

Cu²⁺ complex of *L*-isoleucine: A five-coordinate two-dimensional ferromagnet*

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Magnetic susceptibility and ESR measurements on the Cu²⁺ complex of the amino acid *L*-isoleucine (C₁₂H₂₄CuN₂O₄·H₂O) are reported. Between 4.2 and 0.24 K, the magnetic behavior is best described as due to a two-dimensional ferromagnetic Heisenberg interaction with $J_F/k = 0.120$ K. A transition to a magnetically ordered state takes place at $T_c = 0.117$ K. Well below T_c , a magnetic field of approximately 140 Oe applied in the *ac* plane causes a magnetic phase transition. A zero-temperature Hamiltonian is proposed to explain the behavior in applied field. In the model, spins in each layer are coupled by the ferromagnetic exchange and by an antisymmetric term of the form $\vec{D} \cdot \vec{S}_1 \times \vec{S}_2$ with $D/k = 0.012$ K. An antiferromagnetic exchange between the layers $J_{AF}/k = 0.02$ K produces the three-dimensional ordering.

INTRODUCTION

The Cu²⁺ complex of the amino acid *L*-isoleucine is an example of a five-coordinated transition-element ion in which the local coordination forms a square pyramid. Although there have been extensive spectroscopic measurements of similar systems,¹ and some magnetic measurements,² there have been no reports of the low-temperature magnetic behavior of five-coordinated systems. This paper reports on the magnetic susceptibility and electron-spin-resonance (ESR) spectra of powder and single-crystal samples of Cu²⁺ *L*-isoleucine monohydrate from 0.01 to 4.2 K.

The crystal structure is orthorhombic³ with four chemical formula units (C₁₂H₂₄CuN₂O₄·H₂O) in the unit cell. The unit-cell dimensions are $a = 9.451$, $b = 21.67$, and $c = 7.629$ Å, and the reported space group is $P2_12_12_1$. The copper lies approximately in the center of the base of a square pyramid. Two oxygens and two nitrogens form the corners of the base and a water oxygen completes the top

of the pyramid (Fig. 1). The molecules are hydrogen bonded along the *a* and *c* axes but are well isolated in the *b* direction. These structures will be referred to as "sheets" in the *ac* plane but, in fact, the molecules are very three dimensional; it is only the bonding which is two dimensional. This two-dimensional structure suggests the possibility of two-dimensional magnetic behavior.

EXPERIMENTAL

Copper *L*-isoleucine was prepared by reacting basic copper carbonate in water with *L*-isoleucine. The resulting dark blue solution was filtered and slowly evaporated near room temperature. The complex crystallized into thin deep blue diamond-shaped plates (Fig. 2) which were oriented by comparing the external morphology with the known lattice parameters using x-ray diffractometry. Since the magnetic susceptibility results indicate the possibility of nonstoichiometric copper, the copper content was determined by neutron activation analysis of a 35.6-mg powder sample. The results of this analysis gave 6.8 mg of copper or a concentration of $(19 \pm 2)\%$. The theoretical concentration of copper in the complex is 18.6%, so that to within the accuracy of the analysis there is no uncombined copper.

MAGNETIC SUSCEPTIBILITY—ZERO FIELD

The magnetic susceptibility of powder and aligned single-crystal samples was measured in a field of less than 5 Oe over the temperature range 0.01–4.2 K. Both conventional ac mutual-inductance coils and a superconducting quantum-interference-device (SQUID) magnetometer were used.⁴ The powder susceptibility and that measured along the three crystallographic axes exhibit similar behavior (Fig. 3). In all cases, the susceptibility is Curie-Weiss-like down to ap-

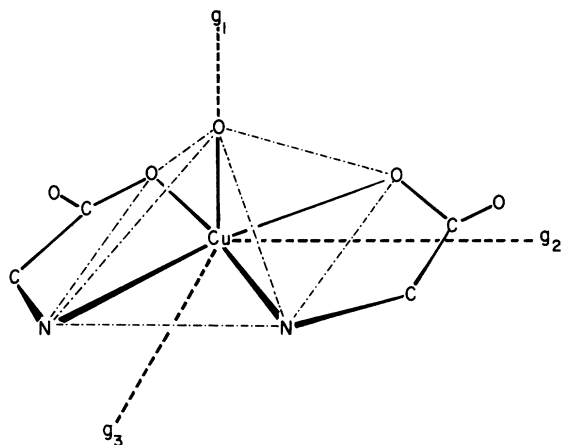


FIG. 1. Fivefold coordination of the Cu²⁺ ion with the principal axes of the *g* tensor.

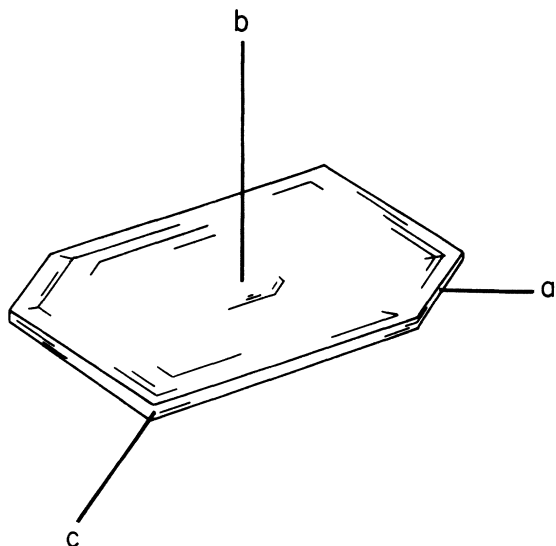


FIG. 2. External morphology of Cu^{2+} *L*-isoleucine monohydrate. The orthorhombic axes are labeled *a*, *b*, and *c*.

proximately 0.5 K and passes through a very large, well-defined peak ($\chi \approx 16$ emu/mole) at 0.117 K. Below this temperature the susceptibility falls, levels off, and begins to rise again near 0.03 K.

APPLIED FIELD

The ac susceptibility has been measured in applied static fields up to 200 Oe in the temperature range 0.01–0.30 K. At low fields the critical temperature is depressed for all orientations of

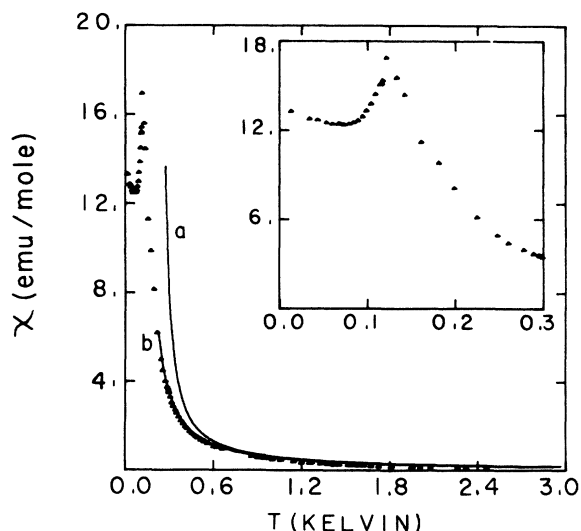


FIG. 3. Powder susceptibility of Cu^{2+} *L*-isoleucine monohydrate. Curve *a* is a Curie-Weiss fit, while curve *b* is the Rushbrooke and Baker high-temperature expansion.

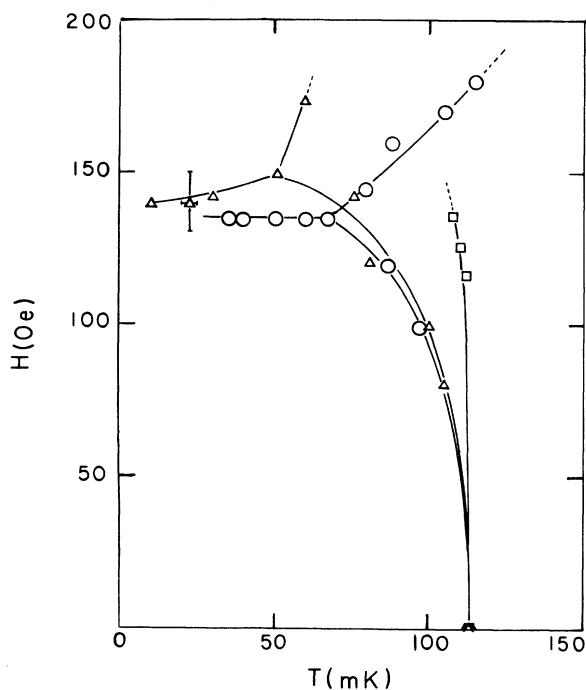


FIG. 4. Composite H - T phase diagram for Cu^{2+} *L*-isoleucine monohydrate. Δ : H parallel to *a*; \square : H parallel to *b*; \circ : H parallel to *c*.

the magnetic field but is somewhat more depressed with H applied parallel to *a* or *c* than with H parallel to *b*. At low temperatures a critical field is observed near $H_c = 140$ Oe with H applied parallel to *a* or *c*, but no such phenomenon is observed with H parallel to *b*. Figure 4 is a composite graph of the data taken along the three axes. There appears to be a triple point near $H_{TP} = 150$ Oe and $T_{TP} = 0.050$ K. We believe that these are the lowest-temperature critical-field experiments reported to date on a magnetic insulator.

ELECTRON SPIN RESONANCE

ESR experiments were performed on aligned single-crystal samples at temperatures near 1 K.

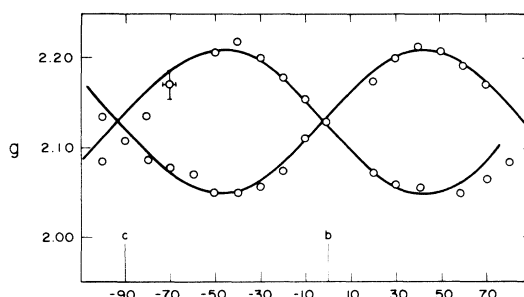


FIG. 5. Angle dependence of the ESR in the bc plane. The data were taken at $T = 1.1$ K and $f = 24.3$ GHz.

Rotation data were taken at X band about all three crystallographic axes. In addition, the *a*-axis rotation data were taken at K band to improve the resolution of the lines (Fig. 5). The rotation diagrams all exhibit twofold symmetry about the crystallographic axes. This is consistent with a point-group symmetry 222, which follows from the space group, $P2_12_12_1$.

The ESR signals for the *b*- and *c*-axis rotations consist of a single line of essentially constant width which exhibits only a slight *g*-factor anisotropy. The *a*-axis data consist of two lines (Fig. 6) with large *g*-factor anisotropy and, in addition, an anisotropy in the linewidth.

The rotation data for each axis was analyzed using the expression⁵

$$g^2 = \alpha + \beta \cos 2\phi + \gamma \sin 2\phi,$$

which determines the value of *g* at the relative rotation angle ϕ . The coefficients in this equation are

$$\alpha = \frac{1}{2}(g_+^2 + g_-^2), \quad \beta = \frac{1}{2}(g_+^2 - g_-^2) \cos 2\phi_+,$$

and

$$\gamma = \frac{1}{2}(g_+^2 - g_-^2) \sin 2\phi_+,$$

where the maximum and minimum *g* values (g_+ and g_-) occur at the relative angles ϕ_+ and ϕ_- , respectively. These parameters were used to calculate the principal values and principal

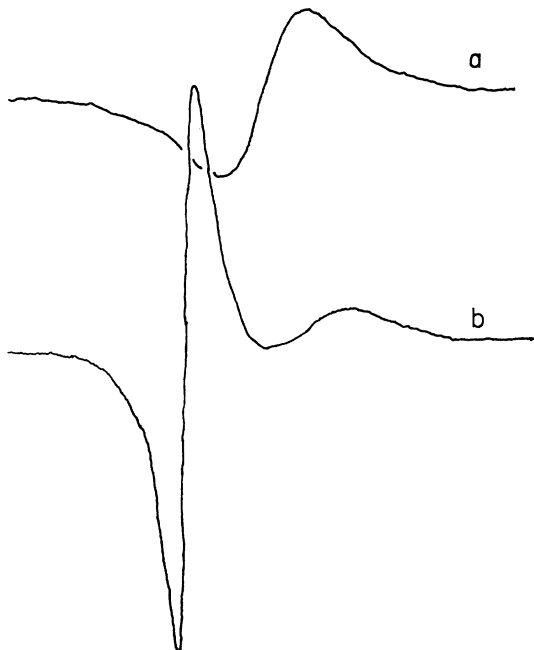


FIG. 6. ESR signals taken at $T = 1.1$ K and $f = 9.2$ GHz with H in the *bc* plane. Curve *b* is for H 50° from the *b* axis and curve *a* is for H parallel to *b*.

TABLE I. Principal values and direction cosines of the principal axes of the two *g* tensors.

	Site 1	Site 2
g_1	2.213 ± 0.005	2.213 ± 0.005
g_2	2.042 ± 0.005	2.042 ± 0.005
g_3	2.142 ± 0.005	2.142 ± 0.005
x_1	(0.00, 0.78, -0.63)	(0.00, 0.78, 0.63)
x_2	(0.00, 0.78, 0.63)	(0.00, 0.78, -0.63)
x_3	(1.00, 0.00, 0.00)	(1.00, 0.00, 0.00)

axes of the two *g* tensors which are listed in Table I. The derived principal axes lie very near the symmetry axes of the local coordination, as shown in Fig. 1. The two *g* tensors differ from one another only in that they are rotated $\pm 51^\circ$ from the crystallographic *b* axis in the *ac* plane.

The *g* values along the crystallographic axes are given in Table II. If one assumes that the anisotropy in the line width is due to unresolved hyperfine structure from the copper nucleus, one can estimate a hyperfine interaction of approximately 0.02 cm^{-1} , which is quite reasonable for copper.

DISCUSSION

The magnetic behavior above and below the transition temperature will be discussed separately. Well above T_c , the susceptibility fits a Curie-Weiss law with a positive (ferromagnetic) Weiss constant of $\Theta = 0.24$ K (Fig. 7). The deviations from Curie-Weiss behavior are best demonstrated by Fig. 8, which is a plot of $C/\chi T$ vs J/kT . On such a plot, a Curie-Weiss law is a straight line which intercepts the x axis at $\Theta = T$ (curve a). The data deviate drastically from Curie-Weiss behavior for $T < 1$ K. Curve *b* is obtained using the first ten terms of a high-temperature expansion by Baker *et al.*⁶ for a two-dimensional square net with (isotropic) Heisenberg exchange. The parameters which give the best fit to the data are $g = 2.15$ and $J/k = +0.120$ K (ferromagnetic). The system is, at best, only approximated by a square net, but a two-dimensional isotropic exchange is consistent with the geometry of the ions as well as the behavior below the transition in applied field.

There are three aspects of the data near and below the transition which are interesting and not entirely understood. The peak in the susceptibility is consistent with two-dimensional ferro-

TABLE II. *g* values along the crystallographic axes.

g_a	2.147 ± 0.005
g_b	2.130 ± 0.005
g_c	2.130 ± 0.005

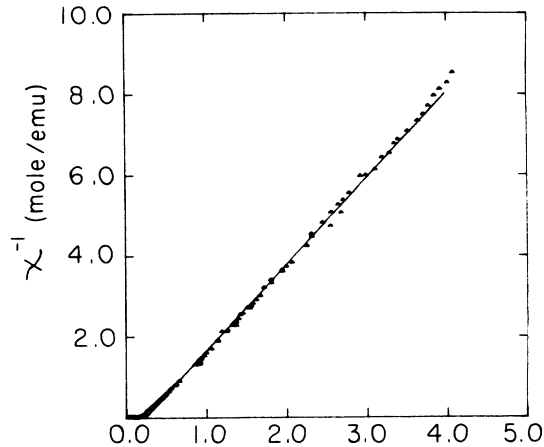


FIG. 7. Reciprocal susceptibility of a powder sample of Cu^{2+} *L*-isoleucine monohydrate. The solid line is a Curie-Weiss fit with $g=2.165$ and $\theta=0.240$ K.

magnetic exchange coupling within the sheets. The three-dimensional ordering then stems from weak antiferromagnetic coupling between the sheets. The weak coupling may be dipolar in nature or a real exchange interaction. In any case, the decrease in susceptibility with decreasing temperature for all three axes is consistent with antiferromagnetic coupling between the sheets. The subsequent rise in susceptibility in all three directions was at first thought to be due to impurities or non stoichiometric copper. A

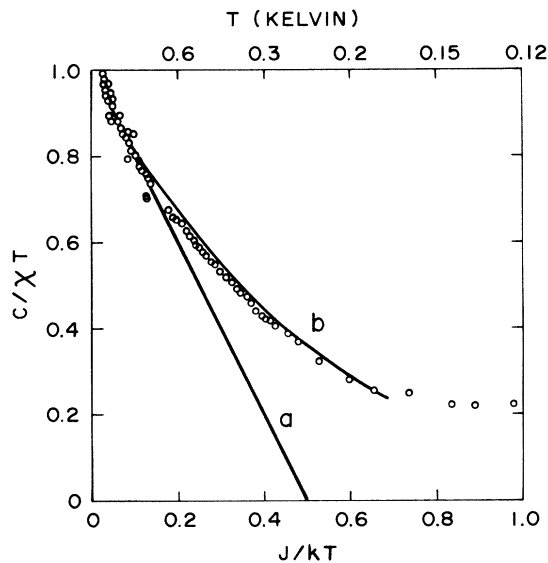


FIG. 8. Powder susceptibility plotted so as to show the deviation of these data from Curie-Weiss behavior. Curve a is a Curie-Weiss fit with $g=2.165$ and $J/k=0.120$ K while curve b represents the first ten terms of the Rushbrooke-Baker high-temperature expansion using the same parameters.

calculation of the impurity concentration necessary to produce the observed susceptibility below 0.03 K, assuming Curie-law behavior, indicates a minimum of 10% $S = \frac{1}{2}$ impurity or 2% $S = 1$ impurity. The neutron activation analysis eliminates the possibility of 10% uncombined copper and the nominal quality of our starting materials eliminated the possibility of as much as a few percent of other transition-metal impurities. It is unlikely that a second transition occurs below 0.1 K, so that the source of the increasing susceptibility at low temperatures remains unclear.

The magnetic phase boundaries exhibited in Fig. 4 indicate that well below the transition temperature the spin system undergoes a phase transition with H parallel to a or c but exhibits no phase transition with H parallel to b . (Owing to the large susceptibility and planar shape of the samples, the maximum internal field with H parallel to b was no more than 150 Oe.) Based on the data, a plausible model of the spin array in zero applied field and an accompanying zero-temperature Hamiltonian can be postulated. Numerical values derived for the parameters of the Hamiltonian agree qualitatively with the observed Curie-Weiss constant, the numerical value of the critical field and its isotropy in the ac plane, the absence of a critical field when H is parallel to b . In spite of this agreement, it should be noted that further evidence is necessary to confirm this model.

Since there are four spins in the unit cell, we postulate a four-sublattice model with the two spins in the same sheet coupled together ferromagnetically by an exchange $J_F/k = 0.120$ K. The ferromagnetic pairs are coupled to one another antiferromagnetically (Fig. 9) by an interaction given by

$$g\mu_B SH_c = 2J_{AF} S^2,$$

which with $g = 2.15$ and $H_c = 140$ Oe gives

$$J_{AF}/k = -0.020 \text{ K.}$$

It is assumed that both exchange interactions are isotropic. (The observed transition in applied field suggests the presence of an additional anisotropic interaction.) In order to maintain the spins in the ac plane, an additional interaction of the form $\vec{D} \cdot \vec{S}_1 \times \vec{S}_2$ will be postulated between the two ferromagnetically coupled spins. \vec{D} is assumed to be parallel to b and to have a magnitude $D \approx (\Delta g/g) J_F$, where Δg is the deviation of the g value from the free-electron value. Such an interaction is allowed by symmetry and in this case $\Delta g/g \sim 0.1$, so that $D/k \approx 0.012$ K. The result of the two interactions J_F and D is to cant the two spins at an angle ϕ given by

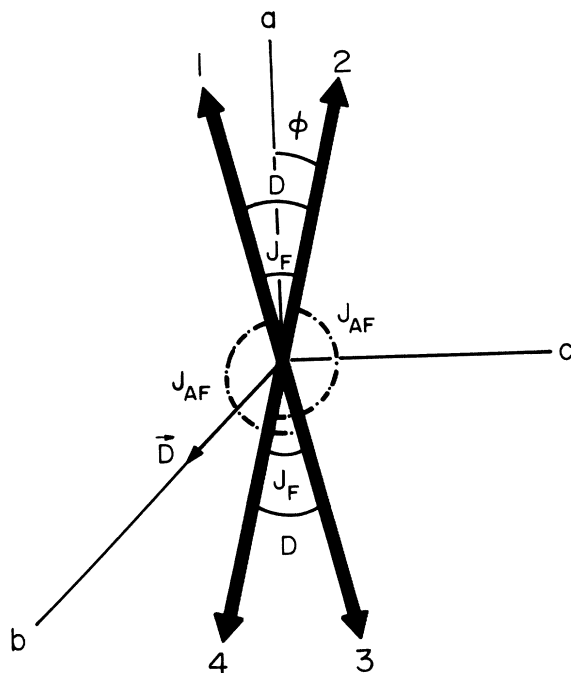


FIG. 9. Proposed spin array with the exchange interactions between the sublattices.

$$\tan 2\phi = D/J = 0.1,$$

so that $\phi = 3^\circ$. The final spin array is shown in Fig. 9. The effect of the field when applied in the ac plane is to produce a metamagnetic transition which "flips" spins 3 and 4 so that they become collinear with spins 1 and 2. A field applied parallel to b tends to tip all four spins toward b . The Zeeman energy must now overcome both J_{AF} and D and in addition produce no sharp phase transition.

There are two possible magnetic space groups⁷ which belong to the crystallographic space group $P2_12_12_1$. They are the group itself and $P2'_12_12'_1$.

Consideration of our proposed spin array leads to the conclusion that it is not possible to differentiate between the two groups based on the evidence at hand.

CONCLUSION

Cu²⁺ *L*-isoleucine monohydrate exhibits several interesting magnetic properties at low temperatures. ESR measurements indicate the g values along the crystallographic axes are essentially equal. The zero-field magnetic susceptibility is also essentially isotropic at all temperatures both above and below the ordering temperature $T_c = 0.117$ K. In contradistinction to this, the system exhibits significant anisotropy in its response to applied fields. A depression of T_c and a magnetic phase transition are observed with H parallel to a or c . With H parallel to b , the depression of T_c is much less pronounced and no magnetic phase transition is observed. The behavior is explainable with a four-sublattice (zero-temperature) model which has ferromagnetic and antisymmetric exchanges coupling the two sublattices in the same sheet to produce a slightly canted array. The canted sublattices are coupled to those in the adjacent sheets by a weak antiferromagnetic interaction. The three exchange constants are $J_F/k = +0.120$ $D/k = 0.012$, and $J_{AF}/k = -0.020$ K. The model is probably not unique. It is likely that a model with an X - Y interaction could be made to agree with the data as well as this one.

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