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Abstract
The magnetic properties of $SrFeO_3$ (SFO), $CaFeO_3$ (CFO) and $Sr_{2/3}La_{1/3}FeO_3$ (SLFO), which are perovskite iron oxides with a high valence state of Fe, have been investigated by high-pressure Mössbauer spectroscopy under external magnetic field. These perovskite oxides have been found to switch electronic ground state drastically from the antiferromagnetic (AF) state to the ferromagnetic (FM) state under high pressure. CFO and SLFO, which show a charge-disproportionation (CD: $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$ and $3Fe^{11/3+} \rightarrow 2Fe^{3+} + Fe^{5+}$, respectively) at low temperature, switch magnetic ordering from the AF state to the FM state simultaneously with the suppression of the CD in a critical pressure of about 19 and 23 GPa, respectively. SFO, which does not show any CD, switches its magnetic ordering from the AF state to the FM state at about 7 GPa. These pressure-induced transitions from the AF state to the FM state are accompanied by the discontinuous reduction of the magnetic hyperfine fields.

1. Introduction

The transition-metal oxides have been investigated and various phenomena have been reported [1]; e.g., high-temperature superconductivity [2], the negative colossal magnetoresistance effect [3] and the coupling or separation of electronic spin, charge and orbital degrees of freedom [4]. In this context perovskites containing iron in an unusually high valence state of Fe^{4+} (d^4) provide us with a unique and interesting class of examples. Measurements of photoelectron spectra and the Hall effect for $SrFeO_3$ (SFO) have suggested that the effective charge transfer energy is largely negative ($\Delta_{eff} \approx -3$ eV) and the electric and magnetic properties are dominated by oxygen hole character [5, 6]. The realistic electronic configuration of the Fe–O octahedron is close to $Fe^{3+}(O_6)^{11-}$ (expressed as $Fe^{3+}\underline{L}$, where $\underline{L}$ stands for a hole in the oxygen octahedron) rather than $Fe^{4+}(O_6)^{12-}$.

 Fe^{4+}-oxides remarkably change their electronic properties at external high pressure [7–11]. Most recently, we showed that the pressure-induced transition from a charge-disproportionated

antiferromagnetic state to a charge-uniform ferromagnetic state occurs at 23 GPa in $Sr_{2/3}La_{1/3}FeO_3$ (SLFO) [12].

In this study we attempt to elucidate the pressure-induced magnetic transition in SFO, $CaFeO_3$ (CFO) and SLFO.

2. Experiment

Polycrystalline samples of CFO and SLFO enriched to 50% in ^{57}Fe were prepared by a solid-state reaction and oxygen-deficient perovskite phases were obtained by repeated heat treatments at high temperature in air; these were subsequently sealed in gold capsules and treated at 6 GPa and 923 K (CFO) and 1273 K (SLFO) for 1 h using a cubic anvil-type high-pressure apparatus. An oxygen generator, $KClO_4$, was sealed together in the capsules to attain oxygen stoichiometry in the final products [13]. ^{57}Fe-enriched (50%) SFO powder was also synthesized by a solid-state reaction. $SrCO_3(4N)$ and α-$Fe_2O_3(4N)$ were mixed in an appropriate stoichiometric proportion (Sr:Fe = 1:1), and annealed for 4 h at 1473 K and then for 24 h at 1373 K in air to prepare a nonstoichiometric phase. Subsequently these powder specimens were annealed for 50 h at 673 K under 1000 atm of O_2. The oxygen deficiency of the specimen was 0.03, which was determined by the iodometric titration method.

Using a diamond anvil cell (DAC) of Bassett type [14], ^{57}Fe Mössbauer spectroscopy of these specimens has been carried out up to 70 GPa. A pair of 0.3 carat diamond anvils was used with a culet of 600 and 400 μm to attain pressures up to 40 and 70 GPa, respectively. In the case of the culet of 600 μm the initial thickness of Re gasket was pressed from 200 to 55 μm with the diamond anvils. The samples were inserted into a 350 μm hole of the Re gasket. In order to measure the gradient of the pressure in the whole of the sample hole in detail, the samples were covered with ruby powder. The pressure-transmitting medium was a 4:1 = methanol:ethanol solution [15]. The pressure was determined from ruby fluorescence manometry. For the transmission Mössbauer measurements, high-density γ-ray sources of 370 MBq and a standard γ-ray sources of 925 MBq ^{57}Co in Rh were used. The usual measuring periods of the high-pressure Mössbauer spectroscopy were from 3 to 10 days. The velocity scale of the spectrum was relative to α-Fe at room temperature.

3. Results and discussion

We now discuss the pressure-induced magnetic transition of perovskite high valence iron oxides of SFO, CFO and SLFO.

High-pressure Mössbauer measurements of SFO have been previously performed, and they showed that the antiferromagnetic state changes to the ferromagnetic state at 74 GPa and 298 K under external magnetic fields [16]. However, the critical pressure of the transition from the AF state to the FM state is not given. In order to ascertain the critical pressure of the transition from the AF state to the FM state, we have conducted a high-pressure Mössbauer study under external magnetic fields at 4.5, 7 and 13 GPa and 4.5 K.

As shown in figure 1, the second and fifth line intensities of the spectra at 4.5 GPa and 4.5 K do not decrease with the increase of external magnetic fields up to 7.8 T and the magnetic hyperfine fields does not change so much (figures 1(a) and (b)). These spectra obtained under external magnetic fields showed only the AF state.

The two magnetically split components have been observed at 7 GPa and 4.5 K. The two hyperfine magnetic fields are determined to be 35.6 and 30.7 T without external magnetic field (figure 1(c)). It should be noted that the magnetic hyperfine fields and the second and fifth line
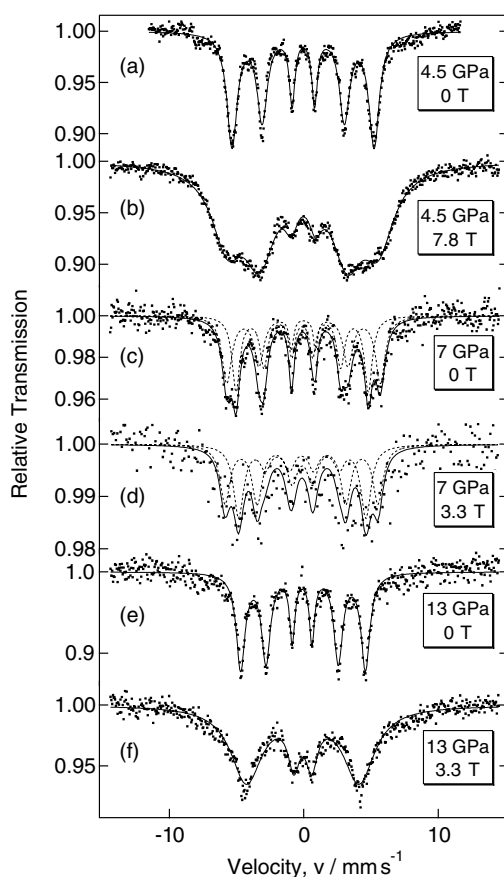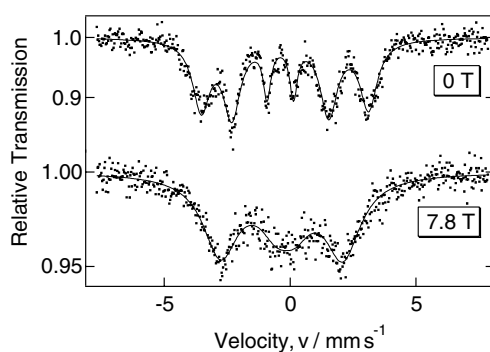
Figure 1. Mössbauer spectra obtained from SrFeO₃ at 4.5, 7 and 13 GPa and 4.5 K under external magnetic fields applied longitudinally to the γ-ray propagation direction. The appreciable line broadening was due to the broadening of the source line caused by application of the magnetic field.

intensities of the two components show different magnetic properties under external magnetic fields. The magnitude of the hyperfine magnetic field of the component with smaller value decreases from 30.7 to 29.8 T with the increase of an external magnetic field from 0 to 3.3 T and the second and fifth line intensities also decrease (figures 1(c) and (d)). Therefore this small component changes from the AF state to the FM state. On the other hand, the component with larger hyperfine field does not show any change with the increase of external magnetic fields like the component at 4.5 GPa (figures 1(c) and (d)). So the component with larger hyperfine field shows the retained AF state. The FM state coexists with the AF state at 7 GPa.

The spectra at 13 GPa consist of one component. Under external magnetic fields the second and fifth line intensities drastically decrease and the magnetic hyperfine fields linearly decrease from 28.9 T at an external magnetic field of 1.1 T to 21.8 T at an external magnetic field of 7.8 T, as shown in figures 1(e) and (f). From the spectra obtained from these high-pressure FM states the magnetism of SFO at 13 GPa is rather soft and it easily aligns to the parallel direction with the external magnetic field.

From the above results it is clear that the pressure-induced transition onset from the AF state to the FM state occurs at about 7 GPa.

Figure 2. Mössbauer spectra obtained from $CaFeO_3$ at 39 GPa and 4.5 K under external magnetic fields. The appreciable line broadening was due to the broadening of the source line caused by application of the magnetic field.
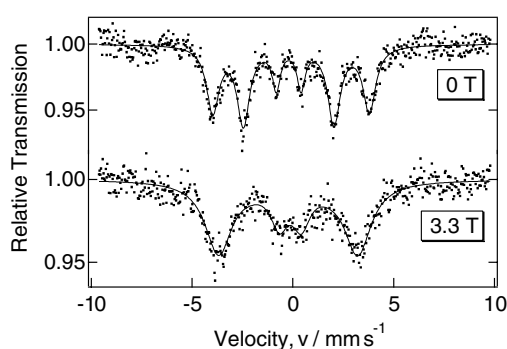
Figure 3. Mössbauer spectra obtained from $Sr_{2/3}La_{1/3}FeO_3$ at 42 GPa and 4.5 K under external magnetic fields. The appreciable line broadening was due to the broadening of the source line caused by application of the magnetic field.

The perovskite oxide CFO has already been investigated by high-pressure ^{57}Fe Mössbauer spectroscopy without an external magnetic field [7, 10]. We specifically attempted to investigate the magnetic transition from the AF state to the FM state under high pressure.

It is interesting to note that the second and fifth line intensities decrease with the increase of external magnetic field at 39 GPa, as shown in figure 2. The angle between the incident γ-ray and the magnetization direction gradually changes from random to parallel with the increase of external magnetic field. The orientation of the magnetization is parallel to the incident γ-ray with the external magnetic field of 7.8 T. With the increase of external magnetic field up to 7.8 T the second and fifth peaks tended to disappear and the magnetic hyperfine fields decreased from 20.7 to 15.1 T, indicating that the atomic moments align to the direction of the external magnetic field (figure 2).

The high-pressure Mössbauer spectra of SLFO under external magnetic fields in the charge-uniform state at 42 GPa are shown in figure 3. The second and fifth line intensities of the spectra decreases and become nearly zero with the increase of external magnetic field up to 3.3 T. From the above results, we conclude that the external pressure switches the ground state from the AF state to the FM state. Considering the inhomogeneity of pressure in the sample cell, the critical pressure has been determined to be 23 GPa [12].

4. Conclusions

High-pressure Mössbauer spectroscopy with an applied external magnetic field found that the pressure-induced transition from the AF state to the FM state appeared at about 7, 19 and 23 GPa in SFO, CFO and SLFO, respectively. Changes in the magnetic state are not associated with any detectable anomaly in the pressure dependence of the lattice parameters. The switching occurs at a lattice volume of $V(7 \text{ GPa})/V_0(0.1 \text{ MPa}) = 0.95$, $V(19 \text{ GPa})/V_0 = 0.91$ and $V(23 \text{ GPa})/V_0 = 0.89$ in SFO, CFO and SLFO, respectively [10, 12, 18].

We have been led to a hypothesis that the charge-uniform and FM states common to these oxides result from the formation of a band in which the electrons of the $e_g(\text{Fe})$–$p_\sigma(\text{O})$ parentage are delocalized. Comparing the e_g–p_σ hybridization and the t_{2g}–p_π hybridization, the former must be enhanced to a large extent than the latter as the Fe–O distance is reduced under high pressure. The small saturated hyperfine magnetic fields result from the polarization of t_{2g} electrons only. Although we have not tested the conductivity, the high-pressure phase of CFO, SLFO and SFO is expected to be a better electrical conductor. The FM and metallic high-pressure phase is, however, not the one expected from a band structure calculation where the hole carriers are delocalized but the $e_g(\text{Fe})$ electrons are localized and polarized [17]. Calculations with small unit cells are necessary to check the above points.

Acknowledgments

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