Observation of magnetically hard grain boundaries in double-perovskite \text{Sr}_2\text{FeMoO}_6

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Abstract – Unusual low-temperature magneto-resistance (MR) of ferromagnetic \text{Sr}_2\text{FeMoO}_6 polycrystals has been attributed to magnetically hard grain boundaries which act as spin valves. We detected the different magnetic hysteresis curves for the grains and the grain boundaries of polycrystalline \text{Sr}_2\text{FeMoO}_6 by utilizing the different probing depths of the different detection modes of x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD), namely, the total electron yield (TEY) mode (probing depth \(\sim 5\) nm) and the total fluorescence yield (TFY) mode (probing depth \(\sim 100\) nm). At 20K, the magnetic coercivity detected in the TEY mode \(H_{c,TEY}\) was several times larger than that in the TFY mode \(H_{c,TFY}\), indicating harder ferromagnetism of the grain boundaries than that of the grains. At room temperature, the grain boundary magnetism became soft and \(H_{c,TEY}\) and \(H_{c,TFY}\) were nearly the same. From the line-shape analysis of the XAS and XMCD spectra, we found that in the grain boundary region the ferromagnetic component is dominated by \(\text{Fe}^{2+}\) or well-screened signals, while the non-magnetic component is dominated by \(\text{Fe}^{3+}\) or poorly screened signals.

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Introduction. – Colossal magneto-resistance (CMR) \cite{1}, a giant decrease of the electrical resistivity under a magnetic field, is a remarkable property that can be applied to spintronics devices. CMR has been observed in many complex oxides of \(\text{Mn}\) such as \(\text{La}_{1-x}\text{Ca}_x\text{MnO}_3\) \cite{2}, \(\text{La}_{1-x}\text{Ba}_x\text{MnO}_3\) \cite{3}, and \(\text{Tl}_2\text{Mn}_2\text{O}_7\) \cite{4}. However, it needs high magnetic fields in the 1 T range, making the practical use of these materials difficult. On the other hand, low-field grain boundary magneto-resistance has been discovered in the pyrochlore-type \(\text{Tl}_2\text{Mn}_2\text{O}_7\) \cite{5}. The polycrystalline double-perovskite \(\text{Sr}_2\text{FeMoO}_6\) (SFMO), which has a high Curie temperature \(T_C = 415\) K, has also been discovered to show CMR at low magnetic field and room temperature \cite{6} and therefore has become one of the most promising materials for the application of CMR. Because the same low-field magneto-resistance (LFMR) has not been observed in single crystalline samples \cite{7}, tunneling magneto-resistance (TMR) between ferromagnetic grains via insulating grain boundaries has been proposed as a mechanism of the LFMR of SFMO \cite{8}. However, a recent study of polycrystalline SFMO has shown unusual magneto-resistance (MR) that cannot be explained by the conventional TMR mechanism, according to which the peak MR should occur at a magnetic field which coincides with the magnetic coercivity \(H_c\) \cite{8}. At low temperatures, the MR peak of SFMO occurs at

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magnetic fields ($H_{c,MR}$) about 6 times larger than $H_c$ [9] as shown in fig. 1, while such a difference between $H_c$ and $H_{c,MR}$ disappears at high temperatures [10]. It has been suggested [9] that the unusual MR in SFMO is controlled by the spin polarization of grain boundary regions acting as spin valves, and is called spin-valve-type MR (SVMR), in contrast to the conventional MR in which the tunnel barriers are non-magnetic. If the $H_c$ of the magnetic tunnel barrier is larger than that of the grains, the discrepancy between $H_c$ and $H_{c,MR}$ can be understood. However, it is difficult to differentiate between the magnetic states of the grains and the grain boundaries using conventional magnetization measurements.

In this work, we have investigated the different coercivities between the grains and the grain boundaries by using x-ray magnetic circular dichroism (XMCD) at the Fe $L_{2,3}$ edges. We have utilized the different probing depths of different detection modes, namely, the total electron yield (TEY, probing depth $\sim$5 nm) and total fluorescence yield (TFY, probing depth $\sim$100 nm) modes.

**Experimental.** Polycrystalline samples were prepared by arc melting and annealing in 2% hydrogen and 98% argon atmosphere at 1250°C (see footnote 1). Electron microscopy observation showed that the average grain size was 5–10 $\mu$m. The grain boundaries are expected to have the thickness of order $\sim$1 nm. X-ray absorption spectroscopy (XAS) and XMCD measurements were carried out at the Dragon beam line 11A of National Synchrotron Radiation Research Center (NSRRC), Taiwan. The monochromator resolution was $E/\Delta E > 10000$ and the degree of circular polarization of x-rays was $\sim$60%. The angle between the incident light and the magnetic field was 30°, and magnetic fields (from $-1$ T to 1 T) were applied parallel to the sample surface. The measurement temperatures were 20 and 300 K. The samples were scraped in situ by a diamond file under an ultrahigh vacuum of $\sim 1 \times 10^{-9}$ torr. When sintered polycrystalline samples are scraped, if intergranular fracture dominates the intragranular one, the scraped surface would largely consist of grain boundaries. Because the thickness of the grain boundaries of our samples is expected to be of the order of a few nm as reported by a SEM study [10] or on the analogy of another transmission electron microscopy study for polycrystalline Al$_2$O$_3$ samples [11], it is comparable to the probing depth of the TEY mode. Therefore, spectra taken in the TEY mode would be dominated by spectra of grain boundaries. On the other hand, the TFY mode has a much deeper probing depth ($\sim$100 nm) than the thickness of grain boundaries, and signals from the interior of grains would be dominant in the spectra.

**Results and discussion.** In fig. 2, we show the XAS [$(\mu_+ + \mu_-)/2$] and XMCD ($\Delta \mu = \mu_+ - \mu_-$) spectra at the Fe $L_{2,3}$ ($2p_{1/2,3/2} \rightarrow 3d$) absorption edges normalized to the $L_3$ XAS peak intensity. Here, $\mu_+$ and $\mu_-$ denote the absorption coefficients for the photon helicity parallel and antiparallel to the Fe 3d majority spin, respectively. In these spectra, the higher- and lower-energy parts of the Fe $L_{2,3}$ peaks are expected to originate mainly from the Fe$^{3+}$ and Fe$^{2+}$ components in the ground state [12], respectively. The Fe$^{2+}$ signals may also originate from the screening of the core hole for the Fe$^{3+}$ ground state. If we compare the spectra taken at 20 and 300 K, the XMCD intensity decreases with increasing temperature by about 30% as can be seen from figs. 2(a) and (b), which reflects the decrease of the ferromagnetic moment with increasing temperature. By applying the XMCD sum rules [13,14], we have estimated the orbital magnetic moments to be 0.03 $\mu_B$/Fe at 20 K and $< 0.01$ $\mu_B$/Fe

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1This sample is similar to sample C in ref. [9]. Details of the sample preparation are given in ref. [9].
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Fig. 3: (Color online) Line-shape analysis of the Fe $L_{2,3}$ XAS and XMCD spectra of Sr$_2$FeMoO$_6$ polycrystal using cluster-model calculation. (a) 20 K, (b) 300 K. Each of the calculated Fe$^{2+}$ and Fe$^{3+}$ spectra is shown. The vertical bars indicate their $L_3$ peak positions. The Fe valence ratios deduced from each spectrum are also indicated. (c) Ratios of the magnetic and non-magnetic components at 20 and 300 K within the probing depth (~5 nm) of the TEY detection. Each component is decomposed into the Fe$^{2+}$-like and Fe$^{3+}$-like components. The error bars in each component are also indicated.

at 300 K, respectively, by using the Fe valences obtained from the XAS spectra in fig. 3. The XMCD spectra taken in the bulk-sensitive TFY mode (figs. 2(c) and (d)) show the same trend but the intensity of the Fe $L_3$ peak relative to the $L_2$ peak is lowered due to self-absorption and quantitative analysis is hindered. Nevertheless, the TFY spectra clearly show a higher Fe$^{2+}$-like intensity than the TEY ones, indicating that the grain interior has more Fe$^{2+}$ component or stronger core-hole screening due to the higher density of conduction electrons than the grain boundaries. In addition, the XMCD intensity of the Fe $L_2$ edge in the TFY mode, which is less affected by the self-absorption, is higher than that in the TEY mode, indicating that the grain interior has a larger magnetic moment than the grain boundaries. This suggests that Fe atoms inside the grains are almost fully spin polarized with an insignificant amount of non-magnetic component. The XMCD intensity in the TFY mode also decreases with increasing temperature, corresponding to the decrease of magnetization in the grain interior [6].

From now on, we focus on the grain boundary region within the TEY probing depth, where the ferromagnetism is weaker than the interior of the grains, in order to obtain the quantitative information about the Fe valence and magnetization. We performed line-shape analysis of the experimental XAS and XMCD spectra by least mean square fitting to a superposition of the Fe$^{2+}$ and Fe$^{3+}$ spectra calculated using the cluster model, as shown by the dotted curves in fig. 3. Parameters used in this calculation are as follows (in units of eV): Fe$^{2+}$: $\Delta = 6.0$, $V_{Fe} = 2.1$, $10Dq = 0.5$, $T_{pp} = 1.2$; Fe$^{3+}$: $\Delta = 3.0$, $V_{Fe} = 2.5$, $10Dq = 0.5$, $T_{pp} = 0.7$ (see footnote 2). Figures 3(a) and (b) show that the Fe valence deduced from the XAS spectrum is quite different from that deduced from the XMCD spectrum. This indicates that the apparent valence of the ferromagnetic Fe ions is more Fe$^{2+}$-like while that of the non-magnetic Fe ones is more Fe$^{3+}$-like.

The experimental XMCD intensities are lower than those expected for fully spin-polarized Fe$^{2+}$ and Fe$^{3+}$ components, indicating that part of the Fe$^{2+}$ and Fe$^{3+}$ ions are in the paramagnetic or antiferromagnetic state. We have obtained the weight of the Fe$^{2+}$-like and Fe$^{3+}$-like components in each of the ferromagnetic and non-magnetic (i.e., para/antiferromagnetic) components, as shown in fig. 3(c). In going from 20 to 300 K, the amount of the ferromagnetic component decreases by 12%, in agreement with the temperature dependence of magnetization [6]. Therefore, the ferromagnetic component of the grain boundary is not much different from the ferromagnetic bulk material. The amount of the Fe$^{2+}$-like component in the non-magnetic component increases with increasing temperature, which may partly be due to the actual increase of Fe$^{2+}$ but also

at the B site of Fe$_3$O$_4$, respectively [15].

Fig. 4: (Color online) Hysteresis loops of the Fe $L_3$ XMCD intensities of the Sr$_2$FeMoO$_6$ polycrystal taken in the TEY and TFY modes at 20 K (a) and 300 K (b). The inset shows an expanded view near $H = 0$. The vertical scales of the inset are arbitrary.

$V_{Fe} = 2.1$, $10Dq = 0.5$, $T_{pp} = 1.2$; Fe$^{3+}$: $\Delta = 3.0$, $V_{Fe} = 2.5$, $10Dq = 0.5$, $T_{pp} = 0.7$ (see footnote 2).
to the enhancement of screening effect related to the decrease of the resistivity with increasing temperature [6].

Figure 4 shows $M$-$H$ curves obtained from the XMCD intensity in both detection modes. Hereafter, the $H_c$ of the hysteresis loop of the TEY mode and that of the TFY mode are denoted by $H_c,_{TEY}$ and $H_c,_{TFY}$, respectively. Figure 4(a) shows that at 20 K $H_c,_{TEY}$ is 0.02 T, 6 times larger than $H_c,_{TFY}$ of 0.003 T. The difference between $H_c,_{TEY}$ and $H_c,_{TFY}$ is similar to the different $H_c$ values between the magnetization and MR measurements [9]. Because TEY and TFY have the probing depths of several nm and ~100 nm, respectively, $H_c,_{TEY}$ and $H_c,_{TFY}$ correspond to the $H_c$ of grain boundaries and that of grains, respectively. This is consistent with the scenario that SVMR is driven by the large coercivity of the grain boundaries at low temperatures [9]. At 300 K, $H_c,_{TEY}$ is reduced and becomes as small as $H_c,_{TFY}$ as shown in fig. 4(b), resulting in the absence of coercivity difference between TEY and TFY, that is, between the grain boundaries and the grain interior. This explains the disappearance of SVMR at high temperatures [10].

Summary. – In conclusion, we have performed detailed XAS and XMCD studies of polycrystalline SFMO. The different magnetic hardness of the grain boundaries and the grains was observed at 20 K as different $H_c$ values in the hysteresis loops recorded in the surface-sensitive TEY and bulk-sensitive TFY modes. These results are consistent with the SVMR mechanism proposed for the unusual MR in SFMO polycrystals. From the line-shape analysis of the XAS and XMCD spectra, we revealed that in the grain boundary region the Fe valence in the magnetic component is more Fe$^{2+}$-like than that in the non-magnetic component.

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