Supplementary Information for *Preparation, Magnetism and Electronic Structures of Cadmium Technetates*

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1 Further details on synthesis

[**Caution:** ^{99}Tc is radioactive with a specific activity of 17 mCi/gram. To prevent contamination and ensure personal safety, all preparations were performed in a fume hood. A polycarbonate shield with a thickness of 1 cm was used when manipulating the powders. In addition, standard practices of a radiochemistry laboratory must be followed.]

The $CdTcO_3$ phase was prepared by heating a stoichiometric mixture of CdO and TcO_2 at 850 °C in a fused quartz boat under flowing Ar gas for 12 hours. The start-

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ing powders were first ground in a mortar and pestle as a methanol slurry. The CdO was purchased from Sigma-Aldrich and TcO_2 was prepared by thermal decomposition of NH_4TcO_4 as described in previous work.[?] The resulting powder, which appears light grey metallic, was treated with 2M HCl to remove any remaining CdO and subsequently washed with water and acetone. Preliminary powder XRD data showed a pattern with Bragg peaks matching the orthorhombic lattice of the perovskite $CdTiO_3$.

Similarly, we used Tc_2O_7 as a starting material to react with Cd metal, previously cleaned with 2M HCl to remove any oxide on the surface. For the preparation of Tc_2O_7, TcO_2 was combusted in pure, dry oxygen in a sealed quartz ampoule heated to 450 °C for two hours. The pure oxygen atmosphere can be established by backfilling the tube with dry oxygen, isolating it from the double vacuum/gas lines, and dipping it in a liquid nitrogen bath to condense the O_2 gas while torch sealing. Extreme caution must be followed during this last procedure to avoid condensing too much O_2 since this can lead to dangerous over-pressurization in a closed system, and liquid O_2 will readily ignite organics.

Previous preparations of the heptoxide in the literature included combusting Tc metal in a stream of oxygen gas, which always produced a pink or red volatile oxide that could not be separated from the product due to its similar volatility.[1–3] We find our preparation of Tc_2O_7 to be an improvement since it always led to bright yellow Tc_2O_7 with no sign of a reduced, colored species. Also, our preparation lowers the risk of ^{99}Tc contamination since it is performed in a closed system. The heptoxide is extremely hygroscopic and readily reduced by organics. A typical preparation used 40 mg of TcO_2 sealed in a 20 cm quartz tube (outer diameter = 10 mm, wall thickness of 1.5 mm) with an approximate O_2 pressure of 2.5 atm at room temperature.

After complete oxidation of TcO_2 to Tc_2O_7, the tube was opened and a stoichiometric amount of clean Cd metal inserted (2:1 ratio for metal:Tc_2O_7). The tube was then immediately connected to the vacuum/Ar double manifold to purge the oxygen atmosphere and subsequently sealed under vacuum. The reactants were heated to 800 °C for ten hours and then furnace cooled. The product appeared as clusters of blue-green metallic crystals. Lacking a quality single crystal, the product was cleaned with

2M HCl and ground into a powder. The XRD powder pattern indicated a highly crystalline, cubic cell with Bragg peaks matching those of $Cd_2Re_2O_7$. Care must be taken to remove any moisture from the system as Tc_2O_7 will take up water to form $HTcO_4$ and the subsequent reaction with Cd metal will lead to the formation of a water soluble, yellow powder, presumably the known salt $Cd(TcO_4)_2$.

2 High-resolution X-ray diffraction and magnetometry

To obtain the structures of the new Cd-Tc-O phases, powder diffraction studies were performed. Since ^{113}Cd has a prohibitively high neutron absorption cross-section and accounts for nearly 12% of naturally abundant Cd, XRD studies were pursued instead of neutron powder diffraction. However, laboratory X-rays do not provide enough information at high 2θ or enough resolution, so high-resolution synchrotron powder XRD measurements were performed to obtain accurate structural parameters. The powder patterns of $CdTcO_3$ and $Cd_2Tc_2O_7$ were collected with the high-resolution beamline 11-BM diffractometer at the Advanced Photon Source at Argonne National Laboratory. The powder samples were doubly encased in Kapton tubing, and mounted onto a rotating platform for better averaging of the powder pattern. For both samples, diffraction patterns were collected at beam energies of 15 keV ($\lambda = 0.82654$ Å) and 30 keV ($\lambda = 0.41326$ Å).

For the SQUID magnetometry measurements, the powder samples of $Cd_2Tc_2O_7$ and $CdTcO_3$ were measured at 0.1 T and 5 T from 2 K to 300 K. The samples, doubly contained in plastic tubes and gelatin caps, were cooled with no field down to 10 K where the field was turned on upon cooling down to 2 K; the susceptibility was then measured upon heating up to 300 K under the 0.1 T or 5 T field and corrected for the weak contribution from sample-encapsulation tubes.

3 Electronic structure calculations

To investigate the electronic band structure of $Cd_2Tc_2O_7$ and $CdTcO_3$, linear muffin-tin orbital (LMTO) calculations were performed within the atomic sphere approximation.[4,5] The scalar-relativistic Kohn-Sham equations were solved within the generalized gradient approximation.[6] For $Cd_2Tc_2O_7$, the calculations were performed on 72 irreducible *k* points within the primitive wedge of the Brillouin zone; 245 irreducible *k* points were used for $CdTcO_3$ since it has lower symmetry than $Cd_2Tc_2O_7$. The crystal structures reported in the Results section were used for the calculations of the electronic density of states (DOS). Since the DOS of $CdTcO_3$ indicated possible magnetic instability (large density of states at the Fermi level), nonspin and spin-polarized calculations were run. In the case of the spin-polarized calculations, two separate magnetic structures were chosen: a ferromagnetic arrangement of the Tc moments and an antiferromagnetic arrangement of the Tc moments. The Stuttgart TB-LMTO-ASA program (version 47C) was used for all the computational work.[7]

References

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