

An operator is derived for the electric quadrupole-quadrupole interaction between the unfilled shell of a paramagnetic ion and the nucleus of this ion. Calculations are carried out for certain iron-group and rare-earth ions. The cases in which this interaction can be reflected in the hyperfine structure of the ESR spectrum are discussed.

1. Introduction

The hyperfine structure of magnetic-resonance lines reveals extremely interesting information about the microscopic structure of solids. This structure is also of applied interest, in that it can be used to select targets for dynamic polarization of nuclei.

All mechanisms for the hyperfine interactions of electrons and nuclei in condensed media which have been studied have been magnetic in nature. We will show below that an interaction occurs between nuclear electric quadrupole moments and the atomic electronic shells which should be reflected as a hyperfine structure of paramagnetic-resonance spectra, if the paramagnetic atoms do not have a purely spin magnetic moment.

When there is a change in the orientation of the electronic magnetic moment (in resonant transitions), a change occurs in the gradient of the electric field at the nucleus produced by the unfilled electronic shell. There is also a change in the electric quadrupole energy of the nucleus; the magnitude of this change depends on the orientation of the nuclear quadrupole moment or nuclear spin. The electric-quadrupole hyperfine interaction increases in intensity as the contribution of the orbital angular momentum to the effective magnetic moment of the paramagnetic ion, measured by the deviation of the g -factor from 2, increases. For resonant lines corresponding to transitions within the Kramers doublet, there can be no quadrupole hyperfine structure, since the electrons at the Kramers sublevels produce the same electric field at the nucleus. It is thus interesting to consider substances in which paramagnetic ions are in a high-symmetry crystalline field and for which the low-symmetry field components are so weak that the spacing between spin levels (which are not sublevels of a single Kramers doublet) corresponds to the rf range ($\sim 1 \text{ cm}^{-1}$). The constant D of the electric-quadrupole interaction is given in order of magnitude by $(e^2 Q r^{-3})/4I(2I-1)$, while the constant A of the hyperfine interaction for electrons of the d and f shells is $g\beta g_n \beta_n r^{-3}$; where β and β_n are the electronic and nuclear magnetons; g and g_n are the electronic and nuclear g -factors; I and Q are the spin and quadrupole moments of the nucleus; and r^{-3} is the mean reciprocal cube of the radius of the d or f shell. With $g = 2$, $g_n = 1$, $I = 3/2$, and $Q \sim 5 \cdot 10^{-25} \text{ cm}^2$, we thus find $(A/D) \sim 10$. Since, in addition, even a slight s -state admixture greatly increases A , we conclude that the inequality $A > D$ is apparently always satisfied. Estimates show that in favorable cases we have $D \sim 100 \text{ MHz}$.

Below we will calculate the operator for the electric-quadrupole hyperfine interaction for iron-group and rare-earth ions; spin systems having properties favorable for this effect are selected from the paramagnetic substances which have been studied previously by magnetic-resonance methods or for which wave functions have been found.

2. The Iron Group

The lower Stark level of an iron-group ion in a cubic field may be a singlet, a doublet, or a triplet. Ions having a lower singlet or doublet orbital level are not of interest here; in the case of a singlet the

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gradient of the electric field at the nucleus is the same for all the Zeeman sublevels, so there is a contribution to the ordinary quadrupole energy of the nuclei, but there is no hyperfine interaction; in the case of the doublet, on the other hand, the lower level turns out to be a singlet or a doublet after the spin-orbit interaction is taken into account. For ions in the sixfold coordination, we are thus left with the possible configurations d^1 , d^2 , and d^6 , which contribute the lower orbital triplets Γ_4 and Γ_5 ; in the eightfold coordination the triplet ground states are those of ions having d^3 , d^4 , d^8 , and d^9 configurations [1]. If, after the spin-orbit splitting of these ground states is taken into account, the magnetic levels have an effective spin S^* higher than $1/2$, we can expect an electric hyperfine structure in the resonance lines.

The energy associated with the interaction of the nuclear electric-quadrupole moment with the electric field of the surrounding charges is [2]

$$\begin{aligned} \mathcal{H}_Q &= \frac{eQ}{2I(2I-1)} \sum_{q=-2}^2 (-1)^q Q_q(I) \nabla E_{-q}(x, y, z), \\ Q_{\pm 2}(I) &= \sqrt{\frac{3}{2}} (I_x \pm iI_y)^2 \equiv \sqrt{\frac{3}{2}} I_{\pm}^2, \quad Q_{\pm 1} = \mp \sqrt{\frac{3}{2}} (I_{\pm} I_z + I_z I_{\pm}), \\ Q_0 &= 3I_z^2 - I(I+1), \end{aligned} \quad (1)$$

where I_x, I_y, I_z are the components of the nuclear spin. The $\nabla E_q(x, y, z)$ are the components of the tensor corresponding to the electric-field gradient, produced by charges at point $\vec{r}(x, y, z)$; these components are given by

$$\begin{aligned} \nabla E_0 &= -\frac{e}{2r^3} \frac{3z^2 - r^2}{r^2}, \quad \nabla E_{\pm 1} = -\frac{3e}{\sqrt{6}r^3} \frac{(x \pm iy)z}{r^2}, \\ \nabla E_{\pm 2} &= -\frac{3e}{2\sqrt{6}r^3} \frac{(x \pm iy)^2}{r^2}. \end{aligned} \quad (2)$$

We must evaluate the contribution to ∇E_q of the entire electronic charge of the d shell; i.e., we must evaluate the matrix elements of the operators ∇E_q with wave functions of the magnetic levels under consideration. According to the Wigner-Eckart theorem [3] these matrix elements are proportional to the matrix elements of certain combinations of spin operators which transform like ∇E_q under the influence of symmetry elements of the crystal.

If all the magnetic levels belong to the same irreducible representation of the cubic group, there will be only a single proportionality factor, so we can write

$$\nabla E_q = -\frac{e}{2r^3} \alpha Q_q(S^*), \quad (3)$$

where the operators $Q_q(S^*)$ are constructed from the components of the effective spin S^* in precisely the same manner used to construct $Q_q(I)$ from the components of the vector I . The coefficient α is found by a direct evaluation of one matrix element with the wave functions of the magnetic levels.

We consider the case of an ion having the d^6 configuration (5D ground level) in an octahedral field. After the crystal field and the spin-orbit coupling are taken into account, the ground state of the ion is found to be a Γ_5 triplet with the wave functions [4]

$$\begin{aligned} \Psi_{\pm 1} &= \pm \sqrt{\frac{1}{10}} |\pm 1, 0\rangle \mp \sqrt{\frac{3}{20}} (2|\pm 1, -2\rangle + |\pm 2, \pm 1\rangle - |\mp 2, \mp 1\rangle), \\ \Psi_0 &= \sqrt{\frac{1}{5}} (|2, 0\rangle - |-2, 0\rangle) + \sqrt{\frac{3}{10}} (|1, 1\rangle - |-1, -1\rangle), \end{aligned} \quad (4)$$

where the first index in $|M_L M_S\rangle$ denotes the projection of the orbital angular momentum of the d electron, while the second denotes the projection of the angular momentum of spin S . We can describe these levels by introducing the effective spin $S^* = 1$; the functions $\Psi_{M_S^*}$ are eigenfunctions of the operator S_z^* .

By a direct evaluation of the matrix elements of operators (2) with functions (4) we can show that relation (3) actually holds and that the value of α is $-1/35$. Substituting (3) into (1), we find the operator for the electric-quadrupole hyperfine interaction:

$$\mathcal{H}_Q = \alpha D \sum_{q=-2}^2 (-1)^q Q_q(I) Q_{-q}(S^*), \quad (5)$$

where

$$D = -\frac{e^2 Q r^{-3}}{4I(2I-1)}.$$

Of the paramagnetic ions in this state, only Fe^{2+} has been studied [4]; the form of functions (4) has been experimentally verified for this ion. However, there is no \mathcal{H}_Q interaction in this case, since the Fe nucleus has a vanishing quadrupole moment.

We turn now to a paramagnetic ion having a d^1 configuration (2D ground level) in an octahedral field. Examples of these states are found in the Ti^{3+} , Mn^{6+} , $\text{Mo}(\text{V})$, and $\text{W}(\text{V})$ ions [5]. After the spin-orbit interaction is taken into account, the lower level is a Γ_8 quartet with the wave functions

$$\begin{aligned} \Psi_{\pm 3/2} &= -\sqrt{\frac{1}{3}} \left| 2, \mp 1/2 \right\rangle + \sqrt{\frac{1}{3}} \left| -2, \mp 1/2 \right\rangle \pm \sqrt{\frac{1}{3}} \left| \pm 1, \pm 1/2 \right\rangle, \\ \Psi_{\pm 1/2} &= \mp \left| \pm 1, \mp 1/2 \right\rangle. \end{aligned} \quad (6)$$

An effective spin of $3/2$ and a g -factor of 1 correspond to these levels. Splitting occurs in a magnetic field because of the admixture to wave functions (6) of the wave functions of excited states, which give $g \sim 1/50$ [6]. This effect arises in the zeroth approximation in terms of wave functions (6); the operator corresponding to the quadrupole hyperfine structure is (5), and the value of α turns out to be $-2/21$.

3. The Rare-Earth Group

For the rare-earth ions the spin-orbit energy is much more higher than the energy of the crystal field. The basic characteristic of these energy levels is thus the total angular momentum J . When the crystal-field levels are not taken into account, the levels with a given J are $(2J+1)$ -degenerate. This degeneracy is removed partially or completely, depending on the symmetry of the crystal field.

a) Let us consider the Dy^{2+} ($4f_{10}, {}^5I_8$) ions in the CaF_2 crystal. The paramagnetic ion is in the electric field produced by eight F ions at the vertices of a regular cube [7]. The 5I_8 ground level of the free ion is split by the crystal field into the representations $2\Gamma_5 + 2\Gamma_4 + 2\Gamma_3 + \Gamma_1$. The lower Γ_3 level is nonmagnetic. A resonance is observed at the first excited level, Γ_4 , 4.9 cm^{-1} from the ground level. The Γ_4 levels are characterized by an effective spin of $S^* = 1$ and have the wave functions

$$\begin{aligned} \Psi_{\pm 1} &= \mp 0.223 \left| \pm 5 \right\rangle \pm 0.119 \left| \pm 1 \right\rangle \pm 0.770 \left| \mp 3 \right\rangle \mp 0.585 \left| \mp 7 \right\rangle, \\ \Psi_0 &= 0.636 \left| 4 \right\rangle - 0.636 \left| -4 \right\rangle - 0.310 \left| 8 \right\rangle + 0.310 \left| -8 \right\rangle. \end{aligned} \quad (7)$$

Calculations in terms of these wave functions yield operator (5) with $\alpha = 0.004$ for the quadrupole hyperfine structure.

The Dy^{3+} ion can also be added to the CaF_2 crystal [8]. In this case the free-ion state ${}^6H_{15/2}$ is split by the crystal field into the representations $\Gamma_6 + \Gamma_7 + 2\Gamma_8$. The lower level is a Γ_8 quartet corresponding to an effective spin of $3/2$. When the magnetic field is along the $[100]$ direction, three lines are observed, having g -factors $g_1 = 2.63 \pm 0.05$, $g_2 = 5.48 \pm 0.15$, and $g_3 = 14 \pm 1$. These g -factors are reproduced by the wave functions

$$\begin{aligned} \Psi_{\pm 3/2} &= 0.1353 \left| \mp \frac{13}{2} \right\rangle + 0.1509 \left| \mp \frac{5}{2} \right\rangle - 0.1322 \left| \pm \frac{3}{2} \right\rangle + 0.9703 \left| \pm \frac{11}{2} \right\rangle, \\ \Psi_{\pm 1/2} &= 0.0847 \left| \mp \frac{15}{2} \right\rangle + 0.5541 \left| \mp \frac{7}{2} \right\rangle - 0.4994 \left| \pm \frac{1}{2} \right\rangle + 0.6606 \left| \pm \frac{9}{2} \right\rangle. \end{aligned} \quad (8)$$

Carrying out calculations analogous to those described above for functions (8), we find Hamiltonian (5) with $\alpha = 0.054$.

b) We turn now to the case of the Ho^{3+} ion (5I_8) in the axisymmetric electric field of an yttrium ethylsulfate single crystal. Baker and Bleaney [9] have established that the two lower levels of the Ho^{3+} ion have the wave functions

$$\begin{aligned} \Psi_{\pm 1} &= 0.933 \left| \pm 7 \right\rangle + 0.342 \left| \pm 1 \right\rangle + 0.111 \left| \mp 5 \right\rangle, \\ \Psi_0 &= \frac{1}{2} \left| 6 \right\rangle + \frac{1}{2} \left| -6 \right\rangle + \frac{1}{\sqrt{2}} \left| 0 \right\rangle, \end{aligned} \quad (9)$$

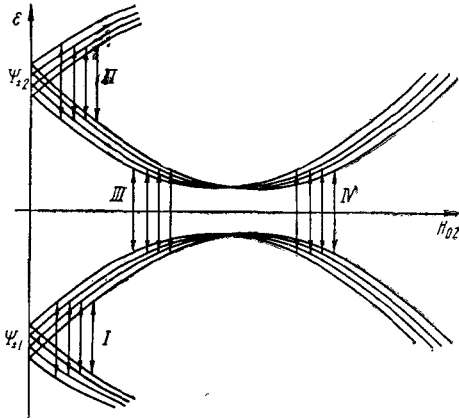


Fig. 1. Energy levels of Tb^{3+} in a BaF_2 single crystal as functions of magnetic field H_{0z} applied along the trigonal symmetry axis. The arrows show the individual hyperfine transitions within the four ESR lines [10],

and can be characterized by an effective spin of $S^* = 1$ and the spin Hamiltonian

$$\mathcal{H} = D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + AS_z I_z + B(S_x I_x + S_y I_y) + P \left[I_z^2 - \frac{1}{3} I(I+1) \right], \quad (10)$$

where $D = 5.8 \text{ cm}^{-1}$ is the zero-splitting energy; A and B are the constants of the anisotropy magnetic hyperfine-structure interaction; g_{\parallel} and g_{\perp} are the effective g -factors; and P is the constant of the ordinary electric-quadrupole interaction. Baker and Bleaney emphasize that P in Hamiltonian (10) is not the same for the $|\pm 1\rangle$ and $|0\rangle$ levels, so they introduce P_1 and P_0 . Calculation of the matrix elements of tensor (2) corresponding to the electric-field gradient in terms of wave functions (9) and substitution of these elements into (1) yield the interaction of the nuclear quadrupole moment with f -shell electrons:

$$\mathcal{H}_Q = \mathcal{H}'_Q + \mathcal{H}''_Q, \quad \mathcal{H}'_Q = 0.071 D Q^0(I),$$

$$\mathcal{H}''_Q = D \{ 0.056 Q^0(S) Q^0(I) - 0.049 [Q^1(S) Q^{-1}(I) + Q^{-1}(S) Q^1(I)] + 0.017 [Q^2(S) Q^{-2}(I) + Q^{-2}(S) Q^2(I)] \}. \quad (11)$$

Here \mathcal{H}'_Q is the ordinary energy, and \mathcal{H}''_Q is the hyperfine-structure energy. Hamiltonian (11) offers a natural explanation for the experimental difference between P_1 and P_0 by treating these quantities as the eigenvalues of the operator

$$\hat{\mathcal{P}} = (\zeta + 0.071) D + 0.056 D \hat{Q}^0(S) \quad (12)$$

in states $|\pm 1\rangle$ and $|0\rangle$; term ζD is due to the electric field of the crystal, and the other terms are due to the f shell. The difference between P_1 and P_0 is wholly due to the f shell. The \mathcal{H}'_Q contribution to the positions of the resonance lines is of the same order of magnitude as the second approximation of the magnetic hyperfine-structure interaction. Accordingly, it is meaningful to treat only the first approximation in \mathcal{H}'_Q . In the first approximation, interaction \mathcal{H}'_Q shifts the resonant frequency only for the $|1\rangle \leftrightarrow |0\rangle$ transition in a strong magnetic field (cases d and e) [9]. The term $3 \cdot 0.056 D Q_0(I)$ (1) must be added to the expression for the resonant frequency in (1). In all other cases the \mathcal{H}'_Q interaction is an additional source of line broadening.

c) We turn finally to the Tb^{3+} ($4F_8^7F_6$) in a BaF_2 single crystal. It has been shown by ESR methods [10] that Tb^{3+} ions are in a trigonal field in this case and that the lower levels are two doublets 4.23 cm^{-1} apart. In weak magnetic fields two resonant lines with hyperfine structure are observed, corresponding to transitions between the sublevels of a given doublet (line groups I and II). In intense fields we find two more groups of lines (III and IV), corresponding to transitions between sublevels of different doublets. There are four components in each line, in accordance with the nuclear spin of $I = 3/2$.

In an interpretation of the experimental data it was found [10] that in the absence of a magnetic field the wave functions of the doublets are

$$\Psi_{\pm 1} = \mp 0.815 |\mp 5\rangle - 0.561 |\mp 2\rangle \mp 0.120 |\pm 1\rangle + 0.082 |\pm 4\rangle,$$

$$\Psi_{\pm 2} = \mp 0.084 |\pm 5\rangle + 0.091 |\pm 2\rangle \pm 0.366 |\mp 1\rangle + 0.922 |\mp 4\rangle,$$
(13)

where $|m\rangle$ is the state having a total angular momentum of $J = 6$ and a projection of $J_z = m$. The behavior of the levels in a magnetic field is described roughly by the Hamiltonian [10]

$$\hat{\mathcal{H}} = \beta (L_z + 2S_z) H_{0z} + a J_z I_z \quad (14)$$

(Fig. 1). Here L_z is the z component of the orbital angular momentum, and the z axis coincides with the symmetry axis of the crystal field. Line groups I and II are described well (and simply) by Hamiltonian (14).

The magnetic fields H_{0z} at which the hyperfine components of lines III and IV are observed at a fixed frequency of $\nu = 37.47 \text{ kHz}$ are shown in the second column of Table 1; the third column shows the corresponding resonant frequencies, obtained by diagonalizing Hamiltonian (14).

TABLE 1

Line group	III				IV			
	H_{0z}, G	6014	6279	6555	6796	8465	8740	8993
ν, kMHz	37,42	37,42	37,33	37,53	37,04	37,32	37,41	37,40

The deviations of these frequencies from the working spectrometer frequency of $\nu = 37.47$ kHz are apparently due to the hyperfine-interaction terms neglected in (14). The Hamiltonian for these hyperfine interactions can be written as

$$\hat{\mathcal{K}}_{\text{hy}} = \frac{a}{2} \{J_+ I_- + J_- I_+\} - \frac{e^2 Q \alpha}{4I(2I-1)} \left\langle \frac{1}{r^3} \right\rangle Q_0(J) Q_0(I), \quad (15)$$

where the first term is the part of the magnetic-dipole hyperfine interaction not taken into account in Hamiltonian (14), and the second term is the part of the Hamiltonian corresponding to the electric-quadrupole hyperfine interaction (5) which contributes to the line position in the first approximation. Calculations analogous to those above yield $\alpha = 0.01$. Hence, substituting in $e = 4.8 \cdot 10^{-10}$ esu, $Q = 0.5 \cdot 10^{-24}$ cm², $I = 3/2$, and $\langle 1/r^3 \rangle = 68 \cdot 10^{-24}$ cm⁻³, we find $\alpha D = -(e^2 Q \alpha / 4I(2I-1)) \langle 1/r^3 \rangle$ to be ≈ 1 MHz. Characteristically, the quadrupole interaction contributes only to the positions of the III and IV components. Evaluation of the matrix elements of the operator $Q_0(J)$ in terms of the wave functions of the perturbed levels reveals that the quadrupole interaction changes sign in the transition from group III to group IV; the correction to the transition frequencies for group III is found to be $-4.9 \{3m^2 - J(J+1)\}$ MHz, while that for group IV is $+0.5 \{3m^2 - J(J+1)\}$ MHz.

However, the quantitative validity of these values is somewhat dubious, since the calculations are based on approximation wave functions (since the exact crystal potential is not known), and we do not have an accurate value for quadrupole moment Q .

The corrections to the transition frequencies in the second approximation in the magnetic part of Hamiltonian (15) and in the first approximation in the electrical part have the general form

$$\Delta\nu = F \{I(I+1) - m(m+1)\} + K \{3m^2 - I(I+1)\}, \quad (16)$$

where F and K are certain coefficients formed from the matrix elements of operators consisting of the components of total angular momentum J evaluated in terms of the wave functions of the levels of different doublets. These coefficients depend on magnetic field H_{0z} and differ in value for groups III and IV.

We will treat coefficients F and K as certain free parameters and determine them by the method of least squares, assuming that the experimental errors obey a normal distribution law. Setting $K = 0$ in (16), we find

$$F_{III} = 15.6 \text{ MHz}, \quad F_{IV} = 26.4 \text{ MHz}, \quad (17)$$

Analogously, for $K \neq 0$ we find

$$F_{III} = 11 \text{ MHz}, \quad F_{IV} = 39.7 \text{ MHz}, \quad K_{III} = -13 \text{ MHz}, \quad K_{IV} = 37.4 \text{ MHz}. \quad (18)$$

The rms deviation of the theoretical resonant frequencies from the experimental values is 20% less for parameters (18) than for parameters (17). We note that coefficient K changes sign, but F does not, in the transition from group III to group IV, in agreement with the previous calculation. A numerical agreement of the αD and K values can be achieved with $Q \langle 1/r^3 \rangle$ on the order of 10^3 cm⁻¹.

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