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# The $Li_2O$-NiO-$O_2$ system at 670°C and the consequences of non-stoichiometry on the magnetic properties of the $Li_xNi_{1-x}O_{1\pm y}$ phases

HENRI-NOËL MIGEON, MICHEL ZANNE, CHARLES GLEITZER, JACQUES AUBRY
*Laboratoire de Chimie du Solide, Associé au CNRS No 158, Service de Chimie Minéral A, Université de Nancy I, Case Officielle No 140, 54037 Nancy Cédex, France*

The $Li_2O$–NiO–$O_2$ system is described at 670° C in the oxygen pressure range $1.3 \times 10^{-8}$ to 150 bars (and the phase diagram is extended up to $Li_2NiO_3$). The consequences of oxygen stoichiometry are emphasized in relation to the magnetic properties.

## 1. Introduction

In the Li–Ni–O system, it is mostly the region near NiO which has been previously studied, since the discovery by Verwey of the valence induction phenomenon (that is substitution of nickel by lithium with a compensating change of nickel oxidation degree). Much work has been devoted by physicists to the lithium-doped nickel oxide system. It was therefore decided to extend the researches in this system towards high lithium and oxygen concentrations and study that region where oxygen pressure influences the nature and properties of known phases.

In a previous article [1], we studied the preparation and the physical properties of $Li_2NiO_3$ which accept a non-stoichiometry with an oxygen deficit. On decomposition, under oxygen pressures varying between 20 and $1.3 \times 10^{-8}$ bars, there appear to be multiphased regions. In order to interpret our results we studied the NiO–$Li_2NiO_3$ line which consequently led to the determination of the Li–Ni–O diagram.

## 2. Background

On the $Li_2O$–NiO line, only one compound, $Li_2NiO_2$, is known [2]. The line joining NiO to $Li_2NiO_3$ has been studied much more [3–6]; the compounds obtained are formulated $Li_xNi_{1-x}O$ with $0 \leqslant x \leqslant 0.67$. The results can be summarized as follows: (i) From NiO to $Li_{0.28}Ni_{0.72}O$ a solid-solution designated $\delta$ is observed, with the NaCl structure. (ii) From $Li_{0.30}Ni_{0.70}O$ to $Li_{0.38}Ni_{0.62}O$ a cubic superstructure of NiO designated $\gamma$ appears, the symmetry of which is rhombohedral of the $\alpha NaFeO_2$ type. (iii) From $Li_{0.42}Ni_{0.58}O$ to $Li_{0.61}Ni_{0.39}O$ a rhombohedral compound appears with the $\alpha NaFeO_2$ structure, designated $\beta$. (iv) For $Li_{0.65}Ni_{0.35}O$ whose composition is near $Li_2NiO_3$, Klemm [4] obtains a compound of monoclinic structure with: $a = 4.906$ Å; $b = 8.492$ Å; $c = 9.549$ Å.

When preparations are carried out at high temperatures (1000 or 1100° C the experimental results are significantly different. The superstructure 2a was no longer observed [9, 10], the upper limit of the cubic phase being $Li_{0.395}Ni_{0.605}O$ [9]. According to Perakis and Kern (based on magnetic and crystallographic properties) this system is represented by $(NiO)_{1-2x}(LiNiO_2)_x$ for $0.02 \leqslant x \leqslant 0.37$. By heating under vaccum, Gallezot [11] observed only a rhombohedral structure for $x \leqslant 0.35$.

The magnetic properties were studied successively by Goodenough [3] and Klemm [4]. Their results are in agreement: (1) The compounds with NiO structure corresponding to a statistical distribution of lithium on the nickel planes are antiferromagnetic, (2) for $0.30 < x < 0.50$ the compounds are ferrimagnetic, (3) according to Klemm, the phases obtained for $x \geqslant 0.5$ are paramagnetic. However, a recent article by Kern [12] assigns ferromagnetic properties to $LiNiO_2$, the Curie temperature being 82 K.

## 3. The phase diagram

### 3.1. Experimental method

The more oxidized compounds of the $Li_xNi_{1-x}O$ system are obtained through calcination at 670° C for 3 days under oxygen pressure ($P_{O_2} < 150$ bars in the presence of $P_2O_5$ and soda lime) of $Li_2O +$ NiO mixtures such that $Li/Ni = x/(1-x)$ with $x \leqslant 0.67$.

The equilibrium is then obtained through heating to 670° C for 20 h under oxygen pressures varying from $1.3 \times 10^{-8}$ to 20 bars accompanied by a decrease of the average oxidation state of nickel (this mean oxidation number is determined by hydrochloric dissolution [7]).

### *3.2 Results*

Crystallographic studies of compounds of variable oxidation number and Li/Ni ratios gave the following results.:

#### *3.2.1. NiO–$Li_2NiO_3$ line*

We observed from NiO to $Li_{0.32}Ni_{0.68}O$, a single phase $\delta$ identical with the one pointed out by Klem, from $Li_{0.32}Ni_{0.68}O$ to $Li_{0.44}Ni_{0.56}O$, the 2a superstructure $\gamma$ phase, from $Li_{0.44}Ni_{0.56}O$ to $Li_{0.57}Ni_{0.43}O$ the single $\beta$ phase, and from $Li_{0.57}Ni_{0.43}O$ to $Li_{0.63}Ni_{0.37}O$ a two-phase domain $(\alpha + \beta)$, not observed by Klemm. From $Li_{0.63}Ni_{0.37}O$ to $Li_{0.67}Ni_{0.33}O$ ($Li_2NiO_3$) only the single phase $\alpha$ was observed. For $x \leqslant 0.57$, when the mean oxidation number of nickel varies, it is possible to characterize a non-stoichiometry on each side of the line corresponding to the $Li_xNi_{1-x}O$ system. For instance, with $x = 0.28$ the single phase $\gamma$ is observed from $Li_{0.28}Ni_{0.72}O_{1.0256}$ to $Li_{0.28}Ni_{0.72}O_{0.986}$. On the other hand, for the composition $Li_{0.28}Ni_{0.72}O_{0.968}$, $Li_2O$ appears. Nevertheless, as the detection of $Li_2O$ is rather difficult with X-rays, we have confirmed this non-stoichiometry with the help of magnetic measurements (cf. Section 4).

In the same way, a study of the compound $LiNiO_2$ ($\beta$ phase) shows the existence of a non-stoichiometry; the system is single phase up to $LiNiO_{1.96}$. Density measurements in this region allow us to conclude a non-stoichiometry with oxygen vacancies. The change from $LiNiO_2$ to $LiNiO_{1.96}$ might correspond to a decrease of the density of 0.6%, which agrees with the measured value (0.6%), while the formation of interstitial cations ($Li_{1+x}Ni_{1+x}O_2$) would give an increase of 1.4%.

Taking account of previous work the structural development along the line NiO–$Li_2NiO_3$ is the following. When the substitution level is low ($x \leqslant 0.32$) the lithium is statistically distributed on the nickel planes [3, 4], so that the NaCl type structure is preserved. When the lithium level is such that $0.32 < x \leqslant 0.44$ the observed superstructure may be interpreted as deriving from $\alpha NaFeO_2$ type structure by substitution of lithium by nickel on the lithium planes [4]. For $0.44 < x \leqslant 0.57$, we observe an $\alpha NaFeO_2$ type structure which corresponds to a sequence along the "$c$" axis: Li–O–Ni–O–Li for $x = 0.5$. When $x$ is lower than 0.5, nickel is statistically substituted on the lithium planes, while for $x$ greater than 0.5 the lithium is introduced into the nickel planes in an unordered manner [4]. For $x$ greater than 0.63 the $Li_2NiO_3$ type phase corresponds to the sequence Li–O–(1/3 Li + 2/3 Ni)–O–Li with an ordered distribution in the mixed planes [1], this order being appreciably different from the former. It is understandable that the transition from one to the other is not gradual (as for the phases $\alpha$ and $\beta$), which proves the existence of the two phase region $\alpha + \beta$. The non-stoichiometry of $Li_2NiO_3$ along the line NiO–$Li_2NiO_3$ may be considered under three aspects: (1) substitution of nickel in the lithium planes, (2) substitution of a part of the lithium by nickel on the ordered mixed planes, (3) equipartition of the excess nickel on all the cationic planes. We carried out a calculation of the structure factors with the atomic positions determined in the structural study of $Li_2NiO_3$ [1]. We have compared the intensities calculated in this way with those measured on a diffractogram of $Li_{1.9}Ni_{1.1}O_3$ (the limiting composition of this non-stoichiometry). The values of the residual factor $R = \Sigma (I_O - I_C)/\Sigma I_O$ for the three assumptions are 0.20, 0.11 and 0.16 respectively. These results indicate that for a Li/Ni ratio lower than two, the excess nickel can be substituted preferentially for the lithium of the Li–Ni mixed planes.

#### *3.2.2. $Li_2NiO_2$–$Li_2NiO_3$ line*

When the mean oxidation number of nickel ($n$) progressively increases from 2 to 4, the following series of single phase and multiphase domains appears (Fig. 1): $Li_2NiO_2$ for a mean oxidation number of 2, a three phase domain $Li_2O + Li_2NiO_2 + Li_xNi_{1-x}O$ (NaCl type with $x \simeq 0.12$) for 2.01 <

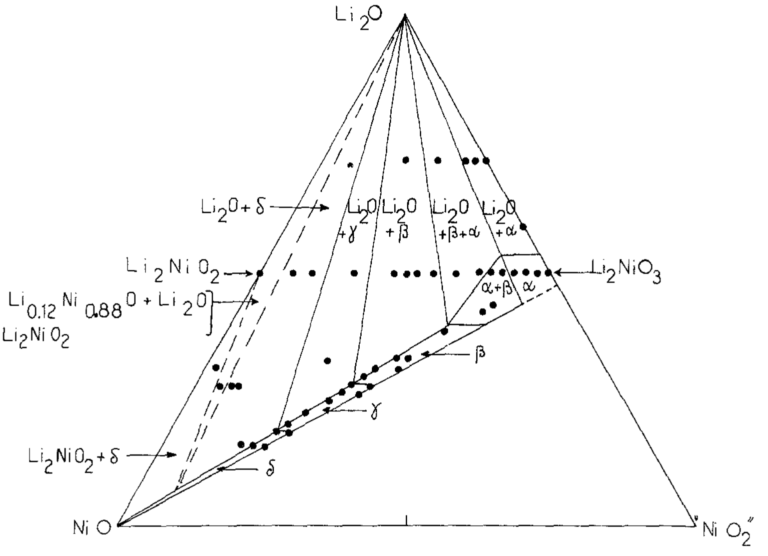


*Figure 1* Ternary diagram $Li_2O$–NiO–"$NiO_2$".

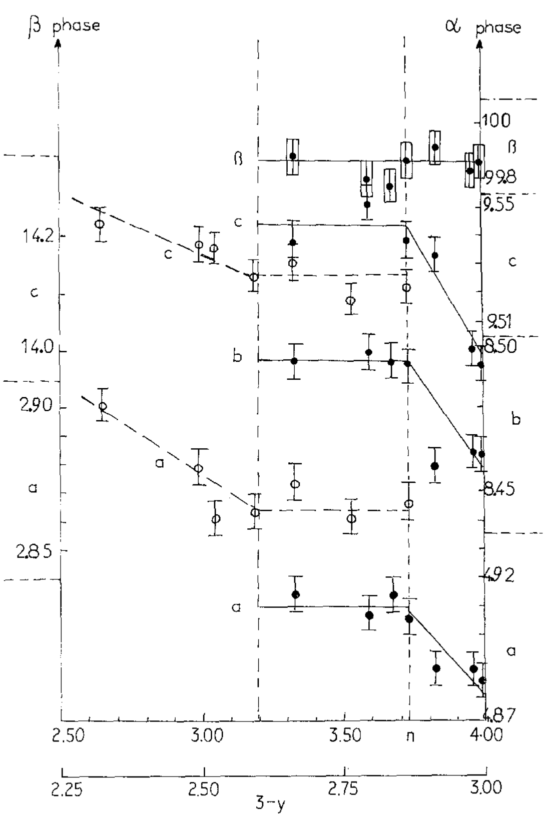


*Figure 2* Cell parameter variations of the phases α and β with the mean oxidation number of nickel (*n*).

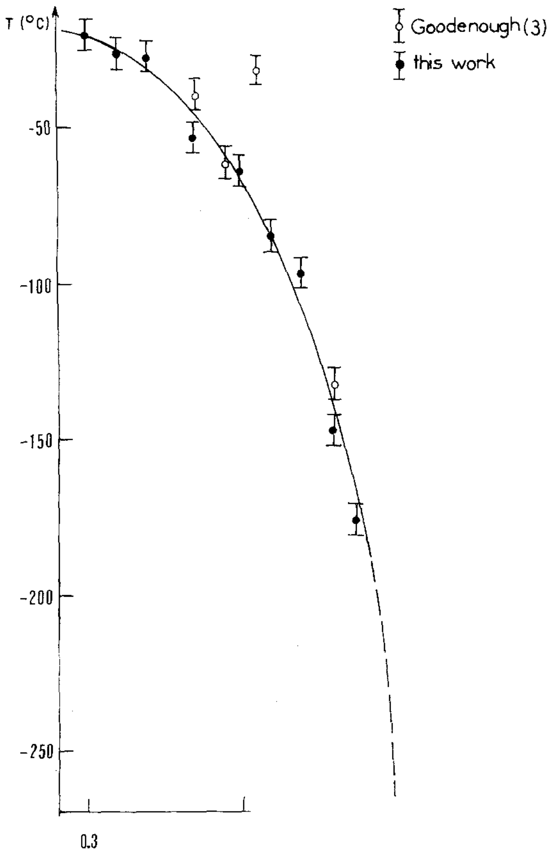
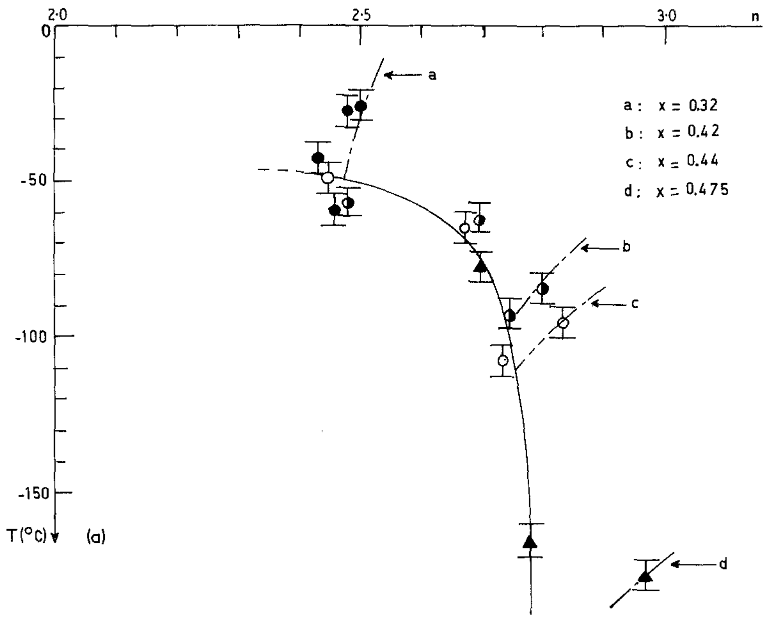


*Figure 3* Variation of the Curie temperature with *x* for $Li_xNi_{1-x}O_{1+y}$.

$n \leqslant 2.14$, and a two phase domain $\delta + Li_2O$ for $2.14 < n \leqslant 2.45$. A measurement of the parameters of $Li_xNi_{1-x}O$ indicates a decrease of the cell volume when the oxidation number of nickel increases, which indicates that the value of *x* becomes greater with *n* inside this domain. For $2.45 < n \leqslant 2.74$ a two phase domain $\gamma + Li_2O$ was observed, while for $2.74 < n \leqslant 3.24$ a domain $\beta + Li_2O$ was observed. The cell parameters of the single phase β decrease as the value of *n* increases (Fig. 2) which is in agreement with an

*Figure 4* (a) Variation of the Curie temperature with the mean oxidation number of nickel ($n$) for different values of $x$. (b) Representation of the variation of the Curie temperature for a given value of $x$ in relation to the displacement of the point representative of the composition on the ternary diagram $Li_2O$–NiO–"$NiO_2$".

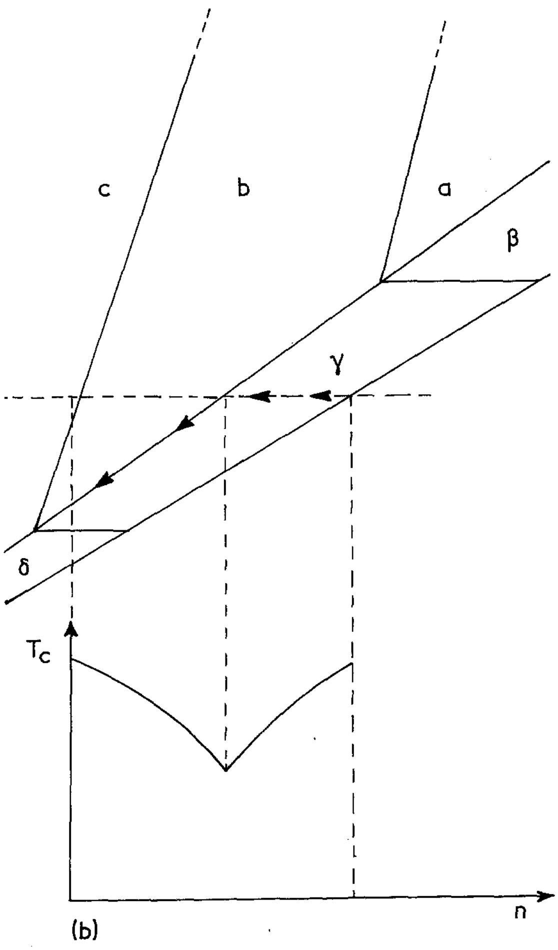


increasing substitution of nickel by lithium on the cationic planes of the $\alpha NaFeO_2$ type structure. For $3.24 < n \leqslant 3.56$ a three phase domain $\alpha + \beta + Li_2O$ was observed, then a two phase domain $\alpha + \beta$ when $3.56 < n \leqslant 3.73$, for which the cell parameters of $\alpha$ and $\beta$ keep the same values (Fig. 2). In agreement with our experimental results, the ternary diagram $Li_2O$–NiO–"$NiO_2$" is given in Fig. 1.

## 4. Magnetic properties

In order to define the non-stoichiometry on the oxygen sublattice of the phases $\beta$, $\gamma$ and $\delta$ deduced from crystallographic evidence, a thermomagnetic study was carried out in the domain 300 to 90 K on a range of compounds with $0.3 \leqslant x < 0.5$. The ferrimagnetic properties are characterized in agreement with previous authors [3, 4]. For the most oxidized compounds, the transition temperature decreases as $x$ increases (Fig. 3). Our results allow us to define more precisely those previously obtained by Goodenough [3].

With a constant value of $x$, a decrease in the mean oxidation number of nickel is accompanied by a significant variation in the Curie temperature as Fig. 4a indicates for different values of $x$. We observe first a decrease of the transition temperature (as the oxidation number of nickel decreases) then an increase (Fig. 4b), the observed value then



only depending on the mean oxidation number of nickel. This confirms the existence of a non-stoichiometry characterized by the decreasing part of each curve, the increasing part (left) corresponding to the lower limit of existence of the single phases.

The extent of the non-stoichiometry thus determined leads to the formula

$$\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}_{1\pm y} \quad \text{with} \quad y \simeq \frac{x}{30}$$

A study of the saturated magnetic moment variation measured at 90 K and with a field of 8200 Oe is given in Table I. As $y$ decreases we observe a decrease of the saturation magnetization. The values of $\sigma_s$ are lower than those given by previous authors; this may be explained by the higher measurement temperature (90 K instead of 4 K) and also by the fact that saturation is probably obtained (in agreement with Kern [6]) higher field strengths being necessary.

TABLE I

| $x$ | $y$ | $\sigma_s(\mu_B\,(\text{g at. of Ni})^{-1})$ |
|---|---|---|
| 0.44 | + 0.0124 | 0.233 |
|  | − 0.0128 | 0.215 |
| 0.42 | + 0.0205 | 0.243 |
|  | + 0.0046 | 0.224 |
| 0.32 | + 0.0100 | 0.042 |
|  | + 0.0032 | 0.030 |
|  | − 0.0036 | 0.006 |

## 4.1 Magnetic properties of the single phase $\mathrm{LiNiO}_{2-y}$

Kern indicated ferromagnetic properties at $T \leqslant 82$ K for a compoung whose formula approaches that of $\mathrm{LiNiO_2}$. Above 82 K the Curie–Weiss law is obeyed with $\theta_p = 100$ K, this leads to a magnetic moment of $1.73\,\mu_B$ in agreement with Klemm [4]. A similar study has been undertaken on the series $\mathrm{LiNiO}_{2-y}$ with $y \leqslant 0.04$.

Within the range 90 to 300 K, the Curie–Weiss law is obeyed and leads to positive Curie paramagnetic temperatures. However, when the deviation from stoichiometry decreases, $\theta_p$ decreases and the magnetic moment increases as indicated in Table II where $n_c$ represents the number of single electrons calculated with the spin only hypothesis. The value of $\mu_B$ is higher than the theoretical value corresponding to $\mathrm{Ni}^{3+}$ in a low spin state ($1.73\,\mu_B$) and may be explained by a bonding between the fundamental level $^2$E (coming from a $^2$G state of the free ion) and the upper term $^2\mathrm{T}_2$ (coming from the same state) under the influence of the spin-orbit coupling. The shell being more than half-filled, the coefficient $\lambda$ is negative and the magnetic moment is then higher than the spin only magnetic moment [8].

TABLE II

| $y$ | $\theta_p$(K) | $\mu(\mu_B)$ | $n_c$ |
|---|---|---|---|
| 0.012 | + 57 | 2.34 | 1.545 |
| 0.027 | + 68 | 2.09 | 1.310 |
| 0.035 | + 86 | 1.91 | 1.155 |

By using the representation of Goodenough [3] and Klemm [4] to characterize the magnetic properties if the phases $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$, $\mathrm{LiNiO_2}$ should be paramagnetic because the $\mathrm{Ni}^{3+}$ ions have only the $\mathrm{Li}^+$ ions as neighbours on the upper layer, which is incompatible with any coupling. The fact that ferromagnetic properties have been characterized by Kern [6] may signify either the existence of indirect interactions at 90°, or the existence of direct interactions between the orbitals $d_{x^2-y^2}$ and $d_{zx}$ or $d_{x^2-y^2}$ and $d_{yz}$ which would lead to ferromagnetic order.

## 5. Electrical properties

Electrical measurements have been made on the system $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$ with $0.34 < x \leqslant 0.5$. These compounds are all semiconductors whose concuctivity follows the classical law $\sigma = \sigma_0 e^{-E/kT}$. For all values of $x$, the conductivity varies little ($0.35 < \sigma < 0.15$ mho cm$^{-1}$); similarly the thermoelectric power is almost constant with the chemical composition ($\alpha \simeq +90\,\mu$V° C$^{-1}$), but it decreases as the temperature increases, as for NiO slightly doped with lithium. In the case of $\mathrm{LiNiO_2}$, the conductivity is rather high for an oxide of this type ($\sigma = 0.2$ mho cm$^{-1}$) with an activation energy of 4.8 kcal mol$^{-1}$. Its thermoelectric power is $2\,\mu$V° C$^{-1}$ at 25° C and − 14 $\mu$V° C$^{-1}$ at 110° C.

The appearance of the non-stoichiometry provokes no significant variations of conductivity or thermoelectric power but on the other hand, the activation energy decreases ($E = 3.65$ kcal mol$^{-1}$ for $\mathrm{LiNiO}_{1.96}$). The electrical properties of $\mathrm{LiNiO_2}$ suggest a situation similar to a delocalized electron state as in $\mathrm{SrFeO_3}$ [8] and which could be explained by direct Ni–Ni interactions or indirect 90° Ni–O–Ni interactions.

## 6. Conclusion

The study of the Li–Ni–O system has allowed us to show the following points:

(1) A non-stoichiometry is characterized on the oxygen sublattice on both sides of the NiO–$LiNiO_2$ line. Study of the obtained phases as a function of the Li/Ni ratio and of the mean oxidation number of nickel leads to the establishment of a ternary diagram $Li_2O$–NiO–"$NiO_2$".

(2) For the compounds $Li_xNi_{1-x}O_{1\pm y}$ with $0.30 \leqslant x < 0.5$, the non-stoichiometry modifies significantly the magnetic properties: a decrease of the oxidation number is accompanied by a decrease of the ferrimagnetic Curie temperature.

(3) In the case of $LiNiO_{2-y}$ the measured magnetic moment may be explained by low-spin nickel III with a low orbital contribution. The electrical conductivity is high and suggests evolution towards a delocalized electron state.

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