

Low-Temperature Electron Transport Properties of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ with $0.5 \leq x \leq 1.3$

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IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

Electrical resistivity (ρ) measurements have been carried out on the quasi-two-dimensional oxide $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($0.5 \leq x \leq 1.3$) in the temperature (T) range 4.3–300 K. A progressive decrease in resistivity and a change from semiconducting- to metallic-type behavior is observed with increasing Sr content. The $\rho(T)$ data of samples in the composition range $0.5 \leq x \leq 0.9$ closely follow the Mott variable-range-hopping-type model, whereas samples with $x > 1.0$ show correlated metallic-type conduction, with a weak upturn in $\rho(T)$ at low temperatures. This resistivity upturn follows a $T^{1/2}$ dependence below ~ 25 K, indicative of electron–electron interaction in a disordered, poorly conducting metallic phase. In the overdoped ($x > 1.0$) samples a progressive decrease in this upturn indicates a reduction in the electron–electron interaction strength with increasing Sr (hole) content. © 1994 Academic Press, Inc.

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INTRODUCTION

Electronic properties of oxide systems showing insulator-to-metal (I-M) transition as a function of carrier doping continue to be of considerable current interest (1). In this connection, the structure and electron transport properties as a function of Sr doping in quasi-two-dimensional $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ have been investigated by several groups (2–10). Although this system is structurally analogous to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, its electronic transport properties are markedly different from those of the Cu analogue. One important distinction is that the doped cuprate becomes metallic and superconducting in the range $0.06 < x < 0.30$, whereas no bulk superconductivity has been observed for the nickelate. Instead, the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system exhibits semiconducting $\rho(T)$ behavior in this composition range. Also, compared to the Cu analogue, a considerably higher Sr concentration is required to attain metallic properties in the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system (5–11). A changeover from semiconducting- to metallic-type conduction occurs in the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system in the range $x = 0.9$ to $x = 1.0$. In all prior studies a weak resistivity

upturn was encountered at low temperatures for the barely metallic samples with $x \approx 1.0$. This upturn has been linked to a metal-insulator transition by Takeda *et al.* (4).

Our primary motivation for the present study was to understand the low-temperature electron transport properties of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system. We wish to establish the nature of the upturn in resistivity with decreasing temperature and to clear up some reported discrepancies concerning whether strontium nickelate samples with x close to 1.0 are metallic or insulating. Toward this end we have studied the Sr composition range $0.5 \leq x \leq 1.3$. The low-temperature electron transport properties $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ with $0.5 < x < 0.9$ are consistent with nonmetallic properties for which the resistivity closely follows the Mott variable-range-hopping (VHR) law, whereas samples in the range $1.0 < x < 1.3$ are poor metallic conductors. We will also show that the weak resistivity upturn observed at low temperatures for the metallic samples likely arises from the combined effects of strong electron–electron interactions in correlated metals with weak disorder.

EXPERIMENTAL

$\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ samples were prepared by dissolving stoichiometric amounts of La_2O_3 , SrCO_3 , and NiO in nitric acid and decomposing the nitrate mixture. The initial decomposition was carried out at 850°C in air. The products were then pressed into pellets after regrinding and annealed in flowing oxygen at 950 – 1000°C . The process was repeated several times until X-ray pure single-phase material with K_2NiF_4 -type structure was obtained. Powder X-ray diffraction patterns were recorded by a SIEMENS D-500 diffractometer using $\text{CuK}\alpha$ radiation. Oxygen stoichiometry was determined by iodometric titration. Electrical resistivity was measured on sintered pellets by the standard four-probe technique in the range 4.2–300 K.

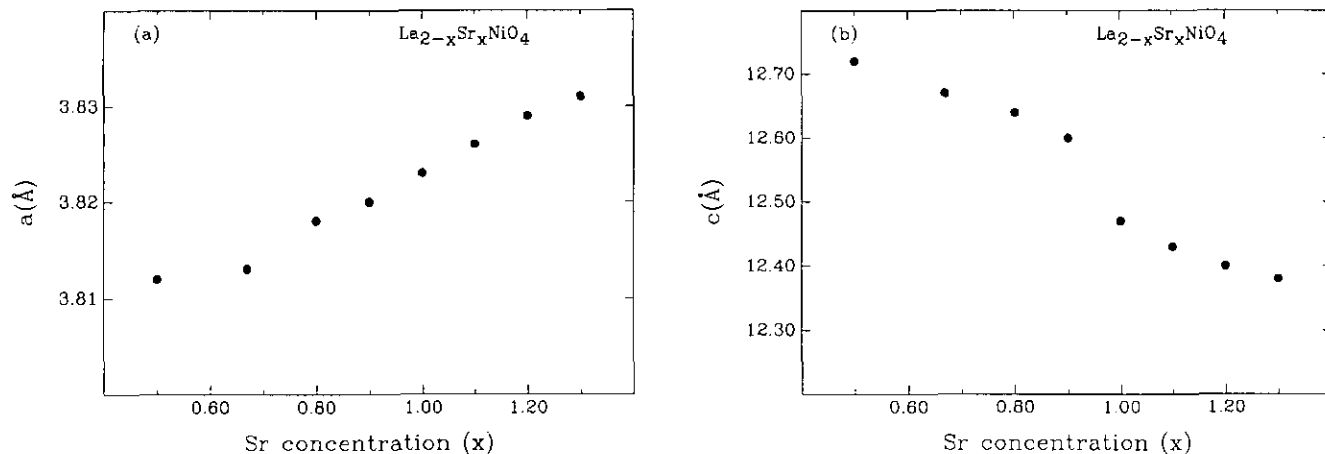


FIG. 1. Variation of (a) a - and (b) c -lattice parameters as a function of Sr content for the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($0.50 \leq x \leq 1.3$) system.

RESULTS AND DISCUSSION

Samples of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ in the composition range $0.5 \leq x \leq 1.3$ crystallize in the tetragonal K_2NiF_4 -type structure. Figure 1 shows the changes in the a - and c -lattice parameters at room temperature as a function of Sr content (x). With increasing x the a -lattice parameter increases slightly, whereas the c -lattice parameter diminishes. These variations are within the range of lattice parameter values reported earlier (4–7). However, there are significant differences both in the values and in the trends of the parameters as reported by different investigators. Presumably, these variations reflect differences in the oxygen stoichiometry and/or inhomogeneity in the Sr distribution of samples prepared by a variety of techniques: X-ray diffraction peaks (especially the $00l$ reflec-

tions) show considerable broadening for the samples with a high Sr content.

Figure 2 shows the temperature-dependent electrical resistivity of samples in the composition range $0.50 < x < 0.90$; these exhibit semiconducting properties. These data follow reasonably well a Mott VRH type conduction law in three dimensions, given by $\rho = \rho_0 \exp(T_0/T)^{1/4}$, as shown in Fig. 3. Similar resistivity characteristics have been reported by other groups (8–10). The characteristic temperature T_0 decreases from -2.3×10^7 to $\sim 2.1 \times 10^3$ K as the Sr content (x) increases from 0.5 to 0.9; this is consistent with the observed decrease in the resistivity. However, for the $x = 0.80$ and 0.90 compositions, which approach nearly metallic characteristics, increasing deviations from the Mott VRH law are observed below ~ 50 K.

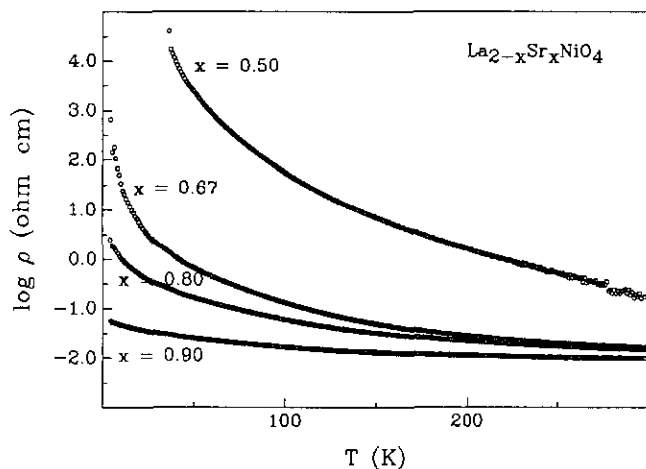


FIG. 2. Temperature-dependent electrical resistivities of various $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compositions with $0.5 \leq x \leq 0.9$.

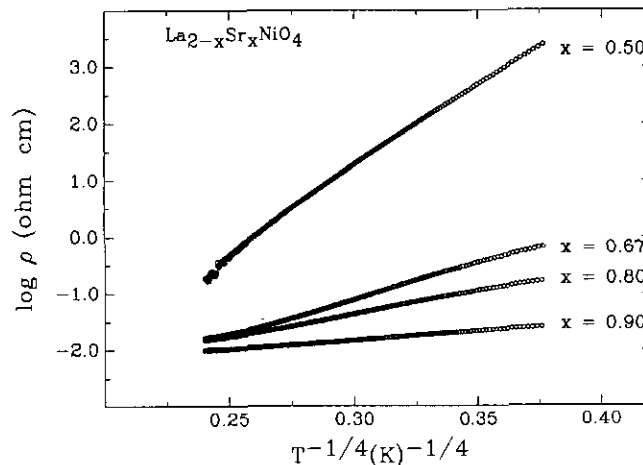


FIG. 3. Plot of $\log \rho$ vs $T^{1/4}$ for various $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compositions in the range $0.5 \leq x \leq 0.9$.

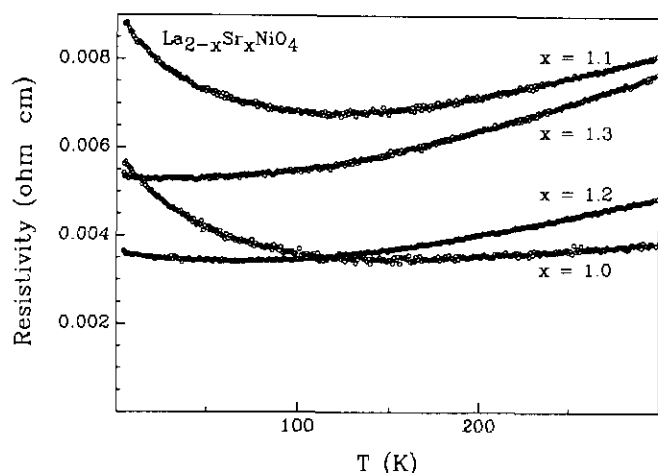


FIG. 4. Temperature-dependent resistivities of various $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compositions in the range $1.0 \leq x \leq 1.3$.

The $\rho(T)$ data of the $1.0 \leq x \leq 1.3$ composition range are shown in Fig. 4, and a normalized set of curves is shown in Fig. 5. The $x = 1.0$ sample exhibits a nearly T -independent resistivity at high temperatures ($T > 100$ K), but below ~ 100 K a significant rise in $\rho(T)$ is encountered. This upturn becomes progressively smaller with increasing Sr content. The resistivities shown in Fig. 4 fall in the range 3.5×10^{-3} to 10^{-2} ohm cm, which is larger by roughly three orders of magnitude than the resistivities encountered in conventional metals. The $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system thus displays correlated electron properties for $x \geq 1$. One should note the smooth progression as one passes from the semiconducting (Fig. 2) to the barely metallic (Fig. 4) regime. The $\rho(T)$ data follow a $T^{1/2}$ dependence below 25 K, as documented in Fig. 6. Such a feature is generally encountered in systems where strong

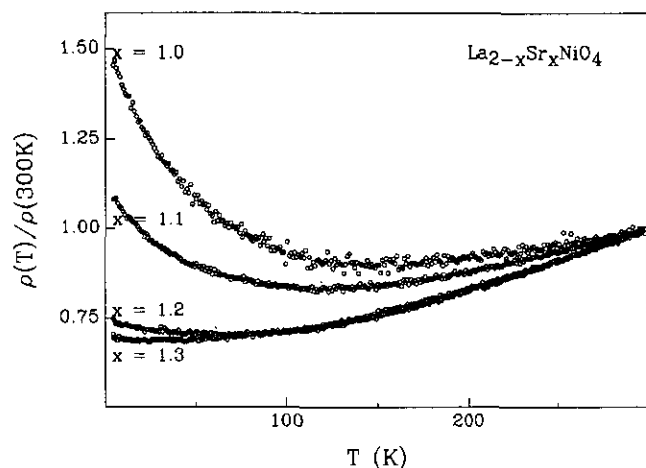


FIG. 5. Plot of normalized resistivities vs temperature for various $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ samples in the composition range $1.0 \leq x \leq 1.3$.

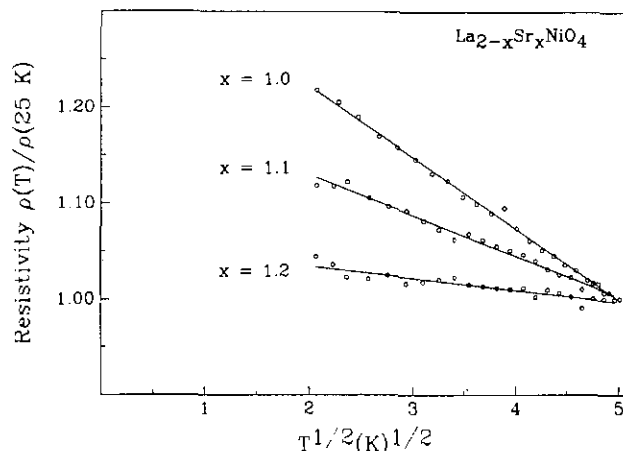


FIG. 6. Plot of normalized resistivity $\rho(T)/\rho(25 \text{ K})$ vs $T^{1/2}$ for various $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compositions in the range $1.0 \leq x \leq 1.3$.

electron–electron interactions occur in the presence of disorder in a diffusive metallic phase (11). Figure 6 also demonstrates a significant decrease in the contribution of the $T^{1/2}$ term with increasing Sr (hole) content.

One possible explanation of the above trend is as follows: At the stoichiometric $x = 1$ composition (LaSrNiO_4) Ni is in the formal $3+$ valence state with the $3d^7$ electronic configuration. Hence, the e_g band, which may be split into two Hubbard subbands, contains one electron/Ni site. The electron-hopping process between different Ni sites in this case generates doubly occupied as well as unoccupied sites with corresponding configurations in the e_g band. The double occupancies lead to strong $e-e$ interaction effects in the split-band interactions. However, when the formal valence state of Ni exceeds 3, the density of electrons in the e_g band is decreased, thereby largely obviating the need for doubly occupied configurations. This decreases the degree of $e-e$ interactions, thereby producing a concomitant decrease in the resistivity upturn at low temperatures. In this overdoped ($x > 1.0$) regime the formal valence state of Ni in excess of 3 is accompanied by a change in color from black to brown.

From iodometric titration of the $x = 1.0, 1.1, 1.2,$ and 1.3 samples we obtain an average valence state of Ni close to 2.94, 3.02, 3.10, and 3.20, respectively. This corresponds to an increasing oxygen deficiency such that the oxygen content decreases from 3.97 to 3.95 with increasing Sr content. These values are slightly lower relative to the ideal composition for which the oxygen content is 4.00. The increasing Sr content thus gives rise to an increase the density of holes, although to a lower than expected degree. The data also suggest that the reduction in $e-e$ interaction with increasing hole content in this composition range outweighs the disorder effects arising from

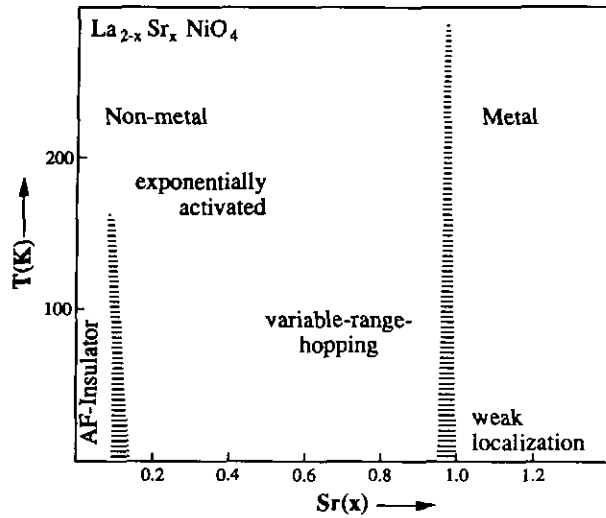


FIG. 7. Schematic diagram describing the changes in the electronic transport properties as a function of Sr doping in the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system.

oxygen deficiency in determining the low-temperature transport properties of the system.

A schematic diagram showing the changes in the electronic transport properties of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system as a function of Sr doping is shown in Fig. 7. The parent $x = 0$ composition is an antiferromagnetic (AF) insulator with an exponentially activated type conduction at low temperatures (12). Doping of Sr introduces holes in the NiO_2 plane which destroy the long-range AF ordering and also decrease the resistivity. However, the system remains nonmetallic and strongly localized up to $x \approx 0.90$. When $x \geq 1.0$ the system shows metallic-type conduction with strong $e-e$ correlations.

Both $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are AF insulators for $x = 0$; their Néel temperatures T_N exceed 300 K (13, 14). With increasing Sr (hole) content the cuprate changes from an AF insulator to a superconductor and then to a normal metallic phase with increasing x in the range 0 to 0.30 (15). The nickelate switches from the AF insulator to a correlated metallic phase at sufficiently high doping levels ($x \approx 1.0$), with no intervening superconducting phase. These differences have been rationalized (6) in terms of an increase in charge-transfer energy in the nickelate as compared to the cuprate; this would also account for the relatively large Sr concentration required to cross into the metallic $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ phase. However, the absence of bulk high- T_c superconductivity in the hole-doped metallic $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system is not understood. However, with Sr (hole) doping the changes in the electronic configurations of the transition metal involved in the two cases are different, viz. $3d^9/3d^8$ in the cuprate and $3d^8/3d^7/3d^6$ in the nickelate systems.

In conclusion, low-temperature electrical resistivity measurements have been carried out on the quasi-two-dimensional $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system in the composition range $0.5 < x < 1.3$. A progressive decrease in the electrical resistivity and a change from semiconducting- to correlated metallic-type behavior is observed with increasing Sr (hole) content. We have shown that the samples in the composition range $0.5 \leq x \leq 0.9$ are nonmetallic and closely follow Mott VRH-type conduction, whereas samples in the range $1.0 \leq x \leq 1.3$ are barely metallic. We have also shown that a weak resistivity upturn at low temperatures closely follows a $T^{1/2}$ dependence below ~ 25 K, suggesting $e-e$ interactions in the presence of disorder. Further, in the overdoped regime ($x > 1.0$) evidence for a reduction in the strength of $e-e$ interaction with increasing Sr (hole) content is found as the system enters further into the correlated metallic phase.

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