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Progressive change with T from hopping to random phase propagation in $\text{La}_{2-x}\text{NiO}_{4-\delta}$ ($\delta \geq 0$)

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Abstract. Electronic properties of $\text{La}_{2-x}\text{NiO}_{4-\delta}$ ($0 \leq x \leq 0.15$, $0 \leq \delta \leq 0.15$) have been investigated for $77 \leq T$ (K) ≤ 800 . Charge compensation between La vacancies and O vacancies makes the hole concentration approximately constant in the series. In the low-temperature range, hopping conduction between localized states dominates. The activation energy of this process increases with increasing structural distortion. In the high-temperature range, close to 650 K, both thermal excitation and broadening of the band contribute to make the carriers delocalized and the conductivity a slow function of T . The mobility at 650 K remains low, i.e. $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, from which we conclude that the carriers move according to a random phase propagation. In this regime, the O vacancies scatter charge carriers and increase the resistivity.

1. Introduction

High- T_c superconductors have novel physical properties, which sustain large interest because the physics of their metallic normal state is not understood well [1, 2]. Due to its similarities with $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ (LSCO), a large amount of research has been performed on structural, magnetic and electronic properties of La_2NiO_4 [3–8]. However rather few works have aimed at understanding what is occurring in the temperature range where a progressive change from semiconducting to ‘apparent metal’ resistivity is observed upon raising T above 600 K [9–11]. This is perhaps reminiscent of what occurs in the incompletely oxygenated high- T_c superconductors. In this case a transition from a metal conductivity to an activated-type one occurs below room temperature, but above the superconductive transition [12]. The study of nickelates is then of importance, although no reproducible superconductivity has been found in this compound up to now.

The electrical conductivity of La_2NiO_4 is characterized by a thermally activated behaviour, with a small activation energy W (typically in the range 50–100 meV) below 600 K [7, 11, 13, 14] and a flat minimum between 600 and 700 K. An upturn is observed above this range, where we discussed recently the contribution of O departure [15, 16]. In fact, in this temperature range the thermal energy (kT) becomes of the order of magnitude of the activation energy and the conductivity is presumed to change in character.

A characteristic of the $\text{La}_{2-x}\text{NiO}_{4-\delta}$ family is its high tolerance to non-stoichiometry, on cationic as well as on anionic sites. First, significant excess O may be introduced into this structure [17, 18]; this induces ordered phases [18] in a very complex phase diagram, still not known in detail [3, 6]. Second, we recently suggested elsewhere the existence of a La non-stoichiometry range: $1.85 \leq \text{La}/\text{Ni} \leq 2$ [16]. This is another parameter that may be used in addition to T and P_{O_2} to investigate the transport properties of $\text{La}_{2-x}\text{NiO}_{4-\delta}$.

In this paper we study the electrical properties of various non-stoichiometric $\text{La}_{2-x}\text{NiO}_{4-\delta}$ compounds, for $77 \leq T$ (K) ≤ 800 . Two conduction mechanisms are involved, depending on the temperature range considered. For each one, effects of deviations from stoichiometry are taken into account. A progressive change from a hopping conduction between localized states to a random phase propagation between extended states is proposed. The electronic (hole) mobility is deduced.

2. Experimental details

The samples were prepared by using aqueous solutions of La and Ni nitrates. In the first method, a flash decomposition of the mixed nitrates is performed in a ventilated furnace, at $T = 970$ K. Samples were held for at least 2 h in the furnace. The powder was then disagglomerated by zirconia ball milling in isopropyl alcohol. The second method is a modified sol/gel route [19]. The solution containing the cations is stabilized by adding an appropriate amount of citric acid and ammonia. It is then gelified with the help of acrylamide polymerization. The gel is calcinated at $T = 1170$ K in an air-ventilated oven. The resulting powder is sufficiently aerated to avoid further disagglomeration or grinding steps; it is then suitable for oxidizing processes performed by solid-gas exchanges. In both cases an initial calcination is performed under pure O_2 flow, with increasing temperature up to 1270 K for 10 h. A slow cooling procedure (100°C h^{-1}) is used with an additional step at $T = 700$ K for 2–4 h, to fully oxygenate the compounds. Several calcination cycles ($1370 < T$ (K) < 1520 in air for 10–15 h) and grinding enables us to obtain phases pure by x-ray diffraction (Cu $K\alpha$ radiation).

Sintering is performed above 1570 K on isostatically compacted powders (300 MPa); higher temperatures are needed for increasing cationic deficiency. The densities of the sintered samples were measured at room temperature by the Archimedes method using pure water. These are compared with theoretical values calculated from crystal lattice parameters. Relative values are given in table 1.

Table 1. The chemical composition (at $T = 300$ K) and relative density of non-stoichiometric $\text{La}_{2-x}\text{NiO}_{4-\delta}$.

La/Ni	1.85	1.9	1.95
O/Ni	3.85	3.9	4
Measured hole concentration (%)	4	2.8	3.5
Calculated hole concentration (%)	3.75	2.5	3.75
Experimental relative density (%)	85	87	89

O and hole concentrations have been determined by using two independent methods: first, they are obtained from the weight change measured during total reduction under Ar/5% H_2 in a TGA apparatus; full reduction is achieved at 1270 K for a gas flow of 10 l h^{-1} and a temperature rising rate of 300 K h^{-1} . After the reduction x-ray diffraction spectra showed a mixture of La_2O_3 and Ni patterns. Secondly, quantitative determination of the hole concentration has been obtained by an indirect chemical redox procedure [16, 20].

The DC electrical conductivity was measured in static air on sintered bars of the same batches as those previously used for chemical analysis. The measurements were made in the temperature range $77 < T$ (K) < 800 by the conventional four-probe technique described elsewhere [13].

3. Results

This work concerns three different pure non-stoichiometric La nickelates, i.e. $\text{La}_{2-x}\text{NiO}_{4-\delta}$ ($\delta \leq 0$) with $x = 0.05, 0.1, \text{ and } 0.15$ [16]. La vacancies should be electrically balanced by holes, i.e. the partial oxidation of Ni^{2+} to Ni^{3+} , and/or O^{2-} to O^- . Referring to XAS data [21, 22], we choose to give here the hole concentration as a percentage of the total number of O sites; this is preferred to the more conventional normalization to Ni sites.

Air-synthesized compounds contain O vacancies, the concentration of which increases linearly with that of La vacancies. Table 1 summarizes both O stoichiometry deviation and hole concentration for the three compositions. The electroneutrality criterion

$$3[V_{\text{La}}^{3'}] = [\text{holes}] + 2[V_{\text{O}}^{2'}]$$

is well fulfilled proving that $V_{\text{La}}^{3'}$ and $V_{\text{O}}^{2'}$ are the main defects. $V_{\text{La}}^{3'}$ and $V_{\text{O}}^{2'}$ represent the ionized La or O vacancies and $[\]$ their concentration; they are respectively negative and positive with respect to the lattice periodic potential. The hole concentration remains almost constant, its value ranging from 2.8 to 4% with respect to O sites. This result traduces the fact that O vacancies are more easily formed than holes.

The measured relative density of the sintered samples is given in table 1; it decreases slightly with increasing deviation from stoichiometry.

The lattice parameters are useful data to compare samples having various defect concentrations; results are given in table 2. First, note that $\text{La}_2\text{NiO}_{4+\delta}$ is orthorhombic. This sample was quenched from high T under low O_2 partial pressure, and using the work of Schartman and Honig [23], its O stoichiometry can be estimated to be 4.015. The compound is therefore nearly stoichiometric and it is orthorhombic in agreement with the phase diagram [6]. Its symmetry and equivalent lattice parameters differ strongly from the lacunar compounds, which are indexed in a tetragonal cell.

Table 2. Lattice parameters of $\text{La}_{2-x}\text{NiO}_{4-\delta}$; for $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta \simeq 0.015$) the equivalent tetragonal unit-cell parameter (a_t) is given for comparison.

	$\text{La}_{1.85}\text{NiO}_{3.85}$ (tetragonal)	$\text{La}_{1.9}\text{NiO}_{3.9}$ (tetragonal)	$\text{La}_{1.95}\text{NiO}_4$ (tetragonal)	$\text{La}_2\text{NiO}_{4+\delta}$ (orthorhombic) ($\delta \simeq 0.015$, estimated from [11])
a (Å)	3.8607(3)	3.8586(2)	3.8585(2)	$a = 5.468$ $b = 5.535$ $a_t = 3.8901$
c (Å)	12.679(1)	12.6624(7)	12.6647(7)	12.547

Figure 1 gives the conductivity versus T , measured between 300 and 800 K for La deficient compounds. As a general feature, a thermally activated behaviour is observed in the lowest temperature range, while for $T > 650$ K a conductivity decrease is seen. The latter has been interpreted in the past as an indication of a semiconductor-to-metal transition. However we recently showed that loss of O must be taken into account above 600 K and therefore the high-temperature part is not necessarily characteristic of a metallic state [15, 16]. For $400 < T$ (K) < 800 , the absolute conductivities increase slightly when decreasing the number of La or O vacancies, consequently each conductivity curve is progressively shifted upward for reduced non-stoichiometry. However, in the low-temperature part the experimental conductivity curves intersect for $T \simeq 250\text{--}300$ K. A

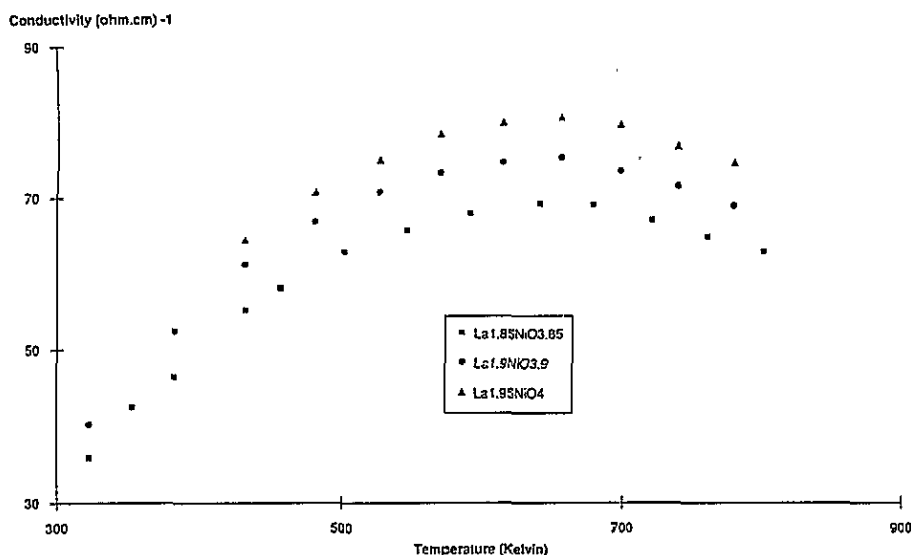


Figure 1. The conductivity versus temperature for polycrystalline $\text{La}_{2-x}\text{NiO}_{4-\delta}$, $300 < T \text{ (K)} < 800$.

different mechanism is then anticipated in the low-temperature range, which modifies the activation energies.

In the following, we consider the conductivity to be the result of two contributions occurring at different energy levels. This is justified according to the general definition of conductivity [24]. We will then analyse the data by using two terms, one dominating at low temperature where conductivity is mainly thermally activated hopping, i.e. σ_h , and one dominating at high temperature where the conductivity changes slowly with T (see figure 1). In this range, the conductivity, i.e. σ_p , is a propagating conductivity. The simplest way to take account of a constant charge carrier concentration below room temperature is to consider σ_h to be given by

$$\sigma_h = (\sigma_h^0/T) \exp(-W/kT) \quad (1)$$

which describes correctly disordered solids, glasses and NiO [24]. Figure 2 reports the electrical conductivity versus T ($125 < T \text{ (K)} < 300$) for different compositions, $0.05 \leq x \leq 0.15$. Activation energies W have been calculated and are reported in figure 3. In addition the activation energy of the compound with no La vacancies ($\text{La}_2\text{NiO}_{4.015}$) has been deduced from previous work involving one of the present authors [11]; W is 134 meV in this sample. The activation energies are found to be almost constant for $0.05 \leq x \leq 0.15$, except for a small increase (around 6%) that is noticed when decreasing the number of vacancies. In contrast, a significant jump occurs (20%) between $\text{La}_{1.95}\text{NiO}_4$ and $\text{La}_2\text{NiO}_{4.015}$. Notice an increasing deviation from (1) at low T ($< 180 \text{ K}$). In contrast $\sigma = \sigma_0 \exp(-A/T^{1/n})$ is more appropriate, indicating a possible variable-range hopping conduction [24].

Figure 4 reports the experimental data $\ln(\text{conductivity} \times T)$ versus inverse T for $\text{La}_{1.95}\text{NiO}_4$ in the entire temperature range. The choice of this particular composition will be justified further; however, the results are similar for the other oxides studied here. The slope of the curve is the activation energy at any temperature. In a first approximation, the

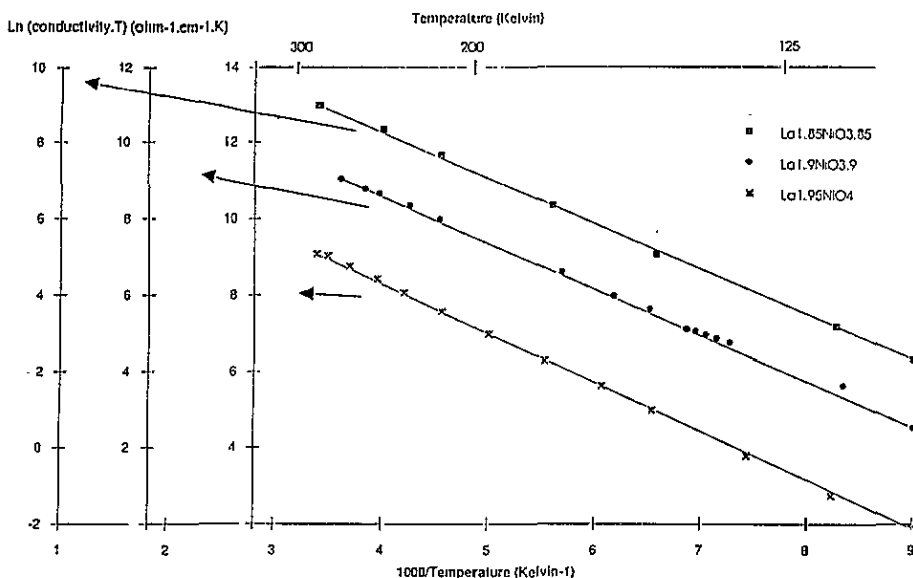


Figure 2. $\ln(\text{conductivity} \times \text{temperature})$ versus inverse temperature for polycrystalline $\text{La}_{2-x}\text{NiO}_{4-\delta}$, $125 < T \text{ (K)} < 300$.

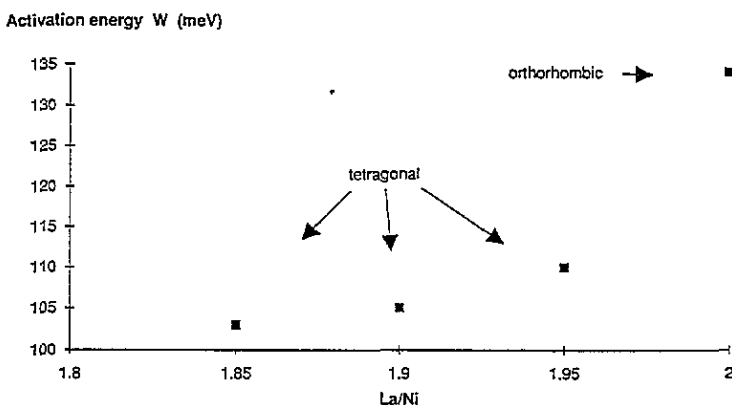


Figure 3. The hopping energy (for $125 < T \text{ (K)} < 300$) versus La vacancy concentration in $\text{La}_{2-x}\text{NiO}_{4-\delta}$.

activation energy is approximately constant in the temperature range $125 < T \text{ (K)} < 300$; it then decreases between 300 and 650 K down to 56 meV. Notice that the activation energy 56 meV in this high- T part is of the order of magnitude of kT .

The drift mobility μ is calculated from conductivity data since the hole concentration is known from chemical titration (table 1). The mobility is

$$\mu = \sigma / ([\text{holes}]e) \tag{2}$$

where σ is the conductivity and $[\text{holes}]$ the hole concentration. This assumes that holes are the main carriers with a constant concentration with T . This is justified in section 4

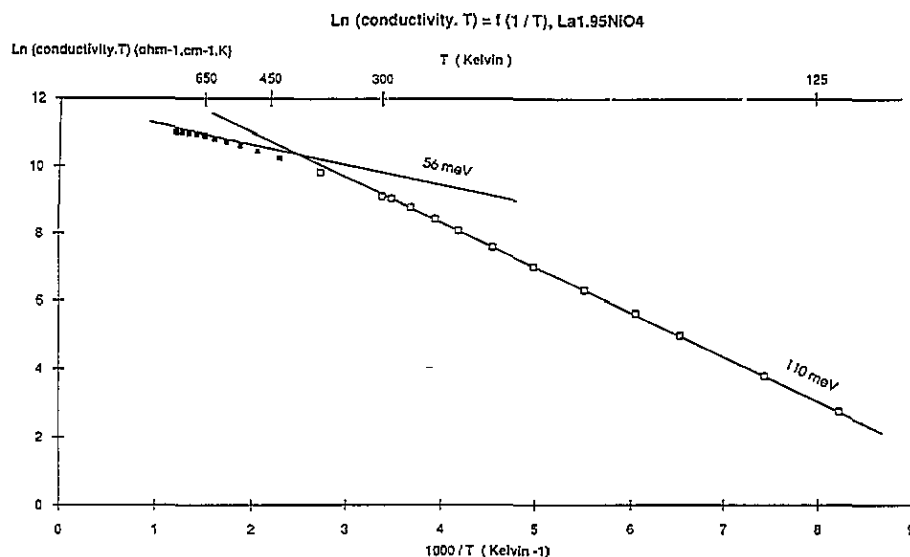


Figure 4. $\ln(\text{conductivity} \times \text{temperature})$ versus inverse temperature for polycrystalline $\text{La}_{1.95}\text{NiO}_4$, $125 < T \text{ (K)} < 800$.

below. The mobility has been calculated for the three La lacunar compounds at $T = 125$, 300 and 650 K (table 3). These mobilities are rather low; this is in agreement with previous measurements at 300 K by the Hall effect on an $\text{La}_{1.93}\text{NiO}_{4.05}$ single crystal [25], the mobility of which was below the detection limit of the apparatus, i.e. $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Table 3. The drift mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for La lacunar compounds, calculated at $T = 125$, 300 and 650 K.

	La/Ni = 1.85	La/Ni = 1.9	La/Ni = 1.95
125 K	8.6×10^{-4}	1.4×10^{-3}	5.4×10^{-4}
300 K	0.12	0.15	0.13
650 K	0.29	0.31	0.34

4. Discussion

4.1. Transport properties for $125 < T \text{ (K)} < 300$

In the following, we consider this low-temperature part to be dominated by a hopping conductivity of holes in localized states of a valence band tail above a mobility edge (the conductivity is p type). The activation energy is an increasing function of the energetic difference between the Fermi level and the energy of the mobility edge [24]. Accordingly, the band width B is of prime importance in determining W ; raising B will decrease W . The band width is linked with the transfer integral, which is related to lattice distortions in the following way. In the Ln_2NiO_4 ($\text{Ln}=\text{rare earth}$) family, due to the small rare-earth size, the 'LnO plane' is under tension while the conducting NiO_2 plane is under compression. In the stoichiometric compounds the strain is released by an orthorhombic distortion [26],

due to an alternate tilt of O octahedra in the [110] direction of the tetragonal phase [3]. The Ni–O orbital hybridization is directly linked with the electronic transfer integral, and therefore with the charge carrier mobility and its activation energy. Any tilt of the octahedra is then liable to increase it. This basis is an appropriate frame to explain the evolution of the electrical properties of $\text{La}_{2-x}\text{NiO}_{4-\delta}$ versus La vacancy concentration (table 2). First, comparing $\text{La}_2\text{NiO}_{4.015}$ and $\text{La}_{2-x}\text{NiO}_{4-\delta}$ evidences a significant decrease in W between the orthorhombic structure and the tetragonal one. Clearly the tilt of O octahedra in the orthorhombic structure accounts for its larger (30%) activation energy. Hole doping also contributes to enhance Ni–O hybridization and therefore goes in the same sense because it significantly decreases the equivalent tetragonal parameter a_t as is shown by comparing $\text{La}_2\text{NiO}_{4.015}$ and $\text{La}_{1.95}\text{NiO}_4$ (table 2). Notice that introducing La vacancies in the tetragonal form tends to increase the volume occupied by La ions and therefore to decrease the bond mismatch between $(\text{LaO})_2$ blocks and NiO_2 layers. This will decrease the activation energy for transport as well, as is observed here between $\text{La}_{1.95}\text{NiO}_4$ and $\text{La}_{1.85}\text{NiO}_{3.85}$.

The Seebeck coefficient has been measured for one intermediate composition, i.e. $\text{La}_{1.9}\text{NiO}_{3.9}$, below 300 K. It is small, positive and almost constant with T , a confirmation that conduction is ensured by hopping carriers of constant concentration. The O vacancies, which are expected to be located principally in the basal plane [27–29], do not contribute in this temperature range, where hopping dominates the conductivity.

4.2. Transport properties for $300 < T \text{ (K)} < 650$

When the temperature is raised, several new features occur. At high temperature, above 650 K the O starts to leave the oxide [16]. Consequently, we have restricted our analysis below this limit, ensuring a constant composition. Next, the intrinsic lattice strain is expected to decrease due to thermal expansion. This is effectively observed for cationic stoichiometric compounds when the O excess is smaller than 0.15, a range where the average structure is $I4/mmm$ [30,31]. As a consequence the term W is expected to decrease with T above 300 K. However the way of decreasing the lattice strains is not known and it seems difficult to model more with our present knowledge. In fact the appearance of the maximum in the conductivity in polycrystalline La_2NiO_4 is not directly related to a structural transition as is explained now. First, Tamura *et al* [6] have reported a phase transition in $\text{La}_2\text{NiO}_{4.15}$ occurring at 450 K in O, while no anomaly appears in the conductivity curve at this temperature. Second, recent experiments on $\text{Pr}_2\text{NiO}_{4+\delta}$ show that there exists a structural transition in this material at 720 K in a range where the maximum of the conductivity has yet been reached [32]. The effect of this transition on the resistivity is also small.

On raising T , thermal excitation promotes trapped carriers into the valence band and the concentration of free holes becomes a determining parameter. In other words, when the thermal energy reach the order of magnitude of the energetic separation between the Fermi level and the mobility edge, i.e. 56 meV at 650 K, which is the activation energy of electrical conductivity at this temperature (figure 4), then the majority of trapped carriers (involved in table 1) are excited into the extended states of the valence band. As a consequence the conductivity is carried out by delocalized carriers. In this regime, the impurities act as diffusive centres according to Mattheissen's rule. We think that O vacancies then play a significant part in diffusing wave functions of free holes for the following reasons. First, it is established that conductivity is very anisotropic in this oxide [13, 33, 34] as a consequence of the structural characteristics, and the easy path for charge transport is the basal plane. Second, from studies on the reduced form of this oxide [27–29], one can presume that O vacancies are formed principally in the basal plane. Therefore they are expected to

play a role in conductivity when the transport is ensured by extended waves. In the low-temperature regime, there also exists O vacancies (in the same amount), but, as conduction is ensured by hopping, the influence of O vacancies is less probable. As a consequence, in this high-temperature range the conductivity increases when decreasing the O vacancy concentration, as is observed in figure 1. One can attempt to quantify the contribution of the O vacancies in terms of additional resistivity, the compound $\text{La}_{1.95}\text{NiO}_4$, having no O may serve as a reference. Taking its minimal resistivity (at 650 K) one obtains an additional impurity contribution to the resistivity of $5 \times 10^{-4} \Omega \text{ cm}$ per % of O vacancy concentration.

The electronic drift mobility may be calculated from conductivity and carrier concentration. In the low-temperature regime (table 3), the drift mobility is below $\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is well within the range of hopping conductivity according to Cohen [35]. This may be consistent with the fact that Hall mobility was not detected in a similar sample (a single crystal, the composition of which was $\text{La}_{1.93}\text{NiO}_{4.05}$ [25]). Conversely, at high temperature, the calculated drift mobility reaches $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 650 K, that is, below $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a threshold limiting the range where particles can coherently propagate according to Cohen. The particles are here considered to have extended wave functions but they propagate incoherently in a so-called random phase propagation mechanism [35, 36]. The conduction ($\leq 90 \Omega^{-1} \text{ cm}^{-1}$) is not that of a normal metal; effectively it remains smaller than that of the minimal metallic conduction defined by Mott and Davis [24], $350 \Omega^{-1} \text{ cm}^{-1}$. Note that in $\text{La}_{1.2}\text{Sr}_{0.8}\text{NiO}_{3.77}$, which has a similar room-temperature (calculated) drift mobility as in $\text{La}_{1.95}\text{NiO}_4$ at 650 K, we measured at this T a Hall mobility of $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [25], that is, of the same order of magnitude, in favour of the existence of extended state in this compound too.

5. Conclusion

$\text{La}_{2-x}\text{NiO}_{4-\delta}$ accommodates a significant amount of non-stoichiometry on the La sites, i.e. $\text{La}_{2-x}\text{NiO}_{4-\delta}$ can be formed with $x \leq 0.15$. For standard synthesizing conditions, O vacancies compensate La vacancies in such a way that hole concentration is approximately constant.

The transport properties in the low-temperature region are characteristic of a hopping conduction of localized carriers in the valence band tail above a mobility edge. The activation energy appears to be related to structural strain modifying the band width.

In the high-temperature range, both thermal excitation and broadening of the band contribute to make the carriers delocalized. The conductivity then varies slowly with T . The mobility at 650 K remains low, i.e. $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, from which we conclude that the carriers move according to a random phase propagation. In this regime, the O vacancies scatter free holes and increase the resistivity.

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