Unintended consequence of topochemical reduction of SrFeO_3 to SrFeO_2 : Design of infinite layered oxides

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The infinite layer structure type has been known to host high-temperature superconductivity since the discovery of $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$, yet little progress has been made to synthesize many analogs. Here, using SrFeO_x as a prototype system, we explore the thermodynamic obstacles behind the scarcity of $3d$ elements adopting the infinite layer structure type. In this context, synthetic considerations to achieve the ABO_3 to ABO_2 transformation are discussed. Specifically, we demonstrate that the conventionally reported topochemical reduction can result in hydride incorporation into SrFeO_2 , causing a decrease in the magnetic ordering temperature of the infinite layered oxide. First-principles simulations further confirm that the incorporation of H is necessary for stabilizing the SrFeO_2 phase by decreasing the thermodynamic cost of individual steps required to transform SrFeO_3 into SrFeO_2 , and is the driving factor behind the changes in magnetic exchange interactions that ultimately change the Néel temperature (T_N). Additionally, inspired by recent reports of superconductivity in another low-dimensional oxide $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$, $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$ was synthesized via a more traditional topochemical reduction procedure. Both physical characterization and accompanying density-functional theory calculations show that this A-site doping can have similar effects on AFeO_2 stability and magnetic ordering temperatures as with the incorporation of hydrogen. Ultimately, these results suggest that charge doping either through the incorporation of H or A-site substitution may be fruitful routes in tuning stability and magnetic properties, with direct consequences on superconducting behavior.

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I. INTRODUCTION

The interest in a class of materials known as infinite layer oxides, of the general formula ABO_2 , first began with the discovery of the high-temperature superconductor $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$ [1]. The “infinite layer” is composed of a network of corner-sharing BO_4 units in a square planar coordination environment that extends along the ab plane [2–4]. These networks are separated by large, often nonmagnetic A-site cations that serve as interlayer spacers. In addition to the novelty of high-temperature superconductivity, this structure type is crystallographically unique as square planar coordination environments are uncommon in complex oxides, and even rarer still are structure types constructed entirely of such local environments. For these reasons, it is unsurprising that among the few reported examples of infinite layer oxides, the

B-site is often a Jahn-Teller ion such as Ni(II) or Cu(II) [1]. The tetragonal distortion of the more common octahedral, O_h , local environment results in strong equatorial bonds and weak axial ones that stabilize the square planar configuration.

Aside from the well-studied cuprates, this infinite layer structure has also been observed in LaNiO_2 [5,6] but no superconductivity has been reported. More recent studies into the LnNiO_2 family have shown that Nd can also be stabilized in NdNiO_2 , and with slight Sr doping onto the Ln site forming $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$, low-temperature superconductivity ($T_c = 9\text{--}15\text{ K}$) can be induced [7]. The realization of superconductivity in the nickelate infinite layer oxide has renewed interest in the field [8–10] and serves as a motivating factor for the herein described work that analyzes the synthetic considerations and thermodynamic limitations that complicate selectively targeting novel ABO_2 structures for potential superconducting behavior.

A number of energetic barriers preclude the direct synthesis of the infinite layer ABO_2 structure type from ABO_3 . The requirement for the B-site ion to occupy an unusual square planar environment in addition to an unusually low oxidation state hinders the formation of such structures from conventional high-temperature synthetic methods. Additionally, the low oxidation state severely limits synthetic options to those without using oxidizing agents such as oxygen-rich environments or most solution chemistry. For these reasons, such

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FIG. 1. Representative crystal structure of a cubic perovskite of the general formula ABO_3 (left) and the infinite layer ABO_2 structure (right) after topochemical reduction. The Sr, Fe, and O atoms are represented by dark blue, gray, and red spheres, respectively.

structure types have only been made through a postsynthesis modification method known as topochemical reduction first employed by Hayward *et al.* [5,11–13]. This synthetic strategy consists of reducing a presynthesized perovskite of the general formula ABO_3 with an alkali metal or alkaline earth hydride, thereby reducing the oxidation state of the B -site ion. This fosters the removal of axial oxygens, thus severing the c -axis connectivity of the cubic perovskite structure type. Perovskites are ideal structural templates for this reduction, as they consist of a stable sublattice resistant to postsynthesis modification, from which a metastable sublattice can be topochemically cleaved. By reducing the metastable sublattice, the thermodynamic barrier associated with the direct synthesis of such a phase is effectively circumvented. Examples of this can be found in the syntheses of $LaNiO_3$ [5,6], $NdNiO_3$ [7], and $SrFeO_3$ [14–19] and their subsequent reduction to ABO_2 with the use of an alkali or alkaline earth metal hydride reductant to cleave axial oxygens from BO_6 units, producing stable sublattices composed entirely of square planar BO_4 units (Fig. 1).

In addition to the thermodynamic cost associated with oxygen vacancy formation that prevents the transformation of ABO_3 to ABO_2 , several chemical considerations must be taken into account. Most reported cases of the topochemical reduction of oxide materials involve an alkaline earth or lanthanide A -site, [5,11–13] which limits possible transformations from $A(II, III)B(IV, III)O_3$ to $A(II, III)B(II, I)O_2$, although a few exceptions do exist. This immediately rules out B -site ions that do not adopt such oxidation states, such as Sc, Ti, and Zn. The required square planar coordination environment is uncommon in oxides, so elements such as V or Cr that have few to no reported cases in such an environment can safely be avoided. Furthermore, previous studies of $4d$ and $5d$ B -site ion-containing perovskites reported instabilities of such ions in low oxidation states in a square planar environment, except when doped with more favorable $3d$ ions such as Fe [20,21]. As no reported cases of infinite layer structures boasting high-temperature superconductivity have B -site mixing, this structural motif was ruled out. Here, given the fact that the planar nature of the infinite layer reduced structure is essential to potentially superconducting behavior, and due to the smaller size of Ca relative to Sr which may result in a buckling of the FeO_4 square planar units in $CaFeO_2$, we focus our study on $SrFeO_3$ as a starting point for understanding the thermodynamic path to achieve the infinite layered $SrFeO_2$ compound.

The $SrFeO_{3-x}$ is a robust material that has been reported for values of ($x = 0, 0.125, 0.25, 0.5$), demonstrating significant modularity. As a function of increasing oxygen vacancy, the structure shifts from cubic $Pm\bar{3}m$ ($x = 0$) to tetragonal $I4/m\bar{m}$ ($x = 0.125$) to orthorhombic $Cmmm$ ($x = 0.25$), and finally the brownmillerite structure $Ibm2$ ($x = 0.5$). Throughout this reduction process, some FeO_6 octahedra are successively reduced to square pyramidal FeO_5 units ($x = 0.125, 0.25$) and eventually to FeO_4 tetrahedra ($x = 0.5$) but the full reduction to a square planar FeO_4 unit is never achieved via direct methods.

To achieve the reduction of $SrFeO_3$ to $SrFeO_2$, a number of studies [22–26] have employed a CaH_2 reducing agent for the topochemical reduction. The reported $SrFeO_2$ was found to be a nonsuperconducting isostructural analog to the infinite layer cuprates with a fairly high magnetic ordering temperature ($T_N = 473$ K). In these studies, the reduction of either bulk powder or thin films was achieved by using similar synthetic conditions first determined by Tsujimoto *et al.* [22]. Despite the inability to synthesize $SrFeO_2$ via traditional high-temperature methods that produce only the most thermodynamically stable phases, this structure has been reported to be thermally stable up to 960 K [23], significantly higher than the synthesis temperature. The robust capacity of $SrFeO_3$ to undergo a variety of oxygen vacancies while maintaining the same genetic structure in addition to the unique thermal stability of the fully reduced $SrFeO_2$ makes this material an ideal model to better understand the ABO_3 to ABO_2 transformation.

Herein, using $SrFeO_3$ as a prototype example, we discuss the thermodynamics that determine whether it will crystallize into the infinite layer structure type, with particular emphasis on the enthalpy of formation for oxygen vacancies. We demonstrate that through careful control of synthetic parameters, namely the molar ratio of $SrFeO_3$ to electropositive hydride CaH_2 , hydride incorporation is achieved. Density-functional theory (DFT) calculations are employed to quantify the thermodynamic costs of reducing $SrFeO_3$ to $SrFeO_2$ in terms of stability of a phase against possible decomposition into binary oxides, the enthalpy of formation of oxygen vacancies, the preferential hydride doping sites, and their effects on the exchange constants and magnetic transition temperature. Our results indicate that the compositions $SrFeO_{3-x}H_{0.25}$ ($x = 0.25, 0.5, 1.0, 1.25$) are more stable and have relatively small thermodynamic costs for successive reduction steps than their pristine counterparts. This offers the possibility of tuning T_N with H-incorporation. We also explore the effects of doping

on the A-site (again using SrFeO_3 as the example via the novel material $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$). Similar effects on magnetic transition temperatures as hydride incorporations on the O-site are observed. Together these results help us understand the thermodynamic limitations in the formation of ABO_2 compounds while presenting routes to tuning the magnetic (and potentially superconducting) properties of related compounds.

II. METHODS

A. Experimental methods

1. Synthesis

Polycrystalline samples of SrFeO_3 , the precursor to all subsequent topochemical reduction methodologies, were prepared by intimately grinding SrCO_3 (99.99%) and Fe_2O_3 (99.9%) in stoichiometric amounts and heating the resultant powder in air in an alumina crucible with a loose-fitting lid. The samples were heated at a rate of 200 °C/h to 800 °C for 24 h, 1000 °C for 24 h, and then 1200 °C for 48 h with intermediate grindings in a programmable furnace. To produce SrFeO_2 , the resultant SrFeO_3 was intimately ground with CaH_2 in a molar ratio of 3.0:1 (CaH_2 : SrFeO_3) in a glove box, and placed in an alumina crucible with a loose-fitting frit for a lid. This alumina crucible was placed in a vacuum-sealed quartz tube and heated at a rate of 100 °C/h to 280 °C for 48 h, and allowed to fast cool. Once cooled, the quartz tube was placed into an oxygen-free glove bag, and the reduced powder, still mixed with residual CaH_2 , was vacuum filtered with a 0.4 molar (M) solution of NH_4Cl in methanol. A total of 300 mL of solution was used per reaction to achieve complete removal of any remaining CaH_2 . To produce $\text{SrFeO}_{2-x}\text{H}_x$, a likely hydrogen-doped system, the above method was modified such that the molar ratio of CaH_2 : SrFeO_3 was increased to 3:1, the reaction temperature was increased to 300 °C, and a second open alumina crucible was added to the sealed evacuated quartz tube containing 1 millimole (mmol) well-ground CaH_2 to provide a stronger reducing atmosphere within the tube. The removal of CaH_2 from the resultant powder was achieved in the same method described above but a total of 500 mL of the 0.4 M solution of NH_4Cl in methanol was needed. The synthesis of $\text{Sr}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.05, 0.1$) and the reduced $\text{Sr}_{1-x}\text{Nd}_x\text{FeO}_2$ ($x = 0.05, 0.1$) was achieved using the same conditions as described for SrFeO_3 and SrFeO_2 , except with the addition of Nd_2O_3 (99.99%) that was preheated in an oven at 1000 °C overnight to remove any residual carbonates or hydroxides. Removal of the remaining CaH_2 after completion of the reaction was achieved by washing with a total of 300 mL of 0.4 M NH_4Cl in a vacuum filtration system held within an oxygen-free glove bag.

2. Powder x-ray diffraction

Powder x-ray diffraction (PXRD) data were collected on a PANalytical X'Pert Pro MPD diffractometer with $\text{Cu K}\alpha 1$ radiation ($\lambda = 1.5418 \text{ \AA}$). An angular range of 10°–70° with a step size of 0.02° was used. No impurities were observed for SrFeO_2 , $\text{SrFeO}_{2-x}\text{H}_x$, and $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$, with a small impurity found for $\text{Sr}_{0.9}\text{Nd}_{0.1}\text{FeO}_2$. The experimental and calculated PXRD patterns are shown in Figs. 2(a)–2(d), which show the lattice parameters barely change ($a = 3.992 \text{ \AA}$,

TABLE I. EDS data for $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$ and $\text{Sr}_{0.9}\text{Nd}_{0.1}\text{FeO}_2$.

Composition	$\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$	$\text{Sr}_{0.9}\text{Nd}_{0.1}\text{FeO}_2$
Sr	43.72	41.75
Nd	5.29	9.62
Fe	50.99	48.63

$c = 3.478 \text{ \AA}$) and the space group $P4/mmm$ remains the same with respect to the SrFeO_2 structure.

3. Energy-dispersive spectroscopy

Energy-dispersive spectroscopy (EDS) was performed using a Hitachi S-3400 scanning electron microscope equipped with an OXFORD EDX microprobe to confirm the elemental composition of the polycrystalline samples. The presence of Sr, Nd, Fe, and O was verified, and the absence of any extraneous elements was confirmed. EDS data for $\text{Sr}_{1-x}\text{Nd}_x\text{FeO}_2$ ($x = 0.05, 0.1$) can be found in Table I.

4. Magnetic susceptibility

Temperature-dependent magnetic susceptibility measurements were taken using the Quantum Design Superconducting quantum interference device Magnetic Properties Measurement System (MPMS). Susceptibility was measured under zero field-cooled (ZFC) and field-cooled (FC) conditions from 4 to 500 K under applied fields of 1 T.

B. Computational methods

To computationally explore the possibility of reducing SrFeO_3 to SrFeO_2 , we computed the oxygen vacancy formation energies of SrFeO_x compounds ($\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x}$) ($x = 3.0, 2.75, 2.5, 2.0$) as a surrogate model for the reduction steps. In all cases, we performed spin-polarized density-functional theory calculations [27,28] as implemented in the plane-wave based Vienna *Ab initio* Simulation Package (VASP 5.4.4) [29]. The generalized gradient approximation (GGA), Perdew-Burke-Ernzerhof revised for solids (PBEsol) [30] was used for the exchange-correlation (XC) functional. Projected augmented wave [31,32] potentials were used to treat the electron-ion interactions with the following valence electronic configurations: Sr: $4s^2 5s^2 4p^6$, Fe: $3s^2 3p^6 4s^1 3d^7$, O: $2s^2 2p^4$, Nd: $5s^2 5p^6 6s^2 5d^1$, and H: $1s^1$. A plane-wave kinetic energy cutoff of 850 eV was employed for all calculations. An electronic convergence criterion of 10^{-8} eV was used, and all structure models were relaxed until the Hellmann-Feynman forces on each atom were less than 10^{-2} eV/Å. A $\sqrt{2} \times \sqrt{2} \times 2$, 20-atom supercell for SrFeO_3 , SrFeO_2 , and $\text{SrFeO}_{2.75}$, and the brownmillerite structure with a $\sqrt{2} \times \sqrt{2} \times 4$ 40-atom supercell for $\text{ABO}_{2.5}$, were employed. In all cases, we examined five different Fe-site spin orientations: ferromagnetic (FM), A-type antiferromagnetic (A-AFM), C-AFM, G-AFM, and E-AFM with magnetic wave vector $k = [0, 0, 0] \frac{\pi}{a}$, $k = [0, 0, \frac{1}{2}] \frac{\pi}{a}$, $k = [\frac{1}{2}, \frac{1}{2}, 0] \frac{\pi}{a}$, $k = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}] \frac{\pi}{a}$ and $k = [0, \frac{1}{3}, 0] \frac{\pi}{a}$, respectively. The schematic representation of spin orientations of these configurations are provided in the Supplemental Material (SM) [33]. The E-AFM structure with a $2 \times 1 \times 1$

FIG. 2. Powder x-ray diffraction patterns of (a) SrFeO_2 , (b) $\text{SrFeO}_{2-x}\text{H}_x$, (c) $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$, and (d) $\text{Sr}_{0.9}\text{Nd}_{0.1}\text{FeO}_2$ (shown in blue) overlaid with their corresponding calculated powder pattern (shown in green).

supercell was necessary to compute the exchange interactions in the SrFeO_2 structure. The $4 \times 4 \times 4$ and $4 \times 4 \times 2$ Monkhorst-Pack set of k points [34] were used for the Brillouin-zone integration of the 20- and 40-atom unit cells, respectively.

To overcome the well-known limitation of DFT to properly treat the self-interactions of the localized d orbitals of Fe, we used the rotationally invariant DFT+ U method [35] with $U = 5.0$ eV for Fe d electrons. Using these parameters, SrFeO_3 was determined to be FM with a cubic lattice constant of 3.839 Å, in good agreement with the experimental value of 3.85 Å [36]. Similar values were obtained for other DFT calculations [19,37,38].

As a proxy for understanding the reducibility of SrFeO_3 to SrFeO_2 , we examined both the stability against decomposition into binary oxides ($\Delta H_f^{\text{SrFeO}_x}$) and the oxygen vacancies formation enthalpy ($\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x}$), which were calculated as

$$\Delta H_f^{\text{SrFeO}_x} = E_{\text{SrFeO}_x} - E_{\text{SrO}} - \frac{E_{\text{Fe}_2\text{O}_3}}{2} + \frac{(x-2.5)}{2} E_{\text{O}_2}, \quad (1)$$

$$\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x} = E_{\text{SrFeO}_{x-0.25}} - E_{\text{SrFeO}_x} + 0.25 \mu_{\text{O}}(T, P). \quad (2)$$

In Eq. (1), E_{SrFeO_x} , E_{SrO} , $E_{\text{Fe}_2\text{O}_3}$, and E_{O_2} refer to the DFT energies of the initial SrFeO_x structure, the reference binary

oxides SrO and Fe_2O_3 , and an O_2 molecule, respectively. In Eq. (2), $E_{\text{SrFeO}_{x-0.25}}$ refers to the energy of the SrFeO_x structure with additional oxygen vacancies and μ_{O} refers to the oxygen chemical potential (reference to the total energy of an oxygen molecule, E_{O_2}) at a specific temperature, T , and pressure, P , as defined by

$$\begin{aligned} \mu_{\text{O}} &= \frac{1}{2} \left[E_{\text{O}_2} + \mu_{\text{O}_2}(T, P^0) + k_B T \ln \left(\frac{P_{\text{O}_2}}{P^0} \right) \right] \\ &= \frac{1}{2} E_{\text{O}_2} + \Delta \mu_{\text{O}}. \end{aligned} \quad (3)$$

Assuming negligible zero-point energy, $\mu_{\text{O}_2}(T, P^0)$ is the T -dependent chemical potential of the O_2 molecule at $P^0 = 1$ atmosphere reference pressure, whose value can be obtained from the JANAF thermochemical tables [39] following the procedure laid out by Reuter and Scheffler [40]. P_{O_2} represents the partial pressure of oxygen during the reaction. The value of E_{O_2} is computed to be -10.256 eV from a spin-polarized O_2 calculation which gives μ_{O} (0 K) of -5.128 eV, in good agreement with the experimental O_2 bond dissociation energy of -5.11 eV [41]. Note that negative values of $\Delta H_f^{\text{SrFeO}_x}$ reflect the energetically favored SrFeO_x relative to reference binary oxides. The values of $\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x}$ refer to the thermodynamic cost for the oxygen vacancy formation in SrFeO_x ,

FIG. 3. The decomposition energy into binary oxides (height of bar) and the formation energy of successive oxygen vacancies (height difference between bars) in the unassisted reduction of SrFeO_x , $x = 3.0, 2.75, 2.5, 2.0$, and 1.75 (low-intensity solid bars) and topochemical reduction of $\text{SrFeO}_x\text{H}_{0.25}$, $x = 2.75, 2.5, 2.0$, and 1.75 with CaH_2 (high-intensity bars with hatch).

with negative values indicating energetically favored final reduced compounds. For the topochemical reduction with CaH_2 , $\Delta H_f^{\text{SrFeO}_x\text{H}_{0.25}}$ and $\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x\text{H}_{0.25}}$ of the hydrogenated perovskites with $x = 2.75, 2.5, 2.0$, and 1.75 are calculated using

$$\Delta H_f^{\text{SrFeO}_x\text{H}_{0.25}} = E_{\text{SrFeO}_x\text{H}_{0.25}} - E_{\text{SrO}} - \frac{E_{\text{Fe}_2\text{O}_3}}{2} - \frac{E_{\text{CaH}_2}}{8} + \frac{E_{\text{CaO}}}{8} - \frac{(x - 2.375)}{2} E_{\text{O}_2}, \quad (4)$$

$$\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x\text{H}_{0.25}} = E_{\text{SrFeO}_{x-0.25}\text{H}_{0.25}} + \frac{1}{2} E_{\text{O}_2} - E_{\text{SrFeO}_x\text{H}_{0.25}}. \quad (5)$$

III. RESULTS AND DISCUSSION

A. Thermodynamic considerations to achieve the SrFeO_3 to SrFeO_2 transformation

Focusing on thermodynamic stability, we first examine the energetics for reducing SrFeO_3 successively to SrFeO_2 . Of particular interest is the decomposition energy ($\Delta H_f^{\text{SrFeO}_x}$) for the various oxygen-deficient phases as well as the corresponding oxygen vacancy formation enthalpies ($\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x}$) and magnetic properties.

Figure 3 depicts $\Delta H_f^{\text{SrFeO}_x}$ and $\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_x}$ for SrFeO_3 being reduced to $\text{SrFeO}_{1.75}$. Here, we see that SrFeO_3 forms a thermodynamically stable perovskite phase with $\Delta H_f^{\text{SrFeO}_3} = -1.003$ eV. The SrFeO_3 compound is determined to be cubic with lattice constant $a_0 = 3.839$ Å, in good agreement with the experimental value of 3.851 Å [42]. We also find SrFeO_3 to have a FM ground state with Fe moments in the octahedral environment to be $3.71 \mu_B$, in agreement with previous computational reports of $3.61 \mu_B$ [19]. This value, however, is larger than the reported experimental values of $2.96 \mu_B$ [16] and $2.7 \pm 0.4 \mu_B$ [36] but is in good agreement with the extrapolated value of $3.73 \mu_B$ for SrFeO_3 from ferromagnetic $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$, $0.2 < x \leq 1$ [43].

The projected density of states used to extract charge distribution of the $3d^4$ valence electrons of Fe in SrFeO_3 shows a high-spin $t_{2g}^3 e_g^1$ configuration with the itinerant e_g orbitals forming broad σ bonds with O $2p$ orbitals, giving a metallic state that explains the absence of the Jahn-Teller distortion expected for a localized d^4 electron system. The geometrical parameters and magnetic moments of the various systems under discussion are presented in Table II.

As shown in Fig. 3, the removal of oxygen from SrFeO_3 to form $\text{SrFeO}_{2.75}$ requires $\Delta H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_3} = 0.185$ eV implying 0.74 eV for 1 O removal from a 20-atom supercell. This value is in agreement with the measured value of 0.829 eV [45] and previous computed values of $0.73(16)$ eV [46] and 0.71 eV [19]. Here, we found the most favorable oxygen vacancy site is one of the axial oxygen sites, in agreement with previous experimental observations [16]. This reduction to $\text{SrFeO}_{2.75}$ results in a change in the magnetic ordering from FM to A-AFM. The calculated Fe magnetic moments of $3.53 \mu_B$ and $4.04 \mu_B$ are in agreement with the reported values of $3.3 \mu_B$ and $3.9 \mu_B$ from a *first-principles* study in an orthorhombic unit cell, [19] and the only reported experimental value of $3.55 \mu_B$ [16]. The two values of the Fe magnetic moments of $3.53 \mu_B$ and $4.04 \mu_B$ reflect the presence of a combination of square pyramidal Fe^{3+}O_5 units arising from the charge transfer due to the missing oxygen ions and the unreduced Fe^{4+}O_6 octahedral units, respectively. We note the reduced moment of $3.53 \mu_B$ from the values $5 \mu_B$ and $4 \mu_B$ of free Fe^{3+} and Fe^{4+} , respectively, resulting from the significant Fe $3d$ -O $2p$ hybridization, typical of perovskite compounds [47,48]. Our computed value of 0.516 eV for one O vacancy formation energy for $\text{SrFeO}_{2.75}$ is smaller than the prior computed value of 1.25 eV [19]. However, we note that the prior calculation employed PBE+ U with $U = 3$ eV while our calculations used PBEsol with $U = 5$ eV and gave a better value for E_{O_2} . In addition, the prior work showed a decrease in the oxygen formation energy as function of increasing U suggesting that those results would approach ours for larger U values.

The $\text{SrFeO}_{2.5}$ (brownmillerite) phase formed by alternating rows of corner-sharing BO_6 octahedra and BO_4 tetrahedra is determined to be stable with a formation enthalpy of $\Delta H_f^{\text{SrFeO}_{2.5}} = -0.688$ eV. Here, a G-AFM configuration is found to be the energetically favored magnetic orientation with Fe moments of $4.08 \mu_B$ and $3.97 \mu_B$ in the octahedral Fe^{3+}O_6 units and square pyramidal Fe^{3+}O_4 units, respectively. The values are close to the reported moments of $4.0(2) \mu_B$ and $3.7(1) \mu_B$ from Rietveld refinement measurement [42] and $4.11 \mu_B$ and $4.22 \mu_B$ from first-principles calculations [19]. However, these values differ significantly from $1.99 \mu_B$ and $2.05 \mu_B$ [44] measured from profile refinement of neutron diffraction data. The Fe atom in the octahedral coordination has a magnetic moment of $4.08 \mu_B$ for its insulating electronic state implying a high spin state of d^4 electronic configuration. Despite the significant change in coordination environment, the magnetic moment of Fe atoms in a tetragonal environment is $3.97 \mu_B$, again indicating high-spin d^4 electronic configuration. The Fe^{4+} atoms in Fe^{4+}O_6 units are positioned symmetrically next to four O atoms within an equatorial plane with Fe-O bond lengths of 1.986 Å but asymmetrically with the axial O atoms with bond lengths of

TABLE II. Geometrical parameters and magnetic moments of Fe in pristine, reduced SrFeO_x ($x = 3.0, 2.75, 2.5, 2.0$) and hydrogenated SrFeO_2 structures with their corresponding available experimental values in parentheses. O_6 , O_5 , O_4 , Eq., and Ax. refer to the FeO_6 , FeO_5 , and FeO_4 coordination environments, equatorial and axial Fe–O bond lengths, respectively.

System (magnetic configuration)	a (Å)	c (Å)	Fe–O (Å)	Fe–Fe (NN) (Å)	Fe magnetic moment (μ_B)
SrFeO_3 (FM)	3.839 (3.851)	3.848 (3.851 [42])	O_6 : Eq.:1.919, Ax.:1.924	3.839	3.71 (3.73 μ_B [43], 2.96 [16], 2.7 $\pm$ 0.4 [36])
$\text{SrFeO}_{2.75}$ (A-AFM)	3.867, 3.864 ($a = 3.88$, $b = 3.839$ [16])	3.855 (3.857)	O_6 : Eq.: 2.023, Ax.:1.97,1.896 O_5 : Eq.:1.86,1.853 Ax.:1.859	3.788	3.53 (Fe in Fe^{3+}O_5) 4.04 (Fe in Fe^{4+}O_6) (3.55 [16])
$\text{SrFeO}_{2.5}$ (G-AFM)	3.898 (3.911 [44])	3.872 (4.009)	O_6 : Eq.:1.986 (1.99) Ax.: 2.23,2.121 mean = 2.175(2.20) O_4 : Eq.:1.861,1.874,1.895 Ax.:1.897 mean = 1.881(1.874)	3.854	3.97, 4.08 (1.99, 2.05 [44] 3.7 (1), 4.0(2) [42])
SrFeO_2 (G-AFM)	3.985 (3.991)	3.441 (3.474)	O_4 : Eq.:1.993	3.442 (Interplanar)	3.563 (3.6 [22])
SrFeO_2 $\text{H}_{0.25}$ (C-AFM)	3.970	3.496	Eq.: 1.982	3.429, 3.451(H on apical site)	3.565 3.756 (H on apical site)
$\text{SrFeO}_{1.75}\text{H}_{0.25}$ (C-AFM)	3.968	3.492	Layer without H: 1.971, Layer with H: Fe–O = 1.935, Fe–H = 2.059	3.487 (interplanar)	3.598 (layer without H) 3.507 (layer with H)

2.239 and 2.121 Å. This is likely due to Jahn-Teller distortions leading to an insulating state. In Fe^{4+}O_4 units, Fe–O bond lengths are the shortest among the nonstoichiometric SrFeO_{3-x} compounds with values of 1.861, 1.874, 1.897, and 1.895 Å. The strong Fe–O bonding might offer similar local environments as that in high coordinated octahedral environments as reflected from the magnetic moment of 3.96 μ_B leading to the d^4 electronic configuration. The O vacancy formation energy of 3.408 eV per O from $\text{SrFeO}_{2.5}$ in our calculation is close to 3.0 eV reported from a prior computational study [19].

The removal of two remaining O ions from the axial sites in the brownmillerite structure transforms it into the layered SrFeO_2 structure. We find that with $H_{\text{O}_{\text{vac}}}^{\text{SrFeO}_{2.5}} = 1.703$ eV, this oxygen reduction step is energetically the most costly process in the transformation of SrFeO_3 to SrFeO_2 . In addition, the SrFeO_2 structure is found to be unstable with $\Delta H_f^{\text{SrFeO}_x} = 1.015$ eV. The G-AFM ordering remains the energetically favored magnetic orientation with Fe magnetic moments of 3.56 μ_B , in agreement with the experimental value of 3.6 μ_B [22]. All of the O atoms in the tetrahedral environment are symmetrically positioned around the Fe atom with O–Fe bond lengths of 1.993 Å. The Fe^{2+} atoms are in perfect square planar coordination with interplanar Fe–Fe distances of 3.442 Å, shorter than the interplanar Fe–Fe distances of 3.985 Å. The buckling angle Fe–O–Fe along the [101] tetragonal axis of 179.77° indicates a nearly perfect planar arrangement. The arrangement relies on the double occupancy of the $3d_z^2$ orbitals of high-spin Fe^{2+} cation [49].

We note that the calculated collinear ferromagnetic ground-state spin ordering of SrFeO_3 differs from the helical

G-AFM observed in experiment [16] and previous non-collinear GGA+ U calculations [50]. Using an effective Heisenberg Hamiltonian [Eq. (6)], the magnetic coupling between the first-, second-, third-, and fourth-nearest neighbor Fe atoms are found to be $J_1 = 17.17$ meV, $J_2 = 17.29$ meV, $J_3 = 1.27$ meV, and $J_4 = 0.82$ meV, respectively. These interaction parameters are close to previously reported values [51]. The negative and almost equal values of intraplanar superexchange (J_1) and interplanar direct exchange interactions (J_2) between Fe cations suggest that FM coupling is favored for nearest-neighbor interactions while the positive J_3 and J_4 values imply AFM exchange interactions are favored further distances. The competition between FM and AFM interactions may lead to a noncollinear AFM with helical structure. For $\text{SrFeO}_{2.75}$, $J_1 = -6.16$ meV, $J_2 = 14.84$ meV, $J_3 = 3.48$ meV, and $J_4 = -0.03$ meV imply an AFM configuration with strong intralayer direct exchange. In this case, our computed $T_N = 288$ K is in close agreement with the measured $T_N = 232$ K [16]. Furthermore, the agreement of the Fe magnetic moment with the experimental measurement for $\text{SrFeO}_{2.5}$ [42] and SrFeO_2 [22] suggests that the collinear magnetism considered in this study is a valid approximation for the reduced compounds.

It is worth noting that the above calculations assume 0 K behavior at $\Delta\mu_O = 0$ eV. To further explore the reducibility of SrFeO_3 at finite temperatures and oxygen partial pressures, we examined the temperature- and pressure-dependent formation enthalpies for multiple oxygen vacancies in SrFeO_3 which is shown in Fig. 4. To obtain the phase diagram, the oxygen partial pressure at different temperatures (T) were calculated using Eq. (3).

FIG. 4. The temperature and oxygen partial pressure-dependent phase diagram for the formation energy of two (green area), and four (blue area) oxygen vacancies on SrFeO_3 .

In Fig. 4, one can see that at low temperatures and relatively high oxygen partial pressures, SrFeO_3 is the most stable phase. As the temperature increases and the partial pressure of O_2 decreases, there is a transformation to the brownmillerite ($\text{SrFeO}_{2.5}$) phase, which encompasses much of the phase diagram, then to the less stable SrFeO_2 at relatively high temperatures and very low O_2 partial pressures. We note that this phase-stable region is accessible experimentally but requires ultrahigh vacuum/reducing conditions and high temperatures. Our thermodynamic results indicate the formation of a reduced $\text{SrFeO}_{2.5}$ phase at lower temperature and low O_2 partial pressure. Furthermore, they confirm the necessity to significantly reduce the O_2 partial pressure to further reduce $\text{SrFeO}_{2.5}$, thus, agreeing with coulometric titration measurements at 1223 K [52].

B. Synthetic considerations

While direct synthesis methods may be possible, in the following text we consider approaches to reducing the barriers towards the synthesis of SrFeO_2 . SrFeO_2 was previously synthesized at 280 °C with a 2:1 molar ratio of CaH_2 : SrFeO_3 and an undisclosed molarity of NH_4Cl in methanol [22]. In this attempt to reproduce the previous experimental process, we find that by increasing the synthesis temperature to 300 °C, raising the molar ratio of CaH_2 : SrFeO_3 to 3.0:1, and increasing the partial pressure of H in the evacuated reaction vessel by adding 1 molar thoroughly ground CaH_2 in a separate alumina crucible, a structure can be achieved as a polycrystalline powder. The PXRD for this structure is shown in Fig. 2(b), and the temperature-dependent magnetic susceptibility overlaid with that of the undoped SrFeO_2 is depicted in Fig. 5.

In the absence of single-crystal data, exact structural determination is difficult. Additionally, for the case of potential hydrogen incorporation, hydrogen is too light for detection via EDS, and the uncertainty of the atomic positions for H

FIG. 5. ZFC temperature-dependent magnetic susceptibility data for SrFeO_2 (shown in green) synthesized via previously reported methods [22], and $\text{SrFeO}_{2-x}\text{H}_x$, a likely hydrogen-doped system (shown in blue) synthesized with a stronger reducing environment at an elevated temperature.

makes knowledge about the local coordination environments ambiguous, causing x-ray absorption near-edge spectroscopy to be unreliable. Rietveld refinement revealed negligible differences in lattice parameters compared to SrFeO_2 . The ZFC susceptibility data for the hydrogen-doped SrFeO_2 exhibit a sharp upturn in the susceptibility. The value of T_N determined from the inflection point on $\frac{d(\chi T)}{dT}$ plot becomes 370 K. This value differs significantly from $T_N = 471$ K obtained with a broader upturn in the susceptibility for SrFeO_2 . The $T_N = 471$ K at the weaker reducing environment is in closer agreement with previously measured $T_N = 473$ K [22].

C. Prediction of the doping-dependent magnetic ordering transition temperature (T_N)

To computationally decipher the source of the significant decrease in the value of T_N , we employ Monte Carlo (MC) simulations with an effective Hamiltonian:

$$H = E_n + \frac{\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j}{2} + \sum_i D S_{iz}^2, \quad (6)$$

where E_n is a nonmagnetic part that mimics the chemical configuration of a system. The spin-dependent contributions are represented by a Heisenberg model with coupling constant J_{ij} between spins $\mathbf{S}_i$ and $\mathbf{S}_j$ located at sites i and j , respectively. A mapping assuming Fe interactions up to the second-nearest neighbors in both the ab - and ac -plane directions are shown in Fig. 6. As in Ref. [26], the spin anisotropy term DS_{iz}^2 is taken to be 4 meV to incorporate the results of spin-orbital coupling calculations of the ferromagnetic state which indicate that states with spin moments parallel to the ab plane are more stable than states with spin moments parallel to the c axis by 4 meV/Fe.

To explore different spin ordering, a $\sqrt{2} \times \sqrt{2} \times 2$ supercell containing four Fe cations is constructed for FM, A-AFM, C-AFM, and G-AFM spin configurations, while a $2\sqrt{2} \times 2\sqrt{2} \times 2$ supercell with 16 Fe is constructed for

FIG. 6. Spin-exchange parameters between Fe atoms in the tetragonal SrFeO_2 structure. The J_1 , J_2 , J_3 , and J_4 refer to the interaction between Fe atoms on the cube edge within a layer, on the cube edge between layers, on the face diagonal within a layer, and on the face diagonal between layers, respectively.

E -AFM. The mapping of the total energy E of the five spin configurations results in the following equations:

$$E_{FM} = E_n + \frac{4J_1S^2 + 2J_2S^2 + 4J_3S^2 + 8J_4S^2}{2}, \quad (7)$$

$$E_{G-AFM} = E_n + \frac{-4J_1S^2 - 2J_2S^2 + 4J_3S^2 + 8J_4S^2}{2}, \quad (8)$$

$$E_{A-AFM} = E_n + \frac{4J_1S^2 - 2J_2S^2 + 4J_3S^2 - 8J_4S^2}{2}, \quad (9)$$

$$E_{C-AFM} = E_n + \frac{-4J_1S^2 + 2J_2S^2 + 4J_3S^2 - 8J_4S^2}{2}, \quad (10)$$

$$E_{E-AFM} = E_n + \frac{2J_2S^2 - 4J_3S^2}{2}. \quad (11)$$

After solving Eqs. (7)–(11), one gets

$$J_1 = \frac{[(E_{FM} - E_{C-AFM}) + (E_{A-AFM} - E_{G-AFM})]}{16S^2}, \quad (12)$$

$$J_2 = \frac{[(E_{FM} - E_{A-AFM}) + (E_{C-AFM} - E_{G-AFM})]}{8S^2}, \quad (13)$$

$$J_3 = \frac{[(E_{FM} + E_{C-AFM}) - 2E_{E-AFM}]}{16S^2}, \quad (14)$$

$$J_4 = \frac{[(E_{FM} - E_{A-AFM}) - (E_{C-AFM} - E_{G-AFM})]}{32S^2}. \quad (15)$$

TABLE III. The values of the spin-exchange interaction parameters (as illustrated in Fig. 6) of different systems calculated using Eqs. (12)–(15). The available measured values are in parentheses.

System	J_1 (meV)	J_2 (meV)	J_3 (meV)	J_4 (meV)	m_{avg} of Fe (μ_B)	T_N (K)
SrFeO_2	7.662	2.809	0.477	−0.291	3.578	327 (471, Fig. 5; 473 [22])
SrFeO_2 [26] (Experimental crystal structure from Ref. [22])	7.04	2.18	0.43	−0.23		
SrFeO_2 [26] (Computationally optimized structure)	7.91	2.29	0.30	−0.30		354
SrFeO_2 [49]	6.58	1.75		−0.26		
$\text{SrFeO}_2\text{H}_{0.25}$	7.173	−2.973	0.616	0.998	3.668	398
$\text{SrFeO}_{1.75}\text{H}_{0.25}$	6.794	−9.878	0.223	−1.163	3.533	284
$\text{Sr}_{0.9375}\text{Nd}_{0.0625}\text{FeO}_2$	4.536	11.159	4.479	−2.276	3.594	233

The positive and negative values of J_s indicate AFM and FM spin-exchange interactions, respectively.

The calculated values of the spin-exchange constants (J_s) for each system are presented in Table III. These values for SrFeO_2 are in agreement with the values computed from previous experimental and optimized crystal structures. Here we find that J_1 is the strongest, J_2 is significant, indicating a three-dimensional spin lattice, while J_3 and J_4 have relatively small values. The signs of these interactions support a G -AFM ground state for SrFeO_2 .

Using these J values, we performed Metropolis Monte Carlo simulations to evaluate T_N using the Oak-Ridge Wang-Landau (OWL) code [53]. A $12 \times 12 \times 12$ spin lattice was used, and the spin length of all spins were randomly assigned to be $S = \frac{m_{\text{avg}}}{2}$, where m_{avg} is the average value of the magnetic moment of an Fe atom obtained from DFT calculations and the factor 2 converts electron number into spin equivalent. Periodic boundary conditions were applied to reduce finite-size effects. At each temperature T , 100 000 MC steps were used for thermalization and statistics were taken from another 100 000 MC steps. The specific heat (C_v) was calculated from the fluctuations in energy using

$$C_v(T) = \frac{\langle E^2 \rangle_T - \langle E \rangle_T^2}{T^2}, \quad (16)$$

where $\langle E \rangle_T$ and $\langle E^2 \rangle_T$ denote the canonical ensemble average of the energy E and energy-squared E^2 at T . The transition temperature T_N was identified as the temperature where the specific heat peaks. The standard error (S.E.) of C_v at a temperature was computed using

$$\text{S.E.} = \sqrt{\frac{\sum_{i=1}^N (C_{vi} - \overline{C_v})^2}{N(N-1)}}, \quad (17)$$

where C_{vi} , $\overline{C_v}$, and N represent the value of C_v for the i th simulation, the mean value of C_{vi} , and the number of independent simulations (ten here), respectively.

Figure 7 shows the C_v for SrFeO_2 , $\text{SrFeO}_2\text{H}_{0.25}$, $\text{SrFeO}_{1.75}\text{H}_{0.25}$, and $\text{Sr}_{0.9375}\text{Nd}_{0.0625}\text{FeO}_2$, each of which was averaged over ten independent simulations with different random seeds. The maximum S.E.'s are about 1% of the absolute value of C_v . From Fig. 7, the computed value of T_N for SrFeO_2 is 327 K, which is in agreement with the reported computed value of 354 K [26] but is smaller than the measured value of 471 K.

FIG. 7. The specific-heat capacity (C_v) of SrFeO_2 , $\text{SrFeO}_2\text{H}_{0.25}$, $\text{SrFeO}_{1.75}\text{H}_{0.25}$, and $\text{Nd}_{0.0625}\text{Sr}_{0.9375}\text{FeO}_2$ systems vs absolute temperature calculated using Metropolis Monte Carlo simulations with a classical spin Hamiltonian [Eq. (6)].

D. Magnetic ordering transition temperature (T_N) and thermodynamic considerations of the oxyhydrides

To explore the possible source of the difference in T_N of 101 K under the two different synthetic conditions previously discussed, we consider the presence of hydrogen (H). H incorporation into SrFeO_2 can occur in one of two ways: (1) interstitial doping, i.e., onto sites previously occupied by apical oxygen ions in SrFeO_3 that are no longer present in SrFeO_2 ; we denote this as SrFeO_2H_y , and (2) substitutional doping onto existing oxygen sites resulting in $\text{SrFeO}_{2-x}\text{H}_x$, as observed in other oxides [54,55]. The geometry of the ground state of the energetically favored $\text{SrFeO}_2\text{H}_{0.25}$ and $\text{SrFeO}_{1.75}\text{H}_{0.25}$ are presented in the SM [33]. The computed T_N of $\text{SrFeO}_2\text{H}_{0.25}$ is found to be 398 K, which is increased from the computed $T_N = 327$ K of SrFeO_2 and is close to

the measured value 471 K. The slightly larger J_2 and J_4 of $\text{SrFeO}_2\text{H}_{0.25}$ compared to SrFeO_2 increase the T_N . In contrast, the T_N of $\text{SrFeO}_{1.75}\text{H}_{0.25}$ formed by the substitution of O with H is found to be 284 K which is 114 K less than that of $\text{SrFeO}_2\text{H}_{0.25}$. The reduction here agrees with the reduction of 101 K measurements. Interestingly, the magnetic moment of Fe changes slightly due to H incorporation where the H incorporation on O site in the Fe-containing plane changes interlayer interactions, possibly due to an increase in interlayer Fe-Fe distances (Table II), relative to the intralayer ones. These results imply that H incorporation in the layered SrFeO_2 system through topochemical reduction may be a fruitful approach to tuning T_N . In the absence of direct experimental evidence for H incorporation in our sample, the experimentally measured differences in T_N indirectly support the presence of hydrogen. In other words, the results suggest the possibility of likely interstitial hydrogen-doped SrFeO_2 as a result of topochemical reduction.

Figure 8(a) depicts the most stable phases of $\text{SrFeO}_x\text{H}_{0.25}$ as a function of chemical potential $\Delta\mu$ of hydrogen (H_2) and oxygen (O_2) while Fig. 8(b) transforms the data to a function of partial pressure of H_2 and O_2 at 1000 K. In Fig. 8(a), one can see that the different hydrogen incorporated compounds are energetically favored than pristine SrFeO_x compounds under hydrogen-rich environments. For hydrogen-rich conditions $\Delta\mu(\text{O}_2) > -2$ eV, the $\text{SrFeO}_{2.75}\text{H}_{0.25}$ phase is favored for $1 \text{ eV} < \Delta\mu(\text{H}_2) < 3 \text{ eV}$ while interestingly the $\text{SrFeO}_{1.75}\text{H}_{0.25}$ is favored for $\Delta\mu(\text{H}_2) > 3 \text{ eV}$. Despite the extended favorable region of the $\text{SrFeO}_{2.5}$ and SrFeO_2 phases, their hydrogenated counterparts have small regions of preference for $\Delta\mu(\text{H}_2) < 3 \text{ eV}$. As shown in Fig. 8(b), SrFeO_2 may be stabilized under an ultrahigh vacuum environment while the hydrogenated $\text{SrFeO}_{1.75}\text{H}_{0.25}$ and $\text{SrFeO}_2\text{H}_{0.25}$ compounds would be stable in strong reducing environments.

FIG. 8. Phase diagrams showing the formation of SrFeO_{3-x} and $\text{SrFeO}_{3-x}\text{H}_{0.25}$ ($x = 0, 0.25, 0.5, 1.0$) compounds as function of (a) the change in chemical potential of hydrogen ($\Delta\mu_{\text{H}_2}$) and oxygen molecules ($\Delta\mu_{\text{O}_2}$), and (b) the partial pressure of hydrogen and oxygen molecules at 1000 K.

FIG. 9. Temperature-dependent magnetic susceptibility for $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$ with FC data shown in blue and ZFC data shown in green.

E. Magnetic ordering transition temperature (T_N) for A-site doped SrFeO_2

In addition to the H doping on the O site in SrFeO_2 , we explored the effects of Nd doping onto the Sr site, inspired by the recent discovery of superconductivity in $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ [7]. $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$ was synthesized via the previously reported method for SrFeO_2 [22]. Attempts to synthesize this material via the modified synthesis aforementioned resulted in incomplete reduction. The powder x-ray diffraction for $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$ is shown in Fig. 2(c), and temperature-dependent magnetic susceptibility is shown in Fig. 9.

As shown in Fig. 9, a slight field dependence is observed, and an inflection point can be observed in the ZFC data at $T_N = 327$ K, a feature not observed in SrFeO_2 nor the H-doped analog. In addition, $\text{Sr}_{0.9}\text{Nd}_{0.1}\text{FeO}_2$ was also synthesized, but it was found that at higher concentrations of Nd, complete reduction was not achieved, and small impurities presented. The reduction of T_N emphasizes the role of electron doping on the A-site for SrFeO_2 for controlling T_N .

The atomic structure of the energetically favored $\text{Sr}_{0.9375}\text{Nd}_{0.0625}\text{FeO}_2$ model and its geometrical and magnetic parameters are presented in SM [33]. The computed value of T_N is found to be 233 K, lower than that of SrFeO_2 and so qualitatively captures the experimental trend of reduction of T_N with Nd doping on A-site of SrFeO_2 . However,

quantitatively, the computed T_N difference of 94 K between SrFeO_2 and $\text{Sr}_{0.9375}\text{Nd}_{0.0625}\text{FeO}_2$ is lower than our measured difference of 144 K. Interestingly, the measured T_N difference of 144 K is close to the difference of 165 K between T_N of $\text{SrFeO}_2\text{H}_{0.25}$ and $\text{Sr}_{0.9375}\text{Nd}_{0.0625}\text{FeO}_2$ models, as in the hydrogenated case discussed previously.

IV. CONCLUSIONS

We discuss the synthetic considerations necessary for the hydride reduction of a perovskite oxide, and present $\text{SrFeO}_{2-x}\text{H}_x$ as an addition to the family of infinite layer structures. Such hydride doping is shown to decrease the Néel temperature of SrFeO_2 by 101 K. Density-functional theory calculations support the thermodynamic stability of SrFeO_2 at low O_2 pressure and at temperatures greater than 700 K. These calculations further demonstrate the formation of hydrogenated SrFeO_2 under high- H_2 partial pressures. Interestingly, $\text{SrFeO}_2\text{H}_{0.25}$ with H incorporated at axial O vacancy sites exhibits an increase in T_N , while H incorporated at substitutional sites in the infinite layer plane favors ferromagnetic interlayer exchange interactions and a reduction in T_N . The composition $\text{Sr}_{0.95}\text{Nd}_{0.05}\text{FeO}_2$ is also presented; both physical characterization and density-functional theory parametrized Monte Carlo calculations show the A-site electron doping may play a similar role in tuning T_N . Together these results serve as a blueprint for tuning the magnetic/electric properties of future infinite layer compounds, which may be potential hosts for high-temperature superconductivity.

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