



CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

High-density electron doping of SmNiO_3 from first principles

Michele Kotiuga and Karin M. Rabe

Phys. Rev. Materials **3**, 115002 — Published 15 November 2019

DOI: [10.1103/PhysRevMaterials.3.115002](https://doi.org/10.1103/PhysRevMaterials.3.115002)

High-density electron doping of SmNiO₃ from first principles

Michele Kotiuga¹ and Karin M. Rabe¹

¹*Department of Physics and Astronomy, Rutgers,
The State University of New Jersey, Piscataway, NJ, USA*

(Dated: October 19, 2019)

Recent experimental work has realized a new insulating state of samarium nickelate (SmNiO₃), accessible in a reversible manner via high-density electron doping. To elucidate this behavior, we use the first-principles density functional theory (DFT) + U method to study the effect of added electrons on the crystal and electronic structure of SmNiO₃. First, we track the changes in the crystal and electronic structure with added electrons compensated by a uniform positive background charge at concentrations of $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and 1 electrons per Ni. The change in electron concentration does not rigidly shift the Fermi energy; rather, the added electrons localize on NiO₆ octahedra causing an on-site Mott transition and a change in the density of states resulting in a large gap between the occupied and unoccupied Ni e_g orbitals at full doping. This evolution of the density of states is essentially unchanged when the added electrons are introduced by doping with interstitial H or Li ions.

I. INTRODUCTION

Doping as a means to control the properties of a material is a well established practice. For conventional semiconductors, the conductivity can be manipulated through low density chemical doping and further altered via the field effect, which is the basis of operation in many electronic devices¹. In transition metal oxides (TMOs) coupling between lattice, charge, spin and orbital degrees of freedom often give rise to many competing phases and interesting properties. Via doping, one can engineer completely new phases, which in some cases possess vastly different properties, such as superconductivity in the cuprates² and recently, the nickelates³. More recently high-concentration doping effects have been observed in the interfacial layers of oxide heterostructures^{4,5} and superlattices⁶⁻¹¹. The short screening length in oxides and the high concentration makes such doped materials useful in nanoscale field-effect devices¹². Beyond interfacial effects, doping by substitution and interstitials allows one to access these doped phases in bulk, and in some instances, can reach the high densities observed at interfaces.

The well-known rare-earth nickelates, $R\text{NiO}_3$ ($R=\text{La-Lu}$), exhibit a rich temperature-composition phase diagram involving various charge and magnetic orderings that can be manipulated via doping^{13,14}. Except for LaNiO_3 , all $R\text{NiO}_3$ have a metal-to-insulator transition (MIT) accompanied by a symmetry lowering NiO₆ octahedral breathing distortion of the metallic $Pbmn$ structure resulting in an insulating $P2_1/n$ structure. For $R=\text{Ce-Nd}$, an antiferromagnetic (AFM) ordering coincides with the MIT and for $R=\text{Sm-Lu}$, the magnetic ordering occurs at a lower temperature. These materials are negative charge-transfer compounds in which the O-2p orbitals span the Fermi energy while overlapping the Ni-3d orbitals, resulting in strongly hybridized Ni-O states and unoccupied oxygen states: ligand holes^{15,16}. When electron doping the nickelates, these states are paramagnetic in the electron localization and are filled by

the added electrons.

Rare-earth nickelates have been electron doped at low concentrations via cation substitution^{17,18}, oxygen deficiency¹⁹⁻²², and electrolyte gating²¹⁻²³. An increase in resistivity observed with electron doping in rare-earth nickelates and other TMOs has been attributed to the localization of carriers^{24,25}. Electron doping at higher concentrations has been engineered through extreme oxygen deficiency^{20,26-30}, and through electron rearrangement at the interface within a superlattice^{6,7,11}. Recent experimental work has shown SmNiO₃ (SNO) can be electron doped at extremely high concentrations via intercalated hydrogen, small alkali and alkaline earth metal ions³¹⁻³³ and the doping can be easily reversed, unlike synthesis-based doping methods. SNO, a narrow-gap semiconductor with a MIT at $\sim 400\text{K}$, when fully doped becomes a Mott insulator with a gap on the order of 3 eV³¹, akin to electron-doped strontium titanate^{34,35}. Such a phase transition leads us to ask how the added electrons act at the nanoscale resulting in this insulating state. First-principles calculations are uniquely positioned to quantify the changes to the electronic structure and explore how and why the added electrons localize.

In this paper, we systematically investigate the effect of electron doping on room temperature SNO using first-principles calculations. We study the effect of added electrons on the structure, density of states, orbital occupation and magnetic moments of the nickel. Furthermore, we compare electron doping with added electrons and a positive compensating background charge to the inclusion of interstitial hydrogen and lithium to study the effect of the doping mechanism and separate the effect of the added electron from that of the doping mechanism. The added electrons do not introduce typical defect-like states³⁶ or a rigid shift of the Fermi energy, but rather localize on NiO₆ octahedra, moving an unoccupied state to the valence band. At a doping concentration of 1 added e^-/Ni , a novel insulating Mott phase of SNO is realized. These localized electrons open up a new class of materials and phases.

TABLE I. Structural and electronic properties of undoped SNO for various magnetic and charge orderings. For the bond disproportionated structures ($P2_1/n$), two NiO_6 octahedral volumes and magnetic moments are given. The non-disproportionated structures relax back to the high symmetry $Pbnm$ space group.

Magnetic Ordering	a (Å)	b (Å)	c (Å)	β (°)	NiO_6 Volume (Å ³)	Total Energy/Ni (eV)	Band Gap (eV)	Magnetic Moment (μ_B)
FM	5.328	5.553	7.600	90.031	10.99/9.69	-33.753	0.30	1.49/0.84
AFM(A)	5.332	5.548	7.594	90.053	11.38/9.35	-33.720	0.77	$\pm 1.61/\pm 0.27$
AFM(G)	5.278	5.818	7.421	90	10.62	-33.648	0.43	± 0.92
AFM(C)	5.270	5.812	7.441	90	10.62	-33.661	0.43	± 1.00
AFM(A)	5.300	5.724	7.481	90	10.52	-33.700	0.54	± 1.11

II. METHODS

Our first-principles DFT + U calculations are carried out using the Perdew-Burke-Ernzerhof (PBE) functional^{37,38} as implemented in VASP^{39,40} with an energy cutoff of 520 eV and the Sm_3, Ni_pv, O projector augmented wave (PAW)⁴¹ potentials provided with the VASP package. The Sm_3 PAW potential includes the f -electrons in the core. When treating interstitial hydrogen or lithium, we use the H or Li_sv potentials, respectively. In both DFT+U and dynamical mean field theory (DMFT) calculations of nickelates⁴²⁻⁴⁹, large values of U are used to reproduce thermodynamic quantities^{50,51}, intermediate values to reproduce insulating states, and small values to reproduce the low temperature magnetic properties⁴⁶⁻⁴⁹. We include a Hubbard U (within the rotationally invariant method of Liechtenstein et al.⁵²) with $U=4.6$ eV and $J=0.6$ eV. We choose this intermediate value as we are not focusing on low temperature or magnetic properties. Using a smaller U ($U=2.6$ eV), there is no qualitative change to the results (see Supp. Mat. sec. II⁵³). To accommodate the $a^-a^-c^+$ tilt pattern present for all phases of SNO, we used a 20 atom $\sqrt{2} \times \sqrt{2} \times 2$ supercell containing four Ni sites. To explore monoclinic phases a $\beta = 90.75^\circ$ was introduced in the starting structures. Structural relaxations of both the internal coordinates and the lattice parameters were carried out with Gaussian smearing with $\sigma = 0.1$ eV and a Monkhorst-Pack k -mesh of $6 \times 6 \times 4$ such that the forces are less than 0.005 eV/Å. The density of states calculations were performed using the tetrahedral method with Blöchl corrections⁵⁴. The projected density of states (PDOS) plots were generated using a Γ -centered k -mesh and the site projected scheme of pymatgen⁵⁵.

To study the effects of high-density electron doping, we increase the number of electrons while adding a uniform positive compensating background charge, or “jellium”⁵⁶. By using this method to model doping, we separate the effects stemming from the added electrons from the effects due to specifics of the doping mechanism. We explore the changes to electronic structure, Ni magnetic moments and local structural changes. When using a uniform positive compensating background charge, which is unphysical in itself, an unphysically large expansion

of the total volume (25% at a concentration of 1 added e^-/Ni) occurs. We, therefore, keep the total volume fixed while only relaxing the internal coordinates.

We added one electron to a $\sqrt{2} \times \sqrt{2} \times 2$ supercell of undoped SNO, a doping concentration of $\frac{1}{4} e^-/\text{Ni}$, relaxing only the internal coordinates. To clearly track the changes as the doping concentration increases, we used this relaxed structure as the starting structure for a doping concentration of $\frac{1}{2} e^-/\text{Ni}$. Thus, we added one electron per supercell to this structure and, again, relaxed only the internal coordinates. We continued in this manner until we reached a doping concentration of 4 electrons per supercell, or 1 e^-/Ni . For doping concentrations of $\frac{1}{4}$ and 1 e^-/Ni , we compare doping with a jellium background to interstitial hydrogen and lithium ions.

To find the low energy structure for added H atoms at a concentration of $\frac{1}{4} \text{H}/\text{Ni}$, we constructed a series of $\sqrt{2} \times \sqrt{2} \times 2$ supercells of undoped SNO with an added H atom placed in the plane bisecting the Ni-O-Ni bonds at the O for both an apical and basal sites. The H atoms were placed approximately $\pm 1\text{Å}$ away from the O along the crystallographic axes lying in the plane. For added Li, we followed the same procedure placing the Li atoms approximately $\pm 2\text{Å}$ away from the the apical or basal O. For the higher concentrations of added atoms, we followed a prescription analogous to that for added electrons: using the relaxed structure at a given concentration as the starting structure for the next highest concentration. We used the lowest energy position of the added ion from the $\frac{1}{4}$ doping case to determine where to place the additional ions^{32,33}. We performed relaxations of the internal coordinates with fixed volume, constrained to (110) epitaxial strain, as well as a full volume relaxation.

III. RESULTS AND DISCUSSION

A. Pristine SmNiO_3

Results for the properties of undoped SNO are reported in Table I. The lowest energy structure exhibits a bond disproportionation ($P2_1/n$), consistent with previous calculations^{24,46} (see Supp. Mat. sec. I⁵³ for electronic structure). As room temperature SNO does not

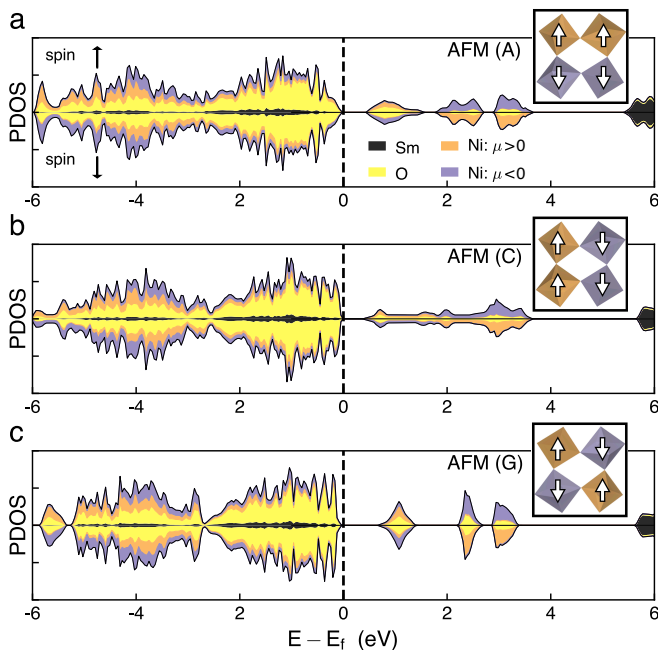


FIG. 1. Projected density of states (PDOS) for undoped SNO for the non-disproportionated cases in Table I, which are dominated by O (yellow) and Ni (orange for a positive magnetic moment and purple for a negative moment), while Sm (dark gray) has a minimal contribution. Insets: the four NiO_6 octahedra supercell with the Sm and O atoms omitted for clarity. The arrows schematically denote the spin of the occupied Ni e_g levels.

display a strong bond-disproportionation signature^{57,58}, we focus on metastable non-disproportionated structures. Initializing the magnitude of all Ni moments to be the same value of $5\mu_B$, we find that the structure relaxes back to a non-disproportionated orthorhombic ($Pbnm$) structure. We find three stable magnetic orderings: layered (A), columnar (C), and rock-salt (G), all of which share the same key features of their electronic structures (see Fig. 1). Both the occupied and unoccupied states within the vicinity of the Fermi level are dominated by O- $2p$ and Ni- $3d$ states with minimal Sm character. The large hybridization along with the O- $2p$ character in the unoccupied states is consistent with the electronic structure of a negative-charge transfer compound. The electronic structure has a more dispersive unoccupied states when neighboring Ni sites have aligned spins, Fig. 1 (a) & (b), stemming from an increased overlap of these states. The unoccupied DOS is comprised of Ni e_g states hybridized with O- $2p$ states. There are three unoccupied states per Ni site, two in one spin channel and one in the other. All Ni have a magnetic moment $\sim 1\mu_B$, suggesting the presence of low-spin Ni^{3+} . Considering the hybridized states as ones associated with the entire NiO_6 octahedron, it is more appropriate to write the electronic configuration as $d^8\bar{L}$, i.e. d^8 with an oxygen ligand-hole. Schematically, we view this as one occupied Ni e_g state (Fig. 1 insets)

B. Electron doped SmNiO_3 : Jellium Background

The PDOS of electron doped SNO is reported in Fig. 2; and the corresponding changes to local Ni moments and the structural changes are summarized in Fig. 3. Adding one electron to undoped SNO with G-type magnetic ordering (i.e. a doping concentration of $\frac{1}{4} e^-/\text{Ni}$) results in dramatic changes as the added electron localizes on one NiO_6 octahedron. Without a loss of generality, we break symmetry and localize the electron on the NiO_6 octahedron containing Ni(1) (inset Fig. 3). As shown in Fig. 2(b), the integrated unoccupied density of states of the feature closest to the Fermi energy decreases from 4 to 3: now with one unoccupied state associated with each of the unaffected Ni sites: Ni(2)-(4).

The spin-down Ni- $3d$ /O- $2p$ state associated with Ni(1) occupied by the added electron moves to the top of the valence band and is dominated by oxygen character essentially filling the ligand hole. The two remaining unoccupied Ni(1) $3d$ -states are spin-up e_g bands. These states, in dark purple, are pushed up in energy from $\sim 3\text{eV}$ to $\sim 3.5\text{eV}$ above the Fermi energy and show a noticeable decrease of hybridization with oxygen. The splitting of the features of the PDOS from Fig. 2(a) to (b) results from local symmetry breaking in the distorted structure. Due to Hund's coupling, Ni^{2+} is in a high-spin $S = 1$ configuration and the magnitude of the magnetic moment of Ni(1) increases from $0.92\mu_B$ to $1.65\mu_B$, while all moments on the other nickels remain relatively unchanged decreasing from $0.92\mu_B$ to 0.81 - $0.86\mu_B$ (Fig. 3(a)). The volume of the NiO_6 octahedron containing Ni(1) increases by $\sim 12\%$. To accommodate this expansion, all octahedra tilt more while the volumes of the three other octahedra slightly decrease as the total unit-cell volume is kept constant (Fig. 3(b) & (c)).

For two added electrons we find that the lowest energy configuration has zero net magnetization, thus the second added electron localizes on Ni(2), which has a positive magnetic moment resulting in no net magnetization of the cell while restoring some symmetry. The added electron occupies the spin-up Ni(2)- $3d$ /O- $2p$ state, moving it to the top of the valence band and, again, decreases the integrated unoccupied density of states by one. The new state in the valence band is again dominated by oxygen character while the remaining unoccupied (spin-down) Ni(2) states are pushed away from the Fermi energy and show a marked decrease in the oxygen hybridization (Fig. 2(c)). The magnetic moment of Ni(2) increases to $1.63\mu_B$ and the moment of Ni(1) decreases slightly to match. The moments of Ni(3) & (4) again decrease very slightly to $0.80\mu_B$. The two octahedra containing localized electrons are now the same so the volume of the octahedron containing Ni(1) decreases slightly and the volume of the octahedron containing Ni(2) increases such that both are $\sim 7\%$ larger than those of undoped SNO. All the octahedra tilt more while the volumes of the remaining octahedra slightly decrease. The third electron localizes on Ni(3), again

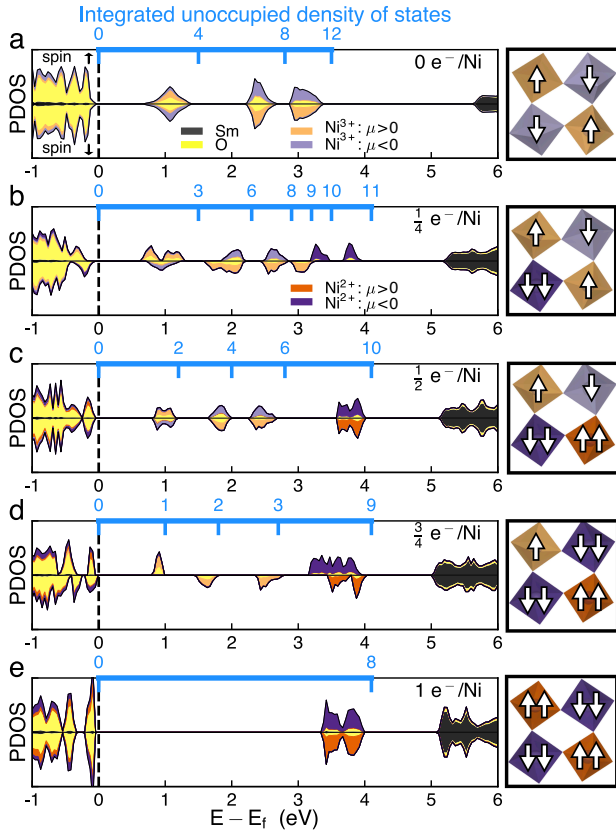


FIG. 2. (a)-(e) Spin-polarized PDOS for electron-doped SNO and schematic of Ni e_g occupation at concentrations of 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and 1 electron/Ni for an AFM G-type magnetic ordering. The integrated unoccupied DOS is displayed along the top axis for $E - E_f \in [0, 4.5]$. The element specific PDOS is shown in dark gray for Sm, yellow for O, orange and purple for Ni. Ni^{3+} with a positive moment is shown in light orange and with a negative moment in light purple and Ni^{2+} with a positive moment is shown in dark orange and with a negative moment in dark purple. The same color scheme is used for the octahedra in the panels to the right where the arrows schematically denote the spin of the occupied Ni e_g levels.

breaking symmetry, leaving only one unoccupied state within 1 eV of the Fermi energy as yet another oxygen dominated state is moved to the top of the valence band. The remaining unoccupied states associated with Ni(3) are pushed up in energy (Fig. 2(d)). At the same time, the magnetic moment of Ni(3) increases to $1.61\mu_B$, while the moments of Ni(1) & Ni(2) decrease to match. The moment of Ni(4) decreases to $0.75\mu_B$ as its octahedron is quite compressed by the other NiO_6 octahedra, which have all expanded.

Upon adding the fourth electron, localizing on Ni(4), we reach a doping concentration of $1 e^-/\text{Ni}$. The last remaining unoccupied state within 1 eV of the Fermi energy moves to the top of the valence band and the remaining states associated with Ni(4) are pushed up in energy. The remaining unoccupied Ni states have been pushed up in

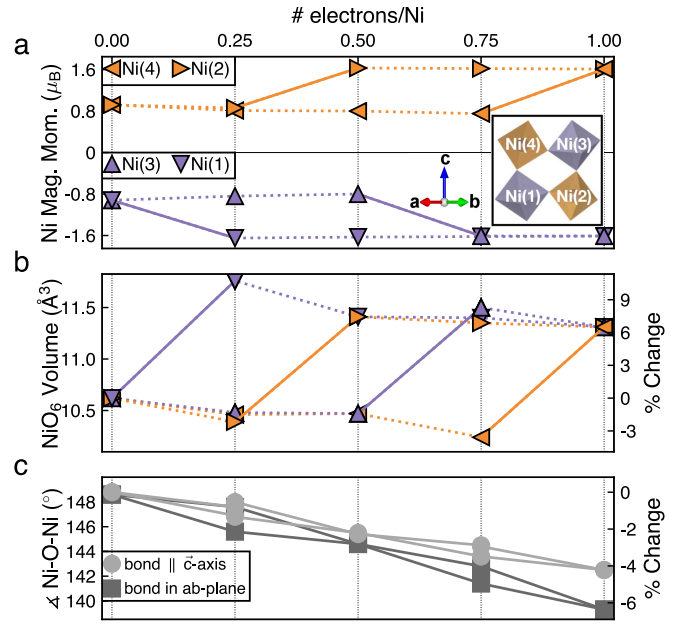


FIG. 3. The change in (a) the magnetic moment and (b) the NiO_6 octahedral volume (b) for each Ni site, with orange and purple denoting the Ni sites with a positive and negative moment, respectively. Inset: the calculation supercell relative to the crystallographic axes with each Ni numbered. (c) The change in the Ni-O-Ni angles with electron doping. The bonds parallel to the \bar{c} -axis are in light gray circles and those parallel to the \bar{ab} -plane are in dark gray squares.

energy and are now ~ 3.5 eV above the Fermi energy with negligible oxygen hybridization. Furthermore, all nickels have a similar magnetic moment and are situated in a similarly sized NiO_6 octahedron.

Although our calculations use the AFM (G) case as a starting point, we find similar results for electron doping the AFM (A) or (C) cases: for a given electron doping concentration, we find the lowest energy configuration has the lowest net magnetization. The localized electrons result in high-spin Ni^{2+} , consistent with Hund's rules. In fact we find the low-spin configuration is ~ 0.5 eV/Ni higher in energy. At a doping concentration of $1 e^-/\text{Ni}$, we find the energy difference from the top of the unoccupied Ni states to the top of the valence band is insensitive to magnetic order (see Fig. 4). The band width of the unoccupied Ni states increases when neighboring Ni sites have aligned spins, as seen in undoped SNO, resulting in the smallest band gap for FM ordering. The top of valence band, comprised of unoccupied states of undoped SNO now occupied by added electrons, is chiefly of oxygen character: the filled ligand holes. Minimal oxygen character is found in the unoccupied DOS: all Ni sites now have an d^8 configuration with no oxygen ligand holes (See Supp. Mat. sec. III⁵³ for band structures).

Even though the band gap remains relatively constant for a doping concentration of less than $1 e^-/\text{Ni}$, the integrated density of states of the unoccupied states de-

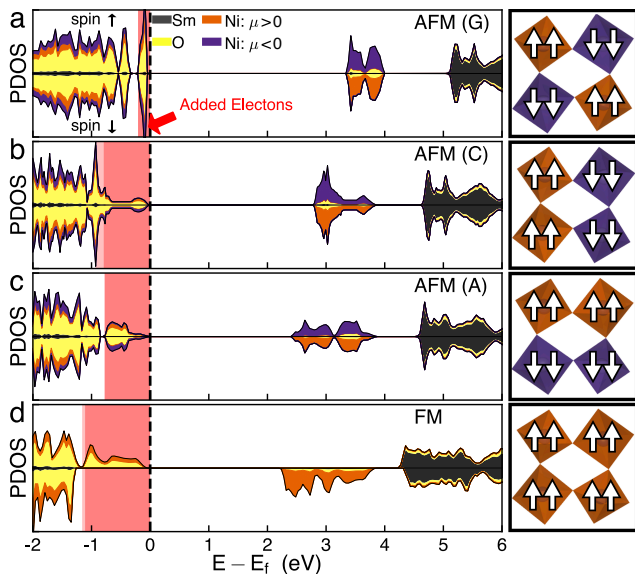


FIG. 4. Spin-polarized PDOS for electron-doped SNO and schematic of Ni e_g occupation at a concentrations of 1 electron/Ni for various magnetic orderings: (a) AFM G-type, (b) AFM C-type, (c) AFM A-type, (d) FM. The portion of the valence band associated with the added electrons is shaded in red, which is dominated by oxygen for all magnetic orderings. The states associated with the added electrons are separate from the original valence band for AFM-G and AFM-A orderings. For AFM-C and FM orderings, these state partially overlap with the top of the original valence band. Where they overlap they are shaded in a lighter red. The element specific PDOS is shown in dark gray for Sm, yellow for O, orange for Ni with a positive moment and purple for Ni with a negative moment. The arrows schematically denote the spin of the occupied Ni e_g levels.

creases as the doping concentration increases, consistent with the experimentally observed increase in resistivity as a function of doping. Ultimately, the experimentally observed resistivity saturates at a concentration of $1 e^-/Ni$, again consistent with the radical increase in the band gap. Thus, by modeling electron doping with a positive compensating jellium background, we have successfully captured the changes in the electronic structure and local properties of the NiO_6 octahedra. To better understand why this works, in the next section we compare these results with a jellium background to results with explicitly added ions.

C. Electron doped $SmNiO_3$: Interstitial Ions

To explore the effect of explicitly including ions in our calculations, we electron dope SNO by adding a neutral hydrogen or lithium. In both cases, the valence electron of the added ion localizes on a nearby NiO_6 octahedron resulting in a $\sim 10\%$ expansion of the octahedron similar to the jellium case. The lowest energy configuration

for both ions is to reside in the tetrahedral space formed between two NiO_6 octahedra that have a relative out-of-phase tilt while canting toward one another. In the case of hydrogen, the H^+ ion sits off center and binds to a basal oxygen (see Fig. S4)³². For lithium, the Li^+ ion is centered and is tetrahedrally coordinated by oxygen (see Fig. S5)³³. At a concentration of $\frac{1}{4} e^-/Ni$, one Ni-3d/O-2p state is occupied and moved to the top of the valence band, as we found in the jellium case (see Fig. 5(a-c)). Furthermore, the localized electron increases the magnetic moment of one Ni to $1.65\mu_B$ for an added H or $1.67\mu_B$ for an added Li, leaving the other moments relatively unchanged. For higher concentrations, the total magnetization is minimized as is observed in the jellium case. At a concentration of $1 e^-/Ni$ a large gap is observed similar to the jellium case (see Fig. 5(d-f)). Unlike the jellium case, the expansion changes the shape of the octahedron and prioritizes creating a binding environment for the ion. The only difference in the electronic structure arises from the local distortion of the NiO_6 octahedra due to the added ions causing a splitting of the unoccupied Ni e_g states. Finally, we allow the volume to relax the epitaxial constraint of the experimental thin films, namely an expansion of the (110) orthorhombic direction. We find a volume increase of $\sim 6\%$ and $\sim 11\%$ for added H and Li, respectively, in good agreement with experiment^{32,33}. This expansion does not impact the qualitative nature of the electronic structure, leading only to a small decrease in the band gap (see Supp. Mat. Fig. S6⁵³).

This analysis shows that for doping by intercalation the changes to the magnetic properties and electronic structure are captured by adding electrons with a uniform jellium background charge: it is only necessary to explicitly include the interstitial ions to study structural changes. This positions jellium background calculations to help us in predicting new phases of materials enabled by high-density doping, not only via electrolyte gating but via doping by intercalation and oxygen deficiency. New phases stemming from carrier localization have already been realized in several $RNiO_3$ ³³, and are expected to occur in other negative charge-transfer compounds where unoccupied ligand states would play a part in the electron localization.

IV. CONCLUSION

In summary, electron doping of SNO results in dramatic changes to the electronic structure. These changes to the electronic structure cannot be understood by rigidly shifting the Fermi energy, but stem from electron localization causing an on-site Mott transition. At a doping concentration of one electron per Ni, all Ni^{3+} are converted to Ni^{2+} resulting in a Mott gap between occupied Ni e_g states hybridized with O and unoccupied Ni e_g states of the opposite spin with negligible O hybridization. This behavior is captured in first-principles

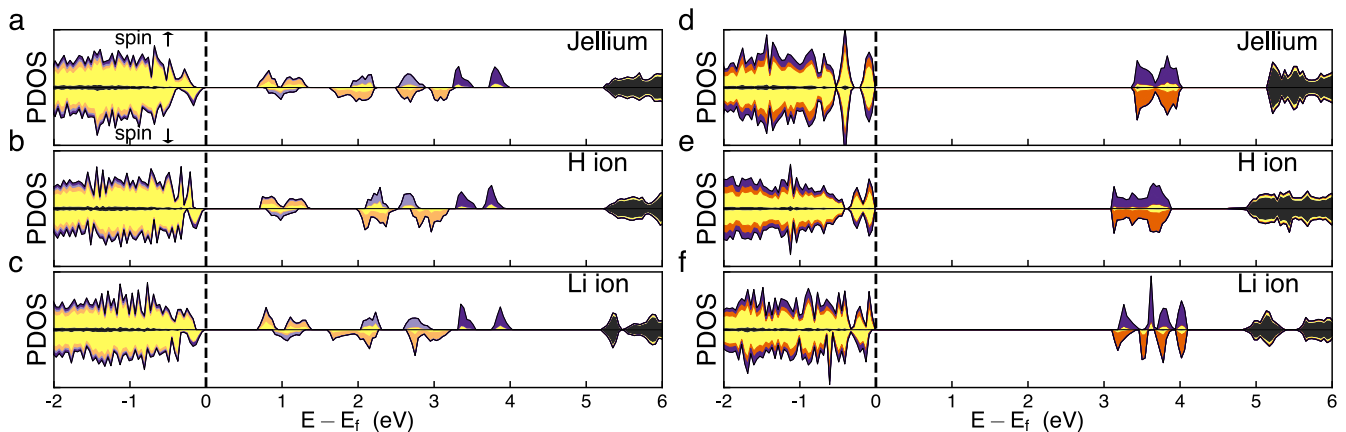


FIG. 5. Spin-polarized PDOS for electron-doped SNO with (a) $1/4$ added e^-/Ni with a positive compensating background charge; (b) $1/4$ H/Ni; (c) $1/4$ Li/Ni; (d) 1 added e^-/Ni with a positive compensating background charge; (e) 1 H/Ni; and, (f) 1 Li/Ni. The element specific PDOS is shown in dark gray for Sm, yellow for O, orange and purple for the Ni with a positive and negative moment, respectively. Ni^{3+} with a positive moment is shown in light orange and with a negative moment in light purple and Ni^{2+} with a positive moment is shown in dark orange and and with a negative moment in dark purple.

calculations with the added electrons accompanied by a jellium background, enabling the identification of new systems with these electron-doping-induced effects.

ACKNOWLEDGMENTS

We thank Cyrus E. Dreyer and Shriram Ramanathan for useful discussions and acknowledge financial support

from Office of Naval Research Grant N00014-17-1-2770.

-
- ¹ S. S. Li, *Semiconductor Physical Electronics*, 2nd ed. (Springer, 2006).
 - ² P. A. Lee, N. Nagaosa, and X.-G. Wen, *Reviews of Modern Physics* **78**, 17 (2006).
 - ³ D. Li, K. Lee, B. Y. Wang, M. Osada, S. Crossley, H. R. Lee, Y. Cui, Y. Hikita, and H. Y. Hwang, *Nature* **572**, 624627 (2019).
 - ⁴ A. Ohtomo and H. Y. Hwang, *Nature* **427**, 423 (2004).
 - ⁵ J. Mannhart and D. G. Schlom, *Science* **327**, 16071611 (2010).
 - ⁶ H. Chen, D. P. Kumah, A. S. Disa, F. J. Walker, C. H. Ahn, and S. Ismail-Beigi, *Physical Review Letters* **110**, 186402 (2013).
 - ⁷ H. Chen, A. J. Millis, and C. A. Marianetti, *Physical Review Letters* **111**, 116403 (2013).
 - ⁸ H. Chen, H. Park, A. J. Millis, and C. A. Marianetti, *Physical Review B* **90**, 245138 (2014).
 - ⁹ M. Marshall, A. Malashevich, A. S. Disa, M.-G. Han, H. Chen, Y. Zhu, S. Ismail-Beigi, F. Walker, and C. Ahn, *Physical Review Applied* **2**, 051001 (2014).
 - ¹⁰ A. S. Disa, D. P. Kumah, A. Malashevich, H. Chen, D. A. Arena, E. D. Specht, S. Ismail-Beigi, F. Walker, and C. H. Ahn, *Physical Review Letters* **114**, 026801 (2015).
 - ¹¹ X. Liu, M. Kotiuga, H.-S. Kim, A. T. NDiaye, Y. Choi, Q. Zhang, Y. Cao, M. Kareev, F. Wen, B. Pal, J. W. Freeland, L. Gu, D. Haskel, P. Shafer, E. Arenholz, K. Haule, D. Vanderbilt, K. M. Rabe, and J. Chakhalian, *PNAS*, *in press* (2019).
 - ¹² C. H. Ahn, J.-M. Triscone, and J. Mannhart, *Nature* **424**, 10151018 (2003).
 - ¹³ S. Middey, J. Chakhalian, P. Mahadevan, J. Freeland, A. Millis, and D. Sarma, *Annual Review of Materials Research* **46**, 305 (2016).
 - ¹⁴ S. Catalano, M. Gibert, J. Fowlie, J. Íñiguez, and J.-M. Triscone, *Reports on Progress in Physics* **81**, 046501 (2018).
 - ¹⁵ V. Bisogni, S. Catalano, R. J. Green, M. Gibert, R. Scherwitzl, Y. Huang, V. N. Strocov, P. Zubko, S. Balandeh, J.-M. Triscone, and et al., *Nature Communications* **7**, 13017 (2016).
 - ¹⁶ K. Haule and G. L. Pascut, *Scientific Reports* **7**, 10375 (2017).
 - ¹⁷ J. L. Garcia-Munoz, M. Suaaidi, M. J. Martinez-Lope, and J. A. Alonso, *Physical Review B* **52**, 13563 (1995).
 - ¹⁸ I. Vobornik, L. Perfetti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, *Physical Review B* **60**, R8426R8429 (1999).
 - ¹⁹ I. Nikulin, M. Novojilov, A. Kaul, S. Mudretsova, and S. Kondrashov, *Materials Research Bulletin* **39**, 775791 (2004).

- ²⁰ M. Kawai, S. Inoue, M. Mizumaki, N. Kawamura, N. Ichikawa, and Y. Shimakawa, *Applied Physics Letters* **94**, 082102 (2009).
- ²¹ J. Shi, S. D. Ha, Y. Zhou, F. Schoofs, and S. Ramanathan, *Nature Communications* **4** (2013), 10.1038/ncomms3676.
- ²² Y. Dong, H. Xu, Z. Luo, H. Zhou, D. D. Fong, W. Wu, and C. Gao, *APL Materials* **5**, 051101 (2017).
- ²³ R. Scherwitzl, P. Zubko, I. G. Lezama, S. Ono, A. F. Morpurgo, G. Catalan, and J.-M. Triscone, *Advanced Materials* **22**, 55175520 (2010).
- ²⁴ Q. Liu, G. M. Dalpian, and A. Zunger, *Physical Review Letters* **122**, 106403 (2019).
- ²⁵ P. Yoo and P. Liao, *Mol. Syst. Des. Eng.* **3**, 264 (2018).
- ²⁶ M. Crespín, P. Levitz, and L. Gatineau, *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **79**, 11811194 (1983).
- ²⁷ M. J. Sayagús, M. Vallet-Reg, A. Caneiro, and J. M. González-Calbet, *Journal of Solid State Chemistry* **110**, 295304 (1994).
- ²⁸ I.-C. Tung, G. Luo, J. H. Lee, S. H. Chang, J. Moyer, H. Hong, M. J. Bedzyk, H. Zhou, D. Morgan, D. D. Fong, and et al., *Physical Review Materials* **1**, 053404 (2017).
- ²⁹ L. Wang, S. Dash, L. Chang, L. You, Y. Feng, X. He, K.-j. Jin, Y. Zhou, H. G. Ong, P. Ren, and et al., *ACS Applied Materials & Interfaces* **8**, 97699776 (2016).
- ³⁰ M. Kotiuga, Z. Zhang, J. Li, F. R., H. Zhou, R. Sutarto, F. He, Q. Wang, Y. Sun, Y. Wang, N. A. Aghamiri, S. B. Hancock, L. P. Rokhinson, D. P. Landau, Y. Abate, J. W. Freeland, R. Comin, S. Ramanathan, and K. M. Rabe, *PNAS*, *in press* (2019).
- ³¹ J. Shi, Y. Zhou, and S. Ramanathan, *Nature communications* **5**, 4860 (2014).
- ³² Z. Zhang, D. Schwanz, B. Narayanan, M. Kotiuga, J. Dura, M. Cherukara, H. Zhou, J. Freeland, J. Li, R. Sutarto, F. He, C. Wu, J. Zhu, Y. Sun, K. Ramadoss, S. Nonnenmann, N. Yu, R. Comin, K. Rabe, S. Sankaranarayanan, and S. Ramanathan, *Nature* **553** (2018).
- ³³ Y. Sun, M. Kotiuga, D. Lim, B. Narayanan, M. Cherukara, Z. Zhang, Y. Dong, R. Kou, C.-J. Sun, Q. Lu, and et al., *Proceedings of the National Academy of Sciences* **115**, 96729677 (2018).
- ³⁴ L. Bjaalie, A. Janotti, B. Himmetoglu, and C. G. Van de Walle, *Physical Review B* **90**, 195117 (2014).
- ³⁵ A. Janotti, J. B. Varley, M. Choi, and C. G. Van de Walle, *Physical Review B* **90**, 085202 (2014).
- ³⁶ C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, *Reviews of Modern Physics* **86**, 253 (2014).
- ³⁷ J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
- ³⁸ J. P. Perdew, K. Burke, and M. Ernzerhof, “Erratum: Generalized gradient approximation made simple (*Physical Review Letters* (1996) 77 (3865)),” (1997).
- ³⁹ G. Kresse and J. Furthmüller, *Physical Review B* **54**, 11169 (1996).
- ⁴⁰ G. Kresse and D. Joubert, *Physical Review B* **59**, 1758 (1999).
- ⁴¹ P. E. Blöchl, *Physical Review B* **50**, 17953 (1994).
- ⁴² H. Park, A. J. Millis, and C. A. Marianetti, *Physical Review Letters* **109**, 156402 (2012).
- ⁴³ H. Park, A. J. Millis, and C. A. Marianetti, *Physical Review B* **89**, 245133 (2014).
- ⁴⁴ H. Park, A. J. Millis, and C. A. Marianetti, *Physical Review B* **90**, 235103 (2014).
- ⁴⁵ A. Subedi, O. E. Peil, and A. Georges, *Physical Review B - Condensed Matter and Materials Physics* **91**, 075128 (2015).
- ⁴⁶ J. Varignon, M. N. Grisolia, J. Íñiguez, A. Barthélémy, and M. Bibes, *npj Quantum Materials* **21** (2017).
- ⁴⁷ A. Mercy, J. Bieder, J. Íñiguez, and P. Ghosez, *Nature Communications* **8**, 1677 (2017).
- ⁴⁸ A. Hampel and C. Ederer, *Physical Review B* **96**, 165130 (2017).
- ⁴⁹ A. Hampel, P. Liu, C. Franchini, and C. Ederer, *npj Quantum Materials* **4**, 5 (2019).
- ⁵⁰ L. Wang, T. Maxisch, and G. Ceder, *Physical Review B* **73**, 195107 (2006).
- ⁵¹ Y.-L. Lee, J. Kleis, J. Rossmeisl, and D. Morgan, *Physical Review B* **80**, 224101 (2009).
- ⁵² A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Physical Review B* **52**, R5467 (1995).
- ⁵³ See Supplemental Material at [URL will be inserted by publisher] for DOS of disproportionated SNO; effects of $U = 2.6$ eV; band structure of doped structures; and, structures with explicit ions along with additional DOS.
- ⁵⁴ P. E. Blöchl, O. Jepsen, and O. K. Andersen, *Physical Review B* **49**, 16223 (1994).
- ⁵⁵ S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, and G. Ceder, *Computational Materials Science* **68**, 314319 (2013).
- ⁵⁶ This achieved by increasing the flag NELECT in our VASP calculations.
- ⁵⁷ J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, M. A. G. Aranda, and M. T. Fernández-Díaz, *Journal of the American Chemical Society* **121**, 4754 (1999).
- ⁵⁸ M. Medarde, C. Dallera, M. Grioni, B. Delley, F. Vernay, J. Mesot, M. Sikora, J. A. Alonso, and M. J. Martínez-Lope, *Physical Review B* **80**, 245105 (2009).