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Approximation to the metal–insulator transition by Gd^{3+} doping in Pauli $LaNiO_3$ perovskite

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Abstract

The effect on electrical and magnetic properties of Gd^{3+} doping of $LaNiO_3$ was studied for Gd concentration $x \leq 0.1$. The electrical resistivity ρ increases with x, being $d\rho/dT > 0$ for all samples studied. The magnetic susceptibilities were fitted by the function $\chi(T) = \chi_0 - aT^2 + xC_{Gd^{3+}}/T$. The EPR results are discussed in terms of the Gd^{3+} paramagnetic moment interactions with the crystal field and with the conduction electron spins.

Keywords: $LaNiO_3$ perovskite; Gd doping; Resistivity; ESR; Magnetic susceptibility

1. Introduction

Research on the properties of the strongly electron correlated system has been a field of intense activity in recent years. The specific heat and metallic properties of $LaNiO_3$ were studied by the authors in a previous report [1], and also by Sreedhar et al. [2]. The $LaNiO_3$ behavior, which is characteristic of a correlated metallic system, was described in Ref. [2] in terms of a Fermi liquid composed of almost localized Ni 3d electrons. Metal–insulator transitions were detected in $RNiO_3$ (R = Pr, Nd, Sm, Eu) at temperatures T_{MI} dependent on the ionic radius of R. T_{MI} rises systematically as the size of R decreases and as the subsequent distortion from the ideal cubic perovskite increases [3]. We are studying the system $La_{1-x}Gd_xNiO_3$, where the compounds for $x = 1$ ($GdNiO_3$) and $x = 0$ ($LaNiO_3$) are respectively insulating and metallic at room temperature. In this work we present the results obtained for $0 \leq x \leq 0.1$.

2. Experimental

The polycrystalline samples were prepared by a sol-gel method. Stoichiometric amounts of $La(NO)_3$ $6H_2O$, $Gd(NO)_3$ $6H_2O$ and $Ni(NO)_3$ $6H_2O$ were dissolved in a solution of urea to obtain a green gel after removing excess water. Annealing at 250 °C for 3 h decomposed the gel into a brown powder. This powder was ground and heated for 12 h at $T = 800$ °C. After this procedure a change of color from brown to black was observed. Finally, the powder was ground again and, in order to homogenize the oxygen composition in the samples, was annealed at 450 °C in an oxygen atmosphere for 12 h. The structural characterization of the $La_{1-x}Gd_xNiO_3$ system was carried out by X-ray powder diffraction. The spectra were matched to $LaNiO_3$ diffraction patterns from the total access diffraction database (TADD). Small amounts (around 1%) of NiO were detected in addition to the $LaNiO_3$ phase. The samples were pressed into small pellets for the electrical measurements, which were performed using a d.c. four probe method in the 77–300 K temperature range. Magnetization was measured using a SQUID magnetometer between 5 and 300 K with an applied magnetic field H of 10 kG. Measurements at higher temperatures (77–600 K) were made with a vibrating sample magnetometer having $H = 5$ kG. EPR spectra were taken at 9.5 GHz (X-band) between 10 and 300 K with a Bruker ESP-300 spectrometer.

3. Results and discussion

Resistivity as a function of T for different x values is shown in Fig. 1. The experimental data were fitted by $\rho(T) = \rho_0 + AT^2$ between 77 and approximately

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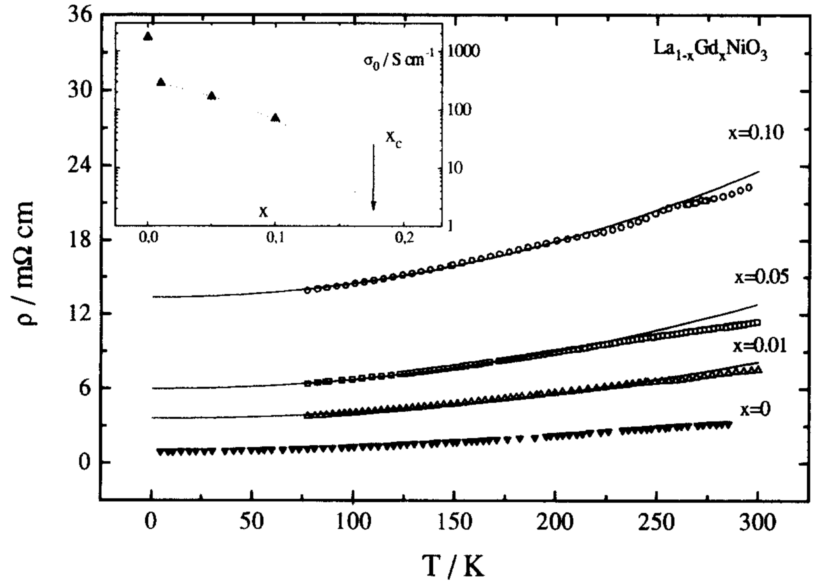

Fig. 1. Electrical resistivities as a function of T for different x values. The solid lines are fittings to $\rho = \rho_0 + AT^2$ with ρ_0 and A from Table 1. In the inset we show the experimental log σ_0 vs. x, and in the broken line the expected behavior near the metal–insulator transition.

200 K, where ρ changes to a linear behavior. The parameters obtained are shown in Table 1. In the inset to Fig. 1 we show $\sigma_0 = 1/\rho_0$ as a function of x. Assuming that $\sigma_0 \sim (x_c - x)^{1.9}$ [4], a percolation concentration for the metal–insulator transition $x_c = 0.18$ is obtained (see Fig. 1). This value is close to other perovskite percolation values [5]. Magnetization measurements are shown in Fig. 2 as $\chi^{-1} = H/M$ vs. T. The susceptibility χ increases with Gd doping. The tendency to a Currie-like behaviour observed for higher x (see Fig. 2) is a consequence of the increasing weight of the Gd susceptibility in the measured χ. The data were fitted by $\chi(T) = \chi_0 - aT^2 + xC_{Gd^{3+}}/T$, where $\chi_0 - aT^2$ is the Stoner metallic susceptibility [6] and $xC_{Gd^{3+}}/T$ (with $C_{Gd^{3+}}$ the Curie constant of Gd^{3+}) is the contribution of the paramagnetic localized moments of Gd^{3+}. The results of the fitting procedure, taking χ_0, a and x as free parameters (see Table 1), are plotted in Fig. 2 with and without T^2 dependence. In Fig. 3 we show the EPR spectra taken at 20 K. The fine structure observed is a consequence of the interaction between the Gd spins and the crystal field. The most important contribution would come from the twelve nearest neighbor oxygen ions. The lines are broadened with increasing x because of dipolar interactions between the Gd spins. As a consequence the spectrum resolution is deteriorated

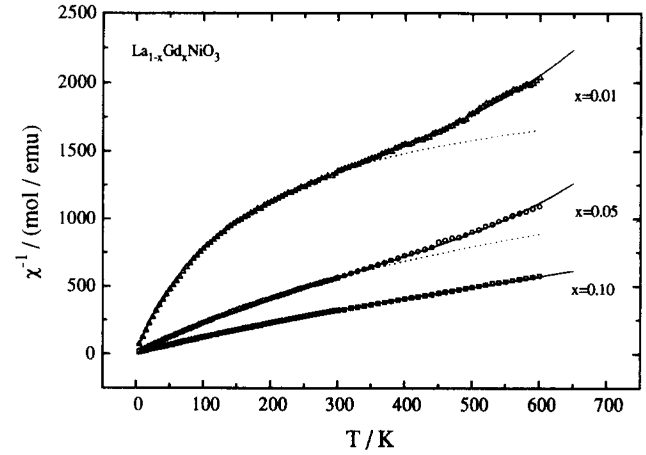

Fig. 2. χ^{-1} vs. T for different x values. The solid lines are fittings to $\chi(T) = \chi_0 - aT^2 + xC_{Gd^{3+}}/T$ with χ_0, a and x from Table 1. The broken lines show the fitting for $a = 0$.

Table 1

$La_{1-x}Gd_xNiO_3$ resistivity and susceptibility parameters obtained by fitting the data to $\rho_0 + AT^2$ and $\chi_0 - aT^2 + xC_{Gd^{3+}}/T$ respectively ($C_{Gd^{3+}} = 7.869$ emu K mol^{-1} is the free-ion value for the Gd^{3+} Curie constant).

Sample x (nominal)	Resistivity parameters		Susceptibility parameters		
	ρ_0/mΩ cm	A/μΩ cm K^2	$\chi_0 \times 10^4$/emu mol^{-1}	$a \times 10^{10}$/emu mol^{-1} K^{-2}	x
0			5.1[a]	2.9[a]	
0.01	3.6	0.0509	5.4	4.8	0.0096
0.05	6	0.0762	5.6	8.6	0.049
0.1	13.3	0.1146	5.9	3.3	0.099

[a] From Ref. [2].

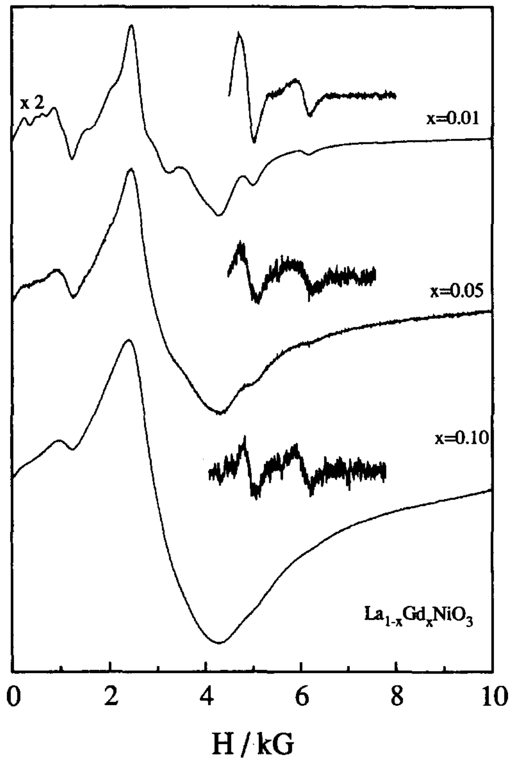

Fig. 3. EPR spectra for different x values taken at $T = 20$ K. The $x = 0.01$ spectrum was amplified by a factor 2. Above each spectrum are shown amplified well resolved resonance lines, with H between 4 and 8 kG and without the base line. These lines do not change position with concentration of Gd.

(see Fig. 3). However, at least two lines are well resolved in all the samples. It can be seen in Fig. 3 that the H positions of these lines remain unchanged when going from $x = 0.01$ to $x = 0.1$. Therefore, we can infer that the oxygen polyhedron surrounding the Gd sites is the same (and not distorted) in all the $x = 0.01$, $x = 0.05$, and $x = 0.1$ samples. Upon increasing the temperature some fine structure lines lose their amplitude, an effect probably related to the interaction between Gd and the conduction-electron spins [7]. In conclusion, we found that the metallic character of $LaNiO_3$ remains unchanged by the (up to 10%) Gd^{3+} substitution. Simultaneously, no structural distortions were detected by EPR. However, the enhancement of the Pauli susceptibility χ_0 and of the electrical resistivity ρ_0 suggests that the metal-insulator transition is being approached. In order to verify this hypothesis we are presently synthesizing samples with higher Gd content, which require high oxygen pressure techniques.

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References

[1] R.D. Sánchez, M.T. Causa, M.J. Sayagués, M. Vallet-Regí and J.M. Gónzalez-Calbet, *J. Alloys Comp.*, *191* (1993) 287.
[2] K. Sreedhar, J.M. Honing, M. Darwin, M. McElfresh, P.M. Shand, J. Xu, B.C. Crooker and J. Spalek, *Phys. Rev. B*, *46* (1992) 6382.
[3] J.B. Torrance, P. Lacorre, A.I. Nazal, E.J. Ansaldo and Ch. Niedermeyer, *Phys. Rev. B*, *45* (1992) 8209.
[4] N.F. Mott and E.A. Davies, *Electronic processes in non-crystalline materials*, Oxford University Press, 2nd edn., 1979; S. Kirkpatrick, *Phys. Rev. Lett.*, *27* (1971) 1722.
[5] A.K. Raychaundhuri, K.P. Rajeev, H. Srikanth and R. Mahendiran, *Physical B*, *197* (1994) 124.
[6] N.F. Mott, *Metal insulator transitions*, Taylor and Francis, London, 1974.
[7] R. Odermatt, *Helv. Phys. Acta*, *54* (1981) 1.