Formation of hydrogen chains in $ABO_2$ nickelate superconductors

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Despite enormous experimental and theoretical efforts, obtaining generally accepted conclusions regarding the intrinsic magnetic and electronic properties of superconducting nickelates remains extremely challenging. Experiments show a large degrees of uncertainty, indicating hidden factors in the synthesized films which call for further investigations. Here, we reveal the formation of one-dimensional hydrogen chains in infinite-layers LaNiO$_2$ superconductors using density-functional theory and dynamical mean-field theory (DFT+DMFT) calculations. The formation of such hydrogen chains induces a coexistence of different oxidation states of Ni and competing magnetic phases. Furthermore, it contributes to the difficulty of synthesizing homogeneous nickelates and of determining their ground states. The smoking gun to detect access hydrogen in nickelates are flat phonon modes, which are quite insensible to the exact arrangement of the H atoms.

I. INTRODUCTION

Efforts to achieve higher and higher superconducting transition temperatures already last for more than a century, starting with the original discovery of superconductivity in mercury by Kammerlingh Onnes. For the first 75 years research focused on what we now call the conventional superconductors. While their microscopic mechanism is understood by now within the framework of the Bardeen, Cooper, and Schrieffer (BCS) theory, no superconductor at that time exceeded a transition temperature of 30 K. This changed with the major breakthrough by Bednortz and Müller [2], who discovered superconductivity in a copper oxide compound. Still to this day members of those cuprates hold the record for superconductivity in a copper oxide compound. (i) There is one orbital at the Fermi-surface, which is a Cu $3d_{x^2−y^2}$ and O $2p$ hybrid in the spirit of the Zhang-Rice singlet [20]. (iv) Superconductivity is observed in a range of roughly 5 − 25% hole-doping in the effective $3d_{x^2−y^2}$ orbital, with details depending on the compound.

Following these simple ingredients already early simulations have predicted the possibility of nickelates superconductors [21] and heterostructures thereof [22–24]. However, a superconducting nickelate was experimentally only confirmed in 2019 for Sr-doped NdNiO$_2$ by Li et al. [25], opening the door to a new playground of superconductivity after a long search. Nickelate superconductors have attracted intensive attention in the last three years, marked by an enormous theoretical and experimental activity, including, but not restricted to, Refs. [25–49] on both infinite- and finite-layers nickelates [30, 50].

Compared to cuprates, which are considered charge-transfer insulators with a Coulomb interaction larger than the charge transfer gap ($U > \Delta$), the situation is reversed in nickelates, i.e., $\Delta > U$, placing them rather in the Mott-Hubbard regime. Additionally, the Ni-O hybridization is reduced and the doped holes thus reside predominantly in the Ni $d$-band, specifically the $d_{x^2−y^2}$ orbital [37, 51–53], while in cuprates they are more located at the O sites. An additional aspect to consider is the Ni-La(Nd) hybridization [54] and in particular the electron pockets at the Τ- and Λ-points, even though they seem not to be essential for superconductivity. This was concluded by calculations using the dynamical vertex approximation (DΓA) [55–58] for nickelates [46], which is unbiased with respect to charge and spin fluctuations.

These calculations find that spin fluctuations dominate and successfully predicted the superconducting dome prior to experiments in Nd$_{1−x}$Sr$_x$NiO$_2$ [26, 59]. The recent measurements on defect-free (Nd,Sr)NiO$_2$ samples yield an even better agreement regarding $T_C$ and the dome structure as predicted by DΓA [60].

While the parent compound of cuprates orders antiferromagnetically, there is still some uncertainty on the ground state magnetic and electronic structure of nickelates. Resonant inelastic x-ray scattering (RIXS) [52, 61] indicate the existence of CDW order including both the Ni and Nd sites. Moreover, coexistence of Ni$^{1+}$ and Ni$^{2+}$...
was reported, the later is, however, incompatible with monovalent Ni$^{1+}$ in LaNiO$_2$. Additionally, no long-range (anti-ferromagnetic) magnetic order has been observed in LaNiO$_2$ and NdNiO$_2$, even in their bulk states [62, 63]. Let us note at this point that while the Nd pockets seem not to be relevant for superconductivity, they quite distinctly alter the parent compound of nickelates compared to cuprates. Specifically, the pocket “self-dopes” the Ni $3d_{x^2-y^2}$ orbital such that its filling is only $\sim 0.94$ in the parent compound instead of 1 as for cuprates. Hence, a comparison to $\sim 6\%$ hole-doped cuprates is more qualified. Indeed such a doping is already at the very edge, or even already outside the AFM dome [64] in cuprates. Furthermore, magnetic excitations consistent with the AFM (para)magnon dispersion, which is expected for doped cuprate-like anti-ferromagnetic order, have recently been observed in NdNiO$_2$ films by RIXS [65]. Similarly, nuclear magnetic resonance (NMR) indicates AFM fluctuations [66]. The $\mu$SR and low-field static and dynamic magnetic susceptibility measurements performed by Ortiz et al. reveal the presence of short-range magnetic correlations and glassy spin dynamics that hint to a possible (local) magnetic-frustration [63]; and these effects have been attributed to local oxygen nonstoichiometry. Recently, by performing $\mu$SR measurements [67], Fowlie et al. investigated the magnetic ground states of four infinite-layers compounds, and concluded that an intrinsic magnetic ground state exists in them, regardless of the rate earth ion or doping concentration.

The above work reveals (1) the coexistence of various oxidation states and (2) various magnetic signals which were recently observed to be (short-range) AFM correlations. These measurements strongly highlight further similarities and differences between nickelates and cuprates. Previous theoretical [40, 68–71] and experimental [66] studies demonstrated the possibility of intercalating topotactic hydrogen (H) defects and their consequences in nickelates. Those theoretical studies focused primarily on the hydrogen saturated compound, i.e. (Nd)LaNiO$_2$H$_x$. A natural question arising is how low-density hydrogen defects will arrange in the crystal and alter the magnetic and electronic properties of the corresponding synthesised crystals. Especially interesting is here the question, how much of the observed experimental uncertainties can be explain and attributed to such defects.

In this paper, we go beyond [40] that reported $E_b$ of various ABO$_2$ compounds by investigating $E_b$ of LaNiO$_2$H$_4$ systems with $\delta=0\%-100\%$. The structural, electronic and magnetic properties of LaNiO$_2$H$_4$ are studied using density-functional theory (DFT) [72] and dynamical mean-field theory (DMFT) calculations [73–76].

A special behaviour of topotactic hydrogen (H) is evidenced by our computations: topotactic-H in infinite-layers tend to form one-dimensional (1D) chains along the $z$-direction. The captured H atoms are mainly confined by the Ni-sublattice while the La(Nd)-sublattice plays the role of distributing the H-chains along the (110)-direction by forming La-$d_{xy}$-H-1s bonds. Such 1D H-chains affect the local properties by leading to various oxidation states in Ni and enhancing the 3D character of magnetism, giving rise to inhomogeneity and uncertainty of experimental observations. Finally, we predict that the formation and existence of 1D H-chains can be detected by techniques such as resonant inelastic x-ray scattering, with the emergence of flat phonon modes being an important indicator.

The paper is organized as follows: Section II provides the computational details and crystal structures considered; in Section III we present corresponding results and discussions: Specifically Sections III A, B, C, D, E, F are dedicated to the results and discussions of (A) structural, (B) energetic, (C) dynamical (phonon), (D) electronic, (E) Fermi-surface and (F) magnetic properties, respectively. Section IV presents a conclusion and outlook.

II. METHODS

The ground state crystal structures with lowest total energies of LaNiO$_2$H$_{\delta}$ ($\delta=12.5\%$ to $87.5\%$) are shown in Fig. 1. To obtain these results, DFT-level structural relaxations and static calculations for all possible phases are performed using the VASP code [77, 78] with the Perdew-Burke-Ernzerhof version for solids of the generalized gradient approximation (GGA-PBESol) [79] and a dense $13\times13\times15$ $k$-mesh for the unit cells of $\delta=0$ and $100\%$ (LaNiO$_2$ and LaNiO$_2$H$_{\delta}$), and a $9\times9\times11$ $k$-mesh for the $2\times2\times2$ supercell of $\delta=0\%$, $12.5\%$, $25\%$, $37.5\%$, $50\%$, $62.5\%$, $75\%$, $87.5\%$, $100\%$. For each H concentration, structural relaxation and static total energy calculations for all possible structures are carried out and shown in Fig. 1 (and in Fig. 7 and Table II in Appendix I). Phonon spectra calculations are performed with the frozen phonon (finite displacement) method using the PHONOPY code [80] interfaced with VASP for the relaxed ground state structures of each H concentration.

In both our previous theoretical study [40] and in this article, the binding energy $E_b$ of hydrogen atoms is computed as:

$$E_b = \{E[\text{LaNiO}_2] + n \times \mu[H] - E[\text{LaNiO}_2\text{H}_\delta]\}/n. \quad (1)$$

Here, $E[\text{LaNiO}_2]$ and $E[\text{LaNiO}_2\text{H}_\delta]$ are the total energy of the infinite-layer LaNiO$_2$ and the hydride-oxides LaNiO$_2$H$_\delta$ supercell consisting of $2\times2\times2$ chemical units, while $\mu[H] = E[H_2]/2$ is the chemical potential of H, and $n = \delta \times 2^4$ is the number of H atoms in the supercell. A positive (negative) $E_b$ indicates that the topotactic H process is energetically favorable (unfavorable) and LaNiO$_2$H$_\delta$ will be formed instead of LaNiO$_2$ and H$_2/2$. 

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A. Formation of one-dimensional H-chains

In Fig. 1 we show the ground state crystal structure with lowest total energy for each concentration of topotactic-H LaNiO$_2$H$_{\delta}$ (δ=0.0% to 100%). The case with 0% and 100% topotactic-H corresponds to LaNiO$_2$ [Fig. 1(a)] and LaNiO$_2$H [Fig. 1(i)], respectively. The simulation of the process of gradual increasing topotactic-H in LaNiO$_2$ is achieved by intercalating H atom(s) to the pristine 2×2×2 LaNiO$_2$ supercell of Fig. 1(a). This process enables us to investigate the energetic, crystal, electronic and magnetic properties for LaNiO$_2$H$_{\delta}$ with δ=0.0%, 12.5%, 25.0%, 37.5%, 50.0%, 62.5%, 75.0%, 87.5% and finally 100%. For each concentration, the ground state crystal structure is predicted by computing the total DFT energy of all possible structures. For the details of possible structures and $E_b$ see Appendix I Fig. 7 and Table II.

For the compounds LaNiO$_2$ [Fig. 1(a)], LaNiO$_2$H$_{0.125}$ [Fig. 1(b)], LaNiO$_2$H$_{0.875}$ and LaNiO$_2$H, the ground state structures are not named as there is only one inequivalent structure for these cases in the 2×2×2 supercell. In Fig. 1(b,c), the formation of 1D H-chains can clearly be seen: the second H atom [Fig. 1(c)] is energetically favourable to occupy the apical position on top of the first H atom [Fig. 1(b)], thus forming a 1D H-chain. Similar to Fig. 1(b,c), Fig. 1(d,e) shows the process of the formation of the second H-chain when the third and fourth H atom are intercalated into the supercell. One notable observation is the favourable position for the third and fourth H atom, both the single third H atom [Fig. 1(d)] and the second H-chain [fourth H atom; Fig. 1(e)] are energetically favourable to occupy the empty space in the (110) direction instead of (100)//(010). Combining this tendency with the formation of 1D H-chain in Fig. 1(b,c), we conclude that the formation of the 1D H-chains are driven by the bonds between H-1s and Ni-d$_{xy}$ orbitals, and the bonds between H-1s and La-d$_{yz}$ orbitals play important roles concerning the detailed arrangement of the H-chains. Finally, further chains are formed when intercalating more H in Fig. 1(f-i).

B. Topotactic-H reshapes the magnetic structures

To further prove the formation of 1D H-chains in nickelate superconductors, we perform DFT-level calculations on the topotactic-H binding energy $E_b$ for all ground state structures (as shown in Fig. 1). Fig. 2(a) shows $E_b$ of different topotactic-H concentration. Beyond Ref. [40] that reports $E_b$ obtained from non-spin-polarized DFT...
calculations without a DFT+U treatment, here we also performed spin-polarized DFT+U calculations, and the magnetically spin-polarized total energies are used to compute $E_b$ according to Eq. (1). Such setups are closer to the real conditions within nickelates, where local Ni moments form.

As shown in Fig. 2(a), $E_b$ reaches a local maximum when the topotactic-H concentration is 25%, 50%, 75% and 100%, corresponding to 1, 2, 3 and 4 H-chains in the supercell. Please note, according to Eq. 1, local maxima of $E_b$ indicate the energetically most stable structures of LaNiO$_2$H$_5$. Hence the results in Fig. 2(a) demonstrate that topotactic-H atoms in infinite-layers nickelates tend to form 1D H-chains, especially for $E_b$ obtained from spin-polarized DFT+U computations. In this context, another important question is: when there is certain amount of H atoms remaining in samples, will they form H-chains (e.g. in the structure of LaNiO$_2$H$_5$) or a locally full topotactic phase (i.e. LaNiO$_2$H)? For non-spin-polarized (DFT) and spin-polarized (DFT+U) calculations, the $E_b$ of LaNiO$_2$H$_5$ is always higher than that of LaNiO$_2$H, by 68 meV and 27 meV per H, respectively, which corresponds to temperatures of 789 K and 313 K. This consistently indicates that the formation of H-chains is energetically favorable even at room temperature, although at such elevated temperatures some degree of disorder can be expected.

To show that this 1D H-chains formation is unique, i.e., other intercalated elements fail to form such chains, we also compute the binding energy $E_b$ for oxygen. In fact such a simulation is effectively equivalent to the reduction process from LaNiO$_3$ to LaNiO$_2$ under the participation of CaH$_2$. The energy cost in the process from LaNiO$_3$ (i.e., $\delta=100\%$ in LaNiO$_{2+\delta}$) to LaNiO$_2$ ($\delta=0\%$) reflects the difficulty of removing oxygen atoms gradually as the binding energy increases with decreasing concentration. However, this trend is monotonous as shown in Fig. 2(b). That is, the oxygen binding energy is only sensitive to the density of oxygen in LaNiO$_{2+\delta}$. This is distinctly different to the hydrogen case (LaNiO$_2$H$_3$).

As discussed in Ref. [40], a complete intercalation of H triggers a transition from a quasi-2D strongly correlated single-band ($d_{x^2-y^2}$) metal to a two-band ($d_{x^2-y^2}+d_{z^2}$) anti-ferromagnetic 3D Mott insulator. Here, by changing the density of topotactic-H we investigate how the formation of 1D H-chains reshapes the magnetic order of LaNiO$_2$H$_5$. Fig. 2(c) shows the spin-polarized total energy per unit cell of LaNiO$_2$H$_5$ obtained from DFT+U calculations by setting the supercell in Fig. 1 to ferromagnetic (FM), A- (AFM-A), C- (AFM-C) and G-type anti-ferromagnetic (AFM-G) orders. For LaNiO$_2$ ($\delta=0\%$), the AFM-C and AFM-G state have similar total energies, which are $\sim$32 meV/Ni lower than those of FM and AFM-A, indicating that the system is dominated by its quasi-2D character with strong intra-layer coupling, but only weak inter-layer coupling ($\sim$2 meV/Ni). At a doping of $\delta=12.5\%$, the AFM-C state becomes the magnetic ground state being $\sim$1.3 meV/Ni lower in energy than AFM-G. However, such a small energy difference is likely not strong enough to pin the AFM-C state, and can thus lead to magnetic frustration, including suppression of long-range order, which could lead to a spin-ice or glassy behaviour. As $\delta$ further increases, AFM inter-layers coupling starts to become dominant and for $\delta>12.5\%$ AFM-G becomes energetically favourable. Between $\delta=12.5\%-100\%$, the energy curve of AFM-G shows a step-like tendency, with remarkable energy gains at $\delta=25\%, 50\%, 75\%$ and 100%, indicating that the formation of the 1D H-chains causes this energy gain. Another notable change with H concentration occurs at $\delta>75\%$, where AFM-A order starts to be favourable compared to AFM-C by $\sim$77 meV/Ni, indicating that the inter-layer coupling increases in strength as the topotactic-H concentration increases. This observation is in agreement with the observed increase of three-dimensionality as we go towards the fully intercalated compound.

We further investigate how multiple H-chains will arrange themselves in infinite-layers nickelates. This simulation is done by employing a $5\times5\times1$ supercell and locating 2 H-chains at different positions. As shown in the inset of Fig. 2(d), the second H-chain tends to occupy the next site along the (110) crystal cell vector (“2”) rather than along the (100)/(010) direction (“1”). In fact the nearest-neighbour location is the place where the second chain wants to be the least, evidenced by a relative energy gain of $\sim$11 meV for locations further away (“5”). This result reflects the importance of bonds between La-$d_{xy}$ and H-1s regarding the distribution of H-chains, when the local density of topotactic-H does not reach 100%. This conclusion will be further discussed in the context of phonon calculations, see Fig. 3 below.

**C. Phonon vibrations induced by topotactic-H**

To further investigate the effects induced by topotactic-H, we perform phonon calculations with the frozen phonon method (finite displacement method) using the PHONONY [80] code interfaced with VASP, and recapitulate the results of Ref. [68] for completing the physical picture. As shown in Fig. 3(a), LaNiO$_2$ is dynamically stable, being consistent with the previous report on NdNiO$_2$ [35]. Its highest frequency optical phonon mode at around 14 to 16 THz has also been observed in recent experimental resonant inelastic x-ray scattering (RIXS) measurements [52] showing a weakly dispersive optical phonon at $\sim$60 meV (~15 THz).

From the right panels of Fig. 3, one can see the low-frequency region (0-6 THz) is mainly stemming from La, while Ni contributes to the signal at 2-8 THz and the high frequency region (6-17 THz) is from O atoms. This can easily be understood as La is the heaviest atom and O is
the lightest one among the three. For the phonon spectra of LaNiO$_2$H$_3$ at other H concentrations, see Appendix II and Fig. 8.

Fig. 3(b) shows, in comparison, the phonon mode of LaNiO$_2$H ($\delta=100\%$ for LaNiO$_2$H$_3$) which is also dynamically stable as evidenced by its positive frequencies. Please note that the phonon dispersions between 0 to 20 THz are essentially the same as those in LaNiO$_2$, indicating that the phonon modes of topotactic-H and the LaNiO$_2$-superlattice are well decoupled. As shown in the phonon density of states (right panel), topotactic-H only contributes to two distinct high-frequency modes at $\sim$25 and 43 THz, corresponding to 103 and 178 meV, respectively. From our phonon eigenvector analysis, the single peak at 42 THz is formed by the vibration of H atoms along (001)-direction ($z$-direction) while the double peaks at 25 THz are generated by the doubly degenerate in-plane (100)/(110) vibrations ($xy$-plane). The formation of the double degenerate modes around $\sim$25 THz is because there is always another symmetrically protected orthogonal direction for the vibrations along the $xy$-plane.

We explain these phonon modes in detail by computing the bonding strength between H-1$s$-Ni-$d_{z^2}$ and H-1$s$-La-$d_{xy}$. Our tight-binding calculations yield an electron hopping term of $-1.604\, eV$ between H-1$s$ and Ni-$d_{z^2}$, while it is only $-1.052\, eV$ from La-$d_{xy}$ to H-1$s$. That is, the larger H-1$s$-Ni-$d_{z^2}$ overlap leads to a stronger $\delta$-type bonding and, together with the shorter c-lattice constant, to a higher phonon frequency. Additionally, the shorter c-lattice in LaNiO$_2$ is also expected to increase the strength of the H-1$s$-Ni-$d_{z^2}$ bond.

So far we have obtained several important conclusions concerning properties and arrangements of topotactic-H in infinite-layers nickelate superconductors: (1) first, our previous band character computations for LaNiO$_2$H [40] reports that the H-1$s$ band at $\sim$7 eV (-2 eV) is composed of an H-1$s$ and Ni-$d_{z^2}$ bonding (anti-bonding) state; (2) the Ni-$d_{z^2}$-H-1$s$ bond plays the most important role at forming 1D H-chains; (3) the La-$d_{xy}$-H-1$s$ bond is decisive for the structural arrangement of H-chains; (4) the Ni-sublattice is more relevant for capturing topotactic-H atoms than the La-sublattice.

D. Electronic structure of LaNiO$_2$H$_3$

In this subsection we study the electronic structure of LaNiO$_2$H$_3$ ($\delta=0.5$). Fig. 4 shows the $k$-integrated spectral functions $A(\omega)$ of LaNiO$_2$H$_3$, as obtained by DMFT. Note that in this setup there are only two inequivalent Ni sites and one Nd site (see Fig. 5 for structural details). In this respect, we define the “normal” Ni, which are in the
center of the NiO$_4$ square, as “Ni-2” and the ones that are between topotactic-H as “Ni-1”. As can be seen, the La-Ni hybridization is not fully eliminated by H-chains. This is in contrast to the fully H-intercalated LaNiO$_2$H (see Ref. [40]). In particular, the La density of states below the Fermi energy in Fig. 4(b) originates mainly from the La-$d_{xy}$ hybridization in the energy range -3 to -1 eV and a La-$d_z^2$ pocket at the Fermi energy (0 eV). The former is a consequence of the $A$-pocket [31], which is mainly composed by La-$d_{xy}$, and the later is from the hybridization between Ni-$d_{xy}$ and La-$d_z^2$ at the $\Gamma$-momentum. The hybridization also reflects in a larger occupation per La which is 0.24 electrons/site, see Table I.

As shown in Fig. 4(b) and (c), Ni-2 hosts a single-band $d_{x^2-y^2}$ picture while Ni-1 has to be described by a two-band model including both $d_{x^2-y^2}$ and $d_{z^2}$. Unlike the two-band Mott-insulating state in LaNiO$_2$H [40], Ni-1 is a two-band correlated metal with a strongly renormalized effective mass $m^*/m_b$ (see Table I). As Ni-2 has a strongly correlated $d_{x^2-y^2}$ orbital ($n \sim0.83$) and a (nearly) fully filled $d_{z^2}$ orbital ($n \sim1.96$), its configuration is close to Ni$^{1+}$ and 3$d^9$ [96]. As table Table I shows, topotactic-H absorbs nearly one electron from the Ni-1 $d_{z^2}$ orbital, i.e., the Ni-1 $d_{x^2}$ orbital in Table I has $n = 1.11$ and an effective mass enhancement $m^*/m_b=2.85$. The correlations of the Ni-1 $d_{x^2-y^2}$ orbital are stronger than those of Ni-2: $m^*/m_b=4.13$ for Ni-1 instead of $m^*/m_b=2.77$ for Ni-2 concomitant with an increase of the $d_{x^2-y^2}$ occupation from $n = 0.83$ for Ni-2 to 1.05 for Ni-1. Altogether, the electronic state of the Ni-1 site adjacent to the topotactic-H is essentially Ni$^{2+}$ and 3$d^8$. Let us note here, that the H-defect mostly changes the local electronic structure of the nearest Ni site, while leaving already the next-nearest Ni sites mostly unchanged compared to LaNiO$_2$ without H.

As reported in previous research [40], 100% topotactic-H eliminates the hybridization between La(Nd)-$d$ and Ni-$d$ by reversing (shifting up) the $A$-pocket ($\Gamma$-pocket) in LaNiO$_2$H. Hence an open question is up to which doping the pockets and the La-$d$-Ni-$d$ hybridization survive in LaNiO$_2$H$_\delta$ ($0<\delta<1$). Table I shows the La-site occupation under different concentrations of topotactic-H. With increasing the concentration of topotactic-H, the electron occupation at La, which is a consequence of La-$d$-Ni-$d$ hybridization and the La-derived pockets, is remarkably reduced.

The above computations in fact explain the recent experimental observations of the existence of Ni$^{2+}$ in undoped LaNiO$_2$ [52, 61]. Existing 1D H-chains reconstruct a 3D character of the Ni sites between topotactic-H
without affecting other Ni sites. This allows for the coexistence of Ni$^{2+}$ and Ni$^{1+}$. Unlike in the 100% case (LaNiO$_2$H), 1D H-chains allow a slight La-$d$-Ni-$d$ hybridization, which has been extensively observed in recent resonant inelastic X-ray scattering (RIXS) measurements [52, 61, 65, 97]. Additionally, the existence of 1D H-chains connects the degree of La-$d$-Ni-$d$ hybridization and a possible charge ordering state induced by disproportionate Ni oxidation states (nominal 3$d^9$ Ni$^{1+}$ and high-spin 3$d^8$ Ni$^{2+}$). Lastly, the uncertainty in concentration of topotactic-H may contribute to the sign change of the low temperature Hall coefficient measurements [25, 26, 59], as it induces a coexistence of single/two/multi bands pictures that are composed by $d_{x^2-y^2}/d_{x^2-y^2}$ and high-spin $3d^{8}(2H^2)$. Additionally, the existence of Ni site (Ni-1) and (c) second Ni site (Ni-2).

Table I. DMFT occupation at (a) the La-site for different concentrations $\delta$ of topotactic-H and (b) effective mass enhancement ($m^*/m_0$) and occupation $n$ of the different Ni orbitals for LaNiO$_2$H$_0.5$.

| (a) LaNiO$_2$H$_\delta$ | $\delta$ | $n$(La-site) |
|-------------------------|---------|-------------|
|                         | 0.25    | 0.32        |
|                         | 0.50    | 0.34        |
|                         | 0.75    | 0.20        |
|                         | 1.00    | 0.00        |

| (b) LaNiO$_2$H$_0.5$ orbital | Ni-1 $d_{x^2-y^2}$ | Ni-1 $d_{z^2}$ | Ni-2 $d_{x^2-y^2}$ | Ni-2 $d_{z^2}$ |
|-----------------------------|-------------------|----------------|-------------------|----------------|
| $m^*/m_0$                   | 4.13              | 2.85           | 2.77              | 1.19           |
| $n$                         | 1.05              | 1.11           | 0.83              | 1.96           |

E. Fermi surface of LaNiO$_2$H$_\delta$

In this subsection we compute the Fermi surface of LaNiO$_2$H$_\delta$, and choose $\delta=50\%$ as it leaves only one inequivalent Nd and two inequivalent Ni sites for the computationally heavy DMFT calculations. As shown in Fig. 5(a), the normal Ni is again defined as “Ni-2” while the one between topotactic-H as “Ni-1”.

As one can see in Fig. 5(b), the FS of LaNiO$_2$H$_0.5$ not only contains the single-band $d_{x^2-y^2}$ character [labelled by the yellow area in Fig. 5(b)], but also hosts an enhanced $\Gamma$-pocket. Please note that the original $\Delta$-pocket of undoped LaNiO$_2$ now seems absent. This is because employing a $\sqrt{2} \times \sqrt{2} \times 1$ supercell in computations rotates the BZ by 45°, and shrinks its volume [see Fig. 5(a,b) for details], which leads to the overlap of the $\Delta$- and $\Gamma$-pocket. Fig. 5(d,f) indicates that the $\Gamma$-pocket is mainly constructed from La-$d_{z^2}$ and Ni-1-$d_{z^2}$. The former contribution is the same as in pure La(Nd)NiO$_2$ while the later one from Ni-1-$d_{z^2}$ is due to the formation of H-chains. Besides La-$d_{z^2}$ and Ni-1-$d_{z^2}$, Ni-2-$d_{z^2}$ also play a tiny role at the $\Gamma$-pocket, which originated from the hybridization between La(Nd)-$d_{z^2}$ and Ni-$d_{z^2}$. Another notable feature is the hybridization between Ni-1-$d_{x^2-y^2}$ and Ni-1-$d_{z^2}$. The complex reconstruction of the Fermi surface caused by the H-chains will also affect the Hall coefficient. For the $k_z$-dependence of the DMFT FS see Appendix III and Fig. 9.

F. Magnetic properties and electronic correlations of LaNiO$_2$H$_\delta$

In order to study the modifications of magnetic properties due to topotactic-H, we define and compute local (impurity) spin-spin correlation functions $\chi(\tau) = \sum_{mn}(S_z^m(\tau)S_z^n(0))$ of LaNiO$_2$ with different concentrations of topotactic-H using DFT+DMFT. Here, $S_z^m(\tau)$ is the $z$ component of the spin operator of orbital $m$ and $\tau$ the imaginary time. Here, $\chi$ can generally be divided into orbital-diagonal (when $m=n$) and off-diagonal contributions (when $m\neq n$) for all interacting sites. Further, the value of $\chi(\tau)$ at $\tau=0$ can be interpreted in terms of
FIG. 5. DMFT Fermi surface (FS) of LaNiO$_2$H$_4$ ($\delta=50\%$) at $k_z = 0$ (for other $k_z$ momenta, see Appendix Fig. 9). (a) Crystal structure and definition of Ni-1 and Ni-2 sites, the $\sqrt{2} \times \sqrt{2} \times 1$ supercell indicated by the La-La bonds (yellow lines) is the computational model with one inequivalent Ni-1 and Ni-2 site. (b) Total Fermi surface. (c-h) Site- and orbital-resolved Fermi surface of La, Ni-1 and Ni-2. All Fermi surfaces are plotted in an extended Brillouin zone (BZ) for clarity. In (b) the dashed green square is the first BZ of the computational model as the crystal sublattice contains only two equivalent Nd and two non-equivalent Ni sites, while the dashed red square is the BZ that enables a comparison with the FS of the LaNiO$_2$ unit cell. The solid green circle encircles the $\Gamma$-pocket and the yellow shadow labels one quarter piece of Ni-$d_{z^2}$ FS.

the instantaneous local magnetic moment. As we again employed a La-$5d$+Ni-$3d$ Kanamori-type multi-site and multi-orbital model, it is instructive to study the importance of topotactic-H and La(Nd)-site. Fig. 6(a) shows the results of bulk LaNiO$_2$ without topotactic-H. As one can see, the instantaneous moment of La at $\tau=0$ is merely 0.268 $\mu_B$, and as indicated by the inset zoom-in of the orbital-resolved contributions, it originates mostly from the La-$d_{xy}$ and La-$d_{z^2}$ orbitals, which correspond to the contribution from the A-pocket and the $\Gamma$-pocket, respectively. The moment of Ni is 1.163 $\mu_B$ at $\tau=0$ and decays to 0.323 $\mu_B$ at $\tau=\beta/2$. The magnetic moment of Ni can be attributed predominately to the Ni-$d_{x^2-y^2}$ orbital, indicating the essentially single-band nature of nickelate superconductors. Other orbitals that are not shown, including Ni-$t_{2g}$ and La-$d_{yz/zx}$ and La-$d_{z^2-y^2}$ orbitals, have basically no or only negligible contributions.

The observed fast decay of $\chi$ for both La and Ni at finite $\tau$ reflects a dynamical screening and strong damping of the local moment, and may contribute to the absence of long-range magnetism in (undoped) infinite-layer nickelates. This fast screening is a consequence of self-doping of and charge transfer away from the Ni-$d_{x^2-y^2}$ orbital even without Sr(hole)-doping [98].

Fig. 6(b-d) shows $\chi(\tau)$ of LaNiO$_2$H$_{0.25}$, which corresponds to a single H-chain in a $2 \times 2 \times 2$ supercell as shown in Fig. 1(c). Such a configuration leads to three inequivalent Ni sites; and Ni-1, Ni-2 and Ni-3 denote the first, second and third nearest Ni neighbour from the H-defect. As shown in Fig. 6(b), the moment of Ni-1 is remarkably enhanced from 1.163 $\mu_B$ in LaNiO$_2$ to 2.161 $\mu_B$ in Ni-1 of LaNiO$_2$H$_{0.25}$. $\chi(\tau)$ of Ni-2 and Ni-3 are, on the other side, however basically identical to the Ni site in LaNiO$_2$ [Fig. 6(a)]. Orbital-diagonal contributions from the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals of Ni-1 do not fully account for the magnetic moment enhancement. In fact they only show a finite enhancement of the $d_{z^2}$ contribution while the $d_{x^2-y^2}$ contribution remains unchanged. To identify the origin of such an enhanced moment, we further compute the site-resolved off-diagonal contribution for Ni-1 to Ni-3, as shown in the insets of Fig. 6(b-d). This off-diagonal contribution is similarly large as the orbital-diagonal contribution of the $d_{z^2}$ orbital, and explains the missing contribution to the magnetic moment. This enhanced off-diagonal contributions of the instantaneous moment in Ni-1 is a consequence of Hund’s exchange $J$, the reduced occupation and enhanced correlations of the Ni-1 $d_{z^2}$-orbital. The boosted local magnetic moment is rather robust against dynamical screening, compared with the systems without H pollution. Since H-chains only affect the first nearest neighbour Ni sites in between H atoms, such an effect is not observed in Ni-2 and Ni-3.
The results of $\chi(\tau)$ for LaNiO$_2$H$_{0.5}$ which corresponds to a structure with two H-chains arranged along the (110)-direction in a 2x2x2 LaNiO$_2$ supercell [Fig. 1(e)] are shown in Fig. 6(e,f). As one can see Ni-1 is basically identical with Ni-1 in LaNiO$_2$H$_{0.25}$ [Fig. 6(b)] and Ni-2 is basically identical with Ni in LaNiO$_2$ [Fig. 6(a)] and Ni-2/Ni-3 in LaNiO$_2$H$_{0.25}$ [Fig. 6(c,d)]. This shows us that not only with respect to the occupation but also with respect to the local magnetic moment, only the Ni sites next to the H-chain are modified.

Finally, we study the degree of electronic correlations in undoped LaNiO$_2$, LaNiO$_2$H$_{0.25}$ and LaNiO$_2$H$_{0.5}$, as shown in Fig. 6(g). The effective masses of the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals in LaNiO$_2$ are 5.35 and 1.12, respectively. That is, the $d_{x^2-y^2}$ orbital is strongly correlated as it is nearly half-filled while the $d_{z^2}$ orbital is essentially uncorrelated as it is basically fully filled. For LaNiO$_2$H$_{0.25}$ [that hosts one H-chain as shown in Fig. 1(c)], the correlations of the $d_{z^2}$ orbital at Ni-1 site are boosted as indicated by a mass enhancement $m^*/m_0=3.28$. On the contrary, and consistent with the previous discussion, $m^*/m_0$ of the $d_{x^2-y^2}$ orbitals of Ni-2 and Ni-3 remain close to one, i.e., 1.17 and 1.04, respectively, as this orbital is almost completely filled and essentially the same as for the defect-free compound. This again indicates that topotactic-H only affects the nearest-neighbor Ni site. The mass enhancement of the $d_{x^2-y^2}$ orbitals of Ni-1 to Ni-3 in LaNiO$_2$H$_{0.25}$ shows a similar trend as that of the $d_{z^2}$ orbital: Ni-1 $d_{x^2-y^2}$ is the most correlated one, while correlations at the Ni-3 site are weakest. Correlations of all the $d_{x^2-y^2}$ orbitals are weaker for compounds with H-chains compared to LaNiO$_2$. This is because we are further away from half-filling: As shown in Table I for LaNiO$_2$H$_{0.5}$, the topotactic-H absorbs electrons from nearby Ni-sites, thus the mass of the $d_{x^2-y^2}$ orbital at the Ni-2 site reduces from half-filling (1/orbital) to 0.83/orbital. Consequently its correlations are reduced. Let us reiterate here that low-density H-defects in LaNiO$_2$H$_3$ alter valence, magnetic moment and the degree of correlations mainly on the closest Ni site, while leaving other sites mostly unchanged. This might explain the coexistence of different valence states in experiments, when such defects are present. Moreover, previous work focusing on the critical temperature $T_C$ of NdNiO$_2$ demonstrated that correlations are decisive for $T_C$ [46]. Also the additional $d_{z^2}$ Fermi surface for the doped compound is expected to be unfavourable for superconductivity. Hence our results may explain why $T_C$ in nickelates varies more strongly from sample to sample and the transition is generally more broad than in other superconductors [25, 26, 59].

### IV. CONCLUSIONS AND OUTLOOK

Our DFT and DMFT computations demonstrate the general tendency to form 1D H-chains in the infinite-layer nickelate LaNiO$_2$ if access hydrogen is available, e.g., from the CaH$_2$ reducing agent. The topotactic-H atoms are confined in the z-direction (001) if LaNiO$_2$ is grown on a SrTiO$_3$ substrate, due to formation of Ni-$d_{xy}$-H-1s bonds. If the access hydrogen exceeds a single chain, additional chains are formed at neighboring sites in the $xy$-direction (110) due to the La-$d_{xy}$-H-1s $\delta$-type bonds. The existence of H near the boundary of infinite-layers nickelates was confirmed by Ref. [70, 99], and its existence in deeper parts is worth to be investigated further. In Ref. [68] we proposed flat phonon vibrations near $\sim$103 and $\sim$178 meV as possible indications for topotactic H, which is a key characteristic as both of these peaks are located at energies that are perfectly separated from the Ni $d$-$d$ transition peak: $\sim$130 meV [65]. Such 1D H-chains can be expected to result in several uncertainties regarding the following aspects in infinite-layers nickelate superconductors: (1) structural distortion; (2) magnetism; (3) coexistence of various oxidation states of Ni ions.

More specifically, (1) our phonon computations reveal that LaNiO$_2$H$_d$ is dynamically stable, and DFT structural relaxations predict a lattice expansion as $\delta$ increases from 0% (LaNiO$_2$) to 100% (LaNiO$_2$H). In realistic samples the topotactic-H may distribute inhomogeneously. Hence, this lattice expansion effect may be rather local, leading to non-zero internal stress near individual H-chains. The experimentally observed “shear fault” phase [26, 60] is expected as an effective way to eliminate internal stress, i.e., when the internal stress is accumulated and exceeds a threshold value, “shear fault” is generated by removing a Nd(La)O layer once along the $z$-direction and a NiO$_2$ layer once along the $xy$-plane to release internal stress. In fact, one notable feature of the experimentally observed “shear fault” [26, 60] is its rectangle shape along the $z$-direction, which hints at a 1D character of the driving force or defect details. H-chains, which are difficult to detect, might explain this.

(2) The general experimental consensus is an absence of long-range magnetic order in pure and doped La(Nd)NiO$_2$ [63], which differs from cuprates and several theoretical computations that yield C- [100, 101] or G-type [102] AFM order as energetically stable compared with ferromagnetic or A-type AFM order. Observations supporting short-range AFM correlations have been reported by nuclear magnetic resonance spectroscopy (NMR) measurement that indicates local AFM spin fluctuations in (Nd,Sr)NiO$_2$ [66] while the presence of FM-like short-range order was supported by the slow magnetically dynamical process under external strong field [63]. Additionally, spin-glassy and spin-freezing behaviour, which are commonly induced by local geomet-
ric/magnetic frustrations, have been observed in both infinite-\cite{62} and finite-layer nickelates\cite{103} through powder-neutron diffraction, magnetization, and muon-spin rotation ($\mu$SR) measurements. Ref.\cite{104} reported a coexistence of FM and AFM regions, and short-range AFM order by observing large exchange bias effects and performing magnetic linear dichroism measurements, respectively. Another strong evidence for a sizable AFM exchange interaction between Ni sites is the direct observation of a dispersive magnetic excitation that shares some common features with spin waves in spin-1/2 AFM square lattice in cuprates\cite{105–107}. While the absence of AFM order may be explained by the self-doping of the Ni $d_{x^2-y^2}$ orbital even for the parent compound due to the La(Nd) pockets, topotactic-H can further diversify the picture and explain the quite different experimental observations.

Our spin-polarized DFT and DMFT spin-spin correlation $\chi(\tau)$ computations demonstrate that the formation of H-chains triggers a 2D intra-layer AFM order to 3D AFM order transition, with enhanced inter-layers coupling. Both the spin-spin correlations of the total, $d_{x^2-y^2}$ and $d_{z^2}$ components are boosted by nearby topotactic-H. The enhanced instantaneous magnetic moment and competing magnetic orders can be expected to contribute to the formation of local magnetic frustration, leading to the observed spin-glass and/or spin-freezing behaviour\cite{62}.

(3) Ni$^{2+}$ (3$d^8$) oxidation states have been reported in a recent study\cite{52} and our previous research\cite{40} was recalled to explain the origin of Ni$^{2+}$. However, in their XAS spectra, a Ni-Nd hybridization was observed, which is in contradiction to the theoretical results of LaNiO$_2$H, where the La(Nd)-Ni hybridization is fully eliminated by H-defects\cite{40}. In the present paper we resolve this apparent contradiction: the formation of H-chains naturally leads to coexisting Ni$^{3+}$ and Ni$^{2+}$ states. Indeed, any topotactic-H concentration below 100% (pure LaNiO$_2$H) is able to split the Ni atoms into two subgroups: nominal $S=1/2$ Ni$^{1+}$ (3$d^9$) and unusual $S=1$ Ni$^{2+}$ (3$d^8$), while keeping the La-Ni hybridization. The degree of La-Ni hybridization is tuned by and anti-proportional to the topotactic-H density.

Finally, our predictions of 1D H-chains in infinite-layer nickelates may explain the previously experimental observations regarding uncertainties of their electronic structures, magnetic orders, and lastly, the hidden superconducting mechanism and pairing interactions. We expect the areas with stoichiometric LaNiO$_2$ to exhibit purely $d$-wave superconductivity and antiferromagnetic fluctuations. The H-polluted regions are expected to exhibit magnetic and structural frustration as well as a suppression of superconductivity. Currently, the difficulties of identifying such H-chains in experiments stem from: (1) the radius and mass of H is negligible compared with those of La(Nd), Ni and O. This makes them hard to be detected by commonly employed techniques such as X-ray powder diffraction (XRD) or scanning transmission electron microscopy (STEM). (2) As revealed by the above phonon computations, the dynamical stability of La(Nd)NiO$_2$ does not rely on the concentration of topotactic-H atoms. Hence, the $ABO_2$ infinite-layer structure should be detected by STEM even in the
presence of H. (3) As revealed by the above presented DMFT spectra and spin-correlations functions (instantaneous magnetic moment), topotactic-H atoms merely affect the closest Ni atoms by absorbing one electron from the Ni-d_{x^2} orbital and forming La-d_{xy}-H-1s and Ni-d_{z^2}-H-1s \delta-bonds. Hence further x-ray spectra and precise chemical measurements are worth to perform in order to achieve a final conclusion on the existence of diffused H-defects or chains.

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APPENDIX

I. Ground state structures of LaNiO$_2$H$_5$

Altogether we have analyzed the all of the possible structures of LaNiO$_2$H$_5$ (0.0%<δ<100%) shown in Fig.7. Their total energies as obtained by DFT calculations are shown in Table II. This supplements Fig. 1 of the main text where only the stable structures of selected filling are presented. Please note that for LaNiO$_2$, LaNiO$_2$H$_{0.125}$, LaNiO$_2$H$_{0.875}$ and LaNiO$_2$H there is only one possible structure.

II. Phonon of LaNiO$_2$H$_5$

Fig. 8 supplements Fig. 3 and shows additional phonon spectra for various H concentrations. This demonstrates that the optical phonon modes induced by topotactic H around ~25 and 43 THz are quite insensitive to the concentration of hydrogen or the chain formation.

III. $k_z$-dependence of Fermi surface of LaNiO$_2$H$_5$

Finally, we present supplemental information for the Fermi surface in Fig. 9. That is, we plot it for other $k_z$ momenta than the $k_z = 0$ of Fig. 5.

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FIG. 7. All possible crystal structures of LaNiO$_2$H$_{\delta}$ for $\delta=0.0\%$, 12.5\%, 25\%, 37.5\%, 50\%, 62.5\%, 75\%, 87.5\% and 100\%. The structures labelled by red texts are the corresponding ground states with the lowest DFT total energy for each concentration.
TABLE II. DFT computed total energies of LaNiO$_2$H$_4$ (LNO$_2$H$_4$: 12.5%<$\delta<$87.5%). For the concentrations (δ=25%, 37.5%, 50%, 62.5%, 75%) with more than one possible crystal structures (STR), the total energy of $A$ and AC phases are set as zero. The structures and relative energies labelled with boldface are the ground states. The last two rows show the $E_0$ (in unit of meV) from non-spin-polarized DFT and spin-polarized DFT+$U$ calculations, respectively.

| $\delta$ (100%) | LNO$_2$H$_0.125$ | LNO$_2$H$_0.25$ | LNO$_2$H$_{0.375}$ | LNO$_2$H$_0.5$ | LNO$_2$H$_0.625$ | LNO$_2$H$_0.75$ | LNO$_2$H$_0.875$ | LNO$_2$H$_1$ |
|----------------|------------------|------------------|------------------|----------------|----------------|----------------|----------------|-------------|
| STR-1          | 0.0              | AC (0.0)         | A (0.0)          | A (0.0)        | A (0.0)        | AC (0.0)       | AC (0.0)       | 0.0          |
| STR-2          | -                | AG (-51.5)       | AC1 (-311.3)     | C1 (-763.3)    | AC1 (-417.3)   | AC (115.0)     | -              | -           |
| STR-3          | -                | C1 (-302.5)      | AC2 (-15.0)      | C2 (-924.9)    | AC2 (-16.7)    | C1 (-454.0)    | -              | -           |
| STR-4          | -                | C2 (54.7)        | AG1 (-449.1)     | C3 (-336.6)    | AG1 (-438.2)   | C2 (60.3)      | -              | -           |
| STR-5          | -                | G (-96.9)        | AG2 (84.2)       | C4 (-436.3)    | AG2 (82.8)     | G (83.5)       | -              | -           |
| STR-6          | -                | -                | -                | C5 (-1.4)      | -              | -              | -              | -           |
| STR-7          | -                | -                | -                | G (114.3)      | -              | -              | -              | -           |
| STR-8          | -                | -                | -                | New-1 (-385.3) | -              | -              | -              | -           |
| STR-9          | -                | -                | -                | New-2 (-389.9) | -              | -              | -              | -           |

$E_0$ (DFT) 54.3 183.9 169.8 226.3 146.8 182.5 130.4 158.5

$E_0$ (DFT+$U$) 75.0 327.3 214.9 330.1 215.8 306.6 234.9 303.9

FIG. 8. DFT phonon spectra of LaNiO$_2$H$_4$ for $\delta=25\%$ , 37.5\%, 50\%, 62.5\%, 75\% and 82.5\%. For results of $\delta=0\%$ (LaNiO$_2$) and 100\% (LaNiO$_2$H$_4$) see main text Fig. 3, and for result for $\delta=12.5\%$ (LaNiO$_2$H$_0.125$) see Ref. [68].

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FIG. 9. DMFT Fermi surfaces for additional \( k_z \)'s besides the \( k_z = 0 \) of Fig. 5 for \( \text{LaNiO}_2\text{H}_0.5 \).

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