The oxygen vacancy at the surface and in bulk MgO: An embedded-cluster study

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The oxygen vacancy in bulk MgO and at its (001) surface have been studied by means of the EMBED program which adopts an embedded-cluster approach in the frame of the Hartree–Fock (HF) approximation [Comp. Phys. Comm. 82, 139 (1994); 96, 152 (1996)]: A spin restricted (RHF) or unrestricted (UHF) method has been used according to whether the vacancy contains an even number (F⁺ and F²⁺ centers) or an odd number (F⁻ center) of electrons. The semi-infinite crystal has been simulated with a three-layer slab. Particular attention has been given to the optimization of the basis functions which serve to describe the trapped electron(s) in the vacancy. The correlation energy was estimated using second order Møller–Plesset theory. The three electronic configurations have been studied by allowing for relaxation of all neighboring ions. For the paramagnetic center, spin density data are provided and discussed with reference to results from EPR experiments and molecular cluster calculations. © 1997 American Institute of Physics. [S0021-9606(97)02346-5]

I. INTRODUCTION

Among the various intrinsic defects of MgO, the oxygen vacancy at the surface has received particular attention both from experimentalists and theoreticians because it is a relatively common defect which has interesting properties in spite of its simplicity. According to the number of electrons trapped in the vacancy (2, 1, or 0) this defect is called F⁺, F° or F²⁺, center, F standing for Farbe, the German word for color, because of its optical activity, and the s subscript recalling its location at the surface. The neutral F° center, either alone or in association with an alkali ion impurity, is believed to contribute to the catalytic activity of MgO in reactions like the dehydrogenation of methane. The charged F⁺ center, corresponding to a lone electron trapped at the anion vacancy, is detectable by electron paramagnetic resonance (EPR) spectroscopies, and is therefore a source of valuable information about the structural characteristics of the surface. The much less stable F²⁺ center, although never detected with certainty, is believed to form at the surface of MgO after treatment of the hydrated surface at high temperatures or following the interaction of molecular oxygen with MgO.7

This paper is concerned with the quantum-mechanical characterization of the three centers at the (001) surface of MgO, with reference to the corresponding defects in the bulk. The ab initio simulation of defects in crystals or at crystal surfaces is not simple. One must adopt a reasonable description of the “infinite” host system, while accounting for disruption of translational symmetry induced by the defect. The supercell approach circumvents this difficulty by creating an artificially periodic structure where the defect is translationally reproduced in correspondence to a given super-lattice of the host. This procedure has the advantage that very efficient computer programs are available for the treatment of periodic systems. Kantorovich et al. have used the CETEP code in a comprehensive study of the neutral F center in bulk MgO and at different crystal faces. CETEP is an ab initio program for periodic systems which adopts density functional theory (DFT) in the local density approximation (LDA); pseudopotentials are used for core electrons, while a basis set of plane waves is adopted to describe valence electrons: The plane-wave cutoff was set at 600 eV. More recently, Orlando et al. have used the program CRYSTAL which adopts the Hartree–Fock (HF) approximation with a basis set of localized functions for an analysis of the catalytic properties of the neutral defects F°, F°/Li:Mg° in the reaction of hydrogen abstraction from methane. An all-electron basis set was used derived from previous studies of bulk MgO and its surfaces. Correlation corrections to the energy were estimated using the Perdew functional applied to the HF charge density. More details on these supercell studies are given in the following discussion. Both exploit the fact that neutral oxygen vacancies do not interact appreciably except if they are very close to each other, so that rapid convergence is achieved with increasing size of the supercell. With charged defects the supercell approach is feasible but less reliable because of the long range Coulomb interaction between the periodic array of defects. Corrections have been suggested to account for these spurious interactions, but they are neither general enough nor sufficiently tested to be used routinely.

With cluster calculations, where only one defect is present, there are no such problems. An example of this approach is provided by the paper by Ferrari and Pacchioni concerning charged and neutral oxygen and magnesium vacancies at the surface of MgO. The clusters, comprising 18, 26, or 42 atoms, were surrounded by an array of point charges (±2ε) to create the correct Madelung field of the host at the central zone of the cluster. The HF approximation
was used, with a basis set of quality comparable to that of Orlando et al.11 The different types of defect were simulated by removing an ion at the center of the cluster, assigning a definite number of electrons to the system, and allowing for relaxation of the ions close to the defect. More sophisticated “embedding” techniques can be used. The use of un-screened point charges can cause polarization of the anions at the border of the cluster resulting in an incorrect value of the electrostatic potential at the vacancy. Effective core potentials (ECP) superimposed to the +2 point charges in the immediate neighborhood of the cluster can partly solve this problem. Very recently, Ferrari and Pacchioni19 have introduced this improvement in their cluster technique as applied to the study of the surface reactivity of oxygen vacancies with respect to molecular oxygen and carbon monoxide. The addition of ECPs resulted in a lowering of the ionization potentials of the F⁻ and F⁺ defects by about 3 eV with respect to the preceding study. Pandey and Vail24 have determined the HF ground states of F-type centers and hydrogen anions in bulk MgO by means of the ICE-CAP program.25 For many respects this calculation resembles that of Ferrari and Pacchioni, in particular as concerns the use of ECPs at the border of the cluster.26 However, instead of point charges, their cluster was surrounded by polarizable ions described according to the shell model;27 in this way, the polarization response of the host was taken into account self-consistently up to infinite distance.

The perturbed cluster (PC) method used in the present work has been described previously.28,29 It relies on the knowledge of the one-electron Green function \( G^f(\varepsilon) \) for the unperturbed host crystal. A cluster (C) is defined containing the defect and comprising a number of host system atoms which are deemed sufficient to screen the perturbation from the rest (D) of the host. The molecular solution for the cluster C in the field of D is corrected self-consistently by exploiting the information contained in \( G^f(\varepsilon) \) so as to ensure a proper coupling of the local wave function to that of the outer region. The theory has been implemented in a computer code (whose present public version is EMBED9630) which uses the CRYSTAL program previously mentioned17 for calculating \( G^f(\varepsilon) \). For that reason, all the fundamental techniques are the same in the two programs: In particular, the basis set consists of localized functions and the HF approximation is adopted both in its spin-restricted (RHF) and unrestricted (UHF) formulation, the latter to describe paramagnetic defects.

The most critical aspect of the PC method is the evaluation of the defect formation energy. While different opinions have been expressed on this point,31,32 it is generally agreed that reliable results can be achieved for the case of large gap insulators if suitable correction terms are included (see next section). In particular, the PC technique has proved capable of providing useful information on simple defects in MgO.22,33,34 Of particular relevance for the present investigation is our study of core holes in magnesium and in substitutional alkali ions (X:Mg; X=Li,Na) in MgO.34 The two studies are similar as regards the description of the host system, the comparison of bulk with surface defects, the choice of the embedded clusters, the techniques used for calculating the energy and the equilibrium geometry and for the treatment of the spin-polarized defects. Special attention was devoted in that paper to the analysis of the stabilization of charged centers by the polarization of the surrounding ions: A linear correlation was found between the gain in energy and the number of oxygens in the first coordination sphere. A novel feature of the present investigation is the attempt to estimate electron correlation effects (which are disregarded in the HF approximation) on defect energy. For this purpose, molecular cluster models are used.

The plan of this work is as follows. In Sec. II the computational method is presented; special attention is given to the choice of the basis set apt to describe the electrons trapped in the vacancy, and to the analysis of the various terms that contribute to the defect formation energy. The results are presented and discussed in Sec. III. The defect formation energies are first discussed, with reference to previous studies. The role of ion relaxation and of oxygen polarization in the stabilization of charged defects is demonstrated. The electronic structure of the defects is analyzed in terms of one-electron energy levels and electron charge density maps. For the paramagnetic center, electron spin density data are reported as well and discussed with reference to experimental EPR data.

II. THE METHOD OF COMPUTATION

A. Geometry

The description of the host systems is essentially the same as in the periodic study by Orlando et al.,11 except that a three-layer instead of a four-layer slab has presently been used to simulate the semi-infinite crystal. For the neutral defect at the surface this slab thickness has been proved to be sufficient;11 thicker slabs would probably be required for an adequate description of polarization effects in the presence of charged defects, but their use would entail excessive computational costs. The lattice parameter (421 pm) is the same as was determined for the bulk;19 no relaxation or rumpling was allowed in the defect-free two-dimensional system following the indications of a previous study.20 Figure 1 shows the embedded Mg₁₄O₁₈ and Mg₁₇O₁₃ clusters used for the bulk and surface defect calculations. Their shape is selected especially to permit the study of ion relaxation around the defect.

B. Basis set

The all-electron basis set adopted for the host system ions is the same as in previous calculations concerning MgO:11,19,20 it corresponds to 8–61 (Mg) and 8–51 (O) contractions of Gaussian type functions. In the following section, we discuss the possible inadequacy of these basis sets for ions close to the defect. Much more delicate is the problem of selecting appropriate basis functions for describing electrons trapped at the anion vacancy, especially for the case of the neutral F⁻ center where two electrons are involved. Since no experience is available from molecular quantum chemistry and only few cases have been treated in
the condensed matter literature with ab initio techniques so far, this is still an open problem. If the basis set is poor, one can proceed to a variational optimization of all parameters: In their study of F centers in bulk MgO, Pandey and Vail\(^24\) have used a single s-type function resulting from the contraction of two and one Gaussians for F and F\(^2\), respectively; the resulting \(\alpha\) exponents were 0.096; 0.067 Bohr\(^{-2}\) in the former case, and 0.079 Bohr\(^{-2}\) in the latter. Another possible strategy is to make reference to the basis set of the missing anion, either by using it unchanged,\(^8\) or by optimizing its most diffuse functions. The latter step proves very important in the case of surface defects where one must allow trapped electrons to spill over from the basin of the surrounding cations. Following this procedure, Orlando et al.\(^11\) have obtained a stabilization of the F\(_5\) defect by as much as 83 kcal/mol by simply changing the exponent of the outermost \(sp\) functions from 0.21 (the optimum value for O\(^2\) in bulk MgO) to 0.07 Bohr\(^{-2}\). The use of an anion derived basis set is however not fully justified: It contains very localized functions apt to describe core states which are unnecessary for trapped electrons and thus may produce unphysical features in the variational solution. We have therefore followed a procedure similar to that adopted by Pandey and Vail;\(^24\) however, we did not perform a fully self-consistent optimization because a much richer basis set was adopted, comprising four independent single-Gaussian s-type plus one polarization single-Gaussian p-type function. The exponents were optimized for the surface defects in a sequence starting from the least diffuse ones. The resulting values in Bohr\(^{-2}\) for the F\(_5\) center were: 3.21034, 1.23514, 0.53642, 0.0700 \((s)\); 0.2100 \((p)\). In the other two and much less critical cases it was sufficient to re-optimize the exponent of the most diffuse s function, resulting in 0.1300 \((F\(_5^+\))\) and 0.1700 \((F\(_5^2+\))\).

For the charged centers in the bulk we used the same basis sets as for the case of the surface. For the neutral defect in the bulk, the basis set was partially re-optimized, resulting in 0.1100 \((s)\); 0.1700 \((p)\) for the two outermost exponents. This shows that there is no need for very diffuse functions when the electrons are confined by Pauli forces in the cage of the surrounding cations. The more diffuse optimized basis set found by Pandey and Vail\(^24\) is most probably to be attributed to their use of a rather poor basis set for host atoms: The functions at the vacancy not only serve to describe the trapped electrons, but also improve the description of the surrounding ions.

### C. Energy and relaxation

The formation energy \(\Delta E_{\text{Fn}}\) of the F\(^n+\) defect \((n=0,1,2)\) at the surface or in the bulk will be referred to the formal reaction:

\[
S^f \rightarrow S(F:O^2-)^{n+} + O^{n-} + ne^- ,
\]

where \(S^f\) corresponds to the unperturbed system, and \(S(F:O^2-)^{n+}\) to the system with the defect. Note that we make reference to atomic oxygen, O\(^n\), as the extracted species, and the additional n electrons removed from the crystal are set at rest to infinity. We have preferred this convention with respect to that adopted by Ferrari and Pacchioni\(^8\) who considered in each case O\(^-n\) as the extracted species, in order to avoid problems associated with the calculation of the electron affinities of oxygen. All energy data cited from that work are corrected accordingly. The following expression has been used for calculating \(\Delta E_{\text{Fn}}\):

\[
\Delta E_{\text{Fn}} = -E^f[S^f] + E^f[S(F:O^2-)^{n+}] + E[O^{n-}] + \mu \cdot (n)
- q_{\text{net}}[S(F:O^2-)^{n+}] + q_{\text{net}}[S^f]) + \delta E_{\text{ovlcor}}(x)
+ \Delta E_{\text{Vzero,n}}[\delta E_{\text{polar,n}} + \delta E_{\text{correl,n}}].
\]

In this equation, all terms refer to the HF defect formation energy except for the last one which gives the electron correlation correction (see below). The two \(E^f\) terms in the first line are the HF local energies\(^20\) of the crystal before \(S^f\) and after \((S(F:O^2-)^{n+})\) the defect is created; in the latter case, the system has a formal charge \(q_{\text{for}} = n\); \(E[O^{n-}]\) is the HF energy of the oxygen atom with the basis set adopted for the
host oxygens (−74.7874 Hartree). The second line corresponds to the charge balance correction, and serves to correct for the fact that in the local region the net charge \( q^\text{net} \) does not coincide with the formal crystal charge. The electrochemical potential \( \mu \) corresponds to the energy associated with the transfer of a unit charge from the external D region to the local region in the perfect host crystal: More precisely, if one looks to these two regions as electron reservoirs, and \( dq \) is the charge transferred from the external to the local region, then \( dE_C = \mu \times dq \) and \( dE_D = -\mu \times dq \) are the respective changes in energy. \( \mu \) depends on the shape, composition and size of the cluster and is determined by the EMBED program.\(^{35} \) The \( \mu \) values for the clusters of Fig. 1 are 0.5748 Hartree/|e| (surface) and 0.6722 Hartree/|e| (bulk); the difference is due to the different stoichiometry of these two clusters.\(^{34,35} \) The \( \delta E^{\text{ovlcor}}(x) \) term in the third line is the overlap correction needed in the case where host crystal atoms are moved by \( x \) with respect to their unrelaxed positions, if they are not sufficiently far from the cluster boundary.\(^{36} \) This correction was estimated according to the procedure described in detail in previous work.\(^{34} \) In its essence, it corresponds to comparing the energy versus displacement curves for an ion at the center of the cluster (where the approximations presently adopted are very well justified) and for the same ion at the cluster boundary, in the absence of any other perturbation. In principle the two curves should coincide: The difference between the two, \( \delta E^{\text{ovlcor}}(x) \), provides an estimate of boundary effects on relaxation. The \( \delta E^{\text{zero,n}} \) term only matters when defects in the bulk are considered which are associated with a transport of charges out of the crystal. It takes account of the fact that the potential zero for an infinite three-dimensional crystal cannot be uniquely defined. Following the discussion given in Ref. 34, this term can be estimated as follows:

\[
\delta E^{\text{zero,n}} = n \times (\varepsilon_{\text{bulk}} - \varepsilon_{\text{slab}}) = n \times 0.03025 \text{ Hartree. (3)}
\]

Here \( \varepsilon_{\text{bulk}} \) and \( \varepsilon_{\text{slab}} \) are the one-electron HF 1s levels of a magnesium ion in the bulk and at the center of a thick enough slab parallel to the selected face, respectively, as determined with the CRYSTAL program.

The two terms in braces are not obtained directly from the EMBED program but can be estimated independently. Their importance in the determination of the defect formation energy will be discussed in the next section.

The \( \delta E^{\text{tripol,n}} \) term is the long-range polarization energy, that is, the contribution to the stabilization of charged defects by the polarization response of the infinite region around the cluster which is neglected in the present approach. Following Grimes et al.,\(^{37} \) for a spherical cluster of radius \( R \) with an effective charge \( q \) immersed in an isotropic medium with static dielectric constant \( \varepsilon_0 \), this term is given approximately by the classical formula

\[
\delta E^{\text{tripol,n}} = -q^2 / 2 R (1 - 1/\varepsilon_0). \tag{4}
\]

This quantity must be divided by two for a defect at the surface. Given the "radius" of the cluster used here (8.85 bohr), the arithmetic average between the distances from the center of the farthest anion included and the closest one excluded) and the value of the dielectric constant of MgO (9.78), this correction amounts to about −0.063 \( q^2 \) and −0.031 \( q^2 \) atomic units for the bulk and the surface defects, respectively. For the effective defect charge we shall use the net charge \( q^\text{net} \), that is, the formal defect charge screened by the charge transferred from the D region to the cluster. Note that while the charge balance correction is linear, the present term is quadratic in \( q^\text{net} \) and matters only for small clusters, large values of the dielectric constant and large values of \( q^\text{net} \). It is in all cases at least an order of magnitude smaller than the other one.

The last term, \( \delta E^{\text{correl,n}} \), gives the difference between the electron correlation energy of "products" (the MgO crystal with the F center plus the isolated oxygen atom) and of "reagents" (the perfect MgO crystal). In principle, we are dealing with a difference between two infinite terms, but all effects are expected to cancel almost perfectly except for the correlation energy in the isolated oxygen atom plus that of the \( 2 - n \) trapped electrons on the one hand, and that of the oxygen ion (\( O^2^- \)) in the crystalline matrix on the other. We can formally write

\[
\delta E^{\text{correl,n}}(\text{O}_\text{at}) + E^{\text{correl}}(\text{O}^2-)_{\text{cry}} - E^{\text{correl}}(\text{O}^2-)_{\text{cry}}. \tag{5}
\]

In order to estimate this difference, cluster calculations have been performed using the Gaussian 94 program.\(^{38} \) The technique adopted is described in more details elsewhere.\(^{39} \) Essentially, it consists in providing Gaussian 94 with the full set of eigenvalues and eigenvectors evaluated by the EMBED program for the embedded C cluster, and to force Gaussian to use them instead of those resulting from the normal SCF procedure. The fundamental justification for this technique is that the embedded cluster solution faithfully reproduces the electronic structure in the local region, as is shown in the next section. Different clusters have been used to simulate the \( [O^2^-]_{\text{cry}} \) ion and the associated defects in the bulk, while for the surface only the largest cluster was considered. For comparison, the same calculations were performed for the isolated clusters. The correlation energies were calculated using Möller–Plesset perturbation theory at the second order level (MP2). The MP2 energy for the isolated oxygen atom in its triplet ground state \( E^{\text{correl}}(\text{O}^2) \) obtained with the present basis set and to be used in Eq. 5 amounts to −0.047 447 Hartree. The results of this study are reported in Table I. They will be discussed in the next section.

D. Computational data

All calculations have been performed using "very good tolerances"\(^{32} \) for the truncation of infinite sums within the CRYSTAL and EMBED programs. In spite of the slightly larger size of the cluster used to describe bulk (33 atoms, 297 AOs) with respect to surface defects (31 atoms, 279 AOs), the former calculations were considerably less demanding because of the higher symmetry. For example, the total number of two-electron integrals were 322 and 634 millions in the two cases. Most of the time of an EMBED run, up to 95%, is spent in the self-consistent-field (SCF) procedure. This is the
III. RESULTS AND DISCUSSION

A. Energy data

Tables II and III report net charge, geometric relaxation, and energy data concerning the three defects for both the unrelaxed and the relaxed systems. We first comment on the formation energies $\Delta E_{\text{F}(\text{Embed})}$ purely based on the EMBED calculation. The long range polarization [Eq. (4)] and correlation [Eq. (5)] contributions are reported separately and are discussed later. The following comments apply to these data.

(1) When considering the relative stability of the defects at the surface and in the bulk, three main effects must be considered, apart from relaxation. The first one comes into play for the neutral defect only, where the two trapped electrons interact repulsively with each other: At the surface, they can reduce very effectively their mutual repulsion without losing much of the attraction from neighboring cations by expanding their distribution just above the surface (see below). This justifies the larger stability of the $F_s$ with respect to the $F$ center. The other two effects matter only for charged defects and act in opposite directions. On the one hand, the crystalline field is stronger at a six-coordinated site, and thus a surface anion is easier to remove, which would favor a defect location at the surface. On the other hand, the polarization response of the host to the defect charge is more effective in the case of the bulk, where twelve nearest anions surround the color center instead of only eight: This last effect is roughly proportional to $n^2$, the preceding one to $n$. For the unrelaxed centers, the surface defects with $n = 0, 1, 2$ are more stable than the bulk ones by 47, 22, 45 mHartree, respectively, which shows that these effects largely balance each other.

(2) Figure 2 shows the effect of the sequential relaxation of the different types of symmetry equivalent ions. From left to right, the defect formation energies at the HF level for the unrelaxed systems are first reported, next those obtained after relaxation of the magnesium ions nearest to the defect, finally those resulting from the movement of nearest oxygens. Consider first the neutral centers. Due to the fact that the two electrons at the surface spill out of the basin, the neighboring magnesium ions experience a reduced attraction with respect to the missing $O^{2-}$, and thus approach slightly the oxygen ions opposite to the $F_s$ defect, with a further gain in energy. For the corresponding defect in the bulk, on the other hand, the relaxation of host ions was found to be negligible. Relaxation is of course much more important for the charged defects, which reduces substantially the ionization energy of the color centers. The main contribution to stabilize the surface defects $F_s^+$ and $F_s^{2+}$ is seen to come from the relaxation of equatorial magnesiums which approach appreciably (about 6% and 11% of the interatomic distance, respectively) the oxygens opposite the defect. By the way, the contribution to the surface defect formation energy from the relaxation of subsur-
The data reported in Table III and concerning the long-


gap gives rise to unreasonable estimates of the correla-


tion energy. This is due to the very effective screening of the defect charge inside the cluster; the highest value of the net charge for the charged defect is less than one fourth of the formal charge (see Table II).

(3) The data reported in Table III and concerning the long-
range polarization correction, $\delta E_{\text{polar,n}}$, indicate that this term, though not negligible, is much less important than other contributions to the defect formation energy. This is due to the very effective screening of the defect charge inside the cluster; the highest value of the net charge for the charged defect is less than one fourth of the formal charge (see Table II).

(4) The correlation correction $\delta E_{\text{corr,n}}$ has been estimated using the data reported in Table I. Let us first comment briefly on these data which will be analyzed more deeply in a separate work. For the defects in the bulk, clusters of different size have been considered, in order to explore the convergence of the procedure adopted. This is rather satisfactory in all cases, better of course for the neutral with respect to the charged defects. For comparison, the results obtained for the isolated clusters are reported as well. As expected, the convergence properties are worse for the isolated than for the embedded clusters; in particular, for the charged defects at the surface the wrong distribution of one electron levels near the main gap gives rise to unreasonable estimates of the correlation energy. $\delta E_{\text{corr,n}}$ is positive in all cases, showing that the correlation of electron motions is more effective for the $\text{O}^{2-}$ ion in the crystal environment than for the {[(2 − n)e$^{-}$:O$^{2-}$]$_{\text{cry}}$+O$^{\text{aq}}$} case. The $\delta E_{\text{corr,n}}$ values obtained for the largest clusters (those shown in Fig. 1) have been adopted as estimates of the correlation energies without further corrections. Note however that the MP2 approximation usually accounts only for about 70%–80% of the correlation energy.

(5) From Table III, it is seen that correlation makes an important contribution to the defect formation energy, but does not introduce changes in the order of stabilities. For the neutral defects, in particular, the two electrons of the F center in bulk have larger correlation energy than those at the surface, as expected, but the difference is not such as to reverse the order of stability. The spectacular decrease of the correlation energy following relaxation for the $\text{F}^{2+}$ defect is due to the fact that in the unrelaxed structure the lowest virtual level is very close to the occupied manifold (0.31 Hartree), and the corresponding excited configurations contribute noticeably to the ground state; this level is destabilized by as much as 0.16 Hartree after relaxation has taken place.

Let us now compare the present results with those reported in the literature.

Relaxation around neutral defects has been found to be almost negligible in most previous studies, the most relevant effect being a slight displacement of magnesium ions away from the color center at the surface by 0.02–0.10 Bohr, in full agreement with the present results. As the only exception to this general finding, Pandey and Vail quote a displacement of magnesiums as large as 0.60 Bohr towards the F defect in bulk: This casts some doubts about the fact that their model system is at equilibrium, even in the absence of defects. Concerning the displacement of magnesium ions

<table>
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<th>TABLE III. Defect formation energies (Hartree). $\Delta E_{\text{F0}}$(Total) refers to the complete formation energy [see Eq. (2)], while $\Delta E_{\text{F0}}$(Embed) denotes the defect formation energy as resulting from the embedded calculations (that is, not including $\delta E_{\text{polar,n}}$ and $\delta E_{\text{corr,n}}$), and can be compared directly to the HF energies of Refs. 8 and 11.</th>
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<td><strong>Unrelaxed</strong></td>
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*HF energies: The (DFT) estimated correlation correction for the surface defect is 38 mHartree.

*HF energies: The results for the largest cluster (42 atoms) are reported.

*DFT energies: For the surface defect, the results for the thickest slab (six layers) are reported.
around the neutral and charged defects at the surface, the agreement of the present results with those obtained by Ferrari and Pacchioni is impressive; on the contrary, the relaxation of oxygens appears overestimated in that study, probably due to the fact that these ions are too close to the cluster boundary even for the largest cluster considered there.

As concerns energetics, the present results confirm the general qualitative picture emerging from the literature which can be summarized as follows:

1. The order of stability is: neutral > singly charged > doubly charged;
2. each type of defect is more stable at the surface than in bulk;
3. relaxation plays a very important role for charged defects.

Again, Pandey and Vail make an exception, since they report the paramagnetic center in the bulk to be more stable than the neutral one both in the unrelaxed and relaxed situation. One possible reason for this anomaly is the same as proposed above for the abnormally high importance of relaxation around the neutral center in their study; another is their use of an inadequate basis set for the F center. The present estimate of defect formation energies for neutral defects at the HF level (that is, without considering the correlation correction), coincides practically with that calculated by Orlando et al. This is not surprising in a sense, since the basic approximations are the same in the two approaches, and in particular the model of the host crystal is identical. The formation energy of the neutral defect at the surface from HF cluster calculations is also in close agreement with the present calculation: The reported values range from 0.2635 to 0.2818 Hartree according to the size of the cluster. This agreement among HF results is gratifying, since completely different computational schemes and formulas for evaluating the energy have been used, and different basis sets for describing the trapped electrons have been adopted in the three cases. It also shows that for the description of the neutral defect it is not necessary to take into account long range interactions. The formation energies of neutral defects reported by Kantorovich et al. are appreciably larger than the HF ones (about 0.09 Hartree). This is due in part to electron correlation effects, which are included in the local DFT Hamiltonian adopted in that study. By using a functional derived from DFT theory and applied a posteriori to the HF electron density, Orlando et al. estimate a correlation contribution of 0.0382 Hartree to the stability of the F defect. The present MP2 estimate is larger, 0.0491 Hartree, which brings the present results closer to the DFT ones. Apart from the uncertainty in these estimates, the rest of the difference can perhaps be attributed to an inadequacy of the local formulation of DFT in the description of the present systems (from a comparison of the calculated with the experimental lattice energy of the host crystal, Kantorovich et al. estimate that their defect formation energies are affected by a systematic error of about +0.03 Hartree).

The HF cluster calculations by Ferrari and Pacchioni concerning defects at the surface permit a direct comparison of ionization energy estimates:

$$I' = \Delta E(F^+_{\text{surf}}) - \Delta E(F^+_{\text{sub}}); \quad I'' = \Delta E(F^2+_{\text{surf}}) - \Delta E(F^+_{\text{surf}}).$$

The values resulting from that study: $I' = 0.1731$ and $I'' = 0.3561$ Hartree for the largest cluster are about three times as large as the present ones: 0.0584 and 0.1223 Hartree, respectively, (see Table III). In a more recent study, those same authors have reviewed critically their previous calculations. They have found that the electrostatic potential at the center of the cluster, and hence the stability of non-neutral defects, is largely dependent on the distribution of charges at the cluster boundary. The introduction of pseudo-atoms at the cluster border, described by suitable effective core potentials, reduces by far this effect. For an O$_{12}$Mg$_9$ cluster surrounded by 20 pseudo-atoms plus a large number of point charges, and after taking relaxation into account, they obtained $I' = 0.0768$ and $I'' = 0.2737$ Hartree, which is much closer to the present results.

### B. One-particle spectra

To understand the electronic structure of the F defects, it is expedient to consider the distribution of the one-electron levels of the clusters embedded in the crystal field. This is done in Fig. 3 for the surface and in Fig. 4 for the bulk. The levels are divided according to the irreducible representation (IRREP) they belong to; for comparison, the bands of the host system are reported as well.
Consider first the data for the surface defect. The self-embedded cluster (that is, the cluster without defects) closely reproduces the band structure of the perfect host. There are altogether 42 electron levels (accounting for degeneracy) between $-0.52$ and $-0.37$ Hartree and 14 levels between $-1.17$ and $-1.11$ Hartree which correspond to the number of $2p$ and $2s$ orbitals, respectively, of the $O^{2-}$ ions in the embedded cluster. The main band gap is also reproduced accurately. The creation of the neutral defect introduces no appreciable changes in the spectrum except for the appearance of one level in the main gap (the 32nd of the $A_1$ IRREP) which hosts the two trapped electrons and the disappearance of four levels (three of the $A_1$, and a degenerate one of the $E$ IRREP) associated with the missing oxygen. This level is above the valence band maximum by 0.169 Hartree before, and 0.200 after relaxation: The destabilization of the
defect level in the relaxed case is associated with the displacement of magnesium ions towards the oxygens, which lowers the electrostatic potential in the central cage. The corresponding values reported by Kantorovich et al.\textsuperscript{10} are 0.084 and 0.073 Hartree. This large difference can be explained in terms of the well known overestimation of interlevel distances in a vicinity of the Fermi energy in the frame of the HF approximation, and of their underestimation in DFT calculations; note however that relaxation has an opposite effect in the two cases.

For creating the paramagnetic defect, we have chosen the 32nd state of the $A_{1g}$ IRREP by imposing its occupation by a lone $\alpha$ electron in the open-shell calculation.\textsuperscript{30} The removal of the spin degeneracy causes a very large energy splitting (0.355 Hartree) of the corresponding $\alpha$ and $\beta$ levels. The positive defect charge shifts downwards all levels by roughly 0.1 Hartree on average; bandwidths are increased because of the “band-bending” effect (states localized nearer to the positive center are stabilized more than farther ones) which is particularly evident in the $2p$ Mg band around $-2.1$ Hartree.

The latter effects are enhanced in the case of the doubly charged defect. The vacant defect state appears at 0.005 Hartree, slightly below the center of the main band gap of the host system; before allowing for relaxation it was much lower, at $-0.174$ Hartree.

Similar comments apply to the structure of levels obtained from the bulk computations and described in Fig. 4. In this case, when passing from the self-embedding to the F center case, the disappearance of the $2s$ level of the central oxygen atom at $-1.1$ Hartree and its re-appearance as a defect level in the main gap at $-0.1$ Hartree is more clearly discernible. It also appears, in accordance with the experiment,\textsuperscript{40} that photon adsorption would excite an electron from the $1A_{1g}$ ground state of the F center to the first excited state of symmetry $1T_{1u}$. However, the transition energy is grossly overestimated (0.519 versus 0.184 Hartree which is the accepted experimental value\textsuperscript{40}). As stated above, this corresponds to the well known “stretching” of HF interlevel distances near the Fermi level, resulting in particular in a main band gap $\Delta E_g = 0.728$ Hartree versus an experimental value of 0.29 Hartree. The stretching is known to be rather uniform in that region: In fact, the defect level is situated almost correctly inside the main band gap (30% above the valence band maximum, the experimental value being 0.36%\textsuperscript{40}). For comparison, the DFT calculation gives a main band gap of 0.176 Hartree, and locates the F defect level at 56% of the gap.\textsuperscript{10}

**C. Charge and spin density**

The electron density maps reported in Fig. 5 describe the spatial distribution of electrons in a vicinity of the defects at the surface. The same figure reports the corresponding **dif-**
ference density maps, with reference to the superposition of HF electron densities for the free ions obtained with the same basis set. These difference maps have no real physical meaning, but they allow us to distinguish more clearly the effects of the perturbation. While the anisotropy of the distribution of the trapped electron $s$ in a vertical direction is visible in both types of representation, only the difference maps show in full evidence the polarization of neighboring ions in the presence of the charged centers. Consider for instance the $F_s^2$ defect, and the oxygens in the sub-surface layer: The isotropic distribution around these ions, which is maintained in the defect-free crystal even close to the surface, is badly distorted: The outer electrons are moving towards the positive center, while in the vicinity of the nucleus electrons are displaced in the opposite direction due to over-screening of the perturbing field.

Figure 6 plots total electron densities for the three defects in the bulk and at the surface along the three crystallographic directions $[001]$, $[100]$, $[110]$ of the neutral (continuous line), singly charged (dashed line) or doubly charged (dotted line) defects in bulk (above) and at the surface (below), as indicated. The left and central plot above are identical by symmetry.

For the bulk, our calculated maximum density is $0.0314 \, |e| \, \text{Bohr}^{-3}$, while Kantorovich et al.\textsuperscript{10} give 0.022 in the same units. The increase of the maximum electron density when passing from the surface to the bulk is expected. The fact that this increase is much smaller in the periodic calculation is not easily explained, and perhaps has its origin in the fact that the periodic defect state is more delocalized (the width of defect band is 0.6 eV, even with the smallest concentration of defects, one every 54 sites).\textsuperscript{10}

The local character of the defect states in the present study can be made more evident by plotting the wave function $\psi_l(r)$, labeling a level in the main gap. This is done in Fig. 7 for the defects at the surface. They look very similar to each other: They all are essentially localized in the central cavity, and exhibit local nodal structures in a vicinity of the surrounding ions which reveal a participation of valence orbitals to these states. They do not extend much beyond the first coordination sphere which justifies \textit{a posteriori} the use of the basic approximation implicit in the present technique.\textsuperscript{29,30}

When comparing the paramagnetic defect states corresponding to $\alpha$ spin (occupied) and $\beta$ spin (vacant), the most evident difference consists in the fact that the former exploits more efficiently the Madelung field by occupying the center of the cavity; the virtual $\beta$ electron feels the Coulomb repulsion from the $\alpha$ electron and thus is pushed to the borders of the cavity with a consequent increase of kinetic energy.

Figure 8 shows the spin density maps for the paramagnetic defect in bulk and at the surface. A more detailed description of the spin density is provided in Fig. 9, which also shows the effect of relaxation. The shape of these curves in a vicinity of the magnesium ions nearest to the defect corre-
sponds essentially to an \( \alpha \)-spin hybrid orbital \( 3sp \) of magnesium which participates in the defect state illustrated in Fig. 7(b). Of particular interest is the value \( \rho_s(r_0) \) of the spin density at the position of the nuclei of magnesium, since it can directly be compared with EPR data for the isotropic hyperfine splitting (hfs) constant, \( A_0 \), corresponding to the contact interaction of the electronic spin with the nuclear spin of \( ^{25}\text{Mg} \) (natural abundance: 10.00\%, nuclear spin: \( I/2 \), \( g_n \): \(-0.342 \pm 0.025 \)). The two are related through the well known expression:

\[
A_0 = \frac{2 \mu_0/3}{\beta_0 g_s g_n} \rho_s(r_0) \beta_0 \rho_s(r_0).
\]

Experimental data of \( A_0 \) are available for the paramagnetic defect both in bulk MgO\(^{3,43-45}\) and at its (001) surface.\(^{2-5}\) In the following, for the sake of simplicity, all these data are expressed in terms of \( \rho_s(r_0) \) in units of \( |e|/\text{Bohr}^3 \) (the conversion factor from Gauss to atomic units is \( 0.01023 \)). By the way, we have found that the basis set of contracted Gaussians here adopted is fully adequate for an accurate description of the spin density at the magnesium cores.

Consider first the bulk results. The calculated value of \( \rho_s(r_0) \) is 0.0313 (0.0363 for the unrelaxed structure) not too different from the well established experimental value of 0.0403.\(^{3,43-45}\) Note that the influence of relaxation is modest in contrast to the findings of Pandey and Vail\(^{32}\) who report a decrease of the spin density from 0.0778 to 0.0253 corresponding to a displacement of magnesium ions similar to the present one.

For the defect at the surface, we must distinguish the spin density at the four equivalent magnesium nuclei in the surface plane from that below; the latter will be reported in parentheses. The calculated values are 0.0392 (0.0269) for the relaxed, and 0.0463 (0.0322) for the unrelaxed structure. Note the difference between the two types of magnesium which exhibit spin densities larger and smaller, respectively, with respect to that in the bulk. The present results are similar to those reported by Ferrari and Pacchioni following the cluster calculations previously discussed.\(^8\) For three different clusters (relaxed structures), they obtain the following values: 0.053 (0.074); 0.056 (0.036); 0.043 (0.053). These theoretical values are much smaller than the reported experimental ones, which are around 0.11 at room temperature.\(^2-5\)

In particular, Tench\(^4\) found a strong temperature effect, much larger than for the F\(^+\) defect in bulk: The observed value was approximately stable around 0.09 from 0 to 120 K, and then increased almost linearly up to 0.11 at 470 K. This author interpreted his findings according to a model where the lone electron trapped in a surface oxygen vacancy interacts about ten times as strongly with the magnesium in the plane below the surface with respect to the equatorial ones. The strong dependence on temperature was attributed to the abnormally large vibrational amplitude of the involved ion with respect to the corresponding situation in the bulk. This model, which is still widely accepted, is in deep contrast with the present findings. One could try and attribute the reasons for these discrepancies to the inadequacy of the theoretical method. The quality of the basis set is again one of the most critical aspects to look carefully into. The discussion of the data of Fig. 9 has shown that the spin density at the nucleus depends on the participation of valence orbitals in the defect state. Since the basis set of magnesium has been designed to reproduce the characteristics of the defect-free crystal where this species is essentially deprived of its valence electrons, it may be argued that it is inadequate to describe the interaction of magnesium with the unpaired electron. We have changed the exponent of the outermost \( sp \) Gaussian orbital of the magnesium ions near the defect from 0.4 to 0.3 atomic units; the value of \( \rho_s(r_0) \) on those ions correspondingly increased by about 7\%. However, no new features appeared, and the energy of the system was slightly worse. We expect that basis set effects can justify the relatively small discrepancy with respect to the experimental bulk results, but they cannot explain the departure from Tench’s findings. A clue for the
solution of this problem is probably to be found in the fine experimental EPR study by Lunsdorf and Jayne. By progressively heating and irradiating with ultraviolet light samples of degassed magnesium oxide powder, they recognized the appearance of three-types of surface paramagnetic centers. Among these, the one that appears at temperatures around 1200 K, labeled $S_8$, presents the same features as the $F_s$ center described by Tench, in particular the same hfs constant for $^{25}$Mg. By considering the role of trivalent impurity ions in increasing the concentration of these centers, they propose that this species is the surface analog of the $F_{2s}$ center in bulk MgO, which consists in an electron trapped in a cation-anion divacancy. The similarity between the $F_{2s}$ bulk center and the surface center analyzed by Tench had been noted by this author, with reference to the highly anisotropic distribution of the unpaired electron in both cases: For the $F_{2s}$ center, the hfs constant gives $\rho_s(r_0) = 0.179$ for the magnesium ion along the tetragonal axis, and less than 0.03 for the four equatorial ions. Also the marked temperature effect is more easily explained for a magnesium ion which is not so strongly bound to the oxygen below. We can then suppose that the oxygen vacancy at the surface, the subject of the present study, does not correspond to the center $S'$ characterized by the high value of the hfs constant, but rather to the defect labeled $S_2$ in Ref. 2, whose hfs constant is similar to that of the $F$ defect in the bulk, and therefore is more difficult to detect. Preliminary calculations have been performed by us with the same techniques as in the present work and concerning an $F_{2s}$ center, that is, an electron trapped at a surface divacancy where a surface magnesium and the underlying oxygen are missing. The results seem to indicate that this is a suitable model for the interpretation of the EPR data: The calculated spin density at the axial Mg is 0.13, while it is 0.04 at the magnesium ions in the equatorial plane. These calculations do not include relaxation effects, which will be considered in a work in preparation. Also a plausible explanation has to be found for the formation of this defect in appreciable concentration.

An interpretation of the same observations has been given recently by Giamello and co-workers, which differs in a more essential way from the model of Tench. It is based on new and more accurate EPR experiments and on quantum-mechanical cluster calculations. First, it is demonstrated that the large majority of paramagnetic centers at the surface are associated with the evidence of a nearby proton; this is also true for the data obtained by Lunsford and Jayne, whose spectra reveal the characteristic doublet attributable to the proton. Next, the hypothesis is formulated that this proton distorts the distribution of the trapped electron, in such a way as to increase the spin density at the nucleus of the Mg ion(s) which are situated between the proton and the vacancy; the opposite would happen at Mg ions near the vacancy but away from the proton. This interpretation is supported by computer simulation of $F_{2s}^+(H)$ defects at the perfect (001) face and at edges or steps, by means of quantum-mechanical cluster calculations. The expected effect was found indeed to take place, though with various characteristics from case to case. An interesting feature of this model is that it allows more than one Mg ion to experience the same increase in the spin density; this seems in

FIG. 9. Linear plots of spin density for the paramagnetic defect along lines joining the missing atom with the nearest magnesium ions: (a) Defect in bulk; (b) defect at the surface, direction [001]; (c) defect at the surface, direction [100]. Continuous and dashed lines refer to the relaxed and unrelaxed structures, respectively. The plots below describe in more detail the structure in a vicinity of the magnesium nucleus. The distances from the defect center are indicated in Bohr; the nucleus is located in exact correspondence to the maximum of the spin density.

IV. SUMMARY AND CONCLUSIONS

We have adopted a rather sophisticated quantum-mechanical \textit{ab initio} approach for a comprehensive investigation of the oxygen vacancy in magnesium oxide. A critical analysis of the results of our calculations with reference to other theoretical investigations and to experimental observation has shown that in order to obtain reliable results many aspects of the problem must be taken in careful consideration, especially as regards defect formation energies and ion relaxation. They are summarized briefly here:

1. **Host system.** The defect must be created within a host structure corresponding to an equilibrium configuration. Otherwise, relaxation effects (both geometric and electronic) due to the defect are superimposed or in competition with those of the host itself. Furthermore, the electrostatic field created by the host must be accurately reproduced at the center of the cluster when charged defects are used.

2. **The local defect region.** Designing properly the defect region while keeping it to a reasonable size is a very important problem which takes different aspects according to the technique adopted (supercell, isolated, or embedded cluster). In the present case, special attention has been given to incorporate into the “active” cluster the main effects due to relaxation of nuclei around the defect.

3. **Defect charge screening and polarization response.** The response of the external region is very important in the case of charged defects in two respects: Screening of the local charge through charge flow from the surroundings, and polarization up to infinite distance. The former effect is accounted for rather accurately in the present scheme, the second one is estimated only \textit{a posteriori}. More sophisticated, self-consistent approaches could be employed in the latter respect.

4. **Basis set.** This problem does not exist when a universal set of plane waves is used, while it represents a most delicate issue if localized basis functions are employed. Not only sufficient variational freedom must be allowed to describe the defect states which may be formed, but the basis set of host crystal atoms, designed to reproduce the electronic structure of the defect-free system, may require modifications at least for the atoms closest to the defect.

5. **Correlation effects.** Correlation effects do not appear to play a crucial role in the present application, where they increase appreciably the formation energy of the defects but leave their ionization energies almost unchanged. This is surely not the case generally. We think that the technique presented in the second section, and consisting in performing molecular correlation calculations on the embedded cluster, can at least provide an estimate of the importance of these effects.

Heavy computations are needed to satisfy these requirements even for simple defects like the ones treated here. For this reason, compromise solutions have been adopted which are only partially adequate: The use of a rather thin slab (three layers) to treat the surface defects, relatively small embedded clusters, and a quite limited basis set. In spite of that, interesting results have been obtained which can be summarized as follows:

1) The anion vacancy at the surface and in the bulk have been compared accurately. In all respects (energy, relaxation, electronic structure, spin density) no important qualitative difference has been found to exist between the two situations, but the defect is more stable at the surface than in the bulk for all three charge states. 2) The spin density of the $\mathrm{F}^-$ defect is markedly anisotropic, but not as much as it would appear from EPR studies. The discussion of this discrepancy has lead us to support the hypothesis that the experimental EPR spectrum, usually attributed to the isolated anion vacancy at the surface is due instead to a surface divacancy. This hypothesis will be critically tested against the other one which assigns a decisive role to surface protons in determining the observed anisotropy of the distribution of the spin density.

From the present results we feel encouraged to apply this method to other similar problems. As anticipated in the preceding section, the first application will concern the divacancy at the surface and in bulk MgO. But other interesting and important problems are worth being investigated which may help experimentalists in the interpretation of the results of surface EPR studies, and thus enhance the importance of this technique in the determination of surface structures. As an example, we can consider the recent study by Pacchioni and co-workers, concerning the reactivity of oxygen vacancies with $\mathrm{O}_2$ and $\mathrm{CO}$ at different types of site at the MgO surface. Other interesting applications could concern the interaction of these centers or divacancies with alkali atoms.

Work is in progress to extend the possibility of comparison of the theoretical with the experimental EPR data, by allowing the calculation of the anisotropic part of the hyperfine interaction and of the effective electronic $g$-tensor within the present scheme.

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