High-Field Magnetic Phase Transition in $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$

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Proton magnetic-resonance measurements are carried out on a single crystal of $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$ in magnetic fields up to 50 kOe at temperatures below 1 K. The copper ions form pairs with an exchange interaction $-J/k$ of about 5 K. In magnetic fields around 36 kOe the much weaker interpair exchange J' leads to short- and long-range order below 0.35 and 0.16 K, respectively. The phase transition at 0.16 K is characterized by a spontaneous component of the time-averaged magnetic moment of the Cu ions perpendicular to the external field, and disappears below 29 and above 42 kOe.

In the past few years the hydrated copper nitrate $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$ has aroused a considerable amount of interest because of its special magnetic characteristics. The Cu^{++} ions in this substance are coupled in relatively isolated pairs by an isotropic antiferromagnetic exchange interaction, as shown by Berger, Friedberg, and Schriempf[1] and Wittekoek.[2] Such an isolated pair of $S=\frac{1}{2}$ ions can be described adequately by the Hamiltonian

$$\mathcal{H} = -J\vec{S}_1 \cdot \vec{S}_2 - g\beta(S_{1z} + S_{2z})H.$$

Here J is the intrapair exchange constant, g the g factor, β the value of the Bohr magneton, and H the applied magnetic field directed along the z axis. The pair ground state is a singlet, separated from the excited triplet by the exchange J/k of about 5 K (3.5 cm^{-1}). The lowest triplet level crosses the singlet at a magnetic field of 36 kOe. From anomalies in adiabatic magnetization experiments[3] and from magnetization isotherms[4] there is also evidence of an interpair coupling J'. Although J' is much weaker than the intrapair coupling J, it causes a considerable amount of mixing between the singlet and the lowest triplet state in the vicinity of the level crossing. Recently several theoretical investigations have been reported concerning the effect of this mixing on the spin structure and the magnetic properties of the crystal.[5-8] The interpair interaction can be accounted for by adding to the Hamiltonian an extra term

$$\mathcal{H}' = -J' \sum_{i=1}^{z} (\vec{S}_1 \cdot \vec{S}_{1i} + \vec{S}_2 \cdot \vec{S}_{2i}).$$

Here $\vec{S}_{1i}$ and $\vec{S}_{2i}$ are the spin operators for the two members of the ith neighbor pair. If the temperature is low with respect to J/k, the system can be described by the two lower energy levels only, and thus for each pair a pseudospin $S'=\frac{1}{2}$ is created in an effective field $H' = g\beta H + J + \frac{1}{2}zJ'$, while the interpair exchange becomes anisotropic. If the number of neighboring pairs z over which the sum extends is equal to two, we have a model of a one-dimensional linear chain of copper pairs in which only short-range order is possible. Bonner *et al.*[5] propose two models of this type for $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$. They fit their models to the existing thermal and magnetic data and find a striking correspondence with a single choice of parameters. If $z=4$ or 6 the description fits a two- or three-dimensional system of coupled pairs. In such systems it can be shown[5] that in the vicinity of the level crossing, apart from the z component of the time averaged Cu magnetic moment, there will also exist a component perpendicular to the external magnetic field below a critical temperature.

In order to investigate the behavior of the spin pairs in the vicinity of the level crossing we studied proton magnetic resonance between 25 and 45 kOe in the temperature range from 50 mK to 1 K. A single crystal of $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$, oriented with its b axis along the magnetic field of a superconducting magnet, was connected to an adiabatically demagnetized cooling salt. Measurements were done with a marginal oscillator while the temperature was determined with a Speer carbon resistor, which was calibrated against the susceptibility of cerium magnesium nitrate.

From the splitting Δ of the proton resonance lines from the free-proton resonance frequency, the magnetization M is determined as a function of the external field H at different temperatures (Fig. 1). The most significant feature of these isotherms is that they have the same linear field dependence in a certain field region around $H = 36.0$ kOe. As a result, each field determines a temperature T_s below which the splitting Δ is temperature independent. However, T_s is not a sharp critical temperature, but indicates only the bend in the Δ vs T curves. This is demonstrated clearly in Fig. 2, where, for a number

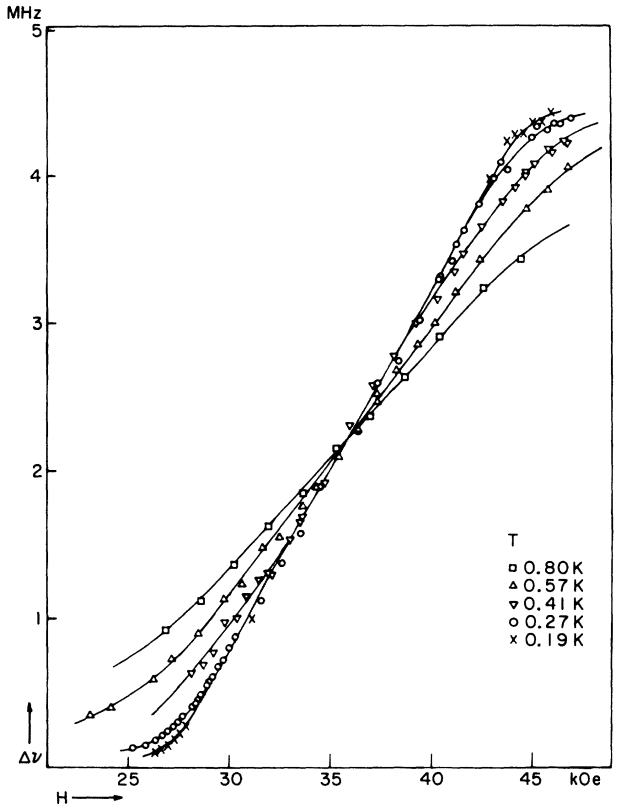

FIG. 1. Splitting Δ for the best distinguishable proton-resonance line as a function of the external field at several temperatures. Lines are drawn only for visual aid.

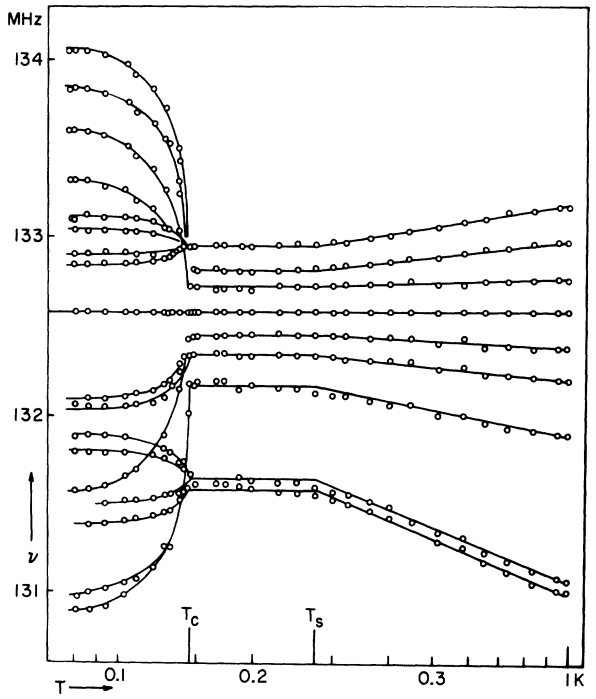

FIG. 2. Resonance frequency ν for a number of well-distinguishable proton lines as a function of temperature at a magnetic field of 31.12 kOe. The logarithmic scale is used only to expand the low-temperature part.

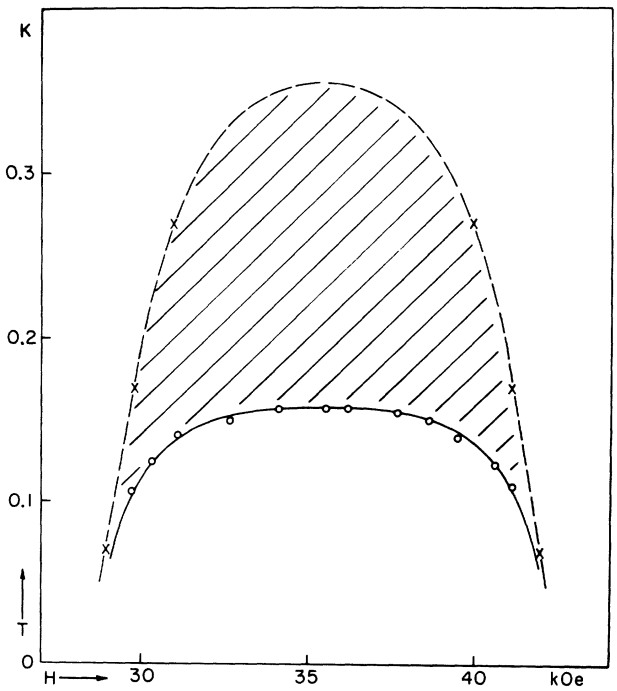

FIG. 3. Critical temperature T_c versus the external magnetic field. For dashed line and shaded area see text. The crosses represent minima of isentropes in adiabatic magnetization experiments.

of well-distinguishable proton resonance lines, Δ is plotted against temperature at a field of 31.1 kOe. The values of T_s for different fields are indicated by the dashed curve in Fig. 3, which forms as a consequence the boundary of the field and temperature region where the splitting Δ is linearly dependent on the field and not dependent on temperature.

Moreover, in extending our NMR measurements to lower temperatures we found a real phase transition which is very interesting. An abrupt change in Δ appears at $T_c = 0.14$ K for all proton-resonance lines as can be seen in Fig. 2. The extra splitting below this critical temperature is clearly due to a spontaneous magnetization effect. Above $T_c = 0.14$ K the resonance spectrum can be described by the form

$$\Delta_i = G_i \mu_z(T). \quad (1)$$

Here G_i is a geometrical factor, determined by the ith proton position and the field direction; $\mu_z(T)$ is the time-averaged magnetic moment of

the copper ions, which is directed along the z axis. However, Fig. 2 shows clearly that below T_c the ratio Δ_i/Δ_j for any two resonance lines is no longer constant, as it is above T_c. This experimental result necessitates an extra term in formula (1) so that below T_c

$$\Delta_i = G_i\mu_z(T) + G_i'\mu'(T),$$

where the factors G_i' are different from the G_i. It must be concluded that the function $\mu'(T)$ represents a spontaneous magnetization perpendicular to μ_z. We have repeated the experiment at other fields between 29 and 42 kOe and found the same behavior of the resonance lines, except that the critical temperature is strongly field dependent. The measured values of T_c are indicated by the drawn line in Fig. 3.

The field and temperature region defined by the the temperature independence of the resonance spectrum (shaded area in Fig. 3) is the same as that found by Haseda *et al.*,[3] whose adiabatic magnetization experiments we extended to 50 mK. The proton resonance experiments show that in this region the interpair coupling J' leads only to short-range order, probably in linear chains of spin pairs. Below 0.16 K long-range order sets in, characterized by a spontaneous component of the time-averaged magnetic moment of the Cu^{++} ion perpendicular to the external field. Comparing our results with those of Bonner *et al.*,[5] we are led to the conclusion that the interpair interaction consists of a dominant exchange in one dimension and two weaker components, just strong enough to arrange long-range order below 0.16 K.

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Critical Behavior of the Heisenberg Ferromagnets EuO and EuS†

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Neutron-scattering measurements have been made of the critical parameters of the simple Heisenberg ferromagnets EuO and EuS. Values of the critical exponents β and ν and the amplitudes of B and F describing, respectively, the reduced magnetization and the inverse correlation range (above T_c) are in good accord with theory. The measured values of the exponent γ, describing the static susceptibility, support the recent prediction that $\gamma \approx 1.40$ in a simple nearest-neighbor Heisenberg ferromagnet. The scaling relation between β, ν, and γ is fulfilled.

Although ferromagnets have been extensively studied, most are so complicated that their critical behavior cannot reliably be compared with the simple Heisenberg or Ising models for which theoretical predictions exist.[1] Among the rare exceptions are EuO and EuS. We have used neutron-scattering techniques to investigate the spontaneous magnetization below the Curie temperature T_c and the spatial critical fluctuations above T_c in these two materials, both of which are insulators with almost ideally localized Heisenberg exchange interactions. Since the Eu^{2+} ions are in the $^8S_{7/2}$ spin state and the magnetic structure of both compounds is fcc, the exchange is also nearly