A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

International Edition

www.angewandte.org

Accepted Article

Title: LaSr3NiRuO4H4: a 4d transition-metal oxide-hydride containing metal hydride sheets.

Authors: Lun Jin, Michael Lane, Dihao Zeng, Franziska Kirschner, Franz Lang, Pascal Manuel, Stephen Blundell, John McGrady, and Michael A. Hayward

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201800989
Angew. Chem. 10.1002/ange.201800989

Link to VoR: http://dx.doi.org/10.1002/anie.201800989
http://dx.doi.org/10.1002/ange.201800989

WILEY-VCH

$LaSr_3NiRuO_4H_4$: a 4d transition-metal oxide-hydride containing metal hydride sheets.

Lun Jin, Michael Lane, Dihao Zeng, Franziska K. K. Kirschner, Franz Lang, Pascal Manuel, Stephen J. Blundell, John E. McGrady and Michael A. Hayward*

Abstract: We report the synthesis of the first 4d transition metal oxide-hydride, $LaSr_3NiRuO_4H_4$, prepared *via* topochemical anion exchange. Neutron diffraction data show that the hydride ions occupy the equatorial anion sites in the host lattice and as a result the Ru and Ni cations are located in a plane containing only hydride ligands – a unique structural feature with obvious parallels to the CuO_2 sheets present in the superconducting cuprates. DFT calculations confirm the presence of $S = ½$ Ni^{1+} and $S = 0$, Ru^{2+} centres, but neutron diffraction and μSR data show no evidence for long-range magnetic order between the Ni centres down to 1.8 K. The observed weak inter-cation magnetic coupling can be attributed to poor overlap between Ni $3d_{z^2}$ and H 1*s* in the super-exchange pathways.

Complex transition metal oxides continue to be the subject of extensive study because they exhibit a wide variety of interesting physical and chemical properties. These range from magnetoresistance, high-temperature superconductivity and collective magnetism to ferroelectricity, ionic conductivity and unusual catalytic and photocatalytic behavior.[1] Typically the properties of complex oxides are tuned *via* cation substitutions, but modifications to the anion lattice, either by the introduction of anion vacancies or by substituting non-oxide hetero-anions, can also be used to modify the chemical and physical behavior of oxides. For example, 'anion doping' allows metal oxidation states to be adjusted, the on-site electronic configuration of transition metal centers to be modified (through ligand-field interactions) and inter-cation couplings to be tuned (though cation-anion-cation linkages), providing access to novel electronic states.

The contrasting features of oxide (O^{2-}) and hydride (H^-) anions offer many attractive opportunities to modify the electronic properties of 'host' oxide phases by anion substitution. The most obvious difference between oxide and hydride ions is their charge, as a result of which, hydride-for-oxide substitution necessarily involves reduction, allowing access to unusually low transition-metal oxidation states. The conversion of insulating $A^{II}TiO_3$ oxides into metallic $A^{II}TiO_{3-x}H_y$ oxide-hydrides is a classic example of the use of hydride-for-oxide substitution to modify materials properties.[2] The lower electronegativity of hydride compared to oxide also implies a higher degree of covalency and orbital mixing in M-H bonds compared to M-O analogues, and as a result the band structures of oxide-hydrides will be qualitatively different from their parent oxides. In addition, magnetic coupling strengths can be strongly enhanced in oxide-hydride phases, resulting in the high magnetic ordering temperatures observed for $LaSrCoO_3H_{0.7}$, $SrVO_2H$ and $SrCrO_2H$.[3] A final, more subtle difference between oxide and hydride ions is the absence of π-symmetry valence orbitals on the H^- anion. The 'orbital connectivity' of a phase can therefore be altered dramatically, especially if the oxide and hydride anions adopt an ordered arrangement. For example, the anion-ordered oxide-hydride $SrVO_2H$, where the hydride ions form V-H-V chains along the *z*-axis, is an antiferromagnetic insulator at ambient pressure, but undergoes a metal-to-insulator transition when pressurized to ~50 GPa.[4] The resulting metallic state exhibits significant 2-dimensional character because the hydride ions limit dispersion of the π-symmetry bands, which span the Fermi level, along the *z*-axis.

Despite their many attractive features, only a handful of transition-metal oxide-hydride phases have been prepared to date. The few reported systems can be separated into different groups on the basis of the mechanism by which the metastable oxide-hydride phase is stabilized with respect to decomposition to the elemental transition metal and water (AMO_xH_y => AO + M + H_2O), the thermodynamic sink in all cases. Early transition metal oxide-hydrides such as those containing titanium ($ATiO_xH_y$)[5] vanadium ($Sr_{n+1}V_nO_{3n-1}H_n$)[3b] and chromium ($SrCrO_2H$)[3c] can be thought of as ionically stabilized – these transition metals resist reduction due to their low electronegativities, and their high oxidation states help to stabilize the H^- anion through columbic interactions. In contrast 'late' transition metals such as cobalt (as in $LaSrCo_3H_{0.7}$, $Sr_3Co_2O_{4.33}H_{0.84}$)[3a, 6] stabilize the oxide-hydride phases through strong Co_{3d}-H_{1s}-O_{2p} covalent interactions.[7] This covalent stabilization of cobalt oxide-hydrides has direct parallels to the strong σ-bonds observed in molecular hydride systems of late 4d and 5d transition metals such as Ru, Rh and Ir, suggesting that it should be possible to prepare covalently stabilized oxide-hydride phases based on the same metals. Following this logic, we have chosen to explore the reduction/anion-exchange chemistry of a number of complex oxides containing 4d transition metal cations using CaH_2 as a reductant and source of hydride ions. We have noted in previous work, however, that 4d transition-metal oxide perovskite and Ruddlesden-Popper phases tend to decompose to yield elemental metals on reaction with CaH_2 unless they are stabilized by the presence of a 3d transition metal ion.[8] For example, reaction of $SrRuO_3$ with CaH_2 yields SrO and Ru but $SrFe_{0.5}Ru_{0.5}O_3$ and $LaSrNiRuO_6$

---

[*] Miss L. Jin, Mr. M. Lane, Mr. D. Zeng, Professor J. E. McGrady, Professor M. A. Hayward.
Department of Chemistry, Inorganic Chemistry Laboratory,
University of Oxford, South Parks Road, OX1 3QR, UK.
E-mail: michael.hayward@chem.ox.ac.uk
Ms F. K. K. Kirschner, Dr. F. Lang, Professor S. J. Blundell
Department of Physics, Clarendon Laboratory,
University of Oxford, Parks Road, OX1 3PU, UK.
Dr. P. Manuel
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxon OX11 0QX, UK.

[**] Experiments at the Diamond Light Source were performed as part of the Block Allocation Group award "Oxford Solid State Chemistry BAG to probe composition-structure-property relationships in solids" (EE13284). Experiments at the ISIS pulsed neutron facility were supported by a beam time allocation from the STFC. Part of this work was performed at the Swiss Muon Source

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

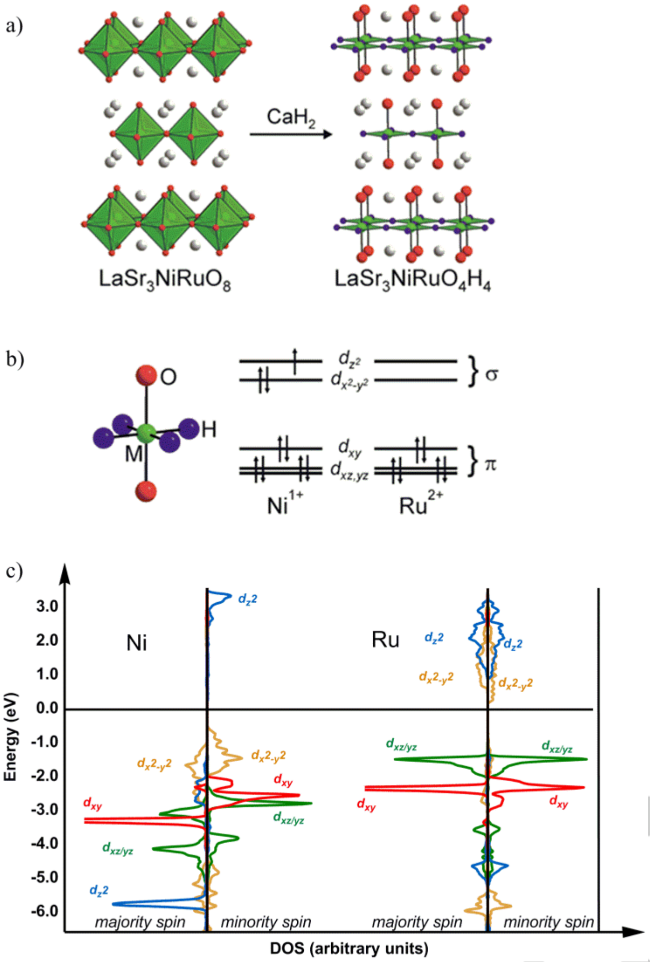


Figure 1. Crystal structure and transition-metal electronic configurations of $LaSr_3NiRuO_4H_4$ a) The Ruddlesden-Popper phase $LaSr_3NiRuO_8$ is transformed topochemically into the oxide-hydride $LaSrNiRuO_4H_4$ by the action of CaH_2 at 450 ºC. La/Sr, Ni/Ru, O and H are represented as grey, green, red and blue spheres respectively. b) The O_2H_4 coordination of Ni^{1+} and Ru^{2+} results in S = ½ and S = 0 spin states respectively. c) Spin-polarised projected density of states (Ni and Ru) for $LaSr_3NiRuO_4H_4$ (U_{eff}(Ni) = 6.0 eV, U_{eff}(Ru) = 3.0 eV). The Ni^{1+} ions are coupled ferromagnetically within the $NiRuH_2$ layers, but coupling between adjacent layers is antiferromagnetic. Majority- and minority-spin components are shown to left and right of the vertical axes, respectively. Complete DOS plots, including contributions from the oxide and hydride ligands are shown in supporting information, Figure S8)

yield $SrFe_{0.5}Ru_{0.5}O_2$ and $LaSrNiRuO_4$ respectively.[8a, 9] We have therefore focused our investigations on the anion exchange chemistry of the 3d/4d Ruddlesden-Popper oxide $LaSr_3NiRuO_8$ in which the combination of late-3d (Ni) and 4d (Ru) transition metal ions should both help to covalently stabilize any oxide-hydride phase formed.

Reaction between the Ruddlesden-Popper phase $LaSr_3NiRuO_8$ and CaH_2 proceeds initially via the topochemical deintercalation of oxide ions. Reaction at 400 ºC leads to the formation of the orthorhombic phase $LaSr_3NiRuO_7$ (a = 3.907 Å, b = 3.789 Å, c = 12.689 Å), which is then converted into $LaSr_3NiRuO_6$ (a = 3.853 Å, b = 3.593 Å, c = 13.011 Å) when the temperature is raised to 425 ºC, with CaO and H_2 being the other reaction products. On raising the temperature to 450 ºC, however, an anion exchange reaction occurs which converts orthorhombic $LaSr_3NiRuO_6$ into tetragonal $LaSr_3NiRuO_4H_4$ (a = 3.6226 Å, c = 13.317 Å) while CaH_2 is converted into CaO. Neutron powder diffraction data reveal that the net result of the conversion of $LaSr_3NiRuO_8$ into $LaSr_3NiRuO_4H_4$ is to exchange the 'equatorial' oxide ions in the former phase for hydride ions, as shown in Figure 1 (Full details of the structural refinement of $LaSr_3NiRuO_4H_4$ are given in the Supporting Information). The –(La/Sr)O–(Ni/Ru)O_2–(La/Sr)O– stacking sequence of the parent oxide is converted to a –(La/Sr)O–(Ni/Ru)H_2–(La/Sr)O– sequence in the oxide-hydride, with the Ru and Ni cations located in a plane containing only hydride ligands. The coordination spheres of the corner-linked square-planar MH_4 units in this plane are completed by two axial oxide ions that link the planes to the neighboring (La/Sr)O layers. To the best of our knowledge $LaSr_3NiRuO_4H_4$ is the first reported example of an oxide-hydride phase containing a 4d transition metal, and the 1:1 ratio of hydride to oxide is the highest yet reported. Moreover, the ordering of the anions generates a unique structural motif wherein the MH_2 planes containing the transition metals are completely devoid of oxide ions, with obvious parallels to the CuO_2 sheets present in the superconducting cuprates.

Magnetization data collected from $LaSr_3NiRuO_4H_4$ are consistent with the presence of a small amount (~ 2 mole %) of elemental nickel in the sample, although this could not be observed in diffraction data. As a result magnetization data were collected using a 'ferromagnetic subtraction' technique, described in the Supporting Information, which utilizes the fact that the magnetization of elemental nickel saturates in applied fields greater that 2T. Figure 2 shows a plot of the paramagnetic susceptibility of $LaSr_3NiRuO_4H_4$ as a function of temperature. These data can be fitted to the Curie-Weiss law ($\chi = C/(T-\theta)$) in the temperature range $10 < T/K < 300$ to yield a Curie constant of 0.374(2) cm^3 K mol^{-1} consistent with a Ni^{1+} S = ½, Ru^{2+} S = 0 electronic configuration as shown in Figure 1. A complementary electronic structure investigation using density functional theory confirmed this simple picture. The density of states, projected onto the individual angular momentum components of the Ni and Ru d orbitals (Figure 1c), shows only the minority-spin component of Ni d_{z^2} above the Fermi level: the bands formed by the other 9 spin orbitals are occupied. The strong splitting of the majority- and minority-spin components of the Ni bands is consistent with the presence of a single unpaired electron on the Ni^+ centers (0.91 μ_B). The Ru centers, in contrast, are diamagnetic, with minority- and majority-spin components of $d_{xz/yz}$ and d_{xy} occupied in a typical low-spin t_{2g}^6 (Ru^{2+}) arrangement.

The paramagnetic susceptibility of $LaSr_3NiRuO_4H_4$ goes through a maximum at 10 K and this is accompanied by an increase in the saturated ferromagnetic moment of the sample (Figure 2). These data in combination suggest the onset of magnetic order. However, neutron powder diffraction data collected from $LaSr_3NiRuO_4H_4$ at 2 K show no additional diffraction features that would support the presence of a long-range magnetic ordered state, although we note that the relatively small size of the Ni moment (S = ½) could account for our failure to observe magnetic diffraction features in low-temperature neutron diffraction data. We have therefore collected μ^+SR data as an

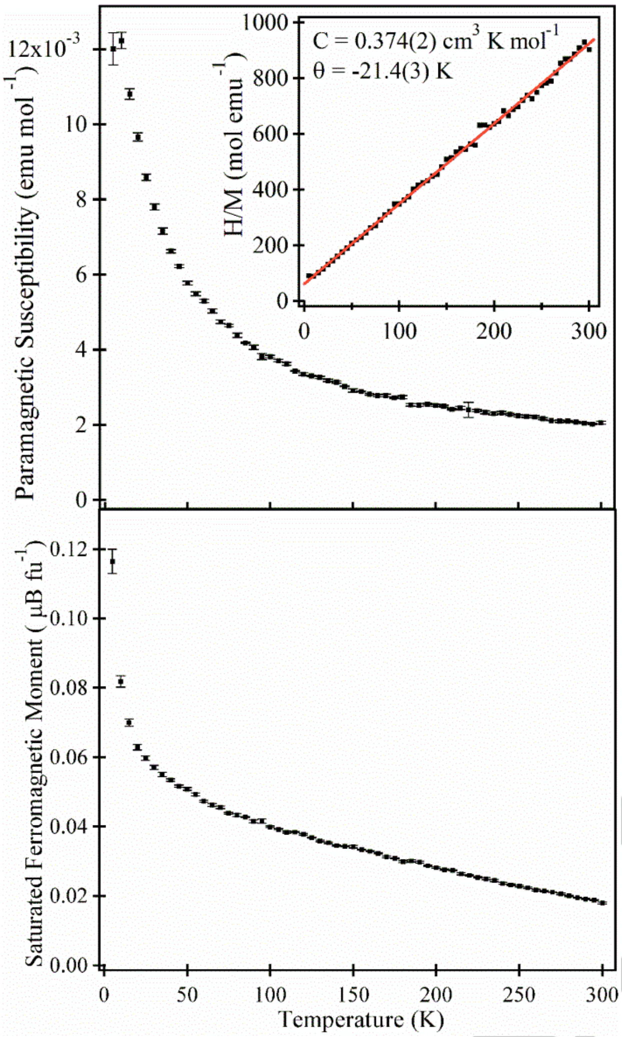


Figure 2. The paramagnetic susceptibility (top) and saturated ferromagnetic moment (bottom) of $LaSr_3NiRuO_4H_4$ collected as a function of temperature. The inset in the top panel shows the fit to the Curie-Weiss law in the temperature range 10 < T/K < 300.

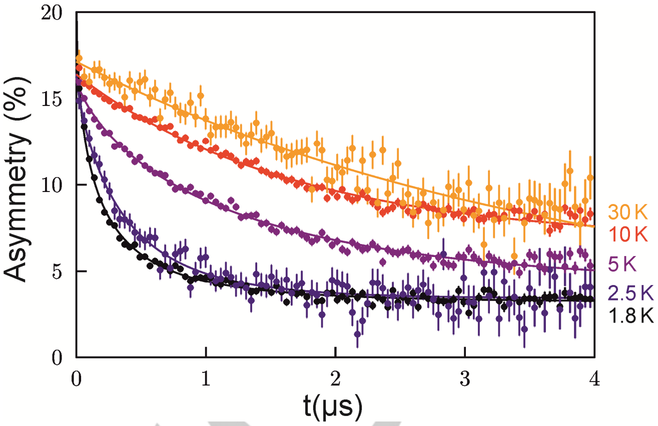


Figure 3. Plots of the asymmetry of μ^+SR data collected from $LaSr_3NiRuO_4H_4$ at various temperatures.

independent probe of local magnetic order: μ^+SR data collected from $LaSr_3NiRuO_4H_4$ are shown in Figure 3 and show no evidence for magnetic order down to a temperature of 1.8 K, in agreement with the neutron powder diffraction data. The muon polarization simply relaxes with a rate which increases as the sample is cooled, consistent with fluctuations that slow down on cooling, but not to the point where long range order is obtained. This suggests that if $LaSr_3NiRuO_4H_4$ does adopt an antiferromagnetic ground state, the ordering temperature is extremely low. The apparent weakness of the magnetic coupling is consistent with orientation of the magnetic orbital, Ni^{1+} d_{z^2}, which overlaps only very weakly with the 1s orbitals of the hydride ligands *via* the torus. The complete density of states plot shown in Figure S8 confirms the absence of significant H 1s character in the same energetic window as Ni^{1+} d_{z^2}.

In conclusion, we have reported the synthesis of an anion-ordered mixed oxide/hydride phase, where the transition metals, Ni and Ru, reside in a tetragonal MO_2H_4 coordination environment. The presence of a plane that is entirely devoid of oxide ligands is, to the best of our knowledge, a unique feature in oxide-hydride chemistry, and provides an elegant comparison to the extensively studied $SrVO_2H$ phase, where the metal coordination is MO_4H_2. The measured structural and magnetic data, along with the computational study, are consistent with the presence of transition metal ions in remarkably low oxidation states, Ru^{2+} and Ni^{1+}, for an oxide lattice.

Keywords: oxide-hydride • neutron diffraction • density functional theory • transition metals

[1] a) P. Schiffer, A. P. Ramirez, W. Bao, S. W. Cheong, *Phys. Rev. Lett.* **1995**, *75*, 3336-3339; b) J. G. Bednorz, K. A. Müller, *Z. Phys. B* **1986**, *64*, 189-193; c) R. E. Cohen, *Nature* **1992**, *358*, 136-138; d) P. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux, Y. Laligant, *Nature* **2000**, *404*, 856-858; e) R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, *293*, 269-271.

[2] a) G. Bouilly, T. Yajima, T. Terashima, W. Yoshimune, K. Nakano, C. Tassel, Y. Kususe, K. Fujita, K. Tanaka, T. Yamamoto, Y. Kobayashi, H. Kageyama, *Chem. Mater.* **2015**, *27*, 6354-6359; b) T. Yajima, A. Kitada, Y. Kobayashi, T. Sakaguchi, G. Bouilly, S. Kasahara, T. Terashima, M. Takano, H. Kageyama, *J. Am. Chem. Soc.* **2012**, *134*, 8782-8785.

[3] a) M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer, M. J. Rosseinsky, C. J. Kiely, S. J. Blundell, I. M. Marshall, F. L. Pratt, *Science* **2002**, *295*, 1882; b) F. Denis Romero, A. Leach, J. S. Moller, F. Foronda, S. Blundell, M. A. Hayward, *Angew. Chem., Int. Ed.* **2014**, *53*, 7556-7559; c) C. Tassel, Y. Goto, Y. Kuno, J. Hester, M. Green, Y. Kobayashi, H. Kageyama, *Angew. Chem., Int. Ed.* **2014**, *53*, 10377-10380.

[4] T. Yamamoto, D. Zeng, T. Kawakami, V. Arcisauskaite, K. Yata, M. A. Patino, N. Izumo, J. E. McGrady, H. Kageyama, M. A. Hayward, *Nature Communications* **2017**, *8*, 1217.

[5] Y. Kobayashi, O. J. Hernandez, T. Sakaguchi, T. Yajima, T. Roisnel, Y. Tsujimoto, M. Morita, Y. Noda, Y. Mogami, A. Kitada, M. Ohkura, S. Hosokawa, Z. F. Li, K. Hayashi, Y. Kusano, J. E. Kim, N. Tsuji, A. Fujiwara, Y. Matsushita, K. Yoshimura, K. Takegoshi, M. Inoue, M. Takano, H. Kageyama, *Nat. Mater.* **2012**, *11*, 507-511.

[6] R. M. Helps, N. H. Rees, M. A. Hayward, *Inorg. Chem.* **2010**, *49*, 11062.

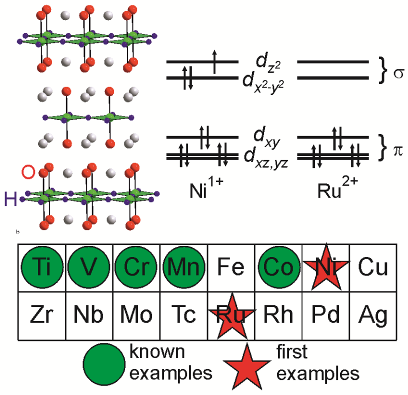
[7] C. A. Bridges, G. R. Darling, M. A. Hayward, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2005**, *127*, 5996.

[8] a) F. Denis Romero, S. J. Burr, J. E. McGrady, D. Gianolio, G. Cibin, M. A. Hayward, *J. Am. Chem. Soc.* **2013**, *135*, 1838-1844; b) F. Denis Romero, D. Gianolio, G. Cibin, P. A. Bingham, J.-C. d'Hollander, S. D. Forder, M. A. Hayward, *Inorg. Chem.* **2013**, *52*, 10920-10928.

[9] M. Amano Patino, D. Zeng, R. Bower, J. E. McGrady, M. A. Hayward, *Inorg. Chem.* **2016**, *55*, 9012-9016.

COMMUNICATION

A 4d transition-metal oxide-hydride, $LaSr_3NiRuO_4H_4$, is prepared *via* topochemical anion exchange. Hydride ions occupy equatorial anion sites in the lattice and as a result the Ru and Ni cations are located in a plane containing only hydride ligands.



Ti ●	V ●	Cr ●	Mn ●	Fe	Co ●	Ni ★	Cu
Zr	Nb	Mo	Tc	Ru ★	Rh	Pd	Ag

● known examples ★ first examples

*Lun Jin, Michael Lane, Dihao Zeng, Franziska K. K. Kirschner, Franz Lang, Pascal Manuel, Stephen J. Blundell, John E. McGrady and Michael A. Hayward**

Page No. – Page No.

$LaSr_3NiRuO_4H_4$: a 4d transition-metal oxide-hydride containing metal hydride sheets.