Investigation of hydrogen incorporations in bulk infinite-layer nickelates

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Infinite-layer (IL) nickelates are an emerging class of superconductors, where the Ni\textsuperscript{3+} valence state in a square planar NiO\textsubscript{2} coordination can only be reached via topotactic reduction of the perovskite phase. However, this topotactic soft chemistry with hydrogenous reagents is still at a stage of rapid development, and there is a number of open issues, especially considering the possibility of hydrogen incorporation. Here we study the time dependence of the topotactic transformation of LaNiO\textsubscript{3} to LaNiO\textsubscript{2} for powder samples with x-ray diffraction and gas extraction techniques. While the hydrogen content of the powder increases with time, neutron diffraction shows no negative scattering of hydrogen in the LaNiO\textsubscript{2} crystal lattice. The extra hydrogen appears to be confined to grain boundaries or secondary-phase precipitates. The average crystal structure, and possibly also the physical properties, of the primary LaNiO\textsubscript{2} phase are therefore not noticeably affected by hydrogen residues created by the topotactic transformation.

I. INTRODUCTION

Superconductivity exists in various hydrogen containing compounds, highlighted by the recent discoveries of critical temperatures \(T_c\) as high as room temperature for hydride compounds formed under extreme pressures [1, 2]. Metal hydroxide-intercalated iron chalcogenides, such as (Lio.3FeO.2)O/HFeSe [3], show coexistence of antiferromagnetic order and superconductivity, a feature known from some high-\(T_c\) superconductors [4]. Electron-doped 1111 iron pnictides as RFeAsO\textsubscript{1−\textit{x}}H\textsubscript{\textit{x}} [5, 6], CeFeAsO\textsubscript{1−\textit{x}}H\textsubscript{\textit{x}} [7], and the pnictogen-free LaFeSiH [8] are a class, where the introduction of charge carriers via doping with hydrogen drives the system from an antiferromagnetically ordered state towards superconductivity. In layered sodium cobalt oxyhydrate, Na\textsubscript{x}CoO\textsubscript{2}·H\textsubscript{2}O [9], superconductivity with a similar hole/electron-doping behavior by chemical substitution is observed as in the cuprate high-\(T_c\) superconductors [10].

For IL nickelates, a close relation and possible analogy to cuprate superconductors was suggested already in 1999 [11] and since the first discovery of superconductivity in the IL nickelate (Nd,Sr)NiO\textsubscript{2} [12], the observation of superconductivity has been confirmed [13–15] and extended to (Pr,Sr)NiO\textsubscript{2} [16], (La,Sr)NiO\textsubscript{2} [17], (La,Ca)NiO\textsubscript{2} [18], and Nd\textsubscript{6}Ni\textsubscript{2}O\textsubscript{12} [19]. Furthermore, a recent work reported superconductivity not only for films grown on SrTiO\textsubscript{3} substrates, but also on LSAT [20], which provides enough evidence to consider thin film nickelates as a novel class of superconductors. The possible presence of topotactic hydrogen in IL nickelates, which depends on the rare-earth ion and/or epitaxial strain [21, 22], was proposed in theoretical studies [23, 24], and might have substantial influence on the electronic and magnetic properties of the IL nickelates, as LaNiO\textsubscript{2}H would realize a two-orbital Mott insulator [23]. A hint towards the possibility of hydrogen incorporation was provided by an early study of topotactically reduced NdNiO\textsubscript{3} films, which showed an oxyhydride NdNiO\textsubscript{4−\textit{x}}H\textsubscript{\textit{x}} phase with a defect-fluorite structure in the surface region [25]. Furthermore, topotactic hydrogen can be found in SrTiO\textsubscript{3} thin films [26], i.e. the material that is commonly used as substrate and capping layer for IL nickelate films, which again provides a possible route for inclusion of hydrogen in infinite-layer nickelates thin films. While superconductivity has remained elusive in IL nickelates in bulk form, with studies on powder samples reporting insulating behavior [27, 28], a first step towards superconductivity was taken by our recent investigation of (La,Ca)NiO\textsubscript{2} single crystals [29], where metallicity was observed.

In this work, we address the issue of possible hydrogen incorporations in IL nickelates by examining bulk LaNiO\textsubscript{3−\textit{x}}H\textsubscript{\textit{x}} powder samples with a combination of x-ray and neutron diffraction studies, gas extraction, as well as complementary high pressure synthesis attempts of LaNiO\textsubscript{2}H.

II. METHODS

LaNiO\textsubscript{3} powder samples with grain sizes of 0.5 \(\mu\)m were synthesized via the citrate-nitrate method as described in Ref. [30]. The method is optimal as the relatively small grains enhance the surface to bulk ratio, reducing the reduction times. Moreover, a higher purity can be reached than by high pressure powder synthesis. The IL phase LaNiO\textsubscript{2} can be obtained solely through topotactic reduction of the perovskite LaNiO\textsubscript{3} phase, which is here achieved by using CaH\textsubscript{2} as the reducing agent [27, 28]. We reduced 50 mg of LaNiO\textsubscript{3} powder wrapped in aluminum foil, spacially separated from 250 mg CaH\textsubscript{2} pow-

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As a first step, we checked the purity and stoichiometry of our starting material in the perovskite phase. In PXRD we found no detectable impurities, and ICP combined with measurements of gas extraction indicated a starting stoichiometry of $\text{La}_{0.99(1)}\text{Ni}_{0.99(1)}\text{O}_{2.98(3)}\text{H}_{0.005(2)}$. We studied the reduction progress with time in detail by preparation of several ampules and extracting samples after varying reduction times and analyzed all the products with PXRD. We noticed that the progress of the reduction depends on the purity and sample amount and grain size for a given time, as the reduction process is surface dependent. Motivated by these observations, we carried out a standardized reduction on the same batch of perovskite precursors. After one day of reduction in the described process (see Methods) we found a full structural transition to $\text{LaNiO}_2$ (see Fig. 1). Our Rietveld refinement of the $\text{LaNiO}_2$ crystal structure is in good agreement with previous reports on reduced powder [32–34]. Notably, reduction times of one day and longer are in stark contrast to thin film samples, which can be fully reduced to the IL phase within hours [12–18, 35, 36], presumably due to the enhanced thickness of our grains, with sizes of 0.5 μm as extracted from scanning electron microscopy (SEM) images. The reduction appears to be happening in domains, as we found cluster spin glass behavior in a detailed magnetic characterization [30] and thus after longer reduction times than one day, we observe phase mixtures of $\text{LaNiO}_2$ in $P2_1/n$ (#14) [33], and $\text{LaNiO}_2$ in $P4/mmm$ (#123) [37], with a slowly increasing fraction of the $\text{LaNiO}_2$ phase as a function of time (see Fig. 2). Extracting the weight percentages from our refinement, we present the reduction progress for the $\text{CaH}_2$ reduction in analogy to a thermogravimetry (TG) curve, which is shown in Fig. 2. The reduction process follows an exponential decay, which we also observed in thermogravimetry studies in hydrogen gas flow (not shown here). After a reduction time of approximately 316 h, the crystal structure can be refined assuming a single phase of IL $\text{LaNiO}_2$ (Fig. 2, and Ref. [30]). Notably, while the structural transition does not progress further on an exponential time scale, a small amount of apical oxygen remains in the crystal lattice, as will be revealed by neutron diffraction below. However, for even longer reduction times, the sample begins to decompose, forming Ni and La$_2$O$_3$, which becomes clearly visible in PXRD after 400 h (Fig. 1 and Fig. 2).

In the inset of Fig. 2 we plot the hydrogen content in the resulting powder samples versus the reduction time, obtained by a gas extraction method. While the initial perovskite nickelate shows a hydrogen content of 0.005(2) wt%, we find an increase of hydrogen with time (opposite to the oxygen content), with 0.065(3) wt% for 24 h, 0.094(3) wt% for 38 h, 0.015(5) wt% for 240 h and finally 0.169(7) wt% after 320-376 h. Via gas extraction we find an oxygen content of 14.1(2) wt% after 316 h and 14.0(2) wt% after 320-376 h of reduction, where 14 wt% corresponding to a full reduction to the $\text{LaNiO}_2$ IL phase. If we assume that the amount of hydrogen would be incorporated into the average crystal structure, the corresponding effective stoichiometry of the sample investigated with neutrons would be $\text{La}_{0.99(1)}\text{Ni}_{0.99(1)}\text{O}_{2.00(2)}\text{H}_{0.39(2)}$, where La and Ni are de-
FIG. 2. Oxygen and hydrogen content of reduced LaNiO$_3$ after different reduction times. Red symbols correspond to the oxygen content $x$ in LaNiO$_{3-x}$, extracted from Rietveld refinements of the PXRD data shown in Fig. 1. The blue datapoint is extracted from Rietveld refinement of our neutron diffraction data shown in Fig. 3. The solid red line is a guide to the eye. The black symbols in the inset correspond to the hydrogen content $y$ in LaNiO$_{3-x}$H$_y$, obtained from gas extraction. The solid black line is a guide to the eye.

TABLE I. Refined atomic coordinates of LaNiO$_2$ in tetragonal space group $P4/mmm$ with preferred orientation extracted from powder neutron diffraction data at 1.5 K [Fig. 3].

| Atom     | $a$, $b$ = 3.9550(3) Å, $c$ = 3.3588(3) Å | $x$ | $y$ | $z$ | $U[Å^2]$ | Occ. |
|----------|------------------------------------------|-----|-----|-----|-----------|------|
| La (1d)  | 0.5 0.5 0.5 0.0036(6)                  | 1   |     |     |           |      |
| Ni (1a)  | 0 0 0 0.0057(5)                         | 1   |     |     |           |      |
| O (2f)   | 0.5 0 0 0.0098(5)                       | 1   |     |     |           |      |
| O (1b)   | 0 0 0.5 0.0098(5)                       | 0.06(1) |     |     |           |      |

Reliability factors $\chi^2$, $R_B$, $R_f$

1.89 3.53 2.79

determined via ICP. However, a first hint that this might not be the case comes from the presence of small amounts of elemental Ni in the PXRD of the 400 h sample (Fig. 1), which is known to trap hydrogen [38]. The Rietveld refinement of the neutron diffraction data below also indicates a small amount of Ni. Furthermore, signatures of Ni precipitates (below detection threshold of our PXRD) were also detected in powders after shorter reduction times, since they give rise to ferromagnetic contributions in the magnetic signal [30]. The amount of Ni likely increases with reduction time, which could explain the increasing capability of incorporating hydrogen.

As a next step, we performed high resolution neutron diffraction experiments on 340 mg of a sample prepared by mixing batches that had been subject to reduction times of 320, 350 and 376 h, respectively, which are all in the range just before the start of the clear decay shown in Fig. 2. The obtained neutron diffraction pattern can be well refined (see Fig. 3) assuming LaNiO$_2$ in the IL $P4/mmm$ structure (see Tab. I), with a $c$-axis parameter of 3.3588(3) Å, which is lower than previously reported values [29, 30, 37], and 1.1(2) wt% of elemental Ni was included as a secondary phase.

The data is taken from mixed samples reduced in the range of 320-376 h. The Rietfeld refinement includes the LaNiO$_2$ phase and a Ni minority phase. Data were collected at 1.5 K with a neutron wavelength of 1.15 Å.
itive scattering observed at this site could be a mixture of negative scattering H and positive scattering O, which effectively clouds the negative scattering. Realized in a substitution series with LaNiO$_3$-$\delta$H$_x$, which would yield occupations of O: 0.430(8) and H: 0.570(8) in refinements of our data, but this oxygen content is way higher than what can be found in multiple gas extraction experiments (La$_{0.99(1)}$Ni$_{0.99(1)}$O$_{2.00(2)}$H$_{0.39(2)}$). Most importantly, the scenario of LaNiO$_3$-$\delta$H$_x$ would hint towards the possibility to synthesize the phase directly, similar as observed in the iron pnictides. However, such synthesis attempts have been carried out as described below and were not successful. Furthermore, in the case of iron pnictides the hydrogen substitution leads to no structural transitions [5–7] contrasting the evolution of the underlying structural transitions in LaNiO$_3$-$\delta$ according to the PXRD data (see Fig.1) and literature [37]. Another possibility to refine mixed occupancy is by constraining an equal occupation of O and H as LaNiO$_2$(OH)$_x$, which converges to 0.18(4). However, this would rather suggest an OH molecule with typical distances around 0.84 Å, which would realize negative scattering [39] and thus reduces the quality of the fit and shifts the occupation again down to 0.06(1). Thus, we conclude that intercalated hydrogen is unlikely in our LaNiO$_{2+\delta}$ powder sample. Nevertheless, we find the presence of a small amount of residual apical oxygen in Wyckoff position (1b), which corresponds to a deviation $\delta = 0.06(1)$ from the ideal stoichiometry.

Additionally, we attempted direct synthesis approaches of LaNiO$_3$-$\delta$H$_x$ as e.g. LaNiO$_2$H via a Walker-type high pressure synthesis in NaCl crucibles. We mixed La$_2$O$_3$ and NiO with NaH or CaH$_2$ and heated it to 650°C - 1000°C under a pressure of 5-7 GPa, but were unable to synthesize any oxyhydride nickelate. Instead we obtained La(OH)$_3$ and Ni, which is in contrast to related cases, such as SmFeAsO$_{1-x}$H$_x$ [5], BaCrO$_2$H [41], BaScO$_2$H [42], and SrVO$_2$H [43].

IV. CONCLUSION

In summary, we have synthesized high quality LaNiO$_{2+\delta}$ powders and found some density of residual oxygen ($\delta = 0.06(1)$) even at the final stage of the topotactic reaction, just prior to decomposition of our samples. While our gas extraction method reveals partial hydrogen inclusions in the powder samples, high resolution neutron diffraction refinements show that there is no clear topotactic hydrogen in LaNiO$_2$, and direct attempts to synthesize LaNiO$_3$-$\delta$H$_x$ were unsuccessful. The hydrogen detected by gas extraction could be trapped in Ni impurities that increase with increasing reduction time and/or ascribed to phenomena at surfaces or grain boundaries such as water adsorption/intercalation [44] on powder surfaces, or partial formation of LaNiO$_{3-x}$H$_x$ on the nm scale [25]. Notably, a relatively high density of grain boundaries/crystallographic defects was reported for IL nickelate thin films [45], and also surface effects can play a more decisive role in films. Thus, future studies clarifying the presence and the impact of hydrogen in nickelate thin film samples are highly desirable.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.
AUTHOR CONTRIBUTIONS

PP, MI, BK, and MH conceived the project. RO carried out the topotactic reductions. SH executed the ICP and gas extractions. PP and VP conducted the neutron diffraction experiments. PP analyzed the data and prepared the manuscript with input from all authors.

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