

# Ferrimagnetic structures with rare-earth induced spin-reorientation in the Mn self-doped perovskite (Er<sub>0.7</sub>Mn<sub>0.3</sub>)MnO<sub>3</sub>

Andreas Dönni,<sup>1</sup> Vladimir Y. Pomjakushin,<sup>2</sup> Martin Rotter,<sup>3</sup> Lei Zhang,<sup>1,4</sup>  
Kazunari Yamaura,<sup>1,4</sup> Alexei A. Belik<sup>1,\*</sup>

<sup>1</sup> *Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan*

<sup>2</sup> *Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*

<sup>3</sup> *McPhase Project, 30121 Venice, Italy*

<sup>4</sup> *Graduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan*

\* Corresponding Author: Alexei.Belik@nims.go.jp

Ceramics International **50**(21), 43414-43423 (2024)

<https://doi.org/10.1016/j.ceramint.2024.08.191>

Accepted manuscript

11 August 2024

**Keywords:** Perovskites; Crystal structure; magnetic structure; spin-reorientation; ferrimagnets

## Abstract

The search for spin-reorientation (SR) phase transitions, a spontaneous rotation of ordered magnetic moments, in ferrimagnetic (FiM) materials, which carry a net magnetization, is of fundamental and practical interest for applications in the field of spintronics. In this work, we have investigated Mn self-doped  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  solid solution with  $\text{GdFeO}_3$ -type *Pnma* perovskite structure by combining specific heat, magnetic susceptibility and neutron powder diffraction measurements. We provide experimental evidence for FiM order below  $T_C = 104$  K, and a spontaneous SR transition at  $T_{\text{SR}} = 11$  K. A FiM structure appears in all  $(\text{R}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds with  $\text{R} = \text{Dy-Lu}$  for  $x \geq 0.2$ . But in this structural family,  $\text{R} = \text{Er}$  is the only material with a SR transition. Below  $T_C = 104$  K, FiM order in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  appears with ferromagnetic (FM) ordering of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations at the B site pointing along the *a*-direction, which are antiferromagnetically (AFM) coupled with  $\text{Er}^{3+}$  and  $\text{Mn}^{2+}$  cations at the A site. At  $T_{\text{SR}} = 11$  K, ordered  $\text{Er}^{3+}$  cations change direction from the magnetically harder *a*-axis to the magnetically easy *b*-axis and induce a change of the whole FiM structure, including the direction of all Mn spins from the irreducible representation  $m\text{GM}3+$  to  $m\text{GM}4+$ . We calculated the crystal-field (CF) anisotropy for  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  and  $\text{Er}^{3+}$  in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , based on the point charge model. The results show large magnetic anisotropies. For the FiM structure of  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$ , the magnetically easy *a*-axis of  $\text{Ho}^{3+}$  keeps the high-temperature magnetic directions along the *a*-axis and gives rise to a pronounced magnetization reversal effect at low temperature because of a significant rise of the  $\text{Ho}^{3+}$  ordered moments. On the other hand, for the FiM structure of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , the magnetically easy *b*-axis of  $\text{Er}^{3+}$  gives rise to a SR phase transition at  $T_{\text{SR}}$ , which does not lead to magnetization reversal even though the  $\text{Er}^{3+}$  ordered moments rise significantly at low temperatures.

## 1. Introduction

Spin-reorientation (SR) phase transitions involve a spontaneous rotation of ordered magnetic moments [1, 2]. They are an important phenomenon of rare-earth perovskites containing unpaired  $3d$  and  $4f$  electrons and arise from competing rare-earth and transition metal anisotropies that are coupled by magnetic exchange interactions. The structural families of the orthoferrites  $R\text{FeO}_3$  [3] and orthochromites  $R\text{CrO}_3$  [4] have been extensively studied. In both cases, rare-earth and transition metal cations are located on different sublattices and the temperature of the SR transition depends on the rare-earth (R) cation.

Compounds with SR transitions have the potential to be utilized for ultrafast repeatable magnetization switching in spintronic components [5, 6]. Ferrimagnetic (FiM) materials are particularly attractive because they carry a net magnetization [7, 8]. Using a FiM  $\text{GdFeCo}$  thin film, a magnetization reversal in the time scale of  $\sim 10$  picoseconds has been reported [6]. In this sense, the search for new FiM materials with SR phase transitions is both, of fundamental and practical interest. In this work, we provide experimental evidence that  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  is a new FiM material ( $T_C = 104$  K) with a SR phase transition ( $T_{\text{SR}} = 11$  K).

Perovskite-structure rare-earth manganites,  $\text{R}^{3+}\text{Mn}^{3+}\text{O}_3$ , have received a lot of attention in literature [9-15]. They possess different degrees of freedom, such as, spin and orbital, and a variety of electric and magnetic phases appear as a function of temperature, magnetic field and size of the  $\text{R}^{3+}$  cation, including structural orbital-order transitions and spin-order transitions involving  $3d$   $\text{Mn}^{3+}$  cations. Of particular interest are compounds with smaller  $\text{R}^{3+}$  cations ( $\text{R} = \text{Tb-Lu}$ ) as Mn spin order produces spin-induced ferroelectric properties [9-13]. Doping of  $\text{RMnO}_3$  by aliovalent A cations,  $(\text{R}_{1-x}\text{A}_x)\text{MnO}_3$ , introduces a charge degree of freedom and mixed valent  $\text{Mn}^{3+}/\text{Mn}^{4+}$  cations. Interactions between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations give rise to high-temperature (above room temperature) ferromagnetic properties [16, 17]. Aliovalent doping is usually realized with  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  cations, which have comparable sizes with  $\text{R}^{3+}$  cations. However, aliovalent doping can also be realized with small  $\text{Mn}^{2+}$  cations. In such a case,  $(\text{R}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds can be called as self-doped by Mn. The coexistence of three different valence states ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ ) in  $(\text{R}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds has been experimentally confirmed by Hard X-ray Photoelectron Spectroscopy (HAXPES) spectra measured for two members  $(\text{Lu}_{0.6}\text{Mn}_{0.4})\text{MnO}_3$  and  $(\text{Er}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  [18].

A conventional solid-state synthesis at ambient pressure results in very limited ranges ( $x$ ) of solid solutions  $(R_{1-x}Mn_x)MnO_3$  [19-22]. In addition, it is difficult to control the oxygen content in  $(R_{1-x}Mn_x)MnO_3$  during conventional solid-state reactions. We, however, found that a high-pressure high-temperature synthesis method can significantly expand solid solution limits in  $(R_{1-x}Mn_x)MnO_3$  and allows controlling the oxygen content more precisely [18, 23-26]. The solubility limit of  $(R_{1-x}Mn_x)MnO_3$  solid solutions decreases with increasing size of the rare-earth cation (from  $x$  slightly above 0.4 for  $R = Lu$  [18], to  $x$  close to 0.33 for  $R = Tm$  [24], to  $x$  slightly above 0.3 for  $R = Er$  [18] and to  $x$  slightly below 0.3 for  $R = Ho$  [26]).

Magnetic property measurements (magnetic susceptibility, magnetization and specific heat) of Mn self-doped orthorhombic perovskite  $(Er_{1-x}Mn_x)MnO_3$  compounds with  $x = 0.333$ , 0.3 and 0.2 have been reported in [18]. The parent compound  $ErMnO_3$  ( $x = 0$ ) shows two antiferromagnetic phase transitions at 42 and 28 K originating from Mn ordering [27, 28], and spin-induced ferroelectricity appears below 28 K. When self-doping Mn onto the A site, it appears as  $Mn^{2+}$  and produces a charge transfer from the A site ( $Er^{3+}$ ,  $Mn^{2+}$ ) to the B site ( $Mn^{3+}$ ,  $Mn^{4+}$ ). For  $x = 0.2$  and larger, ferroelectricity disappeared and a ferrimagnetic (FiM) structure appears with a macroscopic ferromagnetic (FM) moment. The fact that  $(Er_{0.667}Mn_{0.333})MnO_3$  contained an impurity phase (about 4 wt %  $Er_{0.88}Mn_3O_{5.82}$  [29]) indicated that the substitution limit at the A site is a little bit smaller than 33% at the synthesis conditions used.  $(Er_{1-x}Mn_x)MnO_3$  compounds with  $x = 0.2$  and  $x = 0.3$  were both single phase. The FiM ordering temperature  $T_C$  increased with increasing  $Mn^{4+}$  content from 75 K ( $x = 0.2$ ) to 104 K ( $x = 0.3$ ) and 109 K ( $x = 0.333$ ).  $(Er_{1-x}Mn_x)MnO_3$  compounds show an additional first-order phase transition with the ordering temperature  $T_{SR}$  decreasing with decreasing  $Er^{3+}$  content from 16 K ( $x = 0.2$ ) to 10 K ( $x = 0.3$ ) and 9.5 K ( $x = 0.333$ ).  $(R_{1-x}Mn_x)MnO_3$  compounds with  $x \geq 0.2$  and  $R = Ho, Tm, Yb, Lu$  generally show FiM ordering [23-26]. But an additional phase transition at  $T_{SR}$  has not been observed in any of these materials.

In this work we have selected  $Er_{0.7}Mn_{0.3}MnO_3$  ( $x = 0.3$ ) and used neutron diffraction to measure the crystal structure (structural parameters, strain broadening) and magnetic structures (to clarify the nature of the phase transition at  $T_{SR}$ ). We performed additional magnetic property measurements (magnetic susceptibility and specific heat) and present a calculation of the crystal field (CF) anisotropy based on the point charge model to compare magnetic

properties of the two compounds  $\text{Ho}_{0.8}\text{Mn}_{0.2}\text{MnO}_3$  and  $\text{Er}_{0.7}\text{Mn}_{0.3}\text{MnO}_3$  with large rare-earth moments.

## 2. Experimental

For magnetic properties measurements and neutron diffraction experiments, several batches of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  solid solution (with the total weight of 3 g) were synthesized from a stoichiometric mixture of  $\text{Er}_2\text{O}_3$  (99.9%) and  $\text{Mn}_2\text{O}_3$ . Single-phase  $\text{Mn}_2\text{O}_3$  was prepared from commercial  $\text{MnO}_2$  (99.99%) by heating in air at 923 K for 24 h. The mixture was placed in a Pt capsule and treated at 1670 K and 6 GPa for 2 h in a belt-type HP apparatus. The heating time to the synthesis temperature was about 10 min. After the heat treatment, the  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  sample was quenched to room temperature (RT), and the pressure was slowly released.

All measurements reported in this work were performed on this  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  sample. The magnetic susceptibility was measured on a SQUID magnetometer (Quantum Design MPMS-XL-7T) between 2 and 300 K in a very small applied magnetic field of  $H = 1$  Oe under field-cooled upon cooling (FCC) condition. The specific heat ( $C_p$ ) values were recorded in magnetic fields of 0 and 70 kOe between 2 and 300 K upon cooling and heating by a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS).

To determine the magnetic structures of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , powder neutron diffraction experiments were performed at the Paul Scherrer Institute, Switzerland, on the high-resolution powder diffractometer for thermal neutrons (HRPT) [30] using an incident neutron wavelength of  $\lambda = 1.886$  Å. Data were collected in the magnetically ordered and paramagnetic states at temperatures between 1.8 and 130 K for a  $2\theta$  range of  $3.55^\circ - 164.50^\circ$  and a step width of  $0.05^\circ$ . The diffraction patterns were analyzed by the Rietveld method using the FullProf Suite [31]. Possible models for the magnetic structures were deducted based on a group theory analysis using the programs ISODISTORT [32] and BASIREPS in the FullProf Suite program package [31].

The shapes of the Bragg peaks were refined using a Thompson-Cox-Hastings pseudo-Voigt function that consists of a Gaussian and a Lorentzian component. The correlation length ( $L$ ) of the magnetic structure has been estimated from the Lorentzian peak broadening of the

resolution parameter  $Y$  ( $Y_m$  of the magnetic structure compared to  $Y_n$  of the crystal structure), by using the well-known Debye-Scherrer formula  $\sigma_1 = Y_m - Y_n = \lambda/L$  [33]. Here,  $\lambda = 1.886$  Å is the neutron wavelength. Strain broadening was modeled for (100) anisotropic broadening in an orthorhombic lattice using quartic form in reciprocal space [34, 35]. Orthorhombic symmetry allows six independent strain parameters  $S_{HKL}$  [35]. Four of them (e.g.,  $S_{040}$ ,  $S_{004}$ ,  $S_{220}$ , and  $S_{022}$ ) turned out to be zero within experimental error, whereas the other two parameters,  $S_{400}$  and  $S_{202}$ , significantly deviated from zero and were refined.

Calculations of the CF anisotropy were performed for the compounds  $(Er_{0.7}Mn_{0.3})MnO_3$ ,  $(Er_{0.8}Mn_{0.3})MnO_3$  and  $(Ho_{0.8}Mn_{0.2})MnO_3$ , using the McPhase program [36-38].

### 3. Results and discussion

#### 3.1. Structural Properties of $(Ho_{1-x}Mn_x)MnO_3$

The orthorhombic perovskite crystal structure of  $(Er_{0.7}Mn_{0.3})MnO_3$  (space group  $Pnma$ , No. 62) is shown in Fig. 1. Magnetic ions are located on alternating layers of A site (70%  $Er^{3+}$ , 30%  $Mn^{2+}$ ) and B site (70%  $Mn^{3+}$ , 30%  $Mn^{4+}$ ). Room temperature lattice constants (based on laboratory powder X-ray diffraction) have been reported in Ref. [18], but no structural parameters. We have determined the structural parameters of paramagnetic  $(Er_{0.7}Mn_{0.3})MnO_3$  at  $T = 130$  K by neutron diffraction. The results are summarized in Table 1. Calculated values for selected bond lengths, Mn-O-Mn bond angles, and bond-valence sums (BVS) [39] are given in Table 2. Doping on the A site of 70%  $Er^{3+}$  and 30%  $Mn^{2+}$  ions with different sizes and mass causes micro strain effects and anisotropic broadening of some Bragg reflections. The refinement of the crystal structure of paramagnetic  $(Er_{0.7}Mn_{0.3})MnO_3$  at  $T = 130$  K shown in Supplementary Fig. S1 gives a rather poor agreement ( $\chi^2 = 4.03$ ). A refinement that includes corrections for strain broadening (details as described in section 2) shown in Fig. 2a gives a much better agreement ( $\chi^2$  improved from 4.03 to 2.28). Such strain effects are a common feature in orthorhombic Mn self-doped  $(R_{1-x}Mn_x)MnO_3$  materials ( $R = Ho-Lu$ ) [23-26]. Fig. 3 shows the temperature dependence of the lattice constants  $a$ ,  $b$ ,  $c$  and the volume  $V$  of  $(Er_{0.7}Mn_{0.3})MnO_3$  below  $T = 130$  K based on neutron diffraction data. A pronounced anomaly (maximum) is observed at  $T_{SR}$  for all four parameters due to spin lattice coupling. Below  $T_C = 104$  K, the inter-layer distance (lattice constant  $b$ ) increases with decreasing temperature,

whereas the intra-layer distances (lattice constants  $a$ ,  $c$ ) as well as the volume  $V$  decrease. Such a behavior has already been observed at the FiM phase transition  $T_C$  of other Mn self-doped  $(R_{1-x}Mn_x)MnO_3$  materials ( $R = \text{Ho-Lu}$ ) [23-26].

Fig. 4a shows the temperature dependence of the specific heat  $C_p/T$  (measured at zero field) and the magnetic susceptibility  $\chi$  (measured in a very small applied magnetic field of  $H = 1$  Oe) for our  $(Er_{0.7}Mn_{0.3})MnO_3$  sample. These data provide evidence for magnetic phase transitions at  $T_C = 104$  K (second order) and  $T_{SR} = 11$  K (first order). As shown in Fig. S3b of [18], for our  $(Er_{0.7}Mn_{0.3})MnO_3$  sample,  $T_{SR} = 11$  K is found to be slightly larger than  $T_{SR} = 10$  K measured for  $(Er_{0.7}Mn_{0.3})MnO_3$  sample No. 2. In the  $C_p/T$  curves a very sharp anomaly appears at  $T_{SR} = 11$  K for heating but not for cooling which is an artifact of the pulse relaxation method used in the measurement. The maximum of  $C_p/T$  at  $T = 5$  K indicates magnetic saturation. The magnetic field dependence of the  $C_p/T$  anomaly at  $T_{SR}$  is displayed in Fig. 4b. The peak position decreased from 11 K ( $H = 0$  T) to 7 K ( $H = 30$  kOe) and the peak broadens with increasing field. Specific heat curves  $C_p/T$  measured in an external magnetic field of  $H = 70$  kOe are shown in Supplementary Fig. S2. The magnetic phase transition at  $T_{SR}$  has disappeared and the maximum at magnetic saturation has slightly increased to  $T = 8$  K. Magnetic susceptibility data measured in larger magnetic fields of  $H = 100$  Oe and  $H = 10$  kOe have been published in Fig. 4b of [18].

### 3.2. Magnetic structures of $(Er_{0.7}Mn_{0.3})MnO_3$

Fig. 2 shows the refinement of neutron diffraction patterns of  $(Er_{0.7}Mn_{0.3})MnO_3$  measured in the paramagnetic state at (a)  $T = 130$  K, and in the magnetically ordered states at (b)  $T = 20$  K (between  $T_{SR}$  and  $T_C$ ) and (c)  $T = 1.8$  K (below  $T_{SR}$ ). Simultaneous refinements of crystal and magnetic structures were performed in the full range of scattering angles  $2\theta$  up to  $162^\circ$ . The inset of Fig. 2a shows a very weak Bragg peak near  $2\theta = 20.9^\circ$  from an impurity phase. This peak has been excluded from the refinements in the magnetically ordered state. Below  $T_C = 104$  K, all observed magnetic Bragg peaks can be indexed with a propagation vector  $\mathbf{k}_1 = (0, 0, 0)$ . At  $T_{SR} = 11$  K, a drastic change of intensities of magnetic Bragg peaks is observed (Figs. 2b, 2c), but no change of the propagation vector  $\mathbf{k}_1$ . For the space group  $Pnma$ , the propagation vector  $\mathbf{k}_1$  and sites 4c (A site) and 4b (B site), representation analysis for the possible magnetic

structures gives the result summarized in Table 3. There are eight irreducible representations (irreps) with different symmetry. Three of them,  $mGM3+$ ,  $mGM4+$  and  $mGM2+$ , allow a FM moment ( $F, f$ ) at both, A- and B sites, along the  $a$ -,  $b$ - and  $c$ -directions, respectively. The  $2\theta$  values of the Bragg peak positions of magnetic and crystal structures are the same for the FM components ( $F, f$ ) and are different for the AFM components ( $C, c, G, g, A, a$ ). As shown in the inset of Fig. 2c, observed intensities of the AFM Bragg peaks are extremely weak. No intensity was detected for the (0, 0, 1) peak. The (1, 0, 0) peak has intensity at  $T = 20$  K, but not at 1.8 K. On the other hand, for the (0, 1, 0) peak, intensity was detected at  $T = 1.8$  K, but not at 20 K.

At  $T = 20$  K, the observed magnetic structure of  $(Er_{0.7}Mn_{0.3})MnO_3$  belongs to the irrep  $mGM3+$  ( $\Gamma_7$ ). Mn2 at the B site can have ordered moments ( $F_x, A_y, C_z$ ) along all 3 directions. For Er and Mn1 at the A site, ordered moments ( $f_x, 0, c_z$ ) lie within the  $ac$ -plane. The result of the refinement of the average ordered moments at A- and B sites at  $T = 20$  K is given in Table 4. The magnetic structure is FiM and dominated by large values for  $F_{x,ave} = 2.95(5) \mu_B$  and  $f_{x,ave} = -2.00(4) \mu_B$  with AFM coupling between A- and B sites. There is a macroscopic FM moment of  $F_a = F_{x,ave} + f_{x,ave} = 0.96(9) \mu_B$  along the  $a$ -direction. At  $T = 20$  K, the purely magnetic weak Bragg peak (1,0,0) at  $2\theta = 19.6^\circ$ , shown in the inset of Fig. 2c, gives rise to an AFM component  $c_{z,ave} = 1.01(6) \mu_B$  at the A site and a small canting of the FiM structure. The magnetic structure of  $(Er_{0.7}Mn_{0.3})MnO_3$  at  $T = 20$  K is shown in Fig. 5a.

At  $T = 1.8$  K, the observed magnetic structure of  $(Er_{0.7}Mn_{0.3})MnO_3$  belongs to the irrep  $mGM4+$  ( $\Gamma_5$ ). Mn2 at the B site can have ordered moments ( $C_x, F_y, A_z$ ) along all 3 directions, whereas the ordered moments of Er and Mn1 at the A site point along the  $b$ -direction ( $0, f_y, 0$ ). The result of the refinement of the average ordered moments at A- and B sites is given in Table 4. The magnetic structure is FiM and dominated by large values for  $F_{y,ave} = -3.05(3) \mu_B$  and  $f_{y,ave} = 4.60(3) \mu_B$  with AFM coupling between A- and B sites. There is a macroscopic FM moment of  $F_b = F_{y,ave} + f_{y,ave} = 1.55(6) \mu_B$  along the  $b$ -direction. At  $T = 1.8$  K, the purely magnetic weak Bragg peak (0,1,0) at  $2\theta = 14.6^\circ$  shown in the inset of Fig. 2c gives rise to an AFM component  $A_{x,ave} = -0.44(3) \mu_B$  at the B site and a small canting of the FiM structure. The magnetic structure of  $(Er_{0.7}Mn_{0.3})MnO_3$  at  $T = 1.8$  K is shown in Fig. 5b.

Fig. 6a shows the temperature dependence of the average ordered moments.  $T_{\text{SR}} = 11$  K is a spin-reorientation (SR) temperature, where all FM components change direction from the  $a$ -direction (above  $T_{\text{SR}}$ ) to the  $b$ -direction (below  $T_{\text{SR}}$ ). At  $T_{\text{SR}}$ , the magnitude of the ordered Mn moments at the B site ( $F_{x,\text{ave}}, F_{y,\text{ave}}$ ) doesn't change, whereas the average ordered FM moment at the A site ( $f_{x,\text{ave}}, f_{y,\text{ave}}$ ) jumps to a larger value at lower temperature. A coexistence of both phases (28% GM3+, 72% GM4+) is observed in the measurement at  $T = 10$  K, which indicates that  $T_{\text{SR}}$  is a first-order magnetic phase transition. Above  $T_{\text{SR}}$ , the temperature dependence of the macroscopic average FM moment,  $F_a$ , agrees with that of the FCC magnetic susceptibility  $\chi$  measured in a very small magnetic field of  $H = 1$  Oe (Fig. 6b). The temperature dependence of the correlation length of the magnetic structure is shown in Fig. 6c. The correlation length (determined as described in section 2) strongly increases towards low temperature from 242(26) nm at  $T = 20$  K to 593(15) nm at  $T = 1.8$  K (Table 4).

In the refinement, we have determined the average values for the ordered moments at the A site, ( $f_{x,\text{ave}}, c_{z,\text{ave}}$ ) above  $T_{\text{SR}}$  and ( $f_{y,\text{ave}}$ ) below  $T_{\text{SR}}$ . Since, apart from the difference of the magnetic form factors for  $\text{Er}^{3+}$  and  $\text{Mn}^{2+}$  (not accurate), our neutron diffraction data cannot distinguish between the contributions from 70% of  $\text{Er}^{3+}$  and 30% of  $\text{Mn}^{2+}$  to the average value at the A site, it is necessary to use an approximation. It is reasonable to assign the AFM component  $c_z$  to  $\text{Er}^{3+}$ , since magnetic intensity appears close to  $T_{\text{SR}} = 11$  K and not close to  $T_C = 104$  K.

Then, for  $m\text{GM3+}$  (above  $T_{\text{SR}}$ ), we have

A site: Mn ( $f_{x,\text{Mn}}, 0, 0$ ), Er ( $f_{x,\text{Er}}, 0, c_{z,\text{Er}}$ );

B site: Mn ( $F_{x,\text{Mn}}, 0, 0$ ).

For  $m\text{GM4+}$  (below  $T_{\text{SR}}$ ), we have

A site: Mn ( $0, f_{y,\text{Mn}}, 0$ ), Er ( $0, F_{y,\text{Er}}, 0$ );

B site: Mn ( $A_{x,\text{Mn}}, F_{y,\text{Mn}}, 0$ ).

Following the data analysis of the magnetic structure of  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  in the previous work [26], we correlate the ordered Mn moments at B and A sites as follows:

(Model #1):  $-f_{x,\text{Mn}} = 1.53 \cdot F_{x,\text{Mn}}$  and  $-f_{y,\text{Mn}} = 1.53 \cdot F_{y,\text{Mn}}$ .

(Model #2):  $-f_{x,\text{Mn}} = 1.23 \cdot F_{x,\text{Mn}}$  and  $-f_{y,\text{Mn}} = 1.23 \cdot F_{y,\text{Mn}}$ .

The factor 1.53 of Model #1 is based on the experimentally observed ratio of the ordered Mn moments at B and A sites in  $(\text{Lu}_{0.6}\text{Mn}_{0.4})\text{MnO}_3$  [23]. The factor 1.23 of Model #2 has been used to refine the magnetic structure of  $(\text{Tm}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  [24]. The temperature dependence of the magnetic structure of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  calculated for Models #1 and #2 is shown in Fig. 7 and Supplementary Fig. S3, respectively. Near  $T_{\text{SR}}$ , the magnitude of the ordered Mn moments at A site ( $f_{x,\text{Mn}}$  and  $f_{y,\text{Mn}}$ ) and B site ( $F_{x,\text{Mn}}$  and  $F_{y,\text{Mn}}$ ) both show a continuous behavior, whereas ordered Er moments jump from a smaller ( $f_{x,\text{Er}}$ ) to a larger value ( $f_{y,\text{Er}}$ ). At the lowest measured temperature  $T = 1.8$  K,  $f_{y,\text{Er}}$  reaches a similar value as  $f_{y,\text{Mn}}$  for Model #1 and a larger value for Model #2. Our powder neutron diffraction data can't distinguish between Model #1 and Model #2.

### 3.3. Calculations of the crystal-field anisotropy

FiM order appears in both Mn-self doped compounds  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  [this work] and  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  [26]. To compare magnetic properties of the two compounds, the CF anisotropy of  $\text{Er}^{3+}$  in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  and  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  was calculated based on the point charge model using the McPhase program [36-38]. With the structural parameters of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  at  $T = 130$  K (Table 1) as input, the CF energy splitting for  $\text{Er}^{3+}$  at the A site (4c), was calculated by considering all neighboring ions up to a distance of 20 Å with average charges of +2.71 on the A site (for  $0.71 \cdot \text{Er}^{3+} + 0.29 \cdot \text{Mn}^{2+}$ ), +3.29 on the B site (for  $0.71 \cdot \text{Mn}^{3+} + 0.29 \cdot \text{Mn}^{4+}$ ), and -2 for  $\text{O}^{2-}$  on sites (4c and 8d). The number of neighboring ions was 3125. For  $\text{Er}^{3+}$  ( $^4\text{I}_{15/2}$ ) with a total angular momentum  $J = 15/2$ , a Landé factor  $g_J = 6/5$  and a magnitude of moment  $g_J J = 9 \mu_B$ , we obtained a splitting into sixteen ( $2J + 1 = 16$ ) CF levels (eight doublets) due to the charges of the surrounding ions. The calculated CF energy levels are given in Table 5. For applying an external magnetic field of  $H = 10$  T along the three axes  $a$ ,  $b$ ,  $c$ , we calculated the induced ordered magnetic Er moments at  $T = 1$  K. The results shown in Table 6, contain a FM component parallel to the field direction and components perpendicular to the field direction due to the CF anisotropy. The obtained induced  $\text{Er}^{3+}$  moments for  $H \parallel a$ ,  $H \parallel b$  and  $H \parallel c$ , belong to the irreps  $m\text{GM}3^+$ ,  $m\text{GM}4^+$  and  $m\text{GM}2^+$ , respectively (Table 3). For  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , the lowest 8 CF levels have an energy separation of only 6.7 meV (Table 5). The CF levels are found to be very sensitive to small changes of

the structural parameters inside the  $ac$ -plane, but not along the  $b$ -direction. As a result, in Table 6, the errors turn out to be larger for  $\langle Ma \rangle$  and  $\langle Mc \rangle$ , compared to  $\langle Mb \rangle$ . The field dependence of the single-ion magnetization (induced FM component parallel to the field) of  $\text{Er}^{3+}$  at  $T = 1$  K is plotted in Fig. 8a for magnetic fields up to 10 T applied along the  $a$ -,  $b$ - and  $c$ -axes.  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  shows a large CF anisotropy that favors the  $b$ -direction over the  $a$ - and  $c$ -directions.

We performed a similar calculation for  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$ , based on the structural parameters at  $T = 130$  K published in Table 1 of [26]. The CF energy splitting for  $\text{Ho}^{3+}$  at the A site ( $4c$ ), was calculated by considering all neighboring ions up to a distance of 20 Å with average charges of +2.83 on the A site (for  $0.83 \cdot \text{Ho}^{3+} + 0.17 \cdot \text{Mn}^{2+}$ ), +3.17 on the B site (for  $0.83 \cdot \text{Mn}^{3+} + 0.17 \cdot \text{Mn}^{4+}$ ), and -2 for  $\text{O}^{2-}$  on sites ( $4c$  and  $8d$ ). The number of neighboring ions was 3059. For  $\text{Ho}^{3+}$  ( $^5\text{I}_8$ ) with a total angular momentum  $J = 8$ , a Landé factor  $g_J = 5/4$  and a magnitude of moment  $g_J J = 10 \mu_B$ , we obtained a splitting into seventeen ( $2J + 1 = 17$ ) CF levels (all singlets) due to the charges of the surrounding ions. The calculated CF energy levels are given in Table 5. The two lowest CF singlets form a quasi doublet that is well separated (by at least 11.39 meV) from the higher energy CF levels. The ordered magnetic  $\text{Ho}^{3+}$  moments at  $T = 1$  K induced by an external magnetic field of  $H = 10$  T applied along the three axes  $a$ ,  $b$ ,  $c$ , are summarized in Table 7. Fig. 8b displays the calculated field dependence of the single-ion magnetization of  $\text{Ho}^{3+}$  at  $T = 1$  K for magnetic fields up to 10 T applied along the  $a$ -,  $b$ - and  $c$ -axes. For  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$ , the CF anisotropy has a magnetically easy  $a$ -direction and a magnetically hard  $b$ -direction.

The calculated CF anisotropies for  $\text{Er}^{3+}$  in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  and  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  correspond to different rare-earth elements with different compositions (70%  $\text{Er}^{3+}$  versus 80%  $\text{Ho}^{3+}$ ). The FiM structure is observed for  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ ,  $(\text{Er}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  and  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$ , whereas the composition  $(\text{Ho}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  lies outside the solubility limit. To investigate the composition dependence, we performed an additional calculation of the CF anisotropy for  $(\text{Er}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$ , a material for which no structural parameters have been published. As an approximation, we used the structural parameters determined for  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  (Table 1 of this work) together with the room temperature lattice constants of  $(\text{Er}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  measured by x-ray diffraction (Table 1 in

[18]). The results of the CF anisotropy calculated for  $(\text{Er}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  are shown in the Supplementary in Table S1 (CF levels), Table S2 (Induced magnetic  $\text{Er}^{3+}$  moments) and Fig. S4 (Field dependence of single-ion magnetization). Comparing the results obtained for  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  and  $(\text{Er}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  (Fig. S4), suggests that the large CF anisotropy with a magnetically easy  $b$ -direction is independent of the composition for  $(\text{Er}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds within the stability range of the FiM structure  $x \geq 0.2$ . In both compounds the overall energy splitting of the CF levels is similar (Table S1). But small differences in the energies of the CF levels give rise to a composition dependence of  $\langle \text{Ma} \rangle$  and  $\langle \text{Mc} \rangle$  along the magnetically harder directions inside the  $ac$ -plane (Fig. S4, Table S2 and Table 6).

### 3.4. Comparison of the ferrimagnetic structures of $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$ and $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$

The determination of the FiM structure of  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  has been reported in [26]. Below  $T_C = 76$  K, FM order along the  $a$ -direction appears for the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations at the B site, and for the  $\text{Ho}^{3+}$  and  $\text{Mn}^{2+}$  cations at the A site. AFM coupling between the B and A sites gives rise to a FiM structure. With decreasing temperature, the ordered magnetic moment of the  $\text{Ho}^{3+}$  cations increases significantly and overcomes the saturated magnetic moment of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations at the B site, resulting in a magnetization reversal behaviour below a compensation temperature of about 35 K (Fig. 5a of 26). The calculated large CF anisotropy for  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  shown in Fig. 8b has a magnetically easy  $a$ -axis, similar to the high-temperature magnetic directions. Therefore, a spin-reorientation temperature  $T_{\text{SR}}$  is not observed. The FiM structure of  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  is collinear below  $T_C = 76$  K and develops of a spin canting of  $\text{Ho}^{3+}$  at the A site below 40 K (non-zero  $c_{z,\text{Ho}}$  component).

Below  $T_C = 104$  K, the FiM structure of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  (Fig. 6b) is similar to that of  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  with the FM moments pointing along the  $a$ -direction. However, the calculated large CF anisotropy of  $\text{Er}^{3+}$  favours the  $b$ -direction (Fig. 8a) and limits the development of a large FM  $\text{Er}^{3+}$  moment along the magnetically harder  $a$ -direction. A magnetization reversal behaviour as in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  is not observed in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ . In order to grow to a large value, the FM component of the  $\text{Er}^{3+}$  ions changes direction at  $T_{\text{SR}} = 11$  K from the magnetically harder  $a$ -axis to the magnetically easy  $b$ -axis. Mn cations are magnetically coupled to  $\text{Er}^{3+}$  cations and follow the first-order phase transition at  $T_{\text{SR}}$  from

$m\text{GM}3+$  to  $m\text{GM}4+$ , which is induced by the CF anisotropy of  $\text{Er}^{3+}$  ions. Similar to  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$ , the FiM structure of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  is collinear below  $T_C = 104$  K and develops a spin-canting (non-zero  $c_{z,\text{Er}}$  component) below about 30 K (Fig. 6a).

For rare-earth perovskites, orthoferrites  $\text{RFeO}_3$  and orthochromites  $\text{RCrO}_3$ , a simple but realistic microscopic theory of spontaneous spin reorientation [42] suggested that both the temperature and the nature of the spin-reorientation transition are the result of competition between the second- and fourth-order spin anisotropy of the  $3d$  sublattice, the crystal field of  $4f$  cations, and  $4f$ - $3d$  magnetic exchange interactions. For all FiM members of  $(\text{R}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds ( $x \geq 0.2$ ,  $\text{R} = \text{Ho-Lu}$  [23-26]), the Mn cations select the  $a$ -axis for the FM components below  $T_C$ . The occurrence of a spontaneous spin reorientation in these compounds may have some requirements like a  $\text{R}^{3+}$  cation with a large enough ordered moment. But when comparing  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  and  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , the results presented in this work suggest that the large CF anisotropy is the decisive factor for the absence and appearance, respectively, of the spontaneous spin reorientation.

### 3.5. Mn self-doping and magnetic exchange interactions

In intermetallic compounds, competing magnetic exchange interactions among and between unpaired  $3d$  and  $4f$  electron spins may account for complex magnetic properties with multiple phase transitions.  $3d$ - $3d$ ,  $3d$ - $4f$  and  $4f$ - $4f$  exchange interactions have different strengths and shape the magnetic structures at different temperatures, as illustrated by recent neutron diffraction measurements on the isostructural spin-chain compounds  $\text{BaRFeO}_4$  ( $\text{R} = \text{Yb, Tm, Er}$ ) [43, 44]. These orthorhombic compounds (space group  $Pnma$ ) undergo three successive magnetic phase transitions (at  $T_{N1}$ ,  $T_{N2}$  and  $T_{N3}$ ), and magnetic  $\text{Fe}^{3+}$  and  $\text{R}^{3+}$  cations are located on different sublattices. At the highest Néel temperature ( $T_{N1}$ ), only  $\text{Fe}^{3+}$  ions order due to the strongest  $3d$ - $3d$  interactions. At the lowest Néel temperature ( $T_{N3}$ ),  $4f$ - $4f$  interactions dominate in  $\text{BaYbFeO}_4$  (long-range magnetic  $\text{Yb}^{3+}$  order), whereas  $3d$ - $4f$  interactions dominate in  $\text{BaTmFeO}_4$  (ordered  $\text{Tm}^{3+}$  moments on one sublattice coexist with disordered  $\text{Tm}^{3+}$  moments on the other sublattice). In  $\text{BaErFeO}_4$ ,  $3d$ - $4f$  interactions dominate at  $T_{N2}$  (change of magnetic propagation vector and induced  $\text{Er}^{3+}$  order) and  $4f$ - $4f$  interactions at  $T_{N3}$  (modified magnetic structure with constant magnetic phase inside each chain of  $\text{Er}^{3+}$  cations).

For orthoferrites  $\text{RFeO}_3$ , orthochromites  $\text{RCrO}_3$  as well as undoped  $\text{RMnO}_3$  perovskites, transition metal  $3d$  ions and rare-earth  $4f$  ions are located on different sublattices with only  $3d$ - $4f$  exchange interactions between them and only  $3d$ - $3d$  or  $4f$ - $4f$  interactions inside one sublattice. Mn self-doping in  $(\text{R}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds creates a different group of materials with a coexistence of unpaired  $3d$  and  $4f$  electrons on the same sublattice (A site). Here three kinds of exchange interactions ( $3d$ - $3d$ ,  $3d$ - $4f$  and  $4f$ - $4f$ ) are present at the A site and two kinds ( $3d$ - $3d$ ,  $3d$ - $4f$ ) between A- and B sites. When the self-doping reaches a certain threshold ( $x \geq 0.2$ ), the FiM structure appears at  $T_C$ , fully stabilized by  $3d$ - $3d$  interactions, with FM components along the  $a$ -direction, independent of the kind of the  $\text{R}^{3+}$  cation (even for nonmagnetic  $\text{R} = \text{Lu}^{3+}$ ). Below  $T_C$ , the FM structure at the A site is collinear and contains only FM components for Mn1 (due to  $3d$ - $3d$  interactions) and R (small moment induced by  $3d$ - $4f$  interactions). With decreasing temperature,  $4f$ - $4f$  interactions become stronger and at some temperature create magnetic  $\text{R}^{3+}$  order with a larger FM component and a nonzero AFM component. Magnetization reversal has been observed in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  [26] and in  $(\text{Tm}_{0.7}\text{Mn}_{0.2})\text{MnO}_3$  [24], but not in  $(\text{Yb}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  [25] (because of too small ordered  $\text{Yb}^{3+}$  moments), and not in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  (this work, because of the CF anisotropy). Compared to the parent compound  $\text{ErMnO}_3$ , Mn self-doping in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  increases the number of magnetic Mn ions by 30%. They are coupled by the strongest  $3d$ - $3d$  exchange interactions and give rise to a large increase of the highest ordering temperature of Mn from  $T_{N1} = 42$  K in  $\text{ErMnO}_3$  to  $T_C = 104$  K in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ . This argument is also valid for  $(\text{R}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds with other rare-earth cations. Furthermore, Mn self-doping and magnetic exchange interactions can rationalize why magnetic order of  $\text{Er}^{3+}$  appears at  $T_C = 104$  K in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , but is absent at the highest two phase transitions (42 K, 28 K) in the parent compound  $\text{ErMnO}_3$ .

#### 4. Conclusions

$(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  solid solution with  $\text{GdFeO}_3$ -type perovskite structure was successfully prepared by a high-pressure high-temperature method at 6 GPa and 1670 K. By combining specific heat, magnetic susceptibility and neutron diffraction, we have investigated the magnetic phase transitions ( $T_C = 104$  K,  $T_{SR} = 11$  K) and determined crystal and magnetic

structures. When self-doping Mn onto the A site, it appears as  $\text{Mn}^{2+}$  and produces a charge transfer from the A site ( $\text{Er}^{3+}$ ,  $\text{Mn}^{2+}$ ) to the B site ( $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ ). Mn self-doping creates a different group of materials with a coexistence of unpaired  $3d$  and  $4f$  electrons on the same sublattice (A site). In contrast, in the undoped parent compound  $\text{ErMnO}_3$ , rare-earth cations (A site) and transition metals (B site) are located on different sublattices. Compared to  $\text{ErMnO}_3$  with the highest ordering temperature of Mn at  $T_{\text{N1}} = 42$  K, an increase of the number of magnetic Mn ions by 30% in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  gives rise to FiM order at much higher temperature  $T_{\text{C}} = 104$  K. This work reports the discovery of a spontaneous SR transition in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  at  $T_{\text{SR}} = 11$  K, where all FM components of Mn and Er ions change direction from the  $a$ -axis (above) to the  $b$ -axis (below). In the family of  $(\text{R}_{1-x}\text{Mn}_x)\text{MnO}_3$  compounds ( $\text{R} = \text{Dy-Lu}$ ), FiM order appears at  $x \geq 0.2$  for all members. But  $\text{R} = \text{Er}$  is the only material with a spontaneous SR transition. Our calculation of the CF anisotropy of  $\text{Er}^{3+}$  in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , and  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  revealed large magnetic anisotropies that can explain the appearance and absence of the SR transition for  $\text{R} = \text{Er}$  and  $\text{Ho}$ , respectively.

FiM materials with spontaneous SR transitions are of practical interest because deterministic magnetization switching may be used in nanoscale functional spintronic components [6]. Fundamental understanding of the origin and mechanisms of the spontaneous SR transition in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ , a member of a new group of materials, is important for the design of future materials that can be used in spintronics.

### **CRedit authorship contribution statement**

**Andreas Dönni:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Vladimir Y. Pomjakushin:** Investigation. **Martin Rotter:** Investigation. **Lei Zhang:** Investigation. **Kazunari Yamaura:** Investigation, Funding acquisition. **Alexei A. Belik:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization.

### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **Acknowledgements**

This study is partially based on experiments performed on HRPT diffractometer (Proposal No. 20180113) at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institute, Switzerland. This study was supported in part by the World Premier International Research Center Initiative (WPI), the Japan Society for the Promotion of Science KAKENHI (Grant No. JP22H04601), and a grant from the Kazuchika Okura Memorial Foundation (No. 2022-11).

### **Appendix A. Supplementary data**

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2024.08.191>.

## References

- [1] H. Horner, C.M. Varma, Nature of Spin-Reorientation Transitions, *Phys. Rev. Lett.* 20 (1968) 845–846, <https://doi.org/10.1103/PhysRevLett.20.845>
- [2] J.P. Bolletta, F. Pomiro, R.D. Sánchez, V. Pomjakushin, G. Aurelio, A. Maignan, C. Martin, R.E. Carbonio, Spin reorientation and metamagnetic transitions in  $R\text{Fe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  perovskites ( $R=\text{Tb, Dy, Ho, Er}$ ), *Phys. Rev. B* 98 (2018) 134417, <https://doi.org/10.1103/PhysRevB.98.134417>
- [3] R.L. White, Review of Recent Work on the Magnetic and Spectroscopic Properties of the Rare-Earth Orthoferrites, *J. Appl. Phys.* 40 (1969) 1061–1069, <https://doi.org/10.1063/1.1657530>
- [4] R.M. Hornreich, Magnetic interactions and weak ferromagnetism in the rare-earth orthochromites, *J. Magn. Magn. Mater.* 7 (1978) 280–285, [https://doi.org/10.1016/0304-8853\(78\)90203-2](https://doi.org/10.1016/0304-8853(78)90203-2)
- [5] N. Locatelli, V. Cros, J. Grollier, Spin-torque building blocks, *Nature Mater.* 13 (2014) 11–20, <https://doi.org/10.1038/nmat3823>
- [6] Y. Yang, R.B. Wilson, J. Gorchon, C.H. Lambert, S. Salahuddin, J. Bokor, Ultrafast magnetization reversal by picosecond electrical pulses, *Sc. Adv.* 3 (2017) e1603117, <https://doi.org/10.1126/sciadv.1603117>
- [7] A.M. Vibhakar, D.D. Khalyavin, P. Manuel, L. Zhang, K. Yamaura, P.G. Radaelli, A.A. Belik, R.D. Johnson, Magnetic structure and spin-flop transition in the A-site columnar-ordered quadruple perovskite  $\text{TmMn}_3\text{O}_6$ , *Phys. Rev. B* 99 (2019) 104424, <https://doi.org/10.1103/PhysRevB.99.104424>
- [8] A.M. Vibhakar, D.D. Khalyavin, P. Manuel, J. Liu, A.A. Belik, and R.D. Johnson, Spontaneous Rotation of Ferrimagnetism Driven by Antiferromagnetic Spin Canting, *Phys. Rev. Lett.* 124 (2020) 127201, <https://doi.org/10.1103/PhysRevLett.124.127201>
- [9] A. Muñoz, M.T. Casáis, J.A. Alonso, M.J. Martínez-Lope, J.L. Martínez, M.T. Fernández-Díaz, Complex Magnetism and Magnetic Structures of the Metastable  $\text{HoMnO}_3$  Perovskite, *Inorg. Chem.* 40 (2001) 1020–1028, <https://doi.org/10.1021/ic0011009>

- [10] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, Magnetic control of ferroelectric polarization, *Nature* 426 (2003) 55-58, <https://doi.org/10.1038/nature02018>
- [11] T. Goto, T. Kimura, G. Lawes, A.P. Ramirez, Y. Tokura, Ferroelectricity and Giant Magnetocapacitance in Perovskite Rare-Earth Manganites, *Phys. Rev. Lett.* 92 (2004) 257201, <https://doi.org/10.1103/PhysRevLett.92.257201>
- [12] M. Kenzelmann, A.B. Harris, S. Jonas, C. Broholm, J. Schefer, S.B. Kim, C.L. Zhang, S.-W. Cheong, O.P. Vajk, J.W. Lynn, Magnetic Inversion Symmetry Breaking and Ferroelectricity in  $\text{TbMnO}_3$ , *Phys. Rev. Lett.* 95 (2005) 087206, <https://doi.org/10.1103/PhysRevLett.95.087206>
- [13] T. Kimura, G. Lawes, T. Goto, Y. Tokura, A.P. Ramirez, Magnetoelectric phase diagrams of orthorhombic  $\text{RMnO}_3$  ( $\text{R}=\text{Gd}$ ,  $\text{Tb}$ , and  $\text{Dy}$ ), *Phys. Rev. B* 71 (2005) 224425, <https://doi.org/10.1103/PhysRevB.71.224425>
- [14] J.-S. Zhou, J.B. Goodenough, Unusual Evolution of the Magnetic Interactions versus Structural Distortions in  $\text{RMnO}_3$  Perovskites, *Phys. Rev. Lett.* 96 (2006) 247202, <https://doi.org/10.1103/PhysRevLett.96.247202>
- [15] T. Finger, K. Binder, Y. Sidis, A. Maljuk, D. N. Argyriou, M. Braden, Magnetic order and electromagnon excitations in  $\text{DyMnO}_3$  studied by neutron scattering experiments, *Phys. Rev. B* 90 (2014) 224418, <https://doi.org/10.1103/PhysRevB.90.224418>
- [16] M.B. Salamon, M. Jaime, The physics of manganites: Structure and transport, *Rev. Mod. Phys.* 73 (2001) 583, <https://doi.org/10.1103/RevModPhys.73.583>
- [17] J.M.D. Coey, M. Viret, S. von Molnár, Mixed-valence manganites, *Adv. Phys.* 58 (2009) 571–697, <https://doi.org/10.1080/00018730903363184>
- [18] L. Zhang, D. Gerlach, A. Dönni, T. Chikyow, Y. Katsuya, M. Tanaka, S. Ueda, K. Yamaura, A.A. Belik, Mn Self-Doping of Orthorhombic  $\text{RMnO}_3$  Perovskites:  $(\text{R}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  with  $\text{R} = \text{Er-Lu}$ , *Inorg. Chem.* 57 (2018) 2773-2781, <https://doi.org/10.1021/acs.inorgchem.7b03188>

- [19] H. Zhang, R. Flacau, J.L. Sun, G.B. Li, F.H. Liao, J.H. Lin, Synthesis, Structure, and Magnetic Properties of  $(\text{Tb}_{1-x}\text{Mn}_y)\text{MnO}_{3-\delta}$ , *Inorg. Chem.* 53 (2014) 4535–4540, <https://doi.org/10.1021/ic500222y>
- [20] J.M. Deng, M.A. Farid, M. Zhang, A. Yang, H.X. Zhang, H. Zhang, G.F. Tian, M.M. Wu, L.J. Liu, J.L. Sun, G.B. Li, F.H. Liao, J.H. Lin, Enhancement of Ferroelectricity for Orthorhombic  $(\text{Tb}_{0.861}\text{Mn}_{0.121})\text{MnO}_{3-\delta}$  by Copper Doping, *Inorg. Chem.* 56 (2017) 3475–3482, <https://doi.org/10.1021/acs.inorgchem.6b03024>
- [21] J.M. Deng, A. Yang, M.A. Farid, H. Zhang, J. Li, H.X. Zhang, G.B. Li, L.J. Liu, J.L. Sun, J.H. Lin, Synthesis, structure and magnetic properties of  $(\text{Eu}_{1-x}\text{Mn}_x)\text{MnO}_{3-\delta}$ , *RSC Adv.* 7 (2017) 2019–2024, <https://doi.org/10.1039/C6RA25951K>
- [22] J.M. Deng, M.A. Farid, A. Yang, J.X. Zhang, H. Zhang, L. Zhang, Y.M. Qiu, M.H. Yu, H. Zhu, M.Y. Zhong, J. Li, G.B. Li, L.J. Liu, J.L. Sun, J.H. Lin, The origin of multiple magnetic and dielectric anomalies of Mn-doped  $\text{DyMnO}_3$  in low temperature region, *J. Alloys Comp.* 725 (2017) 976–983, <https://doi.org/10.1016/j.jallcom.2017.07.223>
- [23] L. Zhang, A. Dönni, V.Y. Pomjakushin, K. Yamaura, A.A. Belik, Crystal and Magnetic Structures and Properties of  $(\text{Lu}_{1-x}\text{Mn}_x)\text{MnO}_3$  Solid Solutions, *Inorg. Chem.* 57 (2018) 14073–14085, <https://doi.org/10.1021/acs.inorgchem.8b01470>
- [24] A. Dönni, V.Y. Pomjakushin, L. Zhang, K. Yamaura, A.A. Belik, Origin of negative magnetization phenomena in  $(\text{Tm}_{1-x}\text{Mn}_x)\text{MnO}_3$ : A neutron diffraction study, *Phys. Rev. B* 101 (2020) 054442, <https://doi.org/10.1103/PhysRevB.101.054442>
- [25] A. Dönni, V.Y. Pomjakushin, L. Zhang, K. Yamaura, A.A. Belik, Temperature evolution of 3d- and 4f-electron magnetic ordering in the ferrimagnetic Mn self-doped perovskite  $(\text{Yb}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$ , *J. Phys.: Condens. Matter* 33 (2021) 205804, <https://doi.org/10.1088/1361-648X/abe516>
- [26] A. Dönni, V.Y. Pomjakushin, L. Zhang, K. Yamaura, A.A. Belik, Magnetic properties and ferrimagnetic structures of Mn self-doped perovskite solid solutions  $(\text{Ho}_{1-x}\text{Mn}_x)\text{MnO}_3$ , *J. Alloys Comp.* 857 (2021) 158230, <https://doi.org/10.1103/PhysRevB.101.054442>

- [27] F. Ye, B. Lorenz, Q. Huang, Y.Q. Wang, Y.Y. Sun, C.W. Chu, J.A. Fernandez-Baca, P.C. Dai, H.A. Mook, Incommensurate magnetic structure in the orthorhombic perovskite  $\text{ErMnO}_3$ , *Phys. Rev. B* 76 (2007) 060402(R), <https://doi.org/10.1103/PhysRevB.76.060402>
- [28] M. Tachibana, T. Shimoyama, H. Kawaji, T. Atake, E. Takayama-Muromachi, Jahn-Teller distortion and magnetic transitions in perovskite  $\text{RMnO}_3$  (R=Ho, Er, Tm, Yb, and Lu), *Phys. Rev. B* 75 (2007) 144425, <https://doi.org/10.1103/PhysRevB.75.144425>
- [29] L. Zhang, Y. Matsushita, K. Yamaura, A.A. Belik, Five-Fold Ordering in High-Pressure Perovskites  $\text{RMn}_3\text{O}_6$  (R = Gd–Tm and Y), *Inorg. Chem.* 56 (2017) 5210–5218, <https://doi.org/10.1021/acs.inorgchem.7b00347>
- [30] P. Fischer, G. Frey, M. Koch, M. Könnecke, V. Pomjakushin, J. Schefer, R. Thut, N. Schlumpf, R. Bürge, U. Greuter, S. Bondt, E. Berruyer, High-resolution powder diffractometer HRPT for thermal neutrons at SINQ, *Physica B* 276 (2000) 146-147, [https://doi.org/10.1016/S0921-4526\(99\)01399-X](https://doi.org/10.1016/S0921-4526(99)01399-X)
- [31] J. Rodriguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Physica B* 192 (1993) 55-69, [https://doi.org/10.1016/0921-4526\(93\)90108-I](https://doi.org/10.1016/0921-4526(93)90108-I)
- [32] B.J. Campbell, H.T. Stokes, D.E. Tanner, D.M. Hatch, ISODISPLACE: a web-based tool for exploring structural distortions, *J. Appl. Crystallogr.* 39 (2006) 607-614, <https://doi.org/10.1107/S0021889806014075>  
Information on the program ISODISTORT is described in the following URL <https://doi.org/10.1107/S0021889898006001>
- [33] V. Yu. Pomjakushin, D.V. Sheptyakov, K. Conder, E. V. Pomjakushina, A.M. Balagurov, Effect of oxygen isotope substitution and crystal microstructure on magnetic ordering and phase separation in  $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , *Phys. Rev. B* 75 (2007) 054410, <https://doi.org/10.1103/PhysRevB.75.054410>
- [34] R. Rodriguez-Carvajal, M.T. Fernandez-Diaz, J.L. Martinez, Neutron diffraction study on structural and magnetic properties of  $\text{La}_2\text{NiO}_4$ , *J. Phys. Condens. Matter* 3 (1991) 3215–3234, <https://doi.org/10.1088/0953-8984/3/19/002>

- [35] P.W. Stephens, Phenomenological model of anisotropic peak broadening in powder diffraction, *J. Appl. Cryst.* 32 (1999) 281–289,  
<https://doi.org/10.1107/S0021889898006001>
- [36] M. Rotter, Using McPhase to calculate magnetic phase diagrams of rare earth compounds, *J. Magn. Magn. Mater.* 272 (2004) E481-E482,  
<https://doi.org/10.1016/j.jmmm.2003.12.1394>
- [37] M. Rotter, M.D. Le, A.T. Boothroyd, J.A. Blanco, Dynamical matrix diagonalization for the calculation of dispersive excitations, *J. Phys.: Condens. Matter* 24 (2012) 213201, <https://doi.org/10.1088/0953-8984/24/21/213201>
- [38] T. Stöter, M. Doerr, M. Rotter, A new theoretical approach to the strain dependence of magnetic crystal-field anisotropy, *Eur. Phys. J. B* 94 (2021) 125,  
<https://doi.org/10.1140/epjb/s10051-021-00133-8>
- [39] N.E. Brese, M. O’Keeffe, Bond-Valence Parameters for Solids, *Acta Crystallogr. B* 47 (1991) 192-197, <https://doi.org/10.1107/S0108768190011041>
- [40] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.* 44 (2011) 1272-1276,  
<https://doi.org/10.1107/S0021889811038970>
- [41] D.B. Litvin, Magnetic Group Tables (International Union of Crystallography, 2013), <https://doi.org/10.1107/9780955360220001>
- [42] A. Moskvina, E. Vasinovich, A. Shadrin, Simple Realistic Model of Spin Reorientation in 4f-3d Compounds, *Magnetochemistry* 8 (2022) 45,  
<https://doi.org/10.3390/magnetochemistry8040045>
- [43] A. Dönni, V.Y. Pomjakushin, K. Yamaura, A.A. Belik, Cycloidal spiral magnetic structures in the spin-chain compounds BaRFeO<sub>4</sub> (R = Yb and Tm): Ordered Yb versus partly ordered Tm, *Phys. Rev. B* 107 (2023) 134412,  
<https://doi.org/10.1103/PhysRevB.107.134412>
- [44] A. Dönni, V.Y. Pomjakushin, A.A. Belik, Er-driven incommensurate to commensurate magnetic phase transition of Fe in the spin-chain compound BaErFeO<sub>4</sub>, *Phys. Rev. B* 109 (2024) 064403,  
<https://doi.org/10.1103/PhysRevB.109.064403>

**Table 1**

Structural Parameters of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  at  $T = 130$  K refined from powder neutron diffraction data (HRPT,  $\lambda = 1.886$  Å,  $\mu\text{R} = 0.6$ ). Space group  $Pnma$  (No 62), occupation factor ( $g$ ). The lattice constants are  $a = 5.5416(3)$  Å,  $b = 7.3912(4)$  Å,  $c = 5.2250(3)$  Å, and the volume  $V = 214.01(2)$  Å<sup>3</sup>. Strain parameters [in units of  $10^{-4}$ ] are  $S_{400} = 1.52(5)$ ,  $S_{202} = 1.02(16)$ . Reliability indices of the refinement are  $\chi^2 = 2.28$ ,  $R_{\text{wp}} = 3.91\%$ ,  $R_{\text{exp}} = 2.59\%$ , and  $R_{\text{Bragg}} = 4.80\%$ .

| Atom | Site | $g$      | $x$              | $y$       | $z$              | $B$ (Å <sup>2</sup> ) |
|------|------|----------|------------------|-----------|------------------|-----------------------|
| Er   | $4c$ | 0.709(3) | 0.0740(4)        | 0.25      | 0.9823(4)        | 0.17(7)               |
| Mn1  | $4c$ | 0.291(3) | $= x(\text{Er})$ | 0.25      | $= z(\text{Er})$ | $= B(\text{Er})$      |
| Mn2  | $4b$ | 1        | 0                | 0         | 0.5              | 0.38(6)               |
| O1   | $4c$ | 1        | 0.4600(4)        | 0.25      | 0.1063(3)        | 1.04(5)               |
| O2   | $8d$ | 1        | 0.3152(3)        | 0.0533(2) | 0.6950(3)        | 1.20(4)               |

**Table 2**

Calculated values for selected bond lengths (Å), bond angles (deg), Bond Valence Sums, BVS, and distortion parameter  $\Delta(\text{Mn2})$  of  $\text{MnO}_6$  for  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  at  $T = 130$  K based on powder neutron diffraction data.

| $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$<br>$T = 130$ K |                      |
|---------------------------------------------------------------|----------------------|
| Er/Mn1 – O1                                                   | 2.235(3)             |
| Er/Mn1 – O1                                                   | 2.240(3)             |
| Er/Mn1 – O2 ( $\times 2$ )                                    | 2.242(2)             |
| Er/Mn1 – O2 ( $\times 2$ )                                    | 2.481(2)             |
| Er/Mn1 – O2 ( $\times 2$ )                                    | 2.5765(17)           |
| BVS( $\text{Er}^{3+}$ )                                       | +3.14                |
| BVS( $\text{Mn1}^{2+}$ )                                      | +1.73                |
| Mn2 – O1 ( $\times 2$ )                                       | 1.9349(16)           |
| Mn2 – O2 ( $\times 2$ )                                       | 1.9422(5)            |
| Mn2 – O2 ( $\times 2$ )                                       | 2.0602(16)           |
| BVS( $\text{Mn2}^{3+}$ )                                      | +3.36                |
| $\Delta(\text{Mn2})$                                          | $8.4 \times 10^{-4}$ |
| Mn2 – O1 – Mn2 ( $\times 2$ )                                 | 144.13(2)            |
| Mn2 – O2 – Mn2 ( $\times 4$ )                                 | 144.80(7)            |

Note:  $\text{BVS} = \sum_{i=1}^N v_i$ ,  $v_i = \exp[(R_0 - l_i)/B]$ ,  $N$  is the coordination number,  $B = 0.37$ ,  $R_0(\text{Er}^{3+}) =$

2.01,  $R_0(\text{Mn}^{2+}) = 1.79$ , and  $R_0(\text{Mn}^{3+}) = 1.76$  [39].

$\Delta = (1/N) \sum_{i=1}^N [(l_i - l_{\text{av}})/l_{\text{av}}]^2$ , where  $l_{\text{av}} = (1/N) \sum_{i=1}^N l_i$  is the average Mn-O distance and  $N$  is the coordination number.

**Table 3**

Group theory analysis for the magnetic structure of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  calculated using the programs ISODISTORT [32], BasIreps [31] and Magnetic Space groups [41]. The character set corresponds to the following symmetry elements [31]: Symm(1): 1; Symm(2): 2 (0,0,1/2) 1/4,0,z; Symm(3): 2 (0,1/2,0) 0,y,0; Symm(4): 2 (1/2,0,0) x,1/4,1/4; Symm(5):  $-1$  0,0,0; Symm(6): a x,y,1/4; Symm(7): m x,1/4,z; Symm(8): n (0,1/2,1/2) 1/4,y,z. irrep denotes irreducible representation. The crystallographic space group is  $Pnma$  (No. 62). The magnetic propagation vector is  $\mathbf{k}_1 = (0, 0, 0)$ . Magnetic ions  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  are located on a 4b site (B site).  $\text{Er}^{3+}$  and  $\text{Mn}^{2+}$  are on a 4c site (A site).

| irrep<br>(Isodistort)                                                                                               | irrep<br>(BasIreps) | Character set                                                                                                                                           | Magnetic<br>space group                                                                                             | 4 <i>b</i> site<br>(B site)                                               | 4 <i>c</i> site<br>(A site)                          |
|---------------------------------------------------------------------------------------------------------------------|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|------------------------------------------------------|
| <i>m</i> GM1+                                                                                                       | Γ <sub>1</sub>      | (1, 1, 1, 1, 1, 1, 1, 1)                                                                                                                                | 62.1.502                                                                                                            | ( <i>G</i> <sub>x</sub> , <i>C</i> <sub>y</sub> , <i>A</i> <sub>z</sub> ) | (−, <i>c</i> <sub>y</sub> , −)                       |
| <i>m</i> GM1−                                                                                                       | Γ <sub>2</sub>      | (1, 1, 1, 1, −1, −1, −1, −1)                                                                                                                            | 62.9.510                                                                                                            | −                                                                         | ( <i>g</i> <sub>x</sub> , −, <i>a</i> <sub>z</sub> ) |
| <i>m</i> GM2+                                                                                                       | Γ <sub>3</sub>      | (1, 1, −1, −1, 1, 1, −1, −1)                                                                                                                            | 62.6.507                                                                                                            | ( <i>C</i> <sub>x</sub> , <i>G</i> <sub>y</sub> , <i>F</i> <sub>z</sub> ) | ( <i>c</i> <sub>x</sub> , −, <i>f</i> <sub>z</sub> ) |
| <i>m</i> GM2−                                                                                                       | Γ <sub>4</sub>      | (1, 1, −1, −1, −1, −1, 1, 1)                                                                                                                            | 62.5.506                                                                                                            | −                                                                         | (−, <i>g</i> <sub>y</sub> , −)                       |
| <i>m</i> GM3+                                                                                                       | Γ <sub>7</sub>      | (1, −1, −1, 1, 1, −1, −1, 1)                                                                                                                            | 62.5.508                                                                                                            | ( <i>F</i> <sub>x</sub> , <i>A</i> <sub>y</sub> , <i>C</i> <sub>z</sub> ) | ( <i>f</i> <sub>x</sub> , −, <i>c</i> <sub>z</sub> ) |
| <i>m</i> GM3−                                                                                                       | Γ <sub>8</sub>      | (1, −1, −1, 1, −1, 1, 1, −1)                                                                                                                            | 62.5.504                                                                                                            | −                                                                         | (−, <i>a</i> <sub>y</sub> , −)                       |
| <i>m</i> GM4+                                                                                                       | Γ <sub>5</sub>      | (1, −1, 1, −1, 1, −1, 1, −1)                                                                                                                            | 62.5.509                                                                                                            | ( <i>A</i> <sub>x</sub> , <i>F</i> <sub>y</sub> , <i>G</i> <sub>z</sub> ) | (−, <i>f</i> <sub>y</sub> , −)                       |
| <i>m</i> GM4−                                                                                                       | Γ <sub>6</sub>      | (1, −1, 1, −1, −1, 1, −1, 1)                                                                                                                            | 62.5.505                                                                                                            | −                                                                         | ( <i>a</i> <sub>x</sub> , −, <i>g</i> <sub>z</sub> ) |
| <i>F</i> = <i>f</i> = <i>m</i> <sub>1</sub> + <i>m</i> <sub>2</sub> + <i>m</i> <sub>3</sub> + <i>m</i> <sub>4</sub> |                     |                                                                                                                                                         | <i>C</i> = <i>c</i> = <i>m</i> <sub>1</sub> − <i>m</i> <sub>2</sub> + <i>m</i> <sub>3</sub> − <i>m</i> <sub>4</sub> |                                                                           |                                                      |
| <i>G</i> = <i>g</i> = <i>m</i> <sub>1</sub> − <i>m</i> <sub>2</sub> − <i>m</i> <sub>3</sub> + <i>m</i> <sub>4</sub> |                     |                                                                                                                                                         | <i>A</i> = <i>a</i> = <i>m</i> <sub>1</sub> + <i>m</i> <sub>2</sub> − <i>m</i> <sub>3</sub> − <i>m</i> <sub>4</sub> |                                                                           |                                                      |
| Site 4 <i>b</i> (B site):                                                                                           |                     | Mn2 <sub>1</sub> (0, 0, 1/2); Mn2 <sub>2</sub> (1/2, 0, 0); Mn2 <sub>3</sub> (0, 1/2, 1/2); Mn2 <sub>4</sub> (1/2, 1/2, 0)                              |                                                                                                                     |                                                                           |                                                      |
| Site 4 <i>c</i> (A site):                                                                                           |                     | Er1 <sub>1</sub> / Mn1 <sub>1</sub> ( <i>x</i> , 1/4, <i>z</i> );<br>Er1 <sub>3</sub> / Mn1 <sub>3</sub> (− <i>x</i> , 3/4, − <i>z</i> );               |                                                                                                                     |                                                                           |                                                      |
|                                                                                                                     |                     | Er1 <sub>2</sub> / Mn1 <sub>2</sub> (− <i>x</i> +1/2, 3/4, <i>z</i> +1/2)<br>Er1 <sub>4</sub> / Mn1 <sub>4</sub> ( <i>x</i> +1/2, 1/4, − <i>z</i> +1/2) |                                                                                                                     |                                                                           |                                                      |

**Table 4**

Result of the refinement of the average ordered moments of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  at  $T = 20$  and  $1.8$  K based on powder neutron diffraction data. The refinement is based on the occupation factor given in Table 1 ( $g = 0.709$  for  $\text{Er}^{3+}$  and  $\text{Mn}^{2^{3+}}$ , and  $g = 0.291$  for  $\text{Mn}^{1^{2+}}$  and  $\text{Mn}^{2^{4+}}$ ) using magnetic form factors for  $\text{Er}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ . As an approximation, in the refinement, the ordered moments of  $\text{Er}^{3+}$  and  $\text{Mn}^{1^{2+}}$ , as well as of  $\text{Mn}^{2^{3+}}$  and  $\text{Mn}^{2^{4+}}$ , were fixed to equal values, respectively.

|                                                                                                                                           |                                                                                                                |
|-------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| $T = 20$ K:                                                                                                                               | $\mathbf{k}_1 = (0, 0, 0)$ ; irrep: $m\text{GM}3^+ (\Gamma_7)$                                                 |
| A site (Er, Mn1)                                                                                                                          | $(f_x, 0, c_z)$                                                                                                |
| B site (Mn2)                                                                                                                              | $(F_x, A_y, C_z)$ ; $A_y = 0, C_z = 0$                                                                         |
| Average moments:                                                                                                                          | $f_{x,\text{ave}} = -2.00(4) \mu_B$ ; $c_{z,\text{ave}} = 1.01(6) \mu_B$ ; $F_{x,\text{ave}} = 2.95(5) \mu_B$  |
| Ferromagnetic moment:                                                                                                                     | $F_a = F_{x,\text{ave}} + f_{x,\text{ave}} = 0.96(9) \mu_B$ ; along $a$ direction                              |
| Correlation length:                                                                                                                       | 242(26) nm                                                                                                     |
| $T = 1.8$ K:                                                                                                                              | $\mathbf{k}_1 = (0, 0, 0)$ ; irrep: $m\text{GM}4^+ (\Gamma_5)$                                                 |
| A site (Er, Mn1)                                                                                                                          | $(0, f_y, 0)$                                                                                                  |
| B site (Mn2)                                                                                                                              | $(A_x, F_y, G_z)$ ; $G_z = 0$                                                                                  |
| Average moments:                                                                                                                          | $f_{y,\text{ave}} = 4.60(3) \mu_B$ ; $A_{x,\text{ave}} = -0.44(3) \mu_B$ ; $F_{y,\text{ave}} = -3.05(3) \mu_B$ |
| Ferromagnetic moment:                                                                                                                     | $F_b = F_{y,\text{ave}} + f_{y,\text{ave}} = 1.55(6) \mu_B$ ; along $b$ direction                              |
| Correlation length:                                                                                                                       | 593(15) nm                                                                                                     |
| $\chi^2 = 2.00$ ; $R_{\text{wp}} = 4.11$ %; $R_{\text{exp}} = 2.91$ %; $R_{\text{Bragg}} = 4.22$ %; $R_{\text{mag}} = 6.69$ % (at 20 K).  |                                                                                                                |
| $\chi^2 = 2.67$ ; $R_{\text{wp}} = 4.28$ %; $R_{\text{exp}} = 2.62$ %; $R_{\text{Bragg}} = 4.70$ %; $R_{\text{mag}} = 3.06$ % (at 1.8 K). |                                                                                                                |

**Table 5**

Energy levels of the crystal field (CF) splitting of  $\text{Er}^{3+}$  in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  and  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  based on the point charge model, calculated by McPhase. Energies are given in absolute values (second and fourth columns) and relative to the CF ground-state (third and fifth columns). Uncertainties due to the experimental errors in the crystal-structural parameters were evaluated using gauss law of error propagation and are shown in parentheses.

| Number of<br>CF level | $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$<br>$\text{Er}^{3+}$ energy (meV) |           | $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$<br>$\text{Ho}^{3+}$ energy (meV) |           |
|-----------------------|---------------------------------------------------------------------------------|-----------|---------------------------------------------------------------------------------|-----------|
| 17                    |                                                                                 |           | 14.23                                                                           | 38.66(41) |
| 16                    | 23.72                                                                           | 36.96(39) | 13.99                                                                           | 38.42(42) |
| 15                    | 23.72                                                                           | 36.96(39) | 10.67                                                                           | 35.10(41) |
| 14                    | 12.63                                                                           | 25.87(25) | 10.33                                                                           | 34.76(38) |
| 13                    | 12.63                                                                           | 25.87(25) | 8.89                                                                            | 33.32(32) |
| 12                    | 4.12                                                                            | 17.36(20) | 8.47                                                                            | 32.90(35) |
| 11                    | 4.12                                                                            | 17.36(20) | 8.05                                                                            | 32.48(40) |
| 10                    | -0.70                                                                           | 12.54(25) | 5.46                                                                            | 29.90(32) |
| 9                     | -0.70                                                                           | 12.54(25) | 4.78                                                                            | 29.22(30) |
| 8                     | -6.54                                                                           | 6.70(16)  | -0.24                                                                           | 24.19(45) |
| 7                     | -6.54                                                                           | 6.70(16)  | -0.65                                                                           | 23.79(44) |
| 6                     | -9.69                                                                           | 3.55(25)  | -4.52                                                                           | 19.91(30) |
| 5                     | -9.69                                                                           | 3.55(25)  | -4.55                                                                           | 19.88(30) |
| 4                     | -10.32                                                                          | 2.92(27)  | -13.00                                                                          | 11.43(20) |
| 3                     | -10.32                                                                          | 2.92(27)  | -13.04                                                                          | 11.39(20) |
| 2                     | -13.24                                                                          | 0.00(0)   | -24.43                                                                          | 0.01(0)   |
| 1                     | -13.24                                                                          | 0.00      | -24.43                                                                          | 0.00      |

**Table 6**

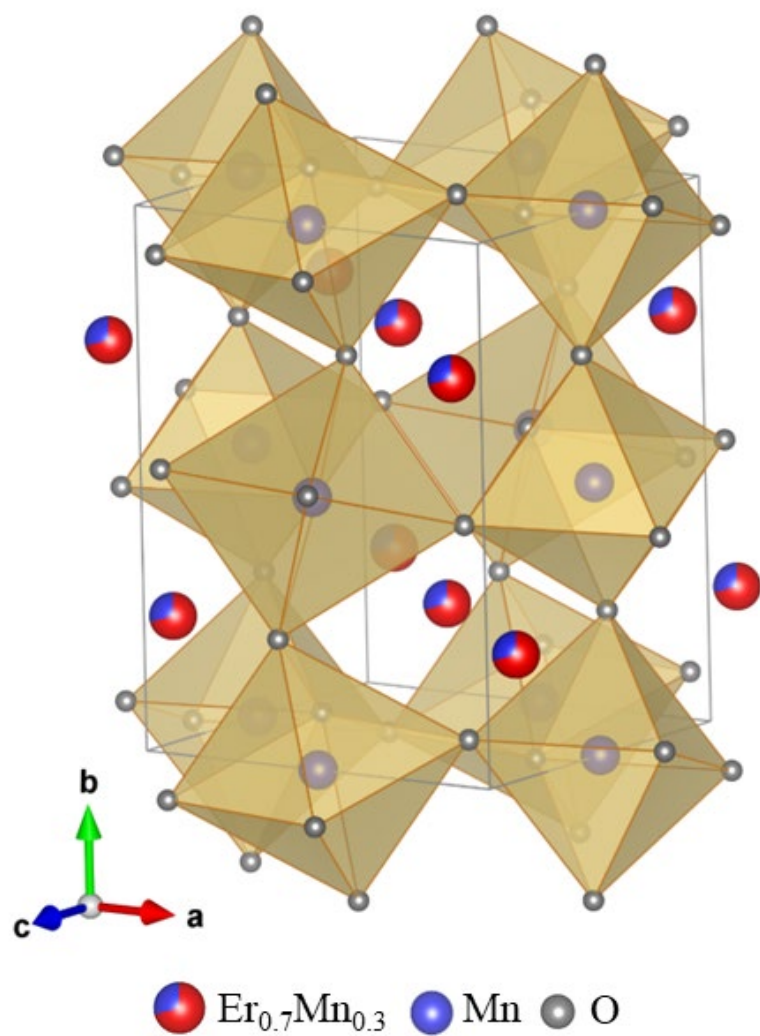
Induced magnetic  $\text{Er}^{3+}$  moments in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  at  $T = 1$  K in an external magnetic field of  $H = 10$  T applied along the three axes  $a$ ,  $b$ ,  $c$  calculated by McPhase. Uncertainties due to the experimental errors in the crystal-structural parameters were evaluated using gauss law of error propagation and are shown in parentheses only for Er1<sub>1</sub> for simplicity.

| $H \parallel a$  | $\langle M_a \rangle$ | $\langle M_b \rangle$ | $\langle M_c \rangle$ | $\langle M \rangle$ |
|------------------|-----------------------|-----------------------|-----------------------|---------------------|
| Er1 <sub>1</sub> | 6.177(435)            | 0(0)                  | -3.041(280)           | 6.885(514)          |
| Er1 <sub>2</sub> | 6.177                 | 0                     | 3.041                 | 6.885               |
| Er1 <sub>3</sub> | 6.177                 | 0                     | -3.041                | 6.885               |
| Er1 <sub>4</sub> | 6.177                 | 0                     | 3.041                 | 6.885               |
| $H \parallel b$  | $\langle M_a \rangle$ | $\langle M_b \rangle$ | $\langle M_c \rangle$ | $\langle M \rangle$ |
| Er1 <sub>1</sub> | 0(0)                  | 8.329(26)             | 0(0)                  | 8.329(26)           |
| Er1 <sub>2</sub> | 0                     | 8.329                 | 0                     | 8.329               |
| Er1 <sub>3</sub> | 0                     | 8.329                 | 0                     | 8.329               |
| Er1 <sub>4</sub> | 0                     | 8.329                 | 0                     | 8.329               |
| $H \parallel c$  | $\langle M_a \rangle$ | $\langle M_b \rangle$ | $\langle M_c \rangle$ | $\langle M \rangle$ |
| Er1 <sub>1</sub> | -1.074(101)           | 0(0)                  | 5.030(258)            | 5.143(274)          |
| Er1 <sub>2</sub> | 1.074                 | 0                     | 5.030                 | 5.143               |
| Er1 <sub>3</sub> | -1.074                | 0                     | 5.030                 | 5.143               |
| Er1 <sub>4</sub> | 1.074                 | 0                     | 5.030                 | 5.143               |

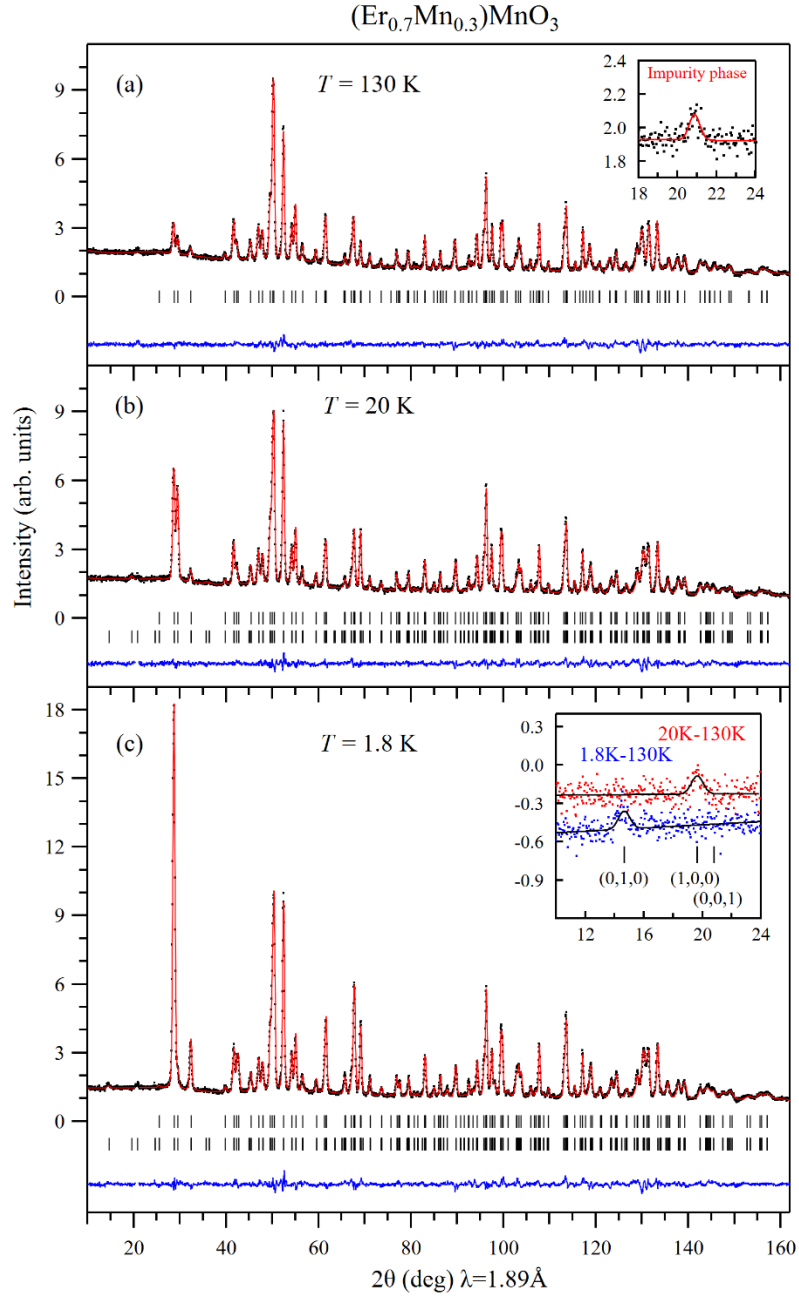
**Table 7**

Induced magnetic  $\text{Ho}^{3+}$  moments in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  at  $T = 1$  K in an external magnetic field of  $H = 10$  T applied along the three axes  $a$ ,  $b$ ,  $c$  calculated by McPhase. Uncertainties due to the experimental errors in the crystal-structural parameters were evaluated using gauss law of error propagation and are shown in parentheses only for Ho1<sub>1</sub> for simplicity.

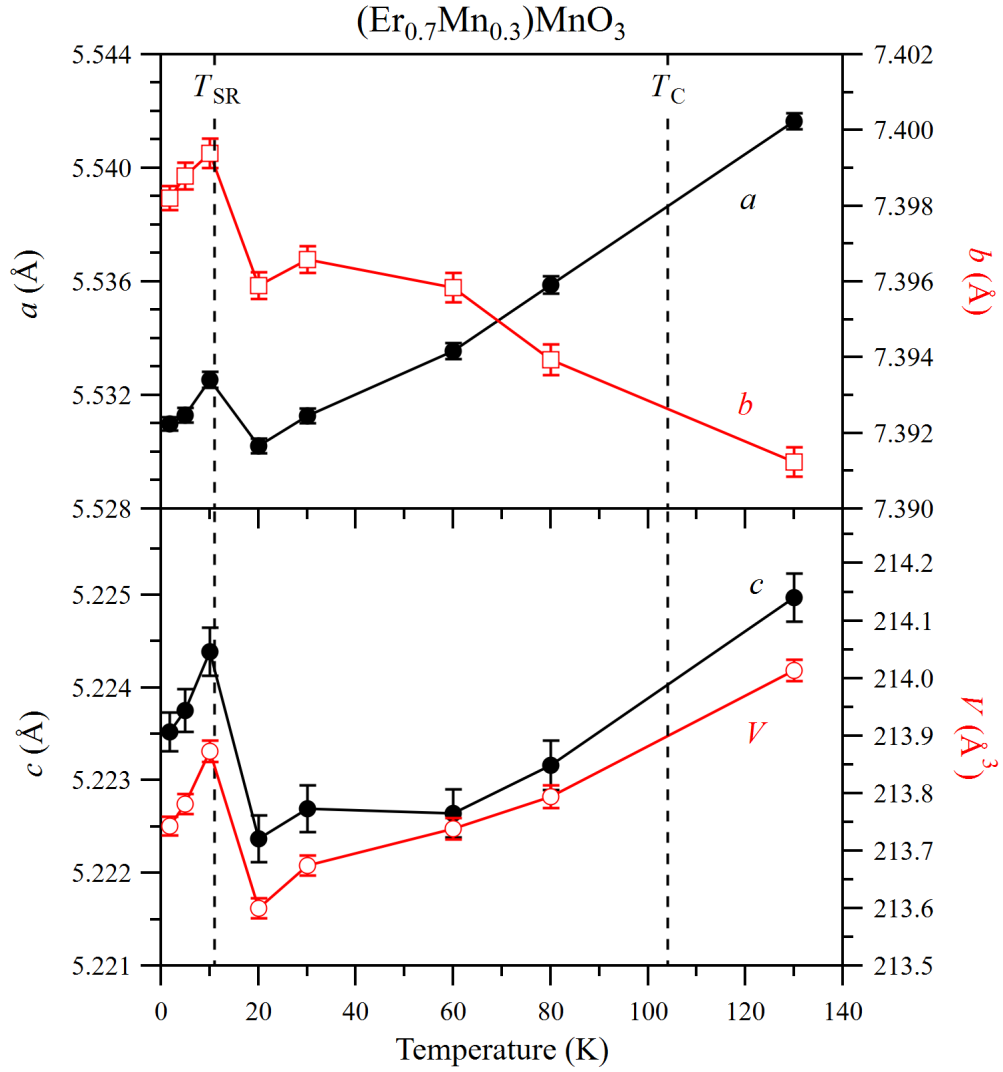
| $H \parallel a$  | $\langle M_a \rangle$ | $\langle M_b \rangle$ | $\langle M_c \rangle$ | $\langle M \rangle$ |
|------------------|-----------------------|-----------------------|-----------------------|---------------------|
| Ho1 <sub>1</sub> | 8.932(9)              | 0(0)                  | 4.112(17)             | 9.833(15)           |
| Ho1 <sub>2</sub> | 8.932                 | 0                     | -4.112                | 9.833               |
| Ho1 <sub>3</sub> | 8.932                 | 0                     | 4.112                 | 9.833               |
| Ho1 <sub>4</sub> | 8.932                 | 0                     | -4.112                | 9.833               |
| $H \parallel b$  | $\langle M_a \rangle$ | $\langle M_b \rangle$ | $\langle M_c \rangle$ | $\langle M \rangle$ |
| Ho1 <sub>1</sub> | 0(0)                  | 1.218(80)             | 0(0)                  | 1.218(80)           |
| Ho1 <sub>2</sub> | 0                     | 1.218                 | 0                     | 1.218               |
| Ho1 <sub>3</sub> | 0                     | 1.218                 | 0                     | 1.218               |
| Ho1 <sub>4</sub> | 0                     | 1.218                 | 0                     | 1.218               |
| $H \parallel c$  | $\langle M_a \rangle$ | $\langle M_b \rangle$ | $\langle M_c \rangle$ | $\langle M \rangle$ |
| Ho1 <sub>1</sub> | 8.692(23)             | 0(0)                  | 4.505(28)             | 9.790(33)           |
| Ho1 <sub>2</sub> | -8.692                | 0                     | 4.505                 | 9.790               |
| Ho1 <sub>3</sub> | 8.692                 | 0                     | 4.505                 | 9.790               |
| Ho1 <sub>4</sub> | -8.692                | 0                     | 4.505                 | 9.790               |



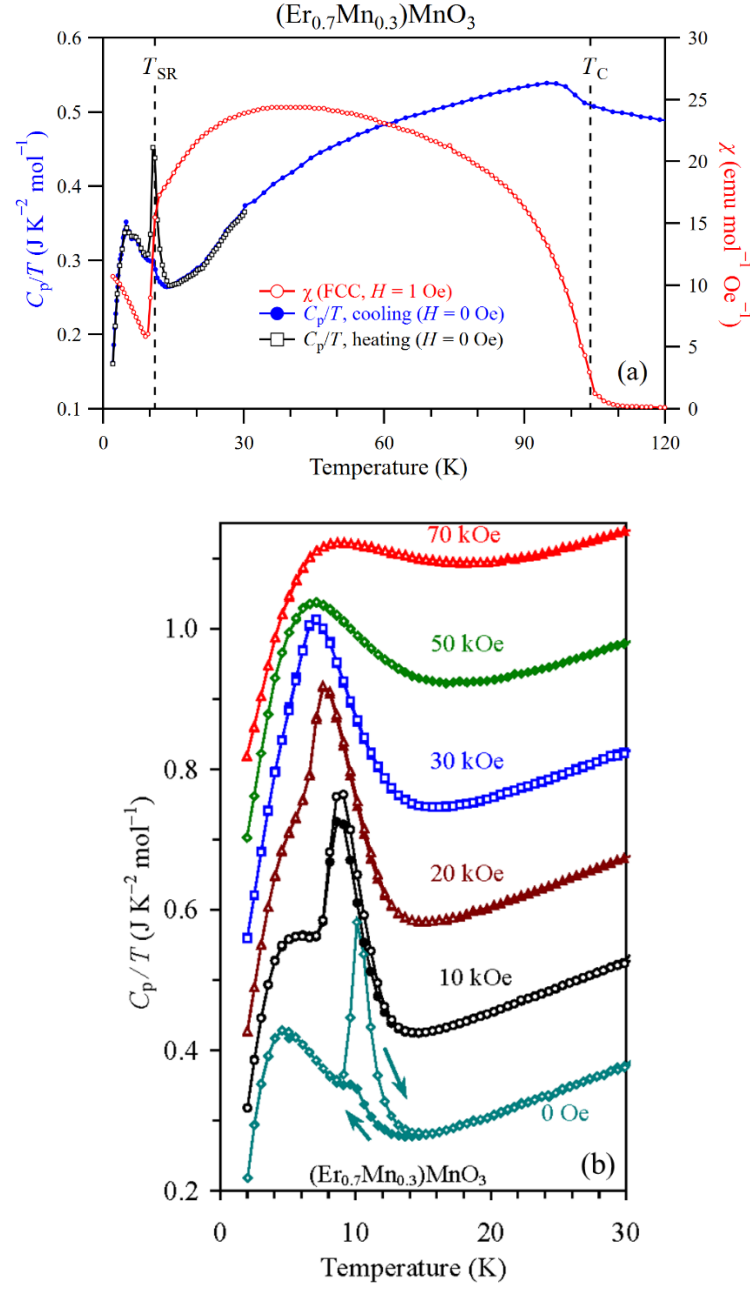
**Fig. 1.** Orthorhombic perovskite crystal structure of Mn self-doped  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ . The drawing was made using the program VESTA [40].



**Fig. 2.** Experimental (black dots), calculated (red line), and difference (blue line) neutron diffraction patterns of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  in the paramagnetic state at  $T = 130$  K (a) and in the magnetically ordered states at  $T = 20$  (b) and  $1.8$  K (c). The tick marks indicate Bragg peak positions: the first row is for the nuclear peaks, and the second row is for the magnetic peaks. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

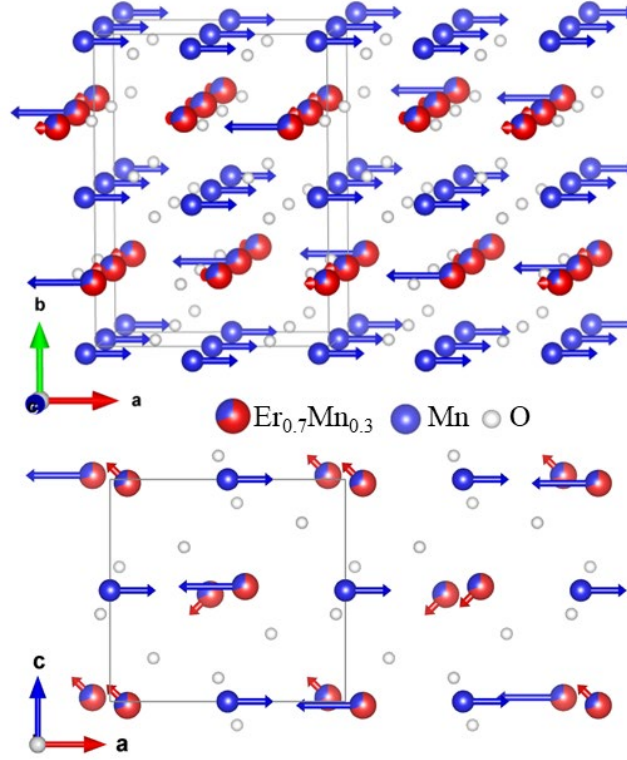


**Fig. 3.** Temperature dependence of the orthorhombic lattice parameters ( $a$ ,  $b$ , and  $c$ ) and the unit cell volume ( $V$ ) of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  refined from neutron diffraction data. The vertical dashed lines indicate the FiM phase transition at  $T_{\text{C}} = 104$  K and the SR temperature at  $T_{\text{SR}} = 11$  K.

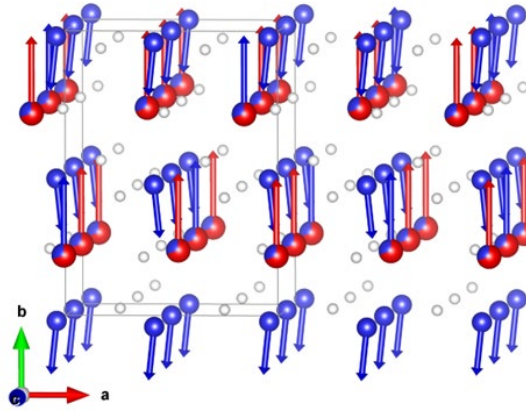


**Fig. 4.** (a) Temperature dependence of the specific heat  $C_p/T$  and magnetic susceptibility  $\chi$  of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  providing evidence for two successive magnetic phase transitions. The vertical dashed lines indicate the FiM phase transition at  $T_C = 104$  K and the SR temperature at  $T_{\text{SR}} = 11$  K. (b)  $C_p/T$  versus  $T$  curves of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  measured on cooling (filled symbols) and heating (empty symbols) at different magnetic fields between 0 and 70 kOe. The curves are shifted by  $0.1 \text{ J K}^{-2} \text{mol}^{-1}$  from each other for clarity.

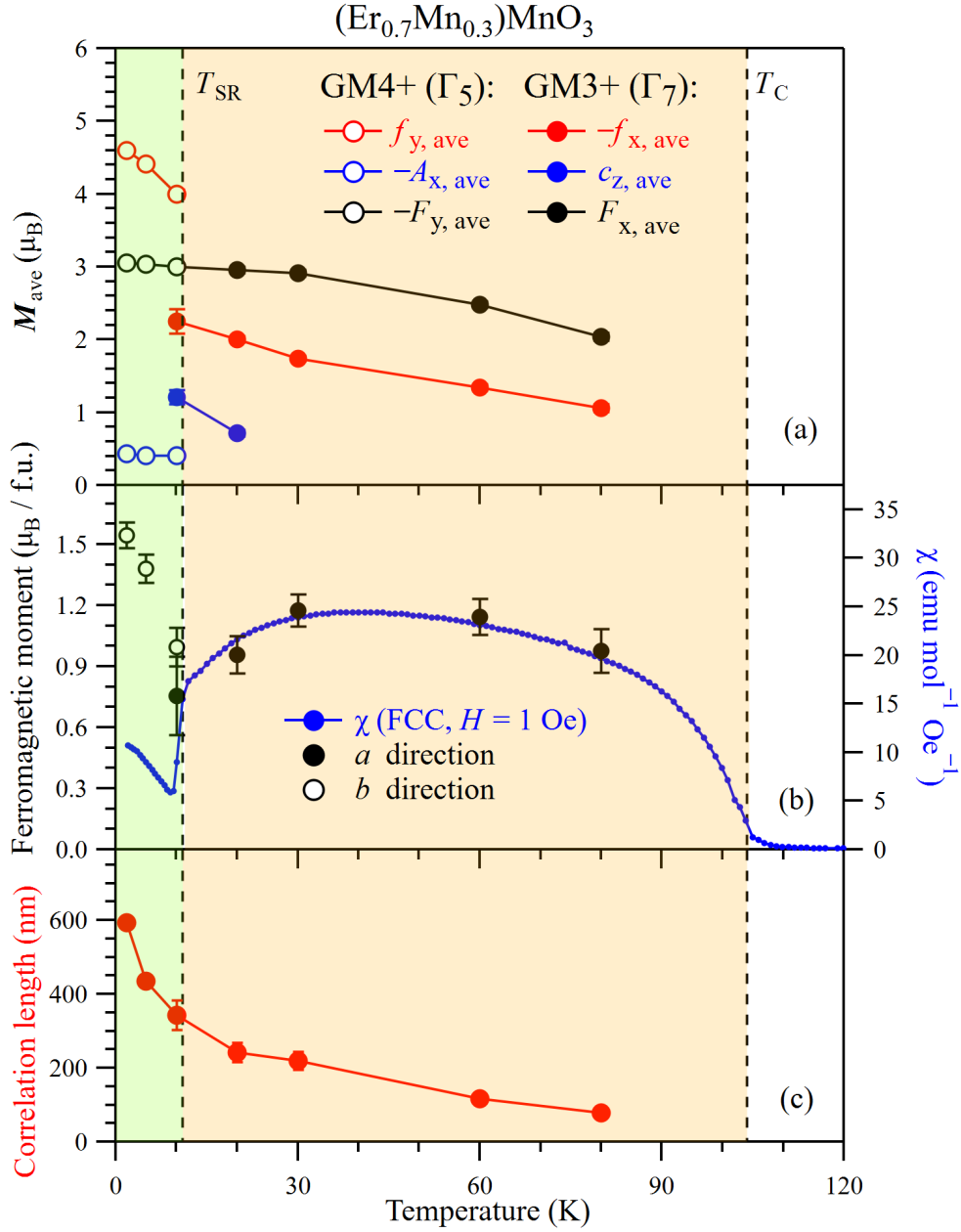
(a)  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ ,  $T = 20 \text{ K}$ , GM3+ ( $\Gamma_7$ )



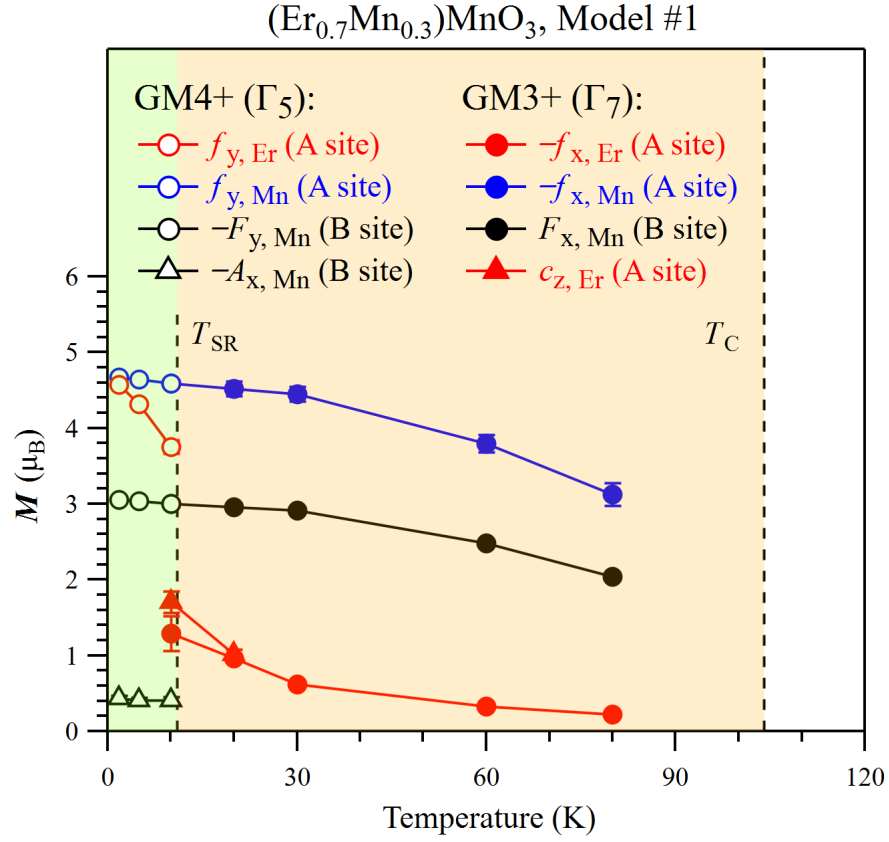
(b)  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$ ,  $T = 1.8 \text{ K}$ , GM4+ ( $\Gamma_5$ )



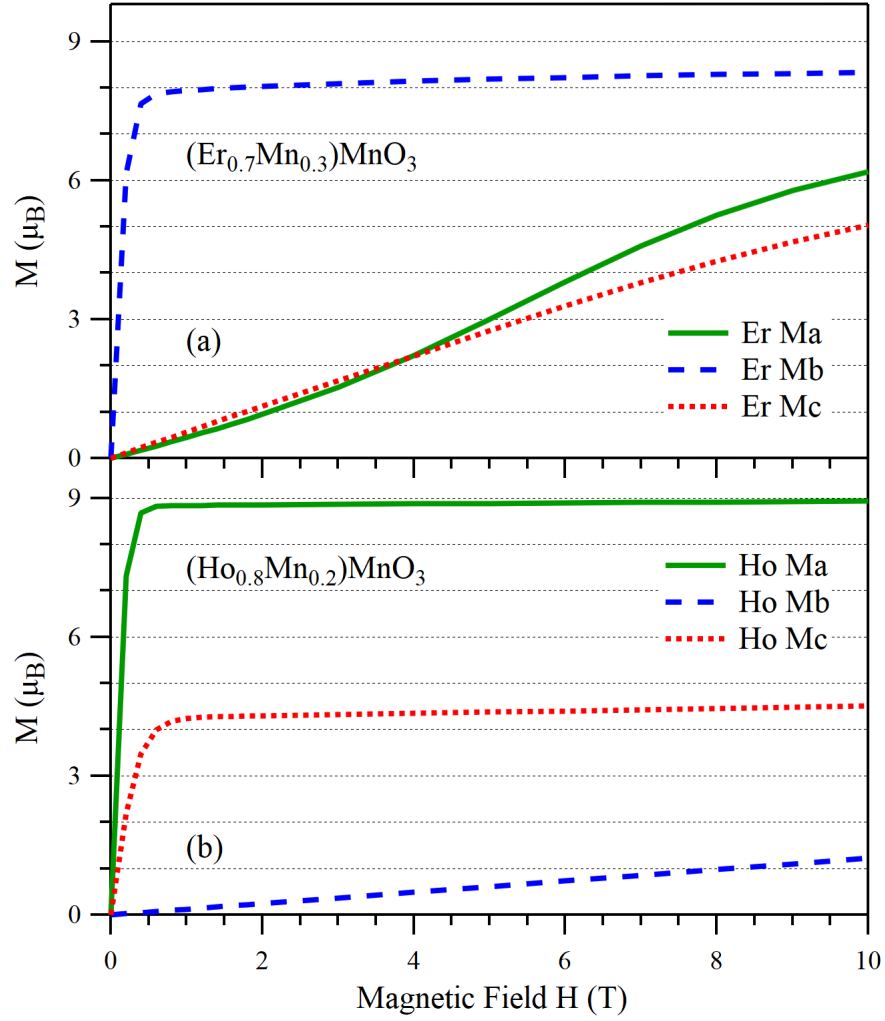
**Fig. 5.** Magnetic structures of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  at  $T = 20 \text{ K}$  (a) and  $1.8 \text{ K}$  (b) refined from neutron diffraction data. Ordered magnetic moments (based on Model #1) are shown by arrows in blue (Mn) and red (Er). The drawings were made using the program VESTA [40]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 6.** Temperature dependence of the FiM structure of  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  refined from neutron diffraction data. Left hand axes show (a) the average ordered Mn and Er moments  $M_{\text{ave}}$ , (b) the macroscopic FM moment per formula unit, and (c) the correlation length of the magnetic structure. Right hand axes display the magnetic susceptibility  $\chi$ . The vertical dashed lines indicate the FiM phase transition at  $T_C = 104$  K and the Spin-reorientation temperature at  $T_{\text{SR}} = 11$  K.



**Fig. 7.** Temperature dependence of the ordered Mn and Er moments of (Er<sub>0.7</sub>Mn<sub>0.3</sub>)MnO<sub>3</sub> based on Model #1. The vertical dashed lines indicate the FiM phase transition at  $T_C = 104$  K and the Spin-reorientation temperature at  $T_{\text{SR}} = 11$  K.



**Fig. 8.** Field dependence of the single-ion magnetization in an external magnetic field applied along the  $a$ -,  $b$ - and  $c$ -axes for  $\text{Er}^{3+}$  in  $(\text{Er}_{0.7}\text{Mn}_{0.3})\text{MnO}_3$  (a) and  $\text{Ho}^{3+}$  in  $(\text{Ho}_{0.8}\text{Mn}_{0.2})\text{MnO}_3$  (b) at  $T = 1$  K calculated by McPhase.