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# High temperature magnetic ordering in the 4d perovskite SrTcO<sub>3</sub>

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We present evidence for possibly the highest magnetic ordering temperature in any compound without 3d transition elements. Neutron powder diffraction measurements, at both time-of-flight and constant wavelength sources, were performed on two independently prepared SrTcO<sub>3</sub> powders. SrTcO<sub>3</sub> adopts a distorted perovskite structure with *G*-type antiferromagnetic ordering and has a moment of 1.87(4)  $\mu_B$  per Tc cation at room temperature with an extraordinarily high Néel point close to 750°C. Electronic structure calculations reveal extensive mixing between the technetium 4d-states and oxygen states proximal to the Fermi level. This hybridization leads to a close relationship between magnetic ordering temperature and moment formation in SrTcO<sub>3</sub>.

The mixed metal oxides of the second transition series exhibit a diverse range of interesting electronic properties. For example, the perovskite Sr<sub>x</sub>NbO<sub>3</sub> is a poorly conducting Pauli paramagnet,[1] and SrRuO<sub>3</sub> a rare example of a metallic ferromagnetic oxide,[2, 3]; SrMoO<sub>3</sub> shows one of the highest electrical conductivities for oxides,[4] while SrRhO<sub>3</sub> exhibits evidence of being affected by quantum critical fluctuations.[5, 6] Other oxides of these elements are also of great interest, such as the superconducting Sr<sub>2</sub>RuO<sub>4</sub>[7] and the pyrochlores A<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>, which undergo metal to semiconductor transitions.[8–10] Technetium lies between molybdenum and ruthenium, but since all of its isotopes are radioactive, its solid state chemistry and physics have not been widely studied. Building on earlier work by Muller, White and Roy,[11] its metal oxides have recently come under scrutiny by modern physical methods.[12–14] In the present work we describe the synthesis of the perovskite SrTcO<sub>3</sub> and discuss its unusual magnetic and electronic properties.

Separate samples of SrTcO<sub>3</sub> were prepared by the groups in Australia and the USA. The Sydney sample was obtained from a solid state reaction between NH<sub>4</sub>TcO<sub>4</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> at 700° C for 1 hour under argon and then ball-milled in cyclohexane for 16 hours, dried, pelleted, and then sintered under argon for 4 hours at 1150° C. The UNLV sample was prepared by a solid state reaction between SrCO<sub>3</sub> and TcO<sub>2</sub> at 850° C in a fused quartz boat under argon gas. Sample purity was confirmed by X-ray powder diffraction in each case.

Powder neutron diffraction data for the Sydney sam-

ple were collected on the high-resolution Echidna diffractometer at ANSTO's Opal facility at Lucas Heights using neutrons of wavelength 1.538 Å; data were obtained between room temperature and 750° C in a standard vacuum furnace. The corresponding neutron data for the UNLV sample were collected on the NPDF diffractometer at the Manuel Lujan Neutron Scattering Center at LANL, where the data were collected in the time-of-flight mode between 4 K and 500 K.

The room temperature constant wavelength data for SrTcO<sub>3</sub> were indexed on the basis of a perovskite cell in space group *Pnma* with  $a \approx c \approx \sqrt{2}a_p$  and  $b \approx 2a_p$  (where  $a_p$  is the lattice parameter of the cubic perovskite sub-cell) and refined by the Rietveld method[15] to yield the parameters given in Table I. The structure is that of the well-known GdFeO<sub>3</sub>-type perovskite. The corresponding parameters for the time-of-flight refinement are given in parentheses.[16] Careful inspection of the Rietveld fit for the constant wavelength data reveals a peak at  $\approx 19.4^\circ 2\theta$  that is not accounted for by the structural refinement (Fig. 1a). The same peak is visible at a *d*-spacing of 4.546 Å in the time-of-flight data, but was absent in the X-ray data (See Supporting Information).

The extra peak that is observed in both the constant wavelength and time-of-flight data can be indexed on the basis of the magnetic scattering expected from the *G*-type antiferromagnetic structure with the moment directed along the *c*-direction (Shubnikov group *Pn'ma'*) shown in Fig. 2a. Final refinement of the nuclear and magnetic structure yielded a magnetic moment of 1.87(4)  $\mu_B$  at room temperature, which increases to 2.13(4)  $\mu_B$

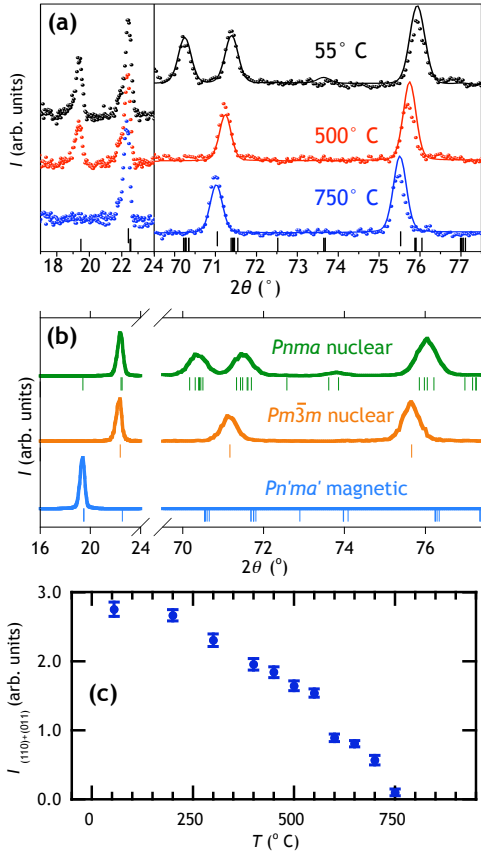


FIG. 1: (a) Observed constant wavelength NPD profiles of SrTcO<sub>3</sub>; select  $2\theta$  regions are shown to highlight the change from  $Pnma$  symmetry to  $Pm\bar{3}m$  symmetry and the loss of the magnetic peak at  $19.4^\circ$   $2\theta$  upon heating. Tickmarks for the cubic and orthorhombic structures are shown below the patterns, respectively. (b) Simulated contributions to the NPD patterns from the nuclear  $Pnma$  and  $Pm\bar{3}m$  structures and the magnetic  $Pn'ma'$  structure. (c) Temperature evolution of the magnetic peak from the CW data.

on cooling to 4 K. This is substantially lower than the spin only value of  $3.87 \mu_B$  for a spin-only  $d^3$  ion, probably due to covalency in the Tc–O bonds.[17]

The possibility that the low-angle peak is due to some structural distortion of the oxygen atoms, and therefore missed by X-rays, was considered. Since the (110) and (011) reflections are allowed for  $Pnma$  symmetry, the loss of the  $19.4^\circ$   $2\theta$  peak at  $750^\circ$  C could indicate a crystallographic transition at higher temperatures (as is common in perovskite oxides) rather than a magnetic one. This scenario, however, is irrefutably excluded by the fact that SrTcO<sub>3</sub> undergoes a crystallographic transition to the highest symmetry space group for a perovskite,  $Pm\bar{3}m$ , at  $500^\circ$  C—well below the temperature at which the intensity of the peak is lost (Fig. 1a). Thus, at temperatures above  $500^\circ$  C, this reflection is already prohibited by symmetry and must be due to magnetic scattering from the Tc cations. Furthermore, the NPD pattern sim-

TABLE I: Structural parameters for SrTcO<sub>3</sub> at 300 K. The lattice cell is orthorhombic with space group  $Pnma$  (62), and cell parameters are given below the table. Atomic displacement parameters are given in  $\text{\AA}^2$  and standard uncertainties are shown in parentheses. Structural and cell parameters from the time-of-flight results are shown in *italics* below those of CW data for comparison.

Atoms	site	x	y	z	$B_{iso}$
Sr	4c	0.001(3)	1/4	0.507(3)	0.85(9)
		<i>0.0086(5)</i>	<i>1/4</i>	<i>0.4995(5)</i>	<i>0.78(1)</i>
Tc	4a	0	0	0	1.01(5)
		<i>0</i>	<i>0</i>	<i>0</i>	<i>0.14(1)</i>
O1	8d	0.262(2)	0.0327(5)	0.257(2)	0.76(14)
		<i>0.2633(3)</i>	<i>0.0225(1)</i>	<i>0.2624(3)</i>	<i>0.82(2)</i>
O2	4c	0.494(4)	1/4	0.524(5)	0.60(7)
		<i>0.4961(8)</i>	<i>1/4</i>	<i>0.5416(3)</i>	<i>0.82(2)</i>
<hr/>					
$a = 5.5797(6) \text{ \AA}, b = 7.8774(8) \text{ \AA}, c = 5.5575(7) \text{ \AA}$					
$a = 5.5768(1) \text{ \AA}, b = 7.8485(1) \text{ \AA}, c = 5.5468(1) \text{ \AA}$					

ulations show that nuclear contribution is negligible even for the  $Pnma$  symmetry (Fig. 1b). Observation of only one magnetic reflection is no doubt a consequence of the sharp drop-off of the magnetic form factor for 4d and 5d electrons due to their highly delocalized nature; the second magnetic peak would appear at  $\approx 38^\circ$   $2\theta$ , where the magnetic form factor has decreased strongly. Indeed, for ferromagnetic SrRuO<sub>3</sub> with a moment size of  $\approx 1.6 \mu_B$ , the magnetic contribution to the NPD patterns is also minimal and confined to one peak at low  $2\theta$ . [2, 18]

The integrated intensity of the (110)/(011) reflections was used to follow the temperature evolution of the magnetic ordering. As can be seen from Fig. 1c, SrTcO<sub>3</sub> shows very robust magnetic ordering up to  $750^\circ$  C, which is entirely unprecedented for an oxide of the second transition metal series. Indeed, one of the unusual features of second row oxides is that magnetic ordering, if it occurs at all, is only observed at quite low temperatures. SrRuO<sub>3</sub>, for example, has a Curie temperature of  $\approx 160$  K, whereas the analogous SrCoO<sub>3</sub> has a  $T_c$  of 280 K. [19]

In order to shed further light on the magnetic ordering of SrTcO<sub>3</sub>, we performed electronic structure calculations within the local density approximation using the general potential linearized augmented planewave (LAPW) method including local orbitals. [20] These were done in a scalar relativistic approximation using the experimental orthorhombic crystal structure. Well-converged basis sets and other parameters were used, with LAPW sphere radii of 2.1 Bohr and 1.6 Bohr for the metal and oxygen atoms, respectively.

The non-spin-polarized (NSP) density of states (DOS) is shown in Fig. 3a. The NSP system is metallic, with a Fermi energy,  $E_F$ , in the middle of a manifold of nominal

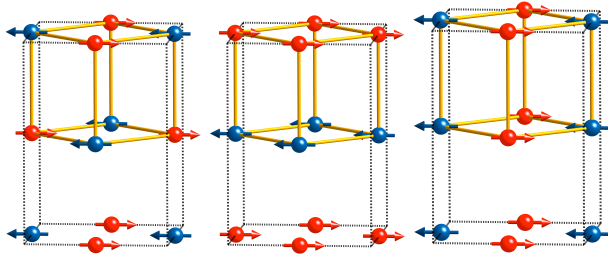


FIG. 2: (a) *G*-type antiferromagnetic ordering in the orthorhombic unit cell used for the structural refinement with the NPD data. (b) The *A*-type antiferromagnetic ordering and (c) *C*-type ordering. The sublattice with sides  $\approx a_p$  (orange line) corresponding to the cubic perovskite is drawn within the orthorhombic cells (thin dashed line).

$t_{2g}$  states, as expected from the electron count. However, unlike typical  $3d$  oxides, these states are strongly hybridized with O. The Fermi energy is at the center of a prominent peak in the DOS, leading to a rather high  $N(E_F) = 4.3 \text{ eV}^{-1}$  per Tc for both spins. This is a value that would substantially exceed the Stoner condition for a  $3d$  based material leading to magnetism. However, the energy as a function of constrained ferromagnetic spin moment from fixed spin moment was calculated and resulted in no stable or metastable ferromagnetic state.

The nonexistence of ferromagnetic ordering can be inferred from the DOS. The projections show very strong covalency between O and Tc even for the nominal  $t_{2g}$  manifold (Tc  $t_{2g}$ -O  $p$   $\pi$ -type antibonding combinations). Indeed, this is probably the cause for the reduced moment obtained from the neutron experiments. Because of this strong covalency, the Tc  $d$  character, as measured by the weight inside the 2.1 Bohr LAPW sphere, amounts to only  $\approx 60\%$  of the total  $N(E_F)$ . Furthermore the Hunds coupling on  $4d$  atoms is smaller than that on  $3d$  atoms because of the more extended orbitals. The combination of these two factors takes  $\text{SrTcO}_3$  away from a Stoner instability even though  $N(E_F)$  is high. Besides the ferromagnetic fixed spin moment calculations, we also did calculations for other spin orders compatible with the primitive unit cell. These include the so-called *A*-type ordering, consisting of ferromagnetic sheets of Tc moments stacked antiferromagnetically along the  $[010]$  direction (Figure 2b), the *C*-type arrangement with ferromagnetic sheets anti-aligned along the  $[100]$  and  $[001]$  directions (Figure 2c), and finally the *G*-type nearest neighbor antiferromagnetic arrangement (Figure 2a). The *A*-type arrangement had no stable moments, while the *C*-type showed a very weak magnetic solution, with moments in the Tc LAPW spheres of  $0.44 \mu_B$  and an energy lower than the NSP state by only  $0.4 \text{ meV} / \text{Tc}$ . In contrast, a very robust solution was found for the *G*-type ordering. This has an energy  $192 \text{ meV} / \text{Tc}$  below the NSP with a Tc moment of  $1.3 \mu_B$ . The *G*-type DOS (Fig. 3b) is strongly reconstructed by this ordering, and a small

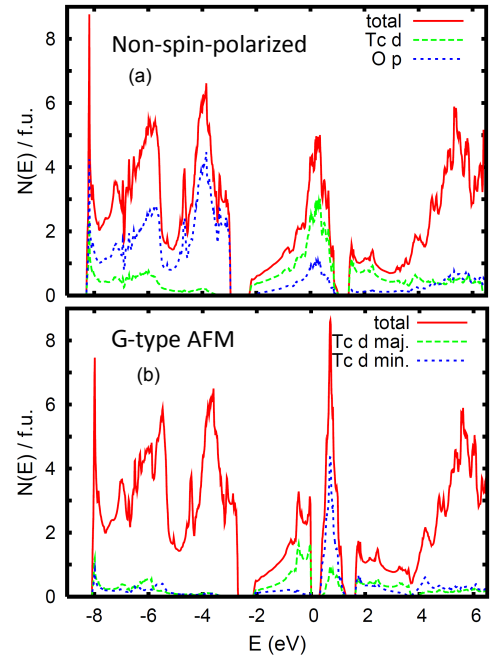


FIG. 3: (a) Electronic DOS and projections onto LAPW spheres for non-spin-polarized  $\text{SrTcO}_3$ . (b) Electronic DOS and majority and minority spin  $d$  projections onto the Tc LAPW sphere for *G*-type  $\text{SrTcO}_3$

insulating band gap of  $0.3 \text{ eV}$  is opened.

In most oxide magnets there are two energy scales. The first is a scale set by intra-atomic Coulomb repulsions, particularly the Hunds coupling, which drive moment formation. This is typically a high energy scale and leads to stable moments at all solid state temperatures. The second scale controls the ordering temperature, and is associated with the relative orientation of moments on neighboring sites. This is determined by interatomic hopping, as for example in the superexchange mechanism. In perovskites it arises from the hybridization between transition metal  $d$  orbitals and oxygen  $p$  orbitals.[21, 22] Importantly, the ordering temperature is set by the energy differences between different configurations of the moments, and these differences in turn are related to metal oxygen covalency and details of the bonding topology. In  $\text{SrTcO}_3$  the larger extent of the Tc  $4d$  orbitals relative to *e.g.* the  $3d$  orbitals of Mn lowers the onsite interactions that underlie moment formation, but strongly increases the amount of covalency as seen in the DOS projections. The result is that the two energy scales become comparable and moment formation and ordering are intertwined. This type of situation is often described as itinerant magnetism. This term should however be used with caution, since the moments are not small, and as a result there is a rearrangement of the DOS not only near  $E_F$  but over most of the  $\approx 3 \text{ eV}$  wide  $t_{2g}$  manifold.

The *G*-type state can be understood in a simple chemical bonding type of picture. Hybridization occurs be-

tween states of the same global spin direction and gives the strongest energy lowering when occupied states mix with unoccupied states. With  $G$ -type ordering, the occupied majority spin states on a given site hybridize with unoccupied minority states in the neighboring sites and vice versa. This is exactly the same mechanism that leads to  $G$ -type ordering in the analogous  $3d\ t_{2g}^3$  materials,  $\text{CaMnO}_3$  and  $\text{SrMnO}_3$ . [21, 22]

There are two important differences between the perovskite manganites and  $\text{SrTcO}_3$  that could result in a high ordering temperature in the latter. First, the energy scale is increased because of the greater hybridization and the smaller energy splitting between majority and minority spin orbitals (this enters in the denominator). Second, because the moment formation is intimately connected to the magnetic order, competing states, such as the  $C$ -type pattern, are suppressed. This is related to the physics that leads to high ordering temperatures in low moment itinerant magnets such as Cr and Ni metal. These two facts provide a qualitative explanation for the high Néel temperature of  $750^\circ\text{C}$  in  $\text{SrTcO}_3$ . This result is in marked contrast to the behavior of  $\text{SrMoO}_3$  and  $\text{SrRuO}_3$ , which are a highly conducting Pauli paramagnet and a metallic ferromagnet ( $T_c \approx 160\text{ K}$ ), respectively. There is no significant structural difference between  $\text{SrMoO}_3$ ,  $\text{SrRuO}_3$  and  $\text{SrTcO}_3$ , since their bridging M–O–M angles are  $170^\circ$ ,  $163.6^\circ$  and  $167.4^\circ$ , respectively. Rather, the unique properties of  $\text{SrTcO}_3$  stem from the high covalency of the Tc–O bonds combined with the outer  $4d^3$  electron configuration of the  $\text{Tc}^{4+}$  cation.

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