

Lattice Parameter and Density in Germanium-Silicon Alloys¹

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The lattice parameter and density of chemically analyzed samples of homogeneous Ge-Si alloy have been measured throughout the entire alloy system. The temperature dependence of the lattice parameter was measured from 25 to 800°. Compositional dependences of the lattice parameter and density are accurate to about ± 0.3 atomic % in alloy composition. Lack of chemical analysis or sample inhomogeneity may explain the large discrepancies between previous investigations of these properties. The excess volume of mixing is given by $\Delta V_m^{xs} = -0.24c_{Ge}c_{Si}$ cm.³ mole⁻¹. Deviations from Vegard's law are negative as predicted by models based on first-order elasticity theory, but smaller in absolute magnitude. This discrepancy is about the size of the positive deviations calculated from second-order elasticity theory.

Introduction

Composition in the Ge-Si alloy system can be accurately determined from measurements either of density or of lattice parameter provided the dependences of lattice parameter and density on composition are known. However, the large discrepancy between the results of previous investigations of these properties²⁻⁵ corresponds to an uncertainty in composition for a definite value of lattice parameter or density of ± 4 atomic % Ge throughout most of the system. This discrepancy can be attributed to the fact that no previous investigator has both evaluated sample homogeneity and determined composition by chemical analysis. Therefore the variation of lattice parameter and density at room temperature has been reinvestigated throughout the Ge-Si alloy system, using chemically homogeneous specimens. The temperature dependence of lattice parameter has also been measured in the range 25-800° for several alloy compositions.

Experimental Procedure

Homogeneous Ge-Si alloy ingots were prepared from high purity Ge and Si by zone leveling using the procedure described by Dismukes and Ekstrom.⁶ Typical mass spectrographic analyses of impurities in these materials are shown in Table II. The procedure for this study consisted of first measuring the density and then measuring either the lattice parameter or the chemical composition of the material.⁷

Table I: Previous Investigations of Lattice Parameter and Density in the Ge-Si Alloy System

Authors	Method of preparation	Lattice parameter	Density ^a	Method of analysis
Stöhr and Klemm ^b	Sintering	D	ND	None ^c
Johnson and Christian ^d	Slow cooling from the melt	D	D	Polarographic
Wang and Alexander ^e	Zone leveling	D	D	None ^f
Busch and Vogt ^g	Zone leveling	D	D	None ^h
Sandulova, <i>et al.</i> ⁱ	Vapor transport	D	ND	None ^j

^a D = determined; ND = not determined. ^b See ref. 2a. ^c Composition assumed to be that of the mixed components before sintering. ^d See ref. 2b. ^e See ref. 3. ^f Composition assumed to be that of the mixed components before some leveling. ^g See ref. 4. ^h Composition determined from the results of Johnson and Christian. ⁱ See ref. 5. ^j Composition assumed to be that of the mixed components before vapor transport.

(1) This research has been supported by the U. S. Navy Bureau of Ships under Contract No. N0bs-88595.

(2) (a) H. Stöhr and W. Klemm, *Z. anorg. allgem. Chem.*, **241**, 313 (1939); (b) E. R. Johnson and S. M. Christian, *Phys. Rev.*, **95**, 560 (1954).

(3) C. C. Wang and B. H. Alexander, Final Technical Report on Investigation of Germanium-Silicon Alloys, Bureau of Ships Contract No. N0bsr-63180, Feb. 17, 1955.

(4) G. Busch and O. Vogt, *Helv. Phys. Acta*, **33**, 437 (1960).

(5) A. V. Sandulova, P. S. Bogoiavlenski, and M. I. Droniuk, *Dokl. Akad. Nauk SSSR*, **143**, 610 (1962).

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(7) K. L. Cheng and B. L. Goydich, *Anal. Chem.*, **35**, 1273 (1963).

Table II: Mass Spectrographic Analyses for Impurities in Ge, Si, and Ge-Si Alloy

Materials	Typical impurity contents, atomic p.p.m.						
	Fe	Cu	Al	Mg	O	C	H
Ge-Si	1	0.2	5	1	300	30	100
Ge	6	ND ^a	0.4	0.4	10	100	30
Si	1	0.2	1	1	300	100	10

^a ND = not detected.

Densities were measured by the method of hydrostatic weighing,⁸ employing Archimedes' principle. The samples in the form of slices weighed 0.7–1.5 g., and the weight loss in water was 0.1–0.3 g. The samples were suspended from a 0.003-in. diameter tungsten wire and were weighed to a precision of 0.02 mg. using a semimicrobalance. Water, to which a small amount of wetting agent had been added to reduce the surface tension, was used as the immersion liquid. The measurements were corrected for water temperature and for the air displaced by the sample, but not for effects due to the wetting agent, dissolved air, or atmospheric pressure. The absolute accuracy of these density measurements is shown to be within $\pm 0.1\%$ by comparison in Table III of measurements made on Si and Ge corrected to 25° with the values of Smakula and Sils.⁸

Samples for lattice parameter measurements were ground to pass through a 325-mesh screen. The sieved powder was mixed with Duco cement and was then rolled into a fiber approximately 0.1 mm. in diameter. The fiber was mounted in a 114.6-mm. diameter camera using the asymmetric method of mounting the film. Powder patterns were obtained using Ni-filtered Cu radiation, with an exposure time of about 24 hr. and at room temperature of $25 \pm 1^\circ$. The back reflection lines, both $K\alpha_1$ and $K\alpha_2$, were measured to within ± 0.05 mm. The lattice parameter for each reflection was calculated, and the final value was obtained by extrapolation using the Nelson-Riley function. The absolute accuracy of the lattice parameter measurements is shown to be within ± 0.0005 Å. by comparison in Table III of measurements made on Si and Ge with the values of Smakula and Kalnajs.⁹ The variation of lattice parameter with temperature in the range 25–800° was determined by scanning the (531) and (620) diffraction peaks with a diffractometer. Values of the lattice parameter at each temperature were obtained by averaging the lattice parameter values for the two peaks. Good agreement between the diffractometer

Table III: Experimental Values of Density, Lattice Parameter, and Chemical Composition for Ge-Si Alloy Samples

d , g. cm. ⁻³	a , Å.	C , at. % Ge
2.6382	...	7.5
2.6319	...	8.0
2.6357	...	8.0
2.6330	5.4492	..
3.0047	...	18.9
3.0098	...	20.0
3.0710	...	21.4
3.0830	...	21.7
3.0120	5.4726	..
3.0822	5.4772	..
3.0884	...	22.6
3.1118	...	23.5
3.2723	...	28.2
3.2844	5.4898	..
3.3634	...	30.5
3.3585	...	31.6
3.4735	5.5032	..
3.4762	...	35.4
3.5181	...	35.5
3.5715	...	36.6
3.6312	5.5151	..
3.6313	...	38.8
3.6340	...	39.8
3.6874	...	40.3
3.6766	...	41.4
3.7750	5.5250	..
3.7827	...	44.5
3.7883	...	44.6
3.9915	5.5404	..
3.8944	...	48.0
3.9940	...	49.9
4.0037	...	50.6
4.0749	5.5475	..
4.0673	...	53.8
4.0897	...	54.8
4.1652	...	57.0
4.1923	5.5567	..
4.5289	5.5841	..
4.5170	...	68.0
4.4969	...	68.9
4.6817	5.5966	..
4.6652	...	71.9
4.6735	...	72.3
4.8246	...	79.4
4.8513	...	79.4
4.8410	5.6112	..
5.0752	5.6325	..
5.0754	...	87.3
5.0728	...	87.9
5.0970	...	88.8
5.0410	...	89.4
5.1090	...	90.8
5.1697	5.6419	..
5.1669	...	94.8
5.3256	5.6575	Ge ^a
5.32674	5.65754	Ge ^b
2.3277	5.4310	Si ^a
2.32902	5.43072	Si ^b

^a Present work. ^b See ref. 9 and 10.(8) A. Smakula and V. Sils, *Phys. Rev.*, **99**, 1744 (1955).(9) A. Smakula and J. Kalnajs, *ibid.*, **99**, 1737 (1955).

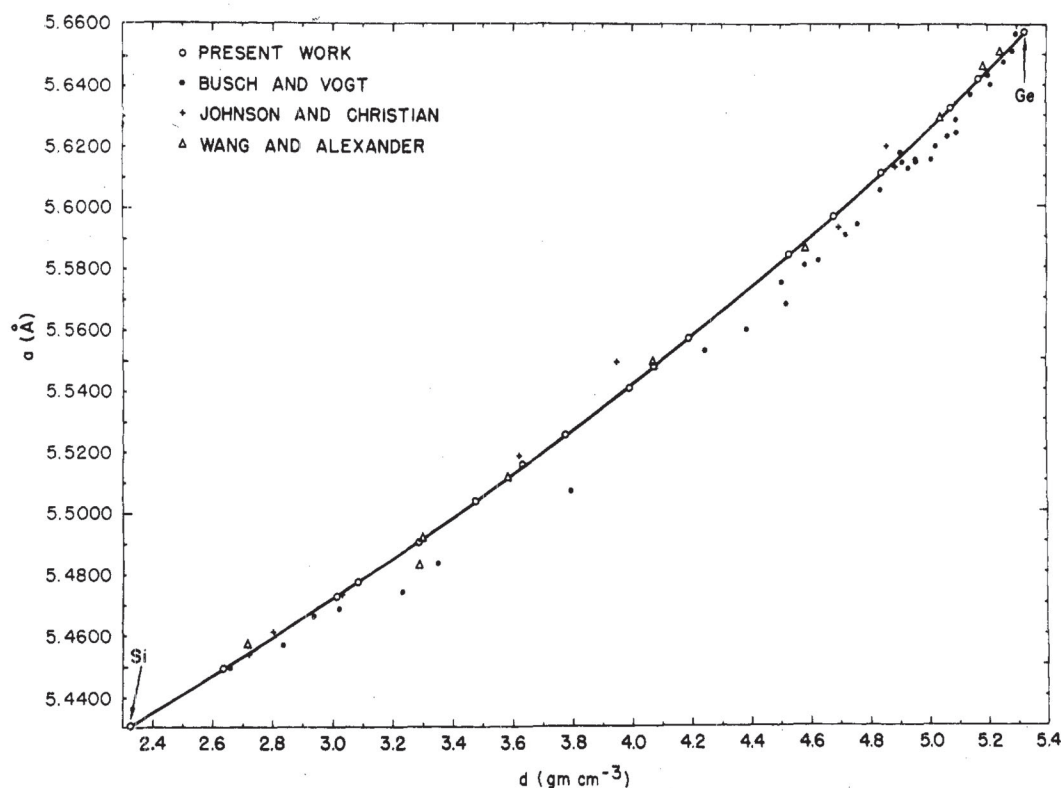


Figure 1. Variation of lattice parameter with density in the Ge-Si alloy system.

method and the Debye-Scherrer method was obtained at room temperature.

Chemical composition was determined by analyzing the material for its Ge content by the method of Cheng and Goydich⁷ using samples containing 150–300 mg. of Ge.

Results

Data on measurements of density and lattice parameter at 25° for different alloy compositions are listed in Table III. The variation of lattice parameter with density is shown in Fig. 1, and this is compared with published data. The curve is drawn through the data from the present study.

The scatter in the data of Johnson and Christian^{2b} and of Busch and Vogt,⁴ and the large systematic error in the latter data, may be due to sample inhomogeneity. The preparative procedure employed by Johnson and Christian, slow cooling from the melt, could lead to this condition, since the growth rate was not controlled and the melt composition changed during growth. The growth rates employed by Busch and Vogt⁴ appear to have been too large for preparing homogeneous material by zone leveling in the middle

of the system,⁶ where the discrepancy is greatest. There is good agreement between our results and the data of Wang and Alexander,³ who have shown that their material was homogeneous.

The curve for the variation of density with chemical composition, shown in Fig. 2, was drawn through the points determined by chemical analysis. Uncertainty in the recovery factor for Ge, $\pm 0.3\%$, is probably the largest source of error in the analysis.⁷ This effect contributes to the relatively large scatter at the Ge-rich end of the system. We also calculated from the curve in Fig. 1 the average atomic weight, $\bar{A}$, using the relation

$$\bar{A} = da^3N/8 \quad (1)$$

where N is Avogadro's number,¹⁰ and from this the

(10) The value of N on the universal C¹² scale, 6.02311×10^{23} (mole)⁻¹, was obtained from the value of Cohen and DuMond¹¹ on the O¹⁶ scale using the conversion factor of Cameron and Wichers.¹² Spectroscopically determined atomic weights on the C¹² scale were 72.628 and 28.086 for Ge and Si, respectively.¹²

(11) E. R. Cohen and J. W. M. DuMond, *Phys. Rev. Letters*, **1**, 291 (1958).

(12) A. E. Cameron and E. Wichers, *J. Am. Chem. Soc.*, **84**, 4175 (1962).

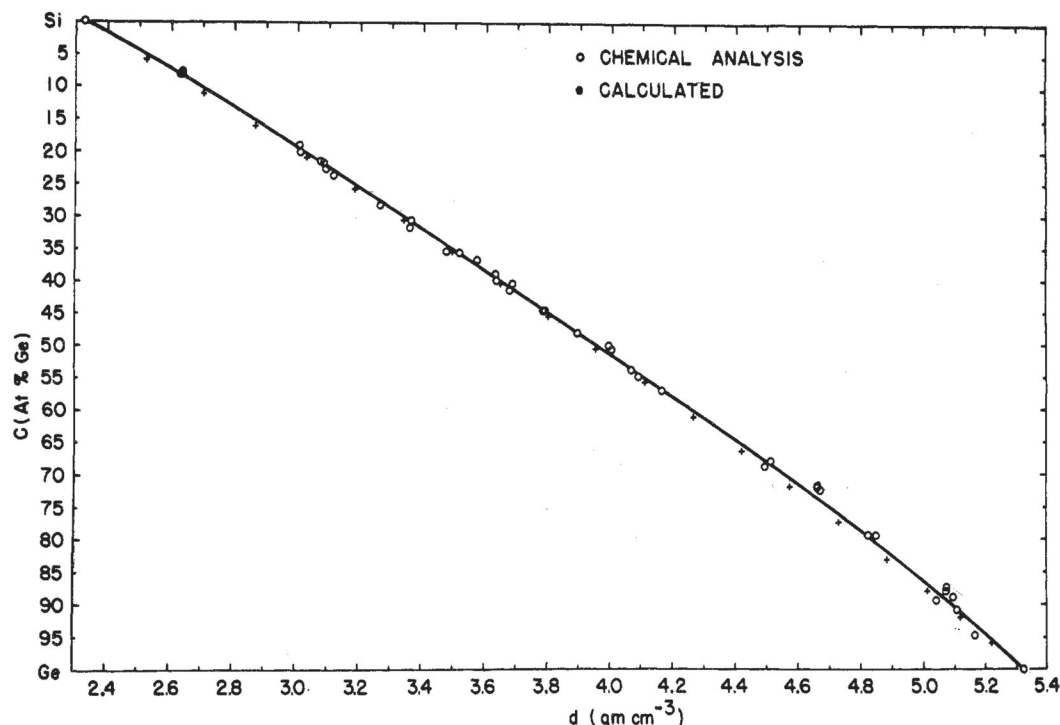


Figure 2. Variation of density with chemical composition in the Ge-Si alloy system.

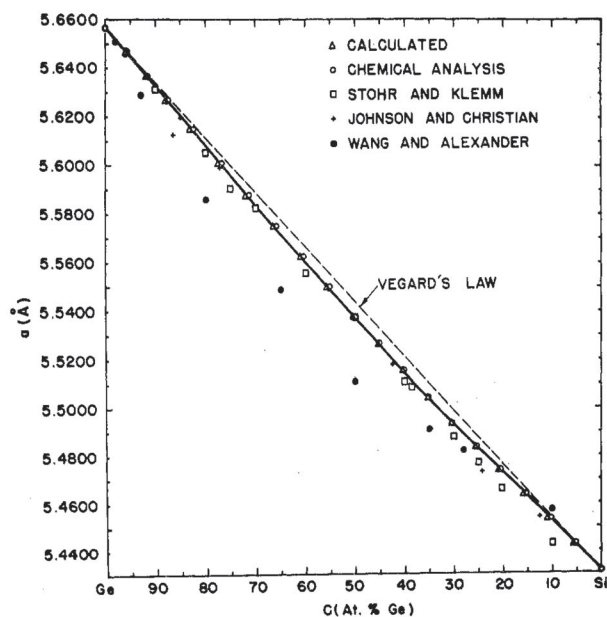


Figure 3. Variation of lattice parameter with composition in the Ge-Si alloy system.

alloy composition. Points for density *vs.* composition determined in this manner are also shown in Fig. 2.

The variation of lattice parameter with composition is shown in Fig. 3. The chemical composition was determined by (a) combining Fig. 1 and 2, and (b) using eq. 1. The results of Johnson and Christian^{2b} (Fig. 3) show some scatter, which could be due to sample inhomogeneity as discussed above, or to error in the polarographic analytical method as was pointed out by Cheng and Goydsh.⁷ The results of Stöhr and Klemm^{2a} are in better agreement with our data, but they show a large deviation at low Ge concentration. The values of Wang and Alexander³ show a large disagreement when plotted against the given compositions. This suggests that their specimens, though chemically homogeneous, differed in composition from the intended values by an average of about 7 atomic % Ge. The lattice parameter data of Busch and Vogt⁴ were not compared with the results of the present work, because of both the lack of chemical analysis and of the large deviation observed in Fig. 1.

In Table IV are listed values of density and lattice parameter at 25° for composition intervals of 5 atomic % Ge. These values are derived from Fig. 1-3, and their absolute accuracy is probably within ± 0.3 atomic % Ge. Values of density were taken as the mean of those from the curve in Fig. 2 and of those calculated from eq. 1. The departure in lattice

Table IV: Accurate Values of Density and Lattice Parameter for Ge-Si Alloy Derived from Fig. 1-3

C, at. % Ge	d, g. cm. ⁻³	a, Å.	a - a _v , Å.
0	2.3277	5.4310	...
5	2.5100	5.4419	-0.0004
10	2.6825	5.4522	-0.0014
15	2.8490	5.4624	-0.0026
20	3.0075	5.4722	-0.0041
25	3.1660	5.4825	-0.0051
30	3.3265	5.4928	-0.0062
35	3.4840	5.5038	-0.0065
40	3.6405	5.5149	-0.0067
45	3.7950	5.5261	-0.0068
50	3.9470	5.5373	-0.0069
55	4.0990	5.5492	-0.0063
60	4.2465	5.5609	-0.0060
65	4.3905	5.5727	-0.0055
70	4.5335	5.5842	-0.0053
75	4.6730	5.5960	-0.0048
80	4.8115	5.6085	-0.0027
85	4.9445	5.6206	-0.0019
90	5.0740	5.6325	-0.0023
95	5.1990	5.6448	-0.0013
100	5.3256	5.6575	...

parameter from Vegard's law, Δ , given by

$$\Delta = a_{\text{Ge-Si}} - \{a_{\text{Si}} + (a_{\text{Ge}} - a_{\text{Si}})c_{\text{Ge}}\} \quad (2)$$

where c_{Ge} = atomic fraction Ge is also listed in Table IV. This quantity is negative throughout the system and reaches a broad minimum in the middle of the system.

The excess volume of mixing, ΔV_m^{xs} , calculated using the expression

$$\Delta V_m^{\text{xs}} = \frac{N}{8} [a_{\text{Ge-Si}}^3 - \{a_{\text{Si}}^3 + (a_{\text{Ge}}^3 - a_{\text{Si}}^3)c_{\text{Ge}}\}] \quad (3)$$

is also small and negative throughout the alloy system. From the plot of $\Delta V_m^{\text{xs}}/(c_{\text{Ge}}c_{\text{Si}})$ against c_{Ge} given in Fig. 4, it is seen that ΔV_m^{xs} can be expressed by the empirical relation

$$\Delta V_m^{\text{xs}} = -0.24c_{\text{Ge}}c_{\text{Si}} \text{ cm.}^3 \text{ mole}^{-1} \quad (4)$$

where c_{Si} is the atomic fraction of Si.

The temperature dependence of the lattice parameter of Ge, Si, and three Ge-Si alloys is shown in Fig. 5 together with the average values of the linear expansion coefficient, $\bar{\alpha}$, between 25 and 800°. For Ge and the Ge-Si alloys, α is independent of temperature, but the data for Si indicate an increase in α of about 50% from 25 to 800°. A larger increase in α with temperature has been reported by Dutta.¹³

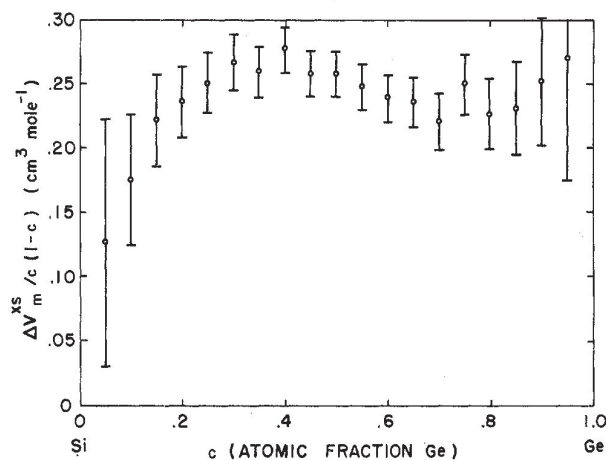


Figure 4. Variation of reduced volume of mixing, $\Delta V_m^{\text{xs}}/c_{\text{Ge}}c_{\text{Si}}$, with c_{Ge} at 25°.

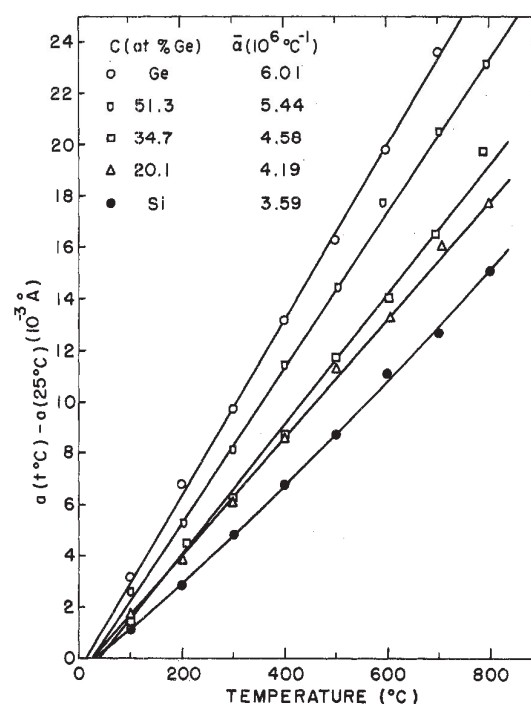


Figure 5. Variation of lattice parameter with temperature for Ge, Si, and some Ge-Si alloys.

For the alloys containing 20.1 and 34.7 atomic % Ge, the deviation from Vegard's law and the excess volume of mixing are constant with temperature within the experimental uncertainty of about $\pm 15\%$ of these quantities. In the 51.7 atomic % Ge alloy, these deviations decrease about 25% between 25 and 800°.

(13) B. N. Dutta, *Phys. Status Solidi*, 2, 984 (1962).

Discussion

Volume of Mixing. The observation that ΔV_m^{xs} can be expressed by eq. 4 suggests that the Ge-Si alloy system might show a simple type of thermodynamic behavior.¹⁴ Since ΔV_m^{xs} is not zero, the system is not an ideal solution, in agreement with Thurmond's¹⁵ conclusion from the nature of the phase diagram. The next simplest type of behavior is regular solution theory in which $\Delta S_m^{xs} = 0$. The quasi-chemical approach to regular solution theory¹⁶ leads to the expression

$$\Delta H_m^{xs} = \Omega c_{Ge} c_{Si} \quad (5)$$

where Ω is related to the bond energies H_{Ge-Ge} , H_{Si-Si} , and H_{Ge-Si} by

$$\Omega = 4[H_{Ge-Si} - \frac{1}{2}\{H_{Ge-Ge} + H_{Si-Si}\}] \quad (6)$$

From quasi-chemical theory one would expect that Ω and ΔV_m^{xs} have the same sign. Rastogi and Nigam^{17a} have calculated a value of +20 kcal. mole⁻¹ for Ω from a quasi-chemical regular solution treatment of the Ge-Si alloy phase diagram. We have repeated their calculation considering a larger section of the phase diagram, and obtain the value +2.4 kcal. mole⁻¹. This is in good agreement with the value +2.2 kcal. mole⁻¹ obtained by Romanenko and Ivanov-Omskii.^{17b} Thus while the value of Ω is quite uncertain, the sign is probably correct. Since Ω and ΔV_m^{xs} are not of the same sign, a more refined model will be required to explain the thermodynamic properties of the Ge-Si alloy system.

Deviations from Vegard's Law. The Ge-Si alloy system is an attractive one for comparing experimental deviations from Vegard's law with theoretical calculations, since there is only one crystal structure in the system, no relative valency effect, and only small differences in size and electronegativity between the constituents. A summary of the theoretical work on this topic was recently given by Gschneidner and Vineyard.¹⁸ The deviations from Vegard's law predicted by theories which require data only on the elastic properties of the pure components are shown in Fig. 6. Pines¹⁹ used an elastic sphere model to derive the equation

$$\Delta = c_A c_B (a_B - a_A) \left[\frac{\frac{4}{3} \mu_A (\chi_A - \chi_B)}{1 + \frac{4}{3} \mu_A (c_B \chi_A + c_A \chi_B)} \right] \quad (7)$$

where A refers to the solvent, B to the solute, μ is the shear modulus, and χ is the compressibility. Fournet²⁰ considered the effects of nearest neighbor interactions to obtain the equation

$$\Delta = c_A c_B (a_B - a_A) \left[\frac{(\chi_A / \chi_B) - 1}{c_A + c_B (\chi_A / \chi_B)} \right] \quad (8)$$

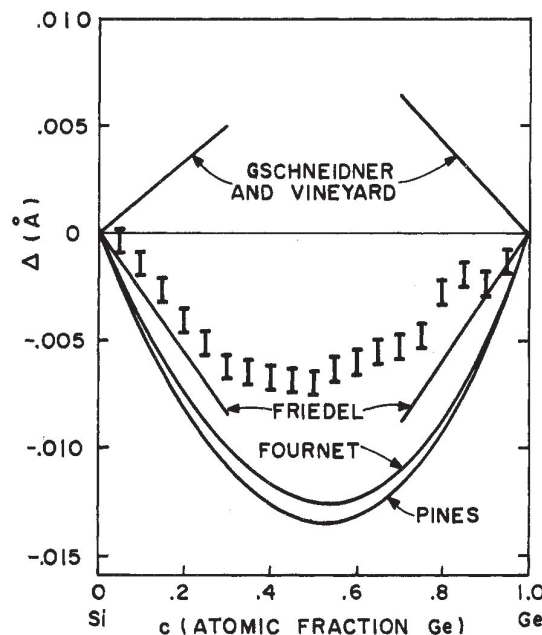


Figure 6. Deviations from Vegard's law in the Ge-Si alloy system predicted by several theories.

Both eq. 7 and 8 predict negative deviations when the element with the larger atom is softer. Thus they give the correct sign of the deviation for the Ge-Si alloy system, but the predicted magnitude is about twice the experimental value.

Friedel²¹ treated the elastic sphere model so as to obtain the equation

$$\Delta = c_B (a_B - a_A) \left\{ (\chi_A / \chi_B) - 1 \right\} / \left[\frac{(1 + \sigma_A) \chi_A}{2(1 - 2\sigma_A) \chi_B} + 1 \right] \quad (9)$$

where σ_A is Poisson's ratio. This equation is valid only for dilute solutions, but within this limit it is in better agreement with experiment than those of Pines¹⁹ and Fournet.²⁰

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(20) G. Fournet, *J. phys. radium*, **14**, 374 (1953).

(21) J. Friedel, *Phil. Mag.*, **46**, 514 (1955).

Gschneidner and Vineyard¹⁸ applied second-order elasticity theory to obtain the equation

$$\Delta = 2 \left(\frac{d\mu}{dp} - \frac{\mu}{B} \right) \frac{(a_A - a_B)^2}{a_A} c_B \quad (10)$$

where p is pressure and B is the bulk modulus. This equation is also valid only for dilute solutions. They suggest the approximation

$$\left(\frac{d\mu}{dp} - \frac{\mu}{B} \right) \cong 6\alpha V\mu/c_V \quad (11)$$

where V is the molar volume and c_V is the molar heat capacity. This equation predicts only positive devia-

tions from Vegard's law. However, the magnitude of its effect is comparable to the amount by which the first-order theories overestimate the negative deviations. This suggests that a theory combining both first- and second-order elasticity effects would be a considerable improvement over current theories for predicting deviations from Vegard's law.

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Kinetic Study on the Reaction of Sodium Chlorite with Potassium Iodide

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The rate of the reaction of sodium chlorite with potassium iodide was measured by the polarized platinum electrode method at 25° and at different concentrations of the reactants. The orders with respect to the hydrogen, iodide, and chlorite ions were substantially one in all cases. The reaction shows a negative salt effect in the presence of NaNO₃ and Ba(NO₃)₂, a stronger retardation in the presence of Th(NO₃)₄, and a remarkable acceleration in the presence of UO₂(NO₃)₂ and a trace of FeSO₄. From the rates at different temperatures, ranging from 15 to 50°, an activation energy of 14.4 kcal. can be calculated.

The oxidation of the iodides by the oxyacids of the halogens has been investigated by several authors since 1890¹; recently, the effects of different salts on the reaction between iodate and iodide has been studied in this department,² and earlier a similar research had been carried on the reaction between bromate and iodide.³ No data seem to exist on the analogous reaction between chlorite and iodide, despite the fact that the chlorites are now widely used as bleaching agents in the textile industry.⁴ A better knowledge of the oxidizing characteristics of the chlorites seems therefore desirable, and a comparison with the other oxyacids of the halogens could also be interesting.

Experimental

Materials. Sodium chlorite was prepared from a technical B.D.H. product, containing about 80%

- (1) G. Magnanini, *Gazz. chim. ital.*, **20**, 390 (1890); (b) S. Dushman, *J. Phys. Chem.*, **8**, 453 (1904); (c) A. A. Noyes, *Z. physik. Chem.*, **19**, 599 (1896); E. Abel and F. Stadler, *ibid.*, **122**, 49 (1926); (d) K. Weber and R. Vališ, *Ber.*, **72B**, 1488 (1939); (e) E. Abel, *Helv. Chim. Acta*, **33**, 785 (1950); (f) K. J. Morgan, M. G. Peard, and C. F. Cullis, *J. Chem. Soc.*, 1865 (1951).
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