

FORBIDDEN HYPERFINE TRANSITIONS IN ELECTRON SPIN RESONANCE OF Mn^{2+} IN NaCl SINGLE CRYSTAL

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ABSTRACT

Forbidden hyperfine transitions are observed in the electron spin resonance spectrum of divalent Mn^{55} ion in NaCl single crystal for a particular associated pair. From the measurements of the $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $\Delta m = \pm 1$ transitions the parameters Q' and Q'' of the nuclear electric quadrupole part of the spin-Hamiltonian $H_o = Q' [I_z^2 - \frac{1}{3}I(I+1)] + Q'' (I_x^2 - I_y^2)$ are found to be $+1.70 \times 10^{-4}$ cm. $^{-1}$ and $+0.16 \times 10^{-4}$ cm. $^{-1}$ respectively.

INTRODUCTION

FORBIDDEN hyperfine transitions ($\Delta m \neq 0$) have been observed in the electron paramagnetic resonance spectra of Mn^{2+} in MgO ,^{1, 2} CaO ,³ $MgAl_2O_4$,⁴ Al_2O_3 ,⁵ ZnO ,⁶ $CaCO_3$,⁷ $ZnSiF_6 \cdot 6H_2O$,^{8, 9} $(NH_4)_2 Zn (SO_4)_2 \cdot 6H_2O$,⁹ $ZnCO_3$,¹⁰ and $Ca_{10}(PO_4)_6 (F, Cl)$.¹⁰ Attempts have been made to explain the variation of intensities by Drumheller and Rubins² by perturbation expressions involving the fine structure a term and the hyperfine A term, and by Friedman and Low,⁸ Ludwig and Woodbury¹¹ and Bleaney and Rubins¹² by perturbation expressions involving D and A terms. A detailed theory is developed by Bir.¹³ The allowed $\Delta M = \pm 1$, $\Delta m = 0$ transitions of Mn^{2+} ion associated with different point defects and impurity ions in NaCl single crystal have been discussed by the authors in an earlier paper.¹⁴ In the present paper the so-called forbidden hyperfine transitions ($\Delta m = \pm 1$) in the paramagnetic resonance spectrum of this ion in NaCl for the spectrum IV referred to in the earlier paper are analysed and from that an anisotropic quadrupole interaction is deduced.

THEORY

The spin-Hamiltonian for a Mn^{2+} ion in orthorhombic symmetry is given by¹⁵

$$H = g\beta H.S + D [S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + S.A.I - \gamma\beta_n H.I. + Q' [I_z^2 - \frac{1}{3}I(I+1)] + Q'' (I_x^2 - I_y^2) \quad (1)$$

where g is the spectroscopic splitting factor, β the Bohr magneton, H the external field, S the electron spin operator, D the axial and E the orthorhombic crystal field splitting parameter. A is the hyperfine coupling constant, γ the nuclear splitting factor, β_n the nuclear magneton, I the nuclear spin operator and Q' and Q'' are the nuclear electric quadrupole interaction parameters.

By making use of earlier literature^{5, 10, 13, 15} one can show that the hyperfine part of the energy of the state $|M, m\rangle$ is given by

$$\begin{aligned}
 E^h_{Mm} = & AMm + \frac{mB^2}{2g\beta H_0} \{M^2 - S(S+1)\} + \frac{MB^2}{2g\beta H_0} \{I(I+1) - m^2\} \\
 & - \gamma\beta_n H m + \frac{1}{2} Q' \{m^2 - \frac{1}{3} I(I+1)\} R \\
 & + \frac{1}{3} Q'' \{m^2 - \frac{1}{3} I(I+1)\} N + \frac{2AMm}{(g\beta H_0)^2} \\
 & \times \{2M^2 + 1 - S(S+1)\} |\rho|^2 + \frac{Am}{2M(g\beta H_0)^2} \\
 & \times \{(M^2 - S(S+1))^2 - M^2\} |\lambda|^2 + \frac{B^2 DR}{8(g\beta H_0)^2} \\
 & \times [3 \{I(I+1) - m^2\} (2M+1) - m \{2S(S+1) \\
 & + 3(-2M^2 + 2M+1)\}] \\
 & + \frac{A^3}{2(g\beta H_0)^2} [\dots]
 \end{aligned} \tag{2}$$

where

$$N = \sin^2\theta \cos 2\phi$$

$$R = 3 \cos^2\theta - 1$$

$$\rho = \frac{1}{2} [D \sin^2\theta + E (\cos^2\theta \cos 2\phi - \sin^2\phi) + 2iE \cos\theta \cos 2\phi]$$

$$\lambda = \sin^2\theta [\cos\theta (D - E \cos 2\phi) + iE \cos 2\phi]$$

and M and m are the electronic and nuclear magnetic quantum numbers respectively. Here g and γ are assumed isotropic and the hyperfine interaction is taken to be isotropic in all terms other than the first. For $E = 0$ this equation applies to the case where there is a mixing of hyperfine levels by the terms involving D and A .*

* Equation so obtained will not be the same as used by Folen⁶ since he did not include some of the third order terms.¹²

From the above equation the separation of the forbidden doublets ($M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $\Delta m = \pm 1$) is found to be

$$\begin{aligned} \Delta H = & \frac{17B^2}{H_0} + 2 \frac{\gamma\beta_n}{g\beta} H - \left[Q'(3\cos^2\theta - 1) + 3Q''\sin^2\theta \cos 2\phi \right. \\ & \left. - 4 \frac{B^2D}{H_0^2} (3\cos^2\theta - 1) \right] (2m + 1) - \frac{25}{2} \frac{A^3}{H_0^2} (2m + 1). \quad (3) \end{aligned}$$

EXPERIMENTAL RESULTS AND DISCUSSIONS

The experimental procedure is the same as in authors' earlier paper.¹⁴ Quenched crystals that show only the spectrum IV with no trace of any other spectra are taken for the present observations. The analysis^{14, 16} of the allowed transitions of spectrum IV gives $A = -84.71$ gauss, $B = -85.63$ gauss, $D = -549.6$ gauss, $E = +21.57$ gauss, $g = 2.0017 \pm 0.002$, $h\nu/g\beta = H_0 = 3373.45$ gauss.

At values of θ between 25° and 65° the magnetic field being rotated in a (100) plane, doublets appeared between $M, m \rightarrow M - 1, m$ transitions. The central part of the spectrum for which $\theta = 45^\circ$ is shown in Fig. 1. Equation (3) represents the theoretical expression for this doublet separation. The first two terms in this equation give essentially equal doublet separation, the third causes angular dependence and the third and fourth terms together cause its asymmetry. The analyses at $\theta = 30^\circ$ and 45° show that a small nuclear electric quadrupole interaction exists which amounts to $Q' = +1.80$ gauss and $Q'' = +0.17$ gauss. From the measurements of the doublet spacings the ratio $\gamma\beta_n/g\beta = -0.38 \times 10^{-3}$ is deduced which gives $\gamma = 1.38$. It is interesting that this value of γ is incidentally the same as the one determined from nuclear magnetic resonance measurements by

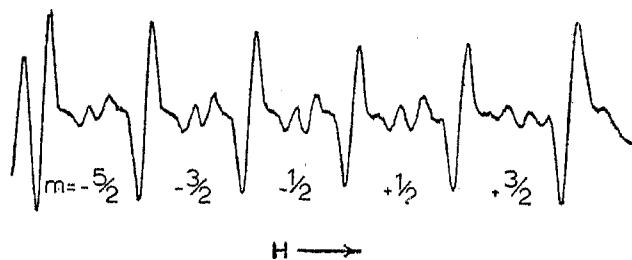


FIG. 1. Showing allowed $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $\Delta m = 0$ intense lines and forbidden $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $\Delta m = \pm 1$ doublets in the E.P.R. spectrum of Mn^{2+} in $NaCl$ single crystal for spectrum IV with $\theta = 45^\circ$.

Sheriff and Williams.¹⁷ Tables I and II show the experimental and theoretical values of the $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $\Delta m = \pm 1$ doublet separations at $\theta = 30^\circ$ and 45° . Good agreement is obtained only when the quadrupole interaction is included. It may be noted that the forbidden transitions ($\Delta m = \pm 1$) are observed for the first time for a Mn^{2+} ion in a crystalline field of orthorhombic symmetry and are due to mixing of hyperfine levels by the interactions

TABLE I

Theoretical and experimental $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $\Delta m = \pm 1$ doublet separation at $\theta = 45^\circ$

m	ΔH measured gauss	ΔH calculated gauss
-5/2	13.08 \pm 1.0	13.29
-3/2	14.75	14.68
-1/2	16.0	16.06
1/2	17.24	17.45
3/2	18.91	18.83

TABLE II

Theoretical and experimental $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $\Delta m = \pm 1$ doublet separations at $\theta = 30^\circ$

m	ΔH measured gauss	ΔH calculated gauss
-5/2	13.0 \pm 1	11.95
-3/2	14.58	14.01
-1/2	16.66	16.06
1/2	19.08	18.62
3/2	20.43	20.17

of the crystal field splitting terms D and E with the hyperfine interaction term A. The forbidden transitions observed by earlier workers¹⁻¹⁰ were due to interaction of D or a with A. There is an indication of $\Delta m = \pm 2$ transitions but they are too weak to be investigated in detail.

A number of models were proposed¹¹ to explain the origin of the spectrum IV. However, since they failed to explain some of the experimentally observed properties of this spectrum the authors have proposed¹⁴ a model where an O_2^{2-} occupies the nearest neighbour anion site. From the experimental evidence for nuclear electric quadrupole interaction in Mn^{2+} , it appears that the O_2^{2-} molar ion distorts the spherically symmetric (⁶S) electron cloud of Mn^{2+} and this distortion produces an electric field gradient at the Mn^{55} nucleus thus explaining a comparatively high value of Q'.

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