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Structure and Physical Properties of $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$

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Abstract. We describe the high-pressure (4 GPa) high-temperature (~ 1100 K) synthesis of the solid solution series $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ ($0 < x < 1$) using H_2SeO_4 and transition metal oxide mixtures sealed in Pt capsules. Neutron powder diffraction has been performed to determine progression of the structure across the solution. All samples crystallise with orthorhombic $Pnma$ symmetry, and octahedral tilting is determined to increase with Mn content. SQUID magnetometry measurements were performed, and reveal that the Néel temperature shifts only by approximately 1 K over the series.

Keywords: High pressure synthesis, neutron diffraction, functional oxides, orthorhombic perovskite structure

PACS numbers:

1. Introduction

Perovskite materials continue to be the subject of extensive research due to their high degree of tunability, which gives rise to a variety of magnetic, catalytic [1], pyroelectric, piezoelectric, ferroelectric [2], dielectric [3], electronic conduction and photovoltaic properties amongst others, all of which are of potential technical significance [4] (and references within).

The ideal perovskite structure (with the generalised formula ABX_3) is cubic, and may generally be described as a three dimensional array of corner sharing BX_6 octahedra, with a typically larger A-cation sited at the centre of eight octahedra, each located at the corner of a cube [5]. The X-site is usually occupied by oxygen, though may also be occupied by other anions. Despite this description of a cubic structure, the majority of perovskite materials are far from ideal and are found to crystallise in tetragonal, orthorhombic, rhombohedral, monoclinic and triclinic symmetries. For example, the archetypal perovskite CaTiO_3 is orthorhombic [6], though it is still helpful to describe the structure in terms of distortions from the ideal cubic crystal symmetry (see Figure 1). These distortions give rise to the wide variety of physical properties found in perovskite compounds, and can be a result of one of three mechanisms; either tilting of the BX_6 octahedra, distortions within these octahedra, or cation displacements within the BX_6 octahedra [7]. The tilting of the octahedra may be driven by the size of the A-cation. When it is small compared to the BX_6 corner sharing octahedral network, the A-X distances will shorten whilst the six fold co-ordination around the central B atom is maintained. This causes the octahedra to rotate around one, or more, of the four-fold axes to compensate.

SeMO_3 (where M = transition metal in 2+ oxidation state) contains Se^{4+} cations with a lone electron pair in the 4s-orbital [8]. This small cation, sits on a relatively large void A-site of a perovskite structure, which leads to highly tilted and distorted crystal structures, with Se^{4+} coordinated to three oxygens forming pyramidal units [8]. This contrasts strongly with perovskites with trivalent A-site cations, which are coordinated by eight oxygens forming a polyhedral unit. In both cases, the contents of the B-site tunes the magnetic properties through altering the superexchange interactions mediated by the M-O-

M angles [9, 10]. Due to the highly distorted crystal structure, high-pressure, high temperature synthesis is required to stabilise these materials, and allow for uniform and complete crystallisation.

Figure 1. Characteristic tilts ($\phi_M^-, \phi_R^+, \phi_M^-$) of the BO_6 octahedra in orthorhombic symmetry, space group $Pnma$. (a) out of phase tilt, ϕ_M^- , and (b) in phase tilt, ϕ_R^+ shown for SeCoO_3 . (c) ϕ_M^- shown for CaTiO_3 , a structurally related but considerably less distorted perovskite. For clarity the B-site cations are only partially shown, but sit at $4b (0,0,\frac{1}{2})$ positions (in the orthorhombic cell) near the centre of the highly distorted octahedra, as shown in (b). The A-site atoms sit at the void sites between these octahedra, note that the A-O bonds are omitted for clarity. (d) Evolution of both the octahedral tilts, relative to the cubic parent structure (see text), as a function of Mn content in $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$.

In this work we have synthesised a series of perovskites in the solid solution $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$. Co and Mn in perovskite solid solutions with larger A-site atoms results in a series of materials exhibiting a variety of structures and physical properties controlled by the Co/Mn ratio [11, 12]. It is of interest to investigate if such systematics occur with a more highly distorted system. We report the crystal structure, as determined from neutron powder diffraction, SQUID magnetometry results and Raman spectroscopic data.

Figure 2. Top: Neutron powder diffraction and Rietveld fit for SeCoO_3 , data are shown as open black circles, the solid red trace shows the calculated profile and the bottom blue trace shows the residual of the fit. The vertical marks show the expected reflection positions for orthorhombic symmetry (space group $Pnma$) of SeCoO_3 . Bottom: Pseudocubic unit-cell volumes (determined from diffraction data, described in the text) as a function of composition for the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series (solid squares) and $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ (solid triangles). Across the $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series there is a transition from orthorhombic to trigonal symmetry at $x \sim 0.4$, and as a result there is a discontinuity in the slope (with phase coexistence at $x=0.4$) [12].

2. Experimental

A number of compositions in the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series were synthesised by a high pressure-temperature route. Stoichiometric quantities of CoO (>99.99%), MnO (>99.99%) and H_2SeO_4 (>99.999%) from Sigma-Aldrich, were ground and loaded into Pt capsules and sealed using a tungsten-inert-gas (TIG) welding technique. The resulting Pt capsule was then encapsulated in MgO , and loaded into a pyrophyllite gasket and graphite heater assembly [13]. The Paris-Edinburgh press [14] with WC anvils was used to pressurise the assembly to ~ 4 GPa, and the graphite

was resistively heated to achieve a sample temperature of ~ 1100 K. The samples were held at these conditions for 1 h prior to cooling and depressurisation to ambient conditions.

The phase purity of the sample was confirmed through X-ray diffraction using a Bruker D2 diffractometer with $\text{Cu K}\alpha$ radiation. Neutron powder diffraction patterns were obtained using the Polaris instrument at the ISIS Neutron and Muon Source, UK [15]. Time-of-flight diffraction patterns were collected from samples held in 1 mm diameter quartz glass capillaries in vacuum. Data acquisition times were of the order of 12-24 hours per sample. Rietveld refinement was performed using GSAS [16].

Magnetisation measurements were performed using a Quantum Design MPMS-XL7 SQUID magnetometer. A finely ground sample was placed into a gelatine capsule and mounted into a straw, loaded into the instrument at 300 K, and cooled to 1.8 K. Measurements of the DC magnetisation were made as a function of temperature on warming (M vs. T) over the range 1.8–300 K in an applied field of 1 kOe. Both field- and zero field-cooled data were collected.

Raman spectra were measured for all samples at ambient temperature. Spectra were recorded in backscattering using an in-house system comprising a Princeton Instruments SP2500i spectrometer equipped with a 1800 g holographic blaze grating. A diode laser ($\lambda = 532$ nm) was focused using a 20x Mitutoyo objective lens with a laser power of 5 mW at the sample position.

3. Results

Across the solid solution $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ all stoichiometries crystallise with orthorhombic symmetry in the space group $Pnma$. The neutron diffraction pattern of SeCoO_3 and associated Rietveld fit is shown in Figure 2. Considering that the data were obtained from very small quantities of powdered samples (~ 15 mg), the quality of the patterns collected on the Polaris instrument is sufficient for a full structure refinement [15]. With increasing Mn content the unit-cell volume increases linearly as do all three unit-cell lengths (Figure 2, Table 1). The refinement of the structural model against the neutron diffraction data allows for the precise determination of the oxygen atomic positions (Table 1), and permits the determination of the octahedral tilts (see Table 2). In the $Pnma$ structure the selenium atom sits on the 4c Wyckoff site, the transition metal on the 4b Wyckoff site, and the two oxygens on the Wyckoff 4c and 8d sites. Using the Glazer notation, the distortion of this crystal can be described by the tilt notation $a^-b^+a^-$, referring to the in-phase tilt around the [010] pseudocubic edges

and the antiphase tilts around the [100] and [001] pseudocubic edges [17]. By use of mode decomposition it is possible to describe the orthorhombic perovskite structure in terms of distortions away from the ideal cubic crystal structure. This permits the derivation of standard crystal-chemical structural relationships between properties such as the octahedral tilt angles, polyhedral volumes, and bond lengths [18]. Figure 1 shows the refined crystal structure of SeCoO_3 , highlighting the octahedral tilts which are of the order of $20\text{--}25^\circ$ away from the idealised cubic structure. For comparison, the structurally related, though significantly less distorted CaTiO_3 is also shown in Figure 1. The variation in the octahedral tilts ϕ_R and ϕ_M with manganese content is shown in Figure 1 (and Table 2), and shows a reduced distortion with increasing cobalt content. Full crystallographic structures are detailed in Table 1.

All members of the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series are antiferromagnetic in character, with a Néel transition around 53 K (see Figure 3). The behaviour above the Néel transition was fitted using the Curie-Weiss law (Equation 1) over the temperature range 240–300 K.

$$\chi = \frac{N_A \mu_B^2 \mu_{eff}^2}{3k} \frac{1}{T - \Theta_W} \quad (1)$$

The values of the fit for each member of the series are reported in Table 2. Below the Néel temperature (T_N) the field-cooled and zero field-cooled behaviour of the samples vary widely; this is partly consistent with differences in the magnetic structure of the two end members of the series, as determined by Muñoz et al. [10] and Alonso et al. [19], who found that SeCoO_3 orders noncollinearly in the ac -plane with a basis vector $(\mathbf{A}_x, \mathbf{G}_y, \mathbf{0})$, whilst SeMnO_3 orders in a collinear fashion along the z -axis with $(\mathbf{0}, \mathbf{0}, \mathbf{A}_z)$. The field-cooled and zero field-cooled are very different in form for all members in the series apart from the $x = 0$ compound. Despite this, only a relatively small shift in T_N is observed across the series (see inset Figure 3, Table 2), though there is an observed maximum in the region of the 50% Mn. The fitted effective paramagnetic moments for the $x = 0, 0.5$ samples are enhanced by a factor $\sim 15\%$, and $\sim 35\%$ respectively compared with the 100% Mn composition (See Table 2). This can be explained by small levels of an Fe impurity in the sample, introduced by the use of steel tooling during the recovery of the sample from the Pt capsule. All other fitted moments are in good agreement with that expected for high-spin $\text{Co}^{2+}/\text{Mn}^{2+}$, or that reported previously [8, 10]. The large differences in field-cooled and zero field-cooled measurements, and the observed abrupt changes in slope for $x \neq 0$, suggest that below the Néel the effect of increased Mn concentration is much more dramatic. Such abnormalities may be indicative of strong domain activity in the samples, or

perhaps secondary magnetic transitions in the sample, which are beyond the scope of this study.

Figure 3. Representative magnetisation-temperature data from the two end members of the series, both field-cooled (dashed) and zero field-cooled (solid) in 1 kOe. (inset) Shift in Néel temperature as a function of Mn content as determined from field-cooled data, dashed line is only a guide to the trend centred around 50% Mn.

The measured Raman signal from each of the samples is shown in Figure 4 (see also Table 3). Assignments were made following work on the related LaMnO_3 compound [20]. The dominant mode in all samples was found to be the in-phase MO_6 stretching mode (‘breathing’ mode) at around 750 rel cm^{-1} , with a relatively weak collection of three modes around 680 rel cm^{-1} . These modes are likely in- and out-of-phase bending, and in-phase concatenating stretching modes. The signal was considerably weaker for the high cobalt content materials (note the intensity is normalised in Figure 4). Additional modes around 400 rel cm^{-1} are from the in- and out-of-phase octahedral rotation, and oxygen $\text{O}1z$ vibration. The out-of-phase rotation is seen to soften with increasing Mn content, whereas the in-phase MO_6 stretch is seen to stiffen. The higher energy modes are all observed to stiffen with increased Mn content.

4. Discussion

Across the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series, the material remains orthorhombic in the $Pnma$ space group. This is in contrast to that observed for the related lanthanum containing $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series, which form more typical, less distorted perovskites, closer to the archetypal cubic structure. In the latter series, a low cobalt content crystallises with orthorhombic symmetry, whilst at $x \leq 0.4$ there is a change to trigonal symmetry (with space group $R\bar{3}c$) [12].

Table 1. Crystallographic data for the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series of materials determined from Rietveld analysis of the Polarized neutron powder diffraction datasets. All refinements performed using the $Pnma$ orthorhombic space group with Se: $(x, 1/4, z)$, Co/Mn: $(0, 0, 1/2)$, O1: $(x, 1/4, z)$, O2: (x, y, z)

x	0	0.125	0.25	0.5	0.75	0.875	1
a -axis ($\text{\AA}$)	5.9306(1)	5.9521(2)	5.9728(3)	6.0078(3)	6.0586(2)	6.0762(2)	6.0921(1)
b -axis ($\text{\AA}$)	7.5961(1)	7.6330(3)	7.6705(3)	7.7315(4)	7.8100(3)	7.8379(3)	7.8621(1)
c -axis ($\text{\AA}$)	5.0302(1)	5.0435(2)	5.0587(2)	5.0813(3)	5.1178(2)	5.1310(2)	5.1427(1)
V_{cell} ($\text{\AA}^3$)	226.608(6)	229.133(10)	231.763(17)	236.023(14)	242.163(13)	244.359(9)	246.318(5)
Se x	0.0221(2)	0.0223(4)	0.0221(3)	0.0250(4)	0.0279(3)	0.0252(4)	0.0257(2)
Se z	-0.0161(3)	-0.0147(5)	-0.0155(4)	-0.0160(6)	-0.0155(5)	-0.0143(5)	-0.0163(3)
O1 x	0.0700(3)	0.0715(5)	0.0723(4)	0.0754(6)	0.0760(6)	0.0784(6)	0.0788(4)
O1 z	0.3196(4)	0.3164(6)	0.3157(5)	0.3142(7)	0.3118(14)	0.3105(7)	0.3089(4)
O2 x	0.1838(2)	0.1828(4)	0.1835(3)	0.1811(4)	0.1789(4)	0.1788(4)	0.1786(2)
O2 y	0.0772(2)	0.0790(2)	0.0789(2)	0.0796(3)	0.0821(3)	0.0825(3)	0.0829(2)
O2 z	0.8660(3)	0.8625(6)	0.8666(4)	0.8678(6)	0.8704(6)	0.8691(6)	0.8697(4)
ρ (gcm^{-3})	5.449	5.369	5.296	5.175	5.013	4.958	4.905
wR_p	5.4	7.7	5.6	6.3	5.5	6.8	6.9
χ^2	4.4	5.1	9.3	13.7	4.6	3.8	6.6

Figure 4. Measured Raman signal at ambient temperature. Intensities normalised against the intensity of the dominant mode for ease of comparison. The dominant mode D is of B_{2g} character, from in-phase MO_6 stretching ('breathing' octahedral mode), A and B are from in- and out-of-phase octahedral rotation respectively, and C is an in-plane vibration mode of the oxygen O1(z). The shift of each of these modes as a function of Mn composition is shown inset, error bars shown but not visible, dotted lines are a visual guide only.

For the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series, the octahedral tilts show an almost linear increase with increasing Mn content with ϕ_M and ϕ_R ranging from $\sim 19 - 22.5^\circ$ and $\sim 25 - 26.5^\circ$ respectively (see Table 2). In contrast the octahedral tilt found in trigonal LaCoO_3 is $\sim 9.7^\circ$ at 300 K [21] and based upon the crystal structure determined by Rodriguez-Carvajal et al.[22] we determined the tilts of the orthorhombic LaMnO_3

to be $\sim 15.11^\circ$ [22].

Despite the smaller size of the Se^{4+} cation compared with La^{3+} , 0.5 $\text{\AA}$ and 1.22 $\text{\AA}$ respectively, the pseudocubic unit cell volume ‡ of the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series is of the order of 17% larger than that of the equivalent $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series (see Figure 2) [23, 24]. This is counterintuitive, as for example in the $\text{LnCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ series, it is reported that decreasing the lanthanide (Ln) ionic radii results in a corresponding decrease in unit-cell volume [25]. However, considering the structure (Figure 1) there are two factors contributing to this discrepancy. Firstly, there is a difference in the oxidation state of the B-site cations, Co^{3+} and Co^{2+} , driven by the electrostatic balance with the La^{3+} and Se^{4+} cations respectively. This leads to a difference in the M-O bond distances within the octahedra, for example the Co-O bond distances are 1.93 $\text{\AA}$ [21] and 2.08-2.22 $\text{\AA}$ for LaCoO_3 and SeCoO_3 respectively. The M-O bond distances increase linearly with increasing manganese content to values of 2.17-2.29 $\text{\AA}$ for SeMnO_3 §. As a result of this, the octahedral volumes (V_{octa}) [26] are approximately 26% larger across the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series than the $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series (SeCoO_3 : 13.0835 $\text{\AA}^3$, LaCoO_3 : 9.6062 $\text{\AA}^3$ [21], and SeMnO_3 : 14.7802 $\text{\AA}^3$,

‡ Shown at the equivalent pseudocubic unit-cell volumes $V_{pc} = a_{pc}b_{pc}c_{pc}$. For the orthorhombic lattice, $a = \sqrt{2}a_{pc}$, $b = \sqrt{2}b_{pc}$, and $c = 2c_{pc}$. For the rhombohedral lattice, $a = \sqrt{2}a_{pc}$.

§ It should be noted that for the orthorhombic perovskite structure in the $Pnma$ space group, the transition metal cation is sited on only one Wyckoff site (4b). When there are multiple cations occupying this site, they are modelled as being disordered, and hence the determined bond distances are only an average of the Mn-O and Co-O bonds.

LaMnO_3 : $10.8997 \text{ \AA}^3$ [22]), see Table 2. Secondly, the larger unit-cell volume is also partly due to the greater degree of rotation and distortion of the MO_6 octahedra within the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ octahedra than for the $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series. This is clear from the range of M–O lengths within the octahedra for each composition in the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series.

A useful metric for quantifying the structural distortion of a perovskite material is the tolerance factor [27], calculated from the ratio of the ionic radii of the cations and anions $\parallel$. For the ideal cubic perovskite the tolerance factor is unity. For the orthorhombic mineral perovskite CaTiO_3 the tolerance factor is 0.946. For LaCoO_3 and LaMnO_3 the tolerance factors are 0.97 and 0.942 respectively. In contrast, the tolerance factors for SeCoO_3 and SeMnO_3 are 0.75 and 0.712 respectively. Such low values are believed to be outside the stability region for a perovskite structure, where 0.8 is considered the lower limit of stability. However, more recently it has been shown that below a value of 0.71 it is expected that the material will adopt the trigonal ilmenite structure of FeTiO_3 [28]. This could suggest that although apparently stable, the perovskite-structured $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series is in fact metastable, and the thermodynamically stable phase should crystallise with a different ilmenite structure. However, the stereochemically active lone pair associated with the selenium cation would suggest that the octahedral environment present within the ilmenite structure is unlikely, and it is possible that this stabilises the perovskite structure.

Another method to quantify the structural instabilities is to consider the magnitudes of the seven orthogonal, symmetry adapted basis-vectors of the aristotype cubic phase. This permits direct comparison to other related materials in terms of displacive modes as described elsewhere [18]. For each composition in the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series the determined lattice parameters and fractional coordinates were decomposed in this way, with respect to an aristotype phase consistent with the space group $Pbnm$ ¶ [29]. The displacements of the Se cation along the orthorhombic a - and b -axes, are each described by the sum of two basis-vectors of equal magnitude. These transform as the irreducible representations (irreps) of the cubic aristotype phase, R_5^+ and X_5^+ along the a -axis and b -axis respectively. Neither vary significantly across the series, and are low in amplitude, which is indicative of the stability of the SeO_3 flattened pyramidal unit (See Se–O bond lengths in Table 2).

$\parallel$ Defined as $t = (r_A + r_X)/(\sqrt{2}(r_B + r_X))$, where r_A is the radius of the A cation, r_B is the radius of the B cation, and r_X is the radius of the X anion.

¶ Transformed from space group $Pnma$.

The primary order parameters for a perovskite-structured compound with space group $Pnma$, or any one of its alternative space group settings, are associated with the in-phase and anti-phase tilting modes that transform as the irreps M_3^+ and R_4^+ respectively [30], and these are both found to increase linearly across the series with increasing manganese content. The MO_6 octahedra are also potentially deformed from the cubic structure by modes that transform as the irreps X_5^+ , M_2^+ and R_5^+ [29, 31, 32]. In all compositions, the magnitudes of the tilting modes (M_3^+ and R_4^+) are larger than the octahedral deformation mode with irrep X_5^+ . However, the amplitudes of the octahedral deformation modes (irreps M_2^+ and R_5^+) are large compared to other orthorhombic systems [33], providing further evidence that these materials are highly unstable. It has been suggested that the amplitude of the M_2^+ mode is only appreciable when the B-site cation displays a Jahn-Teller distortion [29].

In contrast to other systems, there is very little change in the antiferromagnetic magnetic ordering temperatures with x , there is only a 1 K change in Néel temperature over the entire compositional range of $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$. The $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series (Co^{3+d6}) is reported to be predominantly ferromagnetic [12], this is suggestive of a mixed valence Co/Mn [34]. The Curie temperature is reported to vary from 224 K to 177 K over the compositional range [12], with a change in superexchange angle (M–O–M) from 155.43° for LaMnO_3 to 163.9° for LaCoO_3 [22, 35]. The $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series shows a consistently smaller variation in superexchange angle across the series, 126.94° for SeMnO_3 to 129.67° for SeCoO_3 , while their significantly lower values compared with the $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series are consistent with weaker superexchange and therefore lower transition temperatures. Both of the M–O–M bond angles are observed to increase approximately linearly towards the 180° with increased Co content (see Table 2). As the cell volume also reduces with Co content, it is expected that the superexchange coupling would be enhanced with increased concentration. Instead the Néel temperature is observed to decrease again above 50% Co. It is possible that a change in the overall spin-state of the B-site cation results in reduction in the superexchange interaction. However, Alonso et al. [19] reported that the Co^{2+} in SeCoO_3 has a moment of $3.37(3) \mu_B$ at 2.2 K, suggesting that it is present in a high-spin $5t_{2g}2e_g$ configuration. The authors also reported that the Mn^{2+} in SeMnO_3 has a moment of $4.64(2) \mu_B$ at 2.6 K, indicating that Mn^{2+} is present in either a high-spin $3t_{2g}2e_g$ configuration, or a mixed low/high-spin configuration. An alternative reason for the reduction in Néel temperature above

Table 2. Selected bond distances and angles for the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series of materials determined from the crystallographic structures. Also shown are the octahedral volumes (MO_6) [26] and tilts (ϕ_R & ϕ_M) as determined from the mode analysis[18]. Finally the Néel transition temperature determined from the SQUID measurements is also detailed. The orbital mixing coefficients c_1 and c_2 , relating the bonding (ψ_g) and antibonding (ψ_e) orbitals to a linear combination $\psi_g = c_1\Phi_{x^2-y^2} + c_2\Phi_{3z^2-r^2}$, and $\psi_e = c_2\Phi_{x^2-y^2} - c_1\Phi_{3z^2-r^2}$, are derived as explained elsewhere [22].

x	0	0.125	0.25	0.5	0.75	0.875	1
$V_{\text{octa}} (\text{\AA}^3)$	13.0835	13.3022	13.5125	13.8839	14.5216	14.6111	14.7802
M-O1 ($\text{\AA}$)	2.145(1)	2.163(2)	2.176(1)	2.199(2)	2.232(1)	2.239(2)	2.249(1)
M-O2 ($\text{\AA}$)	2.219(2)	2.212(3)	2.238(2)	2.248(3)	2.281(1)	2.277(3)	2.286(2)
M-O2 ($\text{\AA}$)	2.077(1)	2.100(2)	2.097(2)	2.212(3)	2.155(1)	2.163(2)	2.170(1)
M-O1-M ($^\circ$)	124.55(10)	123.80(14)	123.63(12)	123.09(17)	122.56(15)	122.15(16)	121.82(9)
M-O2-M ($^\circ$)	129.67(7)	129.57(12)	129.02(9)	128.37(28)	127.08(11)	127.16(12)	126.94(7)
Se-O1 ($\text{\AA}$)	1.712(2)	1.695(4)	1.702(3)	1.705(4)	1.698(1)	1.698(4)	1.704(2)
Se-O2 ($\text{\AA}$)	1.731(2)	1.732(2)	1.734(2)	1.722(3)	1.701(1)	1.718(3)	1.714(2)
O1-Se-O2 ($^\circ$)	103.4(1)	103.8(2)	103.0(1)	103.9(2)	103.9(1)	104.9(1)	104.2(1)
ϕ_R ($^\circ$)	23.6	24.11	24.04	24.24	24.96	25.00	25.12
ϕ_M ($^\circ$)	20.01	19.8	20.12	20.47	20.59	20.81	20.92
c_1	0.698	0.681	0.680	0.664	0.639	0.637	0.628
c_2	0.716	0.732	0.733	0.748	0.769	0.771	0.778
T_N (K)	52.4(2)	52.6(2)	53.0(2)	53.4(2)	52.9(2)	52.4(2)	52.0(2)
μ_{eff} (μ_B)	8.01(2)	6.56(2)	6.39(2)	9.35(3)	6.19(2)	6.83(2)	6.96(2)
Θ_W (K)	-236(2)	-154(2)	-110(2)	-267(3)	-79(2)	-114(2)	-117(2)

Table 3. Raman mode assignments, and fitted peak positions (in rel cm^{-1}) for selected members of the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series. Data were background subtracted and fitted using a Lorentzian peak profile. The reported mode assignments are estimated from the work of Iliev et al.[20], and are consistent in notation. For the $x = 0.125, 0.25$, and 0.75 only the $B_{2g}(1)$ mode could be measured, at positions 743.90(13), 745.9(1), and 753.6(9) respectively.

x	0	0.5	0.875	1
$A_g(2)$	380.2(2)	380.2(2)	380.3(2)	380.40(12)
$A_g(4)$	410.0(6)	404.5(3)	400.91(9)	399.87(5)
$B_{2g}(\text{O1z})$	438.2(6)	437.5(3)	435.9(2)	435.89(11)
$B_{2g}(3)$	641.1(4)	657.9(4)	666.1(2)	666.73(7)
$A_g(3)$	652.6(3)	672.7(5)	682.70(12)	684.37(3)
$A_g(1)$	664.2(6)	689.8(5)	695.2(3)	696.6(1)
$B_{2g}(1)$	742.90(3)	749.65(5)	755.08(2)	756.860(5)

50% Co may be linked to a more complex exchange environment for SeCoO_3 , resulting in a non-collinear magnetic state. Additional low-temperature neutron diffraction measurements would be required to shed further light on the magnetic structure evolution across the series.

The differences between the M-O bond lengths can be used to directly infer information related to the degeneracy lifting of the e_g orbitals due to the Jahn-Teller effect. Following the formalism

reported by Rodriguez-Carvajal et al.[22] in the study of LaMnO_3 , this breaking of degeneracy can be delineated using mixing coefficients which describe bonding and antibonding orbital occupations, full details are reported elsewhere [36]. In the case of the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series, the mixing coefficients (reported in Table 2) show a definitive convergence to a single value, and thus a lessening of the Jahn-Teller distortion with increased Co content. While both high-spin and low-spin $\text{Co}^{2+}(\text{d}^7)$ show degeneracy, high-spin $\text{Mn}^{2+}(\text{d}^5)$ does not. For comparison, the orbital mixing coefficient $c_2 = 0.8074$ for LaMnO_3 at room temperature [22].

The Raman spectra don't show any significant change over the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series, other than a shift in the position of the observed vibrational modes (see Table 3). The large differences in intensity between the octahedral bending modes and the 'breathing' mode in all the samples suggests that electronically, the covalency is strong in the octahedral unit. The M-O stretching vibration mode is seen to stiffen with increasing Mn content, consistent with Mn-O having a slightly greater bond dissociation energy. Comparing the spectra with those reported for the $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ [37] it is clear that the principal M-O in-phase stretching mode is consistently at higher energies for the Se series. This is perhaps counterintuitive, as a reduction in ionic radius of the A-site cation corresponds to an increase in M-O bond length, which is reported in the literature to result in

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a lower energy mode [38]. As lattice effects don't fully account for the large stiffening of the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series, it is possible that the significantly smaller ionic radius of the Se cation results in a stronger covalency of the M–O bonds, and hence a stiffening of the mode [25].

5. Conclusion

It is clear that the Se cation is the controlling element of the distorted structure in the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series, and that varying the Co/Mn ratio has relatively little effect on the crystallographic structure. Furthermore, the Néel transition is not changed significantly with B-site composition in this series, despite the known difference in magnetic structure at low temperatures. This is in contrast to that of the $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series which shows both significant crystallographic and physical property changes with Co/Mn ratio. The B-site composition seemingly has more influence over the properties of the $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ series, compared with the more distorted $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series which is dominated by the excessively tilted octahedra, driven by the small A-site cation. Despite only causing small changes to the crystal structure at room temperature, increased Mn concentration shows anomalies in the field-cooled/zero field-cooled magnetometry data of the $\text{SeCo}_{1-x}\text{Mn}_x\text{O}_3$ series, and may be indicative of more dramatic changes to the magnetic structure below the Néel transition.

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