

X-ray spectroscopic study of BaFeO₃ thin films; An Fe⁴⁺ ferromagnetic insulatorTomoyuki Tsuyama^{1*}, Wadati Hiroki¹, Suvankar Chakraverty², Jun Okamoto³, Arata Tanaka⁴, Harold Y. Hwang^{2,5}, Yoshinori Tokura^{1,2}¹Department of Applied Physics and Quantum-Phase Electronics Center (QPEC), University of Tokyo, Tokyo 113-8656, Japan.²RIKEN Center for Emergent Matter Science (CEMS), Wako 351-0198 Japan.³Condensed Matter Research Center (CMRC), High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan.⁴Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan.⁵Department of Applied Physics, Stanford University, Stanford, CA 94305, USA

1 Introduction

Strongly correlated transition-metal oxides have shown interesting physical properties. In this class, high valence-metal compounds, such as SrFeO₃ have attracted great attention due to their rich and anomalous physical properties. The recent success of the fabrication of BaFeO₃ thin films showed the large saturation magnetization (in-plane; 3.2 μ_B /f.u., out-of-plane; 2.8 μ_B /f.u.) in ferromagnetic-insulating phases with the lattice constant of 3.97 Å in a cubic crystal structure [1]. The origin of the highly insulating properties, however, had not yet been clarified. The spectroscopic studies of the electronic and magnetic structure would be invaluable to reveal the mechanisms. To achieve the purpose we performed Fe 2*p* and O 1*s* edge soft x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). The obtained results were analyzed by configuration-interaction cluster-model calculations. We clarified that the ground state were dominated by the $d^5\bar{L}$ configuration (\bar{L} ; ligand hole) rather than the d^4 configuration due to the negative charge transfer energy resulting in the presence the substantial magnetic moment even in oxygen sites. We also clarified the unusual insulating phase in BaFeO₃ thin films in the negative charge transfer energy derives from the significant stabilization of its ground state via the strong Fe 3*d* - O 2*p* hybridization.

2 Experiment and calculation

A single crystalline, cubic, fully oxidized 50 nm thin film of BaFeO₃ (with lattice parameter 3.97 Å) was grown on SrTiO₃ (001) substrate, using pulsed laser deposition. The details of fabrication are described in Ref. [1]. XAS and XMCD were carried out at BL-16A in Photon Factory at a temperature of 20 K. The magnetic of ~ 1 T was applied perpendicular to the thin film surface, strong enough to saturate the out-of-plane magnetization. XMCD was measured by under fixed circular polarization

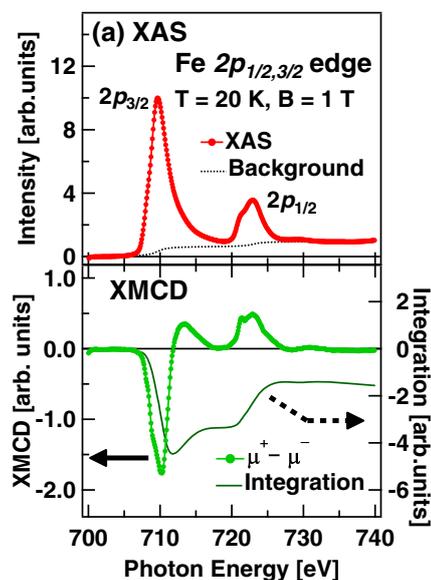


FIG. 1: XAS (top) and XMCD (bottom) spectra of BaFeO₃ thin films are shown for Fe 2*p* edges obtained by experiment

of the incident beam incident on the sample perpendicular to its plane. The XAS and XMCD spectra were collected with the total-electron-yield mode with the probing depth of ~ 20 Å [2]. The obtained results were analyzed by configuration interaction cluster-model calculations. The cluster-model calculations are one of the most suitable methods to analyze the those core-level spectra. In this model calculations we consider the electronic structure of Fe⁴⁺ ion surrounded by 8 O²⁻ ions octahedrally including the charge transfer effect from oxygen sites to iron site. The parameters to be fitted were the charge transfer energy from the O 2*p* orbitals to the empty Fe 3*d* orbitals

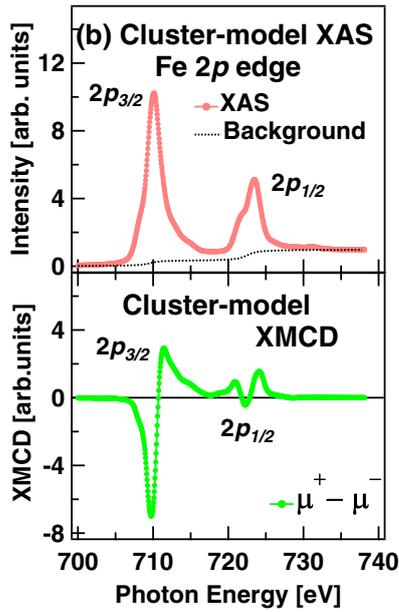


FIG. 2: XAS (top) and XMCD (bottom) spectra calculated by configuration-interaction cluster-model calculations.

denoted by Δ , the strength of Fe $3d$ - O $2p$ hybridization denoted by Slater-Koster parameters (pd), the $3d$ - $3d$ on-site Coulomb interaction energy denoted by U_{dd} , and the on-site $3d$ - $2p$ core hole Coulomb interaction denoted by U_{pd} . The set of the parameters were optimized near the phase boundary of ferromagnetic and A-type helicoidal magnetic phase in Ref. [3], explaining the magnetism of BaFeO₃ thin films.

3 Results and Discussion

The Fe $2p$ edge XAS (top) and XMCD (bottom) spectra are shown in Fig. 1. The broad XAS $2p_{3/2,1/2}$ peaks without shoulder structures reflects the heavily mixed state due to the strong hybridization in BaFeO₃, which is quite similar to that in SrFeO₃, and also suggests that the valence of Fe is not 3+ but 4+ [4]. XMCD shows a large peak intensity of $\sim 18\%$ of the XAS peak intensity. The XMCD intensity of BaFeO₃ thin film is approximately twice as large as that of bulk BaFeO₃ [5]. The orbital moment (M_{orbital}) and spin moment (M_{spin}), we applied sum-rule analysis [6, 7]. By applying the sum-rule analysis, we obtained a large magnetic moment of $M_{\text{total}} = 2.1 \pm 0.3 \mu_B/\text{f.u.}$, composed of $M_{\text{spin}} = 1.8 \pm 0.2 \mu_B/\text{f.u.}$ and $M_{\text{orbital}} = 0.3 \pm 0.1 \mu_B/\text{f.u.}$. Note that we considered the correction coefficient of $1/0.58$ for M_{spin} due to strong electronic correlations [8]. Corrections of $1/0.88$ for M_{spin} and $1/0.49$ for M_{orbital} were also considered to compensate for the saturation effect in total-electron-yield mode [2]. Here, we assumed that the x-ray attenuation length at the $2p_{3,2}$ edge is $\sim 200 \text{ \AA}$ [2]. Since both the $M_{\text{spin}} (>0)$ and $M_{\text{orbital}} (>0)$ have the same sign in BaFeO₃, it suggests the substantial weight of the d^6L^2 configuration due to the negative charge transfer energy. The XMCD result gave a smaller M_{total} than the value obtained by magnetization measurement [1]. The cause of the deviation is not clear

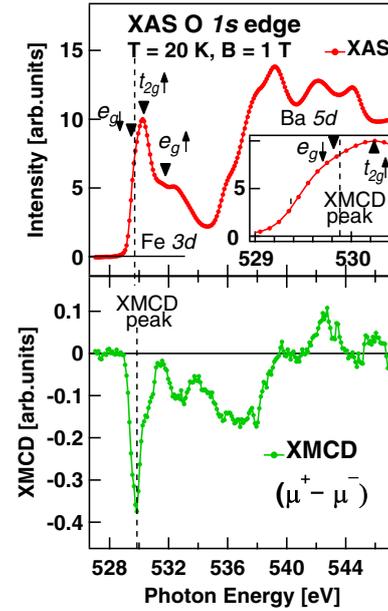


FIG. 3: O $1s$ edge XAS and XMCD spectra of BaFeO₃ thin films are presented. The vertical dashed line represents the XMCD peak energy and the triangles show the XAS structures

at this moment, but there is a possibility that the magnetic moment on the oxygen site might cause the underestimation based on the total magnetic moment in the iron site.

In Fig. 2, the calculated Fe $2p$ edge XAS (top) and XMCD (bottom) spectra are presented. The spectrum reproduces the features of the experimental results very well, unlike the atomic multiplet calculation for d^6 in Ref.[4], suggesting the importance of charge transfer effects in those systems.

The O $1s$ edge XAS (top) and XMCD (bottom) spectra are presented in Fig.3. The inset in the top panel shows the expanded XAS spectrum around the main peak. O $1s$ edge XAS spectra of correlated compounds originate from transitions into unoccupied states with O $2p$ character hybridized with transition metal $3d$ states. Therefore, the structure of the spectrum is qualitatively related to empty bands of primarily Fe $3d$ weight. The structure from 528 eV to 534 eV, mainly Fe $3d$ -related, is similar to that of SrFeO₃[4]. The O $1s$ edge XAS of La_{1-x}Sr_xFeO₃ spectrum shows that a new structure below the threshold of LaFeO₃ grows rapidly with increasing Sr, and dominates the spectra at high concentrations, corresponding to the Fe related main structure in our spectrum. These features seen in SrFeO₃ and BaFeO₃ are attributed to an effective state created by strong Fe $3d$ - O $2p$ hybridization. Such effective states are also seen in La_{2-x}Sr_xCuO₄ and Li_{1-x}Ni_xO due to the anomalously strong antiferromagnetic coupling between Cu or Ni $3d$ and O $2p$ [9, 10]. The O $1s$ edge XMCD spectrum directly shows that the effective state in BaFeO₃ has heavily O $2p$ character with the peak intensity of $\sim 4\%$ versus that of XAS. This is the evidence for significant O $2p$ hole character in the ground state due to the negative charge transfer energy and strong Fe $3d$ - O $2p$ hybridization.

The energy position of the XMCD peak, which is lowered by 400 meV from that of XAS, corresponds to the shoulder structure in XAS assigned by $e_g \uparrow$ as shown in the inset. Since the threshold of XAS is dominated by the transition of $d^5 \bar{L} \rightarrow 1s d^5$, the strong intensity of XMCD was observed at the XAS structure of the lowest energy even in the usually non-magnetic oxygen. Here, $1s$ denotes the O $1s$ core-hole created by the incident x-ray. Thus, when an extra electron is added to the ground state, the electron will be introduced into the ligand hole at the affinity level. By considering Hund's rule, the net spin moment of O $2p$ is parallel to that of Fe $3d$, because the XMCD spectra showed that their orbital moments are parallel. Since there is no spin-orbit interaction in the O $1s$ core-hole, O $1s$ edge XMCD just shows not spin moment but orbital moment in the O $2p$ orbital. The oxygen hole usually antiferromagnetically couples to the net spin on the iron site due to the $p - d$ exchange interaction, which is consistent with the experimental oxygen $1s$ edge XMCD.

The ground states dominated by the $d^5 \bar{L}$ configurations and the presence of the effective states in the final state of O $1s$ XAS spectrum strongly suggest the origins of the insulating properties in BaFeO₃ thin films are the high covalency between Fe $3d - O 2p$ state, often called as covalent insulator [11]. If the ground states are dominated by the configurations including ligand holes, the compounds can be expected to be metallic due to the continuum state in the ground state. If the hybridization between transition metal $3d - O 2p$ is strong, the discrete state would be generated under the continuum state. As a result, the compounds would show the insulating properties. In the case of the hole doped high T_c superconducting copper oxides, the discrete states are often called as Zhang-Rice singlet state. NaCuO₂ has an insulating properties due to the ground state including of the discrete state generated by the strong hybridization between Cu $3d - O 2p$ corresponding to the Zhang-Rice singlet state [12]. In the case of the perovskite structure, those discrete states in a single cluster are expected to be strongly hybridized between each site and often collapses the band gap in a crystal. The lattice constant of BaFeO₃, however, is so large that the hybridization between sites is greatly reduce. As a result the band gap is remained to open in BaFeO₃ thin films.

4 Conclusion

We performed Fe $2p$ and O $1s$ edge XAS and XMCD measurements to clarify the electronic structure of BaFeO₃. We clarified the valence of Fe in BaFeO₃ is Fe⁴⁺ by Fe $2p$ edge XAS and it has large saturation magnetic moment of 2.1 μ_B /f.u. by Fe $2p$ edge XMCD. Those spectra were well reproduced by the cluster-model calculations with negative charge transfer energy. O $1s$ edge XAS revealed the presence of the effective state in BaFeO₃ due to the strong Fe $3d - O 2p$ hybridization which has substantial magnetic moment due to the oxygen holes in the ground state of BaFeO₃ thin films. Those results were suggested that the mechanism of the insulating properties in BaFeO₃ is strong Fe $3d - O 2p$

hybridization under the negative charge transfer energy and classified as a covalent insulator.

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