

In the case of the garnets, an exchange field of the order of 10^5 oe acts on the rare earth ion, due to the interaction between the iron and rare earth sublattices.^{4,5} This exchange field is sufficient to produce saturation magnetization of rare earth ions at room temperatures, so that one would still expect that paramagnetic relaxation might broaden the individual absorption lines. At lower temperatures, however, and possibly even at liquid air temperatures, one might expect to see some line structure, in view of the magnitude of the exchange field acting on the rare earth ion.

The exchange field should decouple the nuclear and electron spins. The over-all maximum width of the

nuclear ground state can then be written as $2\mu H_{av}$, where H_{av} is the effective field at the Dy nuclei averaged over the different Stark levels operative at room temperatures. If we ignore, again, the hyperfine splittings of the excited state, and take $\mu=0.35$ nm,⁷ then, from the experimental width of the absorption line with garnets at room-temperatures, we obtain $H_{av}\sim 2\times 10^6$ oe.

ACKNOWLEDGMENTS

We would like to thank Mr. Schieber and Mr. Gilat for preparing the garnets, and Professor W. Low for helpful discussions.

Paramagnetic Resonance Spectrum of Mn^{2+} in $ZnSiF_6\cdot 6H_2O$, $\Delta m = \pm 1$ Transition*

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(Received June 13, 1960)

In the spectrum of Mn^{2+} in $ZnSiF_6\cdot 6H_2O$ a number of weaker lines are observed at intermediate angles of the magnetic field H with respect to the crystal axis, in addition to the 30 allowed transitions $\Delta M = \pm 1$, $\Delta m = 0$. These lines have been measured and assigned to $\Delta M = \pm 1$, $\Delta m = \pm 1$ transitions. The relatively strong intensity is explained and the intensity of the lines is shown to be proportional to $(D/A)^2 \cos^2\theta \sin^2\theta$. These forbidden transitions can be utilized for dynamic polarization of manganese nuclei.

INTRODUCTION

THE paramagnetic resonance spectrum of Mn^{2+} in single crystals of zinc fluosilicate ($ZnSiF_6\cdot 6H_2O$) has been analyzed by Bleaney and Ingram.¹ The spectrum consists of 5 groups of 6 lines each corresponding to $\Delta M = \pm 1$ and $\Delta m = 0$. In addition Bleaney and Ingram observed a number of weaker lines when the external magnetic field was not directed along or perpendicular to the trigonal axis of the crystal. We have studied these absorption lines and are able to assign these to $\Delta M = \pm 1$, $\Delta m = \pm 1$ transitions. The relatively strong intensity of these so-called "forbidden" transitions is explained. These transitions can be utilized for dynamic polarization of manganese nuclei.

THEORY

The conventional spin Hamiltonian pertaining to an ion in an axial symmetry is given by^{1,2}

$$\begin{aligned} \mathcal{H} = & g\beta\mathbf{H}\cdot\mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + F(a) \\ & + AS_xI_x + B(S_xI_x + S_yI_y) \\ & - \gamma\beta_N\mathbf{H}\cdot\mathbf{I} + Q'[I_x^2 - \frac{1}{3}I(I+1)]. \quad (1) \end{aligned}$$

In the case of manganese $S=I=\frac{5}{2}$. The symbols in (1) have their usual meaning. Taking the direction of the magnetic field as the axis of quantization, the allowed transitions pertaining to the electronic part of the spectrum are given to second order by

$$\begin{aligned} M = \pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2} \quad H = H_0 \mp 2D(3\cos^2\theta - 1) - (32D^2/H_0)\cos^2\theta\sin^2\theta + (D^2/H_0)\sin^4\theta \mp 2pa, \\ M = \pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2} \quad H = H_0 \mp D(3\cos^2\theta - 1) + (4D^2/H_0)\cos^2\theta\sin^2\theta - (5/4)(D^2/H_0)\sin^4\theta \pm \frac{5}{2}pa, \\ M = +\frac{1}{2} \leftrightarrow -\frac{1}{2} \quad H = H_0 + (16D^2/H_0)\cos^2\theta\sin^2\theta - (2D^2/H_0)\sin^4\theta, \end{aligned} \quad (2)$$

where H is the magnetic field at which the transition is observed, $H_0 = h\nu/g\beta$, $p = 1 - 5\Phi$, $\Phi = l^2m^2 + m^2n^2 + n^2l^2$, (l, m, n) being the direction cosines of the magnetic field relative to the cubic axes.

In addition we need the matrix elements resulting from the interaction between the nucleus and the electron

* Supported in part by the U. S. Office of Scientific Research, Air Research and Development Command, through its European Office.

¹ B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

² W. Low, *Paramagnetic Resonance in Solids* (Academic Press, New York, 1960).

spins, and the direct interaction between the nucleus and the external magnetic field. These are given by²

$$\begin{aligned} \langle Mm | \mathcal{H}C | Mm \rangle &= KMm + (Q'/2)m^2(3 \cos^2\Psi - 1) - \gamma\beta_N H m \cos(\Psi - \theta), \\ \langle Mm | \mathcal{H}C | M\pm 1, m \rangle &= \pm i[(B^2 - A^2)/2K]m \cos\theta \sin\theta [S(S+1) - M(M\pm 1)]^{\frac{1}{2}}, \\ \langle Mm | \mathcal{H}C | M\pm 1, m\pm 1 \rangle &= (B/4)[1 - (\mp)(\mp)(A/K)][S(S+1) - M(M\pm 1)]^{\frac{1}{2}}[I(I+1) - m(m\pm 1)]^{\frac{1}{2}}, \\ \langle Mm | \mathcal{H}C | M, m\pm 1 \rangle &= \pm iQ'(m\pm \frac{1}{2}) \sin\Psi \cos\Psi [I(I+1) - m(m\pm 1)]^{\frac{1}{2}} \\ &\quad \pm (1/2i)\gamma\beta_N H \sin(\theta - \Psi)[I(I+1) - m(m\pm 1)]^{\frac{1}{2}}, \\ \langle Mm | \mathcal{H}C | M, m\pm 2 \rangle &= -Q'(\sin^2\Psi/4)[I(I+1) - m(m\pm 1)]^{\frac{1}{2}}[I(I+1) - (m\pm 1)(m\pm 2)]^{\frac{1}{2}}, \end{aligned} \quad (3)$$

where

$$K^2 = A^2 \cos^2\theta + B^2 \sin^2\theta, \quad \cos\Psi = (A/K) \cos\theta, \quad \sin\Psi = (B/K) \sin\theta.$$

In the case of manganese the contribution of the quadrupole interaction Q' and the direct effect of the magnetic field are negligible and may be omitted in the calculation of the energy levels. The significant matrix elements are, therefore, the first and, in our case of particular importance, the third, which involves transitions of $\Delta M = \pm 1$, $\Delta m = \pm 1$. If we consider only transitions involving $\Delta m = 0$ we have to add to (2) to second order the term

$$-Km - (B^2/4H_0)[(A^2 + K^2)/K^2](35/4 - m^2) - (B^2/2H_0)(A/K)[m(2M - 1)]. \quad (4)$$

For transitions involving a nuclear spin flip ($\Delta m = \pm 1$) we have to add to Eq. (2) the following terms (we assume $A = B = K$ in the second-order correction):

$$Mm \leftrightarrow M-1, m+1 \quad K(M-m-1) + (B^2/2H_0)[-35/2 - 2(m+1)(M-1) + (M-m)(M-m-1)] - \gamma\beta_N H \cos(\Psi - \theta), \quad (5)$$

$$Mm \leftrightarrow M-1, m-1 \quad -K(M+m-1) + (B^2/2H_0)[(m-M)(M+m-1)] + \gamma\beta_N H \cos(\Psi - \theta).$$

EXPERIMENTAL RESULTS

When the spectrum is observed at 3-cm wavelength at intermediate angles, a number of weaker lines can be detected which are scattered between the 4th and 25th lines of the 30 "allowed" transitions. We have measured these additional lines at four angles: 12° , 18° , 34° , and 78° from the crystal axis. Tables I and II give the observed transitions of $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ and $M = -\frac{1}{2} \leftrightarrow -\frac{3}{2}$, $\Delta m = \pm 1$. The levels as well as transitions have been calculated using the diagonal and off-diagonal matrix elements in Eq. (3) and Eq. (5), and using the values of the parameters D , a , A , and B as measured by Bleaney and Ingram. Since the magnetic field at which these "forbidden" transitions occur are very sensitive to the

TABLE I. Observed and calculated transitions of $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$, $\Delta m = \pm 1$ for various angles θ . The separation ΔH of the forbidden transitions is measured from a nearby allowed transition. The starred number refers to a stronger allowed transition, belonging to the next group of electronic transitions, whose position nearly coincides with a forbidden transition.

Transition $\frac{1}{2}m \leftrightarrow -\frac{1}{2}m\pm 1$	Measured separations ΔH in gauss				Calculated ΔH in gauss relative to $\frac{1}{2}m' \leftrightarrow -\frac{1}{2}m'$
	$\theta = 12^\circ$	$\theta = 18^\circ$	$\theta = 34^\circ$	$\theta = 78^\circ$	
$\frac{1}{2} \leftrightarrow -\frac{1}{2}$	-40	-39	-41	-36	$m' = \frac{5}{2}$ -42
$\frac{3}{2} \leftrightarrow -\frac{1}{2}$	-63*	-63	-63	-66	$m' = \frac{3}{2}$ -65
$\frac{5}{2} \leftrightarrow -\frac{1}{2}$	-36	-38	-35	-36	$m' = \frac{1}{2}$ -36
$\frac{7}{2} \leftrightarrow -\frac{1}{2}$	-62*	-63	-60	-64	$m' = \frac{3}{2}$ -61
$\frac{9}{2} \leftrightarrow -\frac{1}{2}$	+62	+68	+64*	+61	$m' = -\frac{1}{2}$ +62
$\frac{11}{2} \leftrightarrow -\frac{1}{2}$	+36	+41	+39	+35	$m' = -\frac{3}{2}$ +38
$\frac{13}{2} \leftrightarrow -\frac{1}{2}$	-35	-29	-37	-33	$m' = -\frac{5}{2}$ -36
$\frac{15}{2} \leftrightarrow -\frac{1}{2}$	-59	-58	-67*	-67	$m' = -\frac{7}{2}$ -61
$\frac{17}{2} \leftrightarrow -\frac{1}{2}$	+56*	+59	+50*	+56	$m' = -\frac{9}{2}$ +53
$\frac{19}{2} \leftrightarrow -\frac{1}{2}$	+34	+37	+37*	+35	$m' = -\frac{11}{2}$ +35

TABLE II. Observed and calculated transitions of $M = -\frac{1}{2} \leftrightarrow -\frac{3}{2}$, $\Delta m = \pm 1$ for various angles θ . The separation ΔH of the forbidden transitions is measured from a nearby allowed transitions. The starred number refers to a stronger allowed transition, belonging to the next group of electronic transitions, whose position nearly coincides with a forbidden transition.

Transition $-\frac{1}{2}m \leftrightarrow -\frac{3}{2}m$	Measured separations ΔH in gauss				Calculated ΔH in gauss relative to $-\frac{1}{2}m' \leftrightarrow -\frac{3}{2}m'$
	$\theta = 12^\circ$	$\theta = 18^\circ$	$\theta = 34^\circ$	$\theta = 78^\circ$	
$-\frac{1}{2} \leftrightarrow -\frac{3}{2}$	+39*	+36	+38		$m' = -\frac{3}{2}$ +35
$-\frac{3}{2} \leftrightarrow -\frac{3}{2}$	-34	-34	-36	-36*	$m' = -\frac{5}{2}$ -36
$-\frac{5}{2} \leftrightarrow -\frac{3}{2}$	-32	-32	-40	-40*	$m' = -\frac{7}{2}$ -37
$-\frac{7}{2} \leftrightarrow -\frac{3}{2}$	+36	+35	+36		$m' = -\frac{9}{2}$ +36
$-\frac{9}{2} \leftrightarrow -\frac{3}{2}$	-34	-40*	-37*	-36*	$m' = -\frac{11}{2}$ -38
$-\frac{11}{2} \leftrightarrow -\frac{3}{2}$	+39*	+40	+34*		$m' = \frac{3}{2}$ +39
$-\frac{13}{2} \leftrightarrow -\frac{3}{2}$	+62	+63	+60		$m' = -\frac{13}{2}$ +64

accurate values of these parameters, and since these parameters have not been measured to a sufficient accuracy, a slightly different procedure was adopted. We measured the relative position of these "forbidden" transitions, $\Delta m = \pm 1$, from the nearest or next-nearest allowed $\Delta m = 0$ hyperfine transitions. In this case the electronic part of Eq. (2) does not affect the relative separations to first order. We assumed in these calculations for simplification's sake that $A = B = K$ in the second-order corrections and that the second-order correction to the hyperfine structure ($-B^2/2H_0)[I(I+1) - m^2 + m(2M-1)]$ is not a function of the angle. This last assumption involves an inaccuracy in the calculated spectrum of less than 2 gauss in the extreme cases. We also neglected the diagonal elements of $\gamma\beta_N H$. From the first and second order corrections in γ the magnitude

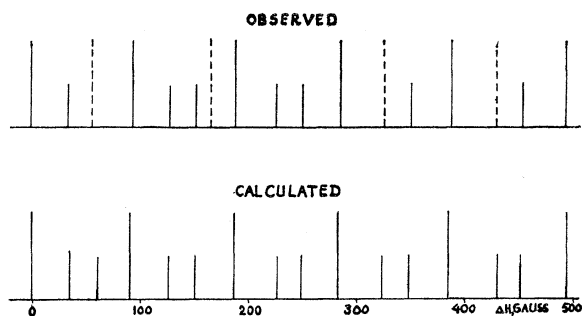


FIG. 1. Observed and calculated spectrum of $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ and $\Delta m = 0$, $\Delta m = \pm 1$ transitions using the parameters of the spin Hamiltonian given in the text. The intensity is arbitrary. The forbidden transitions are drawn with one half of the intensity of the allowed transitions. The dashed line in the observed spectrum refers to $\Delta M = \pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ which falls within the $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ spectrum.

and relative sign of γ can be obtained in favorable cases. As seen from Tables I and II the calculated and observed spectra agree well. We feel, therefore, certain of the assignment of these forbidden $\Delta M = \pm 1$, $\Delta m = \pm 1$ transitions. Figure 1 shows the central part $M = \frac{1}{2} \rightarrow -\frac{1}{2}$ of the observed and calculated spectrum for the angle of $\theta = 12^\circ$.

TRANSITION PROBABILITIES

The experiment was carried out with the rf field H_1 perpendicular to the plane defined by the magnetic field H and the crystal axis. Since the nuclear magnetic moment is very much smaller than the electronic spin moment, the transitions probabilities can be calculated from the matrix elements $\langle Mm | S_x | M-1, m \pm 1 \rangle$. If we use conventional perturbation theory we would obtain transitions probabilities of the order of $(AD \cos \theta \sin \theta)^2 / (g\beta H)^4$ or $(\gamma\beta_N / g\beta H)^2$. This would yield very weak forbidden lines. The significant experimental fact is however that the intensity of these "forbidden" $\Delta m = \pm 1$ lines is of the same order (up to 0.5) of the "allowed" $\Delta m = 0$ lines. Further the intensity is a strong function of θ going to zero intensity at $\theta = 0^\circ$ and $\theta = 90^\circ$. Indeed it is very convenient to align the crystal by means of these forbidden transitions. These observations would lead us to suspect that the intensity should be proportional to $(D/A)^2 \sin^2 \theta \cos^2 \theta$. Physically this means that there is a competition between the axial electric field and the magnetic field set up by the electrons at the nucleus in lining up the nuclei. In the particular case of the fluosilicate D and A are of the same order of magnitude and the usual selection rules of $\Delta M = \pm 1$, $\Delta m = 0$, break down.

This can of course be inferred from the inspection of the 36×36 matrix corresponding to the spin Hamiltonian (1). The conventional perturbation theory breaks down since the off-diagonal elements in D and A are of the same order of magnitude. They are also of the same order of magnitude as the difference of the respective diagonal elements differing in m . Their contribution to the unperturbed wave function comes via

an intermediary which heavily admixes states of the same M but differs in m . This hardly affects the position of the energy levels in the second-order perturbation calculations.

A closed expression for the transition probability is difficult to give. An elementary example however will illustrate this. Assume a matrix of the form

$$\begin{pmatrix} U & \alpha & \beta \\ \alpha & W & 0 \\ \beta & 0 & W - \epsilon \end{pmatrix},$$

where U and W are very large corresponding to $g\beta H$, α , β , and ϵ are small corresponding to A , D , and K , respectively. It can be shown that the wave function corresponding to W is admixed with that of $W - \epsilon$ with amplitude $\{2\beta[\alpha/(U-W)]\}/\{\epsilon + 2\alpha[\alpha/(U-W)]\}$. The admixture coming from U is small but that with $W - \epsilon$ is very considerable. Assuming $\epsilon = 0$ the admixture is (β/α) or $(D/A) \sin \theta \cos \theta$. Obviously the admixture is a strong function of ϵ . The experimental intensities indicate that the $\Delta m = \pm 1$ transitions corresponding to $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ are by far the strongest, followed by the $M = \frac{3}{2} \leftrightarrow \frac{1}{2}$ transitions and about ten times stronger than the $M = \frac{5}{2} \leftrightarrow \frac{3}{2}$ transitions. This is explained by the fact that ϵ is largest for the $\frac{5}{2} \leftrightarrow \frac{3}{2}$ transitions and smallest for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions. Further in the case of the $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$ and $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions the levels are being perturbed from both the higher and lower M levels giving an effective small ϵ . The $\pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$ interacts only with the $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$ level and is therefore perturbed in one direction. The detailed behavior of the transition probability as a function of M and m can of course be calculated using a computer.

Jeffries³ has recently discussed in detail the mechanism of dynamic orientation of nuclei by forbidden transitions in paramagnetic resonance. He calculates in a few cases the transition probability for a general anisotropic spin Hamiltonian. His calculations indicate transition probabilities which are proportional to $(B/g\beta H)^2$ and are in general rather small. The forbidden transitions observed here can be utilized with much greater efficiency in simultaneously flipping the electron and the nucleus without the use of large rf power and over a range of angles.

Zinc fluosilicate could, therefore, be used in dynamically polarized Mn^{52} and Mn^{54} . Similar cases might occur in other paramagnetic systems with initial splittings comparable with the hyperfine structure. Examples of such cases might be selected crystals of axial symmetry containing V^{2+} and possible rare earth ions in cubic or near cubic symmetry.

ACKNOWLEDGMENT

The authors are grateful to Professor G. Racah for valuable discussions of the calculations of the transition probabilities.

³ C. D. Jeffries, Phys. Rev. **117**, 1056 (1960).