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Neutron and EPR Study of $Cu(tn)Cl_2$ – a Two-Dimensional Spatially Anisotropic Triangular-Lattice Antiferromagnet

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We have studied the temperature dependence of the lattice parameters and the influence of spin anisotropy on the electron paramagnetic spectra of $Cu(tn)Cl_2$, an $S = 1/2$ quasi-two-dimensional spatially-anisotropic triangular-lattice Heisenberg antiferromagnet. The variation of the resonance fields with temperature reflects the presence of an easy-plane exchange anisotropy with $J_z/J_{x,y} < 1$ and g-factor anisotropy, $g_z/g_{x,y} > 1$.

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1. Introduction

$Cu(tn)Cl_2$ (tn= 1,3-diaminopropane) has been previously identified as a potential realization of a spin 1/2 frustrated quasi-two-dimensional spatially-anisotropic triangular-lattice Heisenberg antiferromagnet, with intralayer exchange coupling $J/k_B \approx -3$ K, and interlayer exchange coupling $J' \approx 0.001J$. Specific-heat studies did not show a phase transition to an ordered state down to 50 mK [1].

We report the analysis of neutron diffraction and electron paramagnetic resonance (EPR) powder spectra of $Cu(tn)Cl_2$ with the aim to extract information on the spin anisotropy and its impact on the magnetic properties.

2. Experimental details

The crystal structure of $Cu(tn)Cl_2$ is orthorhombic (space group $Pna2_1$) with lattice parameters a = 17.956 Å, b = 6.859 Å, and c = 5.710 Å [1]. The structure consists of covalent ladders running along the c axis, while adjacent ladders are linked through hydrogen bonds. The polycrystals of $Cu(tn)Cl_2$ have been prepared using a procedure described in Ref. [1].

Powder neutron-diffraction studies were performed at Helmholtz-Zentrum Berlin using the powder diffractometer E6 equipped with the VM-1 magnet and ^{3}He insert. A partially deuterated polycrystalline sample of total mass of 1 g was powdered, pressed into a pellet, and stored in a copper can filled with ^{3}He exchange gas. Diffraction patterns were collected with a long counting time at several temperatures between 0.4 and 100 K in zero magnetic field using an incident-neutron wavelength $\lambda = 2.45$ Å. The patterns were analyzed by use of the Rietveld method employed in the software package FULLPROF.

EPR measurements were performed at the Dresden High Magnetic Field Laboratory using an X-band spectrometer (Bruker ELEXSYS E500) at a fixed frequency of 9.4 GHz in the temperature range from 2 to 300 K and magnetic fields up to 0.5 T. The powdered sample mixed with Apiezon N was glued on a Suprasil-quartz rod.

3. Results and discussion

The analysis of the neutron-diffraction patterns (Fig. 1) revealed a rather significant contraction of the lattice parameters a and b with temperature which can be

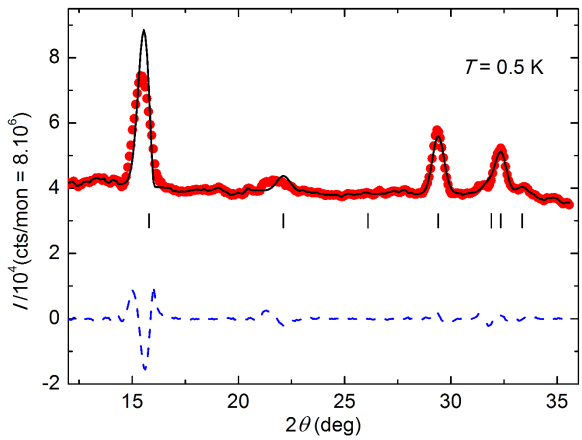

Fig. 1. Diffraction pattern of $Cu(tn)Cl_2$ collected at 0.5 K. Circles represent measured data, the solid line is the calculated pattern fitted to the data. The vertical lines indicate the positions of Bragg nuclear reflections and the dashed line represents the difference between the data and the calculated pattern.

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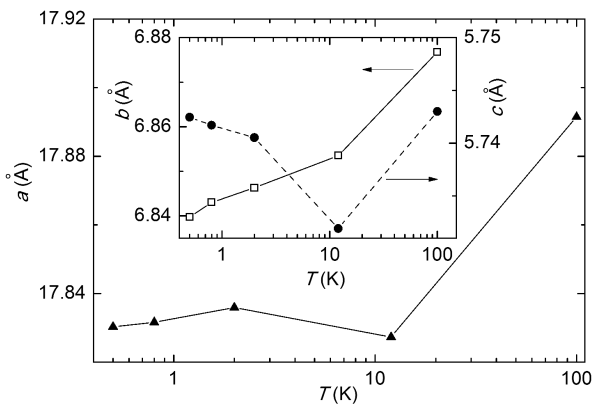

Fig. 2. Temperature evolution of the Rietveld-refinedlattice parameter a of Cu(tn)Cl$_2$. Inset: Temperature evolution of the Rietveld-refinedlattice parameters b and c.

ascribed to hydrogen-bond effects. The relatively weak temperature-dependent change of the lattice parameter c can be associated with the covalent bonds within the ladders (Fig. 2). It should be noted that the appearance of significant lattice contractions correlates with the onset of short-range magnetic order [1]. The EPR powder spectra are characterized by an asymmetric shape, typical for a system of randomly oriented crystallites having a g tensor with axial symmetry. Analysis of the data by use of a model described in Ref. [2] yields the temperature dependence of the g-factor and the linewidth, ΔB (Fig. 3).

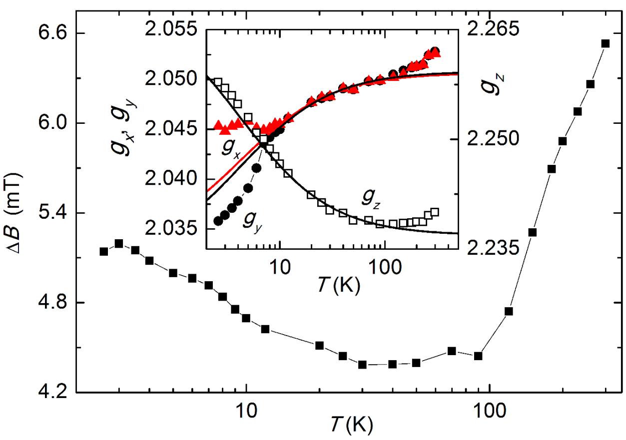

Fig. 3. Temperature dependence of the EPR linewidth of Cu(tn)Cl$_2$. Inset: Temperature dependence of the anisotropy of the g-factor in Cu(tn)Cl$_2$. The lines represent fits (see text).

Below 100 K, the temperature dependence of g_z is opposite to that observed for g_x and g_y. Such a behavior reflects the presence of an exchange anisotropy in Cu(tn)Cl$_2$. The fits performed in the temperature interval from 10 to 120 K, using equation (5) in Ref. [3], yield the high-temperature values $g_x^0 = 2.05$, $g_y^0 = 2.05$, $g_z^0 = 2.24$ and effective spin-anisotropy parameters $J_{xx}/k_\mathrm{B} = 0.04$ K, $J_{yy}/k_\mathrm{B} = 0.05$ K, and $J_{zz}/k_\mathrm{B} = -0.08$ K. The anisotropic exchange couplings, $J_i = J + J_{ii} (i = x, y, z)$ evaluated using $J/k_\mathrm{B} = 3$ K and the J_{ii}'s found above, indicate an easy-plane anisotropy. The increase of all g parameters observed above 100 K can be associated with structural changes.

Similarly, the increase of the EPR linewidth above 100 K correlates with the increase of the g-factors and can be ascribed to the phonon modulation of the spin anisotropies [4]. The upturn of the linewidth appearing below 20 K corresponds to the development of intralayer magnetic correlations.

4. Conclusions

The temperature dependence of the resonance fields reflects the presence of an exchange anisotropy with $J_z/J_{x,y} < 1$. The combined effect of the easy-plane spin anisotropy and weak interlayer coupling might be responsible for the absence of a phase transition in the specific-heat data. The variation of the lattice parameters observed at low temperatures may affect the formation of two-dimensional magnetic correlations. Analogous effects might be obtained by application of pressure - the goal of further studies.

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