

The half-width of the electron-spin absorption band of the Z₃ center, 39 Oe, is less than that of the F center in KCl which is 58 Oe.¹⁶ This difference can be understood qualitatively in terms of our Z₃-center model since there is no hyperfine interaction between the electron and the strontium nucleus which has zero magnetic moment.

ENDOR studies should provide an important test

¹⁶ A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.* **91**, 1066 (1953).

of the Z₃-center model that is proposed in this paper. Such measurements and photoconductive studies have been planned.

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Theory of the Absorption and Emission of the F Center in Alkali-Halide Crystals*†

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The absorption and emission processes of the F center and their relationship to each other are treated using a model which contains many of the features of an exact treatment. The calculations are based on a formulation in which the total energy of the crystal in the ground and excited states is expressed as a function of the variational parameters in the F-center wave functions and of the displacements of the neighboring ions. The F electron is treated quantum-mechanically, but classical ionic crystal theory is used for all other terms in the total energy. A modified method of steepest descents is used to minimize the total energy. The electronic structure of the outer shells of the first nearest neighbor ions is taken into account in detail in the expression for the energy of the F-center electron. Simple, one-parameter, vacancy-centered wave functions are used to describe the F electron. A large Stokes shift is obtained in all crystals. The distortions are small in the ground state but, in the relaxed excited state, they are of the order of 10% of the nearest-neighbor distance and have a pronounced asymmetry.

I. INTRODUCTION

THE F-center lattice defect in alkali-halide crystals consists of an electron trapped at a vacant negative ion site. This defect is one of the simplest which can occur in ionic crystals, and in the physics and chemistry of lattice defects in these crystals it occupies a position of importance roughly comparable to that of the hydrogen atom in ordinary chemistry. It is not surprising, then, that many calculations of the electronic structure of the F center have appeared. The most detailed of these have been made by Kojima,¹ Gourary and Adrian,² Pekar,³ and Wood and Korrington.⁴ Gourary and Adrian⁵ have given a review of many of the theoretic

calculations carried out up until about 1960. Most of the calculations have been limited to an investigation of the ground and first excited states of the center in a rigid, undistorted lattice. The lattice has usually been treated either as a continuum or as made up of simple point ions, although in Refs. 1, 4, and 5 an effort has been made to take into account the structure of the lithium ions which are first-nearest-neighbors (1nn) to the vacancy in LiF^{1,5} and LiCl.⁴ The effect of lattice distortions on the energy levels has not yet been treated in a consistent manner, although a first step has been made in Ref. 4. The importance of lattice distortions can be inferred from the emission spectra of the F center.

The principal emission band of the F center in alkali-halide crystals exhibits a large Stokes shift. In these crystals, the peak of the emission band corresponds to a transition energy $\Delta\epsilon_e$ which is usually about half as large as the F-band absorption energy $\Delta\epsilon_a$; that is, $\Delta\epsilon_e \approx 0.5\Delta\epsilon_a$. To understand how this large Stokes shift can come about, we must consider that the electronic wave function of the ground state of the F-center elec-

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¹ T. Kojima, *J. Phys. Soc. Japan* **12**, 918 (1957).

² B. S. Gourary and F. J. Adrian, *Phys. Rev.* **105**, 1180 (1957).

³ S. I. Pekar, *Uspekhi Fiz. Nauk* **50**, 197 (1953).

⁴ R. F. Wood and J. Korrington, *Phys. Rev.* **123**, 1138 (1961).

⁵ B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. 10.

tron is of Γ_1^+ symmetry of the octahedral group, whereas that of the first excited state is of Γ_4^- symmetry. The excited state is long-lived compared to the characteristic time of lattice relaxation ($\sim 10^{-11}$ sec) and hence the lattice will adjust locally to the symmetry of the excited-state wave function before emission occurs. During the emission process the Franck-Condon principle is assumed to apply. It may happen that both the ground- and excited-state energies calculated with the excited-state distortions are considerably different from those calculated with the ground-state distortions. We shall see that this is, indeed, the case for the F center in the alkali halides. Evidently, the distortion of the lattice in the vicinity of the defect is quite important.

Swank and Brown⁶ have found that the lifetime of the excited state of the F center is considerably longer than might be expected from the usual arguments applicable to atomic systems. Fowler and Dexter⁷ have discussed this result and several possible explanations of it, some of which we shall consider later. One suggestion which has been made by various people is that there is a level of Γ_1^+ symmetry, lying below the first excited level, which serves as an electron trap and thus increases the lifetime. One of the present authors⁸ carried out calculations on LiCl which indicated that this is apparently not the case, although it cannot yet be ruled out completely. Those calculations indicated that there is a state of Γ_1^+ symmetry lying just above the first excited state, but at least part of the K band was attributed to transitions to this state. It is not inconceivable that, after lattice relaxation, this level or another one of forbidden symmetry lies below the first Γ_4^- level. Detailed calculations are needed on this point.

Pekar, in Ref. 3, has treated the F center in a continuum approximation in an attempt to understand the emission spectra and the temperature broadening of the lines. His approach gives some striking results, but Fowler and Dexter,⁹ among others (including Pekar himself), have criticized it and we shall not discuss it here.

From the foregoing it should be apparent that the F center is of considerable interest in its own right. There are two additional reasons which make it interesting as a specific center. The first derives from the experimentally well-established fact that F centers can aggregate to form other defects such as the M and R centers. The electronic structure of the M center has been investigated with reasonably good results on the basis of the model of two F centers bound together at neighboring halide sites.^{10,11} The second reason is that the F center and its aggregates are somewhat unusual

defects, in that there are no sources of potential at the vacant lattice sites. Thus, these defects, especially in their ground states, appear to conform more closely to a particle-in-a-box model than to that of a hydrogenic impurity imbedded in a crystal. While it is not yet clear that this gives them any distinctive properties, it is possible that it may do so. For example, it may be that these centers are unusually sensitive to the movement of neighboring ions.

For the theoretician, the F center seems destined to serve as a test case for various methods of calculating the electronic structure of lattice defects in ionic crystals. The F center is a deep trap compared to those found in doped silicon and germanium. The perturbation of the host lattice is well localized and fairly strong, at least in the ground state. Lattice distortions are present and may be important but, as far as we know, very little detailed work has been done to date on the effects of local distortions on the optical properties of defects. The F center is a one-electron defect which very nearly preserves the over-all charge distribution of the perfect crystal, a characteristic which reduces the importance of electronic polarization effects, although these effects may become important in the excited states. The interactions of defects with the phonon field are important for both optical and thermal properties and the F center, because of its simplicity, may serve as a model when investigating these properties.

In this paper, we attempt to treat the absorption and emission spectra of the F center and their relationship to each other in a consistent way, using just about the simplest model which contains most of the features of an exact treatment, with the notable exception of the dynamic electron-phonon interaction. We take distortions of the lattice into account in all of the states which we treat, but the distortions are limited to displacements of the nearest-neighbor ions. We do this by obtaining an expression for the total energy of the crystal in the ground and excited states as a function of the variational parameters in the F -center wave functions and of the displacements of the neighboring ions. The F electron is treated quantum-mechanically, but classical ionic crystal theory is used for all other terms in the total energy. A modified method of steepest descents is used in an iterative procedure to minimize the total energy. The electronic structure of the outer shells of the first nearest-neighbor ions is taken into account in detail in the expression for the energy of the F -center electron. Simple, one-parameter, vacancy-centered wave functions are used to describe the F electron.

In the next section, we shall discuss the Hamiltonian and the wave functions which we used to obtain the expressions for the energy of the F center in a distorted crystal. In Sec. III, we expand that part of the total energy of the crystal derived from classical ionic crystal theory up to second order in small displacements and combine the results with those of Sec. II to obtain an expression for the total energy of the crystal. In Sec.

⁶ R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

⁷ W. Beall Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962).

⁸ R. F. Wood, Phys. Rev. Letters **11**, 202 (1963).

⁹ W. Beall Fowler and D. L. Dexter, Phys. Stat. Solidi **2**, 821 (1962).

¹⁰ Axel Meyer and R. F. Wood, Phys. Rev. **133**, A1436 (1964).

¹¹ R. A. Evarestov, Opt. i Spektroskopiya **16**, 361 (1964) [English transl.: Opt. Spectry. **16**, 198 (1964)].

IV, some equations for oscillator strengths and lifetimes are set forth. In Sec. V, the details of the calculations and the results are given, and in the last section we discuss the results.

II. THE F -CENTER HAMILTONIAN AND WAVE FUNCTIONS

Of course, it is evident from the outset that in treating this problem of a crystal containing an F center we are severely limited in what we can handle. The most we can hope for at this time is to get at least an approximation to the Hartree-Fock problem for the crystal with the F center. We approach the problem in the same spirit in which Landshoff,¹² Löwdin,¹³ and Howland¹⁴ calculated the cohesive energy of the alkali halides. One of the characteristics of this approach is that the free ion Hartree-Fock orbitals of the alkali and halide ions are assumed to be unchanged when the ions come together to form a crystal. However, since this assumption cannot be rigorously correct, we shall not be too concerned about the exact form of the ion orbitals which we use. The total wave function of the many-electron system is written as an antisymmetrized product of the free ion space-spin orbitals, i.e.,

$$\Psi(1,2,\dots,n) = A\phi_1(1)\phi_2(2)\cdots\phi_n(n). \quad (1)$$

A is the antisymmetrizing operator given by

$$A = (n!)^{-1/2} \sum_P (-1)^p P, \quad (2)$$

in which n is the number of electrons and p is the parity of the permutation operator P . It is a relatively simple task to write down the formal expressions for the equations which determine the one-electron orbitals of the entire crystal in this approximation.¹⁵ This is most easily done for orthogonal orbitals and so we shall assume that the orbital of the F -center electron can be obtained from an effective Hamiltonian equation appropriate for such orbitals. We further assume that the electronic structures of the rest of the ions in the crystal are undisturbed from their perfect crystal forms, and when it is necessary to take this structure into account we use analytic approximations to the free ion Hartree-Fock orbitals as discussed above. This approximation means that, among other things, we are neglecting electronic polarization by the F center, but we shall be able to take into account the effects of the ionic displacements. As was mentioned in the Introduction, the neglect of electronic polarization is probably a fairly good approximation for a highly localized defect in its ground state, but it is not clear that it will be an adequate one for the more diffuse excited states.

¹² R. Landshoff, Z. Phys. **102**, 201 (1936).

¹³ P.-O. Löwdin, *Theoretical Investigation into Some Properties of Ionic Crystals*, University of Uppsala Dissertation (Almqvist and Wiksells Boktryckeri, A.B., Uppsala, 1948).

¹⁴ L. P. Howland, Phys. Rev. **109**, 1927 (1958).

¹⁵ See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

We split the effective Hamiltonian of the F center in the crystal into its one- and two-body parts and write

$$h = h_1 + h_2, \quad (3)$$

where

$$h_1 = -\frac{1}{2}\nabla^2 - \sum_{\nu=1}^{N-1} \frac{Z_\nu}{|\mathbf{r} - \mathbf{R}_\nu|} \quad (4)$$

and

$$h_2 = \int \frac{\rho(2,2) - \rho(1,2)P_{12}}{r_{12}} d\tau_2, \quad (5)$$

in which ρ is the Fock-Dirac density matrix defined by

$$\rho(1,2) = \sum_{\nu=0}^{N-1} \sum_{j=1}^{n_\nu} \phi_{\nu,j}(1)\phi_{\nu,j}^*(2). \quad (6)$$

In the above expressions, $\phi_{\nu,j}$ is the j th atomic space-spin orbital¹⁶ on the ν th ion, Z_ν is the nuclear charge, P_{12} is the permutation operator, and r_{12} is the interelectronic distance. The wave function of the F electron is referred to a coordinate system with origin at the vacant ion site given by $\nu=0$ and it is denoted by $\phi_{0,1}$. The form of the Hamiltonian given by Eqs. (3)–(6) is appropriate when a basis set of orthogonal orbitals is being used, that is, the $\phi_{\nu,j}$ should be orthogonal. We have included finite size effects only for the first nearest-neighbor ions. Furthermore, we assume that the orbitals on alkali ions which are $2nn$ to each other do not overlap so that in order to have an orthogonal set we need only to make the F -electron function orthogonal to the $1nn$ ions. To conform to this condition we take $\phi_{0,1}$ to be of the general form

$$\phi_{0,1}(\mathbf{r}) = N_F [\phi_0(\mathbf{r}) + \sum_{\nu=1}^6 \sum_{j=1}^{n_\nu} c_{\nu,j} \phi_{\nu,j}(\mathbf{r} - \mathbf{R}_\nu)], \quad (7)$$

in which ϕ_0 is a vacancy-centered function and ν runs over only $1nn$ ion sites, which we number 1 through 6. The $c_{\nu,j}$'s in Eq. (7) are determined by the orthogonality condition

$$\langle \phi_{0,1} | \phi_{\nu,j} \rangle = 0, \quad (8)$$

and they are a function of the orbital parameters, as is N_F . Of course, $\phi_{0,1}$ is automatically orthogonal to half of the ion functions through the spin coordinate.

Substitution of Eqs. (3) and (7) into the expression

$$\epsilon = \langle \phi_{0,1} | h | \phi_{0,1} \rangle \quad (9)$$

gives

$$\begin{aligned} \epsilon = N_F^2 \{ & \langle \phi_0 | h | \phi_0 \rangle + \sum_{\mu=1}^6 \sum_{k=1}^{n_\mu} c_{\mu,k} \langle \phi_{\mu,k} | h | \phi_0 \rangle \\ & + \sum_{\nu=1}^6 \sum_{j=1}^{n_\nu} c_{\nu,j} \langle \phi_0 | h | \phi_{\nu,j} \rangle \\ & + \sum_{\mu=1}^6 \sum_{k=1}^{n_\mu} \sum_{\nu=1}^6 \sum_{j=1}^{n_\nu} c_{\mu,k} c_{\nu,j} \langle \phi_{\mu,k} | h | \phi_{\nu,j} \rangle \}. \quad (10) \end{aligned}$$

¹⁶ Throughout the discussion given in this paper, we assume the spatial part of all of the orbitals, other than $\phi_{0,1}$, to be doubly occupied.

We examine the term $\langle \phi_0 | h | \phi_0 \rangle$ first and from h_1 get just the kinetic energy, which we denote by T , and the nuclear attraction energy. When finding the expectation value of h_2 , we divide ρ into a contribution ρ_0 from the term $\nu=0$, and a contribution $\rho-\rho_0$ from all other terms. We shall show in the Appendix that the contribution of ρ_0 to $\langle \phi_0 | h | \phi_0 \rangle$, which is a self-energy term, cancels against corresponding contributions to the other terms in Eq. (10). We then have to consider here the electronic structure of only the $1nn$ ions, and therefore for more distant ions the exchange terms vanish and the first term in h_2 combines with the nuclear attraction terms to give the point ion approximation. Furthermore, for the $1nn$ ions it is possible to write the electronic repulsion part of h_2 as a contribution from a point ion (of charge $Z_\nu-1$) plus a correction Δ due to the electronic structure of the ion. For very compact ions such as lithium, the correction will be small, but for larger ions it may be quite substantial. Combining the nuclear attraction and the electronic repulsion terms for the $1nn$ then allows us to treat them as point ions plus the correction. It is easily shown that a point ion lattice will give a potential energy composed of a Madelung contribution plus terms, which we call A terms, and which come about because the charge density of the F electron extends out beyond the shells of neighboring ions. We have included these corrections out to $3nn$ in our calculations. The expectation value of the second term in h_2 is the exchange energy E_{ex} between ϕ_0 and the orbitals on the neighboring ions. We obtain then

$$\langle \phi_0 | h | \phi_0 \rangle = T - (a_M - 6)R_{10}^{-1} - \sum_{\nu=1}^6 R_\nu^{-1} + \sum A \text{ terms} \\ + \sum \Delta - E_{\text{ex}} + \int \frac{\phi_0^*(1)\rho_0'\phi_0(1)}{r_{12}} d\tau_2 d\tau_1, \quad (11)$$

where a_M is the Madelung constant, R_{10} the $1nn$ distance in the undistorted crystal;

$$\sum A \text{ terms} \equiv \sum_{\nu=1}^{3nn} [\langle \phi_0 | (|\mathbf{r}-\mathbf{R}_\nu|^{-1}) | \phi_0 \rangle - R_\nu^{-1}], \quad (12)$$

$$\Sigma \Delta \equiv \sum_{\nu=1}^6 \sum_{j=1}^{n_\nu} [\langle \phi_0(1)\phi_{\nu,j}(2) | r_{12}^{-1} | \phi_0(1)\phi_{\nu,j}(2) \rangle \\ - \langle \phi_0 | (|\mathbf{r}-\mathbf{R}_\nu|^{-1}) | \phi_0 \rangle], \quad (13)$$

$$E_{\text{ex}} \equiv \sum_{\nu=1}^6 \sum_{j=1}^{n_\nu} \langle \phi_0(1)\phi_{\nu,j}(2) | r_{12}^{-1} | \phi_0(2)\phi_{\nu,j}(1) \rangle, \quad (14)$$

and

$$\rho_0' \equiv \rho_0(2,2) - \rho_0(1,2)P_{12}. \quad (15)$$

The form of Eq. (11) shows that we have removed from the Madelung energy the effect of the six $1nn$ when they are in their perfect crystal position and replaced it by a term

$$\sum_{\nu=1}^6 R_\nu^{-1}$$

evaluated when the ions are in their distorted positions.

The terms in ϵ which contain the c 's we group together and call the overlap energy E_{ov} . In the Appendix, we carry out the reduction of these terms and obtain the expression

$$E_{\text{ov}} = - \sum_{\nu=1}^6 \sum_{j=1}^{n_\nu} c_{\nu,j}^2 [\epsilon_j + (2F_{\nu,j} - 1)(a_M - 1)R_{10}^{-1}] \\ + (\text{terms containing } \rho_0'), \quad (16)$$

in which ϵ_j is the Hartree-Fock energy of the j th orbital. $F_{\nu,j}$ is a factor which allows us, in effect, to approximate some small three-center integrals which enter into the problem. This is discussed in the Appendix. The term

$$\int \frac{\phi_0^*(1)\rho_0'\phi_0(1)}{r_{12}} d\tau_2 d\tau_1$$

cancels with the terms containing ρ_0' in Eq. (16) and for ϵ we obtain, with $E_{\text{ov}}' = E_{\text{ov}} - (\text{terms containing } \rho_0')$,

$$\epsilon = N_F^2 [T - (a_M - 1)R_{10}^{-1} - \sum_{\nu=1}^6 R_\nu^{-1} \\ + \sum A \text{ terms} + \sum \Delta - E_{\text{ex}} + E_{\text{ov}}'] \quad (17)$$

and

$$N_F^2 = (1 - \sum_{\nu=1}^6 \sum_{j=1}^{n_\nu} c_{\nu,j}^2)^{-1}. \quad (18)$$

This is the expression which we have used in our calculations. Although we limited ourselves here to a consideration of the electronic structure of the $1nn$ ions, the equations above can be easily extended to include more distant ions. The function ϕ_0 is still quite general and it could even be given in numerical form. For most purposes it is better at this point to sacrifice some accuracy for simplicity, and so we have chosen ϕ_0 to be of a very simple analytical form. In order to take advantage of the extensive literature on the calculation of molecular integrals, we represent the radial part of ϕ_0 by a single term of the form

$$\phi_0(r) \approx r^n e^{-\beta r}, \quad (19)$$

where n is an integer and β is a variation parameter. An analysis of the potential at the center of the vacancy shows that this form violates the boundary condition at the origin. To get around this in a more exact treatment, ϕ_0 can be expressed as a sum of terms of the form (19) and a secular determinant set up.

We may sometimes refer to our wave functions as being of s type or p type in correspondence with the symmetry of ϕ_0 . Due to the orthogonalization to the ion cores the symmetry designations of the irreducible representations of the octohedral group are the appropriate ones, even for the simple wave functions used here. Thus, our usage of s type and Γ_1^+ , and p type and Γ_4^- interchangeably, while not quite correct, should cause

no confusion and it may aid in visualizing the wave functions. In fact, in this paper we shall limit our starting functions ϕ_0 to s and p types and neglect the g_j , etc., terms which also contribute to Γ_1^+ and Γ_4^- .

III. TOTAL ENERGY OF THE CRYSTAL

In order to find the distortions around an isolated defect, we obtain an expression for the total energy of the crystal containing an F center and then minimize it with respect to small displacements of the ions neighboring the defect. Following Ref. 4, we write for the total energy of the distorted crystal

$$\mathcal{E}_T^d = \mathcal{E}_L^d + \mathcal{E}_e^d. \quad (20)$$

Here \mathcal{E}_L^d is the energy of a fictitious crystal in which a complete halide ion has been removed without permitting any rearrangement of the valence or core electrons other than those connected with the (still arbitrary) displacements of the ions. \mathcal{E}_e^d is the energy of the F -center electron in this fictitious crystal. \mathcal{E}_L^d was calculated classically and was written in the form

$$\mathcal{E}_L^d = \mathcal{E}_1 + \mathcal{E}_2 - \mathcal{E}_1^h - \mathcal{E}_2^h. \quad (21)$$

\mathcal{E}_1 is the Coulomb energy of the complete, but distorted, lattice; \mathcal{E}_2 is the repulsive energy of interaction between the ionic cores of that lattice; and \mathcal{E}_1^h , \mathcal{E}_2^h are those terms in \mathcal{E}_1 and \mathcal{E}_2 involving the removed halide ion. We assumed that only nearest-neighbor ions experience core interaction, and this was represented by a two-body potential of the form

$$V_r(R) = b/R^\lambda. \quad (22)$$

The values of the parameter λ were taken from the literature. The quantities \mathcal{E}_1 , \mathcal{E}_2 , \mathcal{E}_1^h , and \mathcal{E}_2^h were expanded in Taylor series in the ionic displacements. All cubic and higher order terms in this expansion were neglected.

Two types of deformation were considered:

(a) An isotropic distortion, applicable when the electron is in its relaxed ground state, and characterized by a radial displacement *inward* of the $1nn$ ions by the amount

$$\Delta_1 = \delta_1 R_{10}. \quad (23)$$

Second-nearest-neighbor displacements can be treated in this case but they are more difficult to deal with in the excited state where anisotropic distortions occur. The work of Ref. 4 indicated that $2nn$ displacements were very small in the ground state. We expect them to be larger in the excited state, but since they are difficult to handle we have considered only $1nn$ displacements in all cases.

(b) An anisotropic distortion, applicable when the electron is in the relaxed excited state, and characterized by radial displacements inward of the $1nn$ by the amounts

$$\Delta_1' = \delta_1' R_{10} \quad \text{and} \quad \Delta_2' = \delta_2' R_{10}. \quad (24)$$

Here Δ_2' applies to the two neighbors in the direction of the principal symmetry axis of the excited state wave function and Δ_1' applies to the four other neighbors. Displacements of the $2nn$ ions would involve at least four Δ_2' 's.

From Ref. 4, we have obtained the following expressions for the changes in \mathcal{E}_1 , \mathcal{E}_2 , \mathcal{E}_1^h , and \mathcal{E}_2^h in the excited state. The ground state expressions follow simply by putting $\delta_1' = \delta_2'$:

$$\Delta \mathcal{E}_1' = (3/R_{10})[(\sqrt{2}/2 + \frac{1}{6})\delta_1'^2 + \sqrt{2}\delta_1'\delta_2' + \frac{1}{12}\delta_2'^2], \quad (25)$$

$$\Delta \mathcal{E}_2' = [a_M(\lambda - 1)/3R_{10}][2\delta_1'^2 + \delta_2'^2], \quad (26)$$

$$\Delta \mathcal{E}_1^h = -(2/R_{10})[2\delta_1' + \delta_2' + 2\delta_1'^2 + \delta_2'^2], \quad (27)$$

$$\Delta \mathcal{E}_2^h = (a_M/3R_{10}) \times [2\delta_1' + \delta_2' + \frac{1}{2}(\lambda + 1)(2\delta_1'^2 + \delta_2'^2)]. \quad (28)$$

We then write

$$\mathcal{E}_T^d = \mathcal{E}_T^u + \Delta \mathcal{E}_1' + \Delta \mathcal{E}_2' - \Delta \mathcal{E}_1^h - \Delta \mathcal{E}_2^h + \mathcal{E}_e'(R_1', R_2'), \quad (29)$$

where

$$R_1' = (1 - \delta_1')R_{10}, \quad (30)$$

$$R_2' = (1 - \delta_2')R_{10}. \quad (31)$$

$\mathcal{E}_e'(R_1', R_2')$ is given by Eq. (17) of the preceding section, i.e., $\mathcal{E}_e'(R_1', R_2') = \epsilon'$.

In order to get the energy of absorption, we minimize \mathcal{E}_T^d for the ground state with respect to δ_1 and β and then find \mathcal{E}_e . Next, assuming the Franck-Condon principle to hold, we calculate \mathcal{E}_e' using the δ_1 found for the ground state. For the emission energy, Eq. (29) is minimized with the F electron in the excited state and the new distortions found. With these distortions the ground-state energy of the F electron is minimized as a function of β .

Since we have allowed $\delta_1' \neq \delta_2'$, we have gone beyond the case dealt with by simple configuration coordinate diagram theory. In this theory, the total energy of the crystal is treated as a function of a single parameter called the configuration coordinate which describes the position of the neighboring ions. In fact, the total energy is a complicated surface which may require many parameters to describe adequately. We thought it would be interesting to see what results the simple theory gave for one or two of the crystals. In this case, we have only to keep $\delta_1' = \delta_2'$ when allowing the lattice to relax with the F electron in the excited state.

IV. THE LIFETIME OF THE EXCITED STATE

It was mentioned in the Introduction that the first excited state of the F center in KCl has a lifetime appreciably longer than might be expected from considerations appropriate to atomic systems. Fowler and Dexter in their discussion (Ref. 7) of defects in dielectric media suggest a number of possible explanations for this. The most obvious causes are those connected with the large

Stokes shift and we are now in a position to investigate some of these.

The oscillator strength for the transition from level a to level b is given by

$$f_{ab} = \frac{2m}{3\hbar^2} \Delta\epsilon_{ab} \sum_{i,j} \frac{|\langle a,i|\mathbf{r}|b,j\rangle|^2}{2J_a+1}, \quad (32)$$

in which $\Delta\epsilon_{ab} = |\epsilon_a - \epsilon_b|$, m is the electronic mass, $2J_a+1$ gives the degeneracy of the a th level, and i and j are summation indices for the components of levels a and b , respectively. Equation (32) neglects the shape function for the line given by the transition $a \rightarrow b$. This may be rather important for a center which interacts strongly with the phonon field, but we shall use Eq. (32) as it stands.

In terms of the oscillator strength, the lifetime for a transition from level b to level a is given by

$$\tau_{ba} = \left[\frac{\mathcal{E}_0}{\mathcal{E}_{\text{eff}}(\Delta\epsilon_{ba})} \right]^2 \frac{\hbar^2 c^3 m^*}{2e^2 n (\Delta\epsilon_{ba})^3} \frac{\Delta\epsilon_{ab}}{(\Delta\epsilon_{ba})^3} \times \frac{\sum_{i,j} |\langle a,i|\mathbf{r}|b,j\rangle|^2 (2J_b+1)}{\sum_{j,i} |\langle b,j|\mathbf{r}|a,i\rangle|^2 (2J_a+1)} f_{ab}^{-1}. \quad (33)$$

Here, \mathcal{E}_0 is the average field throughout the specimen and $\mathcal{E}_{\text{eff}}(\Delta\epsilon_{ba})$ is the effective field at the defect when it is in state b . m^* is the effective mass, which we take to be the true mass; n is the index of refraction; e is the electronic charge; and c is the velocity of light. $\langle a,i|\mathbf{r}|b,j\rangle$ is not, generally, equal to $\langle b,j|\mathbf{r}|a,i\rangle$ because of lattice relaxation.

The principal quantities of interest to us here are the transition energies $\Delta\epsilon_{ab}$ and $\Delta\epsilon_{ba}$, the transition matrix elements $\langle a,i|\mathbf{r}|b,j\rangle$, etc., and the ratio of the effective field \mathcal{E}_{eff} to the average field \mathcal{E}_0 . This last quantity is difficult to treat correctly with any rigor and we will not consider its evaluation here. We do feel, however, that it may be a source of some of the discrepancies which may exist between theory and experiment.

In an atomic system, the lifetime is given by

$$\tau_{ab}^a = \frac{\hbar^2 m c^3}{2e^2 (\Delta\epsilon_{ba})^2} \frac{(2J_b+1)}{(2J_a+1)} f_{ab}^{a-1} \quad (34)$$

and $\Delta\epsilon_{ba} = \Delta\epsilon_{ab}$. Roughly speaking, we can say that the ratio of the lifetime of this two-level system imbedded in a dielectric medium to its lifetime when it is treated as an "atomic system" is

$$\frac{\tau_{ba}^m}{\tau_{ba}^a} = \frac{1}{n} \left[\frac{\mathcal{E}_0}{\mathcal{E}_{\text{eff}}(\Delta\epsilon_{ba})} \right]^2 \left(\frac{\Delta\epsilon_{ab}}{\Delta\epsilon_{ba}} \right) \times \frac{\sum_{i,j} |\langle a,i|\mathbf{r}|b,j\rangle|^2 f_{ab}^a}{\sum_{j,i} |\langle b,j|\mathbf{r}|a,i\rangle|^2 f_{ab}^m}. \quad (35)$$

We note that both of the oscillator strengths on the

right-hand side are for transitions from level a to level b and that, whereas $f_{ab}^a = f_{ba}^a$, it is certainly not true that $f_{ab}^m = f_{ba}^m$. We expect the ratio f_{ab}^a/f_{ab}^m to be between 1 and 3 for the F center in the alkali halides and here we just put it equal to 2. We also put the ratio $\mathcal{E}_0/\mathcal{E}_{\text{eff}} = 1$ for simplicity. We then have

$$\frac{\tau_{ba}^m}{\tau_{ba}^a} = \frac{2}{n} \left(\frac{\Delta\epsilon_{ab}}{\Delta\epsilon_{ba}} \right) \frac{\sum_{i,j} |\langle a,i|\mathbf{r}|b,j\rangle|^2}{\sum_{j,i} |\langle b,j|\mathbf{r}|a,i\rangle|^2}. \quad (36)$$

We shall use our wave functions to calculate the above ratio in the case of KCl. $\langle a,i|\mathbf{r}|b,j\rangle$ will be calculated with the ground- and excited-state wave functions going with the ground-state distortions and $\langle b,j|\mathbf{r}|a,i\rangle$ will be calculated with the corresponding functions going with the excited-state distortions.

V. CALCULATIONS AND RESULTS

The minimization of Eq. (29) with respect to δ_1' , δ_2' , and β' is not simple. The greatest difficulty arises in the calculations of the two-center, two-electron integrals appearing in Eqs. (13) and (14). These must be re-evaluated repeatedly in the modified method of steepest descent which we are using for the minimization process. We are very grateful to J. C. Browne of the University of Texas for making available to us his programs for calculating the two-center integrals. The entire problem has been programmed for computation on the CDC-1604 at ORNL.

The quantities in Eq. (29) which change from crystal to crystal are R_{10} , λ , the $F_{v,j}$'s and the orbitals on the neighboring ions.

The factors $F_{v,j}$ have been set equal to 1 in all of the calculations reported here. The justification for this is that ϵ_j in Eq. (16) is much larger (by about a factor of 10) than the other terms appearing there, so even a fairly large error in $F_{v,j}$ will have a relatively small effect on the energy. This should be a very good approximation in the case of the lithium halides but somewhat poorer in the cases of more extended alkali ions. In truly accurate calculations, however, this factor will need to be investigated carefully.

We took the values of λ from the literature; they are the ones obtained by Pauling¹⁷ from an approximate quantum-mechanical calculation of the interaction between ions in an ionic crystal. It is well known that the total energy of a crystal does not depend strongly on the value of λ , but it might be that the energy levels and distortions of a defect such as the F center are affected rather strongly by small changes in λ . We did not check this point in any detail, but we did try using a value of λ ($\lambda=9.1$) obtained from compressibility data in NaCl and found no very large differences from the results obtained with the Pauling value, $\lambda=8$.

For the nearest-neighbor distances R_{10} , we took those

¹⁷ See Ref. 15, p. 81, and references therein.

TABLE I. Values of R_{10} (in atomic units) and λ used in the calculations. Values of the experimental absorption and emission energies (where known) are also given, in electron volts.

		F	Cl	Br
Li	R_{10}	3.80	4.86	5.18
	λ	6.0	7.0	7.5
	$\Delta\epsilon_a$	4.82	3.22	2.74
	$\Delta\epsilon_e$
Na	R_{10}	4.37	5.31	5.63
	λ	7.0	8.0	8.5
	$\Delta\epsilon_a$	3.70	2.71	2.30
	$\Delta\epsilon_e$...	1.03	...
K	R_{10}	5.05	5.936	6.22
	λ	8.0	9.0	9.5
	$\Delta\epsilon_a$	2.73	2.23	1.98
	$\Delta\epsilon_e$...	1.22	0.94

listed by Ivey.¹⁸ The values of λ and R_{10} which we used are given in Table I, together with the experimental values of the absorption and emission energies which will be used later for comparison. The values of the absorption energies are taken from Ref. 18. There are some rather large variations in the values reported by different investigators, but for our purposes these are not important. Where values of the emission energy are shown, we have taken them from Schulman and Compton,¹⁹ and where they are not shown we assume them to be approximately one-half of the absorption energies.

For the orbitals on the neighboring ions, we have made the following choices. For the lithium and sodium ions, we have used the analytical Hartree-Fock func-

 TABLE II. Some results for LiF, LiCl, and LiBr using $2s$ and $3p$ functions. The excited-state quantities are indicated by primes. Subscripts a and e stand for absorption and emission, respectively. All quantities are in atomic units except for $\Delta\epsilon_a$ and $\Delta\epsilon_e$, which are given in electron volts.

	LiF	LiCl	LiBr
$\Delta\epsilon_a$	-0.20406	-0.20483	-0.20138
β_a	0.9265	0.7570	0.7240
δ_1	-0.0120	+0.0054	+0.0102
ϵ_a	-0.19127	-0.20965	-0.21006
β_a'	0.4150 (0.9405) ^a	0.7700	0.7510
ϵ_a'	-0.07146 (-0.02247) ^a	-0.09133	-0.10251
$\Delta\epsilon_a$	3.26 (4.59) ^a	3.22	2.93
$\Delta\epsilon_e'$	-0.13853	-0.11765	-0.11225
β_e'	0.3790	0.3358	0.3269
δ_1'	-0.1123	-0.1016	-0.0972
δ_2'	-0.1547	-0.1448	-0.1399
ϵ_e'	-0.06390	-0.06274	-0.06222
β_e	0.7685	0.6393	0.6095
ϵ_e	-0.08861	-0.11171	-0.11505
$\Delta\epsilon_e$	0.67	1.33	1.44

^a These are the data for the other minima in ϵ_a' , which are discussed in the text. They appear to be consistent with the LiCl and LiBr data.

¹⁸ H. F. Ivey, Phys. Rev. **72**, 341 (1947).

¹⁹ J. H. Schulman and W. Dale Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

 TABLE III. Some results for NaF, NaCl, and NaBr using $2s$ and $3p$ functions. The excited-state quantities are indicated by primes. Subscripts a and e stand for absorption and emission, respectively. All quantities are in atomic units except for $\Delta\epsilon_a$ and $\Delta\epsilon_e$, which are given in electron volts.

	NaF	NaCl	NaBr
$\Delta\epsilon_a$	-0.21653	-0.20345	-0.19838
β_a	0.7926	0.6964	0.6670
δ_1	0.0013	0.0165	0.0187
ϵ_a	-0.21782	-0.21758	-0.21359
β_a'	0.7794	0.7329	0.7087
ϵ_a'	-0.08975	-0.11765	-0.12210
$\Delta\epsilon_a$	3.49	2.72	2.49
$\Delta\epsilon_e'$	-0.13421	-0.11747	-0.11293
β_e'	0.3820	0.3521	0.3651
δ_1'	-0.0998	-0.0898	-0.0828
δ_2'	-0.1448	-0.1297	-0.1183
ϵ_e'	-0.07331	-0.07043	-0.07038
β_e	0.6755	0.5500	0.5684
ϵ_e	-0.12565	-0.13095	-0.13517
$\Delta\epsilon_e$	1.42	1.65	1.76

tions supplied to us by T. L. Gilbert²⁰ of Argonne. These functions are constructed using a minimal basis set. The radial part of the Li⁺ function is simply $\varphi_{1s}(r) = Ne^{-2.6875r}$ and the energy $\epsilon_{1s} = -2.77148$ a.u. The radial part of the Na⁺ $2s$ function is given by $\varphi_{2s} = -0.26883 N_1 r e^{-10.626r} + 1.03279 N_2 r e^{-3.281r}$ and the energy is $\epsilon_{2s}(\text{Na}^+) = -2.89334$ a.u. The radial $2p$ function is $\varphi_{2p} = N_2 p r e^{-3.403r}$ and the energy -1.52886 a.u. Already, in the case of this simple sodium function, the calculation is very expensive in terms of computer time. A more accurate representation of the Hartree-Fock approximation would greatly increase the time and probably could not be justified in light of all of the other approximations which have been made. Recogniz-

 TABLE IV. Some results for KF, KCl, and KBr using $2s$ and $3p$ functions. The excited-state quantities are indicated by primes. Subscripts a and e stand for absorption and emission, respectively. All quantities are in atomic units except for $\Delta\epsilon_a$ and $\Delta\epsilon_e$, which are given in electron volts.

	KF	KCl	KBr
$\Delta\epsilon_a$	-0.17375	-0.16694	-0.16534
β_a	0.7393	0.6660	0.6410
δ_1	0.0308	0.0205	0.0203
ϵ_a	-0.20229	-0.18292	-0.18046
β_a'	0.7576	0.6832	0.6653
ϵ_a'	-0.09910	-0.09497	-0.09738
$\Delta\epsilon_a$	2.81	2.39	2.26
$\Delta\epsilon_e'$	-0.10237	-0.09245	-0.08790
β_e'	0.2979	0.2737	0.2648
δ_1'	-0.1011	-0.0937	-0.0909
δ_2'	-0.1341	-0.1268	-0.1240
ϵ_e'	-0.05185	-0.05037	-0.04997
β_e	0.6632	0.5918	0.5706
ϵ_e	-0.07596	-0.09245	-0.09549
$\Delta\epsilon_e$	0.66	1.14	1.24

²⁰ P. S. Bagus and T. L. Gilbert (to be published). We wish to thank Dr. Gilbert for supplying us with these functions.

TABLE V. Various results for absorption and emission in KF, KCl, and KBr. The excited-state quantities are indicated by primes. Subscripts a and e stand for absorption and emission, respectively. All quantities are in atomic units except for $\Delta\epsilon_a$ and $\Delta\epsilon_e$, which are given in electron volts.

	KF	KCl	KBr
(a) 3s absorption			
$\Delta\mathcal{E}_a$	-0.16079	-0.15869	-0.15792
β_a	0.9770	0.8999	0.8660
δ_1	0.0308	0.0205	0.0203
ϵ_a	-0.19001	-0.17469	-0.17305
(b) 4p absorption			
β_a'	1.0037	0.8953	0.8718
ϵ_a'	-0.10740	-0.09763	-0.09957
$\Delta\epsilon_a$ (2s \rightarrow 4p)	2.58	2.32	2.20
(c) 4p \rightarrow 2s emission			
$\Delta\mathcal{E}_e'$	-0.10237	-0.09286	-0.08925
β_e'	0.3800	0.3380	0.3271
δ_1'	-0.1036	-0.0972	-0.0947
δ_2'	-0.1384	-0.1309	-0.1275
ϵ_e'	-0.05452	-0.05191	-0.05110
β_e	0.6608	0.5888	0.5682
ϵ_e	-0.07385	-0.09017	-0.09325
$\Delta\epsilon_e$	0.53	1.04	1.15

ing this, we decided to use the simplest possible functions for the potassium halides. We used the orbital formed by the Slater prescription, namely, $\varphi(r) = N_{3p} r^2 e^{-2.533r}$ for the radial part of both the 3s and 3p functions. For the energies, we chose those used by Howland in Ref. 14, namely, $\epsilon_{3s} = -1.965$ a.u. and $\epsilon_{3p} = -1.1705$ a.u.

We tried 1s, 2s, and 3s functions for the ground state of the lithium halides and found that the 2s function gave the lowest value of \mathcal{E}_T^d in all three cases. A 3p function was somewhat better than a 2p function in the excited state, both before and after relaxation. In the sodium and potassium halides, we at first simply used a 2s function in the ground state and a 3p function in the excited state without searching for the optimum value of n in Eq. (19), since it seemed likely to us that the 2s and 3p functions were adequate to give the essential features of the absorption and emission processes. The results of these calculations are shown in Tables II-IV. Most of the quantities appearing in the tables have already been defined. $\Delta\mathcal{E}$ is the right-hand side of Eq. (29)

TABLE VI. Results for the second minimum in the excited-state energy surface of the sodium halides. In NaF, the program does not become stuck in this minimum if it exists. The notations and units follow those of the preceding tables.

	NaF	NaCl	NaBr
$\Delta\mathcal{E}_e'$	-0.13421	-0.11947	-0.12156
β_e'	0.3820	0.6770	0.6711
δ_1'	-0.0998	-0.0437	-0.0394
δ_2'	-0.1448	-0.0177	+0.0036
ϵ_e'	-0.07331	-0.09568	-0.10524
β_e	0.6755	0.6535	0.6330
ϵ_e	-0.12565	-0.18348	-0.18693
$\Delta\epsilon_e$	1.42	2.39	2.22

TABLE VII. Results for the potassium halides when δ_1' is forced to be equal to δ_2' while calculating the lattice distortions in the relaxed excited state. 3p and 2s functions are used in the excited and ground states, respectively. The notation and units follow those in the preceding tables.

	KF	KCl	KBr
$\Delta\mathcal{E}_e'$	-0.10198	-0.09073	-0.08751
$\delta_1' = \delta_2'$	-0.1126	-0.1052	-0.1019
β_e'	0.2961	0.2709	0.2690
ϵ_e'	-0.05106	-0.04959	-0.04922
β_e	0.6632	0.5914	0.5682
ϵ_e	-0.07559	-0.09214	-0.09545
$\Delta\epsilon_e$	0.67	1.16	1.26

minus \mathcal{E}_T^u , $\Delta\mathcal{E}$ is the transition energy. Primes denote excited state quantities and the subscripts a and e denote absorption and emission, respectively.

Because the potassium halides (especially KCl) are of particular interest to experimentalists and as a study of the sensitivity of the energy and distortions to the form of the trial function, we tried using a 3s ground state function and a 4p excited-state function for the absorption process in these crystals. The results are shown in Table V. Also shown in Table V are the results using a 4p excited state and a 2s ground state in the emission process. We did not try a 3s function here.

Our calculations indicate that the energy surface given by $\mathcal{E}_T^d = \mathcal{E}_T^d(\delta_1', \delta_2', \beta')$ is rather bumpy. We encountered a number of local minima in the various calculations, but the program, with one exception, never became stuck in any of these. This one exception occurred in almost all of the crystals in the emission state; as an example, we give the data for the sodium halides in Table VI. The values of $\Delta\mathcal{E}_e'$ for NaCl and NaBr in this table are actually lower than the corresponding values in Table III and would thus seem to imply that Table VI represents the true state of affairs. Table VI indicates that this difficulty did not occur in NaF. We shall discuss this problem further in the next section.

In Table VII, we show results for the emission states when δ_1' is kept equal to δ_2' in conformity with the simple configuration coordinate theory as described in Sec. III. A 3p function is used in the excited state and a 2s in the ground state.

In Table VIII, we give some data on the oscillator strengths, dipole matrix elements, lifetimes, etc., of KCl.

TABLE VIII. Transition matrix elements, oscillator strengths, and lifetime data for KCl. τ_{ba}^a in Eq. (36) is taken to be 10^{-8} sec.

	Absorption	Emission
$\langle\phi_{0,1} \mathbf{r} \phi_{0,1}'\rangle^2$	4.953	2.316
f	0.87	0.19
$\tau_{\text{exp}} = 60 \times 10^{-8}$ sec		$\tau_{\text{theory}} \approx 20 \times 10^{-8}$ sec

We show, in Fig. 1, the picture which emerges from these calculations in a typical case, namely, that for KCl. We constructed this figure by taking Howland's results on KCl for the position of the maximum and the total width of the valence band. We located the bottom of the conduction band relative to the valence band in the pure crystal, roughly, from experimental data by adding 1 eV to the first exciton peak (~ 7.6 eV).

VI. DISCUSSION

The absorption energies given in Tables II-IV differ from the experimental values by about 0-10% except in the case of LiF, where the error is much larger. In the LiF calculation, however, there is a local minimum in the excited state (shown in parentheses in Table II) which fits in much better with the over-all picture and we believe that this is the appropriate minimum to consider here. From a comparison of the data in Tables II-IV with those in Table I, it is apparent that there is a systematic, nonuniform error in all of the absorption energies. We do not yet know the origin of this error, but it seems likely to us that it is caused by one or more of the following three factors: The first is that the trial functions used here are too simple and inflexible to describe all of the details of the center. For one thing, the radial part of the s function violates the boundary condition at the center of the vacancy. Also, group theoretical considerations show that appropriate linear combinations of g terms, as well as s terms, transform according to the Γ_1^+ representation and that g and f terms can contribute to functions which transform like the Γ_4^- representation. We feel that the contribution of g terms to both the ground and excited states is very small, but we are much less certain about the contribution of f terms to the first excited state. Thus, even within the framework of the simple model which we are using, our trial functions leave something to be desired. The second factor which may be of importance is our neglect of the finite size of the $2nn$ ions. This may be particularly important in the cases where the interionic distance is small and the radii of the alkali and halide ions are greatly different, e.g., in LiF. The third factor is our neglect of polarization, which is probably quite all right in the ground state but may not be permissible in the excited state. The calculations of Gourary and Adrian in Ref. 2 indicate that polarization is small in both the ground and excited states, but it seems to us that this problem needs further investigation.

The ground-state distortions obtained from these calculations are rather small and in most cases in toward the center of the vacancy. In Ref. 4, Wood and Korringa reported a small outward displacement in LiCl. The only essential differences between the LiCl ground-state calculation reported here and the one reported in Ref. 4 are that here we have included exchange and Coulomb repulsion terms with the electrons on the neighboring ions and the computer has carried the iterative procedure used to minimize the total energy to completion.

It is most likely the exchange interaction which makes the biggest difference.

Improvements of our very simple treatment of the classical ionic theory part of the calculation will influence the distortions somewhat. We have used the simplest Born theory with a Coulomb attractive term and a repulsive term of the form $bR^{-\lambda}$. Of course, the use of the more accurate Born-Mayer theory with an exponential repulsive term, van der Waals terms, etc., would be desirable. However, we feel that our result which shows that the distortions are small in the ground state is quite valid.

Parts a and b of Table V are included in order to give some idea of the sensitivity of the calculations to changes in the form of the wave functions. With the $3s$ function, the total energy \mathcal{E}_T^d is higher than it is for the $2s$ function and so we conclude that the $2s$ function is slightly better. It also results in a somewhat lower energy for ϵ_a but the values of the distortions are not greatly affected by this change in the form of the function. Taking the distortions given by the $2s$ function, we tried using a $4p$ function for the excited state, with results which are slightly better than those for a $3p$ function. Thus, using energy minimization as the criterion, the $2s$ - $4p$ description is the best of those tried here.

Another problem somewhat related to the above is that of other minima in the energy surface. That such minima exist might be surmised from the results on lithium fluoride. We have already mentioned that there is a minimum in the curve $\epsilon_a' = \epsilon_a'(\beta_a')$ at a value of 0.9405 for β_a' for which $\epsilon_a' = -0.02247$ a.u. We studied this problem in the ground state of the lithium halides by starting the energy minimization procedure with values of β_a about half as large as those shown in Table II. The results were no different from those shown in Table II, so we conclude that, in the ground state, relative minima pose no great problem for the computer program.

The most striking result shown by the emission data is that the theory does indeed give a large Stokes shift, which in many cases results in the relationship $\Delta\epsilon_e \simeq 0.5\Delta\epsilon_a$ being obtained. However, a systematic error similar to the one which occurred in the absorption energies seems to be operating here, too. We assume that the origin or origins of these errors are the same, with the possibility of one additional factor in the excited state. In general, for a given crystal, the greater the distortions the larger the Stokes shift will be. This suggests that in all three groups of three crystals the tendency is for the distortions to be too great in the crystals with small interionic distances and too small for the crystals with large interionic distances. Of if other factors operate, it may be that the distortions are just too great for the crystals with small interionic distances. The causes of excessive distortions could be many, but it seems to us that the principal one is again that of oversimplified trial functions. In the relaxed excited

state, where distortions are large and the wave functions quite diffuse, $2m$ and polarization effects may be even more important than they are in the absorption states. Finally, the additional factor, unique to the relaxed excited state, is that, because of the large distortions, the Taylor series expansion of the classical part of the energy expression may be beginning to lose validity.

The distortions in the relaxed excited state obtained from the calculations reported here are substantially different from those reported by Wood and Korrington for LiCl in Ref. 4. There appear to be three reasons for this, two of which we have already mentioned above in discussing the ground-state distortions. The third reason is that the quadrupole terms introduced by the asymmetrical distortions have been treated much more accurately here than they were in Ref. 4.

Part c of Table V indicates that a $4p$ function gives a slightly better representation of the excited state in the emission process. We did not try a $3s$ ground-state function, since it seemed that little was to be gained in the way of getting better agreement with experiment.

The data in Table VI illustrate the difficulties encountered with the minima in the energy surface. In the sodium halides, the minima shown in Table VI for NaCl and NaBr are close to, but somewhat lower than, those shown in Table III and would therefore seem to be the appropriate ones. Since they fit in so poorly with the data for the other crystals and do not agree at all with experiments, we conclude that the ones shown in Table III are the appropriate ones. There are corresponding relative minima in the cases of the lithium and potassium halides and it may be that they actually do exist and have some physical significance, but we have no way of knowing from these calculations. Experimentally, their existence would presumably show up as an emission line shifted only a slight amount from the absorption line.

From Table VII, we can see the results obtained from a model which corresponds to that used in obtaining conventional configuration coordinate diagrams. We were somewhat surprised to find so little differences between these data and those in Table IV. Apparently, fairly large asymmetrical distortions produce about the same effect on the energy levels as do symmetrical distortions whose magnitude is the average of the asymmetrical distortions. Just what implications, if any, this has for the interaction of the defect with the phonon field we do not know at this time.

To a very limited extent, we studied the effect of the form of the core orbitals on the energies and distortions. In the preceding section, we described the orbitals which we used on the neighboring ions. We note here that the single term $Li^+ 1s$ function is a rather good analytical fit to the doubly occupied Hartree-Fock spatial orbital, and that a linear combination of two such exponentials is a very good fit. We assume then that, as far as the energy calculations are concerned,

our $1s$ lithium function is essentially the Hartree-Fock function. For the sodium ions, we have used fairly adequate representations of the $2s$ and $2p$ Hartree-Fock orbitals, but we have neglected the $1s$ core orbitals. In the potassium halides, we have made no attempt to use even approximate Hartree-Fock functions but instead use the very simple Slater functions, albeit with the Hartree-Fock energies, for the $3s$ and $3p$ electrons. We neglect the inner electrons altogether. A survey of the results in Tables II-IV indicates that the over-all accuracy of the absorption calculations is about the same in all of the crystals. In the emission calculations, however, the Stokes shift is consistently less in the sodium halides than in the other crystals, although the magnitudes of the distortions do not seem unreasonable. In a calculation on the absorption process, which we have not reported here, we included the $1s$ orbitals on NaCl and found that they could affect the transition energy by about two-tenths of an electron volt. Unfortunately, their inclusion makes the calculation much more complex and time consuming, and we felt that other aspects of the work need further refinement before a thorough quantitative study could be made of the role of the structure of the neighboring ions.

In this connection, it would be interesting to try a pseudopotential²¹ type of calculation on the F center. The last three terms in Eq. (17) tend to cancel each other somewhat and their resultant contribution, though by no means negligible, may be small enough to treat by first-order perturbation theory. A pseudopotential approach might be adequate for the energy calculation, but it is not obvious that it would deal with the hyperfine interaction, oscillator strength, distortions, etc., in a satisfactory way. A rigorously constructed pseudopotential operator is nonlocal and probably as difficult to construct as is the solution of the problem it was originally intended to circumvent. It is, therefore, customary to replace the exact pseudopotential with some approximation thereof. Once this has been done, however, the question arises as to whether or not it might have been easier to make similar simplifying assumptions in an approach of the type used here. Actually, a fairly simple model formulation may be all that is needed in many defect calculations. Thus, using the approach we have taken here but assuming a very simple pseudo- or effective potential for the neighboring ions may give results accurate enough for most purposes.

The picture of the absorption and emission processes which emerges from these calculations is indicated roughly in Fig. 1. The excited state after lattice relaxation appears to move up into the conduction band, but this has no significance, for a number of reasons. For one thing, in drawing the diagram we did not attempt to locate the bottom of the conduction band with any great accuracy. This would have been difficult enough to

²¹ See, for example, B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962) and references therein.

do for a perfect crystal, but even more so for a crystal containing a defect where local distortions of the band in the vicinity of the defect may occur. Another reason for the roughness of the diagram is the fact that our energy levels for all states undoubtedly lie lower than we indicate here. Within the framework of our model and the variation principle, as we make the F -center trial function ϕ_0 more flexible, the energy levels will go down. Subsequent calculations have indicated that a shift downward of the order of 1 eV may easily occur. In spite of the approximate nature of the figure, we do feel that it is instructive and illustrates an effect which is important, i.e., that the excited state before relaxation lies further below the conduction band than it does after relaxation. The interpretation of the Faraday rotation experiments of Lüty and Mort²² involves the first excited state before relaxation, and Smith and Fowler²³ have given preliminary results on the calculation of the spin-orbit interaction in the unrelaxed excited state. On the other hand, luminescence and lifetime experiments give considerable information on the relaxed excited state and it may be possible soon to do spin resonance experiments on this state. Therefore, it seems that eventually a fairly exact treatment of this effect may be obtained.

In Table VIII, the data on the oscillator strengths and lifetimes in KCl tend to indicate that the long lifetime reported in Ref. 6 is at least partially understandable through our calculations. The matrix element effect is not as large as we had guessed it would be, but this may be a fault of our wave functions. The excited-state wave function after relaxation is evidently rather diffuse and therefore probably more affected by polarization effects than is the ground state. Because the wave function is already diffuse and much of the charge density lies in regions of slowly varying, weak potentials, it may be that the wave functions could spread out much more without changing the energy greatly. That is, the energy may no longer be very sensitive to the spatial extension of the wave function. The wave functions are already sufficiently diffuse to suggest that a perturbed band calculation approach to the relaxed excited state might be more appropriate than the method which we have used. Unfortunately, very few calculations have been carried out on the conduction band of alkali-halide crystals.

We summarize the results reported here as follows: The distortions in the ground state are small but in the excited state they are of the order of 10% of the nearest-neighbor distance and have a pronounced asymmetry. The treatment we have given can explain the large Stokes shift and perhaps the long lifetime, although further work is needed on this latter point. Our wave functions are still too inflexible to allow us to locate the position of the individual levels with any great

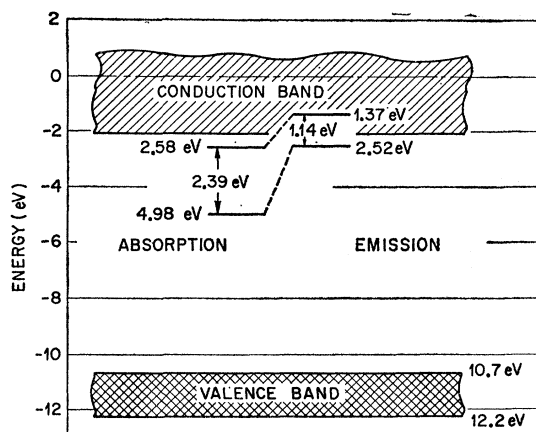


FIG. 1. Energy level diagram of the absorption and emission processes in KCl.

accuracy. We feel that the approach to the problem which we have used is basically sound, but it needs further refinement. These refinements should be concerned with (1) adding greater flexibility to the trial functions, (2) including $2nn$ effects, (3) including polarization effects, and (4) improving the classical ionic theory part of the calculation. At present, we are concentrating our attention on the first of these refinements and we shall report on the results at a later date.

Note added in proof. W. Beall Fowler has informed us of calculations of his which indicate that, because of electronic polarization effects, which we have neglected, there occurs a much greater spreading out of the relaxed excited-state wave function than that which we have obtained in these calculations. This would tend to confirm our own qualitative ideas about the effects of polarization. However, we prefer to withhold comment about their magnitude until our own calculations have progressed further.

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APPENDIX

We continue here the reduction of the right-hand side of Eq. (10). We have assumed that all free ion orbitals which appear in Eq. (7) are orthogonal. This will be true on any one ion because of the symmetry of the orbitals. A few simple calculations show that, for $\mu \neq \nu$, $\langle \phi_{\mu,k} | \phi_{\nu,j} \rangle$ is much smaller than $\langle \phi_0 | \phi_{\nu,j} \rangle$, provided the latter integral does not vanish from symmetry, and so we put the former integral equal to zero. This is a good approximation for the lithium ions in the lithium halides and not at all bad even for the potassium ions in potassium fluoride. It is a good approximation because the overlap charge density $\phi_{\mu,k}(1)\phi_{\nu,j}(1)$ is very small, so that we are justified in assuming the

²² F. Lüty and J. Mort, Phys. Rev. Letters 12, 45 (1964).

²³ D. Y. Smith and W. Beall Fowler, Bull. Am. Phys. Soc. 9, 240 (1964).

condition

$$\phi_{\mu,k}(1)\phi_{\nu,j}(1)=0, \quad (\text{A1})$$

which, of course, is stronger than

$$\langle \phi_{\mu,k} | \phi_{\nu,j} \rangle = 0. \quad (\text{A2})$$

As we shall see, the condition (A1) enables us to make a number of simplifying approximations.

When h operates on $\phi_{\nu,j}$, we separate it into a part $h_{\nu,j}$ which is the effective Hamiltonian for the j th orbital on the ν th ion $\phi_{\nu,j}$, and the part which remains,

$$h_{\nu,j}' = h - h_{\nu,j}. \quad (\text{A3})$$

$h_{\nu,j}$ is given by

$$h_{\nu,j} = -\frac{1}{2}\nabla^2 - \frac{Z_{\nu}}{|\mathbf{r}-\mathbf{R}_{\nu}|} + \int \frac{\rho_{\nu}(2,2) - \rho_{\nu}(1,2)P_{12}}{r_{12}} d\tau_2 \quad (\text{A4})$$

and $h_{\nu,j}'$ by

$$h_{\nu,j}' = - \sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} \frac{Z_{\nu'}}{|\mathbf{r}-\mathbf{R}_{\nu'}|} + \int \frac{\rho_{\nu'}(2,2) - \rho_{\nu'}(1,2)P_{12}}{r_{12}} d\tau_2, \quad (\text{A5})$$

in which

$$\rho_{\nu}(1,2) = \sum_{j=1}^{n_{\nu}} \phi_{\nu,j}(1)\phi_{\nu,j}^*(2) \quad (\text{A6})$$

and

$$\rho_{\nu'}(1,2) = \sum_{\substack{\nu'=0 \\ \nu' \neq \nu}}^{N-1} \sum_{j=1}^{n_{\nu'}} \phi_{\nu',j}(1)\phi_{\nu',j}^*(2). \quad (\text{A7})$$

We take

$$h_{\nu,j}\phi_{\nu,j} = \epsilon_j\phi_{\nu,j} \quad (\text{A8})$$

and use the Hartree-Fock energies for ϵ_j , although the use of experimental ionization energies would not affect the results greatly. We then have that

$$\langle \phi_{\mu,k} | h | \phi_{\nu,j} \rangle = \epsilon_j \delta_{\mu,\nu} \delta_{k,j} + \langle \phi_{\mu,k} | h_{\nu,j}' | \phi_{\nu,j} \rangle \quad (\text{A9})$$

and

$$\begin{aligned} \langle \phi_{\nu,j} | h | \phi_0 \rangle &= \langle \phi_0 | h | \phi_{\nu,j} \rangle \\ &= \epsilon_j \langle \phi_0 | \phi_{\nu,j} \rangle + \langle \phi_0 | h_{\nu,j}' | \phi_{\nu,j} \rangle. \end{aligned} \quad (\text{A10})$$

Because of Eq. (A1) the second term in Eq. (A9) can be written as

$$\begin{aligned} \langle \phi_{\mu,k} | h_{\nu,j}' | \phi_{\nu,j} \rangle &= - \sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} Z_{\nu'} \langle \phi_{\mu,k} | (|\mathbf{r}-\mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle \delta_{\mu,\nu} \delta_{k,j} + \int \frac{\phi_{\mu,k}^*(1)\rho_0'\phi_{\nu,j}(1)}{r_{12}} d\tau_2 d\tau_1 \\ &\quad + \sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} \sum_{j=1}^{n_{\nu'}} \int \frac{\phi_{\mu,k}^*(1)[\phi_{\nu',j}(2)\phi_{\nu',j}^*(2) - \phi_{\nu',j}(1)\phi_{\nu',j}^*(2)P_{12}]\phi_{\nu,j}(1)}{r_{12}} d\tau_2 d\tau_1, \end{aligned} \quad (\text{A11})$$

in which ρ_0' is the operator defined in Eq. (15).

If we again use Eq. (A1) and the fact that the sums over ν' now run over lattice sites which have been assumed to be occupied by point ions, the exchange integrals in the last term of Eq. (A11) will vanish; the Coulomb integrals in the same term will combine with the nuclear attraction integrals of the first term to give a point ion approximation. We then get

$$\langle \phi_{\mu,k} | h_{\nu,j}' | \phi_{\nu,j} \rangle = - \sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} (\pm)_{\nu'} \langle \phi_{\mu,k} | (|\mathbf{r}-\mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle \delta_{\mu,\nu} \delta_{k,j} + \int \frac{\phi_{\mu,k}^*(1)\rho_0'\phi_{\nu,j}(1)}{r_{12}} d\tau_2 d\tau_1. \quad (\text{A12})$$

Using the same type of arguments we reduce $\langle \phi_0 | h' | \phi_{\nu,j} \rangle$ to

$$\langle \phi_0 | h_{\nu,j}' | \phi_{\nu,j} \rangle = - \sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} (\pm)_{\nu'} \langle \phi_0 | (|\mathbf{r}-\mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle + \int \frac{\phi_0^*(1)\rho_0'\phi_{\nu,j}(1)}{r_{12}} d\tau_2 d\tau_1. \quad (\text{A13})$$

We can get rid of the last term in both Eqs. (A12) and (A13) by remembering that from $\langle \phi_0 | h | \phi_0 \rangle$ we have the term

$$\int \frac{\phi_0^*(1)\rho_0'\phi_0(1)}{r_{12}} d\tau_2 d\tau_1.$$

When Eqs. (A12), (A13), and this term are substituted in Eq. (10), they give a contribution, which, it is easy to see, can be written as

$$\int \frac{\phi_{0,1}^*(1)\rho_0'\phi_{0,1}(1)}{r_{12}} d\tau_1 d\tau_2.$$

However, this is identically zero as can be seen by writing ρ_0' in terms of the ϕ 's.

We then write Eq. (10) as

$$\epsilon = N_F^2 \{ T - (a_M - 1)R_{10}^{-1} - \sum_{\nu=1}^6 R_{\nu}^{-1} + \sum A \text{ terms} + \sum \Delta - E_{\text{ex}} + 2 \sum_{\nu=1}^6 \sum_{j=1}^{n_{\nu}} c_{\nu,j} [\epsilon_j \langle \phi_0 | \phi_{\nu,j} \rangle - \sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} (\pm)_{\nu'} \langle \phi_0 | (|\mathbf{r} - \mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle] + \sum_{\nu=1}^6 \sum_{j=1}^{n_{\nu}} c_{\nu,j}^2 [\epsilon_j - \sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} (\pm)_{\nu'} \langle \phi_{\nu,j} | (|\mathbf{r} - \mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle] \}. \quad (\text{A14})$$

In this expression, we note that $\phi_{\nu,j}$ is a highly localized, very compact, positive-ion wave function, whereas ϕ_0 is a much more diffuse function. We can make the sums over ν' go from 0 to $N-1$ by adding and subtracting a term due to $\nu'=0$. Then we can write the last term in Eq. (A14) as

$$\sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} (\pm)_{\nu'} \langle \phi_{\nu,j} | (|\mathbf{r} - \mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle = (a_M - 1)R_1^{-1} + \sum (\text{ionic } A \text{ terms}). \quad (\text{A15})$$

The compact nature of the ion orbitals makes the sum of the ionic A terms very small and we shall neglect them. Also, because of the small spatial extent of $\phi_{\nu,j}$, we can put

$$\langle \phi_0 | (|\mathbf{r} - \mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle \simeq f_{\nu,j,\nu'} \frac{\langle \phi_0 | \phi_{\nu,j} \rangle}{|\mathbf{R}_{\nu} - \mathbf{R}_{\nu'}|}. \quad (\text{A16})$$

Here, $f_{\nu,j,\nu'}$ is a factor which takes into account the fact that the overlap charge $\phi_0(1)\phi_{\nu,j}(1)$ may not be centered exactly at the ν th ion site as is assumed in the denominator of Eq. (A16). The approximation given by Eq. (A16) is actually a device for avoiding the calculation of many small three-center integrals. It is probably a very good approximation for the lithium halides but somewhat less valid for the potassium halides. With this approximation the second term in the

first square bracket in Eq. (A14) becomes

$$\sum_{\substack{\nu'=1 \\ \nu' \neq \nu}}^{N-1} (\pm)_{\nu'} \langle \phi_0 | (|\mathbf{r} - \mathbf{R}_{\nu'}|^{-1}) | \phi_{\nu,j} \rangle = \langle \phi_0 | \phi_{\nu,j} \rangle \left\{ \sum_{\substack{\nu'=0 \\ \nu' \neq \nu}}^{N-1} \frac{(\pm)_{\nu'} f_{\nu,j,\nu'}}{|\mathbf{R}_{\nu} - \mathbf{R}_{\nu'}|} - \frac{f_{\nu,j,0}}{|\mathbf{R}_{\nu} - \mathbf{R}_0|} \right\}. \quad (\text{A17})$$

Now we rather arbitrarily replace the sum over ν' in this equation by the Madelung potential times a factor $F_{\nu,j}$ which is meant to account for the factors $f_{\nu,j,\nu'}$. The Madelung potential is rather slowly varying in the immediate vicinity of any ion, so this should be a better approximation than Eq. (A16). For simplicity we put

$$f_{\nu,j,0} = F_{\nu,j}. \quad (\text{A18})$$

Noting that, because of Eqs. (7) and (8), $c_{\nu,j} = -\langle \phi_0 | \phi_{\nu,j} \rangle$, we obtain from Eq. (A14)

$$\epsilon = N_F^2 \{ T - (a_M - 1)R_{10}^{-1} - \sum_{\nu=1}^6 R_{\nu}^{-1} + \sum A \text{ terms} + \sum \Delta - E_{\text{ex}} - \sum_{\nu=1}^6 \sum_{j=1}^{n_{\nu}} c_{\nu,j}^2 [\epsilon_j + (2F_{\nu,j} - 1)(a_M - 1)R_1^{-1}] \}, \quad (\text{A19})$$

which is the expression we have used in our work.

Our treatment of the three-center integrals via the approximation given by Eq. (A16) and the introduction of $f_{\nu,j,\nu'}$, $F_{\nu,j}$ and the relation Eq. (A18) is certainly not very rigorous, but, in fact, it is probably a fairly good one. We have not checked it in any great detail simply because, in any case, the energy ϵ_j in the square bracket is much larger than the other terms therein.