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Point Defects in Ionic Crystals. II. The F Center in KCl, KBr, KI, and NaCl†

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Methods described in a previous paper are applied to the calculation of the electronic structure of the F center in KCl, KBr, KI, and NaCl. Structure of the ions is explicitly taken into account in a region close to the defect site, and an effective-mass method is used in the more distant regions. Dielectric polarization effects are included on the basis of the formulation due to Toyozawa, Haken, and Schottky, but results in best agreement with experiment are obtained by a procedure which deviates somewhat from that formulation, as might be expected also on purely theoretical grounds. It does not appear to be possible to obtain agreement with experiment even for absorption energies if polarization effects are neglected. The calculated energy differences of the $1s$, $2p$, $3p$, and $2s$ states in absorption agree very well with presently available experimental data. Agreement with experiment is fairly good for the $1s$, $2s$, and $2p$ energies in emission. The calculated optical transition matrix elements are very sensitive to the details of the model; those obtained from our best model and wave functions are compatible with experimental results. The results for the spin density at the nearest-neighbor ions are reasonably close to the experimental values.

I. INTRODUCTION

This is the second of a series of papers dealing with calculation of the electronic structure of point defects in ionic crystals. The work reported here treats the electronic structure of the localized states of the F center in KCl, KBr, KI, and NaCl and is meant to be an extension of the work of Wood and Joy.[1]

In Ref. 1, an attempt was made to calculate the absorption and emission energies and the lifetimes for the F center in nine different alkali halide crystals. The calculations were carried out in a greatly simplified Hartree-Fock approximation in which only the electronic structure of the outer shell of the 1nn (first-nearest-neighbor) ions was taken into account and this only approximately, i.e., the free-ion Hartree-Fock functions were replaced by their corresponding Slater orbitals,[2] except for the $2s$ orbital of sodium, for which a somewhat better approximation was used. Furthermore, the trial functions for the ground and first excited states before orthogonalization to the core orbitals consisted of single functions of the Slater type $[f(r)\sim r^n e^{-\beta r}]$ with the exponential parameter determined to minimize the energies of the various states both before and after lattice relaxation. All dielectric polarization effects were neglected. In spite of these shortcomings, fair agreement with the absorption and emission energies for most of the crystals was obtained. As we shall see later, this agreement was probably fortuitous in that the effects of some of the approximations made tend to cancel each other in a more complete treatment. For example, there is a pronounced tendency for the energy contributions from the structure on ions more distant than 1nn to cancel against those due to polarization effects. The lifetime of the excited state of the defect in KCl in the calculations turned out to be substantially shorter than that measured experimentally.[3]

At about the same time, Fowler[4] reported calculations on the F center in NaCl, using a semicontinuum model, which apparently accounted for the long lifetimes measured experimentally. Although we now believe the agreement of his results with experiment also to have been somewhat fortuitous, they did point up the importance of polarization effects on the wave functions of the relaxed excited state. However, the question has persisted as to the degree to which such effects are important in understanding those states involved in producing the main F-center absorption band. The point-ion calculations of Gourary and Adrian[5] and the calculations in Ref. 1 suggest that they are unimportant, whereas the semicontinuum calculations of various people, e.g., Tibbs[6] and Krumhansl and Schwartz,[7] make the answer to the question uncertain.

The main purposes of this paper are to explore further than was done in Ref. 1 and in Paper I[8] the Hartree-Fock approximation and to investigate the changes brought about by the inclusion of dielectric polarization effects. Some of the experimental quantities to which the results of our calculations can be compared

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

[2] See, for example, H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1954), p. 162.

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

[4] W. B. Fowler, Phys. Rev. **135**, A1725 (1964).

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

[6] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).

[7] J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953).

[8] U. Öpik and R. F. Wood, preceding paper, Phys. Rev. **179**, 772 (1969).

are the F- and K-band absorption energies and oscillator strengths, the F-band emission energy, the relative positions of the $2s$- and $2p$-like levels in absorption and emission which are important for the Stark effect and the lifetime of the excited state, and the hyperfine interaction of the F electron with the neighboring ions in the ground state. Generally, our results agree well with these experimental quantities, particularly in the potassium halides.

In Sec. II, we shall review briefly the work in Paper I and in Sec. III we give the equations from classical ionic-crystal theory which enter into our treatment of lattice relaxation. In Sec. IV we give the details of our calculations and their results. Section V contains a discussion of the results and some concluding comments.

II. REVIEW AND DISCUSSION OF THE METHODS AND MODELS DEVELOPED IN THE FIRST PAPER

In Paper I,[8] we formulated a quantum-mechanical treatment of the F-center electron in ionic crystals which can be modified in various ways to yield different models. We also described methods which we have used to reduce the computer time for the numerical calculations with the models. We give a brief review and a discussion of our treatment here.

A. Hartree-Fock Treatment

We denote by $\mathcal{H}_{\mathrm{HF}}$ the effective Hamiltonian of the defect electron in what we shall refer to, rather loosely, as a Hartree-Fock approximation. It is given, in atomic units, by

$$\mathcal{H}_{\mathrm{HF}}=-\tfrac{1}{2}\nabla^2-\sum_{\nu}\frac{Z_\nu-N_\nu}{|\mathbf{r}-\mathbf{R}_\nu|}+\sum_{\nu}\mathcal{V}_\nu\,, \qquad (1)$$

with

$$\mathcal{V}_\nu u(\mathbf{r})=\left(-\frac{N_\nu}{|\mathbf{r}-\mathbf{R}_\nu|}+2\sum_i\int\frac{[\phi_{\nu i}(\mathbf{r}')]^2}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'\right)u(\mathbf{r})-\sum_i\phi_{\nu i}(\mathbf{r})\int\frac{\phi_{\nu i}(\mathbf{r}')u(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'\,, \qquad (2)$$

where $u(\mathbf{r})$ is an arbitrary one-electron wave function, Z_ν is the charge number, $\mathbf{R}_\nu$ the position vector of the νth ion, and N_ν the number of electrons in closed shells on that ion. The $\phi_{\nu i}$ are the core orbitals and in a true Hartree-Fock calculation they would have to be determined self-consistently since they will depend on the wave function of the defect electron. This would partly introduce dielectric polarization effects explicitly even in the Hartree-Fock approximation. Since we are unable to treat this problem as yet, we shall assume that the $\phi_{\nu i}$ are unpolarized orbitals closely related to the free-ion Hartree-Fock orbitals and introduce polarization effects through a polarization potential.

In principle, the summation index ν should run over all of the ions in the crystal, but in practice this would give rise to formidable computational problems if the wave function of the defect electron were to extend much beyond the vacancy. To see this, let us write, as in Paper I, Eq. (11), the wave function of the defect electron, as

$$\psi(r,\theta,\phi)=f(r,\theta,\phi)-\sum_{\nu,i}\phi_{\nu i}\langle\phi_{\nu i}|f\rangle\,. \qquad (3)$$

Here, $f(r,\theta,\phi)$ is the "smooth" component of ψ which we can express as a linear combination of some basis functions and the $\phi_{\nu i}$ are again the core orbitals. In a band calculation, the basis functions would be plane waves and the core orbitals would be core band functions, thus giving rise to the orthogonalized-plane-wave (OPW) method. If the usual secular determinant generated by a variation calculation is set up using the Hamiltonian in Eqs. (1) and (2), numerous two-center, one- and two-electron integrals involving the $\phi_{\nu i}$ and the basis functions will occur.[9] In quantum chemistry, these integrals are frequently evaluated by a method employing elliptic coordinates, and this method was used in Ref. 1. It is both more accurate than we need and entirely too time-consuming even on a large computer. We therefore developed an approximate method based on l-dependent effective exchange potentials and expansions of $f(r,\theta,\phi)$ about the ion sites which greatly reduced the computing time. We then saw that the orbitals $\phi_{\nu i}$ to be used in Eq. (3) are not the free-ion Hartree-Fock orbitals that are used in Eq. (2), but new ones, say $\phi_{\nu i}'$, generated by the effective exchange potential. Indeed, the use of $\phi_{\nu i}$ in place of $\phi_{\nu i}'$ in Eq. (3) would not be incorrect, but it would probably make the calculation as complicated as that by the old, conventional method. On the other hand, even these orbitals $\phi_{\nu i}'$ are not entirely satisfactory, and an attempt was made to improve them by orthogonalizing those on negative ions to the orbitals on the neighboring positive ions.

B. Treatment of Distant Ions

Even with the computational methods we have developed, it would be too time-consuming to extend the detailed, accurate treatment of the structure on the neighboring ions beyond third-nearest neighbors. We considered two methods of treating the structure on more distant ions. The "extended-ion" method considered the structure on individual ions beyond 3nn but in a very rough manner which was described briefly in Paper I. The second method was based on the effective-mass approximation and gave good agreement with the experimental absorption energies in NaCl and KCl, whereas the extended-ion method did not. In the effective-mass approximation, we choose a radius R_a inside which $\mathcal{H}_{\mathrm{HF}}$ is given by Eqs. (1) and (2) and outside

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[9] Three-center integrals will also occur, but these are expected to be small; our approximations, in effect, circumvent the need to calculate them directly.

which it is given by

$$\mathcal{H}_{\mathrm{HF}} = -(2m^*)^{-1}\nabla^2 - 1/r + \epsilon_{\mathrm{HF}}, \quad r > R_a. \tag{4}$$

ϵ_{HF} is supposed to represent the energy of the bottom of the conduction band in a Hartree-Fock band calculation. Our method of determining it will be given shortly. The impurity potential is taken to be $-r^{-1}$ in the exterior region in our unpolarized ion orbital Hartree-Fock approximation. m^* is the effective mass, also in the Hartree-Fock approximation.

C. Dielectric Polarization

The F-center electron may produce a local polarization of the crystal, and so we add to our Hartree-Fock Hamiltonian a polarization potential $U(r)$ given by

$$U(r) = U_{\mathrm{el}}(r) + U_{\mathrm{ion}}(r), \tag{5}$$

in which $U_{\mathrm{el}}(r)$ is the contribution due to the distortion of the electronic orbitals and $U_{\mathrm{ion}}(r)$ is that due to the displacement of the ions.

There are several different forms of U_{el} and U_{ion} which we could employ; however, here we shall study the applicability to our problem of those following from the work of Toyozawa[10] and Haken and Schottky[11] (THS) on Wannier excitons. We can begin by considering the forms

$$U_{\mathrm{el}}(r) = (1-\kappa_\infty^{-1})[-\tfrac{1}{2}\rho_e + \rho_h) + (2r)^{-1} \times (2 - e^{-\rho_e r} - e^{-\rho_h r})] \tag{6}$$

and

$$U_{\mathrm{ion}}(r) = (\kappa_\infty^{-1} - \kappa_{\mathrm{st}}^{-1})[-\tfrac{1}{2}(v_e + v_h) + (2r)^{-1}(2 - e^{-v_e r} - e^{-v_h r})]. \tag{7}$$

κ_∞ and κ_{st} are the high-frequency and static dielectric constants, respectively. The constants ρ_e, ρ_h, v_e, and v_h were discussed in I, but we wish to extend that discussion here. In I, we decided to fix ρ_h by the equation

$$U_{\mathrm{ML}}^- = \tfrac{1}{2}(1-\kappa_\infty^{-1})\rho_h, \tag{8}$$

in which U_{ML}^- is the polarization energy associated with the removal of a negative ion from the crystal in a Mott-Littleton–type calculation[12] without lattice relaxation. ρ_h is of the order of 0.2 a.u.$^{-1}$ for the crystals considered here. Fowler[13] has suggested that ρ_e should be determined from a similar calculation with U_{ML}^+, the polarization energy associated with the removal of a positive ion, replacing U_{ML}^-. However, we have found that this does not give satisfactory results with our models unless we introduce cutoff radii R_{ce} and R_{ch} inside of which the electron and hole terms, respectively, in U_{el} are put equal to zero. This is perhaps not surprising, since the THS theory may break down for small electron-hole separation even though it approaches what would appear to be the correct limiting behavior, i.e., $U_{\mathrm{el}}(r) \to 0$ as $r \to 0$. As we shall see, we obtain satisfactory agreement with experiment for the absorption process by determining ρ_h from Eq. (8) and putting $\rho_e = \rho_h$ and $R_{ce} = R_{ch} = 0$.

We follow Haken and Schottky's work and determine v_e from the equation

$$v_e = (2m_e^*\omega_{\mathrm{LO}}/\hbar)^{1/2}, \tag{9}$$

where ω_{LO} is the longitudinal optical phonon frequency. The determination of v_h is more difficult. Since the hole in the case of the F center is an immobile vacancy, we can consider it as having an infinite effective mass. Fowler[4] has considered the modification to the ionic part of the THS expression (Eq. 7) for this case. He concludes that it should be a fairly good approximation to determine v_h from the equation

$$v_h = 2/a, \tag{10}$$

where a is the nearest-neighbor distance. Thus, whereas v_e is of the order of 0.03 a.u.$^{-1}$, v_h is of the order of 0.3 a.u.$^{-1}$, and so the vacancy is much more effective in displacing the ions of the crystal than is the electron. This seems quite likely to be the case, but for reasons to be given below we have carried out extensive calculations with $v_h = v_e$.

Difficulties will arise if Eq. (7), as it stands, is used in the calculation of the structure of defects.[14] First, let us consider the ground state of the F center, in which there can be little doubt that the electron is well confined to the vacancy. Even in this state there may be small displacements of the ions neighboring the vacancy and one might expect at least a small contribution from U_{ion}. Nevertheless, it seems best, as far as U_{ion} is concerned, to argue that the screening of the vacancy by the electron in this state, beyond the first nearest neighbors, is complete, and to put $v_e = v_h = 0$ or $\kappa_{\mathrm{st}} = \kappa_\infty$, so that U_{ion}, as given by Eq. (7), becomes zero. We can still include some of the effects of ionic polarization by explicitly allowing the 1nn ions to be displaced, using classical ionic-crystal theory as we shall describe in Sec. III. If we assume the Franck-Condon principle to hold during an optical transition, the ions in the vicinity of the vacancy and the defect electron will retain the positions they occupied in the ground state. Therefore, if U_{ion} is assumed zero in the ground state, we should expect no contribution from it when we calculate the

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[10] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **12**, 422 (1954).

[11] H. Haken and W. Schottky, Z. Physik. Chem. (Frankfurt) **16**, 218 (1958).

[12] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[13] W. B. Fowler, Phys. Rev. **151**, 657 (1966).

[14] In fact, if we used Eq. (7) in both absorption and emission and did not explicitly introduce the displacements of the 1nn ions in $\mathcal{H}_{\mathrm{HF}}$, as we have done, we would obtain no Stokes shift at all. This is because the effects of the motion of the ions are incorporated into U_{ion} through parameters whose values have not been allowed to depend on the electronic state. It is easy to see from the form of our complete Hamiltonian under these conditions that a straightforward application of the THS forms [Eqs. (6) and (7)] would give the same energy levels in both absorption and emission.

energy of the excited states involved in an optical-absorption experiment. One could argue that a slight breakdown of the Franck-Condon principle might be expected and therefore contributions from U_{ion} should be considered. In principle this may be true, but with the form of U_{ion} given in Eq. (7) and the value of v_h suggested by Fowler for an immobile vacancy we would, in effect, be assuming that rather large ionic displacements can occur during an absorption process to a diffuse excited state (e.g., those involved in the K band), and this is very unlikely to be the case. Therefore, in our calculations of the states involved in absorption we shall always take $v_e = v_h = 0$.

The emission process is more troublesome. Let us suppose the electron is in an excited state for which the wave function gives a rather large value for the expectation value of r. Then the ions may be able to follow, to some extent, the motion of the electron. More important, though, is the fact that the immobile vacancy will be almost completely unscreened and will therefore have large displacements of the neighboring ions associated with it since these have ample time to occur before emission takes place. Since we intend to take into account the relaxation energy of the 1nn ions surrounding the vacancy by classical ionic-crystal theory, we might argue that we should keep v_h small so as not to obtain a large additional contribution to the self-energy of the vacancy from U_{ion}. On the other hand, a small value of v_h means that that part of the effective dielectric constant associated with the vacancy will not approach the static dielectric constant very rapidly as a function of r as we expect it to. We have found this to be not too important for the energy of a given state but of considerable importance for the wave function.

While it is thus clear that for emission states a small value of v_h in Eq. (7) is not entirely satisfactory, the use of a large value of v_h also seems unsatisfactory, because it implies that the motion of the ions is so correlated with that of the electron that the ions go back very nearly into the positions appropriate to the ground state in absorption whenever the electron is in the vacancy. Thus, for the compact ground state involved in the emission process, the ionic self-energy would be almost completely turned off and that part of the effective dielectric constant associated with ionic polarization reduced. This is inconsistent with the assumption of the approximate validity of the Franck-Condon principle. If we keep v_h small, the inconsistency is not very important; but if v_h is given the large value suggested by Fowler, it becomes very important. There does not appear to be any completely satisfactory way of overcoming this difficulty when attempting to employ Eq. (7) for the emission states. However, in addition to our calculations with both v_e and v_h small ($v_e = v_h \simeq 0.03$ a.u.$^{-1}$), we have carried out calculations along the following lines. We use Eqs. (6) and (7) and Fowler's suggested value of v_h to argue that in the excited state of the center involved in emission the effective dielectric constant κ_{eff} should be between the high-frequency (κ_∞) and static (κ_{st}) limits. We could determine κ_{eff} approximately in a manner suggested by Fowler's work by estimating the effective radius R_{eff} of the excited state and then employing the equation

$$-1/\kappa_{\text{eff}}r - \tfrac{1}{2}(1-\kappa_\infty^{-1})(\rho_e+\rho_h) - \tfrac{1}{2}(\kappa_\infty^{-1}-\kappa_{\text{st}}^{-1})(v_e+v_h) = -1/r + U_{\text{el}} + U_{\text{ion}} \quad (11)$$

and $r = R_{\text{eff}}$ to determine κ_{eff}. Since this can only give an approximate value of κ_{eff} in any case, we have found it more conveneint to use the following device. We recognize that the energies E of the relaxed excited states of the defect are probably given fairly accurately by effective-mass theory, and write

$$E - E_{\text{cond}} = -(m^*/n^2\kappa_{\text{eff}}^2)13.6 \text{ eV}, \quad (12)$$

where E_{cond} is the energy of the bottom of the conduction band. We then set the difference $E - E_{\text{cond}}$ equal to the experimentally determined thermal ionization energy of the excited state, put $n = 2$, and determine κ_{eff}. With the value of κ_{eff} set, we then take U_{ion} to be given, except for the constant polarization self-energies, by

$$U_{\text{ion}}' = (\kappa_\infty^{-1} - \kappa_{\text{eff}}^{-1})/r, \quad r \geq R_{\text{st}} \quad (13a)$$

and

$$U_{\text{ion}}' = 0, \quad r < R_{\text{st}}. \quad (13b)$$

R_{st} is a cutoff radius for U_{ion}' which is necessary because the effects of the displacements of the 1nn ions on the potential within the radius R_a introduced earlier are to be taken into account explicitly. Apparently, then, R_{st} should be put equal to R_a, although arguments for making it slightly different from R_a can be made. The limiting behavior of $U_{\text{el}} + U_{\text{ion}}'$ for large r is

$$U_{\text{el}} + U_{\text{ion}}' \xrightarrow[r \text{ large}]{} (1-\kappa_{\text{eff}}^{-1})(1/r) - \tfrac{1}{2}(1-\kappa_\infty^{-1})(\rho_e+\rho_h). \quad (14)$$

According to Eqs. (13a), (13b), and (6), that part of the dielectric constant associated with ionic displacement cannot follow the F-center electron's transition, whereas that part associated with electronic polarization will still be given by the THS form. This seems to us to be at least reasonably consistent with the Franck-Condon principle. Our concern with this problem will be more apparent in Sec. IV, where we give the results of our calculations.

In the limit of very large r we have from Eqs. (4)–(7)

$$\begin{aligned}\mathcal{H}_{\text{HF}} + U_{\text{pol}} \rightarrow & -(2m^*)^{-1}\nabla^2 - (\kappa_{\text{st}}r)^{-1} + \epsilon_{\text{HF}} \\ & - \tfrac{1}{2}(1-\kappa_\infty^{-1})(\rho_e+\rho_h) - \tfrac{1}{2}(\kappa_\infty^{-1}+\kappa_{\text{st}}^{-1})(v_e+v_h) \\ = & -(2m^*)^{-1}\nabla^2 - (\kappa_{\text{st}}r)^{-1} + \epsilon_{\text{expt}} - \tfrac{1}{2}(1-\kappa_\infty^{-1})\rho_h \\ & - \tfrac{1}{2}(\kappa_\infty^{-1}+\kappa_{\text{st}}^{-1})v_h, \quad (15)\end{aligned}$$

where we have put

$$\epsilon_{\text{expt}} = \epsilon_{\text{HF}} - \tfrac{1}{2}(1-\kappa_\infty^{-1})\rho_e - \tfrac{1}{2}(\kappa_\infty^{-1}-\kappa_{\text{st}}^{-1})v_e. \quad (16)$$

ϵ_{expt}, the bottom of the conduction band of the perfect crystal, is assumed to be given by the negative of the measured electron affinity, χ_{expt}. We consider it to be composed of a contribution obtainable in principle from a Hartree-Fock band calculation, a polarization self-energy term arising from the distortion of the cores by the additional electron, and a corresponding contribution from the motion of the ions. It is not obvious that this last term should be included, since it is not clear to what extent the ions can follow the electron in a process which measures the electron affinity experimentally. Since the term is only of the order of $\frac{1}{10}$ eV it does not matter greatly whether we include or exclude it. Note that ϵ_{expt} and E_{cond} of Eq. (12) are the same. The terms containing ρ_h and v_h in Eq. (15) represent the polarization self-energy of the hole, in this case a vacancy.

Finally, the expectation value of the effective one-electron energy of the F-center electron is written as

$$E_F=[\langle\psi|h|\psi\rangle_{r\leq R_a}+m^*\langle g|h|g\rangle_{r>R_a}]/[\langle\psi|\psi\rangle_{r\leq R_a}+m^*\langle g|g\rangle_{r>R_a}], \quad (17)$$

in which $h=\mathcal{H}_{\mathrm{HF}}+U(r)$. g is the envelope function of effective-mass theory. The manner in which m^* appears in this equation may seem somewhat peculiar, but, following a suggestion by Tseng,[14a] we have written it this way in order to avoid discontinuity of the kinetic-energy operator at R_a, Such a discontinuity would make the operator non-Hermitian, and, as a consequence, a variational principle could not be derived for the energy. See Paper I for more details.

III. LATTICE RELAXATION

The term $-\frac{1}{2}(\kappa_\infty^{-1}+\kappa_{\mathrm{st}}^{-1})v_h$ in Eqs. (7) and (15) ostensibly takes into account in some sense the energy due to ionic relaxation around the vacancy. However, we wish to include this energy more directly by a calculation employing classical ionic-crystal theory. Thus, to obtain configuration coordinate curves, the effective one-electron energy E_F as a function of the positions of the neighboring ions calculated in the manner outlined in Sec. II must be added to the change in the lattice energy of the crystal as the neighboring ions relax. This problem of the change in lattice energy is one which has received a great deal of attention in the literature in connection with the calculation of the energy of creation of positive- and negative-ion vacancies in ionic crystals. Recently, Boswarva and Lidiard[15] have carried out extensive calculations of these energies in alkali halide crystals and their work indicates how complicated the problem can become. Here we shall employ a very simplified version of their equations.

We write the crystal energy exclusive of E_F as

$$E_{\mathrm{cr}}=E_{\mathrm{cr}}(\mathbf{R}^0)+\Delta E_{\mathrm{cr}}(\mathbf{R}), \quad (18)$$

where $E_{\mathrm{cr}}(\mathbf{R}^0)$ is the energy at the equilibrium position of the ions in the perfect crystal and $\Delta E_{\mathrm{cr}}(\mathbf{R})$ is the change in this energy as a function of the new positions of the ions represented collectively by $\mathbf{R}$.

We shall use the Born-Mayer form for the repulsive potential $V_{\mu\nu}$ between ions μ and ν at a distance $R_{\mu\nu}$ apart. It is given by

$$V_{\mu\nu}=a_{\mu\nu}\exp(-|R_{\mu\nu}|/\rho), \quad (19)$$

with

$$a_{\mu\nu}=b(1+Z_\mu n_\mu^{-1}+Z_\nu n_\nu^{-1})\exp[(R_\mu'+R_\nu')/\rho]. \quad (20)$$

Z_μ and Z_ν are the charges on the ions, n_μ and n_ν the number of electrons in their outer shells, and b and ρ are constants. The effective radii given by Tosi and Fumi[16] for the generalized Born-Mayer potential have been used throughout for R_μ' and R_ν'. The values for the positive (R_+') and negative (R_-') ions of interest here are given in Table I. Note that these are not the same as the crystal radii. The Z's are either $+1$ or -1, and $n_\mu=n_\nu=8$ for all ions considered here.

We consider displacement of the 1nn ions only in a "breathing" mode and express the relaxation parameter as

$$\delta=(R-a)/a, \quad (21)$$

so that a positive δ means an *outward* displacement. a is the nearest-neighbor distance in the perfect crystal, and R is the distance of the 1nn ions from the defect site as relaxation proceeds. The change in the electrostatic energy of the ions treated as point charges is given in atomic units by

$$\Delta E_{\mathrm{Coul}}=\frac{6}{a}\left(\frac{2.6642}{1+\delta}-\frac{1}{2+\delta}-\frac{4}{[1+(1+\delta)^2]^{1/2}}+0.6642\right). \quad (22)$$

TABLE I. Input data for the four crystals considered. m_e is the mass of the electron. χ_{expt} has been varied somewhat from the values shown here for KBr, KI, and NaCl, as described in the text.

	KCl	KBr	KI	NaCl
a (Å)	3.14	3.30	3.53	2.82
R_+' (Å)	1.554	1.554	1.554	1.252
R_-' (Å)	1.678	1.814	2.013	1.678
ρ (Å)	0.324	0.333	0.346	0.317
κ_∞	2.13	2.33	2.69	2.25
κ_{st}	4.68	4.78	4.94	5.62
ρ_h (a.u.$^{-1}$)	0.1969	0.1822	0.1640	0.1972
$v_e=v_h$ (a.u.$^{-1}$)	0.0339	0.0297	0.0275	0.0299
m^* (m_e)	0.5	0.43	0.4	0.6
χ_{expt} (eV)	0.6	0.9	1.6	0.8

[14a] R. Tseng (private communication).

[15] I. M. Boswarva and A. B. Lidiard, Atomic Energy Research Establishment Report No. T.P. 232 (revised), Harwell, England (unpublished), and Phil. Mag. **16**, 805 (1967).

[16] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25**, 45 (1964).

The corresponding change in the repulsive energy arising from the finite extent of the ions is

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\begin{aligned}
\Delta E_{\text{rep}}=12C\{&\exp[-\sqrt{2}(1+\delta)x]-\exp(-\sqrt{2}x)\}\\
&+24B\{\exp[-(1+\delta^2)^{1/2}x]-\exp(-x)\}\\
&+6B\{\exp[-(1-\delta)x]-\exp(-x)\}\\
&+24C\{\exp[-(1+(1-\delta)^2)^{1/2}x]\\
&\quad+\exp[-(2+\delta^2)^{1/2}x]-2\exp(-\sqrt{2}x)\}\,, \qquad (23)
\end{aligned}
$$

where

$$x=a/\rho\,.$$

B and C are the values of $a_{\mu\nu}$, as given by Eq. (20) for negative-positive and positive-positive interactions, respectively. $\Delta E_{\text{cr}}(\mathbf{R})$ is then given by the sums of Eqs. (22) and (23). We have taken these expressions from Ref. 15, but it is easy to see their origins by a simple sketch of the lattice around the defect.

Boswarva and Lidiard obtain considerable variations in their results for the relaxation around positive and negative ion vancancies with their various models and assumptions about the form of the repulsive potential between ions. Also, the displacements of the 2nn ions are not necessarily negligible as we have assumed. Thus, our results calculated with the above equations cannot be considered as more than approximations to a very complicated problem.

IV. CALCULATIONS AND RESULTS

In Paper I, we presented results of calculations of the absorption energy in KCl and NaCl using several different models derivable from the basic computer program. We found that when all polarization effects were excluded the agreement with experiment was poor, whereas when they were included it was much improved. The models in which the effective-mass formulation was used outside of R_a apparently gave good results. Furthermore, in the case of KCl, it did not seem to matter greatly whether we took R_a between the third- and fourth-nearest neighbors or between the first and second. In the latter case, the details of the electronic structure on the negative ions have been eliminated altogether and the model can be extended very easily to the other potassium halides, provided the requisite experimental data are available. The results in Paper I for NaCl seemed to be somewhat more sensitive to the inclusion of 2nn and 3nn ions, and we shall see that it is more difficult to obtain agreement with the experimental results for NaCl than for KCl, KBr, and KI. Before turning to the results of the calculations, however, we shall discuss briefly our choice of input parameters and give some experimental data with which to compare our results.

A. Input Parameters and Experimental Data

The interionic distances and the parameters in the Born-Mayer form of the repulsive potential for the classical ionic-crystal part of the calculation have been taken from Tables III and I, respectively, of Tosi and Fumi (Ref. 16). The second set of data in their Table I has been used. These values are shown in Table I of this paper. In constructing the effective exchange potential and for the hyperfine interaction, we need free-ion Hartree-Fock orbitals, and these we have taken from the work of Bagus.[17] In addition to these data, there are other parameters in the model whose values must be assigned. These are the four parameters in the polarization potential, i.e., ρ_e, ρ_h, v_e, and v_h, which we have already discussed; the high-frequency κ_∞ and static κ_{st} dielectric constants; the experimental electron affinity χ_{expt}; the effective mass m^*; the radius R_a marking the boundary between the region in which the ions are treated in detail and the region in which effective-mass theory is employed; and the cutoff radii R_{ce} and R_{ch} of the polarization potential, if these are used. Actually, we shall always put $R_{ce}=R_{ch}$ when these parameters are introduced. R_a, ρ_e, and the cutoff radii are the parameters with which we have experimented extensively, as will be seen below. We have taken the high-frequency and static dielectric constants in Table I from the literature.[18]

In assigning values of the electron affinity χ_{expt} we have been guided by the work of Timusk and Martienssen,[19] whose values are also shown in Table I. They estimate the error in their determination of the values of χ_{expt} to be not more than 0.2 eV, and we have not hesitated to vary their values by this much, or slightly more in the case of KI,[20] if this would give improved agreement with experiment. The values of the effective mass m^* for KCl, KBr, and KI shown in Table I have been taken from Hodby *et al.*[21]

Table II shows some of the experimental data with which we shall compare our results. The absorption and

TABLE II. Experimental data for the four crystals. As far as we know, the K band in NaCl has not been resolved. ΔE denotes the transition energy for the band, F or K, indicated by the subscript; f denotes an oscillator strength; $E_{\text{th}}(\text{ex})$ is the thermal ionization energy from the relaxed excited state; ab—absorption; em—emission.

	KCl	KBr	KI	NaCl
$\Delta E_F(\text{ab})$	2.313 eV	2.064	1.875	2.770
$\Delta E_K(\text{ab})$	2.71 eV	2.36	2.12	···
$\Delta E_F(\text{em})$	1.215 eV	0.916	0.827	0.975
$E_{\text{th}}(\text{ex})$	0.15 eV	0.135	0.11	0.11
f_F	0.854	0.748	0.827	0.87
f_K	0.107	0.193	0.083	···
$\|\Psi_F(100)\|^2$	0.667 (Å)$^{-3}$	0.589	···	0.351

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[17] P. S. Bagus, Phys. Rev. **139**, A619 (1965).

[18] We have used the values in N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1948).

[19] T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).

[20] E. Taft and L. Apker [J. Phys. Chem. Solids **3**, 1 (1957)] estimate a value of 1.1 eV for the electron affinity in KI.

[21] J. W. Hodby, J. A. Borders, F. C. Brown, and S. Foner, Phys. Rev. Letters **19**, 952 (1967).

emission energies for the main F band and the thermal ionization energies have been taken from the compilation of Podini and Spinolo.[22] These values are for 0°K, while the interionic distances we use are supposedly correct at room temperature. The values of the K-band absorption energy and the oscillator strengths for the F band, f_F, and the K band, f_K, have been taken from Lüty[23] and are appropriate at -180°C, The values of $|\Psi_F(100)|^2$ we have taken from Holton and Blum.[24]

B. Energy Calculations on KCl, KBr, and KI with $\varrho_e=\varrho_h$ and $v_e=v_h$

To obtain an indication of how the computed energy levels are related to some of the parameters of the models, especially the value of the radius R_a, we may consider first the results for KCl given in Fig. 1. This figure shows the energy of the F-center electron, E_F, for the $1s$- and $2p$-like states as a function of the lattice relaxation parameter, δ, which is given there as a percentage of the 1nn distance. The curves labeled 1 on the figure show the results of a calculation for $R_a=11.048$ a.u. (1 a.u. of length$=0.529$ Å), which is between the 3nn and 4nn distances, $\chi_{\rm expt}=0.6$ eV, and $m^*=0.5$. This value of R_a was obtained from the equation

$$\tfrac{4}{3}\pi R_a^3=(3a)^3. \qquad (24)$$

That is, we have equated the volume of a sphere of radius R_a to the volume of a cube which, when it is centered at the defect site, has its faces midway between the first and fourth neighbors.

The curves labeled 2 are for essentially the same calculation but with $R_a=7.427$ a.u., so that only the 1nn ions are considered in detail. This value was obtained from the equation

$$R_a=\sqrt{3}a-R_{\rm alk}, \qquad (25)$$

in which $R_{\rm alk}$ is the classical ionic radius (from Tosi and Fumi) of the alkali ion. The idea here was that the bottom of the conduction band at the Γ point to which the effective-mass treatment is referred is assumed to be composed primarily of $4s$ potassium orbitals in the case of the potassium halides. This suggested that we choose an R_a related to the size of the alkali ion and its distance from the defect site. Experimentation showed that Eq. (25) would accomplish this in a simple way while giving values of R_a sufficiently different from the others we have chosen below to make a meaningful study of the effect of varying R_a.

The curves labeled 3 show the results for calculations in which $m^*=0.6$, $\chi_{\rm expt}=0.6$ eV, and $R_a=6.749$. This value of R_a is determined from the prescription

$$R_a=1.137a. \qquad (26)$$

This is approximately the smallest radius at which the spherically symmetric part of the point ion potential just equals the $1/r$ potential which replaces it beyond R_a. This may be seen from Fig. 6 of the review article of Gourary and Adrian[25] by sketching in the $1/r$ potential.

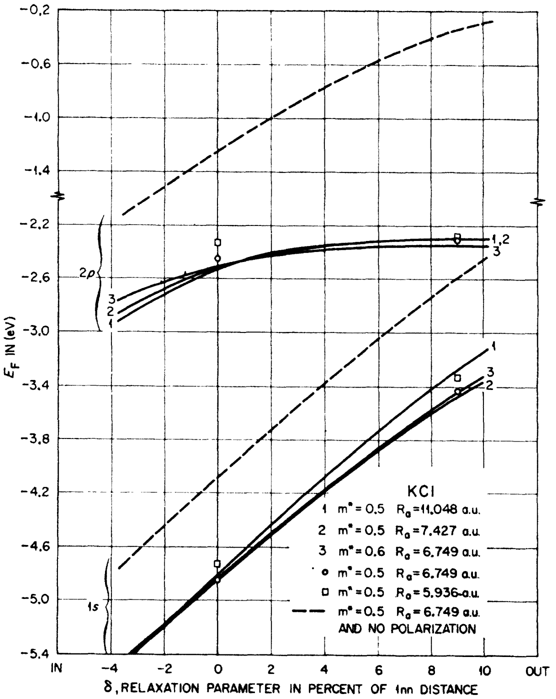

FIG. 1. Curves of E_F [Eq. (17)] versus displacement of the first-nearest-neighbor ions in KCl for various combinations of m^* and R_a. See the text for a more complete description. Note the break in the vertical scale.

The points marked with ○ and □ were calculated with the values of $m^*=0.5$, $\chi_{\rm expt}=0.6$ eV, and $R_a=6.749$ and 5.936 a.u., respectively. The last value of R_a is the same as the 1nn distance a and was chosen in order to study the effects of what we consider a value of R_a which is probably too small when the 1nn ions are treated in detail. We also determined the values of R_a from volume considerations, i.e.,

$$\tfrac{4}{3}\pi R_a^3=(2R_{\rm ha})^3+6(2R_{\rm alk})^3,$$

in which $R_{\rm ha}$ and $R_{\rm alk}$ are the radii of the halide and alkali ions, respectively (again from Tosi and Fumi). The values of R_a determined in this way were not substantially different from those obtained by Eq. (26) for any of the crystals considered, and so no calculations were carried out with them.

There are a number of points to be made from the calculations described thus far. For one thing, the results, over the whole range of δ, with $a\leq R_a<\sqrt{2}a$, do not differ greatly from those with R_a chosen by Eq. (24). This extends the results of Paper I, which were carried out only for $\delta=0$, and further suggests that a model in

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[22] P. Podini and G. Spinolo, Solid State Commun. **4**, 263 (1966).

[23] F. Lüty, Z. Physik **160**, 1 (1960).

[24] W. C. Holton and H. Blum, Phys. Rev. **125**, 89 (1962).

[25] B. S. Gourary and F. J. Adrian, Solid State Phys. **10**, 127 (1960).

which the detailed treatment of the electronic structure on the 2nn and 3nn ions is neglected and effective-mass theory is used just beyond the 1nn may give satisfactory results. However, as in Paper I, we shall see that the results with $a \leq R_a < \sqrt{2}a$ and with R_a chosen by Eq. (24) show a greater difference in NaCl then they do in KCl over the entire range of δ and so we cannot conclude that it is entirely satisfactory to neglect the details of the electronic structure on the 2nn negative ions in all crystals.

If we compare curves 3 and the points ○, we see that the ground state is practically insensitive to small changes in the value of the effective mass. This is to be expected if the ground state is well localized in the negative-ion vacancy. The excited state is somewhat more sensitive, as might be expected for a more diffuse wave function.

We note that from all of the data considered thus far, the energy of the relaxed 2*p*-like state ($\delta \simeq 8.5\%$) is almost totally insensitive to the choice of R_a. The reason is that the wave function in this state is so diffuse that there is very little probability of finding the electron in the vicinity of R_a even when R_a is chosen according to Eq. (24). Also from these data, if we exclude that for $R_a = 5.936$, it appears that the ground state in absorption ($\delta \simeq 0$) is insensitive to the value of R_a. This appears to be due in large part to the compact nature of the ground-state wave function.

The energies indicated by the points □ on the figure are not appreciably worse than any of the other results. However, the excited-state calculations for the □ point at $\delta = 0$ show the wave function to be quite diffuse, as we might expect for emission rather than absorption, while the wave function for point ○ at $\delta = 0$ is relatively compact. This indicates that small changes in the energy can correspond to wave functions of markedly different character.

Finally, in Fig. 1, we show with the dashed curves the results when polarization effects are neglected altogether by putting $\kappa_{\mathrm{st}} = \kappa_\infty = 1$ with $R_a = 6.749$ a.u., $m^* = 0.5$, and $\epsilon_{\mathrm{HF}} = +0.0346$ a.u., as determined from Eq. (16). The results are obviously quite different from those obtained with polarization included and do not agree well with experiment.

We can now combine some of the above results with the calculation of the change in the energy of the crystal due to the relaxation of the 1nn ions as given by Eqs. (22) and (23). Figure 2 shows the results using curve 2 of Fig. 1; the results are very nearly the same if we use the data represented by the ○ points on Fig. 1. We have included on this figure the curves for the 2*s*- and 3*p*-like states, which we omitted in Fig. 1 in order to avoid confusion. We also calculated the energies of the lowest t_{2g} and e_g states for $\delta = 0$. The e_g state is just slightly higher than the t_{2g} state, and both are nearly degenerate with the 3*p* state. The curve we have labeled "conduction band" includes the lattice relaxation energy of Eqs. (22) and (23) and it is, therefore, not a straight line as it would be [see Eq. (16)] if only the one-electron energy corresponding to E_F were plotted. Furthermore, since we assume the Franck-Condon principle to hold during absorption, the curves in the vicinity of $\delta = 0$ have been calculated with $v_e = v_h = 0$, while those in the vicinity of $\delta = 8.5$ have been calculated with $v_e = v_h = 0.0339$ a.u.$^{-1}$. This fact is emphasized in the conduction-band and "3*p*" curves by the break (which is, of course, not physical) at $\delta = 4$, while the other curves, which would show a less pronounced break, have been joined smoothly. In the ground state there is practically no difference at all between the calculations with $v_e = v_h = 0$ and with $v_e = v_h = 0.0339$ a.u.$^{-1}$. It should be noted that two different values of ϵ_{expt} are involved here. First, we determine ϵ_{HF} from Eq. (16), with $v_e = 0.0339$ a.u.$^{-1}$ and $\epsilon_{\mathrm{expt}} = -\chi_{\mathrm{expt}}$. Then we use Eq. (16) again, but with $v_e = 0$ to determine a value of ϵ_{expt} to be used for $\delta \leq 4$.

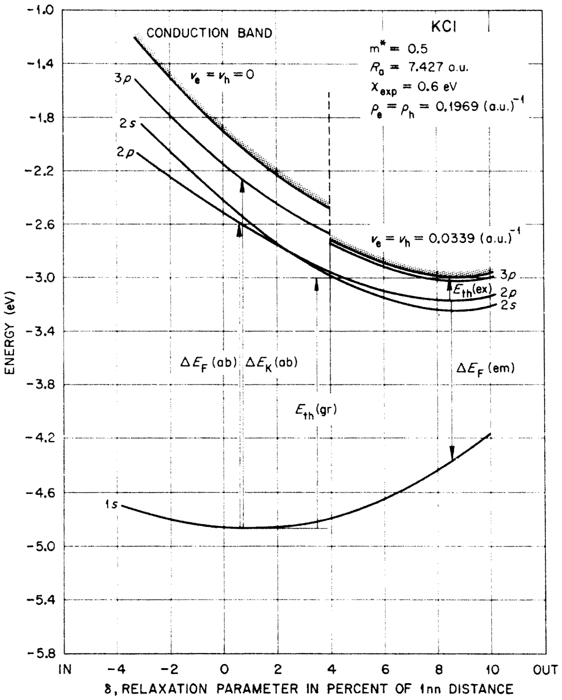

FIG. 2. E_F plus lattice relaxation energy as a function of the positions of the 1nn ions in KCl. Note that the 2*s* level is above the 2*p* in absorption but below it in emission.

We have carried out calculations such as those described above for both KBr and KI. ρ_e and ρ_h were again set equal and R_a was determined from Eq. (25). We again took $v_e = v_h = 0$ for absorption and $v_e = v_h \simeq 0.03$ a.u.$^{-1}$ for emission. The configuration coordinate curves are quite similar to those in Fig. 2 for KCl. Some results for the absorption calculations are shown in Table III. The quantity E_F(cond) is the same as ϵ_{expt} calculated with $v_e = 0$ as explained in the preceding paragraph. We do not give the results for emisson yet, because

TABLE III. Some energy results for absorption (in eV). The values in the first KCl column were obtained with all polarization effects neglected (N.P.). All other results were obtained with $\rho_e=\rho_h$ and $v_e=v_h=0$. Positive δ means an outward displacement of the 1nn ions [Eq. (21)]. E_F is the one-electron energy [Eq. (17)] and does not contain the lattice relaxation energy. $E_{\text{th}}(\text{gr})$ is an estimate of the thermal ionization energy from the ground state obtained as indicated in Fig. 2. We have not shown experimental values for this quantity in Table II because it is difficult to determine their reliability.

	KCl (N.P.)	KCl	KBr	KI	NaCl
δ	0.005	0.006	0.004	0.000	0.004
$E_F(1s)$	-4.00	-4.76	-4.88	-4.95	-5.77
$E_F(2s)$	$\cdots$	-2.43	-2.79	-3.00	-2.86
$E_F(2p)$	-1.18	-2.49	-2.85	-3.07	-3.03
$E_F(3p)$	$+0.01$	-2.15	-2.59	-2.82	-2.45
$E_F(\text{cond})$	$+0.94$	-1.90	-2.43	-2.69	-2.40
$\Delta E_F(1s\rightarrow 2p)$	2.82	2.27	2.03	1.88	2.74
$\Delta E_K(1s\rightarrow 3p)$	4.01	2.61	2.27	2.13	3.32
$E_{\text{th}}(\text{gr})$	$\cdots$	1.9	1.6	1.4	2.2

there is a difficulty, already mentioned in Sec. II C, associated with the ground-state wave function in emission when v_h is assumed to be small. First, however, we shall describe the results of calculations on KBr with ρ_e not equal to ρ_h.

C. Energy Calculations on KBr with $\rho_e\neq\rho_h$

A comparison of the results in Fig. 2 with the experimental quantities in Table II shows that the restriction $\rho_e=\rho_h$ which was employed above gives good agreement with the experimental results on KCl (corresponding agreement is found for KBr and KI). However, since it appears to be a somewhat artificial assumption, we have carried out considerable experimentation on the point.

Figure 3 shows some of the results. The solid curve gives the results of the calculations with $R_a=7.899$ a.u., $\rho_e=\rho_h=0.1822$ a.u.$^{-1}$, and $R_{ce}=R_{ch}=0$. The various circumscribed points give the results of varying R_{ce} and R_{ch}, always keeping $R_{ce}=R_{ch}$. These calculations were carried out with the values $\rho_e=0.2645$ a.u.$^{-1}$ and $\rho_h=0.18515$ a.u.$^{-1}$, as suggested by Fowler from the work of DuPré *et al.*[26] [see Eq. (8) and following text].

It is apparent that with these values and no cutoff both the absorption and emission energies are too great. The reason is that the large value of ρ_e produces a polarization contribution to the energy of the ground state which is evidently too great. Introducing the cutoff radii and increasing their value decreases this polarization contribution until at $R_{ce}=R_{ch}=3.2$ a.u., we are almost back to the curve obtained for $\rho_e=\rho_h=0.1822$ a.u.$^{-1}$ and no cutoff. The compact nature of the ground-state wave function makes the ground-state energy more sensitive than the energies of other states to the effects of the cutoff. Because of this it also appears likely that many different combinations of ρ_e and R_{ce} and R_{ch} can be found which will give approximately the same results. Careful study of energy levels and wave functions might enable one to pick out a combination which is better in some sense than the others, but we have not attempted to do this.

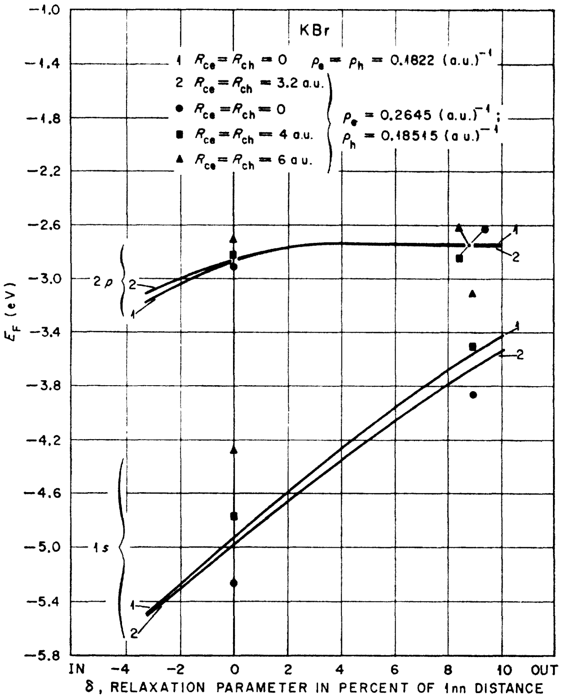

FIG. 3. Curves of E_F versus displacement of 1nn ions in KBr. Here we keep m^* and R_a fixed and vary the polarization parameters ρ_e and ρ_h and the cutoff radii R_{ce} and R_{ch} as discussed in the text.

D. Calculations with v_h Large

From the calculations described in Sec. IV B and C it is possible to obtain rather good agreement with the experimental absorption and emission energies. However, when we compared the computed value of the $\langle 1s|z|2p\rangle$ matrix element in emission to its value in absorption, we found that there was not a very large difference. This was attributable to the fact that the square of the emission matrix element had a value an order of magnitude larger than that deduced by Bogan and Fitchen[27] from experiments on the Stark effect. They obtained $|\langle 1s|z|2p\rangle|^2=9.0\times10^{-18}$ cm^2, whereas we obtained 102×10^{-18} cm^2 for KCl. We have been able to ascertain that our large value comes about because of the development of a substantial tail on the ground-state wave function in emission, i.e., at $\delta=0.085$ when the ions are in their positions corresponding to the relaxed excited state. In KCl this tail has a maximum somewhere in the region between 10 and 15 a.u. This suggests that the THS potential [as given by

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[26] F. K. DuPré, R. A. Hutner, and E. S. Rittner, J. Chem. Phys. **18**, 379 (1950).

[27] D. Bogan and D. B. Fitchen, Bull. Am. Phys. Soc. **12**, 280 (1967).

TABLE IV. Some energy results for emission (in eV). With the exception of the values in the first KCl column, no polarization (N.P.), these results were obtained with U_{ion}' given by Eqs. (13a) and (13b), with κ_{eff} determined from Eq. (12) and the experimental thermal ionization energies given in Table II. $E_{\text{th}}(\text{ex})$ is the computed thermal ionization energy from the 2*s*-like state.

	KCl (N.P.)	KCl	KBr	KI	NaCl
δ	0.04	0.087	0.084	0.085	0.104
$E_F(1s)$	−3.39	−3.38	−3.56	−3.64	−3.81
$E_F(2s)$	···	−2.13	−2.64	−2.87	−2.57
$E_F(2p)$	−0.76	−2.05	−2.56	−2.80	−2.50
$E_F(\text{cond})$	+0.94	−2.02	−2.52	−2.75	−2.49
$\Delta E_F(2s\to 1s)$	···	1.25	0.92	0.77	1.24
$E_{\text{th}}(\text{ex})$	···	0.11	0.12	0.12	0.08

Eqs. (6) and (7)] is too deep in this region even when v_h is kept small. A larger value of v_h, again using Eq. (7), would make the problem worse. It appears that we must make v_h large but abandon Eq. (7) and arrange to keep those effects associated with ionic displacement the same in both the excited and ground states. This would be consistent with the Franck-Condon principle and it is what we have sought to provide for by Eqs. (13a) and (13b).

The results of calculations at $\delta=0.085$ with U_{ion}' given by Eqs. (13a) and (13b) show that indeed the value of the $\langle 1s|z|2p\rangle$ matrix element in emission is now of the right order of magnitude in all three of the crystals. The absorption calculations are, of course, unchanged since for them there is no contribution from U_{ion} at all, as has already been explained. Table IV shows the results of these energy calculations for emission. In obtaining these results (as well as those in Table III) we found it necessary to take $\chi_{\text{expt}}=1.1$ eV for KBr and 1.35 eV for KI, somewhat different from the values of Timusk and Martienssen shown in Table I but very nearly within their range of estimated error (±0.2 eV).

E. Wave-Function Calculations on KCl, KBr, and KI

Most of the above calculations were carried out with wave functions whose smooth part $f(r,\theta,\phi)$ in Eq. (3) was expanded in terms of five Slater-type orbitals of the form

$$f_\kappa(r,\theta,\phi)=[(2\beta_\kappa)^{2n_\kappa+1}/(2n_\kappa)!]^{1/2}r^{n_\kappa-1}e^{-\beta_\kappa r}Y_{l_\kappa}(\theta,\phi)\,, \quad (27)$$

where $Y_{l_\kappa}(\theta,\phi)$ is a Kubic harmonic of degree l referred to a coordinate system located at the missing-ion site. In the ground state, the first three functions were chosen to be $1s(n=1,\ l=0)$, $2s(n=2,\ l=0)$, and $5g$ $(n=5,\ l=4)$ and the exponential parameters β, as well as the expansion coefficients, were determined to minimize the ground-state energy. Two other functions (2*s* and 4*s*) were then added and the parameters in them varied to minimize the second level of *s*-like symmetry. Similarly, in the excited states of *p*-like symmetry, five *p*-type Slater orbitals were used for those calculations in which $\delta\leq 4$, the first three being chosen to minimize the lowest state of this symmetry and the next two to minimize the next-lowest state. For $\delta>4$ only three *p* functions were used and no attempt was made to minimize the 3*p*-like state. A function with $l=3$ was included initially, but its contribution was small and we subsequently neglected it. The contribution of the $l=4$ term in the ground state is also generally small, but since it is of some interest for the spin-orbit interaction we carried it along in the absorption calculations. In emission, this $l=4$ component was replaced by an *s* function in the final calculations described in Sec. IV D.

Rather than giving long tables of the exponential parameters and linear coefficients for $f(r,\theta,\phi)$, we show in Tables V and VI some of the matrix elements which have been calculated with the wave functions associated with the various levels. From Paper I and Eq. (17) of this paper it can be seen that our wave functions are of the form

$$\Psi_F=\psi_{r\leq R_a}+(m^*)^{1/2}g_{r>R_a}\,, \quad (28)$$

with the smooth part of ψ and the envelope function g expanded in terms of the same Slater orbitals of the form given in Eq. (27). The wave function is automatically normalized by the computer program so that the matrix elements of r^n between the smooth parts of any two wave functions are given by

$$\langle 1|r^n|2\rangle=\langle f_1|r^n|f_2\rangle_{r\leq R_a}+m^*\langle g_1|r^n|g_2\rangle_{r>R_a}. \quad (29)$$

The values in Table V were calculated with the radial parts of the wave functions. In Table V we also list the oscillator strengths for $1s\to 2p$ and $1s\to 3p$ transitions obtained from the equation

$$f(1s\to np)=\tfrac{2}{3}\Delta E_n|\langle 1s|r|np\rangle|^2\,, \quad (30)$$

where ΔE_n is the $1s\to np$ transition energy and again only the radial parts of the wave functions are to be used.

TABLE V. Various calculations related to the wave functions for $\delta=0$, i.e., absorption. 1 a.u. of length $=0.529\times10^{-8}$ cm. The starred quantities should be considered less accurate than the others because the minimization of the 3*p* level in NaCl was not carried as far as it was in KCl, KBr, and KI. This is not particularly important for the energy, but the wave function could change significantly. See Sec. V for a discussion of the calculated values of $|\Psi(100)|^2$.

	KCl	KBr	KI	NaCl
$\langle 1s|r|1s\rangle$ (a.u.)	3.93	4.12	4.35	3.58
$\langle 2s|r|2s\rangle$ (a.u.)	18.85	21.60	22.58	16.27
$\langle 2p|r|2p\rangle$ (a.u.)	9.61	12.14	11.17	7.02
$\langle 3p|r|3p\rangle$ (a.u.)	30.20	39.58	45.51	19.00*
$\langle 1s|r|2p\rangle$ (a.u.)	3.89	3.91	4.36	3.71
$\langle 1s|r|3p\rangle$ (a.u.)	1.02	1.50	1.44	0.94*
$\langle 2s|r|2p\rangle$ (a.u.)	10.22	13.84	12.60	7.23
$f(1s\to 2p)$	0.867	0.781	0.878	0.940
$f(1s\to 3p)$	0.069	0.129	0.108	0.073*
$|\Psi(100)|^2$ (Å^{-3})	0.889	0.753	0.565	0.421

All of the above matrix elements should involve the terms arising from the orthogonalization of the smooth function $f(r,\theta,\phi)$ to the core orbitals on the six 1nn ions. We have established that these terms lower the oscillator strength of the $1s \rightarrow 2p$ transition by 5–10%. They probably decrease the effective radii of the $1s$ and $2p$ states by about the same amount, but their effect on the other matrix elements involving more diffuse functions should be much less. We have not included these corrections for the values in the table, since it is likely that these results will most often be compared with the results of semicontinuum calculations where such corrections do not arise explicitly.

We also show in this table the square of the ground-state wave functions at a 1nn ion site. This was calculated by orthogonalizing the smooth part of the wave function to the Hartree-Fock free ion orbitals rather than to the modified core orbitals discussed in Paper I. It would appear to be more consistent to use the modified core orbitals in this calculation, but it is unlikely that this would change the results very much.

F. Calculations on NaCl

We have carried out extensive calculations on NaCl, only a few of which we shall describe here. Figure 4 shows four sets of curves of the energy of the F-center electron versus relaxation parameter for NaCl. The curves labeled (1) were obtained from calculations with $R_a = 9.92$, from Eq. (24); $m^* = 0.6$; $\chi_{\text{expt}} = 0.8$ eV, the value given by Timusk and Martienssen; and $\rho_e = \rho_h = 0.1972$ a.u.$^{-1}$. v_e was taken to be 0 for $\delta < 4$ and 0.02994 a.u.$^{-1}$ for $\delta \geq 4$. The curves marked (2) were obtained with the same values of all of these parameters except R_a, which was taken to be 6.06 a.u., as obtained from Eq. (26). At $\delta = 0$ both of these sets give fairly close agreement with the experimental F-band absorption energy. However, at $\delta = 10.4$, the approximate position of the 1nn ions after lattice relaxation, the calculated value of the emission energy for curves (1) is smaller than the experimental value (~ 1 eV) and for curves (2) they are larger. Thus, following exactly the same procedure as we did for KCl, the results of going from the larger value of R_a to the smaller show rather larger discrepancies than did those for KCl. Since the principal difference between the results for the two values of R_a is in the treatment of the 2nn ions, we conclude that these ions are in some way the major source of the discrepancies. We are fairly certain that our neglect of orthogonalization of the outer orbitals on the Cl$^-$ ion to those on neighboring Cl$^-$ ions is less justified for NaCl than for KCl. This might suggest that the model leading to curves (2) is somewhat superior to that leading to curves (1), but it would be difficult to substantiate this at present.

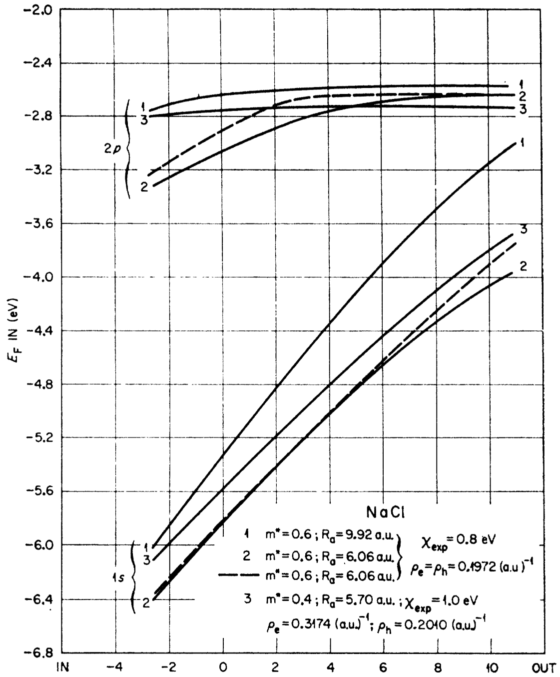

FIG. 4. Some of the results of E_F versus 1nn displacements for NaCl. Curves 2 and the dashed curves differ only because the latter were obtained with less flexible wave functions than the former.

TABLE VI. Various calculations related to the wave functions in emission. $\delta = 0.085$ for KCl, KBr, and KI; $\delta = 0.10$ for NaCl. $\langle 1s|r|2p\rangle^*$ is the matrix element between wave functions obtained when Eq. (7) is used for U_{ion} with $v_h \simeq 0.03$ a.u.$^{-1}$. Only the radial parts of the wave functions have been used in these calculations and the corresponding ones in Table V.

	KCl (a.u.)	KBr (a.u.)	KI (a.u.)	NaCl (a.u.)
$\langle 1s\|r\|1s\rangle$	4.16	4.66	5.22	4.23
$\langle 2s\|r\|2s\rangle$	28.77	28.38	32.19	27.19
$\langle 2p\|r\|2p\rangle$	35.24	39.45	43.64	43.49
$\langle 1s\|r\|2p\rangle$	1.36	1.25	1.31	0.61
$\langle 1s\|r\|2p\rangle^*$	3.31	4.42	3.99	3.71
$\langle 2s\|r\|2p\rangle$	30.86	30.28	34.76	30.00

With these results in mind, we carried out considerable experimentation on varying R_a within the vicinity of 6.06 a.u. Fairly large changes did not improve the agreement with experiment markedly. We tried changing χ_{expt} to 1 eV, which is still within the estimated error of Timusk and Martienssen, and changing m^* to 0.4. We also tried increasing ρ_e while at the same time introducing cutoff radii in the polarization potential as described above for KBr. With $\rho_e = 0.3174$ a.u., $\rho_h = 0.2010$ a.u., and $R_a = 5.70$ a.u., $\chi_{\text{expt}} = 1$ eV, and $m^* = 0.4$, we obtained the curves labeled (3) on Fig. 4. Energetically the results of these calculations compare favorably with the experimental ones shown in Table II. The results for the absorption calculations from curves (2) are shown in Table III.

In the above calculations on NaCl, the $1s$- and $2s$-like states for both absorption and emission were expanded in terms of four s-type and one g-type Slater functions. The $2p$- and $3p$-like states were expanded in terms of five p-like Slater functions for absorption and three for emission. With these wave functions we again found that our $\langle 1s|z|2p\rangle$ matrix element in emission seemed too large. In order to test the effect of using less flexible wave functions, we carried out calculations with the ground state as a linear combination of a $1s$- and a $2s$-type Slater function and the excited state expressed as a single $2p$-type function. In the ground state, the exponential parameters [see Eq. (27)] for the $1s$ and $2s$ functions were forced to be equal but the linear coefficients were allowed to take on the values which minimized the energy. These coefficients could have been determined so as to give zero slope for the radial part of the wave function at $r=0$. Had we done this, we would have had exactly the same forms for the $1s$- and $2p$-like functions as Fowler used in the semicontinuum calculations [see Eqs. (34a) and (34b) below]. The results of the energy calculations with these more restricted functions are shown by the dashed curves in Fig. 4. The $\langle 1s|z|2p\rangle$ matrix element in this case is much smaller than it is in the preceding calculations because the ground-state trial function is not sufficiently flexible to describe the wave function outside of the vacancy.

We also carried out calculations on NaCl at $\delta=0.10$ with U_{ion}' given by Eqs. (13a) and (13b). We found that even with our most flexible wave function the $\langle 1s|z|2p\rangle$ matrix element remained of the right order of magnitude. However, the emission energy from all of the calculations was several tenths of an eV greater than the experimental value. The results of the calculation with $R_a=6.06$, $\chi_{\text{expt}}=1$ eV, $m^*=0.4$, $\rho_e=\rho_h=0.1972$, and $\kappa_{\text{eff}}=3.69$ are shown in Table IV.

G. Semicontinuum Calculations

Our experience with the calculations described above prompted us to investigate the semicontinuum model used by Fowler[4] in his work on the F center in NaCl. His calculations are based on the following Hamiltonian:

$$h=-\tfrac{1}{2}\nabla^2-\frac{\alpha_M}{a}+\frac{6}{a}\left(1-\frac{1}{(1+\delta)}\right)+\frac{1}{2R}(1-\kappa_\infty^{-1})+W_2-\chi_{\text{expt}},\quad r<R \tag{31a}$$

$$h=-\frac{1}{2m^*}\nabla^2-1/\kappa_\infty r+(\kappa_\infty^{-1}-\kappa_{\text{st}}^{-1})[2-(e^{-v_e r}+e^{-2r/a})]/2r,\quad r>R. \tag{31b}$$

W_2 is given by one or the other of the following expressions:

$$W_2=(\kappa_\infty^{-1}-\kappa_{\text{st}}^{-1})\int_R^\infty\left[\int_r^\infty|\psi(s)|^2d^3s\right]r^{-2}dr, \tag{32}$$

where $\psi(s)$ is the wave function of the state from which the optical transition starts; and

$$W_2=\tfrac{1}{2}(\kappa_\infty^{-1}-\kappa_{\text{st}}^{-1})(v_e+2/a). \tag{33}$$

Fowler points our that for large-orbit excited states these two expressions for W_2 are approximately equal but that the second is more consistent with the modified form of the Haken-Schottky expression used in Eq. (31b).

In the model he actually uses in his calculations, which we shall refer to as $F1$, for absorption, Fowler finds that W_2 from Eq. (32) is quite small because the wave function $\psi(s)$ of the initial state is well confined to the vacancy. He also assumes that ionic polarization does not contribute during the absorption process and retains only the first two terms on the right side of Eq. (31b). In the emission process Fowler uses the first expression for W_2, which now gives a large contribution due to the diffuse nature of the wave function of the relaxed excited state. Also in emission rather than using the complete expression for h when $r>R$, he estimates the mean radius of the relaxed excited-state wave function and then evaluates an effective dielectric constant κ_{eff} from the Haken-Schottky expression. κ_{eff} turns out to be 4.2. With this value of κ_{eff} he takes the potential in the external region to be $-(\kappa_{\text{eff}}r)^{-1}$.

In the more consistent model which we shall refer to as $F2$, he suggests that for emission the second expression for W_2 should be used, and presumably the full form for the Haken-Schottky expression in Eq. (31b).

For his wave functions Fowler takes the simple forms

$$\psi_{1s}=[\alpha^{3/2}/(7\pi)^{1/2}](1+\alpha r)e^{-\alpha r}, \tag{34a}$$

$$\psi_{2p}=(\beta^{5/2}/\pi^{1/2})re^{-\beta r}\cos\theta, \tag{34b}$$

where α and β are variational parameters. Fowler obtained rather good agreement with experiment for both the absorption and emission energies. More importantly, he found that the squared ratio of the $\langle 1s|z|2p\rangle$ matrix element in emission to that in absorption was small, and he attributed the long lifetime of the excited state to this result.

We have carried out semicontinuum calculations on NaCl with both of Fowler's models. We obtain agreement with his results so long as we use the $F1$ model and the wave functions given in Eqs. (34a) and (34b) in a variational calculation. However, when we integrate the radial Schrödinger equation appropriate to the $F1$ model numerically,[28] we find that the $\langle 1s|z|2p\rangle$ matrix element is no longer small, and a similar calculation on the $F2$ model gives an even larger value for that matrix element. Quantitatively, the value of $\langle 1s|z|2p\rangle$ in emission for the model $F1$ is 1.96 and for the model $F2$, 2.67 a.u., while that for absorption (where there is no need to distinguish between $F1$ and $F2$) is 2.50 a.u. Thus, we find the ratio of $|\langle 1s|z|2p\rangle|^2$

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[28] In this calculation we used Fowler's Eq. (14) (Ref. 4) for V_0 with $\beta=0.08$ a.u.$^{-1}$.

in emission to that in absorption to be 0.611 and 1.14 for models $F1$ and $F2$, respectively, whereas Fowler obtains the value 0.13 for this ratio. As in the calculations reported in Sec. III B, we find that a tail develops on the $1s$ wave function in emission. This tail is not very important in determining the mean radius of the $1s$ state, but it contributes substantially to the $\langle 1s|z|2p\rangle$ matrix element. This again indicates that considerable care must be exercised in obtaining wave functions from variational calculations, to ensure that the trial functions are flexible enough.

It should also be noted that our treatment of the ionic polarization as discussed before and immediately after Eqs. (13a) and (13b) differs from that of Fowler in a fundamental manner. Fowler has retained the term W_2 within the vacancy when calculating the emission states, whereas we have argued that it should not appear. We contend that this potential has already been included by the outward displacement of the six 1nn ions, and its retention amounts to a double counting of the effects of the displacement of these ions. However, since W_2 is substantially smaller than the effect on the potential of the displacements of the first nearest neighbors, it is possible that the retention of W_2 to some extent compensates for the omission of the effect of the displacements of more distant ions.

We have done calculations with Fowler's model also on KCl, KBr, and KI, and the resulting absorption energies are not nearly as close to the experimental values as in NaCl.

V. DISCUSSION

We have discussed some aspects of the calculations and their results as we proceeded. Here we shall continue the discussion and summarize some of the results obtained in the last section.

It is apparent from Fig. 1 that the results of calculations in which polarization effects are neglected (dashed curves) are quite different from those when it is included (all other curves and points). Since the two dashed curves remain almost parallel throughout the range of δ, there is only a small Stokes shift, a result which does not agree with experiment. The results in the first KCl column of Table III were extracted from the configuration coordinate curve for the case in which polarization was neglected. The disagreement with the corresponding experimental results in Table II is great, especially for the K band in absorption and the F band in emission.

On the other hand, from both Fig. 1 and the results in Tables III and IV, we see that as soon as dielectric polarization is included the calculated and experimental results become quite comparable. The differences between the dashed curves and the curves labeled 3 on Fig. 1 are a quantitative indication of the importance of polarization effects. We can see that they are quite important even in the compact ground state. Is this a model-dependent result? The results of calculations on KBr shown in Fig. 3 lead us to believe that it may be, to a limited extent. From this figure it can be seen that it is possible to move the ground-state curves around readily by introducing cutoff radii for the polarization potential $U(r)$, but they are insensitive to the value of the experimental electron affinity, whereas the excited state is not. Thus, if we were to assume that χ_{expt} is 0.7 eV for KBr, which is still within the estimated error in Ref. 19, rather than 1.1 eV as we have assumed, the excited state would be raised by 0.4 eV in emission and somewhat less in absorption. It should then be possible to find values of the cutoff radii which raised the ground state a corresponding amount by reducing the contribution from the polarization potential. However, such a procedure cannot be carried very far without assuming substantially different values of χ_{expt} from those obtained by Timusk and Martienssen. Therefore, we are now inclined to believe that there really are important polarization contributions even to the compact ground state.

The results in the last four columns of Tables III and IV were taken from configuration coordinate curves like those of Fig. 2. The results, with few exceptions, are in good agreement with the experimental results in Table II. However, it should be kept in mind that the agreement for emission has been forced to a certain extent by our choice of the values of χ_{expt}. Furthermore, since we cannot be sure of the exact position of the 1nn ions and because of other effects such as neglect of the displacement of 2nn ions which we have not included in the calculations, we must conclude that some of these results, especially in emission, may be somewhat fortuitous. Nevertheless, the maxima of the F and K absorption bands (in KCl, KBr, and KI) are given quite well, and slightly different values of χ_{expt} and of the equilibrium positions of the 1nn ions would not affect these results greatly. The results of Boswarva and Lidiard indicate that the uncertainty in the position of the 1nn ions after relaxation may be fairly large, and this would affect the emission energies as would 2nn displacements.

The high-energy side of the K band undoubtedly has contributions from $1s\rightarrow np(n=4,\cdots)$ transitions, as suggested by Mott and Gurney (Ref. 18) and substantiated by the calculations of Smith and Spinolo,[29] but our wave functions are not flexible enough to give these higher p levels with any accuracy. The position of our $3p$ level relative to the conduction band is about right to explain the width and asymmetrical shape of the K band if the $4p$, $5p$,$\cdots$levels were included. We expect most of the oscillator strength of the K band to come from the $1s\rightarrow 3p$ transition and this seems to be indicated by the calculations. It is interesting, although perhaps only accidental, that $f(1s\rightarrow 2p)$ is smaller in KBr than it is in KCl and KI, in agreement

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[29] D. Y. Smith and G. Spinolo, Phys. Rev. **140**, A2121 (1965).

with Lüty's results. The calculations indicate that there are s- and d-like levels in close proximity to the $3p$ level which could be mixed with it by thermal vibrations, but the experimental evidence[30] now seems rather conclusive that appreciable admixing does not occur.

The calculated values of $|\Psi_F(100)|^2$ shown in Table V are somewhat larger than the experimental ones; however, there is a correction to these values which should be taken into account but which we have evaluated approximately only for KCl. This correction comes about because it is necessary to orthogonalize the negative-ion orbitals to the positive-ion orbitals as we have already discussed. This has the effect of introducing a non-negligible spin density at the (1,0,0) site indirectly through the overlap of the smooth trial function with the negative-ion core orbitals. Even when the structure of the negative ions is not taken into account explicitly, this correction should, in principle, be necessary. In KCl, according to our calculations, it lowers the value of $|\Psi_F(100)|^2$ shown in Table V by about 35%, so that the calculated value with this correction is approximately 15% below the experimental value. Although calculations of the spin density at a given ion site are subject to a number of inaccuracies, it does seem that the calculated values obtained from our model should be somewhat smaller than the experimental ones for the following reason. Calculations[31] of the hyperfine interaction of the free potassium atom with restricted Hartree-Fock wave functions give values of the spin density at the nucleus which are about 62% of the measured value. To obtain better agreement one must go to the unrestricted Hartree-Fock scheme or use correlated wave functions. Our approximate wave functions are of the restricted Hartree-Fock type, since the spatial core orbitals are assumed to be doubly occupied. Even if we had a completely rigorous solution within this scheme, we could still not get perfect agreement with experiment.

Examining the results displayed in Fig. 2 further, we note the following. The $2s$ level in absorption is very close to but slightly higher than the $2p$ level, in agreement with the experimental results on the Stark effect.[32] In emission, the $2s$ level is *lower* by a few hundredths of an eV than the $2p$ level, which again is in qualitative agreement with recent experiments on the Stark effect (Ref. 27). This result, which is significant for the interpretation of the lifetime of the excited state, has been obtained in all of the calculations for KBr, KI, and NaCl in which we minimized the $2s$ level after relaxation. Our values of the $2s$-$2p$ splitting ($\sim$0.08 eV) are substantially greater than those derived from the experimental results ($\sim$0.02 eV), but with calculations of this type not much better agreement can be expected unless one adjusts the various parameters in the model to force it. The important point is that there is no reason for the $2s$ and $2p$ levels to be degenerate as in a purely hydrogenic model. We have also calculated $3p$-like, t_{2g}, and e_g levels in emission. They all lie just slightly higher than the $2p$ level, and their wave functions are quite diffuse, as would be expected from the present model.[33]

We feel that we can summarize the results of these calculations as follows. Dielectric polarization effects are important for both absorption and emission. The Toyozawa–Haken-Schottky expressions for the polarization potential appear to be satisfactory for the absorption calculations, but cannot be applied without modification to the emission process because of the difficulties with U_{ion}. The trial wave functions in the variation calculation need to be more flexible than those which have been used frequently in the past. Because of the nature of a variation calculation, this is particularly true for the calculation of quantities other than the energy levels. Finally, the model which we have set up and solved here apparently can give reasonably satisfactory agreement with many of the known properties of the F center in the four crystals we have treated. However, the difficulties we have encountered with the emission results, especially in NaCl, indicate that the model is by no means entirely satisfactory.

ACKNOWLEDGMENTS

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[30] S. E. Schnatterly, Phys. Rev. **140**, A1364 (1965).

[31] D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

[32] G. Chiarotti, U. M. Grassano, and R. Rosei, Phys. Rev. Letters **17**, 1043 (1966).

[33] In a recent publication W. B. Fowler, E. Calabrese, and D. Y. Smith [Solid State Commun. **5**, 569 (1967)] have attributed to one of us (RFW) the suggestion that whereas the $2p$ wave function in emission is diffuse the $3p$ function is compact. These authors have apparently misinterpreted some of the contents of an earlier paper [R. F. Wood, Phys. Rev. **151**, 629 (1966)]. It was never intended that any remarks in that paper should be construed as suggesting that the $3p$ function was less diffuse than the $2p$.

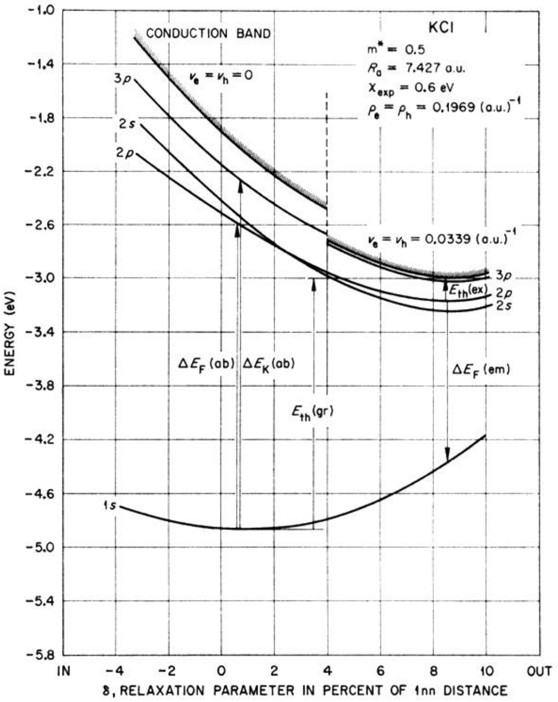

FIG. 2. E_F plus lattice relaxation energy as a function of the positions of the 1nn ions in KCl. Note that the 2*s* level is above the 2*p* in absorption but below it in emission.