# **3 Oxide Heterostructure Project**

 Observation and control of novel quantum phenomena in superstructures of strongly correlated oxides –

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#### **3-1 Introduction**

The goal of this project is to design novel physical properties that appear at the heterointerface of strongly correlated oxides. The physical properties arise from strong mutual coupling among the spin, charge, and orbital degrees of freedom in the interface region between two different oxides [1]. To control such properties, one must clarify the interfacial electronic, magnetic, and orbital structures. Therefore, we are using synchrotron radiation spectroscopic techniques that have elemental selectivity to probe these structures in the nm-scale region at the oxide heterointerface. For example, the electronic structure at the interface is determined by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS), the magnetic structure by magnetic circular dichroism (XMCD) of XAS, and the orbital structure by linear dichroism (LD) of XAS. Furthermore, the electronic band structures near the Fermi level  $(E_{\rm F})$ , which dominate the novel physical properties of oxide nanostructures, were investigated by angle-resolved PES (ARPES). We aim to design and create novel quantum materials by optimally combining sophisticated oxide growth techniques using laser molecular beam epitaxy (MBE) and advanced analysis techniques that use quantum beams.

### **3-2 MUSASHI beamline for surface and interface studies of oxide superstructures**

Our developed system "*in-situ* photoelectron spectrometer – laser MBE" was installed at the new undulator beamline MUSASHI (<u>Multiple Undulator beamline for Spectroscopic Analysis on</u>



**Fig. 1**: Photograph of (a) BL-2A MUSASHI beamline and (b) *"in-situ* ARPES – Laser MBE system" which is installed as an endstation of BL-2A MUSASHI.

Surface and HeteroInterface) as an endstation (Fig. 1). At the new BL-2A MUSASHI, we performe both vacuum ultraviolet (VUV: 30–300 eV) and soft X-ray (SX: 250–2000 eV) spectroscopic measurements at the same time, for the same grown sample, with the same experimental setup. This approach guarantees the quality of the experimental data and offers numerous benefits to

the field of surface science. The newly developed system enables us to obtain complete information on the electronic and chemical structures of oxide nanostructures fabricated by laser MBE with high reproducibility. For example, the chemical states and band lineup of heterostructures are characterized by XAS and PES using SX light, confirming the quality of the heterostructures. Subsequently, their band structures are investigated by ARPES using VUV light.

In addition, we have developed a vacuum suitcase to carry the sample to other beamlines under an ultra-high vacuum (Fig. 2). This equipment enables us to conduct XMCD measurements and other synchrotron analyses on the samples measured at the MUSASHI beamline without surface degradation. Further, synchrotron radiation spectroscopy of the sample prepared by MBE located in the laboratory will be available.



**Fig. 2**: Photograph of the developed vacuum suitcase to carry samples with keeping ultrahigh vacuum condition.

## 3-3 Science topic: Relationship between charge redistribution and ferromagnetism at the heterointerface between perovskite oxides LaNiO<sub>3</sub> and LaMnO<sub>3</sub>

Heterostructures composed of different perovskite transition-metal oxides have attracted considerable attention because of the wide variety of novel electronic and magnetic properties that emerge at their interfaces, which cannot be accomplished in bulk constituents [1, 2]. These exotic phenomena appearing at the interfaces are attractive from the viewpoint not only of fundamental physics but also of their potential for technological application in future electronics, such as magnetic field sensors and memory devices [3]. One of the most interesting properties is the ferromagnetism at the interface formed between "non-ferromagnetic" compounds of LaNiO<sub>3</sub> (LNO) and LaMnO<sub>3</sub> (LMO) [4].

Charge transfer across interfaces is one of the most important factors responsible for this exotic interfacial ferromagnetism [4]. The valence changes of the constituent transition-metal ions stemming from the interfacial charge transfer, accompanied by the reconstructions of the orbital and spin degrees of freedom, have a significant effect on magnetic exchange interactions. In addition, to better understand the novel magnetic properties emerging at the interfaces, it is important to elucidate not only the valence change but also the spatial redistribution of the transferred charges. For the case of the LNO/LMO interface, the valence changes in transition-metal ions due to the charge transfer should significantly affect the interfacial ferromagnetism [5-7]. Charge transfer Ni<sup>3+</sup> + Mn<sup>3+</sup>  $\rightarrow$  Ni<sup>2+</sup> + Mn<sup>4+</sup> has been reported to occur across the LNO/LMO interface [6-8], analogous to the double perovskite La<sub>2</sub>NiMnO<sub>6</sub> (LNMO) system [9,10]. As a result of this interfacial charge transfer, ferromagnetically coupled magnetization is induced between Ni and Mn ions owing to the Kanamori-Goodenough (KG) rules [11], although the constituent LNO and LMO are paramagnetic metals and antiferromagnetic insulators in their bulk forms, respectively.

Recently, we have revealed the existence of a characteristic spatial redistribution in the transferred charges at the (001)-oriented LNO/ LMO interface [12]. A detailed analysis of the thickness dependence of X-ray absorption spectroscopy (XAS) results revealed that the spatial redistributions of the transferred charges in the two layers are significantly different. Specifically, the transferred electrons are confined inside the one monolayer (ML) LNO, while the holes are distributed over 3-4 ML LMO. Therefore, the origin of the interfacial ferromagnetism observed in the (001)-oriented LNO/LMO heterostructures should be addressed considering the spatial charge redistribution in the charge transfer region. Thus, in this study, we investigated the relationship between the charge redistribution due to interfacial charge transfer and the resultant ferromagnetism at the LNO/LMO interface by using XMCD mea-



**Fig. 3**: Ni- $L_{2,3}$  XMCD spectra of the LMO/LNO (*n* ML)/LMO trilayer structures (n = 2, 3, 4, and 5) measured under the magnetic field of 1 T at 70 K. The spectrum of a 20 ML LNO film is shown for reference. The corresponding Mn- $L_{2,3}$  XMCD spectra of the trilayers are shown in the inset.

surements.

Digitally controlled LMO/LNO/LMO and LNO/ LMO/LNO trilayer structures were fabricated on atomically flat TiO<sub>2</sub>-terminated Nb:SrTiO<sub>3</sub> (STO) (001) substrates inside the laser MBE chamber installed at beamline BL-2A MUSASHIXAS (see Fig. 1). XAS and XMCD measurements were carried out at BL-2A and BL-16A at KEK-PF, respectively. XAS spectra were recorded at 300 K using horizontally polarized light, while XMCD spectra were obtained at 70 K using circularly polarized light under a magnetic field of 1 T. All XAS and XMCD spectra were obtained by measuring the sample drain current.

Figure 3 shows the Ni- $L_{2,3}$  XMCD spectra of the sandwiched LNO layers with various thicknesses n in the LMO/LNO/LMO trilayers. The spectrum measured for the paramagnetic 20 ML LNO film is also shown as a reference. As expected, no XMCD signal was observed for the LNO film, indicating its paramagnetic properties [12]. In contrast, distinct XMCD signals are obtained for the Ni- $L_{2,3}$  edges of these trilayers, whose intensities monotonically decrease with increasing n. These results indicate that the magnetization of Ni ions emerges at the interface. As for the LMO layers



**Fig. 4**: Mn- $L_{2,3}$  XMCD spectra of the LNO/LMO (*m* ML)/LNO trilayer structures (*m* = 2, 6, and 12) obtained under the magnetic field of 1 T at 70 K. The spectrum of a 20 ML LMO film is shown for reference. The inset shows the corresponding Ni- $L_{2,3}$  XMCD spectra. Note that Ni XMCD signal is observed for *m* = 6 and 12, while it is negligible for *m* = 2.

of these trilayers, Mn-L<sub>2,3</sub> XMCD signals were also clearly detected, as shown in the inset of Fig. 3. Notably, the signs of the Ni- $L_{2,3}$  and Mn- $L_{2,3}$ XMCD signals are the same, indicating that the magnetization vectors induced in both ions align ferromagnetically. Furthermore, the line shapes of the Ni-L<sub>2</sub> XMCD spectra for all LMO/LNO/LMO trilayers remain almost unchanged within experimental accuracy. This invariance indicates that the electronic states of Ni ions contributing to the magnetization are the same, regardless of the thicknesses of the sandwiched LNO layers. Considering that Ni<sup>2+</sup> states are present only in the 1 ML LNO at the interface [11], it can be concluded that magnetization is induced only in the Ni<sup>2+</sup> ions of the 1 ML LNO adjacent to the interface as a result of the interfacial charge transfer.

To examine the behavior of the corresponding Mn ions, the Mn- $L_{2,3}$  XMCD spectra of the LNO/LMO (*m* ML)/LNO sandwiched structures are shown in Fig. 4. In contrast to the LNO film, the LMO film exhibits a clear XMCD signal due to its ferromagnetic nature [8,13], which likely originates from excess oxygen and/or cation vacancies or compressive strain effects from lattice mismatch with the STO substrate [14]. At first glance, the XMCD spectra of the trilayer structures appear similar to that of the Mn<sup>3+</sup> ions of the LMO film. However, upon closer inspection, the Mn XMCD

signals of the trilayer structures with m = 6 and 12 ML have additional Mn<sup>4+</sup> contributions, which correspond to the shoulder features centered at approximately 641.1 and 643.4 eV. In addition, these spectral shapes are very similar to those of the hole-doped manganite La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> [15,16], indicating that Mn<sup>3+</sup> and Mn<sup>4+</sup> contributed to the ferromagnetism of both the 6 and 12 ML LMO layers. Meanwhile, for the 2 ML trilayer structure, the spectral shape resembles that of La<sub>2</sub>Ni<sup>2+</sup>Mn<sup>4+</sup>O<sub>6</sub> [9,10], suggesting that its magnetization results from the valence states approaching Mn<sup>4+</sup>.

Since transferred charges are distributed across the 3-4 ML LMO next to the interface following an attenuation function [12], the increased magnetic moment in the trilayer structures suggests the following. Due to the charge distribution (effective hole doping), the ferromagnetism of Mn ions in the interfacial region is more stable than that of Mn ions in the inner region, which are away from the interface and do not experience the charge transfer. The magnetic phase diagram of hole-doped LaMnO<sub>3</sub> [17,18] suggests that this stabilized ferromagnetism in the interface region of the LMO layer can be explained by the increased ferromagnetic double exchange (DE) interactions between Mn<sup>3+</sup> and Mn<sup>4+</sup> ions due to holes distributed from the interface. This doped-hole DE phenomenon is further supported by suppressed ferromagnetism in the trilayer structure with m = 2ML, as evidenced by the reduction of the XMCD signal. In the trilayer structure with m = 2 ML, the holes transferred from the top and bottom LNO layers are accommodated in the 2 ML LMO sandwiched layers, and consequently, the hole doping level becomes too high to stabilize the ferromagnetic DE interactions, as observed for the overdoped region of hole-doped LMO [18].

These results suggest that the stabilization of the ferromagnetism in LMO layers due to the interfacial charge redistribution and simultaneous ferromagnetic coupling between Ni and Mn spins due to the KG rule [11] are the key factors inducing the interfacial magnetism of the (001)-oriented LNO/LMO interface. Based on these observations, we proposed a possible model to describe the interfacial magnetism of the LNO/LMO interface [19], as schematically illustrated in Fig. 5.

The model suggests that an appropriate LMO thickness that stabilizes the ferromagnetism is also necessary to magnetize the Ni ions in the



**Fig. 5**: Schematic illustrations of possible interfacial magnetic structures with (a) symmetric and (b) asymmetric charge redistributions. Here, SE denotes superexchange interaction, DE means double exchange interaction, AFM is antiferromagnetism, and FM means ferromagnetism. The magnetization vector of Mn ions is aligned along the direction of incident x-ray (applied magnetic field) under the present experimental conditions. Meanwhile, there is an arbitrary possibility for the direction of antiferromagnetic order for Ni ions.

LNO layer of the (001)-oriented LNO/LMO heterostructure. The close relationship between the charge redistribution and ferromagnetism is further supported by the fact that the LNO/LMO (2 ML)/LNO sandwiched structure, in which the magnetic moment of Mn ions is significantly suppressed, exhibits a negligible XMCD intensity at the Ni absorption edge [the inset of Fig. 4]. The present study demonstrates that not only the charge transfer but also its spatial redistributions of the transferred charges must be considered to describe the interfacial ferromagnetism of these oxide heterostructures. To more comprehensively understand the origins of interfacial magnetism appearing oxide heterostructures, further systematic investigation is required. In particular, the effects of different constituent transition metals on the charge spreading and the resultant interfacial magnetism are especially important to examine.

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