Magnetic properties of the S = 1/2 quantum chain systems CuX_2O_6 (X = Sb, Ta)

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In the past years the efforts to understand the physics of high-T_c superconductors have refocused attention on the magnetism of low-dimensional antiferromagnetic (afm) quantum spin $S = 1/2$ systems. A great number of hitherto unknown magnetic systems with unusual low-temperature magnetic behavior and ground-state properties have been synthesized and investigated experimentally and theoretically. New and unexpected phenomena have been observed which stimulated broad theoretical activity. Two recent one-dimensional quantum systems that attracted particular interest are $CuGeO_3$ and α'-NaV_2O_5 about which we have reported in preceding annual reports (see the annual reports of 1995, 1996, 1998 and 1999).

Some years ago we have identified the compounds MX_2O_6 (X = Sb, Ta) with M being magnetic Co^{2+}, Ni^{2+} and Fe^{2+} ions as magnetic systems with characteristic signatures of low-dimensional afm properties, mostly however, with strong Ising anisotropy as e.g., found for $CoTa_2O_6$. MX_2O_6 phases with Cu^{2+} ($S = 1/2$) as magnetic cations may be expected to show Heisenberg-type exchange coupling. The knowledge of the magnetic properties of $CuSb_2O_6$ and $CuTa_2O_6$, however, is only very preliminary, particularly, because of experimental difficulties encountered in the preparation of large single crystals (in the case of $CuSb_2O_6$) and because of the thermal instability of $CuTa_2O_6$ avoiding preparation routes employing typical solid state preparation techniques.

The phases MX_2O_6 (X = Sb, Ta) crystallize in the tri-rutile structure type which is related to the well-known rutile structure via a tripling of the *c*-axis occurring as a consequence of the chemical ordering of the divalent and pentavalent cations. The cations are octahedrally coordinated by oxygen atoms. The cation-oxygen octahedra form edge-sharing chains which are occupied alternately by MO_6 and XO_6 octahedra in a ratio 1:2 with complete chemical ordering (Fig. 1). $CuSb_2O_6$ undergoes a structural phase transition from the tetragonal to a monoclinic structure above room temperature at $\approx 125°C$, however, the deviation of the monoclinic structure from the tri-rutile structure type is only very small.

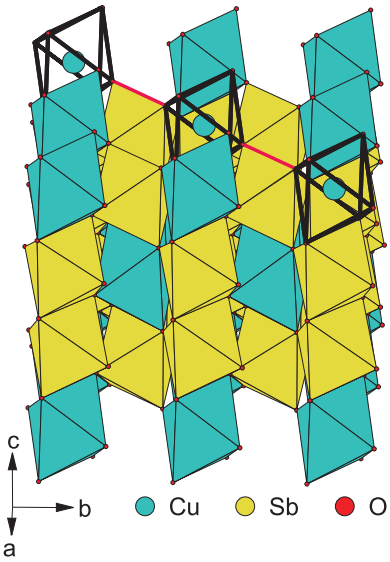

Figure 1: Crystal structure of $CuSb_2O_6$ with distorted oxygen octahedra around Cu and Sb drawn with the respective colors. Red solid lines connecting open-face octahedra around Cu^{2+} indicate the Cu–O–O–Cu bonds which promote strongest afm exchange interaction.

In the tri-rutile structure type two-dimensional character of the magnetic coupling between the divalent cations may be inferred. A closer inspection of the exchange paths, however, reveals the connection of the magnetic ions via

the stretched O–O bonds along face diagonals as the most likely paths for the largest exchange coupling. Bonds via O^{2-} ions to cations in neighboring face diagonals include bonding angles close to 90° and increased bond lengths and exchange is expected to be significantly smaller.

Single crystals of $CuSb_2O_6$ were grown by chemical vapor transport at the University of Frankfurt. Magnetic, thermodynamic properties and magnetic structure solutions were determined in Stuttgart. Single-crystal neutron diffraction measurements on $CuSb_2O_6$ were carried out at the Institut Laue-Langevin in Grenoble. $CuTa_2O_6$ is not accessible via the standard preparation routes from CuO and Ta_2O_5, It has successfully been prepared at the TU Dresden via a careful decomposition of precursor oxalates at 300°C.

$CuSb_2O_6$ had been reported to exhibit magnetic strong short-range order signalled by a broad susceptibility maximum centered around 60 K. The susceptibility fitted well to an afm uniform $S = 1/2$ Heisenberg chain ($J \approx -50$ K) model with nearest-neighbor coupling. A sharp decrease in the susceptibility below ≈ 9 K indicated the long-range afm order due to interchain interactions. Preceding powder neutron diffraction experiments performed by Greedan and collaborators resulted in a propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$ for the afm ordered phase and the suggestion of various ordering schemes. A conclusive magnetic structure solution was pending.

Figure 2 displays the magnetic susceptibility and the heat capacity of a crystal of $CuSb_2O_6$. Long-range order is evident from the heat capacity anomaly and the kinks in the susceptibility below $T_N = 8.68(5)$ K. The fit of the susceptibility with the model of an $S = 1/2$ Heisenberg chain with uniform afm nearest-neighbor coupling yields close to perfect agreement in a temperature range above long-range ordering ($10\,\mathrm{K} < T < 350\,\mathrm{K}$) with an exchange parameter of $J = -48.0(5)$ K. The low-temperature heat capacity ($T < 10$ K), in addition to a phonon term ($\propto T^3$), contains the typical linear magnetic term ($\propto T$) in very good agreement with the expected value $C_{mag}/R = T/3J$ for a uniform afm $S = 1/2$ Heisenberg chain. Long-range ordering arises from finite interchain coupling. Using standard theoretical results from $T_N \approx 8.7$ K and $J = -48$ K the ratio of interchain to intrachain exchange constant is estimated to 3%.

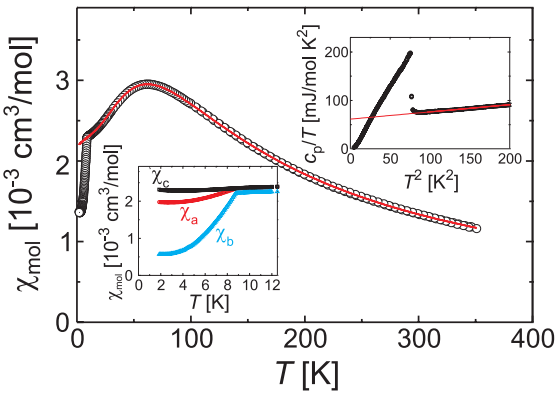

Figure 2: Susceptibility of a single crystal of $CuSb_2O_6$ measured in a field of 0.1 T along the *b*-axis (○). The full line is a fit to the susceptibility of a $S = 1/2$ Heisenberg chain with afm nearest-neighbor interaction with exchange constant $J = -48$ K. Insets: Heat capacity with an anomaly at 8.68(5) K indicating long-range ordering and the linear magnetic contribution above T_N. Susceptibilities along the *c*-, *a*-, and *b*-axis as indicated.

Below T_N the magnetic susceptibility exhibits pronounced anisotropy. With the field aligned along the *a*- or *b*-axis, the susceptibility drops while for the field along the *c*-axis no decrease below T_N can be detected. This observation suggests that the ordered moment lie in the *ab*-plane with their major component along *b*. Single crystal neutron diffraction on $CuSb_2O_6$ at room temperature and at low temperatures revealed additional weak Bragg reflections below T_N which can be indexed on the basis of a propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$. A refinement of the nuclear structure at low temperature gave no indication of a structural phase transition. The refinement of the magnetic structure converged equally well to two alternative models with moments either in the *ab*- or the *bc*-plane,

respectively. For both models the ordered moment at 2 K amounts to 0.51(2) μ_B. On the basis of the anisotropy of the susceptibility we suggest a magnetic structure as displayed in Fig. 3 with moments tilted 103(6)° (Cu1: (0, 0, 0)) and 70(5)° (Cu2: $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$) away from the *a*-axis and oriented antiparallel along (1 1 0).

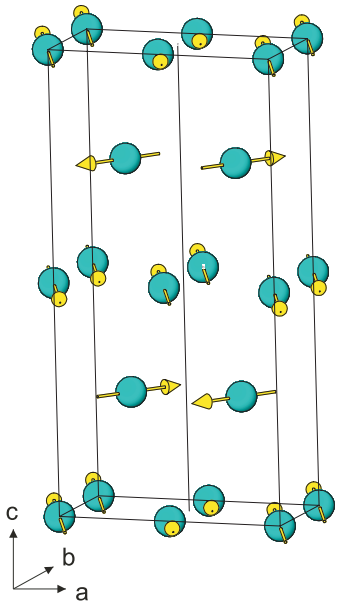

Figure 3: Magnetic structure of $CuSb_2O_6$ at 2 K.

Figure 4 displays first magnetic susceptibility measurements on a polycrystalline sample of $CuTa_2O_6$. A fit to the prediction for a $S = 1/2$ afm Heisenberg chain model with nearest-neighbor coupling indicates that $CuTa_2O_6$, like $CuSb_2O_6$, closely follows theory with an exchange constant $J \approx -25$ K which indicates a reduction by a factor of two as compared to $CuSb_2O_6$. An indication for long-range ordering has not been found yet.

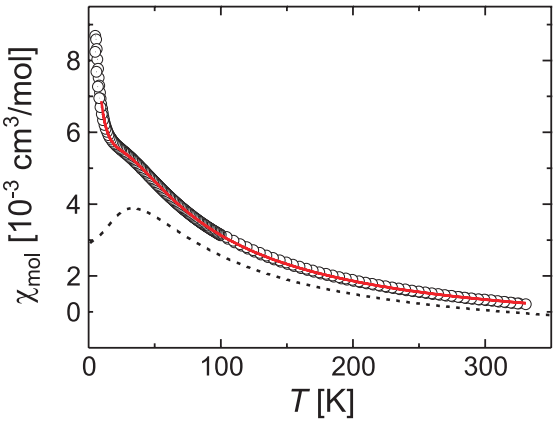

Figure 4: Magnetic susceptibility of $CuTa_2O_6$ (○). The solid line is a fit to the susceptibility of an afm $S = 1/2$ Heisenberg chain with nearest-neighbor interaction with exchange constant $J = -25$ K. A Curie-type contribution has been added to take into account magnetic impurities ($\approx 10\%$ $S = 1/2$ impurities) from a partial decomposition of the sample. The dashed line indicates the contribution from the $S = 1/2$ Heisenberg chain.

In summary, $CuSb_2O_6$ and $CuTa_2O_6$ crystallize with structures which promote predominant exchange coupling along a diagonal direction involving exchange via a O–O bond. Magnetic susceptibility experiments clearly prove that the magnetism of Cu^{2+} in $CuSb_2O_6$ and $CuTa_2O_6$ can be understood as that of a $S = 1/2$ Heisenberg linear chain behavior with afm nearest-neighbor coupling of the order of –50 K and –25 K, respectively. Heat capacity experiments and elastic neutron diffraction experiments prove $CuSb_2O_6$ to undergo long-range afm ordering below 8.7 K due to interchain coupling. The resulting spin structure is commensurate with the nuclear structure with the moments $\approx 0.5\,\mu_{Bohr}$ pointing essentially along (0 1 0).