Ground state order and spin-lattice coupling in tetrahedral spin systems Cu$_2$Te$_2$O$_5$X$_2$

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High-resolution ac susceptibility and thermal conductivity measurement on Cu$_2$Te$_2$O$_5$X$_2$ (X=Br,Cl) single crystals are reported. For Br-sample, sample dependence prevents to distinguish between possibilities of magnetically ordered and spin-singlet ground states. In Cl-sample a three-dimensional transition at 18.5 K is accompanied by almost isotropic behavior of susceptibility and almost switching behavior of thermal conductivity. Thermal conductivity studies suggest the presence of a tremendous spin-lattice coupling characterizing Cl- but not Br-sample. Below the transition Cl-sample is in a complex magnetic state involving AF order but also the elements consistent with the presence of a gap in the excitation spectrum.

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In quantum magnets a nonmagnetic spin singlet ground state, an intriguing hallmark of their quantum nature, and a sizeable reduction of the range of magnetic correlations, are two inseparable phenomena [1]. Thus, unlike classical spin systems, characterized by some kind of low-temperature magnetic long range order, quantum magnetic systems may reveal just a short range ordered -a spin liquid- ground state [1], separated by a spin gap from the excitation spectrum. However, the presence of a gap in properties of real physical quantum system, does not necessarily grant a short-range ordered nonmagnetic singlet ground state: from various reasons a long-range ordered ground states are even more frequent in known quantum magnets [2].

Addressing the general problem of ground-state order we report in this work our studies on recently discovered copper telluride Cu$_2$Te$_2$O$_5$X$_2$ systems (where X=Cl or Br), attracting a lot of attention [4].[6]. These systems belong to a category of Cu$^{2+}$, S=1/2, quantum magnets featuring antiferromagnetic (AF) Heisenberg interaction and a rich variety of quantum spin phenomena [2]. Both Cu$_2$Te$_2$O$_5$Br$_2$ and Cu$_2$Te$_2$O$_5$Cl$_2$ single crystals thus combine intrinsic magnetic low-dimensionality (related to the quasi-zero-dimensional contribution of weakly interacting clusters) and built-in frustration (related to tetrahedral topology). There is a common opinion that the full spectrum of properties may be reconstructed by including additional -inter-tetrahedral- magnetic interactions into the isolated-clusters model Hamiltonian [6].[7]. Even unperturbed, the model of isolated clusters comprises intriguing excitation spectrum [8][9]: Its ground state is always a singlet (involving a quadrumer of all four spins or a product of the two individual dimers) while the first excited state can be either singlet or triplet, depending on the relative sizes of the two involved exchange interactions $J_1$, $J_2$.

Experimentally supported equality of these interactions, $J_1 = J_2 = J$, leads to a double degenerated singlet ground state, separated from the lowest excitation by a gap $\Delta = J$.

Although Cu$_2$Te$_2$O$_5$Cl$_2$ and Cu$_2$Te$_2$O$_5$Br$_2$ samples are isostructural their low-temperature properties are significantly different [4]. The most pronounced reported difference is that the Cl-system develops a 3D magnetic order below about 18 K while the Br-system builds up, below 11 K, a phase revealing specific, Raman active low-lying longitudinal magnetic modes [4]. However, the specific nature and details of both of the mentioned transitions/transformations have not been clarified enough by previous studies [4][6][9].

Targeting the problem of intrinsic ground state and its order, in this work we report ac susceptibility and thermal conductivity studies of high-quality Cu$_2$Te$_2$O$_5$X$_2$ single crystals. AC susceptibility was measured using a commercial CryoBIND set-up. The apparatus reaches its high resolution (better than 2·$10^{-9}$ emu) employing measuring fields of the order of 1 Oe only. Low measuring fields are advantageous in studies of spontaneous magnetic ordering. The field level of a few Oersteds is three to four orders of magnitudes smaller than the typical field values used in previous DC-SQUID studies on powder [9] and single-crystalline [9] forms of Cu$_2$Te$_2$O$_5$X$_2$ samples. Under conditions of our measurements we are thus pretty confident that the low-temperature behavior we report on in this work originates from the evolution of intrinsic ground state of Cu$_2$Te$_2$O$_5$X$_2$.

The single crystals we used were grown by the usual halogen vapor transport technique, using TeCl$_4$, Cl$_2$ or TeBr$_4$ as transport agents. Semi-transparent dark (Cu$_2$Te$_2$O$_5$Br$_2$) or light-green (Cu$_2$Te$_2$O$_5$Cl$_2$) samples grow as needle-like single crystals with the apparent chain morphology. The stoichiometry of the obtained single crystals were quantitatively probed by electron-probe mi-
mum. whole temperature range below the susceptibility maxi-
distinct susceptibility feature, could be detected in the
magnetic ordering, in the form of a kink or any other
from evolution of susceptibility anisotropy, in our low-
electron diamagnetism) in ‘orthogonal’ geometry satu-
ability (sum of the Van Vleck paramagnetism and core
ration level was found close to the value of orbital suscep-
tability (c-axis collinear with magnetic field direction) the satu-
ments on Cu$_2$TeO$_5$Br$_2$ samples (Fig.1) reveals exponent-
ally decreasing featureless susceptibility. At low tem-
peratures susceptibility saturates at different levels de-
ment (related to impurities and/or unpaired spins) has
been observed down to 1.5 K. Our results show that
below the respective maxima the susceptibility behav-
our of Br- and Cl-samples are very different. Measure-
ments of Cu$_2$TeO$_5$Br$_2$ reveals exponential suscep-
tivity maxima coincide with the values reported previously [3, 4]. Illustrat-
ing the quality of the single crystals used in our mea-
urements, we point out that no sizeable Curie-like up-
turn (related to impurities and/or unpaired spins) has
stated full compatibility with the elementary spin-gap ex pres-
sion (thin solid line).

The results of our ac susceptibility studies on Br- and
Cl-single crystals are shown in Fig.1 and Fig.2, respec-
tively. The positions of the susceptibility maxima coin-
stoichiometry of copper.

In contrast to Br-sample, in Cu$_2$TeO$_5$Cl$_2$ there is a
sharp, almost isotropic, kink at $T_c=18.5$ K followed by
an exponential susceptibility decay down to the relatively
high level of low temperature susceptibility saturation,
Fig.2. However, we note that fine details of our results,
like the mentioned level of low-temperature saturation,
are somewhat sample- and thermal- (and/or magnetic)
history-dependent. The latter dependence could proba-
be related to extrinsic magnetic contributions [7].

Verifying compatibility of our results with those pub-
ished earlier we found out that the suggested suscepti-
form for isolated tetrahedra (Figs.1,2, thin line) of Ref.3 describes our data reasonably well. In fact, there
is a perfect fit to the results for Cl-samples (Fig.2), using
the same choice of interaction parameters as those iden-
tified earlier [3], i.e., $J_1 = J_2 = 38.5$ K. Quantitative
accordance with the results for Br-sample is not that good.
Naturally, one can interpret the quantitative deviation
from the model prediction as an evidence of the inter-
shaped corrections to the unperturbed model Hamilton-
ian.

Thermal conductivity was measured along the long
sample axis (c-axis). Magnetic susceptibility and ther-
conductivity were measured on the samples from
the same batch. The results for Cu$_2$TeO$_5$Br$_2$ and
Cu$_2$TeO$_5$Cl$_2$ samples are shown in Fig.3, covering the
temperature range 8 K-150 K. (8 K represents the lower
margin of the temperature range of our set-up). Ther-
conductivity reveals even more striking differences
between the two compounds. By lowering temperature
thermal conductivity of Cu$_2$TeO$_5$Br$_2$ just monotonously
increases forming a characteristic low-temperature max-
imum, typical for phonon thermal transport in crys-

![FIG. 1: AC susceptibility of one Cu$_2$TeO$_5$Br$_2$ single crystal (m=6.7 mg). Measurements were taken in two orientations to applied measuring field $H_{ac}=2$ Oe, at frequency 433 Hz. Rectangular area designates the range of a sample-dependent saturation levels reached in measurements on different samples. Thin solid line plots the isolated-tetrahedra model from Ref. 3, taken with the choice $J_1 = J_2 = 48K$. Inset demonstrates full compatibility with the elementary spin-gap expression (thin solid line).](image1)

![FIG. 2: AC susceptibility of one Cu$_2$TeO$_5$Cl$_2$ single crystal (m=17.6 mg). Measurements were taken in three orientations to applied measuring field $H_{ac}=2$ Oe, at frequency 433 Hz. The result for the third orientation was very similar and has been omitted for clarity. Thin solid line plots the isolated-tetrahedra model from Ref.3, taken with the same choice $J_1 = J_2 = 38.5K$. Magnetic transition region is shown in the Inset. Thick gray line marks the position of the temperature-independent susceptibility part, as determined in Ref.3.](image2)
talline solids. In contrast, thermal conductivity of Cu$_2$Te$_2$O$_5$Cl$_2$, showing up a similar value and temperature dependence above 150 K as the Br-sample, first anomalously levels-off and saturates for temperatures below 40 K and then, below 15 K, very sharply increases and approaches the respective thermal conductivity value of the Br-sample.

We first discuss our results for Cu$_2$Te$_2$O$_5$Br$_2$. Vanishing susceptibility shown in Fig.1 for parallel geometry usually demonstrates a spin singlet ground state stabilizing in a compound: according to best of our knowledge it would be the first known spin singlet among the tetrahedral S=1/2 systems. In this case the singlet state would rely on tetrahedral quadrumers (or dimer products, depending on $J_1$ vs. $J_2$ relationship). Limiting the temperature interval arbitrarily to the temperature range (4.2 K-16 K) a fit to the generic gap form $e^{-\Delta/T}$ identifies the spin gap value of $\Delta = 38K$. However, in orthogonal geometry susceptibility saturates at elevated but sample-dependent levels approaching the vanishing level characterizing parallel-geometry in cases of one or two measured samples only. Elevated susceptibility in any geometry is of course inconsistent with spin-singlet ground state. The susceptibility anisotropy shown in Fig.1 is, on the other hand, fully compatible with magnetic ordering scheme proposed by Jensen et al. [7] thus the result for this particular sample would favor magnetically ordered ground state. Still, due to mentioned sample dependence the question of ground state of Br-compound is not entirely resolved as yet. In our opinion a small amount of non-magnetic impurities, possibly present in our samples [7], might play a crucial role in stabilization of a particular (magnetic or non-magnetic) ground state at low temperatures.

Focusing Cu$_3$Te$_2$O$_5$Cl$_2$ we discuss now its intriguing susceptibility and thermal conductivity behavior below 18 K. The susceptibility kink was observed previously [8] and our low field ac susceptibility measurements on single crystals confirm that there is indeed a spontaneous 3D transition underlying the kink feature. In vast majority of quantum magnets 3d transition stabilizes the antiferromagnetically ordered ground state: only in CuGeO$_3$ spin-Peierls mechanism [8], that involves also a symmetry breaking, stabilizes a dimerized, non-magnetic singlet ground state. The respective magnetic excitation spectrum can be either gapless or gapped, in cases of magnetically ordered or spin singlet-ground states, respectively. (Of course, a gap can be introduced into the magnetic spectrum of magnetically ordered systems by presence other effects, like magnetic anisotropy, into the effective Hamiltonian). However, as shown by numerous studies [8] on doped CuGeO$_3$ these two ground states are not entirely exclusive and locally coexisting AF ordered and dimerized phases cannot be excluded as well. Positioning the nature of the transition in the Cl-compound inside these possibilities [8] is not an easy task. Discussing first the possibility of a long range AF order one immediately notes (Fig.2) that our susceptibility results cast some doubts at least about the classical uniaxial Néel transition scenario: there is almost isotropic susceptibility drop below $T_n=18.5$ K. (Generally, in an AF transition there is a sizeable susceptibility decrease along one (easy) magnetic axis while in the two orthogonal orientations susceptibility hardly changes). Indeed, an independent susceptibility anisotropy study by torque magnetometry [10] identified the presence of magnetic ordering below 18.5 K; the order is however substantially more complex than the standard uniaxial Néel one. Also, a spin flop phenomenon, a decisive feature of AF-ordered substances, could not be identified in these studies. Noteworthy, Cl-compound was found magnetically inhomogeneous [2] thus making it difficult at present to separate intrinsic from extrinsic components in low temperature magnetism.

As far as the possibility of spin-Peierls transition is concerned one first notes that the observed isotropy of ac susceptibility would be consistent with this type of transition: isotropic susceptibility has been observed [8] in spin-Peierls transition of CuGeO$_3$ and spin-Peierls-like transition [11] of NaV$_2$O$_5$. From Fig.2 one however realizes that the value of temperature independent orbital susceptibility is obviously much smaller than the low temperature susceptibility saturation in either directions, inconsistent with nonmagnetic spin-singlet ground state.

On the other hand the thermal conductivity anomaly (Fig.3) would be difficult to interpret without the participation of a gap in magnetic excitation spectrum of Cl-compound. Namely, there are generally very little changes of thermal conductivity at (or in vicinity of) Néel transition point of AF substances. There are however several examples of pronounced anomalies either due scattering on critical fluctuations (e.g., in CoF$_2$) or magnon-phonon interaction (e.g., in FeCl$_2$). Still, to the best of our knowledge there are no examples of AF transition underlying the switching behavior of thermal conductivity like the one we report on for Cu$_2$Te$_2$O$_5$Cl$_2$. Instead, the assumption of a gap enables more natural interpretation of our thermal conductivity results (Fig.3). Br-sample reveals a typical phononic thermal transport down to low temperatures. Pronounced sample dependence, indicating the presence of 3D transition below 11 K in some samples, has been also observed. No evidence for a combined (phonon-magnon) thermal transport or pronounced phonon scattering on magnons can be identified in our result [12]. One concludes therefore that there is intrinsically small magneto-elastic coupling, as well as spin-phonon scattering, characterizing the Br-compound. Surprisingly, the opposite is true for Cu$_2$Te$_2$O$_5$Cl$_2$: Fig.3 shows that the spin-lattice coupling is unexpectedly large in this compound. (Unexpectedly, because of isomorphic structure of the two compounds). In interpreting
stabilizes a complex low temperature magnetic state involving equally the spins and their couplings to lattice, singlet ground states. An intriguing 3D transition, in-between the possibilities of magnetically ordered and spin-Peierls-like ordering [14] in NaV almost identical experimental observation has been realized for Cu₂Te₂O₅Cl₂ at low temperatures. Very similar interpretation and the explosive growth of thermal conductivity below the intermediate temperature range but being very efficiently suppressed in the Cu₂Te₂O₅Cl₂ single crystal. Microscopic background and details of the transition are unknown as yet.

Thus the assumption of a gap in the excitation spectrum of Cu₂Te₂O₅Cl₂ is effective as long as there are magnetic excitations. The abrupt and sizeable (factor of 4) thermal conductivity enhancement below 15 K reflects opening of the latter transport channel for thermal transport. A sharp increase of thermal conductivity below 15 K, as illustrated in Fig. 3, is observed in ground-state-singlet systems precludes to resolve clearly being very efficiently suppressed phonon conduction in intermediate temperature range but being very efficiently swept away below susceptibility kink -3D ordering- temperature Tc. We find a pronounced spin-phonon scattering responsible for the latter mechanism. The scattering is effective as long as there are magnetic excitations. Thus the assumption of a gap in the excitation spectrum of Cl-compound provide a simple interpretation for the explosive growth of thermal conductivity below the mid-gap temperatures. Very similar interpretation and almost identical experimental observation has been reported for spin-Peierls-like ordering [14] in NaV₂O₅, as well for thermal transport [13, 14] in ground-state-singlet system SrCu₂(BO₃)₂. Compared to NaV₂O₅ there are however significant differences: charge ordering (of V⁵⁺ and V⁴⁺) takes plays the main role in low temperature dynamics of the latter system. In Cu₂Te₂O₅Cl₂ we find no grounds for charge ordering of this sort. We suggest therefore that a strong spin-lattice coupling represents an important ingredient in the 3D transition of this compound. Microscopic background and details of the transition are unknown as yet.

In summary, pronounced sample dependence of Cu₂Te₂O₅Br₂ samples precludes to resolve clearly between the possibilities of magnetically ordered and spin-singlet ground states. An intriguing 3D transition, involving equally the spins and their couplings to lattice, stabilizes a complex low temperature magnetic state of Cu₂Te₂O₅Cl₂. As there are evidences for both, long range AF magnetic order and the presence of a gap, our results suggest coexisting magnetically ordered and disordered spin-singlet domains characterizing Cu₂Te₂O₅Cl₂ at low temperatures.

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FIG. 3: Thermal conductivity of Cu₂Te₂O₅Cl₂ and Cu₂Te₂O₅Br₂ single crystals. A sharp increase of thermal conductivity of the Cu₂Te₂O₅Cl₂ sample, shown in the Inset on expanded scale, takes place below the 3D ordering temperature (see text).