crystals

Supplementary Materials

Oxygen Inhomogeneity and Reversibility in Single Crystal Lanio$_{3-\Delta}$

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I. Structures of Oxygen Deficient Phases

Figure S1 shows the crystal structures of $La_2Ni_2O_5$ and $La_4Ni_4O_{11}$. Octahedrally coordinated nickel cations are shown in orange, while square-planar coordinated nickel cations are shown in blue. Lanthanum cations are not depicted. The $La_2Ni_2O_5$ structure was constructed from the coordinates given in Ref. [1]. The $La_4Ni_4O_{11}$ was constructed by removing the expected pattern of oxygen anions from the $LaNiO_3$ structure. The actual octahedral rotations in $La_4Ni_4O_{11}$ are unknown, and for this reason it is labeled as "proposed." In both cases, the common motif are rows of NiO_4 square planes separated by rows of NiO_6 octahedra. The thickness of the row of octahedra is determined by the oxygen stoichiometry, with a general building rule for this homologous series $La_nNi_nO_{3n-1}$.

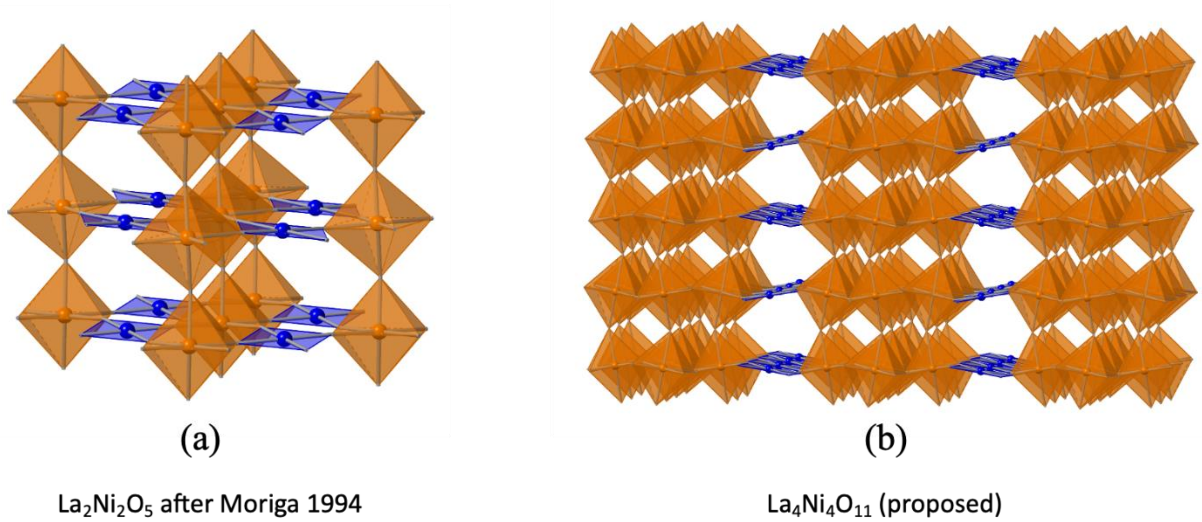

Figure 1. Crystal structures of (a) $La_2Ni_2O_5$ and (b) $La_4Ni_4O_{11}$.

II. Magnetic Susceptibility

Figure S2 shows the results of magnetometry from the pieces cut from the single crystal boule as described in the text. The measurements were taken under $\mu_0 H$=0.2 T.

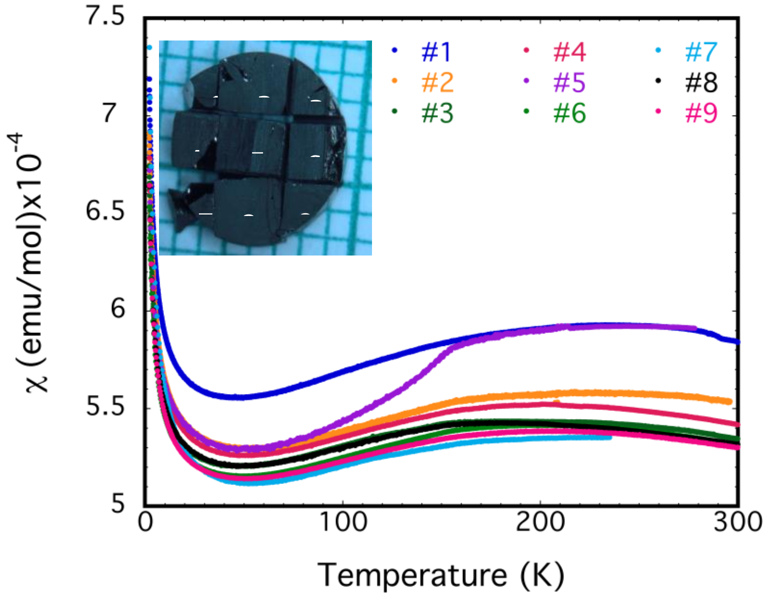

Figure 2. Magnetic susceptibility (χ) vs Temperature for samples #1 to #9.

III. Oxygen Vacancy Structures

As discussed in the main text, we find evidence in as-grown single crystals for an antiferromagnetic (AFM) phase, which is identified as $La_2Ni_2O_5$, and a second apparently nonmagnetic phase that has a 4-fold superlattice. The composition of this latter phase is not known, but evidence from the literature points to $La_4Ni_4O_{11}$ ($LaNiO_{2.75}$), which exhibits alternating stripes of octahedra and square planes in a 3:1 ratio (Hypothetically, $La_4Ni_4O_9$ is another potential phase which could have a 4-fold superlattice with rows of octahedra separated by three rows of square planes; however, there is no evidence in the literature for this highly reduced phase). Low temperature H_2-reduction of a pristine $LaNiO_3$ crystal results in a magnetic susceptibility that shows both an AFM and ferromagnetic (FM) transition at 150 K and 230 K, respectively. Diffraction from this reduced crystal also shows evidence of 4-fold superlattice. Thus, we expect this specimen to likewise have both $La_2Ni_2O_5$ (AFM) and $LaNiO_{2.75}$. Notably, Sanchez *et al.* have reported that a sample of composition $LaNiO_{2.75}$ is FM with T_C ~240 K [2]. Thus, the appearance of the FM component in our H_2-reduced crystal but not in the as-grown crystal (both of which show evidence for a 4-fold superlattice in at least some of the specimen) leads to an apparent paradox. We offer here one possible solution to this puzzle, shown schematically in Figs. S3-S4.

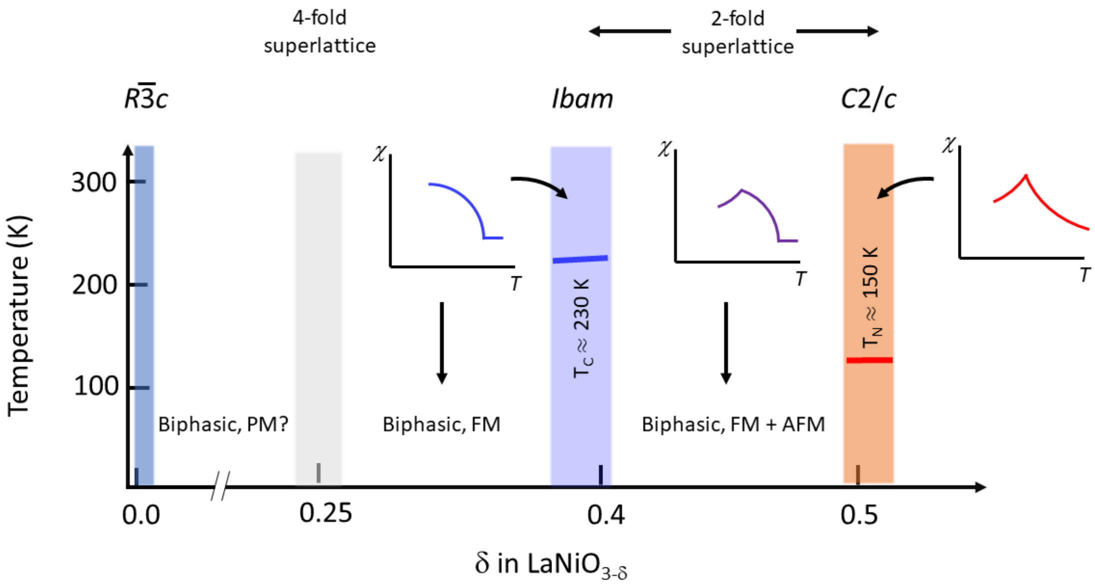

Figure 3. Proposed phase behavior of the oxygen-deficient perovskite system, $LaNiO_{3-\delta}$. Narrow homogeneity regions are denoted by colored bands. Symmetry of the phases identified at the top. Magnetic characteristics of single- and biphasic mixtures shown as insets. PM = paramagnetic, FM=ferromagnetic, AFM=antiferromagnetic. Bold lines represent T_C and T_N.

Fig. S3 schematically represents a proposed phase behavior of the $LaNiO_{3-\delta}$ system, $0 \le \delta \le 0.5$, based largely on the work of Moriga [1,3]. All of Moriga's samples, as well as that of Sanchez [2], were prepared by low temperature reduction either with H_2 mixtures or with metallic getters. We speculate that narrow homogeneity ranges or nearly line phases exist at δ=0, 0.25, and 0.5 as well as at $\delta \approx 0.4$. The δ=0.5 phase is established to be AFM with $T_N \approx 150$ K via susceptibility [1,3], and antiferromagnetic order has been observed via neutron diffraction [4]. Moriga has shown a FM (T_C = 230 K) phase which was identified as δ=0.4 [3]. We suggest that the $LaNiO_{2.75}$ phase, which will have a 4-fold superlattice, does not possess an identifiable magnetic ordering (perhaps it is paramagnetic). We base this conjecture on the absence of FM in our as-grown crystal sample #5 discussed in the main text. Moriga demonstrated that the FM δ=0.4 phase has an *Ibam* symmetry and is effectively an O interstitial phase formed by adding O randomly into the $La_2Ni_2O_5$ structure while retaining a 2-fold superlattice rather than creating a 4- or 3-fold supercell line phase (i.e., $La_3Ni_3O_8$). Despite speculation [5] for the existence of $La_3Ni_3O_8$ (δ=0.33, $LaNiO_{2.67}$) as part of the homologous series $La_nNi_nO_{3n-1}$ [6], we are unaware of any experimental evidence of $La_3Ni_3O_8$. Such a period-3 supercell has been reported for Nd and Pr [5,7].

For our H_2-reduced specimens, we see both a FM and AFM component, as well as a 4-fold superlattice. We suggest a way to understand this by asserting that we have a non-equilibrium sample with an oxygen gradient that leads to a phase mixture in which regions of the sample have δ=0.25 (nonmagnetic, 4-fold superlattice) and others have $0.4 < \delta < 0.5$ (biphasic FM and AFM, 2-fold superlattice). An alternative model in which we have a biphasic sample with δ =0.75 and δ =0.25 contradicts both Moriga's reports as well as our own data from as-grown sample #5. However, this alternative model would comport with the data of Sanchez, whose sample of composition $LaNiO_{2.75}$ is reported to be both FM and evidence a 4-fold superlattice based on electron diffraction. One possible way to reconcile our model, that of Moriga, and that of Sanchez is to speculate that Sanchez's sample, although $O_{2.75}$ on average, has some composition spread that includes regions with δ>0.25, which would be FM, while the remaining regions exhibiting the 4-fold supercell would be nonmagnetic. Even this explanation is difficult to reconcile with the observation that susceptibility of Sanchez's δ =0.25 sample [2] is larger than that of Moriga's δ =0.4 sample [3]. It is clear that further work is needed to definitively understand this complex system.

For our as-grown crystal, we would propose that the phase $LaNiO_{3-\delta}$ with δ =0.4 becomes unstable, see Fig. S3. In this case, samples with overall O content $0.25 < \delta < 0.5$ are biphasic with regions of AFM $LaNiO_{2.5}$ and the presumably nonmagnetic $LaNiO_{2.75}$, the latter accounting for the 4-fold superlattice observed in X-ray diffraction (main text, Fig. 3).

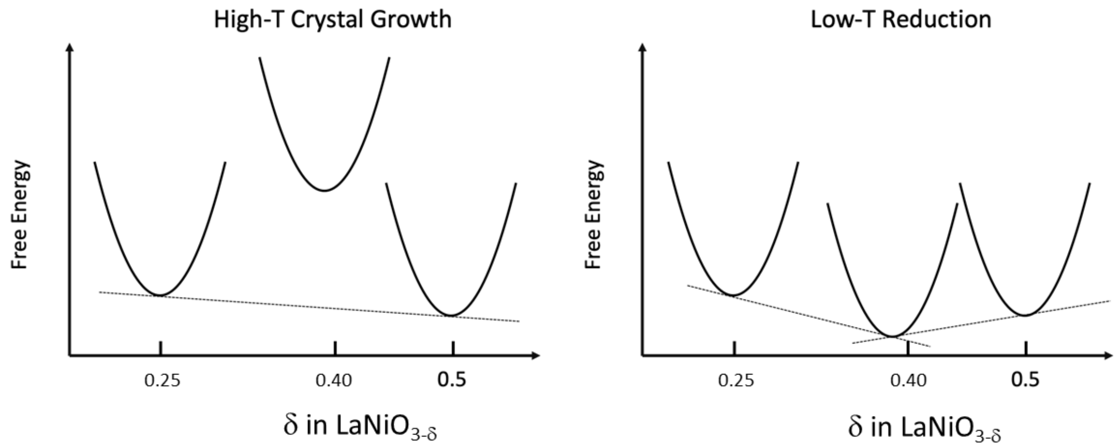

Figure 4. Schematic free energy diagrams for oxygen-deficient phases under conditions associated with high temperature crystal growth (left) and low-temperature reduction via H_2 or metallic getters (right). Dotted lines represent a Maxwell construction.

We emphasize that the explanations offered here are very much ad hoc and will require careful study of well-defined specimens to test. Nonetheless, they provide a plausible means to rationalize the data presented in the main text in a way that is consistent with the body of literature previously published on these complex phases. They also offer a framework of hypotheses to test for future studies on this system.

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