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Structure and magnetism of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ ($0 < x < 1$) iridium-containing oxyhydride phases†

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Ruddlesden-Popper oxide phases in the $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($0 < x < 1$) solid solution can be converted to the corresponding $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ oxyhydride phases, by topochemical reaction with LiH, in which the hydride ions are substituted exclusively onto the equatorial anion sites of the host framework. Analysis reveals that oxyhydride phases in the range $0.5 < x < 1$ adopt $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2+x}\text{H}_{2-x}$ compositions which maintain a constant Co^{1+} , Ir^{3+} oxidation-state combination (confirmed by Co K-edge XANES data), with the presence of low-spin d^6 Ir^{3+} being consistent with the covalent stabilization of the metastable oxyhydride phases *via* strong Ir–H σ -bonds. Phases at the lanthanum-poor end of the solid solution ($x < 0.5$) adopt $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ compositions with lower hydride concentrations ($y < 1.5$). Magnetisation and μSR data indicate that all the $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ oxyhydride phases exhibit strong magnetic frustration, attributed to the large-scale cation and anion disorder, and resulting in glassy magnetic behaviour at low temperature.

Introduction

Complex transition-metal oxides with perovskite or related structures have been, and continue to be, extensively studied due to the wide range of physical and chemical properties they exhibit.¹ The diverse and often complex physical behaviour of perovskite oxides can be attributed to the structural topology of these phases which consists of a network of apex-linked, transition-metal centred BO_6 octahedra. This arrangement naturally co-aligns the d-orbitals of the transition metals on neighbouring BO_6 units, both with each other and with the p-orbitals of the bridging oxide ions, facilitating the formation of relatively wide transition-metal d-bands and a variety of magnetic exchange couplings. Much work has gone into modifying the subtle structural distortions exhibited by materials with perovskitoid structures to tune the B–O–B bond angles, and thus modify the couplings between the transition-metal centres.

Partial chemical substitution of the oxide ions in phases with perovskite-like structures also offers the opportunity to modify the behaviour of materials by both tuning the tran-

sition-metal oxidation states (in the case of aliovalent anion substitutions) and changing the inter-cation couplings which make use of the anion orbitals. The preparation of oxyhydride phases, *via* the partial replacement of O^{2-} oxide ions with H^- hydride ions, is particularly attractive given the strong contrast between the two anions. For example, the lower ionic charge and lower electronegativity of the hydride ion means oxyhydride phases tend to stabilize transition metals in lower oxidation states, and exhibit stronger magnetic super-exchange couplings, than all-oxide analogues.^{2,3} In addition, the lack of π -symmetry valence orbitals on the hydride ion, means that anion-ordered oxyhydride phases exhibit band structures which are qualitatively different to all-oxide analogues.^{3,4}

Unfortunately, the vast majority of transition-metal oxyhydrides are unstable at ambient pressure with respect to decomposition *via* the reduction of the transition metal and formation of water (*e.g.* $2\text{SrVO}_2\text{H} \Rightarrow 2\text{SrO} + \text{VO} + \text{V} + \text{H}_2\text{O}$)³ so must either be prepared *via* reductive topochemical anion exchange or *via* high pressure synthesis routes. Recently we have shown that late transition-metals can kinetically stabilize oxyhydride phases *via* strong M–H Sigma bonds, as observed initially in $\text{LaSrCoO}_3\text{H}_{0.7}$ ⁵ and then subsequently in ruthenium and rhodium phases such as $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$,⁶ $\text{LaSrCoRuO}_{3.2}\text{H}_{1.8}$ ⁷ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$.⁸ Building on this idea, we reported the first iridium-containing oxyhydride phases, $\text{Sr}_2\text{Mn}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ and $\text{Sr}_2\text{Mn}_{0.5}\text{Ir}_{0.5}\text{O}_{2.66}\text{H}_{1.33}$, prepared *via* the reductive topochemical anion exchange of $\text{Sr}_2\text{Mn}_{0.5}\text{Ir}_{0.5}\text{O}_4$.⁹ Here we further investigate the formation and properties of iridium-containing oxyhydride phases by study-

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ing the anion exchange chemistry of the $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($0 < x < 1$) series of phases.

Experimental

Synthesis of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($0 \leq x \leq 1$) phases

Samples of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75, 1$) were prepared by a high-temperature ceramic synthesis method. Suitable stoichiometric ratios of La_2O_3 (99.999%, dried at 900 °C), SrCO_3 (99.99%), Co_3O_4 (99.7%) and IrO_2 (99.99%, dried for 2 hours at 700 °C) were thoroughly ground together in an agate pestle and mortar and pressed into pellets. Samples of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ were heated in air for 2 days at 950 °C, followed by 2 further 2-day periods at 1000 °C. Samples of $\text{La}_{0.25}\text{Sr}_{1.75}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ were heated in air for 2 days at 1000 °C, followed by a further period of 2 days at 1100 °C and then 2 days at 1200 °C. Samples of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ and $\text{La}_{0.75}\text{Sr}_{1.25}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ were heated in air for 2 days at 1000 °C, followed by 2 further periods of 2 days at 1300 °C. Samples of $\text{LaSrCo}_{0.5}\text{Ir}_{0.5}\text{O}_4$ were heated for 2 days at 1000 °C in an approximately 0.5 : 99.5 O_2 : Ar atmosphere (to favour formation of Ir^{4+} whilst also minimising reduction to Ir metal), followed by 2 further cycles of 2 days at 1300 °C in the same atmosphere. All samples were reground and pressed into pellets between heating periods.

Topochemical reduction of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($0 \leq x \leq 1$) phases

Topochemical reduction of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ phases was performed using LiH. Initially, small-scale reactions were performed by grinding ~200 mg of each $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ phase with 4 mole-equivalents of LiH in an argon-filled glovebox. The resulting mixtures were then sealed in evacuated Pyrex ampoules and heated at 1 °C min^{-1} to temperatures in the range 150–400 °C for periods of 2 days, to assess reactivity, which was monitored by powder X-ray diffraction. CAUTION: Heating LiH mixtures in sealed apparatus can release H_2 gas and thus represents an explosion hazard.

$\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ was observed to begin reacting with LiH at 150 °C, with non-topochemical, decomposition reactions observed at temperatures above 250 °C. $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ phases with $0.25 < x < 1$ were observed to react with LiH at temperatures above 250 °C, with non-topochemical decomposition reactions occurring above 430 °C.

Large-scale, topochemically-reduced samples were prepared as follows: $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_z$ was prepared by grinding ~2 g of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ with 4.5 mole-equivalents of LiH in an argon-filled glove box, the resulting mixture was then sealed in an evacuated Pyrex ampoule and heated for 7 days at 195 °C. $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_z$ ($0.25 < x < 1$) samples were prepared by grinding ~2 g of the corresponding $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ phase with 4.5 mole-equivalents of LiH in an argon-filled glovebox, sealing the resulting mixture in an evacuated Pyrex tube and heating for 2 days at 385 °C, followed by 2–4, 5-day periods at 410 °C. Samples were reground between heating

periods and reaction progress was monitored by powder X-ray diffraction. Grinding and heating cycles were continued until reactions were deemed complete. After reaction, samples were washed with MeOH under a nitrogen atmosphere, to remove LiOH by-products and any unreacted LiH.

Characterisation

Sample purity and reaction progress were monitored by powder X-ray diffraction (PXRD), using a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and a Lynx-eye PSD detector. High-resolution synchrotron X-ray powder diffraction (SXRD) data were collected using instrument I11 at the Diamond Light Source. SXRD data were collected using Si-calibrated X-rays with an approximate wavelength of 0.825 Å from samples sealed in 0.3 mm diameter borosilicate glass capillaries. Neutron powder diffraction (NPD) data were collected using the POLARIS instrument¹⁰ at the ISIS neutron and muon source from samples sealed under argon in vanadium cans. Analysis of the diffraction data was performed using the Rietveld method utilizing the Topas Academic software suite (v7).¹¹ DC and AC magnetisation data were collected using a Quantum Design MPMS-3 SQUID magnetometer. Thermogravimetric measurements were performed by heating powder samples at a rate of 10 °C min^{-1} under flowing oxygen using a PerkinElmer TGA 8000, with the exhaust gases monitored using a Hiden Analytical HPR-20 EGA mass spectrometer. Muon spin rotation (μSR) experiments were carried out at the Swiss Muon Source, PSI, Switzerland. Spin-polarised muons were implanted in the bulk of the sample and the time-dependence of their polarisation was monitored by recording the angular distribution of the subsequent positron decay.

Co K-edge XANES spectra were collected using an EasyXAFS300+ laboratory spectrometer based on Rowland circle geometry and operating in transmission mode. The desired energy range was selected using an Si(511) spherically bent crystal analyser and the instrument's chamber was purged with He gas to minimize absorption. Samples were diluted in dried cellulose to reach appropriate mass loading, pelletized and packed in sealed plastic bags in order to avoid exposure to moist air. Spectra were energy calibrated using a Co foil and subsequently background subtracted and normalized using Athena from the demeter software package.¹²

Results

Structural characterisation of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($0 \leq x \leq 1$) phases

SXRD data collected from $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75, 1$) phases can be indexed using body-centred tetragonal cells, with lattice parameters consistent with $n = 1$ Ruddlesden-Popper phases. Data collected from $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ can be fit using previously reported, A- and B-site disordered structural models for these phases,^{13,14} to give good fits to the data, as detailed in the ESI.† Likewise, data from $\text{La}_{0.25}\text{Sr}_{1.75}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$, $\text{La}_{0.75}\text{Sr}_{1.25}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ and



LaSrCo_{0.5}Ir_{0.5}O₄ can also be fitted well by analogous A- and B-site disordered, $n = 1$ Ruddlesden-Popper structural models as detailed in the ESI.† In the case of LaSrCo_{0.5}Ir_{0.5}O₄ a small amount of iridium metal (1.3 weight percent) was observed in the sample, highlighting the challenge of stabilizing low oxidation states of iridium in oxides. The refined lattice parameters of the La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ phases are listed in Table 1. The *a*-lattice parameters of the La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ materials contract from $x = 0$ to $x = 0.5$ and then expand for $x > 0.5$, while the *c*-lattice parameters follow the opposite trend. The *a*-lattice parameter variation can be attributed to the competition between two competing factors. Firstly, the smaller ionic radius of La³⁺ compared to Sr²⁺ leads to a contraction of the *a*-lattice parameter with increasing x . However, substitution of Sr²⁺ with La³⁺ reduces the transition metals, expanding the Co–O and Ir–O bonds counter-acting the first trend. The combination of these two effects leads to the observed behaviour. The two-dimensional nature of the (Co/Ir)–O network means that the expansion of the (Co/Ir)–O bonds, driven by a reduction of the transition metals, doesn't have to lead to an expansion in the *c*-axis. Therefore, the lattice strain that would build up from competition between the opposing contraction of the A-site and expansion of the B-site, with increasing x , can be relieved by the *c*-axis following the opposite expansion/contraction trend to the *a*-axis.

Structural characterisation of La_xSr_{2-x}Co_{0.5}Ir_{0.5}O_{4-y}H_y ($0 \leq x \leq 1$) phases

SXRD data collected from the products of reaction between La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ ($x = 0, 0.25, 0.5$) phases and LiH could be indexed using body-centred tetragonal unit cells with reflection conditions consistent with *I4/mmm* space group symmetry. The lattice parameters of the reduced phases, listed in Table 1, exhibit a contraction in the *xy*-plane and an expansion parallel to the *z*-axis, compared to the corresponding 'parent' La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ phases, consistent with the small size of the H⁻ hydride ion, compared to the O²⁻ oxide ion.

SXRD data collected from the products of reaction between La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ ($x = 0.75, 1$) phases and LiH could only be indexed using two closely related body-centred tetragonal unit cells, both of which have reflection conditions consistent with *I4/mmm* space group symmetry. Again, the lattice parameters

of the reduced phases exhibit a contraction in the *xy*-plane and an expansion parallel to the *z*-axis, compared to the corresponding parent La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ phase.

In an attempt to determine the oxygen content of the reduced phases, thermogravimetric data were collected as a function of temperature while heating samples under oxygen, as described in detail in the ESI (Fig. S6–S10†). All samples exhibit a mass gain under these conditions and exhaust gas monitoring reveals that the $x = 0$ and $x = 0.25$ samples release water on oxidation, while the $x = 0.5, x = 0.75$ and $x = 1$ samples release both water and hydrogen on oxidation, indicating that all 5 reduced phases are oxyhydrides rather than oxygen-deficient oxides. Analysis of samples after these measurements revealed that in common with previously reported Sr₂Mn_{0.5}Ir_{0.5}O_xH_y phases,⁹ the TGA conditions did not lead to complete oxidation of samples. Thus, the oxygen contents listed in Table 2, determined from the relative mass gain of samples (which assume complete oxidation back to the corresponding La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ phase) should be considered as maximum limits for the value of the oxygen content, with real values being significantly lower.

NPD data collected from the reduced La_xSr_{2-x}Co_{0.5}Ir_{0.5}O_{4-y}H_y phases could be indexed using the tetragonal unit cells used to index the SXRD data. Thus, models based on the structures of the corresponding La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ phases were refined against the data, with the occupancies of the anion sites allowed to vary. These models achieved good fits to the data and yielded structures with full oxygen occupancy on the apical (4*e*) anion sites, but reduced occupancy on the equatorial (4*c*) anion sites. Thus, hydride ions were introduced onto the equatorial anion sites along with the constraint that the oxide and hydride occupancies summed to 1, *i.e.* compositions of La_xSr_{2-x}Co_{0.5}Ir_{0.5}O_{4-y}H_y. These models refined smoothly to give good fits to the data and yielded compositions listed in Table 2, which have oxygen contents that are lower than the maximal values determined from the TGA data. In the case of the $x = 0.75$ and $x = 1$ samples, it was possible to refine 2-phase models in which the structures and compositions of the two phases could be refined independently. In both cases the data indicate samples contain a more reduced majority phase (weight fraction >80%) and a less reduced minority phase, as shown in Table 2, suggesting that the reduction reac-

Table 1 Lattice parameters of La_xSr_{2-x}Co_{0.5}Ir_{0.5}O₄ and La_xSr_{2-x}Co_{0.5}Ir_{0.5}O_{4-y}H_y phases

| <i>x</i> | La _x Sr _{2-x} Co _{0.5} Ir _{0.5} O ₄ | | La _x Sr _{2-x} Co _{0.5} Ir _{0.5} O _{4-y} H _y | |
|----------|--|--------------|---|---|
| | <i>a</i> (Å) | <i>c</i> (Å) | <i>a</i> (Å) | <i>c</i> (Å) |
| 0 | 3.91778(6) | 12.4770(2) | 3.8058(3) | 13.037(1) |
| 0.25 | 3.88836(3) | 12.5844(1) | 3.6888(5) | 13.172(1) |
| 0.5 | 3.87999(4) | 12.5927(1) | 3.6596(5) | 13.266(2) |
| 0.75 | 3.90328(7) | 12.5893(2) | 3.6896(7) | 13.233(2) |
| 1 | 3.89677(2) | 12.5777(1) | (3.7661(8)) 3.7070(6) (3.7789(8)) | (13.029(5)) 13.342(4) (13.040(2)) |

Table 2 Sample compositions determined by TGA and NPD analysis

| <i>x</i> | Composition from TGA data | Composition from NPD data |
|----------|--|---|
| | 0 | Sr ₂ Co _{0.5} Ir _{0.5} O _{3.47} H _y |
| 0.25 | La _{0.25} Sr _{1.75} Co _{0.5} Ir _{0.5} O _{3.16} H _y | La _{0.25} Sr _{1.75} Co _{0.5} Ir _{0.5} O _{2.75} H _{1.25} |
| 0.5 | La _{0.5} Sr _{1.5} Co _{0.5} Ir _{0.5} O _{2.97} H _y | La _{0.5} Sr _{1.5} Co _{0.5} Ir _{0.5} O _{2.5} H _{1.5} |
| 0.75 | La _{0.75} Sr _{1.25} Co _{0.5} Ir _{0.5} O _{2.92} H _y | La _{0.75} Sr _{1.25} Co _{0.5} Ir _{0.5} O _{2.75} H _{1.25} (La _{0.75} Sr _{1.25} Co _{0.5} Ir _{0.5} O _{3.4} H _{0.6}) |
| 1 | LaSrCo _{0.5} Ir _{0.5} O _{2.96} H _y | LaSrCo _{0.5} Ir _{0.5} O ₃ H (LaSrCo _{0.5} Ir _{0.5} O _{3.5} H _{0.5}) |



tions did not reach completion during the preparation of the samples. Full details of the refined structures of the $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases are given in the ESI,[†] along with plots of fits to the diffraction data. Fits to the data collected from $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ are shown in Fig. 1 as a representative data set.

Fig. 2 shows XANES data collected from the cobalt K-edges of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$, $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.5}\text{H}_{1.5}$ and $\text{LaSrCo}_{0.5}\text{Ir}_{0.5}\text{O}_3\text{H}$ along with data from $\text{Sr}_2\text{CoIrO}_6$ and YBaCo_2O_5 to act as Co^{3+} and $\text{Co}^{2.5+}$ standards respectively. The edge position of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ is at lower energy than either of the two standards, consistent with a Co^{2+} oxidation state, while the edges of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.5}\text{H}_{1.5}$ and

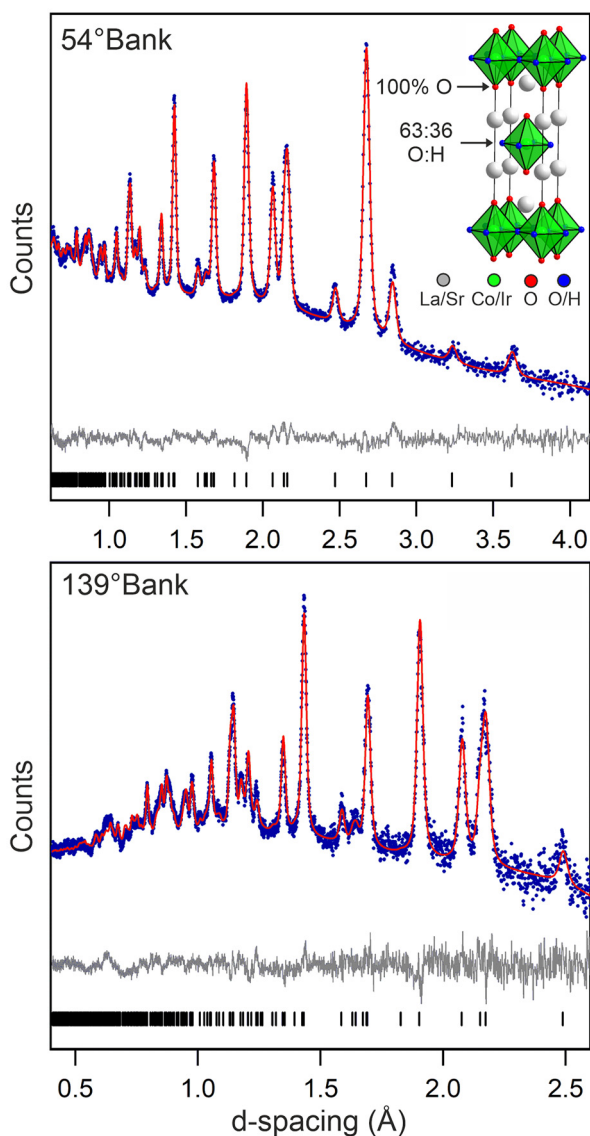


Fig. 1 Observed, calculated and difference plots from the structural refinement of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ against NPD data collected at room temperature from 2 of the detector banks of the POLARIS instrument. Inset show representation of the structure of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.27}\text{H}_{0.73}$.

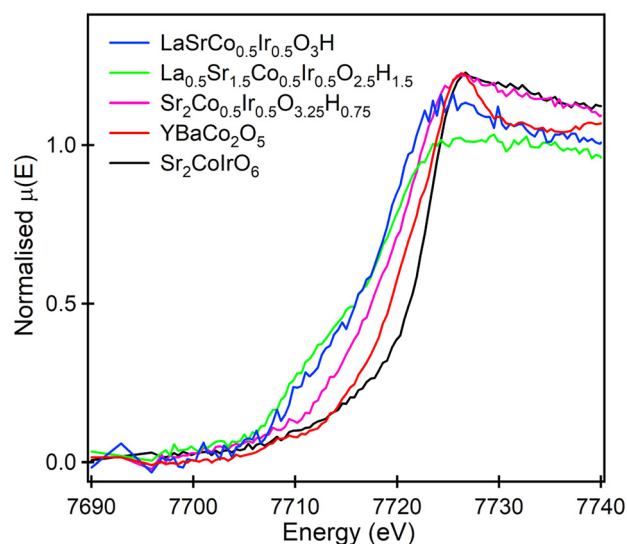


Fig. 2 XANES data collected from the Co K-edges of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$, $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.5}\text{H}_{1.5}$ and $\text{LaSrCo}_{0.5}\text{Ir}_{0.5}\text{O}_3\text{H}$ with data from YBaCo_2O_5 and $\text{Sr}_2\text{CoIrO}_6$ acting as $\text{Co}^{2.5+}$ and Co^{3+} standard respectively.

$\text{LaSrCo}_{0.5}\text{Ir}_{0.5}\text{O}_3\text{H}$ are at even lower energy, consistent with an oxidation state of Co^{1+} in these materials.

Magnetic characterisation of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases

Magnetisation-field data collected from $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases at 300 K are sigmoidal, consistent with the presence of 3–6 mol% ferromagnetic elemental cobalt, as shown in the ESI.[†] Thus, magnetisation data were collected using a ‘ferrosubtraction’ method described in detail in the ESI.[†] The paramagnetic susceptibility of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases measured by this procedure are plotted in Fig. 3a and b.

The paramagnetic susceptibility of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ (Fig. 3a) can be fit by the Curie–Weiss law with the addition of a temperature independent component, in the range $35 < T/\text{K} < 200$, to yield values of $C = 1.17(1) \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -30.5(6) \text{ K}$, $K = 0.0077(5) \text{ cm}^3 \text{ mol}^{-1}$, broadly consistent with the value expected for a combination of Co^{2+} and $\text{Ir}^{4+/5+}$ with the temperature independent contribution being consistent with the strong spin–orbit coupling expected for both Co^{2+} and $\text{Ir}^{4+/5+}$ centres. Below this temperature range the susceptibility increases sharply and magnetisation-field data collected at 5 K, after cooling in an applied field of 5 T, are off-set from the origin (Fig. S16[†]), suggesting a transition to a glassy magnetic state at low temperature. AC susceptibility data collected from $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ (Fig. 4a) show a strong frequency dependence consistent with the freezing of a spin glass at $T \sim 20 \text{ K}$ and μSR data (Fig. 4b) show a change in relaxation between 27.5 and 35 K, consistent with such a transition.

Plots of the paramagnetic susceptibility of the remaining $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases (Fig. 3) become increasingly temperature independent with increasing lanthanum content,



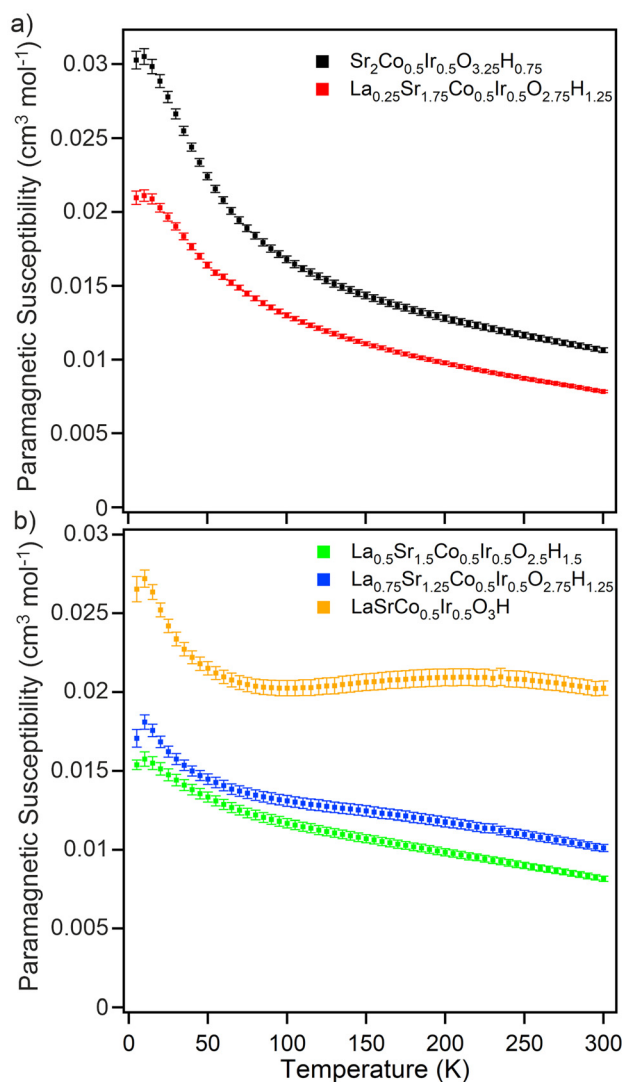


Fig. 3 Paramagnetic susceptibility of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases obtained via the 'ferrosubtraction' method.

so cannot be fit by the Curie–Weiss law. In addition, with the exception of the data from the $x = 1$ sample which shows a sharp increase in magnitude for $T < 60$ K, none of the data show obvious features indicative of phase transitions, such as a precession signal resulting from static ordered moments (as found in ordered materials).^{2,3} μSR data collected from the $x = 0.5$ and $x = 1$ samples (Fig. 4b) exhibit a slowing down of spin fluctuations on cooling, but that the dynamics saturate below around 40 to 50 K. It is hard to definitively describe the magnetic behaviour of the oxyhydride phases from these data. However, on balance, given the large-scale chemical disorder in the materials, we think glassy behaviour at low temperature is the most likely scenario which is consistent with the data. This is consistent with the observation that magnetisation-field data collected from all reduced phases at 5 K, after cooling in an applied field of 5 T, are off-set from the origin (Fig. S17–S20†).

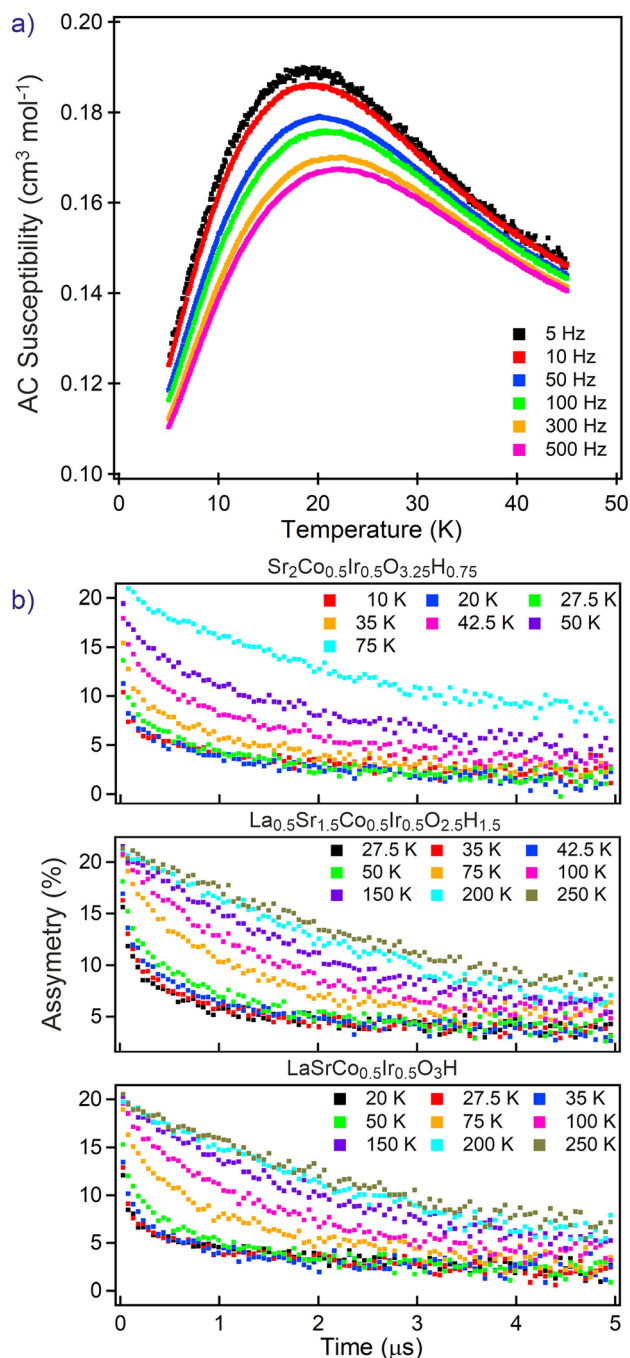


Fig. 4 (a) The real component of AC susceptibility data collected as a function of temperature from $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ (b) μSR data collected from $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$, $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.5}\text{H}_{1.5}$ and $\text{LaSrCo}_{0.5}\text{Ir}_{0.5}\text{O}_3\text{H}$.

Discussion

Reaction between $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ phases and LiH leads to topochemical, hydride-for-oxide, reductive anion-exchange and the formation of the corresponding $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases, with the hydride ions residing in the equatorial anion sites of the phases formed. The selective substitution of equa-



torial, not axial, oxide ions by hydride ions is also observed for other transition-metal oxyhydride phases with $n = 1$ Ruddlesden-Popper structures, such as the 3d transition-metal systems $\text{LaSrCoO}_3\text{H}_{0.7}$,² $\text{Sr}_3\text{CoO}_{4.33}\text{H}_{0.84}$,¹⁵ $\text{Sr}_2\text{VO}_3\text{H}^{3,16}$ and $\text{LaSrMnO}_{3.3}\text{H}_{0.7}$ ¹⁷ or the 3d/4d transition-metal phases $\text{LaSr}_3\text{NiRuO}_4\text{H}_4$,⁶ $\text{LaSr}_3\text{CoRuO}_4\text{H}_4$ ¹⁸ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Rh}_{0.5}\text{O}_3\text{H}$.⁸

This strong preference for locating hydride ions within the equatorial anion sites of A_2BO_4 $n = 1$ Ruddlesden-Popper phases can be rationalized by observing that the equatorial anion sites have an A_4B_2 coordination compared to the A_5B coordination of the axial sites. Thus, replacing the equatorial O^{2-} oxide ions with H^- hydride ions lowers the bond valence sum of the B-cations more (changes more B-anion interactions) than the equivalent change to the axial anion sites. Given that the B-cations are reduced on hydride-for-oxide exchange and the A-cations are not, locating the hydride ions on the equatorial sites leads to oxyhydride phases with lower lattice strain. The same argument has been made previously to rationalise the analogous preference for locating anion vacancies on the equatorial sites of A_2BO_4 phases.¹⁹

Recently we reported that $\text{Sr}_2\text{Mn}_{0.5}\text{Ir}_{0.5}\text{O}_{2.66}\text{H}_{1.33}$ adopts an $n = 1$ Ruddlesden-Popper structure in which some of the hydride ions reside in axial anion sites, violating the 'equatorial hydride' selectivity observed for other $\text{A}_2\text{BO}_{4-x}\text{H}_x$ phases.⁹ In this instance it is argued that a strong *trans*-influence arising from strong Ir–H Sigma bonds disfavors the local *mer* configuration (which forces two hydride ligands to be *trans* to each other) which the IrO_3H_3 units must adopt if the hydride ions are only to be located on equatorial sites of $\text{A}_2\text{BO}_{4-x}\text{H}_x$ phases with $x > 1$. In addition, it was also noted that strong spin-orbit coupling favours the pseudo degeneracy of the $5d_{xy}$, $5d_{xz}$ and $5d_{yz}$ orbitals which occurs when IrO_3H_3 units adopt a *fac* configuration, which actively favours locating anions on axial coordination sites.

Given that both the strong *trans* influence and strong spin-orbit coupling arise from the presence of iridium, it may be expected that other iridium-containing, $\text{A}_2\text{BO}_{4-x}\text{H}_x$ oxyhydride phases with $x > 1$ would also violate the equatorial hydride rule. However, as detailed above $\text{La}_{0.25}\text{Sr}_{1.75}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.75}\text{H}_{1.25}$, $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.5}\text{H}_{1.5}$ and $\text{La}_{0.75}\text{Sr}_{1.25}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.75}\text{H}_{1.25}$ adopt structures in which the hydride ions are located exclusively on equatorial sites, despite containing iridium. We suggest this restoration of the equatorial hydride preference can be attributed to the increased A-site charge in the $\text{La}_{1-x}\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases, compared to $\text{Sr}_2\text{Mn}_{0.5}\text{Ir}_{0.5}\text{O}_{2.66}\text{H}_{1.33}$, which enhances the bond-valence-sum/strain effects disfavoring the location of hydride ions on axial anion sites. However, further study is required to fully understand the anion configuration preferences of iridium-containing oxyhydride phases.

Table 2 shows that the degree of hydride exchange (y) in $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases depends strongly on the La : Sr ratio (x), taking a maximum value of $y = 1.5$ at $x = 0.5$. Fig. 5 plots the observed $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases on a composition-space diagram, with the La : Sr A-site ratio varying

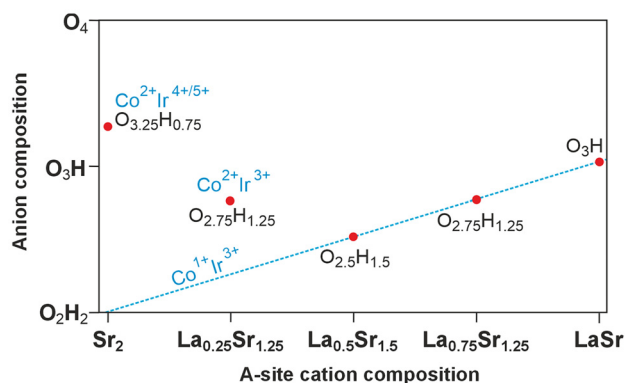


Fig. 5 Composition diagram of $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases.

along the x -axis, and the O : H ratio varying along the y -axis. Thus, moving to the right, or moving down on the diagram requires a reduction in transition-metal oxidation states, and moving left, or moving up on the diagram requires an oxidation of the transition-metals. It can be seen on Fig. 5 that $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.5}\text{H}_{1.5}$, $\text{La}_{0.75}\text{Sr}_{1.25}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.75}\text{H}_{1.25}$ and $\text{LaSrCo}_{0.5}\text{Ir}_{0.5}\text{O}_3\text{H}$ all lie on the line for which the sum of the cobalt and iridium oxidation states is equal to 4. XANES data (Fig. 2) indicate a cobalt oxidation state of Co^{1+} for $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.5}\text{H}_{1.5}$ and $\text{La}_{0.75}\text{Sr}_{1.25}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.75}\text{H}_{1.25}$, consistent with the observation that all the $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases in the range $0.5 < x < 1$ have a Co^{1+} , Ir^{3+} transition-metal oxidation-state combination.

As noted above, the low-spin d^6 configuration of Ir^{3+} is consistent with the 'covalent stabilization' of transition-metal oxyhydrides observed previously for ruthenium and rhodium phases.^{6,8} It is interesting to note that in the case of the $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ ($0.5 < x < 1$) phases shown here, the transition-metal oxidation states appear to define the final hydride concentration, with compounds maintaining the Co^{1+} , Ir^{3+} combination as x rises by lowering the extent of hydride-for-oxide anion exchange. This contrasts with the behaviour of the $\text{La}_x\text{Sr}_{4-x}\text{NiRuO}_4\text{H}_4$ series in which the ' O_4H_4 ' anion composition of the $x = 1$ phase, $\text{LaSr}_3\text{Ni}^{1+}\text{Ru}^{2+}\text{O}_4\text{H}_4$, remains constant across the $0.5 < x < 1.5$ range, with increases in Sr^{2+} content ($x < 1$) accommodated by the partial oxidation of Ni^{1+} to Ni^{2+} and increases in La^{3+} content ($x > 1$) by the partial reduction of Ru^{2+} to Ru^{1+} .²⁰

This contrasting behaviour of the Ir and Ru systems can be rationalized by observing that the enhanced M–X σ -bonding of Ir compared to Ru makes the ligand-field splitting of 5d Ir much greater than 4d Ru and thus makes the $(t_{2g})^6(e_g)^1$ configuration of Ir^{2+} ions energetically unfeasible. As a result, it is not possible to reduce the Co^{1+} , Ir^{3+} oxidation-state combination in $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases as x increases, so the hydride concentration must decline.

The hydride content of $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{3.25}\text{H}_{0.75}$ and $\text{La}_{0.25}\text{Sr}_{1.75}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{2.75}\text{H}_{1.25}$ do not appear to be defined by the transition metal oxidation states, but are instead limited by the robustness of the (La/Sr)–Co–Ir–O framework, with the



reaction conditions required to achieve higher levels of hydride-for-oxide anion exchange leading to non-topochemical reactions and the destruction of the $n = 1$ Ruddlesden-Popper structure.

Magnetisation and μ SR data collected from $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases (Fig. 3 and 4) are indicative of strong interactions between local spins which appear to be strongly frustrated – a combination of behaviours which is particularly evident in phases with $x > 0.25$. The ‘parent’ phases $\text{Sr}_2\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ and $\text{La}_{0.5}\text{Sr}_{1.5}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ exhibit spin glass behaviour at low temperature^{13,14} consistent with disorder of the Co and Ir centres within the $n = 1$ Ruddlesden-Popper framework, with magnetic frustration arising from competition between Co–O–Co, Co–O–Ir and Ir–O–Ir super-exchange interactions.

It may be expected that the reduction of the iridium centres on oxyhydride formation, to adopt diamagnetic, low-spin, Ir^{3+} configurations, may reduce the frustration in the system. However, diamagnetic Ir^{3+} can participate in super–super–exchange coupling in which the empty σ -symmetry iridium d-orbitals provide a pathway to couple neighbouring Co

centres in an antiferromagnetic manner, as shown in Fig. 6a, by a mechanism analogous to the super–super–exchange couplings mediated by Ir^{5+} in double perovskite phases such as LaSrNiIrO_6 .²¹ This super–super–exchange interaction, utilizing O 2p or H 1s anion orbitals, acts to couple next–next–nearest neighbouring cobalt centres in an antiferromagnetic manner, a coupling which would lead to a ‘Type II’ antiferromagnetic structure in a rocksalt ordered array of Co and Ir centres.^{22,23} However, in a cation disordered system, this super–super–exchange coupling competes with simple nearest-neighbour super–exchange couplings between cobalt centres (Fig. 6b) and is likely to be one source of the strong magnetic frustration observed in the $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ phases.

The substitution of oxide ions by hydride ions is not expected to change the sign of any of the dominant σ -symmetry exchange interactions, but is likely to strengthen them due to the enhanced covalency of M–H compared to M–O interactions.

Conclusions

Reaction between $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_4$ ($0 < x < 1$) phases and LiH yields the corresponding $\text{La}_x\text{Sr}_{2-x}\text{Co}_{0.5}\text{Ir}_{0.5}\text{O}_{4-y}\text{H}_y$ oxyhydride phases *via* topochemical anion exchange at the equatorial anion site. Phases in the range $0.5 < x < 1$ have anion compositions defined by a Co^{1+} , Ir^{3+} transition-metal oxidation-state combination, consistent with covalent stabilization of the oxyhydride phase *via* strong Ir–H σ -bonds. Magnetisation data indicate strong magnetic interactions between local cobalt spins, which are strongly frustrated, consistent with the disorder on both the cation and anion lattices.

Author contributions

JIM prepared the samples and performed the structural and chemical analysis, RW assisted with the XANES data, SJB, HCHW and BMH collected the μ SR data and managed the analysis of this data, RIS assisted with the collection of the NPD data, MAH conceived the study, wrote the manuscript and supervised the study.

Conflicts of interest

There are no conflicts to declare.

Data availability

Neutron Powder diffraction data can be found at: (doi.org/10.5286/ISIS.E.RB2310613). Additional data are available in the ESI.†

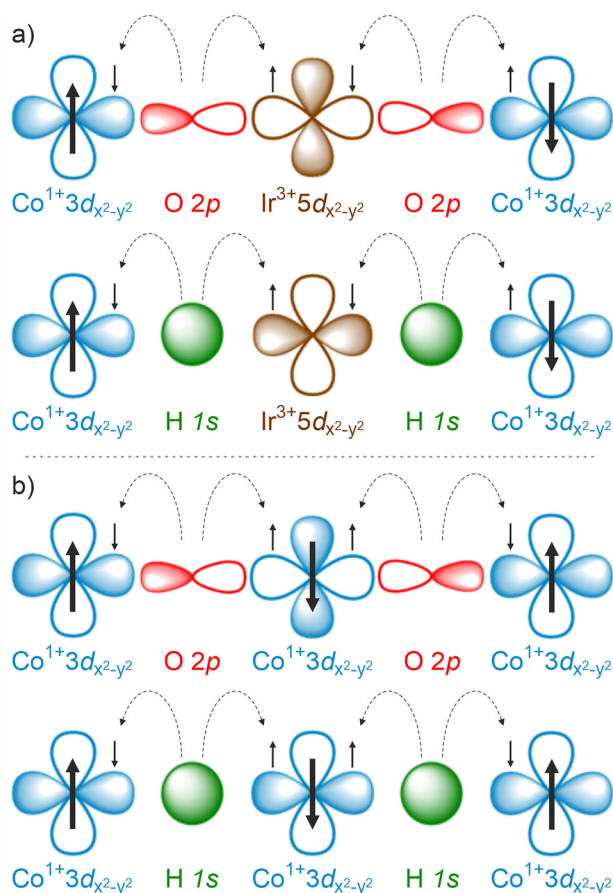


Fig. 6 (a) Super–super–exchange coupling between next–next–nearest neighbour cobalt centres mediated by empty Ir σ -symmetry d-orbitals (b) nearest-neighbour super–exchange couplings between cobalt centres.



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