

The Semiconductor-to-Metal Transition in Question in $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$)

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Nonstoichiometric phases of the compound La_2NiO_4 have been synthesized and chemically characterized. Their defect chemistry involves interstitial oxygens, oxygen vacancies, and lanthanum vacancies. The nonstoichiometric phases follow the general formula $\text{La}_{2-x}\text{NiO}_{4+\delta}$, with $0 \leq x \leq 0.15$ and $\delta \geq 0$ or $\delta < 0$.

The electrical properties of these compounds have been measured between 300 and 1200 K. They are characterized below 600 K by a hopping conduction having a low and almost constant hopping energy (≈ 80 meV). Above 600 K, the resistivity measured under isobaric conditions shows an upturn which for a long time has been interpreted as an indication of a semiconductor-to-metal transition. Careful measurements of the sample weight in this temperature range show, in fact, that the oxide does not maintain constant composition. Taking this fact into account provides evidence suggesting that the "transition" to a metallic state does not take place. Instead a diffusive-type charge transport is involved in the high temperature range. © 1994 Academic Press, Inc.

BaBiO_3 is perfectly insulating, while appropriate substitution on the barium site ($\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-y}$, $x > 0.4$) leads to superconducting compositions (4). Similar results were also obtained recently in our group in the quasi-bidimensional system $\text{Ba}_{2-x}\text{K}_x\text{Pb}_{1-y}\text{Bi}_y\text{O}_4$ (5). Stoichiometric La_2CuO_4 exhibits semiconducting behavior (6), while it becomes superconductive when efficient oxygenation is achieved (introduction of interstitial oxygen) (7).

The study of the "normal" state is an important path to the understanding of the high- T_c superconducting phenomena, and an essential parameter to control is the influence of the various kinds of defects formed. Therefore, intense efforts were devoted to structural characterizations of oxygen-excess compositions in lanthanum nickelates. For example, Jorgensen *et al.* interpreted their data by involving ordered phases (at least at room temperature) in the excess oxygen range $0 \leq \delta \leq 0.18$ (8). Demourgues *et al.* (9) were able to oxidize $\text{La}_2\text{NiO}_{4+\delta}$ up to $\delta = 0.25$ by electrochemical oxidation in alkaline media, finding new ordered phases in this process. More recently, Tranquada *et al.* (10) published a reinvestigated phase diagram ($0 \leq \delta \leq 0.15$) showing the existence of a phase separation and charge-density waves for $\delta = 0.105$. Curiously, the effects of a slight nominal deficiency concerning lanthanum site have rarely been investigated. One study (11) by X-ray refinement reported on the existence of a single crystal whose composition was lanthanum deficient ($\text{La}/\text{Ni} = 1.9$); it was further chemically analyzed as $\text{La}_{1.93}\text{NiO}_{4.05}$ (12). A few studies were also performed in lanthanum cuprate (13, 14) or lanthanum cobaltate (15).

Generally speaking, the dependence of electrical resistivity on temperature for $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$) type compounds may be described as follows: at low temperatures ($80 < T(\text{K}) < 250$), thermally activated behavior is observed with weak activation energies, i.e., in the range 50–100 meV (16–19). For $T > 500$ K, the experimental resistivity displays a broad minimum in the range 500–700 K. In the high-temperature range, the conduction is "metal like," according to the criterion of an increasing resistivity versus temperature (16, 20), *al-*

I. INTRODUCTION

Increasing interest is being devoted to mixed lanthanum-nickelate phases. At least two major reasons justify such efforts: first, an obvious question relates to the existence of superconductivity in nickelates. First, some years ago, there were claims of superconductivity in reduced forms of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compounds, obtained under particular conditions of annealing and thermal cycling (1). Only anomalous diamagnetism results supported these conclusions, giving rise to significant controversies about such reports. However, the same authors recently published another set of results from which they concluded that the existence of "granular superconductivity" was proven by adapted surface resistance (high-frequency) measurements (2). Second, in connection with the above question, note the important structural similarities between semiconducting nickelates and superconducting cuprates.

As claimed by Jorgensen and Hinks, "the oxide superconductors are doped insulators" (3). For example,

though the increase of resistivity versus temperature ($\approx 10^{-5} \Omega \text{ cm K}^{-1}$) (21) is much higher than that generally expected in conventional metals ($\approx 10^{-7}-10^{-8} \Omega \text{ cm K}^{-1}$). Strontium substitution on the lanthanum site appreciably decreases resistivity values (22), and transition temperatures to the metallic state depend on the substitution level (23). In the "metallic" range, the resistivity slope versus temperature of such oxides changes with chemical composition: it may be either close to zero or larger than that generally observed in conventional metals.

Electrical properties are highly anisotropic as shown by studies on single crystals grown by skull melting (20), and afterwards in our group by the floating-zone method (19, 24). Effectively, the ratio $\rho_{(001)}$ (resistivity measured perpendicular to the (001) plane) over $\rho_{(ab)}$ (resistivity within the basal (a , b) plane) is found to be larger than 1000 at room temperature and still rises with decreasing temperature. Such behavior was also reported by Rao *et al.* some years ago (18). This result is correlated with the two-dimensional character of La_2NiO_4 , whose structure belongs to the K_2NiF_4 family (25, 26). According to Goodenough and co-workers (27, 28), the $\text{Ni}^{+II}-d_{x^2-y^2}$ orbitals bonding with O_{2p} orbitals in the basal plane form a narrow $\sigma_{x^2-y^2}^*$ band of strongly correlated itinerant electron states while the $\text{Ni}^{+II}-d_{z^2}$ orbitals are more localized.

Stoichiometric La_2NiO_4 is a 3D antiferromagnet with $T_N > 300 \text{ K}$. There remain discrepancies with regard to the exact value of T_N : from neutron-diffraction experiments, Rodriguez-Carvajal *et al.* (29) reported $T_N = 330 \text{ K}$, in agreement with the results of Yamada *et al.* (30) obtained by magnetic susceptibility measurements. In contrast, Schartman and Honig (31) reported $T_N = 650 \text{ K}$ for strictly stoichiometric ($\delta = 0.0$) La_2NiO_4 . Some doubt remains about T_N because 650 K is very close to the Curie point of metallic nickel (634 K), which according to Shimokawara and Kohn could have been precipitated during the synthesis (under reducing condition) of the oxygen-stoichiometric compounds (32). The magnetic correlations in La_2NiO_4 are highly sensitive to the oxygen content, and the three-dimensional antiferromagnetic order is progressively suppressed when the amount of interstitial oxygen increases (33). In this case short-range antiferromagnetic interactions¹ remain in the basal plane (2D-AF) according to several authors (29, 31, 33-35). The main conclusion is that in La_2NiO_4 -type compounds both $d_{x^2-y^2}$ and d_{z^2} electrons are strongly correlated; consequently, the $\sigma_{x^2-y^2}^*$ and d_{z^2} bands are split. This was the basis of the model proposed by Goodenough and co-workers (28, 36); the Fermi level lies between the two $\sigma_{x^2-y^2}^{*1}$ and $\sigma_{x^2-y^2}^{*2}$ subbands, leading to semiconducting behavior below 600 K. This model of the semiconducting properties of La_2NiO_4 attributes the essential role to Hubbard band splitting.

Electrical properties of La_2NiO_4 -type compounds were more frequently studied in the low temperature range, i.e., for $T \leq 300 \text{ K}$. The high temperature range has received little attention, for example the nature of the "semiconductor-to-metal transition" observed for $T > T_{\min} 640 \text{ K}$ is not clearly established (T_{\min} is here the temperature of the minimal resistivity). In light of the previous discussion, one might consider the possibility of a correlation between the magnetic and electrical transitions. In one paper, Goodenough and Ramasesha (28) proposed that a vanishing band splitting may occur upon raising the temperature, and supposed that the 2D antiferromagnetic ordering extends even about $\theta > 400 \text{ K}$, where θ is the Weiss constant. However, in a more recent work (36), Goodenough argued that the smooth semiconductor-to-metal transition can be interpreted in terms of an orthorhombic-tetragonal transition, with small-polaron holes in the orthorhombic phase and itinerant holes of short mean-free path (diffusive motion) in the tetragonal phase. This interpretation does not require the suppression of the gap established in the low temperature range, and would also explain the absence of magnetic susceptibility anomaly in the Curie-Weiss law, through T_{\min} .

An alternative way to discuss the transport properties of such transition-metal oxide compounds has been introduced by Zaanen *et al.* (37). In this so-called ZSA model both the charge transfer energy (Δ) and the intra-Coulomb energy (U) are taken into account. The charge transfer energy is the energy required to transfer an electron from the oxygen to the cation, the U term being representative of the $d-d$ Coulomb and exchange interactions, which involve charge fluctuations of the type $d_i^n d_j^n \rightarrow d_i^{n-1} d_j^{n+1}$. According to experimental results, stoichiometric La_2NiO_4 is considered as a charge-transfer insulator, that is $\Delta < U$. The insulator is then built with an anionic valence band and d -type empty levels. Indeed, the optical gap would be close to 4 eV, according to Ido *et al.* (38) and Kuiper *et al.* (39). On the other hand, the intra-Coulomb energy is estimated at around 6 eV. Experimentalists have tried to obtain information concerning the hole symmetry. Studies performed by XAS at the oxygen 1s edge show that the doping holes are principally located in the O_{2p} bands, with a hybridization highly polarized in the basal plane (39). However, doping the compounds with interstitial oxygen or strontium (on La sites) suppresses the anisotropy. Such data concerning hole location are in agreement with previous results of Buttrey *et al.* (40). This experimental model then disagrees with the predictions of the "ionic" model built by Torrance *et al.* (41) in which $\Delta = 16 \text{ eV}$ and $U = 13 \text{ eV}$: La_2NiO_4 is here described as a Mott-Hubbard insulator ($\Delta > U$).

La_2NiO_4 -type compounds exchange oxygen with the gas phase quite easily (22), especially in the high temperature range where the semiconductor-to-metal transition

has been postulated. As an example, annealing under various Po_2 conditions can change significantly the oxygen stoichiometry of La_2NiO_4 and therefore its electrical properties (42). Note that this behavior is also well known for cuprates (see for example Refs. (43, 44) concerning $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$). Consequently, *in the high temperature range the electrical properties have to be correlated with oxygen exchange especially in the high temperature range*. For this purpose, it is interesting to compare the behavior of various compounds having different oxygen compositions, fixed by substitutions on the cationic sites and characterized at room temperature. In this respect we have worked on compounds belonging to the $\text{La}_{2-x}\text{NiO}_{4+\delta}$ family ($\delta < 0$ or $\delta > 0$). For $x = 0$ ($\text{La}/\text{Ni} = 2$), an excess-oxygen phase is formed under air, the composition of which is close to $\text{La}_2\text{NiO}_{4.16}$. This result confirms similar findings by other authors (8, 40). On the other hand, the structure is able to accommodate a significant deviation from stoichiometry with respect to the nominal La/Ni ratio. Chemical analysis of several $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$) compounds is made and discussed, with emphasis on the various kinds of defects expected.

We have then investigated the effect of high temperature on the defect chemistry of this oxide. Significant weight losses are measured and their influence is directly taken into account in interpreting the electrical conductivity behavior. This is discussed together with the evolution of the tetragonality ratio c/a reported in the past (45). Conclusions are drawn regarding the electrical properties of this oxide.

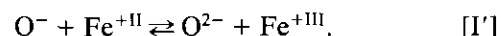
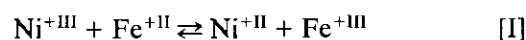
II. EXPERIMENTAL DETAILS

Reactive and chemically homogeneous powders of $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$) were prepared by using two chemical routes involving liquid precursors. This is preferred with respect to the classical solid-state reaction technique because of sluggish cationic diffusion in this kind of perovskite. In both cases the starting aqueous solution is a mixture of nitrates or carbonates in the appropriate stoichiometric proportions. In one procedure, a gel process is used (46), which achieves a better reactivity: we use an *in situ* polyacrylamide gelified liquid containing the cations in solution; it is stabilized by the addition of an appropriate amount of citric acid and ammonia. The gel is then calcined at 1170 K in an air-ventilated oven. In the other procedure, the solution is directly dried at $T = 970$ K in a furnace equipped with an efficient ventilation system. Powders obtained by this flash decomposition of liquids need to be further deagglomerated (this is done by zirconia ball milling in isopropyl alcohol). Compounds resulting from the sol-gel route do not need such treatment; owing to their much more aerated microstructure, they are particularly well suited to efficient

gaseous exchanges. In both cases, an annealing step in an alumina crucible is used. This takes place at 1270 K under a continuous flow of oxygen for 10 hr in order to remove all traces of carbonates. Several calcination cycles ($1370 < T(\text{K}) < 1520$ in air for 10–15 hr) and grinding give single phase samples as determined by X-ray diffraction ($\text{CuK}\alpha$ radiation). Efficient sintering after isostatic compaction (300 MPa) is achieved for $1570 < T(\text{K}) < 1620$; the sintering temperature apparently increases with cationic deficiency. A slow cooling procedure (100°C/hr) is used in order to obtain well-oxygenated compounds; note that a thermal stage ($T = 700$ K for several hours) is included in this schedule.

Heating $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$) under a 95%Ar–5% H_2 flow to 1270 K reduces it to the most stable entities, La_2O_3 and metallic Ni. Measuring simultaneously the weight loss by thermogravimetric analysis (TGA) provides a way to determine the initial oxygen amount of the compounds. X-ray diffraction spectra demonstrate the total reduction of the samples, at least to within detection limits ($\sim 1\%$).

Independently, direct quantitative determination of the total hole concentration is necessary. Chemical redox procedures are convenient for this purpose; however, they are intrinsically incapable of distinguishing between $\text{Ni}^{+\text{III}}$ and holes on oxygen sites (which will be denoted as O^-). Here the hole concentration is obtained by an indirect titration method (47). $\text{Ni}^{+\text{III}}$ (or O^-) species are first reduced in $\text{Ni}^{+\text{II}}$ (or O^{2-}) by the action of $\text{Fe}^{+\text{II}}$; the residual holes amount is then titrated independently. The $\text{Fe}^{+\text{II}}$ is added in excess through the Mohr salt ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), then displacing the equilibria (I) or (I') to the right,



$\text{Fe}^{+\text{II}}$ is titrated afterward by oxydo-reduction with bi-potassium chromite ($\text{Cr}^{+\text{VI}} \rightarrow \text{Cr}^{+\text{III}}$) with the help of barium di-phenylsulphonate used as a color indicator. This is a convenient procedure since both $\text{Ni}^{+\text{II}}$ (or O^{2-}) and $\text{Fe}^{+\text{III}}$ are stable entities in *acidic* conditions. Several samples of the same batch were measured by this procedure proving a quite good reproducibility. Moreover, a complementary set of titration experiments were performed by the classical iodometric method in collaboration with another chemistry laboratory (L. C. S.–C. N. R. S., Bordeaux).

Weight loss measurements were performed up to $T = 1200$ K under air, oxygen, or argon flow by TGA. Careful degassing of the installation precedes the measurements, which were done under 1 atm of total pressure. Experiments were carried out on 100 mg of sintered ceramic samples from the same batch as those chemically titrated.

We used a highly sensitive double cell apparatus, the noise level of which is below $\pm 4 \mu\text{g}$. A blank test run and a careful preliminary calibration of the thermobalance (for T and Δm) are done prior to the experiments by recording the thermogram of a high-purity $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ compound. This sulfate is suitable because its water molecules are liberated in well-separated steps, which allows a calibration over a wide temperature range.

Resistivity measurements are made in static air on sintered bars of the same batch as those used previously by using the conventional four-probe technique with a d.c. current. The measurement was made in the temperature range $300 < T(\text{K}) < 1200$ according to a classical method described elsewhere (19, 24).

The magnetic susceptibility was measured in air from 300 to 1250 K by using the Faraday method ($H = 1.3 \text{ T}$; $H \cdot dH/dx = 4.1 \text{ T}^2/\text{m}$).

III. RESULTS

This work concerns five different compositions having the general formulation $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$), with $x = 0, 0.05, 0.10, 0.15$, and 0.20 . However, the maximum lanthanum deficiency is probably limited to $x \sim 0.16$ – 0.18 , since the X-ray diffraction spectrum of $\text{La}_{1.8}\text{NiO}_{4+\delta}$ ($\delta < 0$, see the following) clearly reveals the patterns of NiO; this composition was not studied further. The cell parameters for $0 \leq x \leq 0.15$ gradually increase versus the lanthanum deficiency; see Table 1. No trace of obvious NiO segregation could be detected by using EDAX.

The formation of lanthanum vacancies must be electrically balanced by the partial oxidation of Ni^{+II} to Ni^{+III} , and/or O^{2-} to O^- . Simultaneously, for air-synthesized compounds, oxygen vacancies exist *in increasing amount with the lanthanum deficiency*, as proved by the chemical analysis reported in Table 2. It summarizes both the oxygen content determined by TGA and the hole concentration by chemical titration for the compounds of the explored series, i.e., $0 \leq x \leq 0.15$. The titration measurement concerning the composition with $x = 0$ is not reported since the result looks very dependent on the experimental procedure used and therefore could be doubtful. This is possibly connected with an increased

TABLE 1
Cell Parameters for $\text{La}_{2-x}\text{NiO}_{4+\delta}$, $0 \leq x \leq 0.15$ and $\delta > 0$ or $\delta < 0$

| | $\text{La}_{1.85}\text{NiO}_{3.85}$ | $\text{La}_{1.9}\text{NiO}_{3.9}$ | $\text{La}_{1.95}\text{NiO}_4$ | $\text{La}_2\text{NiO}_{4.16}$ |
|---------|-------------------------------------|-----------------------------------|--------------------------------|--------------------------------|
| a (Å) | 3.8607(3) | 3.8586(2) | 3.8585(2) | 3.8561(5) |
| c (Å) | 12.679(1) | 12.6624(7) | 12.6647(7) | 12.661(2) |

TABLE 2
Chemical Composition (at $T = 300 \text{ K}$) of the Studied Polycrystalline Nickelates

| La/Ni | 1.85 | 1.9 | 1.95 | 2 |
|------------------------|------|------|------|--------------|
| Hole concentration (%) | 4 | 2.75 | 3.5 | ^a |
| Total oxygen content | 3.85 | 3.9 | 4 | 4.16 |

Note. For the sake of simplicity, the hole concentration is given arbitrarily as a percentage of the total amount of oxygen sites.

^a Unknown.

lability of the excess oxygen. As one could easily verify, the electroneutrality criterion is fulfilled for these compounds, giving us confidence in the reliability of our data. The hole concentration is found to be almost constant upon varying the amount of lanthanum vacancies; we choose in the following to give it as a percentage of the amount of total oxygen sites rather than a proportion of the total nickel; the measured values are then between 2.75 and 4%.

As noted in the introduction, the synthesis of the stoichiometric cationic compound, formally written $\text{La}_2\text{NiO}_{4+\delta}$, allows the confirmation of an excess-oxygen phase— $\text{La}_2\text{NiO}_{4.16}$ —obtained under air. Excess oxygen has been quantified by others (8) using refinement of neutron powder diffraction data; it is accommodated in cuprates or nickelates as interstitial oxygen. In lanthanum nickelate the amount of oxygen interstitial reaches values as large as 4% (4.16) (8, 29, 40) for conventional synthesizing conditions. Recently by electrochemical oxidation, $\text{La}_2\text{NiO}_{4.14}$ has been oxidized up to $\text{La}_2\text{NiO}_{4.25}$ and characterized structurally (9). For comparison, the oxygen-excess concentration in $\text{La}_2\text{CuO}_{4+\delta}$ is limited to $\delta = 0.05$ (1.25%), and the synthesis needs to be made at 1070 K and under 230 MPa of O_2 (48); however, δ may increase up to 0.09 if the oxidation stage is performed by electrochemical oxidation on alkaline medium (49).

Electrical resistivity data versus temperature are reported for $300 < T(\text{K}) < 1200$ in Fig. 1; the behavior agrees with the general description made in the introduction. Note the relatively insensitive resistivity against composition in this series. For $300 < T(\text{K}) < 550$, data are well fitted with the general law derived by Mott and Davis for glasses containing transition-metal ions as well as for nickel oxide (50):

$$\rho = \rho_0 T \exp(W/kT). \quad [1]$$

These results have been interpreted according to a hole-hopping mechanism between localized states (22). For all these compositions, the activation energy W varies less than 15%, i.e., $74 < W(\text{meV}) < 84$ (Table 3); it is constant

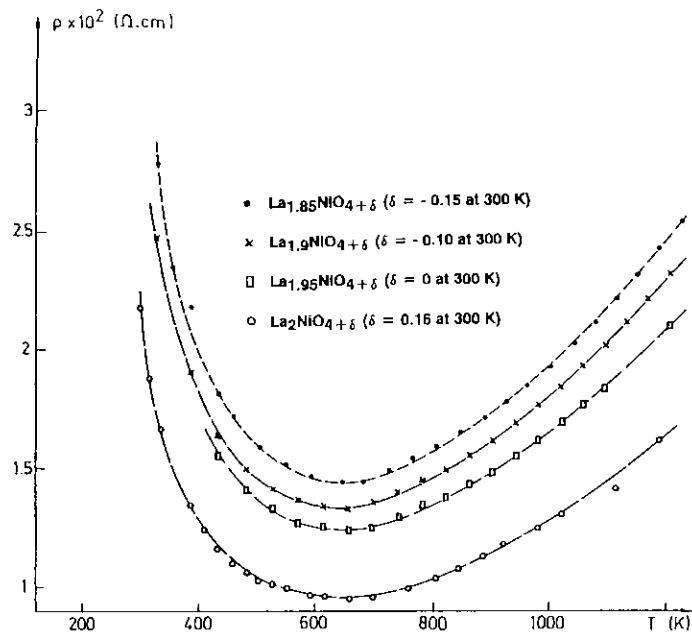


FIG. 1. Resistivity versus temperature for polycrystalline $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$), $300 < T(\text{K}) < 1200$.

(within 3%) for $0.05 < x < 0.15$ and slightly higher for $x = 0$. When $T > 550$ K, a broad resistivity minimum is observed—it extends over 100 K—and in the highest temperature range the conduction appears “metallic” with a positive temperature coefficient.

TABLE 3

Activation Energies W , Calculated for Polycrystalline $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or $\delta < 0$) According to Eq. [1] ($\rho = \rho_0 T \exp(W/kT)$), for $300 \text{ K} < T < 550 \text{ K}$

| Chemical composition | $\text{La}_{1.85}\text{NiO}_{3.85}$ | $\text{La}_{1.9}\text{NiO}_{3.9}$ | $\text{La}_{1.95}\text{NiO}_4$ | $\text{La}_2\text{NiO}_{4.16}$ |
|-------------------------|-------------------------------------|-----------------------------------|--------------------------------|--------------------------------|
| Activation energy (meV) | 75 | 76 | 74 | 84 |

The evolution of the reciprocal magnetic susceptibility versus temperature is reported for $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta = 0.16$ at 300 K) in Fig. 2. A Curie–Weiss law is obeyed in the entire temperature range (400–1300 K); the Curie and Weiss constants are, respectively, $C = 1.49 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ and $\theta \approx -700 \text{ K}$.

As previously discussed, a careful investigation of oxygen exchange in the temperature range where the semiconductor-to-metal transition occurs is highly justified. A weight-loss measurement is therefore an essential tool in this respect as long as one has proven that oxygen is the main component leaving the heated sample because species such as H_2O , CO , or CO_2 may also contribute to the overall weight loss (51). In this respect, evolved gas analysis (EGA) is under investigation using a separate quadrupole mass spectrometer. Preliminary results

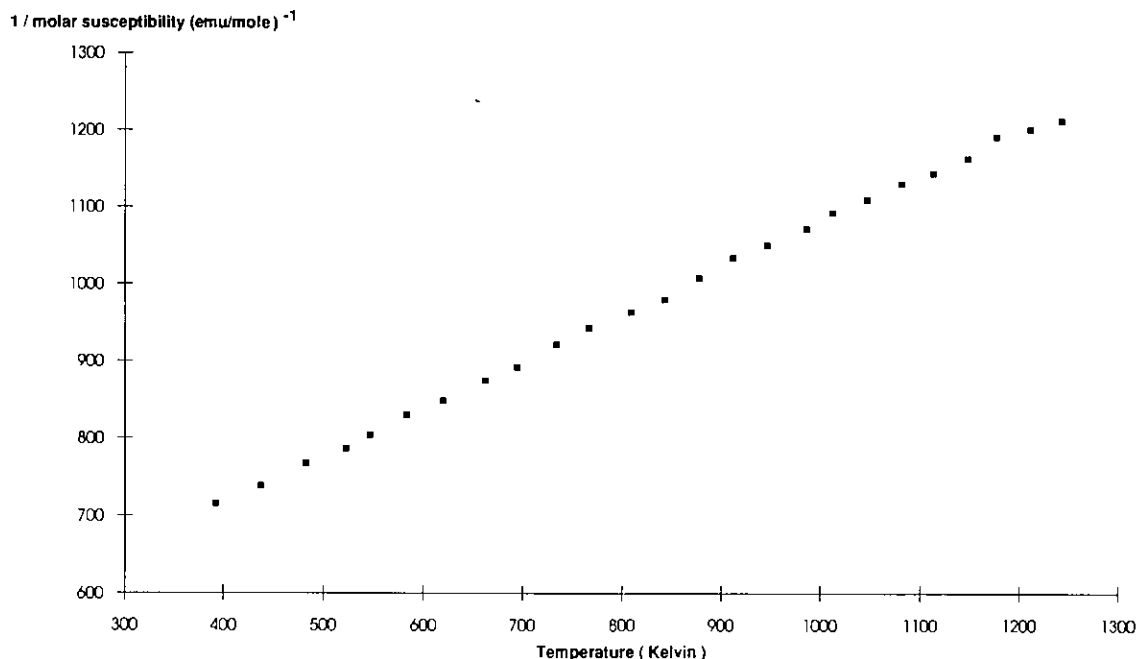


FIG. 2. Temperature dependence of reciprocal molar magnetic susceptibility of $\text{La}_2\text{NiO}_{4.16}$ ($\delta = 0.16$ at 300 K), $300 < T(\text{K}) < 1250$.

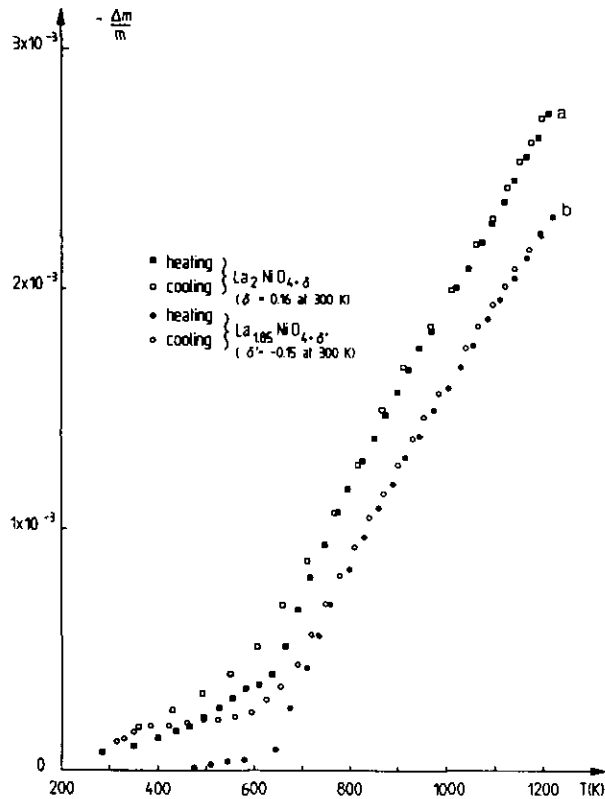


FIG. 3. Thermogravimetric analysis versus T obtained for (a) polycrystalline $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta = 0.16$ at 300 K) and (b) $\text{La}_{1.85}\text{NiO}_{4+\delta}$ ($\delta = -0.15$ at 300 K). Experiments were performed under air upon heating and cooling, $300 < T(\text{K}) < 1200$.

clearly indicate that oxygen is the principal gas evolving from heated $\text{La}_2\text{NiO}_{4.16}$, at least below 1000 K (52).

Figure 3, curve a, reproduces thermogravimetric measurements performed under air for $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta = 0.16$ at 300 K) upon heating in the range 300–1200 K. It shows a weak oxygen loss for $300 < T(\text{K}) < 650$ ($-\Delta m/m_0 \approx 2 \times 10^{-4}$), but a sudden increase at 650 K; finally the oxygen loss reaches $-\Delta m/m_0 \approx 2.5 \times 10^{-3}$ at $T = 1200$ K. Consequently, the composition reaches $\text{La}_2\text{NiO}_{4.09}$ at 1200 K. Note that the oxygen exchange is perfectly reversible when cooling to 700 K. Curve b of Fig. 3 shows the oxygen loss observed upon heating $\text{La}_{1.85}\text{NiO}_{3.85}$ under similar conditions. We focus here on the most oxygen-deficient compound for which the results are very similar to those of $\text{La}_2\text{NiO}_{4+\delta}$, except for a shift of the curve toward higher temperatures. The weight loss is slightly smaller for the La-deficient compound: at 1200 K, $-\Delta m/m_0 \approx 2.2 \times 10^{-3}$. The chemical composition of the oxide is then close to $\text{La}_{1.85}\text{NiO}_{3.79}$ at this temperature. The reversibility of the oxygen exchange, at least down to 700 K, is noted.

In addition, further experiments on $\text{La}_2\text{NiO}_{4.16}$ were performed at different oxygen partial pressures by using

pure oxygen or argon. In Fig. 4, curve a is a plot of the total weight loss measured under 99.9% pure oxygen (Air Liquide Paris, France, B type); for comparison, curve b reproduces a similar experiment, but under highly (99.998%) pure oxygen atmosphere (Air Liquide "N 48" type). Our aim was to avoid difficulties that could be induced by residual moisture in the flowing gas. Note that this high-quality oxygen contains less than 3 ppm of water vapor and 0.2 ppm of CO and/or CO_2 . Obviously this rules out artifacts concerned with higher levels of impurities.

Lastly, Fig. 5 reports the measurements performed under low oxygen partial pressure, i.e., argon flow. The weight-loss behavior (heating) is similar to that previously observed, but it is more intense with a significant hysteresis being visible upon cooling.

Important information is extracted from this set of measurements:

(i) The effect of residual gas impurities on the oxygen evolution is negligible, at least below 1200 K. The weight loss under air or oxygen is reversible. Both these properties assert that weight variations against temperature are mainly due to oxygen transfer between solid and gas, in agreement with EGA.

(ii) Thermodynamic equilibration of the sample, i.e., reversibility of the weight variations, is ensured provided that the oxygen partial pressure and the temperature (then kinetic) are high enough.

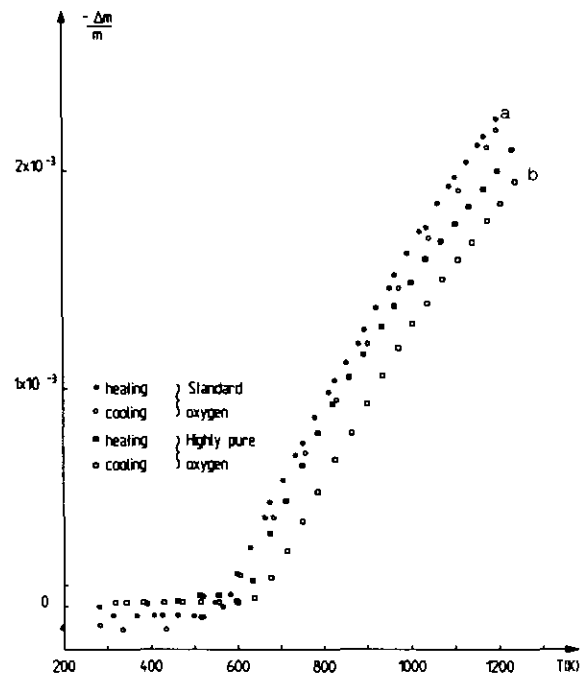


FIG. 4. Thermogravimetric analysis versus T obtained under oxygen for polycrystalline $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta = 0.16$ at 300 K). Experiments are performed upon heating and cooling, $300 < T(\text{K}) < 1200$; measurements carried out (a) under standard oxygen and (b) under high purity oxygen.

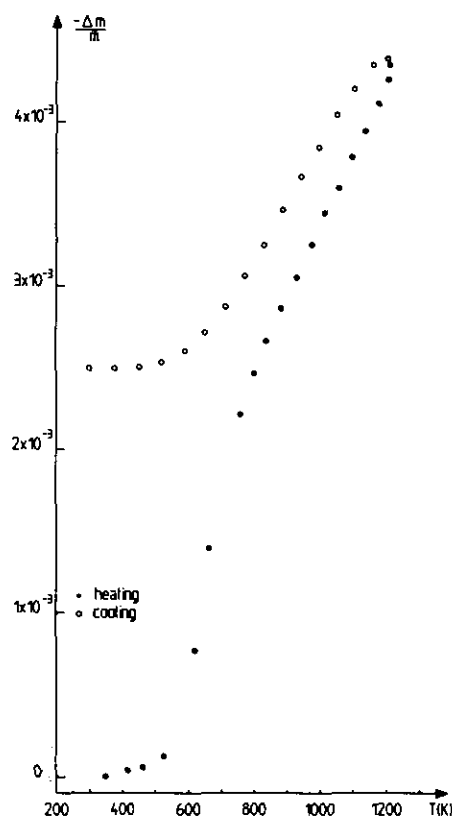


FIG. 5. Thermogravimetric analysis versus T obtained under argon for polycrystalline $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta = 0.16$ at 300 K). Experiments are performed upon heating and cooling, $300 < T(\text{K}) < 1200$.

(iii) In all cases there is a clear oxygen-loss acceleration occurring at around 600 K, the temperature where the resistivity versus T increases.

IV. DISCUSSION

IV.1. Nature of Defects

One of the important points raised by these results is the probable existence of a nonstoichiometric range extending in the lanthanum-deficient side of the composition. Several strong arguments support this assumption. First, the cell parameters increase gradually with the lanthanum vacancy concentration as expected. Second, the X-ray lines are not broadened as they would have been if NiO intergrowth had occurred. Third, the chemical composition obtained by structural refinement of the X-ray diffractogram on a batch of our crystals pointed to a lanthanum-deficient composition ($\text{La}/\text{Ni} = 1.9$) (11). SEM inspection of this crystal did not show any evidence of a secondary phase such as intergrown NiO. Finally, the oxygen content of the mixture $(1 - m)\text{La}_2\text{NiO}_{4.16} + m\text{NiO}$ ($\text{La}/\text{Ni} = 2(1 - m)$), which is supposed to equilibrate

under air cooling if lanthanum-deficient phases do not form, is systematically larger than that measured by TGA ($\text{La}_2\text{NiO}_{4.16}$ is the phase normally formed under air cooling). This indicates that lanthanum vacancies have been created in the compound and have formed oxygen vacancies as a consequence. Indeed several papers already cited in the introduction (11, 13–15) deal with the existence of such defects in K_2NiF_4 -type oxides. However, more definite conclusions will be made when TEM data become available.

The compound with $x = 0$ treated under air contains interstitial oxygens as previously stated, but the charges carried by these ions may be in question. One could propose that interstitial oxygens are doubly charged as are the other oxygen sites. In this case the hole concentration would be simply twice that of the excess oxygen concentration. On the other hand, using the interstitial concept developed by Kröger and others (53), one should allow for the possibility of having neutral oxygen or also singly charged interstitial oxygens, i.e., O_i^- . Due to its high electron affinity, we exclude neutral oxygen, and therefore consider the case where O_i^- is an acceptor and has trapped an electron. This electron is removed from Ni or oxygen orbitals and creates a hole there. We assume in the following that the negative charges on the interstitial oxygens are not mobile while the corresponding hole may contribute to the conductivity. We thus consider the two limiting cases: (i) if interstitial oxygens are only incorporated as O_i^- , the hole concentration is then 4% of the total oxygen sites; (ii) if O_i^{2-} only is to be considered, then the hole concentration with respect to the O sites will be 8%. Our samples are probably in an intermediate situation.

By chemical analysis we have some proof that the oxygen vacancy concentration is correlated with those of lanthanum vacancies. The defect involved is in fact a Schottky defect whose presence has already been discussed in perovskite structures in many papers (see for example (54)). In a recent paper on $\text{LaSrNiO}_{3.1}$, a reduced form of La_2NiO_4 , we have observed that oxygen vacancies are preferentially located in the (a, b) plane (55); we assume it is the same in the present structure.

IV.2. Transport Properties for $T > 300$ K

The point to be discussed now is the implication of the oxygen loss on the electrical properties, especially in the temperature range $600 < T(\text{K}) < 1200$. As reported in Section III, electrical conductivity data are well fitted by the general Eq. [1] for $300 < T(\text{K}) < 550$. More precisely (50, 56), the term ρ_0 is inversely proportional to:

(i) the hole concentration ([holes]):

$$[\text{holes}] = c[A].$$

Here [] stands for the atomic concentration expressed in cm^{-3} , [A] is the nickel or oxygen site concentration, depending on whether the holes are located on nickel or oxygen atoms as previously discussed in the Introduction. Indeed, for $T > 400$ K we suppose that the main charge carriers are holes as proved by the positive sign of the thermoelectric power (16). The term c is the oxygen atomic fraction.

(ii) The constant term $\mu_0(1 - c)$, part of the pre-exponential factor of the thermally activated carrier mobility μ , written as $\mu = (\mu_0/T)(1 - c)\exp(-W/kT)$.

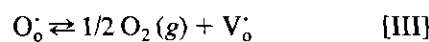
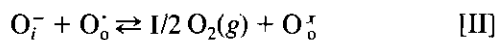
(iii) The electron charge e .

Finally, the complete expression of Eq. [1] may be written as

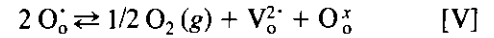
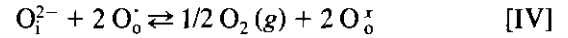
$$\rho = (T[A]\exp(W/kT))/(e\mu_0[\text{holes}]([A] - [\text{holes}])). \quad [2]$$

Equation [2] involves a temperature-dependent mobility. The evolution with temperature of the so-called "plasma frequency" ν_p measured in the basal plane of $\text{La}_{1.93}\text{NiO}_{4.05}$ single crystals (19, 57) is relevant in this case. Indeed, we claimed in a recent note that the plasma frequency is directly linked to the hopping frequency of charge carriers, and then to the mobility (57). Experimentally, ν_p increases continuously with T , at least up to $T = 800$ K (19); we then assumed (57) that the mobility is thermally activated for $300 < T(\text{K}) < 800$. This evolution is not found in La_2CuO_4 ($\nu_p = \text{constant}$) (19, 26). The electrical resistivity of La_2CuO_4 along the (001) face depends little on temperature (58) which is consistent with the observation above.

Equation [2] also shows the dependence of the electrical resistivity versus [holes]. It is quite obvious, as stated in our previous work (21, 42) and more recently by Schartman and Honig (59), that in the high temperature range the hole content is subjected to variations caused by oxygen exchange with the gas phase. According to the weight measurements with temperature, the oxide $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ($\delta > 0$ or < 0) may be considered as having a constant composition up to 600 K. Above this temperature, resistivity measurements made under constant oxygen partial pressure (air, oxygen, or other) are not recorded at constant composition. This has to be taken into account if one wants to interpret the electrical data correctly, and particularly the existence of a "semiconductor-to-metal transition." Measurements reported in Figs. 3 and 4 evidence oxygen loss above 600 K; this may correspond to one of the following equilibria, when assuming that holes are located on lattice oxygen:



or



In these equilibria O_o^{\cdot} is formally equivalent to O^- ; it represents an O site having trapped an effective positive charge with respect to the periodic potential of the lattice. The charge is supposed mainly to be localized on O sites as suggested by the results of the literature (see Introduction); O_o^{\times} is a normal O site with an effective neutral charge, i.e., O^{2-} ; V_o denotes an oxygen vacancy. It becomes V_o^{\cdot} or $\text{V}_o^{2\cdot}$ when one or no electrons remain on this site. This is the symbolic notation for defects introduced by Kröger (53). Equilibria II and IV simply express that when interstitial oxygens are transferred to the gas phase, their electronic charges are simply released toward an oxygen site, reducing it from O_o^{\cdot} to O_o^{\times} . This is one of the possible ways for reducing the hole concentration. Equilibria III and V express a similar phenomenon, but involving oxygen exchange from the lattice and consequently oxygen vacancy formation.

For $T > 300$ K, the combination of O_i^- or O_i^{2-} with O_o^{\cdot} becomes increasingly important with temperature, leading to the oxygen loss observed experimentally; equilibria III and V are also favored in the same way. This results in consumption of holes which is in good agreement with an increasing positive thermoelectric power above room temperature (16). The O_o^{\cdot} consumption being directly bound with the oxygen loss, it is possible to estimate the hole concentration for each temperature from the experimental $\Delta m/m_0$ data. To perform the calculations one needs to know the hole concentration for one temperature—for example room temperature—and the activation energy of the electrical resistivity W (Tables 2 and 3). We use here the hole amount determined by chemical titration, assumed to be equal to the hole concentration at 300 K for lanthanum lacunar compounds. For $\text{La}_2\text{NiO}_{4+\delta}$, the room T hole concentrations are the calculated ones, as discussed in Section IV.1.

We have calculated the resistivity, ρ , versus temperature. Computations were performed for both $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta = 0.16$ at RT and decreases with T) and $\text{La}_{1.85}\text{NiO}_{4+\delta}$ ($\delta = -0.15$ at RT and increases with T) which are the two limiting compositions and involve different kind of defects. The results are reported in Figs. 6 and 7, respectively. For $T < 600$ K the oxygen loss is negligible and the data are well fitted in both cases by Eq. [1]. We have extended this fit in the high temperature range, to give what one would expect for experiments carried out at constant composition. Holes are assumed to sit in O_{2p} orbitals, but identical results are found if they are sup-

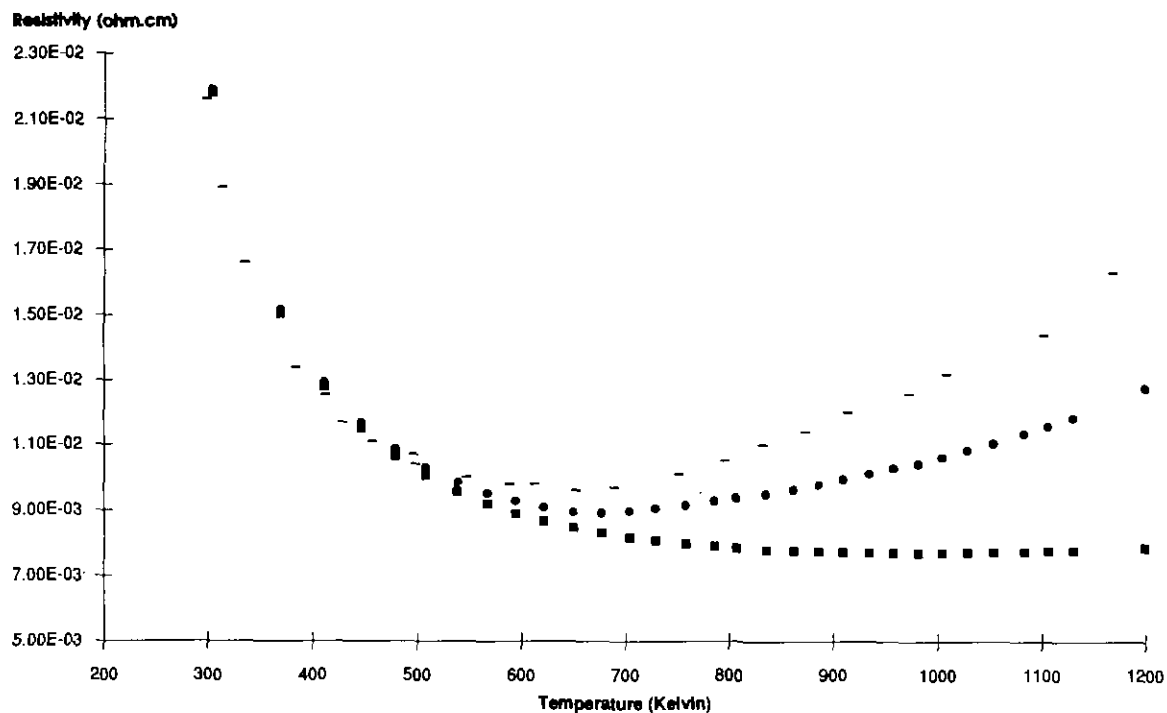


FIG. 6. Calculated resistivity versus temperature, according to Eq. [2], for $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta = 0.16$ at 300 K), $300 < T(\text{K}) < 1200$. Both equilibria II and IV are used for the calculations. The results are indistinguishable and are collected on the curve with circles (\bullet). The experimental data (\circ) and their fit with Eq. [1] (\blacksquare) are added for comparison.

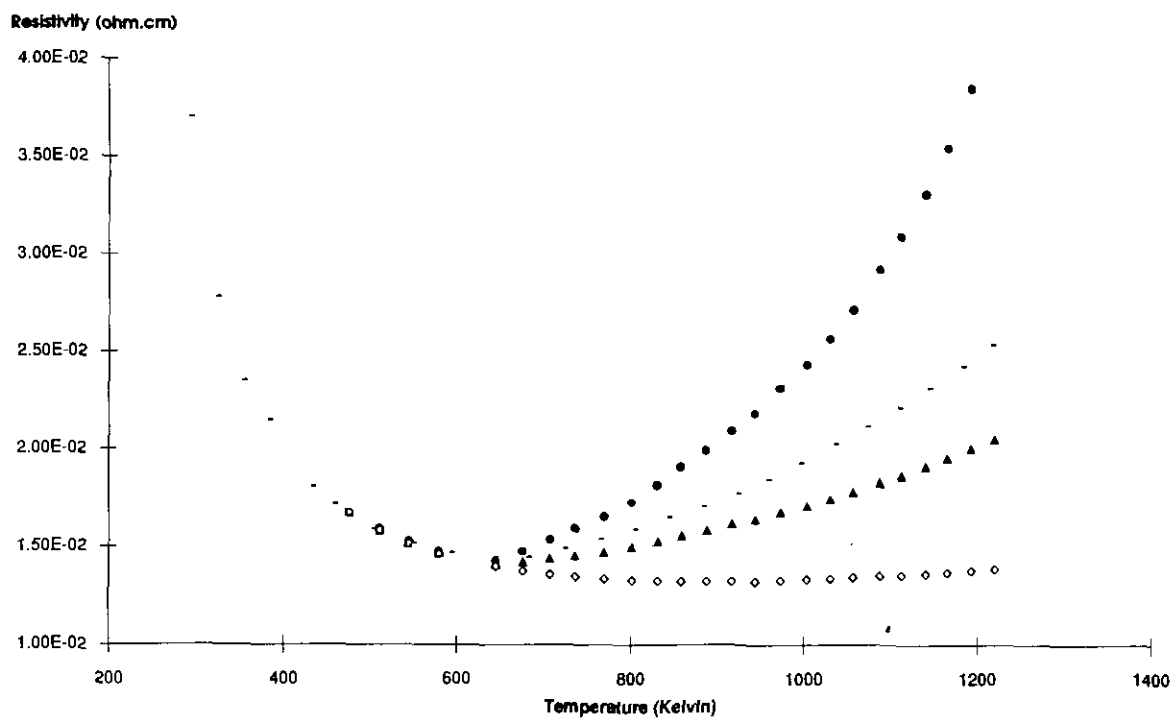


FIG. 7. Calculated resistivity versus temperature, according to Eq. [2], for $\text{La}_{1.83}\text{NiO}_{4+\delta}$ ($\delta = -0.15$ at 300 K), $300 < T(\text{K}) < 1200$. Both equilibria III and V are used for the calculations (denoted \blacktriangle and \bullet , respectively). The experimental data (\circ) and their fit with Eq. [1] (denoted \diamond) are added for comparison.

posed to sit on Ni_{3d} . For $T > 600$ K, Eq. [2] was used to calculate the resistivity versus T . For $\text{La}_2\text{NiO}_{4.16}$, we supposed that interstitial oxygen is the preferential species involved in gaseous oxygen loss, with respect to the normal oxygen lattice type; this hypothesis is in good agreement with the “lability” of interstitial species noted in the titration experiments (Section III). Consequently equilibria II and IV are applied for $\text{La}_2\text{NiO}_{4.16}$ (involving interstitial oxygen), while equilibria III and V are preferred for $\text{La}_{1.85}\text{NiO}_{3.85}$, in which no interstitial oxygen exists. As a first result, a qualitative agreement concerning the general trend of the experimental and fitted curves is observed for both $\text{La}_2\text{NiO}_{4.16}$ and $\text{La}_{1.85}\text{NiO}_{3.85}$. Therefore, clearly, the oxygen exchange between the solid and the gas phase has to be considered to explain electrical resistivity variations. In the case of $\text{La}_2\text{NiO}_{4.16}$, similar fits are obtained with equilibria II or IV because of identical mathematical expressions taken by Eq. [2]. One sees in Fig. 6 that the calculated resistivity curve is found below the experimental one. Concerning $\text{La}_{1.85}\text{NiO}_{3.85}$, equilibria III and V have to be considered a priori (Fig. 7). Unambiguously equilibrium III is the more appropriate one to fit the experimental curve; the calculated resistivity curve is also found below the experimental one. Then clearly oxygen exchange has to be one of the ingredients to be taken into account to model electrical resistivity data of $\text{La}_{2-x}\text{NiO}_{4+\delta}$ versus T .

Oxygen losses may induce structural modifications which in turn may influence charge transport. Structural aspects are discussed first. Arguments may be found in previous work (45) concerning the evolution of the tetragonality ratio c/a for air-prepared samples. First, this ratio increases with δ as evidenced from the comparison between $\text{La}_2\text{NiO}_{4+\delta}$ compounds annealed under low oxygen pressure (45) and those after high oxygenation ($\delta = 0.18$) (8, 33). Secondly, the c/a ratio is temperature dependent: it increases with T (28), but reaches a maximum at ≈ 600 K (45) then decreases at higher temperature. In connection with these results, an obvious question relates to the existence of a structural transition occurring at $T \approx 600$ K. In our opinion, data in the literature are still incomplete and there are no high temperature X-ray or neutron diffraction studies enabling closure of this point. Recent data of high T neutron diffraction on $\text{La}_2\text{NiO}_{4+\delta}$ are not conclusive on this (60). They, however, clearly show a decrease of δ with T under vacuum, in agreement with our data. Moreover, it is meaningful to note that the c/a downturn is observed in the same temperature range as the oxygen departure acceleration and the electrical resistivity minimum, clearly indicating a correlation between these facts (52). Why oxygen loss acceleration is observed at the same T for excess-oxygen phases and oxygen-deficient ones is not clear to us and will have to be studied in the future. Previous heat-capacity measure-

ments performed on $\text{La}_2\text{NiO}_{4+\delta}$ in air for $570 < T < 680$ K (61) attempted to prove the existence of a phase transition in this temperature range. A sharp rise of C_p (endothermic variation) followed by a sharp fall (exothermic variation) was observed for $T = 640$ K. In our opinion, the endothermic variation could correspond to the oxygen departure (reduction) while the exothermic part would then be associated to a structural reorganization following the oxygen loss; this one would have an energetic stabilizing role. To recap, since at the moment there is no clear signature of a structural transition related with the oxygen loss, more work is needed in this area.

The decrease of the hole concentration observed above 600 K has an indirect influence on the hole mobility as suggested now. In $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4-y}$ -type compounds, the decrease of the amount of holes is linked to a progressive elongation of the NiO_6 octahedra (23) and a decrease of the c parameter for low strontium concentrations ($x < 0.4$). The same trend is observed in $\text{La}_2\text{NiO}_{4+\delta}$ upon decreasing δ from 0.18 to 0 (8). When the octahedra become more and more elongated, the so-called tolerance factor decreases and structural strains increase. Such structural strains certainly induce a decrease of the electronic mobility because of a smaller transfer integral in the basal plane. This factor was not taken into account in our calculations; it then may explain qualitatively why the calculated curves are found below the experimental ones (Figs. 6 and 7).

One important aspect of this discussion is to point out that a semiconductor \rightarrow metal transition is not needed in order to model the electrical properties of $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta > 0$) and $\text{La}_{1.85}\text{NiO}_{4+\delta}$ ($\delta < 0$) between 300 and 1200 K, provided that one takes account of oxygen exchange. In addition, and this in agreement with the previous assertion, it should be underlined that no change is observed in the paramagnetic behavior of $\text{La}_2\text{NiO}_{4.16}$ through 640 K, as proved in Fig. 2. These results are understandable in terms of a “diffusive-type” conductivity, with small polarons in the low temperature range and diffused itinerant charges of short mean-free path at high T (36), owing to the similarity between the hopping energy W and the thermal energy (kT) in this high temperature range. Further work is needed on this point.

V. CONCLUSION

Several important findings regarding the properties above room temperature have been obtained for La_2NiO_4 . This is a nonstoichiometric oxide in which oxygen excess via interstitial oxygen, oxygen vacancies, and lanthanum vacancies have been identified. Oxygen vacancies are probably preferentially located in the basal (a , b) plane; they are expected to play an important role in charge transport occurring principally in this plane owing to the

high anisotropy of the compound. This may be important in the superconducting cuprate family also.

The resistivity versus T in the range 300–600 K is that of a doped p -type disordered compound; it is characterized with an almost constant and low (70–80 meV) hopping energy.

On heating under constant oxygen pressure, this oxide starts to lose oxygen above 600–700 K; consequently the hole concentration is reduced and the resistivity increased. This resistivity upturn has been misinterpreted as an indication of a semiconductor-to-metal transition. It is due to a normal nonstoichiometric effect and has, to our knowledge, nothing to do with magnetism as it is sometimes suggested. On the contrary, we show that this oxide behaves intrinsically as a semiconductor, in agreement with previous optical data versus T , with a consequently diffusivity-type charge transport model at high temperature.

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