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NUCLEAR MAGNETIC RESONANCE STUDY
OF THE HEISENBERG FERROMAGNET Cu(NH₄)₂ Br₄, 2 H₂O

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Abstract. — The nuclear magnetic resonance (NMR) of protons, Br⁷⁹ and Br⁸¹ has been studied in single crystals of Cu(NH₄)₂ Br₄, 2 H₂O between 0.4 and 4.2 K. In the paramagnetic phase, two transitions of pure quadrupole resonance were observed at 8.345 and 6.973 MHz. In the ferromagnetic phase below 1.831 K, the observed splittings of these transitions by the internal magnetic fields are in good agreement, as the susceptibility measurements, with an easy axis along c. The deduced relative spontaneous magnetization fits the law

\[ m(T) = 1.54(1 - T/T_c)^{1/4} \]

for \( T < 1 - T/T_c < 0.10^{-3} \). At low temperature the magnetization has been found in agreement with the spin wave theory.

I. Introduction. — The double salt Cu(NH₄)₂ Br₄, 2 H₂O crystallizes in the tetragonal system with a small deviation from the bcc one [1]: \( a = 7.98 \) Å, \( c = 8.41 \) Å. There are two Cu²⁺ ions per unit cell, each one surrounded by two water molecules and four Br⁻ ions. By studying the Cu²⁺ ESR, Suzuki and Watanabe [2] found only one magnetic copper site and axial symmetry of the g tensor with respect to the c axis: \( g_1 = 2.04, g_2 = 2.196 \). Below about 1.8 K, Cu(NH₄)₂ Br₄, 2 H₂O becomes ferromagnetic. The interactions between the Cu²⁺ spins are nearly isotropic, therefore Cu(NH₄)₂ Br₄, 2 H₂O might be a good Heisenberg ferromagnet as the isomorphic salts Cu(NH₄)₂ Cl₄, 2 H₂O, CuK₂ Cl₄, 2 H₂O and CuRb₂ Cl₄, 2 H₂O [3]. The aim of this work is to get precise informations on the transition temperature and on the spontaneous magnetization by nuclear magnetic resonance (NMR) of Br and H in the ferromagnetic region.

II. Experimental methods. — Single crystals of Cu(NH₄)₂ Br₄, 2 H₂O have been grown by evaporation of the saturated aqueous solution. From the same large crystal, two samples of ellipsoidal shape have been formed, one I with the long axis along c and the other II along a. The samples have been immersed in a helium bath between 1.2 and 4.2 K and in a helium bath below 1.2 K. In the vicinity of the phase transition, a temperature stability better than 10⁻⁶ K was achieved by means of an electronic regulation. Temperature was measured from helium vapour pressure above 0.6 K. Below 0.6 K, a germanium thermometer which had been calibrated at high temperature against He³ vapour pressure was used.

The magnetic susceptibilities of the two samples have been measured in the range 1.2-4.2 K with a mutual inductance bridge at 65 Hz.

III. Magnetization measurements. — III. 1 PRINCIPLE. — The nuclei inside the domains of the ferromagnetic crystal experience internal magnetic fields \( H_i \) due to the magnetic moments of the copper ions inside the lattice. These fields are proportional to the spontaneous magnetization \( M(T) \) of the domains, neglecting thermal expansion effects. For the proton which has a spin 1/2, the NMR frequency without applied field is related to \( H_i \) by \( v = \gamma_p/2 \pi H_i \) and is therefore proportional to \( M(T) \); \( \gamma_p \) is the proton gyromagnetic ratio. For the bromine nucleus which has a spin 3/2, there is also an interaction between the Br nuclear quadrupole moment and the electric field gradient (EFG) at the Br position. In the paramagnetic region, above \( T_c \), the pure quadrupole transition associated with each Br isotope has been observed with the following frequencies:

\[ v_0(Br^{81}) = (6.973 \pm 0.002) \text{ MHz}, \]
\[ v_0(Br^{79}) = (8.345 \pm 0.002) \text{ MHz}. \]

We have determined the corresponding EFG by studying the Zeeman splittings of the NQR transitions in the paramagnetic phase [4]. Two EFG were found with \( Z \) axis along \((1, 1, 0)\), \((1, 1, 0)\), \(Y \) axis along \((1, 1, 0)\), \((1, 1, 0)\) and \(X \) axis along \((0, 0, 1)\). In the ferromagnetic region, without applied field, each pure quadrupole transition is split by the internal field into two \( \alpha \) transitions and two \( \beta \) transitions. The observed frequencies of these lines are in agreement.
with an internal field, and therefore a Cu$^{2+}$ spin direction, parallel to $c$.

A computation of the Br frequencies shows that the separation between the $\beta$ transitions is well given by the relation $\Delta\nu_{\beta} = 2 \gamma_B H_z/2 \pi$ for fields up to 1 000 Oe. Therefore $\Delta\nu_{\beta}$ is proportional to the spontaneous magnetization. On another side $\Delta\nu_{\beta}$ strongly depends on the EFG asymmetry parameter $\eta$, which allows us to determine $\eta = 0.897$ below $T_c$.

III.2 Vicinity of the phase transition. — The NMR line shape of Br in the crystal shows a rapid evolution below 1.831 °K. Weak $\alpha$ lines appear above and below the pure quadrupole transition $\nu_0$ and their intensities increase drastically with $T_c - T$ (Fig. 1).

![Fig. 1. NMR spectra of Br$^{115}$ in the crystal II in the phase transition region. The asymmetrical shape of the $\beta$ lines and the rapid evolution of their intensities with temperature indicate coexistence of the para- and ferromagnetic phases over a few millidegrees.](image)

The extrapolation of the frequencies of these $\beta$ lines leads to a $T_c$ value equal to (1.831 ± 0.001) °K. The relative magnetization $m(T) = \Delta\nu_{\beta}(T)/\Delta\nu_{\beta}(0)$ is well described for $10^{-3} < T/T_c < 60.10^{-3}$ by

$$m(T) = A(1 - T/T_c)^{\beta}$$

where $A = 1.56 \pm 0.04$, $\beta = 0.40 \pm 0.01$.

This $\beta$ value is higher than the values found in other ferromagnets [5] and is in reasonably good agreement with the value $\beta = 0.38$ observed in the same salt by Wielinga and Huiskamp [6] using a different experimental method.

![Fig. 2. Relative spontaneous magnetization versus 1 - $T/T_c$ on a logarithmic scale for two crystals. The straight line represents the fit: $m = A(1 - T/T_c)^{\beta}$ with $\beta = 0.40 \pm 0.01$ and $A = 1.56 \pm 0.04$; $A$ crystal ($T_c = 1.831$ °K); $\circ$ less pure crystal ($T_c = 1.801$ °K).](image)

III.3 Low temperature region. — Below 1.6 °K, the proton lines become visible and their frequencies lead to a precise measurement of the spontaneous magnetization. In order to get the relative magnetization $m(T) = M(T)/M(0)$, an extrapolation to 0 °K of the proton frequencies was performed using the Bloch law between 0.4 and 0.6 °K.

The experimental results were compared to a spin-wave calculation of $m(T)$ taking into account an anisotropy field $H_A$ along $c$ of 200 Oe and using for the nearest neighbours and the next-nearest neighbours exchange integrals the following values derived by Miedema et al. [3], $J_1/kT_c = 0.35$, $J_2/J_1 = 0.25$. The integration was performed over the first Brillouin zone approximated by an ellipsoid. Using the renormalization method of Seiden and Papoular [7], a good fit with experiment is found up to $T/T_c = 0.5$ (Fig. 3).

![Fig. 3. Relative magnetization of Cu(NH$_4$)$_2$Br$_4$, 2 H$_2$O at low temperature versus the reduced temperature $T/T_c$. The solid curve is the result of the spin wave calculation using $J_1/kT_c = 0.35$, $J_2/J_1 = 0.25$ and $H_A = 200$ Oe. The dotted curve is the result of the renormalized spin-wave calculation.](image)
IV. Susceptibility measurements. — The measured susceptibilities along $\chi_{||}$ and along $\chi_{\perp}$ are shown in figure 4. As a striking effect of anisotropy, the maximum value of $\chi_{\perp}$ is far from the limiting value $1/\rho N_{II}$, where $N_{II}$ is the demagnetizing factor and $\rho$ the crystal density.

Using the calculated value $N_{II} = 2.80$ and $H_A = 200$ Oe, we found $\chi_{||} = 4.15 \times 10^{-2}$ c. m. u. at $T_C = 1.825$ K in the range $4 \times 10^{-3} < T/T_C < 1/2$. This $\gamma$ exponent is far from the theoretical value which is equal to 1.43 for the Heisenberg model.

V. Discussion. — The behaviour of the intensities of the Br NMR lines and of the magnetic susceptibility in the phase transition region, suggest coexistence of the para and ferromagnetic phases over a few millidegrees. Furthermore our $T_C$ value differs noticeably from previous determinations, 1.74 [6], 1.773 [8], 1.789 K [9]. We suggest that $T_C$ and magnetic susceptibility may be strongly dependent on the crystal purity. To check this assumption, the $T_C$ of various powdered samples were measured by the method used by Turrell and Yue [9].

The results in table I show a decrease of $T_C$ with increasing the Cl content and also a decrease of $T_C$ with deuteration. $T_C$ values in various Cu(NH$_3$)$_2$Br$_4$. 2 H$_2$O samples

<table>
<thead>
<tr>
<th>$T_C$ (K)</th>
<th>$\delta T_C/T_C$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominally pure sample</td>
<td>1.832</td>
</tr>
<tr>
<td>Sample obtained from a solution with 0.5 % Cl</td>
<td>1.824</td>
</tr>
<tr>
<td>Sample obtained from a solution with 1 % Cl</td>
<td>1.818</td>
</tr>
<tr>
<td>Deuterated sample</td>
<td>1.818</td>
</tr>
</tbody>
</table>

Further experiments with very pure crystals are therefore needed. However we expect that our magnetization data are good because there is no noticeable difference between the data obtained from the crystal II ($T_C = 1.831$ K) and a less pure crystal having $T_C = 1.801$ K (Fig. 2).

References

[4] Renard (J.-P.) and Velu (E.), to be published.