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COMMUNICATION

## Mn<sub>2</sub>CoReO<sub>6</sub>: A Robust Multisublattice Antiferromagnetic Perovskite with Small A-Site Cations

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**Mn<sub>2</sub>CoReO<sub>6</sub>, the fourth known magnetic transition-metal-only double perovskite oxide (space group  $P2_1/n$ ) was synthesized at high pressure and temperature (8 GPa, 1350 °C). Large structural distortions are induced by the small A-site Mn<sup>2+</sup> cations. Mn<sub>2</sub>CoReO<sub>6</sub> exhibits complex magnetic properties with a robust antiferromagnetic order ( $T_N = 94$  K) involving all the cation sublattices.**

The search for new materials with potential spintronics applications is increasingly important to the future of microelectronics as the limit of Moore's Law approaches.<sup>1, 2</sup> Double perovskite (DP) oxides ( $A_2BB'O_6$ ) ( $A =$  alkali or rare earth metal,  $B =$  3d transition metal,  $B' =$  4d/5d transition metal) have been particularly important to this search since the discovery of Sr<sub>2</sub>FeMoO<sub>6</sub>.<sup>3-8</sup> The interesting magnetic and transport properties in these materials are primarily driven by interactions between the B and B'-cations, for which large spin orbit coupling and spin polarization of a late transition metal appears to be required.<sup>9, 10</sup>

In an archetypical DP, a large A-cation is 12-fold coordinated by oxygen while the smaller B-cations form a three dimensional

(3D) array of corner sharing  $B/B'O_6$  octahedra. DPs in which A and B are of similar size (possible through  $B/B'O_6$  tilting) are known to exhibit large structural distortions and distinct magneto-structural coupling behaviours. While there are exceptions, DPs with small A-site cations frequently require high pressure (>3 GPa) and temperature for their synthesis.<sup>11-14</sup>

In the so-far-rare cases in which all cations are transition metals, multiple magnetic sublattices can arise with unusual and intense interactions.<sup>15-20</sup> In this work, we present the fourth transition-metal-only DP (TMO-DP), Mn<sub>2</sub>CoReO<sub>6</sub>. Co and Re were selected as the B and B' site cations due to the interesting magnetic interactions exhibited in A<sub>2</sub>CoReO<sub>6</sub> DPs such as Pb<sub>2</sub>CoReO<sub>6</sub>.<sup>21-24</sup> Small black, plate-like crystals of Mn<sub>2</sub>CoReO<sub>6</sub> were synthesized at high pressure and temperature (8 GPa, 1625 K) in a Walker-Type multi-anvil device.

Analysis of neutron powder diffraction (NPD) data revealed a trace spinel-like impurity (Mn<sub>3</sub>O<sub>4</sub> or Mn<sub>3-x</sub>Co<sub>x</sub>O<sub>4</sub>)<sup>25</sup> which was included in refinements. Refinements indicated that the crystal structure of Mn<sub>2</sub>CoReO<sub>6</sub> (space group  $P2_1/n$ ) is analogous to preceding TMO-DPs Mn<sub>2</sub>MnReO<sub>6</sub>, Mn<sub>2</sub>FeReO<sub>6</sub>, and Mn<sub>2</sub>(Fe<sub>0.8</sub>Mo<sub>0.2</sub>)MoO<sub>6</sub>.<sup>17, 18, 20</sup> and to non-magnetic A site A<sub>2</sub>MnReO<sub>6</sub> ( $A =$  Ca, Sr) phases.<sup>26, 27</sup> (See ESI for concurring single crystal and powder X-ray and synchrotron results) Good contrast in neutron scattering lengths of the cations<sup>28</sup> means that NPD data are sensitive to antisite disorder. Refinements revealed almost complete ordering of Co and Re on the  $B/B'$  sites (referred to as Co<sub>B</sub> and Re<sub>B</sub>), and ~16% disorder between Mn on the A site (Mn<sub>A</sub>) and Co on the B site. The crystal structure has significant octahedral tilts, with Co – O – Re angles between 135 – 142° (relative to 180°). These tilts ( $a^+a^-c^+$  in Glazer notation) are similar to those in previous TMO-DPs<sup>17, 18, 20</sup> and noticeably larger than those in A<sub>2</sub>MnReO<sub>6</sub> ( $A =$  Ca, Sr).<sup>26, 27</sup> Large tilting optimises bonding around the small Mn<sup>2+</sup> ion (0.96 Å, 8-coordinate)<sup>29</sup> on the A site and emphasises the difficulty in introducing small ions into the perovskite lattice. The average Re – O bond length (1.939(2) Å at 200 K) observed for Mn<sub>2</sub>CoReO<sub>6</sub> is similar to that observed for Mn<sub>2</sub>MnReO<sub>6</sub> (1.930(2) Å at 300 K)<sup>17</sup> containing Re<sup>6+</sup>, and shorter than that

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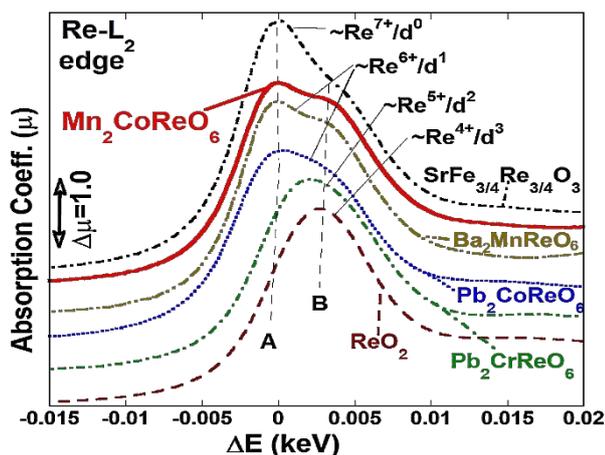
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**Figure 1.** The Re  $L_2$  edge for  $Mn_2CoReO_6$  compared to those of other standard octahedral Re-O compounds (spanning  $Re^{7+}/d^0$  to  $Re^{4+}/d^3$ ). Spectra have been shifted in energy to approximately align the B ( $e_g$ -hole-related) features. The zero of the relative energy scale ( $\Delta E$ ) was chosen as the nominal position of the A ( $t_{2g}$ -hole-related) features. Spectra have been displaced vertically for clarity.

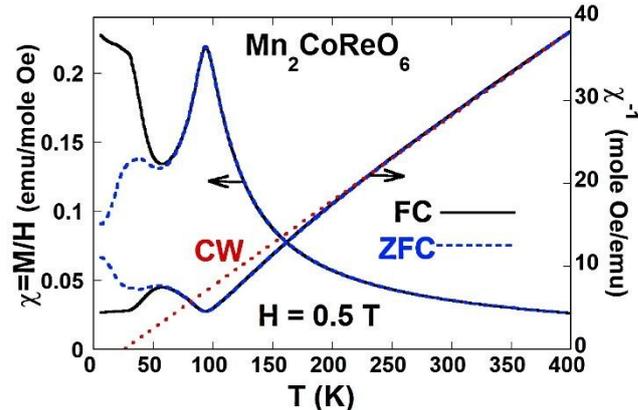
observed in  $Mn_2FeReO_6$  (1.961(9) Å), which contains both  $Re^{6+}$  and  $Re^{5+}$ .<sup>18</sup> X-ray absorption near-edge spectroscopy (XANES) was used to investigate the transition metal oxidation states and analysis of the Mn and Co K edges (and pre-edge features) suggested that both are in 2+ oxidation states, while the Re  $L_{2,3}$  edges (Figures 1 and ESI6.3) were consistent with  $Re^{6+}$  ( $5d^1$ ).

Magnetic susceptibility ( $\chi$ ) measurements (Figure 2) show a local maximum at 94 K, which coincides with the asymmetric peak in heat capacity (Figure ESI9.1), suggesting long-range magnetic order below  $T_N = 94$  K, while below  $\sim 50$  K, field-cooled and zero-field-cooled (FC and ZFC) measurements diverge. At high temperatures,  $\chi^{-1}$  is close to CW behaviour and suggests a paramagnetic moment of  $8.84 \mu_B$  per formula unit and a positive intercept (Weiss temperature) of 25.6 K. The paramagnetic moment is slightly lower than the theoretical moment for  $Mn_2CoReO_6$  ( $9.38 \mu_B$ ) and may reflect a slight reduction in  $Re^{6+}$  moment due to spin-orbit coupling. The positive x axis intercept of  $\chi^{-1}$  may indicate some underlying ferromagnetic (FM) interactions (despite long-range AFM order), although the temperature dependence of  $\chi$  may also arise from crystal field effects as reported for  $Sr_2CoReO_6$ <sup>22</sup> or be influenced by the presence of a trace ferrimagnetic  $Mn_3O_4$ -like phase.

Magnetisation measurements were also carried out as a function of applied field (Figure ESI7.1) and indicate very robust AFM order below 94 K with only a very slight decrease in  $T_N$  at higher fields. This implies that magneto-crystalline anisotropy appears strong enough that the applied H-field is unable to induce any significant continuous canting of the AFM order away from its preferred crystalline ordering direction.

Isothermal magnetization measurements (Figure ESI7.1) are consistent with paramagnetic behaviour for  $T \geq 150$  K. At lower temperatures, magnetization vs field is not linear. At 5 K, magnetization varies smoothly with field (giving no evidence for a field-induced magnetic transition), but gives a small total magnetization ( $\sim 1 \mu_B$ , more than an order of magnitude less

than the potential  $13.5 \mu_B$  /f.u.), consistent with the modest field response within an AFM state, small remnant

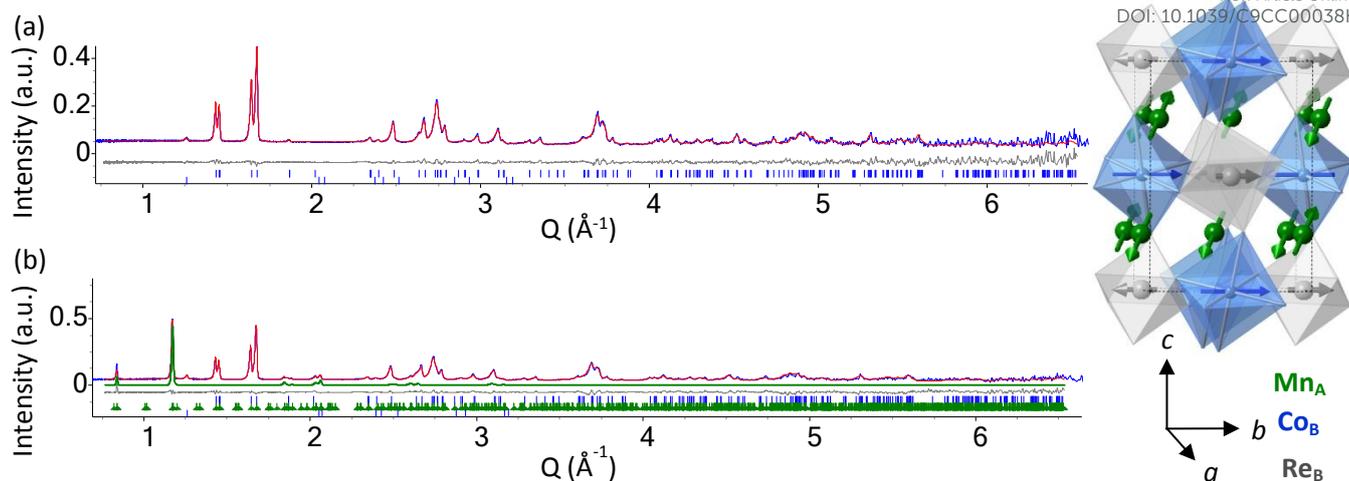


**Figure 2.** The  $H=0.5$  T, temperature dependent magnetic susceptibility,  $\chi$ , and the inverse susceptibilities,  $\chi^{-1}$ , for  $Mn_2CoReO_6$  collected under field cooled (FC) and zero field cooled (ZFC) conditions. The Curie Weiss (CW) fit to the high temperature  $\chi^{-1}$  data is indicated by a dotted line.

magnetization ( $\sim 0.1 \mu_B$ ), and a coercive field of  $\sim 0.5$  T. There are several possible explanations for this magnetization behaviour at low temperatures, including the presence of trace amounts of a ferrimagnetic phase as noted above. It is also possible that some form of spin reorientation transition (or evolution) is active in this temperature range. A change in the Re contribution in the magnetic order is also possible. Such changes are not inconsistent with the temperature dependent NPD results and are discussed further below. It is also possible that AFM domain effects are responsible for this  $T < 50$  K magnetic behavior. The NPD refinement found an  $\sim 16\%$  antisite disorder between A-site Mn and B-site Co. Such interchanging of  $S = 5/2$  and  $3/2$  at sites allows for a local uncompensated moment that, when coupled to other disorder effects, can enhance the coupling of external magnetic field. Above  $T_N$ , AFM fluctuations with modest net magnetic moments would respond to an external field and could motivate the FM components observed in  $\chi^{-1}$  for  $T > T_N$  (see Figure 2) and in the  $M(H)$  at 100 K (see Figure ESI7.1). Similarly, FC conditions would lead to a nucleation and growth of AFM domains with larger net moments aligned with the field, whereas ZFC conditions would lead to a low-magnetization/random-domain growth.

The electrical resistivity of  $Mn_2CoReO_6$  was measured and increased smoothly on cooling (Figure ESI8.1). The zero-field resistivity at 300 K ( $8.32 \Omega \text{ cm}$ ) is similar to  $Mn_2MnReO_6$  ( $6.80 \Omega \text{ cm}$  at 300 K)<sup>17</sup>.  $Mn_2CoReO_6$  shows semiconductor-like behaviour and the temperature-dependence of resistivity could be fitted by a variable-range hopping model ( $T_0^{1/2} = 157.04 \text{ K}^{1/2}$ ,  $\rho_0 = 6.208 \times 10^{-4} \Omega \cdot \text{cm}$ , see ESI) for  $T > 60$  K (below which  $Mn_2CoReO_6$  becomes too resistive). The temperature-dependent resistivity measured under a magnetic field of 7 T results were practically identical to those measured at 0 T, confirming a lack of magnetoresistance.

Low temperature NPD data were used to investigate the magnetic ordering further. On cooling below  $\sim 100$  K, additional magnetic Bragg reflections, consistent with magnetic ordering vector  $k = (\frac{1}{2} \frac{1}{2} 0)$ , were observed and increased in intensity on cooling. ISODISTORT<sup>30</sup> was used to explore possible magnetic



**Figure 3.** Refinement profiles for  $\text{Mn}_2\text{CoReO}_6$  using (a) 200 K NPD data (upper and lower blue ticks show peak positions for the main phase  $\text{Mn}_2\text{CoReO}_6$  and for  $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$  (fitted with Pawley phase), respectively) and (b) 60 K NPD data showing  $58^\circ$  bank data (upper, middle and lower ticks show peak positions for nuclear and magnetic phases and  $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$  Pawley phase, respectively). Observed, calculated and difference profiles are shown in blue, red and grey, respectively and in (b), magnetic scattering is highlighted in green. (c) shows 60 K magnetic structure with  $\text{Mn}_A$ ,  $\text{Co}_B$  and  $\text{Re}_B$  moments in green, blue and grey, respectively (oxides omitted for clarity).

structures and while irreps  $\text{mD1}+\text{mD2}$  only allowed magnetic moments on the  $A$  sites,  $\text{mD1}-\text{mD2}$  gave antiferromagnetic models with moments on  $\text{Mn}_A$  as well as  $\text{Co}_B$  and  $\text{Re}_B$  sites. The ‘mode inclusion’ method<sup>31, 32</sup> was used to consider possible symmetry adapted magnetic modes (by this method, the improvement in fit between observed and calculated diffraction patterns is compared for possible magnetic models). Ordered moments were indicated on all three sites. At temperatures down to  $\sim 50$  K, the best fit was obtained with  $\text{Co}_B$  and  $\text{Re}_B$  moments along  $[010]$  (with constraints to give equal moments for all crystallographically equivalent sites). The  $\text{Co}_B$  and  $\text{Re}_B$  moments were strongly correlated in refinements (as noted for the  $B$  site ions in  $\text{Mn}_2\text{MnReO}_6$ <sup>16</sup>) and so the  $\text{Re}_B$  moment was constrained to be collinear and a third of the magnitude of the  $\text{Co}_B$  moment. The absolute orientation of the  $\text{Mn}_A$  site moments is hard to determine from powder diffraction data due to peak overlap and the slight monoclinic distortion. Good fits were obtained with  $\text{Mn}_A$  moments close to the  $[101]$ , although other models of the same symmetry cannot be ruled out. This model, with collinear  $\text{Mn}_A$  moments nearly perpendicular to the  $B$  site moments, suggests two magnetic sublattices only weakly coupled and is consistent with the  $M(H)$  measurements that suggest a non-null anisotropy of the antiferromagnetic structure. This magnetic model was used in subsequent sequential refinements using data collected on warming (see ESI). This magnetic structure can also be described using the smaller triclinic cell of  $P_3-1$  symmetry with basis  $(-1\ 1\ -1)(-1\ 1\ 0)(0\ 2\ 0)$  relative to the nuclear unit cell. Final refinement details and bond lengths at 60 K are given in Tables ESI10.1-10.3, and refinement profiles and illustration of the 60 K magnetic structure are shown in Figure 3.

While most magnetic reflections increase smoothly on cooling (see ESI), some very weak reflections (at the gamma point, and indexed by the nuclear unit cell) are only observed at lower temperatures (e.g. 110 reflection observed below 40 K). We note that this is close in temperature to the FM-like feature

suggested by magnetic susceptibility measurements and may indicate a second magnetic transition on cooling, although the feature in susceptibility measurements may also be attributed to the trace of ferrimagnetic impurity or by domain effects. The additional magnetic reflections observed for  $T < 40$  K require some extra component described by a gamma point irrep of the parent structure, and all such possible magnetic modes on either the  $A$  or  $B$  sites were considered. It is likely that this component arises from the  $\text{Co}_B$  site, because the ordered moment on this site shows an anomaly around 40 K (Figure ESI11.2), but none of our models gave significant improvement in fit. A single peak is observed in heat capacity data at 94 K, which suggests a single magnetic phase transition in the bulk material. However, we note a slight change in the slope of heat capacity and a change in the lattice parameters, particularly the monoclinic  $\beta$  angle, at  $\sim 40$  K are observed (Figure ESI9.1). This may indicate a change in magnetic behaviour correlated with a slight structural change e.g. magnetic phase segregation, perhaps resulting from the cation  $\text{Mn} - \text{Co}$  antisite disorder. Further analysis to understand this low temperature magnetism is needed.

The 60 K magnetic structure described above is similar to that reported for  $\text{Mn}_2\text{MnReO}_6$ <sup>16</sup> in that spins on both the  $A$  and  $B$  sites are close to perpendicular. This implies that, despite description by the same irreducible representation, the coupling between the  $A$  and  $B$  sublattices in  $\text{Mn}_2\text{CoReO}_6$  is weak. This might explain the difference in transport properties between semiconducting  $\text{Mn}_2\text{CoReO}_6$  (with no magnetoresistance) and the half-metallic  $\text{Mn}_2\text{FeReO}_6$ .<sup>18</sup> From the evolution of the  $\text{Mn}_A$  and  $\text{Co}_B$  site moments and magnetic peak intensities (see ESI), these two sublattices may order at slightly different temperatures, with the  $\text{Co}_B$  site ordering a few Kelvin above the  $\text{Mn}_A$  sublattice (analogous to the magnetic ordering reported for  $\text{Mn}_2\text{MnReO}_6$ <sup>16</sup>), but NPD data collected at smaller temperature intervals would be necessary to confirm this. The low moment observed for the  $\text{Co}^{2+}$  site from NPD is

surprising and may indicate deficiencies of our model; the low temperature magnetic behaviour is not yet understood and the change in magnetic behaviour suggested by magnetic susceptibility measurements below ~40 K may arise from the B-site ions and further investigations are needed.

In conclusion, we have studied the nuclear and magnetic structures of Mn<sub>2</sub>CoReO<sub>6</sub>. Transport measurements suggest that Mn<sub>2</sub>CoReO<sub>6</sub> is an Efros–Shklovskii variable-range-hopping semiconductor with negligible magnetoresistance. Magnetization versus temperature measurements over fields from 0.5 T – 7 T indicate that the transition at 94 K is very robustly antiferromagnetic. According to NPD, all the magnetic cations order with a  $k = (\frac{1}{2} \frac{1}{2} 0)$  propagation vector below ~100 K. The Mn A site cations order with moment close to the [101] direction, whereas the B/B' cations order along the [010] direction. The different moment directions indicate a weak inter-sublattice coupling. NPD data suggests a possible second magnetic transition at ~40 K, with propagation vector  $k = 0$ , likely due to a spin reorientation involving the B/B' ions, but further investigation is required to fully understand this transition. Future investigations, such as first principles calculations and further neutron experiments, will help to understand the electronic and magnetic structures.

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### Conflicts of interest

The authors declare that there are no conflicts of interest.

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