

# Forbidden Transitions ( $\Delta m = \pm 1$ ) in the Paramagnetic Resonance Absorption of $\text{Mn}^{2+}$ in Calcite†

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The forbidden transitions of the type  $\Delta m = \pm 1$  for  $\text{Mn}^{2+}$  in single crystals of calcite have been investigated at X-band frequencies. The results can be fitted with the spin Hamiltonian  $\mathcal{H} = g\mu_B \vec{H} \cdot \vec{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^2 O_4^2 + C_4^3 O_4^3 + A(S_x I_x + S_y I_y) - g_N \mu_N (\vec{H} \cdot \vec{I}) + Q' [I_x^2 - \frac{1}{3} I(I+1)] + Q'' [I_x^2 - I_y^2]$ . At room temperature, the best computer fit for the parameters is

$$g_{||} = 2.0019 \pm 0.0006,$$

$$B_2^0 = 24.99 \pm 0.10,$$

$$A = 87.01 \pm 0.04,$$

$$Q' = 0.174 \pm 0.1,$$

$$g_{\perp} = 2.0018 \pm 0.0006,$$

$$B_4^0 = 0.0397 \pm 0.0002,$$

$$B = 87.26 \pm 0.04,$$

$$Q'' \cos 2\phi = -0.065 \pm 0.1,$$

$B_4^3 \cos 3\phi - C_4^3 \sin 3\phi = -0.542 \pm 0.04$  (all in units of  $10^{-4} \text{ cm}^{-1}$ );  $g_N \mu_N = (10.11 \pm 2.0) \times 10^{-24} \text{ erg/G}$ .

## I. INTRODUCTION

The paramagnetic resonance spectrum of  $\text{Mn}^{2+}$  in calcite has been investigated by Mataresse and Kikuchi<sup>1</sup> and the isoelectronic ion  $\text{Fe}^{3+}$  in calcite by Marshall and Reinberg.<sup>2</sup> These authors have measured the allowed transitions and have pointed out the importance of the term  $B_4^3$  in the spin Hamiltonian for ion of  $S = \frac{5}{2}$ . The forbidden transitions, however, have not been previously measured. These transitions involve terms of the quadrupole and nuclear moment of the manganese ions. Since the lines in calcite are very sharp, they lend themselves to evaluation of the total Hamiltonian.

Another aspect of this paper is a comparison of the fit of the parameters obtained from the conventional expansion of the Hamiltonian to the second order of perturbation with the parameters obtained by diagonalization of the full matrix.

## II. THEORY

Calcite ( $\text{CaCO}_3$ ) has a rhombohedral symmetry. The crystal structure gives rise to two inequivalent calcium sites, each with the point symmetry  $S_6$ . The spin Hamiltonian for  $\text{Mn}^{2+}$ , substituting for the calcium, is given by

$$V = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^2 O_4^2 + C_4^3 R_4^3, \quad (1)$$

where  $B_4^3$  and  $C_4^3$  are real and correspond to the real and imaginary parts of  $B_4^3$  as defined by Marshall and Reinberg.<sup>2</sup> The other inequivalent site has the same spin Hamiltonian, except that one replaces  $B_4^3$  with  $-B_4^3$ . The operators of  $O_2^0$  and  $O_4^0$  are defined in terms of spherical harmonics by Low,<sup>3</sup> Prather,<sup>4</sup> and Hutchings.<sup>5</sup> We give only the expressions for  $O_4^3$  and  $R_4^3$  which are not commonly used:

$$O_4^3 = \frac{1}{4} [S_x(S_x^3 + S_z^3) + (S_x^3 + S_z^3)S_x], \quad (2)$$

$$R_4^3 = -\frac{1}{4} i [S_x(S_x^3 - S_z^3) + (S_x^3 - S_z^3)S_x].$$

The values of these operators in different  $S$  manifolds have been tabulated by Low and by Hutchings.

If we include the nuclear part and the effect of the magnetic field, the spin Hamiltonian takes the form

$$\begin{aligned} \mathcal{H} = & g\mu_B \vec{H} \cdot \vec{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^2 O_4^2 + C_4^3 R_4^3 \\ & + A S_x I_x + \frac{1}{2} B (S_+ I_- + S_- I_+) - g_N \mu_N \vec{H} \cdot \vec{I} \\ & + Q' [I_x^2 - \frac{1}{3} I(I+1)] + \frac{1}{2} Q'' [I_+^2 + I_-^2], \end{aligned} \quad (3)$$

$$S = \frac{5}{2}, \quad I = \frac{5}{2}.$$

Here  $A$  and  $B$  determine the hyperfine components and  $\gamma$  the gyromagnetic ratio, and  $Q'$  and  $Q''$  the components of the quadrupole tensor in an axial field.

We assume, as indeed this is true in our experiments at a wavelength of 3 cm, that  $g\mu_B \vec{H} \cdot \vec{S}$  is larger than any of the other terms of the Hamiltonian. Choosing the axis of quantization along  $H$ , which makes an angle of  $(\theta, \phi)$  with respect to the crystal axes  $x, y, z$  where  $z$  is the  $c$  axis of the crystal and  $x$  and  $y$  are the axes in a plane perpendicular, then the Hamiltonian takes the form

$$\begin{aligned} \mathcal{H} = & g\mu_N H S_z - g_N \mu_N H I_x + B_2^0 [\frac{1}{2} (3 \cos^2 \theta - 1) O_2^0 \\ & - 6 \sin \theta \cos \theta O_2^1 + \frac{3}{2} \sin^2 \theta O_2^2] + B_4^0 [\frac{1}{8} (35 \cos^4 \theta \\ & - 30 \cos^2 \theta + 3) O_4^0 - 5 \sin \theta \cos \theta (7 \cos^2 \theta - 3) O_4^1 \\ & + \frac{5}{2} \sin^2 \theta (7 \cos^2 \theta - 1) O_4^2 - 35 \sin^3 \theta \cos \theta O_4^3 \\ & + \frac{35}{8} \sin^4 \theta O_4^4] + (B_4^3 \cos 3\phi - C_4^3 \sin 3\phi) \\ & \times [\frac{1}{8} \sin^3 \theta \cos \theta O_4^0 + \frac{1}{4} \sin^2 \theta (4 \cos^2 \theta - 1) O_4^1 \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \sin \theta \cos^3 \theta C_4^2 + \frac{1}{4} (4 \cos^4 \theta + 3 \cos^2 \theta - 3) O_4^3 \\
& - \frac{1}{8} \cos \theta \sin \theta (3 + \cos^2 \theta) O_4^4 + (B_4^3 \sin 3 \phi + C_4^3 \cos 3 \phi) \\
& \times [\frac{3}{4} \sin^2 \theta \cos \theta R_4^1 + \frac{1}{4} \sin \theta (3 \cos^2 \theta - 1) R_4^2 \\
& + \frac{1}{4} \cos \theta (9 \cos^2 \theta - 5) R_4^3 - \frac{1}{8} \sin \theta (1 + 3 \cos^2 \theta) R_4^4] \\
& + (A \cos^2 \theta + B \sin^2 \theta) S_z I_z + \frac{1}{4} [A \sin^2 \theta + B (1 + \cos^2 \theta)] \\
& \times [S_+ I_- + S_- I_+] + \frac{1}{4} (A - B) \sin^2 \theta [S_+ I_+ + S_- I_-] \\
& - \frac{1}{2} (A - B) \sin \theta \cos \theta [S_z (I_+ + I_-) + (S_+ + S_-) I_z] \\
& + [\frac{1}{2} Q' (3 \cos^2 \theta - 1) + \frac{3}{2} Q'' \sin^2 \theta \cos^2 \phi] \\
& \times [I_z^2 - \frac{1}{3} I(I+1)] . \quad (4)
\end{aligned}$$

The very small nondiagonal part of  $Q$  has been neglected in the above transformation.

A second-order perturbation gives the following expressions for the resonance field.

#### A. Fine Structure

$$\begin{aligned}
H_{FS} &= H_0 + T + (1/H_0) [\zeta^2 - 5\tau^2 + 190\lambda\zeta - 90\sigma\tau], \\
\Delta M &= \pm \frac{3}{2} \mp \pm \frac{1}{2}, \\
H_{FS} &= H_0 + (1/H_0) [4\zeta^2 - 8\tau^2 - 120\lambda\zeta + 360\sigma\tau], \\
\Delta M &= + \frac{1}{2} \mp - \frac{1}{2}, \\
T &= [3B_2^0(3 \cos^2 \theta - 1) - \frac{75}{2} B_4^0(35 \cos^4 \theta - 30 \cos^2 \theta + 3) \\
& + \frac{75}{2} \bar{B}_4^3 \sin^3 \theta \cos \theta], \\
\bar{B}_4^3 &= B_4^3 \cos 3\phi - C_4^3 \sin 3\phi, \\
H_0 &= \frac{h\nu}{g\mu_B}, \text{ where } \nu = \text{frequency of rf field.} \quad (5) \\
\zeta &= -6B_2^0 \sin \theta \cos \theta, \\
\tau &= \frac{3}{2} B_2^0 \sin^2 \theta, \\
\lambda &= -5B_4^0 \sin \theta \cos \theta (7 \cos^2 \theta - 3) \\
& + \frac{1}{4} \bar{B}_4^3 \sin^2 \theta (4 \cos^2 \theta - 1), \\
\sigma &= \frac{5}{2} B_4^0 \sin^2 \theta (7 \cos^2 \theta - 1) + \frac{1}{2} \bar{B}_4^3 \sin \theta \cos^3 \theta.
\end{aligned}$$

All the constants above are expressed in Gauss, by the conversion  $B_2^0/g\mu_B \rightarrow B_2^0$ , etc.

#### B. Hyperfine Structure

The hyperfine contribution to the energy of the state  $|M, m\rangle$  is given by

$$\begin{aligned}
E_{HFS} &= (A \cos^2 \theta + B \sin^2 \theta) Mm - g_n \mu_n Hm \\
& + [\frac{1}{2} Q' (3 \cos^2 \theta - 1) + \frac{3}{2} Q'' \sin^2 \theta \cos 2\phi] \\
& \times [m^2 - \frac{1}{3} I(I+1)] + \frac{B^2}{2gBH_0} \{m[M^2 - S(S+1)] \\
& + M[I(I+1) - m^2]\} + (\text{third and higher orders}). \quad (6)
\end{aligned}$$

The positions of the lines involving a nuclear

TABLE I. Expression for  $a_{mm'}$ ,  $b_{mm'}$ ,  $c_{Mmm'}$ , as used in first-order Hamiltonian [Eq. (7)].

	$m' = m + 1$	$m' = m - 1$
$a_{mm'}$	$-\frac{g_N \mu_N}{g \mu_B}$	$+\frac{g_N \mu_N}{g \mu_B}$
$b_{mm'}$	$2m + 1$	$-2m + 1$
$c_{Mmm'}$	$M - m - 1$	$-(M + m - 1)$

flip ( $\Delta m = \pm 1$ ) are given to first order by

$$H(M, m \mp M - 1, m') = H_{FS} + a_{mm'} H + b_{mm'} Q + c_{Mmm'} K + H_c,$$

$$Q = \frac{1}{2} Q' (3 \cos^2 \theta - 1) + \frac{3}{2} Q'' \sin^2 \theta \cos 2\phi, \quad (7)$$

$$K = A \cos^2 \theta + B \sin^2 \theta.$$

$H_c$  is the correction to the field from higher-order perturbing terms. The expressions  $a$ ,  $b$ , and  $c$  are given in Table I. The second order correction is

$$\begin{aligned}
H_c^{(2)} &= (B^2/2H_0) [-\frac{35}{2} - 2(m+1)(M+1) \\
& + (M-m)(M-m-1)], \quad m' = m + 1 \\
& = \frac{B^2}{2H_0} [(m-M)(M+m-1)], \quad m' = m - 1. \quad (8)
\end{aligned}$$

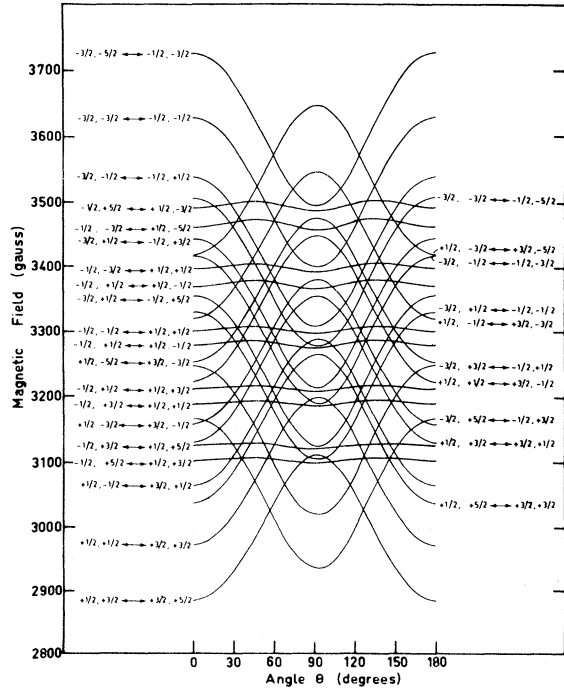


FIG. 1. Angular dependence of the forbidden transition of the  $Mn^{2+}$  spectrum in calcite.

TABLE II.  $\Delta = H$  (calculated)  $- H$  (measured). A comparison of the field values, calculated using second-order perturbation terms and by diagonalizing the complete spin Hamiltonian.  $H = H(M, m \pm M-1, m')$ .

M	m	m'	H (measured)	$\theta = 0^\circ$		H (measured)	$\theta = 90^\circ$	
				$\Delta$ (Gauss)			$\Delta$ (Gauss)	
				Pertur- bation 2nd order	Diag		Pertur- bation 2nd order	Diag
$\frac{3}{2}$	$-\frac{3}{2}$	m - 1	3285.9	-1.3	0.1	3510.3	3.7	4.6
	$-\frac{1}{2}$		3188.0	-0.8	-0.1	3414.4	2.7	2.0
	$+\frac{1}{2}$		3093.2	-0.7	-0.6	3320.6	2.2	0.8
	$+\frac{3}{2}$		2999.4	1.0	0.5	3228.8	2.4	0.7
	$+\frac{5}{2}$		2908.6	2.2	0.9	3140.1	2.0	0.3
	$-\frac{5}{2}$	m + 1	3453.2	2.2	1.5	3686.7	2.5	-3.0
	$-\frac{3}{2}$		3354.3	0.4	0.0	3582.7	3.7	-0.6
	$-\frac{1}{2}$		3255.3	0.2	0.5	3482.8	3.5	1.0
	$+\frac{1}{2}$		3159.5	-0.5	0.8	3388.9	-0.3	-0.4
	$+\frac{3}{2}$		3064.6	0.4	2.7	3297.1	-3.5	-1.0
$\frac{1}{2}$	$-\frac{3}{2}$	m - 1	3527.6	-0.9	0.7	3522.5	-0.9	0.9
	$-\frac{1}{2}$		3432.8	-3.4	-2.8	3426.7	-1.9	-0.9
	$+\frac{1}{2}$		3334.9	-0.3	-0.4	3330.8	-0.3	0.1
	$+\frac{3}{2}$		3244.1	-1.7	-2.4	3240.0	-1.2	-1.4
	$+\frac{5}{2}$		3154.4	-1.5	-3.0	3150.3	-0.5	-1.5
	$-\frac{5}{2}$	m + 1	3497.0	2.2	1.0	3492.9	4.3	0.1
	$-\frac{3}{2}$		3404.0	-1.5	-1.9	3401.2	-1.5	-2.8
	$-\frac{1}{2}$		3311.4	-2.7	-2.2	3307.3	-2.6	-1.5
	$+\frac{1}{2}$		3219.6	-2.2	-1.0	3216.6	-4.2	-1.0
	$+\frac{3}{2}$		3130.9	-2.2	-0.6	3128.9	-6.3	-1.6
$-\frac{1}{2}$	$-\frac{3}{2}$	m - 1	3766.3	0.0	1.4	3530.7	0.0	2.0
	$-\frac{1}{2}$		3667.3	1.5	2.0	3435.8	-2.0	-0.2
	$+\frac{1}{2}$		3575.6	-1.5	-1.6	3342.0	-2.5	-0.9
	$+\frac{3}{2}$		3478.7	3.2	2.6	3245.1	2.8	3.6
	$+\frac{5}{2}$		3389.9	2.4	1.1	3154.4	4.5	4.1
	$-\frac{5}{2}$	m + 1	3542.9	1.7	0.2	3311.4	0.6	-0.7
	$-\frac{3}{2}$		3452.2	1.1	0.9	3220.7	-1.0	0.6
	$-\frac{1}{2}$		3364.5	0.1	0.7	3135.0	-5.1	-1.6
	$+\frac{1}{2}$		3279.8	-1.3	-0.4	3048.3	-5.6	-1.2
	$+\frac{3}{2}$		3196.2	-1.2	-0.5	2962.7	-4.5	-0.4
$\Delta_{\text{rms}}$			1.7	1.5	$\Delta_{\text{rms}}$	3.1	1.8	

TABLE III.  $\Delta_{\text{rms}} = [\frac{1}{30}(H_{\text{calc}} - H_{\text{meas}})^2]^{1/2}$ . Comparison of values obtained using second-order perturbation results, and by numerical diagonalization of the spin Hamiltonian.

$\theta$	$\Delta_{\text{rms}}$ (Gauss)													
	0°	15°	30°	45°	60°	75°	90°	105°	120°	135°	150°	165°		
2nd order pert	1.7	1.7	2.3	2.4	2.7	2.7	3.1	2.8	2.9	2.7	2.3	1.8		
Diag matrix	1.5	1.5	1.8	1.8	1.7	1.6	1.8	1.5	1.8	1.8	1.9	1.5		

TABLE IV. Spin Hamiltonian parameters obtained from the forbidden transitions of  $\text{Mn}^{2+}$  in  $\text{CaCO}_3$ .

$g_{\parallel} = 2.0019 \pm 0.006$	$g_{\perp} = 2.0018 \pm 0.0006$
$B_2^0 = 24.99 \pm 0.10$	$B_4^0 = 0.0397 \pm 0.0002$
$A = 87.01 \pm 0.04$	$B = 87.26 \pm 0.04$
$Q' = 0.17 \pm 0.1$	$Q'' \cos 2\Phi = -0.065 \pm 0.1$
$B_2^3 \cos 3\Phi - C_2^3 \sin 3\Phi = -0.542 \pm 0.04$ all in units of $10^{-4}$	
$\text{cm}^{-1} \gamma \beta_N = (10.11 \pm 2.0) 10^{-24} \text{ erg/G}$	

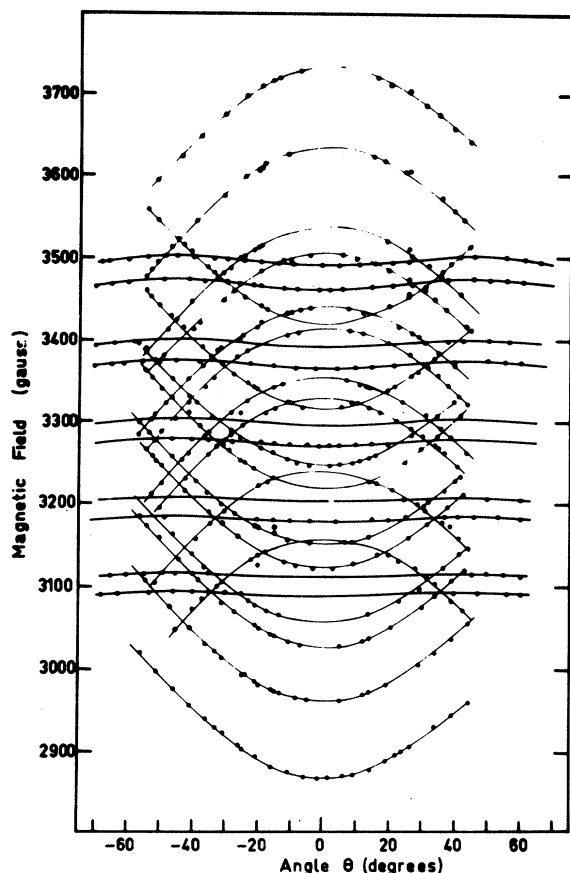


FIG. 2. Angular dependence of the forbidden transition of  $\text{Mn}^{2+}$  in calcite near  $\theta = 0^\circ$  but with a different value of the azimuthal angle.

It is worth while to note that the Hamiltonian contains linear terms in  $g_n\mu_n$  and  $Q$ , and hence a careful measurement permits the evaluation of these terms.

In most publications, the Hamiltonian is evaluated using the expansion of the spin Hamiltonian to second or higher perturbation. We have compared the values of the parameters obtained using the above approximate Hamiltonian with those parameters obtained by direct diagonalization of the  $36 \times 36$  matrix.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

The crystal was oriented in the following manner. The crystal was cleaved to give a rhombohedron of 2-mm edge. A special crystal holder was constructed so that the  $c$  axis was exactly defined with respect to the crystal holder and hence with respect to the resonance cavity. There were two possibilities of mounting the crystal with (i) either  $c$  axis in the horizontal or (ii) in the ver-

tical plane and perpendicular to the magnetic field. In the first orientation,  $\phi$  is fixed and  $\theta$  is varied, or the magnetic field direction is changed. In the second case,  $\theta = 90^\circ$  and one measures the changes of the spectrum with respect to  $\phi$ .

Figure 1 shows the angular dependence of the spectrum of one of the two inequivalent sites. In principle, the values of  $H$  at  $\theta = 0^\circ$  and  $90^\circ$  are sufficient to establish all parameters except  $B_4^3$  and  $C_4^3$ . These two may be obtained as the linear combination  $B_4^3 \cos 3\phi - C_4^3 \sin 3\phi$  from intermediate angles. Figure 2 shows the spectrum about  $\theta = 0^\circ$ , but with a different azimuthal angle  $\phi$ . It is clearly seen that the spectrum is not symmetrical about  $\theta = 0^\circ$  because of the change of  $\phi \rightarrow \pi + \phi$  as  $\theta$  goes through zero.

In Table II, we present the measured values of the various transitions, the calculated position using second-order perturbation theory, and the calculated position by direct diagonalization of the complete spin Hamiltonian. The results are given both for  $\theta = 0^\circ$  and  $90^\circ$ . Similar results are obtained for  $\theta = 0^\circ$  and  $180^\circ$ .

The root mean square deviation is given both for the perturbation theory and direct diagonalization. In Table III are listed the rms deviations for different angles of  $\theta$  from  $0^\circ$  to  $165^\circ$ .

Comparison of the data using these two methods shows that there is a better fit at all angles using the direct diagonalization of the total matrix.

We have also measured the forbidden transitions corresponding to  $\Delta M = \pm \frac{5}{2} \approx \pm \frac{3}{2}$  at angles close to  $\theta = 0^\circ$  and  $180^\circ$  and between  $10^\circ$  and  $40^\circ$ . However, at other orientations, the lines could not be followed because of the lower intensity and in the main because of the over-lap with the stronger allowed transitions. The measured values are not included in Tables. They do not change the obtained values of the different parameters.

The values of the parameters obtained are given in Table IV.

These results are in agreement with those found earlier by Hurd *et al.*,<sup>6</sup> although there is a slight deviation in the value of  $A$  which is outside the combined error.

Evaluation of the nuclear moments and the quadrupole moment depends on the knowledge of the  $\langle 1/r^3 \rangle$  and the gradient in the crystal.

The value of  $\gamma B_n$  found by us is somewhat larger than that obtained by NMR methods.

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<sup>1</sup>L. M. Mataresse and C. Kikuchi, *J. Chem. Phys.* **33**, 601 (1960); see also L. M. Mataresse, *J. Chem. Phys.* **34**, 336 (1961), who has also observed some of the forbidden transitions.

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<sup>5</sup>M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Chap. XVI.

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PHYSICAL REVIEW B

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## Jahn-Teller Distortions of $\text{Ag}^{2+}$ Ions in $\text{SrF}_2$ and $\text{CaF}_2$ by Odd Modes

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An anisotropic EPR spectrum of  $\text{Ag}^{2+}$  ions has been observed at 4.2 °K in single crystals of  $\text{CaF}_2$  and  $\text{SrF}_2$  that have been doped with silver. X rays convert the silver from the  $\text{Ag}^{1+}$  to the  $\text{Ag}^{2+}$  state. The results may be fitted with spin Hamiltonians with  $S = \frac{1}{2}$ ,  $g_{\parallel} = 1.997 \pm 0.001$  and  $g_{\perp} = 2.106 \pm 0.001$  for  $\text{CaF}_2$ , and  $g_{\parallel} = 1.988 \pm 0.001$  and  $g_{\perp} = 2.130 \pm 0.001$  for  $\text{SrF}_2$ . Hyperfine interactions with the silver nucleus are not resolved, but are expected to be small from symmetry considerations. Hyperfine interactions with two equivalent fluorines are observed and have the characteristic 1:2:1 intensity ratio with  $A_{\parallel} = 58.6 \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\perp} = 14.5 \times 10^{-4} \text{ cm}^{-1}$  for  $\text{CaF}_2:\text{Ag}^{2+}$ , and  $A_{\parallel} = 30.6 \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\perp} = 14.6 \times 10^{-4} \text{ cm}^{-1}$  for  $\text{SrF}_2:\text{Ag}^{2+}$ . Additional hyperfine structure from four other fluorine nuclei can be resolved when the magnetic field is along a  $\langle 110 \rangle$  direction. Optical absorption bands are observed in the x-rayed  $\text{CaF}_2:\text{Ag}^{2+}$  at 25 550 and 19 000  $\text{cm}^{-1}$ . One of the optical absorption bands and the  $g$  shift can be correlated by assuming that the  $\text{Ag}^{2+}$  excited state mixes with the fluorine ligands. This physical system is unusual in that the silver ions distort from cubic symmetry by moving off center in  $\langle 110 \rangle$  directions away from the central position and should have an electric dipole moment. In the distorted position, the hole in the  $d$  shell of  $\text{Ag}^{2+}$  is shared with a pair of  $\langle 100 \rangle$ -oriented fluorine ions.

### I. INTRODUCTION

Jahn-Teller effects<sup>1</sup> have been a subject of increasing attention recently. A considerable amount of theoretical effort has gone into the study of static and dynamic Jahn-Teller effects for the doublet ( $\Gamma_3^-$ ) ground state. Bersuker,<sup>2</sup> Ham,<sup>3</sup> and O'Brien<sup>4</sup> have made important contributions beyond the earlier work of Opik, Pryce, and others.<sup>5</sup> Coffman<sup>6</sup> and Höchli<sup>7</sup> have recently found some experimental evidence for tunneling effects in the electron-paramagnetic-resonance (EPR) spectrum of  $\text{Cu}^{2+}$  in  $\text{MgO}$  and  $\text{Sc}^{2+}$  in  $\text{CaF}_2$  and  $\text{SrF}_2$ .

Far less information is available on the distortions of triplet ground states, and the theory appears to be more complicated and less developed. Ham<sup>3</sup> has developed a theory of dynamical quenching of the orbital angular momentum to successfully explain the reduced  $g$  shifts of some para-

magnetic ions that have triplet ground states.

Both Ham<sup>8</sup> and Sturge<sup>9</sup> have recently reviewed the experimental and theoretical status of Jahn-Teller effects.

Relatively few examples of static Jahn-Teller effects have been observed for triplet states. One example is the work of Estle *et al.*<sup>10</sup> and Morigaki<sup>11</sup> who have attributed an anisotropic spectrum of  $\text{Cr}^{2+}$  to distortions along a line bisecting the angle to a nearest-neighbor pair of sulphurs in  $\text{CdS}$ . Similar spectra have been observed for  $\text{Cr}^{2+}$  in  $\text{ZnSe}$ ,  $\text{CaF}_2$ , and  $\text{CdF}_2$ . A model related to the one presented in this paper may apply to the above-mentioned experiments. Recently, Ham<sup>8</sup> has reviewed the experimental situation for Jahn-Teller effects in orbital triplet states.

In this article, we will present results for the static distortions of the  $\text{Ag}^{2+}$  ion in  $\text{CaF}_2$  and  $\text{SrF}_2$ ,<sup>12</sup> where the ground electronic state is a  $\Gamma_5^-$  triplet