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Resisitivity, thermopower, and susceptibility of RNiO$_3$ (R =La,Pr)

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We report the resistivity, thermopower, and dc susceptibility of $R\mathrm{NiO}_3$ (R=La,Pr) ceramic samples for $1.4\ \mathrm{K} \leq T \leq 300$ K. The resistivity of LaNiO$_3$ shows a T^2 dependence below 80 K and changes over to a $T^{1.5}$ dependence at higher temperature (100–300 K). The resistivity of PrNiO$_3$ exhibits a metal-insulator transition at $T_{\mathrm{MI}}=130$ K with a linear temperature dependence above T_{MI}. The thermopower of both LaNiO$_3$ and PrNiO$_3$ is linear and negative in the metallic region. The susceptibility of LaNiO$_3$ is Pauli-like with a Curie-Weiss contribution at low temperature. The Pauli term is enhanced well above the free-electron value. Our samples have smaller resistivity and larger resistivity ratio than previously reported. Thermogravimetric analysis shows that there is excess oxygen ($\delta > 0$) in our samples of LaNiO$_{3+\delta}$, which suggests that the oxygen content of LaNiO$_3$ is important for its physical properties.

I. INTRODUCTION

Transition-metal (TM) perovskite oxides ($AB\mathrm{O}_3$) have been studied extensively in the past[1,2] because of their simple cubic structure and the occurrence of interesting and unusual physical properties. The discovery of high-temperature superconducting copper oxides[3] has drawn new interest to noncopper oxides, as studies of other oxides may give insight which will contribute to the understanding of high-temperature superconductivity. Most TM perovskite oxides are insulating, a few are metals, and others are known to exhibit a metal-insulator (MI) transition as a function of temperature or pressure.[4] Torrance *et al.*[5] used the idea proposed by Zaanen, Sawatzky, and Allen[6] and a simple ionic model to suggest why some oxides are metals while most are insulators. However, the origin of the metal-insulator transition is not well understood in most cases. Detailed transport studies of the perovskite oxides may help us to understand the anomalous normal-state properties of oxide superconductors and to explain why superconductivity occurs in copper oxides but not other oxides similar to it.

One perovskite oxide, LaNiO$_3$, best known among nickelates, has been studied in some detail before.[7–11] It is rhombohedrically distorted in structure and known to be a metal.[8] The nominal electronic structure of Ni^{3+} is $t_{2g}{}^6 e_g^1$. The t_{2g} levels are filled and the conduction band σ^* is formed by the hybridization of low-spin nickel e_g orbitals and oxygen $2p$ orbitals. In this simple picture the antibonding σ^* conduction band would be one-quarter filled. There have been some resistivity measurements of LaNiO$_3$ recently.[10,11] Both showed large room-temperature resistivity ($\sim 1.6\ \mathrm{M}\Omega$) and residual resistivity ($\sim 0.5\ \mathrm{M}\Omega$). A resistivity upturn was observed[10] at low temperature which was attributed to the electron-electron interaction in a disordered system. An earlier susceptibility measurement[9] of LaNiO$_3$ showed Pauli paramagnetism that is anomalously higher than that expected from a simple band model. This, together with the enhanced linear term in the heat capacity,[10,11] suggests that the conduction electrons are highly correlated.

On the other hand, PrNiO$_3$ is a relatively new material that was recently synthesized.[12] It has a smaller ionic radius than that of La and therefore a more distorted structure. It exhibits a metal-insulator transition near 130 K with a temperature hysteresis.[12] However, rather few measurements have been done on it because of the difficulty in synthesizing the material. In this RNiO$_3$ system, distortion occurs since the size of the rare earth is too small to form a cubic structure. NiO$_6$ octahedra tilt and rotate to fill the extra space otherwise occupied by a larger ion. According to a recent neutron-scattering experiment[13] a small distortion like the one in LaNiO$_3$ will result in rhombohedral symmetry while a larger distortion will produce an orthorhombic structure as in the case of PrNiO$_3$. It was suggested by Torrance *et al.*[14] that the metal-insulator transition in PrNiO$_3$ is of a charge-transfer type, in which the charge-transfer gap Δ is smaller than the Coulomb correlation energy U. However this metal-insulator transition is complicated by an antiferromagnetic ordering of the Ni ions at the same temperature.[14] It appears that the origin of this transition is still not completely determined.

The oxygen content has never been directly determined in LaNiO$_3$. A recent paper[15] showed that the nickel ions in LaNiO$_3$ synthesized by the conventional method have mixed valences of Ni^{2+} and Ni^{3+}, or alternatively, that there are oxygen vacancies in these LaNiO$_3$ samples. Oxygen stoichiometry has always been an important factor, not only in the properties of the copper oxides, but also in other oxides (for example, LaTiO$_x$).[16] Since LaNiO$_3$ and PrNiO$_3$ can be synthesized under various conditions which result in different oxygen content, it is important to relate their electronic properties with their oxygen content.

In this paper, we have made a systematic investigation of the properties of LaNiO$_3$ and PrNiO$_3$ by measuring resistivity, thermopower, and dc susceptibility on ceramic samples that are synthesized using O$_2$ pressure and high temperature. Our new measurements on PrNiO$_3$ show a similar magnitude of resistivity and thermopower to that of $LaNiO_3$ in the metallic state. However the linear T dependence of ρ in $PrNiO_3$ is different from the $T^{1.5}$ dependence found in $LaNiO_3$, which may suggest different electron-scattering mechanisms in these two compounds. The Pauli paramagnetic susceptibility of $PrNiO_3$ is larger than that of $LaNiO_3$. This is consistent with a suggestion[14] that the bandwidth of $LaNiO_3$ may be larger than that of $PrNiO_3$.

II. EXPERIMENT

The samples of RNiO$_3$ (R = La,Pr) were prepared by dissolving La_2O_3/Pr_6O_{11} and NiO in concentrated nitric acid. The excess nitric acid was removed by heating it to 200 °C in air. The remaining intimately mixed nitrates were green in color and decomposed to black powder at 450 °C in air. After grinding, the black powder was heated at 650 °C in an O_2 atmosphere for about 24 h. After a second grinding, the powder was pressed into small pellets. The pellets were then fired at 1000 °C for about 70 h under 195 bars of oxygen. The x-ray powder diffraction patterns of RNiO$_3$ indicated a single phase within the resolution of the x ray (3–5%). In a hexagonal unit cell, the lattice parameters for $LaNiO_3$ are $a_{\mathrm{hex}}=5.453$ Å and $c_{\mathrm{hex}}=13.122$ Å. This is close to previous reports.[9,11] For $PrNiO_3$, the orthorhombic lattice parameters are $a=5.405$ Å, $b=5.393$ Å, and $c=7.633$ Å. These parameters are also similar to earlier data.[13] The resistivity ρ was measured using a four-probe method on bar-shaped ceramic samples. The thermopower S was measured by a slow ac method[17] and the dc susceptibility was done using a Quantum Design SQUID magnetometer. All electrical contacts for resistivity and thermopower measurements were made with silver paste without any heat treatment. The contact resistance was usually less than 20 Ω for one pair of contacts. We used thermogravimetric analysis (TGA) to determine the oxygen content in $LaNiO_{3+\delta}$. The TGA was carried out by flowing forming gas (6% H_2, 94% N_2) through the sample chamber. Under H_2 atmosphere, the $LaNiO_{3+\delta}$ ceramics were easily decomposed into La_2O_3 and Ni by high-temperature annealing. The reduction reaction is as follows:[19]

$$2LaNiO_{3+\delta}+(3+2\delta)H_2 \rightarrow La_2O_3+Ni+(3+2\delta)H_2O \; . \tag{1}$$

The final products La_2O_3 and Ni were identified by x-ray powder diffraction. No trace of any other phase was seen within the resolution of x-ray diffraction. We ramped the temperature from room temperature to 950 °C at a rate of 10 °C/min. Using the value of initial weight (m_i) and final weight (m_f) and the above equation, we calculated δ. TGA experiments were performed on two samples of $LaNiO_{3+\delta}$ with $\delta \approx 0.2 \pm 0.03$ in one sample and $\delta = 0.23 \pm 0.03$ in the other. This means, instead of possibly having oxygen vacancies as in samples published earlier,[15] we have excess oxygen in our samples of $LaNiO_{3+\delta}$. This is probably due to our synthesis method which uses a high synthesis temperature and a high oxygen pressure. A TGA was also performed on $PrNiO_3$. Not all of the final products of this process could be identified by x-ray diffraction and therefore we cannot estimate the oxygen content in $PrNiO_3$ at this time. Other techniques, e.g., chemical analysis methods will be tried in the future.

III. RESULTS

Figure 1 shows ρ vs T for $LaNiO_3$ and $PrNiO_3$ ceramic samples for $4.2 \mathrm{~K} < T < 300 \mathrm{~K}$. Two ceramic samples of $LaNiO_3$ were measured and they exhibit metallic conductivity for the entire measured temperature range. Their resistivity is nonlinear even at room temperature. At lower temperatures ρ saturates to a constant value near 4.2 K. The room-temperature resistivity is 380 $\mu\Omega$ cm. Since the density of the ceramic sample that we measured is about 60% that of a crystal, the intrinsic ρ is lower (≈ 320 $\mu\Omega$ cm). In addition we find $\rho_{300 \mathrm{~K}}/\rho_{4 \mathrm{~K}} \approx 11$. We can analyze the resistivity data in two regions. At low temperature ($T < 80$ K), as shown in Fig. 2, ρ fits to the following equation:

$$\rho(T) = A + BT^2 \; , \tag{2}$$

with $A = 34.1$ $\mu\Omega$ cm and $B = 6.14 \times 10^{-3}$ $\mu\Omega \mathrm{~cm/K}^2$. Here A is the residual resistivity at low temperature and the T^2 term is possibly due to electron-electron scattering. At higher temperatures, from 100 to 300 K, ρ follows a simple power law, $\rho = A' + B'T^{1.5}$, where $A' = 22.0$ $\mu\Omega$ cm and $B' = 6.93 \times 10^{-2}$ $\mu\Omega \mathrm{~cm/K}^{3/2}$. The fit is shown in Fig. 3. The origin of this temperature dependence is still unknown.

The resistivity for $PrNiO_3$, also shown in Fig. 1, is metalliclike with a *linear* temperature dependence between 300 and 130 K with $(1/\rho)(d\rho/dT) = 3.6 \times 10^{-3}$ K^{-1}. The *linear* resistivity extrapolates close to the origin, similar to that of the normal state of some high-T_c oxides

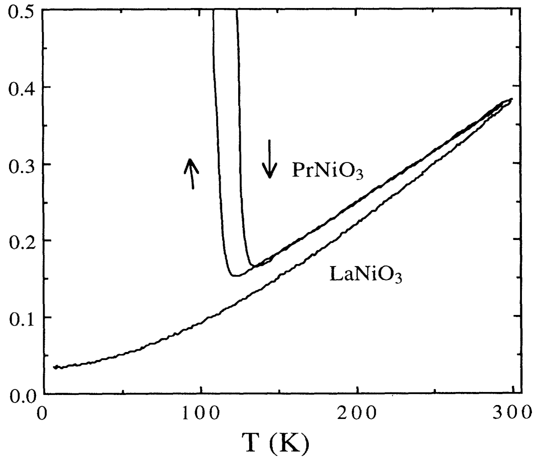

FIG. 1. Resistivity vs temperature for $LaNiO_3$ and $PrNiO_3$ ceramic samples. The temperature hysteresis for $PrNiO_3$ is also seen in the thermopower (see Fig. 4).

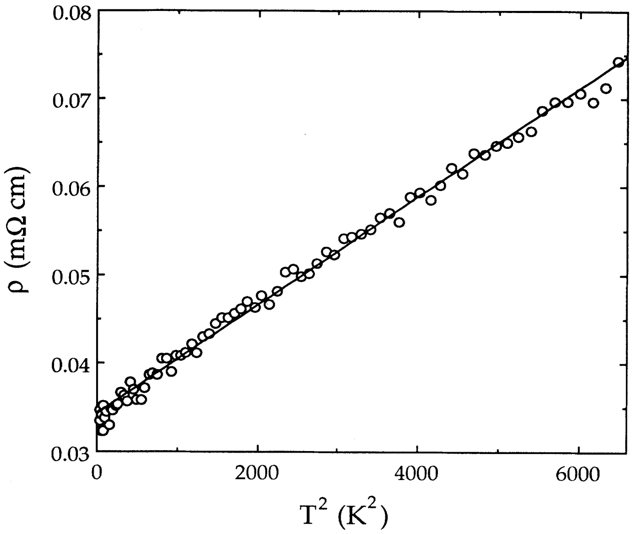

FIG. 2. Resistivity vs T^2 for a $LaNiO_3$ ceramic sample below 80 K. The solid line is the best fit to $\rho = A + BT^2$; $A = 34.1$ μΩ cm; $B = 6.14 \times 10^{-3}$ μΩ cm/ K^2.

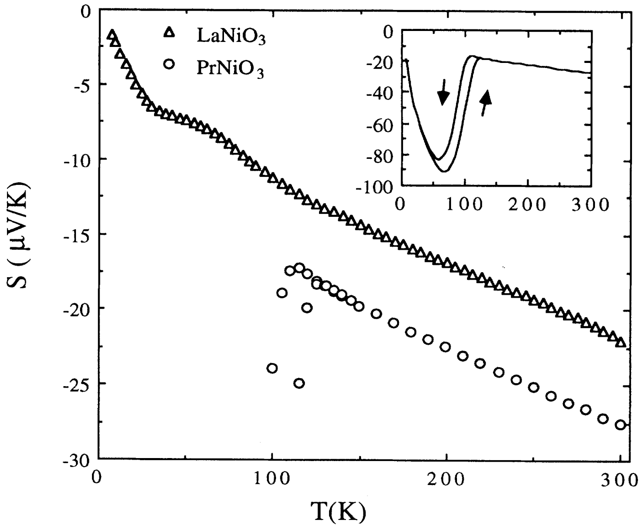

FIG. 4. Thermopower vs temperature for $LaNiO_3$ and $PrNiO_3$ ceramic samples. Inset: S vs T of $PrNiO_3$ for the entire measured temperature range.

like Y-Ba-Cu-O. We measure the metal-insulator transition temperature T_{MI} when the sample is warmed from 4.2 K. At $T_{MI} = 130$ K, we find a metal-insulator transition and a large temperature hysteresis is observed.

The thermopower (S) of $LaNiO_3$ and $PrNiO_3$ between 4 and 300 K is shown in Fig. 4. Both show a linear and negative T dependence above 130 K, typical of metals. A negative thermopower suggests *electronlike* carriers in both samples. The S of $LaNiO_3$ shows a small kink around 30 K, possibly caused by phonon drag. The S of $PrNiO_3$ shows a metal-insulator transition at the same temperature as the resistivity measurement. A hysteresis in S is also observed as shown in the inset. The implications of these new transport data will be discussed later.

Figure 5(a) shows the dc magnetic susceptibility of $LaNiO_3$ which is positive and almost constant at high temperature. It can be fit by the form $\chi = \chi_0 + C/(T - \theta)$, where χ_0 is a temperature-independent contribution, θ is the Curie-Weiss tempera-

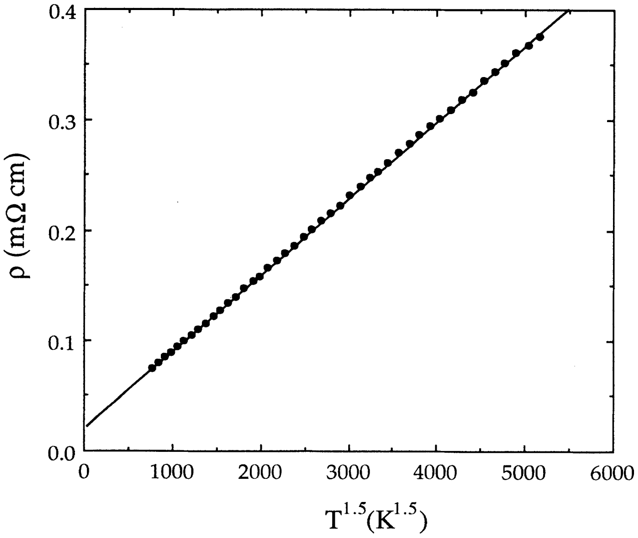

FIG. 3. Resistivity vs $T^{1.5}$ for $LaNiO_3$ from 100 to 300 K. The solid line is the best fit to $\rho = A' + B'T^{1.5}$; $A' = 22.0$ μΩ cm; $B' = 6.93 \times 10^{-2}$ μΩ cm/$K^{3/2}$.

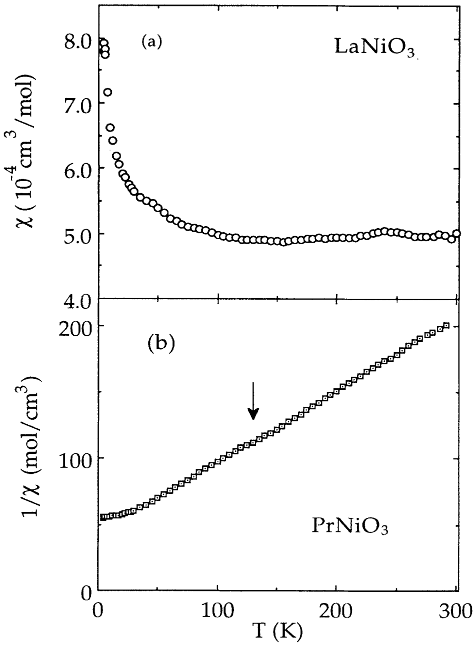

FIG. 5. (a) Susceptibility vs temperature for a $LaNiO_3$ ceramic sample. (b) $1/\chi$ vs temperature for a $PrNiO_3$ ceramic sample. The arrow indicates the metal-insulator transition temperature.

ture, and C is the Curie constant. A least-square fit gives $\chi_0=4.9\times 10^{-4}$ cm^3/mol, $\theta=-4.6$ K, and $C=2.5\times 10^{-3}$ cm^{3}K/mol. From the Curie constant we can estimate the density of magnetic impurities. Assuming the impurities are spin-$\frac{1}{2}$ magnetic ions, the density of impurities is estimated to be 7.1×10^{19} cm^{-3}. This is much smaller than the density of electrons ($\sim 10^{22}$ cm^{-3}).

We analyze the rest of the susceptibility by writing the temperature-independent part χ_0 as follows:[19]

$$\chi_0=\chi^{\text{Core}}+\chi^{\text{Pauli}}+\chi^{\text{Landau}}+\chi^{\text{V.V.}}\ , \tag{3}$$

where χ^{Core} is the core diamagnetism term, χ^{Pauli} is the Pauli paramagnetism term due to the conduction electrons, χ^{Landau} is the diamagnetic orbital contribution due to the conduction electrons, and $\chi^{\text{V.V.}}$ is the Van Vleck susceptibility. The lack of knowledge about crystal-field energy-level splittings forces us to assume that any Van Vleck contribution is small and can be ignored. The core diamagnetism is estimated from tabulated values[18] for La^{3+}, Pr^{3+}, Ni^{2+}, and O^{2-}. By assuming that the core diamagnetic susceptibility of Ni^{2+} is equal to that of Ni^{3+}, we find $\chi^{\text{Core}}=-68\times 10^{-6}$ cm^3/mol. Representing the conduction-electron band effect by an effective mass m^* permits one to relate χ^{Pauli} to χ^{Landau} as follows:[19] $\chi^{\text{Landau}}=-(1/3)[m/m^*]^2\chi^{\text{Pauli}}$. Since the effective mass m^* is estimated[10] to be significantly greater than the free-electron mass m we can neglect χ^{Landau} and Eq. (3) is reduced to $\chi^{\text{Pauli}}=\chi_0-\chi^{\text{Core}}$. This yields an estimate for χ^{Pauli} of 5.6×10^{-4} cm^3/mol. This is very close (within about 10%) to a recent result[11] and about 60% of the value found earlier.[9] Using the relation $\chi^{\text{Pauli}}=\mu_{\text{B}}^2 N_b(E_F)$, where μ_{B} is the Bohr magneton, we find an experimental band-structure density of electron states $N_b(E_F)$ at the Fermi level (for both spin directions) of $N_b(E_F)\approx 1.8\times 10^{23}$ eV^{-1}cm^{-3}. From a band-structure calculation,[20] $N_b(E_F)$ is estimated to be $(0.55-1.1)\times 10^{22}$ eV^{-1}cm^{-3}. So the experimental density of states is significantly enhanced over the band-structure value suggesting strong correlations in this material.

Figure 5(b) shows the behavior of the inverse of the magnetic susceptibility of $\mathrm{PrNiO_3}$ as a function of temperature. Whereas the susceptibility of $\mathrm{LaNiO_3}$ is nearly temperature independent above 100 K, that of $\mathrm{PrNiO_3}$ is temperature dependent. The Pr^{3+} ions contribute to the total susceptibility paramagnetically. For $\mathrm{PrNiO_3}$, χ_{tot} can be written as $\chi_{\text{tot}}=\chi_0+\chi^{\mathrm{Ni}^{3+}}+\chi^{\mathrm{Pr}^{3+}}$, where χ_0 is the temperature-independent part, $\chi^{\mathrm{N}^{3+}}$ is the susceptibility of the Ni^{3+} ion and $\chi^{\mathrm{Pr}^{3+}}$ is that of the Pr^{3+} ion. We find a kink in $\chi(T)$ near the metal-insulator transition temperature T_{MI} (130 K) for $\mathrm{PrNiO_3}$ as shown by the arrow in Fig. 5(b). The data can be fitted in two separate regions (above T_{MI} and below T_{MI}). Using a Curie-Weiss law, the best-fit values of C, θ, and χ_0 above T_{MI} are 1.37 cm^3/mol, -33.7 K, and 7.4×10^{-4} cm^3/mol, respectively. In this temperature region, we expect $\chi^{\mathrm{Ni}^{3+}}$ to have a Pauli susceptibility contribution. By using the same analysis as for $\mathrm{LaNiO_3}$, we find a core diamagnetic susceptibility $\chi^{\text{Core}}=-68\times 10^{-6}$ cm^3/mol for $\mathrm{PrNiO_3}$. Then from Eq. (3) the estimated value of χ^{Pauli} for $T>T_{\text{MI}}$ is 8.7×10^{-4} cm^3/mol. In this temperature range, the paramagnetic contribution to the total susceptibility may come from the Pr^{3+} ions alone, i.e., $\chi^{\mathrm{Pr}^{3+}}$. Using the Curie constant C, we find the experimental effective moment to be 3.31 μ_{B}, which is nearly the same as the theoretical effective moment of 3.58 μ_{B} for the free ion Pr^{3+}. From the Pauli susceptibility, the density of states at Fermi level is estimated to be $N_b(E_F)=2.8\times 10^{23}$ eV^{-1}cm^{-3}, again significantly enhanced over the free-electron value.

Below T_{MI}, χ_0 should only come from the core diamagnetism, which is -68×10^{-6} cm^3/mol. We find the best-fit parameters of C and θ are 1.81 cm^3/mol and -76 K, respectively. The effective moment is 3.80 μ_{B}, which is larger than that above T_{MI} because now both Pr^{3+} and Ni^{3+} ions are contributing to the susceptibility. It should be noted here that the change of χ at T_{MI} is so small that a temperature hysteresis, if any, cannot be observed.

IV. DISCUSSION

Our resistivity results on $\mathrm{LaNiO_3}$ differ from earlier reports[10,11] in having a lower resistivity and a higher resistivity ratio ($\rho_{300}=380$ $\mu\Omega$ cm and $\rho_{300}/\rho_4\approx 11$). A T^2 dependence of the resistivity has been seen before[11] for $T<50$ K. Our data confirm that up to $T=80$ K. The T dependence of ρ was found to be linear at room temperature previously, however our new results show a change from T^2 at low temperature to $T^{1.5}$ at higher temperature. Further resistivity measurements need to be performed at higher temperatures to see if this $T^{1.5}$ dependence changes over to the usual T dependence expected for electron-phonon scattering.

Using a free-electron model we can roughly estimate the electron density of states at Fermi level $N_b(E_F)$ using an effective mass of $m^*=10m_e$ from the earlier specific-heat measurement[10] and with E_F estimated[21] from our thermopower data [from $S=-(\pi^2k_B^2T)/(3eE_F)$]. Here we have assumed that the mean free path l is independent of energy. For $\mathrm{LaNiO_3}$ we find $E_F\approx 0.50$ eV and $N_b(E_F)=1.1\times 10^{23}$ eV^{-1}cm^{-3}. This seems to agree well with the number obtained from our susceptibility measurement. A similar analysis has been done recently by others.[11]

We can calculate k_F for $\mathrm{LaNiO_3}$ using a free-electron model.[22] We find $k_Fl\approx 3.8$ at $T=300$ K and $k_Fl\approx 42$ at $T=4.2$ K, which is larger than a previous estimate ($k_Fl\approx 1$ at 300 K).[10] Most likely we have fewer oxygen vacancies or other defects in our samples and thus our samples have lower resistivity and a longer mean free path at low temperature.

It is interesting to compare the resistivity of $\mathrm{LaNiO_3}$ to $\mathrm{Nd_{1.85}Ce_{0.15}CuO_{4-\delta}}$. They have almost the same room-temperature resistivity (~ 400 $\mu\Omega$ cm) and a very similar temperature dependence. At low temperature, both can be fitted to the formula $\rho=A+BT^2$. The coefficients for a typical $\mathrm{Nd_{1.85}Ce_{0.15}CuO_{4-\delta}}$ crystal[17] are $A=40$ $\mu\Omega$ cm and $B=4.0\times 10^{-3}$ $\mu\Omega$ cm/K^2. The T^2 coefficient is close to that of $\mathrm{LaNiO_3}$ and is much larger than that found in conventional metals. This large T^2 term, though not well understood, may come from electron-electron scattering in both systems.

The resistivity of the $PrNiO_3$ sample is linear in temperature from the MI transition temperature to room temperature. If one assumes this temperature dependence is caused by electron-phonon scattering, then the electron-phonon coupling constant λ can be estimated from the slope of the resistivity[23] using

$$\lambda=\frac{\hbar\omega_P^2}{8\pi^2k_B}\frac{[\rho(T)-\rho(0)]}{T}\ , \qquad (4)$$

where ω_P is the plasma frequency. An electron energy-loss experiment[20] on $LaNiO_3$ showed that $\hbar\omega_P\approx 1$ eV. If we assume a similar ω_P in $PrNiO_3$ as in $LaNiO_3$ then we estimate $\lambda\approx 0.3$ from our resistivity data on $PrNiO_3$ using Eq. (4). This suggests that the electron-phonon coupling is weak in $PrNiO_3$. This is probably also true in $LaNiO_3$ although our analysis cannot be justified for a resistivity that is not linear in temperature. The nonsaturation of $\rho(T)$ at 300 K for both $LaNiO_3$ and $PrNiO_3$ shows that the mean free path is much longer than the lattice constant, i.e., $k_F l > 1$.

According to the Brinkman-Rice theory[24] of correlated electrons, the effective mass is enhanced above the free-electron or band-structure value by antiferromagnetic correlations. In this situation the electronic susceptibility and specific-heat coefficient (γ) can be expressed as follows:

$$\gamma=\gamma_0(1+\lambda)/\Phi_0\ ;\quad \chi=\chi_0/\Phi_0(1-S)\ , \qquad (5)$$

where γ_0 and χ_0 are the nonenhanced values; S is an effective Stoner factor and $\Phi_0=(m^*/m)^{-1}$ is the enhanced effective mass due to correlations. Assuming our estimation of λ of 0.3 in $PrNiO_3$ is approximately the same as in $LaNiO_3$, our experimental value of χ and earlier reports of γ from specific measurements,[10,11] we estimate $S\approx 0.64$. Therefore, in $LaNiO_3$, the Stoner enhancement of susceptibility is small compared to the electron correlation enhancement.

In Fig. 6 we show $\ln\rho$ vs $1/T$ for $PrNiO_3$. If the insulating state has a gap Δ, then $\rho\sim\rho_0\exp(\Delta/kT)$ and $\ln\rho$ vs $1/T$ should be linear with a slope of Δ/k. We find this is only approximately true just below T_{MI} and there is a large change of slope below $T=80$ K. We estimate Δ to be 0.20 eV just below T_{MI}. Below 80 K, it appears that impurities in the gap become important, dominating the resistivity, and leading to a nearly constant ρ at low T. It has been found in a neutron-scattering experiment[13] that there is no change of lattice symmetry and only a slight change in lattice constant through the MI transition. However, the temperature hysteresis that we have observed is fairly large. More studies need to be done to determine whether this is a first-order transition and its exact origin.

Our thermopower data of $LaNiO_3$ are similar to previously published data.[10] Our measurement of S on $PrNiO_3$ can give information about the electronic state below T_{MI}. If we have an insulator with a gap Δ, then $S\sim(k_B/e)(\Delta/2k_BT)$. Using our thermopower data for temperatures just below the MI transition, Δ is estimated to be 0.040 eV. It is not clear why the Δ obtained here is smaller than the Δ estimated from the resistivity data. This suggests that the nature of the electronic state below T_{MI} is more complicated than the simple single gap picture that we have used here. The thermopower of insulators should be divergent at low temperature. However $|S|$ reaches a maximum value at $T=55$ K, below which S approaches zero. This is another indication that we probably have impurity states in the gap.

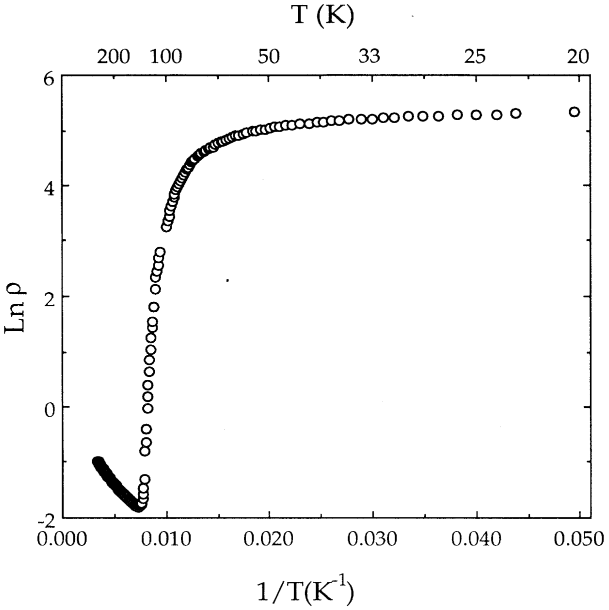

FIG. 6. $\ln[\rho(\Omega)]$ vs $1/T$ for a $PrNiO_3$ ceramic sample.

The resistivity and thermopower in the metallic state are very similar in magnitude for both $PrNiO_3$ and $LaNiO_3$. Also both compounds show a linear and negative thermopower with almost the same slope. This suggests the same order of carrier density in $LaNiO_3$ and $PrNiO_3$. However, there is a distinct difference between them in the temperature dependence of the resistivity. For the $LaNiO_3$ sample $\rho\sim T^{1.5}$ while the ρ of the $PrNiO_3$ sample has a linear T dependence. The origin of the $T^{1.5}$ dependence in $LaNiO_3$ is not known. It could be a combination of a T^2 term and an electron-phonon scattering resistivity term, however higher-temperature measurements will be needed to sort this all out. The linear T dependence in the metallic state of $PrNiO_3$ extrapolates to zero at $T=0$ which may mean it has a similar origin as in the normal state of high-T_c superconductors. On the other hand, it could be due simply to electron-phonon scattering as we have suggested with our analysis above, using Eq. (4). Other measurements will be needed to understand this in more detail.

The size of the Pr^{3+} ion is smaller than that of La^{3+} and therefore $PrNiO_3$ is more distorted than $LaNiO_3$. The Ni-O-Ni angle gets smaller with increasing distortion of the perovskite structure and it has been shown[25] that the bandwidth is closely associated with this angle. It has also been suggested[14] that the bandwidth may be increased by increasing the rare-earth size. Our susceptibility measurements show that Pauli susceptibility in $PrNiO_3$ is larger than that in $LaNiO_3$. This indicates a narrower bandwidth for $PrNiO_3$ than for $LaNiO_3$, which is consistent with the above suggestion.

The oxygen stoichiometry of 3.2 means that there is excess oxygen in our samples which is likely to affect the physical properties. This occurred in $LaTiO_x$, where it was found[16] that when x changes from 3.0 to 3.5, the compound changes from a three-dimensional (3D) weak ferromagnetic semiconductor to a metal and then to a 2D layered ferroelectric insulator. Our results show that the oxygen content has a strong effect on the magnitude of the resistivity of $LaNiO_3$ but the material remains metallic as found previously. Also, the resistivity of our $LaNiO_3$ samples does not exhibit an upturn down to a temperature of 1.4 K. This is in contrast with earlier results[10] that showed a resistivity increase below 10 K. This indicates that our samples are less disordered than previous ones. Since we have excess oxygen in our $LaNiO_3$ sample, the valence of Ni would be between $+3$ and $+4$ if we assume that La has a valence of $+3$ and oxygen has a valence of -2. This is similar to the case of $La_{2-x}Sr_xCuO_4$ where the copper valence is between $+2$ and $+3$. The role of these high-valence states in transition-metal oxides needs further study.

Excess oxygen was also observed[26] in $La_2NiO_{4+\delta}$. $LaNiO_{3+\delta}$ is a 3D perovskite structure with Ni^{3+}, while $La_2NiO_{4+\delta}$ is a layered perovskite with Ni^{2+}. An experiment by Buttrey *et al.* has shown that oxygen nonstoichiometry arises from the presence of excess oxygen in $La_2NiO_{4+\delta}$, possibly in the form of an $O_2{}^{2-}$ species.[26] The excess oxygen δ in both $La_2NiO_{4+\delta}$ and $Pr_2NiO_{4+\delta}$ changes the antiferromagnetic ordering temperature greatly.[27,28] It is also possible that the excess oxygen in our $LaNiO_{3.2}$ sample is also in the form of $O_2{}^{2-}$ which would imply that the Ni valence remains $+3$. Further study will be necessary to determine this. Since the MI transition and the antiferromagnetic ordering are closely related in $PrNiO_3$, it will be interesting to study their oxygen dependence.

In summary, we have measured resistivity, thermopower, dc susceptibility, and oxygen content of $LaNiO_3$. Our $LaNiO_3$ samples have excess oxygen which appears to result in lower room-temperature resistivity and residual resistivity than in previously published data. The T dependence in our resistivity data is different and the ρ at low temperature does not have an upturn in contrast with earlier data, suggesting that our samples are probably less disordered than previous ones. However $S(T)$ and $\chi(T)$ of $LaNiO_3$ are similar to prior data indicating strong electron correlations and enhanced effective mass. We have made quantitative measurements of S, ρ, and χ in $PrNiO_3$. We find a metal-insulator transition at 130 K. Above the transition, the S of $PrNiO_3$ is similar to that of $LaNiO_3$, showing that the carrier densities are of the same order in both oxides. The ρ of $PrNiO_3$ has the same magnitude as $LaNiO_3$ but its temperature dependence is linear and extrapolates to the origin. This indicates that the anomalous linear behavior in ρ is not unique to the "hole-doped" high-T_c oxides. The larger Pauli susceptibility in $PrNiO_3$ than in $LaNiO_3$ suggests a narrower bandwidth for $PrNiO_3$ than for $LaNiO_3$. This is consistent with the suggestion that the bandwidth of RNiO$_3$ may be larger with larger rare-earth ions or less perovskite distortion.

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[22] $k_F l$ can be estimated as follows: $l=(m^* v_F)/(ne^2\rho)=(\hbar k_F)/(ne^2\rho)$, therefore $k_F l=(\hbar k_F^2)/(ne^2\rho)$. Replacing k_F by $(3\pi^2 n)^{1/3}$ we have $k_F l=[\hbar(3\pi^2)^{2/3}]/(e^2\rho n^{1/3})$.

$n \approx 1.7 \times 10^{22}$ cm^{-3} if there is one conduction electron per Ni atom.

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