

Stability of vacancy defects in MgO: The role of charge neutrality

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The energetics and electronic structure of a series of neutral and charged oxygen and magnesium vacancy defects (F , F^+ , F^{2+} , V , V^- , V^{2-} , and P centers) in MgO have been computed using the stationary total-energy functional. We find that contrary to the charge-compensation model for anion-cation defect pairs in ionic materials it is energetically unfavorable for an isolated neutral oxygen vacancy (F center) to transfer electrons to an isolated neutral magnesium vacancy (V center), and form isolated F^{2+} and V^{2-} centers. Charge compensation is unfavorable because additional electrons at the V center induce new occupied states in the gap, which increase the energy of the defect. This result is consistent with the interpretation of spectroscopic experiments on MgO, in which the ground-state defects are either neutral or singly charged. The computed formation energies of both the F and V centers are larger than the cohesive energy of MgO per formula unit, but the binding energy of the defects in the P center configuration is 12.16 eV. This attraction between the F and V centers is enhanced when the defects carry a net charge. The position of the vacancy defect state in the fundamental energy gap of MgO is found to be in qualitative agreement with a model for optical absorption and emission, and is used as a simple model for the formation energies of the defects. The contribution of the band-structure energy to the stationary functional is found to account for more than 90% of the defect energies. This component of the defect formation energy is computed directly, using the recursion method, rather than as the difference between the total energies of our 8000-atom cluster with and without the defect.

I. INTRODUCTION

MgO is an important material for understanding the electronic structure of defects in ionic materials.^{1,2} The material crystallizes in the rocksalt structure, with each Mg and O atom sixfold coordinated. The experimentally determined band gap of MgO is 7.8 eV.³ As with most insulators and semiconductors, the presence of lattice defects in MgO has been shown to give rise to a variety of optical, catalytic, and electrical conductivity phenomena which are absent in the crystalline material.⁴⁻¹⁰ Interpretations of these and allied phenomena are usually based upon an ionic model of the solid, in which each oxygen site has associated with it a charge of $-2e$, which is compensated by $+2e$ charge on each Mg site.^{11,12} This ionic picture of bonding has also been the basis for several descriptions of lattice vacancies in these materials, in which the ground states of the vacancies are doubly positively charged in the case of the oxygen vacancy, and doubly negatively charged for the Mg vacancy.¹³⁻¹⁶ Results from recent *ab initio* density-functional computations for the doubly positively charged oxygen vacancy, designated an F^{2+} center, and the doubly negatively charged magnesium vacancy, the V^{2-} center, qualitatively agree with empirical shell models for the energetics and mobilities of these charged vacancies.¹⁶ The presence of these charged defects is also the basis for the traditional model of ionic conduction via diffusion of lattice vacancies in MgO.¹⁷

Explanations for the optical and electron-energy-loss

experiments on MgO are based almost exclusively on models for the defect levels of the neutral, singly charged, or aggregate oxygen vacancies.^{4-6,18,19} The position and occupation of the defect level associated with the various charged states of the oxygen vacancy has been the subject of experimental⁴⁻⁸ and theoretical^{14,18,20,21} investigations. Optical-absorption and reflectance studies have found broad emissions at approximately 2.3 and 3.2 eV, which are attributed to excited states of the F and F^+ centers, respectively.⁴⁻⁸ A feature at 3.58 eV, observed with electron-energy-loss spectroscopy, has suggested the involvement of oxygen vacancy aggregate centers.²² A strong absorption band centered at 5 eV has been assigned to contributions from F and F^+ centers, and has been observed in the additively colored MgO crystals even when they are produced in a vapor of metals other than magnesium.² A model which has been used to explain the optical experiments is based on the assumption that the observed feature is due to threshold absorption (from the defect state to the conduction band minimum), and therefore that the lowest defect level of the F center is close to the bottom of the fundamental gap.⁴ A consideration of the symmetries and energies of the states at the top of the valence band and bottom of the conduction band suggest, in agreement with our calculations, that the defect level of the F center is at a higher energy in the gap, and close to the conduction-band minimum. A different model for explaining the optical measurements has been proposed for the surface oxygen vacancies,²³ and this model for the bulk defects is briefly discussed in

Sec. IV of this paper.

In this paper we report on calculations of the relative formation and interaction energetics of different charged states of lattice vacancy defects in MgO. Approximate structural energies are obtained by evaluating the stationary functional in density-functional theory. The primary purpose of the current investigation is to explain some of the defect processes which take place in MgO crystals which have been heated to approximately 2000 K, such as the formation energy of the *F* center in and additive coloring experiment.²⁴ More accurate self-consistent calculations are not required, since the explanation of these fundamental phenomena in MgO requires estimates of the defect energies to within several tenths of an eV. Instead, the stationary functional, which has established itself as a useful method for estimating cohesive and structural properties of molecules and solids, is used in this work.^{25–27} The details of this method are presented in Sec. II of this paper. The functional is introduced in Sec. II A, and the accuracy to which calculations are performed is described. The solution to the Schrödinger equation is obtained using the recursion method. This approach enables the treatment of systems with many atoms, due to the scaling of the algorithm which is described in Sec. II B. Section II C describes the treatment of long-range electrostatic interactions for charged defects. The estimates for the charge density and potential used with the stationary functional are based upon atomic rather than ionic magnesium and oxygen. The justification for this approach is discussed in detail in Sec. III, where the self-consistent charge density is compared to a superposition of free-atom charge densities. The results of the defect calculations for the oxygen, oxygen aggregate, magnesium, and MgO divacancy defects are presented in Sec. IV. In Sec. V we discuss our results in relation to the available experimental and other theoretical works, and consider the implications of our results in the context of the ionic model. The conclusions of the work are summarized in Sec. VI.

II. COMPUTATIONAL METHOD

A. The stationary energy functional

The stationary energy functional in density-functional theory has been used to provide quantitative descriptions of the energetics of bonding in a variety of molecules and solids.^{26–30} Evaluation of the functional differs from tight-binding or extended Huckel total-energy methods by the inclusion of the three-center contributions to the Hamiltonian matrix elements.²⁶ The method is an approximation of self-consistent density-functional theory, but unlike the Kohn-Sham energy functional it does not require a calculation of the output charge density from the one-electron Schrödinger equation. By choosing the input electronic charge density and potential in a mathematically convenient form, direct evaluation of point defect energies is computationally more tractable than with self-consistent algorithms. Since the energy functional is stationary about the self-consistent ground-state electronic charge density, a reliable estimate for the

ground-state energy, with errors to second order, is obtained by inserting a suitable trial charge density and potential into the functional. By constructing a trial charge density for homonuclear molecules from a superposition of free-atomic charge densities, and computing a potential from that charge density in the local-density approximation (LDA), Harris²⁷ derived cohesive energies and structural parameters for these molecules which were accurate to within a few percent. Polatoglou and Methfessel²⁹ applied the same method to the *sp*- and *d*-bonded metals Be, Al, V, and Fe, to the covalently bonded semiconductor Si, and to the ionic compound NaCl. The computed cohesive energies and structural quantities compared closely with those derived from self-consistent calculations.

Foulkes²⁶ showed that the stationary functional, introduced independently by other workers,^{25,27} is not only stationary in the input charge density, from which a potential may be calculated, but that it may be written in the form

$$E[n_{\text{in}}(r), V_{\text{in}}(r)] = \sum_{i=1}^N \epsilon_i - \int V_{\text{in}}(r) n_{\text{in}}(r) d^3r + F[n_{\text{in}}(r)], \quad (1)$$

where it is explicitly stationary in both the input charge density $n_{\text{in}}(r)$ and the input potential $V_{\text{in}}(r)$. The first term in Eq. (1) is the sum over the eigenvalues of the N occupied states of the independent electron Schrödinger equation (in atomic units)

$$\left\{ \frac{-\nabla^2}{2} + V_{\text{in}}(r) \right\} \psi_i = \epsilon_i \psi_i, \quad (2)$$

and $F[n_{\text{in}}(r)]$ is the sum of the electrostatic and exchange correlation energies. The input charge density used in this work is a superposition of free-atomic charge densities, which were computed self-consistently using the LDA approximation for exchange and correlation. The Wigner-Seitz cellular potential^{31–33} is used as the input electronic potential $V_{\text{in}}(r)$ in Eq. (1). In the limit of weak coupling between the atoms, and assuming only occupation of states below the Fermi level, the band-structure energy with the Schrödinger equation solved with the Wigner-Seitz potential gives the binding energy of the solid. This result was used by Wigner and Seitz in their calculation of the binding energy of alkali metals.³² The Wigner-Seitz potential is defined to take the value of the most dominant atomic potential in a particular region of space. The physical assumption made by this choice of the potential is that the extra Hartree energy, due to the charge of other atoms in the system, is canceled by the reduced exchange and correlation energy in the interstitial region of the solid. Inglesfield³³ has considered the Wigner-Seitz potential in the context of the single particle Schrödinger equation, and has shown that it is an approximate potential for excitation energies. The solution to the Schrödinger equation with the Wigner-Seitz cellular potential is found to give a significantly larger band gap in MgO compared with computations performed using the LDA for exchange and correlation.²³ Self-

consistent LDA calculations for crystalline MgO find a band gap of between 4 and 5 eV depending upon the particular choice of parametrization for the exchange-correlation functional.^{20,21} By comparison, the band gap computed in this work, 7.31 eV, is closer to the experimental value of 7.8 eV. The computed band gap was found to be insensitive to additional basis set elements on adjacent magnesium and oxygen atoms close to the center of the cluster. In MgO the atomic orbitals were found to be a much better basis set in the Wigner-Seitz approximation than when the potential was constructed from a superposition of atomic charge densities using the LDA. The improved band gap with the Wigner-Seitz approximation facilitates comparison with optical experiments, and enables more accurate estimation of the formation energy of the charged vacancies.

B. The recursion method for computing defect energies

The recursion method is used in this work to compute the components of the solution of the Schrödinger equation necessary for the evaluation of point defect energies. The formal aspects of this approach have been the subject of previous publications.³⁴ Here we describe the applicability of the recursion method for computing point defect energies.

The recursion method is used to compute diagonal elements of the resolvent for localized orbitals in the region of the defect, rather than the eigenfunctions and eigenvalues of the system Hamiltonian. [The diagonal resolvent element $R_{00}(E)$ of a Hamiltonian \mathbf{H} for the state $u_0(\mathbf{r})$ is $\langle u_0(\mathbf{r}) | [E - \mathbf{H}]^{-1} | u_0(\mathbf{r}) \rangle$.] The computation of $R_{00}(E)$ with the recursion method scales linearly with the number of relevant degrees of freedom. A degree of freedom is considered relevant if its exclusion from the basis set would affect $R_{00}(E)$ at the level of accuracy required in the calculation. By comparison, matrix diagonalization and the computation of eigenvalues scale with the cube of the total number of degrees of freedom in the system.

The set of diagonal elements of the resolvent for the localized electronic basis functions in the vicinity of the localized defect are used to compute the quantity

$$\Delta U = \sum_i^{E_F^D} E_i^D - \sum_i^{E_F^R} E_i^R, \quad (3)$$

where E_i^D and E_i^R are the eigenvalues of the defect and reference systems, respectively, and the sums in Eq. (3) are performed over eigenvalues up to the Fermi levels of the appropriate system. The quantity ΔU is constructed explicitly in the recursion method from the zeros and poles of $R_{00}(E)$, instead of the difference between the two individual terms in Eq. (3).³⁴ The explicit computation of this energy difference avoids the problem of noncancellation of random errors which arises when the terms in Eq. (3) are computed individually.

The calculations presented in Sec. III are performed on a cubic cluster of MgO containing 8000 atoms when there are no lattice vacancies. The advantage of using such a large cluster is that the electronic levels localized at the surfaces have a negligible weight close to the center

of the cluster, and therefore it is not necessary to modify the Hamiltonian matrix elements for orbitals localized at the surface. These computations employ a minimal atomic basis set consisting of Mg 3s, O 2s, and O 2p orbitals, supplemented by two energy-optimized spherically symmetric Gaussian orbitals at each vacancy site. The overlap and Hamiltonian hopping matrix elements were calculated, in the frozen-core approximation, by performing nested Gaussian quadrature integrations over a spatial region consisting of up to the seventh nearest neighbors in the rocksalt structure. The computed band gap at the (001) surface is reduced by 1 eV from the value in the bulk, and this effect is detectable at the center of a 1000-atom cluster, but is not detectable in the 8000-atom cluster with double precision arithmetic. The difference in the defect energies computed with the 8000-atom cluster instead of the 1000-atom cluster is much less than the 0.01-eV precision to which the results in this paper are reported.

C. Computation of charged defect energies with the stationary functional

The calculation of the defect energy for an isolated and charged point defect is complicated by the presence of a long-range Coulomb tail in the defect potential. The central problem in formulating the defect energy is how to separate and recombine short- and long-range effects. Baraff and Schluter³⁵ have proposed a methodology for this problem in which they define a sphere of radius R_1 , containing region 1 in which strong chemical effects occur as a result of creation of the defect. Region 1 is surrounded by a much larger region, region 2, in which the crystal's response to the defect can be described by dielectric theory. In region 2 small polarizations persist over an infinite range. The charge disturbance in region 2 is a polarization charge, varying on a length scale of the bonds. The electric field of the defect pushes charge along, or across, bonds, but no macroscopic charge is accrued except at the surface of the solid. Provided region 1 is sufficiently large to fully screen the defect, reducing its nominal charge from n to n/ϵ_e , where ϵ_e is the electronic contribution to the dielectric constant of the crystal, then the finite polarization in the outer region makes no contribution to the energy of the system.³⁵ The electrons move onto or away from the defect until the energy cost associated with moving more electrons is balanced by the electrostatic energy of accruing charge at the surface. The screening of a defect such that the nominal charge is reduced by the dielectric constant arises from the boundary condition for the normal component of the polarization at the outer surface, and its relationship to the surface charge density. The charge which resides on the outer surface of the crystal is $n(1 - 1/\epsilon_e)$, and the fraction n/ϵ_e remains at the defect to interact with any locally inserted charge. Since charge is moved to the surface of the crystal, the zero wave-vector component of the charge density and potential behaves discontinuously when charged defects are present. These results, which

are physically intuitive from classical electrostatics, have been derived from the solution to the Schrödinger equation for the $N + 1$ body problem.³⁶

A choice of charge density and corresponding potential in Eq. (1) to simulate the nominal charge, rather than the reduced charge, at the defect neglects the screening of the bound charge in the insulator, and is found to give comparatively larger defect formation energies. The stationary functional may be exploited with a choice for the potential and charge density which accounts for this screening, by using the dielectric constant as an empirical parameter. When the defect carries a nominal charge n , the input charge density should differ from that of the neutral defect by a total electronic charge of n/ϵ_e in region 1. Similarly the change in the potential should reflect a change in the electronic charge density of n/ϵ_e in the defect region. For the F^+ and F^{2+} defect centers the defect charge is removed in equal proportions from the six vacancy neighbor Mg atoms. The Schrödinger equation is solved for the appropriate fractionally charged Mg ion to compute this charge density. The Wigner-Seitz potential is used in these computations, except that the stronger potential of the Mg ion is used in place of the neutral Mg atoms adjacent to the defect. Similarly, the input charge densities and potentials for the charged states of the V center are obtained by assuming that the nearest-neighbor oxygen atoms share the excess charge density and have their potentials modified accordingly.

An estimate of the importance of the long-range lattice relaxation can be obtained by using the static dielectric constant instead of the high-frequency electronic dielectric constant to determine the residual charge n/ϵ at the defect. The electronic dielectric constant in MgO is 3.01, while the static dielectric constant, which includes the effects of both lattice polarization and electronic contributions, is 9.64.³⁶ When the lattice relaxes, dipole moments are induced which cancel the electric field due to the nominal charge at the defect. The approximation, which is presumably crude, is that the energy gained by the lattice relaxation may be modeled in the same way as the electronic dielectric response. An important virtue of this approximation is that the Schrödinger equation is solved with the appropriate classical potential $n/\epsilon r$ at a large distance r from the charged vacancy. The application of this method to the charged vacancy centers in bulk MgO leads to an energy difference of less than 0.1 eV for both the F^+ and the V^- centers when the static dielectric constant is used instead of the electronic dielectric constant. This suggests that lattice relaxation plays a much less significant role in the formation energies of charged defects in MgO than do electronic structure effects. A much larger estimate for lattice relaxation energies has been obtained in a LDA supercell calculation for charged defects.¹⁶ These calculations smear a uniform compensating charge density in each supercell to cancel the divergent electrostatic energy which arises when each cell carries a net charge. An estimate of the energy due to interaction between the defects in each supercell is modeled with the static dielectric constant of MgO.

III. ATOMIC CHARGE DENSITIES AND IONIC SOLIDS

The energetics and structural parameters of NaCl were evaluated in Ref. 29 using a charge density constructed from a superposition of free-atom charge densities. The energy and bulk modulus differ from the self-consistent result by less than 10%, and the lattice constant by less than 1%. In the case of NaCl, Slater pointed out, that there is very little difference between a superposition of free atoms, a superposition of free ions, and the self-consistent charge density.³⁷ A similar comparison for the charge density in the (100) plane passing through the MgO nuclei is shown in Fig. 1. The self-consistent charge density for MgO (n_{sc}) was computed using the full-potential linearized augmented plane-wave (FLAPW) method in the LDA.³⁸ The convergence of the charge

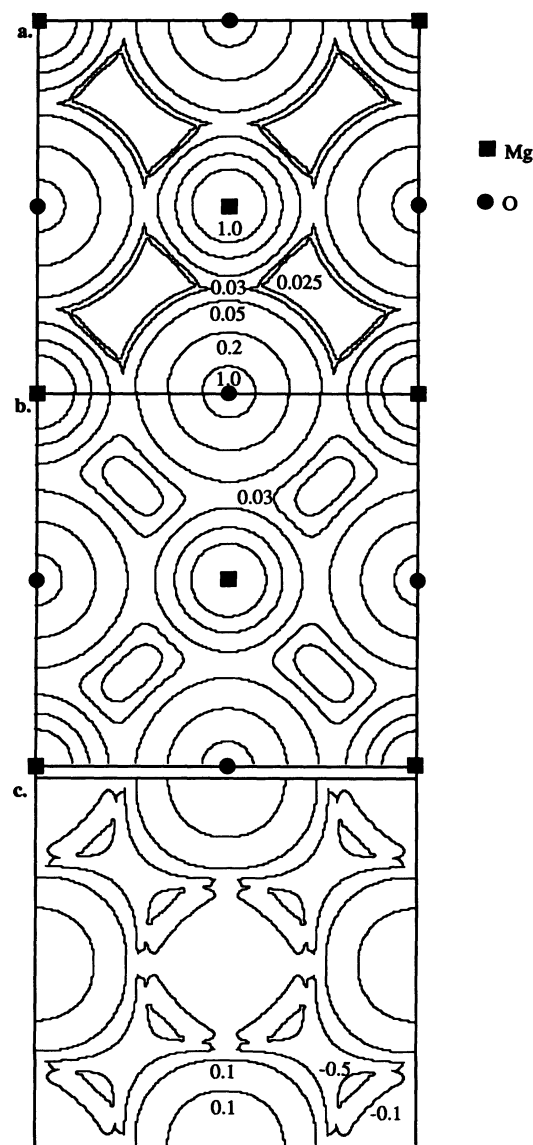


FIG. 1. (a) Self-consistent charge density n_{sc} , computed with the FLAPW method. (b) A superposition of free-atom charged densities, n_a . (c) Fractional difference $(n_{sc} - n_a)/n_{sc}$.

density is several orders of magnitude beyond that which can be determined from Fig. 1(a). For comparison, a superposition of atomic charge densities (n_A) is shown in Fig. 1(b), and the fractional difference, $(n_{SC} - n_A)/n_{SC}$, in Fig. 1(c). It is worth remarking that the size of the oxygen, defined by the position of the minimum contour along an Mg-O bond, is larger than that of the magnesium in both Figs. 1(a) and 1(b). While this ioniclike density is expected for n_{SC} , the result is more surprising for n_A , since a Mg atom has 12 electrons compared to eight in oxygen. This effect may be understood from a consideration of the shell structure of the isolated atoms. The atomic Mg 3s electronic distribution, containing two electrons, is spatially more delocalized than the atomic O 2p orbital, occupied by four electrons, and possesses a maximum close to the O nuclei at the equilibrium Mg-O bond separation. As a consequence, the atomic charge density of an oxygen atom becomes greater than that of a magnesium atom between 1.0- and 2.3-bohr radii from the nucleus. At distances less than 1.0-bohr radii the Mg core states dominate the charge density, and beyond 2.3-bohr radii the Mg 3s charge distribution is larger than that of the oxygen atom. Hence it is the shell structure of the atoms which gives rise to the ioniclike charge density in Fig. 1(a). Representing the charge density as a superposition of atomic charge densities leads to certain contradictions with the classical point-ion model of ionic materials. For example, there are no long-range electrostatic forces. The Madelung potential is therefore not the most natural framework for understanding the cohesive energy in these calculations. This issue is further discussed in Sec. V of this paper.

The superposition of atomic charge densities overestimates the charge in the interstitial region between like atoms. This is illustrated by the negative contours in Fig. 1(c). The charge removed from this interstitial region resides almost entirely between two approximately spherical contours centered on the oxygen atom and with value +0.1. The fractional charge-density difference has a local maximum with the value 0.141 between these two contours. The corresponding charge-density difference at this local maximum in the fractional difference is only 0.013 electrons/bohr³. While there is a peak of 14.1% error in the charge density in a spherical region surrounding the oxygen lattice site, and a significant absolute value of the charge density in this region, the second-order error in the energy associated with a 14% error in the charge density will be sufficiently small to obtain an approximate description of the relative importance of the vacancy defects considered in this paper. In this sense the charge density in Fig. 1(b) can be considered sufficiently self-consistent for use with the stationary functional. This assumption can be tested by comparing the stationary energy functional and self-consistent calculations for bulk energies. The cohesive energy of MgO computed using the stationary functional with n_A as the input charge density is 11.03 eV. Self-consistent calculations have reported results in the range of 9.96–10.56 eV, and the experimentally determined value is 10.35 eV.²¹ The discrepancy between self-consistent and stationary functional results is consistent with other works, which

have found the stationary energy functional to be maximal when the input parameters $n(\mathbf{r})$ and $V(\mathbf{r})$ are derived from their atomic values.²⁹ The agreement is within the 10% error necessary for a description of vacancy energetics in MgO. The energy of the (001) surface in MgO has also been computed using the method used in this paper, and was found to compare closely with the results from other calculations.^{39–41}

The description of the vacancy energetics in Sec. III of this paper is based upon an analysis of the eigenvalue spectrum of the one-electron Schrödinger equation, as in a tight-binding picture of ionic materials. In the case of MgO, the material is fully ionic in the sense that the valence-band eigenfunctions are of O 2p symmetry, and the conduction band is of Mg 3s symmetry. The degree of covalency is less than 5% in the crystalline material. Therefore, modeling the charge density in MgO as a superposition of atomic charge densities is not in contradiction with the laws of valence.

IV. ENERGETICS OF VACANCY DEFECT FORMATION

The formation energies of all defects computed in this work are displayed in Table I. The corresponding defect geometry of the lattice vacancies are illustrated in Fig. 2. We find that more than 95% of the computed defect formation energies arises in the eigenvalue contribution to the stationary energy functional in Eq. (1). The computed defect energies are therefore most readily understood from an analysis of the difference in electronic structure between the solid and isolated atoms in these calculations, and not in terms of Madelung energies which are often used to provide a simple framework for understanding bonding in ionic materials. As the starting point for understanding the defect electronic structure it is useful to consider the symmetry of the wave functions in crystalline MgO. The electronic states at the top of the valence band and the bottom of the conduction band are shown in a minimal atomic basis set representation in Figs. 3(a) and 3(b), respectively. These two states are at

TABLE I. The computation formation energies of the various defects, and the percentage contribution of the band-structure energy to each energy. The superscripts * and ** indicate the energy required to remove an oxygen atom minus the cohesive energy per formula unit, and the energy required to remove two oxygen atoms minus twice the cohesive energy per formula unit, respectively. The percentage contributions to the defect energies are shown before the cohesive energy is subtracted.

Defect	Formation energy	Band-structure percentage of formation energy
F	1.82 eV*	97.7
F^+	3.67 eV*	
F^{2+}	5.47 eV*	
F_2	3.23 eV**	96.1
V	13.82 eV	95.2
V^-	14.83 eV	
V^{2-}	16.35 eV	
P	3.48 eV*	92.0

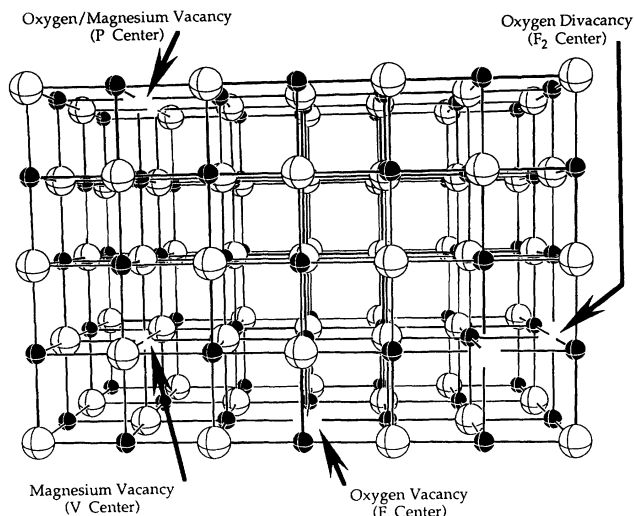


FIG. 2. Lattice vacancies in MgO.

the Γ point in the band structure, and the top of the valence band is approximately a nonbonding superposition of the O $2p$ orbitals, and the bottom of the conduction band is approximately a bonding superposition of Mg $3s$ orbitals. A basic understanding of the oxygen vacancy, magnesium vacancy, and MgO divacancy defects discussed here can be understood qualitatively from a consideration of the position and occupation of the defect state in the energy gap associated with each vacancy.

A. Oxygen vacancies

The formation energy of the neutral oxygen vacancy in bulk MgO has been determined in an additive coloring experiment to be 1.53 eV above the 10.35-eV cohesive energy per MgO formula unit.²⁴ In this experiment, MgO is heated to 1800 K in an environment of magnesium vapor, and vacancy production involves the diffusion of surface oxygen vacancies into the bulk material. In the remainder of this section the formation energy of the F center is referenced to the cohesive energy per MgO formula unit in accordance with the convention in these experiments. If MgO were to be described by a nearest-

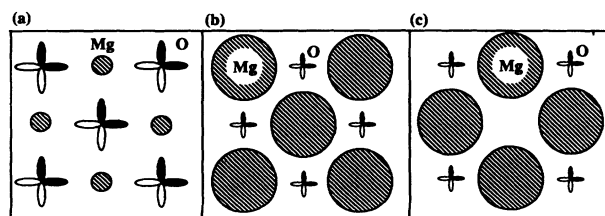


FIG. 3. Schematic representations of the electronic wave function at various energies, and in the minimum atomic basis (Mg $3s$, O $2p$), (a) Valence-band maximum in crystalline MgO, (b) Conduction-band minimum in crystalline MgO, (c) Defect wave function 1.22 eV below the conduction-band minimum at the neutral oxygen vacancy.

neighbor pair-potential model the defect formation energy would be zero. By comparison, the computed formation energy of the F center with the stationary energy functional is 1.82 eV. The implications of the experimental and computed result being larger than that obtained with the pair-potential model are discussed in Sec. IV.

When an oxygen atom is removed, a doubly occupied electronic state appears in the fundamental gap of MgO, as shown schematically in Fig. 4(a). The tightly bound O $2p$ orbitals, which were used to describe the wave function of six electrons in this region of space in the crystalline material, are no longer characteristic of occupied electronic states. The removal of a neutral oxygen atom leaves behind two of these six electrons at the defect. In order for the electrons to minimize their kinetic energy, the wave function must be nodeless at the vacancy site. Despite the addition of two energy-optimized Gaussian functions as variational degrees of freedom in our calculation, a bonding superposition of the six Mg $3s$ orbitals adjacent to the vacancy, as shown schematically in Fig. 3(c), is found to be a good approximation of the electronic wave function. The defect wave function is therefore similar to a conduction-band state, as would be expected for a defect level close to the conduction-band minimum (CBM). The defect level is not actually degenerate with the CBM, but falls 1.22 eV below the CBM in the gap [see Fig. 4(a)], because the defect wave function at the vacancy is not constrained to be orthogonal to the valence-band wave function at the site of the oxygen atom which has been removed.

The position of this defect level can explain qualitatively the formation energy of the oxygen vacancy. That is, when the vacancy is formed, two electrons are promoted from within the O $2p$ valence band to the defect level, which is 6.09 eV above the top of the valence band. For the two electrons, this 12.18-eV contribution accounts for most of the energy required to remove an O atom. There are further contributions due to the change in the shape of the local density of states of the valence-band region, and the noneigenvalue contributions to the stationary functional in Eq. (1). Klein *et al.*²⁰ performed a LDA calculation for F centers and applied the scissors operator

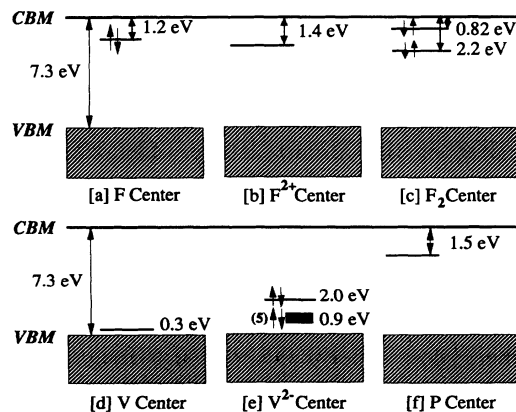


FIG. 4. Position and occupation of defect levels in the fundamental gap of MgO for some of the neutral and charge states of the defects.

to obtain the experimental band gap. They also found that the defect level is significantly above midgap for the self-consistent computation. The formation energy computed in this work, 1.82 eV, is in qualitative agreement with the value 1.53 eV determined in an additive coloring experiment.²⁴

The computed formation energies of the F^+ and F^{2+} centers in MgO are 3.67 and 5.47 eV, respectively. The F^+ and F^{2+} defects are formed by removing one and two electrons, respectively, from the highest occupied localized state of the F center. The formation energies for these defects are the computed energy differences between the charged and neutral vacancies, with the displaced electron(s) moving to a reservoir with a chemical potential μ at the bottom of the conduction band. This arbitrary choice for the chemical potential of the reservoir obtains an estimate for the minimum formation energy of the isolated defect assuming that any excited states lie close to the conduction-band minimum, and in the absence of other defects. The eigenvalue contribution to the energy functional in Eq. (1) accounts for a substantial fraction of the defect formation energy. This result is not quoted in the case of the charged defects, since it is dependent upon the choice of the reservoir's chemical potential.

The additive coloring experiments used to determine the formation energy of the F center also detected substantial concentrations of the F^+ center.^{2,24} The computed difference between the formation energies of the F and F^+ centers, 1.85 eV, is the same order of magnitude as the formation energy of the F center, 1.82 eV. In this sense our results are consistent with the experimental data. The position of the F -center defect level is found to be only weakly sensitive to the charge state of the defect. In particular, our calculations find that the defect level moves below that of the neutral vacancy by 0.13 and 0.16 eV for the F^+ and F^{2+} defects, respectively. The electronic configuration of the F^{2+} center is shown schematically in Fig. 4(b). This displacement of the defect level in the F^+ center is qualitatively consistent with the observed 5-eV peak absorption shift of 0.1 eV from the F to the F^+ centers.²⁴ A similar result has been obtained in another LDA calculation.²¹

B. F_2 centers

An F_2 center consists of two oxygen vacancies on adjacent lattice oxygen lattice sites, or second-nearest-neighbor sites of the atomic lattice. Uniaxial stress-splitting patterns of zero-phonon lines associated with a defect with the orthorhombic symmetry of the F_2 center have been observed at 3.43 and 1.18 eV. The experimental intensities of these lines were found to move in parallel under stress, leading to the suggestion of the involvement of the F_2 center.^{2,7} A feature at 3.58 eV in the electron-energy-loss experiments was also assigned to an oxygen vacancy defect aggregate on the basis of the temperature dependence of the loss measurement.²² The interaction energy, defined as the difference in energy between nearest-neighbor and isolated F centers, is -0.41 eV. A schematic representation of the electronic struc-

ture is shown in Fig. 4(c). The F -center defect level has split into bonding and antibonding superpositions of the isolated vacancy level, both of which are doubly occupied when the defect is charge neutral. In our calculations both of these lines are present when the density of states (DOS) is projected onto a Mg 3s orbital adjacent to one of the F centers, but a third-nearest neighbor of the other F center. However, the DOS projected onto a Mg 3s orbital adjacent to both vacancies does not contain any component of the higher-energy state which is spatially antisymmetric with respect to this magnesium site. The states are referred to as bonding and antibonding on the basis of these symmetries. The defect states lie 2.18 and 0.82 eV below the CBM, compared to 1.22 eV in the case of the F -center state. This splitting between levels is more complicated than the case in diatomic molecules, where the antibonding superposition of s states is moved further in energy than the bonding superposition. The result for the F_2 center depends upon an increase in the Hamiltonian matrix element of the Mg 3s orbitals adjacent to both vacancies, and the additional variational degrees of freedom afforded by the two energy optimized and spherically symmetric Gaussian orbitals used in our calculations, which are found to have a positive-energy expectation value. Both of these factors contribute to a reduction in the charge density at the center of each vacancy and in the region between the two vacancies. The energy due to a node in the wave function is significantly reduced because the charge density of the electronic state in the vicinity of the node is very small. A simple molecular model of the vacancies parametrized with matrix elements of similar magnitudes gives rise to degeneracy splitting with the character of the F_2 center.

The splitting of the level gives an approximation to the binding energy of the defects of 0.54 eV, compared with the evaluation of Eq. (1), which reduces the attraction to 0.41 eV. We do not find any direction correlation between these results and the experimental observations, other than the attractive nature of the interaction between oxygen vacancies which suggests observable concentrations of F_2 centers in the additively colored samples. The computed interaction between second-nearest-neighbor F centers, fourth-nearest neighbors on the atomic lattice, was smaller than the accuracy of the method.

C. Magnesium vacancies

The computed formation energy of the magnesium lattice vacancy, or V center, is 13.82 eV, where in this case the formation energy is defined to be the energy required to completely remove a magnesium atom from the material. It is inconvenient to define the formation energy of the V center as the energy above the cohesive energy per formula unit in MgO, as this definition would require an estimate for the spin-polarization correction to the energy of the isolated oxygen atom. Also, there is no obvious analog of the additive coloring experiment to produce these defects at temperatures below the melting point for MgO, due to the additional energy necessary to dissociate the oxygen molecule.

The electronic structure for the V center is shown schematically in Fig. 4(d), with a triply degenerate defect level containing only four electrons, and located 0.3 eV above the valence-band maximum. The triply degenerate defect level is approximately described by a nonbonding superposition of the $2p$ orbitals associated with the six oxygen atoms adjacent to the defect. The splitting of this degeneracy by a Jahn-Teller distortion is the subject of further work. The 13.82-eV defect formation energy of the V center is readily understood from a consideration of the position of this defect level in the gap. The energy required to take the two electrons from a state close in energy to the valence band of the crystal to the isolated atomic Mg $3s$ orbital energy is approximately 7.6 eV. There is a further significant contribution to the defect energy from the DOS of the oxygen $2p$ -derived valence bands projected onto the oxygen atoms adjacent to the defect. These states are pushed to higher energies in the absence of the magnesium potential. The computed formation energy suggests that the isolated V center does not occur in high concentrations in high-purity MgO below the melting point of the material.

Transferring an electron from a reservoir with a chemical potential at the conduction-band minimum into this state, and thereby forming the V^- center, is found to be an energetically unfavorable process. This is despite the fact that the electron gains almost the entire band-gap energy when it moves from the reservoir to the defect level. The essential feature is that additional electrons at the V center increases the energy of the electronic states associated with the 18 oxygen $2p$ orbitals of the six oxygen atoms adjacent to the lattice vacancy. An additional triply degenerate level moves into the gap when the defect is singly or doubly charged. The highest energy state contains five and six electrons in the V^- and V^{2-} centers, respectively. This feature is shown in Fig. 4(e) for the V^{2-} center, where the electronic states close to the bottom of the gap are fully occupied. The energy of the charge transfer becomes positive, as a result of this rearrangement of the electronic structure. The defect formation energies are tabulated in Table I. Hartree-Fock supercell calculations with a 64-atom supercell have estimated the energy of the V^{2-} center, defined as the energy to remove a magnesium ion, to be 1.54 and 1.44 hartrees before and after structural relaxation, respectively.⁴² By comparison, our calculations predict the unrelaxed energy to be 1.549 hartrees. In order to make this comparison it was necessary to evaluate, using the self-consistent density-functional algorithm, the energy of the doubly charged free magnesium ion. The dielectric screening of the electric field due to the charged defect was observed in the Hartree-Fock calculation.

The position of states in the gap being dependent on their occupation at the magnesium lattice vacancy is unlike the results for the oxygen vacancy, where the position of the defect levels was largely unaffected by the occupation. In the case of the V^- center an electron is being added to a state of valence-band character, and is therefore spatially distributed in a way which is similar to the other valence electrons in the system. By contrast, the defect level electrons at the F center are in a state of

conduction-band character, and are therefore spatially distributed differently from valence-band electrons. When electrons are removed from this state to form the positively charged oxygen vacancies, the electronic structure of the occupied valence band is affected less than when the charge is added to the V center. The position of the V -center defect level close to the valence-band maximum arises due to an unoccupied and tightly bound O $2p$ -derived state which largely feels the potential of the O atom, and does not extend significantly into the defect region. We would expect that a more ionic potential, defined here in the context of the point ion model where the oxygen atoms adjacent to the magnesium lattice vacancy are doubly negatively charged, would bring the V -center defect level even closer to the valence-band maximum. This is because the potential would be more repulsive to the additional electrons.

In real material, where there are always traces of trivalent impurity ions, combined electron-spin resonance and optical studies have inferred the presence of V and V^- centers.⁴³ The presence of V^- centers has been shown to be correlated with substantial concentrations of OH^- .^{44,45} Optical features at 2.37 and 2.33 eV have been attributed to the V and V^- centers, respectively.⁴⁶ The unoccupied V -center defect level appears within an eV of the bottom of the gap in our calculation, as shown in Fig. 4(d). On this basis we are unable to understand the origin of the 2.3-eV optical feature associated with the V center in terms of the electronic structure. Other theoretical work has also suggested that the 2.3-eV optical feature cannot be explained as a crystal-field transition, but corresponds to a polaron transition.¹⁹

D. P center

It is interesting to remark that the formation of F and V centers is controlled by the same mechanism; the F - and V -center formation energies involve a transfer of electrons from oxygen symmetry (valence band) states to magnesium symmetry (conduction band) states. This is not surprising since this bond energy is the first-order contribution to the cohesive energy in MgO. In real materials the F and V centers are not necessarily entirely isolated from each other, but may interact strongly when in close proximity. To investigate this interaction we have considered the MgO divacancy, where Mg and O are missing on adjacent sites. This defect is referred to as a P center, and the formation energy is computed to be 3.48 eV above the cohesive energy of MgO per formula unit. This corresponds to a binding energy of 12.16 eV between the neutral F and V centers, from a manipulation of the values presented in Table I. The extra electrons from the Mg-rich F -center environment are compensated for, in a P center, by the electron deficit at the oxygen-rich V center. The P center could equally be viewed as adjacent F^{2+} and V^{2-} centers. The energy gained by forming the P center from isolated F^{2+} and V^{2-} centers is 18.34 eV, which is greater than the energy gained when the P center is formed from F and V centers, due to the electrostatic attraction between defects of opposite charge. The Wigner-Seitz potential used as the input in Eq. (1), and

derived from neutral atoms, should be a good approximation because the potential in the vacancy region is closer to the limit of weakly coupled atoms than is the crystalline solid. The unoccupied defect level of the V center is approximately a nonbonding combination of O $2p$ orbitals, but the removal of the additional oxygen atom to form the P center allows the new delocalized wave function to possess more bonding character. No defect state is found close to the valence-band minimum in the P center, as shown in Fig. 4(f). An unoccupied defect level is found 1.51 eV below the conduction-band minimum at the P center. This state is analogous to the defect level in the F center, and arises from a superposition of the Mg $3s$ states in the conduction band. It falls below the conduction-band minimum, since the kinetic energy is lowered by the removal of the constraint that it be orthogonal to the occupied state at the oxygen atom.

V. DISCUSSION

Optical spectroscopy has been one of the primary experimental tools used to investigate the properties of defects in ionic material. As a result, many features have been assigned as characteristic of certain types of defect. For example, in MgO the 5-eV optical-absorption band is attributed to F and F^+ centers.²⁴ This absorption band is thought to be a threshold absorption in which electrons are promoted from the defect level, conjectured to be 5 eV below the CBM, to a state close in energy to the CBM.^{4-7,21} The observed 2.7-eV Stokes shift between the 5-eV absorption and 2.3-eV luminescence has been explained in terms of a lattice-relaxation when the electron is in the excited state. While lattice relaxation may be useful for explaining much smaller Stokes shifts of approximately 0.1 eV in less rigid materials with open structures such as GaAs or Si, it is difficult to conceive of a lattice relaxation of 2.7 eV in MgO associated with the excitation of a single electron. This is because much larger changes to the Hamiltonian than placing one electron in an excited state, such as creating a surface, are known to give rise to lattice relaxation energies per formula unit which are smaller by more than two orders of magnitude.

A model for the absorption and luminescence at the oxygen vacancy, based upon the F -center defect level lying closer to the top of the gap as computed in this work, would involve excitation of the electron into the conduction band, nonradiative decay of the electron to the CBM, and luminescence to the defect level close to the CBM in the gap. This model for the observed optical spectra does not require an anomalous lattice relaxation of 2.7 eV to explain the Stokes shift, and has been discussed by the authors in the context of surface oxygen vacancies.²³ Excitation of an electron from the F -center defect state (with s symmetry) in the gap is to a conduction-band state with p symmetry at the oxygen vacancy. The peak in the density of states projected onto a p -symmetry superposition of Mg $3s$ orbitals adjacent to the F center is approximately 4 eV above the defect level in the gap. The experimental optical absorption is close to 5 eV. It is important to emphasize that our calcula-

tions cannot be used quantitatively to predict optical transitions, but we speculate that the computed density of states distinguishes between states at the top and bottom of a 7.31-eV band gap. If the F -center defect level was positioned close to the bottom of the fundamental energy gap, it would be difficult to explain the experimentally determined formation energy of the F center. Further evidence for this picture of the optical absorption and luminescence is the observed photoelectron yield, which results from the absorption of 4-eV photons in defective samples of MgO.⁴⁷ This is inconsistent with excitations from a defect level close to the valence-band maximum, unless MgO is a negative electron affinity material.

Formation energies for the F and V centers provide a useful interpretation of the bonding in MgO. The single largest contribution to the formation energy of the F center is the energy required to remove electrons from the valence band and put them into the defect level close to the conduction-band minimum. Similarly, a substantial fraction of the formation energy of the V center is the energy required to take electrons from the crystalline valence band to the isolated atomic magnesium $3s$ energy. The formation energies for the F and V centers are both above the cohesive energy of MgO. In the limit that the crystal is destroyed by making each site a vacancy, the average energy of forming additional Mg and O vacancies must be equal to the crystalline cohesive energy per formula unit. The 12.16-eV binding energy between the F and V centers, forming the P center, is consistent with this result, as is the less significant binding energy between F centers. Hence the cohesive energy in MgO can be viewed as arising from the removal of an oxygen atom, forming an F center with a doubly occupied state at the top of the gap, followed by the removal of a neighbor magnesium atom which takes with it the electrons from the F -center defect level. In this picture the material is ionic: the Mg $3s$ electrons are donated to the O atom in the sense that the valence electronic states are O $2p$ in character. It is this aspect of the electronic structure which causes the nearest-neighbor pair-potential model to fail in predicting the formation energetics in MgO, as there is a strong asymmetry between removing oxygen and magnesium individually, compared to forming the MgO divacancy.

If there is a large concentration of P centers in a defective sample of MgO, there is the possibility of ultraviolet absorption from the valence band to the defect level at an energy close to the 5-eV absorption. In this case the transition would be from a state of p symmetry in the valence band to the state of s symmetry in the energy gap. Other workers have considered the P^- center, where an extra electron is placed in the defect level close to the conduction-band minimum.² Absorption from the valence-band maximum to the P or P^- level should, by analogy with the F center, be at approximately similar energies since the additional electron in the P^- center is in a state of conduction-band character.

Bombarding crystalline MgO with high-energy particles such as electrons, gamma rays, or neutrons gives rise to an optical-absorption spectrum in which a feature at 2.3 eV has been attributed to the magnesium vacancy, or

V center.^{19,46} Experiments have suggested that the irradiation results in a redistribution of cation vacancies in the crystal by a mechanism in which the newly created magnesium interstitials combine with the V centers in the lattice.⁴³ Furthermore the concentration of V centers has been correlated with the presence of trivalent metals and OH^- in the lattice.^{44,45} The large formation energy of the V center computed in this work is consistent with the density of these magnesium vacancies being small. Since there is no obvious analog of the additive coloring experiment to produce V centers, they are probably less abundant than the F centers. We speculate that the 2.3-eV feature may be a consequence of the gap state associated with the F center, for which luminescence is also observed at 2.3 eV.

The F center is likely to be the dominant defect in additively colored materials, where anion vacancy concentrations, determined by optical absorption, of $6 \times 10^{18} \text{ cm}^{-3}$ are obtained.² If each vacancy possessed a single charge, a cubic centimeter of isolated material would contain close to a Coulomb of net charge in the absence of defects with a compensating charge. As the density of extrinsic impurities may be much lower than $6 \times 10^{18} \text{ cm}^{-3}$ and very few V centers are to be expected in an additively colored material, the neutral F center is believed to be the dominant defect in this material. Hence the Schottky defect, consisting of isolated V^{2-} and F^{2+} vacancies, is not the prevalent defect in all samples of lattice defective MgO, as may be expected from a simple point-ion model of the material. The results of the computations in this paper suggest that charge compensation between isolated neutral anion and cation vacancies is energetically unfavorable in MgO. Hence the Schottky defect is not the ground-state defect structure of isolated Mg and O lattice vacancies, even when the lattice vacancies are present in equal concentration. This result contradicts the mechanism by which ionic conduction is believed to take place in MgO.¹⁷ That is, via migration of the V^{2-} and F^{2+} defects. Furthermore, the formation energy of the P center suggests that migrating V^{2-} and F^{2+} vacancies would prefer to associate, forming a neutral defect which cannot produce a current in the standard ionic model. The optical experiments find agreement with this result in the sense that the F^{2+} defect is extremely short lived. The luminescence is observed on a time scale much faster than that associated with the migration of an F^{2+} across a macroscopic sample. When hydrogen is present in the sample the electrons which have been photoexcited to the conduction band to form the F^{2+} center may become trapped at a defect associated with the hydrogen. The luminescence is then observed at times as large as 1 s.⁴

Structural relaxation energies in metallic, semiconducting, and some ionic insulating materials are found to be comparable in magnitude to electronic energies. The electronic energies of the vacancies in MgO are found to be so large in our calculations that, even after taking into account an upper bound for an estimate of the structural relaxation energy, the defects remain correctly described by their electronic component. For example, supercell density functional calculations for the V^{2-} center have

computed a lattice relaxation energy of -1.300 eV .¹⁶ The lattice relaxation for the neutral defect is likely to be less than for the charged system, since the nuclei do not move in attempt to screen the field. Hence the V -center formation energy of 13.82 eV is not qualitatively affected by lattice relaxation in the sense that the processes by which the defect could be created would remain unaffected if the structural relaxation reduced the formation energy to 13 eV.

The binding energy in classical ionic models is due to the Madelung energy associated with an array of point charges. However, a recent multiconfiguration interaction calculation has considered the binding energy of small molecules of MgO embedded in a point-ion medium, representing the Madelung potential of the ionic crystal.⁴⁸ The computed energies were found to be insensitive to the numerical charge of the point ions in the embedding region. This calculation elegantly demonstrates that the short-range chemical interactions are largely unaffected by the Madelung field. Despite this result, it is still possible to partition the self-consistent charge density in Fig. 1(a) such that the magnesium and oxygen lattice sites have their formal charges $+2$ and -2 , respectively. The Madelung energy associated with these charges is not small on the scale of bond energies. Similarly, however, the partitioning of space chosen for the self-consistent charge density [Fig. 1(a)] which led to the formal charges of the point ions, also provides a quantitatively very similar result for the superposition of atomic charge densities [Fig. 1(b)]. This is because the charge density of the oxygen atom is larger than that of the magnesium atom in the critical bonding region, as has been previously described.

VI. CONCLUSIONS

This paper has concentrated on explaining the properties of intrinsic lattice vacancy defects in MgO using elementary ideas in electronic structure. *Ab initio* calculations were necessary in order to compare reliably the defect energies in the various charged states. The most surprising result is the relatively large formation energies of charged defects compared with the neutral vacancies. Electron transfer between isolated F and V centers was found to be energetically unfavorable, even when the macroscopic dielectric response, which reduces the net charge at the defects, was taken into account. The reason for this is the large energy cost resulting from an additional electron in a state with O $2p$ valence-band character at the negatively magnesium lattice site vacancy.

A simple model for explaining the experimentally observed Stokes shift for electrons associated with the F center has been presented. Further work is required to determine the coupling constant between the s -symmetry defect level and the p -symmetry electronic states in the conduction band. This coupling constant is known to be large in experiments. The P center is predicted to have an unoccupied state close to the top of the fundamental gap in MgO, and we conjecture that an absorption band associated with this level may be observable. The strong

attraction between F and V centers to form a P center suggest that the defect may occur in high concentrations in real materials.

The calculations in this paper have made use of the linear scaling of a density-functional computation with the number of degrees of freedom. The mathematical basis of this scaling is that diagonal elements of the resolvent are exponentially insensitive to successively more distant environments. The recursion method is used in this work to compute the diagonal elements of the resolvent, which can be related to the difference in the eigenvalue spectrum for the defective and reference systems. The energy difference is calculated explicitly in this approach, instead of as a difference between total energies for which random errors do not cancel. The formation energies of charged defects in this paper have used an experimentally determined parameter, the electronic dielectric constant, to estimate the residual charge at the de-

fect. This is necessary with the stationary functional, because errors are first order and not second order, if the wrong number of electrons are placed at the defect. Our calculations are in quantitative agreement with the experimental formation energy of the F -center defect, and with the Hartree-Fock supercell calculation of the V^{2-} center.

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