

Line-Intensity Angular Dependence in Paramagnetic-Resonance Spectrum of S-State Ions with Axial Crystalline Environments

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(Received 7 August 1972)

An intensity spin operator that leads to a simple description of the intensity of electron-paramagnetic-resonance lines is derived in the case of comparable crystal field and hyperfine interactions. These theoretical results are compared with the descriptions given by the method of Bir and by first-order-perturbation calculations, then with experimental measurements on $\text{Al}_2\text{O}_3:\text{Mn}^{2+}$ EPR spectra.

I. INTRODUCTION

Three methods have been used to predict the angular dependence of transition probabilities in electron-paramagnetic-resonance (EPR) spectra. For the case where the crystal field splitting is comparable to the Zeeman splitting, only diagonalization of the full Hamiltonian is adequate. For the case of small crystal field splitting, correct values may be obtained using perturbation techniques and have been given by some authors.¹⁻⁵ For the case of small hyperfine interaction compared with crystal field and Zeeman interactions Bir⁶ has considered the direction of the effective magnetic field associated with the hyperfine interaction and has derived elegant expressions of EPR transition probabilities. It has been shown by Bir and Sochava⁷ and Dickey and Drumheller⁸ to give results in good agreement with experimental measurements. In this method the electronic wave functions are obtained by perturbation theory applied to the electronic part, only, of the Hamiltonian and then nuclear states are defined for a given electronic state.

When crystal field and hyperfine interactions are comparable, this separation must not be considered and the complete spin Hamiltonian of paramagnetic ions must be taken with electronic and nuclear spin operators. In the present paper we have considered S-state ions with axial crystalline environments, when both crystal field and hyperfine interactions are small compared with the Zeeman interaction, and we have derived an "intensity" spin operator that leads to a simple description of the angular variations of the allowed

transition intensities ($\Delta M = 1$, $\Delta m = 0$). These theoretical results have been compared with experimental measurements of $\text{Al}_2\text{O}_3:\text{Mn}^{2+}$ EPR spectra and with the descriptions given on the one hand by Bir's method and on the other hand by a first-order perturbation calculation that considered the correct hyperfine operator⁹—when there is crystal field interaction.

II. THEORY

In an EPR spectrum, the line intensity between levels $\Psi_{M,m}$ and $\Psi_{M',m'}$ may be found from the matrix element of a spin operator:

$$I \propto |\langle \Psi_{M,m} | \Psi_{M',m'} \rangle|^2. \quad (1)$$

The eigenfunctions $\Psi_{M,m}$ of the spin Hamiltonian of the paramagnetic ion can, in perturbation-theory approximation, be obtained as linear combinations of zero-order $|M, m\rangle$ eigenstates of the diagonal part of the Hamiltonian:

$$\Psi_{M,m} = \sum_{i,j} \alpha_{i,j}^{M,m} |M+i, m+j\rangle. \quad (2)$$

Combining Eqs. (1) and (2) gives

$$\begin{aligned} |\langle \Psi_{M,m} | S_x | \Psi_{M-1,m} \rangle|^2 = & \frac{1}{4} |\hbar(M-1) + \hbar(M)\alpha_{2,0}^{M-1,m} \\ & + \hbar(M-2)(\alpha_{-2,0}^{M,m})^* + \sum_{i,j}' \alpha_{i,j}^{M-1,m} (\alpha_{i,j}^{M,m})^* \hbar(M-1+i) \\ & + \sum_{i,j}' \alpha_{i+2,j}^{M-1,m} (\alpha_{i,j}^{M,m})^* \hbar(M+i)|^2. \quad (3) \end{aligned}$$

with $\hbar(M) = [S(S+1) - M(M+1)]^{1/2}$. The coefficients $\alpha_{i,j}^{M,m}$ measure the admixture of the states $|M+i, m+j\rangle$ and must be computed in second-order approximation. The nondiagonal part of the Hamiltonian (Hamiltonian of perturbation) may be written for S-state ions in axial symmetry

$$\begin{aligned} \mathcal{H}_1 = & \frac{D}{2} [S_+(2S_z+1) + (2S_z+1)S_-] \sin\theta \cos\theta + \frac{D}{4} (S_z^2 + S_z) \sin^2\theta \\ & + i \frac{DAB}{4KH_0} \sin^2\theta (3S_z^2 - S^2) (I_+^z - I_-^z) + \frac{D}{4KH_0} (A^2 \sin^2\theta + B^2 \cos^2\theta) \sin^2\theta (3S_z^2 - S^2) S_z^{-1} (S_+ + S_-) I_+^z \end{aligned}$$

$$+i \frac{B}{4} \left(1 - \frac{A}{4K}\right) (S_+ I'_+ - S_- I'_-) + i \frac{B}{4} \left(1 + \frac{A}{4K}\right) (S_+ I'_- - S_- I'_+), \quad (4)$$

where θ is the angle between the applied static magnetic field (z direction) and the C axis of the crystal, A and B determine the hyperfine components, and K is defined by $K = (A^2 \cos^2 \theta + B^2 \sin^2 \theta)^{1/2}$. In this expression the last four terms come from the expression of the hyperfine operator which considers the actual quantization axes of electronic and nuclear spin operators.⁹ In the case of S-state ions, to a good approximation electronic spins are aligned by the static magnetic field which is considered in (4) as the electronic axis of quantization. The crystalline electric field gradient that exists at the cation sites distorts the spherically symmetrical electron cloud in the ion, so the nuclear spins are not acted upon by the external magnetic field alone but by a much

greater effective field associated with hyperfine interaction. Therefore the nuclear spin operators I'_z, I'_+, I'_- are defined relative to the Z direction of the effective field and taken as the nuclear spin axis of quantization.

The most important contribution in (3) arises in first order from $S_z I'_+$ operators of \mathcal{H}_1 and in second order from cross products of the terms in D and

The evaluation of each coefficient $\alpha_{i,j}^{M,m}$ leads to long and uninteresting calculations. Let us show how to calculate the sum of the first three terms of the right-hand side of Eq. (3) by deriving a spin operator whose matrix element between zero-order $|M, m\rangle$ and $|M-1, m\rangle$ states is equal to this sum. With the Hamiltonian of perturbation (4) we obtained

$$\begin{aligned} h(M-1) + h(M)\alpha_{2,0}^{M-1,m} + h(M-2)(\alpha_{-2,0}^{M,m})^* &= h(M-1) + h(M) \left[-\frac{1}{H_0} \langle M+1, m | S_+^2 | M-1, m \rangle \frac{D}{8} \sin^2 \theta \right. \\ &+ \frac{1}{H_0^2} \langle M+1, m | (2S_z - 1) S_+ | M, m \rangle \langle M, m | (2S_z - 1) S_+ | M-1, m \rangle \left. \left(\frac{D}{2} \sin \theta \cos \theta \right)^2 \right] \\ &+ h(M-2) \left[\frac{1}{H_0} \langle M-2, m | S_-^2 | M, m \rangle^* \frac{D}{8} \sin^2 \theta + \frac{1}{H_0^2} \langle M-2, m | S_- (2S_z - 1) | M-1, m \rangle^* \langle M-1, m | S_- (2S_z - 1) | M, m \rangle^* \right. \\ &\left. \times \left(\frac{D}{2} \sin \theta \cos \theta \right)^2 \right]. \quad (5) \end{aligned}$$

In the case we are dealing with, D is small compared to Zeeman energy and we have taken energy denominators as

$$E_{Mm}^0 - E_{M'm}^0 = (M - M') H_0. \quad (6)$$

If we write

$$h(M-1) = \langle M, m | S_+ | M-1, m \rangle, \quad (7)$$

$$h(M) = \langle M, m | S_- | M+1, m \rangle, \quad (8)$$

$$h(M-2) = \langle M-2, m | S_- | M-1, m \rangle, \quad (9)$$

Eq. (5) can be reduced to

$$\begin{aligned} h(M-1) + h(M)\alpha_{2,0}^{M-1,m} + h(M-2)(\alpha_{-2,0}^{M,m})^* &= \langle M, m | S_+ \\ &- \frac{D}{8H_0} \sin^2 \theta (S_- S_+^2 - S_+^2 S_-) + \frac{D^2}{4H_0^2} \sin^2 \theta \cos^2 \theta \\ &\times [S_- (2S_z - 1) S_+ (2S_z - 1) S_+ \\ &+ (2S_z - 1) S_+ (2S_z - 1) S_+ S_-] | M-1, m \rangle. \quad (10) \end{aligned}$$

The products $S_\mp S_\pm$ are diagonal in the representation $|M, m\rangle$, so that Eq. (10) takes the form

$$\begin{aligned} h(M-1) + h(M)\alpha_{2,0}^{M-1,m} + h(M-2)(\alpha_{-2,0}^{M,m})^* \\ &= \langle M, m | \left(1 + \frac{D}{4H_0} \sin^2 \theta (2S_z - 1) \right. \\ &+ \frac{D^2}{4H_0^2} \sin^2 \theta \cos^2 \theta (-8S_z^4 + 16S_z^3 \\ &+ 8S_z^2 S^2 - 34S_z^2 - 8S_z S^2 + 26S_z + 2S^2 - 6) \\ &\left. \times S_+ | M-1, m \rangle. \quad (11) \end{aligned}$$

If we consider all the contributions of Eq. (3) and use the normalization condition for the perturbed functions we obtain¹⁰

$$I \propto \frac{1}{4} |\langle M, m | J | M-1, m \rangle|^2 \quad (12)$$

with

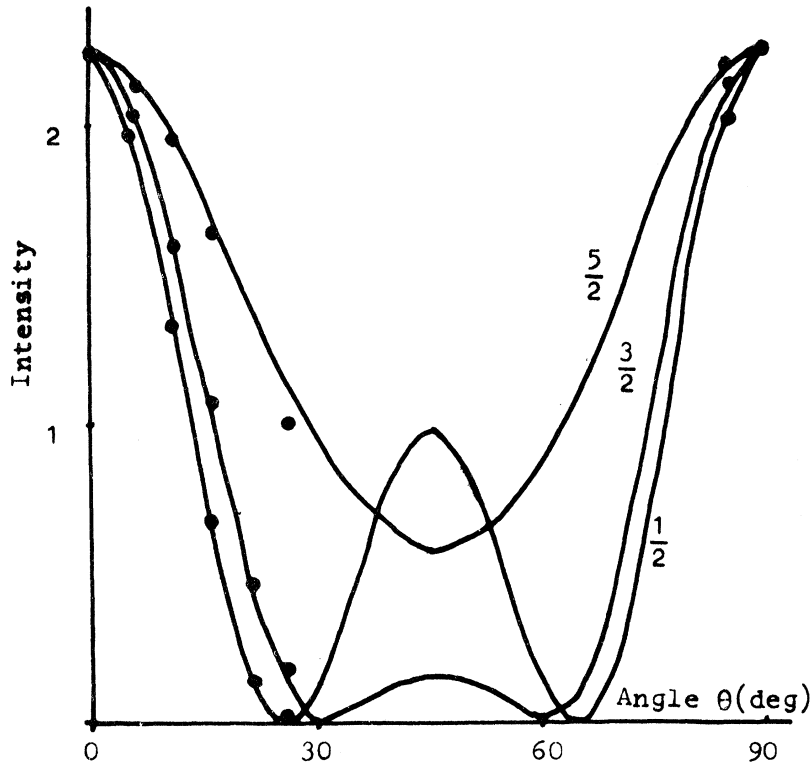


FIG. 1. Intensity of the $\frac{1}{2}, m \rightarrow -\frac{1}{2}, m$ lines as a function of the angle between external field and crystal C axis. The points show measured values for $\text{Al}_2\text{O}_3: \text{Mn}^{2+}$ while the solid curves are drawn from the values calculated with the intensity operator.

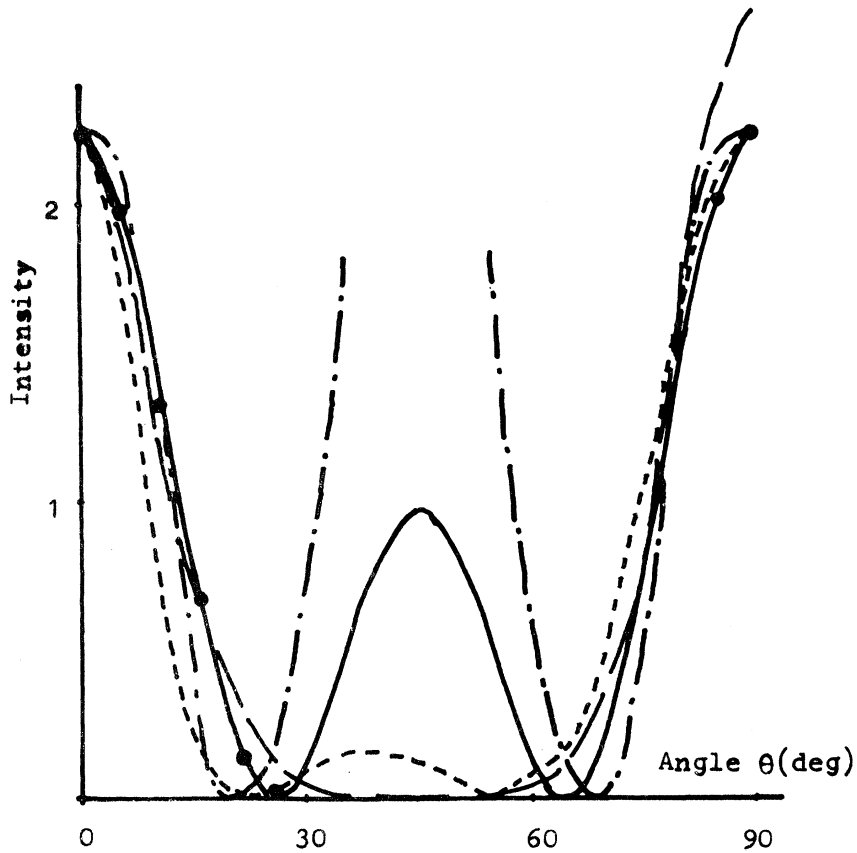


FIG. 2. Calculated intensity of $\frac{1}{2}, \frac{1}{2} \rightarrow -\frac{1}{2}, \frac{1}{2}$ lines as a function of the angle between external field and crystal axis: solid line, intensity operator; dashed line, method of Bir; dash-dot line, first-order perturbation with conventional Hamiltonian; broken line, first-order perturbation with correct hyperfine operator; solid circle, measured values ($\text{Al}_2\text{O}_3: \text{Mn}^{2+}$).

$$\begin{aligned}
J = S_+ &+ \frac{D}{4H_0} \sin^2\theta(2S_z - 1)S_+ + \frac{9}{32} \left(\frac{D}{H_0}\right)^2 \frac{A^2 B^2}{K^4} \sin^2\theta \cos^2\theta S_z^{-1}(S_z - 1)^{-1}(3S_z^2 - S^2)(3S_z^2 - 6S_z - S^2 + 3)(I^2 - I'^2)S_+ \\
&- \left(\frac{D}{2H_0}\right)^2 \frac{A^2 B^2}{K^4} \sin^2\theta \cos^2\theta [S_z^{-2}(3S_z^2 - S^2)^2 + (S_z - 1)^{-2}(3S_z^2 - 6S_z - S^2 + 3)](I^2 - I'^2)S_+ \\
&+ \left(\frac{D}{2H_0}\right)^2 \sin^2\theta \cos^2\theta (-4S_z^4 + 8S_z^3 + 4S_z^2 S^2 - 29S_z^2 - 4S_z S^2 + 25S_z - 3S^2 - 3)S_+ \\
&+ \frac{1}{2} \left(\frac{D}{4H_0}\right)^2 \sin^4\theta (-3S_z^4 + 6S_z^3 + 6S_z^2 S^2 - 45S_z^2 - 6S_z S^2 + 24S_z - 3S^4 + 7S^2 - 6)S_+ . \quad (13)
\end{aligned}$$

The spin operator J appears as an intensity operator expanded in terms of the powers of D/H_0 and A/H_0 and it is very easy to use.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The crystals were α - Al_2O_3 single crystals, obtained from Baikowsky Co. (France), doped with approximately 0.1 wt% divalent manganese ions. The ESR spectra were obtained with a Varian V-4502 apparatus working in the X band. The modulation frequency of the static field was 100 kHz and the amplitude was about 0.3 G. The linewidth was 6 G at $T = 295^\circ\text{K}$.

Measurements of the fine and hyperfine structures yielded the values $D = 207.4 \pm 0.2$ G, $A = -85.1 \pm 0.2$ G, $B = -83.7 \pm 0.2$ G. Figure 1 shows the angular dependence of the intensities of the central $\frac{1}{2}, m \rightarrow -\frac{1}{2}, m$ electronic transition as predicted by the intensity operator (13). The measurements were made relative to the intensity of the corresponding line at $\theta = 0^\circ$. No experimental results can be obtained for the orientations defined by $30^\circ \leq \theta \leq 80^\circ$ because of the superposition of the lines. Some results are plotted in Fig. 2 for comparison with the results given by the method of Bir and by simple first-order perturbation calculations with the conventional spin Hamiltonian and with the spin Hamiltonian given by Eq. (4). These results give evidence of the good description of the angular variation predicted by the intensity operator. The method of Bir predicts too

great a decrease in the intensities with θ increasing and a shifting of the minima towards the small values of θ , which does not agree with experiments. Such results must be ascribed to the electronic-state approximation which is not perturbed by the hyperfine interaction. The comparison of the theoretical results given by first-order calculations shows the importance of expressing properly the hyperfine operator and it also shows the importance of second-order contributions for $30^\circ \leq \theta \leq 60^\circ$. To provide a basis for comparison with results predicted by the intensity operator in this range, we have calculated the intensity by diagonalization of the spin Hamiltonian at $\theta = 50^\circ$ and 35° . The values obtained were about 0.85 times those computed with the intensity operator. In this calculation, we used the magnetic field computed by third-order perturbation theory, rather than the exact value.

IV. CONCLUSION

We have shown that precise descriptions of EPR line intensity of S-state ions in axial crystal field needed the consideration of both exact electronic and nuclear quantization axes. The intensity operator is easy to use, and it enables us to find an operator associated with the physical quantity intensity, not by expanding the wave functions, but by expanding the operators. This expanded operator clearly depends on the physical system considered (ions and crystal environments).

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