Here η has been defined in (2) and q_x, q_y, and q_z are the components of a wave number vector $\mathbf{q}$. The triple integral in (3) can be easily reduced to a single integral. This single integral was evaluated by an electronic computer. The results[9] for various η are shown in Table I. Inserting the numerical values, $T_N = 0.37$, $|J_1|/k = 3$, $S = \frac{1}{2}$ into (3) and using Table I, we obtain $\eta \approx 0.01$.

TABLE I. Numerical values for the integral $I(\eta)$.

η	$I(\eta)$
1	0.505
0.1	1.963
0.01	6.405
0.001	20.323

The expression for T_N obtained by the modified molecular field theory or the Bethe-Peierls theory contains only the number of neighbors z. Consequently, these theories do not take account of dependence on structure. On the other hand, the expression of T_N by the Green function method contains $\sum \mathbf{q}$, where $\mathbf{q}$ is the wave number vector. This indicates the Green function method takes account of structure much more precisely than the other theories. In the present problem the structure dependence is essentially important. In other words, the magnetic property of $Cu(NH_3)_4SO_4 \cdot H_2O$ is well described by the linear chain model, but it is slightly modified by the exchange interactions between the chains. This is the reason why the Green function method can give a reasonable value for $|J_2|/|J_1|$, although the other theories fail.

ACKNOWLEDGMENT

The author thanks J. Skalyo for calculating the numerical values in Table I by the computer.

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[9] Dr. E. W. Montroll informed me that he has calculated the triple integral analytically. [*Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability, December 1954 and June and July 1955* (University of California Press, 1955), p. 209.] The numerical values in Table I are in quite good agreement with his results.

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"Forbidden" Hyperfine Transitions in the Electron Paramagnetic Resonance of Mn^{++} in Cubic MgO

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The so-called "forbidden" hyperfine transitions of the S-state ion Mn^{++} with selection rules $|\Delta M| = 1$, $\Delta m = \pm 1$ have been observed in the cubic field of MgO. These transitions are shown to be observable in cubic fields because of the mixture of the zero-field splitting parameter a with the off-diagonal hyperfine terms in the spin Hamiltonian which mixes neighboring hyperfine levels. Until now the intensities of these transitions had been calculated only in crystals of axial symmetry and were due to the mixing of levels with axial-field splitting D. The intensity for the cubic-field case is calculated and shows an interesting $(\sin 4\theta)^2$ dependence, as compared with $(\sin 2\theta)^2$ in the axial field case. The splittings of the "forbidden" doublets are calculated to third-order perturbation theory and both the intensities and the splittings agree well with the experimental data.

INTRODUCTION

THE electron paramagnetic spectra of divalent manganese in several single crystals of axial symmetry have shown weak lines occurring between the usual intense main hyperfine lines.[1–7] These were first observed by Bleaney and Ingram[8] and are due to the mixing of hyperfine levels by the interaction of the axial-field splitting D with the hyperfine interaction A. Bleaney and Rubins, however, point out that this mixing should occur whenever the magnetic field is not directed along an axis of twofold or higher symmetry.[3] In the present paper, we have observed the forbidden lines in the cubic field of MgO and have shown that they are due to hyperfine mixing with the zero-field cubic splitting a.

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The intensity calculation for the cubic field case is presented and is based on the simpler example of the axial-field case. The forbidden doublet splitting is also evaluated to third-order perturbation using the operator equivalent notation. A comparison between theory and experimental results is made.

THEORY

So-called forbidden hyperfine transitions occur through the mixing of neighboring hyperfine levels by off-diagonal matrix elements in the spin Hamiltonian. Allowed transitions induced by the component of the rf magnetic field perpendicular to the axis of quantization are those for which $|\Delta M|=1$, $\Delta m=0$, where M and m are, respectively, the electron- and nuclear-magnetic quantum numbers. Forbidden hyperfine transitions are then those for which $|\Delta M|=1$, $\Delta m=\pm1$, ±2, etc. Whether or not a transition is considered as forbidden depends upon the manner in which the energy states are labelled. For this paper, we choose a representation in which the external magnetic field H forms the axis of quantization. Off-diagonal matrix elements arising from other terms in the spin Hamiltonian are then treated by perturbation theory and lead to an admixture of zero-order wave functions.

Apart from transitions induced by the parallel component of the rf field, for which $\Delta M=\pm1$, $\Delta m=\mp1$, two other mechanisms are known to produce forbidden hyperfine lines. These are through the nuclear-quadrupole interaction, the effects of which should not be observable in a cubic field, and second-order crossterms between the hyperfine and fine-structure operators in the spin Hamiltonian. The latter have been considered by Bleaney and Rubins for the case of a second-order axial term in the crystalline field. The method depends upon the presence of crystal-field terms containing odd powers of S_x and S_y which may form operators to raise or lower M by unity, without affecting m.

Intensity

To illustrate the calculation, we first consider the simpler case of an axial field with the magnetic field along the z axis and at an angle θ to the crystalline axis in the $x'z'$ plane. The relevant part of the nondiagonal term is then equal to

$$\mathcal{H}_1=\frac{D}{2}(S_zS_++S_zS_-+S_+S_z+S_-S_z)\cos\theta\sin\theta\,, \qquad (1)$$

where $S_\pm=(S_x\pm iS_y)$. The first-order admixtures of the states $|M\pm1,m\rangle$ to $|M,m\rangle$ are given by the perturbation expression

$$\langle M\pm1,m|\mathcal{H}_1|M,m\rangle/(E_{M,m}-E_{M\pm1,m})\,, \qquad (2)$$

where $E_{M,m}-E_{M\pm1,m}\cong\mp g\beta H$. In the second order, it is possible to mix neighboring hyperfine levels $|M,m\rangle$ and $|M,m\pm1\rangle$ by use of off-diagonal elements in the hfs interaction, written for simplicity as

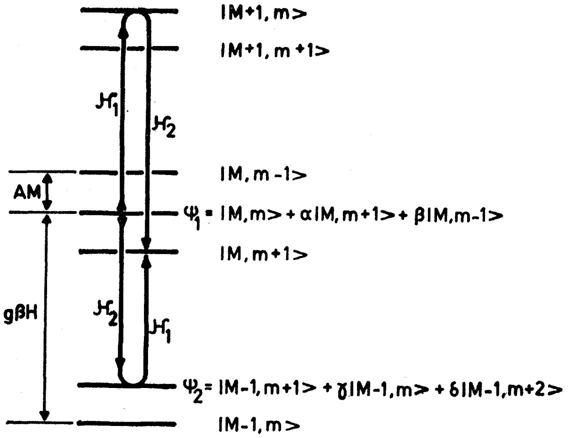

FIG. 1. An example of the mixing of neighboring hyperfine states. The operations shown form α, where $\mathcal{H}_1$ is a raising operator-like S_+ and $\mathcal{H}_2$ is S_-I_+. Similar operations will form β, ϑ, γ, and δ. When the "allowed" selection rules $|\Delta M|=1$, $\Delta m=0$ are applied between levels ψ_1 and ψ_2, the intensity is then seen to be proportional to $(\alpha+\gamma)^2$.

$$\mathcal{H}_2=AS_zI_z+\tfrac{1}{2}A(S_+I_-+S_-I_+)\,. \qquad (3)$$

The second-order admixture may be written immediately as

$$\frac{\langle M,m\pm1|\mathcal{H}_2|M\pm1,m\rangle\langle M\pm1,m|\mathcal{H}_1|M,m\rangle}{(E_{M,m}-E_{M,m\pm1})(E_{M,m}-E_{M\pm1,m})}\,. \qquad (4)$$

$E_{M,m}-E_{M,m\pm1}$ is only $\pm AM$, so that the denominator is proportional to $AM(g\beta H)$ and the numerator to AD. The admixture of neighboring hyperfine levels is thus proportional to $D/g\beta H$. Although obtained by a second-order calculation, the magnitudes are effectively an order lower. It is, of course, possible to take $\mathcal{H}_1$ and $\mathcal{H}_2$ in the reverse order. In Fig. 1, the operations connecting states $|M,m\rangle$ and $|M,m+1\rangle$ are shown schematically. A similar sequence of operations connects $|M,m\rangle$ and $|M,m-1\rangle$. If only these admixtures are considered, the perturbed function $|M,m\rangle$ may be written

$$\psi_1=|M,m\rangle+\alpha|M,m+1\rangle+\beta|M,m-1\rangle\,. \qquad (5)$$

If the transition between the levels $|M,m\rangle$ and $|M-1,m\rangle$ is considered to have unit probability, then that between $|M,m\rangle$ and the perturbed level

$$\psi_2=|M-1,m+1\rangle+\gamma|M-1,m\rangle+\delta|M-1,m+2\rangle \qquad (6)$$

must have probability $(\alpha+\gamma)^2$. The same expression can be shown to hold for the transition between the unperturbed levels $|M,m+1\rangle$ and $|M-1,m\rangle$. An alternate though equivalent formalism was used by Bleaney and Rubins who combined $\mathcal{H}_1$ and $\mathcal{H}_2$ to form an equivalent operator to connect neighboring hyperfine levels. Thus, in the axial field, the off-diagonal terms DS_zS_+ and $(A/2)S_-I_+$ are combined to form an equivalent operator proportional to $(AD/g\beta H)(S_zS_+S_-)I_+$. In the remainder of this section, we calculate $(\alpha+\gamma)^2$ for the case of a cubic fourth-order crystal field.

The spin Hamiltonian describing the d^5 (S state) ion in a cubic crystalline field may be written

$$\mathcal{H}=g\beta H_zS_z+A\mathbf{S}\cdot\mathbf{I}+V_{\text{cubic}}-g_n\beta_nH_zI_z\,, \tag{7}$$

where the terms are given in the order of magnitude observed for Mn^{2+} in cubic oxide lattices.[9] V_{cubic} represents the fine-structure term and may be written

$$V_{\text{cubic}}=\frac{a}{6}\Big[S_{x'}^4+S_{y'}^4+S_{z'}^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)\Big], \tag{8}$$

where the three fourfold axes of the cube lie in the x', y', and z' directions. Alternatively, in the notation of Jones, Baker, and Pope,[10] the cubic term is

$$V_{\text{cubic}}=B_4^0(O_4^0+5O_4^4)\,, \tag{9}$$

where $B_4^0=a/120$, and quantization is along one of the three fourfold axes.

For the relative-intensity calculation, we consider the case when the magnetic field H_z lies in the $x'z'$ plane of the cube, making an angle θ with the z' axis. Then, we have $x=x'\cos\theta-z'\sin\theta$, $y=y'$, $z=z'\cos\theta+x'\sin\theta$, which, when substituted into Eq. (8) and considering only odd terms of S_x and S_y, gives

$$V_{\text{cubic(odd)}}=a(P-R)\sin4\theta/24\,, \tag{10}$$

where

$$P=(S_x^3S_z+S_xS_zS_x^2+S_x^2S_zS_x+S_zS_x^3)$$

and

$$R=(S_z^3S_x+S_zS_xS_z^2+S_z^2S_xS_z+S_xS_z^3)\,.$$

In the operator equivalent notation, the terms of $P-R$ that raise and lower the electronic wave function by one step are proportional to O_4^1 and form the operator $\mathcal{H}_1$, which is substituted into Eq. (4) together with $\mathcal{H}_2=A\mathbf{S}\cdot\mathbf{I}$. Equation (4) has then been evaluated to give

$$\frac{a\sin4\theta}{192M}\left\{\frac{[S(S+1)-M(M+1)](2M+1)[3S(S+1)-7M^2-7M-6]}{E_M-E_{M+1}}+\frac{[S(S+1)-M(M-1)](2M-1)[3S(S+1)-7M^2+7M-6]}{E_M-E_{M-1}}\right\}[I(I+1)-m(m+1)]^{1/2}. \tag{11}$$

For the case of the central electronic transitions $M=\frac{1}{2}\leftrightarrow M=-\frac{1}{2}$ with $S=\frac{5}{2}$, Eq. (11) reduces to

$$\alpha=\gamma=-\frac{5a\sin4\theta}{2g\beta H}[I(I+1)-m(m+1)]^{1/2}, \tag{12}$$

so that the relative intensity of the transitions $|\frac{1}{2},m\rangle\leftrightarrow|-\frac{1}{2},m+1\rangle$ and $|\frac{1}{2},m+1\rangle\leftrightarrow|-\frac{1}{2},m\rangle$ is given by

$$I=\frac{25a^2}{(g\beta H)^2}[I(I+1)-m(m+1)](\sin4\theta)^2. \tag{13}$$

The distinguishing feature of these forbidden transitions is their $(\sin4\theta)^2$ angular dependence, which may be contrasted with the $(\sin2\theta)^2$ variation from forbidden transitions in an axial field. Their intensities relative to allowed transitions are proportional to $a^2/(g\beta H)^2$. Consequently, they diminish in intensity as the measuring frequency is increased. Taking the particular case of Mn^{2+} in MgO, $a/g\beta H$ is approximately 1/150 at 3 cm wavelength, so that the relative intensities of the central pair of forbidden lines $|\frac{1}{2},\pm\frac{1}{2}\rangle\leftrightarrow|-\frac{1}{2},\mp\frac{1}{2}\rangle$ should be $(\sin4\theta)^2/100$ to that of the allowed transitions $|\frac{1}{2},\pm\frac{1}{2}\rangle\leftrightarrow|-\frac{1}{2},\pm\frac{1}{2}\rangle$.

Doublet Splitting

Here, we shall confine our discussion to the central electronic transition $M=\frac{1}{2}\leftrightarrow M=-\frac{1}{2}$. The spectrum is basically the same as that described for axial-field cases: a pair of small "forbidden" lines lying between each two main hyperfine lines. Figure 2 shows an example of the allowed lines $|\frac{1}{2},m\rangle\leftrightarrow|-\frac{1}{2},m\rangle$ and $|\frac{1}{2},m+1\rangle\leftrightarrow|-\frac{1}{2},m+1\rangle$, with the forbidden lines $|\frac{1}{2},m\rangle\leftrightarrow|-\frac{1}{2},m+1\rangle$ and $|\frac{1}{2},m+1\rangle\leftrightarrow|-\frac{1}{2},m\rangle$ between them. For comparison with experiment, we shall be concerned with the separations δH (in gauss) of the two forbidden lines as a function of m. To the second order, the splittings are given by

$$\delta H=\frac{A^2}{2g\beta H_0}[2S(S+1)-\tfrac{1}{2}]+2g_n\beta_nH\,, \tag{14}$$

where $g\beta H_0=h\nu$. Third-order contributions to δH have been considered for the case of an axial field by Folen,[4] Schneider and Sircar,[5] Waldner,[6] and Odenhal.[7]

The relevant contribution of third-order energy term may be written

$$E_m^{(3)}=\sum_{n\neq m}\frac{(\mathcal{H}_{nn}-\mathcal{H}_{mm})|\mathcal{H}_{nm}|^2}{(E_m-E_n)^2} \tag{15}$$

as no terms proportional to $\mathcal{H}_{mn}\mathcal{H}_{nk}\mathcal{H}_{km}(m\neq n\neq k)$ are present. There are only two terms in third order which will contribute to the splitting. The most impor-

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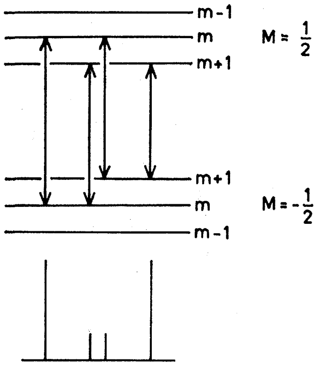

FIG. 2. Schematic of the $M=\pm\frac{1}{2}$ fine-structure levels split by the hyperfine interaction. The outer two transitions shown are allowed while the center two are so-called "forbidden." The spectrum is shown below the energy levels with arbitrary scale.

tant of these is[11]

$$\delta H'=-\frac{25}{32}\frac{A^3}{(g\beta H_0)^2}[2S(S+1)-\tfrac{3}{2}](2m+1). \quad (16)$$

The second term will be proportional to A^2a/H_0^2 and has not previously been calculated. Clearly, the off-diagonal matrix elements $|\mathcal{H}_{nm}|^2$ are produced by the hfs operator $A\mathbf{S}\cdot\mathbf{I}$ and the diagonal operator $(\mathcal{H}_{nn}-\mathcal{H}_{mm})$ by the diagonal part of the cubic field. When the axis of quantization is at an angle θ to a cubic axis, Table 5 of Ref. 10 shows that this operator is given by

$$B_4{}^0(\tfrac{3}{8}+\tfrac{5}{8}\cos4\theta)O_4{}^0, \quad (17)$$

where $B_4{}^0=a/120$. Matrix elements of $O_4{}^0$ have been tabulated by Stevens.[12] This contribution to the splitting is then calculated to be

$$\delta H''=-\frac{5A^2a}{4(g\beta H_0)^2}[S(S+1)-\tfrac{3}{4}]\times(2m+1)(\tfrac{3}{8}+\tfrac{5}{8}\cos4\theta). \quad (18)$$

In the above, only the first-order contribution of the nuclear Zeeman term $g_n\beta_n\mathbf{H}\cdot\mathbf{I}$ has been considered.

EXPERIMENTAL APPARATUS

The sample crystal was mounted in the center of a TE_{011} cylindrical reflection cavity with the longitudinal axis perpendicular to the magnetic field such that there would be no component of the rf field H_1 parallel to the steady magnetic field H_0. The Q of the cavity was about 10 000 and most measurements were made at room temperature. The system was also suitable for liquid-air temperature by the insertion of a quartz Dewar finger into the cavity. The spectrometer used was a high-sensitivity superheterodyne X band system and was operated near 10 Gc/sec with the signal klystron locked to the sample cavity with a 22-kc/sec feedback loop. The magnetic field was modulated at 390 cps and was phase-detected such that the first derivative of the absorption signal was recorded. All field measurements were made with a nuclear magnetic resonance proton probe.

EXPERIMENTAL RESULTS

From Eqs. (14), (16), and (18), the splittings of the forbidden doublets in the central electronic transitions for $S=\frac{5}{2}$ may be written as

$$\delta H=\frac{17}{2}\frac{A^2}{H_0}+2\frac{g_n\beta_n}{g\beta}H-\frac{25}{2}\frac{A^3}{H_0{}^2}(2m+1)-\frac{A^2a}{H_0{}^2}\left(\frac{25}{4}\cos4\theta+\frac{15}{4}\right)(2m+1), \quad (19)$$

where H_0 has been substituted for $g\beta H_0$. The first term is the only constant term and gives the main contribution to the splitting. Table I shows the contributions of each term and compares the total to a typical experimental run. The m value signifies the next main hyperfine line below the doublet; i.e., $m=-\frac{5}{2}$ means the doublet which occurs between the hyperfine lines $m=-\frac{5}{2}$ and $m=-\frac{3}{2}$. The second term varies only with the changing magnetic field and the last two terms change with the different m values. Only the last term varies with angle, but in such a way that the maximum and minimum splittings are at positions of zero intensity (zero, 45, 90 degrees) and the splittings of the forbidden doublets are the same at each position of maximum intensity ($22\frac{1}{2}$, $67\frac{1}{2}$ degrees). Because of the highly anisotropic behavior of the fine-structure pentad of Mn^{2+} in MgO, the doublets were easily observable only over small ranges of angles of about 10–14 degrees each in several positions; but, fortunately, these are at the most interesting positions: namely, zero, $22\frac{1}{2}$, 45, $67\frac{1}{2}$, and 90 degrees. The value given for this term in Table I, therefore, has not taken into account the angular part as $\cos4\theta$ is zero at the maximum intensity positions. Because of the small value of a in MgO:Mn^{2+} the magni-

TABLE I. This table shows the contribution in gauss to each term in the equation for the splitting of the forbidden doublet. The calculated total is compared to the experimentally measured value.

δH	m: $-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
$17A^2/2H_0$	17.6±0.1	17.6	17.6	17.6	17.6
$2(\gamma\beta_n/g\beta)H$	2.6	2.7	2.7	2.8	2.9
$-(25A^3/2H_0{}^2)(2m+1)$	−2.5	−1.2	0	1.2	2.5
$-(15A^2a/4H_0{}^2)(2m+1)$	0.2	0.1	0	−0.1	−0.2
Theoretical total δH	17.9±0.1	18.8	20.3	21.5	22.8
Experimental δH	18.0±0.5	19.0	20.2	21.9	23.2

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[11] Equation (16) contains the correction to third order which is obtained from the second-order contribution by replacing H by H_0+Am in the denominator of the first term of Eq. (14). Waldner had neglected the contribution from the first term in Eq. (15) but it is given in his corrigendum, Helv. Phys. Acta (to be published). The calculation of Schneider and Sircar appears to give the correct result.

[12] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

tude of the term is comparable to the experimental error and, therefore, the magnitude of the change in separation due to angle is unnoticable.

Figure 3 shows the low-field half of the usual spectrum of $MgO:Mn^{2+}$ with the magnetic field oriented about 25 degrees from the z' axis in the $x'z'$ plane. The arrows point to the positions of the "forbidden" hyperfine doublets. Figure 4 shows the doublet between $m=-\frac{3}{2}$ and $m=-\frac{1}{2}$ on an expanded horizontal scale and a signal-gain increase of 28 dB. The entire spectrum shows the doublets to have the usual relative intensity ratios to each other of 5:8:9:8:5 and the relative intensity to the main hyperfine line of about 1:100 as predicted. Runs were made at liquid-air temperatures, but no changes within experimental error were observed.

DISCUSSION

The most distinctive feature of the forbidden doublets is the angular dependence of their intensity. Unlike the axial case, there is an intensity minimum at $\theta=45°$ and equivalent orientations. As may be seen from the experimental data, the intensities are extremely small, which is probably why these lines have previously escaped serious consideration. Also, because of the small magnitude of a, the lines are centered between the main hyperfine lines and are almost isotropic.

In the case of a field of tetragonal or trigonal symmetry, both cubic and axial components will be present, so that the angular variation of intensity will be more complicated. For example, in a tetragonal field the intensity will vary as $A(\sin 2\theta)^2+B(\sin 4\theta)^2$. In the lower-symmetry cases considered, the axial component has been much greater than the cubic component so that the forbidden transitions produced by the sixth-order cubic field may be calculated in a similar manner to that of the fourth-order field, and the intensity variation would again be as $(\sin 4\theta)^2$.

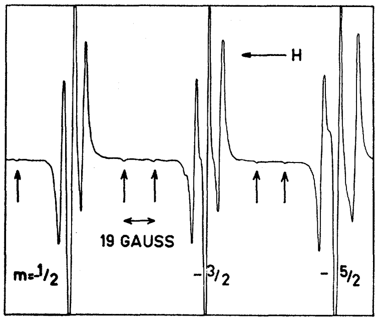

FIG. 3. The low-field half of the usual spectrum for Mn^{2+} impurities in MgO. The arrows point to the positions of the very low intensity "forbidden" hyperfine transitions. The magnetic field is oriented at about 25 degrees from the z' axis in the $x'z'$ plane.

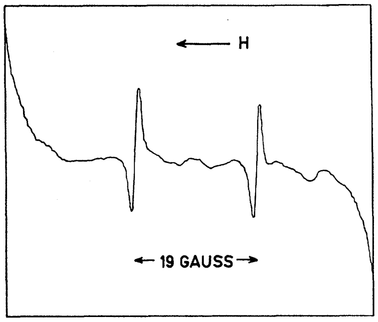

FIG. 4. An example of the data showing the forbidden doublet between the $m=-\frac{3}{2}$ and $m=-\frac{1}{2}$ hyperfine lines. This is the same doublet as shown in Fig. 3 but on an expanded horizontal scale and a signal-gain increase of 28 dB.

The calculations carried out in this paper have been those which could be compared directly with experiment. For this reason, the results for forbidden lines in the outer electronic transitions have not been given here. Their approximate positions have been indicated by Bleaney and Rubins.

The agreement with the theory, which was well within the experimental error, ruled out any need to extend the calculations to higher order. The fourth-order contribution to the splitting is probably well within 0.5 G, and, like the second-order, probably does not produce terms proportional to $(2m+1)$. Also, because the symmetry is cubic, the effect of the manganese nuclear quadrupole moment should not be observable; this term, therefore, does not appear in our Hamiltonian. The good results would therefore indicate that the method of Folen, Waldner, Schneider and Sircar, and Odenhal in fitting their data with an effective Q is basically valid. However, our results have shown that there is a small cubic contribution which should be considered for accurate work or narrow-line spectra in order to improve the results of the effective quadrupole determination. Measurements at higher frequencies to reduce the magnitude of the second- and higher-order effects would improve the degree of certainty of the result.

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