

THE ALLOWED AND FORBIDDEN TRANSITIONS
IN THE PARAMAGNETIC RESONANCE OF THE MANGANESE ION
IN TRIGONAL SITES IN APATITE AND SMITHSONITE

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Summary

The allowed and forbidden paramagnetic resonance transitions of Mn^{2+} ions in single crystals of apatite $[Ca_{10}(PO_4)_6(F, Cl)]$ and smithsonite $[ZnCO_3]$ have been investigated. The spin Hamiltonian parameters, describing the spectra observed at 300°K, were found from a third-order perturbation-theory estimate of the eigenvalues, calculated for the cases in which the magnetic field was parallel and perpendicular to the trigonal axis. Since in the case of apatite the D term was not very small compared with the Zeeman term, it had to be included also in the zeroth-order Hamiltonian.

I. INTRODUCTION

The author has been able to observe for the first time the forbidden $\Delta M = 1$, $\Delta m = 1$ and $\Delta M = 2$, $\Delta m = 0$ transitions due to Mn^{2+} in trigonal sites in apatite $[Ca_{10}(PO_4)_6(F, Cl)]$. These were studied and compared with the results obtained from the allowed $\Delta M = 1$, $\Delta m = 0$ transitions, previously observed by Bil'dyukevich *et al.* (1960). In addition, both allowed and forbidden transitions due to Mn^{2+} in rather similar sites in smithsonite were analysed.

Smithsonite ($ZnCO_3$) has the calcite structure and so the Zn^{2+} sites, into which the Mn^{2+} ions substitute, are arranged in two sets of inequivalent positions on trigonal axes which are parallel to one another. It should be noted that, apart from the orientation of the threefold component of the electric field, the environment is the same at both sites.

The paramagnetic resonance spectra of Mn^{2+} ions substituted into compounds with a similar crystal structure have been reported: Hurd, Sachs, and Hershberger (1954) have discussed the case of calcite and Vinokurov, Zaripov, and Stephanov (1961) obtained rather similar results from dolomite, ankerite, breunerite, and magnesite. However, good crystals of smithsonite are extremely rare (Dana 1932) and so it is not surprising that its Mn^{2+} spectrum has not been reported up till now.

In this investigation several crystals of naturally occurring smithsonite containing small quantities of manganese were obtained from South-west Africa and studied with the aid of the superheterodyne spectrometer described by Cavenett (1964).

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II. THEORY

In the coordinate system of a trigonal crystal field the spin Hamiltonian for the Mn^{2+} ion can be written (Bleaney and Ingram 1951; Stevens 1952; Judd 1955)

$$\begin{aligned} \mathcal{H} = & g_{\parallel}\beta H \cos \theta S_z + \frac{1}{2}g_{\perp}\beta H \sin \theta [S_+\exp(-i\phi) + S_-\exp(i\phi)] \\ & + D[S_z^2 - \frac{1}{3}S(S+1)] - \frac{(a-F)}{180} \left\{ 35S_z^4 + 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2 \right\} \\ & + \frac{2^2a}{36} \left\{ S_z[S_+^3\exp(-3i\phi) + S_-^3\exp(3i\phi)] + [S_+^3\exp(-3i\phi) + S_-^3\exp(3i\phi)]S_z \right\} \\ & + AS_zI_z + \frac{1}{2}B(S_+I_- + S_-I_+) + P[I_z^2 - \frac{1}{3}I(I+1)] \\ & - g_{\parallel}\beta H \cos \theta I_z - \frac{1}{2}g_{\perp}\beta H \sin \theta [I_+\exp(-i\phi) + I_-\exp(i\phi)]. \end{aligned} \quad (1)$$

The various substitution sites in both apatite and smithsonite differ only in the direction of the threefold component of the electric field and so the spin Hamiltonians will be the same for all sites in each material (apart from a phase factor in ϕ whose effect on the energy levels becomes irrelevant when θ equals either 0° or 90°).

The observed absorption of microwave energy is due to transitions between the energy levels given by the action of the spin Hamiltonian operator on the 6S ground term of Mn^{2+} . Since in this case $S = 5/2$, and $I = 5/2$ (for the 100% abundant ^{55}Mn), the resulting secular determinant is of order 36. This would be difficult to solve exactly, but good approximate solutions may be obtained by perturbation theory. Thus to second-order in perturbation theory the allowed $\Delta M = 1$, $\Delta m = 0$ transitions have been described by Bleaney and Ingram (1951), and may be put in the following form.

For H parallel to the trigonal axis

$$g_{\parallel}\beta H_{M,m:M-1,m} = h\nu - D(2M-1) + k(a-F) - Am - \frac{B^2}{2h\nu} \left\{ \frac{3^5}{4} - m^2 + m(2m-1) \right\}, \quad (2)$$

where $k = -4/3, 5/3, 0, -5/3, 4/3$ for $M = 5/2, 3/2, 1/2, -1/2, -3/2$, and for H perpendicular to the trigonal axis

$$\begin{aligned} g_{\perp}\beta H_{M,m:M-1,m} = & h\nu + D(M - \frac{1}{2}) + k(a-F) - \frac{D^2}{8h\nu} \left\{ \frac{2^2}{2} - 6M(M-1) \right\} - Bm \\ & - \frac{A^2 + B^2}{4h\nu} \left\{ \frac{3^5}{4} - m^2 + m(2M-1) \right\}, \end{aligned} \quad (3)$$

where $k = 1/2, -5/8, 0, 5/8, -1/2$ for $M = 5/2, 3/2, 1/2, -1/2, -3/2$.

In addition to these allowed transitions of the Mn^{2+} ion in a trigonal field, the forbidden $\Delta M = 1$, $\Delta m = 1$ transitions have been reported by Bleaney and Ingram (1951), Friedman and Low (1960), Mataresse (1961), Folen (1962), Schneider and Sircar (1962), and Wolga and Tseng (1964). The last three papers show that, in order to account for the spacing of the forbidden line doublets to within a possible experimental error of a fraction of an oersted, it is necessary to go to third-order

in perturbation theory. However, they make significant calculational errors and so the following independent derivation was made by the author.

To third-order in perturbation theory (and using $g_{\parallel}\beta HS_z + DS_z^2$ as the unperturbed operator) we obtain as estimates of the energy levels derived from the unperturbed $M = \pm\frac{1}{2}$ states, when the magnetic field is parallel to the C -axis,

$$\begin{aligned}
 E_{\pm i, m} = & \pm\frac{1}{2}g_{\parallel}\beta H - \frac{8}{3}D - \frac{2}{3}(a - F) \mp \frac{20a^2}{27(g_{\parallel}\beta H \pm 2D)} \pm \frac{1}{2}Am - g\beta Hm + P(m^2 - \frac{3}{4}) \\
 & \pm \frac{9B^2}{4g_{\parallel}\beta H} \left\{ \frac{3}{4} - m(m \mp 1) \right\} \mp \frac{8B^2}{4(g_{\parallel}\beta H \pm 2D)} \left\{ \frac{3}{4} - m(m \pm 1) \right\} \\
 & - \frac{B^3}{4(g_{\parallel}\beta H)^2} \left\{ 9 \left[\frac{3}{4} - m(m \pm 1) \right] \left(\frac{1}{2} \pm m \right) + 8 \left[\frac{3}{4} - m(m \mp 1) \right] \left(\frac{3}{2} \mp m \right) \right\} \\
 & - \frac{B^2D}{3(g_{\parallel}\beta H)^2} \left\{ 18 \left[\frac{3}{4} - m(m \pm 1) \right] + 4 \left[\frac{3}{4} - m(m \mp 1) \right] \right\}. \quad (4)
 \end{aligned}$$

Here we ignore some very small corrections to the denominators of the third-order terms in B^3 and B^2D , and neglect altogether the remaining third-order terms containing factors of a , since these represent corrections very much less than the experimental error (Cavenett 1964).

Hence it can be shown that the spacings ΔH between the $|\frac{1}{2}, m\rangle \rightarrow |-\frac{1}{2}, m-1\rangle$; $|\frac{1}{2}, m-1\rangle \rightarrow |-\frac{1}{2}, m\rangle$ doublets are approximately

$$\Delta H = \frac{1}{g_{\parallel}\beta} \left[\frac{9B^2}{2h\nu} + \frac{8B^2}{2h\nu} \left(\frac{h^2\nu^2}{h^2\nu^2 - 2D^2} \right) + \frac{2g_I h\nu}{g_{\parallel}} \right] - \frac{1}{g_{\parallel}\beta} \left[\frac{67B^3}{4h^2\nu^2} - \frac{22B^2}{3h^2\nu^2} + 2P \right] (2M-1), \quad (5)$$

where ν is the microwave frequency.

The terms in the first set of square brackets give the average spacing of the doublets, while those in the second set indicate the systematic change in spacing as m ranges from $-3/2$ to $5/2$ in unit steps.

When D is very small compared with $h\nu$, equation (5) may be written

$$\Delta H = \left[\frac{17B'^2}{2H_0} + \frac{2g_I H_0}{g_{\parallel}} \right] - \left[\frac{67B'^3}{4H_0^2} - \frac{22B'^2 D'}{3H_0^2} + 2P' \right] (2m-1), \quad (6)$$

where $H_0 = h\nu/g_{\parallel}\beta$, and the primes indicate that the parameters include a factor of $1/g_{\parallel}\beta$ and so are now measured in oersteds. This is consistent with the expression derived by Folen (1962) except that he omits the term in B'^3/H_0^2 . It also agrees with the expressions used by Schneider and Sircar (1962) and Wolga and Tseng (1964), except that these authors incorrectly use $25/2$ instead of $67/4$ as the coefficient of the term in B'^3/H_0^2 .

An expression analogous to that in (6) can be derived for the case in which the magnetic field is perpendicular to the C -axis

$$\Delta H = \left[\frac{17(A'^2 + B'^2)}{4H_0} + \frac{2g_I H_0}{g_{\perp}} \right] - \left[\frac{67B'^3}{4H_0^2} - \frac{22B'^2 D'}{6H_0^2} + P' \right] (2m-1). \quad (7)$$

III. THE APATITE SPECTRUM

The allowed $\Delta M = 1$, $\Delta m = 0$ transitions in the paramagnetic resonance spectrum of Mn^{2+} in trigonal sites in apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{Cl})]$ have been reported by Bil'dyukevich *et al.* (1960). Similar observations have been made by the author, who obtained the following parameters on using third-order perturbation theory to account for the X -band and Q -band spectra at room temperature:

$$\begin{aligned} g &= 2.000(\pm 0.001) \text{ isotropic,} \\ D &= \mp 404.3(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\ (a-F) &= 2.8(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\ A &= \mp 89.8(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\ B &= \mp 89.2(\pm 1) \times 10^{-4} \text{ cm}^{-1}. \end{aligned}$$

These results differ slightly from the values obtained by Bil'dyukevich *et al.* This may result from the use of specimens with a different fluorine and chlorine content; such variations are common and are known to cause structural changes (Thewlis, Glock, and Murray 1939).

TABLE I
SPACING OF THE FORBIDDEN DOUBLETS

ΔH (Experiment) (Oe)	ΔH (Theory, $P = 0$) (Oe)	ΔH (Theory, $P = 0.19$) (Oe)
31.3(± 0.4)	31.8	31.1
29.2(± 0.4)	29.2	28.8
26.9(± 0.4)	26.5	26.5
24.6(± 0.4)	23.8	24.2
22.2(± 0.4)	21.2	21.9

The five forbidden $\Delta M = 1$, $\Delta m = \pm 1$ doublets associated with the allowed central sextet could be clearly resolved only for the case in which the direction of the magnetic field was close to that of the C -axis. Far away from the C -axis they were obscured by allowed transitions, and directly along the C -axis they became rigorously forbidden (Bleaney and Rubins 1961).

A comparison between the experimental values of the spacing between these forbidden doublets, taken with the magnetic field inclined at 2° to the C -axis, and the theoretical values of ΔH given by equation (5) is indicated in Table 1.

The average spacing of the observed doublets is 26.8 Oe which compares to within experimental error with the 26.5 Oe predicted by equation (5), but is not in agreement with the 26.1 Oe predicted by equation (6) (which corresponds to the usual theoretical approach in which the D term is not included in the zeroth-order of the perturbation treatment).

The quadrupole coupling parameter, which represents the interaction between the quadrupole moment of the ^{55}Mn nucleus and the gradient of the electric field, was observed to have the value $P = 0.19(\pm 0.05) \times 10^{-4} \text{ cm}^{-1}$.

The forbidden $\Delta M = 2$, $\Delta m = 0$ transitions were also observed, but could not be accounted for in terms of third-order perturbation theory. Discrepancies of the order of 100 Oe were noted, but these were attributed to the poor convergence of the perturbation series. It was expected that a good fit could be obtained only by computer diagonalization of the secular determinant (which can, of course, be factorized into dimensions lower than the formidable 36×36 of the general case).

IV. THE SMITHSONITE SPECTRUM

The paramagnetic resonance spectrum was investigated at X-band frequencies for magnetic fields up to 7000 Oe. For most orientations of the crystal axis with respect to the magnetic field there were a large number of poorly resolved lines, but as the trigonal axis was turned into the direction of the magnetic field the lines joined up in pairs and intensified giving the spectrum shown in Figure 1. Actually this trace was taken when θ was 5° in order to show clearly the forbidden lines, which became very weak when θ was zero.

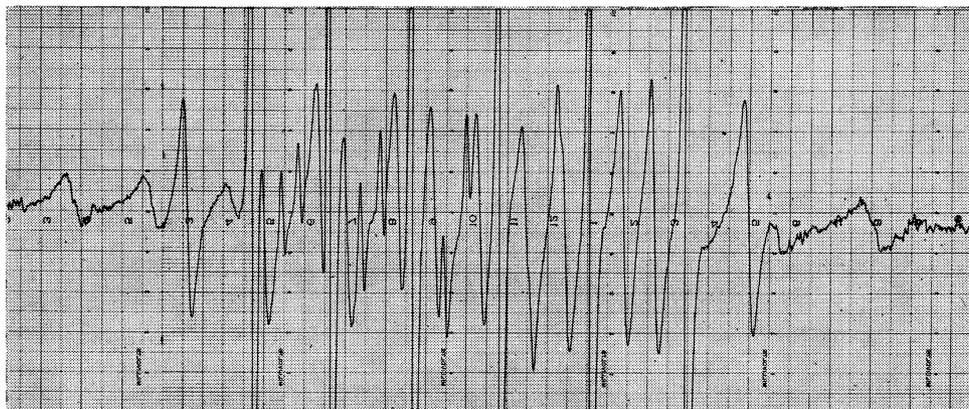


Fig. 1.—The smithsonite spectrum taken for $\theta = 5^\circ$ and showing both the allowed and forbidden lines near $g = 2$.

With the magnetic field perpendicular to the C -axis the lines again paired up, giving a spectrum which was isotropic in the perpendicular plane. Here again the forbidden lines became very weak.

Using the formulae of the previous section, both the allowed and forbidden spectra, taken at 300°K with H both parallel and perpendicular to the C -axis, could be accounted for (to within an experimental error of ± 1 Oe for the position of the allowed lines and ± 0.4 Oe for the spacing of the forbidden doublets) by the parameters:

$$\begin{aligned}
 g &= 2.003(\pm 0.001) \text{ isotropic,} \\
 D &= \mp 41.4(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\
 (a-F) &= \pm 11.4(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\
 A &= \mp 85.9(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\
 B &= \mp 86.7(\pm 1) \times 10^{-4} \text{ cm}^{-1}, \\
 P &= \pm 0.01(\pm 0.05) \times 10^{-4} \text{ cm}^{-1}.
 \end{aligned}$$

The ambiguity in sign of these experimentally measured parameters could be removed by measurements at liquid helium temperatures. However, at this stage we may note that all experience with Mn^{2+} spectra to the present time and the theoretical predictions of Powell, Gabriel, and Johnston (1960) would suggest that a is positive. Hence if we assume that F is small (as its fourth-order character would indicate) we can see that $(a-F)$ also must be positive, and that consequently D , A , and B are negative. The negative signs thus predicted for A and B accord with all observations made so far.

Since the quadrupole coupling parameter P represents the interaction between the quadrupole moment of the ^{55}Mn nucleus and the gradient of the electric field acting on it, and since this gradient is zero in the case of a purely cubic field (assuming we have point charges or multipoles), it is not surprising that no evidence of any such interaction is obtained in smithsonite, where the axial component of the electric field (as measured by the D term) is small; although such evidence has been obtained in apatite where the D term is large.

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