

## Magnetic Properties of $\text{La}_2\text{NiO}_{4.16}$ and $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$

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**Magnetic properties of  $\text{La}_2\text{NiO}_{4.16}$  and  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$  are studied by dc susceptibility in a wide temperature range, i.e., 4–1200 K. The principal aim is to investigate the modifications of magnetic interactions in the  $\text{NiO}_2$  plane by inserting a magnetic ion in the  $\text{LaO}$  layer. Magnetic properties are considerably different with and without praseodymium. When  $0 < x \leq 2$  the solid solution follows the Curie–Weiss law and the Curie constant varies linearly with  $x$ . For  $x = 0$ , the susceptibility is smaller and another contribution appears above 200 K that is treated as the result of clusters of AF-coupled spins of two-dimensional character. Our model fits very well the data from 4 to 1000 K. Comparing the Curie–Weiss temperature with and without Pr suggests that small Pr quantities modify the in-plane Ni–O–Ni magnetic interactions and, thus, decrease the Curie–Weiss temperature. We think this is not a structural effect; it might correlate with an increased resistivity when Pr is substituted. For larger substitution, i.e.,  $x > 0.5$ , a single  $\text{Pr}^{3+}$  effect might dominate.** © 1998

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### INTRODUCTION

Rare earth nickelates,  $\text{Ln}_2\text{NiO}_{4+\delta}$ , have remarkably interesting physical properties resulting from a subtle interplay of several ingredients such as structural constraints, hole density, and magnetism among others. Their structures are known, i.e.,  $\text{K}_2\text{NiF}_4$ , and are commonly described as intergrowth of  $\text{LnO}$  and  $\text{NiO}_2$  layers (1). The hole density is a key factor in the control of electronic and magnetic properties. It is fixed by the oxygen stoichiometry or substitutions on the rare earth site. Some years ago, comparing the infrared response of  $\text{Pr}_2\text{NiO}_{4.22}$  with that of  $\text{Pr}_2\text{NiO}_{4.0}$  (2), we showed that oxygenation modifies the oxygen effective charge (measured by the splitting between LO and TO frequencies) in an anisotropic manner: the component along the  $c$  axis, where bonding is 60% ionic, is insensitive to hole doping by oxygenation, whereas the  $a, b$  component

changes in proportion to the injected hole density. Hence, the injected holes affect essentially the oxygen of the basal plane to which they are hybridized, supplementary proof that the electronic properties of these compounds are quasi-bidimensional (3).

When stoichiometric ( $\delta = 0$ ), the nickelate orders magnetically (three-dimensionally) below  $T_N$  [325 K for lanthanum nickelate (4)]. This order is progressively suppressed on increasing  $\delta$  (5);  $T_N$  decreases and becomes minimal for  $\delta = 0.11$ . It increases again when oxygen tends to order three-dimensionally along the  $c$  axis while incommensurate charge and spin order take place in the  $a, b$  plane (6), as proved by neutron diffraction. Charge and spin ordering suggest that magnetism interferes with transport properties, although no magnetoresistance has been reported up to now in nickelates. Inserting a magnetic ion in the  $\text{LnO}$  layer would then be an interesting way to probe for such a possibility. In other words, is there an interaction between the  $4f$  shell of the rare earth element in the  $\text{LnO}$  layer and Ni–oxygen bonds in the  $\text{NiO}_2$  layer where AF interactions dominate? Certainly this problem is connected to the charge transfer phenomena from the reservoir to the conducting plane in the cuprate series (7) and to the poisoning of superconductivity by praseodymium in Ln-123 compounds (8).

In a previous paper (9), we reported results concerning the solid solution  $\text{Pr}_{2-y}\text{La}_y\text{NiO}_{4+\delta}$ . Praseodymium goes in the  $\text{LnO}$  layers where the  $\text{Ln–O}$  bonds are in extension due to the small size of the rare earth ion. This effect is stronger in praseodymium nickelate than in lanthanum nickelate, and accordingly, for stability reasons, praseodymium is not expected to have an oxidation degree larger than 3+.  $\text{Pr}_2\text{NiO}_{4+\delta}$  has an average structure described by the  $Bmab$  space group while  $\text{La}_2\text{NiO}_{4+\delta}$  is more likely  $Fmmm$ . We expect, then, a phase transition in the solid solution for  $y \sim 1$ –1.2 according to the variations of the unit cell parameters (9). Looking at transport properties, we observed a localization effect of the charge carriers attributed to praseodymium that lowered the conductivity, even for small Pr content ( $1.5 < y < 2$ ), that is in the  $Fmmm$  range. We suggested a possible magnetic origin of this effect.

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$\text{Pr}^{3+}$  ( $4f^2$ ) has magnetic properties ( $S = 1$ ,  ${}^3\text{H}_4$ ,  $\mu_{\text{eff}} = 3.578\mu_{\text{B}}$  when isolated). This solid solution is then an interesting system to study to probe magnetic effects in transport properties.

In the present paper we investigate magnetic properties of the same solid solution  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$  (where  $x = 2 - y$ ) with the purpose of detecting a possible effect of praseodymium on the magnetic coupling in the  $\text{NiO}_2$  plane. In this preliminary approach we use dc susceptibility measurements on ceramics and observe a modification of the susceptibility versus  $T$  affecting significantly the Curie–Weiss temperature for small substitutions (close to  $\text{La}_2\text{NiO}_{4+\delta}$ ), suggesting a magnetic coupling of praseodymium with the  $\text{NiO}_2$  layer.

### EXPERIMENTAL

Compositions of  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$  with  $x$  varying from 0 to 2 were synthesized according to the procedure already described (9) and their oxygen excess ( $\delta$ ) deduced from TGA measurements. It increases regularly with  $x$  from  $\delta = 0.16$  to  $\delta = 0.22$  for air-prepared samples.

Magnetic susceptibility was measured from 4 to 1200 K in a set of two devices. Below room temperature we used an automated susceptometer DSM8 (Manics, France) based on the pendulum principle. The temperature was controlled between 4 and 300 K with an ITC4 controller (Oxford Instruments, France). A ferrite was used as a standard to calibrate the magnetic field measured with a Hall sensor placed a few centimeters from the sample. The sample holder contribution was subtracted from the measurement and the calibration of the system was checked on a gadolinium oxide powder (4N, Johnson Matthey). High-temperature measurements were carried out using a Faraday microbalance. The sample was placed in the isothermal zone of a platinum furnace equipped to work under controlled atmosphere. To minimize the buoyancy correction, we worked with a reduced pressure of 100 mm Hg. The suspensions and sample holder were of fused quartz and their very small contributions are subtracted from the data after blank measurements. The high sensitivity of the balance ( $\pm 10 \mu\text{g}$ ) and the high field constant  $HdH/dx = 6 \times 10^6 \text{ G}^2/\text{cm}$ , stable in a large domain (30 mm), allow very high sensitivity of susceptibility detection ( $10^{-8} \text{ emu}$ ), ensuring the measurement with an excellent precision for susceptibility in the range of  $10^{-4} \text{ emu/mol}$ . This system was also calibrated with the same powder of gadolinium oxide, the susceptibility of which follows well the function  $\chi = 15.757/(T + 16.9) \text{ emu mol}^{-1}$  between 2 and 1400 K. Both apparatus give very good agreement in the overlap regime and allow measurement of the magnetic susceptibility in a fairly large temperature range. Hereafter, the magnetic susceptibility is given in  $\text{emu mol}^{-1}$  and we have subtracted the core diamagnetic contribution of the constituent ions. The

magnetization of  $\text{La}_2\text{NiO}_{4.16}$  has also been measured on a pellet (300 mg) in a SQUID device (Quantum Device) from 300 to 4 K.

### RESULTS AND DISCUSSION

The magnetic susceptibility of  $\text{Pr}_2\text{NiO}_{4+\delta}$  ( $x = 2$ ) has been measured up to 1400 K under air flow. At high temperature some oxygen is lost due to chemical equilibration of the sample with the ambient oxygen partial pressure; this causes a decrease in the oxygen excess  $\delta$ . This quantity, initially stated at  $\delta = 0.22$ , is constant from 4 to 600 K and then decreases progressively to reach 0.14 at 1400 K (10). The molar susceptibility of  $\text{Pr}_2\text{NiO}_{4+\delta}$  and its inverse are reported in Fig. 1, from which it is obvious that the oxygen loss has a negligible effect on it. The data are well fitted by Curie–Weiss law plus a constant term  $\chi_0$  (Table 1). High-temperature measurements ensure good precision in estimating  $\chi_0 \sim 1.8 \times 10^{-3} \text{ emu mol}^{-1}$ . This sample is not metallic (9), and thus a Pauli contribution is not expected (usually smaller than  $1 \times 10^{-3} \text{ emu mol}^{-1}$ ). This constant term could be due to a Van Vleck contribution that is, however, generally small; hence this term traduces more likely an additive term that will be discussed later. The susceptibility is then

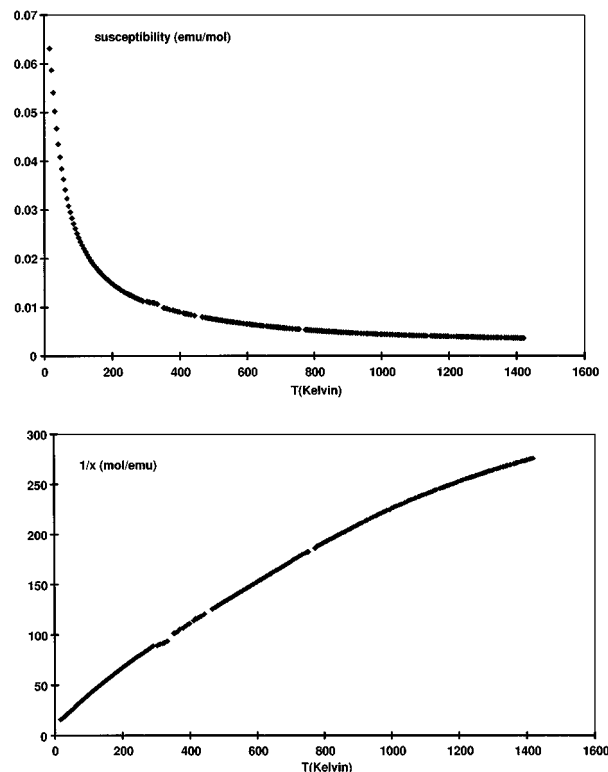


FIG. 1. Magnetic susceptibility of  $\text{Pr}_2\text{NiO}_{4.22}$  (measured at 13 kG).

**TABLE 1**  
**Refined Parameters  $C$ ,  $\theta$  and  $\chi_0$  versus Praseodymium Fraction  $x$  by Fitting the Experimental Data<sup>a</sup>**

Composition	$C$ measured (emu · K mol <sup>-1</sup> )	$-\theta$ (K)	$\chi_0$ (emu · K mol <sup>-2</sup> )
La <sub>2</sub> NiO <sub>4.16</sub> <sup>a</sup>	1.49	700	$4 \times 10^{-4}$
La <sub>2</sub> NiO <sub>4.16</sub> <sup>b</sup>	0.33	65	
La <sub>1.5</sub> Pr <sub>0.5</sub> NiO <sub>4.17</sub>	0.88	25	$1.3 \times 10^{-3}$
LaPrNiO <sub>4.18</sub>	1.64	28	$1.3 \times 10^{-3}$
La <sub>0.5</sub> Pr <sub>1.5</sub> NiO <sub>4.20</sub>	2.4	33	$1.3 \times 10^{-3}$
Pr <sub>2</sub> NiO <sub>4.22</sub>	3.02	32	$1.8 \times 10^{-3}$

<sup>a</sup>Fit by Eq. [1] in the range 200–700 K.

<sup>b</sup>Fit by Eq. [3] of  $\chi_{\text{meas}} - (M/H)_{\text{ferro}}$  by a Curie–Weiss law plus a cluster contribution (see text). The value reported is the mean value of  $C_{\text{CW}}$  and  $C_{\text{spin}}$  as determined in the fitting procedure.

written as

$$\chi = \frac{C}{T + \theta} + \chi_0, \quad [1]$$

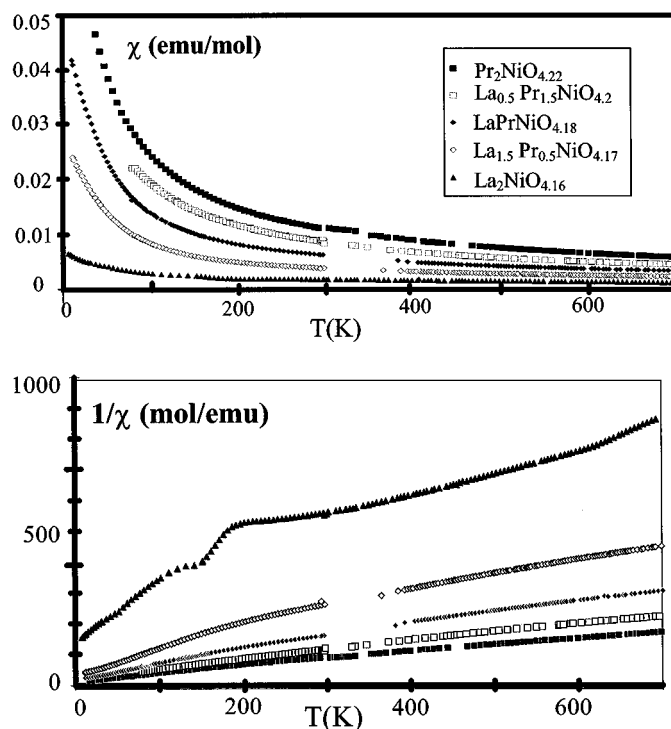
where  $C$  is the Curie constant and  $-\theta$  the Curie–Weiss temperature. In the following we propose values for these quantities in the series La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub>.

Figure 2 shows the molar susceptibility  $\chi$  and  $1/\chi$  versus  $T$  for a set of samples having  $0.16 \leq \delta \leq 0.22$ . In these series of experiments, the temperature is limited to 700 K to avoid oxygen losses. The measurements concerning La<sub>2</sub>NiO<sub>4.16</sub> have been extended to higher temperatures (1200 K) and are reported below. Susceptibility increases with praseodymium content, reflecting in a simple way the progressive introduction of paramagnetic species in the  $LnO$  layers. The evolution with  $T$  is similar for all compositions containing praseodymium ( $x > 0$ ) and Eq. [1] fits well all these data in the large temperature range 4–700 K. La<sub>2</sub>NiO<sub>4+δ</sub> behaves differently and will be considered afterward. The quantities  $C$ ,  $\theta$ , and  $\chi_0$  for these compounds are reported in Table 1.

The Curie constant  $C$  ( $C = (N/3k_B)\mu_{\text{eff}}^2 = \mu_{\text{eff}}^2/2.829$ , where  $N$  is Avogadro's constant and  $\mu_{\text{eff}}$  is in Bohr magneton) is plotted versus  $x$  in Fig. 3, which shows a linear increase in  $C$  with praseodymium concentration when  $x \geq 0.5$ . The system is composed of two sublattices of spins formed by Pr<sup>3+</sup> and Ni<sup>2+</sup> species, and assuming to first order that they can be treated as noninteracting systems of isolated spins, a simple dilution law enables the evaluation of a total effective magnetic moment:

$$\mu_{\text{eff}_T}^2 = 2x\mu_{\text{eff}}^2(\text{Pr}^{3+}) + \mu_{\text{eff}}^2(\text{Ni}^{2+}). \quad [2]$$

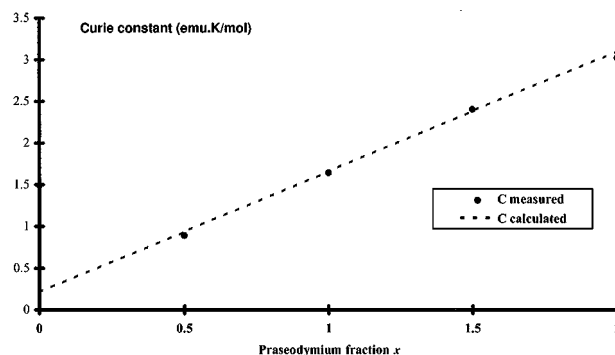
From the linear dependence of  $\mu_{\text{eff}_T}^2$  one can get  $\mu_{\text{eff}}(\text{Ni}^{2+}) = 1.3\mu_B$  and  $\mu_{\text{eff}}(\text{Pr}^{3+}) = 3.4\mu_B$ ; the latter value is only 5% smaller than the known value for the free Pr<sup>3+</sup> ion



**FIG. 2.** Magnetic susceptibility of La<sub>2-x</sub>Pr<sub>x</sub>NiO<sub>4+δ</sub>.  $1/\chi$  is also plotted in the bottom figure.

( $3.58\mu_B$ ). The small value of  $\mu_{\text{eff}}(\text{Ni}^{2+})$  compared with  $3.9\mu_B$  observed in octahedral symmetry is a common feature of transition elements in K<sub>2</sub>NiF<sub>4</sub>-type compounds and especially in cuprates (11). To explain such a small value, one can suggest that first a certain fraction ( $< 20\%$ ) of nickel ions is in a  $3 +$  state (LS:  $\mu_B = 1.73$ ) while the remaining spins are coupled in a cluster of spins. Note that one spin shared by four Ni ions would provide an ad hoc solution.

The fit according to Eq. [1] is only a raw approximation for  $x = 0$  as can be seen in Fig. 2; this is particularly obvious



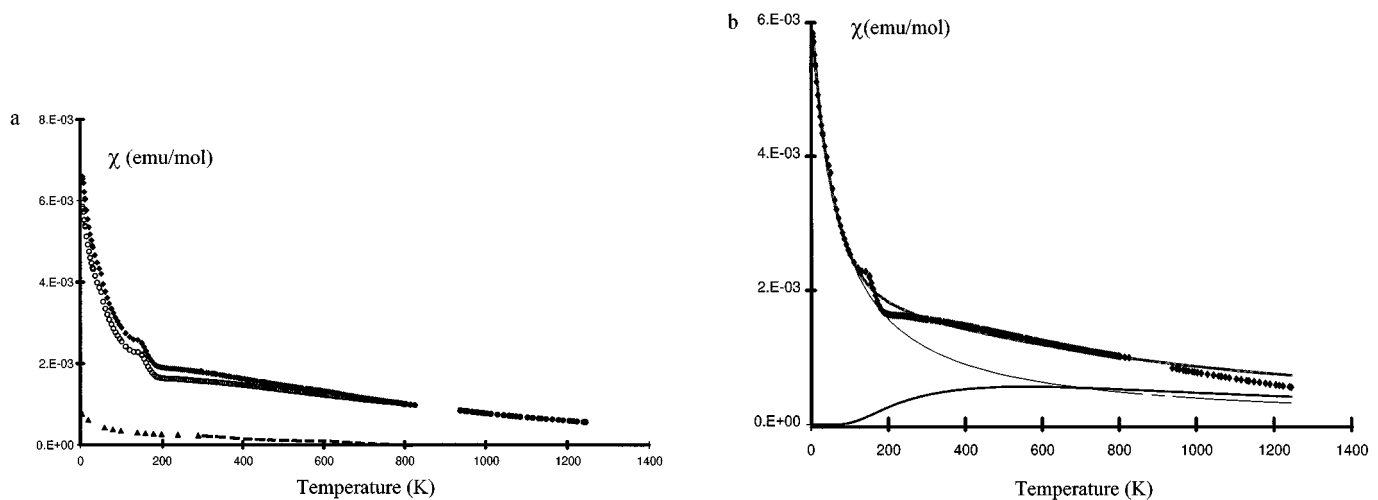
**FIG. 3.** Curie constant deduced from curve fitting of the data in Fig. 2 according to Eq. [1].

for  $\chi^{-1}$  (at bottom). To provide a wider range of fitting we have extended the temperature range to 1200 K, where possible modifications of  $\delta$  could have only secondary effects; that is reported in Fig. 4. In this figure  $\chi_{\text{meas}}$  represents the measured susceptibility; it shows an anomaly at 150 K corresponding to the magnetic order reported by Yamada *et al.* (5) and further ascribed by Tranquada *et al.* (12) to spin order in stripe correlation. The same authors have also reported a divergence of the magnetization at 110 K in  $\text{La}_2\text{NiO}_{4.133}$  characteristic of O-centered domain walls, providing evidence for a ferrimagnetic response in the paramagnetic phase (13). We suspect the accident seen here and the one reported by Tranquada *et al.* to have a similar origin. In many cases, low-temperature magnetizations have shown thermoremanent phenomena (5, 14, 15). We have effectively observed a systematic difference between field-cooled (FC) and zero-field-cooled (ZFC) procedures when measuring magnetization below 50 K. Moreover, in the compound  $\text{La}_2\text{NiO}_{4.05}$  (ceramic sample) we have followed the magnetization decay versus time at 4 K after a FC procedure (16). Its spin-glass-like behavior at low temperature traduces a heterogeneous magnetic structure that appears in all samples with  $0.02 \leq \delta \leq 0.17$ . Consequently, the magnetization is nonlinear and hysteretic below 2000 G. This is observed even at room temperature in dc but also in the low-field part of the magnetic resonance measured at 9.4 GHz (17). Figure 5 shows such a cycle for  $\text{La}_2\text{NiO}_{4.16}$  at room temperature. The ferromagnetic part must be considered in any fit of the susceptibility and might

explain at least part of the constant term in  $\chi(T)$  found in Eq. [1].

This ferromagnetic behavior is very similar to previous observations on nearly stoichiometric  $\text{La}_2\text{NiO}_4$  obtained by annealing the oxidized precursor under reducing conditions (14, 15). In these samples, the ferromagnetic contribution could be suspected to originate from  $\text{Ni}^0$  species. This is definitely not the case here and we anticipate this phenomenon to be intrinsic to oxygen-doped nickelate. In Fig. 4a, we have represented the ferromagnetic contribution  $(M/H)_{\text{ferro}}$  calculated at the same field as that used in the susceptibility measurement. It has been measured from 4 to 300 K; it falls for  $T > 300$  K (dotted line), as explained elsewhere (16, 17, 19). This contribution is lost at around 640 K where there occur (i) a structural transformation to tetragonal symmetry ( $I4/mmm$  SG), (ii) a thermal signal (endothermic at heating), (iii) loss of magnetic resonance, and (iv) onset of an oxygen departure. It is remarkable that this phenomenon is close, but distinct, to that of the Curie transition of  $\text{Ni}^0$  (627 K); this has not been explained up to now.

We now attempt to fit  $\chi_{\text{meas}} - (M/H)_{\text{ferro}}$  (open circle in Fig. 4a) in the largest possible range; it represents the paramagnetic contribution of  $\text{La}_2\text{NiO}_{4.16}$ . Its low-temperature part ( $< 200$  K) falls approximately in Curie-Weiss behavior (the continuous line); it is, however, inappropriate in the intermediate temperature range, i.e., 200–900 K, as seen in this figure. This range has been tentatively modeled by a system of independent clusters of spins (20, 21).



**FIG. 4.** (a) Magnetic susceptibility of  $\text{La}_2\text{NiO}_{4.16}$ . The data are those of Fig. 2 to which we have added subsequent measurements at higher temperature. Triangles represent  $(M/H)_{\text{ferro}}$  as discussed in the text. This contribution goes to zero above 640 K and the low-temperature part of the data has been extrapolated from 300 to 600 K. Diamonds represent  $\chi_{\text{meas}}$ , and open circles,  $\chi_{\text{meas}} - (M/H)_{\text{spin}}$ . (b) Fitting of  $\chi_{\text{meas}} - (M/H)_{\text{spin}}$ . The thin continuous line fits the low-temperature part by Curie-Weiss law ( $C_{\text{cw}}, \theta$ ). The thick black continuous line shows the fit by the cluster model ( $C_{\text{spin}}, J$ ), Eq. [3]. The thick gray line is the addition of both previous laws fitted to the experimental data. The fitted parameters are given in the text. The reliability of the fit is 99.7%.

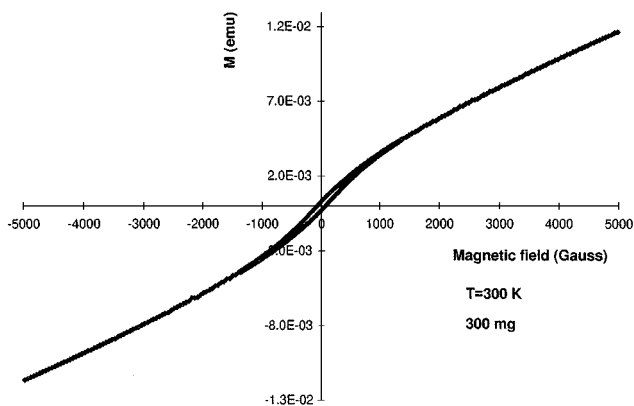


FIG. 5. Hysteresis loop for  $\text{La}_2\text{NiO}_{4.16}$  measured at 300 K for a pellet of 300 mg.

Considering the high density of holes (0.32/Ni atom), we assume the system to be rather heterogeneous, composed of clusters of antiferromagnetically coupled spins. More precisely, we consider the clusters as formed by four antiferromagnetically coupled spins by analogy with previous works in cuprates (21, 22). As the orthorhombic distortion is very small in  $\text{La}_2\text{NiO}_{4.16}$ , we use a tetragonal equivalent unit cell. The four nickel sites are located at the corners of this unit cell and we have to take into account two next neighbors and two next-nearest neighbors at respective distances  $a$  and  $a\sqrt{2}$ , leading to two intracluster exchange interactions  $J$  and  $J'$ . In a first approximation, we suppose  $J'$  negligible compared with  $J$ , because of the larger distances between next neighbors. No interplane interactions are considered; it is then a strictly two-dimensional model. The Heisenberg Hamiltonian can thereby be written as

$$H = -2J(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_3\mathbf{S}_4 + \mathbf{S}_4\mathbf{S}_1),$$

leading to a set of 27 energy levels, some of them being degenerate. Their filling according to Boltzmann statistics gives the expression in parentheses in Eq. [3] with  $x = e^{J/kT}$ , where  $T$  is temperature and  $k$  is the Boltzmann constant. The spin susceptibility is simply obtained by multiplying by the prefactor  $C_{\text{spin}} = Ng^2\mu_B^2/3k$ , where  $N$  is Avogadro's number,  $g$  the gyromagnetic factor, and  $\mu_B$  the Bohr's magneton. To account for low-temperature AF fluctuations, we should add AF interactions between clusters as explained by Wang *et al.* (21); this results in dividing  $C_{\text{spin}}$  by  $(T + \theta)$  where  $-\theta$  is the Curie-Weiss temperature. The susceptibility  $\chi_{\text{spin}}$  is then

$$\chi_{\text{spin}} = \frac{C_{\text{spin}}}{T + \theta} \left( \frac{6x^2 + 42x^6 + 12x^8 + 66x^{10} + 153x^{12} + 30x^{14} + 168x^{16} + 180x^{20}}{1 + 3x^2 + 2x^4 + 13x^6 + 7x^8 + 15x^{10} + 24x^{12} + 5x^{14} + 14x^{16} + 9x^{20}} \right) \quad [3]$$

if one considers only the first five levels. The  $\chi_{\text{spin}}$  follows the thick continuous line in Fig. 4b. We have fitted the experimental data  $[\chi_{\text{meas}} - (M/H)_{\text{ferro}}]$  by adding the Curie-Weiss law, valid at low temperature, to  $\chi_{\text{spin}}$ , which accounts for the intermediate temperature range. The four parameters of the fit, i.e.,  $C_{\text{CW}}$ ,  $\theta$ ,  $C_{\text{spin}}$ , and  $J$  adjust themselves respectively to  $C_{\text{CW}} = 0.42 \text{ emu} \cdot \text{K/mol}$ ,  $-\theta = 65 \text{ K}$ ,  $C_{\text{spin}} = 0.25 \text{ emu} \cdot \text{K/mol}$  and  $J = -295 \text{ K}$  (AF coupling), providing a very small standard deviation to the curve ( $R_1 = 99.7\%$ ) in the temperature range 4–1000 K. This fit is represented by the gray continuous line in Fig. 4b. The divergence at 150 K has not been explained yet. Between 1000 and 1200 K the measured data differ slightly from the calculated data because of some oxygen loss that contributes to a faster decrease in the susceptibility with  $T$ . Note that the dependence of  $T$  in the range 200–1000 K has the same shape as that of a spin 1/2 square-lattice Heisenberg antiferromagnet qualitatively describing the behavior of the LSCO phase (23, 24). There still remains important debate about this model, which does not quantitatively describe the  $\chi$  reduction below  $T_{\text{max}}$  (24).

Summarizing this part, we have shown that the linear part of the susceptibility  $[\chi_{\text{meas}} - (M/H)_{\text{ferro}}]$  of  $\text{La}_2\text{NiO}_{4.16}$  is well described by a Curie-Weiss contribution ( $C_{\text{CW}} = 0.42$ ,  $\theta = -65 \text{ K}$ ), to which is added a spin contribution that we calculate by a cluster model in the intermediate- and high-temperature range. The mean value of both Curie constants is exactly equal to the value extrapolated from the solid solution  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$ . The Curie-Weiss temperature,  $-65 \text{ K}$ , is much smaller than that extrapolated using a Curie-Weiss analysis of the data in the intermediate-temperature range ( $-700 \text{ K}$ , Table 1) and seems more reasonable.

Comparing the Curie-Weiss temperatures for various  $x$  in the series  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$  is interesting with respect to the effect of Pr on in-plane Ni-O-Ni magnetic coupling. There is a clear tendency of Pr to decrease the Curie-Weiss temperature  $-\theta$ , as shown in Fig. 6. The decrease is very fast in the range  $0 \leq x \leq 0.5$  and remains approximately constant for  $x > 0.5$ . For small  $x$ , i.e.,  $x < 0.5$ , this effect is not attributed to a structural modification expected to occur only for larger  $x$  (9). Exchanges between Pr and  $\text{NiO}_2$  layers occurring through the apical oxygen might modify the Ni-O-Ni magnetic interactions. Because of structural distortions the Pr-O-Ni bond angles are not strictly  $180^\circ$  and therefore ferromagnetic exchanges are anticipated to be enhanced by Pr substitution of the LaO layer and consequently to reduce  $-\theta$  (25). Unfortunately, the effect saturates rapidly for  $x > 0.5$  where  $-\theta$  is almost constant

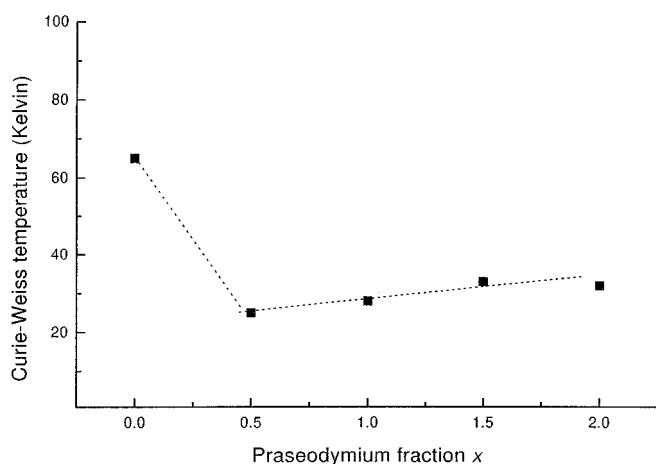


FIG. 6. Curie-Weiss temperature versus  $x$  in  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$ .

or increases slightly. This might be accounted for by decreases in structural parameters as observed elsewhere (26) or suggests that  $-\theta$  is controlled by single-ion effect of  $\text{Pr}^{3+}$ . Clearly more studies for small substitutions are necessitated on powders and also on single crystals because of the intrinsic anisotropy of the system.

### CONCLUSIONS

In praseodymium-substituted lanthanum nickelate, magnetic susceptibility is modeled by classic Curie-Weiss law plus a constant term proved to have a ferromagnetic origin in  $\text{La}_2\text{NiO}_{4.16}$ . Although not checked for  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$  we anticipate the ferromagnetic contribution to increase with  $x$ ; it is probably the main ingredient of the constant  $\chi_0$  term.

The Curie constant increases proportionally with the amount of praseodymium traducing the increasing concentration of magnetic ions. The corresponding effective moment for praseodymium ( $3.4\mu_B$ ) is in close agreement with that of the free ion, in contrary to the moment of nickel ( $1.3\mu_B$ ), which is smaller than usual in a tetragonal field ( $3.2\mu_B$ ).

The susceptibility for  $\text{La}_2\text{NiO}_{4.16}$  is tentatively modeled by considering a cluster contribution in the temperature range 200–1000 K that superposes to a Curie-Weiss contribution at lower temperature. Therefore, three-dimensional interactions dominate the low-temperature regime, whereas a spin susceptibility, two-dimensional in character, accounts for data at increasing temperatures. It explains the very flat temperature dependency of the susceptibility of this oxide in the temperature range 200–1000 K. No such effects appear in  $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$  probably because of the single-ion effect involving  $\text{Pr}^{3+}$ .

For small Pr substitution in the LaO layer, i.e., below  $x = 0.5$ , the Curie-Weiss temperature is significantly depressed. This might be due to an enhanced contribution from ferromagnetic exchange interaction following  $\text{Pr}-\text{O}_{\text{apical}}-\text{Ni}$  bonding. Curiously, this effect occurs in the same range of substitution where the resistivity is enhanced with respect to that in  $\text{La}_2\text{NiO}_{4.16}$  (8) and we are tempted to correlate both phenomena. The confirmation of this hypothesis would provide interesting insight into the transport properties on a microscopic scale in this compound.

### ACKNOWLEDGMENTS

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