Stoichiometry, Structure, and Properties of \( \text{La}_2\text{NiO}_{4+\delta} \) and \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta} \)

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ABSTRACT

The oxygen content phase diagram of \( \text{La}_2\text{NiO}_{4+\delta} \) has been studied in detail using x-ray and neutron diffraction data from well-characterized specimens. There are numerous phase separations and phase transitions which are observed with changes in temperature and composition. The complexity of the phase diagram arises primarily from oxygen defect interactions, however we have also obtained evidence for coupled charge and spin ordering at \( \delta = 0.125 \) corresponding to organization of holes into ordered domain walls. These domain walls act as antiphase boundaries between stripes of antiferromagnetically ordered nickel moments. Neutron scattering data on Sr-substituted compositions with well-defined oxygen content indicate incommensurate charge and spin correlations closely related to those in the \( x = 0, \delta = 0.125 \) composition. The incommensurability approaches \( 1/4 \) and the correlation length increases as the hole concentration approaches \( p = x + 2\delta = 0.25 \).

KEYWORDS: \( \text{La}_2\text{NiO}_{4+\delta} \), phase separations, Sr substitution, defect ordering, charge and spin order.

INTRODUCTION

\( \text{La}_2\text{NiO}_4 \) and its doped variants have been the subject of rather extensive investigation in recent years owing in large part to the close relationship between these materials and their cuprate counterparts. The broader range of both accessible oxygen stoichiometry and strontium solubility make the nickelate a particularly interesting system for systematic study of defect interactions, as well as factors influencing electronic localization and magnetic correlations. As with its copper analog, \( \text{La}_2\text{NiO}_{4+\delta} \) also exhibits phase separations as a function of the level of loading of intercalated oxygen, \( \delta \). For both \( \text{La}_2\text{CuO}_{4+\delta} \) and \( \text{La}_2\text{NiO}_{4+\delta} \), the stoichiometric phases are antiferromagnetic insulators with \( T_N \approx 330 \) K. Upon loading with a small amount of excess oxygen both the cuprate [1] and nickelate [2] become biphasic, separating out a well-defined higher-\( \delta \) phase from the more nearly stoichiometric one. In both systems, multiple biphasic envelopes and single-phase compositional ranges are observed as oxygen loading is increased. Unlike the cuprate, for which the higher-\( \delta \) phases are superconducting, the nickelates remain localized and antiferromagnetic to much higher \( \delta \) [3,4]. Similarly, with Sr-doping the nickelate remains insulating to quite high doping levels whereas the cuprate is metallic or superconducting.
In this report, trends in structure and properties will be examined for nickelates as a function of oxygen stoichiometry (δ), strontium content (x), and overall hole concentration (p = x + 2δ). Oxygen content variations above the nominal stoichiometry arise from intercalation of excess oxygen into the La2O2 rock salt layer; whereas, substoichiometric compositions involve formation of normal site oxygen vacancies (presumably within the basal planes) and are only observed for x > 0 such that p ≥ 0 for all compositions. In this presentation we will restrict our attention to compositions for which either \( x = 0.00 \) with 0 ≤ δ ≤ 0.125 or for which \( δ = 0.000 \) with 0.135 ≤ x ≤ 0.20. In this way similar ranges of hole concentration can be achieved either exclusively by oxygen doping or by strontium doping.

EXPERIMENTAL PROCEDURE

High-purity (99.995%+) single crystals were prepared by radio frequency induction skull melting [5]. Growth is congruent for La2NiO4; however, the largest Sr-substituted crystals show homogeneous Sr content with x slightly less than that of the melt from which they were grown.

Oxygen stoichiometry variations were investigated using a combination of thermogravimetric and iodometric analyses. The thermogravimetric studies were made while varying the \( P_{O_2} \) under fixed total flow rates using mixtures of oxygen/argon or CO/CO2 depending on the oxygen partial pressure range to be reached. The actual in situ \( P_{O_2} \) was measured electrochemically using an Y-ZrO2 cell positioned immediately below the crystal for temperatures above 700°C. Iodometric measurements were made under an inert atmosphere on samples quenched from fixed \( P_{O_2} \) and temperature. The thermogravimetric measure provides a relative measurement of δ at high temperature, while the iodometric determination provides an absolute measure at room temperature. Based on the \( \delta(T, P_{O_2}, x) \) data obtained, conditions were chosen for preparation of crystals with desired compositions.

X-ray powder diffraction data were obtained on specimens ground from (small) annealed single crystals using graphite-monochromated Cu Kα radiation. An internal silicon standard was used for all powder measurements to provide accurate 2θ calibration. Triple-axis neutron scattering data were obtained on various beam lines at the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory using a wavelength of 2.35Å (\( E_i = 14.7 \) meV). Graphite filters were used to suppress higher-order contamination and various combinations of collimators were employed depending on the competing requirements for intensity and resolution. Temperature control was achieved by mounting specimens inside a He-filled aluminum can mounted on a closed-cycle displux refrigerator. In all cases, indexing will be based on the \( \sqrt{2}a \times \sqrt{2}b \times 1c \ K_2NiF_4 \) supercell.

RESULTS AND DISCUSSION

Oxygen Intercalation in La2NiO4+δ

A large number of specimens were prepared under various temperature and \( P_{O_2} \) conditions for X-ray powder diffraction analysis in order to closely survey trends in lattice constants and symmetry at room temperature [2]. From these measurements, phase diagrams were constructed to indicate ranges of δ in which single phases or biphasic assemblages exist. Below δ = 0.007, a single orthorhombic phase with \( Bmab \) symmetry is observed at room temperature, for which NiO6 octahedra are rotated antiferrodistortively about the [100] axis. With 0.020 < δ < 0.030, a distorted tetragonal phase with space group \( P42_{2}ncm \) is observed for which octahedra cant alternately about the [110] axis in one layer and [110] in the next.
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Compositions intermediate between 0.007 and 0.020 are biphasic, as are those with 0.030 < δ < 0.058. For the broad range from 0.058 < δ < 0.14, specimens appear single-phase tetragonal; however, we have recently reported a 3a x 5b x 5c supercell (relative to the doubled-base cell described above) for δ = 0.125, which we ascribe to oxygen defect ordering. Hiroi, et al. [6] have observed evidence for other 3D ordering of intercalated oxygen in electron diffraction patterns; however, their proposed ordering scheme conflicts with single crystal neutron data showing only 1D order in most cases as we will describe below. Although levels of oxygen above δ = 0.14 can be achieved, this will not be discussed here. Excess oxygen intercalates into the (1/4,1/4,1/4)-type sites within the La₂O₂ bilayer [7,8].

On cooling, the most stoichiometric phase undergoes a first-order transition from Bmab to Pccn symmetry near T = 70K [9]. The next-higher δ phase (P42/nmc) shows no structural transitions below room temperature and has a Néel point in the range 153 ≤ T ≤ 204 K, depending on δ. We have so far been unable to observe any evidence of oxygen defect ordering in this composition range.
The behavior below room temperature for compositions with \( \delta \geq 0.058 \) is quite complex (see Figure 1). We have recently shown that just below room temperature, oxygen defects order one-dimensionally such that only certain \( \text{La}_2\text{O}_2 \) layers contain the intercalated defects [10]. Superlattice reflections appear at incommensurate positions \((0,k,\ell \pm D)\) with \( k \) odd, \( \ell \) even, and with the incommensurability falling between \( 1/4 \) and \( 1/2 \). Using a model for one-dimensional disorder in layered systems by Hendricks and Teller [11], the incommensurability can be characterized in terms of intercalated layers which are spaced from two to four \( \text{La}_2\text{O}_2 \) layers apart. This ordering is rather similar to the “staging” of alkali metals that is observed in intercalated graphite, except that in the present case phase separation occurs between compositions with different staging patterns. We have prepared the pure stage-2 composition \( \text{i.e.} \), that for which the intercalated oxygens occupy every other \( \text{La}_2\text{O}_2 \) layer) for which \( \delta = 0.105 \). For pure stage-3, the composition appears to be close to \( \delta = 0.070 \). In the range \( 0.058 < \delta < 0.070 \) a microscopic integrowth of stage-3 and stage-4 ordering seems to exist. The kinetics of stage-2 ordering have been studied in some detail recently [12] by neutron scattering. The ordering occurs by homogeneous nucleation and growth. All of the staged compositions become antiferromagnetically ordered below about 75K. Commensurate antiferromagnetic ordering is observed [10] for each of the staged compositions with Néel points that are below 80K and decrease somewhat with increasing \( \delta \). Magnetic reflections are observed at \((h0\ell)\) with \( h \) odd and \( \ell \) integer.

The oxygen defect ordering becomes 3D at \( \delta = 0.125 \) and sets in upon cooling from just above room temperature. As mentioned earlier, the superstructure reflections observed by neutron scattering indicate a cell which is \( 3a \times 5b \times 5c \), although with the resolution used we were unable to distinguish orthorhombic \( a \) and \( b \) in the parent structure. The intensities of these superlattice reflections are significantly more intense with a slow rate of cooling than when the specimen is quenched. With further cooling, additional incommensurate reflections appear below about 110K. First harmonic peaks of magnetic origin are characterized by modulation wavevector \((\pm \varepsilon,0,0)\) centered about the commensurate antiferromagnetic superlattice positions. Second harmonics have a modulation wavevector \((\pm 2\varepsilon,0,1)\) centered about the fundamental nuclear peaks. The value of \( \varepsilon \) follows a “devils-staircase-like” pattern with cooling, tending toward \( \varepsilon = 0.25 \). The nuclear and magnetic contributions follow the same temperature dependence suggesting that there is coupling of charge and spin here. This has been modeled in terms of a structure in which the holes order into stripes which act as antiphase domain walls separating rows of antiferromagnetically ordered spins. At \( \varepsilon = 0.25 \), every forth row of nickel sites in the basal plane is associated with the stripe of holes.

Strontium Substituted Compositions With \( \delta = 0.00 \)

In order to study the dependence of structure and properties of heterovalently-substituted compositions such as \( \text{La}_{x-x'}\text{Sr}_{x'}\text{NiO}_{4+\delta} \) it is again important to be concerned about oxygen nonstoichiometry. In this case, unlike the unsubstituted composition, it is expected that the oxygen content will become substochiometric before the reduction boundary is encountered, such that if the divalent nickel limit is approached, the oxygen content may fall to as low as \( 4 - x/2 \). Based on both thermogravimetric and iodometric data, we find that compositions do become significantly substochiometric but do not reach this limit on approach to the reduction boundary. For the present study we wish to examine the effects of hole-doping by Sr substitution to compare with the oxygen nonstoichiometry results discussed above. In order to eliminate oxygen defect interactions it is necessary to establish conditions for preparation of materials with stoichiometric oxygen content, \textit{i.e.}, \( \delta = 0.00 \). This has been studied by using parallel thermogravimetry (PTGA) to study
oxygen uptake and loss as a function of temperature and $P_{O_2}$ for crystals with various values of $x$. A typical PTGA isotherm is shown in Figure 2 for a crystal having $x = 0.20$. This is in effect a titration curve for which we assume that the plateau represents the stoichiometric equivalence point resulting from competition between vacancy and interstitial defect reactions similar to that observed in other oxide systems [15]. The absolute scale for $\delta$ is set using this assumption and is currently being tested both by iodometric analysis of quenched specimens and by defect modeling. Based on these and other PTGA data, crystals with several values of $x$ have been annealed to have $\delta = 0.00$.

![Figure 2. A representative thermogravimetric isotherm for $La_{1.8}Sr_{0.2}NiO_4+\delta$. Note that $\delta = 0.00$ is taken to be at the inflection point.](image)

X-ray powder and single crystal neutron diffraction data have been obtained for oxygen stoichiometric ($\delta = 0.00$) crystals with $x = 0.135$ and $x = 0.20$, for which $p = x$. In both cases, these compositions are tetragonal with no apparent superstructure reflections at room temperature and become orthorhombic on cooling. For $x = 0.135$, $T_s = 230K$ below which the orthorhombic strain grows to 0.48% on cooling to 10 K. With $x = 0.20$, the orthorhombic splitting was too small to measure directly. Line broadening, accompanied by the appearance of superlattice reflections associated with octahedral tilting, indicates a transition at $T_s = 70 K$. It is interesting to note that the correlation of $T_s$ with $x$ is in very good agreement with values measured for $La_{2-x}Sr_xCuO_4$ [16].

Incommensurate magnetic ordering appears at $(h \pm \varepsilon,0,l)$ with $h$ odd, $l$ integer below $T = 100K$. For $x = 0.20$, $\varepsilon = 0.25$ as is illustrated in Figure 3. These peaks are sharp in-plane indicating a static correlation of about 40Å, but broad along $l$. Nuclear peaks are also observed for even harmonics with $n=2$, suggesting
that this is closely related to $\delta = 0.125$ with $x = 0.00$; however, in the $x = 0.20$ case correlations never become long range. The incommensurability is present but smaller for $x=0.135$. With $T < 65K$, similar reflections are observed with an incommensurability $\varepsilon = 0.12\pm0.01$ and width in-plane corresponding to a correlation length of about $10\AA$. Comparing with results of Hayden et al. [17], for which they observed $\varepsilon = 0.16$ with $x = 0.20$ and $\delta = -0.04$, we are led to believe that the incommensurability may be closely tied to the hole concentration such that $\varepsilon = p$ and that the nature of charge and spin ordering may be closely related to the ordering we have observed for $x = 0.00$, $\delta = 0.125$ [13]. It appears that as $p$ gets near 0.25, the incommensurability may lock-in.

While the phase separations of oxygen defects and structural transitions may be similar to those observed in the cuprates, it is apparent that the strong tendency toward freezing out of holes in the nickelate tends toward formation of coupled charge and spin order. In the cuprate, similar correlations may be present, but dynamical rather than static in nature. This is likely to be an important factor in rationalizing the absence of superconductivity in the nickelates at similar hole concentrations to those found in doped La$_2$CuO$_4$ superconductors.

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REFERENCES