Exceptionally strong magnetism in 4d perovskites $RTcO_3$ (*R*=Ca, Sr, Ba)

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The evolution of the magnetic ordering temperature of the 4$d^3$ perovskites $RTcO_3$ (*R*=Ca, Sr, Ba) and its relation with its electronic and structural properties has been studied by means of hybrid density functional theory and Monte Carlo simulations. When compared to the most widely studied 3d perovskites the large spatial extent of the 4d shells and their relatively strong hybridization with oxygen weaken the tendency to form Jahn-Teller like orbital ordering. This strengthens the superexchange interaction. The resulting insulating G-type antiferromagnetic ground state is characterized by large superexchange coupling constants (26-35 meV) and Neél temperatures (750-1200 K). These monotonically increase as a function of the *R* ionic radius due to the progressive enhancement of the volume and the associated decrease of the cooperative rotation of the TcO$_6$ octahedra.

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Intermediately located between manganese and rhenium, technetium (5s²4d⁵) shares with its isovalent neighbors the intriguing possibility to form oxides with a complex structural, electronic and magnetic phase diagram. However, the rare occurrence of natural Tc (Tc is essentially an artificial product of fission reactions) and the related radioactive risks (Tc is the lightest radioactive element, whose most abundant isotope, $^{99}$Tc, decays with a half-life of 10⁵ years), have made investigations of Tc-based oxides very sparse [1–6]. Overcoming these difficulties, Avdeev et al. [5] and Rodriguez et al. [6] have recently reported the successful synthesis of the first ever fabricated Tc-based perovskites, namely CaTcO$_3$ and SrTcO$_3$. Furthermore they have shown that these compounds display the anomalously high Neél temperatures ($T_N$) of 800 K for CaTcO$_3$ and 1000 K for SrTcO$_3$, by far the highest among materials not incorporating 3d transition metals. These results are surprising and challenge our understanding of the magnetic interaction in perovskites. In particular they pose three fundamental questions: i) is the origin of such a large magnetic ordering temperature related to the strong Tc 4d-O p hybridization ?, ii) what is the role played by the structural degrees of freedom? and iii) is the enhancement of $T_N$ upon Ca$\rightarrow$Sr substitution related to the observed increase in unit cell volume and the corresponding modification of the internal atomic positions [7, 8] ?

In the present letter, by using a combination of hybrid density functional theory [8] and Monte Carlo (MC) simulations [10], we address these issues at the microscopic level through a systematic study of the series $RTcO_3$ (*R*=Ca, Sr, Ba). Our aim here is twofold. First we wish to interpret and understand the experimental findings for CaTcO$_3$ and SrTcO$_3$, which can be only captured by beyond-local density functional theory (DFT), due to the incorrect treatment of the residual exchange-correlation effects still present in 4d compounds [11]. Secondly we anticipate the experiments predicting the properties of the technetiates series end member BaTcO$_3$.

We have employed the Heyd, Scuseria and Ernzerhof (HSE) [12] scheme as implemented in the VASP code [13–16], using a 4×4×4 k-points set, a cutoff energy of 300 eV, a mixing parameter of $a$=0.1 [17] and standard structural optimization conditions [18]. RTcO$_3$ compounds adopt the same distorted $Pnma$ perovskite structure as LaMnO$_3$ [19], characterized by a GdFeO$_3$-like (GFO) tilting of the TcO$_6$ octahedra caused by the R-O and R-Tc covalencies, and a concomitant Jahn-Teller (JT) Tc-O...
bond length disproportionation, with long (l) and short (s) Tc-O2 in-plane distances and medium (m) Tc-O1 vertical ones (see Fig. 1 and Table I). When compared to LaMnO3, the experimental values of the JT modes $Q_2 = 2(l - s)/\sqrt{2}$ and $Q_3 = 2(2m - l - s)/\sqrt{6}$ in CaTcO3 and SrTcO3 (see Table I) are significantly smaller due to the intrinsically different electronic configuration of the transition metal ions. In LaMnO3 the Mn$^{3+}$ ions 3d states are in a $t_{2g}^2e_g^1$ configuration and a strong JT effect is required to release the degeneracy of the $e_g$ orbitals and to form an orbitally ordered state $\hat{R}^{2}$.

In contrast in RTeO3 the Tc$^{4+}$ ions ($4d^3$: $t_{2g}^3e_g^0$) have completely filled (empty) $t_{2g}(e_g)$ orbitals, similarly to Mn$^{4+}$ ions in CaMnO3 [22], a configuration which inhibits the occurrence of electronic and structural JT instabilities, and leads to an insulating G-type antiferromagnetic (AFM-G) ground state [23]. However, at variance with 3d transition metal (TM) ions in perovskites, where $d^3$ configurations unavoidably lead to fully polarized $m = 3\mu_B$ moments on TM (e.g., CaMnO3), here due to the much larger extension of the 4d electrons and in turns a much stronger hybridizations with O p states, a sizable amount of charge fills the 4d minority states as well, with a consequent reduction of magnetic moment and an overtly evident intra-atomic Hund’s rule violation.

The structural parameters obtained by a full geometry optimization for the AFM-G ground state (Table I) are in excellent agreement with the available low temperature experimental data and the overall relative error is smaller than 1%. The Tc-O2 distances in SrTcO3 are the only exceptions since a deviation of almost 2% is observed. Notice that, at variance with CaTcO3, in SrTcO3 experiment finds an appreciable planar bond length anisotropy, i.e., the two Tc-O2 bond lengths differ by about 0.07 ˚A (at 3 K) [6, 20]. This appears quite anomalous if one considers that the 5% volume expansion associated to the substitution of Ca with the heavier Sr is expected to induce the quenching of the cooperative $Q_2$ and $Q_3$ JT modes. This translates in a reduction of the Tc-O disproportionation, similarly to the trend observed in the most widely study R MnO3 series [7, 8, 22]. The relatively strong Tc-O2 bond length anisotropy found in the experiments is comparable to that found in LaMnO3, and would suggest the presence of an orbitally ordered state in SrTcO3. This is unexpected for a 4d perovskite, given the abovementioned extendend character of the 4d manifold. On the other hand, HSE yields a Tc-O2 bond length anisotropy smaller for SrTcO3 (0.005) than for CaTcO3 (0.007), thus drawing a globally consistent picture. Our results describe clear trends going from small (Ca) to large (Ba) cation size: the increase of volume, the stretching of Tc – O – Tc bond angles, the consequential decrease of tilting distortion and the quenching of the Q2 mode, which controls the relative difference between the in-plane Tc-O2 bond lengths.

How these subtle structural properties affect the magnetism and how they can explain the observed surprisingly large $T_N$ is discussed next.

By mapping the HSE total energies for different magnetic configurations onto a Heisenberg Hamiltonian (for unitary spins) we have evaluated the nearest-neighbor (NN, $J_1$) and next-nearest-neighbor (NNN, $J_2$) magnetic exchange parameters as a function of the ionic radius $r_{R}$ [25]. The results are summarized in Fig. 1. The NN superexchange (SE) Tc-O-Tc path, as illustrated in Fig. 1 connects NN Tc atoms via planar (Tc-O2-Tc) and apical (Tc-O1-Tc) oxygen atoms. Because of the almost identical Tc-O distances and Tc – O – Tc angles (see Table I) we have found that the in-plane ($J_1$) and out-of-plane ($J_1^+$) values of $J_1$ are equal, both in sign (thus establishing the AFM-G ordering) and magnitude (within 10$^{-1}$ meV). Therefore we have finally adopted an effective Hamiltonian including an isotropic $J_1$ magnetic interaction.

In addition to the ferromagnetic (FM) alignment three additional AFM configurations have been considered in fitting the $J’s$: AFM-A ([100] planes of like spins alternating along the c axis), AFM-C (antiferromagnetic order in the xy plane with a ferromagnetic order along z) and

| CaTcO3 | SrTcO3 | BaTcO3 |
|--------|--------|--------|
| Expt. | HSE | Expt. | HSE |
| a (˚A) | 5.526 | 5.527 | 5.543 | 5.559 | 5.678 |
| b (˚A) | 7.695 | 7.695 | 7.854 | 7.856 | 8.038 |
| c (˚A) | 5.389 | 5.386 | 5.576 | 5.592 | 5.688 |
| V (˚A$^3$) | 229.15 | 229.04 | 242.74 | 244.20 | 259.59 |
| Tc – O1 – Tc ($^\circ$) | 150.43 | 150.52 | 161.57 | 164.74 | 178.89 |
| Tc – O2 – Tc ($^\circ$) | 151.53 | 150.84 | 166.96 | 168.76 | 179.22 |
| Tc-O2’ (˚A) | 2.002 | 1.998 | 2.015 | 1.983 | 2.010 |
| Tc-O2$^\ast$ (˚A) | 1.990 | 1.993 | 1.942 | 1.979 | 2.010 |
| Tc-O1 (˚A) | 1.985 | 1.988 | 1.990 | 1.981 | 2.010 |
| Q2 | 0.017 | 0.007 | 0.103 | 0.005 | 0.000 |
| Q3 | -0.018 | -0.012 | 0.018 | 0.001 | 0.000 |
TABLE II: Compilation of measured and calculated magnetic moment $m$, exchange coupling constants, $T_N$ and relative stability of the different magnetic phases considered ($\Delta E_{AFM-C}=E(AFMC)-E(AFMG)$, $\Delta E_{AFM-A}=E(AFMA)-E(AFMG)$ and $\Delta E_{FM}=E(FM)-E(AFMG)$) for $RTcO_3$ ($R=Ca, Sr$ and $Ba$). Experimental data ($m$, taken at 4 K, and $T_N$) are only available for $CaTcO_3$ [3] and $SrTcO_3$ [6].

|          | $CaTcO_3$ | $SrTcO_3$ | $BaTcO_3$ |
|----------|-----------|-----------|-----------|
| $m \,(\mu_B)$ | $\sim 2.0$ | 2.10      | 2.13      |
| $\Delta E_{CG}$ (meV/f.u.) | -78       | 121       | 139       |
| $\Delta E_{AG}$ (meV/f.u.) | -191      | -289      | 299       |
| $\Delta E_{FG}$ (meV/f.u.) | -313      | -449      | 439       |
| $J_1$ (meV) | -26.2     | -35.3     | -34.0     |
| $J_2$ (meV) | -1.3      | -0.7      | 0.1       |
| $T_N$ (K) | 800       | 750       | 1020      |

AFM-G (all spins are antiferromagnetically coupled to their nearest neighbors). At variance with what found with conventional local DFT functionals [3, 6], HSE provides very stable magnetic solutions for every spin ordering with almost identical values of the magnetic moment of $Tc$ ($\approx 2 \mu_B$, see Table I). Furthermore the AFM-G phase turns out to be the most stable (see Table II). The Heisenberg Hamiltonian is then used to evaluate $T_N$ via MC calculations [20]. Note that in doing that we have rescaled the $J$’s by a factor $S^2/(S(S+1))$ ($S=3/2$), which accounts for quantum fluctuations [27]. The results are summarized in Table II. The calculated $T_N$ for $CaTcO_3$ (750 K) and $SrTcO_3$ (1135 K) are in very good agreement with experiments and the $T_N$ predicted for $BaTcO_3$ (1218 K), if experimentally confirmed, would represent the highest magnetic ordering temperature for any system without 3d states.

These unexpectedly large magnetic ordering temperatures can be understood in the framework of Anderson’s theory of SE interactions [28], which links the strength of the SE coupling constant with the actual hybridization between the metal and the mediating atom, and Van Vleck’s theory of antiferromagnetism [29], which connects the strength of the SE interaction with the magnetic ordering temperature. The calculated inter-atomic NN and NNN coupling constants listed in Table II show that the antiferromagnetic NN $J_1$ is the dominating parameter ($\sim 30$ meV) and that it is almost two orders of magnitude larger than $J_2$ ($\sim 0.5$ meV). The calculated density of states (DOS) displayed in Fig. 2 shows that these huge $J_1$ value arises from the strong covalency between the Tc $t_{2g}$ and O $p$ orbitals evolving along the wide 4d $t_{2g}$ manifold, in particular for the topmost valence states spreading from -1.5/2 eV to the Fermi level ($E_F$). The increasing bandwidth ($w$) of this group of hybridized bands observed when going from $CaTcO_3$ ($w=1.5$ eV) to $SrTcO_3$ and $BaTcO_3$ ($w=2.0$ eV) associated with the enhanced $t_{2g}-p$ hybridization in the 3 eV wide $t_{2g}$ band around -5.5 eV explains the larger $J_1$ and the corresponding larger $T_N$ for $SrTcO_3$ and $BaTcO_3$. At this point a fundamental question naturally arises: Why the $Tc-O$ hybridization increases along the $RTcO_3$ series when $r_R$ get larger?

In order to answer to this question we analyse the coupling between the structural changes, caused by the substitution of Ca with bigger isovalent atoms (Sr and Ba), and the electronic and magnetic properties, as exemplified in Fig. 3. We recall, that the most significant effects on the crystal structure caused by increasing $r_R$ are (i) the volume enhancement, (ii) the quenching of the JT distortions $Q_2$ and $Q_3$ and (iii) the decrease of the cooperative rotation of the TcO$_6$ octahedra represented by the Tc-O-Tc bond angles. The angles Tc-O1-Tc and Tc-O2-Tc are crucial quantities to explain the evolution of the SE interactions and of the magnetic ordering temperature. In fact, the monotonic increase of the Tc-O-Tc bond angles (in brief the average between Tc-O1-Tc and Tc-O2-Tc, see Fig. 3) leads to the progressive rectification of the NN superexchange paths. This generates, in a tight-binding framework, an enhanced Tc-$t_{2g}$/O-$p$ hybridization, as confirmed by the DOS (see Fig. 2). As displayed

FIG. 2: (Color online) HSE calculated density of states for the $RTcO_3$ series in the G-type AFM ground state decomposed over majority and minority O $p$ and Tc $t_{2g}$ and $e_g$ states. The calculated band gaps are: 1.4 eV ($CaTcO_3$), 1.48 eV ($SrTcO_3$) and 1.57 eV ($BaTcO_3$).
in Fig. 3, $T_N$ steeply increases from CaTcO$_3$ (750 K) to SrTcO$_3$ (1135 K) as a consequence of the observed larger change in Tc – O – Tc, which goes from 151° to 167°. When moving from SrTcO$_3$ to BaTcO$_3$ (1218 K) the rise of $T_N$ is weaker due to a smaller change of Tc – O – Tc (from 167° to 179°) and to a further reduction and sign change in $J_2$. In analogy with the RMnO$_3$ perovskites, the increase of $T_N$ for larger Tc-O-Tc angles correlates with a progressive reduction of the JT distortions (i.e. a decrease of the associated structural ordering temperature). [7]

In conclusion we remark that our findings for the 4$d$ RTcO$_3$ series are consistent with the Goodenough-Kanamori rules [3] and follow the general trend observed in 3$d$ RMnO$_3$, namely that $T_N$ increases by increasing the Tc – O – Tc angles. The remarkably different $T_N$’s in manganites ($T_N < 150$ K) and technetiates ($T_N > 750$ K) can be explained with the reduced spatial extension of 3$d$ shell, which suppresses the $d$-$p$ hybridization in manganites and thereby inhibits strong SE interactions. We also emphasize, that the correct description of this complex class of materials can be only achieved within a beyond-local functional method such as HSE. HSE is capable of capturing the delicate balance between the SE mechanism and both, the Hund’s coupling (unlike local functionals, HSE provides well defined magnetic solutions for different spin configurations) and the intraatomic Coulomb repulsion (though substantially reduced with respect to 3$d$ perovskites, on site Coulomb interaction survives in 4$d$ technetiates and contributes to the formation of a rather large gap which local functionals seriously underestimates).

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