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The quest for a Ni-based oxide analog to cuprate $Cu^{2+}$([illegible]$^{9}$) superconductors was long known to require a reduced form of $Ni^{1+}$([illegible]$^{9}$) as in $A^{3+}Ni^{1+}O_2$, being an extremely oxygen-poor form of the usual $A^{3+}Ni^{3+}O_3$ compound. Through $CaH_2$ chemical reduction of a parent [illegible]$^{3+}Ni^{3+}O_3$ 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 $\frac{1}{2}[Nd_2O_3 + NiO + Ni]$ with exothermic decomposition energy of +176 meV atom, a considerably higher instability than that for common ternary oxides. This poses the question of whether the [illegible] $NdNiO_2$ 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 [illegible] in $NdNiO_2$, 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 [illegible] factors (the basic chemical constitution and bonding in nickelates vs cuprates), as opposed to [illegible] 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 $A^{3+}Ni^{3+}$([illegible]$^{7}$)$O_3$ compound to $A^{3+}Ni^{1+}$([illegible]$^{9}$)$O_2$, comparing the latter to the isoelectronic $A_2^{3+}Cu^{2+}$([illegible]$^{9}$)$O_4$ compound. The literature [2–13] electronic structure calculations on $NdNiO_2$

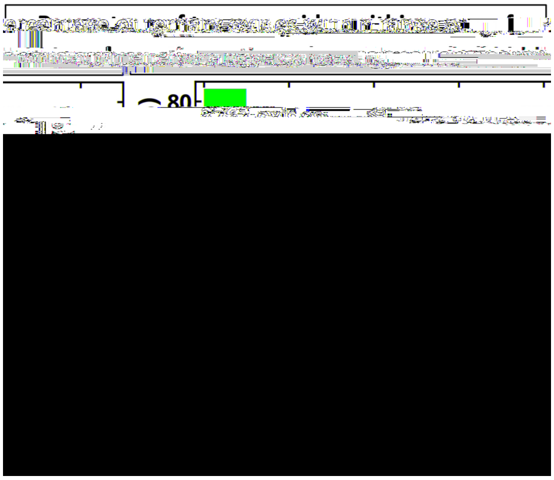

FIG. 1. Distribution of energy above the DFT convex hull for 3262 experimentally reported ternary oxides (see details on a dataset in the Supplemental Material [19]) using the data available in the Materials Project database (accessed on March 20, 2021; note that

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 | *F* -3 | 0 | – |
| Nd | $6_3$. | 0 | – |
| $O_2$ | Molecule | 0 | – |
| NiO | *F* -3 | 0 | – |
| $Ni_3O_4$ |  | 0 | – |
| $Nd_2O_3$ | -3 | 0 | – |
| $NdO_2$ | 2/ | 0 | – |
| NdNi |  | 0 | – |
| $NdNi_2$ | $4_1$ | 0 | – |
| $NdNi_3$ | R-3 | 0 | – |
| $NdNi_5$ | 6/ | 0 | – |
| $Nd_3Ni$ |  | 0 | – |
| $Nd_5Ni_{19}$ | $6_3$. | 0 | – |
| $Nd_2Ni_7$ | $6_3$. | 0 | – |
| $NdNiO_3$ | $2_1$. | 0 | – |
| $Nd_4Ni_3O_{10}$ | $2_1$. | 1 | $NdNiO_3$, $Nd_2O_3$, NiO |
| $Nd_7Ni_3$ | $6_3$ *-.0001 08* |  |  |

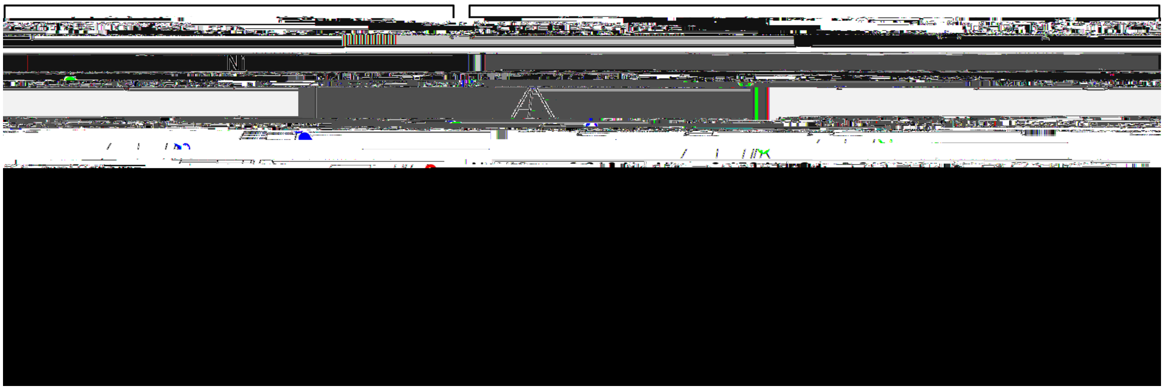

FIG. 2. Summary of Nd-Ni-O convex hull. (a) Nd-Ni-O convex hull showing the stable phases ($O_2$, Ni, Nd, NiO, $Ni_3O_4$, $NdO_2$, $Nd_2O_3$, NdNi, $NdNi_2$, $Nd_3Ni$, $NdNi_5$, $Nd_5Ni_{19}$, $NdNi_3$, $Nd_2Ni_7$, and $NdNiO_3$) as blue dots. (b) Main decomposition reactions for $NdNiO_2$ and corresponding decomposition energies ([illegible]). The results are presented for the SCAN XC functional. The decomposition energies for other compounds are shown in Table I.

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

BULK $NdNiO_2$

zero [35,48–51]. In fact, paramagnets have different local spin environments $\{\ ;\ = 1\ \}$, and hence then its physical property (e.g., electronic structure) cannot be approximated as the property $\langle\ \rangle = (\ _0)$ of the macroscopically averaged structure $_0$, instead of the correct average $_{\mathrm{obs}} =$ P(S