Different routes to charge disproportionation in perovskites-type Fe oxides

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Iron perovskites CaFeO₃ and La₀.₃₃Sr₀.₆₇FeO₃ show charge disproportionation, resulting in charge-ordered states with Fe³⁺:Fe⁵⁺ = 1 : 1 and = 2 : 1, respectively. We have made photoemission and unrestricted Hartree-Fock band-structure calculation of CaFeO₃ and compared it with La₀.₃₃Sr₀.₆₇FeO₃. With decreasing temperature, a gradual decrease of the spectral weight near the Fermi level occurred in CaFeO₃ as in La₀.₃₃Sr₀.₆₇FeO₃ although lattice distortion occurs only in CaFeO₃. Hartree-Fock calculations have indicated that both the breathing and tilting distortions are necessary to induce the charge disproportionation in CaFeO₃, while no lattice distortion is necessary for the charge disproportionation in La₀.₃₃Sr₀.₆₇FeO₃.

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Recently charge ordering phenomena in transition-metal oxides have been extensively studied, particularly in relation to charge stripes in the high-$T_C$ cuprates 1 and giant magnetoresistance in the manganites 2. Charge ordering in highly covalent transition-metal oxides containing $d^1$ (Fe$^{3+}$, Mn$^{3+}$) or $d^2$ (Ni$^{3+}$) ions often exhibit so-called charge disproportionation, in which a charge state is thought to be separated into two different charge states as $2d^n \rightarrow d^{n-1} + d^{n+1}$. A clear fingerprint of charge disproportionation is the breathing-type distortion of metal-oxygen octahedra since the different charge states of the transition-metal ion take different ionic radii. Indeed, a breathing-type lattice distortion has been found for YNi$^{3+}$O$_3$ 3, NdNi$^{3+}$O$_4$ 4 and CaFe$^{3+}$O$_3$ by neutron diffraction studies 5, 6 and a thermally fluctuating charge disproportionated state has been postulated for LaMnO$_3$ at high temperatures 7. However, charge disproportionation in La$_{1-x}$Sr$_x$FeO$_3$ with $x \approx 0.7$, which occurs as a first-order phase transition from the paramagnetic-average-valence state (Fe$^{3.7+}$) above 200 K to the antiferromagnetic charge-disproportionated state (Fe$^{3+}$:Fe$^{5+}$ = 2 : 1) below that temperature 8, is not accompanied by an appreciable lattice distortion 9 although an electron diffraction study has shown extra spots 10 and two charge states of Fe with different hyperfine fields have been detected by Mössbauer spectroscopy 11. The neutron diffraction study of La$_{0.3}$Sr$_{0.7}$FeO$_3$ 12 has revealed a spin-density wave (SDW) of six-fold periodicity along the $(110)$ direction with two inequivalent spin states of Fe, suggesting a charge-density wave (CDW) of three-fold periodicity along the same direction.

Recent photoemission studies have revealed that the electronic structure of Fe$^{4+}$ oxides is rather unique: the charge-transfer energy $\Delta$, the energy required to transfer an electron from the oxygen $p$ to the Fe 3$d$ level, is extremely negative ($\sim -3$ eV including Hund’s coupling energy) 12, and the ground state of the formal Fe$^{4+}$ (“$d^3$”) state is in fact dominated by the $d^5_L$ configuration, where $L$ denotes a hole in the oxygen $2p$ band. The charge disproportionation is therefore more correctly described as $2d^n_L \rightarrow d^{n-1}_L + d^{n+1}_L$ rather than $2d^4 \rightarrow d^3 + d^5$. To understand the interesting physical properties of Fe$^{4+}$ oxides such as the helical antiferromagnetic metallic state in SrFeO$_3$, the Co-substitution induced ferromagnetism in SrFe$_{1-x}$Co$_x$O$_3$ 13, 14, and magnetic and electric phase transitions under high pressure 5, 6, 7, therefore, one has to take into account the negative $\Delta$, namely, the oxygen-hole character of charge carriers. Especially, the $d^5_L$ ground state naturally explains the fact that SrFeO$_3$ shows no charge disproportionation yet no Jahn-Teller effect since the $d^4$ ion necessarily undergoes a Jahn-Teller distortion.

In a recent photoemission and unrestricted Hartree-Fock band-structure calculation study of La$_{1-x}$Sr$_x$FeO$_3$ 15, we have shown that the charge disproportionation is purely electronically driven and that the ordering of oxygen holes plays an important role in the charge disproportionated state of La$_{0.3}$Sr$_{0.7}$FeO$_3$. In this Letter, we present a photoemission study of CaFeO$_3$, which unlike La$_{0.3}$Sr$_{0.7}$FeO$_3$ shows a breathing-type lattice distortion in the charge disproportionated state. Using photoemission we have studied how the charge disproportionation influences the electronic structure near the Fermi level ($E_F$) in comparison with La$_{0.3}$Sr$_{0.7}$FeO$_3$. We have also
performed unrestricted Hartree-Fock band-structure calculations on CaFeO₃ taking into account the realistic lattice distortion. Based on those results, different driving mechanisms are proposed for the charge disproportionation in the seemingly very similar systems CaFeO₃ and La₀.₃₃Sr₀.₆₇FeO₃.

A polycrystalline sample of CaFeO₃ was prepared by a solid state reaction and a subsequent treatment under high-pressure oxygen [13]. The electrical resistivity of the present CaFeO₃ sample is shown in Fig. 1 and is compared with that of La₁₋ₓSrₓFeO₃ (x = 0.67) [13]. It shows a gradual increase below the anomaly at 290 K due the gradual charge disproportionation 2Fe⁴⁺ → Fe⁵⁺ + Fe³⁺ while no anomaly due to the antiferromagnetic ordering is seen at the Néel temperature T_N = 115 K.

Ultraviolet photoemission (UPS) measurements were made using the He I resonance line (hν = 21.2 eV). The He I spectra have been corrected for the He I* satellite. In order to calibrate binding energies and to estimate the instrumental resolution, gold was evaporated on the sample surface after each series of measurements. The energy resolution was 48 meV. The samples were repeatedly scraped in situ with a diamond file. We have adopted the spectra taken within 40 minutes after scraping and the reproducibility of the spectra was confirmed by repeated measurements.

![Figure 1: Electrical resistivities of CaFeO₃ and La₀.₃₃Sr₀.₆₇FeO₃.](image1)

Figure 2 shows the temperature dependence of the He I spectra of CaFeO₃ near E_F. The spectra have been normalized to the integrated intensity of the entire valence band. A clear change in the intensity from the Fermi level to 0.4 eV below it has been observed as in the case of La₀.₃₃Sr₀.₆₇FeO₃. One can see that the spectral weight near E_F show a gradual decrease of the spectral weight with decreasing temperature. The most prominent temperature dependence occurs just below 300 K, followed by more gradual changes below ~270 K. In order to illustrate this, we have plotted the spectral weight integrated from −0.20 to +0.05 eV as a function of temperature in Fig. 2(a), where the previous result on La₀.₃₃Sr₀.₆₇FeO₃ is also plotted [13]. One can see a more gradual decrease as a function of temperature in CaFeO₃ than in La₀.₃₃Sr₀.₆₇FeO₃ corresponding to the more gradual change in the electrical resistivity below the charge disproportionation temperature, although the total spectral change in the wide temperature range is similar between the two systems. We also note that this temperature dependence of the spectral weight is qualitatively similar to the temperature dependence of the Fe-O bond length [6] as shown in Fig. 2(b), suggesting that the lattice deformation is related to the change of the photoemission spectra in CaFeO₃. It is remarkable that, although La₀.₃₃Sr₀.₆₇FeO₃ shows negligibly small structural changes across the transition [13], it shows spectral changes as strong as CaFeO₃. These observations imply different mechanisms for the charge disproportionation
Hartree-Fock calculations for the multi-band in La$_{0.33}$Sr$_{0.67}$FeO$_3$ (a supercell model for La$_{0.33}$Sr$_{0.67}$FeO$_3$) [18], where charge ordering with Fe$^{3+}$ : Fe$^{5+} = 2 : 1$ causes an SDW with six-fold periodicity along the (111) direction [Fig. 3(a)], we assumed an SDW with four-fold periodicity, namely $\uparrow\uparrow\downarrow\downarrow$, for CaFeO$_3$, where ordering with Fe$^{3+}$ : Fe$^{5+} = 1 : 1$ occurs in the same direction. This assumption is compatible with the alternating charge order of Fe$^{3+}$ and Fe$^{5+}$ in CaFeO$_3$. Under this assumption we obtained an insulating solution but this was not a disproportionated one. The reason why we could not explain both charge-ordered and insulating ground state within the $\uparrow\uparrow\downarrow\downarrow$ model is schematically shown in Fig. 3(b). The tendency that holes enter oxygen orbitals between the iron sites of the parallel spins also holds in this case, but all the iron sites become equivalent in spite of the hole ordering in this geometry, as can be seen from Fig. 3(b). Thus the origin of the disproportionation in CaFeO$_3$ and in LaSr$_2$Fe$_3$O$_9$ cannot be the same. In other words, the kinetic exchange interaction derived from the particular magnetic structure as in the case of La$_{0.33}$Sr$_{0.67}$FeO$_3$ cannot drive the charge disproportionation in CaFeO$_3$.

In order to clarify this, the difference spectrum divided by the Fermi-Dirac distribution function is also shown in the bottom panel. The obtained spectral DOS is nearly flat around the $E_F$, in contrast to the corresponding spectrum for La$_{0.33}$Sr$_{0.67}$FeO$_3$, where a pseudo-gap-like DOS has been observed [18]. This is consistent with the transport properties, which show more conducting and metallic behavior in CaFeO$_3$ than in La$_{0.33}$Sr$_{0.67}$FeO$_3$ above the transition temperature.

In order to study the driving force for the phase transition and the origin of the band gap below the transition temperature in CaFeO$_3$, we have carried out unrestricted Hartree-Fock calculations for the multi-band $d$-$p$ lattice model, in which the full degeneracy of the Fe $3d$ and oxygen $2p$ orbitals are taken into account [19]. Parameters in the model are the charge-transfer energy $\Delta$, the multiplet averaged $d$-$d$ Coulomb interaction $U$ and Slater-Koster parameters ($pd\sigma$), ($pd\pi$), ($pp\sigma$) and ($pp\pi$), which represent transfer integrals between the transition metal $3d$ and oxygen $2p$ orbitals. The values of $\Delta$, $U$ and ($pd\sigma$) were chosen to be 0, 6 and $-1.8$ eV, respectively. The ratio ($pd\sigma$)/($pd\pi$) was fixed at $-2.16$ and ($pp\sigma$) and ($pp\pi$) at $-0.60$ and $0.15$ eV, respectively [20].

First, in analogy with LaSr$_2$Fe$_3$O$_9$ (a supercell model for La$_{0.33}$Sr$_{0.67}$FeO$_3$) [18], where charge ordering with Fe$^{3+}$ : Fe$^{5+} = 2 : 1$ causes an SDW with six-fold periodicity along the (111) direction [Fig. 3(a)], we assumed an SDW with four-fold periodicity, namely $\uparrow\uparrow\downarrow\downarrow$, for CaFeO$_3$, where ordering with Fe$^{3+}$ : Fe$^{5+} = 1 : 1$ occurs in the same direction. This assumption is compatible with the alternating charge order of Fe$^{3+}$ and Fe$^{5+}$ in CaFeO$_3$. Under this assumption we obtained an insulating solution but this was not a disproportionated one. The reason why we could not explain both charge-ordered and insulating ground state within the $\uparrow\uparrow\downarrow\downarrow$ model is schematically shown in Fig. 3(b). The tendency that holes enter oxygen orbitals between the iron sites of the parallel spins also holds in this case, but all the iron sites become equivalent in spite of the hole ordering in this geometry, as can be seen from Fig. 3(b). Thus the origin of the disproportionation in CaFeO$_3$ and in LaSr$_2$Fe$_3$O$_9$ cannot be the same. In other words, the kinetic exchange interaction derived from the particular magnetic structure as in the case of La$_{0.33}$Sr$_{0.67}$FeO$_3$ cannot drive the charge disproportionation in CaFeO$_3$.

Then we introduced the lattice distortion in CaFeO$_3$ explicitly because in CaFeO$_3$, lattice distortion has been found to be substantial unlike La$_{0.33}$Sr$_{0.67}$FeO$_3$. CaFeO$_3$ has the GdFeO$_3$-type tilting distortion as well as the breathing distortion [3, 8, 21] and the Fe-O-Fe bond angle is determined to be ~158°. In order to take into account these distortions, a unit cell has been selected as containing four FeO$_6$ octahedra. The breathing distortion, which results in two kinds of Fe-O bond lengths, has been treated by scaling the transfer integrals with respect

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**FIG. 3:** (a) Spectral weight integrated from $-0.20$ to $+0.05$ eV for CaFeO$_3$ and La$_{0.33}$Sr$_{0.67}$FeO$_3$ [18] as functions of temperature. (b) Average Fe-O bond lengths observed by neutron diffraction [4].

**FIG. 4:** Schematic descriptions of the spin and charge configurations in LaSr$_2$Fe$_3$O$_9$ (La$_{0.33}$Sr$_{0.67}$FeO$_3$) (a) and CaFeO$_3$ (b). Black and white arrows represent the spins at the Fe sites and those of the oxygen holes, respectively.
to the bond lengths ($d$) following Harrison’s rule \cite{22} $(pd\sigma) \propto d^{-3.5}$. In order to simulate the effect of both the breathing and the tilting, we calculated the magnitude of the band gap as a function of the degree of the breathing distortion $R = d_{\text{long}}/d_{\text{short}}$ and the Fe-O-Fe bond angle. As for the magnetic structure, we assumed the ferromagnetic structures considering that the spin alignment between neighboring iron sites is almost ferromagnetic in the screw antiferromagnetic structure with a long wave vector \[= 0.161(111)2\pi/a\] observed in CaFeO$_3$ \cite{3}. The results are shown in Table I. We have obtained the charge-disproportionated solution for $R \neq 1$ as expected. The experimental values for CaFeO$_3$ are $R = 1.022$ and $\angle$Fe-O-Fe = 158° for CaFeO$_3$, however, the breathing distortion of $R = 1.022$ alone or the tilting of $\angle$Fe-O-Fe = 158° alone does not open a gap although Hartree-Fock calculations tend to overestimate band gaps. In order to open a band gap (and to lower the total energy of the system), the two types of lattice distortions should occur simultaneously. If the bond angle is 180° as in the case of SrFeO$_3$, one needs an unreasonably large breathing distortion to open the gap. In order to confirm the co-operative nature of the two types of distortions, first-principles total-energy calculations would be necessary in future work.

The present scenario for the charge disproportionation in CaFeO$_3$ naturally explains why the iso-electronic SrFeO$_3$ remains free from charge disproportionation: since the ionic radius of Sr$^{2+}$ is large, no tilting distortion is possible for SrFeO$_3$ and hence the breathing is also blocked. This picture may be analogous to the case of the distorted perovskite BaBiO$_3$, in which freezing of a breathing phonon mode is well known \cite{23}. Liechtenstein et al. \cite{24} calculated the total energy of BaBiO$_3$ as a function of tilting and breathing distortions and found that the instability and the gap opening occurs only when the two kinds of distortions are combined; in the presence of the tilting distortion, the nesting instability of the Fermi surface emerges, leading to the alternating breathing distortion of Bi-O octahedra. If the same nesting instability is confirmed for CaFeO$_3$ by first-principles band-structure calculations, then the quite different mechanism of the charge disproportionation would be established between La$_{0.33}$Sr$_{0.67}$FeO$_3$, where the ordering of holes at oxygen sites is purely electronically driven, and CaFeO$_3$, where the lattice distortion and associated electron-phonon coupling is important.

In conclusion, we have shown that the driving force for the charge disproportionation is quite different between the two apparently very similar compounds La$_{0.33}$Sr$_{0.67}$FeO$_3$ and CaFeO$_3$. The present finding implies that there exists subtle interplay between electron-electron interaction, magnetic interaction, and electron-lattice interaction in realizing charge ordering (or more generally charge inhomogeneity) and charge fluctuations in transition-metal oxides. This means that dominant interaction may change within the same family of compounds, and calls for a critical re-examination of charge ordering/transition phenomena depending on the chemical composition (hole concentration) and crystal distortion even for an apparently similar class of materials.

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| $\angle$ Fe-O-Fe | $R = 1$ | $R = 1.022$ | $R = 1.043$ |
|------------------|--------|-----------|-----------|
| 180°             | 0      | 0         | 190       |
| 158°             | 0      | 30        | 300       |

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