Wave Functions for F Centers in MgO†

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A calculation of the ground $\Gamma_1{}^e$ and first excited $\Gamma_4{}^o$ states of the simple F center in MgO is described, using a mixed linear combination of atomic orbitals (LCAO)–point ion lattice scheme. An estimated transition energy of 4.7 eV and oscillator strength near unity is compared with various observed absorption peaks in the middle ultraviolet. Including estimated polarization and deformation corrections we give for the $\Gamma_1{}^e$ energy E_0, with respect to the vacuum, $E_0 \lesssim -13.0$ eV, i.e., below the presently assumed valence band maximum of about -9.5 eV. Implications of such a result, e.g., that the O^{2-} vacancy trap may not be bleachable by ionizing radiation, are discussed, especially with reference to mixed electron spin resonance (ESR)–optical experiments.

1. INTRODUCTION

EVIDENCE for the existence of F-like centers in MgO was first presented by Wertz, Auzins, Weeks, and Silsbee.[1] They described an electron spin resonance (ESR) spectrum in neutron-irradiated MgO consisting of a prominent single line with essentially $g=2.0023$, centered in a complex of weaker lines which they identified with hyperfine splitting by the 10%-abundant Mg^{25} nuclei. The center was taken to be that of a single electron trapped in an O^{2-} vacancy. The hyperfine pattern was explained in terms of a linear combination of atomic orbitals (LCAO) wave function composed of Mg $3s$ and $3p$ orbitals, analogous to that used earlier for alkali halide F centers.[2] The predicted hyperfine pattern from this simple LCAO agrees closely with that observed.[1] The reality of F centers in MgO has been regarded as well established by the ESR data.[3] A certain problem with the g shift remains to be cleared up and will be discussed below (Sec. 5).

Optical absorption studies in MgO were described by Clarke.[4] Energy levels associated with several possible defects, induced by irradiation or present in nonstoichiometric samples, were tentatively assigned positions in the forbidden band gap in such a way as to explain optical absorption, bleaching, and other observations. A sizeable concentration ($\gtrsim 10^{18}$/cc) of negative ion vacancies can be induced in MgO by neutron bombardment, as suggested by ESR intensities.[1] However, one does not see, in such a crystal, any prominent optical absorption band readily identifiable as an F band, such as in alkali halides.[5] Several peaks in the visible spectrum are observed; the strongest peaks, however, are in the ultraviolet. The visible coloration at least does not seem closely tied to the F-center ESR intensity. A motivation for the present work was to aid in establishing the location in the spectrum of the principal F-center transition.

We shall present here wave functions for the ground and first excited states of the MgO F center, and estimate a transition energy. More than one defect structure, plus invariably certain impurities, are needed to explain the several optical bands seen, and in our opinion experiment alone has not indicated with any certainty which peak or peaks is an F-center transition. Thus, our comparison with experiment (Sec. 6) will be mainly suggestive.

The degree of ionicity of MgO, or more specifically the reality of the O^{2-} ion, is a matter of dispute. Though the O^{2-} overlap severely, the Mg^{2+} at least are fairly compact and well defined. On the validity of an ionic model we note that Yamashita[6] has made use of O^{2-} $2p$ wave functions in a calculation of the valence band. His predicted band is 9 eV wide with the maximum some 8 eV below the vacuum, a result claimed reasonably consistent with x-ray emission and other data.[6] It seems that a purely ionic model of MgO and of other oxides is surely useful for many purposes. In using this model one must assign to the O^{2-} ion a large polarizability, varying considerably for O^{2-} in the various oxides.[7] We work with the ionic model, with some reservations when it comes to including polarizability and exchange effects (Sec. 3).

2. THE POINT-ION LATTICE–LCAO SCHEME

In a divalent crystal we expect greater localization of an F-center wave function than in alkali halides, because of the $+2$ vacancy charge. Thus, a purely continuum model, based on a simple central potential modified by dielectric constant assumptions,[8] is less promising as a starting point here than in alkali halides. Ionic Mg^{1+} $3s$ and $3p$ wave functions[9] centered on the six nearest-neighbor cations (nc) and perhaps also on the eight next-nearest-neighbor cations (nnc) surrounding the vacancy ought to be prominent in the wave function, especially in view of their obvious role in the description of the ESR spectrum.[1] We considered two

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[1] J. E. Wertz, P. Auzins, R. A. Weeks, and R. H. Silsbee, Phys. Rev. **107**, 1535 (1957); J. E. Wertz, J. W. Orton, and P. Auzins, Suppl. J. Appl. Phys. **33**, 322 (1962).
[2] A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. **91**, 1066 (1953); A. H. Kahn and C. Kittel, *ibid.* **89**, 315 (1953).
[3] J. E. Wertz, J. W. Orton, and P. Auzins, Discussions Faraday Soc. **31**, 140 (1961).
[4] F. P. Clarke, Phil. Mag. **2**, 607 (1957).
[5] F. Seitz, Rev. Mod. Phys. **26**, 7 (1957).

[6] J. Yamashita, Phys. Rev. **111**, 733 (1958).
[7] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).
[8] References to the continuum models of Tibbs, Simpson, and others are found in Refs. 5 and 12, which are review articles.
[9] L. Biermann and K. Lübeck, Z. Astrophys. **25**, 325 (1948).

approaches used in alkali halides, the "large molecule" of Inui and Uemara[10] and the "point ion lattice" scheme of Gourary and Adrian.[11,12] The first is purely an LCAO method, using a few near neighbors, and cannot readily take account of the potential falloff for large r. The second uses variational wave functions in a potential $V(\mathbf{r})$ consisting of purely Coulomb potentials of all the crystal ions. The potential is expanded in kubic harmonics about the vacancy center. Gourary and Adrian in fact used only $V_0(r)$, the spherically symmetric part of $V(\mathbf{r})$. In this sense their calculation was not different from early continuum models,[8] except that they used a V_0 which is the actual one in an ionic crystal if polarization and the potential drop inside ion cores is ignored. The effects of the ion cores would appear to have small effect on the energies of the Gourary and Adrian wave functions, or at least on the transition energies. Their predicted values of which are within 10% of those observed in the alkali halide series. Their method seemed attractive in the MgO case. Their wave functions are, however, surely incorrect in the vicinity of the ion cores, and thus, for one thing, cannot directly give correct ESR parameters. For the latter purpose they can of course be orthogonalized to the cores[11-14] or projected onto unoccupied cation states. LCAO functions on the other hand, made up of unoccupied cation states, are automatically almost orthogonal to the cores, to the extent that overlap on "other ion" cores is small, thus they may be intrinsically more accurate. Most of the overlap takes place in the interior of the vacancy (at least in the Γ_1 ground state—see below), and the wave function near the cores may remain well described by ionic orbitals.

Though the Gourary-Adrian method will predict the same energies (see Sec. 4) in the lowest approximation, we use here a different scheme combining LCAO wave functions with the point-ion lattice Hamiltonian. Group theoretical analysis yields several linearly independent LCAO functions, using the nc and nnc Mg^{1+} $3s$ and $3p$ orbitals, for each possible representation of the full cubic group O_h. We expand each such LCAO about the vacancy center, using Löwdin's α functions.[15] The mth LCAO belonging to the jth row of the ith representation Γ_i^p of O_h can be written,

$$\psi_{im}^j(r\theta\phi)=\sum_{(l)}^{\infty} \alpha_l(NLM\,|\,a,r)Q(\Gamma_i^p l j\,|\,\theta,\phi) \qquad (1)$$

where the Q are appropriate kubic harmonics.[16] The Q

notation is used in Ref. 11. For Γ_i^p, where p represents even or odd, we use simple Γ_i for even and Γ_i' for odd representations, respectively. The α notation is Löwdin's.[15] The NLM quantum numbers for a particular LCAO, specified by (ijm), may be considered to refer to a particular typical component orbital, centered on one of the Mg ions at a distance a from the vacancy center. All component orbitals in one LCAO actually have the same expansion. Strictly speaking, M differs for the several component orbitals, if we refer the expansion to a fixed xyz system[15]; in fact, of course, we need expand only one orbital in each LCAO. The sum over l in (1) runs over all l for which Q_l is contained in the representation involved, e.g., $l=0, 4, \cdots$ for Γ_1, and $l=1, 3, \cdots$ for Γ_4'. [In (1), N, L, M, and a implicitly all bear the subscripts ijm.]

Anticipating further application of this method to F centers in other alkaline earth oxides as well as MgO, we have analyzed all possible ψ_{im}^j involving nc and nnc s, p, and d cation functions in crystals with the MgO (i.e., NaCl) structure, and list them here. (The d functions would be needed, for example, in CaO.[17])

nc s functions: $\Gamma_1, \Gamma_3;\ \ \Gamma_4'$.
    p functions: $\Gamma_1, \Gamma_3, \Gamma_4, \Gamma_5;\ \ 2\Gamma_4', \Gamma_5'$.
    d functions: $\Gamma_1, \Gamma_2, 2\Gamma_3, \Gamma_4, 2\Gamma_5;$
    $\qquad\qquad\qquad\qquad\qquad \Gamma_2', \Gamma_3', 2\Gamma_4', 2\Gamma_5'$.

nnc s functions: $\Gamma_1, \Gamma_4;\ \ \Gamma_2', \Gamma_4'$.
     p functions: $\Gamma_1, \Gamma_3, \Gamma_4, 2\Gamma_5; \Gamma_2', \Gamma_3', 2\Gamma_4', \Gamma_5'\rangle$
     d functions: $\Gamma_1, 2\Gamma_3, 2\Gamma_4, 3\Gamma_5;$
     $\qquad\qquad\qquad\qquad\qquad \Gamma_2', 2\Gamma_3', 3\Gamma_4', 2\Gamma_5'$.

An entry in this tabulation such as $n\Gamma_i^p$ means that n linearly independent (and not unique) LCAO's belonging to Γ_i^p, made up of (say) d atomic orbitals centered on nnc ions, may be constructed. The geometry of many of these LCAO's is obvious and familiar, but some is not. It is worth observing that a complete decomposition of this sort would have no great practical importance in the theory of alkali halide F centers because only two or three states, of Γ_1, Γ_4', and maybe one or two other types would seem to represent localized states. In MgO, since the divalent trap is deep, it may be that localized states belonging to several of the representations exist, though the sum rule for transitions from the Γ_1 level will turn out to be almost used up with transition to the Γ_4' level (Sec. 6).

To the ψ_{im}^j we apply the Hamiltonian, written in Hartree atomic units,

$$\mathfrak{IC}= -\tfrac{1}{2}\nabla^2+ \sum_{l=0,4,\cdots} V_l(r)Q_l(\theta,\phi), \qquad (2)$$

i.e., the point-ion lattice Hamiltonian.[11,12] We use here an abbreviated but adequate notation for the potential expansion [see Eq. (5) of Ref. 11]. The $V_l(r)$ are derived from the doubly-charged MgO lattice, which has the

[10] T. Inui and Y. Uemura, Prog. Theoret. Phys. (Kyoto) **5**, 252 (1950).

[11] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

[12] B. S. Gourary and F. J. Adrian, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull, (Academic Press, Inc., New York, 1960) Vol. 10. See also B. S. Gourary and A. F. Fein, Suppl. J. Appl. Phys. **33**, 331 (1962).

[13] W. E. Blumberg and T. P. Das, Phys. Rev. **110**, 647 (1958).

[14] A. Gold, J. Chem. Phys. **35**, 2180 (1961).

[15] P. Löwdin, Advan. Phys. **5**, 1 (1956).

[16] H. A. Bethe and F. C. von der Lage, Phys. Rev. **71**, 612 (1947).

[17] J. C. Kemp and V. I. Neeley, J. Phys. Chem. Solids **24** 332 (1963).

Madelung depth 0.88 Hartree units (interionic distance $a_0 = 3.97$ Bohr radii). Application of $\mathfrak{IC}$ to the several $\psi_{im}{}^j$ with given ij, with m restricted to include say only nc and nnc orbitals, then gives a secular equation for the energies E_{im} (these we shall need denote only by E_i, which will mean the lowest E_{im}). Since we will in this computation use only the lowest-l terms in $V(r)$ and the wave-function expansions, we use simply

$$\mathfrak{IC} = -\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{l(l+1)}{2r^2} + V_0(r). \qquad (2')$$

The effect of including the next V term, V_4, was not investigated quantitatively but presumably its neglect here may not be more serious than in the alkali halide case.[11] V_4 behaves like r^4 inside the vacancy but is of the order of V_0 in the vicinity $r = a_0$ (nc distance). Its angular function Q_4 is such that the energies would tend to be lowered since (when one includes higher-l terms in the $\psi_{im}{}^j$ also) the electron would appear more concentrated on the nc magnesiums. (This would be partly balanced by the higher kinetic energies of the higher-l parts of the $\psi_{im}{}^j$.)

We now discuss the lowest-l approximation to the wave functions. For this purpose we write (1) as follows:

$$\psi_{im}{}^j = d_{im}{}^j \sum_{(\mu)}^{S} \phi_\mu = c_{im}{}^j\alpha_l(NLM \,|\, a,r)Y_{lm}(\theta,\phi) + \cdots$$

$$\equiv \tilde{\psi}_{im}{}^j + \cdots \qquad (1')$$

where the $d_{im}{}^j$ and $c_{im}{}^j$ are normalization constants; μ runs over the particular set of S single-ion functions ϕ_μ involved in the $\psi_{im}{}^j$ LCAO; and l means specifically the lowest l in $\psi_{im}{}^j$. Here we have replaced the lowest-l kubic harmonic with a spherical harmonic, which is allowed in the case of at least the simpler LCAO's which we shall use in the computations of this paper. The truncated expansion consisting of the lowest-l term is denoted $\tilde{\psi}_{im}{}^j$. Supposing neglected terms as negligible, we now may assume *both* $\psi_{im}{}^j$ and $\tilde{\psi}_{im}{}^j$ to be normalized to unity and the $d_{im}{}^j$ and $c_{im}{}^j$ adjusted accordingly. Using Löwdin's[15] normalization conventions for the α functions and spherical harmonics, and assuming separately normalized ϕ_μ, in the lowest-l approximation, (1') implies

$$d_{im}{}^j S k_{LM}\alpha_l(NLM \,|\, a,r)Y_{lM}$$
$$= c_{im}{}^j\alpha_l(NLM \,|\, a,r)Y_{lM} = \tilde{\psi}^j{}_{im},$$

or $d_{im}{}^j = c_{im}{}^j/(Sk_{LM})$. In practice it is simplest to normalize the $\tilde{\psi}_{im}{}^j$ empirically, which determines the $c_{im}{}^j$ and $d_{im}{}^j$. The latter are needed to decompose our approximate eigenfunctions, composed of $\tilde{\psi}_{im}{}^j$, back into ϕ_μ, for calculating wavefunctions amplitudes at ion sites and estimating ESR parameters (Sec. 5). For computing optical energies these normalization considerations have no essential importance, although in what follows the $\tilde{\psi}_{im}{}^j$ and also the linear combinations $\bar{\Psi}_{i0}{}^j$ of the $\tilde{\psi}_{im}{}^j$ (see below) will all be taken as normalized.

It is worth noting that the "completeness ratios"[15] for our interrupted (lowest-l) expansions of the LCAO's here are much closer to unity than are the completeness ratios for similarly interrupted expansions of *individual* one-ion wave functions. This is due to the high symmetry of the cubic representation LCAO's. For example, the next term after $l = 0$ in the Γ_1 expansion is an $l = 4$ term; in the expansion of an individual cation function the next term would have $l = 1$ and would be relatively large. Thus, the lowest-l approximation is better than it might seem at first, especially for the most symmetric LCAO's.

A secular equation for the F-center energies may now be derived by minimizing $\langle\mathfrak{IC}\rangle$, using (2'), with respect to the a_m, applied to

$$\bar{\Psi}_{i0}{}^j \equiv \sum_m a_m\tilde{\psi}_{im}{}^j, \qquad (3)$$

where $\bar{\Psi}_{i0}{}^j$ corresponds to a lowest energy state belonging to the ith representation. To calculate $\langle\mathfrak{IC}\rangle$ one needs to evaluate kinetic energy matrix elements $T_{mm'}$ between the $\tilde{\psi}_{im}{}^j$; overlap integrals $S_{mm'}$; and matrix elements $V_{mm'}$ of $V_0(r)$, the point-ion lattice potential.

We now center attention on the ground and first excited states, assumed to be of the s-like and p-like Γ_1 and Γ_4' types, respectively. We actually use only the nc LCAO's, built from the $3s$ and $3p$ functions. Owing to the strong localization in the vacancy it quickly became apparent that addition of nnc functions would not lower the energies seriously enough to warrant their inclusion in this preliminary calculation. (The excited state would no doubt be lowered slightly more by the nnc's, but we will find that even in this state the F electron appears localized about 80% within the nc sphere in MgO.) The nc Γ_1 and Γ_4' $\psi_{im}{}^j$ may be written, where the ϕ are ion orbitals and we choose for example the x-like member of each of the threefold-degenerate Γ_4' levels,

$$\Gamma_1: \quad \psi_{01}{}^0 \doteq \sum_1^6 \phi_{3s}{}^{(i)} \doteq \alpha_0(300\,|\,a,r) + \cdots \doteq \bar{\psi}_{01}{}^0 + \cdots;$$

$$\psi_{02}{}^0 \doteq \sum_1^6 \phi_{3p}{}^{(i)} \doteq \alpha_0(310\,|\,a,r) + \cdots \doteq \bar{\psi}_{02}{}^0 + \cdots;$$

$$\Gamma_4': \quad \psi_{11}{}^1 \doteq \phi_{3s}{}^{(1)} - \phi_{3s}{}^{(2)}$$
$$\doteq \alpha_1(300\,|\,a,r)\cos\theta + \cdots \doteq \bar{\psi}_{11}{}^1 + \cdots;$$

$$\psi_{12}{}^1 \doteq \phi_{3p}{}^{(2)} - \phi_{3p}{}^{(1)}$$
$$\doteq \alpha_1(310\,|\,a,r)\cos\theta + \cdots \doteq \bar{\psi}_{12}{}^1 + \cdots;$$

$$\psi_{13}{}^1 \doteq \sum_3^6 \phi_{3p}{}^{(i)*}$$
$$\doteq \alpha_1(311\,|\,a,r)\cos\theta + \cdots \doteq \bar{\psi}_{13}{}^1 + \cdots. \qquad (4)$$

The $\phi_{3p}{}^{(i)}$ orbitals are taken as those with positive lobes pointing into the vacancy. The geometry of the nc Γ_1 LCAO's is well known.[1,2] In (4), θ is the polar angle with respect to, for example, the [100] direction. We sketch the three x-like Γ_4' LCAO's in Fig. 1. The four $\phi_{3p}{}^{(i)*}$ orbitals are oriented as shown in Fig. 1. The $\doteq$ equality
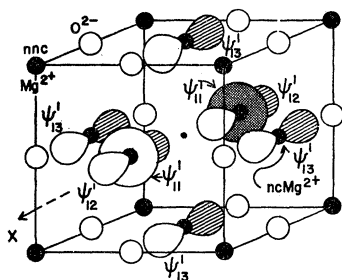
FIG. 1. The geometry of the three linearly independent Γ_4' LCAO's, using nc Mg^{1+} $3s$ (large spheres at 100 and $\bar{1}00$ positions) and $3p$ orbitals. We show the x-like partner function for each of the threefold-degenerate LCAO's. Signs, indicated by shading, of the three orbitals correspond to the choice in Eq. (3) of the text.

in (4) means that normalization constants are omitted, although the signs of the several ϕ are chosen correctly, that is, consistent with the signs of the a_m in $\Psi_{00}{}^0$ and $\Psi_{10}{}^1$ in (6) below and with sign choices for the $\psi_{1m}{}^1$ in Fig. 1.

In computing the necessary α functions it was found that the use of Hartree-Fock Mg^{+1} $3s$ and $3p$ radial functions seemed an unnecessary complication here, and normalized Slater functions $kR^2 \exp(-\lambda R)$ were used. The λ were chosen for a good average fit of the α expansions of the Slater functions to those of the Hartree-Fock functions over the range $0 \leq r \lesssim 8$, for the two easiest-to-evaluate α functions; see Fig. 2. For $3s$ and $3p$ we used $\lambda = 0.9$ and 0.8 a.u., respectively. In the present context, using the point-ion lattice Hamiltonian, it is, in fact, not necessarily true that use of more accurate atomic functions should yield lower energies; their use, however, might be called for in certain modifications of the present scheme (see remarks in Sec. 4). It is clear that for estimating ESR quantities and the like, dependent largely on wave function amplitudes inside ion cores, after obtaining relative amplitudes of the several LCAO's by minimizing the optical energies,
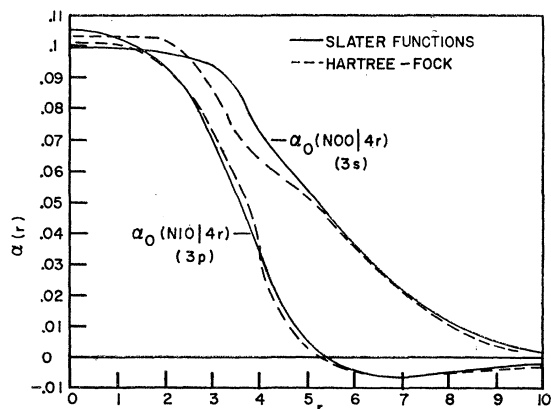

FIG. 2. Similarity of two of the α functions, used in the Γ_1 computation, as computed from Slater functions for the Mg^{1+} $3s$ and $3p$ nc orbitals, versus those computed from the Hartree-Fock functions of Ref. 9. The vacancy center and nc radial positions are $r = 0$ and $r = 4.0 = a_0$ respectively (atomic units).

we are free to replace Slater functions in the LCAO's by Hartree-Fock or other atomic functions. When we use Slater functions, the α functions needed can be quickly written out in closed form. The integrals $T_{mm'}$ and $S_{mm'}$ defined above can then also, in principle, be written out in closed form, as can also the integrals of $V_0(r)$, the latter as explicit infinite series. However, the closed forms for even the simplest of these integrals are surprisingly unwieldy and were deemed not worth the effort to derive.[18] We obtained the integrals for our Γ_1 and Γ_4' computation by numerical integration of the Slater-orbital α functions.

The energies E_0 and E_1 computed for the lowest Γ_1 and Γ_4' states, respectively, using the $\tilde{\psi}_{im}{}^j$ in (4), were

$$\Gamma_1: \quad E_0 = -0.704 = -19.1 \text{ eV},$$
$$\Gamma_4': \quad E_1 = -0.530 = -14.4 \text{ eV}, \qquad (5)$$

and the (normalized) wave functions corresponding to these energies were

$$\Gamma_1: \quad \bar{\Psi}_{00}{}^0 = +0.396\tilde{\psi}_{01}{}^0 + 0.710\tilde{\psi}_{02}{}^0,$$
$$\Gamma_4': \quad \bar{\Psi}_{10}{}^1 = -0.355\tilde{\psi}_{11}{}^1 - 0.577\tilde{\psi}_{12}{}^1 + 1.186\tilde{\psi}_{13}{}^1. \qquad (6)$$

The unmodified point-ion lattice potential (dashed line in Fig. 3) was used here. The energy levels in (5) are, as expected in view of the deep doubly charged well, very deep indeed. An obvious large upward correction to be added is that due to polarization, considered along with other corrections in the next section. Our eventual conclusion will be, however, that the transition energy $E_1 - E_0 \simeq 4.7$ eV is probably not very greatly changed by such corrections. The radial density functions, the Ψ of (6) multiplied by r, are sketched in Fig. 4.

3. CORRECTIONS: POLARIZATION AND LATTICE DISTORTION

Three principal corrections to the simple point-ion lattice model were discussed by Gourary and Adrian[11,12]: ion-core polarization, lattice distortion, and exchange. In MgO, attention centers on displacement of the small Mg^{2+} ions; on the large polarizability of the O^{-2}; and on exchange effects, presumably mostly with the oxygen $2p$ electrons. The second two are really inter-related, and the most satisfying approach would of course be a many-electron calculation, utilizing, for example, the twelve nearest-oxygen $2p$ electrons plus the F electron. Aside from remarks below relative to the

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[18] Using Slater or other analytic atomic functions, the kinetic energy and overlap integrals of the *exact* LCAO's, i.e., of the $\psi_{im}{}^j$, may be expressed in terms of integrals found in standard molecular theory tabulations. The $S_{mm'}$ and $T_{mm'}$, defined as integrals over the truncated-expression functions $\tilde{\psi}_{im}{}^j$, may *not* be so expressed since they are not identical with integrals over the $\psi_{im}{}^j$. They are approximately equal to the latter integrals, however, if the lowest-l approximation is good, thus standard tabulated integrals might be useful here. But one would then be working in the framework of a pure LCAO method (Ref. 10) and for numerical consistency one ought to then calculate the potential energy by means of the usual two- and three-center integrals. The simplicity of the present scheme, in which $V(\mathbf{r})$ is replaced by $V_0(r)$, would then be lost.
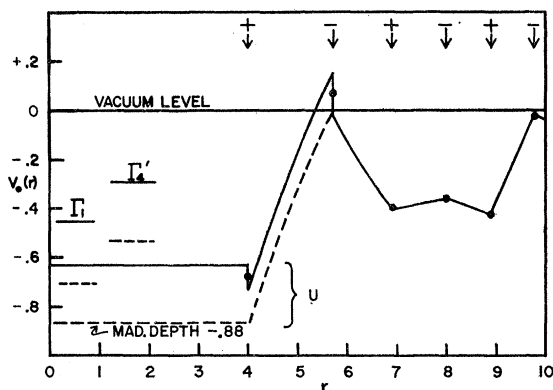
FIG. 3. The radial potential $V_0(r)$ for the MgO F center. Plus and minus signs indicate radial coordinates of various ions. The dashed line (coincident with the solid line for $r > \sqrt{2}a_0$) is the simple point ion lattice $V_0(r)$. "Madelung depth" here denotes the potential energy of an *electron* in the (unpolarized, undistorted) O^{-2} vacancy well; the Madelung depth of an *ion* in MgO of course is twice this depth. The solid line is V_0 corrected for lattice distortion and polarization according to the simplest model. The effect of radial distortion of the nc positions is idealized as a positive potential step at $r = a_0$, shown here with a height corresponding to $\sigma_0 = +0.05$. Polarization of the twelve nearest O^{2-} gives a step at $r = \sqrt{2}a_0$. The shift U in the trap depth is taken here as $+0.230 = +0.145 + 0.085$ as per the estimates of Sec. 3 of the text. The energy levels E_0 and E_1 (meaning levels defined by direct transition to the vacuum) are shown for the two potentials.

ESR g shift, we do not in this paper consider many-electron aspects, and hopefully their inclusion will not completely upset our estimates for the energies. Alkali halide experience suggests that the transition energy is much less affected by all these three above-listed effects than are the absolute energies.[11] Due to the stronger localization, in MgO this may be even more true. We are, however, also interested in the absolute (with respect to the vacuum level and band edges) energies. We have adapted Gourary and Adrian's model for lattice distortion[11] in order to deal simultaneously, but in the simplest possible way, with distortion, polarization, and the interaction of the F electron with the polarization and distortion fields. We allow the six nc Mg^{2+} to be displaced radially an amount σa_0, where positive σ means away from the vacancy. In estimating an equilibrium value σ_0, we examine the energy change $\Delta W(\sigma)$ associated with the distortion, in the presence of O^{2-} polarization. We have

$$\Delta W(\sigma) = \Delta W_e^{(0)} + \Delta W_{ion}^{(0)} + \Delta W_{ion}^p. \qquad (7)$$

Here $\Delta W_e^{(0)}$ and $\Delta W_{ion}^{(0)}$ are the changes in the F electronic ground-state energy and the lattice energy, respectively, if ion-core polarization is ignored. The third term involves polarization and will be considered subsequently. Our expressions for the first two terms, to second order in σ, are essentially those in Ref. 11, with a minor addition, and will not be given explicitly here. For dealing with core repulsion we used[19] $n = 7$, in the

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[19] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

expression $V_{rep} = \lambda R^{-n}$ for MgO. The distortion potential acting on the electron is taken as that of two spherical shells with radii a_0 and $a_0(1+\sigma)$, bearing charges minus and plus $6 \times 2 = 12$, respectively. To first order in σ,

$$\Delta W_e^{(0)} = \frac{12\sigma}{a_0} \int_0^{a_0} |\Psi_{00}^0|^2 r^2 dr \qquad (8)$$

while σ^2 contributions come from more exact evaluation of the expectation value of the distortion potential in the ground state, plus from an estimate of the mixing of excited Γ_1 states into Ψ_{00}^0. The integral in (8) is 0.87. Numerically we obtained

$$\Delta W_e^{(0)} = +2.60\sigma - 2.00\sigma^2 \qquad (9)$$

and

$$\Delta W_{ion}^{(0)} = -4.60\sigma + 15.94\sigma^2. \qquad (10)$$

In the absence of polarization, minimizing the sum of (9) and (10) with respect to σ gives

$$\sigma_0 = +0.072, \quad \Delta W_e^{(0)} = +0.178 = 4.85 \text{ eV}. \qquad (11)$$

The Γ_4' energy E_1 is raised by a slightly smaller amount 0.165, the localization integral [see (8)] being 0.77. Thus, clearly the levels may be seriously shifted; $E_1 - E_0$, however, is changed (reduced) only slightly.

Polarization has an even larger effect, though in our model it interacts with distortion and the two effects do not merely add. The polarizability of Mg^{2+} is a small fraction of that of O^{-2} and will be ignored. Also it is easy to show that the sum of polarization effects on the energy due to all oxygens other than the twelve bordering the vacancy is, though not negligible, only a fraction of that due to these twelve and is ignored here. (Interaction of a charge with a polarizable ion falls off as r^{-4}.) Though the polarizability α assigned to O^{2-} depends on the crystalline environment we did not look into reasons why we should use a value much different from that quoted for O^{2-} in the bulk crystal, as derived from the refractive index. We used the value for MgO (Tessman, Kahn, and Shockley[7]) $\alpha = 1.6510^- \times^{24}$ cm^{-3} = 11 a.u.

In discussing polarization of the twelve O^{2-} at $r = \sqrt{2}a_0$, we deal first with the dipole-dipole interaction among
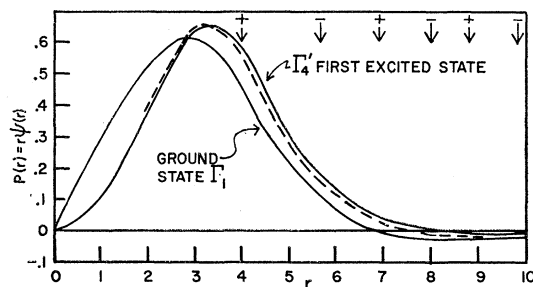

FIG. 4. Normalized radial functions $r\psi$ for the Γ_1 and Γ_4' states, from solution of the secular equation for nc LCAO's using the uncorrected $V_0(r)$ (dashed curve) and a polarization-corrected $V_0(r)$ (solid curves). The difference between the Γ_1 functions for the two cases is not large enough to show on this scale.

the twelve by calculating a "reduction factor" (a local depolarization factor) k for symmetric impressed fields $\mathbf{E}_0$, i.e., those of symmetry O_h. One computes, in the presence of such a field (such as that due to the net charge in the vacancy) plus the induced depolarizing field $\mathbf{E}_1$ (which also has O_h symmetry), the actual polarization $p = \alpha(E_0 - E_1) = \alpha E'$, yielding the linear relation $E' = kE_0$, E' being the actual field polarizing the O^{2-}. We obtained $k = 0.75$ (this value depends on the α used and on the interionic distance). This k must now multiply all fields which polarize the twelve O^{2-}.

We now denote all fields acting on the twelve O^{2-} by the letter E, those acting on the six cations by F. (E means symmetric fields other than the dipole-dipole fields, which must be accounted for by multiplying E by k in computing the polarization.) We calculate first $E_{\text{dist}}(\sigma)$, a dipole-like field due to the σ displacement of the nc Mg^{2+}:

$$E_{\text{dist}} = -(1/a_0^2)(+4.58\sigma + 3.51\sigma^2 + \cdots). \quad (12)$$

Also F_p, the field on an Mg^{2+}, displaced to $a_0(1+\sigma)$, due to the symmetrically disposed O^{2-} dipoles each of moment $p = \alpha k E$ (where E is the total impressed polarizing field), is

$$F_p(\sigma) = [p(\sigma)/a_0^3]$$
$$\times (+4.576 + 7.180\sigma - 13.32\sigma^2 + \cdots). \quad (13)$$

In (13), $F_p(\sigma)$ depends on σ not only through the geometrical factor in parentheses, but also through the fact that the polarization is partly σ-dependent, $p = \alpha k E(\sigma)$. Here $E = E_q + E_{\text{dist}}(\sigma)$, where E_q is due explicitly to the net vacancy charge. For the present purpose we take E_q as simply $1/(2a_0^2)$, i.e., as the Coulomb field of a $+1$ central charge. Strictly speaking, E_q depends on σ, but only to an insignificant extent since in the ground state the F electron appears localized to within over 95% inside the sphere of radius $\sqrt{2}a_0$, and this localization is scarcely changed by the polarization and distortion.

We now define the third term $\Delta W_{\text{ion}}{}^p$ in (7). It is the work done in displacing the six nc cations, in the field F_p of the twelve O^{2-} dipoles, through the radial distance σa_0 from perfect lattice positions:

$$\Delta W_{\text{ion}}{}^p = 2 \times 6a_0 \int_0^\sigma F_p(\sigma')d\sigma'. \quad (14)$$

Numerically we found

$$\Delta W_{\text{ion}}{}^p = +0.88\sigma - 3.34\sigma^2. \quad (15)$$

The sum of (9), (10), and (15) then yields the total energy change:

$$\Delta W = -1.12\sigma + 10.60\sigma^2, \quad (16)$$

which minimizes to $\sigma_0 = +0.053$ for the equilibrium lattice distortion. In view of the simplifications used, such as representing the large polarized oxygens by point

dipoles, this result is obviously on shaky ground. A semiquantitative check on the size of the quadratic term in (16) may be made as follows. Consider $X = \sigma a_0$ as a normal coordinate for a simple local lattice vibration mode[20] of Γ_1 symmetry, in which only the six cations move. The associated potential for such a mode is then, roughly,

$$\Delta W(\sigma^2) = \tfrac{1}{2}(2 \times 10.6/a_0^2)(\sigma a_0)^2 = \tfrac{1}{2}CX^2. \quad (17)$$

Using the mass of six magnesium atoms with the force constant C of (17) gives a frequency corresponding to about $20\ \mu$, which is near the 17.3-μ MgO infrared absorption peak.[21] This is consistent with a tendency that has been noted[20] for local modes about a defect to lie between the optical and acoustic branches of the bulk crystal phonon spectrum. As for the linear term in (16), this depends on partial cancellation of several terms of comparable magnitude, and could even have the wrong sign. However, pending more elaborate analysis, if the model involving only the nc σ displacement is at all realistic we conclude that σ_0 is small and probably positive (outward nc displacement). Assuming $|\sigma_0| < 0.1$, the F-center energies will be shifted somewhat less by lattice distortion than by core polarization.

We now compute U, which we define as the work that must be done against polarization and distortion fields in bringing the F electron to $r = 0$ from $r = \infty$, with σ held fixed at σ_0. U then is the estimated shift in the effective F electron potential minimum, which because of the strong localization will be close to the corrections to the energy levels. Fixing σ_0 means that we are concerned with the level positions defined by direct transitions to the vacuum level—see Fig. 3. We write

$$U = \Delta W_e{}^{(0)} + \Delta W_e{}^p. \quad (18)$$

The first term appeared in (7) and is work done against the cation distortion field. The second term is work done on the electron against the O^{2-} polarization fields. The latter are proportional to the O^{2-} polarization p, which depends on the σ distortion and on the net vacancy charge. By considering the electron charge as brought into the vacancy in infinitesimal increments[22] we may write

$$\Delta W_e{}^p = \frac{-12}{(\sqrt{2}a_0)^2} \int_{+2}^{+1} p\,dq$$

$$= \frac{-12\alpha k}{(\sqrt{2}a_0)^2} \int_{+2}^{+1} \left[\frac{q}{(\sqrt{2}a_0)^2} + E_{\text{dist}}(\sigma_0)\right]dq. \quad (19)$$

[20] J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).
[21] M. Parodi, Compt. Rend. **204**, 1111 (1937).
[22] There has been some controversy in the past over the way one should add polarization corrections to a one-electron F-center potential. See, for example, J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953), and page 195 of Ref. 12. We believe we have treated the effect of polarization in a consistent way. Following usual custom, we assume the O^{-2} polarization, but not lattice distortion, to follow the F electron adiabatically.

Using (12), $\Delta W_e{}^p(\sigma_0)$ may be written out explicitly. Numerically, we obtained

$$\Delta W_e{}^p = +0.145 - 0.89\sigma_0 - 0.68\sigma_0{}^2 \qquad (20)$$

which, added to (9), gives

$$U(\sigma_0) = +0.145 + 1.71\sigma_0 - 2.68\sigma_0{}^2. \qquad (21)$$

As would be expected, the interaction of distortion and polarization reduces the effect of the distortion field alone on U.

In spite of the uncertainty in our σ_0 estimate, U seems undoubtedly positive, due to the large O^{2-} polarizability. With $\sigma_0 = +0.05$, the second two terms in (21) sum to $+0.085$. Simple addition of (21) to (5) then gives estimates of the corrected Γ_1 and Γ_4' energies. If distortion were absent ($\sigma_0 = 0$), we would have

$$E_0 = -0.559 = -15.2 \text{ eV},$$
$$E_1 = -0.385 = -10.5 \text{ eV}, \qquad (5')$$

while with $\sigma_0 = +0.05$, thus with $U = +0.230$, we would have

$$E_0 = -0.474 = -12.9 \text{ eV}$$
$$E_1 = -0.300 = -8.2 \text{ eV}. \qquad (5'')$$

More accurate evaluation of the energies in the presence of distortion and polarization seemed called for, since U is not small compared to the Madelung depth. A correction term $\Delta V_0(r)$, consisting of potential steps at $r = a_0$ and $r = \sqrt{2}a_0$ to account for distortion and polarization, respectively, might be added to $V_0(r)$ (see Fig. 3), and the secular equations for E_0 and E_1 solved again. We carried out such a computation with a simpler ΔV_0, composed of a single step at $r = \sqrt{2}a_0$ of height 0.254, somewhat larger than $U(+0.05) = 0.230$. The resulting energies were only a percent or so lower than those obtained by simply adding 0.254 to the energies of (5), and the transition energy $E_1 - E_0$ was reduced less than 1%. The very small change in the wave functions is shown in Fig. 4. With a polarization-corrected $V_0(r)$, addition of nnc LCAO's might lower the energies perceptibly (particularly E_1), probably a few percent at most. Comments on the meaning of our energy level estimates will be made in Sec. 6.

4. ALTERNATE CALCULATIONS

The Gourary-Adrian alkali halide calculation[11] is adaptable in simple fashion to our case by extrapolation of their variational parameters ξ and η to fit the ionic spacing and double ionic charge of MgO, using their Type III wave function for the Γ_1 state and Type II for the Γ_4' state. (Values $\xi = 2.42$ and $\eta = 2.81$ were used for Γ_1, and $\xi = 3.47$ and $\eta = 4.32$ for Γ_4'.) The resulting energies, uncorrected for polarization and distortion and to be compared with (5), were

$$E_0 = -0.706, \quad E_1 = -0.530. \qquad (22)$$

Since we did not calculate ξ and η directly,[11] the agreement is to a minor extent fortuitous, but is in any case remarkable. However, though the Gourary-Adrian wave functions are not inherently related to our LCAO expansion, in the present framework any sequences of well-chosen wave functions must surely converge to the same energy, the same point-ion lattice Hamiltonian being used in both calculations. In retrospect, each method has advantages and disadvantages. Once the appropriate α expansions and the matrix elements (Sec. 2) are at hand, in our method we need only solve an algebraic secular equation and can deal more easily with certain perturbations. If carried further than the lowest-l terms, the LCAO expansion can deal automatically with the V_4 and higher potential terms, neglected as yet.

A different approach involving, at least implicitly, features of the detailed atomic core potentials as well as their Coulomb falloff will now be described. In this scheme we use the Mg^{1+} free-ion energies, as in standard molecular orbital theory.[23] The $3s$ and $3p$ ionization energies are 0.553 and 0.390 Hartree units, respectively.[24] We write the Hamiltonian for the F electron,

$$\mathcal{3C} = T + \sum_i V_i, \qquad (23)$$

T being the kinetic energy and V_i being an effective one-electron potential (not merely Coulombic) due to lattice ion i (i runs over all cations and anions in the crystal). The nature of $\mathcal{3C}$ is that if the ions were infinitely separated some eigenvalues of $\mathcal{3C}$ would be precisely Mg^{1+} free-ion energies. We now consider the F-center wave function to consist of a set of linearly independent LCAO's belonging to a given representation, as in Sec. 2, each LCAO consisting of Mg^{1+} functions. Let

$$\psi^a = \sum_j \phi_j{}^a \qquad (24)$$

be such an LCAO, made entirely of $3s$, $3p$, or higher, functions with free-ion energy $E_a{}^0$. Then

$$\mathcal{3C}\psi^a = (T + \sum_i V_i)\sum_j \phi_j{}^a = \sum_j (T + V_j + \sum_{i \neq j} V_i)\phi_j{}^a$$

$$= E_a{}^0\psi^a + \sum_j \phi_j{}^a \sum_{i \neq j} V_i. \qquad (25)$$

The expectation value of $\mathcal{3C}$ for a linear combination of type (24) LCAO's consists of, apart from division by the normalization integral, a sum of matrix elements of type

$$(\psi^{a'}, \mathcal{3C}\psi^a) = E_a{}^0(\psi^{a'}, \psi^a) + (\psi^{a'}, \sum_j \phi_j{}^a \sum_{i \neq j} V_i). \qquad (26)$$

The second term consists entirely of two-center and three-center integrals. Since the Mg^{2+} cores are well separated, while on the other hand the $3s$ and $3p$ functions are somewhat distended, we shall suppose that

[23] H. Eyring, J. Walter, and G. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 192.
[24] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D. C., 1949).

most of the contribution to these integrals comes from regions in which the V_i are Coulombic, i.e., in which they are of the form $\pm 2/R_i$, where R_i is the distance from the F electron to a lattice point bearing ionic charge plus or minus (depending on the ion) two. We can then introduce the point-ion lattice potential here by writing

$$V_i \cong V_i' \equiv \pm 2/R_i, \tag{27}$$

in which case

$$\sum_j \phi_j{}^a \sum_{i \neq j} V_i \cong \sum_j \phi_j{}^a \sum_{i \neq j} V_i' = \sum_j \phi_j{}^a \sum_i V_i' - \sum_j \phi_j{}^a V_j'$$

$$= V'(\mathbf{r})\psi^a + 2 \sum_j R_j{}^{-1}\phi_j{}^a, \tag{28}$$

where we denote the point-ion lattice potential by $V'(\mathbf{r})$. In this approximation (26) then involves merely the $E_a{}^0$, overlap integrals $S_{aa'}$, $V'(\mathbf{r})$ integrals, and what we call "Coulomb compensation" integrals

$$C_{aa'} = 2(\psi^{a'} \sum_j R_j{}^{-1}\phi_j{}^a)_J. \tag{29}$$

We now may apply the vacancy-centered α-function expansion of Sec. 2 to this scheme. The functions $\sum R_j{}^{-1}\phi_j{}^a$ have precisely the same symmetry as the corresponding ψ^a and have an expansion identical in form; we denote the α functions in their expansion as β functions.

This development leads to a secular equation determining the F-electron energies and the LCAO expansion coefficients as in Sec. 2. Our results, using where applicable the same approximations used in the preliminary Sec. 2 calculation (lowest-l terms only, nc functions only, etc.), and without the Sec. 3 corrections, were

$$E_0 = -0.615, \quad E_1 = -0.463. \tag{30}$$

These are substantially higher than the result (5), but are immediately subject to at least one criticism. As in Sec. 2, we used here Slater functions for the ϕ_i. Though this was justified in the straight point-ion scheme, there is a reason why it is apparently not so here. The β functions used in evaluating the $C_{aa'}$ of (29), especially those involving $3s$ functions, are more sensitive to behavior of the ion wave functions near the ion nuclei than are the ordinary wave-function expansions (α functions). [This fact does not necessarily invalidate the central approximation of this scheme, contained in (28).] A qualitative check showed that the $C_{aa'}$ containing $3s$ β functions would definitely be smaller if Hartree-Fock $3s$ functions were used. Since at least the diagonal $C_{aa'}$ are positive, this would mean a lowering of the energies. Consistent with these remarks, the $\psi_{01}{}^0 : \psi_{02}{}^0$ coefficient ratio for the minimized Γ_1 function we obtained, using Slater functions in this scheme, was 0.8 times smaller than in (6), i.e., the $3s$ functions tended to raise the energy and to be, therefore, rejected. Carrying this scheme through for both Γ_1 and Γ_4' with Hartree-Fock $3s$ and $3p$ functions would have entailed an additional numerical program for the nine $C_{aa'}$ involved

and was not done. Since this scheme actually involves a Hamiltonian different in some respects from that of Sec. 2 (the kinetic energy term has been assimilated into the free-ion energies), it should not of necessity lead to precisely the same energies. However, if the method is properly carried through, we believe the energies might well come out as low or lower than those of (5).

5. PARAMAGNETIC RESONANCE PARAMETERS

The theory of the g shift and of hyperfine splitting in alkali halide F centers, in terms of LCAO and other wave functions, is well known.[2,12–14,25] In Sec. 1 we referred to the explanation by Wertz et al.[1] of the hyperfine pattern of the MgO F center, in terms of the Γ_1 nc Mg^{1+} $3s$ and $3p$ LCAO's. They adjusted the $3s:3p$ ratio to fit the observed splittings. In principle, this ratio, which is (apart from a normalization correction[18]) the Γ_1 coefficient ratio in (6), should be a check on our calculation, in which the ratio came from minimizing the optical energy. Our wave function (6) gives 3.1 G for the isotropic part of the splitting, versus the observed[1] 4 G interval between adjacent hyperfine peaks (for a single nc Mg^{25} nucleus). In view of the sensitivity of the splitting to small corrections to $|\psi|^2$ at the nucleus and since we are more interested in the optical levels, which are less sensitive to such corrections, we considered this agreement adequate here.

The predicted g shift from our Γ_1 function is -0.0005. Adrian[25] has observed that a wave function made of available (e.g., Mg^{1+} $3s$ and $3p$) cation functions inevitably gives a negative g shift. Wertz[1,3] measured 0.0000 (zero) g shift in MgO; we have measured[26] $(+0.0004\pm0.0002)$. This anomaly, analogous to the LiF case,[25] has been discussed also in connection with F centers in other alkaline earth oxides and sulfides,[3] and the probable role of the anions was mentioned. In CaO, SrO, and BaO the net shift is negative,[3,17] increasing with Z of the cation, while in MgO plus and minus contributions apparently just cancel. The question of exchange or exchange-polarization with the O^{2-} is presumably involved. One speculation we may project is to suppose that a $2p^5$, i.e., O^{1-}, configuration plays a role, via attraction (in a manner of speaking) of a $2p$ electron into the singly charged F center. The spin-orbit coupling constant of the O^{1-} ground term should be like that of F^0, which is negative (actually[24] -270 cm^{-1}, rather large negative) as required for a positive g-shift contribution. A different suggestion was made by Wertz,[3] that O^{3-} (i.e., unoccupied O^{2-}) states must be involved, the d levels of which are inverted; the estimated g shift from this mechanism is, though, too small.[3] A many-electron calculation involving the O^{2-} $2p$ electrons is surely indicated, not only to explain the g shift but to further establish the optical F levels.

[25] F. J. Adrian, Phys. Rev. 107, 488 (1957).
[26] V. I. Neeley and J. C. Kemp (unpublished).

6. ENERGY LEVELS AND TRANSITIONS. COMPARISON WITH EXPERIMENT

The predicted energy levels from our lowest-order application of the point-ion lattice-LCAO scheme of Sec. 2 are subject to the following corrections, which include the two estimated in Sec. 3, due to (1) polarization, (2) lattice distortion, (3) higher-l terms in the potential- and wave-function expansions, (4) inclusion of nnc (and more distant) functions, and (5) exchange. The level difference E_1-E_0 from (5) is $0.174=4.73$ eV. The oscillator strength, computed to two figures only, using the wave functions (6), is 1.0. Then if the sum of the corrections leaves E_1-E_0 little changed, which as we have seen is quite possible even though the absolute energies are substantially shifted, we expect to find the main F-center transition in the vicinity of 2600 Å, or stated conservatively, in the middle ultraviolet.

The experimental description of optical absorption in MgO with defects produced by irradiation or other means has many complexities. We refer to Clarke's paper[4] and to the work of others discussed by him. The attempt is made[4] to interpret all or most of the absorption bands, as well as thermoluminescence peaks, photoconductivity peaks, and the like, in terms of cation and anion vacancies, hole, and electron traps, respectively. Partial discrimination between peaks due to impurities, anion vacancies, or cation vacancies by various techniques is described,[4] but there remains much ambiguity. (Clarke's tentative energy level diagram for the position of the trap levels now appears definitely wrong at least from a numerical standpoint since he used a 7.2-eV band gap, a better number being 8.7—see below.) In magnesium-excess MgO, one sees[4] bands at 2.35 (in the visible), 3.6, and 4.95 eV. In the neutron-irradiated crystal the first and third of these are also prominent, the third being typically several times as intense as the first, and other less well defined peaks are mentioned. One hope for isolation of the F-center transition is through correlated optical and ESR experiments.[27] The results of the latter so far have argued against the visible peaks as being cadidates for the F band and tend to favor the 4.95 eV peak. Clarke[4] seems to imply that the latter is the transition from the F ground level to the

conduction band. The energy we would estimate from the present paper for such a transition would be E_0 from (5') or (5''), minus the conduction band width ($\lesssim 1$ eV), i.e., over twice 4.95 eV, and we feel Clarke's implication is wrong.

We now discuss the position of the Γ_1 level E_0 with respect to the MgO band scheme. The most reliable value for the band gap that we know of at present[28] is 8.7 eV, and indications are that the distance from the vacuum to the conduction band minimum is quite small,[6] probably less than 1 eV. Our highest E_0 estimate is -12.9 eV from (5''). In view of the simplicity of the model used in Sec. 3, we do not place great faith in this number; however, we have some reason to view it as an upper limit. Of the five corrections listed in the first paragraph of this section, the third and fourth [see remarks following (2')] would be negative and the fifth could be also. Thus, at this juncture it seems likely that E_0 falls *below* the maximum of the oxygen $2p$ valence band. Such a trap after all might be expected for an anion vacancy in a divalent crystal. It could be objected that in this case the state would be coupled strongly to band functions and could not be strongly localized. However, the F center here has charge $+1$, and one could picture the valence band as locally depressed, over several lattice constants (this would surely happen whether E_0 were really below the band maximum or not), and this would decouple the trap from the band.

The suggestion that E_0 is below the valence band maximum has interesting implications. It would mean that, contrary to the situation in alkali halides, MgO F centers are essentially unbleachable by ionizing radiation, some very preliminary evidence for which exists.[27] "Unbleachable" here means that the anion vacancy tends to always contain at least one electron. The simple F center, on the other hand, must then have some affinity for attracting another electron, producing an F' center. Charge exchanges connected with the O^{2-} vacancy traps would, on this picture, tend to involve only adding or subtracting the second electron. *Note added in proof.* Some experimental support for our 4.7 eV estimate for the F-band energy has come from results of Professor Wertz's group, recently submitted for publication. They have found a very close connection between the ESR signal and the optical peak near 4.9 eV.

[27] V. I. Neeley and J. C. Kemp, unpublished work in progress, have found in neutron-irradiated samples a factor of at least 3 discrepancy between the relative growth of the 2.15-eV visible band (see a comparison spectrum in Ref. 17 also) versus the F-center ESR intensity, as a function of neutron dosage. Correlation with the 4.95-eV band is closer, but correlation with other uv bands has not been ruled out. We have also looked for uv effects on the ESR signal at 4.2°K, and found at least no large effect, though spurious thermal effects made results inconclusive. If MgO F centers are indeed unbleachable (short of actual heat treatment, which anneals vacancies), uv or x rays still ought to cause ESR signal changes due to $F-F'$ conversions, one way or the other.

[28] G. H. Reiling and E. B. Hensley, Phys. Rev. 112, 1106 (1958).