Interface polarity plays a key role in transition metal oxide heterostructures, since it can drive the emergence of physical properties that are absent in the respective bulk compounds [1–3]. A prominent example is the LaAlO$_3$/SrTiO$_3$(001) system (LAO/STO [4, 5]), in which a correlated two-dimensional electron gas (2DEG) is formed at the interface by occupation of Ti $3d$ conduction band states beyond 4 unit cells of LAO [6, 7] that shows intriguing physics, for instance, superconductivity [8]. Electronic reconstructions such as this can accommodate the polarity mismatch and thereby circumvent the polar catastrophe, i.e., the infinite build-up of electrostatic potential [5, 9].

The very recent observation of superconductivity in Sr-doped NdNiO$_2$ films grown on STO(001) by Li et al. [10] has sparked considerable interest in infinite-layer nickelates, since their formal Ni$^{3+}$($3d^9$) valence state renders them close to cuprates. Most of the theoretical efforts to explain the phenomenon so far have concentrated on the electronic properties of bulk compounds [11–15]. However, superconductivity could not be confirmed experimentally in Sr-doped bulk NdNiO$_2$ [16]. This raises a question about the role of the interface to the substrate that has hardly been addressed so far.

Here we explore the impact of the polar interface on the structural and electronic properties of NdNiO$_{n}$/STO(001) ($n = 2, 3$) by performing first-principles calculations including a Coulomb repulsion term. For infinite-layer nickelate films ($n = 2$), electronic reconstruction drives the emergence of a two-dimensional electron gas (2DEG) at the interface involving a strong occupation of the Ti 3d states. This effect is more pronounced than in the paradigmatic LaAlO$_3$/SrTiO$_3$(001) system and accompanied by a substantial reconstruction of the Fermi surface as well as strong ionic relaxations and Ni valence modulations. The Ni $e_g$ orbital polarization increases throughout the film and exceeds 35% at the surface. In contrast, no 2DEG forms for films in the perovskite structure ($n = 3$) or if a single perovskite layer persists at the interface, and the polarity mismatch is exclusively accommodated by electrostatic doping of the nickelate, accompanied by ionic relaxations. We analyze the topotactic reaction from the perovskite to the infinite-layer phase and show why the reduction is confined to the nickelate film, whereas the SrTiO$_3$ substrate remains intact.

Fundamental difference in the electronic reconstruction of infinite-layer vs. perovskite neodymium nickelate films on SrTiO$_3$(001)

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Motivated by the recent reports of superconductivity in Sr-doped NdNiO$_2$ films on SrTiO$_3$(001) [Li et al., Nature (London) 572, 624 (2019)], we explore the role of the polar interface on the structural and electronic properties of NdNiO$_{n}$/SrTiO$_3$(001) ($n = 2, 3$) by performing first-principles calculations including a Coulomb repulsion term. For infinite-layer nickelate films ($n = 2$), electronic reconstruction drives the emergence of a two-dimensional electron gas (2DEG) at the interface involving a strong occupation of the Ti 3d states. This effect is more pronounced than in the paradigmatic LaAlO$_3$/SrTiO$_3$(001) system and accompanied by a substantial reconstruction of the Fermi surface as well as strong ionic relaxations and Ni valence modulations. The Ni $e_g$ orbital polarization increases throughout the film and exceeds 35% at the surface. In contrast, no 2DEG forms for films in the perovskite structure ($n = 3$) or if a single perovskite layer persists at the interface, and the polarity mismatch is exclusively accommodated by electrostatic doping of the nickelate, accompanied by ionic relaxations. We analyze the topotactic reaction from the perovskite to the infinite-layer phase and show why the reduction is confined to the nickelate film, whereas the SrTiO$_3$ substrate remains intact.

Methodology. — We performed first-principles calculations in the framework of density functional theory [17] (DFT) as implemented in the Quantum ESPRESSO code [18]. The generalized gradient approximation was used for the exchange-correlation functional as parametrized by Perdew, Burke, and Ernzerhof [19]. Static correlation effects were considered within the DFT+$U$ formalism [20] employing $U = 4$ eV on Ni and Ti sites, in line with previous work [15, 21–25]. We model (NdNiO$_{n}$)$_m$/STO(001) ($n = 2, 3$) by using $\sqrt{2}a \times \sqrt{2}a$ supercells with two transition metal sites per layer to account for octahedral rotations, strained to the STO substrate lattice parameter 3.905 Å. The supercells contain 5 layers of STO substrate and $m = 1-6$ layers of nickelate film, subsequently doubled to obtain symmetric slabs (the figures only show half of the supercell). The vacuum region spans 20 Å. We focus here on structural and electrostatic effects and therefore discuss nonmagnetic results in the following [10, 26], noting that spin-polarized calculations with ferromagnetic or A-
and G-type antiferromagnetic order in the nickelate films resulted in qualitatively identical results with respect to 2DEG formation for both \( n = 2 \) and \( n = 3 \). Wave functions and density were expanded into plane waves up to cutoff energies of 45 and 350 Ry, respectively. Ultrasoft pseudopotentials [27] as successfully employed in previous work [22–25, 28–30], were used in conjunction with projector augmented wave datasets [31]. The Nd 4\( f \) electrons are frozen in the core [11, 21]. We used a 12 \( \times \) 12 \( \times \) 1 Monkhorst-Pack \( k \)-point grid [32] and 5 mRy Methfessel-Paxton smearing [33] to sample the Brillouin zone. The ionic positions were accurately optimized, reducing ionic forces below 1 mRy/\( \text{a.u.} \).

**Ionic relaxation.** — We focus our discussion on \((\text{NdNiO}_3)_n/\text{SrTiO}_3(001)\) heterostructures with a representative film thickness of 4 unit cells. The lattice parameters of bulk \( \text{NdNiO}_2 \) (\( \alpha = 3.92, c = 3.28 \text{ Å} \) [11, 34]) imply that the film is subject to compressive strain if grown epitaxially on \text{SrTiO}_3(001) \( [\alpha = 3.905 \text{ Å}, \text{Fig. 1(a)}] \). Consequently, the infinite-layer film expands vertically (\( \sim 2.6\% \)). Interestingly, we find that this expansion is not homogeneous; instead, the distances between the distinct Nd layers increase continuously from the interface (3.29 Å) to the surface (3.47 Å). An analogous trend is observed for the perovskite film \( [n = 3, \text{tensile strain, Fig. 1(b)}] \) with even larger distances. The Nd-Sr distance at the interface is particularly enhanced for the infinite-layer film (4.15 Å), slightly more pronounced than for the perovskite film (4.13 Å). A similar expansion at the interface (4.06 Å) has been observed in \( n \)-type \((\text{LaNiO}_3)_{3.5}/\text{SrTiO}_3(001)\) superlattices on \text{SrTiO}_3(001) [22].

The perovskite film exhibits considerable octahedral rota-
tions [Fig. 1(b)], particularly at the interface with an apical Ni-O-Ti bond angle of 155° and basal Ni-O-Ni and Ti-O-Ti bond angles of 155.5° and 157.7°, respectively. We find the rotational pattern of bulk NdNiO$_2$ (a$^-$a$^-$c$^+$) to be reflected in the film geometry. Owing to the octahedral connectivity, the rotations in the film extend into the STO substrate. In contrast, in the infinite-layer heterostructure, the small intrinsic octahedral rotations of STO are removed near the interface, and the NiO$_2$ squares show no rotations around the c axis [Fig. 1(a)].

For $n = 2$, the central NiO$_2$ layers are coplanar, whereas the surface (interface) layer is buckled, the Ni ion being vertically displaced outwards (inwards) from the respective oxygen layer by $\Delta z = 0.29$ Å ($-0.17$ Å), a response to the internal electric field build-up in the polar films [Fig. 1(a,c)]. The distance between the surface NiO$_2$ layer and the subsurface Nd layer is considerably contracted and amounts to only 1.17 Å. The Ti ions in the STO substrate show a sizeable inwards vertical displacement (away from the interface), particularly at the interface ($\Delta z \sim -0.35$ Å), that decays exponentially as $\Delta z \approx -0.35$ Å $\exp(-d/7.42$ Å) with the distance $d$ to the interfacial TiO$_2$ layer [S = 4; Fig. 1(c)]. This trend is also expressed in strong oscillations of the apical Ti-O bond lengths around the bulk value [1.96 Å; Fig. 1(c)]. Our observations for $n = 3$ are in sharp contrast: In the nickelate, the Ni displacements are smaller than 0.05 Å; in the STO substrate, the Ti displacements almost vanish. This qualitatively different structural response to the polar discontinuities in infinite-layer vs. perovskite nickelate films points at fundamentally distinct accommodation mechanisms, which we unravel in the following.

**Electronic reconstruction.** — For infinite-layer nickelate films ($n = 2$), we observe a considerable electronic reconstruction. The polar discontinuities at the interface and the surface induce a substantial charge transfer, expressed in a depletion (relative to bulk) at the Ni sites (i.e., of the delocalized NiO$_2$ bands), in particular at the surface, whereas the Ti ions gain charge in the localized 3d states, particularly at the interface, with rapid decay into the substrate [Fig. 1(d,f)]. A 2DEG emerges at the interface with considerable band bending in the nickelate film and the STO substrate, as can be seen from the layer-resolved density of states [Fig. 1(d)] and the band structure [Fig. 2(a)]. The strong Ti 3d occupation at the interface is in stark contrast with (LAO)$_x$/STO(001), which is just at the verge of a metal-insulator transition [7]. Already for ultrathin (NdNiO$_2$)$_x$/STO(001) films, we observe a 2DEG, albeit with reduced Ti 3d occupation ($-0.076$ e$^-$ at the interface). In contrast, increasing the film thickness from 4 to 6 layers induces only negligible changes in the surface and interface electronic structure. Since the apical Ti-O bond length at the interface is contracted [1.86 Å, Fig. 1(c)] relative to STO bulk (1.96 Å), predominantly the 3d$_{ez}$ orbital gets occupied due to its lowered energy. This can clearly be seen in the distribution of electronic density [Fig. 1(d)] and resembles the situation in LAO/STO(001) [36, 37]. This orbital order persists for three layers and then develops into a uniform occupation of the $t_{2g}$ manifold.

In contrast, we find no tendency towards 2DEG formation in the perovskite ($n = 3$) heterostructures and only negligible charge redistribution, as shown for the representative (NdNiO$_2$)$_3$/STO(001) system in Fig. 1(e,g), despite a clearly visible electric field in the layer-resolved density of states of the film.

In addition to the charge transfer, we observe a strong modulation of the Ni $e_g$ orbital polarization throughout the infinite-layer nickelate films [Fig. 1(f)] defined from the orbital occupations $n$ by $P = (n_{3d_{yx}} - n_{3d_{yz}})/(n_{3d_{x^2-y^2}} + n_{3d_{x^2-y^2}})$ and increasing from the interface ($P \sim 12\%$) to the surface ($P > 35\%$), indicating a preferential occupation of the 3d$_{xz/yz}$ orbitals. These values exceed attainable values in nickelate/aluminate SLs on a variety of different substrates [25, 38–40]; the incomplete orbital polarization has been discussed as a major hindrance for superconductivity [10]. For reference, in bulk NdNiO$_2$ we find a Ni $e_g$ orbital polarization of 17%. Interestingly, even the interfacial Ti ions exhibit a finite orbital polarization ($P \sim 12\%$) due to a partial occupation of the 3d$_{xz/yz}$ orbital. Again, the behavior of perovskite films is distinct, with only moderate orbital polarization ($P \sim 11\%$) exclusively at the surface [Fig. 1(g)].
The layer-resolved band structures in Fig. 2(a) show that at the interface, the Ti 3d$_{xy}$ band is bent down to $\sim -0.55$ eV at the $\Gamma$ point. Moreover, we observe a hybridized Ni 3d$_{z^2}$–Ti 3d$_{x^2-y^2}$ state at the interface, visible for instance at $\sim -0.65$ eV at the $\Gamma$ point, that extends into the nickelate. In the surface layer, the Ni 3d bands are only occupied around the $\Gamma$ point; from the subsurface layer on, also an electron pocket around the $M$ point emerges. In the STO region, only an electron pocket around the $\Gamma$ point is occupied, having 3d$_{xy}$+3d$_{z^2}$ character at the interface and 3d$_{xy}$+3d$_{x^2}$+3d$_{yz}$ character deeper in the substrate. Therefore, the Fermi surfaces of infinite-layer heterostructures experience considerable reconstructions with respect to bulk [Fig. 2(b)].

Interestingly, the Nd 5d states, which might be relevant for the superconductivity mechanism [26], are strongly affected by the band bending. The layer-resolved density of states for $n = 2$ shows that the Nd 5d states are generally empty and $\sim 2$ eV above $E_F$ near the surface [Fig. 1(d)]. Only at the interface, they are bent down to $\sim -0.6$ eV, leading to a small but finite occupation as reported for bulk NdNiO$_2$ [11]. Therefore, their contribution to the conductivity of a real heterostructure is much smaller than expected from bulk. For $n = 3$, occupied Nd 5d–O 2p$_{x,y}$ hybrid states form $\sim 1$ eV below the Fermi energy at the interface that reach up to the Fermi energy near the surface [Fig. 1(e)].

**Oxygen deintercalation.** We now address the topotactic oxygen deintercalation reaction from the perovskite to the infinite-layer phase. As a first approach, Fig. 3(a) displays single-layer reduction energies (i.e., apical oxygen vacancy layer formation energies), defined from DFT total energies as $E_{\text{f},i}^{i,0} = E_{\text{f},i}^{\text{single layer } i \text{ reduced}} - E_{\text{ideal perovskite film}} + \mu_O$ with $\mu_O = \frac{1}{2}E_{\text{O}_2}$, i.e., in the oxygen-rich limit. The formation energies are lowest at the surface ($\sim 0.5$ eV) and increase to $\sim 1.8$ eV in the third layer. At the interface, the oxygen ions are moderately bound ($\sim 3.5$ eV), and very strongly in the STO substrate ($\sim 4.8$ eV). This is in line with an oxygen vacancy formation energy of $\sim 5.5$ eV in bulk STO [41] and comparable to values near the LAO/STO(001) interface [42]. The values in nickelates are generally lower (e.g., bulk LaNiO$_3$: 2.8 $\pm$ 0.2 eV [43], (LaNiO$_3$)$_3$/LaO$_x$(001) superlattices on STO(001): 2.3 eV [25]). The nickelate layers are therefore easily reduced, whereas oxygen deintercalation in the STO substrate is inhibited by the high formation energies.

In a second and more realistic approach, we model successive layer-by-layer reduction, $E_{\text{f},i}^{i,i-1} = E_{\text{topmost } i \text{ layers reduced}} - E_{\text{topmost } i-1 \text{ layers reduced}} + \mu_O$, which largely concurs with the results of the first approach. Peculiarly, we find that the oxygen binding is enhanced at the interface if the above nickelate layers are already reduced. This leads to the surprising situation that the interfacial Nd layer may retain its oxygen under appropriately chosen experimental conditions. Figure 3(b) shows the corresponding electronic structure and optimized geometry. The single non-reduced (i.e., perovskite) layer at the interface inhibits the formation of a 2DEG. Instead, the STO conduction band aligns with the Fermi energy, and only little band bending can be observed directly at the interface. No layer exhibits Nd 5d states near the Fermi energy. While for ideal infinite-layer films the octahedral rotations are removed at the interface [Fig. 1(a)], here they are enhanced even beyond values of perovskite films. The Nd layer distances show ionic relaxations of comparable magnitude to the ideal infinite-layer case. The NdO-Nd layer distance at the interface (3.52 Å) is considerably larger (smaller) than for ideal infinite-layer (perovskite) films and thus may act as a fingerprint in transmission electron microscopy to detect the interface layer stacking even if oxygen sites are difficult to resolve.

**Summary.** We investigated the electronic reconstructions in NdNiO$_n$/SrTiO$_3$(001) ($n = 2, 3$) driven by interface polarity from first-principles. The results show that the polar discontinuities at the interface and the surface considerably affect the electronic structure throughout infinite-layer nickelate films and several layers (at least 5 unit cells) into the STO substrate. Moreover, the accommodation mechanism is fundamentally different for infinite-layer and perovskite nickelates. The substantial modulations of the Ni and Ti valence and orbital polarization observed for the infinite-layer films on SrTiO$_3$(001) are likely to impact superconductivity considerably, which implies that modeling the epitaxial films simply as strained bulk is only of limited relevance. Hence, interface polarity emerges as a key aspect in understanding superconductivity in infinite-layer nickelates and requires further consideration in future studies. Parallels to other superconducting systems such as LAO/STO(001) [8] and FeSe/STO(001) [44] may point to a more general phenomenon.
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[1] J. Mannhart and D. G. Schlom, Science 327, 1607 (2010).
[2] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, Nat. Mater. 11, 103 (2012).
[3] A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, Nature 419, 378 (2002).
[4] A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004).
[5] N. Nakagawa, H. Y. Hwang, and D. A. Muller, Nat. Mater. 5, 204 (2006).
[6] S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, Science 313, 1942 (2006).
[7] R. Pentcheva and W. E. Pickett, Phys. Rev. Lett. 102, 107602 (2009).
[8] N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Rüetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, Science 317, 1196 (2007).
[9] C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000).
[10] D. Li, K. Lee, B. Y. Wang, M. Osada, S. Crossley, H. R. Lee, Y. Cui, Y. Hikita, and H. Y. Hwang, Nature 572, 624 (2019).
[11] Y. Nomura, M. Hirayama, T. Tadano, Y. Yoshimoto, and R. Arita, Phys. Rev. B 100, 205106 (2019).
[12] H. Sakakibara, H. Usui, K. Suzuki, T. Kotani, H. Aoki, and K. Kuroki, (2019), arXiv:1909.00060 [cond-mat.supr-con].
[13] M. Jiang, M. Berciu, and G. A. Sawatzky, (2019), arXiv:1909.02557 [cond-mat.supr-con].
[14] A. S. Botana and M. R. Norman, (2019), arXiv:1908.10946 [cond-mat.supr-con].
[15] Q. Li, C. He, J. Si, X. Zhu, Y. Zhang, and H.-H. Wen, (2019), arXiv:1911.02420 [cond-mat.supr-con].
[16] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[17] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter 21, 395502 (2009).
[18] D. Li, K. Lee, B. Y. Wang, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, Nat. Mater. 11, 103 (2012).
[19] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[20] M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005).
[21] J. Liu, M. Kargarian, M. Kareev, B. Gray, P. J. Ryan, A. Cruz, N. Tahir, Y.-D. Chuang, J. Guo, J. M. Rondinelli, J. W. Freeland, G. A. Fiete, and J. Chakhalian, Nature Communications 4, 2714 (2013).
[22] B. Geisler, A. Blanca-Romero, and R. Pentcheva, Phys. Rev. B 95, 125301 (2017).
[23] F. Wrobel, B. Geisler, Y. Wang, G. Christiani, G. Logvenov, M. Bluschke, E. Schierle, P. A. van Aken, B. Keimer, R. Pentcheva, and E. Benckiser, Phys. Rev. Materials 2, 035001 (2018).
[24] B. Geisler and R. Pentcheva, Phys. Rev. Materials 2, 055403 (2018).
[25] B. Geisler and R. Pentcheva, Phys. Rev. Applied 11, 044047 (2019).
[26] G. A. Sawatzky, Nature 572, 592 (2019).
[27] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
[28] B. Geisler, P. Kratzer, and V. Popescu, Phys. Rev. B 89, 184422 (2014).
[29] B. Geisler and P. Kratzer, Phys. Rev. B 92, 144418 (2015).
[30] B. Geisler and P. Kratzer, Phys. Rev. B 99, 155433 (2019).
[31] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[32] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[33] M. Methfessel and A. T. Paxton, Phys. Rev. B 40, 3616 (1989).
[34] M. Hayward and M. Rosseinsky, Solid State Sci. 5, 839 (2003).
[35] K.-W. Lee and W. E. Pickett, Phys. Rev. B 70, 165109 (2004).
[36] R. Pentcheva and W. E. Pickett, Phys. Rev. B 78, 205106 (2008).
[37] R. Pentcheva, M. Huijben, K. Otte, W. E. Pickett, J. E. Kleibekaer, J. Huijben, H. Boschkher, D. Kockmann, W. Siemons, G. Koster, H. J. W. Zandvliet, G. Rijnders, D. H. A. Blank, H. Hilgenkamp, and A. Brinkman, Phys. Rev. Lett. 104, 166804 (2010).
[38] A. Blanca-Romero and R. Pentcheva, Phys. Rev. B 84, 195450 (2011).
[39] M. Wu, E. Benckiser, M. W. Haverkort, A. Frano, Y. Lu, U. Nwankwo, S. Brück, P. Audehm, E. Goering, S. Macke, V. Hinkov, P. Woerner, G. Christiani, S. Heinze, G. Logvenov, H.-U. Habermeier, and B. Keimer, Phys. Rev. B 88, 125124 (2013).
[40] F. Belviso, V. E. P. Claerbout, A. Comas-Vives, N. S. Dalal, F.-R. Fan, A. Filippetti, V. Fiorentini, L. Foppa, C. Franchini, B. Geisler, M. G. Ghiringhelli, A. Groß, S. Hu, J. Íñiguez, S. K. Kauwe, J. L. Musfeldt, P. Nicoloni, R. Pentcheva, T. Polcar, W. Ren, F. Ricci, F. Ricci, H. S. Sen, J. M. Skelton, T. D. Sparks, A. Stroppa, A. Urru, M. Vandichel, P. Vavassori, H. Wu, K. Yang, H. J. Zhao, D. Puggioni, R. Cortese, and A. Cammarata, Inorg. Chem. 58, 14939 (2019).
[41] M. T. Curnan and J. R. Kitchin, J. Phys. Chem. C 118, 28776 (2014).
[42] L. Yu and A. Zunger, Nat. Commun. 5, 5118 (2014).
[43] A. Malashevich and S. Ismail-Beigi, Phys. Rev. B 92, 144402 (2015).
[44] J.-F. Ge, Z.-L. Liu, C. Liu, C.-L. Gao, D. Qian, Q.-K. Xue, Y. Liu, and J.-F. Jia, Nat. Mater. 14, 285 (2015).