Magnetic and Mössbauer Study of $\text{Sr}_2\text{FeMoO}_6$ Partially Ordered Double Perovskite

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Double perovskite $\text{Sr}_2\text{FeMoO}_6$ was successfully synthesized by a solid state reaction technique. The ordering parameter of Fe and Mo ions on the B site of the perovskite structure was estimated to be 62% by Rietveld analysis. Saturation magnetization at 5 K was $1.9 \mu_B$ per formula unit, which is about half the theoretically predicted value. The Mössbauer spectrum at 20 K can be fitted by the two magnetic sextets that correspond to valence-fluctuated $\text{Fe}^{2.5+}$ and Fe^{3+} . The reduced magnetization and the valences of Fe ions can be understood by considering the partially ordered atomic arrangement of Fe and Mo on the B site.

Key words: double perovskite, ion ordering, Rietveld refinement, magnetic structure, electronic structure, Mössbauer spectroscopy

1. Introduction

Since a revival of double perovskite $\text{Sr}_2\text{FeMoO}_6$ due to a large magnetoresistance at room temperature¹⁾, many studies²⁾⁻¹¹⁾ on this compound have been performed. In spite of intensive investigations, some parts of the electronic and magnetic structures are still controversial. One of the complicating characters is the presence of the disordered atomic arrangement of Fe and Mo ions on the B site. In perfectly ordered double perovskite, Fe and Mo of $\text{Sr}_2\text{FeMoO}_6$ alternately occupy on the B site of the perovskite structure. Considering the ionic valence of Fe^{3+} and Mo^{5+} , 3d electrons of Fe and 4d ones of Mo has $t_{2g}^3 e_g^2$ and t_{2g}^1 configurations in the ground state, respectively. In this configuration, the Fe up-spin t_{2g} and e_g bands are located below the Fermi level, providing localized Fe magnetic moments of $5 \mu_B$ per formula unit. On the other hand, the down-spin t_{2g} band of Mo which couples antiferromagnetically with Fe is located on the Fermi level and hybridized with Fe down-spin t_{2g} band. Thus, the net magnetic moments should be $4 \mu_B$ per formula unit and the valence fluctuating state between Fe^{2+} and Fe^{3+} ($\text{Fe}^{2.5+}$) can be observed^{1), 5)}. The conduction mechanism due to the down-spin bands hybridization is closely associated with the magnetoresistance observed in $\text{Sr}_2\text{FeMoO}_6$. However, when some imperfection of doubled atomic arrangement is introduced in $\text{Sr}_2\text{FeMoO}_6$, different electronic and magnetic structures could be established and this complicates the magnetic and magnetotransport nature.

In this study, we examined the electronic and magnetic properties of $\text{Sr}_2\text{FeMoO}_6$ by magnetic measurements and Mössbauer spectroscopy, considering the degree of B

ions-disordering.

2. Experimental

The sample was synthesized by solid state reaction. Mixture of SrCO_3 , Fe_2O_3 and MoO_3 was pressed into pellets and calcined at 1100°C for 6h in air. The product was pulverized, pressed into pellets, and heated at 1100°C for 6h in atmosphere of low oxygen partial pressure. The oxygen partial pressure was controlled by mixing of H_2 and CO_2 ; the pressure ratio of CO_2 to H_2 was 0.2.

X-ray diffraction (XRD) data were analyzed by Rietveld analysis¹²⁾ to obtain the information about the atomic ordering of Fe and Mo on the B site.

The magnetization of powder sample was measured at temperatures of 5-300 K by Quantum Design PPMS and the saturation magnetization was obtained. The ^{57}Fe Mössbauer spectra of powder sample were collected at 20 K to room temperature. The Mössbauer data were fitted to obtain the hyperfine information.

3. Results and discussion

The XRD pattern of the synthesized sample confirms a single phase of $\text{Sr}_2\text{FeMoO}_6$ as shown in Fig. 1. The Rietveld refinement was performed on the conditions shown in Table 1. The obtained occupation factors are also summarized. Although the R factor and the goodness-of-fit S are somewhat large, the occupation factor g can be attained within small errors. It is also noted that the results based on the ionic valences of Fe^{3+} and Mo^{5+} scarcely change when using the different valences of Fe^{2+} and Mo^{6+} . In order to obtain quantitative information on the degree of B ions-ordering, we define the B ions-ordering parameter x as follows.

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

where g is the occupation factor of Fe or Mo. The ordering parameter x clearly reflects the number of the Mo (Fe) ions replaced by Fe (Mo) ions at the B site. In this manner, when the sample has perfect ordering, $x = 100\%$, while the Fe and Mo ions occupy randomly, $x = 0\%$. The B ions-ordering parameter x of our sample is calculated to be 62%.

The magnetization curves at 5-300 K are shown in Fig. 2. The magnetization decreases with increasing temperature. The saturation magnetization M_s at 5 K is $1.9 \mu_B$ per formula unit which is about half of the theoretically predicted value of $4 \mu_B$ per formula unit for the perfectly ordered structure. In some disordered arrangement, it is

Fig. 1 Rietveld refinement plot of single phase $\text{Sr}_2\text{FeMoO}_6$.

likely that Fe ions partially occupy the nearest neighbor B sites and couple antiferromagnetically. In this arrangement, each magnetic moment of Fe ion cancels with each other and the net magnetization should be decreased. Thus this is a possible cause for the decrease in the magnetization in our sample. Previous report by Kobayashi *et al.*¹⁾ is also in agreement with the above model, in which the M_s of $3 \mu_B$ was obtained for the polycrystalline ceramic sample with the B ion occupation factor g_B of 0.87 ($x=74\%$).

Figure 3 shows the ^{57}Fe Mössbauer spectra at various temperatures from 20 K to room temperature. All the spectra show magnetically split component. With increasing temperature, paramagnetic singlet appears around the center of the spectra and the absorption intensity of the singlet grows corresponding to the decrease in the magnetization. The spectrum at 20 K can be fitted using the distribution of the hyperfine field shown in Fig. 4. The distribution of the hyperfine field has the two peaks around 48 T and 54 T, necessitating us the

Fig. 2 Magnetization curves of $\text{Sr}_2\text{FeMoO}_6$ at different temperatures.

two magnetic sextets with different hyperfine fields to represent the spectrum. Thus we fit the data using a superposition of two sextets. The fitted results are summarized in Fig. 5 and Table 2. The subspectrum 1 and 2 correspond to those with the hyperfine field of about 48 T and 52 T, respectively. The linewidth of subspectrum 2 is quite large compared with subspectrum 1. This is presumably associated with the disordered atomic arrangement as described below.

The obtained isomer shifts are 0.59 and 0.36 mm/s for the two subspectra. Similar behaviors were reported by Lindén *et al.*⁵⁾ It is well known that the isomer shift gives the information about the chemical state of Fe ion, *i.e.*, valence state. Generally, the isomer shifts of high-spin Fe^{2+} and Fe^{3+} drop in the two regions of 0.8–1.4 mm/s and 0.2–0.6 mm/s, respectively¹³⁾. In the present case, the isomer shift of subspectrum 1 is located between the two regions corresponding to high-spin Fe^{2+} and Fe^{3+} , while that of subspectrum 2 is within the region of Fe^{3+} .

Table 1 Conditions and results for Rietveld refinement.

Ion	Position	g	x	y	z	$B (\text{\AA}^2)^a$
Sr^{2+}	4d	1	0	0.5	0.25	0.5
Fe^{3+}	2a	$0.81 \pm 0.01^{b,c}$	0	0	0	0.5
Mo^{5+}	2a	$0.19 \pm 0.01^{b,c}$	0	0	0	0.5
Fe^{3+}	2b	$0.19 \pm 0.01^{b,c}$	0	0	0.5	0.5
Mo^{5+}	2b	$0.81 \pm 0.01^{b,c}$	0	0	0.5	0.5
O^-	4e	1	0	0	0.26 ± 0.01^b	1
O^-	8h	1	0.248 ± 0.005^b	0.248 ± 0.005^b	0	1
Space group $I4/mmm$ (tetragonal)						
Lattice parameters $a = 5.577 \pm 0.001^b$, $c = 7.911 \pm 0.002^b$ (Å)						
$R_{wp}=13.17\%$, $S=1.47$						

^a Isotropic atomic displacement parameter.

^b Refined parameters.

^c Linear constraint that the total occupation factors of Fe (Mo) is unity was applied.

Fig. 3 ^{57}Fe Mössbauer spectra of $\text{Sr}_2\text{FeMoO}_6$ at various temperatures.

Fig. 4 Distribution of hyperfine field obtained by fitting the spectrum at 20 K.

Fig. 5 Fitted Mössbauer spectrum of $\text{Sr}_2\text{FeMoO}_6$ at 20 K.

Considering the time scale of Mössbauer measurement, the isomer shift of subspectrum 1 can be understood by the fluctuated valence between Fe^{2+} and Fe^{3+} , i.e., $\text{Fe}^{2.5+}$ for the perfectly ordered $\text{Sr}_2\text{FeMoO}_6$.

It is also noteworthy to comment on the possible causes of the presence of subspectrum 2. As we mentioned before, some Fe clusters, in which Fe ion is surrounded by six nearest neighbor Fe ions on the B site, exist when the imperfection of ordering is introduced. In this situation, the Fe cluster forms SrFeO_3 tiny phases possessing Fe^{3+} or Fe^{4+} valence state and electron hopping is rather restricted, which results in the isomer shift identified to be Fe^{3+} . Moreover, if the number of the nearest neighbor Fe ions in the cluster changes, other magnetic environments which in turn make the wide distribution of hyperfine field are realized. Thus it is plausible that the broadness of the subspectrum 2 is attributed to the disordered atomic arrangement. A similar broadening of Mössbauer spectra has been reported⁸⁾. The spectra of a highly disordered sample synthesized by melt-quenching shows the large linewidth of 6 T, in contrast to that of 1 T for an ordered sample synthesized by solid state reaction. This also supports the existence of different chemical environments at disordered B ion sites.

4. Summary

$\text{Sr}_2\text{FeMoO}_6$ synthesized by solid state reaction exhibited the partially ordered arrangement of Fe and Mo ions and the B ions-ordering parameter estimated by Rietveld analysis was 62%. The saturation magnetization at 5 K was about half of the theoretical value, $1.9 \mu_B$ per formula unit. The ^{57}Fe Mössbauer spectrum at 20 K was fitted considering two subspectra showing magnetic sextets which are assigned to be valence fluctuating $\text{Fe}^{2.5+}$ and Fe^{3+} . On the consideration of the valence and hyperfine field, $\text{Fe}^{2.5+}$ and Fe^{3+} are ascribed to the Fe ions in the ordered and disordered part of the partially ordered perovskite $\text{Sr}_2\text{FeMoO}_6$ sample. The broad subspectrum corresponding to Fe^{3+} can be also explained by introducing some Fe clusters due to disordered atomic arrangement.

Table 2 Best-fit hyperfine parameters for the Mössbauer spectrum at 20 K.

Subspectrum	Hyperfine field (T)	Isomer shift (mm/s)	Quadrupole splitting (mm/s)
1	47.73 $\pm$ 0.04	0.589 $\pm$ 0.004	- 0.017 $\pm$ 0.008
2	52.2 $\pm$ 0.2	0.36 $\pm$ 0.02	0.05 $\pm$ 0.04

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