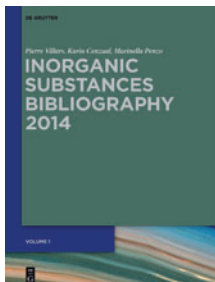


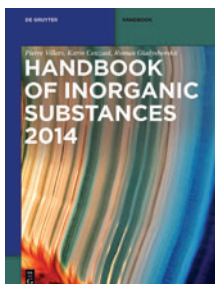
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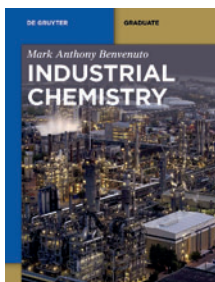
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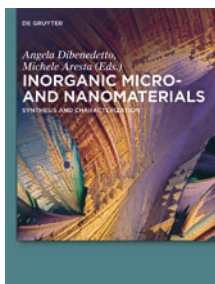
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Rainer Pöttgen · Dirk Johrendt

Intermetallics

Synthesis, Structure, Function

DE GRUYTER

Prof. Dr. Rainer Pöttgen

Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrasse 30
48149 Münster
Germany
E-mail: pottgen@uni-muenster.de

Prof. Dr. Dirk Johrendt

Department Chemie
Ludwig-Maximilians-Universität München
Butenandtstraße 5-13 (Haus D)
81377 München
Germany
E-mail: johrendt@lmu.de

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To our academic teachers

Bernard Chevalier, Wolfgang Jeitschko, Albrecht Mewis,
Jean Rouxel[†], and Arndt Simon

Preface

Inorganic solid state chemistry is a still growing field which covers a broad diversity of compounds from salts via semiconductors to intermetallics. The key topics concern materials synthesis, structure determination and systemization, bonding analyses as well as the characterization and understanding of the physical properties. While halides, chalcogenides, nitrides, and basics on semiconductors are frequently implemented in fundamental inorganic chemistry textbooks, the large family of intermetallics is still stepmotherly treated. Motivated by several colleagues we wrote the present book in order to close a gap for Master and PhD students. Our contribution summarizes basic data for the synthesis and crystal chemistry of intermetallic compounds and gives an outlook on the many physical properties.

The present contribution summarizes selected examples from the huge family of intermetallic compounds, well understood, from a solid state chemistry point of view. The standardized crystallographic data were taken from the Pearson data base. Structure drawings were performed with the DIAMOND software and refined with CORELDRAW or ADOBE ILLUSTRATOR.

The basic research of the authors on intermetallics has generously been supported by the *Deutsche Forschungsgemeinschaft* (DFG) and the *Bundesministerium für Bildung und Forschung* (BMBF) over the last fifteen years, and is gratefully acknowledged.

Such a project is not realizable without the help of colleagues and co-workers. We thank Gudrun Lübbering for continuous help with literature search, Prof. Dr. Hubert Huppertz for several technical photos and critical reading of the manuscript, Thomas Fickenscher for photos of chapter 2, and Dr. Manfred H. Möller, M. Sc. Christine Hieke and M. Sc. Franziska Hummel for proof reading. We are indebted to the editorial and production staff of de Gruyter. Our particular thanks go to Kristin Berber-Nerlinger for her continuous support during conception, writing and producing the present book.

Münster, München, 24 March 2014

Rainer Pöttgen, Dirk Johrendt

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1 Introduction

Intermetallic compounds and alloys are a highly important class of modern functional and construction materials, *e. g.* steels, bronzes, brasses, light-weight alloys for aerospace and vehicle construction, permanent magnetic and magnetic recording materials, shape memory metals, solders, jewelry metal, cutting tools, catalysts, thermoelectric materials, superconductors, battery materials, and many more. In view of the high impact on the gross national product, basic knowledge of these materials should be a prerequisite for a chemist, physicist and materials scientist.

More than 80 elements of the Periodic Table are metals. They crystallize with the closest-packed structure types or the *bcc* structure, but also more complicated normal- and high-pressure modifications are known. Thus, already the metallic elements show a broad range of structures, bonding peculiarities and physical properties. In going to binary, ternary, quaternary or even multinary compounds one ends up with an incredible amount of phases. The plethora of crystallographic data of these phases is compiled in different data bases, *e. g.* the Pearson [1] or the ICSD [2, 3] data base. These modern data bases allow for efficient search of element combinations, cell sizes and diverse crystallographic parameters like Pearson symbols, Wyckoff sequences, etc. Phase diagram information is available in different compilations [4–6].

The incredible amount of structures and crystallographic data readily calls for systematization. Different classes of alloys and intermetallic compounds have already been summarized and reviewed in different books [7–10]. These books mostly cover very specialized topics of the field of intermetallics and they might be too comprehensive for a Master or PhD student interested in this kind of chemistry. The present initiative is not just another compilation on intermetallics. It is meant as an introduction to this broad field on the level of final Master studies. An inevitable prerequisite for the study of this book is the knowledge of basic inorganic crystal chemistry [11–13] as well as some basics in space group and X-ray crystallography [14, 15].

The book is written from a synthetic solid state chemist's points of view. Due to the enormous combinatorial variety, it is impossible to know and consider all classes of intermetallic compounds. Nevertheless, we hope that we made a good compromise and covered most of the basic materials. In all subchapters we present a broad literature overview. The interested reader can use this secondary literature (books and review articles) for further, deeper information. The book is divided into three larger topics (i) Synthesis, (ii) Structure, and (iii) Function, which cover most basic aspects. In those cases where properties are directly related to a special compound, they are already mentioned along with the structural data in Chapter 3.



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2 Synthesis

The synthesis of alloys, solid solutions, and intermetallic compounds has important impact for daily life and covers a broad part of the gross domestic product, keeping the huge amounts of steel, light-weight alloys, solders, prosthetic alloys and super-alloys in mind. On the other hand there is a broad community of solid state chemists, physicists, metallurgists, and materials scientists working in diverse areas of fundamental research of intermetallics. The purity of the elements and the technical requirements are different, whether one works with several tons of a material or uses samples on a milligram scale in research. Concerning the important technical processes we refer to the well known *Ullmann's Encyclopedia of Technical Chemistry*. Herein we focus on the requirements for sample preparation on the laboratory scale in order to perform structural analyses and property investigations for basic materials characterization.

2.1 Starting Materials – Crucible Materials

Most intermetallic compounds are synthesized directly from the elements using the techniques that are discussed in the following subchapters. The use of very pure starting materials is an indispensable prerequisite for the synthesis of pure samples. Today many elements can be purchased directly from the suppliers in pure form, however, the experimentalist should always be extremely vigilant, since introduced impurities can irreversibly affect the reactions and thus the product formation. Often purities of metals are only given with respect to other metallic impurities and it is then not clear to what degree non-metallic impurities might be present as well. Especially if the form of the used metals exhibits a large surface, this is the case for fine powders, these metals might easily react with moisture. Typical impurity phases are then oxydic or hydroxidic surface cusps. Such surface impurities are generally observed *e. g.* on the cauliflower-like surface of electrolytically reduced manganese chips. The dark-brown layer can easily be removed by diluted nitric acid. As an example we show a contaminated and a cleaned manganese chip in Fig. 2.1. Transparent oxydic or hydroxidic coatings often occur on compact pieces of aluminum or magnesium. These elements are mostly purchased in the form of rods. Prior to use one should carefully mill a small surface layer on a turning lathe in order to obtain a pure surface. Generally, when available and suitable, it is always advantageous to use large metal pieces in order to keep the surface area minimal.

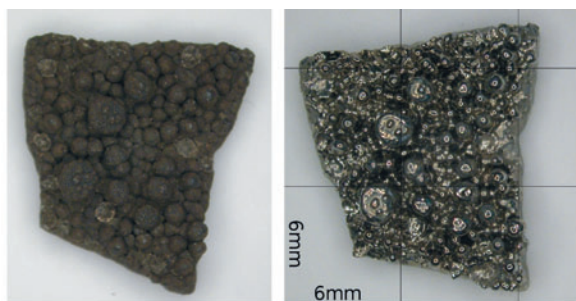


Fig. 2.1 A surface oxidized/hydrolyzed manganese chip (left) which was subsequently cleaned with diluted nitric acid (right). One square has a size of $6 \times 6 \text{ mm}^2$.

Oxidic impurities can also occur in rare earth metals. Especially europium and ytterbium are susceptible to such impurities. Small amounts of ferromagnetic EuO ($T_c = 70 \text{ K}$) or antiferromagnetic Yb_2O_3 ($T_N \sim 3 \text{ K}$) in the starting materials can irreversibly affect magnetic property measurements. These two elements should exclusively be used in freshly distilled form in order to get phase pure samples.

Arsenic lumps are often covered by a thin film of arsenic oxide. Such lumps can easily be purified by fractional sublimation under vacuum. Small quantities of contaminated arsenic are sealed in a long evacuated silica tube. First, the sesquioxide As_2O_3 is sublimed with the hot end of the tube at 570 K and the other end at room temperature. After separation of the cold end, containing the sesquioxide, the tube is sealed again, and the arsenic is sublimed with the hot end of the tube at 870 K . Lead is mostly purified by repeated liquation.

Small oxidic impurities in the starting materials can result in small quantities of by-products, astonishingly, sometimes with good crystal quality. A prominent example concerns the phosphide oxides $\text{AE}_4\text{P}_2\text{O}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$) [1] which are valence precise according to $(4\text{AE}^{2+})(2\text{P}^{3-})\text{O}^{2-}$. Initially the phosphide oxides were thought to be binary compounds, but they were obtained only in low yield and the Zintl concept was violated. Detailed X-ray investigations indeed showed that ternaries and binaries like Sr_2P or Ba_2P do not exist. Similar behavior was observed for various arsenides, antimonides, and bismuthides.

The heavy alkaline earth metals as well as the rare earth metals can be contaminated by hydrogen. Vacuum re-distillation/sublimation prior to use is an essential prerequisite. Again, the formation of hydride by-products in low yield might affect the desired synthesis or lead to completely different compounds if the hydrogen contamination is even large. Striking examples for such synthetic disasters are the electron precise Zintl phases $\text{Ca}_5\text{Sb}_3\text{H}$ [2] and $\text{Ba}_5\text{Ga}_6\text{H}_2$ [3] which were formerly reported as binaries. The quaternary hydride $\text{Ba}_{21}\text{Ge}_2\text{O}_5\text{H}_{24}$ [4] was originally placed as binary barium-rich germanide in the Ba–Ge system.

Lithium can directly react with water, oxygen and nitrogen from the air. This leads to a mixture of surface contaminations, *e. g.* LiOH and Li₃N as well as their hydrated and/or hydrolyzed derivatives, resulting in dark gray cusps on lithium rods or foil.

An almost ubiquitous impurity that does not greatly affect the synthesis of bulk samples is iron. Many of the rare earth elements contain trace amounts of iron that can react with the second or third reaction component, forming magnetically ordering impurity phases that might agglomerate at the grain boundaries. These tiny impurities are mostly not visible on X-ray powder patterns, but can irreversibly affect the magnetic property measurements. This is especially the case for the diamagnetic rare earth elements Sc, Y, La, and Lu and for those with small magnetic moments, *e. g.* Ce with only 2.14 μ_B .

The aim of a reaction should be an intermetallic compound in bulk quantity, *i. e.* at least pure on the level of X-ray powder diffraction. **There is always a reason, why only small product quantities or even only few crystals form!** In most cases, when the reason/origin of an impurity was clear, bulk amounts could be synthesized without problems.

Solid state reactions, especially in the field of intermetallics, are mainly single step syntheses; mostly no further purification steps are possible. A targeted reaction strategy is thus indispensable, especially if property investigations follow. *Harald Schäfer* published a remarkable review article [5] on the situation of preparative solid state inorganic chemistry. He critically addressed all these preparative problems. Although the article dates from 1971, all key topics are and remain timely!

Since solid state reactions are typical high-temperature reactions, normal laboratory glassware cannot be used. In the following paragraph we introduce the most frequently used crucible materials. Sealed evacuated silica tubes are often used for flux synthesis (Chapters 2.7 and 2.8) as oxidation protection for metallic or carbon-based crucibles or simply for annealing/sintering samples. Silica tubes contain surface absorbed water. Prior to all reactions, the tubes must be flame-dried under vacuum. Silica is not a totally inert crucible material. Diverse samples can react with silica forming either oxides or silicides as side-products. During tin flux synthesis of phosphides one frequently observes minor silicon occupancy on the phosphorus sites originating from the crucible material. To avoid these side reactions, one can wrap the samples in zirconium, niobium, tantalum or molybdenum foil (Fig. 2.2) to suppress the contact with the silica wall. Silica has a softening point at ca. 1800 K. The use as container material should be limited to a maximum temperature of 1350 K. Longer annealing at higher temperature enhances recrystallization and the tubes are no longer gas-tight.

For direct reactions of the elements, for flux reactions, or for annealing sequences, ceramic crucibles are frequently used. The most important commercially available crucible materials (Al₂O₃, MgO, and ZrO₂) in different forms are presented in Fig. 2.3. Considering the ionic nature of the three oxides one would expect colorless

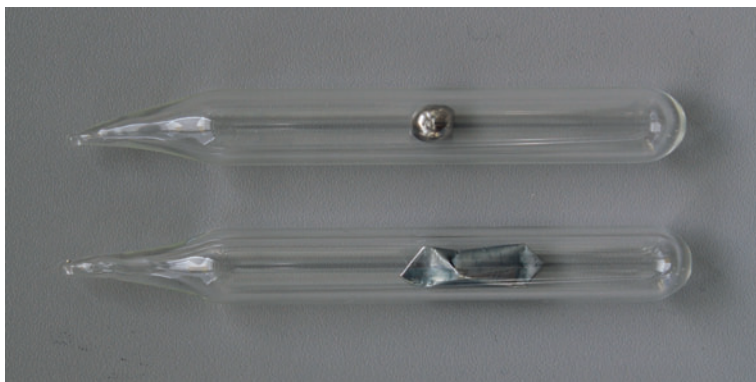


Fig. 2.2 Pre-melted intermetallic compounds in evacuated sealed silica tubes: Without protection (top) and wrapped in molybdenum foil (bottom).

materials. This is not the case, since these crucibles contain sintering additives. One should carefully check the data sheets of these materials in order to know which side reactions might occur with the crucible material. Similar to silica, also the ceramic crucibles might contain surface humidity. They need to be dehydrated at high temperature under vacuum prior to use. In many cases, the ceramic crucibles can be reused after cleaning with oxidizing acids and finally with demineralized water.

For most flux reactions and annealing experiments, the ceramic crucibles can be considered as inert. However, there are few examples where the crucible can unexpectedly react with a sample. A remarkable example is $\text{U}_4\text{Te}_3\text{O}_4$ [6]. This oxide telluride was obtained during recrystallization experiments of binary U_3Te_4 in alumina crucibles, and the oxygen apparently came from the crucible material.

CeO_2 (ceria) can also be used as crucible material, however, it does not belong to the common commercially available ones. Ceria has a high stability even in oxidizing atmosphere up to about 2150 K. The advantage is the possibility of self-fabrication of ceria crucibles, since ceria has an excellent sintering ability in the range of 1550–1750 K. Addition of 5–6 % water to ceria powder leads to a kneadable paste with which one can form or press the desired crucible. After drying in air, the crucible is first annealed at a rate of 7–8 K/min to 970 K, then at a rate of 10–12 K/min at 1670 K, followed by 2 h sintering at that temperature.

Further crucible materials are hexagonal boron nitride (*h*-BN), graphite, and glassy carbon (Fig. 2.4). These can be used under inert gas conditions, if the samples do not react with the crucible walls. *h*-BN and graphite are soft crucible materials. They are available as rods and crucibles can easily be home-made in the desired form on a turning lathe. This is especially the case for the tiny crucibles for high-pressure cells [7]. Graphite crucibles are frequently used for thermal treatment of dental alloys. The experimentalist should be aware of the porous surface and the different wetting abilities, especially of graphite-based crucibles.

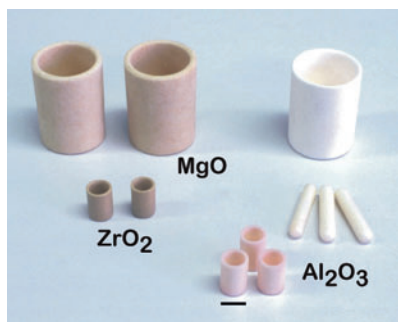


Fig. 2.3 Typical crucibles of MgO, ZrO₂, and Al₂O₃. The different coloring of the ceramics results from sintering additives. The small black bar corresponds to 1 cm.

A highly sophisticated, but expensive crucible material is glassy carbon. These crucibles are produced by thermal decomposition of highly unsaturated hydrocarbons. In contrast to graphite, glassy carbon is a comparatively hard material and it shows poor wettability for metallic fluxes. Prior to use, these crucibles must be heated under dynamic vacuum in order to remove remaining volatile impurities and surface water. Glassy carbon crucibles can be cleaned with oxidizing acids and demineralized water and can be reused after careful drying.

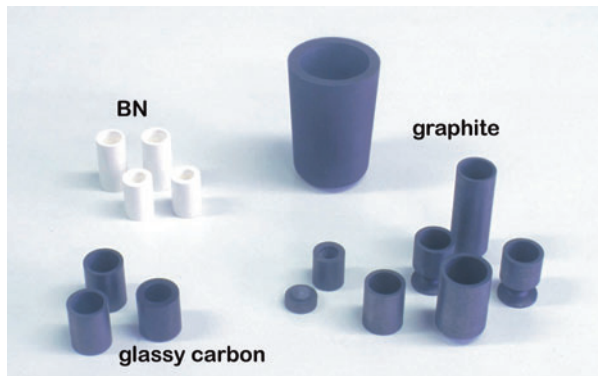


Fig. 2.4 Typical crucibles of hexagonal boron nitride (*h*-BN), graphite, and glassy carbon. The *h*-BN crucibles have a diameter of 1 cm.

Reactions with highly volatile elements, *e. g.* magnesium, zinc, cadmium, europium, or ytterbium, as well as with the alkali and alkaline earth metals require sealed containers. High-melting inert metal tubes made of niobium, tantalum, and molybdenum (Fig. 2.5) are commonly used in preparative solid state inorganic chemistry. Such containers are always self-made from tubes and lids. An overview on the use of tantalum as high-temperature container material was given by *Corbett* and *Simon* [8]. The com-

mercially available tubes and plates need to be cleaned from grease and the surface is finally etched in order to get a pure crucible material.

Two different tube designs are possible. The tubes can be squeezed at both ends [9] and arc-welded or small formed lids are driven into the tube ends, leading to cylindrical crucibles. The welding procedure (electron beam welding) takes place under purified inert gas (argon), using a high-quality welding generator with a high-frequency ignition in order to ensure contact-free welding [10]. After reaction, the solid product is carefully cleaved from the crucible using hammer and anvil. The tubes are then opened with a pipe cutter. For all annealing purposes, the metal crucibles or metal tubes need to be kept either under vacuum or purified inert gas in order to avoid oxidation. In some cases, especially when annealed long and at very high temperature, niobium, tantalum, and molybdenum tend to recrystallization and the ductile crucible material becomes brittle. Mostly, the metal tubes are not reusable. Crucibles with larger wall size can mechanically be cleaned inside (abrasion and polishing) and reused.

Niobium, tantalum, and molybdenum do not always act as inert crucible materials. Especially in the field of rhodium-based intermetallics reactions with the tantalum walls have repeatedly been observed. The exact reason for this behavior is not fully understood. Also the p elements might react with the crucible. Stable borides, silicides etc. can form as coatings on the crucible surface or even completely react. For all reactions, one must carefully check for contaminations with the crucible material.

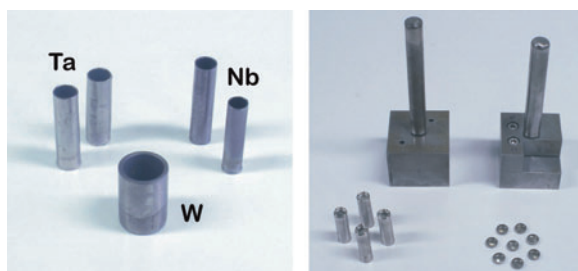


Fig. 2.5 High-melting metal crucibles of Nb, Ta, and W (left) and cylindrically sealed tubes of tantalum. The lids can be stamped and formed by home-made cutting and forming tools (right).

Many elements and reaction mixtures, especially at elevated temperatures are sensitive to oxygen, nitrogen, and moisture. The handling of elements and samples proceeds in commercially available glove boxes (details are available from the leading glove box producers from the internet) or using the Schlenk techniques. For details we refer to the *Handbuch der Präparativen Anorganischen Chemie* [11], to *Synthetic Methods of Organometallic and Inorganic Chemistry* [12], and the careful experimental work by Zintl [13].

Argon is the commonly used inert gas in laboratories, either supplied in bottles or in liquid form in larger tanks. The main impurity components in commercial argon

are water, oxygen, and nitrogen, which can irreversibly affect a reaction. Today, the commercial glove-box systems have automated gas purification supplies along with permanent water and oxygen control.

For gas bombs ready-to-use purification cartridges are meanwhile commercially available, but most solid state labs use home-made gas purification lines. Typical components of such purification lines are columns with the oxysorb catalyst (Cr^{II} / Cr^{III}) [14] or nowadays the commercially available BTX catalyst (Cu/CuO), phosphorus pentoxide, molecular sieves, as well as getter furnaces with magnesium pieces or titanium sponge.

CAUTION: Magnesium and titanium might cause severe metal fires when exposed to oxygen. The purified gas should then be transported exclusively *via* absolutely tight tubes, either laboratory glass, flexible inox, or copper tubes. Several polymer tubes have too high humidity permeability.

Summing up, the synthetic part of a publication on an intermetallic compound is the heart of the experimental work and the indispensable prerequisite for subsequent property studies. This part should be described with all relevant details so that everyone can repeat the experiment independently! To give an example, all reactions reported in *Inorganic Syntheses* [15] have been repeated successfully by independent researchers. These synthesis instructions have high quality standard.

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2.2 Phase Diagrams – Metallography

The basic thermodynamic data for solid state synthesis are the corresponding phase diagrams. Many handbooks and compendia summarizing binary and ternary inter-metallic phase diagrams are available in the literature [1–3]. The binary phase diagrams document the stability of a given binary phase as a function of temperature and the ternary ones are mostly isothermal sections. The thermodynamic and theoretical background for the construction and interpretation of binary and ternary phase diagrams is not the topic of the present book. These topics have repeatedly been summarized in basic textbooks [4–6]. Herein we focus on practical applications for the synthetic solid state chemist.

The experimental construction of phase diagrams depends on many parameters. Often these data resulted from thermal analyses of different starting compositions. This technique led to many phases with approximate compositions, where the structure is not yet known. This is a severe problem. In such cases, where either the composition is not completely known or where a supposed binary (*e. g.* Ca_5Sb_3) or ternary compound (*e. g.* $\text{Ba}_{21}\text{Ge}_2\text{O}_5$) is indeed a ternary or quaternary one, the phase diagrams are incorrect. One should not be too worried about that. Those few binary or ternary phase diagrams where compounds with high technological relevance occur (*e. g.* the Fe–C diagram) have thoroughly been investigated. Many others, especially binary phase diagrams have been studied long time ago, and the composition of a phase was often only derived from the starting composition. Especially for structurally very complex phases, the precise structure determination on the basis of single crystal X-ray data (and thus the exact composition) was not possible at the time where the phase diagrams were gained only on the basis of thermal analyses. Still now, each year several phase diagrams are revised and completed. Many data are summarized in the CALPHAD periodical [7].

Metallography in combination with microscopy is a fast and efficient complementary tool to thermal analysis and X-ray diffraction for phase analysis. Melted or annealed samples are therefore embedded in a polymer matrix (often methylmetacrylate), cut and polished with different silica or diamond suspensions. The resulting sample surface can be analyzed as is or it can be etched in order to remove part of the phases, *e. g.* grain boundaries. Cutting and polishing machines along with complete sets of suspensions and grinding/polishing disks are meanwhile commercially available. The working techniques are well documented in basic textbooks of metals science and metallography [8–10].

In the beginnings, analyses of the polished surfaces were performed with metallographic microscopes. Nowadays these analyses are exclusively carried out by scanning electron microscopy in combination with EDX. Good resolution pictures are taken in backscattering mode [11]. Domains with different electron concentration arise in different gray scales, mostly with sharp contrast between the domains. Domain compositions and grain boundary compositions can be determined with good

precision. In many cases WDX analysis [11] is more accurate. The metallographic/scanning electron microscopic analyses allow for determination of trace amounts of by-products which are not detectable by powder X-ray diffraction. This information is especially important with respect to property studies, where impurity phases can play an important role.

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2.3 Melting, Annealing and Sintering

For the synthesis of an intermetallic compound the elements are usually heated until at least one component melts and reacts with the other ones, or one heats sufficiently high in order to have an adequate diffusion rate (at least $10^{-12} \text{ cm}^2/\text{s}$). According to the empirical Tammann rules, at least one of the reaction partners should reach 2/3 of his melting temperature to enable diffusion at a reasonable time scale. Today, there are many suppliers that offer different *muffle* and *tube furnaces* with maximum heating temperatures up to 1770 K. Such furnaces can also be equipped for operation with inert gas or under vacuum. Different models and resistance wire types are easily accessible by an internet search using the two keywords.

Many university groups need a larger number of furnaces for long-term annealing sequences and explorative solid state synthesis. Keeping the high costs for commercial furnaces in mind, usually the mechanical and electronic workshops of the solid state

chemistry and physics institutes construct their own home-made tube and muffle furnaces. A typical setup is presented in Fig. 2.6 An alumina tube is taped by a calculated number of windings of the resistance wire. These windings are subsequently fixed on the alumina tube by a high-temperature cement in order to avoid electric shortening. The outgoing wires are insulated by small ceramic rings. Thermal insulation of the heating tube is ensured *via* a direct coating with synthetic fiberfrax® ceramic wool, and additionally by commercial vermiculite plates (chimney construction). The whole furnace is capsuled with stainless steel plates.

The home-made tube furnaces can usually be operated up to 1270 K. The single components are all commercially available and not expensive. The length and diameter of the heating tube can then be adapted to the desired experiment. This setup (in modified form) is also used for two-zone tube furnaces for chemical vapor transport reactions (Chapter 2.10). For lower-temperature annealing experiments home-made aluminum block furnaces (Fig. 2.7) can be used. The temperature measurement is performed with commercial thermocouples and the programmable power supplies allow almost any temperature program. Such block furnaces are frequently used for reaction series in explorative flux synthesis, since metal and salt fluxes (Chapters 2.7 and 2.8) often do not require such high temperatures.



CAUTION: Such furnaces are strictly limited to 770 K to avoid melting of the aluminum block; danger of a metal fire.

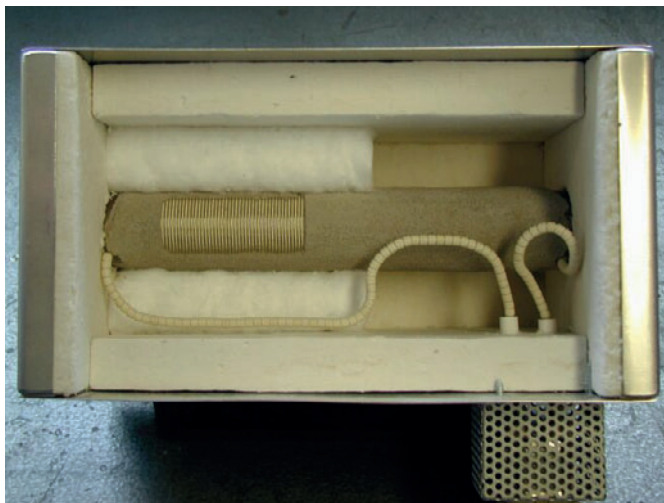


Fig. 2.6 Set-up of a home-made tube furnace. For details see text.



Fig. 2.7 Set-up of a home-made aluminum block furnace. For details see text.

Typical solid state reactions without a liquid phase are diffusion determined and thus highly depend on the reactive surface (Fig. 2.8). Increase of the reaction temperature and densely pressed pellets of the polycrystalline reaction powder enhance the diffusion rate. Such reactions are often interrupted. The reaction products are carefully ground (high surfaces can be obtained with ball, planetary or mixer mills), pressed again into dense pellets and sintered again. Hot isostatic pressing (HIP) can increase the pellet density. Such repeated annealing sequences (a dozen of grindings have been reported in several papers) are typically used for the flux free synthesis of phosphides, arsenides, antimonides, and bismuthides in order to obtain phase-pure samples for property investigations.

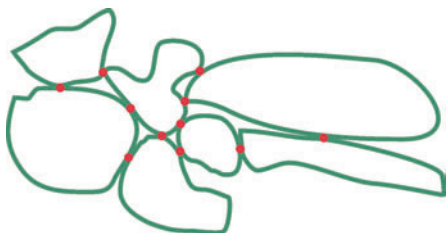


Fig. 2.8 A sketch for a typical sintering reaction. The grains touch each other only at the red points. Only at these points diffusion can occur.

2.4 Arc-Melting

The generation of very high temperatures through electric arcs (a plasma volume heated by an electron beam between two electrodes) is used for many metallurgical processes since decades. Well-known textbook examples are the synthesis of calcium carbide or the carbothermal reduction of phosphorite to white phosphorus. On the industrial scale, such large arc-melting furnaces work with thick carbon electrodes, and temperatures up to 4000 K are achievable. The industrial setups for large-scale production are readily available through an internet search using ‘Lichtbogenofen’ or ‘arc melting furnace’ as keywords. Application of this high-temperature technique to the lab-scale was realized much later [1, 2].

Today, several commercial arc-melting furnaces for research laboratory applications are available. All these models have water-cooled copper hearths for one or more samples. The furnaces are operated with a tungsten electrode (up to 1 cm diameter) under reduced argon pressure (700–800 mbar), and the complete setups are equipped with vacuum/gas delivery supplies. The copper hearths can have different sizes, depending on the sample quantity, either a research sample with some hundred mg, or a 5 g sample for neutron diffraction purposes. For high quality samples, the argon atmosphere in the sample chamber is important. Since most metals that are melted in the arc vigorously react with oxygen (high lattice energy of the oxides), the use of high-purity argon is a prerequisite. The usual purification techniques have been summarized in Chapter 2.1. Before melting, the sample chambers are evacuated and re-filled with purified argon three times. As an additional security one can melt a piece of titanium or zirconium sponge (getter materials) prior to the desired reaction. In order to avoid contamination with evaporated metals, only one sample should be prepared at a time, although many of the commercial furnaces allow for parallel melting of several samples. Evaporated metals of a sample might condensate on the neighboring sample and affect its purity.

Miniaturized arc-melting furnaces [3] usually use commercial CeO_2 doped tungsten electrodes of 1.5–2.4 mm diameter. It is highly recommended to use a high quality welding generator with a foot pedal for dosing the power and a high-frequency ignition. This way one avoids contact of the tungsten electrode with the copper crucible. Thus, arc-melting is frequently called quasi-crucible-free melting technique. The setup for such an arc-melting sample chamber is shown in Fig. 2.9. The copper crucibles are coupled to the quartz sample chamber by a brass flange. The sample chamber can be evacuated and refilled by argon. The melting or welding procedure is typically carried out under reduced argon pressure of 700–800 mbar.



CAUTION: The operator of such an arc-melting device needs to wear welding safety glasses with sufficient shading. Complete insulation of the home-built devices is indispensable.

If one keeps the general operating conditions, mainly the use of pure elements and pure argon, the arc-melting technique is efficient, relatively fast, and straightforward. Best results are obtained if a reaction is carried out with elements with comparable melting and boiling points. In the case of largely differing melting and boiling points, it is possible that one element already evaporates before the other one melts. This leads to weight losses and wrong sample compositions. In any case, the resulting arc-melted buttons should be weighed after each melting step in order to be sure about eventual evaporation losses. In order to ensure homogeneity of the sample, the product buttons are normally re-melted twice, turned around and re-melted again. Very often the resulting samples are quite brittle. Due to many micro-cracks in the button, it may splash during re-melting, again leading to a weight loss.

Many elements like Mg, Cd, Zn, Sm, Eu, or Yb are difficult to handle in an arc-melting furnace. They have too low boiling temperatures and considerable vapor pressures. This leads to uncontrolled reaction conditions. Sample preparations with those elements should be carried out in sealed metal tubes (Chapter 2.1).

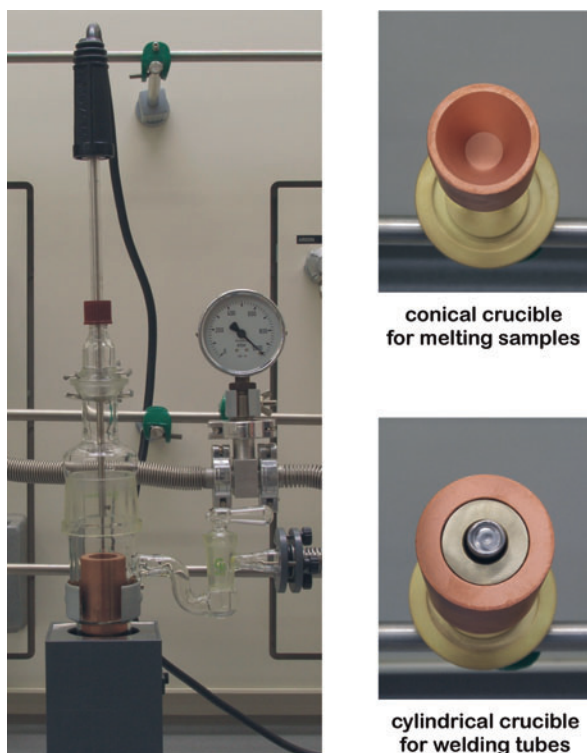


Fig. 2.9 A typical miniaturized arc-melting/welding setup (left). Crucibles used for melting samples and welding tubes (right).

If one melts very small samples in the order of 100–200 mg, the melted sample still has sufficient surface tension in order to keep the sample in spherical shape during solidification. Larger samples flatten under their own weight upon cooling. Special copper hearths allow for melting of several buttons to small bars. Specimens of well-defined dimensions can be cut from those bars for property measurements. Figure 2.10 shows three different sample forms.

Since arc-melting is a typical high-temperature technique, it is usually used for the synthesis of borides, carbides, silicides, and germanides, but also for the lower melting aluminides, gallides, indides, stannides, and partly for antimonides. All starting compositions with volatile components are not adequate for arc-melting, which is a quasi-open system.

The miniaturized arc-melting chambers [3] can be used in parallel for arc-welding metal tubes (cramped tubes or tubes with lids), mainly niobium and tantalum (Fig. 2.9). As compared to the larger setups [4–6], the miniaturized setup has the big advantage of water-cooling of the tubes. This way, also the lower-melting alkali and alkaline earth metals can safely be sealed into the tubes without a risk for reaction during the arc-melting procedure.

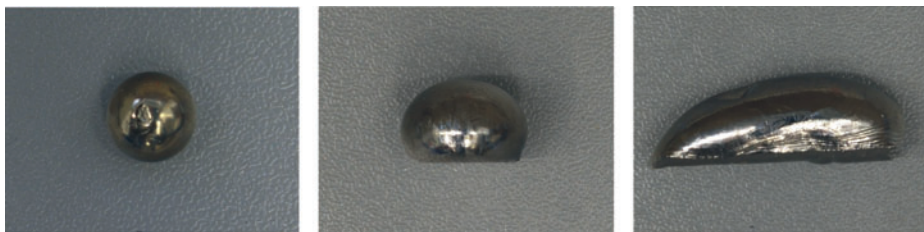


Fig. 2.10 Three different arc-melted titanium samples. The button shown in the middle has ~ 8 mm diameter.



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2.5 Induction Melting

Melting of metallic materials in induction furnaces is a widely used technique also on the large industrial scale. Induction melting is a well controllable, energy-efficient process that is applicable up to a scale of 100 tons in iron, copper, steel, aluminum, and precious metal industry. Due to the efficient energy dosage, one can regulate the temperature just as high as the material melts, thus minimizing any energy loss.

Only electrically conducting, metallic materials can be heated by electromagnetic induction. An eddy current is generated within the metallic specimen and the materials resistance leads to Joule heating. The center piece of an induction generator is an electromagnet which is passed by a high-frequency alternating current. Alternatively one can generate the heat through magnetic hysteresis losses in materials with sufficient relative permeability. The power supplies range from 1.5 kW up to about 15 MW and the operating frequencies cover the broad range from 50 Hz to about 400 kHz. These data basically depend on the nature of the material, on the volume, and the required melting speed. Small sample volumes generally request higher frequency. Herein we only focus on small lab-size experimental setups for the synthesis of sample quantities on the research scale.

The generators that are usually used on the lab scale have power supplies of 1.5 up to 10 kW, rarely 25 kW. The operating frequencies are in the range of 30–300 kHz. The advantage of the smaller generators is their small size and they can routinely be used on a lab bench. The working distance, the diameter, and the number of windings of the water-cooled working coil (usually made of round or square copper tubing) depends on the sample chamber. Usually the coil and the chamber are harmonized with the supplier. This guarantees an optimal coupling of the sample and an effective heat generation.

CAUTION: For all home-built sample chambers the electromagnetic compatibility needs to be fulfilled.



An experimental setup for annealing arc-melted buttons [1] is shown in Fig. 2.11. This technique is especially useful for growing small single crystals for structure determination. The pre-melted button is sealed in an evacuated silica tube and fixed with a silicone tightening into a water-cooled sample chamber. The bottom of the inner silica tube is positioned in the middle of the high-frequency coil. The cooling water prevents an attack of the silica tube. Due to the use of a soft tightening one can still slightly knock at the sample silica tube and guarantee that the button is not gluing at the silica wall. Generally, if one approaches the melting point the buttons give another sound when knocking at the silica tube. One can approach this point empirically and thus find the optimal annealing temperature for the sample. Slightly below the melting point the samples are still solid and one has high diffusion rates.

Besides the annealing of buttons in sealed tubes, one can also react elements or anneal samples in crucibles. For annealing metallic samples one can use ceramic crucibles, carbon-based materials or metallic crucibles that are inert towards the melt. For ceramic, non-conducting samples only an indirect heating with a surrounding niobium/tantalum or graphite/glassy carbon crucible is possible. The sample chamber presented in Fig. 2.12 allows for reactions in open glassy carbon crucibles as well as annealing sequences for sealed niobium or tantalum tubes [2, 3]. The reactions or annealing sequences are carried out under a constant flow of pure argon. The top of the sample chamber is equipped with an observation window through which either the reaction can be monitored *via* a camera or the temperature is controlled *via* a pyrometer. High-frequency generators are available in standard settings from different suppliers. Meanwhile several home-built sample chambers have been constructed. Pictures are readily available through an internet search using the keywords ‘high frequency furnace’ or ‘induction furnace’. For all home-built sample chambers it is important to completely protect the copper coil.

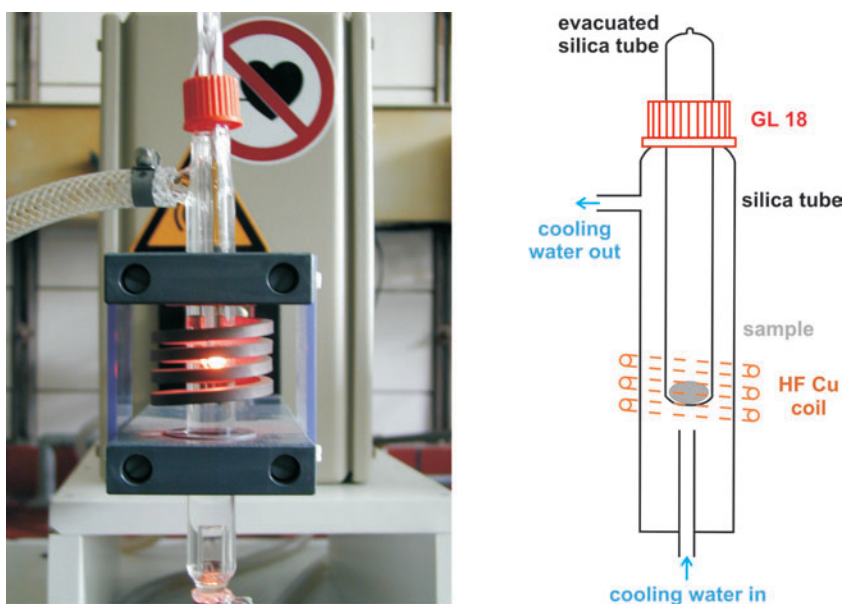


Fig. 2.11 A water-cooled sample chamber in an induction furnace (left) for annealing metallic buttons in sealed silica tubes. A sketch is presented on the right.

A more specialized technique is induction levitation melting. The use of a special coil with well-defined counter-windings allows for a levitation of the melted sample, thus allowing crucible-free melting. The dimensions and windings of such a coil need to be adapted to the material which should be melted. Levitation melting is also possible

with a cold wall induction crucible. Setups of these techniques can be found by a picture search on the internet via the keywords ‘cold wall induction crucible’, ‘levitation melting’, or ‘Schwebeschmelzen’.

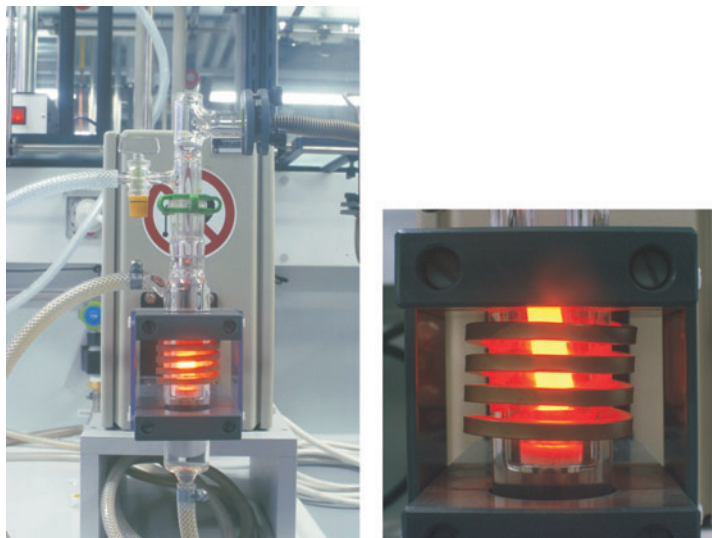


Fig. 2.12 A double-walled water-cooled sample chamber [2, 3] made of silica for inductive heating of sealed metal tubes or reacting elements in glassy carbon crucibles. The center of the copper coil is shown in enlarged scale on the right.

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2.6 Spark Plasma Sintering

Many solid state reactions are carried out by conventional sintering, however, this classical technique often does not provide a dense sample. The main disadvantages of natural sintering are the low mass transport, the required high temperatures, and the long reaction times for densification. To overcome these insufficiencies at least partly, hot-pressing and hot-isostatic-pressing (sintering techniques under pressure) have been developed, mainly for fabrication of dense ceramics. Application of pressure allows lower temperatures and shorter sintering periods.

Activation of the sintering process is also possible by use of electromagnetic fields. This is possible through the application of microwaves or by spark plasma sintering, where pressure is applied simultaneously. These techniques have broadly been used for diverse ceramic materials, but meanwhile many hard materials, composite materials, and intermetallics also have been prepared and heat-treated by spark plasma sintering. Overviews are given in [1–4]. The applied current creates Joule heating and has a remarkable influence on the mass transport. This reduces the sintering temperature and sintering time.

The effect of electric discharge on the sintering behavior of powders has been known for decades. Commercial devices for sample preparation are available for some years. A typical experimental setup is shown in Fig. 2.13. The spark plasma sintering combines the application of external pressure and electric current on the sample. The setup is equipped with a uniaxial pressure device, a pulsed direct current generator, and a die around the sample chamber. The latter is typically made of carbon or tungsten carbide. Pressure and temperature can be controlled electronically. The die and the sample are heated simultaneously. Temperatures up to 2300 K and heating rates of up to 1300 K/min are possible. The sample needs to be inert towards the die material. The rapidity of the thermal treatment allows for complete sintering reactions within several minutes. Reactions can be carried out under argon, nitrogen, hydrogen, or helium gas pressure.

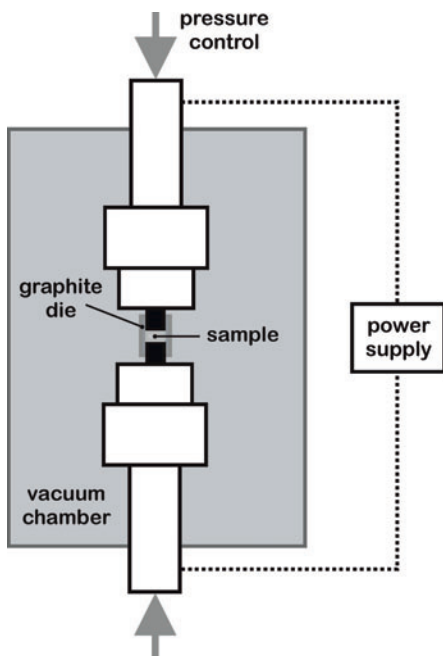


Fig. 2.13 Scheme of a typical spark plasma sintering setup.

Spark plasma sintering certainly has a broad potential for solid state synthesis of intermetallics. So far, most systematic investigations have been carried out for oxide and nitride ceramics. In the field of intermetallics the sintering behavior of high-melting carbides like WC, ZrC, or Ti_3SiC_2 has been studied. Furthermore it is possible to control the microstructure of the samples by carefully choosing the die size and the power parameters. In the field of inorganic materials synthesis, Zintl phases like Mg_2Si , several transition metal borides, the superconductor MgB_2 , silicides and some clathrate compounds have been prepared as bulk samples.

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2.7 Metal-flux assisted Synthesis

The use of metallic fluxes (auxiliary bath method, *Hilfsmetallbadtechnik*) as high-temperature solvents date back to the experimental work in *Moissan's* labs. First systematic synthetic studies were carried out by *Paul Lebeau*, a co-worker of *Henri Moissan* at around 1900 who obtained silicides from copper fluxes [1]. *Jolibois* then grew the first phosphides from tin fluxes [2k], a technique that is meanwhile widely used as preparative tool. Overviews on metal flux synthesis are available in textbooks and review articles [3–7]. Table 2.1 summarizes some typical examples for crystals of intermetallic compounds grown from metal fluxes. In the beginnings, molten metals have been used to grow larger single crystals of known compounds for diverse physical property investigations. The metal flux, however, is an excellent preparative tool for explorative synthesis of new materials.

The use of a metal flux as crystal growth solvent has several prerequisites. The crucible material (mostly Al_2O_3 crucibles) needs to be inert towards the flux, in order to avoid sample contamination. In that view it is also important to know the sintering additives of the crucible material. Many binary and ternary rare earth and transition metal phosphides have been synthesized in tin fluxes using evacuated silica tubes as crucible materials. EDX measurements often revealed non-negligible silicon content in the resulting crystals. Such impurities might irreversibly affect the physical property measurements.

The flux media listed in Table 2.1 can be used in small or large excess, depending on the composition of the desired product. To give some examples, the starting compositions were 1:2:10 for a tin flux synthesis of CuP_2 [8] or 1:1:10:5 for an aluminum flux

Table 2.1 Examples of intermetallic compounds crystallized from metal fluxes. The references are summarized in [2a-p]. The annealing sequences are also given.

Compounds	Metal flux	Temperature	Cooling rate
YbAl_3C_3 ^[a]	Li	1070 K, 1d	7 K/h to RT
NaBa_3N ^[b]	Na	670 K, 3.5 h	20 K/h to 370 K
ReAl_6 ^[c]	Al	1070 K, 14 d	40 K/h to RT
MoAlB ^[d]	Al	2070 K	20 K/min to 1270 K
$\text{Ho}_6\text{Mo}_4\text{Al}_{43}$ ^[e]	Al	1070 K, 21 d	5 K/h to RT
$\text{Th}_2\text{AuAl}_2\text{Si}_3$ ^[f]	Al	80 K/h to 1270 K, 15 h	quenched to RT
$\text{Sm}_2\text{NiGa}_{12}$ ^[g]	Ga	70 K to 1170 K, 4 d	10 K/h to 420 K
YbIrIn_5 ^[h]	In	1300 K, 6 h	5 K/h to RT
CeCu_2Si_2 ^[i]	In	1670 K	4 K/h to 770 K
RhSn_4 ^[j]	Sn	820 K, 2 d; 570 K, 5 d	quenched to RT
NiP_3 ^[k]	Sn	970 K, 7 d	quenched to RT
Ti_2NiP_5 ^[l]	Sn	720 K, 1 d; 920 K, 30 d	quenched to RT
MgRh_6P_4 ^[m]	Pb	1270 K, 48 h	25 K/h to RT
MoCoB ^[n]	Co	1220 K, 21 d	quenched to RT
MnSi ^[o]	Cu	1470 K, 12 h	10 K/h to 770 K
$\text{Ti}_3\text{Zn}_{22}$ ^[p]	Zn	1120 K, 2 d	5 K/h to 770 K

synthesis of $\text{Th}_2\text{AuAl}_2\text{Si}_3$ [2f]. The starting compositions are loaded into the crucibles and annealed with well-defined temperature programs which are well documented in the original literature. Some synthesis strategies simply use one isothermal period with subsequent quenching of the sample, while in most cases the flux is slowly cooled to enhance crystal growth. The slow cooling should generate only few seed crystals which then grow to larger specimens. For samples with volatile components like phosphides and arsenides, the heat treatment is different. Such samples are first annealed at lower temperature in order to react the phosphorus or arsenic. Otherwise the ampoules might burst.

Another important parameter for flux growth is the wettability of the reagents by the flux. In this context tin is one of the best fluxes. Two different techniques are known, (i) the flux is inert towards the sample and (ii) the flux itself is reactive and the flux material is used for crystal growth. This is possible for different fluxes, *e. g.* NiP_3 crystallizes from liquid tin as solvent, while RhSn_4 (Fig. 2.14) forms

upon reaction of rhodium metal with the flux medium. Another pair of compounds is CeCu_2Si_2 and YbIrIn_5 grown from liquid indium. In the first case indium acts as solvent; in the second case it delivers the indium for compound formation and serves as solvent as well.

After the annealing and cooling sequence one obtains crystals that are embedded in the mostly ductile matrix of the flux. For removal of the flux, one can use mechanical, wet-chemical or electrochemical methods. In some cases it is possible to break the brittle crystals out of the matrix. If this is not possible, one dissolves the flux, keeping in mind, that the crystals must resist the solvent. In many cases the crystals are much more stable than the matrix. Tin is frequently dissolved with diluted hydrochloric acid. In Fig. 2.14 we present a sample of RhSn_4 , where just the surface of the flux is dissolved. The diverse crystallites look out of the matrix. The insert of the figure shows one clean crystal with small accretions. Hydrochloric acid is also used for most aluminum-flux-grown intermetallics. Indides are chemically not as stable as stannides. The indium flux is often dissolved in acetic acid. If a lead flux is used, hydrochloric acid would produce too much insoluble PbCl_2 . Therefore, lead fluxes are dissolved in concentrated acetic acid and H_2O_2 (30 %).

In rare cases the flux is removed by electrochemical oxidation. Some examples of bismuthides are reported. With low-melting fluxes, especially gallium and tin, it is possible to use the melt-centrifugation technique [9, 10]. In many cases, thin films of the flux can remain on the surface of the crystals, even if they have been cleaned several times. Another severe problem of flux growth is the incorporation of the flux medium into the crystal. This behavior is well known from many inorganic and organic molecular compounds which crystallize together with a certain amount of the solvent. In metallic flux grown crystals the problem is more delicate, since the flux atoms can substitute for other atoms within the crystal. One problem is the already

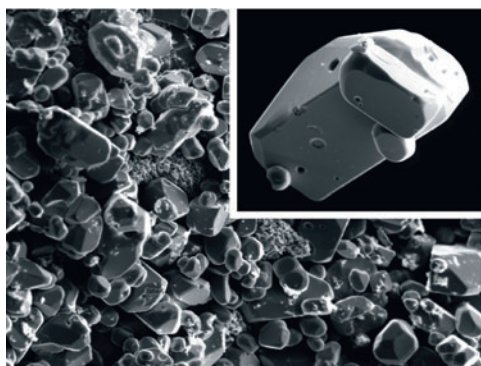


Fig. 2.14 Crystals of RhSn_4 grown from a tin flux. The main photo shows the surface of the sample after partial dissolution of the tin flux with diluted hydrochloric acid and a selected single crystal with small accretions is shown in the insert. The crystals have edge lengths up to 100 μm .

mentioned silicon incorporation in phosphides, a contamination resulting from the crucible material silica. Furthermore, precise DSC measurements of many flux grown phosphides showed signals close to 231 °C, the melting point of tin. This is a clear hint, that tiny segregations of tin either remain within the crystal, or one observes surface contamination with the flux material. A recent example is tin incorporation into BaFe₂As₂ [11]. A combined neutron and X-ray diffraction study revealed a composition close to Ba_{0.95}Sn_{0.05}Fe₂As₂.



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2.8 Salt-flux assisted Synthesis

Salt fluxes have long been used as additives for brazing and welding applications. The salts (diverse borates have been used) can dissolve surface impurities and enable a reaction of the contact materials with the solder, forming the joint. Upon solidification, brittle intermetallic compounds can form as precipitations, a kind of an inadvertent flux synthesis.

For decades, salt fluxes have been used as high-temperature solvents for many sintering applications and for the synthesis of ceramic/oxidic materials. The alkali metal halides have most frequently been used in the form of eutectic mixtures. In terms of costs, NaCl/KCl mixtures have most frequently been applied. An extensive list of suitable fluxes can be obtained from the *Brauer Handbook* [1]. The broad use in the field of crystal growth for complex oxides has been reviewed [2–4].

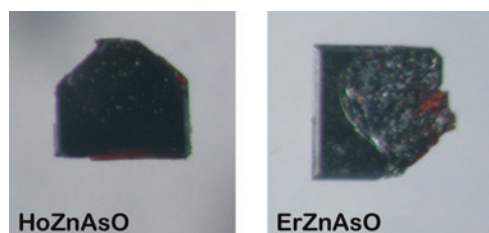
In contrast to oxide chemistry, comparatively few examples are known in the field of intermetallics. Some representative examples are shown in Table 2.2. The salt mixture is mainly chosen by the temperature of the eutectic. Other important parameters are the chemical resistance of the crucible material towards the flux and the wettability of the elements or the precursor compounds. The crucible stabilities towards salt fluxes are also summarized in the *Brauer Handbook* [1].

Salt-flux synthesis can either directly be run in sealed silica tubes or within crucibles that are sealed in tubes for hydrolysis protection. Al_2O_3 is the most commonly used crucible material for the majority of research samples. The amount of flux depends on the specific sample. Usually ten times the sample mass is used as a flux medium. The flux does not necessarily need to completely dissolve the precursors. It can also partly dissolve them and transport the material to the place of recrystallization. Typical annealing sequences (realized *via* programmable temperature control) are listed in Table 2.2. Best results are obtained by low cooling rates in the order of 1–5 K/h. In rare cases pressure is applied in order to improve crystallization. Mostly, the salt fluxes can easily be dissolved in cold or hot demineralized water, provided that the product is insoluble.

Table 2.2 represents approximately the classes of materials that can be grown under salt flux conditions. Most studies have been performed for arsenides and antimonides [6] and the respective pnictide oxides. Well-shaped crystals of HoZnAsO and ErZnAsO [7] are presented as an example in Fig. 2.15. The salt flux medium normally acts as an inert solvent, however, similar to the metal fluxes, rare examples of reactive fluxes are known. A recent example is the quinary oxide chloride $\text{La}_5\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$ [8]. Crystals of this chloride were originally obtained during crystal growth experiments of $\text{La}_3\text{Cu}_4\text{As}_4\text{O}_2$ in a NaCl/KCl flux.

Table 2.2 Examples of intermetallic compounds crystallized from salt fluxes. The references are summarized in [5a-l]. The annealing sequences are also listed.

Compound	Salt flux	Temperature	Cooling rate
$\text{RFeAsO}^{[a]}$	NaCl/KCl	1070 K, 14 d	quenched to RT
$\text{BaCuZn}_3\text{As}_3^{[b]}$	NaCl/KCl	1130 K	15 K/h to RT
$\text{FeSe}_x^{[c]}$	NaCl/KCl	1120 K, 2 h	3 K/h to 870 K
$\text{SmFeAsO}_{1-x}\text{F}_x^{[d]}$	NaCl/KCl	1620–1720 K (4–10 h, 30 bar)	55–290 K/h to RT
$\text{NdFe}_4\text{As}_{12}^{[e]}$	NaCl/KCl	50 K/h to 1170 K, 2 d	5 K/h to RT
$\text{Fe}_{1.04}\text{Te}_{0.66}\text{Se}_{0.34}^{[f]}$	NaCl/KCl	1223 K, 24 h	3.5 K/h to 873 K
$\text{KSm}_2\text{Sb}_3\text{Se}_8^{[g]}$	NaCl/KCl	1020 K, 10 d	2 K/h to RT
$\text{La}_2\text{AuP}_2\text{O}^{[h]}$	NaCl/KCl	1223 K, 3d	2 K/h to 873 K; 5 K/h to RT
$\text{NdFeAsO}^{[i]}$	NaI/KI	40 K/h to 1320 K, 6 d	1 K/h to 870 K, quenching
$\text{PrAgAs}_2^{[j]}$	LiCl/KCl	15 K/h to 1023 K, 96 h	2 K/h to 623 K
$\text{PrZnSbO}^{[k]}$	NaCl/KCl	770 K, 1 d, 1170 K, 24 d	5 K/h to RT
$\text{Cr}_8\text{P}_6\text{C}^{[l]}$	NaCl/KCl	1070 K, 14 d	quenched to RT

**Fig. 2.15** Photographs of HoZnAsO and ErZnAsO single crystals grown from NaCl/KCl fluxes. The edge lengths of the crystals are about 500 μm .

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2.9 Thin Films

Besides classical bulk materials thin films play an important role in materials science in the form of protective coatings or for miniaturized devices with special properties. Broadly used protective coatings concern hard materials. Typical transition metal coatings for drilling tools or watch cases (transition metal carbides and nitrides) are discussed in Chapters 3.9.1 and 3.10.1. Such coatings are typically generated *via* gas phase deposition methods. Furthermore, thin films have a high surface-to-volume ratio and this often influences the physical properties, since the surface often differs from the bulk. Some techniques for the growth of thin films and examples for selected intermetallics are briefly summarized in the present chapter.

A simple technique is the cathodic reduction of metal ions from aqueous solutions on a metal or polymer surface. This is known as electroplating. A well-known example is the electroplating of coins (1 and 2 Euro cent coins) with copper. Other protective metal coatings can be made of nickel, chromium, zinc, or tin. Besides corrosion resistance, especially nickel and chromium coatings are used for many decorative purposes (bathroom fixtures, kitchen utensils, candlesticks). Depending on the composition of the electrolyte such coatings can be of high aesthetic standard (decorative chrome) or wear-resistant (hard chrome). Other high quality thin film coatings can be made from silver and gold.

Many mechanical tools are plated with ductile metals in order to improve their surface corrosion but also to improve the surface sliding properties, *e. g.* for bending tools. Suitable metals for such platings are cadmium and indium. Although the cadmium platings have excellent corrosion resistance even at low film thickness, they are no longer used for common application due to heavy metal toxicity. Today cadmium platings find only application for special military and aerospace applications. Substitution materials are indium and zinc.

Generally, thin film formation is called epitaxy. Depending on whether the film is grown on the same or another material, the terms homoepitaxy and heteroepitaxy are used. Homoepitaxy is frequently used in microelectronics for the growth of silicon films which have higher purity than Czochralski (Chapter 2.11) grown substrates. The silicon can be deposited from the gas phase through thermal decomposition reactions: (i) $\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$, (ii) $\text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{HCl}$, or (iii) $\text{HSiCl}_3 + \text{H}_2 \rightarrow \text{Si} + 3\text{HCl}$. Such procedures which use hydrogen, ammonia, or chlorides are called hydride vapour phase epitaxy (HVPE). Special films can also be grown *via* liquid phase epitaxy (LPE).

A special technique of chemical vapour deposition (CVD) is metal organic chemical vapour deposition (MOCVD). The film growth results from a chemical decomposition reaction of suitable gases at moderate pressures and temperatures. This technique allows for film growth of a broad variety of materials. Typical sources are among others: Trimethylaluminum for Al, trimethylgallium for Ga, trimethylindium for In, isobutylgermane for Ge, phenylhydrazine, or ammonia for N, phosphine, arsine and stibine for P, As, Sb, dimethylzinc and dimethylcadmium for Zn and Cd, dimethylselenide and dimethyltelluride for Se and Te, and titaniumalkoxides for Ti. Combination of different sources allows for film growth of diverse binary and ternary materials.

The second technique for thin film generation is physical vapour deposition (PVD). The frequently used methods are molecular beam epitaxy (MBE), ion beam assisted deposition (IBAD), and cathode sputtering; typical vacuum deposition techniques. The gaseous phase of the respective element is generated by high temperature vacuum evaporation with subsequent condensation or plasma sputter bombardment.

Besides single layers, the PVD techniques also allow for layer by layer depositions at lower temperatures and subsequent reaction of the layers upon increasing the temperatures. In this way it is possible to obtain even new metastable materials in the form of thin films.

The coatings/platings with the pure elements discussed at the beginning of this chapter show random orientation. However, it is also possible to grow oriented films (single crystalline films) by using well-defined oriented substrate crystals. Typical template materials (with their frequently used abbreviations in parentheses) are: Oriented silicon wafers, (La,Sr)(Al,Ta)O₃ (LSAT), LaAlO₃ (LAO), YAlO₃ (YAO), SrTiO₃ (STO), or BaTiO₃ (BTO) substrates, Al₂O₃, (110) GdScO₃, or ion-beam-assisted-deposition (IBAD)-MgO. Meanwhile, these oriented crystalline materials are commercially available.

Since the properties of the films are strongly template dependent, correct choice of the template material is an important prerequisite for good growth conditions in

heteroepitaxy. The oriented surface of the chosen crystal and the unit cell of the material that will be grown need to match as good as possible. Three examples of intermetallics are presented in the following.

Layer-by-layer deposition with subsequent reaction was used for the growth of skutterudite substrate films [1]. These materials were intensively studied in the 1990ies while searching for good thermoelectric materials [2]. The films were deposited on silicon wafers. The samples could be removed from the substrates by soaking with acetone. This allows conventional powder X-ray diffraction studies of the products as well as property investigations.

In recent years misfit layer compounds have intensively been studied with respect to their excellent thermoelectric properties [3]. Preparation of thin films is a very useful technique in order to obtain well-defined samples. Representative examples are $[(\text{PbSe})_{0.99}]_m(\text{WSe}_2)_n$ [4] and binary WSe_2 [5]. Both materials were deposited on (100) silicon wafers.

High-quality epitaxial thin films of the iron arsenide and iron chalcogenide superconductors were grown as thin film samples shortly after the discovery of superconductivity in doped BaFe_2As_2 and LaFeAsO . Such films are required in order to elucidate the intrinsic electromagnetic properties of these materials as well as potential device applications. Overviews on the ongoing work in this field are given in detailed review articles [6–8].

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2.10 Chemical Vapor Transport

Chemical vapor transport is a broadly used technique for the purification of solids or the growth of small single crystals for structure determination. The technique itself is very old and was first observed in nature for the transport of Fe(III) oxide with HCl in volcanoes according to the following transport reaction: Fe_2O_3 (solid) + 6HCl (gaseous) $\leftrightarrow$ 2FeCl₃ (gaseous) + 3H₂O (gaseous). Generally, in such a transport reaction, a solid is dissolved by reaction with the transport agent. The gaseous product shows vapor transport either to a hotter (endothermal transport) or colder (exothermal transport) part of the transport ampoule and decomposes (back reaction) under deliberation of the transport agent which can be used again. After the discovery of the Fe₂O₃ transport by *Bunsen* [1] many experimental work has been performed in the field of halides, oxides, the higher chalcogenides, and chalcogenide halides. The data have first been summarized in 1962 by *Harald Schäfer* in his ‘transport book’ [2]. This was the first systematic work, including the thermodynamic background. Subsequent work has been summarized in further review articles [3, 4] and a new transport book [5].

First examples in the field of intermetallics were the pioneering experiments by *van Arkel* and *de Boer* [6] for the purification of early transition metals. They used the exothermal reaction of the metal with iodine, leading to the gaseous iodide, *e. g.* Ti (solid) + 2I₂ (gaseous) $\leftrightarrow$ TiI₄ (gaseous). The decomposition of titanium tetraiodide then proceeds at a hot tungsten wire (back reaction). This process was then applied to other metals. It was called the iodide process and paved the way for many technologically important processes. In the last 20 years there appeared an increasing number of publications related to such chemical vapor transport reactions. Generally it is important that all reaction products that are formed through the transport reaction are gaseous, and that the equilibrium constant is not extreme.

Transport reactions are usually carried out in sealed silica tubes. The handling of the tubes and the filling of the transport agent are meticulously summarized and described in [5]. The ampoules are then placed in so-called two-zone furnaces in order to achieve the desired temperature gradient. Such furnaces are usually home-made and equipped with thermocouples and electronic, programmable power supplies. For more sophisticated experiments it is possible to use a transport balance.

Based on the pioneering work of *van Arkel* and *de Boer*, many other transport reactions for metals have been developed. Transport reactions are known for more than 40 metals. Most of them had been realized with iodine as transport agent. Besides, some elements can also be purified through transport reactions with chlorine and bromine. In some special cases hydrogen chloride and water can be used as transport reagents. Typical examples are the transport of copper *via* 3Cu (solid) + 3HCl (gaseous) $\leftrightarrow$ Cu₃Cl₃ (gaseous) + 3/2H₂ (gaseous) or the platinum transport according to Pt (solid) + O₂ (gaseous) $\leftrightarrow$ PtO₂ (gaseous). The different transport agents for the metal transports, the temperature ranges, and the literature are summarized in [5].

The only technical application besides the iodide process [8] is the Mond-Langer process [9] for the purification of nickel on an industrial scale according to the reversible transport reaction $\text{Ni (solid)} + 4\text{CO (gaseous)} \leftrightarrow \text{Ni(CO)}_4 \text{ (gaseous)}$. Nickel powder is reacted with carbon monoxide at 320–350 K at a pressure of 1 bar and the resulting pure Ni(CO)_4 decomposes in the back reaction at 470 K on nickel granules to pure nickel and CO. This is an effective purification step, since the main impurity elements cobalt and copper do not form carbonyls under these reaction conditions.

Next to the pure metals it is also possible to grow crystals of binary intermetallic phases *via* chemical vapor transport. Since the desired compounds have no noticeable vapor pressure, they need to react with a transport agent forming two gaseous products. An example is the transport of chromium disilicide with iodine: $\text{CrSi}_2 \text{ (solid)} + 5\text{I}_2 \text{ (gaseous)} \leftrightarrow \text{CrI}_2 \text{ (gaseous)} + 2\text{SiI}_4 \text{ (gaseous)}$. In general, such transport reactions of binary intermetallic phases take place at much lower temperature than an arc-melting synthesis. Furthermore it is possible to grow single crystals of low-temperature modifications and compounds that decompose peritectically before melting. Similar to these elements, also for binaries iodine is the most important transport agent. Further ones are AlCl_3 , GaCl_3 , or InCl_3 .

Iodine is also often used as a so-called mineraliser in isothermal reactions. The addition of a small amount of mineraliser enables a constant transport between the solid and the gas phase. Since in such preparations, the educt and the product are generally not well separated from each other, this reaction type is called a shortcut transport or a micro diffusion.

Most studies on binary intermetallics have been performed for the transition metal tetrelides, but also some aluminides, gallides, and indides have been tested with respect to crystal growth. No systematic data are available for borides and antimonides, although chemical transport reactions are possible. The binary transition metal phosphides have broadly been investigated. In most cases a chemical transport is possible with iodine, but also PI_3 and HgBr_2 have been used. Generally the metal-rich phosphides show excellent crystal growth, while only few examples are known for polyphosphides. Also crystals of ternary phosphides like LaSiP_3 or SmZn_3P_3 have been grown.

Chemical transport of metal arsenides has been reported for many binary and ternary examples. Again, iodine is the most important transport agent besides hydrogen halides (e. g. $\text{SiAs (solid)} + 4\text{HI (gaseous)} \leftrightarrow \text{SiI}_4 \text{ (gaseous)} + 1/4\text{As}_4 \text{ (gaseous)} + 2\text{H}_2 \text{ (gaseous)}$) and water (e. g. $\text{GaAs (solid)} + 1/2\text{H}_2\text{O (gaseous)} \leftrightarrow 1/2\text{Ga}_2\text{O (gaseous)} + 1/2\text{As}_2 \text{ (gaseous)} + 1/2\text{H}_2 \text{ (gaseous)}$). In contrast to the phosphides, the transport-active arsenic transmitting species are As_4 (gaseous) and As_2 (gaseous). A typical example is $\text{YbAs (solid)} + \text{I}_2 \text{ (gaseous)} \leftrightarrow \text{YbI}_2 \text{ (gaseous)} + 1/2\text{As}_2 \text{ (gaseous)}$. The main problem for most transport reactions of arsenides is the lack of detailed thermodynamic data.

The chemical and thermodynamical basics for transport reaction are meanwhile well established. Two different computer programs [10, 11] are available for the calculation of optimal reaction conditions and transport rates, given that reliable thermodynamic data are available for the specific system.



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2.11 Crystal Growth Techniques

Metal and salt fluxes and chemical vapor transport reactions have been described in Chapters 2.7, 2.8, and 2.10 as preparative methods for the growth of single crystals. In most cases these techniques are used in order to obtain small single crystals for determination of the crystal structure by X-ray diffraction. In the case of metal fluxes, selective cases for the growth of larger crystals are known which allow direction-dependent property measurements.

Mostly, the crystal size is not large enough for experiments beyond the X-ray structure determination. Already neutron diffraction experiments warrant larger crystal sizes. The growth of large single crystals deserves more sophisticated techniques [1].

A broadly used crystal growth technique from the melt was discovered in 1916 by Czochralski [2]. He accidentally tipped a fountain pen into a tin flux and obtained a tin single crystal when slowly removing the pen [3]. Later on, this technique found broad interest in industry. Today more than 95 % of silicon single crystals are grown by the Czochralski technique. The typical size of a single crystal is 300 mm diameter and a length of 2 m. This corresponds to approximately 265 kg silicon.

Generally, the melt of the element or compound is kept at a temperature only slightly above the melting point, just avoiding the spontaneous formation of crystal nuclei. An oriented seed crystal is subsequently tipped into the melt. The end of the seed crystal melts, and one obtains a homogeneous layer between the crystal and the melt. The crystal is then slowly removed and the melt solidifies step by step at the

interface. A rotation of the seed crystal inverts the direction of convection and enables an oriented growth of the crystal. The size of the crystal depends on the temperature and velocity.

The Czochralski technique is applicable for many congruently melting compounds. Besides metals and intermetallic compounds, also halides, oxides and silicates can be grown. This is especially important for optical materials for diverse sensors and lasers. A miniaturized version is used for crystal growth on a lab-scale. So-called tri-arc furnaces use the arc-melting setup with three tungsten electrodes combined with the Czochralski technique. Those crystals typically have cm size in diameter and length. Such crystal growth experiments are expensive and they need high technical know-how, excellent knowledge of the underlying phase diagrams, and patience of the operator.

Higher purity crystals of silicon can be obtained by zone-melting. Comparing a solid and its corresponding melt, the impurities have lower chemical potential in the melt. Consequently one observes an accumulation of the impurities in the melt, however, with different segregation coefficients for each element. Usually large polycrystalline rods are inductively melted at one end and similar to the Czochralski technique a seed crystal is used for oriented recrystallization. The small melted zone is then moved through the rod and the recrystallized silicon has higher purity. This purification process can be repeated. In order to achieve homogeneous melting of the zone, the rod rotates smoothly. A typical diameter on the industrial scale for semiconductor silicon is 20 cm. A smaller diameter occurs in lab-scale zone-melting furnaces. Although the zone-melting technique allows for the production of high-purity silicon, it is much more expensive than the Czochralski technique.

A frequently used technique on the laboratory scale is the Bridgman-Stockbarger method [4, 5]. The polycrystalline material is placed in a high-melting metal tube, typically tantalum, and placed in a horizontal furnace. The upper part of the furnace is kept at a temperature above, and the lower part below the melting temperature of the respective material. The smoothly rotating sample tube is then lowered to the colder part of the furnace. The special design of the crucible allows for seed crystal generation. The lower part of the tube which is first heated is strongly narrowed. As soon as the melt recrystallizes in polycrystalline form in this narrowing, only one single crystal continues growing which is then the seed crystal for the remaining melt.

Also the Bridgman-Stockbarger technique deserves broad know-how from the experimentalist. A problem that might occur for these crystal growth methods can be the difference in composition between the melt and the crystal. In such cases it is possible that a grown crystal looks optically quite well, but the composition at both ends might vary. Careful analysis of the crystal edges by powder X-ray diffraction is an important must.



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3 Structure

The peculiar electron configuration of a given element has drastic influence on its size (covalent radius) and coordination requirements. Keeping just the metallic elements in mind, besides the simple *fcc*, *hcp*, and *bcc* arrangements, already these elements show a diversity of singular structures that account for the individual bonding characteristics. In going to binary and ternary intermetallic phases, these sometimes tiny differences lead to a manifold of interesting crystal structures. Knowledge of the structure is an indispensable prerequisite for the understanding and tuning of structure-property relationships.

The present chapter summarizes the crystal chemistry of the metallic elements followed by a short insight into the field of alloys, solid solutions, and ordered close-packed structures. After a short introduction into the bonding peculiarities of intermetallic phases first the so-called *phases*, *i. e.* Hume-Rothery phases, Laves phases, and Zintl phases are summarized, discussing the influence of valence electron concentrations, radii criteria and the large crystal chemistry of Zintl anions. The following subchapters then present the basic data of intermetallic phases, regrouped along the Periodic Table.

3.1 The Metallic Elements

Most of the metallic elements crystallize either with one of the closest-packed structures or with the cubic body-centered structure. The many crystallographic data have competently been summarized by *Donohue* [1]. The three basic structure types Mg, Cu, and W are presented in Fig. 3.1. Since these structures are basic knowledge [2], the structural principles are only briefly described. The close-packed layers are stacked in the sequences ABAB and ABCABC in Mg and Cu, respectively. This leads to an *anti*-cuboctahedral coordination (CN 12) for the hexagonal-closest packing (*hcp*) and to a cuboctahedral one (CN 12) for the cubic-closest packing (*ccp* or *fcc*). If one considers ideal spheres, both packings have 74 % space filling. Besides the ABC notation we have also given the Jagodzinski *hc* notation in that figure. According to *Jagodzinski* a layer is called *h* if the layer above and below is the same (*anti*-cuboctahedral coordination) and *c* if it is different (cuboctahedral coordination). The structures of Mg and Cu can then be classified as pure *h* and *c* stackings, respectively. Other metals have more complex stacking sequences, ABAC resp., *hc* for the neodymium structure or ABACACBCB resp., *hhc* for the samarium structure.

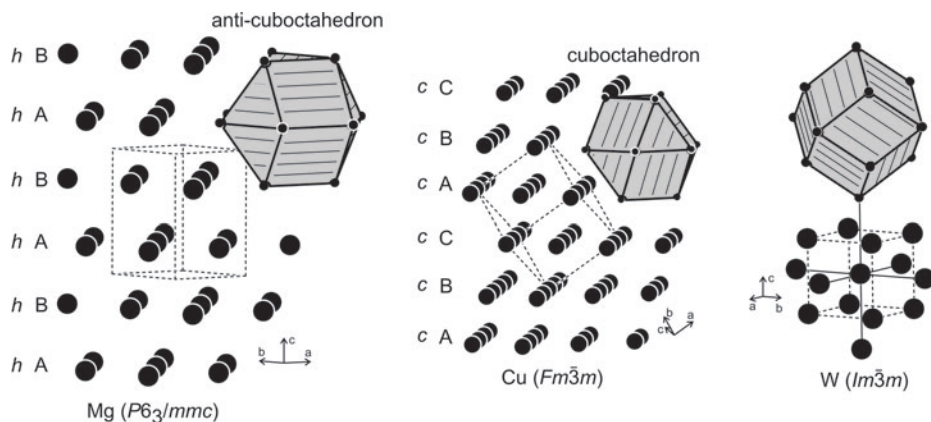


Fig. 3.1 The crystal structures of Mg, Cu, and W. The characteristic coordination polyhedra and stacking sequences (in AB/ABC and *hc* notation) are indicated.

The cubic close-packed structures (typical examples are Al, Ca, Sr, Ni, Cu, Pd, Ag, Au, Pb) have glide planes perpendicular to all space diagonals. They belong to the family of very ductile metals, whereby gold is one of the extreme examples. Gold leaf for gilding applications can easily be produced at thicknesses of 100 to 1000 atomic layers through carefully hammering thin gold foil. The hexagonally close-packed metals (typical representatives are Mg, Sc, Ti, Zr, Hf, Ru, Co, Zn, Cd, Tl) have these glide planes only perpendicular to the *c* axis, leading to reduced ductility. Another important parameter of the hexagonally close-packed metals is the *c/a* ratio (*i. e.* the distance between the close-packed layers) of the unit cell. The calculated ideal value for the *hcp* model is 1.633. This value is almost reached by magnesium (1.62) and nickel (1.63), while beryllium (1.56), zinc (1.86), and cadmium (1.89) differ considerably. Coupled cluster calculations for zinc and cadmium showed that the origin of the anisotropic structures of these two elements results from correlations of the *d*-electrons [3]. The large *c/a* ratios lead to a coordination of six shorter and six longer near-neighbor distances.

The W-type structure (Fig. 3.1) contains no close-packed layers. Among the metals which crystallize with this structure type (typical representatives are Li, Na, K, Rb, Cs, Ba, V, Nb, Ta, Cr, Mo, W, Eu) are hard metals, especially tungsten itself. The cubic body-centered W structure is only considered as close, not as closest packing, since the packing density is only 68 %. Every tungsten atom has eight nearest tungsten neighbors at 274 pm and six further ones at 317 pm (8 + 6 coordination).

Most metallic elements crystallize with one of the three structure types presented in Fig. 3.1. Some, however, show distortions from these highly symmetric structures or even build completely new structural motifs. We start the discussion of these unusual structures with the triel elements indium and gallium (Fig. 3.2).

The indium structure is a stretched version of the *fcc* type. The space group symmetry is reduced to *I4/mmm* and the unit cell (sheared *fcc* cell) contains two atoms. Each indium atom keeps coordination number 12 but with 8×338 and 4×325 pm in a more open-packed atomic arrangement. The *c/a* ratio of the tetragonal cell is 1.52 and drastically deviates from the ideal value of $\sqrt{2}$. The origin of this distortion was studied on the basis of reliable electronic structure calculations [4]. Total energy calculations as a function of the *c/a* ratio nicely reproduced the experimental *c/a* ratio as minimum. The calculations revealed the band energy to be the structure determining parameter and the bonding is significantly influenced by the low lying 5s valence band. A simple close-packed arrangement for indium with unhybridized bands would produce an occupied 5s valence band with essentially antibonding character. The indium structure thus distorts and the *s-s* antibonding states are raised above the Fermi level.

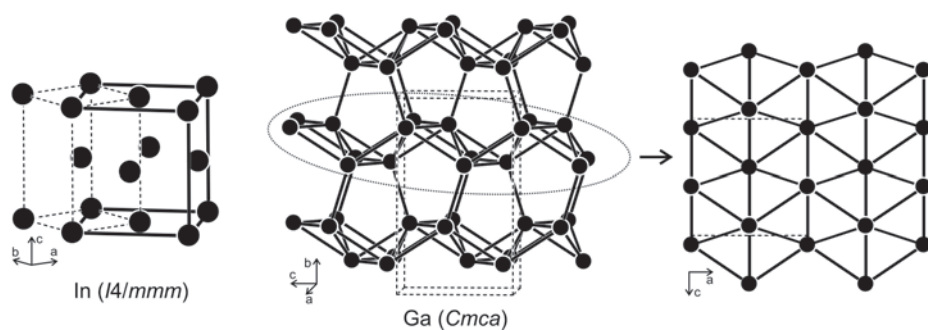


Fig. 3.2 The crystal structures of In and Ga. The relation of the In structure with the *fcc* type is shown. One puckered network of the gallium structure is emphasized at the right-hand part of the drawing.

Also gallium shows similar electronic instability [5] and crystallizes with a strongly orthorhombically distorted structure (Fig. 3.2). The gallium atoms form strongly puckered layers with the motif of close-packing. These layers extend in the *xz* plane with Ga–Ga distances in the range of 269–279 pm. The striking motif in the gallium structure are the short Ga–Ga distances of 248 pm between the layers which can be considered as covalently bonded Ga_2 pairs. This unusual structure is also expressed in the very low melting point of 29.8 °C.

Tin has two modifications (Fig. 3.3) under ambient pressure conditions. Tetragonal metallic $\beta\text{-Sn}$ (*I4₁/amd*, $\rho = 7.285 \text{ g/cm}^3$) transforms at 13.2 °C to semi-metallic $\alpha\text{-Sn}$ with diamond structure (*Fd $\bar{3}m$* , $\rho = 5.769 \text{ g/cm}^3$) [1]. Both modifications are related *via* a *translationengleiche* symmetry reduction [6]. The phase transition usually proceeds slowly. However, if small nuclei of $\alpha\text{-Sn}$ have formed, the transformation proceeds rather fast and destroys the metallic $\beta\text{-Sn}$ (tin pest). Each tin atom in $\alpha\text{-Sn}$ has tetrahe-

dral coordination with 281 pm Sn–Sn. The coordination number in β -Sn is increased to $4 \times 302 + 2 \times 318$ pm.

Tin is a soft metal with good ductility and it is frequently used for tin foil (so-called silver-paper), e. g. capsules for wine bottles. When bending tin pieces small fractures remain at the surface and one notices a peculiar sound which is known as the tin cry which results from the friction of small crystallites in the β -modification. A sound reception of the tin cry can be obtained from the internet [7].

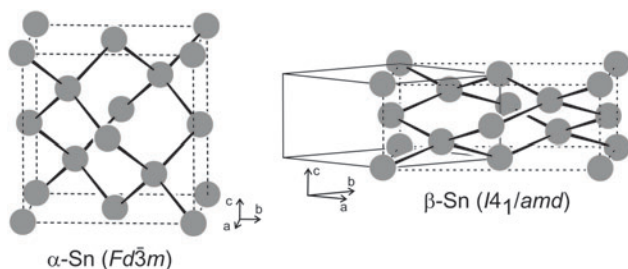


Fig. 3.3 The crystal structures of α - and β -Sn. For better comparison the tetragonal (full lines) and a sheared stuffed cubic cell (dotted lines) are shown for β -Sn.

α -Po (Fig. 3.4) has the simplest inorganic crystal structure. It crystallizes with a primitive cubic cell with one formula unit per cell and a space filling of 52 %. This structure type is at the border between close-packed elements and covalently bonded ones. Each polonium atom has regular octahedral polonium coordination (in direction of the p orbitals) with 336 pm Po–Po. β -Po is stable above 36 °C. It is a slightly rhombohedrally distorted variant of α -Po. The Po–Po distances of 337 pm are slightly longer and the bond angles of 98.2 and 81.8 ° $\angle$ Po–Po–Po significantly deviate from an ideal octahedron. A similar structure is observed for mercury with 299 pm Hg–Hg and 109.3 and 70.7 ° $\angle$ Hg–Hg–Hg.

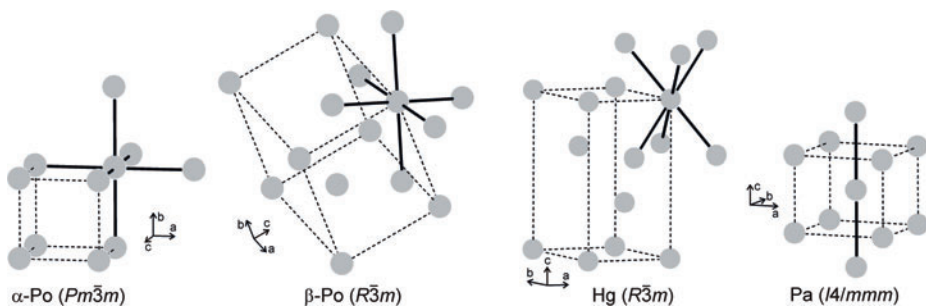


Fig. 3.4 The crystal structures of α - and β -Po, Hg, and Pa.

Protactinium (Fig. 3.4) crystallizes with a compressed version of the W structure with a c/a ratio of 0.82. This leads to changes in the near neighbor coordination. Instead of $8 + 6$ for tungsten we observe an $8 + 2$ coordination with Pa–Pa distances of 321 ($8\times$) and 324 pm ($2\times$). Much more complicated structures occur for α -U, β -U, and Np. Plutonium metal shows complex temperature and pressure driven phase transitions.

The most complex structure among the transition metals occurs for manganese. α -Mn (Fig. 3.5) crystallizes with a body-centered cubic structure with 58 atoms per cell. The four crystallographically independent manganese atoms have the following coordination numbers and ranges of Mn–Mn distances: Mn1, CN 12, 225–289 pm; Mn2, CN 13, 234–292 pm; Mn3, CN 16, 257–292 pm; Mn4, CN 16, 275–280 pm. The CN 12 and CN 16 coordination polyhedra belong to the Frank-Kasper family [8]. The drastically different ranges of Mn–Mn distances clearly underline, that the different manganese sites have different crystal chemical functions [9]. The β -Mn structure (high-temperature phase) (Fig. 3.5) adopts the chiral space group $P4_132$ with 20 atoms per unit cell: Mn2, CN 14, 258–327 pm and Mn1, CN 12, 236–268 pm, where both polyhedra show stronger distortion.

The structures of the elements not only react to temperature but also to external pressure, leading to different coordination modes and properties. In general, the application of pressure tends to delocalization of electrons. A well-known example is iodine. The covalently bonded structure of I_2 molecules transforms to metallic *fcc* iodine at around 30 GPa. Many of the rare earth elements change their stacking sequences under pressure, *e. g.* Pr and Nd from *hc* to *c* and Sm from *hhc* to *hc*. The stronger compression of the outer electron shells leads to a stronger influence of the *f* electrons which then force different stacking sequences. For iron, the polymorphism is not only driven by temperature but also by a change in the magnetic properties.

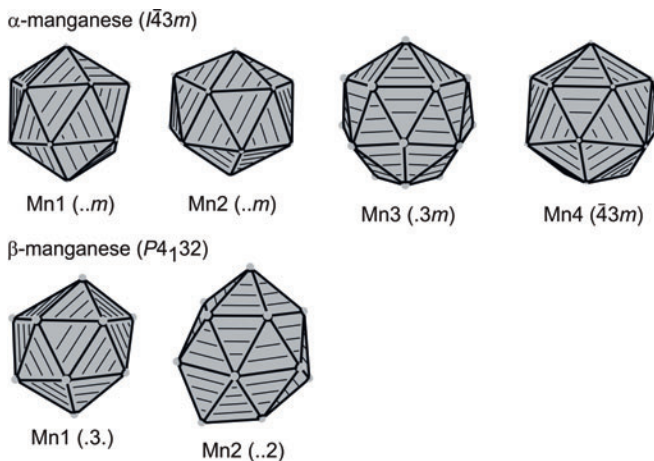


Fig. 3.5 The manganese coordination polyhedra in α - and β -manganese. The site symmetries are indicated.

Very interesting pressure-driven phase transitions have been observed for the alkali metals as well as silicon and germanium, with partly isotypic high-pressure phases [10]. Most of these investigations are quite young, since the experiments request diamond anvil cells with pressures in the order of 100 GPa and high-resolution synchrotron radiation with area detectors in order to get reliable data quality. The alkali metals are considered as free-electron systems and their transport properties are consistent with almost spherical Fermi surfaces. The application of external pressure changes the structures and the bonding properties fundamentally. The alkali metals lose their nearly free-electron character and with increasing density they more and more resemble monovalent *d* transition metals. The driving force for the destabilization of the highly symmetric normal-pressure structures is ascribed to the pressure-driven *s*→*d* transitions, leading to lower symmetric structures. The coordination modes in the high-pressure structures often resemble typical transition metal compounds. To give an example, the Rb-IV structure resembles the metal substructure of W₅Si₃.



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3.2 Alloys, Solid Solutions, Compounds

Having introduced the structures of the metallic elements, the next step in intermetallic chemistry consequently is the reaction between metals. In many general and

inorganic chemistry textbooks all these products are simply called alloys, whatever the composition and nature of chemical bonding is. Some words of rectification seem appropriate at this point.

High purity metals, especially the *fcc* ones are soft, ductile, and malleable. This property is advantageous for the production of gold leaf and diverse metal foils, but not for the production of work pieces for high mechanical claim. The pure metals are thus reacted with a second, a third, or even multiple elements in order to produce alloys with different properties. To give an example, copper for electrical conductivity purposes is used in almost pure form, while copper for construction purposes is alloyed in order to enhance hardness and workability. Generally pure metals have higher conductivity than alloys, while alloys are harder than the pure metals. Alloys are not only produced for enhancing the strength, corrosion and chemical stability, but also to design materials with well defined low melting points like Woods metal, $\text{Bi}_{50}\text{Pb}_{25}\text{Sn}_{12.5}\text{Cd}_{12.5}$ which has a melting temperature of 66 °C. Such materials are not the main point of the present book. For further reading on such materials we refer to special text books [1–8].

To our understanding, the term alloy is directly related to structural disorder. The small, medium or even larger amounts of the alloying elements can substitute on the sites of the metal structure itself or on different interstitial sites. The more alloying components are used in a material, the more complex is the structure. Technically important alloys are the many hundred steel varieties, the copper, lead, zinc, nickel, and tin alloys, the light-weight alloys on aluminum and magnesium basis, as well as a broad variety of special alloys like alkali metal alloys, nuclear reactor alloys, prosthetic alloys, precious metal alloys, or rare earth alloys. All these materials have well defined thermal, magnetic, electrical, and especially mechanical properties allowing a precise technical or medical application.

Alloys can have homogeneous or heterogeneous grain structures and they might show grain boundaries, hot cracks, or whisker growth. In many cases the main component metal directly reacts with one of the alloying components forming an intermetallic compound of defined composition. Such a compound formation is also called a precipitation and these grain structures may then be considered as composite materials, where the precipitation is embedded in the metal matrix. Cementite (Fe_3C) or stellite (Cr_{23}C_6) are typical precipitation components in steels, the stannides Cu_6Sn_5 , Cu_3Sn , Ni_3Sn_4 , Au_5Sn , AuSn , and AuSn_4 or the indides Cu_3In , Cu_9In_4 , Ni_3In , NiIn , Ni_2In_3 , Ni_3In_7 , Ag_3In , AgIn_2 , AuIn , AuIn_2 , Pd_3In , Pd_2In , PdIn , Pd_2In_3 , Pt_2In_3 , PtIn_2 , and Pt_3In_7 are typical precipitations in solder joints. The same holds true for many welded steel joints and light-weight alloys on aluminum and magnesium basis.

Solid solutions might be considered as a sub-group of alloys. They also show some kind of disorder, but one keeps a given structure type. This is possible, if the size of the different metal atoms does not differ by more than about 15 %. The most prominent example is the complete solid solution $\text{Ag}_{1-x}\text{Au}_x$. The metallic radii of silver and gold are similar and one can synthesize samples with all x values with statistical occupan-

cies on the sites of a *fcc* packing. Other examples concern the systems Cu-Ni, Mo-W, Na-Cs, or K-Rb. In some cases the elements are only partially soluble. Homogeneous melts can separate on solidification, leading to a composite with different grains.

Alloys and solid solutions should clearly be distinguished from intermetallic compounds. Metals with different size and different chemical potential react to varieties of binary, ternary and multinary intermetallic compounds with defined compositions and sometimes very small or even no homogeneity range. Such compounds can simply be ordered close-packed structures (Chapter 3.3) or compounds with directed chemical bonding with well defined charge transfer between the elements. This leads to covalent bonding contributions and brittleness. The structural chemistry, structural principles and some structure-property relations of such intermetallic compounds are the key topic of the present book.



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3.3 Ordered Close-packed Structures

The three types of closest (*fcc* and *hcp*) and close packing (*bcc*) have been briefly summarized in Chapter 3.1. A clear differentiation between solid solutions, alloys, and intermetallic compounds is given in Chapter 3.2. In the present chapter we focus on structures which derive from the *fcc*, *hcp*, and *bcc* aristotypes. Such structures are formed if the sizes of the two atom types or the chemical potential differ significantly. In going from a disordered phase to an ordered one, one observes a negative enthalpy. The corresponding structure shows optimized space filling and mostly a defined composition (stoichiometric ratio of the elements) and we call this an intermetallic compound. The formation of such an ordered arrangement is also driven by a maximization of bonding energy and a higher contribution to the lattice energy. Similar to ionic compounds, also in ordered intermetallics, one kind of atoms tends to coordinate the other one and vice versa. The most frequent two-dimensional ordering patterns for general compositions AB, AB₂, AB₃, and AB₄ are presented in Fig. 3.6.

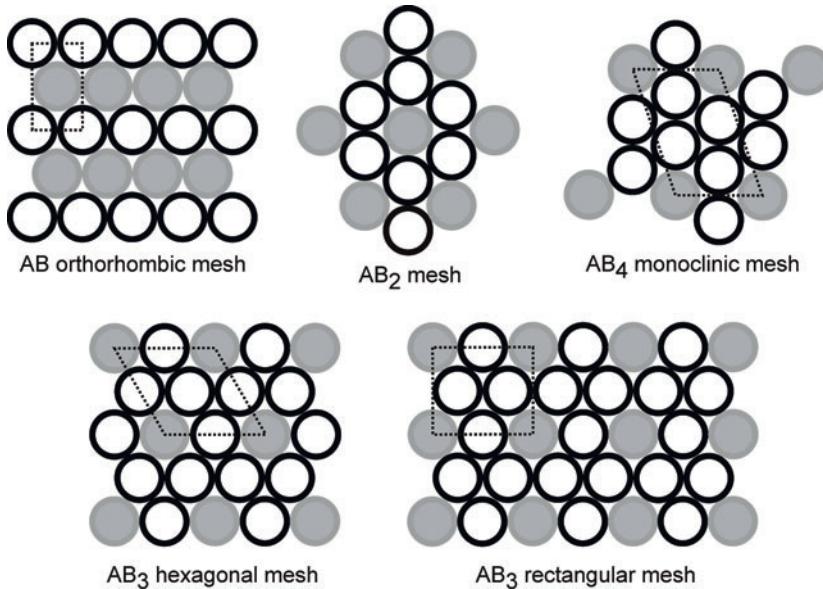


Fig. 3.6 The two-dimensional close-packed arrangements for compositions AB, AB_2 , AB_3 , and AB_4 . Relevant meshes that occur in the three-dimensional structures are emphasized.

For binary compounds AB_x with $x < 3$ it is not possible to surround each kind of atoms solely with the second one, although one can construct a two-dimensional ordering pattern AB_2 . In such structures direct A–A or B–B contacts are inevitable. Three different stacking variants of such ordered layers occur in the structure types $MoSi_2$, $CrSi_2$, and $TiSi_2$ (Chapter 3.9.2), however, not with the sequence of a closest packing. With $x \geq 3$ it is possible to construct ordered close-packed motifs without direct A–A and B–B contacts. Stacking of the two-dimensional AB, AB_3 , and AB_4 nets leads to many different structure types which all derive from one of the closest-packed structures. As examples, the structures of CuAu, Cu_3Au , $TiAl_3$, $ZrAl_3$, and $HfGa_2$ are presented in Fig. 3.7.

The superstructures of CuAu and Cu_3Au are textbook examples. Quenching of Cu–Au melts of 1:1 and 3:1 compositions leads to solid solutions with random Cu–Au occupancy, while slow cooling of these melts leads to well-ordered superstructures. This order-disorder phase transition is accompanied by a well-defined peak in the specific heat. The phase transition is driven by the difference in size between copper and gold with metallic radii of 128 and 144 pm, respectively. The random structure (statistical *fcc* arrangement) and the two superstructures are related by a group-subgroup scheme. The copper-gold ordering can be detected by X-ray powder diffraction. The powder patterns of quenched samples $Cu_{0.5}Au_{0.5}$ and $Cu_{0.75}Au_{0.25}$ show the simple fingerprint of a *fcc* structure. The calculated pattern for the high-temperature *fcc* phase of CuAu is shown in Fig. 3.8 (top). The Cu–Au ordering leads to a tetragonal distor-

tion ($c/a = 0.925$) and the *klassengleiche* symmetry reduction forces the formation of superstructure reflections. The latter are drawn in red color in the calculated powder pattern (Fig. 3.8 (bottom)). The 2θ shifts of the subcell reflections arise from the cubic-to-tetragonal distortion.

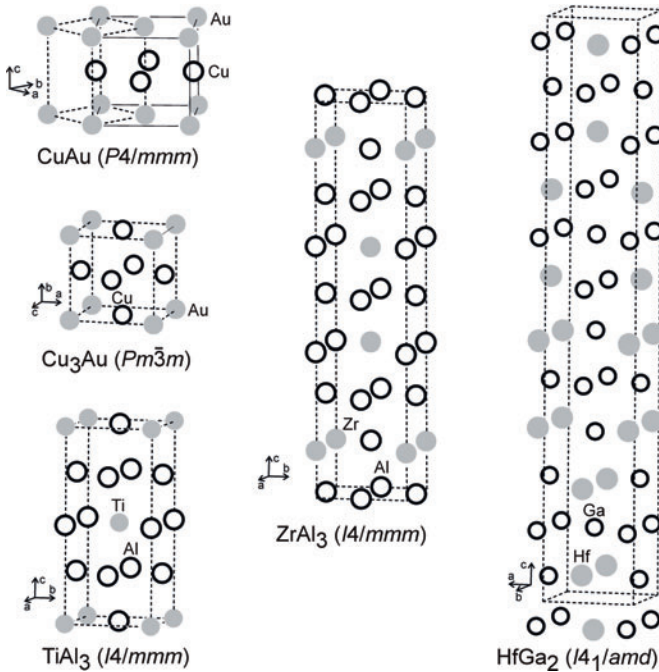


Fig. 3.7 The crystal structures of CuAu, Cu₃Au, TiAl₃, ZrAl₃, and HfGa₂. For CuAu a sheared cell is emphasized in order to underline the relationship with a *fcc* packing.

The Cu₃Au type is closely related to the perovskite structure insofar as the octahedral void remains empty. The Cu₃Au core corresponds to the CaO₃ substructure of CaTiO₃. Together, the Cu₃Au and CuAu types have several hundred representatives. These ordered variants are realized for transition metal binaries with *T* atoms of different sizes as well as binaries of a transition metal and a *p* element. Larger unit cells occur for the structures of TiAl₃, ZrAl₃, and HfGa₂. Here, 2, 4, and 6 *fcc* like cells are stacked in *c* direction. Again, the three structures derive from the *fcc* subcell by a group-subgroup relation [1]. The structures are all tetragonal. The *T*–*p* element ordering thus plays only on the *c/a* ratios of the *fcc* subcells which are slightly smaller or larger than 1. The titanium and zirconium atoms in TiAl₃ and ZrAl₃ have distorted cuboctahedral aluminum coordination. Since the Hf:Ga ratio in HfGa₂ is smaller than 3, one observes pronounced Ga–Ga bonding (283 pm).

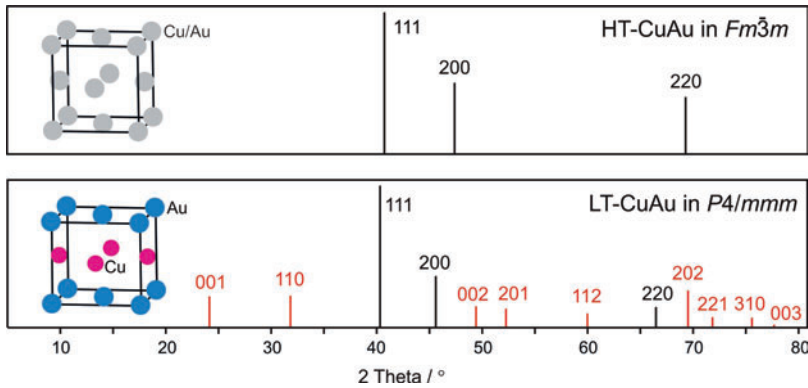


Fig. 3.8 Calculated powder patterns ($\text{CuK}\alpha_1$ radiation) for HT- and LT-CuAu. The hkl indices are given. Superstructure reflections for LT-CuAu are marked in red.

An interesting case occurs for MoNi_4 [2]. The quenched sample crystallizes with a *fcc* cell with Mo/Ni statistics. Annealing of the sample below the critical temperature of 1141 K leads to Mo/Ni ordering (Fig. 3.9). Each molybdenum atom has distorted cuboctahedral nickel coordination (254 pm Mo–Ni). The MoNi_4 structure also derives from an *fcc* subcell *via* three subsequent steps (t_3 , t_2 , and i_5) in the symmetry reduction [3]. These steps of symmetry reduction are the prerequisites for twin domains and antiphase boundaries. The latter have all been observed for MoNi_4 during detailed electron microscopic studies [4, 5]. Keeping the indices of the symmetry reduction steps in minds, one ends up with $3 \times 2 \times 5$ domain types [6].

Four structures that derive from the *hcp* subcell are presented in Fig. 3.10. Ni_3Sn , AuCd , and TiCu_3 have pure hexagonal stacking sequences of the ordered layers, while an *hcc* sequence occurs in the structure of TaRh . Several other mixed stacking sequences are possible. The coordination polyhedra in such structures are cuboctahedra in the cubic and *anti*-cuboctahedra in the hexagonal layers.

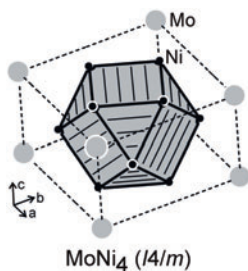


Fig. 3.9 The crystal structure of MoNi_4 . One distorted Mo@Ni_{12} cuboctahedron with a view approximately along the pseudo threefold axis is emphasized.

The structure of Ni_3Sn is the hexagonal equivalent to the Cu_3Au type with a 3:1 ordering on the *hcp* sites. Similar to Cu_3Au one observes distinct $\text{Ni}_{6/2}$ octahedra. The latter share common faces along the *c* axis and these rows build the motif of a hexagonal rod packing (Fig. 3.10). The Ni_3Sn structure is also the substructure of the hexagonal perovskite family with filled octahedral voids. An example is CsNiCl_3 with rods of face-sharing $\text{NiCl}_{6/2}$ octahedra. The coloring in the TiCu_3 structure leads to an orthorhombic distortion and no distinct copper octahedra. The equiatomic composition of AuCd and TaRh leads to homoatomic bonding as discussed above.

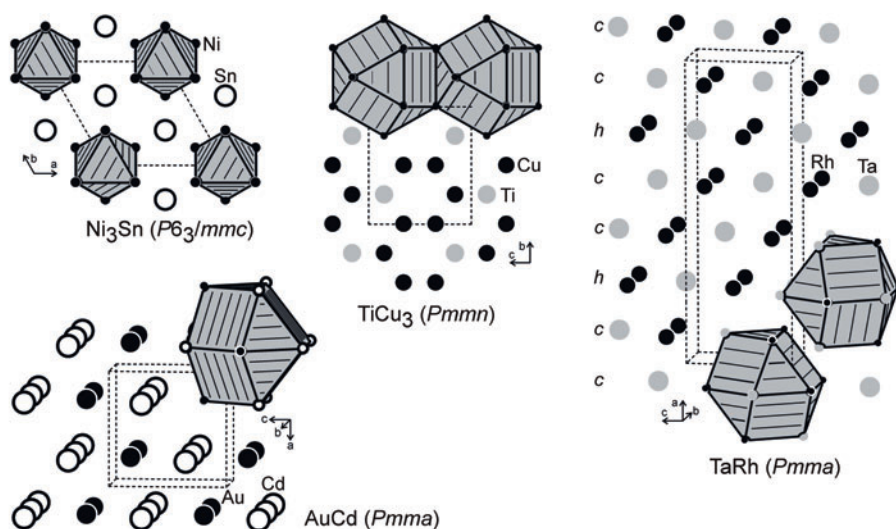


Fig. 3.10 The structures of Ni_3Sn , TiCu_3 , AuCd , and TaRh . The Ni_6 octahedra in Ni_3Sn and distorted cuboctahedra or *anti*-cuboctahedra are emphasized for the other structures.

The third large family of compounds concerns the superstructures of the W type. The simplest ordering variant concerns the 1:1 coloring, leading to the well-known CsCl type which is exemplarily shown for BePd in Fig. 3.11. The coordination number for each beryllium atom is $8\text{Pd} + 6\text{Be}$. For the ideal W-type structure the space filling is only 68 % (Chapter 3.1) and these W superstructures belong to the close-packed but not the closest-packed variants.

Also the structures of ZrAu_2 and Zr_2Au derive from the W type. The deviation from the equiatomic composition forces another ordering pattern, a tripling of the *c* axis with three successive distorted cubes. The difference in size between zirconium (160 pm) and gold (144 pm) leads to compressed cubes in ZrAu_2 ($c/a = 2.32$) while they are elongated in Zr_2Au ($c/a = 3.54$). Considering these drastic differences in chemical bonding, one should call these structures isopointal rather than isotypic [7–9]. The stacking of *bcc* subcells in *c* direction offers many coloring variants, e. g. the se-

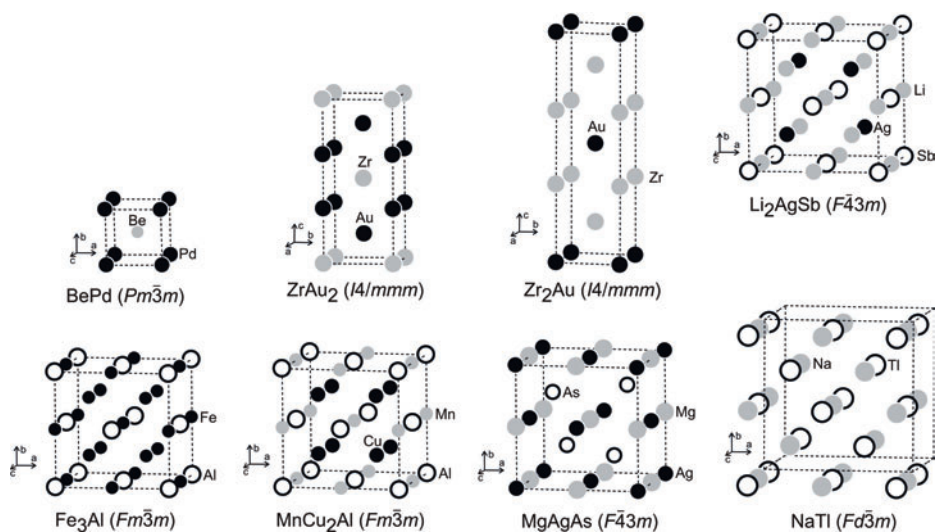


Fig. 3.11 The structures of BePd, ZrAu₂, Zr₂Au, Li₂AgSb, Fe₃Al, MnCu₂Al, MgAgAs, and NaTi.

ries of RE_2RuMg_2 , RE_2RuMg_3 , and RE_3Ru_2Mg compounds. Their structures derive from the aristotype by group-subgroup relations (Chapter 3.17) with tripled or quintupled cells [10, 11]. The most complex ordering pattern has been observed for Ta₉(S,Se)₄ [12], which shows an isomorphic superstructure of index 13. All of these superstructures show largely differing c/a ratios for the distorted subcell cubes, much smaller or much larger than 1. Thus, one observes a continuous decrease of the coordination number from $8 + 6$ for $c/a \approx 1$ to 12 (cuboctahedron) for $c/a \approx \sqrt{2}$ and this transition allows for a compromise between the cubic body-centered and the cubic closest-packing [9, 13].

The five remaining structures have another common geometrical building principle. Here the subcell is doubled in all three directions, leading to eight *sub*-cubes. All 16 sites are occupied in the unit cells of Li₂AgSb, Fe₃Al, MnCu₂Al, and NaTi. Li₂AgSb and NaTi are classical Zintl phases while Fe₃Al and MnCu₂Al are typical intermetallics. These few examples readily show the possibilities in bonding variations for this structural arrangement. Again, these coloring variants are only isopointal. Another Zintl phase is MgAgAs. Since magnesium and silver already deliver three valence electrons for the formation of As³⁻ Zintl anions, half of the tetrahedral sites remain unoccupied.

The structure of MnCu₂Al is the so-called Heusler phase [14] which is the prototype for hundreds of intermetallic compounds. These compounds attracted broad interest among physicists and chemists when the mining engineer *Fritz Heusler* discovered that it is possible to get a ferromagnetic material out of non-magnetic elements. Diverse substitutions on the metal sites in the Heusler structure effectively lead to changes in the magnetic ordering behavior [15, 16]. Also ferrimagnetic and antifer-

romagnetic ordering has been observed as well as giant-magnetoresistance [17] and good thermoelectric properties. Some of the Heusler compounds like YPd_2Sn show superconductivity at low temperatures. First-principles total energy calculations indicated that much more Heusler compounds with interesting magnetic properties might exist [18]. The most deeply investigated phases are MnT_2Ga ($T = \text{Co, Ni}$), MnT_2Al ($T = \text{Co, Ni, Cu, Pd}$), MnT_2In ($T = \text{Cu, Ni, Pd}$), MnT_2Sn ($T = \text{Cu, Ni, Pd}$), MnT_2Sb ($T = \text{Ni, Pd}$), MnCo_2Si , MnCo_2Ge , and Co_2FeSi .

The structural arrangement of MgAgAs might be considered as the ordered defect variant of the Heusler structure. These compounds are frequently called *half*-Heusler phases. They are studied in the same context as well as for topological insulators [19]. Since many of the *half*-Heusler compounds have almost similarly scattering elements, it is often difficult to determine the ordering of the atoms on the basis of X-ray diffraction, especially in the cases of extended solid solutions!

One of the most complex *bcc* superstructures is the ternary gallide $\text{V}_{11}\text{Cu}_9\text{Ga}_{46}$, a 512-fold superstructure ($8 \times 8 \times 8$ subcells) [20].



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3.4 Chemical Bonding

In spite of the rich empirical knowledge about the extremely diverse crystal chemistry and manifold physical properties, chemical bonding in intermetallic compounds is still only rudimentarily understood [1]. No comprising ordering scheme seems to be discernable, thus intermetallics apparently defy the generalities of chemical bonding concepts with its effective valence rules for covalent and ionic solids. However, chemists grow up with the conception of chemical bonding categorized into covalent, ionic, or metallic according to the Van-Arkel-Ketelaar triangle proposed in the 1950ies [2, 3]. Such an extreme diversification is relativized in the context of quantum chemical calculations, where in the end any solid state compound is reduced to a spectrum of energy eigenvalues based on the chosen basis set. It is this eigenvalue spectrum which inherently produces covalence, ionicity or metallicity in arbitrary combinations and with continuously varying contributions. In line with this it has been argued that the term metallic bond should be completely dropped because it is fully encompassed by electronic band structure theory and the broader concept of covalent bonding [4, 5]. Nevertheless it may be useful to maintain the extreme cases of ionic, covalent and metallic bonds in the ‘toolbox of solid state chemists’ [6] together with classical ideas of classifying solids by the Laves, Hume-Rothery, and Zintl concepts (see Chapters 3.5, 3.6, 3.7). However, especially intermetallic compounds teach us the limitations of all these descriptions, which effectively work only for certain classes of materials and completely fail for others. As mentioned above, quantum chemical approaches are independent from any preconceived definition of chemical bonding, and are therefore a good choice to improve our understanding of such complex materials. Many compounds have been studied using quantum theory of solids during the last decades, and it is merely impossible to even summarize only a fraction of the obtained results within this book. We will therefore briefly outline some characteristics of the metallic state of matter followed by short descriptions of the most popular quantum chemical methods that are widely used to analyze chemical bonding and physical properties of intermetallics. For more detailed information we refer to the literature. A comprehensive overview well suited for chemists is the textbook by *Dronskowski* [7].

3.4.1 The Metallic State of Matter

Crystal structures of elemental metals are dominated by close sphere packing (*ccp*, *hcp*, and *bcc*) with large coordination numbers. The principle of close packing remains generally important for intermetallic compounds, even though their structures often become very complicated in detail. Independent of the structure, the metallic state of a compound inherently emerges from certain features in the electronic band structure. The highest occupied electronic level (named the Fermi-level, ϵ_F) is within

at least one of the energy bands, thus at least one partially filled band exists. An important consequence is that occupied electronic states now exist at energies infinitesimally close to the Fermi-level, and unoccupied excited states are also infinitesimally close. In other words, the excitation energy of the electrons with energies $\varepsilon = \varepsilon_F$ is virtually zero. From this it becomes clear why in metals electrons remain mobile and conduct electricity even at temperatures close to absolute zero. It is very important to note that this virtually zero excitation energy concerns only few electrons in close vicinity of ε_F at room temperature. Because electrons are fermions (particles with half integer spins) they underlie the Pauli Exclusion Principle, and the occupation probability of a certain energy level $f(\varepsilon)$ is determined by Fermi-Dirac statistics. This function is plotted in Figure 3.12 for different temperatures. At absolute zero, the occupation probability $f(\varepsilon)$ drops abruptly from one to zero at ε_F .

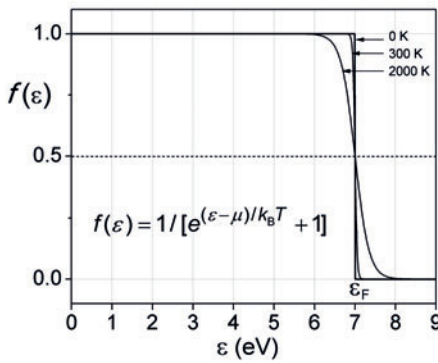


Fig. 3.12 The Fermi-Dirac distribution function plotted for different temperatures. The Fermi energy ε_F is at 7 eV; μ is the chemical potential which is equal to ε_F at $T = 0$ K.

If the temperature increases, a non-zero occupation probability of energy levels emerges above ε_F as shown in Fig. 3.12. The dotted horizontal line marks the probability 0.5 which cuts the curves for all temperatures exactly at the Fermi energy $\varepsilon_F = 7$ eV, which is the approximate value of copper metal. The Fermi energy ε_F is always a large energy. As an example, 7 eV corresponds to a Fermi-temperature $T_F = 8.13 \times 10^4$ K ($T_F = \varepsilon_F/k_B$), which is huge when compared to room temperature. Thus the fraction of excitable electrons with $f(\varepsilon) \neq 1$ is very small at ambient temperatures, approximately the total number of electrons multiplied by the factor T/T_F . In the case of copper this factor is $300 / 8.13 \times 10^4 \approx 0.0037$ at room temperature. Only this small fraction of the valence electrons actually contributes to the conduction electrons, because all others are 'stuck' and not allowed to change their energy level due to the Pauli Exclusion Principle. It is therefore not entirely correct to say that e. g. in copper one electron per Cu contributes to the conduction electrons according to $\text{Cu}^+ \cdot e^-$. From this one gets a

‘conduction’ electron density of $8.5 \times 10^{22} / \text{cm}^3$ which is often listed in textbooks. But this is the total electron density, while the actual conduction electron density is by some orders of magnitude smaller. This explains why the early Drude-Lorentz theory of metals which treated the electrons as a classical gas failed to describe properties like the specific heat of the electrons and the Pauli paramagnetism in metals. Both properties were predicted several magnitudes larger than the experimental values, because all electrons were considered to participate, which is not the case.

This short excursion into basic metal physics has an important consequence regarding concepts of chemical bonding in metals and intermetallic compounds. We have seen that typical physical properties of metals like electrical conductivity or Pauli paramagnetism emanate from a very small fraction (mostly $< 0.5\%$) of the valence electrons near ϵ_F . But the majority of electronic states below this small energy range are in band states which are principally not different from those in semiconducting or insulating materials. In terms of chemistry, all these states have bonding, non-bonding or antibonding characters no matter if the compound is metallic or not. There is no need to introduce a specific metallic bond. The only difference is that the metal has partially filled bands, which means that bonds in metals can be considered as unsaturated covalent bonds. Thus the electronic structure and its analysis in terms of chemical bonding can be treated by the same methods regardless whether the compound is a metal or not.

3.4.2 Approaches to Electronic Structure and Bonding in Extended Structures

Molecular orbital theory is among the most used and widely accepted approaches to chemical bonding in molecules. Pioneering work that has translated the electronic structure of extended solids into the language of the chemist’s orbital picture have been contributed by *J. K. Burdett* [8–10] and *R. Hoffmann* [11, 12] in 1980ies. Therein, the method to construct molecular orbitals through linear combinations of atomic wave functions (LCAO) was applied to extended solids by using Bloch wave functions which are delocalized over the entire crystal:

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}_i} e^{i\vec{k}\vec{R}_i} \varphi_n(\vec{r} - \vec{R}_i)$$

The Bloch wave function $\psi_{n\vec{k}}(\vec{r})$ is the symmetry-adapted linear combination of atomic wavefunctions (strictly speaking, a set of atomic wavefunctions is not orthogonal; therefore one often uses orthogonal Wannier functions as convenient basis for the expansion of electronic states; for details see [13]) φ_n under the action of the infinite translation group [9]. $\vec{R}_i$ with dimensions of length maps out a direct space, and $\vec{k}$ with dimensions of reciprocal length maps out a reciprocal space. The Bloch wave functions are solutions of the Schrödinger equation resulting in the energy disper-

sion $E(\vec{k})$ called the band structure. Such an expansion of the crystal orbitals as *Bloch* sums over a set of local atomic orbitals φ_n can be regarded as a small perturbation of tightly bound atomic states, therefore this approach is referred to as a *tight binding* (TB) method. A semi-empirical version is the Extended-Hückel (EH) method which is based on the Hartree-Fock formalism, but uses fixed orbital energies and expansion coefficients calculated by other methods or fitted to experimental data. The energy-independence makes this small basis set less flexible and allows only qualitative results. On the other hand EH calculations are often easy to grasp for chemists who are familiar with thinking in orbital interactions.

Going beyond the empirical methods, one faces basically two main difficulties: (i) Finding a very flexible but computationally feasible basis set, and (ii) managing the electron-electron interactions. In translational invariant systems, local basis functions like STOs (Slater-type orbitals) or GTOs (Gaussian-type orbitals) are rather unsuitable. However, the Bloch theorem already suggests appropriate basis functions, namely sets of plane waves (PW) of the type $e^{i(kr)}$. The problem is that the wave functions in the atomic core areas have many nodes and oscillate strongly, while they behave rather smooth in the interstitial areas between the atoms. Thus one needs a very large number of high energy plane waves for a reliable description of the core. Indeed the size of a pure PW basis of an atom scales with Z^3 which is computationally not manageable. Basically three methods are established to overcome this problem. The first is simply ignoring the core wave functions as in the empirical TB-approach. The second approach is using a so-called pseudopotential (PP), which still means ignoring the explicit core wave functions, but modifying (or better: simplifying) the core potential in a way that the wave function runs smoother also in the core. The third method is splitting the basis in core- and beyond-core functions. For this purpose a so-called muffin-tin sphere (MT) with radius r_{MT} around each atom is defined. Spherical harmonics are used inside and plane waves outside the MT sphere. A process called augmentation is used to ensure a continuous progression of the wave function at the sphere border r_{MT} .

Augmented plane waves (APWs) are extremely flexible basis sets, but the resulting nonlinear eigenvalue problem makes the APW method [14] slow. Linearization methods [15] have been developed that speed up the method, then called linearized augmented plane wave (LAPW) or FLAPW if the potentials inside the MT are not restricted to be spherical (full potential). FLAPW is among the most accurate methods for electronic structure calculations, but can get expensive for larger systems. In such cases pseudopotential methods are often the better choice. Especially the projected augmented wave (PAW) method [16] is frequently used, where the pseudopotential adapts to the electronic environment and is therefore less artificial than conventional PPs. Finally we mention the Korringa-Kohn-Rostoker (KKR) method which is based on scattering theory. A linearized form of the KKR approach is the linearized muffin tin orbital (LMTO) method [17], which is mostly used within the atomic sphere approximation (ASA) with space-filling MT spheres and spherical potentials. If the basis is transformed to a localized set one arrives at the TB-LMTO-ASA method [18, 19] which

enables tight-binding calculations from first principles. Due to the spherical potentials the method is extraordinarily fast. Equipped with tools for electron- and bond partitioning, TB-LMTO-ASA became quite popular for solid-state chemists. The serious drawback is that the ASA allows exclusively static calculations, thus no structural optimizations are possible.

We turn to the second problem, namely how to handle exchange and correlation. The Hartree-approach approximates the electron-electron interaction by considering the movement of one electron in the field generated by the total of the other electrons. Hartree-Fock includes the spin states (α/β or up/down spins) with respect to the antisymmetry of the wave function at electron exchange. Unfortunately, the bare HF method contains no correlation which causes serious problems especially for metals. So-called post-HF or HF-SCF methods were developed to improve HF through adding correlation. Examples are the configuration interaction (CI), coupled cluster (CC) or Møller-Plesset perturbation (MP) techniques. HF-SCF calculations of extended structures are generally possible but often quite expensive, *viz.* slow.

Today the workhorse for electronic structure calculations is based on density functional theory (DFT). The 1964 Hohenberg-Kohn theorem states that in a system with N electrons only one electron density $\rho(\vec{r})$ exists for one potential $V(\vec{r})$. Thus within DFT the N -particle problem is replaced by the self-consistent iterative solution of N one-electron Kohn-Sham (KS) equations. This is less difficult than solving the Slater determinant in the HF method, mainly because the KS functions are independent solutions of the Schrödinger equation. As basis sets for the KS equations serve either atomic functions or (mostly) plane waves. DFT is restricted to ground-state properties, and in some sense it moves the many-body problem to the exchange-correlation term of the potential $V_{XC}(\vec{r})$. The latter can be calculated exactly within DFT only for a constant electron density ρ , while for real varying electron densities $\rho(\vec{r})$ approximations are necessary. The most successful are the local density approximation (LDA) which assumes that $V_{XC}(\vec{r})$ is a function of the density $\rho(\vec{r})$, and the generalized gradient approximation (GGA) which takes also the gradients of $\rho(\vec{r})$ into account. Several flavors of LDA and GGA exist, among them the widely used PBE-GGA [20] as well as hybrid functionals like B3LYP [21] that incorporate a portion of exact exchange from Hartree-Fock theory with exchange and correlation from other sources.

In the end DFT is as accurate as the used $V_{XC}(\vec{r})$ parameterization scheme. LDA mostly overestimates bond strengths, and band gaps calculated with LDA- or GGA functionals are notoriously smaller than experimental values. Also Van-der-Waals forces which base on long range correlations in the electron density cannot be treated with standard DFT methods, while recently a semi-empirical dispersion correction to the GGA functional has been implemented [16]. Further difficulties occur in compounds with strong Coulomb interactions, so called highly correlated materials. What sounds exotic concerns many simple compounds like NiO or La_2CuO_4 and many others with partially filled $3d$ - or $4f$ -orbitals. The strong repulsion between electrons in spatially localized orbitals prevents them from moving at all, thus these compounds are

Mott-insulators even though conventional band structure methods predict them as metals. One method to circumvent this problem is to apply an extra potential U on the affected orbitals, which makes the orbital energy dependent on its occupation. The LDA+ U method [22] works for many 3d- and 4f-compounds, however, the U is rather an arbitrary parameter and makes the *ab-initio* aspect of DFT calculations at least questionable. Another approach is called dynamical mean field theory (DMFT) which is based on the spectral function of the solid and uses a local impurity model [23].

After the calculation of the band structure by any method, tools are necessary to analyze the often complicated dispersion relations (spaghetitis) in terms of chemical bonding. The perhaps most decisive one for solid-state chemists were already introduced by *Ronald Hoffmann* within the EH method. A bonding indicator was constructed by generating an overlap population weighted density of states, the crystal orbital overlap population (COOP) [11]. It adopts positive values (bonding, because of the positive overlap population) and negative values (which identify antibonding interactions). Similar partition schemes have been developed for DFT methods, where the overlapping orbital picture actually gets lost, especially when plane wave basis sets are used. The Crystal Orbital Hamilton Population (COHP) [24] is an energy partition scheme (in contrast to the electron partitioning COOP), which calculates the energy contributions of the electronic states of a selected pair of atoms to the total electronic energy. Bonding interactions lower, antibonding ones increase the energy, therefore the signs of COHP and COOP are reversed and one usually plots $-COHP$ against the energy. Very recently a method to analyze chemical bonding in terms of COHP and COOP from the output of DFT calculations with plane wave basis sets has been reported and implemented [25]. Therein, the plane wave functions are projected onto Slater-type orbitals, which reconstruct the more chemical view of bonding.

Meanwhile a large number of electronic structures of intermetallic compounds have been analyzed by the COOP [26–28] or COHP [29–32] method, which cannot be discussed in here. A very instructive example is given in [33].

Beyond these momentum space based bonding indicators, also real space visualization tools have been developed which analyze directly the electron density [34]. The latter is an observable quantity (in contrast to orbitals), thus these methods are also applicable to experimentally determined electron densities. A real space partitioning scheme is the electron localization function (ELF), which is the pair probability of like spins $p\uparrow\uparrow(r,r')$, which in some sense measures the Pauli repulsion. It was originally proposed within HF theory [35] and later generalized for DFT methods [36]. ELF values are typically normalized to unity so that high values mean a high probability of paired electrons at a certain position in the unit cell and vice versa. Indeed the ELF provides descriptive images of chemical bonding, which mostly fit very well to chemical intuition [37]. The other popular electron partitioning scheme is the atoms-in-molecules (AIM) approach [38, 39]. It uses the gradients of the density ($\nabla\rho$) and defines zero-flux surfaces ($\nabla\rho\cdot\vec{n}=0$) as bonds for the atoms. The density inside these ‘basins’ is integrated and provides the Bader-charge and the shape of the atom. Bonding is described

in terms of critical points in the electron density where the gradient vanishes ($\nabla p = 0$), and is characterized by the properties of the Laplacian $\nabla^2 p$ at this point. Distinctions are made between bond critical points, ring critical points, and cage critical points according to the components of the Laplacian. As an example, chemical bonding of the intermetallic carbides Sc_3FeC_4 and Sc_3CoC_4 has been analyzed by the AIM formalism using both experimental and calculated electron densities [40].

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3.5 Hume-Rothery Phases

The so-called Hume-Rothery phases [1] are a large number of intermetallic compounds whose structures solely depend on the valence electron concentration, not on the composition of a given phase. They have been named after the British metallurgist *William Hume-Rothery*. The best example for explanation of the Hume-Rothery rule is the phase sequence of intermetallics in the Cu–Zn phase diagram (brass phases). Fig. 3.13 shows the phase sequences schematically. Copper with a valence electron concentration (VEC) of 1.0 adopts a *fcc* structure and zinc with VEC = 2.0 crystallizes with the hexagonal-closest packing.

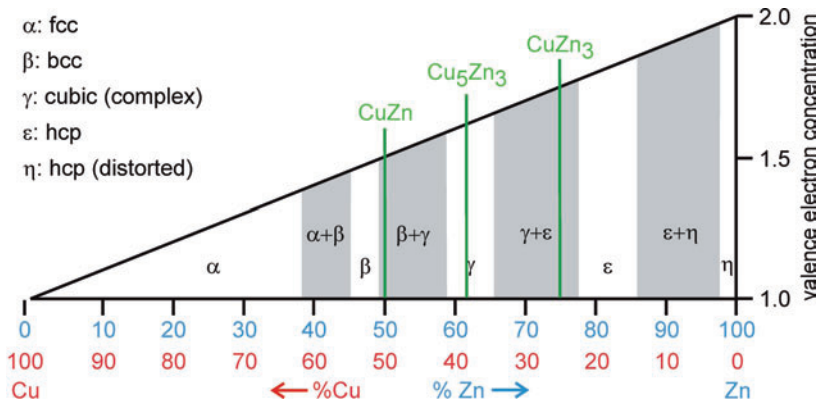


Fig. 3.13 Sketch of the phase sequences in the copper-zinc phase diagram at room temperature. Formation of the Hume-Rothery phases depends on the valence electron concentration. The biphasic areas are shaded in light gray. For details see text.

Copper can form a solid solution with zinc. Up to about 38 % of the copper sites can be substituted, keeping the *fcc* structure (α phase), leading to an increase of VEC. Increasing the zinc content leads to formation of the β phase (45–49 % Zn) whose structure derives from the *bcc* arrangement. CuZn crystallizes with the ordered primitive CsCl-type structure below 740 K, while disorder (*bcc* W type) occurs above. Close to the composition Cu_5Zn_8 one observes the γ phase (58–66 % Zn) which adopts a complex cubic structure with 52 atoms per unit cell. This structure can be considered as an ordered version of the *bcc* type; $3 \times 3 \times 3$ *bcc* subcells form the superstructure cell with 54 atoms. In the ordered version two of the 54 sites remain unoccupied.

The ϵ phase is realized from 78–86 % Zn, close to the composition CuZn_3 . Its structure derives from a hexagonal-closest packing. Finally one gets the *hcp* η phase. In contrast to copper, zinc can only dissolve about 2 % Cu. The difference in structure of the Hume-Rothery phases has direct consequences on the mechanical properties. Pure copper is a ductile and forgeable element. Alloying with zinc leads to an enhancement of the hardness. The γ and ϵ phases are brittle. The brass phases that are technically used (cast brass and diverse utensils) have up to 41 % Zn content.

The VEC (the average number of valence electrons per atom) of Hume-Rothery phases are calculated with the following valences: (i) 0 for transition elements with non-filled *d*-shells, (ii) 1 for Cu, Ag, Au, (iii) 2 for Mg, Zn, Cd, Hg, (iv) 4 for Sn, Si, Ge, and (v) 5 for Sb. Table 3.1 gives some examples for β , γ , and ϵ phases. The striking VECs for these phases are 21/14 for the β , 21/13 for the γ , and 21/12 for the ϵ phases.

Table 3.1 VECs for selected Hume-Rothery phases with the β , γ , and ϵ structures.

Composition	No. VE	No. Atoms	VEC
β phase			
CuZn	1 + 2	2	3:2 = 21/14
Cu_3Al	3 + 3	4	6:4 = 21/14
γ phase			
Cu_5Zn_8	5 + 16	13	21/13
Cu_9Al_4	9 + 12	13	21/13
ϵ phase			
CuZn_3	1 + 6	4	7:4 = 21/12
Au_5Al_3	5 + 9	8	14:8 = 21/12

If one surpasses a certain VEC value, one observes a switch in structure type. All of the Hume-Rothery phases show at least small homogeneity ranges. Extended biphasic

ranges occur in the phase diagram (Fig. 3.13). The decisive role of the valence electron concentration is also paralleled by the solubility of different metals in the copper structure. Zinc with only two valence electrons dissolves up to about 38 %, while aluminum and gallium with three valence electrons show much smaller solubility of 20 %. In going to tetravalent germanium and tin the solubility decreases to 12 and 9 %, respectively. All these phases have VEC between 1.28 and 1.41, in agreement with the requirements for the α phase.



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3.6 Laves Phases

The Laves phases are named after the German mineralogist *Fritz Laves*, one of the pioneers in crystal chemistry of intermetallics [1–3]. A memorial issue was published in *Z. Kristallogr.* (issues 5–7, 2006) on the occasion of Laves' 100th birthday, summarizing state-of-the-art work on Laves phases and further intermetallics. Today more than 4000 entries occur in the *Pearson Crystal Data Base* [4] for the prototypes MgCu_2 , MgNi_2 , and MgZn_2 (Fig. 3.14) [5]. More than 60 % of these compounds contain a rare earth element, which is favorable in view of their magnetic properties. An overview on the binary rare earth containing Laves phases has been given recently [6]. The diverse structural facets of the Laves phases have been summarized [7, 8 and references therein]. Although the Laves phases have first been discussed nearly one hundred years ago, this research topic is still broadly covered. Several of the Max-Planck Institutes recently started a joint program (laves.mpie.de) for the theoretical and experimental investigation of the nature of Laves phases in order to get a deeper understanding of some fundamental questions.

The Laves phases have the general composition AB_2 and they can be considered as line-compounds without noticeable homogeneity ranges, in contrast to the Hume-Rothery phases. The structures are closely packed and they form with a typical ratio of the atomic radii of $r_A/r_B = (3/2)^{1/2} \approx 1.225$. An inspection of all known Laves phases reveals that the AB_2 compounds form in the range from about 1.1 to 1.7. The three representative structure types shown in Fig. 3.14 have common structural principles. The transition metal atoms form tetrahedra and the latter are condensed to three-dimensional networks *via* common corners and/or common faces. In the cubic MgCu_2 type the condensation proceeds exclusively *via* common corners and consequently each copper atom belongs to two tetrahedra. The magnesium atoms fill large cavities left by the tetrahedral network and the magnesium substructure

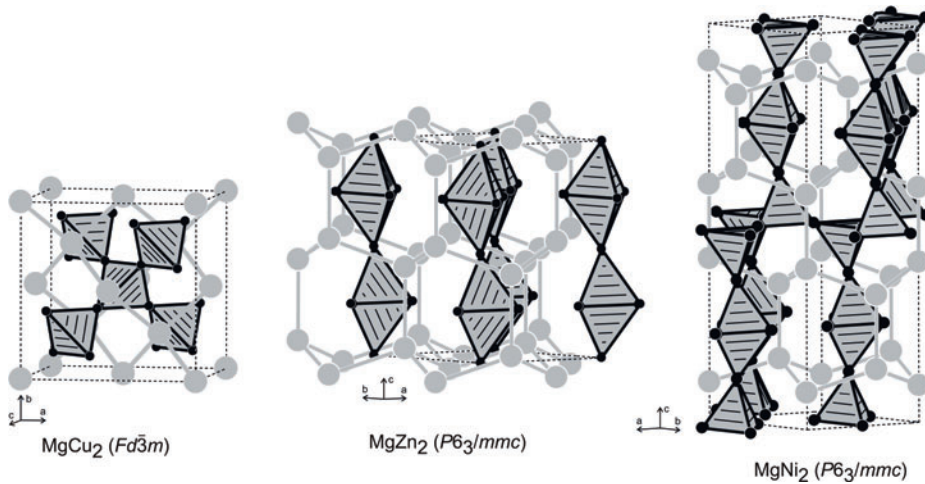


Fig. 3.14 The crystal structures of the Laves phases MgCu_2 , MgZn_2 , and MgNi_2 . Magnesium and transition metal atoms are drawn as light gray and black circles, respectively. The networks of condensed $T_{A/4}$ tetrahedra are emphasized. The magnesium substructures are indicated by light gray lines which do not correspond to chemical bonds.

is of a diamond type. The magnesium atoms have CN 16 (12 Cu at 291 and 4 Mg at 304 pm) and the copper atoms CN 12 (6 Cu at 248 and 6 Mg at 291 pm). Both polyhedra belong to the Frank-Kasper family [9]. These coordinations also occur in the structures of MgZn_2 and MgNi_2 , however, with a different connectivity of the polyhedra. In the hexagonal MgZn_2 structure the Zn_4 tetrahedra share corners and triangular faces and the magnesium substructure corresponds to hexagonal diamond (the mineral lonsdaleite). The structure of MgNi_2 is the most complex one. It contains motifs of both the MgCu_2 and MgZn_2 types. Examples for the three types of Laves phases are given in Table 3.2. Some more complex stacking variants have been observed [10].

Table 3.2 Selected examples for Laves phases.

MgCu_2 type	MgZn_2 type	MgNi_2 type
CaAl_2	CaLi_2	TaCo_2
CaIr_2	TaFe_2	ScFe_2
CeCo_2	CeMn_2	HfMo_2
ZrMo_2	ZrRe_2	TaZn_2

Although the criterion for formation of the Laves phases is a purely geometrical one that works well, the influence of electronic factors cannot be neglected. This point

has repeatedly been discussed [7, 11], however, no general electronic concept exists. Nevertheless one has to keep in mind that the Laves phases cover a very broad range of composition, compounds where A and B have small as well as those with large electronegativity differences. A typical pair would be $\text{CaLi}_2 \leftrightarrow \text{CaIr}_2$. These differences certainly impose shifts in electron density, inducing covalent bonding portions.

Besides the many binary Laves phases and several phases from solid solutions, also ordered ternary compounds with well-defined compositions are known. One example for the hexagonal phases is the structure of $\text{Mg}_2\text{Cu}_3\text{Si}$ [12], where the copper and silicon atoms are ordered within the tetrahedral network. A second possibility is an ordered replacement on the magnesium site. For the cubic structure type this is realized in the MgCu_4Sn ($\equiv \text{Mg}_{0.5}\text{Sn}_{0.5}\text{Cu}_2$) structure [13, 14]. The magnesium/tin ordering results in a symmetry reduction from centrosymmetric $Fd\bar{3}m$ to non-centrosymmetric $F\bar{4}3m$. This structure type has more than 100 representatives [4].



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3.7 Zintl Phases

Zintl phases form with an electropositive metal (alkali, alkaline earth, or rare earth element) and a half-metal of the *p* block. Formally, the electropositive metal transfers

valence electrons to the p element and the latter forms an anionic substructure that corresponds to the structure of an element with the same valence electron configuration. The resulting connectivity is given by the $8-N$ rule where N is the number of electrons at the p element. Such compounds generally form with elements that are on the left- and right-hand part of the so-called Zintl-line. This line runs in between the third and fourth main group of the Periodic Table.

The calcium-silicon system is an excellent example for explaining the Zintl principle. Let us take the silicides Ca_2Si , CaSi , and CaSi_2 . The calcium atoms donate two valence electrons to the silicon atoms. This way we obtain the electron-precise descriptions $(2\text{Ca}^{2+})\text{Si}^{4-}$, $\text{Ca}^{2+}\text{Si}^{2-}$, and $\text{Ca}^{2+}(\text{2Si}^-)$ with distinctly different charges on the silicon atoms. The Si^{4-} anions have a filled octet, similar to argon. Consequently one observes no Si–Si bonding in the Ca_2Si structure. Each silicide anion has tricapped trigonal prismatic calcium coordination. The CaSi structure contains Si^{2-} anions that are formally isoelectronic with sulphur. Again, each silicon atom has trigonal prismatic calcium coordination, but these prisms are condensed *via* common rectangular faces, leading to silicon zig-zag chains. In calcium disilicide one obtains a formal charge of -1 per silicon atom. This results in three-connected silicon atoms that are arranged in a puckered network of hexagons, similar to gray arsenic. The three structures are summarized in Fig. 3.15.

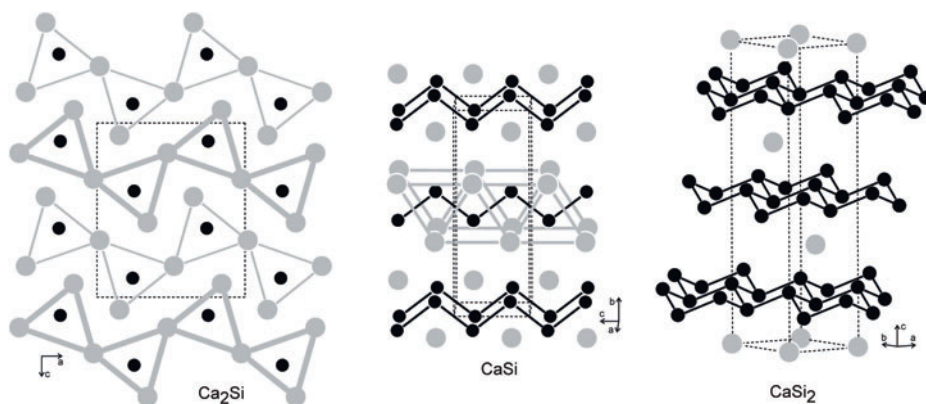


Fig. 3.15 The crystal structures of Ca_2Si , CaSi , and CaSi_2 . Calcium and silicon atoms are drawn as medium gray and black circles, respectively.

The Zintl concept can only predict the connectivity pattern based on the VEC of the Zintl anion, not the concrete structure type. Figs. 3.16 and 3.17 give two examples. For both, BaGa_2 and CaIn_2 we get Ga^- and In^- Zintl anions with an electron count that matches with the fourth main group. The gallium atoms in BaGa_2 build up two-dimensional networks like in graphite while the indium atoms in CaIn_2 form puckered hexagons in ABAB stacking sequence like in hexagonal diamond, lonsdaleite.

The second example concerns the disilicides of calcium, strontium, and thorium. The silicide polyanions are three-dimensional in SrSi_2 and $\alpha\text{-ThSi}_2$ but two-dimensional in CaSi_2 with three-connected silicon in each structure.

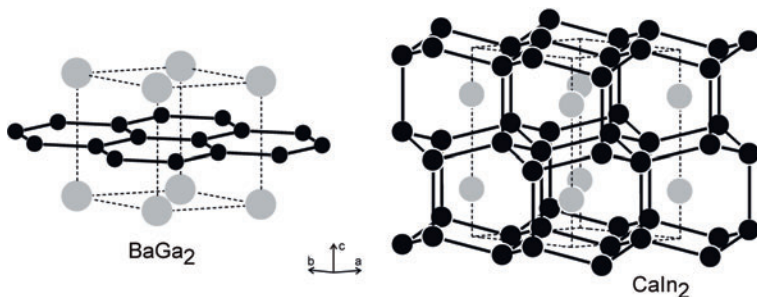


Fig. 3.16 The crystal structures of BaGa_2 and CaIn_2 . Calcium (barium) and indium (gallium) atoms are drawn as medium gray and black circles, respectively. The gallium and indium networks are emphasized.

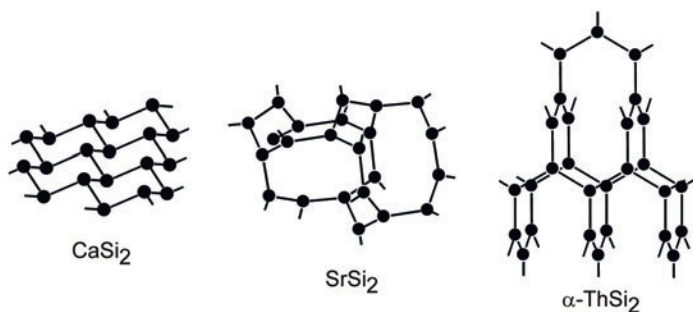


Fig. 3.17 The silicon substructures of CaSi_2 , SrSi_2 , and $\alpha\text{-ThSi}_2$.

The essential ideas of this concept are the merit of *Eduard Zintl*, one of the pioneers in the field of synthesis and crystal chemistry of intermetallic compounds. The fundamental work was already published in 1933 [1]. Later on the concept was extended by *Klemm* and *Busmann* [2]. The huge variety of binary alkali and alkaline earth metal Zintl phases has been summarized by *Schäfer*, *Eisenmann* and *Müller* [3]. *Zintl* studied the solubility of metal halides in liquid ammonia with sodium solutions in the same solvent and investigated these systems by potentiometric and conductometric titrations. These studies led to the assumption that negatively charged ions of diverse elements are possible. *Zintl's* merits were not only the crystal chemical significance of these findings but also the high quality of experimental standard for handling extremely moisture sensitive samples for Debye-Scherrer diagrams and other physico-

chemical characterizations. The key points of these achievements are summarized in [4]. Meanwhile a huge number of binary and ternary Zintl phases exist. Table 3.3 lists selected phases with respect to the dimensionality of the Zintl anion.

Table 3.3 Selected examples for Zintl phases.

Compound	No. VE	Formal charge	Connectedness	Anionic substructure
isolated Zintl anions				
Ca_2Si	4	4–	0	Si^{4-}
Na_3As	5	3–	0	As^{3-}
pairs				
Ca_5Si_3	4/3	4–/3–	0/1	Si^{4-} and Si_2^{6-} pairs
Yb_2MgSi_2	3	3–	1	Si_2^{6-} pairs
clusters				
Na_4Si_4	4	1–	3	Si_4^{4-} tetrahedra
chains				
CaSi	4	2–	2	zig-zag-chains
LiAs	5	1–	2	spiral chains
rings				
InP_3	5	1–	2	P_6^{6-} chairs
layers				
CaSi_2	4	1–	3	puckered hexagons
networks				
NaTl	3	1–	4	diamond network
BaGa_2	3	1–	3	graphite network

Zintl phases can be synthesized by different routes. In the early work of *Zintl* the alkali metals were dissolved in liquid ammonia and reacted with the *p* group element. Since such reactions were often slow, the *p* element salts were used. A typical reaction in liquid ammonia is $22\text{Na} + 9\text{PbI}_2 + n\text{NH}_3 \rightarrow \text{Na}_4\text{Pb}_9 \cdot n\text{NH}_3 + 18\text{NaI}$. That way many of the Zintl phases were obtained only as ammoniates which decomposed when releasing the ammonia. Meanwhile many of these compounds have structurally been characterized, *e. g.* in the *Korber* group [5]. Most of the binary and ternary Zintl phases have directly been synthesized from the elements. Usually niobium and tantalum were used as crucible materials. Further possibilities are

metathesis reactions or electrochemical synthesis (cathodic dissolution of precursor compounds).

The Zintl phases listed in Table 3.3 mostly have the same connectivity for all atoms within the Zintl polyanion. Besides there exist several examples of polyanions with different connectivities. Selected binary compounds are presented in Fig. 3.18. The binary antimonide $\text{Sr}_2\text{Sb}_3 \equiv \text{Sr}_4\text{Sb}_6$ contains a six-membered chain. The four antimony atoms within the chain have the formal oxidation number -1 and a connectivity of 2, similar to the atoms in elemental tellurium with spiral chains. The terminal ones have the formal oxidation number -2 and consequently have only one antimony neighbor. The chain then has a formal charge of -8 , compensating for the eight valence electrons delivered from the strontium atoms. The butterfly-type $[\text{Si}_4]^{6-}$ polyanion in Ba_3Si_4 has silicon in the formal oxidation states -1 and -2 and a Si–Si bond in between.

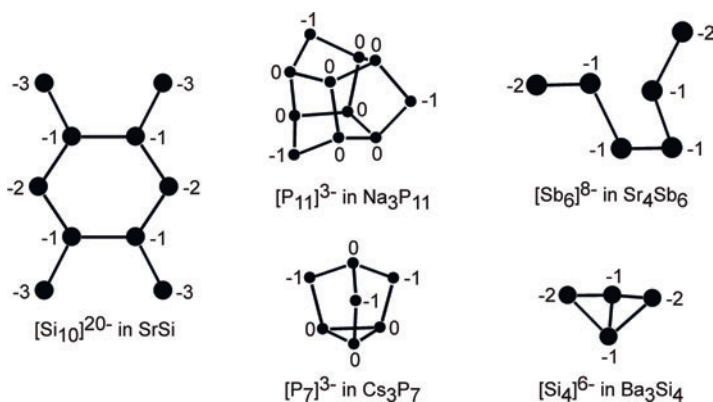


Fig. 3.18 Zintl anions in the structures of SrSi , Na_3P_{11} , Cs_3P_7 , Sr_4Sb_6 , and Ba_3Si_4 . The formal charges are indicated.

The polyphosphides Na_3P_{11} and Cs_3P_7 contain cluster-like Zintl anions $[\text{P}_{11}]^{3-}$ and $[\text{P}_7]^{3-}$. In both clusters only the two-connected phosphorus atoms have the formal charge -1 . $[\text{P}_7]^{3-}$ is isoelectronic with P_4S_3 . Although equiatomic SrSi has a comparatively simple composition, its Zintl anion is rather complex with silicon in three different formal oxidation states. Six silicon atoms build up a Si_6 hexagon which connects four terminal silicon atoms. The three-, two-, and mono-connected silicon atoms have formal charges of -1 , -2 , and -3 , and they are isoelectronic with P, S, and Cl, and the electron-precise description is $10\text{Sr}^{2+}[\text{Si}_{10}]^{20-}$.

Examples for heteropolyanions are shown in Fig. 3.19. The structures of Na_5SiP_3 and Ba_4SiAs_4 contain isolated Zintl anions $[\text{Si}_2\text{P}_6]^{10-}$ and $[\text{SiAs}_4]^{8-}$. In both cases the silicon atoms keep coordination number 4 and the pnictide atoms are either bridging (formal oxidation number -1) or terminal (formal oxidation number -2). A

chain-like polyanion occurs in K_2SiP_2 . Four phosphorus atoms coordinate to silicon and these tetrahedra are *trans*-edge-shared with phosphorus in the formal oxidation -1 . The $[\text{SiP}_2]^{2-}$ substructure is isostructural to binary SiS_2 .

The tin and arsenic atoms in KSnAs form puckered hexagons like in the structure of elemental gray arsenic. The valence electron of potassium is transferred to the tin atom and the Sn^- Zintl anion is then isoelectronic with arsenic enabling the three-connected network. A similar structural motif occurs in $\text{Sr}(\text{SnAs})_2$. Here, the strontium atoms deliver two valence electrons. Consequently one observes two subsequent $[\text{SnAs}]^-$ layers that are separated and charge-balanced by layers of strontium cations. The gallium atoms in LiGaGe obtain the valence electron of the lithium atom. Then, the Ga^- anions are isoelectronic with germanium thus forming the wurtzite-like tetrahedral network, a heteropolyanion with lonsdaleite-like structure.

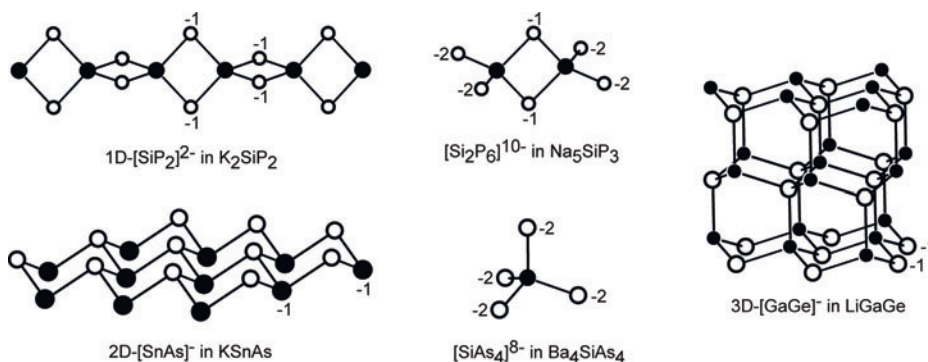


Fig. 3.19 Zintl anions in the structures of K_2SiP_2 , KSnAs , Na_5SiP_3 , Ba_4SiAs_4 , and LiGaGe . The formal charges are indicated.

Some compounds contain Zintl-like anions, however, the overall structure does not fulfill the Zintl rule. This is the case for the structure of the calcium-rich germanide Ca_7Ge (Chapter 3.9.3) which contains isolated Ge^{4-} anions. Since only two calcium atoms are requested for transfer of sufficient electron density, one can describe the structure as $\text{Ca}_2\text{Ge} \cdot 5\text{Ca}$. One can consider the Zintl phase as embedded in a metallic matrix of calcium, similar to the description of subnitrides (Chapter 3.10.1) and suboxides (Chapter 3.11.1). Many other binary phases containing Zintl anions show such behavior, often leaving only few excess valence electrons. The crystal chemical details and consequences on chemical bonding of such compounds at the Zintl border have been reviewed by *Miller* [7]. High-pressure phases like GdSi_5 , CeSi_5 , or Ce_2Si_7 [8] also belong to this family. They show silicon atoms with increased coordination numbers. Also the high-pressure phase EuSi_6 [9] shows four-connected silicon and the formal electron count is $\text{Eu}^{2+}[\text{Si}^0]_6 \cdot 2e^-$, leading to metallic behavior.



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3.8 Group III Elements

3.8.1 Borides

Boron reacts with metals forming a large diversity of binary, ternary and multinary borides [1, 2]. These materials are available either through direct reactions of the elements or through metallothermic or electrochemical reactions. However, the synthesis of pure materials is not that simple. According to the Tammann rule for solid state reactions, sufficient reaction velocity (a sufficiently high diffusion rate) is achieved at around 70–80 % of the melting point. Since boron has a comparatively high melting point, especially reactions with the low-melting alkali and alkaline earth metals are difficult to handle [3, 4]. Through pure powder metallurgical techniques (sintering reactions) it is often difficult to obtain single crystals, a noticeable disadvantage for structure determination. The use of low-melting metal fluxes (Chapter 2.7) is a useful technique for the explorative synthesis of borides.

The many crystal structures of metal borides are best classified by the boron substructures which cover a very broad range from isolated boron atoms (*i. e.* no B–B bonding) to complex three-dimensional networks with polyhedral substructures. In Fig. 3.20 we give a schematic overview on the most frequent boron substructures in metal borides. Some of these motifs, especially the layers, occur sometimes in puckered form. Many borides contain two or even three different boron substructures.

In very metal-rich structures, the boron atoms fill octahedral voids of the metal substructure. These borides can be considered as interstitial compounds. There is no change of the metal substructure. If the boron content increases slightly, the metal-

boron coordination switches from octahedral to trigonal prismatic, the typical boron coordination. Isolated boron atoms in trigonal prismatic coordination occur in metal borides of the general compositions T_4B , T_3B , T_2B , T_5B_2 , T_5B_3 , or T_7B_3 . The Re_3B structure is given as an example in Fig. 3.21. Such metal-rich borides are mostly accessible *via* direct arc-melting of the metal with boron. $Nd_2Fe_{14}B$ is one of the technically important metal-rich borides since it has excellent properties as permanent magnetic solid. This ternary boride paved the way for a new series of permanent magnetic materials. Several iron- and cobalt-rich rare earth-based compounds with boron, carbon, or nitrogen in octahedral or trigonal prismatic voids are today's hard magnetic materials (Chapter 4.1).

Increasing boron content leads to B_2 pairs, then to linear or zig-zag chains, branched chains, double or triple chains, and finally planar or puckered layers. Boron-rich borides contain octahedral, cuboctahedral, or icosahedral boron polyhedra which can be condensed directly or *via* bridging B_2 units.

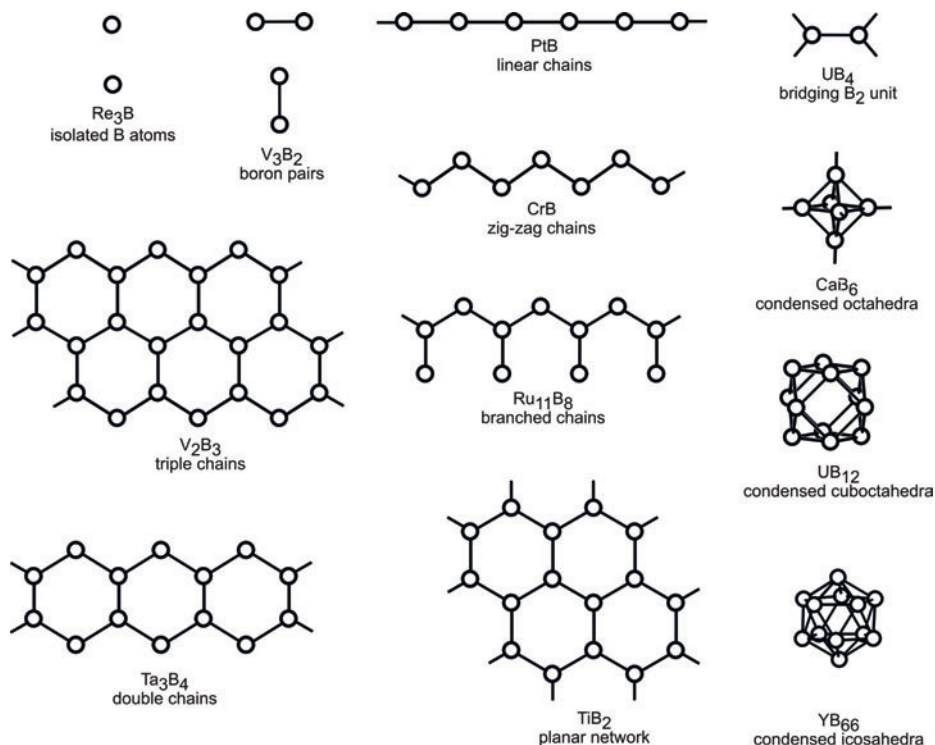


Fig. 3.20 The most frequent boron substructures in metal borides. A representative compound for each motif is given.

The Re_3B structure type (Fig. 3.21) occurs only for few borides [5]. The two crystallographically independent rhenium sites can be substituted in an ordered manner by two different elements, leading to the MgCuAl_2 type [6], the so-called S-phase structure, one of the important precipitation phases in modern magnesium and aluminum based light-weight alloys. Another important binary boride with isolated boron atoms is Ni_3B with the cementite (Fe_3C type) structure, also with a trigonal prismatic coordination.

Increasing the boron content one observes first pair formation and then smaller chains. The structures of Mo_2FeB_2 (181 pm B–B) and Mo_2IrB_2 (182–183 pm) are shown in Fig. 3.21. Again, the boron atoms have trigonal prismatic metal coordination. Mo_2FeB_2 is used as a hard surface coating. Elemental boron is synthesized as an intermediate product *via* $2\text{BCl}_3 + 3\text{H}_2 \rightarrow 2\text{B} + 6\text{HCl}$ at 770–1170 K which then reacts with molybdenum and iron. Another important application is the use of Mo_2FeB_2 as hard component in cermets (**ceramics** + **metals** composite materials). The iron atoms in Mo_2FeB_2 have square-prismatic molybdenum coordination. This motif readily reminds of the CsCl structure. The Mo_2FeB_2 type can therefore be described as an intergrowth variant of CsCl and AlB_2 related slabs. Besides the borides, this structure type occurs for a very large series of silicides, germanides, stannides, plumbides, indium, magnesium, and cadmium compounds with highly interesting magnetic and electrical properties [6].

The trigonal prismatic units in the Mo_2IrB_2 structure are at two different heights. Neighboring blocks are shifted by half a translation period. The boron atoms in the middle of the B_4 chain have similar coordination as in Mo_2FeB_2 while the terminal ones have one edge of the trigonal prism formed by iridium atoms.

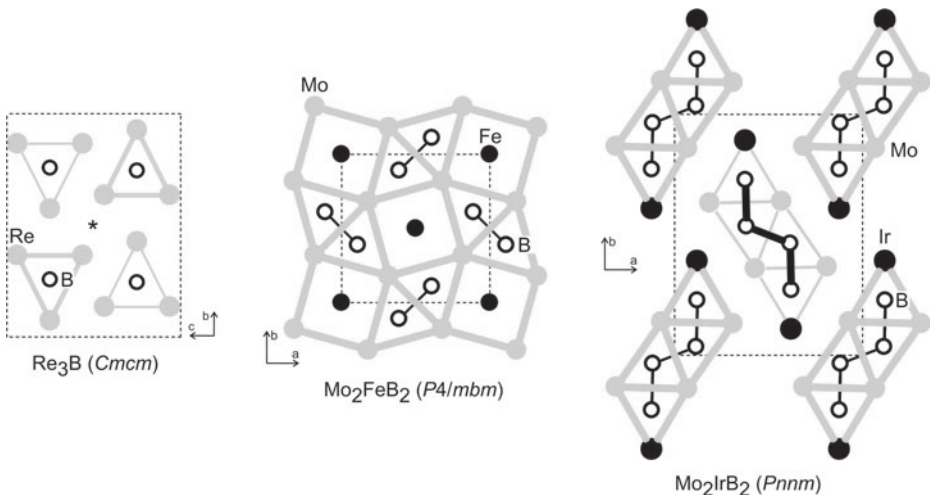


Fig. 3.21 The crystal structures of Re_3B , Mo_2FeB_2 , and Mo_2IrB_2 . Every other unit of trigonal prisms is shifted by half a translation period in the projection direction, indicated by thin and thick lines, respectively. The star in the Re_3B structure indicates an octahedral void.

Three important structure types occur among the transition metal monoborides: CrB, FeB, and α -MoB (Fig. 3.22). The common structural motifs of the three structures are infinite zig-zag chains of boron atoms in trigonal prismatic metal coordination. The B–B distances of 178 pm (CrB), 179 pm (FeB), and 174 pm (α -MoB) are comparable to those in Mo_2FeB_2 and Mo_2IrB_2 discussed above. The high stability of these monoborides arises from strong metal-boron bonding. The T –B distances are 219–229 pm (CrB), 215–218 pm (FeB), and 223–234 pm (α -MoB). The columns of boron-centered trigonal prisms show different condensation patterns in the three structure types. FeB is an important coating material which is produced in a similar way as Mo_2FeB_2 . Such coating can typically be used for cutting and drilling tools. FeB also occurs in ferroboron, a technically important iron-boron alloy. Some of the nickel and cobalt containing borides show catalytic activity for dehydrogenation reactions. Transition metal substitutions in such and related structure types lead to interesting tuneable magnetic properties [7].

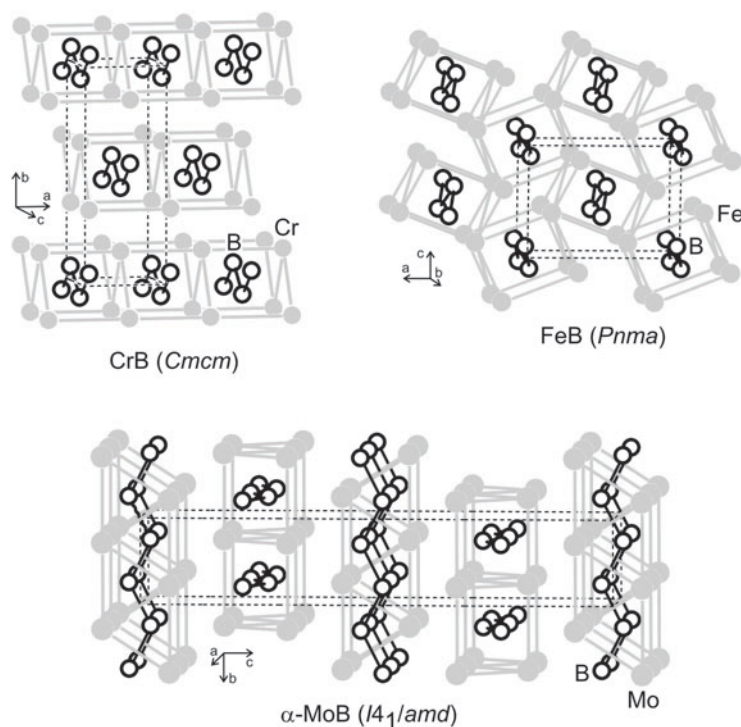


Fig. 3.22 The crystal structures of CrB, FeB, and α -MoB. The trigonal prismatic metal coordinations around the infinite boron zig-zag chains are emphasized.

Further condensation of the monoboride zig-zag chains leads to branched (Ru_{11}B_8), double and triple chains. The structures of V_2B_3 and Ta_3B_4 are presented as examples

in Fig. 3.23. Condensation of the zig-zag chains leads to the formation of condensed boron hexagons with 173–176 (V_2B_3) and 157–184 pm (Ta_3B_4) B–B distances. The boron centered trigonal prisms are condensed *via* the rectangular faces in the direction of the boron chains and *via* the triangular faces perpendicular to them. Similar to the Mo_2IrB_2 structure, adjacent blocks are shifted by half a translation period. The stability of these borides arises from strong metal-boron and metal-metal bonding as well. The technical application of these borides is limited, since those of the much cheaper iron metal are preferably used.

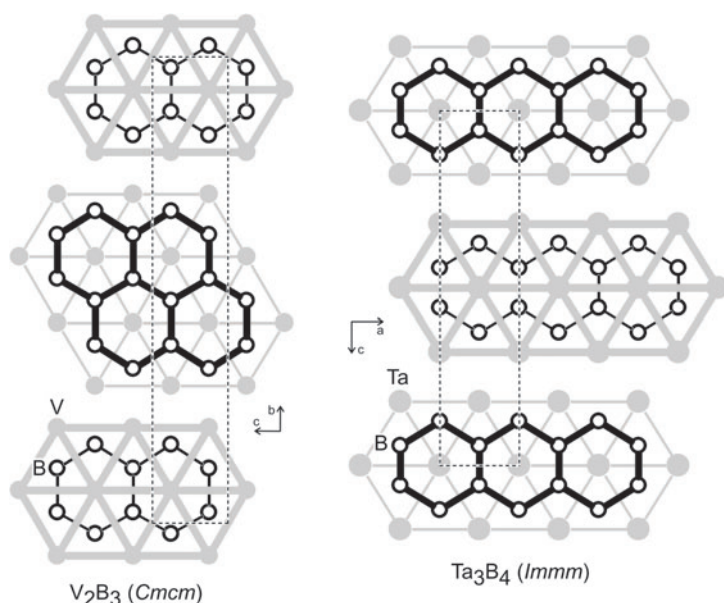


Fig. 3.23 The crystal structures of V_2B_3 and Ta_3B_4 . Every other unit of trigonal prisms is shifted by half a translation period in the projection direction, indicated by thin and thick lines, respectively.

The most important technical boride is TiB_2 (Fig. 3.24). It crystallizes with the well-known AlB_2 -type structure. The boron atoms build up two-dimensional honeycomb-like networks (175 pm B–B) which are stacked in AA sequence, leading to hexagonal prismatic coordination for the titanium atoms. TiB_2 has a high melting temperature of 3470 K. It is the transition metal boride with the highest hardness. Further advantages are its excellent chemical and thermal stability up to ca. 2000 K and a comparatively low density. The technical synthesis of TiB_2 proceeds *via* a carbothermal reduction of a TiO_2/B_2O_3 mixture: $TiO_2 + B_2O_3 + 5C \rightarrow TiB_2 + 5CO$. Most other isotypic TB_2 diborides (*e. g.* ZrB_2 , HfB_2 , VB_2 , NbB_2 , CrB_2 , MoB_2 , and WB_2) either have higher density or they are much more expensive. One of the exciting AlB_2 -type borides is MgB_2 . Although this

compound is known since many years, its 39 K superconducting transition has not been observed before 2001 [8] (Chapter 4.2).

The metal sites of the TiB_2 structure can be substituted, leading to solid solutions $Ti_{1-x}T_xB_2$ or generally written $T_{1-x}T'_xB_2$. The AlB_2 -type can only be retained if the different transition metal atoms are of comparable size. In the case where the radii of the two transition metal atoms are distinctly different, the boron network is reorganized, leading to pentagons and heptagons, accounting for the different coordination requirements. The structures of $ThMoB_4$ and Y_2ReB_6 show this coloring (Fig. 3.24). The larger thorium and yttrium atoms have distorted hexagonal and heptagonal prismatic boron coordination while the smaller molybdenum and rhenium atoms fill slightly distorted pentagonal prisms. Due to the distortions within the boron network one observes a broader range of B–B distances, *i. e.* 180–185 pm in $ThMoB_4$ and 166–213 pm in Y_2ReB_6 . A word of caution is appropriate at this point. Many of such boride structures have been determined many years ago. The difficulty was the precise location of the weakly scattering boron atoms besides heavy metal atoms. Especially the old structure refinements from X-ray film data resulted in enhanced standard deviations for the boron sites. Chemical bonding in these ternary borides is again governed by strong $T-T$ and $T-B$ bonding. $ThMoB_4$ and Y_2ReB_6 are only two representatives of a large family of ternary borides of the rare earth and actinoid metals in combination with a transition metal. The rich crystal chemistry of these compounds has been reviewed [9, 10]. Several of the ternary boride structures are rather complex. A nice example is the $U_5Mo_{10}B_{24}$ structure [11] which contains three different types of boron polyanions. Some of these compounds have peculiar physical properties. A striking family of compounds are the series $RERu_4B_4$ and $RERh_4B_4$ where coexistence of superconductivity and magnetism has been observed [12].

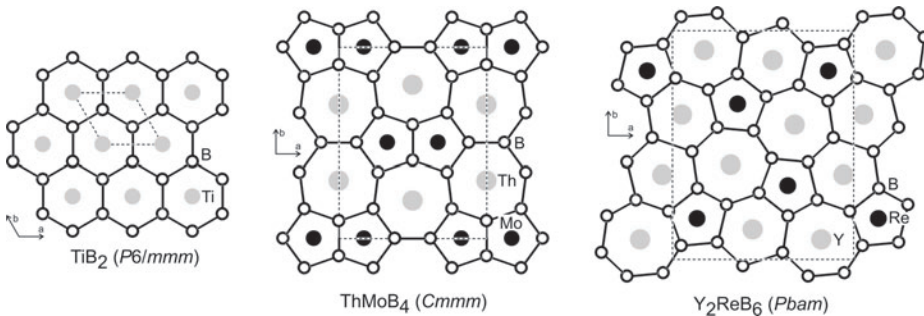


Fig. 3.24 The crystal structures of TiB_2 , $ThMoB_4$, and Y_2ReB_6 . The two-dimensional boron networks and the prismatic metal coordinations are emphasized.

The next step is the condensation of the boron substructure into the third dimension. In the structure of CrB_4 one observes a three-dimensional network, but the normal

case for boron-rich borides is the formation of cluster units. As examples we present the structures of CaB_6 , UB_4 , and UB_{12} in Fig. 3.25. The CaB_6 structure can be considered as a substitution variant of the CsCl type with Ca on the Cs- and the B_6 octahedra on the Cl sites. The B_6 octahedra are connected in all three directions, leading to a three-dimensional network. Each calcium atom is coordinated by eight triangular faces of the B_6 octahedra, *i. e.* $\text{Ca}@\text{B}_{24}$. B_6 octahedra are also the striking structural motifs in UB_4 , however, due to the lower boron content, these octahedra show different condensation. In the *c* direction they are condensed *via* direct B–B bonding like in CaB_6 , but in the *ab* plane we observe bridging B_2 units. These dumb-bells have 172 pm B–B distance and trigonal prismatic uranium coordination for each boron atom, similar to the Mo_2FeB_2 structure. The boron atoms in UB_{12} form cuboctahedral clusters. The packings of the uranium atoms and the cuboctahedra are similar to NaCl, namely *fcc* substructures for both motifs. Each uranium atom is coordinated by six B_4 squares from the cuboctahedra, *i. e.* $\text{U}@\text{B}_{24}$. The boron-rich borides find broad technical use. Since the ^{10}B isotope has a high capture cross section for neutrons ($^{10}\text{B} + ^1_0\text{n} \rightarrow ^7_3\text{Li} + ^4_2\text{He}$), materials like SmB_6 , EuB_6 , GdB_6 , ThB_4 , or ThB_6 can be used for control rods in nuclear reactors. LaB_6 is a thermo-ionic emitter with a very low work function and is used as electron source in plasma technique and electron microscopy.

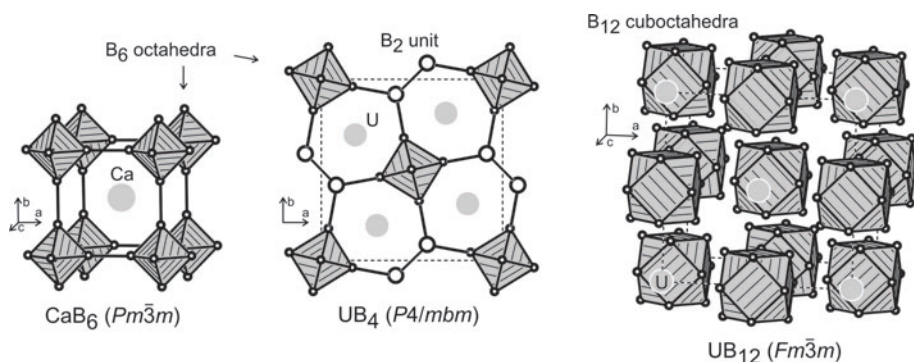


Fig. 3.25 The crystal structures of CaB_6 , UB_4 , and UB_{12} . The boron clusters are emphasized.

The alkali metals form the binary borides LiB_{1-x} , Li_2B_6 , Li_3B_{14} , LiB_{10} , Na_2B_{29} , Na_3B_{20} , and KB_6 and the compositions BeB_3 , BeB_{15} , MgB_2 , MgB_7 , Mg_3B_{44} , MgB_{12} , $\text{MgB}_{17.9}$, CaB_6 , SrB_6 , and BaB_6 have been observed with alkaline earth elements [3, 4]; some of them have comparatively complex crystal structures. LiB_{10} and $\text{MgB}_{17.9}$ derive from the β -B structure with the metal atoms on interstitial sites between boron polyhedra. A severe problem in boride chemistry is the contamination with carbon atoms, mostly arising from carbon contaminated boron or a small B_4C content in the starting materials. In such cases the carbon atoms can bridge the B_{12} icosahedra through CBC or C_2 units like in $\text{LiB}_{13}\text{C}_2$ or $\text{MgB}_{12}\text{C}_2$. The carbapentaborides NaB_5C and KB_5C show random carbon occupancy on

the octahedral building units (CaB_6 type). Besides the few binary alkali (A) and alkaline earth (AE) borides, a large family of ternary $A_xT_yB_z$ and $AE_xT_yB_z$ borides has been synthesized. Most phase analytical work in this field arises from the *Jung* group [13].

The boride chemistry has been extended to heteropolyanions, including carbon and nitrogen. The simplest example is the heterographite LiBC , an electron-precise compound with graphite like $[\text{BC}]^-$ networks which are charge-compensated and separated by the lithium atoms. The borocarbide chemistry has especially been developed with rare earth elements. Numerous $\text{RE}_x\text{B}_y\text{C}_z$ borocarbides have structurally been characterized [14]. These compounds are accessible *via* arc-melting, however, they are extremely sensitive to moisture. The simplest polyanionic unit that occurs in the borocarbides is the $[\text{BC}_2]$ polyanion which is exemplarily shown for Sc_2BC_2 in Fig. 3.26. Besides $[\text{BC}_2]$ also other finite chains like $[\text{B}_4\text{C}_7]$, $[\text{B}_5\text{C}_6]$, $[\text{B}_5\text{C}_8]$ etc. occur, or the chains are infinite and branched. For the complex chains a distorted square *anti*-prismatic coordination by the metal atoms is often observed. Several other borocarbides have two- or three-dimensional polyanions. A severe problem for these borocarbides is the correct assignment of the boron and carbon sites by X-ray diffraction, since both light elements differ only by one electron.

To illustrate this problem we discuss the structures of Sc_2BC_2 and ScB_2C_2 (Fig. 3.26). The linear BC_2 units in Sc_2BC_2 have 148 pm B–C distance, while in the two-dimensional B_2C_2 polyanion of ScB_2C_2 one observes 145 pm C–C, 152–161 pm B–C, and 159 pm B–B bond distances. This readily demonstrates that high quality diffraction data are required for an unambiguous structure determination. The two-dimensional B_2C_2 polyanion of ScB_2C_2 has pentagonal and heptagonal rings. Due to size reasons, the scandium atoms only fill the slightly distorted heptagonal prisms. The $[\text{B}_2\text{C}_2]$ network of ScB_2C_2 is an ordered version of the boron network of the ThMoB_4 type (Fig.

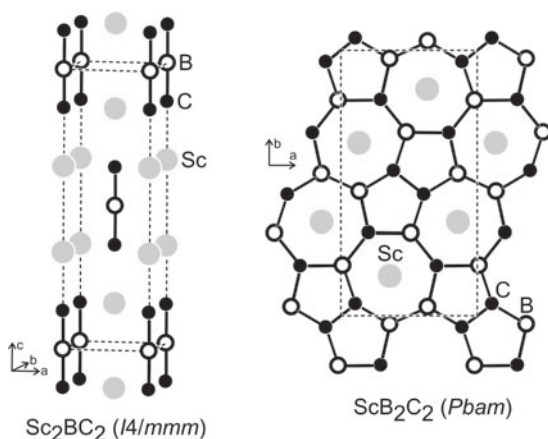


Fig. 3.26 The crystal structures of Sc_2BC_2 and ScB_2C_2 . The $[\text{BC}_2]$ and $[\text{B}_2\text{C}_2]$ boron substructures are emphasized.

ure 3.24). Additionally, the pentagonal prismatic voids are filled by molybdenum in the ThMoB_4 structure, while they remain unoccupied in ScB_2C_2 . The different coloring of the network also leads to different space group symmetry.

Many of the rare earth borocarbides have thoroughly been investigated in detail by electronic structure calculations in order to manifest the boron-carbon ordering, especially for chains that contain all three bonding types. The rare earth borocarbides are mostly metallic conductors with silvery or bronze metallic luster. Several of these materials exhibit interesting magnetic properties at low temperatures. Parallel investigations of rare earth-silicon-boron systems showed only few ternary compounds [15]. One of the well characterized phases is $\text{Gd}_5\text{Si}_2\text{B}_8$ with Si_2 units and B_6 octahedra.

Ternary $(A,AE,RE)_x\text{B}_y\text{N}_z$ compounds show two bonding patterns. In pure boride nitrides like Nb_2BN one observes segregation into a boride and a nitride substructure, similar to the binary compounds. If boron-nitrogen bonding is present, these compounds are called nitridoborates. Meanwhile, a variety of different nitridoborate substructures is known [16]. As examples we present the structures of LaNiBN and $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ in Fig. 3.27. The nickel atoms form square nets in both tetragonal compounds. The $[\text{BN}]$ units (199 pm in LaNiBN and 182 pm in $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$) are connected to these square nets *via* the boron atoms in a chequered pattern. The resulting layers are charge-compensated and separated by the lanthanum atoms in LaNiBN , while a layer of nitrogen-centered lanthanum octahedra (rock salt slab) occurs in $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$. The

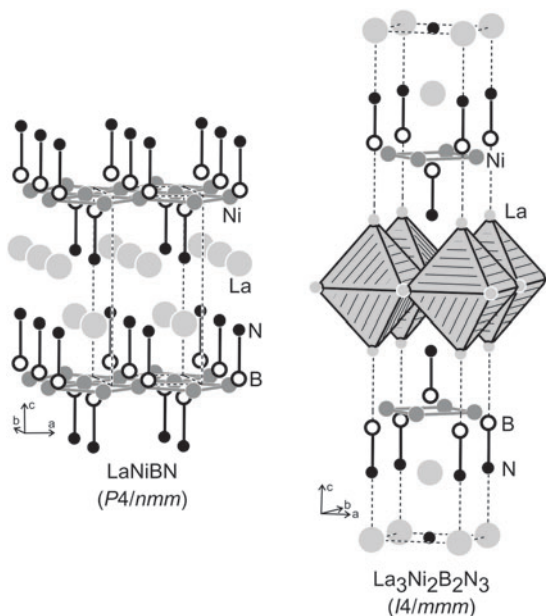


Fig. 3.27 The crystal structures of LaNiBN and $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$. The nickel square nets, the $[\text{BN}]$ units, and the condensed nitrogen-centered octahedra are emphasized.

nitrogen atoms of the [BN] units in both nitridoborates have similar lanthanum coordination. Such tetragonal structures are also known with [BC] units instead of [BN]. These materials have intensively been investigated with respect to their magnetic and superconducting properties [17], starting with the indicatory work on LuNiBC and LuNi₂B₂C [18].

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3.8.2 Aluminides

Aluminum is the most important metallic material after iron and the many steel varieties. It plays the major role in most modern light-weight alloys. Aluminum has an

excellent capacity for secondary generation. For aluminum recycling only a small fraction of energy is needed as compared to Al_2O_3 production and melt-electrolyses. Today already a high percentage of aluminum is taken from these so-called secondary resources. Aluminum is an element with a positive energy balance, when accounting for the whole life cycle. It has low density (2.70 g/cm^3) and high corrosion resistance (formation of thin oxide coatings), good prerequisites for long-living construction materials. The low melting (973 K) and high boiling ($\sim 2770 \text{ K}$) temperature lead to a high liquid range. Due to its extremely broad use, all physical properties of aluminum are well known. The basic data for aluminum and its alloys are competently summarized in the *Aluminium Taschenbuch* [1].

Since pure *fcc* aluminum is too ductile, exclusively aluminum alloys are used for technical applications. Besides aluminum itself, the main components of such modern light-weight alloys are Cu, Si, Mg, Zn, and Mn. Also small additions of Fe, Cr, and Ti are frequently used. For special alloys Ni, Co, Ag, Li, V, Nb, Zr, Sn, Pb, and Bi additions find application. Elements like Be, B, Na, Sr, and Sb are only used as trace components. The exact alloy composition has drastic influences on the specific alloy microstructure and the physical properties.

Generally one has to distinguish the formation of solid solutions from the formation of compounds with a precise composition. Due to the broad application of many aluminum alloys, most binary and several ternary phase diagrams of aluminum based materials are well known. Some key compounds in the alloys are the S-phase precipitate MgCuAl_2 , the T-phase Mg_4CuAl_4 , or the binary aluminide MnAl_6 .

Similar to the many steel varieties, also for the aluminum-based alloys there is good knowledge on the influence of *T/X* solid solutions as well as the history of the heat treatment on the microstructure and the properties, although many of such correlations still rely on empirical research. Theoretical modulation of such multi-parameter systems is difficult. The many parameters have influence on the following materials properties: (i) Density, (ii) strength, (iii) formability, (iv) castability, (v) machinability, (vi) ability for connectivity with other materials, (vii) chemical resistance, (viii) surface treatability, (ix) non-sparkability and non-flammability, (x) electrical and thermal conductivity, (xi) optical properties, (xii) magnetic neutrality, (xiii) neutron absorption cross section, (xiv) biocompatibility and toxicity. Turning back to the first point, the most effective way to reduce the aluminum density is the modification of the dense bulk material into metal foam. This is possible by an up-blow with hydrogen or through in-situ decomposition of titanium hydride. Today many tube and plate materials based on diverse metal foams with high mechanical strength are technically used.

The many influences of the solid solutions/doping and the thermal treatment on the workability and other more technical questions are not subject of this chapter. Here we refer to more specialized technical/application-oriented textbooks. The key subject herein is a short overview on the crystal chemical details of basic aluminides along with some representative properties.

Among the alkali metals only lithium forms binary aluminides. The Zintl phase LiAl (isotypic with NaTl reported in Chapter 3.7), Li_3Al_2 , and Li_9Al_4 have been reported, while no aluminides are known for the heavier alkali metals. Considering the more electronegative character of lithium, the charge transfer proceeds from the lithium to the aluminum atoms, leading to an aluminide character. This is also the case for the calcium (Ca_8Al_3 , $\text{Ca}_{13}\text{Al}_{14}$, CaAl_2 , CaAl_4), strontium (Sr_8Al_7 , SrAl , Sr_5Al_9 , SrAl_2 , SrAl_4), and barium (Ba_3Al_5 , Ba_4Al_5 , $\text{Ba}_7\text{Al}_{13}$, $\text{Ba}_{21}\text{Al}_{40}$, BaAl_2 , BaAl_4) aluminides. Magnesium is the less electropositive element in the series of alkaline earth elements and the electronegativity difference is smaller, but still one can assume a charge transfer from magnesium to aluminum. These two elements form the intermetallic compounds $\text{Mg}_{17}\text{Al}_{12}$, $\text{Mg}_{23}\text{Al}_{30}$, $\text{Mg}_{32}\text{Al}_{49}$, Mg_3Al_5 , Mg_2Al_3 , $\text{Mg}_{28}\text{Al}_{45}$, $\text{Mg}_9\text{Al}_{11}$, and MgAl_2 . The simplest of these structures is MgAl_2 with HfAl_2 type, a tetragonally distorted, ordered variant of an *fcc* arrangement. The other phases have very complex crystal structures, partly with giant unit cells and different approaches have been used for their explanation [2]. A severe problem for structure determination of these phases is the small difference in X-ray scattering power between these two neighboring elements.

The structures of Ba_3Al_5 [3] and BaAl_4 [4] are exemplarily presented in Fig. 3.28. They display different aluminum substructures. The aluminum atoms in Ba_3Al_5 form a two-dimensional network of connected Al_5 bipyramids with Al–Al bond lengths ranging from 274–325 pm. These $[\text{Al}_5]^{6-}$ networks are charge-compensated and separated by the barium atoms. Chemical bonding in this phase can be understood starting from a MO diagram of an $[\text{Al}_5]$ bipyramid [5]. BaAl_4 has a three-dimensional $[\text{Al}_4]$ network of condensed Al_4 tetrahedra with a smaller range of Al–Al distances (267–269 pm). Crystal orbital overlap population analyses for both aluminides showed optimized Al–Al bonding. BaAl_4 is a parent structure for a large family of ternary intermetallic compounds. The two crystallographically independent aluminum sites can be occupied in an ordered manner by a transition metal and a *p* element, first observed for ThCr_2Si_2 [6]. Meanwhile hundreds of representatives of this structure type as well as many more complicated occupancy and deformation variants (superstructures) have been reported [7].

The transition metals react with aluminum forming a manifold of binary aluminides with a broad variety of different crystal structures. If elemental aluminum is allowed to coordinate with other metals, the structural chemistry varies significantly and is drastically different from the simple *fcc* structure of the element. Similar to the complex crystal chemistry of magnesium aluminides this is most likely a result of the smaller electronegativity differences. Many of the transition metal aluminides crystallize with their own structure type; only representative examples are discussed herein.

The chemistry of transition metal aluminides with respect to technical applications is directly coupled to titanium. Binary and multinary titanium aluminides play an important role for a huge number of modern light-weight alloys. The many data

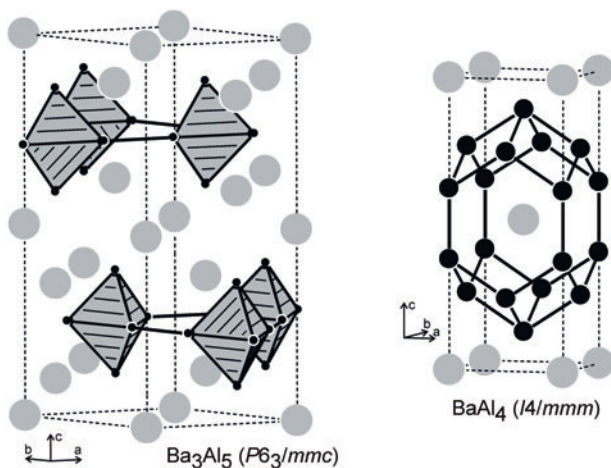


Fig. 3.28 The crystal structures of Ba_3Al_5 and BaAl_4 . Barium and aluminum atoms are drawn as light gray and black circles, respectively. The Al_5 bipyramids in Ba_3Al_5 and the three-dimensional aluminum network in BaAl_4 are emphasized.

have been summarized in a textbook [8]. Such alloys find application in automobile and aircraft construction, plant manufacturing as well as in diverse medical applications like artificial knee and hip joints or tooth implants.

Ti_3Al is the titanium-rich phase. It crystallizes with the hexagonal Ni_3Sn -type structure, space group $P6_3/mmc$, an ordering variant of the *hcp* packing (Chapter 3.3). The titanium atoms form a substructure of chains of face-sharing Ti_6 octahedra, separated by the aluminum atoms. Ti_3Al can alloy with many substitutional and interstitial elements; especially niobium improves the ductility of the Ti_3Al -based alloys. The high oxidation resistance of Ti_3Al results from a protective Al_2O_3 coating. The perovskite Ti_3AlC (where the carbon atoms exclusively fill the octahedral voids formed by titanium) plays an important role as a component for precipitation hardening in titanium based alloys.

Besides precipitation hardening surface oxidation with respect to the formation of chemically and thermally stable protection coatings is an important research activity. The oxidation mechanisms of many titanium-based alloys are well known. Important parameters are a good adherence of the coating on the metal surface, a low self-diffusion of the elements forming the coating, and a low vapor pressure of the oxide. One main problem concerns chromium-containing alloys, since volatile CrO_3 might form at high temperatures.

TiAl with CuAu-type structure has lower density than Ti_3Al . This equiatomic phase is excellent for materials/alloys with good strength and ductility, parameters that are an important prerequisite for a good control of the microstructure. Generally, the phase equilibria of the titanium aluminides are highly sensitive to interstitial

impurities, especially oxygen. The high lattice energy of TiO_2 and Al_2O_3 is the driving force for materials oxidation. The aluminum-rich part of the phase diagram shows the phases TiAl_2 (ZrGa₂ type) and TiAl_3 (own type) which are both ordered *fcc* derivatives (Chapter 3.3).

Zr_3Al (Cu₃Au type) has a low cross section for the absorption of thermal neutrons and it has been tested as a cladding material for water-cooled nuclear reactors. VAL_3 with TiAl_3 -type structure is discussed as a promising material for application in nuclear reactor technology. Nb_3Al (Cr₃Si type) was studied in detail in view of its superconducting properties, but this material has too high brittleness. NbAl_3 (TiAl_3 type) is a candidate for high-temperature applications; however, a severe problem for NbAl_3 is its high ability for grain boundary oxidation.

Tantalum forms the aluminides Ta_5Al_3 (Mn₅Si₃ type) and TaAl_3 (TiAl_3 type) with comparatively simple structure types. Especially TaAl_3 is discussed for composite materials development. The tantalum-rich part of the phase diagram has intensively been investigated [9]. The tantalum-rich phases have large unit cells, complex structures and show substantial degrees of Ta/Al mixing on several Wyckoff positions. Structure determination was possible by combinations of X-ray diffraction with lab and synchrotron sources accompanied by electron diffraction.

The WAl_{12} structure, space group $Im\bar{3}$ (Fig. 3.29) [10] is discussed as an example for a group VI aluminide. Each tungsten atom has icosahedral aluminum coordination with W–Al distances of 273 pm. One can easily derive the WAl_{12} structure from that of elemental tungsten by a replacement of each tungsten atoms by the building unit W@Al_{12} . The change in space group symmetry from $Im\bar{3}m$ to $Im\bar{3}$ results from the orientation of the polyhedra. MoAl_{12} , MnAl_{12} , TcAl_{12} , and ReAl_{12} are isotypic with the tungsten compound.

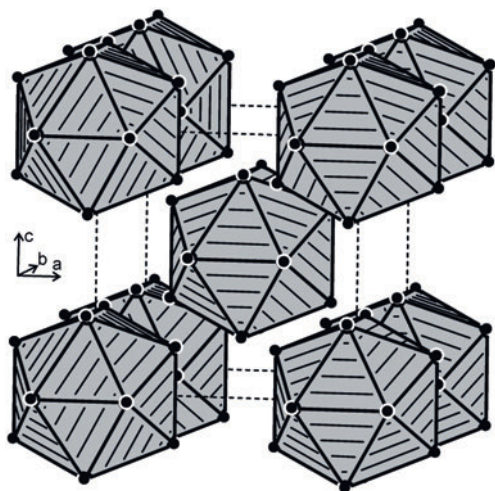


Fig. 3.29 The crystal structure of WAl_{12} . The W@Al_{12} icosahedra are emphasized.

Fe_3Al (Cu₃Au type) has large capacity for dissolving carbon, leading to a perovskite-related phase Fe_3AlC_x . Possible applications are resistance heating elements or steam turbine discs. Simple structure types occur for FeAl, CoAl, RuAl, RhAl, and OsAl (CsCl type), RuAl_2 and OsAl_2 (TiSi₂ type), and RuAl_3 (TiNi₃ type). Many of the aluminum-rich phases crystallize with complex structure types which often form only with one transition metal.

Ni_3Al (Cu₃Au type) is one of the best known and most intensively studied intermetallic compounds. It has good ability to dissolve other transition metals and it has high chemical resistance through Al_2O_3 protective coating. Ni_3Al is discussed for steam, gas, and water turbines, aircraft fasteners, tooling moulds, and diverse automotive components. Nickel aluminides are the basic materials for the production of so-called Raney Nickel, a highly efficient and sensitive catalyst in organic synthesis. The nickel-aluminum phases Ni_2Al_3 or NiAl_3 (which can also be promoted with iron or copper for special catalytic activity) are quenched from high temperature and subsequently ground to fine powder. The aluminum is dissolved with sodium hydroxide solution, leaving highly porous nickel. The latter is sensitive to oxidation and must be kept under inert conditions prior to use.

Liquid aluminum readily reacts with platinum metals with a large heat of formation. This has been observed *e. g.* in the Pt–Al system [11]. Besides aluminides with simple structure types like Pd_2Al and Pt_2Al (Co₂Si type), PdAl and PtAl (CsCl type), or PtAl_2 (CaF₂ type), many complicated structures form, especially in the aluminum-rich region. One example is the structure of PtAl_4 . The phase is known since the phase analytical studies of Huch and Klemm [11], but the complex twinned structure was determined much later on the basis of synchrotron diffraction data in combination with high-resolution transmission electron diffraction [12].

The structure of the palladium-rich phase Pd_5Al [13] is presented as an example for the platinum metal aluminides in Fig. 3.30. Pd_5Al forms from the pure metals in the presence of small amounts of iodine, bromine, or tellurium, another example for a mineralizer-promoted synthesis. The aluminum and palladium atoms are well ordered. One observes segregation of the aluminum atoms within the palladium matrix; aluminum atoms form zig-zag chains that extend in *b* direction. Looking at the projection in Fig. 3.30, the resemblance with the *fcc* structure is readily evident. One distorted *fcc* subcell is shaded in medium gray color. The distortions are driven by the zig-zag chain formation of the aluminum atoms and the difference in size between aluminum and palladium. As compared with *fcc* palladium with an isotropic coordination with twelve equal Pd–Pd distances of 275 pm, the Pd–Pd (269–289 pm), Pd–Al (253–279 pm) and Al–Al (316 pm; no bonding interactions) distances show comparatively large ranges. In comparison with the examples of ordered *fcc* variants discussed in Chapter 3.3, Pd_5Al is a more complex one. Also the aluminum-rich phase WAl_5 [14] shows an ordered close packing, again with a more complex structure.

The highly electropositive rare earth metals form a variety of aluminides. Their crystal chemistry is characterized by several simple compositions: REAl_3 and

RE_3Al (Cu_3Au type), RE_3Al_2 (Zr_3Al_2 type), $REAl$ ($CsCl$ type), $REAl_2$ ($MgCu_2$ type), $REAl_4$ ($BaAl_4$ type), and RE_2Al_{17} (Th_2Ni_{17} type). With a slightly lower aluminum content than $REAl_4$, some of the rare earth elements form binary aluminides RE_3Al_{11} . The structure was first determined for La_3Al_{11} [15], space group $Immm$ (Fig. 3.31). The substructure of the rare earth atoms resembles the $BaAl_4$ type discussed above. Three body-centred lanthanum subcells are condensed. The left-hand and right-hand subcells have different aluminum coordination as compared to the subcell in the middle. Nevertheless, both crystallographically independent lanthanum sites have the coordination number 16. The Al–Al distances within the complex three-dimensional network range from 266–313 pm, which is much broader than in the highly symmetric $BaAl_4$ structure. Similar to the $BaAl_4$ type, ternary ordered versions also exist for La_3Al_{11} . The four crystallographically independent aluminum sites can be occupied in an ordered manner by cobalt and tin, leading to the series $RE_3Co_6Sn_5$ [16].

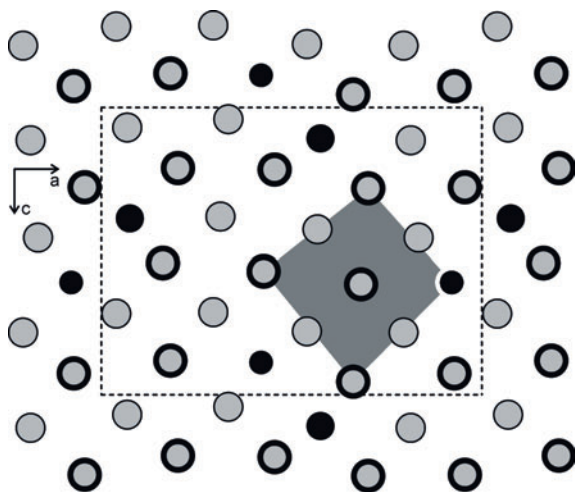


Fig. 3.30 The crystal structures of Pd_3Al . Palladium and aluminum atoms are drawn as light gray and black circles, respectively. One distorted fcc subcell is shaded.

The different cerium aluminides Ce_3Al , $CeAl$, $CeAl_2$, $CeAl_3$, and Ce_3Al_{11} have intensively been studied with respect to their physical properties. Ce_3Al is a heavy fermion material [17], $CeAl_2$ [18] shows the Kondo effect, and incommensurate magnetic ordering is detected at very low temperatures. A ferromagnetic ground state has been observed for Ce_3Al_{11} [19] on the basis of magnetic susceptibility and neutron diffraction data.

The aluminides $EuAl$ (own type), $EuAl_2$ ($MgCu_2$ type), and $EuAl_4$ ($BaAl_4$ type) have been reported with europium as rare earth element. Temperature-dependent magnetic susceptibility measurements showed stable divalent europium in all these aluminides [20], while ytterbium shows intermediate-valence in $YbAl_2$ and $YbAl_3$ [21].

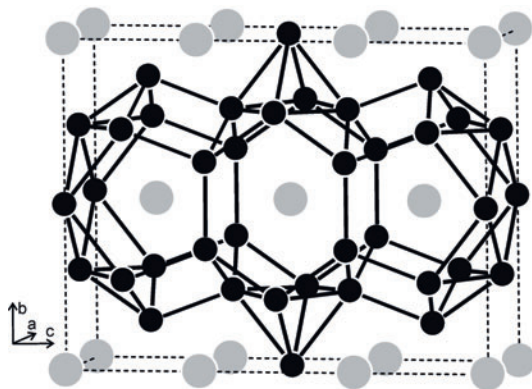


Fig. 3.31 The crystal structure of $\text{La}_3\text{Al}_{11}$. Lanthanum and aluminum atoms are drawn as light gray and black circles, respectively. The three-dimensional aluminum substructure is emphasized.

Thorium forms six aluminides, *i. e.* Th_2Al (CuAl_2 type), Th_3Al_2 (U_3Si_2 type), ThAl (FeB type), ThAl_2 (cubic Laves phase), ThAl_3 (Ni_3Sn type), and Th_2Al_7 . The aluminum-rich phase crystallizes with its own structure type [22]. Each thorium atom has 14 aluminum neighbors at Th–Al distances ranging from 323–337 pm. The coordination polyhedron (Fig. 3.32) derives from a hexagonal prism which is capped by two further aluminum atoms on one rectangular site. Condensation of these Th@Al_{14} polyhedra *via* common hexagon faces leads to a complex three-dimensional network. The thorium coordination includes all three crystallographically independent aluminum atoms. The most aluminum-rich phase of uranium is UAl_4 [23]. Due to the smaller size of the uranium atoms (as compared to thorium), each uranium atom has only 13 aluminum neighbors with shorter U–Al distances ranging from 305–313 pm. These CN 13 polyhedra derive from a cuboctahedron in which one of the triangular faces is substituted by a rectangle. Condensation of these U@Al_{13} polyhedra leads to the network presented in Fig. 3.32.

The uranium and thorium aluminides have intensively been studied with respect to their use as nuclear materials and the uranium ones especially as nuclear fuels. Also their magnetic behavior is of interest. The cubic Laves phase UAl_2 is a spin fluctuation system and Cu_3Au type UAl_3 shows enhanced Pauli paramagnetism. UAl_4 is paramagnetic without any sign for magnetic ordering down to 1.8 K [24].

Besides the many multinary aluminide phases [1, 8, 25], a huge number of structurally well-ordered ternary aluminides are known. They can roughly be subdivided into three groups: (i) Aluminides with two different transition metals, (ii) alkaline earth-transition metal-aluminides and (iii) rare earth-transition metal-aluminides.

Representative examples for the first group are the so-called *AlNiCo* magnets, cheap magnetic materials based on Fe–Ni–Al or Co–Ni–Al alloys. $\gamma\text{-TiV}_4\text{Al}_6$ (and related alloys within a broad range of solid solutions) is one of the technologically most important alloys which are also used for artificial hip and knee joints. Cu–Zn–Al and

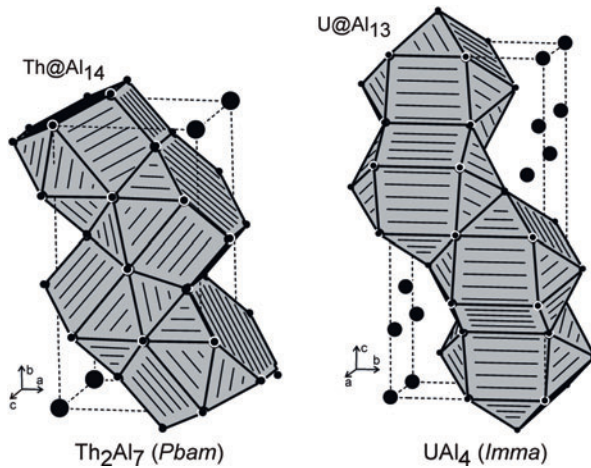


Fig. 3.32 The crystal structures of Th_2Al_7 and UAl_4 . The Th@Al_{14} and U@Al_{13} polyhedra are emphasized.

Cu–Ni–Al based alloys are basic materials for shape memory alloys [26]. Ternary aluminides can also form as precipitations during welding or laser processing. Typical examples are $\text{Ti}_6\text{Fe}_7\text{Al}_{16}$ and $\text{Ti}_6\text{Ni}_7\text{Al}_{16}$ [27]. Ti_2NbAl is the basic alloy of so-called orthorhombic titanium aluminides. This material has a broad solid solution range for all three elements. Cr, Mn, and Mo are the most important alloy additions for property changes. Many aluminum-based Heusler phases (Chapter 3.3) find application with respect to their magnetic and magneto-optical properties [28].

Most ternary transition metal aluminides have complex crystal structures. So far not all element combinations are tested and the structures of several known phases are not yet solved. A recent example is the cubic phase $\text{Cu}_{12.3}\text{Ir}_{24.4}\text{Al}_{63.3}$ [29]. The main structural problems derive from void formation or mixed occupied sites. The complex crystal structures can best be described by cluster building units. Such complex structures also occur in the technically important system Zn–Mg–Al. Ternary alloys/intermetallics from this system are important in the development of light-weight and high strength alloys. Again, also for this system the phase equilibria are still not completely understood. The complex crystal structures belong to Bergman cluster approximant phases [30]. Determination of the phase equilibria and structures of such complex phases requires a combination of state of the art diffraction techniques in combination with thermal analyses and theoretical calculations [31].

The largest family of ternary aluminides concerns those that are formed with an alkaline earth or rare earth metal (*RE*) in combination with a transition metal (*T*). Such aluminides can form as precipitations in multinary alloy systems. The main interest in these compounds, however, lies in their highly interesting magnetic and electrical properties. In that view especially the rare earth-based ones and in parallel also some actinoid compounds have been studied.

Typical compositions of ternary rare earth aluminides are $REAl$, RE_4Al , $REAl_3$, or RE_2Al_2 . Many ternary solid solutions form with comparatively simple binary structure types, e. g. α -ThSi₂, AlB₂, MgCu₂, CaCu₅, BaCd₁₁, or NaZn₁₃. Furthermore one observes several ternary aluminides, which crystallize with their own structure types, similar to the binary compounds. In recent years especially the aluminum-rich parts of the RE - T -Al phase diagrams have been studied. The typical structure types that form are CeCr₂Al₂₀ [32], YbFe₂Al₁₀ [33], CaCr₂Al₁₀ [34], the RE_4Al_8 series with ordered ThMn₁₂ type, or Ho₆Mo₄Al₄₃ [35]. Larger single crystals of such aluminides are available through self-flux crystal growth. This allows for direction-dependent physical property studies.



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3.8.3 Gallides

Gallium is one of the strategic elements with high demand in future, especially due to the enormous use in semiconductor technology (GaAs for LED applications). Apart from this applied field, gallium forms a huge amount of binary and ternary intermetallic compounds with fascinating crystal structures and interesting chemical and physical properties. Pioneering work on gallide crystal chemistry is the merit of *Yu. Grin*. A lot of the basic work started in the renowned inorganic chemistry department of Lviv University (Ukraine) and is compiled in a book [1]. The basic crystal chemistry of gallium-containing intermetallics is summarized in the present chapter, again starting with the alkali metal compounds.

The lithium-gallium phase diagram has intensively been studied by *Müller* and *Schäfer*, and the gallides $\text{Li}_3\text{Ga}_{14}$, Li_5Ga_4 , Li_3Ga_2 , LiGa , and Li_2Ga have been reported [2, 3]. Further investigations of the gallium-rich parts of the phase diagram led to the gallides Li_5Ga_9 , Li_3Ga_8 , Li_2Ga_7 , and LiGa_6 [4]. The structurally simplest compound is the Zintl phase LiGa which crystallizes with the NaTl -type structure (Chapter 3.8.5) with four connected Ga^- species (267 pm Ga–Ga). Li_2Ga and Li_5Ga_4 contain single or double (with inter-layer Ga–Ga bonding) layers of puckered gallium hexagons which are separated and charge-balanced by the lithium atoms. With increasing gallium

content the crystal chemistry becomes more complex with comparatively large unit cells. Basic building units in such phases are gallium octadecahedra (Ga_{11}), icosahedra (Ga_{12}), or $[\text{Ga}_{11}\text{LiGa}_{11}]$ polyhedral chains which are condensed *via* isolated three- or four-connected gallium atoms or Ga_2 dumb-bells. The structure of Li_2Ga_7 is presented as an example in Fig. 3.33. The layers of icosahedra show the typical rhombohedral ABC stacking sequence. They are connected *via* Ga_2 dumb-bells. The lithium atoms fill cavities within this complex three-dimensional network and they have nine nearest gallium neighbors.

Molten and crystalline lithium gallides have intensively been investigated with respect to a potential use in lithium ion- and lithium thermal batteries. These studies revealed a substantial charge transfer from lithium to gallium. Solid state NMR data showed good lithium mobility in LiGa and Li_2Ga_7 and precise diffusion pathways could be deduced. The spectroscopic and electrochemical data on the lithium gallides are summarized in [4].

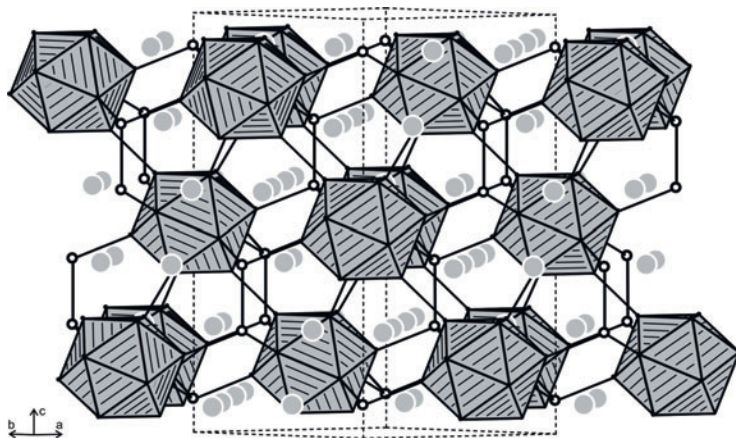


Fig. 3.33 The crystal structure of Li_2Ga_7 , space group $R\bar{3}m$. Lithium and gallium atoms are drawn as medium gray and black open circles, respectively. The network of condensed Ga_{12} icosahedra and Ga_2 dumb-bells is emphasized.

Phase analytical data on the gallides with the heavier alkali metals trace back to the work of *Thümmel* and *Klemm* [5]. These phase diagrams are less complex as compared to Li–Ga. Sodium forms the gallide NaGa_4 with BaAl_4 -type structure and the complex gallides $\text{Na}_7\text{Ga}_{13}$ and $\text{Na}_{22}\text{Ga}_{39}$ which are very close in composition. The latter contain icosahedra and larger Ga_{15} units, while the network in NaGa_4 is composed of simple condensed square pyramids. Complex building units also occur in the potassium gallides K_2Ga_3 , KGa_3 , and K_3Ga_{13} . Rubidium and cesium have quite simple phase diagrams with compounds AGa_3 and AGa_7 ($A = \text{Rb}, \text{Cs}$). The Ga_{12} icosahedra in the AGa_7 phases are connected *via* four-bonded gallium atoms, leading to an electron-precise formula-

tion $(2A^+)(Ga_{12}^0)(2Ga^-)$. A broad overview on this complex crystal chemistry is given by *Belin and Tillard-Charbonnel* [6].

The smallest alkaline earth element beryllium forms no binary gallide. Five phases have been reported for the Mg–Ga system: Mg_2Ga_5 , $MgGa_2$, $MgGa$, Mg_2Ga , and Mg_5Ga_2 . Calcium forms the gallides $Ca_{28}Ga_{11}$, Ca_5Ga_3 , $Ca_{11}Ga_7$, $CaGa$, Ca_3Ga_5 , $CaGa_2$, Ca_3Ga_8 , and $CaGa_4$ of which the structures of $Ca_{28}Ga_{11}$ and $Ca_{11}Ga_7$ are quite complex with huge unit cells. The heavy alkaline earth metals react with gallium forming $SrGa_4$, $Sr_{3-x}Ga_{8+x}$, $SrGa_2$, Sr_8Ga_7 , $Ba_{10}Ga$, Ba_8Ga_7 , $BaGa$, $BaGa_2$, and $BaGa_4$. As examples, the structures of Ba_8Ga_7 and $BaGa_4$ are presented in Fig. 3.34. They contain distinctly different gallium substructures. In the metal-rich structure of Ba_8Ga_7 one observes Ga_3 triangles (263 pm Ga–Ga) besides Ga_4 tetrahedra (268–275 pm Ga–Ga) in 1:1 ratio. These units are well separated by the barium cations. Tetrahedral gallium coordination also occurs in $BaGa_4$ (BaAl₄-type structure) with 266 pm Ga–Ga. These tetrahedra are condensed *via* common edges and corners leading to the three-dimensional network presented in Fig. 3.34. The barium atoms fill large cages formed by 16 gallium atoms (349–354 pm Ba–Ga).

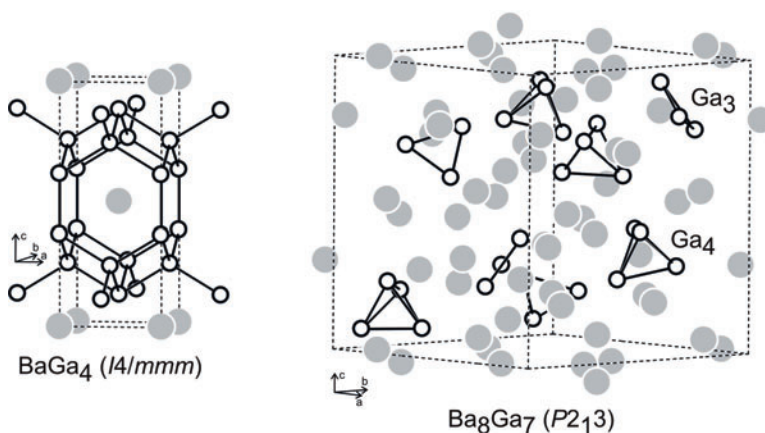


Fig. 3.34 The crystal structures of $BaGa_4$ and Ba_8Ga_7 . Barium and gallium atoms are drawn as medium gray and black open circles, respectively. The gallium substructures are emphasized.

The synthesis of barium containing intermetallic phases deserves high-purity barium metal. Often commercial barium contains substantial hydrogen impurities which can irreversibly affect the synthesis conditions [7]. In the case of gallides, binary Ba_5Ga_6 had been reported which indeed is the electron-precise Zintl phase $Ba_5Ga_6H_2$ ($\equiv (5Ba^{2+})(Ga_6^{8-})(2H^-)$) [8] with distorted octahedral gallium clusters.

An interesting possibility to modify the complex crystal chemistry of the gallide substructures is the introduction of cations of different size and charge. This leads to even more complex cluster units [6, 9] and structures with giant unit cells. Besides the well-known Ga_{12} icosahedra Ga_{21} and Ga_{28} clusters frequently occur in ternary gallides

like $\text{Li}_9\text{K}_3\text{Ga}_{28.83}$ or $\text{Na}_{6.25}\text{Rb}_{0.6}\text{Ga}_{20.02}$. Such cluster frameworks have intensively been studied in order to understand the complex bonding situation and comparison with the Wade rules.

Different crystal chemistry is observed for the gallides of the transition metals. These phases cover a broad range of compositions from metal- to gallium-rich. Many of these gallides crystallize with ordering variants of the close-packed structures (Chapter 3.3). Some prominent examples are TiGa_3 (TiAl_3 type), HfGa_2 (own type), CoGa (CsCl type), or Ni_3Ga (Cu_3Au type). Further gallides adopt frequently occurring binary structure types (with a gallide representative in parentheses) like Cr_3Si (V_3Ga), Mn_2Hg_5 (Mn_2Ga_5), Mg_3Cd (Ti_3Ga), Mn_5Si_3 (Zr_5Ga_3), CuAu (TiGa), CuAl_2 (Hf_2Ga), Zr_2Al_3 (Hf_2Ga_3), U_3Si_2 (Ta_3Ga_2), Ti_6Sn_5 (V_6Ga_5), IrIn_3 (FeGa_3), or Ru_3Sn_7 (Ni_3Ga_7). Others form more complicated structures with large unit cells (with Pearson symbols (Chapter 3.17) in parentheses), e. g. $\text{Mo}_6\text{Ga}_{31}$ (*mP148*), $\text{Mo}_8\text{Ga}_{41}$ (*hR147*), $\text{Rh}_4\text{Ga}_{21}$ (*oS100*), or $\text{Rh}_3\text{Ga}_{16}$ (*oS76*).

Some of the binary gallides have intensively been studied in recent years with respect to their outstanding chemical and physical properties. The gallides TGa_3 ($T = \text{Fe}, \text{Ru}, \text{Os}$) show good thermoelectric properties and are narrow-bandgap semiconductors [10–12]. Pd_2Ga , PdGa , and Pd_3Ga_7 are highly effective semihydrogenation catalysts [13–15] which show large advantages as compared to conventional catalysts like $\text{Pd}/\text{Al}_2\text{O}_3$.

As examples for transition metal gallides the structures of the catalytically important compounds PdGa [16] and Pd_3Ga_7 [17], as well as the gallium-rich phase PdGa_5 [18] are presented in Fig. 3.35. The gallium coordination of the palladium atoms is a function of the gallium content. The lowest coordination number (CN 7) occurs for PdGa (254–271 pm Pd–Ga). The CN 7 polyhedra are condensed *via* common edges, leading to a complex three-dimensional network which crystallizes in the non-centrosymmetric cubic space group $P2_13$. Fig. 3.35 shows a view along a three-fold axis. Also the gallium atoms have seven nearest palladium neighbors and both atom types are well separated from each other. The shortest Ga–Ga distance of 303 pm is much longer than a classical Ga–Ga single bond (250 pm).

Square anti-prisms (253–259 pm Pd–Ga) are the basic building unit in the structure of Pd_3Ga_7 (Ir_3Ge_7 type). Always two of such anti-prisms are condensed *via* a square face. These double prisms (277 pm Pd–Pd) lie on all edges of the cubic unit cell. Always six terminal square faces condense to gallium cubes at the corners of the cell (273 pm Ga–Ga; the higher gallium content leads to an overall increase of Ga–Ga bonding as compared to PdGa). For reasons of clearness, only one ring of four condensed units is presented in Fig. 3.35. This network is penetrated by an independent identical one. Pd_3Ga_7 belongs to a larger family of binary and ternary intermetallics with Ir_3Ge_7 -type structure. Further typical examples are Ru_3Sn_7 , $\text{Nb}_3\text{Sb}_2\text{Te}_5$, or the solid solution $\text{Li}_x\text{Rh}_3\text{Sn}_{7-x}$, where the Ir_3Ge_7 type is only realized through Sn/Li substitution. The bonding peculiarities of this family of compounds have intensively been investigated [19].

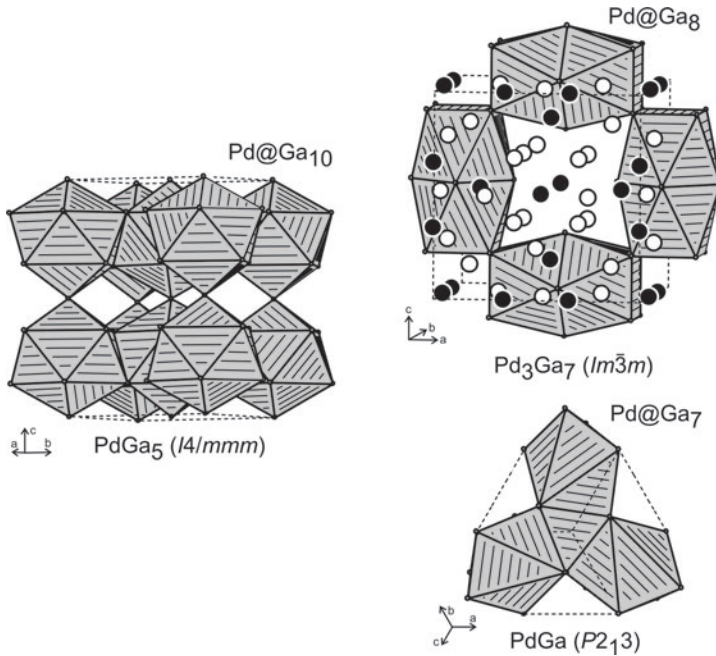


Fig. 3.35 The crystal structures of PdGa_5 , Pd_3Ga_7 , and PdGa . Palladium and gallium atoms are drawn as medium black filled and open circles, respectively. The palladium-gallium polyhedra are emphasized.

PdGa_5 is the gallide with the highest gallium content in the Pd–Ga system. Each palladium atom has CN 10 in form of di-capped square anti-prisms (250–270 pm Pd–Ga). The Pd@Ga_{10} polyhedra are condensed in the ab planes via four common edges and these layers are condensed along c via common corners, leading to the polyhedral framework presented in Fig. 3.35. Every gallium atom belongs to two $\text{Pd@Ga}_{10/2}$ polyhedra. Besides the shorter Pd–Ga contacts (which compare well with the sum of the covalent radii of 253 pm [20]), the PdGa_5 structure also shows a broader range of Ga–Ga distances (267–291 pm), however, mostly longer than in elemental gallium (1×244 and 6×270 pm [21]).

Besides the research in catalysis, gallium is frequently used as alloying component in various technical alloy systems. To give an example, nickel aluminide is microalloyed with gallium leading to improved ductility. Gallium is also used for hardening of palladium based alloys for dental applications.

The rare earth elements form many gallides of compositions RE_3Ga , RE_3Ga_2 , RE_5Ga_3 , RE_3Ga_5 , REGa_2 , and REGa_3 , similar to the aluminum and indium-based systems. A unique situation of the RE–Ga systems is the formation of gallium-rich phases REGa_6 with PuGa_6 -type structure (*vide infra*). Due to their divalent character, the europium-gallium and ytterbium-gallium systems show more similarities with the alkaline earth ones. EuGa_4 and YbGa_4 form with these divalent rare earth elements,

similar to BaGa_4 . Also some unique compositions like Eu_5Ga_9 or YbGa_5 have been determined.

The actinoid-gallium systems with thorium, uranium, neptunium, and plutonium have at least partially been investigated. Representative compounds are ThGa_2 with $\alpha\text{-ThSi}_2$ -type structure, UGa_2 , NpGa_2 , and PuGa_2 with AlB_2 -type, the gallides NpGa_4 and PuGa_4 with UAl_4 -type structure (Chapter 3.8.2), and PuGa_6 [22]. The latter gallide crystallizes in space group $P4/nbm$ and the plutonium atoms have coordination number 12 (310–323 pm Pu–Ga). Eight gallium atoms form a stuffed cube and two opposite faces are capped by another pair of gallium (Fig. 3.36). These Pu@Ga_{12} polyhedra are condensed *via* the rectangular faces in *ab* direction. The layers of condensed polyhedra are connected along the *c* direction by short Ga–Ga bonds of 252 pm.

The two shortest Ga–Ga bonds in the PuGa_6 structure are emphasized in the right-hand drawing of Fig. 3.36. There are two types of dumb-bells which are aligned parallel or in a tilted fashion with respect to the *c* axis. The Ga–Ga distances of 252 and 254 pm are only slightly longer than in the dumb-bell of the element (244 pm). These dumb-bells condense with neighboring ones forming the polyhedra around the plutonium atoms.

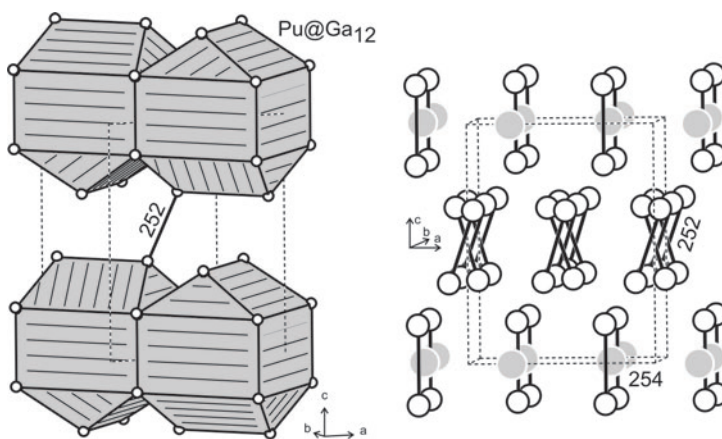


Fig. 3.36 The crystal structure of PuGa_6 . Plutonium and gallium atoms are drawn as medium gray and open circles, respectively. The Pu@Ga_{12} polyhedra are emphasized at the left-hand part of the figure while the right-hand drawing focusses on the shortest Ga–Ga distances.

The large family of ternary metal gallides can roughly be divided into three subgroups: $A\text{-}T\text{-Ga}$, $AE\text{-}T\text{-Ga}$, and $RE\text{-}T\text{-Ga}$. So far the alkali metal (*A*) containing systems have only scarcely been investigated. Most compounds have been prepared with lithium: $\text{Li}T\text{Ga}$ ($T = \text{Pd, Ir}$), Li_2IrGa , and $\text{Li}T\text{Ga}_2$ ($T = \text{Ru, Rh, Pd, Ir, Pt, Au}$) [23]. Although such compounds are potentially interesting with respect to lithium mobility and application as electrode material, the basic characterization of these series of

gallides concerned their intrinsic color, *e. g.* gray LiRuGa_2 , pale violet LiRhGa_2 , silvery LiIrGa , or light yellow LiPtGa as obtained by reflexion spectroscopy.

Among the alkaline earth metal (AE) compounds those with calcium have most intensively been studied. Representative compounds are $\text{Ca}_2\text{Cu}_2\text{Ga}$, CaCuGa [24], $\text{Ca}_3\text{T}_2\text{Ga}_2$ ($T = \text{Pd}, \text{Pt}$), and $\text{Ca}_3\text{T}_2\text{Ga}_3$ ($T = \text{Rh}, \text{Ir}$) [25]. The transition metal and gallium atoms generally build up two- or three-dimensional $[\text{T}_x\text{Ga}_y]^{6-}$ polyanionic networks which are separated (or filled) and charge-balanced by the alkaline earth cations. The crystal chemistry of these gallides is closely related to the corresponding aluminides and indides.

Finally we focus on the rare earth (RE)-transition metal-gallides. The ternary phase diagrams $\text{RE}-T-\text{Ga}$ have thoroughly been studied and the structures of several hundred ternary gallides have been determined. The considerable crystal chemical data are summarized in a handbook [1]. Similar to the alkaline earth metal compounds, also the crystal structures of the ternary rare earth gallides show large similarities with the aluminides and gallides. Generally, the gallides with cerium, europium, and ytterbium have most intensively been investigated, since such compounds are interesting with respect to their valence behavior. Several compositions like RETiIn , RE-TIn_5 , and RE_2TIn_8 exist with different transition metals. Often the gallide structures tolerate a certain valence electron count range.

From the large series of compounds only two important structure types are presented in this chapter, *i. e.* HoCoGa_5 and Ho_2CoGa_8 [26]. The unit cells of both gallides are presented in Fig. 3.37. They have simple building units: Slightly compressed Co@Ga_8 cubes for the cobalt atoms and slightly tetragonally distorted Ho@Ga_{12} cub-

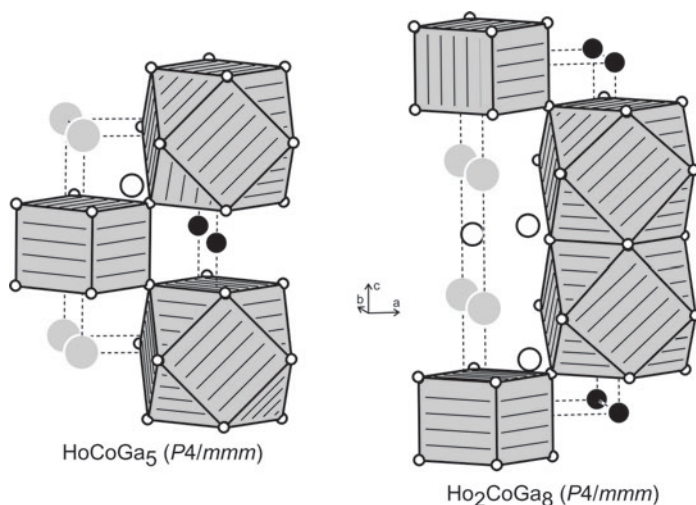


Fig. 3.37 The crystal structures of HoCoGa_5 and Ho_2CoGa_8 . Holmium, cobalt, and gallium atoms are drawn as light gray, medium black filled and open circles, respectively. The Co@Ga_8 and Ho@Ga_{12} polyhedra are emphasized.

octahedra for the holmium atoms. The undistorted versions of both types of polyhedra occur in binary CoGa with CsCl- and HoGa₃ with Cu₃Au-type structures. The HoCoGa₅ type is a 1:1 stacking variant of these building units, while Ho₂CoGa₈ shows insertion of an additional slab, *i. e.* HoCoGa₅ + HoGa₃ $\equiv$ Ho₂CoGa₈. This is a general structural principle. The recently synthesized indides Ce₃PdIn₁₁ and Ce₅Pd₂In₁₁ [27] are 3:1 and 5:2 stacking variants of similar slabs.

Gallides and indides with HoCoGa₅- (> 60 representatives) and Ho₂CoGa₈- (> 30 representatives) type structures have intensively been studied in the last years with respect to their interesting physical properties. Especially the cerium based representatives are highly interesting materials in view of heavy fermion behavior associated with superconductivity. Important results are summarized in [28].



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3.8.4 Indides

Indium belongs to the low-melting elements with a melting temperature of 430 K. It is one of the technologically very important elements which, however, has low abundance. Today we have high demand for low-melting alloys for solders, for sprinkler devices, or thermal fuses. Indium tin oxide is the most important conducting oxide for application in flat screens and touch screens. Keeping the low abundance in mind, there is high necessity for recycling in order to meet the growing demand, especially in the electronic industry. The different intermetallic indium compounds are presented herein with respect to the metal counterparts.

We start with the binary indides formed by the alkali and alkaline earth metals. Lithium reacts with indium forming the binary indides $\text{Li}_{13}\text{In}_3$, Li_2In , Li_3In_2 , Li_5In_4 , LiIn , and LiIn_3 . The first four compounds crystallize with complex structure types. LiIn and LiIn_3 adopt the NaTl - and Cu_3Au -type structures, respectively. Especially the Zintl phase LiIn has intensively been studied with respect to phase transitions depending on temperature and pressure. Applying 11 GPa in a diamond anvil cell, LiIn transforms to the CsCl -type structure [1], while the structure becomes tetragonal upon lowering the temperature below 170 K under normal pressure conditions [2].

The Na-In phase diagram shows the indides Na_2In , NaIn , $\text{Na}_7\text{In}_{11.8}$, and $\text{Na}_{15}\text{In}_{27.4}$ [3]. Some of these indides do not have simple compositions and the crystal structures are comparatively complex. This is also the case for the indides of the heavier alkali metals: K_8In_{11} , $\text{K}_{21.33}\text{In}_{39.67}$, $\text{K}_{39}\text{In}_{80}$, $\text{K}_{17}\text{In}_{41}$, KIn_4 , $\text{Rb}_8\text{In}_{11}$, Rb_2In_3 , RbIn_4 , Cs_2In_3 , and CsIn_4 . The Cs-In phase diagram [4] shows the smallest number of binary compounds. Many of the complex binary indides can be described through their indium substructures. A selection is presented in Fig. 3.38. The smallest units are the $[\text{In}_3]$ triangle in $\text{Na}_{15}\text{In}_{27.4}$ and the $[\text{In}_4]$ tetrahedron in Na_2In . The latter is a rare structural motif in molecules and solids. Another example is discussed at the end of this chapter for rare earth-transition metal-indides. Examples for larger cluster units are the *nido*- and *arachno*- $[\text{In}_{11}]$ clusters and the $[\text{In}_{16}]$ cluster in $\text{Na}_{15}\text{In}_{27.4}$. Often these cluster units do not occur as isolated building units. They are linked *via* In-In bonds to two- or three-dimensional networks. The In-In distances in these cluster units cover a large range with short In-In distances down to 276 pm in $\text{Na}_{15}\text{In}_{27.4}$. Many of these In-In distances are distinctly shorter than in body-centered tetragonal indium, where each indium atom has four nearest indium neighbors at 325 pm and eight further neighbors at 338 pm (Chapter 3.1). This is indicative of strong In-In bonding. A broader comparison of these indium clusters with other triel clusters is given by Corbett [5]. Many clusters obey the Wade- and Zintl rules. An interesting extension

concerns the synthesis of ternary indides with two alkali metals that significantly differ in size. To give an example, the structure of $\text{Rb}_3\text{Na}_{26}\text{In}_{28}$ [6] is a three-dimensional polyanionic indium network of *arachno*- $[\text{In}_{12}]$ drums and $[\text{In}_{12}]$ icosahedra (Fig. 3.38).

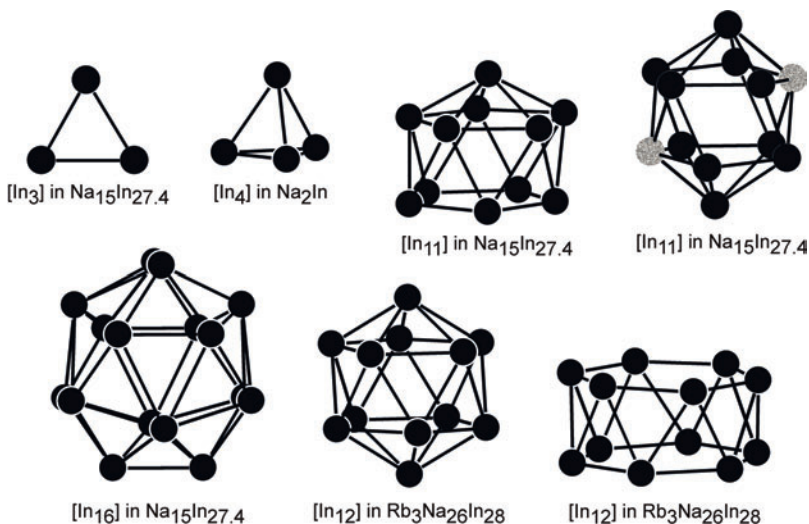


Fig. 3.38 Selected indium clusters in alkali metal indides. The shaded indium atoms in the $[\text{In}_{11}]$ cluster of $\text{Na}_{15}\text{In}_{27.4}$ have only 50 % occupancy.

The alkaline earth metal indides exhibit different structure types. The binary compounds Mg_3In , Mg_5In_2 , Mg_2In , MgIn , MgIn_3 , CaIn_2 , CaIn , Ca_2In , Ca_8In_3 , Ca_3In , SrIn_2 , $\text{Sr}_{28}\text{In}_{11}$, Sr_5In_3 , $\text{Sr}_7\text{In}_{11}$, SrIn , SrIn_3 , $\text{Sr}_3\text{In}_{11}$, SrIn_4 , SrIn_5 , BaIn_2 , Ba_9In_4 , BaIn , and BaIn_4 are known [7]. Again, many of these structures are quite complex, but there are also simple examples. MgIn (CuAu type) and MgIn_3 (Cu_3Au type) crystallize with ordered close-packed structures (Chapter 3.3). As examples for a two- and a three-dimensional indium network the structures of CaIn_2 [8] and Rb_2In_3 [9] are presented in Fig. 3.39. Both compounds can be considered as Zintl phases $\text{Ca}^{2+}(\text{In}^-)_2$ and $(4\text{Rb}^+)(\text{In}_6^{4-})$. The In^- Zintl ions in CaIn_2 are formally isoelectronic with the fourth main group elements and build up a three-dimensional network of condensed tetrahedra, similar to the structure of hexagonal diamond, lonsdaleite. The indium substructure of Rb_2In_3 is two-dimensional. It is composed of indium octahedra which are connected through In–In bonds within the *ab* plane. Adjacent polyanionic layers are shifted by $1/2a + 1/2b$ (body-centered space group). The layers are separated and charge compensated by the rubidium cations. In the case of CaIn_2 the calcium cations fill cages within the three-dimensional network.

Several of the indide Zintl phases have been studied with respect to their magnetic and electrical behavior. Diamagnetism as well as Pauli paramagnetism have been

observed. The Pauli paramagnetic ones show lower electrical specific resistivities and can be classified as metallic Zintl phases [10]. Several data are tabulated in [5].

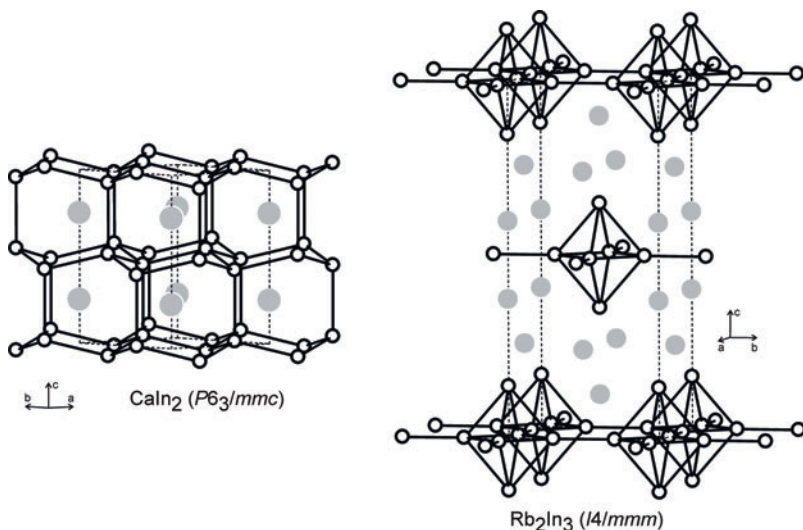


Fig. 3.39 The crystal structures of CaIn_2 and Rb_2In_3 . Calcium (rubidium) and indium atoms are drawn as medium gray and black open circles, respectively. The indium substructures are emphasized.

The binary transition metal-indium systems have intensively been studied; however, not all existing phases have yet been structurally characterized. Only few compounds exist with the electron-poor transition metals, while the systems with elements from the nickel and copper group show many binary phases. Some of the binary indide structures show simple structure types: RhIn and PdIn crystallize with the CsCl type, PtIn_2 and AuIn_2 adopt the CaF_2 type, and the structures of Zr_3In , ZrIn_2 , ZrIn_3 , and Pt_3In derive from ordered *fcc* packings (Chapter 3.3).

As examples for the more complex indides we present the Ti_2In_5 [11] and RuIn_3 [12] structures in Fig. 3.40. The indium atoms in Ti_2In_5 build up two-dimensional networks in the *ab* plane which can be considered as a tessellation of triangles, squares, and pentagons. The AA stacking of these network layers leads to three different prism types. Only the pentagonal prisms are filled with titanium atoms leading to infinite linear chains with 300 pm Ti–Ti which extend in *c* direction. This structure is an excellent example for anisotropic chemical bonding. Electronic structure calculations on isotypic Hf_2In_5 [13] showed pronounced two-dimensional In–In bonding within the layers and strong Hf–Hf bonding within the chains.

Also the RuIn_3 structure shows a two-dimensional indium network; a tessellation of distorted triangles and squares. The square-prismatic voids are filled by additional indium atoms, leading to tungsten-like centered cubes. On the other side, only half of

the trigonal prisms are filled with ruthenium, but in a pair-wise manner. One can thus describe the RuIn_3 structure also as an intergrowth of W and AlB_2 related slabs. The dotted lines in Fig. 3.40 indicate that Ru–Ru bonding plays only a subordinate role in RuIn_3 . The main bonding interactions arise from Ru–In and In–In. RuIn_3 belongs to a series of FeGa_3 -type compounds which have broadly been studied in recent years with respect to their thermoelectric properties [14].

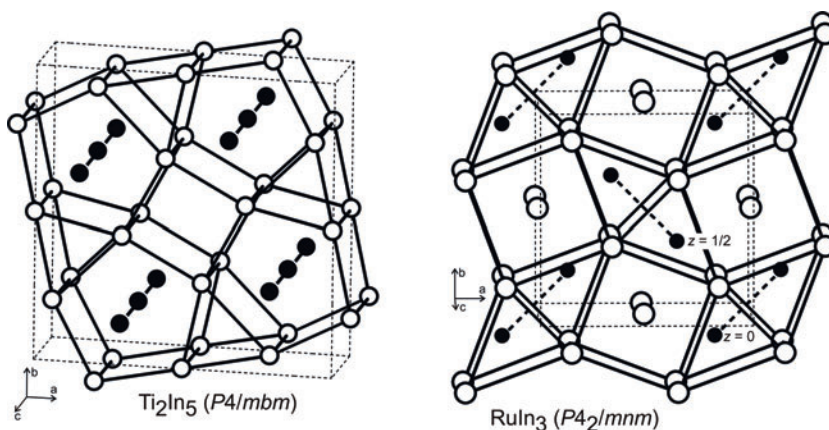


Fig. 3.40 The crystal structures of Ti_2In_5 and RuIn_3 . Titanium (ruthenium) and indium atoms are drawn as black open and filled circles, respectively. The indium substructures are emphasized.

Transition metal-indium compounds are a necessary evil for contact formation in electronics. The problem is their brittleness. The intermetallic compound with directed covalent T –In bonds shows much higher brittleness than the surrounding solder alloy and is thus responsible for fracture of the joints. For joint formation one needs a delicate equilibrium with respect to the layer thickness of the intermetallic compound. It should be large enough to ensure the contact, but not too large to cause fracture. Two important parameters for the formation of intermetallics as precipitations is the temperature of the solder and the soldering time. Generally higher temperature and longer time enhance the formation of stable intermetallics. These processes are diffusion driven. For many of such materials the growth rate curves as a function of temperature and time have been measured and documented. Along with these studies, also the phase diagrams such as Cu–In, Ag–In, and Au–In have thoroughly been examined.

A widely used soldering system is Cu–In, especially for joints with brasses and bronzes. Over time indium can diffuse into the copper-based material, leading to brittle copper indides, weakening the solder joints. For long lasting applications one can coat the copper-based pieces with a 50 micron nickel film. The latter then acts as a kind of diffusion barrier for the indium atoms. Since diffusion of indium into copper, silver, and gold already proceeds at room temperature, precise estimations for long

term (*i. e.* over years) layer growth have been made. Generally, the binary intermetallic compound has a higher melting temperature than the surrounding indium-based solder material. This further causes differences in thermal expansion and heat conductivity.

AuIn and AuIn₂ are frequently used as conducting, but brittle joint materials. Since such materials have high technical importance, all basic mechanical properties of these binaries have been investigated in detail, such as the micro-hardness or the shear resistance. AuIn₂ can act as a barrier against further dissolution of gold in the solder. Ag₂In and AgIn₂ are important intermetallics for the contact on silver-based pieces. Other binaries like Pd₃In, Pd₂In, PdIn, Pd₂In₃, Pt₂In₃, PtIn₂, and Pt₃In₇ play only a subordinate role, mostly for specialized applications.

Indium has long been tested as a substitute for lead-based solders; however, this is limited, since indium is one of the critical raw materials for which the long term availability cannot be guaranteed. Furthermore indium is a very high energy consuming material taking mining, production, and recycling into account; around 400 times more for one kg of indium as compared to lead.

The binary rare earth indides of the trivalent rare earth elements show simple structure types: RE₃In and REIn₃ (Cu₃Au type), RE₃In₅ with Pu₃Pd₅ type, and REIn with CsCl type. Europium and ytterbium show exceptions. They form Zintl phases EuIn₂ and YbIn₂ with CaIn₂-type structure (*vide supra*).

Concerning ternary indides, those with the alkali and alkaline earth metals structurally differ from those of the rare earth metals. We start with the description of the ternary alkali metal-transition metal-indides. Lithium forms a series of indides Li₂TIn, LiT₂In, and LiTIn₂ with ordering variants of the cubic BiF₃ type. These and other intermetallic lithium indides have repeatedly been studied with respect to lithium mobility for potential battery materials [15, 16]. Representative compounds with sodium are Na₂Au₆In₅ [17] and Na₃TIn₂ (*T* = Ag, Au) [18]. Depending on the transition metal (*T*)-to-indium ratio, chemical bonding in these ternary indides is characterized by strong *T*-In, and/or *T*-*T*, respectively In-In bonds. Similar bonding features occur in the potassium compounds KAu₄In₆ [19], KAu₄In₂ [20], and KT₂In₉ (*T* = Co, Ni) [21]. The KAu₄In₂ and KAu₄In₆ structures are exemplarily shown in Fig. 3.41. Both structures have covalently bonded three-dimensional gold-indium networks which leave larger tunnels for the potassium atoms. The [Au₄In₂] network is stabilized also by Au-Au bonding, while the indium-rich [Au₄In₆] network exhibits a variety of In-In bonding interactions. Other structural features have been observed in K₈ZnIn₁₀ [22] and K₁₀NiIn₁₀ [23] which contain [ZnIn₁₀]⁸⁻, respectively [NiIn₁₀]¹⁰⁻ cluster units.

Among the ternary alkaline earth metal indides we observe a clear difference between the magnesium compounds as compared to those with the heavier ones. Magnesium can substitute for indium and play part of the covalently bonded networks. During systematic phase analytical studies of the Mg-*T*-In systems many solid solutions have been observed: (i) Magnesium solubility in binary indides and (ii) indium solubility in binary magnesium compounds. Prominent examples are IrIn_{3-x}Mg_x

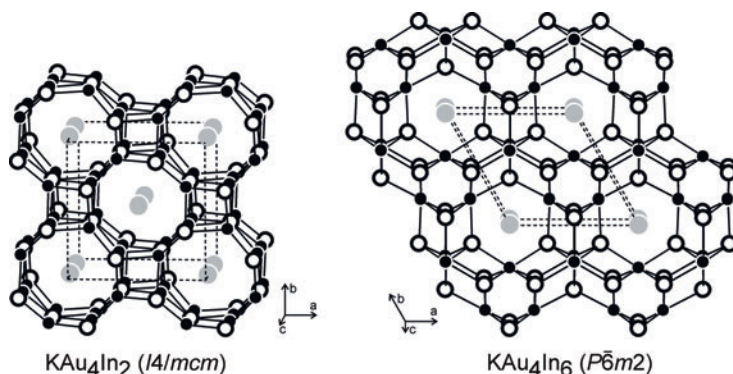


Fig. 3.41 The crystal structures of KAu_4In_2 and KAu_4In_6 . Potassium, gold, and indium atoms are drawn as medium gray, black open and filled circles, respectively. Only Au–In bonds are drawn.

[24], $\text{IrIn}_{2-x}\text{Mg}_x$ [25], or $\text{Ir}_3\text{Mg}_{13-x}\text{In}_x$ [26]. Many other binaries show similar behavior. This covalent behavior of magnesium was later also observed for AEMg_5In_3 ($\text{AE} = \text{Sr}, \text{Ba}$) [27].

Before we discuss the crystal chemical details of the calcium, strontium, and barium containing compounds we briefly refer back to the synthesis conditions. Generally one can directly synthesize the $\text{AE}_x\text{T}_y\text{In}_z$ indides from the elements. The synthesis can be observed in a water-cooled sample chamber equipped with an observation window [28]. To give an example, CaAuIn_2 can be synthesized by induction melting from calcium granules, pieces of gold wire and indium tear drops. Glassy carbon is a suitable crucible material. In a typical experiment, indium first melts and reacts with the gold wire forming a liquid gold-indium alloy. In a second step the liquid alloy is heated up to the melting temperature of the alkaline earth element which then vigorously reacts with the gold-indium alloy. The transfer of the alkaline earth metal valence electrons to the gold-indium alloy is visible through a strong heat flash.

As examples for the ternary alkaline earth metal indides the structures of SrPtIn_2 [29] and $\text{Sr}_2\text{Pt}_3\text{In}_4$ [30] are presented in Fig. 3.42. The platinum and indium atoms form covalently bonded three-dimensional $[\text{PtIn}_2]$ and $[\text{Pt}_3\text{In}_4]$ polyanionic networks which leave larger cavities for the strontium atoms: Distorted pentagonal prisms in SrPtIn_2 and two types of distorted hexagonal prisms in $\text{Sr}_2\text{Pt}_3\text{In}_4$. The Pt–In distances range from 278–282 pm in SrPtIn_2 and 265–290 pm in $\text{Sr}_2\text{Pt}_3\text{In}_4$, close to the sum of the covalent radii of 279 pm [31]. The strontium atoms bond to the polyanions via shorter Sr–Pt contacts, as expected from the course of their electronegativities. Many of the $\text{AE}_x\text{T}_y\text{In}_z$ indides show similar crystal chemical and bonding characteristics. Depending on the transition metal-to-indium ratio, the polyanions additionally show either T–T or In–In bonding. This feature is further addressed for the series of ternary rare earth-transition metal-indides.

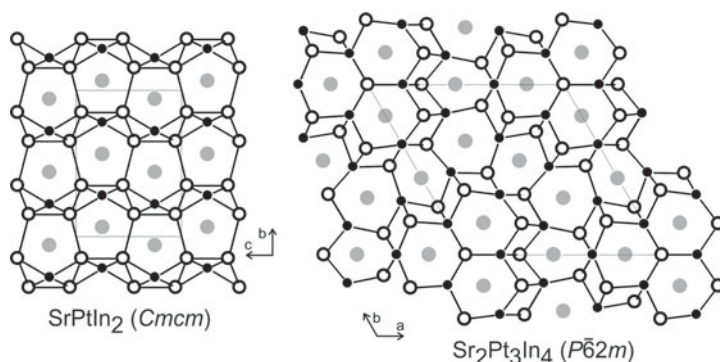


Fig. 3.42 The crystal structures of SrPtIn_2 and $\text{Sr}_2\text{Pt}_3\text{In}_4$. Strontium, platinum, and indium atoms are drawn as medium gray, black filled and open circles, respectively. The three-dimensional platinum-indium polyanions are emphasized (only Pt–In bonds).

The $\text{AE}_x\text{T}_y\text{In}_z$ indides mostly tolerate small ranges in the valence electron concentration (VEC). To give an example, the SrTIn_2 indides exist for $T = \text{Rh, Ir, Pd, Pt}$ and $\text{Sr}_2\text{Au}_3\text{In}_4$ is isotypic with $\text{Sr}_2\text{Pt}_3\text{In}_4$. NaAuIn_2 and CaAuIn_2 crystallize with the MgCuAl_2 type, similar to the SrTIn_2 series. An increase or decrease in VEC can often be equilibrated by small changes in the lattice parameters (isotropic or even anisotropic) and thus variations in interatomic distances. Many of the $\text{AE}_x\text{T}_y\text{In}_z$ indides are stable in air while the binary alkaline earth indides show fast hydrolysis when exposed to traces of water.

With increasing indium concentration in the $\text{AE}_x\text{T}_y\text{In}_z$ indides one observes pronounced formation of In–In bonds. The structures of SrPtIn_2 and SrPtIn_4 [32] are presented in Fig. 3.43. The indium atoms in SrPtIn_2 build up a network of condensed $\text{InIn}_{4/4}$ tetrahedra which resembles the structure of hexagonal diamond, lonsdaleite (AB stacking sequence of the puckered hexagons). This arrangement readily reminds of the CaIn_2 structure discussed above and one can formally describe the SrTIn_2 compounds as transition metal filled Zintl phases. Since the transition metal atoms are the most electronegative component in the SrTIn_2 compounds and tend to fill their d bands, the indium network of the electron-precise binary compound ($\text{Sr}^{2+}(\text{In}^-)_2$) is oxidized, leading to longer In–In distances and orthorhombic distortions for the ternary compounds. This has been underlined by electronic structure calculations [29]. Keeping the strong transition metal-indium bonding in mind, an electron partitioning scheme $\text{Sr}^{2+}[\text{TIn}_2]^{2-}$ is a good approximation.

Even higher indium content occurs in SrPtIn_4 . The indium atoms show distorted bcc cubes, resembling the tetragonal body-centered structure of the element [33]. This structural motif occurs in many indium-rich intermetallic compounds. These cubes can flexibly distort and meet the crystal chemical requirements of the other elements. An overview of a variety of such distorted cubes is given in [34, 35]. The In–In distances in the ternary phases are close to those in the element. Compounds like SrRh_2In_8 [35] belong to the most indium-rich intermetallics with a well ordered structure.

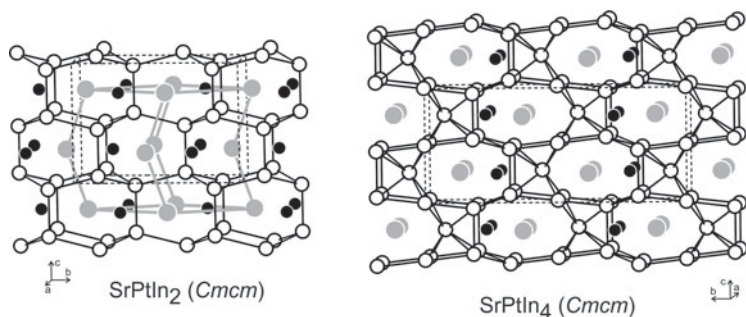


Fig. 3.43 The crystal structures of SrPtIn_2 and SrPtIn_4 . Strontium, platinum, and indium atoms are drawn as medium gray, black filled and open circles, respectively. The indium substructures and the orthorhombically distorted SrIn_2 -related subcell of SrPtIn_2 are emphasized.

The last family of indium compounds concerns those with a rare earth element. Such intermetallics can be synthesized by arc-melting. In the case of europium, ytterbium, and sometimes samarium, the low boiling temperature of the rare earth element hampers such simple synthesis, and better results can be obtained in sealed high-melting metal tubes. Single crystals of $\text{RE}_x\text{T}_y\text{In}_z$ indides can be obtained directly from the arc-melted samples. In many cases, however, special annealing sequences followed by slow cooling of the samples are necessary in order to get crystals of sufficient quality for structure determination. The indium-rich compounds can be obtained in well crystallized form using the self-flux technique (see Chapter 2.7). The excess indium matrix can be dissolved under mild conditions in acetic acid. Not all ternary indides resist 2N hydrochloric acid which is usually used for stannides.

The structural chemistry of $\text{RE}_x\text{T}_y\text{In}_z$ indides is extremely rich. Several hundred ternary phases have been reported and their crystal chemistry has been reviewed [36]. The compositions of the many ternary phases are plotted in a general phase diagram in Fig. 3.44. Four pronounced regions of different substructures can roughly be distinguished. In the rare earth metal-rich regions of the respective phase diagrams (magenta shading) complex structures with large unit cells and high coordination numbers occur. Such structures can often be described as intergrowths of selected polyhedra. The largest family of compounds concerns the large area shaded in blue color. Here one observes formation of two- or three-dimensional covalently bonded $[\text{T}_y\text{In}_z]$ polyanionic networks with larger cavities for the rare earth cations, similar to SrPtIn_2 [29] and $\text{Sr}_2\text{Pt}_3\text{In}_4$ [30] discussed above.

Within the latter family two further distinctions can be made. Most compounds with high indium content (green shaded area) again show pronounced formation of distorted *bcc* indium cubes. This is independent of the nature of the rare earth and transition metals. A recent further example of this family is $\text{Eu}_3\text{Co}_2\text{In}_{15}$ [21] in which all indium atoms participate in the network of condensed cubes. Segregation

of the transition metal atoms is observed in the T -rich part (gray shading). T_2 pairs (e. g. in $\text{Er}_{12}\text{Fe}_2\text{In}_3$), one-, two-, or three-dimensional T clusters are the typical building units.

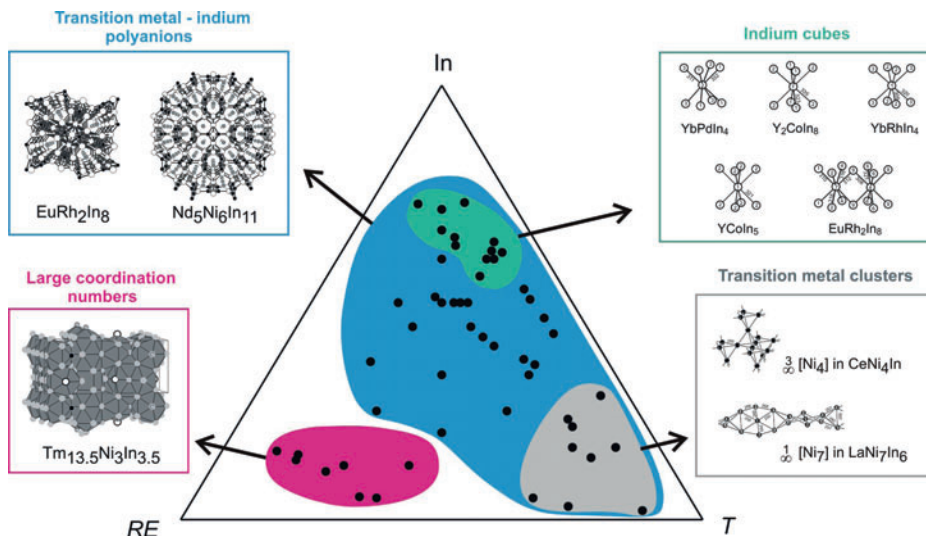


Fig. 3.44 The general phase diagram rare earth metal-transition metal-indium. The shaded areas correspond to different substructures. Representative examples for these substructures are shown on the left- and right-hand parts of the drawing.

The europium and ytterbium compounds contain divalent rare earth elements and their structures are often isotypic with those of the respective alkaline earth elements (calcium and strontium are close in size). The indium substructures of the $\text{RE}_x\text{T}_y\text{In}_z$ phases are not only dominated by the distorted InIn_8 cubes and the lonsdaleite-related networks. An interesting observation is the segregation of In_2 pairs (e. g. in $\text{Ho}_{14}\text{Co}_3\text{In}_3$) and In_4 tetrahedra (e. g. in Gd_4RhIn) in metal-rich indides.

The $\text{RE}_x\text{T}_y\text{In}_z$ indides have intensively been studied with respect to their magnetic properties. Especially the cerium, europium, and ytterbium containing ones and the phases of compositions RETiIn , RETiIn_5 , and RE_2TIn_8 were investigated. Important results are summarized in [36].

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3.8.5 Thallides

Thallium is a ductile metal, similar to lead. Due to its high heavy metal toxicity intermetallic thallium compounds find no technical application. Previously thallium has been used for the hardening of lead-based electrodes. Nevertheless, thallium intermetallics are highly interesting from a basic research point of view. The most prominent thallide is the Zintl phase (Chapter 3.7) NaTl [1]. Formally, the sodium atoms transfer their valence electrons to the thallium atoms which then obtain the electron configuration of a group IV element. The thallium atoms can then form four two-electron-two-center bonds (324 pm Tl–Tl) leading to a diamond-related three-dimensional network (Fig. 3.45) with $\text{TlTl}_{4/4}$ tetrahedra.

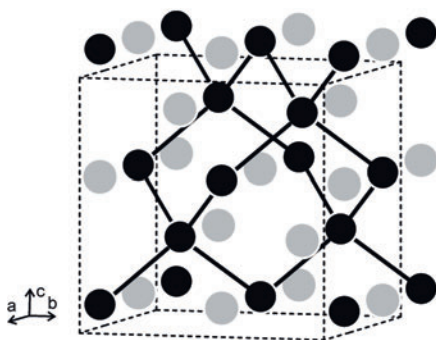


Fig. 3.45 The crystal structure of NaTl. The three-dimensional, diamond-related thallium network is emphasized.

Lithium forms binary thallides of compositions LiTl (CsCl type), Li_2Tl (Li_2Ga type), Li_5Tl_2 (Li_5Sn_2 type), Li_3Tl (BiF_3 type), and $\text{Li}_{22}\text{Tl}_5$ ($\text{Li}_{22}\text{Pb}_5$ type). These structures very much resemble the typical intermetallics of lithium observed with the tetrrels (Chapter 3.9). Besides NaTl sodium forms a structurally complex cubic sodium-rich thallide of composition $\text{Na}_{44}\text{Tl}_7$ [2]. Na_2Tl [3] contains isolated Tl_4 cluster units (Fig. 3.46) (318–330 pm Tl–Tl).

Larger thallium cluster units occur in the phases with the heavier alkali metals. KTI is dimorphic. Under ambient pressure conditions KTI crystallizes with its own structure type [4]. Again the potassium atoms transfer their valence electron to the thallium atoms and one observes formation of Tl_6^{6-} hypoelectronic clusters with 12 ($\equiv 2n$) skeletal p electrons which are embedded within the potassium matrix (Fig. 3.47). The potassium atoms (a similar situation is observed in CsTI) are too large for the cavities left by the diamond-like network in NaTl. The way out is the formation of clusters. The centers of these Tl_6^{6-} clusters show a *fcc* packing. The Tl–Tl distances within the compressed octahedra vary from 306–347 pm. Application of high pressure

in the order of 20 kbar in a diamond anvil cell leads to a reconstructive phase transition. The high-pressure phase of K₂Tl [5] is isotypic with Na₂Tl with 327 pm Tl–Tl in the diamond-like network.

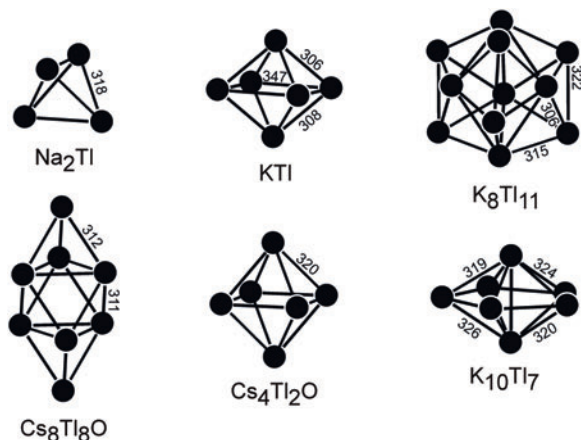


Fig. 3.46 Thallium clusters in selected binary and ternary thallides. Relevant Tl–Tl distances are indicated.

Besides the tetrahedral and filled octahedral clusters in Na₂Tl and K₂Tl, a variety of more complex cluster units has been observed [6]. Some examples are presented in Fig. 3.46. If two alkali metals with different size are used, the variety of clusters is even larger. Typical examples are the complex structures of Na₂K₂₁Tl₁₉ or Na₃K₈Tl₁₃. The clusters can also be substituted by an electron-rich transition metal, *e. g.* Au₂Tl₉^{9–} or Cd₃Tl₈^{10–}, centered by thallium itself (Tl₁₃^{11–}, a thallium-centered Tl₁₂ icosahedron), or by a transition metal, *e. g.* NiTl₁₀^{10–}. This cluster chemistry is not restricted to these pure intermetallics. The structures of Cs₈Tl₈O [7] and Cs₄Tl₂O [8] exhibit Tl₈^{6–} *closo*-deltahedra, respectively, regular Tl₆^{6–} octahedra as cluster units which are charge balanced and separated by poly-nuclear cesium-oxygen cations. All these cluster units exhibit complex chemical bonding features that are strongly influenced by relativistic effects (contraction and energetic stabilization of the thallium 6s orbital). Several cluster anions are classified as Zintl anions, some obey the Wade rules and some are denoted hypoelectronic; they cannot be explained with the aforementioned rules. For details we refer to [6–8].

The alkaline earth metals form several binary thallides, but with much simpler crystal chemistry. CaTl and MgTl crystallize with the CsCl type with well separated thallium atoms. Further examples are Mg₂Tl (Fe₂P type), Mg₅Tl₂ (Mg₅Ga₂ type), Ca₃Tl (Cu₃Au type), and CaTl₃ (BiF₃ type).

A remarkable binary compound is BaTl₂ (Fig. 3.48) which adopts the CaIn₂ type. It can be considered as an electron-precise Zintl phase according to Ba²⁺(Tl[–])₂. The

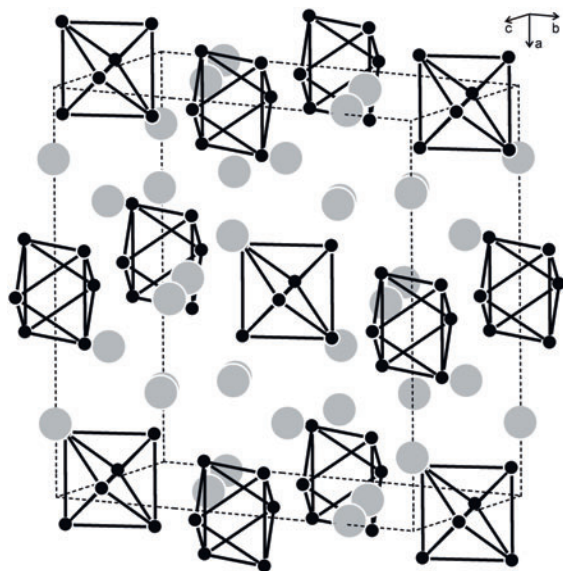


Fig. 3.47 The crystal structure of KTi (space group *Cmce*). The compressed octahedral thallium clusters are emphasized.

thallium atoms adopt the electron configuration of a tetrel (similar to NaTl discussed above), however, the $\text{TlTi}_{4/4}$ tetrahedra show a different arrangement. The thallium substructure of BaTl_2 corresponds to the structure of hexagonal diamond, lonsdaleite. The hexagonal structure offers the c/a ratio as a degree of freedom and consequently each thallium atom has a 3+1 coordination with Tl–Tl distances of 310 and 348 pm, shorter and longer than in NaTl (324 pm). The diamond-like networks are stacked in ABC sequence in NaTl, but in AB sequence in BaTl_2 . Thus, BaTl_2 can be considered as the hexagonal counterpart of NaTl. We come back to this thallium network in the discussion of ternary thallides (*vide infra*).

Only few transition metal thallides have been reported. This might be a consequence of the heavy metal toxicity of thallium. Representative compounds are $\text{Ti}_{3.2}\text{Tl}_{0.8}$, $\text{Zr}_{3.2}\text{Tl}_{0.8}$, and Nb_3Tl with cubic Cr_3Si -type structure (Chapter 3.9.2), PdTi_2 , PtTi_2 , and AuTi_2 with CuAl_2 type, NiTi (NiAs type), Pd_2Tl (Co_2Si type), PtTi (CoSn type), or Pd_3Tl ($\text{TiAl}_3/\text{ZrAl}_3$ type, *fcc* superstructure). Pd_{13}Tl and Pt_3Tl_2 crystallize with their individual more complex structure types.

Except for scandium, thallides have been reported for all rare earth elements. Typical compositions are RETi (CsCl, CuAu, or CuTi type), RE_5Tl_3 (Mn_5Si_3 or W_5Si_3 type), RE_3Tl_5 (Pu_3Pd_5 type), RETi_3 and RE_3Tl (Cu_3Au type). Europium and ytterbium behave like divalent elements in such series. Consequently they do not show the same structure types. The Zintl phase EuTi_2 is isotypic with CaIn_2 and BaTl_2 discussed above. Ytterbium forms the thallides Yb_8Tl_3 (Ca_8In_3 type) and Yb_2Tl (Co_2Si type). Among the rare earth thallides those with cerium have most intensively been studied with respect to

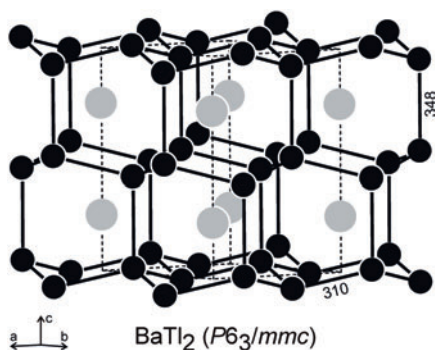


Fig. 3.48 The crystal structure of BaTl_2 . The three-dimensional thallium network and relevant Tl–Tl distances are emphasized.

their magnetic properties. The trivalent cerium atoms in CeTl_3 [9] show strong crystal field splitting of the $J = 5/2$ level. The cerium magnetic moments order antiferromagnetically below 3.85 K.

CsCl type CeTl shows a cubic-to-tetragonal structural transition at 193 K and a comparatively high Néel temperature of 25.5 K [10]. The structural phase transition temperature increases with increasing pressure. The phase transition is expressed by a large hysteresis in the temperature dependence of the electrical resistivity.

The thallium-rich actinide compounds UTl_3 and ThTl_3 both crystallize with the Cu_3Au -type structure. Further thorium thallides are Th_3Tl_5 (Pu_3Pd_5 type), ThTl (ThIn type), Th_5Tl_3 (Mn_5Si_3 type), and Th_2Tl (CuAl_2 type). The magnetic structure of UTl_3 has been determined from neutron diffraction data. The uranium magnetic moments order antiferromagnetically below a Néel temperature of 90 ± 5 K [11] with an alignment of the spins in adjacent (111) planes.

Concerning ternary thallides, the data base is very small. Several series of equi-atomic compounds REMgTl , RECuTl , REZnTl , and REPtTl [12] have been reported. Not all of these compounds exist for the whole series of rare earth elements. An interesting compound within the magnesium-based series is $\text{EuMg}_{1-x}\text{Tl}_{1+x}$ ($x = 0.013\text{--}0.058$) which exhibits a small solid solution within the polyanionic network as well as intermediate europium valence [13].

Only few, but highly interesting ternary compounds have been synthesized with the alkali and alkaline earth metals. The thallides $\text{A}_8\text{PdTl}_{11}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) [14] can be considered as palladium-filled variants of the binaries. The palladium atoms are located within the Tl_{11} cluster units. SrPdTl_2 , SrPtTl_2 [15], and EuPdTl_2 [16] are transition metal filled variants of the binary Zintl phases SrTl_2 and EuTl_2 . They are isotypic with the corresponding indium compounds (Chapter 3.8.4). Another thallium-rich compound, Ba_2AuTl_7 [17] is presented in Fig. 3.49. The gold and thallium atoms build up a complex three-dimensional $[\text{AuTl}_7]$ network which leaves larger cavities for the barium atoms. The gold atoms have slightly distorted square-pyramidal thallium co-

ordination (280–301 pm Au–Tl). These AuTl_5 units are condensed *via* Tl–Tl bonds and additional thallium atoms.

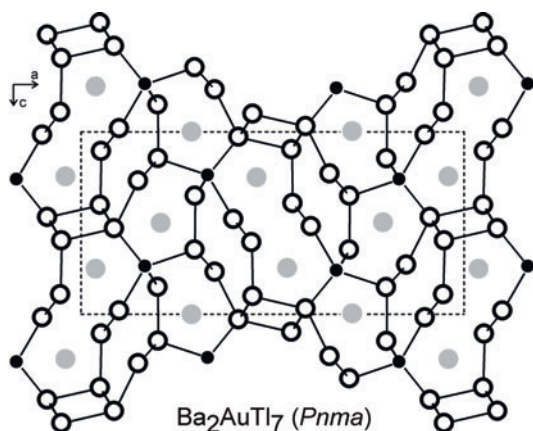


Fig. 3.49 The crystal structure of Ba_2AuTl_7 . Barium, gold, and thallium atoms are drawn as medium gray, black filled and open circles, respectively. The three-dimensional $[\text{AuTl}_7]$ network is emphasized. Only the shortest Tl–Tl bonds (303–312 pm) are drawn.

BaHg_2Tl_2 [18] is one of the spectacular thallide structures (Fig. 3.50). The mercury and thallium atoms show clear segregation. Chains of condensed Hg_6 hexagons and trans-edge-sharing Tl_4 tetrahedra extend in *c* direction. The Hg–Hg (287 and 291 pm) and Tl–Tl (304 and 336 pm) distances are both slightly shorter than in α -mercury (6×299 and

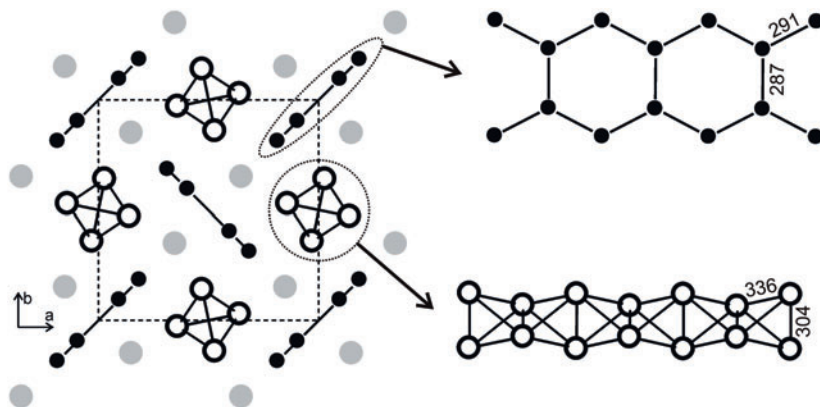


Fig. 3.50 The crystal structure of BaHg_2Tl_2 . Barium, mercury, and thallium atoms are drawn as medium gray, black filled and open circles, respectively. The chains of condensed Hg_6 hexagons and trans-edge-sharing Tl_4 tetrahedra are emphasized at the right-hand part of the drawing. Relevant interatomic distances are indicated.

346 pm) and *hcp* thallium (6×341 and 6×342 pm). Adjacent chains are connected via Hg–Tl bonds (306–309 pm) forming a three-dimensional network in which the barium atoms have Ba@Hg₉Tl₆ coordination. Electronic structure calculations showed strong scalar relativistic contributions to the Hg–Hg bonding within and the Hg–Tl bonding between the chains.



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3.9 Tetrelides

3.9.1 Carbides

In classical inorganic chemistry textbooks, carbides are usually divided into three major groups, depending on their chemical bonding characteristics, i. e. salt-like, covalently bonded, and metallic carbides. Typical examples for the first group are Li₂C₂ [1],

CaC_2 [2], or Al_4C_3 [3]. Pure samples of these acetylides or methanides show essentially ionic bonding and they are white, transparent solids. Due to the absence of *d*-electrons, the hydrolyses of such compounds usually leads to pure hydrocarbons, e. g. $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$ or $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4$. In the beginnings, these reactions have widely been used for the production of acetylene (miner's lamp) and methane (Moisson technique). The acetylides show peculiar structural behavior, since the C_2 dumb-bells show different ordering as a function of temperature [4]. Silicon carbide is a prominent example for the group of covalently-bonded carbides. SiC adopts the blende-type structure, or in other words, every other carbon atom in the diamond structure is substituted in an ordered manner by silicon. Besides the blende-type, SiC can adopt a large variety of other ordered stacking variants of the $\text{SiC}_{4/4}$ tetrahedra [5]. Silicon carbide and also covalently bonded boron carbides are widely used abrasive materials [6]. In the present chapter we will focus essentially on carbides with metallic character.

It is well known from the very beginning of steel manufacturing, that carbon plays a crucial role in steel production and steel hardening. Carbon atoms fill voids in the metallic matrix and enforce strong covalent metal-carbon bonding. Frequently such carbides are called interstitial carbides (Hägg nomenclature [7]). However, this is only correct if the metal substructure is kept also in the binary carbide phase. To give an example, hexagonally close packed titanium transforms to TiC where all octahedral voids are filled by carbon atoms within a cubic close packed titanium substructure. Thus, the titanium atoms in Ti and TiC belong to different structural branches and therefore TiC is not an interstitial carbide as such. Formally, the TiC structure might be seen as isotypic to NaCl, and this comparison is made in many textbooks. Nevertheless, we should call the structural relationship between TiC and NaCl isopointal [8] rather than isotypic. Although we have similar occupancy of the *4a* and *4b* Wyckoff sites, NaCl is a classical salt, while strong Ti–Ti and Ti–C bonding lead to the metallic hard material TiC.

Chemical bonding in such transition metal carbides has first been studied for the rock salt phases TiC, VC, and NbC on the basis of augmented-plane-wave (APW) [9–11] and extended Hückel [12] calculations. The computations revealed charge transfer from the transition metal to the carbon atoms and crystal orbital overlap population analysis (COOP) showed strong *T*–C besides *T*–*T* bonding, an essential prerequisite for the chemical inertness, the extreme hardness, and the high melting points of these materials. Refractory carbides like HfC or TaC have much higher melting points than usual crucible materials like Al_2O_3 . For an overview we refer to [6].

The transition metal carbides have intensively been studied in the early research on steel production and properties. These investigations focused on the phase analysis, the construction of the corresponding phase diagrams, the determination of the crystal structures and the phase width, since several transition metal carbides showed extended homogeneity ranges.

A broad overview on the many transition metal carbides was given by *Frad* already in 1968 [13]. Herein we only focus on the technically most relevant carbides WC, TiC, and TaC, which are produced in large scale (several thousand tons per year). Further industrially important carbides are VC, NbC, ZrC, HfC, Mo₂C, Cr₂₃C₆, Cr₃C₂, Cr₇C₃, and Fe₃C. The structures of TiC and WC are presented in Fig. 3.51. In TiC the carbon atoms fill octahedral voids, the usual carbon coordination in TC_x carbides of the early (electron poor) transition metals [14], while trigonal prisms are occupied in WC.

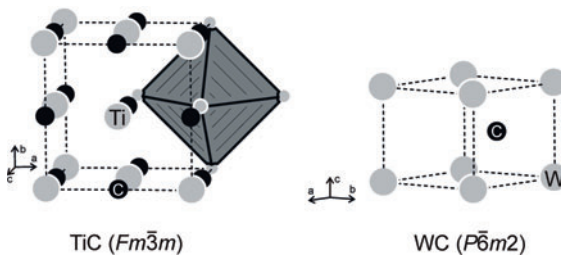


Fig. 3.51 The crystal structures of TiC and WC.

In all of these transition metal carbides one observes isolated carbon atoms (no C–C bonds). The W–C and W–W distances in WC are 220 and 284 pm, respectively, again, indicating strong W–C and W–W bonding. The carbon-poorer phase W₂C crystallizes with an *anti*-CdI₂-type structure. Such structure type relationships between intermetallic and salt-like (covalent) structure types are frequently observed. Again, in W₂C the carbon atoms fill octahedral voids. For such structures with face-sharing octahedra, the Parthé-Yvon rule (adjacent face-sharing octahedra are not occupied) [15] is generally obeyed. Exceptions have been observed for complex hydrides (see Chapter 3.16).

Filling of the trigonal prismatic or octahedral voids is not always complete and most of the binary transition metal carbides show homogeneity ranges. The defects are generally randomly distributed at high temperature, while ordering is frequently observed at low temperature. This is especially expected for most rock salt-derived TC_{1-x} phases, however, only few have been studied in detail. Fully ordered variants have been observed for V₈C₇ and V₆C₅ with bigger empty and smaller filled V₆ octahedra, again, nicely underlining the strong covalent V–C bonding. For a broader overview we refer to [6].

Cubic face centered γ -Fe dissolves up to 8 atomic-% carbon, a well known process from steel production (cast iron formation). Besides this solid solution Fe₃C (cementite) precipitation plays an important role. The carbon atoms in the cementite structure (Fig. 3.52) have trigonal prismatic iron coordination with Fe–C distances of 199 and 204 pm, in agreement with substantial covalent Fe–C bonding. These trigonal prisms form columns via common iron edges that extend along the *x* axis. The carbon coordination sphere is completed by three additional iron neighbors at the longer Fe–C distances of 2×239 and 283 pm, leading to tricapped trigonal prismatic coordination,

frequently observed in such structures [16]. Adjacent columns of condensed trigonal prisms are further condensed via a variety of Fe–Fe bonds (250–270 pm, close to 248 pm in *bcc*-Fe [17]), leading to a bonding pattern similar to TiC. Fe_3C is significantly harder than pure iron, but metastable.

The binary carbides Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6 (Stellite®), as well as the double carbides $(\text{Fe,Cr})_3\text{C}_2$, $(\text{Fe,Cr})_7\text{C}_3$, and $(\text{Fe,Cr})_{23}\text{C}_6$ play an important role in chromium containing steels. These phases enhance hardening and increase the pyrophoric stability as well. The structures of Cr_3C_2 and Cr_7C_3 both show trigonal prismatic carbon coordination, while the unusual coordination number 8 (square anti-prisms) is observed in the cubic structure of Cr_{23}C_6 . The stabilities of the chromium carbides again results from strong Cr–C and Cr–Cr bonding.

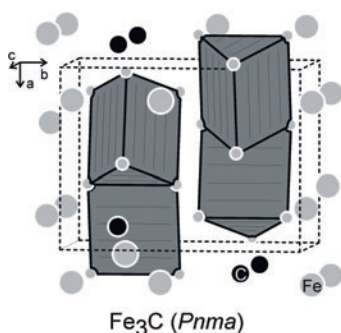


Fig. 3.52 The crystal structure of cementite, Fe_3C . The C@Fe_6 trigonal prisms are emphasized.

The so-called η -carbides, *e. g.* $\text{W}_3\text{Fe}_3\text{C}$ or $\text{W}_3\text{Co}_3\text{C}$, are ternary transition metal carbides which are also important in steel production. Such compounds also form with molybdenum and nickel. The carbon atoms are located in octahedral voids of the higher-melting metal, *i. e.* Mo or W. Thus (for $\text{W}_3\text{Fe}_3\text{C}$), one observes a kind of segregation into a W_6C and an iron substructure. Chemical bonding in these complex carbides is governed by strong W–C, Fe–Fe, and W–Fe bonding.

The usual synthesis for the transition metal carbides proceeds directly from the elements by arc-melting or sintering techniques. For technical applications often a carbothermal reduction, *e. g.* $\text{TiO}_2 + 3\text{C} \rightarrow \text{TiC} + 2\text{CO}$, is used. Coatings of non-abrasive TiC can be obtained *via* chemical vapor deposition, *e. g.* $\text{TiCl}_4 + \text{CH}_4 \rightarrow \text{TiC} + 4\text{HCl}$ [18]. A typical application is the surface refinement of a watch case, a drill, or a saw-blade.

Besides precipitation hardening in steel and steel-related materials, the transition metal carbides are used as hard materials. However, the extreme brittleness is a severe problem for technical applications. The solution is a composite material, Widia®, where hard but brittle WC (ca. 92 %) is embedded in a binder matrix (ca.

8 % Co) which supplies the necessary tenacity. Such composites are the usual hard component in cutting tools, drills, wire drawing dies and further wear resisting materials.

Due to their extremely wide use in all kinds of steel-based and hard materials, all these binary and multinary transition metal carbides have enormous technical and economic importance. Together with construction chemicals (cement, gypsum etc.) they take an immense significance on the global market.

The second group of metallic carbides is formed by the rare earth (*RE*) and actinoid (*An*) elements. The *RE*-C and *An*-C phase diagrams have intensively been studied and metal-rich as well as carbon-rich compounds have been discovered [19]. A variety of rare earth-rich carbides with compositions RE_3C and RE_2C are known. These carbides contain isolated carbon atoms in octahedral rare earth coordination, similar to the NaCl-related carbides ThC and UC. While all octahedral voids are filled in the latter compounds, a random distribution is observed in RE_3C , and the RE_2C carbides show an *anti*-CdCl₂ arrangement with ordered carbon occupancy.

With slightly higher carbon content the cubic RE_2C_3 carbides (Pu_2C_3 type) are formed. They contain C₂ pairs (a structural feature that has not been observed in pure transition metal carbides) with C-C bond lengths ranging from 124–154 pm. Some of the rare earth elements form carbides of more complex compositions and structures. Relevant structure types are Y_4C_5 and the modifications of Lu_4C_7 . The latter carbides contain C⁴⁻ besides C₂⁴⁻ (Y_4C_5) and C⁴⁻ besides C₃⁴⁻ (Lu_4C_7). The most peculiar structure among the rare earth carbides is Sc_3C_4 [20]. This binary metallic carbide contains isolated carbon atoms (C⁴⁻ species) beside C₂ pairs and allene-related C₃ units. The Sc_3C_4 unit cell contains 10 formula units and a formal ionic formula splitting leads to $(30Sc^{3+})(12C^{4-})(2C_2^{2-})(8C_3^{4-})(6e^-)$. As is evident from the ionic formula splitting, in agreement with electronic structure calculations [20], the six excess electrons lead to the metallic properties. The binary rare earth carbides have silvery to brass-like color with metallic lustre. The quite rare C₃ units have also been observed in RE_3C_4 and RE_4C_7 with the smaller rare earth elements, in Mg_2C_3 , $Ca_3Cl_2C_3$, $Sc_5Re_2C_7$, and Ca_2LiC_3H .

The so far highest carbon content has been observed for the acetylides REC_2 and UC_2 . They crystallize with the tetragonal CaC₂-type structure, space group *I4/mmm*. As an overview we present the different carbon species with typical rare earth or actinoid metal coordinations in Fig. 3.53. The isolated carbon atoms in ThC have regular octahedral thorium coordination, while three different kinds of metal coordination are observed for the C₂ pairs in UC_2 , Er_2C_3 , and Sc_3FeC_4 . The C₂ pair in UC_2 is located in a stretched octahedron, while we observe eight erbium atoms around the C₂ pair in Er_2C_3 . This way each carbon atom has distorted octahedral erbium coordination. In the ternary acetylide Sc_3FeC_4 the coordination of the C₂ pair can be considered as a tricapped trigonal prism. This type of coordination is widely known for related rare earth-transition metal-carbides [21]. The C₃ unit in Sc_3C_4 has highly distorted bicapped square-antiprismatic scandium coordination.

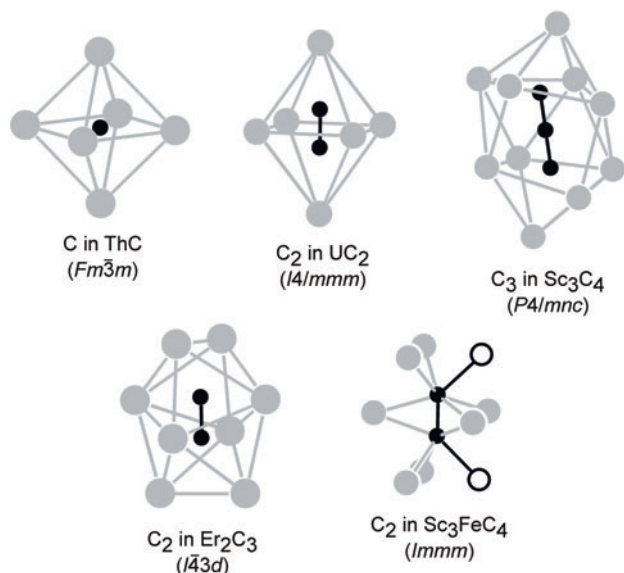


Fig. 3.53 Selected carbon coordinations in the structures of ThC, UC₂, Sc₃C₄, Er₂C₃, and Sc₃FeC₄. Rare earth (actinoid), iron, and carbon atoms are drawn as medium grey, black open, and filled circles, respectively.

The striking difference between the prototype CaC₂ and the rare earth carbides is the surplus valence electron according to $\text{Ca}^{2+}\text{C}_2^{2-}$ and $\text{RE}^{3+}\text{C}_2^{2-}\text{e}^-$. In agreement with the transparent salt-like appearance, CaC₂ is an ionic compound. For the REC_2 acetylides it would be possible to accommodate the surplus electron within the C₂ unit with a formal charge C_2^{3-} and consequently, a lengthening of the C–C distance. This is only partly realized in REC_2 and UC₂. The latter compounds show covalent metal–C₂ bonding, leading to significant broadening in the density-of-states and a closing of the gap at the Fermi level. Consequently REC_2 and UC₂ show metallic character. In contrast to the transition metal carbides, the rare earth carbides are highly sensitive to moisture. They readily hydrolyze, leaving rare earth hydroxides and diverse hydrocarbons. Due to the *d*- and *f*-electron contributions one observes a broader range of hydrocarbon products, most likely due to catalysis and radical reactions [22].

A much larger group of carbides is formed by combinations of rare earth and transition metals with carbon. A simple structure type that occurs in this family of compounds is the perovskite type with compositions $\text{RE}\text{T}_3\text{C}$ or RE_3MC ($M = \text{Al, Ga, In, Tl, Sn, Pb}$) [23]. Such carbides generally show broad homogeneity ranges with partial up to full occupancy of the octahedral voids. The $\text{RE}_x\text{T}_y\text{C}_z$ compounds cover a broad range of structures. In the rare earth- and transition metal-rich parts of the $\text{RE}–\text{T}–\text{C}$ phase diagrams one usually observes carbides with isolated carbon atoms in octahedral or trigonal prismatic voids. Typical examples are $\text{Ce}_2\text{Ni}_{22}\text{C}_{3-x}$, $\text{Yb}_{11}\text{Ni}_{60}\text{C}_6$, $\text{RE}_2\text{Fe}_{14}\text{C}$, or $\text{RE}_2\text{Fe}_{17}\text{C}_{3-x}$. Such phases have intensively been studied with respect to permanent magnetic materials.

With increasing carbon content one observes the formation of transition metal-carbon networks. Interestingly such ternary compounds also form with the noble metals, *e. g.* $\text{Er}_8\text{Rh}_5\text{C}_{12}$, GdRuC_2 , Sc_3OsC_4 , or U_2PtC_2 , although no binary carbide is known for these electron-rich transition metals. As an example we present the CeRhC_2 structure [24] in Fig. 3.54. The cerium atoms transfer their valence electrons to the rhodium and carbon atoms, enabling strong covalent Rh-C and C-C bonding. Together, the rhodium and carbon atoms build up a three-dimensional $[\text{RhC}_2]$ network which leaves larger voids that are filled by the cerium atoms. The rhodium atoms are bonded side-on to the C_2 -pairs. A large variety of such structures has been determined in the last thirty years [19]. Examples are known for pure carbometallates [25], where only isolated carbon atoms bond to the transition metal atoms besides those with $\text{C} + \text{C}_2$ and compounds containing only C_2 pairs. Only the carbides $\text{RE}_5\text{Re}_2\text{C}_7$ ($\text{RE} = \text{Sc}, \text{Er}, \text{Tm}, \text{Lu}$) contain C_3 units (besides isolated carbon atoms) in a bicapped square-prismatic coordination.

Depending on the nature of the transition metal and the metal-to-carbon ratio in the respective structure one observes zero-, one-, two-, and three-dimensional $[\text{T}_y\text{C}_z]^{q-}$ polyanionic units. Selected examples are presented in Fig. 3.55. These polyanions can be considered as metal-organic fragments that are charge compensated and separated by the rare earth or actinoid atoms. In some of the polyanions one also observes T-T bonding. Similar structural units occur with alkali and alkaline earth metals [26], however, many of these compounds show ionic bonding and are not in the scope of this book.

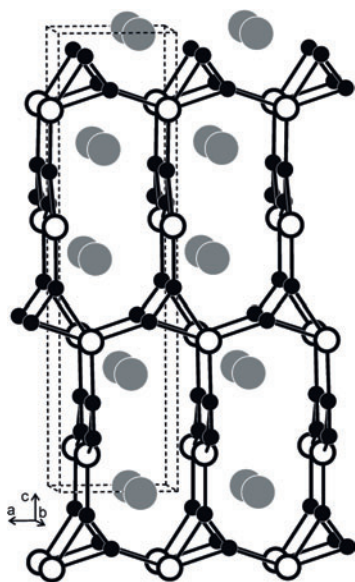


Fig. 3.54 The crystal structure of CeRhC_2 . Cerium, rhodium, and carbon atoms are drawn as medium gray, black open, and filled circles, respectively. The three-dimensional $[\text{RhC}_2]$ network is emphasized.

To a first approximation, chemical bonding in the $RE_xT_yC_z$ carbides can be rationalized by electron counting, assuming that the electropositive rare earth atoms transfer their valence electrons to the transition metal and carbon atoms. These considerations readily showed that the transition metal atoms mostly obey the 18-electron rule [27]. This view of chemical bonding has been underlined by extended Hückel calculations [28]. Chemical bonding has intensively been investigated for the series of Sc_3TC_4 ($T = Fe, Co, Ni$) carbides both by experimental electron density studies and state-of-the-art electronic structure calculations [29]. These data strongly underlined three main bonding contributions, (i) $\sigma(T \leftarrow C)$ donation, (ii) $T \rightarrow \pi^*(C-C)$ back donation and (iii) partially covalent $Sc(\eta^2(C_2))$ bonding.

Finally we draw back to hydrolysis experiments on diverse $RE_xT_yC_z$ carbides. A broader overview is given in [21]. Hydrolysis of such carbides in 2N hydrochloric acid at different temperatures leads to a broad range of hydrocarbons (detected by gas chromatography) up to small amounts of C_6H_{14} . The distribution of hydrocarbons in the hydrolysis products was not representative for the carbon species present in the structure. Again, this is related to transition metal catalysis and radical reactions.

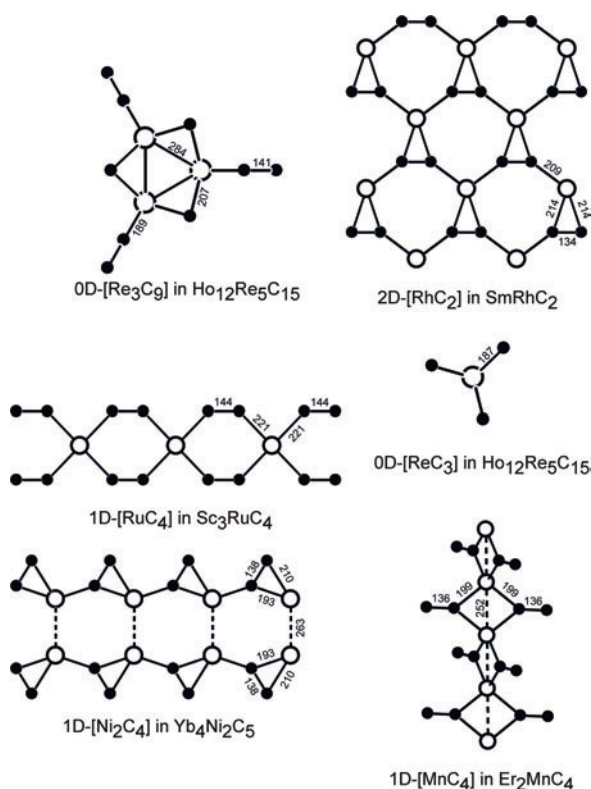


Fig. 3.55 Cutouts of transition metal-carbon polyanions in diverse $RE_xT_yC_z$ carbides. Transition metal and carbon atoms are drawn as medium black open, and filled circles, respectively. Relevant interatomic distances are indicated.



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3.9.2 Silicides

Most metals directly react with elemental silicon forming silicides. Roughly one can subdivide this topic into alkali metal and alkaline earth metal silicides, transition metal silicides, and rare earth/actinoid silicides. These three groups have different structures, bonding patterns and applications. First we focus on the binary compounds and then give an extension to ternary metal silicides and silicide carbides.

The alkali and alkaline earth metals form a variety of binary silicides, most of them obey the Zintl-Klemm-Busmann concept (*vide ultra*) with electron precise Zintl anions. Especially the lithium silicides have recently been reinvestigated thoroughly with respect to their use in lithium ion batteries [1]. Since representative examples of these silicide Zintl anions have already been discussed in Chapter 3.7, here we focus on another interesting family of compounds, the clathrate materials. The existence of such tetrel clathrates has first been reported by *Kasper et al.* [2]. The silicon substructures of $\text{Na}_4\text{Si}_{23}$ (Fig. 3.56) and $\text{Na}_{10}\text{Si}_{136}$ (Fig. 3.57) have four-bonded silicon with Si–Si distances ranging from 234–241 pm, similar to the diamond-type modification with ideal tetrahedra and 235 pm Si–Si.

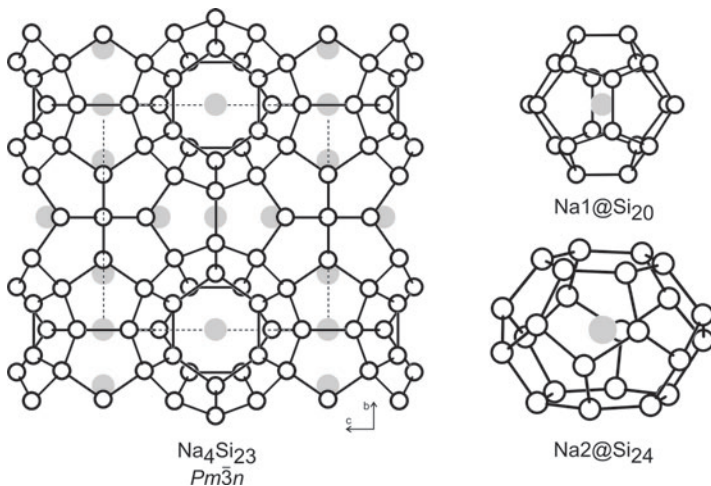


Fig. 3.56 Projection of the $\text{Na}_4\text{Si}_{23}$ structure along the a axis (left). Sodium and silicon atoms are drawn as medium gray and black open circles, respectively. The three-dimensional silicon network is emphasized. The Na1@Si_{20} and Na2@Si_{24} polyhedra (right).

In contrast to the chair conformation of Si_6 rings in the element, in the silicon network of the clathrate structures one observes almost planar Si_5 and Si_6 rings and the Si–Si–Si bond angles substantially deviate from the ideal tetrahedral angle. The two structure types have cages of coordination numbers 20, 24, and 28 which are filled by the sodium atoms. The different sizes of the silicon cages lead to a *rattling* of alkali metal ions, an excellent prerequisite for thermoelectric materials (Chapter 4.3). Thermal decomposition of the Zintl phase NaSi under vacuum leads to almost sodium-free $\text{Na}_x\text{Si}_{136}$ ($x < 1$). Such a precursor can electrochemically be loaded with lithium [3]. Such clathrates also form with germanium and tin. The structural features, diverse substitutions on the cation sites and within the silicon framework as well as the physical properties (thermoelectricity and optoelectronics) of these clathrate materials have broadly been studied [4].

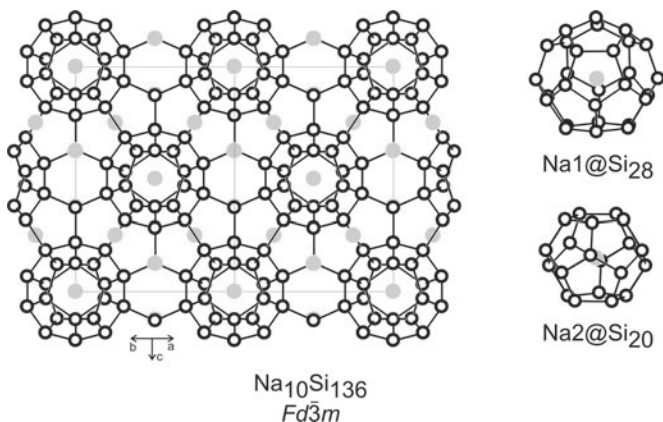


Fig. 3.57 Projection of the $\text{Na}_{10}\text{Si}_{136}$ structure along the $[110]$ direction (left). Sodium and silicon atoms are drawn as medium gray and black open circles, respectively. The three-dimensional silicon network is emphasized. The Na1@Si_{28} and Na2@Si_{20} polyhedra (right).

Many of the alkali metal and alkaline earth metal silicides are moisture sensitive. The hydrolysis leads to silanes. A typical experiment of a practical course is the reaction of magnesium with silica, $4\text{Mg} + \text{SiO}_2 \rightarrow 2\text{MgO} + \text{Mg}_2\text{Si}$, and the subsequent hydrolysis with diluted hydrochloric acid to monosilane *via* $\text{Mg}_2\text{Si} + 4\text{H}^+ \rightarrow 2\text{Mg}^{2+} + \text{SiH}_4\uparrow$. Silicides with *d*-electrons and those with more complicated Zintl anions result in mixtures of silanes, similar to the uncontrolled hydrolyses reactions discussed for carbides (*vide ultra*).

The transition metal silicides can roughly be subdivided into two groups, *i. e.* silicides of the early and late transition metals. Those of the early transition metals are used as hard materials, although their hardness is lower than that of comparable carbides. These silicides have relatively high melting points, a remarkable resistance against acids and good thermal stability even in air, since they form protective surface

coatings of SiO_2 and silicates. Out of the large number of such TSi_x phases we can only consider some representative compounds here. A broader overview is given by *Miglio* and *d'Heurle* in a large proceedings compendium on a silicide workshop [5]. Typical compositions are $T_3\text{Si}$, $T_2\text{Si}$, $T_5\text{Si}_3$, TSi , and TSi_2 .

The technically most important compounds are MoSi_2 and WSi_2 which are used as protective coatings for sheets and wires. Such a coating can easily be generated by CVD, e. g. $\text{Mo} + 2\text{SiCl}_4 + 4\text{H}_2 \rightarrow \text{MoSi}_2 + 8\text{HCl}$. As an example we present the structure of MoSi_2 in Fig. 3.58. The unit cell consists of three successive centered cubes which are occupied in an ordered manner by the molybdenum and silicon atoms. This coordination readily reminds of the W/CsCl-type structure. From a group-theoretical point of view we can describe MoSi_2 as a W superstructure. We draw back to this classification scheme in Chapter 3.17.

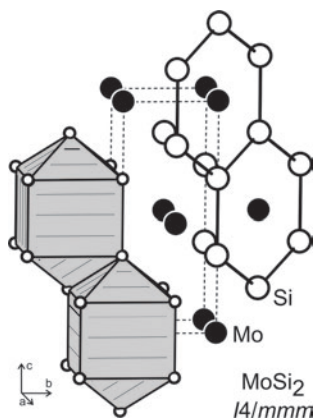


Fig. 3.58 The structure of MoSi_2 . The MoSi_{10} polyhedra are emphasized at the left-hand part. A cutout of a two-dimensionally close-packed layer is drawn at the right-hand side. For the packing pattern of these layers see Fig. 3.59.

The molybdenum atoms have ten silicon neighbors in bi-capped square-prismatic coordination. These polyhedra are condensed *via* common edges. As emphasized in Fig. 3.58, the molybdenum and silicon atoms form two-dimensionally ordered layers. These layers are the basic building units for the closely related structure types CrSi_2 , TiSi_2 , and MoSi_2 [6]. The packing principle of these layers is shown in Fig. 3.59. As emphasized in the upper left-hand part of that figure, the central transition metal atoms of layer A is shifted to the positions B, C, and D in the successive layers, leading to the three different structure types with the stacking sequences AB for MoSi_2 , ABC for CrSi_2 , and ABCD for TiSi_2 . However, at this point it is important to remind that these stacking sequences are just a geometrical tool to explain the three silicide structures and should not be confused with the closest-packed layers in the classical closest-packed metal structures. CrSi_2 , TiSi_2 , and MoSi_2 are characterized by strong T–Si as

well as substantial Si–Si bonding. The Si–Si distances within and between the layers range from 247–279 pm, slightly longer than in elemental silicon (235 pm), as a result of the higher coordination numbers in the binaries.

The A15-type compound Cr_3Si is another metal-rich silicide of an early transition metal. Cr_3Si contains isolated silicon and it is the prototype of the so-called beta tungsten-type structure. This type is discussed for the superconductor Nb_3Sn in Chapter 3.9.4.

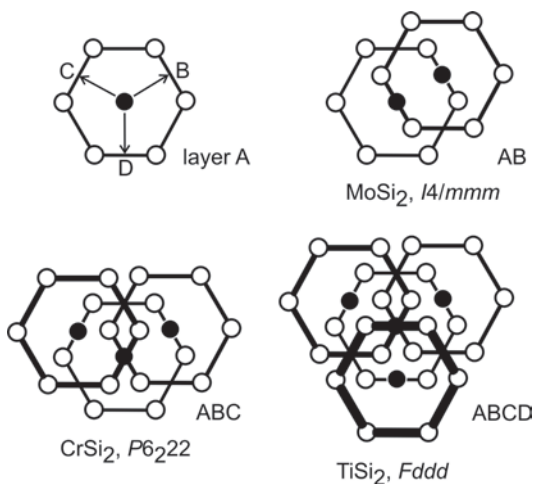


Fig. 3.59 Packing of hexagonal close-packed layers TSi_2 in the structures of MoSi_2 , CrSi_2 , and TiSi_2 . The central transition metal atoms of the basic layer A is shifted to the positions B, C, and D in successive layers to generate the three stacking variants. For details see text.

Transition metal silicides are broadly used to form both ohmic and rectifying contacts to silicon. Interconnections in electronic devices were first made of WSi_2 , then TiSi_2 and also CoSi_2 and platinum metal silicides. Our broad daily use of microelectronics makes such binary silicides indispensable. Besides their use as interconnections, such silicides have also widely been studied with respect to their conductivity behavior (metals and semiconductors) and with respect to their potential use as thermoelectric materials.

Four examples out of the large number of platinum metal silicides are presented in Fig. 3.60. They are representative for the diverse structural motifs. RuSi crystallizes with the simple CsCl-type structure with coordination number 8 for both the ruthenium and silicon atoms. The metal-rich silicides $\text{Rh}_{20}\text{Si}_{13}$ and Ru_2Si show trigonal prismatic metal coordination for the silicon atoms. These prisms are condensed *via* common edges within the layers and *via* the triangular face perpendicular to the layers. Such a structural description is purely geometrical, however, it is extremely efficient to distinguish the many complex silicide structure types. Adjacent chains and blocks

of the trigonal prismatic units are shifted by half a translation period in the projection direction. The stability of these silicides arises from both, strong covalent T -Si bonding as well as a broad range of T - T interactions. $\text{Rh}_{20}\text{Si}_{13}$ and Ru_2Si show no close Si-Si contacts.

As an example for a silicon-rich platinum metal silicide we show the relatively complex Ir_3Si_5 structure in Fig. 3.60. The silicon atoms build up a two-dimensional substructure with fragments of distorted cubes. All Si-Si distances up to 273 pm are drawn in that figure. Again, the longer Si-Si distances are a consequence of the higher coordination number. These silicon layers are condensed *via* the iridium atoms by strong covalent Ir-Si bonds.

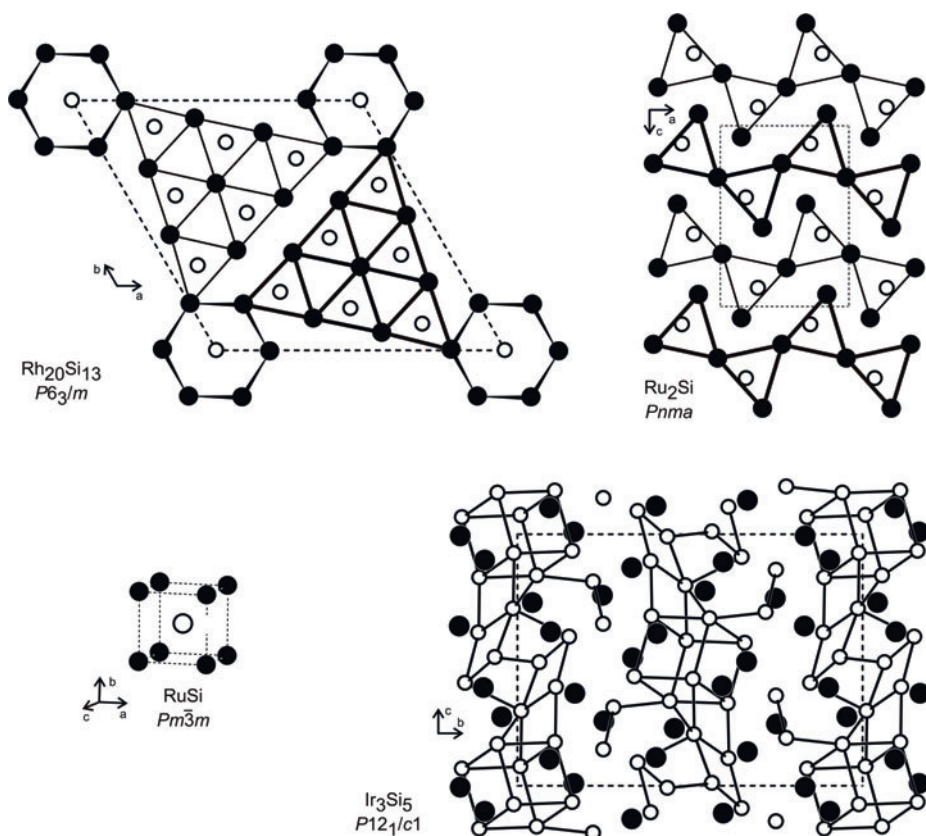


Fig. 3.60 The crystal structures of $\text{Rh}_{20}\text{Si}_{13}$, Ru_2Si , RuSi , and Ir_3Si_5 . Transition metal and silicon atoms are drawn as black filled and open circles, respectively. For crystal chemical details see text.

All rare earth elements form silicides. Typical compositions are RE_5Si_3 , RE_3Si_2 , RE_5Si_4 , RESi , and RESi_2 . Europium and in some cases also ytterbium act as divalent elements

in such silicides and they show similar crystal chemistry as the alkaline earth elements, forming Zintl phases (see Chapter 3.7). The structure of the RE_5Si_3 silicides is discussed at the end of this chapter as host for the carbon atoms in Mo_5Si_3C . As an example for a $RESi$ silicide we present the LT-LaSi modification in Fig. 3.61. Again we observe trigonal prismatic metal coordination for the silicon atoms. These prisms are condensed *via* the rectangular faces, leading to Si–Si zigzag chains with Si–Si distances of 248 and 261 pm. These two-dimensional fragments can be considered as a cut-out of the well-known AlB_2 structure, which is observed for the silicon-rich rare earth silicides, *e. g.* in $LuSi_{2-x}$ (Fig. 3.61). Depending on the size of the rare earth element and the heat treatment of the sample, these silicides show defects in the silicon substructures which might be ordered or statistical. Especially $ErSi_{2-x}$ samples have been studied in detail by high-resolution electron microscopy in order to study the ordering phenomena in the silicon substructure. Many $RESi_2$ silicides crystallize with the α - $ThSi_2$ type (*vide infra*).

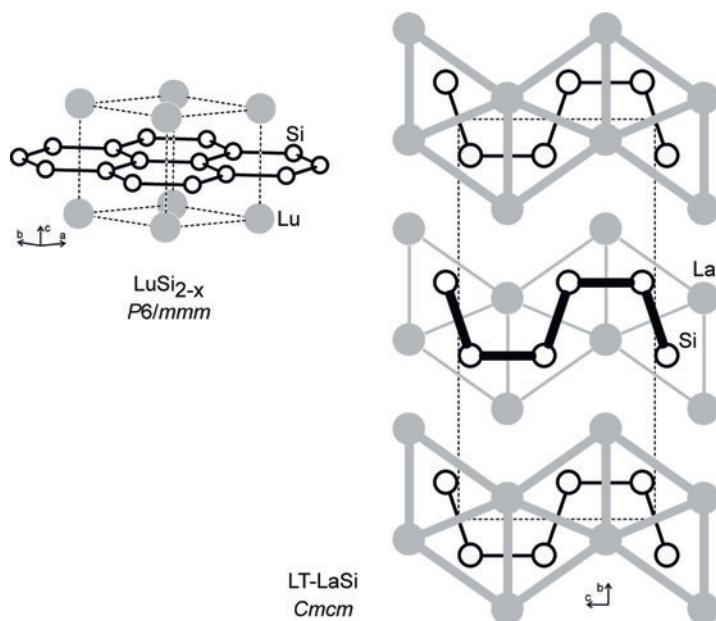


Fig. 3.61 The crystal structures of $LuSi_{2-x}$ and LT-LaSi.

From the group of actinoid metals especially the uranium silicides have intensively been studied with respect to their use as fuel in nuclear reactors. Two important structure types in this field are U_3Si_2 [7] and α - $ThSi_2$ [8]. As emphasized in Fig. 3.62, one can describe the U_3Si_2 structure as an intergrowth variant of slightly distorted W

and AlB_2 related slabs. The silicon atoms form dimers (240 pm Si–Si) and always four AlB_2 slabs are connected to a uranium-centered cube. The U_3Si_2 structure is a very important structure type. The center of the W related slab can be substituted by a p element, by Mg, or by Cd (X component), leading to a large family of ordered compounds [9]. This arrangement has first been observed in the boride $\text{Mo}_2\text{B}_2\text{Fe}$ and later in a variety of $\text{RE}_2\text{T}_2\text{X}$ and $\text{Ac}_2\text{T}_2\text{X}$ intermetallics which show highly interesting magnetic and transport properties.

The $\alpha\text{-ThSi}_2$ structure (Fig. 3.62) consists of a three-dimensional silicon substructure in which every silicon atom is connected to three silicon neighbors (238–240 pm Si–Si; *i. e.* single bond character). The large cavities left by this network are filled by the thorium atoms. Similar to the AlB_2 slabs in the U_3Si_2 structure, also the silicon atoms in $\alpha\text{-ThSi}_2$ have trigonal prismatic metal coordination. Also for the $\alpha\text{-ThSi}_2$ type a ternary ordered version exists. In LaPtSi [10] the lanthanum atoms take the thorium sites and every other silicon atom of the silicon substructure is substituted in an ordered manner by platinum. This leads to local $\text{PtSi}_{3/3}$ and $\text{SiPt}_{3/3}$ coordination. The ordering has a drastic effect on the space group symmetry. Due to the *translationengleiche* symmetry reduction of index 2 from $I4_1/amd$ to $I4_1md$ the ternary ordered structure is non-centrosymmetric. Several representatives of that structure type with diamagnetic rare earth elements are superconductors.

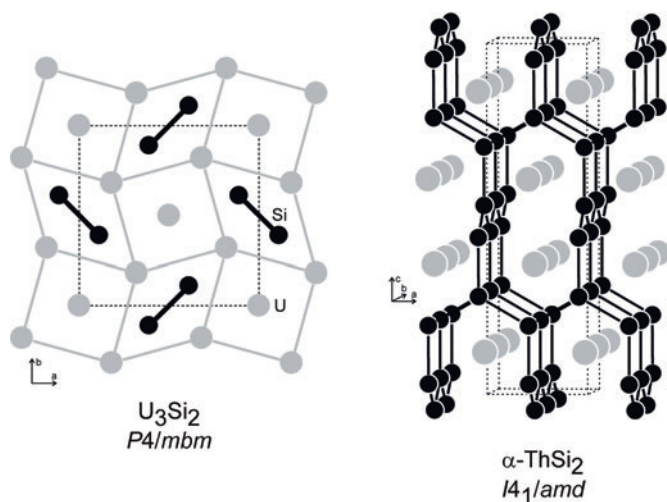


Fig. 3.62 The crystal structures of U_3Si_2 and $\alpha\text{-ThSi}_2$. Actinoid and silicon atoms are drawn as medium gray and black filled circles, respectively. The Si–Si bonds are emphasized.

The combinatorial variety of silicides is much broader in ternary systems. In extension of the basic work on binary rare earth and binary transition metal silicides, the

RE-T-Si and also the *An-T-Si* systems have systematically been studied regarding phase formation, crystal structures, and especially the magnetic and electrical properties of the ternary silicides. The huge number of compounds can only briefly be summarized. For details we refer to review articles [11, 12]. In the *RE-T-Si* and *An-T-Si* systems one observes compounds with distinctly different compositions, rare earth-, transition metal-, or silicon-rich.

Exemplarily we present the structures of CeCu_2Si_2 , $\text{La}_5\text{Ni}_2\text{Si}_3$, and $\text{U}_3\text{Ni}_4\text{Si}_4$ in Fig. 3.63. Generally, the shortest interatomic distances in these structures are observed between the transition metal and silicon atoms. They are mostly close to the sums of the covalent radii, indicating strong *T-Si* bonding. The *T* and Si atoms build up $[\text{T}_x\text{Si}_y]$ polyanionic networks in which the rare earth or actinoid atoms fill larger cavities (see CeCu_2Si_2 and $\text{U}_3\text{Ni}_4\text{Si}_4$ in Fig. 3.63). This is also the case in the rare earth- or actinoid-rich compounds [13]. However, the sometimes very complex structure types can easily be classified by the connectivity pattern of the silicon-filled trigonal rare earth or actinoid prisms. The structural relationship between $\text{Rh}_{20}\text{Si}_{13}$ (Fig. 3.64) and $\text{La}_5\text{Ni}_2\text{Si}_3$ is then readily evident [14].

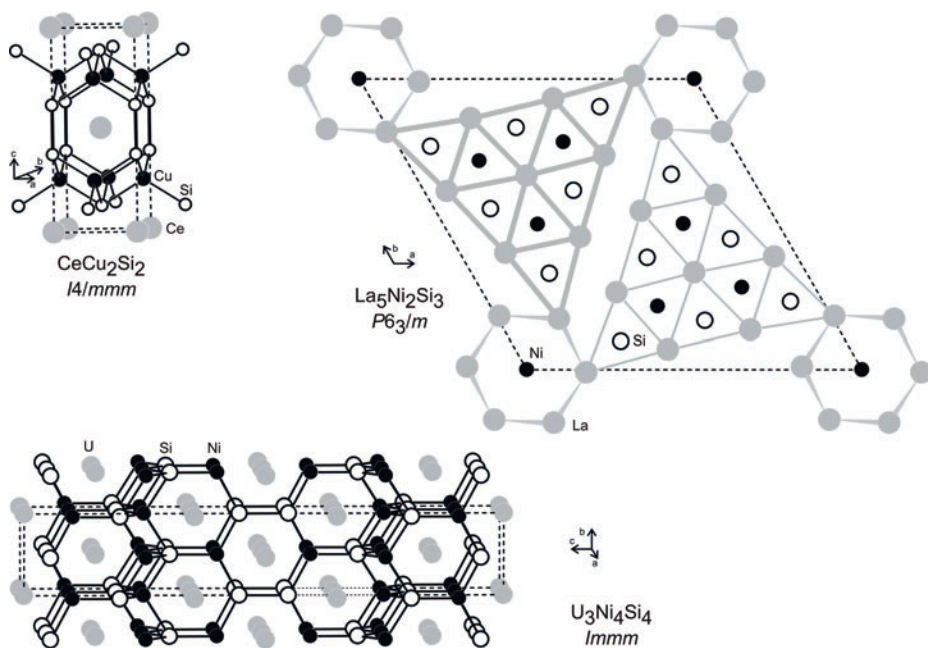


Fig. 3.63 The crystal structures of CeCu_2Si_2 , $\text{La}_5\text{Ni}_2\text{Si}_3$, and $\text{U}_3\text{Ni}_4\text{Si}_4$. The three-dimensional $[\text{Cu}_2\text{Si}_2]$ and $[\text{Ni}_4\text{Si}_4]$ networks of CeCu_2Si_2 and $\text{U}_3\text{Ni}_4\text{Si}_4$ are emphasized. The trigonal-prismatic silicon coordination in $\text{La}_5\text{Ni}_2\text{Si}_3$ is outlined.

Concluding this chapter we concentrate on interesting intermetallic compounds with two anionic units, the silicide carbides. Although large families of binary and ternary carbides and silicides exist, only few silicide carbides have been reported. The structures of Ti_3SiC_2 [15] and $\text{Mo}_5\text{Si}_3\text{C}$ [16] have been studied already forty years ago. $\text{Mo}_5\text{Si}_3\text{C}$ is a filled-up variant of the well known Mn_5Si_3 type [17], the so-called D8_8 or Nowotny phases. A projection of the $\text{Mo}_5\text{Si}_3\text{C}$ structure is presented in Fig. 3.64. Part of the molybdenum atoms form chains of face-sharing octahedra along the c axis. These octahedra are partly filled with carbon atoms. $\text{Mo}_5\text{Si}_3\text{C}$ is the idealized composition. According to the Parthé-Yvon rule (*vide ultra*), such adjacent voids should not be occupied. According to neutron diffraction data [16] the composition $\text{Mo}_{4.8}\text{Si}_3\text{C}_{0.6}$ was determined. Besides strong Mo–C bonding in the carbidic part of the structure, one observes additional Mo–Mo and Mo–Si contacts which stabilize this peculiar structure type. Besides filling of the octahedral voids by small atoms (hydrogen, carbon, boron, oxygen, and nitrogen), also main group elements and transition metals can fill these sites. Representative compounds are Ti_5Ga_4 or $\text{Hf}_5\text{Sn}_3\text{Cu}$. Today more than 300 representatives of these empty, partially or fully filled variants are known.

Also the structure of Ti_3SiC_2 [15] shows a clear segregation into a carbide and a silicide substructure. The platelet-like crystals of Ti_3SiC_2 can be plastically deformed. Ti_3SiC_2 has a high melting point of ca. 3200 °C, comparably good chemical and also thermal shock resistance. In the last twenty years Ti_3SiC_2 has intensively been studied with respect to its high potential as a component in ceramic and composite materials. The carbon atoms in Ti_3SiC_2 have octahedral titanium coordination, similar to TiC (Chapter 3.9.1). These Ti_6C octahedra are condensed *via* common edges. Double-layers of condensed octahedra then alternate in the unit cell with layers of silicon atoms. Similar to $\text{Mo}_5\text{Si}_3\text{C}$ one observes no Si–C bonding.

Few silicide carbides have also been synthesized with the rare earth and actinoid metals. Here we briefly discuss the structures of $\text{RE}_3\text{Si}_2\text{C}_2$ ($\text{RE} = \text{Y}, \text{Pr}, \text{Tb}, \text{Dy}$) [18] and $\text{U}_3\text{Si}_2\text{C}_2$ [19]. Similar to the structure of Ti_3SiC_2 (*vide ultra*), also in the $\text{RE}_3\text{Si}_2\text{C}_2$ silicides carbides one observes a clear segregation into a carbide substructure with C_2 pairs in slightly distorted rare earth octahedra, and an AlB_2 related substructure with silicon zig-zag chains where each silicon atom has distorted trigonal prismatic rare earth coordination. These two substructures show an ABA'B' stacking sequence. So far, Si–C units (193 pm) have only been observed in $\text{U}_3\text{Si}_2\text{C}_2$ [19] (Fig. 3.64).

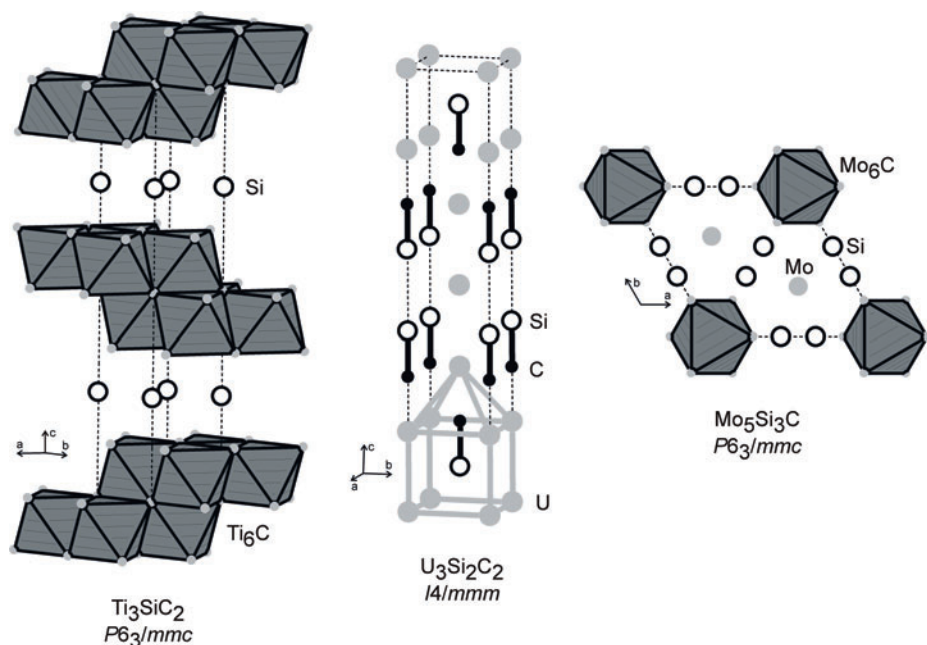


Fig. 3.64 The crystal structures of $\text{Mo}_5\text{Si}_3\text{C}$, Ti_3SiC_2 , and $\text{U}_3\text{Si}_2\text{C}_2$. The carbon-filled octahedra in Ti_3SiC_2 and $\text{Mo}_5\text{Si}_3\text{C}$ and the Si-C units in $\text{U}_3\text{Si}_2\text{C}_2$ are emphasized.

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3.9.3 Germanides

The crystal chemistry of the germanides shows parallels to that of the corresponding silicides. The alkali metals form typical Zintl phases, *e. g.* the monogermanides NaGe, KGe, RbGe, CsGe [1] with Ge^- entities which are arranged as tetrahedra, similar to white phosphorus. The structures of K_4Ge_9 , Rb_4Ge_9 , and Cs_4Ge_9 [2] contain the Ge_9^{4-} anion (Fig. 3.65). The Ge–Ge distances with the Ge_9^{4-} cluster of K_4Ge_9 range from 252–291 pm. Similar cluster units also occur in $\text{Na}_{12}\text{Ge}_{17}$. Although this cluster unit looks quite simple, the structures are often very complicated with large unit cells and the arrangement of the clusters leads to twinning and structural disorder.

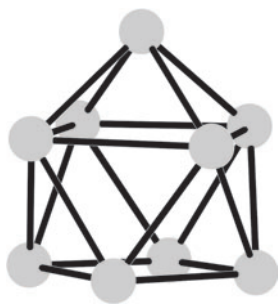


Fig. 3.65 The Ge_9^{4-} cluster.

Similar to the silicides discussed above, clathrate phases have also been observed for the germanides, like $\text{Na}_x\text{Ge}_{136}$ with the clathrate-II structure (by vacuum decomposition of NaGe) as well as the germanium-rich phases K_4Ge_{23} and $\text{Rb}_4\text{Ge}_{23}$. A guest free germani-

um clathrate $\square_{24}\text{Ge}_{136}$ [3] can be obtained from the oxidation of Ge_9^{4-} Zintl anions in ionic liquids under ambient conditions. A similar complex germanium substructure occurs in $\text{Na}_{1-x}\text{Ge}_{3+z}$ [4]. The germanium atoms build up a three-dimensional zeolite-like framework which leaves channels for the sodium atoms (Fig. 3.66). Most of the germanium atoms in the framework have tetrahedral coordination with a comparably small range of Ge–Ge distances of 244–252 pm. The sodium sites in the larger channel can be fully or partially occupied and the germanium atoms around the origin show disorder, leading to the small homogeneity range. Sodium can be removed by vacuum degassing at 620 K.

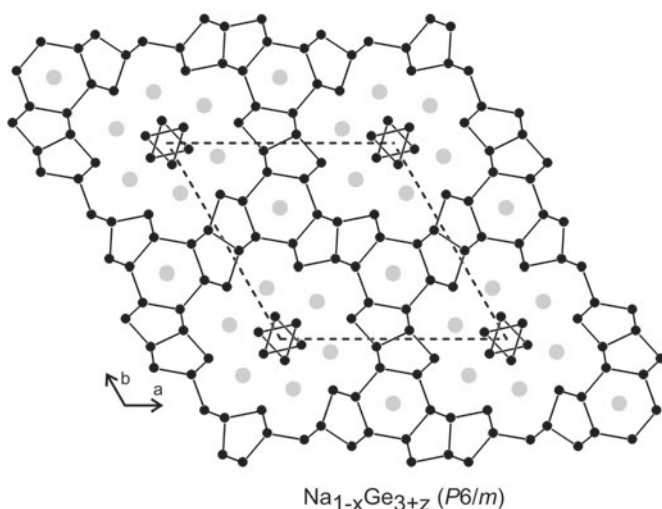


Fig. 3.66 The structure of $\text{Na}_{1-x}\text{Ge}_{3+z}$. The three-dimensional zeolite-like germanium substructure is emphasized. The germanium atoms around the origin of the unit cell show disorder.

The small lithium atoms lead to distinctly different crystal chemistry of the Li_xGe_y phases with the complex compositions LiGe , $\text{Li}_{12}\text{Ge}_7$, $\text{Li}_{11}\text{Ge}_6$, Li_9Ge_4 , Li_7Ge_2 , $\text{Li}_{15}\text{Ge}_4$, and $\text{Li}_{22}\text{Ge}_5$. Some of the germanides are structurally related to the silicides, *e. g.* $\text{Li}_{12}\text{Ge}_7$, while the lithium-rich phase $\text{Li}_{22}\text{Ge}_5$ is isotypic with the corresponding stannide. LiGe has a simple germanium substructure. The Ge^- Zintl anion is three-dimensional and contains three-bonded germanium. These germanides have attracted interest for battery materials. Solid state NMR spectroscopy showed high ionic lithium conductivity for $\text{Li}_{12}\text{Ge}_7$ [5].

The alkaline earth elements show slightly different crystal chemical behavior. So far, no beryllium germanide has been reported and magnesium only forms the *anti*-fluorite type Zintl phase Mg_2Ge . Mg_2Ge is studied as component for composite electrodes in rechargeable lithium batteries as well as for thermoelectrics. Calcium and germanium form the Zintl phases Ca_2Ge , Ca_5Ge_3 , Ca_7Ge_6 , CaGe , and CaGe_2 . A peculiar metallic compound is the calcium-rich germanide Ca_7Ge [6] with CuPt_7 -type

structure, which has also been observed for CePd_7 , LiPd_7 , LiPt_7 , MgPt_7 , Pt_7Sb , Zn_7Mo , or Zn_7Tc . The calcium and germanium atoms show an ordered cubic closest packing (Fig. 3.67). Starting from the simple *fcc* structure, we observe a doubling of the unit cell in all three directions. The corresponding group-subgroup relation is discussed in Chapter 3.17.

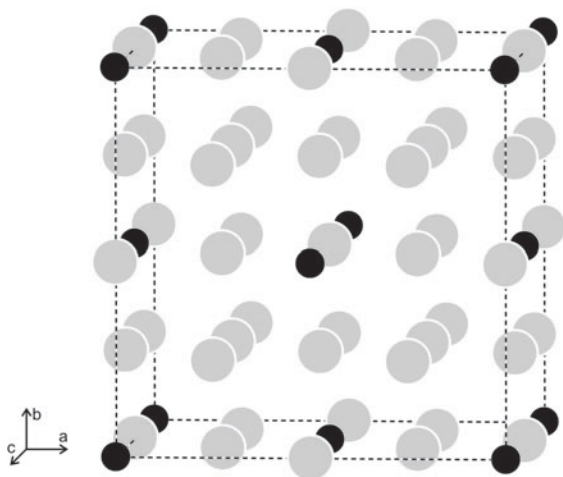


Fig. 3.67 The structure of Ca_7Ge_7 , space group $Fm\bar{3}m$. Calcium and germanium atoms are drawn as light grey and black circles, respectively.

Strontium and barium form the Zintl phases SrGe_2 (BaGe_2), SrGe , Sr_5Ge_3 (Ba_5Ge_3), and Sr_2Ge (Ba_2Ge) with Ge^- , Ge^{2-} , Ge_2^{6-} , and Ge_4^{6-} Zintl anions. Sr_5Ge_3 , Ba_5Ge_3 , and several other tetrelides with the Cr_5B_3 -type structure form hydrides with up to two hydrogen atoms per formula unit [7]. The hydride containing structures can be considered as stuffed Cr_5B_3 variants. This is a severe problem during sample preparation, if hydrogen contaminated alkaline earth elements are used.

Ba_3Ge_4 [8] is dimorphic. At high temperatures (β) this germanide is isotypic to Ba_3Si_4 and transforms to a low-temperature (α) modification below a transition temperature of 630 K. β - Ba_3Ge_4 contains the butterfly-type Zintl anion Ge_4^{6-} (Fig. 3.68) with two two- and two three-bonded germanium atoms. In the low-temperature modification one still observes this monomer, but part of the anions shows polymerization, again, with two- and three-bonded germanium. In the germanium-rich part of the Ba–Ge phase diagram one observes the type-I clathrates $\text{Ba}_8\text{Ge}_{43}$ and $\text{Ba}_6\text{Ge}_{25}$.

The rare earth elements form a broad variety of binary germanides. Depending on the valence and the size of the respective rare earth element (lanthanoid contraction) one does not observe full series for all structure types. Here we list some of the most important general compositions with the germanium substructures in

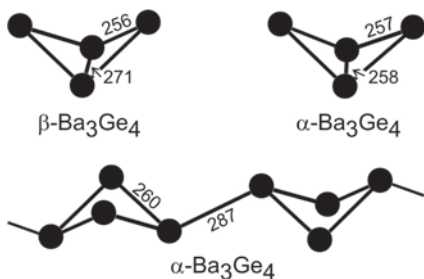


Fig. 3.68 The Zintl anions in α - and β - Ba_3Ge_4 . Relevant Ge–Ge distances (pm) are given.

parentheses: RE_3Ge (Ge units), RE_5Ge_4 (Ge and Ge_2 units), RE_5Ge_3 (Ge units), REGe (Ge zig-zag chains), $\text{RE}_{11}\text{Ge}_{10}$ (Ge, Ge_2 , and Ge_4 units), RE_3Ge_4 (two-dimensional Ge substructure), REGe_2 (three-dimensional Ge substructure), and REGe_5 (three-dimensional Ge substructure). One of the best investigated rare earth germanide is Gd_5Ge_4 and its solid solution $\text{Gd}_5\text{Ge}_{4-x}\text{Si}_x$. These materials have been studied thoroughly with respect to their good thermoelectric properties (giant magnetocaloric effect) [9]. The Gd_5Ge_4 structure (Fig. 3.69) seems quite complex at first sight, but it can easily be described as a stacking of three different layers A, B, and C. Layers A and B also occur in the U_3Si_2 type (*vide ultra*) and layer B is a simple, slightly distorted square net. Besides the Sm_5Ge_4 type (isotypic with Gd_5Ge_4), also the distortion variants Gd_5Si_4 (*Pnma*), $\text{Gd}_5\text{Si}_2\text{Ge}_2$ ($P2_1/a$), and $\text{Tm}_5\text{Si}_2\text{Sb}_2$ (*Cmca*) are known. One of the decisive structural parameters responsible for varying physical properties in this family of compounds is the inter-slab Ge–Ge distance. The latter is 359 pm in Gd_5Ge_4 , but 262 pm in Gd_5Si_4 . For the many structural details we refer to the review articles.

Besides UGe_3 , UGe , U_5Ge_4 , and U_5Ge_3 , the digermanide UGe_2 [10] is the most intensively studied uranium germanide. The structure of UGe_2 (ZrGa_2 type) derives from the *fcc* packing. Three slightly distorted *fcc* cell are stacked in *b* direction. Due to the uranium-germanium ordering one observes slightly distorted germanium square nets and Ge–Ge zig-zag chains with 269 pm Ge–Ge distances (Fig. 3.70). UGe_2 is a collinear ferromagnet with a Curie temperature of 53 K. The strong interest in UGe_2 concerns the coexistence of superconductivity and ferromagnetism [11], similar to UCoGe (Fig. 3.70) and URhGe [12]. The superconducting transition temperatures are 0.8, 0.26, and 0.7 K for UGe_2 , URhGe , and UCoGe , respectively, with somehow higher Curie temperatures of 52 (UGe_2), 9.5 (URhGe), and 3 (UCoGe) K. A still unresolved problem with this kind of germanides still is the unavailability of large high quality single crystals for reliable physical property measurements.

Important thorium germanides are ThGe_2 (isotypic with UGe_2), ThGe with NaCl-type structure, Th_3Ge_2 (isotypic with U_3Si_2), and Th_2Ge with an *anti*- CuAl_2 type.

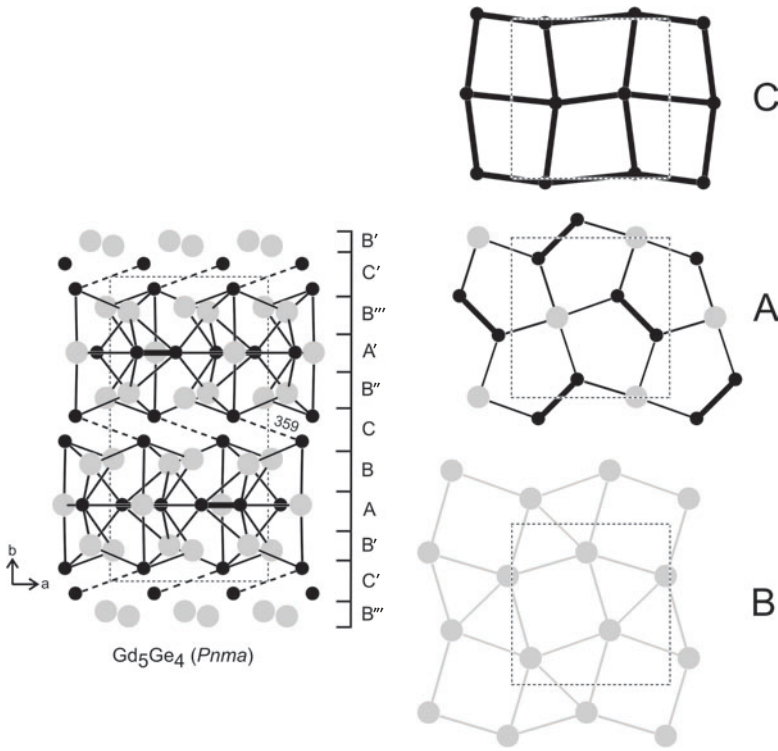


Fig. 3.69 The crystal structure of Gd_5Ge_4 . Gadolinium and germanium atoms are drawn as light gray and black filled circles, respectively. The unit cell is drawn at the left-hand side. Inter-slab Ge–Ge distances are drawn with dotted lines. The stacking sequence of the three different layers is indicated. Layers marked with a tick have the same composition, but different orientation imposed by the space group symmetry. Cutouts of the layers are drawn at the right-hand side.

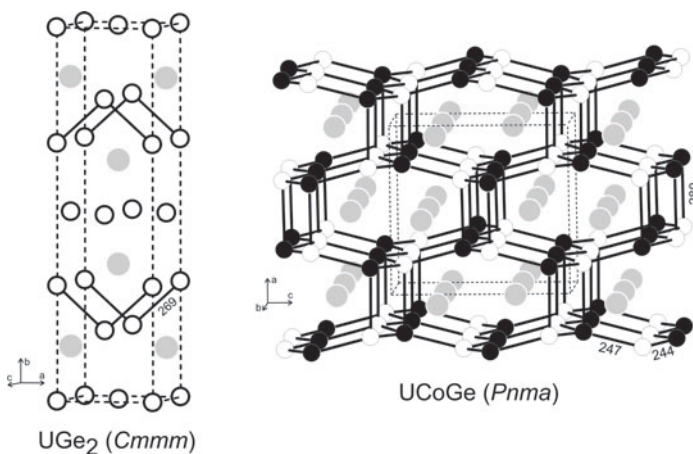


Fig. 3.70 The crystal structures of UGe_2 and UCoGe . Uranium, cobalt, and germanium atoms are drawn as light gray, black filled, and open circles, respectively. Relevant interatomic distances (pm) are given.

Except silver and gold, all transition metals (T) form stable germanides. The most important general compositions are $T_3\text{Ge}$ (Cr_3Si or Ti_3P type), $T_5\text{Ge}_3$ (Mn_5Si_3 or W_5Si_3 type), $T\text{Ge}$ (FeSi type), and $T\text{Ge}_2$ (CrSi_2 , MoSi_2 , or TiSi_2 type). The transition metal germanides are known for their high thermal stability. They are used as Schottky barriers and for contact formation in electronic devices (contact phase between transition metal wires and a germanium wafer). The most intensively studied transition metals for that purpose are titanium, platinum, and nickel. Exemplarily we present the crystal structures of NiGe , Cu_3Ge , and Pt_2Ge_3 in Fig. 3.71. The nickel and platinum atoms in NiGe and Pt_2Ge_3 both have octahedral germanium coordination with short Ni-Ge (233–249 pm) and Pt-Ge (248–262 pm) distances. The NiGe_6 octahedra are face-shared in a direction and these chains are connected with neighboring NiGe_6 octahedra *via* common edges. Pairs of face-sharing PtGe_6 octahedra occur in Pt_2Ge_3 . They are condensed with neighboring pairs *via* common edges and corners, leading to a three-dimensional framework. A different coordination is observed in the copper-rich phase Cu_3Ge . Each germanium atom has almost regular bicapped square-prismatic copper coordination with Cu-Ge distances ranging from 234–265 pm. The $T\text{-Ge}$ distances in these germanides compare well with the sum of the covalent radii and one observes a high degree of $T\text{-Ge}$ bonding. This leads to brittleness for most of the $T\text{Ge}_x$ phases. Thus, the $T\text{Ge}_x$ contact materials are not that shock resistant.

A much larger family occurs for ternary germanides which form with the alkali, alkaline earth, transition, and rare earth metals as well. Equiatomic germanides $TT'\text{Ge}$ have intensively been studied some twenty years ago by combining an electron poor (Ti or V group) with an electron-rich (Fe–Cu group) transition metal. Such germanides frequently crystallize with ordering variants of the Fe_2P (ZrNiAl) or Co_2Si (TiNiSi)-type structure. The main interest in these germanides was their superconducting behavior at low temperatures [13], e. g. ZrIrGe with $T_c = 2.75$ K.

The largest family of compounds comprises the $RE_xT_y\text{Ge}_z$ germanides. The $RE\text{-}T\text{-Ge}$ phase diagrams and the structural chemistry of these compounds have been reviewed by Salamakha [14, 15]. Several hundred $RE_xT_y\text{Ge}_z$ germanides are known. They crystallize in more than 130 different structure types. The crystal chemistry of the $RE_xT_y\text{Ge}_z$ germanides has different facets of chemical bonding as a consequence of the composition, i. e. whether the compounds are $RE\text{-}$, $T\text{-}$, or Ge -rich. For many compounds one observes the formation of $[\text{T}_y\text{Ge}_z]^{6-}$ polyanionic networks in which the more electropositive rare earth elements fill cages or channels. The same holds true for the alkali, alkaline earth, or actinoid compounds. Here we focus on three selected germanides. Although gold and silver form no stable binary germanide, many ternary compounds are known. The structures of $\text{K}_4\text{Au}_7\text{Ge}_2$ [16], UAuGe [17], and YbAgGe [18] are presented in Fig. 3.72.

The gold-germanium network in rhombohedral $\text{K}_4\text{Au}_7\text{Ge}_2$ is three-dimensional. The gold atoms form corner-sharing double tetrahedra which are linked *via* Ge_2 dumbbells. The Au-Au , Au-Ge , and Ge-Ge distances within the $[\text{Au}_7\text{Ge}_2]$ network are again

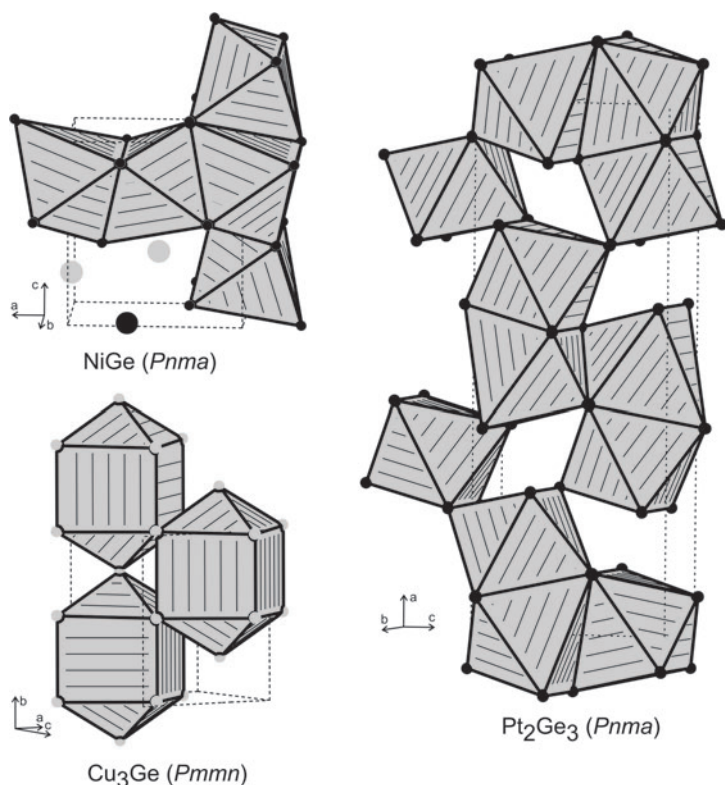


Fig. 3.71 The crystal structures of NiGe, Cu₃Ge, and Pt₂Ge₃. Transition metal and germanium atoms are drawn as light gray and black filled circles, respectively. The distorted octahedra TGe_6 in NiGe and Pt₂Ge₃ and the distorted bicapped square prisms $GeCu_{10}$ in Cu₃Ge are emphasized.

indicative of strong bonding. Slightly longer Au–Ge distances occur in the ordered Au₃Ge₃ hexagons of UAuGe. The hexagons are slightly puckered and one observes weak inter-layer Au–Au bonding (aurophilic interactions). This germanide is an ordered superstructure of AlB₂. Three Au₃Ge₃ hexagons in different orientations are stacked along the hexagonal *c* axis. Also UCoGe (orthorhombic TiNiSi type) presented in Fig. 3.70 derives from the aristotype AlB₂, however, one observes significant orthorhombic distortions and strongly puckered Co₃Ge₃ hexagons. Such AlB₂ superstructures are discussed in more detail in Chapter 3.17 along with the group-subgroup relations.

The germanium atoms are isolated in YbAgGe, *i. e.* no Ge–Ge bonding occurs. The two crystallographically independent germanium sites have trigonal prismatic, respectively trigonal-planar silver coordination. These two building units form a three-dimensional [AgGe] network. The formation of isolated germanium atoms is underlined by the formal electron counting $Yb^{3+}Ag^+Ge^{4-}$ and the trivalent ytterbium is evident from magnetic susceptibility data.

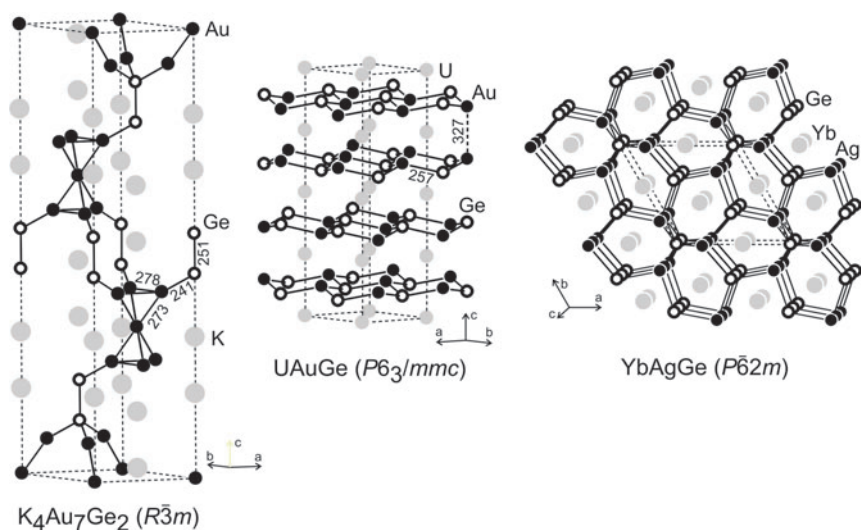


Fig. 3.72 The crystal structures of $K_4Au_7Ge_2$, $UAuGe$ and $YbAgGe$. Atom designations and relevant interatomic distances are indicated. The transition metal-germanium networks are emphasized.



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3.9.4 Stannides

The alkali metals form a variety of binary stannides: NaSn, Na₇Sn₁₂, NaSn₂, NaSn₅, KSn, K₄Sn₉, the clathrate phases K₆Sn₂₅ and K₄Sn₂₃, RbSn and CsSn, and tin-rich clathrate phases of rubidium and cesium. These phases can directly be synthesized from the elements in sealed inert metal tubes. The equiatomic stannides contain tetrahedral Sn₄⁴⁻ Zintl anions, similar to the silicides and germanides and the Sn₉⁴⁻ cluster occurs in K₄Sn₉. Again, due to the small size of the lithium cation, the lithium stannides show different compositions: LiSn, Li₇Sn₃, Li₇Sn₂, Li₅Sn₂, Li₁₃Sn₅, Li₁₇Sn₄, and Li₂₂Sn₅ [1]. These stannides have repeatedly been studied in the last years with respect to their use in lithium ion battery materials [2–4]; see Chapter 4.4. The crystal chemistry and chemical bonding of the alkali metal stannides is reviewed in [5].

Beryllium forms no binary stannide. Magnesium reacts with tin to the Zintl phase Mg₂Sn. High-pressure high-temperature treatment of Mg₂Sn leads to the high-pressure phase Mg₉Sn₅. A much broader range of compounds has been observed with the heavier alkaline earth elements: The calcium stannides Ca₂Sn, Ca₅Sn₃, Ca₃₆Sn₂₃, Ca₃₁Sn₂₀, Ca₇Sn₆, CaSn, CaSn₃, the strontium stannides Sr₂Sn, Sr₅Sn₃, SrSn, Sr₃Sn₅, SrSn₃, SrSn₄, and the barium stannides Ba₂Sn, Ba₅Sn₃, BaSn, Ba₃Sn₅, BaSn₂, BaSn₃, BaSn₅. Some of the strontium and barium stannides show superconductivity at low temperature.

Tin is a dimorphic (Chapter 3.1) low-melting (505 K) metal with excellent wetting behavior. Thin plates and foils of tin have good ductility. Foils are frequently used as capsules for wine bottles and more compact tin plates are the basis for vessels, pewterware and art objects. The high ductility of pure tin often hampers the broad use of such objects. Alloying of tin significantly enhances the hardness and also the mechanical workability. Well known examples are the copper bronzes (Cu–Sn alloys) or britannia metal (Cu–Sn–Sb alloys). The excellent wetting and alloying behavior is the important prerequisite for the broad technical use of tin. In preparative solid state chemistry tin fluxes are frequently used as preparation medium for crystal growth. This is explicitly described in Chapter 2.7. Alloy formation is an important process for all kinds of multinary solder applications. All the facets of these industrially important materials are summarized in the *Tin Handbook* [6], while the fundamental crystal chemical details on stannides are summarized in a review article [7].

Solders are fusible metal alloys which are used to join metallic workpieces. The most often used solders for electronic devices are so-called soft-solders which have melting temperatures in the range of 360–720 K. The main components of the traditional solders are lead and tin. Transition metal stannides can form during the reaction of contact wires with the solder or during the solidification process. The binary or ternary stannides can occur as inclusions within the ductile solder matrix. These stannides are much more brittle than the solder matrix and this drastically reduces the mechanical stability of the joint. In some cases layers of different intermetallic compounds form between the wire material and the solder, *e. g.* $\text{Sn-Cu}_6\text{Sn}_5\text{-Cu}_3\text{Sn-Sn}$. Formation of the stannides further increases the electrical resistivity. The most important transition metals that occur in electronic devices and cause reactions with solders are Fe, Cu, Ni, Pd, Ag, Au, and Pt. In this chapter we mainly focus on the stannides of these transition metals. A severe problem of tin-based solders is the growth of hair-like tin whiskers out of the joint. The whisker formation seems to be encouraged through mechanical stresses and such whiskers might cause short circuits in electronic devices. A manifold of impressive pictures can be found by a simple internet search.

The important binary stannides that might form in solder joints are Cu_6Sn_5 , Cu_3Sn , Ni_3Sn_4 , Au_5Sn , AuSn , AuSn_4 , and also the palladium and platinum stannides. As an example we present the structures of AuSn and Ni_3Sn_4 in Fig. 3.73. AuSn crystallizes with the nickel arsenide structure type. The gold atoms have slightly compressed octahedral tin coordination and the tin atoms have six gold neighbors in trigonal-prismatic coordination. The Au–Sn distances of 285 pm are close to the sum of the covalent radii of 274 pm, indicating substantial Au–Sn bonding. The Au–Au distances of 276 pm along *c* and 433 pm along *a* show drastic differences. Here, only the shorter one can be considered as bonding. Thus one observes pronounced one-dimensional Au–Au bonding in AuSn . These bonding differences lead to anisotropic thermal and electrical conductivity in such NiAs phases.

The Ni_3Sn_4 structure is more complex. It contains two crystallographically independent nickel sites. The Ni1 atoms have slightly distorted octahedral tin coordination with Ni1–Sn distances ranging from 254–261 pm. These NiSn_6 octahedra are condensed in the *b* direction *via* common tin edges. In *a* direction, every other row is shifted by half the translation period, a consequence of the *C*-centered lattice. These rows are further condensed *via* the Ni2–Ni2 zig-zag chains. The Ni2–Ni2 distances of 265 pm point to a distinct nickel substructure. Using the structural description with condensed octahedra one should not neglect the tin substructure. The NiSn_6 octahedra are connected by a broad range of Sn–Sn distances (293–337 pm).

Another technically important stannide is Nb_3Sn with an A15 (W_3O)-type structure. Nb_3Sn is a superconductor with a transition temperature of $T_c = 18$ K. The structure is presented in Fig. 3.73. The niobium atoms form linear infinite chains with 265 pm Nb–Nb distances, which are located on all faces of the cubic unit cell, however, with different orientations. These chains are connected *via* the tin atoms with 296 pm Nb–Sn

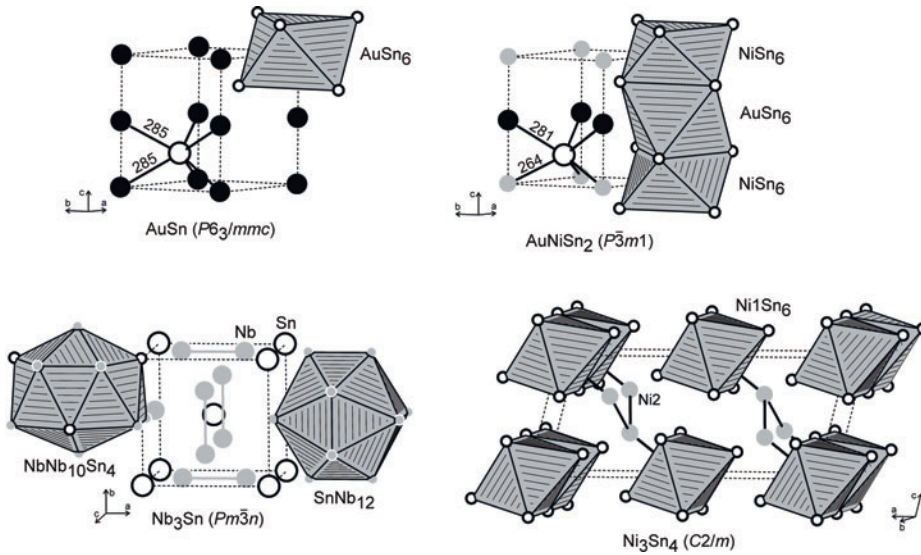


Fig. 3.73 The crystal structures of AuSn, AuNiSn₂, Nb₃Sn, and Ni₃Sn₄. Relevant coordination polyhedra, interatomic distances, and atom designations are indicated.

distances. Both atom types have high coordination numbers. Each tin atom has icosahedral SnNb₁₂ coordination and the niobium atoms have a NbNb₁₀Sn₄ near-neighbor environment. Both coordinations belong to the family of Frank-Kasper polyhedra [8]. Although the electronegativity difference between niobium and tin induces some degree of covalent Nb–Sn bonding, Nb₃Sn still has sufficient ductility for mechanical treatment and the formation of wires. Today Nb₃Sn is still one of the most important intermetallics in superconducting coils of NMR spectrometers, SQUID magnetometers, and computer tomographs.

Besides the binary transition metal stannides a variety of ternary ordered stannides is known. As an example we present the AuNiSn₂ [9] structure in Fig. 3.73. The gold and nickel atoms show a 1:1 ordering on the gold sites of the AuSn structure discussed above. The Au/Ni ordering drastically reduces the space group symmetry from $P6_3/mmc$ to $P\bar{3}m1$. The difference in size between gold and nickel leads to a stacking of larger AuSn₆ and smaller NiSn₆ octahedra along the *c* axis with Au–Sn and Ni–Sn distances of 281 and 264 pm, respectively. The knowledge on noble metal stannides is important, since in high-value electronic devices more and more contacts and joints are based on noble metals in order to reduce corrosion phenomena.

A second example concerns the ternary zirconium stannides ZrNiSn and ZrNi₂Sn [10]. In both structures, the zirconium and tin atoms build up a rock salt-type substructure. Half of the tetrahedral voids left by this substructure are filled in ZrNiSn and all of them in ZrNi₂Sn (Fig. 3.74). Alternatively one can describe ZrNi₂Sn as a filled

version of ZrNiSn . However, these two stannides do not form a continuous solid solution $\text{ZrNi}_{1+x}\text{Sn}$. The different occupancy of the tetrahedral voids has a drastic effect on the space group symmetry. The half-Heusler phase crystallizes with a non-centrosymmetric space group. ZrNiSn and other half-Heusler type stannides (MgAgAs type), have intensively been investigated with respect to their thermoelectric properties [11]. Improvement of the properties is possible by different dopings. Such Heusler phases have been prepared with many transition metals. Even if the properties are promising, in those cases where neighboring transition metals are used, the site assignments on the basis of X-ray data often remains an open question.

The family of binary and ternary rare earth stannides is much larger than the one of the transition metal stannides. The crystal chemical details of these stannides have been reviewed by Skolozdra [12]. The research concerned the determination of the phase diagrams (isothermal sections at different temperatures) as well as the structure determinations of new phases. Depending on the $\text{RE}_x\text{T}_y\text{Sn}_z$ composition, the stannides show different crystal chemical peculiarities. Most structures contain two- or three-dimensional $[\text{T}_y\text{Sn}_z]$ polyanionic networks which leave cavities or channels for the rare earth elements. Within the networks one can observe also $\text{T}-\text{T}$ bonding and especially in the tin-rich compounds extended tin substructures. Some of the T -rich stannides show segregation of the transition metal, leading to interesting structures. So far, the rare earth-rich parts of the $\text{RE}-\text{T}-\text{Sn}$ systems have only scarcely been studied.

The cerium, europium, and ytterbium based stannides have intensively been investigated with respect to their physical properties, when searching for intermetallics with valence instabilities. To give some examples, CeNiSn [13] and CeRhSn [14] show intermediate cerium valence. Both structures contain only one crystallographic cerium site. CeRuSn [15] is a static intermediate-valent cerium compound with one purely trivalent cerium site and one $\text{Ce}^{(4-\delta)+}$ site. Such compounds are in the focus of solid state physicists since many years and have thoroughly been investigated.

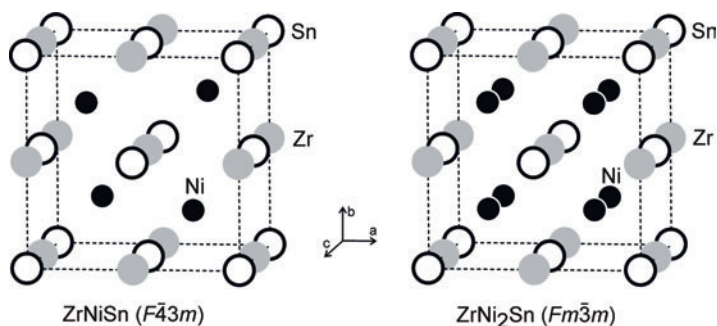


Fig. 3.74 The crystal structures of the half-Heusler phase ZrNiSn and the full-Heusler phase ZrNi_2Sn .

The crystal chemistry of the ternary actinoid stannides is similar to the rare earth ones. Here, especially the uranium-based compounds are in the focus due to their interesting magnetic behavior. Especially the $UTSn$ [16] and U_2T_2Sn [17] stannides have been investigated. Many ternary stannides have also been synthesized with the alkali and alkaline earth metals. Their crystal chemistry has been reviewed [7]. The lithium containing compounds [18] are of interest as model compounds for lithium battery materials. All the $(A,AE,RE,An)-T-Sn$ phase diagrams are by far not completely explored. These phases remain an exciting field in future.

The whisker formation observed in the solder joints also occurs in diverse ternary $RE_xT_ySn_z$ stannides, especially in the tin-rich ones. Such whiskers can grow up to several hundred micrometers. The mechanism is still not understood. Besides the mechanical stress discussed for the solders, certainly also oxidation/hydrolysis might play a role. As an example we present an aged $LuAgSn$ sample in Fig. 3.75.

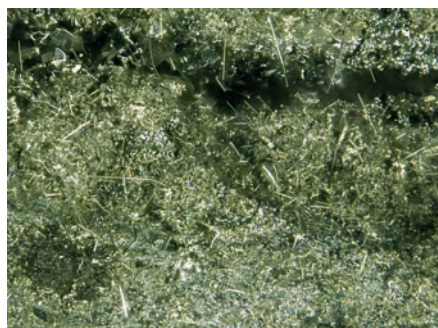


Fig. 3.75 Optical micrograph (magnification 400 ×) of the corroded surface of a $LuAgSn$ sample.

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3.9.5 Plumbides

The alkali metals directly react with lead forming a variety of binary plumbides. The most important phases are NaPb, NaPb₃, Na₁₅Pb₄, KPb, KPb₂, K₄Pb₉, K₅Pb₂₄, RbPb, Rb₄Pb₉, CsPb, and Cs₄Pb₉ with Zintl anions that are similar to the stannides. Again, the small lithium atoms lead to different compositions, *i. e.* LiPb, Li₈Pb₃, Li₃Pb, Li₁₀Pb₃, Li₇Pb₂, and Li₂₂Pb₅. Beryllium forms no plumbide and with magnesium only Mg₂Pb with an *anti*-fluorite-type structure is known. The heavier alkaline earth elements built the plumbides Ca₂Pb, Ca₅Pb₃, CaPb, CaPb₃, Sr₂Pb, Sr₅Pb₃, Sr₃₁Pb₂₀, SrPb, Sr₂Pb₃, SrPb₃, Ba₂Pb, Ba₅Pb₃, CaPb, Ca₃Pb₅, and BaPb₃.

Transition metal plumbides played an important role as precipitations in the classical lead-tin solders. The main plumbides that occur are Au₂Pb, AuPb₂, Pt₃Pb, PtPb, and PtPb₄. Today solders are free of lead in order to avoid environmental contamination. Lead-based solders are only used for extremely specialized applications where no substitute material with equivalent properties is available. The reason for using lead as primary component in multinary solders was the massive suppression of whisker growth.

The transition metal plumbides are less frequent than the respective stannides. Several transition metals form solid solutions with lead with the *fcc*, *hcp*, and *bcc* atomic arrangement besides pure binary compounds. The general compositions are T₃Pb (Cr₃Si or Cu₃Au type), T₅Pb₃ (Mn₅Si₃ type), T₅Pb₄ (Ti₅Ga₄ type), TPb (CoSn or NiAs type), T₄Pb₅ (Rh₄Pb₅ type), TPb₂ (CuAl₂ type), and TPb₄ (PtPb₄ type). As representative examples for the transition metal plumbides we present the structures of PtPb₄ and Rh₄Pb₅ in Fig. 3.76. The platinum atoms in PtPb₄ have square anti-prismatic lead coordination with Pt–Pb distances of 290 pm. These PtPb_{8/2} square anti-prisms are condensed *via* common edges in *ab* direction and these layers are stacked in an *ABAB* sequence. These building units also occur in diverse TSn_x structures [1]. The shortest

Pb–Pb distance of 325 pm between the prisms is shorter than in *fcc* Pb (350 pm) indicating substantial Pb–Pb besides Pt–Pb bonding in PtPb_4 .

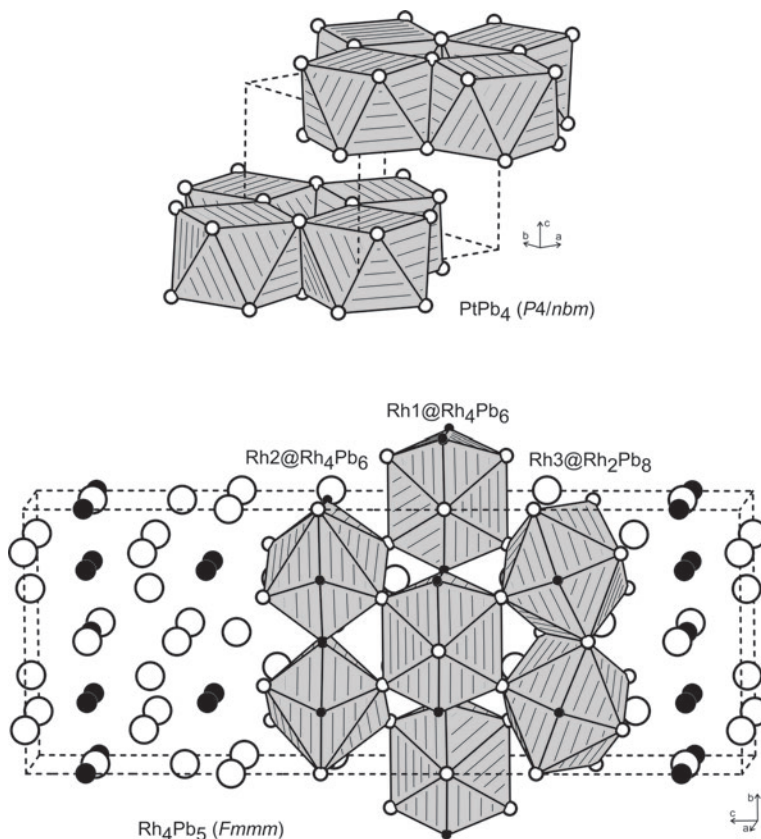


Fig. 3.76 The crystal structures of PtPb_4 and Rh_4Pb_5 . Transition metal and lead atoms are drawn as black filled and open circles, respectively. The characteristic coordination polyhedra around the transition metal atoms are emphasized.

The structure of Rh_4Pb_5 is more complex. It contains three crystallographically independent rhodium sites, all with coordination number 10: $\text{Rh1Rh}_4\text{Pb}_6$, $\text{Rh2Rh}_4\text{Pb}_6$, and $\text{Rh3Rh}_2\text{Pb}_8$. The Rh_4Pb_5 structure is stabilized by Rh–Rh (285–286 pm), Rh–Pb (273–301 pm), and Pb–Pb (323–360 pm) interactions as well. The complete structure of Rh_4Pb_5 can be explained by an edge- and corner-condensation of all three types of rhodium-based polyhedra.

Ternary plumbides are formed with the alkali, alkaline earth, rare earth, and actinoid metals. Exemplarily we only present the $\text{K}_3\text{Au}_5\text{Pb}$ [2] and Rb_3AuPb_4 [3] structures in Fig. 3.77. These two structures show different clustering. The gold atoms in $\text{K}_3\text{Au}_5\text{Pb}$

build a two-dimensional network of corner-sharing Au_4 tetrahedra that extends in the ac direction. The different layers of condensed gold tetrahedra are separated by the potassium atoms and zig-zag chains of lead atoms (316 pm Pb–Pb) which extend in a direction. This description is purely geometrical and explains the different substructures. The zig-zag chains are connected to the network of gold tetrahedra *via* shorter Au–Pb bonds of 269 pm and the $[\text{Au}_5\text{Pb}]$ polyanionic network is charge-compensated by the potassium atoms.

The Rb_3AuPb_4 structure shows the other extreme. The lead atoms are the majority component and they form slightly distorted tetrahedra with 306–328 pm Pb–Pb distance. These Pb_4 tetrahedra are edge-on coordinated to gold atoms (288–289 pm Au–Pb) leading to chains that extend in the c direction. The chains have the motif of a distorted hexagonal rod packing. They are separated and charge-balanced by the rubidium atoms.

Compared with the huge number of $\text{RE}_x\text{T}_y\text{Sn}_z$ stannides, only few data are available about $\text{RE}_x\text{T}_y\text{Pb}_z$ plumbides. The phase diagrams seem to contain less compounds and the low boiling point of lead is a synthetic hindrance. The crystal chemistry of the $\text{RE}_x\text{T}_y\text{Pb}_z$ plumbides [4] largely resembles the respective stannides. The RETPb and $\text{RE}_2\text{T}_2\text{Pb}$ plumbides are the best studied compounds. These plumbides have been prepared in extension of the stannides in order to compare the magnetic properties. One of the very interesting compounds is the magnetically frustrated Shastry-Sutherland lattice $\text{Yb}_2\text{Pt}_2\text{Pb}$ [5] which orders antiferromagnetically at the low Néel temperature of 2.07 K.

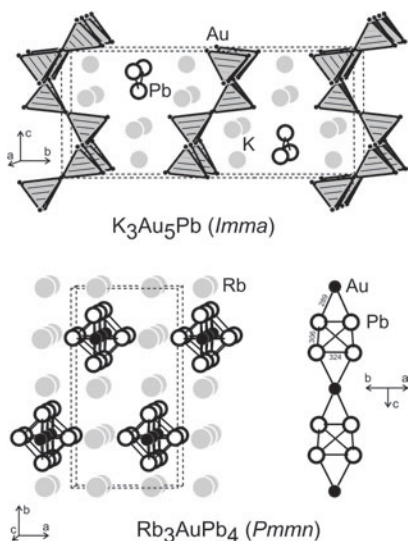


Fig. 3.77 The crystal structures of $\text{K}_3\text{Au}_5\text{Pb}$ and Rb_3AuPb_4 . Alkali metal, gold, and lead atoms are drawn as light gray, black filled and open circles, respectively. The characteristic tetrahedral gold coordination is emphasized. The lower left-hand drawing shows a cutout of the one-dimensional $[\text{AuPb}_4]$ polyanionic chain.

In view of the heavy metal toxicity, lead intermetallics are certainly only of fundamental interest. Nevertheless, many of these compounds have fascinating crystal structures and interesting physical properties. Of the series of ternary rare earth tetrelides, the plumbides are the least investigated ones.

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3.10 Pnictides

3.10.1 Nitrides

The formation of nitrides is generally more difficult than the synthesis of oxides, sulphides, or carbides, since the high bonding energy of 945 kJ/mol of dinitrogen is a severe barrier to overcome. One of the industrially most important reactions is the adsorption of dinitrogen on iron-containing surfaces in the Haber-Bosch process and the subsequent reduction to ammonia. The iron-nitrogen bonding plays a crucial role in this process. The first reduction process is the formation of a diazenide ion, recently observed in SrN_2 and BaN_2 . Similar to the carbides (Chapter 3.9), also nitrides are traditionally subdivided into salt-like, covalent, and metallic nitrides.

Typical ionic nitrides are the ion conductor Li_3N which already forms upon reaction of lithium metal with atmospheric nitrogen, or Mg_3N_2 which is the reaction product of magnesium burning in a pure nitrogen atmosphere. These nitrides are highly sensitive to moisture. Hydrolysis ($\text{N}^{3-} + 3\text{H}_2\text{O} \rightarrow \text{NH}_3\uparrow + 3\text{OH}^-$) readily leads to the formation of ammonia. The well-known covalent nitrides are the two modifications of BN, soft hexagonal *h*-BN and super-hard cubic *c*-BN, the α - and β -modifications of the nitride ceramic Si_3N_4 , the normal- and high-pressure modification of P_3N_5 , and wurtzite-type AlN which exhibits anomalously high thermal conductivity and is used as support material for electronic devices. For an overview we refer to review articles [1].

Herein we focus on nitrides with metallic properties. Besides electron-precise alkaline earth nitrides like Be_3N_2 or Mg_3N_2 , an interesting family of ternary nitrides

has been discovered. First hints at such compounds were obtained by Addison [2] who studied reactions of barium and nitrogen in liquid sodium. Later, systematic studies by Simon and co-workers lead to a variety of ternary and quaternary subnitrides [3]. We start with the structure of binary Sr_2N which crystallizes with an *anti*- CdCl_2 -type structure (Fig. 3.78). The nitrogen atoms fill octahedral voids of the strontium substructure, leading to an ABC stacking of layers of edge-sharing Sr_6N octahedra. Electron counting leads to a description $2\text{Sr}^{2+}\text{N}^{3-}\text{e}^-$. This readily explains the black color of Sr_2N . The remaining octahedral voids between the layers can be filled with hydrogen. The absorption of one equivalent of hydrogen per formula unit Sr_2N leads to the electron-precise yellow nitride hydride $\text{Sr}_2\text{NH} \equiv 2\text{Sr}^{2+}\text{N}^{3-}\text{H}^-$.

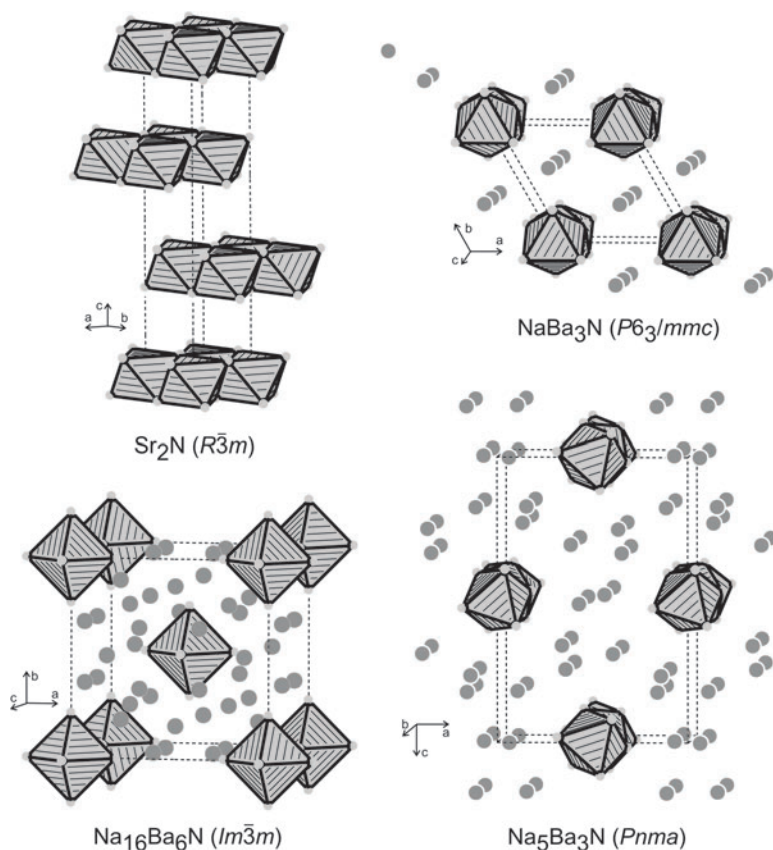


Fig. 3.78 The crystal structures of Sr_2N , NaBa_3N , $\text{Na}_{16}\text{Ba}_6\text{N}$, and $\text{Na}_5\text{Ba}_3\text{N}$. The nitrogen-centered alkaline earth metal octahedra are emphasized. Surrounding sodium atoms are drawn in medium gray color.

The synthesis of the subnitrides is the consequent extension of suboxide chemistry (Chapter 3.11.1). Three representative structures are presented in Fig. 3.78. They all

have the same structural principle. The nitride anions are captured in octahedra of barium and these substructures are embedded in a sodium matrix. In the $\text{Na}_{16}\text{Ba}_6\text{N}$ structure one observes a *bcc* packing of the Ba_6N octahedra which are well separated from each other. In the structures of NaBa_3N (an occupancy variant of the hexagonal perovskite type) and $\text{Na}_5\text{Ba}_3\text{N}$ the Ba_6N octahedra share common faces and one observes hexagonal rod packings of these octahedral chains. The space between the chains is filled by different amounts of sodium atoms. The Ba–N distances in the three structures are characteristic for ionic bonds and one can explain these subnitrides as salt-like alkaline earth nitride substructures in metallic sodium matrices (nanodispersion of a salt in a metal).

A more complicated unit of condensed nitrogen-centered octahedra has been discovered in $\text{Na}_{14}\text{Ba}_{14}\text{CaN}_6$. In Fig. 3.79 we present one of the cluster units. Here, the nitride anions are located in Ba_5Ca octahedra. Six $\text{N@Ba}_5\text{Ca}$ octahedra are condensed *via* common faces and the central calcium atom is part of all octahedra. In $\text{Na}_{14}\text{Ba}_{14}\text{CaN}_6$ the $[\text{Ba}_{14}\text{CaN}_6]$ cluster units build an *fcc* packing and the clusters are well separated by the sodium matrix. Considering the chemical bonding within the cluster unit as fully ionic, one obtains an electron-precise partition within the cluster besides the metallic $[\text{Na}_{14}\text{Ba}_6]$ matrix, *i. e.* $[\text{Na}_{14}\text{Ba}_6][(\text{Ba}^{2+})_8\text{Ca}^{2+}(\text{N}^{3-})_6]$. The $[\text{Ba}_{14}\text{CaN}_6]$ cluster unit is extremely stable. Several other nanodisperse systems of the salt in metal $\text{Na}_x[\text{Ba}_{14}\text{CaN}_6]$ with $x = 14, 21, 22$ have been observed.



Fig. 3.79 The $[\text{Ba}_{14}\text{CaN}_6]$ cluster unit in the structure of $\text{Na}_{14}\text{Ba}_{14}\text{CaN}_6$. The calcium atom in the center of the cluster units belongs to each of the $\text{N@Ba}_5\text{Ca}$ octahedra.

The technically most important nitrides are those containing transition metals [4]. They play an important role for surface coatings and in steel production. Similar to the rock salt-type carbides discussed in Chapter 3.9.1, also the nitrides TiN (yellow golden color) and HfN (yellow brownish color) have very high melting points of ca. 3220 and 3500 K, respectively. Bulk samples of TiN can be obtained by the reduc-

tion of titanium dioxide with carbon in the presence of nitrogen: $2\text{TiO}_2 + \text{N}_2 + 4\text{C} \rightarrow 2\text{TiN} + 4\text{CO}\uparrow$. Surface coatings are available from CVD: $2\text{TiCl}_4 + \text{H}_2 + 2\text{NH}_3 \rightarrow 2\text{TiN} + 8\text{HCl}\uparrow$. The bulk nitrides as well as the coatings show good electrical and thermal conductivity, excellent corrosion stability and hardness. The color of these rock salt-type carbides depends on the anion substructure. Titanium mononitride shows a broad range of homogeneity TiN_{1-x} down to $\text{TiN}_{0.5}$. The defects influence the melting point and the hardness as well. Partial replacements of nitrogen by oxygen and/or carbon result in $\text{Ti}(\text{C}/\text{N}/\text{O})$ materials with varying color. Such colored abrasion-proof surface coatings are frequently observed on watch casings, drills, or saw blades. Besides, the pure mononitrides diverse $\text{Al}_2\text{O}_3/\text{TiN}/\text{TiC}$, TiN/AlN , or $\text{Si}_3\text{N}_4/\text{TiN}$ composite ceramics find technical applications. The mononitrides NbN and ZrN are superconductors with transition temperatures of 16.8 and 10.0 K, respectively.

Besides the rock salt-type phases TiN_{1-x} ($x = 0.5$ to 1.0) three other titanium nitrides are known. Ti_2N crystallizes with an *anti*-rutile-type structure. The nitrogen atoms fill titanium octahedra which are *trans*-edge shared and the resulting chains are further condensed *via* common corners, leading to a three-dimensional network. The other nitrides have the compositions $\text{Ti}_3\text{N}_{2-x}$ and $\text{Ti}_4\text{N}_{3-x}$ with homogeneity ranges. They are only stable in the temperature range 1320–1570 K.

The iron nitrides are of fundamental significance in steel hardening. Although such precipitations are technically produced in huge amounts, not all of the crystal structures and reaction mechanisms are fully determined. In most cases it is difficult to grow single crystals of such materials, therefore the structures were often determined by combinations of neutron and synchrotron powder diffraction [5].

The structures of Fe_4N and Fe_2N are shown as examples in Fig. 3.80. The iron atoms in Fe_4N are packed in an *fcc* arrangement and the nitrogen atoms fill every fourth octahedral void (190 pm Fe–N) in an ordered manner. Thus, the nitrogen atoms no longer fulfil the requirement for the translations of a face-centered lattice and one observes a *klassengleiche* symmetry reduction of index 4 from $Fm\bar{3}m$ to $Pm\bar{3}m$. Fe_4N is the so-called nitrogen martensite. The nitrogen site can rapidly be substituted by carbon. Fe_2N adopts the *anti*- α - PbO_2 -type structure. Similar to the *anti*-rutile-type structure of Ti_2N (*vide ultra*), also Fe_2N can be described as a network of condensed Fe_6N octahedra (189–201 pm Fe–N). In contrast to Fe_4N we now observe a distorted hexagonal close packing of the iron atoms and the nitrogen atoms fill half of the octahedral voids in an ordered manner. Also, the structure of Fe_3N derives from such hexagonal close packing [5], however, only corner-sharing octahedra are occupied.

In the case where thin-film coatings or composites of TiN/AlN are used, ternary nitrides like Ti_3AlN , Ti_2AlN , or $\text{Ti}_3\text{Al}_2\text{N}_2$ might form. The common structural motif of these three nitrides is the close packing of the metal atoms. Similar to the complex carbides discussed in Chapter 3.9.1, the nitrogen atoms fill only octahedral voids formed by the early transition metal. As an example we present the Ti_3AlN structure in Fig. 3.80. It is an *anti*-perovskite ($\text{Ca} \leftrightarrow \text{Al}$, $\text{Ti} \leftrightarrow \text{N}$, $\text{O} \leftrightarrow \text{Ti}$) with a network of corner-sharing Ti_6N octa-

hedra. Zr_3AlN with similar composition also contains Zr_6N octahedra, however, layers of edge- and corner-sharing octahedra are separated by the aluminum atoms, leading to a two-dimensional octahedral substructure.

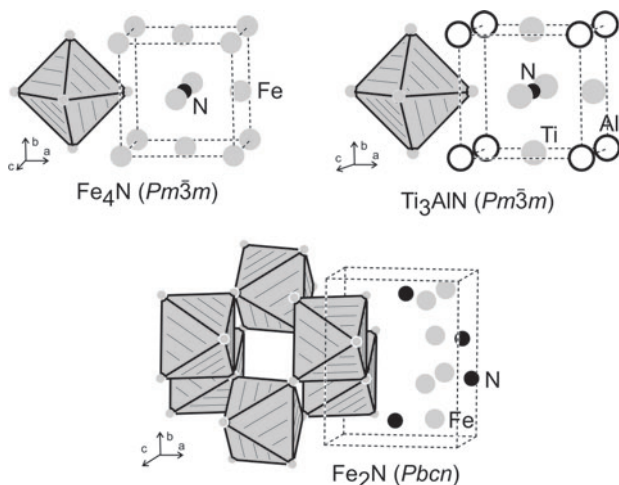


Fig. 3.80 The crystal structures of Fe_4N , Ti_3AlN , and Fe_2N . The striking Fe_6N and Ti_6N octahedra are emphasized.

The rare earth and actinoid metals form nitrides with the rock salt structure which are sometimes nitrogen deficient, *i. e.* REN_{1-x} , leaving part of the valence electrons in metal-centered bands. These nitrides are generally hard materials. Important actinoid nitrides besides UN and ThN are Th_3N_4 (own type) and bixbyite-type U_2N_3 .

Combining the binary alkali, alkaline earth, or rare earth metal nitrides with those of the transition metals leads to a large family of nitridometalates [1, 6]. Many of these structures display electron-precise nitridometalate anions which resemble well-known silicate structures. The nitridometalate anions are charge balanced and separated by alkali, alkaline earth, or rare earth cations. An interesting exception in this family of structures is the metallic auride nitride Ca_3AuN [7] which crystallizes with an *anti*- CaTiO_3 -type structure. Considering the auride and nitride anions, an electron-precise description $3\text{Ca}^{2+}\text{Au}^{-}\text{N}^{3-}2\text{e}^{-}$ leaves two excess electrons, leading to metallic behavior.

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3.10.2 Phosphides

Phosphorus reacts with almost every metal of the periodic system under formation of negatively charged species, referred to as phosphides. It is therefore not surprising that metal phosphides represent a huge family among solid-state compounds, which counts more than 3000 entries in *Pearson's Crystal Database* [1]. Besides the large number of compounds with isolated P^{3-} anions, phosphorus has a strong tendency to the formation of homonuclear P-P bonds, which results in polyphosphides mostly according to Zintl's concept (Chapter 3.7). On the other hand, also many metal-rich phosphides are known, where bonds between the (transition) metal atoms play a dominant role. The exceptional structural variety of phosphides has been reviewed frequently [2–4]. Selected examples for the diverse families of phosphides are summarized in the following. Several of the crystal chemical concepts also apply for the higher congeners arsenic, antimony and bismuth.

Polyphosphides Combinations of phosphorus with electropositive alkali and alkaline earth metals mostly lead to polyphosphides. The electron transfer from the metal to the phosphide-polyanion is presumably complete, thus these polyphosphides are mostly classical valence compounds and show typical P-P bond lengths between 215 and 230 pm. A plethora of polyphosphides with $[P_2^{4-}]$ dumbbells ($|\bar{P}-\bar{P}|$), as well as with two- ($-\bar{P}-$) or threefold- ($-\bar{P}-$) connected phosphorus atoms are known. Figure 3.81 shows the structures of NaP with $[P^-]$ helices, Li_3P_7 with $[P_7^{3-}]$ cages and K_4P_6 with $[P_6^{4-}]$ planar six-membered rings as examples. The $[P_6^{4-}]$ ring in K_4P_6 had been discussed to be aromatic, but NMR experiments revealed that no aromaticity is present [5]. Calculations indicated that a free $[P_6^{4-}]$ would not be planar, and can rather be formulated as $[P_2^0P_4^{1-}]$ with one double-bond in the ring. For a comprehensive overview on polyphosphides we refer to [3].

The simplest polyphosphide motif $[P_2^{4-}]$, also referred to as P_2 -dumbbell, occurs in many transition metal compounds. It is partially combined with other P–P bonded

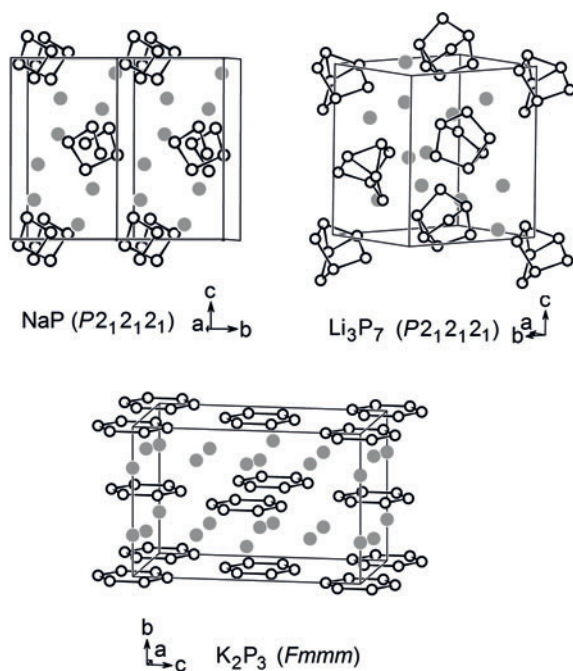


Fig. 3.81 The crystal structures of NaP, Li_3P_7 , and K_2P_3 . The phosphorus substructures (open circles) are emphasized.

fragments, and often with isolated P^{3-} ions. The pyrite type (cubic FeS_2) and variants like the $FeAs_2$ (orthorhombic) and $CoSb_2$ type (monoclinic) are formed by the binary phosphides TP_2 ($T = Fe, Co, Ni, Ru, Rh, Os, Ir, Pt$). The structure of $FeAs_2$ (mineral löllingite) is an orthorhombic variant of the pyrite type, and also referred to as anomalous markasite (orthorhombic FeS_2) [6], because of short distances between the iron atoms (288 pm), which do not occur in the original markasite. Figure 3.82 shows the structures of NiP_2 with the pyrite-type structure and FeP_2 with the $FeAs_2$ -type structure. Note the different orientations of the P_2 -dimers, which are aligned along the body-diagonals of the cubic unit cell only in NiP_2 with pyrite-type structure.

Beyond the pyrite-derivatives, another group of transition metal diphosphides TP_2 ($T = V, Nb, Ta, Cr, W$) crystallizes in the $OsGe_2$ -type structure [7]. Figure 3.82 shows the structure of VP_2 which contains isolated P^{3-} as well as P_2 -dimers with a P–P bond length of 221 pm.

P_2 -dimers with a relatively long P–P bond (243 pm) are present in orthorhombic NiP , which transforms under high pressure to a structure with P_2 -dimers and P_3 -trimers with even longer P–P bonds of 254 pm [8]. The latter structure is closely related to the frequently observed MnP type with weakly bonded $[P^{n-}]$ zigzag-chains (Figure 3.82). Due to the relatively long P–P bonds and significant contributions of metal-

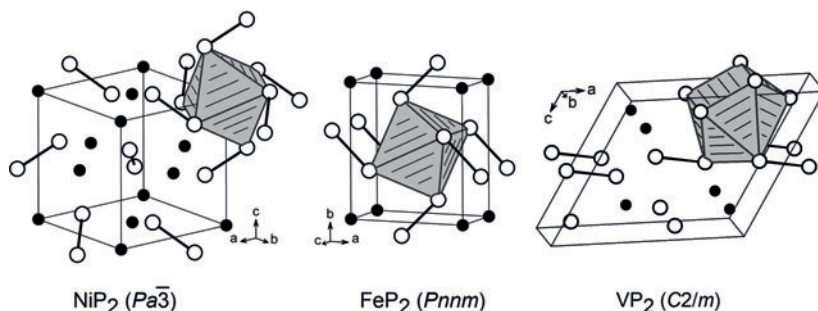


Fig. 3.82 P_2 -dimers in binary transition metal phosphides: The crystal structures of NiP_2 (pyrite type), FeP_2 (FeAs_2 type), and VP_2 (OsGe_2 type). The phosphorus coordination of the transition metal atoms is emphasized.

metal-bonding in NiP - and MnP -type compounds [9], these should be classified in between metal-rich compounds with isolated P^{3-} and true polypnictides.

This is different in PdP_2 without significant Pd-Pd bonding, where helical chains run perpendicular to layers of corner-sharing $\text{PdP}_{4/2}$ -squares [10], as emphasized in Figure 3.83. The P-P bond lengths are 222 and 223 pm, and correspond to a typical P-P single bond. This structure is a good example of how polypnictide fragments are arranged together with the special coordination requirement of the transition metal, in this case with the typical planar square coordination of Pd^{2+} (d^8). NiP_2 forms the same type of structure, which is apparently confined to the phosphides of palladium and nickel, because all higher pnictide homologues as well as PtP_2 crystallize with pyrite- or marcasite-type structures.

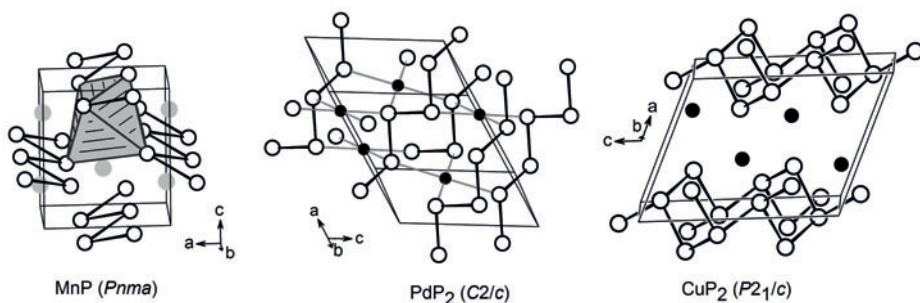


Fig. 3.83 Polyphosphide chains and rings in the crystal structures of MnP , PdP_2 , and CuP_2 .

Examples for increasing complexity of polyphosphide fragments are the structures of CuP_2 [11] and AgP_2 with connected cyclo-P_{10} rings build up by $[\text{P}_4]^{2-}$ units as shown in Figure 3.83. Such rings have also been found in the phosphides TP_4 with

$T = \text{Cr, Mo, and V}$ [12]. Finally, also combinations of different polyphosphide fragments are known, for example in the triclinic structure of Re_2P_5 with dimers, chains and branched chains [13].

Binary phosphides with isolated P^{3-} ions Binary phosphides with isolated P^{3-} ions are formed with nearly all transition and rare earth metals. Considering the coordination of the pnictide by the metal atoms, the by far most common polyhedron is PT_9 , forming a trigonal prism with additional metal atoms located over the three rectangular faces (so-called tricapped trigonal prisms). Besides, also octahedral and trigonal prismatic sixfold coordinations are frequently observed.

Binary compounds TP with the NaCl-type structure are known with all trivalent rare earth ions La–Lu [14] and with Sc, Y [15] as well as with some actinides [16]. On the other hand, the NaCl type is not found among the d -metal pnictides, which mostly crystallize in the NiAs ($T = \text{Al, V}$) and related structure types like the FeAs ($T = \text{Cr, Fe, Co, W, Ru}$), TiP ($T = \text{Ti, Zr, Hf}$), or NbAs types ($T = \text{Nb, Ta}$) [17–20] shown in Figure 3.84, where the trigonal prismatic PT_6 coordination is realized. The orthorhombic MnP-type structure, also referred to as FeAs-type, is a common derivative of the NiAs-type structure. However, P–P distances and electronic structure calculations suggest weakly

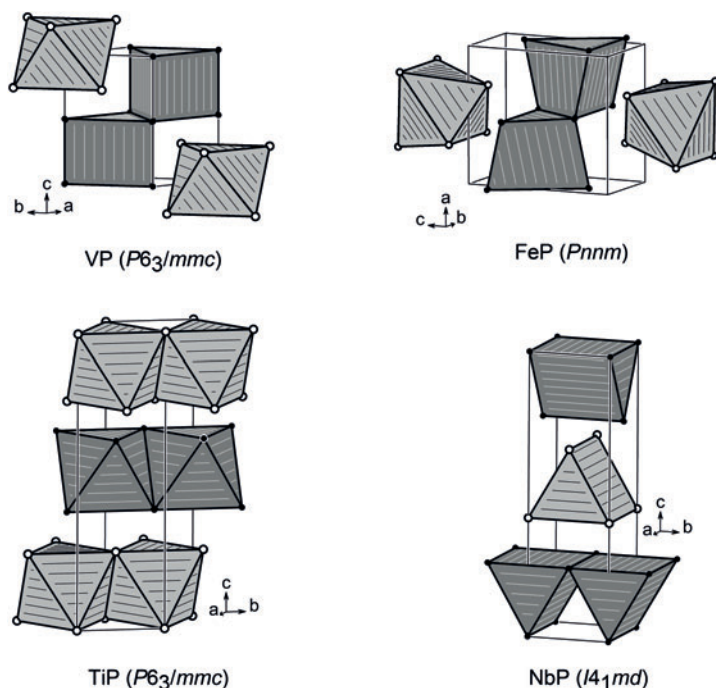


Fig. 3.84 Crystal structures of VP (NiAs type), FeP (FeAs type), TiP, and NbP (NbAs type), emphasizing the trigonal prismatic and octahedral coordinations.

bonded $^{1-}_\infty[\text{P}^{n-}]$ chains in MnP-type pnictides [21], which may rather be considered as polypnictides. It is important to note that the extremely common NiAs-type structure (especially with higher pnictides), one of the most fundamental structures of intermetallic compounds, is actually still not completely understood. Phase widths frequently occur, and the ordering of either additional atoms or vacancies can create superstructures that may easily be missed, especially if we keep in mind that many of these structures have been determined in the early days of X-ray crystallography. Indeed deviations have been found even in stoichiometric NiAs by electron diffraction experiments [22], and it has been argued if the ideal NiAs-type structure exists at all [23].

Equiatomic ternary phosphides Ternary equiatomic compounds ATP (A = electropositive metal of the groups 1, 2, or rare earths) mainly crystallize in six different structure types. A covalently bonded and negatively polarized $[\text{TP}]^{6-}$ network is formed by the transfer of electrons from the electropositive $A^{\delta+}$ ions, which are located in appropriate vacancies of the network. The structures are mainly determined by the size ratio between the A and T atoms r_A/r_T ($r_{A,T}$ = ionic radii). If $r_A \approx r_T$, the cubic MgAgAs-type structure [24] with a three-dimensional network of corner-sharing $\text{TP}_{4/4}$ tetrahedra

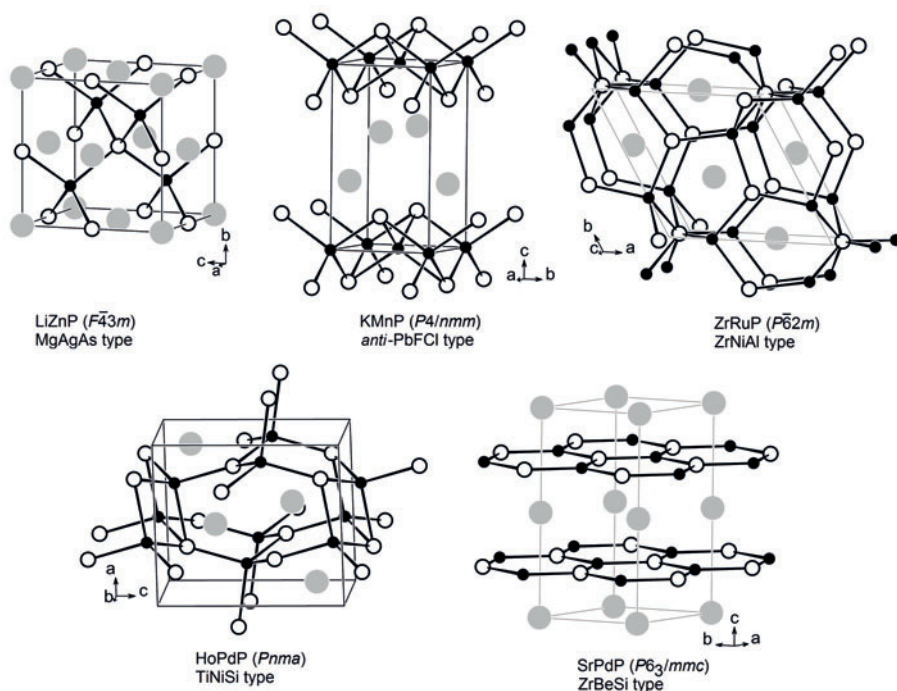


Fig. 3.85 The crystal structures of equiatomic ternary transition metal phosphides ATP. The $[\text{TP}]$ polyanionic networks are emphasized. T and P atoms are drawn as black filled and open circles, respectively.

(filled ZnS type) is formed, an example is LiZnP. As the size of the atom A increases, *anti*-PbFCl-type or ordered ternary variants of the *anti*-PbCl₂-type (TiNiSi-type), and Fe₂P-type (ZrNiAl-type) structures were observed, which still contain distorted TP_4 tetrahedra. Examples are KMnP and HoPdP. Finally, if $r_A \gg r_T$, the coordination of the transition metal changes from tetrahedral to trigonal, and structures with graphite-like (actually BN-like) layers occur, mostly ternary variants of the AlB₂ or Ni₂In type (ZrBeSi type), *e. g.* in the compounds SrPdP, SrAuP [25], and EuTP with $T = \text{Cu, Ag, Pt, Pd}$ [26]. These typical crystal structures of the ATP compounds are collected in Figure 3.85.

It should be noted that the probably oversimplified concept of the size ratio is not always successful to rationalize the formation of different structure types of the ATP compounds. Examples are certain platinum and palladium pnictides of the alkaline earth metals, which are actually expected to form ZrBeSi-type structures because $r_A \gg r_T$. Indeed, trigonal coordination of the transition metal is present, but the connections are quite different from the planar hexagons of the ZrBeSi-type structure [27–29].

The ThCr₂Si₂-type and related structures Ternary phosphides with the composition AM_2P_2 are known with virtually all transition metals (T) in combination with electro-positive elements (A) of the groups 1–3 or rare earth elements. Most of them crystallize in the tetragonal ThCr₂Si₂-type structure or variants thereof [30–36]. The ThCr₂Si₂-type structure is a ternary variant of BaAl₄, and characterized by layers of edge-sharing $TP_{4/4}$ tetrahedra, separated by the larger electropositive atoms. The latter are eightfold coordinated in a tetragonal prism of pnictides (Figure 3.86). It is an extraordinary property of this structure, that the interlayer P–P distances cover a wide range from well above 350 pm to 210 pm. In other words the pnictide atoms can either form covalent single bonds in $[P_2]^{4-}$ dumbbells, or remain non-bonded isolated P^{3-} ions. Actually, two branches of this structure exist, the true ThCr₂Si₂ type with bonds between the layers

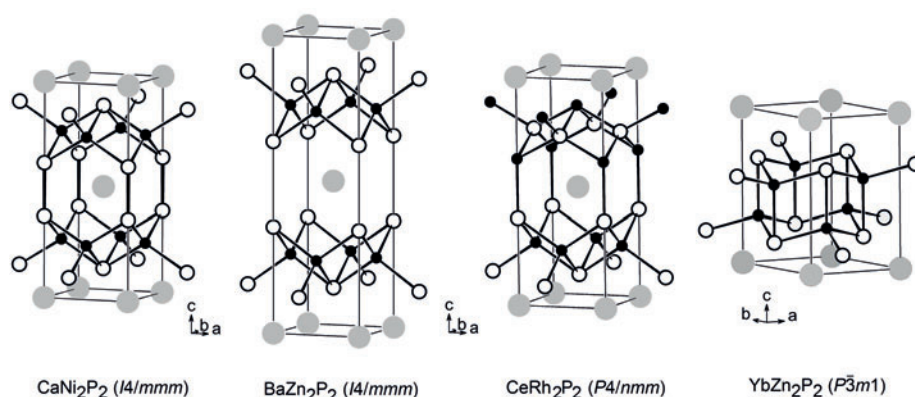


Fig. 3.86 Crystal structures of ternary transition metal phosphides AT_2P_2 . The $[T_2P_2]$ networks are emphasized. Grey: Ca, Ba, Ce, Yb; black: Ni, Zn, Rh, Zn; open circles: P.

like CaNi_2P_2 ($d_{\text{P-P}} = 211.6 \text{ pm}$ [31]) and the BaZn_2P_2 type without interlayer bonds ($d_{\text{P-P}} = 368.5 \text{ pm}$ [37]) (Figure 3.86). However, bonding or non-bonding states are not in all cases obvious, especially at intermediate P–P distances. Moreover, structural phase transitions have been observed, where the interlayer P–P distance changes abruptly by temperature, applying pressure, or by chemical modifications [38–40].

The presence or absence of interlayer P–P bonds in the ThCr_2Si_2 -type structure does not necessarily depend only on the size of the atom between the layers. Typically, the tendency to form bonds increases within the transition metal periods from left to right. A good example is the series CaT_2P_2 , where the P–P distances decrease along the series $T = \text{Fe}$ (271 pm), Co (246 pm), Ni (212 pm), Cu (222 pm), thus traversing from the non-bonding state in CaFe_2P_2 to typical P–P single bonds in CaNi_2P_2 and $\text{CaCu}_{1.75}\text{P}_2$. An at first glance comprehensible explanation has been suggested by *Hoffmann* and *Zheng* [41] based on semi-empirical band structure calculations. They basically argue that P–P σ^* antibonding orbitals become depopulated as the Fermi-level of the metal decreases upon band filling along the 3*d*-series. This sounds plausible, though subsequent DFT calculations did not support this interpretation [42, 43]. A recent study suggests that the formation of the interlayer bonds is intimately connected with the T – T bonds within the layers [44].

Figure 3.86 shows two further structures frequently observed in $AT_2\text{P}_2$ compounds. One is the tetragonal CaBe_2Ge_2 -type [45–47] structure of CeRh_2P_2 , where the T and P atoms are interchanged in every other layer. Consequently, T – P bonds are formed between the layers and the T – T interaction is cancelled in the $\text{PT}_{4/4}$ layer, because the distance between the metal atoms becomes large. The CaBe_2Ge_2 -type structure is preferably formed with late transition metals, which is in line with the above mentioned argument that the electron-rich systems avoid antibonding T – T interactions. The latter has also been suggested to be responsible for the structural distortions observed in CaBe_2Ge_2 -type structure compounds which lead to incommensurable modulations [48].

Another variant of $AT_2\text{Pn}_2$ compounds is the trigonal CaAl_2Si_2 -type structure (Figure 3.86) [49–51]. The transition metal is also tetrahedrally coordinated by the phosphorus atoms, but one threefold axis of the $\text{TP}_{4/4}$ tetrahedra is perpendicular to the layers. Consequently, the tetrahedra in the CaAl_2Si_2 -type structure share only three edges instead of four in the ThCr_2Si_2 -type compounds. Alternatively one may also describe this structure topologically as a hexagonal close packing (*hcp*) of the phosphorus atoms with 1/2 of the tetrahedral vacancies filled by the T atoms and 1/2 of the octahedral vacancies by the A atoms. It turned out that pnictides with the CaAl_2Si_2 -type structure are exclusively valence compounds with a valence electron count (VEC) of 16 electrons per formula unit. As an example $\text{Sr}^{2+}(\text{Zn}^{2+})_2(\text{P}^{3-})_2$ (VEC = 16) forms the CaAl_2Si_2 type, while $\text{Sr}^{2+}(\text{Cu}^+)_2(\text{P}^{3-})_2$ (VEC = 14) crystallizes in the ThCr_2Si_2 type. If the electronic condition is restored in $\text{La}^{3+}(\text{Cu}^+\text{Zn}^{2+})(\text{P}^{3-})_2$ (VEC = 16), the CaAl_2Si_2 -type structure is formed again [52]. However, some compounds do not follow this rule. BaZn_2P_2 is supposed to crystallize in the CaAl_2Si_2 -type structure, but forms the ThCr_2Si_2 type, probably due to the large size of the barium atom, which is not satis-

fied by sixfold coordination. It was also argued that compounds with CaAl_2Si_2 -type structure should be semiconducting because of the valence charge neutrality. However, this has been shown not to be true, even in the prototype compound CaAl_2Si_2 , which is a metal [53] as well as other silicides and germanides with this structure type [54–56]. It turned out that the formation of a band gap depends on the electronegativity difference between the metal and non-metal component, which is smaller in the case of AT_2Si_2 - than in AT_2P_2 -compounds. Therefore metallic silicides and germanides with $\text{VEC} > 16$ and CaAl_2Si_2 -type structure are known, while phosphides (and the other pnictides) strictly keep the 16 electron condition.

Metal-rich phosphides The binary phosphides $T_2\text{P}$ crystallize mainly in the Co_2P -, Fe_2P -, or Ta_2P -type structures, and also with the *anti*- CaF_2 type. Co_2P is also referred to as *anti*- PbCl_2 -type structure with phosphorus in the characteristic PT_9 -coordination. Co_2P and Fe_2P are the parent structure types for a plethora of ternary metal-rich pnictides of the general composition $T_mT'_nP_x$ with $m + n \approx 2x$. In both structures each half of the transition metals is bonded to four P atoms forming TP_4 tetrahedra and to five P atoms forming a square pyramid. The structure is a dense packing of these polyhedra as shown in Figure 3.87. Beyond the T –P bonds also metal-metal bonding plays certainly an important role. The T – T distances are in the range of 260–270 pm which is in the order of the distances in the elemental metals, which are 250 pm (Co) and 248 pm (α -Fe), respectively.

In spite to the complex arrangement of the cation polyhedra, it turned out that the basic building block of these structures is the PT_9 unit with phosphorus in the capped trigonal prism of metal atoms, which occurs extremely frequently in transition metal pnictides. These PT_9 units can be arranged and connected in various ways, but interestingly this occurs in two dimensions mostly. Therefore many of these structures have one short axis which corresponds to the height of the PT_9 prisms. Therefore, it seems natural to use these prism arrangements in order to describe and to systematize these compounds. However, we note that this way of describing a structure is a topological point of view, and does not necessarily reflect the bonding situation. Figure 3.87 shows the structures of Co_2P and Fe_2P where the PT_9 units are emphasized. Actually, only the PT_6 trigonal prisms are drawn, where the additional three atoms located above the rectangular faces are from neighboring prisms, as indicated by the dotted lines in the structure of Co_2P . Furthermore, atoms connected by thick and thin lines are separated from each other by half a translation period of the projection direction. For a comprehensive description on structural systematics based on prism arrangements in metal-rich phosphides see the review by Kuz'ma [4].

The principle of the PT_9 building blocks can easily be expanded to ternary compounds $T_mT'_nP_x$ with $m + n \approx 2x$. One of the most frequent structure types of metal-rich ternary pnictides with more than 100 entries in Pearson's database [1] is the $\text{Zr}_2\text{Fe}_{12}\text{P}_7$ -type structure. The arrangement of the PT_9 units is shown in Figure 3.88 [57]. A large number of $\text{A}_2\text{T}_{12}\text{P}_7$ -compounds has been found with $A = \text{Zr}, \text{Y}, \text{RE}$ [58–60], alkaline earth [61], Li, K [62] and $T = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Pd}, \text{Ti}, \text{Nb}$.

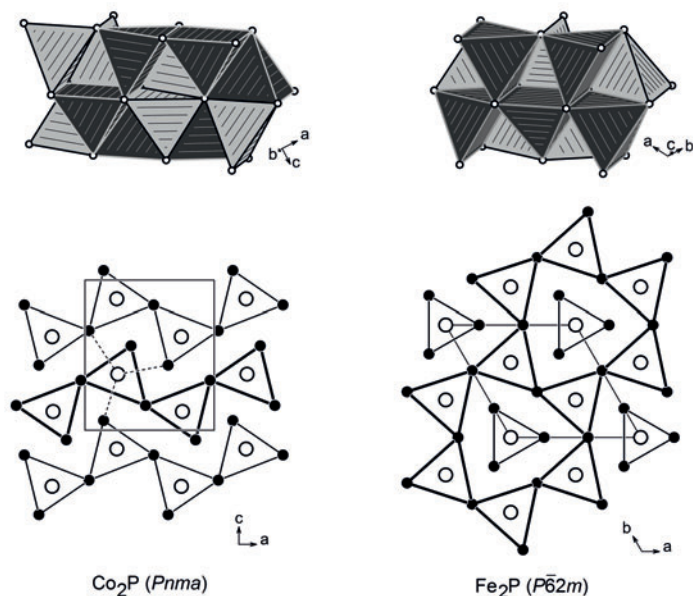


Fig. 3.87 Crystal structures of Co_2P and Fe_2P . Top: Packing of TP_4 tetrahedra (light gray) and TP_5 square prisms (dark gray). Bottom: Projections along the short axis emphasizing the arrangement of PT_6 trigonal prisms as general building block of metal-rich phosphides with a metal-non-metal ratio of 2:1. Atoms connected by thick and thin lines are separated from each other by half a translation period of the projection direction

The series of compounds $RE_6\text{Co}_{30}\text{P}_{19}$ ($RE = \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$) [63] has a slightly smaller $T:P$ ratio of 1.895, but nevertheless the structure can be rationalized by the arrangement of the PT_9 units. As shown in Figure 3.88, the structure consists of condensed propeller-like units made of three prisms with one common edge. This typical building block of ternary metal-rich pnictides is already present in the $\text{Zr}_2\text{Fe}_{12}\text{P}_7$ -type structure. Related structures form with silicon (Chapter 3.9.2).

Even though the structure description with PT_9 building blocks has been successful and occurs frequently in the literature, it is worthwhile to note that the approach can sometimes be misleading. We should keep in mind that the lines connecting the atoms are not bonds but topological lines only, thus the chemical nature of the material may be hidden. As an example, Figure 3.89 shows the prism representation of ZrFe_4P_2 with the tetragonal ZrFe_4Si_2 -type structure [64] which ascribes the structure as a typical member of the metal-rich pnictide family. However, examining the zirconium coordination one finds that it is octahedral, and the octahedra form the pattern known from the rutile-type structure. Nevertheless short Fe–Fe distances (249–255 pm) indicate strong metal-metal bonding. Combining the rutile-type $\text{ZrP}_{6/3}$ octahedra with the transition metal substructure as shown in Figure 3.89, we can understand the ZrFe_4Si_2 -type structure as a rutile type filled by chains of T_4 tetrahedra running along

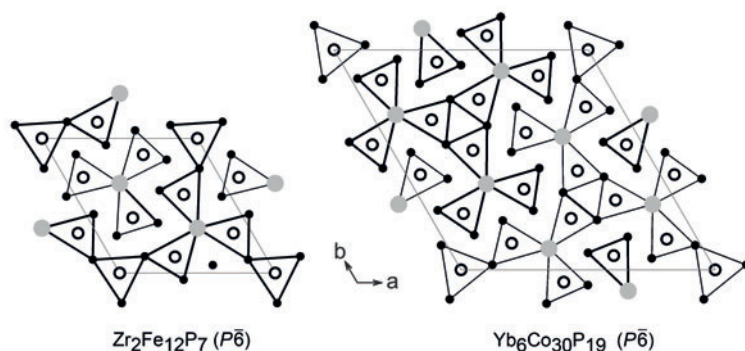


Fig. 3.88 Crystal structures of $\text{Zr}_2\text{Fe}_{12}\text{P}_7$ and $\text{Yb}_6\text{Co}_{30}\text{P}_{19}$. Projections along the short axis emphasize the PT_6 trigonal prisms. Atoms connected by thick and thin lines are separated from each other by half a translation period of the projection direction. Zirconium (ytterbium), iron (cobalt) and phosphorus atoms are drawn as medium gray, black filled and open circles, respectively.

the tetragonal c axis. This approach has been suggested for isotypic CaCu_4P_2 [65]. Note also that rutile and ZrFe_4P_2 share the same space group type $P4_2/mnm$. This is a typical case where the major bonding interactions are not intuitively clear and different interpretations of a crystal structure are possible.

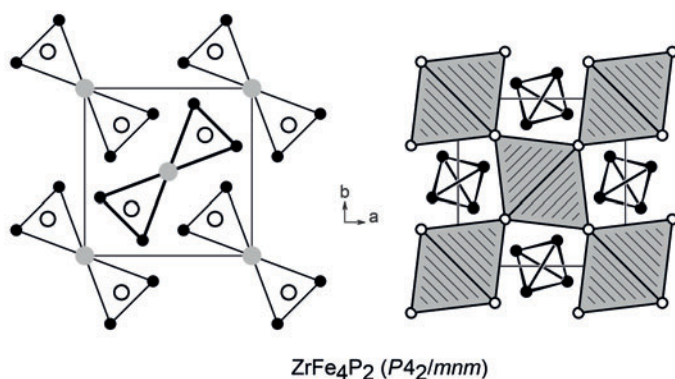


Fig. 3.89 Crystal structure of ZrFe_4P_2 . Left: Arrangement of PT_6 trigonal prisms. Right: ZrP_6 octahedra connected analogously to the rutile type structure, and filled with chains of Fe_4 tetrahedra.

Examples of metal-rich phosphides with ratios $T:P \neq 2$ are the compounds $T_3\text{P}$ with the tetragonal Ni_3P -type structure ($T = \text{V, Mn, Co, Ni}$). Chains of distorted $T_4\text{P}_4$ heterocubanes and the ‘stella quadrangula’ or ‘tetraederstern’ network of T atoms are emphasized in Figure 3.90. The latter is a typical structural motif which often occurs

in intermetallic phases [66]. Ti_5P_3 with the hexagonal Mn_5Si_3 -type structure is shown in Figure 3.90. About 120 binary pnictides crystallize in this structure type, mainly stronger polar compounds with alkaline or rare earth metals, but also compounds with d -metals like V_5P_3 , Ti_5P_3 , Ti_5As_3 , and Nb_5Sb_3 . Columns of face-sharing $[\text{Ti}_{6/2}\text{P}_{6/2}]$ octahedra are arranged as a hexagonal rod packing and form channels that are filled by $[\text{Ti}]$ metal chains with short Ti–Ti bonds. This structure is similar to the famous one-dimensional Mo_6 -cluster compounds $A(\text{Mo}_3\text{Se}_3)$. A second polymorph of Ti_5P_3 with the orthorhombic Yb_5Sb_3 -type structure has been reported, where no Ti_6 -clusters are present, and Ti–Ti bonding seems to be less significant than in the hexagonal Mn_5Si_3 -type structure [67].

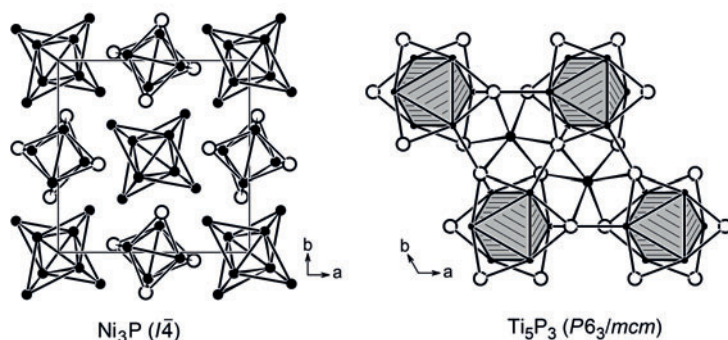


Fig. 3.90 Metal-rich phosphides: The crystal structures of Ni_3P and Ti_5P_3 . For details see text.



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3.10.3 Arsenides

The crystal chemistry of arsenides is largely similar to the phosphides. Binary alkali and alkaline earth arsenides often form polyarsenide anions according to Zintl's concept. The equiatomic compounds AAs with $A = \text{Na–Rb}$ are isostructural to NaP with $[\text{As}]^-$ helices (see Figure 3.81), while for CsAs a unique structure with $[\text{As}_3]^{3-}$ rings has been found (Figure 3.91) [1]. The As–As bond lengths are 243–247 pm, thus very close to the double covalent radius of arsenic (242 pm). Such short As–As bonds are remarkable with respect to the small As–As–As bond angles (60°) and with respect

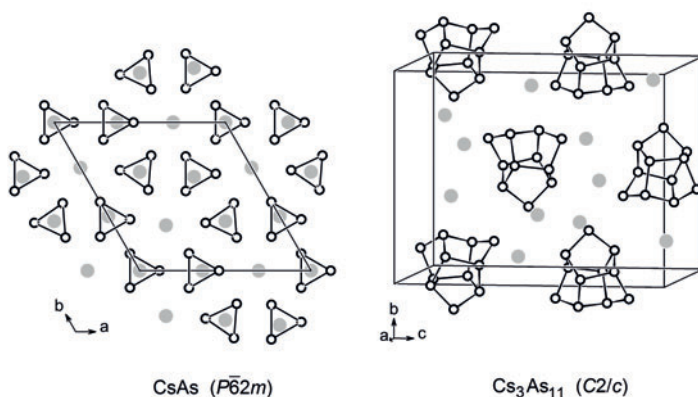


Fig. 3.91 Polyarsenides with molecular entities: The crystal structures of CsAs and $\text{Cs}_3\text{As}_{11}$. Cesium and arsenic atoms are drawn with medium grey and open circles, respectively.

to ring tension. Another example with molecular polyarsenide entities is $\text{Cs}_3\text{As}_{11}$ with $[\text{As}_{11}]^{3-}$ *ufosane* cages as depicted in Figure 3.91. The cesium compound is again unique with arsenic, because the other A_3As_{11} with $\text{A} = \text{K}$ and Rb are isotypic to Na_3P_{11} with another assembly of the ufosane cages [2].

An example of an alkaline earth polyarsenide is SrAs_3 where the arsenic atoms form a strongly puckered two-dimensional net of 14-membered meshes, where two- and three-bonded As atoms occur in the ratio of 2:1 according to $\text{Sr}^{2+}(\text{As}^-)_2\text{As}^0$ (Figure 3.92).

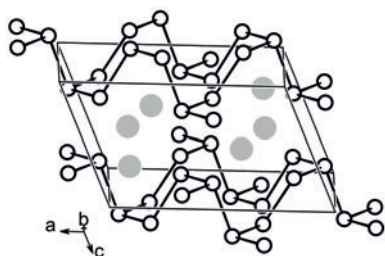


Fig. 3.92 The crystal structure of SrAs_3 with puckered 14-membered As rings.

Similar to the phosphides, many transition metal compounds exist with $[\text{As}_2]^{4-}$ dumbbells and other polyarsenide fragments. The cubic structure of Re_3As_7 [3] with the Ru_3Sn_7 -type structure displays an interesting assembly of As_2 dimers ($d_{\text{As-As}} = 245.5$ pm), which are oriented along [111], and combined with isolated As^{3-} ions according to the formula $\text{Re}_3\text{As}_3(\text{As}_2)_2$. Rhenium is in the center of a square anti-prism of arsenic atoms (Figure 3.93).

Helical chains with short As–As bonds have been found in the structures of CdAs_2 [4] with $[\text{As}_4]^{4-}$ helices ($d_{\text{As-As}} = 244$ pm), and in ZnAs_2 [5] with $[\text{As}_8]^{8-}$ helices ($d_{\text{As-As}} = 241\text{--}243$ pm), shown in Figure 3.94. Cadmium and zinc are tetrahedrally coordinated in both cases.

Among the transition metal polyarsenide compounds the cubic CoAs_3 -type structure [6] (mineral skutterudite) has intensively been studied. The crystal structure contains *cyclo*- $[\text{As}_4]^{4-}$ rings in the compounds $T\text{As}_3$ ($T = \text{Co}, \text{Ni}, \text{Rh}, \text{Ir}$) with the cubic skutterudite-type structure as emphasized in Figure 3.95. The As_4 squares are not regular in spite of the cubic symmetry, in fact the As–As bond lengths in CoAs_3 are 248 pm and 257 pm, respectively. The transition metals are octahedrally coordinated by arsenide ions. The $T\text{As}_6$ octahedra share all corners, thus the structure can be derived from the ReO_3 type by tilting the octahedra in such a way that the As_4 rings emerge [7]. Several phosphides and antimonides also crystallize in the skutterudite-type structure. The Zintl concept may be applied according to $(\text{Co}^{3+})_4[\text{As}_4^{4-}]_3$, however one may keep in

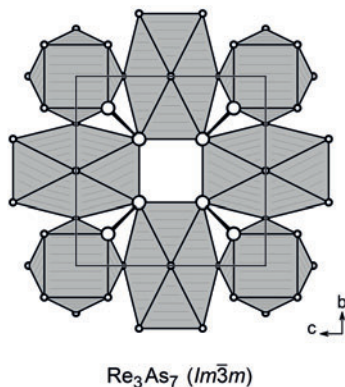


Fig. 3.93 The crystal structure of Re_3As_7 . As_2 dumbbells oriented along $[111]$ and the coordination polyhedra of the rhenium atoms are emphasized.

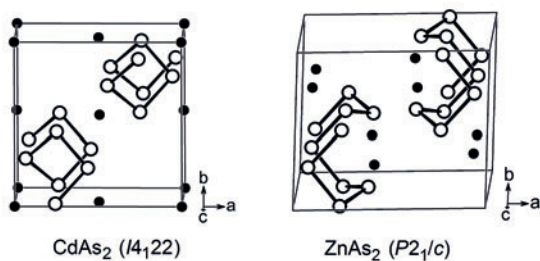


Fig. 3.94 The crystal structures of CdAs_2 and ZnAs_2 . Helical chains of $[\text{As}^{1-}]$ Zintl-polyanions are emphasized. The Cd^{2+} and Zn^{2+} ions are tetrahedrally coordinated by arsenide (not shown).

mind that this compound is metallic and the transfer of electrons from cobalt to arsenic is not necessarily complete.

$\text{LaFe}_4\text{As}_{12}$ with the $\text{LaFe}_4\text{P}_{12}$ -type structure represents a filled skutterudite type [8], where lanthanum fills almost-octahedral voids. More than 160 representatives of filled skutterudites $\text{AT}_4\text{Pn}_{12}$ have been reported ($A = \text{La-Yb, Th, U, Na, K, Sr, Ba}$; $T = \text{Fe, Co, Ni, Ru, Os}$; $\text{Pn} = \text{P, As, Sb}$). Especially the antimonides rank among today's most investigated materials due to their potential as thermoelectric materials [9].

Many binary and ternary arsenides crystallize isotypically to the phosphides described in the previous chapter, and often the arsenide is the actual name giver of the structure type. Examples are the NiAs - and MgAgAs -type structures which have numerous representatives with arsenic, but rather few with phosphorus. Also, the

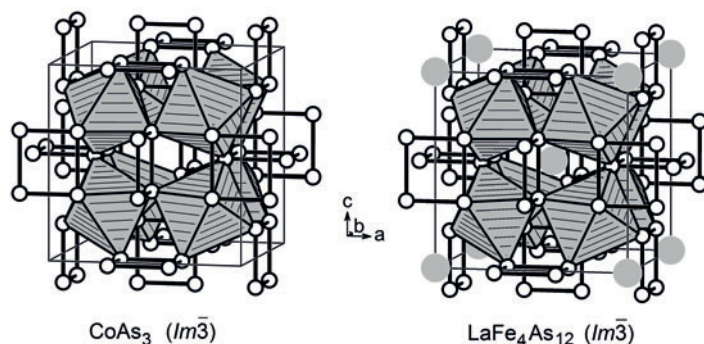


Fig. 3.95 The crystal structures of CoAs_3 (skutterudite) and $\text{LaFe}_4\text{As}_{12}$ (filled skutterudite). Distorted squares of $[\text{As}_4]^{4-}$ Zintl-ions and the octahedral coordination of the Co atoms are emphasized.

above-mentioned equiatomic ternary compounds ATX and the so-called ‘122-type’ compounds AT_2X_2 are well known with $X = \text{As}$ and P , and share common structural features. A large number of compounds with alkali [10], alkaline earth [11–13] and rare earth [14–16] metals at the A position have been studied during the last decades. However, in spite of often identical structure types, the lower electronegativity and the bigger size of the arsenic atoms when compared with phosphorus often have strong influences on the physical properties. As an example BaFe_2P_2 and BaFe_2As_2 are isotypic and crystallize with the ThCr_2Si_2 -type structure (actually the BaZn_2P_2 type because no interlayer bonds are present). The phosphide is a Pauli-paramagnetic metal, while BaFe_2As_2 shows a magneto-structural phase transition at 140 K, and becomes antiferromagnetically ordered below this temperature [17]. If the magnetic ordering is suppressed either by doping or by applying physical pressure, BaFe_2As_2 becomes a high- T_c superconductor with critical temperatures of up to 38 K [18]. None of these properties of BaFe_2As_2 occurs in the isotypic and isoelectronic phosphide BaFe_2P_2 .

Also, the structural principles of metal-rich arsenides are largely similar to those described for phosphorus, for example many representatives with the $T:\text{As}$ ratio close to two and the typical AsT_9 coordination with structures related to the ZrNiAl , $\text{Zr}_2\text{Fe}_{12}\text{P}_7$, and ZrFe_4Si_2 types are known. Nevertheless some compounds may exist with phosphorus which are unknown with arsenic and vice versa.

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3.10.4 Antimonides

The crystal chemistry of antimonides is still similar to the lighter homologues, albeit the stronger metallic character together with lower electronegativity and larger atomic radius causes some differences. Nevertheless, also antimony forms Sb–Sb bonds when combined with electropositive metals, and many polyantimonides are known. The compounds may still be rationalized by Zintl's concept, but due to the lower electronegativity one has to take incomplete electron transfer into account. Figure 3.96 shows crystal structures of CaSb_2 , KSb_2 and Li_2Sb as examples for polyantimonides. CaSb_2 forms the expected $^1[\text{Sb}^{1-}]$ zigzag-chains, while in KSb_2 ribbons of condensed chair-like Sb_6 rings run parallel to the b axis (Figure 3.96). Antimony is formally Sb^{2-} in Li_2Sb , but the crystal structure contains, besides the expected $[\text{Sb}_2^{4-}]$ dumbbells ($d_{\text{Sb-Sb}} = 297 \text{ pm}$), linear Sb chains with significantly longer Sb–Sb bonds ($d_{\text{Sb-Sb}} = 326 \text{ pm}$). The latter can be considered as weak interactions with respect to the Sb–Sb bond length in elementary antimony (282 pm). However, calculations have shown that the antimony atoms in the linear chain are Sb^{2-} with three lone pairs (isoelectronic to the middle iodine in $[\text{I}_3^-]$), and one electron available for bonds to the neighboring atoms [1]. Thus, we have only one electron per Sb–Sb bond in agreement with the relatively long distance. Such an electron-rich bonding situation is sometimes referred to as *hypervalent*, and the $^1[\text{Sb}^{2-}]$ chain as ‘non-classical’ Zintl-ion. The latter means that the number of bonded neighbors does not correspond to the 8- N rule. Thus the seemingly simple binary compound Li_2Sb contains both classical $[\text{Sb}_2^{4-}]$ pairs and non-classical $^1[\text{Sb}^{2-}]$ chains.

A more difficult structure that contains both classical and non-classical Zintl-ions occurs in RE_6TSb_{15} ($RE = La, Ce$; $T = Mn, Cu, Zn$), shown in Figure 3.97. The classical units are isolated Sb^{3-} ions and $[Sb_3^{5-}]$ trimers, the non-classical part is a 3D- Sb_{10} -network of four- and five-bonded antimony atoms. Assuming that lanthanum and manganese together donate 20 electrons, the charge of the 3D-network should be $^{9-}[Sb_{10}]$. This cannot be rationalized with the classical Zintl concept. The theoretical understanding of this bonding situation is still incomplete up to now [2], however one may keep in mind the metallic properties (La_6ZnSb_{15} is a superconductor with $T_c = 3.5$ K [3]) where the assignment of charges to individual atoms may not be straightforward, and the local view of bonding is no longer appropriate.

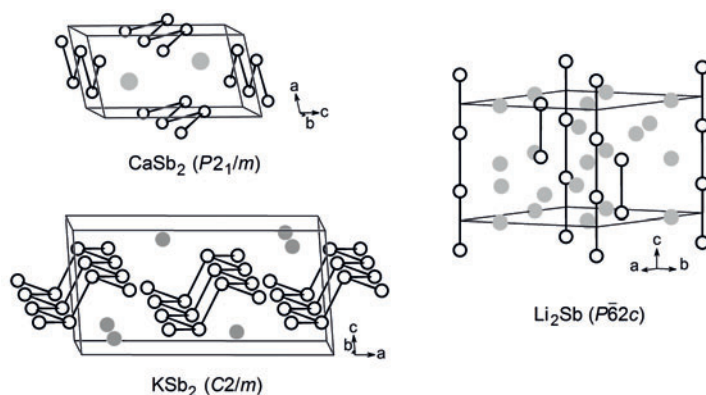


Fig. 3.96 Binary polyantimonides: The crystal structures of $CaSb_2$, KSb_2 and Li_2Sb . The antimony substructures are emphasized. For details see text.

Another example is the structure of $ZrSb_2$ [4] shown in Figure 3.97 (TiAs₂ type, formed by TPn_2 with $T = Ti, Zr, Hf$; $Pn = As, Sb, Bi$). Antimony forms dumbbells and ribbons, and one counts equal amounts of one- (Sb^{2-}), two- (Sb^{1-}), three- (Sb^0), and hypervalent four-bonded (Sb^{x-}) atoms. Thus one may write the compound formally as $(Zr^{4+})_2Sb^0Sb^{1-}Sb^{2-}Sb^{x-}$ and realizes that the electron transfer from zirconium to the anion substructure cannot be complete, otherwise we had to assign a charge of -5 to Sb^{x-} , which is impossible.

Antimonides with AT_2X_2 -type structures are less frequent than arsenides or phosphides, and confined to electron-rich transition metals. Very few compounds exist with the $ThCr_2Si_2$ -type structure, among them $BaPd_2Sb_2$ [5] and $RENi_2Sb_2$ with $RE = La, Nd, Eu, Gd$ [6]. The Sb–Sb bond lengths in the $[Sb_2^{4-}]$ dimers range up to 270 pm in $BaPd_2Sb_2$, remarkably short when compared to the Sb–Sb bond length in elementary antimony (282 pm). The $BaZn_2P_2$ -type structure without homonuclear bonds between the layers does not occur in antimonides, while the $CaBe_2Ge_2$ type has been found for

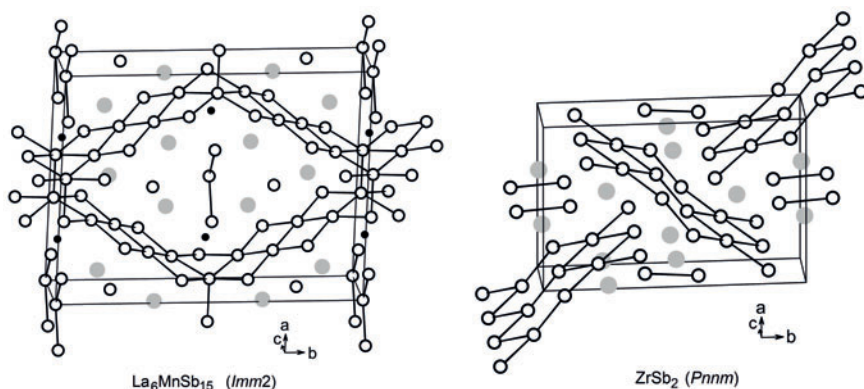


Fig. 3.97 The crystal structures of $\text{La}_6\text{MnSb}_{15}$ and ZrSb_2 . The antimony substructures are emphasized.

AT_2Sb_2 with $A = \text{Sr}, \text{Ba}, \text{La-Er}$, and $T = \text{Li}, \text{Ni}, \text{Pd}, \text{Cu}, \text{Ag}$ [7]. SrPd_2Sb_2 is dimorphic. The room temperature phase has the CaBe_2Ge_2 -type structure, and a high-temperature phase with ThCr_2Si_2 -type can be obtained by quenching the sample at 720 °C.

Beyond such polyanTIMONIDES, many binary and ternary metal-rich compounds with isolated Sb^{3-} ions are known. Their structures often correspond to the types already mentioned for phosphides and arsenides. The equiatomic binaries RESb crystallize with the NaCl type while transition metal compounds TSb ($T = \text{Ti-Ni}, \text{Nb}, \text{Pd}, \text{Ir}, \text{Pt}$) prefer the NiAs-type structure; octahedral vs. trigonal prismatic coordination.

Cu_2Sb has often been referred to as the binary parent of the PbFCl-type structure. A recent analysis of more than 100 representatives of compounds with the Cu_2Sb - and PbFCl-type structures revealed that these structures are more different than initially thought [8]. The PbFCl type is clearly preferred by compounds where ionic bonding is predominant, while the Cu_2Sb type is formed by metallic compounds. The latter can further be subdivided into the ‘true’ Cu_2Sb type which actually occurs rather rarely (Cu_2As , Mn_2Sb , ZrMnSb), and the more frequent Fe_2As type which is also formed by Sc_2Sb . The difference is that in Sc_2Sb the shortest T - T bonds are in the square net of T atoms, while in the Cu_2Sb type the shortest distances are between the copper atoms of the net and the second copper position below and above as emphasized in Figure 3.98. Consequently, these structures are rather isopointal than isotypic [9, 10].

Among the ternary equiatomic series ATSb a large number of compounds is known with the MgAgAs- ($A = \text{Mg}, \text{Sm-Lu}, \text{Th}, \text{U}, \text{Sc}, \text{Y}, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}$; $T = \text{Mn-Zn}, \text{Ru-Cd}, \text{Pt}, \text{Au}$), TiNiSi- ($A = \text{Li}, \text{Ca}, \text{Sr}, \text{Sc}, \text{La-Lu}$; $T = \text{Fe}, \text{Co}, \text{Ni}, \text{Rh}, \text{Pd}, \text{Ag}, \text{U}, \text{Pt}$), PbFCl- ($A = \text{K}$; $T = \text{Mn}$), or ZrBeSi-type structures ($A = \text{Li}, \text{Ca}, \text{Sr}, \text{Ba}$; $T = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Ag}, \text{Au}$). The ZrNiAl-type structure has rarely been found with

antimony, *e. g.* URuSb. Generally, the SbT_9 coordination is not as dominant in antimonides when compared with metal-rich phosphides and arsenides. Thus, the few antimonides with the typical prism motifs are mainly confined to compounds RE_6TSb_2 with the hexagonal *anti*- K_2UF_6 -type structure ($\text{RE} = \text{Sc, Y, Zr, Hf, Tb-Lu}$; $T = \text{Mn, Fe, Co, Ni}$) shown in Figure 3.99. The capped SbZr_6 prisms (thus actually SbZr_9) form a comparatively simple structure arranged around the iron atoms, which are also coordinated by nine zirconium atoms, thus forming FeZr_9 units (tricapped trigonal prisms). Therein, the Zr-Zr distances (330 pm, thick lines in Figure 3.99) are in the range of the bonds in zirconium metal (318 and 323 pm) and much shorter than in the SbZr_9 prisms (419 pm).

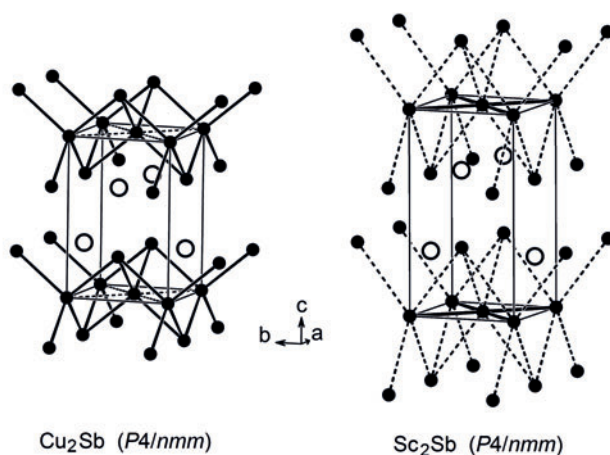


Fig. 3.98 The crystal structures of Cu_2Sb and Sc_2Sb . Black lines represent the shortest $T-T$ distances, while dotted lines are the longer ones. Metal and antimony atoms are drawn as black filled and open circles, respectively.

A considerable number of binary antimonides $T_5\text{Sb}_3$ crystallize in the hexagonal Mn_5Si_3 -type structure ($T = \text{Ca, Sr, Ba, Sc, Y, La-Lu, Ti, Zr, Hf}$), and also ternary filled variants $\text{Zr}_5\text{Sb}_3\text{Z}$ exist [11]. The crystal structure of $\text{Zr}_5\text{Sb}_3\text{Zn}$ is shown in Figure 3.100 and can be described as chains of face-sharing octahedra running along the c axis, where the ZrSb_6 octahedra (light gray in Figure 3.100) additionally share common edges and form a network that surrounds the chains of ZnZr_6 octahedra (dark gray). The latter are empty in the binary host structure Zr_5Sb_3 . The compound $\text{La}_3\text{Sb}_5\text{Zr}$ is an interesting variant of this structure [12], where the La_3Sb_5 host forms the *anti*- Mn_5Sb_3 -type structure and Zr fills the octahedral voids, as depicted in Figure 3.100.

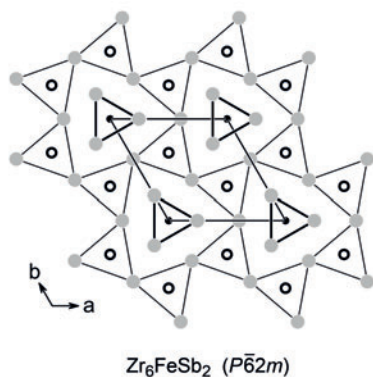


Fig. 3.99 The crystal structure of Zr_6FeSb_2 . Zirconium, iron and antimony atoms are drawn as medium gray, black filled and open circles, respectively. Atoms connected by thin and thick lines are shifted by half the c axis. The trigonal prismatic iron and antimony coordination is emphasized.

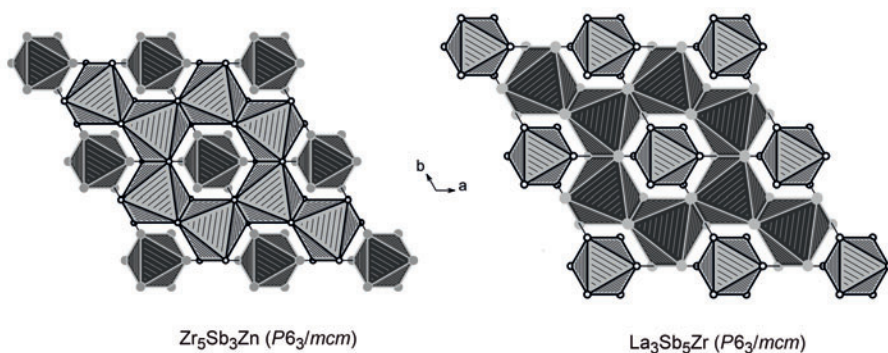


Fig. 3.100 The crystal structures of $\text{Zr}_5\text{Sb}_3\text{Zn}$ and $\text{La}_3\text{Sb}_5\text{Zr}$ with filled Mn_5Si_3 -type structure. Light gray polyhedra are ZrSb_6 , dark gray polyhedra are ZnZr_6 and SbLa_6 , respectively.



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3.10.5 Bismuthides

The majority of bismuthides can be considered as true intermetallic compounds when compared with phosphides, arsenides, or even antimonides. While we have seen a variety of valence compounds understandable through the Zintl concept with the lighter pnictides, such compounds are rare with bismuth. Even combinations of bismuth with electropositive alkali-, alkaline earth and rare earth elements generally result in metallic compounds, often with networks connected through Bi–Bi bonds that cannot be rationalized by simple valence rules. It is therefore not surprising that our understanding of the often unique structures of the bismuthides is still limited [1].

Examples of binary polybismuthides with homonuclear bonds are K_3Bi_2 , K_5Bi_4 and Ba_2Bi_3 . K_3Bi_2 (Figure 3.101) contains dimers which are formally $[Bi_2^{3-}]$ ($d_{Bi-Bi} = 272$ pm) in contrast to the common $[Pn_2^{4-}]$ pnictide dumbbells. DFT calculations revealed that $[Bi_2^{3-}]$ is actually correct, but significant contributions of the potassium orbitals are present and contribute to the overall bonding pattern of this truly intermetallic phase [2]. The situation is similar in K_5Bi_4 with isolated Bi_4 zigzag tetramers [3]. The latter have been interpreted as $[Bi_4^{4-}]$ with an extra electron' based on molecular orbital considerations with delocalized π -bonding within the tetramers. However, actually one cannot expect significant π -contributions for an element of the 6th period of the PSE, thus one may speculate that also the potassium orbitals participate in bonding similar to K_3Bi_2 . The bonding situation is again not completely clear in Ba_2Bi_3 [4] which contains planar sheets of six- and four-membered rings with three- and four-bonded bismuth atoms (Figure 3.101). Calculations have shown that the barium atoms are far from being Ba^{2+} and that the bismuth atoms within the sheets can be considered as $[Bi_3^{3-}]$ by using the hypervalency concept mentioned earlier [5].

These examples may create the impression that bismuth does not form at all classical Zintl-anions, which is not true. The structure of $Ba_{11}Bi_{10}$ is one of the relatively rare representatives where the structure can be understood through the Zintl formalism according to $Bi_{11}^{2+}[Bi_3^{3-}][Bi_2^{4-}][Bi_4^{4-}]$ with isolated atoms, dumbbells and four-membered rings of bismuth. Chemical bonding of $Ba_{11}Bi_{10}$ has been analysed by semi-empirical methods so far [6], however, one can assume that also in this

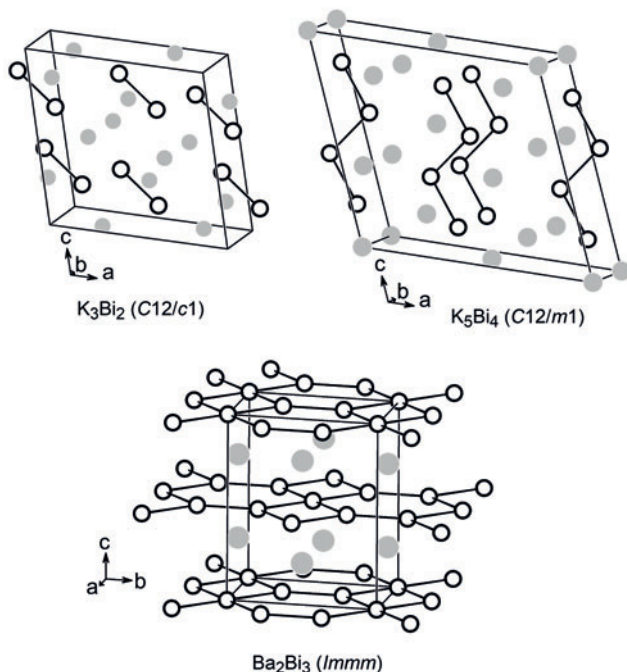


Fig. 3.101 The crystal structures of K_3Bi_2 , K_5Bi_4 , and Ba_2Bi_3 . The bismuth substructures are emphasized.

compound the electron transfer is incomplete as in Ba_2Bi_3 , thus also in this case the seemingly straightforward interpretation of classical Zintl-ions may have to be reconsidered.

Square nets of bismuth atoms occur in the ternary compounds $CeZnBi_2$ with the $HfCuSi_2$ -type structure, and in the closely related structure of $SrZnBi_2$, both shown in Figure 3.102. Square nets and layers on edge-sharing $ZnBi_{4/4}$ tetrahedra are stacked along the c axis of the tetragonal unit cell, separated by cerium- or strontium atoms, respectively. The Bi–Bi distances are similar, namely 323 pm in $CeZnBi_2$ and 328 pm in $SrZnBi_2$. Assuming the bismuth atoms bonded to zinc as Bi^{3-} , the atoms in the square nets are formally -2 in $Ce^{3+}Zn^{2+}Bi^{3-}Bi^{2-}$, but -1 in $SrZnBi^{3-}Bi^{1-}$. The notation $Ce^{3+}Zn^{2+}Bi^{3-}Bi^{1-} \cdot e^-$ forces formally Bi^{1-} in both compounds, but this is artificial because both compounds are metallic. Further $ATBi_2$ compounds with the $HfCuSi_2$ -type structure are known with $A = Y, La, Ce-Dy$ and electron-rich transition metals $T = Ni, Cu, Zn, Ag$. The $SrZnBi_2$ type is less frequent and still confined to $A = Sr, Ba$ and $T = Zn, Cd$, however, both structures are also observed with antimony and a few examples with arsenic and phosphorus exist too.

While more than 200 ternary compounds AT_2X_2 with the $ThCr_2Si_2$ type are known with phosphorus (~ 140), arsenic (~ 60) or antimony (~ 10), it was not until recently that the so far only bismuthide has been reported [7]. $BaMn_2Bi_2$ belongs to the $BaZn_2P_2$ -

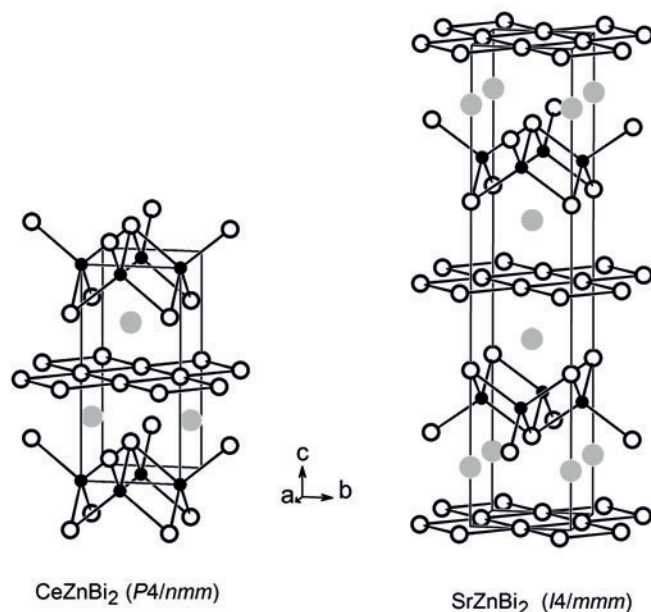


Fig. 3.102 The crystal structures of CeZnBi_2 and SrZnBi_2 . Cerium (strontium), zinc, and bismuth atoms are drawn as medium gray, black filled and open circles, respectively. The tetrahedral zinc coordination and the bismuth substructures are emphasized.

type branch of the 122-type compounds (Figure 3.103), because no bonds are present between the Bi atoms of adjacent layers ($d_{\text{Bi-Bi}} = 384$ pm). Few compounds AT_2Bi_2 are known with the CaBe_2Ge_2 -type structure, examples are $(\text{Ba}, \text{Sr})\text{Pd}_2\text{Bi}_2$, EuPd_2Bi_2 , and $\text{RENi}_{1.5}\text{Bi}_2$. The bismuthides $(\text{Ba}, \text{Sr})\text{Pd}_2\text{Bi}_2$ and BaAu_2Bi_2 also crystallize in a commensurate distorted variant of the CaBe_2Ge_2 type with monoclinic symmetry [8]. An interesting *anti*- ThCr_2Si_2 type is formed by BiN_2U_2 and BiN_2Th_2 [9] which underlines that this structure is extremely flexible.

The structures of binary bismuthides with isolated Bi^{3-} are often analogous to the lighter pnictides. We observe the NaCl-type structure for REBi (RE = trivalent rare earth element) and also some more difficult structures with rare earth elements [1], among them the cubic Th_3P_4 -type structure has been observed for A_3Bi_4 ($\text{A} = \text{Ce-Dy}, \text{Yb}; \text{Ca}, \text{Sr}, \text{Ba}$). Transition metal compounds TBi ($\text{T} = \text{Mn}, \text{Ni}, \text{Rh}, \text{Pt}$) largely crystallize in the NiAs-type structure, a special case is NiBi with a complex superstructure [10]. The phases TBi_2 ($\text{T} = \text{Rh}, \text{Pd}, \text{Ir}, \text{Pt}$) form variants of the pyrite type.

Among the equiatomic compounds ATBi the already mentioned structure types occur, see Figure 3.85. The MgAgAs type ($\text{A} = \text{Li}, \text{Mg}, \text{Sc}, \text{Y}, \text{La-Lu}; \text{T} = \text{V}, \text{Nb}, \text{Fe-Cu}, \text{Rh}, \text{Pd}, \text{Pt}, \text{Au}$), ZrNiAl type ($\text{A} = \text{Ba}, \text{Gd-Er}; \text{T} = \text{Rh}$), TiNiSi type ($\text{A} = \text{Ce-Eu}, \text{T} = \text{Rh}$), and ZrBeSi type ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}; \text{T} = \text{Cu}, \text{Ag}, \text{Au}$). As a variant of the ZrBeSi type also the hexagonal LiGaGe -type structure has been found for YbTBi ($\text{T} = \text{Cu}, \text{Ag}, \text{Au}$). Therein

the symmetry is reduced from $P6_3/mmc$ to $P6_3mc$ (*translationengleiche* transition of index 2), and the T_3Bi_3 hexagons are no longer flat but puckered as depicted in Figure 3.103. This structure also occurs for some antimonides.

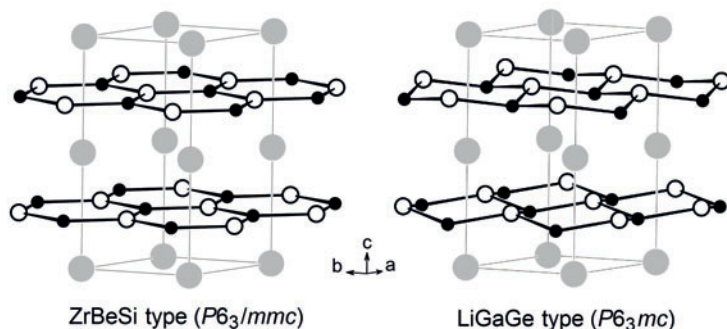


Fig. 3.103 Comparison of the ZrBeSi- and LiGaGe-type structures, both formed by equiatomic ABi -compounds. Zirconium (lithium), beryllium (gallium) and silicon (germanium) atoms are drawn as medium gray, black filled and open circles, respectively. The honeycomb networks are emphasized.

Beyond the compounds described above, a number of metal-rich bismuthides with often complex crystal structures are known, examples are $Ca_3Pd_4Bi_4$, $Nd_6Fe_{13}Bi$, and the compounds RE_6FeBi_2 with the *anti*- K_2UF_6 -type structure (see Figure 3.99). Since all bismuthides are intermetallic compounds, the differentiation to metal-rich compounds is less pronounced. We have defined metal-rich compounds as materials where metal-metal bonding plays the dominant role. However, this is the case in almost all bismuthides because Bi–Bi and T –Bi bonds are on a level with T – T bonds.



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3.11 Chalcogenides

3.11.1 Suboxides

The classical suboxide is W_3O with the so-called β -tungsten structure. Originally this phase was reported to be a new modification of tungsten but two experimental results contradicted this finding: The experimental density of the phase was too low and the phase decomposed into W and WO_2 at 970 K. Subsequent X-ray diffraction studies by Hägg and Schönberg [1] revealed a random distribution of 75 % W and 25 % O on the 2a and 6c Wyckoff sites of space group $Pm\bar{3}n$. Later, an ordered metal-oxygen arrangement was observed for Cr_3O [2]. This structure type (A15, Cr_3Si type) has been discussed in Chapter 3.9.4 for superconducting Nb_3Sn .

The oxygen content of such suboxides mostly derived from small oxygen contaminations, and these phases were first observed as by-products. Some structure types are predestined for oxygen uptake. The Mn_5Si_3 type is such a representative which has octahedral voids where one can host diverse small elements, *i. e.* B, C, N, or O. In Chapter 3.9.2 we presented the silicide carbide Mo_5Si_3C as such a filled-up version. Several transition metal- and rare earth-based suboxides with this structure type are known [3]. Other phases like Zr_4Sn [4] show oxygen-driven decomposition reactions at high temperature. Broader studies have also been performed on oxygen-filled cubic Ti_2Ni phases [5]. These host structures have octahedral voids formed by the electron-poor transition metal (16c site) that are filled by oxygen, a bonding pattern similar to the ternary transition metal carbides. As an example we present the Zr_4Pd_2O structure in Fig. 3.104. The Zr_6O octahedra are condensed *via* common corners, leading to chains that extend parallel to [110]. Detailed phase analytical work on these materials showed solid solutions on the transition metal sites as well as homogeneity ranges $T_4T'_2O_{1-x}$ for the oxygen position. According to single crystal X-ray data, oxygen can also occupy the 8a site (in Nb_6Ni_6O) or partially 8a and 16c sites simultaneously (in $Zr_6Ni_4Ti_2O_{0.6}$). A further interesting result is the significant hydrogen storage capacity of $Zr_4Pd_2OD_{4.5}$.

Oxygen contaminations also played a significant role in pnictide chemistry. The phosphide oxides AE_4P_2O ($AE = Ca, Sr, Ba$) [6], $Na_3M_7(P_3)O$ ($M = Sr, Eu$) [7], and $Th_4Fe_{17}P_{10}O_{0.64}$ [8] were initially obtained only in small yield. The oxygen source was most likely oxygen contaminated metal. In all structures, the oxygen atoms fill octahedral voids AE_6 , M_6 , or Th_4Fe_2 . The large family of quaternary pnictide oxides with $ZrCuSiAs$ -type structure also belongs to these *accidental* oxides. Initially the ternary phases $REFeP$ were reported which were indeed $REFePO$ [9]. These phases are discussed along with the other pnictides in Chapter 3.10.3.

The most remarkable group of suboxides concerns those of the alkali metals. These phases have meticulously been studied by the *Simon* group [10]. The alkali metal suboxides form when the appropriate amount of oxygen is carefully added to the respective melt of the heavy alkali metal. The lighter alkali metals yield the M_2O oxides under similar conditions. Upon the reaction with oxygen rubidium changes its color from silvery to

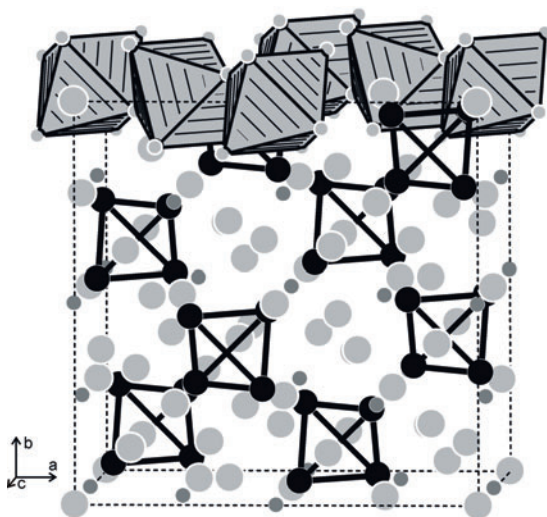


Fig. 3.104 The crystal structure of $\text{Zr}_4\text{Pd}_2\text{O}$ ($Fd\bar{3}m$). Zirconium, palladium, and oxygen atoms are drawn as light gray, black, and small medium gray circles, respectively. The Pd_4 tetrahedra and Zr_6O octahedra are emphasized.

brassy and then to coppery. The structures of the resulting stoichiometric compounds Rb_6O and Rb_9O_2 are presented in Fig. 3.105. The striking structural motifs are face-sharing double octahedra of rubidium atoms which are filled by oxygen atoms. The whole structure of Rb_9O_2 can easily be explained by a stacking of these units (left-hand side of Fig. 3.105). Rb_6O has a higher rubidium content but contains the same cluster units. In contrast to Rb_9O_2 , layers of these condensed octahedra are separated by a layer of rubidium atoms that have no oxygen neighbors. Alternatively one can formulate $\text{Rb}_9\text{O}_2 \cdot \text{Rb}_3$, emphasizing the close relationship with Rb_9O_2 . The Rb–O distances in the slightly distorted Rb_6O octahedra of Rb_6O (270–280 pm) and Rb_9O_2 (264–285 pm) are in the same range.

Cesium loses its golden color upon reaction with oxygen. With increasing oxygen content the phases become bronze, violet and finally almost black. Cs_{11}O_3 is the suboxide with the highest oxygen content. Three oxygen-centered Cs_6O octahedra are condensed *via* common triangular faces, leading to the Cs_{11}O_3 cluster unit (Fig. 3.106). Each cluster is surrounded by six other cluster units, however, with different orientation. In other words, the cluster units derive from a two-dimensional close packing. Similar to the rubidium suboxides discussed above, these cluster units can also be separated by further cesium atoms. In $3\text{Cs}_7\text{O} \equiv \text{Cs}_{11}\text{O}_3 \cdot \text{Cs}_{10}$, the gross motif of a two-dimensional close packing is retained for the Cs_{11}O_3 clusters, but they are well separated by the additional cesium matrix. The Cs–O distances in Cs_7O (275–292 pm) and Cs_{11}O_3 (268–299 pm) cover similar ranges. $3\text{Cs}_4\text{O} \equiv \text{Cs}_{11}\text{O}_3 \cdot \text{Cs}_3$ has the same structural principle. The metallic matrix around the Cs_{11}O_3 clusters can also be built by rubidium atoms, leading to the three suboxides $\text{Cs}_{11}\text{O}_3\text{Rb}$, $\text{Cs}_{11}\text{O}_3\text{Rb}_2$, and $\text{Cs}_{11}\text{O}_3\text{Rb}_7$.

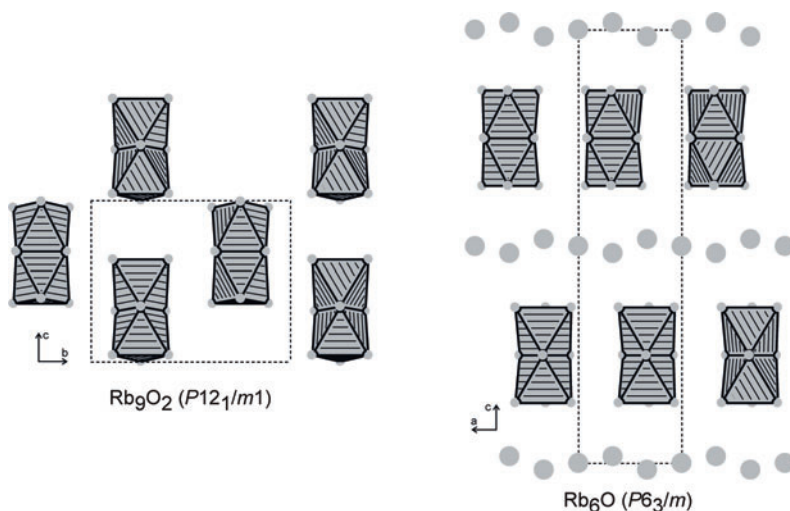


Fig. 3.105 The crystal structures of Rb_9O_2 and Rb_6O . The oxygen centered face-sharing double octahedra are emphasized.

A completely new structural motif has been observed in the ternary suboxide NaBa_2O [11] which was obtained from Ba and BaO_2 in a K-Na alloy as reaction medium. The oxygen atoms in NaBa_2O are located in *trans*-edge-sharing barium tetrahedra. The resulting $[\text{Ba}_2\text{O}]$ cluster chains are embedded in the sodium matrix. The lower coordination number 4 leads to shorter Ba–O distances (253 pm) as compared to BaO (276 pm). A formal electron-precise formulation $\text{Na}^+(\text{Ba}^{2+})_2\text{O}^{2-} \cdot 3e^-$ readily underlines the metallic properties. The negative charge of the oxide anions is cumulated within the cluster units. The conduction electrons fill the space in between. Therefore these materials have been considered as void metals [10]. Consequently, the partial oxidation of rubidium and cesium leads to a reduction of the work function.

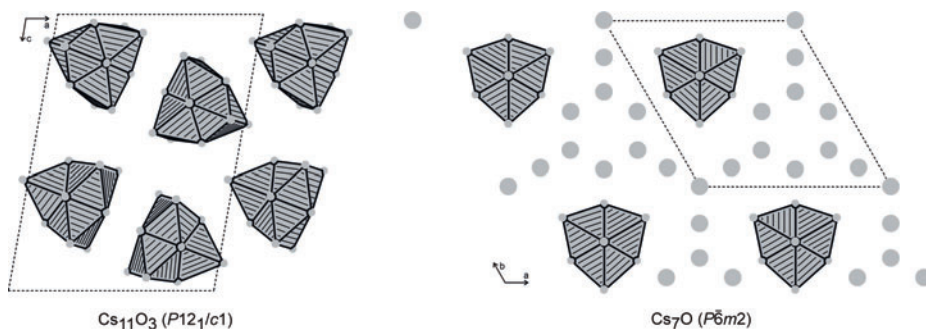


Fig. 3.106 The crystal structures of Cs_{11}O_3 and Cs_7O . The clusters of three oxygen centered face-sharing octahedra are emphasized.

Concluding this subchapter we focus on the suboxides $\text{Ru}_3\text{Sn}_{15}\text{O}_{14}$ [12] and $\text{Ti}_{12}\text{Sn}_3\text{O}_{10}$ [13]. These two structures (Fig. 3.107) comprise intermetallic and oxydic substructures as well. The ruthenium atoms in $\text{Ru}_3\text{Sn}_{15}\text{O}_{14}$ have slightly distorted octahedral tin coordination with Ru–Sn distances ranging from 251 to 262 pm, similar to the condensed RuSn_6 octahedra in CeRu_4Sn_6 (257–277 pm) [14]. The RuSn_6 octahedra are condensed *via* common corners, leading to the blocks emphasized in Fig. 3.107. One of the tin sites is not coordinated to ruthenium. Between the octahedra one observes Sn–Sn distances in the range 333–380 pm, significantly longer than in $\beta\text{-Sn}$ (4×302 and 2×318 pm), indicating only weak interactions. The blocks of condensed octahedra are separated from each other *via* the oxygen atoms (202–234 pm Sn–O), whereby each tin atom has between two and four oxygen neighbors. Strong Ru–Sn and Sn–O but weaker Sn–Sn bonding is in line with extended Hückel electronic structure calculations. $\text{Os}_3\text{Sn}_{15}\text{O}_{14}$ [15] is isotypic with the ruthenium compound. Similar structural features with FeSn_6 and RuSn_6 octahedra in oxydic matrices have been observed in the multinary compounds $\text{Fe}_4\text{Si}_2\text{Sn}_7\text{O}_{16}$ [16] and $\text{RuSn}_6[(\text{Al}_{1/3-x}\text{Si}_{3x/4})\text{O}_4]_2$ [17].

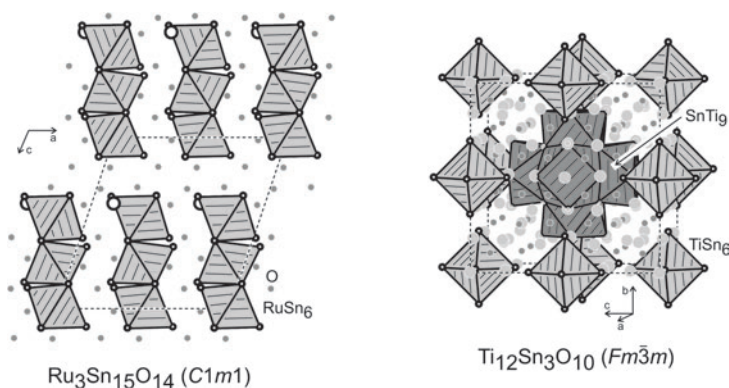


Fig. 3.107 The crystal structures of $\text{Ru}_3\text{Sn}_{15}\text{O}_{14}$ and $\text{Ti}_{12}\text{Sn}_3\text{O}_{10}$. Ruthenium, titanium, tin, and oxygen atoms are drawn as black filled, light gray, black open, and small medium gray circles, respectively. The intermetallic substructures composed of RuSn_6 and TiSn_6 octahedra and SnTi_9 mono-capped square anti-prisms are emphasized. One tin site in $\text{Ru}_3\text{Sn}_{15}\text{O}_{14}$ has no ruthenium neighbors.

The $\text{Ti}_{12}\text{Sn}_3\text{O}_{10}$ structure is cubic. Part of the titanium atoms has octahedral tin coordination with Ti–Sn distances of 261 pm. These TiSn_6 octahedra are packed in an *fcc* fashion. The second intermetallic motif in the $\text{Ti}_{12}\text{Sn}_3\text{O}_{10}$ structure is the SnTi_9 coordination in the form of a mono-capped square anti-prism (261–318 pm Sn–Ti). Always six of such units are condensed (the medium gray cluster in Fig. 3.107) and the capping titanium atoms belong to all six anti-prisms. Again, this motif shows *fcc* packing and the remaining space between the two intermetallic substructures is filled with the oxide matrix which consists of Ti_4O tetrahedra and Ti_5O trigonal bipyramids.

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3.11.2 Metal-rich Sulphides

Metal-rich sulphides occur predominantly with electron poor transition metals of the 4d- and 5d-rows, and have been comprehensively investigated for decades [1–7]. 3d-metals have a less pronounced tendency to form metal-metal bonds, but nevertheless some metal-rich 3d-compounds are known. Examples are the structures of Ti_2S and V_3S shown in Fig. 3.108. Fragments of the elemental metal structures are often conserved in such structures. Thus orthorhombic Ti_2S contains chains of bcc-like blocks as well as titanium octahedra, both running along the *c* axis (left part in Fig. 3.108). The sulphur atoms surround and separate these intermetallic fragments. This principle is also discernible in the tetragonal structure of V_3S where vanadium forms strands of *stella quadrangular* units together with heterocubane-like distorted

V_4S_4 cubes along the c axis. The sulphur atoms bridge the intermetallic parts. Nickel forms the metal-rich sulphide Ni_3S_2 with a hexagonal structure.

Copper sulphides are often complicated, also because copper is relatively mobile in chalcogenides, which can cause considerable ionic conductivity. Several minerals of the composition $Cu_{2-x}S$ are known, among them monoclinic chalcocite Cu_2S , rhombohedral digenite $Cu_{1.8}S$ (Cu_9S_5), orthorhombic anilite $Cu_{1.75}S$ (Cu_7S_4), and rhombohedral geerite $Cu_{1.6}S$ (Cu_8S_5). High-temperature phases of compounds close to the composition Cu_2S were often described with structures derived from the *anti*- CaF_2 -type structure, where the copper atoms are statistically elongated from the centers of the tetrahedral voids. In ordered structures, combinations of fourfold tetrahedral and threefold trigonal planar copper coordinations are observed. Fig. 3.108 shows the structure of Cu_7S_4 with strands of edge- and corner-sharing CuS_4 tetrahedra, which are interlinked through copper atoms with trigonal planar sulphur coordination. The rhombohedral structure of Cu_9S_5 is even more complicated (right part in Fig. 3.108) and can be described as stacked blocks of CuS_4 tetrahedra alternating with honeycomb-like double layers of trigonal coordinated copper. The latter are filled with an additional copper atom between the Cu_3S_3 rings, which is coordinated by six sulphur and six copper atoms. Even though relatively short Cu–Cu distances down to 253 pm occur, bonding in these copper sulphides is dominated by Cu–S bonds. In contrast to the sulphides of electron-poor metals, the structures may rather be rationalized as copper in holes of a more or less complicated packing of sulphur atoms.

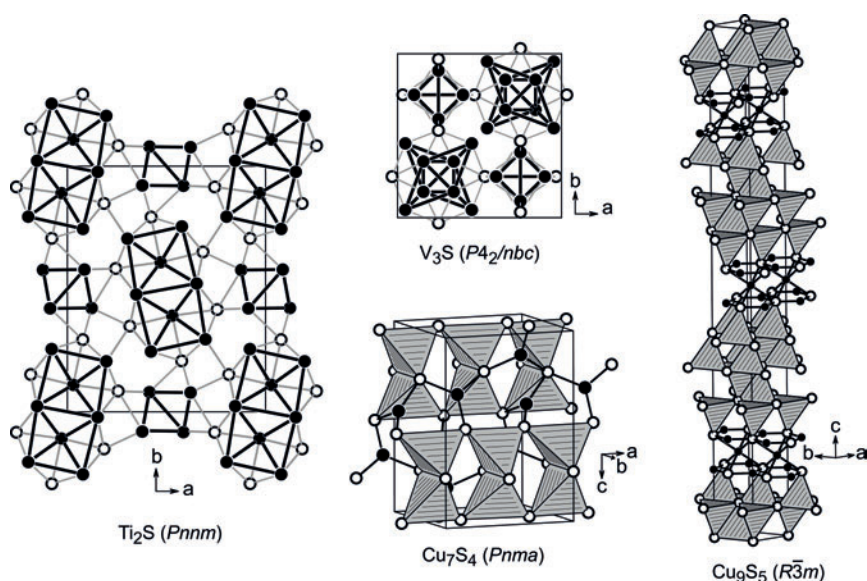


Fig. 3.108 The crystal structures of Ti_2S , V_3S , Cu_7S_4 , and Cu_9S_5 . Titanium, vanadium, and copper are drawn as black filled circles, sulphur as open circles.

The structure of Nb_{21}S_8 is an example for a metal-rich binary compound with $4d$ - and $5d$ -elements. Interestingly, this structure with metal cluster chains running along the c axis (Fig. 3.109) is also formed with molybdenum, tungsten and zirconium, which indicates a high flexibility regarding different electron counts. Nb_{21}S_8 is a superconductor with a critical temperature near 4 K [8].

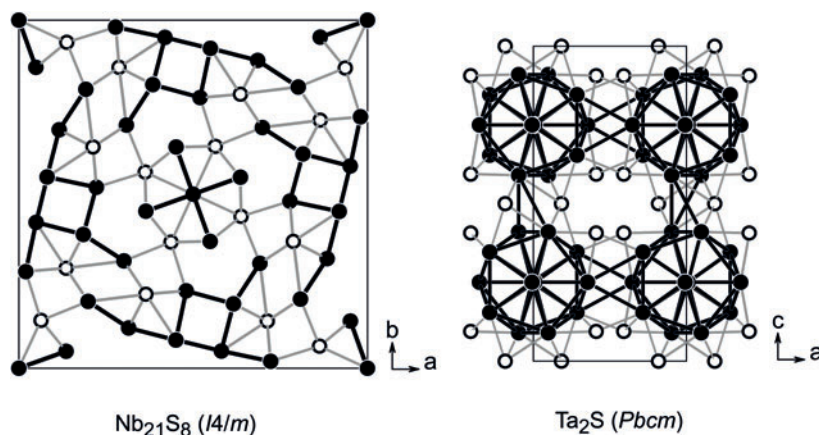


Fig. 3.109 Crystal structures of the metal-rich ternary sulphides Nb_{21}S_8 and Ta_2S . Niobium and tantalum are drawn as black filled circles, sulphur as open circles.

Ta_2S has a complex structure in spite of the simple stoichiometry. Tantalum forms rods of icosahedral units along the b axis of the orthorhombic unit cell. The rods are embedded in sulphur atoms, but also connected through Ta-Ta bonds as shown in Fig. 3.109. In these metal-rich compounds clearly metal-metal bonding dominates and forms a plethora of structures. Further examples with related structures are Ta_6S and Ta_3S_2 [9]. Chemical bonding in this class of compounds has frequently been analyzed, and already early works pointed out the artificiality of separate metallic and covalent bonds [5].

The situation with Ag_2S is similar to Cu_2S , even though Ag_2S is an even better ionic conductor. The structure is monoclinic at room temperature and transforms first to a body-centered pseudo-cubic structure at 177 °C ($\beta\text{-Ag}_2\text{S}$) and to a face-centered cubic one at 593 °C. The mobility of the silver atoms has been studied by single crystal neutron diffraction experiments [10].

With increasing non-metal (sulphur) amount, the at least one-dimensional infinite metal substructures of metal-rich compounds will be broken-up, and zero-dimensional fragments referred to as metal clusters are often formed. Predominantly the refractory metals (Nb, Mo, Ta, W, Re) with strong metal-metal bonds form a large family of compounds with mostly octahedral, but also tetrahedral cluster units. An example with tetrahedral clusters is the cubic compound GaMo_4S_8 , which contains heterocubane-like Mo_4S_4 units and GaS_4 tetrahedra arranged in a NaCl-like manner

(Fig. 3.110). GaMo_4S_8 is a rare example of a $4d$ -ferromagnet, while the isotopic niobium and tantalum chalcogenides have intensively been investigated with respect to superconductivity [11] and field-induced resistive switching [12].

Among sulphides with octahedral clusters, the so-called Chevrel phase PbMo_6S_8 is the best known, because this compound was the first ternary superconductor with a critical temperature of 13 K [13], and at that time (1971), it set a record to the upper critical field ($H_{c2}(0) \approx 60$ T).

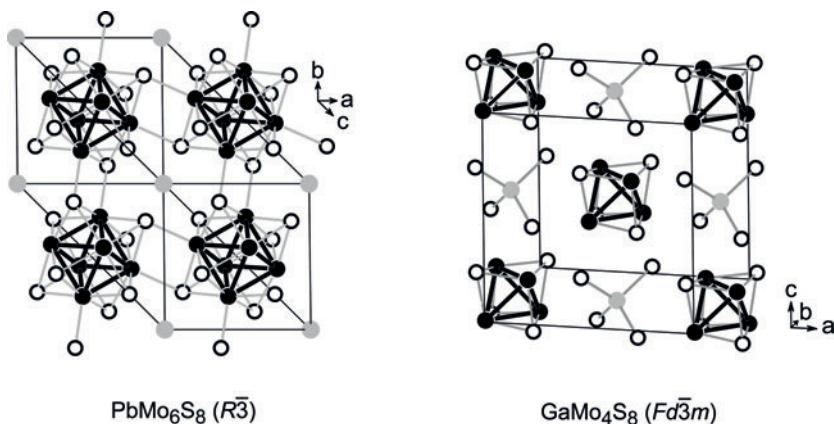


Fig. 3.110 Crystal structures of the molybdenum-cluster compound PbMo_6S_8 (Chevrel-phase) with octahedral clusters, and GaMo_4S_8 with tetrahedral clusters. Molybdenum atoms are drawn as filled black circles, sulphur as white circles and lead or gallium as gray circles.

The rhombohedral crystal structure of PbMo_6S_8 is shown in Fig. 3.110. The Mo_6 octahedra are coordinated by eight sulphur atoms located over each face, and additionally by six sulphur atoms located at every corner. The latter are ligands of the neighboring cluster at the same time, thus forming a three-dimensional net of Mo_6S_8 units with the lead atoms in between. The Mo–Mo bond lengths are 273 pm in the Mo_6 octahedra, and 327 pm between neighboring clusters. Counting electrons leads to $\text{Pb}^{2+}(\text{Mo}^{2.33+})_6(\text{S}^{2-})_8$ which means that each molybdenum atom has 3.67 metal centered electrons, or 22 electrons per Mo_6 cluster. An analysis of the cluster molecular orbitals gives 12 Mo–Mo bonding states, thus 24 electrons per Mo_6 would be the ideal occupation. This is often interpreted as twelve 2-electron-2-center bonds along all edges of the octahedron, however, one should keep in mind that the twelve bonds are not localized between two molybdenum atoms, but delocalized over all cluster atoms [3]. The electron deficiency in PbMo_6S_8 causes metallic properties, and is therefore a crucial prerequisite to superconductivity. The outstanding properties of the Chevrel compounds have been reviewed [14–18].

Beyond the Chevrel phases, a large family of compounds with isolated octahedral metal cluster units is known. The basic units are either M_6X_8 as described above or

M_6X_{12} , where the ligands X are located over the twelve edges of the octahedron. Molecular orbital considerations reveal that 16 valence electrons are needed to fill eight $M-M$ bonding levels of M_6X_{12} , in contrast to 24 electrons in M_6X_8 as mentioned above. Because M_6X_{12} clusters are only formed with halides as ligands X , these compounds are rather salt-like and not in the focus of this book. On the other hand, a large number of M_6X_8 -type chalcogenide-halides are known where the cluster units are connected to one-, two-, or three-dimensional networks. Cluster linkages can occur *via* common ligand atoms in various ways, which is described by the so-called Schäfer-notation. According to this, the ligands are divided in inner ones (i) which are located at the triangular faces and outer ones (a) which are located over the corners of the octahedron. Thus connections through sharing of an X atom of the M_6X_8 cluster core are labelled i-i, while bridging *via* common outer X atoms (over the corners) is a-a, and mixed ones are a-i or i-a, respectively. For example, the structure of $PbMo_6S_8$ (Fig. 3.110) may be written as $PbMo_6S_{6/2}^{i-a}S_{2/2}^{a-i}$: Six of the eight inner sulphur atoms are outer ligands of the neighboring cluster (i-a). The two remaining sulphur atoms are not bridging (i), while all six sulphur atoms at the corners serve as inner ligands for neighboring clusters (a-i). The principle is further illustrated in Fig. 3.111 by means of the sulphide-bromide $Mo_6Br_6S_3$. The cluster core consists of four sulphur and four bromine atoms, while two sulphur and four bromine atoms are the outer ligands. The connectivity is given by $Mo_6Br_4^{i-a}Br_{4/2}^{a-a}S_{2/2}^{i-i}S_{2/2}^{a-i}S_{2/2}^{i-a}$ (Fig. 3.111). Many other cluster connectivities are collected in the recommended review by Simon [3].

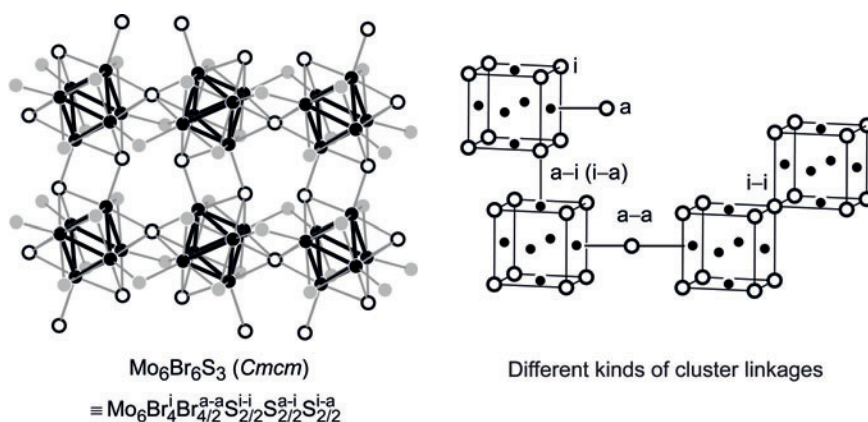


Fig. 3.111 The crystal structure of $Mo_6Br_6S_3$ as an example for connected Mo_6X_8 ($X = S, Br$) cluster units. Molybdenum atoms are drawn as filled black circles, sulphur as white circles and bromine as gray circles. Different kinds of cluster linkages are described by the Schäfer (i, a) notation.

The next step upon further increasing ligand concentration is cluster condensation. Among sulphides, oligomers with two or three face-sharing Mo_6 octahedra have

been discovered, which are interlinked through isolated Mo_6 units in the structures of $\text{Mo}_{15}\text{S}_{19}$ and Mo_9S_{11} presented in Fig. 3.112. However, this is only the tip of the iceberg. A large number of molybdenum selenides continues this condensation principle with even larger one-dimensional oligomers, which ends up in the compound Mo_3Se_3 with infinite one-dimensional chains. We will draw back to this topic in the next chapter.

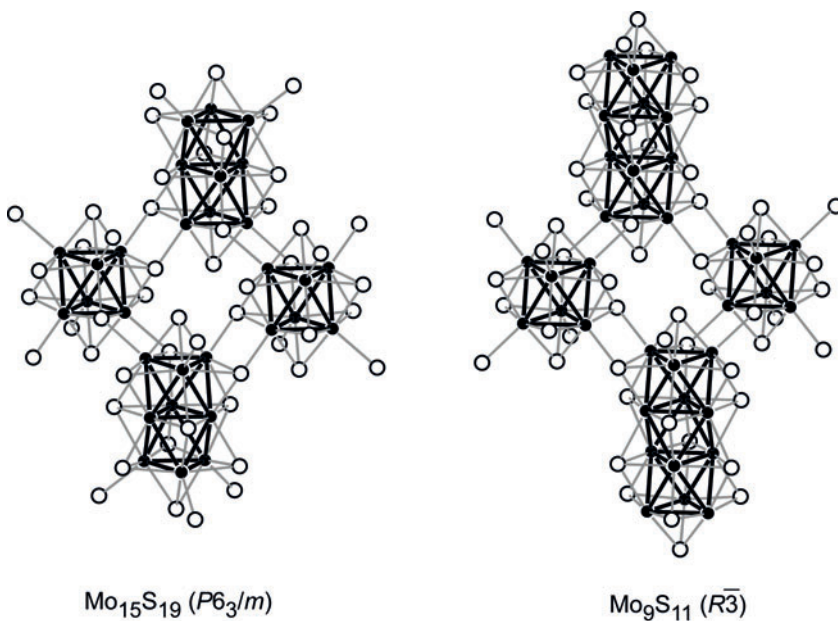


Fig. 3.112 Binary molybdenum sulphides. The crystal structures of $\text{Mo}_{15}\text{S}_{19}$ and Mo_9S_{11} with oligomers of condensed Mo_6 cluster units, interlinked by isolated Mo_6S_8 units. Molybdenum atoms are drawn as filled black circles, sulphur as white circles and bromium as gray circles.

Another large family are the transition metal dichalcogenides MX_2 . Molybdenum disulphide MoS_2 with particle sizes of 1–100 μm is an important dry lubricant which is often used for reciprocating motions, for instance in gears or chains, where liquid lubricants will be squeezed out. MoS_2 is also employed as a co-catalyst for desulfurization in petrochemistry. We count the MX_2 disulphides among metal-rich compounds, because metal-centered electrons are present which form (weak) metal-metal bonds [4]. The structures are built up by slabs of edge-sharing $\text{MX}_{6/3}$ trigonal prisms or antiprisms which are stacked in various ways. The resulting polytypes are classified with the Ramsdell nY notation [19] where n is the number of $X\text{-M-X}$ slabs in the unit cell and Y is the lattice type which can be trigonal (T), hexagonal (H) or rhombohedral (R). Different kinds of slab stacking with the same nY -type are marked by additional subscripts like nY_a , nY_b , and so on. Note that prismatic and octahedral coordination is not

differentiated because the notation bases on $X-M-X$ slabs regardless if X forms a prism or an octahedron. Altogether eleven polytypes of MX_2 chalcogenides are known. Four examples are shown in Fig. 3.113.

MoS_2 (molybdenite) is dimorphic and occurs as $2H_c$ - or $3R$ -polytype with prismatic coordination, shown in Fig. 3.113. TaS_2 forms the most polytypes. Beyond the $1T$ - and $4H_b$ -structures with octahedral or mixed prismatic/octahedral layers shown in Fig. 3.113, TaS_2 also forms the polytypes $2H_a$, $2H_c$, $3R$, $4H_a$, $4H_c$, and $6R$. A complete compilation of all eleven polytypes is given in [20].

Strong intralayer covalent $M-X$ bonding and weak interlayer van der Waals $X-X$ bonding between the layers causes the distinct two-dimensional character, and gives rise to marked anisotropy in physical properties. Most importantly, the weak interlayer bonding permits intercalation of various metal atoms, ions, organic/inorganic molecular species, and salt-like fragments between the layers. Dichalcogenide intercalation chemistry has been studied intensively for decades, and several articles and textbooks review this large field [21–24].

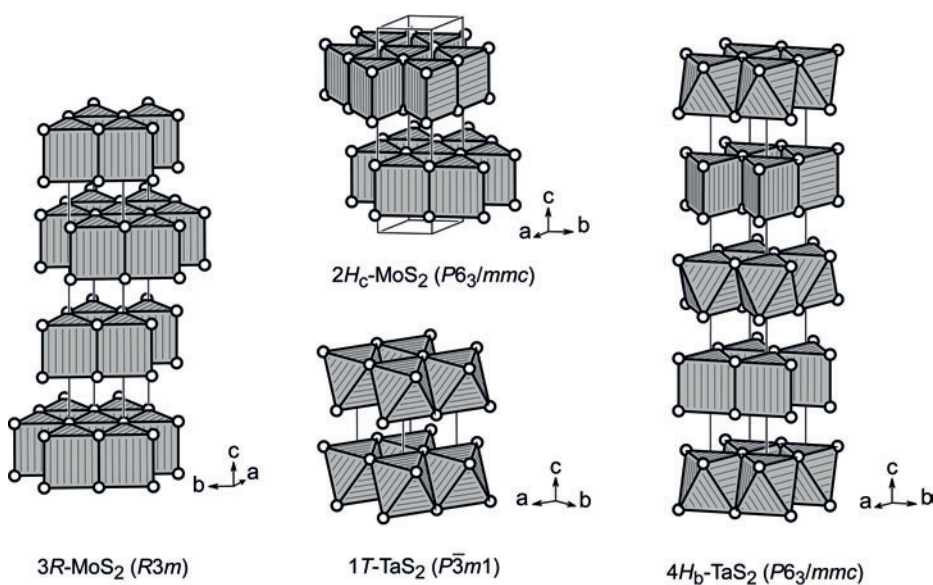


Fig. 3.113 Examples of transition metal disulphides MS_2 with layered structures.

An outstanding family of intercalation compounds are the so-called misfit layer chalcogenides which are composed by two layered subsystems, namely MX_2 layers as described above, and $M'X$ layers which are fragments of rocksalt-type chalcogenides. One in-plane axis (a) of one subsystem is parallel to the a' axis of the second subsystem, but the length ratio a/a' is incommensurable. Thus the in-plane lattices of both layered systems actually do not fit, therefore the name misfit compound.

As an example the commensurable structure approximation of $\text{LaS}_{1.14}\text{NbS}_2$ is shown in Fig. 3.114. The LaS slabs are strongly distorted cubes and constitute fragments of the non-existing compound LaS with NaCl-type structure. The layer stacking is stabilized through charge transfer according to $(\text{LaS})^+$ and $(\text{NbS}_2)^-$. This principle can lead to compounds which consist of layers which are unstable itself. An example is $(\text{LaS})_{1-x}\text{CrS}_2$ where neither LaS nor CrS_2 exists as a separate compound. But the composite is very stable due to transfer of the excess electron of the LaS slab to the chromium in the CrS_2 slab. A large number of misfit layer chalcogenides with the general formula $(M'X)_{1+x}(MX_2)_m$ ($M' = \text{Sn, Pb, Sb, Bi, Rare Earth}$; $M = \text{Ti, V, Cr, Nb, Ta}$; $X = \text{S, Se}$; $0.08 < x < 0.28$) have been described. For a more detailed study we refer to several reviews [25–29].

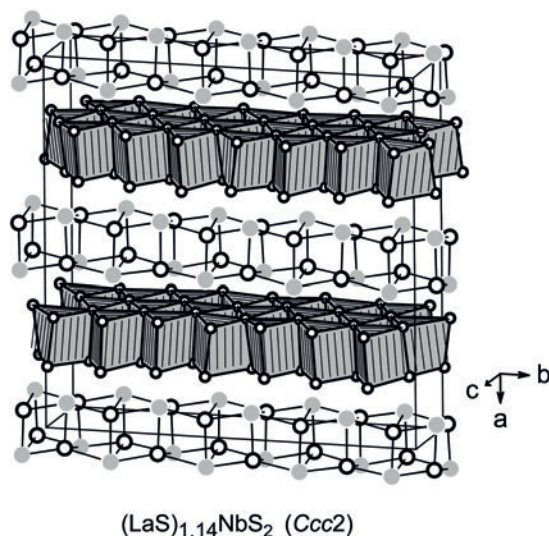


Fig. 3.114 Commensurable structure of the misfit layer compound $\text{LaS}_{1.14}\text{NbS}_2$. The $\text{NbS}_{6/3}$ trigonal prisms are drawn as polyhedra, which are sandwiched between layers of strongly distorted LaS cubes. Lanthanum atoms are drawn as gray circles and sulphur atoms as white circles.



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3.11.3 Selenides

The structural chemistry of transition metal selenides is rather similar to the sulphides described in the previous chapter. However, the lower electronegativity of selenium increases the metallic character, and the bigger radius of Se^{2-} when compared with S^{2-} may also cause some differences. Metal-rich binary selenides with 3d metals are again relatively few. Known compounds are Ti_9Se_2 , Ti_8Se_3 , Ti_2Se , V_5Se_4 , Ni_3Se_2 , and Cu_3Se_2 . As examples we show the crystal structures of Ti_9Se_2 and Cu_3Se_2 in Fig. 3.115. The titanium-selenide shows typical fragments of the underlying metal structure which is *bcc*-Ti in this case. Chains of condensed distorted *bcc*-like cubes run along the *c* axis. These fragments are connected *via* further titanium atoms (connections are not shown for reasons of clarity) and separated by the selenium atoms. While the concept of condensed metal clusters is useful to describe Ti_9Se_2 , it is not appropriate for the copper selenide Cu_3Se_2 (mineral umagite) shown in Fig. 3.115. In this case copper forms corrugated layers (Cu–Cu 267 pm) of five-membered rings, where copper has either three or four copper neighbors. Selenium is located between

the five-membered rings (Cu–S 236–254 pm) and bonded to six copper atoms as illustrated on top right in Fig. 3.115.

Copper is quite mobile in selenides, which is emphasized by an interesting synthesis of Cu_3Se_2 [1]. When pellets of Cu_2Se and CuSe are brought into contact copper begins to diffuse from the Cu_2S to the CuSe until the concentration of copper is equilibrated and both pellets consist of Cu_3Se_2 . This process proceeds at room temperature and is completed after 10 days.

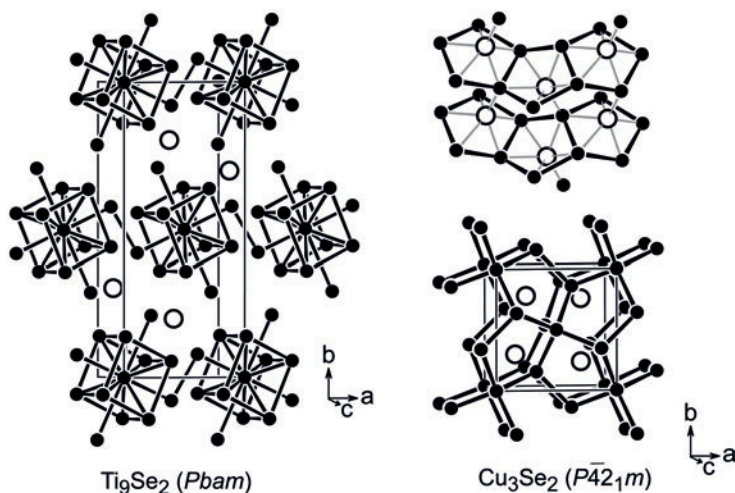


Fig. 3.115 Crystal structures of Ti_9Se_2 and Cu_3Se_2 as examples for metal-rich binary selenides with 3d-metals. Top right shows the coordination of the selenium atoms in Cu_3Se_2 . Titanium and copper are drawn as filled black circles, selenium as white circles.

Iron selenide FeSe is not a typical metal-rich compound, but the PbO -type polymorph (β - FeSe) is mentioned here because it has been intensively investigated after discovery of superconductivity in iron pnictides and pnictide oxides. Tetragonal β - FeSe is a superconductor with a critical temperature of 8 K [2] which increases up to 36 K under pressure [3]. Also potassium intercalation increases the critical temperature to 32 K in samples with the nominal composition $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$. It has been shown that such samples are phase separated in an antiferromagnetic phase with ordered Fe-vacancies and a superconducting phase with ThCr_2Si_2 -type structure which is probably potassium deficient according to $\text{K}_x\text{Fe}_2\text{Se}_2$ [4] shown in Fig. 3.116 (left). The projection of the $^2[\text{Fe}_4\Box\text{Se}_5]$ -layer of $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$ is also depicted in Fig. 3.116 (right). Magnetic moments at the iron atoms are aligned along the c axis, and their orientations are indicated with ‘+’ (up) and ‘−’ (down), respectively. The ordered moment in this so-called block-type antiferromagnetism is $3.3 \mu_B$ per iron.

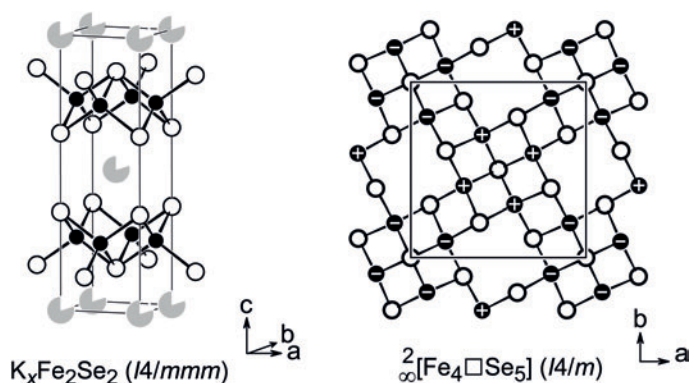


Fig. 3.116 Left: $K_xFe_2As_2$ with $ThCr_2Si_2$ -type structure and statistical K-vacancies. Iron atoms are drawn as filled black circles, selenium as white circles and potassium as gray circles. Right: Iron-selenide layer in $K_2Fe_4Se_5$ ($K_{0.8}Fe_{1.6}Se_2$) with ordered Fe-vacancies that cause a $\sqrt{5} \times \sqrt{5}$ superstructure with respect to the $ThCr_2Si_2$ -type cell of $K_xFe_2As_2$. The magnetic ordering of the iron moments is indicated by + and –, which means moments pointing up or down, respectively.

The materials chemistry of alkali metal iron selenide superconductors is a rapidly growing field, and many questions are still open. The current state is reviewed in [5]. Furthermore the intercalation chemistry of β -FeSe is not restricted to alkali metals. Recently the inclusion of lithium amide at low temperatures in liquid ammonia has been reported [6]. $Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2$ ($x \approx 0.6$; $y \approx 0.2$) becomes superconducting at 43 K. It is a metastable compound which decomposes at 100 °C.

Several metal-rich binary and ternary selenides with 4d- and 5d-metals are known, examples are Ta_2Se , Pd_4Se , Pd_7Se_2 , $Pd_{17}Se_{15}$, and $M_2Ta_{11}Se_8$ ($M = Fe, Co, Ni$). Fig. 3.117 shows

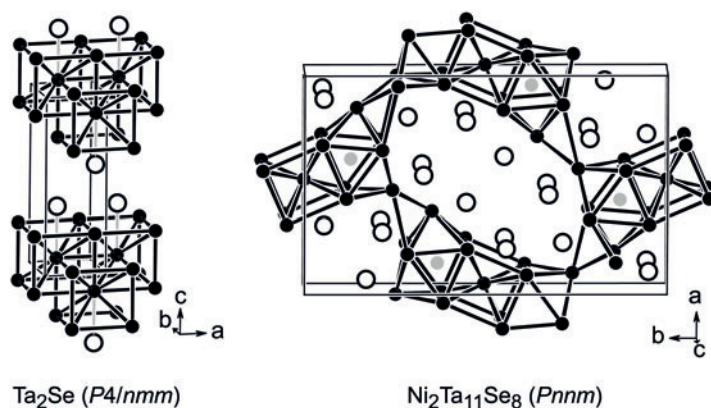


Fig. 3.117 Metal-rich selenides: The crystal structures Ta_2Se and $Ni_2Ta_{11}Se_8$. Tantalum is drawn as black filled circles, selenium as open circles and nickel as gray filled circles. The metal-metal bonded substructures are emphasized.

the crystal structures of Ta_2Se [7] and $\text{Ni}_2\text{Ta}_{11}\text{Se}_8$, both comply with the principle of condensed metal clusters [8, 9]. Ta_2Se is a layered structure with slabs of condensed *bcc*-like tantalum cubes separated by selenium atoms. This structure is reminiscent to the dichalcogenides, because only weak van der Waals bonds are present between the selenium atoms of the adjacent layers.

The structure of the ternary compound $\text{Ni}_2\text{Ta}_{11}\text{Se}_8$ exhibits Ni-centered tricapped trigonal prismatic tantalum clusters condensed *via* trigonal prism faces along the *c* axis and *via* one capping tantalum atom. Thus the clusters form twin columns, which are surrounded by selenium atoms, which also provide the three-dimensional linkage of the metal framework [10].

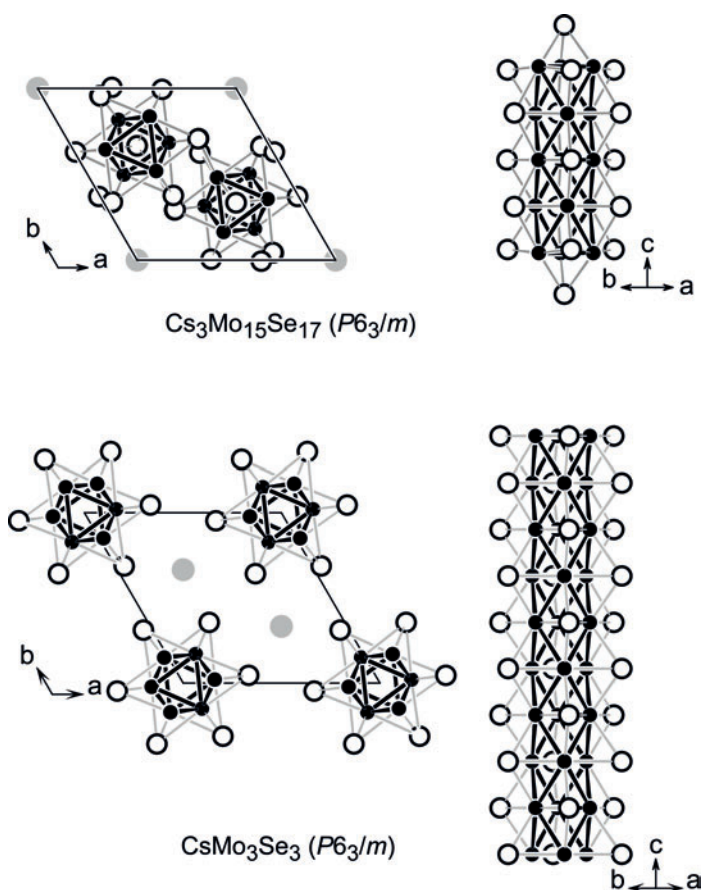


Fig. 3.118 Molybdenum selenides with condensed Mo_6 clusters. $\text{Cs}_3\text{Mo}_{15}\text{Se}_{17}$ (top) contains oligomers of four Mo_6 units, while CsMo_3Se_3 (bottom) is the end member of the series $A_{2n-2}\text{Mo}_{6n}\text{Se}_{2n+2}$ with infinite chains of Mo_6 octahedra. Molybdenum is drawn as black filled circles, selenium as open circles and cesium as gray filled circles.

Ternary metal-rich molybdenum chalcogenides are dominated by compounds with Mo_6 octahedra. The Chevrel-phases AMo_6Se_8 (see Fig. 3.110) exist with $A = \text{La-Lu, Li, Na, Cu, Ag, Zn, Cd, Mn, U-Am, In, Sn, Tl, and Pb}$. Additionally a large number of compounds with condensed $(\text{Mo}_6)_n$ cluster oligomers with $n = 2-5$ are known [11]. They belong to an infinite series with the general formula $A_{2n-2}\text{Mo}_{6n}\text{Se}_{2n+2}$, where the compounds AMo_3Se_3 ($A = \text{Li-Cs, Ba, Ag, In, Tl}$) represent the end members with infinite chains of octahedra. Depending on the linkage of the oligomers *via* selenium atoms also other compositions are possible. Fig. 3.118 shows the structures of $\text{Cs}_3\text{Mo}_{15}\text{Se}_{17}$ and CsMo_3Se_3 .

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3.11.4 Tellurides

Metal-rich tellurides have been investigated for decades and the considerable number of compounds represents an interesting structural chemistry. Many binary transition metal tellurides MTe ($M = \text{Sc-Cu, Zr, Hf, Rh, Pd, Ir, Pt}$) crystallize with the NiAs- and related structures. These are metallic compounds; however, this chapter focuses on metal-rich tellurides where metal-metal bonding plays the dominant role. As shown for the lighter metal-rich chalcogenides, the underlying principle is maintaining fractions of elemental metal structures which are separated by tellurium. Examples are the structures of Hf_3Te_2 , Ti_5Te_4 , and Sc_2Te shown in Figure 3.119. The hafnium and titanium compounds contain *bcc*-like cubes of the metal atoms which form layers parallel to (001) in Hf_3Te_2 and chains along [001] in Ti_5Te_4 . Tellurium atoms are located over the square faces of the cubes and form linkages

between the clusters in Ti_5Te_4 , while only weak van der Waals bonds are present between the layers of Hf_3Te_2 . Sc_2Te forms a complex network of scandium atoms where tellurium fills cavities. This structure is also known with the rare earth elements dysprosium and gadolinium. The rare earth richest tellurides are Lu_7Te and Lu_8Te , whose structures are described as substitutional derivatives of the elemental metals [1].

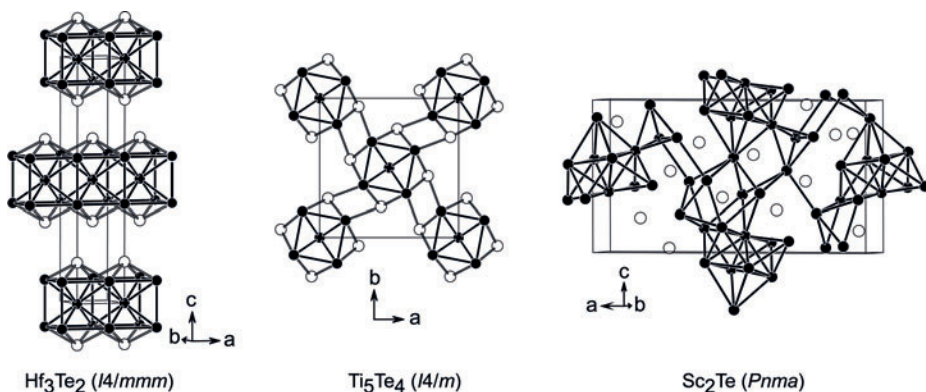


Fig. 3.119 Crystal structures of binary metal-rich tellurides. Hafnium, titanium and scandium are drawn as black filled circles and tellurium as open circles. Thick black lines emphasize the intermetallic framework and are not necessarily the shortest distances between the metal atoms.

The examples shown in Fig. 3.119 are increasingly electron-poor. While hafnium in Hf_3Te_2 has 2.67 metal-centered electrons, titanium in Ti_5Te_4 has 2.4, and scandium in Sc_2Te only 2 electrons available for metal-metal bonds. Chemical bonding of Hf_3Te_2 has been analysed by Extended-Hückel calculations which show that almost all Hf–Hf bonding states are occupied [2]. This is no longer the case in Sc_2Te where the electron count is not sufficient to fill all Sc–Sc bonding states [3].

Several ternary rare earth transition metal tellurides are known, among them $\text{Er}_5\text{M}_2\text{Te}_2$ ($M = \text{Co}, \text{Ni}$) and Gd_4NiTe_2 [4]. Interesting low-dimensional structures have been found for a number of tellurides which contain $3d$ and $4d/5d$ transition metals. In the structure of Ta_4FeTe_4 (Fig. 3.120), tantalum forms quasi one-dimensional strands of square anti-prisms with iron atoms in the centers [5]. Tellurium atoms are located over the triangular faces of these prisms and envelop the metal strands, thus only weak van der Waals forces between tellurium are present between the strands. Also the tetragonal structure of $\text{Ru}_3\text{Sc}_{14}\text{Te}_8$ [6] contains a quasi-one-dimensional motif (Fig. 3.120), which is built up by alternating cubes and anti-prisms of scandium atoms along the c axis. Tellurium atoms link the metal strands which are also connected *via* chains of edge-sharing ScTe_6 octahedra. A third example with quasi one-dimensional building blocks is the orthorhombic structure of Pd_2CoTe_2 [7]. The in-

termetallic framework is made of palladium atoms parallel to the c axis, separated by chains of edge-sharing $\text{CoTe}_{4/2}$ tetrahedra. The structure is isopointal to K_2ZnO_2 . Finally, TaNi_2Te_2 forms a layered structure with slabs made of condensed Ta_2Ni_4 octahedra with tellurium atoms bridging two neighboring octahedra (Fig 3.120). The compound is a Pauli-paramagnetic metal in agreement with electronic band structure calculations [8]. For further information about transition metal tellurides we refer to the review by Tremel [9] and literature cited therein.

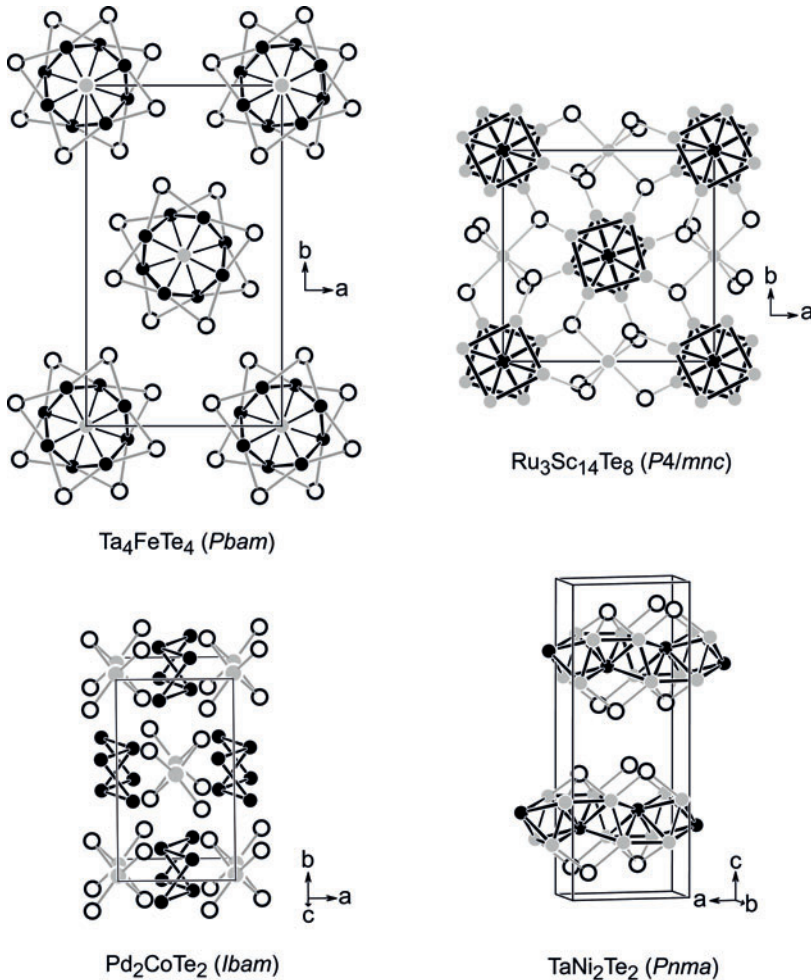


Fig. 3.120 Crystal structures of ternary metal-rich tellurides. The $4d$ -/ $5d$ -metals (Ta, Ru, Pd) are drawn as black filled circles, $3d$ -metals (Fe, Sc, Co, Ni) as gray circles, and tellurium as open circles. Thick black lines emphasize the intermetallic framework and are not necessarily the shortest distances between the metal atoms.



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3.12 Beryllium and Magnesium Intermetallics

Beryllium is an atypical alkaline earth element. It has many similarities to the neighboring elements lithium and aluminum. The *diagonal relationship* well-known in aqueous chemistry is also reflected in the crystal chemistry of beryllium intermetallics. Also, some resemblance to zinc chemistry is evident. Similar structure types form for beryllium and zinc intermetallics (Chapter 3.13).

The prerequisites for the potential high-temperature resistance of beryllium-based intermetallics rely on the high melting (1560 K) and boiling (2745 K) points of beryllium itself. Generally beryllium alloys have high melting points, good thermodynamical stability, but low toughness and brittleness. The good corrosion resistance of beryllium intermetallics is due to a protective BeO coating. The density of beryllium (1.85 g/cm³) is only slightly higher than that of magnesium and beryllium has repeatedly been discussed as construction material for light-weight alloys, primarily since it has an elastic module about 30 % better than steel. The main disadvantage of beryllium and its compounds is the high toxicity [1, 2], although concrete parameters that are responsible for the toxicity are not fully understood. Today most applications of beryllium and its intermetallics are abrasion resistant beryllium-copper-bronzes and beryllium foils (8 μm up to 1 mm thickness) for X-ray tubes.

In view of the toxicity, only few systematic investigations on beryllium intermetallics have been performed and one observes neat crystal chemistry. No compounds have been reported for the alkali metals. The alkaline earth metals form beryllium-rich compounds $AEBe_{13}$ for $AE = \text{Mg, Ca, Sr, and Ba}$ with cubic NaZn_{13} -type structure (Chapter 3.13).

Among the transition metal beryllides several simple structure types occur, *e. g.* CsCl for TBe ($T = \text{Ti, Co, Ni, Rh, Pd, Cu}$), MgCu_2 and MgZn_2 for TBe_2 ($T = \text{Ti, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Cu, Ag, Ru}$), AlB_2 for TBe_2 ($T = \text{Zr, Hf}$), U_3Si_2 for T_3Be_2 ($T = \text{Nb, Ta}$), PuNi_3 for TBe_3 ($T = \text{Ti, Nb}$), CaCu_5 for TBe_5 ($T = \text{Zr, Hf}$), AuBe_5 for TBe_5 ($T = \text{Fe, Pd, Pt, Au}$), $\text{Th}_2\text{Ni}_{17}$ for T_2Zn_{17} ($T = \text{Ti, Zr, Hf, Nb, Ta}$), NaZn_{13} for TZn_{13} ($T = \text{Zr, Hf, Mo}$), ThMn_{12} for

TBe_{12} ($T = \text{Ti, Nb, Ta, V, Cr, Mo, W, Mn, Fe, Os, Co, Pd, Pt, Au}$), and $ZrZn_{22}$ for TBe_{22} ($T = \text{Mo, W, Re}$). Ruthenium, rhodium, and osmium form a variety of complex phases with unique compositions: Ru_2Be_3 , Ru_3Be_{17} and isotypic Os_3Be_{17} , Ru_2Be_{17} and isotypic Os_2Be_{17} , $Rh_{2.36}Be_{15.34}$ and its isotypic iridium compound. Not all binary $T\text{--}Be$ phase diagrams are completely studied. Again, this is most likely due to the toxicity of the beryllides.

Generally these beryllides can be prepared by annealing of cold-pressed pellets at temperatures as high as 1470 K, or simply by arc-melting. The problem of these two preparation techniques is evaporation and dust formation which are harmful for the experimentalist. An interesting technique for very small substance amounts concerns the iodine-catalyzed synthesis which has successfully been tested for the growth of Pd_3Be (Re_3B type) and Pd_2Be (Zr_2Cu type) single crystals [3].

Exemplarily we discuss the structures of $MoBe_{12}$ [4] and Ru_3Be_{17} [5] (Fig. 3.121). The molybdenum compound crystallizes with the tetragonal $ThMn_{12}$ type, space group $I4/mmm$, similar to many other transition metals. The significant difference in size between molybdenum and beryllium allows the high coordination number of 20 with $Mo\text{--}Be$ distances ranging from 254 to 277 pm. These $Mo@Be_{20}$ polyhedra are the monomeric building units of the $MoBe_{12}$ structure. They are condensed *via* common edges and faces in a body-centered manner. The three crystallographically independent beryllium atoms have between 10 and 13 nearest beryllium neighbors at $Be\text{--}Be$ distances in the range from 212 to 261 pm.

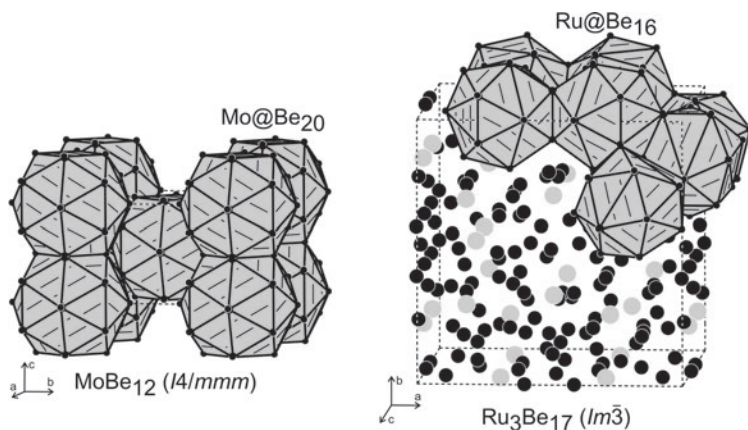


Fig. 3.121 The crystal structures of $MoBe_{12}$ and Ru_3Be_{17} . Transition metal and beryllium atoms are drawn as medium gray and black circles, respectively. Some of the edge- and face-sharing $Mo@Be_{20}$ and $Ru@Be_{16}$ polyhedra are emphasized.

The ruthenium atoms in the Ru_3Be_{17} structure type (space group $Im\bar{3}$) have coordination number 16 with $Ru\text{--}Be$ distances ranging from 238 to 261 pm. The $Ru@Be_{16}$ polyhedra show a complex condensation pattern *via* common edges. Although this struc-

ture type seems complex at first sight, the only monomeric building unit are the Ru@Be_{16} polyhedra. The beryllium atoms have between 6 and 15 beryllium neighbors in the range from 204 to 272 pm, a similar situation to the one in the MoBe_{12} structure.

The smallest rare earth element scandium forms the beryllides ScBe_5 , $\text{Sc}_2\text{Be}_{17}$, and ScBe_{13} . For all other rare earth elements only the REBe_{13} phases with cubic NaZn_{13} -type structure have been reported. This is also the case for the actinide beryllides ThBe_{13} , UBe_{13} , and PuBe_{13} . Very detailed physical property studies have been performed for CeBe_{13} and UBe_{13} . The cerium compound is an intermediate-valence system [6] with a calculated 24 % f electron contribution to the Fermi level and UBe_{13} shows heavy-fermion behavior [7] with a transition to a superconducting state at very low temperatures.

Concerning ternary beryllium intermetallics, only few phases are reported. ZrBeSi [8] is an important structure type. It is a ternary ordered version of the AlB_2 structure, where the beryllium and silicon atoms form a hetero-graphite network that is separated by the zirconium atoms. The corresponding group-subgroup scheme is explained in Chapter 3.17. This structure type has more than 200 representatives in the field of RETX intermetallics with X = element of the 3rd, 4th, or 5th main group [9]. The only other series of ternary compounds concerns the so-called G-phases which exist for different combinations of transition metals: $T_6\text{Co}_8\text{Be}_{15}$ ($T = \text{Zr, Hf}$), $T_6\text{Ni}_8\text{Be}_{15}$ ($T = \text{Zr, Hf, Nb, Ta}$), $T_6\text{Cu}_8\text{Be}_{15}$ ($T = \text{Ti, Zr, Hf, Nb, Ta}$), and $T_6\text{Pd}_8\text{Be}_{15}$ ($T = \text{Zr, Hf}$) [10]. The structure of the first representative, $\text{Ta}_6\text{Cu}_8\text{Be}_{15}$, is discussed. It is a ternary version of the $\text{Th}_6\text{Mn}_{23}$ type with an ordering of the copper and beryllium atoms on the manganese sites. As emphasized in Fig. 3.122 the structure has two striking building units, *i. e.* $\text{Ta@Be}_8\text{Cu}_4\text{Ta}_4$ and $\text{Cu@Be}_7\text{Cu}_3\text{Ta}_3$ polyhedra. The coloring of the polyhedra is somehow more complex than discussed for the two binary structures. The stability of these ternary G-phases is due to short Cu–Be (231–233 pm) and Ta–Be (260 pm) distances as well as Ta–Cu and Cu–Cu bonding. The two types of polyhedra are condensed *via* common edges and faces.

A last example for ternary beryllides concerns compounds of compositions $\text{RE}_2\text{Co}_{17}\text{Be}$ which have been reported for $\text{RE} = \text{Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho}$, and Er [11]. These intermetallics crystallize either with the hexagonal $\text{Th}_2\text{Ni}_{17}$ or the rhombohedral $\text{Th}_2\text{Zn}_{17}$ type (Chapter 3.13). Beryllium incorporation leads to a decrease of the lattice parameters and the magnetic ordering temperatures. Since all these phases have only been investigated on the basis of powder X-ray diffraction data, it is not clear whether the beryllium atoms substitute within the cobalt substructure or fill voids, similar to the magnetic materials discussed in Chapter 4.1.

Magnesium has an abundance of 1.94 % in the earth crust and besides aluminum (7.57 %) it is one of the most important components in modern light-weight alloys. The advantage of magnesium is the low density of only 1.74 g/cm³ as compared to aluminum 2.70 g/cm³. Even lower density is reached with magnesium foam, a technology that is widely developed for aluminum and related alloys. The high relevance of such magnesium-based alloys is well reflected on the *International Conference on Magnesium Alloys and their Applications* which takes place every three years [12]. Important topics in this field are the development of alloys, questions about the microstructure,

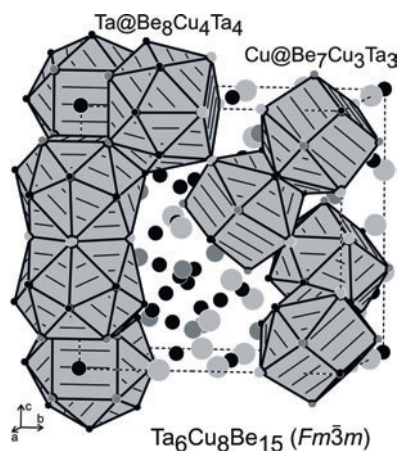


Fig. 3.122 The crystal structure of the G-phase $\text{Ta}_6\text{Cu}_8\text{Be}_{15}$. Tantalum, copper, and beryllium atoms are drawn as large light gray, small medium gray, and black circles, respectively. The condensation patterns of the $\text{Ta@Be}_8\text{Cu}_4\text{Ta}_4$ and $\text{Cu@Be}_7\text{Cu}_3\text{Ta}_3$ polyhedra are emphasized.

casting, corrosion, surface treatment, recycling, etc. In the present chapter we only focus on the structural chemistry and some properties of pure binary or ternary intermetallic magnesium compounds.

The basic textbook on magnesium chemistry with respect to alloy formation is certainly the *Magnesium Taschenbuch* [13] which covers all relevant aspects starting from the abundance of magnesium, its primary and secondary (recycling) exploitation, magnesium-based phase diagrams, metallurgical aspects, shaping, casting, as well as the constitution of multinary magnesium alloys. Out of the huge number of different magnesium alloys we will first concentrate on the compositions of the technologically most relevant ones and then switch to crystal chemical aspects.

Magnesium is not used as a pure element for applications. Alloying with different other elements is necessary in order to improve the properties for shaping (wrought alloys) or casting (cast alloys). The important alloying elements are Al, Zn, Mn, Si, Zr, rare earth elements, Li, and traces of Fe, Ni, and Cu. For special cases alloying with traces of other metals might be favorable. The strategies for alloying are (i) the reduction of density and specific durability, (ii) creep resistance and high-temperature stability, and (iii) rigidity and the elastic module. The structures of these alloys are in principle based on close packing; however, the different chemical potentials of the alloying elements cause different bonding patterns. Well defined intermetallic compounds might occur as precipitations in such alloys. The knowledge of phase formation and determination of the corresponding structures in combination with an evaluation of chemical bonding is important basic knowledge for deeper understanding of the alloy systems. The basic crystal chemical details of magnesium intermetallics are summarized in the following paragraphs. For compounds of magnesium with a p -block element (e. g. phosphides, arsenides, or silicides) we refer to the corresponding chapters.

Lithium shows a small solubility in magnesium while keeping the *hcp* structure. With increasing lithium concentration the structure switches to *bcc* and a model with lithium-magnesium ordering has been discussed [14]. The heavier alkali metals do not form compounds with magnesium. Representative binaries with the alkaline earth elements are MgBe_{13} (NaZn_{13} type), AlMg_2 with Ca, Sr, Ba (MgZn_2 type), SrMg (CsCl type), $\text{Al}_2\text{Mg}_{17}$ with Sr, Ba ($\text{Th}_2\text{Zn}_{17}$ type), and $\text{Al}_6\text{Mg}_{23}$ with Sr, Ba ($\text{Th}_6\text{Mn}_{23}$ type). The structure types of the magnesium-rich phases correspond to those of the zinc-rich phases discussed in Chapter 3.13.

The early transition metals do not react with magnesium. This advantage is used during synthesis procedures in niobium and tantalum tubes (inert crucible materials). For the iron group elements, only the ruthenium-based compounds Ru_2Mg_3 (ordered variant of β -manganese) and $\text{Ru}_{6.5}\text{Mg}_{44.5}$ ($\text{Rh}_7\text{Mg}_{44}$ type) are known. The formulae of the transition metal compounds are written in the same sequence as for the alkaline earth metal ones, just for reasons of systematization. However, the significant differences in electronegativity point to different charge transfers. Analyses of the electronic structure of Ru_2Mg_3 [15] revealed a net charge transfer from magnesium to ruthenium, classifying this compound as a ruthenide. A similar bonding picture certainly holds true also for the other $T_x\text{Mg}_y$ binaries with electron-rich and electro-negative transition metals.

Some of the $T_x\text{Mg}_y$ binaries adopt simple structure types that derive from the close packed structures, their ordered derivatives, or they form Laves phases (Chapter 3.6). The following examples summarize this family of compounds: RhMg , PdMg , AgMg , and AuMg (CsCl type), RhMg_2 (Zr_2Cu type), Ni_3Mg , Pt_3Mg (Cu_3Au type), MgCo_2 , MgNi_2 , MgCu_2 , and MgZn_2 with the Laves phases structure types, Pd_3Mg and $\text{Au}_{3.2}\text{Mg}_{0.8}$ (ZrAl_3 type). Other binaries with comparatively simple structures are Rh_2Mg_5 and Pd_2Mg_5 (Co_2Al_5 type), Pd_2Mg (Co_2Si type), Pd_5Mg_3 (Rh_5Ge_3 type), PdMg_2 (Ti_2Ni type), PtMg (FeSi type), and PtMg_2 (CuAl_2 type). Similar to the beryllides discussed above, also for some magnesium compounds iodine-catalysed syntheses are possible [16].

As an example we present the RhMg_3 structure [17] (Cu_3P type) in Fig. 3.123. The rhodium atoms are at $z = 1/4$ (light gray) and $z = 3/4$ (medium gray) and show a hexagonal closest packing. A subcell of the *hcp* arrangement is presented in the upper left-hand part of the unit cell. Each rhodium atom is surrounded by eleven magnesium atoms with Rh–Mg distances ranging from 264 to 336 pm. These Rh@Mg_{11} polyhedra are the monomeric building units and the RhMg_3 structure can be described by their condensation. The non-centrosymmetric space group $P6_3mc$ of RhMg_3 , as compared to $P6_3/mmc$ for the ideal *hcp* packing, results from the lower site symmetry of the magnesium atoms within the Rh@Mg_{11} polyhedra. PdMg_3 , PtMg_3 , and AuMg_3 are isotypic with RhMg_3 .

Many other binaries crystallize with more complicated/complex structures, e. g. NiMg_2 , $\text{Rh}_7\text{Mg}_{44}$, and $\text{Ir}_7\text{Mg}_{44}$, $\text{Ir}_3\text{Mg}_{13}$, $\text{Ir}_6\text{Mg}_{45}$, $\text{Ir}_4\text{Mg}_{29}$, Ir_3Mg_7 , CuMg_2 , AuMg_2 , Au_3Mg , or $\text{Au}_{14}\text{Mg}_{13}$. Some of them crystallize with their own structure type, often with a

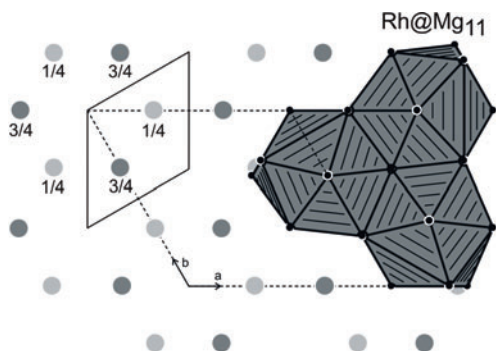


Fig. 3.123 The crystal structure of RhMg_3 . Rhodium and magnesium atoms are drawn as (light at $z = 1/4$ and medium at $z = 3/4$) gray and black circles, respectively. The condensation pattern of the Rh@Mg_{11} polyhedra is emphasized. A *hcp* subcell of the rhodium atoms is emphasized at the upper left-hand part of the drawing.

large unit cell. A very interesting example is the equiatomic compound IrMg [18]. While RhMg crystallizes with the simple CsCl-type structure with just two atoms per unit cell, IrMg adopts a complicated structure in space group $Cmce$ with 304 atoms per cell and a small homogeneity range through Ir/Mg mixing: $\text{Mg}_{1-x}\text{Ir}_{1-x}$ ($x = 0, 0.037$, and 0.054). Such mixed occupancies have been observed also for other binaries. The exact electronic reasons for these peculiar structure types are not yet known.

The rare earth metals form different series of binary magnesium compounds: REMg (CsCl or CuTi type), REMg_2 (hexagonal or cubic Laves phases), REMg_3 (BiF_3 type), $\text{RE}_2\text{Mg}_{17}$ ($\text{Th}_2\text{Ni}_{17}$ type), REMn_{12} (ThMn_{12} type), and $\text{RE}_5\text{Mg}_{41}$ ($\text{Ce}_5\text{Mg}_{41}$ type). Not all rare earth elements form all of these structures. This is a consequence of the difference in size (lanthanoid contraction). For example, scandium only forms the CsCl-type phase ScMg . The structure types that occur for the RE_xMg_y intermetallics are quite variable ones. They are adopted by different compositions and valence electron concentrations as well.

As an example for the $\text{RE}_5\text{Mg}_{24}$ compounds we present the Y_5Mg_{24} structure [19] ($\text{Ti}_5\text{Re}_{24}$ type) in Fig. 3.124. Y_5Mg_{24} is a binary ordering variant of the α -manganese structure. The $2a$ and $8c$ manganese sites are occupied by yttrium and both $24g$ sites by magnesium atoms. Both yttrium sites have coordination number 16 by magnesium and yttrium atoms and the polyhedra have Frank-Kasper shape. The $\text{Y1@Mg}_{12}\text{Y}_4$ polyhedra show *bcc* packing and the $\text{Y2@Mg}_{15}\text{Y}$ polyhedra condense in a tetrahedral manner around the Y1 polyhedra. For reasons of clarity, only two Y2 polyhedra are shown in Fig. 3.124.

The compositions of the binary europium-magnesium compounds are slightly different. Europium is divalent in all these compounds, leading to slightly different crystal chemistry. The compositions EuMg , EuMg_2 , EuMg_4 , EuMg_5 , $\text{EuMg}_{5.2}$, and $\text{Eu}_2\text{Mg}_{17}$ have been reported. Among the actinides only few compounds exist. Uranium shows a large immiscibility gap almost from pure magnesium to pure uranium.

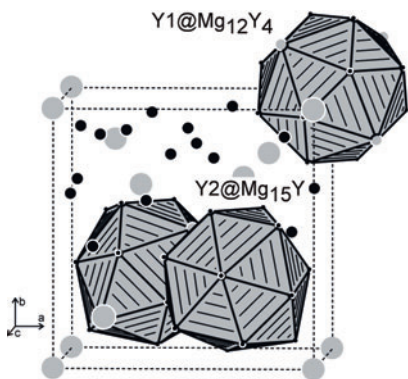


Fig. 3.124 The crystal structure of Y_5Mg_{24} . Yttrium and magnesium atoms are drawn as light gray and black circles, respectively. The coordination polyhedra of the two crystallographically independent yttrium sites are emphasized.

The solubility of uranium into magnesium and *vice versa* is very small. Thorium forms the binaries ThMg_2 , $\text{Th}_6\text{Mg}_{23}$, and ThMg_5 .

Regarding ternary intermetallic magnesium compounds, one can roughly distinguish two families of intermetallics. The first group concerns the RE-T-Mg phase diagrams. First compounds have been reported in the 1990^s, but more systematic phase analytical work has been carried out in the last ten years [20]. These $\text{RE}_x\text{T}_y\text{Mg}_z$ intermetallics are of special interest with respect to hydrogen storage materials and precipitation hardening in modern light-weight alloys. More than 200 ternary compounds have been characterized so far. They crystallize with structure types that are known from stannide and indide chemistry (Chapters 3.9.4 and 3.8.4). In many cases solid solutions $\text{In}_{1-x}\text{Mg}_x$ and $\text{Sn}_{1-x}\text{Mg}_x$ have been observed. Typical compositions are RETMg (ZrNiAl , TiNiSi , or LaNiAl type), $\text{RE}_2\text{T}_2\text{Mg}$ (ordered U_3Si_2 or Zr_3Al_2 type), RE_4TMg (Gd_4RhIn type), RET_4Mg (ordered Laves phases), $\text{RE}_{23}\text{T}_7\text{Mg}_4$ ($\text{Pr}_{23}\text{Ir}_7\text{Mg}_4$ type), or RET_9Mg_2 (ternary ordered RET_3 phases; stacking variants of the $\text{CeNi}_3/\text{PuNi}_3$ structures). So far, only few isothermal sections of the nickel [21], copper [22], and silver [23] containing phase diagrams have been studied.

Similar to indide and stannide chemistry, for many of the $\text{RE}_x\text{T}_y\text{Mg}_z$ intermetallics one observes formation of covalently bonded $[\text{T}_y\text{Mg}_z]$ two- or three-dimensional networks. Comparison of the T-In vs. T-Mg bonding by electronic structure calculations showed weaker T-Mg bonding in all cases. Already in the $\text{RE}_x\text{T}_y\text{Mg}_z$ intermetallics magnesium does not behave like a typical alkaline earth metal. Magnesium takes crystal chemical positions of a typical p element and thus shows its covalent nature.

Some striking properties will also be discussed. Especially the RET_9Mg_2 , RET_4Mg , and RE_4TMg phases have intensively been studied when searching for hydrogen storage materials. An interesting compound is $\text{Gd}_4\text{NiMgH}_{11}$ [24], which shows hydrogen uptake of almost two hydrogen atoms per metal atom. This is a remarkable amount, keeping in mind that the commercially available systems like LaNi_5H_6 and

FeTiH₂ (Chapter 3.16) show an uptake of 1:1 only. Nevertheless, upon hydrogen release decomposition takes place which impedes reversible hydrogen storage. For many $RE_xT_yMg_z$ intermetallics decomposition leads to the REH_3 trihydrides. Among the magnetically interesting compounds it is worthwhile to mention the magnetocaloric material Gd₄Co₂Mg₃ [25], a 75 K antiferromagnet, and the comparatively high Curie temperatures of 150 and 139 K for Eu₄PdMg and Eu₄PtMg, respectively [26]. Further examples are listed in a review article [20].

The second group of ternary magnesium intermetallics comprises those with the alkaline earth elements calcium, strontium, and barium. Here, one strictly observes segregation into two different substructures. The magnesium atoms on one and the calcium (strontium, barium) atoms on the other side, take distinctly different functions in their respective substructures, showing again that magnesium does not behave as a typical alkaline earth element in these structures. This peculiar crystal chemical behavior is related to the smaller size of magnesium and its higher electronegativity (1.23 on the Pauling scale) as compared with calcium (1.04). In contrast to the heavier alkaline earth elements, this leads to Mg–Mg bond formation.

The first example concerns the calcium-rich compounds Ca₄TMg with $T = \text{Pd, Ag, Au}$ [26], which crystallize with the cubic Gd₄RhIn-type structure. The calcium atoms build up trigonal prisms around the transition metal atoms and these Ca₆T prisms are condensed *via* common corners and edges to three-dimensional adamantane-related networks which leave cages for covalently bonded Mg₄ tetrahedra (328 pm Mg–Mg in Ca₄AgMg), a rare crystal chemical motif. The structure shows no solid solution of the calcium and magnesium atoms, but a clear segregation!

The covalent nature of magnesium is also evident in the series of magnesium-rich compounds (Ca,Sr)TMg₂ ($T = \text{Pd, Pt, Au}$) [27] with MgCuAl₂-type structure. This crystal chemical behavior is similar to the corresponding indides [28]. The CaMg₂ and SrMg₂ substructures of these compounds are almost isopointal to the Zintl phase CaIn₂. Thus, we observe clear segregation of calcium and strontium on the cationic position, while the magnesium atoms build up the covalently bonded three-dimensional network of condensed tetrahedra which resemble the structure of hexagonal diamond, lonsdaleit.

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3.13 Zinc and Cadmium Intermetallics

Today elemental zinc is frequently used for different components, sheets (plating, roof gutters), fittings, or injection molding. This broad use in daily life has simple reasons. The zinc surfaces easily oxidize and react with different reactive gases of the air, forming stable, hardly soluble coatings which serve as excellent long lasting corrosion protection. For many iron and steel-based components (guardrails, handrails) hot-dip zinc coating is the usual corrosion protection technique. This is a chemical reaction between the surface of the iron component and the zinc bath, first leading to

formation of $\text{Fe}_3\text{Zn}_{21}$, then FeZn_{10} , then the zinc-richest phase FeZn_{13} , and finally a zinc coating. These multi-layer coatings corrosion-protect the iron and steel component in a similar manner than discussed for pure zinc components. Sheets for roofing and wall cladding consist of fine zinc that is alloyed with small amounts of titanium, copper, and aluminum, increasing the mechanical processability.

Besides this broad technical use, intermetallic zinc compounds show a variety of interesting structural features with high significance in basic research. The low melting point of zinc (692 K) enables flux synthesis of zinc-rich compounds. This technique has been described in Chapter 2.7. The excess zinc flux can easily be removed with 2N hydrochloric acid since in most cases the binary and ternary intermetallic zinc compounds keep stable under these conditions.

Before we start to discuss the structural chemistry of binary and ternary intermetallic zinc compounds we briefly draw back to the alloying behavior of zinc. The brass phases (Cu–Zn alloys) discussed in Chapter 3.5 are probably the most well-known zinc alloys broadly used in daily life. Many other compositions like $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$ or $\text{Al}_2\text{Mg}_5\text{Zn}_2$ are the basis for injection molding. Typical elements for zinc alloying are copper, magnesium, and aluminum. Addition of small amounts of these elements increase strength and hardness of the alloy and improve its fluidity. However, the alloying process needs a critical balance, since adding too much might cause grain growth (precipitation of specific intermetallic compounds) and then lead to inter-granular corrosion.

Turning to the intermetallic zinc compounds we start with the alkali and alkaline earth metals. Knowledge of the phase diagrams and the crystal structures of these compounds is important, since they can form as precipitations in the alloys discussed above. This is also the case for coating formation (see the hot-dip zinc coating), where well defined intermetallic compounds build the interface between iron and zinc. Only few binary alkali metal zinc compounds are known. Lithium forms the equiatomic compound LiZn (NaTl-type structure) with tetrahedral coordination in the lithium and zinc substructures. A peculiar structure type occurs for NaZn_{13} (Fig. 3.125). Although only a minor amount of sodium reacts with zinc, the zinc substructure is completely reorganized and no longer resembles the hexagonal closest packing of the element. The structure contains two crystallographically independent zinc atoms. The Zn2 atoms are directly coordinated to sodium. The large $\text{Na}@\text{Zn}_{24}$ polyhedra share common rectangular faces in all three directions. The cavities left by this three-dimensional network are filled by the Zn1 atoms. The latter have coordination number 12 in the form of $\text{Zn1}@\text{Zn}_{12}$ icosahedra. If one considers the $\text{Na}@\text{Zn}_{24}$ polyhedra as building units, the NaZn_{13} structure can be considered as CsCl derivative (see also CaB_6 in Chapter 3.8.1).

KZn_{13} and RbZn_{13} are isotypic with the sodium compound while $\text{Cs}_{1.34}\text{Zn}_{16}$ forms its own structure type. The zinc substructure of the NaZn_{13} type allows for different coloring with transition metal and *p* element atoms. Small differences in size lead to distortions of the icosahedra. Some ordering variants are presented in Chapter 3.17 with respect to group-subgroup relations.

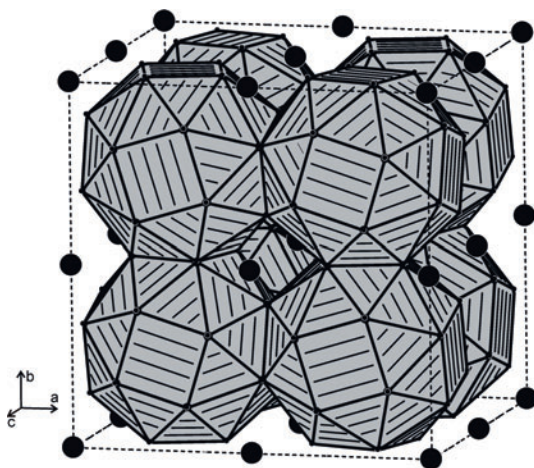


Fig. 3.125 The crystal structure of NaZn_{13} . The face-sharing $\text{Na}@\text{Zn}_{24}$ polyhedra are emphasized. The Zn1 atoms have only zinc neighbors.

A broader variety of zinc intermetallics is formed with the alkaline earth metals. Magnesium reacts with zinc forming the zincides MgZn_2 , $\text{Mg}_2\text{Zn}_{11}$, $\text{Mg}_{21}\text{Zn}_{25}$, $\text{Mg}_{51}\text{Zn}_{20}$, and Mg_4Zn_7 , of which the Laves phase MgZn_2 (Chapter 3.6) is the most prominent one. The zinc-poor phases with calcium, strontium, and barium form comparatively simple structures, e. g. Ca_3Zn (Re_3B type), Ba_2Zn (Zr_2Cu type), AEZn ($\text{AE} = \text{Ca}, \text{Sr}; \text{FeB}$ type), BaZn (CsCl type), or AEZn_2 ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}; \text{KHg}_2$ type). With increasing zinc content the structures increase in complexity. Also, the coordination number of the alkaline earth element becomes significantly larger. As an example we present the CaCu_5 -type structure of the high-temperature phase of SrZn_5 in Fig. 3.126. The zinc atoms build up Kagomé networks (a tessellation of hexagons and triangles) [1, 2] in the ab plane which are condensed to a three-dimensional network by further zinc atoms. Each strontium atom has eighteen zinc neighbors in the form of a hexa-capped hexagonal prism. SrZn_5 shows a reconstructive phase transition upon cooling [3], forming its own structure type. The coordination of the strontium atoms significantly distorts and the coordination number increases to 19. A similar situation, but again with a unique structure type, is observed for BaZn_5 .

CaZn_{11} and SrZn_{11} with much higher zinc content adopt the BaCd_{11} type. This structure is discussed along with the cadmium intermetallics (*vide infra*). AEZn_{13} with $\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$ [4] again crystallize with the cubic NaZn_{13} type. Electronic structure calculations point to a weak charge transfer of the alkali and alkaline earth metals to the zinc network, classifying these intermetallics as zincides with broad ranges of Zn–Zn bonding. Substitution in the zinc substructure is possible in a narrow range with an optimal number of 40 to 42 valence electrons per $[\text{T}_{13-x}\text{X}_x]$ unit ($\text{T} = \text{Li}, \text{Cu}, \text{Zn}, \text{Ag}; \text{X} = \text{Al}, \text{Ga}, \text{In}, \text{Sn}$).

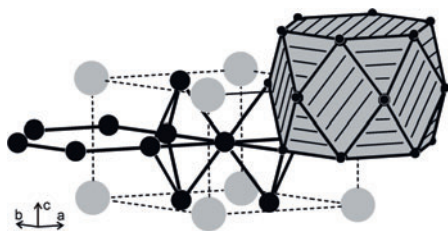


Fig. 3.126 The crystal structure of HT-SrZn₅. Strontium and zinc atoms are drawn as medium gray and black circles, respectively. A Sr@Zn₁₈ polyhedron and part of the Kagomé network are emphasized.

The transition metal zinc compounds show broader structural complexity than the alkali and alkaline earth metals, however, similar situation occurs for the zinc-poor phases. Again one observes simple structure types, *e. g.* Ti₂Zn (Zr₂Cu type), TiZn, RhZn, and IrZn (CsCl type), TiZn₂ (MgZn₂ type), TiZn₃, or NbZn₃ (Cu₃Au type). The complexity arises for the zinc-rich phases. As examples, the structures of TiZn₁₆ (Pearson symbol oC68) and RhZn₁₃ (mS28) are presented in Fig. 3.127.

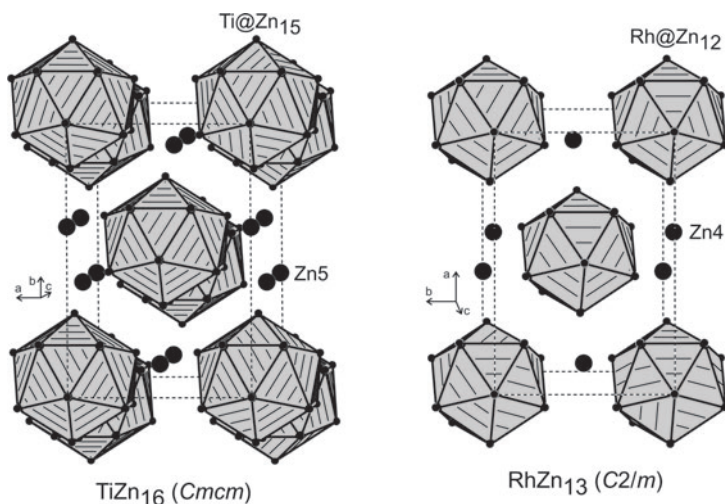


Fig. 3.127 The crystal structures of TiZn₁₆ and RhZn₁₃. The packing of the Ti@Zn₁₅ and Rh@Zn₁₂ polyhedra is emphasized. The Zn5 and Zn4 atoms, respectively, do not participate in the coordination sphere of the transition metal.

Such complex structures are best described by a packing of distinct polyhedra. The titanium and rhodium atoms have 15 and 12 zinc atoms in their coordination shells, respectively. These polyhedra are condensed *via* common corners, forming chains that extend in the *c* directions. If one considers the neighboring chains, both structures show the motif of distorted hexagonal rod packing. The Zn5 atoms in TiZn₁₆ and

the Zn₄ atoms in RhZn₁₃ do not participate in the coordination shells of the transition metal atoms. In both structures these zinc sites have coordination number 12, exclusively by zinc atoms. These Zn@Zn₁₂ polyhedra (not shown in Fig. 3.127) fill the space between the Ti@Zn₁₅ and Rh@Zn₁₂ chains. Such zinc intermetallics are metallic conductors and weak Pauli paramagnets [5]. In some cases they show even negative susceptibility values, indicating that the Pauli susceptibility is overcompensated by the core diamagnetism. Other complex zinc compounds like Ni₂Zn₁₁ or Rh₂Zn₁₁ are Hume-Rothery phases (Chapter 3.5) with cubic Cu₅Zn₈-type structure. Complex γ -brass related structures occur for Ir_{7+7 δ} Zn_{97-11 δ} ($0.31 \leq \delta \leq 0.58$) with partial Ir/Zn disorder [6], for Pt₂Zn_{11- δ} ($0.2 < \delta < 0.3$) and Y₁-Pt₅Zn₂₁ [7]. These phases belong to a large family of compounds which show similar cluster building units [6]. Even more complex is the situation for the solid solution Zn_{1-x}Pd_x ($0.15 < x < 0.25$) [8], where a set of distinct lattice parameters was observed for six different phases which are composed of intergrowths of γ -brass related cluster units.

ZrZn₂₂ [9] is one of the zinc-richest compounds. Its cubic structure contains four crystallographically independent zinc atoms. Only two of them coordinate to zirconium. The Zr@Zn₁₆ polyhedra are then embedded in a matrix of zinc atoms. MoZn_{20.44} [10] has slightly lower zinc content. Its complex cubic structure shows one site with substantial Mo/Zn mixing besides defects on the Zn₁₅ site. The electronic and crystal chemical reasons for this are not yet understood.

Binary rare earth and actinoid zinc compounds can roughly be subdivided into two groups. The zinc-poor phases adopt simple structures. Selected examples are ScZn₂ (UHg₂ type), YZn and PrZn (CsCl type), LaZn₅ (CaCu₅ type), ThZn₂ (AlB₂ type), or ThZn₄ (BaAl₄ type). Several of these structure types form with many of the rare earth atoms. Again, with higher zinc content larger unit cells and more complex structures form. As examples, YZn₁₂ (ThMn₁₂ type) and the two modifications of Th₂Zn₁₇ are presented in Fig. 3.128. The yttrium atoms in YZn₁₂ have coordination number 20. The Y@Zn₂₀ polyhedra are condensed *via* common square faces along the *c* direction. Neighboring rows are shifted by half the *c* axis with respect to each other and are connected *via* common corners. Using the Y@Zn₂₀ polyhedra as monomeric building unit, the YZn₁₂ structure can also be described as tetragonal body-centered packing of these polyhedra (compressed *bcc* packing). Besides Th₂Zn₁₇ and U₂Zn₁₇, also the whole series of RE₂Zn₁₇ intermetallics [11] has been investigated. The β -forms (rhombohedral Th₂Zn₁₇ type) can be obtained from the α -forms (hexagonal Th₂Ni₁₇ type) by heating upon a reconstructive phase transition. The thorium atoms in rhombohedral Th₂Zn₁₇ have the rare coordination number 19. These polyhedra are condensed *via* common hexagonal faces and the resulting dimers condense with neighboring ones *via* common rectangular faces. Two crystallographically independent thorium sites occur in hexagonal Th₂Zn₁₇. Th₂ has the smaller coordination number 18 in the form of hexagonal prisms that are capped by six zinc atoms on the rectangular faces. These Th₂@Zn₁₈ polyhedra are condensed along the *c* axis *via* common hexagonal faces. The Th₁ atoms have two additional zinc neighbors which

further cap the hexa-capped hexagonal prisms on the hexagonal faces. The Th1@Zn_{20} polyhedra share common rectangular faces with the Th2@Zn_{18} ones and common corners with the neighboring Th1@Zn_{20} polyhedra. This polyhedral presentation of the zinc-rich structures facilitates the description and comparison even of more complex structure types.

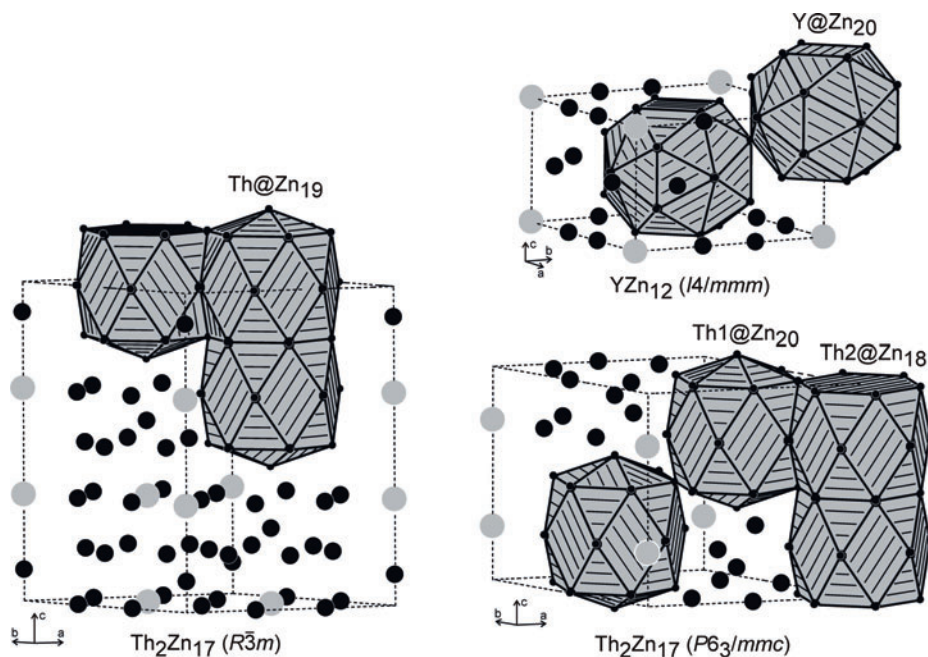


Fig. 3.128 The crystal structures of YZn_{12} and the two modifications of $\text{Th}_2\text{Zn}_{17}$. Yttrium (thorium) and zinc atoms are drawn as medium gray and black circles, respectively. The zinc polyhedra around yttrium and thorium are emphasized.

The zinc-rich phases of cerium and uranium have intensively been studied with respect to their physical properties. CeZn_{11} shows long-range antiferromagnetic ordering at 2.0 K [12], similar to UZn_{12} ($T_N = 5.0$ K) [13] and U_2Zn_{17} ($T_N = 9.7$ K) [14]. The enhanced Sommerfeld coefficients classify UZn_{12} and U_2Zn_{17} as heavy-fermion systems.

Besides the many binary intermetallics, zinc forms several ordered ternary compounds, either in combination with two chemically different transition metals or with a rare earth (actinide) and transition metal. Several equiatomic REZn compounds have been reported [15]. They crystallize with the structure types ZrNiAl or TiNiSi/KHg_2 . In these equiatomic compounds, zinc takes the position otherwise typically occupied by a group III, IV, or V element (Chapters 3.8–3.11). Zinc and the second transition metal build up three-dimensional networks in which larger cavities are filled by the rare earth elements. The ordering variants of the transition metals on the

networks are called the *coloring problem* [16]. Interesting equiatomic compounds are CeNiZn [17] with intermediate cerium valence, ferromagnetic EuAuZn [18], and the heavy-fermion phase YbPtZn [15b].

Ce_2RuZn_4 [19] is one of the outstanding ternary zinc compounds. It adopts a unique structure type (Fig. 3.129) with an ordering of trivalent cerium within Ce1@Zn_{12} and almost tetravalent cerium in $\text{Ce2@Ru}_2\text{Zn}_8$ polyhedra which are condensed *via* common rectangular faces. The Ce2 and ruthenium atoms form infinite linear chains with very short Ce2–Ru distances of 260 pm, much shorter than the sum of the covalent radii of 289 pm, in line with strong Ce–Ru bonding. Only the trivalent cerium atoms carry a magnetic moment and order antiferromagnetically at 2 K. Similar to CeRuSn (Chapter 3.9.4) Ce_2RuZn_4 belongs to a large family of intermetallics with short Ce–Ru bonds and intermediate-valent cerium.

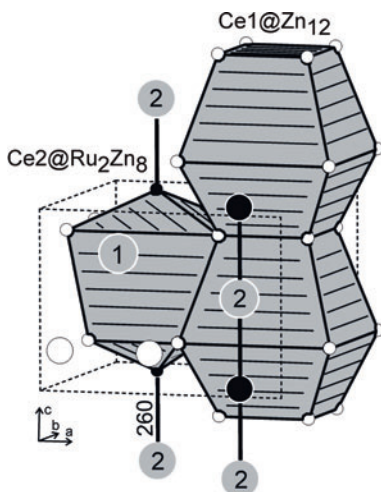


Fig. 3.129 The crystal structure of Ce_2RuZn_4 . Cerium, ruthenium, and zinc atoms are drawn as medium gray, black filled, and open circles, respectively. The zinc polyhedra around cerium and the infinite -Ce2-Ru-Ce2-Ru- chains (260 pm Ce–Ru) are emphasized.

The zinc substructure (four crystallographically independent zinc sites) of the $\text{RE}_2\text{Zn}_{17}$ intermetallics described above (Fig. 3.128) shows solid solutions $\text{RE}_2\text{Zn}_{17-x}\text{T}_x$ with different transition metals ($T = \text{Fe, Co, Ni, Rh, Pd, Pt}$) [20]. Well-shaped single crystals of such zinc-rich intermetallics are easily accessible by the zinc self-flux technique. Single crystal investigations showed completely ordered variants, *e. g.* $\text{Gd}_2\text{Co}_3\text{Zn}_{14}$, where only one site is fully occupied with cobalt, besides substantially mixed occupancies. The latter influence the magnetic ordering temperature, *e. g.* $T_N = 31.5 \text{ K}$ for $\text{Gd}_2\text{Co}_3\text{Zn}_{14}$ and $T_N = 28 \text{ K}$ for $\text{Gd}_2\text{Co}_{4.2}\text{Zn}_{12.8}$ [21]. Generally structural disorder leads to a decrease of the magnetic ordering temperature.

A very large series of more than 40 zinc-rich phases forms for compositions RET_2Zn_{20} and TT^*Zn_{20} with broad ranges of rare earth and transition metals [22]. Also, these phases easily form with the self-flux technique. These compounds crystallize with the cubic $CeCr_2Al_{20}$ -type structure, space group $Fd\bar{3}m$. Although the structure is quite complex with 184 atoms per unit cell, again one can easily describe it with symmetrical polyhedra. A view of the YRu_2Zn_{20} structure along the space diagonal is exemplarily presented in Fig. 3.130 The ruthenium atoms have icosahedral zinc coordination and the yttrium atoms have 16 zinc neighbors in Frank-Kasper coordination. Geometrically, the yttrium and ruthenium atoms occupy the same sites as the magnesium and copper atoms in the cubic Laves phase (Chapter 3.6). One can then describe the YRu_2Zn_{20} structure as a substitution variant of the Laves phase with $Y@Zn_{16}$ and $Ru@Zn_{12}$ polyhedra which are connected *via* common corners. This diamond-related symmetry is observed in many cubic structures with the same space group type.

The growth of well-defined single crystals allows direction dependent measurements of physical properties. Several of the RET_2Zn_{20} phases have intensively been studied with respect to their magnetic behavior. These phases are of special interest, since the rare earth and transition metal atoms are well separated through their Frank-Kasper polyhedra and one observes no direct $RE-RE$, $RE-T$, or $T-T$ contacts. Interesting representatives are the 86 K ferromagnet $GdFe_2Zn_{20}$ [23] and the heavy-fermion ferromagnet UIr_2Zn_{20} [24] with a Curie temperature of 2.1 K.

Cadmium is produced as a by-product mainly during zinc production, but also in the copper and lead purification processes. Due to its high heavy metal toxicity, cadmium is, with very few exceptions, no longer used in devices. Former applications were cadmium plating as corrosion protection and bearing metal, golden greenish Au–Cd alloys for jewellery, low melting alloys and additives for solders. Nevertheless, intermetallic cadmium compounds display very interesting structural chemistry and peculiar bonding patterns. This makes cadmium intermetallics an interesting topic in basic research. The main structural characteristics of these materials are presented in the following paragraphs.

Only few alkali metal cadmium compounds are reported. Lithium forms $LiCd$ which is isotypic with the Zintl phase $NaTl$; the cadmium atoms build up a diamond-analogous substructure. The situation is much more complicated for the Na–Cd system. The compound with the simple composition $NaCd_2$ crystallizes with the diamond-related space group $Fd\bar{3}m$, but with a huge unit cell parameter of 3056 pm and approximately 1192 atoms in the unit cell! The structure determination of this phase is the merit of *Sten Samson* who developed a model of packing maps [25] for the solution of complex cubic structures already in 1964. Some years later an alternative description of this structure based on Friauf polyhedra was published by the *Andersson* group [26]. Another complex phase is $Na_{26}Cd_{141}$ [27] which is closely related to the ternary stannide $Y_{13}Pd_{40}Sn_{31}$. The potassium compound $K_{0.4}Cd_2$ [27] has a zeolite-related cadmium substructure with large channels that are partially filled with potassium

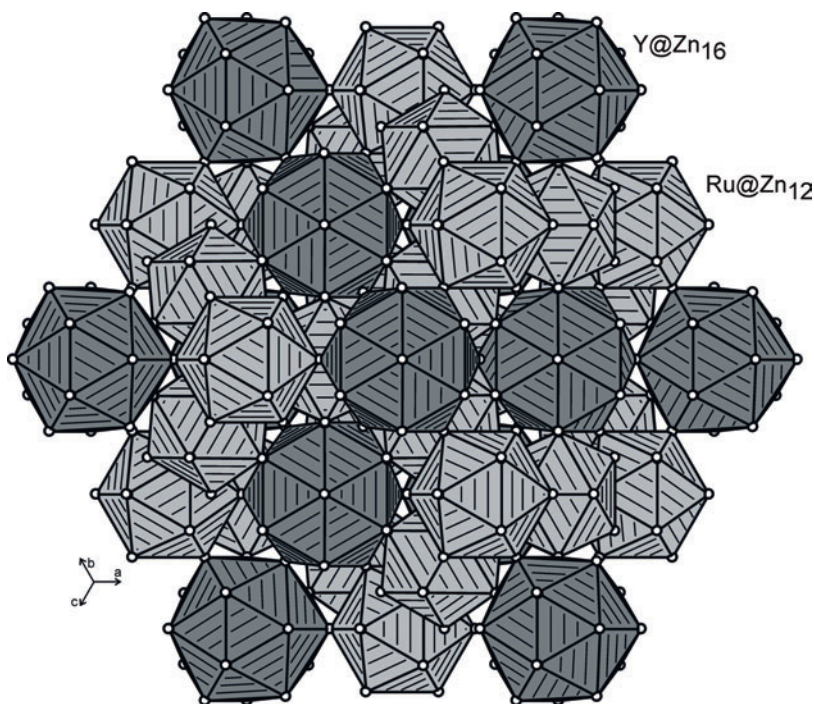


Fig. 3.130 The crystal structure of $\text{YRu}_2\text{Zn}_{20}$ viewed along the space diagonal. The Y@Zn_{16} (medium gray) and Ru@Zn_{12} (light gray) polyhedra are emphasized.

atoms. The cadmium-rich phases ACd_{13} with K, Rb, and Cs crystallize with the cubic NaZn_{13} type (*vide ultra*).

Similar to the zinc intermetallics discussed above, also the cadmium-poor alkaline earth compounds adopt simple, highly symmetric structure types, e. g. Mg_3Cd (own type), Ca_3Cd_2 (Zr_3Al_2 type), or Ba_2Cd (Zr_2Cu type). The cadmium-rich phases are characterized by high coordination numbers around the alkaline earth element. SrCd_{11} and BaCd_{11} are isotypic, space group $I4_1/amd$ (Fig. 3.131). The alkaline earth atoms have coordination number 18. These polyhedra are condensed *via* common corners and faces. Only Cd1 and Cd3 of the three crystallographically independent cadmium sites are part of the alkaline earth coordination sphere. The Cd2 atoms have exclusively cadmium neighbors, forming Cd2@Cd_{10} polyhedra. Also ternary variants of the BaCd_{11} type are known, however, not with cadmium. So far only ternary copper and silver aluminides have been reported with this structure type.

The cadmium-poor transition metal compounds form typical structures that derive from the close packed arrangements or other simple, highly symmetric binary structure types. Representative examples are Zr_2Cd (Zr_2Cu type), ZrCd_3 (stuffed Cu_3Au type), V_3Cd (Cr_3Si type), NbCd_3 and Pt_3Cd (Cu_3Au type), or Au_3Cd (ZrAl_3 type). Nickel forms the binary phases NiCd and NiCd_5 with complex cubic structures. The latter is

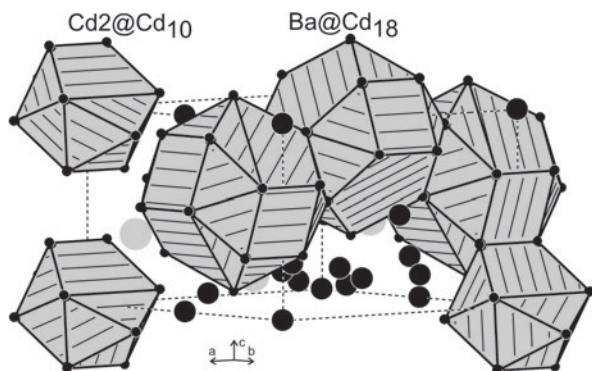


Fig. 3.131 The crystal structure of BaCd_{11} . The Ba@Cd_{18} and $\text{Cd}_2\text{@Cd}_{10}$ polyhedra are emphasized.

still used in rechargeable Ni-Cd accumulators. With higher cadmium content Hume-Rothery phases like $\text{Pd}_2\text{Cd}_{11}$ and Cu_5Cd_8 with Cu_5Zn_8 -type structure form.

The phase diagrams $\text{RE}-\text{Cd}$ have intensively been investigated by metallography and differential thermal analyses [28]. In the cadmium-poor region several phases structurally resemble the zinc compounds discussed above. Representative examples are ScCd and NdCd (CsCl type) or ScCd_3 (Mg_3Cd). In the cadmium-rich portions of the $\text{RE}-\text{Cd}$ phase diagrams several phases $\text{RE}_{13}\text{Cd}_{58}$, $\text{RE}_2\text{Cd}_{17}$, $\text{RE}_{11}\text{Cd}_{45}$, and RECd_{11} with comparatively complex structures form for many of the rare earth elements. Scandium as the smallest rare earth metal deviates from this series. It forms a cadmium-rich compound of composition ScCd_7 [29]. In contrast to the structures discussed above, the coordination number around scandium decreases as a consequence of the small atom size. As emphasized in Fig. 3.132, the ScCd_7 structure (space group Cmcm) is a dense packing of Sc@Cd_{12} and $\text{Cd}_4\text{@Cd}_{10}$ polyhedra which are condensed *via* common corners and faces.

The RECd_6 phases show very large cubic unit cells [30]. They crystallize with the body-centered space group $\text{Im}\bar{3}$. Disordered Cd_4 tetrahedra are located within dodecahedra. These building units have an icosidodecahedron as a next shell, followed by a defect triacontahedron. These RECd_6 phases are 1/1 quasicrystal approximants (Chapter 3.18). Even more complicated is the structure of $\text{Eu}_4\text{Cd}_{25}$ [31]. It is a superstructure of the RECd_6 type upon doubling the unit cell in all three directions, leading to the huge unit cell parameter of 3187 pm. The superstructure formation arises due to partial ordering of the Cd_4 tetrahedra, resulting in two types of triacontahedra which show an *fcc* packing motif.

Besides the interesting crystal chemistry, binary cadmium intermetallics have also been investigated with respect to their magnetic properties. Especially the cerium containing phases were of interest when searching for new heavy-fermion materials [32]. CeCd_2 and CeCd_3 order antiferromagnetically below 20 and 2 K, respectively, while CeCd_6 and $\text{Ce}_{13}\text{Cd}_{58}$ remain paramagnetic down to 1.3 K. UCd_{11} with BaCd_{11} -type

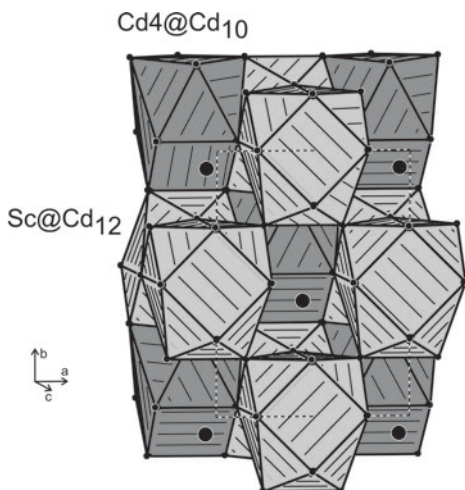


Fig. 3.132 The crystal structure of ScCd_7 . The Sc@Cd_{12} and $\text{Cd}_4\text{@Cd}_{10}$ polyhedra are emphasized. The coordination polyhedra around the Cd_4 atoms in front of the unit cell are not drawn.

structure [33] is a heavy-fermion material that orders antiferromagnetically at 5 K. Single crystals of UCd_{11} were grown from excess molten cadmium.

Several of the ternary phase diagrams $\text{RE}-\text{T}-\text{Cd}$ have been studied with respect to compound formation and the investigation of structures and physical properties. Although such compounds will never find application due to their cadmium content, these materials are very interesting model compounds in basic research [34]. Synthesis of such cadmium intermetallics suffers from the comparatively low boiling point of cadmium (1038 K) and all reactions need to be performed in sealed high-melting metal tubes, e. g. Nb, Ta, or Mo.

The crystal chemistry of the $\text{RE}_x\text{T}_y\text{Cd}_z$ phases depends on their composition. Similar to the zinc intermetallics, also with cadmium a lot of equiatomic phases RETCd with TiNiSi - or ZrNiAl -type structure have been synthesized. The transition metal and cadmium atoms build up covalently bonded three-dimensional $[\text{TCd}]$ networks in which the rare earth atoms fill larger cavities. These structures exclusively contain isolated cadmium atoms, i. e. no Cd–Cd bonding. Several other structures show interesting cadmium substructures. In the metal-rich compounds EuCu_9Cd_2 [35] and EuAu_4Cd_2 [36] one observes segregation of the cadmium atoms into Cd_2 pairs and infinite chains, respectively (Fig. 3.133). The Cd–Cd distances of 273 and 286 pm in these two substructures are significantly shorter than in *hcp* cadmium (6×298 and 6×329 pm), indicating strong Cd–Cd bonding. A three-dimensional cadmium network occurs in LaPdCd_2 [37]. Each cadmium atom has distorted tetrahedral cadmium coordination with Cd–Cd distances ranging from 307–334 pm. This cadmium substructure is closely related to the hexagonal modification of diamond, lonsdaleite. The most remarkable motif concerns the isolated Cd_4 tetrahedra which occur in three series of

compounds, RE_4TCd , $RE_{23}T_7Cd_4$, and $RE_{15}Rh_5Cd_2$ [38]. These three series are structurally closely related. The transition metal atoms are located in RE_6 trigonal prisms and the latter are condensed *via* common edges and corners, leading to different three-dimensional networks in which cavities are filled by the Cd_4 tetrahedra. The Cd–Cd bond lengths in the tetrahedra depend on the size of the rare earth element in the RE_4TCd , $RE_{23}T_7Cd_4$, and $RE_{15}Rh_5Cd_2$ series.

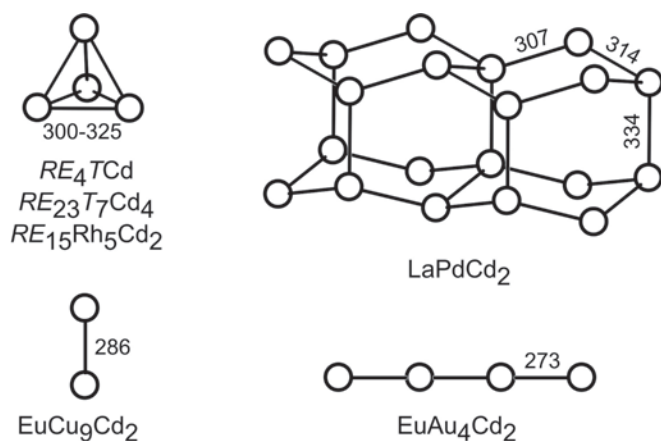


Fig. 3.133 The cadmium substructures in several $RE_xT_yCd_z$ intermetallics. Relevant interatomic distances are indicated.

The structural chemistry of $RE_xT_yCd_z$ intermetallics is closely related to $RE_xT_yIn_z$. Several isotopic compounds are known and in some cases complete solid solutions $Cd_{1-x}In_x$ are possible. In those cases, T –Cd is always weaker than T –In bonding, also observed for corresponding magnesium phases. Several $RE_xT_yCd_z$ intermetallics display interesting magnetic properties. Representative examples are the intermediate-valent compound $Ce_{23}Ru_7Cd_4$ [39] and the 110 K ferromagnet Gd_2Au_2Cd [40]. The solid solutions between cadmium and indium or magnesium and indium, respectively, lead to an increase of the valence electron count and thus influence the magnetic ground states [41].

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3.14 Amalgams

Mercury is the only metallic element that is liquid at room temperature. Although it is toxic and no longer used for broad applications, the basic research on mercury compounds is still an active and fruitful field for the understanding of structure-property relationships [1–3]. Dental amalgams and the chlor-alkali electrolysis are among the last of today's applications.

The alkali and alkaline earth metals, zinc, cadmium, copper, silver, and gold show considerable solubility in liquid mercury. Especially the gold amalgams have long-time been used for gold extraction (amalgam process) and fire gilding. Other elements like molybdenum, manganese, iron, and cobalt are almost insoluble in liquid mercury. That is why iron containers are used for mercury transport. If only small amounts of metals are dissolved in mercury the amalgams keep liquid. With increasing metal content they become viscous and then solid. The reaction of the alkali metals with mercury is accompanied by a substantial reaction heat and in the case of sodium the amalgams are already solid with > 1.5 % sodium content. The alkali amalgams and those of aluminum and zinc are excellent reducing agents. Depending on the type of metal dissolved in mercury, the amalgams have different colors. The silver- and tin-based dental amalgams keep the silvery lustre while the alkali metal amalgams become golden or bronze-golden colored solids.

Although one might think of extended solid solutions for the diverse amalgams, those of the alkali and alkaline earth metals are mostly stoichiometric compounds with small phase widths. These compounds are extremely sensitive to moisture. They readily react with traces of water, liberating mercury and forming alkali hydroxide solutions. Since the alkali and alkaline earth elements have much smaller electronegativity than mercury, one observes a charge transfer to the mercury atoms (partially anionic mercury), leading to brittle compounds. The charge transfer is also expressed in increased melting temperatures for the binary compounds, e. g. 552 K for KHg_2 . The stability and reactivity of the sodium amalgams has been tested in liquid ammonia [4]. It is possible to extract sodium from the alkali metal-rich amalgams. The mercury-rich phases NaHg_2 and NaHg_4 are insoluble in liquid NH_3 .

Some representative structures of binary alkali metal amalgams are presented in Fig. 3.134. LiHg adopts the simple CsCl-type structure with a cubic coordination for

both metal sites. A clustering of the mercury atoms is observed in the mercury-rich amalgam LiHg_3 . The mercury atoms build up rows of face-sharing $\text{Hg}_{6/2}$ octahedra which extend in c direction and form the motif of hexagonal rod-packing. The rows are separated from each other via the lithium atoms. The Li–Hg distances of 285 pm in LiHg and 300 pm in LiHg_3 are comparable. The $\text{Hg}_{6/2}$ octahedra are slightly compressed with 300 and 313 pm Hg–Hg distances.

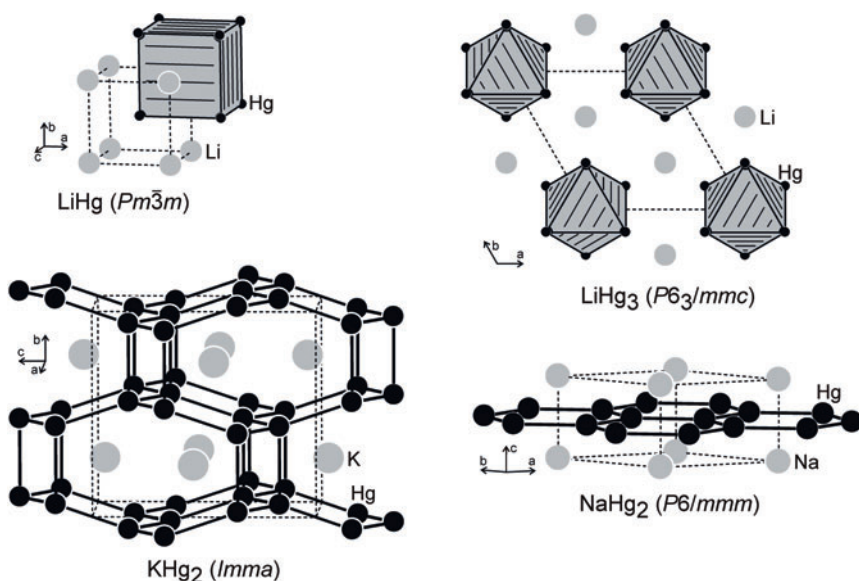


Fig. 3.134 The crystal structures of LiHg , LiHg_3 , KHg_2 , and NaHg_2 .

The structures of AHg_2 ($A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) [5] derive from the AlB_2 type. The mercury atoms in NaHg_2 form planar hexagons with Hg–Hg distances of 290 pm. This structural arrangement readily reminds the well-known AlB_2 structure, however, there are distinct differences in chemical bonding. The very large mercury atoms enforce a larger a axis. Consequently, in order to keep the bonding forces, the c axis needs to collapse and one observes a c/a ratio of 0.64, much smaller than in AlB_2 . Keeping these differences in mind one should call the structural relationship between NaHg_2 and AlB_2 isopointal [6, 7] rather than isotypic. For a further discussion of the pairs $\text{UHg}_2/\text{AlB}_2$ and $\text{CeCd}_2/\text{EuGe}_2$ we refer to a review article [8]. A planar Hg_6 network is no longer possible with the larger potassium atoms. In the KHg_2 structure (a prototype with several hundred binary and ternary representatives) the Hg_6 hexagons are puckered and the structure shows an orthorhombic distortion with a range of Hg–Hg distances from 300–308 pm. NaHg_2 and KHg_2 are related by a group-subgroup relation [8].

With increasing mercury content, the amalgam structures become more and more complex. As an example we present the KHg_{11} structure [9] in Fig. 3.135. The potassium atoms have twenty mercury neighbors and these K@Hg_{20} polyhedra are condensed to a three-dimensional network *via* common edges. An additional mercury atom that is not bonded to a potassium atom is located at the origin of the unit cell. These atoms and the center of gravity of the K@Hg_{20} polyhedra show the structural motif of the Cu_3Au type, an ordered version of the *fcc* arrangement (Chapter 3.3). The Hg–Hg distances within the complex network range from 296 to 318 pm, almost similar to KHg_2 .

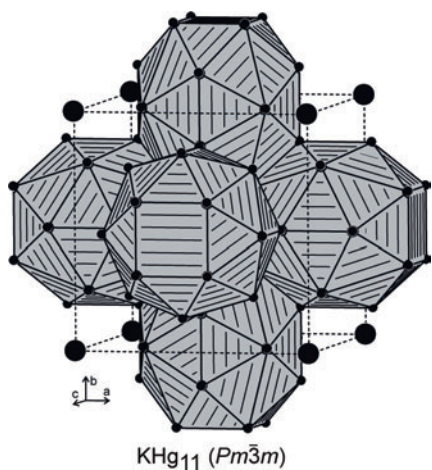


Fig. 3.135 The crystal structure of KHg_{11} . The K@Hg_{20} polyhedra are emphasized.

Further mercury-rich amalgams of the heavier alkali metals have compositions A_3Hg_{20} ($\text{A} = \text{Rb}, \text{Cs}$), K_3Hg_{11} , $\text{Cs}_5\text{Hg}_{19}$, and A_7Hg_{31} ($\text{A} = \text{K}, \text{Rb}$) [10]. All these phases have distinctly different crystal structures, although their $\text{A}:\text{Hg}$ ratios are quite similar. The mercury-richest amalgam, $\text{Cs}_2\text{Hg}_{27}$ [11], has been synthesized by electrolyzing a solution of CsI in *N,N*-dimethylformamide on a mercury electrode. A similar preparation technique has been used for the growth of high quality dendritic crystals of the sodium amalgam $\text{Na}_{11}\text{Hg}_{52}$ [12]. This amalgam is closely linked to the chlor-alkali electrolysis. $\text{Na}_{11}\text{Hg}_{52}$ as the mercury-richest sodium amalgam is dissolved in large amounts of excess mercury in the Castner cells. It crystallizes with a huge hexagonal unit cell of $a = 3970.3$ and $c = 968.1$ pm.

Most of the transition metal amalgams crystallize with classical structure types. Six representative structures are shown in Fig. 3.136. Similar to LiHg , also MnHg adopts the CsCl -type structure. The hafnium-rich amalgam Hf_2Hg (MoSi_2 type) adopts an ordered version of MnHg . Three cubic subcells are stacked in *c* direction and the hafnium-mercury coloring leads to a mercury-centered Hf_8 cube in the middle of the

unit cell and to two hafnium-centered Hf_4Hg_4 cubes. The difference in size between hafnium and mercury leads to an elongation of the cubes and the c/a ratio is 3.44. Cubic coordination occurs also in PtHg_4 . The platinum atoms are located in ideal Hg_8 cubes which share common corners. Since the faces of the cubic cell are not occupied with platinum atoms, one can describe the PtHg_4 structure also as a defect CsCl structure, where every fourth mercury cube is occupied by platinum in an ordered manner. In the same way one can describe the CaF_2 type as an ordered defect variant of CsCl by removing half of the cations, again in an ordered manner.

ZrHg_3 crystallizes with the Cu_3Au type with complete zirconium-mercury ordering. Each zirconium atom has cuboctahedral mercury coordination. The Hg-Hg distances of 309 pm within the cuboctahedral shell correspond to the ones observed for the alkali metal amalgams. Ti_3Hg adopts the Cr_3Si type. This structure has already been discussed for the superconductor Nb_3Sn (Chapter 3.9.4). An interesting and also rare structure occurs for Mn_2Hg_5 . It consists of a two-dimensional mercury network that can be described as a tessellation of triangles, squares, and pentagons. These networks (295–300 pm Hg-Hg) are stacked in an AA sequence and the manganese atoms fill the pentagonal prismatic voids. This structure type also occurs for some transition metal gallides and indides.

Silver, zinc, and copper are the main transition metals in dental amalgam. Powders of these three elements are separately filled with mercury in capsules and freshly mixed before use. The resulting amalgam has silvery color. It is viscous and can me-

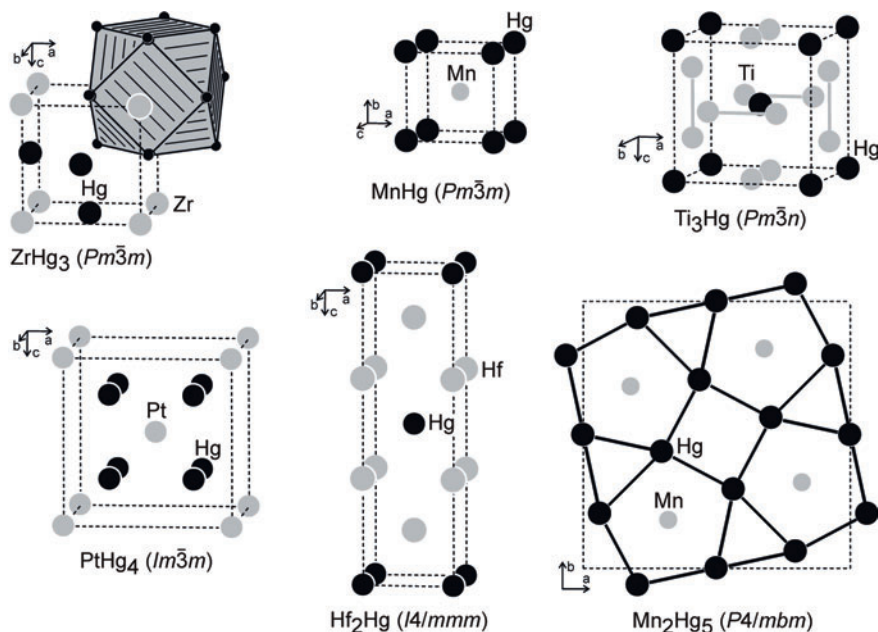


Fig. 3.136 The crystal structures of ZrHg_3 , MnHg , Ti_3Hg , PtHg_4 , Hf_2Hg , and Mn_2Hg_5 .

chanically be treated in order to fill a tooth cavity before it hardens rapidly. X-ray studies revealed that Ag_3Sn , Ag_2Hg_3 , and the $\gamma_2(\text{Sn-Hg})$ phase are important components in such dental amalgams [13].

The rare earth elements form numerous amalgams. Important general compositions are REHg , REHg_2 , REHg_3 , $\text{RE}_{11}\text{Hg}_{45}$, $\text{RE}_{10}\text{Hg}_{42}$, and $\text{RE}_{14}\text{Hg}_{51}$. Thorium forms Th_2Hg and ThHg_3 and uranium $\text{U}_{11}\text{Hg}_{45}$ and UHg_2 besides a broad range of a solid solution with magnesium-type structure. The area of ternary rare earth-transition metal amalgams is only scarcely investigated. So far only the ZrNiAl -type compounds REPdHg ($\text{RE} = \text{La, Ce, Pr, Sm, Gd}$) [14] as well as $\text{Pr}_6\text{Fe}_{13}\text{Hg}$ and $\text{Nd}_6\text{Fe}_{13}\text{Hg}$ [15] have been reported. These phase diagrams have a large potential for new compounds.

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3.15 Aurides and Platinides

Gold and platinum have the by far largest electron affinities of all metals in the periodic system of the elements. This is caused by relativistic effects [1], because the velocity of electrons near the highly charged nuclei reaches a significant fraction of the speed of light. Thus their mass increases and the radii of the s - and p -orbitals decrease. Additionally, spin-orbit coupling becomes significant, and instead of the angular momentum l and spin momentum s their sum $j = l + s$ has to be taken into account. These are so-called direct relativistic effects. Furthermore, the contracted s - and p -shells screen the nuclear attraction more efficiently, and one obtains a relativ-

istic expansion and destabilization of *d*- and *f*-shells. These direct and indirect effects are large enough to cause substantial chemical differences between the elements of the 6th period and the lighter homologues. One is the above-mentioned electron affinity, which amounts to 223 kJ/mol for gold and 205 kJ/mol for platinum. Negatively charged species like the auride- (Au^-) and platinide-anions (Pt^{2-}) are therefore intrinsically stable. They have a rich structural chemistry with a large number of binary and ternary compounds which have been studied intensively.

Cesium auride CsAu with the CsCl-type structure [2] is among the best known compounds with negatively charged gold. Its semiconducting properties are in line with the charge separation Cs^+Au^- [3, 4], which classifies cesium auride as a salt-like compound which is actually not the focus of this book. However, a large number of metallic aurides and platinides have been reported. In this chapter we present some selected examples in order to give an idea about the interesting crystal chemistry. Among the binary alkali aurides are the compounds A_2Au_3 ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$; own structure type), KAu_5 (CaCu_5 type), NaAu_2 (MgCu_2 type), Na_2Au (CuAl_2 type), and Rb_3Au_7 (own structure type). Fig. 3.137 shows the structures of K_2Au_3 , KAu_5 , and Rb_3Au_7 .

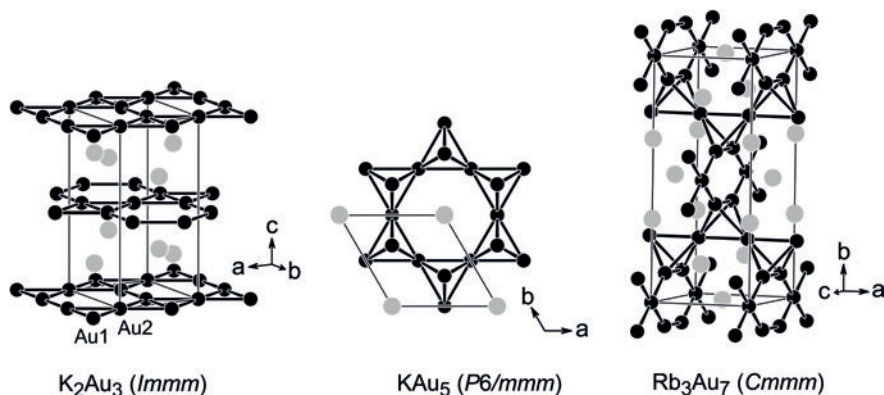


Fig. 3.137 Crystal structures of K_2Au_3 , KAu_5 , and Rb_3Au_7 . Gold atoms are drawn as filled black circles, alkali metals as gray circles. The intermetallic gold networks are emphasized.

K_2Au_3 has a layered structure with two crystallographically different gold atoms. The gold layers can be considered as chains of Au1 atoms (277 pm Au1–Au1) parallel to the *b* axis which are connected through Au2 atoms (280 pm Au1–Au2). KAu_5 crystallizes in the hexagonal CaCu_5 -type structure. Trigonal bipyramids are connected *via* common corners thus forming a three-dimensional network of gold atoms (277–283 pm Au–Au) with potassium atoms in hexagonal channels along the *c* axis (see also Fig. 3.126). This is one of the most common structure types of binary intermetallics with more than 1000 entries in Pearson's database, and closely related to the Laves phases (Chapter 3.6, Fig. 3.14). The structure of Rb_3Au_7 likewise contains building blocks of

the Laves phase MgCu_2 , namely corner-sharing tetrahedra of gold atoms (275–283 pm Au–Au) which form layers in the ac plane. These are connected through gold atoms with fourfold planar coordination (263 pm Au–Au). An overview about binary alkali metal aurides has been given by Zachwieja [5].

Among the aurides with alkaline earth metals we mention MgAu (CsCl type), BaAu_2 (AlB_2 type), BaAu (FeB type), CaAu (CrB type), CaAu_2 (KHg_2 type), and CaAu_5 (Be_5Au type). Rare earth elements also form many aurides like REAu (FeB type, $\text{RE} = \text{La–Eu, Yb}$), REAu_2 (KHg_2 type with $\text{RE} = \text{La–Eu}$; MoSi_2 type with $\text{RE} = \text{Gd–Lu}$), REAu_3 (Cu_3Ti type, $\text{RE} = \text{Sm, Gd–Lu}$), and REAu_4 (MoNi_4 type, $\text{RE} = \text{Ho–Lu}$). As examples we show the structures of CaAu , DyAu_2 , DyAu_3 , and ErAu_4 in Fig. 3.138.

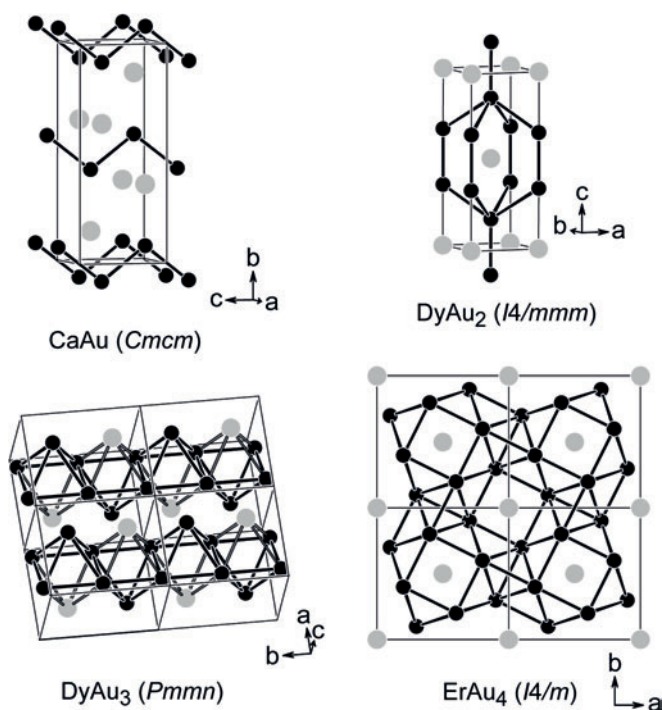


Fig. 3.138 The crystal structures of CaAu , DyAu_2 , DyAu_3 , and ErAu_4 . Gold atoms are drawn as filled black circles, calcium, dysprosium, and erbium as gray circles. The intermetallic gold networks are emphasized.

CaAu with the orthorhombic CrB-type structure contains gold zigzag chains (289 pm Au–Au) separated by calcium atoms. The almost complete charge transfer from calcium to gold according to $\text{Ca}^{2+}\text{Au}^{2-}$, as well as the polar metallic character of CaAu has been demonstrated by DFT band structure calculations [6]. The compounds REAu_2 crystallize in the KHg_2 -type structure (see Fig. 3.134) with $\text{RE} = \text{La–Eu}$, and

in the tetragonal MoSi_2 -type structure with $RE = \text{Gd-Lu}$. DyAu_2 with the MoSi_2 -type structure is shown in Fig. 3.138. Gold atoms are bonded to five neighbors ($4 \times 309 \text{ pm}$, $1 \times 283 \text{ pm Au-Au}$) and form capped square prisms around the dysprosium atoms. DyAu_2 is antiferromagnetic at low temperatures with two magnetic transition temperatures $T_N(\alpha) = 33.8 \text{ K}$ and $T_N(\beta) = 25.0 \text{ K}$ and has a complex incommensurable spin structure determined by neutron scattering [7]. DyAu_3 contains formally Au^- and the structure (Cu_3Ti type) may be described as chains of $\text{DyAuAu}_{4/2}$ octahedra condensed *via* common edges (Fig. 3.138). ErAu_4 with the MoNi_4 -type structure contains chains of face-sharing $\text{Au}_{8/2}\text{Au}_4$ cuboctahedra parallel to the c axis (295 pm , 297 pm Au-Au) [8]. In summary, the binary aurides with electropositive metals often exhibit typical structures of intermetallic compounds, and no concrete relationship is obvious between the electronic configuration and the connectivity of gold in the $(\text{Au}^{\delta-})_n$ polyanions.

Among ternary aurides many compounds with formally Au^- or with negatively polarized ('auridic') gold exist. Examples for the first group are $\text{Rb}_2\text{Au}_3\text{Tl}$ [9] and $\text{Ca}_3\text{Au}_3\text{In}$ [10] according to $(\text{Rb}^+)_2(\text{Au}^-)_3\text{Tl}^+$ and $(\text{Ca}^{2+})_3(\text{Au}^-)_3\text{In}^{3-}$. However, the crystal structures shown in Fig. 3.139 reveal that the assignment of charges is not as straightforward as it seems (and is actually not reasonable) because both compounds have crystallographically different gold atoms with different coordination. $\text{Rb}_2\text{Au}_3\text{Tl}$ contains chains of corner-sharing tetrahedra along the a axis (279 pm or 283 pm Au-Au), separated by Rb and Tl atoms. In $\text{Ca}_3\text{Au}_3\text{In}$ we find gold zigzag chains similar to those in CaAu (compare Fig. 3.138) but also isolated gold atoms. Both are in channel-like cavities of the calcium and indium partial structure parallel to the b axis as emphasized in Fig. 3.139. Pairs of corner-sharing gold tetrahedra occur in the rhombohedral structure of the compounds $\text{A}_4\text{Au}_7\text{X}_2$ ($A = \text{K, Rb, Cs}$; $X = \text{Ge, Sn}$) [11, 12]. These Au_7 clusters are connected *via* X_2 dumbbells. Each X atom has three bonds to gold and one to the neighboring X atom, and it has been argued that no charge transfer occurs from the alkali metal to X ($X^{\pm 0}$), but rather to the gold atoms which have auridic character.

An interesting class of compounds are oxide aurides recently reviewed by Jansen [13]. CsAu reacts with Cs_2O at 573 K quantitatively to the oxide auride Cs_3AuO with a hexagonal perovskite-type structure. The analog compounds Rb_3AuO and K_3AuO crystallize in the cubic perovskite-type structure. The auride anions are surrounded by twelve alkali metal cations in both cases (Fig. 3.140). Cs_3AuO is a yellow transparent semiconductor in agreement with $(\text{Cs}^+)_3\text{Au}^-\text{O}^{2-}$, while the rubidium and potassium compounds are black opaque due to smaller band gaps. The auride subnitride Ca_3AuN also crystallizes with the cubic perovskite-type structure and is metallic [14].

The perovskites A_3AuO form when gold reacts with an excess of heavy alkali metals and the corresponding alkali metal oxides. If less alkali metal is used, the mixed auride aurates $\text{A}_7\text{Au}_5\text{O}_2$ ($A = \text{Rb, Cs}$) form, thus elemental gold disproportionates to Au^- and Au^+ . The compounds contain linear $[\text{AuO}_2]^{3-}$ groups and isolated Au^- anions surrounded by alkali metal ions. The structure of $\text{Cs}_7\text{Au}_5\text{O}_2$ is shown in Fig. 3.140. Cs_3AuO_2 and CsAu slabs are stacked along the c axis, thus the structure is reminiscent

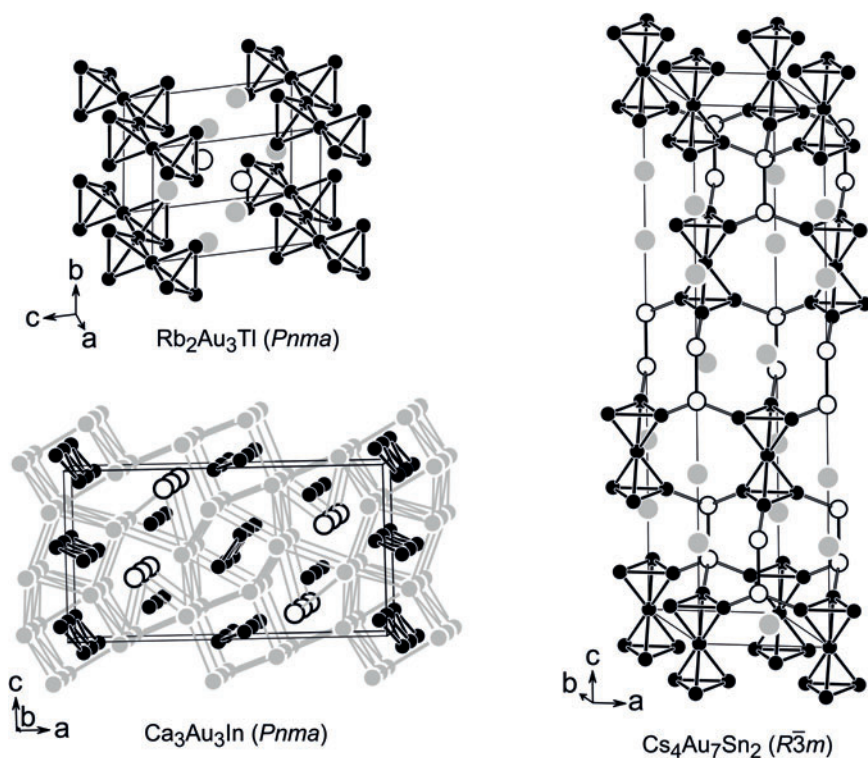


Fig. 3.139 Ternary aurides: The crystal structures of $\text{Rb}_2\text{Au}_3\text{Tl}$, $\text{Ca}_3\text{Au}_3\text{In}$, and $\text{Cs}_4\text{Au}_7\text{Sn}_2$. Gold atoms are drawn as filled black circles, calcium, cesium, or rubidium as gray circles, tin or thallium as white circles. The intermetallic gold networks are emphasized.

to CsCl type CsAu , with one out of five cubes filled by AuO_2 instead of single Au atoms. The coexistence of Au^+ and Au^- in $\text{Cs}_7\text{Au}_5\text{O}_2$ has been verified by ^{197}Au -Mössbauer spectroscopy and quantum chemical calculations [15].

As mentioned at the outset of this chapter, platinum has the second highest electron affinity among the transition metals, thus negatively charged $\text{Pt}^{\delta-}$ species are expected to be stable. Binary platinides with formally Pt^{2-} are Li_2Pt (UHg_2 type), Cs_2Pt (Ni_2In type), and BaPt (NiAs type), however, only Cs_2Pt [16] is transparent to visible light suggesting a complete charge transfer, while the other platinides are metallic [17–19]. Further examples are LiPt (LiRh type), NaPt_2 and BaPt_2 (MgCu_2 type), Ba_3Pt_2 (Er_3Ni_2 type), Ba_2Pt (CdCl_2 type), and BaPt_5 (CaCu_5 type). Among the various patterns of Pt–Pt bonding, Pt_2 pairs occur for instance in Y_5Pt_4 (274 pm Pt–Pt), while $\infty[\text{Pt}]$ chains have been observed in BaPt (270 pm Pt–Pt), SnPt (272 pm), Tl_2Pt (278 pm), and Li_2Pt (266 pm). Examples with rare earth elements are REPt (CrB type, $\text{RE} = \text{La–Nd}$), REPt_2 (MgCu_2 type, $\text{RE} = \text{Y, La–Yb}$), and CePt_5 (CaCu_5 type, $\text{RE} = \text{La–Nd}$). The crystal structures of some alkali platinides and BaPt are depicted in Fig. 3.141.

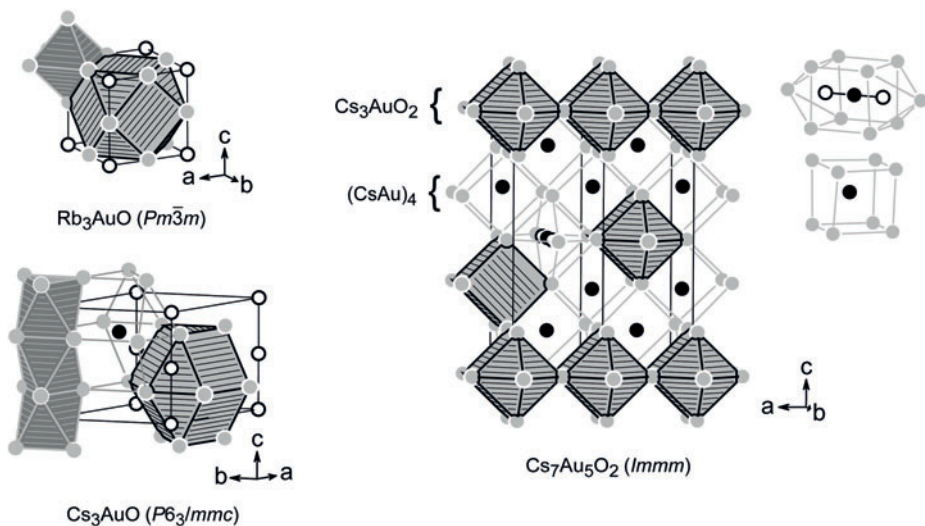


Fig. 3.140 Oxide aurides: The crystal structures of Rb_3AuO , Cs_3AuO , and $\text{Cs}_7\text{Au}_5\text{O}_2$. Gold atoms are drawn as filled black circles, cesium or rubidium as gray circles, and oxygen as white circles.

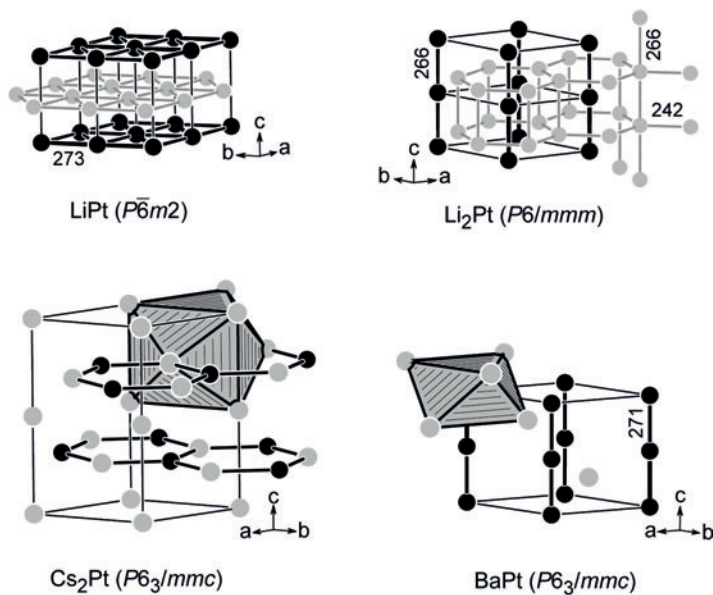


Fig. 3.141 Binary platinides: The crystal structures of LiPt , Li_2Pt , Cs_2Pt , and BaPt . Platinum atoms are drawn as filled black circles, lithium, cesium, or barium as gray circles. The numbers are atomic distances in pm.

The structure of LiPt is a simple hexagonal packing of alternating platinum and lithium layers. The Pt–Pt distance of 273 pm within the hexagonal layers is shorter than in *bcc* platinum metal (278 pm), which suggests strong quasi-two-dimensional Pt–Pt bonding. Li₂Pt forms the UHg₂-type structure which is a variant of the common AlB₂ type. Here the *c* axis is quite short and results in linear ∞^1 [Pt] chains (266 pm Pt–Pt). Also, the bonds within the lithium hexagons (242 pm Li–Li) are much shorter when compared with *bcc* lithium metal (296 pm). The electronic structure of lithium platinides has been studied by DFT methods [18]. It was suggested that the electron configuration of platinum in these compounds is close to $5d^{10}$, and the electrons released from the lithium atoms are delocalized. However, this appears counterintuitive when the higher electronegativity of platinum is taken into account. Moreover, the authors show that the platinum 6s states are almost filled and below the 5d, which strongly suggests negatively polarized platinum. This has been found undoubtedly in BaPt with the NiAs-type structure [20]. The *c* axis is strongly contracted (*c/a* = 1.072 instead of 1.333 in the ideal NiAs-type structure). This leads to ∞^1 [Pt] chains with Pt–Pt distances of 271 pm, which are not as short as in Li₂Pt (266 pm), but nevertheless strong homonuclear bonds are present in the platinum chains of BaPt. Complete charge separation occurs in Cs₂Pt according to band structure calculations and also because of its dark red transparent color. The crystal structure is shown in Fig. 3.141. The Ni₂In-type structure is formed with Pt₃Cs₃ hexagons (328 pm Pt–Cs) stacked along the *c* axis and separated by layers of cesium atoms. The coordination of platinum is completed by six additional cesium atoms (402 pm Pt–Cs), thus the coordination number is nine and the cesium neighbors form a tricapped trigonal prism.

Many ternary compounds are known with negatively polarized platinum. This is expected if both other components are less electronegative than platinum, or if more electrons are released by an electropositive component than the electronegative atom other than platinum can accept. The former is for instance the case in Ce₂Pt₂In [21] with the Mo₂B₂Fe-type structure (Fig. 3.142), which is quite common in intermetallics with more than 200 representatives. Ce₂Pt₂In contains Pt₂ dimers (285 pm Pt–Pt) and may formally be written as (Ce³⁺)₂(Pt²⁻)₂In²⁻ because platinum is significantly more electronegative than indium. This situation is similar in many ternary platinum compounds with a third component from the groups 13 and 14 (except carbon). In the compounds REPt₂X (*X* = Sn, RE = Gd, Tb, Er, Tm, Y, U; *X* = In, RE = Gd–Ho, U) with the hexagonal LiCu₂Sn-type structure, platinum forms a fourfold connected three-dimensional network (299 pm, 301 pm Pt–Pt) analogous to hexagonal diamond (lonsdaleite) filled with the rare earth and tin or indium atoms. Fig. 3.142 shows the structure of ErPt₂Sn as an example [22].

Orthorhombic Ca₃Pt₂Ga₂ [23] is an example where the assignment as platinide is not straightforward. Platinum is trigonal planar coordinated by gallium and forms a three-dimensional network (Fig. 3.142). If we consider gallium as the most electronegative component, we formally get (Ca²⁺)₃(Pt⁰)₂(Ga³⁻)₂. However, it is clear that such a charge separated description is certainly not appropriate for this metallic material, and only a detailed analysis of the electronic structure can reveal the bonding situation.

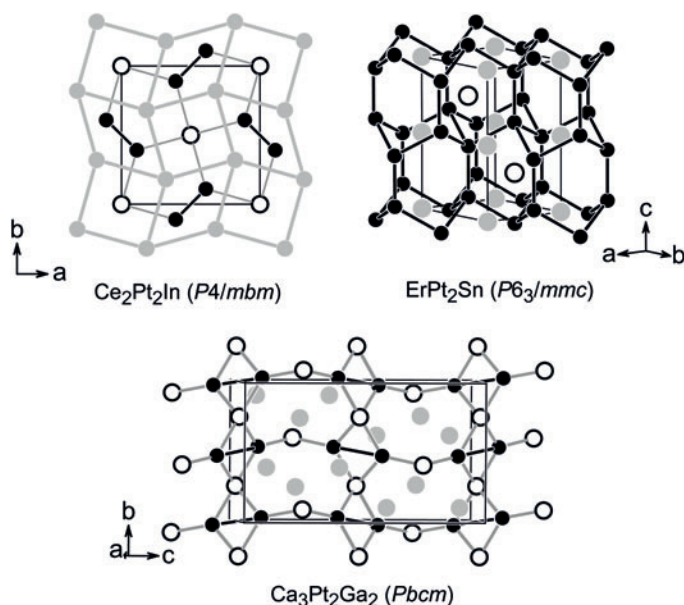


Fig. 3.142 Ternary platinumides: The crystal structures of $\text{Ce}_2\text{Pt}_2\text{In}$, ErPt_2Sn , and $\text{Ca}_3\text{Pt}_2\text{Ga}_2$. Platinum atoms are drawn as filled black circles, cerium, erbium, and calcium as gray circles and indium, tin, or gallium as white circles.

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3.16 Hydrides

Generally hydrides are differentiated into three different categories, *i. e.* salt-like, covalent, and metallic hydrides. The salt-like, ionically bonded hydrides are formed with the alkali and alkaline earth metals. The alkali metals (*A*) react with hydrogen, forming the transparent AH hydrides with rock salt structure. Magnesium hydride MgH_2 crystallizes with the rutile structure, while the heavier alkaline earth (*AE*) elements form dimorphic hydrides AEH_2 . They crystallize with the orthorhombic $PbCl_2$ -type structure at low and with the cubic fluorite-type, structure at high temperatures. These hydrides are all sensitive to moisture and the hydride anions react with protons releasing hydrogen, $H^+ + H^- \rightarrow H_2$ and the corresponding metal hydroxides. The hydride anion shows large polarizability and thus enables the formation of ionic hydrides with alkali and alkaline earth cations with largely differing radii. Furthermore, many ternary salt-like hydrides with two different cations are known, *e. g.* $KMgH_3$, K_2MgH_4 , $LiSrH_3$, or $LiEuH_3$. The crystal chemistry of ionically bonded hydrides very much resembles fluoride chemistry.

Beryllium shows different bonding peculiarities. BeH_2 is a covalently bonded hydride. Each beryllium atom has tetrahedral hydrogen coordination and forms chains of *trans*-edge-sharing tetrahedra, a structural motif also present in SiS_2 and the Zintl phase K_2SiP_2 (Chapter 3.7). Many other *p* elements form molecular, covalently bonded hydrides, however, these compounds are out of the scope of the present chapter. Most of these hydrides are well-known textbook examples [1].

In contrast to the alkali and alkaline earth metal hydrides which are line compounds, transition and rare earth metal hydrides show extended homogeneity ranges. These elements can dissolve small amounts of hydrogen in tetrahedral or octahedral voids. As long as these hydrides keep the metal substructure one may call them interstitial hydrides. Typical boundary compositions are $VH_{0.05}$, $NbH_{0.11}$, or $TaH_{0.22}$. Increasing the hydrogen content the packing of the metal atoms changes. Three different compositions can be discussed. With one hydrogen atom per metal (*M*) atom one obtains the composition MH . The hydrogen atoms fill octahedral voids of the metal substructure. This is the well-known arrangement of the rock salt type. Many hydrides MH and defect monohydrides MH_{1-x} are known. With composition MH_2 the hydrides adopt the fluorite type, but again, homogeneity ranges MH_{2-x} occur. Such hydrides

are known for the group 3–6 transition metals. Typical phase widths are $\text{TiH}_{1.0-2.0}$ or $\text{HfH}_{1.7-2.0}$. Already in the mono- and di-hydrides it is possible that both kinds of voids are partially filled.

With increasing hydrogen content the maximum uptake is at composition MH_3 . This corresponds to the Li_3Bi type with all tetrahedral and octahedral voids filled by hydrogen. This structure is generally observed for rare earth hydrides, except scandium, europium, and ytterbium. ScH_2 , EuH_2 , and YbH_2 are almost stoichiometric compounds. The scandium atoms are most likely too small to allow for further hydrogen uptake. In EuH_2 the europium atoms are in a stable divalent state. EuH_2 shows no further hydrogen uptake up to a pressure of 41 bar. YbH_2 is not that stable and shows hydrogen uptake up to $\text{YbH}_{2.55}$. For the trivalent rare earth elements one also observes extended homogeneity ranges, e. g. compositions like $\text{LaH}_{1.85}$ or $\text{LaH}_{2.90}$ frequently occur.

Since most of the hydrides have extended homogeneity ranges, it is difficult to determine the exact hydrogen content. Many hydrogenation devices allow for direct measurement of volume changes. Another useful technique is X-ray powder diffraction because hydrogen uptake increases the lattice parameters. One can thus precisely determine the lattice parameter as a function of the hydrogen uptake. The most precise way is full oxidation of the sample in an oxygen atmosphere and titrimetric analyses of the resulting water with the Karl-Fischer method [2].

Hydrogenation reactions are not uniform. Mostly, one observes kinetic hindrance and hydrogen is absorbed after a certain period of latency. This hindrance can be due to surface impurities, size of the surface, etc. In some cases hydrogenation already starts under ambient conditions, while other systems need slight heating or even moderate hydrogen pressure.

One of the best analyzed binary systems is Pd–H. *Fcc* palladium absorbs up to one equivalent of hydrogen comparatively fast. The activation energy for hydrogen mobility is only 22 kJ/mol. Starting from $\text{PdH}_{0.8}$ the samples become superconducting with a maximum transition temperature of 9 K for PdH. The different velocity of hydrogen and deuterium diffusion through palladium metal foils can be used for H/D separation. Pioneering work in this field originates from the Wicke group [3].

Metallic substructures are interesting as storage materials for hydrogen. Generally hydrogen can be stored in gaseous or liquid form, or as a metal hydride. For gaseous hydrogen storage pressures of 200 bar are the material's limit. Storage of liquid hydrogen is well known, but the low boiling point of 20.4 K and the low density of 0.071 g/l are not favorable. The alternatively used solid hydrogen storage systems are safe, they allow for hydrogen densities similar to the liquid (or even higher), there is no loss during storage, and the storage is reversible.

Although many binary metal hydrides have intensively been studied, only few have good capability for reversible hydrogen storage. Most hydrides show unfavorable thermodynamics and kinetics. In some cases the metal-to-hydrogen ratio is too small, other compounds show formation of hydrides with high hydrogen content, however, with irreversible desorption. Important parameters for classification of a compound as suitable

hydrogen storage material are not too high heats of formation and a reasonable plateau pressure. In that view, LaNi_5 (CaCu₅ type) and FeTi (CsCl type) are good candidates, especially since they have a low density. Their heat of hydride formation is around 30 kJ/mol with plateau pressures of 2.9 (LaNi₅) and 5 bar (FeTi), respectively. Both intermetallics absorb one hydrogen atom per metal atom, leading to the ternary hydrides LaNi_5H_6 and FeTiH_2 . A severe problem of the hydrides is the drastic change of the cell volume upon hydrogenation, a mechanism that is similar to lithium battery materials (Chapter 4.4). For LaNi_5 the space group symmetry is reduced from $P6/mmm$ to $P31m$ for LaNi_5H_6 and the cell volume increases by about 25 %. Both FeTi and LaNi_5 are already used for diverse technical applications. FeTi and LaNi_5 should be considered as ideal compositions. Mostly, these materials are alloyed in order to enhance their sorption kinetics. Especially for LaNi_5 mostly the less expensive cerium mischmetall (CMM) is used instead of pure lanthanum. These alloys are also used in rechargeable nickel-metal-hydride batteries.

As an example for a typical hydrogen storage material we present the structure of FeTi and its fully deuterated form FeTiD_2 in Fig. 3.143. The CsCl-type unit cell of FeTi has a cell volume of 0.026 nm³ which increases to 0.031 nm³ (~20 %) per FeTi subcell for FeTiD_2 . The FeTi structure has six compressed octahedral voids per cell, however, only two of them are occupied in an ordered manner. The FeTiD_2 cell contains eight occupied voids, $2 \times \text{Fe}_4\text{Ti}_2$ and $6 \times \text{Fe}_2\text{Ti}_4$. These octahedra share common edges and corners, leading to the network emphasized in Fig. 3.143. Since the apices of the octahedra point to different directions, one observes significant displacements of the iron and titanium atoms off the subcell positions.

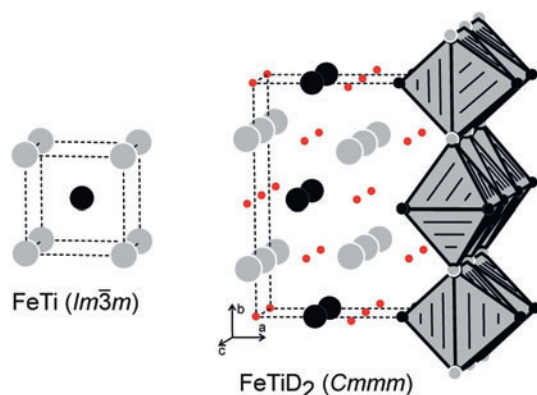


Fig. 3.143 The crystal structures of FeTi and FeTiD_2 . Iron, titanium, and hydrogen atoms are drawn as black, medium gray and red circles, respectively. The network of condensed, deuterium-centered Fe_2Ti_4 and Fe_4Ti_2 octahedra is emphasized.

The search for new hydrogen storage materials still is an active field. A current overview on the crystal chemistry and bonding peculiarities of this class of compounds

was given in a topic issue of *Z. Kristallogr.* [4] and a review article [5]. As soon as large quantities of non-fossil hydrogen (e. g. *via* electrolyses using solar energy) are available, hydrogen will be a safe and ecologically lasting energy source. A problem to overcome for the present materials is the sensitivity against gas impurities. Good sorption-desorption cycle stability is only guaranteed with pure hydrogen. Traces of carbon monoxide and water significantly decrease the storage capacity.

Many ternary intermetallic compounds with complex structures show hydrogen absorption. This leads to both changes in the structure and the physical properties. Many intermetallic cerium and uranium compounds have been studied in order to investigate the hydrogen induced changes of magnetic properties. Even small quantities of hydrogen can induce drastic changes. Only 0.2 equivalents of hydrogen drift the intermediate-valent antimonide CeRhSb to tri-valent CeRhSbH_{0.2} [6] with a Néel temperature of 3.6 K. Many other equiatomic cerium compounds have been studied with respect to such property changes [7]. These compounds keep their metallic behavior also in the hydrogenated form.

An interesting situation was observed with the magnesium-based compounds LaNiMg₂ [8] and La₂Ni₂Mg [9] which form hydrides LaNiMg₂H₇ [10] and La₂Ni₂MgH₈ [11]. While the ternary intermetallic compounds are metals, semiconducting behavior occurs in the hydrides. For both compounds one observes formation of hydridometallate anions with Ni–H distances ranging from 149 to 171 pm. Since lanthanum and magnesium deliver more valence electrons than are needed for formation of the electron-precise hydridometallate anions, additional hydride anions are located in tetrahedral voids of the lanthanum-magnesium substructure. In LaNiMg₂H₇ one observes [NiH₄]⁴⁻ tetrahedra (Fig. 3.144), while [Ni₂H₇]⁷⁻ dimers and [Ni₄H₁₂]¹²⁻ tetramers occur in La₂Ni₂MgH₈, leading to the electron-precise formulations LaNiMg₂H₇ ≡ La³⁺ + 2Mg²⁺ + [NiH₄]⁴⁻ + 3H⁻ and 4La₂Ni₂MgH₈ ≡ 8La³⁺ + 4Mg²⁺ + [Ni₄H₁₂]¹²⁻ + 2[Ni₂H₇]⁷⁻ + 6H⁻. Thus one obtains transitions from intermetallics to electron-precise Zintl phases where the transition metal atoms obey the 18-electron rule. For Ce₂Ni₂Mg one observes a change from intermediate-valence behavior to a non-magnetic strongly correlated electron system in Ce₂Ni₂MgH₈ [12]. All of these compounds show distinct volume increase up to 25 % upon hydrogenation. Quaternary hydrides have been synthesized also with the ZrCuSiAs-type structure [13, 14] with interesting parallels to the field of pnictide oxide superconductors (Chapter 4.2).

Electron-precise hydridometallates have been observed with a variety of ternary alkali and alkaline earth metal hydrides. These ternary systems have intensively been studied by the groups of Bronger and Yvon [15]. The synthesis of these hydridometallates is often accompanied by severe problems. Special CORALLOY 4668 autoclaves are needed in order to allow temperatures up to 900 K and hydrogen pressures up to 5500 bars. Most syntheses only yield powder samples, a massive complication for the solution of the crystal structures. In many cases, the hydrides show crystal chemistry comparable to fluorides and at least the metal sites can be deduced from laboratory X-ray powder data. The hydrogen positions can then be determined from

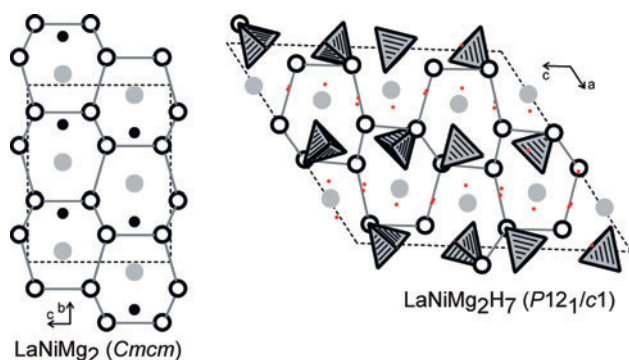


Fig. 3.144 Projections of the LaNiMg₂ and LaNiMg₂H₇ crystal structures along the short unit cell axis. Lanthanum, nickel, magnesium, and hydrogen atoms are drawn as medium gray, black filled, black open and red circles, respectively. The NiH₄ tetrahedra in LaNiMg₂H₇ are emphasized. The magnesium atoms are connected by medium gray lines in order to facilitate comparison of both structures.

high-resolution neutron diffraction data of the corresponding deuterides. The number of crystallographically independent hydrogen sites can also be deduced from ¹H solid state NMR spectroscopy and hints for hydrogen mobility can be obtained through line narrowing experiments. The unequivocal determination of the hydride structures often relies on a combination of different complementary techniques. The high-pressure preparations lead to different, also higher oxidation state of the transition metals. Some selected compounds are listed in Table 3.4.

Table 3.4 Selected alkali- and alkaline earth-transition metal hydrides.

Group VII	Group VIII	Group IX	Group X
K ₃ MnH ₅	Mg ₂ FeH ₆	Mg ₂ CoH ₅	Mg ₂ NiH ₄
K ₂ TcH ₈	Ca ₂ RuH ₆	Na ₃ RhH ₆	CsPdH ₃
K ₂ TcH ₉	Sr ₂ RuH ₆	Sr ₂ RhH ₅	Na ₂ PdH ₄
K ₂ ReH ₉	Mg ₂ OsH ₆	Li ₃ IrH ₆	Li ₂ PtH ₂
BaReH ₉	Na ₃ OsH ₇	Ca ₂ IrH ₅	Na ₂ PtH ₄

In the ternary compounds one observes complex hydridometalate polyanions even of transition metals that do not form stable binary hydrides. In a matrix of large A⁺ or AE²⁺ cations it is possible to stabilize these polyanions with a gain of lattice energy. As an example the structures of the high- and low-temperature modifications of K₂PtD₄ [16] are shown in Fig. 3.145. Due to high hydrogen mobility at room temperature, the hydrogen atoms show hopping and cannot be located. HT-K₂PtD₄ crystallizes with the K₂PtCl₆ type with a 4/6 occupancy of the chlorine site by deuterium. The 15 K neutron diffraction data then revealed deuterium ordering, *i. e.* square-planar [PtD₄]²⁻

units, the typical coordination for d^8 systems. This lock-in phase shows tetragonal symmetry and the $[\text{PtD}_4]^{2-}$ units are aligned along the ab diagonals.

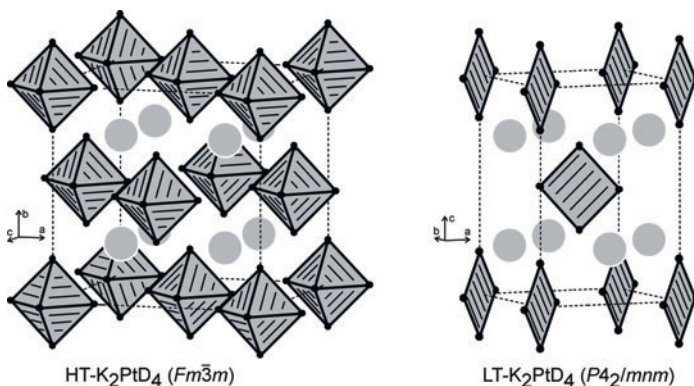


Fig. 3.145 The crystal structures of the high- and low-temperature modifications of K_2PtD_4 . The statistically occupied PtD_6 octahedra (4/6 D) in $\text{HT-K}_2\text{PtD}_4$ and the square-planar PtD_4 units in $\text{LT-K}_2\text{PtD}_4$ are emphasized.

Complex hydrides of the main group elements with low density are in the focus as reversible hydrogen storage materials [17]. Especially NaAlH_4 is discussed as one of the promising materials.

Finally we need to draw back to the possibility of hydrogen as an impurity component in solid state synthesis. Especially the heavier alkaline earth metals might contain hydrogen as trace impurity and synthesis with such precursors often results in very small yields of a product. Such examples are $\text{Ca}_5\text{Sb}_3\text{H}$ [18], $\text{Ba}_5\text{Ga}_6\text{H}_2$ [19], and $\text{Ba}_{21}\text{Ge}_2\text{O}_5\text{H}_{24}$ [20].



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3.17 Classification/Hierarchy

Since the first attempts for structure determination by X-ray film data a huge number of intermetallic structures has been determined and this number is still rapidly growing due to today's extremely efficient scattering and data acquisition techniques. The systematization and understanding of these structures is the main challenge of chemists, metallurgists, and crystallographers in order to avoid data graveyards.

In the *Strukturberichte/Structure Reports* (today continued as the open access journal *Acta Crystallographica E*), starting in 1931, the structure types were assigned letters, *i. e.* A for elements (monoatomic structures), B for AB compounds, C for AB₂ compounds, D for A_mB_n compounds, E for more complex structures and so on. The running numbers for the structure types were then assigned in historical order of the study of the structure. However, this classification scheme readily found its limitations. A striking example is the A15 structure type, wrongly assigned to β -W, which indeed was W₃O (Chapter 3.11.1). Nevertheless, the *Strukturberichte* notation is still used for selected compounds. A selection of structure types is given in [1].

Today, crystal structure data are submitted electronically to collecting agencies, *e. g.* the *Cambridge Crystallographic Data Center* or the *Fachinformationszentrum Karlsruhe*. The data are assigned to depository numbers under which they are available. These data are then transferred to different electronic data bases. So far, more than 240,000 entries occur in *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds* [2], the data base that is relevant for intermetallic compounds. This data base has efficient search routines. Important key points for a given structure are the Pearson symbol, the space group number and the Wyckoff sequence, *e. g.* tI10, 139, *eda* for BaFe₂As₂ or oS16, 63, *fc*² for the S-phase precipitate MgCuAl₂. Us-

ing this basic information, it is readily possible to see whether or not the compound crystallizes with an unknown structure type or, if related entries occur in the data base, it is easy to get sufficient crystal chemical information for comparison.

Nature tries to use simple building units and prefers highly symmetric structures. Thus, one finds many isotypic representatives for simple structure types. An overview of statistics/distributions for frequent binary structure types is given by *Ferro and Saccone* [3]. This building principle is often violated, since radii differences or bonding peculiarities do not allow for the highest possible symmetry. In those cases deviations from high symmetry are mostly small and one can still find similar packing motifs.

In the data bases there exist several entries which are regrouped for a given structure type. The structure type assignment is based on the space group number and the Wyckoff sequence. This purely statistical classification does not consider the different elements occupying the Wyckoff sites nor changes in the lattice parameters. To give an example, NaCl, GdSe, and TiC are listed with the rock salt structure although these three compounds have distinctly different bonding patterns and physical properties. The extreme differences are ionic bonding for NaCl and the use of TiC as hard material. Keeping these differences in mind, one should call the relationship between such structures rather isopointal than isotypic. Many similar examples have been summarized by *Parthé* and coworkers [4].

For space group 62 (*Pnma*) and the Wyckoff sequence c^3 one finds data base entries for assigned structure types PbCl_2 (~280), Co_2Si (~170), and TiNiSi (~1100). These more than 1500 phases belong to a large family of compounds with largely differing element combinations and thus varying bonding patterns. Both, composition and bonding properties lead to large changes in the lattice parameters, which are a crystal chemical variable in the orthorhombic system. This huge number of phases has been regrouped according to their axis ratios [5], leading to different islands in a structure field pattern. Only compounds lying within a certain island are directly comparable and can be called isotypic. Such bonding variabilities occur in many other families of intermetallic compounds.

More complex crystal structures can often be explained by simpler structural motifs, if one considers larger structural fragments as building units. A well-known textbook example from the crystal chemistry of salts is the $\text{K}_2[\text{PtCl}_6]$ type. Considering the $[\text{PtCl}_6]^{2-}$ octahedra as building unit, the structure can be considered as an *anti-fluorite* type with the $[\text{PtCl}_6]^{2-}$ octahedra building a *fcc* pattern and all potassium atoms in the tetrahedral voids. A similar description is possible for molecules. C_{60} bucky balls adopt the *fcc* structure at low temperature, just substituting every Cu site with a C_{60} molecule. This very illustrative kind of description has already been used for the structures of CaB_6 and UB_{12} in Chapter 3.8.1. Also the zinc-rich phase NaZn_{13} (Chapter 3.13) can be described this way. The ZnZn_{12} icosahedra and the sodium atoms formally are arranged in a CsCl-related pattern. In the complex structure of $\text{Mo}_7\text{Sn}_{12}\text{Zn}_{40}$ [6], the CsCl-related pattern is similar, but the building units are $\text{Mo}_{13}\text{Zn}_{42}$ Mackay polyhedra [7] and $\text{MoZn}_{14}\text{Sn}_{14} \equiv \text{Mo}(\text{Zn}_{12})(\text{Mo}_{12}\text{Zn}_{30})$ units with a two-shell coordination. Such de-

scriptions by larger polyhedral units or clusters facilitate the understanding of complex structure types. Even the complex binary phases Cu_4Cd_3 [8–10] and $\beta\text{-Mg}_2\text{Al}_3$ [11, 12] can be explained by packings of Friauf polyhedra (truncated tetrahedra). For further examples and additional descriptions of such complex phases we refer to overviews [10, 12–19, and refs. cited therein].

Another approach to describe complex structures of intermetallic compounds is the concept of intergrowth structures [20–27], where segments of simple structure types are the typical building units. As an example the structures of $\text{Gd}_2\text{Ni}_2\text{In}$ and $\text{Lu}_5\text{Ni}_2\text{In}_4$ are presented in Fig. 3.146. Both structures can be described as intergrowth variants of slightly distorted AlB_2 - and CsCl-related slabs. Although this description is a purely geometrical one, it is extremely efficient in order to distinguish different structure types. Further examples for AlB_2 /CsCl intergrowth variants are presented in [28]. Typical slabs for such intergrowth variants derive from the simple structure types AlB_2 , W/CsCl, $\text{CaCu}_5/\text{CeCo}_3\text{B}_2$, $\alpha\text{-Fe}$, Cu_3Au , $\alpha\text{-Po}$, or BaAl_4 and their ternary derivatives. This way one can geometrically describe dozens of structure types.

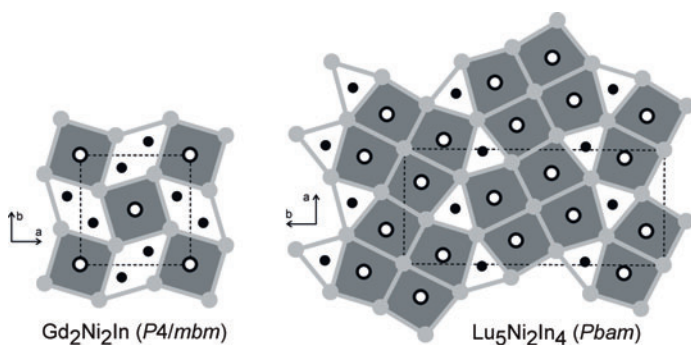


Fig. 3.146 The crystal structures of $\text{Gd}_2\text{Ni}_2\text{In}$ and $\text{Lu}_5\text{Ni}_2\text{In}_4$. Rare earth, nickel, and indium atoms are drawn as light gray, black filled and open circles, respectively. The AlB_2 - and CsCl- (shaded in medium gray) related slabs are emphasized.

The approaches to discuss and classify complex intermetallics presented above rely on geometrical arguments. A group theoretical approach based on group-subgroup relationships is presented in the following. The schemes that are shown in the following figures are based on the Bärnighausen concept [29, 30]. The tools for constructing the so-called Bärnighausen trees are available from the International Tables A1 [31] and a book by *Ulrich Müller* [32]. In the present chapter we focus on selected examples for intermetallic compounds. For details concerning the group theoretical background we refer to the literature [29–32]. To start we present the group-subgroup scheme for the structure types tungsten and cesium chloride in Fig. 3.147.

Tungsten crystallizes with the *bcc* type (Chapter 3.1), space group $Im\bar{3}m$. The W atoms lie on Wyckoff position $2a$. An ordering of two atoms on the tungsten sites is

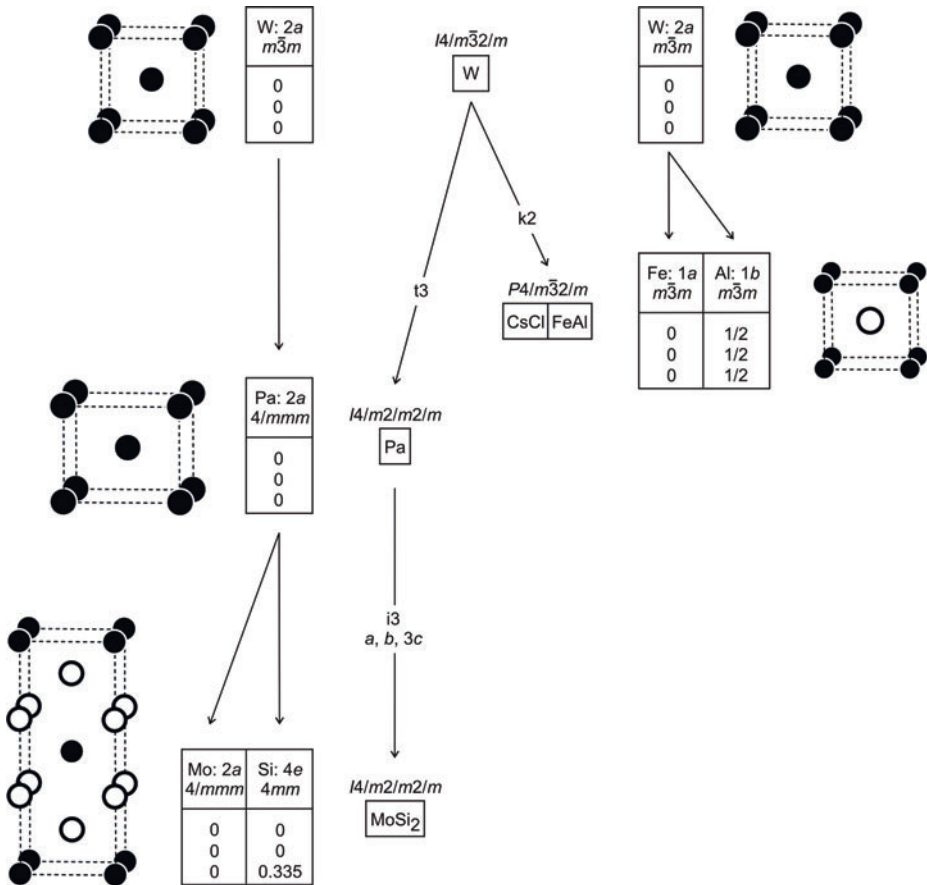


Fig. 3.147 Group-subgroup relation for the structures of W (aristotype), CsCl (FeAl), Pa, and MoSi₂. The indices for the *translationengleiche* (t), *klassengleiche* (k) and isomorphic (i) transitions are given together with the evolution of the atomic parameters.

only possible by lowering the space group symmetry, *i. e.* splitting of the twofold site into two onefold sites. The simplest way to do so is the de-centering of the lattice and one obtains the onefold sites $1a$ and $1b$ in space group $Pm\bar{3}m$. Thus, CsCl (and FeAl as an example for an intermetallic compound) has a primitive structure. Due to the *klassengleiche* symmetry reduction both onefold sites keep their site symmetry, but the site multiplicity is reduced. Furthermore, the *klassengleiche* symmetry reduction leads to superstructure (*primitive*) reflections in the X-ray diffraction patterns.

Also the protactinium structure belongs to this family. Due to its peculiar electronic structure, protactinium does not crystallize with the cubic W type, but with a compressed version. The space group symmetry is reduced from $Im\bar{3}m$ to $I4/mmm$ via a *translationengleiche* symmetry reduction of index 3. The change of the crystal system leads to a lower site symmetry for the protactinium atoms. An ordering of two

different atoms in this structure type is possible for an equiatomic compound in space group $P4/mmm$, corresponding to a compressed tetragonal version of a CsCl-related arrangement. For a general composition AB_2 an ordering is only possible in a tripled unit cell *via* an isomorphic transition of index 3 from $I4/mmm$ to $I4/mmm$, generating a two- and a fourfold site. This is realized for the $MoSi_2$ type. The following example (Fig. 3.148) shows derivatives of the *fcc* structure.

The ordered closest packings have been discussed in detail in Chapter 3.3. Coloring of the *fcc* arrangement with two or more different atoms inevitably leads to lower space group symmetry. In the case of ordered Cu_3Au a *klassengleiche* symmetry reduction of index 4 leads to a de-centering of the lattice and a splitting of the fourfold site into a one- and a threefold site, enabling the copper-gold ordering. Also the ordering variants $CuAu$ and $MoNi_4$ [32] belong to this Bärnighausen tree. A more complex ordering pattern occurs for the platinum-rich compound $CuPt_7$ which also derives from

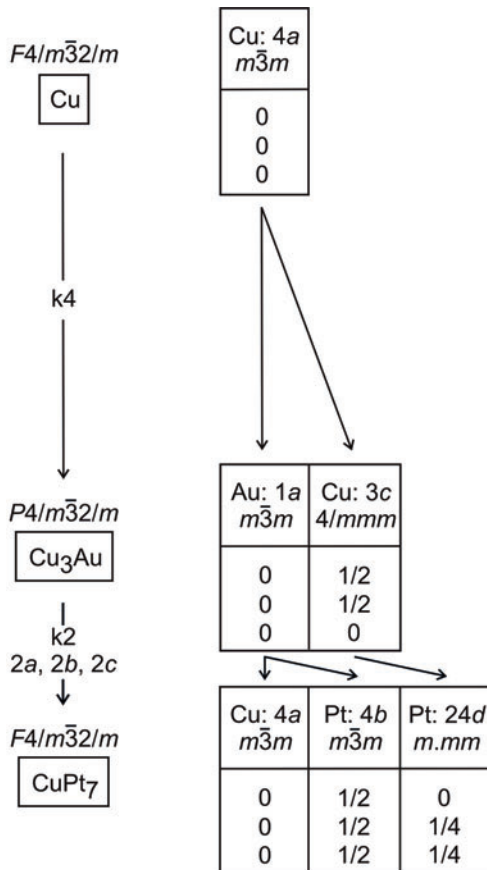


Fig. 3.148 Group-subgroup relation for the structures of Cu (aristotype), Cu_3Au , and $CuPt_7$. The indices for the *klassengleiche* (k) transitions are given together with the evolution of the atomic parameters.

a cubic closest packing. The 1:7 ratio cannot be realized in the small unit cell. Here one observes doubling of all three unit cell parameters and the space group symmetry is reduced from $Pm\bar{3}m$ (Cu_3Au) to $Fm\bar{3}m$ for CuPt_7 via a *klassengleiche* transition of index 2. This structure type has been discussed in Chapter 3.9.3 for Ca_7Ge .

The third example concerns ordered variants of the BaAl_4 type. More than 2500 entries for compounds of this structural family occur in the Pearson database [2]. Most compounds crystallize with the ThCr_2Si_2 -type structure which is a ternary ordered derivative of BaAl_4 (Chapter 3.8.2). Both crystallographically independent aluminum sites are ordered in ThCr_2Si_2 . A change in composition requires a symmetry reduction. As an example we present the structure of BaNiSn_3 . Since a 1:3 ordering is not possible in the high space group symmetry, splitting of one fourfold Wyckoff site is necessary. This can be realized by a *translationengleiche* symmetry reduction of index 2 from $I4/mmm$ to $I4mm$ (Figure 3.149). This corresponds to a loss of the inversion symmetry. Such a *translationengleiche* symmetry reduction just changes the subcell intensities in a diffraction experiment. The whole Bärnighausen tree for the BaAl_4 superstructures comprises some 20 structure types [33].

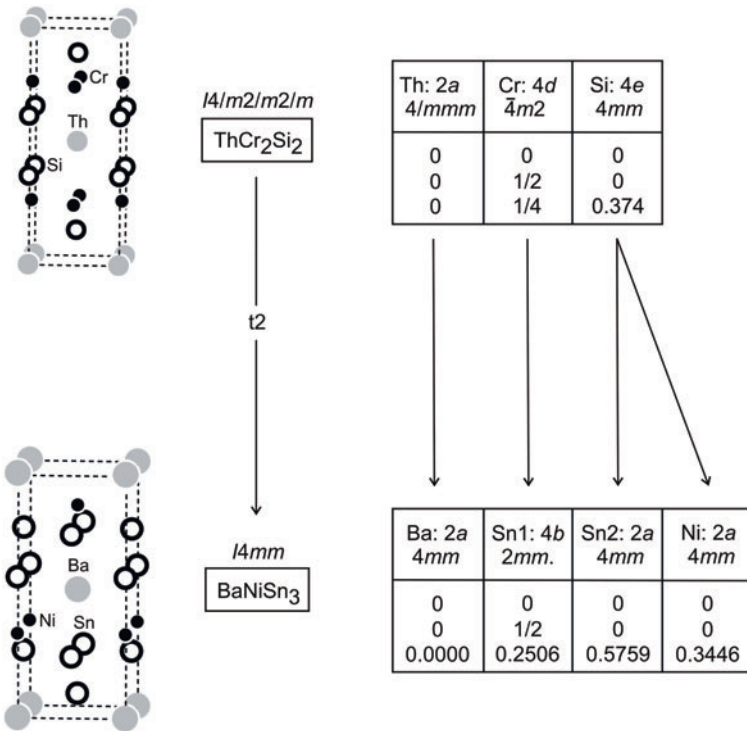


Fig. 3.149 Group-subgroup relation for the structures of ThCr_2Si_2 and BaNiSn_3 . The index for the *translationengleiche* (t) transition is given together with the evolution of the atomic parameters.

The probably largest number of superstructures has been observed for the AlB_2 family [34]. Besides pure binary borides, also ternary ones and a variety of intermetallic compounds show similar topologies. Many equiatomic RTX compounds show an ordered coloring of the T and X atoms within the boron substructure. Due to the difference in size as well as different interatomic interactions, the distortions of the resulting structures are small up to drastic. The basic monomeric units which occur in the different superstructures are presented in Fig. 3.150. The hexagons can be planar, slightly puckered, or even tilted. In the latter case homo- or heteroatomic interactions (e. g. $d^{10}-d^{10}$ interactions) can occur.

The Bärnighausen tree for the AlB_2 superstructures is presented in Fig. 3.151. A hexagonal/trigonal and an orthorhombic/monoclinic branch can be distinguished. Completely tilted hexagons only occur in the latter branch. Group theory can predict further possible superstructure variants, however, it is not possible to predict the corresponding element combination. An example is the structure of $EuAuGe$, space group $Im2m$. From a group theoretical point of view, a tripled and a quintupled cell are possible through isomorphic transitions of index 3 and 5, respectively. The i5 variant had been observed for $EuAuSn$, while the i3 variant was discovered later for $YbAuSn$ [35]. Crystal chemical details on these many superstructures are discussed in [34].

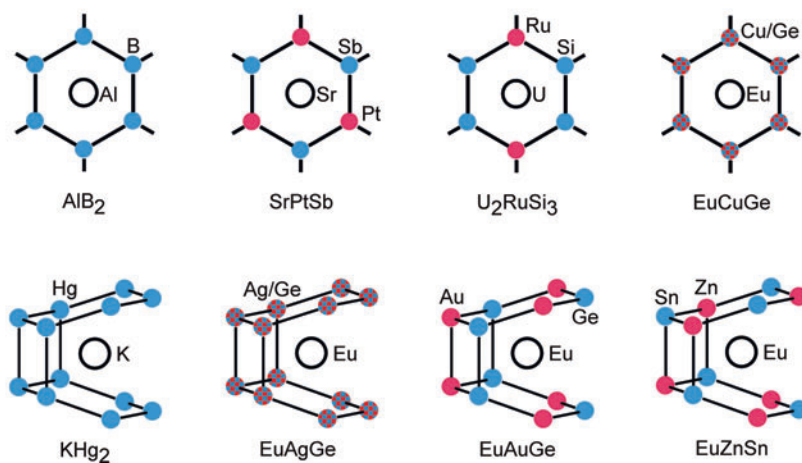


Fig. 3.150 Coloring of the hexagons in different hexagonal/trigonal and orthorhombic/monoclinic superstructures of the AlB_2 family.

The formation of a superstructure always relies on small distortions (an atom or a building group cannot meet the steric requirements for the high-symmetry structure) or peculiar electronic effects. Within the scope of the book one cannot go into

all crystal chemical details which explain such superstructure formations. Just two prominent examples: (i) Size arguments account for many intermetallic scandium compounds. In different series of rare earth compounds scandium is often too small to adopt the structure of the smallest rare earth element, lutetium. However, superstructure formation with only small distortions allows an almost similar atomic arrangement. A recent example concerns the pair LuAgSn [36]/ScAgSn [37]. (ii) Electronic factors like Au–Au interactions account for the superstructure formation of *e. g.* YbAuSn [35] and further gold or platinum containing equiatomic intermetallic compounds.

Selected intermetallic structure types with Bärnighausen trees for superstructures are listed in Table 3.5 together with the relevant literature that discusses the crystal

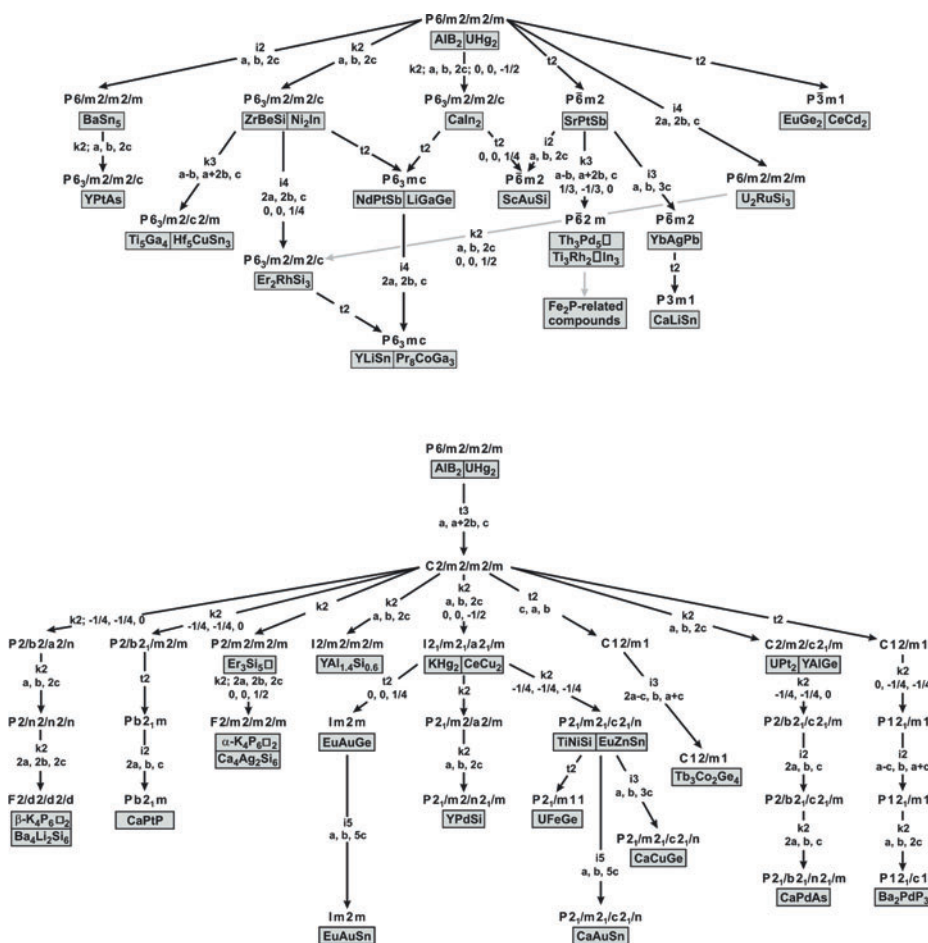


Fig. 3.151 The hexagonal/trigonal (top) and orthorhombic/monoclinic (bottom) branches of the Bärnighausen tree for superstructures of the AlB₂ family [34].

chemical details that are responsible for superstructure formation. For an extension to ionic compounds we refer to the excellent review by Müller [30].

Table 3.5 Selected structure types with Bärnighausen trees. The structures are ordered with decreasing space group symmetry.

Aristotype	Examples for ordered or distorted versions	Reference
<i>bcc</i> , $Im\bar{3}m$	FeAl, β -Cr ₂ Al, Li ₂ In, Pt ₄ PbBi ₇ , Mo ₂ Cu ₃ Ga ₈ , <i>RE</i> ₂ RuMg ₂ , <i>RE</i> ₂ RuMg ₃ , <i>RE</i> ₃ Ru ₂ Mg	[32, 38, 39] [53, 54]
MgCu ₂ , <i>Fd</i> $\bar{3}m$	Cd ₄ Cu ₇ As, YMn ₂ , HfV ₂	[40]
Ti ₂ Ni, <i>Fd</i> $\bar{3}m$	Gd ₄ NiMg, AuSTa ₅	[52]
NaZn ₁₃ , <i>Fm</i> $\bar{3}c$	CeNi ₉ Sn ₄ , SrNi ₇ In ₆ , BaAu _x Zn _{13-x}	[41, 42]
<i>fcc</i> , <i>Fm</i> $\bar{3}m$	CuPt ₇ , Ca ₇ Ge, KHg ₁₁ , MoNi ₄ TiAl ₃	[32, 43]
NaCl, <i>Fm</i> $\bar{3}m$	SrSnP	[44]
NiAs, <i>P6</i> ₃ / <i>mmc</i>	AuNiSn ₂ , LiHg ₃	[45, 46]
AlB ₂ , <i>P6</i> / <i>mmm</i>	TiNiSi, YbAuSn	[34, 35, 38]
Fe ₂ P, <i>P</i> $\bar{6}2m$	HfRhSn	[47]
BaAl ₄ , <i>I4</i> / <i>mmm</i>	ThCr ₂ Si ₂ , CaBe ₂ Ge ₂	[33, 48]
HfCuSi ₂ , <i>P4</i> / <i>nmm</i>	Pr ₃ Zn ₂ As ₆	[49]
U ₃ Si ₂ , <i>P4</i> / <i>mbm</i>	Zr ₃ Al ₂ , Zr ₅ Ni ₄ Al	[50]
Sc ₃ FeC ₄ , <i>Immm</i>	Sc ₃ RhC ₄ , Sc ₃ OsC ₄	[51]
YbMo ₂ Al ₄ , <i>I4</i> / <i>mmm</i>	Ce ₂ RuZn ₄	[55]

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3.18 Quasicrystals

Most intermetallic phases show translational symmetry and obey the well-known laws of classical crystallography. In 1982 the israelian materials scientist *Dan Shechtman* (Nobel Prize in Chemistry 2011) unexpectedly observed icosahedral diffraction symmetry for rapidly solidified metastable Mn-Al phases [1]. The samples were prepared by the melt-spinning technique (Chapter 4.5) upon quenching the melt within milliseconds. In the following years many metastable and stable quasicrystals (QC) were reported. The metastable character of many quasicrystalline phases is certainly due to the absence of periodicity, leading to an energetically less favorable structure. Today several thousand publications on the structures and properties of quasicrystalline materials can be found in literature, however, still fundamental questions on composition and growth conditions (the temperature stability ranges for quasicrystals cover the broad range from a few to several hundred degrees centigrade) remain. Many mathematical approaches have been worked out for the description of their diffraction patterns. Among the tilings and tessellations, the Penrose tiling [2] is widely known.

Besides the initial Mn-Al phases observed by *Shechtman*, a variety of other binary, ternary, and even some multinary materials with quasicrystalline structural characteristics have been studied. Roughly, these phases can be divided into two groups, (i) materials based on transition metal aluminides (typical compositions are Al-Li-Cu, Al-Pd-Mn, or Al-Cu-V) and (ii) Mg-Zn based phases with Frank-Kasper related structural fragments (typical compositions are Zn-Mg-Ho or Zn-Mg-Sc). Interestingly, also a natural (probably of meteoritic origin) quasicrystalline material, $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ (named icosahedrite) was observed. Most of these phases have minutely been studied by electron microscopy. Quasicrystals are (with a few exceptions) almost free of defects and disorder. Their X-ray and electron diffraction patterns show extremely sharp peaks, similar to almost perfect classical crystals. The stability ranges of quasicrystals are similar to other crystalline intermetallic materials. Many of the i-QCs show narrow electron concentration ranges, similar to the Hume-Rothery phases (Chapter 3.5).

Several of the quasicrystalline materials contain well-defined cluster units, called Mackay-, Bergmann, and Tsai-clusters. One observes 'non-crystallographic' 5-, 8-, 10-, or 12-fold rotational symmetry. Such complex clusters occur in a variety of intermetallic structures, very frequently in the alkali and alkaline earth based systems (A, AE)-Au-(Ga, Ge, In, Sn) [3, and references cited therein].

Besides the demanding crystallography, many studies have been devoted to the chemical and physical properties of quasicrystalline materials. They exhibit many features that are unusual for conventional alloys and intermetallic compounds. The detailed property studies have been performed for both families of quasicrystals, the icosahedral i-QCs and the decagonal d-QCs. Their anisotropic structures are also manifested in anisotropic thermal and transport properties. An important parameter for property investigations concerns the structural perfection of the material, single-grain and poly-grain samples show different behavior. Single-grain samples allow for measurements along the distinct crystallographic directions. The property studies mainly concern transport properties (e. g. materials for infrared light absorption), mechanical reinforcement as well as chemical properties (e. g. Ti-Zr-Ni for hydrogen storage applications or $i\text{-Fe}_{12}\text{Cu}_{25}\text{Al}_{63}$ as catalyst for the production of hydrogen from methanol reforming).

Important materials that have broadly been studied are $i\text{-YbCd}_{5.7}$ and $i\text{-Yb}_{16}\text{Al}_{42}\text{In}_{42}$. Single crystals of $i\text{-Yb}_{16}\text{Al}_{42}\text{In}_{42}$ in centimeter size can be grown by the Bridgman technique (Chapter 2.11). Also the Czochralski method (e. g. for $i\text{-Fe}_{13}\text{Cu}_{23}\text{Al}_{64}$) or metal flux synthesis (e. g. Ho-Zn-Mg) are possible. Mostly the bulk and single crystalline materials are too brittle for applications. Suitable coatings can be obtained by thermal or plasma spray techniques and also *via* physical or chemical vapor deposition. Such coatings show reduced adhesion (lower wetting) as compared to conventional intermetallics. The problem of brittleness for bulk materials can be overcome by metal-matrix or polymer-matrix composites, similar to the well-known WIDIA® composit. Although many promising properties are known, commercial products are not yet on the market.

The field of quasicrystalline materials is a rapidly growing one, interdisciplinary in solid state chemistry and physics and of course in crystallography and materials sciences. The interested reader is referred to the relevant literature [4–10] for deeper information.

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4 Function

The metallic elements as well as binary and multinary intermetallic compounds display an extremely broad variety of structural peculiarities which give rise to a manifold of chemical and physical properties. In an introducing textbook on intermetallics it is simply not possible to cover the whole field of properties. In the structural part of this book (Chapter 3) some important properties have been mentioned directly with the respective compound or classes of compounds. Several properties lead to applications in form of materials that carry specific functions. The present chapter reports on five important functions/properties/materials classes.

4.1 Magnetic Properties

One of the broadly used properties of intermetallic compounds is magnetism. Many high-tech applications in daily life are directly related to the magnetic behavior of a given material. Typical examples are magnet boards, permanent magnets for miniaturized motors (there are about 20 in each modern car), rare earth-based magnets for wind turbines (around 150 kg per machine) and magnetocaloric applications, or magnetic anti-theft devices. The field of magnetic properties of intermetallics is rapidly growing and new results are published in specialized solid state journals (*e. g. Journal of Magnetism and Magnetic Materials*) and relevant handbook articles (*e. g. Handbook on Magnetic Materials*). Every three years the *International Conference on Magnetism* (ICM) is one of the leading events covering all aspects of magnetic materials. In the present chapter we do not focus on the fundamental physics of magnetic properties of solids. These basics are well documented in standard solid state physics or magnetochemistry textbooks [1–7]. In the following paragraphs the diverse aspects of magnetic properties are explained phenomenologically from a chemist's point of view. For a practical guide for the experimentalist we refer to a report by *Hatscher et al.* [8]. All species with filled electron shells carry no permanent magnetic moment and contribute to the total susceptibility by a low, negative and temperature independent value in the order of -10^{-6} emu/mol. Such compounds are diamagnets; they are repelled from a magnetic field. For simple ions and fragments of organic compounds the situation is well understood and the total diamagnetism can be calculated from so-called diamagnetic increments [9]. Many of these increments date from the pioneering textbook by *Wilhelm Klemm* [1], the founder of modern magnetochemistry. For metals and intermetallic compounds the situation is somehow more difficult. Copper and silver are diamagnets, but an explanation on the basis of diamagnetic increments is

not straightforward. As examples for ternary intermetallic compounds the temperature dependence of the magnetic susceptibility of $\text{Ca}_2\text{Pd}_2\text{In}$ [10] and LiRuSn_4 [11] is presented in Fig. 4.1.1. The susceptibilities are almost temperature-independent down to about 25 K. The samples then show small upturns in the susceptibility data (Curie tails) which are due to trace amounts of paramagnetic impurities. Since paramagnets have much higher susceptibility, even traces can reliably be detected during the magnetic measurements. Since the susceptibility data of Cu, Ag, and $\text{Ca}_2\text{Pd}_2\text{In}$ are negative, by definition they are diamagnetic, but show metallic conductivity. The true explanation is that the core diamagnetism overcompensates the Pauli susceptibility (*vide infra*), thus resulting in negative susceptibility values.

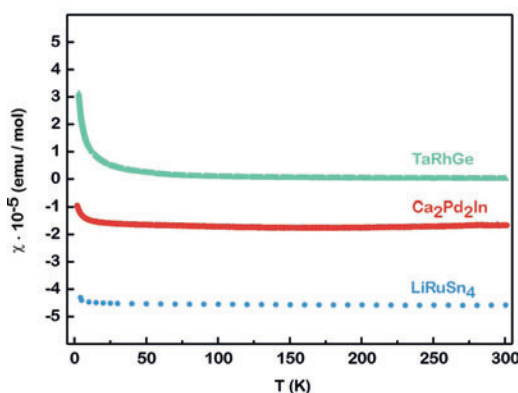


Fig. 4.1 Temperature dependence of the magnetic susceptibility of TaRhGe [12], $\text{Ca}_2\text{Pd}_2\text{In}$ [10], and LiRuSn_4 [11].

The electrons in many metals are itinerant and behave like an electron gas. When such a metal is exposed to an external magnetic field only the electrons close to the Fermi energy will respond and one obtains a weak paramagnetic contribution which is called Pauli paramagnetism. The magnetic susceptibility of Pauli paramagnets is in the order of 10^{-6} emu/mol and thus always competes with the core diamagnetism (with opposite sign). In some rare cases both magnetic contributions can almost compensate each other, leading to a non-magnetic material. The term ‘non-magnetic’ is frequently used in articles dealing with rare earth compounds. In that context it means that a given compound (with diamagnetic scandium, yttrium, lanthanum, or lutetium) does not carry a permanent moment. As an example for a Pauli paramagnetic compound the magnetic susceptibility of TaRhGe [12] is presented in Fig. 4.1. Similar to $\text{Ca}_2\text{Pd}_2\text{In}$ and LiRuSn_4 , also for TaRhGe one observes an upturn of the susceptibility towards low temperatures, again caused by trace amounts of paramagnetic impurities. Such traces are not detectable by powder X-ray diffraction and the susceptibility data for a given compound can vary from sample to sample.

This has exemplarily been tested for several $\text{WNi}_4\text{P}_{16}$ samples [13]. Pauli paramagnets occur within many of the binary and multinary compounds of transition metals with p group elements and for rare earth intermetallics with scandium, yttrium, lanthanum, or lutetium.

Thus, in intermetallic compounds with comparatively good electrical conductivity one observes diamagnetic and Pauli paramagnetic contributions as well. The main interest in magnetic materials with respect to properties/applications concerns paramagnetic ones with much stronger magnetic effects (susceptibilities in the order of 10^{-6} – 10^{-3} emu/mol). Paramagnetism usually occurs if partially filled d - and/or f - shells are present. In the so-called paramagnetic range the moments are not coupled. If an external field is applied the moments tend to align but thermal agitation constantly reorients the moments (statistical orientation). This reorientation is retarded with decreasing temperature and one observes increasing susceptibility. Such paramagnets obey the Curie ($\chi = C / T$) or Curie-Weiss law ($\chi = C / (T - \theta)$), where C is the Curie constant and θ the paramagnetic Curie temperature (Weiss constant). Negative and positive θ values are indicative for antiferromagnetic and ferromagnetic interactions in the paramagnetic regime, respectively. The experimental magnetic moment for a given compound can be calculated by $\mu_{\text{exp}} = (8C)^{1/2}$. As examples the temperature dependencies of the magnetic susceptibilities of TbRhZn [14] and $\text{Gd}_2\text{Cu}_2\text{Mg}$ [15] which are paramagnetic above 25 and 150 K, respectively, are presented in Fig. 4.2. The inverse susceptibility curves often show a slight curvature, indicating a small deviation from Curie-Weiss behavior. This can be due to a small temperature-independent susceptibility contribution χ_0 in the order of magnitude of a Pauli paramagnet and the total susceptibility can be described by a so-called modified Curie-Weiss law $\chi = \chi_0 + (C / (T - \theta))$.

With decreasing temperature the magnetic dipole exchange energy can become higher than the thermal agitation energy. Then the dipoles tend to align along a specific direction within so-called Weiss domains. The magnetic moments are of equal size and aligned in antiparallel fashion in antiferromagnets. Starting from the para-

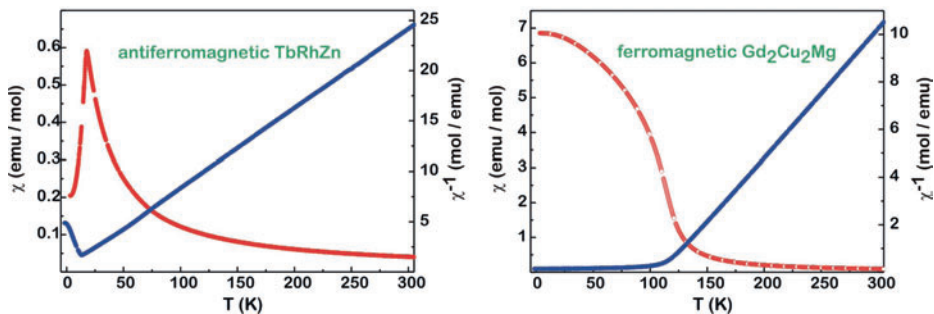


Fig. 4.2 Temperature dependence of the magnetic (red) and inverse magnetic (blue) susceptibility of antiferromagnetic TbRhZn [14] and ferromagnetic $\text{Gd}_2\text{Cu}_2\text{Mg}$ [15].

magnetic regime (Fig. 4.2, left) the susceptibility increases with decreasing temperature and at the Néel temperature antiparallel spin alignment sets in, accompanied by a sudden decrease in susceptibility.

A schematic presentation of different ordering variants is given in Fig. 4.3. In the case of antiferromagnets several ordering variants are possible. The moments can all be aligned in a parallel fashion within one layer and the neighboring layers are antiparallel, or full antiparallel ordering already occurs within the layers. The correct spin structure can only be determined from neutron diffraction data.

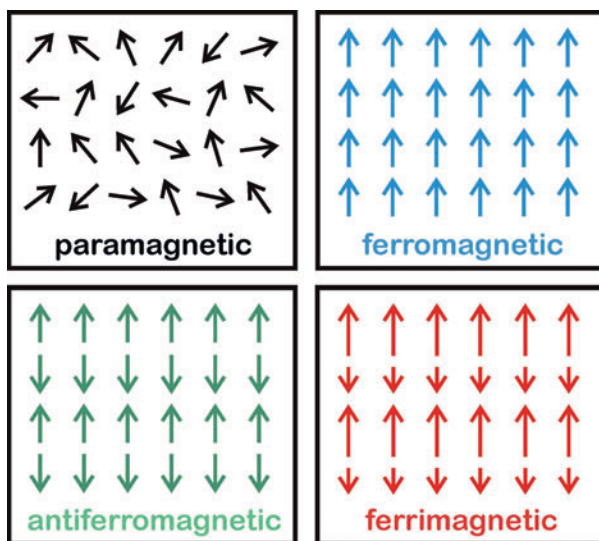


Fig. 4.3 Arrangements of magnetic dipoles in a paramagnet, a ferromagnet, an antiferromagnet, and a ferrimagnet.

If all moments are aligned parallelly the ordering is called ferromagnetic. The parallel ordering sets in at the Curie temperature and is accompanied by a huge increase in the magnetic susceptibility. This is readily visible by comparison of the susceptibility scales for TbRhZn [14] and $\text{Gd}_2\text{Cu}_2\text{Mg}$ [15] in Fig. 4.2, which is an order of magnitude higher for $\text{Gd}_2\text{Cu}_2\text{Mg}$ in the ferromagnetically ordered state. A weak ferromagnetic component also results if magnetic moments of different size are ordered in antiparallel arrangement (Fig. 4.3). The net moment is much smaller than that of a pure ferromagnet, and such materials are called ferrimagnets. The magnetic moments can also show small deviations from strictly parallel or antiparallel alignments. Such magnetic structures are referred to as canted antiferro- or canted ferromagnets (Fig. 4.4). Even more complex is the situation for helical spin alignments. Such sinusoidal spin structures occur for some of the rare earth elements and many rare earth-based compounds [16].

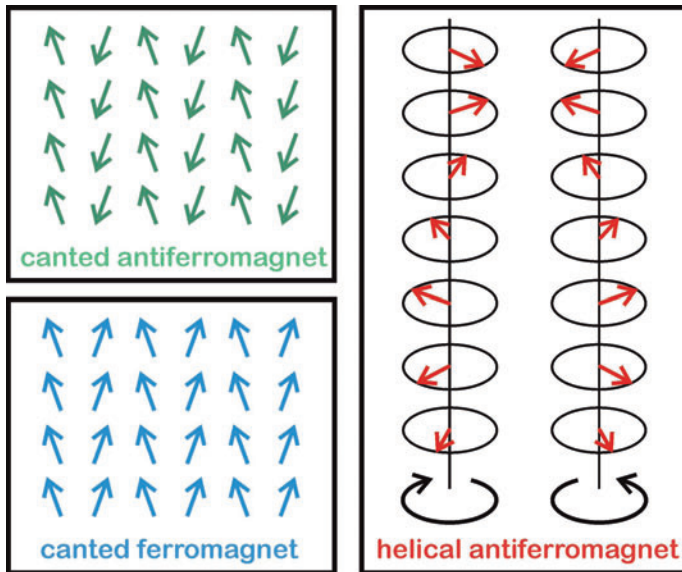


Fig. 4.4 Arrangements of magnetic dipoles in a canted antiferromagnet, a canted ferromagnet, and a helical antiferromagnet.

Today magnetic susceptibility data are determined with automated devices: Faraday balances, SQUID (superconducting quantum interference device) magnetometers, or PPMS (physical property measurement system) equipped with VSM (vibrating sample magnetometers). These instruments are highly sensitive and mostly it is possible to determine the magnetic properties with only some milligrams of the sample. The magnetic ordering temperatures for the arrangements discussed above cover very broad ranges. Typical permanent magnetic materials have Curie temperatures of several hundred Kelvin while some complicated rare earth-based materials on the other hand show magnetic ordering only in the mK range.

The technically most important magnetic materials are ferromagnets. Today we use different permanent magnetic materials for applications in miniaturized motors and loud speakers or wind-driven engines. Straight after synthesis ferromagnetic materials initially show no external permanent magnetization. The Weiss domains are statistically distributed. If such a virgin ferromagnetic material is exposed to a magnetic field, the Weiss domains step by step align parallelly to this field direction. This proceeds by a discrete mechanism. The Weiss domains (with typical sizes in the μm range) are separated by so-called Bloch walls. During the magnetization process one observes rotation of the Bloch walls and the domains align. At a certain field strength all spins are parallel and one reaches the saturation magnetization. If the external field is released, the material remains a permanent magnet with a remanence magnetization that is little smaller than the saturation magnetization. When switching the external field to the opposite direction, the sample can completely be demagnetized

until zero magnetization is attained at the coercive field strength. For every permanent magnetic material the saturation and remanence magnetization as well as the coercive field strength are material constants. This hysteresis behavior of permanent magnets is described in many introducing materials science text books [17, 18] and therefore not illustrated again herein. The area of a hysteresis loop classifies the magnetic material. Narrow hysteresis curves allow for fast magnetization/de-magnetization processes *e. g.* for information storage, while broad hysteresis curves with large remanent magnetizations and high coercive field strengths characterize strong permanent magnets. Of the elements iron, cobalt, and nickel show ferromagnetic behavior. The origin of this has intensively been studied by electronic structure calculations [19].

The composition of permanent magnets influences the strength and the costs of such a material. Weak permanent magnets for typical applications like magnetic boards are so-called AlNiCo magnets, where the name stands for the elements forming the magnet. Such materials (with different ternary and multinary composition, mainly based on aluminum, nickel, and cobalt) can easily be synthesized just by melting (or arc-melting) the respective mixtures of the elements. Broader hysteresis curves occur for a special class of rare earth-based magnets. The first compound was $\text{Nd}_2\text{Fe}_{14}\text{B}$, initially discovered by serendipity. In the following, high-performance permanent magnets like SmCo_5 or $\text{Sm}_2\text{Co}_{17}$ have been characterized. Although these magnets have excellent material characteristics, the comparatively high price of cobalt (one of the strategic elements [20]) limits broad application. Today many permanent magnetic materials $\text{RE}_2\text{Fe}_{17}\text{X}_z$ with different light rare earth elements and $X = \text{B}, \text{C}, \text{N}$ find broad application. The rare earth content of these magnets is a limiting component and many recycling strategies for such materials are in development, *e. g.* large amounts of such materials arise from the first generation of wind turbines.

Finally we draw back to the antiferromagnetically ordered materials. If an antiferromagnet is exposed to an external field, the magnetization linearly increases with increasing field strength. The energy of the external field allows for spin flips and the spins can align step by step. If the external field is sufficiently high, every antiferro-

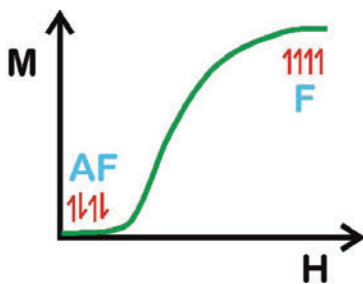


Fig. 4.5 Schematic magnetization isotherm of a metamagnetic material. The spin alignment in the antiferro- (AF) and ferromagnetic (F) ranges are shown.

magnet switches to a ferromagnet. For several compounds the switch in the magnetic ground state already occurs at low field strengths. This is schematically shown in Fig. 4.5. At certain critical field strength the antiparallel spin alignment suddenly switches to parallel. This field-induced spin reorientation is called metamagnetism [21]. Above the critical field strength the magnetization curve corresponds to that of a ferromagnet.

The superexchange mechanism (via $p(z)$ and $d(z^2)$ orbitals) known for $-O-T-O-$ bridges is not possible within intermetallics. Here, the most frequent coupling of the magnetic moments is of the RKKY type [22–24] (named after the physicists *Ruderman-Kittel-Kasuya-Yosida*). It is a coupling mechanism of magnetic moments (or localized inner d or f spins) by an interaction through the conduction electrons. The magnetic ordering is not only evident in the susceptibility data. Mostly also electrical resistivity and specific heat data are recorded in order to monitor the phase transition. In the magnetically ordered state scattering of the conduction electrons is less pronounced and one observes a steeper decrease of the specific resistivity below the ordering temperature. The specific heat data manifest the ordering via typical lambda transitions.

As it concerns basic research, many of the magnetically interesting compounds are based on rare earths. These elements offer a broad diversity of magnetic properties. In the last 40 years a huge number of compounds $RE_xT_yX_z$ have been studied with respect to their magnetic behavior. Often no magnetic moment was found on most of the $[T_yX_z]$ substructures. In these cases the corresponding compounds $RE_xT_yX_z$ with the diamagnetic rare earth cations scandium, yttrium, lanthanum, and lutetium, are all Pauli paramagnets. The other ones show paramagnetic behavior in the high temperature regime. Highly interesting are the compounds with those rare earth elements that are on the border of a magnetic instability. Trivalent cerium has an electron configuration $[Xe]4f^1$ and tends to deplete its f shell. Thus, one observes a huge variety of intermetallic cerium compounds with trivalent, intermediate-valent or even almost tetravalent cerium. These materials are of central interest for solid state physicists since many years. Changes of the valence electron concentration through solid solutions, application of high-pressure, or hydrogenation experiments effectively influence the magnetic behavior.

Europium can be divalent $[Xe]4f^7$ or trivalent $[Xe]4f^6$ with an enhanced stability for the divalent state since the $4f$ shell is half-filled. Eu(II) is isoelectronic with Gd(III) and intermetallic compounds with these rare earth cations often show magnetic ordering at comparatively high temperatures. The latter can nicely be monitored in parallel by ^{151}Eu and ^{155}Gd Mössbauer spectroscopy [25, 26]. Trivalent europium shows van Vleck type paramagnetism.

Two different valence states also occur in ytterbium, Yb(II) with $[Xe]4f^{14}$ and Yb(III) with $[Xe]4f^{13}$. The latter is the hole analog of Ce(III) and shows paramagnetic behavior. Ytterbium (II) compounds carry no magnetic moment and behave like Pauli paramagnets. Furthermore intermediate ytterbium valence is observed, either static or dynamic.

Finally one needs to mention the family of actinide intermetallics where the 5f electrons give rise to a manifold of interesting magnetic properties. Especially uranium intermetallics have deeply been investigated in the context of heavy-fermion materials and superconductivity [27].



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4.2 Superconductivity

Superconductivity is characterized by zero electrical resistivity and the perfect exclusion of magnetic fields from the interior of a material below a critical transition temperature T_c . The superconducting transition is accompanied with a jump in the specific heat (Fig. 4.6).

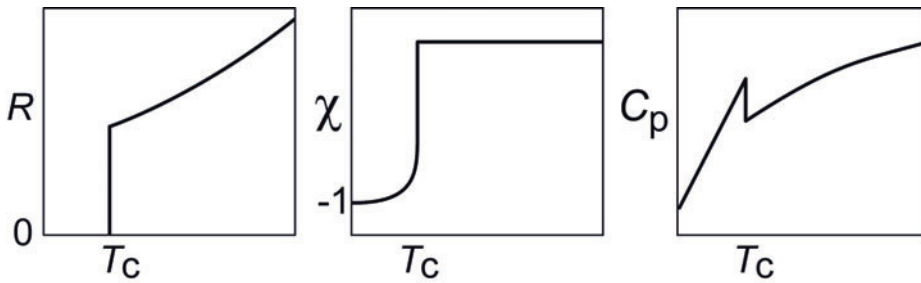


Fig. 4.6 Schematic changes in the electrical resistivity (R), magnetic susceptibility (χ), and heat capacity (C_p) during the superconducting phase transition.

These matchless properties of a superconductor are currently mainly used for the generation of high magnetic fields *e. g.* in medical diagnostic (MRI, magnetic resonance imaging), NMR spectrometers, or high-energy accelerators like the LHC. All these instruments would not be possible without coils made of superconducting wires, because conventional copper conductors cannot carry such enormous current densities. This field is extremely active in both basic and applied research, and the tremendous progress within the last ten years gives reasons to expect a range of innovative applications in energy technology, among them large 10 MW wind turbines, magnetic levitation trains, and smart power grids. An overview about the current state is given in [16]. However, in spite of such bright prospects, there is still a huge material problem which hampers the broader commercialization of superconductors. The perfect superconducting material is still a big ambition, thus here is much space for inventive spirit of solid state chemists.

This macroscopic quantum phenomenon superconductivity has been discovered in 1911 by *Heike Kammerlingh-Onnes* who measured the electrical resistivity of mercury at liquid helium temperatures. Meanwhile thousands of superconducting compounds are known, and one can say that superconductivity is a universal property of metallic matter, at least at very low temperatures, occurring in many elemental metals and a large number of alloys as well as intermetallic compounds. Here we will briefly discuss only the most important intermetallic superconductors. Comprehensive information about the huge research field of superconductivity may be obtained from several textbooks [1–5].

The highest critical temperature of the elements at normal pressure has niobium (9.25 K). Remarkably, metals with the highest normal state conductivities like copper or silver are often no superconductors, while the highest critical temperatures mostly occur in rather poor metals. The dependency of T_c on the valence electron count of metal alloys was among the first studied relations, and led to the Matthias rule proposed in 1955 [6]. It basically states that valence electron counts (VEC) around 4.7 and 6.5 per atom are best. Alloys of niobium with titanium fulfill this concept (NbTi: VEC = 4.5) and up to today, such alloys are the by far most used materials for superconducting wires in coils of high field magnets. Filaments of the superconducting alloy are embedded in a copper matrix (Fig. 4.7), which is necessary to stabilize against degradation at high currents that can otherwise destroy the coil.

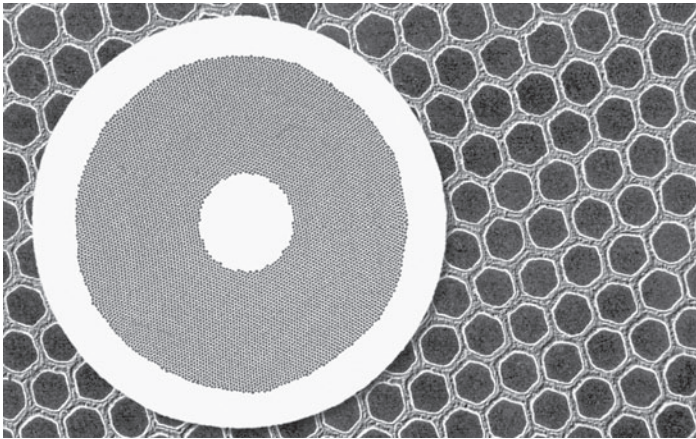


Fig. 4.7 Cross section of a superconducting multicore wire made of NbTi alloy filaments embedded in a copper matrix (reproduced with permission from [7]).

In line with the Matthias rule are the so-called A15-superconductors like V_3Si , Nb_3Sn , or Nb_3Ge with VEC = 4.75. A15 refers to the structure type which is sometimes referred to as the β -tungsten structure, suggesting a polymorph of tungsten. This is incorrect and bases on a wrong structure determination of W_3O where the oxygen has been overlooked due to its small scattering power (Chapter 3.11.1). The correct naming of the structure type is Cr_3Si . Figure 4.8 shows the cubic structure of Nb_3Ge as an example. The first superconductor with this structure was V_3Si discovered in 1954 followed by Nb_3Sn and Nb_3Ge . The latter initially had critical temperatures between 6 and 17 K depending on the synthesis method. In 1973 Nb_3Ge films were produced with $T_c = 23$ K, which was the record until the discovery of the copper oxide superconductors in 1986. Nb_3Sn has a critical temperature of 18 K and is used for wires in high field magnets, because it has a much higher critical field (30 T) than

NbTi (15 T). Such wires are difficult to produce because Nb₃Sn is more brittle than NbTi alloys. Niobium nitride NbN with rock salt structure is a superconductor with T_c around 16 K [8].

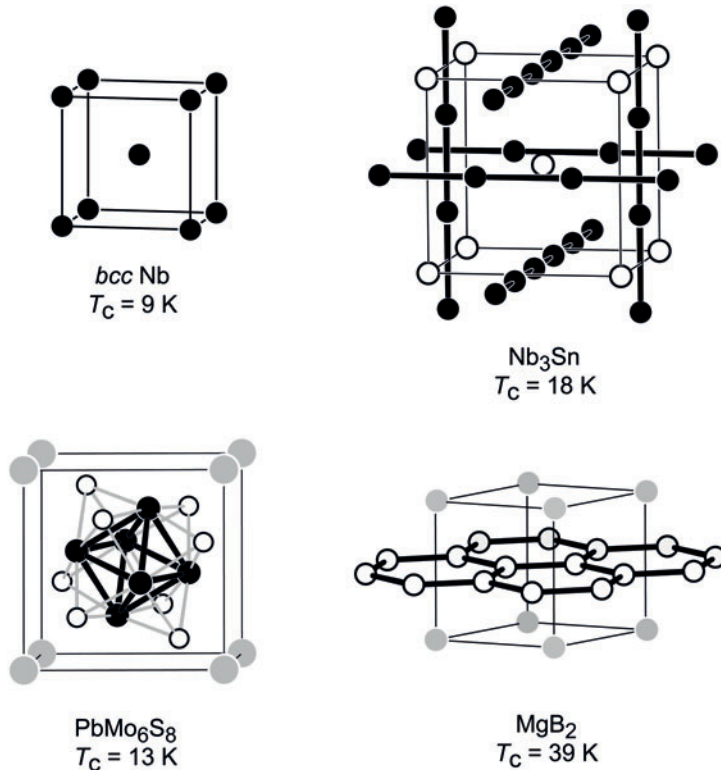


Fig. 4.8 Crystal structures of superconducting intermetallic compounds. The metal atoms niobium and molybdenum are drawn as filled black circles, germanium, sulfur, and boron as white circles, lead and magnesium as gray circles, respectively.

The Chevrel phases are ternary molybdenum chalcogenides like PbMo₆S₈ and contain octahedral molybdenum clusters with μ_3 -connected sulfur atoms located over all faces (Fig. 4.8). The compounds were first described in 1971 by *Chevrel* [9] and exhibit superconductivity up to 13 K [10] with extraordinary high critical fields up to 60 T [11], which was the highest before the discovery of the copper oxides. Chevrel phases became also famous because a number of them where lead is replaced by magnetic rare earth elements showed magnetic order that coexists with superconductivity at low temperatures [12].

Superconductivity in magnesium diboride MgB_2 was not discovered before 2001 [13] even though this intermetallic compound is known since the 1950^s. The structure (Fig. 4.8) is the AlB_2 type and consists of planar layers of boron hexagons separated by magnesium. The boron hexagons are isoelectronic to graphite according to $\text{Mg}^{2+}(\text{B}^-)_2$ and the compound is considered as a metallic Zintl phase. The critical temperature of 39 K is remarkably high especially as it turned out that superconductivity in MgB_2 is conventional and mediated by electron-phonon coupling [14]. Meanwhile MgB_2 wires are commercialized and used for magnet coils in a new generation of cryogen-free cooled magnetic resonance imaging (MRI) instruments. Due to the relatively small critical field, MgB_2 cannot be used for high field applications. For further information about MgB_2 we refer to a recent review [15].

Two classes of high- T_c superconductors with critical temperatures well above 40 K are known, namely the copper oxides and the iron pnictides/chalcogenides. Superconductivity in copper oxides was discovered in 1986 and these materials exhibit the highest transition temperatures up to 138 K under normal pressure. One of the most famous representatives is $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) which was the first superconductor with T_c (93 K) above the boiling point of liquid nitrogen (77 K). Copper oxides are certainly among the most investigated solids, however, these materials are not intermetallic compounds but rather ceramics and therefore outside the scope of this book. We recommend recent reviews for further information [16, 17].

Superconductivity in intermetallic iron pnictides was first reported in 2006 with LaFePO which crystallizes in the tetragonal ZrCuSiAs -type structure, however, the low critical temperature of 4 K caused not much excitement [18]. This changed rapidly when the analog arsenide LaFeAsO exhibited superconductivity at 26 K if doped with fluoride [19], and moreover when the transition temperature was raised to 55 K in $\text{SmFeAsO}_{1-x}\text{F}_x$. It became clear that a second class of high- T_c materials exists, more than 20 years after the copper oxides [20]. Meanwhile a growing family of iron-based superconductors is known. Their crystal structures, collected in Fig. 4.9, contain layers of edge-sharing $\text{FePn}_{4/4}$ ($\text{Pn} = \text{P}, \text{As}$) or $\text{FeSe}_{4/4}$ tetrahedra, separated either by layers of larger ions (alkali or alkaline earth) or by oxide layers as in LaOFeAs or thicker perovskite-like oxide layers like $\text{Sr}_2\text{VO}_3\text{FeAs}$.

These structures belong to well-known types like the ZrCuSiAs -, ThCr_2Si_2 -, PbFCl -, PbO -, and $\text{Sr}_2\text{GaO}_3\text{CuS}$ -type structures. They are often abbreviated by their stoichiometric coefficients according to 1111-, 122-, 111-, 11-, 21311-type superconductors. The stoichiometric compounds are often not superconducting, but show stripe-type antiferromagnetic order at low temperatures [21]. Superconductivity can be induced from such parent compounds by chemical substitution, physical pressure, and chemical pressure. Chemical substitution either decreases the charge of the FeAs -layer (hole-doping) or increases it (electron-doping). Both can induce superconductivity insofar as the substitution suppresses the magnetic ordering. Examples are the substitution of barium for potassium in 122-type compounds (hole-doping) which leads to critical temperatures up to 38 K in $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ [22], or the oxide for fluoride substitution

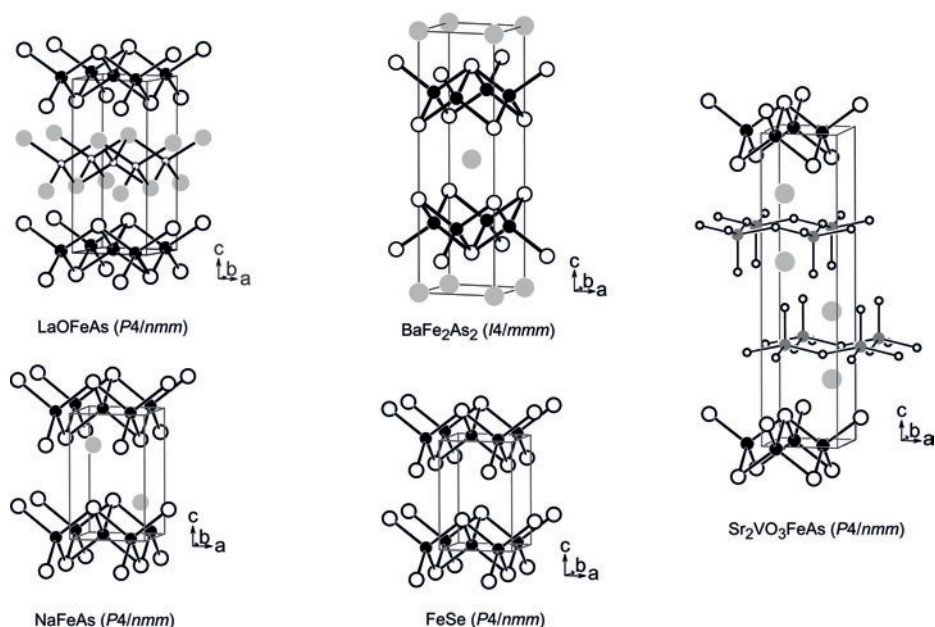


Fig. 4.9 Crystal structures of iron-arsenide and iron-selenide superconductors. Iron atoms are drawn as filled black circles, arsenic or selenium as white circles, lanthanum, barium, sodium, or strontium as large gray circles, vanadium as small gray circles and oxygen as small white circles.

in 1111-type compounds (electron-doping) which produces critical temperatures up to 55 K in SmFeAsO_{0.85}F_{0.15}. Potassium-doped BaFe₂As₂ is among the most investigated iron-based superconductors, and the quite robust superconducting properties in

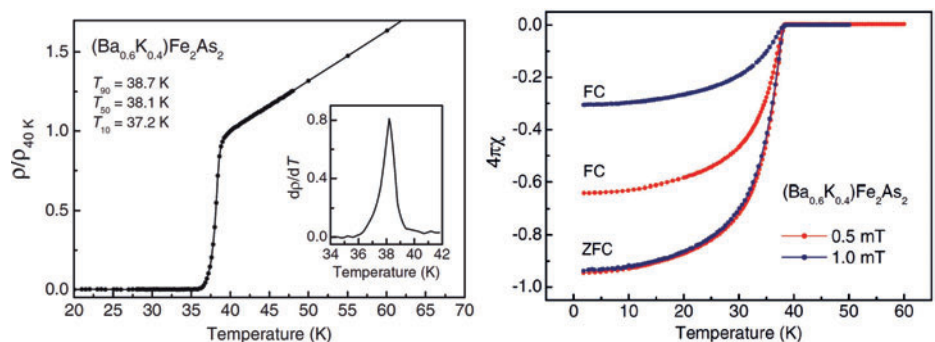


Fig. 4.10 Superconducting transition of Ba_{0.6}K_{0.4}Fe₂As₂. The left panel shows the resistivity transition which starts at 38.7 K and reaches zero resistivity at ≈ 36 K. The right panel shows the low-field magnetic susceptibility which exhibits the Meißner- (field cooled (FC) curves) and the Shielding effects (zero field cooled (ZFC) curves). Reproduced from [22] with permission.

terms of high critical fields ($H_{c2} \approx 70$ T; 30 T @ 20 K) with low anisotropy ($\gamma \approx 2$) are excellent makings for the fabrication of round superconducting wires. The typical superconducting transition of $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ together with the Meißner- and Shielding-effects are shown in Fig. 4.10.

Iron selenide is a special case because superconductivity has been found at 8 K seemingly in the stoichiometric phase [23], which increases to 36 K under pressure [24]. But according to the Fe-Se phase diagram no exact stoichiometric FeSe phase exists, only a composition with a slight excess of iron (Fe_{1+x}Se) should be stable. Thus binary iron selenide is probably intrinsically doped, and therefore superconducting. However, there is evidence for almost ideally stoichiometric FeSe as the superconducting phase [25]. Intercalation of alkali metals between the FeSe layers yields the compounds $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ with defect ThCr_2Si_2 -type structure and critical temperatures around 30 K. It turned out that such samples are intrinsically phase separated in an antiferromagnetic phase with ordered iron vacancies in a $\sqrt{5}a \times \sqrt{5}a$ superstructure, and a superconducting phase without iron deficiency and the probable composition $\text{K}_x\text{Fe}_2\text{Se}_2$ [26]. Also $\text{Sr}_2\text{VO}_3\text{FeAs}$ with perovskite-like oxide slabs between the FeAs-layers is a stoichiometric superconductor with critical temperatures up to 37 K. In this case intrinsic electron doping through a $\text{V}^{3+}/\text{V}^{4+}$ valence mixture is assumed [27].

Iron-based materials exhibit unconventional superconductivity, which means that the formation of the cooper pairs is not mediated by electron-phonon-coupling (alone). It is currently believed that magnetic fluctuations play a key role similar to the copper oxides, and many experiments support this scenario [28, 29]. However, up to now there is no final consent about the mechanism of high- T_c superconductivity in both classes. On the other hand, iron-based compounds have high application potential because of their robust superconducting properties in terms of similar high critical fields and much lower anisotropy when compared to copper oxides. For more details we refer to relevant reviews [21, 30–32].



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4.3 Thermoelectric Materials

The thermoelectric effect is the direct conversion of thermal into electrical energy and of enormous interest with respect to alternative power generation and energy conservation by waste-heat harvesting [1]. A thermoelectric device generates a voltage from a temperature gradient between both ends due to the Seebeck effect. Reversely a temperature gradient occurs if current flows through the device, which is the Peltier effect. The basis of such devices is the Seebeck coefficient α or thermopower of a material, which is defined as the generated voltage V divided by the temperature gradient: $\alpha = V / \Delta T$. Typical Seebeck coefficients range from $-100 \mu\text{V/K}$ to $+1000 \mu\text{V/K}$. Negative values result if electrons are the dominant charge carriers (n -type), whereas

holes are the predominant carriers (*p*-type) in materials with a positive Seebeck coefficient. Note that α is generally not constant in temperature. A thermoelectric circuit is mostly composed by combinations of materials with *n*-type and *p*-type conduction. Schematics of the carrier flow in *n*- and *p*-type materials as well as the principle of a thermoelectric couple are depicted in Fig. 4.11.

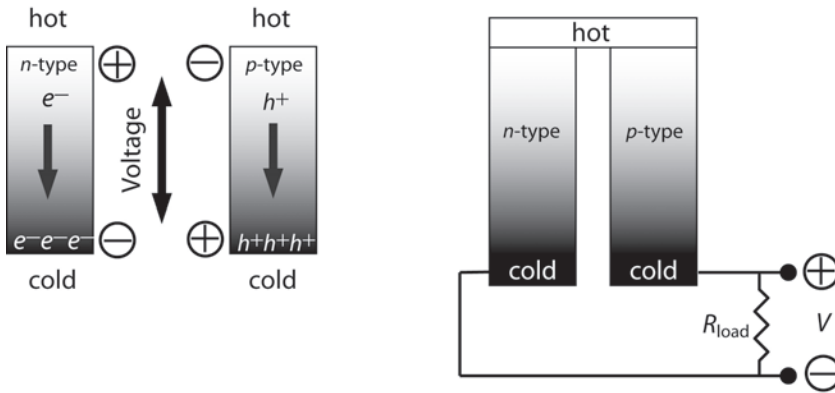


Fig. 4.11 Scheme of charge carriers flowing in materials with negative and positive Seebeck coefficients (left) and general assembly of a thermoelectric device (right).

The physical efficiency limit of a thermoelectric material is the Carnot efficiency $\Delta T/T_{\text{hot}}$ that cannot be exceeded by any heat engine. This is multiplied by a term which contains material specific properties, namely the Seebeck coefficient (α), the electrical resistivity (ρ), and the thermal conductivity (κ) which are combined to the thermoelectric figure of merit zT . The maximal efficiency η_{max} for small temperature differences ($T_{\text{cold}}/T_{\text{hot}} \approx 1$) is then:

$$\eta_{\text{max}} = \frac{\Delta T}{T_{\text{hot}}} \cdot \frac{\sqrt{1+zT} - 1}{\sqrt{1+zT} + 1} \quad \frac{\Delta T}{T_{\text{hot}}} = \text{Carnot efficiency}$$

$$zT = \frac{\alpha^2 T}{\rho \kappa} = \text{Thermoelectric Figure of Merit}$$

For large temperature differences also the thermoelectric compatibility factor $s = (\sqrt{1-zT} - 1)/-\alpha T$ becomes important. For power generation s should not change more than a factor of two between the hot and the cold ends of a thermoelectric couple.

Typical state-of-the-art commercial thermoelectric materials like Bi_2Te_3 , PbTe , or $\text{CeFe}_4\text{Sb}_{12}$ [2] that operate near room temperature have $zT \approx 0.6 - 1.0$, which means the efficiency is at most 17 % of the Carnot limit, in reality rather 10 % is common. Some

30 % would be possible with materials that have $zT \approx 3$, which is a big challenge and currently subject of intense research.

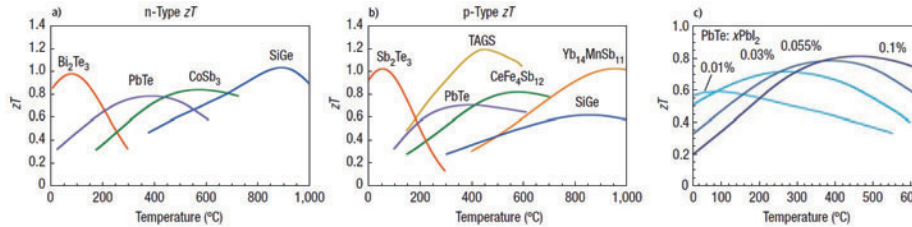


Fig. 4.12 Figure-of-merit zT for currently used thermoelectric materials. a) n -type, b) p -type, c) changes in zT in PbTe with PbI_2 doping (after [2] with permission).

Given $zT = \alpha^2 T / \rho \kappa$ as the quantity to be optimized, the aim is a material with a high Seebeck coefficient and low thermal but high electrical conductivity. Unfortunately, these properties are not independent. In general, increasing α results in higher electrical resistivity ρ , which is furthermore coupled with the electronic contribution to the thermal conductivity κ_e by the Wiedemann-Franz law $\rho \kappa_e = LT$, where L is the Lorenz number. To ensure a large Seebeck coefficient it is important to have only one type of carriers (either n or p), and a relatively low carrier concentration. The latter yields higher resistivity and decreases zT . The best compromise are heavily doped semiconductors with medium carrier densities around $10^{19}/\text{cm}^2$, therefore good metals are not suitable as thermoelectric materials. The thermal conductivity has two components, one comes from the electrons or holes (κ_e) and one from lattice vibrations (phonons) travelling through the lattice (κ_l). Both add to the total thermal conductivity $\kappa = \kappa_e + \kappa_l$. The electron/hole part is directly coupled to the electrical resistivity through the Lorenz number L , which moreover can depend on the carrier concentration. In the end, a material with high electrical but low thermal conductivity remains the inherent conflict for achieving an effective thermoelectric material.

One concept to overcome this problem is based on the fact that glasses have low lattice thermal conductivities. This is because the energy transport by phonons is hampered due to the lack of translation symmetry which reduces κ_l . But for the same reason glasses have low electrical conductivity. Thus, we again require contradictory properties, namely that an efficient thermoelectric material should be a phonon-glass electron crystal (PGEC). It is of course impossible to have a material which is glass and crystal at the same time, but there are at least three approaches to reduce the lattice thermal conductivity in this sense [3].

(i) Scattering of the phonons through so-called ‘rattling’ structures or point defects. Atomic disorder for example has been introduced by alloying $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ or PbTe/GeTe . Furthermore, crystal structures with void spaces open opportunities to re-

duce the lattice thermal conductivity k_l through disorder. Rattling of ions in oversized cages has been discussed in clathrate compounds like $A_8Ga_{16}Ge_{30}$ ($A = Sr, Ba, Eu$) [4, 5] (see Chapters 3.9.2 and 3.9.3) and in filled skutterudites [6] such as $CeFe_3CoSb_{12}$ (see Chapter 3.10.3 and Fig. 3.10.3.5).

(ii) Using large crystal structures which mimic the phonon glass, while the translational symmetry remains intact. An example is $Yb_{14}MnSb_{11}$ [7] which is isostructural to the Zintl phase $Ca_{14}AlSb_{11}$. The tetragonal structure of $Yb_{14}MnSb_{11}$ ($I4_1/acd$, $Z = 8$) has a $6058 \text{ \AA}^3$ unit cell and contains eight $MnSb_4$ tetrahedra, eight Sb_3^{7-} anions and 32 isolated Sb^{3-} . The zT of this material is ≈ 1.0 at 900°C , which is much better than the so far superior high temperature material $SiGe$ ($zT \approx 0.6$) used in spacecrafts. Another example is Zn_4Sb_3 ($zT \approx 1.3$ at 400°C) where zinc atoms are distributed over three interstitial sites, which generates significant disorder and a glass-like thermal conductivity [8]. Good thermoelectric materials are almost always valence compounds, thus complex Zintl compounds with heavy main group elements emerged as new class of thermoelectric materials and are intensively studied [9].

(iii) Scattering phonons through multiphase composites at the nanoscale. There is evidence for enhanced zT in nanostructured thin films and wires due to increased Seebeck coefficients and reduced thermal conductivity [10]. Complex microstructures are discussed as probable reasons for the high zT (1.2–1.3 at $400\text{--}450^\circ\text{C}$) of $(AgSbTe_2)_{0.15}(GeTe)_{0.85}$ (TAGS) and $(AgSbTe_2)_x(PbTe)_{1-x}$ (LAST) materials [11], first studied in the 1950^s. Recent results showed that these materials are not true solid solutions with the rock salt structure, but exhibit complex nanoscale microstructures with twin boundary defects, inhomogeneities and local lattice strain. These materials show that microstructural engineering will become increasingly important in the future development of thermoelectric nanomaterials [12].

Even though thermoelectric materials have been studied since the 1950^s, the interest revived in the 1990^s when the discussion about sustainable energy intensified, and at the same time concepts towards higher efficiency emerged. This field is rapidly growing and many comprehensive reviews and textbooks are available [2, 3, 9–11, 13–16].



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4.4 Battery Materials

Intermetallic compounds are used as basic materials in the field of so-called *energy materials*. One group concerns binary and multinary metal hydrides which find application as hydrogen storage materials (Chapter 3.16) and in metal hydride batteries, where during the charging reaction ($\text{H}_2\text{O} + \text{M} + \text{e}^- \rightarrow \text{HO}^- + \text{MH}$) at the negative electrode the metal (M) reacts with hydrogen. The second group regards intermetallic lithium compounds and their use in rechargeable lithium ion batteries [1–3]. This group of materials is discussed in the present chapter. The focus will not lie on mechanistic effects but on crystal chemical details as well as formation and decomposition of the lithium intermetallics.

If elemental lithium is used as electrode material, reduction of lithium ions often leads to dendrite and whisker formation and causes electric shortening within the electrochemical cells. These shortenings might locally produce high temperatures and in view of the low melting point of lithium (453 K) can lead to severe safety problems. To overcome these inconveniences, binary intermetallic lithium compounds have been used, mainly silicides, stannides, and antimonides [4]. Such binaries show almost similar packing density than metallic lithium. The basic crystallographic data of most binaries are summarized in a review article [5].

Substitution of elemental lithium by binary compounds has two non-negligible disadvantages, (i) the density of the material strongly increases (lithium has only 0.53 g cm^{-3}) and (ii) the potential of the electrode decreases. Due to the charge transfer from lithium to the p element, the compound becomes much more brittle and the melting point strongly increases, up to 1000 K for some of the lithium silicides and stannides. Lithiation of the p element leads to a drastic volume increase and often microcracks within the samples. Repeated cycling can induce a pulverization of the material accompanied by a loss of the electronic interparticle contact. Regarding the capacity fade of the cells, the fracture formation is more important than formation of the solid electrolyte interface.

The maximum lithium uptake corresponds to 4.4 equivalents lithium per silicon or tin atom. The formation of the binary compounds (charging reaction $x\text{Li}^+ + \text{xe}^- +$

$M \rightarrow \text{Li}_x M$) can effectively be monitored by ^7Li solid state NMR [6] and in the case of the stannides also by ^{119}Sn Mössbauer [7] spectroscopy. Especially the silicides have thoroughly been studied [8], since tin and silicon are abundant and environmentally friendly.

A further approach starts from binary transition metal silicides, stannides, phosphides, or antimonides, but also other alloying components are possible [4, 9]. To give an example, lithiation of the iron stannide FeSn_2 leads to the formation of Li_xSn ($x \leq 4.4$) and nano-sized (almost non-crystalline) iron particles. The latter do not react with lithium. They act as a kind of inactive matrix and allow for the intergrain electronic contact, a typical function of a composite material. The dispersion of the lithium stannide into the metal matrix allows for higher cycle life of the electrochemical cells. Even better results occur when the transition metal stannides are directly used as nanomaterials obtained *via* a polyol process [10]. Small particles have less absolute volume change and allow effective lithium conduction due to shortened diffusion distances. The process discussed is the so-called *conversion reaction concept* that is used for improvement of the cells. This concept has also been tested for transition metal oxides, sulphides, and nitrides.

Ternary intermetallic phases $\text{Li}_x\text{T}_y\text{X}_z$ might occur during the first steps of the *conversion reactions*. So far, only few of these phases are known. From a crystal chemical point of view they are composed of $[\text{T}_y\text{X}_z]^{6-}$ polyanions which leave channels or cages for the lithium atoms. The structural data and some properties for the tetrelides are summarized in a review article [11]. The term alloying is misleading in this context. Most of the $\text{Li}_x\text{T}_y\text{X}_z$ phases are well defined inorganic compounds. From an explorative synthesis point of view, many of the $\text{Li}_x\text{T}_y\text{X}_z$ phases have still not been discovered.



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4.5 Metallic Glasses

In Chapters 3.1–3.18 we discussed the crystal chemistry of elemental metals and well-ordered superstructure variants. In these compounds one observes a discrete composition where each atom has well defined near-neighbor coordination in the respective structure. This is not the case in amorphous metals which are also called metallic glasses or glassy metals, since they exhibit structural features similar to the well-known oxide glasses.

To give an example, if a melt of the initial composition 3Cu:1Au is quenched, an *fcc* cell with random copper/gold occupancy results. Each atom has cuboctahedral coordination. Slow cooling of the sample leads to crystallization with copper/gold ordering (Chapter 3.3) with AuCu_{12} and AuCu_4Au_8 cuboctahedra. These order-disorder transitions can easily be explained with the cubic closest packing. On the other hand, if a melt of the starting composition 3Au:1Si is cooled extremely rapidly (in the order of 10^6 K/s), crystallization is suppressed and one obtains an amorphous material [1]. Such rapid quenching of the material is only possible by the *melt-spinning* technique (copper roller quenching method). A schematic presentation of such an experimental setup is shown in Fig. 4.13. The alloy is melted by a high-frequency technique and the liquid alloy is pressed through a very narrow slit using nitrogen or argon gas pressure. The slit is positioned very close to a large water-cooled rotating copper drum. The drum is turning fast and one obtains thin (some microns in diameter) ribbons which can be several hundred meters long within one batch. Another technique is *splat quenching*, where liquid droplets of an alloy are rapidly cooled within fractions of a second. For many years this extreme cooling rate was a prerequisite for the preparation of metallic glasses. Meanwhile alloy compositions are known that require only cooling rates of one Kelvin per second. Such metallic glasses can directly be casted in cold metallic moulds, leading to bulk samples in centimeter size. This technique offers many other possibilities than simple ribbons do.

Metallic glasses form only if at least two different elements are present. Often transition metals (Fe, Zr, Pd) are alloyed with an element near the metal-insulator

borderline in the Periodic Table (often Si, P) and the glass forming ability is frequently associated with the presence of low-melting eutectics. Typical compositions of metallic glasses are $\text{Zr}_{54}\text{Cu}_{46}$, $\text{Pd}_{82}\text{Si}_{18}$, $\text{Fe}_{80}\text{P}_{20}$, or $\text{Fe}_{80}\text{P}_{13}\text{C}_7$. Today much more sophisticated multinary compositions are known, e. g. $\text{Zr}_{60}\text{Ni}_{25}\text{Al}_{15}$, $\text{La}_{55}\text{Ni}_{20}\text{Al}_{25}$, $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$, or $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ [2], and even more complex compositions like the meanwhile commercially available Vitreloy $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ [3]. According to their composition metallic glasses are subdivided into non-ferrous and ferrous ones [2]. A lot of work has been devoted to understand the glass forming abilities and to examine the many glass forming systems. This detailed information is summarized in diverse review articles [2, 4–10]

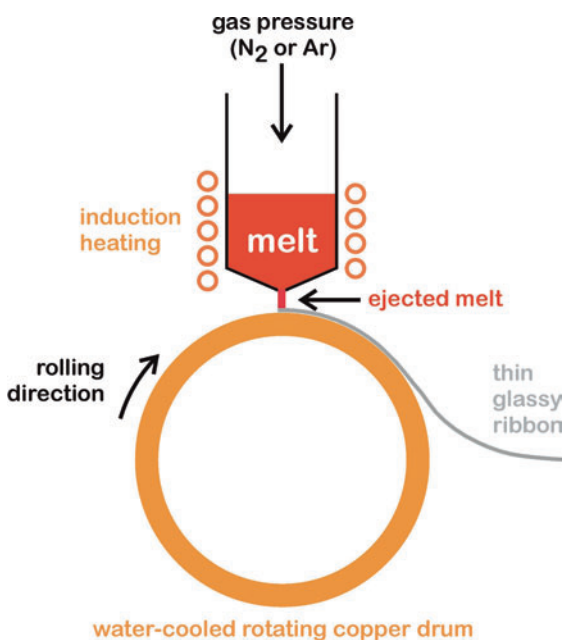


Fig. 4.13 Schematic setup of a melt-spinning device.

Since metallic glasses are amorphous, structural information cannot be deduced from classical diffraction techniques. If a melt with four different elements is quenched rapidly, the structure can be approximated to a random close-packed arrangement of spheres with some degree of short-range but no long-range order. As a conspicuous picture a box with random packing of blue, red, green, and gray spheres is presented in Fig. 4.14. Due to the severe differences in sizes, the atoms have between five and seven nearest neighbors within one layer, similar to the close-packed structures. Information on the local structure in such metallic glasses (similar to conventional oxide glasses) can be obtained through random distribution functions (RDF) which

give hints for the number of neighbors and their average distances. Most effectively this can be done by EXAFS measurements. Upon tuning the absorption edge of each element present in the metallic glass one can get the RDFs for each element. In contrast to silicate glasses a simple description by random networks is not possible for metallic glasses. Packing of the space is achieved by so-called Bernal deltahedra [6]. This already emphasizes the close relationship to quasicrystalline materials. In other cases the local coordination is similar to the crystalline intermetallic phases. To give an example, phosphorus containing metallic glasses often show coordination number nine in the form of a tri-capped trigonal prism of metal atoms around phosphorus, similar to the many metal phosphides (Chapter 3.10.2).

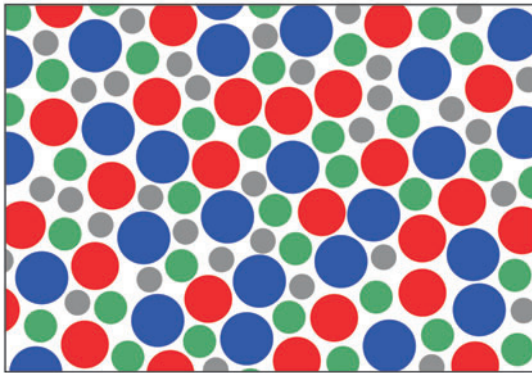


Fig. 4.14 Statistical packing of spheres with four different sizes inside a box.

On the energy scale metallic glasses are metastable materials. They devitrify upon heating, accompanied by crystallization reactions. Polymorphous, primary, and eutectic crystallization are the three main categories [6]. An interesting result in this context is the crystallization of $\text{Zr}_5\text{Ni}_4\text{Al}$ from annealed metallic glass of composition $\text{Zr}_{60}\text{Ni}_{25}\text{Al}_{15}$ [11].

Metallic glasses have very promising properties. They are much stronger than crystalline metals since they contain no dislocations and no grain boundaries. This leads to high strength and high plasticity. Due to this unique combination of strength and toughness, metallic glasses can store a high amount of elastic energy. This property is already commercially used. The heads of high quality golf clubs are made thereof.

Furthermore these glassy metals are more resistant to chemical attack and corrosion (many crystalline materials show enhanced reactivity at dislocations and grain boundaries) and they show good chemical homogeneity. Due to these promising properties about 70 % of implant materials for artificial knee and hip joints, bone plates, bone screws, and dental implants are made of bulk metallic glasses. As bulk

material or in the form of coatings metallic glasses also find application in surgical blades which have much lower surface roughness and improved sharpness.

Due to their low coercivity, several metallic glasses can easily be magnetized and de-magnetized. This behavior is used in very large quantity in anti-theft devices in most supermarkets (electronic article surveillance). Many other promising properties are known [2] and might be commercialized in future.



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