

Surface and Bulk Magnetization in X-ray Magnetic Circular Dichroism Spectroscopy

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Abstract. The magnetic interactions in $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ are investigated by x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism (XMCD), and bulk magnetization measurements. A quantitative procedure is proposed to determine the values of atomic magnetic moments of transition and rare-earth elements, as well as magnetization on the surface and in the bulk from experimental $L_{2,3}$ and $M_{4,5}$ XMCD spectra.

Introduction

X-ray magnetic circular dichroism (XMCD) is a very powerful tool to investigate the internal magnetic structure of compounds in question, including the unique possibility to separate the magnetic moments into their spin and orbital contributions. However XMCD lines often have a complex shape and direct application of the sum rules does not give reasonable values for the magnetic moments of components in compounds. For this reason, researchers have only limited qualitative information about the presence or absence of XMCD signal at various concentrations of atoms, the direction of the magnetic moments of transition and rare-earth atoms [1-3]. Our report provides a method of obtaining magnitudes of the local atomic moments on the surface and in the bulk. We illustrate it on a case study of the compound $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$.

Experimental details

The experiments were performed on $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ single crystals grown by the floating zone technique [4]. XAS and XMCD measurements at the Mn and Ca $L_{2,3}$, La and Pr $M_{4,5}$ and O K edges were carried out on the surface and interface microscopy (SIM) beamline of the Swiss Light Source (SLS). We used the 7 T cryomagnetic TBT-XMCD end station, working with a ^3He - ^4He dilution setup in order to reach base temperatures of around 0.7 K. The sample was cleaved *in-situ* in preparation chamber. The spectra were recorded using the total electron yield (TEY). The undulator-based beamline delivers a flux on the order of 10^{12} photons s^{-1} at Mn L edge photon energies of around 650 eV. Instrumental energy resolution was 0.16 eV. In order to obtain uniform and clean surfaces, the analyzed samples were cleaved under high vacuum conditions in preparation chamber and then moved for XAS measurements without breaking vacuum. The pressure was kept at about 5×10^{-10} mbar during measurements. The spectra were obtained with $\sim 100\%$ circularly polarized beam in the total electron yield mode, and normalized by the incident beam intensity. The XMCD data were taken at 2 K by alternating the ellipticity of the beam between circular left and right, in an applied magnetic field up to 6.9 T along the beam direction by means of a superconducting magnet.

Results and analysis

We measured the XAS spectra at the Mn $L_{2,3}$ edges for the $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ single crystals probing electronic transitions from the Mn $2p$ core levels to Mn $3d$ states above the Fermi level. We studied absorption spectra of circularly polarized X-rays at 2 K in a magnetic field of 6.9 T with the beam helicity parallel I_+ and antiparallel I_- to the applied magnetic field. Fig. 1 (a) shows the x-ray absorption near edge structure (XANES) $(I_+ + I_-) / 2$ averaged over polarization and magnetic field direction and the XMCD difference signal $(I_+ - I_-)$ at the Mn $L_{2,3}$ edges (multiplied by factor 3). The XANES spectrum consists of two peaks in the L_3 edge at 642 and 644 eV and a broad peak in the L_2 edge centered at 654.5 eV with a shoulder at 652.5 eV. The spectrum shows similar line shape of previously reported data for Sr-doped LaMnO_3 [5]. Turning to the XMCD spectrum, we see that it has a rather complicated shape, significantly different from the spectrum of pure transition metals [6].

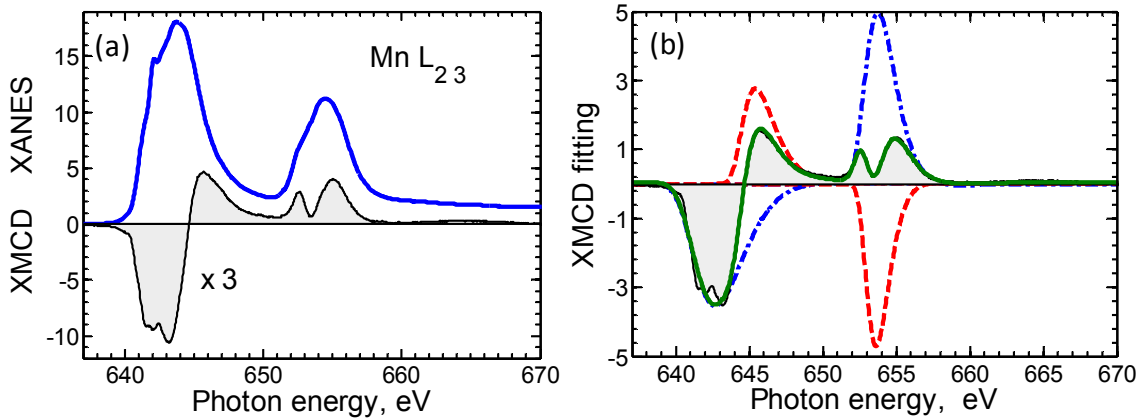


Fig. 1 (a) The Polarization averaged absorption spectra XANES $(I_+ + I_-) / 2$ (blue solid) of $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ and multiplied by factor 3 the XMCD signal $(I_+ - I_-)$ (area) at the Mn $L_{2,3}$ edges performed at 2 K in magnetic field 6.9 T. (b) The Mn $L_{2,3}$ XMCD spectrum (area) and its fitting (green solid) by contribution from up (blue dash-dotted) and down (red dashed) magnetic moments.

The Fig. 2 (a) shows the corresponding XANES and XMCD (multiplied by factor 4) spectra at the Pr $M_{4,5}$ edges probing electronic transitions from the Pr $3d$ core levels to Pr $4f$ valence states above the Fermi energy. The M_5 spectrum shows an intense sharp peak around 932 eV with 1 eV multiplet splitting, while the M_4 line exposed too much stronger splitting into detached peak 948 eV and a group of about 952 eV. Despite the expected high magnetic moment of Pr, the XMCD signal looks very small. Its characteristic feature is a complex form changing the sign as in the M_5 edge, so the M_4 edge. XMCD signals can be noticed for both Mn and Pr edges, indicating that both elements contribute to the magnetic response of these samples at low temperatures. All displayed spectra show a complicated structure with a number of characteristic sharp features. On the other hand, the La $M_{4,5}$ and Ca $L_{2,3}$ does not show any relevant XMCD signal due to the absence of a significant magnetic moments.

In principle, the XMCD signal may provide direct information on Mn $3d$ and Pr $4f$ orbital and spin magnetic moments through the sum rules [7–9]. However, the direct application of the sum rules to extract the magnetic moments of Mn and Pr is unsuccessful. Calculating the area of Mn L_3 and Mn L_2 spectra and Pr M_5 and Pr M_4 , as well as the area of the corresponding XMCD lines, we find the sum rules [6] values for the magnetic moments: $0.79 \mu_B$ per a manganese atom and $-0.35 \mu_B$ per praseodymium. This is much less than the values $3.75 \pm 0.4 \mu_B$ per the formula unit obtained in the bulk magnetization measurements. The standard sum rules approach gives too small moment values not only in this case, but also in many other [10]. This is a common problem for the determination of the magnetic moments in the compounds of the transition and rare earth metals [1–3, 11]. A reason for the discrepancy is that the soft XMCD (and XAS) data taken in the total electron yield mode probes the near-surface layers of the sample within a few nanometers, while dc magnetization shows

a bulk property. To obtain a quantitative description, we propose the following model of the magnetic electronic structure. The magnetization in the surface layers is smaller than in the bulk because atomic magnetic moments at the surface can be directed both along the external magnetic field and in the opposite direction. Accordingly, the XMCD signal is the sum of the two signals of a simple shape with different signs. Summation creates the resulting complex XMCD spectrum.

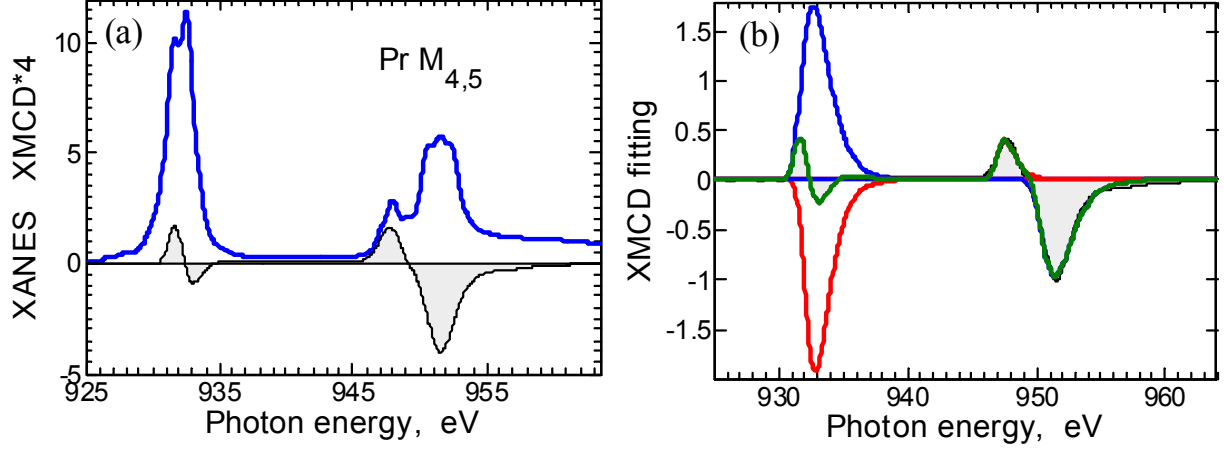


Fig. 2 (a) The Polarization averaged absorption spectra XANES $(I_+ + I_-) / 2$ (blue solid) of $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ and the XMCD signal $(I_+ - I_-)$ multiplied by factor 4 (area) at the Pr $M_{4,5}$ edges performed at 2 K in magnetic field 6.9 T. (b) The Pr $M_{4,5}$ XMCD spectrum (area) and its fitting (green solid) by contribution from up (blue dash dotted) and down (red dots) magnetic moments.

Using standard mathematical fitting procedure, we have identified the signals from the two directions, as shown in Fig. 1 (b). The experimental XMCD spectrum is well described by the green solid curve, which is the sum of the contributions from atoms whose moments are oriented along the external magnetic field (blue dash-dotted line) and against (red dashed line). Applying the sum rules to each signal individually, we find the spin and orbital magnetic moments of up and down atomic subsystems. Table 1 shows the spin, orbital and total magnetic moments of Mn atoms oriented in up and down the magnetic field direction, as well as their sum and difference. According our model the sum value $0.79 \mu_B/\text{Mn}$ is the result for the surface magnetization while the difference $3.32 \mu_B/\text{Mn}$ describes the maximal magnetization achievable in the bulk. The last value agrees well with the dc magnetization measurements which gives $M_s = 3.75 \pm 0.4 \mu_B/\text{f.u.}$ Thus we can conclude that in the strong magnetic field 6.9 T the surface layers (10 nm the total electron yield depth) are not fully magnetized still: 62% Mn atomic moments are oriented along magnetization and 38% in opposite direction, while the bulk state are fully polarized in even significantly weaker fields according to magnetization measurements.

Table 1. The Mn magnetic moments [μ_B/Mn]

Magn. moment	up	down	Surface up+down	Bulk up-down
spin	2.00	-1.30	0.69	3.30
orbital	0.06	0.04	0.10	0.02
total	2.06	-1.26	0.79	3.32

Table 2. The Pr magnetic moments [μ_B/Pr]

Magn. moment	up	down	Surface up+down	Bulk up-down
spin	-0.84	0.07	-0.77	-0.91
orbital	-1.24	1.66	0.42	-2.90
total	-2.08	1.73	-0.35	-3.81

The same results for Pr atoms are presented in the Fig. 2 (b) and the Table 2. The Pr magnetic moments (at 2 K) are directed against the Mn moments (and the external magnetic field). Their magnitudes are equal to $3.81 \mu_B/\text{Pr}$. In the surface layers 55% Pr atomic moments are oriented against the magnetic field magnetization while 45% along. At higher temperatures the Pr moments

can behave like a paramagnetic system without giving a significant contribution to the net magnetization.

Conclusions

Strong contrast of surface and bulk magnetization is quite common in compounds of rare earth and transition elements. We propose the method for separating complex experimental XMCD spectrum into two simple signals originates from the surface atoms with magnetic moments alone and against the applied magnetic field. Applying the sum rules for each signal, it is possible to determine the magnitude of the atomic magnetic moments (orbital and spin) and calculate the magnetization on the surface and in the bulk. We demonstrated the operation of the method on an example of the manganite $\text{La}_{0.5}\text{Pr}_{0.2}\text{Ca}_{0.3}\text{MnO}_3$ but we need that it will be useful in the study of many materials.

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