

Magnetic susceptibility of 1,4-butanediammonium tetrachlorocuprate

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Magnetic susceptibility and magnetization measurements have been made on powdered and single-crystal 1,4-butanediammonium tetrachlorocuprate. The compound is found to be nearly a two-dimensional (2D) ferromagnet with an intraplanar exchange of 13.0 ± 0.2 K and an interplanar exchange of -0.16 K. The transition temperature to 3D antiferromagnetic order occurs at 8.85 ± 0.1 K. The preliminary crystal structure is reported with lattice constants of $a = 9.094$, $b = 7.571$, and $c = 7.375$ in the space group $P2_1/c$. The crystal is monoclinic with $\beta = 13.1^\circ$. Comparisons between this compound and other members of this series are made.

I. INTRODUCTION

The recent investigations¹⁻³ into the layered compounds of the series $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuCl}_4$ ($n = 2, 3, 5$) [ethanediammonium tetrachlorocuprate (EDA CuCl) series] led to the surprising result that the $n = 2$ compound is very nearly a three-dimensional antiferromagnet while the other two members of the series (propane and pentane) are more nearly two-dimensional in their magnetic character. This result was in contradiction with what was expected based on the investigation of the $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ (Refs. 4 and 5) series. However, the crystal structure of the EDA CuCl-type compounds is different in a way such that an increased interlayer exchange should be expected. Specifically, the layers in the EDA series lie with the magnetic ions, copper in this case, for most values of n directly above one another with two intervening overlapping chlorine anions between. This structure is called "eclipsed" and provides an obvious path for enhanced exchange between the layers. We report here the magnetic susceptibility and magnetization of the $n = 4$ member of this series, 1,4-butanediammonium tetrachlorocuprate $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{CuCl}_4$ (BDA), in the temperature range of 4 to 200 K.

The crystal structure of BDA is similar to the other three members of the series, however, there is an interesting difference. As in the other members of the series there are puckered planes of CuCl_4^{2-} which are separated by organic (in the case of BDA) butanediammonium ions. The Cu^{2+} ions in adjacent layers lie nearly above one another though not as much as for the other three members. This is a result of the buckling of the organic chain as will be discussed in the next section. Thus BDA does not have an entirely eclipsed structure but instead is part way

between the eclipsed structure and the staggered arrangement of the $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ series. This apparently causes the interlayer interaction to be somewhat less than would be expected from the Cl-Cl separation alone. The next section will review the structure of all of the series ($n = 2-5$) with emphasis on $n = 4$. Section III will discuss the details of the magnetic properties of BDA.

II. CRYSTAL STRUCTURE

The unit cells and space groups have been determined from precession photographs for ethanediammonium, propanediammonium, and butanediammonium tetrachlorocuprate. These data along with von Känel's² for $n = 2, 3$, and 5 and Phelp's *et al.*³ for $n = 3$ are listed in Table I. So that comparisons can be made, the values for the corresponding tetrachloromanganates are also shown.⁶ Table II shows the interlayer separation in a more convenient form. The two ethanediammonium salts have very similar spacings—the tetrachloromanganate is a bit bigger, perhaps partly because the Mn^{2+} ion is larger than the Cu^{2+} ion. The increase in spacing in the propanediammonium salts compared to the ethanediammonium salts is 0.9 \AA for the tetrachloromanganate and 1.0 \AA for the tetrachlorocuprate. The expected expansion for insertion of one methylene group in a fully extended chain (C-C distance 1.54 \AA) is 1.2 \AA . However, in going from the propanediammonium salts to the butanediammonium derivatives, the tetrachloromanganate increases by 1.2 \AA but the tetrachlorocuprate decreases by 0.1 \AA . This is interpreted to mean that while the chain is fully extended in the tetrachloromanganate, it is kinked or coiled in the tetrachlorocuprate. This should also lead to a consid-

TABLE I. A comparison of the lattice parameters for the EDA CuCl_4 and the EDA MnCl_4 series.

Compound [$\text{NH}_3(\text{CH}_2)_n\text{NH}_3$]	$X\text{Cl}_4$	Crystal system	Space group	a	b	c	γ	Ref.
$n = 2$ (EDA)	$X = \text{Cu}$	Monoclinic	$P2_1/b$	8.109	7.158	7.363	92.37°	a
				8.10				b
	$X = \text{Mn}$	Monoclinic	$P2_1/c^d$	8.110	7.187	7.366	92.46°	c
			$P2_1/b$	8.048	7.319	7.108	$91.6^\circ (= \beta)$	This work
$n = 3$ (PDA)	$X = \text{Cu}$	Orthorhombic	$Pnma$	7.200	18.246	7.451	\dots	e
						≈ 17.88	\dots	b
	$X = \text{Mn}$	Orthorhombic	$Imma$	7.108	18.046	7.466	\dots	This work
				7.172	19.00	7.361	\dots	f
				7.168	7.358	19.004	\dots	g
$n = 4$ (BDA)	$X = \text{Cu}$	Monoclinic	$P2_1/b$	9.094	7.375	7.571	103.1°	This work
			$P2_1/m$	10.770	7.177	7.307	92.66°	f
$n = 5$ (Pent DA)	$X = \text{Cu}$	Monoclinic		≈ 11.94				b
				$X = \text{Mn}$	Orthorhombic	$Imma$	7.152	7.360

^aK. Tichý, J. Beneš, W. Hälg, and H. Arend, Acta Crystallogr. Sect. B **34**, 2970 (1978).

^bReference 2.

^cG. B. Birrel and B. Zaslów, J. Inorg. Nucl. Chem. **34**, 1751 (1972).

^dThis is the same crystal structure. We are just using standard notation.

^eD. W. Phelps, D. B. Losee, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem. **15**, 3147 (1976).

^fR. D. Willett and E. F. Riedel, Chem. Phys. **8**, 112 (1975).

^gH. Arend, K. Tichý, K. Barberschke, and F. Rys, Solid State Commun. **18**, 999 (1976).

erably larger β angle in this compound, which is observed.

It should also be noted that in both series the propanediammonium salt is orthorhombic and has a cell spacing twice the layer spacing. This appears to be a consequence of the fact that a chain with three carbons cannot coordinate equivalently with hydrogen bonds at both ends and still be translation equivalent. The differences the orientation imposes require a doubling of the unit cell. Such a doubling also occurs for both the pentanediammonium tetrachloromanganate and tetrachlorocuprate.

TABLE II. Interlayer Cu-Cu and Cl-Cl distances for the EDA CuCl_4 and MnCl_4 series.

[$\text{NH}_3(\text{CH}_2)_n\text{NH}_3$] $X\text{Cl}_4$		$n = 2$	$n = 3$	$n = 4$	$n = 5$
Cu	$d_{\text{Cu-Cu}}(\text{Å})$	8.10	9.10	9.09	≈ 11.9
	$d_{\text{Cl-Cl}}(\text{Å})$	3.64	4.6	5.0	6.4
Mn	$d_{\text{Mn-Mn}}(\text{Å})$	8.61	9.5	10.77	12.00
	$d_{\text{Cl-Cl}}(\text{Å})$	3.5	4.4	5.4	6.8

A schematic representation of the structures for $n = 2, 3$, and 4 is given in Fig. 1, together with one possible representation of the coiling in the ($n = 4$) butanediammonium tetrachlorocuprate. The main difficulty with this sort of drawing is that it suggests that the chain must be planar, which need not be so. The differences between observation and cal-

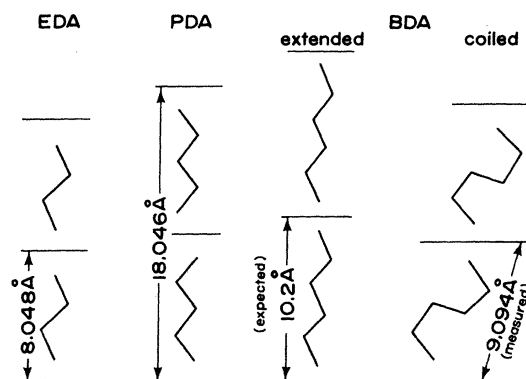


FIG. 1. Schematic representations of the structures for $n = 2, 3$, and 4 with an additional representation of the possible coiling in $n = 4$. Out-of-plane unit-cell dimensions given.

ulation discussed above are probably due mostly to deviations from planarity of this chain in varying degrees for the several compounds.

III. EXPERIMENTAL RESULTS

The susceptibility and magnetization measurements were made with a vibrating sample magnetometer and variable-temperature Dewar system previously described.¹ The only change in that equipment is that a calibrated Lakeshore Cryotronics carbon-glass resistor⁷ was used for temperature measurement to give improved temperature resolution and accuracy. Powdered samples of 0.0451 and 0.0483 g were used to measure the susceptibility over the temperature range of 4 to 200 K and the results are shown in Fig. 2. Typical two-dimensional (2D) ferromagnetic behavior is seen in the sharp decrease occurring on both sides of the susceptibility maximum of 8.95 K.

Figure 3 shows the high-temperature data plotted in the usual fashion of $C/\chi T$ as a function of J/kT . The line through the data is calculated from the 2D quadratic Heisenberg expansion of Baker *et al.*⁸ and shows a fit to the high-temperature expansions with an intralayer exchange, J/k , of 13.0 ± 0.2 K. An averaged sample g value of 2.13 was taken from the measured EPR g values on a single crystal of BDA⁹ to use in the fitting procedure of the powdered sus-

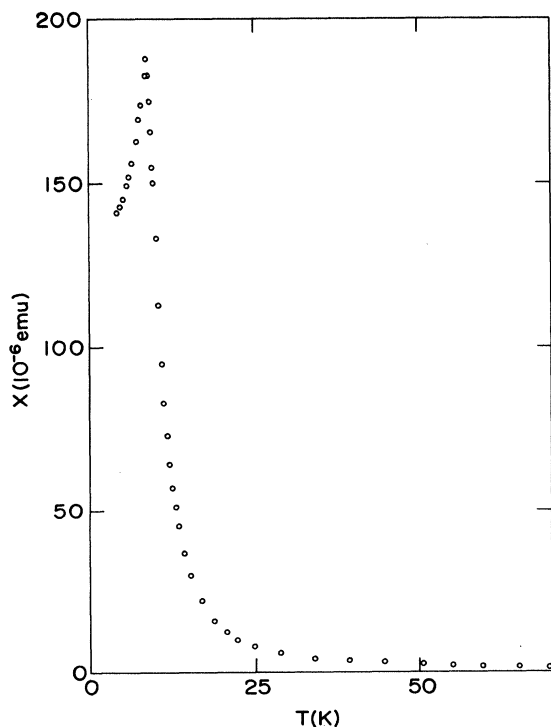


FIG. 2. Magnetic susceptibility of BDA Cu vs temperature.

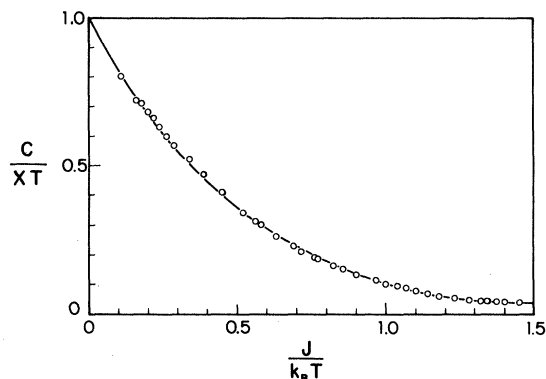


FIG. 3. $C/\chi T$ vs J/kT . Solid line represents the curve for the quadratic Heisenberg high-temperature series expansion of Baker *et al.* for a $J/k = 13.0$ K.

ceptibility. As with EDA the excellent coincidence of the fit to near the transition temperature of $J/kT_c = 1.47$ is surprising and no doubt coincidental. The data have been corrected for diamagnetic contributions.

Because of the low number of terms (5) in the high-temperature series expansion used to fit both intralayer and interlayer exchange, it was not possible to determine the small value of interlayer exchange in BDA in that manner. Thus it was necessary to use the standard mean-field approach using critical fields measured from the magnetization curves. Figure 4

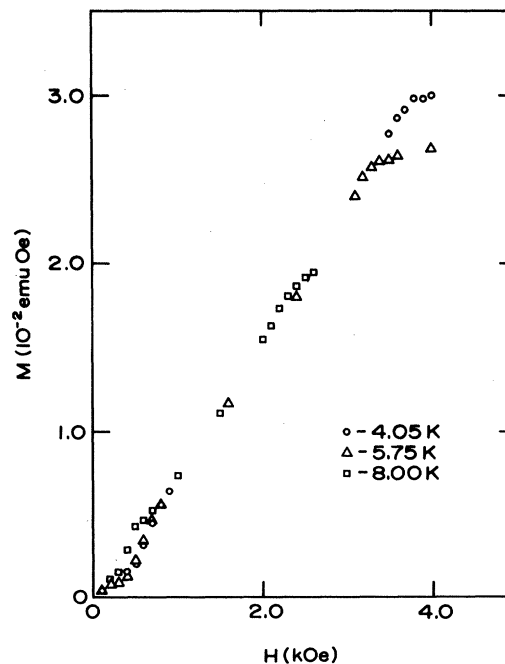


FIG. 4. Magnetization vs applied field. O: 4.0 K; Δ : 5.75 K; \square : 8.00 K.

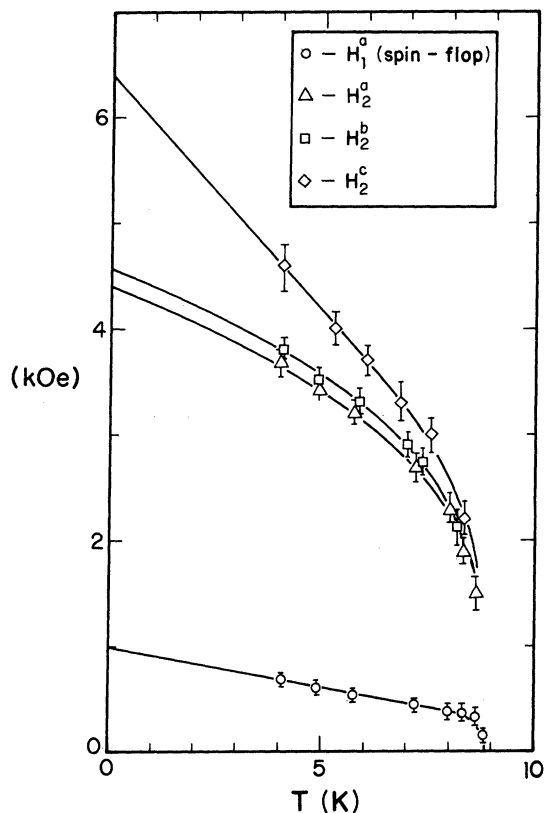


FIG. 5. Critical field vs temperature phase diagram. \circ : easy-axis spin-flop fields; Δ : easy-axis flop-to-paramagnetic fields; \square : next-easy-axis flop-to-para fields; \diamond : out-of-plane flop-to-para fields. Lines are aides to eye only.

shows examples of the isotherms for three different temperatures in the large field region with the field along the easy (a) axis. The external morphology of the very small single crystal has the usual rectangular, flat plate geometry. As with the $n = 2$ and 3 compounds, the a and b axes lie in the plane with c' perpendicular to it. The more useful presentation of the data is Fig. 5 which shows the phase diagram for BDA along all three crystallographic axes. A single crystal weighing 0.0015 g was used for these measurements. The curves through the data are aids for the eye only. Table III lists the values for the four critical fields extrapolated to $T = 0$ K.

Since the value of the spin-flop field is so low in

TABLE III. Exchange constants for $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{CuCl}_4$.

$H_a^1 = 970 \pm 40$ Oe	$H_{af} = 2200 \pm 80$ Oe
$H_a^2 = 4400 \pm 80$ Oe	$J_{\text{out}}/k_B = -0.16$ K
$H_b^2 = 4600 \pm 80$ Oe	$J_{\text{out}}/J_{\text{in}} = -1.2 \times 10^{-2}$
$H_c^2 = 6400 \pm 160$ Oe	

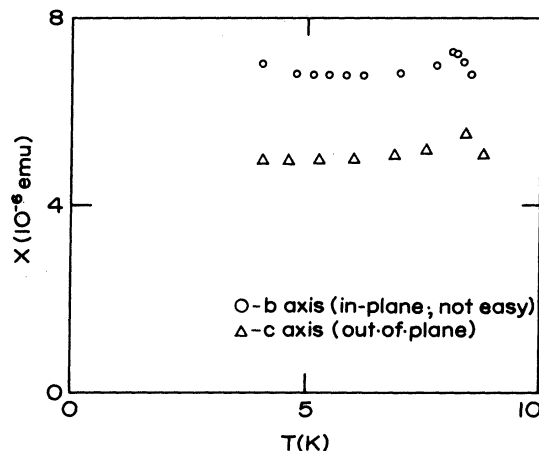


FIG. 6. Single-crystal susceptibility vs temperature below the transition temperature for the b axis (\circ) and c axis (Δ).

this compound and the crystals do not grow very large, it was not possible to take experimentally useful susceptibility data along the easy axis. Thus the transition temperature as determined by the point of largest slope below the susceptibility peak¹⁰ could not be found. An estimate of the transition temperature was therefore made by using the intercept of the easy-axis critical field with the T axis in Fig. 5. The value found of (8.85 ± 0.1) K is consistent with the expected for a 2D antiferromagnet with a χ_{max} at $T = 8.95$ K.⁵

Finally, Fig. 6 is the single-crystal susceptibility below T_c for the two perpendicular axes of the crystal. The χ values at $T = 0$ were used as indicated below to provide a check of the interlayer exchange and also to help determine the anisotropies. The measuring field in both cases was 2 kOe.

The question of the reliability of comparing the exchange values determined by high-temperature series expansions to those determined by using a molecular-field approach should be mentioned. This might be a serious problem considering the two methods of determination use data from different magnetic regimes. von Känel² used the molecular-field expressions for EDA and PDA CuCl_4 getting the values $J_{\text{out}}/J_{\text{in}} = 0.3 \rightarrow 1.0$ and 0.1, respectively, while Snively *et al.*¹ used a high-temperature series expansion getting $J_{\text{out}}/J_{\text{in}} = 0.6$ and 0.1, respectively. Since the values are nearly identical it appears that for this particular series the two techniques lead to the same result. This is not necessarily true in general.

IV. DISCUSSION

Assuming in-plane anisotropies and a simple molecular-field model for the effective exchange, the

usual equations for the critical fields are given by

$$H_{SF}^{q2} = 2H_A^{\text{in}}H_{af}^{\text{in}} - (H_A^{\text{in}})^2, \quad (1)$$

$$H_P^q = 2H_{af}^{\text{in}} - H_A^{\text{in}}, \quad (2)$$

$$H_P^b = 2H_{af}^{\text{in}} + H_A^{\text{in}}, \quad (3)$$

$$H_P^c = 2H_{af}^{\text{out}} + H_A^{\text{out}}, \quad (4)$$

where the a direction is the easy axis, b is the other axis in the plane, and c is the out-of-plane direction. H_A^{in} refers to the in-plane anisotropy and H_{af} is the effective field given by $H_{af} = 2z|J|S/g\mu_B$. The subscripts SF and P refer to the spin-flop and paramagnetic boundaries, respectively. Equations (2) and (3) were used with the values of the critical fields at $T=0$ to find $H_A^{\text{in}} = 100 \pm 80$ Oe and $H_{af}^{\text{in}} = 2250 \pm 80$ Oe. Using that value of H_{af}^{in} and Eq. (1) a second value of H_A^{in} of 220 ± 80 Oe was found. The difference may be attributable to some anisotropy in the exchange.

A second approach to determine H_{af} is to start with the molecular-field expressions

$$\chi_{\perp} = \chi_{\perp}^0(1 + H_A/2H_{af})^{-1}, \quad (5)$$

$$\chi_{\perp}^0 = Ng\mu_B S/2H_{af}, \quad (6)$$

where χ_{\perp}^0 denotes the perpendicular susceptibility corrected for anisotropy effects. From Fig. 6 one gets $\chi_{\perp}(T=0)/C_{\text{in}} = 3.13 \text{ K}^{-1}$ for the in-plane perpendicular susceptibility. Combining Eqs. (5) and (6) give $H_{af}^{\text{in}} = 2150 \pm 80$. Using the same method but solving for H_A with $\chi_{\perp}(T=0)/C_{\text{out}} = 3.26 \text{ K}^{-1}$ gives $H_{af}^{\text{out}} = H_{af}^{\text{in}}(g_{\text{in}}Z_{\text{out}}/g_{\text{out}}Z_{\text{in}})$ and thus gives $H_P^c = 6700 \pm 200$ Oe.

Finally, taking the average value for H_{af}^{in} of 2200 Oe and using the effective exchange field expression $H_{af}^{\text{in}} = 2z^{\text{in}}|J_{af}|S/g_{\text{in}}\mu_B$ the value for the interlayer exchange, J_{af}/k , is found to be 0.16 K. This then gives an exchange ratio $R = 0.012$ which is between those values found for $n=3$ and $n=5$. At first glance this is a surprising result considering the interlayer Cu-Cu distance in BDA is nearly the same as for PDA, approximately 9.1 Å each. However, when the Cl-Cl distance is determined for the two an expected increase is found, 4.6 Å for PDA and 5.0 Å for BDA. The reason for this is because the organic chain is thought to be buckled as indicated earlier. Thus, as suggested previously,¹ the Cl-Cl distance apparently plays a significant role in the strength of the interplanar exchange for the $n=4$ case. The importance of Cl-Cl overlap in this series was also discussed by von Känel²; however he did not attribute a significant effect to it except for the $n=2$ and $n=3$ cases. Algra *et al.*¹¹ have also pointed out the significance of the Cl-Cl distance to the exchange in the Co-Cl-Cl-Co bridge of Cs_2CoCl_4 , however, like the case of CoCl_2 , this bridge is not as linear as the EDA series and therefore not completely analogous. For completeness, we mention the intervening two-oxygen work of Algra *et al.*¹² There is a clear indication that the overlap of the two intervening anions plays a dominant role in the strength of the interplanar exchange.

ACKNOWLEDGMENT

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