Competing antiferromagnetic orders in the double perovskite Mn2MnReO6 (Mn3ReO6)

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Competing antiferromagnetic orders in the double perovskite \( \text{Mn}_2\text{MnReO}_6 \) (\( \text{Mn}_3\text{ReO}_6 \))


The new double perovskite \( \text{Mn}_3\text{MnReO}_6 \) has been synthesised at high pressure. \( \text{Mn}^{2+} \) and \( \text{Re}^{6+} \) spins order antiferromagnetically through two successive transitions that are coupled by magnetoelastic effects, as order of the Mn spins at 109 K leads to lattice distortions that reduce frustration prompting Re order at 99 K.

Double perovskites \( \text{A}_2\text{BB}'\text{O}_6 \) with ordering of \( \text{B}/\text{B}' \) transition metal cations on the \( \text{ABO}_3 \) perovskite-type lattice are an important group of oxide materials. \(^1\) Some examples such as \( \text{Sr}_2\text{FeMoO}_6 \) and \( \text{Sr}_2\text{FeReO}_6 \) are ferrimagnetic, spin-polarised conductors with large low-field tunnelling magneto resistances. \(^2\) Many other double perovskites have antiferromagnetic ground states that may be frustrated due to the tetrahedral geometry of the \( \text{B} \) and \( \text{B}' \) sublattices,\(^3\,4\) leading to a spin liquid ground state in \( \text{Ba}_2\text{MoO}_6 \).\(^5\)

The \( \text{A}^{2+} \) (\( \text{Ca, Sr, Ba, Pb} \)) cations in double perovskites synthesised at ambient pressure are relatively large and non-magnetic. However, perovskites with only the smaller high spin \( \text{Mn}^{2+} \) ion at the \( \text{A} \) sites have recently been synthesised at high pressure and temperature conditions, introducing additional magnetic functionality. \( \text{MnO}_3 \) or \( \text{VO}_3 \) is metallic due to itinerancy of the \( \text{V}^{4+} \) 3d\(^1 \) states, as found in \( \text{CaV}_2\text{O}_5 \) and \( \text{SrV}_2\text{O}_5 \), but also has coexisting helimagnetic order of localised \( S = 5/2 \) \( \text{Mn}^{2+} \) spins. \(^6\) The double perovskite \( \text{Mn}_2\text{FeSbO}_6 \) also has low temperature incommensurate antiferromagnetic \( \text{Mn} \) spin order.\(^7\) \( \text{Mn}_2\text{FeReO}_6 \), also recently discovered through high pressure synthesis,\(^8\,9\) is particularly notable as it has a high Curie temperature (520 K), ferrimagnetic \( \text{Fe}^{3+}/\text{Re}^{5+} \) spin order, and negative tunnelling magneto resistance like other \( \text{A}_2\text{FeReO}_6 \) double perovskites. The \( \text{Mn}^{2+} \) spins enhance the bulk magnetisation giving a record value for transition-metal double perovskites,\(^8\) however, a further Mn magnetic ordering transition at 75 K frustrates and cants \( \text{Fe}^{3+} \) and \( \text{Re}^{5+} \) spins, resulting in a novel switch from negative to large positive magnetoresistances at low temperatures. \( \text{Mn}_2\text{FeReO}_6 \) was the first example of a double perovskite with magnetic transition metal ions at all of the cation sites. Here we have investigated whether \( \text{Fe} \) can be replaced by \( \text{Mn} \) and we report the synthesis and properties of a new double perovskite \( \text{Mn}_2\text{MnReO}_6 \) (\( \text{Mn}_3\text{ReO}_6 \)) which shows successive antiferromagnetic ordering transitions for Re and Mn spins at 99 and 109 K respectively.

10-20 mg samples of \( \text{Mn}_2\text{MnReO}_6 \) were synthesised from a stoichiometric mixture of \( \text{Mn}_3\text{O}_4 \) and \( \text{ReO}_3 \) in a Pt capsule at 8 GPa and 1400 °C in a Walker-type multi-anvil press. The best polycrystalline product was highly phase pure with traces of \( \text{MnO} \) (<3 wt%) also observed. Small single crystals were separated from the walls of the capsule from one run and used for structure determination. Results are summarised in Table I and further details of the single crystal analysis and powder x-ray and neutron studies are in ESI.

\( \text{Mn}_2\text{MnReO}_6 \) has a monoclinic double perovskite structure like those of \( \text{A}_2\text{MnReO}_6 \) (\( \text{A} = \text{Ca and Sr} \)) analogues.\(^10\,11\) A small antisite disorder (3.7 %) for Mn/Re at \( \text{B}/\text{B}' \) sites was observed in the single crystal, showing that the degree of cation ordering is very high. Bond valence sum (BVS) calculations in Table I show that the charge distribution is \( \text{Mn}^{2+}\text{Mn}^{2+}\text{Re}^{6+} \) in contrast to that of \( \text{Mn}^{2+}\text{Fe}^{3+}\text{Re}^{5+} \). The crystal structure is substantially distorted due to the small \( \text{Mn}^{2+} \) cations at the \( \text{A} \) sites. The ideal 12-coordination of the \( \text{Mn}_3 \) site is split into four short (2.10 – 2.16 Å), four medium (2.61 – 2.79 Å) and four long (3.33 – 3.56 Å) \( \text{Mn}_3\text{O} \) distances. The four short bonds create a distorted tetrahedral environment around \( \text{Mn}_3 \). The \( \text{Mn}_8\text{O}_6 \) and \( \text{Re}_6\text{O}_6 \) octahedra are also distorted, with \( \text{ReO}_6 \) showing a small trigonal compression (two 1.88 and four 1.93-1.97 Å bonds) consistent with Jahn-Teller distortion from orbital order of the \( \text{d}^4 \) \( \text{Re}^{5+} \) ions. Large tilts of the octahedra are observed, with \( \text{Mn}_8\text{O}-\text{Re} \) angles of 135 - 140° deviating far from the ideal 180° value.

Magnetic susceptibility measurements in Figure 1 show that \( \text{Mn}_2\text{MnReO}_6 \) is Curie-Weiss paramagnetic at high temperatures. A fit to the inverse susceptibility gives a Weiss
temperature of $\theta = -147(1)$ K, showing that antiferromagnetic exchange interactions are dominant, and a paramagnetic moment of $\mu_{\text{eff}} = 4.9(1)$ $\mu_B$ per transition metal ion, close to the predicted spin-only value of 5.20 $\mu_B$ for Mn$_2^6$Mn$_2^6$Re$_6^{10}$O$_{17}$. The susceptibility maximum at 109 K evidences an antiferromagnetic spin ordering, and a change of slope at 99 K is consistent with the second magnetic transition revealed by neutron diffraction below. Divergence of zero field cooled (ZFC) and field cooled (FC) susceptibilities below ~40 K may evidence a trace of the ferrimagnetic impurity Mn$_3$O$_4$, although this was not seen in the powder diffraction patterns. No magnetic or structural anomalies from Mn$_2$MnReO$_6$ are apparent in the neutron data near 40 K.

Table I. X-ray single crystal refinement results (atomic coordinates, equivalent thermal B-factors, BVS's, and selected bond lengths) for Mn$_2$MnReO$_6$ at 120 K (space group $P2_1/n$; $a = 5.2708(3)$ Å, $b = 5.3869(4)$ Å, $c = 7.7100(5)$ Å; $\beta = 90.097(5)^\circ$).

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$\beta_{eq}$ (Å$^2$)</th>
<th>BVS</th>
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<tr>
<td>Mn$_{\text{Mn}}$</td>
<td>0.5011(1)</td>
<td>0.9516(2)</td>
<td>0.2429(1)</td>
<td>0.68(2)</td>
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<tr>
<td>Mn$_{\text{Re}}$</td>
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<td>1/2</td>
<td>0</td>
<td>0.29(1)</td>
<td>5.9</td>
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<tr>
<td>Re$^*$</td>
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<td>0</td>
<td>0</td>
<td>0.44(2)</td>
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<tr>
<td>O1</td>
<td>0.1212(5)</td>
<td>0.0707(7)</td>
<td>0.2366(3)</td>
<td>0.59(6)</td>
<td>2.0</td>
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<tr>
<td>O2</td>
<td>0.6906(5)</td>
<td>0.1725(5)</td>
<td>0.0577(3)</td>
<td>0.81(6)</td>
<td>2.1</td>
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<tr>
<td>O3</td>
<td>0.8462(5)</td>
<td>0.7020(5)</td>
<td>0.0713(3)</td>
<td>0.75(6)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Bond lengths (Å)

- Mn$_{\text{O1}-\text{O2}}$ (x2) 1.26(4) Re$_{\text{O1}-\text{O2}}$ (x2) 1.96(9)
- Mn$_{\text{O2}-\text{O3}}$ (x2) 1.20(4) Mn$_{\text{O2}-\text{O3}}$ (x2) 1.93(0)
- Mn$_{\text{O3}-\text{O1}}$ (x3) 1.19(3) Mn$_{\text{O3}-\text{O1}}$ (x3) 1.88(1)
- Mn$_{\text{O1}}$ (x1) 1.20(3) Mn$_{\text{O2}}$ (x1) 2.61(4)
- Mn$_{\text{O1}}$ (x1) 1.25(7) Mn$_{\text{O3}}$ (x1) 2.62(3)
- Mn$_{\text{O2}}$ (x1) 1.11(3) Mn$_{\text{O3}}$ (x1) 2.12(5)
- Mn$_{\text{O2}}$ (x1) 2.69(4) Mn$_{\text{O3}}$ (x1) 2.78(7)
- Mn$_{\text{O1}}$ (x1) 3.33(1) Mn$_{\text{O3}}$ (x1) 3.40(1)
- Mn$_{\text{O2}}$ (x1) 3.56(1) Mn$_{\text{O3}}$ (x1) 3.56(2)

Angles (°)

- Mn$_{\text{O1}-\text{Re}}$ 137.7(2)
- Mn$_{\text{O2}-\text{Re}}$ 140.2(2) Mn$_{\text{O3}-\text{Re}}$ 135.2(1)

* Mn$_{\text{Mn/Re}}$ antisite disorder = 3.7(4)%

Fig. 1. Temperature evolution of the direct and inverse magnetic susceptibilities of Mn$_2$MnReO$_6$ under a 0.5 T field showing the 109 K spin ordering transition (open/filled points are ZFC/FC data). The Curie-Weiss fit to the inverse ZFC data is shown as a broken line.

Fig. 2. Fits to powder neutron diffraction data for Mn$_2$MnReO$_6$ at 10 and 200 K. The nuclear structures of Mn$_2$MnReO$_6$ (upper reflection markers) and MnO (1 wt. %; lower markers) are fitted to the 200 K data. Magnetic structures for both phases are additionally fitted to the 10 K pattern.

The onset of antiferromagnetic order in Mn$_2$MnReO$_6$ is marked by the appearance of several magnetic diffraction peaks below 109 K. However, the temperature variation of the magnetic intensities (see inset to Figure 3) shows that a further spin transition occurs at 99 K. All of the Mn$_2$MnReO$_6$ magnetic peaks are indexed by the $k = (1/2 1/2 0)$ propagation vector. Analysis of the 10 K magnetic neutron data reveals that all of the moments lie in the $ab$-plane (details are in ESI). The Mn$_{\text{Mn}}$, Mn$_{\text{Re}}$ and Re spins form three independent antiferromagnetic sublattices. Initial refinements showed that Mn$_{\text{Mn}}$ and Mn$_{\text{Re}}$ spins are approximately perpendicular, and best fits were obtained when they were constrained to be parallel to [110] and [110] directions respectively. Re moments are small and were constrained to be collinear with Mn$_{\text{Re}}$ spins; other directions did not improve the fit. The thermal evolution of the refined model shows that the Mn$_{\text{Mn}}$ and Mn$_{\text{Re}}$ spins order at the upper transition at $T_{\text{Mn}} = 109$ K, whereas Re moments order separately at $T_{\text{Re}} = 99$ K. Thermal variations of the ordered moments and lattice strains are shown in Figure 3, and magnetic structures in the two regimes are in Figure 4.

The (upper) magnetic ordering temperature of 109 K for Mn$_2$MnReO$_6$ is comparable to those of 110 and 120 K for Ca$_2$MnReO$_6$ and Sr$_2$MnReO$_6$.$^{10}$ However the latter materials are both ferrimagnets, with simultaneous $k = (0 0 0)$ order of Mn and Re spins observed in a neutron diffraction study of Sr$_2$MnReO$_6$.$^{15}$ Hence the $k = (1/2 1/2 0)$ antiferromagnetism of Mn$_2$MnReO$_6$ with separate ordering transitions for the two transition metal B-site sublattices, which is very unusual in double perovskites, shows that interactions of B-site spins with

Four high pressure processes were combined to give a ~70 mg sample of Mn$_2$MnReO$_6$ for neutron powder diffraction to investigate the low temperature properties further. Figure 2 displays the profiles at 10 and 200 K. Rietveld refinements showed that the monoclinic $P2_1/n$ structure is retained down to the lowest measured temperature of 10 K. A greater degree (12%) of Mn$_{\text{Mn/Re}}$ antisite disorder was observed than in the single crystal, this probably reflects slight compositional variations between the combined polycrystalline samples.
Mn$_3$ moments are significant and suppress the Re spin order. Antiferromagnetic order within B/B’ tetrahedral networks is frustrated in double perovskites, but Mn$_2$MnReO$_6$ also has frustrated interactions between A and B/B’ cations, as each Mn$_3$ spin has 2 up and 2 down spins from the surrounding Mn$_8$ and Re spin tetrahedra, and each B/B’ site spin has 4 up and 4 down Mn$_3$ spins as neighbours. This results in perpendicular alignment of A and B/B’ spins to maximise antismmmetric Dzyaloshinskii-Moriya interactions. The relative strengths of the competing antiferromagnetic orders are revealed by the moment variations in Fig. 3. Below $T_{\text{Mn}} = 109$ K the ordered Mn$_3$ moment rises rapidly up to 1.9$\mu_B$ at 99 K whereas Mn$_A$ increases more slowly to 1.1 $\mu_B$, showing that dominant Mn$_B$ order partially frustrates Mn$_A$ spins and fully frustrates Re order. However, below $T_{\text{NA}} = 99$ K further Mn$_B$ order is frustrated as the moment saturates at 2.0 $\mu_B$ while less-frustrated Mn$_3$ and Re spins rise to saturated moments of 4.5 and 1.0 $\mu_B$, close to ideal values of 5 and 1 $\mu_B$ respectively.

Although the magnetic structure of Mn$_3$MnReO$_6$ appears frustrated as discussed above, this is not reflected by the ratio $-\theta/T_{\text{NB}} = 1.3$ which is close to unity. This demonstrates that monoclinic lattice distortion relieves much of the frustration by breaking the degeneracy of Mn$_{\mu-\sigma}$–Re superexchange interactions. Further evidence comes from observed anomalies in lattice parameters at the two transitions as shown in Figure 3 and ESI. The change in thermal expansion of $c$ from positive to negative on cooling through $T_{\text{Mn}}$ increases the monoclinic distortion as $a,b < c/\sqrt{2}$. This reduces frustration further and so is the likely factor that drives the long range order of Re spins at 99 K. The proximity of the two antiferromagnetic transitions thus arises from magnetoelastic effects. Re spin order further changes the magnetoelastic coupling as evidenced by the anomaly in $\beta$ at $T_{\text{NB}}$.

In conclusion, Mn$_2$MnReO$_6$ is the first example of a A$_2$B’BO$_6$ double perovskite with antiferromagnetically ordered transition metal spins at all cation sites. Frustration between the three antiferromagnetic sublattices results in perpendicular orientations of the A and B/B’ spins and long range magnetic ordering through two successive antiferromagnetic transitions. These show an unusual coupling through magnetoelastic effects, as order of the Mn spins at $T_{\text{Mn}} = 109$ K leads to lattice distortions that reduce frustration leading to Re spin order at $T_{\text{Re}} = 99$ K. Around 650 A$_2$B’BO$_6$ double perovskite oxides are previously reported but Mn$_3$FeReO$_6$ and Mn$_2$MnReO$_6$ are the only two with magnetic transition metal ions at all sites, and both have novel magnetic properties due to the presence of A-site Mn$^{2+}$, so it is likely that many more interesting ‘all transition metal’ double perovskites will be accessible through high pressure synthesis.

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Notes and references