

Pressure-induced suppression of charge disproportionation in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$

Perovskites containing quadrivalent iron exhibit unique characteristics. Compared with perovskite Fe^{2+} or Fe^{3+} oxides, the lower number of $3d$ electrons and the weaker screening of the nuclear charge result in deepening of the $3d$ orbitals and a strong tendency for them to hybridize with the O $2p$ orbitals. These hybridized electronic states are responsible not only for the good conductivity of the materials but also for their various interesting physical properties.

Typical simple perovskites containing quadrivalent iron are CaFeO_3 , SrFeO_3 , and BaFeO_3 . These perovskites share certain characteristics such as a large negative charge transfer energy and electrical and magnetic properties that are governed by the O $2p$ -hole character. The hole dynamics lead to a variety of electronic states, such as a metal (orthorhombic) to semiconductor ($T < 290$ K, monoclinic) transition coupled to the breathing phonon mode of CFO, where the instability due to orbital degeneracy is lifted through the charge disproportionation (CD: $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$) and the metallic antiferromagnetism with a helical spin structure of cubic SrFeO_3 , and the magnetic-field-induced ferromagnetism of cubic BaFeO_3 .

A-site-ordered perovskite iron oxides $\text{AA}'_3\text{B}_4\text{O}_{12}$ have been synthesized by advanced high-pressure methods. The A'-sites and B-sites are primarily occupied by Cu^{2+} ions and by Fe^{4+} or $\text{Fe}^{3.75+}$ ions, respectively. These oxides undergo two characteristic transitions depending on the size of the ions in the A-site. One is intersite charge transfer (CT), which takes place for comparatively large alkaline-earth metals (e.g., Sr) and rare-earth metal ions (La, Pr, Nd, Sm, Eu, Gd, and Tb) [1-3]. The other is CD, which takes place for comparatively small alkaline-earth metals (Ca) and rare-earth metal ions (Dy, Ho, Er, Tm, Yb, and Lu) [3,4]. These generation mechanisms remove the structural instability caused by metal-oxygen bond strains in the case of the former and by orbital instability in the Fe^{4+} (d^4) state in the case of the latter. The most notable characteristic of the A-site-ordered perovskite oxide $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ (CCFO) is that CD at 210 K is accompanied by ferrimagnetic and metal-semiconductor transitions. The resulting charge-disproportionated $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ is a B-site $\text{Fe}^{3+}\text{-O-Fe}^{5+}$ ferromagnetically coupled compound [4].

We carried out X-ray diffraction, X-ray absorption spectroscopy (XAS), and ^{57}Fe Mössbauer spectroscopy to investigate the effect of pressure on the CD, CT, spin transitions, and crystal structure of CCFO. From our results, we constructed a CCFO P - T magnetic phase

diagram [5].

Typical Mössbauer spectra are shown in Figs. 1(a-j). At ambient pressure, a paramagnetic singlet was observed above 210 K (Fig. 1(a)), while the low-temperature spectra at 8 K consisted of two magnetically split components with hyperfine fields of 41.6 T (Fe^{3+}) and 22.5 T (Fe^{5+}) in the high-spin state (Fig. 1(b)). Essentially the same behavior was observed up to ~ 12 GPa. First, various transitions occur in the pressure range of 13–15 GPa. The transition temperature peaks at approximately 350 K at 15 GPa before entering a perceptible decline. The spectra taken at 15 GPa and 298 and 8 K (Figs. 1(f) and 1(g)) already contained two magnetically split sextets. The shape of the spectra at 15 GPa supports the asymmetry of the intensity and the line width as a cause of the charge-disproportionated state. We concluded that these split components were a new charge-ordering state, which we named a slightly charge-disproportionated state ($\text{Fe}^{(4-\delta)+}$, $\text{Fe}^{(4+\delta)+}$, where δ denotes less than one). As we measured the electrical resistance under pressure, the pressure-induced semiconductor-metal transition appeared around the critical pressure of the first suppression of the CD ($\text{Fe}^{3+} + \text{Fe}^{5+} \rightarrow \text{Fe}^{(4-\delta)+} + \text{Fe}^{(4+\delta)+}$) at ~ 15 GPa. It is contemplated that the delocalization of e_g electrons proceeded upon applying pressure. Therefore, the electron hopping becomes faster and the number

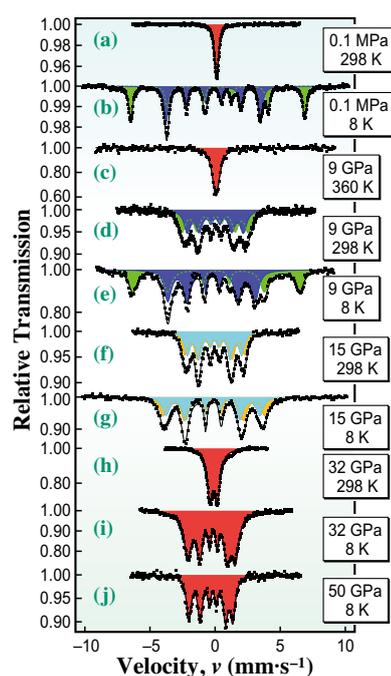


Fig. 1. Typical high-pressure ^{57}Fe Mössbauer spectra.

of electrons that contribute to the magnetic moment decreases. As a result, the valence, which is obtained from the isomer shift, is close to the mean valence (Fe^{4+}) and the hyperfine field decreases; thus, it can be concluded that the slightly charge-disproportionated state was stabilized.

Secondly, various marked changes occurred in the pressure range of 20–32 GPa. At 32 GPa, the 298 K spectrum was fitted to a non-magnetic doublet component (Fig. 1(h)). At 8 K, however, the spectrum changed into a magnetic sextet component with a small hyperfine field of 10.8 T and a quadrupole splitting of -0.14 mm/s (Fig. 1(i)). These spectra indicated a number of changes in the electronic state. The first was a complete suppression of the CD ($\text{Fe}^{(4-\delta)+} + \text{Fe}^{(4+\delta)+} \rightarrow 2\text{Fe}^{4+}$), the second was a low-spin transition, and the third was a rapid decrease in the magnetic ordering temperature to ~ 135 K. The cause of the decrease in the magnetic ordering temperature is thought to be that the superexchange interaction is weak owing to an absence of electrons in the e_g orbital. Similar Mössbauer spectra were maintained up to 50 GPa (Fig. 1(j)). High-spin and low-spin components coexisted in the pressure range of 25–30 GPa. The low-spin transition is complete at ~ 30 GPa.

Figure 2(a) shows XAS spectra around the Cu K edge under various pressures, which we observed at SPring-8 BL39XU. The energy of the absorption edge is around $E = 8.987$ keV. The absorption energies exhibit a very small shift below 0.5 eV with increasing pressure. This result indicated that the valence of the Cu ions in CCFO is almost constant. The energy shift is about 2 eV when the valence of Cu ion changes from divalent to trivalent. As a result of the ^{57}Fe Mössbauer spectroscopy and XAS, no CT between Cu and Fe was detected.

X-ray powder diffraction measurements were carried out at pressures of up to 51 GPa at SPring-8 BL10XU. All the peaks of the diffraction pattern at each pressure could be assigned to a cubic perovskite structure and no additional reflections were detected

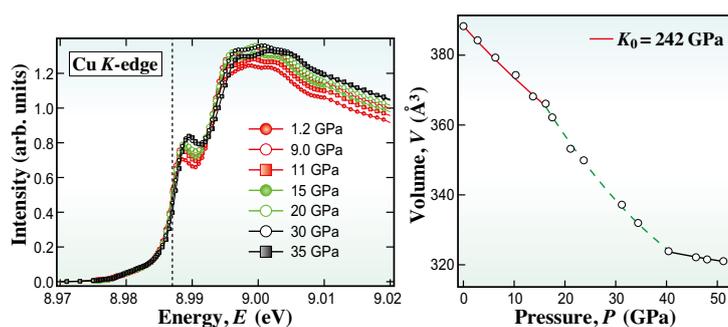


Fig. 2. (a) XAS spectra around the Cu K edge measured under various pressures at $T = 300$ K. (b) Compression curves at $T = 298$ K.

within the resolution of the measurements. The pressure dependence of the volume could be fitted well by the Birch-Murnaghan equation of the state (Fig. 2(b)), yielding a bulk modulus of $K_0 = 242$ GPa below ~ 22 GPa. However, on the application of higher pressure, the volume did not follow this compression curve, which may have been due to the low-spin transition. After the low-spin transition was completed, the compression curve showed a gradual decline.

The high-pressure measurements of CCFO were conducted to investigate changes in its charge, spin configuration, and electrical conduction. The results revealed CD suppression, a high-spin to low-spin transition, and a semiconductor-metal transition. In particular, we found a novel pressure-induced two-step CD suppression ($\text{Fe}^{3+} + \text{Fe}^{5+} \rightarrow \text{Fe}^{(4-\delta)+} + \text{Fe}^{(4+\delta)+} \rightarrow 2\text{Fe}^{4+}$). Finally, the phase diagram is presented in Fig. 3.

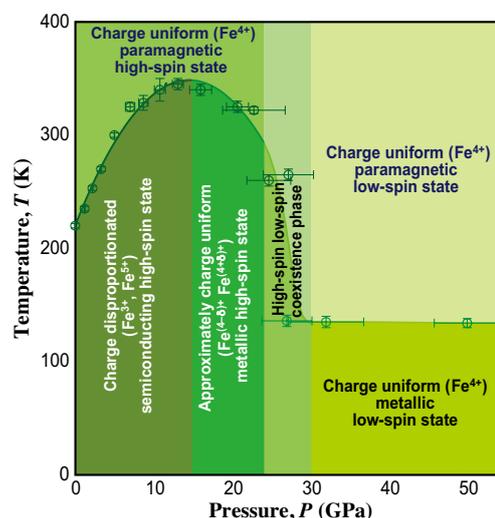


Fig. 3. P - T magnetic phase diagram.

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