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## Forbidden Hyperfine Transitions in the Paramagnetic Resonance of $\text{Mn}^{++}$ in Cubic CaO

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(3. VII. 64)

*Summary.* It has recently been shown that mixing of hyperfine states can be achieved through an interaction with the zero-field cubic splitting. To give further evidence of this mixing, the 'forbidden' hyperfine transitions in the electron paramagnetic resonance of divalent manganese in cubic calcium oxide have been investigated. The five forbidden doublets have been observed and their splittings agree well with theory. Furthermore, the angular dependence of the magnitudes as well as the relative magnitudes of the intensities agree with the theory of cubic field mixing. The intensities have been calculated using operator equivalents.

### 1. Introduction

The forbidden hyperfine lines in the paramagnetic resonance spectrum in cubic fields have been observed for interstitial H atoms in  $\text{CaF}_2$  by HALL and SCHUMACHER<sup>1)</sup> and for  $\text{Mn}^{++}$  ions in MgO by AUZINS et al.<sup>2)</sup>. Recently these transitions have been studied both theoretically and experimentally by DRUMHELLER and RUBINS<sup>3)</sup> and it was shown that the mixing of hyperfine states could occur through a combination of the cubic zero field splitting terms and the hyperfine interaction in second order perturbation theory. The theory was tested on a single crystal of MgO with divalent manganese impurities<sup>4)</sup>. The purpose of this paper is to present further evidence of the cubic interaction and to simplify the theory involved.

BLEANEY and RUBINS<sup>5)</sup> have shown that mixing of the hyperfine states occurs when the magnetic field is rotated away from a two-fold or higher symmetry axis. For cubic fields this means that the mixing will occur when a single electronic raising or lowering term ( $\mathcal{S}_1$ ) resulting from the cubic field fine structure splitting is combined in second order perturbation with a lowering or raising electronic term from the hyperfine interaction ( $\mathcal{S}_2$ ). In the latter expression there is always a corresponding raising or lowering operator for the nuclear wave function resulting in a mixture of neighboring nuclear levels. In the paper by DRUMHELLER and RUBINS, these functions were calculated explicitly. Here, however, the operator equivalent notation will be used resulting in some generalization and simplification in the calculation of intensities.

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## 2. Theory

When the magnetic field is in the  $z$ -direction the cubic potential felt by the impurity manganese ion may be represented in the Spin Hamiltonian as

$$V_{cubic} = B_4 (O_4^0 + 5 O_4^4), \quad (1)$$

where  $B_4$  is a constant and is equal to  $a/120$  and  $a$  is the zero field splitting parameter. The  $O_l^m$  are operator equivalents having the same transformation properties as the spherical harmonics  $Y_l^m$ . If the magnetic field is rotated in the  $xz$ -plane, JONES, BAKER, and POPE<sup>6</sup>) have shown that Equation (1) may be written

$$V_{cubic\ rot} = B_4 \left\{ \frac{3}{8} O_4^0 + \frac{5}{2} O_4^2 + \frac{35}{8} O_4^4 + 5 \left[ \left( \frac{1}{8} O_4^0 - \frac{1}{2} O_4^2 + \frac{1}{8} O_4^4 \right) \cos 4\theta - i(O_4^1 - i O_4^3) \sin 4\theta \right] \right\}. \quad (2)$$

Here we shall be concerned only with the terms that raise and lower the electronic wave function by one step which is represented by  $O_4^1$  in Equation (2).  $O_4^1$  has been evaluated to be<sup>7</sup>)

$$O_4^1 = \frac{1}{4} \{ [7 J_z - 3 J(J+1) J_z - J_z] (J_+ + J_-) + (J_+ + J_-) [7 J_z - 3 J(J+1) J_z - J_z] \}, \quad (3)$$

and with  $\sin 4\theta$  from Equation (2) forms  $\mathfrak{H}_1$ . Using the values for  $Mn^{++}$  of  $J$  and  $J_z$  in Equation (3) with  $\mathfrak{H}_2 = A \bar{S} \bar{I}$  and substituting into the perturbation expression gives the resulting intensity

$$I = \frac{25 a^2}{(g \beta H)^2} [I(I+1) - m(m+1)] (\sin 4\theta)^2 \quad (4)$$

which agrees with Equation (13) of Ref. 3.

## 3. Discussion and Data

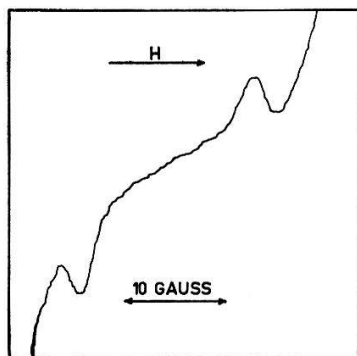
As further evidence of the cubic mixing, the paramagnetic resonance spectrum of divalent manganese in the cubic crystals of calcium oxide, calcium fluoride, and barium fluoride were studied and the forbidden lines were observed in CaO. In this case the cubic field splitting is about 6 gauss<sup>8</sup>) and there is no measured axial field gradient. No forbidden transitions were observed in the spectra of calcium fluoride or barium fluoride, since the zero field splittings are about half a gauss<sup>9</sup>). It can be seen in Equation (4) that since the intensity is proportional to the square of the zero field splitting, the signal would be two orders of magnitude smaller than for CaO. Also in the fluoride crystals, the difficulty of line broadening arises due to the fluorine super-hyperfine interaction. The experiment was performed at room temperature and at X-band in a similar manner described in Ref. 3.

The experimental data shows good agreement with Equation (4) for the intensity including the  $(\sin 4\theta)^2$  dependence. The Figure shows an example of the data for the  $m = -3/2$  doublet, which means the doublet between  $m = -3/2$  and  $m = -1/2$ . The calculated relative intensity of these lines compared to the main hyperfine lines is

about  $5 \times 10^{-4}$ ; this is within a factor of 2 of the measured values. The doublet separation for small  $a$  is given as<sup>3</sup>

$$H = \frac{17}{2} \frac{A^2}{H_0} + 2 \frac{g_n \beta_n}{g \beta} - \frac{5}{4} \frac{A^2}{H_0} (10 A + 3 a) (2 m + 1) \quad (5)$$

where the angular dependent term has been dropped since for maximum intensity it would be zero. The table gives the experimental data for the splitting compared to the values predicted by Equation (5) above.



Data for  $\text{CaO} : \text{Mn}^{++}$

|                         | m              |        |        |       |       |
|-------------------------|----------------|--------|--------|-------|-------|
|                         | $-5/2$         | $-3/2$ | $-1/2$ | $1/2$ | $3/2$ |
| $\delta H$ calculated   | 17.8           | 18.9   | 20.2   | 21.5  | 22.6  |
| $\delta H$ experimental | $17.5 \pm 0.6$ | 18.9   | 19.8   | 21.3  | 22.9  |

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