



# Spin-reorientation magnetic transitions in Mn-doped $\text{SmFeO}_3$

Jian Kang,<sup>a</sup> Yali Yang,<sup>a</sup> Xiaolong Qian,<sup>a</sup> Kai Xu,<sup>a</sup> Xiaopeng Cui,<sup>a</sup> Yifei Fang,<sup>a</sup> Venkatesh Chandragiri,<sup>a</sup> Baojuan Kang,<sup>a</sup> Bin Chen,<sup>b</sup> Alessandro Stroppa,<sup>a,c</sup> Shixun Cao,<sup>a,d</sup> Jincang Zhang<sup>a,d</sup> and Wei Ren<sup>a,d\*</sup>

Received 4 April 2017

Accepted 29 May 2017

Edited by Y. Murakami, KEK, Japan

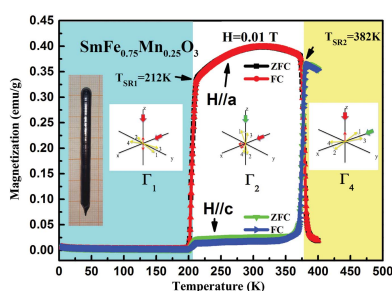
**Keywords:** spin reorientation transitions; rare earth perovskites; magnetic phase transitions; Mn doping.

<sup>a</sup>Department of Physics, International Center of Quantum and Molecular Structures and Materials Genome Institute, Shanghai University, Shanghai 200444, People's Republic of China, <sup>b</sup>Hangzhou Key Laboratory of Quantum Matter, Department of Physics, Hangzhou Normal University, Hangzhou 310036, People's Republic of China, <sup>c</sup>CNR-SPIN, L'Aquila, Italy, and <sup>d</sup>Shanghai Key Laboratory of High-Temperature Superconductors, Shanghai University, Shanghai 200444, People's Republic of China. \*Correspondence e-mail: renwei@shu.edu.cn

Spin reorientation is a magnetic phase transition in which rotation of the magnetization vector with respect to the crystallographic axes occurs upon a change in the temperature or magnetic field. For example,  $\text{SmFeO}_3$  shows a magnetization rotation from the  $c$  axis above 480 K to the  $a$  axis below 450 K, known as the  $\Gamma_4 \rightarrow \Gamma_2$  transition. This work reports the successful synthesis of the new single-crystal perovskite  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  and finds interesting spin reorientations above and below room temperature. In addition to the spin reorientation of the  $\Gamma_4 \rightarrow \Gamma_2$  magnetic phase transition observed at around  $T_{\text{SR}2} = 382$  K, a new spin reorientation,  $\Gamma_2 \rightarrow \Gamma_1$ , was seen at around  $T_{\text{SR}1} = 212$  K due to Mn doping, which could not be observed in the parent rare earth perovskite compound. This unexpected spin configuration has complete antiferromagnetic order without any canting-induced weak ferromagnetic moment, resulting in zero magnetization in the low-temperature regime.  $M$ - $T$  and  $M$ - $H$  measurements have been made to study the temperature and magnetic-field dependence of the observed spin reorientation transitions.

## 1. Introduction

The emerging demand for next-generation spintronic devices calls for more functional materials with outstanding properties. In this context, the  $R\text{FeO}_3$  ( $R$  = rare earth ion) oxide family with the  $Pbnm$  structure are promising candidates, in which not only the magnetic interactions between the  $3d$  spins of the transition metals (Fe–Fe) but also those with the  $4f$  moments of the rare earth ions ( $R$ –Fe) have important roles in their magnetic behaviour and magnetoelectric coupling (Zvezdin & Mukhin, 2009). Up to now,  $R\text{FeO}_3$  compounds have been investigated for future applications such as inertia-driven spin switching (Kimmel *et al.*, 2009), laser-induced spin reorientation (SR) (de Jong *et al.*, 2011), ultrafast manipulation of spins through thermally induced SR transition (de Jong *et al.*, 2012), temperature and magnetic field control of SR (Cao *et al.*, 2014; Hong *et al.*, 2011; Cao *et al.*, 2016; Zhao *et al.*, 2015; Wu *et al.*, 2014; Wang *et al.*, 2016; Yuan *et al.*, 2013) and large rotating-field entropy change (Cao *et al.*, 2016; Huang *et al.*, 2013). The  $\text{RMnO}_3$  family also draws a lot of attention due to spontaneous electric polarizations induced by noncollinear spiral magnetic order (Kenzelmann *et al.*, 2005), a collinear  $E$ -type antiferromagnetic structure (Okuyama *et al.*, 2011) and strong antiferromagnetic pinning effects (Jin *et al.*, 2015). In  $R\text{FeO}_3$  and  $\text{RMnO}_3$  compounds, below their Néel tempera-



OPEN ACCESS

tures ( $T_N$ ), the  $\text{Fe}^{3+}$  or  $\text{Mn}^{3+}$  sublattice will be ordered in a slightly canted antiferromagnetic configuration due to an antisymmetric exchange Dzyaloshinsky–Moriya interaction, while also showing weak ferromagnetism (Dzyaloshinsky, 1958; Moriya, 1960). Magnetoelectric (ME) coupling, which breaks spatial inversion and time-reversal symmetries (Mostovoy, 2006), has been the focus of extensive research to explore the mutual control of electric and magnetic degrees of freedom (Cao *et al.*, 2016; Fina *et al.*, 2010). Various magnetic phase transitions also occur in the presence of ME processes (Hemberger *et al.*, 2007; Kimura *et al.*, 2005) and dielectric properties may also change around the magnetic phase transition, thus providing an approach to trigger magnetodielectric coupling. It is worth noting that  $\text{DyFeO}_3$  has been found experimentally to have a field-induced gigantic ME effect (Nakajima *et al.*, 2015). Consequently, the modification of magnetic and electric polarization by controlling the phase transition is the main theoretical and experimental objective to realise new multiferroic materials that have application at room temperature.

One of the special magnetic phase transitions in  $R\text{FeO}_3$  which might be closely related to magnetically driven ferroelectricity is spin reorientation (SR). According to symmetry considerations and the antiferromagnetic nature of the coupling between the ions, there are three magnetic configurations allowed for the  $\text{Fe}^{3+}$  sublattice, namely  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_4$ , with different major antiferromagnetic directions (White, 1969). Complex  $R^{3+}$ – $R^{3+}$ ,  $R^{3+}$ – $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$ – $\text{Fe}^{3+}$  interactions can lead to competitive anisotropic magnetic features in  $R\text{FeO}_3$ , possessing slightly different free energies when the magnetic moments align along the three main axes over varying temperature ranges. For  $R\text{FeO}_3$ , the  $\Gamma_4$  spin configuration appears in the higher temperature region, while the other two spin configurations can be found when the temperature is reduced (White, 1969). At extremely low temperatures a different spin configuration may appear, due to the more complicated ordering of sets of rare earth ions, such as observed in  $\text{TbFeO}_3$  (Cao *et al.*, 2016) and  $\text{DyFeO}_3$  (White, 1969).

$\text{SmFeO}_3$  has attracted much attention due to its intriguing behaviours, like fast magnetic switching (Jeong *et al.*, 2012), temperature-induced spin switching (Cao *et al.*, 2014), the highest SR temperature ( $T_{\text{SR}}$ ) among the  $R\text{FeO}_3$  system and its curious ferroelectric properties (Lee *et al.*, 2011; Kuo *et al.*, 2014).  $\text{SmMnO}_3$  is one of the *A*-type antiferromagnetic (AFM)  $\text{RMnO}_3$  compounds, showing negative magnetization (Cheng *et al.*, 2011) and magnetocapacitive effects (Jung *et al.*, 2010) as reported recently. In addition, the  $R\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$  ( $R = \text{Dy}$ ,  $\text{Tb}$  and  $\text{Y}$ ) family has been studied a lot due to their varying physical properties and interesting phase transitions (Nair *et al.*, 2016; Mandal *et al.*, 2013, 2011; Hong *et al.*, 2011). Typically, the usual way to control the temperature and configuration of the SR transition is to dope other lanthanides into  $R\text{FeO}_3$ , such as  $\text{Sm}_{1-x}\text{Dy}_x\text{FeO}_3$  (Zhao *et al.*, 2015) and  $\text{Dy}_{0.5}\text{Pr}_{0.5}\text{FeO}_3$  (Wu *et al.*, 2014). Here, we report a new way to change the SR transition by modifying the  $3d$ – $4f$  interaction between  $R^{3+}$ – $\text{Fe}^{3+}$  with  $\text{Mn}^{3+}$  doping in single-crystal  $\text{SmFeO}_3$ .

By doing so, we found that the  $\text{SmFe}_x\text{Mn}_{1-x}\text{O}_3$  family can possess novel properties that are absent from the parent  $\text{SmFeO}_3$  and  $\text{SmMnO}_3$  rare earth perovskites. Here, we focus our investigation on the twofold SR magnetic transitions of  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  and the continuously tunable phase transition as observed from the temperature dependence of the magnetization ( $M$ – $T$ ) under external applied fields and hysteresis loops ( $M$ – $H$ ).

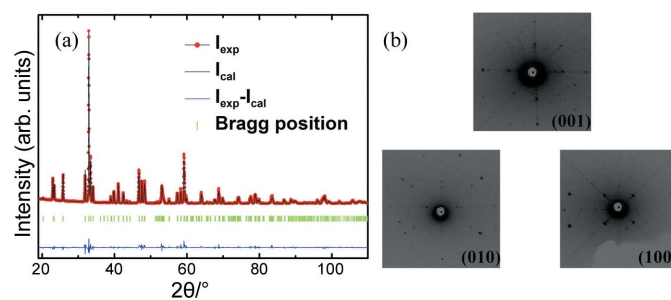
## 2. Experimental

The  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  (SFMO) single crystal was grown by the optical floating-zone method (Crystal System Inc., model FZ-T-10000H-VI-P-SH). The compounds of the feed and seed rods were prepared by a solid-state reaction in which the stoichiometric starting materials were  $\text{Sm}_2\text{O}_3$  (99.99%),  $\text{Fe}_2\text{O}_3$  (99.9%) and  $\text{MnO}_2$  (99.9%) in a properly mixed proportion of 4:3:2. The temperature of the molten zone was controlled by adjusting the power of four lamps. The molten zone moved upwards at a rate of  $3 \text{ mm h}^{-1}$ .

The crystallinity and crystallographic orientations were determined by X-ray Laue photography. The microstructure of the crystal was checked by X-ray diffraction using a Rigaku 18 kW D/MAX-2550 diffractometer ( $\text{Cu K}\alpha$  radiation) with a scanning step of  $0.02^\circ$  and  $2\theta$  from  $10^\circ$  to  $120^\circ$ . The dc magnetization measurements were performed using a Physics Property Measurement System (Quantum Design, PPMS-9). Zero-field-cooling (ZFC) and field-cooling (FC) processes were used to acquire the temperature dependence of the magnetization.

## 3. Results

Fig. 1(a) shows the Rietveld refinement of powder X-ray diffraction (XRD) data from the single crystal of  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  performed using the *AutoFP* (Cui *et al.*, 2015) and *FULLPROF* (Rodríguez-Carvajal, 2001) programs. The diffraction patterns can be assigned to the single-phase orthorhombic perovskite structure with space group *Pbnm* and no impurity phases were detected. The lattice parameters thus obtained are  $a = 5.39392 \text{ \AA}$ ,  $b = 5.63707 \text{ \AA}$  and  $c = 7.67156 \text{ \AA}$  ( $R_{\text{wp}} = 0.133$ ). Fig. 1(b) shows the clear Laue diffraction spots, indicating the high quality of our



**Figure 1**  
(a) X-ray diffraction pattern and (b) Laue back-scattering photography of  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  single crystal along the (001), (010) and (100) crystallographic axes.

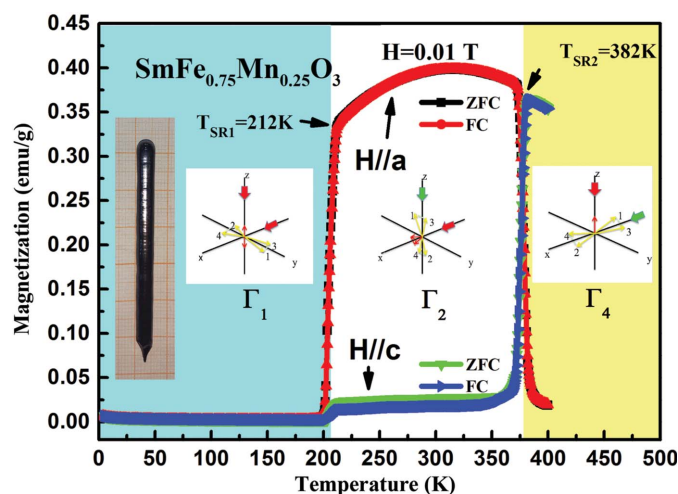


Figure 2

Temperature-dependent magnetizations of  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  along the  $a$  and  $c$  axes under magnetic field  $H = 0.01$  T. Three slightly canted antiferromagnetic phases  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_4$  can be distinguished by the shaded areas. The inset shows the  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  single-crystal sample.

$\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  single crystal. Both XRD and Laue photography confirmed the excellent quality of the sample, and the cutting planes are precisely perpendicular to the  $a$ ,  $b$  and  $c$  axes, respectively.

Fig. 2 shows the temperature dependence of the ZFC and FC magnetizations measured under a field of  $H = 0.01$  T for the  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  single crystal (sample shown in the inset) along the the  $a$  and  $c$  axes, respectively. The second-order transition starting from  $T_{\text{SR}2} = 382$  K is the first spin reorientation, where the  $\text{Fe}^{3+}$  spins reorient from a configuration of canting antiferromagnetism along the  $a$  axis with weak ferromagnetism along the  $c$  axis,  $\Gamma_4(G_x, A_y, F_z)$ , to canting antiferromagnetism along the  $c$  axis with weak ferromagnetism along the  $a$  axis,  $\Gamma_2(F_x, C_y, G_z)$ . Another unique and new feature of the  $M$ - $T$  curve is that at  $T_{\text{SR}1} = 212$  K, the  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  single crystal undergoes a second SR transition at a lower temperature with weak ferromagnetism along the  $a$  axis  $\Gamma_2(F_x, C_y, G_z)$ , changing to complete antiferromagnetism with no net magnetization,  $\Gamma_1(A_x, G_y, C_z)$ . This kind of SR behaviour has never been reported in the literature to the best of our knowledge.

The transition over the whole temperature range might be called a  $\Gamma_4 \rightarrow \Gamma_2 \rightarrow \Gamma_1$  double SR transition. Since pure  $\text{SmFeO}_3$  possesses a spin configuration from  $\Gamma_4$  to  $\Gamma_2$  due to the  $\text{Sm}^{3+}$ - $\text{Fe}^{3+}$  interaction at rather high temperatures (450–480 K), it is reasonable to have such a spin configuration transition in  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  at a lower temperature of 361–382 K. The most interesting finding here is the spin configuration from  $\Gamma_2$  to  $\Gamma_1$  due to  $\text{Mn}^{3+}$  doping in  $\text{SmFeO}_3$  that gives a vanishing effective moment vector below  $T_{\text{SR}1} = 212$  K. It is known that there is no SR in the whole family of the  $\text{RMnO}_3$  system. In addition, it is very rare for a rare earth orthoferrite to possess a  $\Gamma_1$  spin configuration, with the exception of  $\text{DyFeO}_3$  (Fu *et al.*, 2014), for which the SR transition temperature ( $T_{\text{SR}} = 37$  K) is much lower than that of our single crystal here.

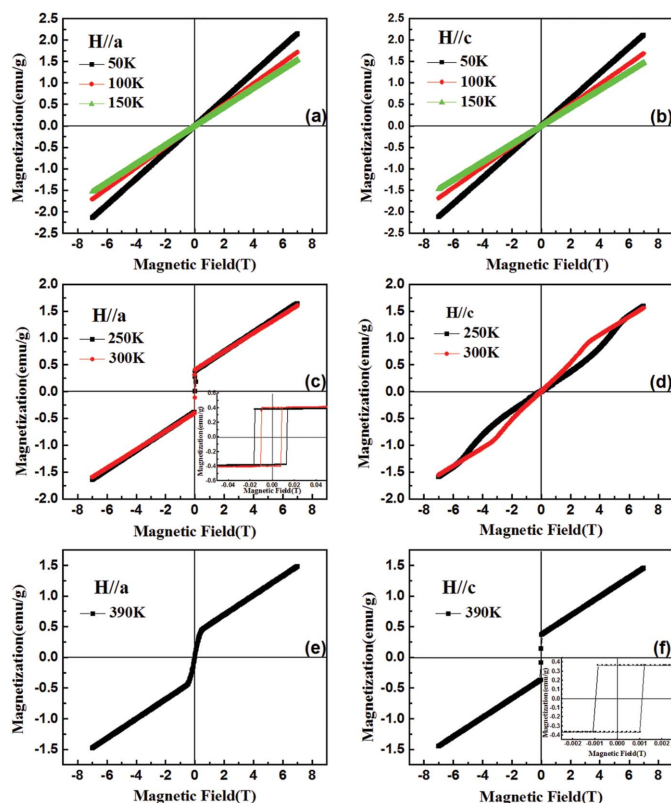


Figure 3

$M$ - $H$  curves for the  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$  single crystal along the  $a$  and  $c$  axes at temperatures of (a), (b) 50 K, 100 K and 150 K, (c), (d) 250 K and 300 K, and (e), (f) 390 K. The insets of (c) and (f) show enlargements of the plots at small magnetic field.

To investigate the SR transition further, the  $M$ - $H$  curves were measured at different temperatures along the  $a$  and  $c$  axes, respectively. Figs. 3(a) and 3(b) show the standard linear AFM behaviour at 50, 100 and 150 K with a change of slope, which corresponds to the feature of  $\Gamma_1$  spin configuration below  $T_{\text{SR}1} = 212$  K. Fig. 3(c) and inset show the uncompensated ferromagnetism component along the  $a$  axis, while Fig. 3(d) shows AFM-like behaviour but with noticeable kinks along the  $c$  axis. Above 382 K, the AFM-like and kink behaviour is more obviously seen in the  $a$  axis  $M$ - $H$ , as shown in Fig. 3(e), while the  $c$  axis shows a ferromagnetism component in Fig. 3(f) and its inset. Inflexion behaviours are observed in Figs. 3(d) and 3(e) when the magnetic fields reach certain critical values, which suggests a field-induced SR. Therefore, according to Fig. 3, we can confirm that the weak ferromagnetism aligns along the  $c$  axis when the temperature is below  $T_N$  (around 600 K), and changes its direction to the  $a$  axis when the temperature drops below  $T_{\text{SR}2} = 382$  K, before disappearing in any direction below  $T_{\text{SR}1} = 212$  K, as shown in Fig. 2. Therefore, such a double SR transition induced by temperature is extraordinary for a single-phase rare earth perovskite.

Fig. 4(a) shows the  $M$ - $T$  curves along the  $c$  axis when we change the magnitude of the external magnetic field. Upon increasing the magnetic field,  $T_{\text{SR}2}$  moves to a lower temperature in a linear-like fashion. For example, we can see

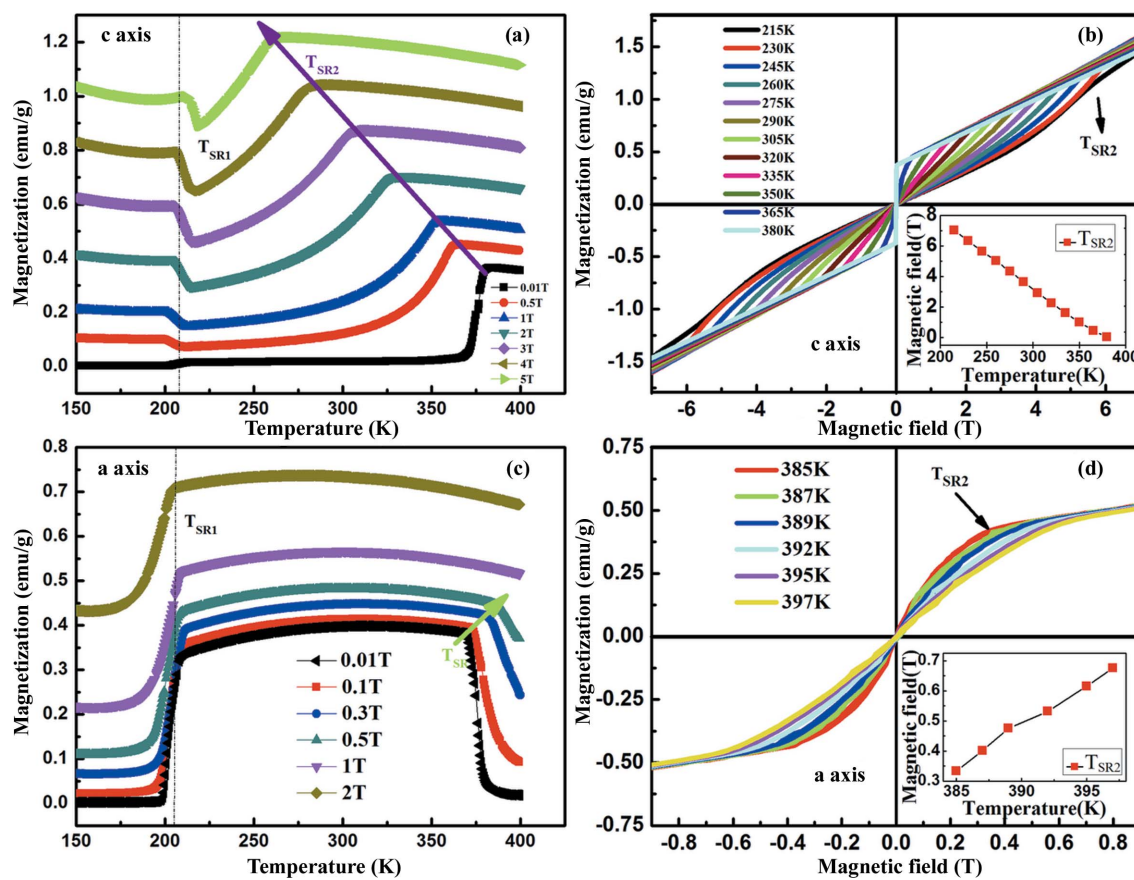


Figure 4

(a) *M-T* curves along the *c* axis at different magnetic fields from 0.01 to 5 T. (b) *M-H* curves along the *c* axis at different temperatures from 215 to 380 K. (c) *M-T* curves along the *a* axis at different magnetic fields from 0.01 to 2 T. (d) *M-H* curves along the *a* axis at different temperatures from 385 to 397 K. The insets in (b) and (d) show the linear temperature dependence of *T*<sub>SR2</sub> along the *c* and *a* axes, respectively.

that the value of *T*<sub>SR2</sub> decreases to 263 K under *H* = 5 T. Thus, we believe that when the magnetic field is high enough, the  $\Gamma_2$  spin configuration will be totally suppressed. On the other hand, *T*<sub>SR1</sub> is found to be almost constant regardless of the magnitude of the external field. Fig. 4(b) shows the measured *M-H* curves at different temperatures ranging from 215 to 380 K. This diagram shows the evolution of the *M-H* curves with a change of slope around *T*<sub>SR2</sub> at different temperatures, illustrating an intermediate state between two different magnetic configurations, corroborating the details of Fig. 4(a). Here, the magnetic order would be stabilized in a  $\Gamma_4$  spin configuration with a moment along the *c* axis after the intermediate state. Furthermore, we also observe from both Figs. 4(a) and 4(b) that, with increasing magnetic field, the inflection points move to low temperature. On the other hand, when we apply the external magnetic field along the *a* axis, Fig. 4(c) shows that the spin reorientation temperature *T*<sub>SR2</sub> will move to the high-temperature region, as indicated by the green arrow. When the magnetic field exceeds 0.5 T, *T*<sub>SR2</sub> moves above 400 K, which is beyond our temperature detection limit. Fig. 4(d) shows the *M-H* curves along the *a* axis at temperatures ranging from 385 to 397 K. The collected data show another linearly increasing behaviour for *T*<sub>SR2</sub> versus magnetic field, consistent with that of the *M-T* curve in Fig. 4(c). In addition, *T*<sub>SR1</sub> remains constant with varying magnetic field, as

indicated by the vertical dashed line. To sum up, the  $\Gamma_4$  to  $\Gamma_2$  SR transition temperature can be easily controlled by magnetic field, whereas the  $\Gamma_2$  to  $\Gamma_1$  transition temperature is insensitive to the magnetic field.

#### 4. Discussion

As mentioned, the rare earth orthoferrites have two kinds of magnetic ion,  $M^{3+}$  and  $R^{3+}$ . So there are three kinds of magnetic interaction,  $M^{3+}-M^{3+}$ ,  $M^{3+}-R^{3+}$  and  $R^{3+}-R^{3+}$ . These three interactions all consist of isotropic, antisymmetric and anisotropic-symmetric super-exchange interactions, which inevitably makes the magnetic properties of RFeO<sub>3</sub> complex. Further, the antisymmetric and anisotropic-symmetric super-exchange interactions of  $M^{3+}-R^{3+}$  are responsible for the temperature-induced SR (Yamaguchi, 1974). In our case, the interaction becomes even more complicated due to the doping Mn<sup>3+</sup> ions and intriguingly introduces all three spin configurations allowed in RFeO<sub>3</sub>. By minimizing the free energy in the  $\Gamma_4$  to  $\Gamma_2$  SR transition with respect to  $\theta$  and  $\Phi$  ( $\theta$  is the rotation angle of the easy axis in the *ac* plane and  $2\Phi$  represents the angle between two sublattices of the  $R^{3+}$  spins), one can obtain the following equation (Yamaguchi, 1974):



$$(J_B - J_C)(\hat{J} + \hat{J}')^2(s_0 + s \cos \Phi) s \sin \Phi + (J_D + J_B)(\hat{J} - \hat{J}')^2 \times (s'_0 \sin \theta - s \sin \Phi) s \cos \Phi = 0, \quad (1)$$

$$\cos \theta \left\{ \left[ 2(D - E) + \frac{(D_z - C_z)^2}{2(J_D - J_C)} - \frac{(B_x - C_x)^2}{2(J_B - J_C)^2} \right] \sin \theta + 2s'_0 \left[ \frac{(\hat{J} - \hat{J}')^2}{(J_B - J_C)} \right] s \sin \Phi \right\} = 0 \quad (2)$$

where  $s$  is the ratio of the mean values of the  $R^{3+}$  and  $M^{3+}$  spins,  $\langle S_R \rangle / \langle S_M \rangle$ , which is the only parameter depending directly on temperature. The other parameters in equations (1) and (2) are different exchange constants. These two equations give the following three sets of solutions, (I), (II) and (III).

$$(I) \quad \sin \Phi = 0. \quad (3)$$

In this case, the stable angle of  $\theta$  is 0 and this gives the  $\Gamma_4$  configuration in the high-temperature phase ( $382 \text{ K} < T < T_N$ ).

$$(II) \quad s \cos \Phi = s_{c1}. \quad (4)$$

where

$$s_{c1} = \frac{-s_0[(\hat{J} + \hat{J}')^2/(J_D + J_B)]}{[(\hat{J} + \hat{J}')^2/(J_D + J_B)] + [(As'_0 - 1)(\hat{J} - \hat{J}')^2/(J_B - J_C)]}, \quad (5)$$

and

$$A = \frac{-2s'_0[(\hat{J} - \hat{J}')^2/(J_B - J_C)]}{2(D - E) + [(D_z - C_z)^2/2(J_D - J_C)] - [(B_x - C_x)^2/2(J_B - J_C)^2]}. \quad (6)$$

The equilibrium values of  $\theta$  can be acquired as

$$\theta = \sin^{-1} \{ [A(s^2 - s_{c1}^2)^{1/2}] \}. \quad (7)$$

From equation (7), we can see that  $\theta$  is zero when  $s = s_{c1}$  and will increase with increasing  $s$ . This implies rotation of the spin system. When  $s$  reaches another critical value of  $s = [s_{c1}^2 + (1/A^2)]^{1/2}$ ,  $\theta$  will take a value of  $\pi/2$ . This process corresponds to the continuous SR intermediate range ( $361 \text{ K} \leq T \leq 382 \text{ K}$ ).

$$(III) \quad \cos \theta = 0. \quad (8)$$

This indicates that the easy axis has rotated to the  $c$  axis and the system is in the  $\Gamma_2$  phase. Briefly, the case when  $s = 0$  corresponds to the state at the Néel temperature. At high temperature  $s$  is small, and when  $s \leq s_{c1}$  the free energy  $F(\Gamma_4)$  is lower and the spin system will be stabilized in the  $\Gamma_4$  configuration due to the anisotropic energy of the  $\text{Fe}^{3+}$  single ions. As the temperature decreases, the sublattice moments of  $\text{Sm}^{3+}$  and  $\text{Fe}^{3+}$  will increase and  $s$  gradually approaches  $s_{c1}$  where the free energy  $F(\Gamma_{24})$  crosses  $F(\Gamma_4)$ . When  $s$  finally surpasses  $[s_{c1}^2 + (1/A^2)]^{1/2}$ , the free energy  $F(\Gamma_2)$  becomes lowest, thus favouring the  $\Gamma_2$  configuration. This is the typical continuous SR transition in most  $R\text{FeO}_3$  systems, but in the  $\text{Mn}^{3+}$ -doped  $\text{SmFeO}_3$  single crystal the situation will become

more complicated. Once the first SR transition is complete, the  $\text{Mn}^{3+}$  ions will be ordered with decreasing temperature and this will consequently influence the distribution of the free energy along the three main axes and  $s$  as well. When  $s$  reaches another critical value  $s_{c2}$ , the free energy of the  $\Gamma_1$  configuration is smaller than that of  $\Gamma_2$  and  $\Gamma_4$ , and the corresponding temperature is 212 K for our case.

So far, we have discussed two critical values of  $s$ , namely  $s_{c1}$  and  $s_{c2}$ . For an un-doped  $R\text{FeO}_3$  system, if  $s_{c1} \leq s_{c2}$ , a  $\Gamma_4$  to  $\Gamma_2$  SR transition will be seen, and if  $s_{c1} \geq s_{c2}$ , a  $\Gamma_4$  to  $\Gamma_1$  SR transition will occur (Yamaguchi, 1974). Indeed, if  $s$  never reaches  $s_{c1}$  or  $s_{c2}$  in the whole temperature range, no SR takes place, and this is the case for  $\text{LaFeO}_3$  and  $\text{YFeO}_3$ . With the appropriate concentration of  $\text{Mn}^{3+}$ , the influence of the  $\text{Mn}^{3+}$  sublattice will make  $s$  grow more rapidly as the temperature decreases and  $s$  will reach  $s_{c2}$  at high temperature where the spin structure transforms to the  $\Gamma_1$  configuration (Hornreich *et al.*, 1975).

The energy of an antiferromagnetic system in a magnetic field is lower when the antiferromagnetic vector is perpendicular to the direction of the field than when the two are parallel (Johnson *et al.*, 1980). A magnetic field applied along the antiferromagnetic axis of the  $\text{Fe}^{3+}$  system in the rare earth orthoferrites acts to cause reorientation of the  $\text{Fe}^{3+}$  antiferromagnetic vector to a perpendicular alignment. It is the competition between this Zeeman energy and the magnetic anisotropy energy of the  $\text{Fe}^{3+}$  system that determines the spin reorientation. In our case, since the antiferromagnetic vector of the  $\Gamma_1$  configuration is along the  $b$  axis, one would not expect a field-induced change in the SR temperature  $T_{\text{SR1}}$  when the external field is along the  $c$  or  $a$  axis. Accordingly, a field-modified spin reorientation is seen when the external field is along the  $c$  axis rather than the  $a$  axis, as the antiferromagnetic vector of the  $\Gamma_2$  configuration is along the  $c$  axis when the temperature is between  $T_{\text{SR1}}$  and  $T_{\text{SR2}}$ . Weak magnetism along the  $c$ -axis direction can be induced by applying an external field along the  $c$  axis. The  $\Gamma_4$  configuration has its antiferromagnetic vector along the  $a$  axis, and an external field along the  $a$  axis can induce another  $\Gamma_2$  spin configuration when the temperature is between  $T_{\text{SR2}}$  and  $T_N$ .

## 5. Conclusions

In summary, we have successfully synthesized a single crystal of  $\text{SmFe}_{0.75}\text{Mn}_{0.25}\text{O}_3$ , which has a single-phase perovskite structure, by the optical floating-zone method. The magnetic properties along different crystallographic axes have been studied in detail. Interesting double spin reorientation transitions  $\Gamma_4 \rightarrow \Gamma_2 \rightarrow \Gamma_1$  were observed above and below room temperature. Field-induced spin reorientation has been investigated along the  $c$  and  $a$  axes in detail, showing the linear dependence and independence of SR temperatures *versus* magnetic field. Delicate interactions between the magnetic sublattices of  $\text{Sm}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  make this unique compound highly sensitive to magnetic field and to temperature. Due to its intriguing magnetic characteristics, novel

magnetic switching devices could be designed based on this finding.

## Funding information

Funding for this research was provided by: National Key Basic Research Program of China (award Nos. 2015CB921600, 2016YFB0700201); National Natural Science Foundation of China (award Nos. 51672171, 11574194, 51372149, 11274222); Eastern Scholar Program from Shanghai Municipal Education Commission; Shanghai Materials Genome Institute from the Shanghai Municipal Science and Technology Commission (award No. 14DZ2261200).

## References

- Cao, Y., Xiang, M., Zhao, W., Wang, G., Feng, Z., Kang, B., Stroppa, A., Zhang, J., Ren, W. & Cao, S. (2016). *J. Appl. Phys.* **119**, 063904.
- Cao, S., Zhao, H., Kang, B., Zhang, J. & Ren, W. (2014). *Sci. Rep.* **4**, 5960.
- Cheng, J. G., Zhou, J. S., Goodenough, J. B., Su, Y. T., Sui, Y. & Ren, Y. (2011). *Phys. Rev. B*, **84**, 104431.
- Cui, X., Feng, Z., Jin, Y., Cao, Y., Deng, D., Chu, H., Cao, S., Dong, C. & Zhang, J. (2015). *J. Appl. Cryst.* **48**, 1581–1586.
- Dzyaloshinsky, I. (1958). *J. Phys. Chem. Solids*, **4**, 241–255.
- Fina, I., Fàbrega, L., Martí, X., Sánchez, F. & Fontcuberta, J. (2010). *Appl. Phys. Lett.* **97**, 232905.
- Fu, X., Liu, X. & Zhou, J. (2014). *Mater. Lett.* **132**, 190–192.
- Hemberger, J., Schrettle, F., Pimenov, A., Lunkenheimer, P., Ivanov, V. Y., Mukhin, A. A., Balbashov, A. M. & Loidl, A. (2007). *Phys. Rev. B*, **75**, 035118.
- Hong, F., Cheng, Z., Zhao, H., Kimura, H. & Wang, X. (2011). *Appl. Phys. Lett.* **99**, 092502.
- Hornreich, R. M., Komet, Y., Nolan, R., Wanklyn, B. M. & Yaeger, I. (1975). *Phys. Rev. B*, **12**, 5094–5104.
- Huang, R., Cao, S., Ren, W., Zhan, S., Kang, B. & Zhang, J. (2013). *Appl. Phys. Lett.* **103**, 162412.
- Jeong, Y. K., Lee, J.-H., Ahn, S.-J. & Jang, H. M. (2012). *Solid State Commun.* **152**, 1112–1115.
- Jin, Y., Cui, X. P., Cheng, J. A., Cao, S. X., Ren, W. & Zhang, J. C. (2015). *Appl. Phys. Lett.* **107**, 072907.
- Johnson, C. E., Prelorendjo, L. A. & Thomas, M. F. (1980). *J. Magn. Mater.* **15–18**, 557–558.
- Jong, J. A. de, Kimel, A. V., Pisarev, R. V., Kirilyuk, A. & Rasing, T. (2011). *Phys. Rev. B*, **84**, 104421.
- Jong, J. A. de, Razdolski, I., Kalashnikova, A. M., Pisarev, R. V., Balbashov, A. M., Kirilyuk, A., Rasing, T. & Kimel, A. V. (2012). *Phys. Rev. Lett.* **108**, 157601.
- Jung, J.-S., Iyama, A., Nakamura, H., Mizumaki, M., Kawamura, N., Wakabayashi, Y. & Kimura, T. (2010). *Phys. Rev. B*, **82**, 212403.
- Kenzelmann, M., Harris, A. B., Jonas, S., Broholm, C., Schefer, J., Kim, S. B., Zhang, C. L., Cheong, S. W., Vajk, O. P. & Lynn, J. W. (2005). *Phys. Rev. Lett.* **95**, 087206.
- Kimel, A. V., Ivanov, B. A., Pisarev, R. V., Usachev, P. A., Kirilyuk, A. & Rasing, T. (2009). *Nat. Phys.* **5**, 727–731.
- Kimura, T., Lawes, G., Goto, T., Tokura, Y. & Ramirez, A. P. (2005). *Phys. Rev. B*, **71**, 224425.
- Kuo, C. Y. et al. (2014). *Phys. Rev. Lett.* **113**, 217203.
- Lee, J. H., Jeong, Y. K., Park, J. H., Oak, M. A., Jang, H. M., Son, J. Y. & Scott, J. F. (2011). *Phys. Rev. Lett.* **107**, 117201.
- Mandal, P., Bhadram, V. S., Sundarayya, Y., Narayana, C., Sundaresan, A. & Rao, C. N. R. (2011). *Phys. Rev. Lett.* **107**, 137202.
- Mandal, P., Serrao, C. R., Suard, E., Caignaert, V., Raveau, B., Sundaresan, A. & Rao, C. N. R. (2013). *J. Solid State Chem.* **197**, 408–413.
- Moriya, T. (1960). *Phys. Rev.* **120**, 91–98.
- Mostovoy, M. (2006). *Phys. Rev. Lett.* **96**, 067601.
- Nair, H. S., Chatterji, T., Kumar, C. M. N., Hansen, T., Nhalil, H., Elizabeth, S. & Strydom, A. M. (2016). *J. Appl. Phys.* **119**, 053901.
- Nakajima, T., Tokunaga, Y., Taguchi, Y., Tokura, Y. & Arima, T. H. (2015). *Phys. Rev. Lett.* **115**, 197205.
- Okuyama, D., Ishiwata, S., Takahashi, Y., Yamauchi, K., Picozzi, S., Sugimoto, K., Sakai, H., Takata, M., Shimano, R., Taguchi, Y., Arima, T. & Tokura, Y. (2011). *Phys. Rev. B*, **84**, 054440.
- Rodríguez-Carvajal, J. (2001). *IUCr Commission Powder Diffraction News*, **26**, 12–19.
- Wang, G., Zhao, W., Cao, Y., Kang, B., Zhang, J., Ren, W. & Cao, S. (2016). *J. Alloys Compd.* **674**, 300–304.
- White, R. L. (1969). *J. Appl. Phys.* **40**, 1061–1069.
- Wu, H., Cao, S., Liu, M., Cao, Y., Kang, B., Zhang, J. & Ren, W. (2014). *Phys. Rev. B*, **90**, 144415.
- Yamaguchi, T. (1974). *J. Phys. Chem. Solids*, **35**, 479–500.
- Yuan, S. J., Ren, W., Hong, F., Wang, Y. B., Zhang, J. C., Bellaiche, L., Cao, S. X. & Cao, G. (2013). *Phys. Rev. B*, **87**, 180405.
- Zhao, W., Cao, S., Huang, R., Cao, Y., Xu, K., Kang, B., Zhang, J. & Ren, W. (2015). *Phys. Rev. B*, **91**, 104425.
- Zvezdin, A. K. & Mukhin, A. A. (2009). *JETP Lett.* **88**, 505–510.