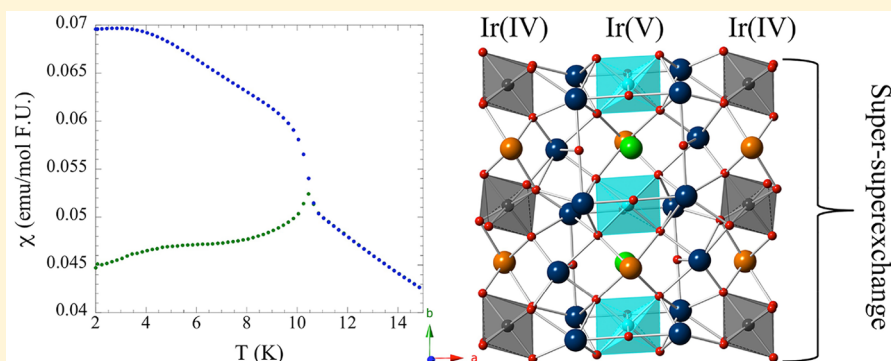


A Family of A-Site Cation-Deficient Double-Perovskite-Related Iridates:  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ )

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## Supporting Information



**ABSTRACT:** The compositions of the general formula  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ;  $1.37 \geq x \geq 2$ ) belonging to a family of A-site cation-deficient double-perovskite-related oxide iridates were grown as highly faceted single crystals from a molten strontium chloride flux. Their structures were determined by single-crystal X-ray diffraction. On the basis of the single-crystal results, additional compositions,  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ), were prepared as polycrystalline powders via solid-state reactions and structurally characterized by Rietveld refinement. The compositions  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ) contain Ir(V) and Ir(IV) in a 1:3 ratio with an average iridium oxidation state of 4.25. The single-crystal compositions  $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$  and  $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$  contain relatively less Ir(V), with the average iridium oxidation states being 4.21 and 4.09, respectively. The magnetic properties of  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ) were measured, and complex magnetic behavior was observed in all cases at temperatures below 30 K.

## INTRODUCTION

The investigation of complex iridates has been pursued for many decades, and numerous compositions containing Ir(IV), Ir(V), and Ir(VI) have been reported to date.<sup>1–5</sup> Investigations of the magnetic properties of iridates have led to the observation that spin–orbit coupling often plays a dominant role in the observed magnetic moments, where the potential of commercial applications<sup>6–8</sup> as well as the desire for a fundamental understanding<sup>9–15</sup> has led to the continuing investigation of complex iridium oxides. Spin–orbit coupling is especially prevalent in the 4d and 5d elements, including iridium for which spin–orbit coupling is often sufficiently strong to affect the crystal-field splitting, leading to a splitting of the  $t_{2g}$  manifold into  $J_{\text{eff}} = 3/2$  and  $J_{\text{eff}} = 1/2$  bands. For that reason, some Ir(IV)-containing compositions,  $\text{A}_2\text{IrO}_4$  ( $\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$ ),<sup>6–8,11,16–21</sup> have garnered significant interest for their  $J_{\text{eff}} = 1/2$  magnetic state because it was proposed that a possible link between this  $J_{\text{eff}} = 1/2$  state and the  $S = 1/2$  state of the layered cuprates may lead to unconventional superconductivity.

The competition between the crystal-field effects and spin–orbit coupling can manifest itself in a variety of ways in iridium-containing oxides. A number of Ir(IV)-containing

compositions exhibit a reduced magnetic moment, such as in  $\text{Sr}_2\text{IrO}_4$  ( $0.50 \mu_{\text{B}}/\text{Ir}$ )<sup>22</sup> and  $\text{Sr}_3\text{Ir}_2\text{O}_7$  ( $0.69 \mu_{\text{B}}/\text{Ir}$ ),<sup>23</sup> while others, such as  $\text{Na}_2\text{IrO}_3$  ( $1.79 \mu_{\text{B}}/\text{Ir}$ ),<sup>24</sup> exhibit a magnetic moment consistent with one unpaired electron. This observation motivated a study conducted by Phelan et al. to investigate a complex iridate of the general formula  $\text{Sr}_x\text{La}_{11-x}\text{Ir}_4\text{O}_{24}$  ( $x = 1–5$ )<sup>10</sup> to measure how the tuning of the valence of iridium via strontium doping, from Ir(IV)  $5d^5$  in  $\text{SrLa}_{10}\text{Ir}_4\text{O}_{24}$  to Ir(V)  $5d^4$  in  $\text{Sr}_5\text{La}_6\text{Ir}_4\text{O}_{24}$ , affected the temperature-dependent magnetic susceptibility. The results of this study determined that the measured  $\mu_{\text{eff}}$  decreased as  $x$  increased, indicating that, as the composition approached  $\text{Sr}_5\text{La}_6\text{Ir}_4\text{O}_{24}$  [all Ir(V)], the magnetic susceptibility decreased. This is consistent with strong spin–orbit coupling interactions in Ir(V), leading to a singlet ground state, demonstrating that this material is a good model structure with which to further study the spin–orbit coupling effects; see Figure S1.

Several compositions isostructural with  $\text{Sr}_x\text{La}_{11-x}\text{Ir}_4\text{O}_{24}$  are known, including  $\text{A}_{11}\text{Re}_4\text{O}_{24}$  ( $\text{A} = \text{Ca}, \text{Sr}$ )<sup>25,26</sup> and  $\text{Ba}_{11}\text{Os}_4\text{O}_{24}$ ,<sup>27</sup> however, to date, no examples of this structure

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type with a magnetic ion on the A site have been reported. In the absence of a magnetic ion on the A site, any magnetic property observed is due to the presence of iridium on the B site, and any magnetic order would be the result of magnetic exchange coupling between them. To expand the investigation of this family of A-site cation-deficient double-perovskite-related oxides, we synthesized compositions having magnetic ions on the A site as well. Herein we report on a series of complex oxides of the general formula  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}; 1.37 \geq x \geq 2$ ), synthesized both as single crystals via chloride flux growth and as polycrystalline powders via traditional solid-state synthesis, to investigate the effect of having magnetic ions on both the A and B sites. We discuss the crystal growth, synthetic considerations, structure determination, and magnetic properties of  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ) as polycrystalline powders and  $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$ ,  $\text{Nd}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ , and  $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$  as single crystals.

## ■ EXPERIMENTAL SECTION

**Reagents.**  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ; Alfa Aesar 99.99%),  $\text{Pr}_6\text{O}_{11}$  (Alfa Aesar 99.9%),  $\text{SrCO}_3$  (Alfa Aesar, 99.9%), Ir powder (Engelhard, 99.9995%), and  $\text{SrCl}_2$  (Macron, ACS Reagent grade) were used as received.  $\text{Pr}_6\text{O}_{11}$  (Alfa Aesar, 99.99%) was reduced to  $\text{Pr}_2\text{O}_3$  under 5% hydrogen at 1000 °C in a tube furnace overnight.

**Synthesis.** Single crystals of  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  [ $\text{Ln} = \text{La}$  ( $x = 1.85$ ),  $\text{Pr}$  ( $x = 1.63$ ),  $\text{Nd}$  ( $x = 2$ )] were grown from a high-temperature chloride flux melt.  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$ ; 1 mmol), Ir (1 mmol), and  $\text{SrCl}_2$  (10 g) were loaded into alumina crucibles with loose-fitting alumina lids. The crucibles were heated to 1150 °C at 600 °C/h, held there for 24 h, slow cooled to 900 °C at 12 °C/h, and then allowed to cool to room temperature by turning off the furnace. The black crystals were removed from the flux by dissolving the flux in water assisted by sonication. The crystals were extracted by vacuum filtration. Polycrystalline samples of  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ) were prepared by intimately grinding  $\text{Ln}_2\text{O}_3$ ,  $\text{SrCO}_3$ , and Ir metal in stoichiometric amounts and heating the resulting powder in air in an alumina crucible with a loose-fitting lid. The crucibles were heated to 1150 °C for 148 h with intermittent grindings in a programmable furnace.

**Single-Crystal X-ray Diffraction.** Crystals grew as clusters of lustrous black polyhedra, from which suitable data crystals were cleaved apart. X-ray intensity data were collected at 303(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo  $K\alpha$  radiation and  $\lambda = 0.71073$  Å). The data collections covered 100% of reciprocal space to  $2\theta_{\text{max}} = 75.6^\circ$ , with high average reflection redundancies ( $>20$ ). The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs. The final unit cell parameters were determined by least-squares refinement of large sets of reflections with  $I > 8\sigma(I)$  taken from the data sets. An initial structural model was obtained with SHELXS using direct methods.<sup>28</sup> Subsequent difference Fourier calculations and full-matrix least-squares refinement against  $F^2$  were performed with SHELXL-2014 using the ShelXle interface.<sup>29</sup>

The compounds are isostructural and crystallize in the tetragonal system. Systematic absences were uniquely consistent with the space group  $I4_1/a$ , which was shown to be correct by structure solution. The asymmetric unit in  $I4_1/a$  (origin choice 2) consists of six metal and six O atoms: two Ir atoms located on the crystallographic inversion centers (Ir1 on site 8d and Ir2 on site 8c), two rare-earth atoms on general positions (RE1 and RE2, site 16f), two mixed RE/Sr sites on 2-fold axes of rotation (RE3/Sr3A and Sr1/RE1A, site 8e, site symmetry 2..), and six O atoms (O1–O6). The six O atoms are located on general positions (site 16f). The mixed RE3/Sr3A site was identified by trial refinements of the site with full occupancy by either RE or Sr, which resulted in either an unreasonably large (100% RE) or small (100% Sr)  $U_{\text{eq}}$  value, both accompanied by poor refinement statistics. Refinement of the occupancy parameter resulted in a

significant decrease (RE) or increase (Sr) from 100% occupancy. Both observations are consistent with RE/Sr mixing on this site. For the final site mixing model, the total site occupancy was constrained to 100% and refined to the following values: La, 0.523(4) La3/0.477(4) Sr3A; Pr, 0.753(3) Pr3/0.247(3) Sr3A; Nd, 0.454(5) Nd3/0.546(5) Sr3A. The mixed Sr1/RE1A position is located on site 8e but is disordered about the nearby 4a site with ( $-4..$ ) site symmetry and was therefore refined with 50% occupancy. In the initial models from all data sets, this site was refined as fully (occupancy 0.50) strontium, leading to a slight buildup of positive electron density (e.g.,  $+1.44/-1.25 \text{ e}^-/\text{\AA}^3$  for RE = La) on the site. Refinement of the Sr1 occupancy resulted in a small increase past full occupancy [to 0.530(2) or 106% in both La and Nd data sets] and a flattened difference map. This was modeled as a small admixture of the RE element onto this site. The final site occupancy was constrained to 0.5 and refined to the following: La, 0.447(4) Sr1/0.053(4) La1A; Pr, 0.439(3) Sr1/0.061(3) Pr1A; Nd, 0.453(4) Sr1/0.047(4) Nd1A. Both Ir and 16f RE sites refined to full occupancy within experimental error. All atoms were refined with anisotropic displacement parameters. The largest residual electron density peak and hole in the final difference map are as follows: La,  $+1.27$  and  $-1.25 \text{ e}^-/\text{\AA}^3$ , located 0.50 Å from Ir1 and 0.54 Å from the Sr1/La1A site, respectively; Pr,  $+1.40$  and  $-1.33 \text{ e}^-/\text{\AA}^3$ , located 0.66 from Ir1 and 0.67 from the Sr1/Pr1A site, respectively; Nd,  $+1.80$  and  $-1.53 \text{ e}^-/\text{\AA}^3$ , located 0.64 Å from Ir1 and 0.29 Å from Nd2, respectively. Final atomic coordinates were standardized with the Structure Tidy program.<sup>30–32</sup> Crystallographic data are listed in Table 1.

**Table 1. Crystallographic Data for  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  [ $\text{Ln} = \text{La}$  ( $x = 1.85$ ),  $\text{Pr}$  ( $x = 1.37$ ),  $\text{Nd}$  ( $x = 2$ )]**

| empirical formula                          | $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$ | $\text{Nd}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ | $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$ |
|--------------------------------------------|------------------------------------------------------------|--------------------------------------------------|------------------------------------------------------------|
| fw (g/mol)                                 | 2586.14                                                    | 2626.34                                          | 2629.91                                                    |
| space group                                | $I4_1/a$                                                   | $I4_1/a$                                         | $I4_1/a$                                                   |
| unit cell dimens                           |                                                            |                                                  |                                                            |
| a (Å)                                      | 11.5955(11)                                                | 11.4244(11)                                      | 11.4576(14)                                                |
| c (Å)                                      | 16.2531(15)                                                | 15.9867(16)                                      | 16.129(2)                                                  |
| V (Å <sup>3</sup> )                        | 2185.3(5)                                                  | 2086.5(5)                                        | 2117.3(6)                                                  |
| Z                                          | 4                                                          | 4                                                | 4                                                          |
| density (calcd) (g/cm <sup>3</sup> )       | 7.860                                                      | 8.361                                            | 8.250                                                      |
| abs coeff (mm <sup>−1</sup> )              | 46.266                                                     | 52.504                                           | 50.229                                                     |
| $F(000)$                                   | 4368                                                       | 4464                                             | 4481                                                       |
| cryst size (mm)                            | $0.05 \times 0.04 \times 0.04$                             | $0.06 \times 0.04 \times 0.04$                   | $0.05 \times 0.04 \times 0.02$                             |
| $\theta_{\text{max}}$ (deg)                | 37.81                                                      | 37.847                                           | 37.936                                                     |
| reflins collected                          | 66209                                                      | 70857                                            | 55953                                                      |
| indep reflins collected                    | 2936 ( $R_{\text{int}} = 0.0449$ )                         | 2805 ( $R_{\text{int}} = 0.0420$ )               | 2875 ( $R_{\text{int}} = 0.0395$ )                         |
| GOF on $F^2$                               | 1.102                                                      | 1.220                                            | 1.12                                                       |
| R indices (all data)                       | $R1 = 0.0275$ , $wR2 = 0.0369$                             | $R1 = 0.0260$ , $wR2 = 0.0435$                   | $R1 = 0.0238$ , $wR2 = 0.0307$                             |
| largest diff peak hole (e/Å <sup>3</sup> ) | $+1.273$ and $-1.248$                                      | $+1.804$ and $-1.532$                            | $+1.401$ and $-1.328$                                      |

**Powder X-ray Diffraction.** Powder X-ray diffraction data were collected on a Rigaku Ultima IV diffractometer using Cu  $K\alpha$  radiation. The step scan covered the angular range 10–120° in steps of 0.02°. Rietveld refinements, using the single-crystal structure solutions as a starting point, were carried out on  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ), prepared via traditional solid-state synthesis, using the FullProf software.<sup>33</sup>

**Energy-Dispersive Spectroscopy (EDS).** Single crystals of  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  [ $\text{Ln} = \text{La}$  ( $x = 1.85$ ),  $\text{Pr}$  ( $x = 1.63$ ),  $\text{Nd}$  ( $x = 2$ )] were analyzed using a TESCAN Vega-3 SBU scanning electron microscope with EDS capabilities. All crystals were mounted on carbon tape, and analysis was carried out using a 20 kV accelerating

voltage and an accumulation time of 20 s. EDS verified the presence of Sr, Ir, O, and the respective Ln elements. The absence of extraneous elements such as Al or Cl was confirmed within the detection limits of the instrument.

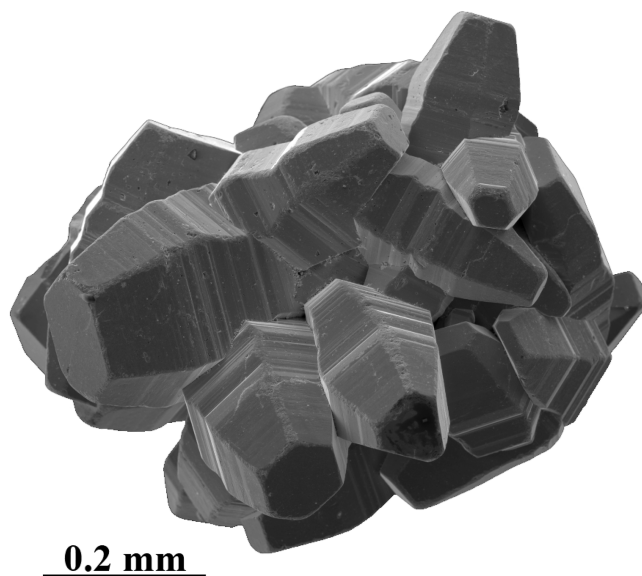
**Magnetic Susceptibility.** The magnetic properties were measured on polycrystalline samples of  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  (Ln = La, Pr, Nd, Sm) using a Quantum Design Magnetic Properties Measurement System (QD MPMS 3 SQUID magnetometer). The magnetic susceptibility data were collected under zero-field-cooled (ZFC) and field-cooled (FC) conditions from 2 to 300 K at an applied field of 0.1 T. Magnetization as a function of the field was measured from 0 to 5 T at 2 K. Data were corrected for the sample shape and radial offset effects, as described previously.<sup>34</sup>

## RESULTS AND DISCUSSION

**Synthesis.** Single crystals of  $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$ ,  $\text{Nd}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ , and  $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$  were grown out of a high-temperature strontium chloride flux, while polycrystalline powders of  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  (Ln = La, Pr, Nd, Sm) were prepared via a standard solid-state route. Previous investigations of the platinum group metal (PGM) containing oxides in our group have focused primarily on using hydroxide fluxes at intermediate temperatures (500–800 °C)<sup>1,2,35–37</sup> and carbonate fluxes at high temperatures (900–1150 °C)<sup>38–41</sup> to obtain single crystals of PGMs. In particular, lanthanide-containing iridates have often been crystallized using reactive alkali-metal hydroxides to synthesize various structure types, including double perovskites such as  $\text{Ln}_2\text{NaIrO}_6$  (Ln = La, Pr, Nd).<sup>42</sup> In the study described herein, the use of alkali-metal fluxes was avoided because, as reactive fluxes, the respective alkali-metal cations are often incorporated into the resulting structure. Because it was known from the work of Phelan et al. that strontium could be incorporated into the  $\text{Ln}_{11}\text{Ir}_4\text{O}_{24}$  structure to prepare  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  and because strontium incorporation was the intent, the use of  $\text{SrCl}_2$  as a flux seemed reasonable and did, in fact, yield the desired single crystals. Because some of the crystals have noninteger stoichiometries, we defaulted to the solid-state method to prepare the integer stoichiometries  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  (Ln = La, Pr, Nd, Sm).

**Structure.** A scanning electron microscopy (SEM) image of the crystal habit observed for the  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  (Ln = La, Pr, Nd, Sm;  $1.37 \geq x \geq 2$ ) series is shown in Figure 1. These crystals grow as black bipyramids, often as intergrown clusters. A shard cleaved from a cluster was used for single-crystal structural determination. As with most structures, there is more than one way to describe it. One way to describe the  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  structure is based on a framework consisting of  $\text{Ln}(1)\text{O}_8$  and  $\text{Ln}(2)\text{O}_9$  polyhedra encapsulating a three-dimensional channel structure in which Ir(1), Ir(2), Ln(3), and Sr(1) are located. The framework is formed by corner-, edge-, and face-sharing  $\text{Ln}(1)\text{O}_8$  and  $\text{Ln}(2)\text{O}_9$  polyhedra, where the  $\text{Ln}(1)\text{O}_8$  polyhedron shares edges with one and faces with three adjacent  $\text{Ln}(2)\text{O}_9$  polyhedra and one common corner with an adjacent  $\text{Ln}(1)\text{O}_8$  polyhedron. The  $\text{Ln}(2)\text{O}_9$  polyhedron shares one corner and one edge with two adjacent  $\text{Ln}(2)\text{O}_9$  polyhedra and faces and edges with an adjacent  $\text{Ln}(1)\text{O}_8$  polyhedron. This arrangement results in three-dimensional intersecting channels in which Ir(1), Ir(2), Ln(3), and Sr(1) are located, as shown in Figure 2a,b. As shown in Figure 2c,d, the Ir(1) and Ir(2) cations are lined up and the Ln(3) and Sr(1) cations are lined up, corresponding to two interpenetrating cation lattices.

A second structural description that emphasizes the iridium locations is best understood as a composition of fundamental



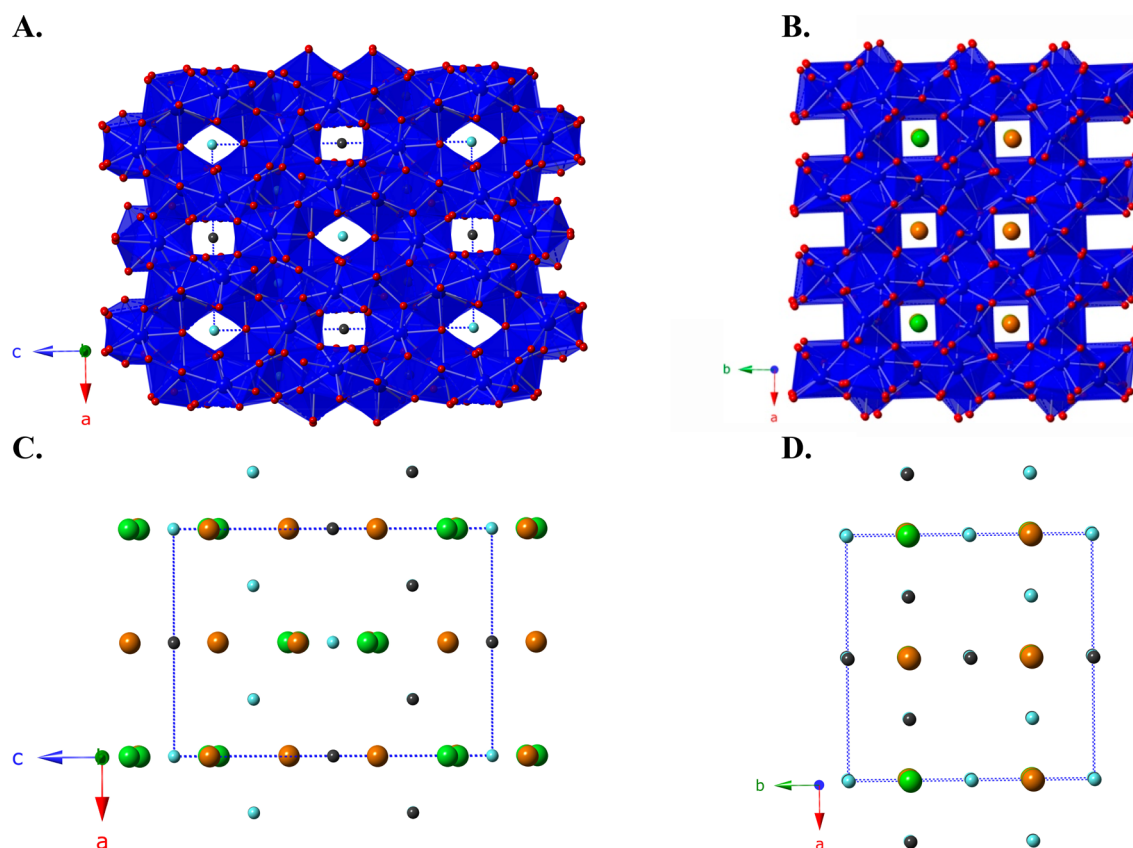
**Figure 1.** SEM image of the crystal habit of  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  (Ln = La, Pr, Nd, Sm;  $1.37 \geq x \geq 2$ ).

building blocks in the form of two unique chains, each composed entirely of edge-sharing polyhedra. The first chain consists of an alternating pattern of Ir(2) $\text{O}_6$  octahedra edge-shared to a split-occupancy (Sr/Ln) $\text{O}_8$  polyhedron. Similar to the first chain, the second chain also consists of an alternating pattern but of Ir(1) $\text{O}_6$  octahedra that are edge-shared to a Sr(1) $\text{O}_8$  site that exhibits mixed occupancy. These two chains are connected via edge sharing between the jointly occupied (Sr/Ln) $\text{O}_8$  polyhedron of the first chain and the position-disordered Sr(1) $\text{O}_8$  site of the second chain. These chains form sheetlike structures containing 10-membered rings in the *ac* plane, as shown in Figure 3a. This sheet interpenetrates an identical orthogonal sheet in the *bc* plane, as shown in Figure 3b. The Sr/Ln chain extends into the *bc* plane by edge-sharing with the Sr site in the *ac* plane, and the same Sr site edge-shares with Ir(1) $\text{O}_6$  to form the second chain in the *bc* plane, completing the sheet structure, creating an alignment of Ir(1) and Ir(2) in the *a*, *b*, and *c* directions.

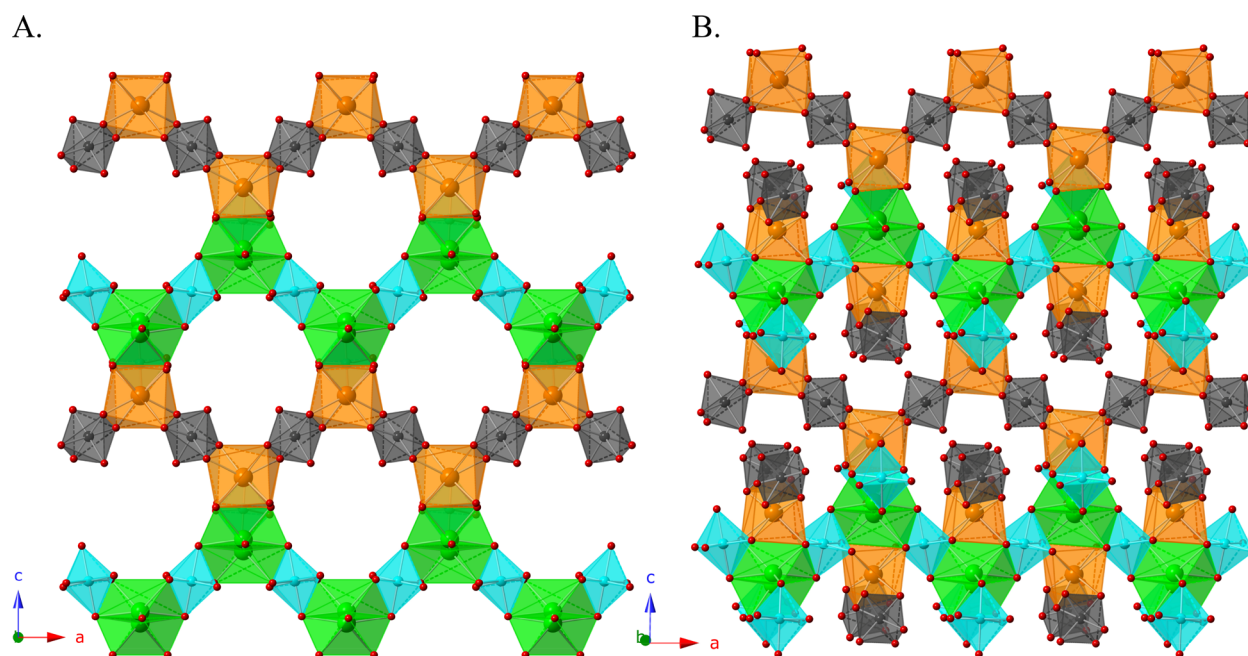
The composition of  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  results in an iridium oxidation state of 4.25, indicating mixed-valent Ir(IV)/Ir(V). For charge balance, we expect  $\text{Ln}_9\text{Sr}_2[\text{Ir(IV)}]_3[\text{Ir(V)}]_{\text{O}_{24}}$ , and we can attempt to assign oxidation states to the two Ir sites using the bond-valence-sum (BVS) approach. The results of this approach for  $\text{Nd}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  indicate that Ir(1) has a BVS of 4.94 and Ir(2) of 4.01, shown in Table 2. This, nonetheless, requires the presence of Ir(IV) on both crystallographically unique Ir sites, even the site that BVS assigns as primarily Ir(V). Because we have a 3:1 distribution of Ir(IV) to Ir(V), this suggests that Ir(2) is predominantly or wholly Ir(IV) while Ir(1) is mixed Ir(IV/V). The other two single-crystal structures,  $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$  and  $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$ , contain relatively less Ir(V) and have average iridium oxidation states of 4.21 and 4.09, respectively. Consistent with this trend, we find that the BVS values for Ir(2) drop to 4.97 and 4.53, respectively, while the BVS values for Ir(1) remain close to 4, 3.91, and 4.00, respectively.

Previously reported examples of this structure type have been described as A-site cation-deficient double-perovskite-related oxides of the general formula  $4[(\text{A}_{7/8}\square_{1/8})\text{BB}'\text{O}_6]$ . For the titled compositions, this would give a formula of





**Figure 2.** Polyhedral representation of the series  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}; 1.37 \geq x \geq 2$ ), viewed as a framework consisting of  $\text{Ln}(1)\text{O}_8$  and  $\text{Ln}(2)\text{O}_9$ , shown in blue, in which Ir(1), Ir(2), Ln(3), and Sr(1) can be found in the resulting channels, shown in light blue, gray, orange, and green, respectively. The framework is shown with Ir(1) and Ir(2) (A) and Ln(3) and Sr(1) (B) in the channels. The corresponding locations of Ir(1), Ir(2), Ln(3), and Sr(1) with the framework removed are shown in parts C and D.



**Figure 3.** Polyhedral representation of the sheet structure of the series  $\text{Ln}_{11-x}\text{Sr}_x\text{Ir}_4\text{O}_{24}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}; 1.37 \geq x \geq 2$ ), composed of two unique chains. The first chain consists of Ir(2) octahedra, shown in gray, and an eight-coordinated Sr/Ln site, shown in orange. The second chain consists of octahedral Ir(1), shown in light blue, and an eight-coordinate disordered Sr site, shown in green. (A) 10-membered rings present in the  $ac$  plane. (B) Second orthogonal  $bc$  plane sheet connecting with the  $ac$  plane sheet.

**Table 2.** Interatomic Distance and BVS Values for Ir–O Bonds in  $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$ ,  $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$ , and  $\text{Nd}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ 

| empirical formula                                          | metal–oxygen bond | bond distance (Å)   | BVS  |
|------------------------------------------------------------|-------------------|---------------------|------|
| $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$ | Ir(2)–O           | $1.990(2) \times 2$ | 3.91 |
|                                                            |                   | $2.021(2) \times 2$ |      |
|                                                            |                   | $2.079(2) \times 2$ |      |
|                                                            | Ir(1)–O           | $1.965(2) \times 2$ | 4.87 |
|                                                            |                   | $1.998(2) \times 2$ |      |
|                                                            |                   | $2.019(2) \times 2$ |      |
| $\text{La}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$           | Ir(2)–O           | $1.987(5) \times 2$ | 3.92 |
|                                                            |                   | $2.024(5) \times 2$ |      |
|                                                            |                   | $2.076(5) \times 2$ |      |
|                                                            | Ir(1)–O           | $1.965(5) \times 2$ | 4.88 |
|                                                            |                   | $1.995(5) \times 2$ |      |
|                                                            |                   | $2.020(5) \times 2$ |      |
| $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$ | Ir(IV)–O          | $1.993(3) \times 2$ | 4.00 |
|                                                            |                   | $2.025(3) \times 2$ |      |
|                                                            |                   | $2.044(3) \times 2$ |      |
|                                                            | Ir(V)–O           | $1.986(3) \times 2$ | 4.53 |
|                                                            |                   | $2.006(3) \times 2$ |      |
|                                                            |                   | $2.073(3) \times 2$ |      |
| $\text{Pr}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$           | Ir(2)–O           | $1.991(6) \times 2$ | 4.01 |
|                                                            |                   | $2.023(6) \times 2$ |      |
|                                                            |                   | $2.042(6) \times 2$ |      |
|                                                            | Ir(1)–O           | $1.984(6) \times 2$ | 4.55 |
|                                                            |                   | $2.005(6) \times 2$ |      |
|                                                            |                   | $2.071(6) \times 2$ |      |
| $\text{Nd}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$           | Ir(IV)–O          | $1.981(3) \times 2$ | 4.01 |
|                                                            |                   | $2.007(3) \times 2$ |      |
|                                                            |                   | $2.075(3) \times 2$ |      |
|                                                            | Ir(V)–O           | $1.956(3) \times 2$ | 4.94 |
|                                                            |                   | $1.992(3) \times 2$ |      |
|                                                            |                   | $2.020(3) \times 2$ |      |
| $\text{Sm}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$           | Ir(2)–O           | $1.961(5) \times 2$ | 4.15 |
|                                                            |                   | $2.001(5) \times 2$ |      |
|                                                            |                   | $2.055(5) \times 2$ |      |
|                                                            | Ir(1)–O           | $1.942(5) \times 2$ | 5.08 |
|                                                            |                   | $1.974(5) \times 2$ |      |
|                                                            |                   | $2.008(5) \times 2$ |      |

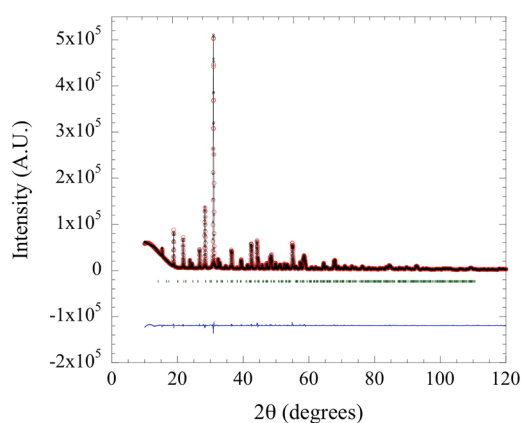
$4([\text{Ln}_{7/8}\square_{1/8}]_2[\text{Ln}_{0.5}\text{Sr}_{0.5}][\text{Ir}]\text{O}_6)$  or  $([\text{Ln}_7][\text{Ln}_2\text{Sr}_2][\text{Ir}_4]\text{O}_{24})$ , with  $[\text{Ln}_7]$  as the “A site”,  $[\text{Ln}_2\text{Sr}_2]$  as the “B site”, and  $[\text{Ir}_4]$  as the “B’ site”. With the exception of the study conducted by Phelan et al. and the compositions described herein, all previously reported examples of this structure type lack site mixing. Specifically, stoichiometric  $\text{Ba}_{11}\text{Os}_4\text{O}_{24}$  contains a  $[\text{BaO}_9]_7$  A site, a  $[\text{BaO}_8]_4$  B site, and a  $[\text{OsO}_6]_4$  B’ site, leading to a rock-salt arrangement of  $\text{OsO}_6$  octahedra and  $\text{BaO}_8$  polyhedra.  $\text{Ba}_{11}\text{Os}_4\text{O}_{24}$  has three crystallographically unique Ba sites, two of which are  $\text{BaO}_9$  polyhedra, which comprise the A site, and one that consists of  $\text{BaO}_8$  polyhedra, making up the B site. In  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ , the doping of Sr introduces site mixing exclusively on the third crystallographically unique Ln(3) site, resulting in a jointly occupied Sr/Ln site. In addition, there is a unique Sr(1) site that suffers from slight positional disorder, and these two sites combined represent the “B site”.

In addition to synthesizing single crystals of  $\text{La}_{9.15}\text{Sr}_{1.85}\text{Ir}_4\text{O}_{24}$ ,  $\text{Nd}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ , and  $\text{Pr}_{9.63}\text{Sr}_{1.37}\text{Ir}_4\text{O}_{24}$ , polycrystalline powders of  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  (Ln = La, Pr, Nd, Sm) were synthesized via solid-state synthesis. Rietveld refinements

were performed on all four polycrystalline samples using the *FullProf Suite* program,<sup>33</sup> with the crystallographic information obtained from single crystals as a starting structural model. Structural information and refinement patterns can be found in Table 3 and Figures 4 and S2 and S3, respectively. These

**Table 3.** Crystallographic Data for  $\text{Ln}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  (Ln = La, Pr, Sm)

| empirical formula | $\text{La}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ | $\text{Pr}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ | $\text{Sm}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$ |
|-------------------|--------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| fw (g/mol)        | 2586.14                                          | 2626.34                                          | 2689.19                                          |
| space group       | $I4_1/a$                                         | $I4_1/a$                                         | $I4_1/a$                                         |
| unit cell dimens  |                                                  |                                                  |                                                  |
| a (Å)             | 11.579(3)                                        | 11.443(2)                                        | 11.313(1)                                        |
| c (Å)             | 16.279(2)                                        | 16.118(4)                                        | 15.940(2)                                        |
| RF factor         | 1.41                                             | 1.47                                             | 2.21                                             |
| $\chi^2$          | 14.7                                             | 6.38                                             | 8.80                                             |



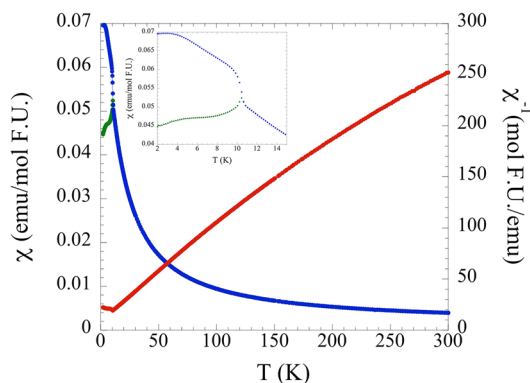
**Figure 4.** Rietveld refinement pattern of  $\text{La}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  collected on a powder X-ray diffractometer. The data are shown in red and fit to the nuclear structure, shown in black. Green tick marks correspond to the nuclear reflections, and the blue line corresponds to the difference between the experimental data and model nuclear phase.

polycrystalline powders were synthesized to ensure that all magnetic data were collected on phase-pure samples with known stoichiometries, and thus equivalent nonmagnetic dopant (Sr) amounts. This makes it possible to assign any significant differences in the magnetic susceptibility across samples to the lanthanide substitution and not to structural distortions resulting from a variation of the Sr content or changes in the iridium valence due to a variation of the Sr content that might occur in a batch of single crystals.

**Magnetism.** The presence of magnetic cations on the  $\text{LnO}_9$  site, in addition to the  $\text{LnO}_8$  site, was a primary motivator for the synthesis of this series of structures. Previously reported examples of this structure contained octahedral  $\text{MO}_6$  magnetic cations separated by nonmagnetic  $\text{MO}_8$  cations in a rock-salt arrangement. This arrangement only allows for magnetic interactions to occur via supersuperexchange, and thus the introduction of a magnetic cation into the  $\text{MO}_8$  polyhedra allows for a variety of superexchange pathways, namely, 5d–4f superexchange interactions between Ir(IV)–Ln alongside both 5d–5d [Ir(IV)–Ir(IV)] and 4f–4f (Ln–Ln) supersuperexchange interactions.

The temperature dependence of the magnetic susceptibility was measured for all samples in an applied field of 0.1 T using both FC and ZFC measurement conditions. The composition  $\text{La}_9\text{Sr}_2\text{Ir}_4\text{O}_{24}$  was studied first, as the simplest example of all

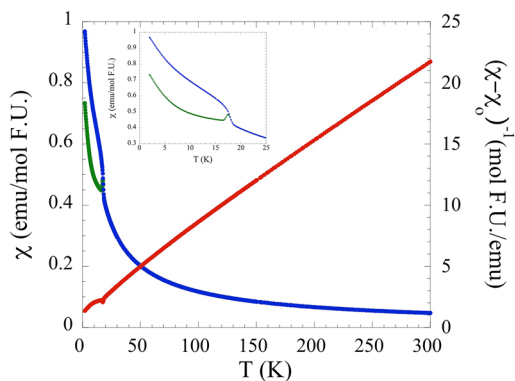
studied materials, with only iridium having unpaired electrons that can couple magnetically through a nonmagnetic Sr/La site. The temperature dependence of the magnetic susceptibility is shown in Figure 5, which indicates low-temperature



**Figure 5.** Temperature dependence of the magnetic susceptibility of  $\text{La}_9\text{Sr}_2\text{IrO}_{24}$  at an applied field of 0.1 T.

field dependence with a  $T_N = 11$  K. The inset shows a ferromagnetic-like transition in the FC data, with a broad antiferromagnetic transition in the ZFC data. No hysteresis was present in the magnetization versus field measurement, as shown in Figure S3, although a positive Weiss constant,  $\theta = 23$ , was observed. The low, yet positive, Weiss temperature suggests a balance of ferromagnetic and antiferromagnetic interactions in this material. On the basis of the low susceptibility and magnetization observed in Figures 5 and S4, respectively, these interactions may result in spin canting. Fitting the high-temperature susceptibility data to the Curie–Weiss law results in an effective moment of  $2.34 \mu_B$ , as shown in Figure S5, which is lower than the calculated spin-only moment of  $3.00 \mu_B$ . This decreased effective moment, likely due to spin–orbit coupling, is consistent with the previous reports for this composition.

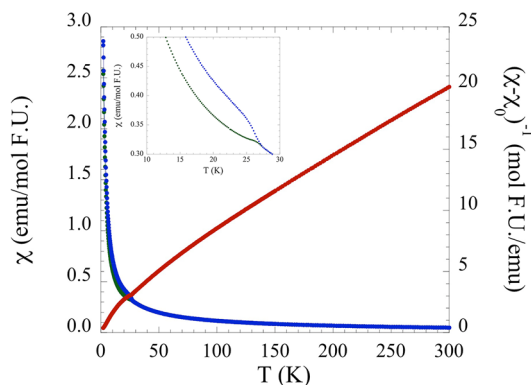
The magnetic susceptibility of  $\text{Pr}_9\text{Sr}_2\text{IrO}_{24}$  at 0.1 T exhibits an even higher magnetic ordering temperature,  $T_N = 18$  K, with a similar ferromagnetic-like transition in the FC data and an antiferromagnetic transition in the ZFC data, as shown in Figure 6. Following this brief antiferromagnetic transition is a very broad and gradual increase in the susceptibility, with the ZFC data following a trend similar to that of the FC data, although with a lower magnitude of the susceptibility. The



**Figure 6.** Temperature dependence of the magnetic susceptibility of  $\text{Pr}_9\text{Sr}_2\text{IrO}_{24}$  at an applied field of 0.1 T.

broadness of this transition may suggest that a variety of magnetic interactions are occurring, possibly coupling between praseodymium and iridium, and cannot be individually identified by a bulk susceptibility measurement. The Weiss constant,  $\theta = -40$ , is significantly lower than that observed for the lanthanum analogue, indicating stronger antiferromagnetic interactions, despite the presence of weak hysteresis at 2 K, as shown in Figure S6. The low magnetization of  $4 \mu_B$  in a material containing 12 magnetic cations suggests that the presence of multiple magnetic exchange pathways is causing competition, resulting in possible spin canting or magnetic frustration. This is further corroborated by the low susceptibility exhibited in the temperature sweep measurement. A fit of the high-temperature inverse susceptibility data results in an effective moment of  $11.17 \mu_B$  per formula unit, which is very close to the calculated moment of  $11.21 \mu_B$ , as shown in Figure S7, determined by treating  $\text{Ir(IV)}$  as a conventional  $S = 1/2$  magnetic cation and  $\text{Ir(V)}$  as a  $S = 0$  cation as a result of spin–orbit coupling.

The  $\text{Nd}_9\text{Sr}_2\text{IrO}_{24}$  composition, a material containing even more unpaired electrons, exhibits field dependence similar to that of the lanthanum and praseodymium analogues, with an increased magnetic ordering temperature of  $T_N = 27$  K, as shown in Figure 7. The low-temperature inset shows the same

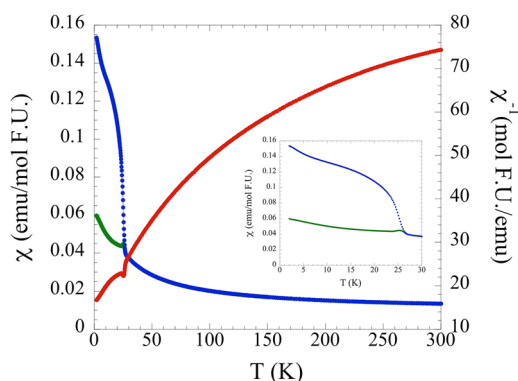


**Figure 7.** Temperature dependence of the magnetic susceptibility of  $\text{Nd}_9\text{Sr}_2\text{IrO}_{24}$  at an applied field of 0.1 T.

ferromagnetic-like transition in the FC data that were present in the lanthanum and praseodymium analogues; however, the previous antiferromagnetic transition in the ZFC is largely gone; it does exhibit the same broad and gradual increase in susceptibility. The absence of hysteresis, as shown in Figure S8, in addition to the larger negative value of the Curie–Weiss  $\theta$  at  $-60$ , indicates stronger antiferromagnetic interactions in this material, although no clear transitions in the susceptibility data are observed. As mentioned for the praseodymium analogue, the existence of a multitude of magnetic exchange pathways likely creates competing interactions resulting in possible spin canting or magnetic frustration. This is corroborated by the low susceptibility and saturation magnetization shown in Figures 7 and S8, respectively. A fit of the high-temperature inverse susceptibility data results in an effective moment of  $11.97 \mu_B$  per formula unit (Figure S9), which is in good agreement with  $11.79 \mu_B$ , determined by treating  $\text{Ir(IV)}$  as a conventional  $S = 1/2$  magnetic cation and  $\text{Ir(V)}$  as a  $S = 0$  cation.

The magnetic susceptibility of  $\text{Sm}_9\text{Sr}_2\text{IrO}_{24}$  (Figure 8) exhibits low-temperature field dependence with a ferromag-





**Figure 8.** Temperature dependence of the magnetic susceptibility of  $\text{Sm}_{0.9}\text{Sr}_{1.1}\text{IrO}_{24}$  at an applied field of 0.1 T.

netic-like transition in the FC data and a very weak antiferromagnetic transition in the ZFC, similar to that observed for the other compositions. The magnetic susceptibility exhibited for this composition is an order of magnitude lower than the other magnetic lanthanide compositions and of the same order of magnitude as the lanthanum analogue. As a composition possessing 48 unpaired electrons per formula unit, in addition to a variety of possible magnetic exchange pathways, it is quite likely that in this material competing interactions are resulting in magnetic frustration, leading to an overall reduced moment. Although the magnetic susceptibility is lower, the ordering temperature of  $T_N = 27$  K is the same as  $\text{Nd}_{0.9}\text{Sr}_{1.1}\text{IrO}_{24}$ . Because of the presence of samarium, this material does not obey Curie–Weiss behavior at elevated temperatures, and thus no effective moment or Weiss constant  $\theta$  was determined. A  $\chi_M T$  plot, as shown in Figure S10, was created to approximate an effective moment, which was determined to be  $5.68 \mu_B$  at 300 K, a value that is consistent with the spin-only moment of  $5.66 \mu_B$ .

## CONCLUSION

A series of heavily distorted A-site cation-deficient double perovskites of the general formula  $\text{Ln}_{1-x}\text{Sr}_x\text{Ir}_2\text{O}_{10}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}; 1.37 \geq x \geq 2$ ) were grown as single crystals from a molten strontium chloride flux. Magnetic measurements were carried out on  $\text{Ln}_{0.9}\text{Sr}_{1.1}\text{Ir}_2\text{O}_{10}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ), synthesized via the solid-state method. The magnetic measurements focused on a versatile structure type that can contain both one or two magnetic cations on a variety of crystallographically unique sites. Temperature-dependent magnetic susceptibility and field-dependent magnetization measurements were conducted for all synthesized compositions. Analysis of the magnetic data indicated that smaller lanthanide cations lead to higher magnetic ordering temperatures and Weiss constants,  $\theta$ , that were more negative. These magnetic data suggest a trend of increased magnetic frustration caused by the introduction of smaller lanthanide cations that contain an increasing number of unpaired electrons into a structure, coupled with the existence of multiple competing magnetic exchange pathways. Because the structure is compositionally quite adjustable, future measurements on additional compositions are certainly of interest.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00887.

Energy splitting, Rietveld refinement patterns, temperature-dependent magnetic susceptibility, field-dependent magnetization, and crystallographic information (PDF)

### Accession Codes

CCDC 1823086–1823088 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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