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PARAMAGNETIC RESONANCE OF F CENTERS IN STATIC MAGNETIC FIELDS OF ARBITRARY STRENGTH

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The hyperfine interaction of an F center electron with the magnetic moments of nuclei of the first coordinational sphere surrounding the vacancy is examined for the case when a static field of arbitrary strength is present. The hyperfine splitting has been evaluated for F centers in a KCl crystal. Transitions between hyperfine levels induced by a radio-frequency field are considered. In the absence of an external static field, these transitions are found to be allowed.

Special attention is paid to paramagnetic resonance of F centers in which only one of the first coordinational sphere has a magnetic moment. In this case the frequencies and intensities of paramagnetic resonance absorption depend on the oriention of the crystal in the static magnetic field. The absorption intensity depends also on the orientation of the crystal relative to the vector of the magnetic field of the wave incident on the crystal.

1. INTRODUCTION

EXPERIMENTAL and theoretical investigations of paramagnetic resonance of F centers in ionic crystals have been reported by several authors.[1-6] An essential feature of all these investigations has been the presence of strong magnetic fields, i.e., the inequality $\mu H \gg A$ (μ is the Bohr magneton, H is the intensity of the external staticmagnetic field, and A is the hyperfine splitting constant). In this case the correct quantum numbers are S_z and I_z.

Quantum transitions under the influence of a microwave field satisfy the condition $\Delta S_z = \pm 1$, $\Delta I_z = 0$. It becomes possible to obtain the shape and half width of the spin-electron resonance curve. The Gaussian form of the curve, which is obtained theoretically, is in good agreement with experiment.

It is of interest to consider paramagnetic resonance of local electron centers for arbitrary value of intensity of external static magnetic field. Judging from references 7 and 8, devoted to an experimental investigation of paramagnetic resonance in hydrogen and deuterium in weak magnetic fields, we can likewise expect qualitatively new features, not inherent in the spin-electron resonance in strong fields, in paramagnetic resonance of local electron centers in crystals.

Of particular interest is an investigation of the possibility of realizing paramagnetic resonance in the absence of an external static magnetic field. We develop below the theory of paramagnetic resonance of F centers for arbitrary value of the intensity of the external static field and, in particular, for zero field.

2. HYPERFINE SPLITTING OF ENERGY LEVELS OF THE F CENTER IN THE PRESENCE OF AN EXTERNAL STATIC MAGNETIC FIELD

The spin-Hamiltonian of the system under consideration can be written[9]

$$\hat{W} = \mu H\Big(g\hat{S}_z - \sum_{k=1}^{6} g_{kI}\,\hat{I}_{kz}\Big) + \sum_{k=1}^{6} a_k(\hat{\mathbf{S}}\cdot\hat{\mathbf{I}}_k) + \sum_{k=1}^{6}\sum_{p,\,q=1}^{3} A_{pqk}\hat{I}_{kq_k}\hat{S}_{p_k}, \qquad (1)$$

and

$$a_k = (4\pi\mu_k\mu/I_kS)\,|\psi(\rho_k = 0)|^2, \quad g_I = g_{\text{nuc}}\mu_N/\mu,$$
$$A_{pqk} = \frac{\mu\mu_k}{SI_k}\int\frac{x_q}{\rho_k^3}\frac{\partial|\psi|^2}{\partial x_p}\,d\tau, \qquad (2)$$

where g is the Landé factor of the electron; g_{nuc} is the nuclear g factor; μ_N is the nucleon magneton; **S**, $\mathbf{I}_k$, S_z and I_{kz} are the spin vectors of the electron and the k-th nucleus and their projections on the z axis, μ_k is the magnetic moment of the k-th nucleus, and ψ is the wave function of the F center. The integration in (2) is in a frame with origin in the k-th nucleus.

Separating the Fermi terms in the last component of (1), the spin-Hamiltonian of the system is more conveniently rewritten as

$$\hat{W} = \mu H\Big(g\hat{S}_z - \sum_{k=1}^{6} g_{Ik}\hat{I}_{kz}\Big) + \sum_{k=1}^{6} A_k(\mathbf{S}\cdot\mathbf{I}_k) + \sum_{k=1}^{6}\sum_{q=1}^{3}\sum_{p=1}^{3} A'_{pqk}\hat{I}_{kq_k}\hat{S}_{p_k}, \tag{3}$$

$$A_k = \frac{8\pi\mu\mu_k}{3SI_k}\,|\psi(\rho_k = 0)|^2, \tag{4}$$

$$A'_{pqk} = \frac{\mu\mu_k}{SI_k}\int|\psi|^2\,\frac{3x_{kp}x_{kq} - \rho_k^2\delta_{pq}}{\rho_k^5}\,d\tau. \tag{5}$$

Estimates show that $A'_{pqk} \ll A_k$ for F centers. Therefore the spin Hamiltonian (3) can be approximately written

$$\hat{W} = \mu H(g\hat{S}_z - g_I\hat{I}_z) + A(\hat{\mathbf{S}}\cdot\hat{\mathbf{I}}). \tag{6}$$

It is taken into account in (6) that for all nuclei of the first coordination sphere the value of A_k is the same ($A_k = A$); I and I_z are respectively the total spin of the nuclei of the first coordinational sphere and its projection on the z axis.

The energy levels of a system with a spin Hamiltonian (6) have been calculated by Breit and Rabi[10] and are written

$$E_1 = AI/2 + \mu H(g/2 - g_I I) \quad \text{for } F_z = S_z + I_z = I + {}^1\!/_2, \tag{7}$$

$$E_2 = AI/2 - \mu H(g/2 - g_I I) \quad \text{for } F_z = -I - {}^1\!/_2, \tag{7a}$$

$$E_{3,4} = -A/4 - \mu H g_I F_z \pm {}^1\!/_2[(g + g_I)^2\mu^2H^2 + 2AF_z(g + g_I)\mu H + A^2(I + {}^1\!/_2)^2]^{1/2}. \tag{7b}$$

In Eq. (7b), F_z assumes values from $-I + \frac{1}{2}$ to $I - \frac{1}{2}$, and the indices 3 and 4 designate the aggregate of energy levels. It follows from (7) that the energy levels correspond to definite values of F_z. This quantum number, however, does not determine the levels uniquely [see (7b)]. It is therefore convenient to describe arbitrarily the energy levels by still another quantum number F, which characterizes the eigenvalue of the square of the total momentum. The latter characteristic has meaning only if $H = 0$ ($F = I + \frac{1}{2}$ and $F = I - \frac{1}{2}$). We shall assign the first value to the E_3 level and the second to the E_4 level. All energy levels of this system are obtained from (7) at different values of F_z and I.

By way of illustration, we calculated the numerical values of the energy levels for the alkali-halide crystals with lattices of the NaCl type (halides of K, Na, Rb, and Li). The spins of the nuclei of the metal ions in these lattices are $^3/_2$. Using the rules for addition of vector operators,[11] we obtain for the total spin of the six nuclei in the first coordinational sphere the following values:

$I =$	0	1	2	3	4	5	6	7	8	9
$N =$	34	90	120	120	96	64	35	15	5	1

N determines the statistical weight of the quantum state corresponding to a definite I.

Available data on double paramagnetic resonance[9,12,13] make it possible to determine the binding constants of the spin Hamiltonian (1). In particular, for the spin-Hamiltonian of the F center in KCl we obtain for the constant A [Eq. (6)] $A/\mu = 15.43$ gausses. We note, furthermore, that in high-accuracy numerical calculations it is possible to neglect the second component of the Zeeman term of (6), since it is on the order of 10^{-4} of the first term.

It is easy to see that the total number of levels in this case is $\sum_{I=0}^{9} 2(2I + 1) = 200$. Numerical claculations of the energy levels in the presence of an external magnetic field have been carried out for H = 50 oersteds. Since we do not wish to clutter up the article with tables, we omit the numerical values of the energy levels and cite only the transition frequencies.

3. QUANTUM TRANSITIONS IN THE SPECTRUM OF HYPERFINE SPLITTING. SELECTION RULES. INTENSITIES OF PARAMAGNETIC-RESONANCE LINES

The wave function of the system is written

$$\Phi = C_1\chi'_I(I_z)\chi_{1/2}(S_z) + C_2\chi'_{-I}(I_z)\chi_{-1/2}(S_z) + \sum_{F_z=-I+1/2}^{I-1/2}[C_3(F_z)\chi'_{F_z+1/2}(I_z)\chi_{-1/2}(S_z) + C_4(F_z)\chi'_{F_z-1/2}(I_z)\chi_{1/2}(S_z)]. \tag{8}$$

Here χ and χ' are the electronic and nuclear spin functions respectively, while C are the linear-combination coefficients.

The inclusion of the perturbation (6) removes the degeneracy completely and leads to the appearance of 200 levels. Each level has its own wave function, obtained from (8) by substituting into this expression the corresponding set of coefficients C. We note that for levels with $F_z = I + \frac{1}{2}$ and $F_z = -(I + \frac{1}{2})$ only one of the coefficients differs from zero. For levels having the same values of F_z only $C_3(F_z)$ and $C_4(F_z)$ differ from zero. They are determined by solving the system of equations

$$\begin{aligned} &[W_{33}(F_z) - E]C_3(F_z) + W_{34}(F_z)C_4(F_z) = 0,\\ &W_{43}(F_z)C_3(F_z) + [W_{44}(F_z) - E]C_4(E_z) = 0, \end{aligned} \tag{9}$$

where $W_{33}(F_z)$ and $W_{44}(F_z)$ are respectively the diagonal matrix elements of the states with $I = F_z + \frac{1}{2}$, $S_z = -\frac{1}{2}$ and $I = F_z - \frac{1}{2}$, $S_z = \frac{1}{2}$, while $|W_{34}(F_z)| = |W_{43}(F_z)|$ is the non-diagonal element, constructed from the wave functions of the state indicated above:

$$W_{33}(F_z) = -\mu Hg/2 - (A/2)(F_z + {}^1/_2),$$
$$W_{44}(F_z) = \mu Hg/2 + (A/2)(F_z - {}^1/_2), \tag{10}$$
$$W_{34}(F_z) = W_{43}(F_z) = (A/2)[(I + F_z + {}^1/_2)(I - F_z + {}^1/_2)]^{1/2}$$

with the normalization condition

$$|C_3(F_z)|^2 + |C_4(F_z)|^2 = 1. \tag{11}$$

We finally obtain the following system of wave functions

$$\Phi_1 = \chi'_I \chi_{1/2}, \tag{12a}$$
$$\Phi_2 = \chi'_{-I}\chi_{-1/2}, \tag{12b}$$
$$\Phi_3(F_z) = C'_3(F_z)\chi'_{F_z+1/2}\chi_{-1/2} + C'_4(F_z)\chi'_{F_z-1/2}\chi_{1/2}, \tag{12c}$$
$$\Phi_4(F_z) = C''_3(F_z)\chi'_{F_z+1/2}\chi_{-1/2} + C''_4(F_z)\chi'_{F_z-1/2}\chi_{1/2}. \tag{12d}$$

In (12c) and (12d) F_z assumes values from $-I + \frac{1}{2}$ to $I - \frac{1}{2}$. C′ corresponds to the value of energy E, obtained from (7b) using the root with the positive sign; C′ corresponds to the negative root. The first three wave functions in (12) describe states characterized by $F = I + \frac{1}{2}$, while the last one describes states with $F = I - \frac{1}{2}$.

It follows directly from (9) and (11) that

$$C_3(F_z) = -W_{34}(F_z)/[W^2_{34}(F_z) + [W_{33}(F_z) - E]^2]^{1/2}, \tag{13a}$$

$$C_4(F_z) = (W_{33}(F_z) - E)/\{W^2_{34}(F_z) + [W_{33}(F_z) - E]^2\}^{1/2}. \tag{13b}$$

Using (13a), (13b), and also (7b), we can show that

$$C'_3(F_z) = -C''_4(F_z), \quad C''_3(F_z) = C'_4(F_z). \tag{14}$$

Going to the limit of strong fields, we obtain the following values for the coefficients:

$$\begin{gathered} C'_3(F_z) \to 0; \quad C''_3(F_z) \to -1; \\ C'_4(F_z) \to -1; \quad C''_4(F_z) \to 0. \end{gathered} \tag{15}$$

A radio-frequency field produces transitions between the stationary states of the system which were considered in Sec. 2.

The solution of the corresponding Schrödinger temporal equation is sought in the following form

$$\varphi = D_1\Phi_1 + D_2\Phi_2 + \sum_{F_z=-I+1/2}^{I-1/2} [D_3(F_z)\Phi_3(F_z) + D_4(F_z)\Phi_4(F_z)], \tag{16}$$

where D are time-dependent coefficients.

As usual, at the instant t = 0 all the coefficients D, with the exception of one, are assumed to be zero. At a time $t \neq 0$, according to perturbation theory,

$$D_i^{(1)} = (1/i\hbar)\int_0^t V_{ik}\exp\{i\omega_{ik}\tau\}\,d\tau + \delta_{ik}, \tag{17}$$

where the index k indicates the level from which the transition takes place to a certain level i, and

$$\hat{V} = -(\boldsymbol{\mu}\cdot\mathbf{H}'(t)), \quad \omega_{ik} = (E_i - E_k)/\hbar. \tag{18}$$

To calculate D_i it is first necessary to determine V_{ik}. It is easy to see that all the matrix elements V_{ik} can be obtained by applying the perturbation operator (18) to the functions Φ_1 and Φ_2, and also to the system of functions $\Phi_3(F_z)$ $\Phi_4(F_z)$.

The first two functions correspond to levels E_1 and E_2, while the third and fourth functions are ascribed to levels E_3 and E_4. We therefore encounter a total of eight different types of matrix elements V_{ik}. The calculations yield

$$V_{12} = 0 \text{ for } I \neq 0,$$
$$V_{12} = {}^1/_2\mu g(H'_x - iH'_y) \quad \text{for } I = 0, \tag{19a}$$
$$V_{13} = {}^1/_2\mu g(H'_x - iH'_y)\,C'_3(F_z)\,\delta(F_z, I - {}^1/_2). \tag{19b}$$

The symbol $\delta(F_z, I - \frac{1}{2})$ indicates that the matrix element (19b) differs from 0 only for transitions from level 3 (when $F_z = I - \frac{1}{2}$) to level 1. For the remaining values of F_z, the transitions from levels 3 to level 1 are forbidden. Inserting into (19b) the values $F_z = I - \frac{1}{2}$ and the values of the coefficient $C'_3(F_z)$ for $F_z = I - \frac{1}{2}$ [from (13a)] we determine V_{13}.

Analogously we have for the matrix element V_{14}, V_{23}, V_{24}, and V_{33}

$$V_{14} = {}^1/_2\mu g(H'_x - iH'_y)\,C''_3(F_z)\,\delta(F_z, I - {}^1/_2), \tag{19c}$$
$$V_{23} = {}^1/_2\mu g(H'_x + iH'_y)\,C'_4(F_z)\,\delta(F_z, -I + {}^1/_2), \tag{19d}$$
$$V_{24} = {}^1/_2\mu g(H'_x + iH'_y)\,C''_4(F_z)\,\delta(F_z, -I + {}^1/_2), \tag{19e}$$
$$V_{33} = {}^1/_2\mu g(H'_x - iH'_y)\,C'_4(F_z^+)\,C'_3(F_z)\,\delta(F_z, F_z^+ - 1). \tag{19f}$$

The matrix element V_{33} corresponds to a transition from the level F_z to the level $F_z^+ = F_z + 1$

$$V_{44} = {}^1/_2\mu g(H'_x + iH'_y)\,C''_3(F_z^+)\,C''_4(F_z)\,\delta(F_z, F_z^+ + 1). \tag{19g}$$

When calculating V_{34} it must be borne in mind that the transitions possible here are both between identical F_z and between different ones. Accordingly, three matrix elements of type V_{34} appear:

$$\begin{gathered} V'_{34} = {}^1/_2\mu gH'_z[C'_4(F_z^+)\,C''_4(F_z) \\ - C'_3(F_z^+)\,C''_3(F_z)]\,\delta(F_z^+, F_z), \end{gathered} \tag{19h}$$

$$V''_{34} = {}^1/_2\mu g(H'_x + iH'_y)\,C'_3(F_z^+)\,C''_4(F_z)\,\delta(F_z, F_z^+ + 1), \tag{19i}$$

$$V'''_{34} = {}^1/_2\mu g(H'_x - iH'_y)\,C'_4(F_z^+)\,C''_3(F_z)\,\delta(F_z, F_z^+ - 1). \tag{19j}$$

It follows from the above that selection rules $\Delta F_z = 0$ apply to transitions caused by the com-

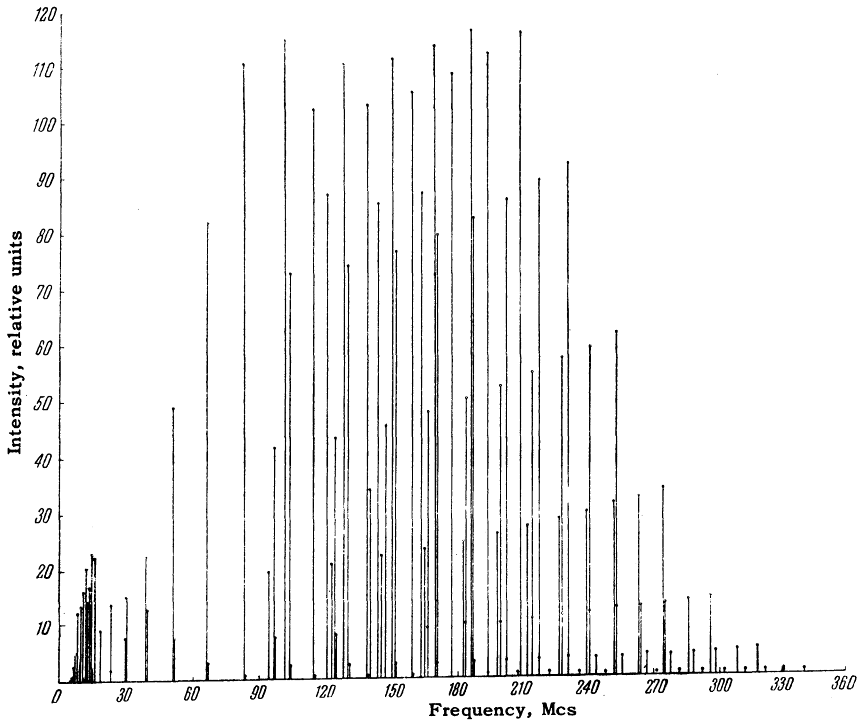

FIG. 1

ponent H'_z of the alternating field, while selection rules $\Delta F_z \pm 1$ hold for the transitions corresponding to the components H'_x and H'_y.

Expressions (19) allow us to determine the probabilities of the corresponding transitions; multiplication of the latter by the statistical weights of the states yields the intensities of the absorption lines in relative units.

The results of calculations are shown in Figs. 1 and 2.

4. FIELD-FREE PARAMAGNETIC RESONANCE

In this case the Hamiltonian (6) becomes

$$\hat{W} = A\hat{S}\cdot\hat{I}. \qquad (20)$$

Its eigenvalues are

$$E = {}^1/_2 A\,[F(F+1) - I(I+1) - S(S+1)]. \qquad (21)$$

In view of the fact that F assumes only two values, two levels $E^{(1)} = AI/2$ and $E^{(2)} = -(A/2)(I+1)$ correspond to each value of I. The transition frequency is $E^{(1)} - E^{(2)} = A(I + \frac{1}{2})$.

It is interesting to investigate the possibility of quantum transitions between levels $E^{(1)}$ and $E^{(2)}$. Using the results of the preceding section, it is easy to show that when $H = 0$ only the matrix elements V_{14}, V_{24}, and V_{34} will play any role (V_{12}, V_{13}, V_{23}, V_{33} and V_{44} are not significant, since the corresponding levels have merged). It is convenient in this case to retain the previous coordinate system

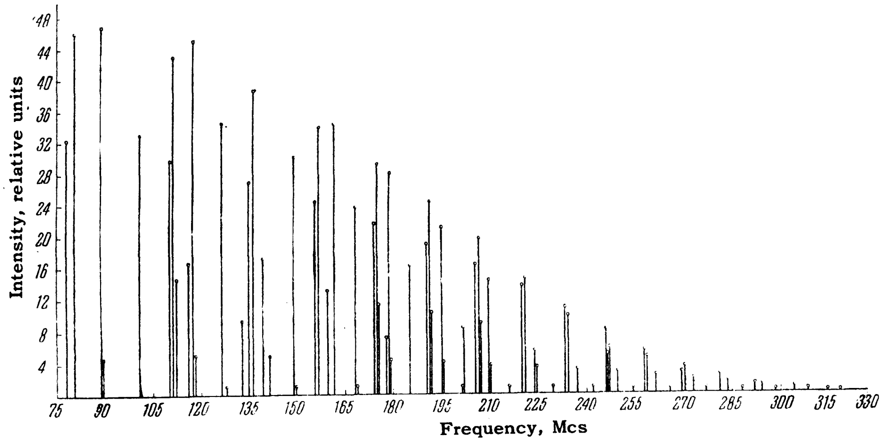

FIG. 2

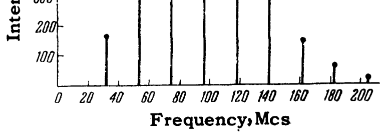

FIG. 3

($H = H_z$) and speak of transitions caused by the alternating-field components H'_x, H'_y and H'_z. If, for example, the vector of the alternating magnetic-field intensity is oriented along z (H'_z component) the intensity of the corresponding transitions is determined from (19h); if we put $H = 0$ in the coefficient C and, taking into account the degeneracy of the levels with respect to F_z, add the intensities of the transitions in the interval from $F_z = -I + \frac{1}{2}$ to $I - \frac{1}{2}$, we obtain

$$J' = 4 \sum_{F_z=-I+1/2}^{I-1/2} [C'_3(F_z)\, C'_4(F_z)]^2. \tag{22}$$

The relations (14) are taken into account here. Putting $H = 0$ in Eqs. (13) we get

$$C'_4(F_z) = -\left[\frac{1}{2}\left(1 + \frac{F_z}{I + 1/2}\right)\right]^{1/2}, \tag{23a}$$

$$C'_3(F_z) = -\left[\frac{1}{2}\left(1 - \frac{F_z}{I + 1/2}\right)\right]^{1/2}. \tag{23b}$$

Inserting (23) into (22) and summing, we get

$$J' = \frac{8I}{3}\,\frac{I+1}{2I+1}. \tag{24}$$

The intensities of the individual lines in relative units are obtained by multiplying (24) by the statistical weights of the states with definite I – N.

Analogous calculations, but using (19i) and (19k), also lead to expression (24) for the two other components.

It is thus obvious that, for an arbitrary orientation of the external alternating magnetic field, the intensity of the lines of field-free paramagnetic resonance is again determined by the product J′N.

The results of the calculation of the frequencies and the transition intensities (in relative units) in field-free paramagnetic resonance are shown in Fig. 3.

It is easy to show that the intensities of the lines of field-free paramagnetic resonance are comparable with the intensities of the lines of spin-electron resonance in strong fields. It therefore becomes possible to realize field-free paramagnetic resonance experimentally.

5. DEPENDENCE OF THE FREQUENCIES AND INTENSITIES OF THE ABSORPTION LINES ON THE ORIENTATION OF THE CRYSTAL IN AN EXTERNAL STATIC MAGNETIC FIELD. DEPENDENCE OF THE LINE INTENSITIES ON THE DIRECTION OF THE POLARIZATION VECTOR OF THE ALTERNATING MAGNETIC FIELD

In Sec. 2, in considering the hyperfine splitting of the energy levels of the F centers, we omitted terms of the form

$$\hat{Q} = \sum_{k=1}^{6} \sum_{p,\,q=1}^{3} A'_{pqk} \hat{I}_{kq_k} \hat{S}_{p_k}. \tag{25}$$

We now find the corrections to the energy levels and to the wave functions of the system, by considering $\hat{Q}$ as a small perturbation. In view of the fact that the energy levels are not degenerate in the zeroth approximation, the correction to the energies in the first approximation are determined by the diagonal elements of the matrix $Q_{\min}$, constructed with the functions Φ_1 and Φ_2, and also with the entire system of functions corresponding to the levels E_3 and E_4. The calculations yield

$$Q_{11} = 1/2 \sum_{k=1}^{6} A'_{k33} (I_k)^I_I I, \tag{26a}$$

$$Q_{22} = Q_{11}, \tag{26b}$$

$$Q_{33} = \left[\frac{F_z}{2}\left(C'^2_4(F_z) - C'^2_3(F_z)\right) - \frac{1}{4} - \frac{1}{2} C'_4(F_z)\, C'_3(F_z) \sqrt{(I + 1/2)^2 - F_z^2}\right] \sum_{k=1}^{6} (I_k)^I_I A'_{k33}, \tag{26c}$$

$$Q_{44} = \left[-\frac{F_z}{2}\left(C'^2_4(F_z) - C'^2_3(F_z)\right) - \frac{1}{4} + \frac{1}{2} C'_4(F_z)\, C'_3(F_z) \sqrt{(I + 1/2)^2 - F_z^2}\right] \sum_{k=1}^{6} (I_k)^I_I A'_{k33}. \tag{26d}$$

The symbol $(I_k)^I_I$ for the matrix elements is borrowed from reference 11. In obtaining formulas (26) we used relations (14) and the equality $A'_{k11} + A'_{k22} + A'_{k33} = 0$. It must be borne in mind that the spin Hamiltonian (1), and consequently also the coefficients, are written in a coordinate system that is connected with the external static magnetic field. In specific calculations it is convenient to calculate expressions for the coefficients in a frame with its origin in the k-th nucleus, but with the z axis along one of the crystallographic axes.

The corrections (26) to the energy depend only on one of the coefficients A'_{k33}. It is easy to show that

$$A'_{k33} = A_{11} + a/3 + (A_{33} - A_{11})\, n_3^2, \tag{27}$$

where

$$a = (4\pi\mu_k\mu/SI)\,|\psi(\rho_k = 0)|^2, \quad A_{11} = A_{22}, \quad 2A_{11} + A_{33} = -a,$$

and A_{33} is given by expression (2), while n_3 is the cosine of the angle between the directions of one of the crystallographic axes and the external static field.

Insertion of (27) into (26) and the subsequent calculation of the energy terms and frequencies of the absorption lines cause, naturally, the position of the line in the spectrum to be a function of n_3, i.e., to depend on the orientation of the crystal in the external static magnetic field.

TABLE I

$\Delta F_z = 0$		$\Delta F_z = \pm 1$	
Frequency, Mcs	**Intensity in relative units**	**Frequency, Mcs**	**Intensity in relative units**
$54.51+5.146\ n_3^2$	0.198	$56.04+8.54\ n_3^2$	0.948
$50.49+0.438\ n_3^2$	0.394	$52.5\ +2.35\ n_3^2$	0.848
$45.22-4.578\ n_3^2$	0.589	$47.85-2.51\ n_3^2$	0.749
$38.51-8,058\ n_3^2$	0.779	$41.86-6.32\ n_3^2$	0.651
$29.45-11,46\ n_3^2$	0.952	$33.98-9.76\ n_3^2$	0.552
		$15.51+0.234\ n_3^2$	0.390

Specific calculations have been made for the F centers in an MgO crystal. In this case the task becomes simpler, for this crystal most probably has two types of F centers:[14] (1) F centers in which the first coordination sphere has no nuclei with magnetic moments different from zero; (2) F centers in which one of the nuclei of the first coordination sphere has a non-zero magnetic moment.

It is obvious that for the F centers of the first there will be no such angular dependence. Calculation of the angular dependence was made for the F centers of the second type. By way of an example, the field was assumed to equal 10 oersteds, and there were calculated frequencies and intensities of lines that are sufficiently remote from each other and were easiest to resolve experimentally in the spectrum. The results of the calculations for two directions of the polarization vector of the incident wave are given in Table I.

The wave functions can be calculated in the first approximation using the ordinary procedure of perturbation theory. Cumbersome calculations, but not difficult in principle, make it possible to determine the wave functions in the first approximation, and to calculate with the aid of the latter the probabilities of the transitions under the influence of the radio-frequency field. By way of an example, the calculations have been made for two arbitrarily chosen levels (with $F = I + \frac{1}{2}$, $F_z = I + \frac{1}{2}$ and $F = I - \frac{1}{2}$, $F_z = I - \frac{1}{2}$), the quantum transitions between which were then considered.

The square of the corresponding matrix element was found to be

$$V_{14}^2 = \mu^2 H_x'^2 \Big\{ C_3''^2(F_z) + 2C_3''(F_z)\Big[\frac{Q_{34}C_3'(F_z)}{E_4^0 - E_3^0} + \frac{(A_{11}' - A_{22}')\sqrt{2I}}{4}\Big(\frac{C_3'^2(F_z^+)}{E_1^0 - E_3^{0+}} + \frac{C_3''^2(F_z^+)}{E_1^0 - E_4^{0+}}\Big)C_4'(F_z)\Big] \times \delta(F_z, F_z^+ + 1)\,\delta(F_z, I - {}^1/_2). \qquad (28)$$

TABLE II

Direction along which the ions are located	**Frequency**	**Intensity according to (29)**
$[0\bar{1}0]$ $[0\bar{1}0]$	$56.04+8.54 \sin^2\Omega$	$0.928 - \cos^2\Omega\,(0.0705 \sin^2\gamma_x - 0.00555)$
$[100]$ $[\bar{1}00]$	$56.04+8.54 \cos^2\Omega$	$0.9225 + \sin^2\Omega\,(0.0705 \sin^2\gamma_x + 0.00555)$
$[001]$ $[00\bar{1}]$	56.04	$0.9225+0.0705 \cos^2\gamma_x$

Inserting into (28) the values A_{11}' and A_{22}' yields, after subsequent calculation,

$$(\mu H_x')^{-2} V_{14}^2 = 0.9225 + 0.00555 n_3^2 + 0.0705 n_1^2, \qquad (29)$$

where n_1 is the cosine of the angle between the x axis (which determines the polarization of the alternating component in the magnetic field) in a coordinate system stationary with respect to the static field, and the z axis of the local system of coordinates.

It follows from (29) that the intensities of the lines will depend on the orientation of the crystal both relative to the external static field and relative to the component of the alternating high-frequency magnetic field that causes the transitions.

To obtain the angular dependences of the intensities and frequencies for any ion of the first coordination sphere, we introduce, as in reference 13, the following angles in the principal system of coordinates: (1) γ and Ω to specify the vector **H**, (2) θ and φ to specify the z axis of the local system of coordinates, and (3) γ_x and Ω_x to specify the x component of the alternating magnetic field.

For $\gamma = 90°$ (intensity vector of the external static field lies in the xy plane of the principal system of coordinates), we obtain, for the sixth of the frequencies (see Table I), the summary of the angular dependences of the frequency and intensity listed in Table II.

Estimates show that the angular dependences of the frequencies and intensities are sufficiently large to be experimentally observable.

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