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Structural aspects of pressure-dependent hole ordering in $\text{La}_{1.67}M_{0.33}\text{NiO}_4$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$)

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A structural aspect of the hole ordering phenomenon in the $\text{La}_{2-x}M_x\text{NiO}_4$ ($x = \frac{1}{3}$, and $M = \text{Ca}, \text{Sr}, \text{or Ba}$) system has been investigated by means of x-ray diffraction experiments and measurements of the hydrostatic pressure dependence of the hole ordering temperature T_c . No significant change of the average lattice parameters was found near T_c , which is consistent with previous arguments that the origin of the ordering is electronic or magnetic in nature. The electrical resistivity conforms to variable range hopping behavior at low temperatures far below T_c and the associated thermal activation energy shows a linear pressure dependence. The highest T_c at ambient pressure was achieved with Sr doping. The pressure dependence of T_c is positive for $M = \text{Ba}$, negative for $M = \text{Ca}$, and very small and negative for $M = \text{Sr}$. The doping and pressure dependences of T_c are examined in the context of the coupling between the holes and the crystal lattice. We suggest that there is an optimum distance of 5.42 Å between the nearest-neighbor ordered holes which gives the maximum T_c .

The compounds $\text{La}_{2-x}M_x\text{NiO}_4$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$) have received considerable attention during the last few years due to their close association with the high-temperature superconducting compounds $\text{La}_{2-x}M_x\text{CuO}_4$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$).¹⁻⁴ Both La_2CuO_4 and its isostructural counterpart La_2NiO_4 belong to the class of charge-transfer insulators, characterized by an oxygen $2p$ -like valence-band and a $3d$ -like upper Hubbard conduction band.⁵ The doping of holes through the substitution of the divalent M ions, however, leads to remarkable different types of behavior in the two systems. For example, no superconductivity is found in the nickelates for any x value, while the cuprates $\text{La}_{2-x}M_x\text{CuO}_4$ exhibit superconductivity for $x \geq 0.05$. Moreover, hole doping in La_2NiO_4 leads to metallic conductivity, but much more slowly than in $\text{La}_{2-x}\text{CuO}_4$; i.e., the cuprate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is metallic for $x \geq 0.05$, while the nickelate $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ becomes metallic only around $x = 1$.⁶ This behavior is probably due to the small mobility of the charge carriers of the nickelates.⁷ It has been suggested that self-localization of holes as a result of the presence of a much stronger electron-phonon coupling in nickelates compared to the $\text{La}_{2-x}M_x\text{CuO}_4$ cuprates,^{8,9} and the large magnetic coupling between Ni and hole spins in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ reduces the metallic behavior and suppresses superconductivity. In $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($x = \frac{1}{3}$ or $\frac{1}{2}$) compounds, recent magnetic and transport anomalies around 230 K as well as electron diffraction

studies have provided evidence for the presence of two-dimensional ordered arrays of localized, doped holes at low temperatures.^{10,11}

In the nickelates, there may be two kinds of coupling mechanisms, one which generates the coupling between the holes and another which produces the coupling between the ordered holes and the crystal lattice to produce a commensurate state. The presence and strength of the latter mechanism could be determined by studying the variation of the hole ordering temperature T_c with the lattice parameters; specifically, if the ordered holes couple to the lattice, the change in the size of the lattice by varying the dopant ions (e.g., Ca, Sr, or Ba) or by applying pressure might change the distance between the ordered holes and, in turn, the strength of coupling, and hence T_c . Moreover, if the coupling mechanism between the ordered holes and the crystal lattice is strong, there should be a structural transition along with the electronic or/and magnetic transition at T_c . Hence, the present study could give further insight into the nature of this coupling mechanism.

In this paper, we determine the presence and strength of the coupling between the ordered holes and the lattice by studying the correlation between the lattice parameters and T_c through x-ray diffraction and pressure dependence of the electrical resistivity measurements on polycrystalline $\text{La}_{2-x}M_x\text{NiO}_4$ ($x = \frac{1}{3}$, $M = \text{Ca}, \text{Sr}, \text{or Ba}$) specimens. For brevity, we designate the Ca, Sr, or Ba

doped materials with $x = \frac{1}{3}$ as LCNO, LSNO, or LBNO, respectively. The basal plane a axis and the apical c axis show an almost linear dependence on the concentration x ($0 \leq x \leq 0.5$), suggesting that there are no abrupt structural changes in this concentration range. The synchrotron x-ray diffraction data show that the specimens are tetragonal and that the lattice constants a and c change smoothly with temperature T , around T_c , which suggests that the phase transition is electronic and/or magnetic, rather than structural, in origin. The electrical resistivity below T_c shows variable range hopping (VRH) behavior, not polaronic hopping conduction, suggesting that all polarons are frozen in the ordered state and do not contribute to the conduction. In addition, the pressure dependence of the thermal activation energy was determined. All of the specimens with different M show small differences in their T_c 's (~ 10 K) in spite of the high values of T_c (~ 230 K). The small variation in T_c among these compounds might be explained by structural changes only, assuming negligible material-dependent effects. Also, the applied pressure P increases T_c for LBNO and decreases T_c for LSNO and LCNO. These results suggest that there is a coupling between the ordered holes and the crystal lattice that produces a commensurate state. The strength of this coupling may be weaker than the coupling between holes. The optimal distance of 5.42 Å between the ordered holes corresponding to the maximum T_c in this system was estimated from the results of compressibility, $T_c(P)$ and $a(P)$ measurements on $\text{La}_{2-x}\text{M}_x\text{NiO}_4$ ($x = \frac{1}{3}$, $M = \text{Ca, Sr, or Ba}$).

High-quality polycrystalline $\text{La}_{2-x}\text{M}_x\text{NiO}_4$ ($0 \leq x \leq 1$, $M = \text{Ca, Sr, or Ba}$) specimens were synthesized by conventional solid-state reaction in air.¹¹ X-ray diffraction measurements were performed on all the samples. The $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($x = \frac{1}{3}$) specimen was examined at Brookhaven National Laboratory with the high-resolution synchrotron x-ray radiation diffractometer installed on beam line X-7A. The wavelength of the radiation was 1.79955 Å with a zero-point offset of $2\theta = -0.045^\circ$. A crystal analyzer was used to achieve high resolution. The typical size of the polycrystalline specimens used in the measurements under hydrostatic pressure is $3.4 \times 1.1 \times 0.9$ mm³. The pressure was applied and maintained with a Be-Cu piston-cylinder self-clamping cell with flourinert (FC 75) as the pressure transmitting fluid. The electrical resistivity was measured by a standard four-wire method.

Figure 1 contains a plot of the a and c axes vs x in the range $0 \leq x \leq 1$ determined from x-ray diffraction measurements on the $\text{La}_{2-x}\text{M}_x\text{NiO}_4$ ($M = \text{Ca, Sr, or Ba}$) samples. For all of the samples, the a axis decreases linearly as x increases up to 0.5. The c axis increases for $M = \text{Ba and Sr}$, and decreases for Ca with increasing x up to $x = 0.5$. The monotonic change of the a and c axes up to $x = 0.5$ suggests that there is no phase separation within this concentration range.

The a axis of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ develops a minimum at $x \approx 0.5$ and increases at higher x values, while the c axis shows a maximum at $x \approx 0.5$ and decreases with further increase in x . If we regard any compound with $0 < x < 1$

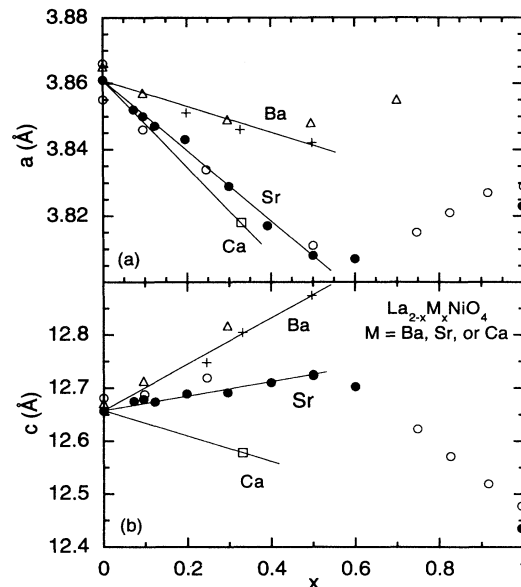


FIG. 1. a and c lattice parameters vs concentration x for $\text{La}_{2-x}\text{M}_x\text{NiO}_4$ ($M = \text{Ca, Sr, or Ba}$) in the range $0 \leq x \leq 1$. For $M = \text{Ba}$, the crosses are from the present work and the open triangles are from Ref. 12; for $M = \text{Sr}$, the open circles are from Ref. 6 and the solid circles from Ref. 10; for Ca the square is from the present work.

as an alloy of La_2NiO_4 and LaSrNiO_4 , then its lattice parameters do not follow Vegard's rule.^{13,14} It is not yet clear why the lattice parameters exhibit such a marked change around $x \approx 0.5$. The linear increase of the c axis for $x < 0.5$ might be due to the fact that the ionic size of Sr^{2+} is slightly larger than that of La^{3+} .¹⁵ We consider the deviation from Vegard's rule for $x > 0.5$ to be related to the appearance of the metallic behavior.¹⁰ Roughly speaking, the behavior of these nickelates at $x \approx 0.5$ is similar to that of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at $x \approx 0.15$ in the sense that both systems deviate from Vegard's rule and charge delocalization starts to develop.^{10,14}

Synchrotron x-ray diffraction measurements show that the space group for the Sr-doped La_2NiO_4 is tetragonal $I4/mmm$. Figure 2 shows the temperature T dependence of the a and c axes of LSNO derived from synchrotron x-ray diffraction measurements. As T decreases from room temperature down to 150 K, both the a and c axes decrease with a slight curvature and without any noticeable change near T_c . Therefore, we conclude that the hole ordering phenomenon is not accompanied by any simple structural phase transition. The slopes of the lattice parameters near T_c are given by $da/dT = 3.20 \times 10^{-5}$ Å/K and $dc/dT = 2.11 \times 10^{-5}$ Å/K.

Figure 3 contains a semilog plot of the electrical resistance R , normalized to the room temperature value, vs T for polycrystalline $\text{La}_{2-x}\text{M}_x\text{NiO}_4$ ($x = \frac{1}{3}$, $M = \text{Ca, Sr, or Ba}$). All of the compounds exhibit a semiconductinglike behavior of $R(T)$ for $100 \text{ K} \leq T \leq 300 \text{ K}$. The sudden increase of the normalized resistance of each compound

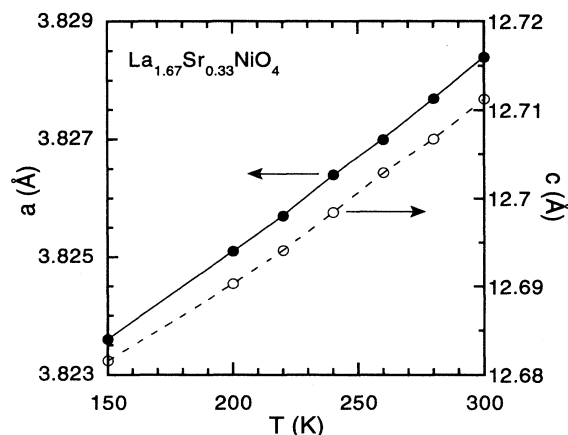


FIG. 2. a and c lattice parameters vs temperature T for $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$.

around 230 K has been attributed to a condensation of the conduction holes into an ordered polaronic state (see the discussion of Fig. 4 and Ref. 11). The hole ordering temperature T_c is determined as the temperature where a minimum in $d \ln R(T)/dT$ occurs. The values of T_c are 224.3, 236.7, and 224.9 K for LCNO, LSNO, and LBNO, respectively.

To determine the low-temperature conduction mechanism, we fitted the $R(T)$ data to different conduction models including polaronic conduction. The best fit comes from VRH conduction.¹⁶ Displayed in Fig. 4 is a semilog plot of the electrical resistivity ρ vs $T^{-1/4}$ of polycrystalline LCNO, LSNO, and LBNO. The thin solid lines are linear fits of the data to the three-dimensional (3D) VRH expression $\rho(T) = \rho_0 \exp(U/k_B T)^{1/4}$, where ρ_0 and U are fitting parameters. The parameter U is proportional to $1/[g(E_F)V]$, where $g(E_F)$ is the density of states at the Fermi energy E_F and V is the localization volume. The sudden increase of the electrical resistivity

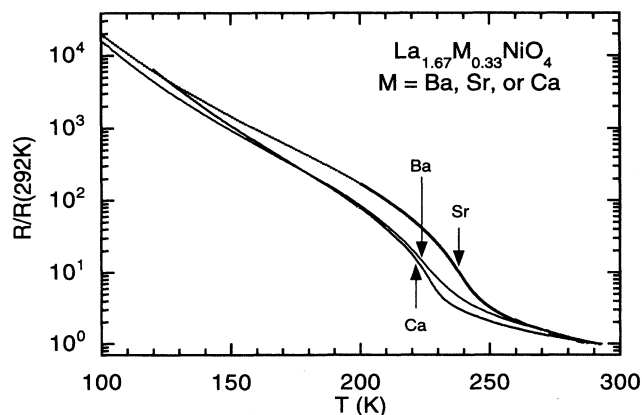


FIG. 3. Electrical resistance R normalized by the room temperature value $R(292 \text{ K})$ vs temperature T , plotted on a semilog scale, for $\text{La}_{1.67}\text{M}_{0.33}\text{NiO}_4$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$).

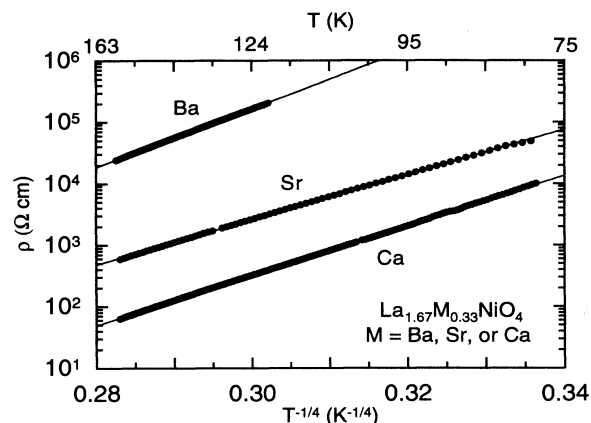


FIG. 4. Electrical resistivity ρ vs $T^{-1/4}$, plotted on a semilog scale, for $\text{La}_{1.67}\text{M}_{0.33}\text{NiO}_4$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$). The corresponding temperature values are shown on the upper abscissa. The thin solid lines are fits of the data to $\rho(T) = \rho_0 \exp(U/k_B T)^{1/4}$ with ρ_0 and U as fitting parameters.

at T_c and the presence of the VRH behavior far below T_c show that the holes in the polaronic states do not contribute to the conduction because they are frozen in the ordered state below T_c . The reason why these materials show VRH behavior is not yet clear. Electron diffraction experiments showed polaron-ordered regions with the in-plane dimension of $\sim 500 \text{ \AA}$.¹⁰ Therefore, the charge carriers outside the ordered states could carry current by thermally activated hopping through the percolating path between the ordered domains.

The parameter U changes with pressure and with divalent ion doping. A fit of the resistivity to the three-dimensional VRH expression yields $U = 7.89 - 6.3 \times 10^{-2}P$ for $M = \text{Ca}$, $U = 7.28 - 8.9 \times 10^{-3}P$ for $M = \text{Sr}$, and $U = 10.9 - 4.4 \times 10^{-2}P$ for $M = \text{Ba}$, where U is given in meV and P in kbar. We found that there is a correlation between T_c and the pressure dependence of the parameter U ; namely, the value of the slope of U in pressure is the smallest for LSNO which has the highest T_c .

Figure 5 contains a plot of the electrical resistivity ρ vs T near T_c for LBNO measured at different hydrostatic pressures. The resistivity shows a very small pressure dependence above T_c , suggesting that the applied pressure does not change appreciably the electronic state of this compound. The other two compounds studied (LCNO and LSNO) show a similar small pressure dependence. Near T_c , the $\rho(T)$ curve exhibits an almost parallel shift to higher temperatures as the pressure increases. This suggests that pressure does not alter much the nature of the transition, but enhances the strength of the coupling between the ordered holes below T_c . For the other two compounds (LCNO and LSNO), we observed a decrease of T_c with increasing pressure.

Figure 6 contains a plot of the pressure dependence of T_c for the three compounds studied. The compound LSNO has the highest T_c of 236.7 K at ambient pressure and a very small negative pressure dependence of T_c .

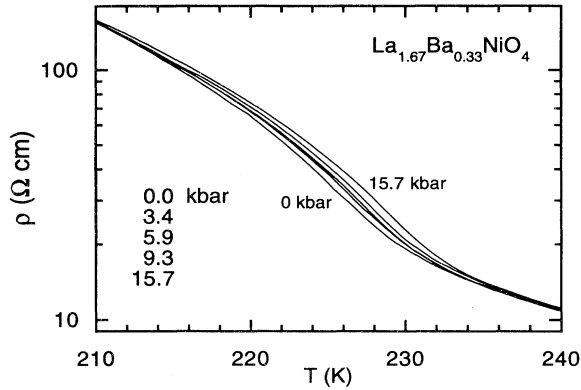


FIG. 5. Electrical resistivity ρ vs temperature T data, plotted on a semilog scale, measured at several pressures between 0 and 15.7 kbar for $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$.

The ambient pressure T_c of LCNO is 224.3 K, a rather low value compared with that of LSNO, and T_c decreases in a parabolic way as the pressure increases. The best fit gives $T_c = 224.3 - 0.248P + 0.0059P^2$, where T_c is given in K and P in kbar. The ambient pressure T_c of LBNO is 224.9 K, a value comparable to that of LCNO; however, it displays a parabolic increase of T_c with increasing pressure given by $T_c = 224.9 + 0.395P - 0.0089P^2$, where T_c is given in K and P in kbar. This is the largest change of T_c with pressure of these three materials.

We have attempted to establish a correlation between the ambient pressure T_c , the pressure dependence of T_c , and the lattice parameters for each sample. The different values of the ambient pressure T_c obtained for the samples studied could be a result of the different values of the ionic size of the divalent dopants that change the lattice parameters. One could test this hypothesis by studying the pressure dependence of T_c , because the applied pressure induces small changes in the a and c axes. The lattice parameter a , rather than c , is associated with the distance between the ordered holes and, hence, the strength

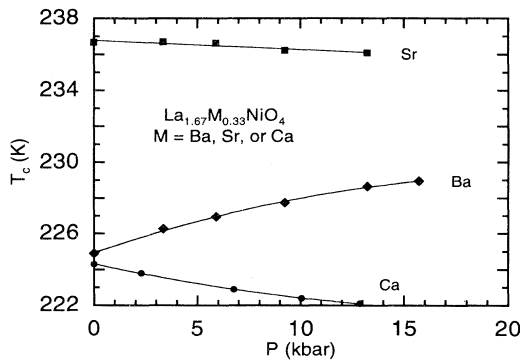


FIG. 6. The hole ordering temperature T_c vs applied pressure P for $\text{La}_{1.67}\text{M}_{0.33}\text{NiO}_4$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$). The solid lines represent parabolic fits of the data for $M = \text{Ba}$ and Ca and a linear fit of the data for $M = \text{Sr}$.

of the coupling (T_c) because (i) the ordered holes form a two-dimensional commensurate superlattice in the ab plane and (ii) the charge ordered region shows a large anisotropy between the a and c directions (~ 500 and ~ 60 Å, respectively) due to hole segregation, as evidenced by the electron diffraction measurements.¹⁰ The pressure dependence of T_c is positive in LBNO (the largest a axis), small and slightly negative in LSNO (the a -axis value is intermediate between those of LBNO and LCNO, and the highest ambient pressure T_c), and negative in LCNO (the smallest a axis). Hence, these results suggest that there is an optimum lattice parameter a_{op} which corresponds to a maximum T_c . Because LBNO has the largest a axis (3.849 Å) and the applied pressure compresses the a axis and increases T_c , one can determine a_{op} by extrapolating the parabolic $T_c(P)$ function to obtain the maximum value of T_c , $T_{c,\text{max}}$, and by attributing its corresponding lattice parameter to a_{op} . The fitting function $T_c(P) = 224.9 + 0.395P - 0.0089P^2$, where T_c is given in K and P in kbar, gives $T_{c,\text{max}} = 229.3$ K and the corresponding pressure $P_{\text{max}} = 22.3$ kbar. Using the compressibility data,¹⁷ P_{max} can be converted to a lattice parameter change, $\Delta a_{\text{max}} = -0.019$ Å and, hence, $a_{\text{op}} = 3.830$ Å. Note that the lattice parameter a_{op} is just slightly larger than the value for LSNO of $a = 3.827$ Å. The fact that the value of the a axis of LSNO is very close to the value of a_{op} is consistent with the pressure dependence of a LSNO having the highest T_c at ambient pressure and the smallest and negative pressure dependence of T_c . Based on the superlattice pattern of ordered holes obtained from electron diffraction measurements,¹⁰ the optimum distance between nearest-neighbor holes, d_{op} , which gives the highest T_c is given by $d_{\text{op}} = \sqrt{2}a_{\text{op}} = 5.416$ Å.

We note that there is a $\sim 3\%$ difference between $T_{c,\text{max}} = 229.3$ K of LBNO and the ambient pressure $T_c = 236.7$ K of LSNO. If T_c is determined only by the structure without any other material dependences, $T_{c,\text{max}}$ of LBNO and the T_c of LSNO should be very close because a of LSNO is very close to a_{op} . This difference could be a result of the assumption of the present calculation that T_c is determined only by the structure and not, for example, by the material dependence of the strength of the electron-phonon coupling and electronic states of the NiO_2 plane. The direction of the present work has been focused on finding d_{op} , and not on the maximum T_c for this nickelate system. Our analysis of d_{op} can be improved by replacing the compressibility data from $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.15$) with that from each of the nickelates at T_c . Pressure-dependent structural data for the nickelates are highly desirable and will be very useful for understanding the complex structural transitions in this system.

In summary, we have performed conventional and synchrotron x-ray diffraction experiments, as well as measurements of the pressure dependence of the electrical resistivity, on the $\text{La}_{2-x}\text{M}_x\text{NiO}_4$ ($x = \frac{1}{3}$, $M = \text{Ca}, \text{Sr}, \text{or Ba}$) system. The conventional and synchrotron x-ray diffraction experiments showed that the hole ordering phenomenon is not a simple structural phase transition.

The electrical resistivity data show semiconductinglike behavior and a sudden increase at T_c . We found that the conduction mechanism far below T_c is governed by VRH. The sudden increase of the electrical resistivity at T_c and the presence of the VRH conduction below T_c indicate that the ordered holes in the polaronic state do not contribute to the conduction. For all of the specimens studied, the thermal activation energy of the localized states decreases with increasing pressure. Of the three compounds, LSNO has the highest ambient T_c , while LCNO and LBNO have comparable values of the ambient T_c . Applied pressure increases T_c for LBNO and decreases T_c for LSNO and LCNO. The T_c of LSNO shows a very small pressure dependence. By combining

lattice parameters, compressibility, T_c 's, and pressure effects of the specimens, we have extracted the optimum distance between the nearest-neighbor ordered holes that gives the maximum T_c in this nickelate system. We hope our structural analyses help to elucidate on the nature of hole ordering in nickelate systems.

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¹⁶The fits of the resistivity to $\rho(T) = \rho_0 \exp(U/k_B T)^{1/3}$ (2D VRH) and $\rho(T) = \rho_0 \exp(U/k_B T)^{1/4}$ (3D VRH) are equally good. A similar situation can be found in the cuprates; e.g. $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. In this paper, we do not attribute any significance to the dimensionality of variable range hopping conduction.

¹⁷Since the compressibility of $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ was not available, we used the compressibility of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ with $da/dP = -8.6844 \times 10^{-4} \text{ \AA/kbar}$ from Shiyu Pei, J. D. Jorgensen, D. G. Hinks, B. Dabrowski, P. Lightfoot, and D. R. Richards, Physica C **169**, 179 (1990).