spectrum.

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Tetramethylammonium Copper Chloride and *tris* (Trimethylammonium) Copper Chloride: $S = \frac{1}{2}$ Heisenberg One-Dimensional Ferromagnets

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The magnetic susceptibilities of powdered samples of Me_4NCuCl_3 (TMCuC) and $[(CH_3)_3NH]_3Cu_2Cl_7$ (TTMCuC) have been measured. Both compounds behave like one-dimensional $S = \frac{1}{2}$ Heisenberg ferromagnets which are weakly coupled antiferromagnetically to adjacent chains. For TMCuC, we obtained $J/k = 30$ K with $|J'| \lesssim 0.003$ K; the ratio $|J'/J|$ is the lowest yet found for a ferromagnetic $S = \frac{1}{2}$ chain. For TTMCuC, we obtained $J_{FM}/k = 50$ K, with $|J'/J_{FM}| \lesssim 10^{-4}$, and $J_{AFM}/k = -10$ K for the antiferromagnetic chains also present.

The magnetic properties of low-dimensional materials continue to be of much interest to physicists and chemists.[1] Of the many possible combinations of space dimensionality, spin dimensionality, and spin quantum number, one combination which has been conspicuous by the lack of suitable realizations is the one-dimensional (1D) spin-$\frac{1}{2}$ Heisenberg ferromagnet. The majority of studies on one-dimensional magnetic systems have been on antiferromagnets, with emphasis on $S = \frac{5}{2}$ Heisenberg (Mn^{2+}), $S = \frac{1}{2}$ Ising (Co^{2+}), and $S = \frac{1}{2}$ Heisenberg (Cu^{2+}) systems. The general lack of one-dimensional ferromagnets, particularly for $S = \frac{1}{2}$ where quantum effects are expected to be most pronounced, has been unfortunate. Recently we reported two pseudo-one-dimensional ferromagnets,[2] $CuCl_2 \cdot$ DMSO [DMSO $\equiv (CH_3)_2SO$] and $CuCl_2 \cdot$ TMSO [TMSO $\equiv C_4H_8SO$] with a strong intrachain coupling, $2J/k$, of ~ 80–90°K but the extent of interchain coupling ($|J'/J| \sim 10^{-2}$) was large enough to preclude their study as ideal systems. The structural insight gained in these studies prompted us to investigate two additional compounds where the interchain coupling, J', could be expected to be minimized.

The results presented in this paper indicate that $(CH_3)_4NCuCl_3$ (TMCuC) is the most one-dimensional $S = \frac{1}{2}$ Heisenberg linear chain ferromagnet yet reported. The other compound discussed here, $[(CH_3)_3NH]_3Cu_2Cl_7$ (TTMCuC), contains a similar set of linear $(CuCl_3)_n$ chains with ferromagnetic interactions and very small interchain coupling.

The room-temperature crystal structure[3] of TMCuC is closely related to, but more complex than, that of the manganese salt (TMMC)[4] and the isomorphic nickel[5] and cadmium[6] analogs (TMNC and TMCC). Distortions of the copper octahedra in the infinite chains lower the symmetry from hexagonal ($P6_3/m$) to monoclinic ($P2_1$). The elongated unit cell reflects the presence of five inequivalent copper sites. Only one of each three bridging chloride ions is symmetrically located between each pair of copper ions. This superexchange pathway will dominate.[2] The symmetric Cu-Cl-Cu bridging angles are in the range 86°–90°, which suggests the presence of ferromagnetic exchange. The variations in these angles will lead to a set of five somewhat different exchange parameters. Hence, we will only be able to derive an average exchange constant. The large distances (~ 9 Å) between neighboring chains indicate good magnetic isolation, and is the basis for assuming that this salt will approximate a one-dimensional system.

The room-temperature crystal structure of the $[(CH_3)_3NH]_3Cu_2Cl_7$ compound consists of two types of copper chains well separated by the trimethyl-ammonium groups[7]: One chain consists of $CuCl_3^-$ groups arranged in face-sharing octahedra, with a symmetric bridging angle of 82° and the other chain consists of discrete tetrahedral $CuCl_4^{2-}$ groups. This is the analog of the $[(CH_3)_3NH]_3Mn_2X_7$ compounds which have recently been studies for $X = Cl$ (Refs. 8 and 9) [and $X = Br$ (Ref. 10)]. In these studies it has been observed that the ions in the tetrahedral chain do interact magnetically via close halide-halide contacts.

The sample of TMCuC was prepared by slow evaporation of a saturated solution of $(CH_3)_4NCl$ and $CuCl_2$ in concentrated hydrochloric acid. The sample of TTMCuC was grown from an ethanol solution. The very small, needle crystals obtained were then washed in acetone, dried, crushed, and dried overnight in a vacuum furnace at 115°C. The susceptibilities were measured in a PAR vibrating sample magnetometer between 2–280 K after magnetization studies had been done at 4 K. Corrections were made to the data for diamagnetic and temperature-independent paramagnetic contributions to the susceptibility.

The magnetization studies of both salts showed a nonlinear field dependence above 2 kOe (Fig. 1). Data for TMCuC were collected at 1 kOe above 4°K and at 0.1 kOe below 4°K while the data for TTMCuC were collected at several field strengths from 1.5 to 8 kOe. Curie-Weiss fits to the high-temperature data yielded $\theta = 31° \pm 3°$ and a Curie constant of 0.403 ± 0.01 ($g = 2.075 \pm 0.025$) for TMCuC and $\theta = 16° \pm 3°$ with $C = 0.885 \pm 0.015$ ($g_{ave} = 2.17 \pm 0.03$) for TTMCuC. The g factors are in good agreement with the EPR g values. Near 80 K there was a change of several percent in the TMCuC data, the data below 80 K being lower when plotted as χT vs T.

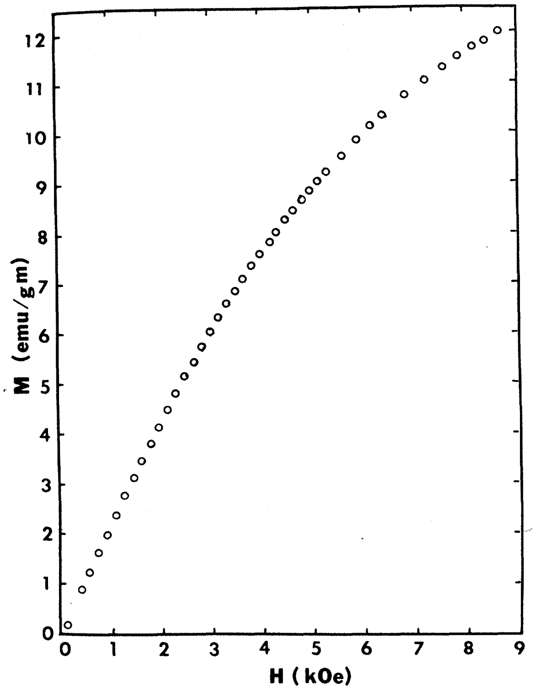

FIG. 1. Magnetization vs applied field at a temperature of 4.1 K for a powdered sample of TMCuC.

The reduced susceptibility, $\bar{\chi} \equiv \chi T$, rises steadily as the temperature decreases (Figs. 2 and 3), indicating ferromagnetic interactions within the chain. Plots of $\ln\chi$ vs $\ln T$ (Fig. 4) give no indication of three-dimensional ordering. In the presence of larger fields, saturation effects are observed as low-temperature maxima.[11] Demagnetization corrections, amounting to several percent at the lowest temperatures, have been applied.

The data for TMCuC have been fitted by a minimization procedure with the theoretical predictions for a $S = \frac{1}{2}$, Heisenberg ferromagnetic linear chain, $H = -2J\sum \vec{S}_j \cdot \vec{S}_{+1}$, as calculated by Baker, Gilbert, and Rushbrooke.[12] This was selected since it has a smooth behavior at low temperatures[2] while agreeing with the results of other calculations[13,14] at higher temperatures. For $T > 85$ K, $J/k = 39 \pm 1$ K while for $T < 55$ K, $J/k = 29 \pm 1$ K.[15] The data in the intermediate regime

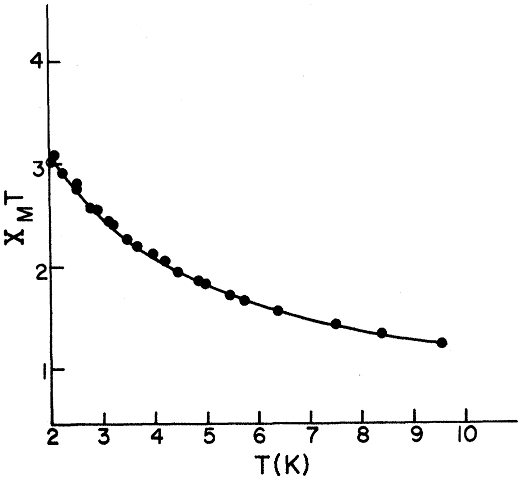

FIG. 2. Product of the magnetic susceptibility and temperature vs temperature for TMCuC in the low-temperature region. The curves are calculated from the series of Baker *et al.* with $J/k = 29$ K and $g = 2.075$.

(55°–80°) deviated from both theoretical curves; this may indicate a structural phase transition such as observed in TMMC, TMNC, and TMCC.

No systematic deviations of the low-temperature data from the predictions of the Heisenberg model are observed. Since interchain coupling, J', of magnitude $|J'/J| = 10^{-4}$ will lead to a 2% correction to χT at 3°K,[16] we can safely place an upper limit of $|J'/J| \sim 10^{-4}$ for TMCuC. This is comparable to the value reported for TMMC. The dipolar energy ($\sim 10^{-19}$ erg) corresponds to a ratio of dipolar-to-intrachain exchange of $\sim 10^{-5}$. Thus TMCuC is significantly more one dimensional than previously reported spin-$\frac{1}{2}$ ferromagnetic chains.

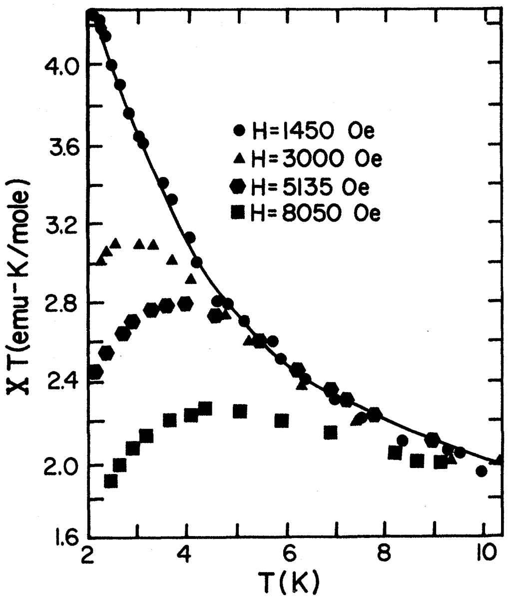

FIG. 3. Product of the magnetic susceptibility and temperature vs temperature for $[(CH_3)_3NH)]_3Cu_2Cl_7$ as a function of applied field. The solid curve is calculated from the series of Baker *et al.*, described in the text with parameters $J_{FM}/k = 50$ K, $J_{AFM}/k = -9.5$ K, and $ZJ'/k = 0$.

For TTMCuC, it was assumed that the magnetic system could be described as two independent linear chains, with exchange parameters J_{FM} (the ferromagnetic exchange parameter of the octahedral chain) and J_{AFM} (the antiferromagnetic exchange parameter of the tetrahedral chain). Fitting the data to a sum of the expression of Baker *et al.*[12] for the 1D FM susceptibility and an expression for the 1D $S = \frac{1}{2}$ AFM susceptibility[12,13] gave a best fit to the data with $J_{FM}/k = 50 \pm 2$ K and $|J_{AFM}|/k = -10 \pm 2$ K with $g_{oct} = 2.12$ and $g_{tetra} = 2.22$. The agreement is good at the high and low extremes of the temperature range but the data are systematically higher than the model between 20 and 160 K with the worst discrepancy being 8% between 60 and 80 K. From a close examination of the crystal structure, it appears likely that the $CuCl_4^{2-}$ anions in the tetrahedral chain are disordered. It is reasonable to assume this discrepancy is due to the effects of that disorder.

The $\ln\chi$ vs $\ln T$ plots in Fig. 4 indicate that, when $T \to 0$, χ diverges as T^n with $n = 1.6$ for both salts. For $CuCl_2 \cdot DMSO$ and $CuCl_2 \cdot TMSO$, the

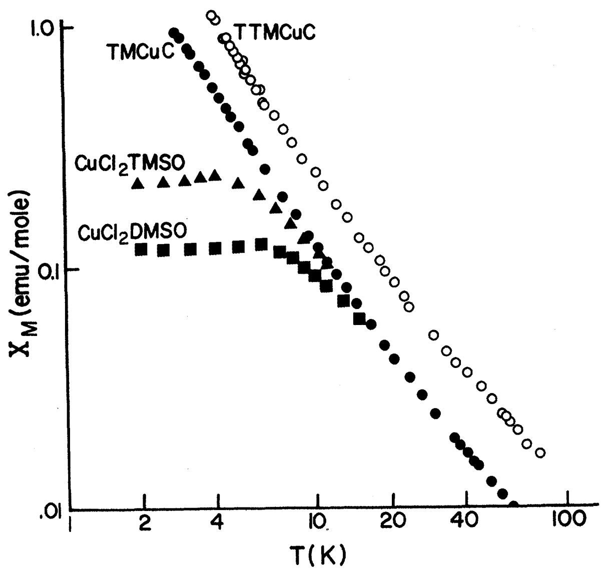

FIG. 4. A plot of $\ln\chi$ vs $\ln T$ for the salts TMCuC, TTMCuC, $CuCl_2 \cdot DMSO$, and $CuCl_2 \cdot TMSO$.

effect of interchain interactions at low temperature is clearly seen. For TTMCuC, the contribution from the antiferromagnetic term is clearly visible above 10°K, but makes no contribution at lower temperatures. This allows an estimation of $J_{\rm FM}$ for TTMCuC independent of $J_{\rm AFM}$. From the values of the extrapolated intercepts of the data in Fig. 4, the ratio $J_{\rm FM,TTMCuC}/J_{\rm TMCuC} = 1.7$ is obtained. This yields $J_{\rm FM,TTMCuC} = 51$ K in good agreement with the value obtained from treatment of the full data set. The value of $n = 1.6$ is in reasonable agreement with the prediction of Baker *et al.*[12] for a spin-$\frac{1}{2}$ Heisenberg chain which predicts $n = \frac{5}{3}$, but in somewhat poorer agreement with Bonner and Fisher's[13] estimate of 1.8. Both of these predictions are based on extrapolations of numerical data, and so are subject to errors of ±10%.

Finally, a word should be included about possible anisotropy in these systems. From EPR analysis underway in our laboratory of the structurally similar $CuCl_2 \cdot$ DMSO and $CuCl_2 \cdot$ TMSO salts, we deduce for the ferromagnetic chains that $g_\parallel < g_\perp$ with $\Delta g/g \sim (3-4)\%$. Bonner *et al.*,[17] have shown that an anisotropy of 10% has a negligible effect on the exchange parameters as determined by susceptibility measurements (although this is for a system in which J' is not negligible). More importantly, no evidence of spin dimensionality crossover is observed in Fig. 4. Thus, the analysis in terms of a Heisenberg Hamiltonian appears to be justified.

In summary, the low-temperature susceptibility of TMCuC behaves like that of a 1D $S = \frac{1}{2}$ Heisenberg ferromagnet with $J/k = 30 \pm 1$ K in which adjacent chains are weakly coupled antiferromagnetically. TTMCuC contains a similar set of ferromagnetic chains with $J/k = 50 \pm 2$ K, as well as a more weakly coupled set of antiferromagnetic chains. The exchange coupling in the latter chain is temperature dependent due to the disorder of the $CuCl_4^{2-}$ anions. The estimated values of $|J'/J|$ are of the order of 10^{-4} for both salts, the lowest yet observed for one-dimensional $S = \frac{1}{2}$ ferromagnets.

Specific-heat measurements to examine both the low-temperature magnetic interactions as well as to determine the existence of order-disorder transitions would be desirable as would the publication of theoretical calculations of the susceptibility of an $S = \frac{1}{2}$ linear chain with anisotropic exchange.

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