Pressure-Induced High-Spin to Low-Spin Transition in $CaFeO_3$

M. Takano,[1],[a] S. Nasu,[1] T. Abe,[1] K. Yamamoto,[1] S. Endo,[1] Y. Takeda,[2]
and J. B. Goodenough,[3]

[1]*Research Center for Extreme Materials and Department of Materials Physics,*
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan
[2]*Department of Chemistry, Faculty of Engineering, Mie University, Tsu 514, Japan*
[3]*Center for Materials Science and Engineering, ETC 5.160, University of Texas at Austin, Austin, Texas 78712-1084*

(Received 29 July 1991)

In situ ^{57}Fe Mössbauer spectroscopy and x-ray diffraction on $CaFeO_3$ (Fe^{4+}:$t_2^3e^1$) under pressure have revealed a first-order high-spin ($S=2$) to low-spin ($S=1$) transition near 30 GPa. The spin and structure transition is an alternative manifestation of the electronic instabilities of the σ-bonding Fe-O-Fe orbitals; at atmospheric pressure a second-order disproportionation $2Fe^{4+} \leftrightarrow Fe^{4-\delta} + Fe^{4+\delta}$, $0 \leq \delta \leq 1$, occurs at a $T_t \approx 290$ K. Such instabilities found at the transition from localized to itinerant σ^*-band electrons reflect a sensitivity to interactions with the lattice.

PACS numbers: 62.50.+p, 61.50.Em, 71.70.Ch, 76.80.+y

The recent discovery of high-temperature superconductivity in copper oxides [1] and a new interpretation of photoemission spectroscopy data [2] have revived interest within the condensed-matter physics community in a fuller understanding of the 3*d* transition-metal oxides. For example, spectroscopic data [3] appear to indicate that the band gaps of insulating late transition-metal oxides like NiO are of a ligand-to-metal charge-transfer type. Perovskite oxides have a relatively simple structure and allow late 3*d* transition metals to be stabilized in unusually high valence states. An increase in formal valency makes the *M*-O bond more covalent, thereby increasing the admixture of O:2*p* and *M*:3*d* wave functions in the electronic states near the Fermi energy. Transitions from more ionic to more covalent bonding may enhance the importance of electron-lattice interactions.

The properties of the perovskites $LaMnO_3$, $CaFeO_3$, and $SrFeO_3$ provide an interesting comparison. Each compound contains an octahedral-site transition-metal ion with a high-spin $d^4 = t_2^3e^1$ configuration at atmospheric pressure. In each case the half-filled t_2^3 orbitals are localized, while an evolution in the strength of the e-O:$2p_\sigma$-e interactions imparts quite distinctive properties to each compound. In $LaMnO_3$, the *e* electrons are sufficiently localized that a classical cooperative Jahn-Teller distortion removes the *e*-orbital degeneracy [4]. Stronger covalent mixing at an Fe^{4+} versus a Mn^{3+} ion increases the ca. 180° e-O:$2p_\sigma$-e interactions, and the localized *e* orbitals become transformed into a narrow σ^* band that is one-quarter filled [5]. Such a band would contribute itinerant-electron ferromagnetic coupling to compete with antiferromagnetic t_2^3-O:$2p_\pi$-t_2^3 superexchange interactions; it would also give metallic conductivity to lowest temperatures. Indeed, $SrFeO_3$ is metallic down to 4 K [6] and has a ferromagnetic nearest-neighbor interaction [7]. On the other hand, $CaFeO_3$ undergoes a second-order phase transition that is typical of a narrower σ^* band at the transition from localized to itinerant-electronic behavior [8]. The transition is a disproportionation reaction expressed formally as

$$2Fe^{4+}(t_2^3\sigma^{*1}) \leftrightarrow Fe^{4-\delta}(t_2^3e^{1+\delta}) + Fe^{4+\delta}(t_2^3e^{1-\delta}) ,$$

where $\delta=0$ for $T > 290$ K increases continuously with decreasing temperature below 290 K; typically δ approaches unity at low temperatures.

A recent x-ray photoemission and ultraviolet photoemission spectroscopic study of $SrFeO_3$ deduced a very small charge-transfer energy of 0–1 eV and also a small charge fluctuation energy, $\ll 1$ eV, for $d^4 + d^4 \rightarrow d^5 + d^4\underline{L}$ ($\underline{L}$ denotes ligand hole) as the common background of the itinerant character of $SrFeO_3$ and the charge disproportionation of $CaFeO_3$ [9]. The disproportionation could be interpreted naturally as the formation of a charge-density wave in which a cooperative oxygen displacement introduces ca. 180° Fe^{5+}-O $\cdots$ Fe^{3+} interactions in all three crystallographic directions. Such a freezing out of a breathing phonon mode has found theoretical support [10]. Where the e-O:$2p_\sigma$-e interactions are stronger, as appears to be the case of $SrFeO_3$ in spite of the larger lattice parameter, the quarter-filled σ^{*1} band of itinerant electrons does not disproportionate.

Mössbauer spectroscopic studies [8,11] of the systems $Ca_{1-x}Sr_xFeO_3$ and $Sr_{1-y}La_yFeO_3$ have revealed a *delicate balance* between the relative strengths of the *Fe-O-Fe interactions* and the *electron-phonon* interactions for the disproportionation reaction to occur. For example, the disproportionation parameter δ was found experimentally to depend monotonically upon the Sr content in each solid solution. It is only pure $SrFeO_3$ that retains the single Fe^{4+} ($\delta=0$) state down to lowest temperatures.

High pressure provides an alternative physical variable in which to compare these three compounds. For example, we may anticipate a transition from high-spin to low-spin Fe^{4+} as an alternative to disproportionation for the creation of empty, itinerant σ^* states and localized electrons—in this case as localized t_2^4 configurations; according to theoretical calculations [12], the gap between the two spin states tends to collapse quickly as the Fe-O bond is contracted. High pressure also changes the relative strengths of the antiferromagnetic t_2^3-O:$2p_\pi$-t_2^3 and either ferromagnetic e^1-O:$2p_\sigma$-e^0 superexchange interactions or ferromagnetic correlations within a quarter-filled σ^{*1} band of itinerant-electron states. We have reported previously [13] on the effect of hydrostatic pressure on $SrFeO_3$; here we report a pressure-induced high-spin to low-spin transition in $CaFeO_3$ found by *in situ* Mössbauer spectroscopy. The transition is accompanied by a serious structural change as found *in situ* by x-ray diffraction (XRD).

$Ca^{57}FeO_3$ was prepared by oxidation of $Ca_2{}^{57}Fe_2O_5$ in a belt high-pressure apparatus using $KClO_4$ as an oxygen source under 6 GPa at 1050 °C for 30 min. The product was shown to be single phase by XRD and Mössbauer spectroscopy. At room temperature, $CaFeO_3$ has the tetragonal perovskite structure with $a_t = 5.332$ Å and $c_t = 7.550$ Å, where $a_t/\sqrt{2} \approx c/2 \approx 3.8$ Å is a typical cubic-perovskite lattice constant [14]. Mössbauer measurements under pressure up to 51 GPa were performed with a diamond-anvil cell of the Bassett type charged with the sample powder in a rhenium gasket with a 0.3-mm-diam hole [12]. The applied pressure was monitored by the fluorescent shift of ruby powder mixed with the sample. XRD was also performed with a similar diamond-anvil cell. A new sample of $SrFeO_3$ was also prepared in the same manner and used for XRD under pressure up to 53 GPa.

The pressure dependence of the room-temperature Mössbauer spectrum is shown in Fig. 1. The ambient-pressure spectrum of a sample containing natural iron, Fig. 1(a), consists of a single narrow line with a CS of 0.048 mm/s relative to α-Fe. At 21 GPa, Fig. 1(b), a broadened singlet and a weak magnetic component are mixed; the broadening is a saturation effect caused by the packing of the ^{57}Fe-enriched (> 90%) sample in the tiny pressure cell. The magnetic component comes from $Ca_2Fe_2O_5$, which is stable under low oxygen pressures and appears to have formed either during a long-term storage of the sample in a desiccator or from heating in the laser beam used for high-pressure calibration. Moreover, the singlet absorption peak from $CaFeO_3$ is more strongly broadened by saturation than is the magnetic component due to the $Ca_2Fe_2O_5$ impurity, which emphasizes the magnetic contaminant.

At 30 GPa, Fig. 1(c), the central singlet peak is beginning to be replaced by a magnetic pattern. At higher pressure, the magnetic splitting becomes clear. Like $SrFeO_3$, but unlike $CaFeO_3$ in its disproportionated state, $CaFeO_3$ under pressure contains only Fe^{4+} ions at room temperature. However, unlike $SrFeO_3$, the CS of $CaFeO_3$ is reduced abruptly at 30 GPa by 0.25 mm/s and a magnetic hyperfine field of $H_i = 16$ T appears, see Fig. 1(e). The H_i value remains constant at higher pressures. The broadened spectrum in the transition region—Fig. 1(c)—can be reproduced by superimposing the paramagnetic singlet of Fig. 1(b) and the magnetic pattern of Fig. 1(d). We are thus led to the conclusion that a first-order transition occurs at a $P_c \approx 30$ GPa.

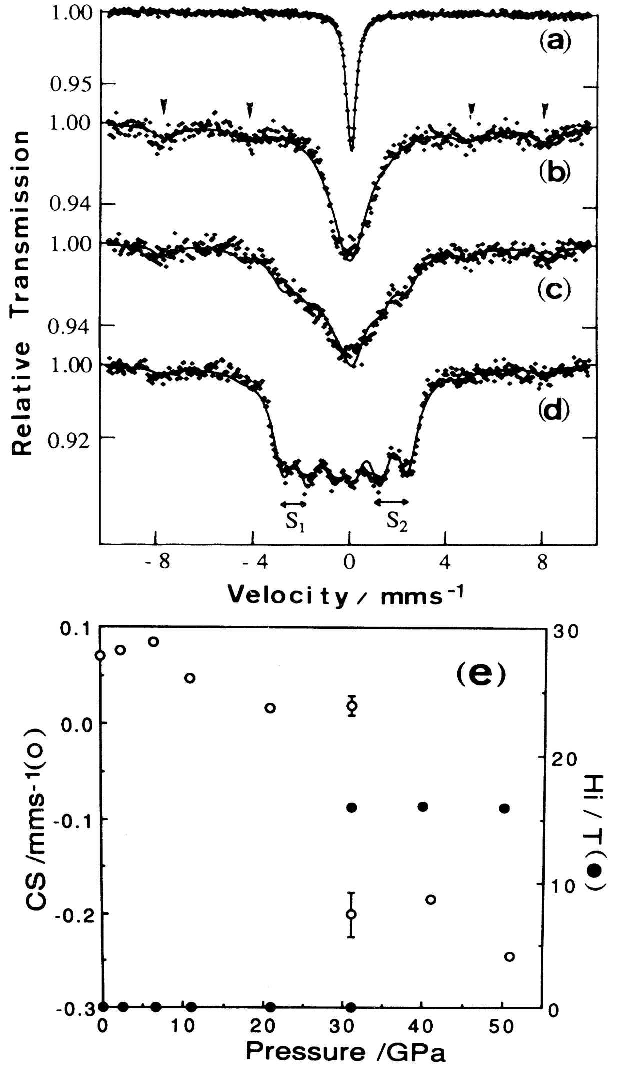

FIG. 1. Pressure-dependent Mössbauer spectra of $CaFeO_3$ at room temperature. Applied pressures are (a) 0.1 MPa, (b) 21 GPa, (c) 30 GPa, and (d) 41 GPa ($S_1 - S_2 = -0.10\ \mathrm{mm\,s^{-1}}$). The sample for (a) contains natural iron, while the other spectra were obtained with an ^{57}Fe-enriched sample. Solid lines are the computer-fitted results. The peaks marked by arrows in (b) come from $Ca_2Fe_2O_5$ (see text). Pressure-dependent center shift (CS) and magnetic hyperfine field (H_i) data for $CaFeO_3$ are shown in (e).

High-pressure XRD shows a change on crossing the transition from the $\sqrt{2}a \times \sqrt{2}a \times 2a$ tetragonal structure to a $2a \times 2a \times 2a$ orthorhombic structure, where a represents the basic perovskite parameter. Shown in Fig. 2 is the pressure-induced splitting of the (220) peak into the (400) and (040) peaks of the high-pressure phase as well as the pressure dependence of the lattice constants on

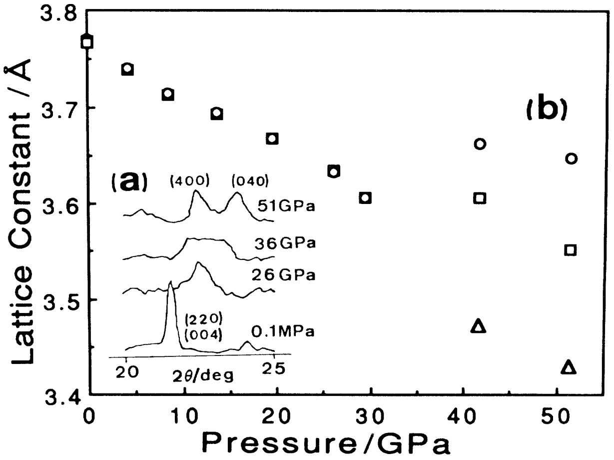

FIG. 2. Pressure-dependent (a) XRD peaks and (b) lattice constants for the hypothetical unimolecular perovskite cell for $CaFeO_3$. In reality $CaFeO_3$ has a tetramolecular tetragonal cell of $a_t \times a_t \times c_t$ for $P \leq 30$ GPa and an octomolecular orthorhombic one of $a_0 \times b_0 \times c_0$. Plotted here are (○) $a_t/\sqrt{2}$ and (□) $c_t/2$ for $P \leq 30$ GPa, and (○) $a_0/2$, (△) $b_0/2$, and (□) $c_0/2$ for $P > 30$ GPa.

crossing the transition. The orthorhombic distortion of the high-pressure phase is quite remarkable. The appearance of a quadruple interaction in the Mössbauer spectra of the high-pressure phase [Fig. 1(d)] provides evidence of the structural change with a microscopic probe. On release of pressure the original low-pressure phase is recovered as seen by both Mössbauer and XRD measurements.

On the other hand, isotropic compression of $SrFeO_3$ up to 53 GPa causes a considerable increase in the Néel temperature T_N ($\simeq 300$ K at 19 GPa), but it does not induce any disproportion or any other transition [13]. The structure remains cubic over the pressure range studied without any noticeable anomaly at T_N.

The first-order phase change at a $P_c \approx 30$ GPa appears to be a high-spin to low-spin transition for the following reasons. First, the drop in CS by ~ 0.25 mm/s is quite remarkable. Such a drop requires a significant electron-density redistribution such that the s-electron density at an ^{57}Fe nucleus is enhanced by $\Delta\rho(0) \sim 0.8$ a.u. [15] in the high-pressure phase. Although we have no quantitative estimates, the observed change in CS is consistent with what has been found at high-spin to low-spin transitions in various iron compounds. Second, the pressure independence of H_i signals that saturation has been reached, yet its value of about 16 T is significantly smaller than the 23.3 T found for $SrFeO_3$ at 53 GPa [13]; it is also smaller than the saturated H_i values of $SrFeO_3$ and $CaFeO_3$ at ambient pressure. The $H_i = 33$–34 T observed for high-spin Fe^{4+} ($S = 2$) [8,11] may be expected to be scaled down by a factor of 2 at a low-spin Fe^{4+} ($S = 1$) ion in high-pressure $CaFeO_3$.

A low-spin state occurs where the cubic-field splitting Δ_c exceeds the intra-atomic-exchange splitting Δ_{ex}. It is reasonable to assume that an external pressure increases Δ_c through a more enhanced increase in covalency for σ vs π bonding; both $CaFeO_3$ and $SrFeO_3$ could exhibit a high-spin to low-spin transition. In order to understand why the low-spin state of $CaFeO_3$ is stabilized for a unit-cell volume $V \leq 47$ Å^3 whereas $SrFeO_3$ remains cubic and retains the high-spin state even for $V = 47$ Å^3 consideration of the differences between Ca^{2+} and Sr^{2+} ions is required.

The Ca^{2+} ion is distinguished from the Sr^{2+} ion not only by its smaller size (1.35 vs 1.44 Å for twelvefold coordination), but also by the greater covalent component in the Ca-O bond. The smaller size of the Ca^{2+} ion induces a distortion of the structure from cubic to tetragonal symmetry whereas $SrFeO_3$ remains cubic to lowest temperatures. The cubic perovskite retains 180° Fe-O-Fe bonding whereas the Fe-O-Fe bonds are bent from 180° in tetragonal $CaFeO_3$. This bending makes the Fe-O bond length greater than half the Fe-Fe distance; it also reduces the strength of the Fe-O-Fe interactions, which is probably why the σ^* band in $CaFeO_3$ appears to be narrower than that in $SrFeO_3$ despite the smaller lattice parameter of $CaFeO_3$.

The covalent component of the A-O bond of an ABO_3 perovskite competes directly with the t_2 orbitals of a transition-metal B cation for the O:$2p_\pi$ electrons. The difference in covalency between the Ca^{2+} and Sr^{2+} ions makes the π component of the covalent Fe-O bond smaller in $CaFeO_3$ than in $SrFeO_3$. Moreover, bending of the Fe-O-Fe bond from 180° reduces the strength of the Fe-O-Fe interactions, but it does not reduce the σ component of the Fe-O bond covalency. Thus, Δ_c in $CaFeO_3$ would be increased relative to Δ_c in $SrFeO_3$, and it should take a smaller increase in Δ_c to make $\Delta_c/\Delta_{ex} \approx 1$ in the case of $CaFeO_3$, which would account for a lower P_c in $CaFeO_3$ than in $SrFeO_3$. Another mechanism mediated by a coupling with the lattice system is a strain-induced splitting and crossing of the highest up-spin levels and the lowest down-spin levels. According to theoretical estimations [12], the gap between the two spin states for a regular $(FeO_6)^{8-}$ octahedron embedded in a Madelung potential representing the host lattice decreases with decreasing bond distance and finally vanishes at $d_{Fe\text{-}O} \simeq 1.7$ Å ($V \simeq 40$ Å^3 for a cubic unit cell). However, the gap may be collapsed at a larger average Fe-O distance if the distortion of the octahedron is serious enough to cause large splittings of the relevant levels. A broader σ^* band in $SrFeO_3$ may allow a more gradual crossover to the low-spin state without any structural distortion.

As noted above, $dH_i/dP \approx 0$ in high-pressure $CaFeO_3$ indicates a magnetically saturated state. From the Brillouin function for $S = 1$ and a saturation $H_i = 16$ T, we estimate a magnetic transition temperature $T_m \gtrsim 800$ K, which is much higher than the $T_N = 116$ K for the high-spin state under ambient pressure. The low-spin t_2^4-O:$2p_\pi$-t_2^4 antiferromagnetic superexchange interactions have no ferromagnetic competition from the empty σ-bonding orbitals. By way of contrast, ferromagnetic $SrRuO_3$ ($T_c = 160$ K) contains degenerate and delocalized t_2 orbitals forming a narrow π^* band that is two-thirds filled. A narrower π^* band in slightly distorted $CaRuO_3$ gives a negative Weiss constant in the Curie-Weiss paramagnetic susceptibility and remains paramagnetic down to 4 K [16]. The localized t_2^4-O-t_2^4 configurations in $CaFeO_3$ give a strong antiferromagnetic superexchange interaction.

In summary, high-pressure Mössbauer spectroscopy and XRD have demonstrated the existence of a first-order phase change at a critical pressure $P_c \approx 30$ GPa from a high-spin to a low-spin state at the Fe^{4+} cations of $CaFeO_3$. Since $CaFeO_3$ exhibits a second-order disproportionation into $Fe^{(4+\delta)}$ and $Fe^{(4-\delta)}$ below a transition temperature $T_t = 290$ K at ambient pressure, the low-spin phase represents a third electronic state in $CaFeO_3$. From the hyperfine field in the high-pressure phase, the low-spin $CaFeO_3$ appears to be antiferromagnetic with a Néel temperature estimated to be $T_N \gtrsim 800$ K. The different electronic behavior of $SrFeO_3$ has been rationalized on the basis of the larger size of the Sr^{2+} ion and smaller covalent component in the Sr-O bond.

(a)Permanent address: Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan.

[1] J. G. Bednorz and K. A Müller, Z. Phys. **64**, 189 (1986).
[2] J. Zaanen *et al.*, Phys. Rev. Lett. **55**, 418 (1985).
[3] A. Fujimori *et al.*, Phys. Rev. B **42**, 7580 (1990).
[4] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).
[5] C. Gleitzer and J. B. Goodenough, Struct. Bonding **61**, 1 (1985).
[6] J. B. MacChesney *et al.*, J. Chem. Phys. **43**, 1907 (1965).
[7] T. Takeda *et al.*, J. Phys. Soc. Jpn. **33**, 967 (1972).
[8] M. Takano *et al.*, Mater. Res. Bull. **12**, 923 (1977).
[9] A. E. Bocquet *et al.*, Phys. Rev. B (to be published).
[10] H. Adachi and M. Takano, J. Solid State Chem. **93**, 556 (1991).
[11] P. K. Gallagher *et al.*, J. Chem. Phys. **41**, 2429 (1964); M. Takano *et al.*, J. Solid State Chem. **39**, 75 (1981). See a review, M. Takano and Y. Takeda, Bull. Inst. Chem. Res., Kyoto Univ. **61**, 406 (1983).
[12] H. Adachi and M. Takano (unpublished).
[13] S. Nasu *et al.*, Hyperfine Interact. (to be published).
[14] Y. Takeda *et al.*, Mater. Res. Bull. **13**, 61 (1978).
[15] R. Ingalls, A. Van der Woude, and G. A. Sawatzky, in *Mössbauer Isomer Shifts,* edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), Chap. 7.
[16] J. B. Goodenough, Prog. Solid State Chem. **5**, 145 (1971); T. C. Gibb *et al.*, J. Solid State Chem. **11**, 17 (1974).