Magnetoresistance of metallic perovskite oxide LaNiO$_{3-\delta}$

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Abstract

We report a study of the magnetoresistance (MR) of the metallic perovskite oxide LaNiO$_{3-\delta}$ as a function of the oxygen stoichiometry $\delta$ ($\delta \leq 0.14$), magnetic field ($H \leq 6T$) and temperature ($1.5K \leq T \leq 25K$). We find a strong dependence of the nature of MR on the oxygen stoichiometry. The MR at low temperatures change from positive to negative as the sample becomes more oxygen deficient (i.e., $\delta$ increases). Some of the samples which are more resistive, show a resistivity minima at $T_{\text{min}} \approx 20K$. We find that in these samples the MR is positive at $T < T_{\text{min}}$ and negative for $T > T_{\text{min}}$. We conclude that in the absence of strong magnetic interaction, the negative MR in these oxides can arise from weak localisation effects.

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I. INTRODUCTION

In recent years the electrical conduction in transition metal perovskite oxides at low temperature has attracted considerable research interest \[1\]. Most of these oxides studied belong to the ABO$_3$ class or its closely linked derivatives. In recent years the observation of colossal magnetoresistance (CMR) in rare-earth maganates belonging to the ABO$_3$ class has added yet another new phenomena \[2\]. These oxides have chemical formula of the type La$_{1-x}$(Sr/Ca)$_x$MnO$_3$ with $x \approx 0.2 - 0.4$. The colossal negative MR seen in these oxides have become a topic of intense research activity. In these mixed valent manganates (doped to create Mn$^{4+}$) the CMR is closely linked to the occurrence of strong ferromagnetism which arises from the Double Exchange (DE) interactions. The additional important contribution to the CMR phenomenon comes from the strong Jahn-Teller effect of the Mn$^{3+}$ ions. In a closely related compound La$_{1-x}$Sr$_x$CoO$_3$ (with Co$^{3+}$ and Co$^{4+}$) which is also a ferromagnetic metallic oxide for $x \geq 0.2$ the MR was found to be much smaller except in the composition range $x \approx 0.2$ where the oxide undergoes a composition driven metal-insulator transition \[3\]. The negative MR in this material for $x \approx 0.2$ is believed to be related to the formation of ferromagnetic clusters. In both these oxides the electron is on the verge of getting localized. On the other hand there are metallic oxides also belonging to ABO$_3$ class like Sr$_x$NbO$_3$ ($x \geq 0.75$) \[4\] and Na$_{0.9}$WO$_3$ \[5\] with relatively high conductivity which have positive MR at all temperatures. In these oxides the MR has a quadratic dependence on the applied field $H$ much like a band metal. The principal differences between the two classes of perovskite oxides seems to be the extent of electron localization and the presence of ferromagnetic interactions. This leads us to the following interesting question: *If we start with a metallic perovskite oxide showing positive MR and gradually make the electrons localized (by some means), will the positive MR change to a negative MR as the electrons get localized?* We investigate this question in the metallic perovskite LaNiO$_{3-\delta}$ in which we find that the MR changes from positive to negative as the material is made more resistive by increasing $\delta$. LaNiO$_3$ belonging to the ABO$_3$ class is structurally similar to LaCoO$_3$ and LaMnO$_3$. 

\[2\]
However unlike the cobaltate and the manganate, it is a fairly good metal with low resistivity \[6–10\]. However, as the oxygen deficiency is increased the resistivity is enhanced. Eventually the material becomes an insulator at \(\delta \gtrsim 0.25\) \[10\]. The investigation of the MR in this oxide is thus of importance because it allows us to investigate the MR in a class of disordered oxides where a change in oxygen stoichiometry leads to a qualitative change in the nature of electronic transport without bringing in strong magnetic effects atleast for \(\delta \leq 0.2\).

LaNiO\(_3\) is an interesting material because of its potential in application as metallic interconnects (or electrodes) in thin film oxide electronics particularly those needing epitaxial multilayer perovskite oxide films \[11\]. The MR data of this oxide will thus be of importance technologically.

II. EXPERIMENTAL DETAILS

The samples of LaNiO\(_{3-\delta}\) were prepared from co-precipitation and subsequent decomposition of nitrates of La and Ni as described in refs. \[8\] and \[12\]. The samples were heat treated under different oxygen atmosphere to get varying oxygen content and the oxygen stoichiometry \(\delta\) was determined by iodometric titration. The grain sizes as measured by scanning electron microscope were typically of the order of 2 \(\mu\)m and there was no variation in the grain sizes of the samples with different \(\delta\). [See ref \[13\] for details of sample preparation and characterisation].

The electrical resistivity \(\rho(T)\) and the MR were measured by a high precision low frequency (20 Hz) ac bridge technique with a precision of \(\pm 10\)ppm. The resistivity was measured in the range 0.4K -300K and the MR was measured in the range 1.5K- 30K in a field of up to 6 Tesla.

III. RESULTS AND DISCUSSION

In figure 1 we present the resistivity measurements for the three samples with the general formula LaNiO\(_{3-\delta}\). We identify the samples in decreasing order of \(\delta\) and have called them
A, B and C for $\delta = 0.14, 0.08$ and $0.02$ respectively. For all the samples the $\rho(T)$ curve show a metallic behaviour although the residual resistivity $\rho_0$ increases by a factor of 30 as $\delta$ changes from 0.02 to 0.14. We restrict our investigations to $\delta \leq 0.14$ to avoid any complications arising from magnetic clusters which appear for $\delta \geq 0.2$ [10].

For the sample with $\delta = 0.14$ which has the highest $\rho_0$ the mean free path ($\ell_{el}$), estimated from the simple free electron approximation, is somewhat smaller than the Ni-O bond length ($\approx 2\text{Å}$). Interestingly, it can be seen that for this sample there is a resistivity minima around 20K. This is very similar to the behavior of highly disordered metallic alloys.

The exact temperature dependence of $\rho(T)$ in LaNiO$_{3-\delta}$ with varying $\delta$ has been critically looked into [13]. We do not discuss these in detail here. We just mention that in the samples B and C which show no resistivity minima we have a power law dependence of the resistivity with $T$ given as [13]:

$$\rho(T) = \rho_0 + \alpha T^{1.5} + \beta f(T)$$

where $f(T)$ is the function giving a linear temperature dependence at high temperature ($T \gtrsim 200\text{K}$) and a $T^n$ ($n \geq 2$) dependence for low temperatures. $\rho_0$ is the residual resistivity and $\alpha$ and $\beta$ are constants. For the sample A, which shows the highest resistivity, we have a resistivity minima at $T_{min} = 20\text{K}$ and $\rho(T)$ for $T < T_{min}$ shows a shallow rise (see figure 1). We find that this shallow rise of $\rho$ below $T_{min}$ can be best accounted for by using expressions for weak localization (WL). We also find below that the MR measurements supports this view. We quantify the weak localization [14] contribution by an additional term $-\gamma T^{0.75}$ which is incorporated into eqn. [1]. Thus, we fit the resistivity of sample A using the expression

$$\rho = \rho_0 - \gamma T^{0.75} + \alpha T^{1.5} + \beta f(T)$$

We find that this relation fits the resitivity curve with an error better than $\pm 0.5\%$ over the entire temperature range. The fits for the samples are shown as a solid line in figure 1.

In figure 2 we show the MR of the three samples as a function of the applied field $H$ at $T = 4.2\text{K}$. We define the MR as $\Delta \rho/\rho_{0H} = (\rho(H) - \rho(0))/\rho_{0H}$, where $\rho_{0H}$ for the zero
field resistivity at a given temperature T. The magnetoresistance of the LaNiO$_{3-\delta}$ system is small but has a distinct dependence on the oxygen stoichiometry. It is positive for the least resistive sample C, it is negative for sample A which has the highest resistivity and it is almost zero (\textless 0.05\%) for sample B with intermediate resistivity. The MR thus becomes progressively negative as the resistivity increases.

The field dependence of MR also changes as \(\delta\) increases. For sample C, MR has a quadratic dependence on H which is shown in figure 3. The MR seems to follow Köhler rule \[15\]. The MR for this sample is positive at all T. According to Koehler rule the dependence of MR on temperature, magnetic field and purity of the sample should be a function of \(H\tau\) only, where \(\tau\) is the relaxation time. Since \(\rho_{0H} \propto \tau^{-1}\), \(\Delta \rho /\rho_{0H} \propto k(H/\rho_{0H})\), where \(k(H/\rho_{0H})\) is a function of \(H/\rho_{0H}\). For normal metals the MR shows a quadratic dependence with field due to the band MR. Hence we can write:

\[
\frac{\Delta \rho}{\rho_{0H}} = \beta_\rho \left(\frac{H}{\rho_{0H}}\right)^2
\]

where, \(\beta_\rho\) is a constant for the material. Fitting the MR of sample C with the above expression we get \(\beta_\rho = 3.98 \times 10^{-12}\) (\(\Omega\text{cm/T}\))^2. For normal metals the value of \(\beta_\rho \approx 10^{-15}\) (\(\Omega\text{cm/T}\))^2. This difference is very interesting because if the positive MR indeed arises from a band mechanism then it is one of the largest MR arising from the band mechanism. It will be of interest to compare the MR of this oxide with other oxides showing positive MR \[4,5\]. The other known metallic oxides showing positive MR, Sr$_x$NbO$_3$ (\(x \leq 0.8\)) \[3\] and Na$_{0.9}$WO$_3$ \[3\] shows a \(H^2\) dependence over a small field range (\(H \leq 3\) Tesla). The values of \(\beta_\rho\) for Sr$_{0.85}$NbO$_3$ (\(\rho_{4.2K} = 1.75\text{m}\Omega\text{cm}\)) and Na$_{0.9}$WO$_3$ (\(\rho_{4.2K} = 3\mu\Omega\text{cm}\)) are 1.127\times 10^{-9} (\(\Omega\text{cm/T}\))^2 and 4\times 10^{-15} (\(\Omega\text{cm/T}\))^2 respectively. It seems therefore in these oxides the constant \(\beta_\rho\) increases as \(\rho\) increases. This observation needs more investigation to establish whether this indeed is a general feature of metallic oxides.

For sample A the MR is not only negative, the field dependence is also qualitatively different. We will show below that it is possible to explain the field dependence of the negative MR as arising from destruction of weak localisation on application of magnetic
field. For sample B, the MR being almost zero we didn’t attempt any fit. Most likely for this sample we have almost equal contribution from both the positive and negative terms.

The temperature dependence of the MR also carries a distinct mark of the oxygen stoichiometry. As shown in figure 4, the MR of sample A is negative for \( T \leq T_{\text{min}} \) and positive for \( T > T_{\text{min}} \), where \( T_{\text{min}} \) is the temperature of resistivity minima (see figure 1). It has been discussed before that the resistivity minima can arise due to the contribution by WL for \( T \leq T_{\text{min}} \). For \( T > T_{\text{min}} \) the MR is positive as in sample C. For \( T \leq T_{\text{min}} \) the WL is suppressed by the application of the magnetic field and hence there will be a negative contribution to the MR. To look at this quantitatively we have fitted the magnetoconductance curves to the WL expression \[16,17\] with an additional \( H^2 \) term to account for the Köhler type negative magnetoconductance (or positive MR). In the following we used conductivity change \( (\delta \sigma) \) instead of resistivity change \( (\delta \rho) \) to follow the customary procedure for WL expressions. The expression thus used was \[17\]:

\[
\delta \sigma = \frac{e^2}{2\pi^2 \hbar} \left( \frac{eH}{\hbar} \right)^{1/2} \mathcal{H} \left( \frac{4D\tau\phi H}{\hbar} \right) - \beta_\sigma H^2
\]

(4)

where

\[
\mathcal{H}(x) = 2 \left[ \sqrt{2 + \frac{1}{x}} - \sqrt{\frac{1}{x}} \right] - \left( \frac{1}{2} + \frac{1}{x} \right)^{-1/2} - \left( \frac{3}{2} + \frac{1}{x} \right)^{-1/2} + \frac{1}{48} \left( 2.03 + \frac{1}{x} \right)^{-3/2}
\]

Here, \( D \) is the electron diffusivity, \( \tau_\phi \) is the electron phase relaxation time and \( \beta_\sigma \) is a constant. In this expression \( \beta_\sigma \) and \( D\tau_\phi \) can be free parameters. However, to restrict the number of free parameters we fixed the parameter \( \beta_\sigma \) following Köhler’s rule using the following strategy.

The Köhler’s rule (see eqn.3) expressed in terms of the conductivity is given by \( \delta \sigma_{\text{Köhler}} = -\beta_\sigma H^2 \) where \( \beta_\sigma = \beta_\rho / \rho_{0H}^3 \). Assuming the validity of the Köhler’s rule for the samples A and C would imply that both samples will have the same \( \beta_\rho \). Thus, using \( \beta_\rho \) as found from sample C in figure 3 we have estimated the value of \( \beta_\sigma \) for sample A. The values of \( \beta_\sigma \) for \( T \leq 4.2K \) are \( \approx 0.01 \) (S/cm)/T$^2$. Using these \( \beta_\sigma \) we fit the magnetoconductance data to eqn.4 using \( D\tau_\phi \) as the only fit parameter. A good fit can be obtained for the magnetoconductance data.
as shown in the inset of figure 4. The $D\tau_\phi$ values (fit parameters) for the two temperatures were obtained as $1.26\times10^{-12}$ cm$^2$ for $T=2.3$K and $1.12\times10^{-12}$ cm$^2$ for $T=4.2$K. Using the above values of $D\tau_\phi$, we have estimated the value of the WL correction to the zero field conductivity of the sample. We get $\delta\sigma_{WL} \approx (e^2/2\pi^2\hbar)(1/\sqrt{D\tau_\phi})$ to be about 12.3 S/cm which is about a factor of 2.5 more than that estimated from the resistivity data of this sample at low temperature ($\approx 4.8$ S/cm). Within the limits of experimental error we can say that this is a good agreement since, the estimate of $\delta\sigma_{WL}$ from the resistivity involves some uncertainties because of the presence of other terms with much larger contributions (see eqn. 2). Also we have only an approximate value for $\beta_\sigma$. We can thus conclude that the negative MR seen in this oxide can arise from the weak localization contribution. At $T=25$ K the positive contribution wins over. But given the smallness of MR it is difficult to obtain any meaningful fit.

One important effect that we should address is the formation of local magnetic moments and any ferromagnetic interaction arising from it which can give rise to negative MR. While stoichiometric LaNiO$_3$ is a Pauli paramagnet, creation of Ni$^{2+}$ ions in oxygen deficient samples can lead to a Curie-Weiss type contribution. We have measured the susceptibility for sample A. The susceptibility and the analysis are reported in ref.[13]. We mention the important results, since they are relevant to this paper. For $T_1100$K we could fit the susceptibility to $\chi = \chi_0 + C/(T-\theta)$. A fit to the expression gives $\chi_0 = 5.95\times10^{-6}$ emu/gm, $\theta = -51$ K and $C = 3.83\times10^{-4}$ emu K/gm. The large value of $C$ can arise from the Ni$^{2+}$ formation as $\delta$ increases [13]. For sample A, for which $\delta = 0.14$, about 30% of the Ni in the system is in the Ni$^{2+}$ state. However, not all of the Ni$^{2+}$ carry moments because part of the Ni$^{2+}$ which are in square planar coordination are diamagnetic. Though there is a net small antiferromagnetic interaction ($\theta \approx -51$ K), the susceptibility shows no sign of any magnetic ordering or cluster formation. It can be contrasted to the composition LaNiO$_{2.75}$ which shows the transition to an insulating state and a clear signature of a spin-glass or cluster glass like transition near 150K [10]. From these observations we conclude that the magnetic interactions will not play an important role for the MR of the samples ($\delta \leq 0.14$)
which we have investigated. It may be that for $\delta \geq 0.2$ the cluster formation can lead to MR dominated by magnetic interaction effects.

In summary, we have measured the magnetoresistance of the metallic perovskite oxide LaNiO$_{3-\delta}$ as a function of the oxygen defect $\delta$. The most metallic sample has a clear positive MR which progressively goes to the negative magnitude as the oxygen defect increases. The positive MR seems to arise from a band-like contribution as seen in normal metals but the magnitude is much larger than that seen in conventional metals. The negative MR seen in the oxygen deficient sample arises from weak-localisation contribution and is not due to any magnetic interactions. Our experiment shows that the effects like weak-localisation of electrons can lead to small but finite negative MR in these oxides which may be masked by stronger negative MR arising from magnetic origin in other oxides.

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**FIGURE CAPTIONS**

**Figure 1** Resistivities ($\rho$) of the three samples of LaNiO$_{3-\delta}$. The samples A, B & C have $\delta = 0.14$, 0.08 and 0.02 respectively. The line shows the fit discussed in the text (see eqns[] and []).

**Figure 2** Magnetoresistance (MR) as a function of field (H) for the three samples A,B and C at T=4.2K. $\rho_{0H}$ is the zero field resistivity.

**Figure 3** MR as a function of $H^2$ for sample C at T=4.2K.

**Figure 4** Magnetoresistance as a function of field for Sample A for three different temperatures 2.3K and 4.2K ($T_\uparrow T_{min}$) and 25K ($T_\downarrow T_{min}$). **Inset:** Fit of the data to the MR relation for weak localisation for $T_\uparrow T_{min}$ (plotted as conductivity $\delta \sigma$).
LaNiO$_{3-\delta}$

\[ \rho/\rho_{0.4K} \]

Temperature (K)

A = 3396 \mu\Omega cm
B = 512 \mu\Omega cm
C = 129 \mu\Omega cm
LaNiO$_{3-\delta}$

$\Delta \rho / \rho_{0\text{H}}$ (%)

$H$ (Tesla)

$T = 4.2$K

$\rho_{0\text{H}} = 130 \mu \Omega \text{cm}$

$\rho_{0\text{H}} = 512 \mu \Omega \text{cm}$

$\rho_{0\text{H}} = 3377 \mu \Omega \text{cm}$
