

Magnetic and electrical properties of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4\pm\delta}$

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(Received 17 August 1990)

The magnetic properties and resistivities of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ solid solution have been investigated with particular emphasis on conductive materials near LaSrNiO_4 . Near that composition, weakly temperature-dependent magnetic susceptibilities, and resistivities, similar in magnitude to those in the isostructural metallic $(\text{La,Sr})_2\text{CuO}_4$ compounds, are found. No superconductivity was found for the highly conductive compositions down to temperatures as low as 30 mK.

Superconductivity in the $(\text{La,Sr})_2\text{CuO}_4$ solid solution with the K_2NiF_4 structure type has been studied extensively in recent years. In particular, the evolution of the system from antiferromagnetism to superconductivity is at the center of the debate on the nature of the microscopic pairing mechanism responsible for high- T_c superconductivity. Studies of the analogous $(\text{La,Sr})_2\text{NiO}_4$ solid solution have been reported by many groups before the advent of the high- T_c copper oxides,¹⁻⁵ and also since then.⁶ The similarity in the energies of the Ni and Cu 3*d* states, the well-known ability of Ni to occur in a low-spin state in oxides, and the observation that both Ni and Cu display Jahn-Teller distortions, suggests that the comparison of the Cu- and Ni-based compounds of the K_2NiF_4 type is of considerable interest.

In agreement with the earlier work, the substitution of Sr for La in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ is found to lead to metallic conductivity, but more slowly than in the cuprate. Significantly more Sr substitution is necessary to induce metallic-type conductivities: the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ solid solution is conductive to low temperatures near $x=1$. The variation of crystallographic cell parameters with Sr content is shown to be similar to that of the cuprate for low doping levels, and, further, indicates a redistribution of charge between the d_{z^2} and $d_{x^2-y^2}$ Ni orbitals at high Sr contents, as has been reported earlier.⁶ In the high-conductivity regime, the lattice parameters suggest that the Ni-O octahedra are nearly equiaxial, in contrast to the superconducting Cu oxides, where there is a Jahn-Teller distortion. The conductive $(\text{La,Sr})_2\text{NiO}_4$ compounds are not superconducting down to temperatures as low as 30 mK. In the same composition regime, it is found that the magnetic susceptibility is paramagnetic and featureless, and similar in magnitude to what is observed in the superconducting cuprates.

Polycrystalline materials were prepared from stoichiometric mixtures of dried La_2O_3 , SrCO_3 , and NiO. Powders were thoroughly mixed, placed in dense Al_2O_3 crucibles, and calcined at 1100°C in air; there were daily grindings for 1 week. Powders were then pressed into 1-g pellets and sintered for 2 d at 1375°C in flowing O_2 and cooled in the oxygen flow (for approximately 4 h) to room temperature. Subsequent annealing at either 800 or 500°C in O_2 for 16 h did not result in weight gain, indicating that the materials have reached their maximum possible oxygen content in a one-atmosphere ambient

pressure. The tendency of $(\text{La,Sr})_2\text{NiO}_4$ compounds to accommodate excess oxygen at low Sr contents under conditions similar to those employed here is well known.² For compositions in the $\text{La}_{1-x}\text{Sr}_x\text{NiO}_4$ solid solution with $x > 0.5$, the oxygen content under synthetic conditions very similar to ours has been found to be 4.0 atoms per formula unit (f.u.).² The same is true for materials prepared at higher oxygen pressures.⁶ Thus in the composition region of the most conductive materials, the formal nickel valence is simply $2+x$. Measurement of the oxygen content of our samples for $0.75 \leq x \leq 1.25$ by reduction in H_2 indicated a stoichiometry of 3.95(2) to 3.97(2) oxygen atoms per formula unit, uncorrelated to the Sr content. Our results are in substantial agreement with other studies on materials with 4.0 oxygen atoms per formula unit. Also, the measured oxygen contents are essentially independent of Sr content for $x > 0.75$, suggesting a structurally determined saturation value. These two facts lead us to believe that there is a small systematic error in our estimate of the oxygen contents of these materials, and that their actual oxygen contents are indistinguishable from the ideal 4.0 atoms/f.u. Under the synthetic conditions employed here, a continuous $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ solid solution exists for compositions between La_2NiO_4 and approximately $\text{La}_{0.6}\text{Sr}_{1.4}\text{NiO}_4$.

Powder diffraction patterns were obtained using high-angle x rays (CuK α radiation). Measurements of three peak positions allowed estimates of the variation in crystallographic unit-cell parameters in the solid-solid solution; see Fig. 1. In agreement with other work,⁶ we observe no discontinuity in lattice parameters or two-phase regions for $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$. Included for comparison in Fig. 1 are the changes in lattice parameters in the $\text{La}_{2-x}\text{Sr}_xCuO_4$ solid solution.^{7,8} Because there is a change in color from black to bronze near $x=1$ we have prepared samples at finer intervals in that region. The *c* lattice parameter is changing continuously near $x=1$, and the *a* parameter displays a subtle but significant saturation in the same composition range after an initial decrease. The peak in *c* is characteristic of a change in the accommodation of the charge for Sr contents smaller than and larger than 0.5. In agreement with others^{2,6} the results suggest to us that the charge first goes into d_{z^2} orbitals and then $d_{x^2-y^2}$ orbitals in a continuous fashion for $x > 0.5$. At the composition LaSrNiO_4 , nickel has a formal +3 valence, and with further Sr content would have a

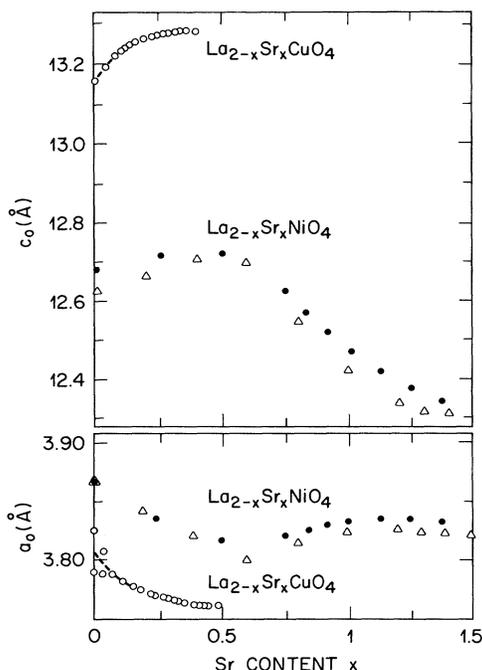


FIG. 1. Comparison of the variation of lattice parameters in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ solid solution (Refs. 7 and 8) and the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ solid solution; triangles, Ref. 6; solid circles, this work.

formal valence between +3 and +4. Although there is a change in color and the general characteristics of the temperature-dependent resistivity at that composition, the crystal structure apparently does not change enough to influence the lattice parameters at our level of precision.

Resistivities were measured in the van der Pauw geometry between room temperature and 4.2 K on the polycrystalline pellets. At the higher Sr contents ($x \geq 1$) the pellets were not well densified and developed cracks if exposed to wet air for several days. Measurements were therefore made on freshly prepared pellets. Due to the relatively low densities for those polycrystalline pellets, the measured values of the resistivities for the highest Sr materials are the least reliable. Representative temperature dependent resistivities for samples with compositions near LaSrNiO_4 are shown in Fig. 2. The most reliable resistivities observed are similar to those for $(\text{La,Sr})_2\text{-CuO}_4$ polycrystalline pellets. For the materials with compositions $\text{La}_{0.75}\text{Sr}_{1.25}\text{NiO}_4$ and $\text{La}_{0.6}\text{Sr}_{1.4}\text{NiO}_4$ (not shown), the resistivity is metallic over the whole temperature range.

The resistivities in the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ solid solution change several orders of magnitude with changes in composition. Our results are summarized in Fig. 3, which shows the measured resistivities at 100 and 300 K. The data show that a dramatic decrease in resistivity begins near $x = 0.5$, the same composition where the c -axis length begins to decrease (Fig. 1). A minimum measured resistivity occurs near $x = 1$, and is relatively sharply defined in composition. Although the temperature-dependent resistivities are weakly monotonically decreasing for $x > 1.12$,

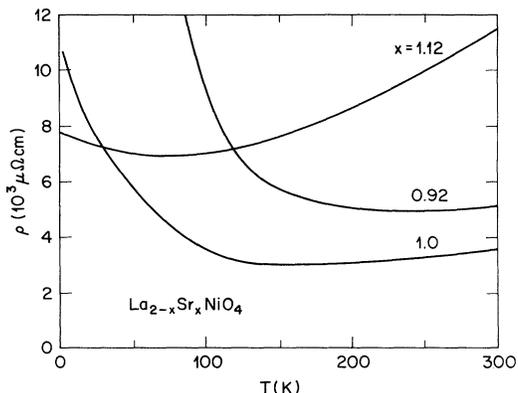


FIG. 2. Temperature-dependent resistivities for various $(\text{La,Sr})_2\text{NiO}_4$ compositions, as measured on polycrystalline pellets.

the absolute magnitudes increase. The increase in measured resistivity for $x > 1$ is no doubt due to the lower densities of the ceramic pellets for $x > 1$, so that the intrinsic resistivities may actually continue to decrease. The temperature dependencies of the resistivities for our materials are similar to those reported in Ref. 6, except that our absolute resistivities are lower than theirs for $x < 1.2$ and their data show a minimum resistivity at $x = 1.2$ instead of $x = 1.0$.

Magnetic susceptibilities were measured between 300 and 5 K in a dc field of 10 kOe in a commercial magnetometer. Representative data are presented in Fig. 4. La_2NiO_4 is a well-studied spin = 1 antiferromagnet with a

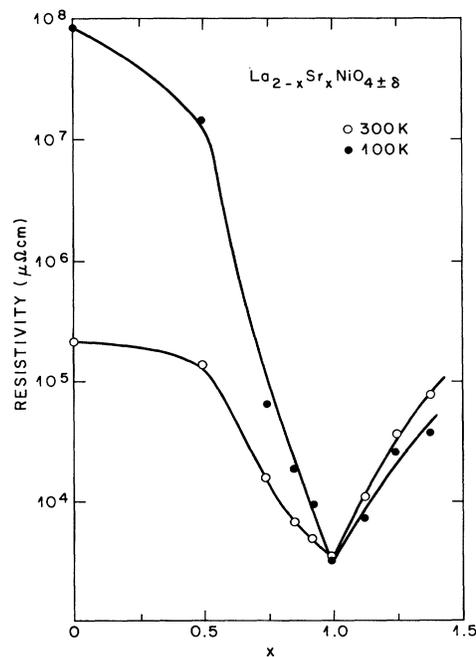


FIG. 3. Room-temperature (open circles) and 100 K (solid circles) resistivities for $(\text{La,Sr})_2\text{NiO}_4$ polycrystalline pellets. The apparent increase in ρ for $x > 1$ may be due to the lower density of these samples.

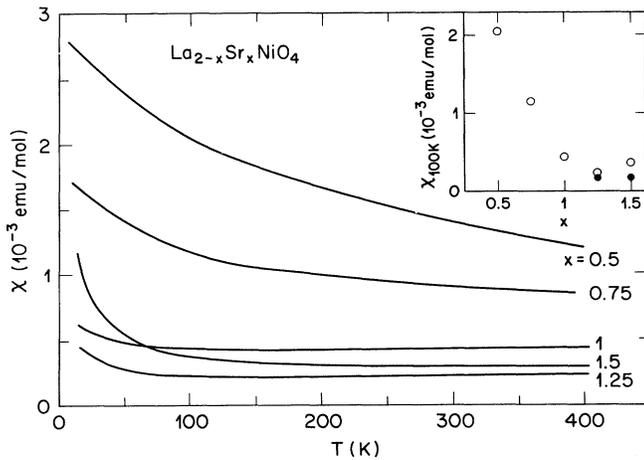


FIG. 4. Representative temperature-dependent magnetic susceptibilities in the $(\text{La,Sr})_2\text{NiO}_4$ solid solution. Inset, susceptibilities at 100 K. Open symbols, measured χ ; solid symbols, after subtraction of a small Curie term as described in text.

Néel temperature that depends sensitively on the oxygen content. The in-plane exchange constant is significantly smaller than in the cuprates.⁹⁻¹² Here we concentrate only on the high Sr compositions in the solid solution. The most striking feature of $\chi(T)$ near $x=1$ is its small overall magnitude compared to the low Sr compositions and its rather weak temperature dependence. For $x=1.25$ and 1.5 the measured $\chi(T)$ can well be analyzed as a superposition of two contributions: an intrinsic part with a linear T dependence ($\chi = \chi_0 + \chi^1 T$) and a Curie-Weiss contribution corresponding to a very small number of extrinsic local moments. The parameters χ_0 and χ^1 for $x=1.25$ are 1.33×10^{-4} emu/mol and 2.3×10^{-7} emu/molK, and for $x=1.5$ are 1.61×10^{-4} emu/mol and 2.3×10^{-7} emu/molK, respectively. (Note the same values of χ^1 , i.e., $d\chi/dT$.) The inset to Fig. 4 summarizes the evolution of χ with Sr content. The open symbols represent the total measured susceptibilities at 100 K and the closed ones for $x=1.25$ and 1.5 represent χ after subtraction of the extrinsic Curie-Weiss term.

The values of $\chi(T)$ for selected $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compositions are compared with various $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compositions^{8,13} in Fig. 5. Shown is $\chi(T)$ after subtracting the Curie-Weiss term. If Ni were in a conventional low-spin state, no paramagnetic contribution would be expected. Since a significant paramagnetism is observed, we suggest that it cannot arise solely from the small expected Pauli contribution of the conduction electrons. When viewed on the scale of Fig. 5, the temperature dependence of χ is quite pronounced, and is of opposite sign to that of highly metallic $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x > 0.2$), but is similar to that in the cuprates at low Sr content. A positive $d\chi/dT$ might be due to a rapidly varying density of states near E_F in a single-band picture, or, in a local-moment picture, due to the fact that the upper limit of the measurement range (400 K) is still well below the peak in $\chi(T)$, given by the exchange constant J , expected for a two-dimensional spin system. The latter was used to explain the low-Sr $\chi(T)$ behavior in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.¹⁴ However, because the ex-

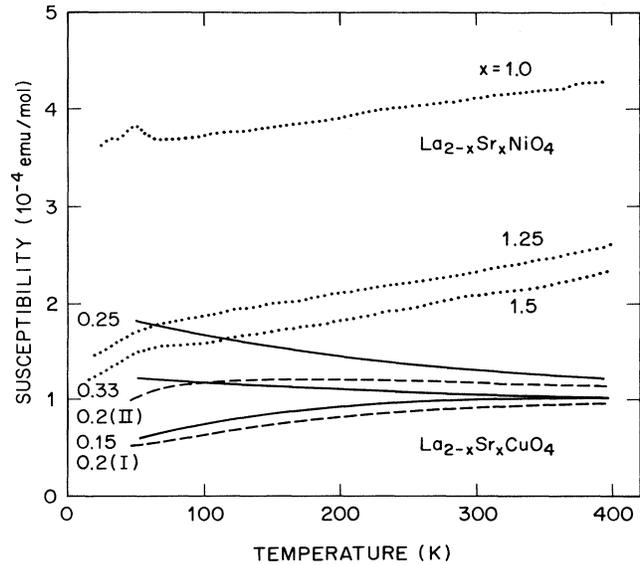


FIG. 5. Comparison of the temperature-dependent magnetic susceptibilities of various $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (Refs. 8 and 13) compositions. A small Curie term was subtracted from the nickelate curves.

change constant is much smaller in the nickelates than in the cuprates, we do not expect that explanation to apply in the current case. Alternatively, the observed paramagnetism is consistent with the Van Vleck susceptibility connecting a ground-state singlet (nickel, low spin) with an excited magnetic state (nickel, high spin). An observation in favor of such an interpretation is the fact that this paramagnetism decreases at higher Sr compositions where the stabilization of the low-spin state might be larger. This kind of analysis concerns only the $3d$ electrons, however, and disregards the important observation¹⁵ made in $\text{Ni}_{1-x}\text{Li}_x\text{O}$: that the extra hole introduced by Li substitution is distributed over the neighboring oxygen p orbitals, not the metal d states. These O $2p$ holes have a very large antiferromagnetic exchange interaction with the $\text{Ni}^{2+}(d^8)$ spins. In a dc magnetization measurement this situation cannot be distinguished from low-spin Ni^{3+} .

Magnetic measurements to check for the presence of superconductivity in the conductive samples near $x=1$ were performed in a dc magnetometer in a field of 20 Oe, to a temperature of 1.5 K. No superconductivity was found. Further, the most conductive samples were cooled to 30 mK in a dilution refrigerator and checked for superconductivity with a 1 kHz ac susceptibility technique, also without the observation of a superconducting transition. We must therefore conclude that the $(\text{La,Sr})_2\text{NiO}_4$ solid solutions, although isostructural with superconducting $(\text{La,Sr})_2\text{CuO}_4$ solid solutions, do not become superconductive to very low temperatures.

The properties of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ are somewhat enigmatic. At compositions where x is between 1 and 1.4 a conductive phase exists with no sign of magnetic ordering, a phase which does not become superconducting down to very low temperatures. An explanation of the evolution of the observed properties by a "high-spin" to "low-spin"

transition of the Ni *d* electrons alone as a function of Sr content appears to be inadequate. We suggest that a microscopic picture which considers the hole distribution among the Ni and the surrounding oxygens, in close analogy to (La,Sr)₂CuO₄ and also (Ni,Li)O is necessary for complete understanding. The lattice parameters for the conductive compositions of the La_{2-x}Sr_xNiO₄ solid solution indicate that the relative charge distribution among the *d*_{z²} and *d*_{x²-y²} orbitals is different from that in the conductive La_{2-x}Sr_xCuO₄ compositions.

More likely to be critical, however, are the relative energies of the nickel *d* and oxygen *p* states, which are considerably further separated in energy (by an additional

1–2 eV) than are those of Cu *d* and O *p*. This difference in energy of a few eV results in a larger charge-transfer gap in La₂NiO₄ than in La₂CuO₄,¹⁶ and is responsible for the necessity for higher Sr concentrations to induce metallic conductivity. This weakening of the metal-oxygen bond hybridization, believed to be critical to the occurrence of superconductivity in copper oxides, may be sufficient to prevent the appearance of superconductivity in nickel-based oxides.

We would like to acknowledge fruitful discussions with G. Sawatzky concerning the results of photoemission spectroscopy measurements on Cu and Ni oxides.

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