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Magnetic hyperfine constants and lattice distortion of the V_k center in CaF_2, SrF_2, and BaF_2†

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The magnetic hyperfine constants of the V_k center in CaF_2, SrF_2, and BaF_2 have been calculated assuming a phenomenological model, based on the F_2^- "central molecule," to describe the wave function of the defect. Calculations have shown that introduction of a small degree of covalency between this central molecule and neighboring ions is necessary to improve the electronic structure description of the defect. It was also shown that the results for the hyperfine constants are strongly dependent on the relaxations of the ions neighboring the central molecule; these relaxations have been determined by fitting the experimental data. The present results are compared with other previous calculations where similar and different theoretical methods have been used.

I. INTRODUCTION

EPR and electron-nuclear double resonance (ENDOR) techniques have been extensively used to characterize unambiguously most point paramagnetic defects present in crystals, in particular color centers produced by different kinds of irradiation. These techniques have in general allowed the proposition of qualitative models for the structure of the defects. However, the extreme accurate measurements obtained using ENDOR can in principle indicate the direction in the formulation of quantitative theories for both the electronic structure and the localization of the ions in the distorted lattice. Usually an *ab initio* calculation for this kind of problem is complicated and for this reason a simpler phenomenological model is a first convenient approach because, besides giving quantitative results, it can indicate important features that must be taken into account when one is dealing with a first-principles formulation.

One of the most studied hole centers is the so-called V_k center which in alkali halides was first positively identified by Kanzig[1] in x-irradiated KCl at liquid-nitrogen temperature as being basically constituted by a Cl_2^- molecule ion oriented in a [110] direction. For alkaline-earth fluorides this center was first studied by Hayes and Twidell[2] and by Kazumata[3] who used the ESR technique; the model was unambiguously established by the ENDOR works done by Marzke and Mieher[4] in CaF_2 and BaF_2 and by Gazzinelli *et al.*[5] in SrF_2. This is basically constituted by a F_2^- molecule ion oriented in a [100] direction. Therefore the local symmetry of the defect in the latter compounds is D_{2h} so that there exist six crystallographically equivalent sites.

The main purposes of the present work are the proposition of a wave function for the electronic structure of the V_k center in CaF_2, SrF_2, and BaF_2 as well as the calculation of the relaxed positions of the ions for which EPR and ENDOR magnetic hyperfine parameters have been measured. We have used a phenomenological model supposing that the electronic structure of this center is essentially described by the $3\sigma_u$ wave function associated with the unpaired electron of the F_2^- molecule ion.[6] To describe more realistically the physical nature of the defect it is necessary to consider corrections to this $3\sigma_u$ wave function. We have calculated the magnetic dipolar tensors and fitted the experimental values by relaxing the positions of the ions; in this manner we obtained a better wave function and determined the relaxations.

Similar unpublished calculations have been done by Marzke[7] for CaF_2 and BaF_2. The main difference between his work and the present one is that, as will be discussed in Sec. III, it is necessary to introduce a small degree of covalency in order to spatially extend the unpaired electron-spin density. For this same defect *ab initio* calculations have been done by Jette and Das[8] for CaF_2 and by Norget and Stoneham[9] for CaF_2, SrF_2, and BaF_2; a comparison between their results and ours will be also made in Sec. III.

In Sec. II we present the theory for the magnetic hyperfine parameters. In Sec. III we present results and discussion and in Sec. IV our conclusions.

We must mention that the present work follows a line similar to that used by Daly and Mieher[10] and Costa Riberio *et al.*[11] who studied respectively the V_k and the H_A (Na^+) centers in LiF.

II. THEORY

The magnetic hyperfine interactions between the unpaired electron of the defect and the nuclei are described by the Hamiltonian

$$\mathcal{H}_{\rm hf} = \sum_i (\mathcal{H}_F^{(i)} + \mathcal{H}_D^{(i)} + \mathcal{H}_L^{(i)}) \equiv \sum_i h^{(i)} , \qquad (1)$$

where $\mathcal{H}_F^{(i)}$, $\mathcal{H}_D^{(i)}$, and $\mathcal{H}_L^{(i)}$ are the Fermi interaction, the spin dipolar interaction, and the orbital angular momentum interaction for the ith nucleus, respectively, given by

$$\mathcal{H}_F^{(i)} = \tfrac{8}{3}\pi g_e g_i \mu_B \mu_N \delta(\vec{r})\vec{I}_i \cdot \vec{S} , \qquad (2)$$

$$\mathcal{H}_D^{(i)} = g_e g_i \mu_B \mu_N [3(\vec{I}_i \cdot \vec{r})(\vec{S} \cdot \vec{r})/r^5 - (\vec{I}_i \cdot \vec{S})/r^3] , \qquad (3)$$

$$\mathcal{H}_L^{(i)} = g_e g_i \mu_B \mu_N (\vec{I}_i \cdot \vec{L})/r^3 , \qquad (4)$$

where g_e is the g factor of the free electron ($g_e = 2.0023$); g_i the g factor of the ith nucleus; $\vec{I}_i$ the angular momentum of the ith nucleus; $\vec{r}$ the position vector of the unpaired electron with respect to the ith nucleus; μ_B the Bohr magneton; μ_N the nuclear magneton; $\vec{L}$ the orbital angular momentum of the unpaired electron; $\vec{S}$ the spin angular momentum of the unpaired electron ($S = \frac{1}{2}$).

Using the perturbation theory we can define an effective spin Hamiltonian for the problem.

A. First-order contribution

In the approximation of independent nuclei we must calculate the matrix element

$$E_{\rm hf} = \left\langle \phi_d \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \middle| h^{(i)} \middle| \phi_d \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \right\rangle , \qquad (5)$$

where ϕ_d is the spatial part of the wave function associated with the unpaired electron, α and β being the eigenstates of S_z corresponding to the eigenvalues $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively. Integrating over the spatial coordinates Eq. (5) gives rise to the spin Hamiltonian

$$H = H_F + H_D , \qquad (6)$$

where

$$H_F = a_i \vec{I} \cdot \vec{S} , \qquad (7)$$

$$H_D = \vec{I} \cdot \overleftrightarrow{B}^{(i)} \cdot \vec{S} , \qquad (8)$$

$$a_i = \tfrac{8}{3}\pi g_e g_i \mu_B \mu_N |\phi_d(0)|^2 , \qquad (9)$$

$$B_{jk}^{(i)} = g_e g_i \mu_B \mu_N \int |\phi_d|^2 \frac{3x_j x_k - r^2 \delta_{jk}}{r^5} d\vec{r} . \qquad (10)$$

The dipolar tensor $\overleftrightarrow{B}^{(i)}$ is symmetric and traceless; a_i is the Fermi contact term. There is no first-order contribution from $\mathcal{H}_L$ because the angular momentum is quenched. Since $\overleftrightarrow{B}^{(i)}$ is traceless in its system of principal axes, it is completely defined by two parameters which were chosen as

$$b_i = \tfrac{3}{2} B_{zz}^{(i)}, \quad b_i' = \tfrac{3}{2}(B_{xx}^{(i)} - B_{yy}^{(i)}). \qquad (11)$$

B. Second-order contributions

If we consider, for instance, the spin-orbit interaction, the contribution of $\mathcal{H}_L$ is no longer zero. This occurs because this interaction partially unquenches the angular momentum $\vec{L}$ and therefore $\langle \phi_d | \mathcal{H}_L | \phi_d \rangle$ can give a contribution to the spin Hamiltonian with bilinear terms in $\vec{I}$ and $\vec{S}$; ϕ_d is the spatial part of the wave function associated with the unpaired electron correction to first order due to the coupling introduced by the spin-orbit interaction between excited states and ground state.

Jette[12] used a second-order perturbation theory formulated by Pryce[13] considering all possible interactions which can give rise to bilinear terms in $\vec{I}$ and $\vec{S}$; these interactions are, besides spin orbit, $\mathcal{H}_F$ and $\mathcal{H}_D$. The Hamiltonian corrected to second order as obtained by Jette,[12] for the central molecule ion is

$$\bar{H} = \vec{I} \cdot \overleftrightarrow{T} \cdot \vec{S} , \qquad (12)$$

where

$$T_{\parallel} = T_{zz} = (1 - \tfrac{1}{8}\Delta g_\perp^2) a + (\tfrac{2}{3} - \tfrac{1}{2}\Delta g_\perp + \tfrac{7}{24}\Delta g_\perp^2) b , \qquad (13)$$

$$T_\perp = T_{xx} = T_{yy} = (1 - \tfrac{1}{8}\Delta g_\perp^2) a - (1 - \tfrac{13}{4}\Delta g_\perp + \tfrac{73}{24}\Delta g_\perp^2)\tfrac{1}{3} b ; \qquad (14)$$

thus

$$b = (T_\parallel - T_\perp)/[1 - (19 - \tfrac{31}{4}\Delta g_\perp)\tfrac{1}{12}\Delta g_\perp] , \qquad (15)$$

$$a = \left(T_\parallel + \frac{(T_\parallel - T_\perp)\frac{1}{2}\Delta g_\perp - \frac{7}{24}\Delta g_\perp^2 - \frac{2}{3})}{1 - (\frac{19}{12}\Delta g_\perp - \frac{31}{48}\Delta g_\perp^2)} \right) \times (1 - \tfrac{1}{8}\Delta g_\perp^2)^{-1} , \qquad (16)$$

where $T_\parallel$, $T_\perp$, and $\Delta g_\perp$ are experimental parameters from which we can extract, using Eqs. (15) and (16), the values of b and a. Now we can fit this "experimental" value of b, evaluating Eq. (11), for different values of the internuclear distance (R) of the F_2^- central molecule ion; the $3\sigma_u$ wave function calculated by Gilbert and Wahl[6] for free F_2^- is given for several values of R. An important point is that the signs of $T_\parallel$ and $T_\perp$ are not determined experimentally, but, as will be discussed in Sec. III, it will be possible to obtain them from theoretical considerations.

It is worthwhile to note that the experimental results presented in Table I indicate that the proposed model, which takes the F_2^- molecule as a first approximation, is well supported since these results are almost independent of the specific crystal.

We should remark that Schoemaker,[15] using a different formulation, obtains

$$b = (T_\parallel - T_\perp)/[1+\tfrac{1}{3}(3\Delta g_\parallel - 5.39\Delta g_\perp)], \qquad (17)$$

and that the use of Eqs. (15) and (17) gives practically the same result for b.

These results hold for the F_2^- molecule ion where axiality exists. For the V_k center this is not rigorously true for the central F_2^- molecule ion because the internuclear axis is only of order 2. However, it is not possible to detect nonaxiality experimentally in either the $\tilde{B}$ or $\tilde{g}$ tensors, the latter describing the Zeeman interaction. $\Delta g_\perp = g_\perp - g_e$, $g_\perp$ being the g value measured when the magnetic field is oriented perpendicularly to the internuclear axis of the F_2^- central molecule ion. As can be seen from Table I, $\Delta g_\perp$ is a small quantity so that these corrections are expected to be small. Of course its importance will be more relevant for the nuclei of the central molecule ion.

III. RESULTS AND DISCUSSION

All calculations have been done using the system of axes defined as (see Fig. 1): X axis, $[1\bar{1}0]$ direction; Y axis $[110]$ direction; and Z axis, Z_c direction, the origin placed on V_1. First, we will try to obtain the wave function for the defect using the F_2^- $3\sigma_u$ wave function, varying the value of R to fit the "experimental" value of b associated with nuclei V_1 and V_2 (see Fig. 1), which belong to the central molecule ion. This value is obtained from EPR measurements. Second, we will use the appropriate wave function to calculate the $\tilde{B}$ tensors of all nuclei which have been measured by ENDOR. As we will show the obtained wave function is not accurate enough to reproduce the experimental values. This necessarily implies a correction to the wave function by considering overlap and a weak covalency with the two fluorines A shown in Fig. 1.

To evaluate all the integrals concerning the $\tilde{B}$ tensors we have used the Gauss-Legendre method, discussed in detail elsewhere.[16]

A. EPR

The curve in Fig. 2 is the one obtained for b as a function of R for CaF_2 and SrF_2. It is necessary to assign a positive value for $T_\parallel$ since its absolute value is much larger than the absolute value of $T_\perp$. The sign of $T_\perp$ still remains undetermined and there are two possible "experimental" values for b (975 G for $T_\perp < 0$ and 875 G for $T_\perp > 0$). From the same figure we can see that just one of these values (875 G) gives a physically acceptable value (3.4 a.u.) for the internuclear distance, as compared with 3.6 a.u. calculated[6] for free F_2^-.

For BaF_2 the results are slightly different but still the lower value for b (881 G), corresponding to $T_\perp > 0$, must be chosen; the value $R = 3.35$ a.u. would then be adequate.

B. ENDOR

Experimental results have been obtained for four fluorine shells which in Fig. 1 we denote A, B, C', and C''. All nuclei of a given shell are equivalent by symmetry, therefore it is only necessary to calculate the $\tilde{B}$ tensor for one nucleus of each shell. The nuclei for which we performed calculations are indicated by the subscript 1 in Fig. 1.

The local symmetry of the defect is D_{2h} as observed experimentally. This allows an immediate shell classification of all nuclei. To simplify the calculation we will separate the nuclei into differ-

TABLE I. EPR parameters of the V_k center in CaF_2, SrF_2, and BaF_2. a_0 is the lattice parameter expressed in Å. The last column indicates the references.

	a_0	$g_\parallel$	$g_\perp$	$T_\parallel$ (G)	$T_\perp$ (G)	Ref.
CAF_2	5.46	2.0010 ±0.0003	2.0200 ±0.0003	899.90 ± 1.0	48.50 ± 0.40	4
		2.001 ± 0.001	2.020 ± 0.001	891.1 ± 1.0	48.50 ± 2.0	14
SrF_2	5.86	2.0024 ± 0.0003	2.0192 ± 0.0003	897.9 ± 0.5	46.3 ± 0.5	5
		2.002 ± 0.003	2.022 ± 0.003	899.0 ± 1.0	45.1 ± 3.0	14
BaF_2	6.20	2.0027 ± 0.0003	2.0226 ± 0.0003	897.50 ± 1.0	37.50 ± 0.50	4
		2.004 ± 0.003	2.024 ± 0.002	897.0 ± 1.0	41.5 ± 5.0	14

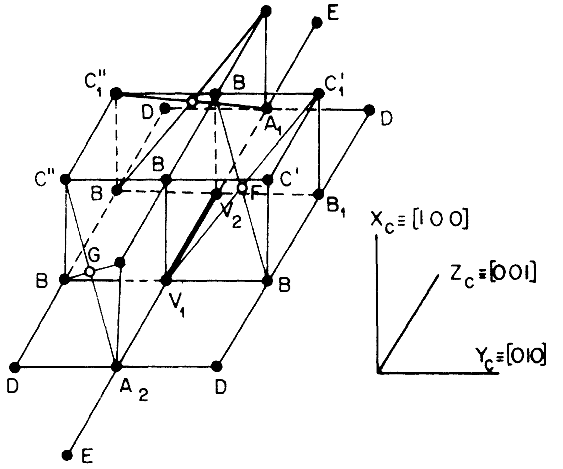

FIG. 1. Part of the crystal structure of a cubic alkaline-earth fluoride containing a V_k center. Nuclei $V_{1,2}$ belong to the "central molecule" F_2^- of the V_k center. Open circles: cations. Full circles: F^- ions. Nuclei for which magnetic hyperfine EPR and ENDOR measurements have been made: V, A, B, C', and C''. Subscript 1 indicates the nucleus, of a given shell, for which the calculation has been made.

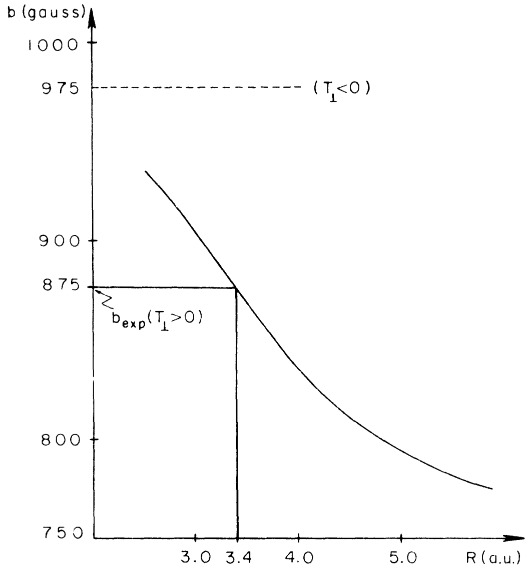

FIG. 2. Plot of the parameter b associated with the V nuclei R of the F_2^- "central molecule." Calculation done using the $3\sigma_u$ wave function, Legendre polynomial of order 96 and integration interval divided in 4 regions.

ent classes characterized by symmetry properties (see Fig. 1).

1. *First class*

All nuclei are situated along the Z_c axis of symmetry of the F_2^- molecule ion. This is an axis of order 2; therefore, in principle, two parameters would be necessary to determine the $\vec{B}$ tensors. This class includes: (i) nuclei V_1 and V_2 of the central molecule ion F_2^-; (ii) two fluorine nuclei belonging to the A shell.

For V_1 and V_2 a deviation from axiality was not experimentally detected. From Table II we can see that for SrF_2 and BaF_2 but not for CaF_2, a certain degree of nonaxiality has been detected for the A-shell nuclei. Nevertheless we assumed within an approximation that the corresponding $\vec{B}$ tensors are axial. This approximation is only relevant for BaF_2. It is clear that relaxation of these nuclei can occur only along the Z_c axis.

2. *Second class*

All nuclei are situated in a plane of symmetry of the defect. In such case the $\vec{B}$ tensor is not axial but the normal to this plane defines necessarily the direction of a principal axis. Therefore the calculation will involve the diagonalization of 2×2 matrices. In this class are: (i) four flourine nuclei belonging to the C' shell; (ii) four fluorine nuclei belonging to the C'' shell. All relaxations will occur in the plane of symmetry.

3. *Third class*

All nuclei belonging to this class are not situated in any symmetry element of the defect. To calculate the $\vec{B}$ tensors we must diagonalize 3×3 matrices. In this class are: eight flourine nuclei belonging to the B shell. All directions of relaxation are allowed. We will now discuss results for these classes of ions.

a. First class. We tried to determine the relaxation of the A-shell ions by fitting their experimental value for b, using the $3\sigma_u$ ($R = 3.4$ a.u.) wave function obtained as explained earlier. The results are shown in Fig. 3 (full curves). In the present work we adopted the following convention: minus sign indicates relaxation toward the molecule ion and plus sign away from the molecule ion. The relaxation obtained for all three crystals are significantly larger than the relaxation of nuclei V_1 and V_2; this is not a physically acceptable result indicating that the wave function is not realistic enough to describe the unpaired spin density.

An immediate correction would be the inclusion of the overlap effect between the $3\sigma_u$ wave function and $2p_z$ fluorine ion functions centered on nuclei A; physically this corresponds to including the Pauli repulsion in our monoelectronic scheme.

TABLE II. Comparison between calculated and experimental principal values of the x, y, and z components and the relevant angles θ of the $\overleftrightarrow{B}$ tensors corresponding to the A-, B-, and C-shell nuclei. The three last columns indicate the values of the relaxations for which the best fit between theoretical and experimental results is obtained.

				B_{xx}	B_{yy}	B_{zz}	θ	Δx	Δy	Δz
A	(CaF_2)		Expt.	−14.27	−14.27	28.55	0.0	0.0	0.0	0.1↔0.9
			Calc.	−14.27	−14.27	28.55	0.0			
	(SrF_2)		Expt.	−6.73	−6.37	12.87	0.0	0.0	0.0	0.0↔1.0
			Calc.	−6.43	−6.43	12.87	0.0			
	(BaF_2)		Expt.	−2.6	−1.6	4.21	0.0	0.0	0.0	0.0↔0.8
			Calc.	−2.1	−2.1	4.21	0.0			
B	(CaF_2)		Expt.	5.15	−1.61	−3.53	2.0	0.0	0.1	−2.0
			Calc.	4.8	−1.97	−2.72	3.7			
	(SrF_2)		Expt.	4.33	−1.62	−2.72	8.5	0.0	0.0	−1.5
			Calc.	4.25	−1.80	−2.44	8.5			
	(BaF_2)		Expt.	3.42	−1.48	−1.94	16.5	0.0	−0.05	−0.4
			Calc.	3.42	−1.52	−1.90	16.1			
C	CaF_2	C'	Expt.	−1.1	1.87	−0.8	14.0	0.0	0.1	−0.2
			Calc.	−1.0	1.87	−0.9	14.1			
		C''	Expt.	−0.8	1.75	−0.9	11.0	0.0	0.4	−0.6
			Calc.	−0.9	1.75	−0.8	11.5			
	SrF_2	C'	Expt.	−0.78	1.52	−0.73	15.0	0.0	0.2	−0.2
			Calc.	−0.82	1.52	−0.70	14.6			
		C''	Expt.	−0.70	1.40	−0.71	11.0	0.0	0.5	−0.8
				−0.76	1.43	−0.67	10.9			
	BaF_2	C'	Expt.	−0.7	1.91	−1.17	40.0	0.0	−2.0	2.0
			Calc.	−1.05	2.00	−0.95	32			
		C''	Expt.	−0.39	1.1	−0.73	6.5	0.0	1.0	−1.5
			Calc.	−0.58	1.1	−0.52	7.3			

In this case the wave function for the unpaired electron becomes[17]

$$|\psi\rangle = N[|3\sigma_u\rangle - (S_t/\sqrt{2})|p_z(A_1)\rangle + |p_z(A_2)\rangle], \qquad (18)$$

where

$$S_t = \sqrt{2}\,\langle 3\sigma_u | p_z(A)\rangle, \qquad (19)$$

N is the normalization constant, and p_z the $2p_z$ F^- ion wave function calculated by Clementi.[18]

Calculation shows that the overlap integral $\langle p_z(A_1)|p_z(A_2)\rangle$ is zero. The results for B_{zz} using $|\psi\rangle$ for several values of relaxation are also shown in Fig. 3 (dashed curves) for the three crystals. This figure shows that only for BaF_2 the experimental result is fitted for a relaxation (−0.8 a.u.) compatible with those of nuclei V_1 and V_2. This suggests that another mechanism of spin transfer must be included in our description; the most obvious one is covalency where charge density is transferred from the fluorine ions A to the central molecule, thus increasing the calculated value of b for a given relaxation. Within the assumption of a small degree of covalency, we can write

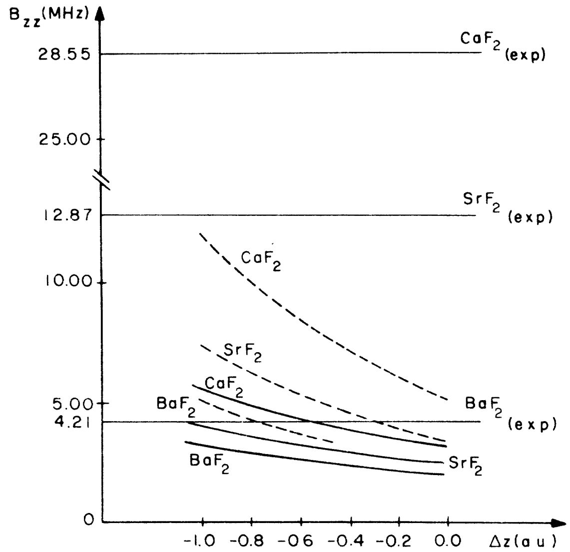

FIG. 3. Plot of the parameter B_{zz} associated with A nuclei as a function of the relaxation Δz along the Z axis. Full curves: using the $3\sigma_u$ wave function. Dashed curves: using the ψ wave function.

the antibonding wave function associated with the unpaired electron as[17]

$$|\psi_c\rangle = N'\left(|3\sigma_u\rangle - \frac{\lambda}{\sqrt{2}}[|p_z(A_1)\rangle + |p_z(A_2)\rangle]\right) , \qquad (20)$$

where $\gamma = S_t + \gamma$, where γ is the covalency parameter, and N' the normalization constant. In the present calculation γ is introduced phenomenologically.

The introduction of these mechanisms can in principle affect the results previously obtained for nuclei V_1 and V_2. Now we have three parameters to be varied (R, γ, and Δz) and we must fit simultaneously the values for b (nuclei V_1 and V_2) and B_{zz} (nuclei A_1 and A_2). The relevant calculated results are shown in Fig. 4 for SrF_2. In this case and for all other nuclei we will only present figures concerning this crystal since this gives an adequate idea of the dependence of the calculations on the parameters involved, avoiding the repetition of similar results for the other two compounds; in Table II we summarize the "best" values obtained.

It is clear that from the formulation we are proposing it will not be possible to fix all three parameters since we have only two experimental data to fit. However, on physical grounds, we can say that the upper limit for Δz is approximately equal to the relaxation of V_1 and V_2; on the other hand, owing to the fact that the V_k center has an effective positive charge it is clear that the lower limit for Δz is the unrelaxed position of nuclei A. In this manner we define the range of variation for R, γ, and Δz. We then obtain the results from the above-mentioned figures, and other calculations not presented, given in Table III. As physically expected the value of $|\gamma|$ decreases with increasing lattice parameter.

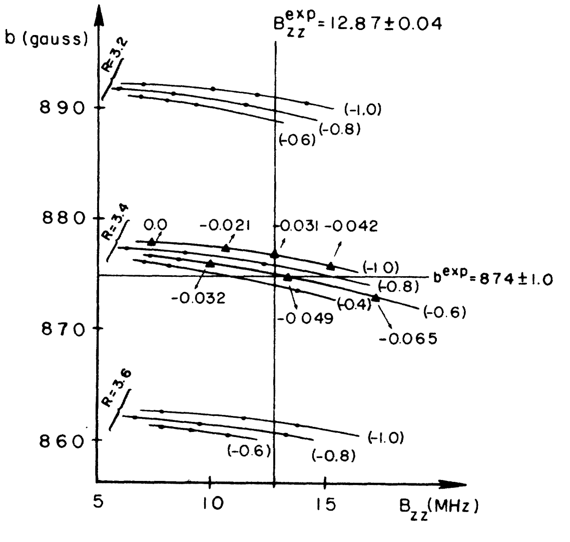

FIG. 4. Plot, for SrF_2, of the parameter b associated to the V nuclei as a function of the parameter B_{zz} associated with the A nuclei, for $R = 3.4$ a.u. and $R = 3.6$ a.u. Each curve corresponds to a given value of Δz indicated inside parentheses. For $R = 3.4$ a.u., several values of the covalency parameter are indicated beside the calculated points.

The percent deviation from the experimental values due to our assumption of axiality for the A shell $\vec{B}$ tensors are: in SrF_2, 4.4% and 4.9% for B_{xx} and B_{yy}, respectively. For CaF_2 nonaxiality is not detected experimentally. These results are physically expected since it is reasonable that the deviation from axiality will increase with increasing ionic radius of the cation. A possible manner to decrease the deviation would be to mix cation wave function with $|\psi_c\rangle$ thus breaking the axial symmetry. We have not included such a correction since the strongest interaction is given by B_{zz} and therefore our results would not be significantly modified by it.

We have verified that, for all nuclei other than those of shell A, the use of $|\psi_c\rangle$ instead of $|3\sigma_u\rangle$ modifies the results for the parameters by less than 1% when one uses $R = 3.4$ a.u. This shows that the suggested correction on $|3\sigma_u\rangle$ is only relevant for the A shell.

Nuclei V_1 and V_2. The values obtained for R are slightly smaller than those obtained by Jette and Das[8] for CaF_2 (3.8 a.u.) and by Norget and Stoneham[9] for all three crystals ($3.47 < R < 3.70$ a.u.) from an *ab initio* calculation that we shall discuss later.

For the other nuclei first we will compare our results with those of Marzke[7] and later with those of the *ab initio* calculations. We note that while Marzke[7] gives the Euler angles that define the principal axes of the $\vec{B}$ tensors we have made a transformation defining the angle θ concerning the relevant principal axis (see Table II).

Fluorines A. For these ions Marzke[7] obtained a relaxation $\Delta z = -1.6$ a.u. for CaF_2 and $\Delta z = -0.5$ a.u. for BaF_2, which corresponds approximately to the result which we have calculated using $|\psi\rangle$, Eq. (18).

b. Second class. Fluorines C'. Figure 5 shows the best fitting of the dipolar tensor for SrF_2. For CaF_2 the corresponding relaxations were Δz

TABLE III. Calculated results for the parameters R, Δz, and γ defined in the text.

CaF_2	SrF_2	BaF_2
$3.3 < R < 3.4$ a.u.	$R \simeq 3.4$ a.u.	$R \simeq 3.35$ a.u.
$0.1 < \lvert\Delta z\rvert < 0.9$ a.u.	$0 < \lvert\Delta z\rvert < 1.05$ a.u.	$0 < \lvert\Delta z\rvert < 0.8$ a.u.
$0.096 < \lvert\gamma\rvert < 0.007$	$0.060 < \lvert\gamma\rvert < 0.031$	$0.020 < \lvert\gamma\rvert < 0$

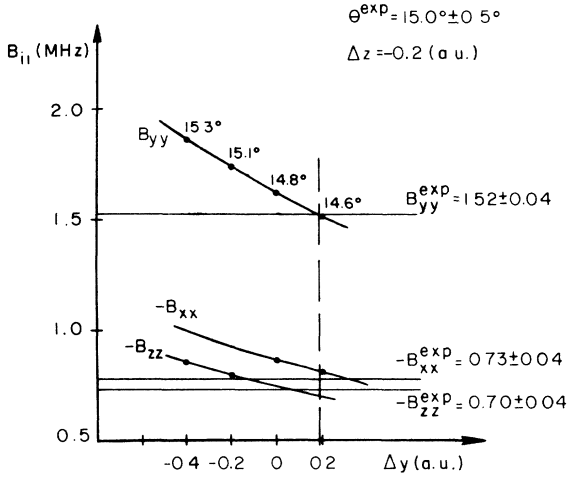

FIG. 5. Principal values B_{ii} of the $\bar{B}$ tensors associated with C' nuclei in SrF_2 plotted as a function of Δy for $\Delta z = -0.2$ a.u. Associated with each point of the curve $B_{yy} = B_{yy}$ (Δy) is the calculated value of the angle θ.

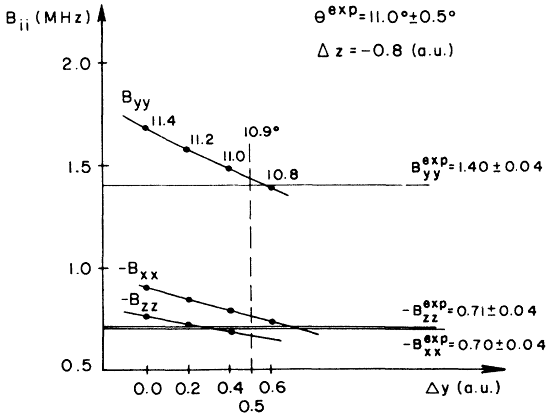

FIG. 6. Principal values B_{ii} of the $\bar{B}$ tensors associated with C'' nuclei in SrF_2 plotted as a function of Δy for $\Delta z = -0.8$ a.u. Associated with each point of the curve $B_{yy} = B_{yy}$ (Δy) is calculated value of the angle θ.

$= -0.2$ a.u. and $\Delta y = -0.1$ a.u.; the experimental results are reproduced. Marzke[7] fitted the experimental results with $\Delta z = \Delta y = 0$. In the case of SrF_2 we reproduced the experimental results with $\Delta z = -0.2$ a.u. and $\Delta y = +0.2$ a.u.

The relaxations obtained for BaF_2 are too large ($\Delta z = 2.0$ a.u. and $\Delta y = -2.0$ a.u.) and we were only able to reproduce exactly the components of the $\bar{B}$ tensor. The calculated value for θ (angle between the z principal axis and the [001] directions), 32°, must be compared with the experimental one, 40.0° ± 1.0°. Marzke[7] has also obtained large relaxations ($\Delta z = 2.06$ a.u. and $\Delta y = -1.8$ a.u.) and $\theta = 33°$. As Ba^{2+} is the largest cation in these alkaline-earth fluorides, one expects that taking into account overlap between its wave functions and $3\sigma_u$ could reduce the values obtained for the relaxations, as well as a better value for θ, because this will significantly increase the spin density near the C' nuclei.

Fluorines C''. Figure 6 shows the best fitting for SrF_2. For CaF_2 the corresponding relaxations were $\Delta z = -0.6$ a.u. and $\Delta y = -0.4$ a.u.; the experimental results were reproduced. Marzke[7] fitted the experimental results with $\Delta z = -0.5$ a.u. and $\Delta y = -0.3$ a.u.

In SrF_2 the best fitting of the experimental results was obtained relaxing the ions −0.8 a.u. in the z direction and 0.5 in the y direction. B_{xx}, B_{yy}, and B_{zz} calculated reproduced the experimental values within 8, 2.5 and 5%, respectively; θ (angle between the z principal axis and the [001] direction) calculated equals the experimental value.

In BaF_2, for relaxations $\Delta z = -1.5$ a.u. and $\Delta y = 1.0$ a.u., the experimental values for B_{xx}, B_{yy}, and B_{zz} were reproduced within 50, 0, and 27%. The calculated value of θ equals the experimental one. Here again the probable reason for these unexpected results is connected with the neglect of the overlap between $3\sigma_u$ and Ba^{2+} wave functions. The results of Marzke[7] ($\Delta z = -1.44$ a.u. and $\Delta y = 0.77$ a.u.) are similar to ours.

It was not possible to distinguish experimentally nuclei C' and C''. We will present a qualitative discussion which we believe can lead to an appropriate assignment. This discussion will be based on the results for BaF_2; because in this crystal the cation has the largest ionic radius it is expected that its presence between the central molecule and fluorines C' will affect relaxations in a manner which will distinguish C' from C''. Figure 7, where the resulting relaxations are indicated by arrows, shows that the distorted position for C' can be "explained" in the following way: the effective positive charge of the central molecule repels the cation Ba^{2+} leading to a larger distance between the C' ions and it will also cause a smaller displacement of these ions toward the central molecule due to the electrostatic attraction between F_2^- and F^- (C') ions. This will necessarily imply a value of θ larger than in the case of the C'' ions. As observed experimentally in all three crystals the value of θ for C' is always larger than for C'' but it was not possible to assign the appropriate position of C' and C'' in the lattice. With this simple qualitative argument we have good reasons to suppose that the cation is situated in the crystal between the central molecule and the C' fluorines.

c. Third class. Fluorines B. Figure 8 shows the best fitting for SrF_2. For CaF_2 the best fitting

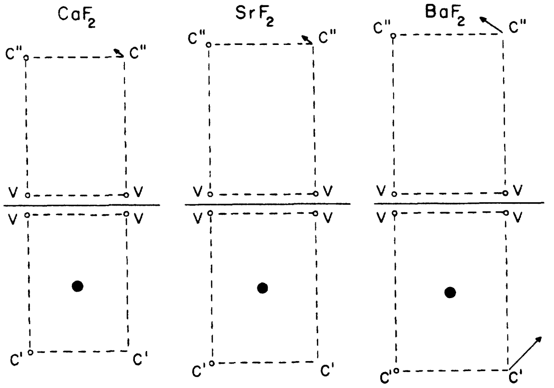

FIG. 7. Arrows indicate in scale the calculated displacements for nuclei C' and C'' in the three crystals studied. For CaF_2 and SrF_2 the displacements of C' ions are too small to be observed in the figure.

was obtained with $\Delta z = -2.0$ a.u., $\Delta y = 0.1$ a.u., and $\Delta x = 0$. This is in good agreement with the results of Marzke[7] ($\Delta z = -2.06$ a.u., $\Delta y = -0.15$ a.u., and $\Delta x = 0$). The theoretical values for B_{xx}, B_{yy}, and B_{zz} agree with the experimental ones within 6, 22, and 22%, respectively. The calculated angle θ between the principal axis x of the $\tilde{B}$ tensor and the [010] direction is 3.7° as compared with the experimental value 2° ± 1°. To obtain a good agreement for θ it was necessary to allow large relaxations in the z direction. The agreement would probably be obtained with a smaller relaxation if one considers the mixing of an appropriate linear combination of $2p_y$ and $2p_z$ centered in fluorine B with $3\sigma_u$. Calculations have shown that the overlap between these functions is not negligible.

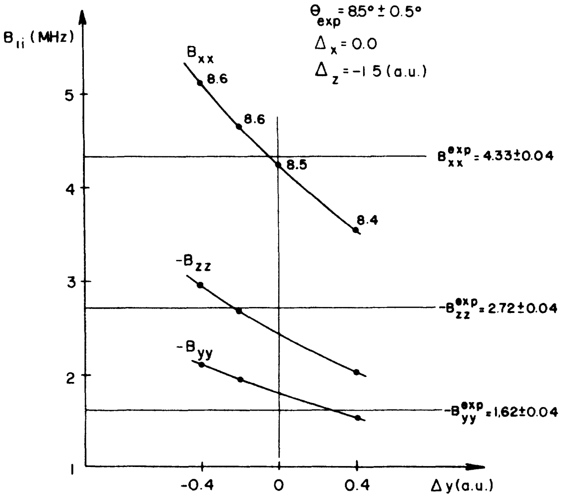

FIG. 8. Principal values B_{ii} of the $\tilde{B}$ tensors associated with B nuclei in SrF_2 plotted as a function of Δy for $\Delta x = 0$ and $\Delta z = -1.5$ a.u. Associated with each point of the curve $B_{xx} = B_{xx}(\Delta y)$ is the calculated value of the angle θ.

In the case of SrF_2, for a relaxation $\Delta z = -1.5$ a.u. and $\Delta x = \Delta y = 0$, the experimental values of B_{xx}, B_{yy}, and B_{zz} are reproduced within 2, 12.5, and 11%, respectively; θ calculated equals the experimental value (8.5° ± 0.5°).

For BaF_2 the best fitting of the experimental results was obtained with the following relaxations: $\Delta z = -0.4$ a.u., $\Delta x = 0$, and $\Delta y = -0.05$ a.u. The theoretical values of B_{xx}, B_{yy}, and B_{zz} reproduce the experimental ones within 7.4, 13, and 7.5%, respectively; θ calculated reproduces the experimental value (16.5° ± 2.0°). We are not able to explain the disagreement between our results and those obtained by Marzke[7] ($\Delta y = -0.5$ a.u. and $\Delta x = \Delta z = 0$); his calculated values for the $\tilde{B}$ tensor agree with ours.

Now we will comment on the *ab initio* calculation done by Jette and Das[8] and Norget and Stoneham[9] who treated the same problem from a different point of view. These authors used a variational procedure to minimize the energy of formation of the defect within the Mott-Littleton[19] approximation where the electrostatic interaction and short-range interactions between the central molecule and some of its neighbors, which are all allowed to relax, are considered in detail whereas the rest of the crystal is treated as a continuum. They have obtained results for the relaxations of all nuclei always smaller than ours, except for the case of nuclei A where our range includes their values. A careful examination of this variational procedure shows that it is strongly sensitive to the value of R but not to small variation in the position of the ions neighboring the central molecule. Substitution of our calculated relaxations in their formulation would certainly not change significantly their results for the formation energy of the defect. On the other hand the type of theory that tries to reproduce measured hyperfine parameters has a strong dependence on the exact position of all nuclei in the lattice. The advantage of their variational theory is that it can be applied to nonparamagnetic defects as well as to paramagnetic defects where the nuclei have no magnetic moment.

As mentioned previously Table II summarizes all the calculated and experimental results for the $\tilde{B}$ tensors as well as the relaxations for which the best fitting was obtained. Figures 7 and 9 show in scale the displacement of the ions in the lattice.

IV. CONCLUSIONS

Summarizing the most relevant results obtained in the present work we can say that this pheno-

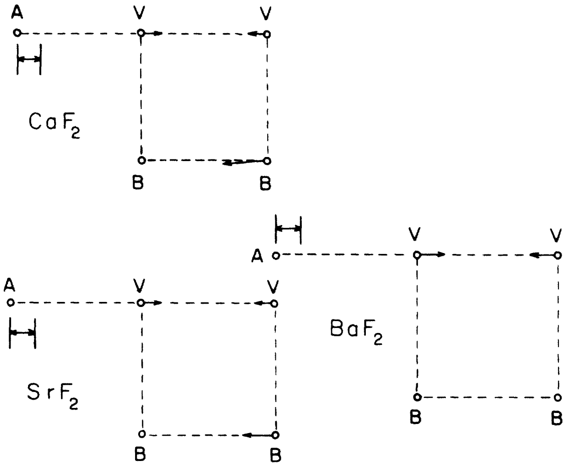

FIG. 9. The arrows indicate in scale the calculated displacements for nuclei V, A, and B in the three crystals studied. For nuclei A there is a range of possible displacements.

menological model provided some quantitative and qualitative information about the electronic and geometric structure of the V_k center in the three studied alkaline-earth fluoride crystals. It was possible to determine the sign of $T_\parallel$ and $T_\perp$ as well as indicate an assignment concerning fluorines C' and C''. Calculations have shown that the electronic structure of the defect is more extended than that of the simple F_2^- molecule ion, and that there exists a certain degree of covalency between the central molecule and the fluorines of the A shell. It also indicates a systematic and physically expected behavior of the covalency parameter since $|\gamma|$ decreases with increasing lattice parameter. The model suggests that to correct some results overlap admixtures of cation wave functions to buildup the unpaired electron wave function are necessary mainly in the case of the heavier cations, and a certain delocalization of the unpaired electron on the fluorine ions of B shell must also be considered.

We have also calculated the Fermi contact terms and, as expected, we verified that a formulation, as the present one, which does not include spin polarization is not appropriate to reproduce the experimental results.

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