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Intensity of forbidden hyperfine ($\Delta m = 2$) transitions in the electron paramagnetic resonance spectra of transition ions

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Abstract. Expressions are derived for determining the angular variation in the intensity of the forbidden hyperfine transitions ($\Delta M = 1$, $\Delta m = \pm 2$) in the EPR spectra of transition ions. The intensities calculated using these expressions are compared with the predictions of Bleaney and Rubins and of Bir. It is found that third-order contributions arising from the nuclear spin operator as well as the quadrupole term are important in interpreting the intensity of forbidden hyperfine lines.

1. Introduction

In the electron paramagnetic resonance (EPR) spectra of ions of electron spin $S > \frac{1}{2}$ and which also have a hyperfine (HF) structure, a number of extra HF lines are usually observed. These 'forbidden' HF lines correspond to transitions in which the nuclear magnetic quantum number m changes by ± 1, ± 2, etc, and arise as a result of the admixing of the various nuclear states corresponding to different m-values (Bleaney and Rubins 1961). The importance of the study of forbidden HF transitions lies in the fact that their intensity and line position can be used to determine the spin–spin interaction and, specifically, the nuclear quadrupole interaction (Misra *et al* 1989). The subject of forbidden HF transitions in EPR has been reviewed by Weil (1987) and the mechanisms responsible for their occurrence and their various applications have been discussed in detail by Misra and Upreti (1987).

Methods for calculating the intensity of the forbidden HF transitions in EPR have been described by Bleaney and Rubins (1961) and Bir (1964). Based on the perturbation method of Bleaney and Rubins (1961), Golding *et al* (1972) and Subramanian and Misra (1989) have derived expressions for the intensity of the forbidden HF transitions, $\Delta m = \pm 1, \pm 2$. The expressions obtained by these workers as well as by Bleaney and Rubins (1961) contain terms only up to second order. Mialhe and Erbeia (1972) and Mialhe (1979) have used the effective magnetic method of Bir (1964) to derive a modified spin Hamiltonian (SH) in order to interpret the angular variation in the EPR line intensities. The perturbation technique of Bleaney and Rubins (1961) was then applied to the complete SH to obtain expressions, in the form of operators, for calculating the intensity of EPR transitions (Mialhe and Erbeia 1973a,b). It has been pointed out that the complete SH derived by Mialhe and Erbeia (1973a,b) to calculate the intensity of the allowed $\Delta m = 0$ and the forbidden $\Delta m = 1$ HF

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transitions is incorrect (Subramanian and Cheung 1990), resulting in incorrect expressions for the angular variation in the EPR line intensity. The expression for the forbidden HF $\Delta m = 2$ transition derived by Mialhe *et al* (1977) does not contain the second-order terms of the expression obtained by Bleaney and Rubins (1961). This has prompted us to re-examine the operator expression for the $\Delta m = 2$ transition reported by Mialhe *et al* (1977).

2. Theory

Consider the spin Hamiltonian for an S-state ion:

$$\mathcal{H} = \mu_{\mathrm{B}} \boldsymbol{S}^{\mathrm{T}} \cdot \mathbf{g} \cdot \boldsymbol{B}_0 + \boldsymbol{S}^{\mathrm{T}} \cdot \mathbf{D} \cdot \boldsymbol{S} + \boldsymbol{S}^{\mathrm{T}} \cdot \mathbf{A} \cdot \boldsymbol{I} + \boldsymbol{I}^{\mathrm{T}} \cdot \mathbf{P} \cdot \boldsymbol{I}. \tag{1}$$

In equation (1), μ_{B} is the Bohr magneton, $\boldsymbol{B}_0$ is the external Zeeman field, $\boldsymbol{I}$ is the nuclear spin and T represents the transpose. $\mathbf{g}$, $\mathbf{D}$, $\mathbf{A}$ and $\mathbf{P}$ are, respectively, the electronic g, zero-field, hyperfine and quadrupole SH 'tensors' and are assumed to be anisotropic and have non-collinear principal axes (Abragam and Bleaney 1970).

The intensity of the EPR transition between the eigenstates $|M', m\rangle$ and $|M, m\rangle$ is given by

$$\mathrm{I}_{\mathrm{M,mM'm'}} = \mathcal{K} |\langle M', m' | \mu_{\mathrm{B}} \boldsymbol{S}^{\mathrm{T}} \cdot \mathbf{g} \cdot \boldsymbol{B}_1 | M, m\rangle|^2. \tag{2}$$

In equation (2) $\mathcal{K}$ is a constant, $\boldsymbol{B}_1$ is the amplitude of the excitation microwave field and $|M, m\rangle$ are the eigenfunctions of the SH (1). In the present paper, $|M, m\rangle$ will be determined using perturbation theory (Landau and Lifschitz 1965). This is conveniently done by first quantizing the electron spin $\boldsymbol{S}$ along the $\boldsymbol{B}_0 \cdot \mathbf{g}$ direction (unit vector $\hat{z}_1$), and then quantizing the nuclear spin $\boldsymbol{I}$ along the direction of the effective magnetic field $\boldsymbol{B}_{\mathrm{eff}}$ (unit vector $\hat{z}_2$) which is defined by (Bir 1964, Bir *et al* 1965)

$$\langle M | \boldsymbol{S}^{\mathrm{T}} \cdot \mathbf{A} \cdot \boldsymbol{I} | M\rangle = g_{\mathrm{n}} \mu_{\mathrm{n}} (\boldsymbol{B}_{\mathrm{eff}} \cdot \boldsymbol{I}) \tag{3}$$

where g_{n}, and μ_{n} are the nuclear g-value and nuclear magneton, respectively. The complete SH can then by written as (Subramanian and Cheung 1990)

$$\begin{aligned}\mathcal{H} = \mu_{\mathrm{B}} g B_0 S_{z1} &+ \sigma[3S_{z1}^2 - S(S+1)] + K_0 S_{z1} I_{z2} + \sigma_1 [3I_{z2}^2 - I(I+1)] \\ &- \tfrac{1}{2}\lambda(S_+ S_{z1} + S_{z1} S_+ + S_- S_{z1} + S_{z1} S_-) + \rho(S_+^2 + S_-^2) \\ &+ S_1(I_+ + I_-) - P(S_+ + S_-) I_{z2} + Q(S_+ I_+ + S_- I_-) \\ &+ R(S_+ I_- + S_- I_+) \\ &- \tfrac{1}{2}\lambda_1 (I_+ I_{z2} + I_{z2} I_+ + I_- I_{z2} + I_{z2} I_-) + \rho_1 (I_+^2 + I_-^2).\end{aligned} \tag{4}$$

In equation (4),

$$\begin{aligned} \sigma &= \tfrac{1}{6} D(3\cos^2\phi - 1) & \sigma_1 &= \tfrac{1}{6} Q'(3\cos^2\phi - 1) \\ \lambda &= D \sin\phi\cos\phi & \lambda_1 &= Q' \sin\phi\cos\phi \\ \rho &= \tfrac{1}{4} D \sin^2\phi & \rho_1 &= \tfrac{1}{4} Q' \sin^2\phi \end{aligned}$$

$$P = [(A^2 - B^2)/2K]\sin\phi\cos\phi + (\lambda/2GKM)(A^2\sin^2\phi + B^2\cos^2\phi)$$
$$\times [3M^2 - S(S+1)]$$

$$Q = \tfrac{1}{4}B(A/K - 1) \qquad R = \tfrac{1}{4}B(A/K + 1)$$

$$S_1 = (\lambda AB/2GK)[3M^2 - S(S+1)]$$

$$K_0 = K + [(A^2 - B^2)D/GKM]\sin^2\phi\cos^2\phi[3M^2 - S(S+1)]$$

$$g^2K^2 = g_{\parallel}^2 A^2\cos^2\theta + g_{\perp}^2 B^2\sin^2\theta$$

$$D = \tfrac{3}{2}D_{zz} \qquad Q' = \tfrac{3}{2}P_{zz} \qquad A = A_{zz} \qquad B = A_{xx} = A_{yy}$$

$$S_{\pm} = S_{x1} \pm \mathrm{i}S_{y1} \qquad I_{\pm} = I_{x2} \pm \mathrm{i}I_{y2}$$

$$\tan\phi = (g_{\perp}/g_{\parallel})\tan\theta \qquad G = \mu_{\mathrm{B}} g B_0 \tag{5}$$

θ is the angle between the Zeeman field B_0 and the z principal axis. The $\mathbf{g}, \mathbf{D}, \mathbf{A}$ and $\mathbf{P}$ tensors are axial. Their principal axes coincide with the laboratory axes x, y, z.

The matrix elements of the forbidden HF transitions $\Delta M = 1, \Delta m = \pm 2$, calculated using equations (2)–(5) for the case of the excitation field B_1 perpendicular to the Zeeman field B_0 are given below.

2.1. *Transitions* $|M-1, m\pm 2\rangle \leftrightarrow |M, m\rangle$

$$\begin{aligned} C_{\pm}[\{[D^2A^2B^2\sin^2(2\phi)]/32G^2K^4\}[[3M^2 - S(S+1)]/M \\ - [3(M-1)^2 - S(S+1)]/(M-1)]^2 \mp (DB^2/32G^2K)(A^2/K^2+1) \\ \times \sin^2\phi[[3M^2 - S(S+1)]/M - [3(M-1)^2 - S(S+1)]/(M-1)] \\ \pm (DB^2/32G^2K)(A^2/K^2-1)(3\cos^2\phi - 1)[[3M^2 - S(S+1)]/M \\ - [3(M-1)^2 - S(S+1)]/(M-1)] + (B^2/8G^2)(A^2/K^2-1) \\ \times [1 - (D\sin^2\phi)/8K][S(S+1) - M^2 + M - 1] \\ - (B^2/16G^2)(A/K+1)^2 \\ - \{[D^4A^4B^4\sin^4(4\phi)]/256G^4K^8\}[[3M^2 - S(S+1)]/M]^2 \\ \times \{[3(M-1)^2 - S(S+1)]/(M-1)\}^2[I(I+1) - m^2 \mp 2m - 2] \\ \mp [(Q'\sin^2\phi)/8K][1/M - 1/(M-1)]] \end{aligned} \tag{6}$$

where

$$C_{\pm}^2 = [S(S+1) - M(M-1)][I(I+1) - m(m\pm 1)][I(I+1) - (m\pm 1)(m\pm 2)].$$

3. Comparison with previous results

The expression for the intensity of the $\Delta m = -2$ transition given by equation (6) above differs significantly from that obtained from the operator expression (equation (4)) of Mialhe *et al* (1977). The reason for the discrepancies between the two results could not be established because the complete SH used by Mialhe *et al* (1977) to derive the operator expressions was not mentioned. The present result (equation (6)) contains all the second-order terms reported by Bleaney and Rubins (1961) whereas that of Mialhe *et al* (1977) does not. The present result (equation (6)) contains the second-order terms of Golding *et al* (1972) and Subramanian and Misra (1989) as well.

Operator expression for the forbidden HF transition, $\Delta m = 2$, is not reported by Mialhe *et al* (1977). Consequently, no comparison with their result was possible. However, equation (6) is in agreement with the second-order expressions of Bleaney and Rubins (1961) and Subramanian and Misra (1989).

4. Illustrative example

The intensity expression given by equation (6) above is now compared with the experimental values on Mn^{2+} for Al_2O_3 reported by Mialhe *et al* (1977). In order to accomplish this, the klystron frequency must be known, which is not reported by Mialhe *et al* (1977). Therefore, it had to be estimated using a least-squares procedure (Subramanian and Cheung 1990). It became apparent during the computation that the fit between the theoretical expression (equation (4)) of Mialhe *et al* (1977) and the corresponding curves drawn by them (their figure 2) was very poor. Since the angular variation in the intensity of the forbidden HF transition, $\Delta m = 2$, predicted from Bir's (1964) theory has also been given by Mialhe *et al*, it was decided that this curve should be used in order to estimate the klystron frequency. The theoretical expression for the intensity needed for this fitting procedure was derived from Bir (1964) and is given by

$$I = K|w_{M,M-1}|^2 |P^I_{m,m+2}(\mu)|^2 \tag{7}$$

where

$$\begin{aligned} w_{M,M-1} = K\{1 &+ (|\rho|^2/G^2)[3M(M-1) - S(S+1) + \tfrac{3}{2}] \\ &- (|\lambda|^2/4G^2)[4S(S+1) - 3] + \rho(2M-1)/G \\ &- \tfrac{3}{4}\lambda^2(2M-1)^2/G^2 + (\sigma\rho/G^2)[S(S+1) - M(M-1) - 1]\} \end{aligned} \tag{8}$$

and

$$P^{5/2}_{-1/2,3/2}(\mu) = -\tfrac{1}{4}(1-\mu)(1+\mu)^{1/2}(1+5\mu) \tag{9a}$$

$$P^{5/2}_{1/2,1/2}(\mu) = 2^{-3/2}(1+\mu)^{1/2}(5\mu^2 - 2\mu - 1) \tag{9b}$$

$$\mu_{M,M-1} = 1 - (9|\lambda|^2/2G^2)[1 + S(S+1)/3M(M-1)]^2. \tag{9c}$$

This procedure resulted in an excellent fit between the angular variation of the line intensity calculated using equations (7)–(9) above and the corresponding curve drawn by Mialhe *et al.* The best-fit klystron frequency was then estimated to be 9.49 GHz. This value of the klystron frequency, together with the reported values of $D = 207.4$ G, $A = -85.1$ G, $B = -83.7$ G and $Q' = 0.87$ G (Mialhe *et al* 1977), was used in equation (6) to compute the intensity. The angular variation in the intensity of the forbidden HF transition $|M-1, m+2\rangle \leftrightarrow |M, m\rangle$ so determined is shown in figure 1. For comparison, the intensity variations predicted by Bleaney and Rubins (1961) and Bir (1964) are also shown in the same figure.

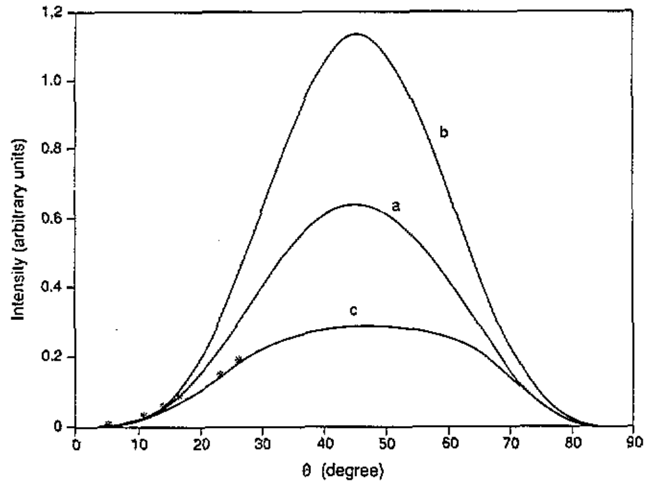

Figure 1. Intensity of the forbidden HF transition $|-\frac{1}{2}, \frac{3}{2}\rangle \leftrightarrow |\frac{1}{2}, -\frac{1}{2}\rangle$ for Mn^{2+} in Al_2O_3 as a function of the angle θ between the external Zeeman field and the z principal axis: curve a, based on equation (6) of the present paper; curve b, according to Bleaney and Rubins (1961); curve c, variation predicted by Bir (1964); *, experimental points from Mialhe *et al* (1977).

As may be seen from figure 1, the experimental values reported by Mialhe *et al* (1977) are in much better agreement with the intensity calculated using equation (6) above than that predicted by Bleaney and Rubins (1961). This would seem to indicate that the third-order contributions from the nuclear spin operator as well as the quadrupole term (not considered by Bleaney and Rubins) are important in computing the intensity of the forbidden HF transitions. The intensity calculated using the method of Bir is also seen to be compatible with the experimental values for angles where data are available. Bir's theory is known to give good agreement with experiment in those cases where the crystal-field splitting is much larger than the HF splitting (Bir *et al* 1965, Jain *et al* 1983). The advantage of the present method is that it is valid even when the crystal-field and HF terms are of comparable magnitude.

5. Conclusion

The intensity calculated using the complete SH gives better agreement with experimental data than that predicted by the second-order perturbation calculations of Bleaney and Rubins. Third-order contributions coming from the nuclear spin operator and the quadrupole term are found to be quite significant in interpreting the intensity of forbidden HF transitions.

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