

# Observation of the cubic-field splitting of an excited $S = 2$ manifold in a cubic copper tetramer

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EPR measurements on single crystals of  $\text{Cu}_4\text{OCl}_6(\text{triphenylphosphine oxide})_4$  at liquid helium temperatures in the frequency ranges 14–17 and 34–35 GHz were fitted to a simple cubic  $S = 2$  spin Hamiltonian with  $g = 2.10 \pm 0.01$  and a zero-field splitting of  $(0.53 \pm 0.01) \text{ cm}^{-1}$ . From the decrease in intensity of the  $S = 2$  spectrum on cooling below 4.2 K and the absence of an  $S = 1$  spectrum, the  $S = 2$  manifold was deduced to lie  $(14 \pm 1) \text{ cm}^{-1}$  above a nonmagnetic ground state. The EPR results are used as a test of the various theories developed to explain the magnetic susceptibility of copper tetramers.

## I. INTRODUCTION

Polynuclear magnetic complexes in organometallic compounds have been used extensively to study exchange interactions in insulating materials.<sup>1–3</sup> Tetrameric complexes are of particular interest, since overall cubic symmetry may occur if the four identical magnetic ions lie at the corners of a regular tetrahedron. Powder magnetic susceptibility measurements have been made on a number of cubic tetrameric compounds of the composition  $\text{Cu}_4\text{OX}_6\text{L}_4$ , where X represents a chloride or bromide ion and L represents a neutral or ionic ligand bonded to a  $\text{Cu}^{2+}$  ion.<sup>4–9</sup> Theoretical studies have focussed on a maximum in the temperature dependence of the effective magnetic moment that is observed for some compounds of this type, which would not occur in the case of a dominant isotropic Heisenberg exchange interaction with equal coupling constants between each pair of  $\text{Cu}^{2+}$  ions of the tetramer.<sup>5,10–13</sup> Such an interaction would lead to a set of energy levels characterized by the total spin  $S$ , spaced according to the Landé interval rule. The various models used to explain the maximum have included appreciable intermolecular exchange,<sup>10</sup> dominant antisymmetric exchange,<sup>3,11</sup> the production of large deviations from the Landé rule by nonequivalent Heisenberg coupling constants,<sup>12</sup> and by a dynamic modulation of the intramolecular exchange interaction.<sup>13</sup>

In this paper, the results of the first electron paramagnetic resonance (EPR) study of single crystals of a cubic copper tetramer are presented and discussed in the light of the models mentioned above. The observed spectrum was fitted to a Hamiltonian for an effective spin  $S = 2$  with Zeeman and zero-field splitting terms. To the best of our knowledge, this is also the first reported EPR study in which the cubic zero-field splitting of an  $S = 2$  manifold has been measured.<sup>14</sup>

## II. EXPERIMENTAL

### A. Material

Single crystals of  $\text{Cu}_4\text{OCl}_6(\text{TPPO})_4$ , where TPPO represents triphenylphosphine oxide  $\text{C}_{18}\text{H}_{15}\text{PO}$ , were prepared

from a mixture obtained by adding cuprous chloride dihydrate to a sample of TPPO dissolved in methyl isobutyl ketone, as described elsewhere.<sup>9</sup>  $\text{Cu}_4\text{OCl}_6(\text{TPPO})_4$  has a structure in which one  $\text{O}^{2-}$  ion is situated at the center of a regular tetrahedron of four  $\text{Cu}^{2+}$  ions.<sup>15</sup> Six Cl ions bridge adjacent  $\text{Cu}^{2+}$  ions. Each  $\text{Cu}^{2+}$  ion lies at the center of a trigonal bipyramidal structure, consisting of an equilateral triangle of Cl ions. The central  $\text{O}^{2-}$  ion and a neutral O atom (from the TPPO) lie on the trigonal axis. Nearest neighbor  $\text{Cu}^{2+}-\text{O}^{2-}$  and  $\text{Cu}^{2+}-\text{Cl}^-$  distances are 1.90 and 2.38 Å, respectively, while  $\text{Cu}^{2+}-\text{Cu}^{2+}$  separations within a molecule are 3.11 Å. There is one formula unit per unit cell with a lattice spacing of 12.22 Å.

### B. Measurements

The EPR measurements were made with conventional spectrometers operating in the frequency ranges 14–17 and 34–35 GHz, with the crystal mounted on a (100) face. The characteristic  $S = 2$  EPR spectra were observed at liquid helium temperatures. The rotational dependence of the 34 GHz EPR spectrum, shown in Fig. 1, demonstrates clearly the cubic symmetry characteristic of the system. Figure 2 shows the 34 GHz EPR spectra at 4.2 K for two [110] type directions separated by a rotation of 90°. Apart from differences in relative intensities, which are due to the orientation of the microwave field in the cavity, the two spectra are identical, consistent with cubic symmetry. A portion of the 34 GHz spectrum in a [100] direction is shown in Fig. 3.

The EPR spectra were fitted to a simple spin Hamiltonian containing an isotropic Zeeman term and a fourth degree cubic zero-field splitting term. With the external magnetic field parallel to a [100] direction, the spin Hamiltonian has the form

$$\mathcal{H}_S = g\beta HS_z + B_4(O_4^0 + 5O_4^4), \quad (1)$$

where  $B_4$  is the cubic field splitting parameter and  $O_4^0$  and  $O_4^4$  are spin operators.<sup>16</sup> The experimental data were fitted to the values

$$g = 2.10 \pm 0.01, \quad \text{and} \quad |B_4| = (0.0044 \pm 0.0001) \text{ cm}^{-1} \quad (2)$$

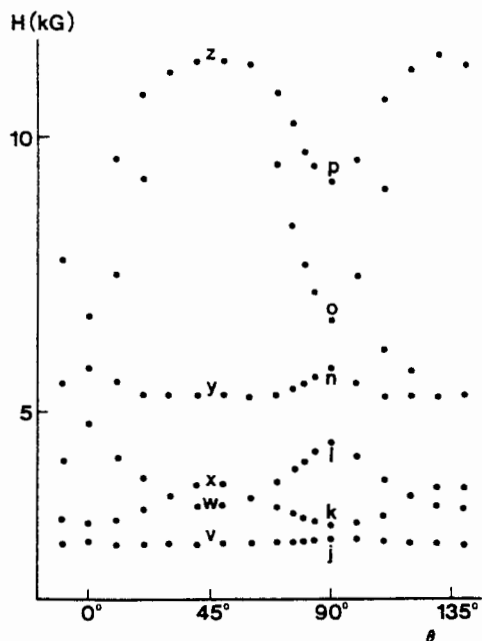


FIG. 1. The positions of the observed EPR resonance lines at 34 GHz are shown for various orientations in a (100) plane. The letters correspond to the spectra in Figs. 2 and 3, and to the transitions in Tables I and II.

leading to a zero field splitting magnitude  $\Delta = 120|B_4| \approx 0.53 \text{ cm}^{-1}$ . The measured and calculated fields and the peak-to-peak linewidths are given in Tables I and II for the [100] and [110] directions, respectively. Energy level diagrams for these two orientations showing the observed transitions are displayed in Figs. 4 and 5, respectively.

The temperature dependence of the EPR spectrum was investigated at liquid helium temperatures. The rapid decrease in intensity of one particular line on cooling below 4.2 K may be seen in Fig. 6. An estimate of  $(14 \pm 1) \text{ cm}^{-1}$  for the excitation energy of the  $S = 2$  manifold was obtained from these measurements, assuming highly excited  $S = 1$  manifolds. We were unable to determine the sign of  $B_4$ .

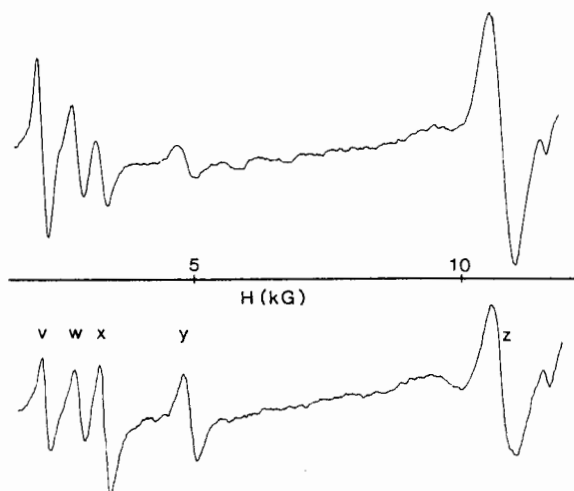


FIG. 2. EPR spectra at 34.6 GHz and 4.2 K in two [110] type orientations related by a  $90^\circ$  rotation in a (100) plane. The measured lines of the  $S = 2$  manifold are denoted by the letters v through z.

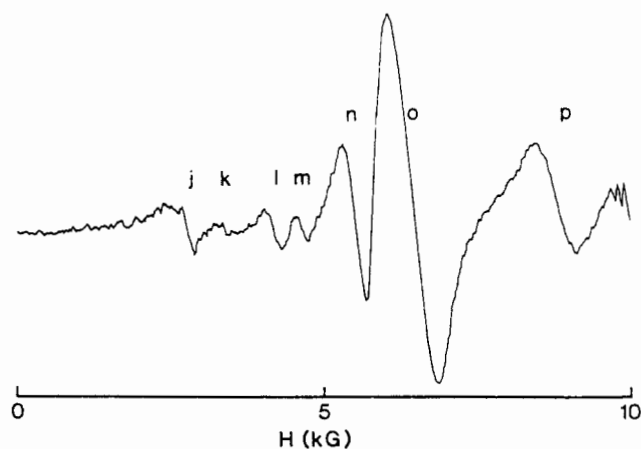


FIG. 3. A portion of the EPR spectrum at 34.6 GHz and 4.2 K in the [100] orientation. The measured lines of the  $S = 2$  manifold are designated by the letters j through p.

### C. Analysis of the EPR results

Since the EPR intensities decreased as the temperature was lowered below 4.2 K, the  $S = 2$  manifold was deduced to lie above a nonmagnetic ground state. Notably absent in the low temperature spectra was the anticipated isotropic resonance from the  $S = 1$  manifolds, which would be expected to occur near  $g = 2.10$ . The absence of this resonance could be due to a number of reasons, such as line broadening, possibly associated with relaxation processes within the three  $S = 1$  manifolds, or modifications of the energy level scheme by interactions other than isotropic Heisenberg exchange. One possibility is the existence of a mechanism which would cause the  $S = 1$  manifolds to lie appreciably above the  $S = 2$  manifold, while retaining an  $S = 0$  ground state. Consistent with this interpretation have been the computer analyses of recent magnetic susceptibility measurements on powdered samples of  $\text{Cu}_4\text{OCl}_6(\text{TPPO})_6$  carried out in these laboratories.<sup>9</sup> With  $g$  fixed at 2.10, the best fit of the data was made with the values  $E(1) = (85 \pm 13) \text{ cm}^{-1}$  and  $E(2) = (10 \pm 1) \text{ cm}^{-1}$ , where the symbol  $E(S)$  refers to the excitation energy level of a manifold of total spin  $S$  and  $E(0)$  is chosen to be

TABLE I. Measured and calculated resonance fields of allowed transitions<sup>a</sup> in the [100] direction at 4.2 K.

Transition <sup>b</sup>	Type	Frequency (GHz)	$\Delta H_{pp}$ (G)	$H_{\text{meas}}$ (kG)	$H_{\text{calc}}$ (kG)
$2 \leftrightarrow -2$ (j)	$\Delta M = 0$	34.63	120	2.55	2.62
$2 \leftrightarrow -1$ (k)	$\Delta M = 1$	34.63	130	2.80	2.82
$1 \leftrightarrow 2$ (s)	$\Delta M = 1$	15.35	140	2.34	2.41
	(m)	34.63	160	4.70	4.70
$0 \leftrightarrow 1$ (o)	$\Delta M = 1$	34.63	510	6.54	6.37
$-1 \leftrightarrow -2$ (t)	$\Delta M = 1$	14.69	260	7.49	7.46
	(t)	16.39	240	8.09	8.05
$2 \leftrightarrow 1$ (r)	$\Delta M = 1$	15.35	450	1.56	1.46
	(p)	34.63	520	8.95	8.87

<sup>a</sup> The transitions are labelled by their quantum numbers in a strong magnetic field. The letters in parentheses refer to the designations in Figs. 2 and 3.

<sup>b</sup> The forbidden transitions  $0 \leftrightarrow -2(1)$  and  $1 \leftrightarrow -1(n)$  were also observed. Near zero field at 15 GHz, several transitions overlap. These are designated (q) in Fig. 3.

TABLE II. Measured and calculated resonance fields of allowed transitions in the [110] direction at 4.2 K.

Transition <sup>a</sup>	Type	Frequency (GHz)	$\Delta H_{pp}$ (G)	$H_{means}$ (kG)	$H_{calc}$ (kG)
$2 \leftrightarrow -2$ (v)	$\Delta M = 0$	34.61	160	2.47	2.50
$1 \leftrightarrow -2$ (w)	$\Delta M = 1$	34.61	200	3.11	3.30
$2 \leftrightarrow -1$ (x)	$\Delta M = 1$	34.61	200	3.59	3.46
$1 \leftrightarrow -1$ (y)	$\Delta M = 0$	34.61	250	5.14	5.23
$2 \leftrightarrow 1$ (z)	$\Delta M = 1$	34.61	420	11.10	11.00

<sup>a</sup> The transitions are labeled by their quantum numbers in a strong magnetic field. The letters in parentheses refer to the designations in Figs. 1 and 4.

zero. The value of  $E(2)$  obtained from the temperature dependence of the EPR spectrum was  $(14 \pm 1) \text{ cm}^{-1}$ .

The absence of hyperfine structure in the observed spectra probably results from the large number of hyperfine configurations associated with the two copper isotopes of the four tetrameric ions together with line broadening due to the intermolecular dipole-dipole interaction between tetramers.

The isotropic  $g$  value may be understood in terms of the single ion Zeeman Hamiltonian<sup>17</sup>

$$\begin{aligned} \mathcal{H}_{ze} &= \beta \sum_{i=1}^4 \mathbf{S}_i \cdot \mathbf{g}_i \cdot \mathbf{H} \\ &= \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \text{smaller terms} \\ &\quad \text{not commuting with } S, \end{aligned} \quad (3)$$

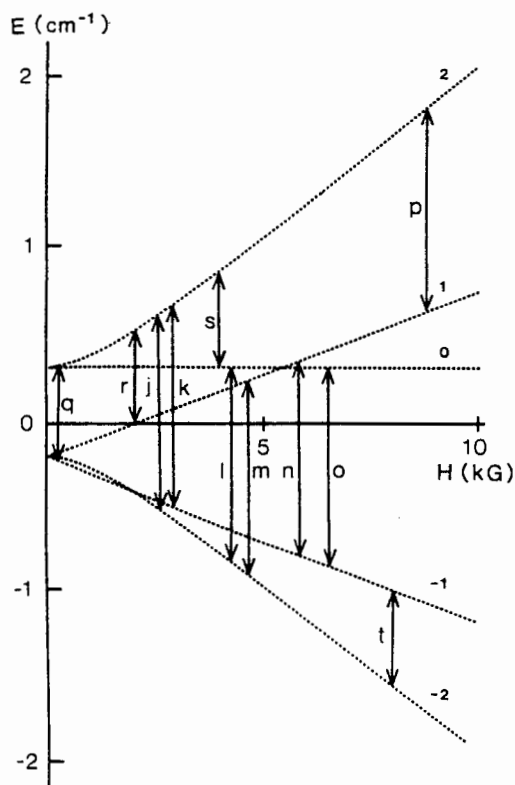


FIG. 4. An energy level diagram for the [100] orientation based on the spin Hamiltonian of Eq. (1). The observed transitions at 15 and 34 GHz are indicated by the double arrows, labeled to correspond to Table I and Fig. 2. The 34 GHz transition *s* has been omitted because of its near overlap with the 15 GHz transition *j*. The five levels are labeled on the right by their high-field values of  $M_S$ .

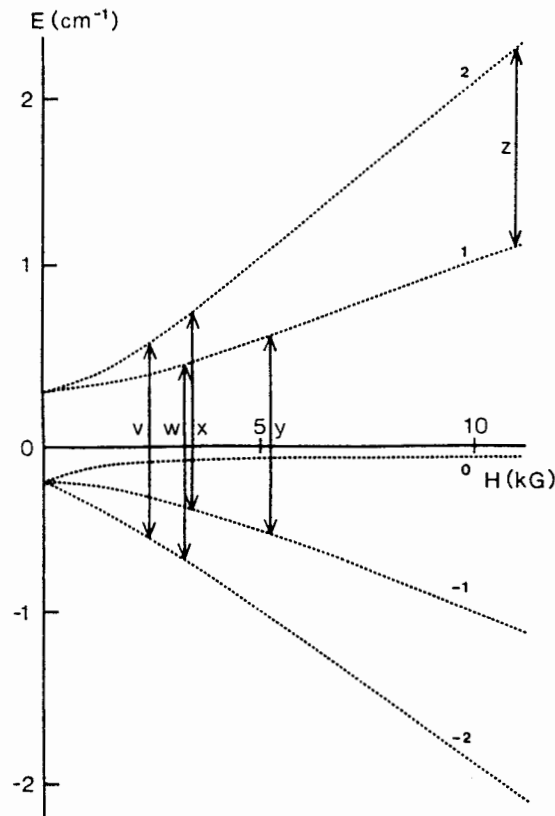


FIG. 5. An energy level diagram for the [110] orientation based on the spin Hamiltonian of Eq. (2). The observed 34 GHz transitions are indicated by the double arrows, labeled to correspond to Table II and Fig. 1. The five levels are labeled on the right by their high-field values of  $M_S$ .

where  $\mathbf{S} = \sum_i \mathbf{S}_i$  and  $\mathbf{g} = \frac{1}{4} \sum_i \mathbf{g}_i$ . The transformation of the single ion  $g$  tensors  $\mathbf{g}_i$  to the same coordinate system leads to the resulting isotropic value

$$g = (g_{\parallel} + 2g_{\perp})/3, \quad (4)$$

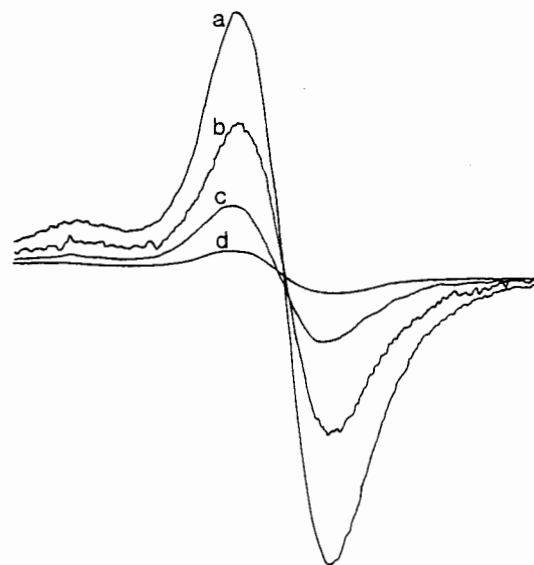


FIG. 6. A superposition of resonance curves for the transition *j* in the [100] direction (see Table II) at 35 GHz is shown for the same observation conditions at (a) 4.0 K, (b) 3.5 K, (c) 3.0 K, and (d) 2.5 K.

where  $g_{\parallel}$  and  $g_{\perp}$  are the principal components of each single ion  $g$  tensor.

Explaining the zero-field splitting  $\Delta$  is a more difficult task, since contributions to  $\Delta$  may be made by a number of additional terms in the magnetic Hamiltonian which do not commute with  $S$ , such as the intramolecular magnetic dipolar and pseudodipolar interactions, and antisymmetric exchange.<sup>18</sup> An order of magnitude calculation has indicated that the dipolar interaction in this case, assuming point  $\text{Cu}^{2+}$  dipoles, produces less than 0.2% of the measured splitting.

### III. DISCUSSION

In the Introduction, mention was made of the various models used to interpret the magnetic susceptibility data for cubic copper tetramers. These models are considered in turn below in the light of the EPR results.

The importance of intermolecular exchange in tetrameric compounds was suggested by Bertrand *et al.*<sup>19</sup> for a nickel tetramer, where the susceptibility data indicated the existence of weak intermolecular ferromagnetic coupling with a Curie temperature of 0.8 K. This model was applied to copper tetramers by Ginsberg and Lines.<sup>10</sup> However, long range ordering effects due to the relatively large intercluster exchange parameter have not been observed experimentally.<sup>12</sup> The EPR evidence against this model is indirect. The measured  $S = 2$  spectrum gives no evidence of long-range order, and the nonappearance of an  $S = 1$  spectrum cannot be explained by this model, which would not affect the Landé interval rule for splittings of the tetrameric levels.

Lines *et al.*<sup>6,11</sup> have suggested that materials containing isolated clusters of magnetic ions are ideally suited for the study of antisymmetric exchange interactions, since they combine high local symmetry with low spin-pair symmetry. Their detailed calculations do not produce an energy level scheme which is consistent with our EPR observations; that is, a slightly split spin quintet above a nonmagnetic ground state. Their justification for the large antisymmetric terms, which were used to fit the susceptibility data for a number of tetrameric copper compounds, was based on the assumption of a  ${}^2E$  orbital ground state for each individual  $\text{Cu}^{2+}$  ion. In such a case, however, one would expect a Jahn–Teller distortion to lift the orbital degeneracy.<sup>20</sup> Evidence in favor of an orbital singlet ground state for a trigonal bipyramidal structure has come from the optical studies of Hatfield *et al.*<sup>21,22</sup> on the complex  $\text{CuCl}_2^{3-}$ , where a singlet ground state was found to lie about  $8000 \text{ cm}^{-1}$  below the nearest excited level. In the case of an orbital singlet ground state, the antisymmetric exchange interaction would be small.<sup>5,18</sup>

Two recent models of Jones, Sams, and Thompson<sup>12,13</sup> have both involved dynamic distortions of the copper tetrahedron. In the earlier model, two nonequivalent coupling constants were used to fit the susceptibility data.<sup>12</sup> Their later model assumed isotropic coupling with a linear dependence on the interatomic separation.<sup>13</sup> The  $E$  and  $T_2$  vibrational modes, which lower the symmetry of the tetrahedron, reduce the degeneracies of the  $S = 0$  and  $S = 1$  manifolds. When applied to the EPR data, the main problem with these theories is in reconciling the best fits of the susceptibility

data with the cubic symmetry of the EPR spectrum. The totally dynamic situation of the later model, termed “fast fluxionality,” appears not to be in conflict with EPR data, since a dynamical averaging of the low symmetry components can occur.

While the recent work of Jones *et al.*<sup>12,13</sup> has been on the dynamic distortions of the tetrahedron, appreciable deviations from the Landé interval rule in exchange-coupled pairs have been attributed to exchange striction, which is a static effect.<sup>18,23</sup> The simplest representation of an exchange striction Hamiltonian for a pair is by means of a biquadratic term  $-j(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ . Of the normal modes of vibration of a regular tetrahedron, only the  $A_1$  mode preserves cubic symmetry, and so can make a static contribution consistent with the symmetry of the EPR spectrum. For this mode, a calculation similar to that given by Owen and Harris<sup>18</sup> leads to an exchange striction Hamiltonian of the form

$$\mathcal{H}_{es}(A_1) = -j \left( \sum_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j \right)^2,$$

which, for a  $\text{Cu}^{2+}$  tetramer, gives an energy contribution

$$E_{es}(A_1) = -\frac{1}{4} j [S^2(S+1)^2 - 6S(S+1) + 9],$$

where  $S$  is the total spin. The presence of such a term leads to deviations from the Landé interval rule, but an unrealistically high ratio of 10 for  $|j/J|$  is needed to fit the proposed energy level scheme for  $\text{Cu}_4\text{OCl}_6(\text{TPPO})_4$  given in Sec. II C.

In a recent study of the four-center Jahn–Teller effect in tetranuclear copper complexes, Polinger, Chibotaru, and Bersuker<sup>24</sup> have apparently obtained agreement with both EPR and magnetic susceptibility data. Unfortunately, details of this work are not yet available.

In conclusion, we note that single crystal EPR work on tetrameric compounds, such as carried out in this study, provides unambiguous information about the symmetry of the cluster and its effective magnetic moment, against which theories designed to explain powder susceptibility data may be rigorously tested.

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