Bulk NdNiO$_2$ is thermodynamically unstable with respect to decomposition while hydrogenation reduces the instability and transforms it from metal to insulator

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The quest for a Ni-based oxide analog to cuprate Cu$_2^+$(d$^9$) superconductors was long known to require a reduced form Ni$^{1+}$(d$^9$) as in A$^{3+}$Ni$^{3+}$O$_2$, being an extreme oxygen-poor form of the usual A$^{3+}$Ni$^{3+}$O$_3$ compound. Through CaH$_2$ chemical reduction of a parent R$^{3+}$Ni$^{3+}$O$_3$ perovskite form, superconductivity was recently achieved in Sr-doped NdNiO$_2$ on SrTiO$_3$ substrate. Using density functional theory (DFT) calculations, we find that stoichiometric NdNiO$_2$ is significantly unstable with respect to decomposition into 1/2[Nd$_2$O$_3$ + NiO + Ni] with exothermic decomposition energy of +176 meV/atom, a considerably higher instability than that for common ternary oxides. This poses the question if the stoichiometric NdNiO$_2$ nickelate compound used extensively to model the electronic band structure of Ni-based oxide analog to cuprates and found to be metallic is the right model for this purpose. To examine this, we study via DFT the role of the common H impurity expected to be present in the process of chemical reduction needed to obtain NdNiO$_2$. We find that H can be incorporated exothermically, i.e., spontaneously in NdNiO$_2$, even from H$_2$ gas. In the concentrated limit, such impurities can result in the formation of a hydride compound NdNiO$_2$H, which has significantly reduced instability relative to hydrogen-free NdNiO$_2$ (decomposition energy of +80 meV/atom instead of +176 meV/atom). Interestingly, the hydrogenated form has a similar lattice constant as the pure form (leading to comparable X-ray diffraction patterns), but unlike the metallic character of NdNiO$_2$, the hydrogenated form is predicted to be a wide gap insulator thus, requiring doping to create a metallic or superconducting state, just like cuprates, but unlike unhydrogenated nickelates. While it is possible that hydrogen would be eventually desorbed, the calculation suggests that pristine NdNiO$_2$ is hydrogen-stabilized. One must exercise caution with theories predicting new physics in pristine stoichiometric NdNiO$_2$ as it might be an unrealizable compound. Experimental examination of the composition of real NdNiO$_2$ superconductors and the effect of hydrogen on the superconductivity is called for.
I. Introduction

The recent observation of superconductivity in Sr-doped NdNiO$_2$ grown on SrTiO$_3$ substrate [1] raised hopes for a new paradigm relative to cuprate superconductivity, but along with it also posed questions about the importance of intrinsic factors (the basic chemical constitution and bonding in nickelates vs. cuprates), as opposed to extrinsic factors (the role of doping, defects, or non-stoichiometry) in comparing the two systems. Interest in nickelates as a comparative paradigm to cuprates has been based on the ability to chemically reduce the stable A$^{3+}$Ni$^{3+}$(d$^7$)O$_3$ compound to A$^{3+}$Ni$^{1+}$(d$^9$)O$_2$, comparing the latter to the isoelectronic A$_2$$^{3+}$Cu$^{2+}$(d$^9$)O$_4$ compound. The literature[2-13] electronic structure calculations on NdNiO$_2$ were consequently based on the ideal stoichiometric and pristine P$_d$/mmm NdNiO$_2$ structure with the Ni$^{1+}$(d$^9$) ion. These calculations, whether using density functional[2-10] or adding dynamical correlation[6,10-13] found for nonmagnetic [2,3,9,10], or antiferromagnetic/ferromagnetic[4-8], or paramagnetic[6,10-12] NdNiO$_2$ a metallic ground state, revealing the first difference with respect to cuprates: the former requires doping to become metallic, unlike the nickelates. Such theoretical investigations of a metallic NdNiO$_2$ phase formed the basis for predicting the role of NdNiO$_2$/SrTiO$_3$ interface in the superconducting properties[3] and the effect of Sr doping[7]. However, recent experimental advances demonstrate that undoped freestanding NdNiO$_2$ has insulator-like temperature-dependent resistivity[14]. Moreover, recent studies indicate that NdNiO$_2$ samples are often non-stoichiometric, for instance, nickel-deficient NdNi$_{1.2}$O$_2$[14], O-rich NdNiO$_{2+y}$[15], and show the coexistence of different phases such as Ni metal and NdNi$_2$O$_3$[16] or NdNiO$_2$ and NdNiO$_3$[17]. These results thus raise the question if pristine stoichiometric NdNiO$_2$ can be used as a model for d$^9$ superconductivity.

DFT is able to assess the stability of a compound with respect to decomposition into competing phases by using the convex hull construct, whereby the lowest formation energy at each composition is contrasted with the formation energies of combinations of competing phases with equivalent composition. Compounds located above the convex hull by an amount $\varepsilon$ are predicted to have exothermic decomposition energy $\varepsilon$. Recognizing that compounds with small metastability energy may still be made as potentially long-lived metastable phases, one generally considers finite but small metastability as potentially realizable [18]. Motivated by this, herein, we study the stability of NdNiO$_2$ with respect to decomposition to competing phases. We find that pure stoichiometric NdNiO$_2$ is a highly unstable phase with the decomposition energy of +176 meV/atom (or +704 meV/formula unit (f.u.)) with respect to 1/2[Nd$_2$O$_3$ + NiO + Ni], questioning if stoichiometric and pristine NdNiO$_2$ compound is ever realized. Our analysis of 3262 experimentally observed ternary oxides (see Supplemental Material[19]) listed in Materials Project[20] demonstrates (see Fig. 1a) that the vast majority of experimentally observed compounds have DFT decomposition energy $\varepsilon$ less than 100 meV/atom above the calculated convex hull[18], so it looks that pristine NdNiO$_2$ is somewhat extra unstable.

Given the distinguishing feature of synthesis of NdNiO$_2$ via chemical reduction of NdNiO$_3$ involving CaH$_2$ or NaH [1,14-16,21-24], and inspired by results of Si et al. on H impurities in AniO$_2$[25], we undertook a broader stability analysis to include the effect of H incorporation into NdNiO$_2$. We find that hydrogen spontaneously incorporated in NdNiO$_2$, resulting in the formation of the hydrogenated and insulating NdNiO$_2$H compound. The resulting compound is significantly more stable with respect to decomposition than pure NdNiO$_2$ and has similar lattice constants (comparable XRD) to NdNiO$_2$. These results (i) suggest that the experimentally NdNiO$_2$ might have a large, hopefully, the detectable concentration of H impurity, which could affect its properties significantly. To the extent that this is so, (ii) this would point to the importance of considering extrinsic factors (such as spontaneous impurity incorporation [26,27]) in assessing the relevant electronic structure of such
compounds; (iii) caution theoreticians from the prediction of new physics and superconductivity mechanisms based on the potentially unrealizable base metallic NdNiO$_2$ compound.

![Graph](image_url)

**Figure 1.** Distribution of energy above the DFT convex hull for 3262 experimentally reported ternary oxides (see details on a dataset in Supplemental Material[19]) using the data available in the Materials Project database (accessed on March 20, 2021; Note that numbers available in Materials Project are changing with time)[20]. The red arrow depicts the energy above the convex hull predicted for NdNiO$_2$ (P$_4$/mmm) in this work using accurate DFT with SCAN functional (i.e., one able to accurately treat localized nature of Ni-$d$ states) calculations and global screening of magnetic orders in competing phases.

II. Methods

The calculations are performed using pseudopotential plane-wave DFT with recently developed SCAN exchange-correlation (XC) functional[28] as implemented in the Vienna Ab Initio Simulation Package (VASP)[29-31]. SCAN does not require the Hubbard-like U parameter to reproduce finite band gaps in both AFM and PM binary and ternary oxides[32-35] and has been shown to describe the formation heats of compounds with higher accuracy than other XC functionals[36]. In all calculations, we treat the f electrons of Nd as part of the core electrons. The cutoff energies for the plane-wave basis are set to 500 eV for final calculations and 550 eV for volume relaxation. Atomic relaxations are performed until the internal forces are smaller than 0.01 eV/Å. Γ-centered Monkhorst-Pack grids[37] with 10,000 k-points per reciprocal atom are used in all calculations. For compounds containing less than 9 metal atoms per primitive cell, we explore ferromagnetic, nonmagnetic, and all antiferromagnetic spin configurations that uniquely decorate cells containing 1 or 2 f.u. For compounds constraining more than 8 metal atoms, only ferromagnetic spin initialization has been used. For NdNiO$_2$ and NdNiO$_2$H, all unique antiferromagnetic spin configurations in the supercells up to 4 f.u. are tested. For the compounds containing over 8 atoms, only ferromagnetic and nonmagnetic spin configurations are used. For each structure and magnetic order, we also apply random atomic displacements with a maximum amplitude of 0.1 Å to ensure that the system is not trapped at local energy minima. The computed results are visualized using the Vesta[38] and pymatgen library [39].
III. Results and Discussion

A. NdNiO$_2$ is substantially unstable with respect to decomposition: calculation of the ternary convex hull

Using the O$_2$ molecule as a reference state for oxygen and stoichiometric compounds available in Inorganic Crystal Structure Database (ICSD)[40] and Materials Project database[20], we consider 105 different competing phases listed in Supplemental Material[19]. By calculating DFT total energies for these compounds, we obtain the convex hull indicating which Nd-Ni-O compounds are stable (residing on the convex hull) with respect to any linear combination of competing phases or unstable by a given amount (placed above the convex hull by that amount). In this way, 15 out of 105 potential competing phases are found to be stable ground states: O$_2$, Ni, Nd, NiO, Ni$_3$O$_4$, NdO$_2$, Nd$_2$O$_3$, NdNi, NdNi$_2$, Nd$_3$Ni, NdNi$_5$, Nd$_3$Ni$_{19}$, NdNi$_3$, Nd$_2$Ni$_7$, and NdNiO$_3$. The other competing phases are above the convex hull with the lowest energy decomposition reactions summarized in Table I. Notably, even the lowest energy magnetic NdNiO$_2$ configuration is above the convex hull (unstable) by +176 meV/atom or +704 meV/f.u. with respect to decomposition to 0.5[Nd$_2$O$_3$ + NiO+ Ni(m)]. There is also a number of other decomposition reactions that have lower decomposition energies (see Fig. 1). While some oxides that are above the convex hull can be realized, as shown in Fig. 1, over 92% of experimentally observed oxides have the decomposition energy below that of NdNiO$_2$ according to the data available in the Materials Project. It should also be noted the ICSD database, which is used in Materials Project for experimental entries, has a number of compounds that are predicted by epitaxial growth, observed only under extreme conditions, and compounds that were shown to be incorrect after more detailed analysis of structural properties. Hence, the high decomposition energy of NdNiO$_2$ suggests that stoichiometric NdNiO$_2$ is a rather unstable phase, raising the question if the compound realized experimentally is indeed undoped pristine stoichiometric NdNiO$_2$.

![Nd-Ni-O convex hull](image)

**Figure 2.** Summary of Nd-Ni-O convex hull. (a) Nd-Ni-O convex hull showing the stable phases (O$_2$, Ni, Nd, NiO, Ni$_3$O$_4$, NdO$_2$, Nd$_2$O$_3$, NdNi, NdNi$_2$, Nd$_3$Ni, NdNi$_5$, Nd$_3$Ni$_{19}$, NdNi$_3$, Nd$_2$Ni$_7$, and NdNiO$_3$) as blue dots. (b) Main decomposition reactions for NdNiO$_2$ and corresponding decomposition energies ($\Delta H_d$). The results are presented for the SCAN XC functional. The decomposition energies for other compounds are shown in Table I.
Table I. Summary of Nd-Ni-O convex hull results including absolutely stable (on hull compounds that do not decompose) as well as metastable (above hull) compounds. Convex hull includes only the lowest energy structure for each composition.

| Compound | Space group | Energy above convex hull (meV/atom) | Decomposition products |
|----------|-------------|-------------------------------------|------------------------|
| Ni       | Fm-3m       | 0                                   | -                      |
| Nd       | P6/m/mmc    | 0                                   | -                      |
| O₂       | molecule    | 0                                   | -                      |
| NiO      | C2          | 0                                   | -                      |
| Ni₃O₄    | Cmmm        | 0                                   | -                      |
| Nd₂O₃    | la-3        | 0                                   | -                      |
| NdO₂     | C2/m        | 0                                   | -                      |
| NdNi     | Cmcm        | 0                                   | -                      |
| NdNi₂    | P1          | 0                                   | -                      |
| NdNi₃    | R-3m        | 0                                   | -                      |
| NdNi₅    | P6/m/mmc    | 0                                   | -                      |
| Nd₃Ni    | Pnma        | 0                                   | -                      |
| Nd₅Ni₁₉  | P6/m/mmc    | 0                                   | -                      |
| Nd₂Ni₇   | P6/m/mmc    | 0                                   | -                      |
| NdNiO₃   | P2₁/c       | 0                                   | -                      |
| Nd₄Ni₃O₁₀| P2₁/c       | 1                                   | NdNiO₃, Nd₂O₃, NiO     |
| Nd₇Ni₃   | P6/m/mmc    | 3                                   | Nd₃Ni, NdNi           |
| NiO₂     | C2/m        | 4                                   | Ni₃O₄, O₂             |
| Nd₂Ni₁₇  | P6/m/mmc    | 17                                  | NdNi₅, Ni             |
| Nd₂NiO₄  | Cmce        | 19                                  | Nd₂O₃, NiO            |
| NdO      | P6/m/mmc    | 62                                  | Nd₂O₃, Nd             |
| Ni₅O₆    | C2/m        | 64                                  | Ni₃O₄, NiO            |
| Ni₅O₇    | P-1         | 70                                  | Ni₃O₄, NiO            |
| Ni₁₅O₁₆  | la-3m       | 72                                  | Ni₃O₄, NiO            |
| Ni₉O₁₀   | P-1         | 73                                  | Ni₃O₄, NiO            |
| Nd₄Ni₃O₈ | l4/m/mmc    | 86                                  | Nd₂O₃, Ni, NiO        |
| Nd₂O₅    | C2/c        | 92                                  | NdO₂, O₂             |
| Ni₅O₁₁   | P1          | 96                                  | Ni₃O₄, O₂             |
| Ni₅O₄    | P1          | 165                                 | Ni, NiO              |
| NdNiO₂   | P4/m/mmc    | 176                                 | Nd₂O₃, Ni, NiO        |
| NdO₃     | P-3         | 285                                 | NdO₂, O₂             |
| Nd₄Ni    | Fd-3m       | 364                                 | Nd₃Ni, Nd             |
B. Hydrogenation diminishes the instability of NdNiO₂

Hydrogen as a common additive solute element in NdNiO₂ and its bonding to the lattice: Hydrogen is one of the most common solutes in insulating solids, which often defines the n- and p-type nature of the compounds even under normal conditions owing to universal pinning of H transition level in insulators[41-44]. The most famous examples of such behaviors are ZnO and SnO₂, which are intrinsic n-type insulators with hydrogen impurities limiting the possibility to realize p-type insulators [41-44]. In general, hydrogen bonds to anion in n-type compounds (e.g., H-O bond in ZnO[43]) and to cation in p-type compounds[42,45]. In specific cases, hydrogen forms multicenter bonds such as H₂O in MgO or ZnO [45], where instead of forming a single bond, it becomes a center of a complex multiple atomic bond inducing charge density rearrangement on multiple atoms. Since NdNiO₂ is usually synthesized by the reduction of the stable parent NdNiO₃ perovskite in the H-rich environment[1,14-16,21-23], hydrogen impurities can be formed in NdNiO₂. To verify it and identify the lowest energy sites, we screen over 35 randomly generated interstitial H positions in NdNiO₂ (for simplicity, the screening calculations are performed using PBE XC functional) and find that in the lowest energy configuration H bonds to Ni atoms forming two Ni-H bonds with a bond length of 1.58 Å (Fig. 3a). In such configuration, H accepts electrons from the Ni atoms as evidenced by the charge density difference plot (see Fig. 3a,b), \( \Delta \rho = \rho(\text{NdNiO}_2: \text{H}) - \rho(\text{NdNiO}_2) - \rho(\text{H}) \), where H refers to atomic hydrogen (spin-polarized) and each charge density \( \rho \) is computed for the lowest energy configuration of H in 32 f.u. NdNiO₂ supercell. These results imply that H acts as the acceptor, restoring part of the charge imbalance caused by the chemical reduction of \( A^{3+}\text{Ni}^{3+}(d^7)\text{O}_3 \) compound to \( A^{3+}\text{Ni}^{1+}(d^9)\text{O}_2 \).

![Figure 3](image-url)

**Figure 3.** 32 f.u. of NdNiO₂ containing 1 H impurity: (a) Difference in wavefunction squared – i.e., NdNiO₂:H – NdNiO₂ -H, where H refers to atomic hydrogen (spin-polarized) and each charge density \( \rho \) is computed for lowest energy configuration of H in 32 f.u. NdNiO₂ supercell, illustrating the nature of bonding. Yellow and blue isosurfaces correspond to charge density increase and charge density reduction, respectively. The isosurface is set up at 0.01 e/bohr³. Only the atomic planes in the vicinity of H are shown. (b) The corresponding counter-plot for the difference in wavefunction squared shown in (a).
**Spontaneous hydrogen incorporation into NdNiO$_2$:** While it usually costs energy to dissolve hydrogen into traditional oxides[41-44], for NdNiO$_2$, the reaction energy $\Delta H_R$ of H addition to NdNiO$_2$ from H$_2$ gas, i.e.,

$$\Delta H_R = E(\text{NdNiO}_2:H) - E(\text{NdNiO}_2) - 1/2\text{H}_2(g)$$

is negative (-350 meV), as found here by DFT calculations for 32 f.u. of NdNiO$_2$ containing one interstitial H. This thus suggests that in the presence of an H$_2$-rich environment, H will be spontaneously (exothermically) introduced into NdNiO$_2$. Hence, hydrogen insertion can reduce the instability of NdNiO$_2$-like structure in the limit of high H concentration, i.e., the formation of (NdNiO$_2$)$_n$H$_m$ compound can be observed as the result of hydrogen interaction with NdNiO$_2$. To reveal that this type of additive/solute can be formed in large H concentrations, we consider the possibility of the formation of (NdNiO$_2$)$_n$H$_m$ with m=n=1 and find that indeed reaction energy of NdNiO$_2$ + 1/2 H$_2$(g) → NdNiO$_2$H is highly negative (-300 meV) (see Fig. 4). These data thus demonstrate that H can be not only a common solute additive but can also lead to the formation of a stoichiometric H-rich NdNiO$_2$H compound, which is more stable with respect to decomposition than hydrogen free NdNiO$_2$. Importantly, the predicted reaction energy for hydrogen insertion into NdNiO$_2$ is comparable to that in the recent study of H insertion into ABO$_2$[25]. The H insertion changes the stability of NdNiO$_2$ itself. As illustrated in Fig. 4, NdNiO$_2$ decomposes to Ni, NiO, and Nd$_2$O$_3$ with the decomposition energy of 176 meV/atom, while although NdNiO$_2$H is still not the ground state – the compound decomposes to Ni, NiO, Nd$_2$O$_3$, and H$_2$, the corresponding decomposition energy is only 80 meV/atom. While this work does not describe the full range of m/n ratio, the above results intimate that it is likely to observe NdNiO$_2$H than NdNiO$_2$ especially taking into account that NdNiO$_2$ is usually synthesized by reduction of NdNiO$_3$ in H-rich environment and pure stochiometric NdNiO$_2$ is a highly unstable phase. We note that the formation of NdNiO$_2.3$H$_{0.7}$ has already been detected experimentally[21], suggesting that NdNiO$_2$ indeed can take a large concentration of H defects. It should be noted that herein the results are presented for bulk NdNiO$_2$ and it is possible that in some experimental studies substrate or competing phases (e.g., SrTiO$_3$) can modify NdNiO$_2$ stability and H intake.

![Reduction of NdNiO$_3$](image)

**Figure 4.** Reduction of NdNiO$_3$ and main decomposition reaction for NdNiO$_2$, demonstrating that NdNiO$_2$ is unstable with respect to decomposition to Nd$_2$O$_3$, NiO, and Ni. Hydrogenation of NdNiO$_2$ reduces the instability of the compound, but even NdNiO$_2$H is still unstable with respect to competing phases.
NdNiO$_2$H and NdNiO$_2$ have comparable lattice constants leading to similar expected X-ray diffraction patterns: One may think that insertion of large H concentration into NdNiO$_2$ leads to a noticeable structural change leading to a new structure which can be detected in the typical XRD analysis of the sample. However, H is a small solute which usually does not provide significant structural changes. The SCAN lattice constants of NdNiO$_2$H are 3.95 and 3.35 Å, which are only slightly larger (within the typical difference range of DFT and experimental lattice constants) than the SCAN values for NdNiO$_2$ (3.91 and 3.27 Å) and corresponding experimental lattice constants (e.g., 3.9 and 3.3 Å[21], or 3.91 and 3.24 Å[14], or 3.92 and 3.28 Å[15]). The main XRD peaks for NdNiO$_2$ and NdNiO$_2$H almost overlap with each other (see Supplemental Material[19]). While a minor difference of lattice vectors between experimental NdNiO$_2$ and theoretical NdNiO$_2$ and NdNiO$_2$H is reflected in the position of the minor peaks in the XRD spectra as compared to the experimental structure, such peaks are usually not used to identify the compound, and it is well known that the presence of H usually cannot be detected by XRD. If the lattice parameters of NdNiO$_2$ and NdNiO$_2$H are aligned to experimental lattice constants, both NdNiO$_2$ and NdNiO$_2$H have the same XRD spectra. Interestingly, NdNiO$_{2.3}$H$_{0.7}$ and NdNiO$_2$ have a more pronounced difference in XRD spectra[21], which is likely due to deviation from stoichiometry on the O site and not caused by H impurity. These results thus demonstrate that while the formation of NdNiO$_2$H is spontaneous its detection is not possible with standard XRD and more accurate methods should be applied. Moreover, since NdNiO$_2$ is rarely synthesized in pure form, e.g., experimentally observed NdNiO$_2$ samples are nickel deficient [14], O-rich [15] or have coexistence of different phases [16,17], the determination of exact composition for different samples is critical step in understanding better current experimental observations.

Possible role of substrate: Examining the simplest substrate effect of potential increase in lattice mismatch between the SrTiO$_3$ substrate due to the presence of H in the NdNiO$_2$ film suggest that this factor may not be a concern. Indeed, the DFT calculated in-plane lattice constant of NdNiO$_2$ changes by H incorporation by only 0.03 Å, having a negligible contribution to the altered strain and altered stabilization of a hydrogen-free NdNiO$_2$ on SrTiO$_3$. However, in general, it is essential to further understand the potential role of the substrate and spontaneous off-stoichiometry in the stability of NdNiO$_2$ and H insertion.

C. Effect of Hydrogen on electronic properties of NdNiO$_2$

Hypothetical NdNiO$_2$: Similar to previous DFT[2-10] and dynamical mean-field theory [6,10-13] studies, we find that unstable pristine NdNiO$_2$ (Fig. 5a) is metallic as confirmed by the analysis of the spin-projected density of states (DOS) for the lowest energy magnetic order (Fig. 5c). The DOS has a strong Ni peak located below the Fermi level, and O-p mainly contributes a few eV below it. Importantly, the majority of previous studies[2,3,9,10] utilized a nonmagnetic spin-configuration. Such selection has been justified by paramagnetic (PM) nature of the experimentally observed Sr-doped NdNiO$_2$ compound. However, as has been demonstrated recently, nonmagnetic approximation cannot be used to describe the PM compounds having a set of local non-zero magnetic moments and total magnetic moment zero[35,46-49]. In fact, paramagnets have different local spin environments $\{S_i;i=1, N\}$, and hence then its physical property P (e.g., electronic structure) cannot be approximated as the property $<P>=P(S_0)$ of the macroscopically averaged structure $S_0$, instead of the correct average $P_{obs} = \sum P(S_i)$ of the properties $P(S_i)$ of the individual, low symmetry microscopic configurations [35,46-49]. Moreover, for the pure NdNiO$_2$, the lowest energy AFM state is about 100 meV/atom lower than high energy hypothetical nonmagnetic state according to our SCAN calculations. These results thus intimate that
some of the early theoretical predictions based on the nonmagnetic assumption may be misleading. It should also be noted that the AFM nature of pure stoichiometric NdNiO$_2$ has been confirmed by other theoretical works as well[5-8], which also reported a noticeable difference in the electronic properties of nonmagnetic and magnetic NdNiO$_2$.

**NdNiO$_2$:** Hydrogenation of NdNiO$_2$ leads to a significant change in electronic properties. For instance, NdNiO$_2$H is predicted to be an AFM insulator with DFT band gap energy of about 0.7 eV (Fig. 5b,d). While we cannot argue that experimentally reported structures are NdNiO$_2$H, we would like to note that experimentally reported freestanding "NdNiO$_2" compound is indeed an insulator as confirmed by measurements of electronic conductivity/resistivity vs. temperature[14], which clearly contradicts to theoretical predictions for pure stoichiometric NdNiO$_2$ in this work and that available in the literature[2-13]. These observations thus suggest that before understanding the physics of superconductivity in nickelates, one might first need to understand the composition of samples and the role of common impurities such as H in the stabilization of NdNiO$_2$-like structure or even more complex deviations from ideal stoichiometry. These results also exercise serious caution to predicting new physics in pristine stoichiometric NdNiO$_2$ as it might be a potentially unrealizable compound.

![Crystal structures](image)

**Figure 5.** Crystal structures of (a) NdNiO$_2$ and (b) hydrogenated NdNiO$_2$H. Orbital projected spin-polarized density of states of pure stoichiometric P4/mmm NdNiO$_2$ (c) and (b) hydrogenated NdNiO$_2$ using the SCAN exchange-correlation functional. Occupied states are shadowed in light blue. The band gap is shown in gray.

**IV. Conclusions**

This study demonstrates that pure stoichiometric NdNiO$_2$ is significantly thermodynamically unstable with respect to decomposition into Nd$_2$O$_3$, NiO, and Ni. Given the distinguishing feature of synthesis of NdNiO$_2$ via
chemical reduction of NdNiO$_3$ involving CaH$_2$ or NaH, we point out that hydrogen inclusions can form spontaneously in stoichiometric NdNiO$_2$. In the concentrated limit, such inclusions can result in formation of NdNiO$_2$H. Although NdNiO$_2$H is also unstable with respect to decomposition, its decomposition energy to $0.5[\text{Nd}_2\text{O}_3+\text{NiO}+\text{Ni}+\text{H}_2]$ is only 80 meV/atom, substantially lower compared to the pristine phase. Hydrogenation introduces a fundamental change in the electronic structure, converting the pristine NdNiO$_2$ from AFM metal to a NdNiO$_2$:H AFM insulator, requiring doping as a prerequisite for superconductivity. These results point to the importance of considering extrinsic factors (such as spontaneous defect physics) in assessing the relevant electronic structure of such compounds. The need for experimental determination of H incorporation in as grown and subsequent H retention: Indeed, there is precedence for incorporation of H as hydride when such reductions are done, as noted in refs. [21,50], in particular, when late row transition metals (e.g., Ni) are present. Such experiments might involve Secondary Ion Mass Spectroscopy (SIMS) or neutron diffraction. This could determine the concentration of hydrogen in the as prepared sample, predicted here thermodynamically to bind significant H concentration, and establish if the processed sample, used in superconductivity measurement, might have retained hydrogen, or else it escaped. Hence, further understanding the physics of superconductivity in reduced nickelates might require investigation of the role of H impurities or even more complex deviations from ideal stoichiometry (e.g., formation of H-doped Nd$_{1-x}$Ni$_{2-y}$O$_2$ compounds). Keeping this in mind, theorists should be aware that pure stoichiometric NdNiO$_2$ may be a “fantasy material”[51] that may never be realized as such, and hence the theoretical predictions based on such material might be misleading.

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