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ESR in a 1D-system with a ferromagnetic coupling

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Résumé. — Nous avons mesuré les dépendances angulaires de la largeur de raie de RPE et du facteur g en bande X et à la température ambiante dans le trichlorure cuivrique de cyclo-hexyl-ammonium (ou CHAC). Nous avons déterminé également la dépendance de la largeur de raie avec la température entre 30 et 300 K.

Abstract. — We have measured the angular dependences of the ESR linewidth and g -factor at X-band and room temperature in cyclo-hexyl-ammonium-trichlorocuprate (II) (CHAC). The temperature dependence of the linewidth between 30 and 300 K has also been determined.

1. Introduction.

The magnetism of one-dimensional (1D) systems has been mainly investigated in manganese compounds presenting an antiferromagnetic coupling such as tetramethyl manganese chloride (TMMC) and cesium manganese chloride (CMC) [1-3]. TMMC can be considered, to date, as the best 1D-system available for experiment. Recent progress in material chemistry has allowed the synthesis of linear Ising-Heisenberg systems with a ferromagnetic coupling [4]. The cyclo-hexyl-ammonium-trichlorocuprate (II) $((C_6H_{11}NH_3)CuCl_3)$, usually termed « CHAC » is a typical example of these materials [5, 6]. The experimental data concerning the magnetic susceptibility [5, 7] and the specific heat [6, 8] indicate that it is very close to the theoretical one-dimensional model, because of a strong interchain exchange and ($J_0 \sim 50$ K) and a weak interchain exchange ($J' \sim 10^{-3} \times J_0$). It shows a small anisotropic exchange so that the Hamiltonian of the symmetrical exchange can be expressed as :

$$H_e^s = - \sum_{i,j} J_{\perp} (S_i^x S_j^x + S_i^y S_j^y) + J_{\parallel} S_i^z S_j^z. \quad (1)$$

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With this type of Hamiltonian two extreme cases may be considered : (i) $J_{\perp}/J_{\parallel} = 1$ which leads to a Heisenberg system, (ii) $J_{\perp}/J_{\parallel} = 0$ which corresponds to an Ising system. In CHAC, $J_{\perp}/J_{\parallel} = 0.99$ [7], it shows a strong Heisenberg interaction and a very weak Ising one.

In this communication, we present experimental data concerning Electron Spin Resonance (ESR) at X-band in CHAC. We have measured the linewidth in the temperature region between 20 and 300 K. Furthermore, we have determined, at room temperature, the dependences of the linewidth and the g -factor with the angle θ between the crystal c -axis and the magnetic field H_0 . Finally, we discuss our data taking into account the various interactions in the sample.

2. Sample.

The crystal was grown from an equimolar solution of ammonium cyclohexyl chloride and anhydrous copper chloride (II) in 1-propanol. The crystallographic structure of CHAC has been determined by Groenendijk *et al.* [7]. The CuCl_3^- -ions are disposed in chains parallel to the c -axis. They are bound by the hydrogen bonds in the $(b-c)$ plane, through the NH_3^+ -groups.

At room temperature the structure is orthorhombic with $a = 19.441 \text{ \AA}$, $b = 8.549 \text{ \AA}$ and $c = 6.190 \text{ \AA}$ [7]. The apical Cu-Cl (1) bond is longer than the equatorial Cu-Cl (2) or Cu-Cl (3) one. The hydrogen bond produces a weak distortion which displaces the Cu^{2+} -ion out of the equatorial plane constituted by the four basal Cl^- -ions, towards the apical chlorine. A Cu-Cl-Cu bridge appears in the chain between two adjacent copper ions with an angle of 86° between the two Cu-Cl bonds. The bridging angle of less than 90° leads to a strong ferromagnetic coupling within each chain [7]. The distance between two adjacent copper atoms is $3.138 \text{ \AA}$ along the c -axis while it is $8.549 \text{ \AA}$ along the b -axis and $10 \text{ \AA}$ along the a -axis. Furthermore, the magnetic ordering occurs below $T_c = 2.18 \text{ K}$ [6, 7].

3. The experimental arrangement.

We have measured the linewidth with an ESR spectrometer operating at the frequency of 9.4 GHz . The sample, of size $3 \times 2 \times 1.5 \text{ mm}^3$, was placed within the resonant cavity. A goniometric device allowed rotations in a plane including the magnetic field H_0 . The angle θ between H_0 and the c -axis was measured with an accuracy of $\pm 0.5^\circ$. The temperature was varied from 20 to 300 K using an « OXFORD instruments » cryostat and it was measured by a thermocouple fixed close to the sample.

4. Experimental data.

First, we have measured the angular dependence of the g -factor in the (a, c) and (b, c) planes. The data are shown in figure 1. They are well described by the following equation, for H_0 in the (α, c) plane and at 300 K :

$$g(\theta) = (g_c^2 \cos^2 \theta + g_\alpha^2 \sin^2 \theta)^{1/2}, \quad (2)$$

where α is the a or b -axis, with :

$$g_a = 2.108 \pm 0.001; \quad g_b = 2.185 \pm 0.003; \quad g_c = 2.129 \pm 0.003.$$

The g_a and g_c -values are in good agreement with those found by Groenendijk *et al.* at 80 K [7], but a difference occurs for the g_b -value. It is due to different temperature dependences. In effect, when the temperature is lowered below 300 K, g_b increases continuously while g_a and g_c decrease below 70 and 30 K respectively.

The angular variations of the linewidth observed at room temperature are shown in figure 2. The measurements have been taken in the (a, c) and (b, c) planes. They are well fitted by the

Fig. 1. — The g -factor in CHAC versus the angle θ between the c -axis and the magnetic field H_0 . The temperature is 300 K and the spectrometer operates at X-band. The circles and the triangles correspond to the magnetic field in the (b, c) and (a, c) planes respectively. The solid line has been drawn from the computation of $(g_c^2 \cos^2 \theta + g_b^2 \sin^2 \theta)$ and the dotted curve from that of $(g_c^2 \cos^2 \theta + g_a^2 \sin^2 \theta)$ with $g_a = 2.108 \pm 0.001$; $g_b = 2.185 \pm 0.003$ and $g_c = 2.129 \pm 0.005$.

following expressions, found from an adjustment by the mean square method :

$$\text{in the } (a, c) \text{ plane} \quad \Delta H(\theta) = 788 - 413 \cos^2 \theta \quad (3)$$

$$\text{in the } (b, c) \text{ plane} \quad \Delta H(\theta) = 860 - 485 \cos^2 \theta. \quad (4)$$

In figure 3 we have drawn the variation of the linewidth with the temperature in the range from 20 to 300 K for the orientations $\theta = 0^\circ$ and $\theta = 90^\circ$, with H_0 in the (a, c) plane.

5. Discussion.

The angular anisotropy and the temperature dependence of the linewidth in CHAC are very different from those usually observed in 1D-systems. In TMMC for instance, the linewidth varies as $|1 - 3 \cos^2 \theta|^{4/3}$ and presents a marked minimum at the magic angle $\theta = 55^\circ$, while in CHAC it increases when θ varies from zero to 90° , in the two planes studied. Another difference concerns the lineshape. In TMMC, the ESR line shows a form intermediate between a Gaussian and a Lorentzian, except at the magic angle where it is purely Lorentzian. In contrast, the lineshape of CHAC remains approximately Lorentzian, whatever the orientation.

In TMMC the linewidth is essentially determined by the dipolar Hamiltonian H_D , presenting an axial symmetry with respect to the chain axis. H_D is also responsible for the breakdown of diffusing modes along the chains, which gives a non-Lorentzian lineshape. Thus, it is clear that

Fig. 2. — The ESR linewidth at room temperature in CHAC *versus* the angle θ . The data are represented by circles when the magnetic field is placed in the (b, c) plane and by triangles when the field is in the (a, c) plane. The smooth lines have been obtained from a mean square adjustment of the functions :

$$\begin{array}{ll} \text{the upper curve} & \Delta H = 788 - 413 \cos^2 \theta \quad (a, c) \text{ plane} \\ \text{the lower curve} & \Delta H = 860 - 485 \cos^2 \theta \quad (b, c) \text{ plane.} \end{array}$$

the results and conclusions drawn in TMMC cannot be applied to CHAC. In this compound, other interactions must be considered.

Groenendijk *et al.* [7] have extracted a value of the isotropic exchange : $J_0/k = 70$ K from their susceptibility data. In addition, they found a 1 % Ising-like anisotropy. From heat capacity measurement, de Jonge *et al.* [8] found a lower value of J_0 (45 K) with a 2 % anisotropy.

Our own high temperature susceptibility measurement gives $J_0/k = 47$ K with an accuracy better than 10 %, in good agreement with the Eindhoven group value. It is highly probable that the anisotropic exchange interaction exceeds the dipolar interaction ($\omega_D = \hbar\gamma e^2/r^3 \sim 10^{10}$ rad.s⁻¹, while $J_0/\hbar \sim 6 \times 10^{12}$ rad.s⁻¹).

The Ising term behaves for the ESR linewidth just like the dipolar interaction, but here with an axial symmetry along the b -axis (as it can be inferred from the g -tensor). If the Ising term was predominant, one would obtain the same symmetry for the ESR spectrum and also a minimum of the linewidth in the $(b-c)$ plane, at about $\theta \sim 35^\circ$ (a new magic angle). However, cross terms involving dipolar and Ising interactions should break this symmetry, but the minimum in the $(b-c)$ plane should persist. This is not observed.

Another puzzling fact is the Lorentzian lineshape. It implies that a cut-off mechanism takes place for the diffusing modes larger (in frequency unit) than the linewidth. This cannot be due to the exchange coupling between chains because it is too weak ($\sim 10^{-3} J_0$). So, another interaction has to be considered. One could think of the antisymmetric exchange interaction $\mathbf{d} \cdot \mathbf{S}_i \mathbf{X} \mathbf{S}_j$. It is known that d can be potentially as large as $(\Delta g/g) J_0$, Δg being the departure of the Lande

Fig. 3. — The ESR linewidth *versus* temperature for $\theta = 0^\circ$ and $\theta = 90^\circ$. The magnetic field is placed in the (a, c) plane. The broken lines are only guides for the eyes.

factor from the value for the free electron [9]. Actually, its value is severely dependent on the crystal symmetry. For example, it vanishes when the two ions have a centre of inversion midway between them. Soos *et al.* [10, 11] have shown that the diffusive modes disappear when the ion sites are themselves centres of inversion. None of these symmetry conditions are strictly fulfilled here and the antisymmetric exchange (with $\mathbf{d} \nparallel \mathbf{c}$) could explain satisfactorily our data. However, information concerning the presence of an antisymmetric exchange is hard to obtain from susceptibility measurement. In effect, such an interaction is not expected to influence static properties, as shown by Groenendijk *et al.* [7]. The surprising characteristics of the ESR in CHAC are probably related to a very strong coupling of the ions to the lattice. In TMMC, the electron spin-lattice relaxation occurs *via* a Bloembergen and Wang process. At high temperature, the relaxation time is very short but it becomes much longer at lower temperature. The situation is different in CHAC. Our measurements, using the modulation method [12], give extremely short times. The relaxation time is shorter for $\theta = 0^\circ$ and its value is about 2×10^{-10} s at $T = 90$ K (measurement at higher temperature could not be carried out). Clearly, it must contribute substantially to the linewidth at this orientation and at least partially at the others.

In a forthcoming publication we shall develop a more complete interpretation.

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