

Forbidden Transitions in the Paramagnetic-Resonance Spectrum of Mn^{2+} in Cubic MgO^+

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The first order "forbidden" transitions, $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$, $\Delta m = \pm 1$, in the paramagnetic-resonance spectrum of Mn^{2+} in cubic MgO have been studied both experimentally and theoretically. A powder sample was used which permitted the resolution of the "forbidden" transitions which would ordinarily have been obscured by the full fine-structure spectrum. The analysis was based on a spin Hamiltonian that included the cubic crystal field interaction with the ${}^6S_{5/2}$ state of Mn^{2+} , magnetic hyperfine interaction with the Mn^{2+} nucleus, and electronic and nuclear Zeeman interactions. Satisfactory agreement between the calculated and observed spectrum was achieved by carrying the hyperfine-perturbation calculation to third order. It was unnecessary to include a trigonal crystal field interaction or a quadrupole interaction in order to satisfactorily explain the spacings of the "forbidden" transitions. On the other hand, the appropriate mixing of states that is required for observation of the forbidden transitions requires the presence of trigonal or lower symmetry crystal field terms. Analysis of the relative intensity of the forbidden to the allowed transitions permitted an estimate to be made of the trigonal crystal field constant D on the basis of an assumed trigonal distortion to the cubic crystal field. By inserting this value of D into the angular dependent terms in the Hamiltonian, an estimate of the expected linewidths was obtained which agreed well with experiment. The contributions of the estimated trigonal distortion to shifts in the spectrum were too small to be observed for those transitions that are resolved with a powder sample.

INTRODUCTION

THE paramagnetic-resonance spectrum of Mn^{2+} ions in the cubic crystalline electric field of MgO and CaF_2 has been studied by Low.¹ In his work he investigated the $\Delta M = \pm 1$, $\Delta m = 0$ transitions between the nondegenerate levels arising from the ${}^6S_{5/2}$ ground-state fine-structure split by a large dc magnetic field and the characteristically large hyperfine interaction of the Mn^{2+} ion. More recently, Friedman and Low,² Folen,³ and Schneider and Sircar⁴ have reported $\Delta M = \pm 1$, $\Delta m = \pm 1$ transitions between the ground-state energy levels of Mn^{2+} in various single crystals. In his work¹ with Mn^{2+} in MgO , Low did not report the "forbidden" $\Delta m = \pm 1$ transitions. In this paper we report the observation of the $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$, $\Delta m = \pm 1$ transitions in the spectrum of Mn^{2+} in cubic- MgO powder. The positions of these lines are satisfactorily explained by including third-order corrections to the expression for the hyperfine-structure splitting. We also comment upon the novel desirability of using a powder sample in this experiment to allow the resolution of the $\Delta m = \pm 1$ transitions.

EXPERIMENTAL METHOD

The experimental apparatus consisted of a Strand Labs Model-601, X-band spectrometer, a Pacific Electric Motor Company 9-in. electromagnet, and a Varian strip-chart recorder. The magnetic field was modulated at 6000 cps with pancake coils fixed to the magnet pole faces and driven by an audio-power amplifier. The

microwave bridge was modified for balanced mixer operation as follows. The microwave power reflected from the cavity containing the sample that was to be used for signal processing was fed into one arm of a matched magic tee. The opposite arm of the tee was fed directly with microwave power of variable amplitude and phase, which was taken from a tee at the input to the bridge and consequently was not modulated as a result of absorption by the sample. The other two arms of the magic tee were terminated in matchable crystal mounts. The output of the balanced mixer was fed to the balanced-input 6000-cps amplifier of the spectrometer.

We obtained samples of MgO powder containing Mn^{2+} as an impurity from three sources (material prepared by the Cornell University Chemistry Dept., Mallinckrodt reagent-grade MgO powder, and some samples prepared by the Towanda, Penna. Division of Sylvania Electric Products Co. through the courtesy of Dr. R. Mooney). The Cornell sample contained the fewest unwanted impurities (principally Cr^{3+} , which gave a single sharp line close to $g = 2.0$), and only the results obtained with this sample will be discussed here. In an attempt to resolve the $\Delta m = \pm 2$ transitions, we tried to obtain MgO powder specifically enriched with Mn^{2+} so as to increase the intensity of the resonances. This approach failed because we were not able to control the introduction of large concentrations of unwanted impurities. The Cornell sample was analyzed by emission spectroscopy and the manganese concentration was found to be approximately 45 ppm.

The dc magnetic field was measured with a transistORIZED proton resonance spectrometer using a marginal oscillator circuit. The spectrometer frequency was measured with a B.C.-221 frequency meter. The proton probe was located at the side of the sample cavity and

* This work was supported in part by the Advanced Research Projects Agency.

¹ W. Low, Phys. Rev. **105**, 793 (1957).

² E. Friedman and W. Low, Phys. Rev. **120**, 408 (1960).

³ V. J. Folen, Phys. Rev. **125**, 1581 (1962).

⁴ J. Schneider and S. R. Sircar, Z. Naturforsch. **17a**, 651 (1962).

therefore did not measure the magnetic field at the sample. Since the theoretical and experimental analysis used only the differences between magnetic fields at resonance, the axial-field gradient of the magnet cancelled out to a good approximation. The klystron frequency was measured before and after each run by zero beating it with the output from a Hewlett Packard 540B transfer oscillator whose primary frequency was measured with a Hewlett Packard 525B frequency counter. The maximum excursion of the klystron frequency from the mean of 9449.553 Mc/sec was 0.3 Mc/sec.

Data were recorded on five runs through the entire $\Delta M = -\frac{1}{2} \rightarrow +\frac{1}{2}$, $\Delta m = 0, \pm 1$ spectrum, and several additional runs over portions of the spectrum, and the results were averaged. The magnetic fields of the $\Delta m = 0$ resonances were measured accurately with the B.C.-221 frequency meter. The magnetic fields of the $\Delta m = \pm 1$ resonances were obtained by linear interpolation from the strip-chart recordings using the $\Delta m = 0$ resonances as end points for the interpolations. The magnetic-field sweep between $\Delta m = 0$ resonances was checked separately and was found to be linear to within the experimental error (about 0.3 G) of interpolation on the chart recordings.

THEORY

A. Fine Structure

The theoretical expressions for the fine-structure separations of the six energy levels arising from the ${}^6S_{5/2}$ state of Mn^{2+} in a cubic crystalline electric field and an applied magnetic field have been given by Low.¹ In a magnetic field the $M = \pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ and the $M = \pm\frac{5}{2} \rightarrow \pm\frac{3}{2}$ energy separations contain a term proportional to ρa , where $3a$ is the zero field splitting parameter¹ (+59 G for Mn^{2+} in MgO); and $\rho = 1 - 5\phi$, where $\phi = l^2 m^2 + m^2 n^2 + n^2 l^2$ with l, m, n the direction cosines of the magnetic field referred to the cubic axes of the crystal. The $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$ resonance has no appreciable first-order dependence on a or ϕ (there is a linear term in ϕ , but its coefficient is $a^2/g\beta H_0$, which is very small at the fields used). Consequently, in a powder sample where a random orientation of the cubic axes of the crystal with the magnetic field is to be expected, all fine-structure transitions except $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$ will be "washed out" into a very broad background upon which these transitions will be superposed. As a result of this random distribution of crystallite orientations, the complete spectrum of 30 $\Delta M = \pm 1$, $\Delta m = 0$ resonances is reduced to the six $\Delta M = -\frac{1}{2} \rightarrow +\frac{1}{2}$, $\Delta m = 0$ resonances observed. The resulting enhanced resolution allowed the observation of the ten $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$, $\Delta m = \pm 1$ resonances which we discuss in detail.

Such an enhancement of resolution is necessary in order to observe the forbidden transitions in the $\text{Mn}^{2+}:\text{MgO}$, because the fine-structure splitting is smaller than the hyperfine-structure splitting; there-

fore, the angular-dependent resonances would overlap the forbidden ones making the latter difficult to observe. In our analysis of the resonance fields for the various transitions, we found no reason to add a trigonal, crystalline, electric-field term to the cubic term. Such a term might arise in a cubic crystal from a local lattice distortion in the vicinity of the impurity ion, or, in a powder from lattice distortion of the crystallites due to strain. The cubic or lower symmetry crystal field contribution to the energy of the $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$ transitions in a powder serves merely to broaden the resonances. These were found to be about two gauss wide (peak to peak of the derivative of the line shape). The broad background arising from the unresolved strongly angular-dependent transitions was several hundred gauss wide.

B. Hyperfine Structure

Expressions for the hyperfine splitting of the $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$ fine-structure energy levels correct to third order in the constant A of the hyperfine structure have been given by Schneider and Sircar.⁴ Because we took the trigonal crystal field parameter D to be zero in the analysis of the resonance positions, we did not include third-order terms proportional to $A^2 D/g^2 \beta^2 H^2$ in our analysis. Nor did we include a quadrupole interaction in our theoretical expressions. First, we did not require such an interaction to secure agreement between theory and experiment. Second, in prior experiments with Mn^{2+} in solids,^{3,4} the quadrupole interaction has been two to three orders of magnitude smaller than the trigonal electric-field interaction, and both have been present simultaneously. Since we took D to be zero, we found it reasonable to ignore the quadrupole interaction as well.

The theoretical expressions we used for the magnetic fields at resonance for a fixed microwave frequency were

$$M = -\frac{1}{2}, m \rightarrow M = \frac{1}{2}, m:$$

$$H_a = H_0 - \left[A' - \frac{15 A'^3}{4 H_0^2} \right] m + \left[\frac{A'^2}{2 H_0} \right] \left[m^2 - \frac{35}{4} \right], \quad (1a)$$

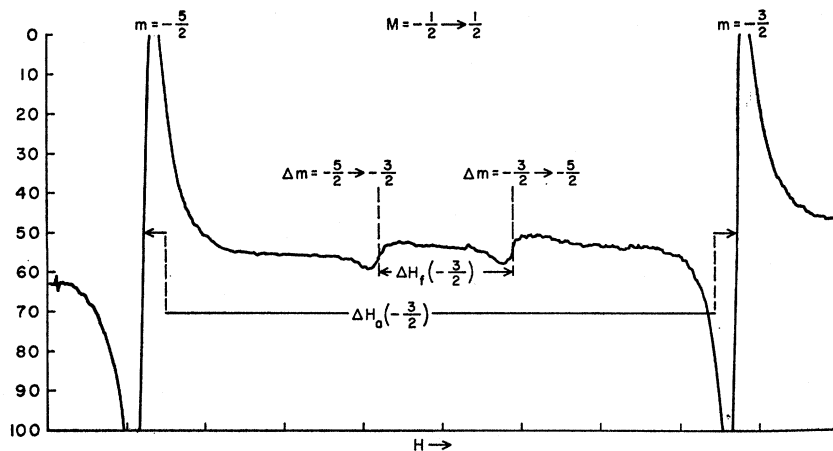
$$M = -\frac{1}{2}, m-1 \rightarrow M = \frac{1}{2}, m:$$

$$H_f^- = H_0 - \left[\frac{A'}{2} \right] [2m-1] + \left[\frac{A'^2}{2 H_0} \right] \left[m^2 - m + \frac{1}{4} \right] - \left[\frac{9 A'^3}{2 H_0^2} \right] [2m-1] + g_N H_0, \quad (1b)$$

$$M = -\frac{1}{2}, m \rightarrow M = \frac{1}{2}, m-1:$$

$$H_f^+ = H_0 - \left[\frac{A'}{2} \right] [2m-1] + \left[\frac{A'^2}{2 H_0} \right] \left[m^2 - m - \frac{67}{4} \right] + \left[\frac{8 A'^3}{H_0^2} \right] [2m-1] - g_N H_0, \quad (1c)$$

FIG. 1. A portion of the full spectrum of Mn^{2+} in cubic MgO is shown as a function of magnetic field. Two allowed transitions $\Delta M = -\frac{1}{2} \rightarrow \frac{1}{2}$, $\Delta m = 0$, and two "forbidden" transitions $\Delta M = -\frac{1}{2} \rightarrow \frac{3}{2}$, $\Delta m = \pm 1$, are shown and identified. The resonance-field spacings ΔH_a and ΔH_f defined in the text are also indicated.



where, $H_0 \equiv h\nu_0/g\beta$ and $A' = A/g\beta$, with ν_0 the constant microwave frequency. We took $g = 2.0014$, the value given by Low,¹ and we redetermined A from the analysis of our data. All calculations were made with $\nu_0 = 9449.553$ Mc/sec, $\beta = 0.9273 \times 10^{-20}$ erg/G, and $g_N = 3.775 \times 10^{-4}$.

In our analysis it was convenient to use the field differences between adjacent resonances, which were readily obtained from Eqs. (1a,b,c). With the definitions, $\Delta H_a(m) \equiv H_a(m) - H_a(m-1)$, and $\Delta H_f(m) \equiv H_f^- - H_f^+$, we obtained

$$\Delta H_a(m) = -\left[A' - \frac{15A'^3}{4H_0^2}\right] + \left[\frac{A'^2}{2H_0}\right][2m-1], \quad (2a)$$

$$\Delta H_f(m) = -\left[\frac{25A'^3}{2H_0^2}\right][2m-1] + \left[\frac{17A'^2}{2H_0}\right] + 2g_N H_0. \quad (2b)$$

THE SPECTRUM

Figure 1 shows a portion of the complete spectrum and includes an allowed transition on either side of a pair of forbidden transitions. The appropriate M , m values for each transition are indicated, as are the field differences $\Delta H_a(m)$ and $\Delta H_f(m)$. There is some indication in portions of our data that $\Delta M = \pm 1$, $\Delta m = \pm 2$ transitions are present, but their intensity is too weak to allow an analysis of their position to be made. In an attempt to study these transitions, a low-temperature run was made at 77°K in order to increase the sensitivity, but this was unsuccessful.

TABLE I. Allowed spectrum: $\Delta H_a(m) = 86.81 + 1.112(2m-1)$ G.

m	Calc.	Obs.	Diff.
$\frac{5}{2}$	91.25	91.36	-0.11
$\frac{3}{2}$	89.03	88.90	+0.13
$\frac{1}{2}$	86.81	87.00	-0.19
$-\frac{1}{2}$	84.59	84.65	-0.06
$-\frac{3}{2}$	82.36	82.74	-0.38

QUANTITATIVE RESULTS

We first analyzed the allowed and forbidden transitions separately and determined the hyperfine constant A' for each. Our results were $A_a' = -86.72$ G and $A_f' = -86.48$ G. The agreement between the calculated and observed resonance-field differences $\Delta H_a(m)$ and $\Delta H_f(m)$ were within the experimental error of ± 0.3 G. For a final, over-all fit to the spectrum, we chose

$$A' \equiv \frac{1}{2}(A_a' + A_f') = -86.6 \text{ G} = -80.92 \times 10^{-4} \text{ cm}^{-1}.$$

With this value of A' , the calculated differences in the resonance field are

$$\Delta H_a(m) = 86.81 + 1.112(2m-1),$$

$$\Delta H_f(m) = 21.44 + 0.713(2m-1),$$

and the comparison between theory and experiment is shown in Tables I and II. The standard deviation for both the allowed and forbidden spectrum is 0.18 G, which is within our maximum experimental error of ± 0.3 G, and therefore shows close agreement between theory and experiment. Our redetermination of A is also consistent with Low's¹ value.

DISCUSSION

We have observed and successfully analyzed the positions of the $\Delta M = \pm 1$, $\Delta m = \pm 1$ forbidden transitions in the spectrum of $Mn^{2+}:\text{MgO}$ powder without the introduction of crystalline electric fields of lower symmetry than cubic into the analysis. On the other

TABLE II. Forbidden spectrum: $\Delta H_f(m) = 2.144 + 0.713(2m-1)$ G.

m	Calc.	Obs.	Diff.
$\frac{3}{2}$	24.29	24.47	-0.18
$\frac{1}{2}$	22.87	23.09	-0.22
$-\frac{1}{2}$	21.44	21.27	+0.17
$-\frac{3}{2}$	20.01	19.72	+0.29
$-\frac{5}{2}$	18.59	18.41	+0.18

hand, the work of Bleaney and Rubins^{5,6} shows that the mixing of states necessary for the observation of the forbidden transitions depends on the existence of higher order cross terms between the hyperfine interaction and a lower symmetry crystal field term such as a trigonal field. It would appear, therefore, that some such lower symmetry crystal field term must be present in order for products of operators of the form $(S_z S_{\pm})(S_{\mp} I_{\pm})$ to exist and thereby permit observation of the forbidden transitions. We therefore assume the existence of a trigonal crystal field term of the form $D[S_z^2 - \frac{1}{3}S(S+1)]$ and investigate its effect upon the positions of the resonances, their intensities, and the observed line-widths.

A. Intensities of the Transitions

Bleaney and Rubins⁶ give the following expression for the relative intensity of a first-order forbidden transition to an allowed transition,

$$\left(\frac{3D}{4g\beta H}\right)^2 \sin^2 2\theta \left[1 + \frac{S(S+1)}{3M(M-1)}\right]^2 \times [I(I+1) - m^2 + m], \quad (3)$$

where the allowed transition is of the type $M, m \rightarrow M-1, m$ and the forbidden transition is of the type $M, m \rightarrow M-1, m-1$ or $M, m-1 \rightarrow M-1, m$. For a powder sample the angular term must be averaged with a weighting factor of $\sin\theta$ thereby yielding 8/15. The measured relative intensity was close to 1/20. By setting the above theoretical expression equal to 1/20 and using the appropriate values for the other constants we infer the value $D \cong 50$ G for the trigonal field parameter.

B. Effects on the Spectrum of D

Strandberg⁷ has given the expression for the trigonal interaction expressed in a coordinate system whose quantization axis makes an angle θ with the C axis of the

$$\begin{aligned} & \frac{D}{2} (3 \cos^2 \theta - 1) (M^2 - \frac{1}{3} S(S+1)) \\ & \times \left\{ \frac{D^2}{16H_0^2} (\sin 2\theta)^2 [(4M^2 - 4M + 1)(S+M)(S-M+1) + (4M^2 + 4M + 1)(S-M)(S+M+1)] \right. \\ & \left. + \frac{D^2}{64H_0^2} (\sin^4 \theta) [(S-M+2)(S+M-1)(S-M+1)(S+M) + (S+M+2)(S-M-1)(S+M+1)(S-M)] \right\}. \quad (6) \end{aligned}$$

It is evident that this expression is symmetrical in M for $M = \pm \frac{1}{2}$ and therefore the difference of this term for $M = +\frac{1}{2}$ and $M = -\frac{1}{2}$ vanishes.

For the mixed terms in the trigonal and hyperfine interactions we find the following expressions for the third-order corrections to the magnetic fields at resonance.

$$H(\frac{1}{2}, m) - H(-\frac{1}{2}, m) = -\frac{16DA^2}{3H_0^2} (3 \cos^2 \theta - 1)m - \frac{2AD^2}{H_0^2} (\sin 2\theta)^2 m - \frac{7AD^2}{4H_0^2} (\sin^4 \theta)m, \quad (7a)$$

⁵ B. Bleaney, *Phil. Mag.* **42**, 441 (1951).

⁶ B. Bleaney and R. S. Rubins, *Proc. Phys. Soc. (London)* **77**, 103 (1961).

⁷ M. W. P. Strandberg, *Phys. Chem. Solids* **16**, 39 (1960).

crystal. He finds this term to be

$$\begin{aligned} & (D/2)(3 \cos^2 \theta - 1)(S_z^2 - \frac{1}{3}S(S+1)) \\ & - (D/4)(\sin 2\theta)[S_z(S_+ + S_-) + (S_+ + S_-)S_z] \\ & + (D/4)\sin^2 \theta[S_+^2 + S_-^2]. \quad (4) \end{aligned}$$

The remainder of our analysis will consider the effects of this expression and of the hyperfine interaction upon the spectrum.

The value $D = 50$ G when inserted into the diagonal trigonal term would make gross changes in the observed spectrum of a single crystal. Such effects were not observed by Low¹ and we conclude that a nonzero D must be characteristic only of the powder and that lattice strain probably accounts for the noncubic component of the crystalline-field interaction. The diagonal term does not contribute in a powder for two reasons. First, only the $M = \pm \frac{1}{2}$ levels are involved and they are equally shifted by the diagonal term. Second, the angular function is zero when averaged.

The trigonal terms also contribute shifts in the positions of the resonances in the second and third orders of perturbation theory, and in mixture with the hyperfine interaction in third order.

Friedman and Low² gave the following expression for the contribution of the off-diagonal trigonal terms in second-order perturbation theory to the magnetic fields at resonance.

$$H(\frac{1}{2}) - H(-\frac{1}{2}) = (16D^2/H_0)\cos^2 \theta \sin^2 \theta - (2D^2/H_0)\sin^4 \theta. \quad (5)$$

These are constant terms, independent of m , and will cancel when field differences between hyperfine lines are measured as in our experiment. The magnitude of this shift when an average over crystallite orientation is made is 0.8 G.

In the third order of perturbation theory we obtain pure trigonal terms, mixed terms in the trigonal and hyperfine interactions, and pure hyperfine terms that we considered earlier. The pure trigonal energy in third order corresponding to a given M is:

$$H(\frac{1}{2}, m) - H(-\frac{1}{2}, m-1) = -\frac{12DA^2}{H_0^2}(3 \cos^2\theta - 1)(2m-1) - \frac{AD^2}{H_0^2}(\sin 2\theta)^2(2m-1) - \frac{7AD^2}{8H_0^2}(\sin^4\theta)(2m-1), \quad (7b)$$

$$H(\frac{1}{2}, m-1) - H(-\frac{1}{2}, m) = +\frac{20DA^2}{3H_0^2}(3 \cos^2\theta - 1)(2m-1) - \frac{AD^2}{H_0^2}(\sin 2\theta)^2(2m-1) - \frac{7AD^2}{8H_0^2}(\sin^4\theta)(2m-1). \quad (7c)$$

The first term in each of these expressions agrees with Folen³ but he did not evaluate the remaining terms. We list the complete expressions for the third-order mixed terms in the Appendix. If we average the angular functions weighted by $\sin\theta$ we obtain

$$H(\frac{1}{2}, m) - H(-\frac{1}{2}, m) = -2(AD^2/H_0^2)m, \quad (8a)$$

$$H(\frac{1}{2}, m) - H(-\frac{1}{2}, m-1) = -(AD^2/H_0^2)(2m-1), \quad (8b)$$

$$H(\frac{1}{2}, m-1) - H(-\frac{1}{2}, m) = -(AD^2/H_0^2)(2m-1). \quad (8c)$$

Inserting the values $D=50$ G, $A=87$ G, and $H_0=3300$ G, we find that the maximum shift for an allowed transition is 0.1 G and the maximum shift for a forbidden transition is 0.05 G. Such shifts were not resolved in our experiments as they were more than an order of magnitude smaller than the observed linewidth.

We conclude from this analysis that a strain-induced trigonal crystalline field parameter D of the order of 50 G would explain the observed intensities of the forbidden transitions but would not result in resolvable shifts in the spectrum of the transitions.

C. Contribution of D to the Linewidth

The dominant effect on the linewidth of a nonzero trigonal interaction will arise from the second-order perturbation terms in D that were considered in Sec. B. The two second-order terms will contribute a spreading of the resonance fields over a range of about two gauss. A detailed analysis of the linewidth in a powder sample is very difficult⁸ and was not attempted. However, the broadening due to second-order and higher terms in D were consistent with the observed linewidths for the inferred value of $D \cong 50$ G. It should be noted that our linewidths were larger than those observed by Low.¹

$$\begin{aligned} E^{(3)}(M, m) = & \frac{A^2D}{8(g\beta H_0)^2}(3 \cos^2\theta - 1) \\ & \times \{ (M^2 - \frac{1}{3}S(S+1))[(S+M+1)(S-M)(I-m+1)(I+m) + (S-M+1)(S+M)(I+m+1)(I-m)] \\ & + (S(S+1) - M(M+1))(I(I+1) - m(m-1))((M+1)^2 - \frac{1}{3}S(S+1)) \\ & + (S(S+1) - M(M-1))(I(I+1) - m(m+1))((M-1)^2 - \frac{1}{3}S(S+1)) \} \\ & + \frac{AD^2}{16(g\beta H_0)^2}(\sin 2\theta)^2 Mm [(4M^2 - 4M + 1)(S+M)(S-M+1) + (4M^2 + 4M + 1)(S-M)(S+M+1)] \\ & + \frac{AD^2}{64(g\beta H_0)^2}(\sin^4\theta) Mm [(S-M+2)(S+M-1)(S-M+1)(S+M) + (S+M+2)(S-M-1)(S+M+1)(S-M)]. \end{aligned}$$

⁸ J. A. Ibers and J. D. Swalen, Phys. Rev. **127**, 1914 (1962).

CONCLUSIONS

We have observed and successfully analyzed the $\Delta M = \pm 1$, $\Delta m = \pm 1$ forbidden transitions in $Mn^{2+}:\text{MgO}$. As suggested by Bleaney,^{5,6} the observation of these forbidden transitions provides a sensitive test for the presence of a lower than cubic distortion of the crystalline electric field in a predominantly cubic crystal. We must conclude that such a distortion exists in the powder we examined. The assumption of a trigonal distortion of appropriate magnitude to yield the observed intensities of the forbidden transitions did not result in measurable shifts in the spectrum predicted from a pure cubic crystalline field but did give rise to line broadening in agreement with the observed linewidths. The analysis of our spectrum and our redetermination of the hyperfine splitting constant were in agreement with Low's¹ results on a single crystal sample. We did not consider a possible quadrupole interaction in our analysis resulting from the lattice strain since such an interaction usually produces shifts that are smaller than those resulting from an axial component of the crystal field.

ACKNOWLEDGMENT

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APPENDIX

We list below the third-order perturbation of the energy of a state (M, m) resulting from the mixing of a trigonal crystal field term and an isotropic hyperfine interaction when the quantization axis is at an angle θ to the trigonal axis.