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HIGH FIELD N. M. R. IN Cu(NO₃)₂·2 $\frac{1}{2}$ H₂O BELOW 1 °K

M. W. van TOL, M. MATSUURA and N. J. POULIS
Kamerlingh Onnes Laboratory, Leiden, Netherlands

Résumé. — On étudie le spectre des protons dans des monocristaux de Cu(NO₃)₂·2 $\frac{1}{2}$ H₂O entre 0,3 et 1 °K. On a utilisé des champs jusqu'à 47 kOe selon l'axe b. On peut décrire les dépendances en champ et en température de l'aimantation obtenues à partir de ces mesures, à l'aide d'un couplage d'échange entre paires $xJ'/k = -1,9$ °K qui produit un ordre transversal au-dessous d'une température antique de 0,45 °K.

Abstract. — The proton spectrum of single crystals of Cu(NO₃)₂·2 $\frac{1}{2}$ H₂O is studied between 0.3 and 1 °K. Fields up to 47 kOe were applied along the b axis. The field and temperature dependence of the magnetization obtained from these measurements can be described by an interpair exchange coupling $xJ'/k = -1.9$ °K that generates a transverse ordering below a critical temperature of 0.45 °K.

Introduction. — Low field susceptibility measurements [1] and specific heat measurements [2] at low temperatures have shown that in cupric nitrate «trihydrate» the spins of the copper ions are associated in pairs by an isotropic Heisenberg coupling.

This results in a pair ground state with total spin $S = 0$ separated by $|J'/k| \approx 5$ K from an excited triplet. The lowest level of this triplet is crossing the singlet at a field of about 36 kOe. Adiabatic magnetization experiments show a decrease of temperature at the point of level crossing [2, 3]. Anomalies found in these experiments when the initial temperature is lower than about 0.7 °K [4] can be explained by the assumption of a weak interpair exchange interaction [5]. This exchange interaction also follows from a small discrepancy between magnetization isotherms in the 1-4°K region and theoretical curves for the isolated pair model [6]. Recently several theoretical investigations are reported concerning this interpair exchange. According to these theories an ordering of the spin component perpendicular to the field can occur in the vicinities of the point of level crossing at sufficiently low temperatures [5, 7]. When the temperature is low compared to the intrapair exchange-energy of 5 °K, as is the case in all our experiments, the upper two triplet levels of the spin pair can be neglected. If the interpair exchange is assumed to be isotropic and of the form:

$$\mathcal{K}' = J' \sum_{i<j} (S_{i1} S_{j1} + S_{i2} S_{j2})$$

projection of the system onto the subspace spanned by the lower two levels leads to a Hamiltonian:

$$\mathcal{K} = g\beta H_{eff} \sum_{i} \sigma_{ix} +$$

$$+ \frac{1}{2} J' \sum_{i<j} \left[ \sigma_{ix} \sigma_{jz} + 2(\sigma_{ix} \sigma_{jx} + \sigma_{iy} \sigma_{jy}) \right]$$

where $H_{eff} = H_0 - |J + \frac{1}{2} \alpha|/g\beta$ is the effective field and $\sigma$ the Pauli spin matrix corresponding to the lower two levels:

$$\sigma_x = 2(S_{i1} + S_{i2}) - 1,$$

$$\sigma_{x,y} = \sqrt{2}(S_{i1,y} - S_{i2,y})$$

and

$$\alpha = \frac{1}{2} zJ'$$

$z$ is the number of nearest neighbours.

The main feature of this transformation is that the interpair exchange interaction is no longer isotropic. Using a two sublattice model and a molecular field approximation [5] the critical temperature at the crossing point (zero effective field) is expected to be:

$$T_c = \frac{\alpha}{2k}$$

while above this temperature the $\frac{1}{2} J' \sum_{i<j} S_{ix} S_{jz}$ term causes the system to follow a Curie-Weiss law with

$$\theta = -\frac{1}{2} T_c.$$

The magnetization $< S_z >$ at zero temperature is expected to be zero for magnetic fields up to $g\beta H = |J - \alpha|$, to increase linearly with $H$ until $g\beta H = |J + 2 \alpha|$ and to remain equal to $H$ above that value. For finite temperatures below $T_c$ the same curve is followed in a part of the field region between $|J - \alpha|$ and $|J + 2 \alpha|$ (Fig. 1).

In this paper we report NMR measurements of Cu(NO₃)₂·2 $\frac{1}{2}$ H₂O in fields up to 47 kOe at temperatures between 0.27 and 1 °K. These were undertaken to study possible ordering effects of the above described nature. A reasonable agreement with the Tachiki theory [5] has been found.

Experimental method. — Single crystals of Cu(NO₃)₂·2 $\frac{1}{2}$ H₂O, grown from an aequous solution at 35 °C, were polished in an ellipsoidal shape with

![Fig. 1. — Theoretical magnetization isotherms in the Tachiki theory.](image-url)
their long axis in the b-direction. They were placed in a glass 3He cryostat in the centre of a superconducting solenoid capable of generating homogeneous magnetic fields up to 47 kOe.

The NMR signals were detected with a marginal oscillator of the Robinson type [8] operating in the 80–200 MHz range.

The field strength was obtained from fluorine resonance in the teflon insulation of the resonance coil before and after the proton spectrum was measured. Frequencies were counted with a Hewlett-Packard type 5253B frequency meter. The magnetization of cupric nitrate is obtained by measuring the shift in the resonance frequency of one of the protons in the crystal water. The crystal was directed with its b-axis parallel to the field. By making resonance diagrams at 3 °K with the (low) field rotating in the ab and ac-plane respectively it was verified that in this direction the observed line showed a maximum shift so that the measured frequency difference \( \Delta \nu \) is proportional to the magnetization within 1%. The ab-diagram clearly shows ten different resonance lines that coincide in pairs in the ac-plane because of symmetry. Therefore we must conclude to a number of 2 \( \frac{1}{4} \) crystal water molecules, in contrast to other publications from this laboratory [9].

**Discussion of the results.** — The level crossing \( \frac{g \beta H}{J + \frac{1}{2} \alpha} \) has been determined to occur at 36.00 (± 0.03) kOe from magnetization curves at 0.3 and 0.8 °K (Fig. 2). Within the measuring accuracy the 0.41 magnetization curve coincides with the 0.27 °K curve between 33 and 39 kOe. Careful measurements at the lowest temperature show a discontinuity in the susceptibility \( dM/dH \) at 28.4 kOe (Fig. 4). Extrapolating the straight part of the 0.27 curve yields the field equivalent for \( |J - \alpha| \) and \( |J + 2 \alpha| \). The \( g \)-value along the b axis is known from EPR measurements [10] and high temperature magnetization measurements [6] to be 2.36 ± 0.02 so that \( J \) and \( \alpha \) can be calculated. The result,

\[
J/k = -5.19 \pm 0.03 \text{ °K}
\]

and

\[
\alpha/k = -0.96 \pm 0.03 \text{ °K}
\]

is in close agreement with the value \( J/k = -5.18 \) from specific heat data [2] although a rather large discrepancy exists between our value for \( \alpha \) and that obtained by high temperature magnetization measurements \( \alpha/k = 0.62 \) °K [6].

To check our measurements in a different way we measured the temperature dependence of the lineshift \( \Delta \nu \) at 33 kOe. The lineshift is proportional to the magnetization and because of the linear behaviour of the magnetization near 36 kOe the difference \( \Delta \nu(36) - \Delta \nu(33) \) is a reasonable estimate for the susceptibility in that region. The inverse susceptibility clearly demonstrates the Curie-Weiss behaviour above 0.45 °K (Fig. 3) with a \( \theta \)-value of about — 0.2 °K. This is in good agreement with our magnetization isotherms and the Tachiki theory [5] that expects these temperatures to be equal to

\[
|\alpha|/2 k = 0.48 \text{ °K and } |\alpha|/4 k = 0.24 \text{ °K}
\]

respectively. Below the critical temperature of 0.45 °K the measured lineshift is not temperature independent. This may be due to a non-negligible perpendicular component of the Cu spins below \( T_c \) or to the fact that only short range ordering occurs [7].

**Conclusion.** — There is evidence of an antiferromagnetic exchange interaction \( zJ'/k = -1.9 \) °K that
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The fact that $T_s \approx -2\theta$ suggests that the spin components perpendicular to the magnetic field play the more important role in this ordering.

References

[10] Van der Ven (N.), private comm.

High field N. M. R. in Cu(NO₃)₂·2 H₂O below 1 °K gives rise to (at least short range) ordering effects at temperatures below 0.45 °K and fields between 27 and 45 kOe.