

Charge-Ordered State in Single-Crystal Like CaFeO_3 Thin Film Studied by X-ray Anomalous Diffraction

Charge ordering (CO) in perovskite-type oxides has been intensively investigated in recent years. CaFeO_3 (CFO) shows the CO transition at 290 K [1] with a change of the crystal space group from $Pbnm$ in the normal state to $P2_1/n$ in the CO state. The transition accompanies the metal-insulator transition, as seen other mixed valence materials. On the other hand, SrFeO_3 (SFO), having the same nominal Fe valence of +4 and nearly the same structure, does not show CO even at 4 K. The CFO crystal has a distorted perovskite-type structure (GdFeO_3 structure) shown in Fig. 1, where each FeO_6 octahedron is tilted. Since the $\text{Fe}^{4+}\text{-O}$ bond has a strong d - p hybridization, oxygen holes on the antibonding band are considered to be generated initially, and consequently, the system becomes metallic. The Fe-O-Fe bond angle in CFO is 160° which is much reduced from the 180° in SFO. This causes the d - p band in CFO to be narrower than that in SFO and, as a consequence, the system transforms to the CO state at a relatively high temperature. In the CFO crystal, two major steric configurations of the excess charge have been proposed for the CO state. One is that fully charged Fe^{3+} ($3d^5$) and Fe^{5+} ($3d^3$) are positioned separately with a rocksalt-type structure. This concept was accepted at an early stage and supported by the experiment of the Mössbauer effect. The other, based on XPS measurements, is that holes, as excess charge, are localized around some Fe^{3+} ions, such as $3d^5 3d^5 \underline{L}^2$ (\underline{L} denotes a ligand hole). This suggests that the Fe ions of CFO in the CO state split into $\text{Fe}^{4+\delta}$ and $\text{Fe}^{4-\delta}$ ($0 < \delta \leq 1$) at the CO transition temperature. More recently, neutron and X-ray diffraction analyses of polycrystalline CFO have been performed [2]. These studies revealed that Fe-O bond lengths for each equivalent Fe site are distinct, e.g., at 15 K for Fe(1) and Fe(2) sites, bond lengths are 0.1872(6) and 0.1974(6) nm, respectively [2]. Even with these explicit studies,

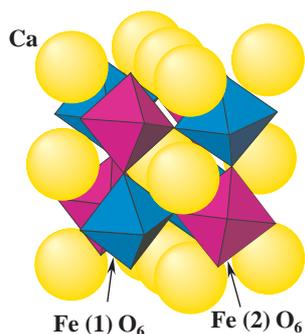


Fig. 1. Crystal structure of CaFeO_3 . Two types of octahedra contain Fe(1) or Fe(2) alternatively. Spheres symbolize calcium ions.

however, the physical picture appropriate for CO in CFO is still controversial, because of a lack of quantitative information on each electronic state of Fe(1) and Fe(2). We present explicit experimental evidence of the CO state realized in CFO, using an X-ray anomalous diffraction (XAD) technique, and a subsequent electronic band-structure calculation is then compared with the experimental results to obtain the physical picture in terms of the quantitative electronic state difference between Fe(1) and Fe(2) in the CO state of CFO [3].

CFO single-crystalline thin films with [001] orientation parallel to the growth direction were fabricated by pulsed laser deposition with epitaxial growth on the SrLaAlO_4 (001) substrate. After the deposition, the films were cooled by blowing partially ozonized oxygen. The size of the films obtained was $10 \times 10 \text{ mm}^2$ in area and 50 nm in thickness. An XAD experiment was carried out near the Fe-K absorption edge ($E = 7112 \text{ eV}$) with the κ -type six-circle diffractometer installed on beamline BL14B1. The X-rays were monochromatized by a Si(111) double-crystal system. The XAD experiment is one of the powerful techniques for studying materials with CO. In the present work, we have focused on a superlattice reflection $(0.5, 0.5, 0.5)p$, where p denotes a primitive perovskite structure. Since a structure factor for this reflection is obtained from the reported crystal structure [2] with two Fe atomic sites Fe(1) and Fe(2), we can estimate the Bragg peak intensity with the anomalous scattering factors for the reflection. If we observe the energy dispersion of such a superlattice reflection, there will be a characteristic structure on the dispersion curve, reflecting the difference between both environments of surrounding Fe(1) and Fe(2). Then, in order to study the physical picture of CO in the CFO, we have carried out the XAD measurements of the superlattice reflection, $(0.5, 0.5, 0.5)p$, for CFO thin film. In our experimental geometry, the incident synchrotron beam was polarized perpendicular to the scattering plane (σ) and the diffracted beam was detected without regarding the polarization (i.e., $\sigma + \pi'$).

Figure 2 shows the energy dependence of the XAD intensity of the $(0.5, 0.5, 0.5)p$ reflection with two different azimuthal angles observed at 150 K. The anomalous diffraction intensity has a significant peak at $E \approx 7124 \text{ eV}$. The antiferromagnetic order ($T_N = 115 \text{ K}$) does not appear at that temperature. Thus the structure of the XAD spectra is considered to derive

from the charge order at the Fe ions. The X-ray absorption spectrum (XAS) of the CFO thin film is shown in Fig. 2(b) and the calculated dispersion curves for the two different azimuthal angles are superposed on the observed XAD curve in Fig. 2(a). Generally, the structure factor of reflections with contributions from ions including electrons with a local anisotropy, such as Fe ions in CFO, should be treated as a tensor and show the azimuthal angle dependence. In the present case, however, the dispersion curves are almost identical. This is reasonably supported by the calculation which expects that azimuthal dependence would not appear in the reflection, as shown in the inset of Fig. 2(b), due to the relatively large Thomson scattering term and our optical configuration where the diffracted beam is collected without polarization. The calculated dispersion of the XAD intensity seems well fitted to the experimentally obtained curve. The procedure of the calculation is briefly explained as follows.

The first-principles electronic structure calculation is performed for the antiferromagnetic CFO in the low-temperature phase with the reported crystal structure data [2]. The full-potential linearized augmented-

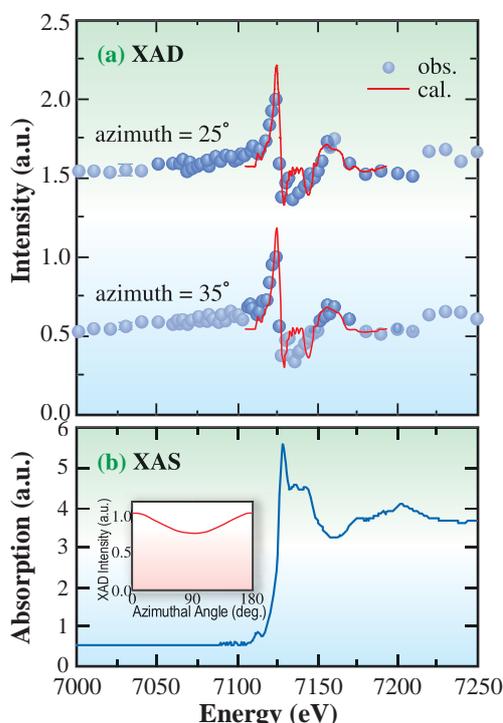


Fig. 2. Energy dependence of (a) the intensity of (0.5, 0.5) ρ with the filled circles for the azimuthal angles of 25° and 35° at 150 K, and (b) the absorption with the solid line at 300 K, near the Fe K edge. A typical error of the intensity is represented only for the point of 7030 eV. The solid lines in (a) show the calculated dispersion curve as described in the text. Inset in (b) shows a calculated azimuthal angle dependence of the XAD intensity at 7124 eV.

plane-wave method is employed with the LDA- U scheme [4]: $U_{\text{eff}} = 2$ eV for the Fe 3d orbital. The theoretical curves in the figure were obtained by calculating the (1s - 4p) dipole-transition amplitude using the Fe 4p states. The calculation scheme was established by Takahashi and Igarashi [5]. The CO state is characterized by the hybridization between the Fe 3d orbital and the O 2p orbital. We show a remarkable feature that is, the total numbers of 3d electrons are almost the same for Fe(1) ~ Fe⁺⁵ and Fe(2) ~ Fe⁺³, as shown in Table I, where Fe 3d electron numbers in the muffin-tin spheres of Fe(1) and Fe(2) are tabulated. Thus, we have a picture for the CO state similar to the oxygen hole scenario in which the 3d electron number at the Fe site is fixed at 5, while the change of the electron number is attributed to the oxygen hole. Our picture, however, asserts that the Fe 3d electron number is larger than 5 and that the minority-spin 3d orbital is also partially occupied; thus, the Fe magnetic moment is significantly reduced from 5 μ_B . This reduction is also observed by the neutron scattering measurement: 2.5 μ_B for Fe(1) and 3.5 μ_B for Fe(2) [2]. The magnetic moments are also consistent with the result of the Mössbauer experiment. Every O atom is a common neighbor on Fe(1) and Fe(2); the charge at the O site is, therefore, unchanged by the CO transition.

Table I. Numbers of 3d electrons and magnetic moments for the two iron sites in CaFeO₃.

Site	Electron number			Magnetic moment / μ_B
	Up	Down	Total	
Fe(1)	4.18	1.41	5.59	2.77
Fe(2)	4.62	0.93	5.55	3.69
Average	4.40	1.17	5.57	3.23

T. Akao^a, J. Mizuki^b and N. Hamada^c

(a) Faculty of Engineering, Tottori University

(b) SPring-8 / JAERI

(c) Faculty of Science and Technology, Science University of Tokyo

E-mail: akao@mech.tottori-u.ac.jp

References

- [1] M. Takano *et al.*: Mater. Res. Bull. **12** (1977) 923.
- [2] P. M. Woodward *et al.*: Phys. Rev. B **62** (2000) 844.
- [3] T. Akao, Y. Azuma, M. Usuda, Y. Nishihata, J. Mizuki, N. Hamada, N. Hayashi, T. Terashima and M. Takano: Phys. Rev. Lett. **91** (2003) 156405.
- [4] I. Solovyev *et al.*: Phys. Rev. B **53** (1996) 7158.
- [5] M. Takahashi and J. Igarashi: Phys. Rev. B **64** (2001) 075110.