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Magnetic susceptibility and electron spin resonance of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$

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The low-temperature magnetic susceptibilities and electron spin resonance of single crystals of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ are reported. The crystal orders magnetically at $T_c = 0.157 \pm 0.003$ K. Above the transition the susceptibility can be fit to the high-temperature expansion for a two-dimensional ferromagnetic square Heisenberg lattice with $J/k = 0.28 \pm 0.02$ K. Below T_c the crystal exhibits behavior characteristic of weak antiferromagnetic coupling between the ferromagnetic layers.

INTRODUCTION

The crystal structure and some magnetic properties of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ have recently been reported by Losee *et al.*[1] The compound is monoclinic and belongs to the space group $P2_1/c$ with $a = 7.479$ Å, $b = 7.864$ Å, $c = 16.730$ Å, and $\beta = 91.98°$ with four chemical-formula units per unit cell. The most significant feature of the structure is the chains of edge-sharing $CuCl_4(OH_2)_2$ octahedra running along the z axis. These chains can be pictured as bonded into layers of composition $CuCl_3 \cdot 2H_2O$ situated at heights 0 and $\frac{1}{2}$ along the c axis.

From such a structure one might expect linear-chain or other low-dimensional magnetic behavior with strong exchange interaction (J_1) along the chains, intermediate exchange interaction (J_2) between the chains within the layers, and weakest exchange interaction (J_3) between the layers.

The susceptibility and specific heat down to 1.5 K as measured by Losee *et al.* do not appear to have any very unusual features. In an attempt to understand the data, they fit the susceptibility to a Curie-Weiss, Ising linear chain, and an isotropic Heisenberg ferromagnetic chain, and the specific heat to an Ising-linear-chain and isotropic-Heisenberg-linear-chain models, as well as a binary-cluster model without any very great success.

The magnetic properties of $(CH_3)_3NHCoCl_3 \cdot 2H_2O$ have been well explained using an essentially two-dimensional rectangular Ising model.[2] Although the cobalt salt is orthorhombic while the copper is monoclinic, the monoclinic salt can be derived from the orthorhombic by a 2° macroscopic distortion so that the microscopic descriptions are similar.

In the light of these results, we felt that extension of the susceptibility measurements to lower temperatures and ESR measurements might prove enlightening.

EXPERIMENTAL DETAILS

Single crystals were grown from a 1 : 1 mixture of $[(CH_3)_3NH]Cl$ and $CuCl_2 \cdot 2H_2O$ in water at room temperature. The crystals were oriented by means of an optical goniometer using the angles of face normals given by Groth[3] and checked by x-ray measurements of the cell parameters. We have followed the convention of Losee *et al.*[1] and have interchanged the a and c axes relative to Groth's morphological description.

The ESR data was taken at $T = 300$, 77, and 4 K using a simple reflection-type X-band spectrometer with fields up to 10 kOe. The sample was mounted on the side wall of a rectangular cavity and rotation data were taken in three orthogonal planes.

The near-zero-field ac magnetic susceptibility was measured using a 17-Hz mutual-inductance bridge. The susceptibility was measured as a function of temperature and orientation from 4.2 to 1.2 K in a ^{4}He cryostat in which the crystal may be rotated about one axis.[4] Susceptibilities were measured along the a, b, and c axes over this entire temperature range on a number of samples.

Below 1.2 K the susceptibility was measured in the same manner using a ^{3}He-^{4}He dilution refrigerator. In this case the orientation is fixed and one obtains χ vs T for only one value of θ. In the dilution refrigerator the temperature was determined by a carbon-resistance thermometer, which was calibrated against the susceptibility of powdered cerium magnesium nitrate. Only one run of the b- and c-axis orientation was made while the a axis was run in two different refrigerators in an attempt to resolve the inconsistencies in a-axis data.

ELECTRON SPIN RESONANCE

Although this is a concentrated salt, the ESR lines are only 250 Oe wide, so that the signals from nonequivalent coppers are resolvable and g-value accuracy of $\frac{1}{2}\%$ can be obtained.

The principal g values and their directions relative to the crystal were determined from measurements of the g-value variation in the ab, bc' and $c'a$ planes. The c' axis is defined as the axis perpendicular to the *ab* plane. It differs from the *c* axis by less than 2°. Following the method of Schonland,[5] these rotation patterns were fit by a least-squares technique to

$$g^2 = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta \ .$$

From α, β, and γ determined for each rotation the *g*-tensor elements can be determined. The principal values and axes are determined by diagonalizing this tensor. Although there are four chemical-formula units and therefore four copper atoms per unit cell, we find no more than two lines in any rotation. Thus we can resolve only two nonequivalent paramagnetic complexes per unit cell. We can interpret the observed rotation patterns by two principal-axis *g* tensors having essentially the same principal values but different principal axes. The principal values and polar and azimuthal angles specifying these two tensors are given in Table I. Note that the principal axes do not coincide with the crystal axes, but that the *g* values for the crystal axes are well determined, being the *g*-value extremes in the *ab* rotation, where only one ESR line is observed, and the values where the two observed lines cross in the other two rotations. These values are $g_a = 2.238 \pm 0.010$, $g_b = 2.037 \pm 0.010$, and $g_c = 2.195 \pm 0.010$. Although this data was obtained at $T = 77$ K no difference was observed in measurements made at 300 and 4 K.

The ESR results do not lend themselves to a simple interpretation. The principal axes do not fall near the Cu-Cl and Cu-O directions of the distorted octahedron surrounding the coppers, as one might expect. The main value of these results arises in the use of the *g* values to calculate Curie constants for the susceptibility.

SUSCEPTIBILITY

The magnetic-susceptibility data is displayed in Fig. 1 where χ^{-1} is plotted for the *a*, *b*, and *c* axes over the entire temperature range for which data was taken. In Fig. 2 we plot the magnetic susceptibility parallel to these three axes at temperatures below 0.45 K. There are three interesting features of the results. The first is that the system does order magnetically at $T_c = 0.157 \pm 0.003$ K, where the ordering temperature is taken as the point of maximum $d\chi_a/dT$. The second interesting feature is that the behavior of χ below T_c appears to be antiferromagnetic in nature, yet χ_a, which most resembles $\chi_\parallel$, does have a nonzero value as $T \rightarrow 0$. Experimental errors due to misalignment and empty-sample-holder contributions are smaller

TABLE I. Principal *g*-tensor values and orientations. θ is measured from the c' axis toward the *ab* plane and ϕ is measured from the *a* axis toward the *b* axis.

g	θ	ϕ
Tensor 1		
2.343 ± 0.010	49.8° ± 2.0°	170.1° ± 2.0°
2.027 ± 0.010	74.4°	273.6°
2.095 ± 0.010	44.4°	20.3°
Tensor 2		
2.333 ± 0.010	140.5°	176.9°
2.029 ± 0.010	76.9°	103.7°
2.101 ± 0.010	42.4°	151.6°

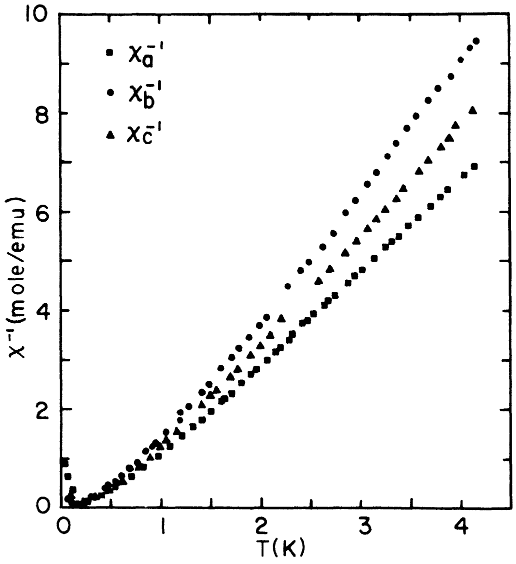

FIG. 1. Inverse magnetic susceptibilities of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ parallel to the *a*, *b*, and *c* axes.

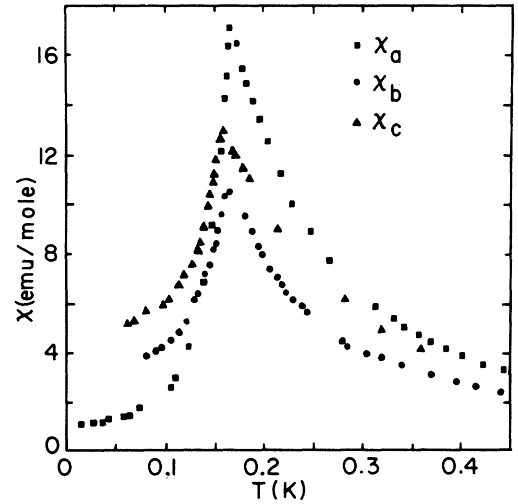

FIG. 2. Magnetic susceptibilities of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ parallel to the *a*, *b*, and *c* axes near the transition temperature.

than this deviation. In addition, χ_b and χ_c exhibit strong temperature dependence below T_c, unlike $\chi_\perp$ for an antiferromagnet. The third feature is the large value of the peak susceptibility for all three axes. Such behavior could arise from antiferromagnetic order with a small net moment due to canting, or it could be the result of ferromagnetic planes weakly coupled antiferromagnetically.

The cobalt salt[2,6] is best explained as an Ising lattice with $J_1/k = 7.7$ K, $J_2/k = 0.09$ K, and $J_3/k \simeq -0.01$ K giving rise to ferromagnetic sheets very weakly coupled antiferromagnetically with a net moment. Our results in trimethylamine copper chloride clearly indicate that J_1 is much smaller than it was in the cobalt salt. Since copper has rather small g-factor anisotropy, and (being $S=\frac{1}{2}$) no zero-field splitting, it is unlikely to be Ising-like.

In the light of these factors we attempt to fit the data above T_c with a two-dimensional ferromagnetic Heisenberg interaction. Since there are no exact solutions available, we used the high-temperature expansion due to Baker *et al.*[7] Figure 3 is a graph of $C/\chi_c T$ vs J/kT. Here C is calculated from $C = N_0 g^2 \mu_B^2 S(S+1)/3k$ using $S=\frac{1}{2}$ and g_c from the ESR results. The solid line 2 is obtained using the first ten terms of Baker's expansion. The best fit is obtained for $J_1/k = J_2/k = 0.28 \pm 0.02$ K. For comparison, curve 1 is the Curie-Weiss law with $\theta = 2zJS(S+1)/3k$, which reduces to $C/\chi T = 1 - 2J/kT$ for the two-dimensional square lattice, while curve 3 is the Bonner and Fisher[8] result for a Heisenberg linear chain with $S=\frac{1}{2}$. Note that the abscissa for the Bonner and Fisher result has been scaled down by a factor of 2. There is no value of J/k for which either of these expressions gives as good an overall fit as does the two-dimensional square ferromagnetic Heisenberg interaction. The b-axis data are fit equally well using $g_b = 2.04$ with the same value of J/k.

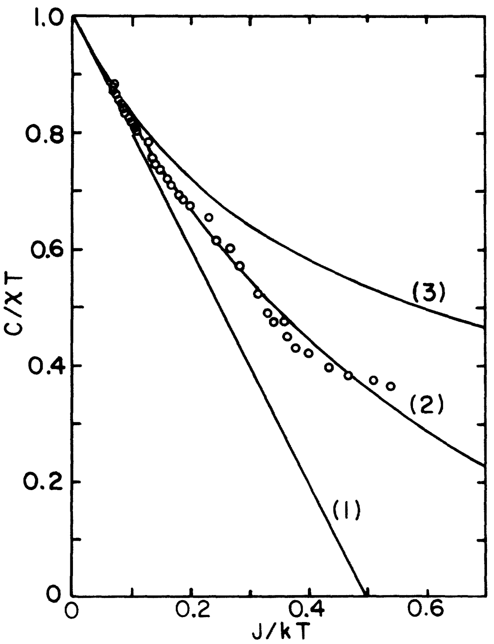

FIG. 3. Magnetic susceptibility of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ parallel to the c axis plotted as $C/\chi T$ vs J/kT. The transition temperature corresponds to $J/kT_c = 1.78$. Solid curve (1) is the Curie-Weiss results with $\theta = 2J/kT$; (2) is the square Heisenberg ferromagnet; and (3) is the Heisenberg ferromagnetic chain (abscissa scaled down by a factor of 2).

The a-axis data present some difficulty in that, using the value of $g_a = 2.24$ found by ESR, no value of J/k gives anything resembling a fit to the two-dimensional high-temperature expansion. If we make a two-parameter fit letting both g and J/k vary, we obtain a fit which is comparable to that obtained for the b and c axes, with $g_a = 2.36 \pm 0.02$ and $J/k = 0.28 \pm 0.02$ K. It is striking that although there is a discrepancy between the ESR g value and the high-temperature expansion g, the same J values are obtained from all three fits.

The susceptibility results above the transition temperature indicate that trimethylamine copper chloride behaves as a two-dimensional Heisenberg ferromagnet. Fitting the results to a square lattice in which $J/k = 0.28$ K may well be an over-simplification, since a rectangular lattice with two different exchange interactions would no doubt be more realistic. Below T_c, the data seem to indicate that the ferromagnetic sheets are antiferromagnetically ordered. The antiferromagnetic interlayer interaction may arise from the dipole-dipole interaction between adjacent planes or from a very weak exchange interaction. We will denote this interlayer interaction J_{AF}, while calling the intralayer ferromagnetic interaction J_F.

The properties of a layered structure with ferromagnetic intralayer exchange and a weaker antiferromagnetic interlayer coupling have been studied by a number of authors[9-13] both theoretically, using a variety of two sublattice models, and experimentally. The considerable success at fitting χ-vs-T curves with such models led us to try a simple molecular-field calculation similar to that of Berger and Friedberg.[12] Using such a model we were unable to fit the data at high T and at the same time obtain meaningful results below T_c.

From measurements made on several systems, deJongh *et al.*[13] have drawn a series of empirical conclusions concerning the magnetic properties of such structures. They observe that on both sides of T_c, χ drops steeply. Above T_c the steep fall occurs because χ is mainly that of the two-dimensional ferromagnetic layer, and the effect of J_{AF} is simply to shift T_c upward in temperature from the value determined by J_F. They also deduce that for the two-dimensional ferromagnetic square Heisenberg lattice $kT_c/J_F \simeq 0.44$, where T_c is the temperature at which χ diverges. Inserting $J_F/k = 0.28$ K into this expression, we obtain $T_c = 0.12$ K. Thus we observe an upward shift in the value of T_c of approximately 25% due to the weak antiferromagnetic interaction between layers. This is in agreement with deJongh's result for $(C_2H_5NH_3)_2CuCl_4$. For the same compound they find a large value of the maximum parallel susceptibility, namely $\chi_{\max}T_c/C \simeq 85$, whereas for a normal antiferromagnetic $\chi_{\max}T_c/C < 1$. We obtain $\chi_{\max}T_c/C \simeq 5$, which is considerably less than their value, but still well above normal and thus is in agreement with large anisotropy in the magnitude of the exchange.

As noted above, the susceptibility in the *a* direction, which we would like to associate with $\chi_{\parallel}$, has a nonzero value as $T \rightarrow 0$. Such behavior could be due to canting of spins on inequivalent ions. Our spin-resonance results show there are two inequivalent *g*-tensor orientations for the copper ion sites. Silvera *et al.*[14] have shown that two anisotropic *g* tensors tilted with respect to each other are sufficient to produce considerable canting of the spins on the inequivalent sites, even with isotropic exchange. For our case we find the *g*-tensor rotational inequivalence would be sufficient to produce approximately 3° of canting away from the *a* axis. Thus we conclude that canting of spins on inequivalent sites probably explains the nonzero value of χ_a as $T \rightarrow 0$.

For a simple antiferromagnet, one would expect little temperature dependence of $\chi_{\perp}$ below T_c, whereas χ_b and χ_c fall quite steeply below T_c. Although our data show strong temperature dependence, we can obtain some estimate of J_{AF} if we assume that the large value of $\chi_{\perp}$ just below T_c is a property of the ferromagnetic layers, and use the value of χ_c extrapolated to $T = 0$ in the molecular-field expression for $\chi_{\perp}$ given by

$$\chi_{\perp} = Ng\mu_B S/2H_{AF} = Ng^2\mu_B^2/2zJ_{AF} .$$

Doing this and assuming $z = 2$, we obtain $J_{AF}/k = -0.023$ K.

CONCLUSION

The susceptibility of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ has been shown to display the properties of a two-dimensional ferromagnet above $T_c = 0.157$ K, while below T_c it exhibits behavior characteristic of antiferromagnetic coupling between the ferromagnetic layers.

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[1] D. B. Losee, J. N. McElearney, A. Siegel, R. L. Carlin, A. A. Khan, J. P. Roux, and W. J. James, Phys. Rev. B 6, 4342 (1972).

[2] D. B. Losee, J. N. McElearney, G. E. Shankle, R. L. Carlin, P. J. Cresswell and W. T. Robinson, Phys. Rev. B 8, 2185 (1973).

[3] P. Groth, *Chemische Kristallographic* (Wilhelm Englemann, Leipzig, 1908), Vol. 1, p. 375.

[4] C. W. Fairall, D. D. Swinehart, and J. A. Cowen, J. Appl. Phys. 41, 2509 (1970).

[5] D. S. Schonland, Proc. Phys. Soc. Lond. 73, 788 (1959).

[6] R. D. Spence (private communication).

[7] G. A. Baker, Jr., H. E. Gilbert, J. Eve, and G. S. Rushbrooke, Phys. Lett. A 25, 207 (1967).

[8] J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1964).

[9] L. Neel, Nuovo Cimento Suppl. 6, 942 (1957).

[10] J. Kanamori, Prog. Theor. Phys. 20, 890 (1958).

[11] B. R. Heap, Proc. Phys. Soc. Lond. 80, 248 (1962).

[12] L. Berger and S. A. Friedberg, Phys. Rev. 136, A158 (1964).

[13] L. J. deJongh, W. D. vanAmstel, and A. R. Miedema, Physica (Utr.) 58, 277 (1972).

[14] I. F. Silvera, J. H. M. Thornley, and M. Tinkham, Phys. Rev., 136, A695 (1964).