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High-pressure Mössbauer study of perovskite iron oxides

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Abstract

The perovskite oxides CaFeO_3 and $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ have been investigated by high-pressure ^{57}Fe Mössbauer spectroscopy. The critical temperatures of the charge disproportionation (CD) and the magnetic order (MO) have been determined as a function of pressure. In CaFeO_3 the CD ($2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$) occurs at an almost constant temperature of 290 K in the pressure range of 0–17 GPa. Above 20 GPa, the CD is suppressed. The MO temperature of 125 K at an ambient pressure rises to 300 K at 34 GPa. In $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ the CD ($3\text{Fe}^{11/3+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}^{5+}$) and the MO occur at the same temperature up to 21 GPa, which decreases from 207 to 165 K with increasing pressure. Above 25 GPa, however, the MO temperature rises above 400 K.

1. Introduction

One of the most interesting problems in condensed-matter systems is metal–insulator transition driven by the correlation effects associated with electron–electron interaction [1]. A charge ordering in perovskite compounds often occurred with their metal–insulator transitions.

The high valence state of Fe in SrFeO_3 , CaFeO_3 and $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ among the perovskite iron oxides is quite important to study, because they show a charge disproportionation (CD) and a magnetic order (MO).

The crystal structure of CaFeO_3 is of GaFeO_3 type [2–5]. CaFeO_3 shows a metal–insulator transition at 290 K. At the same temperature the Mössbauer spectrum begins to split gradually into two paramagnetic absorption lines suggesting a CD ($2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$) with two different valence states with decreasing temperature in a second-order transition. CaFeO_3 below 125 K shows an antiferromagnetic long-range order with a helical spin structure. An x-ray photoemission study of CaFeO_3 deduces that the Fe^{4+} and Fe^{5+} states may consequently

be considered as Fe^{3+} states accompanied by a single and double oxygen holes, $d^5\bar{\underline{L}}$ and $d^5\bar{\underline{L}}^2$, respectively. The CD may be written as $2d^5\bar{\underline{L}} \rightarrow d^5 + d^5\bar{\underline{L}}^2$ [6].

$\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ in the solid solution system shows metal–insulator transition with charge order and antiferromagnetic order at the same temperature of 207 K with narrow thermal hysteresis, suggesting the occurrence of a first-order phase transition. Such an anomalous valence state as well as the real-space ordering of valence-skipping sites is confirmed by neutron scattering measurements [7]. The disproportionated charges are condensed within the (111) plane of the cubic perovskite. From the magnitudes of the respective staggered moments on the Fe sites, estimated from neutron diffraction, the Fe valence is estimated to be +3.4 and +4.2, respectively; these may correspond to the Fe^{3+} and Fe^{5+} detected by Mössbauer spectroscopy. Photoemission spectroscopy and unrestricted Hartree–Fock band structure calculation of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ suggest that the ordering of holes on the oxygen sites plays an essential role in realizing the CD ground state [8].

In this investigation, we examined the effects of pressure on the CD, the MO and the crystal structure of CaFeO_3 and $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ by ^{57}Fe Mössbauer spectroscopy. The results obtained are summarized as P – T magnetic phase diagrams of CaFeO_3 and $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$.

2. Experimental details

^{57}Fe Mössbauer measurements for CaFeO_3 and $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ have been performed under high pressure using a diamond anvil cell (DAC). ^{57}Fe -enriched (50%) $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ powder is synthesized under high oxygen pressure and used as an absorber in transmission geometry. The DAC used in this experiment is of Basset type. The powder sample and a small ruby chip are enclosed in a hole of diameter 200 μm in an Re gasket. The pressure-transmitting medium used is a 4:1 methanol:ethanol solution. The actual pressure is determined from the wavelength shift of the ruby line. All of the Mössbauer spectra have been measured by combination of a specimen powder in DAC and a velocity transducer attached with 370 MBq ^{57}Co in Rh as a high-density γ -ray source. The velocity scale of the spectrum is relative to α -Fe at room temperature.

3. Results and discussion

High-pressure ^{57}Fe Mössbauer spectra of CaFeO_3 are shown in figure 1. At an ambient pressure and at 304 K, the spectrum is a paramagnetic singlet (Fe^{4+}) (figure 1(a)). The spectrum at 130 K consists of two paramagnetic singlets (Fe^{3+} and Fe^{5+}) (figure 1(b)). At 5 K, two components of the magnetically split sextets are observed and their hyperfine magnetic fields are determined as 42.2 T (Fe^{3+} , $t_{2g}^3 e_g^2$) and 28.6 T (Fe^{5+} , $t_{2g}^3 e_g^0$) for high-spin configurations (figure 1(c)).

At the average pressure of 17 GPa, two different hyperfine magnetic fields appear: 34.2 T (Fe^{3+}) and 19.3 T (Fe^{5+}) at 78 K (figure 1(d)), which implies that charge- and spin-ordered lattices exist at 78 K below 17 GPa. However, with increase of the pressure to an average value of 20 GPa, the magnetically split components change drastically and a new magnetically split single component (Fe^{4+}) appears (figure 1(e)), which implies that the CD is suppressed by the high pressure above 20 GPa. The magnitude of the hyperfine magnetic field, whose spectrum first appears in the magnetically split sextet at 298 K and 34 GPa, is determined as 16.6 T (figure 1(f)). The magnitude of the hyperfine magnetic field is reduced to 16.3 T at 65 GPa and 6 K, which suggests that the Fe^{4+} completely transforms to the low-spin state ($S = 1$) (figure 1(g)). T_{CD} and T_{MO} as functions of temperature and pressure are shown in figure 2 as a P – T phase diagram. T_{CD} and T_{MO} are shown up to 65 GPa in the temperature range of 6–400 K [9].

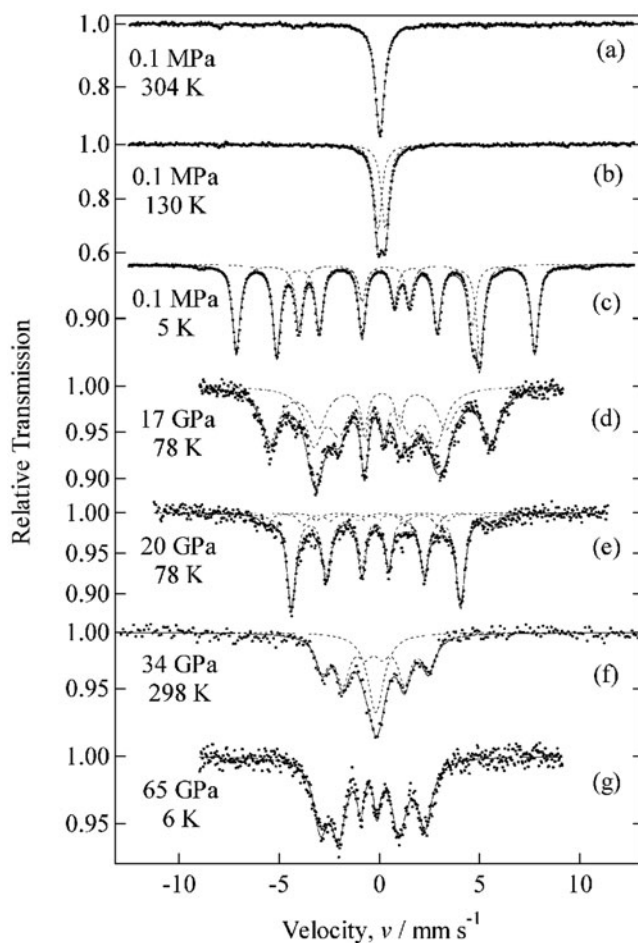


Figure 1. Typical pressure-dependent Mössbauer spectra obtained for CaFeO_3 at various temperatures.

The high-pressure ^{57}Fe Mössbauer spectra of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ are shown in figure 3. At ambient pressure and 298 and 210 K the spectrum is a paramagnetic singlet of average valence $\text{Fe}^{11/3+}$, as shown in figures 3(a) and (b). With decrease of the temperature below 200 K the CD and the MO occur simultaneously as shown in figure 3(c). At 5 K the hyperfine magnetic fields are determined as 46.3 T for Fe^{3+} and 26.5 T for Fe^{5+} , whose values correspond to the Fe with high-spin configurations, as shown in figure 3(d). $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ shows a first-order phase transition which is a simultaneous CD and MO transition at ambient pressure. At 10 GPa and 187 K, the spectrum is a paramagnetic singlet of $\text{Fe}^{11/3+}$. At 173 K, just below T_{MO} , the spectrum shows the occurrence of both the CD and the MO, as shown in figures 3(e) and (f). At pressure between 21 and 25 GPa the Mössbauer spectra are drastically changed and the CD is suppressed although T_{MO} suddenly increases above 400 K at 25 GPa. At 21 GPa and 298 K the spectrum is still a paramagnetic singlet. At 21 GPa and 78 K, the spectrum consists of two magnetically split sextets showing the CD. At 25 GPa and 298 K, the spectrum shows an extra magnetically split sextet. At 78 K, the spectrum is only one magnetically split sextet, in which the CD is suppressed by the high pressure, as shown in figures 3(g)–(j). According

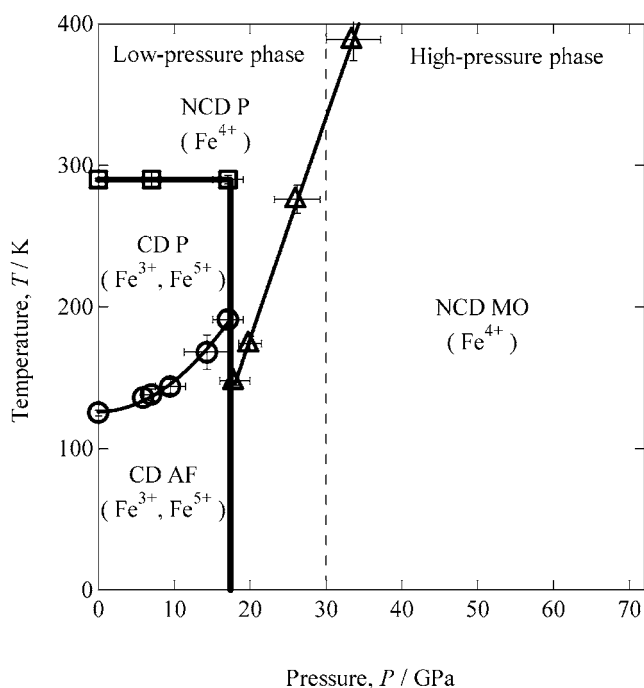


Figure 2. The P - T phase diagram of CaFeO_3 . The critical temperature of the CD and the MO temperature as a function of pressure are shown.

to the measurements of the pressure dependence, the critical pressure for vanishing of the CD reaction is determined as about 23 GPa. T_{CD} and T_{MO} as a function of pressure are shown in figure 4.

4. Conclusions

The p-d hybridization between O 2p and Fe 3d is enhanced with a reduction in Fe-O distance by external pressure. In CaFeO_3 the MO temperature increases with increase of pressure, but T_{CD} does not show any significant change up to 17 GPa and is suddenly suppressed above 20 GPa. Different pressure dependences on the charge and spin order in CaFeO_3 might be interpreted as follows. The CD is controlled mainly by holes and the MO is enhanced by the electron transfer between oxygen and iron.

In $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ the appearance of the CD state below 21 GPa suggests that the localization of the charge at the Fe sites occurs and the resultant Mössbauer spectra consist of two components arising from Fe^{3+} and Fe^{5+} at low temperatures. The spectra above 25 GPa each consist of a single component with an average valence state of $\text{Fe}^{11/3+}$, since the p-d hybridization is enhanced by the pressure and the collective motion of holes can occur between Fe sites. As a result of the collective motion, $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ might show good electrical conductivity, for which appropriate experimental evidence has not yet been obtained. The characteristics of the oxygen holes in $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ and CaFeO_3 with the strong p-d hybridization under high pressure may play an important role in the understanding of its transport and magnetic properties.

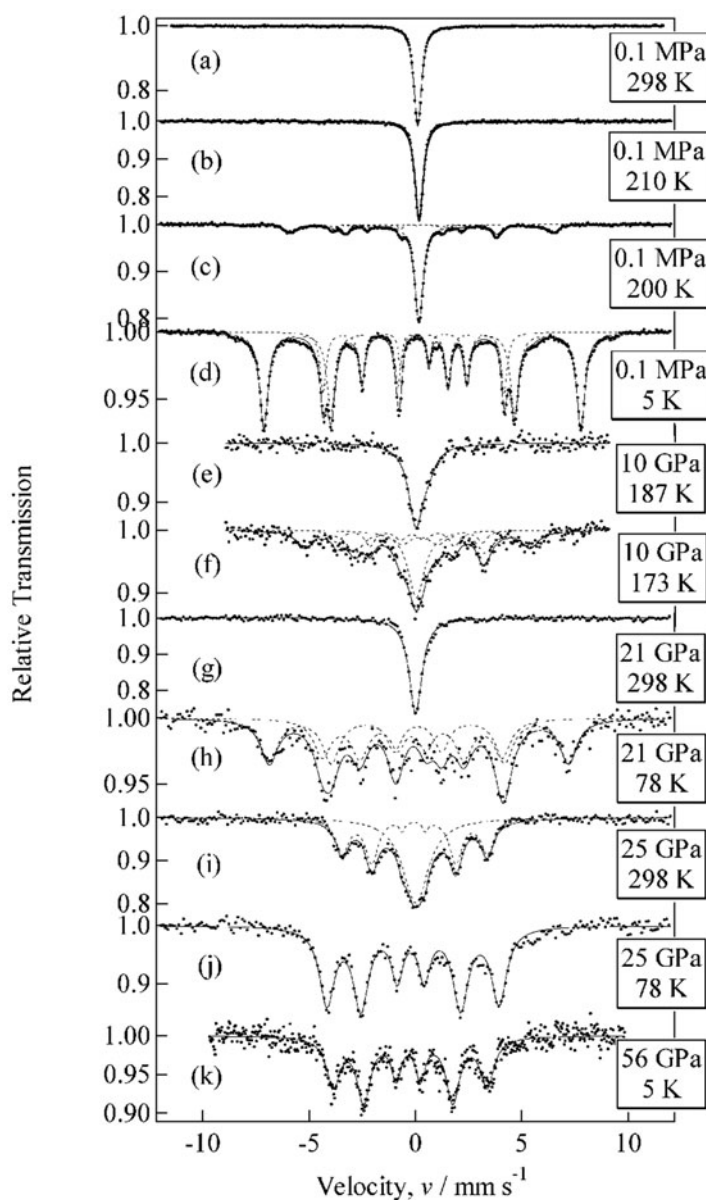


Figure 3. Typical pressure-dependent Mössbauer spectra obtained from $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ at various temperatures.

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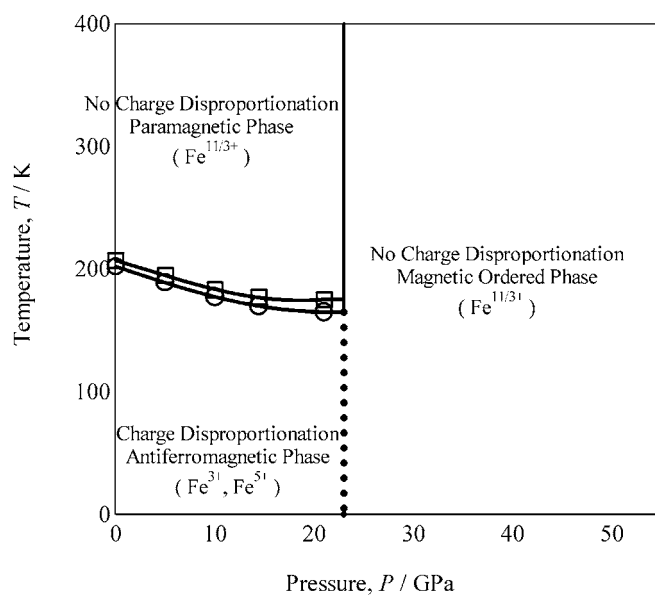


Figure 4. The P - T phase diagram of CaFeO_3 . The critical temperature of the CD and the MO temperature as a function of pressure are shown.

References

- [1] Imada M *et al* 1998 *Rev. Mod. Phys.* **70** 1211
- [2] Bocquet A E *et al* 1992 *Phys. Rev. B* **45** 1561
- [3] Takano M *et al* 1977 *Mater. Res. Bull.* **9** 923
- [4] Morimoto S *et al* 1997 *Physica B* **237-8** 66
- [5] Woodward P M *et al* 2000 *Phys. Rev. B* **62** 844
- [6] Bocquet A E *et al* 1992 *Phys. Rev. B* **45** 1561
- [7] Battle P D *et al* 1990 *J. Solid State Chem.* **84** 271
- [8] Matsuno J *et al* 1999 *Phys. Rev. B* **60** 4605
- [9] Kawakami T *et al* 2001 *J. Phys. Soc. Japan* **70** 1491