Atomic-scale observation of spontaneous hole doping and concomitant lattice instabilities in strained nickelate films

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Abstract

Thin oxide films are of vast opportunities for modern electronics and can facilitate emergent phenomena by factors absent in the bulk counterparts, such as the ubiquitous epitaxial strain and interfacial charge doping. Here, we demonstrate the twisting of intended bulk-metallic phases in 10-unit-cell LaNiO3, PrNiO3, and NdNiO3 films on (001)-oriented SrTiO3 into distinct charge-lattice entangled states by epitaxial strains. Using atomically-resolved electron microscopy and spectroscopy, the interfacial electron doping into SrTiO3 in the conventional context of band alignments are discounted. Instead, spontaneously doped holes that are localized and at the order of $10^{13}$ cm$^{-2}$ are atomically unraveled across all three heterointerfaces and associated with strain mitigations by the accompanied atomic intermixing with various ionic radii. The epitaxial strains also lead to condensations of monoclinic-C2/c lattice instabilities, which are hidden to the bulk phase diagram. The group-theoretical analysis of characteristic transition pathways unveils the strain resurrection of the hidden C2/c symmetry. While this strain-induced monoclinic phase in LaNiO3 remains metallic at room temperature, those in PrNiO3 and NdNiO3 turn out to be insulating. Such strain-induced monoclinic lattice instabilities and parasitic localized holes go beyond the classical elastic deformations of films upon epitaxial strains and hint on plausible hidden orders in versatile oxide heterostructures with unexpected properties, of which the exploration is only at the infancy and full of potentials.

1. Introduction

Rare-earth perovskite nickel oxides, RNO$_3$ (RNO; $R = \text{La–Lu}$), compose the textbook example of metal–insulator transitions (MITs) [1, 2]. The constituent Ni$^{3+}$ ($d^7$) is in the low-spin state ($t_{2g}^6e_{g}^1$) [1–4]. The corner-shared NiO$_6$ octahedra manifest the GdFeO$_3$-type distortion, characterized by antiphase octahedral buckling in the equatorial plane and inphase rotation along the apical direction. The extent of distortions increases upon the decrease in $R$-ionic sizes from La to Lu [3, 5, 6].

The least distorted LaNiO$_3$ (LNO; rhombohedral R$3c$) in the family is metallic and free from magnetic ordering [1, 3]. Neighboring PrNiO$_3$ (PNO) and NdNiO$_3$ (NNO) of increasing GdFeO$_3$-type distortions crystallize in orthorhombic Pbnm at room temperature (RT) and become insulating below the respective MIT temperatures ($T_{MI}$) of 135 and 200 K [1, 3], which coincide with the antiferromagnetic ordering temperatures ($T_N$) [4]. The magnetically-ordered phases show a common modulation vector of...
$k = (\frac{1}{2}, 0, \frac{1}{4})$ in the $Pbnm$ frame [4] and the concurrent gap opening at $k$ conveys the distinct charge order, charge- and bond-disproportionate NiO$_6$ in the reduced monoclinic $P2_1/n$ symmetry (with otherwise similar lattice parameters to the $Pbnm$'s) and corresponding to the softening of an oxygen-breathing phonon mode with alternating dilated and contracted octahedra [6–11]. Considering also the nesting of cube-like Fermi surfaces at $k$, the concomitant magnetic ordering below $T_N$ is recast into a spin-density wave (SDW) [10, 11, 13]. The same breathing-mode order and magnetic modulation robustly emerge in nickelates with reduced $R$ sizes ($Y$, Pr–Lu) [6, 10, 14–18], where $T_{MI}$ systematically increases (>200 K) and $T_N$ simultaneously decreases (<200 K). The bulk phase diagram of RNiO$_3$ thus comprises three states, the charge-order insulator ($P2_1/n$), the insulating SDW ($P2_1/n$), and the paramagnetic metal ($Pbnm$; $R\overline{3}c$, LNO) [6, 10]. The phenomenological Landau-theory elaborations unveil the MIT as an interplay of the charge-order and SDW order parameters, with an increasing GdFeO$_3$-type distortion favoring a predominance of the charge order with elevated $T_{MI}$ [6, 10].

With the above wisdom in bulks, current advances in the nickelates center on emergent properties in thin films [19–21], and the three RT paramagnetic metals of LNO ($a = 5.4573$, $c = 13.1462 \text{Å}$), PNO ($a = 5.4193$, $b = 5.3801$, $c = 7.6263 \text{Å}$), and NNO ($a = 5.3891$, $b = 5.3816$, $c = 7.6101 \text{Å}$) compose the model materials [3]. Notably, whereas the bulk-LNO, -PNO, and -NNO metals feature $n$-type carriers as expected in the context of conducting $e_g^{1}$ electrons [22–25], the films become $p$-type regardless of being subject to tensile or compressive strains [21, 26–30]. Though firstly proposed as an effect of self-hole doping by a strain-induced negative charge-transfer gap [26], it is now understood that the phenomenon arises from the large hole pockets at Fermi surface of the strained films [11, 21, 31–34]. Despite this reconstructed fermiology [21, 31–34], the strained nickelates grown on GdTiO$_3$ were reported to harbor electrons as a result of interfacial charge doping into the nickelates by an elaborately designed chemical-potential difference between the films and GdTiO$_3$ (e.g. $\sim 1.2 \text{eV}$ for LNO/GdTiO$_3$) [19]. The strained NNO/SrTiO$_3$ otherwise constitutes the skeleton for novel hole-doped superconducting NdNiO$_2$ on SrTiO$_3$ (STO), achieved by an exemplificatory chemical reduction of the NNO with resultant Ni $^{2+}$ $\rightarrow$ Ni $^{3+}$, followed by cooling in the oxygen ambience to RT with a cooling rate of 25 $°$C/$\text{min}$ and then subject to post-annealing at the oxygen pressure of 300 T orr to eliminate oxygen vacancies, followed by cooling in the oxygen ambience to RT with a cooling rate of 25 $°$C/$\text{min}$. The layer-by-layer growths were achieved by simultaneous monitoring of the reflection high-energy electron diffraction (ED). Each heterostructure consists of 10 nickelate unit cells (uc) in the quasicubic unit of $a_{STO}$ (3.837, LNO; 3.826, PNO; 3.807 Å, NNO) and all nickelate films are nominally tensile-strained considering the cubic STO of $a_{STO} = 3.905$ Å [21, 26–30]. The resistivity and Hall measurements were performed in a quantum design physical property measurement system. The atomic-resolution structural and electronic investigations were conducted on spherical-aberration corrected JEOL 2100FX scanning transmission electron microscopy (STEM) at 200 kV equipped with Gatan Enfishinium EELS. The STEM high-angle annular dark-field (HAADF) and annular bright-field (ABF) imaging collection angles are of 70–190 and

2. Experimental details

The LNO, PNO, and NNO/STO were grown by pulsed-laser depositions on (001)-oriented STO using sintered bulk targets and the KrF excimer laser with a repetition rate of 3 Hz and a laser energy density of 3 J cm$^{-2}$. The growths were conducted at the substrate temperature of 550 °C under the oxygen pressure of 10 mTorr and then subject to post-annealing at the oxygen pressure of 300 Torr to eliminate oxygen vacancies, followed by cooling in the oxygen ambience to RT with a cooling rate of 25 °C/$\text{min}$. The layer-by-layer growths were achieved by simultaneous monitoring of the reflection high-energy electron diffraction (ED). Each heterostructure consists of 10 nickelate unit cells (uc) in the quasicubic unit of $a_{STO}$ (3.837, LNO; 3.826, PNO; 3.807 Å, NNO) and all nickelate films are nominally tensile-strained considering the cubic STO of $a_{STO} = 3.905$ Å [21, 26–30]. The resistivity and Hall measurements were performed in a quantum design physical property measurement system. The atomic-resolution structural and electronic investigations were conducted on spherical-aberration corrected JEOL 2100FX scanning transmission electron microscopy (STEM) at 200 kV equipped with Gatan Enfishinium EELS. The STEM high-angle annular dark-field (HAADF) and annular bright-field (ABF) imaging collection angles are of 70–190 and
7–19 mrad, respectively, with the HAADF (ABF) for capturing the cations (light-element oxygen in particular). The STEM–EELS spectral collection angle is of 30 mrad. The probe convergence angle is of 20 mrad throughout the work. The electron-microscopy specimens were prepared by mechanical polishing and ion milling, with the studied thin regions of 0.4–0.6λ (λ, inelastic mean-free path) in thickness. The self-consistent electronic band structure calculations were performed on the basis of density functional theory with the generalized gradient approximation (GGA) [41] plus the onsite Coulomb interaction U (i.e., the GGA + U method) [42]. The effective U values used for the R-4f electrons and Ni-3d electrons are of 4.0 and 4.5 eV, respectively. The accurate projector-augmented wave method [43], implemented in the Vienna ab initio simulation package [44, 45], was used. A large plane-wave cutoff of 450 eV and the small total energy convergence criterion of 10\(^{-7}\) eV are exploited.

### 3. Results

Figures 1(a) and (b) show respective bulk LNO and NNO superimposed with quasicubic \(a_P\) (gray). The LNO lattice (figure 1(a)) is projected along vectors equivalent to [110], [100], and [010] in \(Pbnm\) of PNO and NNO (figure 1(b)), highlighting the least distorted oxygen cages, \(a_P\)-cornered La, and \(-\)-centered Ni characteristic of the \(R\3c\) structure [3]. In figure 1(b), the more distorted \(Pbnm\) structure of NNO (also PNO, not shown for brevity) is distinguished by the antipolar Nd displacements of 0.188 (\(d_{b_P}\)), 0.185 (\(d_b\)), and 0.03 Å (\(d_a\)) along the associated \(ab\)-, \(-\)-, and \(a\)-axial directions in figure 1(b) (0.155, 0.152, and 0.03 Å for PNO), with the centering of Ni [3]. The \(d_{b_P}\) and \(d_b\) are so significant that their direct STEM–HAADF and –ABF imaging had been proven straightforward [20, 46].

**Transport Characteristics of the RNO/STO.** Figure 1(c) exhibits the transport properties of LNO/, PNO/ and NNO/STO. The resistivity of LNO/STO is comparable to the previous reports [26, 27]. The positive Hall coefficient of 2.1 × 10\(^{-4}\) cm\(^2\) C\(^{-1}\) (inset, figure 1(c)) corresponds to a hole density of 2.9 × 10\(^{22}\) cm\(^{-3}\), which is customary of tensile-strained LNO/STO with characteristic \(p\)-type carriers [26, 27, 29]. Intriguingly, the LNO/STO displays a MIT at \(~\)20 K that is absent in the bulk [1] and was reported in the earlier study of LNO(7-uc)/STO [27]. A disorder-induced localization that can become growingly important in thinner LNO films with an effectively reduced dimensionality has been proposed for this \(~\)20 K transition [27] and will be addressed in our later STEM-EELS characterizations of the RNO/STO. The PNO/ and NNO/STO surprisingly turn out to be insulating without the anticipated bulk \(T_{\text{MI}}\) (135, PNO; 200 K, NNO; figure 1(c)). While epitaxial strains can attenuate the extent of GdFeO\(_3\)-type distortions and thus modify the \(T_{\text{MI}}\) [6, 10, 12, 20, 21, 30], an elevation above RT is rare. The elevated \(T_{\text{MI}}\) of 319 K is recently established in tensile-strained NNO/NdGaO\(_3\)(101) and ascribed to an enhanced stability of the charge-order insulating \(P2_1/n\) state up to high temperatures by the orthorhombic-substrate anisotropy (magnetic order not experimentally tackled thereby) [46]. Although the isotropic STO is dissimilar to the anisotropic NdGaO\(_3\) [46], the linking of insulating PNO and NNO (figure 1(c)) to the charge-order insulator (\(P2_1/n\)) should be thoroughly scrutinized. Besides, the three resistivity curves in figure 1(c) are immune from a thermal hysteresis (supplemental figure 1 [47]) (https://stacks.iop.org/NJP/24/023011/mmedia), while bulk RNO with close \(T_{\text{MI}}\) and \(T_N\) are characteristic of the hysteresys [48, 49]. The \(T_{\text{MI}}\) and \(T_N\) of the PNO and NNO films shall then be different from the situation of \(T_{\text{MI}} = T_N\) in the bulk counterparts [1, 3, 4] and this argument should also be applicable to the LNO film if a magnetic transition, absent in the bulk, exists [1, 3]. In this work, we focus on the lattice and charge degrees of freedom accessible to our core characterization techniques of STEM and EELS. The determination of \(T_N\) in the RNO films by, for example, dedicated resonant magnetic x-ray diffraction is beyond the current scope [48].

**Structural characterizations by STEM HAADF imaging.** Figures 2(a)–(c) depict the representative HAADF images of respective LNO/, PNO/, and NNO/STO along [110] projection in \(Pbnm\) (LNO, equivalently [42]). No misfit dislocation has been observed in figures 2(a)–(c) and the large field-of-view HAADF images acquired in different sample regions (supplemental figure 2 [47]) with consistent quality to figures 2(a)–(c) refer to the robustness in phenomena observed throughout this report. The in-plane strain maps at the bottom-right corner of figures 2(a)–(c) indicate that the basal plane of the nickelates is coherently tensile-strained to that of the STO (also supplemental figures 4–5 [47]). An inspection of the atomistic contrasts of Pr (figure 2(b)) and Nd (figure 2(c)) around the \(a_P\) corners, however, reveals the absence of anticipated \(d_{a_P}\)-antipolar displacements in figure 1(b) (left panel), of which the nominal magnitude of >10 pm is to be directly discernible in our imaging [20, 50–54]. By contrast, the La in figure 2(a) is indeed corner-centered as indicated in figure 1(a) (left panel). This structural subtlety in the PNO/ and NNO/STO has important correlations later. We first settle the problem of electron doping into STO by the chemical-potential argument [19, 37], though already inconsistent with the \(p\)-type LNO/STO in figure 1(c) (inset).
Figure 1. (a) Projections of the RT rhombohedral-\(R_3\)c structure of bulk LNO along respective \([42\bar{1}]\), \([220]\), and \([\bar{T}11]\) axes. (b) Projections of the RT orthorhombic-Pbnm structure of bulk NNO along respective \([110]\), \([100]\), and \([010]\) axes. \(a_p\), pseudocubic uc. \(d_{ab}\), \(d_{a}\), and \(d_{b}\), characteristic antipolar displacements. (c) Resistivities of LNO, PNO, and NNO/STO upon cooling. Inset, the Hall measurement of LNO/STO at 300 K, with the positive slope indicating hole carriers. The curves of the highly resistive PNO and NNO are grouped for the scale shown on the left (oval and arrow) and the resistivity scale of the LNO is exhibited on the right (separate oval and arrow). The presentation of two different resistivity scales in (c) is for the clarity of three curves in the same figure. The highly resistive nature of the PNO and NNO had refrained us from conducting measurements below 100 K. Otherwise, the LNO/STO was cooled down to 2 K.

Tackling interfacial charge doping by STEM–EELS. In the ionic limit, the presence of charge doping across an interface can be quantitatively measured provided the chemical formula and ionic valences in each interfacial uc are resolvable at atomic accuracy \([50–55]\), e.g. an atomically-elaborated interfacial STO uc with \(\text{Sr}^{2+} (\text{Ti}^{3+}_{0.1} \text{Ti}^{4+}_{0.9}) \text{O}_{2}^{-}\) to be electron-doped by \(-0.1\) e per uc (elementary charge). Figures 2(d)–(f) show the STEM–EELS elemental mapping of LNO, PNO, and NNO/STO, with each atomically-mapped elemental contrast (Sr, Ti, Ni, and R) representing a compositional profile in figure 2(g) (each profile therein, a further average over three separate STEM–EELS maps). The ensemble of figure 2(g) thus manifests the uc-by-uc estimation of chemical formulas in the RNO/STO and the graded profiles around the interface (uc, \(-3\) to \(3\)) refer to the spontaneous atomic intermixing \([50, 51, 53, 55]\). The previously argued disorder-induced electronic localization for the MIT at \(\sim 20\) K in a seven-uc LNO/STO \([27]\) appears to find an experimental correspondence in figure 2(g) by the atomically-unraveled disorders, despite a difference in the LNO thicknesses (10 uc hereby). Similar atomic disorders in the 10-uc PNO/ and NNO/STO (figure 2(g)) may also be susceptible for the disorder-induced localization \([27]\), while the insulating characters of the PNO and NNO (figure 1(c)) would mask such a factor plausibly at play.

We then examine the valences of intermixed Ti and Ni in respective figures 3(a)–(c), (d)–(f). The valences of \(\text{Sr}^{2+}, \text{R}^{3+}\), and \(\text{O}^{2-}\) in nickelates are otherwise robust \([4, 56]\). In figures 3(a)–(c), the Ti-L spectral redshift from STO to RNO uc indicates mixed valences across the interfaces, which are evaluated by linear-least square fitting of each uc-specific Ti spectrum using the bulk STO (\(\text{Ti}^{4+}\); solid blue, figure 3(a))
Figure 2. The Bragg-filtered STEM–HAADF images of (a) LNO/, (b) PNO/, and (c) NNO/STO projected along [421]LNO in bulk R3c and equivalent [110] in bulk Pbnm of PNO and NNO (lattice axes of the LNO/STO denoted in Pbnm’s). Bottom-right panels, ab-plane strain maps with reference to the lattice parameter of STO’s (color scale bar, ±10%). The corresponding STEM-EELS elemental mapping of (d) LNO/, (e) PNO/, and (f) NNO/STO, with Sr in yellow, Ti in blue, Ni in red, and R (La, Pr, and Nd) in green. Red-green-blue (RGB) color mixing, the superposition of Ni, R, and Ti maps. (g) The elemental distribution profiles across the RNO/STO interfaces. Each profile, the integration of each elemental map in (d)–(f) and averaged over three different sets of integrated maps with comparable qualities. Error bars of ±10%, omitted for brevity.

and Ti2O3 (Ti3+; dashed blue) references with the red residuals in figures 3(a)–(c) being the fitting exemplifications for the dotted interfacial 0-uc spectra [50–53, 55]. The thus-derived Ti3+ fractions across the interfaces are shown in figure 3(g) (inset, an atomically-resolved Ti-L dataset for figure 3(a)). In LNO/STO (figure 3(d)), the superposition of La-M4 and Ni-L3 edges does not hinder the Ni-valence examination, since the Ni-L2 edge itself in LNO (also PNO and NNO) is a gauge of the Ni state [19, 57–59]. The monotonic Ni-L3 line shapes in the RNO uc in figures 3(d)–(f) are typical of Ni3+ [19, 57–59].

Upon the otherwise mixed-valence Ni2+ and Ni3+, spectral splitting of >1.4 eV would appear in both the Ni-L2 and -L3 edges [19, 59], while there is no sign on such splitting in figures 3(d)–(f) within the limit of our energy resolution (1.2 eV). The constant Ni-L line shapes and peak positions in all RNO uc (figures 3(d)–(f)) indicate persistent Ni3+ [19, 57–59]. With figures 3(d)–(f) (Ni3+), figure 3(g) (Ti valences), and figure 2(g) (chemical formulas), the uc-by-uc charges across the interfaces are derived in figure 3(h), showing hole distributions over a length scale (uc, −3 to 3) in close coherence with that of atomic intermixing (figure 2(g)). The similar extents of intermixing (figure 2(g)) and mixed-valence Ti
Figure 3. The Ti-L EELS spectra across the (a) LNO/, (b) PNO/, and (c) NNO/STO interfaces, and (d)–(f) the simultaneously acquired Ni-L EELS spectra. Each spectrum, the average over three different spectra acquired at separate sample regions. Dotted black, spectra of the uc at the interfaces (denoted as 0-uc). Gray (black), spectra of the RNO (STO) uc. Solid (dashed) blue, STO Ti$^{4+}$-reference (Ti$_2$O$_3$ Ti$^{3+}$-) spectrum. Red curves in (a)–(c), residuals of the linear least-square fits of the 0-uc spectra using the Ti$^{4+}$-and Ti$^{3+}$-reference spectra. Scale of the red curves, same as those of the Ti$^{4+}$ and Ti$^{3+}$ references. Vertical red bars, guides for the eyes. (g) The least-square fitted Ti$^{3+}$/uc ratio at each individual uc in (a)–(c). Error bars, ±10%.

The spontaneously doped holes in LNO/STO, however, correspond to only $\sim 5.9\%$ of holes unraveled in the Hall measurement (inset, figure 1(c)) and those in insulating PNO/ and NNO/STO are apparently localized. These doped holes are clearly not for enhancing the nominal $p$-type carrier densities of the strained nickelates [11, 21, 31–34]. Instead, the doped holes should be localized by a relevant disorder-induced localization (figure 2(g)) [27, 55] and correlated with the tensile-strain accommodations considering the variant effective ionic radii of the intermixed atoms (La$^{3+}$, 1.16; Pr$^{3+}$, 1.13; Nd$^{3+}$, 1.11; Sr$^{2+}$, 1.26; Ti$^{4+}$, 0.605; Ti$^{3+}$, 0.67; low-spin Ni$^{3+}$, 0.56 Å) [50]. The presence of heterogenous R$^{3+}$ (Sr$^{2+}$) in STO (RNO) can contract (dilate) the uc and the mixed-valence Ti (monotonic Ni$^{3+}$) in RNO (STO) would enlarge (reduce) the lattice volume, all assisting to mitigate the strains. A likewise strain mitigation by a segregation of doped localized electrons into the misfit dislocation cores in
(Nd, Sr)MnO3/STO has been reported [50]. The notion of interfacial charge doping and the strain mitigation by spontaneous hole doping will be further addressed in section 4. Discussion.

Unveiling oxygen by STEM ABF imaging. Figures 4(a)–(c) exhibit the ABF blowups of figures 2(a)–(c) with the superposition of schematic atoms, revealing the oxygen frames of constituent octahedra (namely, oxygen cages; red rhombuses) in addition to the cations already imaged in figures 2(a)–(c). Like figures 2(b)–(c), the $d_{ab}$-antipolar displacements characteristic of the RT bulk-metallic $Pbnm$ structures of PNO and NNO do not appear in figures 4(b)–(c). The oxygen-cage octahedral buckling iconic to the GdFeO3-type distortion in all three bulk-metallic phases (left panels, figures 1(a) and (b)) is, meanwhile, obscure in figures 4(a)–(c), where rather shifts of the oxygen atoms and corresponding cages toward interfaces with respect to the centered Ni and Ti (interface) atoms are seemingly suggested (see the guiding arrows) and will be elaborated in detail in figure 5 with better imaging contrasts due perhaps to characteristic electron-beam scattering conditions along the projections. Indeed, the LNO, PNO, and NNO films appear to crystallize in different structures from the pristine RT bulk-metallic phases [3] and the potential correlation of the insulating PNO and NNO films with the low-temperature (LT) charge-order insulators $P2_1/n$ is carefully examined [46]. In bulk PNO and NNO, the LT insulator ($P2_1/n$) and RT metal ($Pbnm$), in effect, share similar antipolar $d_{ab}$ and in-plane octahedral buckling [7, 8, 20, 46, 59]. The missing $d_{ab}$ and apparently downward-shifted oxygen cages in figures 4(b)–(c) can be incompatible with the RT $Pbnm$ and LT $P2_1/n$ phases. The persistent Ni$^{3+}$ in figures 3(e)–(f) also suggests that the insulating PNO and NNO films shall be irrelevant with the condensation of the LT-insulating $P2_1/n$ state at RT, since the related Ni-charge disproportionation would feature the Ni-$L_2$ splitting by $>1.4$ eV that is absent in our uc-resolved spectra [19, 59]. The tendency of downward-shifted oxygen cages observed in the strained LNO (figure 4(a)) are also unmatched with the bulk GdFeO3-type distortion in $R\bar{3}c$ [3], altogether referring to that the LNO, PNO, and NNO films are all subject to lattice instabilities hidden to the bulk phase diagram [6, 11].

Symmetry and oxygen-displacement scrutiny of the hidden lattice instabilities in RNO/STO. Figures 4(d)–(f) tackle the symmetry essences of these strained nickelate films using finite-beam ED (bottom panels; ~5 Å, beam size; more technically, convergent-beam ED) and the comparison with the systematic extinctions (middle panels) of RT bulk-metallic $R\bar{3}c$ of LNO (figure 4(d)) and $Pbnm$ of PNO (figure 4(e)) and NNO (figure 4(f)). The rather diffused contrasts of the ED patterns in figures 4(d)–(f) are characteristic of the diffraction projections. The top-right panels are the fast Fourier transform (FFT) of respective nickelate-ABF images in figures 4(a)–(c). In the FFT and ED of figures 4(e) and (f), the absence of characteristic $hkl$ reflections with $l = \text{odd}$ (blue arrows and also dashed discs) in the experiments lifts the primitive-$P$ lattice symmetry in the PNO and NNO films, retiring both the RT-$Pbnm$ and LT-$P2_1/n$ options. Whereas the FFT and ED of the LNO film are compatible with $R\bar{3}c$ in the designated orientation (figure 4(d)), the other projection in figures 5(a) and 6(a) revisits the symmetry.

Using atomistic measurements at ~3-pm precision by the in-house developed algorithm based on Atomap-statistical and -vectorial analyses of all comprised oxygen and cations (each type, hundreds of atoms; large field-of-view results, supplemental figures 3 and 5 [47, 60]), we address the downward oxygen shifts in the ABF images of LNO, PNO, and NNO films upon the [010] projection of NNO (figure 5(c)) and LNO (equivalently $\bar{T}1\bar{1}$, figure 5(a)) and the [100] zone axis of PNO (figure 5(b)), with the former orientation practical for examining the characteristic antiphase octahedral buckling of bulk GdFeO3-type distortions (right panels, figure 1(a) and (b)) and the latter for tackling the antipolar $d_{ab}$ (middle panel, figure 1(b)). Figures 5(a) and (c) (also the more extended supplemental figure 3 [47]) reveal the lifting of cooperative antiphase buckling in the bulks by the concerted downward displacements of equatorial oxygen (red arrows). Figure 5(b) unravels the diminished bulk-antipolar $d_{ab}$ and the downward equatorial-oxygen displacements (red arrows; also supplemental figures 3 and 5 [47]). The c-component magnitudes of the downward shifts are derived in figure 5(d). Figure 5(e) shows the accompanied O–B–O angles (B, nominally Ti in STO and Ni in RNO). In figures 5(d) and (e) (also supplemental figure 3 [47]), the signature oxygen-cage buckling of bulk GdFeO3-type distortions (middle and right panels, figures 1(a) and (b)) vanishes in the films and the distorted oxygen patterns propagate to the uc at the interfaces and also the first STO uc beneath the interfaces.

Figures 6(a)–(c) show the FFT (top-right panels) of ABF images in figures 5(a)–(c), finite-beam ED (bottom panels) of the films, and systematic extinctions of RT bulk-metallic phases along the designated projections (middle panels). In the FFT (top, figure 6(a)) and ED (bottom) of the LNO film, weak symmetry-forbidden reflections, e.g. $\bar{T}0\bar{T}$ (blue circle) and other likewise ones in green circles, emerge and cannot be accounted for by multiple scattering due to their robustness upon the suppressed electron multiple scattering by out-of-zone tilting. Accordingly, the LNO film does not comply with the bulk-$R\bar{3}c$ symmetry. Further considering the RT bulk-$Pbnm$ symmetry of PNO and NNO, while the [010]-projected reflections in figure 6(c) agrees with the $Pbnm$’s (red circles, a comparison to the blue and green ones of
LNO in figure 6(a)), the absence of bulk 0 k\(l\) reflections with \(l = \text{odd}\) (red arrows) in figure 6(b) suggests higher symmetry element(s) than the bulk \(Pbnm\)’s should be at play. An orthorhombic subgroup with such elevated symmetry element(s) and broken-\(P\) lattice as indicated in figures 4(e) and (f) does not exist [40, 61].

Notably, the RT-monoclinic and base-centered \(C2/c\) symmetry reported in tensile- and also compressive-strained LNO films on respective STO and LaAlO\(_3\) substrates resolves these structural subtleties in the LNO, PNO, and NNO films [38], though a marginally discussed monoclinic phase in the literature. In figures 7(a)–(c), we show the systematic extinctions of this \(C2/c\) phase in the documented tensile-strained LNO on STO with \(a = 9.406\), \(b = 5.523\), \(c = 5.523\) Å, and \(\beta = 125.95^\circ\) [38]. Figure 7(a) nicely describes the experimental reflection conditions in both figure 6(a) (LNO) and 6(c) (NNO), and figure 7(b) profoundly addresses figure 6(b) (PNO). The orthogonal projection of figure 7(a) with respect to figure 7(b) suggests that the respective [001] and [010] axes, i.e. \(c\) and \(b\), of the \(C2/c\) cell now define the basal planes of the LNO, PNO, and NNO films (supplemental figures 3 and 5 [47]). The associated [011]-projected figure 7(c) in \(C2/c\), namely along the basal-plane diagonal, indeed depicts the reflection characteristics in all related diagonal-projected figures 4(d)–(f). The LNO, PNO, and NNO films crystalize in the strain-induced monoclinic \(C2/c\) symmetry, which is hidden to the bulk phase diagram [6, 10]. Figure 7(d) displays such a monoclinic-\(C2/c\) lattice with \(R-R\) bonds of 3.905 Å [38], corresponding to a coherently strained basal plane by the STO as confirmed in figures 2(a)–(c) (bottom-right insets) and supplemental figures 4 and 5 [47], and also the quenching of GdFeO\(_3\)-type distortions observed in figures 5(a)–(c) (otherwise preserved in the previous report [38]). Despite the difference in oxygen-cage
distortions between our work and reference [38], the same C2/c symmetry is established in the respective strained nickelate films.

4. Discussion

Transition pathways and electronic structures of the strain-resurrected C2/c phases. In the Landau physics of phase transitions, a structural phase transition is underlined by the condensation of a child lattice instability from a high-temperature parent phase and the corresponding transition pathway is delineated by a group-theoretically permitted irreducible representation (irrep) [5, 40, 52, 54]. The common C2/c symmetry in LNO, PNO, and NNO films could, therefore, refer to an identical parent symmetry and a unified transition pathway. Indeed, bulk PNO and NNO have been reported to transform into R3c (like the RT-bulk LNO) at high temperatures [16, 62]. Considering R3c as the parent phase, a pertinent group-theoretical analysis (green, figure 7(e)) unveils the characteristic subgroup of C2/c by the zone-center symmetry breaking pathway of Γ3+ [40]. By contrast, the RT-bulk Pbnm symmetry of PNO and NNO is not a subgroup of R3c (figure 7(e)) [40]. The reported group-theoretical analyses so far (blue, figure 7(e)) center on the transitions in bulks from cubic Pm3m (a ∼ 4 Å) to Pbnm and subsequently to P21/n [5, 6], regardless of the experimentally determined high-temperature symmetry of R3c [16, 62]. To resolve this subtlety on Pm3m, we examine irreps of Pm3m and find a direct link to R3c by the zone-boundary R5− pathway (figure 7(e)) [40].

Figure 7(e) profoundly captures the allowed symmetries and transition pathways in LNO, PNO, and NNO [40]. Since the RT-monoclinic C2/c phase only appears in the strained nickelate films, the
$\Gamma_3^+ + \Gamma_3^-$-transition pathway is to be a hidden one and resurrected by the epitaxial strains. Moreover, the parent $R3c$ symmetry stands at a nodal point, guiding to respective monoclinic $P2_1/n$ and $C2/c$ phases upon relevant unstrained and strained conditions. The $C2/c$ phase in the strained LNO film was theoretically proposed as a metal [38], in agreement with the RT metallicity of LNO/STO (figure 1(c)). In the strained PNO and NNO films, the $C2/c$ phases are, however, unaddressed so far and figure 1(c) suggests their insulating characters. Figure 8 shows the calculated band structures of LNO, PNO, and NNO in the $C2/c$ symmetry with the ubiquitous G-type antiferromagnetic ordering at both the Ni$^{3+}$ and Pr$^{3+}$ sublattices (except for La$^{3+}$ of empty 4$f$) [2, 46]. In our calculations, the lattice parameters (non-orthogonal angle) of the three strain-induced $C2/c$ phases are fixed at the reported values of $a = 9.406$, $b = 5.523$, and $c = 5.523$ Å ($\beta = 125.95^\circ$) for monoclinic-$C2/c$ LNO [38] and the associated atomic coordinates are theoretically optimized. The inherent electronic correlations of Ni$^{3+}$-3$d$, Pr$^{3+}$-4$f$, and Nd$^{3+}$-4$f$ electrons are prone to the magnetically ordered G-type LNO, PNO, and NNO (calculated density of states, supplemental figure 6 [47]), and the previously adopted ferromagnetic order for monoclinic-$C2/c$ LNO was found to be unstable [38]. Figure 8(a) shows the thus-calculated LNO, which is metallic as the previous theoretical study despite the difference in exploited magnetic orders [38]. The metallicity in figure 8(a) provides a further support for the observed MIT at ∼20 K in the LNO/STO (figure 1(c)) as a possible result of the atomic-disorder induced localization [27]. The PNO (figure 8(b)) and NNO (figure 8(c)) manifest the opening up of a finite gap, underlining the insulating features revealed in figure 1(c). We are aware that, in a recent electronic calculation of strained NNO films with a metallic character at RT, an otherwise tetragonal lattice ($P4/mmm$ rather than bulk $Pbnm$) with the $A$-type antiferromagnetic ordering was employed and captures the metallicity [21].

The context of Thomas–Fermi screening on interfacial charge doping. Now, we address the argued chemical-potential difference in nickelate heterostructures [19, 37]. This core conception in interfacial charge doping, in effect, deals with band alignments, which concern the energy-level difference across an interface instead of the wave functions that convey the thorough structural and electronic complexities of oxides [11]. Explicitly, such a band-diagram notion is formulated within the framework of a slowly varying electrostatic potential ($\phi$) compared to the lattice parameter, which is meanwhile the core condition of the Thomas–Fermi screening [63], and is to be warranted by $\phi$ with a characteristically minimal decay term ($e^{-k_0|x|}$), with $\phi(x) = \phi_0 e^{-k_0|x|}$, where $\phi_0$ is the potential at origin, $x$ is the distance from origin, $k_0 = l_{TF}^{-1}$, and $l_{TF}$ is the Thomas–Fermi screening length ($l_{TF} = \sqrt{\pi \varepsilon_0 a_0/(3\varepsilon \rho)^{1/3}}$; $\varepsilon$, the dielectric constant; $a_0$, the Bohr radius ∼0.53 Å; $\rho$, the volume carrier density) [11, 47, 64, 65]. In conventional semiconductors, the
Figure 7. The systematic extinctions of the strained-induced monoclinic-$\text{C}_2/c$ lattice of LNO in (a) [001], (b) [010], and (c) [011] projections [38]. Red circles, comparisons to those in figure 6(c) and blue and green ones in figure 6(a). Red and blue arrows, corresponding to those in figures 6(b) and 4(e) and (f), respectively. (d) A $\text{C}_2/c$ structure with the quenched GdFeO$_3$-type distortion inferred from figures 5(a)–(c). (e) The group-theoretical analysis of allowed symmetries and transition pathways in the RNO. Green $\text{R}_3\text{c}$ ($\text{C}_2/c$), the common parent phase (strain-resurrected hidden lattice instability) of the RNO. Blue $\text{Pm}$3$m$, $\text{Pbnm}$, and $\text{P}_2_1/\text{n}$, the reported group-theoretical analysis of the transition pathways in bulks, with the intermediate $\text{P}_4/\text{mbm}$ and $\text{Imma}$ designating respective octahedral distortion modes [5]. Irreps (e.g. $\Gamma_3^+$), derived from reference [40].

Figure 8. The electronic band structures of G-type antiferromagnetic (a) LNO, (b) PNO, and (c) NNO in the strain-induced monoclinic-$\text{C}_2/c$ symmetry. Fermi level, 0 eV. The calculated LNO is metallic and the PNO and NNO are gapped by 54 and 183 meV, respectively.

typically large $l_{TF}$ (namely, small $k_0$) devises a small variation of $\phi$ in the uc, e.g. the $l_{TF}$ of 12.5–27 Å in silicon ($\varepsilon_r \sim 11.7; \rho \sim 10^{16}$–$10^{18}$ cm$^{-3}$) casting 0.63–0.8 $\phi_0$ at the lattice boundary ($x = a = 5.43$ Å), and the band-diagram notion is generally applicable [11]. In the nickelates with $\varepsilon_r \sim 30$ [65] and $\rho$ at the order of $10^{22}$ cm$^{-3}$ (like LNO, figure 1(c)) [22–24, 59], the $l_{TF}$ ($\sim 3.7$ Å) turns out to be comparable to $a_0$ and the band alignments do not necessarily apply to the nickelate heterointerfaces, as pointed out before [11] and indeed verified in our uc-by-uc charge unveiling (figure 3(h)). The observed length scale of hole spreading in figure 3(h) (6 uc, $\sim 23$ Å) is unmatched with the $l_{TF}$ of $\sim 3.7$ Å and the electrostatic charge-screening essence behind [63], enforcing our arguments on the doped holes for strain mitigations.
Accordingly, oxides prone to effective electrostatic screening by a significant dielectric constant and/or a small carrier density, thus facilitating large $I_{TF}$ (small $k_0$), shall favor the band-diagram notion [63]. The reported electron doping into strained nickelate films on GdTiO$_3$ by the characteristic chemical-potential difference may be an exemplification of this kind, while not specifically discussed [19]. We shed more light on the interfacial charge doping using our works on dislocation-free (Nd, Sr)MnO$_3$/STO (chemical-potential difference, $\sim$0.4 eV; electrons to be doped into the manganese) [55] and LaAlO$_3$/STO (chemical-potential difference, $\sim$0.8 eV; electrons to be doped into the LaAlO$_3$ [66]) [51]. In the (Nd, Sr) MnO$_3$/STO, the $I_{TF}$ of (Nd, Sr)MnO$_3$ of $\sim$8.1 Å ($\varepsilon_r \sim 30; \rho \sim 2.3 \times 10^{20}$ cm$^{-3}$ [50]) is reasonably larger than $\alpha D$ ($\sim$3.797 Å) and the designated electron doping was observed [55]. In the LaAlO$_3$/STO, the $I_{TF}$ of LaAlO$_3$ of $\sim$7 Å ($\varepsilon_r \sim 24; \rho \sim 2.9 \times 10^{20}$ cm$^{-3}$) is also sensibly larger than the $\alpha D$ of $\sim$3.79 Å, whereas does not convey the anticipated electron doping [51, 66]. Instead, electrons spread over $\sim$7 STO uc therein and have been correlated with the electrostatic screening for strain-induced head-to-head ferroelectric-like polarizations across the LaAlO$_3$/STO interface, with the $I_{TF}$ being conversely of $\sim$26 Å (namely $\sim$6.7 $\alpha_{STO}$, close to the experimental observation of $\sim$7 $\alpha_{STO}$) owing to the significant $\varepsilon_r \sim 332$ of STO [51]. Such strain-rejuvenated ferroelectric-like lattice instabilities do not emerge in the (Nd, Sr)MnO$_3$/STO [55]. In oxide heterostructures like the LaAlO$_3$/STO and current nickelates, the existence of strain-reurrected hidden lattice instabilities opens up an extra dimension to the material systems. For the elaborate design and control of related oxide electronics, theoretical advances capable of capturing the hidden states prior to experiments would, therefore, be increasingly important, while challenging [38, 51–53]. Our group-theoretical exemplification (figure 7(e)) manifests an efficient search for the hidden phases and could provide the theoretical advances with a hint on reducing the computational burden.

To date, experimental work on the condensation of RT monoclinic-$C2/c$ phases in thin nickelate films is scarce [38] and may be ascribed to subtle differences in film-growth kinematics from one report to another [19–21, 27–30], remaining an open question to be systematically studied. Moreover, it is to be thoroughly investigated in the future regarding whether the strain-reurrected $C2/c$ phenomena could be general to later rare-earth members of RNO (such as EuNiO$_3$) and would be subject to a critical-thickness effect (e.g. a 13-uc NNO in supplemental figure 1 apparently preserving the MIT [47]). It also deserves mentioning that a paramagnetic insulating phase, not existing in the bulk phase diagram, has been unveiled in the tensile-strained NNO(15-uc)/STO with $>1\%$ of the strain [48]. Although the potential correlation between the paramagnetic-insulating state [48] and currently observed $C2/c$ insulator in 10-uc NNO/STO is unclear, it is obvious that strain engineering in nickelate heterostructures can cast rich opportunities and awaits further explorations [48].

5. Conclusion

The strain-induced entanglement of spontaneously doped holes and concomitant monoclinic-$C2/c$ lattice instabilities is unraveled at the atomic scale in the RT-metallic LNO and $P$-insulating PNO and NNO films. This undocumented conjugation of the charge and lattice degrees of freedom for accommodating the epitaial strain goes beyond the primitive elastic stretching of the films and enriches the established knowledge in the bulk phase diagram by the strain-reurrected hidden $C2/c$ instabilities with quenched GdFeO$_3$-type distortions. By analogy to the LT-bulk monoclinic $P2_1/n$ phase of PNO and NNO with charge disproportionations and SDW, the RT-metallic $C2/c$ LNO and $P$-insulating PNO and NNO may seed intriguing ground states in the films and prompt for further studies in, for example, the charge-order regime by cryogenic STEM--EELS that features the superb spectroscopic charge-valence tackling at the atomic scale (like figure 3), though only down to $\sim$100 K at the moment [54]. Films can be more than the miniaturized counterpart of bulks and decorated by a plethora of hidden orders, of which the experimental and theoretical scrutiny awaits endeavors. This work represents a preliminary momentum toward the addressing of such emergent phases in correlated-oxide films and would draw broad repercussions.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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