STUDY OF FERROMAGNETIC MATERIALS BY MEANS OF MAGNETIC CIRCULAR DICHROISM IN SOFT X-RAY PHOTOABSORPTION

Magnetic circular dichroism (MCD) of core-level X-ray absorption (XAS) has attracted much attention because of its ability to resolve spin and orbital contributions to the magnetic moments in ferromagnetic materials [1]. At the circularly polarized soft X-ray beamline **BL25SU** [2], we have developed an apparatus with which XAS-MCD can be measured with a magnetic field of 1.4 T applied on a sample that can be cooled down to about 25K.

The components of magnetism are electronic spin – the spinning rotation of the electron itself – and orbital angular momentum – the orbital rotation of the electron around the nucleus. In XAS-MCD, core-level electrons are excited to an orbital whose electrons are magnetized, where their spin and orbital angular momentum states are probed. The use of circularly polarized X-ray, which is effectively a rotating electric field, is essential because it can selectively excite electrons whose spin and orbital rotations are in particular directions. This mechanism can be understood by combining the selection rule of the circularly polarized light with the spin-orbit interaction [3].

The experimental setup used for MCD is illustrated in Fig. 1. Circularly polarized soft X-ray from the helical undulator is monochromatized and the incident X-ray is normal to the sample plane. XAS are obtained using the total photoelectron yield method by measuring the sample current and normalizing it with the photon current. The photon current is defined by the total photoelectron yield of the post-focussing mirror (M3) before the measurement chamber. A magnetic field of 1.4 T is applied to the sample by a permanent magnet during the measurement. In order to the reverse magnetic field, one of the two permanent magnets, which have opposing dipoles, is placed upon the optical axis (see Fig. 1). The magnetic field is thus either parallel or antiparallel to the photon's k-vector (Faraday geometry). The magnetization is reversed with each photon's energy to cancel any possible drift or fluctuation of the photon current, or other possible errors. A clean sample surface was obtained by *in situ* scraping in an ultra-high vacuum of about 4×10^{-8} Pa. The sample temperature could be set between about 25 K and room temperature.

Perovskite-type manganites have attracted much attention due to their extensive variety of phase transitions, such as ferromagnetic,
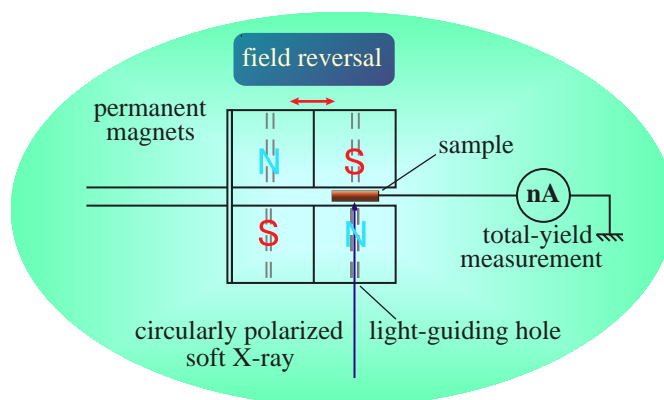

Fig. 1. Illustration of the XAS-MCD setup at beamline BL25SU. Monochromatized circularly polarized soft X-ray is incident normally on the sample and XAS is obtained using the total photoelectron yield method. Magnetic field of 1.4 T is applied to the sample and reversal of the magnetic field is achieved by the linear motion of the permanent-magnets unit.

antiferromagnetic and charge-ordering transitions. We have studied compounds that do not show charge ordering upon a low-temperature-induced phase transition from paramagnetic insulator to ferromagnetic metal. Two compounds are $La_{0.84}Sr_{0.16}MnO_3$ (LSMO 0.16) and the other is $Nd_{0.53}Sr_{0.47}MnO_3$ (NSMO 0.47). The latter is very similar in the composition to a compounds that exhibits a charge-ordering transition.

In Fig. 2, Mn $2p$ XAS under the magnetic fields parallel (I_+) and antiparallel (I_-) to the photon spin are shown by solid and broken lines, respectively [4]. MCD is defined by $I_+ - I_-$. The overall shapes of the XAS and the MCD spectra are quite similar between LSMO 0.16 and NSMO 0.47. However, multiplet structures in both XAS and MCD show clear differences between the two, especially in the $2p_{3/2}$ region (around 640 eV). In the XAS of both samples, a shoulder is seen on the higher energy side of the $2p_{1/2}$ peak (extending from about 657 to 667 eV). A difference in the shape of this shoulder between I_+ and I_-. gives rise to the broad hump in the MCD spectrum around 663 eV.

The origin of the multiplet structures seen in the $2p$ XAS is a combination of the electron-electron interaction within the Mn atom, the crystal field applied to the Mn ion by O^{2-} and the hybridization between the Mn $3d$ orbital and O^{2-} $2p$ orbitals. The shoulder in the higher energy side of the $2p_{1/2}$ peak is not seen in the atomic calculation of $2p$ XAS and MCD spectra for an ion subject to crystal fields. This suggests that the shoulder originates from the hybridization between Mn and the surrounding O^{2-}. The difference in $2p$ XAS curve shape between LSMO 0.16 and NSMO 0.47 is similar to that between LSMO with different Sr composition. Therefore, the difference in the spectra between LSMO 0.16 and NSMO 0.47 is probably derived mainly from the disparity in the $3d$ electronic states due to the different concentrations of the doped hole or, *i.e.*, the average valence of Mn.
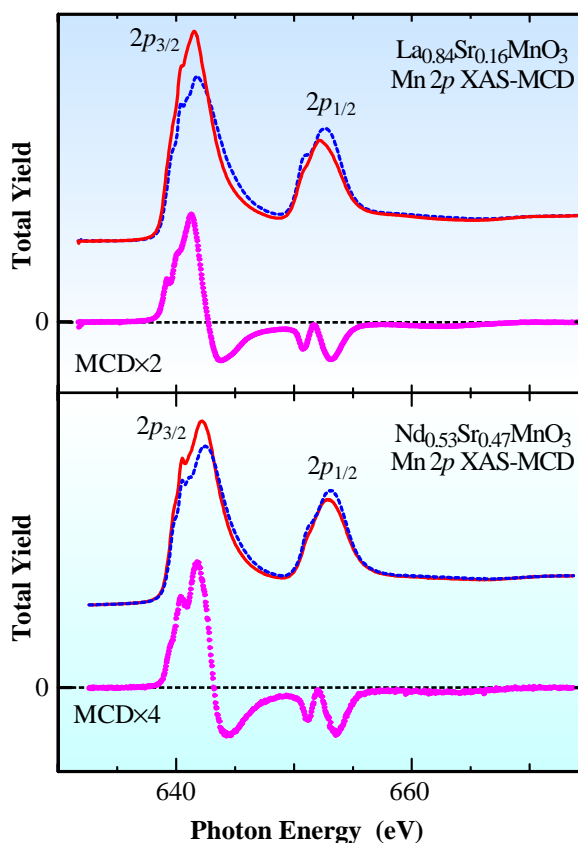

Fig. 2. Mn 2p XAS and MCD of $La_{0.84}Sr_{0.16}MnO_3$ (upper panel) and $Nd_{0.53}Sr_{0.47}MnO_3$ (lower panel). In addition to the splitting between the $2p_{3/2}$ and $2p_{1/2}$ regions due to the spin-orbit coupling of the 2p level, multiplet structures are seen. Clear sample-dependence is seen in both XAS and MCD especially in the $2p_{3/2}$ region.

Small but clear MCD was found in Nd $3d$ ($4f$ XAS of NSMO 0.47 as seen in Fig. 3). Note that the noise in the MCD spectrum is reasonably small if the 50x magnification is considered. The overall profile of XAS is the same as the typical $3d$ XAS for Nd^{3+} ion [5], which is consistent with the general understanding that Nd is trivalent in this compound. However, the shape of MCD spectrum, especially in the $3d_{5/2}$ region, is quite different from that observed for Nd in $Nd_2Fe_{14}B$, in which Nd carries a large magnetic moment [6]. Since the latter was very well reproduced by the atomic MCD calculation for a Nd^{3+} ion placed in a small magnetic field [3], the present MCD directly indicates that the magnetic state of the Nd^{3+} is unusual in NSMO 0.47. The origin for this phenomenon is not yet known and should be resolved. However, the sign and the shape of the $3d_{3/2}$ MCD is the same as that for $Nd_2Fe_{14}B$, in which the Nd magnetic moment is in the same direction as the total magnetic moment. Therefore, the magnetic moment induced on the Nd site of NSMO 0.47 is considered to be in the same direction as that at the Mn site.
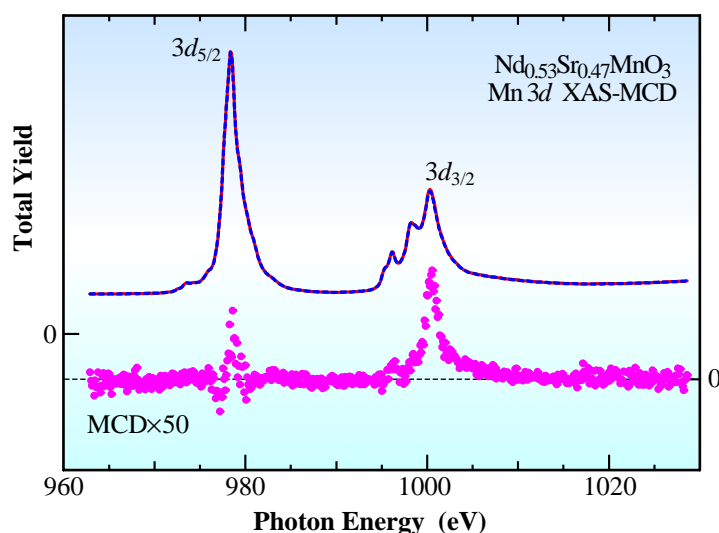

Fig. 3. Nd 3d XAS and MCD of La$_{0.84}$Sr$_{0.16}$MnO$_3$ (upper panel) and Nd$_{0.53}$Sr$_{0.47}$MnO$_3$ (lower panel). Small but clear MCD was found. Note that the noise in the MCD spectrum is reasonably small if the magnification factor of 50 times is considered.

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