Spin Anisotropy in Cu(tn)Cl$_2$: A Quasi-Two-Dimensional $S = 1/2$ Spatially Anisotropic Triangular-Lattice Antiferromagnet

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Abstract. The angular dependence of electron paramagnetic resonance spectra of Cu(tn)Cl$_2$ single crystals has been studied in the X-band frequency range in the temperature range from 2.5 to 300 K. The presence of an easy-plane exchange anisotropy with $J_z/J_{x,y} < 1$ and $g$-factor anisotropy, $g_z/g_{x,y} > 1$ was found from analysis of the variation of the resonance fields with temperature.

1. Introduction

Cu(tn)Cl$_2$ ($\text{tn} = 1,3$-diaminopropane) has been previously identified as a potential realization of a spatially-anisotropic triangular Heisenberg antiferromagnet with spin $1/2$, intralayer exchange coupling, $J/k_B \approx -3$ K, and interlayer exchange coupling, $J' \approx 0.001 J$. Previous specific-heat studies in zero magnetic field did not show a phase transition to long-range magnetic order down to 60 mK. These studies indicated a field-induced anomaly forming below 1 K in magnetic fields up to 7 T and this anomaly was assigned to a Berezinskii-Kosterlitz-Thouless phase transition [1].

In this paper, we focus on the analysis of angular dependence of electron paramagnetic resonance spectra (EPR) of Cu(tn)Cl$_2$ single crystals with the aim to indicate the type of a spin anisotropy in the studied system, which plays an important role in stabilization of magnetic order.

2. Experimental details

The crystal structure of Cu(tn)Cl$_2$ determined at 150 K is orthorhombic, space group $Pna2_1$ with the lattice parameters $a = 17.956$ Å, $b = 6.859$ Å, $c = 5.710$ Å and $Z = 4$ [2]. The structure consists of covalent ladders running along the $c$ axis, while adjacent ladders are linked through hydrogen bonds (Figure 1a).
The 4 + 2 local coordination can be considered to be axially symmetric to a good approximation. The axial symmetry permits choosing a local (xyz) coordinate system with the z axis parallel with the crystallographic c axis and x, y axes parallel with the directions of the chemical bonds within the equatorial plane. The angle between the x, y and a, b axes is about 45° (Figure 1b).

Using a modified method published in Ref. [2], Cu(tn)Cl2 single crystals were prepared in the form of blue flat plates with typical dimensions \(a' \times b' \times c' = 1.5 \times 1 \times 0.5 \text{ mm}^3\). Using X-ray study the longest crystal edge \(a'\) was identified with the crystallographic \(c\) axis, \(b'\) edge is parallel to the \(b\) axis and the shortest crystal edge \(c'\) is parallel to the \(a\) axis.

EPR angular measurements of a single crystal within \(ac\) plane have been performed at Dresden High Magnetic Field Laboratory using an X-band spectrometer (Bruker ELEXSYS E500) at the fixed frequency of 9.4 GHz and magnetic fields up to 0.5 T.

3. Results and discussion

Angular variation of the g-factor of Cu(tn)Cl2 in the \(ac\) plane in the temperature range from 2.5 to 300 K is presented in Figure 2a. Experimental data were fitted using the standard relation

\[
g^2 = g_x^2 \cos^2 \theta + g_y^2 \sin^2 \theta \cos^2 \varphi + g_z^2 \sin^2 \theta \sin^2 \varphi, \tag{1}
\]

where \(g_x, g_y, \) and \(g_z\) are the g- factors corresponding to the local anisotropy axes \(x, y, \) and \(z\). \(\theta\) is the angle between the magnetic field and the local \(z\) axis and \(\varphi\) is the angle between the projection of the magnetic field in the \(xy\) plane and the local \(x\) axis (Figure 1b).

A possible deviation of the (xyz) frame from the actual local anisotropy axes was introduced by free fitting parameters, \(p_\theta\) and \(p_\varphi\), taking \(\theta = \Gamma + p_\theta\) and \(\varphi = p_\varphi\) in Eq. (1). \(\Gamma\) expresses angle of rotation within \(ac\) plane. We found the nearly temperature-independent parameter \(p_\theta = (90 \pm 0.5)^\circ\). The parameter \(p_\varphi\) changed monotonously from 41° at 2.5 K to 52° at room temperature, which is rather close to the value 45°. The obtained corrections correspond to the choice of the coordinate system as depicted in Figure 1b.

The fits also provided \(g_x, g_y, \) and \(g_z\) parameters, which systematically vary with temperature (Figure 2b). The increase of \(g_z\) and decrease of \(g_x, g_y\) parameters at low temperatures, is typical for the presence of an effective exchange anisotropy. At higher temperatures, an increase of the \(g\) parameters appears, probably as a result of a thermal lattice expansion. The fits performed in the temperature
interval from 10 to 100 K using Eq. (5) in Ref. [3] and Curie paramagnetic temperature, $\Theta_C = - 4$ K from Ref. [2], yield the high-temperature values $g_x^0 = 2.035$, $g_y^0 = 2.064$, $g_z^0 = 2.241$ and effective spin-anisotropy parameters $J_{xx}/k_B \approx 0$ K, $J_{yy}/k_B \approx -0.02$ K, and $J_{zz}/k_B \approx -0.17$ K. The latter approximate easy-plane anisotropy in Cu(tn)Cl$_2$. Nearly zero value of $J_{xx}/k_B$ suggests a presence of easy axis within the easy plane, parallel to the $x$-axis.

**Figure 2.** (a) Angular variation of the $g$-factor of Cu(tn)Cl$_2$ in the $ac$ plane. For clarity, only data at selected temperatures are shown. The solid lines represent the fits to Eq. (1). (b) Temperature dependence of $g_x$ (square), $g_y$ (triangle), and $g_z$ (circle) parameters as obtained from the fits of $g$-factor variation within the $ac$ plane. The solid lines represent fitting curves (see text).

4. Conclusions

The analysis of EPR spectra of Cu(tn)Cl$_2$ in the $ac$ plane at various temperatures revealed the presence of a spin exchange anisotropy with the easy-plane character. In future, the presence of easy-plane anisotropy will be verified by single crystal measurement of magnetic susceptibility at temperatures below $0.1/J/k_B$ [4].

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