

# Jahn-Teller EPR spectra of $\text{Cu}^{2+}$ in $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$

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The 34 GHz EPR spectrum of  $\text{Cu}^{2+}$  in  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  showed a "static" Jahn-Teller effect at 4.2 K with two inequivalent Jahn-Teller sites per unit cell. The six axially symmetric sets of  $\text{Cu}^{2+}$  lines had their  $z$  axes parallel to the three tetragonal axes of two cubes, which were rotated by approximately  $40^\circ$  with respect to each other about a common [111] axis, which is the crystal  $c$  axis. The measured spin-Hamiltonian parameters at 4.2 K for each set of lines were  $g_{\parallel} = 2.47 \pm 0.01$ ,  $g_{\perp} = 2.10 \pm 0.01$ , and  $|A_{\parallel}| = (110 \pm 3) \times 10^{-4} \text{ cm}^{-1}$ . There was a gradual decrease in the anisotropy of the spectrum on warming the crystal, with a single, nearly isotropic line being observed above 220 K. At 270 K the spectrum had axial symmetry about the  $c$  axis with  $g'_{\parallel} = 2.23 \pm 0.01$  and  $g'_{\perp} = 2.25 \pm 0.01$ . The temperature evolution of the spectrum was interpreted in terms of a Boltzmann distribution over inequivalent distorted Jahn-Teller configurations, with one potential well lowered by an amount  $\Delta \approx 105 \text{ cm}^{-1}$  below the other two.

## I. INTRODUCTION

Electron paramagnetic resonance (EPR) studies of the Jahn-Teller effect in copper-doped crystals which showed gradual changes in anisotropy over unprecedentedly large temperature ranges have been made by Ziatdinov *et al.*<sup>1</sup> on  $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$  and by De *et al.*<sup>2</sup> on  $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ . In both cases, six inequivalent  $\text{Cu}^{2+}$  spectra, each with  $g_{\parallel} = 2.47$  and  $g_{\perp} = 2.10$ , were observed at low temperatures. In  $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ , the  $z$  axes of the six spectra were found to lie along the three fourfold axes of two cubes sharing a common [111] axis and related to each other by a rotation of approximately  $40^\circ$  about that axis.<sup>2</sup> These low temperature spectra are consistent with a "static" Jahn-Teller effect,<sup>3</sup> and are similar to those observed in the classic case of  $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ ,<sup>4-6</sup> except for the presence of two distinct "Jahn-Teller" sites in these crystals.

In both  $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ , a gradual decrease in the anisotropy of the spectrum was observed on warming the crystal, until a transition was reached in which the multiline anisotropic spectrum was replaced by a nearly isotropic single line. In  $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ , this transition was found to be strongly dependent on the  $\text{Cu}^{2+}$  concentration, occurring in the least concentrated samples roughly 10 K below the structural phase transition of 182 K in the pure material.<sup>7</sup>

While interesting problems exist both in the region of the phase transition and above it, the present paper presents a further investigation of the low temperature region through an EPR study of  $\text{Cu}^{2+}$  in single crystals of  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ , which is probably isomorphous to both  $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ .<sup>8</sup> In  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ , the structural transition between the low temperature monoclinic phase, which belongs to the space group  $C_{2h}^5(P2_1/c)$ , and the high temperature rhombohedral phase, belonging to  $D_{3d}^5(R\bar{3}m)$ , occurs near 295 K in the pure material.<sup>9</sup> The high transition temperature allows the gradual reduction of the anisotropy of the temperature EPR spectrum to be fol-

lowed until it becomes a single line, without the complicating effects of the structural transition.

Experimental data for  $\text{Cu}^{2+}$  in  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  are presented in Sec. II and compared with the corresponding data for  $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ . The temperature evolution of the EPR spectrum is discussed in Sec. III, and (following Ziatdinov *et al.*<sup>1</sup>) interpreted in terms of a Boltzmann distribution over inequivalent potential wells.

## II. EXPERIMENTAL RESULTS

### A. General

EPR in single crystals of  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$  was studied between liquid helium and room temperatures, using a conventional 33–34 GHz spectrometer. The 4.2 K spectra were very similar to those measured in  $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ , with six inequivalent sets of  $\text{Cu}^{2+}$  lines and the hyperfine structure resolved only at the low field end of the spectrum.<sup>2</sup> On warming the crystal, there was a gradual change to a nearly isotropic single line spectrum above 220 K. The spectra at a number of temperatures between 4.2 and 228 K are shown in Fig. 1 for a particular orientation of the crystal. Following

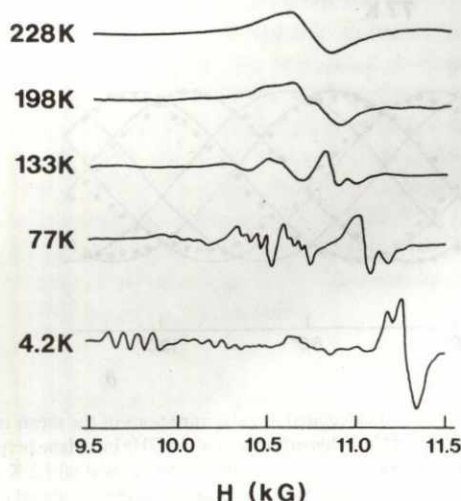


FIG. 1. The evolution of the EPR spectrum at 34 GHz between 4.2 and 228 K for an orientation in which the  $\text{Cu}^{2+}$  lines are well separated.

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TABLE I. Estimate of  $u(T)$  from experiment and theory.

$T$ (K)	$g_{\parallel}$	$u(T)$	
		Experiment <sup>a</sup>	Theory <sup>b</sup>
4.2	2.47	1.0	1.00
79	2.38	0.67	0.67
88	2.37	0.625	0.61
97	2.36	0.58	0.56
108	2.34	0.50	0.51
119	2.33	0.46	0.47

<sup>a</sup>  $u(T)$  was calculated from Eq. (1) with  $g_1 = 2.22$  and  $g_2 = 0.24$ . Estimated errors are  $\pm 0.05$ .

<sup>b</sup> Equation (9) was used to estimate  $u(T)$  theoretically with  $\Delta = 154$  K.

De *et al.*,<sup>2</sup> the temperature dependencies of  $g_{\parallel}$  and  $g_{\perp}$  were interpreted in terms of an empirical parameter  $u(T)$  given by

$$g_{\parallel}(T) = g_1 + u(T)g_2, \quad g_{\perp}(T) = g_1 - \frac{1}{2}u(T)g_2, \quad (1)$$

where  $g_1$  and  $g_2$  are parameters defined by Ham<sup>3</sup> and  $u(4.2)$  was assumed to be unity, so that the 4.2 K values of  $g_{\parallel}$  and  $g_{\perp}$  could be used to determine  $g_1$  and  $g_2$  (see Sec. II B). Values of  $u(T)$  calculated from the measured values of  $g_{\parallel}$  are given in Table I, where they are compared with the theory given in Sec. III. The results at 4.2, 77 and above 220 K are discussed separately below.

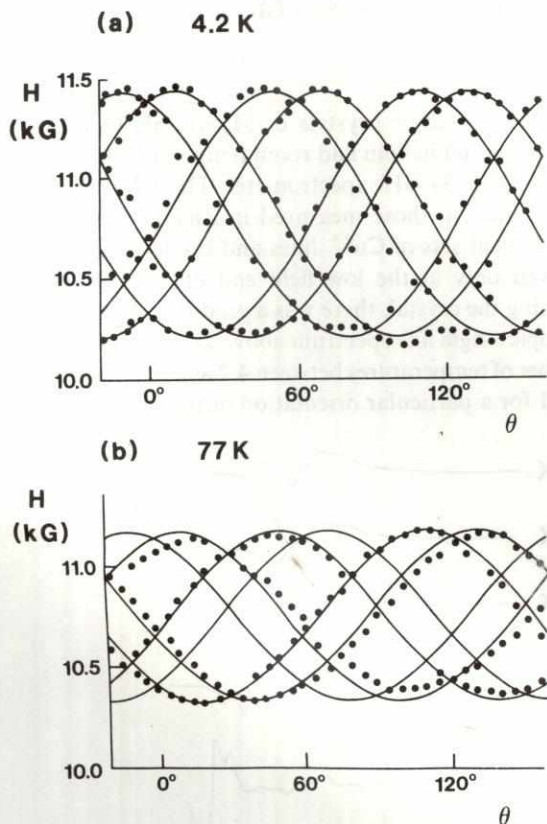


FIG. 2. The observed and calculated angular variations of the mean resonance fields of each set of Cu<sup>2+</sup> hyperfine lines at 34 GHz in a plane perpendicular to a natural face of the crystal containing the  $c$  axis at (a) 4.2 K and (b) 77 K. Points represent experimental data and curves the calculated positions. The angles  $\theta = 0^\circ$  and  $180^\circ$  corresponds to an orientation parallel to the  $c$  axis.

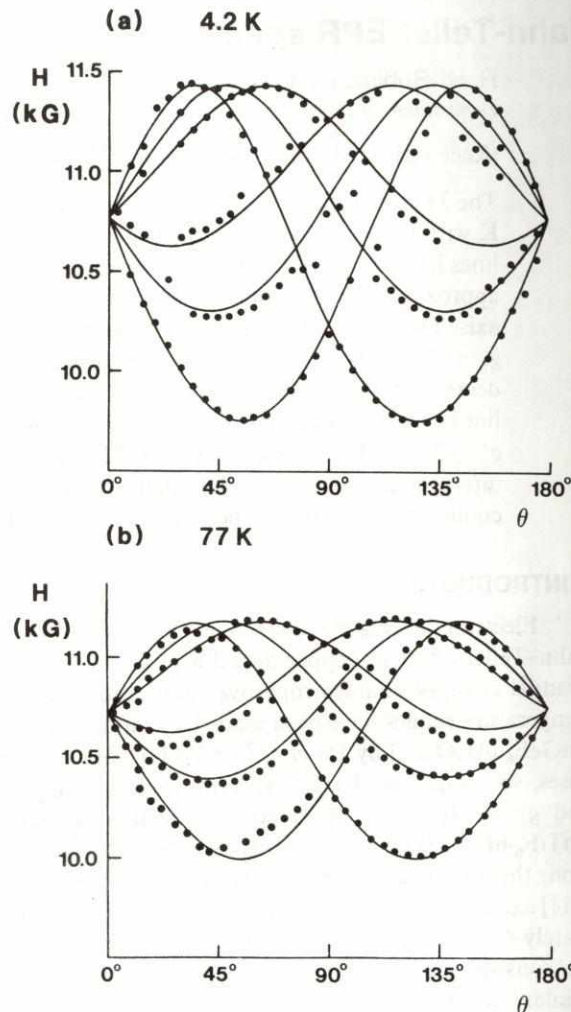


FIG. 3. The observed and calculated angular variations of the mean resonance fields of each set of Cu<sup>2+</sup> hyperfine lines in a plane perpendicular to the crystal  $c$  axis at (a) 4.2 K and (b) 77 K. Points represent experimental data and curves the calculated positions. The angles  $0^\circ$ ,  $60^\circ$ , and  $120^\circ$  correspond to directions perpendicular to hexagonal crystal faces.

### B. Results at 4.2 K

The angular variations of the EPR spectra in two mutually orthogonal planes are shown in Figs. 2(a) and 3(a). The plane of Fig. 2(a) is perpendicular to a natural face of the crystal and contains the pseudotrigonal  $c$  axis of the crystal. The six sets of lines are seen to coincide when the magnetic field is parallel to the  $c$  axis. The plane of Fig. 3(a) is perpendicular to the  $c$  axis. Here the lines clearly belong to two sets of three lines, each set showing  $60^\circ$  rotational symmetry. In both figures, the solid circles represent the centers of each group of hyperfine lines, while the curves represent theoretical fits based on a model of two inequivalent Jahn-Teller ions,<sup>2</sup> with

$$g_{\parallel} = 2.47, \quad g_{\perp} = 2.10, \quad \theta = 55^\circ, \quad \Delta\phi = 40^\circ, \quad (2)$$

where  $\theta$  is the angle between the  $z$  axis of each Cu<sup>2+</sup> spectrum and the crystal  $c$  axis, and  $\Delta\phi$  is the angular separation about the  $c$  axis of the two cubes associated with the Jahn-Teller distortions of the two inequivalent sites in the crystal.<sup>2</sup> Details of the method of computation have been given by Tello.<sup>10</sup> While the general agreement between theory and

experiment seen in these figures appears to be good, there are some discrepancies, which are probably a combination of effects due to slight crystal misalignments, nonaxial *g* tensors arising from the low symmetry components of the crystal field, and to errors in estimating the centers of the sometimes unsymmetrical groups of hyperfine lines.

The best values obtained for the extreme *g* values of the individual Cu<sup>2+</sup> spectra (assuming axially symmetric *g* tensors) and the average hyperfine structure constants of the Cu<sup>63</sup> and Cu<sup>65</sup> isotopes parallel to the *z* axes are

$$g_{\parallel} = 2.47 \pm 0.01, \quad g_{\perp} = 2.10 \pm 0.01, \\ A_{\parallel} = (95 \pm 3), \quad G = (110 \pm 3) \times 10^{-4} \text{ cm}^{-1}. \quad (3)$$

In the perpendicular directions, the hyperfine structure was both asymmetrical and unresolved, so that no precise value could be given for *A*<sub>⊥</sub>. The peak to peak linewidths parallel to the *z* axes were approximately 60 G.

The parameters of Eq. (3) are the same as those measured in ZnTiF<sub>6</sub>·6H<sub>2</sub>O, to within the experimental errors, so that the analysis used by De *et al.*<sup>2</sup> may be followed exactly. Letting

$$g_{\parallel} = g + 2qg_2, \quad g_{\perp} = g_1 - qg_2, \quad (4)$$

where *q* is a reduction factor introduced by Ham,<sup>3</sup> we obtain

$$g_1 = 2.22 \pm 0.01, \quad qg_2 = 0.12 \pm 0.01. \quad (5)$$

Assuming a ratio for  $\lambda/\Delta$  of  $-0.07$ ,<sup>2</sup> where  $\lambda$  is the spin-orbit coupling constant and  $\Delta$  is the cubic field splitting of the <sup>2</sup>*E* and <sup>2</sup>*T*<sub>2</sub> levels derived from the <sup>2</sup>*D* term of the free ion, leads to a value for *q* of 0.50, which corresponds to the strong Jahn–Teller limit.<sup>3</sup>

### C. Results at 77 K

The 77 K spectra were similar to those taken at 4.2 K, except that line separations were reduced and the hyperfine structure was only partially resolved parallel to each *z* axis. A comparison of experiment and theory for the same two planes is shown in Figs. 2(b) and 3(b). The theoretical fit is based on axial symmetry for each Cu<sup>2+</sup> transition with the parameters

$$g_{\parallel} = 2.39, \quad g_{\perp} = 2.14, \quad \theta = 55^\circ, \quad \Delta\phi = 40^\circ. \quad (6)$$

The measured extreme *g* values were

$$g_{\parallel} = 2.39 \pm 0.01, \quad g_{\perp} = 2.14 \pm 0.01, \quad (7)$$

which gives the same mean value  $\bar{g} = (g_{\parallel} + 2g_{\perp})/3 = 2.22$  as at 4.2 K. Precise estimates of the hyperfine structure splittings could not be made.

### D. Results above 250 K

The single observed EPR line was slightly anisotropic, with

$$g'_{\parallel} = 2.23 \pm 0.01, \quad g'_{\perp} = 2.25 \pm 0.01, \quad (8)$$

where the parallel axis is along the *c* axis of the crystal. This high temperature anisotropy has been shown to result from the trigonal component of the crystal field.<sup>6,11</sup> The result  $g'_{\parallel} < g'_{\perp}$  is the same as has been observed in ZnSiF<sub>6</sub>·6H<sub>2</sub>O<sup>6</sup> and ZnGeF<sub>6</sub>·6H<sub>2</sub>O,<sup>1</sup> but is opposite to that observed in ZnTiF<sub>6</sub>·6H<sub>2</sub>O.<sup>2</sup>

The linewidths showed a gradual increase with temperature. At 270 K, the peak-to-peak widths were  $\Delta H_{\parallel} \approx 380$  G and  $\Delta H_{\perp} \approx 300$  G. No sudden changes in either linewidth or line shape were observed in the region of the phase transition in MgSiF<sub>6</sub>·6H<sub>2</sub>O, which occurs near 295 K.<sup>9</sup>

### III. DISCUSSION

The most interesting feature of the EPR spectra of Cu<sup>2+</sup> in the monoclinic phases of crystals such as MgSiF<sub>6</sub>·6H<sub>2</sub>O, ZnGeF<sub>6</sub>·6H<sub>2</sub>O, and ZnTiF<sub>6</sub>·6H<sub>2</sub>O, is the gradual reduction of anisotropy with increasing temperature. This feature has been interpreted as a “pseudo-Jahn–Teller” effect,<sup>3</sup> in which the three distorted configurations associated with each Jahn–Teller ion are inequivalent, with one potential well lowered with respect to the other two by an energy  $\Delta$ .<sup>1,2</sup> The six sets of Cu<sup>2+</sup> lines observed at 4.2 K indicate that the potential well of lowest energy is distributed over the distorted configurations. For a reorientation time between distorted configurations sufficiently short for motional narrowing to occur, the motionally averaged spectrum should reflect a Boltzmann distribution over the lowest vibronic state in each of the distorted configurations. This form of averaging was assumed by Ziatdinov *et al.*<sup>1</sup> to explain the variation of the spin-Hamiltonian parameters in ZnGeF<sub>6</sub>·6H<sub>2</sub>O. In this case, the parameter *u*(*T*) of Eq. (1) would be given by

$$u(T) = [1 - \exp(-\Delta/kT)]/[1 + 2 \exp(-\Delta/kT)]. \quad (9)$$

The denominator of this expression was omitted by De *et al.*,<sup>2</sup> in their paper on ZnTiF<sub>6</sub>·6H<sub>2</sub>O. Use of Eq. (9) leads to a value for  $\Delta$  of approximately 105 cm<sup>-1</sup> in MgSiF<sub>6</sub>·6H<sub>2</sub>O, which may be compared with the values of 140 cm<sup>-1</sup> for ZnTiF<sub>6</sub>·6H<sub>2</sub>O and 154 cm<sup>-1</sup> for ZnGeF<sub>6</sub>·6H<sub>2</sub>O.<sup>1</sup> The calculated values of *u*(*T*) from Eq. (9) are compared with those determined from the experimental data in Table I.

While the estimates of *u*(*T*) were in good agreement with experiment, the measurements of *g*<sub>∥</sub> were not precise enough to provide a rigorous test of the theory. Several complicating factors could occur. At low temperatures, the conditions for motional narrowing may not be satisfied, which could result in deviations from Eq. (9).<sup>6</sup> At higher temperatures, the first excited vibronic states in the lowest potential well may be sufficiently populated to cause an appreciable contribution to *u*(*T*) in Eq. (9). Finally, we note that the splitting  $\Delta$  may itself be temperature dependent, since the orthorhombic *E* term in the spin-Hamiltonian of Ni<sup>2+</sup> in MgSiF<sub>6</sub>·6H<sub>2</sub>O has been found to increase appreciably with temperature in the monoclinic phase.<sup>12</sup> In the recent work of Ziatdinov *et al.*<sup>13</sup> on copper-doped ZnGeF<sub>6</sub>·6H<sub>2</sub>O,  $\Delta$  was found to increase with Cu<sup>2+</sup> concentration and to decrease with increasing temperature.

<sup>1</sup>A. M. Ziatdinov, M. M. Zaripov, Yu. V. Yablokov, and R. L. Davidovich, *Phys. Status Solidi B* **78**, K69 (1976).

<sup>2</sup>D. K. De, R. S. Rubins, and T. D. Black, *Phys. Rev. B* **29**, 71 (1984).

<sup>3</sup>See, for example, F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972), pp. 1–119.

<sup>4</sup>B. Bleaney and D. J. E. Ingram, *Proc. Soc. London Sect. A* **63**, 408 (1950).

<sup>5</sup>B. Bleaney and K. D. Bowers, *Proc. Phys. Soc. London Sect. A* **65**, 667

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		Experiment <sup>a</sup>	Theory <sup>b</sup>
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<sup>a</sup>  $u(T)$  was calculated from Eq. (1) with  $g_1 = 2.22$  and  $g_2 = 0.24$ . Estimated errors are  $\pm 0.05$ .

<sup>b</sup> Equation (9) was used to estimate  $u(T)$  theoretically with  $\Delta = 154$  K.

De *et al.*,<sup>2</sup> the temperature dependencies of  $g_{\parallel}$  and  $g_{\perp}$  were interpreted in terms of an empirical parameter  $u(T)$  given by

$$g_{\parallel}(T) = g_1 + u(T)g_2, \quad g_{\perp}(T) = g_1 - \frac{1}{2}u(T)g_2, \quad (1)$$

where  $g_1$  and  $g_2$  are parameters defined by Ham<sup>3</sup> and  $u(4.2)$  was assumed to be unity, so that the 4.2 K values of  $g_{\parallel}$  and  $g_{\perp}$  could be used to determine  $g_1$  and  $g_2$  (see Sec. II B). Values of  $u(T)$  calculated from the measured values of  $g_{\parallel}$  are given in Table I, where they are compared with the theory given in Sec. III. The results at 4.2, 77 and above 220 K are discussed separately below.

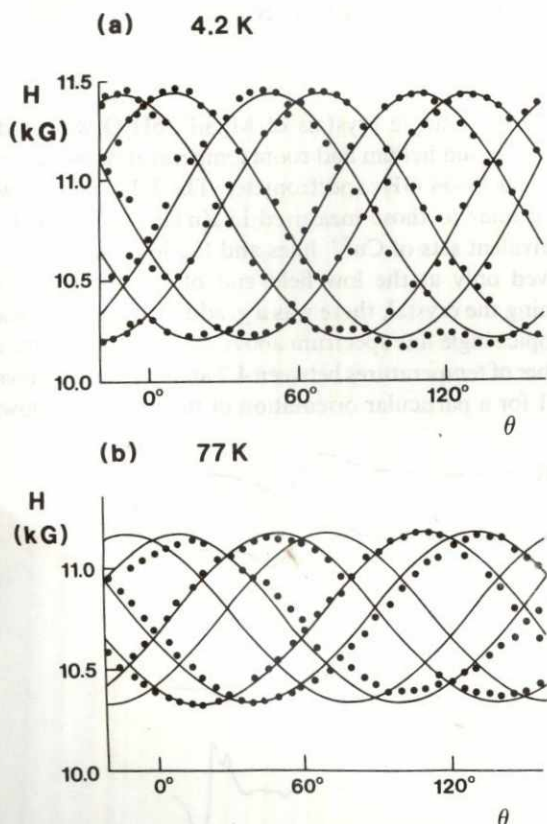


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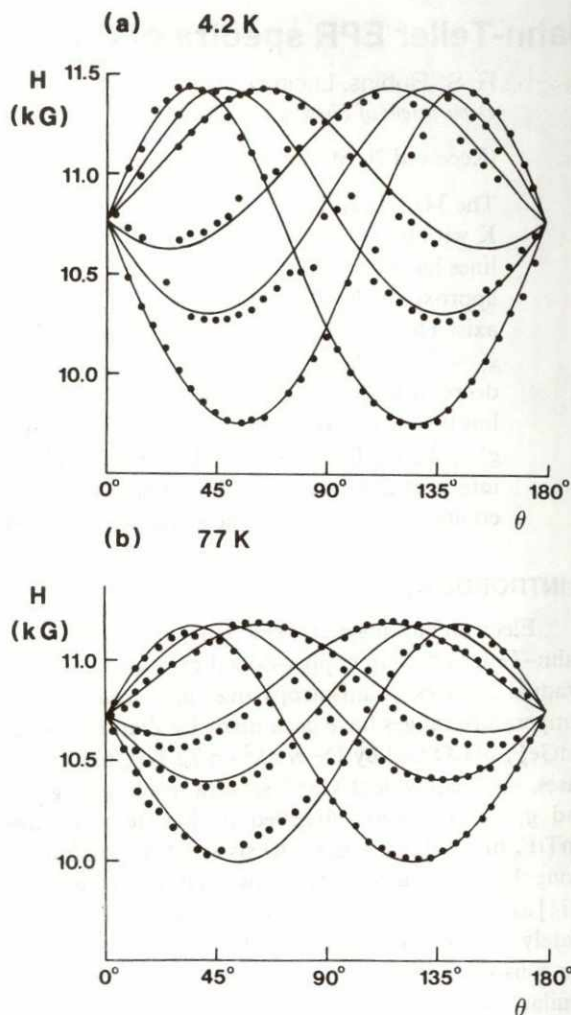


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## B. Results at 4.2 K

The angular variations of the EPR spectra in two mutually orthogonal planes are shown in Figs. 2(a) and 3(a). The plane of Fig. 2(a) is perpendicular to a natural face of the crystal and contains the pseudotrigonal  $c$  axis of the crystal. The six sets of lines are seen to coincide when the magnetic field is parallel to the  $c$  axis. The plane of Fig. 3(a) is perpendicular to the  $c$  axis. Here the lines clearly belong to two sets of three lines, each set showing  $60^\circ$  rotational symmetry. In both figures, the solid circles represent the centers of each group of hyperfine lines, while the curves represent theoretical fits based on a model of two inequivalent Jahn-Teller ions,<sup>2</sup> with

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(1952).

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<sup>7</sup>M. L. Afanasyev, A. F. Lybizikov, V. V. Menshikov, and E. P. Zeer, *Chem. Phys. Lett.* **60**, 279 (1979).

<sup>8</sup>See, for example, R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1965), Vol. 3, pp. 796-797.

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<sup>12</sup>R. S. Rubins and K. K. Kwee, *J. Chem. Phys.* **66**, 3948 (1977).

<sup>13</sup>A. M. Ziatdinov, R. L. Davidovich, V. Ya. Shevchenko, and Yu. V. Yablokov, *Koord. Khim.* **9**, 1644 (1983).