Dynamical structural instability and its implication on the physical properties of infinite-layer nickelates

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Abstract

We use first-principles calculations to find that in infinite-layer nickelates $R\text{NiO}_2$, the widely studied tetragonal $P4/mmm$ structure is only dynamically stable for early lanthanide elements $R = \text{La-Sm}$. For late lanthanide elements $R = \text{Eu-Lu}$, an imaginary phonon frequency appears at $A = (\pi, \pi, \pi)$ point. For those infinite-layer nickelates, condensation of this phonon mode into the $P4/mmm$ structure leads to a more energetically favorable $I4/mcm$ structure that is characterized by an out-of-phase rotation of “NiO$_4$ square”. Special attention is given to two borderline cases: PmNiO$_2$ and SmNiO$_2$, in which both the $P4/mmm$ structure and the $I4/mcm$ structure are local minimums, and the energy difference between the two structures can be fine-tuned by epitaxial strain. Compared to the $P4/mmm$ structure, $R\text{NiO}_2$ in the $I4/mcm$ structure has a substantially reduced Ni $d_{x^2-y^2}$ bandwidth, a smaller Ni $d$ occupancy, a “cleaner” Fermi surface with a lanthanide-$d$-derived electron pocket suppressed at $\Gamma$ point, and a decreased critical $U_{\text{Ni}}$ to stabilize long-range antiferromagnetic ordering. All these features imply enhanced correlation effects and favor Mott physics. Our work reveals the importance of structure-property relation in infinite-layer nickelates, in particular the spontaneous “NiO$_4$ square” rotation provides a tuning knob to render $R\text{NiO}_2$ in the $I4/mcm$ structure a closer analogy to superconducting infinite-layer cuprates.
I. INTRODUCTION

The discovery of superconductivity in infinite-layer nickelates Sr$_x$Nd$_{1-x}$NiO$_2$ [1] has drawn great attention [2–9] because the parent material NdNiO$_2$ has similar crystal and electronic structures to those of infinite-layer cuprate CaCuO$_2$ [10], which exhibits high-temperature unconventional superconductivity upon doping [11, 12]. Both NdNiO$_2$ and CaCuO$_2$ crystallize in a simple tetragonal $P4/mmm$ structure in which Ni (Cu) and O atoms form a flat “NiO$_4$ (CuO$_4$) square” [13–15]. The $P4/mmm$ crystal structure has only two degrees of freedom: lattice constants $a$ and $c$. As for the non-interacting electronic structure, first-principles calculations show that CaCuO$_2$ has only one Cu $d_{x^2-y^2}$-derived band that crosses the Fermi level, while NdNiO$_2$ has two bands crossing the Fermi level [16–20]. One is Ni $d_{x^2-y^2}$-derived band and the other band is derived from Nd $d$ orbitals and an interstitial $s$ orbital [21–23]. So far, the minimum theoretical model that is adequate to describe the low-energy physics of infinite-layer NdNiO$_2$ has been under intensive debate and several different mechanisms for superconductivity in Sr$_x$Nd$_{1-x}$NiO$_2$ have been proposed [24–44]. Albeit there are many important differences, one thing in common is that all first-principles calculations use the $P4/mmm$ crystal structure of NdNiO$_2$ (either experimental one or theoretical optimized one), based on which one-particle band structure calculations (using density functional theory and its Hubbard $U$ extension) [45–50] or more sophisticated many-body electronic structure calculations (such as dynamical mean field theory and GW) [51–63] are performed. On the experimental side, in addition to Sr$_x$Nd$_{1-x}$NiO$_2$, recently superconductivity is also observed in Sr$_x$Pr$_{1-x}$NiO$_2$ [64–66], Sr$_x$La$_{1-x}$NiO$_2$ [67] and Ca$_x$La$_{1-x}$NiO$_2$ [68, 69]. Thus it is anticipated that superconductivity should be observed in the entire lanthanide series of infinite-layer nickelates RNiO$_2$. In particular, Refs. [70, 71] perform a systematic study on the electronic structure of RNiO$_2$ in the $P4/mmm$ structure as $R$ traverses the lanthanide series and find promising trends that favor superconductivity.

In this work, we use first-principles calculations to show that the widely studied $P4/mmm$ structure of infinite-layer nickelates is only dynamically stable for early lanthanide elements $R =$ La-Sm. For late lanthanide elements $R =$ Eu-Lu, an imaginary phonon mode appears at $A = (\pi, \pi, \pi)$ point in the $P4/mmm$ structure of RNiO$_2$. The imaginary phonon mode corresponds to an out-of-phase rotation of “NiO$_4$ square” about the $z$ axis. Condensation of this unstable phonon mode into the $P4/mmm$
structure leads to a more energetically favorable crystal structure with lower symmetry (space group $I4/mcm$). Attention is given to two borderline cases PmNiO$_2$ and SmNiO$_2$, which have two local minimums: the $P4/mmm$ structure and the $I4/mcm$ structure. Epitaxial strain can be used to fine-tune the energy difference between the two crystal structures.

Compared to the $P4/mmm$ structure, infinite-layer $RNiO_2$ in the new $I4/mcm$ structure has a distinct electronic structure: the Ni $d_{x^2-y^2}$ bandwidth is substantially reduced (by about 0.5 eV) and Ni $d$ occupancy decreases; the Fermi surface becomes “cleaner” because one lanthanide-$d$-derived electron pocket disappears at the $\Gamma$ point; the critical $U_{Ni}$ to stabilize a long-range antiferromagnetic ordering in $RNiO_2$ is smaller. All these features imply that with the “NiO$_4$ square” rotation, correlation effects will be enhanced and Mott physics will play a more prominent role in the new $I4/mcm$ structure than in the $P4/mmm$ structure, when local interaction is added on Ni $d$ orbitals [72]. In particular, our results suggest that among the lanthanide series of infinite-layer nickelates, SmNiO$_2$ is the most promising candidate to crystallize in the $I4/mcm$ structure, which renders it a closer analogy to superconducting infinite-layer cuprates.

II. COMPUTATIONAL DETAILS

We perform density functional theory (DFT) [73, 74] calculations within the $ab\ ini-tio$ plane-wave approach, as implemented in the Vienna Ab-initio Simulation Package (VASP) [75, 76]. We use projected augmented wave (PAW) pseudopotentials with the 4$f$ electrons placed in the core (except for La), explicitly to avoid complication that arises from treating the localized 4$f$ electrons. We employ generalized gradient approximation (GGA) for the exchange-correlation functional with Perdew-Burke-Ernzerhof (PBE) parametrization [77]. The theoretical lattice constants of $RNiO_2$ are in good agreement with the available experimental structure information (see Supplementary Materials [78] Sec. I) [15, 50, 79]. We use an energy cutoff of 600 eV. Charge self-consistent calculations are converged to $10^{-7}$ eV. Both cell and internal atomic positions are fully relaxed until each force component is smaller than 1 meV/Å and pressure on the cell is smaller than 0.1 kBar. We use the finite-displacement method to calculate the full phonon dispersion with the aid of Phonopy [80]. A supercell that consists of
3 × 3 × 3 primitive cells is used to calculate the force constants and dynamical matrices. The primitive cell of the $P4/mmm$ structure has one formula of $R\text{NiO}_2$ (i.e. 4 atoms), while the primitive cell of the $I4/mcm$ structure has two formulae of $R\text{NiO}_2$ (i.e. 8 atoms) in order to accommodate the rotation of “NiO$_4$ square”. For the 4-atom $P4/mmm$ cell, we use a Monkhorst-Pack $\mathbf{k}$ mesh of $14 \times 14 \times 14$ to sample the first Brillouin zone. For the 8-atom $I4/mcm$ cell, we use a Monkhorst-Pack $\mathbf{k}$ mesh of $10 \times 10 \times 10$ to sample the first Brillouin zone. For ease of comparison, when calculating the electronic structure, Fermi surface and long-range magnetic ordering, we use the 8-atom cell for both $P4/mmm$ and $I4/mcm$ structures. This cell-doubling is also necessary to accommodate the rocksalt antiferromagnetic ordering in the $P4/mmm$ structure. To study the energy evolution as a function of “NiO$_4$ square” rotation, we use a linear interpolation and generate an intermediate crystal structure between the fully-relaxed $P4/mmm$ and $I4/mcm$ crystal structures. The “NiO$_4$ square” rotation angle continuously changes with an interpolation parameter $\lambda$ (more details are found in Supplementary Materials [78] Sec. II). When we impose a bi-axial strain on infinite-layer nickelates, the out-of-plane $c$ axis is fully relaxed in order to minimize the total energy. When calculating $\text{Sr}_x\text{R}_{1-x}\text{NiO}_2$, we use virtual crystal approximation (VCA) [81]. To break spin symmetry and study magnetic order, we use the charge-only DFT+$U$+$J$ method [82–84] (by setting LDAUTYPE = 4 in VASP). This method is such that the exchange-correlation functional only depends on charge density but not on spin density; thereby, spin symmetry is only broken by the $U/J$ terms that are added to the Kohn-Sham potential, while the exchange splitting that arises from the spin-dependent exchange-correlation functional is disabled. By setting the parameter $U/J = 0$ in the charge-only DFT+$U$+$J$ method, the non-spin-polarized DFT results are recovered. The calculations of Ni $d$ projected magnetic moment and Ni $d$ occupancy use the default VASP value for the radius of sphere which is 1.11 Å. We also use the charge-only DFT+$U$+$J$ method to test phonon spectrum for a few representative $R\text{NiO}_2$ (see Supplementary Materials [78] Sec. VIII) [79, 85, 86].
Figure 1: Phonon properties of infinite-layer $R$NiO$_2$ in the $P4/mmm$ structure. a: The series of lanthanide elements. Different colors are used to distinguish four categories of phonon dispersions, whose prototypes are shown in b-e. b: Phonon dispersion of infinite-layer NdNiO$_2$ in the $P4/mmm$ structure. c: Phonon dispersion of infinite-layer SmNiO$_2$ in the $P4/mmm$ structure. d: Phonon dispersion of infinite-layer EuNiO$_2$ in the $P4/mmm$ structure. e: Phonon dispersion of infinite-layer TmNiO$_2$ in the $P4/mmm$ structure. f: Frequency of the lowest phonon mode at $A=({\pi, \pi, \pi})$ point $\omega^*_A$ for the entire lanthanide series of infinite-layer $R$NiO$_2$ in the $P4/mmm$ structure. g: The lowest phonon mode at $A$ point of infinite-layer $R$NiO$_2$ in the $P4/mmm$ structure.

III. RESULTS AND DISCUSSION

A. Phonon spectrum

We calculate the phonon dispersion of the fully-relaxed $P4/mmm$ structure for the entire lanthanide series of infinite-layer $R$NiO$_2$. We find that the complete set of phonon dispersions (see Supplementary Materials [78] Sec. II) can be classified into four categories, which we use colors to distinguish in panel a. The first category includes $R=$La-Nd (denoted by green). NdNiO$_2$ is the prototype, whose full phonon dispersion is shown in panel b. In this category, the full phonon dispersion is free of imaginary
modes and the $P4/mmm$ crystal structure is dynamically stable. The second category includes $R$=Pm, Sm (denoted by yellow). SmNiO$_2$ is the prototype, whose full phonon dispersion is shown in panel c. In this category, a soft phonon develops at $A = (\pi, \pi, \pi)$ point, implying a potentially unstable mode. The third category includes $R$=Eu-Dy (denoted by orange). EuNiO$_2$ is the prototype, whose full phonon dispersion is shown in panel d. In this category, the frequency of the lowest phonon mode at $A$ point (marked as $\omega_A^*$) becomes imaginary and the $P4/mmm$ crystal structure is dynamically unstable. The last category includes $R$=Ho-Lu (denoted by red). TmNiO$_2$ is the prototype, whose full phonon dispersion is shown in panel e. In this category, the lowest phonon modes at multiple $\mathbf{q}$ points become imaginary in the phonon dispersion, indicating that the $P4/mmm$ crystal structure is far from stable. In panel f, we compare the frequency of the lowest phonon mode at $A$ point $\omega_A^*$ for the entire lanthanide series. We find that $\omega_A^*$ monotonically decreases from La to Lu and becomes imaginary when $R$=Eu and beyond. In panel g, we show the lowest phonon mode at $A$ point of the $P4/mmm$ structure, which is an out-of-phase rotation of “NiO$_4$ square” about the $z$ axis. Infinite-layer nickelates with early lanthanide elements such as NdNiO$_2$ are stable against this “NiO$_4$ square” rotation, and their equilibrium structure is the widely-studied $P4/mmm$ structure. However, infinite-layer nickelates with late lanthanide elements become dynamically unstable when the “NiO$_4$ square” rotates. Condensation of this unstable mode into the $P4/mmm$ structure will lead to a more energetically favorable crystal structure, which in turn results in a new electronic structure.

B. Rotation of “NiO$_4$ square” and the new $I4/mcm$ structure

When the lowest phonon frequency at the $A$ point in the $P4/mmm$ structure of $R$NiO$_2$ becomes imaginary ($R$ = Eu-Lu), it means that condensation of this unstable phonon mode into the $P4/mmm$ structure can decrease the total energy and will result in a new crystal structure with lower symmetry. Such a crystal structure is shown in panel a of Fig. 2, which has space group $I4/mcm$. The primitive cell of the $I4/mcm$ structure has 8 atoms, which has three degrees of freedom: in addition to the two lattice constants $a$ and $c$, there is an angle $\theta$ that characterizes the out-of-phase rotation of “NiO$_4$ square” about the $z$ axis. When $\theta = 0$, the $I4/mcm$ structure is reduced to the $P4/mmm$ structure. For ease of comparison with the $I4/mcm$ structure, we show the
Figure 2:  

a: The primitive cell of infinite-layer nickelate $RNiO_2$ in the $I4/mcm$ structure. $\theta$ is the rotation angle of “NiO$_4$ square” along the $z$ axis.  
b: A doubled unit cell of infinite-layer nickelate $RNiO_2$ in the $P4/mmm$ structure (the $P4/mmm$ primitive cell is doubled along [111] direction). $\theta = 0^\circ$ in the $P4/mmm$ structure.  
c: The energy evolution of $RNiO_2$ ($R =$ Nd, Pm, Sm and Eu) as a function of the “NiO$_4$ square” rotation angle $\theta$. The $P4/mmm$ structure is used as the energy reference.  
d: The zoom-in view of the energy evolution of PmNiO$_2$ and SmNiO$_2$ as a function of the “NiO$_4$ square” rotation angle $\theta$.  
e and f: The phonon dispersions of infinite-layer PmNiO$_2$ and SmNiO$_2$ in the $I4/mcm$ structure, respectively.

two-Ni unit cell of the $P4/mmm$ structure (doubling the 4-atom primitive cell along the [111] direction) in panel b. For subsequent electronic structure, Fermi surface and long-range magnetic ordering calculations of infinite-layer $RNiO_2$, we use the 8-atom cell for both the $I4/mcm$ structure and the $P4/mmm$ structure.

To get a better understanding of the new $I4/mcm$ structure, we calculate the energy evolution of $RNiO_2$ as a function of the rotation angle $\theta$ (see panel c of Fig. 2, the
calculation details can be found in Supplementary Materials Sec. II [78]). We select \( R = \text{Nd, Pm, Sm and Eu} \), which are near the phase boundary where the lowest phonon frequency at \( A \) point becomes imaginary. We find that the total energy of NdNiO\(_2\) monotonically increases with the rotation angle \( \theta \), indicating that the \( P4/mmm \) structure (i.e. \( \theta = 0 \)) is stable against the rotation of “NiO\(_4\) square”. By contrast, the total energy of EuNiO\(_2\) first decreases with the rotation angle \( \theta \) and then increases. The energy minimum is at \( \theta = 7.7^\circ \). This clearly shows that the \( P4/mmm \) structure is not dynamically stable in infinite-layer EuNiO\(_2\). PmNiO\(_2\) and SmNiO\(_2\) (the second category) exhibit more interesting features in that they have two local minima: one is at \( \theta = 0 \) (\( P4/mmm \) structure) and the other is at \( \theta > 0 \) (\( I4/mcm \) structure), as is shown in panel d. For PmNiO\(_2\), the energy of the \( P4/mmm \) structure is slightly lower than that of the \( I4/mcm \) structure by 0.5 meV/f.u. For SmNiO\(_2\), the energy order is reversed and the \( I4/mcm \) structure becomes more stable than the \( P4/mmm \) structure by 10.5 meV/f.u. Furthermore, we calculate the energy barrier from the \( P4/mmm \) structure to the \( I4/mcm \) structure. We find that the barrier decreases from 2.8 meV/f.u. for PmNiO\(_2\) to 0.5 meV/f.u. for SmNiO\(_2\). Next we test that after condensation of the “NiO\(_4\) square” rotation mode, the \( I4/mcm \) structure becomes dynamically stable in some infinite-layer nickelates. We perform the phonon calculation of the \( I4/mcm \) structure for PmNiO\(_2\) and SmNiO\(_2\). The phonon dispersions are shown in panels e and f. We find that the phonon dispersion of the \( I4/mcm \) structure is free from imaginary frequencies for PmNiO\(_2\) and SmNiO\(_2\). We make two comments here. First, while SmNiO\(_2\) has two local minima, considering the facts that 1) its \( I4/mcm \) structure is energetically more favorable than the \( P4/mmm \) structure, 2) the energy barrier for SmNiO\(_2\) to transition from the \( P4/mmm \) structure to the \( I4/mcm \) structure is tiny (0.5 meV/f.u.), and 3) its \( I4/mcm \) structure is dynamically stable, we argue that in experiments SmNiO\(_2\) is most likely stabilized in the \( I4/mcm \) structure. Second, the “NiO\(_4\) square” rotation is the first structural distortion that will appear in the \( P4/mmm \) structure of infinite-layer nickelates \( RNiO_2 \) when the lanthanide element \( R \) traverses from La to Lu. For late lanthanide elements (such as Ho-Lu), more complicated structural distortions are expected to emerge in infinite-layer \( RNiO_2 \). The purpose of the current study is to show that just by including one more degree of freedom in the crystal structure of \( RNiO_2 \) (i.e. “NiO\(_4\) square” rotation), the resulting
Figure 3:  

**a:** The lowest phonon frequency at $A = (\pi, \pi, \pi)$ point of infinite-layer $R\text{NiO}_2$ in the $P4/mmm$ structure ($R = \text{Pm, Sm, Eu and Gd}$) as a function of biaxial strain. Negative (positive) strain means compressive (tensile) biaxial strain. 

**b** and **c:** The phonon dispersions of infinite-layer SmNiO$_2$ in the $P4/mmm$ structure. The cyan curves are the phonon dispersions of fully-relaxed SmNiO$_2$ (i.e. without strain). The red curves in **b** and **c** are the phonon dispersions of SmNiO$_2$ under 1% and 2% compressive strains, respectively. The black arrows highlight that with compressive strain, the lowest phonon mode at $A = (\pi, \pi, \pi)$ point is “hardened”, while the lowest phonon modes at $Z = (0, 0, \pi)$ and $R = (\pi, 0, \pi)$ are “softened”.  

**d:** The energy evolution of infinite-layer SmNiO$_2$ as a function of “NiO$_4$ square” rotation angle $\theta$. The red, cyan and green symbols correspond to 1% compressive strain, no strain and 1% tensile strain, respectively. For each case, the $P4/mmm$ structure is used as the energy reference.  

Electronic structure trends can be qualitatively different from those of the $P4/mmm$ structure (see discussion below).  

**C. Epitaxial strain**  

Before we carefully compare the physical properties of $R\text{NiO}_2$ between the $I4/mcm$ structure and the $P4/mmm$ structure, we study epitaxial strain effects first. That is
because superconductivity in infinite-layer nickelates is observed in thin films rather than in bulk [1, 3, 4, 14, 64–68, 87]. We investigate how epitaxial strain influences the phonon dispersion of infinite-layer RNiO$_2$, in particular, whether it may remove the imaginary phonon mode at $A$ point and thus stabilize the $P4/mmm$ structure. Experimentally, oxide thin films are grown along the $z$ axis with a biaxial strain imposed by substrates in the $xy$ plane. The biaxial strain (either compressive or tensile) typically ranges within 3\% [88].

Panel a of Fig. 3 shows the lowest phonon frequency at $A$ point $\omega_A^*$ of a few infinite-layer $R$NiO$_2$ in the $P4/mmm$ structure as a function of biaxial strain $\xi$. We select $R = \text{Pm, Sm, Eu and Gd}$, which are close to the phase boundary where $\omega_A^*$ becomes imaginary (the complete phonon dispersions of those four nickelates under epitaxial strain are found in Supplementary Materials [78] Sec. III). The biaxial strain is defined as $\xi = (a_{\text{sub}} - a)/a \times 100\%$, where $a_{\text{sub}}$ is the theoretical substrate lattice constant and $a$ is the DFT optimized lattice constant of infinite-layer RNiO$_2$ in the $P4/mmm$ structure. For each infinite-layer RNiO$_2$, we vary the strain $\xi$ and find that $\omega_A^*$ decreases with tensile strain and increases with compressive strain. However, we note that for infinite-layer nickelate GdNiO$_2$, a compressive strain up to 3\% can not remove the “NiO$_4$ rotation” instability in the $P4/mmm$ structure. This is also true for other infinite-layer nickelates RNiO$_2$ with late lanthanide elements ($R = \text{Gd-Lu}$). More importantly, we find that while compressive strain helps remove the phonon instability at $A$ point in the $P4/mmm$ structure, it may induce other phonon instabilities. Panel b compares the phonon dispersions of infinite-layer nickelate SmNiO$_2$ in the $P4/mmm$ structure under 1\% compressive strain versus without epitaxial strain. It shows that compressive strain “hardens” the lowest phonon frequency at $A$ point but “softens” the lowest phonon frequencies at $Z$ and $R$ points. Under a compressive strain of 2\% or larger (see panel c and Fig. S3 in the Supplementary Materials [78]), the lowest phonon frequencies at $Z$ and $R$ points become imaginary in the $P4/mmm$ structure. To summarize, for infinite-layer nickelates, tensile strain increases the phonon instability at $A$ point in the $P4/mmm$ structure; small compressive strain helps remove the phonon instability at $A$ point but larger compressive strain can cause other phonon instabilities at $Z$ and $R$ points. Hence, epitaxial strain alone cannot substantially increase the stability of the $P4/mmm$ structure in infinite-layer nickelates RNiO$_2$. 

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On the other hand, we find that for SmNiO$_2$, epitaxial strain can tune its energetics and structural properties. Panel d of Fig. 3 shows the energy evolution of SmNiO$_2$ as a function of “NiO$_4$ square” rotation angle $\theta$. We compare three different epitaxial strains: 1% compressive (-1%), no strain (0%) and 1% tensile (+1%). From 1% compressive strain to 1% tensile strain, the energy difference between the $I4/mcm$ structure and the $P4/mcm$ structure monotonically increases from 4.8 to 17.5 meV/f.u. in its magnitude (indicating that the $I4/mcm$ structure gradually becomes more stable than the $P4/mmm$ structure). At the same time, the energy barrier from the $P4/mmm$ structure to the $I4/mcm$ structure decreases from 1.5 meV/f.u. (1% compressive strain) to 0.5 meV/f.u. (no strain) and disappears (1% tensile strain). The disappearance of the energy barrier indicates that under 1% tensile strain, the $P4/mmm$ structure is no longer a local minimum in SmNiO$_2$ and it spontaneously transitions into the $I4/mcm$ structure. Furthermore, the equilibrium “NiO$_4$ square” rotation angle $\theta$ in the $I4/mcm$ structure also increases from 6.4° to 7.1° when the epitaxial strain changes from 1% compressive to 1% tensile strain. This shows that epitaxial strain can be used as a fine-tuning knob to delicately control the structural stability of infinite-layer SmNiO$_2$.

In the next three sections, we will study the entire lanthanide series of infinite-layer nickelates in the $I4/mcm$ structure and in the $P4/mcm$ structure. We compare the trends in electronic properties and magnetic properties between the two crystal structures. For demonstration, we use SmNiO$_2$ as a prototype.

D. $P4/mmm$ versus $I4/mcm$ structures: structural properties

Fig. 4 compares the structural properties of $RNiO_2$ between the $I4/mcm$ structure and the $P4/mmm$ structure. For infinite-layer nickelates in the first category ($R =$ La-Nd), we only study the $P4/mmm$ structure because the $I4/mcm$ structure cannot be stabilized in those nickelates. Panels a shows the lattice constants $a$ and $c$ of the $I4/mcm$ and $P4/mmm$ structures. For ease of comparison to the $P4/mmm$ structure, we convert the lattice constants of the $I4/mcm$ structure into the pseudo-tetragonal lattice constants $a$ and $c$ (see Supplementary Materials [78] Sec. I). The general trend is similar in the two structures that $a$ and $c$ get smaller when $R$ traverses the lanthanide series [71]. For a given $R$, the $a$ and $c$ lattice constants are larger in the $I4/mcm$ structure than in the $P4/mmm$ structure. Panel b shows the volume per Ni atom
of the $I4/mcm$ and $P4/mmm$ structures. Consistent with the trends of the lattice constants, the volume decreases as $R$ traverses the lanthanide series. The key difference between the $I4/mcm$ structure and the $P4/mmm$ structure lies in the “NiO$_4$ square” rotation. In panel c, we show the “NiO$_4$ square” rotation angle $\theta$. In the $P4/mmm$ structure, $\theta = 0$ by definition. We find that $\theta$ increases in the $I4/mcm$ structure, as we traverse from Pm to Lu. A finite $\theta$ means that the in-plane Ni-O-Ni bond angle is reduced from the ideal $180^\circ$. A direct consequence of $\theta$ is the elongation of Ni-O bond. In the $P4/mmm$ structure, the Ni-O bond length is simply half of the lattice constant $a$, which decreases as $R$ traverses the lanthanide series. By contrast, in the $I4/mcm$ structure, Ni-O bond length is elongated compared to that in the $P4/mmm$ structure and it slowly increases as $R$ traverses the lanthanide series. We note that the “NiO$_4$ square” rotation $\theta$ and the volume reduction are two competing forces on the Ni-O bond length. The former, which is absent in the $P4/mmm$ structure, is more dominating in the $I4/mcm$ structure. A similar picture of these two competing forces is also found in LiNbO$_3$ under hydrostatic pressure [89]. The different behaviors of Ni-O-Ni bond angle and Ni-O bond length in the $I4/mcm$ structure versus in the $P4/mmm$ structure will have important influences on the electronic properties of $R$NiO$_2$.

E. \textit{P4/mmm versus I4/mcm structures: electronic properties}

Panel a of Fig. 5 compares the Ni $d_{x^2-y^2}$ bandwidth of the $I4/mcm$ structure and the $P4/mmm$ structure. Consistent with the previous studies [70, 71], the Ni $d_{x^2-y^2}$ bandwidth of the $P4/mmm$ structure monotonically increases when $R$ traverses the lanthanide series. That is because the Ni-O bond length of the $P4/mmm$ structure monotonically decreases, which increases the Ni-O hopping and thus the bandwidth. By contrast, we find that the Ni $d_{x^2-y^2}$ bandwidth of the $I4/mcm$ structure monotonically decreases when $R$ traverses the lanthanide series. That is consistent with the trend of a decreasing Ni-O-Ni bond angle and an increasing Ni-O bond length, both of which reduce the overlap between Ni-$d_{x^2-y^2}$ and O-$p$ orbitals and thus suppress the Ni-O hopping [90]. More importantly, for a given lanthanide element $R$, the Ni $d_{x^2-y^2}$ bandwidth of the $I4/mcm$ structure is substantially smaller than that of the $P4/mmm$ structure. For example, for SmNiO$_2$, its Ni $d_{x^2-y^2}$ bandwidth is 3.2 eV in the $P4/mmm$ structure and is reduced to 2.7 eV in the $I4/mcm$ structure. This indicates that for the
Figure 4: Crystal information of infinite-layer nickelates $R\text{NiO}_2$ in the $I4/mcm$ structure (red symbols) and in the $P4/mmm$ structure (blue symbols). a: The lattice constants $a$ (circle symbols) and $c$ (square symbols). For ease of comparison, we convert the lattice constants of the $I4/mcm$ structure into the pseudo-tetragonal lattice constants $a$ and $c$. b: Volume per $R\text{NiO}_2$ formula (f.u.). c: “NiO$_4$ square” rotation angle $\theta$. In the $P4/mmm$ structure, $\theta = 0^\circ$. d: Ni-O bond length.

same value of $U$ on Ni $d_{x^2-y^2}$ orbital, correlation strength is increased in the $I4/mcm$ structure, compared to the $P4/mmm$ structure. In addition, we also compare the Ni $d$ orbital occupancy $N_d$ between the $I4/mcm$ structure and the $P4/mmm$ structure in panel b. Ref. [91] shows that the metal $d$ orbital occupancy $N_d$ is a good measure of $p$-$d$ hybridization in complex oxides. We find that as $R$ traverses the lanthanide series, $R\text{NiO}_2$ in the $P4/mmm$ structure has a progressively increased $N_d$. This is consistent with the previous study [71] which shows that the O-$p$ content monotonically decreases across the lanthanide series. However, for $R\text{NiO}_2$ in the $I4/mcm$ structure, $N_d$ almost stays a constant as $R$ traverses the lanthanide series. By analyzing the density of states of $R\text{NiO}_2$ (see Supplementary Materials [78] Sec. VI), we find that in the $P4/mmm$ structure, running across the lanthanide series, the centroid of O-$p$ states monotonically decreases to lower energy, by about 1 eV from La to Lu [71]. This change increases the charge-transfer energy and decreases the $p$-$d$ hybridization. But in the $I4/mcm$ struc-
Figure 5: Electronic properties of infinite-layer nickelates $RNiO_2$ in the $I4/mcm$ structure and in the $P4/mmm$ structure. 

(a) and (b): bandwidth of Ni $d_{x^2-y^2}$ orbital and Ni $d$ occupancy. The red (blue) symbols refer to the $I4/mcm$ structure (the $P4/mmm$ structure).

(c) and (d): Electronic structure of SmNiO$_2$ in the $P4/mmm$ structure and in the $I4/mcm$ structure, respectively. The red (blue) symbols highlight the atomic projection onto the Ni $d_{x^2-y^2}$ orbital (Sm $d$ orbitals). The purple arrows in (c) and (d) highlight that a Sm-$d$-derived band is removed from the Fermi level and is pushed up to higher energy via the “NiO$_4$ square” rotation in the $I4/mcm$ structure.

(e) and (f): Fermi surface of SmNiO$_2$ in the $P4/mmm$ structure and in the $I4/mcm$ structure, respectively. The red (blue) arrows highlight the Fermi surface sheets that are composed of Ni $d_{x^2-y^2}$ orbital (Sm $d$ orbitals).
ture, the “NiO$_4$ square” rotation counteracts this effect and the centroid of O-$p$ states almost does not move across the lanthanide series. As a result, the Ni $d$ occupancy $N_d$ and $p$-$d$ hybridization change marginally across the lanthanide series of $RNiO_2$. We note that for a given lanthanide element $R$, $N_d$ is smaller in the $I4/mcm$ structure than in the $P4/mmm$ structure. A smaller $N_d$ corresponds to a smaller critical $U$ value for the metal-insulator transition $[91]$, i.e. $RNiO_2$ in the $I4/mcm$ structure is closer to the Mott insulating phase than that in the $P4/mmm$ structure.

Next we study the electronic band structure and Fermi surface of SmNiO$_2$ as a prototype (very similar results are also obtained in infinite-layer nickelates close to the phase boundary $RNiO_2$ with $R = $ Pm, Eu and Gd, see Supplementary Materials $[78]$ Sec. V). Panel c of Fig. 5 shows the band structure of SmNiO$_2$ in the $P4/mmm$ structure. Due to the cell-doubling, there are four bands that cross the Fermi level: two are Ni-$d_{x^2-y^2}$-derived bands and the other two are Sm-$d$-derived bands. In the unfolded Brillouin zone (BZ), the Sm-$d$-derived band crosses the Fermi level and results in two electron pockets: one is at $\Gamma$ point and the other is at $A$ point. After band folding, in the body-centered-tetragonal Brillouin zone (BCT-BZ) $[71]$, the electron pocket that is originally at $A$ point in the unfolded BZ is mapped to $\Gamma$ point, leading to two electron pockets at $\Gamma$ point. This is clearly seen in panel e, which shows the Fermi surface of SmNiO$_2$ in the $P4/mmm$ structure. These $\Gamma$-centered electron pockets are one of the main differences between infinite-layer nickelates and superconducting cuprates and their role is still under debate $[16–23]$. Panel d of Fig. 5 shows the band structure of SmNiO$_2$ in the $I4/mcm$ structure. Compared to the $P4/mmm$ structure, the “NiO$_4$ square” rotation removes one Sm-$d$-derived band (highlighted by the purple arrows) away from the Fermi surface and pushes it to higher energy. In the corresponding Fermi surface (panel f), one $\Gamma$-centered electron pocket vanishes. This is an interesting result in that 1) compared to the $P4/mmm$ structure, the Fermi surface of SmNiO$_2$ in the $I4/mcm$ structure more closely resembles that of CaCuO$_2$; and 2) the “NiO$_4$ square” rotation in the $I4/mcm$ structure effectively acts as hole doping in SmNiO$_2$. To demonstrate the second point more clearly, we calculate the band structure and Fermi surface of Sr$_{0.2}$Sm$_{0.8}$NiO$_2$ in the $P4/mmm$ structure (see the Supplementary Materials $[78]$ Sec. VII) and we find that they are similar to pristine SmNiO$_2$ in the $I4/mcm$ structure.
F. *P4/mmm versus I4/mcm* structures: magnetic properties

Next we study the magnetic properties of $R$NiO$_2$ and compare the $I4/mcm$ structure and the $P4/mmm$ structure. We use the charge-only DFT+$U$+$J$ method [82–84] in which the spin polarization is broken by the $U/J$ extension rather than the spin-dependent exchange-correlation functional. The advantage of using this method is that when $U/J$ parameters approach zero, we will recover our non-spin-polarized DFT results. We first fix the optimized crystal structure that is obtained from the non-spin-polarized (nsp) DFT calculations, upon which the electronic structure calculations are performed. This is the convention of some previous DFT+$U$ and DFT+dynamical mean field theory (DFT+DMFT) studies [46–48, 54–59, 71]. Then we relax the crystal structure within the charge-only DF+$U$+$J$ method and discuss the relaxation effects on magnetic properties.

We first study rocksalt antiferromagnetic ordering (ordering wave vector $q = (\pi, \pi, \pi)$) in SmNiO$_2$ [47]. Panel a of Fig. 6 shows the magnetic moment on Ni atom as a function of $U_{Ni}$ (throughout the calculations, we set $J_{Ni} = 0.15U_{Ni}$ [92]). We compare the Ni magnetic moment between the $I4/mcm$ structure and the $P4/mmm$ structure. We find that within the charge-only DFT+$U$+$J$ method, the critical effective $U_{Ni}$ for rocksalt antiferromagnetic ordering is reduced from 1.8 eV in the $P4/mmm$ structure to 1.5 eV in the $I4/mcm$ structure. This is consistent with the bandwidth reduction effect that correlation strength is increased on Ni $d_{x^2−y^2}$ orbital in the $I4/mcm$ structure, which favors the formation of long-range magnetic ordering. Next in panel b, we study the entire lanthanide series of infinite-layer nickelates RNiO$_2$ and compare the critical $U_{Ni}$ for the $I4/mcm$ structure and for the $P4/mmm$ structure. We find that the critical $U_{Ni}$ for the $I4/mcm$ structure is always smaller than that for the $P4/mmm$ structure, and from PmNiO$_2$ to LuNiO$_2$, the reduction in the critical $U_{Ni}$ becomes more substantial. This feature is consistent with the trend of Ni $d_{x^2−y^2}$ bandwidth reduction (see Fig. 5a). In addition, we study the energy difference between rocksalt antiferromagnetic ordering and ferromagnetic ordering $\Delta E = E_{AFM} − E_{FM}$ as a function of $U_{Ni}$. Panel c shows that for SmNiO$_2$, both in the $I4/mcm$ structure and in the $P4/mmm$ structure, when $U_{Ni}$ exceeds the critical value (highlighted by the two dashed lines), rocksalt antiferromagnetic ordering has lower energy than ferromagnetic ordering ($\Delta E$ is negative). However, the magnitude of $|\Delta E|$ is larger in the $I4/mcm$ structure than in
Figure 6: Magnetic properties of infinite-layer nickelates $R\text{NiO}_2$ in the $I4/mcm$ structure (red symbols) and in the $P4/mmm$ structure (blue symbols). a: The magnetic moment on Ni atom of SmNiO$_2$ in rocksalt antiferromagnetic ordering (AFM) as a function of $U_{Ni}$. b: The critical $U_{Ni}$ for rocksalt antiferromagnetic ordering across the lanthanide series of infinite-layer nickelates $R\text{NiO}_2$. c: The energy difference between rocksalt antiferromagnetic ordering and ferromagnetic ordering of SmNiO$_2$ as a function of $U_{Ni}$. The dashed lines highlight the critical $U_{Ni}$ for rocksalt antiferromagnetic ordering. d: The energy difference between rocksalt antiferromagnetic ordering and ferromagnetic ordering at $U_{Ni} = 3$ eV across the lanthanide series of infinite-layer nickelates $R\text{NiO}_2$.

The results in panel c indicate that given the same value of $U_{Ni}$, the “NiO$_4$ square” rotation in the $I4/mcm$ structure further stabilizes the rocksalt antiferromagnetic ordering over the ferromagnetic ordering. We repeat the same calculations for the entire lanthanide series of infinite-layer nickelates $R\text{NiO}_2$ and show in panel d the energy difference $\Delta E$ at $U_{Ni} = 3$ eV. We find that $\Delta E$ is negative and its magnitude is larger in the $I4/mcm$ structure than in the $P4/mmm$ structure for the entire series of $R\text{NiO}_2$ ($R = \text{Pm-Lu}$).

Next within the charge-only DFT+$U$+$J$ method, we relax the crystal structure of SmNiO$_2$ for each given $U$ and $J$ (see Supplementary Materials [78] Sec. VIII). We
find that adding $U$ and $J$ terms does not considerably change the optimized lattice constants and the “NiO$_4$ square” rotation angle. However, it is noted that a weak “cusp” feature emerges at the critical $U_{\text{Ni}}$ when the long-range magnetic ordering is stabilized. Using the optimized crystal structure from the charge-only DFT+$U$+$J$ method, we still find that 1) the critical $U_{\text{Ni}}$ for the $I4/mcm$ structure is smaller than that for the $P4/mmm$ structure, 2) rocksalt-antiferromagnetic ordering is more stable than ferromagnetic ordering in both crystal structures, and 3) the magnitude of the energy difference between rocksalt-antiferromagnetic ordering and ferromagnetic ordering $|\Delta E|$ is larger in the $I4/mcm$ structure than in the $P4/mmm$ structure. All these results are qualitatively consistent with the previous ones that are obtained by using the nsp-DFT optimized crystal structure.

IV. CONCLUSION

In conclusion, we perform first-principles calculations to study structural, electronic and magnetic properties of the entire lanthanide series of infinite-layer nickelates $RNiO_2$. We find that the widely-studied $P4/mmm$ structure is only dynamically stable when $R$ is an early lanthanide element (La-Sm). For late lanthanide elements (Eu-Lu), an unstable phonon mode appears at $A$ point in the $P4/mmm$ structure, which corresponds to an out-of-phase “NiO$_4$ square” rotation about the $z$ axis. For infinite-layer nickelates with late lanthanide elements, condensation of this phonon mode in the $P4/mmm$ structure lowers the total energy and leads to a new $I4/mcm$ crystal structure. Special attention is paid to two borderline cases $PmNiO_2$ and $SmNiO_2$, in which both the $P4/mmm$ structure and the $I4/mcm$ structure are local minimums. When epitaxial strain is imposed on infinite-layer nickelates, tensile strain further increases the dynamical instability at $A$ point in the $P4/mmm$ structure, while compressive strain “hardens” the phonon at $A$ point but “softens” the phonons at $Z$ and $R$ points in the $P4/mmm$ structure. Furthermore, epitaxial strain can fine-tune the energy difference between the $I4/mcm$ structure and the $P4/mmm$ structure when they are both dynamically stable in $RNiO_2$ (such as $SmNiO_2$).

We use the new $I4/mcm$ crystal structure to study the trends of electronic and magnetic properties of $RNiO_2$. We find that compared to the $P4/mmm$ structure, the Ni $d_{x^2-y^2}$ bandwidth of $RNiO_2$ is substantially reduced in the $I4/mcm$ structure,
which implies an increased correlation strength in the new $I\bar{4}/mcm$ structure. In addition, the Ni $d$ occupancy of $RNiO_2$ gets smaller in the $I\bar{4}/mcm$ structure than that in the $P4/mmm$ structure, which means a small critical $U_{Ni}$ for the metal-insulator transition [91]. Furthermore, the electronic structure and Fermi surface of $RNiO_2$ become “cleaner” in the $I\bar{4}/mcm$ structure than in the $P4/mmm$ structure, because one lanthanide-$d$-derived band is removed from the Fermi level and thus a lanthanide-$d$-derived electron pocket disappears at $\Gamma$ point. Finally, the critical $U_{Ni}$ to stabilize the rocksalt antiferromagnetic ordering in $RNiO_2$ is reduced from the $P4/mmm$ structure to the $I\bar{4}/mcm$ structure. All these results imply that correlation effects are enhanced and Mott physics plays a more important role in the new $I\bar{4}/mcm$ crystal structure of infinite-layer $RNiO_2$. Hence, if $RNiO_2$ in the $I\bar{4}/mcm$ crystal structure can be synthesized in experiment, it will provide a closer analogy to infinite-layer cuprate $\text{CaCuO}_2$.

Our work suggests that among the lanthanide series of infinite-layer nickelates, the most promising candidate to crystallize in the $I\bar{4}/mcm$ structure is $\text{SmNiO}_2$.

We finally note that structure-property relations have been widely studied in complex oxides, such as perovskite nickelates and manganites [93–97]. Spontaneous structural distortions, such as Jahn-Teller, breathing, rotations and tilts of oxygen octahedra, turn out to have substantial impacts on the physical properties of complex oxides [98–102]. Our work reveals a similar coupling between crystal structure and electronic structure in infinite-layer nickelates $RNiO_2$: by substituting the lanthanide element $R$, we can control the rotation of “NiO$_4$ square”, which tunes the underlying electronic structure and may potentially favor superconductivity.

Note added: after the completion of our work, we became aware of Refs. [103–105], which also study structural distortions in infinite-layer nickelates $RNiO_2$ and $YNiO_2$. The authors of Ref. [103] find that $YNiO_2$ is also prone to the “NiO$_4$ square” rotation. The authors of Ref. [104] show that due to the $R$-to-Ni cation mismatch, the “NiO$_4$ square” is prone to various types of rotations. For $R$ of a small ionic radius such as Y, the ground state structure has the orthorhombic $Pbnm$ symmetry with the $a^-a^-c^+$ rotation pattern. For $R$ of a moderate ionic radius such as Gd, the ground state structure has the tetragonal $I\bar{4}/mcm$ symmetry with the $a^0a^0c^-$ rotation, which is consistent with our results. The authors of Ref. [105] also find the dynamical instability of “NiO$_4$ square” rotation in infinite-layer nickelates $RNiO_2$. In addition, they study the electronic and
magnetic properties of $R\text{NiO}_2$ at finite temperatures.

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