

Structural and electronic trends in rare-earth technetate pyrochlores†

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We report the structures and electronic properties of nine novel rare earth technetate pyrochlores with ideal stoichiometry $\text{Ln}_2\text{Tc}_2\text{O}_7$ ($\text{Ln} = \text{Ce-Pm, Gd, Tb, Ho, Tm, Lu}$) predicted within the framework of gradient-corrected density functional theory. The computed structures of $\text{Er}_2\text{Tc}_2\text{O}_7$, $\text{Dy}_2\text{Tc}_2\text{O}_7$, and $\text{Sm}_2\text{Tc}_2\text{O}_7$ also closely match available X-ray diffraction data.

Pyrochlore-structured oxides have received considerable attention in recent years owing to the diversity of their properties and their remarkable stability under extreme conditions.^{1,2} Their range of technological applications encompasses high-permittivity dielectrics,³ electrolytes in solid oxide fuels,⁴ catalysts,⁵ thermal barrier coatings,⁶ and host materials for advanced nuclear fuels or nuclear waste forms.⁷ In the latter, pyrochlores are envisioned as promising radiation-tolerant matrix materials for the transmutation or the immobilization of actinides or lanthanides produced in nuclear power plants. Recent advances have focused on gaining insight into point-defect formation and metamictization induced by radiation damage from radioactive elements contained within these pyrochlores.²

Although numerous pyrochlores bearing fission products have been investigated so far, only few studies have been reported on technetate pyrochlores.^{8,9} This appears particularly surprising in light of the importance of technetium in the field of nuclear waste management. Indeed, although technetium possesses no stable isotopes, its long-lived β -emitting isotope, ^{99}Tc ($t_{1/2} = 2.13 \times 10^5$ years; $E^{\beta} = 294$ keV), is produced in sizable amount from the nuclear fuel cycle (up to a cumulative yield of 6% for the thermal neutron fission of ^{235}U)¹⁰ and constitutes an important challenge for environmental remediation.¹¹

In this Communication, we report the structures and electronic properties of nine novel rare earth technetate pyrochlores with ideal stoichiometry $\text{Ln}_2\text{Tc}_2\text{O}_7$ ($\text{Ln} = \text{Ce-Pm, Gd, Tb, Ho, Tm, Lu}$) predicted within the framework of gradient-corrected density functional theory (DFT). The structures of $\text{Er}_2\text{Tc}_2\text{O}_7$, $\text{Dy}_2\text{Tc}_2\text{O}_7$,

and $\text{Sm}_2\text{Tc}_2\text{O}_7$ pyrochlores previously synthesized by Muller *et al.*⁸ have also been computed and closely match available X-ray diffraction (XRD) crystallographic data. The present calculations indicate that the lattice parameter evolves linearly with the lanthanide ionic radius. Band structure and density of states calculations along the lanthanide series show metallic characteristics stemming from the hybridization of O 2p and Tc 4d orbitals in the vicinity of the Fermi level.

The pyrochlore structure is a super structure derivative of the simple fluorite structure (CaF_2). Ideal stoichiometric pyrochlores $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ considered in this study are cubic with $Fd\bar{3}m$ space group symmetry (IT No. 227, $Z = 8$) and can be described as two interpenetrating networks $\text{A}_2\text{O}'$ (corner-sharing $\text{A}_4\text{O}'$ tetrahedra) and B_2O_6 (corner-sharing BO_6 octahedra), where lanthanide Ln^{3+} and technetium Tc^{4+} cations occupy A and B sites, respectively (*cf.* Fig. 1).

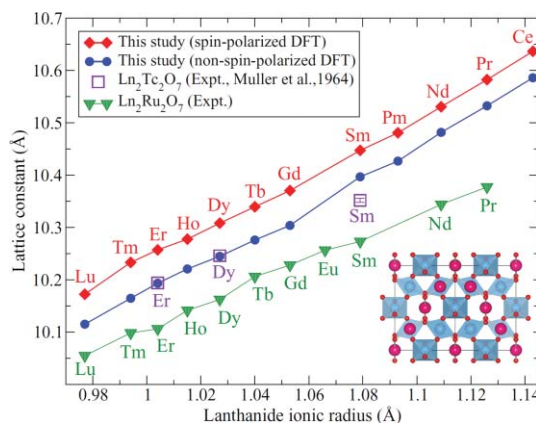


Fig. 1 Evolution of the crystal lattice parameter of $\text{Ln}_2\text{Tc}_2\text{O}_7$ pyrochlores as a function of the lanthanide (Ln) ionic radius. Experimental data^{5,12} for $\text{Ln}_2\text{Ru}_2\text{O}_7$ pyrochlores are also shown for the sake of comparison. The crystal unit cell of an ideal stoichiometric $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ pyrochlore along the [110] direction is represented, where Ln^{3+} and Tc^{4+} cations occupy A sites and B sites, respectively. Color legend: red, O; cyan, Tc; pink, Ln.

First-principles total energy calculations were performed using density functional theory as implemented in the Vienna *ab initio* simulation package (VASP).¹³ The exchange–correlation energy was calculated using the generalized gradient approximation (GGA) with the parametrization of Perdew and Wang (PW91).¹⁴ The interaction between valence electrons and ionic cores was described by the projector augmented wave (PAW) method.¹⁵ The Tc(4p,5s,4d) and Ln(4f,5d,6s) electrons were treated explicitly as valence electrons in the Kohn–Sham (KS) equation and the remaining core electrons together with the nuclei were represented by PAW pseudopotentials. The KS equation was solved using

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the blocked Davidson iterative matrix diagonalization scheme followed by the residual vector minimization method. The plane-wave cutoff energy for the electronic wavefunctions was set to a value of 500 eV, ensuring the total energy of the system to be converged to within 1 meV/atom. A periodic unit cell containing 88 atoms was used in the calculations. Electronic relaxation was performed with the conjugate gradient method accelerated using the Methfessel–Paxton Fermi-level smearing¹⁶ with a Gaussian width of 0.1 eV. Ionic relaxation was carried out using the quasi-Newton method and the Hellmann–Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.01 eV/Å. The Brillouin zone was sampled using the Monkhorst–Pack special k -point scheme¹⁷ with a $3 \times 3 \times 3$ mesh for structural optimization and total energy calculations. Test calculations carried out with a $5 \times 5 \times 5$ mesh resulted in differences typically less than 0.03 eV per unit cell in the total energy and less than 0.005 Å in the lattice constants. Calculations including spin–orbit coupling were also performed for several rare earth technetate pyrochlores to confirm that this term does not affect our results. Differences of *ca.* 0.02 eV/88 atom unit cell were found in the total energy, therefore the spin–orbit term can be safely neglected. For each structure, the density of states was calculated using the linear tetrahedron method with Blöchl corrections.¹⁸ In order to calculate the band structures, a k -point path along the W–L–Γ–X–W symmetry points¹⁹ was used to sample the first Brillouin zone (BZ) with 30 points along high-symmetry lines. Molecular orbitals corresponding to bands near the Fermi level were represented graphically using the DMol3 software.²⁰

The equilibrium lattice parameter of rare earth technetate pyrochlores varies from 10.115 Å for $\text{Lu}_2\text{Tc}_2\text{O}_7$ to 10.586 Å for $\text{Ce}_2\text{Tc}_2\text{O}_7$ using non-spin polarized DFT (*cf.* Fig. 1), while spin polarization produces lattice parameters systematically larger by only ~0.5%. The possibility of non-collinear magnetism, which is not addressed in our formalism, and the small energy difference associated with spin polarization might be the reasons why structural parameters may be better described in this case by ignoring the magnetic structure. The evolution of the lattice parameter abides overall by the lanthanide contraction phenomenon. The XRD values of 10.194 ± 0.004 Å, 10.246 ± 0.004 Å, and 10.352 ± 0.004 Å measured by Muller *et al.*⁸ for $\text{Er}_2\text{Tc}_2\text{O}_7$, $\text{Dy}_2\text{Tc}_2\text{O}_7$, and $\text{Sm}_2\text{Tc}_2\text{O}_7$, respectively, are essentially reproduced by non-spin polarized DFT calculations, *i.e.*, 10.193 Å, 10.245 Å, and 10.397 Å. The residual discrepancies between theoretical and experimental lattice parameters can possibly be ascribed to the presence of small amounts of impurities from the non-volatile starting materials in the pyrochlores synthesized.⁸ The ratio of the ionic radii of A and B cations (r_A/r_B), which seems to govern the stability of pyrochlores, extends from 1.515 for $\text{Lu}_2\text{Tc}_2\text{O}_7$ to 1.772 for $\text{Ce}_2\text{Tc}_2\text{O}_7$ using the 8-fold coordinated Ln^{3+} (VIII) and 6-fold coordinated Tc^{4+} (VI) ionic radii given by Shannon.²¹ These values are within the stability regime ranging from 1.46 to 1.78 for A^{3+}/B^{4+} pyrochlores.²² As can be inferred from Fig. 1, the complete transmutation of ^{99}Tc into the stable ^{100}Ru without radiation damage is expected to be accompanied by a 1.8–4.5% volume collapse of the pyrochlore structure, the largest volume change occurring for pyrochlores containing early lanthanide elements.

Total and partial densities of states (DOS) of $\text{Ln}_2\text{Tc}_2\text{O}_7$ pyrochlores were also calculated using spin-polarized density functional with the tetrahedron method (*cf.* Fig. 2). Lanthanide 4f

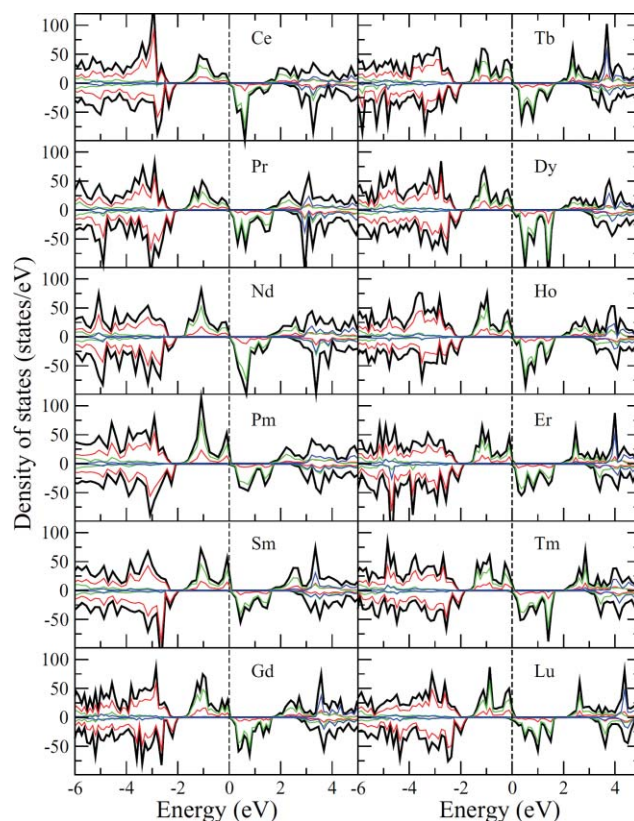


Fig. 2 (a) Density of states (DOS) per unit cell of $\text{Ln}_2\text{Tc}_2\text{O}_7$ ($\text{Ln} = \text{Ce}–\text{Sm}, \text{Gd}–\text{Tm}, \text{Lu}$) pyrochlores calculated using spin-polarized density functional theory. Color legend: Total DOS, black; Partial DOS: O 2p, red; Tc 4d, green; Ln 5d, blue. The Fermi energy is set to 0 eV (dashed line). Positive and negative values of the DOS correspond to spin-up and spin-down contributions, respectively.

electrons were not found to play a significant role in the vicinity of the Fermi level as expected. Most of the contribution to the DOS near the Fermi level originates from the hybridization of Tc 4d and O 2p electrons, which are responsible for the metallic conductivity of rare-earth technetate pyrochlores.

Band structure calculations confirm the weak metallic character of $\text{Ln}_2\text{Tc}_2\text{O}_7$ pyrochlores. As a representative example, we present the band structure of $\text{Ce}_2\text{Tc}_2\text{O}_7$ in the Supporting Information.[†] There, we observe metallic states crossing E_F along the radial L–Γ and Γ–X high-symmetry lines, and a small band gap opening up along the X–W and W–L lines at the surface of the BZ. Although no experimental data on the conductivity of rare-earth technetate pyrochlores are available, recent measurements of the magnetic susceptibility of Bi technetate pyrochlores show that they are Pauli paramagnets and therefore should also be metallic conductors.^{9,23}

The analysis of the frontier molecular orbitals (MOs) calculated at the Γ point corresponding to the lowest-energy conduction band and the highest-energy valence band confirms the importance of Tc 4d₂ and O 2p orbitals near the Fermi level. As an example, the frontier MOs of $\text{Ce}_2\text{Tc}_2\text{O}_7$ are depicted in the pyrochlore primitive cell in Fig. 3.

As shown in Fig. 4, the net electron-spin magnetic moment of $\text{Ln}_2\text{Tc}_2\text{O}_7$ originates essentially from the corner-sharing TcO_6 octahedra constituting the Tc_2O_6 sublattice, while the corner-sharing $\text{Ln}_4\text{O}'$ tetrahedra of the $\text{Ln}_2\text{O}'$ network do not contribute

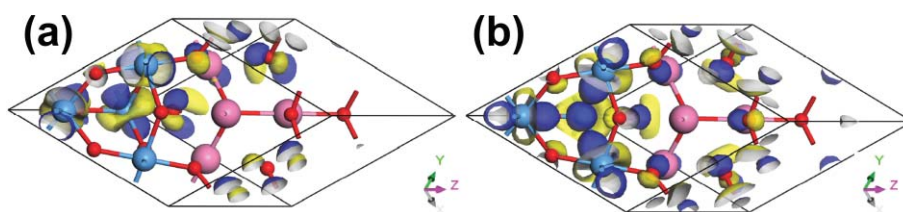


Fig. 3 Frontier molecular orbitals of $\text{Ce}_2\text{Tc}_2\text{O}_7$ pyrochlore calculated at the Γ point using spin-polarized density functional theory. Molecular orbitals corresponding to the (a) lowest-energy conduction band and (b) the highest-energy valence band, both featuring Tc $4d_{z^2}$ and O $2p$ orbitals in the pyrochlore primitive cell. Color legend: red, O; cyan, Tc; pink, Ce. The wavefunction phase is distinguished by yellow and blue colors.

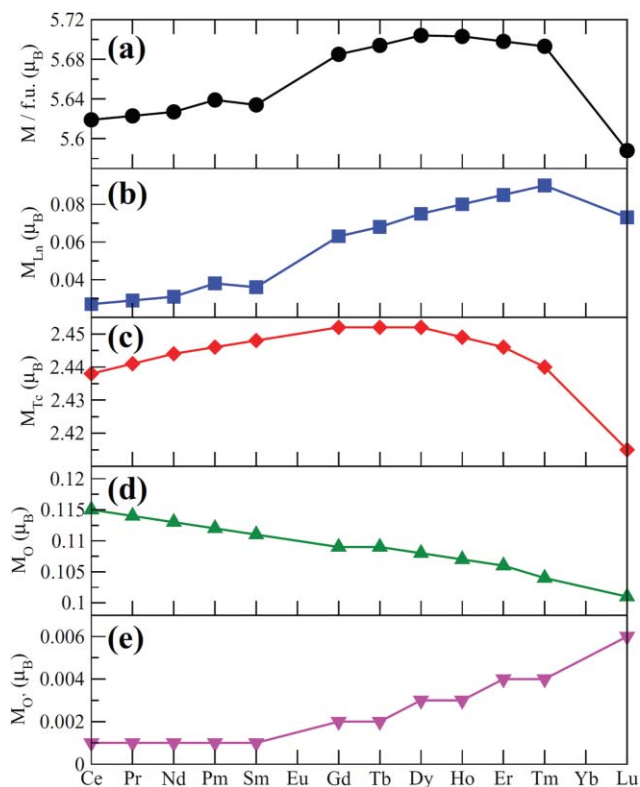


Fig. 4 Evolution of the electron-spin magnetic moments of $\text{Ln}_2\text{Tc}_2\text{O}_6\text{O}'$ pyrochlores calculated using spin-polarized density functional theory. Partial contributions to the magnetic moment are represented (a) per formula unit, and per atom of (b) Ln^{3+} , (c) Tc^{4+} , (d) O, and (e) O' .

significantly to the total magnetic moment. This is consistent with our DOS and band-structure analysis predicting the predominant role of Tc $4d$ and O $2p$ electrons near the Fermi level.

Experimental efforts to synthesize and characterize the technetate pyrochlores reported in this study are underway.

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