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Competing antiferromagnetic orders in the double perovskite Mn₂MnReO₆ (Mn₃ReO₆)†

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The new double perovskite $\rm Mn_2MnReO_6$ has been synthesised at high pressure. $\rm Mn^{2+}$ and $\rm Re^{6+}$ 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 A₂BB'O₆ with ordering of B/B' transition metal cations on the ABO₃ perovskite-type lattice are an important group of oxide materials.¹ Some examples such as Sr₂FeMoO₆ and Sr₂FeReO₆ are ferrimagnetic, spin-polarised conductors with large low-field tunnelling magnetoresistances.² Many other double perovskites have antiferromagnetic ground states that may be frustrated due to the tetrahedral geometry of the B and B' sublattices,^{3,4} leading to a spin liquid ground state in Ba₂YMoO₆.⁵

The A²⁺ (= Ca, Sr, Ba, Pb) cations in double perovskites synthesised at ambient pressure are relatively large and nonmagnetic. However, perovskites with only the smaller high spin Mn²⁺ ion at the A sites have recently been synthesised at high pressure and temperature conditions, introducing additional magnetic functionality. MnVO₃ perovskite is metallic due to itinerancy of the V⁴⁺ 3d¹ states, as found in CaVO₃ and SrVO₃, but also has coexisting helimagnetic order of localised $S = 5/2 \text{ Mn}^{2+}$ spins.6 The double perovskite Mn₂FeSbO₆ also has low temperature incommensurate antiferromagnetic Mn spin order.⁷ Mn₂FeReO₆, also recently discovered through high pressure synthesis,8,9 is particularly notable as it has a high Curie temperature (520 K), ferrimagnetic Fe3+/Re5+ spin order, and negative tunnelling magnetoresistance like other A2FeReO6 double perovskites. The Mn²⁺ 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 Fe3+ and Re5+ spins, resulting in a novel

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switch from negative to large positive magnetoresistances at low temperatures. Mn₂FeReO₆ was the first example of a double perovskite with magnetic transition metal ions at all of the cation sites. Here we have investigated whether Fe can be replaced by Mn and we report the synthesis and properties of a new double perovskite Mn₂MnReO₆ (Mn₃ReO₆) which shows successive antiferromagnetic ordering transitions for Re and Mn spins at 99 and 109 K respectively.

10–20 mg samples of $\rm Mn_2MnReO_6$ were synthesised from a stoichiometric mixture of $\rm Mn_3O_4$ and $\rm ReO_2$ 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 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 1 and further details of the single crystal analysis and powder X-ray and neutron studies are in ESI.†

Mn₂MnReO₆ has a monoclinic double perovskite structure like those of A₂MnReO₆ (A = Ca and Sr) analogues. ^{10,11} A small antisite disorder (3.7%) for Mn/Re at B/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 1 show that the charge distribution is Mn₂²⁺Mn²⁺Re⁶⁺O₆, in contrast to that of Mn₂²⁺Fe³⁺Re⁵⁺O₆. The crystal structure is substantially distorted due to the small Mn2+ cations at the A sites. The ideal 12-coordination of the Mn_A 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) Mn_A-O distances. The four short bonds create a distorted tetrahedral environment around Mn_A. The Mn_BO₆ and ReO₆ octahedra are also distorted, with ReO6 showing a small tetragonal compression (two 1.88 and four 1.93-1.97 Å bonds) consistent with Jahn-Teller distortion from orbital order of the 5d1 Re6+ ions. Large tilts of the octahedra are observed, with Mn_B-O-Re angles of 135-140° deviating far from the ideal 180° value.

Magnetic susceptibility measurements in Fig. 1 show that Mn_2MnReO_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

Angles (°)

 Mn_B -O2-Re

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Table 1 X-ray single crystal refinement results (atomic coordinates, equivalent thermal B-factors, BVS's, and selected bond lengths) for Mn_2MnReO_6 at 120 K (space group $P2_1/n$; a = 5.2708(3) Å, b = 5.3869(4) Å, $c = 7.7100(5) \text{ Å}; \beta = 90.097(5)^{\circ}$

	x	у	z	$B_{\mathrm{eq.}}\left(\mathring{\mathrm{A}}^{2}\right)$	BVS
Mn_A	0.5011(1)	0.9516(2)	0.2429(1)	0.68(2)	2.0
Mn_B^a	1/2	1/2	0	0.29(1)	2.3
Re^a	0	0	0	0.44(2)	5.9
O1	0.1212(5)	0.0707(7)	0.2366(3)	0.59(6)	2.0
O2	0.6906(5)	0.1725(5)	0.0577(3)	0.81(6)	2.1
O3	0.8462(5)	0.7020(5)	0.0713(3)	0.75(6)	2.0
Bond lengths (Å)					
Mn_B -O1 (×2)		2.164(2)	Re-O1 (×2)		1.969(2)
Mn_B -O2 (×2)		2.078(2)	Re-O2 (×2)		1.930(2)
Mn_B -O3 (×2)		2.194(3)	Re-O3 (×2)		1.881(3)
Mn _A -O1		2.103(1)	Mn_A -O2		2.614(2)
Mn _A -O1		2.157(1)	Mn_A -O3		2.622(3)
Mn_A -O2		2.111(1)	Mn_A -O3		2.125(3)
Mn_A -O2		2.694(2)	Mn_A -O3		2.787(3)
Mn _A -O1		3.331(2)	Mn_A -O1		3.400(1)
Mn_A -O2		3.561(2)	Mn_A -O3		3.562(2)

Mn_B-O1-Re

Mn_B-O3-Re

137.7(2)

135.2(1)

140.2(2)

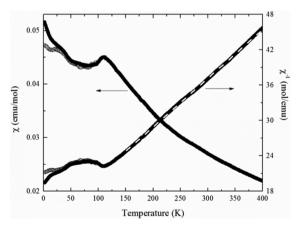


Fig. 1 Temperature evolution of the direct and inverse magnetic susceptibilities of Mn₂MnReO₆ under a 0.5 T field showing the 109 K spin ordering transition (open/filled points are ZFC/FC data). The Curie-Weiss fit to the inverse ZFC data is shown as a broken line

interactions are dominant, and a paramagnetic moment of $\mu_{\rm eff}$ = 4.9(1) $\mu_{\rm B}$ per transition metal ion, close to the predicted spin-only value of 5.20 $\mu_{\rm B}$ for Mn₂²⁺Mn²⁺Re⁶⁺O₆. 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 Mn₃O₄, although this was not seen in the powder diffraction patterns. No magnetic or structural anomalies from Mn₂MnReO₆ are apparent in the neutron data near 40 K.

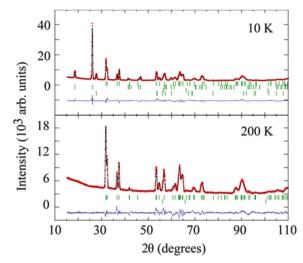


Fig. 2 Fits to powder neutron diffraction data for Mn₂MnReO₆ at 10 and 200 K. The nuclear structures of Mn₂MnReO₆ (upper reflection markers) and MnO (1 wt%; lower markers) are fitted to the 200 K data. Magnetic structures for both phases are additionally fitted to the 10 K pattern.

Four high pressure products were combined to give a \sim 70 mg sample of Mn₂MnReO₆ for neutron powder diffraction to investigate the low temperature properties further. Fig. 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_B/Re antisite disorder was observed than in the single crystal, this probably reflects slight compositional variations between the combined polycrystalline samples.

The onset of antiferromagnetic order in Mn₂MnReO₆ is marked by the appearance of several magnetic diffraction peaks below 109 K. However, the temperature variation of the magnetic intensities (see inset to Fig. 3) shows that a further spin transition occurs at 99 K. All of the Mn₂MnReO₆ magnetic peaks are indexed

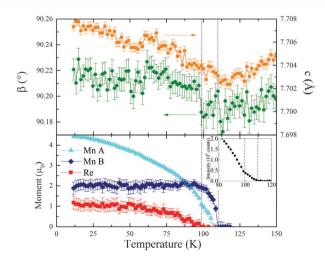


Fig. 3 Temperature evolution of the unit cell parameters c and β (upper panel) and magnetic moments (lower panel) for Mn₂MnReO₆, showing the T_{Re} = 99 and T_{Mn} = 109 K spin transitions. The inset shows the variation of the (1/2 1/2 1) magnetic peak intensity around the transitions.

^a Mn_B/Re antisite disorder = 3.7(4)%.

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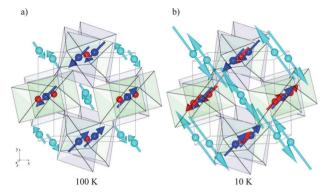


Fig. 4 (a) Crystal and magnetic structures of Mn₂MnReO₆ shown for the nuclear $P2_1/n$ cell at (a) 100 K with order of only Mn_A and Mn_B moments, and (b) 10 K showing order of all spins. Mn_A/Mn_B/Re are cyan/blue/red spheres.

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_A, Mn_B and Re spins form three independent antiferromagnetic sublattices. Initial refinements showed that Mn_A and Mn_B 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_B spins; other directions did not improve the fit. The thermal evolution of the refined model shows that the Mn_A and $\mathrm{Mn_{B}}$ spins order at the upper transition at T_{Mn} = 109 K, whereas Re moments order separately at $T_{\rm Re}$ = 99 K. Thermal variations of the ordered moments and lattice strains are shown in Fig. 3, and magnetic structures in the two regimes are in Fig. 4.

The (upper) magnetic ordering temperature of 109 K for Mn₂MnReO₆ is comparable to those of 110 and 120 K for Ca₂MnReO₆ and Sr₂MnReO₆. 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 Sr₂MnReO₆. ¹¹ Hence the $k = (1/2 \ 1/2 \ 0)$ antiferromagnetism of Mn₂MnReO₆ 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 Mn_A moments are significant and suppress the Re spin order. Antiferromagnetic order within B/B' tetrahedral networks is frustrated in double perovskites, but Mn₂MnReO₆ also has frustrated interactions between A and B/B' cations, as each Mn_A spin has 2 up and 2 down spins from the surrounding Mn_B and Re spin tetrahedra, and each B/B'-site spin has 4 up and 4 down Mn_A spins as neighbours. This results in perpendicular alignment of A and B/B' spins to maximise antisymmetric Dzyaloshinskii-Moriya interactions. The relative strengths of the competing antiferromagnetic orders are revealed by the moment variations in Fig. 3. Below $T_{\rm Mn}$ = 109 K the ordered Mn_B moment rises rapidly up to 1.9 μ_B at 99 K whereas Mn_A increases more slowly to 1.1 μ_B , showing that dominant Mn_B order partially frustrates Mn_A spins and fully frustrates Re order. However, below T_{NA} = 99 K further Mn_B order is frustrated as the moment saturates at 2.0 μ_B while less-frustrated Mn_A and Re spins rise to saturated moments of 4.5 and 1.0 $\mu_{\rm B}$, close to ideal values of 5 and 1 $\mu_{\rm B}$ respectively.

Although the magnetic structure of Mn₂MnReO₆ appears frustrated as discussed above, this is not reflected by the ratio $-\theta/T_{\rm NB}$ = 1.3 which is close to unity. This demonstrates that monoclinic lattice distortion relieves much of the frustration by breaking the degeneracy of Mn_B-O-Re superexchange interactions. Further evidence comes from observed anomalies in lattice parameters at the two transitions as shown in Fig. 3 and ESI.† The change in thermal expansion of c from positive to negative on cooling through T_{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 β at T_{Re} .

In conclusion, Mn₂MnReO₆ is the first example of a A₂BB'O₆ 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_{Mn} = 109 K leads to lattice distortions that reduce frustration leading to Re spin order at $T_{\rm Re}$ = 99 K. Around 650 A₂BB'O₆ double perovskite oxides are previously reported¹ but Mn₂FeReO₆ and Mn₂MnReO₆ 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 Mn2+, so it is likely that many more interesting 'all transition metal' double perovskites will be accessible through high pressure synthesis.

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