

be described. The method is illustrated in Fig. 4, where the second-harmonic power at 9 GHz generated from a 4.5-GHz fundamental is plotted as a function of distance. The calibrating echoes generated and detected at 9 GHz are plotted in an identical manner, their $a=0$ intercept being normalized to equal that of the second harmonic. The zero intercept of the second harmonic measures the nonlinearity in the generating process, while the increase of the second harmonic above the calibrating echoes Δ is a measure of the volume nonlinearity.

The detected second-harmonic microwave power $P_{2m}(a)$ is given by

$$P_{2m}(a) = IF_2(a)[P_2(a) + P_2(0)e^{-2a/l_2}], \quad (\text{B1})$$

where I is the insertion loss or electromechanical conversion efficiency, $F_2(a)$ is the destructive interference factor, which has the property of being equal to one at $a=0$,⁸ and $P_2(a)$ and $P_2(0)$ are the acoustic powers corresponding to the volume and surface terms $S_2(a)$ and $S_2(0)$, respectively. The microwave calibrating pulse $P_c(a)$ which is surface generated and detected at 9 GHz, is given by

$$P_c(a) = IF_2(a)P_2(0)e^{-2a/l_2}, \quad (\text{B2})$$

where $F_2(a)$ is the same as in Eq. (B2), since the frequency is the same. For the present purposes the absolute power level of $P_c(a)$ is arbitrary, and we have chosen $P_c(a)$ in Eq. (B2) to be equal to $P_2(0)$ at $a=0$, as is shown graphically in the top part of Fig. 4. $F_2(a)$ is now eliminated by dividing Eq. (B1) by Eq. (B2):

$$[\Delta(a) - 1]P_2(0) = P_2(a)e^{2a/l_2}, \quad (\text{B3})$$

where $\Delta(a) = P_{2m}(a)/P_c(a)$.

It is convenient for a graphical plot of the experimental results to take the square root of Eq. (B3) and to define a new quantity $S_2'(a)$:

$$\begin{aligned} S_2'(a) &= (\Delta(a) - 1)^{1/2} S_2(0) \\ &= \frac{1}{4} \Gamma S_1^2 k_1 \left[\frac{1 - e^{-2a/l_1 + a/l_2}}{2l_1^{-1} - l_2^{-1}} \right]. \end{aligned} \quad (\text{B4})$$

Here we have used Eqs. (12) and (20). Equation (B4) thus gives a relation for the volume nonlinearity which is independent of the end-surface nonparallelism. Equations (21a) and (21b) in the text come from Eq. (B4).

F Center in Ionic Crystals: Semicontinuum Polaron Models

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The states of the F center are considered on the basis of models which treat the movement of the nearest neighbors to the F center and the F electron in a self-consistent manner. The lattice is described in terms of a classical ionic-crystal theory, and the F electron is treated according to the semicontinuum polaron theory. The absorption energy, the emission energy, the lifetime of the first excited state, the thermal activation energies, and the Huang-Rhys factor are evaluated for two models (Hartree and quasiadiabatic) which differ in the evaluation of the optical polarization. It is shown that the Hartree semicontinuum polaron model agrees best with the experimental results for NaCl, KCl, CaF₂, SrF₂, and BaF₂. In addition, these models show that among the above quantities the thermal activation energies and the lifetime of the first excited state are most sensitive to the physical content of a given model.

I. INTRODUCTION

THE F center in ionic crystals consists of an electron localized about a vacant negative-ion site. Even though the F center is one of the simplest defects which can occur in ionic crystals, calculations of its optical properties have been a challenge to theoreticians ever since Tibbs first undertook such calculations for the alkali halides.¹ Most calculations of the F -center electronic structure consider the ground state and the low-lying excited states in a rigid lattice, are valid only

for optical-absorptive transitions, and view the lattice either as a continuum or as an array of point ions.²⁻⁴ However, electronic polarization (distortion of the closed shells of the ions) and ionic polarization (displacement of the ions) are present and are factors which influence the energy levels of the F electron. Only a few authors have attempted to include these polarizations

² S. I. Pekar, Usp. Fiz. Nauk **50**, 197 (1953).

³ B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

⁴ J. K. Kubler and R. J. Friauf, Phys. Rev. **140**, A1742 (1965).

¹ S. R. Tibbs, Trans. Faraday Soc. **35**, 147 (1934).

in a consistent manner with the F -electron problem.⁵⁻⁹ For example, taking into account the detailed atomic structure of the crystal, the polarization effects, and the lattice relaxation, Kojima⁵ uses a variational procedure to study the F center in LiF. Recent data on the F -center luminescence are not so easy to analyze as data associated with optical absorption.¹⁰⁻¹² In particular, the emission band for many of the alkali halides exhibits a large Stokes shift, and the first excited state has a lifetime which is greater than the lifetime which one would expect by comparison with atomic spectra.¹³⁻¹⁶ These observations strongly suggest that polarization of the lattice and particularly the relaxation of the ions in the immediate vicinity of the defect have a pronounced effect on the electronic states of the F center.

The measurements of the optical absorption, of the emission, and of the lifetime of the first excited state are the more conceptually elementary experiments which one may perform on the F center. All theoretical treatments of the above experiments consider models with mathematical descriptions which are by necessity much simpler than those of the real F center. We usually do not know the exact solution to any physically reasonable model of the F center, and hence we must resort to approximations. Thus we usually have approximate solutions to a model problem. Consequently two questions arise, namely, how well do the approximate solutions give the exact properties of the model, and how well does the model represent the properties of the real system? In this paper, we shall attempt to make statements concerning both of the above questions.

Two basic models from which we may calculate the electronic structure of the F center exist. For brevity, we shall refer to these models as Hartree (or Hartree-Fock) polarizable-ion models (HFPI) and semi-continuum polaron models (SCP). Both types of models reduce a many-electron problem to an effective one-electron (the F electron) problem and treat the lattice polarizations and the F electron in a self-consistent manner. They differ most profoundly in their treatment of the effective interaction between the F electron and the infinite mass hole (the anion vacancy) due to ionic polarization. The HFPI models assume that the F -

electron orbit will not become so large (or, equivalently, that the F electron will not move so slowly) that the ionic polarization can follow the F -electron motion. The SCP models contain an approximate expression for the F -electron-vacancy interaction which is based upon the Haken theory of Wannier excitons,^{17,18} and which thereby allows the ionic polarization to follow to some extent the motion of the F electron when the latter is in a large orbit (or is moving slowly).

The SCP models require a greater amount of experimental input data than do the HFPI models. Both types require the lattice structure, the lattice constant, the repulsive-interaction parameters, the high-frequency dielectric constant ϵ_∞ , and the static dielectric constant ϵ_0 . In addition, however, the SCP models use the longitudinal optical-lattice-vibration frequency ω_l , the Mott-Littleton radius R , the electron effective mass m^* due only to the electron-electron interaction in a periodic lattice potential, and the bottom of the conduction band χ . We readily obtain from the literature values for ω_l and R in ionic crystals. We know the values of m^* and χ only reasonably well for NaCl and KCl, and there is little literature for these quantities in the other ionic crystals. The reason is mainly because measurements of m^* and χ by present techniques require the presence of a large number of electrons in the conduction band. This condition is most difficult to achieve in insulators (ionic crystals) with relatively large band gaps. Another complication arises from the fact that one measures in many of the more common experiments the effective mass due to both the electron-electron interactions and the electron-polarization interactions m^{**} , and that m^{**} depends upon m^* and the coupling constant¹⁹

$$\lambda = e^2 \left\{ (1/\epsilon_\infty) - (1/\epsilon_0) \right\} (m^*/2\hbar^3\omega_l)^{1/2}. \quad (1)$$

On the other hand, many of the HFPI models are computationally much more elaborate than the SCP models. Hence the SCP models demand less sophisticated computer programs and the HFPI models frequently demand less experimental input data.

The experience which we have gained from examining the theoretical predictions of the above models suggests that the optical-absorption energy is rather insensitive to the physics contained in a given model. As long as a model states that when the F electron is near the anion vacancy, it moves in a potential well of depth about the Madelung potential and of width about the lattice spacing, the model will give correct order-of-magnitude or better answers for the absorption energy. When one allows the nearest nearest-neighbor ions to move self-consistently from their perfect lattice sites in order to accommodate the F electron, then the emission energy

⁵ T. Kojima, *J. Phys. Soc. Japan* **12**, 918 (1957).

⁶ R. F. Wood and J. Koringa, *Phys. Rev.* **123**, 1138 (1961).

⁷ R. F. Wood and H. W. Joy, *Phys. Rev.* **136**, A451 (1964).

⁸ W. B. Fowler, *Phys. Rev.* **135**, A1725 (1965). In this paper, the author asserts that the nearest neighbors (Na ions) move radially outward by 10% of the nearest-neighbor distance for the relaxed excited state $|\beta_1, \sigma_1\rangle$.

⁹ S. Wang, *Phys. Rev.* **153**, 939 (1967).

¹⁰ D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. VI.

¹¹ J. J. Markham, *Rev. Mod. Phys.* **31**, 956 (1959).

¹² J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Co., New York, 1962).

¹³ R. K. Swank and F. C. Brown, *Phys. Rev.* **130**, 34 (1963).

¹⁴ G. Spinolo and F. C. Brown, *Phys. Rev.* **135**, A450 (1964).

¹⁵ F. Luty and W. Gebhardt, *Z. Physik* **169**, 475 (1962).

¹⁶ C. C. Klick, D. A. Paterson, and R. S. Knox, *Phys. Rev.* **133**, A1717 (1964).

¹⁷ H. Haken, *Nuovo Cimento* **10**, 1230 (1956).

¹⁸ H. Haken, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, London, 1963), p. 295.

¹⁹ D. Pines, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, London, 1962), p. 33.

is only slightly more sensitive than the absorption energy to the physics contained in the model. The lifetime of the relaxed first excited state is the only quantity among the above three which is sensitive to the physical details of the model.

Researchers have examined the F -center absorption in many systems; for example, the alkali halides (NaCl, KCl, etc.), the alkaline earth fluorides (CaF₂, SrF₂, BaF₂, etc.), and some alkaline oxides (MgO, CaO, etc.). Unfortunately, emission and lifetime measurements are extremely rare for the latter two groups and exist mainly for only the alkali halides. Because the true worth of a model is often determined by how well its predictions agree with experiment, the theorist must exercise great caution when choosing among possible models for the latter two groups.

In this paper, we shall discuss two semicontinuum polaron models. These two SCP models differ in their treatment of the optical polarization which occurs when the F electron is near the vacancy. One model, SCP(QA), asserts that the core-electron dipoles point towards the instantaneous position of the F electron when the latter is near the vacancy [quasiadiabatic approximation (QA)]; and the other model, SCP(HF), asserts that the core-electron dipoles point towards the mean position of the F electron [Hartree or Hartree-Fock approximation (HF)]. We shall see that the latter approximation agrees best with the experiments for NaCl and KCl. We intend to treat the Hartree (Hartree-Fock) polarizable-ion models in a future paper.

The method of the present calculations is essentially a two-parameter variational method. We assume a trial wave function which has a suitable symmetry and which contains a variational parameter η . We then compute the ion displacements σ which are consistent with the assumed trial wave function. In this way, we obtain the total energy of the crystal as a function of η and σ . We finally minimize the total energy as a function of η and σ to obtain the F -electron wave function and the lattice configuration.

In Sec. II, we briefly apply the Born-Oppenheimer approximation to the F center and discuss some properties of the low-lying F -center electron states. Section III contains a discussion of the lattice energy and the important role which next-nearest-neighbor repulsive interactions might play under certain conditions. We present, in Sec. IV, the two semicontinuum polaron models of the F center and, in Sec. V, briefly list additional expressions for some experimentally measured quantities and for an estimate of how well we expect the trial wave functions to exhibit the exact properties of the model. In Sec. VI, we tabulate the numerical results and show that the semicontinuum polaron model with the Hartree evaluation for the optical polarization SCP(HF) gives reasonable agreement with the experimental measurements in the alkali halides NaCl and KCl. We also tabulate the absorption

results for three alkaline earth fluorides. Within the limitations of the trial wave functions, we discuss, in Sec. VII, our conclusions and compare the SCP(HF) model with the model given in Ref. 8. Finally, in the Appendix, we emphasize special features which obtain when hydrogenic trial wave functions are used to compute the total energy of the F center.

II. PRELIMINARIES

In order to gain some insight into our treatments of the F center in ionic crystals, we first consider the Schrödinger equation for the system. Neglecting spin-dependent terms, we write the total crystal Hamiltonian as

$$\mathcal{H} = T_e + T_N + U(\mathbf{r}, \mathbf{x}), \quad (2)$$

where $U(\mathbf{r}, \mathbf{x}) = U_{ee}(\mathbf{r}) + U_{eN}(\mathbf{r}, \mathbf{x}) + U_{NN}(\mathbf{x})$. Here T_e is the electronic kinetic energy, T_N is the nuclear kinetic energy, U_{ee} is the electron-electron potential energy, U_{eN} is the electron-nucleus potential energy, and U_{NN} is the nucleus-nucleus potential energy. The quantity \mathbf{r} denotes the set of electronic coordinates, and \mathbf{x} denotes the set of nuclear coordinates.

From Hamiltonian (2) we see that the total wave function Ψ is a function of all the electronic and nuclear coordinates. Because the heavy nuclei move much more slowly than the electrons, we may use the Born-Oppenheimer approximation which separates the total wave function into electronic and nuclear factors:

$$\Psi_{n,\eta}(\mathbf{r}, \mathbf{x}) \cong \phi_n(\mathbf{r}; \mathbf{x}) \chi_{n,\eta}(\mathbf{x}), \quad (3)$$

where the wave function ϕ_n depends parametrically on the nuclear coordinates, and where the nuclear wave function $\chi_{n,\eta}$ depends not on the electronic coordinates, but on the electronic state n . Using the Born-Oppenheimer approximation, we obtain the following equations for the electronic and nuclear systems:

$$[T_e + U(\mathbf{r}, \mathbf{x})] \phi_n(\mathbf{r}; \mathbf{x}) = E_n(\mathbf{x}) \phi_n(\mathbf{r}; \mathbf{x}), \quad (4)$$

$$[T_N + E_n(\mathbf{x})] \chi_{n,\eta}(\mathbf{x}) = \mathcal{E}_{n,\eta} \chi_{n,\eta}(\mathbf{x}). \quad (5)$$

In these equations $E_n(\mathbf{x})$ is an adiabatic electronic eigenvalue, and both $\chi_{n,\eta}$ and ϕ_n form a complete set of eigenfunctions.

For many physical systems, the pertinent physics contained in the electronic Hamiltonian (4) depends primarily upon the equilibrium position of the nuclei \mathbf{x}_0 , and not on the details of the lattice vibrations. The main reason for this is that the amplitudes of the lattice vibrations are small, and the changes in the potential associated with them may be treated by perturbation theory. Thus in zero order we may write

$$[T_e + U^0(\mathbf{r}, \mathbf{x}_0)] \phi_n^0(\mathbf{r}; \mathbf{x}_0) = E_n^0(\mathbf{x}_0) \phi_n^0(\mathbf{r}; \mathbf{x}_0). \quad (6)$$

However, the lattice vibrations must be considered if matrix elements for a transition are identically zero when the ϕ_n^0 's are used, and if the lattice perturbation

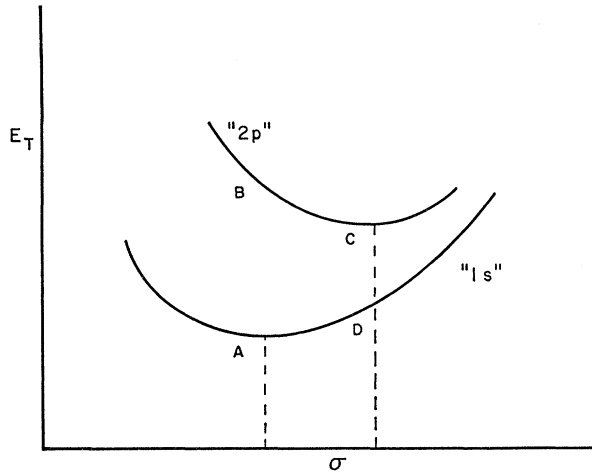


FIG. 1. Schematic configuration coordinate diagram. The quantity E_T is the total energy of the F center, and σ is the nearest-neighbor radial motion; $r_1' = r_1(1 - \sigma)$. The points A , B , C , and D correspond, respectively, to $|\alpha_0, \sigma_0\rangle$, $|\beta_0, \sigma_0\rangle$, $|\beta_1, \sigma_1\rangle$, and $|\alpha_1, \sigma_1\rangle$. The F electron is in the ground-state equation (25) for the lower curve AD and is in the excited-state equation (26) for the upper curve BC .

makes the matrix elements involving first-order ϕ_n 's nonzero. For the most part, we shall assume that $U^0(\mathbf{r}, \mathbf{x}_0)$ is the important term, that ϕ_n^0 is a good approximation to the wave function, and that $E_n^0(\mathbf{x}_0)$ is an accurate eigenvalue.

Schrödinger equation (6) describes a many-electron problem, and we must reduce it to a tractable form. We view an ionic solid as a periodic array of nuclei with charge eA_ν (atomic number) at \mathbf{R}_ν and with $(A_\nu - Z_\nu)$ core electrons localized about \mathbf{R}_ν . The quantity Z_ν is the valence of the ν th ion, and the j th core electron on the ν th ion is assumed to be in the state $\chi_{nj}(\mathbf{r}_{\nu j})$, where $j = 1, 2, \dots, |A_\nu - Z_\nu|$. With this picture in mind, we write the one-electron Hamiltonian for the F center as the sum of two terms,

$$\mathcal{H}_T(\mathbf{r}, \mathbf{x}_0) = \mathcal{H}_F(\mathbf{r}, \mathbf{x}_0) + \mathcal{H}_L(\mathbf{x}_0). \quad (7)$$

The expectation value of the operator \mathcal{H}_F gives us the F -center electron energy in the crystal, while the expectation value of the operator \mathcal{H}_L , which contains no F -electron coordinates, gives us the lattice energy of the crystal.

We shall take the view that the nature of the wave function of the F electron may change substantially between absorption and emission.^{20,21} The F center which is originally in its ground state $|\alpha_0, \sigma_0\rangle$ becomes excited into the state $|\beta_0, \sigma_0\rangle$, which is assumed to be a quasistationary state with an electronic wave function calculated from the same crystal potential as that for the ground state $|\alpha_0, \sigma_0\rangle$. The lattice then relaxes, and thereby the crystal potential which the F electron

experiences changes. The excited electronic state calculated from the relaxed crystal potential $|\beta_1, \sigma_1\rangle$ may differ from the excited state $|\beta_0, \sigma_0\rangle$. The semi-continuum polaron model of Fowler⁸ suggests that the relaxed excited state $|\beta_1, \sigma_1\rangle$ from which emission occurs may be very diffuse. That is to say, the wave function $\langle r | \beta_1, \sigma_1 \rangle$ may have its maximum at four to five nearest-neighbor distances, while the ground state $|\alpha_1, \sigma_1\rangle$ into which emission occurs remains rather compact, with a wave function $\langle r | \alpha_1, \sigma_1 \rangle$ confined mostly to the region within the nearest-neighbor distance. In Fig. 1, we present a simple configuration coordinate diagram which gives the four F -center states treated by our present models.

The electronic part of the Hamiltonian contains the self-consistent potential which the F electron experiences, and which is a function of the lattice configuration. All calculations thus far represent this potential for distances less than the nearest-neighbor distance as a potential well whose depth is determined in part by the Madelung potential. We compute the Madelung potential by viewing the lattice as a collection of point ions, and this suggests that we use the point-ion approximation as a zeroth-order approximation to the lattice. The electronic Hamiltonian yields an electronic wave function which may be either spatially diffuse or compact. This F -electron wave function gives rise to a charge density $\rho_F(\mathbf{r}) = -e\psi^*(\mathbf{r})\psi(\mathbf{r})$. Under certain conditions the F -electron charge density may approximate one of the two extreme cases; namely,

$$\begin{aligned} \text{diffuse: } \rho_F(\mathbf{r}) &\approx 0; \\ \text{compact: } \rho_F(\mathbf{r}) &\approx -e\delta^3(\mathbf{r}). \end{aligned} \quad (8)$$

The compact limit never obtains in real systems, because it demands that the kinetic energy of the F electron, which we may view as an effective repulsive interaction with the neighboring ions, be infinite in accordance with the uncertainty principle. We shall call an F -electron state compact whenever $\int_0^R \psi^* \psi r^2 dr d\Omega \gtrsim 0.5$ and diffuse whenever $\int_0^R \psi^* \psi r^2 dr d\Omega \ll 0.5$. We shall continue in the next section our discussion of the lattice energy.

III. CLASSICAL IONIC LATTICE

The two models for the F center which we shall present below contain the same treatment of the lattice energy and differ in their treatment of the F -electron energy. We shall first present a model of the ionic lattice and then proceed to discuss the semicontinuum polaron model of the F -center electron.

We choose a model of the lattice which is relatively simple, and yet which contains many of the features of a more rigorous treatment. But most important, we require that the same lattice model be able to accommodate either a spatially compact or diffuse vacancy-centered F -electron wave function. We feel that this

²⁰ W. B. Fowler and D. L. Dexter, Phys. Rev. **138**, 2154 (1962).

²¹ W. B. Fowler and D. L. Dexter, J. Chem. Phys. **43**, 1768 (1965).

last condition has not received sufficient consideration in the few previous calculations of the F -electron wave function and the lattice distortions.

Classical ionic-lattice theory gives the interaction energy U_{ij} between two ions i and j at a separation $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$; namely,

$$U_{ij} = (Z_i Z_j / r_{ij}) - (C_{ij}^{(6)} / r_{ij}^6) - (C_{ij}^{(8)} / r_{ij}^8) + \varphi_r(r_{ij}), \quad (9)$$

where the four terms are, respectively, the Coulomb electrostatic, dipole-dipole, dipole-quadrupole, and repulsive contributions to the energy. The charge on the ion i is Z_i ; $C_{ij}^{(6)}$ and $C_{ij}^{(8)}$ are the van der Waals constants for ions i and j , and the repulsive energy is $\varphi_r(r_{ij})$. The cohesive energy $\Phi(r)$ becomes

$$\Phi(r) = \frac{1}{2} \sum_{i \neq j} U_{ij} + U_0, \quad (10)$$

where r is the nearest-neighbor distance for the perfect lattice, and where U_0 is the zero-point lattice energy.

Boswarva and Lidiard have computed the formation energy and nearest-neighbor distortions of Schottky defects by a theory which includes the van der Waals terms and by a theory which omits the van der Waals terms.²² Their results show that the van der Waals terms increase the formation energy by about 5% and decrease the distortion by about 4%. Considering this, and because we do not expect the F -center electronic portion of the Hamiltonian to be accurate to within 5% of the experimental results, we shall not include the van der Waals terms in our expression for the cohesive energy from which we compute the lattice energy.

We want to compute the change in the lattice energy due to replacing an anion with an F -center electron. We first create a vacancy at the anion site $\mathbf{r}_0 = \mathbf{0}$ of charge Z_0 and permit no lattice relaxation. This fictitious lattice state will serve as the reference energy for the lattice part of the F -center Hamiltonian. Neglecting the van der Waals terms, we express the lattice energy as a sum of the electrostatic Coulombic energy E_e and the repulsive energy of interaction between the ionic cores E_r :

$$E_L = E_e + E_r, \quad (11)$$

where

$$E_e = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} Z_i Z_j |\mathbf{r}_i - \mathbf{r}_j|^{-1} - Z_0 \sum_{j \neq 0} Z_j |\mathbf{r}_j|^{-1}, \quad (12)$$

and

$$E_r = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \varphi_r(\mathbf{r}_i - \mathbf{r}_j) - \sum_{j \neq 0} \varphi_r(\mathbf{r}_j). \quad (13)$$

We may interpret the second term of E_e by saying that we create a vacancy by adding an ion of charge $-Z_0$ at $\mathbf{r}_0 = \mathbf{0}$, or, equivalently, by saying that we remove the electrostatic "bonds" involving the point $i=0$. The

second term in E_r means that we remove the repulsive bonds involving the point $i=0$. The repulsive energy $\varphi_r(\mathbf{r}_i - \mathbf{r}_j)$ between the i th and j th ions takes the Pauli exclusion principle between the i th and j th cores into account and is a short-ranged function of $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The function $\varphi_r(r_{ij})$ usually has the empirically determined Born inverse-power-law form

$$\varphi_r(r_{ij}) = a r_{ij}^{-\lambda}, \quad \lambda > 0 \quad (14)$$

the Born-Mayer exponential form

$$\varphi_r(r_{ij}) = b b_i b_j \beta_{ij} \exp(-r_{ij}/\rho), \quad (15)$$

or some combination of the two forms (Born-Mayer-Verwey). The quantities a , λ , $b_i = \exp(\rho_i/\rho)$, $b_j = \exp(\rho_j/\rho)$, and ρ are given in the literature.²³ The quantity ρ_i is the ionic radius of the i th ion, and β_{ij} is the Pauling factor for the i th and j th ions. We determine b from the condition that

$$\left. \frac{d\Phi(r)}{dr} \right|_{r=r_1} = 0, \quad (16)$$

where r_1 is the nearest-neighbor distance in the perfect lattice. Forms (14) and (15) assume no electronic polarization of the ionic cores, and because the experiments which determine their parameters involve only small ion displacements, we must at the least be cautious whenever the distance between the ions becomes substantially less than the sum of their ionic radii.

We now allow the n nearest neighbors of the vacancy (defect ions) to move radially inward or outward to the sites $\mathbf{r}'_i = \mathbf{r}_i(1-\sigma)$ for $1 \leq i \leq n$. All other ions are to remain at their perfect-lattice sites in this model. The change in the lattice energy then assumes the form

$$\Delta E_L(\text{vacancy, distortion}) = E_L' - E_L = \Delta E_e + \Delta E_r, \quad (17)$$

where

$$\Delta E_e = E_1 + E_2 + E_3 + E_4, \quad (18)$$

$$E_1 = n Z_1 \sum_{j \neq 1} Z_j \{ |\mathbf{r}'_1 - \mathbf{r}_j|^{-1} - |\mathbf{r}_1 - \mathbf{r}_j|^{-1} \}, \quad (19)$$

$$E_2 = -n Z_1 \sum_{\substack{j \neq 1, j \neq 0 \\ j \leq n}} Z_j \{ |\mathbf{r}'_1 - \mathbf{r}_j|^{-1} - |\mathbf{r}_1 - \mathbf{r}_j|^{-1} \}, \quad (20)$$

$$E_3 = \frac{1}{2} \sum_{\substack{i \leq n \\ i \neq 0}} \sum_{\substack{j \leq n \\ j \neq 0, i \neq j}} Z_i Z_j \{ |\mathbf{r}'_i - \mathbf{r}'_j|^{-1} - |\mathbf{r}_i - \mathbf{r}_j|^{-1} \}, \quad (21)$$

$$E_4 = -Z_0 \sum_{j \leq n, j \neq 0} Z_j \{ |\mathbf{r}'_j|^{-1} - |\mathbf{r}_j|^{-1} \}, \quad (22)$$

and

$$\Delta E_r = E_r' - E_r. \quad (23)$$

The lattice configuration obtains at that value of σ for which the change in the lattice energy is a minimum.

²² I. M. Boswarva and A. B. Lidiard, Phil. Mag. (to be published).

²³ We refer the reader to the references in Table I.

Keeping the implications of the above paragraph in mind, we pause here for a moment to restate our goals. We are developing two models for the F center from which we will make statements about experimentally observed quantities such as the absorption energy, emission energy, and the lifetime of the excited state. These three quantities are known best for NaCl and KCl. If our models for NaCl and KCl agree reasonably well with experiment, then we shall have more confidence when we use them to make predictions for other ionic crystals. Certain diagonal matrix elements of the F -electron Hamiltonian give us the absorption and emission energies, while the one-electron dipole matrix elements (transition matrix elements) give us the lifetime of an excited state. In the next paragraph, we remark on the effect that angular and radial changes in the potential $U^0(\mathbf{r}, \mathbf{x})$ may have on these matrix elements.

We have just discussed the change in energy of a lattice relaxation in which the nearest-neighbor ions move symmetrically inward or outward (breathing mode). In fact, the ions will relax so as to conform to the symmetry of the F -electron wave function. We would expect the lattice relaxation to occur via the Jahn-Teller effect, which could change the angular dependence of U^0 , as well as its radial dependence. Accordingly, the F -electron wave function would have a different angular dependence, and this might make the emission dipole matrix element smaller than that for absorption. The results of F -center calculations, however, indicate, that the inclusion of modes other than the symmetric breathing mode does not significantly affect the F -electron energy levels.^{7,24} This means that the radial changes in U^0 for the model of Ref. 7 dominate over the angular changes in determining the energy levels. We have no such statements concerning the primary mechanism for the transition matrix elements. In the development of our two models, we shall assume that the radial changes in U^0 , and thereby in the F -electron wave function, dominate over the angular changes in determining both the energy levels and the lifetimes. For this reason, we shall also use the symmetric breathing lattice mode for the relaxed excited state.

One test of a model's worth is whether it produces agreement with experiment. Experience teaches us that many point-ion and continuum models which contain a self-consistent potential well whose depth is approximately the Madelung potential and whose width is approximately the nearest-neighbor distance will agree satisfactorily with the absorption-energy data in, say, NaCl. The theorist must put forth more thought to obtain models which yield satisfactory values for the Stokes shift. But the true test of a model's success is its predictions for the wave-function-sensitive quantities such as the lifetime of an excited state. Let us now return to our lattice-energy discussion.

²⁴ R. F. Wood, Phys. Rev. **151**, 629 (1966).

Because we want to make certain that our lattice model accommodates both compact and diffuse F -electron states in all three groups—the alkali halides ($Z_0 = -e$), the alkaline earth fluorides ($Z_0 = -e$), and the alkaline earth oxides ($Z_0 = -2e$)—we shall consider a fictitious model which neglects all quantum aspects of the F electron. We replace the ions by point charges which experience both electrostatic Coulomb interactions and empirical repulsions in the form of Eq. (14) or Eq. (15). Experience motivates us to use this fictitious model to study some aspects of the delicate balance between the electrostatic and repulsive forces present in the vicinity of the F -center defect.

Past authors⁶⁻⁷ have assumed that the ions experience core repulsions with only their nearest neighbors. These repulsions are quantum-mechanical in origin, and we represent them in classical ionic-crystal theory by empirical laws such as Eq. (14) or Eq. (15). Our initial studies of the F center in the halides show that the assumption of only nearest-neighbor empirical repulsions leads to no inconsistencies. However, the relaxed ground states of the F center in the oxides MgO and CaO (one electron localized about the anion vacancy), which have rather compact F -electron wave functions, produce excessive inward movement of the nearest neighbors to the defect when we use only nearest-neighbor empirical repulsions. The distance between adjacent defect cations in these oxides is less than the sum of their ionic radii. Such a result is not consistent with forms (14) and (15) and with the concept of ionic radii.

A quantitatively delicate balance exists between the electrostatic interactions and the empirical repulsions when we make the anion vacancy (the limit of an extremely diffuse F -electron state) by removing both the electrostatic bonds and the empirical repulsive bonds involving the point $i=0$. When we add the one F electron, this delicate balance depends in a very nonlinear manner upon the F -electron spatial extent and the motion of the n defect ions. The relaxed ground state has among all the possible F -center states the most compact F -electron wave function, i.e., $\int_0^R \psi^* \psi r^2 dr d\Omega$ is closer to 1 than to, say, 0.5. Consequently this state produces the greatest electrostatic attraction with the neighboring n defect cations. Because $\int_0^R \psi^* \psi r^2 dr d\Omega$ is near 1, the electrostatic environment is almost the same as that in the perfect halide lattice for NaCl or CaF₂. However, the electrostatic environment remains substantially different from that in the perfect oxide lattice of MgO and CaO for which a charge of $-2e$ is necessary in order to approximate the electrostatic environment of the perfect lattice. In all cases, however, the electrostatic energy maintains the same analytic Coulombic structure ($Z_i Z_j / r_{ij}$).

The repulsive environment about the defect changes quantitatively, but more importantly, it undergoes a fundamental change for its analytic representation in

the model. The inward motion of the n defect ions deepens and narrows the potential well which the single F electron experiences. The narrowing of the well confines the F electron to a smaller region in space. This increases the F -electron kinetic energy in accordance with the uncertainty principle, and thereby increases the energy of the F center. We may view the tendency to lower the F -electron kinetic energy by an outward motion of the defect ions as a repulsive interaction of the F electron with its neighbors. We will call this mechanism an effective F -electron repulsion (EFER), and we distinguish it from the empirical repulsions (14) or (15) between the ion cores. This EFER repulsion will depend in a very nonlinear manner upon the F -electron wave function (its spatial extent) and the lattice distortion. Note that the empirical repulsive bonds to the point $i=0$ which we remove to make the anion vacancy depend only on the positions of the ions. This is what we mean when we say that the EFER repulsions have an analytic representation which differs substantially from that of the empirical repulsions (14) or (15).

This nonlinear dependence of the equilibrium position of the n defect ions on the F -electron wave function makes it rather difficult to predict by qualitative arguments alone whether the defect ions will move inward or outward. Not only must we consider the values of the many repulsive and electrostatic terms, but we must also consider the rates with which they change and the quantum-mechanical energy of the F electron. We feel that the explicit use of numbers is the best way and perhaps the only reliable way to decide whether a given model predicts inward or outward motion of the n defect ions.

The EFER repulsions replace the empirical repulsions to the point $i=0$ in the F center, and there is no guarantee that they are as effective as the empirical forms (14) or (15) in stabilizing the defect ions. Our initial studies show that the EFER repulsions and the only nearest-neighbor empirical repulsions combine to stabilize the F -center defect in NaCl and CaF₂ lattices, but that these same repulsions do not stabilize the F -center defect in the MgO and CaO lattices. The success in the halides and the failure in the oxides suggest that we also include second-nearest-neighbor empirical repulsions and not reject the empirical forms (14) or (15). In order to clarify the above discussion, we invoke, below, the fictitious (zero quantum mechanics for the F electron) model. We also hope by this study to explain our reasons for employing second-nearest-neighbor repulsions, both between the n defect ions and between the other ions of the crystal, in the work which we are reporting here.

We assume in this fictitious model that the F electron has negligible repulsive interactions (EFER) with the core electrons, i.e., we neglect the quantum-mechanical aspects of the F electron. The limit of a very diffuse

electron state ($\int_0^R \psi^* \psi r^2 dr d\Omega$ is very small) then corresponds in such a model to removing both the electrostatic and empirical repulsive bonds involving the point $i=0$, i.e., we minimize $\Delta E_L(\sigma)$. On the other hand, the limit of a very compact F -electron state corresponds to removing only the empirical repulsive core bonds involving the point $i=0$; i.e., we minimize $\Delta E_L(\sigma; c) \equiv \{\Delta E_L(\sigma) - [eE_A(\sigma)/(-Z_0)]\}$. The second term adds the electrostatic bonds between the single defect electron of charge $(-e)$ and all the other ions which arise from $\int_0^R \psi^* \psi r^2 dr d\Omega$ being close to 1.

We have used a computer to minimize $\Delta E_L(\sigma)$ and $\Delta E_L(\sigma; c)$ for NaCl ($Z_0 = -e$) and for the two oxides MgO and CaO ($Z_0 = -2e$). We find that for the range $-0.06 \gtrsim \sigma_d \gtrsim -0.20$, $\Delta E_L(\sigma_d)$ is a minimum, depending upon which form for φ_r we choose to describe the nearest-neighbor-only repulsive-core interaction. The same examination of $\Delta E_L(\sigma; c)$ yields that $\Delta E_L(\sigma; c)$ will be a minimum only for values of σ_e greater than $+0.30$. This large inward motion of the ions to accommodate a very compact F -electron state results in the n defect ions, which are next nearest neighbors of each other, approaching within a distance roughly equal to the sum of their ionic radii.

As mentioned above, when we include the F -electron quantum-mechanical energy H_F and minimize the total energy of the system $E_T = H_F + \Delta E_L$, then we find that the EFER repulsions contained in H_F are sufficiently strong to bring about reasonable values of σ_e for NaCl, but are not sufficiently strong to bring about reasonable values of σ_e for the two oxides MgO and CaO. Even minimizing $E_T = H_F + \Delta E_L$ for the oxides yields values of $\sigma_e > +0.3$. These large values for σ_e obtain for both HFPI and SCP models of the F center in alkaline earth oxides, and we feel that such large values are not reasonable. We find that second-nearest-neighbor empirical repulsions produce reasonable values of σ_e in MgO and CaO, both when we minimize $\Delta E_L(\sigma; c)$ and $E_T = H_F + \Delta E_L$ for the HFPI and SCP models of H_F .

A qualitative examination of the terms in $\Delta E_L(\sigma)$ and in $\Delta E_L(\sigma; c)$ as functions of σ also reveals the same results for the nearest-neighbor-only core interactions. To facilitate this qualitative examination, we summarize the contents of the terms E_1 to E_4 . The term E_1 is the change in electrostatic energy which occurs when a neighboring cation moves in the background of a perfect-point-ion-lattice potential. We express this term as a series expansion in the distortion σ to terms including σ^8 , and evaluate by Ewald's method the lattice summations which give the series coefficients. The quantity E_2 represents the change in the electrostatic energy which occurs when one of the n defect ions moves in the point-ion potential of the remaining $(n-1)$ defect ions at perfect-lattice sites. The term E_3 is the change in the electrostatic energy of the n defect ions when all n defect ions move radially inward or outward.

TABLE I. Input data for the SCP(HF) and SCP(QA) F -center models. The quantities $\beta_{++}, \beta_{+-}, \beta_{--}, \epsilon_{\infty}^{-1}, \epsilon_0^{-1}, d_{ML}$, and (m^*/m) are dimensionless. The longitudinal optical-phonon frequency ω_l is expressed in units of 10^{13} rad sec $^{-1}$. The Mott-Littleton radius R is given by $R=r_1(1-d_{ML})$. The quantity r_1 is the nearest-neighbor distance (anion-cation) for the NaCl structure and is the lattice constant (cation-cation) for the CaF $_2$ structure. All other quantities are expressed in terms of atomic units; 1 a.u.=27.2 eV for energy and 0.529×10^{-8} cm for length.

	NaCl	KCl	MgO	CaO	CaF $_2$	SrF $_2$	BaF $_2$
β_{++}	1.25	1.25	1.50	1.50	1.50	1.50	1.50
β_{+-}	1.0	1.0	1.0	1.0	1.125	1.125	1.125
β_{--}	0.75	0.75	0.5	0.5	0.75	0.75	0.75
ρ	0.599 ^a	0.637 ^a	0.629 ^b	0.629 ^b	0.546 ^e	0.560 ^e	0.582 ^e
ρ_+	2.21 ^a	2.77 ^a	1.76 ^b	2.21 ^b	2.21 ^d	2.48 ^d	2.76 ^d
ρ_-	3.00 ^a	3.00 ^a	2.55 ^b	2.55 ^b	1.98 ^d	1.98 ^d	1.98 ^d
α_M	1.748	1.748	1.748	1.748	4.071	4.071	4.071
ϵ_{∞}^{-1}	0.444 ^e	0.469 ^e	0.339 ^e	0.305 ^e	0.489 ^f	0.483 ^f	0.463 ^f
ϵ_0^{-1}	0.177 ^e	0.214 ^e	0.102 ^e	0.085 ^e	0.149 ^f	0.152 ^f	0.139 ^f
ω_l	4.88 ^e	3.95 ^e	19.83 ^e	13.07 ^e	1.38 ^f	1.12 ^f	0.977 ^f
d_{ML}	0.069 ^g	0.140 ^g	0.070 ^g	0.120 ^g	0.074 ^g	0.140 ^g	0.197 ^g
r_1	5.31 ^a	5.93 ^a	3.97 ^b	4.54 ^b	10.32 ^d	10.95 ^d	11.71 ^d
C_4	3.579 ^h	3.579 ^h	3.579 ^h	3.579 ^h	1.865 ⁱ	1.865 ⁱ	1.865 ⁱ
C_6	0.9895 ^h	0.9895 ^h	0.9895 ^h	0.9895 ^h
C_8	2.942 ^h	2.942 ^h	2.942 ^h	2.942 ^h
χ	-0.028 ^j	-0.022 ^j	-0.04 ^k
(m^*/m)	0.6 ^l	0.6 ^l	1.0 ^m

^a M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. XVI, p. 52.

^b M. L. Huggins and Y. Sakamoto, *J. Phys. Soc. Japan* **12**, 241 (1957).

^c A. D. Franklin (private communication).

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^e M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1954), p. 85, Table 17.

^f W. Kaiser *et al.*, *Phys. Rev.* **127**, 1950 (1962).

^g F. K. du Pré, *J. Chem. Phys.* **18**, 379 (1950).

^h A. Scholz, *Phys. Status Solidi* **7**, 973 (1964).

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^j T. Timusk and W. Martienssen, *Phys. Rev.* **128**, 1656 (1962).

^k J. Yamashita, *Phys. Rev.* **111**, 733 (1958).

^l W. B. Fowler, *Phys. Rev.* **135**, A1725 (1964); J. Hodby *et al.* (to be published).

^m M. L. Cohen *et al.*, *Phys. Rev.* **155**, 992 (1967). We fit the curves of Fig. 2 to the form $(\hbar^2 k^2 / 2m^*)$ and find that $(m^*/m) \approx 1.01$ for the (110) direction, 1.21 for the (111) direction, and 0.55 for the (100) direction.

And, finally, E_4 represents the change in the electrostatic energy between the effective vacancy charge $Z_V \equiv -Z_0$ and the lattice due to the motion of the defect ions.

To be specific, we use the form (15); but either expression (14) or the Born-Mayer-Verwey expression will lead to the same conclusions. Recall that a diffuse state corresponds to adding an effective charge $-Z_0$ at $i=0$ (remove electrostatic bonds to $i=0$). However, $-Z_0$ has the same sign as the nearest neighbors to $i=0$. Hence the electrostatic terms E_1 , E_3 , and E_4 decrease for $\sigma < 0$. Only the term E_2 increases for $\sigma < 0$. In addition, we have a sufficient number of repulsive nearest-neighbor bonds which decrease in length for $\sigma < 0$. These conditions combine to bring about an accompanying increase in ΔE_r which offsets the decrease in ΔE_e before σ becomes too large. However, such a balance does not obtain for the case of a compact state which is the limit of removing only the repulsive bonds for the case $Z_0 = -e$. In this case, we consider $\Delta E_L(\sigma; c)$. The electrostatic terms E_1 and E_2 decrease for $\sigma > 0$. Only the term E_3 increases for $\sigma > 0$. Thus the electrostatic forces (or the absence of repulsive forces) tend to move the n defect ions inwards, $\sigma > 0$. But most important, because there are no nearest-neighbor repulsive bonds which decrease for $\sigma > 0$, the defect ions move

excessively inward until the weaker (less rapidly varying) electrostatic term E_3 increases sufficiently to offset the decrease in the remaining electrostatic part $\Delta E_e(\sigma; c) - E_3$ and in the repulsive term ΔE_r . Our initial studies in the oxides indicate that even the EFER repulsions in the quantum-mechanical energy H_F are unable to counter the inward motion until $\sigma > 0.3$. They are able, however, to counteract the inward motion in NaCl.

Note that when the next-nearest-neighbor repulsive bonds are included, those bonds among the n defect ions of $i=0$ decrease for $\sigma > 0$. In fact, upon minimizing $\Delta E_L(\sigma; c)$ with next-nearest-neighbor repulsive bonds, we obtain a much smaller inward distortion for the compact F -electron state and about the same outward distortion for the diffuse F -electron state as before. The quantity σ_e is in the range $0.1 \gtrsim \sigma_e \gtrsim 0.01$, depending upon the form and parameters of φ_r . Hence we state that one should include next-nearest-neighbor core repulsions when considering a compact F -electron wave function in a model lattice in which only the nearest-neighbor ions to the defect move in the breathing mode.

Our later research, which we present in the following sections of this paper, includes the second-nearest-neighbor empirical repulsions between the n defect ions and between the other ions of the crystal. Second-

nearest-neighbor empirical repulsions are necessary to yield reasonable values of σ_e for the relaxed ground state in the oxides, and even though they may be a negligible embellishment in the halides, we include them for the halides in order to be consistent. Because essentially the same results obtain for both HFPI and SCP models of H_F , the physical details of H_F play a very minor role in our deciding to include the second-nearest-neighbor empirical repulsions.

The few researchers^{3,5,7} who have considered the local lattice distortions near the F center in a self-consistent manner consider only the alkali halides and include only nearest-neighbor repulsive interactions. They also neglect the term E_1 and expand the remaining terms of ΔE_L in powers of σ . We, however, expand E_1 to eighth order in σ for the NaCl structure and to fourth order for the CaF₂ structure, and treat the remaining terms of ΔE_L (E_2 , E_3 , E_4 , and ΔE_r) rigorously. We write

$$E_1 = - (n/\bar{r}_1)(C_4\sigma^4 + C_6\sigma^6 + C_8\sigma^8 + \dots), \quad (24)$$

where \bar{r}_1 is the cation-anion distance in the NaCl structure and is the lattice constant (cation-cation distance) in the CaF₂ structure. The coefficients c_4 , c_6 , and c_8 are given in Table I in atomic units. In addition, these researchers have not examined the lattice by itself; i.e., they have not minimized $\Delta E_L(\sigma)$ and $\Delta E_L(\sigma; c)$ alone to see if the same lattice model can accommodate the two extreme cases of Eq. (8). They minimize the sum of the lattice energy and the F -electron energy H_F . The combination of limiting oneself to the alkali halides and of considering the total system energy $E_T = H_F + \Delta E_L$, which is, of course, correct for real systems, will not reveal the necessity for the inclusion of second-nearest-neighbor repulsions in the oxides. To repeat, our experience has been the following. When we add the F -electron energy H_F to ΔE_L and minimize the sum $E_T = H_F + \Delta E_L$ for nearest-neighbor-only repulsions, then the compact F -center wave function produces only negligible inward distortion for the alkali halides. However, the same procedure applied to the alkaline earth oxides (MgO and CaO) produces excessive inward distortion. Therefore, unless we include next-nearest-neighbor repulsions for the oxides, the inward distortion compatible with a compact F center will be excessive.

IV. SEMICONTINUUM POLARON MODEL

Neglecting lattice vibrations and magnetic interactions, we shall discuss the semicontinuum polaron Hamiltonian and its expectation value for the F -center electron in a relaxed state and then in an unrelaxed state. We mean by "relaxed" that the electronic state with a given symmetry has existed for a time long enough to allow the lattice to accommodate itself to the defect; in our case, the state $|\eta, \sigma\rangle$ exists long enough for the nearest-neighbor ions to move. The unrelaxed

state arises when the state $|\eta, \sigma\rangle$ has existed for such a short time that the lattice has not had time to accommodate itself to the new charge density associated with the F electron.

The trial wave functions which we shall use in the variational approach are

$$\psi_{1s}(\mathbf{r}) = \langle \mathbf{r} | \alpha, \sigma \rangle_F = (\alpha^3/7\pi)^{1/2}(1 + \alpha r) \exp(-\alpha r) \quad (25)$$

and

$$\psi_{2p}(\mathbf{r}) = \langle \mathbf{r} | \beta, \sigma \rangle_F = (\beta^5/\pi)^{1/2} r \cos\theta \exp(-\beta r), \quad (26)$$

where α and β are the variational parameters and depend implicitly on the displacement of the nearest-neighbor ions. The wave functions are normalized to the crystal volume:

$$\int \psi^*(\mathbf{r})\psi(\mathbf{r})d^3r = 1. \quad (27)$$

In the semicontinuum approximation, we view the vacancy as a spherical cavity of radius R (the Mott-Littleton radius) in a continuous dielectric medium characterized by the static and high-frequency dielectric constants ϵ_0 and ϵ_∞ , respectively. The expression

$$W_{\text{pol}} = Z_0^2 [1 - (1/\epsilon_\infty)]/R \quad (28)$$

relates the Mott-Littleton radius to the polarization energy W_{pol} . This is the energy required to move an ion of charge Z_0 to the surface of a rigid lattice.

We begin with the one-electron Hamiltonian for the F -center electron

$$\mathcal{H}_F = (\mathbf{p}^2/2m) + \sum'_{\nu \neq 0} V_{\text{perf}}(\mathbf{r} - \mathbf{R}_\nu) + V_{\text{pol}}(\mathbf{r}), \quad (29)$$

where $(\mathbf{p}^2/2m)$ is the kinetic energy, V_{perf} is the perfect-crystal potential, and V_{pol} describes the polarization effect. We write the Hamiltonian for the region inside the cavity ($r < R$) in the form

$$\mathcal{H}_< = (\mathbf{p}^2/2m) + V_0 + W_0. \quad (30)$$

The term V_0 is the spherically symmetric part of the point-ion-crystal potential for the region $r \leq r_1$, where r_1 is the nearest-neighbor distance for the rigid lattice; namely,

$$V_0 = Z_0 e [\alpha_M/r_1 + S_1 Q_1 \sigma / r_1 (1 - \sigma)]. \quad (31)$$

The quantity α_M is the Madelung potential constant at the anion site, S_i is the number of ions on the i th shell centered about the vacancy, and Q_i is the charge on one of the ions in the i th shell. The energy W_0 contains a number of terms which we will discuss below. Outside the cavity ($r > R$), we write

$$\mathcal{H}_> = (\mathbf{p}^2/2m) + \sum_{\nu} V_{\text{perf}}(\mathbf{r} - \mathbf{R}_\nu) + V_{\text{pol}}(\mathbf{r}) - V_{\text{perf}}(\mathbf{r}) + V_{\text{sef}} + V_{\text{sev}}, \quad (32)$$

or

$$\mathfrak{H}\mathcal{C}_> = (\mathbf{p}^2/2m^*) + V_{\text{pol}}(\mathbf{r}) - V_{\text{perf}}(\mathbf{r}) + V_{\text{sef}} + V_{\text{sev}}, \quad (33)$$

where V_{sef} and V_{sev} are, respectively, the F -electron and the vacancy self-energies. The quantity m is the bare electron mass, and the quantity m^* is the effective mass at the bottom of the conduction band due to the electron-electron interactions. We assume that m^* is a scalar.

We have added and subtracted $V_{\text{perf}}(\mathbf{r})$ in order to include the $\nu=0$ term in the lattice summation of the second term in Eq. (32). This procedure enables us to introduce the effective-mass approximation for which we replace

$$(\mathbf{p}^2/2m) + \sum_{\nu} V_{\text{perf}}(\mathbf{r} - \mathbf{R}_{\nu})$$

with $(\mathbf{p}^2/2m^*)$. We then write the remaining terms $V_{\text{pol}}(\mathbf{r}) - V_{\text{perf}}(\mathbf{r})$ in a form containing a spatially dependent effective dielectric function $\epsilon_{\text{eff}}(r)$, which we assume is only a function of $r = |\mathbf{r}|$; namely,

$$V_{F-V}(r) = V_{\text{pol}}(\mathbf{r}) - V_{\text{perf}}(\mathbf{r}) \approx [eZ_0/(\epsilon_{\text{eff}}(r)r)]. \quad (34)$$

The potential $V_{F-V}(r)$ represents the effective interaction between the F electron and an infinite-mass hole (a vacancy) of charge $-Z_0$ due to the polarizations. When the F electron is in a compact state (small orbit) or moves very rapidly, then we expect $\epsilon_{\text{eff}} \approx \epsilon_{\infty}$, and when the F electron is in a diffuse state (large orbit) or moves so slowly that the ionic polarization can follow to some extent the electronic motion, then we expect $\epsilon_{\text{eff}} \approx \epsilon_0$. Hence the potential $V_{F-V}(r)$ will act as an interpolation between the two extreme cases. Following the suggestion which was first made by Fowler,⁸ we use the Haken theory of Wannier excitons. Haken's theory^{17,18} treats the manner in which an electron of charge $-e$ interacts with a mobile hole of charge $+e$ in the presence of ionic polarizations. Fowler then extends Haken's theory to the case for which the hole is immobile (the vacancy with an effective charge of $+e$). Because we also want to discuss the F center in systems for which the vacancy has an effective charge $Z_V = -Z_0$ greater than $+e$, e.g., the oxides, we have mathematically generalized the above theories to treat the case of a mobile electron of charge $Z_F = -e$ interacting with an immobile charge Z_V in the presence of ionic polarizations. The result is

$$V_{\text{sev}} = -(Z_V^2/r_1)[(1/\epsilon_{\infty}) - (1/\epsilon_0)], \quad (35)$$

$$V_{\text{sef}} = -(\frac{1}{2}Z_F^2)v[(1/\epsilon_{\infty}) - (1/\epsilon_0)], \quad (36)$$

and

$$V_{F-V}(r) = (Z_V Z_F / r) [(1/\epsilon_{\infty}) + \{ (1/\epsilon_0) - (1/\epsilon_{\infty}) \} \times \{ 1 - \frac{1}{2}(\exp(-vr) + \exp(-2r/r_1)) \}]. \quad (37)$$

Here, $v = (2m^*\omega_l/\hbar)^{1/2}$, and ω_l is the frequency of the longitudinal optical phonon for the crystal.

Let us digress for a moment in order to outline the derivation of Eqs. (35)–(37). The Haken theory addresses itself to the effective interaction in the presence of ionic polarizations between a mobile electron and a mobile hole.²⁵ We then view the F center in an alkali halide, say, NaCl or KCl, as a mobile electron and an immobile hole, and take the limit to which the Haken interaction approaches when the effective hole mass becomes infinite. We use this limit as the effective F -electron potential for the region outside the cavity $r > R$. The mathematically generalized equations (35)–(37) obtain by the following procedure. We write a Hamiltonian for a mobile negative charge Z_F and a mobile positive charge Z_V interacting in the presence of ionic polarizations, i.e., the Fröhlich Hamiltonian.²⁶ We then proceed as in the Haken theory and take the limit as the effective mass of the positive charge becomes infinite. This procedure gives us Eqs. (35)–(37). But we argue that the method may be physically wrong for $Z_F \neq -e$ and for $Z_V \neq +e$ because electrons ($Z_F = -e$) and holes ($Z_V = +e$) give rise to the elementary processes in solids. Another way to state this is that the F center in NaCl is an appropriate limit of the two-body problem (electron and hole) treated by the Haken theory, while the F center in the oxides is an appropriate limit of a four-body problem (two electrons and two holes) in which the two holes both with infinite effective mass become localized about the same point in space, one electron remains at finite distances from the two localized holes, and the second electron moves infinitely far from this point. We call the electron at finite distances from the two holes the F electron. The F center in the oxides is not a neutral system. It is one electron localized about an anion vacancy with an effective charge of $Z_V = +2e$. However, in order to maintain a Hermitian Hamiltonian within the framework of the Haken theory, we view the F center not as a three-body problem (one electron and two holes), but as a four-body problem in which one of the electrons moves to infinity relative to the other three fermions. Our tacit assumption is that the above four-body limit is approximated by Eqs. (35)–(37) for the case $Z_F = -e$ and $Z_V = +2e$. Considering the importance of spin when two particles obeying Fermi statistics approach one another, we suggest that this assumption may be incorrect. When $Z_F = -e$ and $Z_V = +e$, Eqs. (35)–(37) reduce to the correct form given in Ref. 8.

Because the Haken theory neglects the wave-vector dependence of the polaron wave function, expression (37) is justifiable only for large values of r :

$$(e^2/r) \{ (1/\epsilon_{\infty}) - (1/\epsilon_0) \} < \hbar\omega_l. \quad (38)$$

²⁵ We refer the reader to Refs. 17 and 18. The electron-hole system corresponds to $Z_V = +e$ and $Z_F = -e$, i.e., to a neutral system $Z_V + Z_F = 0$. The F center in an alkaline earth oxide is not a neutral system, $Z_V + Z_F = +e$.

²⁶ H. Fröhlich, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, London, 1963), p. 1.

This inequality states that the polarization-energy correction to the electron-vacancy interaction energy due to ionic displacements should be less than the energy to liberate a free phonon. However, a calculation using Feynman techniques²⁷ shows that expression (37) is in fact a qualitative interpolation between large and small r , and is quantitatively correct up to order $1/r$ + const in the $r \rightarrow 0$ limit. The $r \rightarrow 0$ limit of Eq. (37) is

$$\lim_{r \rightarrow 0} V_{F-V}(r) = (Z_V Z_F / r \epsilon_\infty) - Z_V Z_F \{ (1/\epsilon_\infty) - (1/\epsilon_0) \} \{ \frac{1}{2}v + (1/r_1) \}. \quad (39)$$

Observe that the last term in the $r \rightarrow 0$ limit just cancels the self-energy terms V_{sev} and V_{sef} for the electron-hole case ($Z_V = +e$ and $Z_F = -e$) and that this cancellation does not occur for the ($Z_V = +2e$ and $Z_F = -e$) oxide case. This is just what one would intuitively expect, because the electron hole is a neutral system and the F center in the oxide case is not a neutral system.

The negative self-energy terms outside the cavity are equivalent to positive self-energy terms inside the cavity and a change in the zero of energy. That is, we write

$$\int_R^\infty r^2 dr \int d\Omega |\psi|^2 [V_{sev} + V_{sef}] = E_{SE} - \int_0^R r^2 dr \int d\Omega |\psi|^2 [V_{sev} + V_{sef}], \quad (40)$$

where we have used the normalization of the wave functions, and where the change in the zero of energy from which we measure the energy is $E_{SE} = V_{sev} + V_{sef}$. This change is a constant, and hence it will be of no consequence.

We now return to present the several terms contained in the second term W_0 of the well depth ($V_0 + W_0$) which appears in Eq. (30). We have that

$$W_0 = -\chi + W_{inf} + W_{opt}, \quad (41)$$

where χ is the energy at the bottom of the conduction band relative to the vacuum, or, equivalently, relative to an electron at rest infinitely far from the F center, where W_{inf} is the self-energy due to lattice polarization, and where W_{opt} is the potential energy due to the distortion of the ion-core electrons (optical polarization). Recalling the previous paragraph, we express the self-energy due to the infrared polarization in the form

$$W_{inf} = -(V_{sev} + V_{sef}). \quad (42)$$

Two expressions exist for the potential energy of the F electron due to the optical polarization when the F

electron is inside the cavity; the quasiadiabatic approximation gives²⁸

$$W_{opt}(QA) = \{1 - (1/\epsilon_\infty)\} \{Z_V - (\frac{1}{2}e)\} (e/R), \quad (43)$$

and the continuum Hartree approximation gives²⁸

$$W_{opt}(HF) = \{1 - (1/\epsilon_\infty)\} (e/R) \times \left(Z_V - e + eR \int_R^\infty q(s) s^{-2} ds \right), \quad (44)$$

where

$$q(s) = \int_s^\infty |\psi|^2 d^3s. \quad (45)$$

The adiabatic approximation allows the core dipoles to follow to some extent the motion of the F electron when the latter is in the cavity; while the continuum Hartree approximation asserts that the core dipoles do not follow the F electron and that they point towards the mean position of the F electron when it is in the cavity. We call the model with expression (43) the SCP(QA) model and the model with expression (44) the SCP(HF) model. Except for this one difference in the approximation for the optical polarization inside the cavity, the SCP(QA) model and the SCP(HF) model are identical in all other aspects. We shall show by numerical computations that the continuum Hartree approximation SCP(HF) agrees much better with the experiments in KCl and NaCl than does the quasi-adiabatic approximation SCP(QA).

The location of the conduction band enters because the operator $(\mathbf{p}^2/2m) + V_0$ has the vacuum as the zero of energy and the operator $(\mathbf{p}^2/2m^*)$ has the bottom of the conduction band as the zero of energy. We do not explicitly include the self-energy of the F electron due to optical polarization, because the quantity χ will contain this term whenever we use experimentally determined values for χ .

Combining the above terms, we obtain the following expression for the semicontinuum polaron model of the F -electron energy:

$$H_F = H_{<} + H_{>}, \quad (46)$$

where

$$H_{<} = \int_0^R r^2 dr \int dr \psi^* (-\hbar^2 \nabla^2 / 2m) \psi + \int_0^R r^2 dr \int dr |\psi|^2 (V_0 + W_0), \quad (47)$$

and

$$H_{>} = \int_R^\infty r^2 dr \int d\Omega \{ \psi^* (-\hbar^2 \nabla^2 / 2m^*) \psi + |\psi|^2 V_{F-V}(r) \}. \quad (48)$$

²⁸ G. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. X, p. 127.

²⁷ R. P. Feynman, *Phys. Rev.* **97**, 660 (1955).

Combining Eqs. (17) and (46), we obtain the total energy of the F center as a functional of the wave function for the F electron and the lattice configuration σ :

$$E_T(\eta; \sigma) = H_F(\eta; \sigma) + \Delta E_L(\eta; \sigma), \quad (49)$$

where η is either the α or the β which appears in Eqs. (25) or (26), respectively.

We minimize $E_T(\eta; \sigma)$ simultaneously with respect to α (or β) and σ to obtain the energy of the system for the case of a relaxed state of the F -center electron and lattice; i.e., $E_T(\alpha_0; \sigma_0)$ for the relaxed ground state $|\alpha_0, \sigma_0\rangle$ and $E_T(\beta_1; \sigma_1)$ for the relaxed excited state $|\beta_1, \sigma_1\rangle$. For the unrelaxed states which we obtain by either optical excitation from the state $|\alpha_0, \sigma_0\rangle$ or by emission from the state $|\beta_1, \sigma_1\rangle$, we invoke the Franck-Condon principle; i.e., the ions are fixed at their positions in the relaxed initial state. This means that for the unrelaxed state we minimize the total energy $E_T(\eta; \sigma)$ as a function of only η , with σ equal to that value for the initial relaxed state. For the unrelaxed states we must also use the infrared polarization which is appropriate for the relaxed initial state.

V. ADDITIONAL CONSIDERATIONS

In this section, we shall discuss the lifetime of the relaxed excited state, the spatial extent of the F -electron wave function, a procedure by which we may determine how well the variational wave functions give the exact properties of the SCP model, the Huang-Rhys factor, and the thermal activation energies.

Fowler and Dexter²⁰ give the expression for the radiative lifetime of luminescent centers in ionic crystals. For our case, their expression reduces to the expression,

$$\Sigma_{\alpha\beta} \tau_{\alpha\beta} = \left[\frac{\mathcal{E}_{\text{off}}(E_{\alpha\beta})}{\mathcal{E}_{\text{eff}}(E_{\beta\alpha})} \right]^2 \frac{\pi^2 \hbar^3 c^2}{n(E_{\alpha\beta}) n(E_{\beta\alpha})} \times \frac{3E_{\alpha\beta} |\langle \beta_0, \sigma_0 | z | \alpha_0, \sigma_0 \rangle_{\text{abs}}|^2}{E_{\beta\alpha}^3 |\langle \alpha_1, \sigma_1 | z | \beta_1, \sigma_1 \rangle_{\text{emis}}|^2}. \quad (50)$$

The quantity $\Sigma_{\alpha\beta}$ is the absorption cross section, and $\tau_{\alpha\beta}$ is the decay time. The quantities $\mathcal{E}_{\text{off}}(E)$ and $n(E)$ are, respectively, the effective field at the center and the index of refraction evaluated at the peak energy of absorption [$E_{\alpha\beta} = H_F(\beta_0; \sigma_0) - H_F(\alpha_0; \sigma_0)$] or emission [$E_{\beta\alpha} = H_F(\beta_1; \sigma_1) - H_F(\alpha_1; \sigma_1)$]. The effective field is an explicit function of the electronic state and the positions of the ions. Therefore we must evaluate it in a self-consistent manner, and we do not expect

$$\mathcal{E}_{\text{off}}(E_{\alpha\beta}) = \mathcal{E}_{\text{eff}}(E_{\beta\alpha}).$$

Other researchers^{8,20} suggest that the square of the ratio of these two effective fields is of the order of unity, with a change which is no greater than a factor of 4 for most cases, i.e.,

$$1 \lesssim [\mathcal{E}_{\text{off}}(E_{\alpha\beta}) / \mathcal{E}_{\text{eff}}(E_{\beta\alpha})]^2 \lesssim 4. \quad (51)$$

Using the experimental values for the other parameters, we find for NaCl⁸ that the lifetime becomes

$$\tau_{\alpha\beta} = 17.9 \times 10^{-8} \text{ sec} \frac{|\langle \beta_0, \sigma_0 | z | \alpha_0, \sigma_0 \rangle_{\text{abs}}|^2}{|\langle \beta_1, \sigma_1 | z | \alpha_1, \sigma_1 \rangle_{\text{emis}}|^2}. \quad (52)$$

Because many of the above parameters for the other groups of crystals have not been measured, and because the most important terms of Eqs. (50) and (52) are the matrix elements, we shall compute only the square of the ratio of the matrix elements. This will enable us to obtain order-of-magnitude estimates of the lifetime in those systems for which our experimental knowledge is not so complete as that for NaCl and KCl. We define τ_R to be the ratio

$$\tau_R = \frac{|\langle \beta_0, \sigma_0 | z | \alpha_0, \sigma_0 \rangle_{\text{abs}}|^2}{|\langle \beta_1, \sigma_1 | z | \alpha_1, \sigma_1 \rangle_{\text{emis}}|^2}, \quad (53)$$

and referring to Eq. (52), we expect an order-of-magnitude estimate for the radiative lifetime to be given by

$$\tau_{\alpha\beta} \approx \tau_R \times 10^{-7} \text{ sec}. \quad (54)$$

In the above lifetime discussion, we have considered only dipole radiation to the unrelaxed ground state. There are, of course, other processes which may be competitive with the dipole-radiation decay, such as nonradiative decay (high-temperature thermal ionization) of the excited and tunnelling to the conduction band. Hence our present treatment of the SCP model will be least subject to criticism for low temperatures.

The expectation value of a given power of the radial coordinate r gives us a measure of the spatial extent of the F -center electronic wave function. For convenience, we have chosen the first power of r ; namely, we compute

$$r(\eta, \sigma) = R^{-1} \langle \eta, \sigma | r | \eta, \sigma \rangle. \quad (55)$$

There are many possible ways to test how well the variational wave functions approximate the exact eigenfunctions of our model Hamiltonian. We use the following procedure. We take the matrix elements of the operator equations

$$[z, H_{<}] = (i\hbar p_z / m), \quad \text{for } r < R \quad (56)$$

and

$$[z, H_{>}] = (i\hbar p_z / m^*), \quad \text{for } r > R \quad (57)$$

between the states $|\alpha, \sigma\rangle$ and $|\beta, \sigma\rangle$, where $\sigma = \sigma_0$ for absorption and $\sigma = \sigma_1$ for emission; namely,

$$\langle \beta_0, \sigma_0 | z | \alpha_0, \sigma_0 \rangle E_{\alpha\beta} = (i\hbar/m) \langle \beta_0, \sigma_0 | p_z | \alpha_0, \sigma_0 \rangle_{r < R} + (i\hbar/m^*) \langle \beta_0, \sigma_0 | p_z | \alpha_0, \sigma_0 \rangle_{r > R} \quad (58)$$

for absorption and

$$\langle \alpha_1, \sigma_1 | z | \beta_1, \sigma_1 \rangle E_{\beta\alpha} = (i\hbar/m) \langle \alpha_1, \sigma_1 | p_z | \beta_1, \sigma_1 \rangle_{r < R} + (i\hbar/m^*) \langle \alpha_1, \sigma_1 | p_z | \beta_1, \sigma_1 \rangle_{r > R} \quad (59)$$

for emission. We then compute both the left- and right-

hand sides of Eqs. (58) and (59). If the state $|\eta, \sigma\rangle_F$ were an exact eigenstate of \mathcal{H}_F , then the equality would hold. But our variational wave functions are not exact, and then the amount by which the ratio $\tau_M(\sigma)$ of the left-hand side divided by the right-hand side differs from 1 will be a measure of how well we have carried out the mathematics for our model.

The F -center absorption in CaO exhibits some structure which Kemp interprets to be the zero-phonon line.²⁹ The probability for the zero-phonon transition relative to the entire F -center absorption band is $\exp(-s)$, where s is the Huang-Rhys factor³⁰

$$s \approx \{E_T(\beta_0; \sigma_0) - E_T(\beta_1; \sigma_1)\} / \hbar\omega_l. \quad (60)$$

Hence we may observe in practice the zero-phonon transition, if it exists, only for values of $s \lesssim 6$. The energy

$$E_{0-ph} = \{E_T(\beta_0; \sigma_0) - E_T(\beta_1; \sigma_1)\} \quad (61)$$

gives us the location of the zero-order phonon line relative to the F -center absorption peak.

The thermal activation energy $\epsilon_t(\eta; \sigma)$ is the energy difference between the ionized F center (anion vacancy and the F electron in the conduction band) and the F -center total energy $E_T(\eta; \sigma)$. The thermal activation energy from the relaxed ground state $|\alpha_0, \sigma_0\rangle$ is

$$\epsilon_t(\alpha_0; \sigma_0) = \Delta E_L(\sigma_d) - E_T(\alpha_0; \sigma_0) \approx \epsilon_t(0), \quad (62)$$

and the thermal activation energy from the relaxed first excited state $|\beta_1, \sigma_1\rangle$ is

$$\epsilon_t(\beta_1; \sigma_1) = \Delta E_L(\sigma_d) - E_T(\beta_1; \sigma_1) \approx \epsilon_t(1). \quad (63)$$

Relations (62) and (63) are strictly valid only in the limit for which the energy levels have zero width.

VI. RESULTS

We report in this section the results of the preceding variational Hartree and quasiadiabatic semicontinuum polaron models. We shall divide the presentation of our results into three groups: the alkali halides (NaCl and KCl), the alkaline earth fluorides (CaF₂, SrF₂, and BaF₂), and the alkaline earth oxides (MgO and CaO). We use the Born-Mayer empirical form (15) for the repulsive energy. Table I contains the values of the input data which we have used.

To decide which model agrees best with the known experimental results, we consider two questions. First, how well did we solve for the eigenfunctions of our model Hamiltonian, and second, how model-sensitive are those quantities which we compare with the experimental results?

If the ratio τ_M is not close to 1, then we must say that our results are inconclusive, because we have not solved the model Hamiltonian with sufficient rigor. We em-

TABLE II. Numerical results of the SCP(HF) model for NaCl and KCl compared with experiment and with the model of Ref. 8. The quantities χ , E_{BA} , E_{CD} , E_{0-ph} , $\epsilon_t(\alpha_0, \sigma_0)$, $\epsilon_t(\beta_1, \sigma_1)$, $\epsilon_t(0)$, and $\epsilon_t(1)$ are energies expressed in atomic units (1 a.u. = 27.2 eV). All other quantities are dimensionless.

	NaCl	NaCl ^a	KCl	NaCl
χ	-0.028	-0.020	-0.022	-0.04
(m^*/m)	0.6	0.6	0.6	0.6
σ_0	-0.015	0.0	-0.012	-0.015
$r(\alpha_0, \sigma_0)$	0.732	...	0.733	0.744
$r(\beta_0, \sigma_0)$	1.11	...	1.14	5.69
$\alpha_0 R_0$ ^b	2.92	2.77	2.92	2.88
$\beta_0 R_0$	2.25	2.08	2.19	0.439
$\tau_M(\sigma_0)$	0.964	...	0.962	1.07
E_{BA} (theor)	0.109	0.103	0.102	0.099
E_{BA}' (expt)	0.101 ^c	0.101	0.085 ^c	0.101
σ_1 (theor)	-0.103	-0.100	-0.102	-0.103
σ_1' (expt)	-0.07 to	-0.07 to	-0.125 ^d	-0.07 to
	-0.08 ^d	-0.08		-0.08
$r(\alpha_1, \sigma_1)$	0.812	...	0.807	0.837
$r(\beta_1, \sigma_1)$	5.55	...	5.08	5.64
$\alpha_1 R_1$ ^b	2.64	1.94	2.66	2.56
$\beta_1 R_1$	0.451	0.356	0.492	0.443
$\tau_M(\sigma_1)$	0.752	...	0.689	0.653
E_{CD} (theor)	0.051	0.046	0.045	0.042
E_{CD}' (expt)	0.040 ^e	0.040	0.046 ^e	0.040
E_{0-ph}	0.033	...	0.035	0.033
s (theor)	27.6	...	36.8	27.9
s' (expt)	25.0 ^f	25.0	...	25.0
τ_R (theor)	10.9	13.4	8.39	0.473
τ_R' (expt)	10.0 ^g	10.0	5.71 ^g	10.0
$\epsilon_t(\alpha_0, \sigma_0)$ (theor)	0.069	...	0.069	0.059
$\epsilon_t(0)$ (expt)	0.071 ^h	0.071	0.075 ^h	0.071
$\epsilon_t(\beta_1, \sigma_1)$ (theor)	0.004	...	0.005	0.004
$\epsilon_t(1)$ (expt)	0.003 ⁱ	0.003	0.002 ⁱ	0.003

^a This column contains the numerical results of model SCP(QA; WBF) given in Ref. 8.

^b The quantities R_0 and R_1 are given by the relations $R_0 = R(1 - \sigma_0)$ and $R_1 = R(1 - \sigma_1)$.

^c J. J. Markham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. VIII (Suppl.), Table 3.2a.

^d N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938); N. N. Kristofel', *Fiz. Tverd. Tela* **5**, 2367 (1963) [English transl.: *Soviet Phys.—Solid State* **5**, 1722 (1964)].

^e Reference c, Table 8.1.

^f Reference c, Table 3.5. The Huang-Rhys factor is assumed to be 25 for the Poissonian curve.

^g Reference c, Table 8.5.

^h Reference c, Table 11.5.

ⁱ Reference c, Table 7.4.

phasize that even when τ_M equals 1, the variational wave functions may differ substantially from the exact wave functions. The ratio τ_M gives us only first-moment information. The extent to which τ_M may differ from 1 before we must reject the variational wave functions as being too crude for the computed quantities is a subjective decision. This is in part due to the scarcity of experimental data on the emission and thermal activation energies and the lifetime in the non-alkali-halide ionic crystals (e.g., CaF₂, SrF₂, BaF₂, MgO, CaO, etc.). Based upon the agreement of the semicontinuum polaron model SCP(HF) for NaCl and KCl with the experimental values of $E_{\alpha\beta}$, $E_{\beta\alpha}$, τ_R , s , $\epsilon_t(0)$, and $\epsilon_t(1)$, we feel that values of τ_M between 0.5 and 1.3 are reasonable.

²⁹ J. C. Kemp, W. M. Ziniker, and E. B. Hensley (to be published).

³⁰ A. E. Hughes (unpublished).

TABLE III. The numerical results for absorption of the SCP(HF) model for CaF_2 , SrF_2 , and BaF_2 compared with experiment^a and with a point-ion rigid-lattice model.^b The quantities χ and E_{BA} are energies expressed in atomic units (1 a.u. = 27.2 eV). All other quantities are dimensionless.

	CaF_2	SrF_2	BaF_2
χ	-0.04	-0.04	-0.04
(m^*/m)	0.6	0.6	0.6
σ_0	0.005	-0.004	-0.014
$r(\alpha_0, \sigma_0)$	0.744	0.795	0.81
$r(\beta_0, \sigma_0)$	6.39 ^c	6.75 ^c	7.37 ^c
$\alpha_0 R_0^d$	2.77	2.70	2.65
$\beta_0 R_0$	0.391	0.370	0.339
$\tau_M(\sigma_0)$	0.937	0.732	0.546
E_{BA} (theor)	0.120	0.090	0.064
E_{BA} (theor) ^b	0.117 ^b	0.107 ^b	0.096 ^b
E_{BA}' (expt)	0.121 ^a	0.101 ^a	0.069 ^a

^a P. Feltham and I. Andrews, *Phys. Status Solidi* **10**, 203 (1965), Table 3.

^b H. S. Bennett and A. B. Lidiard, *Phys. Letters* **18**, 253 (1965), Table 1.

^c The SCP(HF) model with $\chi = -0.04$ a.u. and $m^*/m = 0.6$ predicts that the excited state to which absorption reaches is very diffuse, while the point-ion rigid-lattice model of Ref. b predicts that it is compact. This contradiction between models, both of which give reasonable values for the absorption energy, dramatizes the need for further theoretical and experimental studies.

^d The quantity R_0 is given by the relation $R_0 = R(1 - \sigma_0)$.

We consider a bound state to be compact for values of $r(\eta, \sigma) \lesssim 1$ and to be diffuse for values of $r(\eta, \sigma) \gtrsim 3$. For values between 1 and 3 the decision is rather subjective.

Among the above quantities, the thermal activation energy and the lifetime are most sensitive to the details of a given model. If they are known experimentally, we give them more weight in our decision on a model's worth than the less model-sensitive absorption and emission energies.

A. Alkali Halides: NaCl and KCl

Using the values $\chi = -0.028$ a.u. and $m^* = 0.6m$, we find that the SCP(QA) model for NaCl gives $\tau_M(\sigma_0) = 0.829$, $\tau_M(\sigma_1) = 0.567$, $E_{BA} = 0.060$ a.u., $E_{CD} = 0.023$ a.u., and $\tau_R \approx 0.231$. Note that we shall now use the notation $E_{BA} \equiv E_{\alpha\beta}$ and $E_{CD} \equiv E_{\beta\alpha}$. The values of τ_M indicate that our variational wave functions are reasonable. However, the predicted E_{BA} , E_{CD} , and τ_R values disagree with the experimental values of 0.101 a.u., 0.040 a.u., and 10.0, respectively. Quantitatively similar results obtain for KCl. We conclude that the SCP(QA) model contains physical statements which do not apply to the above alkali halides.

We present in Table II the SCP(HF)-model predictions for NaCl and KCl. We indicate the experimental value of a quantity by a prime, i.e., E_{BA} is the theoretical value for the absorption energy, and E_{BA}' is the experimental value. The over-all agreement between theory and experiment is very good, particularly when we consider the model-sensitive quantities.

We list in the fourth column of Table II the SCP(HF) results for NaCl, with $\chi = -0.04$ a.u. and $m^* = 0.6m$, in order to illustrate the dangers of those theories which

compute and then compare with experiment only model-insensitive quantities such as E_{BA} and E_{CD} . Even though the absorption and emission energies E_{BA} and E_{CD} agree extremely well with the experimental values E_{BA}' and E_{CD}' for this case, the lifetime τ_R is too small by a factor of 25.

B. Alkaline Earth Fluorides

Because we have sufficient experimental data for the alkali halides, and because the τ_M values were reasonably close to 1, we can state that the SCP(HF) model for NaCl and KCl is superior to the SCP(QA) model. However, because we know among the quantities listed in Table II only E_{BA} for the alkaline earth fluorides, and because we do not have values of χ and m^* for this group, we must be cautious here. Keeping in mind the dangers illustrated in the fourth column of Table II, we proceed as follows. Inserting all possible combinations of $\chi = 0.0$, -0.02 , and -0.04 a.u. and $m^* = 0.6m$ and $1.0m$ into the SCP(QA) and the SCP(HF) models for CaF_2 , we study the theoretical values of $E_{BA}(\chi; m^*)$ as a function of χ and m^* . Within the above range of χ and m^* values, the first variational derivatives for both models satisfy the inequalities

$$(\delta E_{BA}/\delta \chi)_{m^*} > 0 \quad (64)$$

and

$$(\delta E_{BA}/\delta m^*)_{\chi} < 0. \quad (65)$$

The existence of electrons in an ionic crystal dictates that $\chi \leq 0.0$ a.u. Even when $\chi = 0.0$ a.u. and $m^* = 0.6m$, the SCP(QA) model predicts an absorption energy which is 20% less than the experimental value. However, the SCP(HF) model with $\chi = -0.04$ a.u. and $m^* = 0.6m$ predicts that $E_{BA} = 0.120$ a.u. and this agrees very well with the experimental value of $E_{BA}' = 0.121$ a.u. Inserting the values $\chi = -0.04$ a.u. and $m^* = 0.6m$ into the SCP(HF) model, and emphasizing again the potential hazards which are illustrated in column 4 of Table II, we compute E_{BA} for SrF_2 and BaF_2 . We list in Table III the results for the absorption problem. We do not list the emission results, because the values of $\tau_M(\sigma_1)$ are less than 0.5. We obtain reasonable agreement with the experimental absorption energies for SrF_2 and BaF_2 . However, lacking the other experimental values for E_{CD}' and τ_R' and rigorous solutions of the model Hamiltonian for emission, we must view the above results for the alkaline earth fluorides as interim results.

C. Alkaline Earth Oxides

We have reasonable values of $\chi = -0.04$ a.u. and $m^* \approx 1.0m$ for MgO .³¹ We shall use these same values for CaO . This is admittedly questionable, particularly when we remark that ZnO has an effective band mass

³¹ J. Yamashita, *Phys. Rev.* **111**, 733 (1958); M. L. Cohen, P. J. Lin, D. M. Roessler, and W. C. Walker, *ibid.* **155**, 992 (1967).

$m^* \approx 0.24m$.³² The SCP(QA) model for MgO and CaO with $\chi = -0.04$ a.u. and $m^* \approx 1.0m$ yields values of $\tau_M(\sigma_0) \approx 1.1$ and $\tau_M(\sigma_1) \approx 1.1$, but values of the absorption energy which are too small by a factor of 25. We consider the results of the SCP(HF) model for MgO and CaO as inconclusive, because the values of τ_M are too far from 1 for both the absorption and emission problems. We may attribute the SCP(HF) difficulty to the deficiencies of the hydrogenic variational wave functions. We discuss this in the Appendix.

Since most reasonable models give correct order-of-magnitude estimates of E_{BA} , even though E_{CD} and τ_R may be wrong by factors of 2 or more, we feel that the factor of 25 arising between the SCP(QA) model E_{BA} and the experimental value E_{BA}' signals the necessity for more serious thought on the application of Eqs. (35)–(37) to the F center in the oxides, that is, to those cases for which $Z_V \neq +e$ and $Z_F \neq -e$. At least two possible explanations exist. First, Eqs. (35)–(37) may not be correct when $Z_V \neq e$ and $Z_F \neq -e$, as we have already suggested in Sec. IV. The second explanation is that the coupling constant in the Fröhlich Hamiltonian may be too small to be of importance. The coupling constant is about 4.34 for KCl with $m^* = 0.6m$, 2.3 for MgO with $m^* = 1.0m$, and 1.1 for MgO with $m^* = 0.25m$.

VII. COMMENTS AND DISCUSSION

We have shown that our SCP(HF) model with the variational wave functions (25) and (26) agrees reasonably well with experiments for NaCl and KCl. Lacking lifetime measurements and acceptable emission wave functions for the alkaline earth fluorides, we can only remark here that, thus far, the SCP(HF) model with $\chi = -0.04$ a.u. and $m^* = 0.6m$ predicts results which agree with the absorption experiments in CaF₂, SrF₂, and BaF₂ to within 10%. We find that the SCP(QA) model for the alkaline earth oxides gives incorrect results and that the SCF(HF) model gives inconclusive results, because both the absorption and emission wave functions are not acceptable.

Our SCP(HF) and SCP(QA) models differ only by which approximation we choose to represent the optical polarization W_{opt} . The SCP(QA) model contains expression (43), while the SCP(HF) model contains expression (44). Aside from this one difference, all other terms of the Hamiltonian for each model are identical. We also emphasize that our SCP(QA) model differs substantially from the quasiadiabatic approximation of Simpson and of Krumhansl and Schwartz (SKS). Only the optical-polarization term is the same in our SCP(QA) model and in the quasiadiabatic model as formulated by Krumhansl and Schwartz and as discussed by Gourary and Adrian.²⁸ All other terms except the kinetic energy are different. In particular, we use

the infrared-polarization term given by Eq. (42) and the Haken interaction term (37) when the F electron is outside the cavity, while Simpson and Krumhansl and Schwartz use the infrared polarization

$$W_{\text{inf}}(\text{SKS}) = -\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \int_R^\infty q(s)s^{-2} ds \quad (66)$$

and the interaction term

$$V(\text{SKS}) = \frac{Z_F Z_V}{\epsilon_\infty r} + Z_F Z_V \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}\right) \int_r^\infty q(s)s^{-2} ds \quad (67)$$

when the F electron is outside the cavity.

In order to prevent confusion, we list the differences between our SCP(HF) model and the model contained in Fowler's paper.⁸ We shall refer to the latter model as the SCP(QA;WBF) model. Our SCP(HF) model treats the lattice and the F electron self-consistently. We minimize $E_T(\eta; \sigma)$, while the SCP(QA;WBF) model treats only the F -electron term $H_F(\eta, \sigma)$ and contains the assertion that $\sigma_0 = 0.0$ and $\sigma_1 = -0.1$ in the term V_0 . We evaluate the Haken interaction $V_{F-V}(r)$ exactly in the term $H_>$ of Eq. (48), while Fowler approximates this term by an effective dielectric constant within the interval $\epsilon_0 > \epsilon_{\text{eff}} > \epsilon_\infty$. But the most important difference lies in the physical content of the term W_0 of the well depth. Our SCP(HF) model contains the infrared-polarization term W_{inf} which is consistent with the Haken theory. The SCP(QA;WBF) model contains the infrared-polarization term of Simpson and of Krumhansl and Schwartz,⁸ i.e., Eq. (66). Fowler states in the appendix of his paper that consistency requires $W_{\text{inf}} = -(V_{\text{sev}} + V_{\text{set}})$, and then argues that for large-orbit states the difference between W_{inf} and $W_{\text{inf}}(\text{SKS})$ is small. Using $W_{\text{inf}}(\text{SKS})$, we obtain positive energy values for $H_F(\beta_0, \sigma_0)$. This result places the unrelaxed excited state in the conduction band and is not consistent with a bound-state variational wave function. Finally, our SCP(HF) model has the Hartree form for the optical polarization $W_{\text{opt}}(\text{HF})$, and the SCP(QA;WBF) model has the quasiadiabatic form $W_{\text{opt}}(\text{QA})$. Comparing columns 1 and 2 of Table II, we see that the accumulation of all these differences changes only negligibly the final theoretical numbers for the experimentally measured quantities.

One feature is common to the research of Krumhansl and Schwartz, of Fowler, and of the present author; namely, the F electron experiences a constant potential inside the cavity. We expect that more refined treatments of either the quasiadiabatic approximation or the Hartree approximation will lead to spatially dependent potentials for distances less than the nearest-neighbor distance. But again we stress that the functional dependence of the constant potential upon the F -electron wave function undergoes extreme changes among the three above approaches to the F center.

³² W. S. Baer, Phys. Rev. **154**, 785 (1967).

Hence any conclusions which obtain from any of these three treatments of the F center are subject to the validity of a constant potential inside the cavity. Our studies suggest that the Hartree term for the optical polarization is physically correct within the context of the polaron theory for the F center in the alkali halides NaCl and KCl and in the three alkaline earth fluorides CaF₂, SrF₂, and BaF₂, and that it might be correct for the oxides MgO and CaO.

We have used only the spherically symmetric part of the potential $V_{\text{peri}}(\mathbf{r})$. This procedure is exact for matrix elements involving spherically symmetric wave functions or “ $2p$ ”-type wave functions which experience potentials having at least tetrahedral symmetry or higher.³³ The procedure is not exact for “ d ”- or “ f ”-type wave functions.

As we show in Table III, the point-ion calculation of Ref. 34, HFPI(BL), is least successful for the BaF₂ absorption energy in agreeing with experiment. The SCP(HF) model for BaF₂ with $\chi = -0.04$ a.u. and $m^* = 0.6m$ gives much better agreement. This numerical improvement and the 10% agreement for CaF₂ and SrF₂ may be fortuitous. The point-ion calculation HFPI(BL) gives ground-state wave functions which are too compact for the BaF₂ F center and hence a greater absorption energy. The SCP(HF) model for BaF₂ gives a slightly more diffuse ground-state wave function, and this contributes to the better numerical agreement with experiment. The HFPI(BL) model does not contain polarization, while the SCP(HF) model does contain polarization. This suggests that even though we may neglect polarization in CaF₂ and SrF₂ for a zero-order approximation, we must include polarization in BaF₂ from the beginning. The fact that the electronic polarizability of the neighboring Ba⁺⁺ ions, $\alpha(\text{Ba}^{++}) = 2.5 \text{ \AA}^3$, is larger than the electronic polarizabilities of the Ca⁺⁺ and Sr⁺⁺ ions, 1.1 \AA^3 and 1.6 \AA^3 , respectively, provides us with one possible explanation for the above observation. In addition, the HFPI(BL) model predicts compact excited states for the alkaline earth fluorides, while the SCP(HF) model predicts diffuse excited states. This is a most crucial and physical difference between these two models. Because of a lack of experimental excited-wave-function knowledge, we cannot decide whether the HFPI(BL) model or the SCP(HF) model is correct in this case.

We add some critical comments which detract from the validity of the SCP(HF) model for the alkaline earth fluorides and of the SCP models in general when we ask questions about the value of the F -electron wave function at a lattice site. The ENDOR experiments give us such information. The F center in NaCl has cubic symmetry (inversion symmetry), and the F center in CaF₂ has tetrahedral symmetry (no inversion symmetry). This means that the assumption of a

spherically symmetric ground-state wave function is correct for NaCl, but may not be adequate for CaF₂. For the F center in a CaF₂ lattice, we should also consider the admixture of some anisotropic wave-function terms, and such terms could give rise to the more diffuse nature of the ground state in BaF₂ than it is in CaF₂ and SrF₂. All models with built-in spherical symmetry, such as the SCP models, do not recognize these differences in crystal structure. The crystal structure appears in them only numerically through the lattice constant and the Madelung potential. We expect that those quantities computed in this paper, which do not ask for the value of the wave function at the ν th lattice site, are much less sensitive to the lattice-structure details than the information given by ENDOR experiments.

Finally, we observe that perhaps most attention should be directed towards the physical content of the SCP(HF) model, and not towards the mathematical and group-theoretic (lattice-structure) limitations of the model, particularly when one contemplates a theory to explain properly the ENDOR experiments. That is to say, when we assume a constant potential for distances less than the nearest-neighbor distance, the Hartree formulation for the optical polarization is more correct when the F electron is close to the anion vacancy than the quasiadiabatic approximation for the optical polarization, and the ionic polarization follows to some extent the F -electron motion when the F electron is far from the anion vacancy.

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APPENDIX

We add a few remarks on the variational procedure and the inflexibility of the hydrogenic trial wave functions of Eqs. (25) and (26). Based upon our experience with the Gourary and Adrian type-II and type-III trial wave functions,³ we expect that the below remarks also apply to them.

Figure 2 shows the function $E_T(\beta; \sigma)$, which obtains from the NaCl SCP(HF) model, as a function of β for four values of $\sigma = -0.015, -0.02, -0.04, \text{ and } -0.10$. The function $E_T(\alpha; \sigma)$ for $-0.015 \geq \sigma \geq -0.20$ exhibits only one minimum and does not contain the features which we find in $E_T(\beta; \sigma)$. We call the minimum at $\beta_0 \equiv \beta_c$ the compact-state minimum and the one at $\beta_1 \equiv \beta_d$ the diffuse-state minimum. When $\sigma = -0.015$, two minima occur, and the compact one is the absolute

³³ A. M. Stoneham, Proc. Roy. Soc. (London) (to be published).

³⁴ H. S. Bennett and A. B. Lidiard, Phys. Letters 18, 253 (1965).

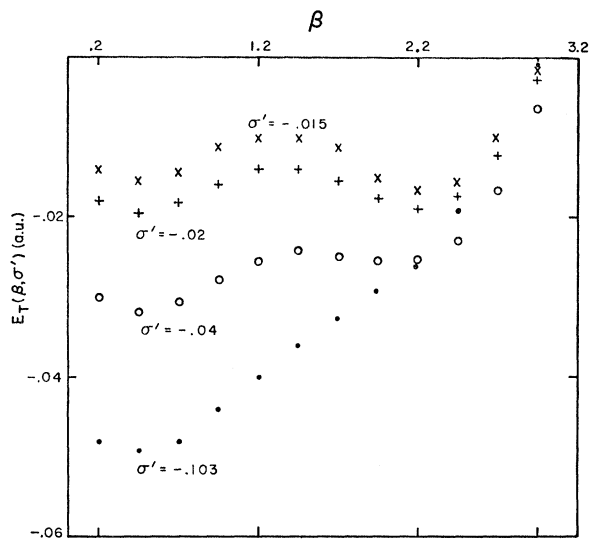


FIG. 2. The total F -center energy $E_T(\beta, \sigma)$ for fixed values of σ as a function of $\beta \equiv \beta_2 R(1 - \sigma)$, where β_2 is the same β which appears in Eq. (26). The F electron is in the excited-state equation (26). The energy is in atomic units (1 a.u. = 27.2 eV), and the wave-function variational parameter β is expressed in a dimensionless manner.

minimum. As σ decreases from -0.015 , the compact minimum rises until at $\sigma = -0.04$ the diffuse minimum becomes the absolute one. When $\sigma = -0.10$, a shoulder, which was first an inflection point, replaces the compact minimum. We report in Tables II and III the results which follow from the use of the absolute minimum. The transition from compact to diffuse states is much more dramatic when we examine the function $r(\beta, \sigma)$ as a function of σ . We fix $\sigma = \sigma'$, vary β until the absolute minimum of $E_T(\beta; \sigma')$ obtains at $\beta = \beta'$, and then evaluate $r(\beta', \sigma')$. Figure 3 presents plots of $r(\alpha', \sigma')$ and $r(\beta', \sigma')$ as functions of σ' . We see that $r(\alpha', \sigma')$ has no rapid variation for $-0.2 \leq \sigma' \leq +0.06$. On the other hand, the function $r(\beta', \sigma')$ exhibits a rather sudden jump from compact to diffuse properties between $-0.035 \geq \sigma' \geq -0.04$, and is a smoothly varying function of σ' for the region $-0.20 \leq \sigma' \leq -0.04$ and $-0.035 \leq \sigma' \leq +0.06$. The results of any model which yields values of σ_0 or σ_1 within this transition region would be rather questionable. Our models using the input data of Table I give values of σ_0 and σ_1 well outside this transition region. In order to make certain that our results are insensitive to the repulsion parameters ρ , ρ_+ , and ρ_- , we change ρ by 20%, and we alter ρ_+ and ρ_- by 15%, but keep the sum $\rho_+ + \rho_- = 5.21$ a.u. We find no detectable change in the location of the transition region and only negligible changes in $r(\alpha', \sigma')$ and $r(\beta', \sigma')$.

Based upon our work, we may attribute the very rapid transition between compact and diffuse states to

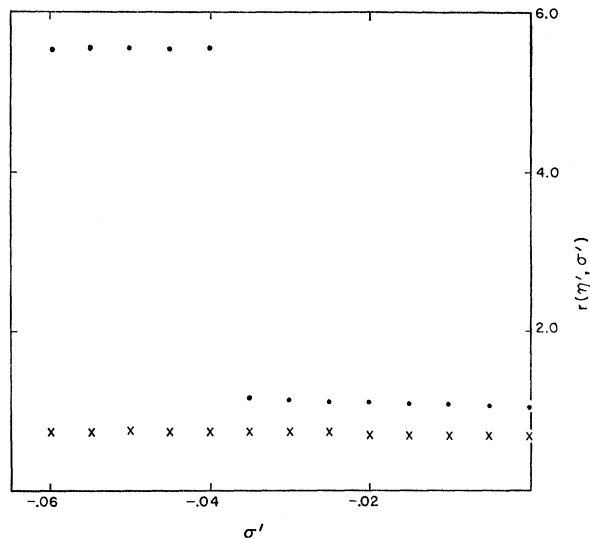


FIG. 3. The spatial extent of the F -electron wave function $r(\eta', \sigma')$ as a function of σ' . For each value of σ' , the wave-function variational parameter η' is such that $E_T(\eta', \sigma')$ is the absolute minimum. The quantities $r(\eta', \sigma')$ and σ' are dimensionless. The dots correspond to the excited F -electron state $\eta' = \beta'$, and the X 's correspond to the ground F -electron state $\eta' = \alpha'$. The quantity $r(\eta', \sigma')$ is given in Eq. (55).

one or more of the following: the inflexibility of the trial wave functions, the discontinuity of the model potential which is experienced by the F electron at $r = R$, and an inherent property of the F center. Wood has also found multiple minima for a model in which the F electron sees a continuous effective potential.³⁵ Therefore we expect the sudden transition to be associated with the inflexibility of the hydrogenic trial wave functions and/or with an inherent property of the F center.

The SCP(QA) model with hydrogenic trial wave functions also has similar behavior. The main difference is that the transition region in NaCl occurs for values of σ in the interval $0.02 \leq \sigma \leq 0.04$. This shift in the location of the transition region means that the SCP(QA) model tends to make the F -electron states more diffuse than the SCP(HF) model. Because only the radial part of the instantaneous polarization vector enters the quasiadiabatic term $W_{\text{opt}}(\text{QA})$, while the radial part of the average polarization vector, which is radial for cubic crystals without lattice distortions, enters the Hartree term $W_{\text{opt}}(\text{HF})$, the $W_{\text{opt}}(\text{QA})$ term produces less optical polarization than the $W_{\text{opt}}(\text{HF})$ term; i.e., the well depth for the $W_{\text{opt}}(\text{QA})$ term is more shallow than that for the $W_{\text{opt}}(\text{HF})$ term. Hence the F electron finds it easier to be outside the quasiadiabatic well than the Hartree well.

³⁵ R. F. Wood (private communication).