PHYSICAL REVIEW B VOLUME 14, NUMBER 7 1 OCTOBER 1976

Intensity operator for forbidden lines in EPR spectra of *S*-state ions

P. Mialhe* and P. Quedec
Centre d'Etudes Mathématiques, Université de Lyon-France, Boîte Postale 38 55 Beyrouth, Liban
and Laboratoire de Spectroscopie et de Luminescence, Université Claude Bernard Lyon I,
43 Boulevard du 11 Novembre 1918, 69621 Villeurbanne, France

(Received 12 December 1975; revised manuscript received 24 May 1976)

An intensity spin operator is derived: it leads to a simple description of the intensity of EPR forbidden ($\Delta M = 2$, $\Delta m = 0$) lines. These theoretical results are discussed and compared with experimental measurements on Al_2O_3:Mn^{2+} EPR spectra.

I. INTRODUCTION

It is known that the selection rules for magnetic-dipole transitions are often broken down and this leads to the observation of forbidden transitions. Bleaney and Rubins[1] ascribed the large intensities of these forbidden lines to cross terms arising from off-diagonal operators in the spin Hamiltonian.

Some authors[2-5] have reported the observation of $\Delta M = 2$ transitions in the EPR spectra of Mn^{2+} ions; only Narayana made an attempt to derive an expression of line intensities but in a particular and incomplete case. It seems of interest to calculate line intensities by using the method proposed by Mialhe and Erbeia[6] who have introduced an intensity operator to describe allowed transitions.

In this paper we have derived an intensity spin operator that leads to a description of $\Delta M = 2$, $\Delta m = 0$ lines of the EPR spectra of S-state ions with axial or cubic environments. We have considered the case when both crystal-field and hyperfine interactions are of the same magnitude and are small compared with Zeeman interaction. These theoretical results have been compared with experimental measurements of Al_2O_3: Mn^{2+} EPR spectra.

II. THEORY

The complete spin Hamiltonian for Mn^{2+} ions may be written as

$$\mathcal{H} = \vec{H}\cdot\underline{g}\cdot\vec{S} + \mathcal{H}_c + \mathcal{H}_a + \vec{S}\cdot\underline{A}\cdot\vec{I}\,. \tag{1}$$

The $\underline{g}$ tensor is approximately isotropic for S-state ions, $\mathcal{H}_c$ and $\mathcal{H}_a$ are the cubic and axial field operators, and $\underline{A}$ is the hyperfine tensor. In the crystal field of corundum (Al_2O_3), the Hamiltonian $\mathcal{H}$ takes the form[7]

$$\mathcal{H} = g\mu_B\vec{H}\cdot\vec{S} + D[S_z^2 - \tfrac{1}{3}S(S+1)] - \frac{a-F}{180}[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2]$$
$$+ \frac{a\sqrt{2}}{36}[S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z] + AS_zI_z + \frac{B}{2}(S_+I_- + S_-I_+)\,. \tag{2}$$

In this expression a is the cubic-crystal-field splitting parameter, D and F correspond to the axial crystal field of the second and fourth degree, respectively, A and B determine the hyperfine components, and the direction of the axial crystal field defines the z axis which lies along the [111] direction when referred to the cube axes. We need $\mathcal{H}$ relative to a coordinate system in which the Zeeman terms are diagonal; this may be obtained by using[8] a rotation operator. Furthermore, the crystalline-electric-field gradient that exists at the cation sites distorts the spherically symmetrical electron cloud in the ion, so that the nuclear spins are not acted upon by the external magnetic field alone, but by a much greater effective field[9] associated with hyperfine interaction as well. For line-intensity calculations, it has been shown[6] that it is important to take the expression of the hyperfine operator, which considers the actual quantization axes of electronic and nuclear spin operators. Then, the nondiagonal part of the Hamiltonian may be written as

$$\begin{aligned}
\mathcal{H}_1 = {} & \frac{D}{2}[S_+(2S_Z+1)+(2S_Z+1)S_-]\sin\theta\cos\theta+\frac{D}{4}(S_+^2+S_-^2)\sin^2\theta \\
& -\frac{a-F}{180}\{-\tfrac{5}{4}\sin\theta\cos\theta(4-7\sin^2\theta)\ [S_+F_1(S_Z)+F_1(S_Z)S_-]-\tfrac{5}{8}\sin^2\theta(6-7\sin^2\theta)[S_+^2F_2(S_Z)+F_2(S_Z)S_-^2] \\
& \qquad +\tfrac{35}{4}\sin^3\theta\cos\theta\ [S_+^3F_3(S_Z)+F_3(S_Z)S_-^3]+\tfrac{35}{16}\sin^4\theta(S_+^4+S_-^4)\} \\
& +\frac{a\sqrt{2}}{36}\{\sin 3\varphi(4\sin^2\theta-3)\sin^2\theta\ [S_+F_1(S_Z)+F_1(S_Z)S_-]+3i\cos 3\varphi\cos\theta\sin^2\theta[S_+F_1(S_Z)-F_1(S_Z)S_-] \\
& \qquad +2\sin 3\varphi\sin\theta\cos 3\theta\ [S_+^2F_2(S_Z)+F_2(S_Z)S_-^2]-i\cos 3\varphi\sin\theta(2-3\sin^2\theta)[S_+^2F_2(S_Z)-F_2(S_Z)S_-^2] \\
& \qquad +\sin 3\varphi\,(4-11\sin^2\theta+4\sin^4\theta)[S_+^3F_3(S_Z)+F_3(S_Z)S_-^3]-i\cos 3\varphi\cos\theta(4-9\sin^2\theta)[S_+^3F_3(S_Z)-F_3(S_Z)S_-^3] \\
& \qquad +\sin 3\varphi\sin\theta\cos\theta(4-\sin^2\theta)(S_+^4+S_-^4)-i\cos 3\varphi\sin\theta(4-3\sin^2\theta)(S_+^4-S_-^4)\} \\
& +i\frac{DAB}{4KH_0}\sin 2\theta\,(3S_Z^2-S^2)(I'_+-I'_-)+\frac{D}{4KH_0}(A^2\sin^2\theta+B^2\cos^2\theta)\sin 2\theta(3S_Z^2-S^2)S_Z^{-1}(S_++S_-)I'_Z \\
& +i\frac{B}{4}\left(1-\frac{A}{4K}\right)(S_+I'_+-S_-I'_-)+i\frac{B}{4}\left(1+\frac{A}{4K}\right)(S_+I'_--S_-I'_+)\ ,
\end{aligned} \tag{3}$$

with

$$F_1(S_Z)=-14S_Z^3-21S_Z^2+6S^2S_Z-19S_Z+3S^2-6\ , \tag{4}$$

$$F_2(S_Z)=-14S_Z^2-28S_Z+2S^2-18\ , \tag{5}$$

$$F_3(S_Z)=2S_Z+3\ . \tag{6}$$

In this expression the electronic axis of quantization is along the magnetic field (Z axis) which makes angles (θ,φ) with respect to the crystal axes, K is defined by $K=(A^2\cos^2\theta+B^2\sin^2\theta)^{1/2}$, and I'_Z, I'_+, I'_- are defined relative to the effective field at the nucleus taken as nuclear-spin axis of quantization.

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

$$\Psi_{M,m}=\sum_{i,j}\alpha_{i,j}^{M,m}|M+i,m+j\rangle\ . \tag{7}$$

The admixture coefficients $\alpha_{i,j}^{M,m}$ enable us to write a simple expression of line intensity I;

$$\begin{aligned}
I\propto|\langle\Psi_{M,m}|S_x|\Psi_{M-2,m}\rangle|^2 = \Big| & (\alpha_{0,0}^{M,m})^*\alpha_{1,0}^{M-2,m}h(M-1) \\
& +(\alpha_{-1,0}^{M,m})^*\alpha_{0,0}^{M-2,m}h(M-2)+(\alpha_{0,0}^{M,m})^*\alpha_{3,0}^{M-2,m}h(M) \\
& +(\alpha_{-3,0}^{M,m})^*\alpha_{0,0}^{M-2}h(M-3)+\sum_{i,j}(\alpha_{i,j}^{M,m})^*\alpha_{i+1,j}^{M-2,m}h(M-1+i) \\
& +\sum_{i,j}(\alpha_{i,j}^{M,m})^*\alpha_{i+3,j}^{M-2,m}h(M+i)\Big|^2\Big/4\ ,
\end{aligned} \tag{8}$$

with $h(M)=[S(S+1)-M(M+1)]^{1/2}$.

The evaluation of each coefficient $\alpha_{i,j}^{M,m}$ that we need in the second-order approximation leads to long calculations. We use the method given in Ref. 6 and recalled in the Appendix.

If we consider all the contributions in Eq. (8) up to second order [we include terms in $(D/H_0)^2$ but we neglect terms in Da/H_0^2 or DF/H_0^2 which are of a lower order of magnitude], we get the intensity of $\Delta M=2$, $\Delta M=0$ lines as matrix elements of a simple spin operator J_2;

$$I\propto|\langle M,m|J_2|M-2,m\rangle|^2/4\ , \tag{9}$$

$$\begin{aligned}
J_2 = {} & \frac{D}{2H_0}\sin 2\theta S_+^2-\frac{D^2}{8H_0^2}\cos\theta\sin^3\theta[2(S_Z-1)S^2-2S_Z^3+6S_Z^2-19S_Z+15)]S_+^2 \\
& +\left(\frac{2a\sqrt{2}}{27H_0}\ [\sin 3\varphi(8\sin^4\theta-4\sin^2\theta-1)+i\cos 3\varphi\cos\theta(4\sin^2\theta-1)]+\frac{a-F}{54H_0}\sin\theta\cos\theta(9-14\sin^2\theta)\right) \\
& \times(S^2-7S_Z^2+14S_Z-9)S_+^2\ .
\end{aligned} \tag{10}$$

The operator J_2 appears as an intensity operator expanded in terms of the powers of $1/H_0$ and is easy to use.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The EPR 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 0.7 G. In order to enhance the signal-to-noise ratio of the forbidden lines, linear sweeps were accumulated in a computer of average transients (CAT) triggered by a NMR signal. The crystals were α-Al_2O_3 single crystals, obtained from Baikowsky Co. (France) and doped with approximatively 0.1-wt% divalent manganese ions. Measurements of the fine and hyperfine structure yielded the values $D = 207.4 \pm 0.2$ G, $A = -85.1 \pm 0.2$ G, $B = -83.7 \pm 0.2$ G, $a = 12.8 \pm 0.3$ G, $F = -11.5 \pm 1$ G.

The half-field spectrum arising from transitions where $\Delta M = 2$ is weak and, compared with the central allowed group, it is 1% in intensity at most. Because of this weak intensity and also because of the superposition of the lines, only a few results are available and these are plotted in Fig. 1.

In first order in D/H_0 and with $a = F = 0$ G we get results derived by Narayana.[3] But the asymmetry given by the intensity operator for results between 0° and 90° compared to results between 90° and 180° shows the importance of terms from the crystal field in a and F. (It may be noted that this asymmetry provides a way to find the relative sign of a and D, the same sign here, and that this justifies the F minus sign proposed elsewhere.[10])

The intensity operator J_2, derived by using the complete spin Hamiltonian with the correct expression of the hyperfine operator, is independent of nuclear-spin operators. This fact must be pointed out when we compare these results with the description of the angular variation of allowed line intensities[6] ($\Delta M = 1, \Delta m = 0$); in this last case the nuclear-spin operators had a great part in the expression of the intensity operator.

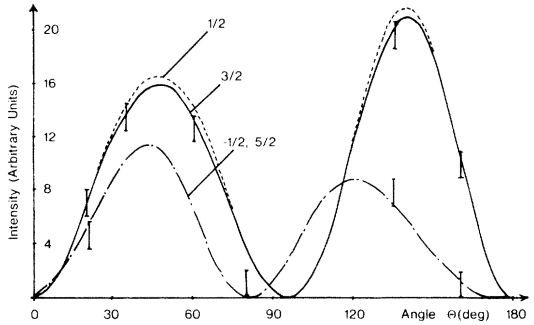

FIG. 1. Intensity of $(M,m) \rightarrow (M-2,m)$ lines as a function of the angle between external field and crystal C axis. (M values are indicated). $\varphi = 30°$. The curves are drawn from values calculated with the intensity operator. The error bars indicate the results of measurements for Al_2O_3: Mn^{2+}.

IV. CONCLUSION

We have shown that a good description of the angular dependence of forbidden $\Delta M = 2$ line intensity is gotten with the intensity operator. This operator is easy to use and depends on the physical system considered. It is an attempt to associate an operator with the physical quantity "intensity" and to derive an approximation method, theoretically more satisfactory, since it makes it possible to work with zero-order wave functions and then to use an expanded operator.

APPENDIX

To show the method we used in the calculations, let us derive in first order the coefficients

$$\alpha^{M,m}_{\pm 1,0} = -\frac{\langle M \pm 1, m | \mathcal{H}_1 | M, m \rangle}{E^0_{M\pm 1} - E^0_{M,m}} . \tag{11}$$

In this case D is small and we have taken energy denominators as

$$E^0_{M\pm 1,m} - E^0_{M,m} = \pm H_0 . \tag{12}$$

We obtain

$$\alpha^{M,m}_{\pm 1,0} = \mp \frac{D}{2H_0} \sin\theta \cos\theta \langle M \pm 1, m | (2S_z \pm 1) S_\pm | M, m \rangle . \tag{13}$$

Assuming here that $\alpha^{M,m}_{0,0}$ is equal to 1, we have

$$\alpha^{M-2,m}_{1,0} h(M-1) + (\alpha^{M,m}_{-1,0})^* h(M-2) = \frac{D}{2H_0} \sin\theta \cos\theta \, [\langle M, m | S_+ (2S_z + 1) | M-1, m \rangle h(M-2) - \langle M-1, m | (2S_z - 1) S_+ | M-2, m \rangle h(M-1)] . \tag{14}$$

If we write in Eq. (14)

$$h(M-1) = \langle M, m | S_+ | M-1, m \rangle , \tag{15}$$

$$h(M-2) = \langle M-1, m | S_+ | M-2, m \rangle , \tag{16}$$

we get

$$\alpha_{1,0}^{M-2,m}h(M-1)+(\alpha_{-1,0}^{M,m})^{*}h(M-2)=\frac{D}{2H_0}\sin\theta\cos\theta\langle M,m\,|\,S_+(2S_z+1)S_+-S_+(2S_z-1)S_+\,|\,M-2,m\rangle$$

$$=\frac{D}{2H_0}\sin 2\theta\langle M,m\,|\,S_+^2\,|\,M-2,m\rangle\,. \qquad (17)$$

It is the first term that appears in J_2.

---

[*] Present address: Le Chastelet, 43000 Le Puy, France.

[1] B. Bleaney and R. S. Rubins, Proc. Phys. Soc. Lond. 77, 103 (1961).

[2] B. Bleaney and D. J. E. Ingram, Proc. R. Soc. A 205, 336, (1951).

[3] P. A. Narayana, J. Chem. Phys. 55, 4283 (1971).

[4] R. M. Golding, R. H. Newman, A. D. Rae, and W. C. Tennant, J. Chem. Phys. 57, 1912 (1972).

[5] A. Serra Walls, C. Gaco-Bousquet, and M. Garcia-Sucre, Phys. Rev. B 9, 4667 (1974).

[6] P. Mialhe and A. Erbeia, Phys. Rev. B 7, 4061 (1973).

[7] J. W. Orton, *Electron Paramagnetic Resonance* (Ilife, London, 1968).

[8] P. Mialhe, J. Phys. Chem. Solids 34, 217 (1973).

[9] P. Mialhe and A. Erbeia, Phys. Status Solidi B 57, 509 (1973).

[10] P. Mialhe, A. Briguet, and A. Erbeia, Solid State Commun. 9, 755 (1971).