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## Structure and magnetoresistance of the double perovskite $\text{Sr}_2\text{FeMoO}_6$ doped at the Fe site

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### Abstract

The structural, magnetic and transport properties of the compounds  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  ( $0 \leq x \leq 0.45$ ) have been studied. The saturated magnetization, Curie temperature and low-field magnetoresistance of the compounds decrease with  $x$ , while the resistivity increases by several orders of magnitude when  $x$  exceeds a critical value. A positive magnetoresistance has been observed for  $x = 0.45$ . A possible percolation mechanism is proposed to elucidate the observations; it also suggests a coexistence of  $(\text{Mn}^{3+}, \text{Mo}^{5+})$  and  $(\text{Mn}^{2+}, \text{Mo}^{6+})$  valence pairs and a saturated substitution of  $\text{Mn}^{3+}$  for  $\text{Fe}^{3+}$ .

### 1. Introduction

$\text{Sr}_2\text{FeMoO}_6$  is known as a double perovskite of ferrimagnetic metal character ( $T_C = 400\text{--}450$  K) [1–5]. Renewed interest in double-perovskite compounds has arisen owing to the recent discovery of a tunnelling magnetoresistance (TMR) at room temperature in polycrystalline  $\text{Sr}_2\text{FeMoO}_6$  and  $\text{Sr}_2\text{FeReO}_6$  [1, 2], which is intriguing from both the fundamental and applied viewpoints. It was elucidated that the valence states are  $\text{Sr}_2\text{Fe}^{3+}\text{Mo}^{5+}\text{O}_6$  [3, 6], in which  $\text{Fe}^{3+}$  and  $\text{Mo}^{5+}$  alternately occupy the B sites in a simple perovskite  $\text{ABO}_3$ . Because of high spin polarization of conduction electrons inherent to this compound, electronic transport across the tunnelling junction depends on the relative angle between the magnetic moments on either side of ferrimagnetic domains, which is controlled by a low external field [2].

$\text{Sr}_2\text{MnMoO}_6$  also crystallizes in the double-perovskite structure and was reported to be an antiferromagnetic (AFM) semiconductor with a valence pair of  $(\text{Mn}^{2+}, \text{Mo}^{6+})$  [3]. However, for Fe-site-substituted  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  and  $\text{Ba}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$ , the valence state of Mn was treated as +3 [4, 7]. In addition, for doped  $\text{Ba}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  [7] and

$\text{Sr}_2\text{Fe}(\text{W}_{1-x}\text{Mo}_x)\text{O}_6$  [8, 9], the magnetic and transport properties were explained by invoking a percolation mechanism. While Kobayashi *et al* [8] suggested persistent existence of ( $\text{Fe}^{2+}$ ,  $\text{W}^{6+}$ ) pairs in  $\text{Sr}_2\text{Fe}(\text{W}_{1-x}\text{Mo}_x)\text{O}_6$ , Ray *et al* [9] argued for a transformation of ( $\text{Fe}^{2+}$ ,  $\text{W}^{6+}$ ) pairs to ( $\text{Fe}^{3+}$ ,  $\text{W}^{5+}$ ) pairs beyond the percolation threshold. A similar phenomenon is expected in other Fe-site-doped double perovskites. In this contribution, we investigate the structure, magnetic and transport properties of  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$ . We show that the saturated magnetization  $M_S$  and Curie temperature  $T_C$  are significantly influenced by the substitution of Mn for Fe and TMR was observed at both low temperature and room temperature. A positive magnetoresistance (PMR) has been observed in  $\text{Sr}_2(\text{Fe}_{0.55}\text{Mn}_{0.45})\text{MoO}_6$  at room temperature, which is less often reported for double perovskites. Our results suggest a coexistence of ( $\text{Mn}^{3+}$ ,  $\text{Mo}^{5+}$ ) and ( $\text{Mn}^{2+}$ ,  $\text{Mo}^{6+}$ ) pairs and the percolation mechanism.

## 2. Experiment

Polycrystalline  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  were prepared by solid-state reaction at high temperature. Stoichiometric amounts of  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MoO}_3$  and  $\text{MnO}$  were mixed and calcined at  $900^\circ\text{C}$  for 10 h in air. The calcined mixture was then finely pulverized and pressed into pellets; this was followed by sintering at  $1280^\circ\text{C}$  for 3 h in a stream of 5%  $\text{H}_2/\text{Ar}$ .

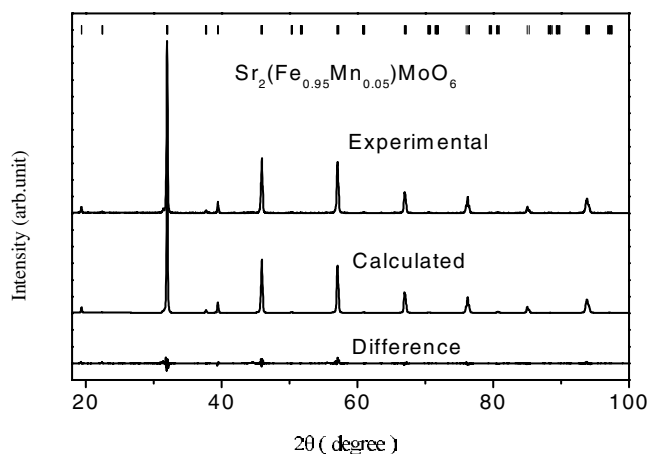
X-ray powder diffraction (XRD) data used for structure refinement were collected on a Rigaku D/max 2500 diffractometer with  $\text{Cu K}\alpha$  radiation ( $50\text{ kV} \times 250\text{ mA}$ ) and a graphite monochromator. A step scan mode was employed with a step width of  $2\theta = 0.02^\circ$  and a sampling time of 1 s. The XRD patterns showed that all the compounds ( $0 \leq x \leq 0.45$ ) are single phase without detectable secondary phase or impurity. The XRD data were analysed by the Rietveld refinement program DBW-9411 [10, 11].

The field dependence of the magnetization was measured at 4.2 K by a superconducting quantum interference device (SQUID) magnetometer. Temperature dependence of magnetization curves were measured by a vibrating-sample magnetometer (VSM) in a field of 0.09 T. The Curie temperature was determined from the inflection point of the  $M-T$  curve. Transport properties were determined by the standard four-probe method using OXFORD MaglabExa measurement system.

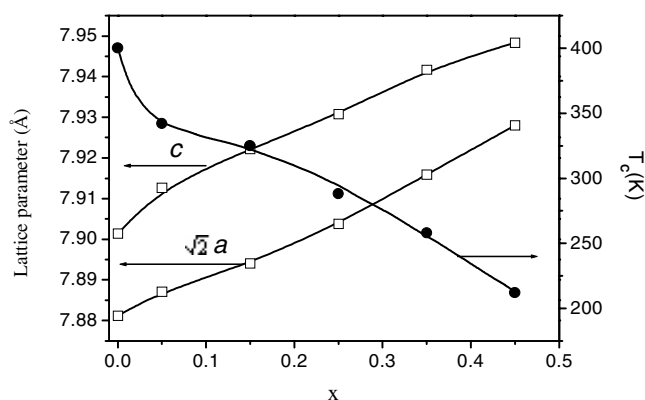
## 3. Results and discussion

A representative XRD pattern of  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  ( $0 \leq x \leq 0.45$ ) is shown in figure 1 for  $x = 0.05$ ; this could be indexed with a tetragonal  $I4/mmm$  lattice. The structure was refined by the Rietveld technique for all the doped samples. The calculated profile gives a good fit to the observed one as shown in figure 1. We did not attempt to distinguish Fe and Mn ions because of the tiny difference between their x-ray atomic scattering factors. Lattice parameters are displayed in figure 2. The lattice parameters  $a$  and  $c$  increase monotonically with increasing  $x$ , which may indicate the appearance of divalent Mn in the compounds (ion radius:  $\text{Mn}^{2+}$ :  $0.72\text{ \AA}$ ;  $\text{Mn}^{3+}$ :  $0.645\text{ \AA}$ ;  $\text{Fe}^{3+}$ :  $0.645\text{ \AA}$ , for CN = 6).

Figure 3 presents the composition dependence of the XRD patterns of the  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$ . The diffractive peak (101) at around  $2\theta = 19.5^\circ$  indicates cationic ordering on the B site, the relative intensity of which varies with the compound. Figure 4 shows that the degree of B-site ordering derived from the Rietveld refinement underwent a sharp drop when a minimal amount of Mn was doped in and then increased gradually with increasing  $x$  until an almost saturated value of 0.97 was reached; the diffractive intensity ratio,  $I(101)/\{I(200) + I(112)\}$ , derived from figure 3, which measures the degree of ordering,



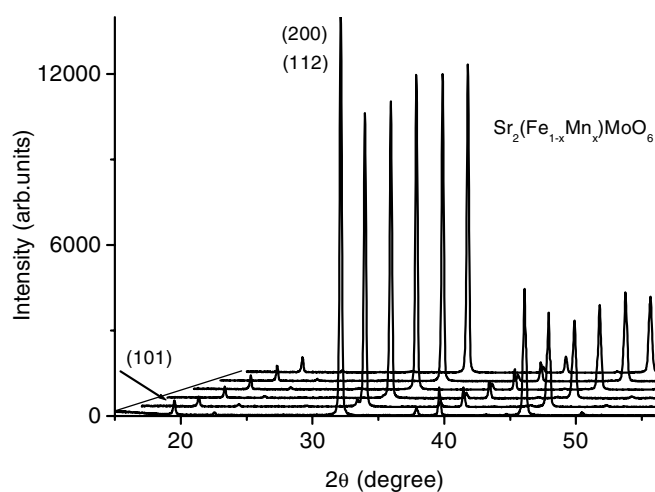
**Figure 1.** The observed and calculated XRD patterns at 300 K for  $\text{Sr}_2(\text{Fe}_{0.95}\text{Mn}_{0.05})\text{MoO}_6$ . The vertical bars at the top indicate Bragg reflection positions and the lowest curve is the difference between observed and calculated patterns.



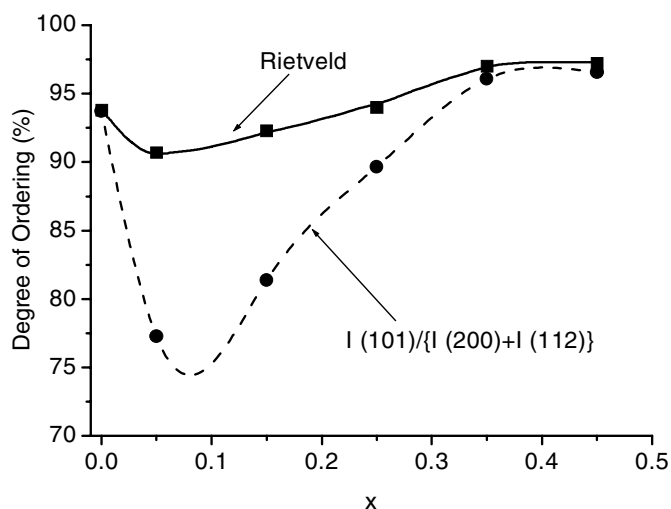
**Figure 2.** Dependences of the lattice parameters and Curie temperature on the doping level. Arrows are guides to the eyes.

exhibits a similar trend. This implies that the substitution of Mn is beneficial as regards reducing the disorder of the B site. The substitution of W for Mo in  $\text{Sr}_2\text{Fe}(\text{W}_{1-x}\text{Mo}_x)$  also enhanced the ordering of the B site [8]. The degree of the B-site ordering is 0.94 in  $\text{Sr}_2\text{FeMoO}_6$ , which is larger than the value of 0.87 reported in [1] because of the higher sintering temperature.

The magnetization curves at 4.2 K show that the magnetic moment of  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  decreases as  $x$  increases, from  $3.6 \mu_B/\text{fu}$  for  $x = 0$  to  $2.5 \mu_B/\text{fu}$  for  $x = 0.45$  (figure 5). The magnetization decreases drastically for  $x \leq 0.05$ , then decreases gradually until  $x = 0.35$ ; this is followed by another noticeable drop for  $x > 0.35$ . Figure 6 shows the composition dependence of the saturated magnetization  $M_S$  at 4.2 K. The reduced magnetization can be attributed to mis-site (Fe–Mo) imperfection [12, 13] or magnetic dilution due to the substitution of Mn for Fe. Based on the false-site imperfection model (the FIM, as in [12]) and the degree of ordering derived from the Rietveld refinement results,  $M_S$  is evaluated as  $3.5 \mu_B/\text{fu}$  for  $x = 0$ , which agrees well with the experimental value. For the doped  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$ , three models might be plausible:



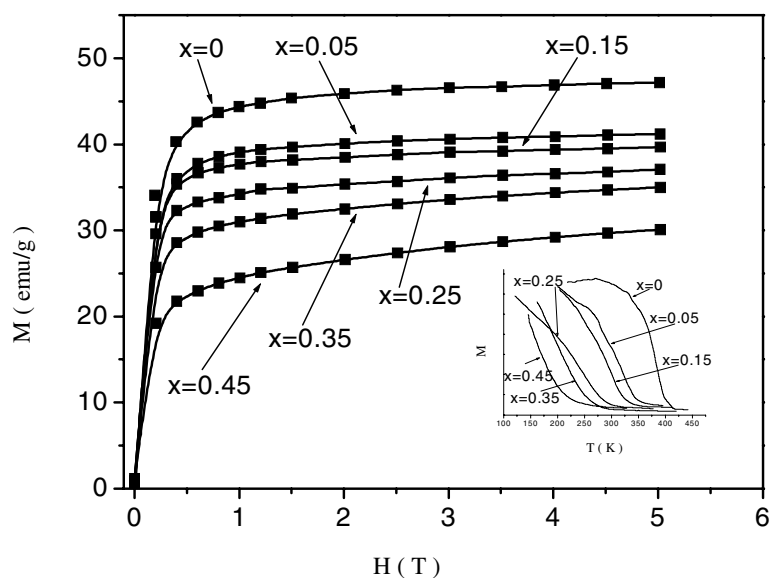
**Figure 3.** The detailed XRD patterns at room temperature for  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  samples. From bottom to top,  $x = 0, 0.05, 0.15, 0.25, 0.35$  and  $0.45$ . The arrow indicates the (101) superstructure peak. The strongest peak corresponds to the (200) and (112) diffractions.



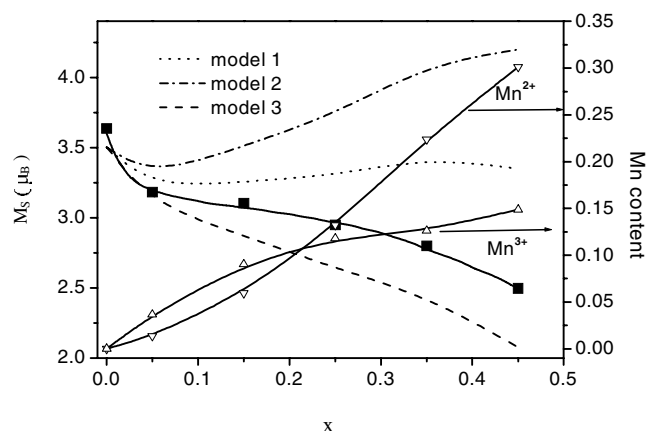
**Figure 4.** The degree of ordering between (Fe, Mn) and Mo in  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$ . Arrows are guides to the eyes.

- (I) the FIM with all Mn in +3 valence states;
- (II) the FIM with all Mn in +2 valence states and accordingly a fraction  $x$  of Mo in +6 valence states; and
- (III) an extreme phase separation model, i.e. a coexistence of content  $(1 - x)$  of ferromagnetic (FM)  $\text{Sr}_2\text{FeMoO}_6$  and content  $x$  AFM  $\text{Sr}_2\text{MnMoO}_6$ .

The  $M_S$ -values evaluated from the three models using the degree of ordering derived are shown in figure 6. None of the models reproduces the observed values, especially for higher Mn content. Nevertheless, model III seems to predict the trend of variation of  $M_S$  with the Mn content, though the values are underestimated.

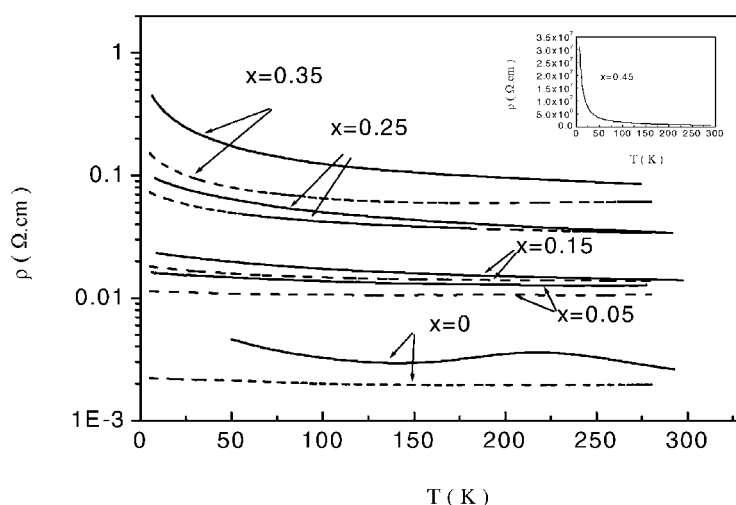


**Figure 5.** Magnetization curves for  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  at 4.2 K. Inset: the temperature dependence of the magnetization in a field of 0.09 T.

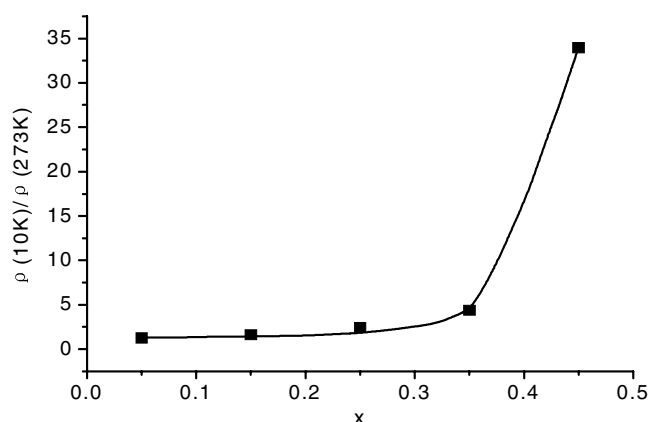


**Figure 6.** The dependence of the saturation magnetization on the doping level. Filled squares show experimental values. The predictions are represented by dotted (model I), dashed-dotted (model II) and dashed (model III) curves. The estimated contents of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions are shown as downward-pointing and upward-pointing triangles. The solid curves are guides to the eyes.

We propose a phase separation model as follows: content  $(x - x')$  of Mn in FM  $\text{Sr}_2(\text{Fe}^{3+}, \text{Mn}^{3+})\text{Mo}^{5+}\text{O}_6$  and content  $x'$  of Mn in AFM  $\text{Sr}_2\text{Mn}^{2+}\text{Mo}^{6+}\text{O}_6$ . The FM domains and the AFM domains are assumed to distribute randomly in the bulk of the compounds. Taking into account that Mn substitution for Fe stabilizes the ordered structure, it is reasonable to assume that the false-site imperfection occurs exclusively in the FM domains. From the Rietveld refinement result and the measured  $M_S$ , the  $\text{Mn}^{2+}$  content  $x'$  and  $\text{Mn}^{3+}$  content  $(x - x')$  can be derived; these are shown in figure 6. The results appear quite intriguing. The  $\text{Mn}^{2+}$  content  $x'$ , or



**Figure 7.** Resistivity under zero field (solid curve) and 3 T (dashed curve) as a function of temperature. Inset: the temperature dependence of the resistivity at zero field for  $\text{Sr}_2(\text{Fe}_{0.55}\text{Mn}_{0.45})\text{MoO}_6$ .

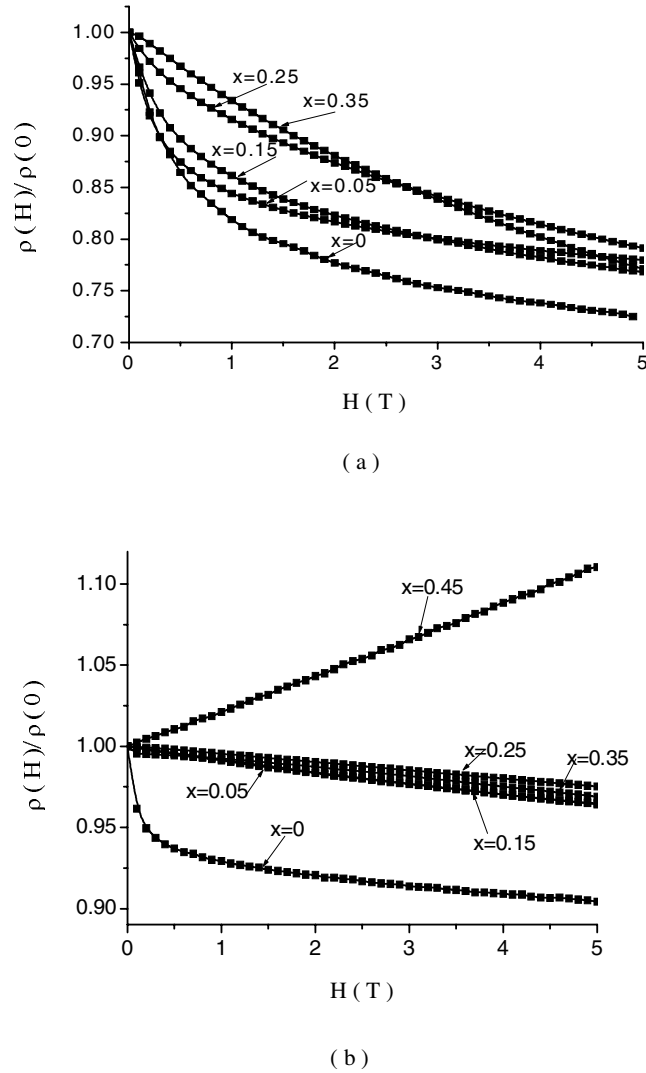


**Figure 8.** Resistivity ratio  $\rho(10\text{ K})/\rho(273\text{ K})$  under zero field versus the doping level in  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$ .

the fraction of the AFM domains, increases slowly at low doping level  $x$  and rapidly at high doping level as  $x$  increases. In contrast, the  $\text{Mn}^{3+}$  content increases strongly at low doping level and gradually at high doping level. The  $\text{Mn}^{3+}$  content seems to approach a saturated value as the doping content increases. This implies that the substitution of  $\text{Mn}^{3+}$  for  $\text{Fe}^{3+}$  in  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  may have a saturated value.

The temperature dependence of the magnetization of the compounds is shown in the inset of figure 5. The derived Curie temperature  $T_C$  is depicted in figure 2. The composition dependence of  $T_C$  mimics that of  $M_S$  shown in figure 6. The Curie temperature  $T_C$  decreases significantly as the doping content increases, from 400 K for  $x = 0$  to 212 K for  $x = 0.45$ .

The  $\rho(T)$  curves registered under zero field and 3 T reveal that all the doped compounds  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  exhibit semiconducting behaviour between 4.2 and 285 K (figure 7), except for the parent compound  $\text{Sr}_2\text{FeMoO}_6$ . Unlike the reported metallic behaviour of



**Figure 9.**  $\rho(H)/\rho(0)$  as a function of the applied field at (a) 5 K and (b) 285 K.

$\text{Sr}_2\text{FeMoO}_6$  below  $T_C$ , our sample exhibits a semiconducting behaviour below 150 K and a resistivity bulking around 225 K under zero field. The resistivity bulking below  $T_C$  is frequently observed in colossal-magnetoresistive perovskite manganites and could result from a contribution of non-conductive domain or grain boundary scattering [14]. The data shown in figure 7 may indicate that the contribution of boundary scattering is significant in our samples. The resistivity increases by several orders of magnitude with the increase of the Mn content. At  $T = 285$  K, the resistivities are  $2.85 \times 10^{-3}$  and  $1.15 \times 10^{-2} \Omega \text{ cm}$  for  $x = 0$  and 0.05 respectively, whereas the resistivity is  $6.02 \times 10^5 \Omega \text{ cm}$  for  $x = 0.45$ . Figure 8 shows the composition dependence of the resistivity ratio  $\rho(10 \text{ K})/\rho(273 \text{ K})$ . The ratio exhibits an abrupt increase around  $x_c \approx 0.35$ . This feature was also observed in  $\text{Ba}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  ( $x_c \approx 0.4$ ) [7] and  $\text{Sr}_2\text{Fe}(\text{Mo}_{1-x}\text{W}_x)\text{O}_6$  ( $x_c \approx 0.75$ ) [8] and was attributed to a percolation mechanism for the electronic transport. The discrepancy between



the observed  $x_c$  and the percolation concentration  $p_c (=1 - x_c)$  for a FCC lattice ( $p_c = 0.195$ ) might be due to an underestimation of the non-conductive fraction caused by neglecting the contribution of grain or domain boundary scattering. Therefore, the deviation of  $x_c$  from the theoretical threshold 0.805 is indicative of lack of sample quality. It is intriguing to note that the  $\text{Mn}^{2+}$  concentration, i.e. the fraction of AFM domains, of 0.195 corresponds to a doping level of about 0.35 (figure 6), at which both  $M_S$  and  $T_C$  start to decrease rapidly.

As reported for other double-perovskite oxides, MR is observed in  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$ . We define  $\text{MR} = \{\rho(H) - \rho(0)\}/\rho(0)$ , where  $\rho(H)$  is the resistivity in a magnetic field  $H$ . From figure 9, we conclude that the MR is significantly higher at 5 K than at 285 K. While the parent compound  $\text{Sr}_2\text{FeMoO}_6$  shows large low-field magnetoresistance (LFMR) at both 5 and 285 K, the doped compounds exhibit decreasing LFMR at 5 K with increasing  $x$  and no appreciable LFMR at 285 K, though  $T_C$  is higher than 285 K for most of them. It seems that Mn substitution for Fe in  $\text{Sr}_2\text{FeMoO}_6$  degrades the intergranular TMR, which is contrary to the report for Fe-site-doped  $\text{Ba}_2\text{FeMoO}_6$  [7] in which the intergranular TMR at low temperature was not degraded by the substitution and in several cases (such as that of zinc substitution) the TMR was even dramatically enhanced. In addition, a PMR of about 12% has been observed at 285 K in  $\text{Sr}_2(\text{Fe}_{0.55}\text{Mn}_{0.45})\text{MoO}_6$  under a field of 5 T. There are extensive reports on large negative MR in half-metallic FM oxides such as perovskite manganites, but PMR is less often reported for these oxides. Nevertheless, a large PMR has been observed in several layered structures and epitaxial  $\text{Sr}_2\text{FeMoO}_{6-y}$  thin films [15]. A PMR cannot be anticipated within the double-exchange scenario and the presence of AFM interaction is one of the important aspects for the PMR [15]. On the basis of the proposed inhomogeneous model in this work, figure 8 reveals that when the doping level is greater than 0.35, the isolated AFM  $\text{Sr}_2\text{MnMoO}_6$  domains can be expected to coalesce and form infinitely extended channels. The existence of well developed and extended AFM  $\text{Sr}_2\text{MnMoO}_6$  domains may be responsible for the observed PMR at 285 K in  $\text{Sr}_2(\text{Fe}_{0.55}\text{Mn}_{0.45})\text{MoO}_6$ .

#### 4. Conclusions

In summary, the crystal structure, magnetization and magnetoresistance of the compounds  $\text{Sr}_2(\text{Fe}_{1-x}\text{Mn}_x)\text{MoO}_6$  ( $0 \leq x \leq 0.45$ ) are investigated. The substitution of Mn for Fe in  $\text{Sr}_2\text{FeMoO}_6$  does not alter the crystal structure, but dramatically reduces the Curie temperature, saturated magnetization and magnetoresistance of the compounds. A percolation behaviour is revealed in the composition dependence of the resistivity and a PMR is observed in  $\text{Sr}_2(\text{Fe}_{0.55}\text{Mn}_{0.45})\text{MoO}_6$ . An inhomogeneous model is proposed to elucidate the observations; it suggests coexistence of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions in the doped compounds and a saturated substitution of  $\text{Mn}^{3+}$  for  $\text{Fe}^{3+}$ .

#### Acknowledgment

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