Revealing the spin/charge modulation in perovskite-type iron oxide $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$

Masaho Onose[1], Ryunosuke Takahashi[2]

[1] Grad. Sch. Eng., Univ. of Tokyo
[2] Grad. Sch. Sci., Univ. of Hyogo

Abstract

Perovskite-type iron oxide $Sr_{2/3}La_{1/3}FeO_3$ has attracted much attention for its characteristic spin/charge ordering, where three-fold charge ordering and six-fold spin ordering are coupled with each other. This spin/charge ordering ranges from $x = 0$ to $x = 0.75$ in its Ba-substituted system $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$, whereas $0.9 \leqq x \leqq 1$ has two-step magnetic transitions. The high-temperature phase has a G-type antiferromagnetic ordering, whereas the low-temperature phase has a six-fold collinear magnetic structure which is the same as that at $x = 0$, revealed by powder neutron diffraction studies at $x = 1$. On the other hand, the existence or absence of charge disproportionation has remained elusive in both phases. In this study, ^{57}Fe Mössbauer spectroscopy measurements were performed at $x = 1$. The spectra in the low-temperature phase are well fitted by the superposition of two sextets corresponding to Fe^{3+} and Fe^{5+}, indicating the existence of the same spin/charge ordered phase as that at $x = 0$. On the other hand, the spectra in the high-temperature phase are asymmetric and significantly broadened, indicating a possible emergence of a glassy electronic state where spin and charge are slowly fluctuating.

About the authors

Masaho Onose:

A Ph.D. student in Kagawa lab. in Grad. Sch. Eng., Univ. of Tokyo. Have been working on high-pressure synthesis of novel perovskite-type iron oxides in Ishiwata Lab. in Grad. Sch. Eng. Sci., Osaka Univ. (Grad. Sch. Eng., Univ. of Tokyo until 2018.) Synthesized the sample and analyzed the Mössbauer spectra in this joint research.

Ryunosuke Takahashi:

A Master's student in Wadati lab. in Grad. Sch. Sci., Univ. of Hyogo. Have been working on EAFS measurements of $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$ and Eu-based compounds. Analyzed the Mössbauer spectra and discussed their consistency with the previous XAFS measurements in this joint research.

Background and purpose

3d transition metal oxides are a typical example of strongly correlated electronic systems and exhibit versatile electronic phases in the vicinity of Mott insulator phase. Among them, perovskite-type oxides with Fe ions in unusually-high-valence state have attracted much attention for their exotic electronic properties arising from the strong d-p hybridization and negative charge-transfer energy. The representative example is $SrFeO_3$ with Fe^{4+} ions, which hosts versatile multi-q helimagnetic phases[1], whose stabilities can be controlled easily by slight chemical substitution[2]. On the other hand, $Sr_{2/3}La_{1/3}FeO_3$ with $Fe^{3.67+}$ ions shows a characteristic spin/charge ordered phase as shown in Fig. 1[3,4]. In this phase, three-fold charge ordering and six-fold collinear magnetic ordering are cooperatively stabilized along the [111] direction of the pseudocubic unit cell. This spin/charge arrangements are reasonable considering the ferromagnetic interaction between $Fe^{3+}-Fe^{5+}$ mediated by localized ligand holes, and the antiferromagnetic superexchange interaction between $Fe^{3+}-Fe^{3+}$.
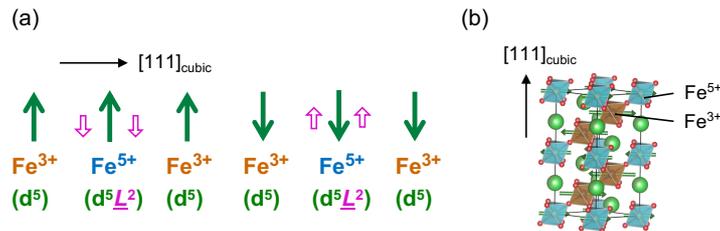
Fig. 1. (a) Spin/charge ordered phase in $Sr_{2/3}La_{1/3}FeO_3$. $\underline{L}$ denotes ligand holes. (b) Crystal structure of $Sr_{2/3}La_{1/3}FeO_3$.

While this spin/charge ordered phase ranges from $x = 0$ to $x = 0.75$ in the Ba-substituted system ($Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$, the existence of two magnetic phases was clarified in $0.9 \leqq x \leqq 1$ by our previous powder neutron diffraction measurements. The low-temperature phase has the six-fold collinear magnetic ordering same as that in the spin/charge ordered phase at $x = 0$, but there was no direct evidence for the corresponding three-fold charge ordering. The high-temperature phase has G-type antiferromagnetic ordering, but the existence or absence of charge disproportionation has not been elucidated. In this study, ^{57}Fe Mössbauer spectroscopy measurements were performed at $x = 1$ to clarify its charge state and get an insight into the whole spin/charge modulation in ($Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$.

Methods

A polycrystalline sample of $x = 1$ was prepared by high-pressure synthesis. The ^{57}Fe Mössbauer spectra were measured with a ^{57}Co source in Rh. The velocity was calibrated with α-Fe. Fits to the spectra were performed by the least-squares method assuming Lorentzian peaks. The Mössbauer spectroscopy measurements were performed in joint research with Prof. S. Kitao and Prof. M. Seto at the Institute for Integrated Radiation and Nuclear Science, Kyoto University.

Results and Discussion

Figure 2 shows the ^{57}Fe Mössbauer spectra and its Lorentzian fitting for ($Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$ ($x = 1$). The spectra in the paramagnetic phase ($180K \leqq T \leqq 300$ K) do not show hyperfine splitting and can be fitted well by quadrupole-splitted doublets. The spectra for 77 K $\leqq T \leqq 140$ K are described by the superposition of two sextets corresponding to Fe^{3+} and Fe^{5+}, indicating the emergence of the same spin/charge ordered phase as $x = 0$. The spectra at $T = 160$ K in the G-AFM phase are significantly broadened and it is difficult to get a satisfactory fitting. We will discuss the possible origin of this peak broadening later.
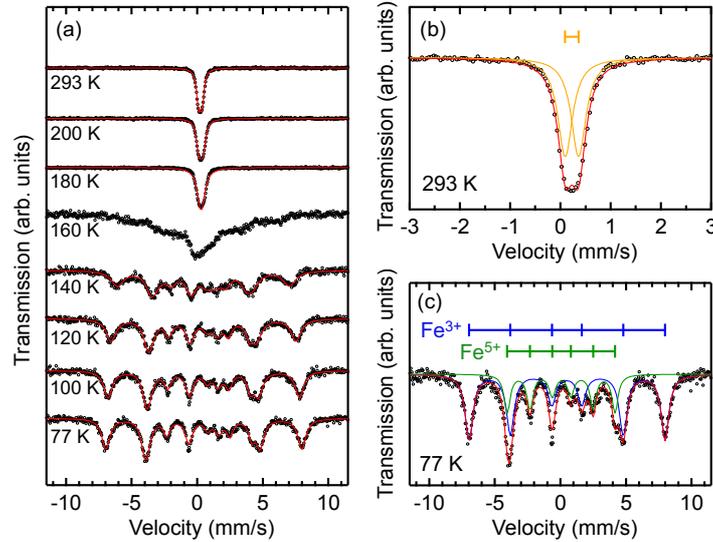
Fig. 2. (a) Temperature dependence of the Mössbauer spectra for ($Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$ ($x = 1$). The red line indicates the Lorentzian fitting. (b) The magnified view of the Mössbauer spectra at $T = 293$ K. The yellow line and yellow vertical ticks indicate the two quadrupole-splitted peaks and their positions, respectively. The red line is their superposition. (c) The magnified view of the Mössbauer spectra at $T = 77$ K. The blue line and green line indicate the hyperfine-splitted peaks for Fe^{3+} and Fe^{5+}, respectively. The red line is their superposition. The vertical ticks indicate the positions for each peak.

Figure 3 shows the temperature dependence of Mössbauer parameters. The data of previous studies at $x = 0$[5] are plotted together for comparison. The hyperfine field is comparable for $x = 0$ and $x = 1$, which is consistent with the emergence of the same spin/charge ordered phase for both compositions. On the other hand, isomer shift (IS) for $x = 1$ is systematically larger than that for $x = 0$ by about 0.01 mm/s. IS reflects the electron density at the nucleus position and the increase in IS is usually considered to be originated from the decrease in the valence of Fe. However, it is unlikely that there is a significant difference in the valence of Fe (i.e. the amount of oxygen deficiency) between x

= 0 and $x = 1$ because the lattice constants for the $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$ varies linearly with x in good accordance with Vegard's rule. Therefore, the difference in IS between $x = 0$ and $x = 1$ is most likely due to the change in the bonding state. The electron density at the nucleus position is expected to decrease at $x = 1$ compared to $x = 0$ because of the following two reasons: (1) the broadening of the 4s electron distribution with the increase in the lattice constant, and (2) the enhancement of screening effect by the localization of 3d electrons. In fact, the IS of the related compounds $SrFeO_3$ and $BaFeO_3$ are reported as 0.07 mm/s[6] and 0.146 mm/s[7], respectively, whose difference is comparable to that for the present case between $x = 0$ and $x = 1$ in $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$.

The quadrupole splitting (QS) shown in Fig. 3(c) is close to zero for both $x = 0$ and $x = 1$ in the spin/charge ordered phase, reflecting the high octahedral symmetry in the electronic configuration of Fe^{3+}($t_{2g}^3e_g^2$) and Fe^{5+} (t_{2g}^3). On the other hand, the QS for $Fe^{3.67+}$ in the paramagnetic phase is larger than that in the spin/charge ordered phase. In addition, QS for $x = 1$ is greater than that for $x = 0$. The origin of this difference has not been completely clarified yet, but given that the resistivity for $x = 1$ is semiconducting in all temperature range, it is possible that incoherent charge disproportionation is developed even near room temperature, resulting in a finite distribution of IS. Since the QS shown in Fig. 3(c) is obtained assuming a single IS, it may be overestimated if the finite distribution of IS exists.
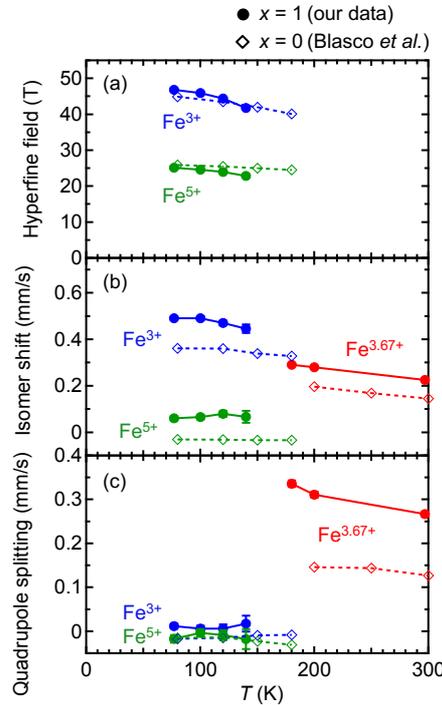
Fig. 3. (a) Hyperfine field, (b) isomer shift, and (c) quadrupole splitting for $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$ ($x = 1$) obtained by the fitting of the Mössbauer spectra. The data of previous studies at $x = 0$[5] are plotted together for comparison.

Next, we will discuss the spectrum at $T = 160$ K in the G-type AFM phase. Although a satisfactory fitting is difficult owing to the significant peak broadening, there are two notable features in this spectrum. The first point is that the transmission reaches a minimum near the center of the spectrum. This suggests a broad distribution of hyperfine field which extends up to zero. Considering the fact that the neutron diffraction pattern does not show significant peak broadening, this broad distribution of hyperfine field is likely to derive from the time-dependent fluctuation of the spin order, not from the spatial inhomogeneity. In other words, this suggests the possibility that spins appear to be ordered in the G-type AFM arrangement in the characteristic timescale of neutron diffraction measurements ($\sim 10^{-13}$ s), while it is fluctuating in the longer timescale of Mössbauer spectroscopy ($\sim 10^{-7}$ s).

The second point is the asymmetric spectral shape, which is likely due to an asymmetric distribution of isomer shift, i.e., an asymmetric charge disproportionation. Although long-range charge ordering has not been developed at this temperature yet, the existence of charge fluctuation as $3Fe^{3.67+} \rightleftarrows 2Fe^{3+} + Fe^{5+}$ is suggested. The characteristic timescale for this charge fluctuation could be as slow as a laboratory timescale, considering the weak anomaly in the temperature derivative of resistivity and the abrupt change in Fe-O bond length obtained by our

previous EXAFS analysis, both of which are observed near the transition temperature of the G-type AFM phase.

These slow dynamics in the spin and charge fluctuation are possibly the manifestation of a glassy electronic feature at this phase. Although further studies are needed to clarify its origin, a possible mechanism is a competition between charge ordering and magnetic ordering. In other words, the incommensurability between the two-fold G-type AFM and the three-fold charge ordering may suppress the formation of long-range order, which results in the appearance of a glassy electronic state. On the other hand, the six-fold spin ordering at the spin/charge ordered phase can coexist with the three-fold charge ordering, which stabilizes the long-range spin ordering and charge ordering.

Conclusions and perspectives

Figure 4 shows the electronic phase diagram for $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$. The Mössbauer spectroscopy performed at $x = 1$ has revealed the existence of the same spin/charge ordered phase as that in $x = 0$ at the low-temperature phase, which is consistent with our previous results of powder neutron diffraction. Besides, the emergence of a glassy electronic state and slow dynamics of spin/charge fluctuation are suggested in the high-temperature G-AFM phase from the broadened and asymmetric Mössbauer spectrum at $T = 160$ K. The characteristic timescale for this spin/charge fluctuation and the origin of the glassy state are expected to be clarified by future studies of AC magnetic susceptibility and dielectric measurements.
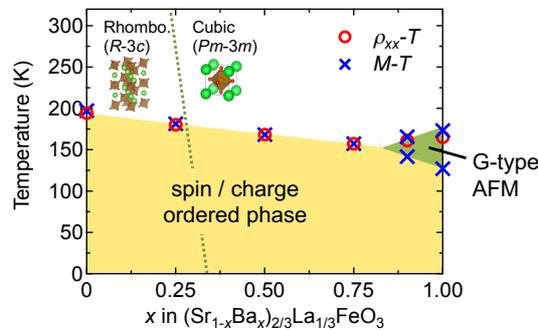
Fig. 4. Electronic phase diagram for $(Sr_{1-x}Ba_x)_{2/3}La_{1/3}FeO_3$.

Acknowledgments

References

[1] S. Ishiwata, M. Tokunaga, Y. Kaneko, D. Okuyama, Y. Tokunaga, S. Wakimoto, K. Kakurai, T. Arima, Y. Taguchi, and Y. Tokura, Phys. Rev. B **84**, 054427 (2011).

[2] M. Onose, H. Takahashi, H. Sagayama, Y. Yamasaki, and S. Ishiwata, Phys. Rev. Mater. **4**, 114420 (2020).

[3] P.D. Battle, T.C. Gibb, and P. Lightfoot, J. Solid State Chem. **84**, 271 (1990).

[4] J.Q. Li, Y. Matsui, S.K. Park, and Y. Tokura, Phys. Rev. Lett. **79**, 297 (1997).

[5] J. Blasco, J.A. Rodríguez-Velamazán, J. García, G. Subías, C. Piquer, V. Cuartero, M.C. Sánchez, and J. Stankiewicz, Phys. Rev. B **98**, 104422 (2018).

[6] P. Adler, A. Lebon, V. Damljanović, C. Ulrich, C. Bernhard, A. V. Boris, A. Maljuk, C.T. Lin, and B. Keimer, Phys. Rev. B **73**, 094451 (2006).

[7] N. Hayashi, T. Yamamoto, H. Kageyama, M. Nishi, Y. Watanabe, T. Kawakami, Y. Matsushita, A. Fujimori, and M. Takano, Angew. Chemie - Int. Ed. **50**, 12547 (2011).