Evidence for an unconventional magnetic instability in the spin-tetrahedra system Cu$_2$Te$_2$O$_5$Br$_2$

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Thermodynamic experiments as well as Raman scattering have been used to study the magnetic instabilities in the spin-tetrahedra systems Cu$_2$Te$_2$O$_5$X$_2$, X=Cl and Br. While the phase transition observed in the Cl system at $T_c=18.2$ K is consistent with 3D AF ordering, the phase transition at $T_c=11.3$ K in the Br system has several unusual features. We propose an explanation in terms of weakly coupled tetrahedra with a singlet–triplet gap and low lying singlets.

Reduced dimensionality of a quantum spin system in combination with frustration leads in many cases to unconventional and interesting ground states or magnetic phase diagrams. Prominent examples are the frustrated and dimerized spin-1/2 chain, represented by the low-temperature phase of CuGeO$_3$, or the two-dimensional Shastry-Sutherland lattice with orthogonally arranged spin dimers and a frustrating inter-dimer coupling, realized in SrCu$_2$(BO$_3$)$_2$. These systems show a spin liquid ground state with a singlet–triplet gap. Frustration is evident in the latter system as dispersionless elementary triplets and multi-particle bound states of triplet and singlet character.

Spin triangles and tetrahedra that are strongly coupled into Kagomé or pyrochlore structures are at the origin of another important class of frustrated spin systems. Although the consequences of the classical ground-state degeneracy for the quantum case have not been fully elucidated theoretically, there are good reasons to believe that such models do not possess magnetic long-range order (LRO) but low-lying singlets. Scenarios leading to the development of LRO within this non-magnetic manifold have been put forward.

The limit of weakly-coupled tetrahedra with spin $S=1/2$ has been studied in some detail in 3D and 1D, and the physics is expected to be very interesting. However, they have not been investigated experimentally so far due to the lack of appropriate materials. The recently found spin system Cu$_2$Te$_2$O$_5$X$_2$, with X=Cl, Br, contains tetrahedral clusters of Cu$^{2+}$ with $S=1/2$ in a distorted square planar CuO$_3$X-coordination. These tetrahedra align to tubes or chains along the [001] direction, as they are separated along [100] and [010] direction by different Te-O coordinations (see Fig. 1a). Substituting Br for Cl in this system widens up the unit cell and increases its volume from 367 to 391 Å$^3$, by 7%, while bond angles or anisotropies do not change essentially. Therefore, this system allows in a unique way to study the interplay of frustration and coupling in a tetrahedra quantum spin system.

Preliminary measurements of the magnetic susceptibility $\chi(T)$ of both compounds showed a maximum at $T_{\chi_{\text{max}}}=23$ K and 30 K for X=Cl, Br and a strong reduction at low temperatures, typical for a spin gap system. Assuming that the compounds consist of weakly-coupled units of 4 spins with couplings $J_1$ and $J_2$ (see Fig. 1b), the best fit of the susceptibility - quite a good one actually - was obtained for $J_1 = J_2 = 38.5$ K and 43 K for X=Cl and Br respectively. The effect of inter-tetrahedra coupling was not included in this fit however.

We present here an investigation of both compounds, using detailed susceptibility, specific heat and Raman measurements. These measurements indicate an onset of antiferromagnetic order in the chloride compound at 18.2 K, pointing to a significant inter-tetrahedra coupling. In contrast, the bromide shows a very unusual phase transition at 11.3 K, at a temperature where a large part of the magnetic excitations have already been frozen out. A possible scenario for this transition shall be discussed.

The preparation of the samples and single crystals used for our measurements is described elsewhere. Specific heat and susceptibility measurements were performed on powder samples using a Quantum Design measurement property system and a SQUID magnetometer, respectively. The Raman scattering experiments were performed with a $\lambda=514$ nm laser line and a power level of 0.05-2 mW focused on a spot of 0.05-0.1 mm diameter. The whisker-like single crystals with typical dimensions 0.1-0.1·1 mm$^3$ and the measurement geometry did allow...
experiments in (cc), (yc) and (yy) light scattering polarizations, with c parallel to the crystallographic [001] direction and y given by a linear combination of the [100] and [010] direction. Based on the tetragonal space group and the missing center of inversion these polarizations correspond to the A symmetry and combinations of B and E symmetry, respectively.

Results of our detailed investigation of the magnetic susceptibility $\chi(T)$ of both compounds are shown in Fig. 2. Whereas the high temperature part of $\chi(T)$ at and above $T_{\chi_{\text{max}}}$ is very similar in both compounds, pronounced differences are observed at low temperatures. In the chloride a clear kink is evident in $\chi(T)$ at $T_N = 18.2$ K. This anomaly corresponds to a pronounced step-like increase of the slope $\partial \chi(T)/\partial T$ with decreasing temperature, as shown in the inset of Fig. 2. In other words, the susceptibility in the ordered state is smaller than it would be in the disordered state. Applying a magnetic field leads to a reduction of the size of this anomaly and thus to an increase of the susceptibility for $T < T_N$.

The specific heat $C_p(T)$ of Cu$_2$Te$_2$O$_5$Br$_2$ (see Fig. 3, upper curves with upper temperature scale) shows a mean field like transition with a sizeable anomaly at $T_N$. A magnetic field of 13.5 T leaves this anomaly almost unchanged, only a slight decrease of $T_N$ from 18.2 K to 18.0 K is discernible. All these features: the reduction of the susceptibility for $T < T_N$, the mean field type of transition, the reduction of the anomaly in $\chi(T)$ in an applied field whereas no reduction is observed in $C_p(T)$ and the very weak decrease of $T_N$ with increasing B, point to a 3D-antiferromagnetic ordering in a system with only weak spin-anisotropies. Since this transition occurs below the well-defined maximum in $\chi(T)$, with $T_N/T_{\chi_{\text{max}}} = 0.78$, these results indicate that Cu$_2$Te$_2$O$_5$Cl$_2$ is a low-dimensional spin systems with a significant inter-tetrahedra (or inter-chain) coupling.

In contrast, the low temperature behavior of Cu$_2$Te$_2$O$_5$Br$_2$ is quite different and rather unusual. For temperatures below $T_{\chi_{\text{max}}}$, $\chi(T)$ decreases considerably, by more than 50%. This indicates the freezing out of a large part of the magnetic triplet excitations as expected in a system with a spin gap. Whereas at first sight no anomaly can be observed in $\chi(T)$ at low fields (0.1 T), the derivative $\partial \chi(T)/\partial T$ reveals a small but well discernible step at $T_o = 11.5$ K. This step however has the opposite sign compared to Cu$_2$Te$_2$O$_5$Cl$_2$, i.e. the slope for $T < T_o$ is smaller than for $T > T_o$. This means, that the susceptibility of Cu$_2$Te$_2$O$_5$Br$_2$ and thus the magnetization in the ordered state is larger than it would be in the disordered state. This is opposite to the expected result for antiferromagnetic ordering. For $T < T_o$, the magnetization is strictly proportional to the applied field between $B = -1$ T and 1 T and shows no remanence. Thus ferromagnetic ordering or canted antiferromagnetism can be excluded for Cu$_2$Te$_2$O$_5$Br$_2$. The anomaly in $\chi(T)$ increases significantly in a magnetic field larger than 1 T. For $B = 5$ T, it is quite evident that $\chi(T)$ is higher in the ordered state than it would be in the disordered state.

The specific heat of Cu$_2$Te$_2$O$_5$Br$_2$ at $B = 0$ (see Fig. 3, lower curves with lower temperature scale) shows a small but well-defined mean field like anomaly at $T = T_o$. This proves that this transition also occurs in the absence of an external field. Applying a magnetic field leads to a very strong increase of the size of the anomaly, by more than a factor of 3 at $B = 13$ T, and to a pronounced shift of $T_o$ to higher temperatures, from $T_o(0) = 11.4$ K to $T_o(B=13T) = 12.4$ K. In thermodynamic terms, this shift corresponds to the larger magnetization of the ordered state compared to the disordered state. Fitting a power law to the field dependence of $T_o$ as determined from $C_p(T)$, $T_o(B) = T_o(0)+a \cdot B^n$, we obtain $n = 1.41 \pm 0.05$. Using the low temperature parts $(T \ll T_o, T_N)$ and the high temperature parts $(T > T_o, T_N)$ of the specific heat results, we made a rough estimate of the magnetic specific heat and of the magnetic entropy $S_m(T)$. For Cu$_2$Te$_2$O$_5$Br$_2$, the magnetic entropy at $T_o$ is only a quite small portion of the total spin entropy expected at high temperatures $S_m(T_o) \simeq 1.8$ J/Kmol = 0.16 · Rln2/spin, whereas for Cu$_2$Te$_2$O$_5$Cl$_2$, the entropy $T_o$ at $T_N$ is much larger, $S_m(T_N) \simeq 4.1$ J/Kmol = 0.36 · Rln2/spin. This is related to the difference in the ratio $T_o/J$ and $T_N/J$ and indicates that in the bromide, a large part of the magnetic degrees of freedom are freezing out at higher temperatures.

Light scattering studies have been performed on both systems as function of temperature. The optic $(q \approx 0)$ phonon frequencies of Cu$_2$Te$_2$O$_5$Br$_2$ are generally smaller compared with Cu$_2$Te$_2$O$_5$Cl$_2$. This is consistent with the larger unit cell volume of the bromide. Details of the phonon spectrum will be given elsewhere. In the low energy range comparable to the spin gap of the systems we observe two signals in Cu$_2$Te$_2$O$_5$Br$_2$ that do not fit to phonon scattering. The excitation spectrum of Cu$_2$Te$_2$O$_5$Cl$_2$ is less spectacular. The corresponding energy regime displays a much weaker temperature dependence and a smaller intensity of scattering. It will not be further discussed here.

In Cu$_2$Te$_2$O$_5$Br$_2$ the high-temperature spectra are dominated by a pyramidal-shaped scattering continuum centered at 61 cm$^{-1}$=88 K, corresponding to $2\Delta = 86$ K previously determined from the magnetic susceptibility [4]. The continuum is attributed to a two-magnon-like scattering process [3]. Its total linewidth and the low energy onset at 40 cm$^{-1}$ both point to an appreciable inter-tetrahedra coupling. For reduced temperatures, $T < 9$ K, a second maximum with smaller linewidth develops. It shows a soft mode-like behavior and reaches its maximum energy of 18 cm$^{-1}$ = 0.62K at lowest temperatures. This intensity is undoubtedly related to the instability observed in our thermodynamic experiments. In the same temperature regime an additional shoulder develops on the high frequency side of the scattering con
tinuum. This leads to a small shift of this signal from 61 to 63 cm$^{-1}$.

These two scattering signals are only observed in (cc) polarization with both electric field vectors parallel to the crystallographic c-axis and the chains of tetrahedra. This symmetry selection rule and the temperature dependence of the low energy mode are similar to the properties of a singlet bound state observed in the dimerized phase (T $\leq$ T$_{SP}$ = 14.5 K) of CuGeO$_3$. In this spin chain system frustration leads to a binding effect of two elementary triplets to a well-defined mode at 1.78$\Delta$ [13]. The "in chain" selection rule that is observed in both systems in combination with the final linewidth of the continuum are the result of an appreciable quasi-one-dimensional inter-tetrahedra coupling.

Let us start the discussion by noting that the main features of the Br system can be understood in terms of weakly coupled tetrahedra. The spectrum of a tetrahedron is depicted in Fig. 1c. If J$_1$ = J$_2$ above T$_o$, as suggested by the fit of the susceptibility at high temperature, then the ground-state is a two-fold degenerate singlet, and the first excitation is a three-fold degenerate triplet located at $\Delta$ = J$_1$ above the GS. These triplets would then lead to Raman scattering at 2$\Delta$ = 86 K, in agreement with our data.

The origin of the phase transition at T$_o$ could be a small distortion of the tetrahedra that leads to different values for J$_1$ and J$_2$, hence to a lifting of the degeneracy between the two GS singlets. This is similar to the spin-Peierls scenario of Yamashita and Ueda [9]. In this picture, the Raman scattering observed below 9 K would involve transitions between the singlet GS and the first excited singlet. Note that the entropy jump of such a transition is expected to be a small fraction of R ln 2/spin, in agreement with the specific heat data.

Let us now discuss all the other issues raised by the present results. First of all, the Cl and Br compounds turn out to be very different. As a first step toward understanding this difference, we have performed ab-initio calculations of the electronic structure of these systems. These results will be reported elsewhere. These calculations give access to the hopping integrals but not to the exchange integrals. So the information is only qualitative. The main difference between the two systems is that the ratio of the intraplaquette hoppings $t_2/t_1$ is closer to 1 in the Br system than in the Cl one. This is consistent with our proposal that the physics of weakly coupled tetrahedra is realized in the Br system but not in the Cl one.

As a first step to understand the Raman continuum we have analyzed the light-scattering cross section of a coupled array of tetrahedra, extending however only in 1D along the c-axis [13]. Based on exact diagonalization and bond-operator theory it is found that in this case the continuum is determined by the spin-zero two-triplet excitations of an effective dimerized spin-one chain. Due to triplet interactions the corresponding Raman continuum is strongly renormalized with respect to the bare two-triplet spectrum. It displays no van-Hove type edge-singularities, a width set by the inter-tetrahedral coupling, and a smooth convex shape with a single maximum. The latter shape is encouraging, yet still different from the pyramid-like spectrum of fig. 8. This is consistent with our ab-initio band structure calculations indicating that the inter-tetrahedral couplings are comparable along and perpendicular to the tubes. A study of the Raman response of a 3D array of coupled tetrahedra is in progress.

Finally a lot remains to be done to understand in detail what happens at T$_o$ in the Br system, in particular whether there is a change of the local geometry, as implied by our interpretation of Raman data, as well as the influence of the magnetic field on the transition, which might require to take into account the Dzyaloshinskii-Moriya interaction which is a priori present in that system.

In summary, our results have revealed that both the Cl and Br compounds undergo a phase transition at low temperatures, but that these phase transitions appear to be of different nature: While there is good evidence in favor of a 3D magnetic ordering in Cl, the transition in the Br compound is very unusual, with the appearance of low energy Raman scattering below the transition. If our interpretation of the origin of this low-energy scattering is confirmed, this makes Cu$_2$Te$_2$O$_5$Br$_2$ the first system with only singlet low-energy excitations that undergo a phase transition involving these singlet low-energy degrees of freedom. Since the Cl and Br systems are very similar a priori, their difference at low temperature suggest that they might be located on both sides of a quantum critical point in a system of coupled tetrahedra.

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FIG. 1. a) Part of the crystal structure of Cu$_2$Te$_2$O$_5$X$_2$ with two Cu tetrahedra, O (filled), Cl or Br (dashed) and Te (empty circles) coordinations. b) exchange topology of a single spin tetrahedron and c) the resulting excitation spectrum with respect to the ground state (GS) energy.

FIG. 2. Magnetic susceptibility $\chi(T)$ of Cu$_2$Te$_2$O$_5$X$_2$, X=Cl and Br, with different magnetic fields applied. The inset shows $\partial \chi(T)/\partial T$.

FIG. 3. Specific heat $C_p(T)/T$ of Cu$_2$Te$_2$O$_5$X$_2$ with X=Cl (upper temperature axis) and X=Br (lower temperature axis). The inset gives a temperature–magnetic field phase diagram.

FIG. 4. Raman scattering spectrum of Cu$_2$Te$_2$O$_5$Br$_2$ in (cc) polarization.