Eq. (6), Q is also proportional to V_M at constant T. We see, therefore, that the total concentration of free carriers, n, is a maximum when V_M is a *maximum*, despite the fact that the relative amount of uncompensated donors, n/D^+, is a minimum under the same conditions. When $Q \gg 1$, as in the II-VI compounds (see Sec. III), the *total* concentration of free carriers is essentially independent of V_M. Thus, as p_M is varied in these systems, only the concentration of compensated donors varies.

It should be noted that the situation is entirely different if the donor impurities reside on N sites rather than M sites. Under such circumstances, the solubility of the impurities is maximized and the degree of self-compensation minimized when V_M is minimized, i.e., when p_M is maximized.

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Theory of the Optical and Magnetic Properties of the Self-Trapped Hole in Lithium Fluoride*

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Using a semiphenomenological method, the energy and wave functions of a self-trapped hole (V_k center) in LiF are obtained as a function of the separation between the two F^- ions at which the hole is assumed trapped. The lattice distortion energy due to the changes in Madelung, repulsive, and polarization energies is calculated as a function of the totally symmetric displacement of the two participating F^- ions and six positive ions adjacent to the F^- ions. This lattice energy is combined with the calculated energy for the F_2^- molecule to obtain the total energy as a function of the distance between the participating F^- ions for both the symmetric (Σ_g) and antisymmetric (Σ_u) states of the hole on the V_k center. Only the energy curve for the ground (Σ_u) state exhibits a minimum in the expected region of F^--ion separation. From the resulting configurational coordinate curves, the optical absorption energy and width are computed and found to be in order-of-magnitude agreement with experiment. Computed values of the experimentally known isotropic and anisotropic hyperfine constants are used to assess the validity of our molecular wave functions, which were obtained in a one-electron approximation.

I. INTRODUCTION

IN recent years, a fairly detailed understanding of the F center in alkali halides has been achieved by concerted theoretical and experimental studies of its electronic structure.[1] The F center consists of an electron bound to a negative-ion vacancy, and is the simplest of several "electron" color centers such as the M, R, and F' centers.[2] A series of "hole" color centers also exists (V_1,H,V_k); these are characterized by optical absorption bands lying at somewhat higher energies than those of electron centers, are generally stable only at low temperatures, and must be formed by high-energy irradiation. The best understood of these, a center which consists of a self-trapped hole, has been studied elaborately by Castner and Känzig.[3] Electron resonance data have conclusively shown that this center is not associated with a vacancy but instead resembles a negative halogen molecule-ion with a hole shared between two adjacent negative ions. Two previous theoretical attempts[4,5] have been made to explain the stability of this self-trapped holes. Yamashita[4] tried to calculate the energy of the hole in KCl as a function of the displacement of the Cl^- ions which trap it. He could not obtain a minimum in the energy as a function of this displacement but suggested that the repulsion between the core electrons of the Cl^- ions, which he had neglected, might provide a minimum in the energy curve at half the usual distance between the ions in the crystal. A subsequent attempt by Nettel[5] gave the result that the energy of a hole trapped as a Cl_2^- ion in the crystal had higher energy than a chlorine atom

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[1] See, for example, the review article by 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.

[2] See, for example, J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1963).

[3] T. G. Castner and W. Känzig, Phys. Chem. Solids **3**, 178 (1957); Nuovo Cimento Suppl. **7**, 612 (1958).

[4] J. Yamashita, work at the University of Illinois, 1958 (unpublished).

[5] S. J. Nettel, Phys. Rev. **121**, 425 (1961).

at a cubic site. It appears that Nettel had not employed adequate variational functions for the hole to take account of the relatively strong distortion of the wave function of one of the trapping ions by the other.

In the present paper we attempt to obtain the energy of the LiF crystal containing a hole relative to that of the perfect crystal. The hole is assumed to be shared between two F^- ions so that we have in effect a F_2^- molecule. The energies of the three σ electrons are calculated as a function of the distance between the ions in the two cases corresponding to the unpaired electron being in a symmetric or antisymmetric state. For each distance between the ions, the repulsive, Madelung, and polarization energies are also calculated allowing for relaxation and electronic polarization of six positive ions in the plane of the F_2^- molecule, which are the nearest neighbors to the two F^- ions forming the molecule. The minimum in the total energy curve plotted as a function of the distance between the fluorine nuclei of the F_2^- molecule then gives the equilibrium configuration of the crystal.

In Sec. II, the various contributions to the energy are discussed qualitatively. In Sec. III, the calculation of the lattice energy change is described and in Sec. IV, the computations for obtaining the electronic energies and wave function of the F_2^- molecule are described. In Sec. V, the configuration coordinate curves for the crystal are presented and the optical absorption energy and width and hyperfine constants are calculated and compared with experiment. The nature of the agreement between theoretical and experimental results is then analyzed. In the last section, limitations of the present work are discussed and suggestions for improvement are listed.

II. ANALYSIS OF THE VARIOUS TERMS IN THE ENERGY OF THE CRYSTAL

Our calculation is based on the variation principle. The energy of the crystal containing the hole is calculated as a function of several variation parameters. Some of these parameters may be regarded as equivalent to the configuration coordinates in calculations on luminescent centers, while others are variation parameters that occur in the electronic wave functions. With respect to the former, our calculation resembles that of Williams,[6] with at least one major exception. He was able to use experimental values of the excitation energy of free Tl^+ ion in constructing his excited state configurational coordinate curves, whereas we must rely on computations of this quantity.

Before we describe our variation parameters in detail, we will list and explain the various terms in the total crystal energy E when a hole is present

$$E=E_0+E_A+(\alpha_M e^2/a)+E_E+\Delta E_M+\Delta E_R+\Delta E_P. \quad (1)$$

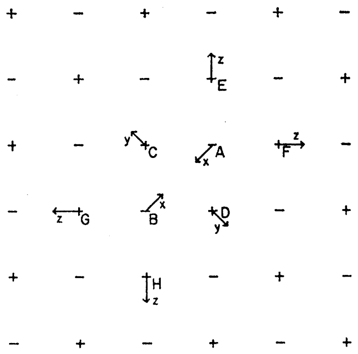

FIG. 1. Diagram showing the ions $A, B, \cdots, H$ which we allow to displace and their directions of displacement.

These terms may be understood in terms of a sequence of events occurring during the removal of an electron from the crystal. E_0 is the energy of the perfect crystal; the next two terms represent the energy required to remove an electron from an F^- ion and place it at infinity; E_A is the electron affinity (work done in taking the electron from F^- itself) and $\alpha_M e^2/a$ is the Madelung energy (work done taking the electron out of the electrostatic potential of the crystal). Here a is the nearest-neighbor distance and α_M the corresponding Madelung constant. Up to this point we have regarded the lattice and remaining electrons as stationary; now let us assume that the hole becomes shared with a nearest neighboring F^- ion so that a molecule F_2^- is formed (see ions A and B in Fig. 1). This will "require" an energy E_E, a quantity which is negative and which will certainly depend on R, the nuclear separation of A and B. The redistribution of charge on the two F^- ions, as well as their relaxation toward each other, will cause a further change in electrostatic energy of the crystal which is included in ΔE_M. In this term is also included the change of electrostatic energy due to the relaxation of neighboring positive ions which will now occur as explained in detail below. Finally, ΔE_R and ΔE_P are the analogous changes in repulsive and polarization energies, respectively, occasioned by the redistribution of charge and motion of the ions.

Of the six terms in (1) which represent the change in the energy of the crystal due to the creation and capture of a hole, the last three and $\alpha_M e^2/a$ may be considered as constituting a change in lattice energy $\Delta E_L=\Delta E_M+\Delta E_P+\Delta E_R+(\alpha_M e^2/a)$. These three contributions are calculated as a function of the fractional displacements (in terms of nearest-neighbor distance in the lattice) x, y, and z of the ions of types A, C, and E shown in Fig. 1. The type-A ions are the two F^- ions (A,B) which share the hole, type C are the two Li^+ ions (C,D) which are the nearest neighbors of A and B. The type E ions are the four Li^+ ions (E,F,G,H) which are the nearest neighbors of the A and B ions. They lie on the same plane as the A- and C-type ions. The relaxation of the four Li^+ ions, which are nearest neighbors of the A and B ions but which do not lie on the plane of the A- and C-type ions, is neglected. Because of the geometry of

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[6] F. E. Williams, J. Chem. Phys. 19, 457 (1951).

the location of these ions, they are an order of magnitude less effective in influencing the lattice energy than the ions C, D, E, F, G, and H. In calculating the repulsive energy change ΔE_R, only nearest-neighbor interactions are considered. The polarization energy of the rest of the lattice as well as of the ions $A, \cdots, F$ is calculated following Mott and Littleton's procedure.[7] The net lattice energy is thus obtained as a function $\Delta E_L(x,y,z)$. Since x represents the major relaxation, $\Delta E_L(x,y,z)$ is minimized with respect to y and z to obtain $\Delta E_L(x,y_0,z_0)$ which is a function of x alone. The details and results of the lattice energy calculation are presented in Sec. III.

The terms E_A and E_E represent the electronic energy changes associated with the creation and capture of the hole. The electron-affinity E_A of the F^- ion is taken as 0.363 eV, from Hartree-Fock calculations[8] on the F^- ion. The F_2^- binding energy E_E is obtained by calculating the energy of three σ electrons in the molecule (two electrons in σ_g state and one in σ_u when the hole is in the antisymmetric state Σ_u, and two electrons in σ_u state and one in σ_g state for the hole in the symmetric state Σ_g) and taking the difference between this energy and the energy of three $2p$ electrons on the F^- ion. The details of the calculation of E_E as a function of the distance between A and B, that is, $E_E(x)$, as well as the potential and the variational form of the wave function employed will be discussed in Sec. IV. $E_E(x)$ is then combined with $\Delta E_L(x)$ to obtain the variation of the total energy of the crystal with x; the position of its minimum gives the equilibrium configuration of the crystal. It will be seen later that a minimum is found only when the hole is in the Σ_u and not in the state Σ_g.

III. CALCULATION OF LATTICE ENERGY CHANGES

We shall first consider the change in the Madelung energy of the lattice due to the presence of the hole. For this calculation, we shall assume that the hole is equally divided between the two F^- ions. This is a fairly good approximation if the bonding between A and B is not too strong so that there is not much migration of charge to the region between the two ions. The general expression for the difference in Madelung energies of the crystal between the two situations in which the ions $A, B, C, \cdots, H$ are displaced, $E_M(x,y,z)$, and undisplaced, $E_M(0,0,0)$, can be shown to be given by

$$E_M(x,y,z)-E_M(0,0,0)$$

$$=\sum_{L=A}^{H}\sum_{M\neq A,\cdots,H}^{\infty}\zeta_L\zeta_M\left(\frac{1}{r_{LM_0}}-\frac{1}{r_{L_0M_0}}\right)$$

$$+\sum_{L=A}^{M-1}\sum_{M=A}^{H}\zeta_L\zeta_M\left(\frac{1}{r_{LM}}-\frac{1}{r_{L_0M_0}}\right). \quad (2)$$

Here ζ_L and ζ_M are the charges on the lattice points L and M, and L_0 and L represent, respectively, the undisplaced and displaced positions of the point L. Thus, for example, r_{LM_0} represents the distance between the displaced position of the point L and undisplaced position of M. If we are interested in an expansion of (2) in powers of x, y, and z correct to second order, we may take

$$\sum_{M\neq L}^{\infty}\frac{\zeta_L\zeta_M}{r_{LM_0}}=\sum_{M\neq L}^{\infty}\frac{\zeta_L\zeta_M}{r_{L_0M_0}}, \quad (3)$$

provided that all ζ_M are equal to $\pm e$ and are situated on a regular cubic lattice. Equation (3) is a result of the fact that in regular cubic crystals, the next multipole interaction between ions after the monopole corresponds to $l=4$. Hence only quartic and higher terms in x, y, or z are to be expected from the summation in (3). It follows that

$$\sum_{M\neq A\cdots H}^{\infty}\frac{\zeta_L\zeta_M}{r_{LM_0}}=\sum_{M\neq L}^{\infty}\frac{\zeta_L\zeta_M}{r_{L_0M_0}}-\sum_{\substack{M=A\\M\neq L}}^{H}\frac{\zeta_L\zeta_M}{r_{LM_0}}, \quad (4)$$

which may be used to simplify Eq. (2) to the following form:

$$E_M(x,y,z)-E_M(0,0,0)$$

$$=\frac{1}{2}\sum_{\substack{M=A\\M\neq L}}^{H}\sum_{L=A}^{H}\zeta_L\zeta_M\left(\frac{1}{r_{LM}}-\frac{2}{r_{LM_0}}+\frac{1}{r_{L_0M_0}}\right). \quad (5)$$

If the charges on the A and B ions are $-qe$ and the charges on the rest of the lattice points are the same as in the perfect lattice, then the above calculation must be modified in an obvious way, and one obtains

$$E_M(x,y,z)-E_M(0,0,0)$$

$$=\sum_{L=A}^{M-1}\sum_{M=A}^{H}\zeta_L\zeta_M\left(\frac{1}{r_{LM}}+\frac{1}{r_{L_0M_0}}-\frac{1}{r_{LM_0}}-\frac{1}{r_{L_0M}}\right)$$

$$+2(q^2-q)\left(\frac{1}{r_{AB_0}}-\frac{1}{r_{A_0B_0}}\right)$$

$$-2(q-1)\sum_{L=C}^{H}\left(\frac{1}{r_{LA_0}}-\frac{1}{r_{L_0A_0}}\right). \quad (6)$$

In the present case we are assuming that $q=\frac{1}{2}$. Also, ζ_L is $+e$ for a positive ion and $-e$ for a negative ion. With the help of Fig. 1, one can calculate the various distances involved in Eq. (6) correct to terms quadratic in x, y, and z. Thus, for example,

$$\frac{1}{r_{AE}}+\frac{1}{r_{A_0E_0}}-\frac{1}{r_{AE_0}}-\frac{1}{r_{A_0E}}=-\frac{\sqrt{2}}{a}xz. \quad (7)$$

Equation (6) includes the repulsive energy between charges $-e/2$ on the ions A and B. This is a spurious

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

[8] C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

term introduced by our assumption that the hole is equally distributed between the two F^- ions, and must be excluded because all such intramolecular interactions are contained in E_E. We therefore obtain the following expression for ΔE_M:

$$\Delta E_M(x,y,z)=E_M(x,y,z)-E_M(0,0,0) -[e^2/4\sqrt{2}a(1-\sqrt{2}x)]. \quad (8)$$

Using equations like (7), Eqs. (6) and (8) may be expanded in powers of x, y, and z, and after a lengthy calculation one obtains

$$\Delta E_M=(e^2/a)(-0.177-0.500x-0.354x^2 -1.414y+1.207y^2+2.358z+3.426z^2 +3.000xy+2.500zx-1.707yz). \quad (9)$$

It should be emphasized that this equation has been derived for a particular (fcc) lattice.

Next, we consider ΔE_R. In keeping with our earlier assumptions for the Madelung energy change we shall not consider the repulsion between the ions A and B. This latter repulsive energy, when it becomes appreciable, will be included in the electronic energy terms. Also, we shall consider repulsion between nearest neighbors alone. There are several choices that one can make for the repulsive interaction energy between the positive and negative ions. One possible choice is the Born-Mayer potential,[9] which has the form

$$V(r)=Be^{-r/\rho}, \quad (10)$$

with B and ρ obtained from the observed compressibility and lattice constant of the crystal. In the determination of B and ρ in the Born-Mayer formula from the perfect crystal, Van der Waals forces were neglected, i.e., their effect is assumed to be adequately included in the exponential parameters. Therefore in using this formula for the imperfect crystal, we should ignore Van der Waals forces for the sake of consistency. Huggins and Mayer[10] have also obtained B and ρ from data on the perfect crystal, but including Van der Waals forces separately. We shall also make use of these constants to test the sensitiveness of the calculated lattice energy to the choice of force constants. Another form for the repulsive energy has been proposed by Pauling,[11] namely

$$V(r)=0.0485e^2r_0^{n-1}/r^n, \quad (11)$$

where r_0 is the sum of the ionic radii of the positive and negative ions and n depends on the nature of the positive and negative ion pair. For LiF one can take $n=6$ so that for the repulsive potential between Li^+ and F^- ion we can rewrite (11) as

$$V(r)=Ae^2/r^6, \quad (12)$$

where $A=0.0485r_0^5$. Using the form in Eq. (10) for the repulsive energy, the expression for $\Delta E_R(x,y,z)$ is given by Eq. (13):

$$\Delta E_R(x,y,z)=4Be^{-a/\rho}\left[\frac{a}{\rho}\left\{\left(-x^2-y^2-2z^2-\frac{xy}{2}\right) +\frac{a}{2\rho}(x^2+y^2+2z^2-xy-\sqrt{2}xz)\right\}\right]. \quad (13)$$

In obtaining Eq. (13), the energy differences between a pair of ions L and M is calculated using the relation

$$\Delta E_R(L,M)=B[e^{-r_{LM}/\rho}-e^{-r_{L_0M_0}/\rho}], \quad (14)$$

where r_{LM} and $r_{L_0M_0}$ have the same meaning as in Eq. (6). The distances r_{LM} between the displaced ions and their nearest neighbors are calculated up to quadratic terms in x, y, and z as before.

Using the Pauling expression (12) for the force law, Eq. (15) is obtained for the change in the repulsive energy as a function of x, y, z:

$$\Delta E_R(x,y,z)=(Ae^2/a^6)[60x^2+60y^2+120z^2 -96xy-84\sqrt{2}xz]. \quad (15)$$

In Table I are tabulated the constants B and ρ both in the Born-Mayer and Huggins-Mayer approximations as well as the value of A in the Pauling approximation. In obtaining A, a value of $r_0=1.95$ Å was used in Eq. (12), this value of r_0 being the sum of the ionic radii of Li^+ and F^- ions. The lattice constant a for LiF is 2.01 Å, only slightly different from r_0. On introducing the values of B, ρ, and A in Eqs. (14) and (15), we get the following equations for $\Delta E_R(x,y,z)$ in the three cases.

Huggins-Mayer:

$$\Delta E_R(x,y,z)=\frac{e^2}{a}[1.664x^2+1.664y^2 +3.328z^2-3.031xy-3.642xz], \quad (16a)$$

Born-Mayer:

$$\Delta E_R(x,y,z)=\frac{e^2}{a}[2.482x^2+2.482y^2 +4.964z^2-3.675xy-4.635xz], \quad (16b)$$

Pauling:

$$\Delta E_R(x,y,z)=\frac{e^2}{a}[2.910x^2+2.910y^2 +5.820z^2-4.656xy-5.762xz]. \quad (16c)$$

The difference between Eqs. (16a) and (16b) which use the same force law but different force constants B and ρ could partly be ascribed to the neglect of the effect of the Van der Waals forces in using the Huggins-Mayer formula. In order to get an expression for

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[9] M. Born and J. E. Mayer, Z. Physik. **75**, 1 (1932); we will use the simple theory given by M. Born and K. Huang, *Dynamics of Crystal Lattices* (Oxford University Press, New York, 1955), p. 26.

[10] M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

[11] L. Pauling, Proc. Natl. Acad. Sci. India Sec. A, Pt. I **25**, (1956). See also Milne and Cubiccoti, J. Chem. Phys. **29**, 846 (1956).

TABLE I. Table of constants in repulsive energy formulas.

	B (ergs)	ρ (Å)	A
Born-Mayer	1.05×10^{-9}	0.244	
Huggins-Mayer	1.3541×10^{-10}	0.345	
Pauling			1.368×10^{-40}

$\Delta E_R(x,y,z)$ which would be comparable to (16b) one would have to include in $\Delta E_R(x,y,z)$ the contribution from the change in Van der Waals energy due to the displacement of the lattice points. We shall not do this but instead use the differences between the lattice energy changes with Huggins-Mayer and Born-Mayer formulas as a measure of the importance of Van der Waals forces. Equations (16a) and (16b) indicate that while the Van der Waals contribution to the lattice energy is significant, it is definitely less important than the repulsive energy change. The difference between the energy expressions in (16b) and (16c) is due to the different formulas [Eqs. (10) and (12)] employed. It is encouraging that the difference between Eqs. (16b) and (16c) is less than that between (16a) and (16b) since both Born-Mayer and Pauling formulas include the effect of the Van der Waals forces indirectly. One last comment about the repulsive energy calculation. We have used Eqs. (10) and (12) together with the constants in Table I which refer to the energy of repulsion between Li^+ and F^- ions. Actually ions A and B are somewhat different from the regular F^- ion because they each contain a total charge $-e/2$, which is less than that of a regular F^- ion. Our belief that the use of Eqs. (10) and (12) does not lead to significant error is based on two considerations. First, that the charge distribution of five and one-half $2p$ electrons is probably not too different from what it would be for six. Secondly, at least in the Σ_u state, the hole probably affects only the charge distribution in the region between the two ions A and B. Hence, to the nearest-neighbor positive ions, $C, D, \cdots, H$, the A and B ions do not "look" very different from perfect F^- ions.

We shall finally consider ΔE_P, the energy associated with the polarization of the lattice due both to the two holes on ions A and B and the displacements of the neighboring points $C, D, \cdots, H$. The polarization energy due to a point charge at a lattice site has been considered in detail by Mott and Littleton.[12] In the zeroth-order approximation, where one considers the crystal as a dielectric continuum in calculating local fields at the ions, the dipole moments on the positive and negative ions are given by

$$N_\pm = \frac{M_\pm a^3 e}{r^2}, \tag{17}$$

with the dipoles directed outwards in the direction of $\mathbf{r}$, the radius vector joining the impurity charge ζ_i and the ion under consideration.

$$M_\pm = \frac{\zeta_i(1-1/K_S)(e^2/A+\alpha_\pm)}{4\pi[(e^2/A)+\frac{1}{2}(\alpha_+ + \alpha_-)]}, \tag{18}$$

where α_+ and α_- are the electronic polarizabilities of the positive and negative ions on the lattice, K_S is the static dielectric constant and $A = 6a/\theta$ is the spring constant with the compressibility $1/\theta$ given by

$$\frac{1}{\theta} = \frac{1}{3a}\left[\frac{1}{\rho^2} - \frac{2}{a\rho}\right] B e^{-a/\rho}. \tag{19}$$

We however follow the first-order approximation of Mott and Littleton in that we permit the nearest-neighbor ions ($B, C, \cdots, H$ in the case of the hole on A) to move discretely and determine their displacements by a detailed consideration of the various terms in the lattice energy. So we have to allow for this difference in nature between the ions $A, \cdots, H$ and the ions in the rest of the crystal. We shall do this by taking into account only the electronic polarization of ions A to H, since their ionic polarizations have already been considered by calculating their electrostatic and repulsive interactions with other ions in the crystal in their displaced positions.

Our polarization energy calculation is also somewhat more involved than the calculation of the polarization energy due to single point charges such as single vacancies and interstitials in a lattice. The ions A and B carry only charges $-e/2$ and are in displaced positions as compared to their original positions A_0 and B_0 in the lattice. Therefore, in the calculation of polarization effects we have in effect to consider four charges, namely $-\frac{1}{2}e$ each at A and B, and $+e$ each at the points A_0 and B_0. The latter two represent the effective charges the vacancies would have if the charges $-\frac{1}{2}e$ were *entirely* removed. Each of these four charges polarizes the ions in the rest of the lattice and the dipole moment on the polarized ion not only interacts with the polarizing charge (direct polarization energy) but also with the other three charges (indirect polarization energy). We shall consider the four ions in six pairs, namely (A_0B_0), (AB), $(AB_0)(A_0B)$, (AA_0), and (BB_0). To avoid counting the direct polarization energy for each of the four charges twice, we shall include the direct polarization energies only while considering the first two pairs (A_0B_0) and (AB). Strictly speaking, one should consider similar pairs for the ions C, D, E, F, G, H because they are also displaced from their original equilibrium positions. A consideration of such effects is equivalent to considering the polarization of the lattice due to the dipoles produced by the displacements of $C, \cdots, H$ from their original positions. Since the displacements of the ions $C, \cdots, H$ are expected to be less important than those of A and B, we shall neglect the

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[12] See Ref. 7; B. G. Dick (private communication).

effects of the dipoles at $C, \cdots, H$ on the polarization energy. Thus we have

$$\Delta E_P = \Delta E_p(A_0B_0) + \Delta E_p(AB) + \Delta E_p(AB_0) + \Delta E_p(A_0B) + \Delta E_p(AA_0) + \Delta E_p(BB_0)\,. \tag{20}$$

$$\begin{aligned}\Delta E_p(A_0B_0) = -\frac{e^2}{a}\Bigg[& M_1 \sum_i \frac{1}{r_{A_0i}{}^4} + M_2 \sum_j \frac{1}{r_{A_0j}{}^4} + M_1 \sum_i \frac{\cos\theta_{A_0iB_0}}{r_{A_0i}{}^2 r_{B_0i}{}^2} + M_2 \sum_j \frac{\cos\theta_{A_0jB_0}}{r_{A_0j}{}^2 r_{B_0j}{}^2} - \frac{M_2}{r_{A_0B_0}{}^4} - 2\left(\frac{M_1}{r_{A_0C_0}{}^4} - \frac{M_1'}{r_{A_0C}{}^4}\right) \\ & - 2\left(\frac{M_1 \cos\theta_{A_0C_0B_0}}{r_{A_0C_0}{}^2 r_{B_0C_0}{}^2} - \frac{M_1' \cos\theta_{A_0CB_0}}{r_{A_0C}{}^2 r_{B_0C}{}^2}\right) - 2\left(\frac{M_1}{r_{A_0E_0}{}^4} - \frac{M_1'}{r_{A_0E}{}^4}\right) \\ & - 2\left(\frac{M_1}{r_{A_0G_0}{}^4} - \frac{M_1'}{r_{A_0G}{}^4}\right) - 4\left(\frac{M_1 \cos\theta_{A_0E_0B_0}}{r_{A_0E_0}{}^2 r_{B_0E_0}{}^2} - \frac{M_1' \cos\theta_{A_0EB_0}}{r_{A_0E}{}^2 r_{B_0E}{}^2}\right)\Bigg], \end{aligned} \tag{21}$$

where

$$\begin{aligned} M_1 &= \frac{[1-(1/K_S)][(e^2/A)+\alpha_+]}{4\pi[(e^2/A)+\frac{1}{2}(\alpha_+ + \alpha_-)]}, \quad M_1' = \frac{\alpha_+}{a^3}, \\ M_2 &= \frac{[1-(1/K_S)][(e^2/A)+\alpha_-]}{4\pi[(e^2/A)+\frac{1}{2}(\alpha_+ + \alpha_-)]}, \quad M_2' = \frac{\alpha_-}{a^3}. \end{aligned} \tag{22}$$

The summation in i in the first and third terms of (21) runs over the positive ions in the lattice while the summation over j in the second and fourth terms runs over the negative ions except that in the fourth term the points $j = A_0$ and $j = B_0$ are excluded. The fifth term arises because (when considering the effect of the charge $+e$ at A_0) we do not have an ion at the B_0 site and vice versa for the charge $+e$ at B_0. The sixth, seventh, eighth, ninth, and tenth terms in (21) take account of the correction to be introduced because we have to consider only the electronic polarization of the displaced ions C, D, E, F, G, and H. The angles like $\theta_{A_0jB_0}$ stand for the angle subtended by the points A_0 and B_0 at the lattice point j.

$$\begin{aligned}\Delta E_p(AB) = -\frac{e^2}{4a}\Bigg[& M_1 \sum_i \frac{1}{r_{Ai}{}^4} + M_2 \sum_j \frac{1}{r_{Aj}{}^4} + M_1 \sum_i \frac{\cos\theta_{AiB}}{r_{Ai}{}^2 r_{Bi}{}^2} + M_2 \sum_j \frac{\cos\theta_{AjB}}{r_{Aj}{}^2 r_{Bj}{}^2} - (M_2 - M_2'')\frac{1}{r_{AB}{}^4} \\ & - 2\left(\frac{M_1}{r_{AC_0}{}^4} - \frac{M_1'}{r_{AC}{}^4}\right) - 2\left(\frac{M_1 \cos\theta_{AC_0B}}{r_{AC_0}{}^2 r_{BC_0}{}^2} - \frac{M_1' \cos\theta_{ACB}}{r_{AC}{}^2 r_{BC}{}^2}\right) - 2\left(\frac{M_1}{r_{AE_0}{}^4} - \frac{M_1'}{r_{AE}{}^4}\right) - 2\left(\frac{M_1}{r_{AG_0}{}^4} - \frac{M_1'}{r_{AG}{}^4}\right) \\ & - 4\left(\frac{M_1 \cos\theta_{AE_0B}}{r_{AE_0}{}^2 r_{BE_0}{}^2} - \frac{M_1' \cos\theta_{AEB}}{r_{AE}{}^2 r_{BE}{}^2}\right)\Bigg], \end{aligned} \tag{23}$$

where M_1, M_2, and M_1' are defined in Eq. (22) and

$$M_2'' = \frac{\alpha_-'}{a^3}. \tag{24}$$

The quantity α_-' represents the polarizability of the π electrons on the F^- ion. The fifth term is introduced to take account of the fact that only the polarization of the π electrons on A and B ions has to be considered; the polarization of the σ electrons will be taken care of indirectly in the electronic energy. The summations in the first and third terms again run over the positive ions alone and those in the second and fourth terms over the negative ions alone, the points $j = A, B$ are again excluded from the fourth summation. The rest of the terms are introduced to avoid introducing the ionic polarization of the ions $C, D, \cdots, H$ in ΔE_P.

$$\begin{aligned}\Delta E_p(AB_0) + \Delta E_p(A_0B) = \frac{e^2}{a}\Bigg[& M_1 \sum_i \frac{\cos\theta_{A_0jB}}{r_{A_0i}{}^2 r_{Bi}{}^2} + M_2 \sum_j \frac{\cos\theta_{A_0jB}}{r_{A_0j}{}^2 r_{Bj}{}^2} - 2\left(\frac{M_1 \cos\theta_{A_0C_0B}}{r_{A_0C_0}{}^2 r_{BC_0}{}^2} - \frac{M_1' \cos\theta_{A_0CB}}{r_{A_0C}{}^2 r_{BC}{}^2}\right) \\ & - 2\left(\frac{M_1 \cos\theta_{A_0E_0B}}{r_{A_0E_0}{}^2 r_{BE_0}{}^2} - \frac{M_1' \cos\theta_{A_0EB}}{r_{A_0E}{}^2 r_{BE}{}^2}\right) - 2\left(\frac{M_1 \cos\theta_{A_0G_0B}}{r_{A_0G_0}{}^2 r_{BG_0}{}^2} - \frac{M_1' \cos\theta_{A_0GB}}{r_{A_0G}{}^2 r_{BG}{}^2}\right)\Bigg]. \end{aligned} \tag{25}$$

In Eq. (25) also, the summation indices (in the first and second terms) refer to positive and negative ions, respectively, the ion B being left out of the summation in j. Finally, we have

$$\Delta E_p(AA_0)+\Delta E_p(BB_0)=\frac{e^2}{a}\Biggl[M_1\sum_i\frac{\cos\theta_{A_0iA}}{r_{A_0i}{}^2r_{Ai}{}^2}+M_2\sum_j\frac{\cos\theta_{A_0jA}}{r_{A_0j}{}^2r_{Aj}{}^2}-2\biggl(\frac{M_1\cos\theta_{A_0C_0A}}{r_{A_0C_0}{}^2r_{AC_0}{}^2}-\frac{M_1'\cos\theta_{A_0CA}}{r_{A_0C}{}^2r_{AC}{}^2}\biggr)$$
$$-2\biggl(\frac{M_1\cos\theta_{A_0E_0A}}{r_{A_0E_0}{}^2r_{AE_0}{}^2}-\frac{M_1'\cos\theta_{A_0EA}}{r_{A_0E}{}^2r_{AE}{}^2}\biggr)-2\biggl(\frac{M_1\cos\theta_{A_0G_0A}}{r_{A_0G_0}{}^2r_{AG_0}{}^2}-\frac{M_1'\cos\theta_{A_0GA}}{r_{A_0G}{}^2r_{AG}{}^2}\biggr)\Biggr]. \quad (26)$$

We can combine Eqs. (21), (23), (25), and (26) to obtain the net polarization energy of the lattice given by Eq. (20). Since we require the energy only up to quadratic terms we have to express the polarization energy in terms of linear and quadratic terms in x, y, and z only. This can be done with the help of Fig. 1 and expressing the distances and angles involving the displaced ions A, B, $\cdots$, H in terms of linear and quadratic terms in x, y, and z. The detailed evaluation of the coefficients of these terms requires several lattice summations, some of them about the single center A and some involving the two centers A and B. A few of these summations were available from the work of earlier authors,[7,13] namely

$$\begin{aligned}&\sum_i\frac{1}{r_{A_0i}{}^4}=10.1977\,,\\&\sum_j\frac{1}{r_{A_0j}{}^4}=6.3346\,,\\&\sum_i\frac{1}{r_{A_0i}r_{B_0i}{}^3}-\sum_i\frac{1}{r_{A_0i}{}^3r_{B_0i}{}^3}=5.036\,,\\&\sum_j\frac{1}{r_{A_0j}r_{B_0j}{}^3}-\sum_j\frac{1}{r_{A_0j}{}^3r_{B_0j}{}^3}=4.152.\end{aligned} \quad (27)$$

These summations are the least convergent of the various sums needed. The rest of the sums have the general form

$$\sum\frac{x_{A_0i}{}^{\alpha}x_{B_0i}{}^{\beta}y_{A_0i}{}^{\gamma}y_{B_0i}{}^{\delta}}{r_{A_0i}{}^{\sigma}r_{B_0i}{}^{\tau}}, \quad (28)$$

with similar expressions involving j. x_{A_0i}, y_{A_0i}, and z_{A_0i} represent coordinates of the ith ion in terms of the crystal axes with respect to the undisplaced position of A. These were performed on the Illiac at the University of Illinois computing center and checked on the IBM-1620 at the computing center of the Riverside campus of the University of California. Their values are presented in Table II. The sums were carried out in all cases up to the eleventh neighbors of the relevant type (positive or negative ion), and the convergence was tested by finding the additional contribution in going to the thirteenth neighbors. The convergence in all cases was better than 0.1%.

Next we have to consider the values of the quantities M_1, M_2, M_1', M_2'' to be used in the calculation. The expressions for these are given in terms of K_S, α_+, α_-, α_-', and the spring constant A in Eqs. (22) and (24). In Table III the values of these quantities are tabulated together with the source from which they were obtained.

TABLE II. Lattice sums involved in the calculation of ΔE_p. The sums and notation are defined in the text [see Eq. (28)].

α	β	γ	δ	σ	τ	Sum over i	Sum over j
0	0	0	0	1	5	4.62961	1.32584
0	0	0	0	3	5	2.79582	0.41540
0	1	0	0	3	3	1.73987	0.54498
0	1	0	0	1	5	0.73710	0.13719
0	1	0	0	3	5	1.11161	0.14987
0	2	0	0	3	5	1.42513	0.34914
0	1	0	1	3	5	0.18422	0.00136
1	1	0	0	3	5	0.31351	0.19927
1	0	0	1	3	5	−0.92679	−0.14850
1	1	0	0	5	5	0.08821	0.04716
0	1	0	1	1	7	0.02760	−0.05133
0	2	0	0	3	7	1.17244	0.12574
0	1	0	1	3	7	0.05051	−0.01262
0	2	0	0	1	7	1.64155	0.41656
0	2	0	0	0	8	2.19260	0.59693
1	0	0	1	5	5	−0.97343	−0.07417

TABLE III. Values of the quantities involved in expressions for M_1, M_2, M_1', and M_2''.

Quantity	Value	Source
K_S	9.27	M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Table 17.
α_+	0.03×10^{-24} cm³	J. R. Tessman, A. H. Kahn and W. Shockley, Phys. Rev. **92**, 890 (1953).
α_-	0.652×10^{-24} cm³	C. Kittel, *Solid State Physics*, (John Wiley and Sons Inc., New York, 1959), p. 165.
α_-'	0.391×10^{-24} cm³	Represents polarizability of π electrons which is $\frac{3}{5}$ of α_- [see R. M. Sternheimer, Phys. Rev. **96**, 951 (1954)].
A	1.17×10^{-12}	M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Table 9.

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[13] J. R. Reitz and Gammel, J. Chem. Phys. **19**, 894 (1951); F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1955).

Using these values, we obtain

$$\begin{aligned} M_1&=0.0624,\\ M_1'&=0.0036,\\ M_2&=0.0796,\\ M_2'&=0.0482. \end{aligned} \tag{29}$$

The result of our expansion and substitution is finally,

$$\begin{aligned} \Delta E_P(x,y,z)=-(e^2/4a)[&1.416-0.505x+0.702x^2\\ &-0.010y-0.007y^2+0.089xy+0.037z\\ &+0.087z^2+0.106xz]. \end{aligned} \tag{30}$$

It is understandable why in the expression for the polarization energy the coefficients of the terms that do not involve x are small. These terms arise out of the electronic polarization of the positive ions which have rather small polarizability. Combining Eqs. (9), (16), and (30) we get the following equation for the net change in the lattice energy, namely,

$$\begin{aligned} \Delta E_L(x,y,z)=(\alpha_M e^2/a)+(e^2/a)[&-0.538-0.374x\\ &-1.416y+2.348z+\alpha x^2+\beta y^2+\gamma z^2\\ &+\lambda xy+\mu yz+\nu xz], \end{aligned} \tag{31}$$

where the coefficients α, β, γ, λ, μ, and ν depend on our choice of the repulsive energy formula. In Table IV, the values of these coefficients are tabulated when the Born-Mayer, Huggins-Mayer, and Pauling repulsive energy formulas are used. The coefficients in the lattice-energy expression are seen to be sensitive to the choice of the repulsive energy formula, as discussed above.

From Eq. (31), one obtains the energy of the lattice as a function of x alone by minimizing the lattice energy with respect to y and z. This leads to the equations

$$\begin{aligned} 2\beta y+\mu z&=1.416-\lambda x,\\ \mu y+2\gamma z&=-2.348-\nu x. \end{aligned} \tag{32}$$

One can now solve Eqs. (32) in terms of x and substitute the following expressions (33) obtained for $y(x)$ and $z(x)$ in Eqs. (31) and hence express the lattice energy in terms of x alone, as in (34):

$$\begin{aligned} y_0(x)&=b+cx,\\ z_0(x)&=d+ex, \end{aligned} \tag{33}$$

and

$$\Delta E_L(x)=A+Bx+Cx^2. \tag{34}$$

From Eq. (34), one can obtain a plot of the lattice energy as a function of x or of R, the distance between the ions A and B, the relation between R and x being given by

$$R=\sqrt{2}a(1-\sqrt{2}x). \tag{35}$$

TABLE IV. Values of coefficients in lattice energy expressions.

Coefficient	Born-Mayer	Huggins-Mayer	Pauling
α	1.953	1.135	2.381
β	3.691	2.873	4.119
γ	8.368	6.732	9.224
λ	−0.698	−0.053	−1.678
μ	−1.707	−1.707	−1.707
ν	−2.162	−1.169	−3.288

In Table V, the values of b, c, d, and e in Eq. (33) and A, B, and C in Eq. (34) are tabulated for our three different repulsive force laws. In Fig. 2, we have plotted $\Delta E_L(R)$ as a function of R and as expected there is great similarity between the Born-Mayer and Pauling curves, there being a minimum in the lattice energy curve in each case. The positions of the minima can be expressed either in terms of x or in terms of R, using Eq. (35). In Table VI, we have tabulated for the cases of the three repulsive formulas employed, the values of x_0, R_0, and $\Delta E_L(R_0)$, the lattice energy at the position of the minimum in $\Delta E_L(R)$. The minimum in the lattice energy curve is rather significant and arises out of a compromise between the energy of interaction between the ions A and B with the ions C, D, E, F, G, H. Thus, the distance between the ions A and C decreases as x increases while the distances between ion A and ions E and F increases as x increases. The fact that we get a minimum in the lattice energy curve indicates that there is self-trapping of the hole even in the absence of appreciable electronic conjugation between the ions A and B leading to the F_2^- molecule ion. As we shall see in the next section, there is also a stable state for the free F_2^- ion. The relative depths and shapes of the lattice energy and electronic energy curves are important in determining the nature of the total energy curve for the crystal. We shall discuss this point further in Secs. IV and V after describing the electronic energy calculation.

IV. ELECTRONIC ENERGY CALCULATIONS

The next quantities that we have to calculate are the energies and wave functions for a F_2^- ion as a function of internuclear separation. There are various standard methods in molecular physics to accomplish this, broadly divided into molecular orbital and valence-

TABLE V. Coefficients b, c, d, e, A, B, and C in Eqs. (34) and (35) for the different choices of repulsive energy formula. A, B, and C are in Ry ($e^2/2a_0$).

Coefficient	Born-Mayer	Huggins-Mayer	Pauling
b	0.163	0.202	0.148
c	0.127	0.036	0.245
d	−0.124	−0.149	−0.114
e	0.142	0.091	0.201
A	0.503	0.473	0.515
B	−0.116	−0.111	−0.131
C	0.923	0.569	0.971

TABLE VI. Positions R_0 of the minima and minimum values $\Delta E_L(x_0)$ of the lattice energy for the various approximations. $\Delta E_L(x_0)$ is expressed in Ry, and R_0 is in units of a_0. For $x=0$, that is, for the undisplaced positions of A and B, $R=5.371a_0$.

Quantity	Born-Mayer	Huggins-Mayer	Pauling
x_0	0.063	0.097	0.068
R_0	4.893	4.680	4.855
$\Delta E_L(x_0)$	0.502	0.470	0.513

bond methods.[14] Both these methods in their improved forms, including configuration interaction in the molecular orbital approach and ionic character in the valence bond approach, are essentially equivalent. In their improved forms they are comparable to variational approaches in the self-consistent procedure for atoms including configuration interaction. In our calculations, we have not attempted to include any configuration interaction or self-consistency requirements, but have adopted a simple molecular orbital procedure. In the usual molecular orbital method, as in the Hartree-Fock approach for atoms, one generally starts from the following many-electron Hamiltonian and computes from it a one-electron Hamiltonian for each state:

$$\mathcal{H}=-\sum_i \nabla_i^2+\sum_i \frac{2z}{r_i}+\sum_{i>j}\frac{2}{r_{ij}}. \tag{36}$$

For simplicity, we have adopted the following approximate one-electron Hamiltonian for the three $2p$ electrons which take part in the σ bond for the F_2^- molecule:

$$\mathcal{H}=-\nabla_i^2+V_A(\mathbf{r}_{Ai})+V_B(\mathbf{r}_{Bi}). \tag{37}$$

The potentials $V_A(\mathbf{r}_{Ai})$ and $V_B(\mathbf{r}_{Bi})$ both represent the one-electron potentials seen by a $2p$ electron on a F^- ion. The justification for choosing (37) is the following. When the unpaired electron in the molecule is in the neighborhood of ion A, then as far as the ion A is concerned, it sees the potential that a $2p$ electron on an F^- ion would see. In the same situation, as far as ion B is concerned, the charge distribution on it looks like a neutral atom to the unpaired electron on A and therefore the electron again experiences the same potential from ion B as a $2p$ electron on an F^- ion would. These arguments are valid when the cores of the F^- are not too distorted by the presence of the hole. This would be true if the distance between the fluorine nuclei in the molecule is not very greatly different from the distance in the perfect crystal.

As basis functions for our determination of the σ_g and σ_u functions for the F_2^- molecule, we have selected the following linear combinations:

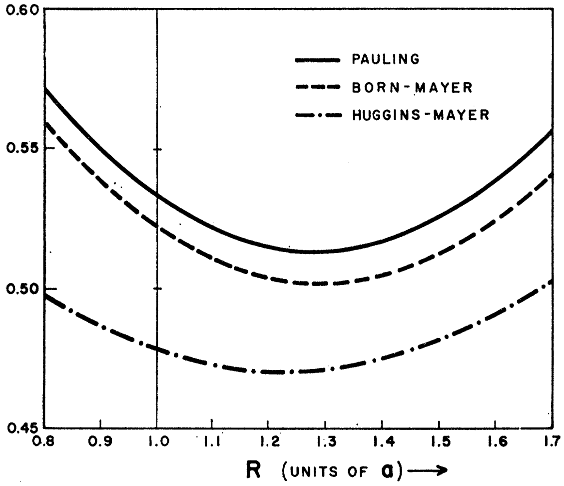

FIG. 2. Curve showing lattice energy ΔE_L as a function of the distance R between the F^- ions A and B. Curves for all three approximations for the repulsive energy, namely Born-Mayer, Pauling, and Huggins-Mayer are given.

$$\Phi_g=\sum_i c_i\phi_{ig}, \qquad \Phi_u=\sum_i d_i\phi_{iu}, \tag{38}$$

where

$$\begin{aligned} \phi_{1g}&=\phi_{1A}-\phi_{1B}, & \phi_{1u}&=\phi_{1A}+\phi_{1B},\\ \phi_{2g}&=\phi_{2A}-\phi_{2B}, & \phi_{2u}&=\phi_{2A}+\phi_{2B},\\ \phi_{3g}&=\phi_{3A}+\phi_{3B}, & \phi_{3u}&=\phi_{3A}-\phi_{3B},\\ \phi_{4g}&=\phi_{4A}+\phi_{4B}, & \phi_{4u}&=\phi_{4A}-\phi_{4B}, \end{aligned} \tag{39}$$

with

$$\begin{aligned} \phi_{1A}&=\frac{P_{2p}(r_A)}{r_A}Y_1^0(\theta_A,\phi_A), & \phi_{3A}&=\frac{P_{2p}(r_A)}{r_A^2}Y_0^0(\theta_A,\phi_A),\\ \phi_{2A}&=P_{2p}(r_A)Y_1^0(\theta_A,\phi_A), & \phi_{4A}&=\frac{P_{2p}(r_A)}{r_A}Y_0^0(\theta_A,\phi_A). \end{aligned} \tag{40}$$

The function $P_{2p}(r_A)$ is taken to be the radial part of the $2p$ wave function of the F^- ion. Ideally one should have used in addition to ϕ_{1A} and ϕ_{2A}, functions whose radial parts are $r_AP_{2p}(r_A)$, $r_A^2P_{2p}(r_A)$, $\cdots$ to include a complete set. We have chosen only two functions out of the complete set as a compromise to reduce the work involved. The same remark applies to the choice of the functions ϕ_{3A} and ϕ_{4A}. Taking the radial parts of all the functions as being related to $P_{2p}(r_A)$ enables us to make use of the known integral and differential properties [Eq. (43)] of this function, especially as they relate to the effective potentials V_A and V_B and the atomic eigenvalues $\mathcal{E}_{2p}$.

To set up secular equations to obtain the coefficients c_i and d_i in Eq. (38), we have to compute matrix ele-

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[14] C. Coulson, *Valence* (Oxford University Press, New York, 1953).

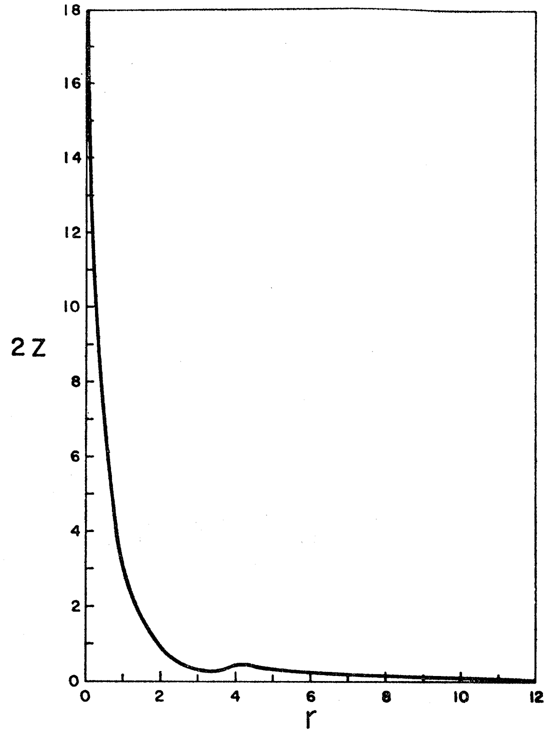

FIG. 3. Plot of $2Z(r)$ versus r.

ments $\mathcal{H}_{ij}=\langle\phi_i|\mathcal{H}|\phi_j\rangle$ for both u and g states. These matrix elements $\mathcal{H}_{ij}$ involve integrals over the orbitals in Eq. (39). Examples of the various types of integrals that have to be calculated are

$$\langle\phi_{iA}|-\nabla^2|\phi_{iA}\rangle,\quad \langle\phi_{iA}|V_A|\phi_{iA}\rangle,\quad \text{and}$$
$$\langle\phi_{iA}|V_B|\phi_{iA}\rangle,\quad \langle\phi_{iB}|-\nabla^2|\phi_{iA}\rangle,\quad \langle\phi_{iA}|V_A|\phi_{iB}\rangle.$$

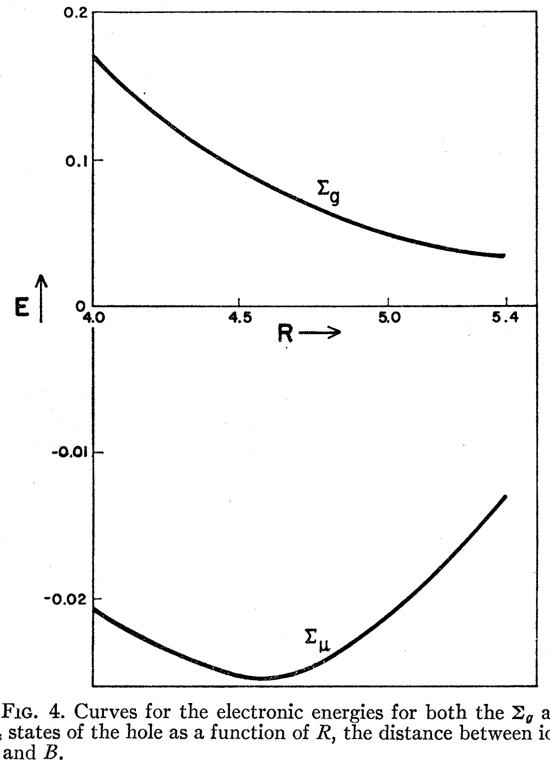

FIG. 4. Curves for the electronic energies for both the Σ_g and Σ_u states of the hole as a function of R, the distance between ions A and B.

Of these integrals only the first two are one-center integrals, the other three are two-center integrals. The one-center integrals can be obtained by direct numerical integration. For example, we have

$$\langle\phi_{1A}|-\nabla^2|\phi_{1A}\rangle=\int_0^\infty\left(\frac{dP_{2p}}{dr}\right)^2dr+2\int_0^\infty\frac{P_{2p}^2}{r^2}dr,$$
$$\langle\phi_{1A}|V_A|\phi_{1A}\rangle=-\int_0^\infty\frac{P_{2p}^2}{r}2Z(r)dr,\qquad(41)$$

where the potential $V_A(r)$ has been expressed as

$$V_A(r)\equiv-2Z(r)/r.\qquad(42)$$

We obtain $V_A(r)$ directly from its definition by the one-electron Hartree-Fock equation:

$$V_A(r)=+\mathcal{E}_{2p}-\frac{P_{2p}''}{P_{2p}}-\frac{2}{r^2}\qquad(43)$$

where $\mathcal{E}_{2p}$ is the one-electron energy for the $2p$ state and $P''=d^2P/dr^2$. The function P_{2p} and the energy parameter $\mathcal{E}_{2p}$ are taken from Froese's calculations.[8] In Fig. 3 we have plotted the values of $2Z(r)$ as a function of r. For the two-center integrals we employ Löwdin's α-function method.[15] The α functions and the integrals involving them that were required [to determine the matrix elements of the Hamiltonian $\mathcal{H}$, Eq. (37)], were obtained at the computing centers of the University of Rochester and Argonne National Laboratory. Since we require the electronic energy as a function of the distance between the ions A and B we have to compute the matrix elements for different values of R. These computations were done for six values of R, namely $4.0a_0$, $4.4a_0$, $4.8a_0$, $5.0a_0$, $5.2a_0$, and $5.4a_0$. Since the functions ϕ_i do not form an orthonormal set, we must take account of the integrals $S_{ij}=\langle\phi_i|\phi_j\rangle$ for both the σ_g and σ_u states and the eigenvalue secular equation then takes the form:

$$\mathrm{Det}|\mathcal{H}_{ij}-S_{ij}E|=0\qquad(44)$$

for both σ_g and σ_u states. The eigenvalues $\mathcal{E}_g$ and $\mathcal{E}_u$ for the six values of R considered are tabulated in Table VII. Also tabulated in Table VII are the quantities

$$E_u=\mathcal{E}_u+2\mathcal{E}_g+(2/R)-3\mathcal{E}_{2p}\qquad(45)$$

and

$$E_g=2\mathcal{E}_u+\mathcal{E}_g+(2/R)-3\mathcal{E}_{2p}.\qquad(46)$$

The quantity E_u represents the decrease in energy of the three σ electrons due to bonding between the ions

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[15] P. O. Löwdin, Advan. Phys. 5, 96 (1956).

TABLE VII. Energy values in rydbergs for electronic and hole states for different values of the internuclear distance of R.

Energy value \ R	4.0	4.4	4.8	5.0	5.2	5.4
$\mathcal{E}_g$	-0.5997	-0.5666	-0.5400	-0.5282	-0.5179	-0.5086
$\mathcal{E}_u$	-0.4103	-0.4352	-0.4498	-0.4534	-0.4558	-0.4552
$\mathcal{E}_u+2\,\mathcal{E}_g+(2/R)$	-1.1097	-1.1137	-1.1131	-1.1098	-1.1070	-1.1020
$\mathcal{E}_g+2\,\mathcal{E}_u+(2/R)$	-0.9203	-0.9823	-1.0229	-1.0350	-1.0414	-1.0486
E_u	-0.0207	-0.0247	-0.0241	-0.0208	-0.0180	-0.0130
E_g	$+0.1687$	$+0.1067$	$+0.0661$	$+0.0540$	$+0.0376$	$+0.0304$

A and B, when the hole is in the Σ_u state; E_g represents the corresponding energy decrease of the three σ electrons for the Σ_g state of the hole. The term $2/R$ represents the Coulomb energy of repulsion between the effective unit positive charges at the A and B ions about which the three σ electrons of the F_2^- molecule can be considered as moving. Thus E_u and E_g give the values of the term E_E in Eq. (1) for the Σ_u and Σ_g states of the hole, respectively. The variations of E_u and E_g with R are shown in Fig. 4. It is seen that while E_u has a minimum at $R=4.56a_0$, E_g has no such minimum. This result indicates that while the Σ_u state for the hole in the free F_2^- molecule is stable, the Σ_g state is not, as expected. Finally, to obtain the variation in total energies of the hole states Σ_u and Σ_g in the crystal with the distance R between A and B, we have to combine the energies plotted in Figs. 2 and 4 which will give us the variation with R of the total energy of the crystal in the presence of the hole.

V. TOTAL ENERGY OF CRYSTAL AND INTERPRETATION OF VARIOUS EXPERIMENTALLY STUDIED PROPERTIES OF THE HOLE

In Table VIII, we tabulate $E-E_0$ of Eq. (1) as a function of R. In addition to the lattice energy calculated from Eq. (34) and the electronic energy tabulated in Table VIII we have added the electronic affinity E_A which we have taken as 0.363 Ry from Froese's calculations.[8] For the lattice energy, in view of the inaccuracy in principle in the use of the Huggins-Mayer expression, as mentioned earlier, we have only used the Born-Mayer and Pauling expressions. Also tabulated is δE which is the difference between E and the quantity

$$\frac{\alpha_m e^2}{a}+E_A=1.283\text{ Ry},\qquad(47)$$

representing the increase in energy of a crystal when an electron leaves the crystal (or a hole is produced in the crystal) excluding the energy change due to relaxation of the ions of the lattice and the electronic binding between the ions A and B. The suffixes g and u to δE and E are added in Table VIII to indicate the corresponding states Σ_g and Σ_u of the hole. The negative values of δE_u and δE_g indicate that the combined effects of the lattice distortion and electronic conjugation between A and B ions is to stabilize the hole center. In the case of the Σ_u state both the lattice distortion and electronic conjugation lead to stabilization. For the Σ_g state, the lattice distortion leads to stabilization while the presence of two antibonding σ_u electrons and only one bonding σ_g electron leads to destabilization. In Fig. 5 the energies δE_u and δE_g are plotted as functions of R for both the Pauling and Born-Mayer approximations. The zero ordinate on this plot would represent the energy of the undisturbed crystal after the hole has been removed, while the energy of the perfect crystal E_0 lies at -1.283 Ry. As was found in Fig. 4 with the electronic energy, again we have a minimum only in the Σ_u state and none in the Σ_g state suggesting that only the Σ_u state for the hole has a stable minimum. This result cannot be taken too literally, however, because we must realize that when R corresponds to the normal lattice distance or greater distances, our de-

TABLE VIII. Energy in Ry of the crystal due to the presence of the hole.

Energy \ R	4.0	4.4	4.8	5.0	5.2	5.4
E_u (Pauling)	0.869	0.855	0.852	0.855	0.860	0.868
E_u (Born-Mayer)	0.858	0.845	0.841	0.844	0.848	0.856
E_g (Pauling)	1.058	0.987	0.942	0.930	0.915	0.911
E_g (Born-Mayer)	1.047	0.976	0.931	0.919	0.904	0.899
δE_u (Pauling)	-0.415	-0.428	-0.431	-0.428	-0.424	-0.416
δE_u (Born-Mayer)	-0.425	-0.439	-0.442	-0.439	-0.435	-0.428
δE_g (Pauling)	-0.225	-0.297	-0.341	-0.353	-0.368	-0.372
δE_g (Born-Mayer)	-0.236	-0.307	-0.352	-0.364	-0.380	-0.384

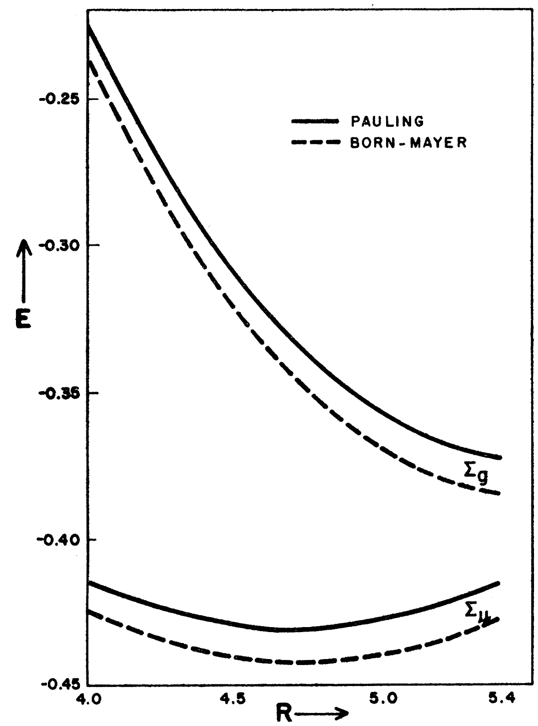

FIG. 5. Curves for the total energies δE_u and δE_g for the Σ_u and Σ_g states, respectively, of the hole as a function of R.

scription is not a complete one. In that case, there is high probability of the hole hopping to a new pair of F^- ions.

A comparison of Figs. 2, 4, and 5 indicates that the depths and rates of variation around the minimum of the Born-Mayer and Pauling curves are comparable. Also it is seen that the minima of the lattice energy curves for the Pauling and Born-Mayer approximations are at $R=4.89a_0$ and $4.92a_0$, respectively, while the minimum in the E_u curve for the electronic energy occurs at about $4.56a_0$. In comparison, the minimum in the δE_u curves for the total energy occurs at about $4.72a_0$ for both the Pauling and Born-Mayer approximations. These considerations indicate that according to our calculations, the lattice distortion around the V_k center and the electronic binding within the F_2^- molecule are comparable in importance in contributing to the stabilization of the V_k center.

From Fig. 4 one can also obtain the absorption energy for transitions between the Σ_u and Σ_g hole states. By the Franck-Condon principle, we expect the transition energy to be obtained vertically from the minimum in the E_u curve. From Fig. 5, the absorption energy for both the Born-Mayer and Pauling approximations is 0.097 Ry, which corresponds to 1.32 eV. This is to be compared with the experimentally observed[16] position of the absorption peak at 3.54 eV. We thus obtain only order-of-magnitude agreement with experiment. There are two possible sources of error which might be responsible for the disagreement between theoretical and experimental absorption energies. Our molecular calculations are approximate and perhaps a better calculation would lead to a stronger binding that is, a deeper energy curve for the Σ_u state of the hole and move the Σ_g state correspondingly upwards in energy.[14] The other possibility is the lack of self-consistency in our calculation which is implied by the direct addition of E_E and ΔE_L.

From the ground state and excited state curves for the energy as a function of R, we can also obtain the width of the absorption band. Assuming a linear dependence on the excited state configuration coordinate (R in our case)[17] one obtains the following expression for the width at an intensity equal to one half of that at the maximum, namely:

$$\Delta W = 27A(\mu K)^{-1/4}\,\text{eV}, \tag{48}$$

where A is the excited state slope in Ry$/a_0$, μ is the effective mass of the oscillator in units of the electron mass, and K is the ground-state force constant in Ry$/a_0^2$. Properly, one should use not only the reduced mass of the two F atoms A and B but include a small correction from the ions $C, D, \cdots, H$ which relax. However this last correction is rather difficult to calculate and is not warranted because of the various approximations that we have made so far in our calculations. So we take

$$\mu = 9.5 m_e \times 1837,$$

where the electron mass, $m_e = 9.11\times10^{-28}$ g. From the Born-Mayer curve in Fig. 5, we get $K=0.1$ Ry$/a_0^2$, $A=0.1$ Ry$/a_0$. Substituting these numbers in (48) we have

$$\Delta W = 0.58\ \text{eV} \tag{49}$$

as compared to the experimental value of 0.95 eV found by Delbecq *et al.*[16] So the calculated value of the half-width is about a factor of 2 less than experiment. An improved electronic energy calculation would lead to a deeper potential well for the Σ_u state implying an increase in K, while the Σ_g state would get steeper leading to an increase in A. These two consequences are opposite in their influence on ΔW but perhaps their combined effect would lead to better agreement with experiment. Another quantity that can be derived from Fig. 5 from the ground-state curve is the half-width of the lowest vibrational state. One can deduce the following expression for this latter half-width, namely

$$(\Delta R)_{1/2} = (0.996)(\mu K)^{-1/4} a_0. \tag{50}$$

Using the values of μ and K for the Born-Mayer curve

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[16] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).

[17] See, for example, D. L. Dexter in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353.

we get $(\Delta R)_{1/2}=0.015a_0$. The Pauling curves in Fig. 5 yield almost exactly the same values for ΔW and $(\Delta R)_{1/2}$ as the Born-Mayer curves. This small value of $(\Delta R)_{1/2}$ assures us that the actual inter-nuclear distance in the F_2^- molecule is always well within the region in which our calculation is valid.

With the wave functions that we have obtained for the V_k center, we can make an approximate calculation of the hyperfine coupling constants between the unpaired electron spin and the F^{19} nucleus. The Hamiltonian describing the magnetic hyperfine interaction between a nucleus and the spins of the orbital electrons is given by

$$\mathcal{H}=\mathcal{H}_{\text{dip}}+\mathcal{H}_F, \tag{51}$$

where

$$\mathcal{H}_{\text{dip}}=\frac{2\mu_N\mu_B}{I}\sum_i\left[\frac{\mathbf{S}_i\cdot\mathbf{I}}{r_i^3}+\frac{3(\mathbf{S}_i\cdot\mathbf{r}_i)(\mathbf{I}\cdot\mathbf{r}_i)}{r_i^5}\right] \tag{52a}$$

and

$$\mathcal{H}_F=(16\pi/3)(\mu_N\mu_B/I)\textstyle\sum_i \mathbf{S}_i\cdot\mathbf{I}\delta(\mathbf{r}_i). \tag{52b}$$

In Eqs. (52), μ_N and $\mathbf{I}$ are, respectively, the magnetic moment and spin of the nucleus, μ_B is the Bohr magneton, $\mathbf{S}_i$ and $\mathbf{r}_i$ are, respectively, the spin and position vectors of the ith electron. The summation in i runs over all the electron spins in the atomic or molecular system under consideration. When we have a system with one unpaired electron and the wave functions for the various electronic states of the system are orthogonal we can drop the summation over i in Eqs. (52a) and (52b) and take expectation values over the orbital corresponding to the single unpaired electron. However, when the wave function for the orbital of the unpaired electron is not orthogonal to the wave functions for other states one has to take the expectation values of the summations in (52a) and (52b) over the entire determinantal wave function involving both the outer unpaired electronic state and all other paired states of the molecule. It can be shown[18] however, that in such cases, one can simplify the calculation by making the unpaired electron wave function orthogonal to the wave functions for the paired states by the Schmidt orthogonalization procedure. One then has to take the expectation value of only one term out of the summations in (52a) and (52b) over the orthogonalized wave function. For the ground state Σ_u of the hole, the unpaired electron will be in a σ_u state. The orthogonalized wave function for the unpaired electron will therefore be of the form:

$$\psi=\frac{\psi_u-S_1(\psi_{1SA}+\psi_{1SB})-S_2(\psi_{2SA}+\psi_{2SB})}{N[1+2S_1^2\langle\psi_{1SA}|\psi_{1SB}\rangle+2S_2^2\langle\psi_{2SA}|\psi_{2SB}\rangle+4S_1S_2\langle\psi_{1SA}|\psi_{2SB}\rangle]^{1/2}}, \tag{53}$$

where

$$S_1=\langle\psi_u|\psi_{1SA}\rangle=-\langle\psi_u|\psi_{1SB}\rangle,$$
$$S_2=\langle\psi_u|\psi_{2SA}\rangle=-\langle\psi_u|\psi_{2SB}\rangle,$$
$$N^2=\langle\psi_u|\psi_u\rangle.$$

The overlap integrals $\langle\psi_{1SA}|\psi_{1SB}\rangle$, $\langle\psi_{1SA}|\psi_{2SB}\rangle$, and $\langle\psi_{2SA}|\psi_{2SB}\rangle$ are all one order of magnitude less than the overlap integrals S_1 and S_2, so we shall neglect them. Using Eq. (53) for the wave function ψ of the unpaired electron and Eq. (52a) for $\mathcal{H}_{\text{dip}}$, we obtain Eq. (54) for the hyperfine constant "b". Since we want to express "b" in Oersteds we have divided the hyperfine constant in energy units (ergs) by $2\mu_B$.

$$\begin{aligned}b=(3\mu_N/2IN^2)[&\langle\psi_u|0|\psi_u\rangle+S_1^2\langle\psi_{1SA}|0|\psi_{1SA}\rangle\\&+S_2^2\langle\psi_{2SA}|0|\psi_{2SA}\rangle-2S_1\langle\psi_u|0|\psi_{1SA}\rangle\\&-2S_2\langle\psi_u|0|\psi_{2SA}\rangle+2S_1S_2\langle\psi_{1SA}|0|\psi_{2SA}\rangle],\end{aligned} \tag{54}$$

with

$$0=(3\cos^2\theta_A-1)/r_A^3,$$

where r_A and θ_A refer to the polar coordinates of the electron with respect to A and with the AB direction as the Z axis. Equation (54) is approximate because a number of cross terms, involving $1S$ and $2S$ orbitals on atom B have been dropped. These terms are three orders of magnitude less than the leading term $\langle\psi_u|0|\psi_u\rangle$. Furthermore it is clear that the second, third, and sixth terms in (54) are identically zero. The fourth and fifth terms are two orders of magnitude smaller than the leading term. Therefore we can write, using (38) and (39),

$$\begin{aligned}b=(3\mu_N/2IN^2)[\sum_{ij} d_id_j\{&\langle\phi_{iA}|0|\phi_{jA}\rangle\\&+\langle\phi_{iA}|0|\phi_{jB}\rangle+\langle\phi_{iB}|0|\phi_{jA}\rangle+\langle\phi_{iB}|0|\phi_{jB}\rangle\}].\end{aligned} \tag{55}$$

In Eq. (55) the fourth term in brackets is two orders of magnitude smaller than the contribution from the first term while the second and third terms are each more than one order of magnitude smaller. Also, when either i or j is three or four, the contribution to the first term is identically zero. We thus have finally,

$$\begin{aligned}b=(6\mu_N/5IN^2)[&d_1^2\langle\phi_{1A}|r_A^{-3}|\phi_{1A}\rangle+d_2^2\langle\phi_{2A}|r_A^{-3}|\phi_{2A}\rangle\\&+2d_1d_2\langle\phi_{1A}|r_A^{-3}|\phi_{2A}\rangle].\end{aligned} \tag{56}$$

Using Eq. (39) for ϕ_{1A} and ϕ_{2A} we then obtain for b the value 747.3 Oe for both the Pauling and Born-Mayer approximations. More than 99% of the contribution to b comes from the first term in (56). Since our wave functions were tabulated for the points listed in Table VIII, we had to interpolate the coefficients d_i in Eq. (55) at R equal to $4.72a_0$. The calculated value

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[18] See, for example, B. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957); W. Blumberg and T. P. Das, *ibid.* **110**, 647 (1959).

TABLE IX. Contributions from the various terms in Eq. (57) to the isotropic hyperfine interaction constant for F^{19} nucleus in the V_k center. The wave function densities are in units of a_0^{-3} and the contributions to a_F in Oe.

Term in Eq. (57)	Wave function density	Contribution to hyperfine constant a_F
First	0.00012	0.175
Second	0.00684	10.317
Third	0.00604	9.099
Fourth	−0.00178	−2.679
Fifth	−0.00167	−2.516
Sixth	0.01288	19.384
Total	0.02243	33.780

of the hyperfine constant b is in fair agreement, certainly in much better agreement, with experiment than the optical absorption frequency and width. The experimental value of b is not known unambiguously[3] because it depends on the sign of a which is not known. If the sign of a is assumed negative, the experimental value of b would be 946 Oe while for a positive the value would be 828 Oe. The hyperfine constant a is given by

$$a=a_F-(b/3)\,, \tag{57}$$

where

$$a_F=(8\pi\mu_N/3IN^2)[\psi_u^2(A)+S_1^2\psi_{1SA}^2(A)+S_2^2\psi_{2SA}^2(A)-2S_1\psi_u(A)\psi_{1S}(A)-2S_2\psi_u(A)\psi_{2S}(A)+2S_1S_2\psi_{1S}(A)\psi_{2S}(A)].$$

The term a_F arises from the Fermi contact term $\mathcal{H}_F$ in the Hamiltonian and $-b/3$ from $\mathcal{H}_{\text{dip}}$. In Eq. (57) we have neglected all the terms that involve $\psi_{1SB}(A)$ and $\psi_{2SB}(A)$. We have done this because the terms involving $\psi_{1SB}(A)$ and $\psi_{2SB}(A)$ are an order of magnitude smaller than the smallest of the terms in Eq. (54). This approximation is in line with our assumption concerning the smallness of the overlaps between the $1S$ and $2S$ orbitals about the two centers. To emphasize the importance of the overlap terms which may also be referred to as the Pauli correlation terms,[19] we have tabulated in Table IX the values of the various terms in the brackets of Eq. (57) in units of a_0^{-3} as well as the value of a_F in Oersteds for $R=4.72a_0$, the equilibrium distances for both the Pauling and Born-Mayer cases.

Combining a_F and $-b/3$ we get for a the value -215.3 Oe. It appears that the constant b is in much better agreement with experiment than the costant a. The reason for this can be gauged by examining Table IX. From Table IX it appears that the major contribution to a comes from the second, third, and sixth terms in Eq. (57). All these terms depend bilinearly on the overlap integrals S_1 and S_2. A stronger conjugation between the two ions A and B, as expected from earlier considerations of the optical data, would reduce the distance corresponding to the minimum in the total energy curve in Fig. 4 and would therefore increase S_1 and S_2 significantly. Such an increase would enhance a_F and therefore cause a greater cancellation between a_F and $-b/3$ leading to a smaller theoretical value of a. The value of b on the other hand, as seen from Eq. (56) does not depend sensitively on R and should therefore be relatively unaffected by a stronger conjugation. This stronger conjugation would also make the electronic energy curve deeper than the lattice energy curve and therefore make the properties of the V_k center less sensitively independent on the lattice potential. Evidence that this is the case has been obtained by Twidell and Hayes[20] in recent work on CaF_2. It should be mentioned here that in addition to the Pauli correlation effect there will be a contribution to a_F from the exchange polarization effect[21] which arises out of the difference in the potentials experienced by electrons in the two spin states of the $1S$ and $2S$ shells. For an order of magnitude estimate of the exchange polarization one could use as a criterion the results from the nitrogen atom. Thus, noting that there are three unpaired $2p$ electrons in the nitrogen atom as compared to approximately one-half of a $2p$ electron per fluorine atom in the present case, one would expect the exchange polarization contribution to a to be about a sixth of the 10 Mc result found for the nitrogen atom. This would correspond to only about 0.25 Oe. While this result is probably an underestimate because the $1S$ and $2S$ wave functions in fluorine atom are more strongly bound than in nitrogen, it is however clear that a consideration of exchange polarization effect alone cannot explain the difference between our calculated values of a and experiment.

VI. CONCLUSION

From the calculations in the previous sections it appears that both the distortion of the lattice around the V_k center and the electronic binding of the σ electrons play important roles in determining the properties of the V_k center. The relative importance of the lattice and electronic energies would of course determine how the properties of the V_k center will vary from one crystal to another. Recent work of Twidell and Hayes,[20] however, indicates that the electronic properties of the V_k center in CaF_2 are almost the same as in LiF. This could be explained either if the electronic binding energy of the F_2^- molecule and the lattice energy are as comparable with each other in importance as in LiF or if the electronic binding energy has been underestimated by us and really involves a curve with a steeper minimum than we have calculated and the lattice effect is of minor importance in determining the equilibrium

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[19] A. Mukherjee and T. P. Das, Phys. Rev. **111**, 1479 (1958).

[20] A. Twidell and W. Hayes, Proc. Phys. Soc. (London) **A79**, 1295 (1962).

[21] V. Heine, Phys. Rev. **107**, 1002 (1957); T. P. Das and A. Mukherjee, J. Chem. Phys. **33**, 1808 (1960).

configuration. The latter possibility seems somewhat more probable, from our considerations of optical and hyperfine data in the last section. Also, we have made an approximate calculation of the energy of a trapped fluorine atom at a F^- site using the Born-Mayer approximation and allowing for displacements of the nearest neighbor Li^+ ions. The procedure employed in the calculations is analogous to that used by Dick[22] in recent work on alkali halide solid solutions. The energy of the trapped fluorine atom relative to the undisturbed crystal after the hole is removed is then found to be -0.441 Ry. Comparing this with the corresponding energy, -0.443 Ry for the V_k center for the Born-Mayer approximation, it is noticed that they are almost equal, although one would expect the V_k center to be lower in energy from a consideration of relative stability. This result seems to substantiate our conclusion that we have underestimated the electronic binding energy of the V_k center and should have a curve with a steeper minimum for the ground state in Figs. 4 and 5.

It would be useful to combine the results of a careful recalculation[23] of the electronic energy of the F_2^- molecule with the results of our lattice energy calculations in Sec. III to obtain a better total energy curve for the V_k center. It would also be interesting to find out if the recalculated wave function for the electronic σ_u state gives better agreement with the experimental value of the hyperfine constant a. It is encouraging that the results of the lattice energy calculations in Sec. III with two widely different repulsive energy formulas, such as the Born-Mayer and Pauling expressions (10) and (12), are not very different from one another and especially that the curves in Figs. 2 and 5 are so similar in shape. This is a very significant result because the effects of such widely different force laws have not been extensively compared in imperfect crystals. In future calculations one could therefore use either the Born-Mayer or Pauling repulsive formula with equal confidence.

One possible source of error in the calculation of the absorption energy should be mentioned here. When we consider the Hartree-Fock approximation for an atomic or molecular system, the net energy of the system is not just the sum of the one-electron energies for the individual states because then the Coulomb and exchange interaction energies get counted twice. One has therefore to subtract off the Coulomb and exchange energies from the sum of one-electron energies for the various states. The difference in E_u and E_g, which are tabulated in the last column of Table VII, is therefore likely to differ from the $\Sigma_u \rightarrow \Sigma_g$ excitation energy for the hole if there is appreciable difference in the exchange and Coulomb integrals occurring in the energy expressions for the σ_g and σ_u states of the electrons. We have not made any estimates of the correction due to this source of error because such a refinement would be inconsistent with the approximations we have already made in our electronic energy calculations in Sec. IV.

There is one other correction that has to be considered in any improved calculations in future. In Sec. IV and in Fig. 5 we have directly added the electronic and lattice energies associated with the V_k center which amounts to a neglect of self-consistency requirements. To be entirely self-consistent, one should consider the change in the potential seen by the electrons due to the distortion and polarization of the lattice. Correspondingly, one has also to consider the change in lattice energy produced by the redistribution of the electron density on the F_2^- molecule due to electronic binding. However, if it turns out in a refined calculation that the electronic binding is much more important than the lattice distortion in determining the equilibrium situation for the V_k center, one would expect the consistency condition involving interaction between lattice and electronic potentials to be correspondingly less important.

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[22] B. G. Dick and T. P. Das, Phys. Rev. **127**, 1053 (1962).

[23] See, for example, A Kolos and C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960); B. Ransil, Rev. Mod. Phys. **32**, 245 (1962). Such calculations are already in progress at Argonne National Laboratory (A. C. Wahl and T. L. Gilbert, private communication).