**Mn₃MnNb₂O₉**: high-pressure triple perovskite with 1 : 2 B-site order and modulated spins

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The first triple perovskite with Mn in A- and 1:2 B-site order Mn₃MnNb₂O₉, prepared by high pressure phase transformation of the magnetodielectric Mn₃Nb₂O₉, is reported herein. It has a complex magnetic behaviour with a transition from a collinear AFM into an evolving incommensurate spin density wave (SDW) further stabilised into a lock-in structure dictated by the B-site order.

ABO₃ materials with perovskite structure (Pv) are of great interest in the search for new compounds with enhanced properties. Pv accommodates a wide range of chemical compositions and possible cation order into both A and B sites. Among these derivatives, several examples are known for 1:1 order into AA′B₂O₆ or A₂B′O₆ double perovskites (DPv) and more complex 1:3 order into AA′₂B₂O₁₂ quadruple perovskites (QPV). However, 1:2 arrangements into A₂B′₂O₉ triple perovskite (TPv) structures are not often observed. The 1:2 TPv aristotype Ba₃SrTi₂O₉ crystallises with P-3m1 symmetry and a = a₁V₂ and c = a₁V₃ supercell (a₁ = 3.8 Å for a cubic Pv). Only examples with A = Ba, Sr, Ca and La are known and they often present typical octahedrally tilted structures. The related A₂CoNb₂O₉ TPvs show notable photocatalytic and dielectric properties, while Ba₃SrTa₂O₉ (B²⁺ = Mn, Ni) TPvs are multiferroic materials.

High pressure and high temperature (HPHT) synthesis method allows the stabilisation of the smaller Mn³⁺ cation into the A site of the Pv, giving rise to the so-called A-site manganeseites. These have attracted much attention in the search for new functional materials, providing accessibility to simple, double and quadruple perovskite derivatives, e.g. Mn⁺²V⁴⁺O₉-²⁻, Mn⁺²⁺Fe³⁺Re⁵⁺O₉⁻¹⁵ and Mn⁺²⁺Mn⁺³⁺Mn⁺³⁺⁺O₁₂⁻₁⁶ with a rich variety of physical properties.

In this article, we present the structure and properties of the first A-site manganeseite with A₂B′₂O₉ TPv structure: HP-Mn₃MnNb₂O₉. The room pressure Mn₃Nb₂O₉ oxide has remarkable magnetoelectric properties and a preliminary microscopy study of the high-pressure modification mentioned a distorted aₘ = V₂V₃a₁, bₘ = V₂a₁ and cₘ = 2V₃a₁ monoclinic supercell, but no further studies have been performed. HP-Mn₃MnNb₂O₉ TPv with a 1:2 Mn:Nb cation order shows a complex magnetic behaviour and we argue that the magnetic ground state is directly driven by the B-site cation ordering.
manganites. Mn2 and Nb2 B-site octahedral distortions are considerably bigger than those observed in other 1:2 TPv and high pressure DPv A-site manganites;\(^{1,2}\) HP-Mn1MnNbO\(_9\) distortion is only surpassed by the MnMnMnO\(_2\) QPV (\(<\Delta> = 16.5 \text{ deg}^2\), \(<\lambda^2> = 1.0295\), \(<\sigma^2> = 0.22)\);\(^3\) and thus, the “all transition metal” (ATM) HP-Mn1MnNbO\(_9\) is the first A-site Mn TPv and the second most distorted A-site manganate oxide up to date.

The coexistence of four independent Mn sites induces a complex magnetic behaviour with subsequent transitions observed in bulk magnetic susceptibility measurements at \(T_N = 52.1(1) \text{ K}, T_M = 27.8(1) \text{ K and } T_L = 4.2(1) \text{ K}\), as displayed in Fig.2, where \(N\), \(M\) and \(L\) stand for Néel, modulated and lock-in respectively. The fit of the inverse susceptibility to the Curie-Weiss law above 125 K (Fig. S4) results in an effective magnetic moment of 5.92 \(\mu\text{B}/\text{Mn}\), in good agreement with the expected value for Mn\(^2+\) \(d^5\) cations, and a Weiss constant of \(\theta = -334 \text{ K}\) showing a large frustration index \(f = |\theta|/T_N = 6.42\). The three transitions are also observed in the magnetic contribution to the heat capacity shown in Fig.2. Integration of the three transitions from \(C_{mag}/T\) (Fig. S6a) reveals a total entropy release of 39(1) J/mol K, which is about 2/3 of the theoretical value \(S = 4^*R\ln(2S+1) = 59.59 \text{ J/mol K for HP-Mn1MnNbO}_9 \ (S = 5/2)\). Deconvolution of the entropy contributions (Fig. S6b) results in 59%, 39% and 2% for \(T_N\), \(T_M\) and \(T_L\) respectively, suggesting a strong entropy release below \(T_N\) and \(T_M\) and even ordering of a fraction of the moments down to \(T_L\) as discussed below.

The temperature dependence of HP-Mn1MnNbO\(_9\) NPD data reveals the appearance of magnetic peaks below \(T_N = 52.1(1) \text{ K}\) and their shift on cooling below \(T_M = 27.8(1) \text{ K}\) (Fig. 3a). All magnetic peaks in the \(T_M < T < T_N\) temperature range can be indexed with the propagation vector \(k_0 = [0 \ 0 \ 0]\). The refined magnetic structure in this interval \((R_{mag} = 14.0\%\) shows A-type AFM sublattices for all Mn sites (Fig. 3b) with spins aligned along the c axis and (101) AFM planes of Mn at the A-sites (dashed lines). All magnetic moments were constrained to the same values and refined to 2.68(1) \(\mu\text{B}\).

Figure 1. a) Rietveld fits against the NPD and SXRD data collected at 300 K for HP-Mn1MnNbO\(_9\) with (002), (200) and (110) superstructure peaks labelled for SXRD. Second and third rows of Bragg ticks are MnO and Pt from the capsule, only observed in the SXRD sample. b) One (11-2) layer of the refined structure, showing the 1:2 B-site order among Mn2 (blue) and Nb (grey) sites and the alternated Mn1 (black), Mn3 (red) and Mn4 (green) in A. c) Coordination environments for each cation site, with schematised octahedral environments and longer Mn-O distances labelled in red.

Table 1. Atomic positions (all Wyckoff 4a sites fully occupied) of HP-Mn1MnNbO\(_9\) as refined from 100 K high resolution NPD. Space group \(Cc\) and cell parameters \(a = 9.9054(5) \text{ Å}, b = 5.3097(2) \text{ Å}, c = 13.2052(7) \text{ Å and } \beta = 92.772(6)\). Agreement factors: \(R_p = 2.97\%, R_w = 3.91 \%, R_B = 6.96\%, R_I = 5.83\%, \chi^2 = 6.75\%\).

<table>
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<th>Site</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
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<td>Mn1</td>
<td>0.735(3)</td>
<td>0.535(3)</td>
<td>0.420(2)</td>
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<td>Mn2</td>
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<td>0.476(4)</td>
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<td>Mn4</td>
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<td>-0.002(5)</td>
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<td>Nb1</td>
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<td>0.508(3)</td>
<td>0.820(1)</td>
</tr>
<tr>
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<td>0.687(2)</td>
<td>0.701(1)</td>
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<td>O3</td>
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<td>0.870(2)</td>
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<td>O4</td>
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<td>0.334(2)</td>
<td>0.538(1)</td>
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<td>O9</td>
<td>0.400(2)</td>
<td>0.291(2)</td>
<td>0.619(1)</td>
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<table>
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<th>(&lt;\lambda&gt;)</th>
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<th>Mn2</th>
<th>Mn3</th>
<th>Mn4</th>
<th>Nb1</th>
<th>Nb2</th>
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<td>(10^3A^2)</td>
<td>1.088</td>
<td>1.036</td>
<td>1.059</td>
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<td>1.012</td>
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<td>(\Sigma^2(\text{deg}))</td>
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<td>86.35</td>
<td>181.05</td>
<td>172.75</td>
<td>36.47</td>
<td>50.39</td>
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The coexistence of a complex magnetic behaviour with subsequent transitions observed in bulk magnetic susceptibility measurements at \(T_N = 52.1(1) \text{ K}, T_M = 27.8(1) \text{ K and } T_L = 4.2(1) \text{ K}\), as displayed in Fig.2, where \(N\), \(M\) and \(L\) stand for Néel, modulated and lock-in respectively. The fit of the inverse susceptibility to the Curie-Weiss law above 125 K (Fig. S4) results in an effective magnetic moment of 5.92 \(\mu\text{B}/\text{Mn}\), in good agreement with the expected value for Mn\(^2+\) \(d^5\) cations, and a Weiss constant of \(\theta = -334 \text{ K}\) showing a large frustration index \(f = |\theta|/T_N = 6.42\). The three transitions are also observed in the magnetic contribution to the heat capacity shown in Fig.2. Integration of the three transitions from \(C_{mag}/T\) (Fig. S6a) reveals a total entropy release of 39(1) J/mol K, which is about 2/3 of the theoretical value \(S = 4^*R\ln(2S+1) = 59.59 \text{ J/mol K for HP-Mn1MnNbO}_9 \ (S = 5/2)\). Deconvolution of the entropy contributions (Fig. S6b) results in 59%, 39% and 2% for \(T_N\), \(T_M\) and \(T_L\) respectively, suggesting a strong entropy release below \(T_N\) and \(T_M\) and even ordering of a fraction of the moments down to \(T_L\) as discussed below.

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Figure 2. FC-ZFC magnetisation (blue, left axis) and magnetic contribution to the heat capacity (orange, right axis) of HP-Mn1MnNbO\(_9\). Transition temperatures are identified with vertical dashed lines.
Considering octahedral environments for all the Mn sites provides an understanding of the interactions involved (ESI): the dominant exchange is between face-shared Mn1-Mn2 octahedra and all MnA-MnB are AFM super-exchange in accordance with Goodenough-Kanamori-Anderson rules (GKA). Thus, Mn2 is AFM to its nearest Mn1 but FM to Mn3 and Mn4, which involves a strong magnetic frustration and triggers the spin modulation observed below $T_M$.

Figure 3c shows the thermal behaviour of the propagation vector. Below $T_M = 27.8(1) \, K$, the abrupt displacements of the magnetic peaks follow a $[K_1, 0, K_2]$ propagation vector with the incommensurate components gradually evolving to $K_1 = 0.337(5)$ and $K_2 = -0.144(9)$ at 5 K and thus suggesting a lock-in transition to $K_1 = [\frac{1}{3} 0 -\frac{1}{3}]$ at $T_1 = 4.2(1) \, K$ as shown by magnetisation and heat capacity measurements in Figure 2. Similar behaviours occur for instance in HP-Mn$_3$InSbO$_9$, which presents a continuous reorientation from $k_0$ into a lock-in transition to $k = [0 0 \frac{1}{3}]$.22

The refined magnetic structure at 5 K (Fig. 4a) presents a sinusoidal modulation of the magnetic moments along c. An elliptical modulation of the magnetic moments is also physically possible; however, Rietveld fits against NPD at 5 K show that the simpler collinear SDW model gives better agreement $R_{mag}$ factor (13% SDW vs. 15.5% elliptical model) and hence it is discussed here. The isotropic nature of Mn$^{2+}$ single ion ($d^5, L = 0$) also supports the preferential alignment of the spins along the c axis in a SDW rather than their rotation into the plane via a poor influence of local orbital overlaps.

The $k_0$ structure minimises its exchange energy between unfavourable FM spins by modulating the magnetic moments between 0 and a maximum amplitude of 5.1(1) $\mu_0$ at 5 K. The thermal evolution of the magnetic moments, Figure 3c, shows a coherent increase of the averaged moment, calculated as $\mu_{mag}/\sqrt{2}$. The averaged ordered moment magnitude at 5 K of 3.6(1) $\mu_0$ is 72% of the ideal value, so one-third of the spins remain dynamic below the magnetic ordering transitions, consistent with the persistence of 1/3 of the theoretical magnetic entropy. The fit of the saturated moment in the $k_0$ region using a critical law $\mu = \mu_0 \ast (1 - (T/T_S))^\beta$ results in $\mu_0 = 3.52(8) \, \mu_0$, $T_S = 52.2(2) \, K$ and $\beta = 0.25(1)$. The critical exponent $\beta$ is intermediate between 2D and 3D systems, the former only ordering in the Ising case. Therefore, the 2D-lattice in the $ab$ plane would predominate but order via weaker interplane exchanges.

2D models are reported for related A$_3$B$^{18}$Nb$_9$O$_2$:1.2 TPv with non-magnetic A-site cations.12,13 There, completely isolated triangular lattice antiferromagnets (TLAs) with the spins confined to the $ab$ plane are stacked along the c axis. Here, the presence of 75% of the magnetic cations in the A-site defines the magnetic backbone of HP-Mn$_3$InSbO$_9$ but the sole presence of one magnetic cation in three in the B lattice enables the A-B frustrated interactions and finally destabilizes the $k_0$ structure at $k_M$ and below.

**Figure 3.** a) Thermal evolution of HP-Mn$_3$InSbO$_9$ NPD data focused in the 24°-35° 2θ region. b) Magnetic structure at $T_M < T < T_{N}$ with $k_0 = [0 0 0]$ and black, blue, red and green arrows representing the magnetic moments of Mn1 – Mn4 sites respectively. Grey spheres are Nb atoms. The red square highlights the frustrated (FM) blue-red and blue-green vs. dominant blue-black AFM interactions. Dashed lines show AFM A-site order. c) Refined magnetic propagation vector (top panel, $k_0$ black and $k_1$ red) and magnetic moment (bottom panel, maximum and averaged amplitudes in black and blue respectively) as a function of temperature. Vertical dashed lines mark $T_M$ and $T_N$ transition temperatures from magnetic susceptibility. Red line in bottom panel shows the fit to the critical law as detailed in the text.

**Figure 4.** a) Magnetic structure at 5 K with $k = [k_0, 0, k_2]$. Orange and purple dashed rectangles mark 2D-like blocks separated by Nb. b) Ideal magnetic structure with $k_1 = [\frac{1}{3} 0 -\frac{1}{3}]$ showing the alternated sinusoidal and UU0DD0 chains of each magnetic site along the c axis. One unit cell is identified for each block using the orange and purple dashed rectangles.
The SDW described by all Mn sites are schematised in Fig. 4b for the ideal $k = [\frac{1}{3} 0 -\frac{1}{3}]$ model below $T_c$. They describe two different types of waves propagating along $a$ and alternating along $c$: i) sinusoidal waves with 3 modulated spins up and 3 down and ii) 2 up-null-2 down-null patterns (UUODDO). The nearly identical phase refined for AFM Mn1 and Mn4 sites at 5 K is reflected in the similar behaviour of their waves, which are coupled in Fig 4b for simplicity. Mn2 and Mn3 waves are almost FM coupled.

Collinearly ordered components with full amplitude modulation within a SDW is very rare in oxides. The only closely related systems we are aware of where the collinear moments of spin chains are fully modulated are MnVO$_3$, NaYNiWO$_6$, Ca$_3$Co$_2$O$_6$, and Fe$_2$GeO$_4$. The two later cases are for $S = 2$ 3d ions with unquenched orbital contributions for the cobalt case. Among all the Pv-type A-site manganites only MnVO$_3$ ($k = [0.29 0 0]$), MnF$_2$SeSbO$_6$ ($k = [0.043 0]$) and MnMn$_3$MnO$_5$ ($k = [0 0.5]$) show incommensurate propagation vectors while HP-Mn$_3$MnNb$_2$O$_9$ exhibits a bidirectional $k = [0 k_0 k_0]$ one. As MnVO$_3$, HP-Mn$_3$MnNb$_2$O$_9$ shows $S = 5/2$ Mn$^{2+}$ with no orbital degeneracy and thus minimises its exchange energy by retaining fluctuating moment components below $T_c$. As detailed in ESI, a hypothetical situation with fully saturated Mn moments for the $k_0$ phase would have an energy of $E_0 = 150^*$ J. Instead, the energy associated with the SDW results in $E(k_0) = 65.4^*$ J. Therefore, a clear benefit is obtained from the modulation, while part of the magnetic moments saturates to their ideal $2S = 5 \mu_B$ value.

Non-magnetic A-site 1:2 PV propagation vectors related to the triangular B-site lattice are usually observed, e.g. $[\frac{1}{3} \frac{2}{3} 0]$ or $[\frac{1}{3} \frac{1}{3} \frac{1}{2}]$. The presence of the A-site manganese in HP-Mn$_3$MnNb$_2$O$_9$ dictates the AFM $k_0$ structure. However, the underlying 1:2 B-site ordering stabilises the frustration via A-B interactions and thus the leitmotiv of the triangular lattice remains, eventually inducing the modulation and the lock-in ground state. In conclusion, the discovery of HP-Mn$_3$MnNb$_2$O$_9$ PVs closes the gap between the known types of cation ordered A-site manganites. HP-Mn$_3$MnNb$_2$O$_9$ shows a full 1:2 Mn:Nb cation order and is also the second most distorted A-site manganese oxide up to date. It presents a simultaneous order of the four independent Mn cations with a simple but highly frustrated $k_0$ magnetic structure. The structure minimises the frustration between unfavourably oriented spins via large amplitude modulations and stabilises in a lock-in structure with $k = [\frac{1}{3} 0 -\frac{1}{3}]$ directly related to the 1:2 cation order.

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**Notes and references**