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FREQUENCY SPECTRUM OF ELECTRON SPIN DOUBLE RESONANCE AT COLOR CENTERS IN ALKALI HALIDE CRYSTALS

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The dependence of frequencies in electron spin double resonance on crystal orientation in an external static magnetic field is found for U_2, F_2^+ and M centers in alkali halide crystals. Angular dependence is determined by the structure of the centers; the double-frequency resonance method can thus be used for a direct experimental study of the structure of color centers in alkali halide crystals.

1. STUDY OF SHORT-RANGE ORDER BY THE DOUBLE-FREQUENCY RESONANCE METHOD

THE electron spin double-resonance method[1,2] furnishes the frequencies of spin-nuclear transitions resulting from interactions between a localized electron and one of the nuclei surrounding the center where the electron is localized. These frequencies depend on the wave function of the localized electron and the direction of the external static magnetic field **H**. The dependence on the angle of **H** can be determined without knowing the analytic form of the electron wave function. This dependence is determined by the structure of the center and the symmetry of its neighborhood. The double-frequency resonance method can therefore be used to study the structure of different localization centers from their frequency spectra and angular dependences. When the wave function ψ falls off rapidly outside of the center the principal contribution to the frequency spectrum comes from nuclei of the first and second coordination spheres (i.e., only small frequencies result from interactions with the spins of distant nuclei). Therefore the frequency spectrum and its dependence on crystal orientation in an external magnetic field are sensitive to the short-range order of the localization centers.

Feher[2] investigated the frequency spectrum and angular dependence of double resonance at F centers in KCl. His experiments agree with the accepted view as to the nature of F centers and give the values of $|\psi|^2$ at the lattice sites which are closest to F centers.[3] Feher points out that the experiments obtain many other frequencies some of which are probably associated with defects other than F centers. It is therefore useful to obtain the dependence of double-resonance frequencies in spin-nuclear transitions on crystal orientation in an external field H when the crystal contains color centers other than F centers. This is all the more important because there is no direct experimental evidence showing the structures of a number of different electron localization centers.

2. SPIN HAMILTONIAN FOR INTERACTION BETWEEN A LOCALIZED ELECTRON AND THE MAGNETIC MOMENT OF A LATTICE NUCLEUS. SIMPLIFICATION OF THE HAMILTONIAN

We denote by **S** and $\mathbf{I}_k$ the spins of the electron and nucleus at the k-th lattice site, by μ, μ_k their magnetic moments and by ρ_k the distance from the k-th site. The spin Hamiltonian $\mathcal{H}_{sk}$ for the interaction between a localized electron and the k-th nucleus can be written as follows:[4]

$$\mathcal{H}_{sk} = 4\pi \frac{\mu\mu_k}{SI_k} |\psi(\rho_k = 0)|^2 (\mathbf{I}_k \cdot \mathbf{S}) + \sum_{p,q} A_{pqk} I_{pk} S_q, \tag{1}$$

$$A_{pqk} = \frac{\mu\mu_k}{SI_k} \int \frac{x_{qk}}{\rho_k^3} \frac{\partial |\psi|^2}{\partial x_{pk}} dV. \tag{2}$$

The axes of the Cartesian coordinate system centered at the k-th site are numbered by the subscripts p and q.

The spin Hamiltonian in (1) agrees essentially with the usual form for $\mathcal{H}_{sk}$ as the sum of a Fermi expression and a dipole-dipole interaction,[5] which is mathematically less accurate than (1) because the dipole-dipole term contains the difference between two divergent integrals. However, it is convenient in (1) to separate the Fermi term, which is proportional to $|\psi|^2$ at the k-th site.

When spherical coordinates are used for A_{pqk} in (2) it is easily shown that

$$A_{pqk} = -\frac{4\pi\mu\mu_k}{3SI_k}\,|\psi(\rho_k = 0)|^2\,\delta_{pq} + \frac{\mu\mu_k}{SI_k}\int|\psi|^2\,\frac{3x_{pk}x_{qk} - \rho_k^2\delta_{pq}}{\rho_k^5}\,dV, \tag{3}$$

where δ_{pq} is the Kronecker symbol. Inserting A_{pqk} from (3) into (1), we obtain

$$\mathscr{H}_{sk} = a(\mathbf{I}_k\cdot\mathbf{S}) + \sum_{p,q} D_{pqk}\,I_{pk}S_q. \tag{4}$$

The first expression on the right is the Fermi term while the second is the mean value of the dipole-dipole interaction. It follows from (1) and (3) that

$$a = \frac{8\pi}{3}\,\frac{\mu\mu_k}{SI_k}\,|\psi(\rho_k = 0)|^2, \tag{5a}$$

$$D_{pqk} = \frac{\mu\mu_k}{SI_k}\int|\psi|^2\,\frac{3x_{pk}x_{qk} - \rho_k^2\delta_{pq}}{\rho_k^5}\,dV. \tag{5b}$$

It is obvious that $D_{pq} = D_{qp}$. From considerations of symmetry the spin Hamiltonian (4) can be simplified further. Let $G_i^{(k)}$ be a symmetry operator satisfy the following requirements: (1) It does not affect the spatial position of the electron localization center. (2) It does not move the k-th nucleus of the lattice. (3) It interchanges identical crystal ions. Then

$$G_i^{(k)}\,|\psi|^2 = |\psi|^2. \tag{6}$$

From (6) we easily obtain the relation between different coefficients in (5b) resulting from symmetry:

$$D_{pqk} \equiv G_i^{(k)}D_{pqk} = \sum_{s,r} b_{isr}\,D_{srk}. \tag{7}$$

The coefficients b_{isr} (which are generally also dependent on p, q, and k) are determined very simply in any specific case.

We note that the set of operations $G_i^{(k)}$ comprises a subgroup of the crystal point symmetry group. The fact that the present problem is subject to less than complete crystal symmetry accounts for the frequency anisotropy of spin-nuclear transitions (the dependence of double-resonance frequencies on crystal orientation in an external magnetic field H).

It is also evident that when the coordinate axes x_{1k}, x_{2k}, x_{3k} transform into each other under the operations of crystal point symmetry leaving lattice defects in their places, the coefficients D_{pqk} will not depend on the subscript k for a group of ions that are arranged identically with respect to the localization center and have the same symmetry elements of $G_i^{(k)}$. Each ion of this group can be transferred to any other site of the group by a crystal symmetry operation without effecting the spatial arrangement of the lattice defect. Hereinafter local coordinate systems will always satisfy the foregoing conditions.

3. U_2 CENTERS

There is indirect experimental evidence that the U_2 absorption band in KCl results from the presence of hydrogen atoms at interstices of the lattice.[6] It was shown in reference 6 that the U_2 optical absorption band is accompanied by the paramagnetic resonance of hydrogen atoms. The paramagnetic resonance line width (≈ 68 gauss) results from the interaction between the electron spin and the magnetic moments of the surrounding nuclei.

We shall now obtain the electron spin double resonance frequencies resulting from the interaction between the U_2-center electron and eight surrounding nuclei, assuming that the hydrogen atom is at the center of a cube (Fig. 1). For each of the eight points the symmetry elements of $G_i^{(k)}$ form a group C_{3v} (a three-fold rotation axis and three planes of symmetry containing the rotation axis). The local coordinate system for ion 1 is chosen such that the axes x_{1k}, x_{2k} and x_{3k} are parallel to X, Y and Z. The coordinate axes for ion 2 are parallel to the directions [0 $\bar{1}$ 0], [1 0 0] and [0 0 1]. The local coordinate systems for other ions in Fig. 1 are then obtained by symmetry operations which leave the U_2 center fixed but transport ion 1 (or 2) together with its local coordinate system to equivalent points. In these coordinate systems all integrals in (5b) are identical for positive and negative ions, respectively.

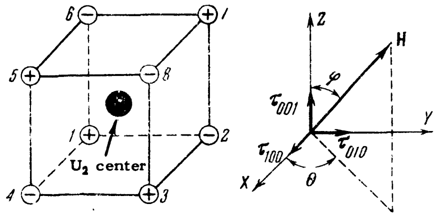

FIG. 1

Performing the symmetry operations of $G_i^{(k)}$ in group C_{3v} on the coefficients D_{pq}, we obtain

$$D_{11} = D_{22} = D_{33} = 0, \quad D_{12} = D_{23} = D_{31}. \tag{8}$$

The vanishing of the coefficients D_{pp} follows from the fact that $D_{11} + D_{22} + D_{33} = 0$. We denote the unit axes of the local systems by τ_{1k}, τ_{2k}, τ_{3k} and the coefficients D_{pq}, $p \neq q$, by $D^{\pm}$, where the upper sign refers to positive ions and the lower sign to negative ions. The spin Hamiltonian (4) with (8) taken into account can then be written as follows:

$$\mathscr{H}_{sk}^{\pm} = a^{\pm}(\mathbf{I}_k\cdot\mathbf{S}) + D^{\pm}\sum_{p\neq q}(\mathbf{I}_k\cdot\boldsymbol{\tau}_{pk})(\mathbf{S}\cdot\boldsymbol{\tau}_{qk}). \tag{9}$$

We assume at first that $a^{\pm} \gg D^{\pm}$, so that the selection rules for double-resonance spin-nuclear transitions are $\Delta M_S = 0$; $\Delta M_I = \pm 1$, where M_S and M_I are the spin projections on the field **H**, which is oriented with respect to the crystallographic axes as shown in Fig. 1. To calculate the mean value of $\mathcal{H}_{sk}$ we must know the projections of τ_{pq} ($p = 1, 2, 3$) on the field direction. It is evident that

$$\tau_{pkH} = \tau_{pkX} \sin\varphi \cos\theta + \tau_{pkY} \sin\varphi \sin\theta + \tau_{pkZ} \cos\varphi. \quad (10)$$

In (10) τ_{pkX} is the projection of τ_{pk} on the X axis etc. In order to obtain the correct frequency the Zeeman energy $g_n\beta_n(\mathbf{I}_k \cdot \mathbf{H})$ must be added to $\mathcal{H}_{sk}$, where g_n and β_n are the nuclear g-factor and nuclear magneton, respectively. Since the isotropic term in (10) makes the isotropic contribution $a^{\pm}/2$ to the frequency and the contribution of $D^{\pm}(\mathbf{I}_k \cdot \tau_{pk})(\mathbf{S} \cdot \tau_{qk})$ is $\frac{1}{2}D^{\pm}\tau_{pkH}\tau_{qkH}$, we obtain the following eight frequencies in the double-resonance spectrum of a U_2 center:

$$\begin{aligned}
h\nu_{1,8}^{\pm} &= g_n\beta_n H + {}^1/_2 a^{\pm} + {}^1/_2 (\sin^2\varphi \sin 2\theta + \sin 2\varphi (\cos\theta + \sin\theta))\, D^{\pm}, \\
h\nu_{3,6}^{\pm} &= g_n\beta_n H + {}^1/_2 a^{\pm} + {}^1/_2 (\sin^2\varphi \sin 2\theta - \sin 2\varphi (\cos\theta + \sin\theta))\, D^{\pm}, \\
h\nu_{5,2}^{\pm} &= g_n\beta_n H + {}^1/_2 a^{\pm} - {}^1/_2 (\sin^2\varphi \sin 2\theta - \sin 2\varphi (\cos\theta - \sin\theta))\, D^{\pm}, \\
h\nu_{7,4}^{\pm} &= g_n\beta_n H + {}^1/_2 a^{\pm} - {}^1/_2 (\sin^2\varphi \sin 2\theta + \sin 2\varphi (\cos\theta - \sin\theta))\, D^{\pm}
\end{aligned} \quad (11)$$

The subscripts of $h\nu$ in (11) refer to the numbered nuclei in Fig. 1.

When **H** lies in the XY plane we have $\varphi = \pi/2$ and

$$\begin{aligned}
h\nu_{1,8}^{\pm} = h\nu_{3,6}^{\pm} &= g_n\beta_n H + {}^1/_2 a^{\pm} + {}^1/_2 D^{\pm} \sin 2\theta, \\
h\nu_{5,2}^{\pm} = h\nu_{7,4}^{\pm} &= g_n\beta_n H + {}^1/_2 a^{\pm} - {}^1/_2 D^{\pm} \sin 2\theta.
\end{aligned} \quad (12)$$

In this case only four frequencies are obtained.

We shall now drop the assumption that $a^{\pm} \gg D^{\pm}$. As previously, the electron spin is oriented in the direction of **H**, so that $M_S = \frac{1}{2}$ and the selection rule is $\Delta M_S = 0$.

Let $\mathcal{H}_{sk}$ be the spin Hamiltonian averaged over the electron spin wave functions. From (9), with $g_n\beta_n(\mathbf{I}_k \cdot \mathbf{H})$ taken into account, we then obtain

$$\overline{\mathcal{H}}_{sk} = g_n\beta_n (\mathbf{I}_k \cdot \mathbf{H}) + {}^1/_2 a^{\pm} I_{kH} + {}^1/_2 D^{\pm} \sum_{\substack{p,q \\ p \neq q}} \sum_{X,Y,Z} I_{kX} \tau_{pkX} \tau_{qkH}. \quad (13)$$

It is convenient to rewrite (13) by introducing the projection I_{kn} of the spin of the k-th nucleus on the "quantization axis."[7] If M_n is the quantum number of this projection of the spin operator the selection rule is $\Delta M_n = \pm 1$. It follows from (13) that

$$\begin{aligned}
\overline{\mathcal{H}}_{sk} = [(m_{1k} + g_n\beta_n\alpha_1 H)^2 &+ (m_{2k} + g_n\beta_n\alpha_2 H)^2 \\
&+ (m_{3k} + g_n\beta_n\alpha_3 H)^2]^{1/2} I_{kn}.
\end{aligned} \quad (14)$$

Here α_1, α_2, α_3 are the projections of **H**/H on the X, Y, and Z axes,

$$m_{1k} = {}^1/_2 \alpha_1 a^{\pm} + \frac{D^{\pm}}{2} \sum_{p \neq q} \tau_{pkX}\tau_{qkH}, \quad (15)$$

and m_{2k} and m_{3k} are given by (15) with τ_{pkX} replaced by τ_{pkY} and τ_{pkZ}, respectively, and α_1 by α_2 and α_3. The frequencies are easily obtained from (14):

$$\begin{aligned}
h\nu_k = [(m_{1k} + g_n\beta_n\alpha_1 H)^2 &+ (m_{2k} + g_n\beta_n\alpha_2 H)^2 \\
&+ (m_{3k} + g_n\beta_n\alpha_3 H)^2]^{1/2}.
\end{aligned} \quad (16)$$

It can be shown that when $a^{\pm} \gg D^{\pm}$ (16) becomes Eq. (11) as an expression for the frequencies.

The coefficients D_{pq} (the dipole-dipole interaction tensor) can most conveniently be written in the principal coordinate system where D_{pq} is diagonal. In the present case the symmetry group C_{3v} determines these coordinates, the x_{3k} axis being the three-fold rotation axis while the other two axes have any mutually perpendicular directions in a plane perpendicular to the C_3 axis. D_{pq} now has only the diagonal components $-D^{\pm}$, $-D^{\pm}$, and $2D^{\pm}$.

4. F_2^+ CENTERS

An F_2^+ center is a system consisting of two negative vacancies and an electron in an ionic crystal.[8] The electron ψ cloud can either be distributed symmetrically with respect to the two vacancies or be concentrated to a large degree around only one vacancy, giving what we shall call the symmetrical and asymmetrical F_2^+-center models, respectively. The second model possesses greater probability but both models are used in the literature.[9,10,11]

The angular dependences of a number of double-resonance frequencies will differ in the symmetrical and asymmetrical models. We shall determine the double-resonance frequency spectrum by considering only the interaction of the electron with the nearest neighbors of the F_2^+ center (Fig. 2). Table I is a list of the symmetry elements of $G_i^{(k)}$ for each of seven groups of "nearest neighbor" ions which are located identically with respect to the F_2^+ center. The spin Hamiltonian for ions of

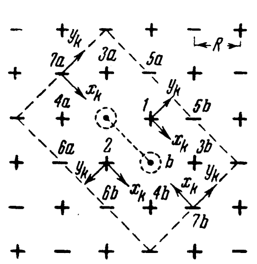

FIG. 2. Immediate neighborhood of an F_2^+ center. Ions located one row above those shown in the figure are denoted by primes (3′a, a′, etc.); those located one row below by double primes (3″a, a″ etc.). The nearest neighbors include ions which are not farther distant than $\sqrt{2R}$ from a (upper circle) or b (lower circle).

groups I and VI will differ in the symmetrical and asymmetrical cases since the symmetry groups of the $G_i^{(k)}$ elements differ; frequencies resulting from interactions with ions of group I will be highest because these ions are closest to the vacant lattice sites a and b simultaneously. Moreover, in the asymmetrical case, the plane σ'' is not a plane of symmetry because the vacancies a and b are not equivalent in this instance. Therefore the coefficients in the spin Hamiltonian for ions of a single group are not equal when these ions have specularly symmetrical positions with respect to σ''. In the symmetrical case the coefficients of the spin Hamiltonian for all ions of a given group are identical. Compared with the asymmetrical case there are now only one half as many frequencies for groups of ions which are not in the σ'' plane. For the sake of simplicity we shall not supply the coefficients a and D_{pq} with additional indices but shall keep in mind the preceding discussion and the fact that the coefficients differ for ions of different groups.

Local coordinate systems are naturally selected so that the x_{1k} axis is parallel to the a-b direction, the x_{2k} axis is perpendicular to this direction and the x_{3k} axis is perpendicular to the plane of the F_2^+ center (the principal axes of D_{pq} can be given without knowing actual magnitudes only for ions of group I in the symmetrical model and for ions of group V; the axes are those already mentioned).

Table II gives the directions of τ_{pk} for some ions. Directions for other local coordinate systems are obtained by the procedure described in Sec. 2.

In the symmetrical model the symmetry group of $G_i^{(k)}$ for group I ions is C_{2v}. Therefore $D_{pqk} = 0$ when $p \neq q$:

$$\mathscr{H}_{sk}^{I} = a(\mathbf{I}_k\cdot\mathbf{S}) + D_{11}(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k}) + D_{22}(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + D_{33}(\mathbf{I}_k\cdot\boldsymbol{\tau}_{3k})(\mathbf{S}\cdot\boldsymbol{\tau}_{3k}) = (a - D_{\parallel} - D_{\perp})(\mathbf{I}_k\cdot\mathbf{S}) + (2D_{\parallel} + D_{\perp})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k}) + (2D_{\perp} + D_{\parallel})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}). \quad (17)$$

In deriving (17) we used the fact that the trace of D_{pq} is 0 and employed the notation

$$D_{11} = D_{\parallel}; \quad D_{22} = D_{\perp}.$$

In the asymmetrical model the symmetry group for the same ions is C_s, so that only the coefficients D_{13} and D_{23} vanish (the x_{3k} axis being perpendicular to the C_s plane). Consequently, in this case,

$$\mathscr{H}_{sk}^{I} = (a - D_{\parallel} - D_{\perp})(\mathbf{I}_k\cdot\mathbf{S}) + (2D_{\parallel} + D_{\perp})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k}) + (2D_{\perp} + D_{\parallel})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + D_{12}[(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + (\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k})]. \quad (18)$$

The spin Hamiltonian of ion groups II and IV in both F_2^+-center models is also given by (18) (see Table I). For ions of Group III we have the following spin Hamiltonian:

$$\mathscr{H}_{sk}^{III} = (a - D_{\parallel} - D_{\perp})(\mathbf{I}_k\cdot\mathbf{S}) + (2D_{\parallel} + D_{\perp})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k}) + (2D_{\perp} + D_{\parallel})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + D_{13}[(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{3k}) + (\mathbf{I}_k\cdot\boldsymbol{\tau}_{3k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k})]. \quad (19)$$

This equation does not contain D_{23} and D_{21} because the x_{2k} axis is perpendicular to the symmetry plane σ'.

For ions of group V the symmetry elements of $G_i^{(k)}$ form the group C_{2v}, and the corresponding spin Hamiltonian is given by (17). In the symmetrical F_2^+ center group VI ions possess a symmetry

TABLE I. Symmetry elements of $G_i^{(k)}$

Ion group	Symmetrical model	Asymmetrical model
I: Ions 1, 2	σ, σ'', C_2	σ
II: Ions 3a, b; 4a, b	σ	σ
III: Ions a′, b′, a″, b″	σ'	σ'
IV: Ions 5a, b; 6a, b	σ	σ
V: Ions 7a, b	σ, σ', C_2'	σ, σ', C_2'
VI: Ions 1′, 2′, 1″, 2″	σ''	–
VII: Ions 3′a, b; 3″a, b 4′a, b; 4″a, b	–	–

σ – plane of F_2^+ center; σ' – plane perpendicular to σ and containing a and b; σ'' – plane perpendicular to σ and containing ions 1 and 2 (Fig. 2); C_2 – a – b axis; C_2^1 – axis through ions 1 and 2.

TABLE II

Local orthogonal unit axes for ions 1,3a,a′, 5a, 7a, 1′,3′a	F_2^+ center in (001) plane		F_2^+ center in (010) plane		F_2^+ center in (100) plane	
	a – b [110]	Along [$\bar{1}$10]	a – b [101]	Along [$\bar{1}$01]	a – b [011]	Along [01$\bar{1}$]
τ_1	110	$\bar{1}$10	101	$\bar{1}$01	011	01$\bar{1}$
τ_2	$\bar{1}$10	$\bar{1}\bar{1}$0	$\bar{1}$01	$\bar{1}$0$\bar{1}$	01$\bar{1}$	0$\bar{1}\bar{1}$
τ_3	001	001	010	010	100	100

plane σ''; consequently D_{12} and D_{13} vanish, so that

$$\mathscr{H}_{sk}^{\mathrm{VI}} = (a - D_{\parallel} - D_{\perp})(\mathbf{I}_k\cdot\mathbf{S}) + (2D_{\parallel} + D_{\perp})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k}) + (2D_{\perp} + D_{\parallel})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + D_{23}[(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{3k}) + (\mathbf{I}_k\cdot\boldsymbol{\tau}_{3k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k})]. \qquad (20)$$

In the asymmetrical case, however, symmetry elements of $G_i^{(k)}$ are absent, so that

$$\mathscr{H}_{sk}^{\mathrm{VI}} = (a - D_{\parallel} - D_{\perp})(\mathbf{I}_k\cdot\mathbf{S}) + (2D_{\parallel} + D_{\perp})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k}) + (2D_{\perp} + D_{\parallel})(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + \sum_{p\neq q} D_{pq}(\mathbf{I}_k\cdot\boldsymbol{\tau}_{pk})(\mathbf{S}\cdot\boldsymbol{\tau}_{qk}). \qquad (21)$$

Group VII ions have the same spin Hamiltonian.

We shall now determine the frequencies for double-resonance spin-nuclear transitions. Let the static magnetic field H lie in the (001) plane forming an angle θ with the [1 0 0] direction. The isotropic part of the spin Hamiltonian is usually considerably larger than the anisotropic part,^{2,3,7} so that for simplicity we shall assume $a \gg D_{pq}$. Therefore, if as previously M_S and M_I are the quantum numbers of the spin projections in the H direction, the selection rules for spin-nuclear transitions will be $\Delta M_S = 0$ and $\Delta M_I = \pm 1$. The frequencies are easily computed without assumptions regarding the orientation of H and the magnitudes of a and D_{pq}, as was shown for U_2 centers.

To determine the frequencies we must know the projections of the local axes on **H**. If the F_2^+ center lies in the (0 0 1) plane and is oriented along [1 1 0] the projections of the unit axes in Table II are given by

$$\tau_{1H} = (\sin\theta + \cos\theta)/\sqrt{2}; \quad \tau_{2H} = (\sin\theta - \cos\theta)/\sqrt{2}; \quad \tau_{3H} = 0. \qquad (22)$$

If the F_2^+ center lies along $[\bar{1}\,1\,0]$ it follows from Table II that

$$\tau'_{1H} = \tau_{2H}; \quad \tau'_{2H} = -\tau_{1H}; \quad \tau'_{3H} = \tau_{3H}. \qquad (23)$$

The primed axes in (23) refer to the case in which the F_2^+ center is directed along $[\bar{1}\,1\,0]$. For local coordinate axes not given in the table projections on H can differ from (22) in sign. If the F_2^+ center lies in the (1 0 0) plane the projections are

$$\tau_{1kH} = \pm\sin\theta/\sqrt{2}; \quad \tau_{2kH} = \pm\sin\theta/\sqrt{2}; \quad \tau_{3kH} = \pm\cos\theta. \qquad (24)$$

The combination of signs in (24) depends on the number k of the ion. Finally, for an F_2^+ center in the (0 1 0) plane the result differs from (24) by the interchange of $\sin\theta$ and $\cos\theta$. The frequencies are determined in the same way as in the preceding section.

When F_2^+ centers lie in the (0 0 1) plane spin-nuclear transitions for ions of the first group in the symmetrical case are represented by

$$\begin{aligned} h\nu &= g_n\beta_n H + \frac{1}{2}\left(a + \frac{D_{\parallel} + D_{\perp}}{2}\right) + \frac{D_{\parallel} - D_{\perp}}{4}\sin 2\theta; \\ h\nu' &= g_n\beta_n H + \frac{1}{2}\left(a + \frac{D_{\parallel} + D_{\perp}}{2}\right) - \frac{D_{\parallel} - D_{\perp}}{4}\sin 2\theta. \end{aligned} \qquad (25)$$

For ions of the second group in the symmetrical case we have

$$\begin{aligned} h\nu^{\pm} &= g_n\beta_n H + \frac{1}{2}\left(a + \frac{D_{\parallel} + D_{\perp}}{2}\right) + \frac{D_{\parallel} - D_{\perp}}{4}\sin 2\theta \mp \frac{1}{2}D_{12}\cos 2\theta; \\ h\nu'^{\pm} &= g_n\beta_n H + \frac{1}{2}\left(a + \frac{D_{\parallel} + D_{\perp}}{2}\right) - \frac{D_{\parallel} - D_{\perp}}{4}\sin 2\theta \pm \frac{1}{2}D_{12}\cos 2\theta. \end{aligned} \qquad (26)$$

In (25) and (26) $h\nu$ and $h\nu'$ refer to two mutually perpendicular orientations of F_2^+ centers in the (0 0 1) plane.

For ions of groups III, V and VI spin-nuclear transition frequencies are given by (25), and for groups IV and VII by (26).

In the symmetrical case for F_2^+ centers in the (0 0 1) plane there are the single frequencies $h\nu$ and $h\nu'$ for groups I, III, V and VI, and pairs of frequencies for groups II, IV and VII.

For F_2^+ centers in the (1 0 0) plane in the symmetrical case spin-nuclear transition frequencies resulting from an interaction between the spin of a localized electron and the magnetic moment of the k-th nucleus are given by the following equations:

For groups I and V:

$$h\nu = g_n\beta_n H + \frac{1}{2}(a - D_{\parallel} - D_{\perp}) + \frac{3}{4}(D_{\parallel} + D_{\perp})\sin^2\theta. \qquad (27)$$

For groups II and IV:

$$h\nu^{\pm} = g_n\beta_n H + \frac{1}{2}(a - D_{\parallel} - D_{\perp}) + \frac{3}{4}\left(D_{\parallel} + D_{\perp} \pm \frac{2}{3}D_{12}\right)\sin^2\theta. \qquad (28)$$

For group III:

$$h\nu^{\pm} = g_n\beta_n H + \frac{1}{2}(a - D_{\parallel} - D_{\perp}) + \frac{3}{4}(D_{\parallel} + D_{\perp})\sin^2\theta \pm \frac{D_{13}}{2\sqrt{2}}\sin 2\theta. \qquad (29)$$

For group VI:

$$h\nu^{\pm} = g_n\beta_n H + \frac{1}{2}(a - D_{\parallel} - D_{\perp}) + \frac{3}{4}(D_{\parallel} + D_{\perp})\sin^2\theta \pm \frac{D_{23}}{2\sqrt{2}}\sin 2\theta. \qquad (30)$$

For group VII:

$$h\nu^{\pm} = g_n\beta_n H + \frac{1}{2}(a - D_{\parallel} - D_{\perp}) + \frac{3}{4}\left(D_{\parallel} + D_{\perp} + \frac{2}{3}D_{12}\right)\sin^2\theta \pm \frac{D_{13}+D_{23}}{2\sqrt{2}}\sin 2\theta;$$

$$h\nu_1^{\mp} = g_n\beta_n H + \frac{1}{2}(a - D_{\parallel} - D_{\perp}) + \frac{3}{4}\left(D_{\parallel} + D_{\perp} - \frac{2}{3}D_{12}\right)\sin^2\theta \pm \frac{D_{13}-D_{23}}{2\sqrt{2}}\sin 2\theta. \quad (31)$$

If the F_2^+ center lies in the (0 1 0) plane the results are the same as in the (1 0 0) plane with $\sin\theta$ in (27) to (31) replaced by $\cos\theta$.

Let us now consider the results for the asymmetrical F_2^+-center model. For ions of groups I and VI and F_2^+ centers in the (0 0 1) plane we have

$$h\nu^{\pm} = g_n\beta_n H + \frac{1}{2}\left(a + \frac{D_{\parallel}+D_{\perp}}{2}\right) + \frac{D_{\parallel}-D_{\perp}}{4}\sin 2\theta \pm \frac{1}{2}D_{12}\cos 2\theta;$$

$$h\nu'^{\pm} = g_n\beta_n H + \frac{1}{2}\left(a + \frac{D_{\parallel}+D_{\perp}}{2}\right) - \frac{D_{\parallel}-D_{\perp}}{4}\sin 2\theta \pm \frac{1}{2}D_{12}\cos 2\theta. \quad (32)$$

For group I and F_2^+ centers in the (1 0 0) plane we have

$$h\nu^{\pm} = g_n\beta_n H + \frac{1}{2}(a - D_{\parallel} - D_{\perp}) + \frac{3}{4}\left(D_{\parallel} + D_{\perp} \pm \frac{2}{3}D_{12}\right)\sin^2\theta, \quad (33)$$

and for group VI the frequencies are given by (31).

For the remaining ion groups the angular dependences of the frequencies are the same as for the corresponding groups in the symmetrical case.

In the asymmetrical model the frequencies for F_2^+ centers in the (0 1 0) plane are given by the symmetrical model in the (1 0 0) plane with $\sin\theta$ replaced by $\cos\theta$.

Each ion group in the asymmetrical case has twice as many different frequencies as the same groups in the symmetrical case.

It is evident from the foregoing that F_2^+ centers lying in mutually perpendicular directions in the (0 0 1) plane are represented by different angular dependences of the frequencies, whereas for F_2^+ centers in the other two planes the frequency spectrum is independent of the F_2^+-center orientation in the plane. If the F_2^+ center lies in the (0 0 1) plane the weight of each frequency for ion groups I, II, IV and V is one-half that of the corresponding frequency when the F_2^+ center lies in the (0 1 0) or (1 0 0) plane and is equal to N/6 and N/3 for the asymmetrical and symmetrical model, respectively (N is the number of F_2^+ centers in the crystal). For other frequencies the weight is independent of the plane in which the F_2^+ center is located and is twice as large as the values just given.

We may now inquire about the difference between the angular dependence of the double-resonance frequency for an F center and that for an F_2^+ center which is regarded as an F center that is polarized by a neighboring negative vacancy (the asymmetrical model). It is simplest to compare the two frequencies in the local coordinate system that was used for the nuclei surrounding the F center.[3] Denoting the coefficient of the dipole-dipole interaction in this system by $D_{p'q'}$, when for the positive ions nearest to the vacancy the primed axes are along the principal crystallographic axes and the x_3' axis passes through the vacancy, for k = 1, for example, we obtain

$$h\nu_{0,0,1}^{k=1} = g_n\beta_n H + \frac{1}{2}(a + D_{2'2'}) + \frac{1}{2}(D_{3'3'} - D_{2'2'})\sin^2\theta + \frac{1}{2}D_{3'2'}\sin 2\theta. \quad (34)$$

For F centers $D_{3'2'} = 0$, and we obtain the already known double-resonance frequency for this case[2,3] (in reference 3 $a + D_{2'2'} = A$, $D_{3'3'} - D_{2'2'} = BR^2$).

The angular dependences of other frequencies for F centers in the asymmetrical model can be determined in the local coordinate systems of the centers. However, without computing a and D_{pq} it is impossible to determine theoretically whether experiment can distinguish F-center and asymmetrical F_2^+-center frequencies (in (25) the difference in the angular dependence results from the term $\frac{1}{2}D_{3'2'}\sin 2\theta$). For an asymmetrical F_2^+ center the second vacancy has little effect on the ψ-cloud distribution of the F center, so that it is difficult to separate the frequencies. It is still an open question which of the frequencies in (25) to (33) can be resolved experimentally and how well this can be done.

5. M CENTERS

An M center is pictured as being formed by an electron localized near three vacancies resulting from two missing anions and one missing cation (Fig. 3).[8,12,13] As for F_2^+ centers, we have both a symmetrical and an asymmetrical model for M centers. In the symmetrical model the ψ cloud of the localized electron is distributed symmetrically with respect to the anion vacancies a and b, so that vacancies a and b are equivalent. In the more probable asymmetrical case the ψ cloud is concentrated to a greater extent around one of the anion vacancies.

Table III gives the symmetry elements of $G_i^{(k)}$ for nearest-neighbor ions. A knowledge of $G_i^{(k)}$ enables us to write the spin Hamiltonian $\mathcal{H}_{sk}$ at once. For ions of the first group in both M-center models

$$\begin{aligned}\mathcal{H}^{\mathrm{I}}_{sk} = (a - D_1 - D_2)(\mathbf{I}_k\cdot\mathbf{S}) + (2D_1 + D_2)(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k})\\ + (2D_2 + D_1)(\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k})\\ + D_{12}[(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + (\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k})].\end{aligned} \tag{35}$$

For group II in the symmetrical model $D_{11} = D_{22}$, so that

$$\begin{aligned}\mathcal{H}^{\mathrm{II}}_{sk} = (a - 2D_1)(\mathbf{I}_k\cdot\mathbf{S}) + 3D_1[(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k}) + (\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k})]\\ + D_{12}[(\mathbf{I}_k\cdot\boldsymbol{\tau}_{1k})(\mathbf{S}\cdot\boldsymbol{\tau}_{2k}) + (\mathbf{I}_k\cdot\boldsymbol{\tau}_{2k})(\mathbf{S}\cdot\boldsymbol{\tau}_{1k})].\end{aligned} \tag{36}$$

In this case the principal axes of the tensor D_{pq} are along C_2 and two mutually perpendicular directions in a plane perpendicular to C_2. The principal values of the tensor are $D_1 - D_{12}$, $D_1 + D_{12}$ and $-2D_1$. In the asymmetrical model the spin Hamiltonian for these ions is given by (36).

For group III in the symmetrical case we have $D_{13} = D_{23}$, and $D_{11} = D_{22}$; otherwise we have (21). The asymmetrical model has the same spin Hamiltonian with different coefficients. Finally, group IV does not possess symmetry elements that simplify the Hamiltonian, so that $\mathcal{H}^{\mathrm{IV}}_{sk}$ is given by (21).

The coefficients a and D_{pq} are identical for ions that are mirror reflections of each other in the σ plane. Moreover, in the symmetrical model there are identical coefficients for ions (k_a and k_b) that are located symmetrically with respect to the σ' plane, while all other ion groups have different coefficients. However, we shall not add additional subscripts to a and D_{pq}.

In calculating frequencies it must be remembered that there are four orientations of an M center in a given plane, which is thus divided into four quadrants by the sides of the M center.

Let the field H lie in the (0 0 1) plane and make an angle θ with the [1 0 0] direction. As previously, we shall assume that $a \gg D_{pq}$. The projections of unit local axes (Fig. 3) on H for M centers with different orientations in different planes will be 0, $\pm\cos\theta$ or $\pm\sin\theta$.

TABLE III. Symmetry elements of $G_i^{(k)}$

Ion group	Symmetrical model	Asymmetrical model
I: Ions 1–6a, b	σ	σ
II: Ions 1, 3, 7	σ, σ', C_2	σ
III: Ions σ', σ'', 1′, 1″, 3′, 3″, 7″, 7″	σ'	–
IV: Ions on both sides of group I ions.	–	–

σ – plane of M center; σ' – diagonal plane; C_2 – intersection of these planes

Spin-nuclear transition frequencies in the symmetrical model for an M center in the (0 0 1) plane are as follows:

For ions of groups I and IV:

$$\begin{aligned}h\nu_a^{\pm} = g_n\beta_nH + \frac{1}{2}(a + D_2)\\ + \frac{1}{2}(D_1 - D_2)\cos^2\theta \pm \frac{1}{2}D_{12}\sin 2\theta;\\ h\nu_b^{\pm} = g_n\beta_nH + \frac{1}{2}(a + D_2)\\ + \frac{1}{2}(D_1 - D_2)\sin^2\theta \pm \frac{1}{2}D_{12}\sin 2\theta.\end{aligned} \tag{37}$$

For groups II and III:

$$h\nu^{\pm} = g_n\beta_nH + \frac{1}{2}(a + D_1) \pm \frac{1}{2}D_{12}\sin 2\theta. \tag{38}$$

For M centers in the (1 0 0) plane in the symmetrical model the frequencies are:

For group I:

$$\begin{aligned}h\nu_a = g_n\beta_nH + \frac{1}{2}(a + D_1) - \frac{2D_1 + D_2}{2}\cos^2\theta;\\ h\nu_b = g_n\beta_nH + \frac{1}{2}(a + D_2) - \frac{2D_2 + D_1}{2}\cos^2\theta;\end{aligned} \tag{39}$$

For group II:

$$h\nu = g_n\beta_nH + \frac{1}{2}(a + D_1) - \frac{3}{2}D_1\cos^2\theta; \tag{40}$$

For group III:

$$\begin{aligned}h\nu^{\pm} = g_n\beta_nH + \frac{1}{2}(a + D_1)\\ - \frac{3}{2}D_1\cos^2\theta \pm \frac{1}{2}D_{13}\sin 2\theta;\end{aligned} \tag{41}$$

For group IV:

$$\begin{aligned}h\nu_a^{\pm} = g_n\beta_nH + \frac{1}{2}(a + D_1) - \frac{2D_1 + D_2}{2}\cos^2\theta \pm \frac{1}{2}D_{13}\sin 2\theta;\\ h\nu_b^{\pm} = g_n\beta_nH + \frac{1}{2}(a + D_2) - \frac{2D_2 + D_1}{2}\cos^2\theta \pm \frac{1}{2}D_{23}\sin 2\theta.\end{aligned} \tag{42}$$

In the asymmetrical model the number of different frequencies for each group is double that in the symmetrical model.

For groups I and IV of an M center in the (0 0 1) plane the angular dependences are the same as in the symmetrical model [Eq. (38)]. For groups II and III

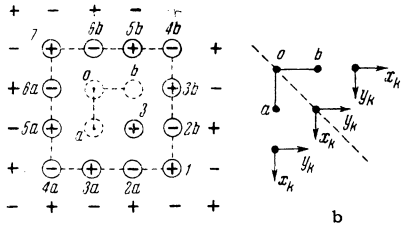

FIG. 3. a) Nearest neighbors of an M center, which include ions in two parallel planes above and below those shown in the figure. The notation is the same as in Fig. 2.

b) Local coordinate systems. The z_k axis is perpendicular to the plane of the M center and is always directed away from it. (As for primed ions, the z_k axis in the figure is always along one of the three directions [0 0 1], [0 1 0] or [1 0 0].

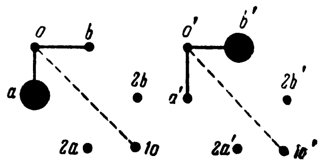

FIG. 4. The Ψ cloud is largely concentrated at a on the left and at b′ on the right.

the frequencies are the same as $h\nu_a^\pm$ of (38) in the symmetrical model.

For M centers in the (1 0 0) plane in the asymmetrical model the frequencies for group I are

$$\begin{aligned} h\nu_a &= g_n\beta_n H + {}^1/_2\,(a + D_1) - {}^1/_2\,(2D_1 + D_2)\cos^2\theta;\\ h\nu'_a &= g_n\beta_n H + {}^1/_2\,(a + D_2) - {}^1/_2\,(2D_2 + D_1)\cos^2\theta;\\ h\nu_b &= g_n\beta_n H + {}^1/_2\,(a' + D'_2) - {}^1/_2\,(2D'_2 + D'_1)\cos^2\theta;\\ h\nu'_b &= g_n\beta_n H + {}^1/_2\,(a' + D'_1) - {}^1/_2\,(2D'_1 + D'_2)\cos^2\theta. \end{aligned} \tag{43}$$

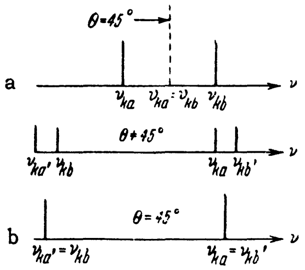

FIG. 5. a) The pair of nuclei k_a and k_b in the symmetrical model result in two frequencies which coincide at $\theta = 45°$.

b) In the asymmetrical model the same ions give four frequencies, two of which are smaller than for the symmetrical case. The weight of each frequency is one half that in the symsymmetrical model.

For group IV we have

$$\begin{aligned} h\nu_a^\pm &= g_n\beta_n H + {}^1/_2\,(a + D_1) - {}^1/_2\,(2D_1 + D_2)\cos^2\theta \pm {}^1/_2\,D_{13}\sin 2\theta;\\ h\nu'^\pm_a &= g_n\beta_n H + {}^1/_2\,(a + D_2) - {}^1/_2\,(2D_2 + D_1)\cos^2\theta \pm {}^1/_2\,D_{23}\sin 2\theta;\\ h\nu_b^\pm &= g_n\beta_n H + {}^1/_2\,(a' + D'_2) - {}^1/_2\,(2D'_2 + D'_1)\cos^2\theta \pm {}^1/_2\,D'_{23}\sin 2\theta;\\ h\nu'^\pm_b &= g_n\beta_n H + {}^1/_2\,(a' + D'_1) - {}^1/_2\,(2D'_1 + D'_2)\cos^2\theta \pm {}^1/_2\,D'_{13}\sin 2\theta. \end{aligned} \tag{44}$$

For group II the frequencies are given by $h\nu_a$ and $h\nu'_a$ of (43) and for group III by $h\nu_a^\pm$ and $h\nu'^\pm_a$ of (44).

For an M center in the (0 1 0) plane in both the symmetrical and asymmetrical models frequencies are given by the preceding expressions for the (1 0 0) plane with cos θ replaced by sin θ. We must expect large differences in the frequencies for ions of a single group even in the symmetrical model because of considerably different positions of ions in the group with respect to the M center.

We can make the following comments regarding the foregoing angular dependences. When an M center is in the (0 0 1) plane the angular dependences for ions k_a and k_b (Fig. 3) differ; also, M centers with sides along [0 0 1], [0 1 0] and [0 0 $\bar{1}$], [0 $\bar{1}$ 0] give frequencies different from the corresponding frequencies due to the two other M-center orientations in this plane (the sign of D_{12} is different). In the asymmetrical model each frequency is split into two. Thus ions 2a, 2a′, 2b, and 2b′ (Fig. 4) give four frequencies and ions 1o and 1o′ give two. (In our local coordinates D_{pq} for 2a and 2b′ coincide, and for ions 1o and 1o′ $D_{11} = D'_{22}$; $D_{22} = D'_{11}$). This is illustrated in Fig. 5.

When an M center lies in the (1 0 0) or (0 1 0) plane all four orientations in the symmetrical model give identical sets of frequencies, while in the asymmetrical model two pairs of orientations give different frequencies. However, the M centers shown in Fig. 4 give identical frequencies in this case.

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