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## Electrical transport in $\text{LaNiO}_{3-\delta}$ ( $0 \leq \delta \leq 0.14$ )

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**Abstract.** We report a systematic study of the effect of increasing oxygen deficiency on the electrical resistivity, tunnelling conductance and thermopower of  $\text{LaNiO}_{3-\delta}$  ( $0 \leq \delta \leq 0.14$ ). Stoichiometric  $\text{LaNiO}_3$  behaves like a normal metal with a positive temperature coefficient of resistivity (TCR) and a negative thermopower which is proportional to temperature over the range 5 K–300 K. As the oxygen deficiency increases, the electrical resistivity ( $\rho$ ) shows a minimum at low temperature which progressively shifts to higher temperature with increasing  $\delta$ . In the low-temperature limit the correction to the electrical conductivity follows a power-law behaviour with an exponent  $\approx 0.5$ . We also find a cusp-like dip in the tunnelling conductance near zero bias voltage. We attribute both of these behaviours to enhanced interaction between the charge carriers in the system occurring because of the disorder. The thermopower of the oxygen-deficient samples is found to vary systematically with  $\delta$ , showing a sign reversal at low temperature.

### 1. Introduction

In the past few years our understanding of electrical conduction in disordered metallic systems [1] has advanced significantly. The effect of disorder on the electrical transport and thermodynamic properties has been found to be extremely important, causing significant corrections to the conductivity and the density of states: a minimum in the temperature dependence of the resistivity and a strong anomaly in the density of states [2] at the Fermi level are frequently observed. Altshuler and Aronov [3, 4] showed that in these systems many-body e–e interactions, are important. Taking into consideration e–e interactions, they predicted [3] a  $T^{1/2}$  temperature dependence for the low-temperature correction to the electrical conductivity and an anomaly in the density of states at  $E_F$ . According to them [4], a modification in the density of states (symmetric about  $E_F$ ) occurs which goes as  $\delta N(E) \propto |E - E_F|^{1/2}$ . Later, McMillan [5], considering both localization and e–e interaction effects, predicted a similar expression for the density of states:

$$N(E) = N(0)[1 + (E/\Delta)^{0.5}]. \quad (1)$$

Here  $\Delta$  is a constant, called the correlation gap [5].

Previously, most of the studies of disordered systems were confined to amorphous metals and doped semiconductors [6], but recently oxides have also attracted considerable attention as subjects for such studies [7–10]. In this paper we have made an effort to investigate the effect of disorder (oxygen deficiency) on the electrical resistivity  $\rho(T)$ , tunnelling conductance  $G(V)$  and thermopower  $S(T)$  of a three-dimensional transition metal perovskite oxide system. For this study we found the  $\text{LaNiO}_{3-\delta}$  system to be the most suitable, for the following reasons:

- (a) The parent compound  $\text{LaNiO}_3$  is a well studied sample [9, 10] and it has been reported to have a high electron density ( $\approx 10^{22} \text{ cm}^{-3}$ ) but a low conductivity ( $\approx 10^3\text{--}10^4 \text{ S cm}^{-1}$ ).

The combination of a low conductivity and a high electron density indicates a low electron diffusivity ( $D$ ) and a sizable amount of disorder. This transition metal oxide seems ideal for a study of the effect of disorder on a metallic system.

- (b) It is possible to exert fine control over the strength of the disorder (and hence the e–e interactions) by controlling the oxygen deficiency  $\delta$ . The nature of the disorder in this case would be mainly oxygen vacancies in the lattice. This would randomize the potential ‘seen’ by the conduction electrons.
- (c) The thermopower of the parent sample  $\text{LaNiO}_3$  varies almost linearly with temperature; a linear temperature dependence suggests that the thermopower of the system mainly arises from the diffusion of electrons, and hence any interaction among the electrons due to disorder may be reflected in the thermopower of the system also [11].

With the above objectives in mind we have carried out precise measurements of the electrical resistivity, tunnelling conductance and thermopower of  $\text{LaNiO}_{3-\delta}$  ( $\delta = 0\text{--}0.14$ ).

## 2. Experimental procedure

All of the samples investigated in this work were prepared by the sol–gel method. Stoichiometric amounts of  $\text{La}_2\text{O}_3$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in nitric acid, and citric acid was added to this solution so as to maintain the ratio of La:Ni: citric acid as 1:1:2.05. The molarity of this solution was maintained at 0.1 M and the solution was refluxed at 360 K for 24 hours. The solution was gently warmed to produce a fluffy gel; this gel was fired at 925 K for 12 hours. The sample thus prepared was pressed to form four rectangular pellets and the pellets were sintered under different conditions to vary the oxygen stoichiometry of the sample. The oxygen concentrations for all of the samples were determined by iodometry (see table 1). The sample sintered in  $\text{N}_2$  has the maximum oxygen deficiency; further attempts to increase the oxygen deficiency led to the decomposition of the material. The crystal structures and lattice parameters for all of the samples were determined by x-ray diffraction using a Rich–Seifert x-ray diffractometer.

**Table 1.** The sintering conditions, oxygen nonstoichiometries ( $\delta$ ) and lattice parameters ( $a$ ) for various  $\text{LaNiO}_{3-\delta}$  samples.

Sintering atmosphere	Duration (days)	Sintering temperature (K)	$\delta$	$a$ (Å)
$\text{O}_2$	7	1100	0.00	3.850
$\text{O}_2 + \text{air}$	7	1100	0.06	3.851
Air	7	1100	0.11	3.853
$\text{N}_2$	7	1050	0.14	3.855

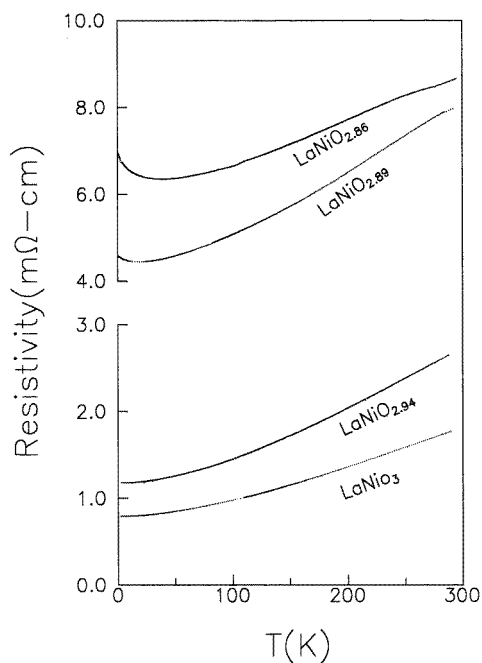
A four-probe ac (1 kHz) technique was employed to measure the electrical resistivities of all of the samples over the temperature range 2.5–300 K. We preferred an ac technique over a dc technique because (i) it is faster, (ii) it gives a better signal-to-noise ratio and (iii) it automatically cancels thermal emfs. A lock-in amplifier (Stanford Research Systems: SR830), a voltage-to-current converter (home-made, driven by the lock-in sine out) and a temperature controller (LakeShore Cryotronics: DRC-82C) were used. A measuring current of 2–5 mA was used. It was ensured that the current did not cause any self-heating. The absolute accuracy of the resistivity is about 10% (this is large, mainly due to uncertainties in the geometrical factor); however, the resolution was much better at 1–5 parts in  $10^5$ .

The tunnelling measurements were carried out on tunnel junctions made with a Pb counter-electrode. The tunnel barrier is formed by the native oxide surface on the Pb. A programmable current source (Keithley Model 220) and a nanovoltmeter (Keithley Model 182) were used to obtain the  $I$ - $V$  characteristics of the junction. The differential conductance was obtained numerically. All of the measurements were performed at 1.2 K by dipping the samples in a pumped  $^4\text{He}$  cryostat.

The absolute thermopower measurements were performed over the temperature range 5–300 K. The home-made apparatus employs a standard dc differential technique with copper as the other arm of the thermocouple. A temperature difference ( $\Delta T$ ) of 1–2 K was maintained across the two ends of the sample and the voltage difference ( $\Delta V$ ) thus developed was measured using a Keithley nanovoltmeter (model 182).  $\Delta V/\Delta T$  gives the thermopower of the sample with respect to that of copper. The absolute thermopower was obtained by adding to this quantity the absolute thermopower of copper which was obtained from reported data. The performance of the apparatus was checked by measuring the thermopower of platinum and comparing it with the reported data and found to be good. The absolute accuracy is  $\sim 0.5 \mu\text{V K}^{-1}$  and the resolution is  $\sim 0.1 \mu\text{V K}^{-1}$ .

### 3. Results

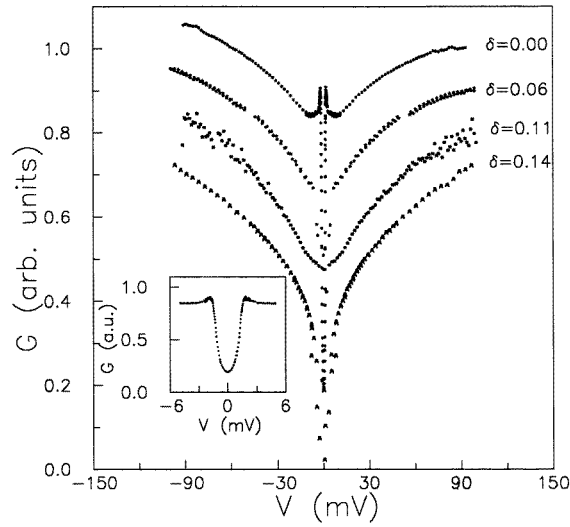
The X-ray diffraction patterns of all of the samples indicate single-phase systems. All of the samples are found to be cubic, with almost identical lattice parameters (see table 1).



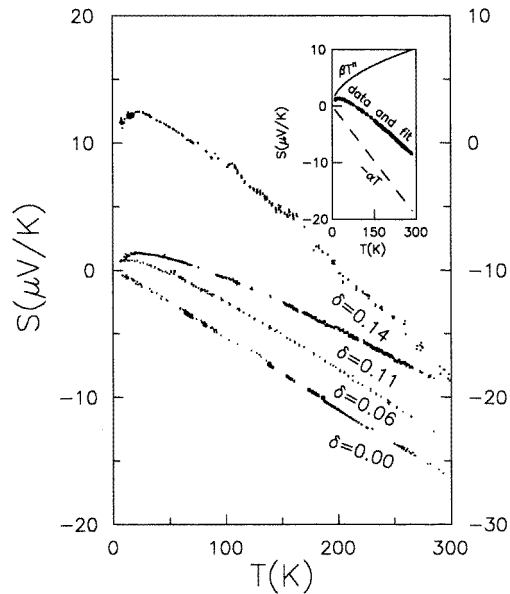
**Figure 1.** The electrical resistivity of  $\text{LaNiO}_{3-\delta}$  ( $\delta = 0.00, 0.06, 0.11, 0.14$ ) from 2.5 K to 300 K.

The electrical resistivity data for  $\text{LaNiO}_{3-\delta}$  samples from 2.5 K to 300 K are shown in figure 1.  $\text{LaNiO}_3$  shows a positive temperature coefficient of resistivity (TCR) throughout the whole temperature range while the oxygen-deficient samples exhibit a minimum in

the resistivity at low temperature ( $T_{min}$ ). At higher temperatures all of the samples show linear variation with temperature, indicating that electron-phonon scattering determines the temperature dependence at high temperature in these metals.



**Figure 2.** The tunnelling conductance ( $G$ ) versus the bias voltage for  $\text{LaNiO}_{3-\delta}$  ( $\delta = 0.00, 0.06, 0.11, 0.14$ ) at 1.2 K. The inset shows the low-bias ( $|V| < 10$  mV) experimental data for  $\text{LaNiO}_3$ , reflecting the signatures of the superconductivity gap of Pb.



**Figure 3.** The thermopower of  $\text{LaNiO}_{3-\delta}$  ( $\delta = 0.00, 0.06, 0.11, 0.14$ ) from 2.5 K to 300 K. For  $\delta = 0.00, 0.06$  and  $0.11$ , the y-scale is on the left-hand side, while for  $\delta = 0.14$ , it is on the right-hand side. The inset shows the fit for  $\text{LaNiO}_{2.89}$  to  $S = -\alpha T + \beta T^n$ .

In figure 2 we show the differential tunnelling conductances  $G(V)$  ( $=dI/dV$ ) of various samples at 1.2 K. We have chosen Pb as the counter-electrode and performed the measurements at 1.2 K where Pb is in the superconducting state. This was chosen because the observation of the superconductivity gap is strong evidence for the quality of the tunnel junction, and ensures that the tunnel injection is indeed the mechanism of charge transfer. For all of the junctions we have observed a well defined dip in conductance for  $|V| < \Delta_{\text{Pb}}$ . In the inset of figure 2 we have shown the superconductivity gap of Pb as observed in the case of  $\text{LaNiO}_3$ . The thermopower data for  $\text{LaNiO}_{3-\delta}$  samples from 5 K to 300 K are shown in figure 3.  $\text{LaNiO}_3$  has a negative thermopower with almost linear thermal variation, while the thermopower of oxygen-deficient samples show a sign reversal from negative to positive and a distinct maximum at low temperature.

## 4. Discussion

### 4.1. Electrical resistivity

The variation of the resistivity with temperature for  $\text{LaNiO}_3$  is very similar to that for good metals except as regards its large magnitude. At higher temperatures,  $\rho(T)$  varies linearly with temperature and at lower temperatures it approaches a residual value following the relation  $\rho(T) = \rho(0) + CT^2$ . Here it is to be noted that, although  $\text{LaNiO}_3$  has a high electron density, its electrical conductivity is very low ( $\approx 2 \times 10^3 \text{ S cm}^{-1}$ ). This implies a low electron diffusivity.

For oxygen-deficient samples, distinct resistivity minima are observed. In metals the low-temperature minima may arise for the following reasons: (i) because of the Kondo effect [13]; and (ii) because of the weak localization and e-e interactions, collectively known as the quantum correction effects [1, 6]. The Kondo effect is encountered in nonmagnetic systems containing small amounts of magnetic impurity. Kondo systems show a giant thermopower, at low temperature. Since none of our samples exhibit giant thermopower the possibility of a Kondo effect is ruled out. Weak-localization and e-e interaction effects are seen in disordered metallic systems. In the case of disordered metals, because of the interference of partial electron waves, weak-localization effects are observed. The correction to the conductivity in the case of weak localization goes as  $\delta\sigma_{\text{WL}} \propto T^{p/2}$  with  $p \approx 1.5-3$ . In the case of strongly disordered metals, the electrons undergo intense elastic scattering from the impurities. This makes their motion diffusive and hence reduces their ability to screen out the electric field of other electrons. Reduced screening causes an enhanced Coulomb interaction between the electrons [1]. The correction to the conductivity due to the enhanced interaction goes as  $\delta\sigma_{\text{e-e}} \propto T^{1/2}$ . Quantum correction effects affect the electrical conductivity at low temperatures; at higher temperatures the usual inelastic contributions become significant [14]. Because of the inelastic scattering, the electrical conductivity has an additional contribution of the form  $\delta\sigma_{\text{inel}} = -cT^p$ .

To get some idea of the real mechanisms involved, we fitted our low-temperature (2.5–

**Table 2.** Parameters used in fitting the low-temperature ( $2.5 \text{ K} < T < 20 \text{ K}$ ) conductivity data for  $\text{LaNiO}_{3-\delta}$  to the empirical relation  $\sigma = \sigma(0) + bT^m - cT^n$ .

$\delta$	$\sigma(0)$ ( $\text{S cm}^{-1}$ )	$b$ ( $\text{S cm}^{-1} \text{ K}^{-m}$ )	$c$ ( $\text{S cm}^{-1} \text{ K}^{-n}$ )	$m$	$n$	$\chi^2$
0.00	1262.07(1)	—	0.0377(1)	—	1.993(1)	1.2
0.06	841.61(2)	3.976(8)	0.0649(4)	0.51(2)	2.026(2)	1.4
0.11	209.18(4)	5.586(9)	0.141(2)	0.49(1)	1.367(3)	1.4
0.14	132.71(3)	7.075(3)	0.244(3)	0.49(1)	1.188(2)	1.3

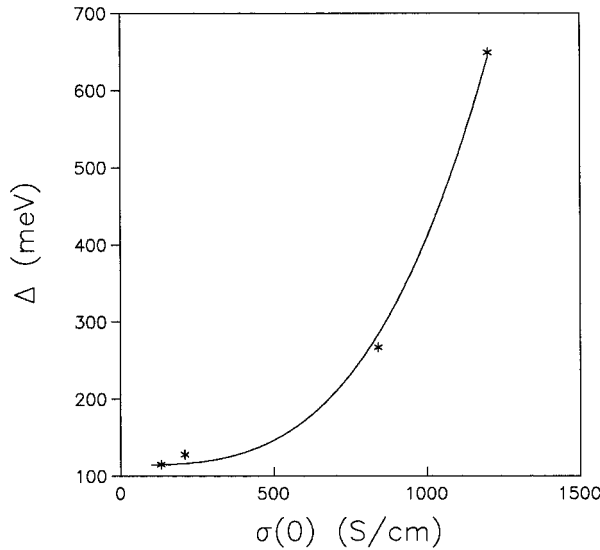
20 K) conductivity data to an empirical relation of the form  $\sigma = \sigma(0) + bT^m - cT^n$ . For all of the samples, the value of  $m$  lies very close to 1/2 (see table 2), thus suggesting that e–e interactions determine the low-temperature behaviour of the electrical resistivity.

#### 4.2. Tunnelling spectroscopy

The tunnelling conductance  $G(V)$  is a direct measure of the single-particle electronic density of states  $N(E)$  at the energy  $E = q_e V + E_F$ . In highly disordered metallic systems, electron–electron interactions give rise to a correction to the density of states  $N(E)$  at  $E = E_F$  (see equation (1)). According to Altshuler and Aronov, for three-dimensional disordered systems this correction to the density of states goes as  $\delta N(E) \propto |(E - E_F)|^{1/2}$  causing a cusp in the tunnelling conductance at  $V = 0$  such that  $G(V) = G_0[1 + (|V|/\Delta)^{0.5}]$ . Here  $G_0$  is the zero-bias conductance and  $\Delta$  is the same constant as appears in equation (1).

**Table 3.** Parameters used in fitting the tunnelling conductance data for  $\text{LaNiO}_{3-\delta}$  to  $G(V) = G_0[1 + (|V|/\Delta)^{0.5}]$ . Data in the range  $10 \text{ mV} < |V| < 100 \text{ mV}$  were used for the fitting.

$\delta$	$G_0$ (S)	$\Delta$ (meV)	$\chi^2$
0.00	0.8473(9)	649(9)	1.7
0.06	0.1203(2)	267(2)	1.3
0.11	0.0410(1)	128(2)	1.6
0.14	0.00273(2)	116(3)	1.7



**Figure 4.** The variation of  $\Delta$  with  $\sigma(0)$ . The solid curve represents the best fit to  $\Delta = u + v\sigma(0)^q$ .

Interestingly, all of the samples under investigation are found to obey the above relation very well. In table 3 we have shown the values of  $\chi^2$  and the parameters used in fitting our data to the above equation. Shown in figure 4 are the values of  $\Delta$  as a function of the extrapolated zero-temperature conductivity  $\sigma(0)$ . Altshuler and Aronov showed [1] that  $\Delta$  should vary as  $\sigma(0)^3$  while McMillan’s model [5] predicts an exponent of 2. Our experimental data are found to

follow an empirical relation,  $\Delta = u + v\sigma(0)^q$  ( $u = 114.5 \text{ meV}$ ,  $v = 0.741 \times 10^{-7} \text{ meV S}^{-q} \text{ cm}^q$ ,  $q = 3.2$ ), which is very close to the prediction of Altshuler and Aronov.

### 4.3. Thermopower

The thermopower of  $\text{LaNiO}_3$  varies linearly with temperature in good agreement with the free-electron expression for the thermopower:

$$S = -\frac{\pi^2 k_B^2 T}{6 e E_F}. \quad (2)$$

Using this expression for the  $\delta = 0$  sample, we found  $E_F = 0.24 \text{ eV}$ , which agrees well with the previously reported value [9] of  $E_F = 0.21 \text{ eV}$ . A linear temperature dependence of the thermopower means that the main contribution comes from the diffusion component. As the value of  $\delta$  increases, some very interesting features appear in the thermopower of the system. It is negative at room temperature and as we go down in temperature at a characteristic temperature  $T_0$  it changes sign from negative to positive. Below  $T_0$  its magnitude further increases to a maximum and then starts falling. Also we observe that the value of  $T_0$  changes with  $\delta$ :  $T_0 = 42 \text{ K}$ ,  $75 \text{ K}$  and  $71 \text{ K}$  for  $\delta = 0.06$ ,  $0.11$  and  $0.14$  respectively. We found that  $S$  fits best to the relation  $S = -\alpha T + \beta T^n$  with  $n \approx 1/2$  (see table 4).

**Table 4.** Parameters used in fitting the thermopower data ( $5 \text{ K} < T < 300 \text{ K}$ ) for  $\text{LaNiO}_{3-\delta}$  to the empirical relation  $S = -\alpha T + \beta T^n$ .

$\delta$	$\alpha$ ( $\mu\text{V K}^{-2}$ )	$\beta$ ( $\mu\text{V K}^{-(n+1)}$ )	$n$	$\chi^2$
0.00	0.05419	—	—	1.6
0.06	0.0739(9)	0.48(1)	0.50(1)	1.3
0.11	0.084(3)	0.505(8)	0.59(1)	1.1
0.14	0.136(4)	0.91(3)	0.56(1)	1.5

For several other materials an additional contribution to the thermopower along with the diffusion component is observed and this is usually attributed to phonon drag. Since all of our samples have similar crystal structures and almost identical molecular weights, their Debye temperatures will also be the same, and hence the phonon drag thermopower is expected to be the same for all of the samples. But in our case a systematic variation in the strength of the  $T^n$ -term with  $\delta$  is observed. These observations suggest that the phonon drag mechanism cannot account for the observed thermopower. Since the presence of enhanced interaction among the charge carriers due to disorder is unambiguously established from the electrical conductivity and tunnelling conductance data, we feel that the thermopower may also be showing the effects of enhanced electron–electron interactions in this system. However, in the absence of any theoretical predictions [11] we cannot make any further progress on this front.

## 5. Conclusions

In this study we have observed the evolution of enhanced electron–electron interaction effects in a three-dimensional perovskite oxide system,  $\text{LaNiO}_{3-\delta}$ .  $\text{LaNiO}_3$  behaves as a normal metal although with a very small electron diffusivity; as oxygen deficiency is introduced into the system, the material becomes more disordered and the electron–electron interactions become quite significant and start to affect the electrical transport. The observed changes in the electrical conductivity and tunnelling conductance agree very well with the theoretical



predictions for e–e interactions. A systematic variation in the thermopower of the system with  $\delta$  is also observed.

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