Pressure-Induced Transition from a Charge-Disproportionated Antiferromagnetic State to a Charge-Uniform Ferromagnetic State in $Sr_{2/3}La_{1/3}FeO_3$

T. Kawakami,[1] S. Nasu,[1] T. Sasaki,[1] K. Kuzushita,[1] S. Morimoto,[1] S. Endo,[2] T. Yamada,[3] S. Kawasaki,[4] and M. Takano[4]

[1]*Department of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[2]*Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[3]*Japan Synchrotron Radiation Research Institute, Sayo-gun, Hyogo 679-5198, Japan*
[4]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

The perovskite oxide $Sr_{2/3}La_{1/3}FeO_3$ has been found to switch its electronic ground state drastically at 23 GPa through measurements of ^{57}Fe Mössbauer spectroscopy and powder x-ray diffraction up to 56 GPa. In the low-pressure region a first-order transition from a charge-uniform paramagnetic metallic phase to a charge-disproportionated ($3Fe^{11/3+} \rightarrow 2Fe^{3+} + Fe^{5+}$) antiferromagnetic insulating phase occurs at 207 K at 0.1 MPa and 165 K at 21 GPa, typically. Above 25 GPa, however, a charge-uniform ferromagnetic (and most probably metallic) phase persists below 300 K. This switching occurs at a lattice volume of $V(23 \text{ GPa})/V_0(0.1 \text{ MPa}) = 0.89$.

Various types of metal-insulator transitions and related phenomena in strongly correlated electron systems such as $3d$ transition metal oxides have been keenly studied [1]. 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 ($\Delta_{\text{eff}} \approx -3$ eV) and the electric and magnetic properties are dominated by oxygen hole character [2,3]: 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 $Fe^{4+}(O_6)^{12-}$. The dynamics of holes leads to a variety of ground states such as metallic antiferromagnetism with a screw spin structure for SFO [4,5], a metal ($T \geq 290$ K, orthorhombic) to semiconductor ($T < 290$ K, monoclinic) transition coupled to the breathing phonon mode in such a way as $2Fe^{3+}\underline{L} \leftrightarrow Fe^{3+}$ (large octahedron) $+ Fe^{3+}\underline{L}^2$ (small octahedron) for $CaFeO_3$ (CFO) [6–9], and metallic ferromagnetism with a relatively high T_C of 340 K and large moments of $4\mu_B/Fe$ and $2\mu_B/Co$ [10,11] for $SrFe_{1-x}Co_xO_3$ with $x \approx 0.5$ containing $Fe^{3+}\underline{L}$ and $Co^{3+}\underline{L}$ [12–14].

$Sr_{2/3}La_{1/3}FeO_3$ (SLFO), with a formal valence of $Fe^{11/3+}$, may be considered as SFO doped with electrons so that the hole concentration is decreased to $2/3$. Although the O $2p$ holes remain delocalized in SFO, those in SLFO become confined in two-thirds of the oxygen (111) layers, or the doped electrons become confined in one-third of these layers, so that two kinds of Fe sites are generated in such a way that $3(Fe^{3+}\underline{L}^{2/3})$ (paramagnetic metal, $T \geq 200$ K) $\leftrightarrow 2Fe^{3+} + Fe^{3+}\underline{L}^2$ [antiferromagnetic (AF) insulator, $T < 200$ K] [15–18]. An accompanying structural change is known to be much smaller [16–19] than for CFO.

Fe^{4+} oxides generally change their electronic properties remarkably under high pressure (HP) [20–23]. Most recently, we showed that the transition of CFO occurred at an almost constant temperature of 290 K below 17 GPa but disappears above 20 GPa [23].

In this Letter, we report the pressure effects on SLFO studied with ^{57}Fe Mössbauer spectroscopy and x-ray diffraction (XRD) using synchrotron radiation. Hereafter, for simplicity, we use the nominal valence and the terminology of charge disproportionation (CD) [6] such as $3Fe^{11/3+} \leftrightarrow 2Fe^{3+} + Fe^{5+}$.

The HP ^{57}Fe Mössbauer measurements were performed in transmission geometry using a diamond anvil cell (DAC) of Basset type [24]. ^{57}Fe-enriched (50%) sample powder, synthesized under high oxygen pressure [11], and a small ruby chip were enclosed in a hole with a diameter of 200 μm in a Re gasket. The pressure-transmitting medium was a 4:1 methanole:ethanol solution. The actual pressure was determined from the wavelength shift of the ruby line using the nonlinear pressure scale of Mao *et al.* [25]. A high-density γ-ray source of 370 MBq ^{57}Co in Rh was used. The velocity scale of the spectrum was relative to Fe at room temperature. The XRD measurements were carried out by using synchrotron radiation at BL-04B2 in SPring-8. The x-ray energy was 37.62 KeV as determined using CeO_2 as a control sample.

The most typical Mössbauer spectra are shown in Figs. 1a–1h. At ambient pressure a paramagnetic singlet corresponding to the average valence of $Fe^{11/3+}$ was observed above 210 K (Fig. 1a), while the low temperature spectra consisted of two magnetically split components with hyperfine fields of 46.3 T (Fe^{3+}) and 26.5 T (Fe^{5+}) at 5 K (Fig. 1b). The change around 200 K was consistent with the known first-order transition mentioned above [15]. Essentially the same behavior was observed up to 21 GPa, except for the decrease of the transition temperature
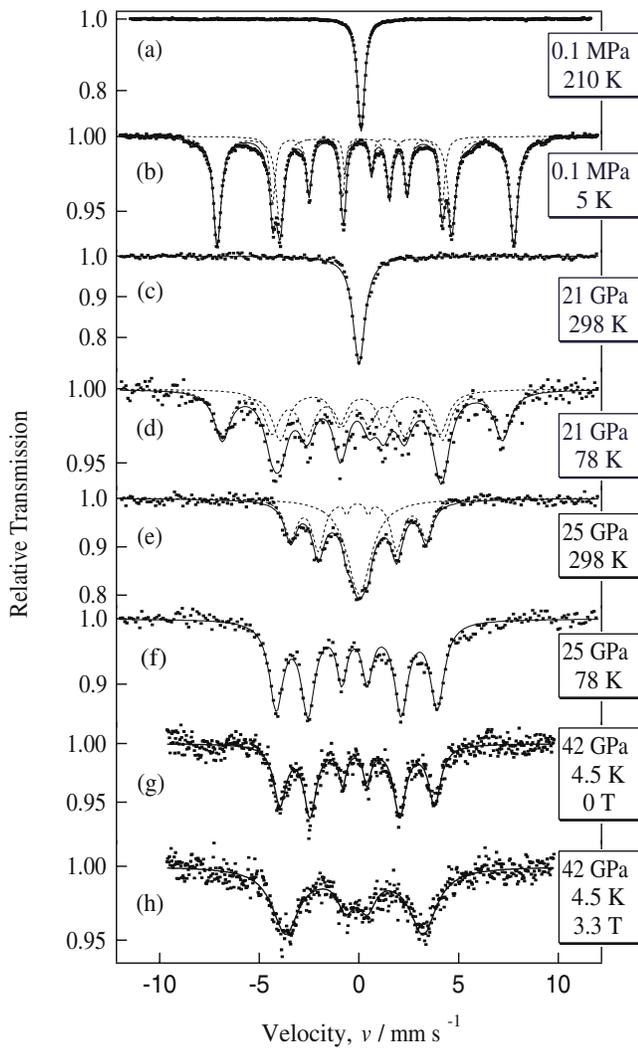
FIG. 1. Typical Mössbauer spectra obtained from $Sr_{2/3}La_{1/3}FeO_3$. The spectrum (h) was measured with a longitudinal external field of 3.3 T. The appreciable line broadening was due to the broadening of the source line caused by the application of the magnetic field. Velocity scale is relative to α-Fe at 298 K.

(165 K at 21 GPa), as revealed in the similarity of the spectra (compare Figs. 1c and 1d with Figs. 1a and 1b, respectively). By measuring the count rate at zero Doppler velocity as a function of temperature (Mössbauer thermal scanning method) it is possible to determine the transition temperature, $T_{CD} = T_{MO}$ (MO: magnetic ordering), at a given pressure in a relatively short time. The T_{CD} at 5 GPa was thus determined to be 189 K in the cooling process but 195 K in the heating process, a hysteretic behavior due to the first-order nature of the transition. At 21 GPa the temperature interval was further increased to 10 K; 175 K (cooling) and 165 K (heating). We thus conclude that the nature of the first-order transition was preserved up to 21 GPa although the transition temperature is decreased considerably with increasing pressure.

What happens in a pressure range of 21–25 GPa is drastic: The CD is suppressed but the magnetic transition temperature is suddenly increased above 400 K. The spectrum taken at 25 GPa and 298 K (Fig. 1e) contains an extra magnetically split sextet indicating such a high T_{MO}, and the uniqueness of the magnetic sextet indicates the suppression of the CD (Figs. 1e–1h). Another remarkable finding is the ferromagnetism of this novel HP phase. In the spectra measured in external fields up to 3.3 T the second and the fifth peaks tended to disappear and the hyperfine field was decreased from 24.2 to 21.5 T, indicating that the atomic moment was aligned parallel to the field (Figs. 1g and 1h). We thus conclude here that pressure switches the ground state from the AF and charge-disproportionated state to the novel ferromagnetic (FM) and charge-uniform state. Considering the inhomogeneity of pressure in the sample cell, the critical pressure has been estimated to be 23 GPa.

The pressure dependences of the Mössbauer parameters across the phase boundary at 300 and 6 K are plotted in Figs. 2a and 2b, respectively. The center shift at 300 K is monotonically decreased with increasing pressure, without any remarkable anomaly at 23 GPa. The magnetic hyperfine field of 21.2 T appearing in the HP phase remains almost constant up to 56 GPa, indicating that the magnetic transition temperature is far above 300 K, at least 400 K even at 23 GPa. A small quadrupole splitting has been found for the HP phase, but what this means is not clear to us because there has not been found any sign of structural transition around 23 GPa. The compression of the rhombohedral cell [15,16] is shown in Fig. 3. The pressure dependence was analyzed using the Brich-Murnaghan equation of state

$$P = \tfrac{3}{2}K_0(x^{7/3} - x^{5/3})[1 + \tfrac{3}{4}(K_0' - 4)(x^{2/3} - 1)],$$

where $x = V_0/V$, V is the volume at pressure P, V_0 is the zero-pressure volume, K_0 is the bulk modulus, and K_0' is its pressure derivative, at zero pressure. However, the scatter of the data points did not allow us to use both K_0 and K_0' as fitting parameters. For most materials, the value of K_0' is close to 4.0 and this has been adopted in the present work [26]. The best fit was obtained with $K_0 = 178$ GPa as shown using a solid line.

The LP-HP phase transition takes place at $V(23\ \text{GPa})/V_0 = 0.89$ at room temperature. The pressure dependence of the Mössbauer spectrum at 6 K indicates that the HP phase is stabilized also around 23 GPa, independent of temperature. The center shift for the HP phase seems, as expected, to be intermediate between those for the two components in the low-pressure (LP) phase, while the hyperfine field is almost the same as that of Fe^{5+} in the LP phase.

It is interesting here to compare the behavior of SLFO with that of SFO [27]. What separates SLFO from SFO definitely is the presence of the charge-disproportionated AF phase in the low-P, T region. At pressures high
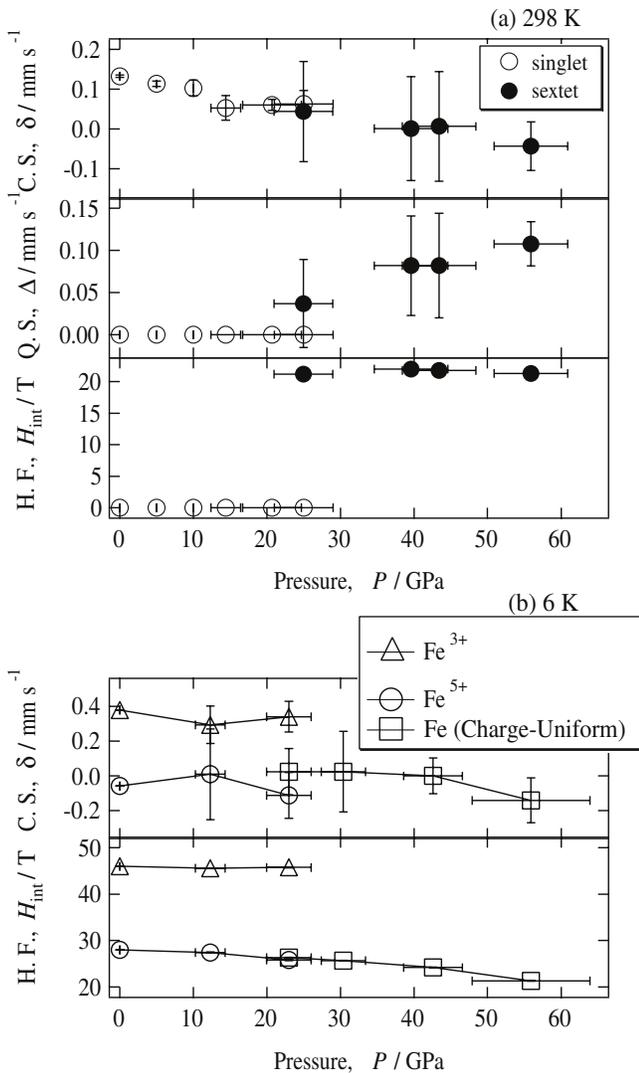
FIG. 2. (a) Center shift, quadrupole splitting, and hyperfine magnetic field measured at room temperature for $Sr_{2/3}La_{1/3}FeO_3$ as a function of pressure. The values for the charge-uniform singlet are denoted with (∘) and those for the charge-uniform sextet are denoted with (•). (b) The data at 6 K.

enough, similarity prevails down to low temperatures. Both these are charge uniform and FM with Curie temperatures well above 300 K, the center shifts, and the saturated hyperfine fields are about 0.0 mm s^{-1} and 25 T, respectively, and the structures are the same except for the slight rhombohedral distortion for SLFO.

We have thus 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 $e_g(Fe)$-$p_\sigma(O)$ parentage are delocalized and unpolarized. Comparing the e_g-p_σ hybridization and the t_{2g}-p_π hybridization, the former must be enhanced to a larger extent than the latter as the Fe-O distance is reduced under pressure. The small saturated hyperfine field of about 25 T results from the polarization of t_{2g} electrons only. Al-
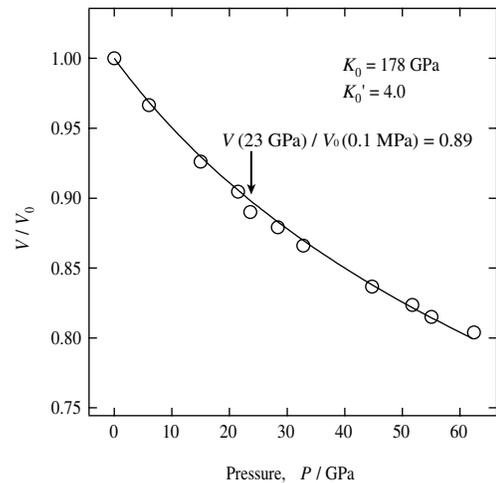
FIG. 3. Compression curve for $Sr_{2/3}La_{1/3}FeO_3$ at room temperature. The solid line is a fit using the Brich-Murnaghan equation of state. Parameters derived from this fit are given in the figure. The arrow indicates the critical pressure [at $V(23\ GPa)/V_0(0.1\ MPa) = 0.89$] for the transformation from the paramagnetic charge-uniform state to the ferromagnetic charge-uniform state.

though yet to be tested experimentally, saying strictly, the HP phase of SLFO must be metallic. The phase diagram together with the schematic band structures is illustrated in Fig. 4. The FM and metallic HP phase is, however, not the one expected from a band structure calculation where the hole carries are delocalized but the $e_g(Fe)$ electrons are
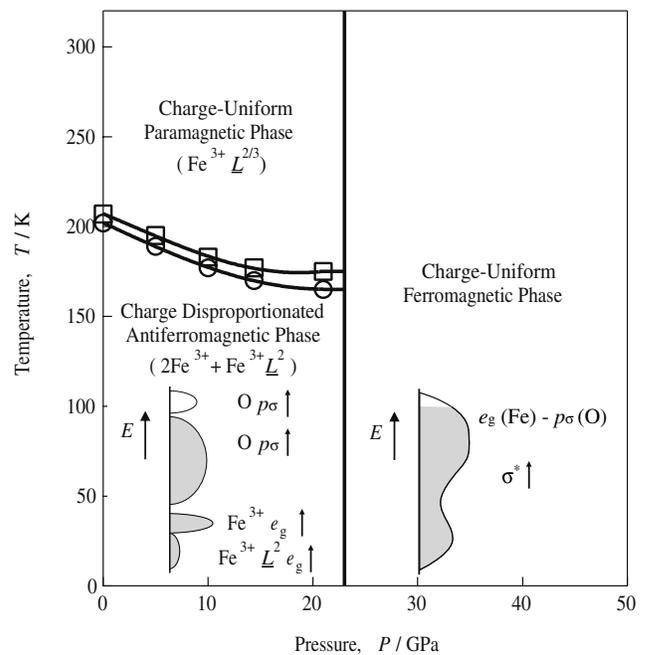
FIG. 4. P-T magnetic phase diagram of $Sr_{2/3}La_{1/3}FeO_3$. The critical temperature of the CD and the MO temperature as a function of pressure are shown. The values obtained from the critical temperature of the CD and the magnetic ordering temperature are denoted by (□) in the heating and (∘) in the cooling.

localized and polarized [19]. A calculation assuming small unit cells is desired.

In summary, we discovered that the contraction of the unit cell volume to $V(23 \text{ GPa})/V_0 = 0.89$ induces the switching of the ground state of $Sr_{2/3}La_{1/3}FeO_3$ from the charge-disproportionated AF state to the charge-uniform (most probably metallic) FM state.

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1211 (1998).

[2] A. E. Bocqest, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, N. Kimizuka, Y. Takeda, and M. Takano, Phys. Rev. B **45**, 1561 (1992).

[3] N. Hayashi, T. Terashima, and M. Takano, J. Mater. Chem. (to be published).

[4] J. B. MacChesney, R. C. Sherwood, and J. F. Potter, J. Chem. Phys. **43**, 1907 (1965).

[5] T. Takeda, Y. Yamaguchi, and H. Watanabe, J. Phys. Soc. Jpn. **33**, 967 (1972).

[6] M. Takano, N. Nakanishi, Y. Takeda, S. Naka, and T. Takada, Mater. Res. Bull. **12**, 923 (1977).

[7] S. Morimoto, T. Yamanaka, and M. Tanaka, Physica (Amsterdam) **237B–238B**, 66 (1997).

[8] P. M. Woodward, D. E. Cox, E. Moshopoulou, A. W. Sleight, and S. Morimoto, Phys. Rev. B **62**, 844 (2000).

[9] T. Takeda et al., Solid State Sci. **2**, 673–687 (2001).

[10] P. Bezdicka, L. Fournès, A. Wattiaux, J. C. Grenier, and M. Pouchard, Solid State Commun. **91**, 501 (1994).

[11] S. Kawasaki, M. Takano, and Y. Takeda, J. Solid State Chem. **121**, 174 (1996).

[12] R. H. Potze, G. A. Sawatzky, and M. Abbate, Phys. Rev. B **51**, 11 501 (1995).

[13] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B **56**, 1290 (1997).

[14] J. Okamoto et al., Phys. Rev. B **62**, 4455 (2000).

[15] M. Takano et al., J. Solid State Chem. **39**, 75 (1981).

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

[17] T. Ishikawa, S. K. Park, T. Katsufuji, T. Arima, and Y. Tokura, Phys. Rev. B **58**, R13 326 (1998).

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

[19] J. Matsuno, T. Mizokawa, A. Fujimori, K. Mamiya, Y. Takeda, S. Kawasaki, and M. Takano, Phys. Rev. B **60**, 4605 (1999).

[20] M. Takano, S. Nasu, T. Abe, K. Yamamoto, S. Endo, Y. Takeda, and J. B. Goodenough, Phys. Rev. Lett. **67**, 3267 (1991).

[21] S. Nasu, T. Abe, K. Yamamoto, S. Endo, M. Takano, and Y. Takeda, Hyperfine Interact. **67**, 529 (1991).

[22] G. Kh. Rosenberg, A. P. Milner, M. P. Pasternak, G. R. Hearne, and R. D. Taylor, Phys. Rev. B **58**, 10 283 (1998).

[23] T. Kawakami, S. Nasu, T. Sasaki, S. Morimoto, S. Endo, S. Kwasaki, and M. Takano, J. Phys. Soc. Jpn. **70**, 5701 (2001).

[24] W. A. Bassett, T. Takahashi, and P. W. Stook, Rev. Sci. Instrum. **38**, 37 (1967).

[25] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[26] J. R. Smyth, S. D. Jacobsen, and R. M. Hazen, Rev. Mineral. Geochem. **41**, 157 (2000).

[27] S. Nasu, K. Wada, K. Kuzushita, S. Morimoto, and M. Takano, in Proceedings of the International Conference on High Pressure Science and Technology (AIRAPT-17), Honolulu, HI, 1999, edited by M. H. Manghnani et al. (Universities Press Ltd., Hyderabad, India, 2000), pp. 763–766.