Magnetic susceptibility of $(NH_3CH_2CH_2NH_3)CuCl_4$: A layered structure with strong interlayer magnetic coupling

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(Received 23 April 1979)

The magnetic susceptibility of single-crystal $(NH_3CH_2CH_2NH_3)CuCl_4$ has been investigated between 4 and 300° K and this compound was found to be a three dimensional antiferromagnet with a nearest-neighbor exchange of $J/k = 23.0 \pm 0.5°$ K and a next-nearest-neighbor exchange of $J'/k = -13.7 \pm 0.5$ °K. The transition to long-range order occurs at $31.5 \pm 0.1°$ K. The structure of $(NH_3CH_2CH_2NH_3)CuCl_4$ is similar to that of other compounds which exhibit a square-planar nature and comparisons to these compounds are made.

I. INTRODUCTION

The interest in the quasi-two-dimensional magnetic structures typically has been because the magnetic planes were well isolated with very small interplanar exchange so that the two-dimensional character could be studied. The archetypical structures are the $(C_nH_{2n+1}NH_3)_2CuCl_4$ [ethylammonium (EA)] series[1,2] in which the planes could be separated at will depending only on how many $(CH_2)_2$ ions were included. In the present work, however, 1,2-ethanediammonium tetrachlorocuprate $(NH_3CH_2CH_2NH_3)CuCl_4$ (EDA) has been studied by magnetic-susceptibility techniques indicating a layered structure in which the planes are slightly closer together but resulting in strong three-dimensional anti-ferromagnetic behavior. Like the EA series EDA has layers of square-planar $CuCl_4^{2-}$ ions which share two chlorides with adjacent ions to achieve a distorted octahedral configuration of ligands about the copper ion.[3a] As usual there is a slight puckering of the layer with the bridging chloride ion somewhat out of the plane defined by the copper atoms. This puckering is less pronounced than that reported in several similar manganese layers.[3b] The NH_3 group occupies a space between four Cl^- ions, and is hydrogen bonded to several of these chlorides. The planes are separated by the 1,2-ethanediammonium ions which are oriented so that the ammonium groups at opposite ends of each ion abut adjacent layers.

EDA differs from the EA series, however, in that instead of the layers being staggered in such a manner that the metal atoms in adjacent layers are positioned over spaces in the reference layer, in EDA the neighboring layers are positioned so that the paramagnetic ions in one layer lie almost exactly over those of the next. Only a few other reported structures have this "eclipsed" arrangement examples of which are $(NH_3CH_2CH_2CH_2NH_3)CuCl_4$ (PDA),[4] $[(NH_3CH_2CH_2)_2NH_2](CuCl_4)Cl,$[5] and $[NH_3(CH_2)_nNH_3]MnCl_4.$[6,7] Yet another similar compound, *bis*(anilinium) $CuCl_4$ has the adjacent layers displaced from the eclipsed position by about $\frac{1}{3}$ of a cell translation.[8]

II. EXPERIMENTAL PROCEDURE

The susceptibility measurements were made using a PAR FM-1 vibrating sample magnetometer and an Andonian variable-temperature Dewar calibrated against an NBS MnF_2 standard. Stability and reproducibility were measured to be better than machine specifications. Magnetic fields between 200 and 22 000 Oe were provided by standard laboratory magnets with field accuracy determined by NMR techniques to be better than 0.1% at 5000 Oe.

Temperature was measured with a gallium arsenide diode[9] excited by a constant current source of 0.005% stability and a Leeds and Northrup K-5 potentiometer. The diode was calibrated *in situ* against a germanium resistor[10] in the range from 4.2 to 100 °K and against a standard Hg laboratory thermometer at room temperature. A Lakeshore cryogenics capacitance temperature controller in conjunction with adjustable cryogen flow rate was used to maintain the temperature to within 0.01°K near the transition to long-range order.

The 0.0602-g single crystal was oriented on a teflon holder with a polarizing microscope. Extinction occurs along the Cu-Cl-Cu directions and is typically quite sharp for single crystals. However, for the EDA sample extinction occured over an approximately 10° range indicating twinning. This problem was also noted by Birrell and Zaslow in their crystallographic studies.[3a]

III. RESULTS

Figure 1 shows the magnetic susceptibility near the transition temperature, T_c. The data reflect the typical antiferromagnetic behavior below T_c as well as the gentle decrease of the $\chi_{\parallel}$ curve on either side of T_c appropriate for a 3-D system. The transition temperature of $31.5 \pm 0.1\,°K$ occurs at the temperature at which there is maximum slope in the $\chi_{\parallel}$ curve on the low-temperature side of the susceptibility maximum[11] of $T_0 = 37.2\,°K$. The difference between these two temperatures is about 18%, which also indicates the 3-D nature of this crystal. For nearly 2-D antiferromagnets the difference is on the order of 50% while 3-D systems will have a difference from 5 to 15%.[1] The 2-D ferromagnetic compounds in the $(C_nH_{2n+1}NH_3)_2CuCl_4$ series have differences on the order of 0.7%.

The fact that $\chi_{\parallel}$ does not go to zero at $T = 0$ may be explained by the possibility that the crystal was twinned. The data do not indicate clearly whether the b axis, the perpendicular direction in the plane, or the c axis, which is the interplanar direction, is favored next. Because of the very large interplanar coupling it was not possible to measure the second-order transition in any of the three crystallographic directions to help estimate the anisotropies and thus determine the next favored axis. However, the spin-flop transition in the $\chi_{\parallel}$ direction, the a axis, was measured to be 8500 ± 500 Oe. The a and b axes are at $45°$ in the
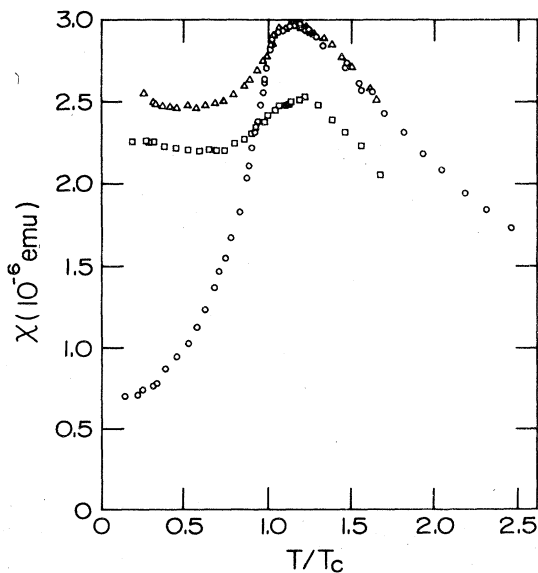
plane with respect to the external rectangular morphology of the crystal.

The high-temperature susceptibility data are presented in Fig. 2. The solid curve through the data was calculated using a five-term high-temperature expansion for Heisenberg interactions of $J/k = 23.0 \pm 0.5\,°K$ between nearest neighbors within layers, and of $J'/k = -13.7 \pm 0.5\,°K$ between neighboring Cu ions in adjacent layers. The expansion and fitting procedure used will be discussed in Sec. IV. The Curie constant was calculated using our measured value of $g = 2.171$ in the direction of $\chi_{\parallel}$. Only the data down to a temperature of $J/kT = 0.6$ were used for the fitting procedure. However, the excellent coincidence continuing through $J/kT = 0.75$ was not expected since the transition occurs at $J/kT = 0.73$. Also shown for comparison are the curves representing the high-temperature expansions for a simple cubic lattice, a square-planar lattice, and mean-field prediction. Finally, the top curve is for the completely 3-D case of $J/k = 23\,°K$, $J'/k = -23\,°K$ as a limiting example.
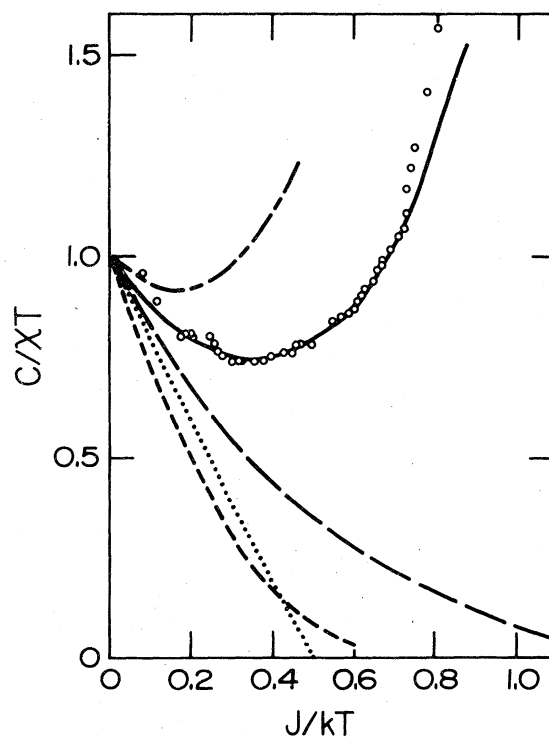

FIG. 1. Antiferromagnetic susceptibility near the transition temperature. $\bigcirc$: $\chi_{\parallel} = \chi_a$, $\triangle$: χ_b, $\square$: χ_c. $H = 5000$ Oe.

FIG. 2. High-temperature data and expansions as a function of inverse susceptibility vs J/kT. $J/kT_c = 0.73$. ....., mean field; — — — —, simple cubic; — — — — — , square planar; ——, second neighbor $J = 23.0°\,K$, $J' = -13.7°\,K$; — — — — —, second neighbor $J = 23°\,K$, $J' = -23.0°\,K$.

TABLE I. Comparison of various layered compounds with the 3-D EDA. sta means the layers are staggered, ecl means they are eclipsed. d_1 is the intraplanar Cu-Cu separation, d_2 is the interlayer separation.

Compound	T_c	J/k	J'/J	d_1	d_2	Orient	Ref.
$(CH_3NH_3)_2CuCl_4$	8.91	19.2	$+5.5 \times 10^{-5}$	5.247	9.97	sta	18
$(C_2H_5NH_3)_2CuCl_4$	10.25	18.6	-8×10^{-4}	5.240	11.21	sta	1
$(NH_3CH_2CH_2CH_2NH_3)CuCl_4$	13.5	15.4		5.18	9.12	ecl	4
$[(NH_3CH_2CH_2)_2NH_2]CuCl_4Cl$	11.8	18.7	-2.8×10^{-3}	5.108	11.89	ecl	5
$(NH_3CH_2CH_2NH_3)CuCl_4$	31.5	23.0	-0.595	5.180	8.11	ecl	this work

IV. DISCUSSION

The most surprising magnetic aspect about this compound is that it has such a large interplanar interaction. We expected the largest interaction to be between nearest neighbors in the a-b plane for which the high-temperature susceptibility expansion starts out[12]

$$\frac{\chi T}{C} = 1 + \left(\frac{2J}{T}\right) + \frac{1}{2!}\left(\frac{2J}{T}\right)^2 + \frac{1}{3!}\left(\frac{2J}{T}\right)^3 + \cdots$$

the same as an exponential. Therefore, to enhance any deviations from purely nearest-neighbor Heisenberg interactions, we used $T \ln(\chi T/C)$, corrected for nonzero magnetic field, as the quantity to fit by least squares to an eight-term polynomial in $1/T$. By expanding the logarithm we converted to a form suitable for comparison to the fitted coefficients the expansions for the square-planar lattice[12] (10 terms), various second-neighbor models[13,14] (5 terms), and anisotropic[15] and Dzyaloshinsky-Moriya[16] contributions to the interaction. To see if the data were consistent with an expansion whose first few coefficients are related as predicted by a model, the theoretical coefficients were calculated using values of the parameters in the model's spin Hamiltonian, consistent with the first two terms in the fit. These were then compared to the fit coefficients using the F distribution test. All models but the interplanar second-neighbor interaction could be rejected at the 99% confidence level.

Because the layers of the series $(C_nH_{2n+1}NH_3)_2CuCl_4$ are isostructural to those of EDA, one would expect the intraplanar interaction to be comparable in magnitude. As can be seen in Table I, the value of J/k for EDA is consistent with those reported for that series. A comparison of the interplanar exchange with the above series is not appropriate.

The reason for the very strong interplanar exchange in EDA is not yet clear. A superexchange pathway through the two chlorides between interlayer

coppers is certainly expected in EDA owing to its eclipsed nature. However, typically for each additional exchange ion between magnetic ions the value of J'/J decreases by 10^{-2}.[17] Thus our value of $|J'/J| = 0.6$ is at least a factor of 60 too large assuming only that superexchange mechanism. In the case of PDA, the value of J'/J was not given, but, the low transition temperature and excellent fit to a square-planar expansion suggests that a value of 10^{-2} or less is not unreasonable.[4] The most significant difference between EDA and PDA is that the layers in the former are about 1 Å closer together. Even though the superexchange interaction typically decreases as r^{-12} that is not sufficient to explain the much stronger exchange in EDA. However, the reduced separation does allow the two interlayer chlorides to fall within their Van der Waal's radii as shown in Fig. 3. It would seem then that the two chloride ions in EDA are acting as a single ion owing to the contact which is occurring between them.

A comparison to the isostructural manganese compounds is not illuminating. (EDA)$MnCl_4$ and (PDA)$MnCl_4$ have both been found to be nearly 2-D antiferromagnets.[6,7] For (PDA)$MnCl_4$ the interlayer chlorines are known to be beyond the Van der Waal's radii but the complete structure for (EDA)$MnCl_4$ has not been reported. If one assumes an average value
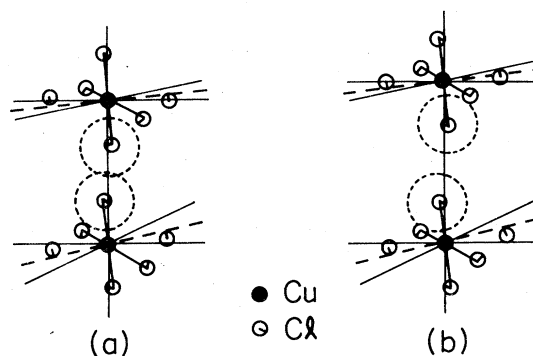

FIG. 3. (a) Interlayer chloride environment for EDA. Dashed circles around chlorides indicate their Van der Waal's radii. (b) Same as (a) for PDA.

for the Mn-Cl interlayer bond length and the reported interplanar separation in $(EDA)MnCl_4$,[6] the two neighboring interplanar chlorides also lie outside their Van der Waal's radii consistent with the 2-D magnetic behavior.

ACKNOWLEDGMENTS

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