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

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

1. Introduction

In recent years the electrical conduction in transition metal perovskite oxides at low temperature has attracted considerable research interest [1]. Most of the 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 manganates belonging to the ABO_3 class has added yet another new phenomenon [2]. These oxides have chemical formulae of the type $\text{La}_{1-x}(\text{Sr}/\text{Ca})_x\text{MnO}_3$ with $x \approx 0.2$ – 0.4 . The colossal *negative* MR seen in these oxides have become a focus of intense research activity. In these mixed-valence 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. An additional important contribution to the CMR phenomenon comes from the strong Jahn–Teller effect of the Mn^{3+} ions. In a closely related compound $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (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 of these oxides the electron is on the verge of becoming localized. On the other hand there are metallic oxides also belonging to the ABO_3 class like Sr_xNbO_3 ($x \geq 0.75$) [4] and $\text{Na}_{0.9}\text{WO}_3$ [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 seem to be as regards the extent of the electron localization and the presence of ferromagnetic interactions. This leads us to the following interesting question: *if we start with a metallic perovskite oxide*

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showing positive MR and gradually make the electrons localized (by some means), will the positive MR change to a negative MR as the electrons become localized? We investigate this question for the metallic perovskite $\text{LaNiO}_{3-\delta}$, for which we find that the MR changes from positive to negative as the material is made more resistive by increasing δ . LaNiO_3 , belonging to the ABO_3 class, is structurally similar to LaCoO_3 and LaMnO_3 . 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 $\delta > 0.25$ [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 the electronic transport without bringing in strong magnetic effects at least for $\delta \leq 0.2$.

LaNiO_3 is an interesting material because of its potential application as metallic interconnects (or electrodes) in thin-film oxide electronics, particularly those needing epitaxial multilayer perovskite oxide films [11]. The MR data for this oxide will thus be of importance technologically.

2. Experimental details

The samples of $\text{LaNiO}_{3-\delta}$ were prepared by co-precipitation and subsequent decomposition of nitrates of La and Ni as described in references [8] and [12]. The samples were heat treated under different oxygen atmospheres to produce varying oxygen contents and the oxygen stoichiometry δ was determined by iodometric titration. The grain sizes as measured by a scanning electron microscope were typically of the order of $2 \mu\text{m}$ and there was no variation in the grain sizes of the samples with different values of δ . We will see that all of the relevant length scales are less than the grain size. (See reference [13] for details of the sample preparation and characterization.)

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 ± 10 ppm. The resistivity was measured over the range 0.4 K–300 K and the MR was measured over the range 1.5 K–30 K in a field of up to 6 T.

3. Results and discussion

In figure 1 we present the resistivity measurements for the three samples with the general formula $\text{LaNiO}_{3-\delta}$. We identify the samples in decreasing order of δ and have called them A, B and C for $\delta = 0.14, 0.08$ and 0.02 respectively. For all of the samples the $\rho(T)$ curve shows a metallic behaviour although the residual resistivity ρ_0 increases by a factor of 30 as δ 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 ρ_0 , the mean free path (ℓ_{el}), estimated from the simple free-electron approximation, is somewhat smaller than the Ni–O bond length ($\approx 2 \text{ \AA}$). Interestingly, it can be seen that for this sample there is a resistivity minimum at around 20 K. This is very similar to the behaviour of highly disordered metallic alloys.

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

$$\rho(T) = \rho_0 + \alpha T^{1.5} + \beta f(T) \quad (1)$$

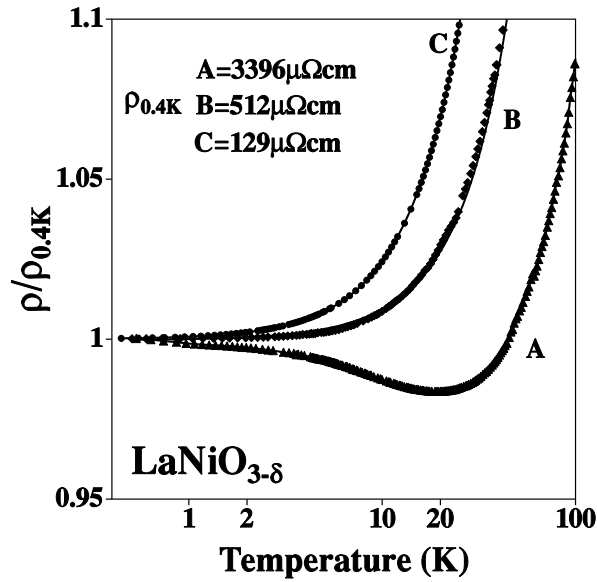


Figure 1. The resistivities (ρ) of the three samples of $\text{LaNiO}_{3-\delta}$. The samples A, B and C have $\delta = 0.14, 0.08$ and 0.02 respectively. The curves show the fit discussed in the text (see equations (1) and (2)).

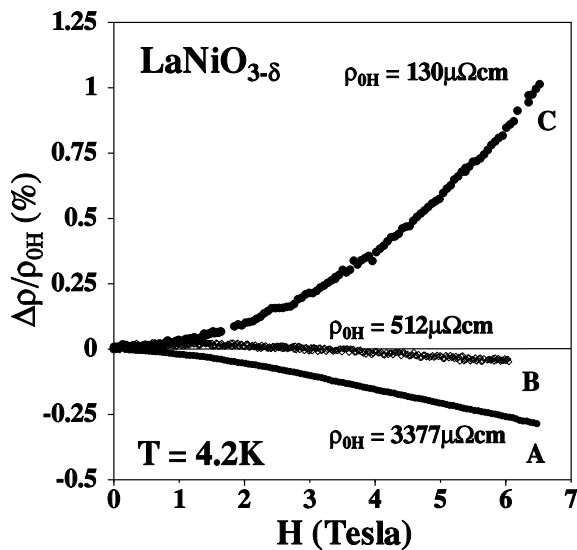


Figure 2. The magnetoresistance (MR) as a function of the field (H) for the three samples A, B and C at $T = 4.2$ K. ρ_{0H} is the zero-field resistivity.

where $f(T)$ is a function giving a linear temperature dependence at high temperature ($T > 200$ K) and a T^n -dependence ($n \geq 2$) for low temperatures. ρ_0 is the residual resistivity and α and β are constants. The $T^{1.5}$ -term is necessary for all of the samples. This term implies that the power-law dependence exponent is greater than unity even at the highest temperatures and the simple $f(T)$ is not adequate to fit the data. Such a strong power-law dependence can

arise due to optical phonons in the system. The significance of this term has been discussed in depth in reference [13].

For sample A, which shows the highest resistivity, we have a resistivity minimum at $T_{min} = 20$ K and $\rho(T)$ for $T < T_{min}$ shows a shallow rise (see figure 1). We find that this shallow rise of ρ below T_{min} can be best accounted for by using expressions for weak localization (WL). We also find below that the MR measurements support this view. We quantify the weak-localization [14] contribution by an additional term $-\gamma T^{0.75}$ which is incorporated into equation (1). This term implies that the weak-localization correction is in the presence of interaction in the dirty limit [14]. Thus, we fit the resistivity of sample A using the expression

$$\rho = \rho_0 - \gamma T^{0.75} + \alpha T^{1.5} + \beta f(T). \quad (2)$$

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

In figure 2 we show the MR of the three samples as functions of the applied field H at $T = 4.2$ K. We define the MR as $\Delta\rho/\rho_{0H} = (\rho(H) - \rho(0))/\rho_{0H}$, where ρ_{0H} is the zero-field resistivity at a given temperature T . The magnetoresistance of the $\text{LaNiO}_{3-\delta}$ 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 ($< 0.05\%$) for sample B with intermediate resistivity. The MR thus progressively moves towards negative values as the resistivity increases.

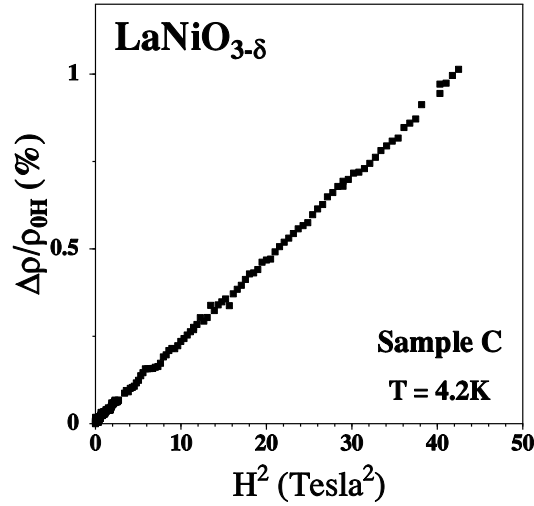


Figure 3. The MR as a function of H^2 for sample C at $T = 4.2$ K.

The field dependence of the MR also changes as δ increases. For sample C, the MR has a quadratic dependence on H which is shown in figure 3. The MR seems to follow Köhler's rule [15]. The MR for this sample is positive at all T . According to Köhler's rule the dependence of the MR on the temperature, magnetic field and purity of the sample should be a function of $H\tau$ only, where τ 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/ρ_{0H} . For normal metals the MR shows a quadratic dependence on the field due to the band MR. Hence we can write

$$\frac{\Delta\rho}{\rho_{0H}} = \beta_\rho \left(\frac{H}{\rho_{0H}} \right)^2 \quad (3)$$

where β_ρ is a constant for the material. Fitting the MR of sample C with the above expression we get $\beta_\rho = 3.98 \times 10^{-12} \Omega^2 \text{cm}^2 \text{T}^{-2}$. For normal metals the value of $\beta_\rho \approx 10^{-15} \Omega^2 \text{cm}^2 \text{T}^{-2}$. This difference is very interesting because if the positive MR does indeed arise from a band mechanism, then it is one of the largest MR arising from a band mechanism. It will be of interest to compare the MR of this oxide with those of other oxides showing positive MR [4, 5]. The other known metallic oxides showing positive MR, Sr_xNbO_3 ($x \leq 0.8$) [4] and $\text{Na}_{0.9}\text{WO}_3$ [5], show H^2 -dependence over a small field range ($H \leq 3$ T). The values of β_ρ for $\text{Sr}_{0.85}\text{NbO}_3$ ($\rho_{4.2\text{K}} = 1.75 \text{ m}\Omega \text{cm}$) and $\text{Na}_{0.9}\text{WO}_3$ ($\rho_{4.2\text{K}} = 3 \mu\Omega \text{cm}$) are $1.127 \times 10^{-9} \Omega^2 \text{cm}^2 \text{T}^{-2}$ and $4 \times 10^{-15} \Omega^2 \text{cm}^2 \text{T}^{-2}$ respectively. It seems therefore that for these oxides the constant β_ρ increases as ρ increases. This observation needs more investigation to establish whether this is indeed a general feature of metallic oxides.

For sample A not only is the MR negative, but also the field dependence is qualitatively different. We will show below that it is possible to explain the field dependence of the negative MR as arising from the destruction of the weak localization on application of a magnetic field. For sample B, as the MR is almost zero we did not attempt any fit. Most probably for this sample the contributions from the positive and negative terms are almost equal.

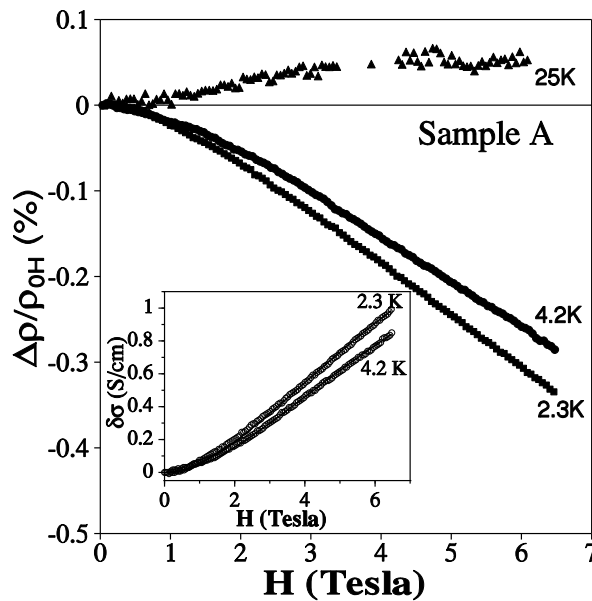


Figure 4. The magnetoresistance as a function of the field for sample A for three different temperatures: 2.3 K and 4.2 K ($T < T_{min}$) and 25 K ($T > T_{min}$). *Inset:* the fit of the data to the MR relation for weak localization for $T < T_{min}$ (plotted as the conductivity, $\Delta\sigma$).

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 $T < T_{min}$ and positive for $T > T_{min}$, where T_{min} is the temperature of the resistivity minimum (see figure 1). It has been discussed before that the resistivity minima can arise due to the contribution from WL for $T < T_{min}$. For $T > T_{min}$ the MR is positive as in sample C. For $T < T_{min}$ 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 the conductivity

change ($\delta\sigma$) instead of the resistivity change ($\delta\rho$), following the customary procedure for WL expressions. The expression thus used was [17]

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

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, τ_ϕ is the electron phase relaxation time and β_σ is a constant. In this expression β_σ and $D\tau_\phi$ can be free parameters. However, to restrict the number of free parameters we fixed the parameter β_σ following Köhler's rule using the following strategy.

Köhler's rule (see equation (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 the two samples will have the same value of β_ρ . Thus, using β_ρ as found from sample C in figure 3 we have estimated the value of β_σ for sample A. The values of β_σ for $T \leq 4.2$ K are ≈ 0.01 S cm⁻¹ T⁻². Using these values of β_σ we fit the magnetoconductance data to equation (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 values of $D\tau_\phi$ (fit parameters) for the two temperatures were obtained as 3.26×10^{-11} cm² for $T = 2.3$ K and 1.21×10^{-11} cm² 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 $\delta\sigma_{\text{WL}} (\approx (e^2/2\pi^2\hbar)(1/\sqrt{D\tau_\phi}))$ to be about 3.53 S cm⁻¹ at 4.2 K. The value estimated from the resistivity data for the sample at 4.2 K is ≈ 2.79 S cm⁻¹. Within the limits of experimental error we can say that this is a good agreement since the estimation of $\delta\sigma_{\text{WL}}$ from the resistivity involves some uncertainties because of the presence of other terms making much larger contributions (see equation (2)). Also we have only an approximate value for β_σ . 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 the MR it is difficult to obtain any meaningful fit.

The presence of local magnetic moments can give rise to spin-flip scattering. The spin-flip scattering in the presence of a magnetic field is suppressed, giving rise to a negative MR. It is thus important to rule out the formation of magnetic moments. While stoichiometric LaNiO₃ is a Pauli paramagnet, creation of Ni²⁺ 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 reference [13]. We mention the important results, since they are relevant to this paper. For $T < 100$ K we could fit the susceptibility to $\chi = \chi_0 + C/(T - \theta)$. A fit to this expression gives $\chi_0 = 5.95 \times 10^{-6}$ emu g⁻¹, $\theta = -51$ K and $C = 3.83 \times 10^{-4}$ emu K g⁻¹. The large value of C can arise from Ni²⁺ formation as δ increases [13]. For sample A, for which $\delta = 0.14$, about 30% of the Ni in the system is in the Ni²⁺ state. However, not all of the Ni²⁺ carry moments because some of the Ni²⁺ 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. This can be contrasted to the case for the composition LaNiO_{2.75} which shows a transition to an insulating state and a clear signature of a spin-glass-like or cluster-glass-like transition near 150 K [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 $\delta \geq 0.2$ cluster formation can lead to MR dominated by magnetic interaction effects.

In summary, we have measured the magnetoresistance of the metallic perovskite oxide $\text{LaNiO}_{3-\delta}$ as a function of the oxygen stoichiometry δ . The most metallic sample has a clear positive MR which progressively becomes negative as the oxygen deficiency increases. The positive MR may 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 the weak-localization contribution and is not due to any magnetic interactions. Our experiment shows that effects like weak localization of electrons can lead to small but finite negative MR in these oxides which may be masked by the stronger negative MR arising from magnetic origins in other oxides.

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