Introduction

Transition metal-based oxide heterostructures exhibit diverse emergent phenomena—e.g., two-dimensional electron gas, superconductivity, non-collinear magnetic phase, ferroelectricity, polar vortices, topological Hall effect, etc.—which are absent in the constituent bulk oxides [1–6]. The microscopic understandings of these properties in such nanometer-thick materials are extremely challenging. Synchrotron X-ray-based techniques such as X-ray diffraction, X-ray absorption spectroscopy (XAS), resonant X-ray scattering (RXS), resonant inelastic X-ray scattering (RIXS), X-ray photoemission spectroscopy, etc., are essential to elucidating the response of lattice, charge, orbital, and spin degrees of freedom to the heterostructure [7–14]. As a prototypical case of complex behavior, rare-earth nickelate-based (RENiO3 with RE = La, Pr, Nd, Sm, Eu…Lu) thin films and heterostructures have been investigated quite extensively in recent years [15–25]. An extensive body of literature about these systems exists; for an overview of the field, we refer interested readers to the recent reviews in [26] and [27]. The bulk properties of RENiO3 have been reviewed by Marder [28] and Catalan [29]. In the present article, we give a brief review that concentrates on the use of synchrotron-based techniques to investigate a specific set of EuNiO3/LaNiO3 superlattices, specifically designed to solve a long-standing puzzle about the origin of simultaneous electronic, magnetic, and structural transitions of the RENiO3 series [30–32].

Apart from the least distorted member LaNiO3 (space group R3c), all other members of the RENiO3 bulk series undergo a temperature-driven metal-insulator transition (MIT), which is also accompanied by lowering of structural symmetry from orthorhombic (Pbnm) to monoclinic (P21/n) [33]. Since the P21/n space group contains two inequivalent Ni sites, the structural transition was also linked to a charge disproportionation (CD) [Ni13+ + Ni3− → Ni13+δ + Ni13−δ] transition [33, 34], which has been further corroborated by RXS experiments [35–37]. In recent years, this MIT has been assigned theoretically as a site-selective Mott transition (d6L2+bd + ddL2, where L denotes a hole in the O p orbital), primarily due to the very small charge transfer energy of these systems [38–41]. Since NiO6 octahedra with d6 (S=1) and ddL2 (S=0) configurations have long and short Ni-O bonds, respectively, this insulating state can also be described as a bond disproportionate (BD) phase. The most important outcome of these theoretical works is that the structural symmetry change and the charge ordering on Ni sublattice are not essential in order to stabilize the insulating phase. Further, Mandal et al. have demonstrated that the BD phase appears when the effective charge transfer energy becomes negative [42]. Surprisingly, signatures of breathing distortion have been also found in the metallic phase of LaNiO3 [43]. On the other hand, there are also reports emphasizing the importance of structural transition [44, 45] and polaron condensation [46]. Fermi surface nesting-driven MIT has been also proposed to explain simultaneous electronic and magnetic transitions of NdNiO3 and PrNiO3 [47, 48]. However, it is extremely difficult to experimentally probe if the MIT can be linked with one of those proposed mechanisms, as the MIT is always accompanied by another two or three transitions in reality.

In order to address this actively debated issue, we focused on epitaxial growth of short periodic superlattices, consisting of two members of the series: LaNiO3 (LNO) and EuNiO3 (ENO). Since the octahedral rotational patterns of LNO and ENO are different (αa ‘a’ vs. a ‘a’ c‘ in Glazer notation [49]), a strong structural competition at the interface between ENO and LNO can be anticipated [50]. Moreover, the ability to grow these materials individually with unit-cell (in pseudo-cubic notation) precision allows us to mismatch the structural periodicity of the superlattice with the periodicity of a particular ordering pattern. For example, the periodicity of a [2 uc ENO/1 uc LNO] SL (uc = unit cell in pseudo-cubic notation) is 3×cpc along [001]pc (pc = pseudo-cubic), which does not match with the periodicity of the bulk-like checkerboard CO pattern (see Figures 1a and 1c). On the other hand, as shown in Figure 1b, the periodicity of 1ENO/1LNO SL (=2×cpc) is exactly the same as the CO periodicity. In this review article, we summarize our findings of electronic and magnetic structure of such m uc ENO/n uc LNO (mENO/nLNO) SLs using synchrotron-based techniques.
Epitaxial growth, structural symmetry, and transport measurement

These samples were grown on NdGaO$_3$ substrate (pseudo-cubic in-plane lattice constant $a_{\text{sub}} = 3.858\,\text{Å}$) by pulsed laser deposition and the layer-by-layer growth of each unit cell of ENO and LNO was confirmed by RHEED (reflection high-energy electron diffraction) [30–32]. Apart from the streaking pattern of RHEED image with specular (0 0) and off-specular (0 ±1) reflections, additional half-order spots (0 ±1/2) were observed for 2ENO/1LNO and 1ENO/1LNO SLs (indicated by arrows in Figures 1e and 1f). The (0 ±1/2) reflections in RENiO$_3$ series arise due to the in-plane doubling of the unit cell with either orthorhombic or monoclinic symmetry [51, 52]. The absence of these half-order spots in 1ENO/2LNO SL (Figure 1d) strongly suggests rhombohedral symmetry of the sample, similar to bulk LNO. The strong structural competition between the ENO and LNO layers was also observed during the growth as the deposition of second LNO layers in each period of 1ENO/2LNO SL results in the disappearance of the half-order spots, which reappear after the growth on ENO layer in the next period. The symmetries of these SLs were further checked by synchrotron X-ray diffraction. As illustrated in Figure 2a, both orthorhombic and monoclinic $\text{ABO}_3$ perovskites have an antiparallel displacement of $A$-sites whereas rhombohedral $\text{ABO}_3$ does not show this kind of behavior. The presence of such antiparallel displacement can be verified by examining half-order X-ray diffraction peaks with the index (odd/2 even/2 even/2) [53]. Our findings of the (0 1/2 2)$_{pc}$ diffraction peaks for both the substrate and the film (Figures 2b and 2c) for 2ENO/1LNO and 1ENO/1LNO SLs clearly establish orthorhombic/monoclinic symmetry. Moreover, the absence of (1/2 0 2)$_{pc}$ peak for the film and substrate confirm that the film is a single domain and has the same in-plane orientation as the substrate. The rhombohedral symmetry of 1ENO/2LNO film is authenticated by the absence of both (0 1/2 2)$_{pc}$ and (1/2 0 2)$_{pc}$ reflections, shown in Figure 2d.

Before discussing the electronic behaviors of these SLs, we note that it is well-established in the literature that the bulk rhombohedral LNO is a paramagnetic metal down to very low temperature. However, a recent claim of an antiferromagnetic metallic phase of LNO in single crystalline form has led to a debate about the actual nature of magnetic ground states [54–56]. On the other hand, bulk ENO undergoes MIT around 460 K and another transition from paramagnetic insulating (PI) phase to antiferro-
magnetic insulating (AFI) around 200 K [28, 29]. In accordance with its rhombohedral structure, 2LNO/1ENO SL remains metallic down to the lowest temperature of measurement of ~ 2 K. On the other hand, both 2ENO/1LNO and 1ENO/1LNO SLs exhibit temperature-driven first-order MIT with strong thermal hysteresis, as shown in Figure 2e. While the resistivity values in the metallic phases of the SLs are very similar, the transition temperature strongly depends on layer numbers m and n.

**Soft X-ray scattering to probe magnetic ordering**

The magnetic structure of polycrystalline NdNiO₃ and PrNiO₃ samples was initially solved by the neutron diffraction experiment [57]. The unusual E′ antiferromagnetic spin configuration is characterized by a magnetic wave vector (1/2 0 1/2)ₚₑ (≡(1/4 1/4 1/4)ₚₑ), which can be viewed as a spin sequence of either ↑↑↓↓ or ↑→↓← along [1 1 1]ₚₑ. Resonant soft X-ray scattering experiments on single crystalline NdNiO₃ films by Scagnolli et al. further confirmed the non-collinear spin arrangements. In these scattering experiments, the presence of a (1/4 1/4 1/4)pc Bragg peak is examined by X-ray photons with energy close to the Ni L₃ edge [58]. This technique has been used extensively to investigate the magnetic ordering of various RENiO₃-based thin films, superlattices, and heterostructures [59–65].

Based on the RXS measurement, the antiferromagnetic transition temperature is found to be 220 ± 5 K for 2ENO/1LNO (Figures 3a and 3b). An energy scan across the Ni L₃ edges for the (1/4 1/4 1/4)pc Bragg peak is compared (Figure 3c) with simultaneously collected fluorescence background, which represents XAS in fluorescence mode. The resonant enhancement is very strong around 852.8 eV, where XAS also exhibits a sharp peak. Recent RIXS measurements and cluster calculations have attributed this XAS feature with a d⁸ state [66, 67]. Moreover, Ni L₃,2 XMCD (X-ray magnetic circular dichroism) of the 2ENO/1LNO SL looks very similar to the S=1 Ni XMCD of Ca₃NiOsO₆ [68]. Furthermore, the magnetic scattering derived from the XMCD spectrum by a Kramers-Kronig (K-K) transformation matches well with the line shape and line position of the scattered intensity, observed in the RXS measurement [30, 69, 70]. All of these studies confirm the presence of an S=1 state in 2ENO/1LNO SL, which is contrary to the ionic picture, where S=1/2 is expected. This result in turn implies that the sequence of the spin arrangement in (1 1 1)ₚₑ planes is ↑ 0 ↓ 0. In addition, the RXS measurements of 1ENO/1LNO SL determined Tᵥ ~ 150 K [30] and the energy scan appear very similar to 2ENO/1LNO SL, shown in Figure 3c).

**Hard X-ray scattering to probe charge ordering**

The checkerboard type charge ordering (CO) in a 50-nm-thick NdNiO₃ film was demonstrated using resonant hard X-ray scattering at the Ni K edge by Staub et al [35]. These experiments are focused on (h 0 l)ₚₑ and (0 k l)ₚₑ reflections with h, k, l being odd integers, as these peaks have no contribution from Ni in Pbnm symmetry and inequivalent Ni sites in the monoclinic structure give rise to a strong energy dependence for these particular Bragg reflections. The observation of CO was further corroborated by polarization-dependent analysis and azimuthal scans [36, 37]. However, it has been argued in very recent years that the Ni resonance features can also be obtained by BD without any CO on the Ni sublattice [71, 72]. Similar experiments on 6 nm thin NdNiO₃ films did not find any signature of Ni resonance, and have been interpreted as a suppression of CO by epitaxial strain [73, 74].

The 1ENO/1LNO SL, which exhibits simultaneous MIT and magnetic transition around 150 K, also showed sharp resonance features in the insulating phase (see Figure 4a). As shown in Figure 4b, the temperature-dependence plot of the resonant intensity demonstrates a CO transition around 150 K. The off-resonant intensity, which depends on the crystal structure, also shows a transition at the same temperature. This result confirms that the structural changes and the CO are cooperative in nature in this system. In contrast, the resonance line shape of the 2ENO/1LNO SL, and resonance and off-resonance intensity, did not show any significant modulation across the Tᵥ ~ 245 K. This observation establishes that a metal-insulator transition can be obtained without any bulk-like charge ordering and structural symmetry change. Moreover, the strong resonance features in the metallic phase of 2ENO/1LNO SL are evidence of a rare monoclinic metal phase. The observation of the S=1 state of Ni, together with negligible orbital polarization, also support the site-selective Mott transition scenario in this artificial material [38–41].

**Effect of epitaxial strain**

So far, all of the results discussed in this article are for ENO/LNO heterostructures grown on NdGaO₃ substrates. In order to investigate the effect of the epitaxial strain on the electronic and magnetic transition, 1ENO/1LNO SLs were also grown on DySeO₃ (in-plane pseudo-
cubic lattice constant $a_{\text{sub}}=3.955\AA$, LaAlO$_3$ ($a_{\text{sub}}=3.794\AA$), and YAlO$_3$ ($a_{\text{sub}}=3.692\AA$) substrates. Interestingly, the electronic transition temperature does not change appreciably with the increase of the tensile strain. Most importantly, both the MIT and antiferromagnetic ordering transition are completely suppressed under the application of compressive strain (Figure 5a). Similar suppression of MIT has been also reported for PrNiO$_3$, NdNiO$_3$, SmNiO$_3$, and EuNiO$_3$ thin films [21, 59, 61, 62, 75, 76].

To understand this strain effect, O $K$-edge resonant X-ray absorption spectra were measured at room temperature on these SLs [77]. In this technique, a pre-peak is observed around 528 eV due to the $d^9_{E_z} \rightarrow d^8_{E_z}$ transition (here, $E_z$ is a hole in the oxygen $1s$ core state) and the intensity, position, and width of this pre-peak depend on the Ni-O covalency (Figure 5b) [18, 59]. As the strain becomes more compressive, the pre-peak shifts towards higher energy (Figure 5c). This signifies a decrease in charge transfer energy ($\Delta$) and is related to the strong modulation of relative Madelung potential between Ni and O by epitaxial strain [18, 59, 78]. Moreover, the increase of FWHM of the pre-peak with the compressive strain implies the increase of Ni-O covalency. Thus, strain-induced modulation of both $\Delta$ and hybridization energy is responsible for the suppression of the antiferromagnetic insulating phase.

### Summary

In this brief review article, we discuss the results of synchrotron-based X-ray diffraction, X-ray absorption spectroscopy, and resonant (soft and hard) X-ray scattering experiments on a series of short-periodic EuNiO$_3$/LaNiO$_3$ superlattices. These experiments demonstrate that the 2EuNiO$_3$/1LaNiO$_3$ SL exhibits a temperature-driven metal-insulator transition without any structural symmetry change and charge ordering, solving a long-standing puzzle about the origin of simultaneous transition in the RENiO$_3$ series. Moreover, the results of these experiments emphasize the unique insights obtained by combining synchrotron-based techniques to understand multiple electronic, spin, and lattice order parameters in nanometer thin artificial quantum materials.

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