

Ab initio theory of point defects in oxide materials: structure, properties, chemical reactivity

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Abstract

Point defects play a fundamental role in determining the physical and chemical properties of inorganic materials. This holds not only for the bulk properties but also for the surface of oxides where several kinds of point defects exist and exhibit a rich and complex chemistry. A particularly important defect in oxides is the oxygen vacancy. Depending on the electronic structure of the material the nature of oxygen vacancies changes dramatically. In this article we provide a rationalization of the very different electronic structure of neutral and charged oxygen vacancies in SiO_2 and MgO , two oxide materials with completely different electronic structure (from very ionic, MgO , to largely covalent, SiO_2). We used methods of ab initio quantum chemistry, from density functional theory (DFT) to configuration interaction (CI), to determine the ground and excited state properties of these defects. The theoretical results are combined with recent spectroscopic measurements. A series of observable properties has been determined in this way: defect formation energies, hyperfine interactions in electron paramagnetic resonance (EPR) spectra of paramagnetic centers, optical spectra, surface chemical reactivity. The interplay between experimental and theoretical information allows one to unambiguously identify the structure of oxygen vacancies in these binary oxides and on their surfaces. © 2000 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

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1. Introduction

Metal oxides are certainly among the most important ceramic materials with wide technological applications in coating, catalysis, electrochemistry, optical fibers, sensors, etc. [1–4]. Very often, however, the most important properties of the materials are directly or indirectly connected to the presence of defects and in particular of point defects [5]. These centers determine the optical, electronic and trans-

port properties of the material and usually dominate the chemistry of its surface. A detailed understanding and a control at atomistic level of the nature (and concentration) of point defects in oxides is therefore of fundamental importance to synthesize new materials with well defined properties. This has lead in recent years to the birth of the new field of defect engineering. Of course, before being created in controlled conditions, all aspects of the point defects' physico-chemical properties must be understood.

The accurate theoretical description of the electronic structure of point defects in oxides is essential for the understanding of their structure–properties relationship. In recent years a great deal of attention

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has been directed to the theoretical study of non-defective bulk oxides, although perfect, defect free, oxides are simply an idealization and do not exist in nature. From a computational point of view the treatment of point defects is particularly challenging. In fact, the electronic properties of a point defect are often determined by its local environment and require a localized description. On the other hand, it is essential to take into account solid state effects by ‘embedding’ the local system in the host crystal. Several theoretical approaches have been proposed to treat neutral and charged defects, and a brief account will be given in the following [6–16].

One of the most important defects in oxides, if not the most important, is the oxygen vacancy. Oxygen vacancies are naturally present in every oxide in the form of Shottky or Frenkel defects and their concentration can be increased or reduced in several ways. Oxides exhibit very different electronic structures: some are highly ionic, some largely covalent. From the point of view of electrical conductivity, in the class of oxides one can find semiconductors, wide-gap insulators, oxides with metallic conductivity and even superconductors. While some oxides are stoichiometric, there are many examples of non-stoichiometric oxides with wide compositional ranges, in particular for transition metal oxides [1–5]. The geometric structure of oxides can go from very simple systems with a NaCl-like structure to complex spinels and perovskites. Finally, the oxidation state of the metal in oxides can vary from very low to very high formal oxidation numbers. The great variety of behaviors implies that the geometric and electronic nature of oxygen vacancies also change dramatically from case to case. In this study we review the present level of understanding of the electronic and geometrical structure of neutral and charged oxygen vacancies in SiO_2 and MgO , two non-transition metal oxides with rather different structural and electronic properties. An oxygen vacancy in SiO_2 can either be neutral, V_{O} , or positively charged, V_{O}^+ . This latter defect is paramagnetic and is also called the E' center. Oxygen vacancies in MgO are known as color centers or F centers (from *Farbe*, the German word for color); if the vacancy is localized at the surface a subscript *s* is added, F_s . F centers exist in three states, depending on their electronic charge. Diamagnetic oxygen vacancies can be either neutral, F, or doubly charged, F^{2+} . In the former case two electrons are associated to the vacancy. Of particular

interest for the characterization of oxygen vacancies are the paramagnetic F^+ centers, consisting of a single electron trapped in the cavity formed by removing an oxygen anion, O^- [16,17]. In a sense, SiO_2 and MgO can be considered as extreme cases of oxide materials with pronounced covalent and dominant ionic character, respectively. The comparison of the electronic nature of oxygen vacancies in the two systems allows one to draw some general rules about the nature of these point defects in other oxide materials.

The paper is organized as follow. First we briefly describe the modern computational techniques which can be used to study point defects in solids. In particular we will focus on the cluster model approach [18] which is particularly appropriate to study localized phenomena, like defects and impurity states, local excitations or core level ionizations, provided that the effect of the rest of the crystal is included. Because of the different nature of SiO_2 and MgO , different approaches are used to take into account the surrounding. Advantages and limitations of the approach are discussed in the perspective of the potential use of quantum-chemical calculations as a practical tool to solve problems in solid state chemistry. In Section 3 we discuss in detail the electronic properties of neutral and oxygen vacancies in SiO_2 , and in Section 4 a similar review is done for the MgO case. In both cases contact with existing experimental data is done by computing directly available observable quantities, like formation energies (hence stabilities), hyperfine coupling constants in electron paramagnetic resonance (EPR) experiments and absorption and emission bands in optical spectra. From the direct comparison of the computed and the measured properties it is possible to gain new insight into the electronic and structural nature of oxygen vacancies in oxide materials.

2. Computational aspects

2.1. Cluster models of solids

The electronic structure of solids is usually described in terms of band structure. To this end, a unit cell containing a given number of atoms is periodically repeated in three dimensions to account for the ‘infinite’ nature of the crystalline solid and the Schrödinger equation is solved for the atoms in

the unit cell subject to periodic boundary conditions [19]. This approach is the method of choice in solid state physics. If one is interested in the study of a point defect, like an impurity atom or a vacancy, the presence of the defect in the unit cell results in a periodic repetition of the defect in the three directions of space, hence in an extremely high concentration of defects. The only way to reduce the defect concentration is to increase the size of the unit cell, but this implies a very large computational cost. Even for large supercells containing several tens of atoms, the defect concentration is orders of magnitude larger than in real systems where 10^{16} – 10^{18} defects/cm³ are usually present [5]. At these concentrations one can reasonably assume that the defects are isolated and do not interact with each other. In the periodic approach, the mutual interaction among the point defects can be strongly reduced but never completely eliminated.

An alternative approach to the periodic band structure methods to study solids is the cluster approach [18]. Here one considers explicitly only a finite number of atoms to describe a section of the solid while the rest of the crystal (or of the amorphous material) is treated in a more or less simplified way (embedding). The main conceptual difference is that in the cluster approach one uses molecular orbitals, MO, instead of delocalized bands. The description of the electronic properties is thus done in terms of local orbitals, allowing one to treat problems in solids with the typical language of chemistry, the language of orbitals. This is particularly useful when dealing with surface problems and with the reactivity of a solid surface. In fact, the interaction of gas-phase molecules with a solid surface can be described in exactly the same way as the interaction of two molecules. Of course, the cluster model is not free from limitations either. The most serious one is that the effect of the surrounding is often taken into account in a more or less approximate way, thus leading to some uncertainties in the absolute values of the computed quantities. It is also possible that some properties are described differently depending on the size and the shape of the cluster used. It is therefore necessary to check the results versus cluster size and shape. Examples of this aspect will be discussed in more detail below. The advantage, however, is that in describing point defects an infinite dilution is considered so that no mutual interaction of the defects is present in the model. There is

another important advantage in the use of clusters which should not be underestimated. This is the possibility to explicitly include correlation effects in the calculations through a configuration interaction (CI) procedure (see below). While this is not the only way to include correlation effects in the model, it is the best way to compute excited state properties, for example, optical transitions and intensities, and therefore optical spectra. While some examples of excited-state calculations based on time-dependent density functional theory (DFT) are now available [20], their application to solid state problems is still in its infancy and the use of cluster models and CI methods represents a valid approach to the study of excited states of point defects in solid matrices.

In this work two completely different strategies have been adopted to ‘embed’ the SiO₂ and the MgO clusters. In both cases we used a simplified approach, although it should be mentioned that more sophisticated schemes have been developed [21,22]. In SiO₂ the cluster dangling bonds have been saturated by H atoms (Fig. 1), a common procedure to terminate clusters of covalent materials [23]. The positions of the cluster atoms were initially fixed to those of α -quartz [24] and the H atoms were fixed at a given distance from the respective O and Si atoms along the O–Si directions. The position of all the Si and O atoms of the cluster has been reoptimised. The fixed H atoms provide a simple representation of the mechanical embedding of the solid matrix. This is an important aspect of the embedding, but not the only one. In fact, in this way one neglects the Madelung field arising from the charge asymmetry of the Si–O bond. In principle, this term can be of some importance, in particular for the description of charged defects.

The very ionic nature of MgO, on the other hand, implies that the Madelung potential is explicitly included in the models. Indeed, several properties of MgO are incorrectly described if the long range Coulomb interactions are not taken into account [25]. To provide a simple representation of the Madelung potential we used large arrays of ± 2 point charges (PC) (Fig. 2). However, the PCs polarize the oxide anions at the cluster border and cause an incorrect behavior of the electrostatic potential [26]. The problem can be substantially reduced by placing at the position of the $+2$ PCs around the cluster an effective core potential (ECP), representing the finite size of the Mg²⁺ core [27]. No basis

functions are associated to the ECP [28], which accounts for the Pauli or exchange repulsion of the O^{2-} valence electrons with the surrounding. This is a very simplified approach compared to more rigor-

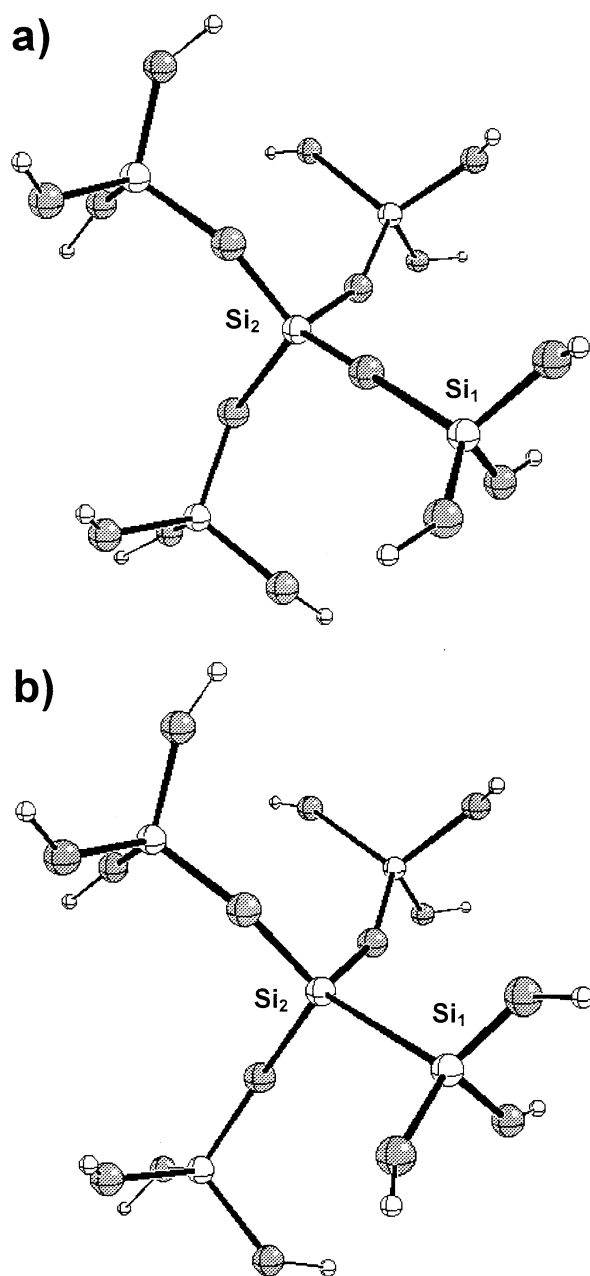


Fig. 1. (a) Model of a four-coordinated Si atom in α -quartz. (b) Model of an oxygen vacancy, V_O , in α -quartz; notice the formation of a direct Si-Si bond after O removal. The cluster dangling bonds have been saturated by H atoms.

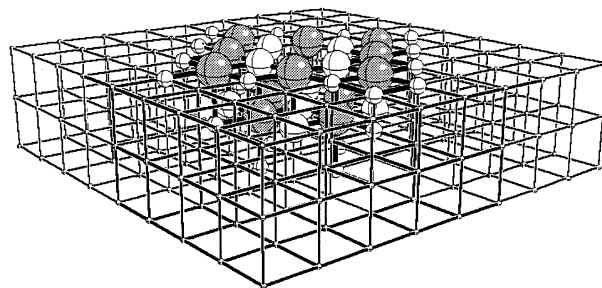


Fig. 2. A cluster model of an oxygen vacancy, F center, at the (100) surface of MgO. The ions in the cluster are represented by gray spheres (oxygen) and large white spheres (magnesium); small white spheres correspond to Mg^{2+} ions described by an ECP (see text). The entire cluster is embedded in a large array of point charges (only partially shown).

ous embedding techniques [29,30], but is computationally simple and reliable.

All geometry optimizations have been performed by computing analytical gradients of the total energy. Clusters of various sizes were used, as described in detail below. The models of an oxygen vacancy have been obtained by removing one oxygen atom from a model of the regular lattice. Also for the defective structures, the cluster geometries have been fully optimized with the boundary condition that the position of the external H atoms or of the ECPs is fixed. This means that only local relaxation effects have been considered; long-range lattice relaxation is not included.

2.2. Methods and basis sets

Two general groups of methodologies are used to solve the Schrödinger equation and to determine the electronic structure of molecules and solids, the Hartree-Fock (HF) approach and related methods to include correlation effects like Møller-Plesset perturbation theory (MP2) or CI [31] and the DFT approach [32]. The main difference between the two methods is that in the HF approach the objective is the determination of the wave function of the system while in DFT the quantity of interest is the charge density ρ ; in fact, the Hohenberg-Kohn theorem [33] ensures that the energy E of a system is a functional of ρ which takes its minimum value E_0 for the ground state density ρ_0 . Despite this profound conceptual difference, the two methods, HF + correlation and DFT, provide in ultimate analysis similar

results and the choice of one approach or the other is largely a matter of convenience.

In this work we have performed both HF + MP2 or HF + CI and DFT calculations. The hybrid exchange-correlation potential of Becke [34] and Lee–Yang–Parr [35] (B3LYP) was employed in the DFT calculations. The wave function or the charge density of the system are expressed in terms of atomic orbital (AO) basis functions. For paramagnetic defects or open shell states we used either the restricted open HF (ROHF) and the unrestricted HF (UHF) approaches, or the spin polarized DFT formalisms.

A problem connected with the description of vacancies in oxide materials is the possible localization of trapped electrons in the cavity (see Section 4.2). A plane wave basis set automatically includes the possibility of electron localization at sites other than nuclei. Using atomic basis sets the same result can be obtained if the set of basis functions is flexible enough, e.g. when it includes diffuse functions at the atomic positions or by placing floating Gaussian functions in the center of the vacancy or in the position previously occupied by the missing O atom. For the case of MgO F centers we have placed floating Gaussians in the center of the vacancy. A different approach has been followed for SiO₂. Since the removal of an oxygen atom leads to the formation of dangling bonds or localized Si–Si covalent bonds, no basis functions have been placed at the position of the missing oxygen. We will see below that this is fully justified.

The previous discussion of the embedding approach and of the basis sets raises the question of the assumptions which are behind a cluster model. In fact, although the calculations are of ab initio type (no parameters are fit to the experiment), some basic assumptions about the nature of the material lead to different treatments of the same problem, the description of the oxygen vacancy. In ultimate analysis, it is the comparison of the results, in particular for observable properties, with the available experimental data which provides a direct validation of the approach used.

2.3. Calculation of observable properties

2.3.1. Formation energies

The calculation of formation energies of defects in oxides is difficult and requires a high level of treatment with the inclusion of electron correlation, in

particular when the bonding has a partial covalent character like in SiO₂. The importance of correlation is expected to be smaller for materials like MgO where electrostatic effects dominate. To determine the formation energies, E_F , of point defects in SiO₂ we have included electron correlation at the second order perturbation theory level, MP2 [36]. In general we have performed a single point MP2 calculation at the HF optimal geometry but we also considered fully optimized MP2 structures; the deviations are always smaller than 0.2 eV¹. The formation energies of the MgO surface F_s centers have been determined at the HF level only. Here we will briefly outline some aspects of the calculations in order to compare MgO with SiO₂. In particular, given the difficulties inherent with the description of charged defects, we will concentrate on the formation energy of neutral F and F_s centers.

2.3.2. Magnetic interactions (hyperfine splitting)

The determination of the hyperfine coupling constants of unpaired electrons with the ²⁹Si or the ²⁵Mg nuclides in EPR experiments is of fundamental importance for the spectroscopic and electronic characterization of paramagnetic defects in SiO₂ and MgO, respectively. The hyperfine Hamiltonian, $H = \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$, is given in terms of the hyperfine tensor $\mathbf{A}$ which describes the coupling of the electron with the nuclear spin. The components of $\mathbf{A}$ can be represented by the following matrix notation:

$$\mathbf{A} = \begin{vmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{vmatrix} = a_{\text{iso}} + \begin{vmatrix} B_1 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & B_3 \end{vmatrix} \quad (1)$$

The isotropic part of the coupling constants, a_{iso} , is related to the spin density at the nucleus (the Fermi contact term):

$$a_{\text{iso}} = (8/3\pi)g_N\beta_N g_0\beta_e |\Psi_s(0)|^2 \quad (2)$$

where g_N and g_0 are the nuclear and electronic g -factors, and β_N and β_e are the nuclear and Bohr magnetons. The anisotropic contribution $\mathbf{B}$ results from the dipolar interaction. The comparison of the computed with the experimental hyperfine constants provides therefore a direct validation of the compu-

¹ We use the notation HF/MP2 for final MP2 energies evaluated on the optimal HF geometry and MP2/MP2 when the energy is that of a fully optimized structure at MP2 level.

tational approach. We have determined the isotropic components of the **A** tensor, a_{iso} , for the paramagnetic oxygen vacancies, V_{O}^+ in SiO_2 and F^+ or F_s^+ in MgO , from UHF and DFT calculations.

2.3.3. Optical spectra

The calculation of transition energies (T_e) in crystalline and amorphous solids is a complex problem which requires an extensive inclusion of correlation effects. We have studied the optical transitions associated to oxygen vacancies in SiO_2 and MgO by performing multireference CI calculations for ground and excited states of the clusters. The basic idea behind this approach is to generate single and double excitations with respect to a set of reference one-electron configurations and to construct a new wave function which is a linear combination of these configurations [37,38]. Since the number of generated excited configurations can be very large (of the order of several millions), various techniques can be employed to deal with this problem, as described in more detail in the paragraphs reporting the results of the calculations on the optical transitions of the point defects.

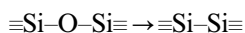
Absorption intensities have been estimated by means of the oscillator strength f , a dimensionless quantity, using the dipole-length operator formula, $f(\mathbf{r}) = 2/3 |\langle \Psi_0 | \mathbf{e} \mathbf{r} | \Psi_n \rangle|^2 (E_n - E_0)$. Typical values of f for allowed transitions are between 0.1 and 1. Radiative lifetimes, τ , have also been determined.

Various quantum-chemical program packages have been used for the calculations described in this paper: HONDO 8.5 for HF and MP2 [39], Gaussian-94 for DFT [40], GAMESS-UK [41] and PSHONDO-CIPSI [42] for excited state calculations.

3. Oxygen vacancies in SiO_2

3.1. Formation energies

The removal of an oxygen from the α -quartz lattice results in a neutral oxygen vacancy, V_{O} , where two Si–O bonds are broken and replaced by a direct two-electrons, two-centers, Si–Si bond (Fig. 1(b)):



+ O ($\equiv$ represents three Si–O bonds)

(3)

After relaxation, the Si–Si distance decreases from 3.06 to 2.50 ± 0.05 Å (the value of the Si–Si distance

changes slightly as function of cluster size). The breaking of two Si–O bonds requires a substantial energy. Thermodynamic criteria suggest 7.3 eV as a lower bound for the formation energy of an oxygen vacancy in SiO_2 [43]. Theoretical estimates differ significantly from method to method [44–46]. Cluster model extended Hückel calculations gave about 10 eV or more for the energy associated to the process [44]. Local density functional (LDF) band structure calculations give $E_{\text{F}} = 7.9$ eV [45], but LDF sometimes overestimates binding energies. Using a formally exact embedding scheme, a much smaller E_{F} , ≈ 5 eV, was obtained by ab initio HF calculations [46].

We have computed $E_{\text{F}}(V_{\text{O}})$ using HF and MP2 wave functions. For comparison we have computed the SiO and O_2 diatomic molecules whose experimental dissociation energies, D_e , are 8.26 and 5.11 eV, respectively [47]. The corresponding MP2/MP2 D_e s, 8.09 and 5.04 eV, respectively, are in excellent agreement with the experiment. At the HF/MP2 level, i.e. the same approach used for the determination of E_{F} in SiO_2 , the computed D_e s, 8.01 eV (SiO) and 4.80 eV (O_2), are also reasonably close to the measured ones. Our computed formation energy for V_{O} in SiO_2 with a small $\text{Si}_2\text{O}_7\text{H}_6$ cluster at the HF/MP2 level is 8.5 eV. This value is consistent with the recent experimental estimate of Boureau and Carniato ($E_{\text{F}} > 7.3$ eV). The discrepancy between other ab initio values reported in the literature, ≈ 5 eV [46] and our calculations [36] is due to the lack of d functions on Si and O and to the neglect of correlation effects in previous estimates. Their simultaneous inclusion however provides reliable formation energies of defects in silica. We also checked the results versus cluster size, computing E_{F} with a $\text{Si}_5\text{O}_{16}\text{H}_{12}$ cluster but we found no significant change in E_{F} with respect to the $\text{Si}_2\text{O}_7\text{H}_6$ model.

3.2. Magnetic interactions

One of the most abundant and best characterized defects in SiO_2 is the E' center, corresponding to a hole trapped at an oxygen vacancy, $V_{\text{O}} + h^+ \rightarrow V_{\text{O}}^+$. The E' center is a fundamental radiation-induced defect in amorphous silica, a- SiO_2 [48,49], and an important source of degradation in Si/SiO₂ based electronic devices [49]. Several variants of the E' centers exist: E'_1 , and the H-associated E'_2 , and E'_4 , in α -quartz; E'_γ and E'_δ centers in a- SiO_2 . E'_γ is the

closest analogue to the E'_1 in α -quartz [48]. Thanks to the combined use of optical and EPR spectroscopies [48,50] and theoretical calculations [45,51–53] the ground state structure of the E'_1 and E'_2 centers is now quite well understood. According to the first model proposed in 1974 by Feigl, Fowler and Yip [51], FFY, the defect consists of a sp^3 hybridized $\equiv Si^\bullet$ dangling bond and of a nearly planar $\equiv Si^+$ unit, $\equiv Si^+ \cdots Si^\bullet$. The FFY model, however, does not account for the large hyperfine coupling constant, hcc , of ≈ 420 G of the unpaired electron with the ^{29}Si nuclide [48,50].

In fact, using a minimum $[Si_2O_6H_6]^+$ model of V_O^+ to compute the hyperfine constants one finds the following a_{iso} values (UHF wave functions): $Si_1 = 172$ G, $Si_2 = 75$ G. Both are substantially different from the measured ones. This is not connected to the basis set or the method used since using larger basis sets and the DFT approach there are only minor changes in the hyperfine constants. Even the use of a

larger cluster, $[Si_5O_{15}H_{12}]^+$, gives a_{iso} values of 161 and 29 G, respectively, with only little improvement compared to the smaller model. Thus, none of the models considered so far accounts for the measured hyperfine constants.

Some years ago, Rudra and Fowler [54] found a structure where one Si atom is oriented towards a lattice oxygen which becomes effectively three-coordinated. The distance between this oxygen and the formally positively charged Si atom of the defect is less than 2 Å [54]. Performing the minimum search using a $[Si_{14}O_{16}H_{26}]^+$ cluster which includes more atoms around the defect one finds two minima (Fig. 3). In the first one, the Si_1 – Si_2 distance is very long, 4.06 Å, while the distance between the positively charged Si_2 atom and the three-coordinated oxygen is very short, 1.81 Å (Fig. 3(a)). The a_{iso} on Si_1 , 364 G, is in reasonable agreement with the experimental value, 420 G [50]. In a metastable variant of the E' ground state structure the unpaired electron is shared among the two Si atoms of the vacancy (Fig. 3(b)). The substantial delocalization of the spin is shown by the existence of two hcc 's of 118 G (Si_1) and 62 G (Si_2). This is the structure found with the smaller $[Si_2O_6H_6]^+$ cluster. In this case the small cluster fails to give the most stable structure simply because some important atoms which are indispensable to describe the overcoordination of the Si_2 atom are not included. In the metastable structure (Fig. 3(b)), the electron remains trapped between the two Si atoms; the Si–Si distance, 2.67 Å, is not too far from that of the neutral oxygen vacancy, ≈ 2.5 Å. This structure E'_δ , has been described by Snyder and Fowler [52] and by Boero et al. [53] and probably observed in Cl-containing glasses by Griscom and Friebele [55]. In the HF approach the metastable E'_δ is 0.64 eV higher than the global minimum, although this value can change by using different methods and basis sets. Thus, the 'puckered' structure where the positively charged Si is electrostatically bound to a lattice oxygen, is more stable and gives hyperfine coupling constants in much better agreement with the experiment. It is very likely that this structure corresponds to that of the E' center in silica.

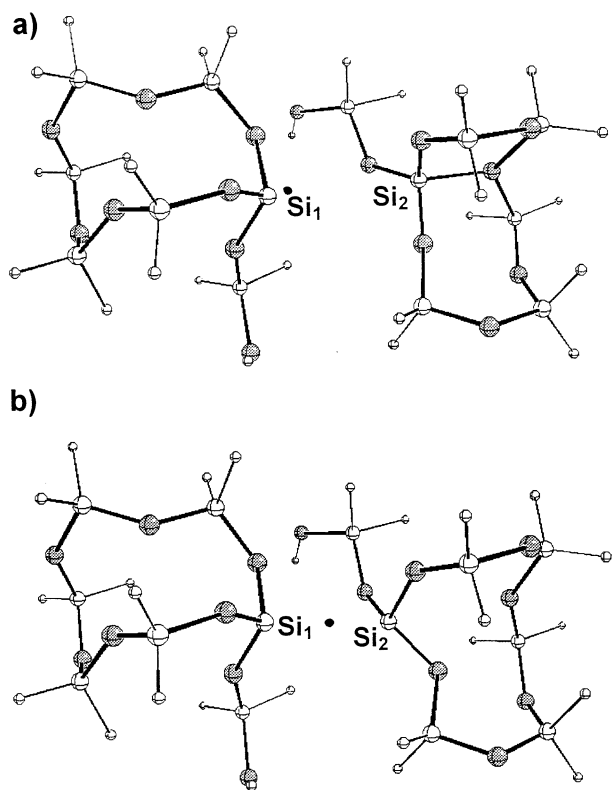


Fig. 3. (a) The ground state structure of an E' center in α -quartz (E'_1). Notice the strong relaxation of Si_2 which is bound to an oxygen atom which becomes three-coordinated. (b) Metastable structure of the E' center in α -quartz (E'_δ).

3.3. Optical transitions

Structural imperfections created during fabrication or generated by heat treatments or irradiation determine the optical absorption (OA) and photolumines-

Table 1

Computed transition energies, T_e , of neutral, V_O , and charged, V_O^+ , oxygen vacancies in α -quartz (CI results [62,67])

Center	Nature of the transition		T_e , eV	$f(r)$	exp., eV
V_O	$\equiv Si-Si \rightarrow \equiv Si^\bullet \cdot Si$	OA	7.5 ± 0.3	0.33	≈ 7.6
V_O	$\equiv Si^\bullet \cdot Si \rightarrow \equiv Si-Si$	PL	4.3 ± 0.3	0.40	≈ 4.4
V_O^+	$\equiv Si_1^\bullet + Si_2 \rightarrow \equiv Si_1^+ \cdot Si_2$	OA	5.9 ± 0.3	0.30	≈ 5.8

cence (PL) properties of crystalline and amorphous silica [56–60]. In particular, oxygen deficient centers give rise to an OA at 5.0 eV (the B_2 band, more pronounced in amorphous silica) and at 7.6 eV (the E band) with a typical PL band at 4.3–4.4 eV. Excitation in both B_2 and E bands absorption regions induces the 4.4 eV fluorescence [57–59]. Recent studies have shown that the 5.0 eV OA and the 4.4 eV PL bands are actually envelopes of several bands [61]. Here we consider only the origin of the 7.6 eV band and we briefly summarize the results of our MRD CI calculations [62] on the optical transitions of a V_O center in α -quartz. For these calculations we used a small cluster, $(OH)_3Si-Si(OH)_3$ to perform accurate calculations of the transition energies, T_e ².

As we mentioned before, the formation of a V_O center results in a short $d(Si-Si) = 2.50 \pm 0.05$ Å. From the combination of the sp^3 hybrids on each Si, a doubly occupied σ bonding and an empty σ^* antibonding state appear in the band gap [62]. The ground state, S_0 , is therefore $(\sigma)^2(\sigma^*)^0$. The first excited state is a triplet, $T_1(\sigma)^1(\sigma^*)^1$, with a MRD CI T_e of 6.3 eV (Table 1). Singlet–triplet transitions, $S_0 \rightarrow T_1$, however, are forbidden and can carry sufficient intensity only through spin-orbit coupling. The first allowed transition is $S_0(\sigma)^2(\sigma^*)^0 \rightarrow S_1(\sigma)^1(\sigma^*)^1$ with formation of two singly occupied dangling bonds, coupled singlet, on the adjacent Si atoms. The vertical T_e computed including diffuse Rydberg s and p functions on Si is 7.5 eV; the oscillator strength, $f = 0.3$, indicates a strong absorption inten-

sity; the computed radiative lifetime is 1 ns (Table 1). These results strongly support the assignment of the E band to a $S_0 \rightarrow S_1$ transition in a neutral oxygen vacancy.

The rupture of the Si–Si bond due to the absorption of a 7.6 eV photon causes a substantial geometrical relaxation of the excited state. In the minimum configuration of the S_1 excited state the Si atoms move ≈ 3.6 Å apart. From the minimum of the S_1 excited state the system decays to S_0 . The computed energy of the emitted photon, 4.3 eV, is consistent with the observed PL band at 4.3–4.4 eV. The Stokes shift is therefore more than 3 eV. The lifetime, 3 ns, is extremely close to the experimental one, $\tau = 2.1$ ns [59]. Thus the calculations support the assignment of the 4.4 eV emission to the radiative $(\sigma)^1(\sigma^*)^1 \rightarrow (\sigma)^2$ decay from the minimum of the $\equiv Si^\bullet \cdot Si \equiv S_1$ excited state. It should be mentioned however, that another defect in silica has been identified as the possible source of the 5.0 eV OA and of the 4.4 eV PL bands. This is the two-coordinated Si, $\equiv Si:$, originally proposed by Skuja [63]. Recent first principle calculations by our group [64] and by Ravagachari and co-workers [65] come to the conclusion that this center has absorption and emission properties fully consistent with Skuja's proposal [63]. It has also been suggested that the neutral oxygen vacancy and the two-coordinated Si defect centers are in some way interconnected [60].

We consider now the excited state properties of an E' center. A typical OA band in bulk silica at 5.85 eV with an oscillator strength of 0.14 ± 0.04 has been assigned to the E'_v center by Weeks and Sonder based on a strong correlation with a characteristic EPR signal [66]. The nature of the transition, however, has been under debate for a long time. It could involve a charge transfer, CT, from $\equiv Si^\bullet$ to $\equiv Si^+$ or simply a transition from the valence band to the partially filled Si sp^3 hybrid orbital (Fig. 4). To study the nature of the lowest excitations we have considered a $(HO)_3Si^\bullet + Si(OH)_3-(OH)_2$ cluster, which in-

² We used all electron double-zeta basis sets augmented by a d function and diffuse s and p functions on Si. Single and double excitations from the 12 highest occupied levels (24 electrons) to all virtual orbitals were generated. The configurations with an estimated contribution to the CI energy larger than 10 μ Hartree (about 10,000) were included in the secular determinant; the contribution of the remaining configurations (more than one million) has been estimated through an extrapolation technique. For further details see Ref. [62].

cludes the three-coordinated oxygen of the E'_γ ground state structure [67].

In the CI calculation we searched the three lowest roots in the secular problem: (1) the ground state, (2) the $O(2p) \rightarrow \equiv Si^\bullet$ transition (a doublet-to-doublet transition corresponding to the excitation of one electron from a non-bonding O 2p valence band orbital to the Si dangling bond), and (3) the charge transfer transition where one electron is excited from Si_1 to Si_2 (strictly speaking the $O(2p) \rightarrow \equiv Si^\bullet$ is also a charge transfer transition, but we refer only to the excitation from the two non-bonded Si atoms as charge transfer for clarity). The CI results (Table 1) show that the two excited states have very small mixing and similar T_e , ≈ 5.7 – 5.8 eV; they are separated by ≈ 0.2 eV only [67] (but the relative ordering depends also on the details of the calculation). It is not possible to predict in a firm way which is the lowest transition based on the T_e s. However, the two transitions exhibit very different intensities: the charge transfer is very strong, about ten times stronger than the $O(2p) \rightarrow \equiv Si^\bullet$ transition. Experimentally, it has been observed that the transition at 5.85 eV associated with the E'_γ center has an oscillator strength of ≈ 0.14 eV [66]. Both T_e and $f(r)$ are in agreement with the charge transfer transition computed here while the predicted intensity of the valence band transition is too low. Consequently, the

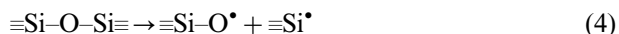
charge transfer transition is expected to have a much shorter lifetime, $\tau \approx 10^{-9}$ s, and to occur much more rapidly than the $O(2p) \rightarrow \equiv Si^\bullet$ transition, $\tau \approx 10^{-8}$ s [67].

The present discussion shows that the excitation mechanisms in silica oxygen vacancies can be described in terms of localized electron pairs, bonding and antibonding states, etc. This is a direct consequence of the covalent (polar) character of the bonding in the material.

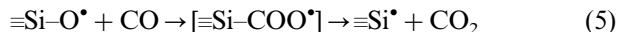
3.4. Surface chemical reactivity

We briefly consider here the general features of the chemical reactivity of the dehydroxylated silica surface, but a quite different behavior is expected for the same surface terminated by hydroxyl groups. In general, the non-defective silica surface is rather unreactive. In fact, the breaking of the Si–O bonds requires about 5 eV [36] and makes most reactions unfavorable from a thermodynamic point of view. Higher reactivity is exhibited by strained Si–O bonds, as probably present on the surface of amorphous silica prepared in special conditions. The low reactivity of the non-defective surface is shown for instance by a recent ab initio study on the interaction of isolated metal atoms on SiO_2 [68]. The results have shown that transition metal atoms form only weak bonds with the surface, mainly of dispersion and polarization type, in agreement with the low sticking coefficient measured experimentally for Cu atoms impinging on SiO_2 [69].

Things are substantially different when point defects are considered. Among these defects, the paramagnetic defects resulting from the breaking of a Si–O bond are particularly abundant on the surface of mechanically activated silica [70]:



These two defects are known as non-bridging oxygen center (NBO), $\equiv Si-O^\bullet$, and as the surface counterpart of the bulk E' center, $\equiv Si^\bullet$. In a series of studies, Radsig and coworkers [70] have shown that these two surface defects dominate the chemistry of mechanically activated silica through reactions which proceed via radical mechanisms:



The presence of surface dangling bonds as in the NBO and E' centers can facilitate the breaking of

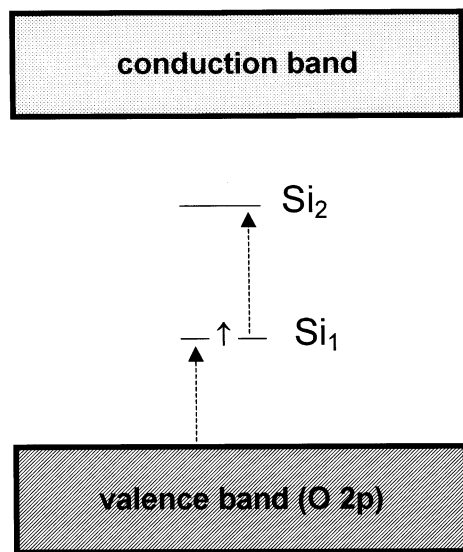


Fig. 4. Schematic representation of the level structure of an E' center in α -quartz and of the corresponding electronic transitions (see also Fig. 3(b)).

small gas-phase molecules like H_2 . The interaction of molecular hydrogen with defect sites (in particular dangling bonds) of SiO_2 is a process which plays a fundamental role in several technological applications. For instance, the dielectric reliability of gate silicon dioxide films is a crucial issue in the design of metal-oxide semiconductor (MOS) devices and oxygen vacancies acting as charge traps at the Si/ SiO_2 interface are known to degrade the dielectric response and the performance of the device [71,72]. In the semiconductor industry, annealing of the SiO_2 films in a hydrogen containing atmosphere is used as a standard technique to reduce the concentration of the defects at the Si/ SiO_2 interface. We have recently shown [73] that the cracking of the H_2 molecule occurs with low activation barrier and with an exothermic process on the NBO centers and, with a less favourable reaction, also at the E' centers:



Therefore, the surface chemistry of mechanically activated silica is dominated by the presence of paramagnetic defects which give rise to a series of reactions determined by radical mechanisms [70]. This is the direct consequence of the almost complete localization of the unpaired electrons to a specific atom (Si or O dangling bonds). In the following we will see that completely different reaction mechanisms dominate the surface chemistry of defect centers on the MgO surface.

4. Oxygen vacancies in MgO

4.1. Formation energies

We discuss first the accuracy of our estimated formation energy of an O vacancy in MgO by comparing the results for a test case with that of other calculations. In particular, there are two aspects to be addressed: the validity of a cluster model in describing the relaxation following the oxygen removal, and the importance of correlation effects. Using a $O_{21}Mg_{21}$ cluster model of the MgO(100) surface and an HF wave function, we computed for the process $O_{21}Mg_{21} \rightarrow O_{20}Mg_{21} + O$ an energy of 8.1 eV (formation of neutral F_s) [74]. This value includes the local geometry relaxation following the vacancy

formation which is not large for a neutral defect (the Mg–O distances around the cavity change by $\approx \pm 1\%$ [16]) although it has some effect on E_F . The formation energy of an O vacancy on the MgO surface has been estimated by means of band structure HF calculations using the Crystal program [75]. The computed value of 7.7 eV is close to our E_F [16], showing that the response of a MgO cluster embedded in PCs is similar to that of an extended system. What is missing from both these calculations are correlation effects. Orlando et al. [75] have estimated that at a correlated level E_F for a surface F center is 8.4 eV. Recent LDA calculations gave $E_F = 9.8$ eV [76], i.e. about 2 eV larger than the HF ones. If one considers that the computed cohesive energy of MgO is overestimated in LDA by about 10% [76], it is possible to conclude that E_F for a F center at a terrace site of the MgO(100) surface should be around 8.5 eV.

Correlation effects, although not negligible, are therefore less important than in SiO_2 where they account for about one third of the formation energy. The reason why HF performs much better for MgO than for SiO_2 is that MgO has a much more pronounced ionic character. HF wave functions describe properly the electrostatic part of the interaction in an ionic crystal, and if the corrections due to covalent bonding contributions are small then the final result is in satisfactory agreement with the experiment. In SiO_2 , where the bonding is much more covalent, the use of a method which includes correlation effects is essential for the proper description of the energetics.

We have determined the energy required to extract a neutral O atom from some clusters modeling O atoms in different environments: a sub-surface, six-coordinated O atom (close to a bulk atom), a surface five-coordinated O atom, a step four-coordinated, oxygen, and finally an oxygen atom at a corner three-coordinated site. The corresponding F centers can be denoted F_{6c} , F_{5c} , F_{4c} , F_{3c} , respectively (Fig. 5). The formation energies computed at the HF level are 9.7, 8.1, 6.9, and 5.6 eV [74], respectively (Table 2). Therefore, the results provide a clear indication that the removal of an O atom from the MgO lattice requires substantially different energies depending on the location.

The results of our studies allow one to draw some general conclusions about the relative stability of oxygen vacancies in MgO. The order of stability is,

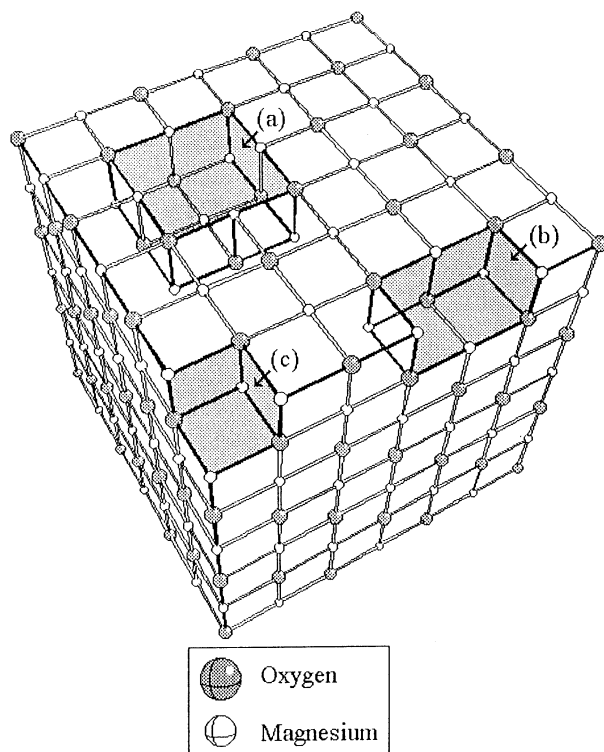


Fig. 5. Possible locations of oxygen vacancies at the surface of MgO: (a) terrace; (b) step; (c) corner.

Table 2

Computed formation energies, E_F , of neutral oxygen vacancies (F centers) at bulk and surface sites of MgO (HF results [74])

F center	Location	E_F (eV)
F (6c)	Bulk	9.7
F_s (5c)	Terrace	8.1
F_s (4c)	Step	6.9
F_s (3c)	Corner	5.6

no matter which is the coordination of the defect, $F > F^+ > F^{2+}$ [16]. This trend is closely connected to the electronic structure and the nature of oxygen vacancies in ionic materials like MgO. Differently from covalent oxides, in MgO the removal of an O atom or ion does not result in the formation of new bonds but rather in cavities which may be filled by one or two electrons trapped by the strong electrostatic potential of the ionic crystal [16,77]. In this respect, it is clear that neutral vacancies, the F centers, are more stable because two electrons interact with the Madelung field of the crystal. F^{2+}

centers, on the other hand, are much less stable since they are very electron deficient.

The relative stability of the neutral oxygen vacancies follows a general trend; F centers at low-coordinated sites are more stable than high-coordinated vacancies [74,76]. Thus, a bulk or sub-surface F center is less stable than the corresponding surface one; a surface F center is less stable than a step one; etc. This is directly connected with the energy required to remove an oxygen atom from the material: bulk (or sub-surface) > surface > step > corner. Thus, low-coordinated F centers are easier to form than the bulk F centers [74]. This is true also for charged vacancies although, in particular for the F^{2+} centers, the difference in stability between low- and high-coordinated sites is not as high as for neutral F centers [74]. From this discussion it follows that electrons trapped by the electrostatic field of the ionic crystal exist also at step and corner sites, a fact which has to be considered in the analysis of the surface reactivity of MgO powders.

4.2. Magnetic interactions

A question related to F and F^+ centers, and their surface counterparts, is that of the electron distribution. In fact the trapped electron(s) can either be localized in the center of the vacancy or delocalized over the Mg^{2+} ions around the cavity (six in bulk case, less for other sites). Attempts to identify the degree of electron localization with common computational techniques, like the Mulliken population analysis, lead to frustrating results [16] because, depending on the basis set used, the results oscillate from almost full localization in the vacancy to complete delocalization over the Mg ions. This is a typical case of failure of the Mulliken analysis due to the strong basis set dependence [16]. A much more reliable description of the electron distribution comes from charge density and spin density plots [16] which show unambiguously that the electron(s) in F_s and F_s^+ centers (as well in bulk vacancies [7,12,75]) are trapped in the cavity with little delocalization over the neighboring Mg ions (Fig. 6).

A direct experimental proof of the charge distribution comes from the hyperfine interactions in F^+ centers. Let us consider the bulk F^+ center and restrict the analysis to the isotropic part, a_{iso} , of the hyperfine coupling constants. The experimental a_{iso} for a F^+ center in bulk MgO is 3.94 G [78]. We used

various models, methods, and basis sets to check the accuracy of the computational approach in determining the a_{iso} values and, at the UHF level, we always found a_{iso} values of 4 ± 1 G [77] (in the UHF wave functions the value of $\langle S^2 \rangle = 0.75$ indicates no spin contamination). We also performed spin polarized DFT-B3LYP calculations using the same clusters and basis sets but we found virtually no

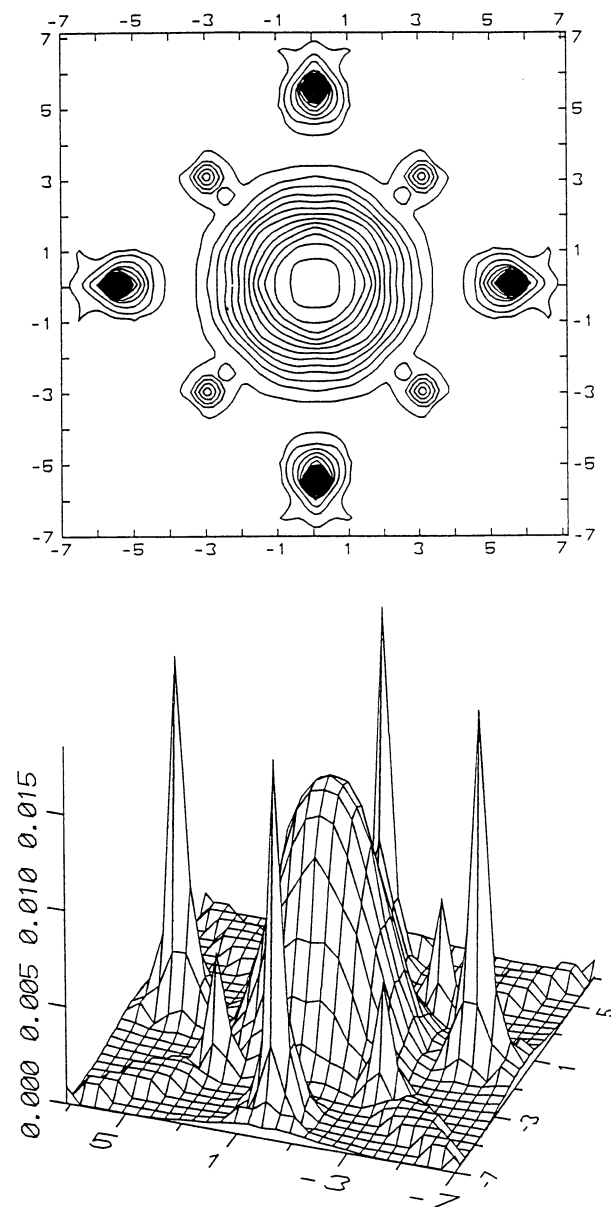


Fig. 6. Spin density plot of an F_s^+ center at the $\text{MgO}(100)$ surface. (top) Isocontour lines in the surface plane; (bottom) three dimensional view. The lines are drawn in intervals of 0.001 e/a.u.^3 .

difference with the UHF values [77]. This is similar to what we observed for the paramagnetic defects of SiO_2 where similar results were obtained using UHF and DFT approaches [77]. Thus, the spin distribution in two of these inorganic materials is properly described already at the UHF level, a conclusion which may not be generally valid. It is important to mention that all the MgO models used give a correct description of the spin density in a F center except those where the Madelung field is not included. In fact, differently from the SiO_2 case, the neglect of the Madelung potential in MgO can give unphysical results [79]. Again, this reflects the much more ionic nature of the alkaline–earth oxide.

In general, the hyperfine interactions in MgO F centers are small. This means that the unpaired electron is interacting only to a minor extent with the Mg ions around the vacancy. A Mg_6^{11+} octahedral cluster with MgO bulk geometry where one unpaired electron is delocalized over the Mg 3s and 3p orbitals shows an a_{iso} value of 17 G, i.e. four times larger than in reality. The localization at the center of the cluster is not possible in this case because of the absence of the electrostatic field of the ionic crystal. Notice that a_{iso} for a free $\text{Mg}^+ (3s)^1$ ion is very large, ≈ 200 G. This also shows the role of the 3s–3p mixing in reducing the Fermi contact term.

We consider now the nature of paramagnetic F centers at the surface of MgO . Recent experiments point towards the possible localization of F centers at low-coordinated sites of the MgO surface (steps, kinks, corners, etc.) [80]. Since the reactivity of the surface may depend critically on the existence of these defect centers (see Section 4.4), their identification with EPR spectroscopy is of great importance. We have seen above that the formation energy of an F center at a low-coordinated site is lower than at terrace and sub-surface sites. Hence, it is not unreasonable to expect that a thermal treatment of MgO , which is usually prepared by thermal decomposition of MgCO_3 or of Mg(OH)_2 , will result in the migration of the vacancies from the bulk to the surface and to the low coordinated sites.

With a O_8Mg_9 model of a F_s^+ center at a five-coordinated terrace site we compute an a_{iso} of 6 G (UHF). As for the bulk, DFT results give the same hyperfine constants, 6.2 G. Larger clusters give values in the same range, 4–6 G [17]. Thus, the coupling constants for the surface are similar to those

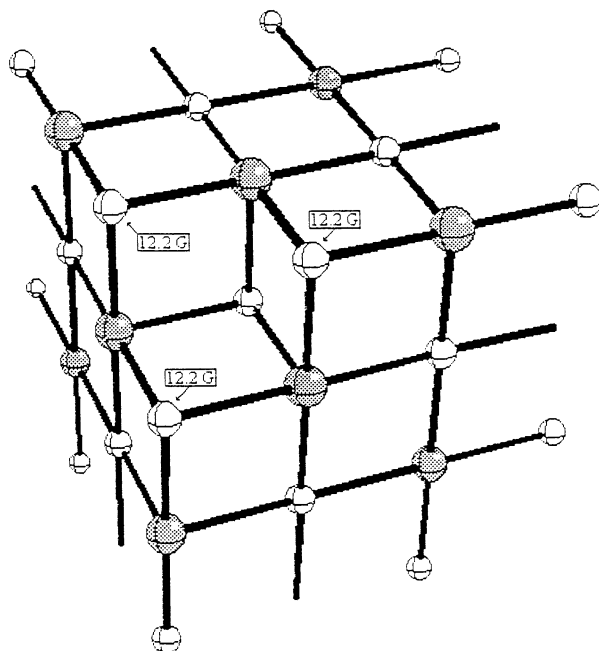


Fig. 7. Structure of a F_{3c}^+ center (an oxygen vacancy at a three-coordinated corner site) and isotropic hyperfine coupling constants of the unpaired electron with the ^{25}Mg nuclide (values in Gauss).

for the bulk. EPR spectra for paramagnetic surface F centers exist only for high surface area polycrystalline MgO. No data are available to date for single crystals in UHV. The original measurements of 10–11 G by Tench and Nelson [81] have been confirmed by very recent data obtained by Giamello et al. [17]. These values are about two times larger than in our calculations. Furthermore, Tench and Nelson observed an inhomogeneous distribution of the electron spin in the cavity [81]. According to their interpretation the spin is preferentially localized on the apical atom in the second MgO layer. Also the experiments of Giamello et al. [17] indicate the existence of an inhomogeneous distribution of the unpaired electron. Our calculations, however, do not support the Tench and Nelson model. We found similar a_{iso} values, about 5 G, for all the five Mg ions of a F_s^+ center, independent of the cluster size [17]. Therefore, not only the absolute values of the constants are different in the experiment and in the calculations, but also the distribution of the unpaired electron seems to be different. This is in contrast with the result obtained for the bulk where the computed values are almost coincident with the experimental ones. The discrepancy between theory and experi-

ment can be due to limitations of the quantum-chemical approach or, more likely, to the fact that the models used do not reflect the ‘real’ situation.

Two possible alternative models can be proposed. One is based on the presence of adsorbed protons in the vicinity of the F centers, giving rise to the so called $F_s(\text{H})$ centers. The second is that the vacancies at the surface of MgO form preferentially at the low-coordinated sites (step, corners) instead of the terrace sites. Both possibilities are consistent with recent careful analyses of the EPR parameters and direct chemical evidences [80].

Better resolved EPR spectra have indeed shown the presence of a hyperfine interaction between the unpaired electron on a F_s^+ center and the H atom of an OH group on the surface [17]. If one considers a model where an OH group is close to a F_s^+ center on a terrace it is possible to see that the unpaired electron becomes polarized by the positively charged H atom. This polarization leads to an inhomogeneous spin distribution and to larger a_{iso} values for some of the Mg ions in the cavity (typically 9–13 G) [17]. These values and the inhomogeneous distribution are therefore consistent with the experimental observations.

The second possibility is that what is actually measured are F centers located at corner sites of the MgO surface (in polycrystalline materials it is expected that the number of such sites is relatively high). The calculations show that one or two electrons can be trapped at such sites; for the case of a single trapped electron the a_{iso} values, 12 G, are in close agreement with the measured one for surface F centers [80] (Fig. 7). In this model however, the three Mg^{2+} ions are equivalent and exhibit the same hyperfine interaction with the unpaired electron. Therefore the distribution is homogenous in a corner site. Things can be different in other three-coordinated sites like the kink sites. In this case in fact the electrostatic potential around the center does not have the three-fold symmetry of a corner site and the charge distribution will be inhomogeneous for symmetry reasons.

To summarize, the electron distribution in paramagnetic F^+ centers has been analyzed by computing the isotropic hcc’s of the unpaired electron with the ^{25}Mg nuclides. The small values of the hcc’s indicate an high degree of localization of the unpaired electron in the vacancy for all sites considered. Going from high-coordinated to

low-coordinated sites there is an increase of the hcc's simply because the spin density is shared among a smaller number of Mg neighbors. A more refined analysis reveals that in the low-symmetry centers the unpaired electron interacts preferentially with the more exposed cations, a fact which is due to the higher electrostatic potential at these sites [74]. These results show that electrons trapped at the MgO surface may exist even at low-coordinated oxygen vacancies.

4.3. Optical transitions

When a neutral O atom is removed from the bulk or from the surface of MgO to form a F center, a doubly occupied electronic state appears in the gap, about midway between the top of the O 2p valence band and the bottom of the Mg 3s and 3p conduction band [16] (Fig. 8). If one of the two electrons is promoted to the conduction band it may move away from the defect leaving a charged defect behind, F^+ (or F_s^+). The singly occupied impurity state moves toward the top of the valence band, but keeps its distinct character. If the electron occupying this state is also removed or promoted to the conduction band, one forms a doubly charged vacancy, F^{2+} (or F_s^{2+}). The occupied impurity states due to MgO

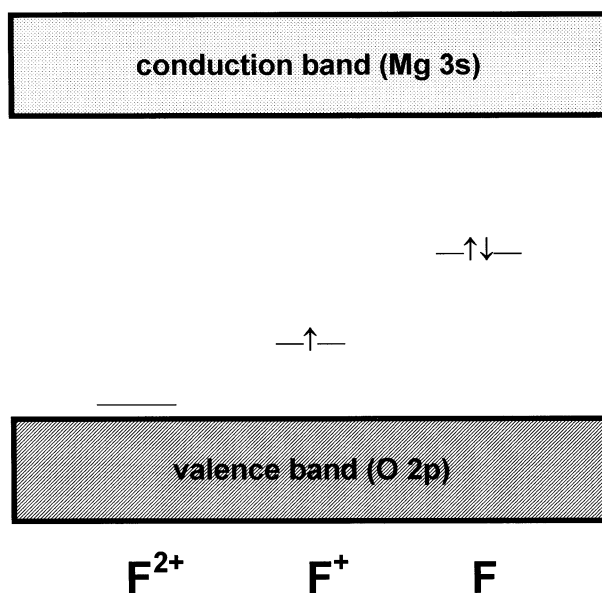


Fig. 8. Schematic representation of the level structure of F, F^+ , F^{2+} centers in MgO.

oxygen vacancies give rise to typical OAs in the region of 5 eV which are responsible for the blue color of the polycrystalline material [82].

Chen and co-workers have been able to decompose the band into two components due to F^+ centers at 4.96 eV and to neutral F centers at 5.03 eV [83]. Optical spectra of MgO surface F centers have been measured on polycrystalline materials [80,84], on single crystals [85] and ultrathin MgO films [86,87]. Optical measurements on fine powder samples of MgO using diffuse reflectance technique showed a feature at 2.05 eV attributed to F_{sc}^+ centers [84]. A peak at 2.3 eV has been observed by Heinrich et al. [85] on MgO single crystals using electron energy loss spectroscopy (EELS). The feature was tentatively assigned to surface F centers, although according to Underhill and Gallon [88] the loss is due to a surface V^- center (a cation vacancy with a hole trapped on an adjacent oxygen ion). Wu et al. [86] have studied with high resolution EELS the defects generated in an ultra-thin film of MgO grown on Mo(100). They observed three features at 1.15, 3.58 and 5.33 eV. The 5.33 eV band was assigned to bulk F centers, the band at 1.15 eV to surface F centers, and the band at 3.58 eV to F aggregates [86]. Very recently the nature of the optical transitions on MgO thin films has been studied by Pfnür and co-workers using EELS [87]. Two sets of bands around 3.3 and 2.4 eV have been measured and tentatively assigned to surface F centers.

We have investigated the optical transitions associated to F centers formed at various sites of the MgO surface [89,90]. The calculations have been performed using cluster models and CI wave functions. For details of the models and basis sets used see Refs. [89,90]. Correlated calculations have been performed for the ground and the low-lying states of each defect by performing DDCI3 calculations [91], a technically different approach with respect to the MRDCI treatment. In general the DDCI3 and the MRDCI approaches give similar results with deviations of ≈ 0.1 eV.

A general comment is required about the use of cluster models to compute excited states in solids. In fact, the finite size of the cluster implies that the extension of the excited state does not exceed the size of the cluster. If the excited state wave function extends beyond the limits of the cluster this may result in an unphysical stabilization of this state. However, both ground and excited state wave func-

Table 3

Computed transition energies, T_c , of neutral, F, and charged, F^+ , oxygen vacancies located at various sites of MgO (CI results [89,90])

Center	Location	Nature of the transition	T_c (eV)		exp. eV
			Computed	Scaled ^a	
F (6c)	Bulk	$(1s)^2 \rightarrow (1s)^1(2p)^1$	6.0	5.1	≈ 5.0
F^+ (6c)	Bulk	$(1s)^1 \rightarrow (2p)^1$	5.8	4.9	≈ 5.0
F_s (5c)	Terrace	$(1s)^2 \rightarrow (1s)^1(2p)^1$	3.4	2.9	≈ 3.3
F_s^+ (5c)	Terrace	$(1s)^1 \rightarrow (2p)^1$	3.6	3.1	
F_s (4c)	Step	$(1s)^2 \rightarrow (1s)^1(2p)^1$	2.9	2.5	$\approx 2-2.4$
F_s^+ (4c)	Step	$(1s)^1 \rightarrow (2p)^1$	2.6	2.2	
F_s (3c)	Corner	$(1s)^2 \rightarrow (1s)^1(2p)^1$	2.6	2.1	$\approx 2-2.4$
F_s^+ (3c)	Corner	$(1s)^1 \rightarrow (2p)^1$	2.4	2.1	

^a A scaling factor of 0.85 has been applied to all computed T_c s.

tions of F and F^+ centers in MgO have radial extensions within the dimension of the cavity and the trapped electron(s) are well confined in the vacancy also when promoted to the lowest excited states [89].

In Table 3 we have summarized the results of the CI calculations on the optical transitions of color centers at the surface of MgO and we compared them with those of the bulk centers and with experimental bands. Three kind of surface F centers have been considered: terrace, F_{5c} , step, F_{4c} , and corner, F_{3c} . For each case the neutral and the positively charged forms of the F center have been considered, with two and one electrons trapped at the vacancy site, respectively. The lowest fully allowed singlet-to-singlet (F centers) and doublet-to-doublet (F^+ centers) transitions are reported. The first excitation corresponds to the promotion of one trapped electron from the 1s-type to a 2p-type state. On the neutral F centers, the corresponding transition energies decrease regularly as the coordination of the defect decreases: 3.4 eV (surface), 2.9 eV (step), 2.6 eV (corner) for the singlet state (Table 3). A similar trend is found for the F^+ centers, where the first doublet-to-doublet excitation energy goes from 3.6 eV for the surface, to ≈ 2.6 eV for the step and the corner sites, respectively [90]. The 1s $\rightarrow$ 2p transitions for a bulk F center occur at about 5.8–6.0 eV according to CI calculations, i.e. about 1 eV higher than experimentally observed [83]. Thus, on the surface the computed transition energies are considerably red-shifted. This can be explained with the fact that the excited state in the bulk is spatially con-

strained by the presence of an octahedral shell of Mg^{2+} cations around the vacancy. This gives rise to a considerable Pauli repulsion when the electron is promoted from the 1s-type to the 2p-type levels and to a consequent destabilization of the excited state. On the surface, on the contrary, the 2p_z-like excited state is free to extend in the direction normal to the surface without constraint, an effect which substantially lowers the cost for the transition. This mechanism is active also on the low-coordinated F centers, like the step and the corner vacancies.

OA bands associated to surface F centers for differently prepared MgO samples (single crystals, thin films, powders) have been observed at 1.15, 2.05, 2.3, 3.3 and 3.58 eV [84–87]; features at 5.03 and 4.96 eV are unambiguously assigned to bulk F and F^+ centers [83]. Our computed transition energies for the bulk F centers are overestimated by about 0.8–1 eV, i.e. $\approx 15\%$. If we apply this correction to the computed excitation energies for surface centers we come to the following estimate of the transition energies: step F_{4c} and F_{4c}^+ , and corner F_{3c} and F_{3c}^+ centers ≈ 2.1 –2.5 eV, surface F_{5c} and F_{5c}^+ centers ≈ 3 eV (Table 3). These values are quite close to those reported recently by Pfnür and coworkers for MgO thin films [87]. They seem to support the idea that F centers at the surface of MgO are located not only on the terrace sites but also on the step and corner sites, in full agreement with the results of other measurements, like the hyperfine coupling constants, and with the trend in thermodynamic stability discussed above.

4.4. Surface chemical reactivity

The exposure of dehydrated MgO to CO at room temperature leads to the formation of complex carbonylic species like ‘carbonite’ molecules, CO_2^{2-} , and other complexes of general formula $\text{C}_n\text{O}_{n+x}^{2-x}$ ($x = 0, 1, 2$) [92]. In a similar way, O_2 does react with a MgO surface where a large number of electron rich centers is artificially created by, e.g. γ - or UV-irradiation followed by doping with alkali metals. O_2 forms adsorbed superoxide anions, O_2^- , and the reaction is accompanied by very characteristic changes in EPR spectra [93,94]. This peculiar reactivity of the surface of polycrystalline MgO contrasts with the very inert nature of the (100) surface of a MgO single crystal. Surface science studies [95] and theoretical calculations (for a brief account see Ref. [96]) have shown that CO is very weakly bound on this surface so that it adsorbs only at temperatures well below liquid nitrogen. Clearly, the high reactivity of the dehydrated MgO surface is connected to the presence of defects, in particular of oxygen vacancies.

We have considered the interaction of CO [97] and O_2 [98] and more recently also of N_2 , molecules with the F centers of the MgO surface (we considered only centers located at the terrace sites, but the conclusions are valid also for F centers at low-coordinated sites). The calculations have been performed at the HF level. As usual, to describe the MgO surface we used stoichiometric MgO clusters and removed the central surface oxygen atom. The clus-

ters can be neutral or positively charged to represent F_s , F_s^+ , or F_s^{2+} surface vacancies, respectively, and the interaction of CO and O_2 with these centers has been considered³.

A neutral oxygen vacancy, F_s , is characterized by two electrons trapped in the cavity. In molecular orbital (MO) terms, there is a doubly occupied $(a_1)^2$ level pointing out from the surface. When a CO or O_2 molecule approaches the surface the occupied levels of the molecule interact in a repulsive way with the $(a_1)^2$ level leading to a strong Pauli repulsion which increases as the surface–molecule distance decreases. Let us consider the CO case in detail. The interaction energy curve for the $^1\text{A}_1$ state, corresponding to $\text{CO } ({}^1\Sigma) + \text{F}_s ({}^1\text{A}_1)$ is purely repulsive and no charge transfer occurs between MgO and CO. To form a bond one electron has to be transferred from the $\text{F}_s (a_1)^2$ orbital to the CO $2\pi^*$ MO (${}^3\text{E } (a_1)({}^2\pi^*)^1$ configuration in C_{4v}). At infinite distance, this state dissociates into ionic fragments, $\text{CO}^- ({}^2\Pi) + \text{F}_s^+ ({}^2\text{A}_1)$. For this ${}^3\text{E}$ state there is a bound minimum which is slightly higher than the neutral dissociation limit. A crossing of the ${}^1\text{A}_1$ and ${}^3\text{E}$ states occurs at about 2.5 Å from the surface. At the minimum of the ${}^3\text{E}$ curve, CO^- is in a metastable state and the reaction is an activated process. At short surface–CO distances a charge transfer from the vacancy to CO occurs, and the resulting F_s^+/CO^- complex is bound by electrostatic forces [97]. The large price for the charge transfer is not fully compensated by the formation of the chemisorption bond and this is why the minimum on the potential energy surface is higher than the energy of the neutral fragments.

The interaction of CO with a paramagnetic F_s^+ center is similar (Fig. 9). The ${}^2\text{A}_1$ curve, which correlates with ‘neutral’ fragments, $\text{CO } ({}^1\Sigma)$ and $\text{F}_s^+ ({}^2\text{A}_1)$, is repulsive. A bound state found at short surface–CO distances corresponds to the transfer of the trapped electron, $(a_1)^1$, to the CO $2\pi^*$ MOs (${}^2\text{E}$ state in C_{4v}). As for the adsorption on F_s , this state is strongly bound with respect to the asymptotic ionic dissociation limit, $\text{CO}^- ({}^2\Pi)$ and $\text{F}_s^{2+} ({}^1\text{A}_1)$, while it is unbound (metastable) compared to the ‘neutral’ dissociation limit, $\text{CO } ({}^1\Sigma)$ and $\text{F}_s^+ ({}^2\text{A}_1)$ [97].

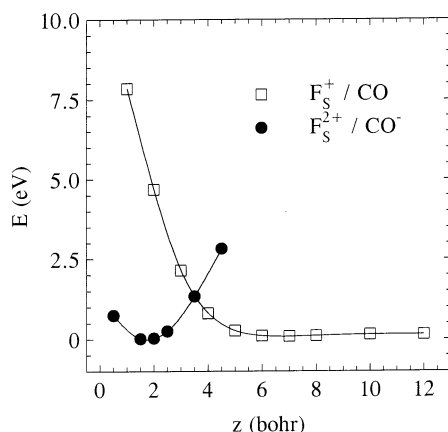


Fig. 9. Potential energy curves for the interaction of CO with a F_s^+ center at the MgO surface.

³ CO was placed normal to the surface, with the C-end down, the usual coordination mode of this molecule. O_2 has been adsorbed with the molecular axis parallel to the surface since EPR experiments show the equivalence of the two O nuclei.

Table 4
Summary of properties of oxygen vacancies in SiO₂ and MgO

Property	SiO ₂	MgO
Bond nature in the material	Covalent polar	Highly ionic
Notation of oxygen vacancy	V _O or V _O ⁺	F or F ⁺
Formation energy of neutral bulk vacancy	8.5 eV	> 10 eV
Electrons in a vacancy	Recombination of dangling bonds; localized electron pair	Trapped in cavity by Madelung potential
Geometrical relaxation	Strong in V _O and very strong in V _O ⁺	Virtually none in neutral F center; ≈ 5% in F ⁺ centers
Nature of ground and excited states	Very localized	Less localized, in particular for excited states
Quantum-mechanical level of description	Well described by CI cluster models (H embedding)	Large clusters and large CI required (PC embedding)
Surface versus bulk electronic transitions	Similar in the bulk and on the surface	Lower on the surface than in the bulk
Unpaired electron distribution in charged vacancy	V _O ⁺ : complete localization on Si (²⁹ Si <i>a</i> _{iso} ≈ 410 G)	F ⁺ : trapping at vacancy center (²⁵ Mg <i>a</i> _{iso} ≈ 4 G)
Surface chemical reactivity	Dominated by radical mechanisms	Dominated by electrostatic interactions

The main ingredient of the interaction is therefore the transfer of one electron from the surface to the adsorbed molecule. This results in a positively charged vacancy on the surface and a negative anion which are bound together by electrostatic forces. The interaction with O₂ is similar; this molecule however forms a stable surface complex with a F_s center, O₂⁻/F_s⁺; in a similar way, O₂ reacts with a F_s⁺ center to form O₂⁻/F_s²⁺. Also in this case a crossing of the ‘neutral’ and ‘ionic’ states occurs at about 2–2.5 Å from the surface, but, at variance with the CO case, for shorter distances the charge transfer complex is considerably more stable than the neutral dissociation limit. This is because the electron affinity of the O₂ molecule is much higher than that of CO so that O₂⁻ is intrinsically more stable than CO⁻. Thus, the reaction is exothermic. The important implication is that O₂ completely removes the trapped electrons from the MgO surface vacancies even at very low temperature, in agreement with the experimental observation [97,98].

To summarize, neutral O₂ and CO molecules interact very weakly with the regular, non-defective MgO(100) surface while the same molecules interact with oxygen vacancies on the MgO surface to form radical anions. The mechanism of the interaction is dominated by electrostatic charge-transfer mechanisms and is strictly connected to the presence of electrons trapped by the Madelung potential in the surface cavities corresponding to the anion vacancy.

5. Conclusions

In the previous paragraphs we have described the main structural, spectroscopic and chemical features of an oxygen vacancy in SiO₂ and MgO. These are summarized and compared in Table 4. On the basis of this comparison, one can conclude that the nature and the electronic properties of an oxygen vacancy in a binary oxide are directly related to the chemical nature of the bonding in the bulk material. In SiO₂, where the lattice is characterized by strong directional bonds (tetrahedral coordination around Si, bent coordination around O), the removal of an oxygen atom results in dangling bonds which recombine to form a new Si–Si bond. This new bond is localized and induces a strong relaxation of the lattice. In MgO, where the position and coordination of the ions is determined by the strong Madelung field, the removal of an oxygen does not result in new bonds. The two electrons formally associated to the O²⁻ anion remain localized in the position previously occupied by this anion. Energetically it is much more convenient to keep the electronic charge in the vacancy than to redistribute it over the neighboring Mg²⁺ cations. In a similar way, a charged oxygen vacancy (paramagnetic) is characterized by the presence of a localized dangling bond in SiO₂ while the unpaired electron does not belong to any specific atom in MgO. Of course, when the defects are located on the surface of the material, the presence

of these imperfections dominates the reactivity towards molecular adsorbates from the gas or from the liquid phase. In SiO_2 the surface chemistry is dominated by radical mechanisms, on MgO by electrostatic contributions.

Clearly, SiO_2 and MgO represent two extreme cases of oxides and the nature of oxygen vacancies in other oxides with mixed ionic-covalent character or where the metal atom can assume different oxidation states (e.g. for transition metal oxides) can lead to a much more complex behavior. In this review we have shown that it is nowadays possible to combine highly accurate quantum-mechanical calculations with spectroscopic measurements to deeply understand the nature of these centers. The development of defect engineering at an atomistic level implies necessarily the complete characterization of these centers, a process where quantum chemistry can significantly contribute.

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