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# Antiferromagnetism in Linear Chain Crystals. Entropy Changes Accompanying Magnetic Ordering in Anhydrous $CuCl_2$ and $CrCl_2$

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The heat capacities of anhydrous $CuCl_2$ and $CrCl_2$ have been measured over the temperature range 11–300°K. Estimates of the lattice contribution to the heat capacity permit the evaluation of the contribution arising from ordering of the magnetic moments. In both these compounds the major portion of the magnetic entropy is lost in the region of short range order where there is a rounded maximum in the magnetic heat capacity curve. The magnetic heat capacity curves have lambda-type peaks at 23.91°K for $CuCl_2$ and 16.06°K for $CrCl_2$. The measurements are interpreted in terms of one dimensional antiferromagnetic ordering caused by strong interactions within linear chains of magnetic ions (one-dimensional Ising model), together with a long-range order induced by weak interactions between chains.

The measurement of low temperature heat capacity is a valuable tool[1] for determining, in an antiferromagnetic substance, the change in the degree of magnetic order as the temperature is varied. As part of a program of investigation of the anhydrous dichlorides and dibromides of the metals of the first transition series, we have measured the heat capacities of anhydrous $CuCl_2$ and $CrCl_2$ over the temperature range from 11° to 300°K. In a typical antiferromagnetic salt there is a lambda-shaped peak in the heat capacity

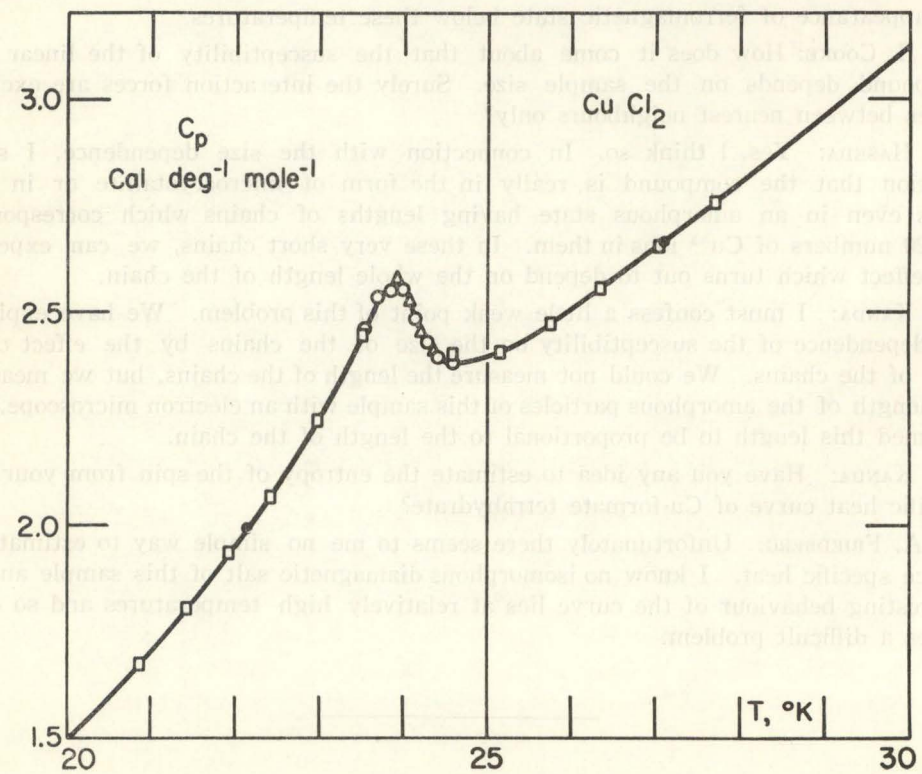



Fig. 1. Heat capacity of $CuCl_2$ *versus* temperature.

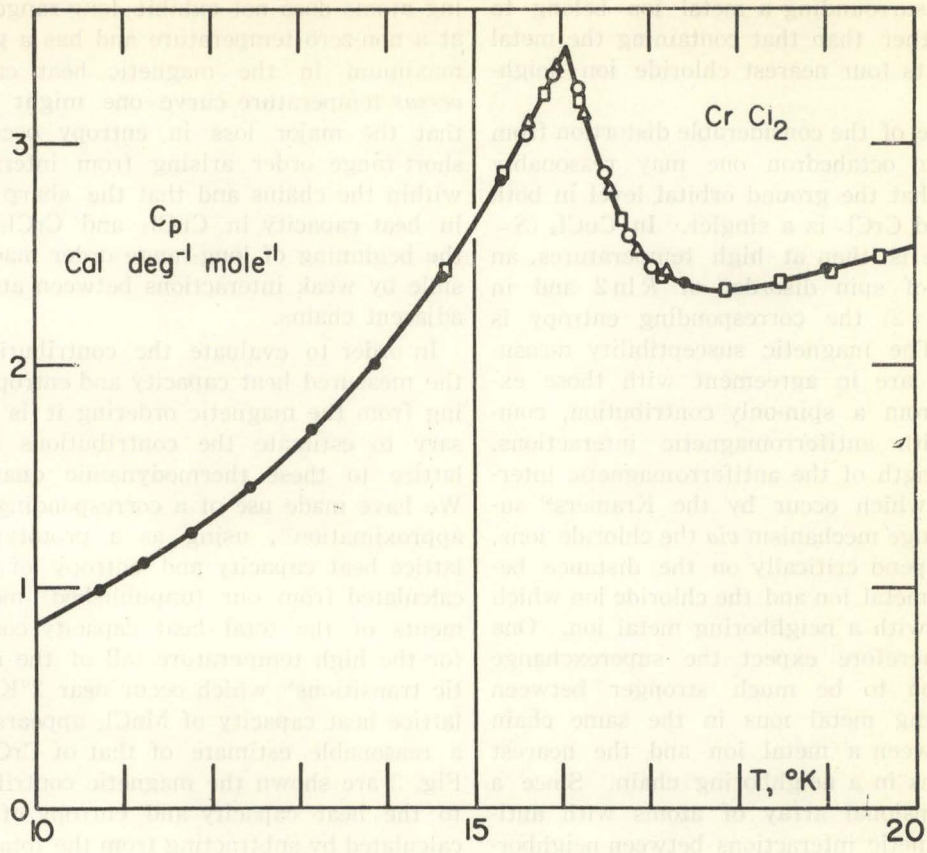
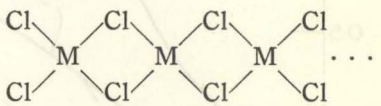



Fig. 2. Heat capacity of $CrCl_2$ *versus* temperature.

at the temperature where long-range ordering of the spins begins and there is a maximum in the powder magnetic susceptibility at approximately the same temperature[2]. The magnetic susceptibilities of powdered $CuCl_2$ and $CrCl_2$ have been measured by Starr, Bitter and Kaufmann[3] who found a maximum in the susceptibility of $CuCl_2$ at 70°K and of $CrCl_2$ at approximately 40°K. We were therefore surprised to find in the corresponding heat capacities no anomalies at these temperatures. Instead, heat capacity peaks were observed at 23.91°K for $CuCl_2$ and at 16.06°K for $CrCl_2$. Fig. 1 and 2 show the measured heat capacities in the anomalous regions for $CuCl_2$ and $CrCl_2$ respectively.

The crystal structure of $CuCl_2$ has been determined by Wells[4] and that of $CrCl_2$ is reported by Cable, Wilkinson and Wollan[5] who also measured by neutron diffraction the ordered magnetic structure. In most dichlorides of the metals of the first transition series, the six nearest anion neighbors of the metal ion are arranged at the corners of a regular octahedron. However, because of the Jahn-Teller effect, in $CuCl_2$ and $CrCl_2$ the octahedron of six chloride ions surrounding the metal ion is greatly distorted from a regular arrangment. In $CuCl_2$ each $Cu^{++}$ ion is surrounded by four chloride ions at a distance of 2.3Å and by two chloride ions at a distance of 2.95Å. In $CrCl_2$ the chromous ion has four chloride ion neighbors at a distance of 2.40Å and two at a distance of 2.89 Å. In both structures there exist infinite chains of the form




where M is the metal ion. The packing of the parallel chains is different in the two structures. The metal ions within a chain are linked by chloride ions at the smaller distance from the metal ions in the chain, and the two chloride ions at the greater

distance surrounding a metal ion belong to chains other than that containing the metal ion and its four nearest chloride ion neighbors.

Because of the considerable distortion from a regular octahedron one may reasonably assume that the ground orbital level in both $CuCl_2$ and $CrCl_2$ is a singlet. In $CuCl_2$ ($S=1/2$) there is, then at high temperatures, an entropy of spin disorder of $R\ln 2$ and in $CrCl_2$ ($S=2$) the corresponding entropy is $R\ln 5$. The magnetic susceptibility measurements[3] are in agreement with those expected from a spin-only contribution, combined with antiferromagnetic interactions. The strength of the antiferromagnetic interactions, which occur by the Kramers[6] superexchange mechanism *via* the chloride ions, would depend critically on the distance between a metal ion and the chloride ion which it shares with a neighboring metal ion. One would therefore expect the superexchange interaction to be much stronger between neighboring metal ions in the same chain than between a metal ion and the nearest metal ions in a neighboring chain. Since a one-dimensional array of atoms with antiferromagnetic interactions between neighboring atoms does not exhibit long-range order at a non-zero temperature and has a gradual maximum in the magnetic heat capacity *versus* temperature curve one might expect that the major loss in entropy occurs as short-range order arising from interactions within the chains and that the sharp peaks in heat capacity in $CuCl_2$ and $CrCl_2$ mark the beginning of long-range order made possible by weak interactions between atoms in adjacent chains.

In order to evaluate the contributions to the measured heat capacity and entropy arising from the magnetic ordering it is necessary to estimate the contributions of the lattice to these thermodynamic quantities. We have made use of a corresponding states approximation[7], using as a prototype the lattice heat capacity and entropy of $MnCl_2$ calculated from our (unpublished) measurements of the total heat capacity corrected for the high temperature tail of the magnetic transitions[8] which occur near 2°K. The lattice heat capacity of $MnCl_2$ appears to be a reasonable estimate of that of $CrCl_2$. In Fig. 3 are shown the magnetic contributions to the heat capacity and entropy of $CuCl_2$ calculated by subtracting from the total func-

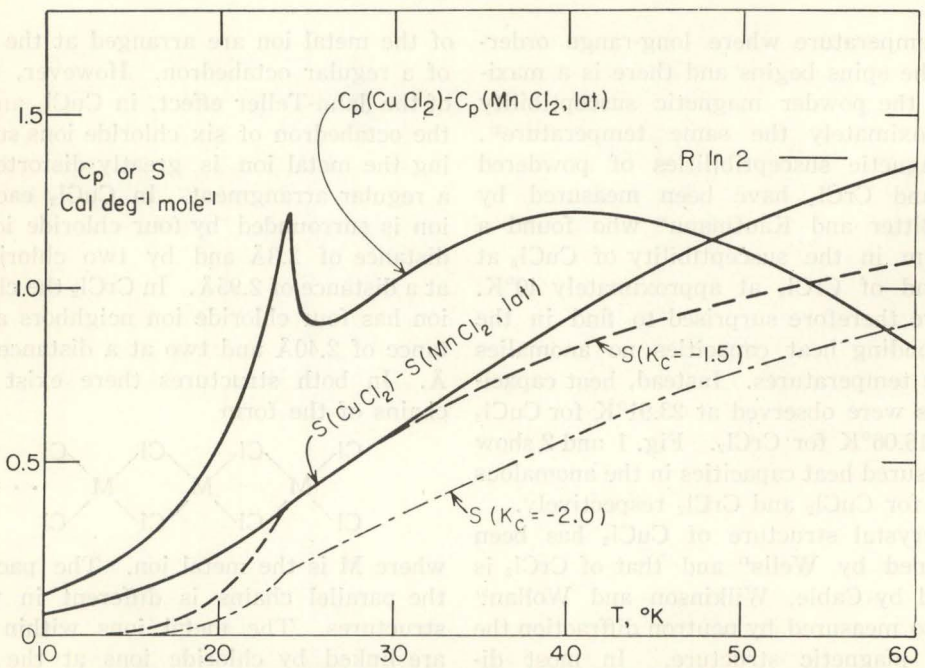



Fig. 3. Magnetic heat capacity and entropy of $CuCl_2$ *versus* temperature. The dashed curves are calculated values of the magnetic entropy (see text).

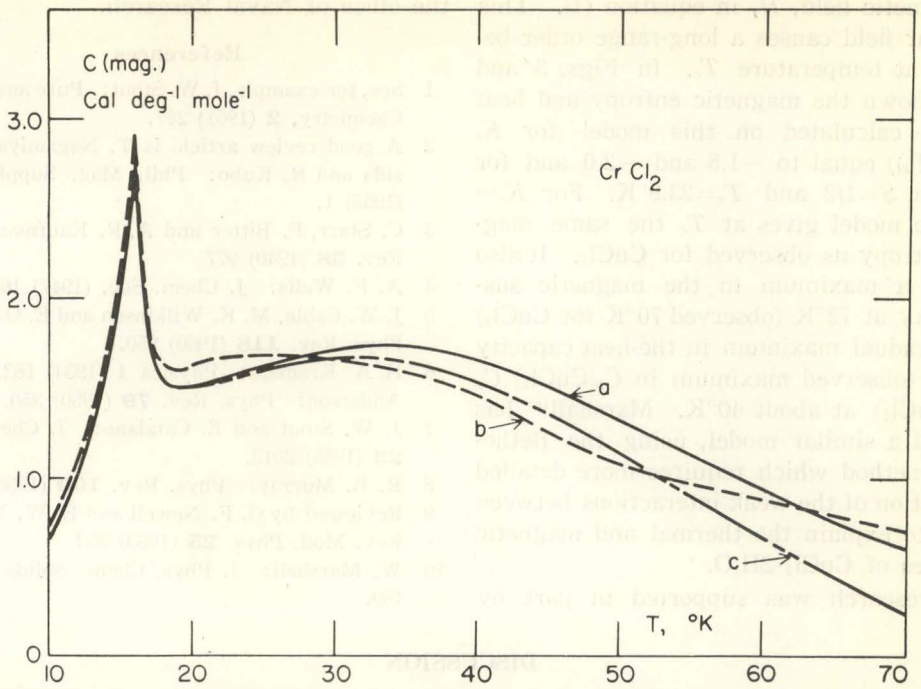



Fig 4. Magnetic heat capacity of $CrCl_2$ *versus* temperature. The three curves correspond to different assumptions as to the lattice contribution to the heat capacity described in the text.

tion for $CuCl_2$ the value for the $MnCl_2$ lattice. In Fig. 4 are shown three different estimates of the magnetic contribution to the heat capacity of $CrCl_2$. Curve (a) is based on a corresponding states approximation, using the lattice heat capacity of $MnCl_2$ as a prototype and adjusting the magnetic entropy of $CrCl_2$ to be $R \ln 5$. Curve (b) is a similar calculation using $ZnCl_2$ (unpublished heat capacity data of E. F. Westrum, Jr.) as a prototype substance. Curve (c) is calculated by taking the lattice heat capacity of $CrCl_2$ at temperature $T$ to be the lattice heat capacity of $MnCl_2$ at temperature 1.048 $T$.

A linear chain with antiferromagnetic or ferromagnetic coupling between nearest neighbors may be approximated by the Ising model[9]. The energy of the chain is represented by the operator

$$\mathscr{H} = -2J \sum_i S_{z,i} S_{z,i+1} + g\beta H \sum_i S_{z,i} \qquad (1)$$

$J$ is the exchange coupling constant, $S_{z,i}$ and $S_{z,i+1}$ are operators representing the component in the direction of the magnetic field, $H$, of the spin angular momentum of adjacent atoms in the chain, and $\beta$ is the Bohr magneton. The heat capacity and magnetic susceptibility may be calculated exactly[9] on this model. To represent the interactions between atoms in adjacent chains we have introduced a molecular field which replaces

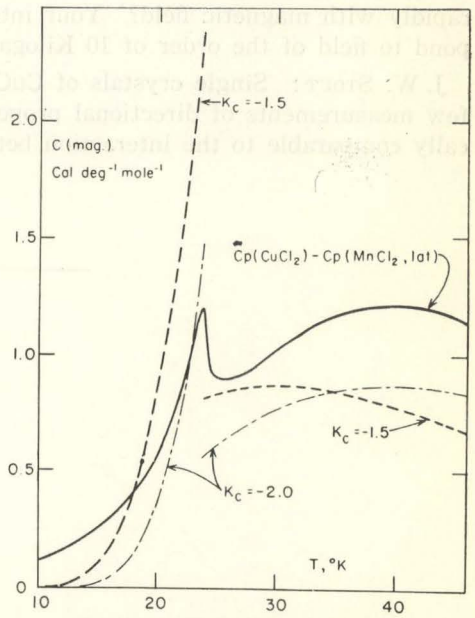



Fig. 5. Magnetic heat capacity of $CuCl_2$ *versus* temperature. The dashed curves are theoretical curves described in the text.

the magnetic field, $H$, in equation (1). This molecular field causes a long-range order beginning at temperature $T_c$. In Figs. 3 and 5 are shown the magnetic entropy and heat capacity calculated on this model for $K_c$ $(=J/(2kT_c))$ equal to $-1.5$ and $-2.0$ and for the case $S=1/2$ and $T_c=23.9°K$. For $K_c=-1.5$ the model gives at $T_c$ the same magnetic entropy as observed for $CuCl_2$. It also predicts a maximum in the magnetic susceptibility at 72°K (observed 70°K for $CuCl_2$) and a gradual maximum in the heat capacity at 30°K (observed maximum in $C_p(CuCl_2)-C_p$ (lat. $MnCl_2$) at about 40°K. Marshall[10] has advanced a similar model, using the Bethe-Peierls method which requires more detailed specification of the weak interactions between chains, to explain the thermal and magnetic properties of $CuCl_2 \cdot 2H_2O$.

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## DISCUSSION

W. MARSHALL: I want to know a rough guess of the ratio of the interaction between chains.

J. W. STOUT: It depends on how many neighbors are involved in the interactions between atoms in different chains, but roughly speaking the interactions within a chain are 30 times as strong as those between chains.

W. P. WOLF: In view of the very small interaction between the linear chains, which you propose, would you expect the magnetic and thermal properties to vary rapidly with magnetic field? Your inter-chain coupling of 1.2°K would only correspond to field of the order of 10 Kilogauss.

J. W. STOUT: Single crystals of $CuCl_2$ have not yet been made and there are very few measurements of directional properties. Attainable fields are certainly energetically comparable to the interaction between chains.