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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  $\lambda$  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



surrounded by two water molecules (on the  $c$ -axis) and four Cl ions (in the  $c$ -plane), forming an octahedron. The local symmetry of the crystalline field at the Cu ion is orthorhombic and the principal values of the  $g$ -tensor are  $g_1=2.10$ ,  $g_2=2.36$  and  $g_c=2.07$ , respectively<sup>11</sup>. The configuration of atoms around the Cu ion at  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  can be derived from that around (000) by  $90^\circ$  rotation about the  $c$ -axis. An exchange interaction acts between these dissimilar ions and only a single line appears in ESR spectrum with  $g_{\parallel}=g_c$  and  $g_{\perp}=(g_1+g_2)/2$ , unless very high frequency microwave is used. The exchange frequency was determined by Abe *et al* for the K-salt to be  $3 \times 10^9 \text{ sec}^{-1}$  using 60Gc/sec microwave<sup>11</sup>.

The displacement of the proton magnetic resonance lines from Zeeman value, after correcting the effect of proton-proton interaction, is proportional to the average magnetization of Cu ions, or, when the crystal is in paramagnetic state, to  $\chi H$  ( $\chi$ , susceptibility;  $H$ , applied field). The displacement was found to follow Curie-Weiss law above  $2^\circ\text{K}$ , with the Weiss temperature of  $1.0^\circ\text{K}$ . Below  $2^\circ\text{K}$ , it shows paramagnetic saturation effect. At  $1.1^\circ\text{K}$  and 7000 oe, over 70% of spins are ordered paramagnetically. No indication of magnetic phase change was observed. In the  $\text{NH}_4$ -salt, the width of proton line of  $\text{NH}_4$  is about 3 oe at room temperature, indicating that the  $\text{NH}_4$  ion is rotating,

just as in  $\text{NH}_4$ -halides. At liquid nitrogen temperature, the width displays full value of the rigid  $\text{NH}_4$ -ion. The spin lattice relaxation time,  $T_1$ , of this proton line will change stepwisely at the temperature where  $\nu_e=\nu_J$ ,  $\nu_e$  being the correlation frequency of

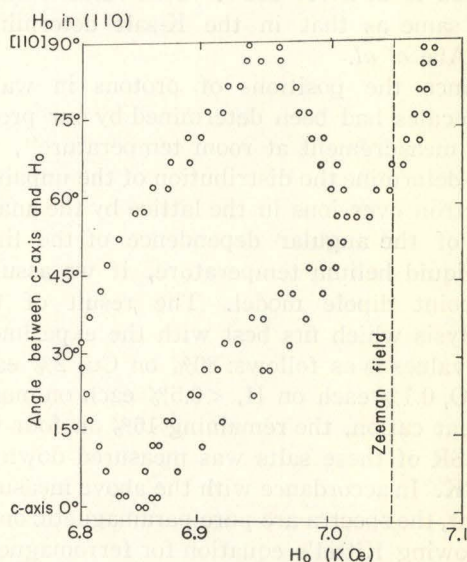


Fig. 2. Proton resonance in  $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$  ( $4.2^\circ\text{K}$ , frequency 30 Mc/sec).

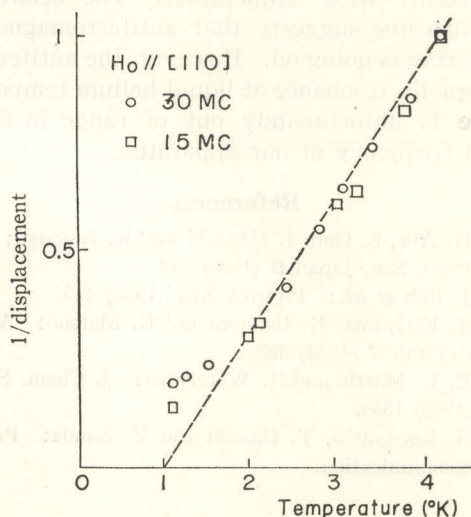


Fig. 1. Temperature dependence of the relative separation between two groups of proton lines in  $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ .

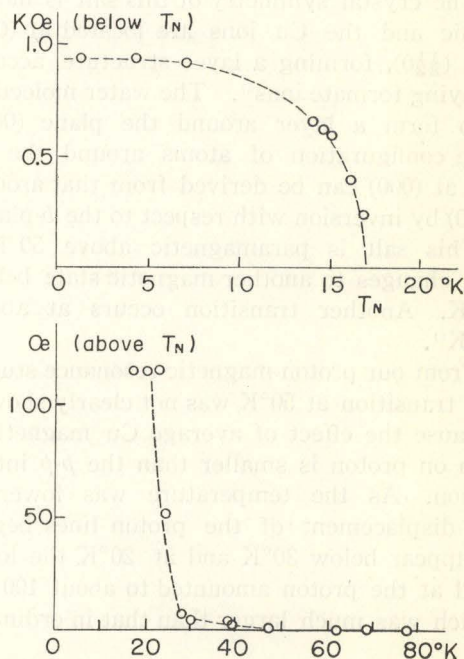


Fig. 3. Temperature dependence of the displacement of the proton lines from Zeeman field in  $\text{Cu-formate} \cdot 4\text{H}_2\text{O}$ .



rotation and  $\nu_J$  the exchange frequency of Cu ions. The temperature dependence of  $\nu_c (= \nu_0 \exp -E/kT)$  was determined by measuring the motional narrowing effect of the width. At about 240°K a stepwise change of  $T_1$  was observed, from which  $\nu_J$  is determined to be  $3 \times 10^9 \text{ sec}^{-1}$ . This value is about the same as that in the K-salt determined by Abe *et al.*

Since the positions of protons in water molecules had been determined by our previous measurement at room temperature<sup>2)</sup>, we can determine the distribution of the unpaired electron over ions in the lattice by the analysis of the angular dependence of the lines at liquid helium temperature, if we assume a point dipole model. The result of the analysis which fits best with the experimental values is as follows: 80% on Cu, 2% each on O, 0.1% each on H, <0.5% each on monovalent cation, the remaining 16% on four Cl.

ESR of these salts was measured down to 1.1°K. In accordance with the above measurement, the spectra are pure paramagnetic ones, following Kittel's equation for ferromagnetic resonance when the paramagnetic ordering increases.

## (2) $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$

The crystal symmetry of this salt is monoclinic and the Cu ions are located at (000) and  $(\frac{1}{2}, \frac{1}{2}, 0)$ , forming a layer structure accompanying formate ions<sup>3)</sup>. The water molecules also form a layer around the plane (002). The configuration of atoms around the Cu ion at (000) can be derived from that around  $(\frac{1}{2}, \frac{1}{2}, 0)$  by inversion with respect to the *b*-plane.

This salt is paramagnetic above 50°K<sup>4)</sup>, and changes to another magnetic state below 50°K. Another transition occurs at about 20°K<sup>5)</sup>.

From our proton magnetic resonance study, the transition at 50°K was not clearly shown, because the effect of average Cu magnetization on proton is smaller than the *p-p* interaction. As the temperature was lowered, the displacement of the proton lines began to appear below 30°K and at 20°K the local field at the proton amounted to about 100 oe, which was much larger than that in ordinary

paramagnetic salts at this temperature. The angular dependence of the proton lines has 180° symmetry, and the displacement was proportional to the applied field strength. But the angular dependence is not consistent with  $(3 \cos^2 \theta - 1)$  law, where  $\theta$  is the angle between *H* and Cu-*p* line. From our experiment alone, the magnetic state of this salt around 20°K is not clear.

Below 20°K, the proton line displacement remained almost constant, indicating that some magnetic ordering began to occur, and, below 17°K, this crystal changed to an antiferromagnetic state. The line displacement followed the Brillouin function with Néel temperature of about 17°K. At liquid helium temperature, the angular distribution of the proton lines had 360° symmetry and the lines appeared as pairs differing 180° in phase with each other, which are typical features of an antiferromagnet. The magnetic unit cell is larger than the crystallographic unit cell, and the direction of the easy axis of spins does not coincide with the principal axes of the crystal, nor with those of the *g*-tensor.

ESR was also measured in the temperature range below 50°K. Below 50°K, only a weak line of residual paramagnetic resonance was observed which disappeared when the temperature was decreased. No other line was found. Below 20°K, a resonance line was again observed, whose resonance field varied markedly with temperature. The behavior of this line suggests that antiferromagnetic ordering is going on. However, the antiferromagnetic resonance at liquid helium temperature is unfortunately out of range in field and frequency of our apparatus.

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