PHYSICAL REVIEW B VOLUME 35, NUMBER 11 15 APRIL 1987-I

Theory of *F* centers in the alkaline-earth oxides MgO and CaO

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(Received 18 August 1986)

We present results of a theoretical study of the electronic structure of isolated anion vacancies (*F*-center-like defects) in the alkaline-earth oxides MgO and CaO using the multiple-scattering-theory—based muffin-tin Green's-function method. These *ab initio* calculations are valence-charge self-consistent for the vacancy and first shell of cation neighbors but, at present, do not include effects due to atomic relaxation around the vacancy site. Different charge states are explored by varying the occupation of the *s*-like bound state from two (neutral *F* center), to one (positively charged F^+ center), including results for the Hubbard Coulomb localization parameter, *U*. Various *ad hoc* "fixes" to the underestimated local-density theory valence-conduction band gap for the perfect crystal are explored, with primary emphasis given to "scissor-operator" type of band-gap widening. Calculated defect charge and state densities are compared with experiment and with other calculations. Although good qualitative, or even semiquantitative, agreement with experiment is obtained as to the nature and locations of the defect-induced ground and excited states, it is concluded that atomic relaxation effects, and extensions to further shells of neighbors, need to be included before a full evaluation of the theory can be made.

I. INTRODUCTION

In recent years there has been an increasing focus on studies of anion vacancy centers (*F*-center-like defects) in alkaline-earth oxides, such as MgO and CaO, for which we report theoretical results in this paper. A recent review of this field has been given by Henderson.[1] The increased interest is related to both the understanding gained in similar studies of simpler vacancy centers in alkali halide systems, and also to the availability of "good" oxide crystals (low impurity concentrations) for experimental studies. Interest is heightened, too, by the fact that the oxides are also highly refractory, high-melting-temperature insulators, leading to a number of important technological applications for these materials.

To study the *F*-like centers we use the muffin-tin Green's function (MTGF) method[2-5] which has been highly successful in describing the electronic structure of point defects in metals, including magnetic properties. Rocksalt (*B*1) structure ionic insulators, such as MgO and CaO, are conceptually ideal examples for extending the realm of application of the MTGF method to nonmetals since the muffin-tin approximation would not seem to be a limitation for these systems. However, there are conceptual and computational difficulties which arise due to problems in quantitatively describing excited states in bulk perfect insulators within the local-density approximation (LDA),[6] which also have an analogue in the defect calculations. We discuss these in some detail in this paper, including an exploration of several "fixes."

In the alkaline-earth oxides, the oxygen atoms reside, to a good approximation, in an O^{2-} state (see below) which, although unstable as a free ion, is stabilized by the crystal field in these systems. Therefore, the charge-neutral *F* center attracts two electrons forming, in zeroth order, a helium-like system, while a one-electron F^+ center is intrinsically a singly (positive) charged state. Both of these *F*-center-like defects are explored, theoretically, in this paper for MgO and CaO.

In Sec. II we give a brief description of the MTGF method used in this work, and the underlying augmented-plane-wave (APW) band-structure techniques used to construct the host electronic structures. In Sec. III we discuss our band-structure results for MgO and CaO, compare them with previous work and experiment, and discuss the band-gap "problem," viz., the fact that LDA-based calculations underestimate the gap by approximately 50% for these materials. We discuss ways we have attempted to "fix" the host band gaps either before implementing, or in conjunction with the defect calculation. In Sec. IV we present our theoretical *F*- and F^+-center results including densities of states, charge densities and Hubbard *U* localization parameters. We also compare our work with previous theoretical studies. In Sec. V we enumerate some of the conclusions which follow from this work.

II. METHOD OF CALCULATION

In this section we describe the muffin-tin Green's function and APW band-structure methods that we have used in our *F*-center calculations. Since recent detailed expositions of the former are in the literature,[2-5] we will be content with giving an outline of the techniques that we use. The interested reader can also find a full description of the APW method in Ref. 7.

A. The muffin-tin Green's-function method

Let G be the Green's function operator for the system with the defect having the Hamiltonian H, with E the energy. G^0 is the equivalent operator for the perfect crystal system which has the Hamiltonian H^0. The Green's functions are given by

$$G=\{E-H\}^{-1} \tag{1}$$

and

$$G^0=\{E-H^0\}^{-1} \ . \tag{2}$$

If $H=H^0+\Delta v$, where Δv is the change in potential due to the defect, we can form the Dyson equation,

$$G=G^0+G^0\,\Delta v\,G \ , \tag{3}$$

which gives a formal solution for the defect system in terms of the host perfect crystal Green's function and the change in potential due to the defect. In an **r**-space muffin-tin representation, both G and G^0 satisfy a single-particle Schrödinger equation, and they can be expanded in terms of muffin-tin eigenfunctions as

$$G(\mathbf{r}+\mathbf{R}^n,\mathbf{r}'+\mathbf{R}^{n'};E)=G_s(\mathbf{r}+\mathbf{R}^n,\mathbf{r}'+\mathbf{R}^{n'};E)\delta_{nn'}+\sum_{L,L'}Y_L(\hat{r})R_l^n(r,E)G_{LL'}^{nn'}(E)R_{l'}^{n'}(r';E)Y_{L'}(\hat{r}\,') \ . \tag{4}$$

Here, $L=(l,m)$ are angular momentum indices, Y_L are spherical harmonics, and $R(r,E)$ are the regular solutions of the radial Schrödinger equation for the spherical (muffin-tin) potential $v_n(r)$. G_s is the Green's function for a single, isolated muffin-tin potential in free space. The structural Green's function $G_{LL'}^{nn'}$ describes multiple scattering between the muffin tins, and it can be related to its counterpart for the host system by the following analog to Eq. (3),

$$G_{LL'}^{nn'}(E)=G_{LL'}^{0nn'}(E)+\sum_{n'',L''}G_{LL''}^{0nn''}(E)\Delta t_l^{n''}(E)G_{L''L'}^{n''n'}(E) \ . \tag{5}$$

In Eq. (5), $\Delta t_l^n=t_l^n-t_l^{0n}$ is the difference between the t matrices for the defect and host-system muffin tin n. At every stage in the iteration procedure for the defect-system Green's functions, Eq. (5) can be used to determine the coefficients $G_{LL'}^{nn'}$ in terms of host quantities $G_{LL'}^{0nn'}$ and Δt. We come back to discuss this below.

Now consider a spectral representation for the Green's function, either the host perfect lattice or the defect system, which can be written in terms of the full eigenfunctions (ψ) and eigenvalues (E_i) of the system,

$$G(\mathbf{r},\mathbf{r}';z)=\sum_i\frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')}{z-E_i} \ , \tag{6}$$

where $z=E+i\epsilon$, with ϵ a positive infinitesimal. From this form for G, one can show that the charge density, $n(\mathbf{r})$, and the density of electronic states, $N(E)$, are given by,

$$N(E)=-\frac{1}{\pi}\int_\Omega d\mathbf{r}\,\mathrm{Im}G(\mathbf{r},\mathbf{r};E) \ , \tag{7}$$

$$n(\mathbf{r})=-\frac{1}{\pi}\int_{-\infty}^{E_F}dE\,\mathrm{Im}G(\mathbf{r},\mathbf{r};E) \ , \tag{8}$$

where Ω is the volume of the unit cell [site and angular-momentum decomposed densities of states are defined similar to Eq. (7)]. In particular, using Eqs. (4) and (6) it can be shown that the imaginary part of the host structural Green's function G^0 can be determined in terms of the wave-function coefficients for the perfect crystal found from an APW or Korringa-Kohn-Rostoker (KKR) band-structure calculations. As shown in Refs. 2–5, the real part of G^0 can be determined by a Kramers-Kronig transformation which, although having the disadvantage of requiring the calculation of band-structure quantities for host for states well above the Fermi level, avoids the calculation of a direct integral form for ReG^0 which presents numerical difficulties. The form of the charge density given in Eq. (8) allows the calculation of the various defect-system potentials needed in each stage of the self-consistent iteration process.

Although, as discussed below, all of the electronic states for perfect-crystal MgO and CaO are calculated self-consistently, we have made the simplifying approximation of freezing all of the electronic states below the highest occupied valence bands (O $2p$ states) in our defect calculations. This frozen-core approximation will be removed in our future work, but we do not believe this to have a significant quantitative effect on the results presented here. The Hedin-Lundqvist[8] form of the local-density approximation (LDA) for exchange and correlation was used throughout.

All of our defect calculations were non-spin-polarized so that defect-related multiplet splittings, observed experimentally, are not available. The lack of spin polarization may introduce some additional errors, especially in our F^+-center calculations where there is an occupied unpaired electron spin. We hope to address spin-polarization effects in our future work where we will also attempt to remove some of the other approximations that we have made (see below).

Equation (5) is a matrix equation for the $G_{LL'}^{nn'}(E)$ coefficients having both angular momentum and site indices. In the present calculations, the potentials on the vacancy (anion) site, and on the first shell of Mg or Ca neighbors are allowed to respond self-consistently to the vacancy, and angular momenta for s, p, and d components are included. Since experience with this method for metallic systems has shown that including the central defect site plus one shell of neighbors is adequate for an accurate description of defect properties,[4] we have tried the same approach for the F-center studies in this paper. Although the work reported here shows this to be a reasonable approximation, it may be necessary to relax this restriction in future studies in order to obtain more accurate quantitative results. Using the above, it is seen that Eq. (5) becomes a 63×63 matrix which is reduced to a set of smaller matrices by making use of the fact that the vacancy defect is at a site of cubic symmetry. The use of symmetry, as well as the technique of complex energy integration,[5] results in an enormous saving of computer time. We have used 32 complex energies for the self-consistent iterations, and 180 complex energy points along a linear path very close to ($\mathrm{Im}z \simeq 0.5$ mRy), but above the real axis for the final-charge-density and density-of-states calculations using the self-consistent (SC) potentials. Determining the host Green's function quantities from the band-structure results takes several minutes of central processing unit time on the U.S. Naval Research Laboratory (NRL) Cray Research X-MP computer. The full SC defect calculation also takes several minutes in total. The major consumption of computer time is the APW band-structure calculation which uses approximately 15 s of Cray time per **k** point. However, it should be noted that in this method the host energy bands need only be calculated once, and that a whole range of defect calculations may then be done.

Finally, we note that the defect calculations are performed for Wigner-Seitz spheres, having radii R_{WS}, which fill the volume of the unit cell. The values of R_{WS}, shown in Table I, were determined by scaling from the muffin-tin volumes, and the appropriate host potentials were extended to R_{WS}, linearly.

B. APW band-structure approach

The muffin-tin version of the APW method,[7] without interstitial or nonspherical corrections, was used. The relevant structural parameters are given in Table I. The core state [He] for O, [Ne] for Mg, and [Ar] for Ca, were treated in the soft-core approximation, whereby their charge densities were recalculated in each SC iteration with the ambient crystal potential. The remaining states were treated as bands. Relativistic effects, except for spin-orbit interactions were included self-consistently.[9] The Hedin-Lundqvist form[8] of the LDA for exchange and correlation was used in all of the SC band-structure calculations. Energies and wave functions needed for the determination of G^0 were obtained for energies up to approximately 20 eV above the top of the valence bands in order to determine the Kramers-Kronig transform for $\mathrm{Re}G^0$. These were calculated on a fine mesh of 324 points in the Brillouin zone for all calculations except for the shifted potential results, discussed below, which were calculated on a 68-point mesh. We believe the resultant host Green's functions are well converged in all cases, since we are not dealing with energy regions where there is fine structure (e.g., narrow bands) in the densities of states.

TABLE I. Lattice constants a, muffin-tin radii R_{MT}, and Wigner-Seitz radii R_{WS}, used in the present calculations.

Structural parameters	MgO (a.u.)	CaO (a.u.)
a	7.958	9.090
R_{MT}(Mg,Ca)	2.170	2.455
R_{MT}(O)	1.800	2.090
R_{WS}(Mg,Ca)	2.670	3.027
R_{WS}(O)	2.215	2.576

III. HOST-CRYSTAL BAND STRUCTURE

In this section we discuss the results of the energy band structures of MgO and CaO, of interest in their own right, and how they impact the defect calculations. In particular, we discuss three ways we have attempted to include corrections to go beyond the ground-state description of LDA in doing these *F*-center calculations. These "improvements" may have more general applicability beyond the specific impurity calculations considered here. We first discuss features of our band-structure results and how they compare with previous work.

A. Present band-structure results

In forming the crystal, the two outer-shell *s* electrons of the alkaline earth are transferred to O, filling its *p* shell, resulting in a sixfold occupied upper valence band of nearly pure O 2*p* character. The resultant crystal electronic structure is closed-shell-like, ionic in nature, with nearly spherically symmetric charge densities and potentials. The approximate charge states of the ions are $\mathrm{Mg(Ca)}^{2+}$ and O^{2-}, so that an oxygen vacancy is inherently doubly positively charged, and the neutral defect system (*F* center) has two trapped electrons (an analogy with a helium-like atom is often made).

Figure 1 shows the upper valence and lower conduction energy bands for MgO and CaO. The occupied valence-band widths, predominantly of O 2*p* character, were found to be 4.48 and 2.70 eV for MgO and CaO, respectively. For MgO the lowest band gap is direct at the zone center Γ and has the value 4.65 eV; while for CaO the lowest calculated gap is 3.48 eV and is indirect from Γ in the valence band to the X point in the conduction band. For MgO the lowest conduction bands are predominantly of Mg *s* character, while for CaO fairly diffuse Ca *d* states dominate. While excitonic effects, for instance, or in the case of CaO the fact that theory predicts an indirect gap, makes a precise experimental determination of the band gaps difficult, good experimental estimates are 7.8 (Ref. 10) and 7.0 eV (Ref. 11) for MgO and CaO, respectively. It is seen that the LDA-based band-structure approach significantly underestimates the band gap in both cases, a result which has been found to be typical for semiconductors and insulators—LDA eigenvalues do not give a proper description of excited-state properties, and indeed the theoretical formalism is not designed to do so.[6] This latter failure extends to other comparisons of one-electron eigenvalues with experiment as well, viz., our theoretical valence-band widths are too small, and the relative locations of the narrow semicore bands (not shown in Fig. 1) below the valence bands deviate significantly from experiment.[12]

This brings up the question of whether uncorrected LDA, or "fixes" which we discuss below, can give a proper description of defects in insulators such as the *F*-center problem we are investigating. This problem forms one of the central themes of this paper. While in the future rigorous methods for going beyond LDA will be developed and applied to defect problems, as they are being implemented for perfect-crystal theory, at the present time these are not available for studying defects. In addi-

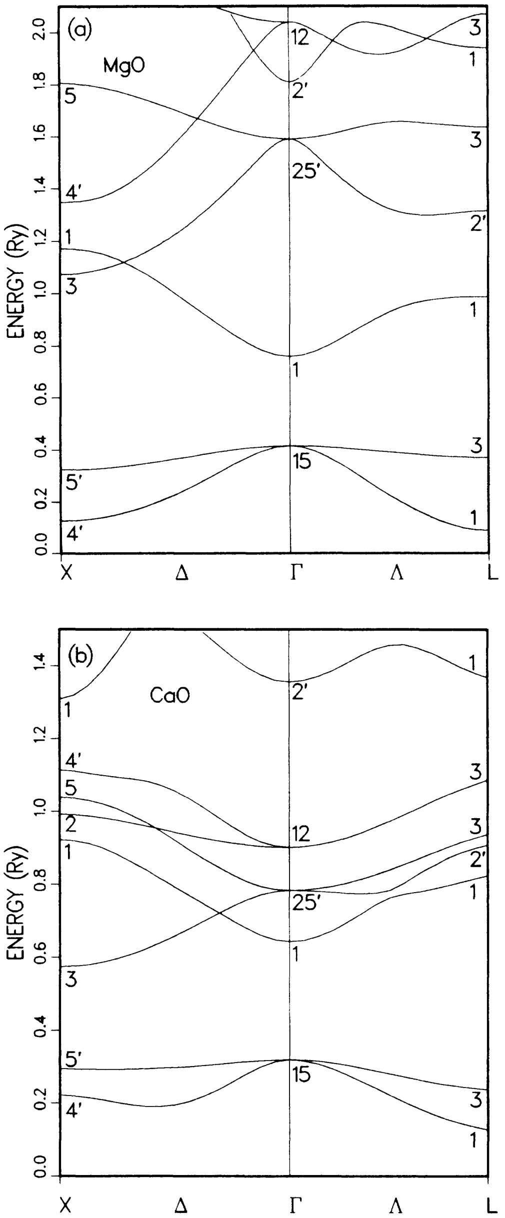

FIG. 1. Energy bands of rocksalt structure (a) MgO and (b) CaO, along the $\Gamma(000)$-$X(200)$, and Γ-$L(111)$ directions, in units of π/lattice constant. The top of the occupied valence bands are at the Γ_{15} state in both cases.

tion, these rigorous approaches will likely be quite cumbersome for some time, so that simpler, more viable approaches would be very valuable in the interim for interpreting experimental results as well as for providing insight into the "band-gap problem."

B. *Ad hoc* corrections to the band gaps

In this paper we will explore three different ways of "improving" upon LDA in a defect calculation. These are the following:

(1) Using the "scissor operator" on the host band structure,[13] which corresponds to uniformly shifting the conduction-band energies but leaving the wave functions unchanged, so that the experimental band gap is obtained. In this procedure, the host Green's function is calculated from these scissored bands and the defect calculation proceeds using the SC-LDA defect procedures discussed above. This "fix" does not make use of any defect-related properties, is easy to implement and, as we shall see, gives improved results for some aspects of the defect calculations. However, in this approach there is no attempt to correct the host wave functions, they simply remain tagged with the shifted energies.

(2) Using a self-energy based picture, where the LDA is used to calculate the density and potential (ground-state characteristics) of the defect, followed by the calculation of the final spectrum with the scissored Green's function, thereby mimicking dynamic self-energy corrections to the LDA eigenvalues. Although this has the appeal that an attempt is made to include corrections to the LDA in both the host and defect properties directly, it has the feature that the final set of defect wave functions are not consistent with the defect potential. This, too, gives improved results regarding agreement with the impurity gap-state locations, but the reliability of the defect wave functions is somewhat more questionable than in (1).

(3) Using a "shifted" host potential, whereby we uniformly shift the O and Mg(Ca) host potentials, analogously to a self-interaction correction, to give the correct host-system band gap. This has the advantage that the host potential is consistent with the host band structure, but suffers the drawback that the host band structure is not charge-density self-consistent. In addition, as might be expected, this procedure pays a penalty in that the resultant host valence bands narrow by several eV, in even worse agreement with experiment than the straight LDA results. In addition, we have found that defect results, such as the potentials and charge densities, using the shifted potential method differ qualitatively from those using the other methods, leading us to have less confidence in this approach. At present, comparisons to experiment tend to favor scissor-type methods for improving upon LDA.

C. Comparison with other band-structure calculations

There have been a number of electronic structure studies of MgO and CaO using a wide range of techniques. A good source of references may be found in the recent papers of Chang and Cohen,[14] Taurian *et al.*,[15] and Bukowinski[16] for MgO; and by Bukowinski[17] for CaO. The literature for CaO is much more limited than for MgO. The above-mentioned works are all parameter-free calculations using either the self-consistent pseudopotential, APW, or the linear muffin-tin-orbital (LMTO) methods. As expected, there is good agreement with the results presented here, for the valence-band widths and energy gaps in particular, with the exception of the gap results of Taurian *et al.*,[15] who find a direct gap for MgO of 6.06 eV in significant disagreement with the other works. One might think that this is due to the inclusion (in some sense) of interstitial corrections to the muffin-tin approximations in the LMTO calculations, but this is contradicted by two pieces of evidence: the calculation of Chang and Cohen involves a general form for the potential (no muffin tins) and their gap agrees with ours and, in addition, unpublished calculations by Feldman *et al.*[18] at the Naval Research Laboratory using the full-potential linearized APW (LAPW) method for MgO also gives good agreement with our APW results to within a 0.1 eV or better. In any case, one would expect non-muffin-tin corrections to be small for these closed-shell-like systems. We refer the interested readers to the above papers for a more thorough discussion of the electronic structure and bonding in these systems.

IV. RESULTS AND DISCUSSION

In this section we present our results for the F and F^+ centers, including the densities of states and charge densities, and their interpretations. We focus particularly on the new defect bound states and resonances induced by the oxygen vacancy, how their characteristics vary with the *ad hoc* host band-gap corrections discussed in Sec. III B, and the localized nature of these states including an estimate of the Hubbard U parameter which will be useful in various model Hamiltonian calculations of the dynamics of F-center—like defects and their interaction with the host lattice.

A. F-center densities of states

Figure 2 shows self-consistent density-of-states results for the F center in MgO obtained using the uncorrected LDA band structure. They are total density of states, $N(E)$, for the oxygen vacancy site, the s, p, and d decompositions for the vacancy, and the total $N(E)$ for the first shell of magnesium neighbors. Figure 3 shows the equivalent results for CaO. It should be noted, as discussed in Sec. II, that all of the density-of-states calculations were determined for energies with a small ($\simeq$0.5 mRy) finite complex part for numerical and visual convenience, so that the $N(E)$ are slightly "broadened." Figures 4 and 5 show, schematically, the other results for MgO and CaO F centers obtained using the *ad hoc* corrections to LDA discussed in Sec. III B.

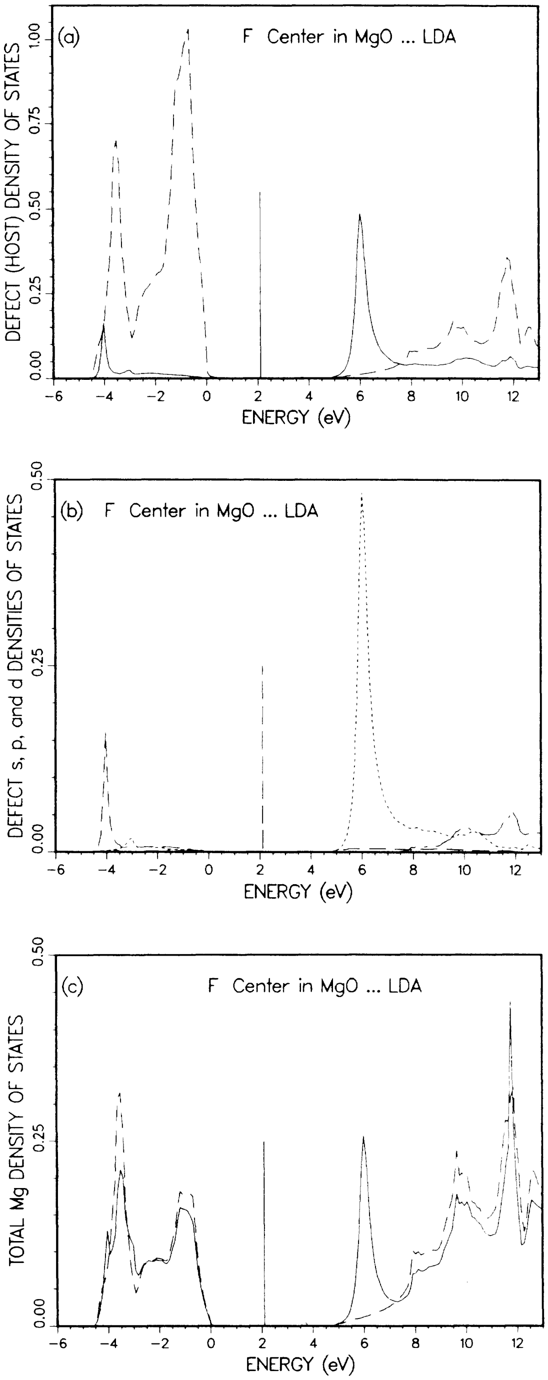

FIG. 2. Densities of states (arbitrary units) for LDA F-center calculations for MgO. (a) Vacancy-site total (solid line) and host O-site total (dashed line). (b) Vacancy s like (dashed line), vacancy p like (dotted line), and vacancy d like (dashed-dotted line). (c) Mg-site total (solid line) and host Mg site (dashed line). The top of the valence bands is at 0.0 eV.

In all of the calculations shown in Figs. 2—5, there is a bound state in the energy gap of the host, having pure s-like character on the F-center site which, by construction, contains two electrons. Table II shows the locations of these gap bound states for the different F-center calculations. The spatial nature of this state will be discussed below. The density of states in the valence-band region is generally very small except for a small resonancelike peak that shows up at the bottom of the MgO valence bands. The integrated strength of this peak is small, however. All of the calculations show a resonancelike peak, of p-like character on the F-center site, in the conduction-band region as seen in Figs. 2 and 3. For the scissor or shifted potential calculations this resonance becomes sharper compared to the LDA results and occurs close to, but above, the conduction-band edge, not quite splitting off as a bound state into the gap. This p resonance is somewhat less narrow for the shifted potential results than for the scissor calculations. For MgO, there is almost no other angular momentum contributions for several eV above the conduction band edge, while for CaO there is a significant

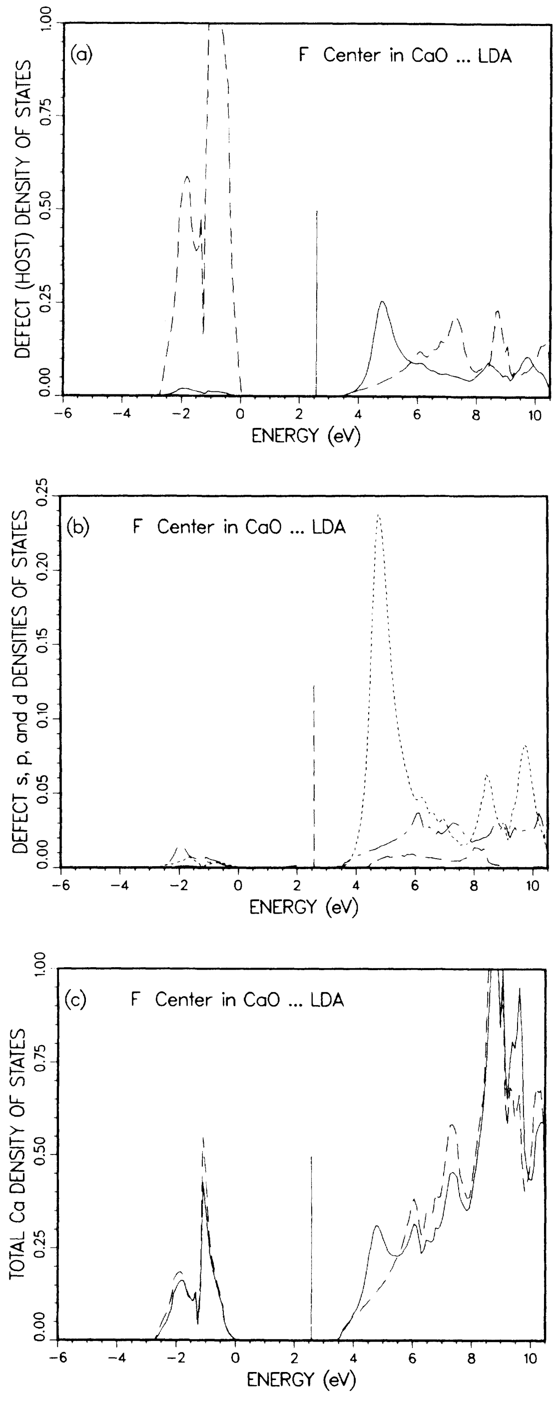

FIG. 3. Densities of states (arbitrary units) for LDA *F*-center calculations for CaO. (a) Vacancy-site total (solid line) and host O-site total (dashed line). (b) Vacancy *s* like (dashed line), vacancy *p* like (dotted line), and vacancy *d* like (dashed-dotted line). (c) Ca-site total (solid line) and host Ca site (dashed line). The top of the valence bands is at 0.0 eV.

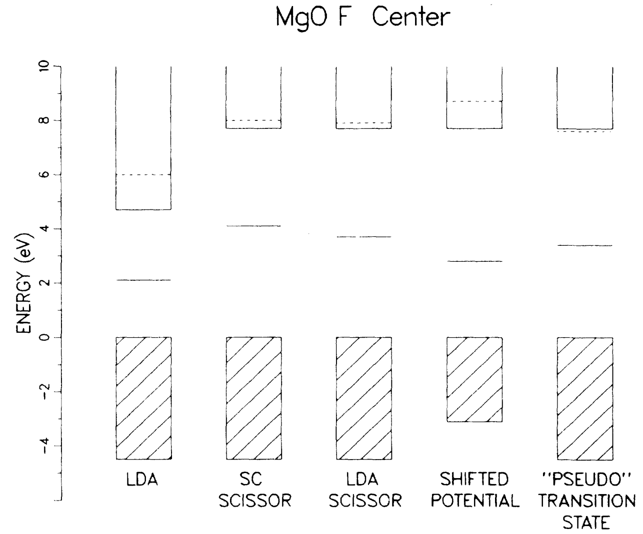

FIG. 4. Schematic diagram showing the locations of the occupied *s*-like bound state in the energy gap (solid line), and the *p*-like resonance or bound state (dotted line) near the conduction-band edge for the different calculations (described in the text) for MgO. The top of the valence bands is at 0.0 eV.

d-like component related to overlap of the Ca *d* states into the O vacancy site (see below). Also noteworthy is the fact that the SC and LDA scissor results are nearly identical except for modest shifts in the gap bound-state locations for the two calculations, leading to some confidence in the use of scissorlike gap-fixing procedures.

In examining the gap-state locations shown in Table II, the reader should take note that we present the values of the separations between the location of the δ function in the gap and the peak of the *p*-like resonance in the conduction band (or, for the "pseudo"-transition-state and

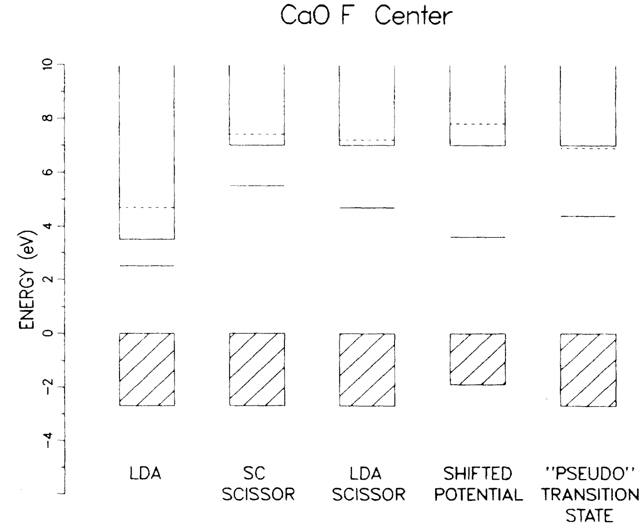

FIG. 5. Schematic diagram showing the locations of the occupied *s*-like bound state in the energy gap (solid line), and the *p*-like resonance or bound state (dotted line) near the conduction-band edge for the different calculations (described in the text) for CaO. The top of the valence bands is at 0.0 eV.

TABLE II. Locations of the F- and F^+-center s-like gap bound-state eigenvalues Δ_1, *below* the conduction-band edge; and separation of the s-like gap bound state and the p-like resonance or gap bound state Δ_2. The absolute values of the energies are shown for the various calculations as described in the text. The experimental absorption energies are also presented. All entries are in eV. Notation: SCS is the self-consistent scissor and PTS the "pseudo"-transition-state.

		MgO		CaO	
	Method	Δ_1 (eV)	Δ_2 (eV)	Δ_1 (eV)	Δ_2 (eV)
F center	LDA	2.55	3.90	0.89	2.17
	SCS	3.60	3.90	1.54	1.91
	LDA scissor	3.94	4.14	2.30	2.50
	LDA PTS	3.00	4.14	1.51	2.46
	SCS PTS	4.30	4.15	2.57	2.47
	Shifted potential	5.00	5.80	3.43	4.20
	Experimental absorption peak	5.01[a]		3.10[b]	
F^+ center	LDA	3.43	4.45	2.23	2.87
	SCS	5.04	4.66	3.85	3.20
	Experimental absorption peak	4.95[c]		3.65[d]	

[a] Reference 19.
[b] Reference 21.
[c] Reference 20.
[d] Reference 22.

F^+-center calculations discussed below, the p gap bound state), and also the absolute location of the gap state with respect to the conduction-band edge. The former values would correspond to peaks in the optical absorption in these materials, whereby an electron from the s gap state is raised to the first "excited" p-like level. This interpretation, based on considerations of associating excitation energies with dipole matrix element allowed transitions in the defect system, is discussed more fully in Sec. IV G. Although LDA-determined excitation energies are known to be quantitatively inaccurate for perfect crystals, leading to a large underestimate of the experimental band gaps, for instance, we see from the comparison with experiment[19–22] shown in Table II that the errors for the calculated defect excitation energies, as we have defined them, are percentage-wise, significantly smaller than the errors for the energy gaps of MgO and CaO; approximately a factor of 2 better. It appears from Table II that although the s-like gap bound state shifts to deeper energies for the scissor-type calculations, there is a kind of "conservation" of excitation energy, in that the location of the higher-lying p-like resonance also is lowered in energy. We also note that the shifted potential excitation energy results are much larger than the LDA or scissor results, a qualitative difference, adding additional weight to our lack of enthusiasm for this approach especially when taken together with the unrealistic change in the host valence-band widths discussed in Sec. III A. There remains the important question of the effect of atomic relaxation on the simple theoretical picture of optical absorption, neglected in the present calculations, which we will discuss in Sec. IV.

The effects of the F center on the first shell of Mg or Ca neighbors can be seen in Figs. 2 and 3. Although the changes from the host density of states are smaller than for the F-center site, the nature of the density of states changes are revealing. For the Mg neighbors there are contributions to both the gap and conduction-band-edge states which come at the expense of a diminution of higher conduction-band states of s, p, and d character, more or less uniformly, and some small changes in the already small Mg valence band states. There is a qualitative difference for the Ca neighbors where the major change is in the Ca d states which decrease to give a large contribution to the p-like F-center resonance at the conduction-band edge. These Ca d states can, as viewed from the anion site, give either s, p, or d contributions; these contribute significantly to the p-like resonance for the F center in CaO (see Ref. 23 for a discussion of the mathematics of d overlap in the rocksalt structure).

B. "Pseudo"-transition-state density of states

In a transition-state calculation one approximates the excitation process by a theoretical construct which is strongly motivated by Hartree-Fock theory for which there is an exact relationship between removal energies and one-electron eigenvalues (Koopmans' theorem), and some exact results from density functional theory. For localized states, such as in atoms or for electronic bound states which arise in defect calculations, the prescription is to do a self-consistent calculation with half of the excited electron in its ground-state level, and the other half in the excited state. The difference in eigenvalues of the partially filled levels usually gives a better description of the excitation energy than using the difference in LDA eigenvalues, which do not have any formal justification as excitation energies. We have attempted to do such calculations in the LDA and SC scissor modes, and the results are shown in Table II and Figs. 4 and 5 (for the SC scissor) for MgO and CaO, respectively. Although the excited p-like resonance did "try" to become a bound state just below the conduction band edge, it was impossible to stabilize this state with $\frac{1}{2}$ electrons, as during the course of self-consistency this bound state or resonance shifted in and out of the bottom of the conduction band, even with very small mixing of old and new charge density components. Therefore, the results presented in Figs. 4 and 5 and Table II are labeled "pseudo"-transition-state calculations because they correspond to SC results with 1.5 electrons in the occupied s bound state, as required, but 0.0 electrons in the p bound-state or resonance just at the gap upper edge. In some sense the "pseudo"-transition-state calculation is an improved description of the excitation process as it further increases the excitation energy, moving it closer to experiment, and moves the excited state down, very close to the conduction-band edge. However, the latter effect makes it practically impossible to stabilize a transition-state calculation in these systems due to numerical difficulties. We also point out, and discuss more fully below, that since the excited p bound state or resonance is diffuse when compared with the s bound state, the SC calculation is fairly insensitive to the occupancy of the former, with a bound-state energy uncertainty of 0.1—0.2 eV, at most.

C. F^+-center density of states

Figures 6 and 7 show the defect-site densities of states for LDA and SC scissor calculations of an F^+ center in MgO and CaO, with the s bound-state locations shown in Table II. There is a qualitative difference between the LDA and SC scissor results in that the s bound state moves further down into the gap and, in addition, there is a p bound state just below the conduction band edge for the latter, both aspects in better agreement with experiment. In these regards the SC scissor results are an improvement over the LDA calculations. Referring now to the SC scissor results, we find for CaO, an increase in separation between the ground state and the first excited p-like states compared to the F-center calculation in agreement with the experimental trend,[21,22] while for MgO this is not the case. Experimental results[19,20] for MgO show that the F and F^+ centers have approximately the same absorption energies, 5.0 eV, while the SC scissor calculations show an increase of nearly 0.7 eV for the F^+ center compared to the F center, although both results are somewhat smaller than experiment. Since atomic relaxation effects, and polarization of the host electrons beyond the first shell are neglected in all of our calculations, it is difficult to pin down the exact cause of this discrepancy, but one would expect both relaxation and polarization effects to be quantitatively different for the neutral F center and charged F^+ center situations and, of course, more rigorous corrections to LDA still lurk in the background. Given the fully first-principles nature of our defect calculations, the semiquantitative agreement with experiment in all cases is gratifying.

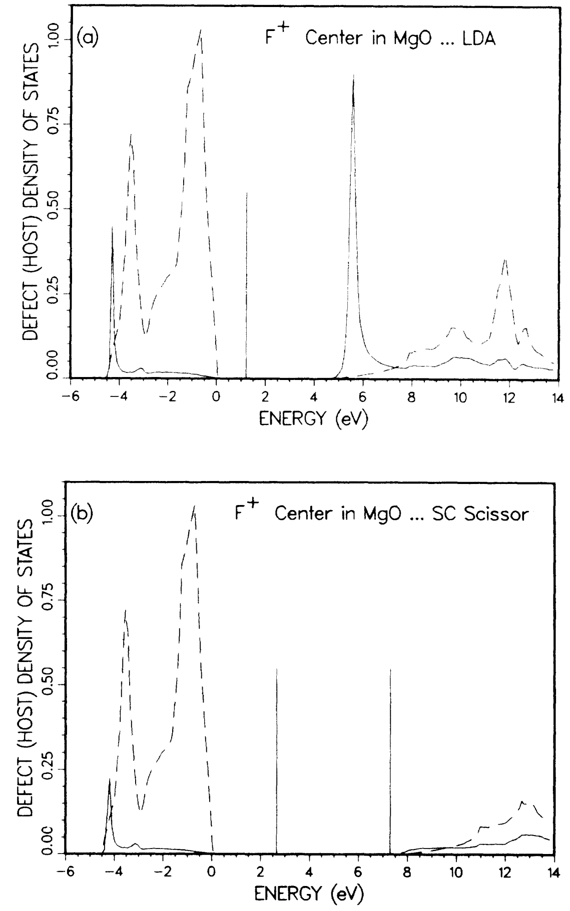

FIG. 6. Vacancy-site (solid line) and host O-site (dashed line) densities of states (arbitrary units) for an F^+ center in MgO: (a) LDA calculation and (b) SC scissor calculation.

D. Charge densities and potentials

The vacancy-site spherical charge densities, $n(r)$, are shown in Fig. 8 for several of the different F- and F^+-center calculations. In Fig. 9 we show the contributions to $n(r)$ for the occupied gap s state, and the unoccupied p-like bound state $n(r)$ for the F^+ center, both determined from the SC scissor calculation.

In Table III we present results for the vacancy-site and first-shell charges, Q_i, defined as the volume integral of the charge density of site i out to the Wigner-Seitz radius. In Table IV we give results of SC scissor calculations for the charges of the occupied F center s-like bound state and the unoccupied F^+ center p-like excited bound state, defined as above, but with only the bound-state contribution to the charge density included in the volume integration. Table V shows results of the charge neutrality of the defect cluster considered, comparing the defect- and host-system cluster charges.

From Fig. 8 and Table III, and the appropriate F-center density-of-states plots, it is seen that the charge densities and Q_i correlate with the locations of the occupied s bound state, viz., the deeper-lying bound states have larger, somewhat more localized charge densities. It is

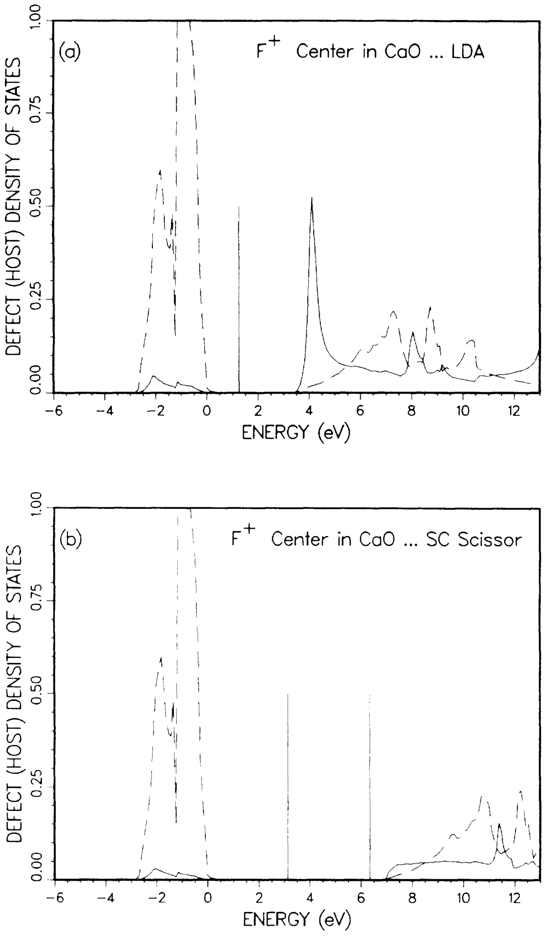

FIG. 7. Vacancy-site (solid line) and host O-site (dashed line) densities of states (arbitrary units) for an F^+ center in CaO: (a) LDA calculation and (b) SC scissor calculation.

also seen from Tables III and IV that the increase in the vacancy-site charges for the SC scissor and shifted potential F-center calculations, compared with the LDA results, come largely at the expense of charge on the neighboring shell of Mg or Ca atoms so that the net cluster charges are quantitatively similar (see Table V). The spatial form of the s-like bound-state charge density shown in Fig. 9 can also be seen to be very similar to the total defect charge density shown in Fig. 8. The differences between the total vacancy-site charge density and Q_{vac}, and the bound-state contributions, can be accounted for by noticing that there is a small amount of vacancy-site charge in the valence-band region.

Examining Table IV, it is clear that the occupied s bound-state charge is well localized in the defect cluster, especially so for CaO, in agreement with the previous results of Wilson and Wood.[24] They found that the s-like bound state contained nearly two full electrons for both CaO and MgO within the nearest *two* shells of neighbors to the vacancy site. More recent theoretical results for MgO reported by Summers *et al.*,[25] maintain this conclusion. Our results, for the vacancy site plus *first* shell of neighbors are similar, and also show that the bound states for CaO are significantly more localized than for MgO. We note that our results for the bound state $n(r)$ and Q were determined by using the SC potentials and choosing an energy integration contour encircling just the respective bound states. From Fig. 9 and Table IV, it is apparent that the unoccupied p bound state is significantly more diffuse compared to the s bound state, as was also

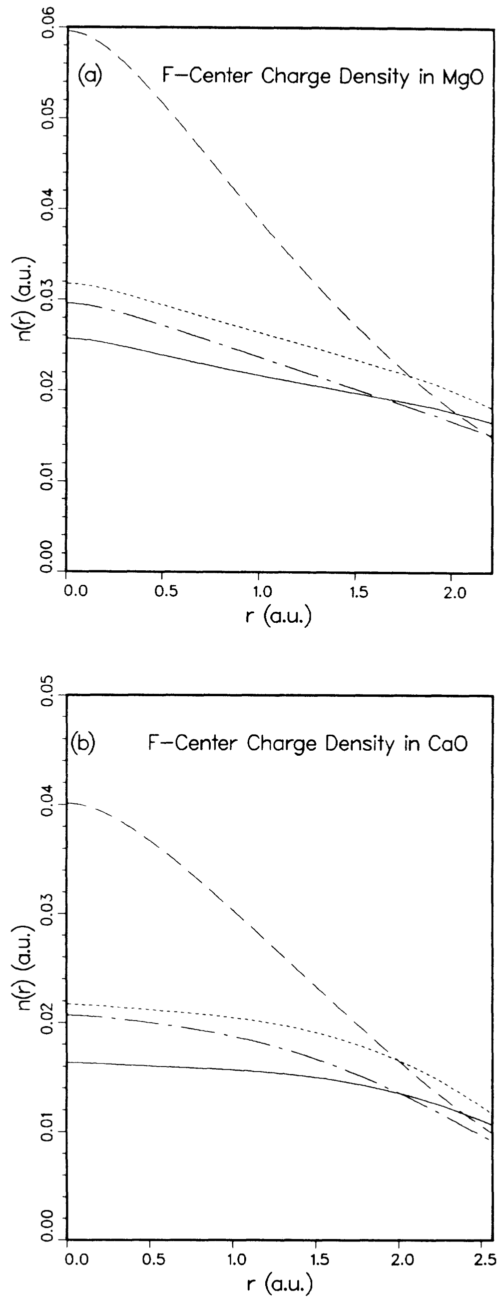

FIG. 8. Vacancy-site charge densities, $n(r)$, for F-center calculations in (a) MgO and (b) CaO. LDA (solid line), SC scissor (dotted line), shifted potential (dashed line), and "pseudo"-transition-state calculations (dashed-dotted line).

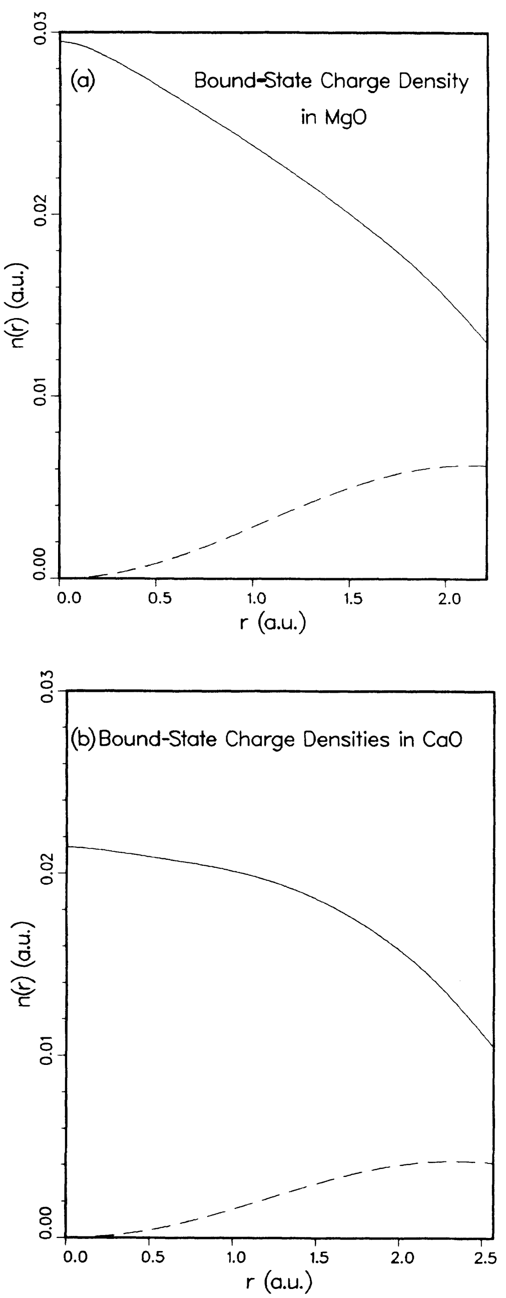

FIG. 9. Vacancy-site s (solid line) and p (dashed line) bound-state charge densities, $n(r)$, for (a) MgO and (b) CaO. The s-like and p-like results are from SC scissor F- and F^+-center calculations, respectively, as described in the text.

found by Wilson and Wood.[24] Since these states are unoccupied, their diffuse nature may not have an adverse effect on the cluster convergence.

The most reliable way to determine if an MTGF defect calculation is converged with respect to cluster size is to increase the size of the cluster and check for sensitivity of the calculated results. Although computational complications have prevented us from doing this, there is a large body of evidence for metallic systems based on the present methods that defect clusters such as we have used are adequate to obtain reliable results for charge-neutral defects; indeed simple central-site calculations are usually quantitatively adequate,[4] contrary to intuitive expectations. However, preliminary single-site calculations for the F center in MgO, using an approach discussed by two of us,[26] gave an s-like bound state just below the conduction-band edge in serious disagreement with experiment and the present results. Therefore, although the present work using a defect cluster with the first shell of neighbors represents a considerable improvement over the single-site results, further studies of more extended defect clusters will be necessary to be assured of adequate convergence.

An alternative indication of cluster-size adequacy can be obtained by comparing the charges in the host and defect clusters as we have done in Table V. These results show that our F-center calculations are relatively charge neutral to within approximately $0.1e$, where e is the electron charge, having this amount of *excess* electronic charge. The F^+-center results are also close to local charge neutrality with an approximate *deficit* of $0.25e$ electrons compared to the host cluster, even though it is intrinsically non-charge-neutral by one electron. Other workers have also found that charged defects tend to be closer to neutrality than initially anticipated.[27] This is, apparently, caused by the F^+-center site "pulling in" additional charge from the neighboring shell and beyond. This leads us to have some confidence in the F^+-center calculation, even though it is not a charge-neutral defect, although these results are on the least firm ground. It is also seen from Table V that the first-neighbor charges (Mg or Ca shell) for the defect calculations are very close to the values for the host cluster, further reinforcing our conclusions as to reasonable convergence, especially so for the F center. This comparison for the F^+ center shows still small, but significantly bigger, changes as compared with the F-center results.

E. Degree of localization of gap states

Although we have discussed aspects of the localization of the defect bound states and resonances in terms of their charges and charge densities, it is instructive to look at localization from the point of view of the Hubbard "U" parameters which enter into model Hamiltonians. These intrasite U parameters relate how the energy of a state depends on its occupancy, essentially measuring the intra-atomic Coulomb potentials between electrons in the same eigenstate. Strong (weak) localization of the electrons corresponds to large (small) values of the U parameters compared to typical kinetic energy contributions to the total eigenenergies. If U is big enough, transitions from extended to localized eigenstates can take place, even in periodic systems.

In the present work, two types of prominent defect-inducted states are obtained: (1) bound s or p gap states splitoff from the continuous, extended valence and conduction bands and (2) conduction-band resonances of p-like character. As might be expected, the former have

TABLE III. Wigner-Seitz sphere charges for the various defect calculations in units of the electron charge. Notation: vac is the vacancy, SCS the self-consistent scissor, and PTS the "pseudo"-transition-state.

Method		MgO		CaO	
		Q_{vac}	Q_{Mg}	Q_{vac}	Q_{Ca}
F center	LDA	0.872	11.279	0.958	19.124
	SCS	1.016	11.257	1.168	19.099
	LDS PTS	0.760	11.271	0.811	19.122
	SCS PTS	0.871	11.248	0.978	19.093
	Shifted potential	1.134	10.970	1.270	18.815
F^+ center	LDA	0.649	11.266	0.643	19.124
	SCS	0.717	11.243	0.751	19.094

been shown to be more localized than the latter from an examination of their electronic charges and charge densities, and here we show that the evaluation of the U parameters gives a consistent picture.

We denote the change in s or p state eigenenergies (ΔE) as a function of s or p occupancy (Δn) as

$$\Delta E_s = U_{ss}\,\Delta n_s + U_{sp}\,\Delta n_p \tag{9}$$

and

$$\Delta E_p = U_{ps}\,\Delta n_s + U_{pp}\,\Delta n_p \ . \tag{10}$$

Since in all of our calculations $\Delta n_p = 0$, we can only calculate U_{ss} and U_{ps}. We do so by plotting $\Delta E_{s(p)}$ as a function of Δn_s for $\Delta n_s = 2$, 1.5, and 1.0, corresponding to our F, "pseudo"-transition-state, and F^+ calculations, respectively. In Fig. 10 we show $\Delta E_{s(p)}$ versus Δn_s for MgO and CaO, respectively, and in Table VI we present our results for U_{ss} and U_{ps}. Two sets of calculations, using our LDA and our SC scissor procedures, are presented.

First of all it is seen from Fig. 10 that $\Delta E_{s(p)}$ are close to linear with respect to changes in s occupancy so that the theoretical construct used, and the meaning of the U parameters, is reasonable. The results from Table VI show that, as expected, $U_{ss} > U_{ps}$ for both materials and, in addition, the U values for CaO are bigger than for MgO indicating greater localization of the wave functions of the former, consistent with our interpretation which followed from examining the charges and charge densities. It is also seen that the U parameters for the SC scissor calculations are larger than those from the LDA results, roughly scaling by the ratio of the shifted to unshifted host band gaps.

TABLE IV. Bound-state charges from SC scissor calculations for the s-like F-center ground state and the p-like excited state of the F^+ center in units of the electron charge. The total charges in the central-site Wigner-Seitz sphere and the spheres of the six surrounding neighbors are shown separately in parentheses below each entry.

State	MgO	CaO
s-like gap state	1.61	2.0
F center (2 electrons)	(0.84+0.77)	(1.11+0.89)
p-like excited state	0.66	0.84
F^+ center (1 electron)	(0.24+0.42)	(0.26+0.58)

F. Comparison with previous work

In a series of papers, Wilson and co-workers,[24,25] have used a combination of theoretical techniques to examine the properties of F centers in alkaline-earth oxides (references to earlier theoretical work may be found in Ref. 1). For the electrons, they use a Hartree-Fock–type approximation near the defect and an effective-mass approximation in the outer regions. Lattice-relaxation energies are included, using an approach based on classical ionic theory, so that configuration-coordinate curves are determined. In general, small adjustments of certain Hartree-Fock parameters (essentially those determining the host band gap) were made so as to give the correct absorption energy, although as discussed by Summers *et al.*,[25] recent improvements in the method require little or no adjustments. Both absorption and emission, including multiplet effects, are determined in this method, but here we focus on the absorption results to compare with our work. They find that (1) the first shell of Mg or Ca neighbors relaxes *outward* by ~3–4 %, (2) nearly the full two electrons in the F center are contained in the first *two* shells of neighbors, and (3) the excited electron (p-like state) is much more delocalized compared to the s-like gap state electron. Points (2) and (3) agree with our results, and point (1) emphasizes a limitation in our work, the lack of inclusion of lattice relaxation. From the work of Wilson and Wood,[24] it also appears that lattice relaxation *decreases* the theoretical F-center absorption energy by approximately 0.5 eV, implying that the present results (too

TABLE V. Charge-neutrality parameter, defined as the sum of the net electronic charge in the defect cluster minus the similar quantity for the host cluster, in units of electron charge. Positive values correspond to an electron excess.

Method	MgO	CaO
F center LDA	0.12	0.06
F center SC scissor	0.13	0.11
F center shifted potential	0.15	0.16
F^+ center SC scissor	−0.25	−0.34

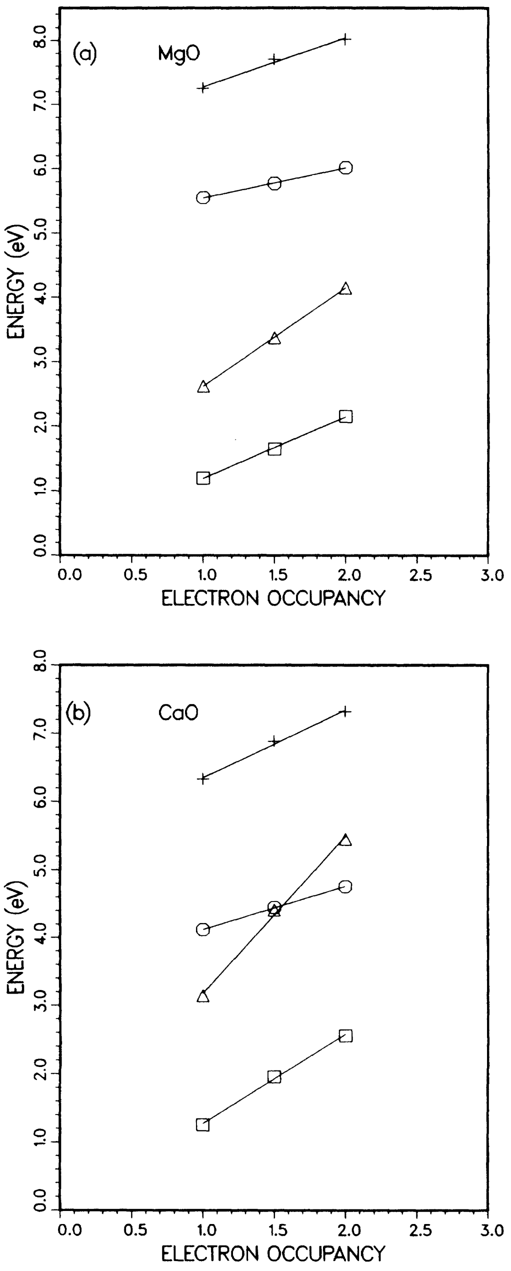

FIG. 10. Variations of the s and p bound state or resonance energies with s bound-state occupation for (a) MgO and (b) CaO. Squares and triangles are for the s bound state for LDA and SC scissor calculations, respectively. Circles and plus signs are for the p bound state or resonance for LDA or SC scissor calculations, respectively.

TABLE VI. Hubbard U parameters, defined in the text, for LDA and SC scissor calculations. All entries are in electron volts.

Hubbard parameter	MgO LDA	MgO SC scissor	CaO LDA	CaO SC scissor
U_{ss}	0.96	1.52	1.31	2.31
U_{ps}	0.46	0.76	0.64	0.99

small already) have this additional amount of disagreement with experiment.

Very recently Vail *et al.*[28] have discussed the F^+ center in MgO using unrestricted Hartree-Fock techniques for the electrons and sophisticated static shell-model techniques for the lattice polarization. Both the electronic and lattice polarization are determined self-consistently. They find good qualitative agreement with experiment, but emphasize that their detailed numerical studies are of limited use due to the extended nature of the perturbations induced by the F^+ center. They suggest that numerical complexities introduced by these extended defect states lead them to conclude that new techniques may be needed to describe them accurately.

Cluster calculations for F and F^+ centers in MgO have been recently reported by Sobolev *et al.*,[29] and for F^+ centers for MgO, CaO, SrO, and BaO by Taurian *et al.*[30] In these calculations exchange and correlation are treated within the $X\alpha$ method (which should be, roughly, equivalent to the LDA approach used here), and transition-state calculations of absorption energies were explored.

In the work of Sobolev *et al.*,[29] atomic relaxation effects for the first *two* shells of neighbors were studied by comparing the calculated absorption energies for the clusters as a function of the shell relaxations (no fully *ab initio* total cluster energies were determined) with *experiment.* They conclude that relaxation of the positions of the second shell of neighbors is quantitatively important, similar to the conclusions of Vail *et al.*[28] However, it is puzzling that Sobolev *et al.*[29] obtain a band gap of 8.14 eV for the perfect MgO cluster, much larger than one would expect from an $X\alpha$ calculation. Although the cause of this discrepancy is, to us, unclear, the cluster sizes and the imbedding procedures used may be a source of considerable error.

The F^+-center calculations of Taurian *et al.*[30] explicitly considered the vacancy plus one shell of neighbors, and yielded absorption energies much too large compared to experiment for all of the alkaline-earth oxides they studied. The inclusion of atomic relaxation (neglected in their work) would probably reduce their absorption energy values, but they would still appear to be much too large. They argue that long-range polarization effects, argued for on theoretical grounds by Vail *et al.*[28] and from experimental results by Halliburton *et al.*,[31] are likely to be important.

In a recent paper,[32] Choi and Takeuchi have discussed electronic states of F-center-type defects in oxide crystals, and propose a "new picture" which they have derived from general arguments using point-ion models of the F-center energetics, and specific calculations for the Al_2O_3 system. From considerations of the Madelung energies of assumed oxidation states of the oxide constituents, they conclude that the F-center occupied bound state is likely to fall *below* the valence-band edge, specifically in the gap below the occupied upper O p states. Their $X\alpha$ self-consistent cluster calculations for Al_2O_3 supports these conclusions. Although we have not searched for defect states below the upper valence-band bottom, given the consistency of our results with optical absorption measurements, and with other theoretical work, we believe that it is extremely unlikely that these low-lying states exist in MgO or CaO *F*-center-like defects.

We believe that the *general* validity of the point-ion arguments of Choi and Takeuchi is questionable since details of the crystal-field effects are neglected. In addition, although we have not done *F*-center calculations in Al_2O_3, we point out that some of the assumptions they have made in doing their cluster calculations, particularly freezing the Al^{3+} electrons, and questions of cluster-size adequacy, should be checked by calculations using alternative methods.

In summary, although different techniques and approximations used by various authors tends to cloud interpretations and comparisons, it is clear that long-range electronic and lattice polarization effects are likely to be important, especially for the F^+ center. We are in the process of extending our numerical capabilities to include both effects, and we will report on this work in the future.

G. Further discussion of excited states

It is generally believed that *F*-center-like defects in ionic insulators should possess a full Rydberg-like series of gap bound states, $s,p,\ldots$, in analogy to a hydrogen atom, with the electron moving in the field of a positively charged vacancy center. Mott and Gurney[33] gave a general proof of the existence of an infinite number of impurity bound-states below the conduction-band edge, subject to the condition that the potential seen by the trapped electron is Coulomb-like at large distances, e.g., falls off as $1/r$ for large r. The latter condition has a great deal of physical appeal. This theorem has been verified by a wealth of experimental results for *F*-center-like defects in alkali halide crystals,[34] and for the alkaline-earth oxides as well (see Ref. 1 and references therein). In particular, it is found that p bound states are in the gap, falling just below the bottom of the conduction bands. However, our straight LDA results show instead a p-like resonance above the conduction-band edge, contradicting the Mott-Gurney theorem. The question is why?

We believe that the answer is related to limitations of the LDA, specifically the fact that the LDA one-electron potential for an *F*-center-like trapped electron does not obey the $1/r$ asymptotic r limit required by the Mott-Gurney theorem. Because of this unphysical limit of the LDA potential, the Mott-Gurney theorem cannot be applied and, hence, there is no requirement for the p, or higher l states to be bound in the gap. This unphysical feature of the LDA is also thought to be a part of the reason that LDA eigenvalue differences do not give a good representation of the energy gaps in semiconductors and insulators. If our interpretation is correct, then one might expect that improvements to the LDA, such as the *ad hoc* scissor operator corrections to the host band-structure and/or the transition-state description of excitation, would lead to an excited p state that moves from being a broad resonance in the conduction bands, to a bound state in the gap, or at least to a sharper resonance closer to the conduction-band edge. It is encouraging that both the scissor and transition-state models lead to such an improved description of the excited p states.

V. CONCLUSIONS

It is gratifying that the MTGF method for these seven-atom defect clusters gives a respectable semi-quantitative picture of vacancy-induced electronic states in the oxides MgO and CaO. Although the first-principles theory yields defect-related ground and excited states of the proper angular momentum character with approximately the correct energies even without considerations of lattice relaxation and extended clusters, it is also clear from the present work and other theoretical studies that including these effects is important for good quantitative accuracy.

The treatment of exchange and correlation effects for ground and excited states is also still a source of contention for perfect and defected semiconductor and insulator systems with, at present, only approximate "fixes" available for the latter studies. In this paper the various attempts to improve the LDA description of the excited defect states were, to a large extent, successful, especially with regard to predicting the widths and locations of the excited states with respect to the conduction-band edges. There was found to be some variation in the energetics of the transitions from the ground states to the excited states, with the "pseudo"-transition-state calculations giving the best overall description.

Although there is still much room for quantitative improvements within the current versions of our MTGF computer codes—more perturbed shells and atomic relaxation, especially—we consider these initial calculations successful. These fully first-principles *F*-center calculations already have yielded a good semi-quantitative picture of the spectrum and spatial dependence of the *F*-center states, and are amenable to systematic improvements which are being developed. We also hope that the Hubbard U parameters we have determined will be useful in other model Hamiltonian studies in these systems.

Note added in proof. N. E. Christensen (private communication) has informed us that including "empty spheres" in the LMTO calculation reported in Ref. 15 results in an LDA gap of ≈ 5.0 eV, in much better agreement with the other band-structure calculations discussed in Sec. III C.

ACKNOWLEDGMENTS

Helpful discussions with R. Cohen, J. Feldman, P. Dederichs, and T. Wilson are appreciated. This work was supported, in part, by the U. S. Office of Naval Research under Contract No. N00014-83-WR-30007.

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