

Ⓜ (Received 5 July 2021; accepted 9 November 2021; published 19 January 2022)

The quest for a Ni-based oxide analog to cuprate $\text{Cu}^{2+}(\text{ }^9)$ superconductors was long known to require a reduced form of $\text{Ni}^{1+}(\text{ }^9)$ as in $\text{A}^{3+}\text{Ni}^{1+}\text{O}_2$, being an extremely oxygen-poor form of the usual $\text{A}^{3+}\text{Ni}^{3+}\text{O}_3$ compound. Through CaH_2 chemical reduction of a parent $\text{A}^{3+}\text{Ni}^{3+}\text{O}_3$ perovskite form, superconductivity was recently achieved in Sr-doped NdNiO_2 on a SrTiO_3 substrate. Using density functional theory (DFT) calculations, we find that stoichiometric NdNiO_2 is significantly unstable with respect to decomposition into $\frac{1}{2}[\text{Nd}_2\text{O}_3 + \text{NiO} + \text{Ni}]$ with exothermic decomposition energy of +176 meV/atom, a considerably higher instability than that for common ternary oxides. This poses the question of whether the NdNiO_2 nickelate compound used extensively to model the electronic band structure of the 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 NdNiO_2 , even from H_2 gas. In the concentrated limit, such impurities can result in the formation of a hydride compound, NdNiO_2H , 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 lattice constants similar to those of 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.

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I. INTRODUCTION

The recent observation of superconductivity in Sr-doped NdNiO_2 grown on a 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 NdNiO_2 factors (the basic chemical constitution and bonding in nickelates vs cuprates), as opposed to NdNiO_2 factors (the role of doping, defects, or nonstoichiometry) in comparing the two systems. Interest in nickelates as a paradigm comparative to cuprates has been based on the ability to chemically reduce the stable $\text{A}^{3+}\text{Ni}^{3+}(\text{ }^7)\text{O}_3$ compound to $\text{A}^{3+}\text{Ni}^{1+}(\text{ }^9)\text{O}_2$, comparing the latter to the isoelectronic $\text{A}_2^{3+}\text{Cu}^{2+}(\text{ }^9)\text{O}_4$ compound. The literature [2–13] electronic structure calculations on NdNiO_2

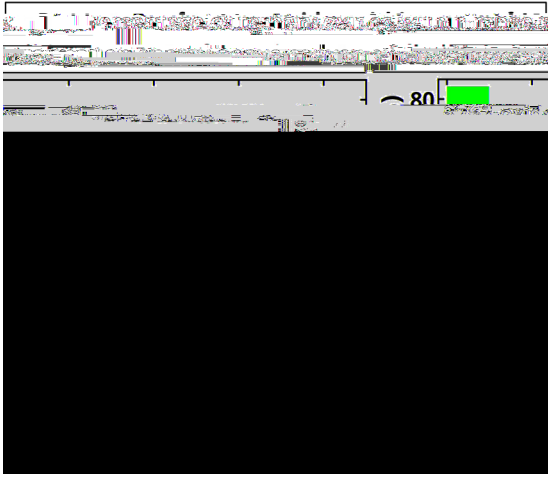


FIG. 1. Distribution of energy above the DFT convex hull for 3262 experimentally reported ternary oxides (see details on a dataset in the Supplemental Material [19]) using the data available in the Materials Project database (accessed on March 20, 2021; note that

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	<i>F</i> -3	0	–
Nd	6 ₃	0	–
O ₂	Molecule	0	–
NiO	<i>F</i> -3	0	–
Ni ₃ O ₄		0	–
Nd ₂ O ₃	-3	0	–
NdO ₂	2/	0	–
NdNi		0	–
NdNi ₂	4 ₁	0	–
NdNi ₃	4 -3	0	–
NdNi ₅	6/	0	–
Nd ₃ Ni		0	–
Nd ₅ Ni ₁₉	6 ₃	0	–
Nd ₂ Ni ₇	6 ₃	0	–
NdNiO ₃	2 ₁	0	–
Nd ₄ Ni ₃ O ₁₀	2 ₁	1	NdNiO ₃ , Nd ₂ O ₃ , NiO
Nd ₇ Ni ₃	6 ₃	3	Nd ₃ Ni, NdNi
NiO ₂	2/	4	Ni ₃ O ₄ , O ₂
Nd ₂ Ni ₁₇	6 ₃	17	NdNi ₅ , Ni
Nd ₂ NiO ₄		19	Nd ₂ O ₃ , NiO
NdO	6 ₃	62	Nd ₂ O ₃ , Nd
Ni ₅ O ₆	2/	64	Ni ₃ O ₄ , NiO
Ni ₆ O ₇	-1	70	Ni ₃ O ₄ , NiO
Ni ₁₅ O ₁₆	-3	72	Ni ₃ O ₄ , NiO
Ni ₉ O ₁₀	-1	73	Ni ₃ O ₄ , NiO
Nd ₄ Ni ₃ O ₈	4	86	Nd ₂ O ₃ , Ni, NiO
Nd ₂ O ₅	2/	92	NdO ₂ , O ₂
Ni ₅ O ₁₁	1	96	Ni ₃ O ₄ , O ₂
Ni ₅ O ₄	1	165	Ni, NiO
NdNiO ₂	4	176	Nd ₂ O ₃ , Ni, NiO
NdO ₃	-3	285	NdO ₂ , O ₂
Nd ₄ Ni	<i>F</i> -3	364	Nd ₃ Ni, Nd

above the convex hull by that amount). In this way, 15 out of 97 potential competing phases are found to be stable ground states: O₂, Ni, Nd, NiO, Ni₃O₄, NdO₂, Nd₂O₃, NdNi, NdNi₂, Nd₃Ni, NdNi₅, Nd₅Ni₁₉, NdNi₃, Nd₂Ni₇, and NdNiO₃. 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 NdNiO₂ configuration is above the convex hull (unstable) by +176 meV. atom or +704 meV. f.u. with respect to decomposition to $\frac{1}{2}$ [Nd₂O₃ + NiO + Ni]. There



FIG. 2. Summary of Nd-Ni-O convex hull. (a) Nd-Ni-O convex hull showing the stable phases (O_2 , Ni, Nd, NiO, Ni_3O_4 , NdO_2 , Nd_2O_3 , NdNi , NdNi_2 , Nd_3Ni , NdNi_5 , $\text{Nd}_5\text{Ni}_{19}$, NdNi_3 , Nd_2Ni_7 , and NdNiO_3) as blue dots. (b) Main decomposition reactions for NdNiO_2 and corresponding decomposition energies (ΔH_f°). The results are presented for the SCAN XC functional. The decomposition energies for other compounds are shown in Table I.

bonds to anions in δ -type compounds (e.g., H-O bond in ZnO [45]) and to cations in δ -type compounds [44,47]. In

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zero [35,48–51]. In fact, paramagnets have different local spin environments $\{S_i = 1/2\}$, and hence then its physical property (e.g., electronic structure) cannot be approximated as the property $\langle S \rangle = \langle S_0 \rangle$ of the macroscopically averaged structure S_0 , instead of the correct average $S_{\text{obs}} = \langle S \rangle$.

