Three Dimensional Spin Web: A New Magnetic Lattice in Cu$_3$TeO$_6$

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We report on magnetic properties of cubic compound Cu$_3$TeO$_6$ studied by ac and dc susceptibility and neutron powder diffraction for the first time. A novel magnetic lattice, three dimensional spin web, composed of almost planar regular hexagons of Cu$^{2+}$ 1/2 spins, defines the properties of Cu$_3$TeO$_6$. The behaviour of the magnetic susceptibility in the paramagnetic state at $\approx 170$ K is suggestive for a competition between local anisotropies of Cu$^{2+}$ hexagons. The resulting frustration is weaker than the antiferromagnetic nearest-neighbor interaction which leads to a collinear (or slightly canted) spin arrangement ($k=0,0,0$) and formation of magnetic domains below $T_N = 61$ K.

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Magnetism relying on 3d$^9$ copper Cu$^{2+}$ ions reveals a striking diversity of magnetic structures. This diversity originates from a broad range of effective magnetic dimensionalities characterizing various 3d$^9$ magnetic systems. Depending, in turn, on the level of frustration and the importance of quantum fluctuations either singlet non-magnetic, disordered spin liquid or magnetically long-range ordered ground states set in at low temperatures. Understanding the magnetic structures underlying each of these ground states represents an issue of central interest for 3d$^9$-magnetism, as well for magnetism in general.

In this article we present magnetic susceptibility and neutron diffraction studies of a copper tellurium oxide, Cu$_3$TeO$_6$. Apart from the crystal structure determination, published for the first time back in 1968 and revised in 1978, no other properties of Cu$_3$TeO$_6$ have, to the best of our knowledge, been ever reported in literature, in spite of tremendous general interest for uniform Néel-ordered systems. This observation might be consistent with more complex (e.g., helicoidal) AF ordering. However, small susceptibility anisotropy can be interpreted by presence of AF domains of different orientations, rendering the effective bulk susceptibility more isotropic. The latter interpretation turns out to be consistent with all other observations presented below.

Figure 2 shows the total dc magnetic susceptibility in a broad temperature range. The spin-only part of susceptibility $\chi_{\text{spin}}$ was calculated by subtracting the temperature independent part $\chi_0$. $\chi_0$ sums the diamagnetic susceptibility of all ions and the paramagnetic Van Vleck contribution of Cu$^{2+}$, thus $\chi_0 = +1.5 \cdot 10^{-4}$ emu/mol. At approximately 170 K a deviation from Curie-Weiss law sets in. Inset to
FIG. 1: Main panel: ac susceptibility measurements on a single-crystalline Cu$_3$TeO$_6$ sample. Applied ac field (2 Oe, 430 Hz) was directed along the specified crystallographic directions. The vertical downward shift for the [-110] sample orientation might originate from reasons specific to ac susceptibility technique. Inset: Magnetic transition on the expanded scale.

Figure 2 shows that $\chi_{\text{spin}}$ follows the Curie-Weiss law, $1/\chi_{\text{spin}} = (T - \Theta_{\text{CW}})/C$, in the temperature range 170–330 K. The fit gives the values $C = 1.18$ emu K/mol and $\Theta_{\text{CW}} \approx -145$ K for the Curie and the Weiss constant, respectively. Large and negative $\Theta_{\text{CW}}$ from the Curie-Weiss law suggests that the copper spins are strongly antiferromagnetically coupled. The value of the g-factor calculated from the determined $C$ equals $g = 2.05$. This value is smaller than the value of $<g> \approx 2.15$ characterizing a large number of investigated copper oxides.

This suggests there is an approximately 5% copper spin-deficiency in our sample. Alternatively, a g-factor deviation could rely on inappropriate use of Curie-Weiss law even at the highest measured temperatures (inset to Figure 2). Below $\approx 170$ K the susceptibility increases less rapidly than the original Curie-Weiss law, reveals a maximum at 69 K and then decreases rapidly below 61 K.

One notes that magnetic ordering introduces susceptibility reduction being almost 5 times bigger in ac-compared to the dc-susceptibility studies. Taking into account that the respective measuring fields differ by 3 orders of magnitude one concludes that a pronounced and unusual magnetic non-linearity characterizes the ordered phase.

Torque magnetometry studies (Inset to Fig 2) reveal a strong deviation from those characterizing single domain antiferromagnet, i.e., sinusoidal angle dependence with $\pi$ periodicity and zeros in the direction of the magnetic axes. In Cu$_3$TeO$_6$ this type of behavior was observed only in low fields ($<0.5$ kOe). In higher fields, instead of a narrow and non-hysteretic spin flop, we observed a sequence of discontinuous jumps and a pronounced hysteresis. Closely related are the observations of the relaxation effects on a long time scale ($\tau \approx 200$ seconds). As the same behavior was observed also for another orientation of the sample one concludes there are at least four AF domains which change their population at fields $>0.5$ kG. The details of these studies will be published separately.

Below $T_N = 61$ K magnetic peaks appear in neutron powder diffraction, Figure 3, at the positions of the crystallographic reciprocal lattice corresponding to the wave vector $k=(0,0,0)$. The temperature variation of the integrated intensity of the magnetic peaks has classical

FIG. 2: dc magnetic susceptibility of Cu$_3$TeO$_6$ in the applied field of 5 kOe. Inset: Torque measurement in field of 1.1 kOe at 4.2 K on the same sample. Applied dc field was swept from $\approx 10^\circ$ up to 220$^\circ$ (solid circles) and than back (empty circles). Positions of the crystal axes [100] and [010] are marked. Solid line represents the $\sin(2\theta)$ curve.

FIG. 3: DMC neutron powder diffraction patterns of Cu$_3$TeO$_6$. Arrows points to magnetic reflections. Inset shows the temperature evolution of the $\langle h0l \rangle$ (open circles) and $\langle hkl \rangle$ (filled circles) lowest angle magnetic peaks intensity.
behaviour; the intensities of the $<hkl>$ and $<hk0>$ contributions vary as the square of the S=1/2 Brillouin function.

The systematic extinction rules observed in 1.5 K-70 K magnetic difference pattern (Figure 4) reveal that the I-translation is not combined with time reversal ($hkl$: $h+k+l = 2n$), while the glide planes are combined with it, if retained ($<hk0>$: $k,l = 2n$; $<hkl>$ denotes cyclical permutation). Note that three-fold rotations are not compatible with time reversal. Our trials to find a model with the cubic magnetic configuration symmetry were unsuccessful. Only models with trigonal symmetry gave good agreement to the observed diffraction pattern. The retention of the unique three-fold axis in the magnetic structure has two consequences. Firstly, there must exist at least four rotation S-domains, each possessing its own $<1±1±1>$ three-fold axis and each having a pair of 180 deg domains. Their presence is fully supported by the torque magnetometry results. Secondly, as the cubic symmetry is lost, the glide planes could not be the elements of the magnetic group. The Cu$^{2+}$ ions related by the glide planes must, however, have the magnetic moments antiparallel to each other, otherwise magnetic intensity would be found at the $hkl$: $h+k+l = 2n$ positions.

The magnetic moment direction is not conditioned by extinctions and must be determined from modeling. Due to the high symmetry of the crystal lattice and the wave vector this task is, however, not easy based on powder data only $^2$. For a collinear antiferromagnetic model with spins aligned along the [111] direction and the 1.5 K moment value of 0.644(7) $\mu_B$/Cu$^{2+}$ a good fit ($R_M = 16.9\%$) has been obtained. However, canted spin arrangements with magnetic moments tilted from the [111] direction, fit the data equally well ($R_M = 13.2\%$). For collinear model spins are aligned along one of the space diagonals of the cubic unit cell. Since each of the four directions is equally probable, domains with four different spin directions must coexist in antiferromagnetically ordered state. In canted model the tilt of the spins from the [111] direction is small, of the order of 6 degrees. Here also four equally probable antiferromagnetic domains could exist. In canted model the angle between two 1st $nn$ moments is 168.7 degrees (in collinear model it is 180 deg) and between two 2nd $nn$ 11.3 degrees (in cantilinear model it is 0 deg). Further neutron diffraction experiments on a single domain crystal are needed to distinguish between the models.

Now we elaborate the magnetic structure of Cu$_3$TeO$_6$. There are 24 copper ions per unit cell, each forming a distorted CuO$_6$ octahedron. Each Cu$^{2+}$ ion has four nearest Cu neighbours ($nn$) at 3.18A (1st $nn$) and the next four $nn$ at 3.6A (2nd $nn$). 1st $nn$ are connected by 2 superexchange paths through two oxygens making Cu-O-Cu angles of 92.4° and 106.2°, while 2nd $nn$ are connected through one oxygen only, forming a Cu-O-Cu angle of 112.5°. Assuming that the interaction between 2nd $nn$ is weaker compared to the 1st $nn$ one, it seems reasonable to restrict consideration of magnetic interactions just to the 1st $nn$ network.

The latter restriction generates a surprisingly interesting outcome, Figures 5,6. The structural building block of the 1st $nn$ sublattice is characterized by almost planar hexagon arrangement of copper ions. As shown in Fig. 5 the hexagons are not isolated, but form a complex three-dimensional network, hereby named a three-dimensional spin web. Note that the web geometry is primarily determined just by copper ion topology: as shown in Figure 6 each Cu$^{2+}$ is coordinated by four nearest neighbors and is shared between the two non-coplanar hexagons.

The results of neutron diffraction studies are indeed consistent with a collinear AF arrangement of spins within hexagons (Figs. 6). The spin web with hexagons as the building blocks strongly resembles the pyrochlore lattice of corner-shared tetrahedra. The latter lattice characterizes AB$_2$O$_4$ spinels, the cubic systems as well. There are, however, important differences: While in the pyrochlore the disconnected hexagons are spanned by a skeleton of spin tetrahedra, in the spin web the hexagons share a common corner and are interconnected by a network of distorted CuO$_6$ octahedra. (The Cu-O distances in each spin web octahedron are: 1.949(2)Å (2x), 2.031(2)Å (2x) and 2.369(3)Å (2x) while the O-Cu-O angles in the octahedron range from 72.6(1)° to 166.3°, none of them being 90° nor 180° as in a regular octahedron).

In the pyrochlore (in particular ZnCr$_2$O$_4$) the pronounced frustration relies on the geometrically frustrated spin tetrahedra building blocks. In the spin web Cu$_3$TeO$_6$ the possible source of frustration is the local
magnetic anisotropy of the hexagons, in addition to the neglected interaction with 2nd nearest neighbors. Each spin shared between the two non-coplanar hexagons experiences frustration. Apparently, this frustration is only modest (the value of frustration parameter $f = \Theta_{CW}/T_N = 2.4$). Alternatively, one can say that the spin web is closer to the over-constrained limit$, preferring magnetic order at higher temperature.

Furthermore, a comparison of the two lattices seems to reveal a route how frustration can affect magnetic clustering in general. In the pyrochlore strong frustration promotes clustering of individual spins into hexagonal loops at low temperatures$. The loop directors - the unique direction along which the spins are aligned - are weakly interacting and slowly varying in space. In the spin web the directors are strongly interacting. This interaction, mediated by a common corner, overcomes the frustration and the collinear order fixes the directors along the common axis.

In conclusion, a new magnetic lattice, the 3d spin web, characterizing magnetic structure of the Cu$_3$TeO$_6$ compound has been found. It’s main building blocks, Cu hexagons, share common corners. The competition between local anisotropy of hexagons and AF nearest neighbors interaction leads to a modest frustration which is resolved below $T_N = 61$ K by formation of AF collinear spin arrangement. The unusual magnetic features of the ordered state, like reduced anisotropy and pronounced magnetic non-linearity, are naturally interpreted by the presence of differently oriented magnetic domains.

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