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Atomic ordering and magnetic properties of non-stoichiometric double-perovskite $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$

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Abstract

The crystal structure and magnetic properties of a new series of ordered double-perovskite oxides $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($0.8 \leq x \leq 1.5$) have been studied. The crystal structure changes from a tetragonal $I4/mmm$ lattice to a cubic $Fm\bar{3}m$ lattice around $x = 1.2$. The degree of ordering in $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ exhibits a maximal at $x = 0.95$ and decreases as x deviates from 0.95. The saturated magnetization increases from $x = 0.8$ to 0.95 and then decreases from $x = 0.95$ to 1.5. The Curie temperature exhibits an abrupt drop around $x = 1.2$, where the structural transition takes place. These complex behaviours are strongly correlated to antisite defect concentration in the compounds.

Although we have known for a long time about double-perovskite oxides of the type $\text{A}_2\text{BB}'\text{O}_6$, where A is an alkaline earth ($A = \text{Sr}, \text{Ca}, \text{Ba}$) and B, B' are heterovalent transition metals (such as $B = \text{Fe}, \text{Cr}, \text{Mn}, \dots$ and $B' = \text{Mo}, \text{W}, \text{Re}, \dots$) [1–3], the recent discovery of metallic ferrimagnetism with an appreciable low-field room temperature magnetoresistance and a relatively high Curie temperature (about 410–450 K), which are of significance for spintronic device applications [4], in $\text{Sr}_2\text{FeMoO}_6$ by Kobayashi *et al* [5] has stimulated both fundamental and applied research on these oxides. It was elucidated that the valence states are $\text{Sr}_2\text{Fe}^{3+}\text{Mo}^{5+}\text{O}_6$ [3, 6], in which Fe^{3+} and Mo^{5+} alternatively occupy the B, B' sites in a double-perovskite $\text{A}_2\text{BB}'\text{O}_6$. The magnetic structure of $\text{Sr}_2\text{FeMoO}_6$ is attributed to an ordered arrangement of parallel Fe^{3+} ($3d^5$, $S = 5/2$) magnetic moments antiferromagnetically coupling with Mo^{5+} ($4d^1$, $S = 1/2$) spins. Because of the high-spin state of Fe^{3+} , its d orbitals are split into spin-up and spin-down states. The empty spin-down states ($\pi^*-\beta$) of Fe^{3+} degenerate to the one-electron-occupied spin-down states ($\pi^*-\beta$) of Mo^{5+} , which may lead to the formation of a narrow band. The electrons in this band have their spins antiparallel to the localized spins

in the spin-up states ($\sigma^*-\alpha$ and $\pi^*-\alpha$) of Fe^{3+} [6]. A ferrimagnetic half-metallic nature was confirmed in this ordered perovskite with localized up-spins of Fe^{3+} and itinerant down-spin electron of Mo^{5+} [7]. Thus a saturation magnetization of $M_S = 4 \mu_B$ is predicted. Accordingly, it is expected that M_S should be sensitively dependent on the ordering of Fe/Mo ions among the B/B' sublattices. Indeed, the M_S values of bulk materials reported so far are systematically much smaller ($3.1 \mu_B$ [4], $3.2 \mu_B$ [7] and $3.5 \mu_B$ [8]) than the predicted $4 \mu_B$. It is commonly accepted that this significant decrease is due to antisite defects resulting from partial disorder of Fe and Mo ions among the B/B' sublattices [9–11].

Monte Carlo simulation indicated that the decrease of the saturation magnetization M_S and the Curie temperature T_C was nearly linear with the increase of the antisite defect concentration for the case of randomly created defects in the double-perovskite $\text{Sr}_2\text{FeMoO}_6$ [12], which is consistent with experimental observations [9, 13, 14].

Recently, many studies have been done on Mo or Fe site doping [14–17], but not on altering the ratio of Fe to Mo. For the $\text{Sr}_2\text{Fe}(\text{W}_{1-x}\text{Mo}_x)\text{O}_6$ system, Kobayashi *et al* [14] and Sugata *et al* [15] reported that the degree of B/B' ordering increases with increasing content of W. In these studies the valence of dopant is assumed to be the same as that of the substituted ions. Nevertheless, experimental observation that the saturated magnetization of $\text{Sr}_2\text{FeMoO}_6$ is usually smaller than the expected value of $4 \mu_B$ indicates that mutual substitution between Fe and Mo can take place. Therefore, it would be interesting to investigate the stability, ionic ordering and magnetic properties of the non-stoichiometric compounds $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$, which will be addressed in this paper.

Polycrystalline samples of $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ with $0.8 \leq x \leq 1.5$ were prepared by solid-state reaction at high temperature. Stoichiometric amounts of SrCO_3 , Fe_2O_3 and MoO_3 were mixed and calcined at 900°C for 10 h in air. The resulting mixture was then pressed into pellets and sintered, with intermediate grindings, at 1280°C for 12 h in a stream of 5% H_2/Ar .

X-ray powder diffraction (XRD) data used for structure refinement was collected at room temperature 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 pattern showed that the compounds with $x \geq 0.9$ were single phase without detectable secondary phase or impurity. When $x < 0.9$, trace amounts of insulating SrMoO_4 (up to 5% for $x = 0.8$) were observed in the XRD patterns. The programme FullProf [18, 19] was used for the Rietveld refinement in order to obtain information on the crystal structure of $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($0.8 \leq x \leq 1.5$).

The field dependence of magnetization was measured at 4.2 K by a superconducting quantum interference device (SQUID) magnetometer. Curves showing the temperature dependence of magnetization were measured by a vibrating sample magnetometer (VSM) in a field of 0.09 T. The Curie temperature was determined from the inflection point on the $M-T$ curve.

The result of Rietveld analysis indicates an occurrence of structural phase transition from a tetragonal $I4/mmm$ ($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$) lattice to a cubic $Fm\bar{3}m$ ($2a_p \times 2a_p \times 2a_p$) lattice around $x = 1.2$ (where a_p is the unit cell of a primitive perovskite). Lattice parameters and unit-cell volume versus x in $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($0.8 \leq x \leq 1.5$) are displayed in figure 1(a). The structural transition is more evident in the splitting of the reflections, i.e. one reflection (620) C splits into three reflections of (116) T, (332) T and (420) T, as shown in figure 1(b) (see also the insets in figure 2, where the doublet of (620) C results from the contribution of the doublet of $\text{K}\alpha$ radiation). As examples, two sets of XRD data on $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($0.8 \leq x \leq 1.5$), including observed and calculated patterns, differences and the expected peak positions, are shown in figure 2 for $x = 1.05$ with the tetragonal $I4/mmm$ lattice and $x = 1.5$ with the cubic lattice. The calculated profiles give good fits to the observed ones.

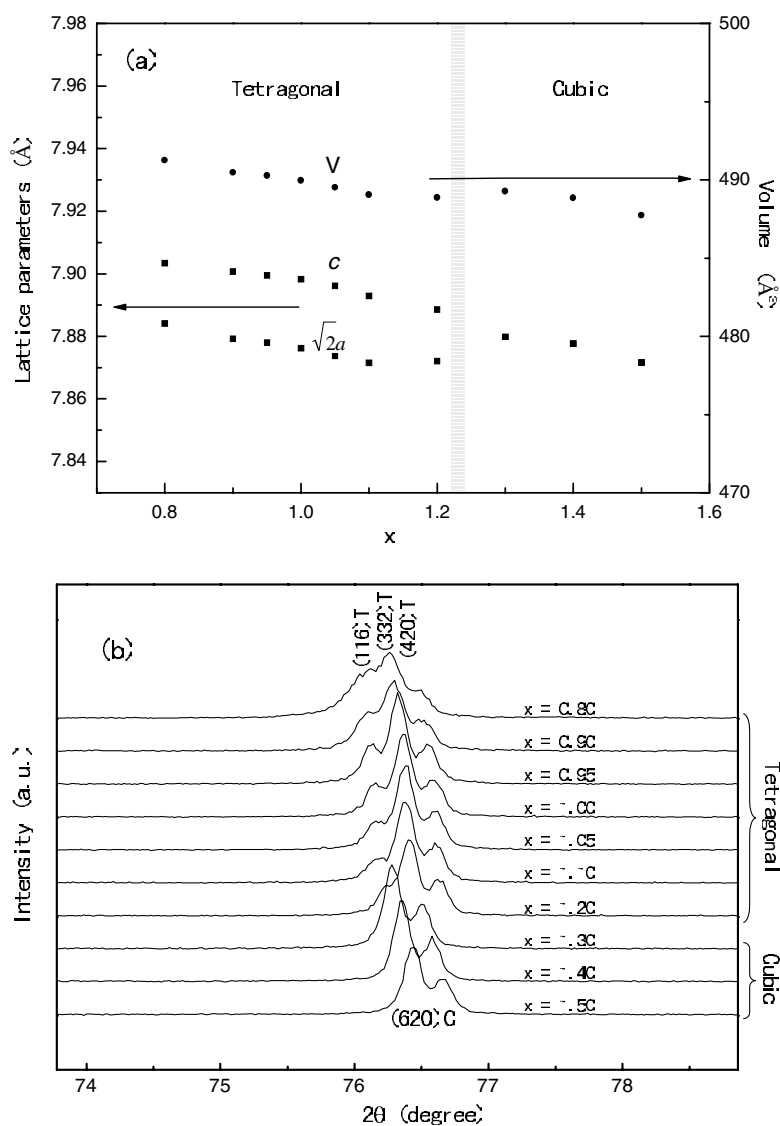


Figure 1. Structural phase transition from the tetragonal $I4/mmm$ ($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$) lattice in a $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ system to the cubic $Fm\bar{3}m$ ($2a_p \times 2a_p \times 2a_p$) lattice, where a_p is the unit cell of the primitive perovskite. (a) Lattice parameters and unit-cell volume versus x . (b) Peak splittings (one peak of (620) C splits into three peaks of (116) T, (332) T and (420) T). The phase boundary is a tentative one.

In figure 3 the diffracted intensity ratio measuring the degree of the B/B'-site ordering, $I(101)/\{I(200) + I(112)\}$ for the tetragonal lattice or $I(111)/I(220)$ for the cubic lattice, is depicted as a function of x in $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ system with ($0.8 \leq x \leq 1.5$). The reflection (101) or (111) is a superstructure reflection which reflects the ordering of Fe/Mo ions at B/B' sites [9]. It is clearly indicated that the degree of the B/B'-site ordering is maximal around $x = 0.95$ (approach to $\text{Sr}_2\text{FeMo}_2\text{O}_6$) and then decreases gradually as x deviates from 0.95. It implies that a departure of x from 0.95 in a $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ system tends to increase the disorder of the B/B' site.

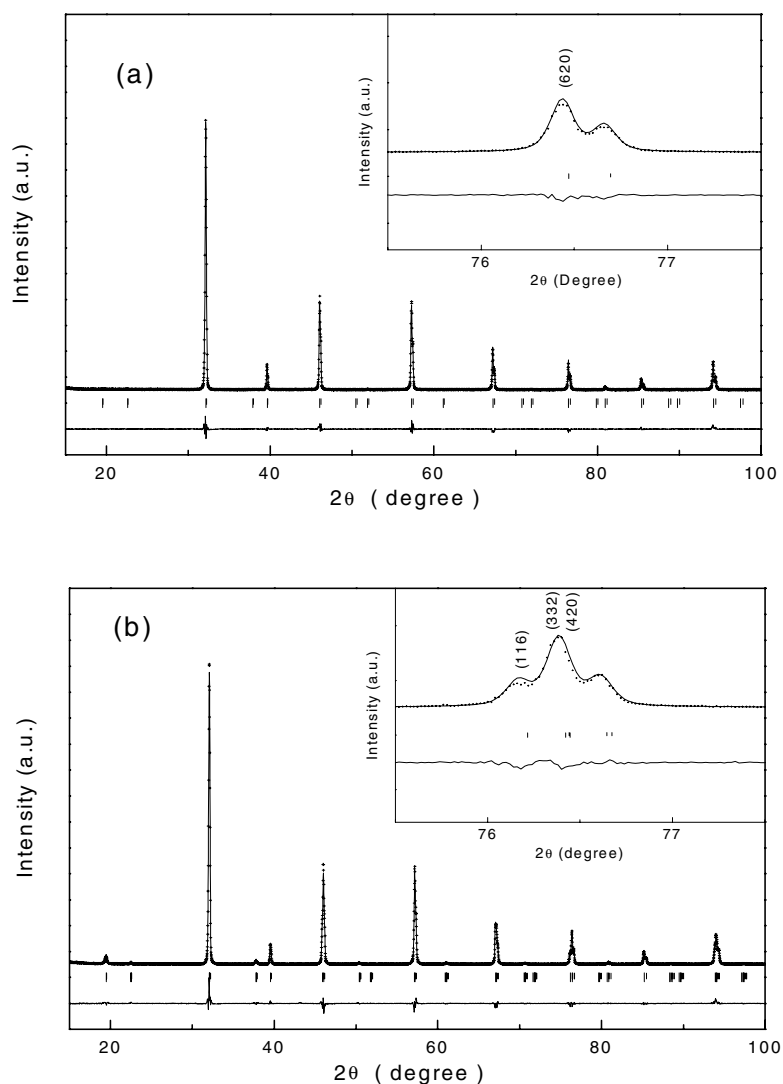


Figure 2. Observed (crosses) and calculated (full curve) XRD profiles of $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ for (a) $x = 1.5$ and (b) $x = 1.05$. The difference between the observed and calculated data is plotted at the bottom of each pattern. The small vertical bars mark the positions of expected reflections (the longer and shorter bars correspond to $\text{K}\alpha 1$ and $\text{K}\alpha 2$ radiation, respectively).

Based on the detailed quantitative Rietveld analysis of the XRD patterns, the degree of ordering η in non-stoichiometric double-perovskite $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ can be determined by $\eta = \text{Occ}_{\text{Fe}}^{\text{B}} - \text{Occ}_{\text{Fe}}^{\text{B}'}$ ($\text{Occ}_{\text{Fe}}^{\text{B}}$ or $\text{Occ}_{\text{Fe}}^{\text{B}'}$ is the occupancy of Fe ions in B/B' sites). Also in figure 3 we show the obtained η as a function of x . The same trend has been observed as the ratio $I(101)/\{I(200) + I(112)\}$ for the tetragonal lattice or the ratio $I(111)/I(220)$ for the cubic lattice. The maximal degree of ordering η_{max} ($x \geq 1.0$: $\eta_{\text{max}} = 2 - x$; $x < 1.0$: $\eta_{\text{max}} = x$) has been shown as a function of x by the chain line in figure 3. It is intriguing that $\eta_{\text{max}} - \eta \approx 0.18$ for $1.0 \leq x \leq 1.2$ and $\eta_{\text{max}} - \eta \approx 0.075$ for $0.8 \leq x \leq 0.95$ (shown as a shaded area in figure 3). It is worth noting that $(\eta_{\text{max}} - \eta)/2$ can be regarded as the actual

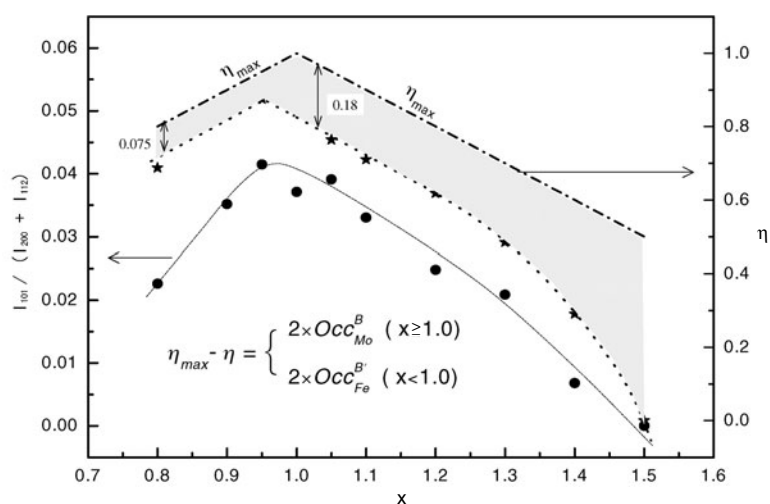


Figure 3. Relative intensity ratio $I_{101}/(I_{200} + I_{112})$ for the tetragonal lattice or I_{111}/I_{220} for the cubic lattice (left axis) and degree of ordering η (right axis) as a function of x in a non-stoichiometric double-perovskite $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ system. The chain curve indicates the expected maximal degree of ordering (see text). The dotted and broken curves are guides for the eyes.

antisite defect concentration $\text{Occ}_{\text{Fe}}^{\text{B}'}$ ($x \leq 1.0$) or $\text{Occ}_{\text{Mo}}^{\text{B}}$ ($x \geq 1.0$) in non-stoichiometric double-perovskite $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$, i.e. if complete ordering occurred, $\text{Occ}_{\text{Fe}}^{\text{B}'} = 0$ for $x \leq 1.0$ and $\text{Occ}_{\text{Mo}}^{\text{B}} = 0$ for $x \geq 1.0$. This observation seems to indicate that an almost constant antisite defect concentration is necessary under our synthesis conditions to stabilize the tetragonal double-perovskite $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$. In addition, the required antisite defect concentration is about three times larger in Fe-rich compounds than that in Mo-rich compounds. The occurrence of the structural phase transition from the tetragonal lattice to the cubic lattice is evidenced by the rapid decrease of η when $x > 1.2$.

The temperature dependence of magnetization is shown in figure 4(a). The Curie temperature (T_C) of each sample was determined from the inflection point on the $M-T$ curve. In figure 4(b) we show the composition (x) dependence of the derived Curie temperature. T_C increases with the concentration x for $0.8 \leq x \leq 1.1$ and $1.3 \leq x \leq 1.5$. In agreement with the result of the structural analysis, T_C exhibits a sharp drop around $x = 1.2$, indicating a structural phase transition from the tetragonal $I4/mmm$ lattice to the cubic $Fm\bar{3}m$ lattice.

The magnetization curves at 4.2 K show that the magnetic moment of $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ decreases when the component x is different from 0.95, from $3.5 \mu_B/\text{fu}$ for $x = 0.95$ – $2.7 \mu_B/\text{fu}$ for $x = 0.80$ and to $0.5 \mu_B/\text{fu}$ for $x = 1.50$ (see figure 5), which has the same trend as the degree of the B/B'-site ordering discussed above. The composition dependence of the saturated magnetization M_S at 4.2 K is depicted by full squares in figure 6. The reduced magnetization can be attributed to mis-site (Fe–Mo) imperfection [9, 13], oxygen deficiency [13] and valence disproportion. The valence disproportion is expected to fulfil the electroneutrality in the compounds provided there is no oxygen deficiency. Both the oxygen deficiency and valence disproportion could lead to a decrease of the unit cell volume with Fe content, as shown in figure 1(a).

In summary, the crystal structure and magnetization of the non-stoichiometric $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ system with ($0.8 \leq x \leq 1.5$) are investigated. The alteration of the relative content between Fe and Mo in $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ exhibits a significant effect on the crystal

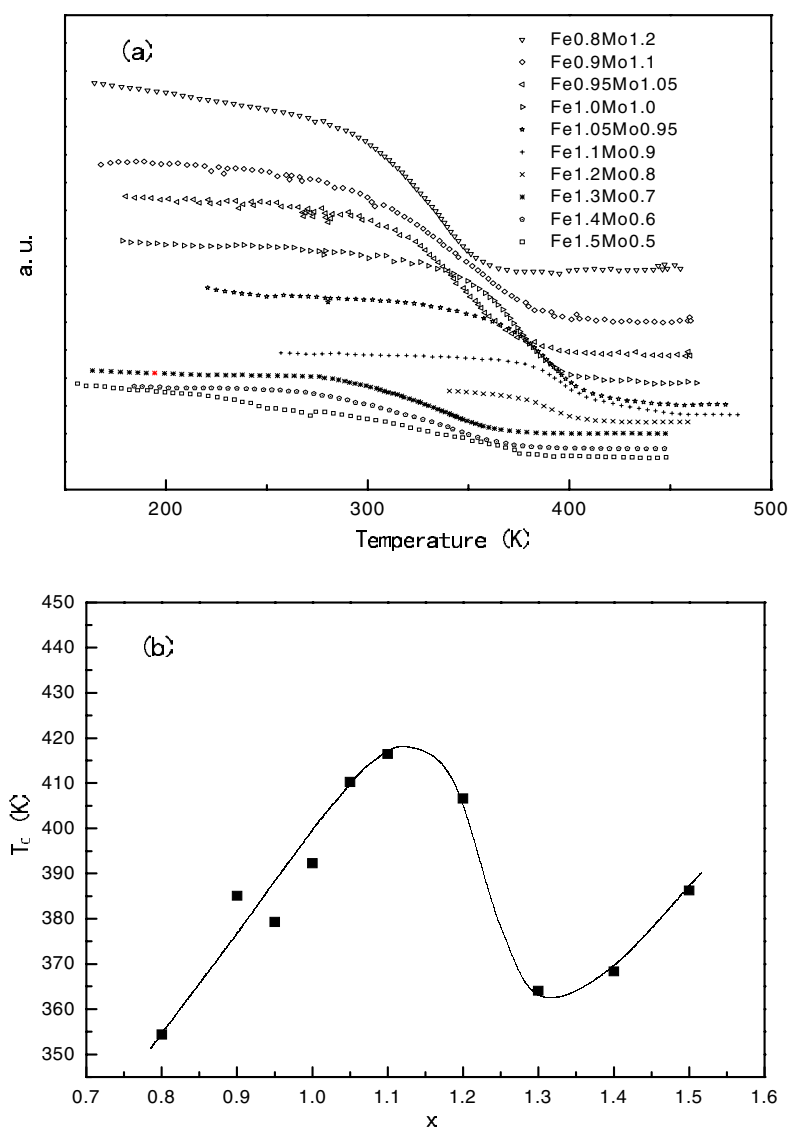


Figure 4. (a) Magnetization versus temperature in a field of 0.09 T, (b) the composition dependence of the Curie temperature (T_c) for $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ system. The curve is a guide for the eyes.

structure, the ionic ordering, the Curie temperature and the saturated magnetization of the compounds. The degree of ordering is maximal at $x = 0.95$ and decreases as x deviates from 0.95. A structural transition from the tetragonal $I4/mmm$ lattice to the cubic $Fm\bar{3}m$ lattice occurs around $x = 1.2$. It seems that an appropriate antisite defect is necessary to stabilize the double-perovskite structure under our synthesis conditions. The saturated magnetization increases from $2.7 \mu_B/\text{fu}$ for $x = 0.8$, approaches a maximum of $3.5 \mu_B/\text{fu}$ for $x = 0.95$ and then decreases to $0.5 \mu_B/\text{fu}$ for $x = 1.5$. The Curie temperature of the compounds increases with the composition x , but exhibits a sharp drop around $x = 1.2$, at which point the structural transition takes place.

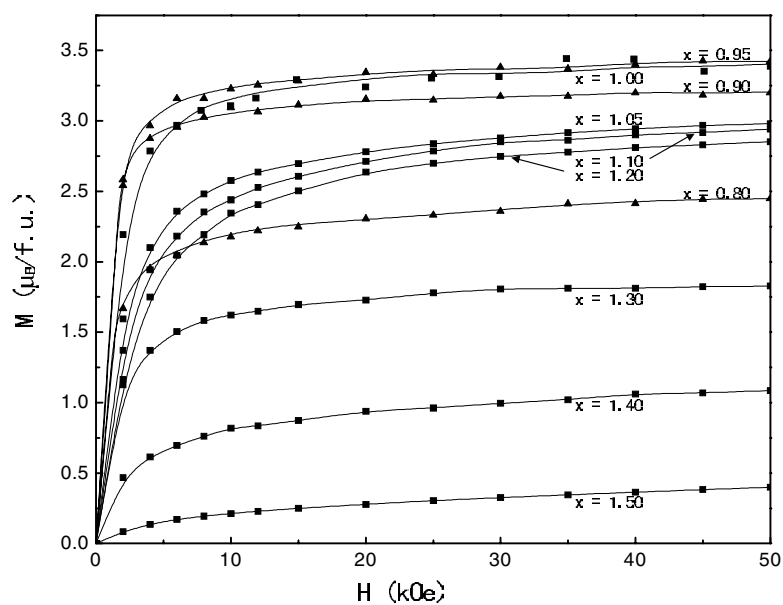


Figure 5. Field dependence of the magnetization of $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ at 4.2 K.

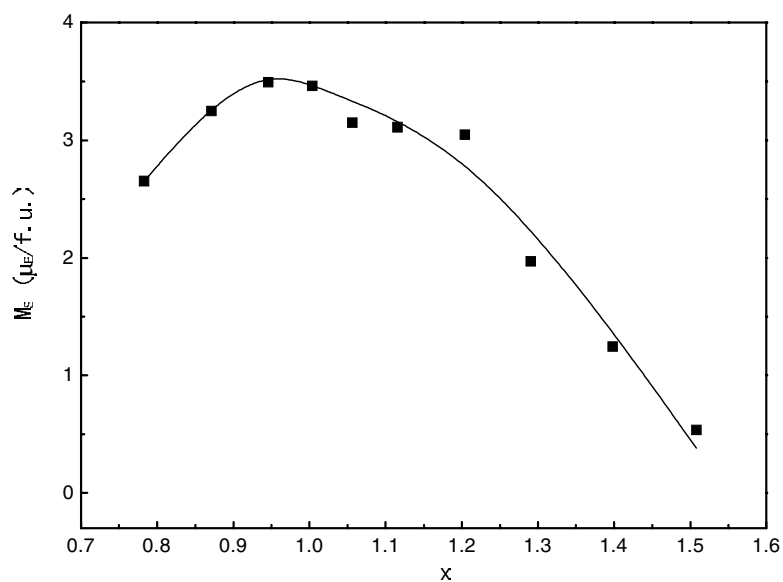


Figure 6. Dependence of the saturation magnetization on the composition x in a $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ system ($0.8 \leq x \leq 1.5$). The curve is a guide for the eyes.

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