to the axial site centers was detected. The spectra are of tetragonal symmetry, and the g values are given in Table IX. Similar results were also recently obtained by McLaughlan and Newman.[29] The deuterium-site g values show the characteristic small shift from the hydrogen-site g values.

Subsequent endor measurements on the same centers confirm the axial-site model proposed on the basis of the optical measurements. Details of the endor and ESR measurements and results will be reported elsewhere.

VIII. SUMMARY AND CONCLUSIONS

Crystals of CaF_2 containing RE ions which are hydrogenated and subsequently quenched possess two hydrogenic centers exclusively characteristic of the RE impurities. One center consists of a RE-hydride pair aligned along the $\langle 100\rangle$ directions of the crystal. It is a stable impurity configuration in which the hydride ion settles as a charge compensator for the adjacent RE ion. The interaction of the two ions causes new infrared H^- lines to appear. It also causes new electronic lines of the RE ion, an isotope shift in all these lines, and vibronic transitions involving the new H^- local modes.

The other center is an isolated interstitial hydride ion. It can only be detected through its infrared absorption and is only observed in crystals doped with trivalent impurities. It is unstable and in crystals of low RE^{3+} concentration, is converted into the former ion-pair site by slow annealing of the crystal. Irradiation of the hydrogenated crystals by uv or x rays converts the hydride negative ion into a neutral hydrogen atom, which may remain in its previous location or may wander to new sites depending on the ambient temperature. This atom is sometimes located adjacent to a RE impurity, giving rise to vibronic emission of the latter. The vibronic frequency shift is due to the local-mode frequency of the neutral hydrogen.

Due to its small mass, the hydrogen can diffuse rapidly between equivalent and nonequivalent sites. Its motion can be traced by the reversible and irreversible changes in the spectra of different sites.

ACKNOWLEDGMENTS

We wish to express thanks to M. Foguel for growing the doped calcium-fluoride crystals, to A. Kafri for providing us with his ESR results before publication, and to M. Presland for checking lifetime measurements on the gadolinium emission lines. One of us (G.D.J.) wishes to thank the Hebrew University of Jerusalem for making his visit to the University possible.

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ENDOR Hyperfine Constants and Lattice Distortion of V_K-Type Centers*†

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The magnetic hyperfine dipole-dipole interaction between V_K-type centers (negatively charged diatomic halide molecule-ions) and the neighboring lattice nuclei has been calculated for the V_K center in LiF and NaF and the V_{KA} (Li) center in NaF using the F_2^- wave function of Wahl. The calculated hyperfine constants are sensitive to the relative positions of the F_2^- molecule-ion and the neighboring nuclei. When the calculated hyperfine constants were compared with those measured in electron-nuclear double-resonance (ENDOR) experiments, the displacements of the nuclei surrounding the V_K-type centers were determined. In the vicinity of the center, the lattice contracts parallel to the axis of the molecule-ion and dilates perpendicular to this axis. The contact hyperfine interaction has been estimated and compared with the values measured in ENDOR experiments. The sign and order of magnitude of the contact hyperfine constants can be explained by assuming that the closed-shell orbitals of the molecule-ion are exchange-polarized.

I. INTRODUCTION

THE V_K center was discovered by Känzig when he irradiated a KCl crystal at liquid-nitrogen temperature with x rays.[1,2] By studying its electron-spin-resonance (ESR) spectrum, he determined that this center was a Cl_2^- molecule-ion oriented in a [110] direction of the cubic lattice (see Fig. 1). Subsequently the optical absorption of this center was identified by Delbecq, Smaller, and Yuster.[3]

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V_K centers have been produced in practically all of the alkali halides, and their ESR and optical spectra have been studied.[4–8] Also, additional information has been obtained about the surroundings of the V_K center in LiF[9–11] and NaF[12] by means of the electron-nuclear double-resonance (ENDOR) technique.[13] These experiments further confirmed the self-trapped hole model for the center and showed that no other lattice defect was present in the immediate vicinity of the V_K center. Similar ENDOR experiments served to identify a V_K center associated with an alkali impurity (V_{KA} center).[14,15]

These ENDOR experiments measure the hyperfine constants which characterize the magnetic hyperfine interaction between the unpaired electron spin of the V_K center and the spins of the neighboring nuclei. This hyperfine interaction is composed of the isotropic part due to the Fermi contact interaction and the anisotropic part due to the dipole-dipole interaction. The main purpose of this paper is to calculate the dipole-dipole hyperfine constants using Wahl's[16] self-consistent-field (SCF) wave function for the F_2^- molecule-ion.

It will be seen that agreement to within a factor of 2 can be obtained for the dipole-dipole hyperfine constants when the neighboring nuclei are taken to be in their perfect lattice positions. However, semiphenomenological calculations by Das, Jette, Knox, and Gilbert[17,18] have shown that two sets of neighboring alkali nuclei (A and E in our notation) should be appreciably displaced from their perfect lattice positions. We calculate the dipole-dipole hyperfine constants for different positions of these and other sets of neighboring nuclei and select the positions that correspond to agreement with the experimental hyperfine constants. These positions can be compared with the distortion of the lattice predicted by Das *et al.*[17,18] Earlier results of these calculations for the V_K center in LiF have been published by the present authors.[19] In this paper we present the calculations for the V_K and V_{KA} centers in NaF, as well as the most recent results for the V_K center in LiF.

With the nuclei at the positions that give agreement for the dipole-dipole interaction, we can proceed to estimate the contact interaction. The contact interaction is proportional to the total spin density at the ENDOR nucleus, and for most nuclei surrounding the V_K center in LiF this has been found experimentally to be negative,[9,10] i.e., the total spin density at the ENDOR nucleus has polarization opposite to the unpaired spin in the open shell of the F_2^- molecule-ion. An order-of-magnitude estimate of this polarization has been made for all the neighboring nuclei for which ENDOR hyperfine constants have been measured.

II. SPIN HAMILTONIAN AND HYPERFINE CONSTANTS

A. Method of Calculation

If the wave function for the unpaired spin $|V_K\rangle$ is known, then a spin Hamiltonian can be derived as follows:

$$\begin{aligned}\mathcal{H}(\mathbf{S},\mathbf{K}_1,\mathbf{K}_2,\mathbf{I}_1,\cdots,\mathbf{I}_n)&=\langle V_K|\sum_{\kappa=1}^{2}\mathcal{H}_{\text{dipole}}(\mathbf{S},\mathbf{K}_\kappa,\mathbf{r})|V_K\rangle+\langle V_K|\sum_{\kappa=1}^{2}\mathcal{H}_{\text{contact}}(\mathbf{S},\mathbf{K}_\kappa,\mathbf{r})|V_K\rangle+\langle V_K|\sum_{\alpha=1}^{n}\mathcal{H}_{\text{dipole}}(\mathbf{S},\mathbf{I}_\alpha,\mathbf{r})|V_K\rangle\\&\quad+\langle V_K|\sum_{\alpha=1}^{n}\mathcal{H}_{\text{contact}}(\mathbf{S},\mathbf{I}_\alpha,\mathbf{r})|V_K\rangle+\frac{\gamma_e\hbar}{g_0}\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H}_0-\sum_{\kappa=1}^{2}\gamma_\kappa\hbar\mathbf{K}_\kappa\cdot\mathbf{H}_0-\sum_{\alpha=1}^{n}\gamma_\alpha\hbar\mathbf{I}_\alpha\cdot\mathbf{H}_0\\&=\frac{\gamma_e\hbar}{g_0}\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H}_0+\sum_{\kappa=1}^{2}\mathbf{K}_\kappa\cdot\mathbf{T}_\kappa\cdot\mathbf{S}-\sum_{\kappa=1}^{2}\gamma_\kappa\hbar\mathbf{K}_\kappa\cdot\mathbf{H}_0-\sum_{\alpha=1}^{n}\mathbf{S}\cdot\mathbf{B}_\alpha\cdot\mathbf{I}_\alpha+\sum_{\alpha=1}^{n}a_\alpha\mathbf{S}\cdot\mathbf{I}_\alpha-\sum_{\alpha=1}^{n}\gamma_\alpha\hbar\mathbf{I}_\alpha\cdot\mathbf{H}_0.\qquad(1)\end{aligned}$$

The $\langle V_K|\mathcal{H}|V_K\rangle$ is an integral over the spatial function $|V_K\rangle$ and the spatial parts of the operator $\mathcal{H}$. $K_\kappa(\kappa=1,2)$ refers to the spin of one of the nuclei comprising the V_K center; $I_\alpha(\alpha=1,n)$ refers to the spin of a neighboring nucleus in the lattice. For comparison with experiment, the hyperfine constants are sometimes combined into a single tensor $\mathbf{A}=a\mathbf{I}+\mathbf{B}$. In Ref. 15, it is shown how the ESR and ENDOR spectra are fitted to this Hamiltonian. The hyperfine constants determined in these experiments are summarized in Table I.

The first requirement for calculating any of the elements of the spin Hamiltonian is to have a good wave

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TABLE I. Hyperfine constants of V_K-type centers.

	Nucleus	A_x	A_y	A_z	a	B_x	B_y	B_z	θ (deg)
V_K in LiF[a]	A(Li)	-8.060 ± 0.005	$+1.020\pm0.005$	-5.320 ± 0.008	-4.120	-3.940	$+5.140$	-1.200	0
	B(F)	-2.840 ± 0.012	-9.055 ± 0.012	-8.170 ± 0.008	-6.688	$+3.848$	-2.367	-1.482	33.75 ± 1
	C(Li)	$+2.800\pm0.010$	-2.450 ± 0.006	-1.820 ± 0.010	-0.490	$+3.290$	-1.960	-1.330	17.0 ± 1
	D(F)	-3.390 ± 0.014	$+2.710\pm0.012$	-2.360 ± 0.012	-1.013	-2.377	$+3.723$	-1.347	12.0 ± 1
	E(Li)	-1.470 ± 0.010	-1.370 ± 0.008	$+2.360\pm0.008$	-0.160	-1.310	-1.210	2.520	39.0 ± 1
	F(F)	-2.090 ± 0.006	-2.050 ± 0.006	$+13.020\pm0.006$	$+2.960$	-5.050	-5.010	$+10.060$	0
V_K in NaF[b]	A(Na)	-7.15 ± 0.04	-4.10 ± 0.04	-6.36 ± 0.04	-5.87	-1.28	$+1.77$	-0.49	0
	B(F)	$+0.85\pm0.05$	-4.57 ± 0.05	-3.74 ± 0.02	-2.49	$+3.34$	-2.08	-1.25	36 ± 1
	C(Na)	$+1.40\pm0.1$	-1.43 ± 0.06	-1.12 ± 0.05	-0.38	1.78	-1.05	-0.74	19 ± 3
	D(F)	-1.56 ± 0.04	$+3.05\pm0.06$	-1.22 ± 0.03	$+0.09$	-1.65	$+2.96$	-1.31	16 ± 1
	F(F)	-1.10 ± 0.03	-1.10 ± 0.03	-3.95 ± 0.03	$+0.58$	-1.68	-1.68	$+3.37$	0
	G(F)	-1.36 ± 0.15	$+4.40\pm0.30$	-1.22 ± 0.30	$+0.61$	-1.97	3.79	-1.83	$35\pm4\,(z,Z)$ $52\,^{+8}_{-2}\,(x,X)$
V_{KA} in NaF[c]	A(Na)	-6.15 ± 0.04	-3.17 ± 0.04	-5.50 ± 0.04	-4.94	-1.21	$+1.77$	-0.56	0
	A'(Li)	-6.04 ± 0.02	$+1.65\pm0.02$	-4.06 ± 0.02	-2.82	-3.22	$+4.47$	-1.24	0
	B(F)	$+1.34\pm0.06$	-3.94 ± 0.02	-3.22 ± 0.02	-1.94	$+3.28$	-2.00	-1.28	38.7 ± 0.5
	B'(F)	-0.22 ± 0.06	-5.85 ± 0.02	-5.01 ± 0.02	-3.69	$+3.47$	-2.16	-1.32	32.2 ± 0.5
	C(Na)	$+2.20\pm0.5$	-1.55 ± 0.10	-1.10 ± 0.10	-0.15	$+2.35$	-1.40	-0.95	$7.5\pm2\,(y,Y)$ $15\pm5\,(z,Z)$
	D(F)	-1.36 ± 0.02	$+2.52\pm0.08$	-1.10 ± 0.04	$+0.02$	-1.38	2.50	-1.12	16.3 ± 1.5
	D'(F)	-2.77 ± 0.02	$+3.35\pm0.08$	-1.73 ± 0.04	-0.38	-2.39	$+3.73$	-1.35	10 ± 2
	F(F)	-1.06 ± 0.04	-1.06 ± 0.04	$+3.77\pm0.02$	$+0.55$	-1.61	-1.61	$+3.22$	2.5 ± 0.5

[a] See Refs. 9–11. [b] See Ref. 12. [c] See Refs. 14 and 15.

function for the unpaired spin $|V_K\rangle$. While wave functions have not been calculated for the V_K center, they have been calculated by Wahl[16] using a SCF technique for the free F_2^- molecule-ion. The electron distribution in this molecule-ion is compact enough to suggest that it can be fitted into the LiF or NaF lattice without serious distortion. In fact, if this wave function is placed in the crystal lattice in the position of the V_K center, the overlap between the open-shell molecular orbital and the neighboring ion-core orbitals (before displacement of the ions) is less than 0.03 in the largest case (F fluorine) and is less than 0.01 for all other orbitals. For this reason it appears safe to use the F_2^- free molecule-ion wave function as a starting point for a calculation of the dipole-dipole hyperfine constants. Since Wahl's calculations are of the restricted Hartree-Fock type, all of the unpaired spin density comes from the molecular orbital of highest energy ($3\sigma_u$) which contains only one electron. There are, however, two important modifications of these wave functions necessary to give an electron-spin distribution that is satisfactory for the calculation of hyperfine constants.

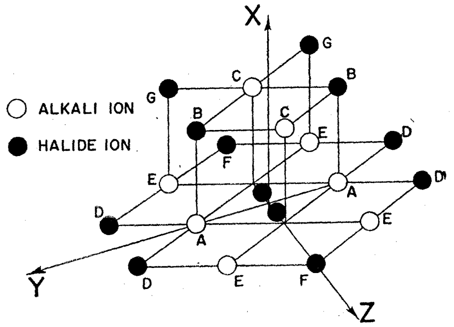

FIG. 1. V_K center and surrounding lattice nuclei.

First of all, within the molecule-ion itself, there is an exchange polarization of the closed-shell molecular orbitals. The exchange interaction between the unpaired (say, spin-up) electron in the $3\sigma_u$ orbital with the spin-up and spin-down electrons in each of the closed-shell orbitals will be different. As a result, the spatial distribution of the electron density in the spin-up and spin-down closed shells is different. Therefore they contribute a net spin density at each point in space that is either parallel or antiparallel to the spin density of the unpaired electron.[20]

Secondly, the wave function of the V_K center must be orthogonal to the wave functions of all the occupied orbitals on the surrounding nuclei in the lattice, if the one-electron expectation value used in deriving the spin Hamiltonian in Eq. (1) is to be valid.[21]

Orthogonalizing by the Gram-Schmidt process gives the following expression for $|V_K\rangle$:

$$|V_K\rangle = N\{|3\sigma_u\rangle - \sum_{l\alpha}\langle 3\sigma_u|\alpha l\rangle|\alpha l\rangle\}, \qquad (2)$$

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where $|\alpha l\rangle$ is the lth ion orbital on the αth site, and

$$N = (1-\sum_{\alpha l} |\langle 3\sigma_u|\alpha l\rangle|^2)^{-1/2}.$$

Orthogonalization to ions other than the one (η) whose ENDOR interaction is being calculated can be ignored, because both the overlap and r_η^{-3} are small for these ions (r_η is the distance between the η site and the electron). Hence the summation over α in Eq. (4) can be dropped. The overlaps, $\langle 3\sigma_u|\alpha l\rangle$, are so small that $N \approx 1.00$.

The elements of the dipole-dipole tensor can now be calculated[22] in the X, Y, Z coordinate system illustrated in Fig. 1:

$$\begin{aligned}\langle V_K|\beta_{ij}|V_K\rangle = N^2\{&\langle 3\sigma_u|\beta_{ij}|3\sigma_u\rangle + \sum_l |\langle 3\sigma_u|\eta l\rangle|^2 \\ &\times \langle \eta l|\beta_{ij}|\eta l\rangle - 2\sum_l \langle 3\sigma_u|\eta l\rangle\langle 3\sigma_u|\beta_{ij}|\eta l\rangle \\ &+ \sum_{l,l';\,l\neq l'} \langle 3\sigma_u|\eta l\rangle\langle 3\sigma_u|\eta l'\rangle\langle l|\beta_{ij}|l'\rangle\}, \quad (3)\end{aligned}$$

where

$$\beta_{ij} = (3x_\eta^i x_\eta^j - r_\eta^2\delta_{ij})/r_\mu^5$$

and

$$x_\eta^1 = x_\eta, \quad x_\eta^2 = y_\eta, \quad x_\eta^3 = z_\eta.$$

The distance between the unpaired electron, which is located by position vector $\mathbf{r}$, and the ENDOR nucleus, which is located by position vector $\mathbf{R}_\eta$, is denoted by $|\mathbf{r}_\eta| = |\mathbf{r}-\mathbf{R}_\eta| = (x_\eta^2+y_\eta^2+z_\eta^2)^{1/2}$ expressed in atomic units (a.u.).[23] Therefore, by comparison with Eq. (2), it is seen that the dipole-dipole term in the spin Hamiltonian can be written

$$\mathcal{H}_{\text{dipole}} = \sum_{i,j=1}^{3} I_i B_{ij} S_j,$$

where

$$B_{ij} = (\gamma_e\gamma_\eta\hbar^2/a_0^3)\langle V_K|\beta_{ij}|V_K\rangle. \quad (4)$$

There are five independent elements in this symmetric traceless matrix. By diagonalizing the matrix, these can be expressed as two principal values and three angles.

In the calculation of the dipole-dipole hyperfine constants described above, we have made the following four approximations:

(1) We use the free molecule-ion wave function. The effect of the crystal field on the $3\sigma_u$ molecular orbit has not been considered. The experimental fact that the ESR hyperfine constants are practically the same for all the alkali fluorides that have been measured[5] suggests that the crystal field does not produce gross distortions of the molecular orbitals. Furthermore, the ESR hyperfine constants and g values and the hyperfine constants of the fluorine F neighboring nuclei are all axially symmetric about the axis of the molecule-ion, even though the crystal has only twofold rotational symmetry in this direction.

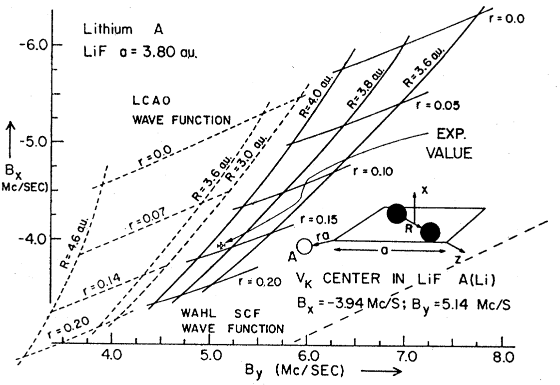

FIG. 2. Comparison of the experimental and the calculated hyperfine constants (B_x and B_y) for the dipole-dipole interaction between the lithium A nucleus and the V_K center in lithium fluoride. Calculations are shown for both the SCF and the LCAO wave functions of the molecule-ion. Calculations are shown for different positions of the lithium nucleus along the Y axis and for different internuclear distances in the molecule-ion. The dashed line in the lower right-hand side of the figure represents the interaction with a point electron magnetic dipole located at the center of the F_2^- molecule.

(2) A one-electron orbital for the unpaired spin of the V_K center is obtained by Gram-Schmidt orthogonalization to free alkali and halide ion orbitals at the sites of the neighboring ions. Crystal field effects and orthogonalization of the ions to each other are not included. This is discussed in Sec. II C 3.

(3) The molecule-ion and the ENDOR nucleus are treated as stationary in the lattice. The effect of lattice vibrations is discussed in Sec. II C 3.

(4) Only the unpaired spin that is in the $3\sigma_u$ orbital orthogonalized to its neighbors is considered. Exchange polarization of the closed-shell orbitals is not included. This is considered in Sec. III.

We have calculated the dipole-dipole hyperfine constants for each nucleus neighboring the V_K center at

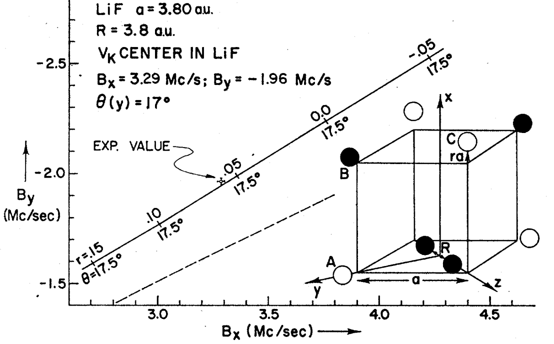

FIG. 3. Comparison of the experimental and the calculated hyperfine constants for the dipole-dipole interaction between the lithium C nucleus and the V_K center in lithium fluoride. The dashed line represents the interaction with a point electron magnetic dipole located at the center of the F_2^- molecule.

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[23] 1 a.u. (atomic unit) = a_0 (Bohr radius) = 0.529 Å.

TABLE II. Displacement of lattice nuclei surrounding the V_K center in LiF.

Displacement from perfect lattice position (in units of LiF nearest-neighbor distance, $a=3.80$ a.u.) Nucleus	ΔX	ΔY	ΔZ	$[(\Delta X)^2+(\Delta Y)^2+(\Delta Z)^2]^{1/2}$	$\delta_{\parallel}$	$\delta_{\perp}$	Molecule-ion internuclear distance (in a.u.)
$V_K(\mathrm{F})$[a]	0	0	−0.192	0.192±0.003			$R=3.91\pm0.01$
$V_K(\mathrm{F})$[b]	0	0	−0.18	0.18			$R=4.0$
$A(\mathrm{Li})$[a]	0	0.141	0	0.141	±0.001		$R=3.8$
$A(\mathrm{Li})$[b]	0	0.167	0	0.167			$R=4.0$
$B(\mathrm{F})$[a]	0.24	0.13	0	0.279	±0.003	±0.020	$R=3.8$
$C(\mathrm{Li})$[a]	0.063	0	−0.016	0.065	±0.002	±0.020	$R=3.8$
$D(\mathrm{F})$[a]	0	0.059	−0.127	0.14	±0.015	±0.05	$R=3.8$
$E(\mathrm{Li})$[a]	0	0.083	0.051	0.095	±0.003	±0.02	$R=3.8$
$E(\mathrm{Li})$[b]	0	0.043	0.043	0.061			$R=4.0$
$F(\mathrm{F})$	0	0	−0.232	0.232	±0.005		$R=3.91$

[a] This work. [b] See Ref. 18.

different displacements from the position they would occupy in the perfect lattice. Because of the r^{-3} dependence and because of the anisotropy of the dipole-dipole interaction, the calculation of the dipole-dipole hyperfine constants is quite sensitive to the relative positions of the V_K center and the ENDOR nucleus. In Figs. 2–8 some of the results of these calculations are displayed. For each displaced position of the neighboring nucleus we have calculated the three dipole-dipole hyperfine constants B_x, B_y, and B_z. Only two of these are independent, since $B_x+B_y+B_z=0$. Therefore the calculated dipole-dipole hyperfine constants for each displaced position correspond to a point on a graph of B_x versus B_y. Also the rotation angle θ required to diagonalize the **B** matrix is calculated and listed for typical points on each diagram. We calculate these constants for a series of displaced positions along the same line as indicated on each graph and the result is a curve on the B_x-versus-B_y plane. Similar curves are calculated for different displacement directions. These curves are then compared with the experimental point (B_x,B_y) to determine at what displaced position the calculated dipole-dipole constants are in agreement with the experimental values. These displaced positions are summarized in Tables II–IV.

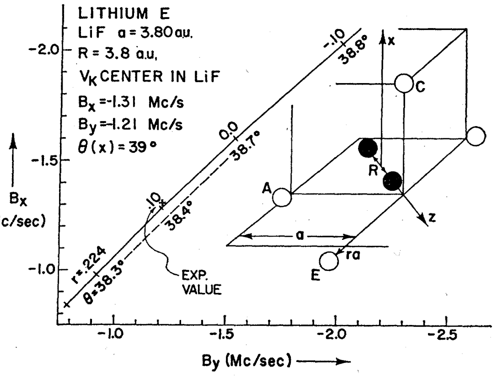


FIG. 4. Comparison of the experimental and the calculated hyperfine constants for the dipole-dipole interaction between the lithium E nucleus and the V_K center in lithium fluoride. The dashed line represents the interaction with a point electron magnetic dipole located at the center of the F_2^- molecule.

B. Results of Static Dipole-Dipole Calculation

1. V_K Center in LiF

The symmetry of the ENDOR spectrum requires that the lithium A lie somewhere along the Y axis. Figure 2 shows that calculated dipole-dipole constants will agree with the experimental constants only if we

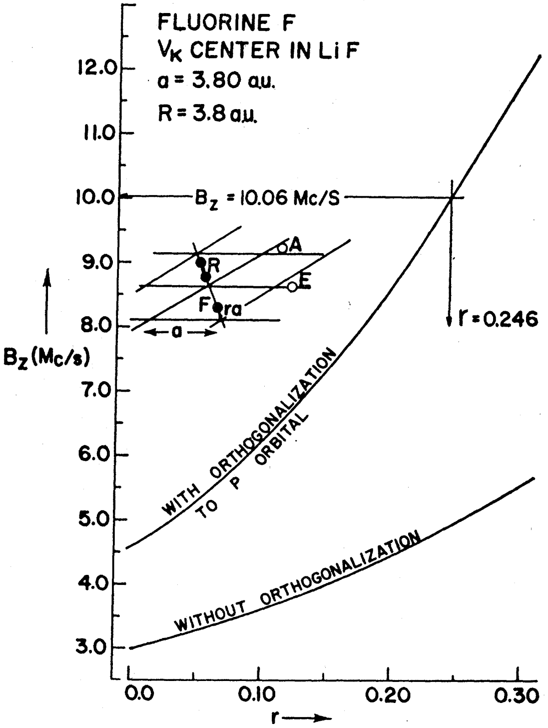


FIG. 5. Comparison of the experimental and the calculated hyperfine constant B_z for the dipole-dipole interaction between the fluorine F nucleus and the V_K center in lithium fluoride. This is a plot of B_z versus displacement of the fluorine F nucleus. Calculations both with and without orthogonalization to the p_z fluorine ion orbital are shown.

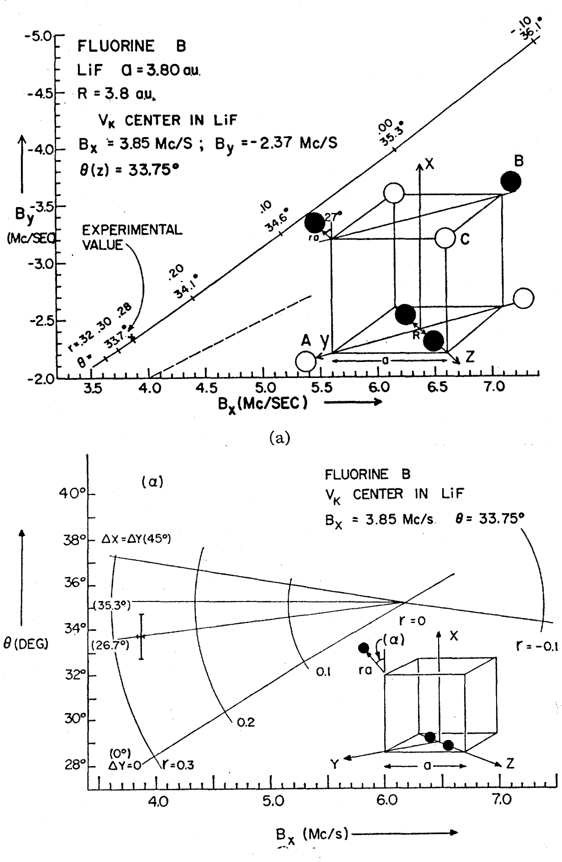
TABLE III. Displacement of lattice nuclei surrounding the V_K center in NaF.

Nucleus	Displacement from perfect lattice position (in units of NaF nearest-neighbor distance, $a=4.37$ a.u.) ΔX	ΔY	ΔZ	$[(\Delta X)^2+(\Delta Y)^2+(\Delta Z)^2]^{1/2}$	$\delta_{\parallel}$	$\delta_{\perp}$	Molecule-ion internuclear distance (in a.u.)
V_K(F)[a]	0	0	−0.193	0.193±0.023			$R=4.50\pm0.10$
V_K(F)[b]	0	0	−0.249	0.249			$R=4.00$
A(Na)[a]	0	0.270	0	0.270	±0.015		$R=4.50$
A(Na)[b]	0	0.20	0	0.20			$R=4.00$
B(F)[a]	0.081	0.081	0	0.115	±0.005	±0.025	$R=4.4$
C(Na)[a]	−0.026	0	0.086	0.09	±0.02	±0.04	$R=4.4$
D(F)[a]	0	−0.030	+0.030	0.042	±0.015	±0.025	$R=4.4$
E(Na)[b]	0	0.0396	0.0396	0.056			$R=4.00$
F(F)[a]	0	0	−0.111	0.111	±0.005		$R=4.5$
G(F)[a]	−0.098	−0.069	−0.100	0.156	±0.05	±0.11	$R=4.4$

[a] This work. [b] See Ref. 18.

displace the lithium A away from its perfect lattice position by $0.141a$, where a is the nearest-neighbor distance. For lithium fluoride, $a=3.80$ a.u. There is also a strong enough dependence of the **B** tensor on the internuclear distance R of the molecule-ion to show that $R=3.91$ a.u. gives agreement. The calculations have been made both by using the SCF wave functions of Wahl[16] and by using a linear combination of atomic orbitals (LCAO) wave function constructed out of tabulated F^- Hartree-Fock atomic orbitals.[24,25]

Wahl[16] has determined that the internuclear distance for his free F_2^- wave function is 3.6 a.u. Das, Jette, and Gilbert,[18] in recent calculations using Wahl's wave function, have obtained a best internuclear distance of 4.0 a.u. for the V_K center in the LiF lattice. They also determine that, for minimum lattice energy, the lithium A should be displaced away from the perfect lattice position by $0.167a$. Notice in Fig. 2 that, even though the two different wave functions would give agreement with the hyperfine constants for very



(a)

(b)

FIG. 6. (a) Comparison of the experimental and calculated hyperfine constants for the dipole-dipole interaction between the fluorine B nucleus and the V_K center in lithium fluoride. Calculated values of B_x versus B_y are shown for displacement of the fluorine B along a line at 27° to the X axis. The principal axis angle θ is also listed for various displacements. The dashed line represents the interaction with a point electron magnetic dipole located at the center of the F_2^- molecule. (b) Dipole-dipole hyperfine constants B_x and θ as a function of displacement magnitude and direction for the fluorine B nucleus.

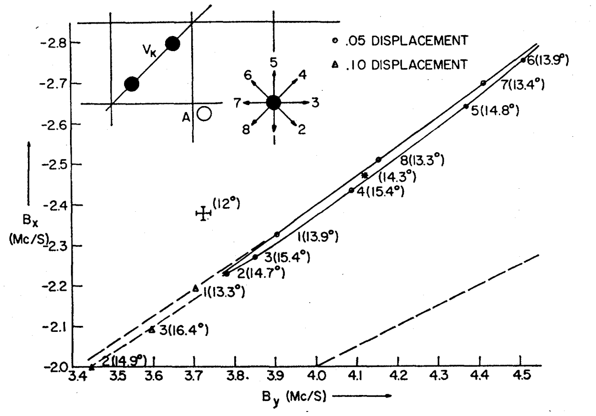


FIG. 7. Experimental dipole-dipole hyperfine constants for the fluorine D nuclei adjacent to the V_K center in LiF ($B_x=-2.38$ Mc/sec, $B_y=+3.72$ Mc/sec $\theta=12°$) are indicated by the cross on this diagram. Also shown are the calculated values of these constants at the perfect lattice position (*) and at positions displaced from it in different directions. The dashed line represents the interaction with a point electron magnetic dipole located at the center of the F_2^- molecule.

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

[25] D. F. Daly, Ph.D. thesis, Columbia University, 1966 (unpublished).

TABLE IV. Displacement of lattice nuclei surrounding the V_{KA} center in NaF.

Displacement from perfect lattice position (in units of NaF nearest-neighbor distance, $a=4.37$ a.u.)							Molecule-ion internuclear distance (in a.u.)
Nucleus	ΔX	ΔY	ΔZ	$[(\Delta X)^2+(\Delta Y)^2+(\Delta Z)^2]^{1/2}$	$\delta_{\parallel}$	$\delta_{\perp}$	
V_K(F)	0	0	-0.222	0.222 ± 0.035			$R=4.25\pm0.15$ [based on A(Na)]
	0	0	-0.273	0.273 ± 0.005			$R=3.80\pm0.02$ [based on A'(Li)]
A(Na)	0	$+0.30$	0	0.30	±0.02		$R=4.25$
A'(Li)	0	$+0.105$	0	0.105	±0.005		$R=3.8$
B(F)	$+0.055$	$+0.137$	0	0.148	±0.010	±0.020	$R=4.4$
B'(F)	$+0.115$	-0.006	0	0.115	±0.010	±0.020	$R=4.4$
C(Na)	-0.102	0	≈0	0.102	±0.015	±0.018	$R=4.4$
D(F)	0	0.035	0.035	0.05	±0.015	±0.040	$R=4.4$
D'(F)	0	-0.161	-0.233	0.283	±0.015	±0.10	$R=4.4$
F(F)	0	0.067	-0.124	0.124	±0.005	±0.015	$R=4.25$

different internuclear distances, the displacement required for the neighboring nucleus would be about the same in both cases. Therefore, despite uncertainties concerning details of the wave function, it is still possible to have considerable confidence in the displacements calculated for the neighbors.

For the lithium C nucleus, as shown in Fig. 3, agreement is obtained between the experimental and theoretical hyperfine constants when the nucleus is moved away from the molecule-ion. Although Das *et al.*[17,18] did not allow the lithium C nucleus to displace, it is expected to move away from the V_K center since it is a positive ion.

The lithium E nucleus, likewise, moves away from the V_K center. Figure 4 shows how the dipole-dipole constants vary as the nucleus is moved along a line 45° to the Y and Z directions. The dipole-dipole hyperfine constants agree for a displacement of $0.095a$. Das, Jette, and Knox[17] state that this nucleus should displace inward. However, recent corrections by Das, Jette, and Gilbert[18] show that it should displace outward in agreement with the dipole-dipole results. They calculate a displacement of $0.061a$.

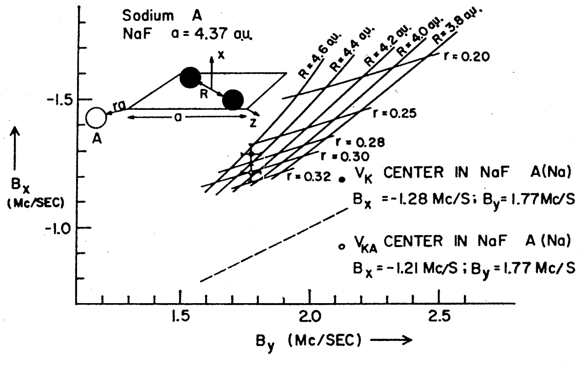

FIG. 8. Comparison of the experimental and the calculated hyperfine constants for the dipole-dipole interaction between the sodium A nuclei and the V_K and V_{KA} centers in sodium fluoride. The dashed line represents the interaction with a point electron magnetic dipole located at the center of the F_2^- molecule.

Since the lithium ion contains only s orbitals, orthogonalization to the ENDOR ion orbitals did not have to be considered in any of these cases. This point will be discussed further in Sec. II C 2.

When we come to calculate the dipole-dipole interaction between the V_K center and the neighboring fluorine nucleus, the effect of orthogonalizing the $3\sigma_u$ orbital to the p orbitals of the fluorine ion[26] must be included. In the case of the fluorine F nuclei, where $\langle 3\sigma_u | p_Z(F)\rangle \approx 0.05$, the contribution to the hyperfine constant from orthogonalization is as large as the contribution from the dipole-dipole interaction between the F nucleus and the $3\sigma_u$ orbital.

The experimental hyperfine interaction between the V_K center and the fluorine F nucleus is almost axially symmetric, i.e., $B_x \approx B_y$. (A 2% deviation from axial symmetry is observed for the fluorine F nuclei neighboring the V_K center in LiF. For the V_K and V_{KA} centers in NaF, the fluorine F hyperfine constants are axially symmetric within experimental error.) Since the sum of the three dipole-dipole constants must be zero, and since in the case of axial symmetry B_z equals $-2B_x$, there is only one independent dipole-dipole hyperfine constant. Therefore it is possible for some displacement of the F fluorines to get agreement for any hyperfine constant. But if orthogonalization to the p orbital is not included, this would require unreasonably large lattice distortions of more than $\frac{1}{2}$ of the nearest-neighbor distance. With orthogonalization to the p orbital, agreement is obtained at a reasonable value, about $\frac{1}{4}$ of a nearest-neighbor distance (Fig. 5).

Orthogonalization is likewise included in the calculations for the fluorine B and fluorine D nuclei. However, the overlap of the fluorine B p orbital with the $3\sigma_u$ orbital is small and the orthogonalization changes the hyperfine constants by less than 0.02 Mc/sec.

In Fig. 7 we present the dipole-dipole hyperfine constants calculated for the fluorine D nucleus as the nucleus is displaced in various directions. The closest

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

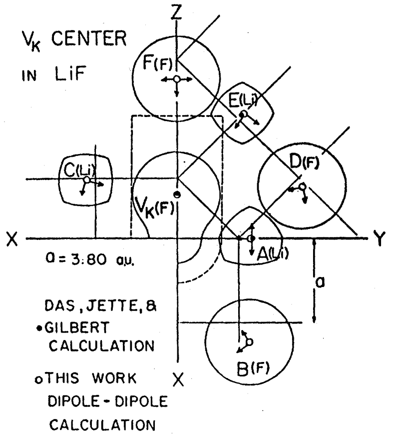

FIG. 9. Displaced positions of the ions surrounding the V_K center in lithium fluoride that give agreement with the measured dipole-dipole hyperfine constants. The electron contours correspond to a density of 0.3 electrons/Å^3 (Ref. 27). Also shown are the positions calculated for the V_K, A, and E nuclei by Das, Jette, and Gilbert (Ref. 18). The arrows indicate the experimental principal axis directions of the hyperfine tensor for each neighboring nucleus. The cylindrical volume enclosed within the dashed lines contains 98.5% of the wave function density for Wahl's $3\sigma_u$ orbital. Uncertainty in the positions of the nuclei due to the experimental uncertainty in the hyperfine constants is comparable to the small circles denoting the nuclear positions.

agreement in magnitude and orientation for the dipole-dipole hyperfine constants is obtained when the nucleus is displaced $0.14a$ at 25° to the $-Z$ direction. The remaining discrepancy, as shown in Fig. 7, is the worst of any set of dipole constants calculated for the V_K or V_{KA} centers.

2. V_K and V_{KA} Centers in NaF

The calculation of dipole-dipole hyperfine constants for a sodium nucleus in the A position in sodium fluoride is presented in Fig. 8. The hyperfine constants measured for the sodium A of the V_K center and the V_{KA} center are both shown on this graph. Because NaF has a larger lattice than LiF, these nuclei are located farther from the F_2^- molecule-ion than the A nuclei in LiF. For NaF, the nearest-neighbor distance a equals 4.37 a.u. As a result, the dipole-dipole hyperfine constants do not depend as sensitively on the internuclear distance of the molecule-ion in NaF as in LiF. The disagreement between the internuclear distance of the molecule of the V_{KA} as determined by the sodium A and lithium A' dipole-dipole calculations (indicated in Table IV) might be due to the bent bond nature of the V_{KA} center which has not been included in these calculations. Also the discrepancy might be due to the fact that the calculations do not include the effect of orthogonalizing the exchange-polarized closed-shell molecular orbitals to the sodium $2p$ electrons (see Sec. III B). Notice in Fig. 2 that the determination of the molecule-ion internuclear distance is sensitive to the choice of wave function, while the magnitude of the displacement of the neighboring ion is quite insensitive. Therefore disagreement on the internuclear distance due to distortions of the wave function does not imply similar uncertainty in the displacement of the neighboring ions.

In both the sodium A and sodium C calculations, the $3\sigma_u$ molecular orbital is orthogonalized to the p orbitals of the sodium ion.[26]

The calculation for the fluorine F nuclei in NaF is very similar to that in LiF. But in this case the nuclei are located farther away, so that both the direct dipole-dipole interaction and the overlap with the p orbital are smaller. The overlap with the p_Z orbital is 0.02 in NaF compared with 0.05 in LiF.

3. Distortion of the Neighboring Lattice

Figures 9–11 show how the ions surrounding the V_K and the V_{KA} centers, whose positions have been determined by the dipole-dipole hyperfine constants, fit together in the lithium fluoride and sodium fluoride lattices. The electron contours in these figures correspond to 0.3 electrons/Å^3 or 0.044 electrons/(a.u.)^3. For the lithium, sodium, and fluorine ions, the density contours were taken from the x-ray diffraction measurements by Witte and Wolfel[27]; for the V_K center the density was taken from Wahl's calculated wave functions. This contour was chosen because it is the lowest one in LiF that closes about the ion. Also the 0.3 electron/Å^3 contour is the lowest contour that remains undistorted for fluorine ions in LiF and for sodium ions in NaCl, so it appears to represent a "hard sphere."

In almost every case there is sufficient room for the neighboring ions to assume the displaced positions determined by the dipole-dipole calculation without the

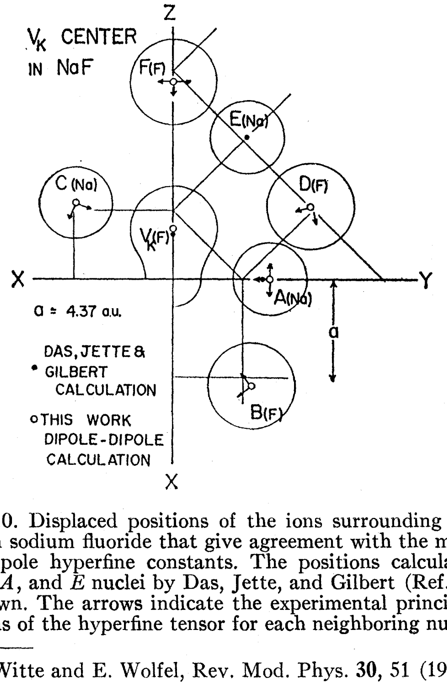

FIG. 10. Displaced positions of the ions surrounding the V_K center in sodium fluoride that give agreement with the measured dipole-dipole hyperfine constants. The positions calculated for the V_K, A, and E nuclei by Das, Jette, and Gilbert (Ref. 18) are also shown. The arrows indicate the experimental principal axis directions of the hyperfine tensor for each neighboring nucleus.

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[27] H. Witte and E. Wolfel, Rev. Mod. Phys. 30, 51 (1958).

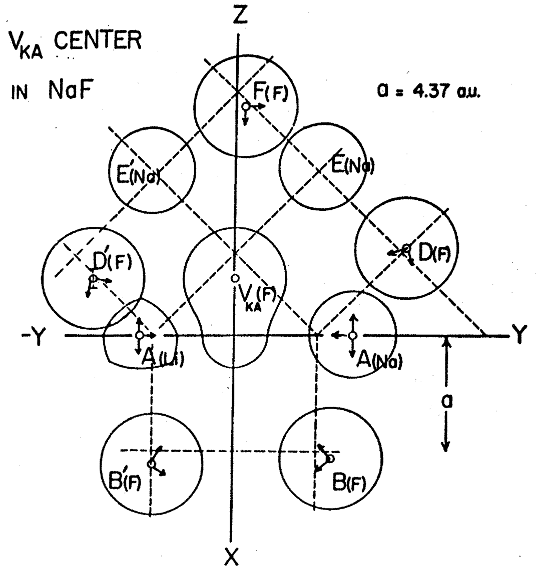

FIG. 11. Displaced position of the ions surrounding the V_{KA} center in sodium fluoride. The choice between primed and unprimed nuclei is made to be consistent with a picture of the molecule-ion moving toward the small lithium A' impurity. For the same reason the F fluorine and the C sodium are placed on the A sodium side of the center. The arrows indicate the principal axis directions. For completeness the sodium E position of Das, Jette, and Gilbert (Ref. 18) for the V_K center has also been included.

"hard spheres" overlapping. For the fluorine D' of the V_{KA} center, the D' and the lithium A' do overlap; however, the magnitude of the ion displacement in this case is determined largely by fitting the principal axis orientation. Experimentally, it was difficult to determine this orientation, which has resulted in the larger than usual error limits assigned to the rotation angle (±2°). This implies an uncertainty in the position of the D' nucleus which includes values around 12° for which there is no overlap of the "hard spheres." This uncertainty is indicated by error bars on Fig. 11.

For the V_{KA} center, the displacements are shown on lattice coordinates fixed with respect to the molecule-ion. These do not coincide with the lattice coordinates of the crystal far from the defect. It is to be expected that a [110] line through the distant lattice sites is closer to a line through the fluorine F nuclei rather than through the molecular nuclei of the V_{KA} center. There is no unambiguous method of distinguishing the primed nuclei (those on the side of the center adjacent to the lithium impurity) from the unprimed nuclei. Likewise, there is no unambiguous way of determining whether the C and F nuclei are displaced to the side of the lithium impurity or away from it. However, since one expects that the molecule-ion is displaced toward the smaller neighbor, the lithium impurity, the primes are assigned to the neighbor with the larger hyperfine interaction. These assignments were initially made on the basis of the contact interaction.[14,15] The primed sites were chosen to be the ones with the larger contact interaction. On the basis of the dipole-dipole constants, the assignments of primed and unprimed sites remain the same. The F and likewise the C nuclei are expected to remain closer to the perfect lattice positions and hence they are left behind. When the molecule-ion displaces, they remain on the side of the sodium A.

Also plotted in Figs. 9 and 10 are the positions of the V_K center fluorines and the A and E neighbors determined in the calculations of Das, Jette. and Gilbert.[18] They minimized the total energy of the molecule-ion and the lattice with respect to the displacement of these three sets of nuclei. In each case the displacements calculated by fitting the dipole-dipole hyperfine constants agree in direction and within about 40% in magnitude of the displacement. These agreements for such completely different theoretical approaches are encouraging. The large displacements indicated for the other neighboring nuclei indicate that future energy calculations, such as those of Ref. 17, should allow more neighbors to move.

C. Discussion

1. Uniqueness of Calculated Displacements

In Figs. 2–8 we have presented the calculated dipole-dipole hyperfine constants as the ENDOR ion is moved along a particular direction in the lattice. For nuclei such as A and F, the line of displacement is fixed by the symmetry of the ENDOR spectrum. For other nuclei, the displacements are restricted to a given plane by symmetry, i.e., the B nuclei are restricted to the XY plane. We have calculated the dipole-dipole hyperfine constants for various nuclear positions within these allowed planes. Two questions arise about our choice of the "best position" to fit the measured hyperfine constants:

(1) Is the agreement forced by the variation of enough parameters to fit any conceivable experimental results? That this is not so can be shown in the following way. It is seen in Fig. 2 that varying the displacement of the lithium A nucleus and the internuclear distance of the V_K center through physically reasonable values only allows coverage of a certain restricted region of the B_x-versus-B_y plane. The fact that the experimental values lie within this region suggests that the calculation is physically correct. The situation is even more restrictive for nuclei like the fluorine D shown in Fig. 7. No matter what direction of displacement we choose for these nuclei, as long as we keep the magnitude of the displacement within physically reasonable limits, all calculated values lie on practically the same line in the B_x-versus-B_y plane.

Only in the case of the A and F nuclei do the number of independent variables equal the number of constants to be fitted. There are two independent variables in the case of the A nuclei: displacement in the Y direction and the V_K-center internuclear distance. Only the calculation for the A nuclei is particularly sensitive to the position of the nuclei in the molecule-ion. Therefore, we use this calculation to determine the internuclear distance, but then keep it fixed for the calculation of the hyperfine constants of all the remaining neighbors.

Results for the fluorine B nuclei give the clearest indication that the agreement between the calculated and the measured hyperfine constants is not merely the result of varying enough parameters. For the fluorine B nuclei, *two* independent hyperfine constants B_x and B_y are obtained by varying only *one* parameter, the distance between the axis of the molecule-ion and the B nuclei. Therefore, no matter what the direction of displacement is, the calculated B_x and B_y must lie on the solid line drawn in Fig. 6(a). The fact that this calculated line, based only on Wahl's wave function and the dipole-dipole interaction, does pass within twice the experimental error (± 0.012 Mc/sec) for the V_K center in LiF suggests that the agreement is physically significant. The orientation of the principal axis is a function of the direction of the nuclear displacement alone. In fact, the angle between the hyperfine principal axis x and the coordinate axis X is simply the angle between the X axis and a line joining the center of the molecule-ion to the B nucleus. The dependence of the orientation of the principal axes on the direction of the displacement for the fluorine B nuclei is shown in Fig. 6(b).

(2) A related question is whether the choice of "best position" is unique or whether there is a locus of positions throughout space that will give equally good agreement with the experimental values. For nuclei that have more than one degree of freedom, a locus of positions sometimes exists that gives equally good agreement with the *magnitudes* of the hyperfine constants. But once we require agreement with the *direction* of the principal axis as well, then the positions at which equivalent agreement might be obtained are limited to a small region of space.

In Tables II–IV, there are two different uncertainties listed for the position of the neighboring nuclei. The uncertainty along the line joining the molecule-ion and the neighboring nucleus due to uncertainty in the magnitudes of the hyperfine constants, called $\delta_{\parallel}$, is typically $\pm 0.01a$. These calculations are most sensitive to the distance between the molecule-ion and the ENDOR nucleus. The dipole-dipole interaction depends on this distance as r^{-3}. The uncertainty in position perpendicular to this line, which is due to uncertainty in the orientation of the principal axes, is called $\delta_{\perp}$ and is typically $\pm 0.02a$.

The quoted error limit on the position of each neighboring ion is merely the uncertainty in position that is a consequence of the experimental uncertainty in the measured hyperfine constants and principal axis orientation. Hence it does not include any uncertainty due to physical effects that would modify the orthogonalized, static, dipole-dipole calculation.

2. *Accuracy of the Calculation*

The integrals required to evaluate the various terms of Eq. (3), i.e., (a) $\langle 3\sigma_u|\beta_{ij}|3\sigma_u\rangle$, (b) $\langle 3\sigma_u|p_k\rangle$, and (c) $\langle 3\sigma_u|\beta_{ij}|p_k\rangle$ ($k=x$, y, or z), were performed by dividing the space surrounding the V_K center and the ENDOR nucleus into small boxes (approximately $\frac{1}{4}$ of a Bohr radius on each side), evaluating the integrand at the center of each box, and summing over all the boxes.[25] This method is likely to be inaccurate in regions of space where the integrand changes rapidly within the dimensions of the box. But for evaluating terms like (a) and (b), the only regions where the integrand changes rapidly are regions where the integrand itself is so small that it makes a negligible contribution to the result. In fact, we have used this method to recalculate the ESR dipole-dipole hyperfine constant that had been calculated using more accurate techniques by Jette,[28] and our answers agree to within $\frac{1}{2}\%$. This is a calculation like that of (a). We have also used this technique to evaluate the normalization integral of the $|3\sigma_u\rangle$ and the $|p_k\rangle$ orbitals. If the boxes with sides of $\frac{1}{4}$ of a Bohr radius are used, these integrals are accurate to about 2%. However, in the regions where the function is varying rapidly, boxes of 0.05 and 0.01 Bohr radius on a side can be used, and then the integral is accurate to about 0.2%. This calculation is similar to that of (b). We have used these smaller box sizes in evaluating the integrals for the fluorine F nucleus in the region of space surrounding the F nucleus.

Integrals like (c) cannot be evaluated as accurately, but these terms contribute 1% or less to the dipole-dipole constants. Therefore the estimated errors of 10% in these terms will contribute only 0.1% error to the calculated dipole-dipole constant.

Similar to the p-overlap cross terms, there are also s-overlap cross terms, such as $\langle 3\sigma_u|s\rangle\langle s|\beta|3\sigma_u\rangle$, which have not been included in this calculation because our technique for evaluating the integrals fails for the $\langle s|\beta|3\sigma_u\rangle$ term. However, we have calculated this term for the case of the fluorine F nucleus using another technqiue.[29] The contribution from the $\langle 2s|3\sigma_u\rangle \langle 3\sigma_u|\beta|2s\rangle$ term is less than $1\frac{1}{2}\%$ of the contribution from the $|\langle p|3\sigma_u\rangle|^2\langle p|\beta|p\rangle$ term. The cross term involving the 1s orbital is at least one order of magnitude smaller. Since the overlap to the p orbitals contributes about half of the dipole-dipole hyperfine constant for the fluorine F nuclei, this would cause an error of about $\frac{3}{4}\%$ in the calculated constant. For other nuclei, where the contribution to the hyperfine constants from orthogonalization to the p orbitals is calculated to be less than 10%, the additional contributions from the s cross terms will be negligible.

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[28] A. N. Jette, Ph.D. thesis, University of California, Riverside, 1964 (unpublished).

[29] This calculation was performed using a computer program prepared by A. N. Jette.

TABLE V. Amplification factors for the contact hyperfine interactions.[a]

Ion	Amplication factor (A_α)
Li^+	57
F^-	350
Na^+	256

[a] See Ref. 21.

3. *Additional Effects*

Some additional physical processes that could modify the results of the semiclassical static dipole-dipole calculation are now considered.

These calculations have assumed a static lattice in which the relative positions of the molecule-ion and the neighboring nuclei are fixed. In fact, all these nuclei are undergoing zero-point and thermal vibrations, which result in an average hyperfine interaction[30]:

$$\langle \mathbf{B} \rangle_{\mathrm{av}} \approx \mathbf{B}(r_0) + \frac{1}{2} \frac{\partial^2 \mathbf{B}}{\partial r^2}\bigg|_{r_0} \langle (r-r_0)^2 \rangle. \tag{5}$$

Since we have shown experimentally that the hyperfine interaction does not change between the temperatures of ≈20 and ≈80°K, it is reasonable to assume an effective characteristic temperature for vibrations around the molecule-ion of 100°K or more. On this basis, the *change* in the hyperfine constants due to the second term in the equation above has a negligible effect on the calculation of the displaced positions.

The ENDOR dipole-dipole hyperfine constants, particularly those of the fluorine F nuclei, depend on the orthogonalization of the wave function for the unpaired spin to the closed-shell orbitals on the surrounding ions. Spaeth[31] has considered that the orbitals on the ions neighboring the paramagnetic center must be orthogonal to each other as well as to the wave function of the center. This results in replacing the overlap term in Eq. (3), $\langle 3\sigma_u | l \rangle$, by $\langle 3\sigma_u | l \rangle - \sum_n \langle 3\sigma_u | n \rangle \langle n | l \rangle$, where n is summed over all the ions neighboring l. Using our numerical integration for calculating the overlap between $|3\sigma_u\rangle$ and the neighboring ion orbitals, and using the results of Hafemeister and Flygare[32] for the overlap between ions in the perfect lattice, we can estimate $\sum_n \langle 3\sigma_u | n \rangle \langle n | l \rangle$. Since the overlap between the V_K center and the neighboring ion is small (the largest case is that of the fluorine F ion in LiF, where the overlap is 0.05), these products of overlaps turn out to be negligible.

Since the F_2^- molecule-ion replaces two F^- ions in the crystal, it will appear in the lattice to carry a single positive charge. The field from this charge will induce electric dipole moments on the surrounding ions, thereby changing the charge distribution of these ions. We have estimated that this could produce an admixture of about 5% of a $3p$ orbital on the neighboring fluorine site. This would make no significant change in the calculated dipole-dipole constant.

In order to explain the ESR and ENDOR hyperfine constants of the U_2 center, Cho, Kamimura, and Uemura[33] considered configuration mixing between the open-shell center with closed-shell neighbor configuration and the closed-shell center with open-shell neighbor configuration. While in principle there could also be such configuration mixing for the V_K center, the fact that the V_K wave function is compact implies that the overlap between these configurations is small. Since the energy difference between the configurations is also appreciable, the configuration mixing should be negligible. We have not made a quantitative estimate of this effect.

The effects of exchange polarization on the dipole-dipole interaction are discussed in Sec. III B.

III. EXCHANGE POLARIZATION

A. Contact Interaction

As indicated in Eq. (1), the isotropic hyperfine interaction between the unpaired spin and the neighboring ENDOR nucleus results from the Fermi contact interaction:

$$\mathcal{H}_{\mathrm{contact}} = (8\pi/3)\gamma_e \gamma_\alpha \hbar^2 \mathbf{I}_\alpha \cdot \mathbf{S} \delta(\mathbf{r} - \mathbf{R}_\alpha), \tag{6}$$

$$\begin{aligned} \langle V_K | \mathcal{H}_{\mathrm{contact}} | V_K \rangle = (8\pi/3)\gamma_e \gamma_\alpha \hbar^2 \mathbf{I}_\alpha \cdot \mathbf{S} | | V_K(\mathbf{R}_\alpha) \rangle |^2 \\ = a_\alpha \mathbf{I}_\alpha \cdot \mathbf{S}. \end{aligned} \tag{7}$$

Hence the contact interaction constant is proportional to the total spin density at the site of the ENDOR nucleus.

To construct the V_K-center wave function, the $3\sigma_u$ orbital of the molecule-ion must be orthogonalized to the closed shells of the neighboring ions, as described in Eq. (2). Only the s orbitals on the ENDOR ion in question make a contribution to the contact interaction. However, that contribution, unlike the orthogonalization to the s orbitals changes the wave-function density, hence the contact interaction, by two to three orders of magnitude. Following the approach of Gourary and Adrian,[21] we can approximate Eq. (2) for the s orbitals at the site of the nucleus as follows:

$$\begin{aligned} | V_K(R_\alpha) \rangle &= N\{ | 3\sigma_u(R_\alpha) \rangle - \sum_l \langle 3\sigma_u | s_l \rangle | s_l(R_\alpha) \rangle \} \\ &\approx N | 3\sigma_u(R_\alpha) \rangle \{ 1 - \sum_l \langle 1 | s_l \rangle | s_l(R_\alpha) \rangle \} \\ &= | 3\sigma_u(R_\alpha) \rangle (A_\alpha)^{1/2}, \end{aligned} \tag{8}$$

where it is assumed that $|3\sigma_u\rangle$ is practically constant over the volume in which $|s_l\rangle$ is nonzero. The amplification factor A_α depends only on the s orbitals of the

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[30] W. M. Walsh, J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965).

[31] J. M. Spaeth, Z. Physik **192**, 106 (1966).

[32] D. W. Hafemeister and W. H. Flygare, J. Chem. Phys. **43**, 795 (1965).

[33] K. Cho, H. Kamimura, and Y. Uemura, J. Phys. Soc. Japan **21**, 2244 (1966).

ENDOR ion and has been evaluated by Gourary and Adrian.[34] These factors are listed in Table V. The Gourary-Adrian amplification factors have been used since this is consistent with the other approximations made in these calculations.

However, when ENDOR measurements on the V_K center in LiF[9,10] revealed that most contact hyperfine constants were negative, it was realized that the contact constant could not be explained merely by the Fermi contact interaction between the neighboring nucleus and the unpaired spin in the $3\sigma_u$ orbital orthogonalized to the ion cores. Since we calculate the dipole-dipole constant using the distribution of unpaired spin in the $3\sigma_u$ orbital of the F_2^- molecule-ion, a negative contact constant a indicates that the spin at the site of the ENDOR nucleus is polarized in the opposite sense from the spin in the $3\sigma_u$ orbital. Furthermore, the largest negative contact interactions are found for the A and B nuclei which lie on the XY plane which bisects the F_2^- molecular bond. This is a nodal plane for the $3\sigma_u$ orbital and, in a one-electron picture, the contact interaction would be expected to be zero for nuclei in this plane.

Two mechanisms would seem capable of explaining the negative contact interaction including the case of zero unpaired spin density at the ENDOR nucleus.

(1) Even if the ENDOR nucleus lies in a nodal plane of the $3\sigma_u$ orbital, there will be an overlap between the $3\sigma_u$ orbital and the ENDOR ion core. This can result in an exchange polarizations of the ion electrons which could produce a negative contact interaction. We have calculated this overlap in several cases and can estimate its order of magnitude. As shown in Refs. 9 and 10, this effect is at least two orders of magnitude smaller than the observed contact hyperfine constants.

(2) Another mechanism that would provide negative contact interactions is exchange polarization of the closed-shell molecular orbitals of the F_2^- molecule-ion. Since unrestricted Hartree-Fock molecular orbitals have not been calculated for molecular systems like the F_2^-, it was necessary in Refs. 9 and 10 to use F^- ion wave functions[34] plus calculations of the exchange polarization for the fluorine atom[35] to construct linear combination of atomic orbitals molecular orbitals (LCAO-MO) that included an estimate of the exchange polarization. This was shown to give order-of-magnitude agreement for the contact hyperfine constants of ENDOR nuclei surrounding the V_K center in LiF.[9,10]

We have recalculated this estimate of the contact hyperfine constant for ENDOR nuclei surrounding the V_K center in LiF and also the V_K and the V_{KA} centers in NaF using the SCF wave functions of Wahl[16] and a similar estimate of the exchange polarization based on the fluorine atom calculations by Goodings.[35] These new calculations are also only order-of-magnitude estimates, but they show that the results of Refs. 9 and 10 were not just an accident due to the LCAO-MO. Also, a new estimate of the polarization was necessary for the investigation of possible effects on the dipole-dipole interactions which are discussed in Sec. III B.

The unrestricted Hartree-Fock wave functions of Goodings for the $2p$ orbitals of the fluorine *atom* may be approximated in the following way:

$$|2p_{F\uparrow}\rangle \approx \left(\frac{3}{4\pi}\right)^{1/2} \frac{P(r)+\frac{1}{2}\Delta P(r)}{r} \cos\theta,$$

$$|2p_{F\downarrow}\rangle \approx \left(\frac{3}{4\pi}\right)^{1/2} \frac{P(r)-\frac{1}{2}\Delta P(r)}{r} \cos\theta,$$

where

$$\Delta P(r) = P_\uparrow(r) - P_\downarrow(r), \quad P(r) = \tfrac{1}{2}[P_\uparrow(r) + P_\downarrow(r)].$$

Then the net spin density in a $2p$ closed shell is

$$\begin{aligned} &||2p_{F\uparrow}\rangle|^2 - ||2p_{F\uparrow}\rangle|^2 \\ &\qquad = \frac{3}{4\pi} \frac{P(r)^2}{r^2} \cos^2\theta \, 2\frac{\Delta P(r)}{P(r)} \\ &\qquad = ||2p_F\rangle|^2 2\frac{\Delta P(r)}{P(r)} \equiv ||2p_F\rangle|^2 \Delta\pi(r). \end{aligned}$$

Since the polarization depends on the density of the unpaired spin, we can express $\Delta\pi(r)$ as a function of $||2p_F\rangle|^2$, i.e., $\Delta\pi(||2p_F\rangle|^2)$. This result as deduced from Goodings calculation is presented in Fig. 12.

Using this definition of $\Delta\pi$, we then determine the spin density for a closed shell λ of the F_2^- molecule-ion:

$$\rho_\lambda = ||\lambda\rangle|^2 (\tfrac{1}{2}\Delta\pi) K \langle ||V_K\rangle|^2 \rangle_{\text{av}}.$$

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[34] The approximations involved in the use of the Gourary-Adrian amplification factors are probably better than the crude estimates of the exchange polarization and the neglect of crystal field distortions of the molecular orbitals. Therefore, we did not calculate the exact overlaps between the F_2^- molecular orbitals and the ENDOR ion s orbitals except for the fluorine F position, where the overlap with the $3\sigma_u$ orbital is large. For this case the exact calculation gives a positive contribution to the a value of 12.37 Mc/sec, whereas the use of the amplification factor of 350 gives 4.90 Mc/sec. Part of this difference could result from the use of different wave functions. However, Edward Y. S. Lee of Purdue University has calculated the amplification factors for some ions using the Bagus (see Ref. 26) wave functions. These values for A_α are 256, 180, and 805 for F^-, Na^+, and Cl^-, respectively. These are to be compared with the values of 350, 260, and 1500 given by Gourary and Adrian (Ref. 21). Therefore, the amplification factor of 256 gives only 3.58 Mc/sec compared to the 12.37 Mc/sec from the exact overlap calculations. This difference of a factor of 4 is caused by approximating the rapidly decreasing tail of the $3\sigma_u$ function by a constant value (the density at the nucleus of the unorthogonalized function) in the amplification factor approximation. If this factor-of-4 difference holds for other lattice positions (it should be less for the smaller Li^+ ion), then we could reduce our estimate of the polarization by 4 and keep the same numbers in Table V. This may indicate that we have overestimated the polarization. However, the values in Tables VI-VIII are intended to demonstrate the physical origin of the contact interaction by an order-of-magnitude estimate. Therefore, we did not believe that it was worthwhile to calculate exact overlaps for the other ion positions.

[35] D. A. Goodings, Phys. Rev. **123**, 1706 (1961); Ph.D. thesis, Cambridge University, 1960 (unpublished).

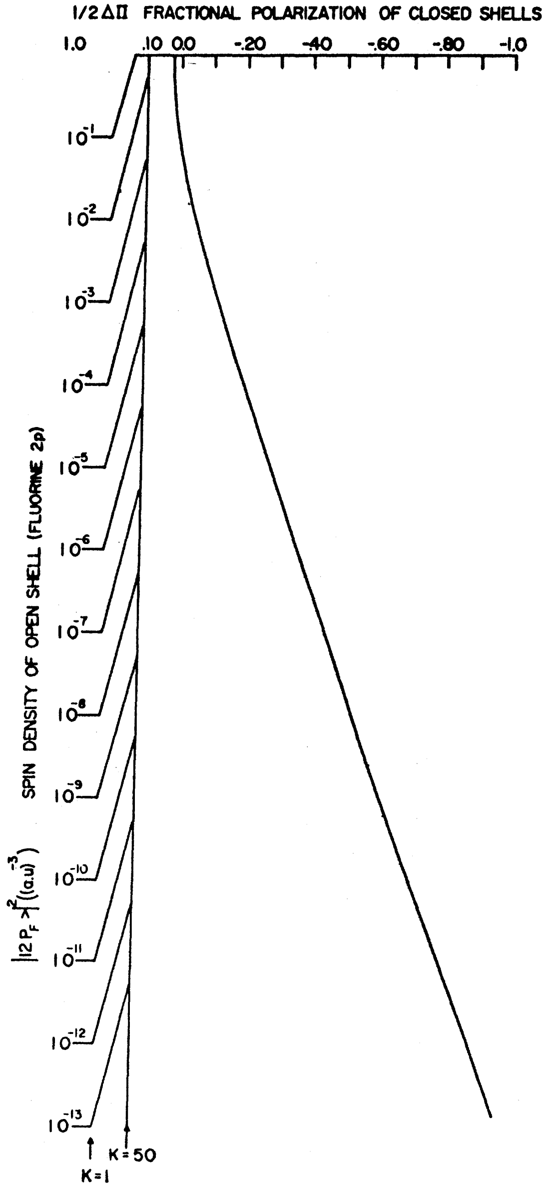

FIG. 12. One-half the fractional spin polarization of the closed shells of the fluorine atom as a function of the wave-function density in the open shell [adopted from the calculations of Goodings (Ref. 35)]. Fractional polarizations of the closed shells of the V_K center can be obtained for different values of the multiplying factor K by choosing the appropriate position of the scale on the left. For $R=3.8$ a.u. the values of K are $\pi_g(23)$, $\pi_u(37)$, $\sigma_g(8)$.

Only $\frac{1}{2}$ the polarization of the fluorine atom is used for the F_2^- molecule-ion. This is done because the one unpaired spin of the molecule-ion must serve to polarize more than twice as many closed shells as the single unpaired spin of the fluorine atom. Furthermore, in determining $\Delta\pi$, the scale of Fig. 12 is moved by the factor K in order to satisfy the requirement

$$\int \rho_\lambda d^3r = \int \{ \| \lambda_\uparrow \rangle |^2 - \| \lambda_\downarrow \rangle |^2 \} d^3r = 0 .$$

To avoid having the polarization dominated by large contributions along the nodal lines of the $3\sigma_u$ orbital, $\Delta\pi \langle (K \| V_K \rangle |^2) \rangle_{\text{av}}$ depends on the average value of the V_K center $3\sigma_u$ orbital over $\frac{1}{2}$ a.u. in a direction perpendicular to the nodal lines:

$$\langle \| V_K \rangle |^2 \rangle_{\text{av}} = \tfrac{1}{3} \{ \| V_K \rangle |_{X,Y,Z-\frac{1}{4}}{}^2 + \| V_K \rangle |_{X,Y,Z}{}^2 + \| V_K \rangle |_{X,Y,Z+\frac{1}{4}}{}^2 \} .$$

This is meant to represent the fact that the true polarization is an average over the diameter of the "Fermi exchange hole." The exchange-polarized closed shells are multiplied by the same Gourary-Adrian amplification factor A_α as was the open shell, since this depends only on the ENDOR ion wave function and not on the wave function of the unpaired spin.

It should be emphasized that this is not a calculation from first principles of the contact interaction, which would be a formidable theoretical problem; rather, it is an attempt to use the existing theoretical results to explain the sign and the order of magnitude of the measured contact interactions. It is then possible to check and see if the dipole-dipole calculations are affected by the modifications of the closed-shell wave functions needed to explain the contact interaction.

Tables VI–VIII present the experimental values of the contact hyperfine constant for nuclei surrounding the V_K center in LiF and NaF and the V_{KA} center in NaF. These values are compared with calculated hyperfine constants obtained using the procedure described above for exchange polarization and with calculated constants obtained using just the unpaired spin density in the $3\sigma_u$ orbital. In both cases the cal-

TABLE VI. Contact-interaction hyperfine constants for the V_K center in LiF (in units of Mc/sec).[a]

		a (calc)		Displacement		
Nucleus	*a* (expt)	With exchange polarization	Without exchange polarization	ΔX	ΔY	ΔZ
A(Li)	−4.120	−10.19	0.0	0.0	0.14	0.0
		−21.55	0.0	0.0	0.0	0.0
B(F)	−6.688	−1.42	0.0	0.240	0.130	0.0
		−15.52	0.0	0.0	0.0	0.0
C(Li)	−0.490	−1.22	+0.27	0.06	0.0	−0.02
		−1.98	+0.45	0.0	0.0	0.0
D(F)	−1.013	−1.14	+0.05	0.0	0.059	−0.127
		−1.45	+0.15	0.0	0.0	0.0
E(Li)	−0.160	+0.37	+0.61	0.0	0.083	0.051
		+0.97	+1.43	0.0	0.0	0.0
F(F)	+2.960	+3.89	+4.90	0.0	0.0	−0.25
		+1.14	+1.50	0.0	0.0	−0.12
		+0.36	+0.50	0.0	0.0	0.0

[a] $R=3.8$ a.u. (displacement in units of the nearest-neighbor distance, $a=3.80$ a.u.).

culated spin density is multiplied by the Gourary-Adrian amplification factor. These calculated values are shown for both the best displaced positions determined by the dipole-dipole calculations described in Sec. II and the undisplaced perfect lattice positions. In all cases it is clear that exchange polarization of the closed-shell orbitals of the F_2^- molecule-ion has the correct magnitude to explain the sign of the contact hyperfine constants measured for these centers. The calculated contact interactions in Tables VI-VIII change rapidly with the relative positions of the molecule-ion and the neighboring nuclei. Therefore a prerequisite for an accurate calculation of the contact interaction, when the other physical problems have been solved, will be accurate knowledge of the position of the neighboring nucleus as determined by the **B** tensor calculations. Also, it is interesting to note that crystal field distortions of the exchange-polarized closed-shell molecular orbitals are just as important as distortions of the unpaired σ_u orbital in an accurate calculation of the contact interactions.

B. Dipole-Dipole Interaction

We shall now discuss the effects that the exchange polarization has on the dipole-dipole interaction due to the altered spin-density distribution of the F_2^- molecule.

If we ignore cross terms which were seen to be negligible in the calculation of the dipole-dipole interaction with the σ_u orbital, the spin density of a closed-shell molecular orbital ($|V_K\lambda\rangle$) orthogonalized to a neighboring ion p orbital ($|2p\rangle$) can be expressed by the following approximation:

$$||V_K\lambda_\uparrow\rangle|^2-||V_K\lambda_\downarrow\rangle|^2\approx||\lambda_\uparrow\rangle|^2-||\lambda_\downarrow\rangle|^2 +\{|\langle 2p|\lambda_\uparrow\rangle|^2-|\langle 2p|\lambda_\downarrow\rangle|^2\}||2p\rangle|^2.$$

By using approximations that are similar to those used in Sec. III A, we obtain the following expression for the spin density:

$$||V_K\lambda_\uparrow\rangle|^2-||V_K\lambda_\downarrow\rangle|^2\approx||\lambda\rangle|^2\tfrac{1}{2}\Delta\pi +|\langle 2p|\lambda\rangle|^2\tfrac{1}{2}\langle\Delta\pi\rangle_{\text{av}}||2p\rangle|^2,$$

where $\langle\Delta\pi\rangle_{\text{av}}$ is an average value for the polarization in the region of space in which the overlap integral $\langle 2p|\lambda\rangle$ is significant.

We have calculated the dipole-dipole hyperfine constants of lithium A and fluorine D in LiF using just the first term of the equation above. For a given displaced position of the lithium A ion, the exchange-polarized wave function yields dipole-dipole constants that are about 0.33 Mc/sec larger than the ones calculated with the $3\sigma_u$ orbital alone. Therefore, to obtain agreement with the experimental dipole-dipole hyperfine constants, the lithium A nucleus would have to be displaced about 0.03 lattice constants further from the V_K than the position shown in Fig. 9. This does not change the qualitative features of the lattice distortion that we have described and illustrated in Fig. 9. For the fluorine D nuclei, this term increases the dipole-dipole constants by about 0.04 Mc/sec. This change falls within the uncertainty of the displaced position. The orthogonalization contributions to the calculated **B** tensor in Sec. II were small because the overlap integrals $\langle 3\sigma_u|p_k\rangle$ were small for all sites except F. On the other hand, the overlap integrals of the π_u and π_g orbitals with ion wave functions on a general site are comparable to the $\langle 3\sigma_u|p_k\rangle$ values for the F site.

TABLE VII. Contact-interaction hyperfine constants for the V_K center in NaF (hyperfine constants in units of Mc/sec).[a]

Nucleus	a (expt)	a (calc) With exchange polarization	a (calc) Without exchange polarization	Displacement ΔX	Displacement ΔY	Displacement ΔZ
A (Na)	-5.87	-3.73	0.0	0.0	0.27	0.0
		-26.35	0.0	0.0	0.0	0.0
B (F)	-2.49	-0.91	0.0	0.081	0.081	0.0
		-2.37	0.0	0.0	0.0	0.0
C (Na)	-0.38	-1.83	$+0.55$	-0.026	0.0	0.086
		-2.23	$+0.30$	0.0	0.0	0.0
D (F)	$+0.09$	-0.32	$+0.03$	0.0	-0.030	$+0.030$
		-0.26	$+0.02$	0.0	0.0	0.0
F (F)	$+0.58$	$+0.10$	$+0.16$	0.0	0.0	-0.11
		$+0.03$	$+0.05$	0.0	0.0	0.0
G (F)	$+0.61$	-0.09	$+0.25$	-0.098	-0.069	-0.100
		-0.03	$+0.05$	0.0	0.0	0.0

[a] $R=4.4$ a.u. (displacement in units of the nearest-neighbor distance $a=4.37$ a.u.).

We estimate this effect by an exact calculation of what the orthogonalization contribution from a closed shell would be if the closed shell were in fact only half filled, i.e., in the same way that the $3\sigma_u$ shell was treated in Sec. II. We then attempt to estimate what fraction of this result an exchanged-polarized closed shell might have. Since most of the contribution to the

TABLE VIII. Contact-interaction hyperfine constants for the V_{KA} center in NaF (hyperfine constants in units of Mc/sec).[a]

Nucleus	a (expt)	a (calc) With exchange polarization	a (calc) Without exchange polarization	Displacement ΔX	Displacement ΔY	Displacement ΔZ
A (Na)	-4.94	-2.95	0.0	0.0	0.30	0.0
		-26.35	0.0	0.0	0.0	0.0
A' (Li)	-2.82	-4.14	0.0	0.0	0.105	0.0
		-8.48	0.0	0.0	0.0	0.0
B (F)	-1.94	-0.82	0.0	0.055	0.137	0.0
B' (F)	-3.69	-1.08	0.0	0.115	-0.006	0.0
		-2.37	0.0	0.0	0.0	0.0
C (Na)	-0.15	-4.92	$+0.93$	-0.102	0.0	0.0
		-2.23	$+0.30$	0.0	0.0	0.0
D (F)	$+0.02$	-0.17	$+0.01$	0.0	$+0.035$	$+0.035$
D' (F)	-0.38	-1.82	$+0.01$	0.0	-0.161	-0.233
		-0.26	$+0.02$	0.0	0.0	0.0
F (F)	$+0.55$	$+0.12$	$+0.18$	0.0	0.0	-0.124
		$+0.03$	$+0.05$	0.0	0.0	0.0

[a] $R=4.4$ a.u. (displacement in units of the nearest-neighbor distance, $a=4.37$ a.u.).

overlap integral comes from the edge of the ion nearest the molecule, we use the density of the $3\sigma_u$ orbital in this region to estimate $\langle\Delta\pi\rangle_{\text{av}}$ as described above. This argument results in the prediction that the contribution from orthogonalization of an exchange-polarized closed-shell molecular orbital to the ion p orbital is between 5 and 10% of the value for the same orbital treated as a half-filled shell. Such a contribution would be important for the determination of the ion positions. For instance, a 10% effect would result in the fluorine B site moving away from the F_2^- molecule only half as far as the displacement listed in Tables II–IV. There is a certain amount of cancellation in the effects of the exchange polarization. At a given position for a lattice ion, the integration over the polarized closed shells increases the B values and the orthogonalization effect decreases the B values. It appears, however, that the orthogonalization contribution is larger, so that the displacements of most ions in Tables II–IV might be decreased. It should be noted that this combined orthogonalization-exchange polarization effect does *not* contribute to the lithium ions but does contribute to the sodium ions. Therefore, the fact that the displacements of lithium and sodium ions are similar when the effect is ignored gives some assurance that it is at most a correction to the displaced positions of the sodium and fluorine ions. Since the distortion of the molecular orbitals by the crystal field (which we have neglected) will change the overlap integrals, it is interesting to note that if the orthogonalization-exchange polarization contribution to the $\mathbf{B}$ tensor is important, then the crystal field distortions of the closed-shell orbitals will be just as important as the distortion of the half-filled $3\sigma_u$ orbital.

We conclude than that exchange polarization will not change the general qualitative picture of lattice distortion presented in Sec. II, but it *might* make significant corrections to the magnitude of the displacements. It is also possible that the polarization contributions to the B tensor discussed in this section are negligible if we have overestimated the polarization by as much as a factor of 4, as discussed in Ref. 34. It is probably not possible to decide between these possibilities until more sophisticated treatments of exchange polarization and crystal field effects on the molecule are available.

IV. CONCLUSIONS

We have presented calculations of the ENDOR hyperfine constants of the V_K center in LiF and NaF and the V_{KA} center in NaF. These calculations are compared with the experimental values of the constants that have been reported previously.[9–12,14,15] First of all, it is seen that the anisotropic or dipole-dipole part of the hyperfine interaction can be explained only by allowing the ENDOR nuclei surrounding the center to be displaced from their positions in the perfect lattice. These displacements are to be expected on the basis of other theoretical studies of the V_K center. We have compared the displacements predicted with our dipole-dipole calculations to the displacements of Das *et al.*,[17,18] and in all cases where results of both techniques are available there is agreement in the direction of the displacement and approximate agreement in magnitude of the displacement.

The displaced positions of the ions neighboring the V_K center in LiF and NaF and the V_{KA} center in NaF are listed in Tables II-IV and the positions are illustrated in Figs. 9–11. For all of the V_K-type centers, the lattice appears to contract along the axis of the molecule-ion (Z axis) and to expand in directions perpendicular to this axis. The largest corrections in the displaced positions of Tables II–IV may be due to the effects of exchange polarization of the closed-shell molecular orbitals.

Using the displaced positions of the ENDOR nuclei determined by the dipole-dipole calculations, we then estimated the ENDOR contact hyperfine interactions. In this case the hyperfine interaction is dominated by the orthogonalization of the closed shell of the ENDOR ion to the wave function of the unpaired spin on the V_K center and the exchange polarization of the closed-shell molecular orbitals of the V_K center itself. Using the amplification factors of Gourary and Adrian to account for orthogonalization and an approximation to the exchange polarization based on exchange polarization of the fluorine atom, we have estimated the contact hyperfine interaction. Order-of-magnitude agreement is obtained for each of the nuclei surrounding the three centers considered. This confirms that the exchange polarization of closed-shell molecular orbitals is the interaction primarily responsible for the experimentally observed negative contact interaction.

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