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# Ground-state order and spin-lattice coupling in tetrahedral spin systems $Cu_2Te_2O_5X_2$ ($X$=Br or Cl)

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High-resolution ac susceptibility and thermal conductivity measurement on $Cu_2Te_2O_5X_2$ ($X$=Br,Cl) single crystals are reported. For Br-sample, sample dependence prevents one from distinguishing 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 sizable 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[3] copper telluride $Cu_2Te_2O_5X_2$ 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 $Cu_2Te_2O_5Br_2$ and $Cu_2Te_2O_5Cl_2$ integrate a common magnetic building block, tetrahedral clusters of $S=1/2$ spins. The $Cu_2Te_2O_5X_2$ systems 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.[5,6] Even unperturbed, the model of isolated clusters comprises intriguing excitation spectrum:[3,4] 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[3] 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 $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$ samples are isostructural their low-temperature properties are significantly different.[4] The most pronounced reported difference[4] is that the Cl-system develops a three-dimensional (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.[3–5]

Targeting the problem of intrinsic ground state and its order, in this work we report ac susceptibility and thermal conductivity studies of high-quality $Cu_2Te_2O_5X_2$ single crystals. ac susceptibility was measured using a commercial CryoBIND setup. The apparatus reaches its high resolution (better than $2\times10^{-9}$ 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[3,4] and single-crystalline[5] forms of $Cu_2Te_2O_5X_2$ 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 $Cu_2Te_2O_5X_2$.

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- ($Cu_2Te_2O_5Br_2$) or light-green ($Cu_2Te_2O_5Cl_2$) 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 micro analysis. This analysis identified a good stoichiometry in all constituents (including Cl and Br), allowing only for a probability of small (1%–2%) systematic under-stoichiometry of copper.

The results of our ac susceptibility studies on Br- and Cl-single crystals are shown in Figs. 1 and 2, respectively. The positions of the susceptibility maxima coincide with the values reported previously.[3,4] Illustrating the quality of the single crystals used in our measurements, we point out that no sizable Curie-like upturn (related to impurities and/or un-

 

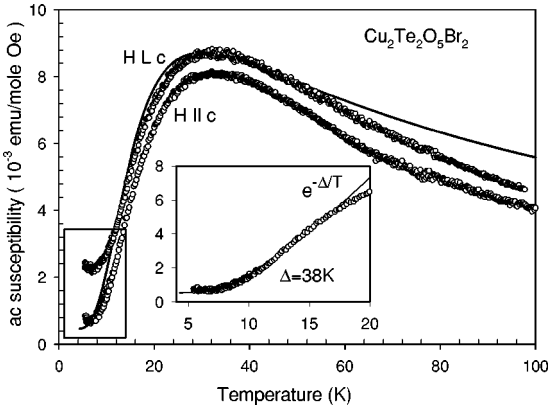


FIG. 1. ac susceptibility of one $Cu_2Te_2O_5Br_2$ single crystal ($m = 6.7$ mg). Measurements were taken in two orientations to applied measuring field $H_{ac} = 2$ Oe, at frequency 433 Hz. Rectangular area designates the range of a sample-dependent saturation levels reached in measurements on different samples. Thin solid line plots the isolated-tetrahedra model from Ref. 3, taken with the choice $J_1 = J_2 = 48$ K. Inset demonstrates full compatibility with the elementary spin-gap expression (thin solid line).

paired spins) has been observed down to 1.5 K. Our results show that below the respective maxima the susceptibility behavior of Br- and Cl-samples are very different. Measurements on $Cu_2Te_2O_5Br_2$ samples (Fig. 1) reveal exponentially decreasing featureless susceptibility. At low temperatures susceptibility saturates at different levels depending, in most of the measured samples, on sample-to-applied field orientation. While in ''parallel'' orientation ($c$-axis collinear with magnetic field direction) the saturation level was found close to the value of orbital susceptibility (sum of the Van Vleck paramagnetism and core electron diamagnetism) in ''orthogonal'' geometry saturation exhibits pronounced sample dependence. Apart from evolution of susceptibility anisotropy, in our low-field measurements on $Cu_2Te_2O_5Br_2$ no explicit sign of magnetic ordering, in the form of a kink or any other distinct susceptibility feature, could be detected in the whole temperature range below the susceptibility maximum.

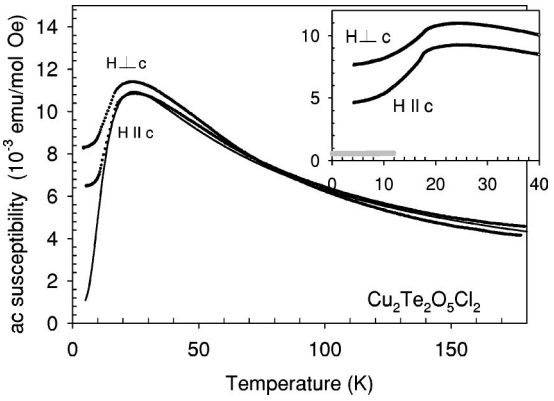


FIG. 2. ac susceptibility of one $Cu_2Te_2O_5Cl_2$ single crystal ($m = 17.6$ mg). Measurements were taken in three orientations to applied measuring field $H_{ac} = 2$ Oe, at frequency of 433 Hz. The result for the third orientation was very similar and has been omitted for clarity. Thin solid line plots the isolated-tetrahedra model from Ref. 3, taken with the same choice $J_1 = J_2 = 38.5$ K. 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.

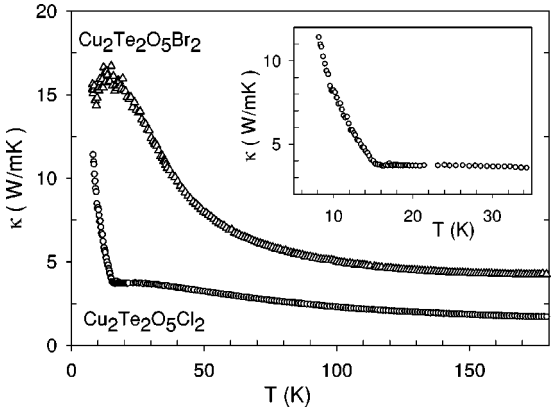


FIG. 3. Thermal conductivity of $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$ single crystals. A sharp increase of thermal conductivity of the $Cu_2Te_2O_5Cl_2$ sample, shown in the Inset on expanded scale, takes place below the 3D ordering temperature (see the text).

In contrast to Br-sample, in $Cu_2Te_2O_5Cl_2$ 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 probably be related to extrinsic magnetic contributions.[7]

Verifying compatibility of our results with those published earlier we found out that the suggested susceptibility form for isolated tetrahedra (Figs. 1 and 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 identified 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-terahedral corrections to the unperturbed model Hamiltonian.

Thermal conductivity was measured along the long sample axis ($c$ axis). Magnetic susceptibility and thermal conductivity were measured on the samples from the same batch. The results for $Cu_2Te_2O_5Br_2$ and $Cu_2Te_2O_5Cl_2$ samples are shown in Fig. 3, covering the temperature range 8–150 K. (8 K represents the lower margin of the temperature range of our setup.) Thermal conductivity reveals even more striking differences between the two compounds. By lowering temperature thermal conductivity of $Cu_2Te_2O_5Br_2$ just monotonously increases forming a characteristic low-temperature maximum, typical for phonon thermal transport in crystalline solids. In contrast, thermal conductivity of $Cu_2Te_2O_5Cl_2$, 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 $Cu_2Te_2O_5Br_2$. 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 (4.2–16 K) a fit to the generic gap form $e^{-\Delta/T}$ identifies the spin gap value of $\Delta=38$ K. 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.*[5] 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 nonmagnetic 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 $Cu_2Te_2O_5Cl_2$ we discuss now its intriguing susceptibility and thermal conductivity behavior below 18 K. The susceptibility kink was observed previously[4] 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 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 of 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[9] 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 $T_c=18.5$ K. [Generally, in an AF transition there is a sizable 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[7] 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 $NaV_2O_5$. 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 direction, 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 $Cu_2Te_2O_5Cl_2$. 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 $Cu_2Te_2O_5Cl_2$: Figure 3 shows that the spin-lattice coupling is unexpectedly large in this compound (unexpectedly, because of isomorphic structure of the two compounds). In interpreting the result for $Cu_2Te_2O_5Cl_2$ one could naively assume that the abrupt and sizable (factor of 4) thermal conductivity enhancement below 15 K reflects opening of an additional—magnetic—channel for thermal transport. However, a simple correlation with the corresponding result for $Cu_2Te_2O_5Br_2$, which represents a natural ''unperturbed'' reference system, tells that the latter interpretation is very unlikely: there is obviously a mechanism that drastically suppress phonon conduction in intermediate temperature range but being very efficiently swept away below susceptibility kink —3D ordering— temperature $T_c$. 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 provides 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 $NaV_2O_5$, as well for thermal transport[15,16] in ground-state-singlet system

$SrCu_2(BO_3)_2$. Compared to $NaV_2O_5$ there are however significant differences: charge ordering (of $V^{5+}$ and $V^{4+}$) plays the main role in low temperature dynamics of the latter system. In $Cu_2Te_2O_5Cl_2$ 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 $Cu_2Te_2O_5Br_2$ 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 $Cu_2Te_2O_5Cl_2$. As there is evidence 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 $Cu_2Te_2O_5Cl_2$ at low temperatures.

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