

Nuclear Resonance and Heat Capacity Studies of Antiferromagnetic $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}^*$

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The Li^{7} and proton nuclear magnetic resonance in $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ shows this compound to be antiferromagnetic below $4.46 \pm 0.02^\circ\text{K}$. The local fields at the Li and H sites indicate that the magnetic symmetry group must be one of three possible types. The sublattice magnetization and spin lattice relaxation time vary more rapidly with temperature than indicated by spin wave theory.

Measurements have also been made on the heat capacity of $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$, yielding a Néel temperature of $4.40 \pm .02^\circ\text{K}$. The entropy change associated with the magnetic ordering process has been calculated. This change agrees within 2% of the theoretical value $R \ln (2S+1)$ if the ground state spin of the magnetic ion is taken as $\frac{1}{2}$.

The crystals of $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ used in the experiments reported here were grown from an aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and LiCl at room temperature. This yielded reddish brown monoclinic crystals.

The Néel temperature in $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ was determined by observing the characteristic change in the Li^{7} or proton nuclear resonance which occurs in passing from the antiferromagnetic to the paramagnetic state. The value $T_N = 4.46 \pm .02^\circ\text{K}$ obtained from such experiments is somewhat lower than the value (5.9°K) obtained by Vossos, Jennings and Rundle¹⁾ from magnetic susceptibility measurements but is in agreement with the specific heat results.

The Li^{7} resonance consists of four lines each showing a quadrupole splitting. Lines for which the quadrupole splitting has the same magnitude and angular variation arise from lithiums on sites related by an inversion center. We find that such lithiums experience reversed local magnetic fields showing that the magnetic symmetry element occupying the crystallographic inversion center is an anti-inversion. This result coupled with the facts that the number of lines is the same as the number of lithiums in the chemical unit cell and that the resonance diagrams show monoclinic symmetry leads to the conclusion that the magnetic symmetry group (Schubnikov group) must be one of three: $P2_1/C'$, $P2_1'/C$, P_a2_1/C . The first two

groups have magnetic unit cells of the same size as the chemical unit cell. The third group has a magnetic unit cell of dimensions $2a, b, c$ where a, b, c are the dimensions of the chemical unit cell.

The proton resonance consists of sixteen lines each showing a dipole-dipole splitting arising from the interaction between hydrogens on the same water molecule. The local magnetic fields at proton sites related by the inversion operation are reversed in sign which again demonstrates that the magnetic element occupying the crystallographic inversion point is an anti-inversion. Thus analysis of the proton resonance spectrum leads to the same possible Schubnikov groups as obtained from the Li^{7} resonance.

The temperature dependence of three of the larger local magnetic fields at the proton sites has been examined by resonance experiments in zero field. We find that the magnetization difference $M(0) - M(T)$ varies as T^3 at low temperatures in contrast with the T^4 dependence observed by Hardeman *et al.*²⁾ for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the T^2 dependence obtained from spin wave theory by Kubo³⁾. We find that the spin lattice relaxation time of the protons varies approximately as T^{-4} which may be compared with the T^{-7} dependence observed by Hardeman *et al.* for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the T^{-3} dependence predicted by the spin wave calculations of Van Kranendonk and Bloom⁴⁾.

The heat capacity of $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ has also been measured. These measurements

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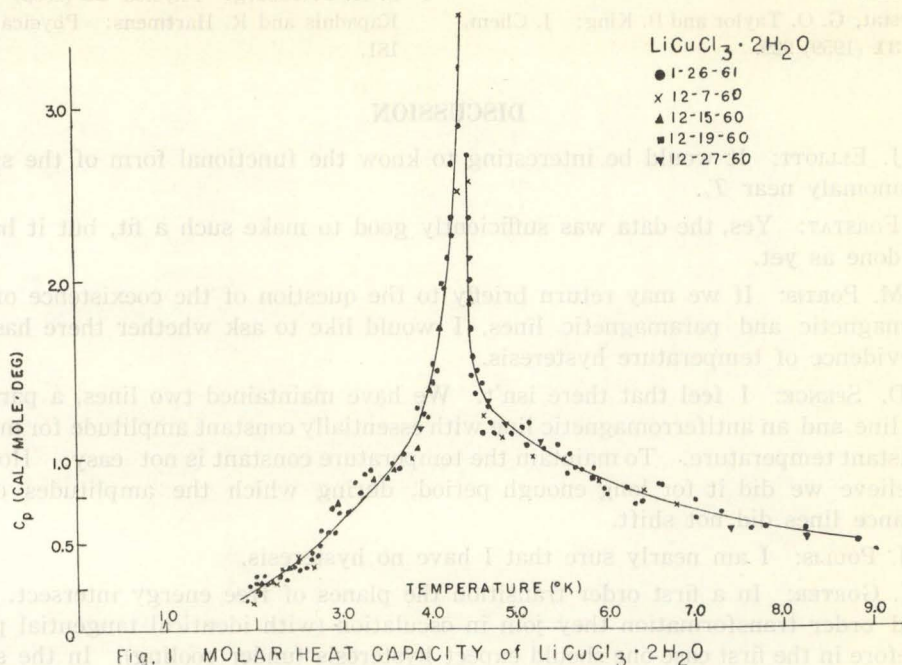


Fig. 1.

on the single crystals were made in the temperature range 2° – 9°K . Three separate crystals were used in the experiments, each weighing approximately 1.5 gm and measuring $1.5 \times 1.0 \text{ cm}$.

Data were taken for five separate runs using a vacuum calorimeter⁵; three on the first crystal (12-7, 12-15, 12-19-60), one on the second crystal (12-22-60), and one on the third crystal (1-26-61). This latter crystal was also used in some of the proton resonance work. Fig. 1 shows the heat capacity curve obtained from these measurements. This λ -type anomaly, occurring at $4.40 \pm 0.02^{\circ}\text{K}$, has been identified as a paramagnetic-antiferromagnetic transition by the proton resonance work of above. The Néel temperature, obtained from the heat capacity data agrees well with that obtained from the proton resonance experiments.

Referring to Fig. 1, it can be seen that the heat capacity curve rises very sharply in the neighborhood of the Néel temperature, but falls less rapidly, producing a large "tail" in the paramagnetic state (above 4.4°K). The "tail" is due primarily to the slow diminution of the short range ordering of the spins of the magnetic ions. It is pos-

sible to determine the total magnetic entropy associated with this antiferromagnetic transition, and consequently to note what fraction is connected with the short range ordering. A method for making this calculation has already been described⁶. It consists essentially of calculating separately, contributions to the magnetic entropy above and below the Néel temperature. This calculation yields 0.70 cal/mol deg and 0.65 cal/mol deg for the regions below and above the Néel temperature respectively. The total entropy change is therefore 1.35 cal/mol deg, of which nearly 50% is associated with the short range ordering effect. In addition, if one assumes a ground state spin, S , of $\frac{1}{2}$ for the copper ion, this calculated value of the magnetic entropy change agrees to within 2% with the value obtained from $R \ln (2S+1)$.

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DISCUSSION

R. J. ELLIOTT: It would be interesting to know the functional form of the specific heat anomaly near T_c .

H. FORSTAT: Yes, the data was sufficiently good to make such a fit, but it has not been done as yet.

A. M. PORTIS: If we may return briefly to the question of the coexistence of anti-ferromagnetic and paramagnetic lines, I would like to ask whether there has been any evidence of temperature hysteresis.

R. D. SPENCE: I feel that there isn't. We have maintained two lines, a paramagnetic line and an antiferromagnetic line with essentially constant amplitude for minutes at constant temperature. To maintain the temperature constant is not easy. However we believe we did it for long enough period, during which the amplitudes of the resonance lines did not shift.

N. J. POULIS: I am nearly sure that I have no hysteresis.

C. J. GORTER: In a first order transition the planes of free energy intersect. In a second order transformation they join in osculation (with identical tangential plane). Therefore in the first case one should expect hysteresis (under cooling). In the second case one might expect a large role to be played by local inhomogeneities and strains. Only the He λ point is free from that as it concerns a liquid and it is therefore ideal for studying the approach of the transition line.

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Magnetic Resonance Studies of Some Copper Salts

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(1) Unpaired electron distribution over various atoms or ions in the lattice of $K_2CuCl_4 \cdot 2H_2O$ and $(NH_4)_2CuCl_4 \cdot 2H_2O$ was determined by analysing the angular distribution of proton magnetic resonance lines at liquid helium temperature. The result is as follows: 80% on Cu, 2% each on O, 0.1% each on H of H_2O , less than 0.5% each on monovalent cation, the remaining 16% on four Cl ions.

(2) Magnetic behavior of $Cu(HCOO)_4 \cdot 4H_2O$ was investigated by proton magnetic resonance. Below 17°K, this crystal is in antiferromagnetic state. Magnetic unit cell is larger than the crystallographic one. Between 20° and about 50°K, the magnetic behavior of this crystal is not simply paramagnetic, but could not be uniquely determined by our experiment alone. Above about 50°K, it is paramagnetic.

Magnetic behavior of some copper salts at low temperature was investigated by means of proton and electron magnetic resonance methods.

(1) $K_2CuCl_4 \cdot 2H_2O$ and $(NH_4)_2CuCl_4 \cdot 2H_2O$

These salts are isomorphic in structure. The crystal symmetry is tetragonal, Cu ions located at (000) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$). Each Cu ion is