(1) An effort should be made to correlate dielectric and internal friction losses in quartz by making both types of loss measurements on the same sample.

(2) Possibly placing the crystal in a strong electric field in the optic axis direction at elevated temperatures, would flush out the impurities responsible for the relaxation peak. Appropriate analyses should be made before and after this experiment.

(3) If a particular impurity were suspected of causing the relaxation peak, possibly the height of the peak could be increased by diffusing in the impurity, again with a high field at elevated temperatures.

ACKNOWLEDGMENTS

The author thanks Dr. R. K. Cook for suggesting this investigation and for many helpful discussions. He also thanks Mr. Martin Greenspan and Professor Karl F. Herzfeld for numerous enlightening discussions.

PHYSICAL REVIEW VOLUME 105, NUMBER 4 FEBRUARY 15, 1957

Approximate Wave Functions for the *F* Center, and Their Application to the Electron Spin Resonance Problem*†

BARRY S. GOURARY AND FRANK J. ADRIAN
Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland

(Received August 23, 1956)

The vacancy model of the *F* center is treated by a simplified Hartree method. The ions are treated as point charges, and the potential of the lattice is computed. The simplified Hartree equation is solved variationally, and the electronic polarization is computed by a self-consistent method which takes account of the screening action of the *F*-center electron. The lattice distortion is then calculated. The resulting energies are compared with the available optical data. The agreement is good.

The hyperfine structure of the *F* center is computed, using a determinantal wave function. The predicted hyperfine splittings agree fairly well with the experimental results of Lord and Jen on the resolved hyperfine structure of LiF.

The effects of exchange and overlap are also discussed.

1. INTRODUCTION

THE study of the *F* center has long occupied a central place in the investigation of the imperfection-determined properties of crystalline solids. An extensive survey of the theoretical and experimental work has been given by Seitz.[1,2] There are two well-known models of the *F* center. The de Boer or vacancy model views the *F* center as consisting of an electron trapped in the field of a negative ion vacancy. The interstitial model, on the other hand, assumes the *F*-center to consist of an electron trapped in the field of an interstitial ion; it is thus an interstitial atom. Thus the interstitial model considers the *F* center to be a primary imperfection while the vacancy model represents it as the stable union of two primary imperfections.[3] Consequently, the understanding of the nature and properties of the *F* center is an essential step in the study of the primary imperfections and their interactions.

The purpose of this paper is to study the vacancy model of the *F* center. A complete solution of the problem of the stationary states of the *F* center at absolute zero requires a careful consideration of a variety of physical factors. The proper tool for such an investigation is a generalized configuration interaction calculation which takes account also of the motion of the ions. Such a calculation is too difficult for present day techniques. We have attempted to set up a Hartree-Fock equation for the *F*-center orbital, taking account of possible displacements of the ions near the vacancy. The complete solution of this problem is still some way off, and it seems reasonable to take stock of the physical results presently available by a simplified method. We shall, therefore, proceed to set up a simplified Hartree equation for the *F*-center orbital, neglecting the effects of the finite size of the ion cores and the effects of exchange. We shall solve this equation by a variational method, and compute the effects of electronic polarization and ion displacement. We shall then set up a method for the calculation of the hyperfine structure, using a determinantal wave function. This will give us a set of theoretical transition energies and hyperfine interactions which we shall proceed to compare with the available experimental

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* Work supported by the Bureau of Ordnance, Department of the Navy.

† Some of the results presented here have been reported at the June, 1956 meeting of the American Physical Society in New Haven, Connecticut.

[1] F. Seitz, Revs. Modern Phys. 18, 384 (1946).

[2] F. Seitz, Revs. Modern Phys. 26, 7 (1954).

[3] We shall follow the usage of F. Seitz [*Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), p. 3] in considering phonons, electrons and holes, excitons, vacant lattice sites and interstitial atoms, foreign atoms, and dislocations as the primary imperfections.

data. We shall then turn to a discussion of the exchange and overlap effects, and the influence they are likely to have on the wave function. From this discussion it will become clear which of our results can be expected to change rather little under the action of exchange and overlap.

2. SIMPLIFIED HARTREE EQUATION

Consider an alkali halide crystal with one *F* center. It has N nuclei, $n-1$ core electrons, and one extra electron, which we shall call the nth electron. By a core electron we mean any electron which is attached to the complete shell of a positive or negative ion. Thus this name includes the electrons belonging to the complete valence shell of a negative ion. For the purposes of Secs. 2, 3, and 4, the core electrons will be considered as point charges. Thus the nth electron may be considered to have a potential energy of the form (a is the nearest neighbor distance)

$$V_L(\mathbf{r})=\sum_{x_i,y_i,z_i=-\infty}^{+\infty}{}' (-1)^{x_i+y_i+z_i} \times[(x-ax_i)^2+(y-ay_i)^2+(z-az_i)^2]^{-\frac{1}{2}}. \quad (1)$$

(We use Hartree atomic units throughout the paper.) The prime on the summation sign means that the point (0,0,0) is omitted. We have assumed that the ion cores were not polarized. This assumption will be shown to be self-consistent in Sec. 3, where we shall evaluate the electric field acting on each ion, and will compute the contribution of the polarization effect to the binding energy. Our present problem is, therefore, the determination of the orbital $\psi_n(\mathbf{r})$ for the *F*-center electron which minimizes the functional[4]

$$E_F{}^{SH}=\int\psi_n(\mathbf{r})[-\tfrac{1}{2}\nabla^2+V_L(\mathbf{r})]\psi_n(\mathbf{r})d\tau, \quad (2)$$

subject to

$$\int[\psi_n(\mathbf{r})]^2d\tau=1.$$

Throughout this section, the lattice will be assumed to be undistorted; that is, the ions will be assumed to occupy the same positions they would occupy in the perfect lattice at $T=0$. Later we shall compute the lattice distortion effects by a perturbation method, permitting only the nearest neighbor ions to move. It will be seen that the distortion effect is small in this approximation.

TABLE I. Reduced form of the spherical harmonics of order l.

Order l	Reduced form
0	$\Gamma_1{}^e$
1	$\Gamma_4{}^o$
2	$\Gamma_3{}^e+\Gamma_5{}^e$
3	$\Gamma_2{}^o+\Gamma_4{}^o+\Gamma_5{}^o$
4	$\Gamma_1{}^e+\Gamma_3{}^e+\Gamma_4{}^e+\Gamma_5{}^e$
5	$\Gamma_3{}^o+2\Gamma_4{}^o+\Gamma_5{}^o$
6	$\Gamma_1{}^e+\Gamma_2{}^e+\Gamma_3{}^e+\Gamma_4{}^e+2\Gamma_5{}^e$
7	$\Gamma_2{}^o+\Gamma_3{}^o+2\Gamma_4{}^o+2\Gamma_5{}^o$
8	$\Gamma_1{}^e+2\Gamma_3{}^e+2\Gamma_4{}^e+2\Gamma_5{}^e$

The usual group theoretical considerations lead one to the conclusion that $V_L(\mathbf{r})$ must belong to the $\Gamma_1{}^e$ (totally symmetric) irreducible representation of the cubic group.[5] Let us denote the linear combinations of the spherical harmonics which belong to a given irreducible representation $\Gamma_i{}^p$ of the cubic group O_h by the symbol

$$Q(\Gamma_i{}^p,l,\mu_l|\theta,\varphi)=\sum_{m=-l}^{+l}C(\Gamma_i{}^p,l,\mu_l;m)Y_{lm}(\theta,\varphi). \quad (3)$$

Here μ_l is an index used to differentiate among several Q's of the same l, belonging to the same $\Gamma_i{}^p$. Thus the maximum possible range of μ_l is $0\leq\mu_l\leq 2l$. Following Bethe and Von der Lage, we shall call the Q's Kubic Harmonics.[6] These Kubic Harmonics are orthonormal, that is

$$\int d\Omega Q^*(\Gamma_i,l,\mu_l|\theta,\varphi)Q(\Gamma_j,l',\mu_{l'}'|\theta,\varphi) =\delta_{\Gamma_i,\Gamma_j}\delta_{l,l'}\delta_{\mu_l,\mu_{l'}'}. \quad (4)$$

Bethe has reduced the spherical harmonics according to the several irreducible representations of the cubic group.[5] He finds that the spherical harmonics of order l belong to the following irreducible representations (Table I). (We have extended his table.) We have appended the superscripts e for even and o for odd, where even and odd retain their usual spectroscopic significance. It follows that

$$V_L(\mathbf{r})=V_{00}(r)Q(\Gamma_1{}^e,0,0|\theta,\varphi)+V_{40}(r)Q(\Gamma_1{}^e,4,0|\theta,\varphi) +V_{60}(r)Q(\Gamma_1{}^e,6,0|\theta,\varphi) +V_{80}(r)Q(\Gamma_1{}^e,8,0|\theta,\varphi)+\cdots. \quad (5)$$

The individual $V_{l,\mu_l}(r)$'s are determined by expanding each term in the potential about the center of the vacancy. Since the potential energy $V_L(\mathbf{r})$ is invariant under the full cubic group, it is clear that every solution of our equation must belong to an irreducible representation of the cubic group. Thus we must have[7]

$$\psi(\Gamma_i{}^p|\mathbf{r})=\sum_{l=0}^{\infty}\sum_{\mu_l}R(\Gamma_i{}^p,l,\mu_l|r)Q(\Gamma_i{}^p,l,\mu_l|\theta,\varphi). \quad (6)$$

In practice it is necessary to terminate the series for $\psi(\Gamma_i{}^p|\mathbf{r})$ after one or two terms for the variational treatment. The higher terms may be added later by

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[4] The wave function ψ_n can be taken real because the Hamiltonian is real in our problem.

[5] We shall denote the irreducible representations of the full cubic group O_h by $\Gamma_i{}^p$ following H. A. Bethe, Ann. Physik **3**, 133 (1929). We have appended the superscript p which stands for "odd" or "even."

[6] H. A. Bethe and F. C. Von der Lage, Phys. Rev. **71**, 612 (1947). It should be noted that our normalization differs from theirs.

[7] For all but the two one-dimensional representations Γ_1 and Γ_2, two or three wave functions belong to the same representation. In the interests of simplicity of notation, we have omitted the index which differentiates the several wave functions belonging to the same representation.

TABLE II. Theoretical ground state energies and parameter values for six alkali halides with the NaCl structure. All quantities are in Hartree atomic units; i.e., the unit of energy is two Rydbergs, and the unit of length is the Bohr radius.

Substance	Interionic distance a	Type I ξ	Type I $E(\Gamma_1^e)$	Type II ξ	Type II η	Type II $E(\Gamma_1^e)$	Type III ξ	Type III η	Type III $E(\Gamma_1^e)$
LiF	3.80	1.71	−0.267	2.38	3.50	−0.257	2.26	1.86	−0.297
NaF	4.37	1.81	−0.244	2.41	3.68	−0.244	2.30	2.06	−0.271
LiCl	4.86	1.87	−0.227	2.43	3.82	−0.232	2.34	2.27	−0.253
NaCl	5.31	1.92	−0.214	2.45	3.96	−0.221	2.36	2.38	−0.238
KCl	5.93	1.99	−0.198	2.47	4.11	−0.207	2.37	2.44	−0.219
RbBr	6.48	2.04	−0.186	2.49	4.26	−0.195	2.40	2.62	−0.205

perturbation theory methods, provided that they are small.

Thus far our efforts have been directed chiefly towards the determination of $R(\Gamma_1^e,0,0|r)$ and $R(\Gamma_4^o,1,0|r)$. These are the familiar s and p states of previous treatments.[1,2] We have tried three types of wave functions for the ground state, which has Γ_1^e symmetry; and three corresponding types of wave functions for the first state to which the electron may be excited by electric dipole radiation, namely, a state with Γ_4^o symmetry. The several trial functions and the corresponding energies are listed below. Later we shall give heuristic reasons for choosing these particular trial functions.

Ground-State Wave Function

$$Q(\Gamma_1^e,0,0|\theta,\varphi)=(1/4\pi)^{\frac{1}{2}},$$

$$\text{I.}\qquad R(\Gamma_1^e,0,0|r)=2(\xi/a)^{\frac{3}{2}}\exp(-\xi r/a);$$

$$\text{II.}\qquad \begin{aligned} R(\Gamma_1^e,0,0|r)&=Aj_0(\xi r/a)\exp(-\eta), & r<a\\ &=Aj_0(\xi)\exp(-\eta r/a), & r>a \end{aligned}\qquad (7)$$

where

$$\eta=1-\xi\cot\xi;$$

$$\text{III.}\qquad \begin{aligned} R(\Gamma_1^e,0,0|r)&=Aj_0(\xi r/a)k_0(\eta), & r<a\\ &=Aj_0(\xi)k_0(\eta r/a), & r>a \end{aligned}$$

where

$$\eta=-\xi\cot\xi,\quad\text{and}\quad k_0(x)=(1/x)\exp(-x).$$

Here the ξ's are variational parameters and the η's are determined by the condition that both the wave function and its radial derivative have to be continuous at $r=a$. A is a normalizing constant, and $j_n(x)$ is the spherical Bessel function of order n.[8]

The corresponding energy functionals are[9]

$$\text{I.}\ E_F{}^{SH}=\xi^2/2a^2-(1/a)\{\alpha_M-\exp(-2\xi)\sum_{z_i\geq y_i\geq x_i\geq 0}{}' h_i(-1)^{x_i+y_i+z_i+1}(1+\rho_i\xi)(1/\rho_i)\exp[-2\xi(\rho_i-1)]\};$$
$$h_i\equiv(3!/n_i!)2^{3-0_i};\quad \rho_i=(x_i^2+y_i^2+z_i^2)^{\frac{1}{2}},\qquad (8)$$

where n_i is the number of times any given number occurs in the triplet (x_i,y_i,z_i), and 0_i is the number of times that zero occurs in this triplet. $\alpha_M=1.747558$ is the Madelung constant for the NaCl lattice. The prime on the summation sign means that the point (0,0,0) is omitted.

$$\text{II.}\ E_F{}^{SH}=(1/2a^2)\{\xi^2-(G(\xi)/\eta)[\eta^2-3\eta-\tfrac{1}{2}+\xi^2(1-1/\eta+\tfrac{1}{2}\eta^{-2})]\}$$
$$-(1/a)\{\alpha_M-\tfrac{1}{2}\eta^{-3}G(\xi)\sum_{z_i\geq y_i\geq x_i\geq 0}{}' h_i(-1)^{x_i+y_i+z_i+1}(1+\eta\rho_i)(1/\rho_i)\exp[-2\eta(\rho_i-1)]\},\qquad (9)$$

where

$$[G(\xi)]^{-1}=(1-(1/2\xi)\sin 2\xi)(\sin\xi)^{-2}+(1/\eta)(1+1/\eta+\tfrac{1}{2}\eta^{-2}).$$

$$\text{III.}\ E_F{}^{SH}=(1/2a^2)\xi^2\eta(1+\eta)^{-1}-(1/a)[\alpha_M-2\eta\xi^2(1+\eta)^{-1}(\xi^2+\eta^2)^{-1}\sum_{z_i\geq y_i\geq x_i\geq 0}{}' h_i(-1)^{x_i+y_i+z_i+1}$$
$$\times\{(2\eta\rho_i)^{-1}\exp[-2\eta(\rho_i-1)]+\exp(2\eta)\,\mathrm{Ei}(-2\eta\rho_i)\}].\qquad (10)$$

The corresponding energies and parameters are tabulated in Table II. We have denoted the stationary value of the $E_F{}^{SH}$ functional for the ground state by $E(\Gamma_1^e)$. About three to eight terms in the series for $E_F{}^{SH}$ actually contributed. It is clear that the type III wave function gives consistently lower energies for the ground state, and it is therefore the better wave function.

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[8] See, for example, P. M. Morse, *Vibration and Sound* (McGraw-Hill Book Company, Inc., New York, 1948), second edition, p. 316.

[9] These expressions for $E_F{}^{SH}$ are easily obtained if one evaluates the expectation value of $V_L(\mathbf{r})$, as given in (1), expanding each term in (1) about the center of the vacancy in a series of spherical harmonics.

First Excited State Wave Functions

$$Q(\Gamma_4{}^o,1,0|\theta,\varphi)=(3/4\pi)^{\frac{1}{2}}\cos\theta,$$

I. $$R(\Gamma_4{}^o,1,0|r)=(2/\sqrt{3})(\xi'/a)^{5/2}r\exp(-\xi'r/a).$$

II. $$R(\Gamma_4{}^o,1,0|r)=A'j_1(\xi'r/a)\exp(-\eta'),\quad r<a$$
$$=A'j_1(\xi')(r/a)\exp(-\eta'r/a),\quad r>a \qquad (11)$$

where

$$\eta'=3-\xi'^2(1-\xi'\cot\xi')^{-1}.$$

III. $$R(\Gamma_4{}^o,1,0|r)=A'j_1(\xi'r/a)k_1(\eta'),\quad r<a$$
$$=A'j_1(\xi')k_1(\eta'r/a),\quad r>a,$$

where

$$\eta'=f(\xi')+\{[f(\xi')]^2+2f(\xi')\}^{\frac{1}{2}},$$
$$f(\xi')=\tfrac{1}{2}\xi'^2(\xi'\cot\xi'-1)^{-1},$$
$$k_1(x)=(1/x+1/x^2)\exp(-x).$$

The corresponding expressions for the energy functionals are

I. $$E_F{}^{SH}=\xi'^2/2a^2-(1/a)\{\alpha_M-\tfrac{1}{3}\sum_{z_i\geq y_i\geq x_i\geq 0}{}' h_i(-1)^{x_i+y_i+z_i+1}(1/\rho_i)\exp(-2\xi'\rho_i)$$
$$\times[3+(9/2)\xi'\rho_i+3(\xi'\rho_i)^2+(\xi'\rho_i)^3]\}. \qquad (12)$$

II. $$E_F{}^{SH}=(1/2a^2)\{\xi'^2-2G'(\xi')[(2\eta')^{-5}(\xi'^2+\eta'^2)((2\eta')^4+4(2\eta')^3+12(2\eta')^2+24(2\eta')+24)$$
$$-2(2\eta')^{-3}((2\eta')^3+3(2\eta')^2+6(2\eta')+6)]\}-(1/a)\{\alpha_M-\tfrac{1}{2}\eta'^{-5}G'(\xi')\sum_{z_i\geq y_i\geq x_i\geq 0}{}' h_i(-1)^{x_i+y_i+z_i+1}$$
$$\times(1/\rho_i)\exp[-2\eta'(\rho_i-1)][3+(9/2)\eta'\rho_i+3(\eta'\rho_i)^2+(\eta'\rho_i)^3]\}, \qquad (13)$$
$$[G'(\xi')]^{-1}=1-j_0(\xi')j_2(\xi')[j_1(\xi')]^{-2}+2(2\eta')^{-5}[(2\eta')^4+4(2\eta')^3+12(2\eta')^2+24(2\eta')+24].$$

III. $$E_F{}^{SH}=(1/2a^2)[\xi'^2-G'(\xi')\eta'^{-2}(1+\eta'/2)(\xi'^2+\eta'^2)]-(1/a)\{\alpha_M-G'(\xi')\sum_{z_i\geq y_i\geq x_i\geq 0}{}' h_i(-1)^{x_i+y_i+z_i+1}$$
$$\times\{\exp(2\eta')[-E_i(-2\eta'\rho_i)]-\tfrac{1}{2}(\eta'\rho_i)^{-2}(\eta'\rho_i-1)\exp[-2\eta'(\rho_i-1)]\}\}, \qquad (14)$$
$$[G'(\xi')]^{-1}=\eta'^{-2}[1+(\eta'/2)]+(1+1/\eta')^2\{[\xi'j_1(\xi')]^{-2}\{\tfrac{1}{2}(1+(2\xi')^{-1}\sin 2\xi')-(j_0(\xi'))^2]\}.$$

About five to sixteen terms in the series actually contribute. The resulting energies and parameters are summarized in Table III. Here type II seems to be a slightly better wave function.

The reasons for choosing trial wave functions of these three types are the following:

Type I. These are hydrogenic functions. They are chosen in accordance with the conventional picture that the potential of the negative ion vacancy is qualitatively similar to a Coulomb potential.

Type II. These are composite functions. They are chosen after an examination of $V_{00}(r)$. This is the only term in the potential energy capable of affecting a trial function which is spherically symmetric. From Fig. 1, it is clear that the potential is constant for $r<a$. For $r>a$, it has a Coulomb-like behavior for a short stretch, and then it breaks into a series of violent oscillations as more and more terms in the sum undergo a series reversal. In the region $r<a$, the solution of the wave equation is therefore of the form $j_n(\xi r/a)$. Outside this region we approximate the wave function by a hydrogenic wave function which would have been appropriate if the potential were actually Coulomb-like for *all* values of $r>a$.

Type III. These are composite wave functions appropriate to a region where for $r<a$ the potential has a constant negative value while for $r>a$ it has a large constant positive value. Thus for $r<a$ the appropriate solution is $j_n(\xi r/a)$ while for $r>a$ the solution takes the form $k_n(\eta r/a)$, where $k_n(x)$ is the modified spherical Hankel function of order n. This choice makes sense if we suspect that the actual energy levels we are computing are so low that the oscillations of $V_{00}(r)$ are of little consequence. Thus this approximation is better for the ground state than for the excited states.

Before we go on to discuss the several correction

TABLE III. Theoretical energy and parameter values for the first excited state. All quantities are in Hartree atomic units.

Substance	Interionic distance a	Type I ξ'	Type I $E(\Gamma_4{}^o)$	Type II ξ'	Type II η'	Type II $E(\Gamma_4{}^o)$	Type III ξ'	Type III η'	Type III $E(\Gamma_4{}^o)$
LiF	3.80	2.00	−0.138	3.03	2.67	−0.150	3.24	0.763	−0.147
NaF	4.37	2.20	−0.137	3.14	3.00	−0.152	3.29	1.02	−0.150
LiCl	4.86	2.30	−0.135	3.21	3.23	−0.152	3.33	1.22	−0.151
NaCl	5.31	2.40	−0.133	3.26	3.40	−0.150	3.36	1.38	−0.149
KCl	5.93	2.50	−0.129	3.32	3.63	−0.146	3.40	1.59	−0.145
RbBr	6.48	2.60	−0.126	3.37	3.84	−0.142	3.40	1.59	−0.141

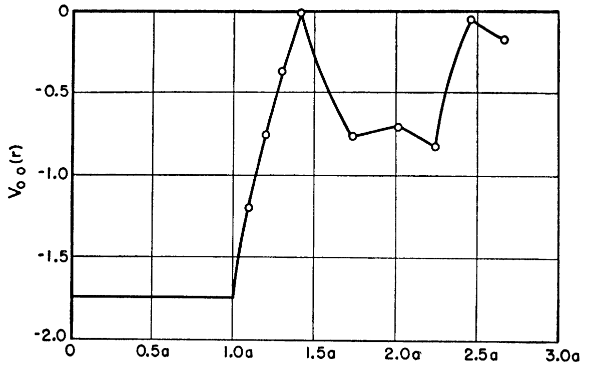

FIG. 1. Spherically symmetric part of the potential energy of the F-center electron, $V_{00}(r)$, as a function of the distance r from the center of the vacancy. r is in Bohr radii; $V_{00}(r)$ is in arbitrary units.

terms, which will be shown to be small, it will be advisable to compare our results with the available experimental data; namely, the peak of the F band at $T=0$. In this comparison, we shall use the energy obtained with a wave function of type III for the ground state and of type II for the first excited state. We shall also list the values of the oscillator strength for the transition under consideration, computed with the aid of the above wave functions. The results are listed in Table IV and a comparison with experiment is made in Fig. 2. We can thus interpolate graphically to find the theoretical value of the F-band energy for those intermediate values of a which correspond to substances measured at very low temperatures by Mollwo[10] and by Russell and Klick.[11] The results of this interpolation are seen to agree with the experimental values to within 15%. It is interesting to note that in this approximation our theory states that the F-band energy is a function of the interionic distance a only. This is in substantial agreement with Ivey's empirical formulas.[12]

We have estimated the magnitude of $R(\Gamma_1{}^e,4,0|r)$ by a variational method. While this estimate is not completely reliable, it would appear that the high angular momentum wave function is so diffuse that its overlap with $R(\Gamma_1{}^e,0,0|r)$ is very small. Consequently, very little g state would seem to be mixed into the ground state. It should be noted, however, that the question of high angular momentum components is intimately tied up with exchange and overlap effects. We shall therefore postpone further discussion of this subject to Sec. 6.

TABLE IV. Theoretical F-band energies and oscillator strengths. All quantities are in Hartree atomic units.

Substance	Interionic distance a	Theoretical $E(\Gamma_4{}^o)-E(\Gamma_1{}^e)$	Oscillator strength
LiF	3.80	0.147	0.997
NaF	4.37	0.119	0.988
LiCl	4.86	0.101	0.967
NaCl	5.31	0.088	0.968
KCl	5.93	0.073	0.985
RbBr	6.48	0.063	0.971

3. POLARIZATION ENERGY

The polarizing forces acting on the core electrons near the F center can be divided into several classes. First, there are the forces acting on the core electrons of an ion placed on a lattice site in a perfect crystal. These have the point symmetry of the lattice. Their only appreciable contribution to the energy of the core electrons is a spherically symmetric one: they raise or lower the potential energy of the core electron by α_M/a. Their polarizing effects involve the admixture of states of much higher angular momentum, and therefore considerably higher energy. They are consequently negligible.

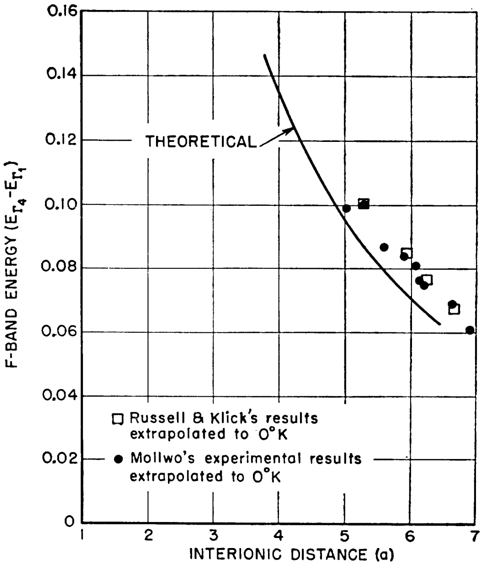

FIG. 2. F-band energies at 0°K for the alkali halides as a function of the interionic distance. All quantities are in Hartree atomic units.

The removal of a negative ion and its replacement by an electron introduces some new forces. The electronic cloud of the ion and the F-center electron overlap and exchange in a manner different from that in which the overlap and exchange between the two ionic cores took place. This phenomenon is appreciable only for the nearest neighbor alkali ions, and it can hardly affect their tightly bound core electrons. Its effects on the F-center electron may be more appreciable, and they will be discussed in Sec. 6.

The final and most important polarizing force is due to the relatively diffuse nature of the F-center electron cloud. Unlike the core electrons of a negative ion, an

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[10] E. Mollwo, Z. Physik **85**, 56 (1933).
[11] C. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).
[12] H. F. Ivey, Phys. Rev. **72**, 341 (1947).

appreciable portion of the electronic charge may be expected to be outside the sphere bounded by the nearest neighbor positive ions, and some of the charge will be even outside the larger sphere bounded by the next nearest neighbor ions. Thus an electric field must be acting at the center of every nearest and next nearest neighbor ion, tending to polarize it. In some previous treatments, this was taken into account by using the dielectric constant technique in the framework of the adiabatic approximation. This led to mathematical difficulties in the computation of the polarization throughout the crystal. The effect of the polarization of the distant parts of the medium was, of course, cancelled by the depolarizing influence of the *F*-center electron cloud, but both of these terms had to be computed in the course of the calculation. In a self-consistent treatment, on the other hand, this mathematical difficulty is avoided because only the net polarization energy must be computed, provided that one starts with appropriate initial wave functions.

We shall, therefore, compute the field at each of the nearest and next nearest neighbors, and then use the usual polarizability theory. This will give us the change in the energy of the *F*-center electron due to polarization. If the energy change is large, we must recompute the wave function. If it is small enough, we shall leave well enough alone.

The change in $V_L(\mathbf{r})$ will evidence itself in two different ways. First, there will be a change in $V_{00}(r)$ and also in the higher coefficients in the expansion of the potential. Secondly, there may appear some new terms in the potential, having a symmetry other than Γ_1^e. These new terms will belong to representations occurring in the reduced form of $\Gamma_i^p \times \Gamma_i^p$ if the *F*-center electron is in a state belonging to the Γ_i^p representation. Thus, for the ground state

$$\Gamma_1^e \times \Gamma_1^e = \Gamma_1^e \tag{15}$$

and no new terms appear. For the first excited state, on the other hand, we have

$$\Gamma_4^o \times \Gamma_4^o = \Gamma_1^e + \Gamma_3^e + \Gamma_4^e + \Gamma_5^e \tag{16}$$

and terms of different symmetry do appear. There is good reason to believe, however, that their effects are no more important than the effects of the changes in $V_{00}(r)$, and therefore we shall content ourselves with showing that the changes in $V_{00}(r)$ are small.

We shall estimate the polarization effects by first computing the polarizing charge q_s acting on the sth ion, and then employing Gauss' theorem. For the ground state, the spherically symmetric part of the polarizing charge density is

$$\delta(\mathbf{r}) - (1/4\pi)[R(\Gamma_1^e,0,0|r)]^2, \tag{17}$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac delta function, centered at the center of the vacancy. For the first excited state, it is

$$\delta(\mathbf{r}) - (1/4\pi)[R(\Gamma_4^o,1,0|r)]^2. \tag{18}$$

Thus the polarizing charge acting on the nearest neighbor cations in the ground state is

$$q_+ = \int_a^\infty [R(\Gamma_1^e,0,0|r)]^2 r^2 dr \tag{19}$$

and the charge acting on the next nearest neighbor anions is

$$q_- = \int_{\sqrt{2}a}^\infty [R(\Gamma_1^e,0,0|r)]^2 r^2 dr. \tag{20}$$

Analogous expressions hold for the excited state, with $R(\Gamma_1^e,0,0|r)$ replaced by $R(\Gamma_4^o,1,0|r)$. In Table V below, we have listed the values of q_s, computed using a type III function for the ground state and a type II function for the first excited state.

The dipole induced on the sth ion is approximately

$$\alpha_s q_s / r_s^2 \tag{21}$$

and it points away from the vacancy in a radial direction. n_s such dipoles situated symmetrically about the vacancy produce a potential whose spherically symmetric component is

$$-n_s \alpha_s q_s / r_s^4 \quad \text{if} \quad r < r_s, \tag{22}$$

and zero otherwise. This leads to a change in the potential energy which may be written in the form

$$\epsilon_s = -n_s \alpha_s q_s^2 / r_s^4. \tag{23}$$

This contribution to the potential energy is tabulated in Table VI. ϵ_+ is the contribution to the energy from the six nearest neighbor cations, and ϵ_- is the contribution of the twelve next nearest neighbor anions. Other ions produce only negligible effects because q_s drops off very rapidly. Clearly the polarization effects are completely negligible for the ground state. For the first excited state, they are of the order of 3% or less, and they may be evaluated in first-order perturbation theory as was done above. For those alkali halides which have the more pronounced polarization effects, it may pay to examine more closely the nonspherical terms in the polarization energy of the first excited

TABLE V. The polarizing charge. These charges are expressed as multiples of the electronic charge.

Substance	Ground state		First excited state	
	$q_+(\Gamma_1^e)$	$q_-(\Gamma_1^e)$	$q_+(\Gamma_4^o)$	$q_-(\Gamma_4^o)$
LiF	0.209	0.045	0.493	0.165
NaF	0.181	0.033	0.416	0.110
LiCl	0.158	0.024	0.368	0.082
NaCl	0.147	0.020	0.335	0.065
KCl	0.141	0.019	0.296	0.048
RbBr	0.126	0.014	0.266	0.037

TABLE VI. The contributions to the electronic polarization energy of the six nearest neighbor cations ϵ_+, and of the next nearest neighbor anions ϵ_-. Energies are in Hartree atomic units.

Substance	Ground state ϵ_+	Ground state ϵ_-	First excited state ϵ_+	First excited state ϵ_-
LiF	−0.0003	−0.0002	−0.0014	−0.0025
NaF	−0.0007	−0.0001	−0.0036	−0.0006
LiCl	−0.0001	−0.0001	−0.0003	−0.0009
NaCl	−0.0002	−0.0000	−0.0011	−0.0004
KCl	−0.0006	−0.0000	−0.0025	−0.0001
RbBr	−0.0006	−0.0000	−0.0025	−0.0001

state. It may then also be necessary to take account of the interactions among the dipoles which tend to decrease the polarization energy.

While the polarization energy is negligible for the two states that we have considered, it is quite large if the F-center electron is ionized to the conduction band, because then its shielding effects are absent. Mott and Littleton[13] have computed this quantity for NaCl; they call this energy $\frac{1}{2}eV$, and give its value as -0.11 atomic units. The energy of the lowest level in the conduction band is given by Tibbs[14] as -0.02 atomic units for NaCl. Using our values for NaCl, we then have for the ground state energy of the F-center electron below the lowest conduction level the value 0.11 atomic units. For the first excited state, the value is 0.02 atomic units.

4. LATTICE DISTORTION EFFECTS

In this section we shall examine the effects of a lattice distortion in the vicinity of the F center on the wave function and energy levels of the F center. This is an effect which cannot be assumed to be negligible *a priori*, and one which is often responsible for the appearance of such physical phenomena as luminescence. In the present paper, we shall confine ourselves to a partial treatment of the problem; that is, we shall allow only the six ions closest to the vacancy to move radially. Clearly this is an oversimplication of a complex situation, and it can give us an approximate result at best.

If the nearest six alkali ions move radially into the vacancy by an amount (σa), where a is the interionic distance, then the corresponding six terms in the potential energy $V_L(\mathbf{r})$ change. The change in the expectation value of the potential energy is

$$-(6/a)\sigma(1-\sigma)^{-1}+24\pi\int_{a(1-\sigma)}^{\infty}[R(\Gamma_1{}^e,0,0|r)]^2 \times[a^{-1}(1-\sigma)^{-1}-(1/r)]r^2dr. \quad (24)$$

This kind of distortion also produces changes in the electrostatic interaction among the ions and in their core repulsions. For our purpose, it will be sufficiently accurate to represent the repulsive potential energy acting between the ions α and β by the expression[15]

$$br_{\alpha\beta}{}^{-\lambda}. \quad (25)$$

Then the change in the repulsive energy becomes

$$(\alpha_M/\lambda a)[(1+\sigma)^{-\lambda}-1] +(4\alpha_M/\lambda a)[(1+\sigma^2)^{-\lambda/2}-1]. \quad (26)$$

It remains to calculate the change in the electrostatic interaction caused by the distortion. In this connection, we must remember that if an ion in a perfect lattice is displaced from its equilibrium position by an amount σa, then the change in its energy is of order $(\sigma a)^4$. This is a change too small to be of concern to us. In our case, of course, the lattice is not perfect because five other ions move. The resulting change in the energy can be shown to be

$$\frac{6\sigma}{a(1-\sigma)}+\frac{12}{a}\left\{\frac{1}{\sqrt{2}(1-\sigma)}-\frac{2}{[1+(1-\sigma)^2]^{\frac{1}{2}}}\right\} +\frac{3}{a}\left[\frac{1}{2(1-\sigma)}-\frac{2}{2-\sigma}\right]+\frac{1}{a}[6\sqrt{2}+\tfrac{3}{2}]. \quad (27)$$

When computing this expression, one must remember to count the interactions between each pair of moving ions only once.

We can now expand the change in the energy as a power series in σ, retaining only terms of first and second order in σ. Thus,

$$\Delta E=C\sigma+\tfrac{1}{2}D\sigma^2 \quad (28)$$

and the total energy is $E_F{}^{SH}+\Delta E$.

Using a wave function of type I, we have

$$C=-(\alpha_M/a)+(6/a)e^{-2\xi}(1+2\xi+2\xi^2), \quad (29)$$

$$D=(6/a)(3/\sqrt{2}+\tfrac{1}{4})+(\alpha_M/a)(\lambda-3) +(12/a)e^{-2\xi}(1+2\xi+2\xi^2+2\xi^3). \quad (30)$$

With a type III wave function, we obtain

$$C=-\alpha_M/a+(6/a)(\eta+1)^{-1}\sin^2\xi, \quad (31)$$

$$D=(6/a)(3/\sqrt{2}+\tfrac{1}{4})+(\alpha_M/a)(\lambda-3)+(12/a)\sin^2\xi. \quad (32)$$

Differentiating with respect to σ and equating the derivative to zero, we obtain the following equations for the equilibrium values of the displacement and the energy change:

$$\sigma_0=-C/D, \quad (33)$$

$$(\Delta E)_0=-\tfrac{1}{2}D\sigma_0{}^2. \quad (34)$$

Table VII lists the values of σ_0 and $(\Delta E)_0$ for several alkali halides. Clearly both the displacement and $(\Delta E)_0$

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

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

[15] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940). We later express the coefficient b in terms of the other constants, using the usual equilibrium conditions.

are very small indeed. This result justifies our procedure of first minimizing the major part of the energy as a function of ξ only, and then minimizing ΔE as a function of σ at constant ξ.

The sign of some of the σ's is at first surprising. One at first tends to reason that in effect a core potential has been removed, and consequently the surrounding ions should move inward. It turns out, however, that there is also another effect; namely, the electron prefers to stay in a region of the lowest potential available. Thus it prefers to remain inside the vacancy. Since it does not like to increase its kinetic energy by concentrating its wave function in the vacancy, it tries instead to enlarge the vacancy by pushing the ions outward.

The effects of the distortion on the predicted transition energy can be estimated in the following manner. The only term whose contribution depends on the electronic state is the integral appearing in Eq. (24). It is readily verified that with $\sigma_0 = 0.03$ or less, only the term linear in σ need be retained in the expansion of this integral. This term is

$$(6/a)q_+\sigma. \tag{35}$$

Thus the correction term which must be added to the predicted transition energy is

$$(6/a)[q_+(\Gamma_4{}^o) - q_+(\Gamma_1{}^e)]\sigma. \tag{36}$$

It is tabulated below in Table VIII, using a wave function of type III for the ground state, and type II for the excited state.

This correction improves appreciably the agreement with the experimental data. It should be remembered, however, that the distortion may depend appreciably on exchange and overlap effects. We shall discuss this further in Sec. 6.

5. HYPERFINE STRUCTURE IN ELECTRON SPIN RESONANCE STUDIES OF THE *F* CENTER

The *F*-center electron spin is unpaired. A strong magnetic field (~3000 gauss) will split the spin degeneracy giving two energy levels whose difference corresponds to a frequency in the microwave region. An applied microwave field of the right frequency will induce transitions between these two energy levels with a consequent absorption of power from the applied field.

TABLE VII. Lattice distortion energies and parameters. Energies are in Hartree atomic units; displacements σ_0 are in lattice distances.

Substance	Type I σ_0	Type I $(\Delta E)_0 \times 10^4$	Type III σ_0	Type III $(\Delta E)_0 \times 10^4$
LiF	−0.0098	−3.4	0.019	−12
NaF	−0.0017	−0.09	0.024	−18
LiCl	0.0027	−0.21	0.029	−24
NaCl	0.0058	−0.94	0.030	−24
KCl	0.0097	−2.5	0.029	−22
RbBr	0.0119	−3.6	0.031	−24

TABLE VIII. Correction to the theoretical *F*-band energy due to lattice distortion. Energy is in Hartree atomic units.

Substance	$(6/a)[q_+(\Gamma_4{}^o) - q_+(\Gamma_1{}^e)]\sigma$
LiF	0.0084
NaF	0.0076
LiCl	0.0076
NaCl	0.0064
KCl	0.0046
RbBr	0.0040

From such an electron spin resonance experiment, one obtains the following two quantities: The electronic g factor (which is usually slightly different from that of a free electron); and the absorption line shape. The observed broadening of the absorption line is thought to be due to the interaction of the electronic magnetic moment with the magnetic moments of the nuclei of the surrounding ions (hyperfine interaction). In one case (LiF), the hyperfine structure of the *F*-center electron spin resonance line has actually been resolved.[16]

If the wave function for a crystal containing an *F* center is known, one can evaluate the energy $E_\alpha{}^{\text{hfs}}$ of the interaction between the unpaired electron magnetic moment and the magnetic moment of nucleus α, using first-order perturbation theory. However, the problem should be treated by an n-electron formalism. The correct expression for $E_\alpha{}^{\text{hfs}}$ is

$$E_\alpha{}^{\text{hfs}} = \int \Phi \mathcal{H}_\alpha{}^{\text{hfs}} \Phi d\tau \bigg/ \int \Phi\Phi d\tau, \tag{37}$$

where

$$\mathcal{H}_\alpha{}^{\text{hfs}} = \sum_{\mu=1}^{n} \mathcal{H}_{\alpha,\mu}{}^{\text{hfs}} \tag{38}$$

gives the interaction of the magnetic moment of nucleus α with all n electrons, and Φ is the appropriate antisymmetrized n-electron wave function.[17] For systems

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[16] N. W. Lord and C. K. Jen, Bull. Am. Phys. Soc. Ser. II, **1**, 12 (1956).

[17] Some previous calculations of hyperfine structure in *F* centers have used the quantity $|\psi_n(0)|^2$ as a measure of the hyperfine splitting. This is obtained from the expectation value of the hyperfine interaction operator for one electron. It is shown in the text that this procedure is entirely valid, provided that two conditions are fulfilled. First, the *F*-center orbital must be orthogonal to the orbitals of all the other electrons. Secondly, the orbitals of all the other electrons must form pairs of orbitals differing only in the spin, i.e., except for the *F*-electron the system consists of a closed shell configuration. Unless the problem is treated as an n-electron problem, it is difficult to fulfill these conditions. If the *F*-center orbital is not orthogonal to the other orbitals, a careful evaluation of the expectation value of the total hyperfine interaction operator for all the electrons of the crystal would lead to a number of overlap terms. If these overlap terms could be summed conveniently, the result would be identical to the one obtained in the text. In some previous work, nonorthogonal *F*-center orbitals were unfortunately used, and the importance of overlap terms was not realized.

The molecular orbital function used by Kip, Kittel, *et al.* [Phys. Rev. **91**, 1066 (1953)] is partially orthogonal to the core orbitals on the alkali ions. This is so because the molecular orbital is written in the LCAO approximation, and a valence orbital centered on a given alkali atom is orthogonal to all the core orbitals of the same atom, even though it may overlap the core orbitals of some adjacent ions. To some extent, this explains the agreement of their work with experiment. For reasons given with only one unpaired electron spin, a good approximation to Φ is the single determinant

$$\Phi=(n!)^{-\frac{1}{2}}\sum_{x=1}^{n!}(-1)^{P_x}P_x\psi_1(1)\psi_2(2)\cdots\times\psi_{n-1}(n-1)\psi_n(n). \tag{39}$$

Here, ψ_n is the F-electron wave function and ψ_1 to ψ_{n-1} are wave functions for the ion-core electrons. Since the results of Sec. 3 show that negligible ion core polarization is produced by the F center, appropriate free-ion wave functions may be used for ψ_1 to ψ_{n-1}.

It can be shown that[18]

$$\mathcal{H}_{\alpha,\mu}{}^{\mathrm{hfs}}=\frac{2\beta\mu_\alpha}{I_\alpha}\left(\frac{8\pi}{3}\mathbf{I}_\alpha\cdot\mathbf{S}_\mu\delta(\mathbf{r}_\mu-\mathbf{r}_\alpha)+\frac{3\mathbf{S}_\mu\cdot(\mathbf{r}_\mu-\mathbf{r}_\alpha)\mathbf{I}_\alpha\cdot(\mathbf{r}_\mu-\mathbf{r}_\alpha)}{|\mathbf{r}_\mu-\mathbf{r}_\alpha|^5}-\frac{\mathbf{S}_\mu\cdot\mathbf{I}_\alpha}{|\mathbf{r}_\mu-\mathbf{r}_\alpha|^3}+\frac{\mathbf{l}_\mu\cdot\mathbf{I}_\alpha}{|\mathbf{r}_\mu-\mathbf{r}_\alpha|^3}\right), \tag{40}$$

where β is the Bohr magneton; μ_α is the magnetic moment of nucleus α; $\mathbf{I}_\alpha$ is the spin of nucleus α; and $\mathbf{S}_\mu$ and $\mathbf{l}_\mu$ are, respectively, the spin and orbital momentum of the μth electron. The term involving $\mathbf{l}_\mu$ represents the interaction of the nuclear dipole moment with the magnetic field arising from the orbital motion of the μth electron. All other terms arise from the interaction between the spin moment of the μth electron and the nucleus. In all subsequent calculations involving $\mathcal{H}_{\alpha,\mu}{}^{\mathrm{hfs}}$, we shall neglect the term involving the orbital momentum $\mathbf{l}_\mu$. The reason for this is that, in the absence of an appreciable coupling between the orbital momentum and the spin momentum of the unpaired electron (the lack of which is attested to by the very small observed g-factor shift), such orbital interactions will merely shift all the magnetic energy levels of the unpaired electron spin by equal amounts.

In evaluating (37), the problem of enumerating the various overlap terms can be avoided by transforming the ψ_i to an orthonormal set φ_j. The counting problem can be further simplified if the orthogonalization process is carried out in such a way as to avoid disrupting the closed shell configuration of electron orbitals ψ_1 to ψ_{n-1}. To do this we proceed as follows: First, we orthogonalize orbitals ψ_1 to ψ_{n-1} using a method due to Löwdin.[19] This method uses the transformation

$$\varphi_j=\sum_{i=1}^{n-1}\psi_iA_{ij},\quad j=1,2,\cdots n-1. \tag{41}$$

The simplest matrix A satisfying the requirement that the φ_j be orthonormal is

$$A=(1+S)^{\frac{1}{2}}=1-\tfrac{1}{2}S+\tfrac{3}{8}S^2-\tfrac{5}{16}S^3+\cdots, \tag{42}$$

where S is the overlap matrix

$$S_{ij}=\int\psi_i\psi_jd\tau-\delta_{ij}. \tag{43}$$

Since the functions ψ_1 to ψ_{n-1} form a closed-shell configuration, any pair of orbitals differing only in their spin function will be transformed in the same way by (41). Therefore, the functions φ_1 to φ_{n-1} also describe a closed-shell configuration. We now construct an orthonormal function φ_n, corresponding to ψ_n, in such a way as to leave this closed-shell configuration unchanged. This can be done by the linear transformation

$$\varphi_n=\left(\psi_n-\sum_{j=1}^{n-1}[n|j]\varphi_j\right)\bigg/\left[1-\sum_{j=1}^{n-1}[n|j]^2\right]^{\frac{1}{2}}=\left(\psi_n-\sum_{i=1}^{n-1}\sum_{k=1}^{n-1}T_{ki}(n|k)\psi_i\right)\bigg/\left[1-\sum_{i=1}^{n-\mathrm{I}}\sum_{k=1}^{n-1}T_{ki}(n|k)(n|i)\right]^{\frac{1}{2}}, \tag{44}$$

where $[n|j]$ is the overlap integral of ψ_n with φ_j and $(n|i)$ is the overlap integral of ψ_n with ψ_i. The last equality in (44) is the result of substituting for φ_j using (41). T is the matrix $\tilde{A}A$. The expansion of T, using (42), is

$$T=(1+S)^{-1}=1-S+S^2-S^3+\cdots. \tag{45}$$

The linear nonsingular transformation described by (41) and (44) is readily shown to possess the inverse transformation

$$\psi_i=\sum_{j=1}^{n}C_{ij}\varphi_j. \tag{46}$$

If we substitute for each ψ_i in the determinantal wave function (39) and use the rule for determinant multipli-

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below, however, the excellence of this agreement is somewhat fortuitous. Kip, Kittel, *et al.* computed the hyperfine splitting with two wave functions. One, the central field wave function, gave results which were one or two orders of magnitude less than the experimental results. The LCAO molecular orbital gave correct results and provided a measure of the amount of s character of the wave function. Unfortunately, these results were obtained by neglecting overlap integrals between two atomic orbitals centered on adjacent K$^+$ ions. These integrals are negligible only in the case that the s and p orbitals combine in such a way as to push the electron away from the vacancy. Our results on the central wave function indicate that this is not the case. In fact, there is a clear indication that the electron spends most of its time inside the vacancy. Thus, we must conclude that the s and p orbitals combine so as to put the electron closer to the center of the vacancy. In this case, however, the overlap integrals are large: four of them are at least 0.3 to 0.6 each. The inclusion of these overlap integrals in the calculation would have reduced the predicted value of the hyperfine interaction by a factor of three or more. This means that even if 100% s character is assumed, the computed hyperfine splitting falls short of the experimental value. The order of magnitude, however, is still correct.

[18] See, for example, H. A. Bethe in *Handbuch der Physik* (Verlag Julius Springer, 1933), Vol. 24, Part I, p. 385. Also A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 137 (1951).

[19] Per-Olov Löwdin, J. Chem. Phys. **18**, 365 (1950).

cation, it can be shown that

$$\Phi=(n!)^{-\frac{1}{2}}\det|C_{ij}|\sum_{x=1}^{n!}(-1)^{P_x}P_x\varphi_1(1)\cdots\varphi_n(n). \quad (47)$$

Therefore, the Eq. (37) for $E_\alpha{}^{\mathrm{hfs}}$ is invariant under the transformation from the ψ_i to the φ_i. Using (47) for Φ, the expansion of (37) follows immediately. The result is

$$E_\alpha{}^{\mathrm{hfs}}=\sum_{i=1}^{n}\int\varphi_i(1)\mathcal{H}_{\alpha,\,i}{}^{\mathrm{hfs}}\varphi_i(1)d\tau_1. \quad (48)$$

Since the orbitals φ_1 to φ_{n-1} form a closed shell of zero total spin and angular momentum, the sum over these orbitals vanishes, and we are left with

$$E_\alpha{}^{\mathrm{hfs}}=\int\varphi_n(n)\mathcal{H}_{\alpha,\,n}{}^{\mathrm{hfs}}\varphi_n(n)d\tau_n=E_\alpha{}^S+E_\alpha{}^{\mathrm{dipole}}, \quad (49)$$

where

$$E_\alpha{}^S=\frac{16\pi}{3}\frac{\beta\mu_\alpha}{I_\alpha}I_{\alpha z}'S_{nz}'|\varphi_n(\alpha)|^2, \quad (50)$$

$$E_\alpha{}^{\mathrm{dipole}}=\frac{2\beta\mu_\alpha}{I_\alpha}I_{\alpha z}'S_{nz}'\int\varphi_n(n)\times\left(\frac{3\cos^2\theta_{\alpha n}-1}{r_{\alpha n}{}^3}\right)\varphi_n(n)d\tau_n. \quad (51)$$

Here, $\varphi_n(\alpha)$ is φ_n evaluated at nucleus α. The hyperfine structure of the electron spin resonance line produced by $E_\alpha{}^S$ will be isotropic in the sense that it will not depend on the orientation of the crystal with respect to the magnetic field. $E_\alpha{}^{\mathrm{dipole}}$, on the other hand, will cause the hyperfine splitting to vary with the orientation of the applied field. In general, however, this effect will be small because $E_\alpha{}^{\mathrm{dipole}}$ is considerably smaller than $E_\alpha{}^S$.

To evaluate (50), φ_n must be re-expanded in terms of the known ψ_i. Since overlap integrals between ion core orbitals are very small (~0.01 for nearest neighbor orbitals), we can neglect all overlap integrals not involving ψ_n without changing the result by more than 20%. With this approximation (44) becomes

$$\varphi_n=\left(\psi_n-\sum_{i=1}^{n-1}(n|i)\psi_i\right)\Big/\left[1-\sum_{i=1}^{n-1}(n|i)^2\right]^{\frac{1}{2}}. \quad (52)$$

The above approximation is quite satisfactory when one considers the accuracy of our present *F*-electron wave function. Should the accuracy of ψ_n be improved, it would be necessary to check this approximation more carefully. Equation (52) shows that φ_n has admixed into it components of the orbital wave functions of all the electrons of the system with the same spin. This admixing arises because ψ_n is not orthogonal to the ψ_i; the terms in (52) which involve orbitals other than ψ_n are analogous to the overlap and exchange energies which appear in the expressions for the binding energy of most molecules. In fact, the overlap terms involving at least one orbital other than ψ_n provide the major contribution to $E_\alpha{}^{\mathrm{hfs}}$. This result follows from the nature of the Hamiltonian $\mathcal{H}_\alpha{}^{\mathrm{hfs}}$ which is very small everywhere except in the immediate vicinity of nucleus α. Consequently the major contribution to $E_\alpha{}^{\mathrm{hfs}}$ will come from those orbitals in φ_n which are centered on nucleus α.

The result obtained by considering hyperfine interactions as due to the lone *F* electron described by the wave function ψ_n has the same form as (50); the only difference is that the orthonormal function φ_n has been replaced by ψ_n. However, it is now clear that unless the ψ_n used was orthogonal to all the other orbitals, such a replacement loses the only terms which give appreciable contributions to $E_\alpha{}^{\mathrm{hfs}}$.

To clarify the previous discussion and to show that calculations based on (50) can give the correct order of magnitude for the *F*-center hyperfine interaction energies, we consider a specific salt, namely, LiF. LiF was chosen for three reasons. First, the *F*-center electron spin resonance hyperfine structure has been resolved in LiF.[16] Secondly, we need compute only $E_\alpha{}^s$ because $E_\alpha{}^{\mathrm{dipole}}$ is negligible for Li nuclei and less than 10% for F nuclei. Finally, LiF has the advantage that relatively few free ion atomic orbitals need be considered and that the necessary data on these orbitals is available.

Following the conventional procedure, we shall actually calculate $|\varphi_n(\alpha)|^2$, which is equivalent to calculating $E_\alpha{}^S$. Furthermore, in calculating $|\varphi_n(\alpha)|^2$ for a given nucleus, it is necessary to include in φ_n only ψ_n and those *s* state orbitals ψ_i which are centered on α. It is shown in the Appendix that when ψ_i is an *s* function, the overlap integral $(i|n)$ can be written in the form

$$(i|n)=B_i\psi_n[\alpha(i)]. \quad (53)$$

Combining (52) and (53) gives

$$|\varphi_n(\alpha)|^2=|1-\sum_{i(\alpha)}B_i\psi_i(\alpha)|^2|\psi_n(\alpha)|^2\Big/\left(1-\sum_{i=1}^{n-1}(n|i)^2\right)=G_\alpha|\psi_n(\alpha)|^2, \quad (54)$$

where $i(\alpha)$ symbolizes those orbitals centered on α. It will be seen that G_α is an amplifying factor which will give $|\varphi_n(\alpha)|^2$ the correct order of magnitude. $|\varphi_n(\alpha)|^2$ is approximately proportional to $|\psi_n(\alpha)|^2$. Any attempt to calculate highly accurate values for the hyperfine interaction energy in *F* centers will, therefore, require a more accurate calculation of ψ_n and an investigation of the question of lattice distortion which could have a marked effect on ψ_n at a given nucleus.

TABLE IX. Theoretical and experimental hyperfine structure results (Hartree atomic units).

Substance	Ion	Exp. $\lvert\varphi\rvert^2$	Theoretical Gourary and Adrian $\lvert\psi\rvert^2$	Theoretical Gourary and Adrian $\lvert\varphi\rvert^2$	Theoretical Dexter $\lvert\varphi\rvert^2$	Theoretical Krumhansl $\lvert\varphi\rvert^2$
LiF	Alkali	0.023	0.00112	0.064	···	0.073
	Halide	0.0031	0.00012	0.042	···	···
NaF	Alkali	0.087	0.00071	···	···	0.213
NaCl	Alkali	0.059	0.00037	···	0.100	···
KCl	Alkali	0.104	0.00026	···	···	0.140

Table IX gives the results for a Li nucleus nearest the vacancy and for an F nucleus nearest the vacancy; $|\varphi_n(\alpha)|^2$ for all other nuclei is very much smaller. The overlap integrals are calculated using Slater orbitals for the ψ_i; it turns out that if ψ_i is a $1s$ function, then $B_i\psi_i(\alpha)$ is quite insensitive to the effective charge of the orbital ψ_i. The value of $\psi_{F-2s}(F)$ is obtained from the Hartree orbital for the F^- ion.[20] The experimental results are those of Lord and Jen.[16]

Results are also given for several other alkali halides. Here also our $|\psi_n(\alpha)|^2$ is used, but the amplifying factors are obtained by the methods of Dexter[21] and of Krumhansl.[22] The experimental values for NaF and NaCl are due to Lord;[23] the values for KCl are taken from the work of Kip *et al.*[24]

The agreement between the calculated and experimental values is only fair. However, one can hardly expect to get highly accurate results when evaluating a rapidly varying Hamiltonian, such as $\mathcal{H}_\alpha^{\mathrm{hfs}}$, and using a wave function which is barely accurate enough to give good results for the slowly varying energy Hamiltonian. Moreover, our present ψ_n is the result of an approximate calculation which neglected exchange insofar as the binding energy of the F-electron was concerned. Nonetheless, these results show that inclusion of the nonorthogonality terms results in a manyfold amplification of the small term $|\psi_n(\alpha)|^2$ to give a result which is of the correct order of magnitude.

6. SPECULATIONS ON THE EFFECTS OF EXCHANGE AND OVERLAP

In a complete Hartree-Fock calculation, terms due to exchange and overlap will appear. Some of these terms involve many-body forces. Thus, for example, the interaction of electrons 1 and 2 is modified by the presence of electron 3. If we neglect the many-body forces (this corresponds to representing the core electrons by free ion wave functions), then it is possible to set up the variational equations for the orthogonalized wave function $\varphi_n(\mathbf{r})$ directly, retaining exchange and overlap terms. We have set up such a calculation for LiF, and have estimated the effects of the orthogonalization, the Hartree potential, and exchange. The sum of these interactions with ion α is approximately proportional to $|\psi_n(\alpha)|^2$. For the nearest neighbor lithium ions, the interaction is repulsive. It tends, therefore, to concentrate the wave function in the vacancy. It is also likely that this effect would tend to push the nearest neighbor cations outward slightly. The transition energy is not likely to be affected greatly.

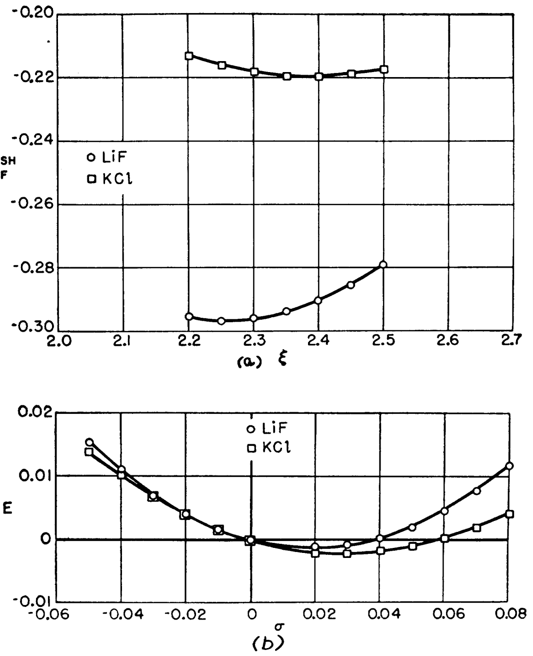

FIG. 3. (a) The energy functional E_F^{SH} for the ground state (type III wave function) as a function of the variational parameter ξ. (b) The energy change ΔE caused by the lattice distortion as a function of the distortion parameter σ.

The above picture is borne out by the graphs of Fig. 3, which give the variation of E_F^{SH} and of ΔE with the variational parameters. These curves are remarkably flat, and consequently the values of the variational parameters may be changed somewhat by the exchange and overlap interactions. It is comforting, therefore, to know that this interaction is likely to push the electron into the vacancy, not out of it. Thus our assumption of zero polarization is not likely to be upset. The predicted oscillator strengths and hyperfine energies will probably decrease, leading to somewhat better agreement with experiment.

7. DISCUSSION

The calculation of the wave functions and energy levels reported in this paper differs from previous work on this subject[15,25] primarily in the following characteristic features. First, we use the actual potential of a point ion lattice, not a smoothed effective potential.

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[20] D. R. Hartree, Proc. Roy. Soc. (London) A151, 96 (1935).

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[22] J. A. Krumhansl, Phys. Rev. 93, 245 (1954).

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[24] Kip, Kittel, Levy, and Portis, Phys. Rev. 91, 1066 (1953).

[25] J. H. Simpson, Proc. Roy. Soc. (London) A197, 269 (1949).

Secondly, the electronic polarization energy is computed by a self-consistent method, which takes advantage of the screening effects of the *F*-center electron. Thirdly, the lattice distortion is computed by permitting only six nearest neighbor ions to displace, and then treating their displacement in detail.

The first two features represent a definite improvement. Thus, the group theoretical treatment of the lattice potential not only gives a clearer picture of the potential in the *F* center, but it is easily generalizable to certain other color centers. It is, of course, simply a generalization of Bethe's theory of the crystalline potential to the case where a power series expansion of the potential about the center of the vacancy is inadequate because of the diffuse nature of the wave function, and a more general expansion in spherical harmonics must be used. The self-consistent estimate of the polarization energy is easier to compute and it is readily obtainable even for color centers of low symmetry.

The third feature is a mixed blessing. The presence of the *F* center produces two effects. One is the displacement of the nearest neighbor ions caused directly by the combined effects of the missing core potential and the strongly screened electric field of the *F* center. This effect is well taken care of by our method. The other is the resulting elastic dilatation. If our crystal were a continuous, isotropic elastic medium, this latter radial displacement would vary as r^{-2}. Thus it would be better to assume that the nearest neighbor ions move radially a distance (σa), and that all other ions move a distance Ca/ρ_i^2, where ρ_i is the distance from the ith ion to the center of the vacancy and C is a parameter. We have not done this because it seemed inconsistent to tackle this aspect of the problem in such detail while neglecting exchange and overlap effects.

The fact that the ions have been treated as point charges and not as extended charge distributions turns out to be of secondary importance. The reason for this is that the *F*-center electron spends most of its time in the region which is outside of the ionic cores (as defined by the ionic radius). In fact, a simple geometrical calculation shows that approximately $\frac{5}{6}$ of the volume of a sphere of radius a, centered at the center of the vacancy, is "empty." More accurate results for the wave function and the energy can be obtained, of course, by actually solving the variational equations (with exchange and overlap) for the orthogonalized trial function $\varphi_n(\mathbf{r})$, but it is likely that the resulting wave function will not differ substantially from the $\varphi_n(\mathbf{r})$ which we have obtained in (52) by simply orthogonalizing our approximate $\psi_n(\mathbf{r})$ to the core orbitals. (*Note added in proof.*—Professor T. Nagamiya informs us that T. Kojima is presently solving the variational equations for $\varphi_n(\mathbf{r})$ in LiF directly by a method similar to the one outlined in the above paragraph.)

The method we have used for the calculation of the hyperfine interaction differs from the approach of Krumhansl[22] and of Dexter,[21] who have treated this problem from the point of view of the band theory. Our approach is based on a purely ionic model, of course, and it does not depend on the validity of the expansion of the *F*-center orbital in the form $u_0(\mathbf{r})f(r)$.[22] Numerically, however, the amplifying factors derived from our theory are very close to those given by the methods of Krumhansl and of Dexter, as can be seen in Table IX.

Our method can be adapted to the treatment of other electron-excess color centers, as well as to the interstitial model of the *F* center. Its applicability to centers possessing low symmetry, such as the *M* center, is in fact one of its greatest assets.

8. ACKNOWLEDGMENTS

The authors are indebted to Dr. C. K. Jen, Dr. N. W. Lord, Dr. J. J. Markham, Dr. F. T. McClure, and Dr. R. F. Wallis for several stimulating discussions. They have had the benefit of an informative conversation with Professor J. C. Slater. They are also indebted to Professor F. Seitz for reading an early draft of this paper and for his comments. The extensive numerical computations have been performed by Mrs. Mary E. Lynam, and the typing was done by Miss Agnes M. Fogelgren.

APPENDIX. EVALUATION OF OVERLAP INTEGRALS INVOLVING THE *F*-ELECTRON ORBITAL

We shall develop formulas for the overlap integrals $(i|n)$. Such integrals are needed for evaluating the hyperfine interaction energy.

From the fact that the overlap charge distribution $\psi_i\psi_n$ is appreciable only in the vicinity of the nucleus $\alpha(i)$, one is led to expand the function ψ_n about this nucleus. This expansion is obtained by writing

$$\begin{aligned} r_1 &= (r_{\alpha 1}^2 + r_\alpha^2 - 2r_{\alpha 1} r_\alpha \cos\theta_{\alpha 1})^{\frac{1}{2}} \\ &= r_\alpha\left[1 - \left(\frac{r_{\alpha 1}}{r_\alpha}\right)\cos\theta_{\alpha 1} + \tfrac{1}{2}\left(\frac{r_{\alpha 1}}{r_\alpha}\right)^2 \sin^2\theta_{\alpha 1} + \cdots\right], \end{aligned}$$

where r_1 is the distance from the center of the vacancy to the electron, $r_{\alpha 1}$ is the distance from nucleus α to the electron, and r_α is the distance from the center of the vacancy to nucleus α. One can now substitute the above expression for r_1 in $\psi_n(r_1)$, expand the various functions in powers of $(r_{\alpha 1}/r_\alpha)$, and evaluate the resulting series of one center integrals. This will lead to an expansion for the overlap integral which is asymptotic in the effective charge δ_i of the wave function ψ_i. The first few terms in the series will provide an adequate approximation, because δ_i is large for the compact ion core orbitals. This procedure has been carried out for the Type III ground-state wave functions $\psi_n(\Gamma_1^e|\mathbf{r})$. The results are

$$(i|n)=\psi_n(\Gamma_1^e|\alpha)\frac{2^{p+1}(p+1)!}{[(2p)!]^{\frac{1}{2}}}\left(\frac{2\pi}{\delta^3}\right)^{\frac{1}{2}}\times\begin{cases}\left[1+\dfrac{(\eta^2-\xi^2)(p+3)(p+2)}{12\delta^2}+\cdots\right], & r_\alpha\leq a\\[2ex] \left[1+\dfrac{\eta^2(p+3)(p+2)}{6\delta^2}+\cdots\right], & r_\alpha>a\end{cases}$$

when ψ_i is the s function

$$\psi_i(1)=\left[\frac{2^{2p}\delta^{2p+1}}{2\pi(2p)!}\right]^{\frac{1}{2}}r_{\alpha1}{}^{p-1}\exp(-\delta r_{\alpha1})$$

and

$$(i|n)=\psi_n(\Gamma_1^e|\alpha)2^{p+1}(p+2)!\left[\frac{6\pi}{(2p)!\delta^5}\right]^{\frac{1}{2}}\times\begin{cases}\left[\dfrac{\eta+1}{3}-\dfrac{(\eta^2+\xi^2)(p+3)}{16\delta}+\cdots\right], & r_\alpha\leq a\\[2ex] \left[\dfrac{\eta r_\alpha+1}{3r_\alpha}+\cdots\right], & r_\alpha>a\end{cases}$$

when ψ_i is the p function

$$\psi_i(1)=\left[\frac{3(2)^{2p}\delta^{2p+1}}{2\pi(2p)!}\right]^{\frac{1}{2}}r_{\alpha1}{}^{p-1}\exp(-\delta r_{\alpha1})\cos\theta_{\alpha1}.$$

If, when ψ_i is an s function, one uses only the first term in the asymptotic expansion for $(i|n)$, then

$$(i|n)=B_i\psi_n(\alpha),$$

where B_i is independent of ψ_n. This result was used in Sec. 5.

PHYSICAL REVIEW VOLUME 105, NUMBER 4 FEBRUARY 15, 1957

Photoconductivity in Lead Selenide: Theory of the Dependence of Sensitivity on Film Thickness and Absorption Coefficients*

JAMES N. HUMPHREY, *United States Naval Ordnance Laboratory, White Oak, Maryland and University of Maryland, College Park, Maryland*

AND

RICHARD L. PETRITZ, *United States Naval Ordnance Laboratory, White Oak, Maryland*

(Received November 12, 1956)

Recently developed theoretical expressions for the responsivity R_s and noise of photoconductive films are examined. Assuming that the time constant is independent of film thickness we express R_s and signal/noise (S/N) in terms of the absorption coefficient α and thickness d. Using a curve of α *vs* λ for lead selenide obtained by Avery from crystal measurements, we calculate R_s *vs* λ for films of different thicknesses. These curves indicate that the photoconductive knee should lie near 5μ for PbSe films of all thicknesses. Experimentally, however, the position of the knee is observed to be a function of film thickness, being near 3.3μ in thin films and 5μ in thick films.

It is then shown from the theory that in very thin films the responsivity is a direct measure of α. Accordingly the wavelength dependence of α is calculated from responsivity data for thin films; the magnitude is determined from the crystal absorption data at 5μ. Curves of responsivity *vs* λ for various film thicknesses are computed, using the α *vs* λ curve derived from responsivity data on thin films. These curves agree with the observed responsivity data; they show the shift of the knee from 3.3 to 5μ with increased film thickness, and show that no increase in responsivity can be obtained at any wavelength by increasing the film thickness.

The dependence of signal/noise on λ and d is calculated, using the same α *vs* λ curve, and found to be in qualitative agreement with experiment. The curves show that for any given wavelength the signal/noise is a maximum at a certain value of film thickness. The maximum occurs at greater thicknesses for longer wavelengths. The dependence of S/N on d and α is given for any material fitting the same general photoconductive model. The same conclusion, that there is an optimum thickness for any particular absorption coefficient, holds in this general case.

Finally, the derived α *vs* λ curve is shown to be consistent with recent theories of indirect optical transitions.

INTRODUCTION

A RECENT experimental study[1] of photoconductive lead selenide films investigates the relationship of film thickness and method of sensitization to magnitude and spectral dependence of sensitivity. Previous workers had shown that at room temperature a knee in the spectral sensitivity curve occurs near 3.3μ in thin films,[2] but near 5μ in thicker films.[3] The sensitivity of the

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* A portion of a dissertation submitted (by J.N.H.) to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Part of this work was reported at the 1955 Washington meeting of the American Physical Society [J. N. Humphrey, Phys. Rev. **99**, 625(A) (1955)].

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