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# Probing the metal-insulator transition in Ni(III)-oxide perovskites

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Systematic measurements of the resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ under hydrostatic pressure have been made on single-valent perovskites of the family $LnNiO_3$ ($Ln=La, Pr, Nd, Sm_{0.5}Nd_{0.5}$); they distinguish the influences of chemical and hydrostatic pressure on the insulator-metal transition occurring at a temperature $T_t$. The data suggest the coexistence above $T_t$ of fluctuations of more localized electrons in a Fermi-liquid background with an ordering of the two phases into a static charge-density/spin-density wave below $T_t$.

The $LnNiO_3$ perovskites contain low-spin $Ni(III){:}t^6e^1$ configurations, and one electron per Ni(III) occupies an orbitally twofold-degenerate $\sigma^*$ band of $e$-orbital parentage of the $NiO_3$ array. The tight-binding width of the narrow $\sigma^*$ band is controlled by the $(180°-\phi)$ Ni-O-Ni interactions and is given by[1]

$$W_b \approx \varepsilon_\sigma \lambda_\sigma^2 \cos\phi, \tag{1}$$

where $\varepsilon_\sigma$ is a one-electron energy and $\lambda_\sigma$ is the $Ni{:}e-O{:}2p_\sigma$ covalent-mixing parameter for the $\sigma$-bonding $d$ electrons of $e$ symmetry. Substitution of a smaller $Ln^{3+}$ ion for $La^{3+}$ increases $\phi$ by increasing the mismatch of the equilibrium Ln-O and Ni-O bond lengths. The critical energy $U$ is, in this case, the on-site coulomb energy to add an electron to a low-spin $Ni(III)t^6e^1$ configuration to make it $Ni(II)t^6e^2$. Metallic $LaNiO_3$ exhibits an enhanced Pauli paramagnetism,[2] which indicates that the bandwidth approaches the Mott-Hubbard transition from the itinerant-electron side. Therefore substitution of a smaller $Ln^{3+}$ ion for $La^{3+}$, which increases $\phi$ in Eq. (1), allows one to study experimentally the Mott-Hubbard transition. Although the metallic character of rhombohedral $LaNiO_3$ was established in 1965,[3] it was not until 1991 that Lacorre *et al.*[4] used high oxygen pressure to obtain the orthorhombic samples from $La_{1-x}Pr_xNiO_3$ to $EuNiO_3$. This family exhibits an insulator-metal transition at a temperature $T_t$ (Ref. 5) and a transition to an unusual long-range antiferromagnetic order below a $T_N \leqslant T_t$ (Ref. 6) that has been interpreted[7] to be a charge-density wave/spin-density wave (CDW/SDW) phase. The metal-insulator transition at $T_t$ was suggested[5,8] to be the opening of a charge-transfer gap between the O-$2p$ and upper Mott-Hubbard band in a globally homogeneous electronic phase and the decrease in $T_N$ with decreasing tolerance factor to indicate that the spins are associated with localized electrons in the antiferromagnetic phase. With this interpretation, the observation[9,10] that $T_t$ decreases sharply with hydrostatic pressure was attributed to an increasing $t$ factor, and a $dt/dP=0.0004$/kbar was calculated. On the other hand, the observation[11] that substitution of $^{18}O$ for $^{16}O$ in $NdNiO_3$ increases $T_t=T_N$ by 10.3 K without introducing any change in $t$ or $W_b$ demonstrated that some oxygen vibrational frequency $\omega_O$ plays an important role in the determination of $T_t$. Retaining the assumption that $T_t$ occurs at a critical bandwidth, it was suggested that the bandwidth has a form analogous to the Holstein[12] polaron bandwidth

$$W = W_b \exp(-\lambda \varepsilon_p/\hbar\omega_O), \tag{2}$$

where $\omega_O^{-1}$ is the period of the cooperative oxygen displacements that define a polaron and stabilize it by an energy $\varepsilon_p$; $\lambda=\varepsilon_p/W_b$ is a measure of the strength of the electron coupling to the atomic displacements. However, the $LnNiO_3$ family is single valent, a condition that is incompatible with polaron formation; and this problem was not addressed.

In this paper we report resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ under different hydrostatic pressures $P$ for $LaNiO_3$, $PrNiO_3$, $NdNiO_3$, and $Sm_{0.5}Nd_{0.5}NiO_3$ in order (1) to clarify the character of the narrow-band electrons both above and below $T_t$, (2) to show that the dramatic effect of pressure is not due to an increase in $t$ that broadens $W_b$, but is primarily due to a stiffening of the frequency $\omega_O$, and (3) to provide a signature that allows monitoring with transport measurements the variation with $P$ of $T_N$ as well as $T_t$.

Our experiments used ceramic samples of $LaNiO_3$, $PrNiO_3$, $NdNiO_3$, and $Sm_{0.5}Nd_{0.5}NiO_3$ that provide the chemical variation needed to cover the important evolution with $t$ of $T_t$ and $T_N$. All samples were synthesized under 600 bar oxygen pressure at 1080 °C, they were shown by x-ray diffraction to be single phase. The oxygen content of each was determined to be $3.00\pm0.01$ by thermogravimetric analysis in 50-50 $H_2$-Ar atmosphere. The transport measurements were made under pressure in a Be-Cu self clamp.

1. $LaNiO_3$. Figure 1(a) shows the $\rho(T)$ and $\alpha(T)$ data for rhombohedral $LaNiO_3$ under pressures $P<14$ kbar. Three features are noteworthy: (a) The $\rho(T)$ curves, which are similar to those reported by others,[13,14] have a temperature dependence typical for a Fermi liquid, but they are too high and pressure sensitive for a conventional metal. (b) The low-temperature phonon-drag enhancement, which has a maximum at $T_{max}\approx70$ K in the oxide perovskites, is largely suppressed; but it is partially restored by pressure. (c) A

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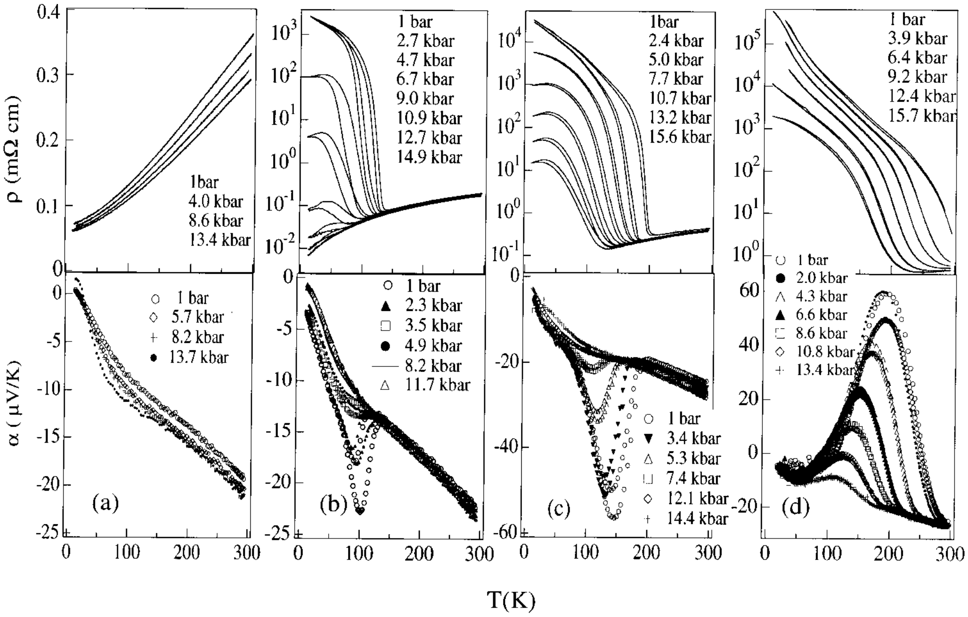

FIG. 1. The resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ under different hydrostatic pressures for (a) $LaNiO_3$, (b) $PrNiO_3$, (c) $NdNiO_3$, and (d) $Sm_{0.5}Nd_{0.5}NiO_3$.

$d|(\alpha(300\,\mathrm{K})|/dP>0$, where $\alpha$ is enhanced by 15% in 14 kbar pressure, indicates an anomalous increase in $m^*$ with pressure. Features (b) and (c) have also been found for $CaVO_3$ and $LaCuO_3$.[15,16] Independently photoemission spectroscopy (PES) has provided direct evidence for coexistence of two electronic phases in the system $Sr_{1-x}Ca_xVO_3$ with a maximum in $m^*$ at an intermediate value of $x$ and a continuous transfer of spectral weight from Fermi-liquid to strong-correlation states with increasing $x$.[17] On the other hand, the unusual relation between bandwidth and effective mass, which is contrary to the prediction from a homogeneous model, could be used as evidence for heterogeneity. Pressure transfers spectral weight from strong correlation to Fermi-liquid states. The unusual pressure dependence of thermoelectric power, shown in Fig. 1(a), therefore indicates that two electronic phases coexist in this ''metallic'' phase of $LaNiO_3$. The features (a) and (c) found for $LaNiO_3$ were also observed in the orthorhombic $LnNiO_3$ samples, Figs. 1(b) and 1(c); feature (b) could not be observed in the orthorhombic samples as the maximum pressure available to us was insufficient to suppress $T_t$ completely. Therefore, we may conclude that the ''metallic'' phase above $T_t$ in the orthorhombic perovskites also contains two electronic phases as a result of the lattice instability associated with a first-order Mott-Hubbard transition. Phase fluctuations in a single-valent system would narrow the bandwidth of itinerant electron to give rise to the bandwidth

$$W=W_b\exp(-\lambda\varepsilon_{sc}/\hbar\omega_O), \tag{3}$$

where $\varepsilon_{sc}$ is the stabilization energy for a cluster defined by cooperative oxygen displacements of period $\omega_O^{-1}$ and $\lambda\sim\varepsilon_{sc}/W_b$.

2. Pressure dependence of $W_b$. Figure 1(b) shows the $\rho(T)$ and $\alpha(T)$ data for orthorhombic $PrNiO_3$ under pressures $P<15\,\mathrm{kbar}$. At atmospheric pressure, the first-order insulator-metal transition at $T_N=T_t\approx130\,\mathrm{K}$ seen in the $\rho(T)$ curve is matched by a sharp increase at $T_t$ in the magnitude $|\alpha(T)|$ of the thermoelectric power. Between 2.7 and 4.7 kbar, the low-temperature ($T\leqslant50\,\mathrm{K}$) $\rho(T)$ curve changes from a semiconductive to a metallic temperature dependence; and with increasing pressure $P\geqslant4.7\,\mathrm{kbar}$, the jump in $\rho(T)$ and $|\alpha(T)|$ at $T_t$ decreases with $T_t$, disappearing above 13 kbar even though a weakly first-order transition is retained at $T_t\approx80\,\mathrm{K}$, Fig. 2. The remarkable change in $\rho(15\,\mathrm{K})$ by six orders of magnitude is an intrinsic phenomenon; it cannot be attributed to a change in grain-boundary conduction under pressure as the $\rho(T)$ curve shows little change with pressure at temperatures $T>T_t$. These unusual data indicate that pressure increases dramatically the number and/or mobility of the charge carriers in the CDW/SDW phase over a limited pressure range $\Delta P\approx10\,\mathrm{kbar}$.

Comparison of Figs. 1(a) and 3(a) shows that O-orthorhombic $PrNiO_3$ at 14.9 kbar has a lower resistivity than $R$-rhombohedral $LaNiO_3$ at a similar pressure. Moreover, $\rho(T)$ retains a significant residual value in $LaNiO_3$ whereas $\rho(T)$ for $PrNiO_3$ under 14.9 kbar extrapolates to a much lower residual value at $T=0\,\mathrm{K}$. In addition, a larger $|\alpha(300\,\mathrm{K})|$ in $PrNiO_3$ than in $LaNiO_3$ increases with pressure. There is no indication of an approach under pressure to the

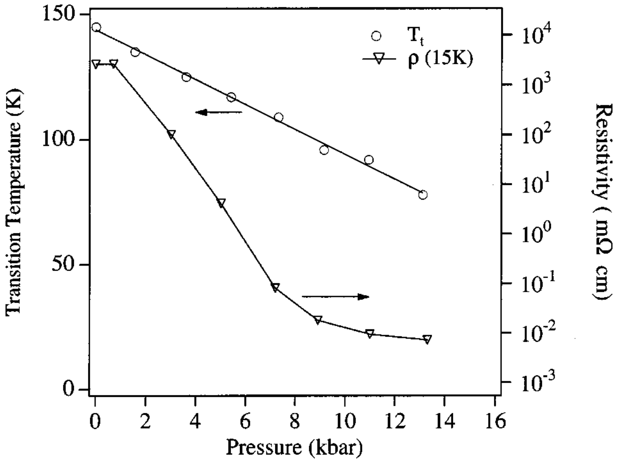

FIG. 2. Variations with pressure of $T_t$ and the resistivity at 15 K for $PrNiO_3$.

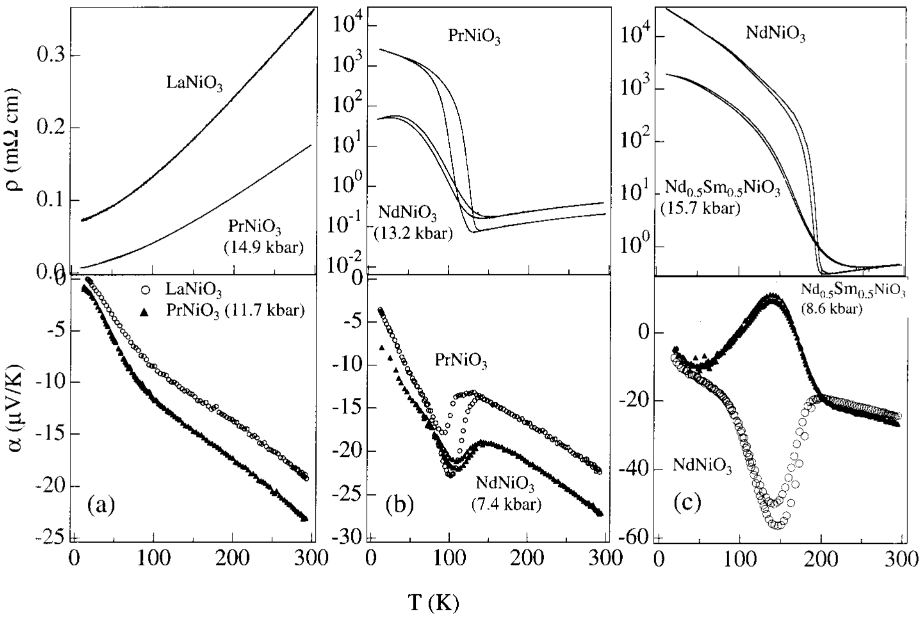

FIG. 3. Comparisons of the resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ for two compounds with approximately the same $T_t$, one at atmospheric pressure and the other under hydrostatic pressure.

O-*R* phase boundary as would be expected from Fig. 2 of Ref. 5 if hydrostatic pressure simply increased *t*.

Figure 1(d) shows that $\alpha(T)$ increases on cooling through the interval $T_N<T<T_t$ in $Sm_{0.5}Nd_{0.5}NiO_3$; the magnitude of this interval changes little as $T_N$ and $T_t$ are lowered with increasing pressure, which again is contrary to what would be expected from Fig. 2 of Ref. 5 if hydrostatic pressure simply increased *t*.

We conclude, therefore, that pressures below 15 kbar have a relatively small influence on $W_b$, which means that, if $T_t$ occurs at a critical bandwidth $W_c$, the principal contribution to the large $dT_t/dP<0$ is associated with a pressure dependence of $\omega_O$ in Eq. (3). It follows that the remarkable change with pressure in the number and/or mobility of the charge carriers in the CDW/SDW phase is also associated with a pressure dependence of $\omega_O$.

3. Comparisons for same $T_t$ with/without pressure. What determines $T_t$ at atmospheric pressure appears to be the bandwidth *W*. The large isotope shift in $T_t$ with no change in $\phi$ can, in principle, be accounted for with a *W* described by Eq. (3). Under pressure, the oxygen vibration frequency $\omega_O$ would increase with a reduction of the (Ni-O) equilibrium bond length. Although $W_b$ appears to change little with pressure, it is narrowed by reducing the size of the $Ln^{3+}$ ion. On the other hand, $\omega_O$ increases sensitively with pressure and may be relatively insensitive to the angle $\phi$. Therefore, the application of pressure to a sample of narrower $W_b$ to make $T_t$ equal to that of a sample with larger $W_b$ would give rise to quite different transport properties and $T_N$ where these properties depend strongly on $\omega_O$. Figure 3 compares the physical properties of two samples with roughly the same $T_t$; the one with the smaller $Ln^{3+}$ ion is under pressure. The figure clearly demonstrates three features: (1) a remarkable difference in $\rho(T)$ below $T_t$, (2) a sharp difference in $\alpha(T)$ below $T_t$ between the samples with $T_N=T_t$ and the one with $T_N<T_t$, and (3) a change from a first-order transition at $T_N=T_t$ to a second-order transition at $T_N$ and $T_t$ where $T_N$ and $T_t$ are separated from one another.

Discussion. Neutron-diffraction data[18] for $PrNiO_3$ and $NdNiO_3$ have shown that the (Ni-O) bond length in the metallic phase is identical and temperature-independent in the two compositions; but on cooling through $T_t$, the (Ni-O) bond length increases discontinuously by 0.0035 Å, which decreases the Ni:$e-$O:$2p_\sigma$ overlap integral and therefore the covalent-mixing parameter $\lambda_\sigma$ entering the bandwidth $W_b\approx\varepsilon_\sigma\lambda_\sigma^2\cos\phi$ of Eq. (1). The data also show a decrease in the $(180°-\phi)$ Ni-O-Ni bond angle with decreasing temperature, a discontinuous change of 0.5° occurring at $T_t$. Although $W_b$ is clearly narrower in the CDW/SDW phase, the changes in $\cos\phi$ and (Ni-O) bond length are not large enough to signal a global change from itinerant to localized electronic behavior. In support of this conclusion, low-temperature neutron-diffraction data[6] have shown an unusual alternation of ferromagnetic and antiferromagnetic Ni-O-Ni interactions below $T_N$; such a long-range ordering would stabilize only a modest increase in the volume of strongly correlated electrons and would therefore require a relatively small discontinuous increase in the mean lattice volume at $T_t$. In fact, the first-order character of the transition decreases as $T_t$ increases as is made even more evident in Fig. 1(d). The change from a weakly first-order to a second-order transition at $T_t>T_N$ gives strong support that an order-disorder transition occurs at $T_t$. We need finally to consider why $T_N$ decreases with increasing angle $\phi$ and how the transport properties become so sensitive to pressure below $T_t$.

A localized spin configuration on the Ni(III) would give a ferromagnetic Ni-O-Ni interaction via coupling to dynamic, cooperative Jahn-Teller deformations of the $NiO_{6/2}$ octahedra.[19] The decrease of $T_N$ with decreasing bandwidth would therefore appear to reflect itinerant-electron behavior with a transition from a SDW toward ferromagnetic order with band narrowing as occurs in the system $La_{1-x}Y_xTiO_3$.[20]

Stabilization of the CDW introduces an energy discontinuity at the Fermi surface in the [111] direction, but two-dimensional conduction is still possible in the (111) planes. Therefore, we conclude that a change of six orders of magnitude in the low-temperature resistivity of $PrNiO_3$ with the application of 15 kbar pressure, Fig. 2, reflects primarily a change in the electron mobility. Formation of a CDW requires a period $\omega_O^{-1} < \tau_h$ for the oxygen displacements that define it; and the time for an electron to tunnel to a neighboring Ni atom is, according to the uncertainty principle, $\tau_h \sim \hbar/W$. Therefore, stabilization of the CDW occurs at a critical ratio $W/\hbar\omega_O$ below which the electron mobility becomes activated. The electron mobility in the $T > T_t$ phase is not activated, so $\rho(T)$ has a metallic temperature dependence. In the CDW phase, pressure increases $\omega_O$ and broadens $W$ according to Eq. (3), which decreases both $T_t$ and more dramatically the activation energy in the mobility. From Figs. 1(b) and 2, the activation energy vanishes below $T_t$ under a pressure $P > 10$ kbar. The CDW appears to stabilize the ratio of the volumes of the strong-correlation and Fermi-liquid phases, preventing further transfer of spectral weight and ''melting'' under pressure in the pressure range studied. Nevertheless, pressure would decrease the energy gap at the Brillouin-zone boundary introduced by the translational symmetry of the CDW, so the change $\Delta n$ in the density of charge carriers on cooling through $T_t$ also decreases with pressure. The activation energy in the mobility vanishes before $\Delta n$ as well as $T_t$, so a metallic temperature dependence of $\rho(T)$ is found below $T_t$ where $\Delta n$ remains finite.

In conclusion, a systematic measurement of the transport properties under pressure provides important insights about nickelates; (1) hydrostatic pressure changes the metal-insulator transition temperature $T_t$ by strengthening the oxygen vibration frequency $\omega_O$ instead of changing the tolerance factor $t$ as previously thought, (2) the metal-insulator transition at $T_t$ has been proven to be incompatible with a Mott-Hubbard transition but consistent with ordering of two phases, (3) the pressure dependence of the thermoelectric power in the normal state is similar to that of $CaVO_3$ in which the coexistence of metallic and Mott-insulator phases has been detected by PES, (4) the paramagnetic insulator phase shows a large positive thermoelectric power. A magnetic-susceptibility study [21] has provided further proof for conclusion (2).

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