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Cation order and magnetic properties of double perovskite $\text{Sr}_2\text{FeMoO}_6$

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A double perovskite type compound $\text{Sr}_2\text{FeMoO}_6$ was synthesized by a solid-state reaction. The order parameter (x) of Fe and Pt ions on the B sites increased from 68% to 82% and the spontaneous magnetization at 5 K increased from 2.1 to 3.0 μ_B per formula unit by lowering the calcination temperature from 1100 to 500 °C. The dependence of the spontaneous magnetization on x was discussed using two models considering the local magnetic interactions between ions on the B sites. ^{57}Fe Mössbauer analysis suggested the existence of tiny areas of $\text{SrFeO}_{3-\delta}$ in $\text{Sr}_2\text{FeMoO}_6$.

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I. INTRODUCTION

A double perovskite-type oxide $\text{Sr}_2\text{FeMoO}_6$ shows large magnetoresistance at room temperature and this property is attractive from the standpoint of both physics and engineering. In $\text{Sr}_2\text{FeMoO}_6$, Fe and Mo ions occupy the B site of the perovskite structure and the alternately ordered structure of these transition metals is stable, taking into account the electrostatic energy of ionic crystal. The ordered structure of Fe and Mo ions can be regarded as a rock salt structure. Therefore, the electrostatic energy of an ordered double perovskite-type compound $\text{A}_2^{2+}\text{B}_a^{(4-n)+}\text{B}_b^{(4+n)+}\text{O}_6^{2-}$ is expressed in the sum of ordinary perovskite $\text{A}^{2+}\text{B}_c^{4+}\text{O}_3^{2-}$ and rock salt-type compound $\text{B}_d^{n+}\text{B}_e^{n-}$, where A is a large metal cation, B_a to B_e are smaller than A and different metal cations with different ionic valences, and n is an integer.¹ Accordingly, the electrostatic energy decreases as n becomes larger.

$\text{Sr}_2\text{FeMoO}_6$ with the ordered structure of Fe and Mo ions has electronic and magnetic structures as follows. The localized magnetic moments of Fe and Mo ion are 5 μ_B ($3d^5$) and 0 μ_B ($4d^0$), respectively. In addition, one itinerant electron per formula unit exists and its magnetic moment is opposite to the localized moment of Fe ions. Therefore, the ionic valences of Fe and Mo ion are 2.5+ and 5.5+ respectively,² and the total magnetic moment is 4 μ_B per formula unit.

In many cases, however, the magnetization is lower than 4 μ_B and this is considered to be due to the disorder of the ionic arrangement.^{3–6} The order parameter of the structure on the B site depends on synthesis conditions, such as heat-treatment temperature, time, and atmosphere.

While the magnetization depends strongly on the order parameter, electrical properties such as magnetoresistance are also affected by external factors, such as grain boundary and packing density of particles regarding the sintered specimen of $\text{Sr}_2\text{FeMoO}_6$. Thus, $\text{Sr}_2\text{FeMoO}_6$ samples were synthesized by varying sintering conditions, and the relationship between magnetic properties, particularly magnetization, and

the order parameter were discussed in this study. Two magnetic structural models in consideration of the local interaction between the ions on the B site were used to explain the experimental data.

II. EXPERIMENT

Samples were synthesized by a solid-state reaction. A mixture of SrCO_3 , Fe_2O_3 , and MoO_3 was pressed into pellets and calcined at temperatures in the range of 500 to 1100 °C for 6 h in air. All of the products after calcination were pulverized, pressed into pellets, and heated at 1100 °C for 6 h in a flow of $\text{H}_2/\text{CO}_2/\text{Ar}$ mixed gas. The pressure ratio of H_2 to CO_2 $P_{\text{H}_2}/P_{\text{CO}_2}$ decides the oxygen partial pressure P_{O_2} . $P_{\text{H}_2}/P_{\text{CO}_2}$ was set at 0.17, and $\log[P_{\text{O}_2}(\text{atm})]$ was calculated to be -14.6 at 1100 °C.

The order parameter of the Fe and Mo arrangement x was evaluated from x-ray diffraction (XRD) patterns.⁷ The ordered structure of Fe and Mo ions form a superlattice and, therefore, the intensities of the superlattice peaks depend on x . Rietveld analysis was performed assuming the space group of $I4/mmm$,⁸ in which an alternate arrangement of $2a$ and $2b$ positions corresponds to the B site of perovskite structure. The occupation factors of Fe^{3+} and Mo^{5+} on the two positions are obtained and the order parameter x was expressed as,⁹

$$x(\%) = |g - 0.5| \times 2 \times 100, \quad (1)$$

where g is the occupation factor of Fe or Mo on the $2a$ or $2b$ position. Four values of g satisfy the following:

$$\begin{aligned} g_{\text{Fe on } 2a} + g_{\text{Mo on } 2a} &= g_{\text{Fe on } 2b} + g_{\text{Mo on } 2b} \\ &= g_{\text{Fe on } 2a} + g_{\text{Fe on } 2b} \\ &= g_{\text{Mo on } 2a} + g_{\text{Mo on } 2b} = 1. \end{aligned} \quad (2)$$

Magnetization curves of the powder samples were measured in a magnetic field up to 9 T at 5 K by a Quantum Design PPMS. ^{57}Fe Mössbauer spectra of the powder samples were taken at various temperatures from 20 to 300 K

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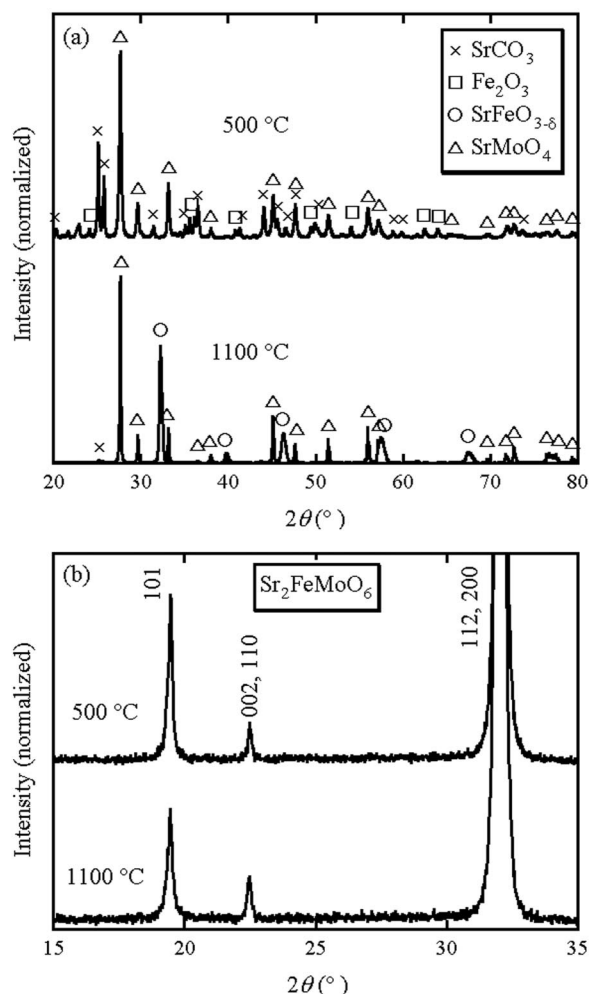


FIG. 1. XRD patterns of the samples, (a) calcined at 500 and 1100 °C in air, and (b) followed by heating at 1100 °C in $\text{H}_2/\text{CO}_2/\text{Ar}$ mixed gas.

in transmission geometry, using a $^{57}\text{Co}:\text{Rh}$ γ -ray source. The Mössbauer spectra were fitted to obtain the hyperfine information.

III. RESULTS AND DISCUSSION

A. Products after calcination

The products after calcination contained several ingredients. XRD patterns of the products calcined at 500 and 1100 °C are shown in Fig. 1(a). The products calcined at low temperatures contained raw materials, SrCO_3 and Fe_2O_3 . As the calcination temperature increased, the quantity of the raw materials decreased, while that of $\text{SrFeO}_{3-\delta}$ (includes SrFeO_3) increased.

B. $\text{Sr}_2\text{FeMoO}_6$ samples

The calcined products were heated at 1100 °C in a low oxygen partial pressure to be formed into $\text{Sr}_2\text{FeMoO}_6$. All of the samples were single phase of $\text{Sr}_2\text{FeMoO}_6$ judging from their XRD patterns [Fig. 1(b)], but the intensities of some peaks varied with calcination temperature. The intensity of the 101 peak compared to the 002 and 110 peaks increased by decreasing the calcination temperature, and that of the

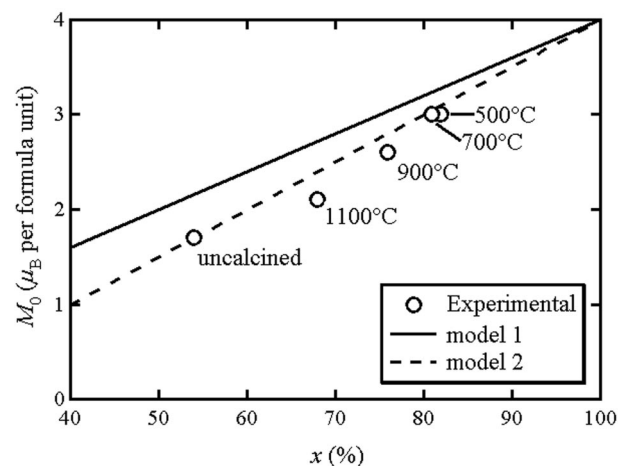


FIG. 2. Relationship between spontaneous magnetization M_0 and order parameter of Fe and Mo ions x . Tags are calcination temperatures.

uncalcined sample was lowest. The order parameter x that depends on the relative intensity of 101 to 002 and 110 peaks is shown in Fig. 2. x was increased from 68% to 82% with decreasing the calcination temperature and that of uncalcined sample was 54%.

We gave attention to SrCO_3 and $\text{SrFeO}_{3-\delta}$ included in the samples before heating in low oxygen partial pressure to understand the dependence of x on the calcination temperature. In the heating process, SrCO_3 decomposes, releases CO_2 gas, and is transformed into perovskite structure with other elements. Since $P_{\text{H}_2}/P_{\text{CO}_2}$ determines the oxygen partial pressure, it is possible that CO_2 originating from SrCO_3 raises the oxygen partial pressure. Until the decomposition of SrCO_3 is finished, high P_{O_2} maintains; net heating time at low P_{O_2} becomes shorter as SrCO_3 concentration in the calcined products becomes higher. $\text{SrFeO}_{3-\delta}$ also can be an obstacle to forming ordered $\text{Sr}_2\text{FeMoO}_6$. Fe ions on B site in $\text{SrFeO}_{3-\delta}$ hardly diffuse because the ions are trapped in a deep potential at the B sites.^{10,11} Therefore, it is energetically unfavorable to form $\text{Sr}_2\text{FeMoO}_6$ by the reaction of Mo and $\text{SrFeO}_{3-\delta}$. Consequently, the sample calcined at 500 °C, which contains less quantity of both SrCO_3 and $\text{SrFeO}_{3-\delta}$, is easier to transform into $\text{Sr}_2\text{FeMoO}_6$ with a high-order parameter.

Although the intermediate products can disturb a formation of ordered $\text{Sr}_2\text{FeMoO}_6$, heating at a higher temperature and/or for a longer time should allow all samples to form highly ordered $\text{Sr}_2\text{FeMoO}_6$.

C. Relationship between magnetization and order parameter

Spontaneous magnetizations M_0 at 5 K of the $\text{Sr}_2\text{FeMoO}_6$ samples were obtained from magnetization curves. The relationship between M_0 and the order parameter x is shown in Fig. 2. M_0 increased with x . As mentioned in Sec. I, at $x=100\%$, the magnetic moments of Fe ions are coupled ferromagnetically, resulting in M_0 of $4\mu_B$ per formula unit. At $x<100\%$, some cations of the same element occupy the B site side by side as shown in Fig. 3. Consider-

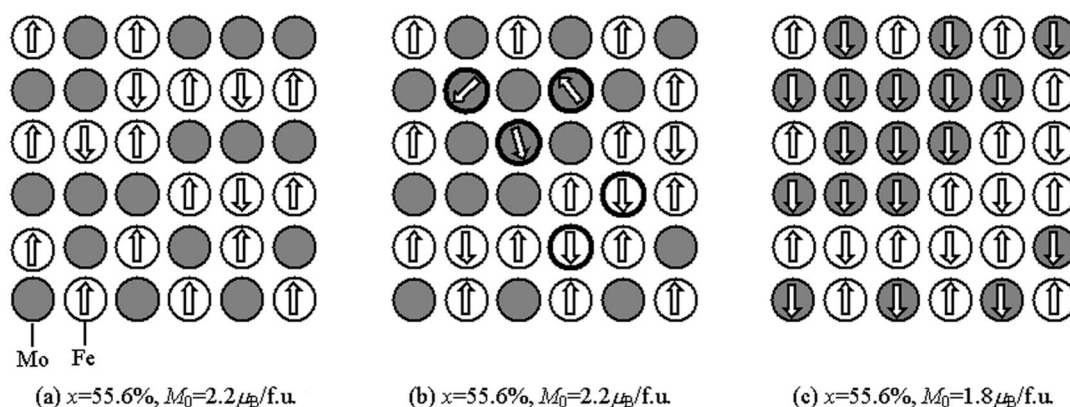


FIG. 3. Ionic arrangements and magnetic structure models of disordered $\text{Sr}_2\text{FeMoO}_6$. (a) Model 1. At least one ion on the nearest-neighbor B site is a cation of different element. (b) Model 1. All of the nearest-neighbor ions around a Fe (or Mo) ion hemmed by bold line are Fe (or Mo) ions. (c) Model 2.

ing the local magnetic interactions between the ions on the B site, two models are presented to discuss the relationship between the magnetization and the order parameter.

One of the two models (model 1) is based on the assumption that two Fe ions that occupy the B site side by side are coupled antiferromagnetically by a superexchange interaction, and two Mo ions in the same situation have no magnetic interactions. These assumptions are based on the facts that $\text{SrFeO}_{3-\delta}$ (includes SrFeO_3) and SrMoO_4 exhibit antiferromagnetic and paramagnetic behavior, respectively.⁴ We assume that the electronic and magnetic interactions between a Fe ion and a Mo ion side by side are identical with those of $\text{Sr}_2\text{FeMoO}_6$ with x of 100%.

We classify the ionic arrangements on the B site into two cases. One case is that at least one site in the nearest-neighbor ones is occupied by the cation of another element as shown in Fig. 3(a), and the other case is that all the nearest-neighbor sites on the B sites around an ion are occupied by the cations of the same element as shown in Fig. 3(b). In the former case, we assumed that an itinerant electron exists between the Fe ion and the Mo ion as seen in 100% ordered $\text{Sr}_2\text{FeMoO}_6$ mentioned in Sec. I. No localized moment exists in Mo ions and localized moment of $5\mu_B$ exists in Fe ions. The magnetic moment of itinerant electron is opposite to the localized moment. Accordingly, the relationship between M_0 and x comes to

$$M_0(\mu_B/\text{f.u.}) = x/25. \quad (3)$$

In the latter case, a cluster of Fe ions or Mo ions exists. The different valence state from that in 100% ordered $\text{Sr}_2\text{FeMoO}_6$ may be shown because the itinerant electron cannot exist due to a lack of the Fe–Mo interaction. However, the relationship between M_0 and x of Eq. (3) roughly holds well because antiferromagnetic couple of Fe ions and paramagnetic couple of Mo ions exhibit no magnetization; that is the same as the case shown in Fig. 3(a). This relationship from model 1 is in agreement with the Monte Carlo simulation on the similar assumption.⁴

Another model (model 2) is based on the assumption that the two Mo ions occupying the B site side by side couple ferromagnetically.⁵ As shown in Fig. 3(c), the magnetic moment of the Mo ion is opposite to the direction of

the net magnetization in Fe ions and decreases the total magnetization. Then, the relationship between M_0 and x is

$$M_0(\mu_B/\text{f.u.}) = x/20 - 1. \quad (4)$$

Experimental data of the relationship between M_0 and x are compared with that calculated from the two models in Fig. 2. The experimental dependence of M_0 on x is rather close to model 2. However, we need more microscopic information for the complete understanding of these features. It is noted that the dependence of M_0 on x reported by Balcells *et al.*⁶ is rather close to model 1.

D. Mössbauer spectroscopy

Figure 4 shows ^{57}Fe Mössbauer spectra at 300 K and Table I shows the results of fitting. The spectra were analyzed as a superposition of a paramagnetic singlet and magnetic sextets. The area of the paramagnetic singlet increased

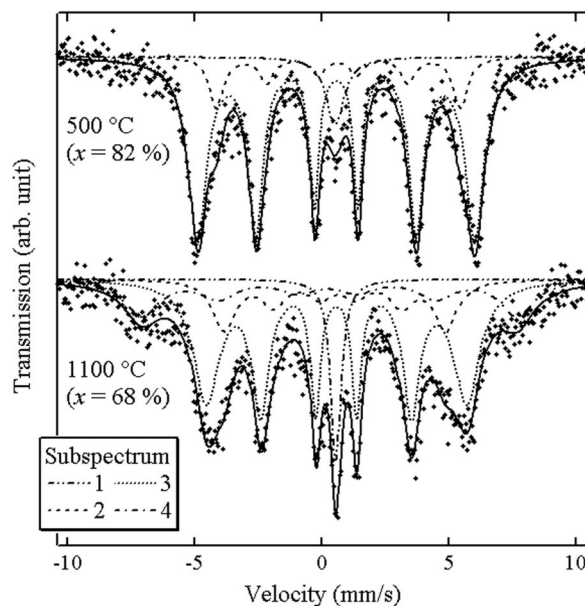


FIG. 4. Mössbauer spectra of the samples calcined at 500 and 1100 °C. The spectra were obtained at 300 K.

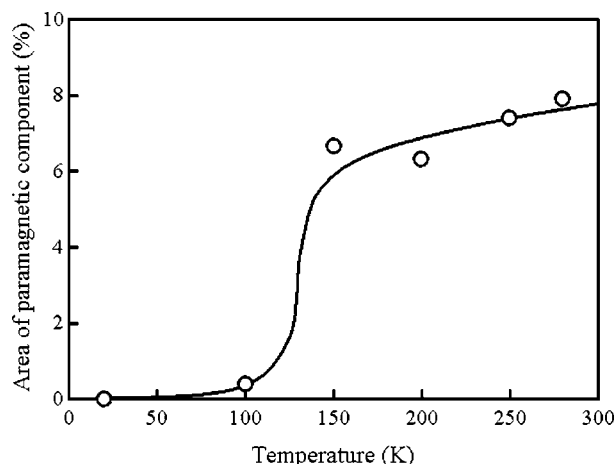


FIG. 5. Temperature dependence of paramagnetic component area in the Mössbauer spectra of the samples calcined at 1100 °C.

with the decrease of x . Because the Curie temperature of $\text{Sr}_2\text{FeMoO}_6$ is about 420 K, in general, the singlet originated in the disordered area of Fe and Mo ion arrangement on the B site. As illustrated in Fig. 3, the Fe ions have various environments, e.g., various numbers of nearest-neighbor Fe ions on the B site. This probably causes several subspectra in the Mössbauer spectra. The spectra of the samples with x of 81% and 82% showed sextets with broad absorption peaks. Although these sextets were fitted by the superposition of two sextets to simplify the analysis, these sextets may include many components. In case of the samples with x of 54% and 68%, obviously distinguishable sextets appeared (subspectrum 4). This small sextet can be assigned to the areas of $\text{SrFeO}_{3-\delta}$, which are clusters of Fe ions on the B site of disordered $\text{Sr}_2\text{FeMoO}_6$. The isomer shift of subspectrum 4 is lower than that of other sextets, indicating the higher valence of Fe ion in the area.

Mössbauer spectra of the sample of $x = 68\%$ were taken at various temperatures in the range of 20 to 300 K and the temperature dependence of the area ratio of the paramagnetic singlet is shown in Fig. 5. The increase of the paramagnetic component between 100 and 150 K indicates the existence of a component having a magnetic transition temperature in this range. It is in agreement with the Néel temperature of SrFeO_3 , 130 K.¹²

As mentioned herein, particular ionic arrangement cannot be derived from x , that is, whether the disordered part is random on an atomic scale or separated to $\text{SrFeO}_{3-\delta}$ and SrMoO_3 is unknown. Although the Mössbauer data show the existence of the $\text{SrFeO}_{3-\delta}$ cluster, no distinguishable peak of

TABLE I. Hyperfine parameters for Mössbauer spectra at 300 K.

Calcination temperature (°C)	Subspectrum	I (%)	B_i (T)	δ (mm/s)	Δ (mm/s) ^a
500	1	7	...	0.55	...
	2 ^b	14	29.8	0.65	0.05
	3	80	33.9	0.584	0.004
1100	1	7.9	...	0.573	...
	2 ^b	17	27.0	0.58	-0.09
	3	56	31.8	0.594	0.02
	4 ^b	19	45.8	0.26	0.01

^a I : relative intensity, B_i : internal magnetic field, δ : isomer shift relative to Fe, and Δ : quadrupole splitting.

^bIntensities of peaks in a sextet were fixed at 3:2:1:1:2:3, and linewidths at 1:1:1:1:1:1.

$\text{SrFeO}_{3-\delta}$ or SrMoO_3 was observed in the XRD pattern. Therefore, Mössbauer data indicate the existence of tiny areas of $\text{SrFeO}_{3-\delta}$ and SrMoO_3 in partially ordered $\text{Sr}_2\text{FeMoO}_6$ samples, which XRD cannot detect.

IV. SUMMARY

Spontaneous magnetization at 5 K of double perovskite $\text{Sr}_2\text{FeMoO}_6$ was increased by increasing the order parameter of Fe and Mo ions on the B site. This dependence was explained using two models. Mössbauer spectra indicated that the arrangement of Fe and Mo ions were not random on the atomic scale, but the clusters of Fe or Mo ions on the B site exist in partially ordered double perovskite structure.

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