XAS and MCD studies in $Eu_{0.6}Sr_{0.4}MnO_3$

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$Eu_{1-x}Sr_xMnO_3$ system is one of the perovskite manganites that exhibit the giant magneto resistance effect and the transition from the insulator phase to the metal. $Eu_{0.6}Sr_{0.4}MnO_3$ behaves as a ferromagnetic semiconductor and has an Insulator-Metal (IM) transition induced by external magnetic field, which could be found only in this system among the perovskite manganites group. The mechanism of the transition was investigated by X-ray Magnetic Circular Dichroism (XMCD) at the Mn $L_{2,3}$-edges of and the Eu $M_{4,5}$ -edges in $Eu_{0.6}Sr_{0.4}MnO_3$.

Keywords: x-ray absorption spectra, magnetic circular dichroism, metal-insulator transition, $Eu_{0.6}Sr_{0.4}MnO_3$

1. Introduction

The perovskite manganites are well known for the Insulator-Metal (IM) transition accompanied by the ferromagnetic-paramagnetic transition. This phenomenon can be interpreted by the double-exchange interaction model. Recently, this perovskite manganites family have been revived because of their giant magnetoresistance effect, charge order effect and orbital order. Unlikely the other manganites, $Eu_{0.6}Sr_{0.4}MnO_3$ behaves as a semiconductor and has the field-induced IM-transition. The change of the resistivity induced by magnetic field was observed at 12 K and estimated to be the order of about 10^6. The tentative interpretation of the substantial change in resistivity was proposed by Nakamura *et al*. (1999). According to them, the total quantum number (J) of the Eu ions supposed to be increased from J=0 to J=7/2 when the external magnetic field induces the change of the electronic state of Eu ions from $Eu^{3+}(4f^6)$ to $Eu^{2+}(4f^7)$. Because of the coupling of the spins between Eu and Mn ions, extra holes at Mn sites will be produced and contribute to the metallic conduction as the carrier. It is, however, not so the mechanism of IM transition as mentioned above is not common. Therefore, our purpose was to determine the mechanism of the magnetic field-induced change of the resistivity. We report X-ray Magnetic Circular Dichroism (XMCD) measurement performed at the $L_{2,3}$-edges of Mn and the $M_{4,5}$-edges of Eu in $Eu_{0.6}Sr_{0.4}MnO_3$ at variable temperature and the strength of magnetic field.

2. Experimental

The MCD and XAS spectra were measured for $Eu_{0.6}Sr_{0.4}MnO_3$ using synchrotron radiation at soft X-ray beamline BL23SU and BL25SU of SPring-8, Japan.

BL23SU has a Hettrik-Underwood type monochromator which consists of, a varied line-spacing plane grating and a post-focusing mirror (Saitoh *et al.*, 2000). One can choose a grating between a groove density 600 *l/mm* grating and a grove density 1000 *l/mm* grating in vacuum for required energy region. For the present measurements both gratings were used.

The monochromator covers the energy region from 0.5 to 2 keV (Yoshigoe *et al.*, 2000). The energy resolution of the monochromator, E/ΔE, was estimated over 7000 during the measurements. The photon flux is expected to be greater than 10^{11} photons/sec on a few-square-millimeter sample in the MCD instrument. The post-focusing mirror current was recorded as an incident photon intensity monitor. The photon energy scale of spectra was calibrated by referring the nickel and titanium $L_{2,3}$ absorption spectra of NiO and TiO_2. The MCD instrument, which was installed in BL23SU, could add the magnetic filed to samples until 10 Tesla and make samples cooled to 10 K.

Sample surfaces were thoroughly field in an analysis chamber before the measurements. At BL25SU, the spectra were obtained from the subtraction of XAS spectra, which were measured at T = 30 K and H = 1.4 T in a total electron yield mode around Mn-$L_{2,3}$, Eu-$M_{4,5}$ edges. A magnetic field of ±1.4 Tesla was applied to samples, and was switched at each photon energy to flip the magnetization. At BL23SU a magnetic field was fixed to +10 Tesla and we could get the MCD spectra by subtracting the two XAS spectra which were measured for the right-handed and left-handed circularly polarized X-rays by the total electron yield method.

$Eu_{0.6}Sr_{0.4}MnO_3$ samples were synthesized by the conventional solid state reaction method. $SrCO_3$(3N), Eu_2O_3(4N) and MnO_2(99.5%) were used starting materials. The starting materials were mixed by stoichiometric ratios. The mixed powders were calcined in air at 1173 K for 12 h. The calcined powders was ground, pelletized, and sintered at 1473 K – 1723 K for 12 h in air, and then furnace-cooled to room temperature. The powder X-ray diffraction patterns revealed that the sample show a single phased the orthorhombic perovskite-type structure without any impurity phases (Tadokoro *et al.*, 1998).

3. Results and Discussion

Figure 1 shows the magnetic field dependence of the Eu $M_{4,5}$ soft x-ray absorption spectra of $Eu_{0.6}Sr_{0.4}MnO_3$. The spectrum (a) was measured at 80 K with the external magnetic fields of 1 T and the spectrum (b) was measured at 80 K with the external magnetic fields of 10 T. Figure 2 shows the $M_{4,5}$ absorption spectra of the $Eu^{3+}(J=0)$ ion and the $Eu^{2+}(J=7/2)$ ion. These spectra were calculated with the complete atomic multiplet terms (Imada, *et al*., 1990; Nakazawa, *et al*., 2000).

If there was the change of Eu ion's valence from trivalent to divalent, the line shape of the Eu 3d-XAS spectra showed the change. But the spectrum (A) and (B) were the same shape. These spectra were similar to the theoretical spectrum of Eu^{3+}. The result revealed that the valence of Eu ions did not change by the magnetic field. In Figure 2 (a) and (b), Mn $L_{2,3}$-edges absorption spectra under the magnetic field parallel (I_+) and antiparallel (I_-) to the photon spin are shown by solid and broken lines, respectively. The MCD spectrum is the difference of these two spectra. Figure 2 (a) was measured at H = 1 T and T= 30 K. Figure 2 (b) was measured at H = 10 T and T= 30 K. The overall line shape of the XAS and the MCD is quite similar between two graphs. The multiplet structures in both XAS and MCD did not show clear differences between two graphs. The intensity of MCD became increasing, as the magnetic field became stronger.

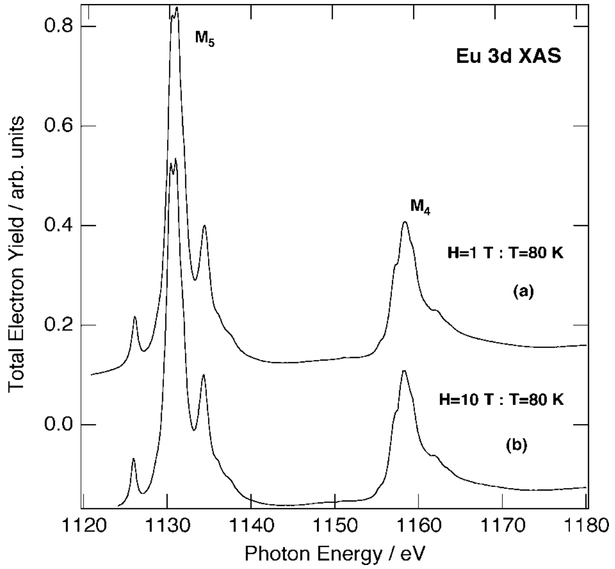

Figure 1
XAS at the Eu $M_{4,5}$ edges in Eu$_{0.6}$Sr$_{0.4}$MnO$_3$, which were measured at 80 K with the external magnetic fields of 1 T and 10 T

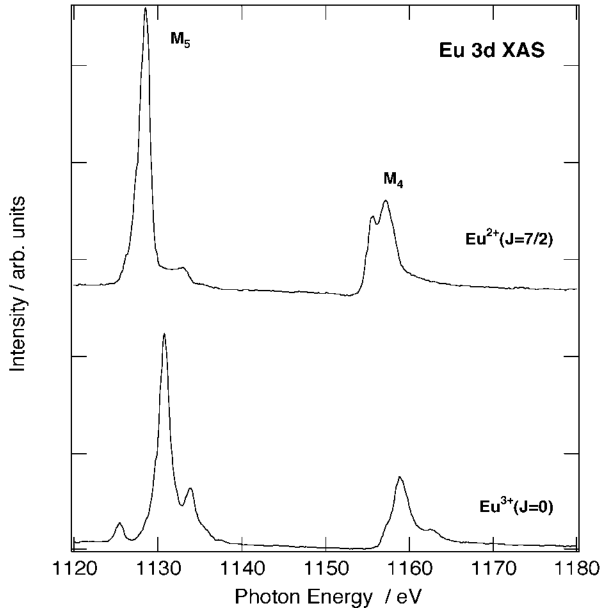

Figure 2
Calculated XAS Eu $M_{4,5}$ edges for the Eu^{2+} and Eu^{3+} ions, which the atomic full mutiplet terms were taken into account.

The origin of the multiplet structures seen in the $L_{2,3}$-edges soft X-ray absorption spectra and MCD spectra is a combination of the electron-electron interaction within the Mn atom, the crystal field applied to Mn ion by O^{2-} and the hybridization between the Mn 3d orbital and the O 2p orbital. It was reported that the difference of Mn $L_{2,3}$-edges soft X-ray absorption spectra line shape comes from the average valence of Mn. (Abatte *et al.*, 1992). Therefore, the average valence of Mn was not changed clearly by the magnetic field.

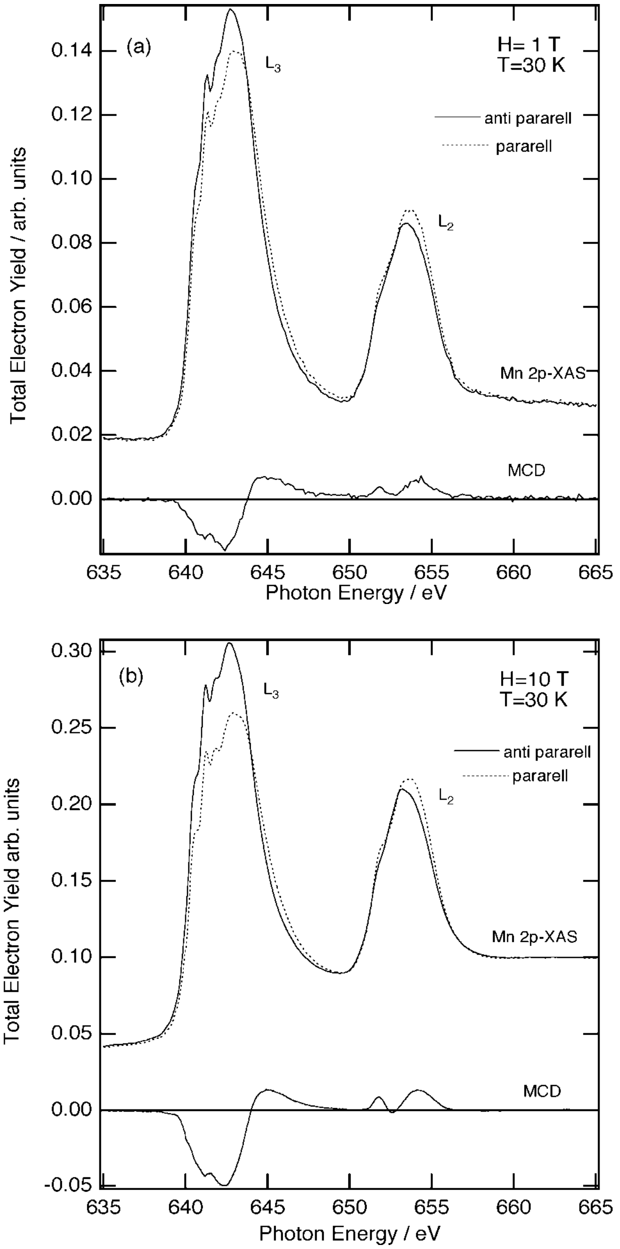

Figure 3
XAS and MCD at the Mn $L_{2,3}$-edges in Eu$_{0.6}$Sr$_{0.4}$MnO$_3$. They were measured at 30 K with the external magnetic fields of (a) 1 T and (b) 10 T. The solid line and the dotted lines in upper part of both panels correspond to XAS when the left- and the right-handed circularly polarized light were used for measurements, respectively.

Figure 4 shows the Eu $M_{4,5}$ soft x-ray absorption spectra and MCD spectra of the Eu$_{0.6}$Sr$_{0.4}$MnO$_3$ taken at T=30 K and at H=1.4 T. The Eu $M_{4,5}$ soft x-ray absorption spectra under the magnetic field parallel (I_+) and antiparallel (I_-) to the photon spin are shown by solid line and dots, respectively. The MCD spectrum is the difference of these two spectra and is shown by dots. The solid line in MCD spectrum corresponds to the smoothed raw data.

The Eu $M_{4,5}$ absorption spectrum shows the complex multiplet structures and the line shape is quite similar to the spectrum of Eu^{3+} ($J=0$) ion. This results show that the valence of Eu ions is trivalent. The Eu $M_{4,5}$-MCD spectrum had the negative peak around the 3$d_{5/2}$ regions and the positive peak around the 3$d_{3/2}$ regions.

According to the theoretical calculation of T. Jo (1993), the MCD intensity of Eu^{3+} was expected to zero. They assumed that Eu^{3+} is taken the lowest state in the Hund's Rule at T=0 K. According to van Vleck (Vleck, 1965), the energy difference between the ground state (*J=0*) and the first excitation state (*J=1*) is very small with compared to other 4*f* elements. Figure 5(a) shows the energy scheme of Eu^{3+} ion. The magnitude of the difference is about 29 meV. In the finite temperature some of the Eu^{3+} ions are excited to the first excitation state (*J=1*).

In Figure 5(b) and (C), the configuration of electrons for *J=0* and *J=1* were shown respectively. When we assume the configuration of electrons and take into considerations for the first excited state, we are able to explain that the MCD of Eu^{3+} ions come out. We calculated the MCD intensity with the atomic model about Eu^{3+} (*J=1*) ions. As the result, the MCD signal is negative around $3d_{5/2}$ regions and positive around $3d_{3/2}$ regions. We conclude that the MCD of the Eu^{3+} ions came from the existence of the first excited state in finite temperature.

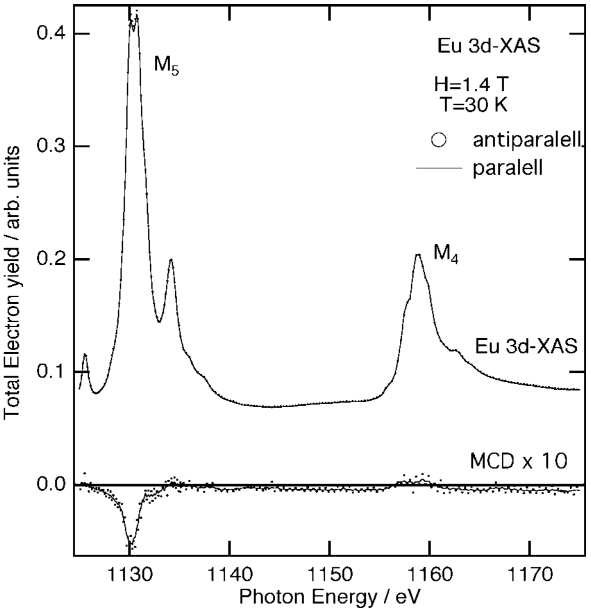

Figure 4
XAS and MCD at the Eu $M_{4,5}$ edges in $Eu_{0.6}Sr_{0.4}MnO_3$, which were measured at 30 K with the external fields of 1.4 T. The dots and the solid line in the MCD spectra correspond to the raw data and the guide to eyes,

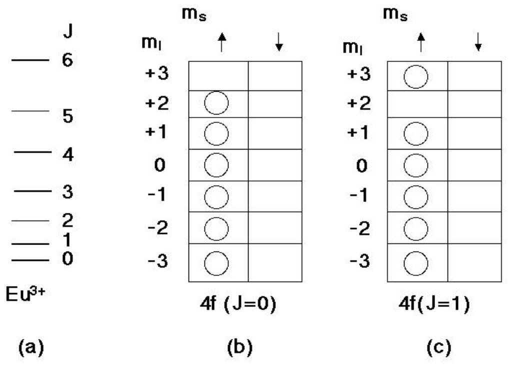

Figure 5
(a) The schematic diagram of energy levels of Eu^{3+} ion. (b) and (c) show the configuration of 4*f* electrons for *J*=0 and for *J*=1, respectively.

4. Conclusion

In summary, we measured the XAS and MCD spectra at the Mn-$L_{2,3}$ and Eu-$M_{4,5}$ edges in $Eu_{0.6}Sr_{0.4}MnO_3$ taken at 30 K and 80 K with the external magnetic fields of 1.4 T and 10 T. The shape of the Eu $M_{4,5}$ x-ray absorption spectra showed the Eu^{3+}(*J=0*) and did not change by the magnetic field. This fact showed that the valence of Eu ions was independent of the external magnetic field. The Mn-$L_{2,3}$ MCD spectra did not show the clear difference by the magnetic field. The results showed that the average valence of Mn was not changed clearly by the magnetic field. In conclusion, the metal-insulator transition in $Eu_{0.6}Sr_{0.4}MnO_3$ induced by the magnetic field did not come from the change of Eu ion's valence. But the double exchange interaction played an important role in the field induced phase transition.

The Eu-$M_{4,5}$ MCD spectra had a negative peak around $3d_{5/2}$ regions and a positive peak around $3d_{3/2}$ regions. We could explain that the MCD of the Eu^{3+} ions came from the existence of the first excited state in finite temperature.

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References

Abbate, M., de Groot, F. M. F., Fuggle, J. C., Fujimori, A., Strebel, O., Lopez, F., Domke, M., Kaindl, G., Sawatzky, G. A., Takano, M., Takeda, Y., Eisaki, H., & Uchida, S. (1992), *Phys. Rev. B* **46**, 4511-4519.
Imada, S., & Jo, T. (1990), *J. Phys. Soc. Jpn.* **59**, 3358-3373.
Jo, T., & Imada, S. (1993), *J. Alloys and Compounds* **193**, 170-174.
Tadokoro, Y., Shan, Y. J., Nakamura, T., & Nakamura, S. (1998), *Solid State Ionics* **108**, 261-267.
Nakamura, S., Tadokoro, Y., Shan, Y. J., & Nakamura, T. (1999), *J. Phys. Soc. Jpn.* **68**, 1485-1487.
Nakazawa, M., to be published.
Saitoh, S., *et al.*, (2000), *Nucl. Instrum. Methods*, to be published.
Van Vleck. J. H. (1965), *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, London.
Yoshigoe, A., Agui, A., Saitoh, Y., & Yokoya, A., (2000), *J. Synchrotron Rad.* to be published.