

Electron Paramagnetic Resonance Study of Copper(II) Fluosilicate Hexahydrate

D. K. DE

*Department of Magnetism, Indian Association for the Cultivation of Science, Calcutta-700032,
India, and Department of Physics, University of Texas at Arlington,
P.O. Box 19059, Arlington, Texas 76019*

AND

J. STHANAPATI, A. K. GHOSHAL, AND A. K. PAL

*Department of Magnetism, Indian Association for the Cultivation of Science,
Calcutta-700032, India*

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An electron paramagnetic resonance study was performed on single crystals of copper fluosilicate hexahydrate. EPR signals correspond to three tetragonally distorted octahedral Cu(II) ions (A site) with g values: $g_{\parallel} = 2.390$, $g_{\perp} = 2.093$, and one regular octahedral Cu(II) ion (B site) with $g = 2.093$. The spectra are thus quite different from those observed earlier by Bleaney and Ingram in $\text{Cu(II):ZnSiF}_6 \cdot 6\text{H}_2\text{O}$.

Fluosilicate hexahydrates of divalent metals belong to a series of crystals well-suited for X-ray, magnetic susceptibility and anisotropy, electron paramagnetic resonance, optical, and other studies (1-4). Observations of an isotropic EPR signal at 90 K and above and anisotropic EPR signals at 20 K by Bleaney and Ingram (1) in $\text{Cu:ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ provided the first experimental evidence of the Jahn-Teller effect. A determination of crystal structures of this series by Ray *et al.* (2, 3) has revealed that copper(II) fluosilicate hexahydrate (3), contrary to earlier belief, is not isomorphous with zinc fluosilicate hexahydrate. The structure is still rhombohedral (space group $R\bar{3}$) with a cell four times as large as that supposed earlier. The unit cell, which has dimensions $a = b = 18.18 \text{ \AA}$ and $c = 9.857 \text{ \AA}$, contains three magnetically nonequivalent tetragonally distorted $\text{Cu(II)} \cdot 6\text{H}_2\text{O}$ octahedra ($\text{Cu-O}(1) = 1.97 \text{ \AA}$, $\text{Cu-O}(2) = 1.97 \text{ \AA}$, $\text{Cu-O}(3) = 2.367 \text{ \AA}$) designated as the A sites; and one regular $\text{Cu(II)} \cdot 6\text{H}_2\text{O}$ octahedron ($\text{Cu-O} = 2.074 \text{ \AA}$) designated as the B site. It was therefore considered of interest to study EPR in single crystals of copper fluosilicate hexahydrate with the object of unravelling the nature of the ligand fields in a crystal where two types of Cu(II) complexes coexist.

EXPERIMENTAL

Single crystals were obtained by the slow evaporation of aqueous solutions of copper fluosilicate, the solutions being prepared by the reaction of CuCO_3 with

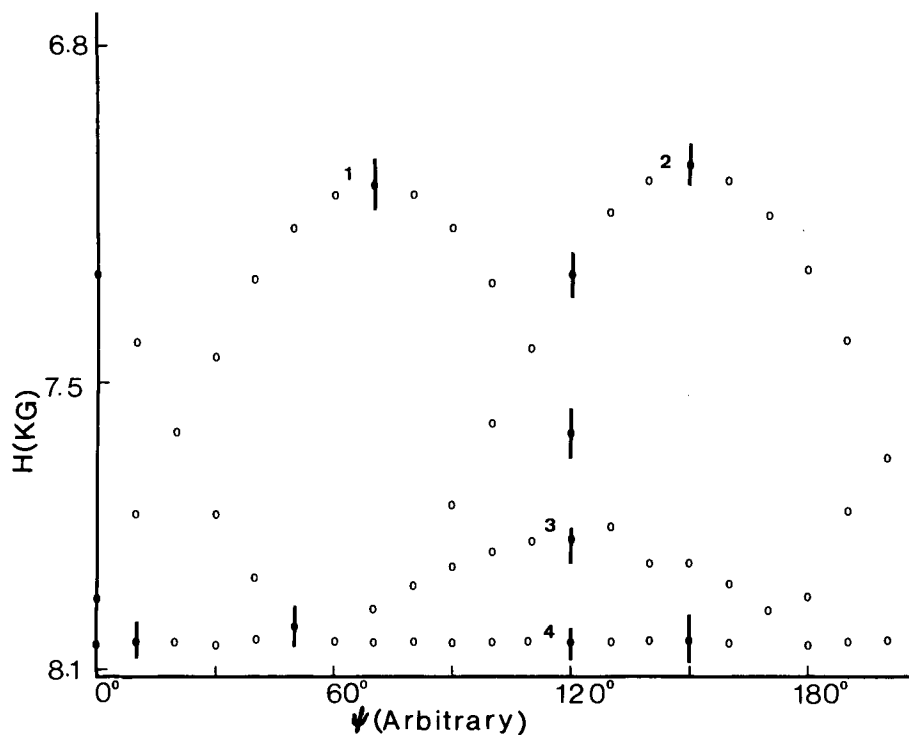


FIG. 1. Observed EPR resonance fields in the rhombohedral plane of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ at 298 K and microwave frequency $\nu = 23.54$ GHz. The minima of curves 1, 2, 3 are described by Eq. [3] (see text).

H_2SiF_6 . The crystallization temperature was chosen to be about 6°C to prevent the growth of $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$ (4). As the crystals were extremely hygroscopic they were coated with a very thin layer of a cyanoacrylate adhesive dissolved in amyl acetate immediately after being taken out of the mother solution. A K-band transmission type EPR spectrometer working in the cavity mode TE_{111} and a magnetic field stabilization system (5, 6) were employed for the room-temperature investigation. Measurements of g values were carried out at intervals of 5° in the rhombohedral (III) plane of the crystal. The angular variations of the resonance magnetic fields in the rhombohedral plane are given in Fig. 1. Derivative linewidths of the anisotropic lines were observed to vary from 88 to 200 G. The anisotropic lines were found to resolve into three distinct signals (1, 2, 3 in Fig. 1). These three signals correspond to the three magnetically inequivalent copper(II) complexes at the A site. Partially resolved hyperfine lines ($I = 3/2$) were observed in some directions.

From the equality of the minima of the curves 1 to 3 (Fig. 1), it follows that the minima correspond to g_{\perp} . An EPR signal (4 in Fig. 1) at high field (with g value close to g_{\perp}) was found to be isotropic. The spin Hamiltonian describing these anisotropic EPR spectra can be written as

$$g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y) \quad [1]$$

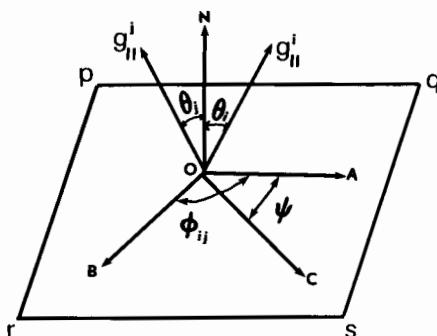


FIG. 2. The angles θ_i between the normal to the rhombohedral plane and the tetragonal axes (g_{11}) of A-type complexes and the angles ϕ_{ij} between their projections.

and that describing the isotropic signal as

$$H_s = \beta H \cdot \mathbf{g} \cdot \mathbf{S}. \quad [2]$$

ANALYSIS OF THE ANISOTROPIC SPECTRA

The angles θ_i between the normal to the rhombohedral plane "pqrs" and the tetragonal axes of the A-type complexes, and the angles ϕ_{ij} between their projections on the rhombohedral plane are shown in Fig. 2. The values of these angles are calculated from X-ray data (3) for $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ and are shown in Table 1. Referred to Fig. 1 the g^2 maxima should correspond to the projections of any of the g_{11} axes on the rhombohedral plane and can be described by

$$g_i^2 = (g_{11}^2 - g_{\perp}^2) \sin^2 \theta_i + g_{\perp}^2 \quad (i = 1, 2, 3). \quad [3]$$

The values of the g_{11} so determined from the three curves 1 to 3 (Fig. 1) are given in Table 2. They are found to be the same for the three ions. The values of g_{11} and g_{\perp} obtained from measurements at different microwave frequencies in different planes (110) and (001) of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ are also found to be nearly the same (7) as those given in Table 2. Values of g_i^2 at any angle ψ to the projection of the g_{11} axes were computed from the equation

$$g_i^2 = (g_{11} - g_{\perp}^2) \sin^2 \theta_i \cos^2 \psi + g_{\perp}^2.$$

They were found to be in good agreement with the observed variation of g_i^2 vs ψ in Fig. 1. The observed angles among the three g^2 maxima agreed quite well with the angle ϕ_{ij} between the projections of the g_{11} axes on the rhombohedral plane (Table 1).

DISCUSSION

The two types of EPR spectrum are discussed separately.

(i) *Anisotropic spectrum of Cu^{2+} at A sites.* Cu^{2+} ions at the A sites are subject to tetragonally distorted octahedral ligand fields (D_{4h} symmetry) so that the 2D ground state of Cu^{2+} is split into $^2B_{1g}$, $^2A_{1g}$, $^2B_{2g}$, and 2E_g ligand field levels. The

TABLE 1

THE ANGLES θ_i AND ϕ_{ij} (FIG. 2) DETERMINED FROM THE X-RAY AND EPR DATA IN $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$

	θ_1	θ_2	θ_3	θ_{12}	θ_{13}	θ_{23}	Ref.
X-ray	75.8°	81.2°	25.3°	85°	29.5°	59°	(3)
EPR				(85 ± 2)°	(30 ± 2)°	(60 ± 2)°	Present work

optical absorption spectra of both $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ and $(\text{Cu:Zn}) \text{SiF}_6 \cdot 6\text{H}_2\text{O}$ have been studied by Pappalardo (8). In $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ the 78 K optical spectrum consists of a weak shoulder at $10,870 \text{ cm}^{-1}$ and a very strong absorption peak at $13,330 \text{ cm}^{-1}$.

Billing and Hathaway (9) have established from polarized optical studies on several tetragonally distorted elongated octahedral copper(II)-oxygen systems (9) that the relative order of the ligand field energy levels is $B_{1g} < A_{1g} < B_{2g} < E_g$.

From our observation that $g_{\parallel} > g_{\perp}$ in $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$, B_{1g} should be the ground state. The double degeneracy of the state 2E_g is also expected to provide a relatively high intensity for the ${}^2B_{1g} \rightarrow {}^2E_g$ transition, as observed (8). In view of the above, the bands at $10,870$ and $13,300 \text{ cm}^{-1}$ may be assigned to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively.

The following expressions for g_{\parallel} and g_{\perp} are obtained from second-order perturbation theory (10):

$$g_{\parallel} = 2 \left[1 - \frac{4\alpha_{\parallel}^2 \lambda_0}{E_{B_{2g}} - E_{B_{1g}}} \right], \quad [4]$$

$$g_{\perp} = 2 \left[1 - \frac{\alpha_{\perp}^2 \lambda_0}{E_{E_g} - E_{B_{1g}}} \right]. \quad [5]$$

The covalent reduction parameters α_{\parallel} and α_{\perp} have been estimated from the experimental g values and the ligand field splittings using Eqs. [4] and [5]. The values so obtained, $\alpha_{\parallel} = 0.80$ and $\alpha_{\perp} = 0.61$, are quite consistent with the elongated octahedral structures of copper(II) complexes at A sites.

TABLE 2

EXPERIMENTAL VALUES OF g_{\parallel} AND g_{\perp} IN $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ OBTAINED FROM FIG. 1 USING THE VALUES GIVEN IN TABLE 1

Curves employed	g_{\parallel} ±0.003	g_{\perp} ±0.003	g ±0.003
1	2.390	2.093	
2	2.390	2.093	
3	2.388	2.093	
4			2.093

(ii) *Nearly isotropic spectrum at high field.* At the microwave frequency $\nu = 23.54$ GHz we found an EPR line at high field (4 in Fig. 1) which is almost independent of orientation of the magnetic field in the rhombohedral plane of the crystal. The corresponding g value was found to be ~ 2.093 . Recent measurements (7) at Ku ($\nu \approx 16.16$ GHz) and Ka band ($\nu \approx 34.6$ GHz) in different planes (001) and (110) of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ confirmed the existence of this line, which remains almost isotropic at 4.2 K. This is significantly different from the isotropic g spectrum ($g = 2.23$) obtained in $\text{Cu(II):ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ (1). The width of this line varied between 50 and 100 G. It may be noted that the isotropic g values of Cu(II) ions (under a trigonally distorted or regular octahedral field) in several other systems, e.g., copper bismuth nitrate, copper lanthanum nitrate, copper magnesium lanthanum nitrate, copper bromate hexahydrate, copper in magnesium oxide (11–13) are close to 2.20 in the dynamic Jahn–Teller regime.

The copper–water (B site) (3) and zinc–water distances (2) are nearly equal (2.074 Å in $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ and 2.078 Å in $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$). As observed by Pappalardo (8) the ligand field splittings are not much different in these complexes. Therefore the low isotropic g value in $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ ¹ is unlikely to be resulting from a much larger covalency than in $\text{Cu:ZnSiF}_6 \cdot 6\text{H}_2\text{O}$.

Ham (14) showed that in the case of ions with 2E orbital doublet ground states, the dynamic Jahn–Teller effect introduces additional reduction parameters in the spin Hamiltonian of the paramagnetic ion when the Jahn–Teller coupling is weak and linear. Such a theory, however, does not seem to be tenable in this case as corresponding spectra should have cubic anisotropy symmetry.

It is to be noted that the situation of the B-site copper complex in $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ is somewhat different from the Jahn–Teller copper systems studied so far in the sense that each dynamic Jahn–Teller Cu(II) ion at a B site in $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ is surrounded by six nearest-neighbor anisotropic Cu(II) ions at A sites, the separation being ~ 9.09 Å (15). Further investigation of the Jahn–Teller aspect of this site is in progress.

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¹ Recent measurements (7) in single crystals of $\text{CuSiF}_6 \cdot 6\text{D}_2\text{O}$ also show the existence of an isotropic line with $g \approx 2.09$.

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