

# Hole and electron doping of the 4d transition-metal oxyhydride $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ .

Lun Jin and Michael A. Hayward\*

**Abstract:** Hole or electron doping of phases prepared by topochemical reactions (e.g. anion deintercalation or anion-exchange) is extremely challenging as these low-temperature conversion reactions are typically very sensitive to the electron counts of precursor phases. Here we report the successful hole and electron doping of the transition-metal oxyhydride  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  by first preparing precursors in the range  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$   $0.5 < x < 1.4$  and then converting to the corresponding  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  phases. This is particularly noteworthy as the  $(\text{Ni/Ru})\text{H}_2$  sheets in the  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  phases are structurally analogous to the  $\text{CuO}_2$  sheets in cuprate superconductors and hole doping ( $\text{Ni}^{1+/2+}$ ,  $\text{Ru}^{2+}$ ) or electron doping ( $\text{Ni}^{1+}$ ,  $\text{Ru}^{1+/2+}$ ) yields materials with partial occupancy in  $\text{Ni/Ru } 3d/4d_{x^2-y^2} - \text{H}1s$  bands which are analogous to the partially occupied  $\text{Cu } 3d_{x^2-y^2} - \text{O}2p$  bands present in the  $\text{CuO}_2$  sheets of doped superconducting cuprates.

Mixed anion solids have been receiving a lot of attention recently because they offer opportunities to tailor and tune the chemical and physical properties of materials in ways which are not available to single anion chemistries.<sup>[1]</sup> For example, by including anions with differing characteristics (size, charge, polarizability, electronegativity, frontier orbital symmetry) in transition-metal systems, novel local electronic configurations can be stabilized on the d-metals, allowing the collective behavior of these states to be tuned and studied.

The strongly contrasting features of  $\text{O}^{2-}$  oxide and  $\text{H}^-$  hydride ions make complex transition-metal oxyhydride phases well placed to exploit these concepts. For example, the most obvious difference between  $\text{H}^-$  and  $\text{O}^{2-}$  is the ionic charge. When combined with the greater polarizability and lower electronegativity of the hydride ion, this charge difference means transition-metal cations tend to be stabilized in lower oxidation states in oxyhydrides ( $\text{Co}^{1+}$ ,  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Ni}^{1+}$ ,  $\text{Ru}^{2+}$ )<sup>[2]</sup> than the corresponding all-oxide systems. In addition, the greater polarizability and lower electronegativity of hydride means that M–H bonds have a greater degree of covalency than M–O bonds, resulting in qualitative differences in the band structures of oxide and oxyhydride phases, and enhanced magnetic coupling in oxide-hydride materials.<sup>[2a, 2c, 3]</sup> A further difference between the  $\text{H}^-$  and  $\text{O}^{2-}$  anions is that the hydride ion lacks  $\pi$ -

symmetry valence orbitals, and as a result cannot form bonds with metal orbitals of  $\pi$ -symmetry ( $d_{xz}$ ,  $d_{yz}$  and  $d_{xy}$  in octahedral coordination). This feature can dramatically change the ‘orbital connectivity’ of anion-ordered systems, leading to low-dimensional electronic behavior, as observed for  $\text{SrVO}_2\text{H}$ .<sup>[4]</sup> In addition to their novel electronic and magnetic properties, oxyhydrides also exhibit unusual chemical behavior and have been proposed as supports for heterogeneous catalysis, particularly for ammonia synthesis,<sup>[5]</sup> and also exhibit appreciable hydride ion conductivity,<sup>[6]</sup> which could lead to their application as electrolyte materials in hydrogen fuel cells.

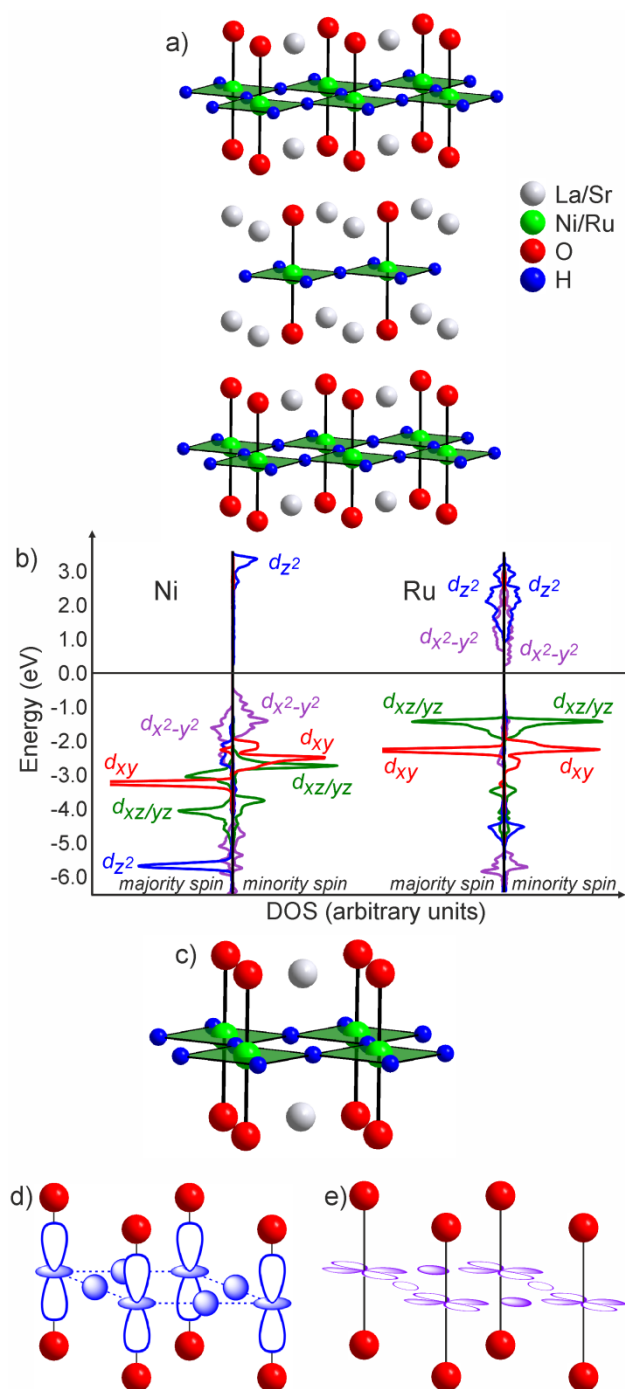
This range of novel physical and chemical behaviors suggests that oxyhydrides could become an important class of functional material, but in order to optimize the behavior of particular oxyhydride phases to a specific application it is likely they will need to be ‘doped’ by compositional modification, in an analogy to the methods which have been applied very successfully to complex oxides such as superconducting cuprates,<sup>[7]</sup> colossal magnetoresistive manganates<sup>[8]</sup> and wide range of other solid-state materials. It is challenging to dope the majority of transition-metal oxyhydride systems because they are prepared by topochemical anion-exchange reactions which convert all-oxide precursor phases into structurally related oxyhydride phases.<sup>[9]</sup> Such reactions operate under kinetic control, with product(s) determined by the relative rates of a number of competing chemical processes which can be very sensitive to the chemical composition of the precursor materials. As a result, relatively small changes to the chemical composition of the precursor can lead to changes to the reaction pathway followed, resulting in dramatically different reaction products. For example, reaction between  $\text{SrVO}_3$  and  $\text{CaH}_2$  yields the anion-ordered oxyhydride  $\text{SrVO}_2\text{H}$ .<sup>[2c]</sup> However reaction between  $\text{SrV}_{0.95}\text{Ti}_{0.05}\text{O}_3$  and  $\text{CaH}_2$  under identical conditions yields the anion-disordered oxyhydride  $\text{SrV}_{0.95}\text{Ti}_{0.05}\text{O}_{1.5}\text{H}_{1.5}$ , with the hypothetical ‘doped’  $\text{SrV}_{0.95}\text{Ti}_{0.05}\text{O}_2\text{H}$  phase being apparently synthetically inaccessible.<sup>[10]</sup> Likewise, reaction of  $\text{SrFeO}_{3-\delta}$  with  $\text{CaH}_2$  yields  $\text{SrFeO}_2$ ,<sup>[11]</sup> but attempts to electron dope samples *via* reduction of  $\text{Ln}_x\text{Sr}_{1-x}\text{FeO}_{3-\delta}$  ( $\text{Ln} = \text{Nd, Sm, Ho}$ ) yields  $\text{Ln}_x\text{Sr}_{1-x}\text{FeO}_{2+x/2}$  retaining an  $\text{Fe}^{2+}$  oxidation state.<sup>[12]</sup> Thus, in general, it is not expected that materials prepared via topochemical processes will be amenable to chemical doping.

Recently we reported the synthesis of  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ ,<sup>[2d]</sup> the first oxyhydride to contain a 4d transition-metal, which is prepared *via* hydride-for-oxide anion exchange from the all-oxide phase  $\text{LaSr}_3\text{NiRuO}_8$ .  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  has a structure based on the  $n = 1$  Ruddlesden-Popper structure of  $\text{La}_2\text{CuO}_4$ ,<sup>[13]</sup> in which the  $\text{CuO}_2$  sheets have been replaced by  $(\text{Ni/Ru})\text{H}_2$  sheets, as shown in Figure 1a. The calculated electronic structure of  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  <sup>[2d]</sup> shown in Figure 1b indicates that  $\text{Ru}^{2+}$  adopts a low-spin  $d^6$ , diamagnetic configuration, while the single unpaired electron of  $\text{Ni}^{1+}$  resides in a  $d_{z^2}$  orbital which has only minimal overlap with the  $1s$  orbital of the in-plane hydride

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Supporting information for this article is given via a link at the end of the document.



**Figure 1** a) the crystal structure and b) the spin-polarized density of states (Ni and Ru) of  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ . c) a section of the  $\text{NiRuO}_4\text{H}_4$  units with d) the Ni/Ru  $3d/4d_{z^2}$  and H1s orbitals and e) the Ni/Ru  $3d/4d_{x^2-y^2}$  and H1s orbitals projected onto it.

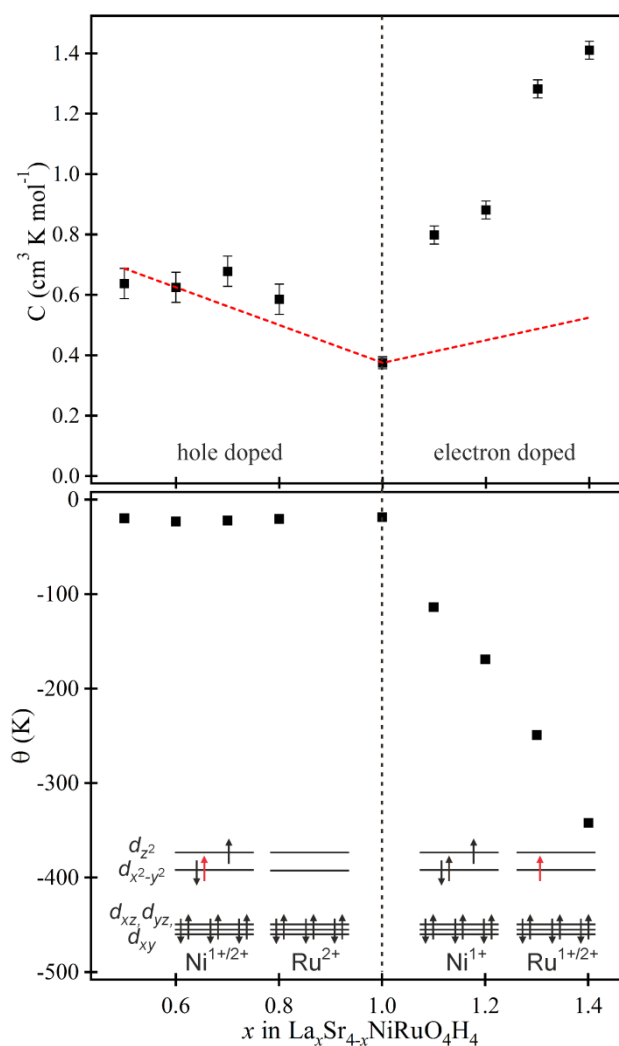
anion (Figure 1d). Thus it is no surprise that  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  is observed to be a simple paramagnet with a moment in excellent agreement with that expected for a spin-only  $S = 1/2$  center, and weak spin-spin coupling ( $\theta = -18.6$  K) and no indication of any magnetic order down to 2 K.<sup>[2d]</sup>

Close inspection of the calculated electronic structure of  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  reveals that the top of the valence band

principally consists of filled Ni  $3d_{x^2-y^2}$  states, while the bottom of the conduction band consists of empty Ru  $4d_{x^2-y^2}$  states. Thus either hole or electron doping of  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  will result partial electron occupation of states based on transition metal  $d_{x^2-y^2}$  orbitals which will interact much more strongly with the H 1s orbitals (as shown in Figure 1e) and can be considered analogous to the partially occupied bands present in hole doped superconducting copper oxides such as  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ .<sup>[7]</sup> To investigate the possibility of compositionally doping  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ , all-oxide samples in the phase range  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$  ( $0.5 < x < 1.5$ ) were prepared. Structural models based on  $\text{LaSr}_3\text{NiRuO}_8$  were refined against synchrotron X-ray powder diffraction data collected from these doped samples, to achieve good fits, revealing that the lattice parameters of these phases varied smoothly across the whole compositional range (Table S1 in the Supporting Information) consistent with the formation of a simple A-site solid solution.

The  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$  samples were reacted with  $\text{CaH}_2$  under conditions analogous to those used for converting  $\text{LaSr}_3\text{NiRuO}_8$  into  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ , described in detail in the supporting information. Structural models based on  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  were refined against synchrotron X-ray powder diffraction data collected from the products of these reactions, to achieve good fits, revealing that the lattice parameters of these phases varied smoothly across the compositional range from  $x = 0.5$  to  $x = 1.4$ , as shown in Figure S1 in the supporting Information. Close inspection of the diffraction data set from the reaction between the  $x = 1.5$  sample,  $\text{La}_{1.5}\text{Sr}_{2.5}\text{NiRuO}_8$ , and  $\text{CaH}_2$  showed that while it could be fitted by a structural model based on  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  the lattice parameters were significantly different to other members of the series, indicating that topochemical reaction which converts  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$  to  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  is limited to the range  $0.5 < x < 1.4$ . In addition close inspection of the diffraction data from the  $x = 0.9$  sample revealed the anion-exchange reaction was incomplete, so this sample was excluded from the magnetic analysis. Iodometric back-titrations and thermogravimetric measurements collected during the oxidation of  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  samples to the corresponding  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$  phases were, with the exception of the  $x = 0.9$  sample, consistent with the stated compositions, as described in the Supporting Information.

Electrical transport measurements performed on cold-pressed powder samples indicated the  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  phases are highly insulating, with all samples exhibiting resistivities greater than  $1\text{M}\Omega\cdot\text{cm}$  at room temperature, and thus too resistive to measure temperature dependent data with our equipment. Magnetization data collected from  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  ( $0.5 < x < 1.4$ ) samples indicated the presence of small amounts of a ferromagnetic impurity, consistent with  $\sim 2$  mole% elemental nickel, as reported previously for  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$ .<sup>[2d]</sup> Therefore the 'ferromagnetic subtraction' method previously used to characterize  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  was also employed for the other members of the  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  ( $0.5 < x < 1.4$ ) series, as described in the supporting information. These measurements reveal that phases in the  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  ( $0.5 < x < 1.4$ ) solid solution can be divided into two groups on the basis of their magnetic behavior. Hole doped phases ( $0.5 < x < 1$ ) have paramagnetic susceptibilities which can be fit by the Curie-Weiss law at temperatures greater than 15 K, once a small temperature independent term ( $\sim 8 \times 10^{-4} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ ) is



**Figure 2.** The Curie constants (top) and Weiss temperatures (bottom) extracted from magnetisation data collected from  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  samples. Dashed line shows the expected, spin-only Curie constant. Spin-states of the Ni and Ru cations are indicated, with partially occupied states shown in red.

included (Figure S4, Supporting Information). The values of the Curie constant extracted from these fits, plotted in Figure 2, are broadly in line with those expected from the combination of  $S = \frac{1}{2}$ ,  $\text{Ni}^{1+}$  and  $S = 1$ ,  $\text{Ni}^{2+}$  and  $S = 0$ ,  $\text{Ru}^{2+}$  centers, while it can be seen that the Weiss temperatures, also plotted in Figure 2, retain an approximately constant value of  $\theta \sim -20$  K for hole doped samples, in line with undoped  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  and consistent with weak coupling between magnetic centers. Electron doped samples ( $x > 1$ ) exhibit different magnetic behavior in which the reciprocal of the paramagnetic susceptibility is linear for  $T > 120$  K (without the addition of a temperature independent term) but shows a strong deviation from Curie-Weiss behavior at lower temperatures, as shown in Figure S5 in the Supporting Information. The Curie constants extracted from these fits, plotted in Figure 2, grow rapidly with increasing strontium substitution, to take values many times that predicted for the combinations of  $S = \frac{1}{2}$ ,  $\text{Ni}^{1+}$ ,  $S = 0$ ,  $\text{Ru}^{2+}$  and  $S = \frac{1}{2}$ ,  $\text{Ru}^{1+}$  indicated by their chemical formulae (We note that this is the first credible report of  $\text{Ru}^{1+}$  in an oxide-based system).

Likewise the Weiss constants (Figure 2) become more negative with increasing  $x$ , indicating strengthening magnetic interactions in hole-doped samples. The large, unphysical values of the Curie constant observed for hole-doped samples suggest that while the susceptibility of these phases has a Curie-Weiss-like temperature dependence, they are not simple paramagnets and the large moments observed are signatures of collective, correlated electronic behavior, consistent with strong interactions mediated by Ru-H-Ni coupling pathways. However, the conservation of insulating behavior over the whole compositional range suggests that the low dimensionality of the structure restricts the electronic band width of the system, preventing itinerant electronic behavior.

The topochemical reaction which converts  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_8$  oxide phases to the corresponding  $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$  oxyhydride phases appears insensitive to the La: Sr ratio in the range  $0.5 < x < 1.4$ , allowing the system to be electronically doped. This insensitivity indicates that the stability of the  $\text{A}_4\text{NiRuO}_4\text{H}_4$  framework directs the hydride-for-oxide anion exchange reaction, overriding any influence from the changing transition-metal oxidation states arising from the A-site doping. This is consistent with the observation that, with the exception of metallic  $\text{Sr}_2\text{TiO}_{3-x}\text{H}_x$ ,<sup>[14]</sup> all the other known insulating transition-metal oxyhydrides based on  $n = 1$  Ruddlesden-Popper structures:  $\text{LaSrCoO}_3\text{H}_x$ ,<sup>[2a, 15]</sup>  $\text{Sr}_2\text{VO}_{3-x}\text{H}_x$ <sup>[2c, 16]</sup> and  $(\text{La/Sr})_2\text{M}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$ <sup>[2e]</sup> locate the hydride ions in the equatorial anion sites of the framework. Thus we conclude that if a suitably favorable oxyhydride network can be formed, topochemically synthesized oxyhydride phases can be electronically doped by chemical substitution of the initial oxide phases allowing highly unusual oxidation states such as  $\text{Ru}^{1+}$  to be stabilized.

**Keywords:** Anion-exchange reactions • Topochemistry • Transition-metals • Transition-metal oxyhydrides • Solid-state reactions

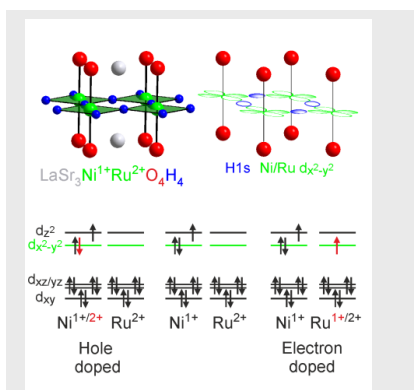
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## COMMUNICATION

Hole or electron doping the oxyhydride  $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$  creates a system with partial occupancy in the Ni/Ru  $3d/4d_{x^2-y^2} - \text{H}1s$  bands located in the  $(\text{Ni/Ru})\text{H}_2$  sheets of these phases, which are analogous to the Cu  $3d_{x^2-y^2} - \text{O}2p$  bands present in the  $\text{CuO}_2$  sheets of hole-doped superconducting cuprates.



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