In the same manner as before, we are led to

$$\mu_{AC}>\mu_{AB}(1-\theta)[\epsilon_0(AC)/\epsilon_\infty(AC)]^{1/2}, \tag{8}$$

which implies that

$$m_C>m_B(1-\theta)[\epsilon_0(AC)/\epsilon_\infty(AC)]^{1/2}, \tag{9}$$

or

$$m_C[\epsilon_\infty(AC)/\epsilon_0(AC)]^{1/2}>m_B(1-\theta). \tag{10}$$

Since $m_C[\epsilon_\infty(AC)/\epsilon_0(AC)]^{1/2}>\mu_{AC}[\epsilon_\infty(AC)/\epsilon_0(AC)]^{1/2}$ and $m_B(1-\theta)<m_B$, we have

$$m_C[\epsilon_\infty(AC)/\epsilon_0(AC)]^{1/2}>\mu_{AC}[\epsilon_\infty(AC)/\epsilon_0(AC)]^{1/2} >m_B>m_B(1-\theta). \tag{11}$$

Thus it is apparent that the nonoverlap requirement is a less restrictive condition than the requirement of inequality (6) and is included in it.

ACKNOWLEDGMENTS

We wish to thank Professor A. Smakula of the MIT Center for Materials Science and Engineering for the pure alkali halides and $KCl_{1-x}Br_x$ samples, and J. Kalnajs for the x-ray measurements and their interpretation. This work forms a part of the thesis of one of us (J.H.F.) to be submitted to the MIT Physics Department in partial fulfillment of the requirements for the Ph.D. degree.

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Theory of the Self-Trapped Hole in the Alkali Halides*

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Combining the self-consistent-field molecular-orbital results for the wave functions and energies of F_2^- and Cl_2^- with a classical calculation of the lattice distortion and polarization energies, we have obtained the ground- and excited-state potential curves of the V_K center in several of the alkali halides. The widths and peak values of the optical-absorption bands have been calculated from these potential curves and are found to be in reasonable agreement with, but somewhat smaller than, the experimental results. The hyperfine constants are obtained as a function of internuclear distance and compared with the experimental results using the internuclear distance at the minimum of the configurational coordinate curves. The significance of the remaining discrepancies between theory and experiment for interpreting still unresolved aspects of the structure of V_K centers is pointed out.

I. INTRODUCTION

THE study of the structure and properties of color centers continues to be a fruitful area of theoretical and experimental research in solid state physics. This study has been made possible by new experimental techniques which provide more accurate probes into properties that were studied earlier and that have also made possible the measurement of properties that were not accessible previously. The experimental results have raised new problems which have stimulated theorists to try to gain further understanding of the structure of these interesting systems and of defects in ionic crystals in general. Efforts in this direction have been helped by refinements in our theoretical understanding of atomic and molecular systems and the rapid advancements in computer technology, which have added a dimension to efforts in the theory of the solid state. The two centers that have been studied most extensively are the F center and its close associates,[1-4] and the self-trapped hole or V_K center.[1,2] The present work is concerned with the theory of this latter type of center.

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* Work supported in part by the National Science Foundation, the U. S. Atomic Energy Commission, and the Bureau of Naval Weapons, U. S. Department of the Navy, under Contract No. NOw 62-0604-c.

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The V_K center was discovered by Känzig,[5] and the early information on its electronic structure was derived from detailed spin-resonance work on selected crystals by Castner and Känzig,[6] and optical work by Delbecq, Smaller, and Yuster.[7] Theoretical attempts to understand qualitatively the self-trapping of holes leading to the formation of the V_K center were made by Yamashita[8] and Nettel.[9] Subsequently, a microscopic theory combining an approximate molecular-orbital treatment for the negative halogen molecule ion with an analysis of the lattice distortion around the V_K center was developed by Das, Jette, and Knox[10] (referred to hereafter as I). This approach was applied to the specific case of LiF, and partial agreement was obtained with optical properties as well as hyperfine effects associated with the F^{19} nuclei of the center. The results indicated that further significant improvements in the theory would require more sophisticated molecular wave functions and energy calculations.

Since these earlier theoretical calculations were published, several additional experimental results have become available. Among these are the study of the hyperfine constants in the series LiF, NaF, KF, and RbF by Bailey[11] and the optical-absorption frequencies and linebreadths in NaF by Jones.[12] Delbecq, Gilbert, Hayes, and Yuster[13] have studied the hyperfine constants and optical spectra in the series of alkali chlorides LiCl, NaCl, KCl, and RbCl. Schoemaker[14] has carried out similar studies in several mixed negative halogen molecule-ion centers. Dreybordt[15] has studied temperature variations of hyperfine constants for V_K centers in a number of alkali halides and attempted to interpret them in terms of the vibrational properties of the V_K centers. Gazzinelli and Mieher[16] measured the hyperfine constants of nuclei adjacent to the V_K center in LiF using electron-nuclear double-resonance (ENDOR) techniques. Using these results, Daly and Mieher[17] obtained information about the displacements of ions adjacent to the V_K center. On the theoretical side, self-consistent-field molecular-orbital (SCF-MO) wave functions have now become available[18] for the ground and excited states of the F_2^- and Cl_2^- molecule ions. We have adapted our lattice-distortion analysis to be able to combine with the SCF-MO results and carried out calculations for F_2^- and Cl_2^- centers in all the alkali fluorides and chlorides for which experimental data are currently available. Finally, mention should be made of the recent experimental measurements of the hyperfine spectra of the F_2^- and Cl_2^- centers by Schoemaker.[19]

Our recent results by the revised procedure are being published at this time with three purposes in mind. The first reason is to make our analysis and results available to experimentalists. Second, we hope, by presenting our results and current theoretical understanding of the structure of these centers, to interest investigators in doing additional experiments which will subject some of the assumptions and predictions of the theory to further test. Finally, from a theoretical point of view, we would like to show the extent of improvement in terms of comparison with experiment that is attained with the use of SCF-MO wave functions. With the closer agreement now possible between experiment and theory, it is possible to assess the need for more sophisticated calculations involving improvements in the treatment of lattice distortion and its influence on the molecular wave functions and more accurate wave functions for the molecule ions. Such an examination is particularly facilitated by the availability of theoretical and experimental results in a number of alkali fluorides and chlorides, so that theoretical and experimental trends of different properties can be compared.

In Sec. II, details of the procedure are described using Paper I as a reference point. Section III deals with the results for both F_2^- and Cl_2^- centers in the crystals studied and comparison with experimentally observed optical and hyperfine properties. Finally, Sec. IV discusses the over-all status of our present understanding of the V_K center, based on the results of Sec. III, and suggests improvements in the theory.

II. PROCEDURE

In order to obtain the energy and configuration of the crystal, we shall broadly follow the approach of Paper I. In this earlier work, the ground and excited states of the V_K center in LiF were calculated using a variation principle in which the energy of the molecule ion and lattice was obtained as a function of several variation parameters. The phenomenological theory of ionic crystals was used to calculate the lattice energy in combination with an approximate quantum-mechanical evaluation of the binding energy of the molecule ion. This procedure will be adjusted to take advantage of improved molecular calculations by the SCF technique which are now available for both F_2^- and Cl_2^-.[18,20]

As is well known, the V_K center in an alkali halide of the rock-salt structure is a halogen molecule ion oriented along a $\langle 110\rangle$ direction. The surrounding ions

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relax, and the energy of the crystal containing a V_K center depends on the resulting configuration. The total energy for a crystal with a self-trapped hole may be written as a "formal" sum of two-body interactions:

$$E_{V_K}=\sum_{l'>l} V_{ll'}. \tag{2.1}$$

The potential interactions $V_{ll'}=V_{ll'}(\mathbf{R}_l-\mathbf{R}_{l'})$ include the Coulomb (monopole) interaction and the core-repulsion and multipole interactions due to induced dipole moments. Let $l=1$ and 2 be the pair of ions at which the hole is self-trapped and let $R=|\mathbf{R}_1-\mathbf{R}_2|$ be the distance between them. $V_{12}(R)$ is the potential curve for the self-trapping pair. The potentials $V_{ll'}$ are not true two-body potentials, because they depend on the configuration of surrounding ions. In order to eliminate irrelevant constant terms, we consider

$$\Delta E_{V_K}(R)=E_{V_K}(Q)-E_{V_K}(Q_0)=\sum_{l'>l} \Delta V_{ll'}, \tag{2.2}$$

where Q_0 denotes the configuration of the perfect crystal, that is, where all ions occupy lattice sites of the undistorted crystal, and $Q=Q(R)$ is the configuration obtained by allowing the ions to relax to give a minimum energy for a fixed value of R. If the minimum value $\Delta E_{V_K}(R_e)$ is negative, then self-trapping can occur for an equilibrium separation R_e of the self-trapping pair.

Before proceeding with a quantitative energy analysis, let us briefly consider the self-trapping process from a qualitative viewpoint in order to gain some intuitive feeling for why and when self-trapping can occur. In the initial configuration with undisplaced ions, the hole will be unlocalized and the total energy of the crystal will be $E_{V_K}(Q_0)$. One may go to the equilibrium self-trapping configuration Q_e with energy $E_{V_K}(Q_e)$ by the following hypothetical three-step process. Let us first localize the hole by constructing a wave packet from crystal eigenfunctions for the valence band. The "localization energy" E_{loc} expended by this step will be positive and roughly equal to half the width of the valence band. We then allow the ions to relax under the influence of the electric field created by the localized hole, keeping the distance between the self-trapping pair fixed. The "polarization energy" E_{pol} expended in this step will be negative and can be estimated from a simple model corresponding to a point charge in a spherical cavity within a continuum dielectric. Finally, we allow the distance between the self-trapping pair to relax to its equilibrium value. If, as is the case for the V_K center, the change in the bond energy of the self-trapping pair is large compared to the energy change due to further rearrangement of neighboring ions, the negative "bonding energy" E_{bond} expended in this last step can be obtained from the potential energy curve for the free molecule ion. Adding up the three contributions from this hypothetical process, we have

$$\Delta E_{V_K}(R_e)=E_{\text{loc}}+E_{\text{pol}}+E_{\text{bond}}. \tag{2.3}$$

Self-trapping will occur if and only if $\Delta E_{V_K}(R_e)<0$.

We find for self-trapped holes in alkali halides that the localization and polarization energies are of the order of 0.5 eV and approximately cancel each other.[21] The estimates indicate that the polarization energy is larger in magnitude by about 0.2 eV, but the model is too crude for us to decide with any certainty whether the positive localization energy or negative polarization energy dominates. The crucial part of the contribution is, therefore, the contribution from the bonding energy. If, as is the case for holes in alkali halides, the equilibrium separation for the free molecule ion is significantly less than the distance between neighboring halide ions in the crystal lattice, the bonding energy gives an appreciable negative contribution, and one may expect self-trapping to occur. Typical estimates of the bonding energy, obtained from SCF-MO calculations of the potential curves for the free molecule ions, are of the order of 1 eV. The same analysis could also be used for self-trapping of electrons. It is clear from this qualitative analysis why hole self-trapping is much more likely to occur than electron self-trapping.

Let us now proceed with a more detailed quantitative analysis of the energy changes. The energy change can by written as

$$\Delta E_{V_K}=\Delta V_{12}+\sum_{l\geq 3} (\Delta V_{1l}+\Delta V_{2l})+\sum_{l'>l>2} \Delta V_{ll'}, \tag{2.4}$$

where

$$\Delta V_{12}=V_{12}(R)-V_{12}(R_0)=\Delta E_B(R) \tag{2.5}$$

is the change in bond energy of the molecule ion and R_0 is the separation of the halogen ions in the undistorted lattice. Note that $\Delta E_B(R_e)\approx E_{\text{bond}}$. The change in bond energy of the molecule ion, $\Delta E_B(R)$, is taken from the SCF calculations.[18] The remaining terms in Eq. (2.4) represent changes in the lattice energy, i.e.,

$$\Delta E_L=E_L(Q)-E_L(Q_0)=\sum_{l\geq 3} (\Delta V_{1l}+\Delta V_{2l}) +\sum_{l'>l>2} \Delta V_{ll'}, \tag{2.6}$$

where $E_L(Q)$ represents the energy of a crystal containing a self-trapped hole in configuration Q excluding the molecular binding energy of the molecule ion.

In order to calculate the changes in the lattice energy, $\Delta E_L(Q)$, we shall limit ourselves to configurations for which the hole remains localized, so that we can ignore changes in the localization energy, ΔE_{loc}. One may justify this assumption for the ground state by noting that delocalization corresponds to a mixing of the localized molecular state with the delocalized states of the valence band, and that the separation between

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[21] T. L. Gilbert, Lecture Notes for the NATO Summer School in Solid State Physics, Ghent, Belgium, 1966 (unpublished).

the ground self-trapping level and the valence-band levels is of the order of 3 eV at the equilibrium self-trapping configuration. [The separation is the sum of the self-trapping energy $E_{ST}=-\Delta E_{V_K}(R_e)$ and the energy required to displace all ions to the self-trapping configuration when there is no hole in the crystal.] The assumption that the hole remains completely localized on the self-trapping pair is probably not justified for the excited $^2\Sigma_g{}^+$ state, but we are, at the moment, interested only in energy changes for the ground state near the equilibrium self-trapping configuration.

The lattice energy $E_L(Q)$ of the crystal for the rock-salt structure was developed in I. Taking the zero point of energy to be that of the perfect crystal plus the electron affinity of Cl$^-$, we can write

$$E_L(Q)=\Delta E_M+\Delta E_R+\Delta E_P+\alpha_M e^2/a\,, \qquad (2.7)$$

where ΔE_M represents the change in electrostatic monopole energy due to the presence of the self-trapped hole, ΔE_R is the change in the short-range repulsive energy, ΔE_P is the electronic and ionic polarization energy of the V_K center, and $\alpha_M e^2/a$ is the energy needed to remove an electron from the electrostatic potential of the crystal. The reader is referred to I for the details. These quantities were calculated using a first-order Mott-Littleton procedure[22] with the variational parameters shown in Fig. 1 to characterize the ionic displacements. The calculation was carried out to second order in the variational parameters, resulting in the following expressions for crystals of the rock-salt structure[23]:

$$\begin{aligned}\Delta E_M=(e^2/a)(&-0.177-0.500x-0.354x^2-1.414y\\&+1.207y^2-2.358z+3.426z^2+3.000xy\\&-2.500xz+1.707yz)\,, \qquad (2.8a)\end{aligned}$$

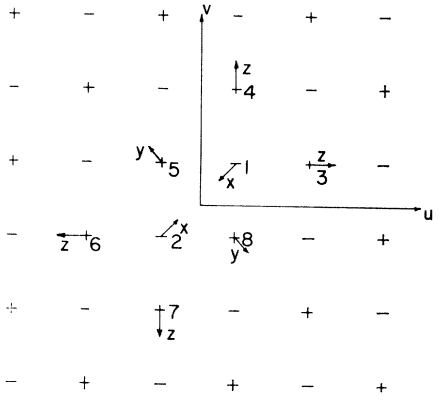

Fig. 1

FIG. 1. Diagrams showing the ions 1–8, which we allow to displace, and their directions of displacement.

$$\begin{aligned}\Delta E_R=(e^2/a)[(\beta-\alpha)(x^2+y^2+2z^2)-(\beta+\tfrac{1}{2}\alpha)xy&\\+\sqrt{2}\beta xz]\,,&\qquad (2.8b)\end{aligned}$$

$$\begin{aligned}\Delta E_P=(e^2/a)(&\gamma_1+\gamma_2x+\gamma_3x^2+0.707M_1'y\\&+0.500M_1'y^2-2.515M_1'z-5.871M_1'z^2\\&-6.000M_1'xy-7.153M_1'xz)\,. \qquad (2.8c)\end{aligned}$$

Here, the variational parameters are in units of the nearest-neighbor distance a. The constants appearing in Eqs. (2.8) are given by

$$\begin{aligned}\alpha&=(4Ba^2/\rho e^2)e^{-a/\rho}\,,\\\beta&=(a/2\rho)\alpha\,,\end{aligned} \qquad (2.9)$$

where B and ρ are the constants in the Born-Mayer short-range repulsive energy formula $Be^{-r/\rho}$ and are determined from the experimental compressibility and nearest-neighbor distance.[24] In Eqs. (2.8), the quantities γ_1, γ_2, and γ_3 are rather complicated expressions involving polarizabilities of the positive and negative ions, the compressibility, and a number of one-center and two-center summations over the lattice sites. The constant M_1' is $(\alpha_+)/a^3$, where α_+ is the polarizability of the positive ions. In obtaining Eq. (2.8c), the term $M_2''=(\alpha'_-)/a^3$ appearing in Eq. (23) of I is not included, since it represents the electronic polarizability of the π electrons of F$_2^-$ and Cl$_2^-$ which is now included in the SCF molecular calculations. We tabulate the quantities appearing in Eqs. (2.8) in Tables I and II for F$_2^-$ and Cl$_2^-$.

To obtain the lattice energy in terms of x, which is related to the internuclear distance of the molecule ion, we minimize Eq. (2.7) with respect to y and z and obtain the following expressions in units of the nearest-neighbor distance a:

$$\begin{aligned}y_0(x)&=b+cx\,,\\z_0(x)&=d+ex\,.\end{aligned} \qquad (2.10)$$

By use of the relation $R=\sqrt{2}(1-2x)$, and Eqs. (2.7) and (2.8), the lattice energy as a function of the internuclear distance of the molecule ion can be ex-

TABLE I. Constants in lattice-energy expressions [Eqs. (2.8a)–(2.8c)] for the alkali fluorides. Repulsive parameters are taken from Table XVII of Ref. 24.

Lattice-energy constants	LiF	NaF	KF	RbF
a (Å)	2.010	2.310	2.665	2.815
ρ (Å)	0.244	0.288	0.302	0.318
$Be^{-a/\rho}$ (10^{-13} erg)	4.05	3.62	2.85	2.70
α	1.163	1.163	1.162	1.167
β	4.797	4.670	5.125	5.163
γ_1	−0.352	−0.365	−0.412	−0.434
γ_2	0.142	0.153	0.177	0.189
γ_3	−0.121	−0.132	−0.157	−0.167
M_1'	0.004	0.033	0.070	0.089

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[22] N. F. Mott and M. J. Kittleton, Trans. Faraday Soc. 34, 485 (1938).

[23] In Ref. 10 there exists an error in sign for the terms linear in z (xz, yz, and z) in ΔE_M and ΔE_R. As a result of this error, ions 3, 4, 6, and 7 have the wrong displacement direction.

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Table II. Constants in lattice-energy expressions [Eqs. (2.8a)–(2.8c)] for the alkali chlorides. Repulsive parameters are taken from Table XVII of Ref. 24.

Lattice-energy constants	LiCl	NaCl	KCl	RbCl
a (Å)	2.572	2.814	3.137	3.270
ρ (Å)	0.332	0.328	0.324	0.338
$Be^{-a/\rho}$ (10^{-13} erg)	3.36	2.78	2.20	2.12
α	1.161	1.163	1.162	1.166
β	4.500	4.982	5.642	5.655
γ_1	−0.353	−0.340	−0.358	−0.380
γ_2	0.147	0.144	0.154	0.165
γ_3	−0.095	−0.099	−0.115	−0.128
M_1'	0.002	0.018	0.043	0.057

Table III. Constants in Eqs. (2.10) and (2.11) for F_2^-.

	LiF	NaF	KF	RbF
A (Ry)	1.067	0.887	0.805	0.749
B (Ry/a)	−0.819	−0.672	−0.652	−0.610
C (Ry/a^2)	0.311	0.257	0.246	0.230
b	0.128	0.127	0.114	0.111
c	0.216	0.298	0.272	0.348
d	0.101	0.109	0.107	0.110
e	−0.222	−0.214	−0.220	−0.218

Table IV. Constants in Eqs. (2.10) and (2.11) for Cl_2^-.

	LiCl	NaCl	KCl	RbCl
A (Ry)	0.806	0.784	0.763	0.723
B (Ry/a)	−0.592	−0.610	−0.630	−0.601
C (Ry/a^2)	0.226	0.232	0.237	0.225
b	0.136	0.122	0.107	0.106
c	0.270	0.304	0.340	0.348
d	0.106	0.100	0.094	0.096
e	−0.214	−0.225	−0.237	−0.236

pressed as

$$E_L(R)=A+BR+CR^2, \tag{2.11}$$

where R is in units of the nearest-neighbor distance of the host lattice. The constants in Eqs. (2.10) and (2.11) are tabulated in Tables III and IV; and for illustration, in Fig. 2, we have plotted $E_L(R)$ for F_2^- and Cl_2^- in LiF and LiCl.

In order to determine the magnetic properties, we require the molecular orbitals to be a function of internuclear distance. The SCF molecular orbitals are expanded into sums of the form

$$\phi_i=\sum_{l,m} c_{i,lm}(\chi_{1,lm}\pm\chi_{2,lm}), \tag{2.12}$$

where

$$\chi_{1,lm}(\mathbf{r}_1)=R_{lm}(r_1)Y_l^m(\theta_1,\phi_1) \tag{2.13}$$

is a normalized atomic component centered on nucleus 1, expressed as a product of a spherical harmonic $Y_{lm}(\theta,\phi)$ and a Slater-type orbital $R_{lm}(r)$. The coefficients $c_{i,lm}$ and potential energy curves $V_{12}(R)$ have been obtained for the ${}^2\Sigma_u{}^+$, ${}^2\Pi_g$, ${}^2\Pi_u$, and ${}^2\Sigma_g{}^+$ states of both F_2^- and Cl_2^-.

III. RESULTS

In Eq. (2.4), by combining the results of the previous section with the SCF-MO calculations of Gilbert[18] and Wahl for the bond energies of F_2^- and Cl_2^-, we obtain the change in energy, ΔE_{V_K}, of the crystal in the presence of a V_K center as a function of the internuclear distance R. This procedure ignores delocalization and also distortion of the molecular orbitals by the crystal environment. As noted above, we have reason to believe that these effects are small for the ground state. Additional support for this assumption is provided by the fact that different host lattices produce only rather small changes in the properties of the V_K center.[25] If the crystal environment introduced any appreciable delocalization or distortion of the localized orbitals, one would expect rather pronounced differences. We will return to this point in Sec. IV. The configuration curves $\Delta E_{V_K}(R)$ obtained in the manner described above are valid for $R\approx R_e$. We shall use them below to determine R_e. Combining this with a calculation of the hyperfine constants as a function of R, we can obtain a predicted hyperfine constant to compare with the experimental value. We can also obtain useful information by comparing the calculated absorption frequencies with observed values, even though the assumption that there is no delocalization is probably not justified for the excited states. We shall first discuss F_2^-.

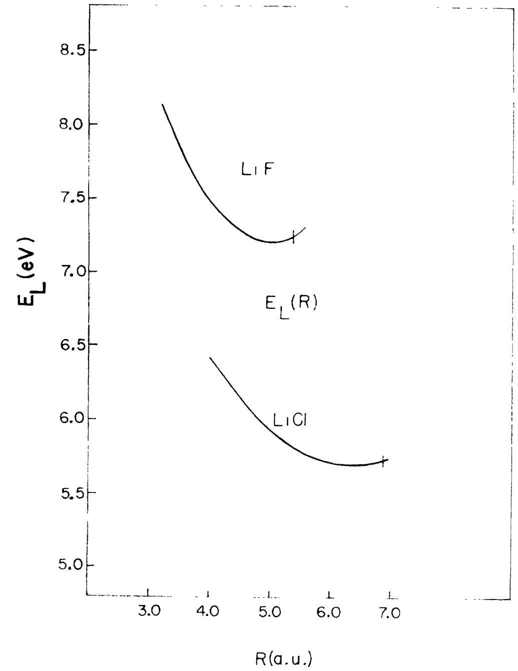

Fig. 2. Lattice energy of LiF and LiCl as a function of R. Vertical bars indicate lattice points of the perfect lattice.

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[25] F. W. Patton and M. J. Marrone, Phys. Rev. **142**, 513 (1966).

F_2^- Center

In Figs. 3 and 4 we have plotted the energy of the free molecule ion and $\Delta E_{V_K}(R)$ for the alkali fluorides, respectively, for the ground and excited states. One notices that the improved molecular calculations give a much deeper potential well than the earlier calculations and that the internuclear distance for LiF at the energy minimum is 4.0 a.u. as compared to 4.72.[10] The effect of the lattice energy is seen to make the curves shallower and to shift the internuclear distance from 3.6 a.u. for the free molecule to the larger distances in the crystals listed in Table V. The slight trend towards increasing R for larger cations is understandable as an effect due to a pushing apart of the molecule ion by the cations at sites 5 and 8 in Fig. 1. One would expect this contribution to become larger for larger cations.

The hyperfine terms of the spin Hamiltonian are taken in the same form as in earlier theoretical[10] and experimental[6] work, namely,

$$H_{\mathrm{hfs}} = a\mathbf{I}\cdot\mathbf{S} + bI_zS_z. \tag{3.1}$$

The constants b and a can be expressed as usual in terms of expectation values over the unpaired $3\sigma_u$ orbital, namely,

$$a_F = (8\pi/3)(\mu_N/I)\,|\phi_{3\sigma_u}(1)|^2, \tag{3.2}$$

$$b = \frac{3}{2}\frac{\mu_N}{I}\langle\phi_{3\sigma_u}|\frac{3\cos^2\theta_1 - 1}{r_1^3}|\phi_{3\sigma_u}\rangle, \tag{3.3}$$

with

$$a = a_F - \tfrac{1}{3}b. \tag{3.4}$$

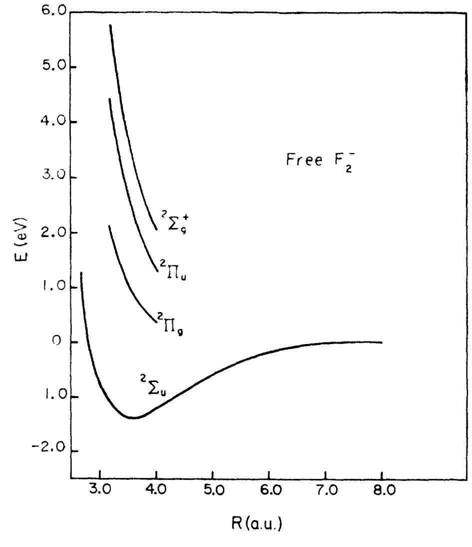

FIG. 3. Potential curves for the ground ($^2\Sigma_u^+$) and excited ($^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_g^+$) states of F_2^-. (From Ref. 18.)

TABLE V. Calculated internuclear distances (R_e) for the F_2^- ion in alkali fluorides.

Crystal	R_e[a]
Free F_2^-	3.6
LiF	4.00
NaF	4.00
KF	4.15
RbF	4.15

[a] Distances R_e are in atomic units (a_0).

TABLE VI. Hyperfine constants in G as a function of internuclear distance for F_2^-. $\Delta g_\perp$ taken to be 0.02.

R (a.u.)	a_F	$\Delta g_\perp b$	a	b	$a+b$
3.6	226.3	17.2	− 60.7	861.2	800.5
3.8	164.4	17.0	−118.1	847.6	729.5
4.0	120.6	16.7	−157.9	835.6	677.7
4.2	89.2	16.5	−185.8	824.9	639.1
4.4	66.4	16.3	−205.3	815.2	609.9
4.6	49.9	16.1	−219.2	807.3	588.1

TABLE VII. Experimental hyperfine constants in G for the V_K center in alkali fluorides. (From Ref. 19.) Constants a and b are defined by Eq. (3.1).

	LiF	NaF	KF	RbF
$a+b$	887	898.1	908.1	908.4
$\|a\|$	58	47	28	...
$b\ \{a>0$	829	851	880	...
$b\ \{a<0$	945	945	936	...

There are additional terms in Eq. (3.1) which arise out of the combined effects of spin-orbit interactions with the nuclear-electron orbital[14] and with the nuclear-electron spin dipolar interactions.[26] Both of these effects may be related approximately to the g-shift tensor. To first order, their combined contribution is given by

$$\begin{aligned} \Delta a &= (\tfrac{5}{6}+\tfrac{1}{4})(g_\perp - g_0)b, \\ \Delta b &= -(\tfrac{5}{6}+\tfrac{3}{4})(g_\perp - g_0)b, \end{aligned} \tag{3.5}$$

where the first numerical coefficient arises from the nuclear-electron orbital interaction and the second from the nuclear-electron dipolar interaction. The above terms are important for the molecule ions with a large spin-orbit interaction. In contrast to the earlier theoretical calculation,[10] no nonorthogonality effects have to be considered, since the molecular orbitals used are orthonormal. All two-center terms in Eqs. (3.2) and (3.3) were included, with Löwdin's[27] α-function techniques being applied to evaluate the two-center integrals of (3.3). It was found that the total contribution from the two-center integrals of (3.3) was nearly zero, since the "distant" terms (both atomic functions centered on site 2 in Fig. 1) were of the same order of magnitude but opposite in sign to the "cross" terms (atomic functions centered on sites 1 and 2). Both types of terms were about two orders of magnitude smaller than the one-center terms for both a_F and b.

In Tables VI and VII we tabulate the calculated

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[26] A. N. Jette, Bull. Am. Phys. Soc. 13, 1670 (1968); (to be published).

[27] P. O. Löwdin, Advan. Phys. 5, 1 (1956); see also, R. R. Sharma, J. Math. Phys. 9, 505 (1968).

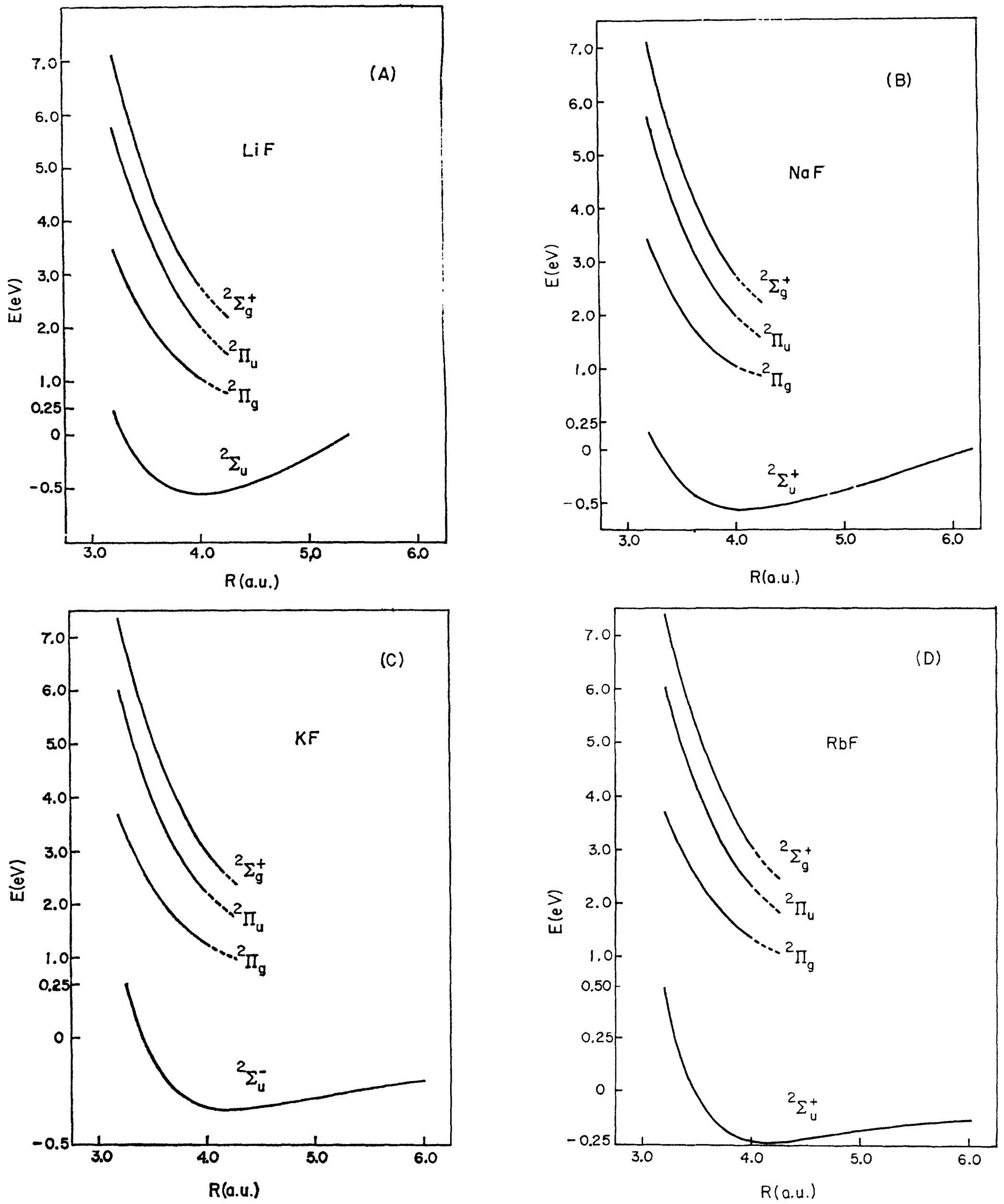

FIG. 4. Potential curves for the ground and excited states of the V_K center in the alkali fluorides.

hyperfine constants as a function of R and the experimental values (as determined by Schoemaker[19]), respectively. These values are essentially the same as those determined earlier by Bailey.[11] The constants at $R=4.0$ a.u. corresponding to the energy minimum for LiF agree better with experiment than the earlier calculation. The sign of a has not been obtained experimentally. From our theoretical results, the sign appears to be negative. This choice would be expected on empirical grounds.[14,19] While improvements in the theory could affect the magnitudes of a significantly, the sign is not expected to change. In Table VII, the two sets of values for b correspond to assuming positive and negative signs for the experimental a used in conjunction with the measured $(a+b)$. The theoretical value of b for LiF is now substantially larger than the earlier theoretical value of 747.3 G and within about 10% of the experimental value. The theoretical value of a is about a factor of 2.5 larger in magnitude than the experimental value. A more meaningful comparison can be made between our theoretical and experimental values of a_F, which arise directly from the Fermi contact term in the hyperfine Hamiltonian. Our theoretical value of $a_F=120.6$ G is about a factor of

2 smaller than the experimental value obtained using Eq. (3.4) and significantly larger than the earlier theoretical result of 33.78 G. This disagreement between theory and experiment is not unexpected in view of the fact that a_F depends on the spin density at one point (the nucleus) and arises out of the s character of the wave function which is very sensitive to the form chosen for the molecular orbitals and the internuclear distance in the crystal, but it is encouraging to note the substantial improvement over the earlier theoretical results. The experimental values of a show some decrease on going from LiF to KF, while our values of R for these crystals would tend to indicate a slight increase. Again this result is not unexpected in view of the uncertainties in our calculated a_F and the neglect of crystal field effects on the molecular orbitals. Both the experimental and theoretical values of b tend to be nearly constant in going from LiF to KF. The better agreement for b is to be expected, since Eq. (3.3) demonstrates that it involves an integration over the wave function rather than its value at one point. Further, it depends on the p character of the molecular orbitals, which are less sensitive to crystal field effects and variations in R.

Dipolar hyperfine constants b of nuclei adjacent to the V_K center in LiF and NaF obtained from ENDOR measurements have been utilized by Daly and Mieher[17,28] to predict the displacements of neighboring ions. The displacements of the nearest-neighbor positive ions can be determined from Eq. (2.10) using our equilibrium internuclear distances for LiF and NaF. These values are tabulated in Table VIII and compared with Daly and Mieher's results. The good agreement between the results of our theoretical calculation and those obtained from experiment lends support to the model we have adopted. Daly and Mieher, however, have also obtained rather large (20–25% of the nearest-neighbor distance) displacements for some of the next-nearest-neighbor F^- ions, which were neglected in our work. These large displacements are puzzling and can perhaps be attributed to the fact that in their analysis of hyperfine data, they treated the F^- ions as unperturbed instead of allowing them to deform upon displacement to sites which lack inversion symmetry.

TABLE VIII. Displacements of nuclei surrounding the V_K center in alkali fluorides in units of the nearest-neighbor distance (2.010 Å in LiF and 2.310 Å in NaF).

	LiF		NaF	
ion	Δu	Δv	Δu	Δv
1[a]	−0.136	−0.136	−0.136	−0.136
1[b]	−0.127	−0.127	−0.176	−0.176
5[a]	−0.100	+0.100	−0.191	+0.191
5[b]	−0.118	+0.118	−0.141	+0.141
3[a]	+0.095	−0.023	...	...
3[b]	+0.061	0	...	...

[a] Daly and Mieher, Refs. 17 and 28.
[b] This work.

TABLE IX. Theoretical and experimental absorption energies and linewidths for the V_K center in the alkali fluorides in eV. (ir = infrared.)

		LiF	NaF	KF	RbF	F_2^-
uv band	Theory	3.30	3.30	2.99	3.00	4.74[a]
	Experiment	3.48[b]	3.38[c]	...	...	...
ir band	Theory	1.60	1.60	1.42	1.46	2.23[a]
	Experiment	1.65[b]	...	...	...	...
Linewidth uv band	Theory	0.99	0.97	0.79	0.68	
	Experiment	1.20[b]	0.66[c]	...	...	
Linewidth ir band	Theory	0.50	0.38	0.44	0.41	

[a] From Ref. 18.
[b] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).
[c] From Ref. 12.

This approximation is more valid for the smaller Li^+ ion than for the larger F^- ions.

The peak optical absorption energies correspond to vertical transitions from the ground-state minima shown in Fig. 4. These are tabulated in Table IX along with the absorption energy for the free molecule ion. The agreement with experiment is reasonable where we have experimental results, and the results for LiF are significantly better than the previous calculation.[10] The fact that the theoretical values are smaller than the experimental values is surprising, however, because one would expect the greatest error to be due to the neglected interaction with the valence band, which would tend to depress the excited level as well as delocalize the excited orbitals. This point will be discussed further below. Also tabulated in Table IX are calculated and measured linewidths. The linewidths are given by[10]

$$\Delta W = 27A(\mu K)^{-1/4}\ \text{eV}, \tag{3.6}$$

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, K is the ground-state force constant in Ry/a_0^2, and a_0 is the atomic unit for distance. Again we have significant improvement over the earlier result for LiF.

Cl_2^- Center

The free-molecule-ion potential curves and ΔE_{V_K} for the alkali chlorides are shown in Figs. 5 and 6 for the ground and excited states, while the equilibrium internuclear distances R_e are listed in Table X. The hyper-

TABLE X. Calculated internuclear distances (R_e) for the Cl_2^- ion in the alkali chlorides.

Crystal	R_e[a]
Free Cl_2^-	5.0
LiCl	5.50
NaCl	5.50
KCl	5.60
RbCl	5.75

[a] Distances R_e are in atomic units (a_0).

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[28] D. F. Daly and R. L. Mieher (to be published).

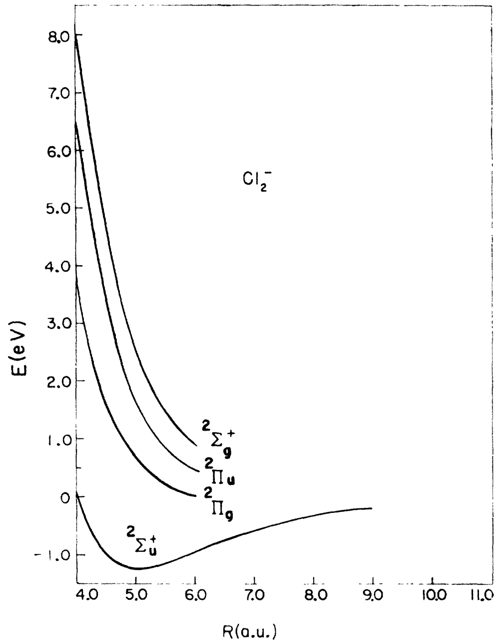

FIG. 5. Potential curves for the ground ($^2\Sigma_u^+$) and excited ($^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_g^+$) states of Cl_2^-. (From Ref. 18.)

fine constants were evaluated using the $\phi_{5\sigma_u}$ orbital for the unpaired electron, and these are tabulated in Table XI as a function of the configuration coordinate R. The experimental values of Schoemaker[19] are given in Table XII.

The choice of the experimental sign of a presents a dilemma. As suggested by Schoemaker[14,19] the correct sign should be that which gives the smaller value for $|\partial b/\partial R|$. This criterion would give $a>0$, which also seems to give better agreement between the calculated and observed values for b. However, it is opposite to the calculated sign of a if we use the calculated values of R_e. We note, however, that a changes sign at a separation very near to the equilibrium value and that the position of the node will be quite sensitive to small errors in the calculated values of a_F and b. In view of this, either a small overestimate of b or R_e, or an underestimate of a_F, could easily lead to a wrong prediction of the sign of a. Since the calculated value of b is less than the predicted value even when a is assumed to be positive, the two most likely possibilities are an underestimate of a_F or an overestimate of R_e. We note that an overestimate of R_e would also resolve a discrepancy in the predicted peak in the optical-absorption spectra, as noted below.

TABLE XI. Hyperfine constants in G as a function of internuclear distance for Cl_2^-. $\Delta g_\perp$ was taken to be 0.04.

R (a.u.)	a_F	$\Delta g_\perp b$	a	b	$a+b$
3.8	105.4	3.0	80.2	75.7	155.9
4.0	85.8	3.2	59.5	78.8	138.3
4.5	48.7	3.2	21.6	81.2	102.6
4.7	38.6	3.2	11.6	81.0	92.6
5.0	27.1	3.2	0.3	80.4	80.7
5.1	24.1	3.2	− 2.6	80.2	77.6
5.5	15.3	3.1	−10.9	78.7	67.8
6.0	8.8	3.1	−16.8	76.9	60.1

TABLE XII. Experimental hyperfine constants in G for the V_K center in the alkali chlorides. (From Ref. 19.) Constants a and b are defined by Eq. (3.1).

		LiCl	NaCl	KCl	RbCl
$a+b$		95.6	98.7	101.3	101.9
$\lvert a\rvert$		8.5	10.5	12.5	13.0
b	$a>0$	87.1	88.2	8.88	88.9
	$a<0$	104.1	109.2	113.8	114.9

TABLE XIII. Theoretical and experimental absorption energies and linewidths in eV for the V_K center in the alkali chlorides. (ir = infrared.)

		LiCl	NaCl	KCl	RbCl	Cl_2^-
uv band	Theory	2.69	2.65	2.37	2.20	3.86[a]
	Experiment	3.15[b]	3.28[b]	3.39[b]	3.40[b]	···
ir band	Theory	1.31	1.35	1.23	1.18	1.87[a]
	Experiment	···	···	1.65[c]	···	···
Linewidth uv band	Theory	0.60	0.45	0.65	0.55	
	Experiment	1.47[b]	1.12[b]	0.81[b]	0.76[b]	
Linewidth ir band	Theory	0.29	0.22	0.27	0.31	
	Experiment	···	···	0.37[c]	···	

[a] From Ref. 18.
[b] From Ref. 13.
[c] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).

The optical-absorption energies and linewidths at half-maximum as obtained from Fig. 6 and Eq. (3.6) are tabulated in Table XIII. The agreement with experiment varies from 15% for LiCl to 35% for RbCl.

IV. CONCLUSIONS

As anticipated in I, the more accurate F_2^- potential curves obtained from SCF-MO calculations have led to substantial improvements in the theoretical predictions of available properties of the F_2^- center in LiF. In addition, for both the F_2^- and Cl_2^- centers in the series of alkali halides considered, there is now reasonable over-all agreement with experiment. In particular, the values of the dipolar hyperfine constant b are within about 10%. The displacements of the nearest-neighbor Li^+ and Na^+ ions have been found to be in substantial agreement with analyses based on the interpretation of the ENDOR data in LiF and NaF. The optical-absorption frequencies and widths are in good agreement with the available experimental data for the fluorides for both the ultraviolet and infrared bands. The theoretical optical-absorption frequencies for the chlorides are all within 35% of experiment.

The agreement between theory and experiment is good enough to give us confidence in the qualitative picture of the structure of a V_K center. However, the remaining quantitative discrepancies merit a more detailed study. Such a study is beyond the scope of

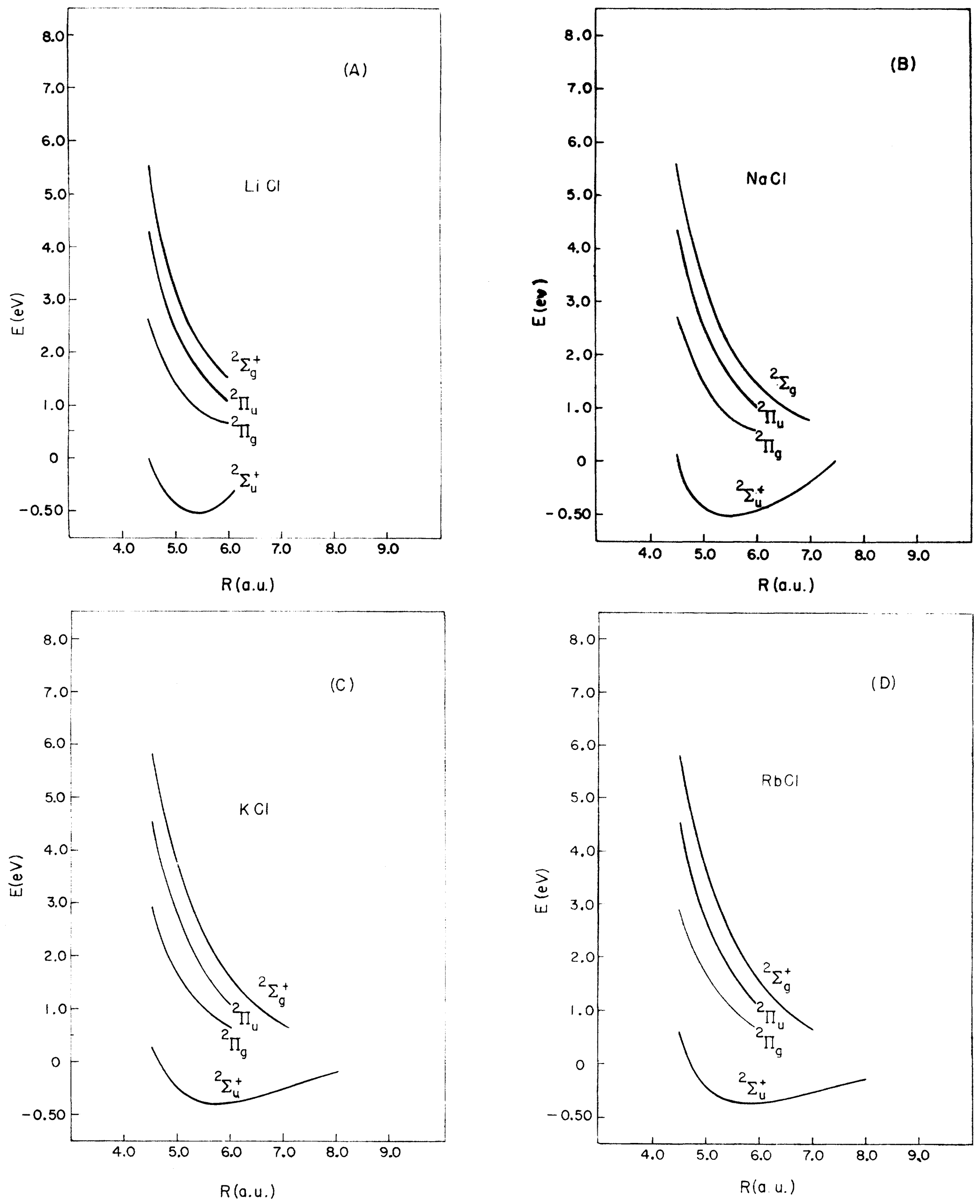

FIG. 6. Potential curves for the ground and excited states of the V_K center in the alkali chlorides.

this work. We will therefore limit ourselves to a discussion of the nature and significance of these discrepancies and the kind of calculations which would be needed to resolve them.

Let us first consider the differences between predicted and observed widths and positions of the optical-absorption curves (the V_K bands). Differences between the optical-absorption curves for an isolated molecule ion and for the same molecule ion embedded in a crystal are expected to arise primarily from two effects: (1) changes in R_e caused by the additional forces provided by the crystal environment, and (2) changes in the energy curve for the $^2\Sigma_g{}^+$ state caused by a mixing of this excited molecular state with the valence band states. This mixing will be much greater for the excited state, which is close to the valence band, than for the ground state. The mixing will also tend to increase as the internuclear distance R approaches the like-neighbor distance for a perfect lattice. The second effect will therefore tend to increase the slope of the excited-state configuration-coordinate curve, which will, in turn, tend to broaden the optical band. Furthermore, one would expect this effect to be greater in LiCl than in RbCl and more pronounced for the chlorides than the fluorides. These trends are, for the most part, in agreement with the observed linewidths in Tables IX and XIII. With the exception of NaF, the observed absorption bandwidths are greater than the predicted values, and the trend is toward broader bands for smaller cations. One could also account qualitatively for the broadening of the absorption bands by an increase in R_e; however, the predicted trend is wrong, since the calculations predict that the internuclear separation for the V_K center increases with increasing cation size, whereas the width of the observed optical-absorption bands decreases. These considerations indicate that although the evidence is by no means conclusive, it is consistent with the assumption that there is an appreciable mixing of the $^2\Sigma_g{}^+$ molecular state and the valence band states of the crystal.

This mixing will cause the hole orbital to spread out onto neighboring halide ions. It will also push the excited molecular level down toward the ground level. We note that the calculated peak values for the absorption bands are consistently smaller than the observed values. A correction for mixing with the valence band would make the predicted peak values still smaller and reduce the agreement. This leaves two likely causes for the discrepancy between observed and predicted peak values: (i) The $^2\Sigma_u{}^+$-$^2\Sigma_g{}^+$ separation for the free molecule ions is larger than indicated by the SCF-MO calculations (which we doubt, but cannot refute until more sophisticated calculations than the present SCF-MO are available); or (ii) the equilibrium internuclear separations are smaller than the values which we have predicted. This latter possibility could lead to an improvement between the calculated and experimental values of a_F. However, a substantial change in R_e for the fluorides could destroy the apparent agreement between our calculated neighboring ion displacements and those determined by Daly and Mieher from ENDOR data.

It is clear, therefore, that further work—in particular, more sophisticated calculations—will be needed before one can claim to have a detailed quantitative understanding of the structure of the V_K center. We suggest that further work should focus on three problems: improving the calculation of $R_e(V_K)$ (which is probably overestimated in our work), improving the calculation of a_F (which is probably underestimated in our work), and taking into account mixing of the valence-band and excited molecular states. Some of the factors that must be considered in making these refinements are indicated below.

In the calculations of the configuration-coordinate curves for the ground state, a likely source of error is in the repulsive potentials used to calculate the displacements. The actual two-body repulsive forces which should be used to calculate the local displacements in the neighborhood of a V_K center may be quite different from the semiempirical two-body forces obtained in the perfect crystal. One should be able to obtain more reliable values for $R_e(V_K)$ by using data obtained from spectroscopic observations on alkali halide diatomic molecules in order to determine the two-body repulsive forces.[29] In addition, no account was taken of the contraction of the Cl^- ions on which the hole is localized. Significant improvements may be obtained by applying corrections to the repulsive forces to take this contraction into account. This would reduce $R_e(V_K)$, which is in the direction needed to resolve the remaining discrepancies.

Refinements in the calculated potential curve for the free molecule ions, taking correlation effects into account, may also be important. Corrections due to distortion of the ground-state molecular orbitals by the crystal environment might be important, but model calculations in which the effect of the crystal environment was simulated by point-ion fields indicated that this effect is probably negligible. Finally, the effect of allowing more ions to relax should also be studied.

The Fermi contact term has a strong R dependence and is also very sensitive to small errors in the wave function. In order to obtain a quantitative check of the theory from the hyperfine data, one must first have a more reliable value for R_e, which could presumably be obtained by introducing the refinements noted above. In order to obtain a more reliable wave function, one needs wave functions for $F_2{}^-$ and $Cl_2{}^-$ which include spin-polarization effects and probably other correlation effects in order to obtain a better estimate of spin-polarization hybridization. In addition, the distortion of the wave functions of the molecule-ion orbitals by the crystal environment should be considered.

The incorporation of these improvements, particularly the mixing of the valence-band state with the molecular states, would require substantially greater effort than has been made so far in the theory of the self-trapped hole centers, and may, in the last analysis, require an SCF calculation for a giant molecule involving the V_K center and its nearest neighbors. However, such efforts should be rewarding, not only in improving our understanding of these interesting centers, but also in furthering our basic understanding of the electronic structure of ionic crystals in general.

ACKNOWLEDGMENTS

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[29] T. L. Gilbert, J. Chem. Phys. **49**, 2640 (1968).