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Electronic properties of the metallic perovskite $LaNiO_3$: Correlated behavior of 3*d* electrons

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Low-temperature electrical resistivity, specific heat, and magnetic measurements have been performed on the distorted perovskite $LaNiO_3$. The electrical resistivity shows a linear temperature dependence at high temperatures and an AT^2 dependence below ~ 50 K. The static paramagnetic susceptibility is nearly Pauli-like with an additional small Curie-law contribution in the range 100–300 K, and shows stronger temperature dependence at lower temperatures. The specific heat can be represented as $\gamma T + \beta T^3 + \delta T^3 \ln T$ at low temperatures. Both the Pauli magnetic susceptibility $\chi = 5.1 \times 10^{-4}$ emu/mol and the linear temperature coefficient of the specific heat $\gamma = 13.7$ mJ/K^2 mol are enhanced well above their electron gas values. The effective Stoner enhancement factor is $S = 0.58$, i.e., far from the ferromagnetic instability. These results are interpreted in terms of a Fermi liquid composed of almost localized Ni 3*d* electrons. Thus, $LaNiO_3$ represents a correlated metallic system.

I. INTRODUCTION

Since the discovery of high-temperature superconductivity in the layered perovskite $La_{2-x}Ba_xCuO_4$ system,[1] the electronic properties of oxides having the perovskite and related structures have been of great interest, particularly those that exhibit metallic properties. Among these may be listed $LaNiO_3$, which has a rhombohedrally distorted perovskite structure, with nominally Ni^{3+} ions in near-octahedral coordination. Hence, to a first approximation, the 3*d* electrons can be represented as occupying a full t_{2g} band and a quarter filled e_g band. Here we consider the properties of electrons in the partially filled band.

The compound was first synthesized and its structure determined by Wold, Post, and Banks.[2] Early neutron-diffraction experiments showed no evidence for magnetic ordering down to 4.2 K.[3] Additional structural studies, as well as magnetic and electronic properties, have been reported.[4-13] It was shown that $LaNiO_3$ is metallic with a large Pauli-type magnetic susceptibility which has been interpreted in terms of a Stoner enhancement, based on ferromagnetic correlation of electrons in the quarter filled e_g band associated with Ni^{3+} ions in the $3d^7$ configuration. Further susceptibility measurements have revealed a weak T dependence of χ at intermediate temperatures and Curie-Weiss behavior above 500 K. A recent study[8,9] of the low-temperature electronic properties of this system has shown that $LaNiO_3$ exhibits a substantial electron-electron interaction which gives rise to low electron diffusivity and a short mean free path. Moreover, from the electrical resistivity and low-temperature heat capacity studies on $LaNiO_3$, an effective mass of the carriers of $m^*/m_0 \sim 10$, was deduced, where m_0 is the free-electron mass.

In order to differentiate between the exchange-enhanced and mass-enhanced susceptibilities in this system, we compare the density of states (DOS) obtained from the Pauli contribution to the magnetic susceptibility with that deduced from the electronic specific heat. In particular, from our measurements of heat capacities (C_p), magnetic susceptibility (χ), and resistivity (ρ) at low temperatures, we show that $LaNiO_3$ should be regarded as a correlated electron system with relatively large electron-electron interactions. This gives rise to the enhancement of the electronic linear specific heat coefficient γ, of the spin susceptibility χ, and to the T^2 coefficient of both the resistivity and the susceptibility, as well as a $T^3 \ln T$ dependence of the specific heat at low temperatures.

II. EXPERIMENT

The compound was synthesized by dissolving appropriate molar ratios of La_2O_3 (99.99%) and NiO (99.99%) in nitric acid. The resulting nitrate mixture was first decomposed at 750 °C in air, and then heated to 800 °C under 1 atm of flowing oxygen, with frequent intermittent grinding, until single-phase perovskite was obtained. The polycrystalline material was finally annealed in an atmosphere of flowing oxygen at 400 °C for 12 h.

The x-ray powder diffraction patterns were recorded using a Siemens D-500 diffractometer with Cu-$K\alpha$ radiation. No secondary phases were observed. dc magnetization measurements were performed in the range 2–400 K using a Quantum Design SQUID magnetometer. ac susceptibility measurements in the range 0.033–4.2 K were performed using a custom SQUID susceptometer attached to a ^3He-^4He dilution refrigerator. Heat-capacity measurements were carried out by the quasiadiabatic heat pulse method between 0.5 and 20 K. The electrical resistivity was measured on sintered bars down to 4.2 K, employing a standard four-probe technique.

III. RESULTS

The x-ray powder diffraction patterns of $LaNiO_3$ is shown in Fig. 1. The pattern is consistent with the assumption that the compound crystallizes in the rhombohedrally distorted perovskite structure at room temperature. The x-ray diffraction pattern can be indexed in a rhombodhedral unit cell or, alternatively, in the hexagonal unit cell, with lattice parameters $a_0 = 5.49$ Å and $c_0 = 13.14$ Å. These lattice parameters are close to those reported earlier.[2,7] Since the Ni^{3+} ions in $LaNiO_3$ are in near-octahedral coordination and are known to have the low-spin electronic configuration[6] $t_{2g}^6 e_g^1$, the doubly degenerate e_g band should be one-quarter filled in this system.

The temperature dependence of the electrical resistivity $\rho(T)$, of $LaNiO_3$, is shown in Fig. 2. The compound has a positive temperature coefficient of resistivity, typical of a metal, down to 4.2 K, with the resistivity varying from ~1.8 mΩ cm at 290 K to ~0.5 mΩ cm at 4.2 K. These resistivity values are nearly two to three orders of magnitude larger than those characterizing ordinary metals and are comparable to those reported earlier.[12,13] Above $T \sim 200$ K the variation of resistivity with temperature is almost linear, but marked deviations from linearity are observed at lower temperatures. As shown in Fig. 3, for $T \leq 55$ K the temperature dependence of the electrical resistivity follows the quadratic relation

$$\rho(T) = \rho_0 + AT^2 \tag{1}$$

with $\rho_0 \sim 0.5$ mΩ cm and $A \sim 0.034$ $\mu\Omega\,\mathrm{cm/K^2}$.

The overall temperature dependence of the magnetic susceptibility, $\chi(T)$, of $LaNiO_3$ is shown in Fig. 4. The susceptibility has a weak temperature dependence and is nearly Pauli-like in the range 300–100 K, but shows a marked temperature dependence at lower temperatures. The molar Pauli susceptibility at 300 K is $\sim 5.1 \times 10^{-4}$ emu/mole, close to that reported earlier.[7–9] This value is more than an order of magnitude larger than the free-electron Pauli susceptibility. The residual resistivity is quite large for a metal suggesting that magnetic impurities may be present in the system. This conjecture may also explain the susceptibility results discussed below. Note also that the T^2 dependence of the resistivity is valid over a wide range, a circumstance that supports strong electron-electron scattering for charge carriers forming a Fermi liquid.[14]

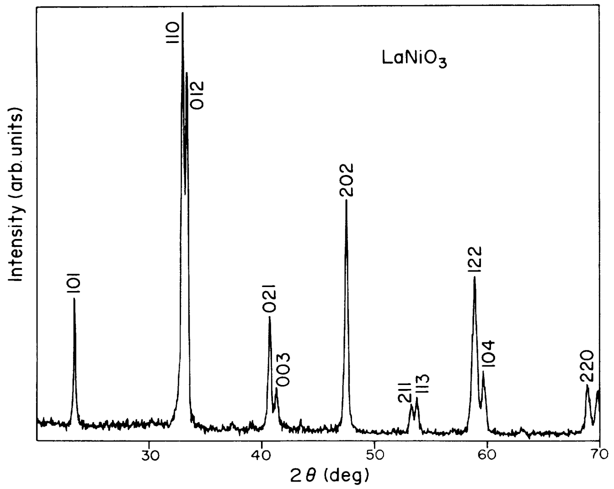

FIG. 1. X-ray powder diffraction pattern of $LaNiO_3$, obtained with Cu-$K\alpha$ radiation, indexed to the hexagonal unit cell with lattice parameters $a = 5.48$ Å and $c = 13.14$ Å.

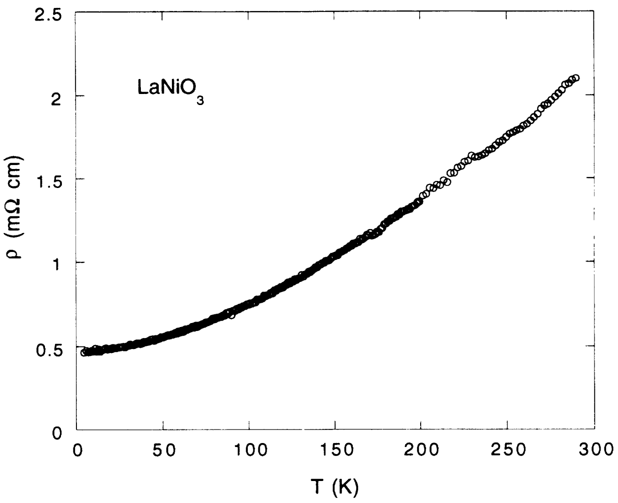

FIG. 2. Temperature dependence of the electrical resistivity of $LaNiO_3$.

To determine the detailed temperature dependence of the magnetic susceptibility $\chi(T)$, we have performed a series of magnetization measurements at various magnetic fields. One notices a number of interesting features. First, the magnetic susceptibility $\chi = M/H$ taken at $H = 10$ kOe for $T > 100$ K, shown in the inset of Fig. 4, can be fitted to the formula

$$\chi(T) = \chi(0) - aT^2 + C/T , \tag{2}$$

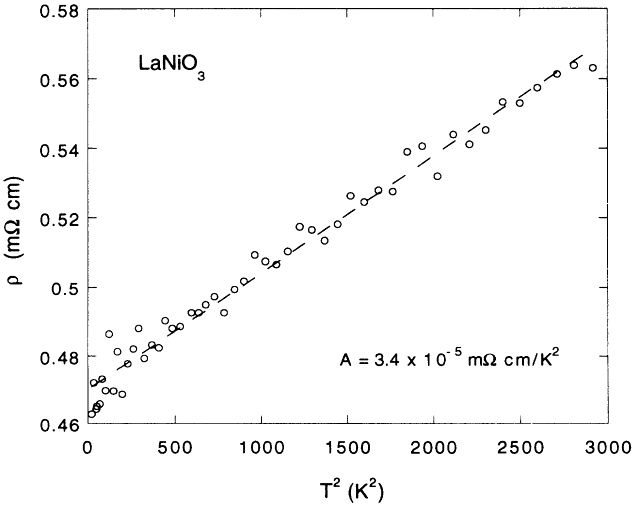

FIG. 3. The resistivity plotted as a function of T^2. The linearity holds for $T \leq 55$ K.

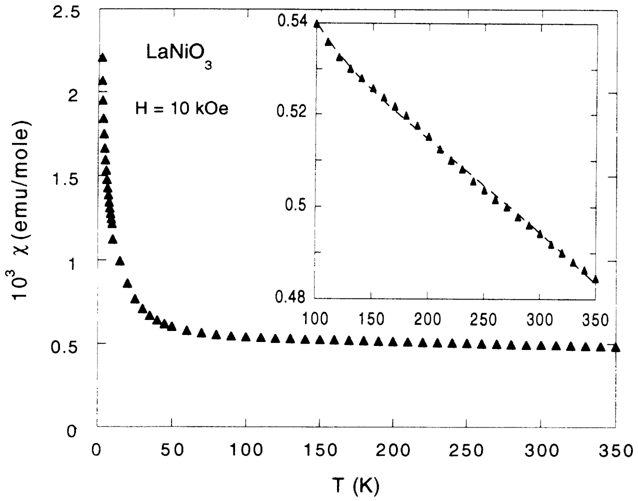

FIG. 4. Temperature dependence of the molar magnetic susceptibility of LaNiO$_3$ in an applied magnetic field of 10 kOe. Inset: the susceptibility in the high-temperature regime. The dashed curve represents the fitting to Pauli and Curie terms described in the text.

with $\chi(0) \sim 5.1 \times 10^{-4}$ emu/mole, $a = 2.9 \times 10^{-10}$ emu/K^2 mole, and $C = 3.4 \times 10^{-3}$ emuK/mole. The second term provides the temperature dependence of the Pauli susceptibility and accounts for a small fraction of the Pauli contribution even at 300 K. The last term represents a Curie law with a small Curie constant. We cannot rule out impurities as a source of this Curie term. It is also possible that it is an intrinsic feature of systems near the metal-insulator transition, as has been suggested previously.[15] However, our data do not support the scaling laws proposed by these authors. Second, a shoulder in the $M(T)$ data is observed in the low-field regime, followed by a rise at still lower temperatures. The detailed behavior in the temperature range $T < 30$ K is shown in Fig. 5, where we show in the lower curve the Pauli and Curie contributions calculated from the fit at high temperatures. We see that Eq. (2) cannot account fully for either of the two features. Additionally, the $M(H)$ curve is nonlinear in the low-T range, as displayed in Fig. 6. The nonlinear behavior cannot be represented by a Brillouin function. In an attempt to interpret the low-T behavior of $M(T,H)$ we have constructed an Arrott plot from which one can estimate the temperature of a possible magnetic transition to a weakly ferromagnetic phase to occur at $T = 12-14$ K. In connection with the last observation one should note that a ferromagnetic phase transition in a quarter-filled and correlated e_g band system was shown to take place for CoS$_2$.[16] Those results can be understood by taking the ferromagnetic kinetic exchange interactions into account.[17] Another possible explanation for this transition is the presence of an antiferromagnetic phase with a small moment. An antiferromagnetic metallic phase is observed in weakly nonstoichiometric V$_2$O$_3$, an almost localized system (cf. Ref. 18). We also cannot rule out an impurity phase at the level of 0.1% or less as an explanation of this apparent transition.

The low-temperature ac susceptibility data is shown in Fig. 7. The susceptometer was calibrated by comparing the data between 2.0 and 4.2 K with that obtained from the dc magnetometer. A small uncertainty is introduced in this calibration by the presence of the phase transition at $T \sim 13$ K. Also shown is a fit to a Curie-Weiss law $\chi = C/(T-\theta)$ with $C = 3.6 \times 10^{-3}$ emu/mole and $\theta = -0.11$ K. The antiferromagnetic value of θ was determined to be insensitive to the calibration. Given the uncertainties involved in the fit, this value of the Curie constant is in good agreement with that obtained from the high-temperature data. This agreement, and the value of θ, suggests that the mechanism involved in the Curie behavior at the lowest temperatures is not dependent on the mechanism producing the ordering at $T \sim 13$ K. The physical origin of the Curie-Weiss behavior over

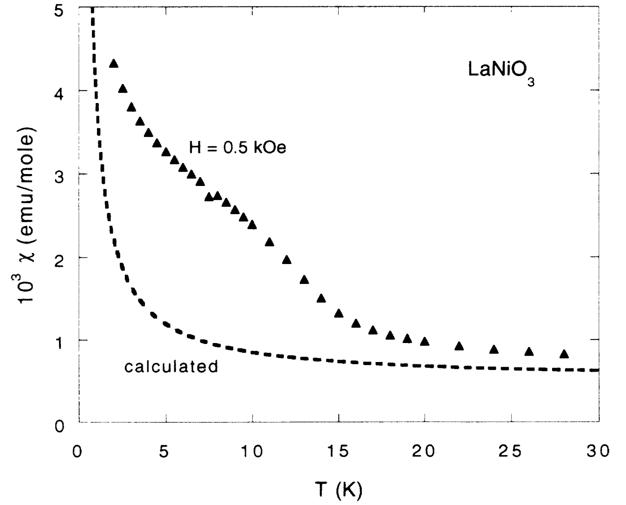

FIG. 5. Temperature dependence of the magnetic susceptibility for $T < 30$ K and $H = 0.5$ kOe as compared to the combined Curie and Pauli contributions calculated from fits to the high-temperature susceptibility.

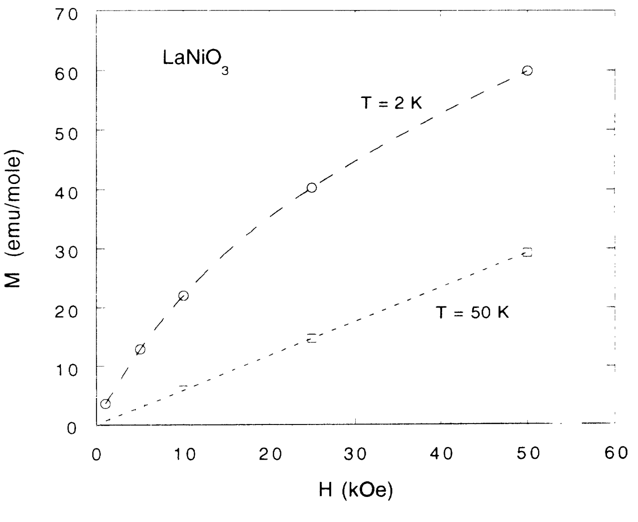

FIG. 6. Applied magnetic-field dependence of the magnetization at $T = 2$ and 50 K. The lines are guides to the eye.

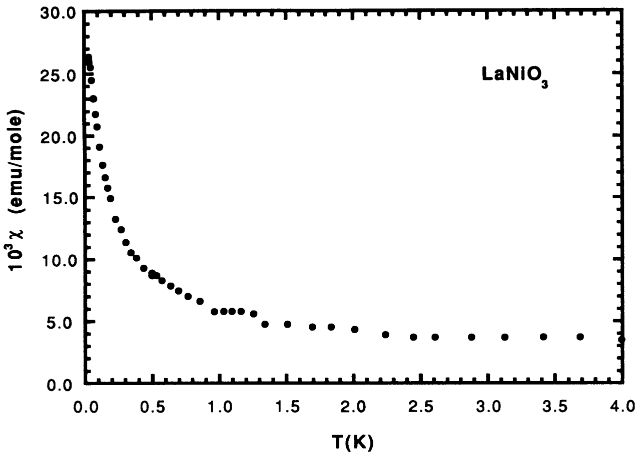

FIG. 7. Low-temperature ac susceptibility of $LaNiO_3$.

the whole range $0.03 \leq T \leq 300$ K requires further study.

The low-temperature heat capacity (C) of $LaNiO_3$, plotted as C/T vs T^2, is shown in Fig. 8. The heat-capacity data below 10 K can be accurately fitted to the relation

$$C=\gamma T+\beta T^3+\delta T^3 \ln T \ . \tag{3}$$

The value of γ obtained from the fit is 13.8 ± 0.04 mJ/mole K^2. The last term in Eq. (3) arises as a consequence of spin fluctuations that are specified by the expression $T^3 \ln(T/T_{sf})$, as shown theoretically by Pethick and Carneiro.[19] The fit gives $\beta=5.8\times10^{-5}$ mJ/K^3 mole and $\delta=0.12$ mJ/K^3 mole. The small value of β is due to a near cancellation between the $-\delta T^3 \ln T_{sf}$ term and the lattice term. The $\delta T^3 \ln T_{sf}$ term has been associated with the contribution of the spin fluctuations in Fermi-liquid systems. Recently, such a term has also been associated with spin fluctuations in almost localized Fermi liquids, as described by Rasul and Li,[20] and Li and Wolfle.[21]

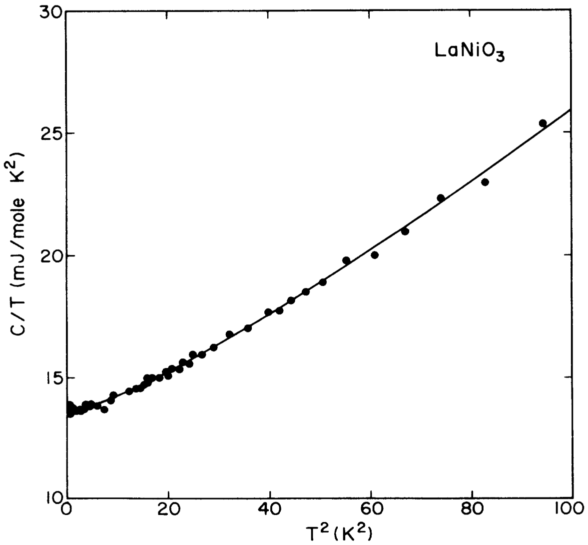

FIG. 8. Low-temperature specific heat of $LaNiO_3$ plotted as C/T vs T^2. The line represents the fitting described in the text.

IV. DISCUSSION

The principal features of the collective electron assembly in $LaNiO_3$ may be rationalized in terms of the model of correlated electrons proposed by Brinkman and Rice,[22] and extended to nonzero temperatures by Spalek *et al.*[23] It was shown that electron-electron interactions in metals should lead to a T^2 dependence of resistivity at low temperatures that characterize Baber-Landau-Pomeranchuk scattering.[24] The relatively large T^2 coefficient of the resistivity, $A \sim 0.034$ $\mu\Omega$ cm/K^2, is close to the A range of 0.025–0.042 $\mu\Omega$ cm/K^2 reported for V_2O_3, which becomes metallic under pressures exceeding 26 kbar.[18] Metallic V_2O_3 is regarded as a canonical example of a system with almost localized $3d$ electrons.[25]

According to the Brinkman-Rice theory of correlated electrons near a metal-insulator transition, the electronic specific-heat coefficient γ and the temperature independent part of the Pauli magnetic susceptibility χ at $T=0$ are enhanced above the free-electron value and are specified respectively by

$$\gamma=\gamma_0/\Phi_0 \ , \tag{4}$$

and

$$\chi=\chi_0/\Phi_0(1-S) \ , \tag{5}$$

where γ_0 and χ_0 are the values for electrons in the bare band. Here

$$\Phi_0=1-(U/U_c)^2=(m^*/m_0)^{-1} \tag{6}$$

is a band-narrowing factor, where U represents the on-site Coulomb repulsion energy between two electrons with opposite spins, and U_c is the critical value at which the system undergoes a phase change from the metallic state to the insulating state with localized electrons. The term on the right-hand side of Eq. (6) represents the inverse ratio of the effective to the free-electron mass, S in Eq. (5) represents the effective Stoner enhancement factor for correlated electrons given by

$$S=UD(\varepsilon_F)[1+U/(2U_c)]/[1+(U/U_c)^2] \ , \tag{7}$$

which reduces to $3UD(\varepsilon_F)/8$ when U/U_c approaches a value of 1. The factor $\frac{3}{8}$ is the reduction in the Hartree-Fock value of the Stoner factor due to electron correlations. The quantity $D(\varepsilon_F)$ is the density of the bare states (DOS) per site per spin at the bare Fermi energy ε_F. We set $D(\varepsilon_F)=1/W$, where W is the effective bare-electron bandwidth; then $U_c=2W$.[23] These latter two relations apply only if the function $D(\varepsilon)$ is featureless, i.e., rectangular in shape. However, it can be shown[26] that the above results are not greatly affected if other types of DOS are adopted.

The factor $1/S$ represents an exchange enhancement factor, while $1/\Phi_0$ is the effective mass enhancement. The positive value of the effective Stoner enhancement factor means that a system of itinerant electrons will not order ferromagnetically. From the value of the χ/γ ratio, we determine a Stoner factor of $S=0.58$, i.e., the system is relatively far from a ferromagnetic instability

($S=1$). Therefore, the electrons must be correlated, since otherwise the values of χ and γ would not be enhanced, and the large T^2 term in the resistivity, as well as the $T^3 \ln T$ term in the specific heat, would not be present.

In conclusion, we have measured the electrical resistivity, magnetic susceptibility, and heat capacity of $LaNiO_3$. We observe poor metallic electrical conductivity, with the electrical resistivity at low temperatures varying as T^2, a $T^3 \ln T$ dependence of the specific heat, and enhanced values of both χ and γ. Our results suggest that $LaNiO_3$ represents a system with correlated $3d$ electrons in a quarter-filled e_g type of band. Further work is necessary to establish the nature of the magnetic phase in the low-temperature regime $T < 15$ K.

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