Universal magneto-orbital ordering in the divalent $A$-site quadruple perovskite manganites $\text{AMn}_7\text{O}_{12}$ ($A = \text{Ca, Sr, Cd, and Pb}$)

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Through analysis of variable temperature neutron powder diffraction data, we present solutions for the magnetic structures of SrMn$_7$O$_{12}$, CdMn$_7$O$_{12}$, and PbMn$_7$O$_{12}$ in all long-range ordered phases. The three compounds were found to have magnetic structures analogous to that reported for CaMn$_7$O$_{12}$. They all feature a higher temperature lock-in phase with commensurate magneto-orbital coupling, and a delocated, multi-k magnetic ground state where incommensurate magneto-orbital coupling gives rise to a constant-moment magnetic helix with modulated spin helicity. CdMn$_7$O$_{12}$ represents a special case in which the orbital modulation is commensurate with the crystal lattice and involves stacking of fully and partially polarized orbital states. Our results provide a robust confirmation of the phenomenological model for magneto-orbital coupling previously presented for CaMn$_7$O$_{12}$. Furthermore, we show that the model is universal to the $A^{2+}$ quadruple perovskite manganites synthesised to date, and that it is tunable by selection of the $A$-site ionic radius.

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I. INTRODUCTION

The quadruple perovskite manganites of general formula $\text{AA}''\text{BB}'\text{O}_{12}$ ($A = \text{Na}^+$, $\text{Mn}^{2+}$, $\text{Ca}^{2+}$, $\text{Cd}^{2+}$, $\text{Sr}^{2+}$, $\text{Pb}^{2+}$, $\text{La}^{3+}$, $\text{Pr}^{3+}$, $\text{Nd}^{3+}$, or $\text{Bi}^{3+}$ [18]), $A'$ and $B = \text{Mn}$), are host to a complex interplay between charge, orbital, and spin degrees of freedom [19-31]. The $A$ and $A'$ sites form a chemically ordered pseudo-cubic sublattice in the ratio $\frac{1}{2} A$ to $\frac{3}{2} A'$, accompanied by large, in-phase rotations of $B$-site oxygen octahedra ($a^+a^-a^+$ in Glazer notation), which also form a pseudo-cubic sublattice displaced from the $A$ and $A'$ sites along the pseudo-cubic body diagonal. In monovalent $A$-site NaMn$_7$O$_{12}$, checkerboard charge ordering of $B$-site Mn$^{3+}$ and Mn$^{4+}$ ions and CE-type orbital order and associated antiferromagnetism have been observed [32-34], which are exactly equivalent to the long-range order found in the canonical manganite La$_0.5$Ca$_0.5$MnO$_3$. To the contrary, in divalent $A$-site CaMn$_7$O$_{12}$ a 75% Mn$^{3+}$ and 25% Mn$^{4+}$ charge ordered phase (rhombohedral space group $R\bar{3}$) develops. This charge order is a crucial precursor to an unusual incommensurate magneto-orbital helix characterised by a multi-k magnetic ground state, which is unlike any ordering phenomena found in the simple perovskite manganites. The trivalent $A$-site compounds LaMn$_7$O$_{12}$ and BiMn$_7$O$_{12}$ are similar to NaMn$_7$O$_{12}$, in that they display collinear, commensurate antiferromagnetic order, but in the absence of charge order [35] (Mn$^{3+}$ only). It has therefore become apparent that the general type of long-range electronic ordering found in the AMn$_7$O$_{12}$ series can be selected by modification of the average valence of the $B$-site Mn ions through choice of the $A$-site cation charge state.

All divalent $A$-site quadruple perovskite manganites synthesised to date ($A = \text{Ca, Sr, Cd, and Pb}$) show a similar sequence of phase transitions. Below $T_{\text{OO}}$, diffraction peaks have been observed [20,21,22] that originate in an orbital density wave propagating along the $c$-axis with wavevector $k_{\text{c}}$ [36]. On further cooling, two magnetic phase transitions at $T_{N1}$ and $T_{N2}$ have been identified [37-39], with the exception of PbMn$_7$O$_{12}$ for which an additional phase transition at an intermediate temperature, $T''$, was reported [40]. The magnetically ordered phases have only been well characterised for CaMn$_7$O$_{12}$ [41]. Below $T_{N1}$ the manganese magnetic structure evolves continuously from a collinear spin density wave towards a constant-moment helix with modulated spin helicity, and the fundamental propagation vector $k_0$ is locked into the periodicity of the orbital modulation with the relation $k_s = 2k_0$ (phase AFM1). At $T_{N2}$ the fundamental magnetic order delocks from the orbital modulation periodicity in order to gain energy from spin exchange interactions, while the same magneto-orbital coupling persists through the creation of additional magnetic order parameters (phase AFM2). In AFM1, the magnetic order is commensurate with the orbital order, and in AFM2 the magnetic order is incommensurate with the orbital order. In both phases of CaMn$_7$O$_{12}$, the magneto-orbital textures are incommensurate with respect to the crystal lattice. Literature values for the transition temperatures of all four compounds are summarised in Table 1. $T_{N1}$ was found to be remarkably similar across the series, however, significant variation was observed in $T_{N2}$.

In this article we present results of neutron powder diffraction experiments, which show that the magneto-orbital phenomenology previously reported in CaMn$_7$O$_{12}$...
is universal to the $A^{2+}$ compounds studied. Furthermore, we show that the periodicity of the magnetic ground state, which is directly related to the variation in $T_{N2}$, can be controlled by the $A$-site cation radius. The article is organised as follows. In Section II we provide experimental details of sample growth, characterisation, and neutron powder diffraction. We present results on the commensurate orbital order in CdMn$_7$O$_{12}$ (Sections III B), followed by results on the magnetic structures of SrMn$_7$O$_{12}$, and PbMn$_7$O$_{12}$ (Sections III C, III D, and III E respectively). The AMn$_7$O$_{12}$ series is then discussed in general in Section IV. Finally, in Section V we summarise our conclusions.

### II. EXPERIMENT

Powder samples of SrMn$_7$O$_{12}$, CdMn$_7$O$_{12}$, and PbMn$_7$O$_{12}$ were prepared from stoichiometric mixtures of Mn$_2$O$_3$, MnO$_1.83$ (Alpha Aesar MnO2 99.997% with the precise oxygen content determined by thermogravimetric analysis), PbO (99.999%), CdO (99.99%), and 4H-SrMn$_3$O$_4$. The mixtures were placed in Au capsules and treated at 6 GPa and 1373 K for 2 h for CdMn$_7$O$_{12}$ and PbMn$_7$O$_{12}$ and at 6 GPa and 1573 K for 2 h for SrMn$_7$O$_{12}$ (the duration of heating to the desired temperature was 10 min) in a belt-type high-pressure apparatus. After the heat treatments, the samples were quenched to RT, and the pressure was slowly released. Data on CaMn$_7$O$_{12}$ presented in this paper has been reproduced from previous studies$^{22,23}$, in which single crystals were grown at ambient pressure by the flux method$^3$ and then ground and sieved through a 35µm mesh. All samples were characterised by laboratory based x-ray powder diffraction, and heat capacity and magnetisation measurements using a Quantum Design PPMS and MPMS, respectively.

Neutron powder diffraction measurements were performed on the WISH time-of-flight diffractometer$^{25}$ at ISIS, the UK Neutron and Muon Spallation Source. Samples were loaded into a cylindrical vanadium can and mounted within a $^4$He cryostat. Data were collected with high counting statistics at a fixed temperature within each magnetic phase, including paramagnetic for reference. Data were also collected with lower counting statistics on warming in the temperature range 1.5 K to 90 K. All diffraction data were refined using Fullpro$^{20}$.

### III. RESULTS

#### A. Average $R3$ crystal structures

Figure 1 shows neutron powder diffraction data measured in the paramagnetic, AFM1, and AFM2 phases of SrMn$_7$O$_{12}$, CdMn$_7$O$_{12}$, and PbMn$_7$O$_{12}$, alongside data previously published on CaMn$_7$O$_{12}$$^{22,23}$. The diffraction patterns measured in the paramagnetic region $T_{N1} < T < T_{OO}$ (panes a-d in Figure 1) were found to be qualitatively the same with the exception of weak superstructure reflections that originate in orbital modulations of differing periodicities. Direct comparisons were made by refining the average rhombohedral crystal structure of CaMn$_7$O$_{12}$ (space group $R3$) against the four diffraction patterns. The respective fits (Figure 1a-d) are in excellent agreement with the data, and the results are summarised in Table II. Systematic variations in the lattice parameters and oxygen positions were observed due to the different ionic radii of the $A$-site cations.

Beyond the average $R3$ structure, CaMn$_7$O$_{12}$, SrMn$_7$O$_{12}$, and PbMn$_7$O$_{12}$ support orbital order below $T_{OO}$ that is commensurate with respect to the crystal lattice (Table II). The complex pattern of atomic displacements has been determined for CaMn$_7$O$_{12}$, in which they corresponded to a sinusoidal modulation of $d_{z^2-r^2}$ and $d_{g^2-r^2}$ orbital occupation of the single $B$-$Mn^{3+}$ $e_g$ electron. This commensurate structure can be described within the four dimensional super-space group $R3'(00γ)$$^{21,23}$. To the contrary, in CdMn$_7$O$_{12}$ the orbital order is commensurate with the crystal lattice (Table II), such that the atomic displacements associated with the orbital order are in register with the average crystal structure. This material therefore presents a model case as it can be fully described within conventional 3D crystallography, as follows in Section III B.

#### B. CdMn$_7$O$_{12}$ commensurate orbital order

The commensurate nature of the orbital ordering in CdMn$_7$O$_{12}$ can be explained by activation of the lock-in free-energy term, $δ^3 + δ'^3$, which selects the $k_s = (0, 0, 2)$ propagation vector (or equivalently $k_s = (0, 0, 1)$). Here $δ$ and $δ'$ are complex conjugate components of the structural order parameter associated with the orbital density wave, which transforms by the $A_1$ irreducible representation (see reference $^{22}$ for details). The presence of the commensurate phase does not exclude the existence of a hypothetical, high-temperature incommensurate orbital modulation similar to other members of the series.

### TABLE I. Literature values for transition temperatures and the length of the orbital order propagation vector, $k_{s} = (0, 0, k_{s})$, of the divalent $A$-site AMn$_7$O$_{12}$ compounds. Note that $T_{N2}$ in PbMn$_7$O$_{12}$ extends over a broad region of thermal hysteresis.

|        | CaMn$_7$O$_{12}$ | CdMn$_7$O$_{12}$ | SrMn$_7$O$_{12}$ | PbMn$_7$O$_{12}$ |
|--------|-----------------|-----------------|-----------------|-----------------|
| $r_0$  | 1.31            | 1.34            | 1.44            | 1.49            |
| $T_{OO}$ [K] | 254           | 250            | 265             | 294             |
| $T_{N1}$ [K] | 88             | 90             | 87              | 83              |
| $T'$ [K]      | -              | -              | -               | 77              |
| $T_{N2}$ [K] | 33             | 48             | 63              | 37-65           |
| $|k_{s}|$  | 2              | 2.0785         | 2.0765          | $\sim$ 2        |
FIG. 1. Neutron powder diffraction data measured in bank 2 (average 2θ = 58.3°) of the WISH diffractometer from CaMn$_7$O$_{12}$, SrMn$_7$O$_{12}$, CdMn$_7$O$_{12}$, and PbMn$_7$O$_{12}$. Diffraction data (red points) collected in the paramagnetic, AFM1, and AFM2 phases are shown in a)-d), e)-h), and i)-l), respectively. The fitted nuclear (top tick marks) and magnetic (bottom tick marks) structural models are shown as a solid black line. A difference pattern ($I_{\text{obs}} - I_{\text{calc}}$) is given as a blue solid line at the bottom of each pane.

it only dictates that the periodicity of any incommensurate order would have to be sufficiently close to the commensurate order such that the lock-in term becomes competitive (and wins) at the measured temperatures.

The commensurate propagation vector implies that the structural modulation on sites related by R-centring translations adopt phase shifts of $2/3\pi$ and $4/3\pi$. There are two isotropy subgroups associated with the $\Lambda_1$ irreducible representation and the $k_o = (0,0,2)$ propagation vector, namely $P3$ and $P\bar{3}$. These two cases correspond to different choices of the global phase of the modulation, which can be anticipated by inspecting the Wyckoff position splitting. The $P3$ and $P\bar{3}$ subgroups split the 9d ($B$-site Mn$^{3+}$) position into two (3f and 6g, see Figure 2) and three (3d, 3d, and 3d) independent positions, respectively. The former implies that the orbital states of Mn$^{3+}$ in the sites related by the R-centring translations are identical (6g positions). In the latter case, Mn$^{3+}$ ions in these sites would be in different orbital states. Based on the orbital modulation measured in CaMn$_7$O$_{12}$, a $B$-site manganese orbital state, $\Psi$, can be defined by an admixture of $\psi_1 = |3x^2-r^2\rangle$ and $\psi_2 = |3y^2-r^2\rangle$ orbitals through the relation $\Psi = \psi_1|\cos(\phi/2)\rangle + \psi_2|\sin(\phi/2)\rangle$, as illustrated in Figure 2. The $P3$ symmetry sets $\phi$ to be 0 (or $\pi$) for the 3f position, and $\phi = 2/3\pi$ or $\phi = 4/3\pi$ for the sites in the 6g position, respectively (Figure 2). Alternatively, the $P\bar{3}$ subgroup implies an arbitrary phase, different from zero (or $\pi$), for all three independent 3d positions.

Our neutron diffraction data (Figure 1) was successfully refined using the $P\bar{3}$ subgroup, and the obtained structural parameters are summarised in Appendix X. Using the non-centrosymmetric $P\bar{3}$ symmetry did not improve the refinement quality. The choice of the global phase in the $P3$ subgroup implies the presence of one third $B$-site Mn$^{3+}$ sites in the fully polarized orbital state ($3f$ Wyckoff position, $\Psi = \psi_1$, see Figure 2). This fully polarised orbital state is unique to the $P\bar{3}$ structure, it is the most efficient configuration for releasing the Jahn-Teller instability, and it is therefore the likely microscopic mechanism behind the phenomenological lock in term $\delta^3 + \delta'^3$. The other two third $B$-site Mn$^{3+}$ cations adopt the electronic configuration dominated by the $\psi_2$ orbital states ($\Psi = 1/2\psi_1 + \sqrt{3}/2\psi_2$).
TABLE II. Crystal structure parameters refined in the average R3 space group for the paramagnetic phases.

|                  | CdMn$_2$O$_{12}$ | CaMn$_2$O$_{12}$ | SrMn$_7$O$_{12}$ | PbMn$_7$O$_{12}$ |
|------------------|------------------|------------------|------------------|------------------|
| $r_{i\text{o}}$  | 1.31             | 1.34             | 1.44             | 1.49             |
| $T$ [K]          | 104              | 110              | 96               | 100              |
| **Lattice Parameters** [Å] |            |              |              |                  |
| $a$              | 10.4394(2)       | 10.4504(1)      | 10.4866(1)      | 10.5044(4)       |
| $c$              | 6.3401(1)        | 6.3472(1)       | 6.3802(1)       | 6.4088(3)        |
| $V$ [Å$^3$]      | 598.40(2)        | 600.31(2)       | 607.63(2)       | 612.42(4)        |
| Atomic fractional coordinates |            |              |              |                  |
| O1 $x$           | 0.2274(4)        | 0.2239(3)       | 0.2260(3)       | 0.2291(5)        |
| $y$              | 0.2779(4)        | 0.2741(3)       | 0.2755(3)       | 0.2794(5)        |
| $z$              | 0.0826(5)        | 0.0827(5)       | 0.0817(4)       | 0.0814(7)        |
| O2 $x$           | 0.3420(4)        | 0.3416(4)       | 0.3412(4)       | 0.3391(7)        |
| $y$              | 0.5226(4)        | 0.5232(3)       | 0.5213(3)       | 0.5210(5)        |
| $z$              | 0.3440(9)        | 0.3391(6)       | 0.3360(5)       | 0.3348(8)        |
| Isotropic atomic displacement parameters, $U_{iso}$ [Å$^2$] |            |              |              |                  |
| $A^{2+}$         | 0.037(3)         | 0.031(3)        | 0.016(2)        | 0.030(2)         |
| A-Mn$^{3+}$      | 0.0013(8)        | 0.017(2)        | 0.007(2)        | 0.018(2)         |
| $B$-Mn$^{3+}$    | 0.0013(8)        | 0.010(2)        | 0.004(2)        | 0.012(3)         |
| $B$-Mn$^{4+}$    | 0.0013(8)        | 0.020(6)        | 0.004(5)        | 0.017(9)         |
| O1               | 0.015(1)         | 0.0121(11)      | 0.001(1)        | 0.002(1)         |
| O2               | 0.017(1)         | 0.0165(12)      | 0.004(1)        | 0.016(2)         |
| Refinement reliability parameters [%] |            |              |              |                  |
| $R_w$            | 5.48             | 4.84            | 4.30            | 4.98             |
| $R_{Bragg}$      | 6.88             | 2.90            | 2.89            | 3.67             |

*a $A^{2+}$: [0,0,0], A-site Mn$^{3+}$: [0.5,0,0], B-site Mn$^{3+}$: [0.5,0,0.5], B-site Mn$^{4+}$: [0,0,0.5]"

The orbital phase, $\phi$, can be found for the measured Jahn-Teller anisotropy of the B-site Mn$^{3+}$ oxygen octahedra using the equation,

$$\tan\left(\frac{2}{3} \phi\right) = \frac{\sqrt{3} (l - s)}{2(m - l - s)}$$  \hspace{1cm} (1)

where $l$, $m$, and $s$ are the long, medium, and short bonds of the octahedron, and the origin of $\phi$ is chosen such that it sweeps out the orbital sector $|3x^2-r^2|$ to $|3x^2-r^2|$. From the empirical bond lengths detailed in Figures 2, and 2a, $\phi \approx 0.18\pi$ and $\phi = 0.62\pi$ for the 3f and 6g sites, respectively. This result is in good agreement with the predicted orbital pattern quantified in Figure 2, which demonstrates that the orbital modulation in CdMn$_7$O$_{12}$ is indeed the commensurate limit of that found in CaMn$_2$O$_{12}$.

**C. SrMn$_7$O$_{12}$ magnetic structures**

Immediately below $T_{N1}$ (panes (e)-(f) in Figure 1) additional diffraction peaks were observed that could be indexed with a fundamental magnetic propagation vector, $k_0$, which lies parallel to the hexagonal $c$-axis. Both the incommensurate length of $k_0$ in the AFM1 phase (Table III), and the transition temperature, $T_{N1}$, were found to be approximately equal for SrMn$_7$O$_{12}$ and CaMn$_2$O$_{12}$. The temperature dependence of $k_0$ is given in Figure 3b, which shows that in both compounds the fundamental modulation remains locked-in to the value $\frac{1}{2} [k_0]$ down to $T_{N2}$ (n.b. $k_0$ is also approximately equal for SrMn$_7$O$_{12}$ and CaMn$_7$O$_{12}$). Throughout AFM1, the fundamental modulation is accompanied by a third harmonic Fourier component with propagation vector $3k_0$, as shown in the inset to Figure 3a. A third harmonic was also observed in CaMn$_2$O$_{12}$, in which it arose through commensurate magneto-orbital coupling of the form $\delta \eta_0 \xi_0^* + \xi_3 \eta_3^* + \text{c.c.}$, where c.c. indicates the complex conjugation, and $\delta$, $\eta_0$, $\xi_0$ and $\eta_3$, $\xi_3$ are components of the orbital ($k_0$), fundamental magnetic ($k_0$) and third harmonic magnetic ($3k_0$) order parameters, respectively. We refer the reader to the Supplemental Information accompanying reference 22 for detailed definitions of the magnetic and orbital order parameters. This coupling results in a modulated spin he-
The helicity, i.e., higher order Fourier components describe a periodic variation in the local spin helicity of an otherwise proper helix magnetic structure, in accordance with the variation in orbital occupation.

The helicity modulated AFM1 magnetic structure has nine parameters - three moment amplitudes of the symmetry inequivalent manganese sites, $A$-$Mn^{3+}$, $B$-$Mn^{3+}$, and $B$-$Mn^{4+}$, for each observed Fourier component (six amplitudes in total), two relative phases between the three sites, and a global phase. For an incommensurate structure the global phase can be arbitrarily set to zero, and the relative phase between $A$-$Mn^{3+}$ and $B$-$Mn^{3+}$ was fixed to a value of $\pi (|k_0| - 1)$ to be consistent with a helical magnetic structure. An insufficient number of third harmonic reflections were observed to reliably refine the respective amplitudes. Therefore, a model based upon just four parameters (three amplitudes and the $B$-$Mn^{4+}$ phase) was refined against the fundamental magnetic diffraction peaks measured in the AFM1 phase of SrMn$_7$O$_{12}$. The fit showed excellent agreement with the data ($R_{\text{Bragg}} = 2.8\%$, $R_{\text{Mag}} = 2.61\%$, Figure 1), the $B$-$Mn^{4+}$ phase refined to a value of $0.60(1)$, and the refined moment magnitudes are given in Table IV. The modulated helicity was found to reside predominantly on the $B$-$Mn^{3+}$ ions, and was negligibly small on the $B$-$Mn^{4+}$ ions. This is consistent with the fact that Mn$^{3+}$ is Jahn-Teller active and primarily responsible for the orbital order.

In summary, SrMn$_7$O$_{12}$ displays the same magneto-
orbital physics as observed in CaMn$_7$O$_{12}$. Below $T_{N1}$ the magnetic and orbital order are both incommensurate with respect to the crystal structure, but their periodicities are locked together by commensurate magneto-orbital coupling. At $T_{N2}$, which was found to be 15 K higher in SrMn$_7$O$_{12}$, the magnetic and orbital periodicities de-lock, but remain incommensurately coupled down to 1.5 K. In both phases magneto-orbital interactions give rise to a modulation of the spin helicity, which is described by higher order Fourier components of the magnetic structure.

### D. CdMn$_7$O$_{12}$ magnetic structures

The magnetic structure of CdMn$_7$O$_{12}$ in the AFM1 phase has been reported, however, the AFM2 magnetic structure and coupling to the orbital physics had not been discussed. For completeness, we will begin with a repeat analysis of the AFM1 structure, and then continue with details of the AFM2 phase. We note that in the previous work crystallographic phase separation was found below 60 K. We did not observe any such phase separation in the sample used in our neutron diffraction experiments, however, it was detected in another sample not reported here.

When CdMn$_7$O$_{12}$ orders magnetically below $T_{N1}$, the magnetic diffraction peaks (Figure 1k) index with the commensurate propagation vector $k_0 = (0, 0, 1)$, as previously observed. Again, the periodicities of orbital and magnetic order within AFM1 are found to be locked together with the relationship $k_s = 2k_0$ (Figure 1h). In this case the third harmonic cannot be identified as it overlaps exactly with much larger nuclear diffraction intensities with Miller indices $(0, 0, l)$: $l = 3m$, $m$ integer, i.e., in AFM1 the modulation of spin helicity occurs within a single conventional unit cell.

In the absence of magneto-orbital coupling the AFM1 magnetic structure of CdMn$_7$O$_{12}$ can be described by a single irreducible representation of space group $R3$. In the commensurate limit manganese spins related by $R$-centring must be equal in magnitude and form a 120° configuration. However, as a result of the commensurate orbital ordering, each manganese sublattice is split into two sublattices, giving six, symmetry inequivalent Mn ions (see Appendix A). One should then expect that, for example, the B-site Mn$^{3+}$ spins in the 3f and 6g Wyckoff positions do not form an exactly 120° configuration, nor should they have exactly the same magnitudes. The latter implies an admixture of a spin-density wave component, which is an essential condition for the lock in mechanism through magnetoelastic coupling. The parametrisation of the magnetic structure should be extended accordingly, however, it is the third harmonic modulation at $3k_0 = (0, 0, 0)$ that captures any departure from the $R3$ AFM1 model - a natural consequence of the magneto-orbital coupling. As this component cannot be reliably refined, we continue with the $R3$ AFM1 model as a good approximation.

A single-$k$ AFM1 magnetic structure model was refined against the neutron powder diffraction data (Figure 1k) with reliability factors of $R_{Bragg} = 5.19\%$ and $R_{Mag} = 6.95\%$. The relative phases A-Mn$^{3+}$:B-Mn$^{3+}$, and A-Mn$^{3+}$:B-Mn$^{4+}$ were fixed to $\pi(|k_0| - 1)$ and freely refined to a value of 0.5(1), respectively. The refined moment magnitudes are plotted in Figure 4b, and the magnetic structure is illustrated in Figure 7. Our results for the AFM1 phase are in good agreement with those previously published.

Below $T_{N2} = 33$ K, the fundamental propagation vector de-locks from the orbital order propagation vector and monotonically increases towards the incommensurate ground state length (Figure 3h). The family of diffraction peaks with propagation vector $k_{-1} = k_s - k_0$ also appears below $T_{N2}$, as shown in Figure 1k, which are consistent with the existence of incommensurate magneto-orbital coupling in the AFM2 phase. Although

### TABLE IV. AMn$_7$O$_{12}$ magnetic moment component magnitudes on each manganese sublattice, refined against data measured at 1.5 K.

| $k_0$ moments ($\mu_B$) | CdMn$_7$O$_{12}$ | CaMn$_7$O$_{12}$ | SrMn$_7$O$_{12}$ | PbMn$_7$O$_{12}$ |
|-------------------------|------------------|------------------|------------------|------------------|
| $A$-Mn$^{3+}$           | 3.14(3)          | 3.71(3)          | 3.64(1)          | 3.64(2)          |
| $B$-Mn$^{3+}$           | 2.24(3)          | 2.69(2)          | 2.58(2)          | 2.34(2)          |
| $B$-Mn$^{4+}$           | 2.67(6)          | 3.09(6)          | 2.92(3)          | 2.94(3)          |
| $k_{1+}$ & $k_{1-}$ moments ($\mu_B$) |     |                 |                 |                 |
| $A$-Mn$^{3+}$           | 0.71(6)          | 0.39(2)          | 0.52(2)          | 0.39(3)          |
| $B$-Mn$^{3+}$           | 1.33(6)          | 1.41(2)          | 1.47(2)          | 1.52(2)          |
| $B$-Mn$^{4+}$           | 0.95(8)          | 0.52(4)          | 0.02(3)          | 0.09(6)          |

FIG. 4. a) Temperature dependence of the observed magnetic propagation vectors of CdMn$_7$O$_{12}$ measured on warming. b) The temperature dependence of the CdMn$_7$O$_{12}$ moment amplitudes of the $k_0$ component. All error bars are smaller than the data points so they are omitted for clarity.
the $k_1^+$ intensities are no longer coincident with the nuclear intensities, they are not sufficiently separated to be observable beyond the experimental resolution. The AFM2 magnetic structure model was refined against the neutron powder diffraction data measured at 1.5 K (Figure 1k) with reliability factors $R_{\text{Bragg}} = 5.30\%$ and $R_{\text{Mag}} = 8.25\%$. The $B$-Mn$^{4+}$ phase refined to a value of 0.5(1), and the refined moment magnitudes are given in Table IV.

### E. PbMn$_7$O$_{12}$ magnetic structures

PbMn$_7$O$_{12}$ was found to magnetically order with the same AFM1 lock-in magnetic structure as observed in CaMn$_7$O$_{12}$ and SrMn$_7$O$_{12}$. The fundamental magnetic diffraction peaks, shown in Figure 1l, could be indexed with the incommensurate propagation vector $k_0 = (0, 0, 1.0248)$. The third harmonic diffraction intensity with Miller indices $(0, 0, 0.0744)$ corresponds to a d-spacing of 86.14 Å, which is just outside the practical measurement range of the WISH diffractometer (the same reflection for CaMn$_7$O$_{12}$ and SrMn$_7$O$_{12}$ could be observed with d-spacing values of 53.67 Å and 54.39 Å, respectively). We note that the observation of a third harmonic in the AFM1 phase provides the strongest evidence for a locked-in magneto-orbital helix. We therefore conclude that the AFM1 magnetic structure in PbMn$_7$O$_{12}$ is a lock-in phase based upon the numerical relationship between the respective propagation vectors alone. The diffraction data collected in the AFM1 phase was fit with the single-$k$ AFM1 model (Figure 1h). Reliability factors of $R_{\text{Bragg}} = 3.43\%$ and $R_{\text{Mag}} = 6.48\%$ were obtained, the relative phase of the $B$-site Mn$^{4+}$ moments was fixed to $\pi$ to achieve convergence of the refinement, and the temperature dependence of the moment magnitudes are plotted in Figure 6.

The ground state magnetic structure of PbMn$_7$O$_{12}$ was found to be delocked from the orbital order periodicity, and the observation of $k_1^+$ and $k_1^-$ magnetic diffraction peaks (Figure 1l) indicated the presence of incommensurate magneto-orbital coupling and the same AFM2 magnetic structure as observed in the ground state of CaMn$_7$O$_{12}$, SrMn$_7$O$_{12}$, and CdMn$_7$O$_{12}$. The AFM2 magnetic structure model was refined against the data giving reliability factors $R_{\text{Bragg}} = 4.23\%$ and $R_{\text{Mag}} = 7.71\%$. The relative phase of the $B$-site Mn$^{4+}$ moments was again fixed to $\pi$ to achieve convergence of the refinement, and the moment magnitudes are given in Table IV.

Whilst the ground state and AFM1 magnetic structures were found to be analogous to those observed in the other AMn$_7$O$_{12}$ compounds, PbMn$_7$O$_{12}$ displayed very different behaviour over an intermediate range of
temperatures (Figure 6). Instead of supporting a single phase transition from the AFM1 phase to the AFM2 phase at $T_{N2}$, the magnetic structure of PbMn$_7$O$_{12}$ is locked on cooling below $T' \approx 78$ K, but orders with a single propagation vector, $k_0$, down to $T_{N2} \approx 43$ K. Below $T_{N2}$ the system entered the AFM2 phase, characterised by the appearance of $k_{1+}$ and $k_{1-}$ Fourier components, as shown in Figure 6. On warming, a large region of hysteresis is observed whereby the system did not leave the AFM2 phase until $T_{N2} \approx 66$ K, above which there exists the same delocated, single-$k$ phase up to $T'$ (Figure 6). The presence of $k_{1+}$ and $k_{1-}$ magnetic diffraction peaks below the lock-in phase transition is a requirement of the magneto-orbital helical state. Hence, their absence in PbMn$_7$O$_{12}$ in the intermediate temperature range $T_{N2} < T < T'$ indicates that either the two electronic textures temporarily decouple, or the orbital modulation is temporarily destroyed. Establishing the true nature of the phase transition at $T'$ will require a detailed study of the crystal structure.

IV. DISCUSSION

As we have seen, the lock-in and ground state magneto-orbital coupling mechanisms, and the resulting magnetic structures are in essence identical in CaMn$_7$O$_{12}$, SrMn$_7$O$_{12}$, CdMn$_7$O$_{12}$, and PbMn$_7$O$_{12}$. The magneto-orbital textures differ only in their periodicity, which is determined in the ground state by the competing magnetic exchange interactions. In the remainder, we demonstrate that the exchange interactions that determine the ground-state propagation vector, $k_0$, are effectively tuned by changing the ionic radius of the A-site cation. Crucially, this can occur without changing the average antiferromagnetic interactions, and hence the Neel temperature $T_{N1}$. We construct a mean field model of the magnetic exchange energy within the average $R3$ Amn$_7$O$_{12}$ crystal structure, which contains 7 symmetry inequivalent nearest-neighbour magnetic exchange interactions, as illustrated in Figure 7. The exchange parameter space can be reduced as geometry allows two pairs of interactions, $(J_1 + J_{II})$ and $(J_{III} + J_{IV})$, to be factorised, and we write the combined exchange interactions as $J_{I+II}$ and $J_{III+IV}$, respectively. The ground state Heisenberg mean field energy was calculated for the five dimensional parameter space, whilst keeping $J_V$ fixed to -1 (ferromagnetic) - consistent with the experimentally determined magnetic structures. By imposing empirical constraints on the relative phases of the three manganese sublattices, one can show that $J_{III} \approx 0$, $J_{I+II}$ and $J_{III+IV} > 0$ (antiferromagnetic), and $J_{VII} < 0$ (ferromagnetic). The exchange energy for Amn$_7$O$_{12}$ can therefore be written in terms of just three interactions, $J_{I+II}$, $J_{III+IV}$, and $J_{VII}$, relative to $J_V$:

$$\Delta E = (6J_{I+II} - 3J_{VII}) \cos(\frac{2}{3}\pi k_z) - 2J_{III+IV} \cos(\frac{3}{2}\pi k_z) - J_V \cos(\pi k_z)$$ (2)

Minimising $\Delta E$ with respect to $k_z$ gives

$$k_z = \frac{3}{\pi} \tan^{-1}\left(\frac{8}{2 + \alpha^2 + \beta - \alpha \sqrt{4 + \alpha^2 + 2\beta}} - 1\right)$$ (3)

where $\alpha = (4J_{I+II} - 2J_{VII})$ and $\beta = \frac{3}{8}J_{III+IV}$. For small $\beta$, the commensurate structure ($k_z = 1$) is approached as $\alpha$ tends to zero. The propagation vector varies rapidly for small, positive alpha, and then asymptotically approaches a value of 1.5. Accordingly, the ground state propagation vector in Amn$_7$O$_{12}$ can be gradually increased by $J_{I+II}$ becoming more positive, $J_{VII}$ becoming more negative, or a uniform increase in the magnitude of both. Figure 7 shows the pseudo-cubic network of $J_{I+II}$ and $J_{VII}$ pathways of the B-site sublattice, centred on the A-site cation. By changing the radius of the central cation, the bonding geometry of the relevant exchange pathways will be modified resulting in a change in the ground state $k_z$, as found experimentally and summarised in Figure 8.

Figure 8 also shows $T_{N2}$ ($T'$ in PbMn$_7$O$_{12}$) plotted against the A-site cation radius, which shows a similar trend to the ground state $k_z$. At all temperatures below $T_{N1}$ the free energy gain from magneto-orbital lock-in is in competition with energy lost from magnetic exchange due to the required deviation from the ground state magnetic propagation vector. The lock-in phase transition therefore arises at a temperature above which the entropy of the system stabilises locked-in magneto-orbital coupling. In this scenario, the lock-in transition temperature would be zero when the energy lost though
exchange exactly equals the energy gain through lock-in. Then by monotonically increasing the difference in exchange energy between the ground state and the lock-in magnetic structure, the transition temperature becomes finite and also increases monotonically, i.e., the lock-in transition temperature is expected to be dependent on the propagation vector difference \( \Delta k_0 = |k_0| - |k_s|/2 \), where \( |k_0| \) is evaluated in the ground state. The inset to figure 8 shows \( \Delta k_0 \) plotted against the lock-in transition temperature for CdMn\(_{7}\)O\(_{12}\), CaMn\(_{7}\)O\(_{12}\), SrMn\(_{7}\)O\(_{12}\), and PbMn\(_{7}\)O\(_{12}\), which clearly demonstrates the expected dependence. Whilst \( T_{N2} \) is mostly determined by the relative magnitude of competing exchange interactions, at the mean field level \( T_{N1} \) is expected to be dependent upon the average magnitude of the exchange interactions, and hence independent of the \( A \)-site cation radius, as observed.

V. CONCLUSIONS

The magnetic structures in all ordered phases of SrMn\(_{7}\)O\(_{12}\), CdMn\(_{7}\)O\(_{12}\), and PbMn\(_{7}\)O\(_{12}\) have been determined. Through comparison with CaMn\(_{7}\)O\(_{12}\), our results have revealed a universal interplay between magnetic and orbital degrees of freedom in this series of divalent \( A \)-site quadruple perovskite manganites. In the high temperature magnetically ordered state the periodicities of the magnetic and orbital subsystems lock together via commensurate magneto-orbital coupling. On cooling, these periodicities delock, allowing the system to evolve towards a multi-\( k \) magnetic ground state in which incommensurate magneto-orbital coupling gives rise to a modulation of the spin helicity. We have shown that the periodicity of the ground state magnetic structure is controlled by the \( A^{2+} \) ionic radius. This in turn determines the temperature at which the magnetic and orbital periodicities de-lock, while the Néel temperature remains approximately constant. The universality of our results suggests that these unusual magnetic textures may be observed in other families of manganites with the same 3:1 ratio of 3+ and 4+ ordered \( B \)-site charge states.

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Appendix A: Crystal structure of CdMn\(_{7}\)O\(_{12}\) below \( T_{OO} \)

The crystal structure of CdMn\(_{7}\)O\(_{12}\) was refined against neutron powder diffraction data measured below \( T_{OO} = 254 \text{K} \), shown in Figure 9. Atomic displacements that result directly from the orbital order give rise to new diffraction peaks that can be indexed with the commensurate propagation vector \( k_s = (0,0,2) \) (see Figure 9 inset). This propagation vector is equivalent to \((0,0,1)\), however we choose the former to be consistent with the description of magneto-orbital coupling presented in the main text. The propagation vector indicates that translational symmetries \([2/3, 1/3, 1/3] \) and \([1/3, 2/3, 2/3] \) within the \( R \)-centred conventional unit cell have been broken by the orbital order, and the pattern of atomic displacements can be fully described within space group \( P\bar{3} \). The refined atomic fractional coordinates and isotropic atomic displacement parameters are given in Table V. Our results are in good agreement with those published in reference [33], with the exception of the fractional coordinates of atom O1-1 (labelled O1 in Table 2 of ref. [33]). In the previously published structure [33] this atom appears to deviate greatly from its nominal position in the higher symmetry \( R\bar{3} \) structure, and as a result bonding with its neighbours would be unphysical.

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[1] S. V. Ovsyannikov, A. M. Abakumov, A. A. Tsirlin, W. Schnelle, R. Egoavil, J. Verbeeck, G. VanTendeloo,
TABLE V. Crystal structure parameters of CdMn$_7$O$_{12}$ below the orbital ordering phase transition, measured at 104 K, and refined in the commensurate $P\bar{3}$ super-cell. Lattice parameters: $a = 10.4394(2)$, $c = 6.3401(1)$. $R_{\text{Bragg}} = 7.24\%$.

| $R\bar{3}$ ($T > T_{OO}$) | $P\bar{3}$ ($T < T_{OO}$) | $x$ | $y$ | $z$ | $U_{\text{iso}}$ |
|--------------------------|--------------------------|-----|-----|-----|----------------|
| Atom Site Sym. | Atom Site Sym. | | | | |
| Cd1 3a | 1a | 3. | Cd1-1 | 0 | 0 | 0 | 0.035(4) |
| Cd1 | 2d | 3. | Cd1-2 | 1/3 | 2/3 | 0.659(6) | 0.035(4) |
| Mn1 9e | 1 | Mn1-1 | 1/2 | 0 | 0 | 0.008(2) |
| Mn1 | 6g | 1 | Mn1-2 | 0.183(2) | 0.337(3) | 0.328(4) | 0.008(2) |
| Mn2 9d | 1 | Mn2-1 | 1/2 | 0 | 1/2 | 0.010(2) |
| Mn2 | 6g | 1 | Mn2-2 | 0.167(3) | 0.327(3) | 0.817(4) | 0.010(2) |
| Mn3 3b | 3. | Mn3-1 | 0 | 0 | 1/2 | 0.010(2) |
| Mn3 | 2d | 3. | Mn3-2 | 1/3 | 2/3 | 0.161(6) | 0.010(2) |
| O1 18f | 1 | O1-1 | 0.237(2) | 0.285(2) | 0.080(3) | 0.0132(9) |
| O1-1 | 6g | 1 | O1-2-1 | 0.895(2) | 0.614(2) | 0.416(4) | 0.0132(9) |
| O1-2-1 | 6g | 1 | O1-3 | 0.549(1) | 0.934(1) | 0.752(3) | 0.0132(9) |
| O2 18f | 1 | O2-1 | 0.346(2) | 0.522(2) | 0.352(2) | 0.0132(9) |
| O2-1 | 6g | 1 | O2-2 | 0.007(2) | 0.860(2) | 0.684(2) | 0.0132(9) |
| O2-2 | 6g | 1 | O2-3 | 0.327(1) | 0.815(2) | 0.010(1) | 0.0132(9) |

FIG. 9. High resolution neutron powder diffraction data measured in bank 5 (average $2\theta = 152.8^\circ$) of the WISH diffractometer from CdMn$_7$O$_{12}$ at 104 K. Diffraction data are shown as red points, the nuclear peak positions are denoted by the black tick marks, and the fit to the data is shown as a solid black line. A difference pattern ($I_{\text{obs}} - I_{\text{calc}}$) is given as a blue solid line at the bottom of the pane. The inset shows a typical $P\bar{3}$ super-structure diffraction peak forbidden in the average $R\bar{3}$ space group.

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