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Anomalies in magnetic susceptibility of nonstoichiometric $Nd_2NiO_{4+\delta}$ ($\delta = 0.049, 0.065, 0.077, 0.234$)

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Abstract

We have investigated the influence of oxygen excess on structural and physical properties of the $Nd_2NiO_{4+\delta}$ compounds. Using the citrate method and subsequent annealing in air and in a reducing atmosphere a various oxygen-doped compounds were prepared. X-ray diffraction at room temperature shows that structure is strongly oxygen excess dependent. Thus, by increasing δ by up to 0.077, the compounds adopt a tetragonal structure gradually with a biphasic domain between orthorhombic and tetragonal structures. And at higher δ values, the structure becomes orthorhombic. Moreover, Rietveld analysis shows that for $\delta < 0.077$ the presence of two crystalline phases with different oxygen excess: it should be the signature of interstitial oxygen, which is distributed in heterogeneous way. The biphasic products are composed of a stoichiometric Nd_2NiO_4 phase (orthorhombic structure) and a tetragonal $Nd_2NiO_{4.077}$ phase. Magnetic susceptibility shows a deviation from Curie–Weiss law for lower oxygen excess ($\delta \leqslant 0.077$). Moreover, some anomalies in dc magnetic susceptibility curves was observed at 45, 95 and 130 K for $\delta < 0.077$. These transitions are connected to the tetragonal phase, and were attributed, respectively, to an antiferromagnetic transition, possible charge ordering and structural transition.

Keywords: Charge and spin ordering; Stripes; $Nd_2NiO_{4+\delta}$; Oxygen nonstoichiometry; Magnetic susceptibility

1. Introduction

The discovery of superconductivity in doped $La_{2-x}A_xCuO_4$ cuprates ($A =$ Ca, Sr, or Ba) [1,2] encouraged many groups to observe this property in other isostructural compounds. The first candidates of these investigations were the nickelates R_2NiO_4 ($R =$ rare earth). However, no superconductivity was found in these materials. $R_{2-x}A_xNiO_{4+\delta}$ compounds remain insulating up to $x = 1.0$. But these oxides present interesting materials due to their large variety of structural, magnetic and electronic properties transitions, which are strongly dependent on rate and nature of doping (holes or electrons).

The R_2NiO_4 structure is K_2NiF_4 type, which can be described as a successive stacking of NiO_2 layers and R_2O_2 layers of NaCl type. The stability of this structure is determined by the Goldshmidt criterion ($t = d_{R-O}/\sqrt{2}d_{Ni-O}$). If $t = 1$, the unit cell is tetragonal, and for $0.86 < t < 1$, the unit cell is tetragonal or orthorhombic. For $t < 0.86$, the structure is not derived from K_2NiF_4. In R_2NiO_4, Nd–O bonds are in extension, while Ni–O bonds are in compression. An alternated of NiO_6 octahedra along [110] the direction of ideal quadratic structure *I4/mmm* allow to minimize these structural strains. Then an orthorhombic symmetry can exist with *Bmab*, *Pccn* or *Fmmm* space groups. To relax the strain in these materials, a large-sized atom can be inserted in *R* site, thereby increasing the *R*–O distance. Another way is to insert an oxygen atom in R_2O_2 block [3]. A simultaneous movement of the NiO_6 octahedra apical oxygen leads to a decrease in *R*–O distance. And a partial oxidation of Ni^{2+} in Ni^{3+} occurs in NiO_2 layers for satisfaction of electroneutrality conservation. However, with oxygen doping, phase separation and interstitial oxygen order have been observed for particular holes concentration, especially for $La_2NiO_{4+\delta}$ [4]. In

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fact, the interstitial oxygen influences all properties of these phases. For example, magnetic and electronic properties change drastically with δ. Indeed, by neutron diffraction on $La_2NiO_{4+\delta}$ monocrystals, Tranquada et al. have shown, for $\delta > 0.105$, a 3D order of interstitial oxygen takes place linked to a particular distribution of charges and spins [5]. In $La_{2-x}Sr_xNiO_4$ compound, for $x = \frac{1}{3}$ and $\frac{1}{2}$, magnetic and resistivity anomalies, already observed by Cheong et al. [6], have been attributed to charge order. This phenomenon has been confirmed by Katsufuji et al., for $x = \frac{1}{3}$, by resistivity measurements and optic spectroscopy [7].

The combined order of holes and spins has been proved to be a common phenomenon in the cuprates and nickelates. The order can be described as stripes phase, where the holes are segregated in domain walls separating periodically non-doped antiferromagnetic domains. Stripes phases have been observed in Sr [8], Zn [9] and oxygen-doped La_2NiO_4 [10]. The first observation of unusual magnetic correlation in the nickelates has been realized by Hayden et al. [11] by neutron diffraction on $La_{1.8}Sr_{0.2}NiO_{3.96}$ crystal; the existence of a holes order in $La_{2-x}Sr_xNiO_4$ has been confirmed by electron diffraction [12] and transport measurements in ceramics [6]. A combined order of Ni spins and holes generated by doping in $La_2NiO_{4+\delta}$ exists for $\delta = 0.133$ too [13].

The majority of investigations of stripe order are devoted to lanthanum compounds, only few were interested in rare earth. In the present paper, we were interested in $Nd_2NiO_{4+\delta}$, in order to observe the influence of rare earth and oxygen excess on structural and magnetic properties. We have chosen to study $Nd_2NiO_{4+\delta}$ system because the rare earth Nd^{3+} allows to insert an elevated interstitial oxygen concentration. In this article, we present synthesis of various $Nd_2NiO_{4+\delta}$ compounds, structural characterizations and magnetic investigations.

2. Experimental details

Polycrystalline $Nd_2NiO_{4+\delta}$ was prepared by citrate method [14] and subsequent annealing in air at 1100°C for 6 h. The determination of oxygen excess was carried out by thermogravimetric analysis (TGA) in a reducing atmosphere using TGA7—Perkin Elmer system. About 30 mg of powder was heated from room temperature to 900°C at the rate of 2°C/min under 1 atm of Ar/H_2 gas. The value of δ was determined from weight loss as shown in Fig. 1. The compounds begin to lose oxygen excess above 200°C. The plateau between 350°C and 500°C corresponds to the stabilization of Ni^{2+} and there is no evidence of Ni^{+} stabilization [15]. Above 500°C, Nd_2NiO_4 is decomposed to metallic Ni and neodymium oxide (Nd_2O_3). After annealing in air, oxygen excess is $\delta = 0.234$. For $\delta < 0.234$, $Nd_2NiO_{4+\delta}$ powders were obtained by the reduction of the oxidized $Nd_2NiO_{4.234}$ at 350°C for a few hours (0.5–2 h) under Ar/H_2 atmosphere.

The powder X-ray diffraction patterns of all samples were collected at room temperature (RT) using Rikagu diffractometer in a $\theta - 2\theta$ geometry. The structural Rietveld refinement was also carried out on these data thanks to FULLPROF 2000 program. dc magnetic susceptibility was carried out with a DC Squid magnetometer (Quantum Design MPMS 5) under a field of 0.3 T in a temperature range of 10–300 K. And magnetization measurements were obtained with a Manics Faraday-based magnetosusceptometer in the range 67–300 K.

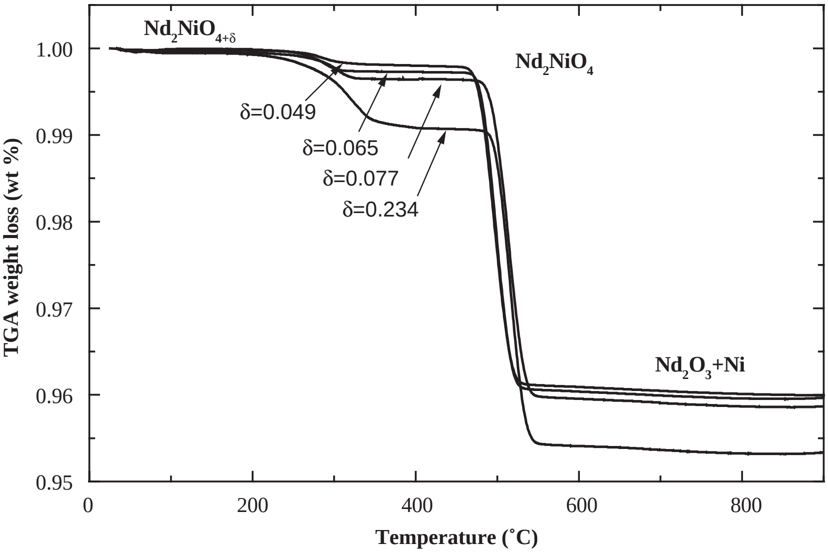

Fig. 1. TGA weight loss curves of $Nd_2NiO_{4+\delta}$ powders in 1 atm Ar/H_2 gas.

3. Results and discussion

3.1. X-ray diffraction

Fig. 2 shows X-ray diffraction patterns of $Nd_2NiO_{4+\delta}$ ($\delta = 0.049$, 0.065, 0.077 and 0.234) samples obtained at room temperature. All products were pure $Nd_2NiO_{4+\delta}$, and no significant impurities have been detected. The ideal stoichiometric Nd_2NiO_4 is orthorhombic at room temperature with *Bmab* space group [16]. Moreover, it appears clearly that oxygen nonstoichiometry has a strong influence on diffraction patterns.

The structural refinement of the powder samples was refined using the Rietveld technique. The refinement results, summarized in Table 1, show evolution of crystal symmetry with δ. Thus, for:

(1) $\delta = 0.049$ and 0.065: The products are biphasic with the coexistence of tetragonal ($I4/mmm$) and orthorhombic (*Bmab*) phases. Fig. 3 shows an example of the observed and calculated profile. It presents results obtained for $Nd_2NiO_{4.065}$ analyzed with a two-phase model.

(2) $\delta = 0.077$: The compound adopts a tetragonal symmetry with $I4/mmm$ cell. In this case, we also use a *Fmmm* space group, but the results are inconclusive.

(3) $\delta = 0.234$: The sample has orthorhombic structure with *Fmmm* space group as reported for $Nd_2NiO_{4.2}$ [17] and $La_2NiO_{4.18}$ [18].

These results were consistent with various studies concerning Nd_2NiO_4 and other isostructural materials like $La_2NiO_{4+\delta}$ [19], $La_2CuO_{4+\delta}$ [20], Eu_2VO_4 [21] and $NdCaCrO_4$ [22].

We can observe that the increasing of excess oxygen, up to 0.077, favors the formation of tetragonal phase. And the structural parameters of each phase practically do not vary with oxygen doping. Moreover the c-axis is higher for tetragonal phase than for orthorhombic phase, whereas the tetragonal unit cell a_t ($a_t = (a+b)/2\sqrt{2}$) is larger in *Bmab* structure than in $I4/mmm$

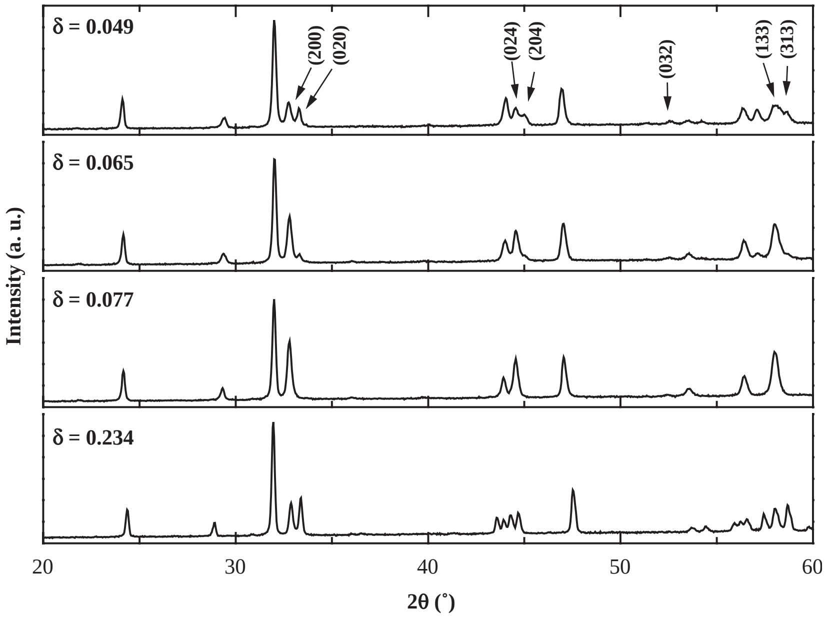

Fig. 2. Room temperature powder X-ray diffraction patterns of the oxidized sample $Nd_2NiO_{4+\delta}$.

Table 1
Refined structural parameters for powder samples of $Nd_2NiO_{4+\delta}$ at room temperature.

δ	Space group	Fraction (%)	a (Å)	b (Å)	c (Å)	R_{Bragg} (%)	R_{wp} (%)
0.049	*Bmab*	41.42	5.5794(4)	5.3788(4)	12.1247(9)	12.0	
	$I4/mmm$	58.58	3.8648(3)		12.1751(1)	10.2	16.1
0.065	*Bmab*	14.45	5.5812(8)	5.3799(6)	12.1227(2)	17.0	
	$I4/mmm$	85.55	3.8647(3)		12.1835(9)	10.0	16.7
0.077	$I4/mmm$	—	3.86556(9)		12.1977(3)	9.64	12.3
0.234	*Fmmm*	—	5.4598(3)	5.3741(3)	12.3802(6)	5.06	17.6

The percentage of *Bmab* and $I4/mmm$ phases is determined by two phases Rietveld refinement.

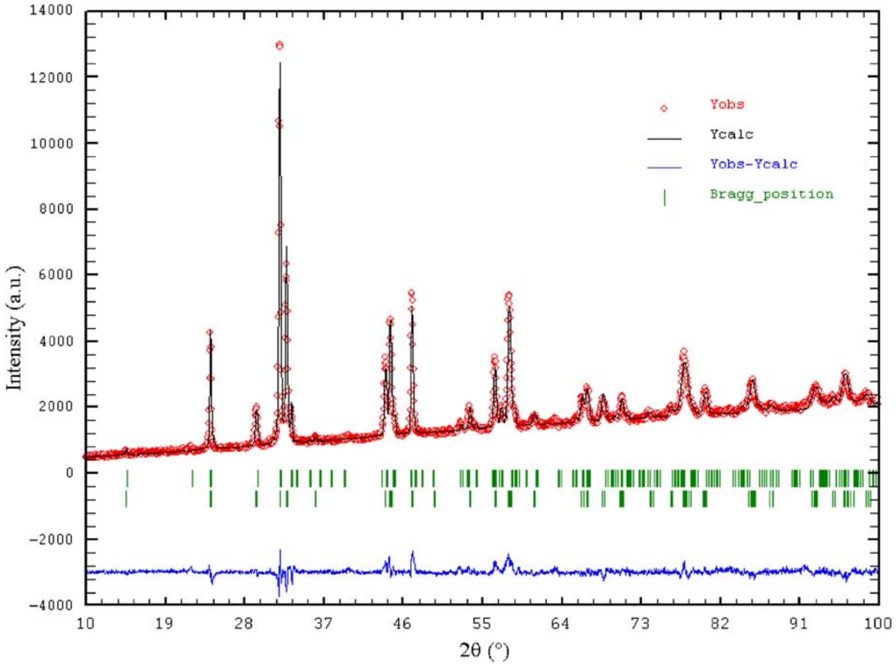

Fig. 3. Typical Rietveld refinement for $Nd_2NiO_{4+\delta}$ powders. This figure presents observed and calculated X-ray diffraction, at room temperature, obtained for the biphasic compound $Nd_2NiO_{4.065}$. The atomic positions in each space group are as follows: for *Bmab* space group the Nd and O2 ions are located at (0,0,z) with $z = 0.36$ and 0.19, Ni ions at (0,0,0) and O1 at (0.25,0.25,0); for $I4/mmm$ space group the Nd and O2 at (0,0,z) with $z = 0.36$ and 0.18, the Ni at (0,0,0) and O1 at (0,0.5,0).

structure. The excess of oxygen is located between NdO layers, which lead to increase of c-axis. And in the NiO_2 sheets, nickel is oxidized to Ni^{3+} smaller than Ni^{2+}, which results in the reduction of a_t axis. For higher doping compounds, Ni^{3+} may be adopt a high-spin configuration ($t_{2g}^5e_g^2$) as reported for $La_{2-x}Ba_xNiO_4$ [23], which has larger size than Ni^{3+} low spin. That will increase the orthorhombic strain and lead to the *Fmmm* cell.

The evolution with oxygen excess δ of the structure of $Nd_2NiO_{4+\delta}$ is very similar to that reported for $La_2NiO_{4+\delta}$ [24]. We could expect that physical properties are strongly dependent on oxygen excess as lanthanum nickelate.

3.2. Magnetic susceptibility

Fig. 4 shows the thermal evolution of dc magnetic susceptibility for $Nd_2NiO_{4+\delta}$ samples with various δ measured under a field of 0.3 T in zero field cooling. It appears that χ is very sensitive to oxygen nonstoichiometry. $Nd_2NiO_{4.049}$ and $Nd_2NiO_{4.065}$ compounds present three anomalies at 45, 95 and 130 K as shown by $\mathrm{d}(1/\chi)/\mathrm{d}T$ in Fig. 4a and b, while $Nd_2NiO_{4.077}$ presents only two transitions at 45 and 95 K (Fig. 4c). Whereas the most oxygenated sample does not show any anomaly in $\chi(T)$ curve and its experimental data follow a Curie–Weiss behavior, $\chi = 0.005 + 2.13/(T + 9)$, in all ranges of temperature from 10 to 300 K. The calculated moment is 4.19 μ_B instead of 6.93 μ_B for the stoichiometric compound [25]. The negative value of the Curie temperature ($-\theta = -9$ K) indicates predominant antiferromagnetic exchange interactions.

In Fig. 5, we show the full hysteretic loops obtained at various temperatures for all samples studied. The applied magnetic field was decreased from 1.5 to −1.5 T, and then increased to 1.5 T again. On the one hand, it appears that the magnetization curves, for $\delta \leqslant 0.077$, are characteristic of mixture of two phases: one ferromagnetic and another antiferromagnetic. It should be noted that hysterisis appears below 130 K for $Nd_2NiO_{4.049}$ and below 95 K for $Nd_2NiO_{4.065}$ and $Nd_2NiO_{4.077}$. Moreover hysterisis of the first compound is broader compared to those of the two other compounds. On the other hand, the magnetization curve of $Nd_2NiO_{4.23}$ is linear as a function of applied field whatever the temperature, which is characteristic of antiferromagnetic phase.

The transition observed at 45 K seems to be δ independent and can be attributed to an antiferromagnetic transition. The increase of susceptibility, below this temperature, is probably due to the large contribution of Nd ions. Obradors et al. also observed this transition in stoichiometric Nd_2NiO_4 [26]. At the same temperature, anomalies in the intensity of some magnetic Bragg reflections and a strong magnetic polarization of Nd^{3+} ions were observed by neutron diffraction [20]. The coworkers explained this anomaly by an internal field

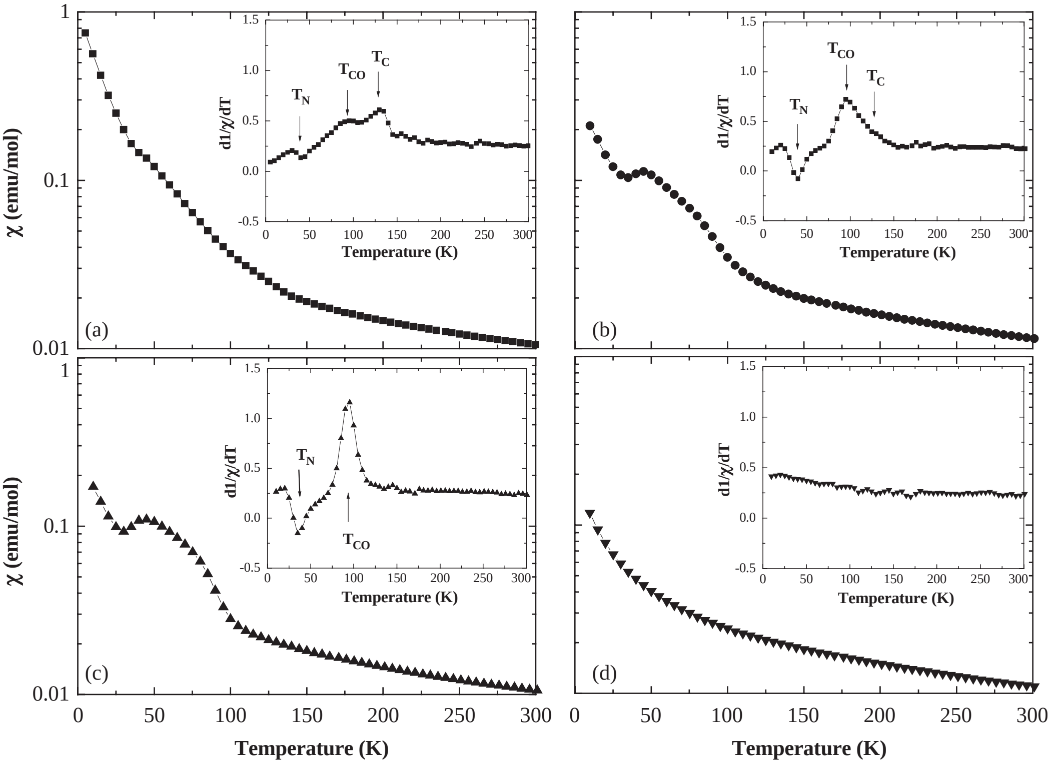

Fig. 4. dc magnetic susceptibility as a function of temperature for varied oxygen excesses: (a) $\delta = 0.049$, (b) $\delta = 0.065$, (c) $\delta = 0.077$ and (d) $\delta = 0.234$. The insets represent temperature derivative of dc magnetic susceptibility inverse versus temperature.

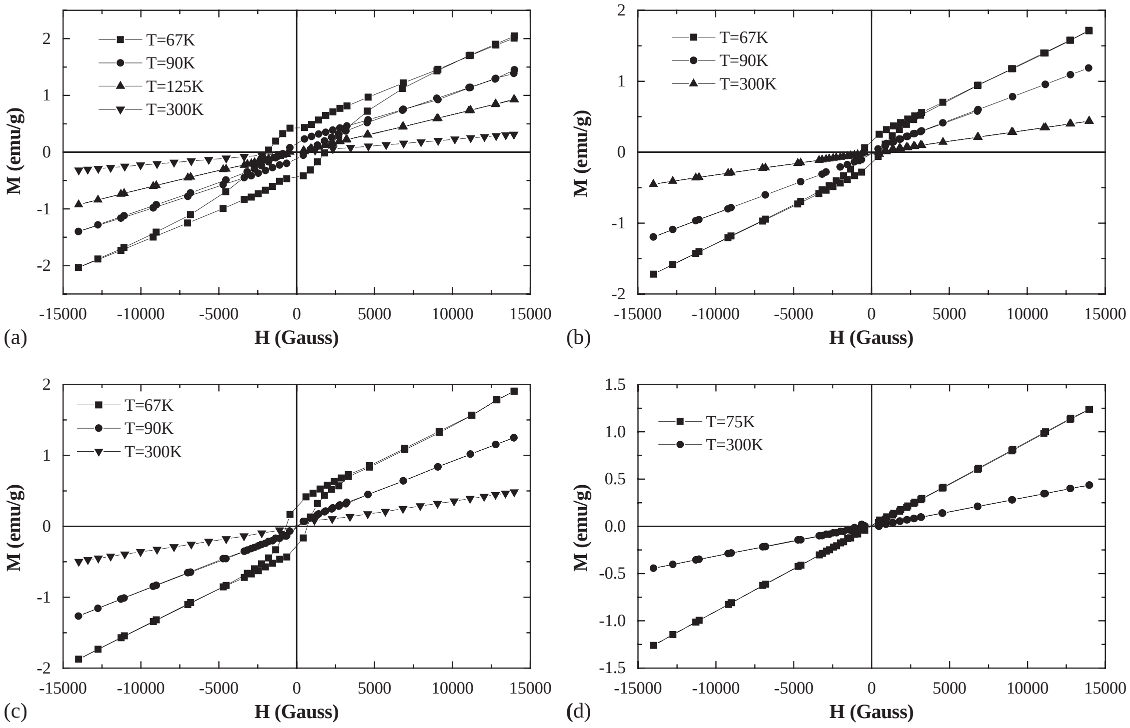

Fig. 5. Magnetization as a function of the magnetic field measured at different temperatures for $\delta = 0.049$ (a), 0.065 (b), 0.077 (c) and 0.234 (d).

due to some kind of spin reorientation of Ni^{2+}, which polarizes Nd ions. Moreover, Fig. 4 shows that this phenomenon is underlying when δ increases up to 0.077. That can be explained by an increase in the ferromagnetic component that appears below 95 K. The fact that the temperature transition is δ independent leads us to say that this transition cannot be attributed to 2D AFM–3D AFM transition as occurs in $La_2NiO_{4+\delta}$ [27], but we will see hereafter that this assumption cannot be turned down. The transition temperature of this type of magnetic phenomenon decreases with increasing holes concentration. In this case, the increase of δ leads to the decrease of AFM interactions in NiO_2 planes, which destroy the 3D AFM order. That could explain the absence of 3D magnetic order in $Nd_2NiO_{4.234}$.

An accident in χ curve, which occurs at $T_C = 130\,K$, is already reported by Batlle et al. in stoichiometric Nd_2NiO_4 [24]. Their investigations on neutrons diffraction revealed the existence of a structural transition of the type orthorhombic *Bmab* (high temperature)→ tetragonal $P4_2/cnm$ (low temperature). This transition is also present in La_2NiO_4 and Pr_2NiO_4 at 80 and 117 K, respectively [25]. At this transition temperature, the NiO_6 octahedra tilt along [100] and [010] axis implies a reorientation of Ni magnetic moments. In our case, the fact that the transition occurs at 130 K only on the compounds, which contain the orthorhombic *Bmab* phase, indicates that it clearly acts, here as well, owing to the same transition.

The anomaly, which occurs at 95 K (noted T_{CO}) for $\delta = 0.049$, 0.065 and 0.077, is more important for $\delta = 0.065$ and 0.077 than for $\delta = 0.049$. Indeed, in the inset in Fig. 4a–c, we observe that the peak at 95 K becomes increasingly intense and less broad when δ increases. The variation of the amplitude of this peak is connected to the evolution of X-ray diffraction patterns. It can be a direct consequence of the presence of tetragonal symmetry. This accident could correspond to a structural transition (X-ray diffraction versus temperature are in progress) or to a charge ordering in NiO_2 plans as found in $La_2NiO_{4+\delta}$. Moreover, the magnetization curves versus magnetic field show apparition of hysterisis below 95 K. This hysterisis is a signature of a weak ferromagnetic.

In the case of $Nd_2NiO_{4.049}$, the broad hysterisis is probably a sum of two contributions:

(i) The first one is due to the presence of $P4_2/ncm$ phase below 130 K. This space group is centrosymmetric and it leads to the apparition of weak ferromagnetism along *c*-axis as observed in stoechiometric Nd_2NiO_4 [24].
(ii) The second contribution is probably due to the presence of tetragonal phase, which develops a ferromagnetic below 95 K.

As we have mentioned below, the transition at 95 K can be a signature of charge ordering in these materials. Indeed, Kajimoto et al. [28] and Tranquada et al. [29] reported that the charge ordering temperature (noted T_{CO}) of neodymium nickelate compounds versus holes concentration are in good agreement with those of lanthanum compounds. It seems that the substitution of La by Nd did not significantly vary T_{CO}, in spite of the magnetic contribution of Kajimoto et al. [27], who reported also a phase diagram of T_{CO} versus holes concentration $n_h (n_h = x + 2\delta)$ of $R_{2-x}Sr_xNiO_{4+\delta}$ (R = La, Nd). The T_{CO} value for $\delta = 0.077$, obtained from this diagram, is very close to 95 K. What leads us to think that this transition can be attributed to charge ordering. In such case, the stripes are bond-centered (localization of holes on oxygen site), leading to apparition of a ferromagnetic component in a stripe-ordered regime [30]. That could explain the appearance of ferromagnetic in samples studied here.

On the other hand, it is known that R_2NiO_4 and R_2CuO_4 have 2D AFM magnetic behavior favored by superexchange interactions in NiO_2 plan. In this way, the susceptibility data were modelled with the 2D Heisenberg ferromagnet approach, using the following expression [31]:

$$\chi = \frac{1}{T}[C_1 \exp(\alpha j/kT) + C_2 \exp(\beta j/kT)],$$

where C_1 and C_2 are constants, k is the Boltzman constant and j is the in-plane exchange interaction. The first member corresponds to a low temperature magnetic contribution and the second to the high temperature contribution. The best values of the parameters obtained are summarized in Table 2. At high temperature and for all the compositions, the dominant in-plane interactions are antiferromagnetic indicated by the negative value of $\beta j/k$. At low temperature, we distinguish two cases:

(i) for $\delta = 0.234$, the still antiferromagnetic interactions indicates the negative value of $\alpha j/k$; and
(ii) for $\delta = 0.049$, 0.065 and 0.077, the positive value of $\alpha j/k$ indicates existence of ferromagnetic interactions.

In addition, $\alpha j/k$ increases between 0.049 and 0.077, whereas $\beta j/k$ decreases. This indicates that the ferromagnetic interactions increase with the detriment of the antiferromagnetic interactions. This can be a consequence of increase of exchange interactions in Ni–O–Ni bond by a localization of holes on the oxygen site (double exchange mechanism), what constitutes another argument in favor of the presence of the stripes bond-centered. Moreover, existence of ferromagnetic

Table 2
Parameters obtained from fitting the dc magnetic susceptibility data for $Nd_2NiO_{4+\delta}$ between 80 and 300 K, using 2D Heisenberg model $\{\chi = 1/T[C_1 \exp(\alpha j/kT) + C_2 \exp(\beta j/kT)]\}$.

δ	C_1	C_2	$\alpha j/k$	$\beta j/k$
0.049	1.33(6)	5.6(6)	98(4)	−417(40)
0.065	0.06(2)	4.6(1)	339(19)	−95(8)
0.077	0.0005(2)	3.80(6)	732(29)	−55(3)
0.234	2.13(1)	1.83(4)	−6.06(6)	−140(4)

interactions leads to the presence of weak ferromagnetic, which appears when the magnetic moments are not perfectly parallel. A small magnetization appears in a perpendicular direction to the average direction of spins, that is the so-called spin canting. This magnetic component will increases the field induced by Ni^{2+} ions and polarize more Nd^{3+} ions, which has a consequence on the evidence of magnetic order occurring at 45 K. For $\delta > 0.077$, it is the opposite situation. We observe an increase of AFM interactions, maybe due to the structural change (from tetragonal $I4/mmm$ symmetry to orthorhombic $Fmmm$ space group). But it is very interesting to study the doping rate between 0.077 and 0.234 in order to confirm or negate this assumption. Thus, these results seem to be in agreement with those reported by Demourgues et al. for $La_2NiO_{4+\delta}$ ($\delta = 0.00$, 0.03, 0.14, 0.18 and 0.25) [26]. They observe that the weak ferromagnetic exists between $\delta = 0.00$ and 0.10. Beyond that, this ferromagnetic component disappears and the 3D AFM order too.

Let us return now to the transitions that occur at T_N and T_{CO}. These transitions are δ independent, whereas we thought that they should vary with holes concentration, as we can observe in other $Nd_2NiO_{4+\delta}$ isostructural samples. Moreover, these transitions become more marked when tetragonal rate increases. Then all these observations lead us to think that our compounds are formed only by two phases: a stoichiometric Nd_2NiO_4 phase, which is orthorhombic; and an oxygen doped $Nd_2NiO_{4.077}$ phase with tetragonal structure. i.e. the interstitial oxygen is not distributed in a homogeneous way. In this case, the global δ determined by TGA measurements is only due to the tetragonal phase. Then, if we assume this, 58.58% and 85.55% (results of Rietveld analysis, see Table 1), of $Nd_2NiO_{4.077}$ present in $Nd_2NiO_{4.049}$ $Nd_2NiO_{4.065}$ samples, give a δ equal to 0.045 and 0.066, respectively. These results are then very close to those measured in TGA. Moreover, no significant variation of tetragonal and orthorhombic structural parameters was observed when δ increases. That consolidates our assumption. This thus enables us to say that the transition occurring at 45 K could also be attributed to 2D AFM–3D AFM transition, which is lower than for stoichiometric sample ($T_N = 320$ K [20]). This could be another explanation of the anomaly that Obradors et al. [25] attributed to some kind of reorientation of Ni^{2+}. The assumption mentioned above thus explains why the transitions, occurring at 45 and 95 K, are δ independent.

4. Conclusion

In conclusion, we have investigated the structure and magnetic susceptibility in powders of $Nd_2NiO_{4+\delta}$ with $\delta = 0.049$, 0.065, 0.077 and 0.234. The oxygen excess has a strong influence on structural and magnetic properties. And the physical properties and structure are connected between them. Moreover, the increase in oxygen excess, up to 0.077, leads to the formation of $Nd_2NiO_{4.077}$ phase with the detriment of the stoichiometric phase.

The thermal magnetic susceptibility measurements display several magnetic and structural transitions, which can be related to the crystallographic structure. Thus, the structural transition at 130 K, charge ordering at 95 K, and antiferromagnetic transition at 45 K was interpreted. Although these results seem to indicate existence of a charge ordering in $Nd_2NiO_{4.077}$ compound, these results show that the presence of stripes state is independent of the nature of rare earth and that this order is of electronic origin. Nevertheless, more investigations are needed. Synthesis of single crystal and investigations of physical properties like thermal resistivity and reflectivity measurements versus temperature measurements could confirm the existence or not of charge ordering in this compound.

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