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Specific heat, magnetic susceptibility and electrical resistivity measurements on $LaNiO_3$

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Abstract

Measurements of specific heat, magnetic susceptibility and electrical resistivity on $LaNiO_3$ are reported. No evidence of magnetic ordering or metal–insulator transitions is found. From the measured electronic specific heat parameter γ and the Pauli susceptibility χ_P, a Stoner enhancement parameter is derived. Comparison with band structure calculations performed by other workers is also made.

1. Introduction

The oxides ABO_3 with perovskite-related structures are very interesting compounds to study in materials science, since high temperature superconductivity has been discovered in perovskite-like oxides.

According to early investigations by Goodenough [1], if the B cation in ABO_3 is a first series 3d ion, the compound will be an antiferromagnetic insulator, except for some rare cases such as $LaNiO_3$. Early neutron diffraction, electrical conductivity and magnetic susceptibility experiments were discussed by Goodenough and Raccah [2] in terms of a cation–anion transfer integral, suggesting that the partially filled e_g orbitals of the low spin state [3] of Ni^{3+} are transformed into partially filled σ^* narrow band states, which do not present spontaneous magnetization.

More recently, Torrance *et al.* [4] have examined the electrical conductivity of a large variety of binary and ternary transition metal oxides characterizing each compound by three parameters: the Coulomb correlation, the charge transfer energy and the bandwidth. In this framework, $LaNiO_3$ is classified as a borderline metal–insulator compound. In the isomorphous compounds $RNiO_3$ ($R \equiv$ Pr, Nd, Sm, Eu) a metal–insulator transition is observed [5] at a temperature which is dependent on the ionic radius of R. In these cases antiferromagnetic ordering is also detected [5]. $LaNiO_3$, by contrast, presents metallic conductivity down to 1.5 K [5, 6]. Nevertheless, a specific heat C_p measurement by Rajeev *et al.* [6] shows a slight rise in C_p with decreasing temperatures for $1.5\ K < T < 2\ K$. This rise could be considered as the onset of a magnetic ordering process. Experiments at lower temperatures should confirm this behaviour.

In this paper, we present a new C_p measurement on $LaNiO_3$ lowering the temperature limit down to 0.45 K. We also measured the electrical resistivity and magnetic susceptibility. All these experiments were performed on samples from the same bulk. They were carefully prepared in order to synthesize a single-phase material with the accurate oxygen stoichiometry required, since some evidence of ordered phases has already been found in the system $LaNiO_{3-x}$ [7, 8].

2. Experimental details and results

The sample was prepared by the so-called liquid mix technique. This technique is based on the formation of metallic complexes from concentrated solutions of polyfunctional organic acids and either salts or oxides of suitable cations for mixed oxide formation. Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot$

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$6H_2O$, were dissolved in hot citric acid. In order to solidify the liquid solution, ethylene glycol (3%, v/v) was added, which increases the solution viscosity due to the formation of ester-type three-dimensional polymers. In this way, a resin is formed and the evaporation of the solution obtained gives a vitreous intermediate polymer containing all the cations in the desired stoichiometric amounts. This resin was heated at 450 °C for 16 h. Several consecutive heat treatments were then performed: 600 °C for 64 h, 700 °C for 1 h, 800 °C for 72 h and, finally, 900 °C for 96 h. In this way, a well-crystallized solid is obtained showing the rhombohedral unit cell of $LaNiO_3$ which, indexed in a hexagonal cell, has the lattice parameters $a = 5.456(1)$ and $c = 13.136(2)$ Å.

The pellets, pressed at 2000 kgf cm^{-2}, were sintered at 800 °C for 24 h in air followed by another 24 h in oxygen. The final pellet density is 3.9 g cm^{-3}.

In Fig. 1 we show the electrical resistivity $\rho(T)$ of $LaNiO_3$ measured in the range 4.2–300 K in an He^4 cryostat, using a standard four-probe d.c. method. In agreement with other workers [6] no $d\rho/dT$ discontinuities were seen. Therefore, there is no evidence of metal–insulator [5] or magnetic ordering [9] transitions.

In Fig. 2 we show the magnetic susceptibility $\chi(T)$ measured with a Faraday magnetometer with an applied magnetic field H of 5000 G between 45 and 300 K. The magnetization is proportional to the magnetic field, without any remanent component over the whole temperature range. The slight dependence of χ on T is in accordance with the results of Goodenough *et al.* [10]. After correcting the extrapolated $\chi(T=0)$ value for core and Landau diamagnetism, we obtain a Pauli paramagnetic susceptibility χ_P of $8.773(4) \times 10^{-4}$ e.m.u. mol^{-1}.

The specific heat C_p was measured in the 0.45–8 K range (see Fig. 3) by a pulsed method in a semi-adiabatic calorimeter equipped with an He^3 cryostat. For $T > 5$ K our results are in reasonable agreement with those reported by Rajeev *et al.* [6]. For lower temperatures we observed a different behaviour. As can be seen in the inset of Fig. 3, C_p/T decreases linearly with T^2. The anomalous dependence reported in ref. 6 was not observed.

In Fig. 3 we also show the best fit of C_p to the function $C_p(T) = \gamma T + \beta T^3$, which results from the addition of the electronic contribution ($\gamma = 13.04(9)$ mJ mol^{-1} K^{-2}) to the lattice contribution ($\beta = 0.14(4)$ mJ mol^{-1} K^{-4}). From such a β value, a Debye temperature θ_D of 385 K is derived, which is similar to that obtained in other metallic oxides [11].

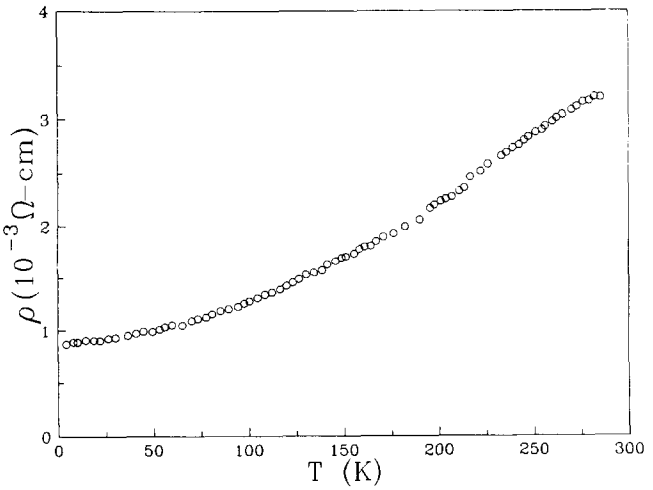

Fig. 1. Electrical resistivity as a function of T.

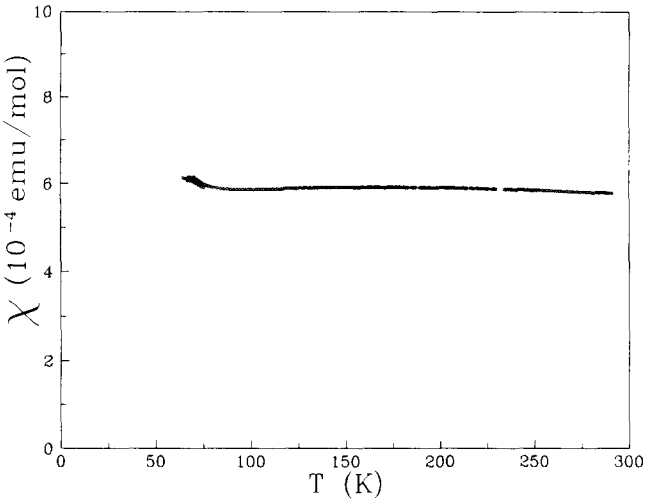

Fig. 2. Magnetic susceptibility as a function of T.

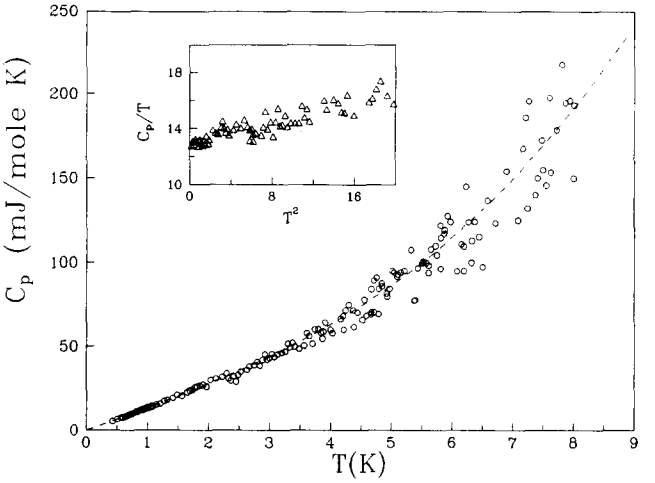

Fig. 3. Specific heat C_p as a function of T. The broken line is the best fit of C_p to the function $C_p(T) = \gamma T + \beta T^3$. Inset: C_p/T *vs.* T^2.

TABLE 1. Experimental parameters of $LaNiO_3$ compared with theoretical calculations of ref. 13

	γ (mJ mol^{-1} K^{-2})	$N(E_F)$ (states eV^{-1} cm^{-3})	χ_P^0 (e.m.u. mol^{-1})	χ_P (e.m.u. mol^{-1})
Experiment	13.04(9)	9.627×10^{22}	1.788×10^{-4}	$8.773(4)\times10^{-4}$
Theory	10.4696	7.6943×10^{22}	1.4332×10^{-4}	

3. Discussion

In Table 1, the experimentally determined γ and χ_P values are shown. The value of the density of states in the Fermi level $N(E_F)$ is also given. This value has been derived from the experimental γ values using the free-electron relation $\gamma=(\pi^2/3)k_B^2N(E_F)$, where k_B is the Boltzmann constant. The Pauli susceptibility, using the same approximation, is $\chi_P^0=\mu_B^2N(E_F)$, where μ_B is the Bohr magneton. It can be seen that the experimental χ_P value is related to χ_P^0 by a Stoner enhancement parameter [12]: $S\approx5$. In a mean-field approximation $S=(1-N(E_F)U_{eff})^{-1}$, where U_{eff} accounts for the intra-atomic correlations. Such a large S value is characteristic of ferromagnetic correlations. Nevertheless, the condition $N(E_F)U_{eff}\geqslant1$ is not accomplished and therefore spontaneous ferromagnetism should not be present, as was observed experimentally.

The results from band structure calculations by Mathi Jaya *et al.* [13] are also shown in Table 1. In view of the approximations involved, the agreement with experiment is quite good. The difference between γ(theory) and γ(experiment) can be attributed to electron–phonon interactions. If γ(theory) is corrected, as suggested in ref. 14, by a factor $(1+\lambda_{e-ph})$, the γ(experiment) value is reached with $\lambda_{e-ph}\approx0.24$. This λ_{e-ph} value is of the same order of magnitude as that found, for example, in the $La_{2-x}Sr_xCuO_4$ system [15].

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