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Magnetic order and transitions in the spin-web compound Cu_3TeO_6

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Abstract

The spin-web compound Cu_3TeO_6, belongs to an intriguing group of materials where magnetism is governed by $3d^9$ copper Cu^{2+} ions. This compound has been sparsely experimentally studied and we here present the first investigation of its local magnetic properties using muon-spin relaxation/rotation (μ^+SR). Our results show a clear long-range 3D magnetic order below T_N as indicated by clear zero-field (ZF) muon-precessions. At $T_N = 61.7$ K a very sharp transition is observed in the weak transverse-field (wTF) as well as ZF data. Contrary to suggestions by susceptibility measurements and inelastic neutron scattering, we find no evidence for either static or dynamic (on the time-scale of μ^+SR) spin-correlations above T_N.

Keywords: Muon-spin relaxation/rotation (μ^+SR), spin-web compounds, short-range magnetic order

1. Introduction

Although magnetism is a quantum phenomenon, properties of most of the magnetic insulators can be understood using a semi-classical approach, i.e. the linear spin-wave theory. Especially in three-dimensional (3D) systems quantum effects are expected to be small and it may be asked whether they are at all relevant. The insulating tricopper-tellurate Cu_3TeO_6 belongs to an intriguing group of compounds where the magnetism is governed by $3d^9$ copper Cu^{2+} ions [1]. This compound can be indexed by the cubic space group $Ia\overline{3}$ [$a = 9.537(1)$ Å] [2, 3]. As shown in Fig. 1, the unit cell consists of 8 regular TeO_6 octahedra and 24 copper ions [3]. Each copper ion is surrounded by six oxygen ions forming a very irregular octahedron. There have been very few experimental studies of Cu_3TeO_6 and in fact only one published investigation is to be found regarding its magnetic properties [4]. The susceptibility-vs.-T [$\chi(T)$] curve [inset of Fig. 2(a)] displays a kink at $T \approx 60$ K indicating long-range magnetic ordering. From a wider temperature range, a good fit of χ^{-1} to a Curie-Weiss law **(CWL)** for $T = 180 - 330$ K gives $\Theta_{CW} = -134$ K [Fig. 2(a)]. This shows that the Cu^{2+} spins are in fact strongly antiferromagnetically (AF) coupled. It is further evident that $\chi(T)$ also starts to deviate from CWL below approximately 180 K, possibly indicating the onset of a short-range spin order. To

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*Corresponding author. Tel.: +41-(0)56-310-5534 ; fax: +41-(0)44-633-1282
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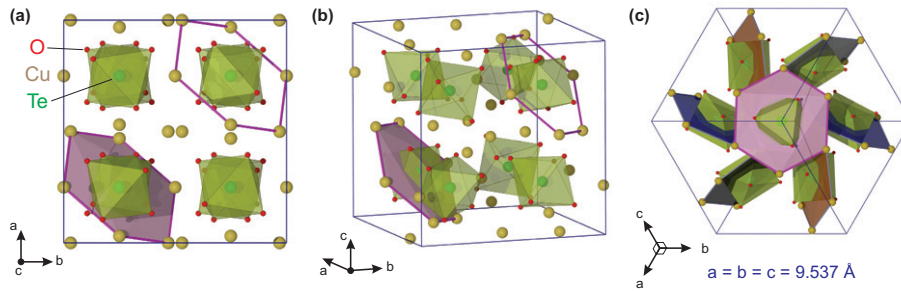Figure 1: The crystal structure of Cu_3TeO_6 [cubic space group $Ia\bar{3}$, $a = 9.537(1)$ Å] viewed along different directions. (c) Emphasizes the four different domains created by the copper planes oriented perpendicular to the space diagonals.
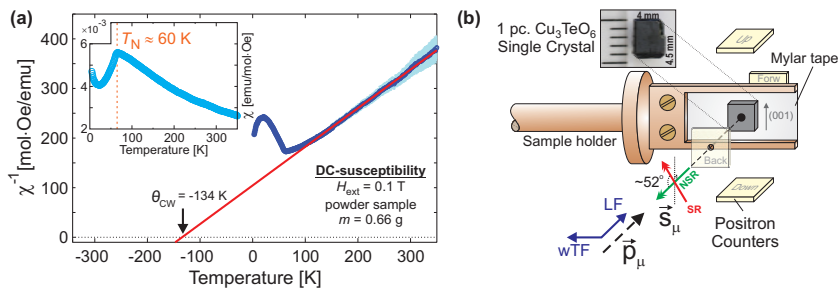

Figure 2: (a) Temperature dependence of the magnetic susceptibility, χ (inset) and χ^{-1}. A clear kink at $T_N \approx 60$ K indicates the onset of long-range magnetic ordering. Solid red line is a fit to Curie-Weiss law yielding $\Theta_{CW} = -134$ K. (b) Schematic view of the experimental setup at the GPS spectrometer showing the direction of magnetic fields for spin-rotated (SR) and non-spin-rotated (NSR) mode.

display a deviation from CWL as high as $3T_N$ is rather unusual for a 3D system and is only expected to be observed in low-dimensional and frustrated spin systems. The explanation is found in the magnetic structure that consists of a 3D "spin-web" lattice of $S = 1/2$ Cu^{2+} ions characterized by low connectivity. Here each spin has only 4 nearest neighbors and 4 next-nearest neighbors, which is comparable to the two-dimensional square lattice antiferromagnets (2DSL-AF), *e.g.* parent compounds of cuprate high-temperature superconductors. Further, the magnetization vs. magnetic field (H) curve displays anomalous behavior that cannot be explained by a simple spin-flip or spin-flop transition, but rather by field induced rotation of magnetic domains. Such situation is also supported by torque measurements [4]. Neutron powder diffraction show clear magnetic peaks below T_N [4] and the magnetic structure is found to be a collinear (possibly canted) Néel order on a bipartite lattice with a wave vector $\vec{k} = (0, 0, 0)$. The ordered moment determined by neutron diffraction is predominantly directed along the $(\pm1, \pm1, \pm1)$ space diagonals and is found to be only 0.64 μ_B/ion, i.e. strongly reduced from the classical 1 μ_B/ion, again similar to the $S = 1/2$ 2DSL-AF. Further, a recent inelastic neutron scattering (INS) study of the magnon dispersion in Cu_3TeO_6 show a large amount of diffuse scattering for $T > T_N$ [5]. In similarity to the deviation from CWL this could possibly indicate the presence of short-range spin correlations above the bulk magnetic transition. Muon-spin relaxation/rotation (μ^+SR) is an optimal technique to study such microscopic magnetic properties and we here present, to the best of our knowledge, the first μ^+SR investigation of the Cu_3TeO_6 compound.

2. Experimental Details

Single crystals of Cu_3TeO_3 can be obtained by a HBr chemical transport method resulting in prisms of approximately 2×2 mm, or even bigger. For this μ^+SR experiment, a single piece of single crystal (4×4×2 mm³) was attached to a low-background (fork-type) sample holder [see Fig. 2(b)] using very thin Al-coated Mylar tape. In order to make certain that the muon stopped primarily inside the sample, we ensured that the side facing the muon beamline was only
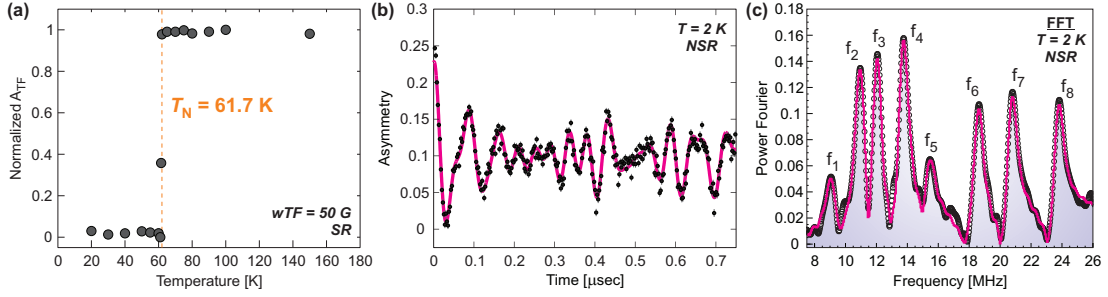
Figure 3: (a) Temperature dependence of the wTF asymmetry (A_{TF}) showing a sharp transition at T_N = 61.7 K. (b) ZF μ^+SR time spectrum at T = 2 K using NSR mode. Fast Fourier transform (FFT) of (b) showing eight different frequencies (f_i). Solid lines in (b-c) are a fits to Eq.(1).

covered by a single layer of mylar tape and in addition, a muon veto counter was used. Subsequently, μ^+SR spectra were measured at the Swiss Muon Source (SμS), Paul Scherrer Institut, Villigen, Switzerland. By using the surface muon beam-line πM3.2, weak transverse-field (wTF) and zero-field (ZF) spectra were collected (see Fig. 3 & 4) at the General Purpose Spectrometer (GPS). Data was collected for both non-spin-rotated mode (NSR) and spin-rotated (SR) mode [see Fig. 2(b)]. The experimental setup and techniques are described in greater detail elsewhere [6].

3. Results & Discussion

In order to obtain an overview of the magnetic transition weak transverse-field (wTF = 50 G) μ^+SR spectra were obtained as a function of temperature. In Fig. 3(a) the T-dependence of the wTF precession asymmetry (A_{TF}) is shown where A_{TF} is completely suppressed below T_N. At T_N = 61.7 K a clear bulk magnetic transition occurs, in accordance with susceptibility measurements, and A_{TF} quickly reaches its expected maximum value. That the full A_{TF} is recovered immediately above T_N is a strong indication that no magnetic order exists above T_N. However, to gain a more robust verification also zero-field (ZF) μ^+SR data was acquired. Below T_N a clear static magnetic order is seen from the obvious oscillation in the ZF time spectrum [Fig. 3(b)] acquired at T = 2 K. From a fast Fourier transform (FFT) of the time spectrum [Fig. 3(c)], eight distinct muon precession frequencies (f_i, where i = 1..8) can be decerned. Consequently, the ZF data was well fitted by the combination of eight damped cosine oscillations and a *tail* signal due to the field component parallel to the initial muon spin:

$$A_0 \, P_{ZF}(t) = A_{tail} \, e^{-\lambda_{tail}t} + \sum_{i=1}^{8} A_i \, e^{-\lambda_i t} \cos(2\pi f_i \cdot t + \phi_i) \, , \tag{1}$$

In order to further investigate the formation of static magnetic order ZF-μ^+SR spectra were collected for 2 K $\leq T \leq$ 70 K. As seen from Fig. 4(a) and from the temperature dependencies of f_i [Fig. 4(c)], as T increases the oscillation frequencies are gradually slowing down and finally disappears around T_N. The magnetic order parameter [Fig. 4(c)] was found to be well fitted to the commonly used phenomenological formula:

$$f_i(T) = f_{T \to 0K} \cdot \left[1 - \left(\frac{T}{T_N} \right)^{\alpha} \right]^{\beta} \, , \tag{2}$$

where β is a parameter describing the dimensionality of the magnetic order [7]. In these fits T_N was fixed to 61.7 K as obtained from the wTF measurements and the values of β was shown to range from 0.4-0.5. Contrary to the proposed 2DSL-AF nature, on the length-scale of μ^+SR, such β-values indicate a fully 3D (possibly Heisenberg) type magnetic order [7]. Further, that all f_i's show the same temperature evolution (i.e. similar β and transition temperature) suggests that the multiple frequencies are not caused by the coexistence of different magnetic phases but rather a result of several inequivalent interatomic muon stopping sites within the crystallographic lattice. Noteworthy is also that the initial phases [ϕ_i in Eq. (1)] of the precession frequencies show (if not fixed) strong deviations from zero and in addition complex T−dependencies. Such non-zero phases along with a rather asymmetric field distribution
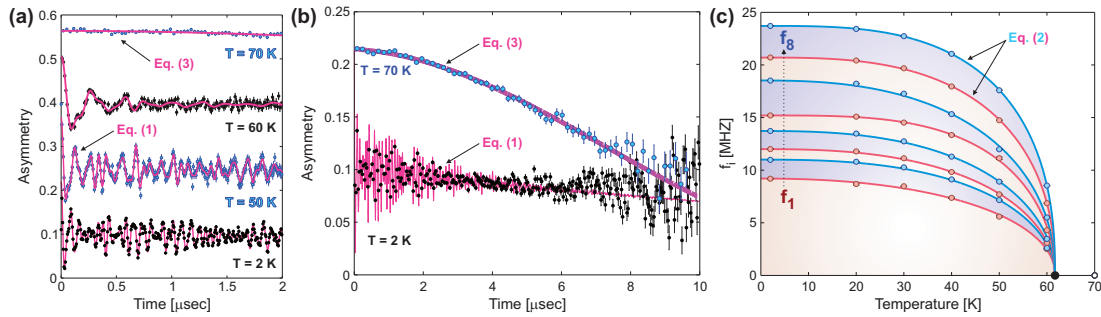
Figure 4: (a-b) Temperature dependence of ZF time spectra using SR mode. Solid lines are fits to Eq. (1) and Eq. (3). (b) Magnetic order parameter showing the temperature dependence of the oscillation frequencies (f_i where $i = 1..8$). Solid lines are fits to Eq. (2).

[see e.g. the FFT spectrum in Fig. 3(c)] could be an indication for incommensurate magnetic order in this compound. However, it is more likely that such phase-delays are caused by a wide field distribution due to the large amount of inequivalent muon sites, as we have previously reported for the $LiCrO_2$ compound [8]. This is clearly also in line with the neutron diffraction data that indeed show a clear commensurate order [4].

Finally, the ZF data obtained just above T_N [$T = 70$ K in Fig. 4(a-b)] show no indication of short-range magnetic order. Instead it is well fitted by a simple static Gaussian Kubo-Toyabe (KT) function [$G^{KT}(\Delta_{KT}, t)$] multiplied by an exponential relaxation:

$$A_0 P_{ZF}(t) = A_{KT} G^{KT}(\Delta_{KT}, t) \cdot e^{-\lambda_{elec}t}, \tag{3}$$

Here $G^{KT}(\Delta_{KT}, t)$ originates from the presence of randomized (nuclear) magnetic moments. From such fit we obtain $\Delta_{KT} = 0.095$ MHz along with $\lambda_{elec} = 0.009$ MHz for $T = 70$ K. The negligible value of λ_{elec} indicates the absence of any strong fluctuations in the electronic moments (spins).

4. Summary

We here present the first study of local magnetic properties of the spin-web compound Cu_3TeO_6. On the length-scale of μ^+SR, both wTF and ZF measurements show a clear long-range 3D magnetic order below $T_N = 61.7$ K. Contrary to suggestions by susceptibility measurements and inelastic neutron scattering, we further find no clear evidence for either static or dynamic (on the time-scale of μ^+SR) spin-correlations above T_N.

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