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Excited state and optical absorption properties of an F center in a lithium fluoride crystal*

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The method of linear combinations of atomic orbitals has been utilized to perform accurate first-principles calculation of the Γ_1^+ ground state and the Γ_4^- excited states for an F center in lithium fluoride. The one-electron Hamiltonian includes the Coulomb and exchange interaction (Slater's approximation) due to all of the ions in the crystal and the trapped electron, and incorporates the effects of lattice relaxation of the neighboring ions due to the presence of the defect as well as the electronic polarization effects. The F-center wave functions are expressed as linear combinations of localized orbitals centered at atomic sites up to the sixth nearest neighbors to the vacancy. Solution of the secular equation yields energies for the Γ_1^+ ground state and Γ_4^- excited states for the F-center electron. Properties of the F-center electron associated with optical absorption, such as absorption energy, orbital g factor of the Γ_4^- excited state, and spin-orbit splitting of the excited state have been calculated and are in excellent agreement with experiment. The oscillator strength for the Γ_1^+ to Γ_4^- transition has also been calculated and is in agreement with the experimental value within its range of uncertainty. A discussion of the effect of lattice distortion upon the properties of the F-center electron will also be presented.

I. INTRODUCTION

The method of linear combination of atomic orbitals (LCAO) has been successful in a recent application to determine the electronic states of an F center in a lithium fluoride crystal.[1] The success of the quantitative application of the LCAO method is primarily due to the simplification in the evaluation of the multicenter integrals obtained by expressing the atomic orbitals in terms of Gaussians. This simplification has enabled the LCAO technique to be used successfully in several applications to study the band structure of electrons in perfect crystals.[2] In the previous defect calculation,[1] the basis functions for the F-center electron were expressed as linear combinations of localized orbitals centered at atomic sites up to the sixth nearest neighbors to the vacancy. The initial crystal potential was constructed from the charge distributions for the Li^+ and F^- ions in the perfect crystal. The solution to this initial Hamiltonian was then used for an iterative calculation to take into account the effect of electronic polarization. This calculation resulted in an accurate ground state (Γ_1^+) wave function which was obtained from an *ab initio* LCAO calculation with the Slater approximation for exchange. The relaxation displacement of the surrounding lattice sites resulting from the presence of the F center, however, was neglected. The energy of the Γ_4^- excited-state calculation was also obtained in Ref. 1. A further approximation which was used in the excited state calculation was to construct the Hamiltonian for the F-center electron ($[H_{Fc}^{(1)}]_{\Gamma_1^+}$ in Ref. 1) by placing the F-center electron in the Γ_1^+ state (the ground-state configuration). It was pointed out in Ref. 1 that the use of the unoccupied orbitals of the ground-state configuration to approximate the Hamiltonian for the excited state can yield an accurate value for the absorption energy, but may possibly lead to less satisfactory results for oscillator strengths.

The properties pertaining to the optical absorption of the F-center electron in lithium fluoride have been studied using a variety of experiments. Absorption measurements have provided the transition energy between the Γ_1^+ ground state and the Γ_4^- excited state.[3] Magnetic circular dichroism experiments have provided the spin-orbit splitting and orbital g factor for the Γ_4^- excited state.[4] For a theoretical study along these directions, we report in the present paper an investigation into the effect of lattice relaxation upon the Γ_1^+ ground state and Γ_4^- excited states of an F center in a lithium fluoride crystal. We will study the properties of the Γ_4^- excited state associated with the absorption process and will, therefore, use the lattice relaxation obtained for the ground state in both the Γ_1^+ ground-state and the Γ_4^- excited-state calculations. We will, however, calculate the Γ_4^- excited-state function using the Hamiltonian for the F-center electron as constructed by placing the F-center electron in the Γ_4^- state. The effect of lattice relaxation on the various absorption properties will also be studied.

Several theoretical studies of the absorption properties of the F-center electron in various host crystals have been performed. Among them, one may point out that Smith has developed techniques for obtaining the spin-orbit splitting[5] and orbital g factor[6] for the excited state and performed explicit calculations for an F center in sodium chloride. Wood and Joy calculated the oscillator strength for an F-center absorption in potassium chloride.[7] The F-center absorption energy is a direct result from most of the F-center calculations and has been used extensively as a test of the accuracy for different techniques for determining the F-center electronic states.[8] We will show by calculating each of these properties, and comparing our results with experiment, that the LCAO method is, indeed, capable of producing an accurate representation of the F-center electron for both the ground and excited states. The technique also results in a wave function in a convenient form for the evaluation of the experimental properties of the F-center electron.

II. LATTICE RELAXATION

The presence of the F-center defect produces a localized distortion of the lattice near to the vacancy site. When the F-center electron is in the Γ_1 ground state, this lattice relaxation corresponds to a displacement radially inward or outward relative to the vacancy. The wave function for the ground state of the F center is a very localized function (Fig. 2 of Ref. 1) and acts as an effective shield for the positive charge produced by the removal of the fluoride ion at the vacancy site. For this reason one might expect the distortion of atoms in shells beyond the nearest-neighbor atoms to be minimal. We will, therefore, adopt the approximation of neglecting lattice relaxation effects for ions beyond the first (or nearest-neighbor) shell. If we define the lattice vectors $\vec{R}_{1i}$, where i ranges from 1 to 6, to represent the locations of the six nearest-neighbor lithium ions in the perfect lattice, we may represent a radial distortion by placing the nearest neighbors at the points $\epsilon\vec{R}_{1i}$. Following a technique similar to the one developed in the previous work,[1] we write the relaxed F-center Hamiltonian as two terms

$$H = [H_{Fc}^{(1)}]_{\Gamma_1^+} + H', \tag{1}$$

where $[H_{Fc}^{(1)}]_{\Gamma_1^+}$ (defined in Sec. IV of Ref. 1) is the Hamiltonian describing the F-center electron in the ground state with electronic polarization taken into account but no allowance for lattice distortion, while H' corresponds to the effect of lattice relaxation. The H' Hamiltonian, therefore, represents the effect upon the Coulomb and exchange potential produced by the displacement of the lithium ions. The Coulomb part V_D^c of H' can be written in terms of the difference between the contributions from the lithium ions at their relaxed and unrelaxed sites as

$$V_D^c(\vec{r}) = \sum_{i=1}^{6} [V_{\text{Li}}^c(\vec{r} - \epsilon\vec{R}_{1i}) - V_{\text{Li}}^c(\vec{r} - \vec{R}_{1i})], \tag{2}$$

where $V_{\text{Li}}^c(\vec{r})$ is the Coulomb potential produced by the lithium ion. The exchange part (V_D^x) of H' is equal to the difference between the relaxed exchange potential and the unrelaxed exchange potential which, according to the Slater approximation, is proportional to the cubic roots of the electron charge density ρ_{cry} corresponding to the relaxed and unrelaxed configuration, respectively. In other words, we write

$$V_D^x = -3[(3\rho_{cry}^R/8\pi)^{1/3} - (3\rho_{cry}^U/8\pi)^{1/3}], \tag{3}$$

where the superscripts R and U refer to the relaxed and unrelaxed cases, respectively. The quantity ρ_{cry}^U has already been evaluated in Ref. 1 and ρ_{cry}^R is similar to ρ_{cry}^U, but contains the modification in electronic charge produced by the displacement of the lithium ions. The difference is appreciable only in the vicinity of the first shell of ions. The Coulomb and exchange part of H' are then curve fitted using Gaussians to facilitate the evaluation of the multicenter integrals.

The basis functions used in this lattice-relaxation calculation are similar to those used in the previous work. They correspond to basis functions which extend up to the sixth shell of atoms. This basis set includes symmetrized LCAO's of the lithium $1s$ optimized orbitals at the $\epsilon(\frac{1}{2}00)$, $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and $(1\frac{1}{2}0)$ shells, of the fluoride $1s$, $2s$, and $2p$ optimized orbitals at the $(\frac{1}{2}\frac{1}{2}0)$, (100), and $(1\frac{1}{2}\frac{1}{2})$ shells and of seven Li s-type and six Li p-type Gaussian-type orbitals (GTO's) at the relaxed $\epsilon(\frac{1}{2}00)$ shell. The choice of the optimized orbitals and the single Gaussians are described elsewhere.[1] The ϵ parameter indicates that the origin for the basis functions at the first shell has been moved to the relaxed site.

The shift of the origin for the basis functions on the first shell necessitates the calculation of some new matrix elements of the Hamiltonian $H_{Fc}^{(1)}$ over those which were done previously. One must also calculate the matrix elements of H' for all of the basis functions. Techniques for evaluating these matrix elements are similar to those which were used to produce the original defect in the crystal and are described elsewhere.[1]

The secular equation is then constructed using these matrix elements and solved for the energy levels of the electrons in the neighboring atoms up to the sixth shell as well as the energy for the ground-state F-center electron as a function of the lattice relaxation parameter ϵ. Looking at the result one finds a substantial contribution to the shift in the electronic energy produced by the ions in the first shell. As one proceeds further out into the lattice, one finds the second-shell shift to be much smaller and the shifts in succeeding shells to be entirely negligible. The change in the total electronic energy must be added to the Coulomb energy corresponding to the shift in the positions of the six nuclei in the first shell. It was found that the contribution from the lithium ions at the first shell dominated the shift in the total energy, and that the value of ϵ corresponding to the minimum in total energy could be computed to the desired accuracy without including contributions to the shift in total energy from ions beyond the first shell. The calculated change in total energy produced for relaxations ϵ of 0.99, 0.98, and 0.97 are −0.59, −1.25, and +5.91 a.u., respectively. The minimum occurs for an ϵ value of 0.98 and corresponds to an inward contraction of 2% of the nearest-neighbor separation. The energy for the ground state of the F-center electron corresponding to this relaxation is −0.261 a.u. This is a shift downward of −0.012 a.u. from its unrelaxed value of −0.249 a.u.

It is interesting to investigate the various contributions to this shift in total energy. The ions in the first shell produce a shift of −1.25 a.u. over the unrelaxed configuration. The ions in the second shell produce a shift of the order of 0.2 a.u. The only other non-negligible contribution results from the shift of −0.012 a.u. in the color center electron, the contributions beyond the second shell being unimportant.

III. Γ_4^- EXCITED STATE AND OSCILLATOR STRENGTH

In order to investigate many of the experimental properties of the F-center electron, it is necessary to obtain an accurate excited-state wave function. We must, therefore, construct the appropriate Hamiltonian for the Γ_4^- excited state; namely, in calculating the charge density for the Coulomb and exchange potential we should populate the Γ_4^- F-center electronic state instead of the ground state Γ_1^+ as was done in Ref. 1 (see Sec. III D and Sec. V of Ref. 1). In order to maintain the octahedral rotational symmetry of the Hamiltonian about the vacancy site, the Γ_4^- F-center charge density was constructed as

$$\rho_F(\Gamma_4^- | \vec{r}) = \tfrac{1}{3}\left[|\Psi(\Gamma_{4x}^- | \vec{r})|^2 + |\Psi(\Gamma_{4y}^- | \vec{r})|^2 + |\Psi(\Gamma_{4z}^- | \vec{r})|^2 \right], \tag{4}$$

where $\Psi(\Gamma_{4x}^- | \vec{r})$, $\Psi(\Gamma_{4y}^- | \vec{r})$, and $\Psi(\Gamma_{4z}^- | \vec{r})$ are the three components of the Γ_4^- wave function which transform like x, y, and z, respectively, about the vacancy site. These wave functions were obtained from the unoccupied state calculation described in Ref. 1. This charge density was then added to the charge density of all of the ions in the crystal in order to obtain the total charge density for the evaluation of the Coulomb and exchange potential. The charge density associated with the ions in the crystal calculated in Sec. IV of Ref. 1, in which the electronic polarization due to the vacancy and the F-center electron has been taken into account, is used here. Strictly speaking, this is an approximation since the F-center electron is placed in the Γ_1^+ state for the polarization calculation in Ref. 1, whereas we are at present dealing with an F center in the Γ_4^- state. The difference between the polarization caused by a Γ_1^+ electron and by a Γ_4^- electron may be expected to be small relative to the total electronic polarization produced by the vacancy and the F-center electron. Furthermore, since it has been shown in Ref. 1 that the major polarization effect occurs in the fluoride ions in the second shell (the first-shell lithium ions being much less polarizable), it is interesting to note the close similarity between the charge density of the Γ_1^+ electron and the Γ_4^- electron for distances r greater than the location of the ions in the first shell. A plot of $\rho_F(\Gamma_4^- | \vec{r})$ and $\rho_F(\Gamma_1^+ | \vec{r})$ along the [110] direction in Fig. 1 indicates that by the time one gets to the fluoride ions at the second shell (0.71) that the charge densities are very similar. For these reasons the use of the result of electronic polarization derived in Ref. 1 is justifiable. The effect of the 2% lattice relaxation of the first shell lithium ions is incorporated into the Hamiltonian using techniques described in Sec. II.

The basis functions included symmetrized LCAO's of the lithium 1s optimized orbitals on

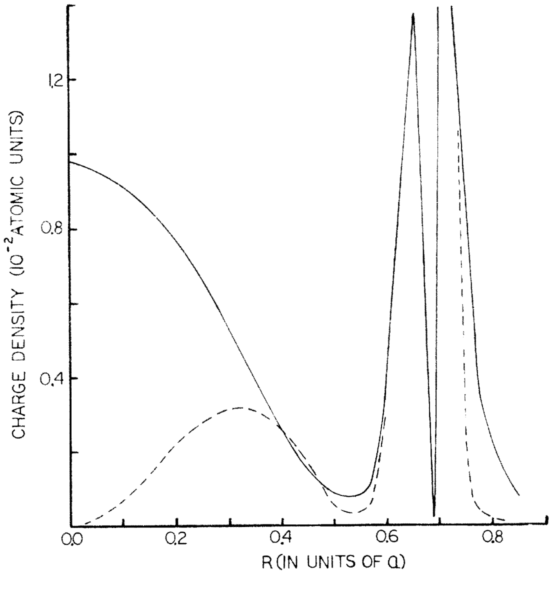

FIG. 1. Comparison of the charge density along the [110] direction obtained from a Γ_1^+ ground-state F-center electron (solid curve) with the corresponding charge density from a Γ_4^- excited-state F-center electron (dashed curve). The abscissa is in units of the lattice constant of the crystal. Note the close similarity of the curves near to the fluoride ion (0.71).

the first, third, and fifth shells, of the fluoride $1s$, $2s$, $2p$ optimized orbitals at the second, fourth, and sixth shells as well as seven lithium s-type and six lithium p-type GTO's at the first shell. We evaluated the matrix elements of the secular equation using this basis set and obtained a value of −0.083 a.u. for the energy of the Γ_4^- excited-state F center. This corresponds to an absorption energy of 4.85 eV, which is in excellent agreement with the experimental value of 4.82 eV.[3] The apparent agreement to within 0.03 eV should not be taken completely literally, as it is probably smaller than the uncertainty of both the experimental and theoretical values. In Fig. 2, a plot of the wave function $\Psi(\Gamma_{4x}^-|\vec{r})$ is compared along the x direction with a similar plot of the Γ_4^- wave function obtained previously using an unoccupied-state calculation without the inclusion of the effect of lattice relaxation. One notes that the two curves are almost the same except in the region near the lithium ions. This deviation is produced by the lattice relaxation.

The oscillator strength for the transition from the ground state to the excited state for the F-center electron is obtained using Eq. (3.2) of Ref. 7 as

$$f = 2\Delta E\, |\langle \Gamma_1^+ | z | \Gamma_{4z}^- \rangle|^2 , \tag{5}$$

where ΔE is the absorption energy in Hartrees. Using this formula we obtained a value of 0.66 for the oscillator strength. This may be compared with an experimental value of 0.54 obtained by Bate and Heer.[8] Their value was obtained from the Smakula equation using the actual area under the F-center absorption band. It has been pointed out by Smith and Dexter[9] that since the F-center defect does not have the same polarization as the host crystal, that one might question the validity of the use of a Lorentz local field in the Smakula equation. They determined that the effective field near the F center was considerably smaller than that predicted by a Lorentz local field model. Since the reciprocal of the square of the local field is used in determining the experimental oscillator strength, one might expect to obtain a larger value than 0.54 if he used the proper local field. For example if one adopts the Onsager approach to the local field[9] instead, the "experimental" value would be revised to 0.69. In light of this, one can say that the agreement of our value of 0.66 with experiment is within the uncertainty of the latter.

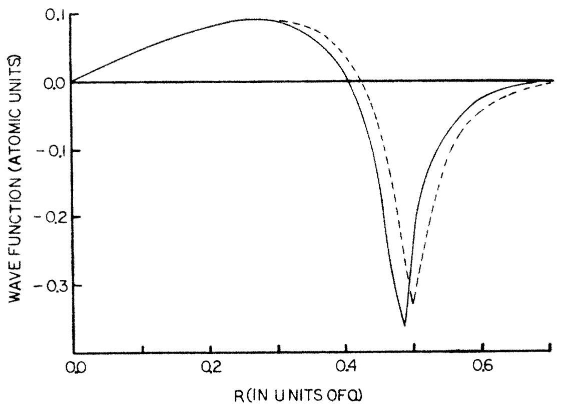

FIG. 2. Comparison of the Γ_4^- excited-state F-center wave function obtained from the occupied-state calculation including the effects of lattice relaxation (solid curve) with the corresponding wave function obtained from the unoccupied-state calculation neglecting effects of lattice relaxation (dashed curve). The abscissa is in units of the lattice constant of the crystal. The primary shift is produced by the lattice relaxation of the lithium ion (near 0.5).

IV. ORBITAL g FACTOR FOR ORBITAL ZEEMAN SPLITTING OF THE Γ_4^- EXCITED STATE

The orbital Zeeman splitting of the F center (g_{orb}) can be expressed in terms of the matrix element for the z component of angular momentum (L_z) corresponding to the excited state Γ_4^- wave function which transforms like $(x+iy)/\sqrt{2}$ about the vacancy site. We may, therefore, write

$$\begin{aligned} g_{\text{orb}} &= \tfrac{1}{2}\langle \Gamma_{4x}^- + i\Gamma_{4y}^- | L_z | \Gamma_{4x}^- + i\Gamma_{4y}^- \rangle \\ &= i\langle \Gamma_{4x}^- | L_z | \Gamma_{4y}^- \rangle , \end{aligned} \tag{6}$$

taking advantage of the fact that g_{orb} must be real and that the matrix elements of L_z are Hermitian. The basis functions for $\Psi(\Gamma_{4x}^-|\vec{r})$ and $\Psi(\Gamma_{4y}^-|\vec{r})$ which are used in the above equation are expressed in terms of Gaussian orbitals centered about atoms in shells near to the vacant site. This means that the matrix element for L_z in Eq. (6) reduces to sums over multicenter integrals involving Gaussian functions. We must, therefore, evaluate the general class of integrals

$$\langle \chi(A, \alpha_1, l_1, m_1, n_1) | L_z | \chi(B, \alpha_2, l_2, m_2, n_2) \rangle ,$$

where $\chi(A, \alpha, l, m, n)$ represents a general Gaussian function centered about A and has the form of

$$\begin{aligned} \chi(A, \alpha, l, m, n) &= (x - A_x)^l (y - A_y)^m (z - A_z)^n \\ &\quad \times \exp(-\alpha |\vec{r} - \vec{A}|^2) \\ &= x_A^l y_A^m z_A^n \exp(-\alpha r_A^2) . \end{aligned} \tag{7}$$

By performing the appropriate differentiation we obtain the L_z matrix element in terms of the following six multicenter overlap integrals:

$$
\begin{aligned}
&\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|L_z|\,\chi(B,\alpha_2,l_2,m_2,n_2)\rangle \\
&\quad=\{m_2\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,\chi(B,\alpha_2,l_2+1,m_2-1,n_2)\rangle+m_2B_x\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,\chi(B,\alpha_2,l_2,m_2-1,n_2)\rangle \\
&\qquad-2\alpha_2B_x\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,\chi(B,\alpha_2,l_2,m_2+1,n_2)\rangle-l_2\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,\chi(B,\alpha_2,l_2-1,m_2+1,n_2)\rangle \\
&\qquad-m_2B_y\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,\chi(B,\alpha_2,l_2-1,m_2,n_2)\rangle+2\alpha_2B_y\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,\chi(B,\alpha_2,l_2+1,m_2,n_2)\rangle\}/i. \qquad (8)
\end{aligned}
$$

The evaluation of the multicenter overlap integrals of this form is described elsewhere.[10]

We computed the matrix elements for each of the Gaussians and summed over the appropriate combinations of the Gaussians to evaluate g_{orb} using Eq. (6). We obtained a value of 0.53 for g_{orb} which compares favorably with the experimental value of 0.59 obtained by Osborne and Stephens using magnetic circular dichroism.[4]

Smith has discussed much of the experimental work in determining the orbital g factor of an F center in an alkali-halide crystal.[6] He states that if one confines himself to values of g_{orb} obtained by moments analysis of the experimental data,[11] that g_{orb} for the excited F center has a value of one or slightly less than one for most of the alkali-halide crystals. This is interesting since a value of one would be expected for a bound electron in a Γ_4^- state in the absence of a host crystal (for example, an atomic p-state electron). The notable exception to this occurs in lithium fluoride, where the value we obtained for g_{orb} for the excited F center is 0.53. It is, therefore, interesting to examine the various contributions to g_{orb}. In order to better understand the different contributions we will split the Γ_4^- excited-state wave function into four parts: (i) the single Gaussians at the first shell which produce the envelope of the F-center function; (ii) the portion of the F-center wave function which results from its orthogonality to the lithium 1*s* core states at the first shell; (iii) the portion of the F-center wave function which results from its orthogonality to the fluoride 1*s* and 2*s* core states at the second shell; and (iv) the portion of the F-center wave function produced by orthogonality to the fluoride 2*p* states. The contribution of the envelope from the first part gives a value for g_{orb} of 1.31. The orthogonality to the lithium 1*s* then reduces this by 0.26 to a value of 1.05. The orthogonality to the fluoride 1*s* and 2*s* states then reduces this by 0.50 to a value of 0.55. The orthogonality to the 2*p* fluoride states produces some fluctuation; however, the different terms cancel each other. The main reason for the fact that g_{orb} is low in an excited F center in lithium fluoride is, therefore, due to the cancellation associated with the orthogonality of the F-center wave function to the lithium 1*s* core electrons at shell one and the fluoride 1*s* and 2*s* core electrons at shell two. The contribution from the third and fourth shells to g_{orb} is insignificant. It may, therefore, be possible to neglect contributions from shells out beyond the second shell in calculating the orbital g factor. This will provide some simplification in the computational procedure.

V. SPIN-ORBIT SPLITTING OF THE EXCITED-STATE Γ_4^- ELECTRON

The Hamiltonian for the spin-orbit interaction is given in atomic units as

$$h_{\text{so}}=-\vec{S}\cdot(\vec{E}\times\vec{p})/2c^2, \qquad (9)$$

where c is the velocity of light, $\vec{S}$ is the electron spin operator, $\vec{p}$ is the momentum operator, and $\vec{E}$ is the electric field through which the electron moves. Since the crystal electric field is greatest in the immediate vicinity of the nuclei and the charge distribution is nearly spherically symmetric near the nuclei, we may approximate the spin-orbit Hamiltonian in a manner similar to Smith[5] and obtain

$$
\begin{aligned}
h_{\text{so}}&=\frac{1}{2c^2}\sum_I|\vec{r}-\vec{R}_I|^{-1}\left(\frac{\partial V_I}{\partial(\vec{r}-\vec{R}_I)}\right)\vec{L}_I\cdot\vec{S} \\
&=\frac{1}{2c^2}\sum_I\xi(\vec{r}-\vec{R}_I)\vec{L}_I\cdot\vec{S}, \qquad (10)
\end{aligned}
$$

where the index I labels the ion at the location $\vec{R}_I$ and V_I is the potential near the Ith ion. $\vec{L}_I$ is the orbital angular momentum operator with respect to the origin on the Ith ion $[\vec{L}_I=(\vec{r}-\vec{R}_I)\times\vec{p}]$. The spin-orbit splitting ΔE_{so} corresponds to the difference between the energy of the $P_{3/2}$ and the $P_{1/2}$ state for the excited F-center electron. Or, alternatively,[5] one writes

$$\Delta E_{\text{so}}=3\langle P_{3/2}|h_{\text{so}}|P_{3/2}\rangle.$$

This equation can be further reduced to

$$\Delta E_{\text{so}}=\frac{3}{8c^2}\langle\Gamma_{4x}^-+i\Gamma_{4y}^-|\sum_I\xi(\vec{r}-\vec{R}_I)(\vec{L}_I)_z\;|\Gamma_{4x}^-+i\Gamma_{4y}^-\rangle, \qquad (11)$$

where Γ_{4x}^- and Γ_{4y}^- have the form defined in Sec. IV and $(\vec{L}_I)_z$ is the z component of the orbital angular momentum about the Ith ion. Using techniques described in Sec. IV this may be reduced to

$$\Delta E_{\mathrm{so}} = \frac{3}{4c^2}\langle \Gamma_{4x}^- \,|\, \sum_I \xi(\vec{r} - \vec{R}_I)(\vec{L}_I)_z |\Gamma_{4y}^-\rangle \;. \tag{12}$$

We must now obtain a form for the potential near the ions in order to evaluate the $\xi(\vec{r} - \vec{R}_I)$ terms in Eq. (12). In the region near the nucleus we may expect that $\xi(\vec{r} - \vec{R}_I)$ is due to the Coulomb potential from the Ith nucleus and the electronic charge near this nucleus. Therefore, we may write

$$\xi(r) = \frac{1}{r}\frac{\partial V_{\mathrm{Coul}}}{\partial r} \,. \tag{13}$$

The function $r^3\xi(r)$ is then curve fitted in the region near the lithium ion and the fluoride ion in terms of a superposition of Gaussians. The r^3 weighting of the function $\xi(r)$ is provided to facilitate the curve fitting procedure by making the function finite at the origin. We then curve fit

$$r^3\xi^{\mathrm{Li}}(r) = \sum_j a_j^{\mathrm{Li}} e^{-\beta_j r^2}$$

and (14)

$$r^3\xi^{\mathrm{F}}(r) = \sum_j a_j^{\mathrm{F}} e^{-\gamma_j r^2},$$

where $\xi^{\mathrm{Li}}(r)$ and $\xi^{\mathrm{F}}(r)$ correspond to the function in Eq. (13) centered about the lithium and fluoride ions, respectively, and the a_j^{Li}, a_j^{F}, β_j, γ_j terms are obtained by a least-squares curve-fitting procedure. Using the functions from Eq. (14) the spin-orbit splitting in Eq. (12) reduces to sums over three center integrals of the form

$$\langle \chi(A, \alpha_1, l_1, m_1, n_1)\,|(1/r_c^3)\exp(-\beta r_c^2) L_z^c \times |\chi(B, \alpha_2, l_2, m_2, n_2)\rangle, \tag{15}$$

where $\chi(A, \alpha_1, l_1, m_1, n_1)$ and $\chi(B, \alpha_2, l_2, m_2, n_2)$ are described in Sec. IV, $(1/r_c^3)\exp(-\beta r_c^2)$ is a term in the curve fit of $\xi(\vec{r} - \vec{C})$ for the ion centered about the point $\vec{C}$, and L_z^c is the z component of angular momentum about $\vec{C}$. Techniques for evaluating this integral are described in the Appendix. It was found that the primary contribution to the spin-orbit splitting resulted from the integrals in Eq. (15) corresponding to the single-center case $\vec{A} = \vec{B} = \vec{C}$. In this case the matrix element is similar to the ones found in the spin-orbit splitting of atomic systems. By analogy with atomic systems one knows that the single center matrix element gives no contribution if $\chi(B, \alpha_2, l_2, m_2, n_2)$ is an s-type Gaussian, therefore, one expects that a large contribution to the spin-orbit splitting should result from p-type Gaussians. Indeed, the major contribution to the spin-orbit splitting of Γ_4^- excited-state function is produced by single-center integrals centered about the fluoride ions at the second shell. This effect is a direct result of the orthogonality of the Γ_4^- function to the $2p$ atomic-like orbitals centered about the fluoride ions. The two-centered integrals $\vec{A} = \vec{C} \neq \vec{B}$ or $\vec{A} \neq \vec{B} = \vec{C}$ produced a much smaller effect (less than 12%) and the contribution from the three-center integrals could be neglected. We obtained a value for the spin-orbit splitting ΔE_{so} of 28 cm^{-1}. This is in excellent agreement with the experimental value of 27 cm^{-1} obtained by Osborne and Stephens.[4]

VI. DISCUSSION

We have shown that the lattice relaxation of the neighboring ions to the defect may be easily incorporated into the LCAO formalism. By putting in the lattice relaxation as well as the electronic polarization effects we have performed *ab initio* calculations of the electronic states of the Γ_1^+ ground-state and Γ_4^- excited-state F-center electron. The accuracy of the wave functions is evident from the excellent agreement of the calculated absorption properties with experiment. The determination of these properties is greatly simplified by the ease of evaluating multicenter integrals when the orbitals are expressed in terms of Gaussians.

A summary of the absorption properties we have calculated for the F-center electron is presented in Table I. The first row in the table corresponds to the wave functions obtained with the inclusion of the effects of lattice relaxation, while the second column represents a similar calculation without lattice relaxation. Since the lattice relaxation is small (only 2% of the nearest-neighbor separation) one does not expect that it will change the electronic properties of the F center drastically. It does, however, shift the oscillator strength and the spin-orbit splitting by almost 10%.

Now that we have obtained the Γ_4^- excited-state wave function using the proper Hamiltonian (see Sec. III) we may compare the absorption properties obtained using an occupied state calculation with those obtained using the unoccupied state calculation of Ref. 1. The calculation of both of these Γ_4^- wave functions did not include lattice distortion. In the unoccupied state calculation we obtained values of 0.68, 0.55, 26 cm^{-1} for the oscillator strength, orbital g factor, and spin-orbit splitting while the corresponding values in the more accurate occupied state calculation were 0.72, 0.55, 25 cm^{-1}. The good agreement of the absorption properties using these two different sets of wave functions indicates that populating the excited-

TABLE I. Examination of the effects of lattice relaxation upon the optical absorption properties of the *F*-center electron.

	Absorption energy (eV) ($\Gamma_1^+ - \Gamma_4^-$)	Oscillator strength	Spin-orbit splitting (cm^{-1})	Orbital *g* factor
With lattice relaxation	4.85	0.66	28	0.53
No lattice relaxation	4.71	0.72	25	0.55

state wave function in constructing the charge density for the Hamiltonian for the excited-state *F* center does not shift these absorption properties significantly over populating the ground-state wave function. If one did not have to change the Hamiltonian for the calculation of the Γ_4^- excited state from the one for the Γ_1^+ ground state, this would represent a considerable simplification in the computation. However, ultimately one should test this effect for other cases before assuming it to be true for the *F*-center electrons in other crystals.

The LCAO method has shown itself to be a very useful technique in describing the properties of an *F*-center defect. It may be utilized to provide accurate values for the energies of the electronic states of the *F* center and results in a wave function in a convenient form for the determination of other electronic properties for comparison with experiment.

APPENDIX

The integral to be evaluated is

$$\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,[\exp(-\beta r_c^2)/r_c^3]L_z\,|\,\chi(B,\alpha_2,l_2,m_2,n_2)\rangle$$

$$\begin{aligned}&=[m_2\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,x_c\exp(-\beta r_c^2)/r_c^3\,|\,\chi(B,\alpha_2,l_2,m_2-1,n_2)\rangle\\ &\quad-2\alpha_2\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,x_c\exp(-\beta r_c^2)/r_c^3\,|\,\chi(B,\alpha_2,l_2,m_2+1,n_2)\rangle\\ &\quad-l_2\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,y_c\exp(-\beta r_c^2)/r_c^3\,|\,\chi(B,\alpha_2,l_2-1,m_2,n_2)\rangle\\ &\quad+2\alpha_2\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,y_c\exp(-\beta r_c^2)/r_c^3\,|\,\chi(B,\alpha_2,l_2+1,m_2,n_2)\rangle]/i,\end{aligned}$$

where we have substituted for the *z* component of angular momentum and performed the appropriate differentiation. Typical of the four integrals in the above expression which give nonzero contribution is

$$\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,x_c\exp(-\beta r_c^2)/r_c^3\,|\,\chi(B,\alpha_2,l_2,m_2,n_2)\rangle,$$

where $l_1, l_2, m_1, m_2, n_1, n_2$ are equal to or greater than zero. This integral may be evaluated in a manner similar to the determination of the nuclear attraction integral in Eq. 3.8 of Ref. 9. The result is

$$\langle\chi(A,\alpha_1,l_1,m_1,n_1)\,|\,x_c\exp(-\beta r_c^2)/r_c^3\,|\,\chi(B,\alpha_2,l_2,m_2,n_2)\rangle$$

$$=\lambda\sum_{t_1=0}^{l_1+l_2} f_{t_1}(l_1,l_2,\overline{AD}_x,\overline{BD}_x)\sum_{t_2=0}^{m_1+m_2} f_{t_2}(m_1,m_2,\overline{AD}_y,\overline{BD}_y)\sum_{t_3=0}^{n_1+n_2} f_{t_3}(n_1,n_2,\overline{AD}_z,\overline{BD}_z)I',$$

where $f_{t_1}(l_1,l_2,\overline{AD}_x,\overline{BD}_x)$ is defined in Eq. 3.2 of Ref. 9; $\overline{AD}_x, \overline{AD}_y, \overline{AD}_z$ are components of $\vec{\mathrm{AD}}=\vec{\mathrm{D}}-\vec{\mathrm{A}}$; $\overline{BD}_x, \overline{BD}_y, \overline{BD}_z$ are components of $\vec{\mathrm{BD}}=\vec{\mathrm{D}}-\vec{\mathrm{B}}$; and

$$\lambda=\exp(-\alpha_1\alpha_2\gamma^{-1}\overline{AB}^2-\gamma\beta\omega^{-1}\overline{CP}^2),\quad \gamma=\alpha_1+\alpha_2\,,\quad \omega=\gamma+\beta,$$

$$\overline{AB}=|\vec{\mathrm{B}}-\vec{\mathrm{A}}|,\quad \vec{\mathrm{P}}=\gamma^{-1}(\alpha_1\vec{\mathrm{A}}+\alpha_2\vec{\mathrm{B}}),\quad \vec{\mathrm{D}}=\omega^{-1}(\gamma\vec{\mathrm{P}}+\beta\vec{\mathrm{C}}),$$

and

$$I'=\int(x-D_x)^{t_1}(y-Dy)^{t_2}(z-Dz)^{t_3}\exp(-\omega\,|\vec{\mathrm{r}}-\vec{\mathrm{D}}\,|^2)x_c r_c^{-3}\,d\tau.$$

The I' integral may be evaluated in terms of the incomplete Γ function as

$$I' = 4\pi\left\{\left[\sum_{q_1}\overline{CD}_x V(t_1, q_1, \overline{CD}_x)\sum_{q_2} V(t_2, q_2, \overline{CD}_y)\sum_{q_3} V(t_3, q_3, \overline{CD}_z)\sum_{k}(-1)^k\binom{q_1+q_2+q_3}{k}F_\nu(\omega\overline{CD}^2)\right]\right.$$
$$-\left[\sum_{p_1}2(p_1+1)(t_1-2p_1-1)^{-1}V(t_1,p_1+1,\overline{CD}_x)\overline{CD}_x\right.$$
$$\left.\left.\times\sum_{p_2}V(t_2,p_2,\overline{CD}_y)\sum_{p_3}V(t_3,p_3,\overline{CD}_z)\sum_{j}(-1)^j\binom{p_1+p_2+p_3}{j}F_\delta(\omega\overline{CD}^2)\right]\right\},$$

where

$$\overline{CD}_i = D_i - C_i \quad\text{and}\quad i = x, y, z,$$

$$V(t,q,\overline{CD}_i) = \frac{(-\overline{CD}_i)^{t-2q}t!}{(4\omega)^q(t-2q)!\,q!},$$

$$\nu = t_1 + t_2 + t_3 - 2q_1 - 2q_2 - 2q_3 + k + 1,$$

$$\delta = t_1 + t_2 + t_3 - 2p_1 - 2p_2 - 2p_3 + j,$$

and

$$\binom{q_1+q_2+q_3}{k}\quad\text{and}\quad\binom{p_1+p_2+p_3}{j}$$

represent binomial coefficients, $F_\nu(\omega\overline{CD}^2)$ is the incomplete Γ function defined in Eq. (3.3) of Ref. 9.

The summations over q_1, q_2, q_3 range from 0 to $[\frac{1}{2}t_1]$, 0 to $[\frac{1}{2}t_2]$, and 0 to $[\frac{1}{2}t_3]$, respectively, where $[\frac{1}{2}t]$ indicates the largest integer less than $\frac{1}{2}t$. The summations over p_1, p_2, p_3 range from 0 to $[(t_1-1)/2]$, 0 to $[\frac{1}{2}t_2]$, and 0 to $[\frac{1}{2}t_3]$, respectively.

One now has the techniques necessary to evaluate the matrix element in Eq. (15).

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