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Magnetism of Some Copper Complexes at Low Temperatures

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The susceptibility of Cu formate $4H_2O$; Cu dihydroxy-para-quinone and $Cu(NH_3)_4 \cdot SO_4 \cdot H_2O$, and the specific heat of the last salt was studied at very low temperatures. The susceptibility of Cu formate $4H_2O$ follows the Curie-Weiss Law above 70°K with a Weiss constant −175°. Below 65°K, susceptibilities of L_1 and L_2 axes become almost constant, while that of L_3 decreases as the temperature is lowered with an anomaly at 65°K. At 17°K, susceptibilities of the L_1 and L_2 axes show very sharp maxima and become temperature independent at liquid He temperatures. Magnetization curves of L_1 and L_2 axes at liquid He temperatures indicate the appearance of weak ferromagnetism along both axes. Susceptibility of Cu dihydroxy-para-quinone was measured on three different samples having different lengths of Cu^{+2} chains. In all three samples, a broad maximum is found at about 20°K suggesting that the magnetic behavior can be understood as a magnetic linear chain with interaction energy of about 20°K. $Cu(NH_3)_4SO_4 \cdot H_2O$ has a crystal structure in which linear chains of Cu^{+2} ions joined by a H_2O between them are found. It was already known that specific heat of this salt has a broad hump with its maximum at about 3.0°K. The second peak is found at 0.37°K which can be attributed to the occurence of long range order at this temperature. Susceptibility of c axis becomes flat at 0.37°K while those of the other two axes continue to diminish with decreasing temperature. These facts are also consistent with the appearence of long range order at 0.37°K.

The magnetic susceptibilities of $Cu(NH_3)_4 \cdot H_2O$, Cu-dihydroxy-para-quinone and $Cu(CHO_2)_2 \cdot 4H_2O$, and the specific heat of the first salt were measured at low temperatures. These coordination compounds were chosen from two points of interest. The first concerns the superexchange interaction through the intervening large diamagnetic molecules and the second with the magnetic behaviours of one- and two-dimensional lattice models.

(1) $Cu(NH_3)_4SO_4 \cdot H_2O$. The specific heat and the magnetic susceptibility along the three crystalline axes of $Cu(NH_3)_4SO_4 \cdot H_2O$ was measured down to 0.03°K[1]. The specific heat shows a broad Schottky type maximum near 3°K, and a small sharp maximum at

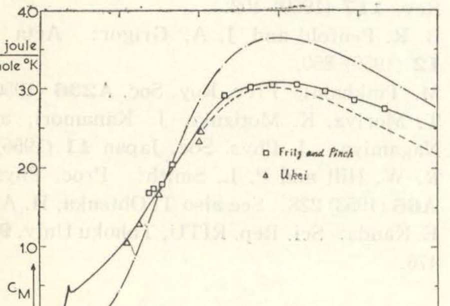


Fig. 1. Specific heat of $Cu(NH_3)_4SO_4 \cdot H_2O$. —·— Ising linear chain.

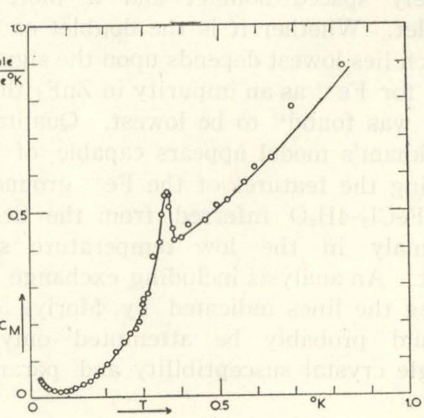
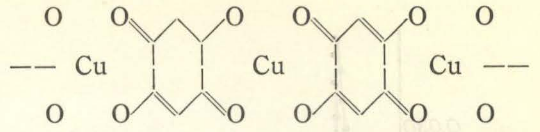


Fig. 2. Specific heat of $Cu(NH_3)_4SO_4 \cdot H_2O$ below 1°K.

0.37°K (Figs. 1 and 2). The susceptibility for the *c* axis becomes flattened below 0.37°K. (Fig. 3) These experimental results are in agreement with the idea that, as far as interactions between magnetic ions are concerned, the Cu^{+2} ions are arranged in linear chains with an exchange constant $J/k = -7.2$°K. The sharp peak at 0.37°K can be attributed to the appearance of long range magnetic order below this temperature[2].

(2) Cu-dihydroxy-para-quinone. This compound is considered to have a linear chain structure, such as the following,



The length of the chain is not so long. The main interaction between Cu^{+2} ions is within the linear chain joined by quinone molecules and the interaction between the chains can be very small. The magnetic susceptibilities of samples containing different lengths of chains are shown in Fig. 4 with a plot of the calculated susceptibility of a linear chain by Ising's model. The deviation from the Ising model in the lower temperature region may be due to the effect of Cu^{+2} ions at the ends of the chains. If the effect is subtracted, the susceptibility agrees with that of an Ising linear chain with J/k about −24°K.

(3) $Cu(CHO_2)_2 \cdot 4H_2O$. This compound has a remarkable layer structure. The following interaction paths between Cu^{+2} ions, (Fig. 5) Cu^{+2}—$OCHO^{-1}$—Cu^{+2} in the layer and Cu^{+2}—O-H-H-O—Cu^{+2} and Cu^{+2}—O-H-O-H-O-Cu^{2+} between layers suggests that the main interaction between Cu^{+2} ions may be considered to be through the formate ion, which is a large organic molecule, within each layer and the interaction between layers may be small.

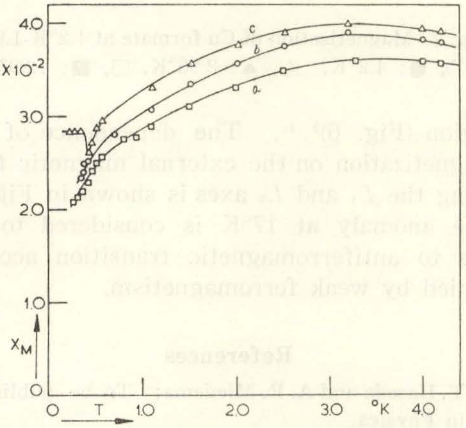


Fig. 3. Susceptibility of $Cu(NH_3)_4SO_4 \cdot H_2O$.

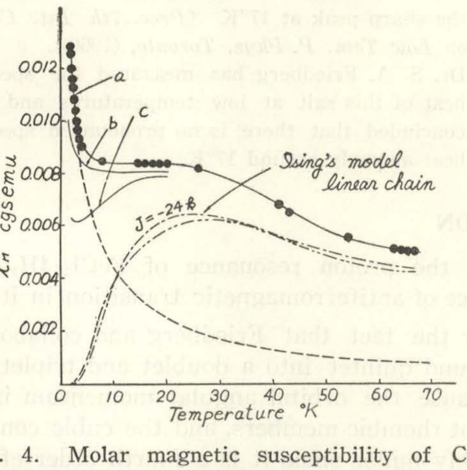


Fig. 4. Molar magnetic susceptibility of Cu-dihydroxyparaquinone. Full curve represents observed values with lengths of chains $a<b<c$. Dotted curve (- - - -) is the extension of the low temperature susceptibility (end effect) assuming Curie-Weiss law with Weiss constant −3°K. —·—·—·— is a plot of values obtained by subtracting the dotted curve from the experimental curve *a*. — · — · — is calculated using Ising linear chain model with $J/k = -24$°K.

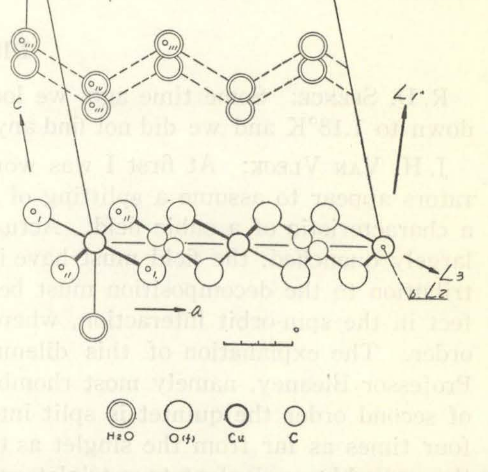


Fig. 5. Atomic arrangement of $Cu(HCO_2) \cdot 4H_2O$ projected on (010). Broken lines show the layer of water molecules.

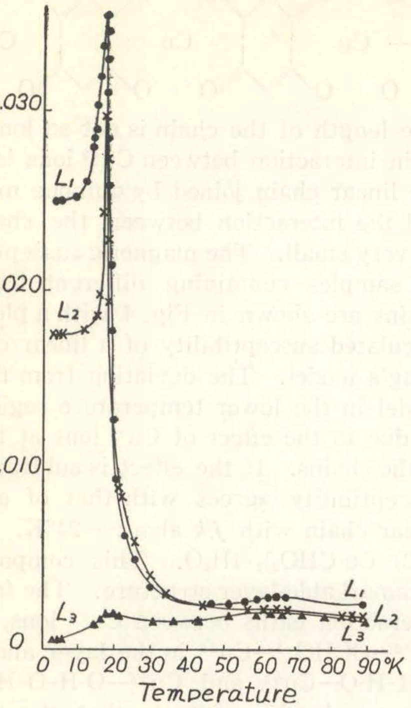


Fig. 6. Molar magnetic susceptibility of Cu-formate tetrahydrate.

The magnetic susceptibility follows the Curie-Weiss law above 65°K and the Weiss constant is about −175°K indicating a large superexchange interaction between Cu^{+2} ions through the formate molecule. At 17°K there are steep maxima of the magnetic susceptibilities along the L_1 and L_2 axes and the susceptibilities become independent of temperature in the liquid He temperature region (Fig. 6)[3),4)]. The dependence of the magnetization on the external magnetic field along the L_1 and L_2 axes is shown in Fig. 7. The anomaly at 17°K is considered to be due to antiferromagnetic transition accompanied by weak ferromagnetism.

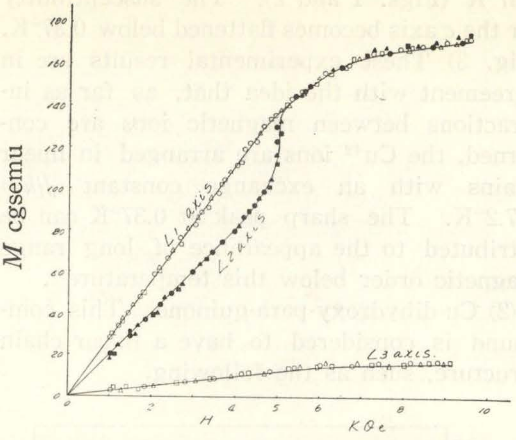


Fig. 7. Magnetization of Cu formate at 4.2°K-1.9°K ○, ●; 4.2°K, △, ▲; 2.96°K, □, ■; 1.99°K.

References

1 T. Haseda and A. R. Miedema: To be published in Physica.
2 L. Onsager: Phys. Rev. **65** (1943) 117.
3 S. A. Friedberg and R. B. Flippen has also found the sharp peak at 17°K (*Proc. 7th Int. Conf. on Low Tem. P. Phys. Toronto,* (1960)),
4 Dr. S. A. Friedberg has measured the specific heat of this salt at low temperatures and has concluded that there is no pronounced specific heat anomaly around 17°K.

DISCUSSION

R. D. SPENCE: Some time ago, we looked at the proton resonance of $FeCl_2 \cdot 4H_2O$ down to 1.18°K and we did not find any evidence of antiferromagnetic transition in it.

J. H. VAN VLECK: At first I was worried by the fact that Friedberg and collaborators appear to assume a splitting of the ground quintet into a doublet and triplet, a characteristic of a cubic field. Actually because the orbital angular momentum is largely quenched, the field must have important rhombic members, and the cubic contribution to the decomposition must be relatively minor since it is a fourth order effect in the spin-orbit interaction, whereas the rhombic contribution is of the second order. The explanation of this dilemma is probably one just mentioned to me by Professor Bleaney, namely most rhombic fields are roughly axial and in an axial field of second order the quintet is split into a singlet, a doublet, and a second doublet four times as far from the singlet as the first one. The singlet and first doublet are thus roughly equivalent to a triplet as regards specific heat behavior. This is presumably the same general sort of explanation as obtained from the calculations of Tinkham quoted in the preprint.

S. A. **Friedberg**: Tinkham model does lead qualitatively to the conclusion cited by Professor Van Vleck. Our measurements, of course, provide no detail about the upper three levels, except that they are apparently close. Single crystal susceptibility measurements now in progress will illuminate this point.

M. **Date**:

1. We observed a peculiar paramagnetic resonance line in Cu-formate near 17°K. Resonance line is similar to that of antiferromagnetic resonance but its absorption intensity is too small.
2. Broadening of the ESR line of $Cu(NH_3)_4SO_4 \cdot H_2O$ was observed at 3 cm region which was reported earlier by us. Recently, however, we observed the frequency dependence of this broadening effect. At higher frequency region, the broadening effect of the resonance line decreases and this may be due to the effect of shortr ange order in this crystal.
3. ESR of $CuK_2Cl_4 \cdot 2H_2O$ was investigated at low temperatures and we found that the resonance line can be explained by using Kittel's ferromagnetic resonance below 1.5°K. This is due to the existence of large magnetization in this crystal at low temperatures arising from ferromagnetic Weiss constant.

N. J. **Poulis**: We found ten years ago that in a single crystal of $CuK_2Cl_4 \cdot 2H_2O$ the proton resonance lines disappeared abruptly at about 1.6°K. No lines could be detected below this temperature. Did you observe any effect like this?

J. **Itoh**: We have measured the proton resonance in $K_2CuCl_4 \cdot 2H_2O$ down to about 1.2°K, but we did not observe any anomalous change in intensity. The angular distribution of proton line structure also showed no anomalous behavior.

T. **Haseda**: Dr. Miedema and myself have recently measured the specific heat and susceptibility of $K_2CuCl_4 \cdot 2H_2O$ and $(NH_4)_2CuCl_4 \cdot 2H_2O$. The first salt shows a sharp λ-type anomaly at 0.8°K and the second one shows 0.6°K. The susceptibility suggests the appearance of ferromagnetic state below these temperatures.

A. H. **Cooke**: How does it come about that the susceptibility of the linear chain compound depends on the sample size. Surely the interaction forces are exchange forces between nearest neighbours only?

T. **Haseda**: Yes, I think so. In connection with the size dependence, I should mention that the compound is really in the form of microcrystallite or in some cases even in an amorphous state having lengths of chains which correspond to 10~20 numbers of Cu^{+2} ions in them. In these very short chains, we can expect an end effect which turns out to depend on the whole length of the chain.

E. **Kanda**: I must confess a little weak point of this problem. We have explained the dependence of the susceptibility on the size of the chains by the effect of the ends of the chains. We could not measure the length of the chains, but we measured the length of the amorphous particles of this sample with an electron microscope. We assumed this length to be proportional to the length of the chain.

E. **Kanda**: Have you any idea to estimate the entropy of the spin from your total specific heat curve of Cu-formate tetrahydrate?

S. A. **Friedberg**: Unfortunately there seems to me no simple way to estimate the lattice specific heat. I know no isomorphous diamagnetic salt of this sample and the interesting behaviour of the curve lies at relatively high temperatures and so it becomes a difficult problem.