JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

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Antiferromagnetism in a Technetium Oxide. Structure of $CaTcO_3$

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Supporting Information

ABSTRACT: The technetium perovskite $CaTcO_3$ has been synthesized. Combining synchrotron X-ray and neutron diffraction, we found that $CaTcO_3$ is an antiferromagnetic with a surprisingly high Neel temperature of ~800 K. The transition to the magnetic state does not involve a structural change, but there is obvious magnetostriction. Electronic structure calculations confirm the experimental results.

That extremely little is known regarding the structure and properties of technetium oxides is not surprising, given the absence of any naturally occurring Tc isotopes and the radioactivity of those available.[1] Nevertheless, Tc oxides are of considerable importance since ^{99}Tc, found in nuclear waste, has a long half-life (2.13×10^5 yr). Under oxidizing conditions, the predominant form is the pertechnetate anion, which is highly soluble in water and thus readily mobile in the environment. Tc has a $5s^24d^5$ electronic configuration and, like its lighter analogue Mn ($4s^23d^5$), adopts a number of oxidation states, some of which contain unpaired d-band electrons. In solids there is an interplay between the Hund's rule coupling, which favors moment formation, and hybridization with ligands, which works against moments. 3d oxides are generally, but not always, magnetic, while 4d and 5d oxides, with their more spatially extended d-orbitals, tend not to be magnetic, although the exceptions are remarkable, for example the ferromagnetism of $SrRuO_3$[2] and its likely connection with the triplet superconductor Sr_2RuO_4.[3]

Here we report the discovery of unusual high-temperature magnetism in the simple Tc^{4+} perovskite $CaTcO_3$ The only previous report on $CaTcO_3$ was by Muller, White, and Roy in 1964.[4] They reported its synthesis and suggested the structure to be orthorhombic. Except for this, little is known about $CaTcO_3$, and there has been no study of its magnetic properties.

Perovskite-type compounds have a general chemical formula ABO_3 and have a crystal structure based on corner-sharing BO_6 octahedra. As a consequence of competition between the bonding requirements of the A- and B-type cations, relatively few perovskites have the ideal cubic structure, but rather cooperative rotation of the BO_6 octahedra lowers the symmetry, with the most commonly observed crystal symmetry being orthorhombic in *Pnma*, as exemplified by $CaTiO_3$ itself.[5]

Caution! *^{99}Tc is a β-emitter (E_{max} = 0.29 MeV). Appropriate shielding was employed during the synthesis and all manipulations.* A polycrystalline sample of $CaTcO_3$ was prepared using solid-state methods from 4.83 g (0.0267 mol) of NH_4TcO_4 (Oak Ridge National Laboratory) and 6.35 g (0.0267 mol) of AR-grade $Ca(NO_3)_2 \cdot 4H_2O$. These were dry-rolled in a polyethylene vial for 16 h to ensure complete mixing and then calcined in flowing Ar for 1 h at 700 °C. The calcine was then reground, wet ball-milled in cyclohexane for 16 h, air-dried, pressed into 1 g pellets, and then annealed under Ar at 1150 °C for 4 h. Heating the sample at higher temperatures resulted in melting and/or decomposition.

The temperature dependence of the structure of a polycrystalline sample of $CaTcO_3$ was established using synchrotron X-ray diffraction (SXRD) data recorded over the angular range $5 < 2\theta < 85°$, with λ = 0.82249 Å, on the powder diffractometer at the Australian Synchrotron.[6] For these measurements, the sample was housed in a 0.3 mm diameter quartz capillary that was continuously rotated. A number of superlattice reflections indicative of tilting of the corner-sharing TcO_6 octahedra were apparent in the diffraction profiles, and the structure was refined in the orthorhombic space group *Pnma* using the Rietveld program RIETICA[7] (see Supporting Information, Figure S1). The temperature dependence of the structure between room temperature and 1273 K was also determined from SXRD data, and there was no indication for any increase in symmetry as the temperature was increased, with the structure remaining in *Pnma* to 1273 K. The temperature dependence of the unit cell parameters, illustrated in Figure 1, clearly demonstrates an anomaly in the thermal expansion of the *a*-axis near 750 K. Although considerably less dramatic, there was a variation in the thermal expansion of both the *b*- and *c*-axes near this temperature. It is apparent from the thermal expansion of the cell that a volume strain is introduced upon cooling below 750 K.

Neutron diffraction profiles for a 2 g sample of $CaTcO_3$ were then measured at 3, 300, 473, 673, and 823 K using neutrons of wavelength 1.538 Å on the high-resolution powder diffractometer Echidna at ANSTO's OPAL facility.[8] These data allowed us to obtain an accurate description of the structure, with the refined lattice parameters being *a* = 5.5327(3), *b* = 7.7224(4), and *c* = 5.4112(3) Å at 300 K. The occupancies of the two oxygen

Received: October 19, 2010
Published: January 26, 2011

dx.doi.org/10.1021/ja109431t | *J. Am. Chem. Soc.* 2011, 133, 1654–1657

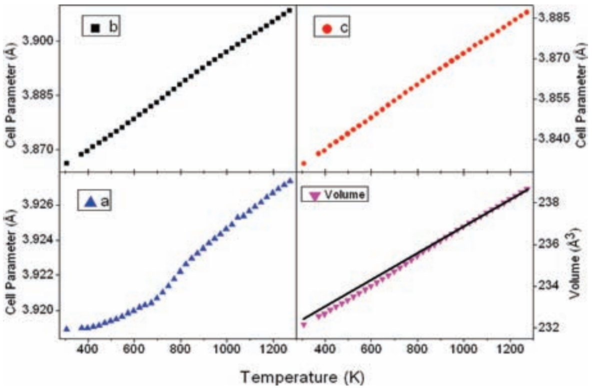

Figure 1. Temperature dependence of lattice parameters (*a*, *b*, and *c* and the unit volume) for $CaTcO_3$, estimated from Rietveld analysis of synchrotron X-ray diffraction data. The structures were refined in an orthorhombic space group *Pnma*. The solid line is a linear extrapolation of the high-temperature volume.

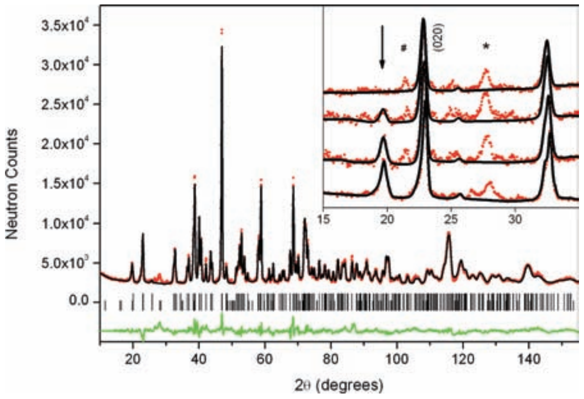

Figure 2. Rietveld plot of the neutron diffraction profiles ($\lambda = 1.538$ Å) for $CaTcO_3$ recorded at room temperature. The upper set of markers show the positions of the allowed nuclear peaks, and the lower set of markers show the allowed magnetic peaks. The inset illustrates the temperature dependence of the (011) magnetic reflection at (from bottom to top) 293, 473, 673, and 823 K. This reflection is lost on heating to 823 K but reappears on cooling the sample to 3 K (see Supporting Information). The intensity of the (020) nuclear reflection is unaltered. The peaks indicated with # are from parasitic scattering in the furnace, and those indicated with * are from poorly crystalline TcO_2 in the sample. The R_p, R_{wp}, and R_{mag} factors are 4.69%, 5.32%, and 3.59%, respectively.

Table 1. Refined Atomic Coordinates and Displacement Factors for $CaTcO_3$ from the Refinement against Powder Neutrons Diffraction Data Obtained at Room Temperature

atom	site	*x*	*y*	*z*	B_{iso} (Å^2)
Ca	4c	0.0440(6)	0.25	0.5139(9)	1.19(6)
Tc	4a	0	0	0	0.94(4)
O1	4c	0.4768(6)	0.25	0.4148(6)	0.95(5)
O2	8d	0.2046(4)	−0.0471(3)	0.2966(4)	1.01(3)

sites were refined, and no evidence for any oxygen vacancies was obtained, suggesting the material to be stoichiometric. The refined atomic coordinates are given in Table 1. The Tc is at the center of a slightly distorted octahedron with two Tc−O(1)'s at 1.9890(8) Å. There are two different Tc−O(2) distances, 1.997(2) and 2.004(2) Å. The absence of appreciable anisotropy in the Tc−O distances is in keeping with the anticipated $t_{2g}{}^3e_g{}^0$ orbital occupancy. There are few well-characterized Tc oxides with which to compare these results; however, the average Tc−O distance, 1.997 Å, appears typical of a Tc^{4+} oxide and is similar to the average Tc−O distances in TcO_2 (1.97 Å)[9] and $Bi_2Tc_2O_{7-d}$ (2.011 Å).[10] The Ca is effectively eight-coordinate, with four Ca−O contacts being longer than 3.1 Å. The bond valence sums for the Tc[11] and Ca cations, 4.14 and 2.01, respectively, are unexceptional.

The initial fit to the room-temperature neutron diffraction profile failed to reproduce the observed intensity of the orthorhombic (011) reflection near $2\theta = 19.4°$ ($d = 4.57$ Å). This reflection was well fitted in the synchrotron profile. As illustrated in Figure 2, heating the sample to above 800 K resulted in the loss of this reflection, with it reappearing upon cooling the sample to 3 K. The most logical postulate for this is that there is a magnetic contribution to the reflection and that $CaTcO_3$ is magnetic to above 800 K. All the diffraction peaks with magnetic contribution could be indexed by the crystallographic unit cell, i.e., with the propagation vector $k = [0,0,0]$. Analysis suggests the magnetic structure is purely collinear G-type antiferromagnetic with Tc moments parallel to the *c*-axis, as also found in $SrTcO_3$.[12] The magnetic moment of the Tc atom is 1.69(3) μ_B at room temperature. The temperature dependence of the Tc magnetic moments estimated by refinements from the neutron diffraction data using Fullprof[13] is illustrated in Figure 3. That only one strong magnetic reflection is observed is due to the rapid decrease in the magnetic form factor of the 4d electrons (see Supporting Information, Table S1).

The robust magnetism in $CaTcO_3$ ($4d^3$) is all the more remarkable considering the magnetic properties of other 4d Ca perovskites, notably $CaMoO_3$ ($4d^2$) and $CaRuO_3$ ($4d^4$). All three oxides are isostructural. $CaMoO_3$ is a metal and displays Pauli paramagnetic-like behavior, although at low temperatures a non-negligible temperature-dependent component due to isolated Mo^{4+} spins is observed.[14] The magnetic ground state of $CaRuO_3$ remains controversial, with recent work indicating paramagnetic behavior (or exchange-enhanced paramagnetism) down to 30 mK. Resistivity results indicate that $CaRuO_3$ is a non-Fermi liquid metal. It is believed that the itinerant 4d bandwidth is too narrow for long-range magnetic ordering, but not so narrow as to cause $CaRuO_3$ to be nonmetallic.[15] Precise structures are available for these three oxides, and the diagnostic M−O(1)−M (152.16°) and M−O(2)−M (150.53°) bond angles in $CaTcO_3$ are intermediate between those of CaMoO3 (153.49 and 152.52)[14] and $CaRuO_3$ (150.15 and 150.27°).[16] There is nothing from the crystal structure to suggest unusual magnetism should be observed in $CaTcO_3$.

We performed electronic structure calculations within the local spin density approximation (LSDA) using the experimental crystal structure. These were done with the general potential linearized augmented planewave (LAPW) method.[17] We used converged basis sets and Brillouin samplings, with LAPW sphere radii of 2.1 and 1.6 bohr for the metal and O atoms, respectively. The calculations were done in a scalar relativistic approximation. We considered four possible magnetic orderings as well as a nonmagnetic case. The calculated electronic density of states (DOS) for the nonmagnetic and lowest energy *G*-type antiferromagnetic (AFM) ordering is shown in Figure 4. The Fermi energy lies in a clearly defined manifold of Tc t_{2g} d states (−2 to 1 eV), which are considerably hybridized with O $p\pi$ orbitals. All the magnetic orders showed finite DOS at the Fermi energy, although for the

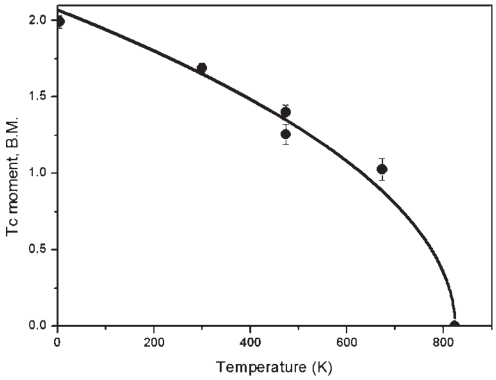

Figure 3. Temperature dependence of the magnetic moment for $CaTcO_3$ reduced from the powder neutron diffraction data. The solid line illustrates the behavior expected for a $(T - T_c)^{0.5}$ type dependence with a transition temperature of around 800 K.

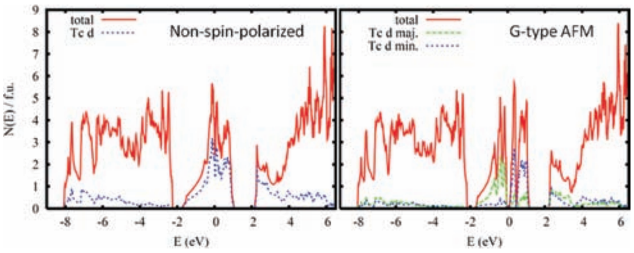

Figure 4. Electronic DOS per $CaTcO_3$ formula unit and Tc d projection as defined by projection onto the LAPW sphere for non-spin-polarized (left) and *G*-type AFM (right) states. The Fermi energy is at 0 eV.

lowest energy configuration there is almost a gap. We find band magnetism, with a strong interplay between moment formation and magnetic ordering. This is distinct from Mn oxides, e.g. $CaMnO_3$, which also has a *G*-type antiferromagnetic ground state. In the Mn compounds, the moments are very stable and fixed at their high-spin values by the strong Hund's interaction, while the ordering temperature is determined by interatomic superexchange interactions that depend on the Mn d−O p hybridization. In $CaTcO_3$, the energy scale for moment formation is lower and the hybridization is larger, so these scales become comparable. On a per formula unit basis relative to the non-spin-polarized case, the energies of ferromagnetic, *A*-type AFM, *C*-type AFM, and *G*-type AFM (using standard notation) are −0.003, −0.005, −0.040, and −0.078 eV, respectively and the moments depend strongly on the particular ordering. Inside the Tc LAPW sphere we find 1.3 μB for *G*-type, but only 0.5 μB for ferromagnetic and 0.4 μB for *A*-type order (n.b., because of the spatial extent of the Tc d orbitals, which extend beyond the LAPW spheres, these numbers are approximately proportional to but should not be directly taken as moments to compare with experiment). We also did calculations using the atomic coordinates obtained from LSDA energy minimization in the magnetic state. While we found some changes in atomic coordinates, possibly due to limitations of the LSDA, we did not find any significant changes in the magnetic properties. For example, the Tc moment changes by only ~3% when the calculated coordinates are used. These results are summarized in the Supporting Information.

It is interesting to consider the magnetism of $CaTcO_3$ in light of the conventional superexchange mechanism. As mentioned, this mechanism depends on covalency between the metal and ligand atoms, with strong covalency leading to strong superexchange.[18,19] Given there are apparently no oxygen vacancies, it appears that only Tc^{4+} is present in the sample. The transition temperature is comparable to that seen in $LaFeO_3$, which has the highest Néel temperature of any of the orthoferrates.[20] That material has a high-spin d^5 configuration and, therefore, e_g-based superexchange involving O pπ orbitals as opposed to the weaker t_{2g}−O pπ interactions relevant in a d^3 material. It seems reasonable that a similar superexchange coupling is important here, although clearly the behavior of the 4d electrons is different from that of the 3d electrons. Finally we note that surprisingly high magnetic ordering temperatures have been observed in other 4d transition metal oxides; for example, Sr_2FeMoO_6 has $T_N \approx 415$ K,[21,22] although in this case the moments reside on Fe. In $CaTcO_3$, the stronger metal−O covalency strengthens the superexchange interaction, thereby raising T_N while making the moments almost unstable. Materials with metallic near-magnetic states with large interatomic exchange interactions and unstable moments can be particularly interesting. Two examples are Fe-based superconductors and metallic high-temperature superconducting cuprates.

In summary, a polycrystalline sample of the perovskite $CaTcO_3$ has been synthesized. Synchrotron X-ray diffraction measurements between 300 and 1273 K show that the material is orthorhombic and displays magnetostriction, although no evidence for any structural transitions is found. Neutron diffraction measurements demonstrate that, at room temperature, $CaTcO_3$ is an antiferromagnet and the magnetic ordering persists until ca. 800 K. The discovery of this unexpectedly high magnetic ordering temperature could open new frontiers in the relation of magnetism and properties of heavy transition metal systems.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Monte Carlo simulation details (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We acknowledge the assistance of Mr. Terry McLeod in sample preparation. This work was, in part, performed at the powder diffraction beamline at the Australian Synchrotron. B.J.K. acknowledges the support of the Australian Research Council. Work at ORNL was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

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