

Theory of the $H_A(\text{Na}^+)$ center in LiF †

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Taking a linear combination of free-molecule F_2^- wave functions for the $H_A(\text{Na}^+)$ -center wave function, the hyperfine tensors have been calculated for several ions neighboring this defect. The theoretical results for each ion have been fitted with the experimental ones by relaxing the ion from its perfect lattice position. These results show that the principal axes of the hyperfine tensors are in good agreement with the experimental data and that the relaxations are small compared with the lattice parameter.

I. INTRODUCTION

From the early work of Duerig and Markham¹ and the ESR work of Känzig and Woodruff² the model for the $H_A(\text{Na}^+)$ center in LiF has been proposed as consisting of an interstitial halogen atom forming a covalent bond with one of the neighboring halogen ions in the $[110]$ crystalline direction. Later on, through the electron nuclear double resonance (ENDOR) experiments done by Dakss and Miehler,³ the model of this defect has been definitely established with the identification of a Na^+ impurity substituting for a Li^+ in the nearest neighborhood of the defect molecule (see Fig. 1).

The ESR lines are characterized by a strong anisotropic primary hyperfine splitting due to the interaction of the hole with the nuclei forming the molecular ion and a secondary splitting of each one of the lines due to the hyperfine interaction with the nearest neighbors situated along the axes of the molecular ion.

There exists a remarkable similarity in the symmetry of the hyperfine interaction between the primary and the secondary spectra and the spectra of the V_k center.

On the basis of these results and the model of the V_k center,⁴ we have proposed a wave function to describe the $H_A(\text{Na}^+)$ center.⁵ The proposed wave function was assumed to be a linear combination of F_2^- molecular wave functions,

$$|\psi_H\rangle = \alpha |3\sigma_u(1, 2)\rangle + (\beta/\sqrt{2}) [|3\sigma_u(1, 3)\rangle + |3\sigma_u(2, 4)\rangle], \quad (1)$$

where $|3\sigma_u\rangle$ is the wave function constructed by Wahl⁶ for the F_2^- free molecule ion and used by several authors in calculations with V_k centers.⁷⁻⁹

The values of β , $R(1-2)$ (distance between fluorines 1 and 2), and $R_1(1-3)$ and $R_1(2-4)$ (distances between fluorines 1-3 and 2-4, respectively) (see Fig. 1) have been chosen to reproduce the experimental results for the hyperfine constants of the $H_A(\text{Na}^+)$ center. The value of α is obtained by imposing normalization.

The best fitting of the experimental value of the hyperfine constants has been obtained for the values of the parameters shown in Table I.⁴

Using these values for the parameters, the components of the dipole-dipole hyperfine tensors have been calculated for several relaxations of the neighboring ions to the $H_A(\text{Na}^+)$ center; the calculation procedure is discussed in Sec. II. The comparison of the calculated results with the ENDOR experimental parameters allowed us to determine most of the distorted positions of these neighboring ions in the lattice. It is necessary to mention here that it has been assumed that the defect molecule is linear although the ENDOR measurements³ indicated a small bending of the internuclear axis due to the presence of the impurity. This simplifying assumption has proved to be not too restrictive but in some cases, as will be discussed, discrepancies between calculated and experimental results can be explained in terms of this small bending.

II. SPIN-HAMILTONIAN AND HYPERFINE TENSORS

The experimental results concerning the hyperfine interaction are described by a phenomenological spin Hamiltonian which can be derived by evaluating¹⁰ the matrix element $\langle \psi | \mathcal{H}_{\text{hf}} | \psi \rangle$. $|\psi\rangle$ is the spatial part of the wave function of the unpaired defect electron; \mathcal{H}_{hf} describes the interaction between this electron and one single nucleus and is given by¹⁰

$$\mathcal{H}_{\text{hf}} = \mathcal{H}_{\text{dipole}} + \mathcal{H}_{\text{contact}}, \quad (2)$$

where

$$\mathcal{H}_{\text{dipole}} = \gamma_e \gamma_n \hbar^2 \left[\frac{3(\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^5} - \frac{\vec{I} \cdot \vec{S}}{r^3} \right],$$

$$\mathcal{H}_{\text{contact}} = \frac{8}{3} \pi \gamma_e \gamma_n \hbar^2 \delta(\vec{r}) \vec{S} \cdot \vec{I},$$

and γ_e , γ_n are the electronic and nuclear gyromagnetic ratios, \vec{S} and \vec{I} are the electronic and nuclear spin operators, and \vec{r} is the position vector of the

electron with respect to the nucleus.

The most convenient form to write the hyperfine

part of the spin Hamiltonian for the $H_A(\text{Na}^+)$ center is⁸

$$\begin{aligned} \mathcal{H}_{\text{hf}}(\vec{S}, \vec{K}_i, \vec{I}_\alpha) = & \langle \psi_H | \sum_{i=1}^4 \mathcal{H}_{\text{dipole}}(\vec{S}, \vec{K}_i, \vec{r}) | \psi_H \rangle + \langle \psi_H | \sum_{i=1}^4 \mathcal{H}_{\text{contact}}(\vec{S}, \vec{K}_i, \vec{r}) | \psi_H \rangle \\ & + \langle \psi_H | \sum_{\alpha=1}^n \mathcal{H}_{\text{dipole}}(\vec{S}, \vec{I}_\alpha, \vec{r}) | \psi_H \rangle + \langle \psi_H | \sum_{\alpha=1}^n \mathcal{H}_{\text{contact}}(\vec{S}, \vec{I}_\alpha, \vec{r}) | \psi_H \rangle, \end{aligned} \quad (3)$$

where \vec{I}_α ($\alpha=1, \dots, n$) is the nuclear-spin angular momentum of the α th neighboring nucleus to the $H_A(\text{Na}^+)$ center, and the \vec{K}_i ($i=1, \dots, 4$) are the spins of the four nuclei which constitute the defect molecule. The values are

$$K = I_F = \frac{1}{2}, \quad I_{Li} = I_{Na} = \frac{3}{2}.$$

Adding to this equation the terms describing the electronic and nuclear Zeeman interactions the complete spin-Hamiltonian which allows one to fit all the ESR and ENDOR experimental results is obtained:

$$\begin{aligned} \mathcal{H}(\vec{S}, \vec{K}_i, \vec{I}_\alpha) = & \frac{\hbar\gamma_e}{g_0} \vec{S} \cdot \vec{g} \cdot \vec{H}_0 + \sum_{i=1}^4 \vec{K}_i \cdot \vec{T}_i \cdot \vec{S} \\ & - \sum_{i=1}^4 \hbar\gamma_i \vec{K}_i \cdot \vec{H}_0 + \sum_{\alpha=1}^n \vec{S} \cdot \vec{A}_\alpha \cdot \vec{I}_\alpha \end{aligned}$$

$$- \sum_{\alpha=1}^n \hbar\gamma_\alpha \vec{I}_\alpha \cdot \vec{H}_0, \quad (4)$$

where the tensors \vec{g} , \vec{T} , and \vec{A} describe, respectively, the electronic Zeeman interaction, the hyperfine interactions with the defect molecule nuclei, and the hyperfine interaction with neighboring nuclei. The first three terms in Eq. (4) fit the ESR measurements and the others the ENDOR ones.

Because of the symmetry of the $H_A(\text{Na}^+)$ center,

$$\vec{T}_1 = \vec{T}_2; \quad \vec{T}_3 = \vec{T}_4.$$

From the axial symmetry of the EPR spectra of this defect, the components of the \vec{T} tensor can be written as

$$\begin{aligned} T_i^{ZZ} = T_i^i = a_i + b_i, \\ T_i^{XX} = T_i^{YY} = T_i^i = a_i, \end{aligned}$$

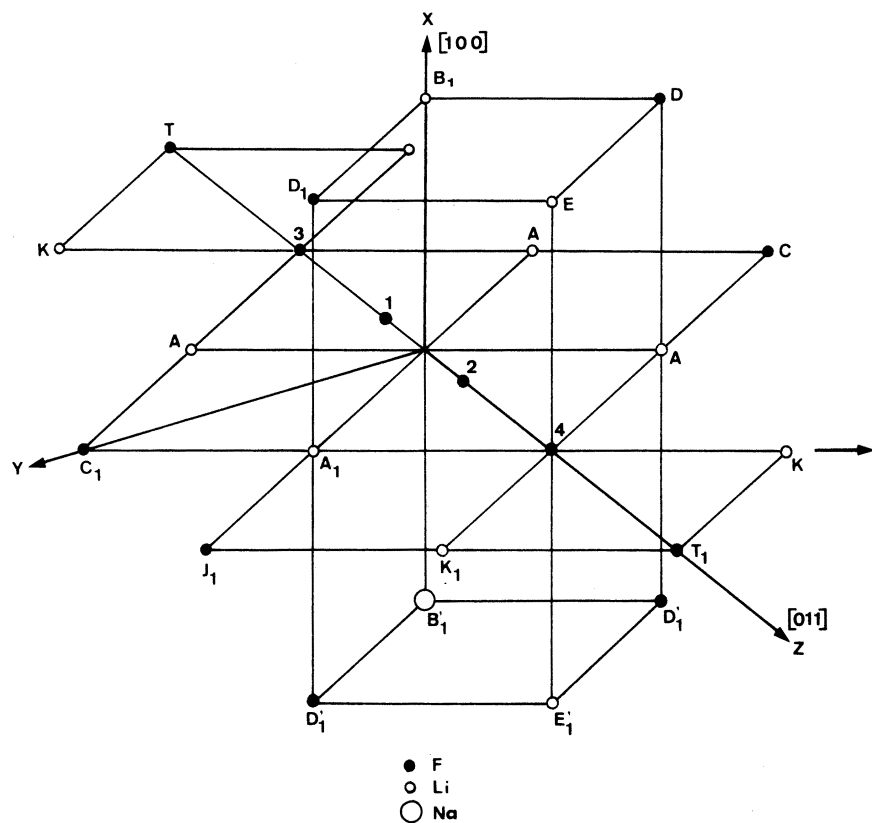


FIG. 1. Ion positions in the neighborhood of the $H_A(\text{Na}^+)$ center in LiF. The relaxations have been calculated for ions denoted by subscript 1 in the Cartesian axes shown.

TABLE I. Theoretical and experimental hyperfine constants for the primary (a_F and b) and the secondary (a'_F and b') EPR spectra of the $H_A(\text{Na}^+)$ center in LiF. The value α , β_* , $R(1.2)$, and $R(1.3)$ are the correspondent parameters of Eq. (1) which best fit the experimental data (see Ref. 4).

	Units	Theory	Expt.	Ref.
$R(1-2)$	a. u.	2.68
$R(1-3)$, $R(2-4)$	a. u.	4.0
$\alpha/\sqrt{2}$...	0.77460
$\beta_*/\sqrt{2}$...	0.22373
a_F	gauss	713	319	3
b	gauss	918	886($a > 0$)	3
a'_F	gauss	4.1	46.3	2
b'	gauss	51.0	64.8($a' > 0$)	2

where a and b are the isotropic and dipolar constants of the spin-Hamiltonian used by Castner and Känzig,¹¹

$$a_i = a_i^F - \frac{1}{3} b_i \quad (5a)$$

and

$$a_i^F = \frac{8}{3} \pi \gamma_e \gamma_i \hbar^2 \langle \psi_H | \delta(\vec{r}_i) | \psi_H \rangle, \quad (5b)$$

$$b_i = \frac{3}{2} \gamma_e \gamma_i \hbar^2 \langle \psi_H | (3Z_i^2 - r_i^2)/r_i^5 | \psi_H \rangle. \quad (5c)$$

The hyperfine tensor \vec{A}_α can be rewritten as

$$\vec{A}_\alpha = a_\alpha^F \vec{1} + \vec{B}_\alpha, \quad (6a)$$

where

$$a_\alpha^F = \frac{8}{3} \pi \gamma_e \gamma_\alpha \hbar^2 \langle \psi'_H | \delta(\vec{r}_\alpha) | \psi'_H \rangle, \quad (6b)$$

$$B_\alpha^{l,m} = \gamma_e \gamma_\alpha \hbar^2 \times \langle \psi'_H | (3x_\alpha^l x_\alpha^m - r_\alpha^2 \delta_{lm})/r_\alpha^5 | \psi'_H \rangle. \quad (6c)$$

$|\psi'_H\rangle$ is the $H_A(\text{Na}^+)$ -center wave function properly orthogonalized to the ion-core wave functions,

$$|\psi'_H\rangle = N \left(|\psi_H\rangle - \sum_\beta \langle \psi_\beta | \psi_H \rangle |\psi_\beta\rangle \right), \quad (7)$$

where N is the normalization constant. In this calculation it was found necessary to orthogonalize only to the p_x wave function of the F^- ions (T and T_I in Fig. 1) nearest neighbors in the axis of the defect molecule. Other overlap integrals were also evaluated but their values were not significant to modify the calculated results.

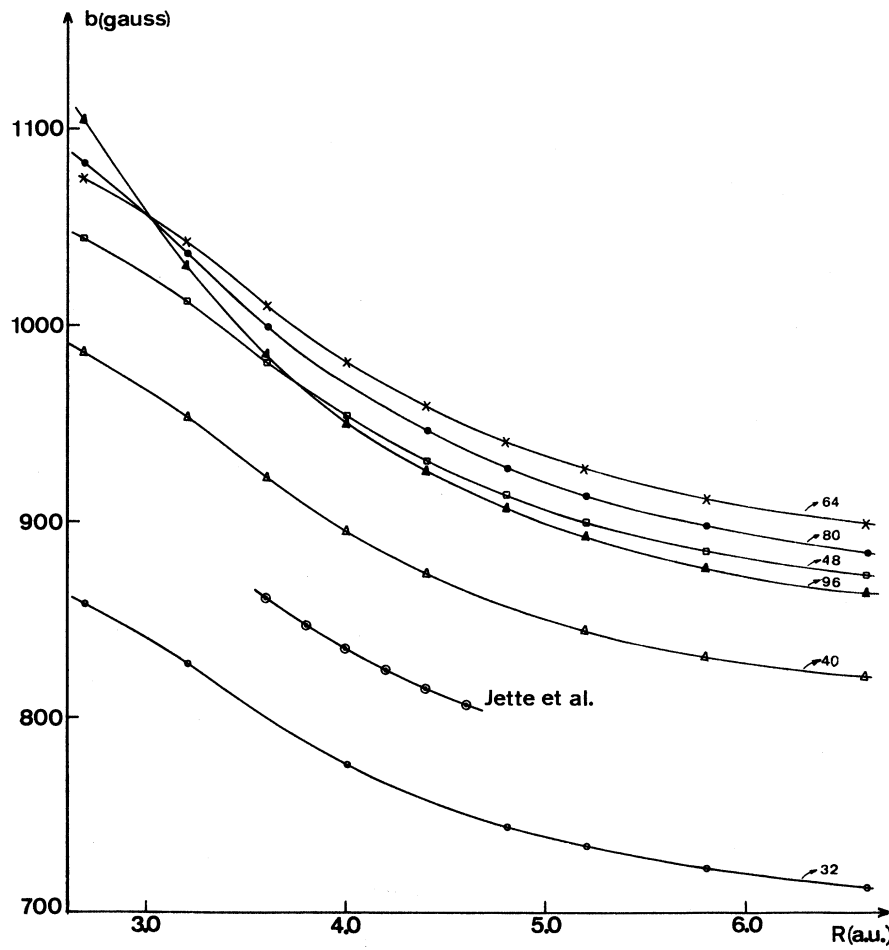


FIG. 2. Anisotropic parameter b for the V_k center in LiF as a function of the internuclear distance R . Calculated by the Gauss method and by Jette *et al.* (Ref. 7).

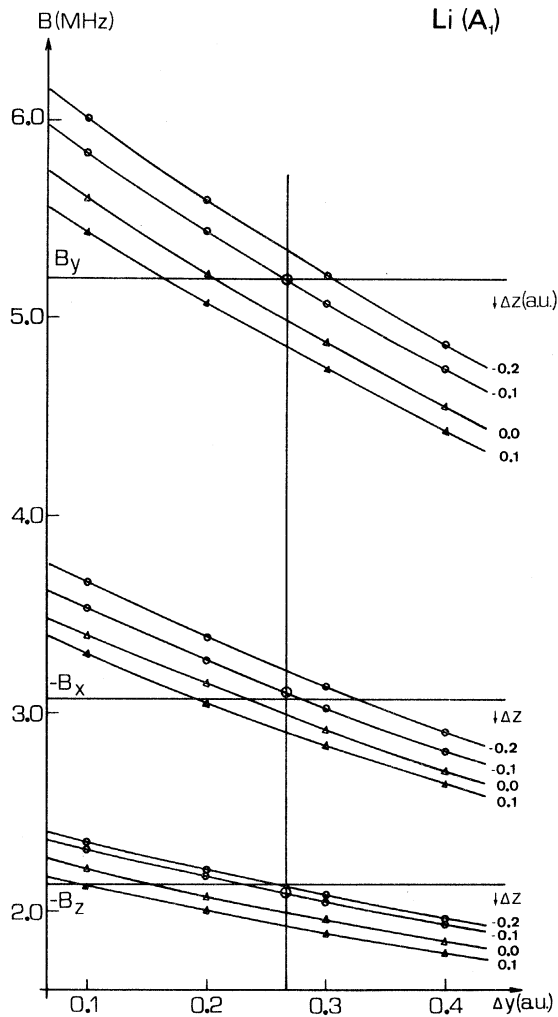


FIG. 3. Calculated \vec{B} -tensor components as a function of the $\text{Li}(A_1)$ displacement from its perfect lattice position. The experimental values (Ref. 3) are shown by horizontal lines.

The theoretical basis and the approximations leading to the present calculation are very well described in the work of Daly and Mieher⁸ who treated a similar problem concerning V_k -type centers in LiF and NaF . One of the features which distinguishes the present work from that of Daly and Mieher⁸ is the fact that here the internuclear distances of the defect molecule are fixed while they tried to fit the experimental results by relaxing simultaneously both the neighboring ions and the internuclear distance of the molecule ion.

In general, it was possible in the present calculations to obtain physically reasonable values for the nuclear displacements except in the case of the fluorine T (see Fig. 1), where the resulting relaxation was unreasonably large. An acceptable value could be obtained if the internuclear distances of

the defect molecule were changed. Nevertheless, to respect the consistency of the model it was decided to introduce for this case a new physical feature instead of varying those internuclear distances. Phenomenologically there was introduced a covalency parameter λ which, as is well known from the theory of small degrees of covalent bonding,¹² modifies the wave function of Eq. (7) to the form

$$|\psi'_H\rangle = N' [|\psi_H\rangle - (\langle\psi_H|\psi_T\rangle + \lambda) |\psi_T\rangle], \quad (8)$$

where N' is the normalization constant. The Clementi wavefunction¹³ has been used for $\psi_T = p_x$.

III. RESULTS AND DISCUSSION

To calculate the integrals involved in the present work, for the magnetic anisotropic hyperfine parameters as well as for the wave function overlaps and normalization, the Gauss method has been used.¹⁴ This method of integration was tested by calculating the ESR anisotropic parameters of the V_k center, for several orders (20, 32, 48, 64, 80, 96) of the Legendre polynomials and the results were then compared with previous calculation of Daly and Mieher⁸ and of Jette, Gilbert, and Das,⁷

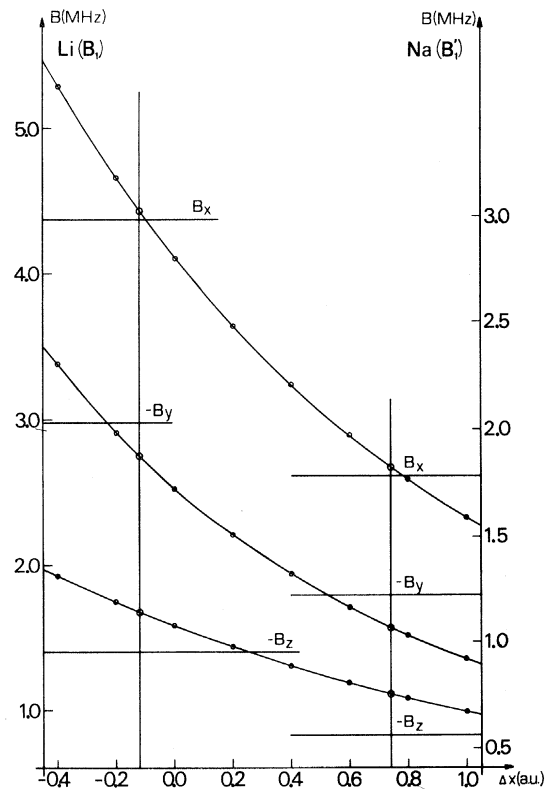


FIG. 4. Calculated \vec{B} -tensor components as a function of the $\text{Li}(B_1)$ and $\text{Na}(B_1)$ displacements from their perfect lattice positions. The experimental values (Ref. 3) are shown by horizontal lines.

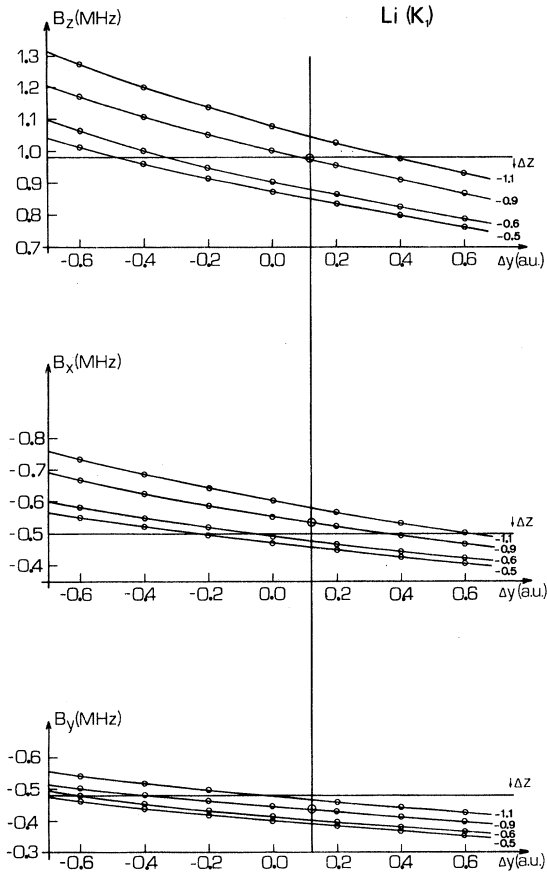


FIG. 5. Calculated \vec{B} -tensor components as a function of the $\text{Li}(K_1)$ displacement from its perfect lattice position. The experimental values (Ref. 3) are shown by horizontal lines.

where other processes of integration had been used. The agreement between their results and those obtained by the Gauss method was excellent when polynomials of order higher than 48 were used, typically 2% (see Fig. 2). For normalization and overlap integrals it has been shown that the Legendre polynomials of order 32 are enough to assure an agreement better than 0.2%. A certain care must be taken when calculating the dipole-dipole integrals because for a given polynomial some of its roots can be in a region extremely close to the positions of the nuclei and because of the particular form of the integrand it may numerically diverge giving spurious results. Changing the order of the polynomial the roots are modified and the integral can be correctly evaluated.

A. EPR

The agreement between the experimental results for the hyperfine constants and those obtained using the wave function defined by Eq. (1) with the parameters presented in Table I can be considered

TABLE II. Summary of the experimental (Ref. 3) and theoretical results: $a_0 = 3.8$ a. u., $B = (B_x^2 + B_y^2 + B_z^2)^{1/2}$, $|\Delta\vec{T}| = [(\Delta X)^2 + (\Delta Y)^2 + (\Delta Z)^2]^{1/2}$, $\Delta B = [(\Delta B_x)^2 + (\Delta B_y)^2 + (\Delta B_z)^2]^{1/2}$, $(\Delta B_i = B_i^{\text{Th}} - B_i^{\text{Expt}}; i = x, y, z)$.

Nuclei	a_F (MHz)	B_x (MHz)	B_y (MHz)	B_z (MHz)	α (deg)	β	γ	ΔX (a_0)	ΔY (a_0)	ΔZ (a_0)	$ \Delta\vec{T} $ (a_0)	$\Delta B/B$ (%)
$A_1(\text{Li})$	Th. 0.11	-3.10	5.19	-2.09	0	25.2°	25.2°	0	0.071	-0.026	0.076	0.9%
	Expt. -0.86	-3.07	5.20	-2.14	~1	23.5° ± 1.0°	23.5° ± 1.0°	0	0	0	0.031	6.8%
$B_1(\text{Li})$	Th. 0.00	4.42	-2.74	-1.68	0	0°	0°	-0.031	0	0	0.031	6.8%
	Expt. -1.89	4.37	-2.98	-1.40	0	0°	0°	-0.168	0	0	0.168	11.2%
$B_1'(\text{Na})$	Th. 0.00	1.81	-1.06	-0.75	0	0°	0°	0	0	0	0	0
	Expt. -4.83	1.78	-1.22	-0.56	0	0°	0°	0	0	0	0	0
$K_1(\text{Li})$	Th. 0.005	-0.533	-0.435	0.970	0	28.9°	28.9°	0	0.031	-0.237	0.239	4.8%
	Expt. 0.17	-0.50	-0.48	0.98	~0	28° ± 1°	28° ± 1°	0	0.281	0	0.281	18.6%
$C_1(\text{F})$	Th. 0.00	-1.68	3.17	-1.47	0	0°	0°	0	0	0	0	0
	Expt. -2.11	-2.22	3.17	-0.96	~1	~1°	0°	-0.026	0.071	0.026	0.080	3.0%
$D_1(\text{F})$	Th. 0.00	-2.49	4.46	-1.97	51.3	55.2°	23.5°	0	0	0	0	0
	Expt. -2.07	-2.60	4.45	-1.85	52° ± 2°	54° ± 2°	15° ± 2°	0	0	0	0	0
$D_1'(\text{F})$	Th. -3.24	-3.57	5.42	-1.86	52 ± 2	54° ± 2°	8° ± 2°	0	0	0	0	0
	Expt. 0.87 × 10 ⁻³	-1.37	-1.37	2.74	0	0°	0°	0	0	-0.131	0.131	0.7%
$T_1(\text{F})$	Th. 1.92	-1.37	-1.38	2.76	0	0°	~0°	0	0	0	0	0
	Expt. 1.92	-1.37	-1.38	2.76	0	0°	~0°	0	0	0	0	0

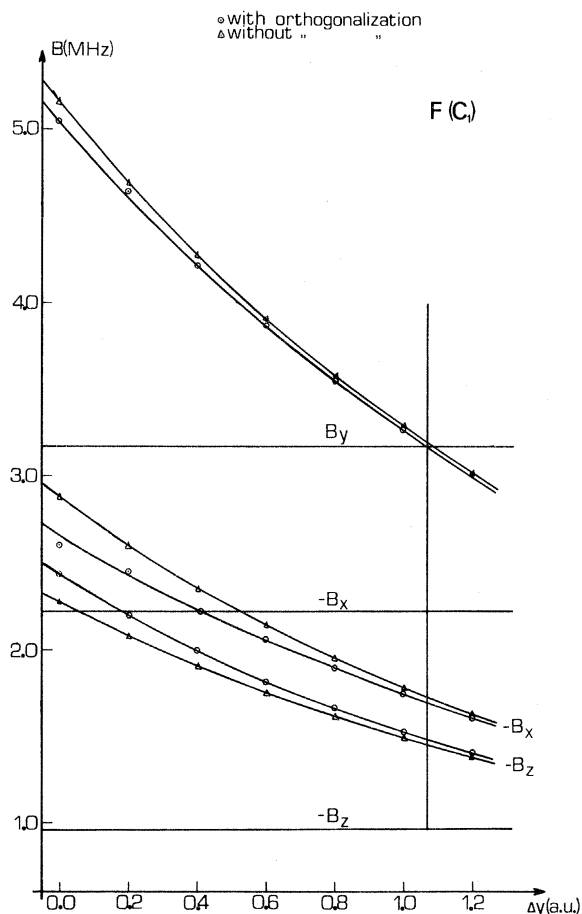


FIG. 6. Calculated \vec{B} -tensor components as a function of the $F(C_1)$ displacement from its perfect lattice position. The experimental values (Ref. 3) are shown by horizontal lines.

very good, but a definite check on the accuracy of this wave function can be obtained by comparing the theoretical results with the experimental ones obtained from the ENDOR spectra.

B. ENDOR

Assuming the parameters for the $H_A(\text{Na}^+)$ -center wave functions to be those presented in Table I, and taking for the ψ_B Clementi's linear combination of Slater function,¹³ the hyperfine tensors \vec{B}_α have been calculated for several displacements of the α th ion from its equilibrium position in the perfect lattice. These are presented in Figs. 3-10 for Li(A, B, K), Na(B'), and F(C, D, D', T). The positions of the ions in the lattice shown in Fig. 1, are those previously defined by Dakss and Mieher.³ For each ion, the relaxations proposed in this calculation are the ones expected by symmetry considerations. The experimental results from Ref. 3 are represented in each figure by horizontal lines.

The best value for the relaxations of each one of the studied ions has been obtained by varying the values of the ion position, in the m directions ΔX_m ($m = x, y, z$), from the perfect lattice site, and then plotting the family of curves generated by the function $\Delta^2(\Delta X_l)$ ($l \neq m$) defined as

$$\Delta^2(\Delta X_l) = \sum_{j=1}^3 [B_{\text{exp}}^j - B_{\text{theo}}^j(\Delta X_l)]^2,$$

$$l = x, y, z.$$

Each one of these curves presents a minimum; the smallest value of all the minima has been chosen to indicate the best theoretical value for the \vec{B} tensor. For some ions, however, there was some ambiguity in the determination of this smallest value, and in this case the value chosen was such that the calculated angle of the principal-axes tensor is the best fitting for the angle of the experimental tensor \vec{B} . A typical plot is shown in Fig. 11.

The results presented in Figs. 3-10, are summarized in Table II. Table II compares the calculated theoretical results for the hyperfine tensors with the experimental ones from Dakss and Mieher³; it presents also the resulting relaxations. Using these results for the relaxed positions, the Fermi contact term a_F [Eq. (6b)] has been calculated, and is also shown in this same table. An estimate of the agreement concerning the anisotropic parameters is given by the last column of Table II.

C. Discussion

Li(A). From symmetry considerations the Li(A) ion should remain in the YZ plane, if it is supposed that the perturbation due to the sodium ion Na(B') will not distort the $H_A(\text{Na}^+)$ -center wave function at the Li(A) site. This assumption is confirmed by the excellent agreement between theoretical and experimental results for all three components of the hyperfine tensor. This agreement has been obtained with an ion relaxation from its normal position of $0.071a_0$ in the positive Y direction, and $-0.026a_0$ in the Z direction, i. e., toward the center of the defect (see Figs. 3 and 9). (a_0 is the interionic distance.)

Previous calculations³ using the F_2^- wave function with internuclear distance of 3.6 a. u. have been fitted to the experimental data, by relaxing the ion $0.14a_0$ in the Y direction, and $-0.1a_0$ in the Z direction.

The difference between the two theoretical results could be expected since the $R(1-2)$ distance used in the present calculations is 2.68 a. u., and the fact that the wave function for the $H_A(\text{Na}^+)$ center is spread over nuclei 3 and 4 reducing the spin density around the Li(A) site.

Li(B) and Na(B'). These ions are situated on the X axis which is a symmetry axis of the defect

and therefore they are constrained to relax along this direction. Figure 4 shows that the agreement between theoretical and experimental results is not as good as in the case of $\text{Li}(A)$. This can be explained by the fact that the presence of the sodium ion will slightly break the axial symmetry of the wave function and this effect should be particularly noted in the nodal plane. The calculated relaxations are in agreement with simple arguments based on hard-sphere models. The difference between the relaxations of $\text{Li}(B)$ and $\text{Na}(B')$ is $0.13a_0$, while $R_{\text{Na}} - R_{\text{Li}}$, calculated by different authors,³ varies between the values of $0.10a_0$ and $0.17a_0$ (see Fig. 10).

$\text{Li}(K)$. For this ion the best fitting has been obtained by relaxing it $-0.237a_0$ in the Z direction and $0.031a_0$ in the Y direction. This result could be expected since $\text{Li}(A)$ and also $F(T)$ both relax toward the center of the defect. A possible explanation for this relaxation could be the decrease in the repulsive energy between $\text{Li}(K)$ and fluorine 3 or 4, due to the hole density at these fluorines, together

with the relaxation obtained for $F(T)$ in the negative Z direction and the probable relaxation of $F(J)$ in this same direction, which should be expected due to the large calculated displacement of $F(C)$ in the positive Y direction (see Fig. 9). It should also be pointed out that a different behavior for the $H_A(\text{Na}^+)$ center, as compared with the V_k center, could be expected since the $H_A(\text{Na}^+)$ center is electrically neutral while the V_k center has a positive charge which surely will make the positive ions relax away from the V_k center.

Calculations have shown that the contribution of the orthogonalization between the $H_A(\text{Na}^+)$ -center wave functions and the Li^+ s functions is less than 0.01% for the dipole-dipole integrals. Therefore the overlap between the s orbitals and $|\psi_H\rangle$ could be neglected. The same is not true for the fluorine ions, because of the p character of its outest-shell electrons.

$F(T)$. Even including orthogonalization it was not possible to obtain a good agreement with the

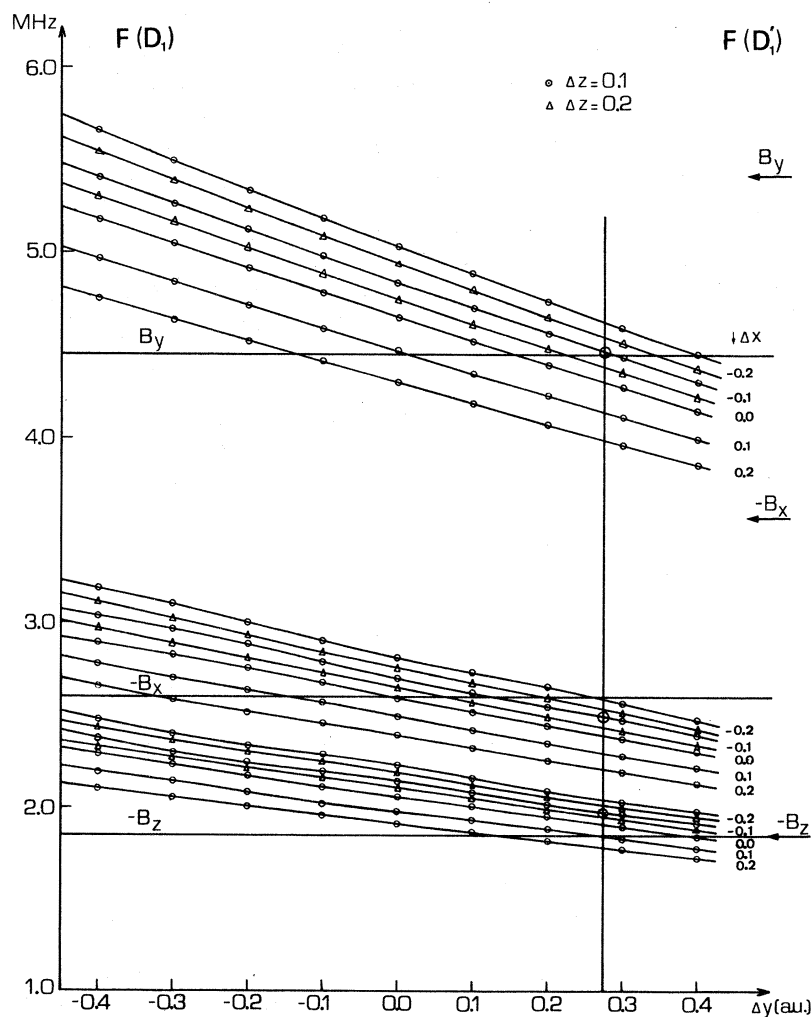


FIG. 7. Calculated \vec{B} -tensor components as a function of the $F(D_1)$ and $F(D_1')$ displacements from their perfect lattice positions. The experimental values (Ref. 3) are shown by horizontal lines.

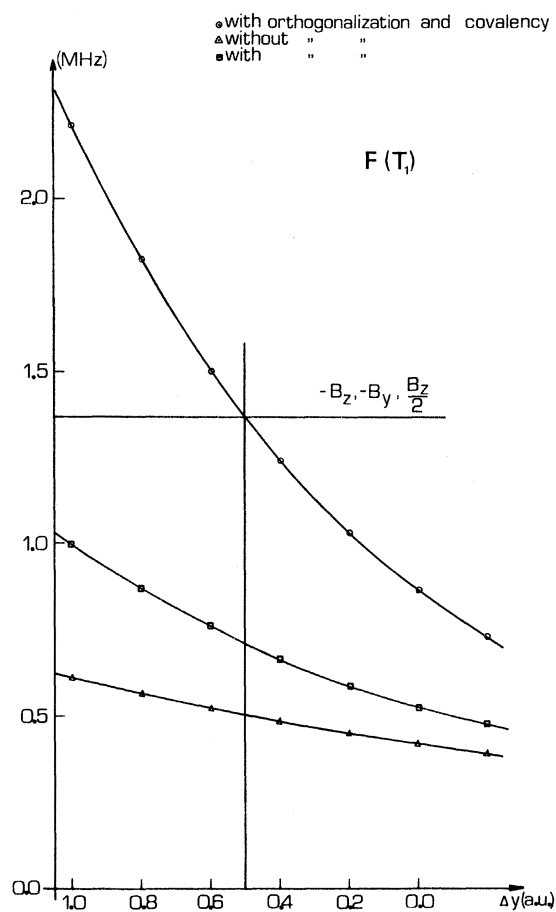


FIG. 8. Calculated \bar{B} -tensor components as a function of the $F(T)$ displacement from its perfect lattice position. The experimental values (Ref. 3) are shown by horizontal lines.

experimental results. To fit these results it would be necessary to relax the fluorine $-0.38a_0$ toward the center of the molecule, which is not a physically reasonable relaxation.

Previous results for interstitial hydrogen in alkali halides,¹⁵ U_2 center, have shown that covalency takes an important role in the interpretation of the experimental hyperfine constants associated with the nuclei which are nearest-neighbors to the defect. Like the $H_A(\text{Na}^*)$ center, the U_2 center is an interstitial and electrostatically neutral defect; therefore it seems reasonable that covalency must be taken into account to interpret the hyperfine results of this $F(T)$ nucleus.

If there is introduced phenomenologically a covalency parameter, arbitrarily assuming it equal to the overlap integral value, the experimental result is reproduced for a slight relaxation of $0.131a_0$ along the Z direction toward the center of the molecule (Figs. 8, 9, and 10). It is observed in these figures that the covalent contribution makes an important shift in the calculated results and that with a little higher value for the covalency parameter it would be possible to fit the experimental result without having to assume any relaxation at all.

It is worthwhile noting that the arbitrary value taken for the covalency parameter is only 10% of the covalency parameter obtained for fluorine 3 or 4 in the "four-fluorine molecule" constituting the basic model for the $H_A(\text{Na}^*)$ center. Thus the fact that the first-neighbor $F(T)$ ions are slightly covalently bonded to this "molecule" is perfectly reasonable, and the consequence is that the unpaired hole is more delocalized onto the $F(T)$ ions than is indicated by just the overlap.

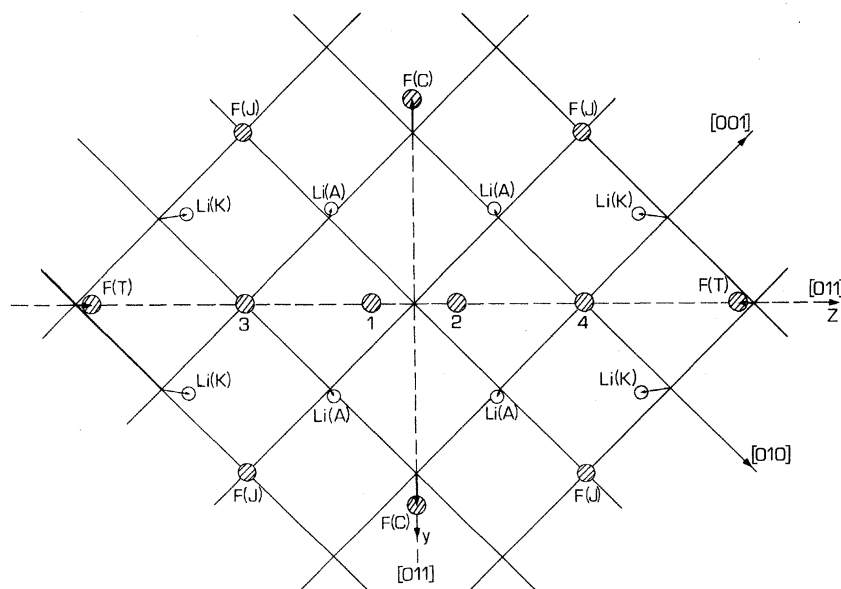


FIG. 9. Calculated displacements for the ions in the YZ plane (in scale).

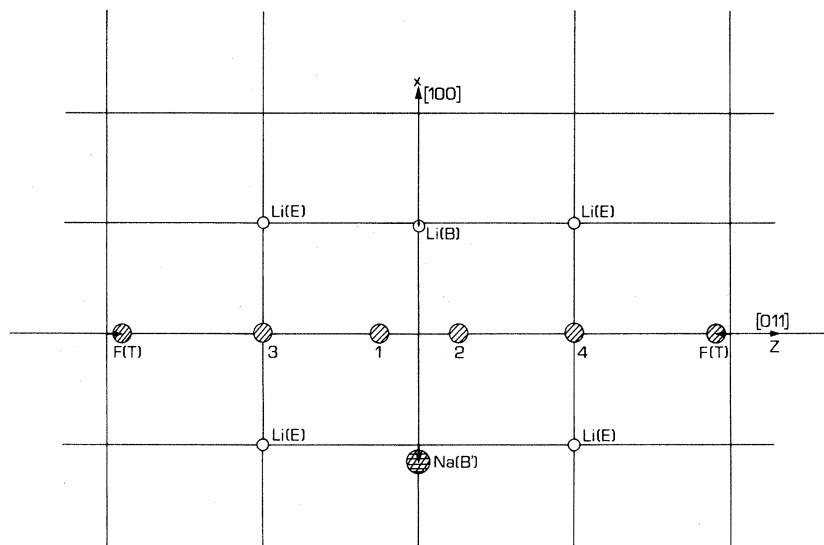


FIG. 10. Calculated displacements for the ions in the XZ plane (in scale).

$F(C)$. For this ion the calculations have shown that orthogonalization has a small influence on the results for the dipole-dipole tensors. The obtained relaxation was $0.281a_0$ in the positive Y direction. This large relaxation could be caused by the presence of the interstitial fluorine which forms the $H_A(\text{Na}^+)$ center.

$F(D)$ and $F(D')$. To identify fluorines D and D' Dakss and Mieher³ have used theoretical results assuming for the $H_A(\text{Na}^+)$ -center wave function the F_2^- -molecule wave function.

In the present work a very good agreement has been obtained between the theoretical results for the \vec{B} tensor for $F(D)$ and the experimental results not for $F(D)$ but for $F(D')$. It could be possible that the use of theoretical results obtained with a less precise wave function misled the proper identification of $F(D)$ and $F(D')$ by Ref. 3.

The wave function used in the present calculations is more accurate than the simple V_k wave functions;

this suggests the possibility that $F(D)$ and $F(D')$ were improperly identified.

For $F(D')$ the ratio between the experimental values for B_Y and B_Z is quite different from the ratio obtained with the theoretical values, as can be seen in Fig. 7. It was not possible to assign a relaxation to this ion. This discrepancy may be explained because of the presence of the $\text{Na}(B)$ ion, which will certainly distort the $H_A(\text{Na}^+)$ -center wave function in the vicinity of the $F(D')$ site.

IV. CONCLUSIONS

The present results seem to indicate that the $H_A(\text{Na}^+)$ center distorts the lattice very little, a result that was not expected by simple hard-sphere arguments. But this small relaxation is consistent with previous work on volume expansion¹⁶ where the annealing of the $H_A(\text{Na}^+)$ center at 130°K does not show a great change in volume.

It will be interesting for a definitive check on the

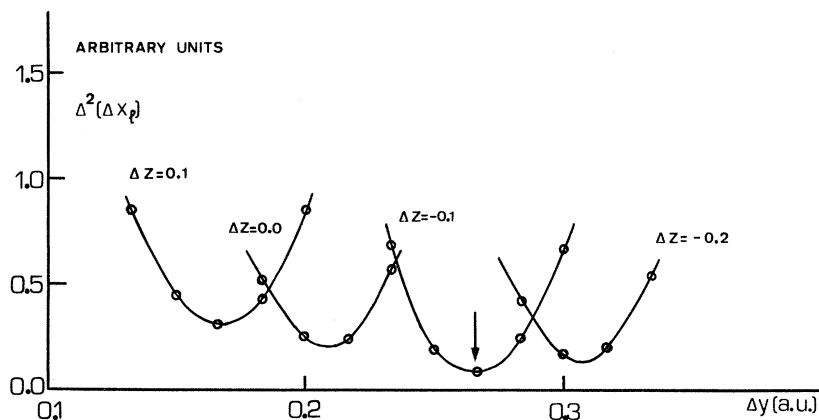


FIG. 11. Plot of $\Delta^2(\Delta X_j) = \sum_{j=1}^3 [B_{\text{expt}}^j - B_{\text{Th}}^j(\Delta X_j)]^2$ for $\text{Li}(A_1)$. The arrow indicates the chosen displacements.

relaxations of the neighbor ions to the $H_A(\text{Na}^+)$ center to perform a calculation of the energy of the lattice as a function of the displacement of the ions similarly to the one made by Jette *et al.*⁷ for the V_k center.

A word should be said about the very bad agree-

ment between the experimental values for the contact interaction and the calculated ones. As in the case of the V_k center a strong exchange polarization is responsible for these discrepancies.⁹ A calculation of the exchange polarization on the $H_A(\text{Na}^+)$ center is in progress.¹⁷

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