Preparation, magnetism and electronic structures of cadmium technetates†‡

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Due to the scarcity of the artificial transition metal technetium, studies on the solid-state properties of its oxides have been rarely undertaken. We have prepared a new technetium metal oxide system that include the 4d metal in two separate oxidation states and have characterized the new phases’ crystal structures and magnetic properties. One phase Cd₄Tc₂O₇ was prepared through the vapor-phase reaction of the heptaoxide Tc₂O₇ with Cd metal; the other phase, CdTcO₅, was prepared through the solid state reaction of TcO₂ with CdO. High-resolution synchrotron X-ray diffraction was used to characterize the crystal structures and stoichiometries of the two new technetates. At room temperature, Cd₄Tc₂O₇ takes on the pyrochlore structure with \( a = 10.18118(1) \) Å, space group, \( Fd\overline{3}m \) and \( Z = 8 \). CdTcO₅ has the GdFeO₃-type structure with space group \( Pbnm \) and \( a = 5.38881(1) \) Å, \( b = 5.46504(1) \) Å, and \( c = 7.71272(1) \) Å. The magnetic susceptibility behavior of Cd₄Tc₂O₇ is strikingly similar to that observed in Cd₂Re₂O₇, with a broad transition close to 200 K. The magnetic behavior of CdTcO₅ is also compared with that of isomorphous Pb₂TcO₅ and Bi₂TcO₅, also presented in this study. The magnetic susceptibility of the distorted perovskite phase CdTcO₅ is weakly temperature dependent, with no obvious signs of an ordering transition below 300 K. Electronic band structure calculations performed to simulate electronic densities of states indicate that the Fermi level is located in a ‘\( t_{2g} \)’ band of the octahedrally coordinated Tc cations and therefore metallic conductivity in both CdTcO₅ and Cd₂Tc₂O₇.

1 Introduction

Among the various subsets of inorganic materials, transition metal oxides have captured the imagination and interest of materials scientists, chemists, and physicists for their diverse physical and chemical properties. Among investigations of electronic properties of transition metal oxides, those on oxides containing ruthenium have produced a wide array of physical phenomenon. The Ru-containing oxides, or ruthenates, can express properties such as superconductivity in \( \text{Sr}_2\text{RuO}_4 \), collective electron ferromagnetism in \( \text{SrRuO}_3 \), and metal-to-insulator (MI) transitions in several \( \text{A}_2\text{RuO}_4 \) compounds (where \( \text{A} \) is a divalent cation). Typically, in the latter compounds, Ru is paired with a heavy post-transition metal as in \( \text{Ti}_3\text{Ru}_2\text{O}_7 \) or \( \text{Hg}_2\text{Ru}_2\text{O}_7 \). In the case of \( \text{Ti}_3\text{Ru}_2\text{O}_7 \), an interesting one-dimensional ordering of the Ru d orbitals within the three-dimensional crystal structure leads to the MI transition, while in \( \text{Hg}_2\text{Ru}_2\text{O}_7 \), the MI transition is thought to be purely electronic. These fascinating electronic and structural properties in the Sr–Ru–O system and the ruthenate pyrochlores motivated our study of mixed-metal oxides of neighboring 4d metal, technetium, an artificial element often overlooked due to its paucity.

For the first time in over 40 years, mixed-metal oxides containing Tc were prepared in a study on the oxides \( \text{Bi}_2\text{Tc}_2\text{O}_7 \), \( \text{Bi}_3\text{Tc}_2\text{O}_7 \), and \( \text{Bi}_1\text{Tc}_2\text{O}_7 \). In the present study, two new Tc-containing oxides with another post-transition metal, cadmium, are presented. Unlike \( \text{Bi}^{II} \) and \( \text{Pb}^{II} \), \( \text{Cd}^{II} \) is a smaller and less polarizable cation due to its higher charge density. Furthermore, the stereochemical effect of an inert pair of s electrons does not play a role in the crystal chemistry of \( \text{Cd}^{II} \) as it does for \( \text{Bi}^{III} \) and \( \text{Pb}^{IV} \). While not as electropositive as the alkaline earth metals, Cd is more so than Bi and Pb, which should also influence the bonding interaction between the Tc and O atoms.

The pyrochlore structure has been found to occur for oxides with the stoichiometry \( \text{Cd}^{II}_{2n-1}\text{M}^{III+n}\text{O}_{3n} \) where \( \text{M} = \text{Nb, Ta, Ru, Re, Os, and Ir} \). These Cd-containing oxides of the 4d/5d series have shown a diverse array of electronic behavior. \( \text{Cd}_2\text{Nb}_2\text{O}_7 \) and \( \text{Cd}_2\text{Ta}_2\text{O}_7 \) are insulating, as expected from the d° configuration, and in the case of the niobate, a complex ferroelectric transition occurs around 180 K. Contrastingly, \( \text{Cd}_2\text{Re}_2\text{O}_7 \) was the first oxide with the pyrochlore structure found to exhibit superconductivity with a \( T_c \) around 1 K. In the homologous oxide of neighboring osmium, a metal-to-insulator (MI) transition occurs instead around 225 K. Since Tc and Re have similar chemistries, studying the structure and properties of the Tc analogue...
would be imperative for further exploring the phenomena of superconductivity and MI transitions in 4d/5d oxides with the pyrochlore structure. Consequently, we have, for the first time, prepared the oxides Cd$_2$Tc$_2$O$_7$ and CdTcO$_3$, with the former adopting the pyrochlore structure and the latter a distorted perovskite structure.

In Cd$_2$Te$_2$O$_7$, the Te$^{4+}$ cations have a 4d$^2$ configuration, whereas in CdTeO$_3$, the Te$^{4+}$ cations have a 4d$^4$ configuration, an interesting state to explore since it might correspond to a half-filled t$_{2g}$ manifold in an octahedral field, and thus a possible instability leading to magnetic ordering. The preparation of the two new cadmium technetates is presented along with high-resolution synchrotron X-ray diffraction (XRD) data to characterize their crystal structures. The magnetic properties of CdTeO$_3$ and Cd$_2$Te$_2$O$_7$ as characterized from SQUID magnetometry measurements are also presented. Finally, electronic structure calculations for the two Cd–Tc–O phases were performed in order to predict possible electronic transport behavior.

2 Experimental

[Caution: $^{99}$Tc is radioactive with a specific activity of 17 mCi/gram. To prevent contamination and ensure personal safety, standard practices of a radiochemistry laboratory must be followed.]

The CdTeO$_3$ phase was prepared by heating a stoichiometric mixture of CdO and TeO$_2$ at 850 °C in a fused quartz boat under flowing Ar gas for 12 h. TeO$_2$ was prepared by thermal decomposition of NH$_4$TeO$_4$ as described in previous work. The resulting powder, which appears light grey metallic, was treated with 2M HCl to remove any remaining CdO and subsequently washed with water and acetone. Preliminary powder XRD data showed a pattern with Bragg peaks matching the orthorhombic lattice of the perovskite CdTiO$_3$.

For the preparation of Cd$_2$Re$_2$O$_7$, Donohue et al. reacted ReO$_3$ with CdO in a sealed quartz ampoule at 1000 °C. After complete oxidation of TcO$_2$ to Tc$_2$O$_7$, the tube was cooled to room temperature over several hours. After complete oxidation of TcO$_2$ to Tc$_2$O$_7$, the tube was opened and the products were washed with water and acetone. Preliminary powder XRD data showed a pattern with Bragg peaks matching the orthorhombic lattice of the perovskite CdTiO$_3$.

Details concerning the high-resolution X-ray diffraction, SQUID magnetometry, and electronic band structure calculations can be found in Supplementary Information. Further details on sample preparation can also be found in the Supplementary Information.

3 Results and discussion

3.1 Structural details

Using the GSAS software package, the crystal structures of Cd$_2$Te$_2$O$_7$ and CdTcO$_3$ were refined with the room temperature, high-resolution powder XRD data. Starting with the structural parameters of Cd$_2$Re$_2$O$_7$, the Rietveld refinement with the 15 keV XRD data of Cd$_2$Te$_2$O$_7$ converged to the parameters shown in Table 1 with an $R_{wp}$ of 12.3% and $\chi^2$ of 2.043. The $R_{wp}$ is high due to the high-resolution and low background quality of the data, and is not necessarily an indication of an insufficient structural model. In Rietveld analysis, the $\chi^2$ is similar to the goodness of fit $G$ of the single crystal literature and equal to $(R_{wp}/R_{exp})^2$ where $R_{exp}$ is the 'best' possible expected $R_{wp}$ for a given data set. Since $\chi^2$ from our refinement is 2.043, then $R_{wp}$ is only equal to about 1.42$R_{exp}$, validating our model for the observed high-resolution, low background data. Furthermore, the accuracy of the model is apparent from the relatively smooth difference curve between the observed and calculated powder patterns for Cd$_2$Te$_2$O$_7$ as shown in Fig. 1.

At room temperature, Cd$_2$Te$_2$O$_7$ takes on the idealized pyrochlore structure (see Fig. 2) with $a = 10.18118(1)$ Å, space group $Fd\bar{3}m$ (origin choice 2), and $Z = 8$ formula units per cell. The high-resolution powder pattern also revealed some impurities in the powder with TcO$_2$ accounting for around 2.7% and CdTeO$_3$ around 1.5%. Unlike Bi$_2$Tc$_2$O$_7$, Cd$_2$Te$_2$O$_7$ was found to be stoichiometric and with a much shorter Tc–O bond length of 1.926(1) Å that found in TcO$_2$ (1.982 Å on average) or in the other pyrochlore Bi$_2$Tc$_2$O$_7$–$\delta$ (2.0108 Å on average). Thus the structural results confirm the presence of Tc$^{4+}$ from the much shorter and therefore more covalent Tc–O bond. The relevant interatomic distances are presented in Table 2.

Like Cd$_2$Re$_2$O$_7$, the new compound Cd$_2$Tc$_2$O$_7$ is a colored oxide with metallic luster. The color of Cd$_2$Tc$_2$O$_7$ is blue-green, whereas that of the Re analogue is purple. The diffraction results support a stoichiometric oxide with Tc$^{4+}$ cations. Excluding salts of [TcX$_6$]$^+$ anions, the only other known solid-state compounds containing Tc$^{4+}$ are the yellow pentafluoride

<table>
<thead>
<tr>
<th>Atoms</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>16d</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.0160(2)</td>
</tr>
<tr>
<td>Tc</td>
<td>16c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0096(1)</td>
</tr>
<tr>
<td>O</td>
<td>48f</td>
<td>0.3175(2)</td>
<td>1/8</td>
<td>1/8</td>
<td>0.017(1)$^*$</td>
</tr>
<tr>
<td>O'</td>
<td>8b</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.009(1)</td>
</tr>
</tbody>
</table>

$^*$ Anisotropic atomic displacement parameters for O: $U_{11} = 0.021(1)$, $U_{22} = 0.015(1)$, $U_{33} = 0.015(1)$; $\epsilon_{12} = 0.0$, $U_{13} = 0.0$, $U_{23} = 0.002(1)$. |
TcF₅,²⁰ the oxyhalides TcOCl₃ and TcOBr₃,²¹ and the alkaline oxides Li₃TcO₄ and NaTcO₃.²² However, the crystal structures of these compounds were never determined. Therefore, the Shannon radius for Tc⁵⁺ was extrapolated from the orthorhombic cell of TcF₅, which is thought to be isostructural to CrF₅.²₀,²³,²⁴ The radius of 0.546 Å for Tc⁵⁺ from our studies (1.926 – 1.38 = 0.546) seems especially small when compared to the Shannon radius of 0.60 Å, indicating the increased covalency in Cd₂Tc₂O₇ compared to the fluoride. The pentavalent state is unusual for Tc and it is remarkable that it does not undergo disproportionation at 800 °C since the pentafluoride decomposes at 60 °C. Furthermore, the preparation did not require high pressures or oxidizing agents, both necessary for the preparation of Cd₂Ru₂O₇.²⁵

While not as common as the A₂³⁺M₂⁴⁺O₇ pyrochlores, the A₂²⁺M₂⁵⁺O₇ pyrochlores can show a diverse array of physical properties, from ferroelectricity to superconductivity. In the case of A = Cd, the pyrochlore oxides exist for M = Nb, Ta, Re, Ru, Ir, Os, and now Tc. For the d² and d⁴ systems (almost nothing is known for the d⁶ Ir-based pyrochlore),²⁶ the M–O–M angle is relatively open for a pyrochlore oxide, pointing towards increased hybridization of the M d orbitals and the O p orbitals. The x parameter of the O atom (see Table 1) is close to the extremal value of 0.3125, which leads to regular octahedral geometry around the M cations.² These values, along with those of the M–O bond distance, are shown for Cd₂Tc₂O₇ and related oxides in Table 3. As can be seen from these values, one would expect high covalency in these Cd-based pyrochlores since they have short M–O bond lengths and are close to possessing true octahedral geometry.

When TeO₂ was reacted with CdO, the perovskite phase Cd₂TcO₃ was prepared. This is in contrast to the same reaction with PbO which led to the oxygen deficient pyrochlore phase instead. This observation can be understood by considering the differences in the calculated densities between the two Cd–Tc–O phases. For Cd₂Tc₂O₇ the calculated density from the XRD data was 6.655 g cc⁻¹ and for Cd₂TcO₇ 7.556 g cc⁻¹. Therefore, the more ionic, close-packed structure of the perovskite Cd₂TcO₃ is found to be more stable than a defect pyrochlore of the type Cd₂Tc₂O₆₊ₓ. This suggests that the high covalency between the Tc⁵⁺ cations and O anions achieved by the high valency of the Tc cations is necessary to form the pyrochlore phase in the Cd–Tc–O system.

Table 2  Selected interatomic distances (Å) and angles (°) in Cd₂Tc₂O₇ from room temperature powder XRD data. Standard uncertainties are shown in parentheses

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cd₂Tc₂O₇</th>
<th>Cd₂Re₂O₇</th>
<th>Cd₂Ru₂O₇</th>
<th>Cd₂Os₂O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc–O (×6)</td>
<td>1.926(1)</td>
<td>1.938(2)</td>
<td>1.924(1)</td>
<td>1.928(1)</td>
</tr>
<tr>
<td>O–Tc–O</td>
<td>92.0(1)</td>
<td>137.7(4)</td>
<td>137.1</td>
<td>137.5(7)</td>
</tr>
<tr>
<td>Tc–O–Tc</td>
<td>88.0(1)</td>
<td>88.0(1)</td>
<td>88.0(1)</td>
<td>88.0(1)</td>
</tr>
<tr>
<td>Cd–O’ (×2)</td>
<td>138.2(1)</td>
<td>138.2(1)</td>
<td>138.2(1)</td>
<td>138.2(1)</td>
</tr>
<tr>
<td>Cd–O’–Cd</td>
<td>2.2043</td>
<td>2.2043</td>
<td>2.2043</td>
<td>2.2043</td>
</tr>
<tr>
<td>Cd–O (×6)</td>
<td>2.587(1)</td>
<td>2.587(1)</td>
<td>2.587(1)</td>
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</tr>
</tbody>
</table>

Table 3  The O x parameter and selected bond distances (Å) and angles (°) for Cd₂Tc₂O₇ and closely related oxides

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cd₂Tc₂O₇</th>
<th>Cd₂Re₂O₇</th>
<th>Cd₂Ru₂O₇</th>
<th>Cd₂Os₂O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–O</td>
<td>1.926(1)</td>
<td>1.938(2)</td>
<td>1.924(1)</td>
<td>1.928(1)</td>
</tr>
<tr>
<td>M–O–M</td>
<td>138.2(1)</td>
<td>137.7(4)</td>
<td>137.1</td>
<td>137.5(7)</td>
</tr>
<tr>
<td>O x parameter</td>
<td>0.3175(2)</td>
<td>0.3184(7)</td>
<td>0.3194(5)</td>
<td>0.319(2)</td>
</tr>
<tr>
<td>Ref.</td>
<td>This</td>
<td>He et al.</td>
<td>Wang and Sleigh</td>
<td>Mandrus et al.</td>
</tr>
</tbody>
</table>

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Starting with the structural parameters of CdTiO$_3$, which has the GdFeO$_3$-type structure (see Fig. 3), the Rietveld refinement with the 30 keV XRD data of CdTcO$_3$ converged to the parameters shown in Table 4 with an $R_{wp}$ of 10.8% and $\chi^2$ of 1.993. Again, due to the high-resolution, low-background quality of the data, the $R_{wp}$ is high but both the value of $\chi^2$ and the relatively smooth difference curve between the observed and calculated profiles shown in Fig. 4 support the accuracy of our structural model. Two impurities were readily seen in the high-resolution data with TcO$_2$ accounting for 2.82 wt.% and CdO 1.28 wt.%. Relevant bond distances and bond angles are shown in Table 5.

The structure of CdTcO$_3$ has orthorhombic symmetry $Pbnm$ and the symbol $a'b'b'$ under the Glazer scheme for labeling the BO$_6$ octahedra in ABO$_3$ perovskites.$^{27,28}$ The effect of the A cation on the Tc–O bonding in these materials can be understood by comparing some key structural data. For oxides with the perovskite structure the tolerance factor, $t = \langle A–O \rangle / \sqrt{2\langle B–O \rangle}$, gives an indication on how distorted the structure is from the ideal perovskite, which has a $t = 1$. Other good measures of these distortions are the M–O–M bond angles and the variation in the oxygen coordination around the A cation. These values and the average M–O distances are listed for CdTcO$_3$ and the closely related oxides of Ti$^{4+}$ and Ru$^{4+}$ with divalent cations in Table 6. One factor influencing the structure is simply one of cation size; in CdTcO$_3$ the octahedral network is more collapsed due the smaller Cd$^{2+}$ (131 pm for 12 CN) when compared to that of CaRuO$_3$ where the bigger Ca$^{2+}$ (134 pm for 12 CN) causes it to be closer to the idealized perovskite structure ($t = 1$). The second factor is related to the electronegativity of Cd.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
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<tbody>
<tr>
<td>Cd</td>
<td>4$c$</td>
<td>-0.0088(1)</td>
<td>0.0443(4)</td>
<td>1/4</td>
<td>0.0076(1)</td>
</tr>
<tr>
<td>Tc</td>
<td>4$b$</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.0023(1)</td>
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<tr>
<td>O1</td>
<td>8$d$</td>
<td>0.6844(4)</td>
<td>0.2987(4)</td>
<td>0.0551(3)</td>
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</tr>
<tr>
<td>O2</td>
<td>4$c$</td>
<td>0.098(1)</td>
<td>0.458(1)</td>
<td>1/4</td>
<td>0.008(1)</td>
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</tbody>
</table>

Fig. 4 Observed and calculated XRD powder profiles for CdTcO$_3$ with the difference curve shown below. Reflection marks are shown for CdTcO$_3$ and impurity phases. Inset shows a zoomed-in section of the powder patterns at higher $2\theta$. The wavelength of the X-rays is $\lambda = 0.41326$ Å.

Table 5 Selected interatomic distances (Å) and angles (°) in CdTcO$_3$ from room temperature powder XRD data. Standard uncertainties are shown in parentheses.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc–O1 ($\times$2)</td>
<td>1.957(2)</td>
<td>144.7(1)</td>
</tr>
<tr>
<td>Tc–O2 ($\times$2)</td>
<td>2.013(1)</td>
<td>146.6(1)</td>
</tr>
<tr>
<td>Cd–O2</td>
<td>2.261(3)</td>
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</tr>
<tr>
<td>O1–Tc–O2</td>
<td>2.13(1)</td>
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<tr>
<td>O1–Tc–O2</td>
<td>2.333(3)</td>
<td></td>
</tr>
<tr>
<td>O1–O2</td>
<td>2.764(2)</td>
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</tbody>
</table>

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Pb$_2$Tc$_2$O$_6$ shows a cusp-like transition around 140 K indicative of superconductivity around 1 K. The sudden drop in susceptibility measured, as shown in Fig. 5. Contrasting to Cd$_2$Tc$_2$O$_7$, the distortions of A cation environment (A–O) and M–O bonding where M is the transition metal. Distances are in Å, angles in °. The values for all the phases are from their room temperature phases, and standard uncertainties are shown in parentheses.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Average bond length (Å)</th>
<th>Average bond angle (°)</th>
<th>t</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTcO$_3$</td>
<td>2.013(1)</td>
<td>144.7(1); 146.6(1)</td>
<td>1.254(3)</td>
<td>0.971 This work</td>
</tr>
<tr>
<td>CaRuO$_3$</td>
<td>1.991(1)</td>
<td>148.9(1); 150.0</td>
<td>1.144(3)</td>
<td>0.979 Kobayashi et al.</td>
</tr>
<tr>
<td>CdTiO$_3$</td>
<td>1.9694(4)</td>
<td>150.5(1); 149.8(1)</td>
<td>1.084(1)</td>
<td>0.978 Sasaki et al.</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>1.9503(3)</td>
<td>156.6(1); 155.7(1)</td>
<td>0.877(1)</td>
<td>0.986 Sasaki et al.</td>
</tr>
</tbody>
</table>

The more electropositive the cation, the more it stabilizes the p orbitals of the O for bonding with the transition metal’s d orbitals. In other words, the more ionic the interaction between the A cation and the O anions, the more covalent the interaction between the transition metal and the O atoms. This can be seen from the large Ti–O bond distances in the CdTiO$_3$ than in CaTiO$_3$ (see Table 6). Since Cd has more covalent interactions with the oxygen atoms, as indicated by its more distorted O coordination and shorter Cd–O bond distances, the interaction between Tc and O atoms becomes more ionic.

3.2 Magnetic and electronic properties

The molar magnetic susceptibility, $\chi_{\text{m}}$, of Cd$_2$Tc$_2$O$_7$ with a 5 T applied field is shown in Fig. 5. The susceptibility indicates that Cd$_2$Tc$_2$O$_7$ does not display Curie (C/T) or Curie–Weiss (C/T − θ) behavior but instead Pauli paramagnetism above 225 K followed by a drop in $\chi$ below 225 K. The SQUID measurement was performed down to 1.8 K; studies below this temperature would determine whether Cd$_2$Tc$_2$O$_7$, like Cd$_2$Re$_2$O$_7$, also displays superconductivity around 1 K. The sudden drop in susceptibility of Cd$_2$Tc$_2$O$_7$ around 4 K may indicate the onset of superconductivity; curiously, this downturn in the magnetic susceptibility is common to several of the oxide samples as seen in Fig. 5.

For comparison with Cd$_2$Tc$_2$O$_7$, the magnetic susceptibilities of the isostructural Pb$_2$Tc$_2$O$_7$ and Bi$_2$Tc$_2$O$_7$ oxides were also measured, as shown in Fig. 5. Contrasting to Cd$_2$Tc$_2$O$_7$, Pb$_2$Tc$_2$O$_7$ shows a cusp-like transition around 140 K indicative of antiferromagnetic ordering. The low temperature region (below 50 K) for the susceptibility of Pb$_2$Tc$_2$O$_7$ shows some Curie behavior, most likely due to impurities. The behavior of Bi$_2$Tc$_2$O$_7$ also suggests some type of magnetic ordering below 150 K, albeit one not as sharp as in Pb$_2$Tc$_2$O$_7$, possibly due to a second-order type nature of the transition. The possible antiferromagnetic ordering in Bi$_2$Tc$_2$O$_7$ and Pb$_2$Tc$_2$O$_7$ would be consistent to that observed in other d$^0$ pyrochlore oxides such as Cd$_2$Os$_2$O$_7$ and Hg$_2$Ru$_2$O$_7$. For the Pb and Bi-based ruthenate pyrochlores, no such changes in their magnetic susceptibilities were observed, and those materials were classified as metallic conductors with Pauli paramagnetism.

It is interesting to compare the known properties of chemical and structurally related oxides to the pyrochlore technetates. The only insulating Cd$_2$M$_2$O$_7$ pyrochlores are those for M = Nb and Ta since they contain d$^0$ cations; the rest are conductors with the Os-based one showing an MI transition around 225 K.

3.2 Magnetic and electronic properties

The molar magnetic susceptibility, $\chi_{\text{m}}$, of Cd$_2$Tc$_2$O$_7$ with a 5 T applied field is shown in Fig. 5. The susceptibility indicates that Cd$_2$Tc$_2$O$_7$ does not display Curie (C/T) or Curie–Weiss (C/T − θ) behavior but instead Pauli paramagnetism above 225 K followed by a drop in $\chi$ below 225 K. The SQUID measurement was performed down to 1.8 K; studies below this temperature would determine whether Cd$_2$Tc$_2$O$_7$, like Cd$_2$Re$_2$O$_7$, also displays superconductivity around 1 K. The magnetic ordering in Cd$_2$Os$_2$O$_7$, however, was not detected by temperature dependent NPD measurements, indicating that the ordering occurs locally and never manifests into long-range order. Furthermore, the MI transition in Cd$_2$Os$_2$O$_7$ occurs without a crystallographic phase transition and is continuous. Measurements of physical properties such as specific heat further support a second-order transition. Singh et al. suggest through electronic structure calculations that the magnetic transition in Cd$_2$Os$_2$O$_7$ is due to the d$^0$ state, which lies at a higher density of states at the Fermi level, leading to a magnetic instability. Likewise, the reason why the pyrochlores Pb$_2$Tc$_2$O$_7$ and Bi$_2$Tc$_2$O$_7$ appear to order magnetically while Cd$_2$Tc$_2$O$_7$ does not may have to do with the fact that Tc is in a d$^0$ configuration in the first two while d$^0$ in Cd$_2$Tc$_2$O$_7$.

In contrast to the MI transition in Cd$_2$Os$_2$O$_7$ at 225 K, a second-order transition in Cd$_2$Re$_2$O$_7$ occurs at 200 K whereby the electrical resistivity decreases continuously down to low temperatures, until a superconducting state is reached around 1.1 K. Although believed to be a purely electronic transition at first, careful single crystal studies revealed a cubic-to-tetragonal and centrosymmetric-to-noncentrosymmetric change coinciding with the drop in resistivity and magnetic susceptibility at 200 K. Although much less studied, Cd$_2$Ru$_2$O$_7$ also displays...
similar features in the magnetic susceptibility data with similar transitions occurring at 100 K instead.\textsuperscript{25} Furthermore, Cd$_2$Ru$_2$O$_7$ is also a metallic conductor, but no one has reported its resistivity below 5 K to check for superconductivity.

For our compound Cd$_2$Tc$_2$O$_7$, the magnetic susceptibility data shows similar features to those of Cd$_2$Re$_2$O$_7$ as shown in Fig. 5. As observed for Cd$_2$Re$_2$O$_7$, the Tc analogue loses its magnetization by about 25–35\% at low temperatures. The density of states (DOS) for Cd$_2$Tc$_2$O$_7$ from our LMTO calculations support conductivity since the Fermi level is located in the $t_{2g}$ band of Tc, as shown in Fig. 6. Since Tc$^{5+}$ is $d^7$, the $t_{2g}$ manifold should be about a third filled. Indeed, the calculated DOS shows the Fermi level to be in a valley located between two of the three ‘peaks’ of the $t_{2g}$ band. Singh et al.\textsuperscript{34} calculated a similar electronic DOS for Cd$_2$Re$_2$O$_7$ where the Fermi level lies in a pseudogap that is a third of the way in the $t_{2g}$ band, suggesting semimetallicity. This could explain the observed blue-green and red colors in Cd$_2$Tc$_2$O$_7$ and Cd$_2$Re$_2$O$_7$, respectively, where interband transitions between the filled $d$-states and the conduction electrons lead to a plasmon absorption band in the visible range as observed in copper, gold, and ReO$_3$\textsuperscript{37}.

An interesting inelastic scattering study of Cd$_2$Re$_2$O$_7$ shows the formation of Raman-active phonon modes known as Goldstone modes that lead to several structural phase transitions below 200 K and therefore a different electronic state at low temperatures.\textsuperscript{38} The space groups of those low-temperature phases of Cd$_2$Re$_2$O$_7$ were found to be non-centrosymmetric, an interesting property for a material that is electrically conducting and even superconducting in its ground state.\textsuperscript{36,39} No doubt, Cd$_2$Tc$_2$O$_7$ along with Cd$_2$Ru$_2$O$_7$ merit more careful study to answer these outstanding questions and to better understand the subtle structure-property relationships in 4$d$ and 5$d$ metal-based pyrochlore oxides.

In contrast to Cd$_2$Tc$_2$O$_7$, the molar magnetic susceptibility of CdTcO$_3$, shown in Fig. 5, does not show the broad transition of Cd$_2$Tc$_2$O$_7$, and is weakly temperature dependent; this behavior does not suggest an ordering transition between 2 K and 300 K since the susceptibility remains mostly constant. However, this does not rule out antiferromagnetic ordering above room temperature. Therefore, LMTO calculations with spin-polarized Tc atoms were undertaken to make predictions. Comparing the calculated relative energies of the non-spin polarized with those of spin-polarized with ferromagnetic ordering shows the spin-polarized to be more stable by about 0.0357 eV. Another type of magnetic ordering was used in which the moments order antiferromagnetically leading to another lowering of the energy by 0.1818 eV. The resulting DOS of this spin-polarized LMTO calculation with antiferromagnetic ordering is shown in Fig. 7. The DOS plot of CdTcO$_3$ shows the Fermi level above filled $d$-states corresponding to half of the $t_{2g}$ band, so that the other half is left unfilled. These results make sense in light of the fact that in CdTcO$_3$, as in Pb$_2$Tc$_2$O$_7$ and Bi$_2$Tc$_2$O$_7$, Tc has a $d^9$ electron configuration. This half-filling of the $t_{2g}$ levels would promote a high-density of states at the Fermi level and therefore a magnetic instability towards ordering.

4 Conclusions and future work

After 40 years of inactivity in the area of ternary technetium oxides, we prepared the bismuth technetates in an earlier study.\textsuperscript{4} In the present study we prepare two new technetates with a different post-transition metal–Cd$_2$Tc$_2$O$_7$ with the pyrochlore-type structure and Cd$_2$TcO$_3$ with a distorted perovskite-type structure. For the pyrochlore, no doubt the highly charged Tc$^{5+}$ cations allow the formation of this phase due to the highly covalent nature of the Tc–O bond. This covalency should lead to metallic conductivity in Cd$_2$Tc$_2$O$_7$ as is the case in structurally related oxides Cd$_2$Re$_2$O$_7$, Cd$_2$Ru$_2$O$_7$, and Cd$_2$Os$_2$O$_7$. In addition, the calculated DOS of Cd$_2$Tc$_2$O$_7$ shows that the Fermi level is in a valley between two high DOS peaks in the $t_{2g}$ band. This leads to the prediction that Cd$_2$Tc$_2$O$_7$ should not have a magnetic instability and therefore no magnetic ordering, which accompanies the metal-to-insulator transition in Cd$_2$Os$_2$O$_7$. Instead, the behavior of Cd$_2$Tc$_2$O$_7$ is much closer to that of Cd$_2$Re$_2$O$_7$, a known superconductor where the value of $\chi_{mol}$ loses about 30\% of its value upon cooling below 200 K.

Future experiments on Cd$_2$Tc$_2$O$_7$ and the Ru analogue would establish what role d electron count plays in observing either superconductivity or an MI transitions. Low-temperature (mK range) electrical resistivity measurements or magnetic susceptibility measurements on Cd$_2$Tc$_2$O$_7$ would corroborate our prediction of metallicity in these oxides, including a possible superconducting ground-state as implied by our electronic structure calculations and magnetization data. For the perovskite phase CdTcO$_3$, the role of the post-transition metal Cd on

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**Fig. 6** Calculated densities of states of Cd$_2$Tc$_2$O$_7$ with the Fermi energy indicated by the dashed line at 0 eV.

**Fig. 7** Calculated densities of states of Cd$_2$Tc$_2$O$_7$ with the Fermi energy indicated by the dashed line at 0 eV.
Tc–O bonding and structure become apparent when compared to closely related perovskites such as SrRuO$_3$. In CdTeO$_3$, the more covalent interaction between Cd and O ions and the smaller size of the Cd$^{2+}$ cation lead to a fairly distorted perovskite with Tc–O–Tc bond angles around 145° and an average Tc–O bond length of around 2.07 Å. Nevertheless, our magnetic susceptibility data and electronic structure calculations point towards metallicity in this compound arising from Tc–O bonding.

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