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Permalink
https://escholarship.org/uc/item/2794v4k6

Journal
Physical Review B, 52(2)

ISSN
0163-1829

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Publication Date
1995

DOI
10.1103/PhysRevB.52.1347

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Peer reviewed
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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(Received 21 February 1995)

A structural aspect of the hole ordering phenomenon in the $\text{La}_{2-x}M_x\text{NiO}_4$ ($x = \frac{1}{4}$, 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 $\text{La}_{2-x}M_x\text{CuO}_4$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$). Both $\text{La}_2\text{CuO}_4$ and its isostructural counterpart $\text{La}_2\text{NiO}_4$ belong to the class of charge-transfer insulators, characterized by an oxygen 2p-like valence-band and a 3d-like upper Hubbard conduction band. 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 $\text{La}_2\text{NiO}_4$ 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. 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 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 $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($x = \frac{1}{4}$ or $\frac{1}{4}$) 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.

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/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 $\text{La}_{2-x}M_x\text{NiO}_4$ ($x = \frac{1}{4}$, $M = \text{Ca}, \text{Sr}, \text{or Ba}$) specimens. For brevity, we designate the Ca, Sr, or Ba...
doped materials with \( x = \frac{1}{2} \) 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 polaronic 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 (\( \sim 10 \text{ K} \)) in spite of the high values of \( T_c \) (\( \sim 230 \text{ K} \)). 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 \( \text{Å} \) 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 \( \text{La}_{2-x}M_x\text{NiO}_4 \) (\( x = \frac{1}{2} \), \( M = \text{Ca, Sr, or Ba} \)).

High-quality polycrystalline \( \text{La}_{2-x}M_x\text{NiO}_4 \) (\( 0 \leq x \leq 1 \), \( M = \text{Ca, Sr, or Ba} \)) specimens were synthesized by conventional solid-state reaction in air.\(^{11}\) X-ray diffraction measurements were performed on all the samples. The \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) \( (x = \frac{1}{2}) \) 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 \( \text{Å} \) 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 mm\(^3\). The pressure was applied and maintained with a Be-Cu piston-cylinder self-clamping cell with fluorinert (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 \( \text{La}_{2-x}M_x\text{NiO}_4 \) \( (M = \text{Ca, Sr, or Ba}) \) 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 \( x \). If we regard any compound with \( 0 < x < 1 \) as an alloy of \( \text{La}_2\text{NiO}_4 \) and \( \text{LaSrNiO}_4 \), then its lattice parameters do not follow Vegard's rule.\(^{12,13}\) 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 \( \text{Sr}^{2+} \) is slightly larger than that of \( \text{La}^{3+} \).\(^{14,15}\) 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 change delocalization starts to develop.\(^{10,14}\)

Synchrotron x-ray diffraction measurements show that the space group for the Sr-doped \( \text{La}_2\text{NiO}_4 \) 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 \( da/dT = 3.20 \times 10^{-5} \text{Å/K} \) and \( dc/dT = 2.11 \times 10^{-5} \text{Å/K} \).

Figure 3 contains a semilog plot of the electrical resistance \( R \), normalized to the room temperature value, vs \( T \) for polycrystalline \( \text{La}_{2-x}M_x\text{NiO}_4 \) \( (x = \frac{1}{2}, M = \text{Ca, Sr, or Ba}) \). All of the compounds exhibit a semiconductinglike behavior of \( R (T) \) for 100 K \( \leq T \leq 300 \text{ K} \). The sudden increase of the normalized resistance of each compound.
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. Displayed in Fig. 4 is a semilog plot of the electrical resistivity \( \rho \) 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 \( \rho_0 \) 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 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 diffusion experiments showed polaron-ordered regions with the in-plane dimension of \( \sim 500 \) Å. 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 \( U = 7.89 - 6.3 \times 10^{-3} P \) for \( M = \text{Ca} \), \( U = 7.28 - 8.9 \times 10^{-3} P \) for \( M = \text{Sr} \), and \( U = 10.9 - 4.4 \times 10^{-3} P \) 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 \( \rho \) 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 \( T_c \).
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 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 ($\sim 500$ and $\sim 60$ Å, respectively) due to hole segregation, as evidenced by the electron diffraction measurements. The pressure dependence of $T_c$, positive in LBNO (the largest $a$ axis), small and slightly negative in LSNO ($a$-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 $T_c$, $T_{c,max}$ 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 $T_{c,max} = 229.3$ K and the corresponding pressure $P_{max} = 22.3$ kbar. Using the compressibility data, $P_{max}$ can be converted to a lattice parameter change, $\Delta a_{max} = -0.019$ Å and, hence, $a_{op} = 3.830$ 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, the optimum distance between nearest-neighbor holes, $d_{op}$, which gives the highest $T_c$ is given by $d_{op} = \sqrt{2a_{op}} = 5.416$ Å.

We note that there is a $\sim 3\%$ difference between $T_{c,max} = 229.3$ 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, $T_{c,max}$ 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 La$_{2-x}$Sr$_x$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 La$_{2-x}$M$_x$NiO$_4$ ($x = \frac{1}{2}$, $M$ = Ca, Sr, 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 semiconducting-like 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.

We would like to acknowledge helpful discussions with C. C. Almasan. The research at U.C.S.D. was supported by the U.S. Department of Energy under Grant No. DE-FG03-86ER-45230. S.H.H. was also supported by LANL/INCOR Grant No. UC-91-6A-110. The research at LANL was supported under the auspices of the U.S. Department of Energy.

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25The 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. PrBa$_2$CuO$_{4-\delta}$. In this paper, we do not attribute any significance to the dimensionality of variable range hopping conduction.
26Since the compressibility of La$_{1.6}$Sr$_{0.3}$NiO$_4$ was not available, we used the compressibility of La$_{1.45}$Sr$_{0.15}$CuO$_4$ with $da/dP = -8.6844 \times 10^{-4}$ Å/kbar from Shiyou Pei, J. D. Jorgensen, D. G. Hinks, B. Dabrowski, P. Lightfoot, and D. R. Richards, Physica C 169, 179 (1990).