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Comparative study of the magnetism of $SrTcO_3$ and $Ca(Sr)MnO_3$

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ABSTRACT

By the first-principles calculations, we studied the electronic structures and the magnetic properties of $SrTcO_3$ and $Ca(Sr)MnO_3$. We found the strikingly high Néel temperature of $SrTcO_3$ is mostly due to the strong Tc(4d)–O(2p) hybridizations, since the Tc-4d states are more extended than the Mn-3d states. Such Tc(4d)–O(2p) hybridizations increase the super-exchange constants, hence increased the Néel temperatures.

1. Introduction

Intermediately located between manganese and rhenium, technetium ($4d^5 5s^2$) shares with its isovalent neighbors the intriguing possibility to form oxides with a complex structural, electronic, and magnetic phase diagram. Tc has a $4d^5 5s^2$ electronic configuration, like its lighter analogue Mn ($3d^5 4s^2$) adopts a number of oxidation states. Since all of its isotopes are radioactive, its properties have not been widely studied. In solids there is an interplay between the Hund's rule coupling, which favors moment formation, and hybridization with ligands, which works against moments. The 3d oxides are generally magnetic, while 4d and 5d oxides, with their more spatially extended orbitals, tend not to be magnetic, although the exceptions are remarkable, for example the ferromagnetism of $SrRuO_3$, with a moment size of $1.1\mu_B$ and Curie temperature $T_c \approx 160$ K [1].

Recently, antiferromagnetism persisting to very high temperatures exceeding 1000 K has been reported for $SrTcO_3$ [2–4] and other Tc^{4+} perovskites [6,5,7,8]. Comparing with its 3d analogue $SrMnO_3$, we find both compounds adopt the same distorted Pnma perovskite structure [9] and have the same G-type antiferromagnetic order. At the same time, the Tc magnetic moment is smaller ($2.1\mu_B$) than the Mn ($2.6\mu_B$) ion in the $SrMnO_3$ compound [9]. However, the Néel temperature of $SrTcO_3$ appears strikingly high compared to $T_N = 233$ K [9] of $SrMnO_3$. In this Letter, we resolve this puzzling question by performing electronic structure calculations on $SrTcO_3$, $CaMnO_3$ and $SrMnO_3$. By mapping the calculated total energies for different magnetic configurations onto a Heisenberg Hamiltonian, we evaluated the nearest-neighbor magnetic exchange parameters J_{ab} and J_c. We found the magnetic exchange parameters of $SrTcO_3$ are about 10 times as large as those of $CaMnO_3$ and $SrMnO_3$. So, we attributed the strikingly high Néel temperature of $SrTcO_3$ to the exceptional strong magnetic exchange parameters, which is derived from the strong hybridizations between the Tc-4d and O-2p states.

2. Method and details

The calculations were done with the BSTATE [10] code, with the ultra-soft pseudopotential plane wave method. We calculated the total energy of different magnetic configurations (FM, A, C, G-type antiferromagnetic states), where FM denotes the ferromagnetic state; A-type represents ferromagnetic in the *a*–*b* plane but antiferromagnetic along the *c*-axis; C-type marks ferromagnetic along the *c*-axis, but antiferromagnetic in the *a*–*b* plane; G-type means antiferromagnetic both in the *a*–*b* plane and along the *c*-axis [10,11]. We appropriately decouple the spin degree of freedom and treat it in terms of the Heisenberg model, then the exchange interaction is estimated by mapping the calculated total energies of each magnetic state [11,12] to the Heisenberg model. So, the nearest neighboring exchange coupling constants are given by

$$J_c = -\left[E(\mathrm{F}) - E(\mathrm{G}) - E(\mathrm{A}) + E(\mathrm{C})\right]/\left(4S^2\right),$$
$$J_{ab} = -\left[E(\mathrm{F}) - E(\mathrm{G}) + E(\mathrm{A}) - E(\mathrm{C})\right]/\left(8S^2\right),$$

where $E(\mathrm{F})$, $E(\mathrm{A})$, $E(\mathrm{C})$ and $E(\mathrm{G})$ are the total energies of ferromagnetic, A, C, G-type antiferromagnetic (AFM) states, respectively, and S is the calculated moment of Tc ion, J_c and J_{ab} are the exchange coupling constants along the *c*-axis and in the *ab*-plane, respectively. This model may miss certain contributions from itinerant electrons [13]. However, we believe that it captures the substantial physics on the magnetic structures. This model has

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Table 1
The experimental and optimized structural parameters for the $SrTcO_3$, $CaMnO_3$ and $SrMnO_3$. B stands for Tc and Mn in the $SrTcO_3$ and $Ca(Sr)MnO_3$. The local modes characterizing the Jahn–Teller effect defined as: $Q_2 = 2(l - s)/\sqrt{2}$, $Q_3 = 2(2m - l - s)/\sqrt{6}$, where l, s, and m indicate the three inequivalent long (B–O_2^l), short (B–O_2^s) and medium (B–O_1) B–O distances, respectively.

	$SrTcO_3$		$CaMnO_3$		$SrMnO_3$	
	Exp [2]	Opti	Exp [9]	Opti	Exp [9]	Opti
a (Å)	5.543	5.656	5.266	5.294	5.381	5.382
b (Å)	5.576	5.610	5.278	5.304	5.381	5.381
c (Å)	7.854	7.943	7.453	7.379	7.610	7.611
V ($Å^3$)	242.740	247.587	207.152	207.198	220.356	220.405
$\angle BO_1B$ (°)	161.57	162.58	158.83	158.88	180.00	179.07
$\angle BO_2B$ (°)	166.96	167.49	157.39	157.22	180.00	179.35
B–O_2^s (Å)	1.942	2.004	1.902	2.014	1.903	1.903
B–O_2^l (Å)	2.015	2.003	1.900	2.022	1.903	1.902
B–O_l (Å)	1.990	2.009	1.896	2.009	1.903	1.903
Q_2	0.1030	0.0004	0.0044	0.0001	0.0000	0.0009
Q_3	0.0181	0.0085	−0.0084	−0.0395	0.000	0.0003

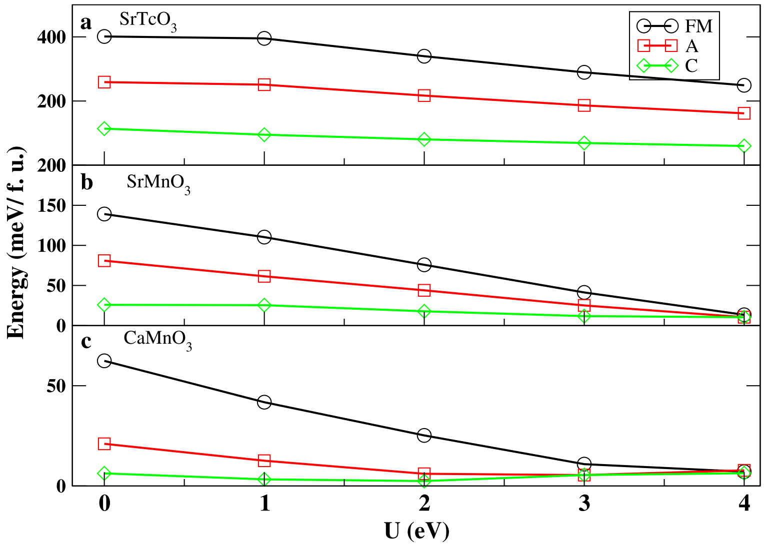

Fig. 1. (Color online.) (a) The stabilization energies (per f.u.) of $SrTcO_3$, $CaMnO_3$ and $SrMnO_3$ in the FM, A-AFM, and C-AFM states, with respective to the G-AFM state, varying with the electronic correlation U.

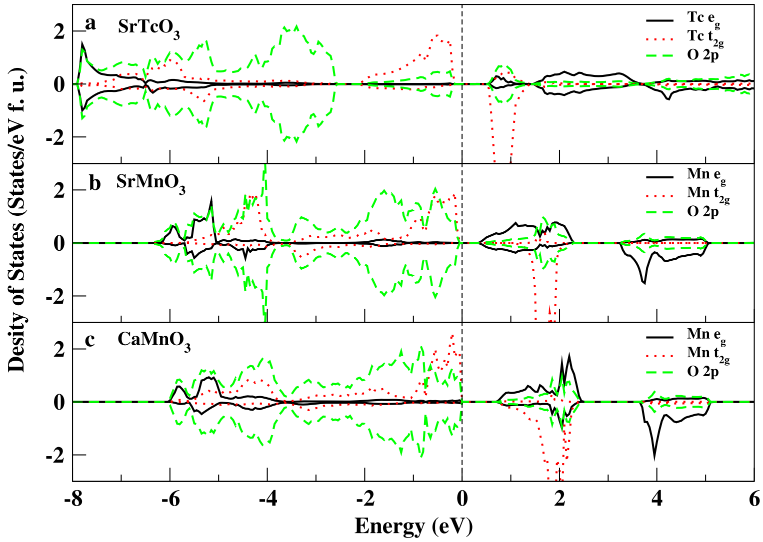

Fig. 2. (Color online.) (a) The calculated density of states of $SrTcO_3$, $CaMnO_3$ and $SrMnO_3$ in the G-type AFM ground state, decomposed over majority and minority O-2p, Tc(Mn) t_{2g} and e_g states.