Interfacial Ferromagnetism of LaNiO$_3$/LaMnO$_3$ Heterostructures Induced by Asymmetric Charge Redistribution

To investigate the relationship between the asymmetric charge redistribution and ferromagnetism at the interface between the perovskite transition-metal oxides LaNiO$_3$ and LaMnO$_3$, we performed X-ray absorption spectroscopy and X-ray magnetic circular dichroism measurements on the sandwiched layer in the trilayer structures. The characteristic length scale of interfacial ferromagnetism is in good agreement with the charge redistribution due to the charge transfer across the interface, indicating the close relationship between the charge transfer and the ferromagnetism of the LaNiO$_3$/LaMnO$_3$ interface. The observed weak magnetization of Ni^{2+} ions in the LNO layer adjacent to the interface probably originates from the spin canting caused by the competition between the in-plane antiferromagnetic and out-of-plane ferromagnetic interactions.

Heterostructures composed of different perovskite transition-metal oxides have attracted considerable attention because of the variety of exotic magnetic properties that emerge at their interfaces, which cannot be accomplished in the bulk constituents [1, 2]. For example, for the heterostructures of LaNiO$_3$ (LNO) and LaMnO$_3$ (LMO), the charge transfer Ni^{3+} + Mn^{3+} → Ni^{2+} + Mn^{4+} occurs across the interface. As a result, ferromagnetically coupled magnetization is induced between Ni and Mn ions [3–5], although the constituent LNO and LMO are a paramagnetic metal and an antiferromagnetic insulator in their bulk forms, respectively. We have recently revealed the existence of an asymmetric spatial redistribution in the transferred charges at the (001)-oriented LNO/LMO interface: the transferred electrons are confined inside the one monolayer (ML) LNO, while the holes are distributed over 3–4 ML LMO [6]. In this study,
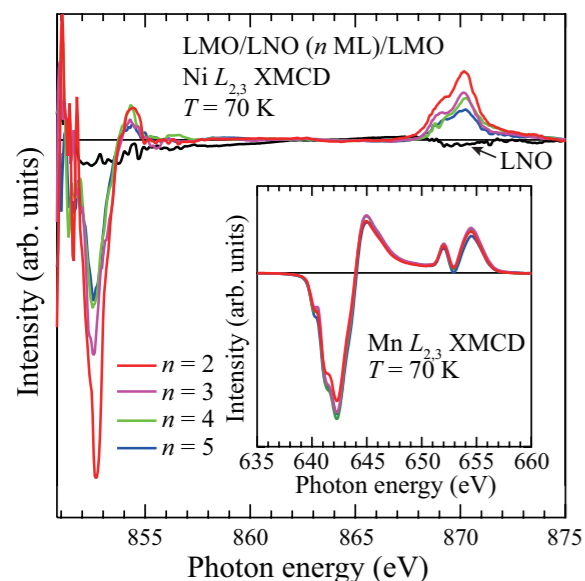
we investigated the relationship between this asymmetric charge redistribution and the resultant ferromagnetism at the LNO/LMO interface by using X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) techniques.

Figure 1 shows the Ni-$L_{2,3}$ XMCD spectra of the sandwiched LNO layers in the LMO 5 ML/LNO n ML/LMO 20 ML trilayers and reference spectrum of the 20 ML LNO film. As expected, no XMCD signal is observed for the LNO film, reflecting its paramagnetic properties. In contrast, clear XMCD signals are observed for the LMO/LNO/LMO trilayers, whose intensities decrease monotonically with increasing n, indicating that the magnetization of Ni ions emerges at the interface. The line shapes of the Ni-L_2 XMCD spectra for all LMO/LNO/LMO trilayers remain almost unchanged within experimental accuracy and closely resemble that of Ni^{2+} states [3]. Considering that Ni^{2+} states are present only in the 1 ML LNO at the interface [6], these results indicate that magnetization is induced only in the Ni^{2+} ions of the 1 ML LNO adjacent to the interface as a result of the interfacial charge transfer. As shown in the inset of **Fig. 1**, the signs of the Ni-$L_{2,3}$ XMCD signals of the sandwiched layer and Mn-$L_{2,3}$ XMCD of the top and bottom LMO layers are the same, indicating that the magnetization vectors induced in both ions align ferromagnetically. Furthermore, element-selective sum-rule analysis has revealed that the induced effective spin moments are about 0.2–0.3 μ_B/Ni ion, which are significantly smaller than the full moments of the Ni^{2+} states (2 μ_B/Ni ion).

As for the corresponding magnetic states of Mn ions, Mn-$L_{2,3}$ XMCD spectra of the LNO 5 ML/LMO 6 and 12 ML/LNO 20 ML sandwiched structures indicated that not only Mn^{3+} states in the original LMO but also Mn^{4+} states which result from the charge transfer contributed to their ferromagnetism. In addition, the magnetization degree of Mn ions in the interfacial region characterized by charge redistribution was higher than that in the inner region of LMO [7].
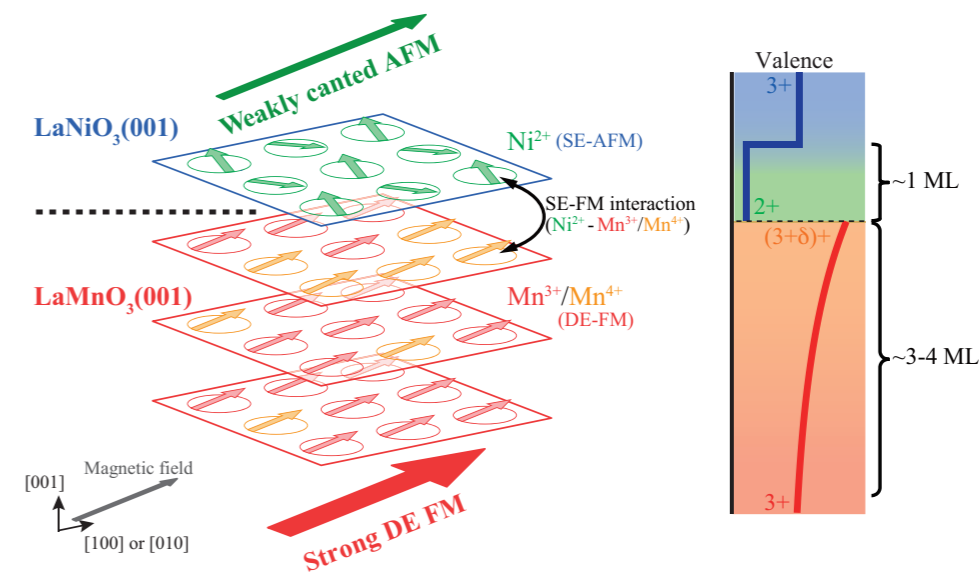

Figure 1: Ni-$L_{2,3}$ XMCD spectra of the LMO 5 ML/LNO n ML/LMO 20 ML trilayer structures (n = 2, 3, 4, and 5) and reference spectrum of a 20 ML LNO film. The corresponding Mn-$L_{2,3}$ XMCD spectra of the top and bottom LMO layers are shown in the inset.

Figure 2: Schematic illustrations of possible interfacial magnetic structures with asymmetric charge redistributions. AFM denotes antiferromagnetism and FM ferromagnetism; SE denotes superexchange interaction and DE double exchange interaction.

Based on the XMCD results, we proposed a possible mechanism for the emergence of the ferromagnetism at the (001)-oriented LNO/LMO interface, as schematically depicted in **Fig. 2**. In the interfacial region of the LMO layer, the ferromagnetic coupling is stabilized by the ferromagnetic double exchange (DE) interactions between Mn^{3+}(d^4 high spin (HS)) and Mn^{4+}(d^3 HS) ions. As for the LNO layer, according to the Kanamori-Goodenough (KG) rules, the spins of Ni^{2+} ions within the 1 ML LNO layer at the interface are expected to couple with each other in antiparallel due to the strong antiferromagnetic superexchange (SE) interaction of Ni^{2+}(d^8)-O-Ni^{2+}(d^8) bonds. Meanwhile, along the out-of-plane direction, ferromagnetic SE interactions obeying the KG rules should exist between Ni and Mn ions bonded via oxygen across the interface, mostly Ni^{2+}(d^8)-O-Mn^{4+}(d^3 HS) bonds and Ni^{2+}(d^8)-O-Mn^{3+}(d^4 HS) bonds. As a result, the delicate balance between the out-of-plane and in-plane exchange interactions may cause spin canting of Ni ions within the 1 ML LNO at the interface, as shown by the green arrows in **Fig. 2**, resulting in the observed weak ferromagnetism.

If the charge redistribution was absent in the LMO layer, the ferromagnetism in the interfacial LMO layer could not exist because Mn^{4+} spins align antiferromagnetically, resulting in the expected absence of macroscopic magnetization of Mn and Ni ions at the (001)-oriented LNO/LMO interface. However, clear XMCD signals were actually observed for both ions. This suggests that the stabilization of the ferromagnetism in LMO layers due to the interfacial charge redistribution

and simultaneous ferromagnetic coupling between Ni and Mn spins are the key factors inducing the unique interfacial magnetism of the (001)-oriented LNO/LMO interface [7].

REFERENCES

[1] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa and Y. Tokura, *Nat. Mater.* **11**, 103 (2012).
[2] A. Bhattacharya and S. J. May, *Annu. Rev. Mater. Res.* **44**, 65 (2014).
[3] C. Piamonteze, M. Gibert, J. Heidler, J. Dreiser, S. Rusponi, H. Brune, J.-M. Triscone, F. Nolting and U. Staub, *Phys. Rev. B* **92**, 014426 (2015).
[4] J. Hoffman, I. C. Tung, B. B. Nelson-Cheeseman, M. Liu, J. W. Freeland and A. Bhattacharya, *Phys. Rev. B* **88**, 144411 (2013).
[5] M. Gibert, P. Zubko, R. Scherwitzl, J. Íñiguez and J.-M. Triscone, *Nat. Mater.* **11**, 195 (2012).
[6] M. Kitamura, K. Horiba, M. Kobayashi, E. Sakai, M. Minohara, T. Mitsuhashi, A. Fujimori, T. Nagai, H. Fujioka and H. Kumigashira, *Appl. Phys. Lett.* **108**, 111603 (2016).
[7] M. Kitamura, M. Kobayashi, E. Sakai, M. Minohara, R. Yukawa, D. Shiga, K. Amemiya, Y. Nonaka, G. Shibata, A. Fujimori, H. Fujioka, K. Horiba and H. Kumigashira, *Phys. Rev. B* **100**, 245132 (2019).

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