

EPR investigation of Cu^{2+} tetramers in ferroelectric CsH_2PO_4

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EPR study of CsH_2PO_4 (CDP) single crystals with 0.005 mol % of Cu^{2+} at room temperature reveals isolated Cu^{2+} ($S = \frac{1}{2}$) complexes with four ligand coordination and spin Hamiltonian parameters $g_{\parallel} = 2.2575$, $g_{\perp} = 2.1866$, $A_{\parallel} = 30$ G, and $A_{\perp} = 27$ G. At temperatures below 250 K the spectra were observed to have fine structure and are described as arising from a Cu^{2+} tetramer with effective spin $S = 2$ and spin Hamiltonian parameters $D = 0.181$ cm^{-1} , $E = -0.081$ cm^{-1} , $a = 0.001$ cm^{-1} , $b = 0$, and $c = -0.021$ cm^{-1} . Also reported are transitions within the $S = 1$ multiplet of the tetramer, and a microscopic model of superexchange interaction has been used to evaluate the parameters $D_x = 0.543$ cm^{-1} and $E_x = -0.159$ cm^{-1} . A tetramer model as well as a temperature dependence of the ratio of tetramer-to-single-ion intensity is presented.

I. INTRODUCTION

In recent years cesium dihydrogen phosphate (CDP) and the deuterated DCDP have been studied with great interest because they have a one-dimensional-like structure of hydrogen (deuterium) bonds.¹⁻⁶ CDP belongs to the space group $P2_1/m$ (C_{2h}^2) in the monoclinic system¹ and undergoes a phase transition to the ferroelectric phase at 154 K with the space group $P2_1$ (C_2^2). In order to study these phase transitions by electron paramagnetic resonance (EPR) methods, we grew single crystals of CDP doped with Cr^{5+} (Ref. 7) and with Cu^{2+} . In the latter case the data show the expected single-ion (Cu^{2+} , $S = \frac{1}{2}$) spectra but, in addition, spectra indicating a rare tetrameric complex with $S = 2$ are observed. In this paper we report the details of these EPR spectra using a spin Hamiltonian model with $S = 2$ to evaluate the fine-structure parameters for the tetramer. A model of four exchange-bonded copper ions in the CDP structure is used to explain the tetrameric complex. In addition, a spectrum suggesting transitions within the $S = 1$ multiplet of the tetramer has been observed and is explained by a superexchange model first proposed by Kurzyński.^{8,9} The details of the ferroelectric properties and phase-transition phenomena as exhibited in the EPR line splitting will be presented elsewhere.

II. CRYSTAL STRUCTURE AND EXPERIMENTAL PROCEDURE

CDP can be described as having two kinds of one-dimensional chains of $(\text{PO}_4)^{3-}$ units connected by hydrogen bonds.^{1,2} One chain is composed of $\text{O}_1-\text{H}\cdots\text{O}_2$ bonds along the c axis with bond lengths equal to 2.537 Å and with the protons already oriented at room temperature. The second chain has $\text{O}_3-\text{H}\cdots\text{O}_4$ bonds along the ferroelectric b axis with lengths of 2.472 Å and with protons that are disordered at $T > T_c$.

Single crystals of CDP were grown by slow evaporation from the saturated water solution of a mixture of Cs_2CO_3

and H_3PO_4 in the molar ratio of 1:2 and containing 0.3 mol % of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. This resulted in a single ion Cu^{2+} replacing Cs^+ to a concentration in the crystal of about 0.005 mol %. The EPR spectrum anisotropy was measured with a Varian Associates X-band spectrometer with 100 kHz modulation and a nitrogen-gas blow-through system for temperature control and stabilization. The orthogonal coordinate system used to interpret the EPR measurements was chosen as follows: $X \parallel c$, $Y \parallel -b$, and $Z \parallel a^*$, with a^* perpendicular to the b - c plane in accord with the crystallographic axis system.¹

III. EXPERIMENTAL RESULTS

At room temperature two magnetically equivalent Cu^{2+} complexes ($S = \frac{1}{2}$) related by a twofold screw axis parallel to the b axis were observed. The spin Hamiltonian parameters and direction cosines for these single Cu^{2+} complexes are listed in Table I. At temperatures below about 250 K a new spectrum with fine structure appears and shows anisotropy for crystal rotation around the ferroelectric b axis. This spectrum is shown in Fig. 1 and is seen to have a minimum between two maxima centered on the principal axis of the crystal field (z). This same behavior was observed by Stankowski and Maćkowiak¹⁰ and by Maćkowiak and Kurzyński in their data for copper-doped triglycine fluoroberyllate (TGFB: Cu^{2+}). They analyzed their data in terms of a Cu^{2+} tetramer and

TABLE I. Spin Hamiltonian parameters and the direction cosines for the CDP Cu^{2+} ion.

| Spin Hamiltonian parameters | Direction cosines of z principal axis | | |
|-----------------------------|---|--------|--------|
| | l | m | n |
| $g_{\parallel} = 2.2575$ | 0.0292 | 0.1736 | 0.9698 |
| $g_{\perp} = 2.1866$ | | | |
| $A_{\parallel} = 30$ G | | | |
| $A_{\perp} = 27$ G | | | |

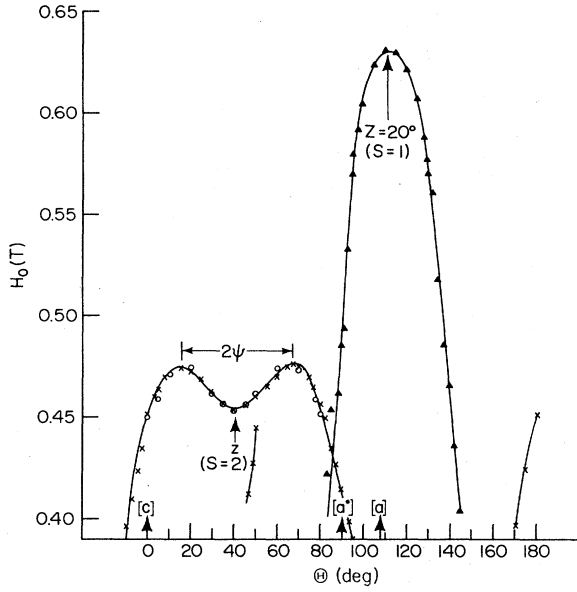


FIG. 1. EPR fine-structure spectrum anisotropy for quintet ($S=2$) and triplet ($S=1$) systems with the b axis as the axis of crystal rotation in the magnetic field. The angle 2Ψ is defined in the text. Solid line with cross points is the experimental anisotropy for $S=2$.

showed that the double minimum curve is characteristic of the $S=2$ state of such a tetramer. Since the space-group symmetry in CDP is the same, namely, $P2_1/m$, we will follow their analysis below to describe our double minimum curve.

Considering the rhombic symmetry of the crystal field, the following spin Hamiltonian at zero magnetic field appears as

$$\begin{aligned} \mathcal{H}(2) = & -\left(\frac{2}{3}\right)^{1/2} DP_0^2(S) + E[P_2^2(S) + P_{-2}^2(S)] \\ & + a\left\{\left(\frac{14}{15}\right)^{1/2} P_0^4(S) + \frac{1}{3}[P_4^4(S) + P_{-4}^4(S)]\right\} \\ & + b\left\{-5\left(\frac{14}{15}\right)^{1/2} P_0^4(S) + \frac{7}{3}[P_4^4(S) + P_{-4}^4(S)]\right\} \\ & + \left(\frac{7}{3}\right)^{1/2} c[P_2^4(S) + P_{-2}^4(S)], \end{aligned} \quad (1)$$

where the irreducible spherical tensor operators are as follows:

$$\begin{aligned} P_0^2(S) = & -\frac{3}{\sqrt{6}}[S_z^2 - \frac{1}{3}S(S+1)], \quad P_{\pm 2}^2 = \pm S_{\pm}^2 \\ P_0^4(S) = & \frac{1}{\sqrt{280}}[35S_z^4 + 25S_z^2 - 30S(S+1)S_z^2 \\ & + 3S^2(S+1)^2 - 6S(S+1)], \\ P_{\pm 2}^4(S) = & \frac{1}{\sqrt{28}}S_{\pm}^2[7S_z^2 \pm 14S_z - S(S+1) + 9], \\ P_{\pm 4}^4(S) = & \frac{1}{4}S_{\pm}^4, \end{aligned} \quad (2)$$

and $S_{\pm} = S_x \pm iS_y$. D, E, a, b, c are the usual crystal-field parameters. In the strong field approximation, i.e., when the Zeeman energy $g\beta H_0 \gg D, E, a, b, c$, one obtains¹¹ the following equations for the resonance magnetic field H_0

for the transition among quintet ($S=2$) levels:

$$B_0 \begin{pmatrix} 1 \leftrightarrow 0 \\ 0 \leftrightarrow -1 \end{pmatrix} = \frac{1}{g\beta} [h\nu \mp \frac{1}{2}(u - 10v)], \quad (3)$$

$$B_0 \begin{pmatrix} 2 \leftrightarrow 1 \\ -1 \leftrightarrow -2 \end{pmatrix} = \frac{1}{g\beta} [h\nu \mp \frac{1}{2}(3u + 10v)],$$

where h is Planck's constant and

$$\begin{aligned} u = & D(3\cos^2\theta - 1) + 3E\cos 2\phi \sin^2\theta, \\ v = & (0.1a - 0.5b)(5\cos^2\theta + 3 - 8\sin^2\theta) \\ & + c\cos 2\phi \sin^2\theta(7\cos^2\theta - 1) \\ & + (0.5a + 3.5b)\cos 4\phi \sin^4\theta. \end{aligned} \quad (4)$$

In these expressions, θ is the polar angle and ϕ is the azimuthal angle of the external magnetic field H_0 with respect to the crystal-field principal axes xyz . The angle ϕ is defined as $\phi=0^\circ$ for H_0 in the x - z plane and $\phi=90^\circ$ for H_0 in the y - z plane.

Equations (3) and (4) are used to evaluate the spin Hamiltonian parameters D, E, a, b, c by assuming single ion g_{\parallel} and g_{\perp} and by fitting the experimental points near the crystal-field z axis in the x - z plane ($\phi=0$) for $S=2$. The fit is shown in Fig. 1 as the solid line through the crosses.

The values of the spin Hamiltonian parameters and of the direction cosines of the xyz axes with respect to the laboratory system XYZ axes are listed in Table II. The accuracy of the fit is checked by evaluating H_0 values from Eqs. (3) and (4), using these parameters. The agreement of H_0 from experimental (solid line with cross points in Fig. 1) and evaluated (circles) values is satisfactory.

The anisotropy of the transition $0 \leftrightarrow -1$ exhibits, for H_0 near the z axis ($S=2$), an additional resonance field extremum due to the a, b, c parameters. This behavior is anomalous when compared with the expected $3\cos^2\theta - 1$ behavior. Defining 2Ψ to be the angle between the maxima (see Fig. 1) and for $\phi=0$ (x - z plane) we find

$$\cos 2\Psi = \frac{-3(D-E) + 60b - 10c}{37a - 125b - 70c}. \quad (5)$$

Substituting the spin Hamiltonian parameter values from Table II into Eq. (5) gives $2\Psi=49^\circ$ which should be compared to the experimental value of 51° . On the other hand, the line with the maximum value of resonance field

TABLE II. Spin Hamiltonian parameters and the direction cosines of xyz axes with respect to XYZ axes for CDP Cu^{2+} quintet ($S=2$) spectrum.

| Spin Hamiltonian parameters | Direction cosines of xyz axes | | | |
|-----------------------------|---------------------------------|---------|-----|--------|
| | l | m | n | |
| $D=0.181 \text{ cm}^{-1}$ | x | -0.6428 | 0 | 0.7660 |
| $E=-0.081 \text{ cm}^{-1}$ | y | 0 | 1 | 0 |
| $a=0.001 \text{ cm}^{-1}$ | z | 0.7660 | 0 | 0.6428 |
| $b=0$ | | | | |
| $c=-0.021 \text{ cm}^{-1}$ | | | | |

$H_0 = 0.635$ T (Fig. 1) for H_0 near around the a^* axis cannot be fitted by the same spin Hamiltonian parameters.

In order to interpret this latter line we turn to the theoretical work of Kurzyński *et al.*⁹ who, also considering the problem of TGFB:Cu²⁺ and extending the earlier work, showed that the remaining single fine-structure line can be interpreted as a transition within one of the triplets. Because the energetic structure of the cluster is complicated, they found it inconvenient to analyze the spectrum by means of a Hamiltonian describing the whole manifold of low-lying levels. Instead they used an effective spin Hamiltonian for the individual multiplets with parameters that more directly describe the interactions within a cluster. This model includes both isotropic and anisotropic superexchange interactions between the four copper ions and leads to a splitting of the 16-fold spin-degenerate ground state of the copper cluster into one quintet ($S=2$), three triplets ($S=1$), and two singlets ($S=0$). The spin Hamiltonian has the following form:

$$\begin{aligned} D &= \frac{1}{4}(B_{0+} + B_{1+}) + \frac{1}{252A} [3(B_{0+}^2 + 9B_{0-}^2) - (B_{1+}^2 + 9B_{1-}^2) - 6(B_{0+}B_{1+} + 9B_{0-}B_{1-})], \\ E &= -\frac{1}{12}(3B_{0+} - B_{1+}) - \frac{1}{252A} [3(B_{0+}^2 + 9B_{0-}^2) - (B_{1+}^2 + 9B_{1-}^2) + 2(B_{0+}B_{1+} + 9B_{0-}B_{1-})], \\ a &= \frac{1}{144A} [3(B_{0+}^2 + 9B_{0-}^2) + (B_{1+}^2 + 9B_{1-}^2)], \\ b &= \frac{1}{6(336A)} [3(B_{0+}^2 + 9B_{0-}^2) - (B_{1+}^2 + 9B_{1-}^2) - 6(B_{0+}B_{1+} + 9B_{0-}B_{1-})], \\ c &= \frac{1}{336A} [3(B_{0+}^2 + 9B_{0-}^2) - (B_{1+}^2 + 9B_{1-}^2) + 2(B_{0+}B_{1+} + 9B_{0-}B_{1-})], \end{aligned} \quad (8)$$

where $B_{0\pm} = B_{0a} \pm B_{0b}$, $B_{1\pm} = B_{1a} \pm B_{1b}$, and $A_{ij} \equiv A$.

If all spin Hamiltonian parameters are different from zero some approximate relation between the parameters is necessary in order to compare the phenomenological parameters of Eq. (8) with the experimental values. For our case of CDP:Cu²⁺, the experimental value for b is $b \equiv 0$ and we can evaluate the B_{0+} and B_{1+} parameters without additional simplification. By combining the remaining expressions of Eq. (8), the following relations are obtained for the quintet transitions:

$$D = \frac{1}{4}(B_{0+} + B_{1+}), \quad (9)$$

$$E = -\frac{1}{12}(3B_{0+} - B_{1+}) + \frac{4}{3}c, \quad (10)$$

which in turn lead to the following B_{0+} and B_{1+} parameters:

$$B_{0+} = D - 3E + 4c, \quad (11)$$

$$B_{1+} = 3(D + E) - 4c.$$

For the transition between triplet levels ($S=1$), the Hamiltonian with rhombic crystal-field symmetry, Eq. (1), is reduced to the form

$$\mathcal{H}(1) = -\left(\frac{2}{3}\right)^{1/2} D_x P_0^2(S) - E_x [P_2^2(S) + P_2^{-2}(S)], \quad (12)$$

where $x = 1, 2, 3$, and¹¹

$$\mathcal{H}_0 = \sum_{i>j} A_{ij} S_i S_j + V, \quad (6)$$

where A_{ij} is the isotropic superexchange constant and V is the anisotropic superexchange Hamiltonian. V is considered to be a perturbation and is given by

$$\begin{aligned} V &= B_{0f}[(S_1 \cdot S_3 - 3S_{1y}S_{3y}) + (S_2 \cdot S_4 - 3S_{2y}S_{4y})] \\ &\quad + B_{0g}[(S_1 \cdot S_2 - 3S_{1y}S_{2y}) + (S_3 \cdot S_4 - 3S_{3y}S_{4y})] \\ &\quad + B_{1f}[(S_{1z}S_{3z} - 3S_{1x}S_{3x}) + (S_{2z}S_{4z} - S_{2x}S_{4x})] \\ &\quad + B_{1g}[(S_{1z}S_{2z} - S_{1x}S_{2x}) + (S_{3z}S_{4z} - S_{3x}S_{4x})]. \end{aligned} \quad (7)$$

Here, B_{0f} , B_{0g} , B_{1f} , and B_{1g} are four independent parameters describing the symmetric anisotropic superexchange in the cluster in accord with the model presented in Fig. 2. Applying perturbation theory to second order, Kurzyński *et al.*⁹ obtain the following expressions for the phenomenological parameters occurring in Eq. (1):

$$\begin{aligned} D_1 = -D_2 &= -\frac{3}{4}B_{1-}, \quad E_1 = -E_2 = -\frac{1}{4}B_{1-}, \\ D_3 &= \frac{3}{4}(B_{0+} + B_{1+}), \quad E_3 = -\frac{1}{4}(3B_{0+} - B_{1+}). \end{aligned} \quad (13)$$

Evaluating Eq. (11) by using the experimental values of

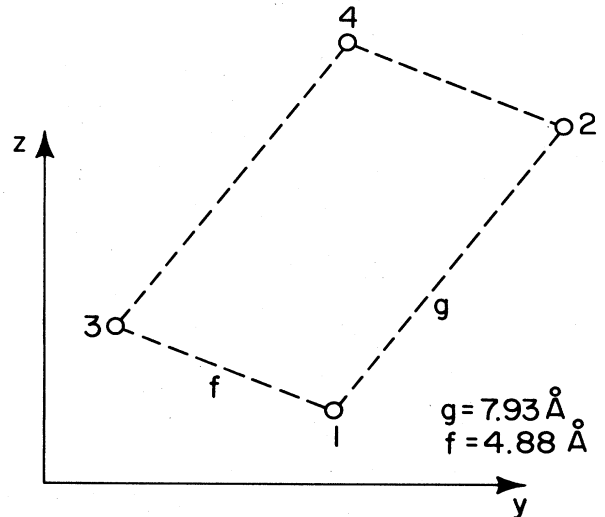


FIG. 2. Labeling of copper ions and their separation distance in the tetramer. $\{xyz\}$ is the space of the spin components and f and g are the actual distances between copper ions.

TABLE III. Direction cosines for xyz axes with respect to XYZ axes for CDP Cu^{2+} triplet ($S=1$) spectrum.

| | l | m | n |
|-----|--------|--------|--------|
| x | 0.8516 | 0.3420 | 0.3971 |
| y | 0 | 0.9397 | 0.8516 |
| z | 0.3971 | 0.3420 | 0.8516 |

D , E , a , b , and c obtained for the quintet transition, we have $D_3=0.543 \text{ cm}^{-1}$ and $E_3=-0.159 \text{ cm}^{-1}$.

Finally these values of D_3 and E_3 may be substituted into the expression for the $0 \leftrightarrow -1$ transition between triplet levels giving a resonance field of

$$H_0 = (1/g\beta) \left\{ h\nu + \left(\frac{1}{2} \right) [D_3(3 \cos^2 \theta_3 - 1) + 3E_3 \sin^2 \theta_3 \cos 2\phi_3] \right\}, \quad (14)$$

where θ_3 and ϕ_3 are the polar and azimuthal angles of the magnetic field H_0 with respect to the xyz crystal-field axes for the triplet spectrum.

The direction cosines for the xyz axes of the triplet system with respect to the XYZ laboratory system are listed in Table III. Figures 3(a) and 3(b) show the xyz axes orientations for both the quintet and triplet spectra. It was found (Table III) that the z axis of the triplet spectrum makes an angle of 25° with the a (Z) axis in the a^*-c plane and $\theta_0=20^\circ$ with the a^*-c plane. These data are shown as triangles on Fig. 1. As a result, the anisotropy in the a^*-c plane for the triplet spectrum can be described by Eq. (14) with $\theta_3 = \arccos(\cos \theta_0 \cos \theta)$ and $\phi_3 = 20^\circ$ where θ is the angle in the a^*-c plane. For $\theta=0^\circ$ and $\phi_3=20^\circ$ (the position of the maximum value of H_0 in the a^*-c plane for the triplet spectrum, Fig. 1), Eq. (14) gives $H_0=0.707 \text{ T}$ which should be compared to the experimental value $H_0=0.633 \text{ T}$.

To compare the expressions of Eq. (8) with experiment we assume $A_{ij} \equiv A$ which is not quite true for our cluster model (see Fig. 2). Nevertheless, the agreement with the experimental values D_x and E_x is qualitatively good.

As mentioned above, the fine structure of the additional spectrum below 250 K is probably caused by the four-ion anisotropic interaction. Although it could also be due to pure magnetic dipole-dipole interactions, that effect is

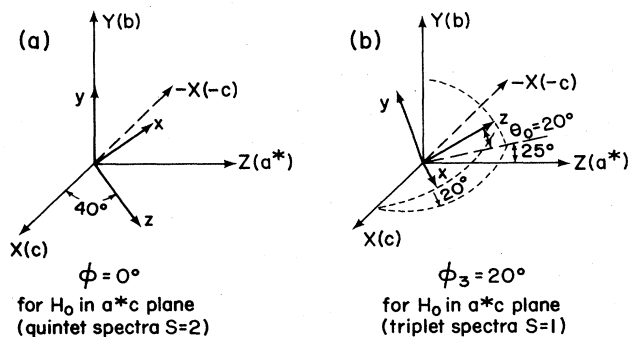


FIG. 3. (a) and (b) xyz axis orientations for the quintet and triplet spectra with respect to the XYZ system.

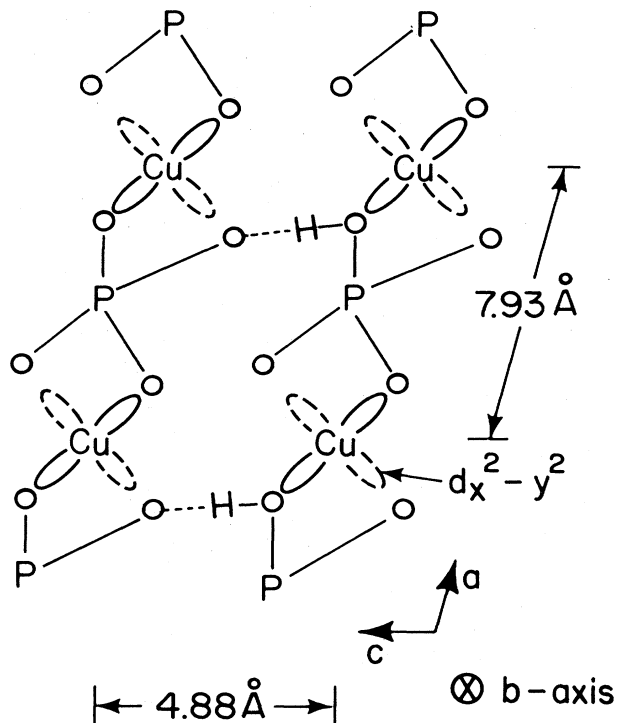


FIG. 4. Model of the tetrameric copper complex showing the superexchange paths.

probably negligible here since the contribution of the dipole-dipole interaction decreases as $(1/r)^3$ and for CDP the two pertinent distances are 4.88 Å and 7.93 Å. The principal crystal-field z axis of each of the four single Cu^{2+} ions lies in the a^*-c plane which is also the plane of the crystal-field z axis of the tetramer. These EPR data as well as neutron and x-ray structural data seem to be convincing evidence for the tetramer cluster model presented in Fig. 4.

The superexchange interaction, also shown in Fig. 4,

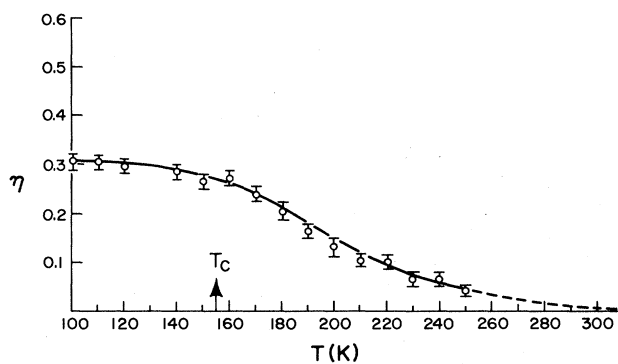


FIG. 5. Ratio η of the total intensity of the tetramer resonance to the intensity of the single-ion resonance as a function of temperature.

arises through Cu-O-P-O-Cu paths between pairs of Cu^{2+} ($S = \frac{1}{2}$) complexes. The superexchange by the hydrogen bonds is also included, but a comparison with $\text{DCDP}:\text{Cu}^{2+}$ data would be useful to corroborate this model.

To show the relationship between the tetramers and the isolated Cu^{2+} ions, we have plotted in Fig. 5 the ratio of the total intensity of the tetramer to that of the isolated ion as a function of temperature. The ratio remains small but clearly shows an increase as temperature is lowered indicating a conversion from single-ion copper to the tetrameric state. By extrapolating to high temperature where no tetramers appear (about 310 K; see Fig. 5) we have a dissociation energy of about 216 cm^{-1} .

It appears that at room temperature at which the $\text{CDP}:\text{Cu}^{2+}$ crystals were grown, both isolated Cu^{2+} complexes and four-ion coupled complexes (tetramers) are formed during crystallization, and that as temperature is lowered some of the isolated Cu^{2+} complexes are coupled to the tetramers.

V. DISCUSSION

Tetramers have been investigated theoretically^{8,9} as well as experimentally¹⁰⁻¹⁴ but examples of high spin value complexes of Cu^{2+} are very rare. We have used the cluster theory developed especially for $\text{TGFB}:\text{Cu}^{2+}$,⁹⁻¹¹ which has the same space group as CDP , to satisfactorily describe the spin Hamiltonian parameters in $\text{CDP}:\text{Cu}^{2+}$. The model used is only phenomenological but is useful in describing the fine structure in higher spin EPR spectra from crystal symmetries as low as rhombic. The line from transitions between the $S=1$ triplet levels could only be fitted qualitatively since we assumed the exchange constant A_{ij} to be isotropic and possibly because of the effects of lower than rhombic symmetry.

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