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Epitaxial strain modulated electronic properties of interface controlled nickelate superlattices
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Phys. Rev. B 98, 045115 — Published 10 July 2018
DOI: 10.1103/PhysRevB.98.045115
I. INTRODUCTION

The sudden change in the electrical conductivity across the metal insulator transition (MIT) of complex oxides remains a topic of long-standing interest in condensed matter physics and materials science\(^1\). Apart from the fundamental physics aspect of understanding the origin of MIT, a lot of attempts are being made towards the realization of next generation functional devices utilizing MIT\(^2\)–\(^4\). Practical realization of such devices depends strongly on the ability to maintain sharp metal-insulator transition as the size reduction of the materials towards the nanometer thick device scale and epitaxial strain can significantly modify MIT\(^5\)–\(^7\).

As a prototypical example having MIT, massive efforts have been made over the last 5 years about the manipulation of the MIT of rare-earth perovskite nickelate (\(\text{RENiO}_3\)) using external perturbation such as light, strain, electric and magnetic fields etc. (see Ref. 8–10 and references therein). Epitaxial strain i.e. mismatch of lattice constants between the single crystalline substrate and \(\text{RENiO}_3\), has been found to be very successful in manipulation of these transitions\(^11\)–\(^20\). For example, the first-order metal to insulator transition (MIT) can be suppressed entirely by compressive strain. Though the MIT is accompanied by spin and charge ordering transitions and structural symmetry lowering in bulk \(\text{NdNiO}_3\)\(^{21\text{–}23}\), the MIT and magnetic transition can be separated by tensile strain, leading to a paramagnetic insulating phase\(^11\). Surprisingly, charge ordering and symmetry lowering transitions are absent in ultra-thin \(\text{NdNiO}_3\) films (thickness \(\sim 6\) nm), grown under tensile strain\(^{24,26}\). Nickelates being a prototypical strongly correlated system, exhibit highly nontrivial transport properties in the metallic phase. One such frequently discussed phenomenon is the non-Fermi liquid (NFL) behavior of the metallic phase, and epitaxial strain is able to control scaling behavior (power exponents) of the NFL phase\(^{12,13}\). In addition, \(\text{RENiO}_3\) members have been combined with dielectric materials such as \(\text{LaAlO}_3\), \(\text{DyScO}_3\) etc. to study the effect of quantum confinement, and the responses of the orbital and spin degrees of freedom to heterostructuring and epitaxial strain\(^{28\text{–}35}\). However, study of ultra-thin superlattices consisting of dissimilar nickelate layers is very limited\(^{36}\) and the response of electronic and magnetic structure to the underlying epitaxial strain is still largely unknown.

The choice of \(\text{RE}\) ions determine the structural symmetry of bulk \(\text{RENiO}_3\) and a very strong connection between the temperature scale of electronic, magnetic transitions and \(<\text{Ni}-\text{O}-\text{Ni}>\) has been observed in bulk \(\text{RENiO}_3\) series\(^{37,38}\). For example, bulk \(\text{LaNiO}_3\) (LNO) with rhombohedral symmetry has the smallest distortion (\(<\text{Ni}-\text{O}-\text{Ni}>\sim 165.2^\circ\)) in the \(\text{RENiO}_3\) series and remains metallic and paramagnetic without any structural transition. On the other hand, bulk \(\text{EuNiO}_3\) (ENO) is strongly distorted (\(<\text{Ni}-\text{O}-\text{Ni}>\sim 147.9^\circ\)) and undergoes a first order MIT around 460 K with a charge ordering transition and structural transition and well separated magnetic transition (paramagnetic to \(E'\)-antiferromagnetic) at \(\sim 200\) K\(^{39}\). Since each \(\text{RENiO}_3\) member has a rather strong propensity for maintaining bulk-like symmetry even in thin film geometry\(^{40}\), a strong structural competition can be anticipated in the ultra-thin limit for the superlattices consisting of dissimilar nickelates layers, and can in turn result in new electronic and magnetic phenomena.

Towards this goal, we have synthesized and investigated the effect of epitaxial strain by growing 1 uc \(\text{EuNiO}_3/\text{LaNiO}_3\) superlattices (1ENO/1LNO SL, uc= unit cell in pseudocubic setting, see Fig. 1) on a variety of substrates. To elucidate the microscopic effect of epitaxial strain on the structural, electronic, and magnetic properties of these superlattices, X-ray diffraction (XRD), dc transport, Hall effect, resonant soft X-ray absorption spectroscopy (XAS) and X-ray linear dichroism (XLD) measurements have been performed. Surprisingly, we have found that in spite of the strong variation of substrate strain and symmetry, the structural response of the SLs in this ultimate interface limit is primarily governed by the ENO layer. The heterostructure grown under tensile strain undergoes a MIT and a magnetic transition below room temperature, emphasizing entire modulation of the electronic properties, sharply contrasted to the bulk ENO and LNO. Moreover, by the judicious application of epitaxial
TABLE I. Symmetry and in-plane pseudo-cubic lattice constants ($a_{sub}$) of the substrates and the corresponding strain ($\epsilon$) for orthorhombic EuNiO$_3$ (3.806 Å), and rhombohedral LaNiO$_3$ (3.855 Å). The lattice constants for the bulk ENO and LNO have been obtained from Ref. 39.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Symmetry</th>
<th>$a_{sub}$ (Å)</th>
<th>$\epsilon$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAIO$_3$</td>
<td>Orthorhombic</td>
<td>3.692</td>
<td>-3.0%</td>
<td>-4.2%</td>
</tr>
<tr>
<td>LaAlO$_3$</td>
<td>Rhombohedral</td>
<td>3.794</td>
<td>-0.3%</td>
<td>-1.6%</td>
</tr>
<tr>
<td>NdGaO$_3$</td>
<td>Orthorhombic</td>
<td>3.858</td>
<td>+1.4%</td>
<td>+0.1%</td>
</tr>
<tr>
<td>DyScO$_3$</td>
<td>Orthorhombic</td>
<td>3.955</td>
<td>+3.9%</td>
<td>+2.6%</td>
</tr>
</tbody>
</table>

strain these transitions can be made to occur simultaneously or separated with temperature or even entirely suppressed. Oxygen K edge XAS measurements revealed that such a drastic change in the electronic behaviour is related to a strain induced self-doping effect$^{31,42}$. Such manipulation of the electronic and magnetic transitions by the application of epitaxial strain highlights the remarkable power of heteroepitaxy in determining physical properties of perovskite nickelates.

II. EXPERIMENTAL DETAILS

[1EuNiO$_3$/[1LaNiO$_3$]$\times10$ superlattices [(1ENO/1LNO) SL], oriented along the pseudo cubic [0 0 1] direction were grown on a variety of single crystal substrates by pulsed laser interval deposition$^{43,44}$ from polycrystalline stoichiometric EuNiO$_3$ and LaNiO$_3$ targets. The substrates used in this work: DyScO$_3$ (DSO), NdGaO$_3$ (NGO), LaAlO$_3$ (LAO), and YAIO$_3$ (YAO) have been selected to avoid polar discontinuity at the film/substrate interface$^{45}$. The symmetry of the substrates and the corresponding expected strain values for ENO and LNO are listed in Table-I. Growth of all samples were monitored by in-situ high pressure RHEED (reflection high energy electron diffraction). All films were grown at 620° C and 150 mTorr of oxygen pressure and were post annealed at growth temperature under 650 Torr pressure of pure oxygen. XRD measurements were carried out around the (0 0 2) reflection of the substrate (pseudocubic notation) with a Panalytical Xpert Pro materials research diffractometer (MRD). X-ray absorption spectra (XAS) of Ni $L_{2,3}$ edges were recorded at the 4-ID-C beam line of Advanced Photon Source (APS). dc transport measurements, using a four probe Van Der Pauw geometry, were performed in Physical Property Measurement System (PPMS Quantum Design). $I$-$V$ measurements confirmed ohmic behavior of all electrical contacts.

III. RESULTS AND DISCUSSION

Epitaxial growth: Since the optimal growth conditions for ENO and LNO thin films are different$^{46,47}$, it is crucial to find out the mutually compatible growth conditions for the layer by layer epitaxial stabilization of both ENO and LNO layers to form high quality 1ENO/1LNO SL. The sequence of layer by layer growth has been shown in Fig. 1(b). The variation of the intensity of the specular spot in the RHEED pattern, recorded during the growth of 1ENO/1LNO superlattice on a NGO substrate, has been plotted in Fig. 1(c). The full recovery of intensity after the deposition of each unit cell confirms the desired layer by layer stabilization of both EuNiO$_3$ and LaNiO$_3$. The RHEED image (Fig. 1(d)), taken after cooling the sample to room temperature, shows the streak patterns of specular (0, 0) and off-specular (0, ±1) Bragg reflections, implying atomically smooth surface morphology. The presence of half order reflections (marked by arrows) due to the in-plane doubling of the unit cell$^{46}$ (also observed for superlattices grown on other substrates), confirm that superlattices have either orthorhombic or monoclinic symmetry at room temperature.

Following Poisson argument about elasticity, it is generally anticipated that the single crystalline thin film should undergo out-of-plane compression (expansion) to accommodate in-plane tensile (compressive) strain. Experimentally, however, the effects of epitaxial strain on nickelate thin films and heterostructures are more complex and markedly depart from the expected tetragonal distortion$^{44,43,32,34,40,48}$. To investigate the effect of epitaxial strain on our 1ENO/1LNO SLs, $2\theta$-$\omega$ scans have been recorded using Cu $K_{\alpha}$ radiation (Fig. 1(e)). Each of the diffraction patterns consist of a sharp substrate peak together with a film peak (indicated by a solid triangle) and thickness fringes confirming the growth along the desired pseudo cubic (0 0 1) direction. Out-of-plane pseudocubic lattice constant ($c_{pc}$) for the SL grown on YAO is found to be 3.875 ± 0.005 Å, which is enlarged compared to both bulk ENO and LNO, and is as expected for a tetragonal distortion under high compressive strain. While the close proximity of the substrate and film peaks for the samples grown on LAO...
and NGO substrates prohibits a reliable estimation of \( c_a \); nevertheless it can be immediately seen that the film peak for the NGO substrate is close to bulk ENO. Interestingly, \( c_{pc} \) (3.798 0.005 Å) of the SL grown on DSO is also very close to the lattice constant of bulk ENO (3.8 Å). The very different orbital responses and electronic properties of the SLs (discussed latter in this paper) suggest that such bulk ENO-like lattice constant of the SLs under tensile strain does not arise from simple strain relaxation. We also note that single layer films of ENO and LNO under tensile strain also show corresponding bulk-like lattice constants \(^{36}^{38}\) and such anomalous behaviors are related to the strain compensation by octahedral tilts, rotations and breathing mode distortions. In contrary to single layer LNO films, LNO layers in the present SLs under tensile strain undergo out-of plane compression so that the resultant \( c_a \) of the SL remains consistent with the bulk ENO value. This indicates that the overall symmetry of the SL takes the lower form as in ENO \((a^- a^- c^+)\)!\(^{19}\), likely due to the inability of the \(a^- a^- a^-\) rotation system seen in bulk LNO to stabilize in the presence of the smaller Eu ions.

Structural responses of these SLs to the epitaxial strain have been further investigated by X-ray linear dichroism (XLD) measurements at room temperature. In such experiment, absorption at Ni \(L_2\) edges are measured with horizontally (H) and vertically (V) polarized X-rays (Fig. 2(a)) and the difference in the energy position and intensity provides information about the splitting between the \(e_g\) orbitals and their preferential electronic occupation \(^{32}^{34},^{44},^{45},^{50}\). The absorptions labeled as \(I_V\) and \(I_H\) after background subtraction of the Ni \(L_2\) edge and the difference signal \((I_V - I_H)\) are shown in Fig. 2(b). As seen, the line shapes of the spectra confirm the expected Ni\(^{3+}\) oxidation state in these superlattices. The ratio, \(X\) of holes on \(d_{3z^2-r^2}\) and \(d_{x^2-y^2}\) orbitals can be obtained from the measured \(I_V\), \(I_H\) using the sum rules \(X = \frac{h_{3z^2-r^2}}{h_{x^2-y^2}} = \frac{3A_V}{4[A_H - A_V]} \) \(^{12,34}\), where \(A_H\) (\(A_V\)) is the integrated area of \(I_H\) (\(I_V\)). We note that bulk \(RENiO_3\) does not show any preference between these two \(e_g\) levels \(^{24,51}\). The variation of \(X\) and the energy splitting between \(d_{3z^2-r^2}\) and \(d_{x^2-y^2}\) orbitals obtained from Fig. 2(b) is plotted in Fig. 2(c) as a function of substrate lattice constant. As immediately seen, the large compressive strain provided by the YAO substrate results in a derivative-like shape of the XLD \((I_V - I_H)\) spectra confirming the expected orbital splitting with \(c_{pc}/a_{pc} > 1\). \(d_{3z^2-r^2}\) orbital is higher in energy compared to \(d_{x^2-y^2}\) by 50 meV and \(X\) is close to unity, emphasizing equal population on both \(e_g\) orbitals. On the other end, the SL on DSO with \(c_{pc}/a_{pc} < 1\) shows a orbital splitting of around 100 meV and much larger hole density in \(d_{3z^2-r^2}\) orbitals. Surprisingly, for intermediate compressive (LAO) and tensile (NGO) strain cases, the holes density is slightly larger in \(d_{x^2-y^2}\) orbitals and the energy separation between two \(e_g\) orbitals is below the accuracy of the XLD measurement (~ 50 meV). This apparently conflicting observation for the film on NGO substrate can be resolved by including complex octahedral distortions acting to accommodate the moderate amount of strain \(^{36,48}\).

The summary of temperature dependent resistivity measurements on these SLs is shown in Fig. 3(a). As reported earlier \(^{36}\), the samples grown on NGO substrate remains metallic down to 125 K and then undergo a MIT. During heating from low temperature it becomes metallic at 155 K. This hysteresis signifies the first order nature of the transition. This behavior is drastically different from the entirely insulating behavior of single layer ENO or entirely metallic behaviour of LNO films grown on NGO substrates below 300 K \(^{14}\). Such a large change emphasizes a complete modulation of the electronic structure by heteropitaxy. Surprisingly, in the metallic phase the resistivity shows an unconventional linear-\(T\) dependence (over 190 K - 280 range, shown in Supplemental Materials \(^{52}\)) while the Debye temperature of bulk nickelates is around 420 K \(^{53}\). Such linear-\(T\) dependent resistivity has been also observed in high \(T_c\) cuprates, pnictide and organic superconductor, ruthenate, heavy fermion metals etc. and has been very often linked to the quantum criticality \(^{54-58}\). Furthermore, the increase of tensile strain on DSO results in a higher resistivity at room temperature. Also, while the insulator to metal transition temperature during heating remains similar to the SL on NGO, the magnitude of thermal hysteresis becomes much smaller. On the other hand, the superlattices grown on LAO and YAO remains metallic down to low temperature without any hysteretic behavior. This suppression of the MIT by compressive strain resembles the behavior of ultrathin films of PrNiO\(_3\), NdNiO\(_3\), SmNiO\(_3\), EuNiO\(_3\) \(^{11-16}\). The dc transport of these metallic samples exhibits a \(T^{4/3}\) dependence over a large range of temperature and then switches to linear-\(T\) dependent behavior (see Fig. 3(b) and Supplemental Materials \(^{52}\)). \(T^{4/3}\) dependence of resistivity is a characteristic of NFL phase proximal to a two-dimensional quantum critical point \(^{58}\). Such switching of \(T^{4/3}\) dependence to linear \(T\) behavior has been also observed in NdNiO\(_3\) thin films under compressive strain and can be accounted by Boltzmann-type
transport theory with multiple bands near a quantum critical point (for details see Refs. 11 and 58).

In the past, long range magnetic orderings of bulk \( \text{RENiO}_3 \), single layer films and superlattice structures consisting of \( \text{RENiO}_3 \) layers have been investigated by neutron diffraction \(^{59}\) and resonant X-ray scattering \(^{11,12,16,24,27,31,35,60,61}\). These investigations showed that the insulating phase of these materials always shows a \( E' \)-antiferromagnetic ordering with the transition temperature \( T_N \) that can be either \( T_{\text{MIT}} \) or \( < T_{\text{MIT}} \) and the magnetic wave vector is \( (1/2, 0, 1/2) \), \( (1/4, 1/4, 1/4) \), \( (0, 1/2, 0) \), and \( (1/2, 0, 1/2) \). In addition, a re-arrangement of the lattice has been further emphasized in several recent theoretical and experimental works \(^{36,73–76}\). In recent investigations, a plot of the thermoelectric power \( T \) vs. \( T_{\text{MIT}} \) and the magnetic wave vector is \( (1/2, 0, 1/2) \), \( (1/4, 1/4, 1/4) \), and \( (0, 1/2, 0) \). In addition, a re-arrangement of the lattice has been further emphasized in several recent theoretical and experimental works \(^{36,73–76}\). In addition, a re-arrangement of the lattice has been further emphasized in several recent theoretical and experimental works \(^{36,73–76}\). In addition, a re-arrangement of the lattice has been further emphasized in several recent theoretical and experimental works \(^{36,73–76}\). In addition, a re-arrangement of the lattice has been further emphasized in several recent theoretical and experimental works \(^{36,73–76}\). In addition, a re-arrangement of the lattice has been further emphasized in several recent theoretical and experimental works \(^{36,73–76}\). In addition, a re-arrangement of the lattice has been further emphasized in several recent theoretical and experimental works \(^{36,73–76}\).

A direct inspection of Figure 4(a) and upper panel of Fig. 4(b) shows the movement of the prepeak towards higher phonon energy as strain becomes more compressive (NGO \( \rightarrow \) LAO \( \rightarrow \) YAO), thus emphasizing a decrease of charge transfer energy \( \Delta \) with compressive strain. Microscopically, at the first approximation \( \Delta \) is related to the electron affinity of oxygen \( [I(O^{2-})] \), the ionization potential of \( \text{Ni}^{3+} \) \( \left[A(\text{Ni}^{3+})\right] \), relative Madelung potential \( \delta V_{\text{Madd}} \) between Ni and O, and the nearest-neighbor distance between Ni and O \( (d_{\text{NN}}-\text{O}) \) as \( \Delta = e\delta V_{\text{Madd}} + I(O^{2-}) - A(\text{Ni}^{3+}) + e^2/d_{\text{NN}}-\text{O} \). This observation implies that strain induced change in \( \Delta \) originates from the strong modulation in the relative Madelung potential. Most importantly, the FWHM of the pre-peak also increases with compressive strain signifying the enhancement of Ni-O hy-
with different electronic occupancies (Fig. 2(c)). This im-

4(c). Such strain-induced ‘self-doping’ of 1ENO/1LNO SL

528.5 eV for 1ENO/1LNO SLs measured at 300 K. The peaks above

an additional strong peak, related to the transition to hybridized Sc 3d-O 2p states is present around 533 eV

Schematic representation of the single-particle density of states in

metal. The electronic and magnetic phases are highly tunable

to the observed shift of O K edge will be required to investigate this scenario83.

IV. CONCLUSION

To summarize, correlated metal LaNiO$_3$ and charge transfer

V. ACKNOWLEDGEMENTS

S.M. and J.C. deeply thank D. Khomskii and K. Haule for theoretical discussion. S.M. is supported by IISc start up


5 D. G. Schlom, L.-Q. Chen, X. Pan, A. Schmehl, and M. A. Zur-


