Low-dimensional Magnetism and Antiferromagnetic Ordering in the Mixed-valence Spin-chain Cuprate TlCu$_2$O$_2$

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Dedicated to Professor Arndt Simon on the Occasion of his 80th Birthday

Abstract. TlCu$_2$O$_2$, a mixed-valence spin-chain cuprate, was synthesized in a piston cylinder system starting from thallium sesquioxide Tl$_2$O$_3$, cuprous oxide Cu$_2$O and copper powder. The main structural characteristics are edge-sharing (CuO$_2$)$_n$ zigzag chains, which are linked in the perpendicular crystallographic direction by Cu$^+$ to form a three-dimensional network. Data from magnetic susceptibility and specific heat measurements show features typical for low-dimensional magnetic exchange interactions. The long-range antiferromagnetic ordering is observed at $T_N = 19.7$ K. No weak ferromagnetic component can be detected, suggesting a plain Néel-type spin-ordered structure.

Introduction

The main structural characteristic of spin-chain cuprates are (CuO$_2$)$_n$ chains formed by edge-sharing [CuO$_4$]$^{n-}$ units, with Cu$^{2+}$ ions with magnetic spin 1/2 in square planar oxygen environment. The combination of these anionic chains with the respective charge compensating counter cations, such as lithium ions in the lithium cuprate(II) Li$_2$CuO$_2$ (Figure 1a), leads to an overall three-dimensional (3D) structure.$^{[1]}$ In mixed-valence spin-chain cuprates(I,II), besides the Cu$^{2+}$ ions in (CuO$_2$)$_n$ chains, Cu$^+$ ions in linear oxygen environment are found in the crystal structure. These copper-oxygen dumbbells are interconnecting the (CuO$_2$)$_n$ chains to higher dimensional polyoxometalates.

This connection of the (CuO$_2$)$_n$ chains via Cu$^+$ ions is realized in the isostructural compounds LiCu$_2$O$_2$,$^{[2]}$ and NaCu$_2$O$_2$.$^{[3]}$ Chains of square planar [CuO$_4$]$^{n-}$ along the crystallographic $a$ and $b$ directions are connected by Cu$^+$ ions along the $c$ direction (Figure 1b). The overall arrangement is that of alternating two-dimensional wave-like sheets in two directions.

TlCu$_2$O$_2$ is another mixed-valence cuprate(I,II), where the (CuO$_2$)$_n$ spin-chains are likewise connected by Cu$^+$ ions.$^{[4]}$ In contrast to LiCu$_2$O$_2$, the (CuO$_2$)$_n$ are forming zigzag chains in TlCu$_2$O$_2$ due to the larger charge compensating cation Tl$^+$. The zigzag (CuO$_2$)$_n$ chains along the crystallographic $a$-direction are connected along the $c$ direction, resulting in a three-dimensional network (Figure 2a). Especially interesting is that Tl$^+$ is not only significantly larger than Li$^+$, but also carries a lone $s$-electron pair. Therefore, TlCu$_2$O$_2$ is also interesting in the context of the inert pair effect, referring to the stabilization of the 6$s$-electron pair due to the lanthanide contraction and relativistic effects.

Spin-chain cuprates display a surprisingly rich diversity of magnetic ground states. In edge-sharing cuprate chains the most important exchange interactions are those between nearest ($J_1$) and next nearest ($J_2$) neighbors within the chain.$^{[5]}$ In contrast to the uniform $S = 1/2$ Heisenberg antiferromagnetic (afm) chain,$^{[6]}$ the $J_1$ is most often ferromagnetic (fm, $J_1 > 0$) whereas $J_2$ is afm ($J_2 > 0$). Thus, there are competing interac-

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The synthesis of TICu2O2 was performed applying hydrostatic pressure in a piston cylinder system, starting from thallium sesquioxide Tl2O3, cuprous oxide Cu2O and copper powder. The product obtained in an optimized synthesis protocol still contained a considerable amount of Cu2O and traces of Cu by-phases. A respective two-phase Rietveld refinement (Supporting Information) confirmed earlier reported lattice parameters[4] (see Table 1). In this work we focus on the magnetic ordering in TICu2O2. For illustrating the most relevant magnetic exchange coupling paths, we present a projection of the crystal structure along [010] in Figure 2b. This view direction visualizes the non-planar nature of the strands of edge sharing CuO4 plaquettes, which constitutes a significant difference to the Li and Na analogues. Neighboring chains are shifted half a unit cell along the crystallographic a direction and are connected via Cu+ ions in linear coordination. Since these O–Cu–O dumbbells are connecting the buckled ribbons alternatingly in both directions of the crystallographic c direction, a 3D network results (Figure 2).

The magnetic susceptibility χ(T) of TICu2O2 (Figure 3) may be described by the Curie–Weiss-law at high temperatures. After subtraction of the sum of diamagnetic increments, a fit in the range 250 K < T < 350 K results in an effective magnetic moment of μ_{eff} = 2.00 μB and θ_{CW} = −77(2) K, thus, in a value typical for one Cu^{2+} (S = 1/2) ion per formula unit. At lower temperature, χ(T) deviates from this behavior and at T_{max} ≈...
47 K a broad maximum is observed. Such a maximum in \( \chi(T) \) is the hallmark of low-dimensional magnetic exchange in the compound, although it is not possible to derive the sign and value of, e.g., \( J_{1} \), from \( \theta_{CW} \). \[^{[8]}\] Below \( T_{\text{max}} \), \( \chi(T) \) decreases to about 70% of the maximum value. In the derivative \( d(\chi(T))/dT \) (Fisher’s heat capacity, Figure 3 inset) a sharp peak at \( T_{N} = 20.0 \) K becomes noticeable. This anomaly marks the long-range afm ordering of the Cu\(^{2+} \) spins. In measurements at low applied fields (e.g., \( \mu_{0}H = 0.01 \) T, see Supporting Information) there is no indication for any weak ferromagnetism below \( T_{N} \). Measurement with increasing and decreasing temperature shows the transition to occur at the same temperature suggesting a negligible magnetoelastic coupling in TlCu\(_{2}\)O\(_{2}\). No further phase transitions are observed in the temperature range investigated here (1.8–350 K), however, in an isothermal magnetization loop measured at \( T = 1.82 \) K (see Supporting Information) indications for field-induced transitions are seen.

The temperature dependence of the specific heat \( c_{p}(T) \) of TlCu\(_{2}\)O\(_{2}\) is shown in Figure 4. Below 5 K, \( c_{p}(T) \) is well described by the standard ansatz \( c_{p}(T) = \gamma T + \beta T^{3} \). The fit results in \( \gamma = -0.2(3) \) mJ mol\(^{-1}\) K\(^{-2}\), i.e., \( \gamma = 0 \), consistent with the insulating character of TlCu\(_{2}\)O\(_{2}\), and \( \beta = 3.1 \) mJ mol\(^{-1}\) K\(^{4}\). Please note that the \( \beta T^{3} \) term is due to the thermal excitation of both lattice phonons and afm magnons. More interesting is the sharp lambda-type peak at \( T_{N} = 19.7 \) K, corroborating the long-range (antiferro-)magnetic order at this temperature.

Figure 4. Temperature dependence of the specific heat \( c_{p}(T) \) divided by temperature \( T \) for the TlCu\(_{2}\)O\(_{2}\) sample. The total specific heat \( c_{\text{tot}} \) and the estimated lattice \( c_{\text{latt}} \) and magnetic contributions \( c_{\text{mag}} \) are shown on the left axis. On the right axis the magnetic entropy \( S_{\text{mag}}(T) \) (see text) is indicated.

In order to obtain the magnetic contribution to the specific heat, the lattice contribution needs to be estimated (total \( c_{p} = c_{\text{latt}} + c_{\text{mag}} \)). Since no nonmagnetic reference compound is available, a reasonable Debye model was constructed. It is expected that above \( T_{N} \) the magnetic short-range order contribution \( c_{\text{mag}} \) decreases slowly, and thus \( c_{\text{latt}} \) has to join smoothly the experimental \( c_{\text{tot}}(T) \) curve well above the transition (cf. Figure 4). The magnetic entropy \( S_{\text{mag}}(T) \) is calculated by integrating \( c_{\text{mag}}/T \). As can be seen in Figure 4, for \( T >> T_{N} \) it approaches the value \( R \ln 2 \), as expected for the magnetic order of one \( S = 1/2 \) ion per formula unit (\( R = N_{A}k_{B} \) is the gas constant).

Conclusions

TlCu\(_{2}\)O\(_{2}\), a mixed-valence spin-chain cuprate, was synthesized for the first time as a bulk material via a new synthesis route using a piston-cylinder system. The reaction product was obtained as air-sensitive, microcrystalline grey powder with cuprous oxide Cu\(_{2}\)O as a secondary phase. The results of crystal structure refinement on powder X-ray diffraction data is in agreement with the published crystal structure solved from single-crystal data, featuring buckled edge-sharing (CuO\(_{2}\))\(_{n}\) chains connected by Cu\(^{+} \) ions. While in some Li-containing mixed-valency cuprates, due to their similar ionic radii, lithium is observed on the Cu\(^{1+} \) site and gives rise to significant disorder, the much larger Tl\(^{+} \) ion is not able to substitute Cu\(^{+} \).

The magnetic susceptibility and specific heat data indicate antiferromagnetic spin ordering below a Néel temperature of \( T_{N} = 19.7 \) K. The Néel temperature is twice as large as observed for NaCu\(_{2}\)O\(_{2}\) but very similar to that of LiCu\(_{2}\)O\(_{2}\).\[^{[9–11,13]}\] Since the long-range ordering temperature is determined by the magnitude of the interchain magnetic exchange such as \( J_{N} \), it can be concluded that such couplings in TlCu\(_{2}\)O\(_{2}\) and LiCu\(_{2}\)O\(_{2}\) are of comparable strength. However, from a crystal chemical point of view the Tl compound appears to have a more three-dimensional character than the Li counterpart. Moreover, no weak ferromagnetic component was detected for the ordered spin structure down to \( T_{\text{min}} = 1.8 \) K, eventually suggesting a simple commensurate Néel-type ordering of the Cu\(^{2+} \) spins in TlCu\(_{2}\)O\(_{2}\) (no canting of spins). This is in contrast to observations in several edge-shared chain cuprates.\[^{[7]}\] Further confirmation requires the detailed determination of the ordered structure and moment size by neutron diffraction.

Experimental Section

TlCu\(_{2}\)O\(_{2}\) was synthesized in a high-pressure/high-temperature reaction using a piston-cylinder press. In an argon glove box, thallium sesquioxide Tl\(_{2}\)O\(_{3}\) (Alfa Aesar, 99.999 %), cuprous oxide Cu\(_{2}\)O (Sigma Aldrich, 99.9 %) and copper powder (Alfa Aesar, 99.9999 %) were mixed in ratios according to Equation (1), thoroughly ground and tightly packed in a stainless steel capsule using a slicer. The reaction product was obtained as air-sensitive, microcrystalline grey powder. The compound was manipulated and stored in a glove box. For the X-ray investigation on flat specimens the powder samples were ground in an agate mortar and glued between two Mylar foils with Apiezon N grease (Sigma Aldrich) in the glove box. PXRD measurements were performed at room temperature with Cu-K\(_{\alpha1}\) radiation (\( \lambda = 1.54178 \) Å) using an image-plate Huber G670 Guinier camera and a germanium monochromator. Rietveld refinement of the PXRD data was performed using the TOPAS software package (Bruker AXS, Germany, version 4.2) (\( R_{wp} 9.1 \% \)) starting from the published single-crystal data.\[^{[4]}\] Multiphase Rietveld refinement calculated the sample to
contain ≈ 18% Cu₂O. Magnetization was measured in a SQUID magnetometer (MPMS XL-7, Quantum Design) on a polycrystalline piece in magnetic fields up to 7 T. The composition of the sample from the refinement of XRD data was estimated as TlCu₂O₂ (82.2%) and Cu₂O (17.8%). Since the side phase is diamagnetic, the susceptibility was corrected accordingly (\(\chi (\text{Cu}_2\text{O}) = -0.2516 \times 10^{-6}\) emu·g⁻¹). For the heat capacity measurement, the HC option of a PPMS-9 (Quantum Design) was employed. The raw heat capacity data were corrected for the contribution of the Cu₂O impurity. The two available data sets in the literature[16] showed some inconsistencies in the overlap region around 20 K. Therefore, the combined data were critically evaluated and the reliable data were then interpolated and subtracted from the raw data.

Supporting Information (see footnote on the first page of this article): Fig. S1 displays a PXRD pattern and Rietveld profile fit for TlCu₂O₂, Tables S1 to S3 present atom coordinates and isotropic temperature factors for TlCu₂O₂ attained from Rietveld refinement, details of the Rietveld refinement, and comparison of space groups, magnetic orderings, and key bond angles and bond lengths of TlCu₂O₂ with LiCu₂O₂ and NaCu₂O₂, respectively.

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Keywords: Mixed-valence compound / Spin-chain cuprate / Copper oxide chains / Copper / Low-dimensional magnetism

References

[1] R. Hoppe, H. Rieck, Z. Anorg. Allg. Chem. 1970, 379, 157–164.
[2] S. J. Hibble, J. Köhler, A. Simon, S. Paider, J. Solid State Chem. 1990, 88, 534–542.
[3] G. Tams, H. Müller-Buschbaum, J. Alloys Compd. 1992, 189, 241–243.
[4] A. Adam, C. Felser-Wenz, H. U. Schuster, R. Hoppe, Z. Anorg. Allg. Chem. 1991, 605, 157–162.
[5] S. Maekawa, T. Toyahma, Rep. Prog. Phys. 2001, 64, 383–428.
[6] A. Klümper, Eur. Phys. J. B 1998, 5, 677–685.
[7] P. Horsch, M. Sofin, M. Mayr, M. Jansen, Phys. Rev. Lett. 2005, 94, 76–403; S. L. Drechsler, J. Richter, K. Kuraz, J. Malek, N. Tristan, B. Büchner, A. S. Moskvin, A. A. Gippius, A. Vasilev, O. Volkova, A. Rokofiev, H. Rakoto, J. M. Broto, W. Schnelle, M. Schmitt, A. Ormeci, C. Loison, H. Rosner, J. Magnetism Magn. Mater. 2007, 316, 306–312; N. Z. Ali, J. Sirkker, J. Nuss, P. Horsch, M. Jansen, Phys. Rev. B 2011, 84, 035113.
[8] F. Sapiña, J. Rodríguez-Carvajal, M. J. Sanchis, R. Ibáñez, A. Beltrán, D. Beltrán, Solid State Commun. 1990, 74, 779–784; W. E. A. Lorenz, R. O. Kuzian, S. L. Drechsler, W. D. Stein, N. Wizent, G. Behr, J. Malek, U. Nitzsche, H. Rosner, A. Hiess, W. Schmidt, R. Klingeler, M. Loewenhaupt, B. Büchner, Europhys. Lett. 2009, 88, 37002.
[9] T. Masuda, A. Zheludev, A. Bush, M. Markina, A. Vasilev, Phys. Rev. Lett. 2004, 92, 177201.
[10] a) L. Capogna, M. Mayr, P. Horsch, M. Raichle, R. K. Kremer, M. Sofin, A. Maljuk, M. Jansen, B. Keimer, Phys. Rev. B 2005, 71, 140402(R); b) L. Capogna, M. Reehuis, A. Maljuk, R. K. Kremer, B. Ouladdiaf, M. Jansen, B. Keimer, Phys. Rev. B 2010, 82, 014407.
[11] S. Park, Y. J. Choi, C. L. Zhang, S. W. Cheong, Phys. Rev. Lett. 2007, 98, 057601.
[12] M. Enderle, C. Mukherjee, F. Fäk, R. K. Kremer, J. M. Broto, H. Rosner, S. L. Drechsler, J. Richter, J. Malek, A. Prokofiev, W. Assmus, S. Pujol, J. L. Ragazzoni, H. Rakoto, M. Rheinstädter, H. M. Ronnow, Europhys. Lett. 2005, 70, 237–243; Y. Naito, K. Sato, Y. Yasui, Y. Kobayashi, Y. Kobayashi, M. Sato, J. Phys. Soc. Jpn. 2007, 76, 023708.
[13] Ph. Leininger, M. Rahlenbeck, M. Raichle, B. Bohnenbuck, A. Maljuk, C. T. Lin, B. Keimer, E. Weschke, E. Schierle, S. Seki, Y. Tokura, J. W. Freeland, Phys. Rev. B 2010, 81, 085111.
[14] R. Berger, A. Meetsma, S. van Smaalen, M. Sundberg, J. Less-Common Met. 1991, 175, 119–129; A. Maljuk, A. B. Kulakov, M. Sofin, L. Capogna, J. Strempfer, C. T. Lin, M. Jansen, B. Keimer, J. Cryst. Growth 2004, 263, 338–343.
[15] P. W. Selwood, Magnetoochemistry, 2nd ed., Interscience Publishers, New York, 1956, p.87.
[16] L. V. Gregor, J. Phys. Chem. 1962, 66, 1645–1647; J.-H. Hu, H. L. Johnston, J. Am. Chem. Soc. 1951, 73, 4550–4551.

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