Enhanced Susceptibility in $L\mathrm{NiO_3}$ Perovskites ($L = \mathrm{La, Pr, Nd, Nd_{0.5}Sm_{0.5}}$)

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The temperature dependence of the resistivity $\rho(T)$ and of the dc magnetic susceptibility $\chi(T)$ were measured on high-quality $L\mathrm{NiO_3}$ ($L = \mathrm{La, Pr, Nd, Nd_{0.5}Sm_{0.5}}$) samples synthesized under high oxygen pressure. Subtraction of the rare-earth contribution to $\chi(T)$ allows the presentation of the evolution of the susceptibility of the $\mathrm{NiO_3}$ array from Pauli to Curie-Weiss paramagnetism with decreasing bandwidth. A metal-insulator transition occurring at a temperature $T_t = T_N$ is first order for $L =$ Pr and Nd; it becomes second order and produces no anomaly in $\chi^{-1}(T)$ at a $T_t > T_N$ for $L = \mathrm{Nd_{0.5}Sm_{0.5}}$. In the antiferromagnetic domain $T < T_N$, the $\chi(T)$ curve for the $\mathrm{NiO_3}$ array resembles that of a paramagnet.

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A systematic study of the transition from Pauli to Curie-Weiss paramagnetism is lacking. The $L\mathrm{NiO_3}$ family offers the opportunity to study the evolution of the paramagnetic susceptibility of the $\mathrm{NiO_3}$ array with decreasing bandwidth on the approach to the Mott-Hubbard transition from the itinerant-electron side. Figure 1, which is adapted from Torrance *et al.* [1], shows that the orthorhombic perovskites of this family undergo two transitions, an insulator-metal transition at T_t and antiferromagnetic order below a $T_N \leq T_t$. Rhombohedral $\mathrm{LaNiO_3}$ is metallic without long-range magnetic order down to lowest temperatures [2]. Where $T_N = T_t$, the transition is weakly first order, but the transition at $T_t > T_N$ is second order [3]. Moreover, T_t decreases sensitively with hydrostatic pressure P [3–5] and the exchange of $^{18}\mathrm{O}$ for $^{16}\mathrm{O}$ [6]. Neutron-diffraction [7] data have revealed an unusual magnetic order below T_N, ferromagnetic Ni (111) bilayers coupling antiferromagnetically. This magnetic order has been interpreted to manifest stabilization of a charge-density wave/spin-density wave (CDW/SDW) in which itinerant electrons are confined to strongly hybridized Ni-O σ^* orbitals within the ferromagnetic bilayers; the bilayers are coupled antiferromagnetically by superexchange across (111) O^{2-}-ion planes [8]. From transport measurements, we [3] have deduced that the phase above T_t is not a conventional metal, but contains strong-correlation fluctuations that order into a CDW below T_t and into a CDW/SDW below T_N. In this Letter, we report the evolution of the magnetic susceptibility $\chi(T)$ of the $\mathrm{NiO_3}$ subarray with narrowing of the bandwidth. We address the following questions: (1) Is the enhancement of the paramagnetic $\chi(T)$ of the metallic phase due to a Brinkman-Rice mass enhancement or a Stoner enhancement in a homogeneous electronic system or to strong-correlation fluctuations in a heterogeneous electronic system? (2) Does the susceptibility change on passing through a $T_t > T_N$ as would be the case for a CDW stabilized by Fermi-surface nesting or a homogeneous Mott-Hubbard transition? (3) Can we determine $T_N < T_t$ from $\chi(T)$ as distinguished from $T_N = T_t$ determined by the resistivity $\rho(T)$? (4) What is the character of $\chi(T)$ below T_N?

The compositions $L\mathrm{NiO_3}$ ($L = \mathrm{La, Pr, Nd, Nd_{0.5}Sm_{0.5}}$) were synthesized under high oxygen pressure. All samples were single phase to x-ray powder diffraction. Thermogravimetric analysis was used to determine an oxygen content 3.00 ± 0.01 (f.u.)$^{-1}$ and an onset of oxygen loss at about 200 °C in $\mathrm{H_2}$ 50%-Ar 50%. Therefore, resistivity $\rho(T)$ and susceptibility $\chi(T)$ measurements were restricted to temperatures $T \leq 150$ °C. The $\chi(T)$ data were obtained with a SQUID magnetometer (Quantum Design) in an applied field $H = 10$ kOe; four-probe $\rho(T)$ data were obtained with a homemade apparatus.

In order to obtain $\chi(T)$ for the $\mathrm{NiO_3}$ subarray, it is necessary to carry out a precise subtraction of the L^{3+}-ion contribution to the measured $\chi(T)$. For this purpose, we prepared the $L\mathrm{AlO_3}$ perovskites by standard solid-state reaction; all were single phase to x-ray diffraction. Interactions between the rare-earth ions cannot be neglected; $\mathrm{PrAlO_3}$ orders magnetically at low temperature, for example, and the short-range order above T_N makes the susceptibility deviate from the Curie-Weiss behavior. Therefore, a polynomial instead of a simple Curie-Weiss

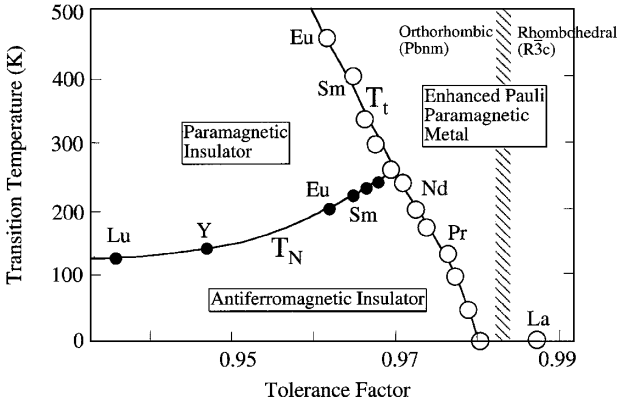

FIG. 1. The insulator-metal transition T_t and the Néel temperature T_N for the $L\mathrm{NiO_3}$ family (adapted from [1]).

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law was used to fit the $\chi(T)$ curve for the $L\mathrm{AlO_3}$ compounds over the entire temperature range measured. However, the curve fitting to a Curie-Weiss law above 100 K gave $C = 3.6$ for $L = \mathrm{Pr}^{3+}$ and Nd^{3+}, which is close to the free-ion values 3.58 (Pr^{3+}) and 3.62 (Nd^{3+}). Subtraction of the polynomial for $\chi(T)$ of $L\mathrm{AlO_3}$ gave a very consistent result for the $\chi(T)$ of the $\mathrm{NiO_3}$ array of $\mathrm{PrNiO_3}$ and $\mathrm{NdNiO_3}$. In the case of $\mathrm{Nd_{0.5}Sm_{0.5}NiO_3}$, subtraction of the polynomial did not work as well at low temperatures. Therefore, a fit to the Curie-Weiss law above 100 K was used. Fortunately, all the transitions we addressed occur above 100 K.

Figures 2–5 show $\chi(T)$, $\chi^{-1}(T)$, and $\rho(T)$ for the $\mathrm{NiO_3}$ array of $\mathrm{LaNiO_3}$, $\mathrm{PrNiO_3}$, $\mathrm{NdNiO_3}$, and $\mathrm{Nd_{0.5}Sm_{0.5}NiO_3}$, respectively. Both Landau diamagnetism and Van Vleck paramagnetism are relatively small in magnitude compared with our measured $\chi(T)$. Therefore, no correction was made for these two contributions to $\chi(T)$. In a homogeneous model, the temperature dependence of $\chi(T)$ for the $\mathrm{NiO_3}$ array may be attributed to the electronic states near the Fermi energy.

Interpretation of the $\chi(T)$ data begins with the observation that the low-spin Ni (III) ions contribute a single electron each to an orbitally twofold-degenerate σ^* band. A quarter-filled band should experience ferromagnetic correlations which introduce a Stoner enhancement in addition to the mass enhancement due to strong electron-electron interactions. A distinction between these two enhancements is that the electronic specific-heat parameter γ increases with mass enhancement, but not with Stoner enhancement [9]. By measuring both $\chi(T)$ and the electronic specific heat at low temperatures, Sreedhar *et al.* [2] determined a Stoner factor $S = 0.58$, well below the $S = 1$ for a ferromagnetic instability. The curvature of the temperature dependence of $\chi(T)$ for mass enhancement is opposite to that for Stoner enhancement. Mott [10] was the first to point out this distinction, but he was unable to find a suitable experimental example to test his prediction that a flattening of the $\varepsilon_{\mathbf{k}}$ vs $\mathbf{k}$ dispersion at the Fermi energy of a mass-enhanced metallic system would give a temperature dependence below a temperature T_d.

Qualitatively, the $\chi(T)$ data for $\mathrm{LaNiO_3}$ in Fig. 2 appears to fit the Mott prediction for a homogeneous electronic system. However, a weak temperature dependence persisting above the apparent $T_d \approx 200$ K in Fig. 2 does not conform to the Mott picture. Alternatively, the $\chi(T)$ curve of Fig. 2 may be described by a two-electronic-phase model in which $\chi = a\chi_0 + b\chi_{CW}$, where χ_0 is the susceptibility of a mass-enhanced, conductive parent phase and χ_{CW} is a Curie-Weiss component coming from strong-correlation fluctuations within the parent phase. We [11] have used this formulation to interpret a similar temperature dependence of $\chi(T)$ found for the $\mathrm{La_{1-x}Nd_xCuO_3}$ perovskite system. Moreover, the model is supported by the evidence from our transport measurements [3] for strong-correlation fluctuations in the metallic phase of the $L\mathrm{NiO_3}$ family. A $T_d \approx 200$ K was also found in the $\mathrm{La_{1-x}Nd_xCuO_3}$ system; why it should occur at this temperature in both systems is not clear. One possibility is that the boundary of the host phase is where the mass enhancement gives a $T_d \approx 200$ K; further narrowing of the band introduces more and more of the strong-correlation second phase and hence a greater temperature dependence of $\chi(T)$ above T_d. Indeed, the temperature dependence of $\chi(T)$ at $T > T_d$ increases on narrowing the bandwidth in Figs. 2–5.

In Figs. 3–5, the onset of the rise in $\rho(T)$ on cooling is a measure of the transition temperature T_t. The thermal hysteresis of T_t decreases as T_t increases, and the transition becomes second order (no thermal hysteresis at T_t) in $\mathrm{Nd_{0.5}Sm_{0.5}NiO_3}$, which has a $T_t > T_N$ (see Figs. 1

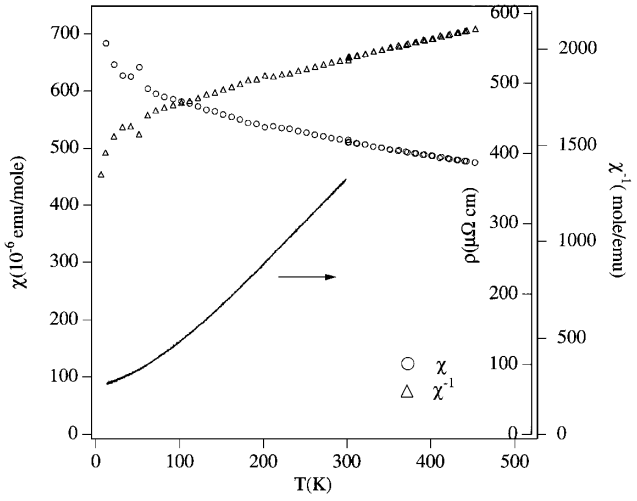

FIG. 2. Temperature dependence of resistivity ρ, magnetic susceptibility χ, and its reciprocal $\chi^{-1}(T)$ for $\mathrm{LaNiO_3}$.

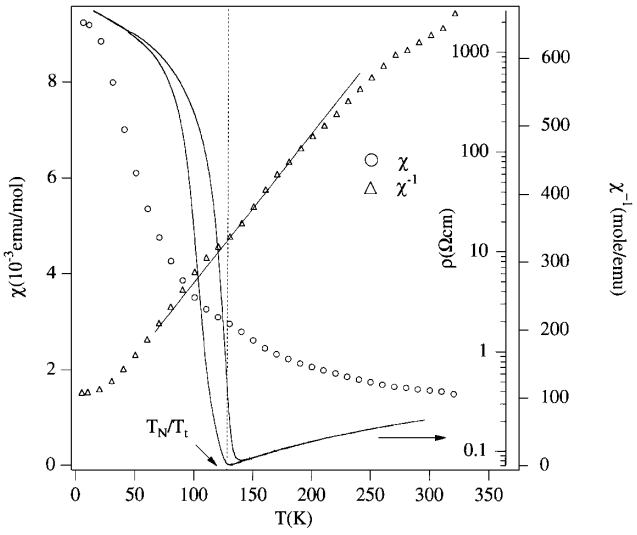

FIG. 3. $\rho(T)$, $\chi(T)$, and $\chi^{-1}(T)$ for $\mathrm{PrNiO_3}$, the line is a guide to the eye.

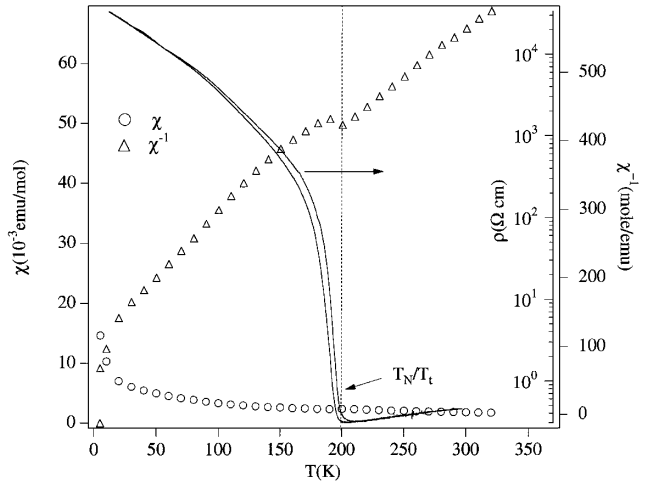

FIG. 4. $\rho(T)$, $\chi(T)$, and $\chi^{-1}(T)$ for $NdNiO_3$.

and 5). Surprisingly, the $\chi^{-1}(T)$ curve shows only a small anomaly at $T_N = T_t$ in $PrNiO_3$ and $NdNiO_3$; in $Nd_{0.5}Sm_{0.5}NiO_3$, there is no observable change in $\chi(T)$ at T_t as defined by $\rho(T)$. *These data clearly demonstrate that the CDW below T_t is not stabilized by either Fermi-surface nesting or the onset of a homogeneous Mott-Hubbard transition.* However, the data are compatible with an order-disorder transition for the strong-correlation fluctuations which we have deduced from transport data [3]. Recent neutron-diffraction data for $YNiO_3$ show an alternative CDW in the range $T_N < T < T_t$ in this compound; $NiO_{6/2}$ clusters of shorter Ni-O bond length alternate with Ni atoms having longer Ni-O bond lengths [12]. This observation was interpreted conventionally as evidence for a negative-U CDW in which charge is transferred from the Ni with shorter Ni-O bond lengths to the one with longer bond lengths. An alternative description would be an ordering of molecular orbitals in $NiO_{6/2}$ complexes of shorter Ni-O bonds with strong

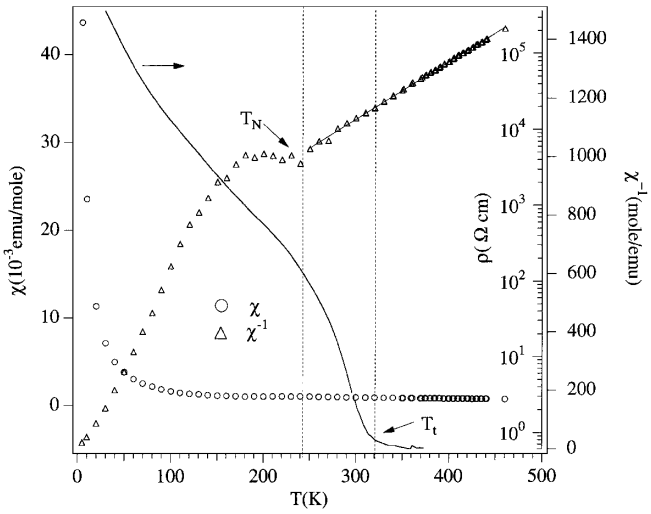

FIG. 5. $\rho(T)$, $\chi(T)$, and $\chi^{-1}(T)$ for $Nd_{0.5}Sm_{0.5}NiO_3$. The line is a linear fit to χ^{-1} versus T above T_N.

correlations localizing electrons on the alternate Ni atoms. The σ^* band of the NiO_3 array is the result of strong hybridization of the σ-bonding Ni-3d and O-2p orbitals, and the CDW may be thought of as an ordering of stronger and weaker hybridization. Strong-correlation fluctuations simply represent clusters with weaker hybridization in a host matrix of stronger hybridization.

The $\chi(T)$ curve below T_N is uncharacteristic of a localized-electron antiferromagnet. Although the anomaly in $\chi^{-1}(T)$ at T_N increases as the band narrows, $\chi(T)$ increases with decreasing T below T_N in all samples. However, there is no difference between the $\chi(T)$ for field-cooled and zero-field-cooled samples, which shows that this anomalous situation is not due to a canted-spin ferromagnetism. The conclusion that the rise in T_N with increasing bandwidth indicates localized electrons below T_N is clearly unjustified. This variation of T_N with bandwidth should be reconsidered in the following context. The ferromagnetic correlations of a quarter-filled band should induce ferromagnetism as the band narrows, and the reduction in T_N with decreasing bandwidth could represent an increasing electron-correlation frustration as occurs in the $La_{1-x}Y_xTiO_3$ system, which undergoes a transition from band antiferromagnetism in $LaTiO_3$ to ferromagnetism in $YTiO_3$. On the other hand, the variation of T_N with tolerance factor t in Fig. 1 could also reflect a competition between different types of CDWs.

The observation [13] of a temperature-dependent paramagnetic susceptibility in the itinerant-electron ferromagnets $ZrZn_2$ and Sc_3In has motivated attempts to describe the evolution from Pauli to Curie-Weiss paramagnetism within an itinerant-electron framework. Whereas Mott [10] starts from the Brinkman-Rice mass enhancement based on a Hubbard Hamiltonian, Moriya [14] has extended the paramagnon theory based on the Hartree-Fock and random-phase approximation to include a higher-order mode-mode coupling of spin fluctuations with a self-consistent renormalization procedure. The Moriya model yields a temperature-dependent paramagnetism for a weakly ferromagnetic metal having no local moments; it appears to be applicable to alloys such as $ZrZn_2$ and Sc_3In, where the Fermi energy just cuts a narrow d band that is overlapped by a broad conduction band. In this model, the Curie constant of the "new Curie-Weiss" behavior is independent of the magnetic-ordering temperature and depends only on the band structure near the Fermi surface. In the $LNiO_3$ family, the slope of $\chi^{-1}(T)$ increases with T_N for $L = \mathrm{La, Pr, Nd}$. Clearly the Moriya description is not applicable.

The $LNiO_3$ family approaches the Mott-Hubbard transition from the itinerant-electron side, but it remains far from a ferromagnetic instability. Our data indicate that, in this case, single-valent perovskites may undergo a dynamic phase segregation in which strong-correlation fluctuations introduce localized spins; these spins would yield a temperature-dependent paramagnetism that is

added to the paramagnetism of a mass-enhanced matrix. Mott argued that the matrix component of $\chi^{-1}(T)$ would increase with T for a $T < T_d$; T_d for the matrix would remain fixed at a phase boundary with strong-correlation fluctuations.

In conclusion, we answer the four questions raised in the introduction. (1) The enhancement of the paramagnetic $\chi(T)$ of the metallic phase exhibits temperature and bandwidth dependencies which are not described by homogeneous models based on mass, Stoner, or spin-fluctuation enhancement; however, they are consistent with a heterogeneous model of strong-correlation fluctuations in a mass-enhanced matrix, as deduced from previous transport measurements. (2) The lack of any change in $\chi(T)$ on traversing the insulator-metal transition at $T_t > T_N$ is incompatible with a homogeneous model of Fermi-surface nesting or a Mott-Hubbard transition, but can be understood as an order-disorder transition of preexisting strong-correlation fluctuations. (3) With proper subtraction of the rare-earth contribution to $\chi(T)$, it is possible to determine $T_N < T_t$ from $\chi(T)$ for the NiO_3 array as distinguished from $T_N = T_t$ determined by $\rho(T)$. It is also possible to determine $T_t = T_N$, but it is not possible to determine $T_t > T_N$ from the $\chi(T)$ data. (4) The character of $\chi(T)$ below T_N is not characteristic of localized-spin antiferromagnetism, including canted-spin antiferromagnetism. In a magnetic field of 1T, it exhibits a behavior like that of a paramagnet. It is as though the NiO_3 array disproportionates into alternating diamagnetic and paramagnetic nickel sites as implied by the observation of Alonso *et al.* [12] for $YNiO_3$, the disproportionation suppressing the long-range magnetic order.

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