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Metamagnetic Behavior of Triethylenetetrammonium Hexachlorocuprate(II), $[C_6H_{22}N_4]CuCl_6$

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The compound triethylenetetrammonium hexachlorocuprate(II), $[C_6H_{22}N_4]CuCl_6$, exhibits two-dimensional magnetic behavior in the temperature range 20–75 K with an exchange constant of $J/k = 19.4$ K derived from a fit of the data by the expansion of Baker *et al.* There is a phase transition to an antiferromagnetic state at 8.95 ± 0.1 K, and the magnetization data suggest metamagnetic behavior.

Metamagnetic behavior in transition-metal antiferromagnets is a phenomenon that has been known both theoretically and experimentally for sometime. In all analyses of this field-dependent behavior, Ising-like properties have been ascribed to the ground state of the ion in question. This has been a natural consequence of having to account for the required anisotropy.

Generally anisotropy arises from single-ion (crystal-field) effects, dipole-dipole considerations, and anisotropic exchange interactions. Until this report, metamagnetism had been found only in compounds where the anisotropy was a result of crystal-field effects within the ground-state manifold, i.e., in compounds containing Fe(II), Co(II), Ni(II), and Dy(III). Here we give a preliminary report of the metamagnetism in triethylenetetrammonium hexachlorocuprate(II), henceforth $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$. This is the first Cu(II)-containing compound to be described which exhibits metamagnetism. It is especially intriguing that the magnetic behavior of the compound could not have arisen from single-ion effects.

Polycrystalline $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ was prepared from a 1:1 mole ratio of triethylenetetrammonium chloride, previously prepared by titration of the amine in ethanol, and $CuCl_2 \cdot 2H_2O$ in an HCl-H_2O solution. Although single crystals are exceptionally difficult to obtain, a few platelike crystals were obtained. These were examined by x rays, and the preliminary results indicate that the material is either hexagonal or more likely monoclinic with $\beta = 120°$ and with successive twinning along the unique axis. This phenomenon is best described by the precession photographs taken normal to the "trigonal or hexagonal" axis of one of the crystals. The size and shape of the spots in the zero layer are those of a normal, well-behaved crystal; however, those of the first layer are characteristic of either badly disordered lattices or lattices with excessively large thermal motion. The same is true of any precession-layer photograph for which the order is not a multiple of 3. Thus, we feel that layers become coincident every $3n$ and scatter in phase while those for which the order does not equal $3n$ are mismatched in such a way as to lead to destructive interference.

A sufficiently large "single crystal" as well as the polycrystalline materials were used for EPR measurements in a Varian E-3 spectrometer operating at X-band frequency. Measurements were carried out at room temperature.

Magnetic-susceptibility and magnetization experiments were carried out on the polycrystalline material as previously described.[1,2]

The results of the magnetic-susceptibility measurements at a field strength of 5.0 Oe from 4.2 to 20 K are shown in Fig. 1. Data at 50, 100, and 500 Oe were extended to 77 K and subsequently used for the determination of the high-temperature magnetic properties of the material. These data were appropriately corrected for temperature-independent paramagnetism and the diamagnetism associated with the protonated amine. No field dependence in the susceptibility was observed above 25 K.

The results of the magnetization experiments, performed in fields ranging from 1.0 Oe to 10 kOe at 4.2 K and 1.0 Oe to 500 Oe for the remaining temperatures, are shown in Figs. 2 and 3.

The polycrystalline magnetic-susceptibility data from 20 to 75 K were fitted by the expansion of Baker *et al.*[3] for a two-dimensional, Heisenberg-ferromagnetic, spin-$\frac{1}{2}$ system. In this expansion the susceptibility is given by

$$\chi = (C/T)[1 + 2(J/kT) + 2(J/kT)^2 + \tfrac{4}{3}(J/kT)^3 + \ldots], \qquad (1)$$

where C is the Curie constant and J the exchange constant. Values of $J/k = 19.4$ K and $g = 2.144$ resulted. The fit is excellent with the maximum deviation for any point on the fitted curve being 2.5%. The data set included values determined at 50, 100, and 500 Oe.

The lowest temperature to which the data were fitted was determined by truncating the series at seven terms and observing if variations in the fitted parameters resulted between the seven-term series compared to the full series. Sufficiently accurate high-temperature data are not available to be fitted by a simple Curie-Weiss relationship in the high-temperature region. The agreement between the EPR-determined g value of 2.134 and the value determined from the fit is excellent.

It is evident from an inspection of the 5.0-Oe data shown in Fig. 1 that a phase transition to an antiferromagnetic state occurs at 8.95± 0.1 K. Although it is difficult to define the Néel temperature accurately from powder data (since it is strictly defined along the easy axis), it is felt that because of the precipitous decrease in the ferromagnetically dominated susceptibility above the transition temperature, the Néel temperature

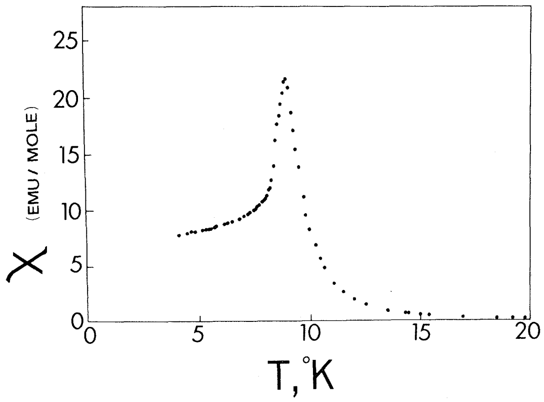

FIG. 1. Magnetic susceptibility of polycrystalline $[(NH_2CH_2CH_2)_3NH][CuCl_4]Cl_2$ at a field strength of 5 Oe uncorrected for demagnetization effects.

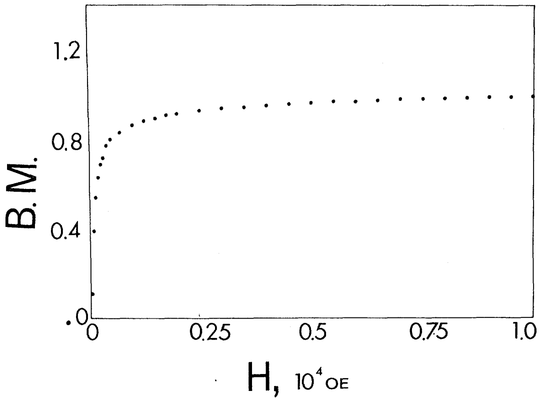

FIG. 2. Magnetization data of polycrystalline $[(NH_2CH_2CH_2)_3NH][CuCl_4]Cl_2$ at 4.2 K.

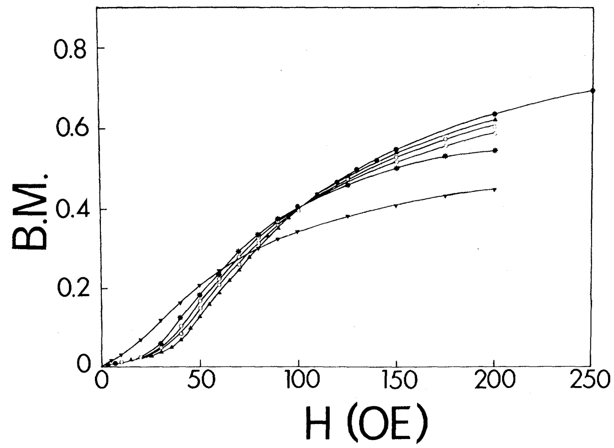

FIG. 3. Polycrystalline magnetization data at 4.2 K (●), 4.52 K (▲), 5.52 K (□), 6.86 K (○), 7.34 K (*), and 8.65 K (▼). Solid lines have been drawn through the data as a visual aid.

is more accurately determined in this system than would be possible in a conventional antiferromagnet. It should also be pointed out that because of this dominant ferromagnetic behavior above the transition temperature, the maximum susceptibility would be a few percent higher if demagnetizing effects could be accounted for.

Magnetization data collected at 4.2 K and shown in Fig. 2 suggest metamagnetic behavior with the sample achieving near-saturation at relatively low field strengths. When the external field reaches 10 kOe, the magnetization is effectively saturated at a value of $1.0\mu_B$ per Cu(II). For full ferromagnetic alignment of all Cu(II) moments a value of $1.08\mu_B$ per Cu(II) is calculated from $M = Ng\mu_B S$, if $S=\frac{1}{2}$ and the EPR-determined g value are used. The occurrence of a metamagnetic transition is further substantiated when the magnetization data are collected along other isotherms. Although it is not possible to determine the precise location of the critical field from polycrystalline data, the decrease of this critical field with increasing temperature is clearly revealed in Fig. 3. This is the expected behavior for the critical field in the metamagnet as a function of temperature below the tricritical point.[4] The reverse temperature dependence is observed in the more frequently occurring antiferromagnetic to spin-flop transition.[2,4]

"Single"-crystal EPR data have been collected as a function of rotation angle and linewidth. The rotation was carried out from a direction parallel to the thin plate to a direction perpendicular to it. The g value was 2.070 perpendicular to the plate and 2.168 parallel to it. Somewhat surprisingly[5] there was no linewidth variation as a function of rotation angle; this may result from accidental cancelation of dipolar effects due to twinning or may be a reflection of antisymmetric exchange contributions to the anisotropy.

From its high-temperature magnetic properties $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ can be characterized as consisting of a two-dimensional ferromagnetic arrangement of spins with an exchange constant of 19.4 K within these isolated layers.

In zero field at 8.9 K these layers ordered antiferromagnetically. This long-range order can be established by the combined effects of antiferromagnetic interlayer exchange and anisotropy. Below this ordering temperature of 8.95 K a metamagnetic transition occurs in the presence of a magnetic field. For this behavior to be observed, the anisotropy must exceed the antiferromagnetic interlayer exchange.[6] In order to obtain an estimate of the amount of antiferromagnetic exchange which is present, the molecular-field treatment given by Jacobs and Lawrence[6] for $FeCl_2$ was used. These authors have shown that the ratio of ferromagnetic exchange, Γ, to antiferromagnetic exchange, A, for a metamagnet is given by

$$\Gamma/A = (kT_N/\mu_B H_c)^{-1}, \tag{2}$$

for $S=\frac{1}{2}$. Further $\Gamma = 2Z_F J_F/N$ while $A = 2Z_{AF} J_{AF}/N$.

At this point some reasonable speculation on the structure of $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ is necessary. Two-dimensional ferromagnetism has been well documented in the series of Cu(II) compounds $[C_nH_{2n+1}NH_3]_2CuCl_4$.[4] In this series puckered sheets of $(CuCl_4)^{-2}$ ions are insulated from adjacent sheets by the appropriate protonated amine. In diethylenetriammonium pentachlorocuprate(II) $[(NH_3CH_2CH_2)_2NH_2]CuCl_4Cl$, these same sheets of $(CuCl_4)^{-2}$ ions are present and are separated by the protonated amine, with the additional chloride ion situated midway between these layers. Although the high-temperature magnetic properties of $[(NH_3CH_2CH_2)_2NH_2][CuCl_5]$ were virtually identical to those of $[C_2H_5NH_3]CuCl_4$, increased anisotropy, introduced by this intervening Cl^-, in both the in-plane as well as the out-of-plane directions, was established by magnetization experiments. With these model compounds in mind, then, it is postulated that $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ consists of isolated layers of $(CuCl_4)^{-2}$ ions separated by the protonated amine, but now with two additional chloride ions between these layers. The increased anisotropy is obvious as well as the two-dimensionality.

Returning to the estimate of interlayer antiferromagnetic exchange given in Eq. (2), it is assumed from the postulated structure that $Z_F = 4$ while $Z_{AF} = 2$. With a reasonable value of 50 Oe for H_c at 4.2 K and $T_N = 8.95$ K, a ratio of $\Gamma/A \approx 2650$ results. Since $\Gamma/A = 2J_F/J_{AF}$, $J_{AF} \approx 0.014$ K. This ratio of ferromagnetic to antiferromagnetic exchange is nearly two and a half to three orders of magnitude larger than that found for $FeCl_2$.

All of the models which predict metamagnetism also predict that this first-order transition will disappear at some temperature (the tricritical point) close to but below T_N. The temperature at which this occurs has been given by Kanamori, Motizuki, and Tosida (summarized by Motizuki[7]) in a molecular-field Ising model by

$$\tau^* = 1 - A/3\Gamma, \qquad (3)$$

where $\tau^* = T^*/T_N$ (T^* is the temperature above which the first-order transition disappears). Using the above ratio for Γ/A we calculate a temperature of 8.86 K. Although there are several other theories which predict this temperature, considering the approximations used in arriving at the above result, the calculated temperature is more than likely an upper limit. It is further noted that the character of the magnetization isotherm at 8.65 K is of a different form than that observed for the data collected at the lower temperatures. Although a definitive statement in regard to the magnetism of $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ cannot be given until single-crystal measurements are made, its high-temperature two-dimensional character and metamagnetism are established.

The exact way in which the various forms of anisotropy enter into the magnetism must also await the structure determination in order to calculate the dipole-dipole contribution to the total anisotropy. However, speculating on the structure as discussed above and with particular attention to the anisotropy in $[(NH_3CH_2CH_2)_2NH_2]$-$[CuCl_4]Cl$, one would expect the out-of-plane anisotropy to increase relative to $[(NH_3CH_2CH_2)_2NH_2]$-$[CuCl_4]Cl$, thereby creating a more planar Heisenberg system. Unfortunately metamagnetism has only been investigated in the Ising limit. It is interesting that insofar as the g values reflect anisotropy, the values determined both parallel and perpendicular to the platelike crystals are very nearly identical in the two systems.

In conclusion these preliminary results on $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ have an important bearing on the problem of two-dimensional magnetism. As mentioned above, the extensive study of $[(NH_3CH_2CH_2)_2NH_2][CuCl_4]Cl$ pointed out the effects of introducing anisotropy via the Cl anions which are positioned between the well-separated layers of Cu(II) ions, and now the results for $[(NH_3CH_2CH_2)_3NH]CuCl_4Cl_2$ reveal even more dramatic effects arising from the introduction of anisotropy into basically two-dimensional lattices.

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