

Controlling the all-in-all-out magnetic domains in pyrochlore iridate thin films and heterostructures

Y. Kozuka¹

¹National Institute for Materials Science, Tsukuba 305-0047, Japan

Domain walls of ferromagnetic or ferroelectric materials have attracted little attention as active elements of devices, but rather are considered to form as metastable objects of ferroic domains. In the case of ferromagnetic metal, domain walls frequently act as scatterers of electrons, deteriorating the device operation. Here we present transport properties of pyrochlore iridate thin films and heterostructures, where metallic conduction at the domain walls are theoretically proposed while the bulk is kept insulating in stark contrast to conventional ferromagnetic metal.

Pyrochlore materials, expressed as $A_2B_2O_7$ (A : rare-earth, B : transition metal), are composed of tetrahedral network of rare-earth and iridium sublattices, respectively as shown in Fig. 1. Characteristic of this compound is the all-in-all-out spin structure, where all the four spins at the vertices of a tetrahedron point inward or outward alternately due to the cooperation of strong spin-orbit interaction and spin frustration. Although the all-in-all-out spin structure is antiferromagnetic, there are clearly distinct two magnetic domains as shown in Fig. 1, which we call A domain and B domain for simplicity. While pyrochlore iridates are metallic in the paramagnetic phase above the Neel temperature T_N , the all-in-all-out spin structure is theoretically predicted to induce intriguing semimetallic or insulating phases below T_N ,¹⁾ depending on the strength of electron correlation tuned by the choice of rare-earth ions; the smaller the rare-earth ions are, the stronger the electron correlation is. Additionally, in the insulating phase, conducting domain walls are theoretically predicted,²⁾ followed by experimental observation by microwave impedance microscopy.³⁾ Although the electronic phases of the pyrochlore iridates have recently been gradually clarified experimentally, thin films are still difficult to fabricate and controlling the domain walls is not easily accessible in heterostructures. In this study, we aim at fabricating pyrochlore iridate thin films and heterostructures to artificially control the all-in-all-out magnetic domains.

The pyrochlore iridate thin films are fabricated by pulsed laser deposition using Y-stabilized ZrO_2 (111) substrates. The oxygen partial pressure and substrate temperatures are varied to find optimum growth conditions but the epitaxial $Eu_2Ir_2O_7$ films are not obtained probably due to low formation energy of pyrochlore iridates. Instead, we anneal the thin films after depositing amorphous films, resulting in successful formation of $Eu_2Ir_2O_7$ thin films. This method, so-called solid-state epitaxy, is also found to be applicable to pyrochlore iridate thin films with other rare-earth ions. X-ray diffraction and transmission electron microscope also show single crystalline $Eu_2Ir_2O_7$ thin films are formed.⁴⁾

For controlling the all-in-all-out magnetic domain wall, we have fabricated $Eu_2Ir_2O_7/Tb_2Ir_2O_7$ heterostructures.⁵⁾ Eu^{3+} is nonmagnetic, while Tb^{3+} has a large magnetic moment of $J = 6$. Thus, we expect that magnetic domains of $Eu_2Ir_2O_7$ is not sensitive to external magnetic field and the domains of $Tb_2Ir_2O_7$ may be switched by magnetic field. Figure 2 shows magnetoresistance (MR) of $Eu_2Ir_2O_7$ and $Tb_2Ir_2O_7$ thin films. In the case of $Eu_2Ir_2O_7$, MR does not show hysteresis, but

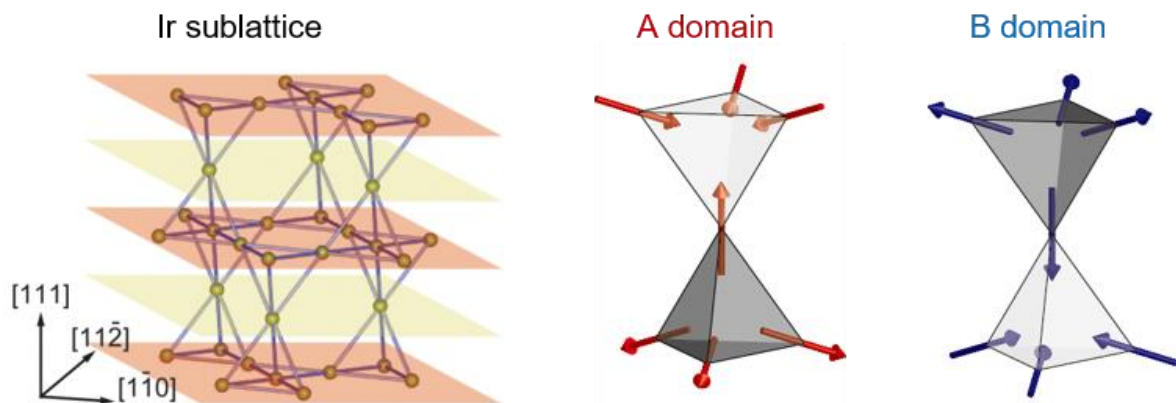


Fig. 1. Ir sublattice of pyrochlore iridate $A_2Ir_2O_7$ (A : rare-earth) and spin structures of two all-in-all-out magnetic domains (A domain and B domain).

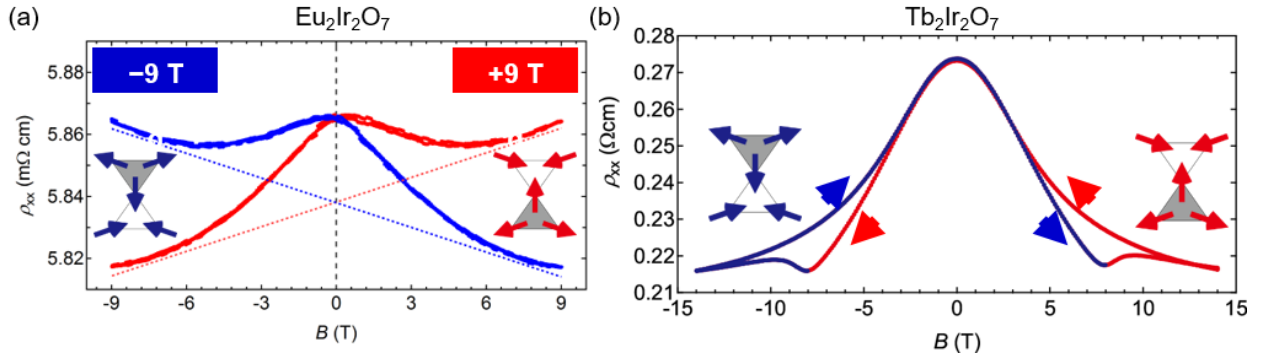


Fig. 2. Magnetoresistance of (a) $\text{Eu}_2\text{Ir}_2\text{O}_7$ and (b) $\text{Tb}_2\text{Ir}_2\text{O}_7$ thin films at 2 K. For $\text{Eu}_2\text{Ir}_2\text{O}_7$ thin film, magnetoresistance is measured after cooling the sample under + 9 T and -9 T, while that of $\text{Tb}_2\text{Ir}_2\text{O}_7$ thin film shows double hysteresis, indicating domain switching. The insets are expected domains of Ir spins.

is asymmetric with respect to magnetic field. The sign of the asymmetric part is inverted between positive and negative field cooling, which suggests that all-in-all-out magnetic domain is selectively stabilized by the polarity of the magnetic field. In contrast, MR possesses double hysteresis for the $\text{Tb}_2\text{Ir}_2\text{O}_7$ thin film, suggestive of magnetic domain switching.⁶⁾ The stabilization of the all-in-all-out domains can be visualized by scanning SQUID microscopy.⁷⁾ Although all-in-all-out spin structure in the cubic symmetry does not produce dipole moment, subtle distortion of the lattice can hold dipole moment, the sign of which depends on the all-in-all-out magnetic domain. Figure 3 shows the images of scanning SQUID microscope. Under zero-field cooling, magnetic domains are clearly observed. After warming up and cooling down the sample from 130 K under positive magnetic field, uniform shift of magnetic field is observed. This result clearly demonstrates the above assumption that the all-in-all-out magnetic domains can be selectively stabilized by cooling magnetic field.

Finally, we fabricated $\text{Eu}_2\text{Ir}_2\text{O}_7/\text{Tb}_2\text{Ir}_2\text{O}_7$ heterostructure and measured the magnetoconductance at the interface as shown in Fig. 4. The interface conductance exhibits hysteresis. Obviously, interface conductance is higher when the magnetic domains of $\text{Eu}_2\text{Ir}_2\text{O}_7$ and $\text{Tb}_2\text{Ir}_2\text{O}_7$ layers are opposite than when those magnetic domains are the same. This result indicates that the domain wall conduction is successfully controlled in the heterostructure with selective domain stabilization.

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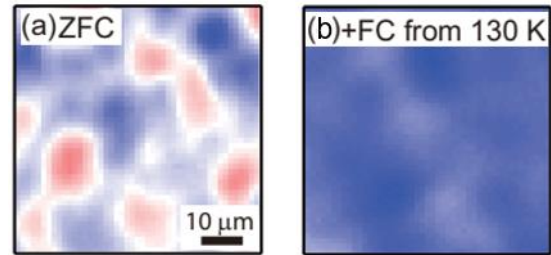


Fig. 3. Scanning SQUID images of a $\text{Tb}_2\text{Ir}_2\text{O}_7$ thin film at 4.7 K after (a) zero-field cooling and (b) cooling under positive magnetic field from 130 K.

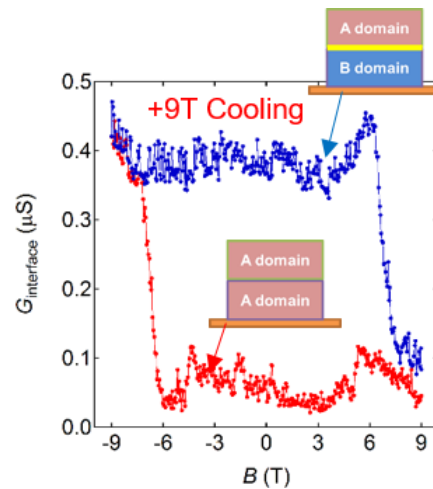


Fig. 4. Conductance at the $\text{Eu}_2\text{Ir}_2\text{O}_7/\text{Tb}_2\text{Ir}_2\text{O}_7$ heterointerface after cooling under +9 T.

Atomic-scale studies of structural and electronic properties in functional transition metal oxide thin films using scanning tunneling microscopy/spectroscopy

Ryota Shimizu^{1,2}

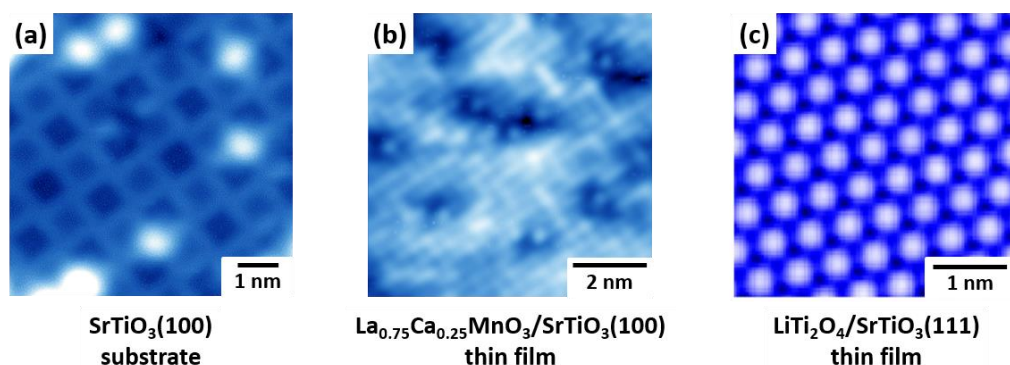
¹School of Materials and Chemical Technology, Tokyo Institute of Technology, ²JST-PRESTO

Discovery of high- T_c superconductivity in cuprate has triggered enormous attention on strongly-correlated electron systems in transition metal oxides for decades. To elucidate the mechanism of exotic physical properties, many progressive efforts have been made to dramatically improve the resolution in measurements such as angle-resolved photoemission spectroscopy and scanning tunneling microscopy/spectroscopy (STM/STS). Nowadays, these techniques are widely used to understand structural and electronic properties in a variety of bulk cleavable materials as well as layered perovskite oxides. However, due to the poor cleavability, there are few reports on atomic-scale studies of three-dimensional perovskite oxides.

To overcome this problem, we focused on high-quality epitaxial thin films as a specimen, and *in-situ* studied the structures and electronic states on the thin film surfaces of transition metal oxides at the atomic level. For this purpose, we constructed ultrastable low-temperature STM combined with pulsed laser deposition (PLD) system[1] to eliminate the influence of surface contamination. In this talk, I show our atomic-scale investigations of SrTiO₃(100) substrates[2] (Fig. 1(a)) and thin film surfaces of perovskite-type La_{0.75}Ca_{0.25}MnO₃ (ferromagnet, Fig. 1(b))[3] and spinel-type LiTi₂O₄ (superconductor, Fig. 1(c))[4] using low-temperature STM/STS.

On a La_{0.75}Ca_{0.25}MnO₃/SrTiO₃(100) thin film surface, we observed uniaxial zigzag ($\sqrt{2} \times \sqrt{2}$) stripes with two orthogonal domains, accompanying an energy gap at the Fermi level. Combined with theoretical calculations, we found that the electrical dead layer (gap opening) at the surface is induced by the relaxation of the topmost truncated octahedra (MnO₅) correlated with the Mn 3d orbital reconstruction[3]. Furthermore, on a LiTi₂O₄/SrTiO₃(111) thin film surface, we succeeded in the observation of clear triangular lattices and superconducting properties (gap and vortex state) in tunneling spectra[4]. Thus, our PLD-STM studies open a path for atomic-scale visualization of functional transition metal oxides with three-dimensional structures.

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Figures: STM images on (a) SrTiO₃(100) substrate and (b) La_{0.75}Ca_{0.25}MnO₃(100) and (c) LiTi₂O₄(111) thin films.

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Origin of interfacial ferromagnetism between perovskite transition-metal oxides LaNiO₃ and LaMnO₃

M. Kitamura^{1,2}, K. Horiba¹, M. Kobayashi¹, E. Sakai¹, M. Minohara¹, R. Yukawa¹, D. Shiga¹, K. Amemiya¹, T. Nagai³, Y. Nonaka⁴, G. Shibata⁴, A. Fujimori⁴, H. Fujioka², and H. Kumigashira¹

¹Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan

²Institute of Industrial Science, The University of Tokyo, Meguro-ku 153-8505, Japan

³National Institute for Material Science, Tsukuba 305-0044, Japan

⁴Graduate School of Science, The University of Tokyo, Bunkyo-ku 113-0033, Japan

Heterointerfaces between perovskite transition-metal oxides have attracted much attention because of their novel electronic and/or magnetic properties that are absent in their bulk form. Recently, it has been reported that an unusual spin order occurs in a paramagnetic LaNiO₃ (LNO) layer in the heterointerface region with a “ferromagnetic” LaMnO₃ (LMO) layer, resulting in the appearance of the exchange bias between the two oxides¹. For understanding these exotic magnetic properties appearing at the heterointerface between LNO/LMO, it is indispensable to elucidate the relationships between the electronic states at the heterointerface, especially the interfacial charge transfer between Ni and Mn ions, and the interfacial ferromagnetism. In this study, we have investigated the electronic and magnetic states of both the transition-metal ions in the interfacial region by utilizing the elemental selectivity and surface (interface) sensitivity of x-ray absorption spectroscopy (XAS): The changes in valence of both ions caused by the interfacial charge transfer and resultant spatial distributions of the transferred charges are determined by XAS, while the induced magnetization by magnetic circular dichroism (MCD) of XAS.

The XAS measurements on toplayer for both LNO/LMO and LMO/LNO bilayers demonstrated the occurrence of the electron transfer from LMO layers to LNO layers ($\text{Ni}^{3+} + \text{Mn}^{3+} \rightarrow \text{Ni}^{2+} + \text{Mn}^{4+}$) in the interface region². Thus, to evaluate the spatial distribution of the interfacial charge transfer, we have measured the thickness dependent XAS spectra of *underlayers* for LNO/LMO and LMO/LNO bilayers as shown in Fig. 1. As can be seen in Fig. 1, the XAS spectra exhibit the small but distinct spectral modulation reflecting the valence changes due to the interfacial electron transfer. Furthermore, a closer look reveals that the spectral change of Mn-*L*_{2,3} XAS are totally saturated by 1-ML LNO deposition on LMO layer, while that of Ni-*L*_{2,3} XAS seems to continue up to 3–4 ML deposition of LMO overlayer on LNO. These results demonstrate that the spatial distribution of the interfacial charge transfer is significantly different between the two layers. Judging from the saturation of spectral change in the underlayer, the interfacial region subject to the charge transfer is evaluated to be about 1 ML for the LNO side, while 3–4 ML for the LMO side². Meanwhile, the Ni-*L*_{2,3} x-ray MCD spectra of LMO/LNO/LMO sandwiched structures revealed that net magnetization was induced only in the Ni²⁺ ions at a 1-ML LNO layer adjacent to the interface owing to the interfacial charge transfer. As for the counterpart Mn ions, the magnetic moment increased from that of LMO bulk within the 3–4 ML LMO layers from the interface where the transferred holes were distributed. Furthermore, both magnetic moments were ferromagnetically coupled to each other. These results suggest that the stabilization of ferromagnetism in LMO layers due to the interfacial charge transfer and the resultant ferromagnetic coupling between Ni and Mn spins are keys to understanding the induced net magnetization in Ni ions at the interface.

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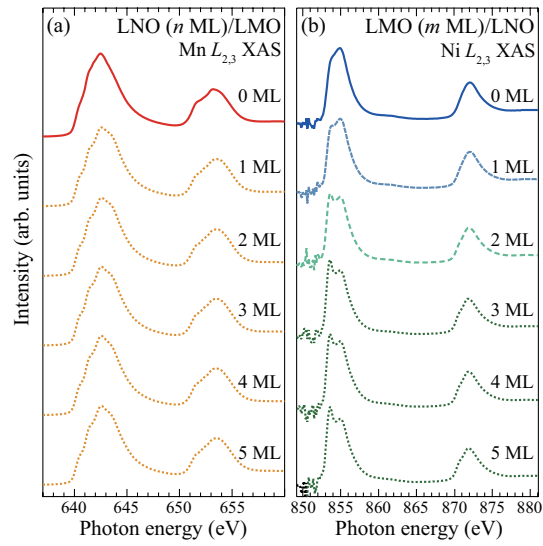


Fig. 1 (a) Mn- $L_{2,3}$ XAS spectra of the LMO *underlayer* of LNO/LMO bilayers (b) Ni- $L_{2,3}$ XAS spectra of the LNO *underlayer* of LMO/LNO bilayers.

Ferroelectric and Magnetic Properties in Room-Temperature Multiferroic GaFeO₃-type Thin Films

T. Katayama¹, S. Yasui², Y. Hamasaki³, and M. Itoh²

¹The University of Tokyo, Tokyo 113-0033, Japan

²Tokyo Institute of Technology, Yokohama 226-8503, Japan

³National Defense Academy, Kanagawa 239-8686, Japan

Multiferroic materials exhibiting ferromagnetic and ferroelectric properties in a single phase have been eagerly studied due to their fascinating physics and novel technological applications such as fast-writing, power-saving, and non-destructive data storage. However, such multiferroic materials rarely exhibit both spontaneous magnetization and polarization at room temperature. GaFeO₃-type iron oxides are promising multiferroic materials due to the coexistence of a large spontaneous magnetization and polarization near and above room temperature as well as their multiferroic properties such as magnetic-field-induced modulation of polarization. GFO consists of one tetrahedral (T_d) Ga1 site and three octahedral (O_h) Ga2, Fe1, and Fe2 sites. The ferrimagnetism in GFO is derived from superexchange antiferromagnetic interactions between Fe ions, where the Fe ion magnetic moments at Ga1 and Fe1 sites are antiparallel to those at Ga2 and Fe2 sites. Especially, the Fe $3d^5$ orbital at the Fe2 site has strong hybridization with O $2p$ orbitals, producing a large spin-orbit interaction. This interaction leads to a much larger coercive field (H_c) of 20 kOe at 300 K in GFO-type Fe₂O₃ nanoparticles compared to other room-temperature multiferroic materials. For the ferroelectricity in GFO films, a unique mechanism of polarization switching is predicted. The displacement length of the metal cations at the Fe1 and Fe2 sites can reach as high as 1.2 Å during polarization switching, whereas that of conventional perovskite ferroelectrics such as BaTiO₃ is about 0.1 Å. Such a large displacement of magnetic Fe ions should realize a novel magnetoelectric effect.

To realize large magnetoelectric properties and applications of GFO films, the ferroelectric and ferrimagnetic properties at room temperature must be controlled. A key point for the existence of both ferroelectricity and ferrimagnetism at room temperature is to understand the relationship between the constituent composition at each cation site and the original character. Thus, a systematic investigation of multiferroicity as a function of the compositional ratio of Ga and Fe is important for a fundamental understanding and future applications. In this study, we fabricate high-quality Ga_xFe_{2-x}O₃ epitaxial thin films ($x = 0.0$ – 1.0) and systematically investigate their ferroelectric and ferrimagnetic properties. All films exhibit out-of-plane ferroelectricity and in-plane ferrimagnetism simultaneously. The coercive electric field (E_c) monotonically decreases with x . Additionally, increasing x reduces the coercive force (H_c) but enhances the saturated magnetization (M_s) at room temperature, according to the site of Ga ions. Finally, we demonstrate the room-temperature magnetocapacitance effects of the GFO films. The E_c , H_c , and M_s values can be widely controlled in ranges of 400–800 kV/cm, 1–8 kOe, and 0.2–0.6 μ_B /f.u at room temperature by changing x , respectively. Because such ferroelectric and magnetic ranges differ from those of well-known room-temperature multiferroic BiFeO₃, GFO-type iron oxides may expand the variety of room-temperature multiferroic materials.

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Synthesis and spectroscopic analysis of novel ordered alloy with large uniaxial magnetic anisotropy

Masaki Mizuguchi and Koki Takanashi
(Institute for Materials Research, Tohoku University, Japan)

A large uniaxial magnetic anisotropy is a fascinating feature for magnetic materials because it gives birth to various intelligent functions. For instance, materials with a large uniaxial magnetic anisotropy are promising for the application to high-density magnetic storage devices since the thermal stability of magnetization is kept even in a nanometer scale. Furthermore, large uniaxial magnetic anisotropy energy (K_u) is one of the crucial matters to realize next-generation strong hard magnets. It is well known that L1₀-ordered alloys such as FePt, CoPt, and FePd show considerably large K_u . However, they include noble metals, thus it is an indispensable subject to find a noble metal-free large magnetic anisotropy ferromagnet. It is known that iron meteorites contain L1₀-ordered FeNi phase, so-called "tetrataenite", which induces unique magnetic properties different from usual Fe-Ni alloys. It has been reported that L1₀-ordered FeNi has a large K_u of 1.3×10^7 erg/cm³ for a bulk sample¹⁾. However, there have been no studies on the fabrication of L1₀-ordered FeNi thin films. We have been trying the fabrication of L1₀-ordered FeNi films by alternate monatomic layer deposition or the sputtering method for several years²⁻¹⁸⁾. In this talk, we present a review on the recent progress of our study on the synthesis and characterization of L1₀-ordered FeNi films. The maximum value of K_u , which was estimated from magnetization curves, reached 9.0×10^6 erg/cm³. The largest order parameter, which was estimated from XRD spectra, was 0.48. K_u monotonously increased with the order parameter. We also fabricated Ni/Fe superlattices with different layer thickness and investigated their magnetic properties to understand magnetic anisotropy in Ni/Fe system including L1₀-ordered FeNi. The spectroscopic analysis of the electronic structures of these films by the photoemission spectroscopy (PES) and the magnetic circular dichroism (MCD) measurements were made using a synchrotron radiation. The origin of the large uniaxial magnetic anisotropy will be discussed. In addition, recent progress on the synthesis of L1₀-ordered FeNi bulks by a chemical method will be also presented¹⁹⁾.

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