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J. Phys.: Condens. Matter 4 (1992) 3559–3568. Printed in the UK

Magnetism and resistivity of $Nd_{2-x}Sr_xNiO_{4+\delta}$ compounds

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Received 24 September 1991, in final form 20 December 1991

Abstract. The Sr-doped neodymium nickelates have similar (K_2NiF_4-type) structures both to the high-T_c superconductor $La_{1.85}Sr_{0.15}CuO_4$ and to $La_{2-x}Sr_xNiO_4$ materials, in which anomalous diamagnetic signals have been observed. We have made AC susceptibility, oxygen content, XRD and resistance measurements on $Nd_{2-x}Sr_xNiO_{4+\delta}$ samples for a wide range of Sr doping levels ($0 \leqslant x \leqslant 1.30$). Metal–semiconductor transitions occur below room temperature in samples with a high Sr concentration ($x \geqslant 0.90$) while more subtle changes in the nature of the electrical conductivity occur in the low-temperature resistance of samples with lower doping levels. These changes in resistance with doping and temperature are closely associated with changes in structure and with the strength of the Ni ion magnetic interactions. Similar changes in resistivity occur in the $La_{2-x}Sr_xCuO_4$ system, although over a much narrower range of Sr doping levels than in the nickelates.

1. Introduction

Undoped La_2NiO_4 is well known for its two-dimensional magnetic properties [1] and for the metal–insulator transition which occurs at a high temperature [2, 3]. After the discovery of the high-temperature superconductor $La_{1.85}Sr_{0.15}CuO_4$, $La_{2-x}Sr_xNiO_4$ compounds were studied as non-superconducting analogues of the cuprate system. Work on the nickelates was further stimulated in 1989 by the observation of small magnetic and resistance anomalies at low temperatures in some samples of $La_{2-x}Sr_xNiO_4$ [4–6]. Substitution of Nd^{3+} for La^{3+} introduces a large magnetic moment onto the rare-earth site which may affect some of the physical properties of the nickelate system. Complete substitution of a magnetic ion is not possible in the cuprate system since a different structure is formed when any ion other than La occupies the rare-earth site.

The physical properties of $La_{2-x}Sr_xNiO_{4+\delta}$ compounds have been extensively studied [7–9]. These are dominated by the structural feature of Ni–O planes, making both electronic and magnetic properties two dimensional. The magnetic susceptibility of the Ni ions varies with oxygen content and with Sr concentration, both of which directly influence the amount of hole doping of the Ni–O plane. Electronic properties are thought to depend on the Ni d orbital and O p orbital energy levels near the Fermi energy. These levels may form narrow hybridized conduction bands in the Ni–O plane and/or along the c axis. Band formation may be sensitive to magnetic correlations between the Ni ions [10] and to certain structural changes characteristic of the K_2NiF_4-type oxides. These include changes in the c/a axis ratio, transitions between tetragonal and orthorhombic symmetry and tilting of the oxygen octahedra

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around the copper or nickel ion. Such structural changes would also affect magnetic superexchange interactions, which depend on bond length. It is clear that the structural, magnetic and electronic properties are closely linked. These properties are also sensitive to oxygen stoichiometry, which is known to affect lattice parameters, the tetragonal-to-orthorhombic transition, carrier concentration and the likelihood of 3D magnetic ordering.

2. Sample preparation and oxygen stoichiometry

The samples were prepared by solid-state reaction in air of Nd_2O_3, $SrCO_3$ and NiO at 1200 °C. The oxides were well mixed and ground before reacting and reground once or twice during the reaction process at the end of which they were quenched in air. X-ray diffraction spectra were taken at room temperature to confirm that the materials were single phase. This was the case until $x > 1.30$, where extra peaks appeared.

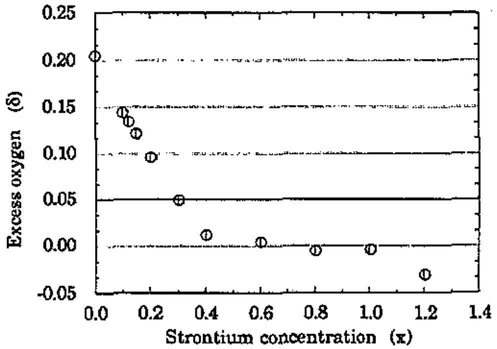

Figure 1. The excess oxygen δ in air-reacted samples of $Nd_{2-x}Sr_xNiO_{4+\delta}$.

Undoped $La_2NiO_{4+\delta}$ and $Nd_2NiO_{4+\delta}$ are known to contain excess oxygen when reacted in air [11–13]. As these parent compounds are doped and Sr^{2+} is substituted for Nd^{3+}, the excess oxygen decreases. In figure 1 the results of iodometric titration measurements on air-reacted samples are shown and the decrease in excess oxygen with increased doping can be clearly seen. Compounds with $0.4 < x < 1.0$ are believed to be stoichiometric as made when reacted in air and to contain no excess oxygen. At higher doping levels the compounds become deficient in oxygen, change in colour from black to brown and will deteriorate when left in the room atmosphere. Excess oxygen can be removed from the low Sr compounds by annealing in hydrogen at 310 °C. The effect of reduction is especially noticeable in $Nd_2NiO_{4+\delta}$ which changes in colour from black to brown.

3. Structure

Lattice parameters at room temperature were calculated from the peak positions of the XRD spectra. The lattice parameters are plotted for different values of x in figure 2 for both hydrogen-reduced and unreduced samples.

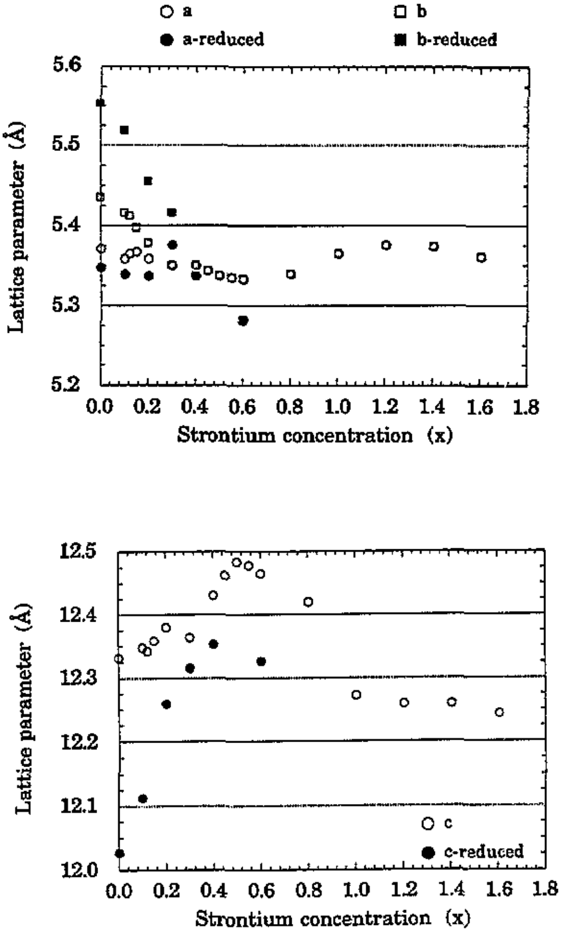

Figure 2. Lattice parameters of $Nd_{2-x}Sr_xNiO_{4+\delta}$ calculated from room-temperature x-ray spectra, for both reduced (●, ■) and unreduced (○, □) samples.

The low-Sr-concentration compounds are orthorhombic at room temperature. The orthorhombic splitting of the a and b parameters is strongly enhanced by hydrogen reduction and the removal of excess oxygen. As doping increases, there is a continuous decrease in orthorhombic distortion with the a and b lattice parameters becoming roughly equal at $x = 0.40$. Above this concentration the air-reacted samples no longer contain much excess oxygen.

The c/a ratio (figure 3) changes with x, reaching a peak at around $x = 0.5$–0.6, then falling steeply with increasing x and finally levelling off above $x = 1.0$. Similar behaviour is observed in $La_{2-x}Sr_xNiO_4$ and in $La_{2-x}Sr_xCuO_4$ [8, 9]. In the cuprates the c/a ratio is generally larger than 3.30, the undistorted ratio for the K_2NiF_4 structure, while in the nickelates for most x the ratio is less than 3.30 [7], showing compression of the c axis. Trends in the c/a ratio with x are similar for both the nickelates and the cuprates.

Neutron diffraction measurements were carried out on three powder samples ($x = 0.40$, $x = 0.55$ and $x = 1.00$) to see whether any significant structural changes accompanied either the metal–semiconductor transition or the magnetic and

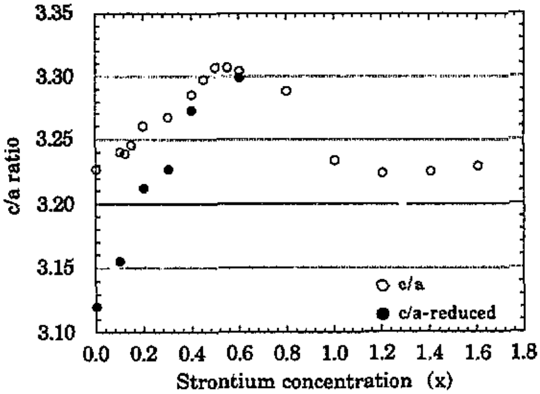

Figure 3. Ratio of c/a_{tet} (where $a_{tet} = (a + b)/2\sqrt{2}$) plotted aginst strontium concentration x.

electronic changes observed in the low-x compounds. Data were acquired at different temperatures below 300 K, using the medium-resolution LAD spectrometer at the ISIS source of the Rutherford–Appleton Laboratory. In all cases, a better fit to the data was achieved by using the orthorhombic space group Abma rather than the tetragonal group I4/mmm even though there was no sign of orthorhombic splitting of the relevant peaks in the diffraction spectra. Rodríguez-Carvajal *et al* [14] reported a similar problem in analysing their data for $La_2NiO_{4+\delta}$. They proposed that the materials contain both tetragonal and orthorhombic phases, causing microstrains that broaden some of the diffraction peaks. A possibly significant difference with our samples is that the undoped lanthanum nickelate contains large amounts of excess oxygen which are likely to contribute to lattice strain, while our doped samples are close to stoichiometric. The lattice parameters (I4/mmm) decreased smoothly with increasing temperature for all three samples and were not noticeably influenced by the metal–semiconductor transition in the $x = 1.00$ sample. The data and fit were not of sufficiently good quality to draw conclusions from the changes in bond lengths.

4. Magnetism

We measured the AC susceptibility below 40 K of both the reduced and the unreduced ceramic samples and observed complicated changes in magnetic properties with doping [15] (figure 4). In the susceptibility of the reduced low-x ($x < 0.20$) samples there are sharp peaks below 20 K which we attribute to 3D AFM ordering of the Nd^{3+} ions. Such ordering has been shown using neutron diffraction to exist below 80 K in a stoichiometric single crystal of Nd_2NiO_4 [12]. It is generally difficult for 3D order to exist in the nickelates. Superexchange interactions between the layers are weak and, because of the symmetry of the K_2NiF_4 structure, interlayer interactions tend to cancel out. It has been suggested [16] that oxides with the K_2NiF_4 structure which do have 3D magnetic order are those in which the transition-metal–oxygen bonds in the c-axis direction have a significant covalent component. This is not the case in the nickelates, in which the strongest interlayer interaction is probably between the Ni and Nd ions in neighbouring planes [12]. The magnetic interactions are also very sensitive to the presence of excess oxygen. In an oxygenated single crystal of Nd_2NiO_4

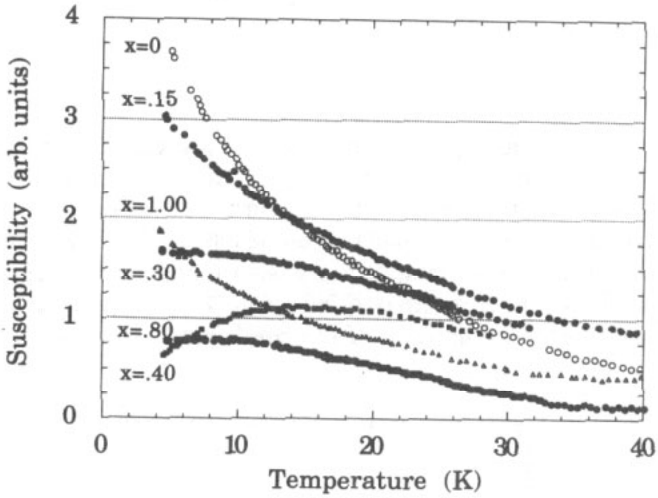

Figure 4. AC susceptibility of $Nd_{2-x}Sr_xNiO_{4+\delta}$ compounds.

no 3D ordering of either the Ni or the Nd ions could be seen down to 1.5 K [12]. Similarly, in our unreduced samples ($x < 0.20$) the susceptibility is paramagnetic and no ordering is apparent.

There are signs, however, of short-range 2D ordering between ions in the Ni–O and Nd–O planes. For samples with $x > 0.30$ and $x < 0.90$ a broad hump appears in the susceptibility as would be expected for 2D ordering. Since the large Nd^{3+} moment dominates the susceptibility below 40 K, 2D correlations must exist between the Nd ions as well as the Ni ions. It has been observed that the interlayer $J_{\mathrm{Ni-Nd}}$ interaction is stronger than the in-plane $J_{\mathrm{Nd-Nd}}$ interaction [12], and so to some extent magnetic order in the Nd–O layers may mirror that in the Ni–O planes.

As Sr doping increases beyond $x = 0.60$, Sr^{2+} ions dilute the Nd^{3+} ions in the Nd–O planes and the lower-moment Ni^{3+} ions are created in the Ni–O planes. The 2D correlations are weakened, and at higher concentrations ($x \geqslant 0.9$) the hump disappears. The susceptibility now shows a low-temperature upturn as expected for the uncorrelated Nd^{3+} ions.

Very similar susceptibility behaviour has been measured in $La_{2-x}Sr_xCuO_4$ compounds [17], although over completely different ranges of doping levels and temperatures. The broad 2D hump is found over the range $0.05 \leqslant x \leqslant 0.11$ and it extends in some of the samples to above 600 K. This indicates that the 2D Cu–Cu correlations are stronger in the cuprate system than the equivalent interactions in the nickelates but are also more easily destroyed by doping.

5. Resistivity

The resistance of the samples was measured using a four-terminal method with silver paint contacts. The samples were all approximately of the same size and shape (half a pellet 13 mm in diameter), except for some of the higher-Sr-content compounds ($x > 1.00$) which were less dense and more fragile than the lower-doped materials.

These samples were all unreduced, having oxygen contents approximately as shown in figure 1.

5.1. $0 \leqslant x \leqslant 0.50$

The compounds with low doping levels have a high resistance, and conduction is by means of activated hopping rather than band processes. The data are more linear when plotted as $\log R$ versus $T^{-1/4}$ than against $1/T$ (figure 5). This suggests variable-range hopping, a type of conduction resulting from hopping around the Fermi energy [18]. This type of conduction is also found in low-doped ($x = 0.05$) $La_{2-x}Sr_xCuO_4$ [19] and in deoxygenated $YBa_2Cu_3O_{7-\delta}$ [20]. In all these materials it is associated with partial localization of the conduction electrons.

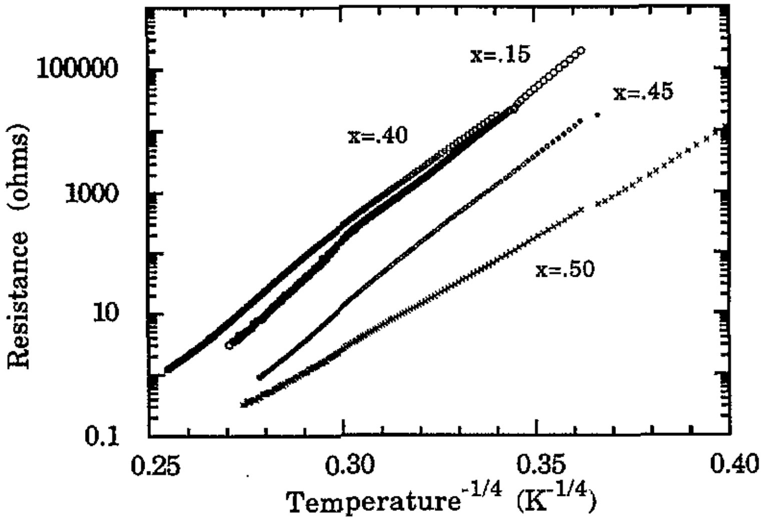

Figure 5. Resistance versus $T^{-1/4}$ of $Nd_{2-x}Sr_xNiO_{4+\delta}$ for $0.15 \leqslant x \leqslant 0.50$.

5.2. $0.50 \leqslant x \leqslant 0.90$

The slope of the resistance curve (equivalent to the value of the activation energy) falls abruptly below $x = 0.5$ (figure 6). One explanation for this drop in resistance considers the possibility of configuration crossover of the Ni^{3+} ions [7]. At low doping levels, as Sr^{2+} is substituted for Nd^{3+}, a reduction in excess oxygen may occur rather than the formation of Ni^{2+}. Above $x \simeq 0.4$, the compounds are stoichiometric, without excess oxygen, and Ni^{2+} is changed to Ni^{3+}. High-spin Ni^{2+} has $S = 1$ with one electron each in the planar $d_{x^2-y^2}$ and c axis d_{z^2} orbitals. Ni^{3+} has one less electron and only the lower-energy orbital is occupied. Gopalakrishnan *et al* [7] suggest that below $x = 0.5$ the d_{z^2} orbital is occupied, in accordance with the stretching of the c axis. With further doping the energies of the d_{z^2} and $d_{x^2-y^2}$ orbitals cross and the electron moves to the planar orbital. This agrees with the observed contraction in the c axis and may also increase conductivity in the Ni–O planes.

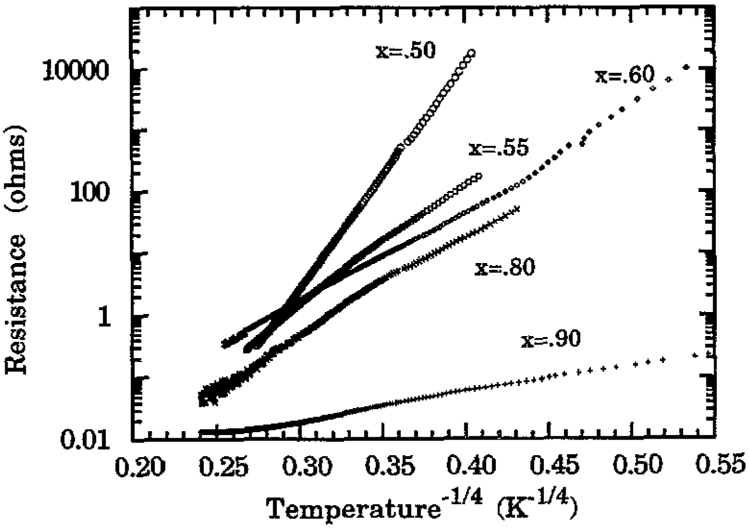

Figure 6. Resistance versus $T^{-1/4}$ of $Nd_{2-x}Sr_xNiO_{4+\delta}$ for $0.50 \leqslant x \leqslant 0.90$.

5.3. $0.95 \leqslant x \leqslant 1.30$

Samples with Sr concentrations in this range exhibit a metal-to-activated conduction (M–I) transition below room temperature (figure 7). The transition is manifested in the R versus T curves by a change from a positive slope at high temperatures to a negative slope below the transition temperature. This transition is well known in $La_{2-x}Sr_xNiO_4$ [8]. The transition temperature increases as doping decreases and moves above room temperature for $x \leqslant 0.90$, reaching a maximum of 500–600 K for undoped La_2NiO_4. Resistivity measurements on single-crystal La_2NiO_4 have shown that the transition is two dimensional and takes place only in the basal plane [3]. Figure 8 is a plot of the transition temperatures T_t for our samples. The transition occurs smoothly over a wide range of temperatures in most of the samples; so the transition temperatures in figure 8 are plotted as vertical bars which represent the approximate temperature range of the transition for each compound. In $Nd_{2-x}Sr_xNiO_4$ the transition occurs at more or less the same concentration and temperature as in the corresponding lanthanum compound. The M–I transition in the lanthanum nickelates is thought to be caused by band splitting [10] and many possible mechanisms for this splitting have been proposed. These include AFM correlations [10, 21], electron–electron correlations [2], changes in bond lengths [22] and a structural transition which occurs at the same temperature as the electronic transition [23].

6. Discussion

The changes in structure and conductivity with strontium doping that we have observed in $Nd_{2-x}Sr_xNiO_{4+\delta}$ are generally the same as those in $La_{2-x}Sr_xNiO_{4+\delta}$. This indicates that the magnetic moment of the Nd^{3+} ion does not significantly affect the properties of the nickelates. The changes in the properties of Nd_2NiO_4 on doping it with Sr can be explained as resulting from a combination of electron delocalization and band formation in the Ni–O planes and from changes in the electronic configuration of the Ni ion.

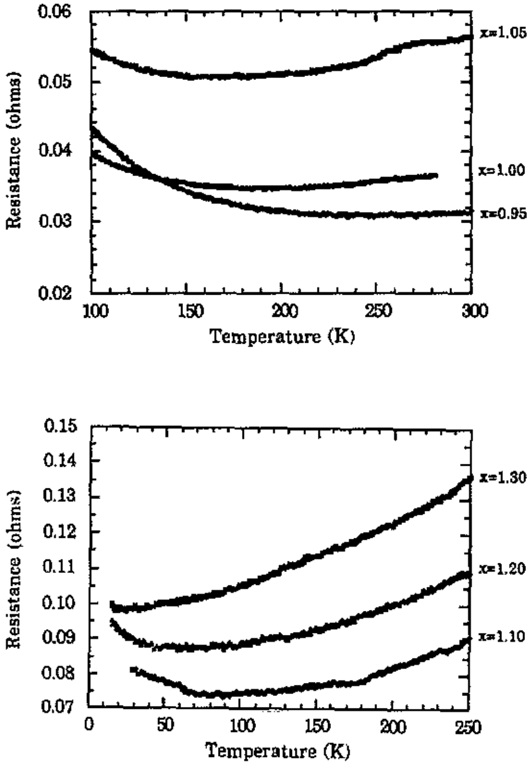

Figure 7. Resistance versus temperature of $Nd_{2-x}Sr_xNiO_{4+\delta}$ for (*a*) $0.95 \leqslant x \leqslant 1.05$, and (*b*) $1.10 \leqslant x \leqslant 1.30$.

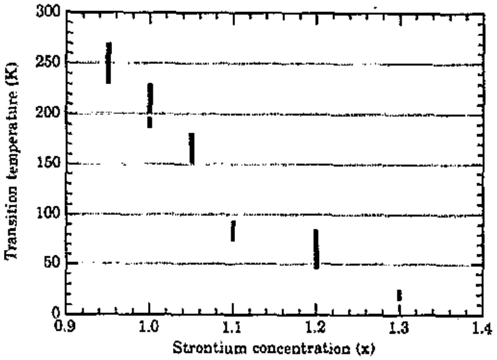

Figure 8. Transition temperature T_t of the metal–semiconducting transition versus strontium concentration x.

The observed changes in conductivity at doping levels below $x = 0.90$ have been explained in the lanthanum compounds as being due to configuration crossover of the Ni^{3+} ion [7]. At strontium concentrations less than $x = 0.50$ there is a single electron in the Ni^{3+} d_{z^2} orbital and an accompanying stretching of the c axis. When $x > 0.5$–0.6 the electron moves from the localized d_{z^2} orbital to the more delocalized $d_{x^2-y^2}$ planar orbital. This increases conductivity and reduces the c/a ratio. It has also been suggested that a different kind of change in spin configuration could be responsible for the small diamagnetic signal seen in some single crystals of La_2NiO_4 [4] and $La_{1.8}Sr_{0.2}NiO_4$ [5]. Takeda *et al* [8] contend that the compressive stress in the a–b planes could force the Ni^{2+} in low-doped materials from the high-spin $S = 1$ state into a diamagnetic low-spin state where two electrons fill the d_{z^2} orbital and the $d_{x^2-y^2}$ orbital is empty. If enough of the Ni^{2+} ions are forced into the low-spin state by temperature cycling, a drop in susceptibility could appear. It is not clear, however, how this situation could contribute to the drops in resistivity seen in $La_{1.8}Sr_{0.2}NiO_4$ by Hoffman *et al* [6] since the d_{z^2} orbital electrons are expected to be more localized than those in the planar orbitals.

The transition seen in the nickelates from a variable-range-hopping material to a metallic conductor is also found in $La_{2-x}Sr_xCuO_4$ [19]. The corresponding phase region in the lanthanum cuprates is $0 < x < 0.05$, just below the doping range in which superconductivity appears, rather than in the region $0 < x < 0.90$ as in the nickelates. If an analogous type of superconductivity were to be found in the nickelates it might be expected at around $x = 1.30$ where the conductivity is metallic down to low temperatures and the Ni^{3+} magnetic moment is small. However, Cava *et al* [9] made susceptibility measurements down to 30 mK and found no sign of superconductivity.

Acknowledgments

We would like to thank Alex Hannon of the Rutherford–Appleton Laboratory for his help with the neutron diffraction measurements.

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