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# Disentangled cooperative orderings in artificial rare-earth nickelates

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Coupled transitions between distinct ordered phases are important aspects behind the rich phase complexity of correlated oxides that hinders our understanding of the underlying phenomena. For this reason, fundamental control over complex transitions has become a leading motivation of the designer approach to materials. We have devised a series of new superlattices by combining a Mott insulator and a correlated metal to form ultra-short period superlattices, which allow one to disentangle the simultaneous orderings in  $RENiO_3$ . Tailoring an incommensurate heterostructure period relative to the bulk charge ordering pattern suppresses the charge order transition while preserving metal-insulator and antiferromagnetic transitions. Such selective decoupling of the entangled phases resolves the long-standing puzzle about the driving force behind the metal-insulator transition and points to the site selective Mott transition as the operative mechanism. This designer approach emphasizes the potential of heterointerfaces for selective control of simultaneous transitions in complex materials with entwined broken symmetries.

Materials exhibiting complex phase diagrams are often characterized by multiple entangled order parameters. Complex oxides in particular show multiple types of phase transformations controlled by various external stimuli [1–7]. However, understanding of the mechanism behind the transitions is quite challenging in compounds which display multiple simultaneous orderings such as cuprates, vanadates, manganites, pnictides, etc. [4–7]. In recent years substantial efforts have been put forward to decouple structural and electronic transitions by external means. For example, these transitions in vanadates can be separated by external stimuli [4, 8] leading to the discovery of a novel monoclinic metallic phase. This surprising finding has triggered the search for alternative methods of materials design in hopes of realizing such unusual phases without external perturbations. In the rapidly progressing field of controllable tunability in complex oxides, a promising emerging method is the heterostructuring of ultra-thin dissimilar layers into a superlattice without bulk analogues [3]. Such artificial structures allow layer-by-layer design and the exploration of unique stacking sequences which offer an unprecedented opportunity for manipulation of materials properties.

Another example of a complex multi-order parameter system,  $RENiO_3$  ( $RE = \text{La, Pr, Nd, Sm, Eu, ...Lu etc.}$ ) [9, 10] have recently undergone intense scrutiny due to their simultaneous metal-to-insulator (MIT), structural, charge-ordering (CO)/bond disproportionation (BD), and unusual  $E'$ -type antiferromagnetic ( $E'$ -AFM) transitions [11]. The combination of multiple transitions occurring at the same temperature (Fig. 1(a)) has fueled an active debate on the origin of the MIT. Among several mechanisms, the CO on  $Ni^{3+}$  with a rock-salt pattern, i.e.  $d^7 + d^7 \leftrightarrow d^{7+\delta} + d^{7-\delta}$ , (Fig. 1(b)) has been fastidiously scrutinized by various probes and shown to accompany the MIT both in bulk and thick films [12–15] with

simultaneous lattice symmetry lowering from orthorhombic to monoclinic. While density functional theory supports the scenario of a CO-driven MIT [16], recent infrared spectroscopy measurements strongly emphasized the importance of Mott physics [17]. However, charge disproportionation is not required for a pure Mott-type MIT [12–15, 18–20] and the expected  $T_{MIT}$  would have been well above  $T_N$  (Néel temperature) irrespective of the choice of a  $RE$  ion, which clearly contradicts experiments. Recent theories [21–26] have instead postulated that this type of MIT is a Ni ‘site selective Mott’ (SSM) transition and occurs without any explicit charge ordering on the Ni sites, i.e.  $d^8\bar{L} + d^8\bar{L} \leftrightarrow d^8 (S=1) + d^8\bar{L}^2 (S=0)$ , where  $\bar{L}$  indicates a hole on oxygen  $p$  orbitals [27]. The insulating phase obtained by the SSM transition does not have conventional charge disproportionation  $Ni^{3\pm\delta}$  and instead the theory implies a ‘bond disproportionation’ (BD) phase as different Ni sites with  $d^8$  and  $d^8\bar{L}^2$  configuration will have longer and shorter Ni-O bond-length respectively. In sharp contrast to SSM, the appearance of the insulating phase with simultaneous  $E'$ -type antiferromagnetic ( $E'$ -AFM) ordering  $T_{MIT} = T_N$  for  $NdNiO_3$  and  $PrNiO_3$  has been explained by Fermi surface nesting [28–30]. Further,  $E'$ -AFM transition has been also reported in the weakly metallic state of  $PrNiO_3/PrLaO_3$  superlattices [20] without or with very weak charge ordering and also in some metallic  $RENiO_3$  [31, 32]. All these conflicting results highlight the need for an alternative approach to materials design to selectively decouple the entangled orderings and elucidate the individual role of each for the MIT.

In this letter, we utilize a new route to control the transitions by mapping the number of dissimilar atomic planes of the heterostructure to the anticipated real-space pattern for a specific ordering. Two different members of the series, insulating  $EuNiO_3$  (ENO) [33, 34] and correlated metal  $LaNiO_3$

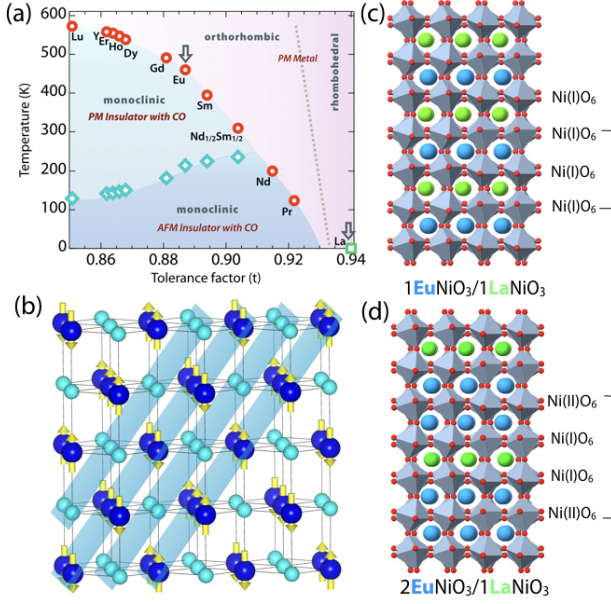


FIG. 1. (a) Phase diagram of bulk  $RENiO_3$  [9–11]. Arrows denote individual members, which are used in this paper to make superlattices. (b) Rock-salt type charge ordering with exaggerated  $Ni^{3\pm\delta}$  radius variations and  $E'$ -AFM spin ordering [25] for bulk  $RENiO_3$  ( $RE$  and O atoms omitted for clarity). Pseudocubic (pc)  $(1\ 1\ 1)$  planes are highlighted. Schematic crystal structure of (c) 1ENO/1LNO and (d) 2ENO/1LNO superlattices grown along pseudocubic  $[0\ 0\ 1]$  direction. All Ni's in 1ENO/1LNO SL have Eu in one side and La on the opposite side along  $[0\ 0\ 1]_{pc}$ . However, 2ENO/1LNO has two types of Ni: NiI with Eu and La on opposite sides and NiII with Eu on both sides.

(LNO) [35] have been heterostructured to stabilize a new quantum material:  $[m\text{ u.c. EuNiO}_3 / n\text{ u.c. LaNiO}_3]$  (Fig. 1(c), (d)) where  $m=1, 2$  and  $n=1$  refer to the individual layer thickness (u.c. = unit cell in pseudo-cubic notation). While  $RENiO_3$  SLs encompassing band-insulating spacing layers are ubiquitous [11], our approach of combining two distinct  $RENiO_3$  layers in the form of short-period superlattices has not been explored so far to the best of our knowledge. The design idea is illustrated in Fig. 1(c), (d). All Ni sites are structurally equivalent in 1ENO/1LNO superlattice (SL) and the checker board type CO can be naturally accommodated within this structure, akin to bulk  $RENiO_3$ . In sharp contrast, for 2ENO/1LNO SL the period of two kinds of inequivalent nickels  $[Ni(I), Ni(II)]$  is  $3 \times c$  along  $[0\ 0\ 1]$  and clearly cannot be matched with the periodicity of the bulk-like checker board CO ( $2 \times c$ ). Though both samples show the first-order MITs and antiferromagnetism, resonant X-ray scattering (RXS) at the Ni  $K$ -edge revealed an unaffected amount of CO across the MIT for 2ENO/1LNO SL whereas the MIT of 1ENO/1LNO was accompanied by a significant modulation of CO. Combined magnetic characterizations using X-ray spectroscopy and scattering at Ni  $L_{3,2}$ -edges confirm  $S=1$  behavior, signifying the critical importance of ligand holes for the magnetic ordering of these materials. The decoupling of the

structural and electronic degrees of freedom and confirmation of  $S=1$  magnetic nature attest to the fact that structural and CO transitions are not the origin of MIT for 2ENO/1LNO, and selects the SSM scenario as the microscopic mechanism for the transition [21–26].

$[2ENO/1LNO] \times 12$  and  $[1ENO/1LNO] \times 18$  SLs were grown on orthorhombic  $NdGaO_3$   $(1\ 1\ 0)_{or}$   $[(0\ 0\ 1)_{pc}]$  (or and pc denote orthorhombic and pseudocubic settings respectively) substrates by laser MBE [33–38]. The growth was monitored by in-situ reflection high energy electron diffraction. X-ray diffraction (XRD) measurements (shown in supplemental [39]), recorded using the six-circle diffractometer at the 6-ID-B beam-line of the Advanced Photon Source (APS) at Argonne National Laboratory confirm high structural quality of the superlattices and also establish that all samples are single domain [18, 34]. Transport properties were measured in 4-probe Van Der Pauw geometry with a Quantum Design physical property measurement system (PPMS). X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) on the Ni  $L_{2,3}$  edges were performed at the 4-ID-C beam line of the APS. Magnetic structure was investigated at the resonant soft X-ray beamline 4.0.2 of the Advanced Light Source (ALS).

Fig. 2 shows the electronic and magnetic properties of the SLs. As immediately seen, both 2ENO/1LNO and 1ENO/1LNO SLs are metallic at room temperature and undergo a first order MIT at 245 K and 155 K respectively with several orders of magnitude resistivity changes, similar to bulk  $RENiO_3$  (upper panels of Fig. 2(a) and (b)). The large dissimilarity in  $T_{MIT}$ , along with the difference in hysteric widths suggests a significant difference between these SLs. As for the magnetic order,  $E'$ -AFM ordering of  $RENiO_3$  is characterized by the  $(1/2, 0, 1/2)_{or}$   $[(1/4, 1/4, 1/4)_{pc}]$  magnetic wave vector, which can be viewed as a stacking of either  $\uparrow\uparrow\downarrow\downarrow$  or  $\uparrow\rightarrow\downarrow\leftarrow$  or  $\uparrow\ 0\ \downarrow\ 0$  of pseudocubic  $(111)$  planes [11]. This type of magnetism is rather robust and has been found in bulk-like thick films, ultra-thin films and superlattices of  $RENiO_3$  [19, 20, 30, 34, 42, 43]. To assess the magnetic structure of our superlattices we performed resonant magnetic X-ray scattering recorded at the Ni  $L_3$  edge resonance energy of 852 eV. The inset in Fig. 2(b) shows the presence of a strong  $(1/4, 1/4, 1/4)_{pc}$  reflection appearing below the transition temperature. The plot of integrated intensity of the peak as a function of  $T$  (lower panel of Fig. 2(a)-2(b)) yields the antiferromagnetic transition temperature of  $T_N=220 \pm 5$  K for 2ENO/1LNO and  $155 \pm 5$  K for 1ENO/1LNO. A direct comparison to the transport data shows that for the 2ENO/1LNO SL there is a finite separation between  $T_N$  and  $T_{MIT}$  that has been additionally confirmed by the magneto-transport measurements [39, 44]. These results demonstrate that by altering the ENO layer thickness within just one period of the superlattice, the temperature driven electronic and magnetic transitions can be made either simultaneous or separate.

After establishing bulk-like magnetic order, we investigate for a possible difference in CO, and the accompanying structural transition, as the progenitor of dissimilar transport be-

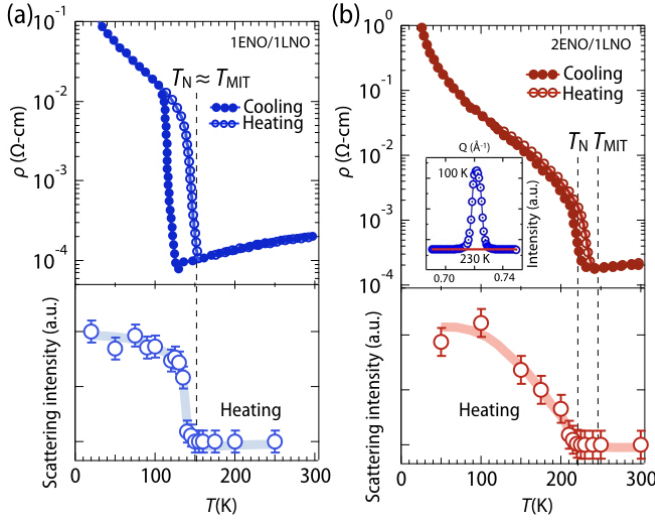


FIG. 2. Upper panel of (a) and (b) displays temperature dependence of the *dc* resistivity of 1ENO/1LNO and 2ENO/1LNO respectively. Lower panels show temperature dependence of the  $(1/2\ 0\ 1/2)_{\text{or}}$  Bragg peak intensity corresponding to  $E'$  type antiferromagnetic state. Magnified view of the resistivity around  $T_{\text{MIT}}$  has been shown in supplemental. Inset of (b) shows measured magnetic scattering for 100 K and 230 K for 2ENO/1LNO.

havior. To probe for the presence of CO, resonant X-ray scattering (RXS) at the *K*-edge ( $1s \rightarrow 4p$  transition) around  $(h\ 0\ l)_{\text{or}}$  and  $(0\ k\ l)_{\text{or}}$  reflections (odd  $h, k, l$ ) has been extensively used as a direct proof of a CO phase [12–15]. Specifically, we performed our RXS measurements on the Ni *K*-edge (8.34 keV) at the  $(0\ 1\ 1)_{\text{or}}$  reflection. The structure factor for this reflection can be written as [12–15]  $F_{011}(\mathbf{Q}, E) = A_{O,RE}(\mathbf{Q}) + 2\Delta f_{\text{Ni}}^0(\mathbf{Q}) + 2\Delta f_{\text{Ni}}'(E) + 2\Delta f_{\text{Ni}}''(E)$  with  $\Delta f_{\text{Ni}}^0(\mathbf{Q}) = f_{\text{Ni}1}^0(\mathbf{Q}) - f_{\text{Ni}2}^0(\mathbf{Q})$ ,  $\Delta f_{\text{Ni}}'(E) = f_{\text{Ni}1}'(E) - f_{\text{Ni}2}'(E)$ ,  $\Delta f_{\text{Ni}}''(E) = f_{\text{Ni}1}''(E) - f_{\text{Ni}2}''(E)$ .  $A_{O,RE}(\mathbf{Q})$ ,  $f_{\text{Ni}}^0(\mathbf{Q})$  are the energy independent Thompson scattering terms for the *RE* and O-sites, and the Ni-sites respectively. The  $f_{\text{Ni}}'(E)$ ,  $f_{\text{Ni}}''(E)$  terms represent the real and imaginary energy-dispersive correction factors which contribute to the resonant behavior. The intensity of the Bragg reflection is then given by  $I_{011} \propto |F_{011}|^2 = A_{O,RE}^2 + 2A_{O,RE} \cdot 2(\Delta f_{\text{Ni}}^0 + \Delta f_{\text{Ni}}' + \Delta f_{\text{Ni}}'') + 4(\Delta f_{\text{Ni}}^0 + \Delta f_{\text{Ni}}' + \Delta f_{\text{Ni}}'')^2$ . As clearly seen, because of the mixing of  $A_{O,RE}$  and  $\Delta f$  parameters, any energy-dependent features at resonance can be due to either a change in the energy dispersive terms themselves, or due to a change in the *Q*-dependent Thompson scattering factors from the *RE* and O-sites,  $A_{O,RE}(\mathbf{Q})$ . Thus, through this entanglement, a significant modulation of  $A_{O,RE}$  may contribute to a large energy-dependent variation at resonance in addition to the Ni charge ordering. However, all energy-dispersive terms go to zero [ $\Delta f_{\text{Ni}}'(E)$  and  $\Delta f_{\text{Ni}}''(E) \rightarrow 0$ ] a few eV away from the resonant energy, and thus isolate changes due to the energy independent terms  $A_{O,RE}$  alone.

The 1ENO/1LNO SL exhibits a sharp appearance of the  $(0\ 1\ 1)_{\text{or}}$  reflection below the MIT as exemplified by the data

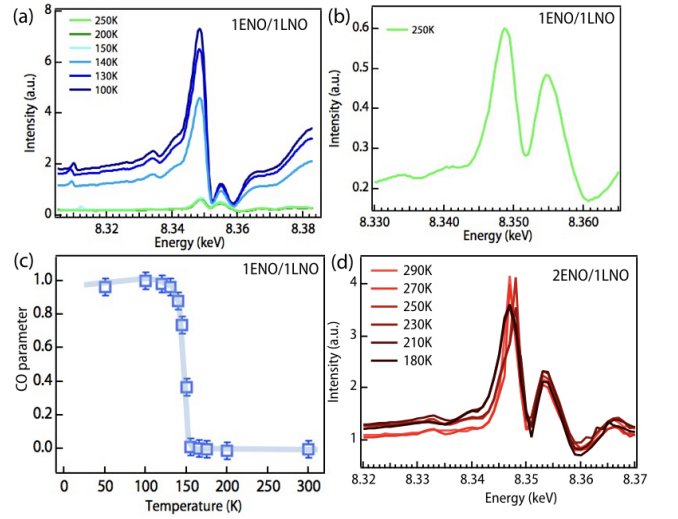


FIG. 3. (a)  $(0\ 1\ 1)_{\text{or}}$  resonance energy scan for the 1ENO/1LNO SL at various temperature. Resonance does also persist in the metallic state (b). (c) Temperature dependence of CO parameter [45] for 1ENO/1LNO. (d)  $(0\ 1\ 1)_{\text{or}}$  resonance for the 2ENO/1LNO SL showing a strong resonance signal but no significant change across  $T_{\text{MIT}} \sim 245\text{ K}$  is observed.

at 100K shown in Fig. 3(a). The result is similar to what is seen in bulk-like films of  $\text{NdNiO}_3$  and has been directly connect to the monoclinic CO phase [12–15]. Upon heating across the MIT, the CO scattering signal from 1ENO/1LNO SL is strongly reduced, but in contrast to the expectations for the bulk nickelates [12], does not completely disappear, and is likely due to the presence of octahedral distortions contributing to the off-diagonal elements of the energy dispersive scattering factors [15]. The large change in the off-resonant scattering intensity for 1ENO/1LNO emphasizes a significant lattice modulation across the MIT. The coupling of the energy-independent and dispersive factors can also affect the resonance intensity and shape, and thus contributes to the strong change across the MIT observed at resonance. The change in CO is quantified in Fig. 3(c) where we plot *T*-dependence of the charge order parameter, defined as  $\alpha = \sqrt{I(E_{\text{res}})} - \sqrt{I(E_{\text{offres}})}$  [12, 45], which is concurrent with both the MIT and antiferromagnetic order present in 1ENO/1LNO SL.

The case of 2ENO/1LNO shown in Fig. 3(d) shows a stark contrast to 1ENO/1LNO. Specifically, no significant change in either the line shape or intensity occurs upon traversing the MIT at  $\sim 245\text{ K}$  for 2ENO/1LNO SL. Moreover, no change in the on- or off-resonant behavior unambiguously implies that there is no significant modulation of the structure factor across the MIT for 2ENO/1LNO, which in turn *excludes* the presence of bulk-like long-range CO and lattice symmetry change within the detection limit of the scattering technique. However, short range CO could still be present [46]. The lack of bulk-like CO or structural symmetry change across the MIT means another driving mechanism is at play. Additionally, the large resonance intensity found

above  $T_{\text{MIT}}$  for 2ENO/1LNO SL signifies the realization of a new monoclinic metallic phase without application of any external field.

Next, we focus on a possible microscopic mechanism responsible for the MIT. In contrast to 1ENO/1LNO SL where the simultaneous transitions can be accounted by a spin-density wave scenario [28–30], the observation of a MIT and magnetic transition in this 2ENO/1LNO SL without CO advocates for a different model such as the site-selective Mott mechanism [22]. The key aspect of the model is that, in contrast to what is expected from a  $\text{Ni}^{3+}$  picture (spin  $S=1/2$  state), an  $S=1$ -like magnetic ground state is predicted. Moreover, as very recently demonstrated in the SSM [25] model, the Ni  $K$ -edge resonance line shape can be successfully generated from inequivalent Ni-sublattices with BD and does not require any real CO among the Ni sites. To test such scenario for 2ENO/1LNO SL, we investigated the magnetic state of the Ni spins by carrying out XMCD measurements which is a local probe of element specific magnetism. Although the antiferromagnetic arrangement of Ni sites does not have any net magnetization, an applied external magnetic field ( $H$ ) can cant the individual spins resulting in a finite XMCD signal. If the applied magnetic field  $H$  energy is weaker than the crystal field, it preserves the intrinsic spin value and thus provides an opportunity to probe the magnitude of spin per nickel site. Figure 4(a) shows the X-ray absorption and XMCD spectra at 50 K under a applied field of 5 Tesla. For comparison, we show the XAS of a well-known  $S=1$  compound  $\text{Ni}^{2+}\text{O}$ . Surprisingly, the most notable feature of the XMCD line shape of the  $L_3$  edge is that the energy corresponding to the (negative) peak of XMCD is at the same position as the peak of  $\text{Ni}^{2+}$  XAS. Moreover, the XMCD line shape of 2ENO/1LNO is strikingly similar to the XMCD of  $\text{Ca}_2\text{NiOsO}_6$  ( $\text{Ni}^{2+}$  with octahedral crystal field analogous to  $\text{RENiO}_3$ ) obtained from Ref. [47] (see [39]). All these similarities point towards the existence of the  $S=1$  state in 2ENO/1LNO SL [48].

To investigate whether  $S=1$  like behavior of the film deduced from XMCD corresponds to the observed  $E'$ -AFM, we have derived magnetic scattering (Fig. 4(b)) from XMCD data [49] by using Kramers-Kronig transformation [50, 51] and compared it with the experimentally observed magnetic scattering data corresponding to the  $(1/4\ 1/4\ 1/4)_{\text{pc}}$  reflection. As clearly seen in Fig. 4(c), the derived magnetic scattering intensity has exactly the same line shape and line positions as the energy scans recorded on  $(1/4\ 1/4\ 1/4)_{\text{pc}}$  reflections in our RXS experiment which in turn unambiguously confirms the  $S = 1$  magnetic state of Ni. To emphasize, the MIT in 2ENO/1LNO without any bulk-like symmetry change, the absence of CO, and  $S = 1$ -like behavior with  $E'$ -AFM provide the first experimental evidence for the theoretically proposed SSM ground state [21–26]. Interestingly, the temperature dependence of out-of-plane lattice constant shows almost negligible lattice expansion ( $\sim 0.18\%$ ) across the MIT [39], which can be also accounted by the bond disproportionation in SSM model as the partial volume compression of octahedra with  $d^8\bar{L}^2$  configuration being compensated by the equal expan-

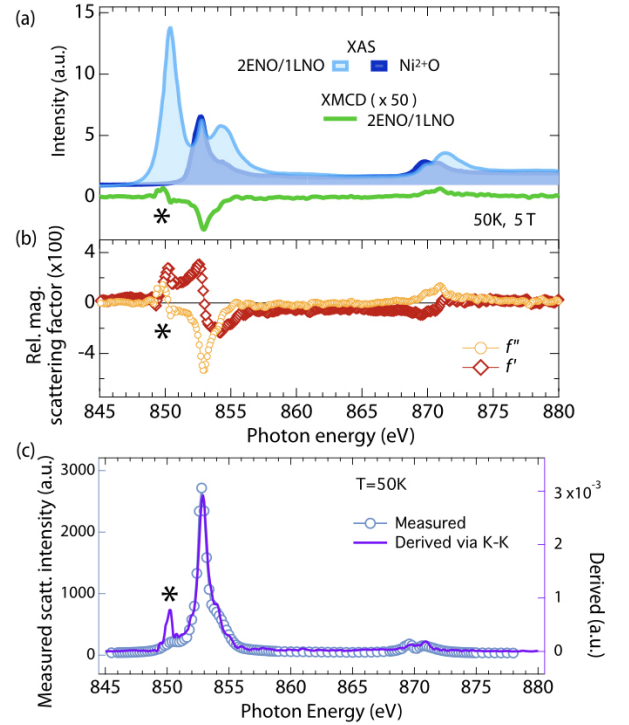


FIG. 4. (Color online) (a) XAS and XMCD of 2ENO/1LNO SL, measured with  $H = 5$  Tesla at 50 K and XAS of  $\text{NiO}$ . To rule out any artifacts, XMCD was measured with both  $+5$  T and  $-5$  T and their difference (divided by 2) has been plotted. The strong artifacts in XMCD at the very strong  $\text{La } M_4$  peak position does not exactly cancel with this field flipping, resulting in the small artifacts indicated by \*. (b) Real and imaginary part of magnetic scattering factor. (c) Energy dependence of magnetic scattering intensity was simulated using the data shown in (b) and is compared with the experimentally observed energy scan of  $E'$  magnetic structure.

sion of the neighboring octahedra with  $d^8$  state [23].

In conclusion, by designing ultra-thin superlattices, we have been able to solve a long-standing puzzle of the MIT in  $\text{RENiO}_3$  by demonstrating that neither charge ordering nor lattice symmetry transition is mandatory for the MIT, and instead it can be accounted by a bond-disproportionation within the pure site-selective Mott transition. The realization of a previously unknown monoclinic metallic phase without any external field demonstrates the utility of interface engineering as a tool for generating novel materials phases of complex oxides. Moreover, the idea of selective suppression of cooperative ordering by mismatching the structural periodicity with the periodicity of the ordering phenomenon can be a promising route to unravel the mystery of competing phases including charge density wave and pseudo gap phase on superconductivity in high  $T_c$  cuprates [7] and may eventually provide a new materials design principle to enhance  $T_c$ .

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- $$\frac{(\sqrt{I(E_{\text{res}})} - \sqrt{I(E_{\text{offres}})})_{T=T_K} - (\sqrt{I(E_{\text{res}})} - \sqrt{I(E_{\text{offres}})})_{T=300K}}{(\sqrt{I(E_{\text{res}})} - \sqrt{I(E_{\text{offres}})})_{T=100K} - (\sqrt{I(E_{\text{res}})} - \sqrt{I(E_{\text{offres}})})_{T=300K}}.$$
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