Magnetic clusters formation in Li$_{1-x}$Ni$_{1+x}$O$_2$ compounds: experiments and numerical simulations.

D. Mertz, Y. Ksari, F. Celestini*, J. M. Debierre, A. Stepanov
Laboratoire MATériaux Organisation Propriétés CNRS, Université d’Aix-Marseille III
Faculté des Sciences de Saint-Jérôme, Case 151, 13397 Marseille Cedex 20, France.

and C. Delmas
Institut de Chimie de la Matière Condensée de Bordeaux CNRS,
Ecole Nationnale Supérieure de Chimie et Physique de Bordeaux,
87 Avenue du Docteur Albert Schweitzer, 33608 Pessac Cedex, France

(Part of a technical report released on April 14th, 1999)

The magnetic properties of Li$_{1-x}$Ni$_{1+x}$O$_2$ compounds with $x$ ranging between 0.02 and 0.2 are investigated. Magnetization and ac susceptibility measured at temperatures between 2 K and 300 K reveal a high sensitivity to $x$, the excess Nickel concentration. We introduce a percolation model describing the formation of Ni clusters and use an Ising model to simulate their magnetic properties. Numerical results, obtained by a Monte-Carlo technique, are compared to the experimental data. We show the existence of a critical concentration, $x_c = 0.136$, locating the Ni percolation threshold. The system is superparamagnetic for $x < x_c$, while it is ferrimagnetic for $x > x_c$. The 180$^\circ$ Ni–O–Ni inter-plane super-exchange coupling $J_{\perp} \simeq -110K$ is confirmed to be the predominant magnetic interaction. From the low temperature behavior, we find a clear indication of a 90$^\circ$ Ni–O–Ni intra-plane antiferromagnetic interaction $J_{\parallel} \simeq -1.5K$ which implies magnetic frustration.

PACS numbers: 75.40.Mg, 75.10.Hk, 75.30.Et, 75.30.Kz

1. INTRODUCTION

Conduction and magnetic properties of Li$_{1-x}$Ni$_{1+x}$O$_2$ compounds have long been studied in relation with their crystallographic structure [1,2]. Two essential conclusions emerge from these studies. First, due to its lamellar structure allowing Lithium desintercalation/intercalation, LiNiO$_2$ is a good candidate as an electrode material in rechargeable Lithium-ion batteries [3,4]. Unfortunately, excess Nickel in the Lithium planes usually alters considerably the intercalation properties. Several synthesis ways have thus been developed in order to approach the stoichiometric composition [5]. Second, even if magnetic properties are known to be very sensitive to the structure, the actual relationship is not fully understood and still under debate. In this paper, we shall focus our attention on this latter point.

For large values of $x$, Li$_{1-x}$Ni$_{1+x}$O$_2$ keeps the rock-salt structure of NiO, in which Oxygen ions occupy one face-centered-cubic (fcc) lattice, while both Nickel and Lithium are randomly distributed over a second fcc frame [6,7]. As $x$ is decreased, the material leaves its cubic structure to adopt an hexagonal one in which the metal ions segregate into alternate Lithium and Nickel (111) planes, respectively denoted (111)$_{Li}$ and (111)$_{Ni}$. A lattice-gas model [8] has demonstrated that the transition occurs at a critical concentration $x^* \simeq 0.38$, in good agreement with X-ray diffraction experiments. When $x$ tends to 0, the segregation tends to be complete and the almost stoichiometric compound shows an alternation of triangular Ni and Li planes (Fig. 1). In this structure, a Ni plane is “magnetically isolated” by two adjacent Li planes so that LiNiO$_2$ can be considered as a model material for a perfect triangular two-dimensional (2D) magnet. Depending on the ferromagnetic or antiferromagnetic (AF) nature of the 90$^\circ$ Ni–O–Ni magnetic coupling, the system could then be respectively ferromagnetic or frustrated at low temperatures. Hirakawa et al. [9] found evidence of a quantum liquid state, as it is suggested by Anderson for a triangular lattice Heisenberg antiferromagnet [10]. Later, Kemp et al. [11] interpreted their experimental results as a consequence of a ferromagnetic intra-plane interaction. Until now the question of the intra-plane coupling thus remains a controversial subject [12,13]. For $x > 0$, two other magnetic interactions should be considered. Charge compensation on Nickel implies that a Ni$^{2+}$ ion sitting in a (111)$_{Li}$ plane has five Ni$^{3+}$ and one Ni$^{2+}$ ions as nearest neighbors (NN) in the adjacent (111)$_{Ni}$ planes. The corresponding magnetic interactions are denoted $J_{\perp}$ and $J'_{\perp}$ respectively (Fig. 2). If $J'_{\perp}$ is known to be strongly antiferromagnetic, no direct conclusions can be made on the sign of $J_{\perp}$. The existence of these inter-plane interactions, due to the Anderson super-exchange [14] and acting in the direction perpendicular to the (111) planes, tends to destroy the 2D magnetic behavior expected in the stoichiometric compound. This is illustrated in Fig. 3(a), where we show a magnetic Ni cluster containing one ion located in a (111)$_{Li}$ plane and six nearest-neighbors (NNs) located...
in the two adjacent (111)$_{Ni}$ planes. The two fundamental spin states, depending on the sign of $J_\perp$, are sketched in Fig. 3(b). Let us note finally that Kuiper et al. [15,16] recently discussed the possibility that substitution of Li by Ni can give rise to a charge compensation on Oxygen rather than on Nickel. The resulting Ni$^{3+}$–O$^-$ exchange interaction being two orders of magnitude larger than the Ni$^{3+}$–O$^{2-}$–Ni$^{3+}$ super-exchange, this point should be easily tested by magnetic measurements.

The aim of this study is to investigate the magnetic behavior of the Li$_{1-x}$Ni$_{1+x}$O$_2$ family through a comparison between experimental and numerical simulation results. We consider here the compositions $x = 0.02, 0.07, 0.08, 0.14$ and 0.2, lying in the region where metal ions segregate in the (111)$_{Li}$ and (111)$_{Ni}$ planes. In section II, we describe the sample preparation and characterisation procedure. We also give experimental results for the magnetization and ac susceptibility as functions of temperature. In section III, a percolation approach is used to simulate the formation of the Ni spin clusters. The magnetic properties of the disordered system are then calculated by performing Monte Carlo simulations in an Ising-like model. We finally present our discussion and conclusions in section IV: we are able to confirm that the inter-plane interactions are two order of magnitude greater than the intra-plane ones, and present arguments in favor of an AF intra-plane interaction leading to magnetic frustration. The scenario consisting in charge compensation on oxygen is ruled out for the low concentrations examined in this paper. We finally demonstrate the existence of a critical concentration, $x_c = 0.136$, for the extra Ni ions. For $x < x_c$, the system behaves as a superparamagnet, while for $x > x_c$ it is a ferrimagnet.

2. EXPERIMENTS

Fifty-mg samples of Li$_{1-x}$Ni$_{1+x}$O$_2$ powder, prepared as reported in Ref. [17], were placed in Pyrex tubes, 4 mm in diameter, filled with Helium gas. The amount of extra nickel was previously determined by Rietveld analysis in the $R\bar{3}m$ crystallographic space group. The magnetic measurements were carried out using an Oxford Instrument Maglab2000 cryostat equipped with a 7 T superconducting magnet and a variable temperature insert allowing temperature scans between 1.8 and 450 K. During experiments at constant field, the magnet was set in the persistent mode.

The measurement system comprises an excitation coil for ac susceptibility, with two inner compensated coils, used either for ac susceptibility or for dc moment measurements. The dc moment and ac susceptibility signals are measured respectively with a Keithley 2001 voltmeter and with a SR830 lock-in-amplifier. The geometry of the system allows a sensitivity of $10^{-5}$ (dc moment) and $10^{-8}$ emu (ac susceptibility).

The static properties were first investigated under external field of 2 and 5 T as a function of $x$. These field values are sufficiently large to suppress the ferromagnetic domains due to dipole-dipole interactions and to make negligible the effect of magnetic anisotropy which reaches 2.5 T in this compound [18]. In these conditions, the system is only subject to local exchange interactions in which we are interested. The data were corrected for demagnetizing effects using a model of spherical thin grains. The correction is only significant below 100 K for the largest $x$ values and does not exceed 5% at 3 K. In Fig. 3 we represent the magnetization curves obtained under 2 T. It is clearly seen that the magnetic response of the Li$_{1-x}$Ni$_{1+x}$O$_2$ family is strongly influenced by the amount of extra nickel ions. The important point is that the topology of the experimental curves changes with $x$. This suggests that, as $x$ changes, the system undergoes a transition between distinct macroscopic magnetic behaviors probably related to Ni clusters formation. Indeed, the lowest ($x < 0.14$) and highest ($x > 0.14$) concentrations present respectively superparamagnetic and ferromagnetic like behavior. To illustrate and quantify this point we measured the ac susceptibility of the samples at a frequency of 10 kHz, with an excitation field of 3 Oe. In Fig. 4 we show the data obtained for $x = 0.02$, $x = 0.14$ and $x = 0.20$. The susceptibility curves display maxima which are characteristic for ferromagnets at temperatures of 116 K and 168 K respectively for $x = 0.14$ and $x = 0.20$. In contrast, for $x = 0.02$, the temperature variation of $\chi_{ac}$ is rather monotonic. These observations confirm the superparamagnetic behavior of compounds with low extra nickel concentrations, in agreement with previous neutron experiments [19]. The second point concerns the magnetization of the different samples at the lowest temperatures. Assuming that all the magnetic moments in Li$_{1-x}$Ni$_{1+x}$O$_2$ are parallel, the magnetization should saturate to:

$$M_s = (1 - x) \frac{N \mu_B g_1 S_1}{2 \pi N \mu_B g_2 S_2} + 2\pi N \mu_B g_2 S_2,$$

where $N$, $\mu_B$, $g$ and $S$ denoting respectively the Avogadro's constant, Bohr's magneton, Landé's factor and spin value. The first term represents the contribution of Ni$^{3+}$ ions in the (111)$_{Ni}$ planes while the second one is related to Ni$^{2+}$ ions in (111)$_{Li}$ and (111)$_{Ni}$ planes. This saturation should be reached when the Zeeman energy exceeds the interplane antiferromagnetic coupling. This cannot be reasonably the case for the moderate magnetic fields involved in this work. In Fig. 5 we plot the magnetization measured at 4.3 K, as a function of $x$, together with $M_s(x)$ (Eq. 1). We can see that the maximum saturation is not reached. This is in good agreement with previous results of Rougier et al. [18] who reported the absence of saturation for $x = 0.02$, even at 11 T. In addition, our results show that the measured magnetization presents a maximum at $x \approx 0.14$. In the light of the experimental results, it is difficult to conclude about the exact nature
of the magnetic order. In the next section, we propose a simple model to investigate this point further.

3. MODEL

Our model incorporates the different magnetic interactions described in Section I. The main ones ($J_\perp$ and $J_\parallel < 0$) are the 180° Ni–O–Ni super-exchange coupling one Ni ion sitting in a (111)$_{Li}$ plane to its six NNs sitting in the adjacent (111)$_{Ni}$ planes. It is reasonable to assume that these two coupling constants are of the same order of magnitude. In the following we suppose $J_\perp = J_\parallel < 0$. It is obvious that changing the sign of $J_\perp$ does not modify the magnetization, the susceptibility and other related quantities, since there is a compensation between the magnetic moments of the two Ni$^{2+}$ ions. We also consider the 90° Ni–O–Ni intra-plane interaction $J_\parallel$. We make no a priori assumption about the sign of $J_\parallel$. Recent neutron diffraction studies on this material family ($x \leq 0.20$) have shown that there is no Lithium in the Nickel planes. We verified this point with the help of the lattice gas structural model introduced by Reimers et al. [8]. For a composition $x = 0.2$, which is the highest considered here, the quantity of Li ions in the (111)$_{Ni}$ planes is not significant (less than 2%) and can be reasonably neglected. Furthermore, we suppose that the excess Ni ions are randomly distributed in the (111)$_{Li}$ planes. Since we assumed that the excess Ni ions are antiferromagnetically coupled to their six NNs, three-dimensional magnetic Ni clusters are formed in the system, as shown in Fig. 2 (for the time being, we neglect intra-plane coupling). For $x < x_c$ all these clusters have a finite size. At the critical concentration $x_c$ the largest cluster percolates and for higher concentrations it grows in size. This percolation transition strongly affects the magnetic properties. One may expect different types of behaviors in samples with $x$ below, at, or above $x_c$. Numerical simulation gave $x_c \simeq 0.136$ for the percolation threshold. The cluster mass distribution $n_s$ was calculated at $x_c$: it follows a power law $n_s \propto s^{-\tau}$ with a critical exponent $\tau = 2.19 \pm 0.01$. This last result indicates a regular three-dimensional percolation transition [20], as predicted in a dedicated study of percolation in multi-layered structures [21]. We note that a small amount of Nickel impurities can give rise to large clusters because each impurity is coupled to six other Ni ions. This is illustrated in Fig. 3 where we represent the Ni ions distribution in a sample with $x = 0.02$. For such a low value of $x$, most of the magnetic clusters contain seven ions, but larger clusters coupling three successive Ni layers are also observed.

In order to calculate the magnetic properties, we use an Ising model in which each Ni ion has a spin $\sigma = \pm 1$. The choice of an Ising-type Hamiltonian is justified by intrinsically high magnetic anisotropy of Ni clusters in LiNiO$_2$ [18], and a posteriori by the good agreement found between the numerical results and the experimental data. In our model, we neglect the differences between the Ni ions. Indeed, the (111)$_{Ni}$ planes are mostly composed of Ni$^{3+}$ ions in a low spin state $S = 1/2$ while extra Nickels are Ni$^{2+}$ ions with $S = 1$. Two types of spin can be easily taken into account in the model, but we checked that it is not a crucial point, probably because we consider small concentrations of extra Nickel ions.

The Hamiltonian then simply reads:

$$H = -g\mu_B B \sum_i \sigma_i - J_\perp \sum_{<i,j>} \sigma_i \sigma_j - J_\parallel \sum_{<i,j>} \sigma_i \sigma_j$$

The first term describes the interaction with the magnetic field $B$. In the second term, $\sigma_i$ sits on a Ni in a (111)$_{Li}$ plane, and the $\sigma_j$'s sit on the six NN Ni ions in the adjacent (111)$_{Ni}$ planes. In the last term, the sum runs over all NN pairs in the same plane. For a given spin configuration, the Boltzmann factor is:

$$\exp \left[ K \left( b \sum_i \sigma_i + \text{sign}(J_\perp) \sum_{<i,j>} \sigma_i \sigma_j + j_\parallel \sum_{<i,j>} \sigma_i \sigma_j \right) \right]$$

where $b = g\mu_B B / |J_\perp|, K = |J_\perp| / kT$, and $j_\parallel = J_\parallel / |J_\perp|$ are respectively the dimensionless field, the inverse temperature, and the ratio of intra- to inter-plane coupling constants.

The classical "single spin flip" Monte Carlo algorithm is not well suited to simulate this system because of critical slowing down around the transition and at low temperatures [23]. To avoid very long simulation times, we adapted Wolff’s algorithm [24] to our system. This method largely compensates the correlation length increase when the temperature is lowered because the system evolves by flipping clusters of ordered spins. One Monte Carlo step (MCS) consists in constructing a Wolff cluster and then trying to flip it. In our case, the construction of a cluster is made as follows: we randomly choose a first spin $\sigma_a$. All the inter-plane bonds (if any) between $\sigma_a$ and the closest spins $\{\sigma_b\}$ are examined in turn. Those with $\sigma_a = \sigma_b$ are discarded; for the other bonds, spin $\sigma_b$ is added to the cluster with an arbitrary probability $p$. Now set $\{\sigma_a\}$ is replaced by set $\{\sigma_b\}$ and the procedure is repeated until an empty set is found. Choosing $p = 1 - e^{-2K}$, as in the classical Wolff algorithm, the expression for the flipping probability satisfying the detailed balance condition simplifies to

$$\min \{1, \exp \left[ -2K \left( bM_c + j_\parallel \Gamma_c \right) \right] \}$$

with

$$M_c = \sum_{\text{cluster}} \sigma_i$$
and

\[ \Gamma_c = \sum_{<i,j>_{surf}} \sigma_i \sigma_j \]  

(6)

The last sum runs over all the pairs of spins at the cluster surface, \( \sigma_i \) being part of the cluster and \( \sigma_j \) at the exterior. The exponential argument is the energy cost to flip the cluster: the first term is due to the field, the second to the intra-plane interactions at the cluster surface.

We considered systems of about 3000 spins (9 pure (111)\( _{Ni} \) planes, each containing 18 \times 18 Ni ions, and \( x\% \) excess Ni in the (111)\( _{Li} \) planes). Periodic boundary conditions were applied in the three directions. To check for finite size effects, we simulated a bigger system of approximately 30000 spins without significant changes in the results. For a concentration \( x \), a spatial configuration was built up by randomly placing Ni excess ions in the Li planes. At each temperature, ranging from 300 K down to 20 K, we first equilibrated the spin system through a Monte Carlo procedure, with about 20 K Monte Carlo steps per spin. We then calculated and are thus "magnetically isolated": they are at the origin of the superparamagnetic behavior observed both numerically and experimentally. For an extra Nickel concentration above the critical value \( x_c \approx 0.136 \), a magnetic cluster spans the sample. When the temperature is decreased, this magnetic cluster undergoes a second order transition to a ferrimagnetic state. Since the external field is high, the transition is broadened on the \( x = 0.14 \) and \( x = 0.2 \) curves. We also calculated magnetization curves for the same concentrations but without external magnetic field. In this case, the sample with \( x = 0.02 \) has no magnetization, as expected for a superparamagnetic system under zero applied magnetic field. On the other hand, in the samples with \( x > x_c \), the transition is well marked with the appearance of a spontaneous magnetization at low temperature.

From the \( M(T) \) curves, it is possible to extract values for the temperature \( T_o \) locating the onset of magnetic ordering. For \( x > x_c \), we first locate the inflexion point \( I \). We then draw the line tangent to the curve at point \( I \), and define \( T_o \) as the intercept with the T axis. For \( x < x_c \), there is no longer an inflexion point, since the system is superparamagnetic. However, we can still estimate the onset of magnetic ordering inside the isolated clusters. To do so, we define \( T_o \) as the temperature at which magnetization reaches 7 percent of its saturation value. For \( x > x_c \), this definition approximately gives the same \( T_o \) as the inflexion point method. In Fig. 8, we represent the onset of magnetic ordering temperatures, \( T_o \) deduced from the experimental and numerical \( M(T) \) curves under an applied field of 2 T. The good agreement confirms that our simple model permits an accurate description of the onset of magnetic ordering, thus providing information for the estimate of \( x \).

Let us now examine more closely the low temperature magnetization. The disagreement between the experimental and numerical results can be traced to the different approximations made in the model. At first, the choice of Ising spins is certainly too crude and it affects more and more the shape of the calculated magnetization curve as \( T \) is decreased. Secondly, we did not yet introduce the intra-plane interaction, known to be weaker than the inter-plane one, and to influence the magnetization at lower temperatures. Assuming a strong AF intra-plane coupling \( J_\perp \) and a weak intra-plane coupling \( J_\parallel \), we still have to discuss the sign of the intra-plane coupling. We consider two different magnetic subsystems: the first one is composed of spins belonging to the ferromagnetic clusters and the second one contains all the remaining spins which lie in the (111)\( _{Ni} \) planes. We denote \( \beta(x) \) the proportion of spins belonging to the clusters.

We calculated \( \beta(x) \) numerically for \( x \) ranging between 0 and 0.2: the results are well fitted by the polynomial \( \beta(x) = 7x - 22x^2 + 40.7x^3 \). Assuming a ferromagnetic coupling, \( J_\parallel \geq 0 \), at low temperature all the Ni\(^{3+} \) ions in the (111)\( _{Ni} \) planes adopt the field direction while the extra Ni\(^{2+} \) spins adopt the opposite one. As one can see on Fig. 8(b) the spin \( S = 1 \) on the extra Ni\(^{2+} \) is exactly compensated by one of his NNs having a spin \( S = 1 \). One can then expect a maximum ferrimagnetic magnetization

\[ \frac{M_1}{N \mu_B g_1 S_1} = (1 - x) . \]  

(7)

On the opposite, an AF coupling, \( J_\parallel < 0 \), leads to frustration in the second subsystem. In the case where this frustration is large enough to cancel the corresponding magnetization, only the ferrimagnetic clusters contribute to the low temperature magnetization. One then obtains
\[ \frac{M_2}{N \mu_B g_1 S_1} = [(1 + x) \beta (x) - 2x]. \] (8)

In Fig. 5 we plot the two curves corresponding to \( M_1(x) \) and \( M_2(x) \) together with the experimental results for \( B = 2 \) T at \( T = 4.3 \) K. Since temperature is too high and magnetic field too low to ensure perfect saturation of the different subsystems, neither \( M_1 \) nor \( M_2 \) fit the experimental data on the whole range. We can however qualitatively discuss the two limits. \( M_1(x) \) decreases linearly with \( x \), in contradiction with the increase of magnetization observed at low \( x \). Conversely, the \( M_2(x) \) curve approximately follows the experimental data points up to a systematic vertical shift. Since Eq. (8) assumes that the second subsystem has no magnetization, this is consistent with an AF intra-plane coupling (\( J_{\|} < 0 \)).

We thus performed additional simulations to examine the effect of the intra-plane interaction \( J_{\perp} \). Our results show that, for a ferromagnetic coupling (\( J_{\|} \geq 0 \)), the magnetization curve changes concavity around 20 K to reach the expected saturation value \( M_1 \) as \( T \to 0 \) K (Fig. 2). For an AF coupling, (\( J_{\|} < 0 \)), the curves at low temperatures behave much more like the experimental ones: saturation is not reached because the AF coupling induces a frustrated state in the triangular (111)\( N_i \) planes. The best qualitative agreement between simulations and experiments is found for \( J_{\|} \simeq -1.5 \) K. Of course, this rough estimate of \( J_{\|} \) is obtained for a given value of \( J_{\perp} \), determined from the high temperature behavior of the model with \( J_{\|} = 0 \). For a better estimate, one would have to take both \( J_{\perp} \), \( J_{\perp}' \) and \( J_{\|} \) as free parameters, simulate several magnetization curves and fit them to the experimental data.

4. SUMMARY AND DISCUSSION

In summary, we introduced a simple model to investigate the magnetic properties of non stoichiometric \( \text{Li}_{1-x} \text{Ni}_{1+x} \text{O}_2 \) layered compounds. The formation of three-dimensional (3D) Ni clusters around the extra Nickel ions was simulated by simple percolation of the Ni ions in the direction perpendicular to the metal layers. An Ising Hamiltonian was then used to compute the magnetic properties of the disordered system made of both 3D Ni clusters (magnetic coupling \( J_{\perp} \)) and 2D intra-plane Ni clusters (magnetic coupling \( J_{\|} \)). The transition from a superparamagnetic to a ferrimagnetic behavior, observed experimentally as \( x \) increases, is interpreted in our model as the onset of percolation for the 3D Ni clusters, at a critical threshold \( x_c \). Our numerical estimate \( x_c \simeq 0.136 \), agrees nicely with the experimental evidence of magnetic ordering at \( x = 0.14 \).

The best fit of our model to the experimental data is found for \( J_{\|} = -1.5 K \) and \( J_{\perp} = -110 K \). The assumption that \( |J_{\perp}| \simeq |J_{\perp}'| \) is validated by the good agreement between the model and the experiments. The order of magnitude found for \( J_{\|} \) allows us to confirm magnetic coupling through the Ni-O-Ni super-exchange interactions. The possibility of charge compensation on Oxygen proposed for \( x \) close to 1 \([3]\) is thus inadequate for the low \( x \) values considered in this paper. Another important outcome of our work is the relation found between the ordering temperature \( T_o \) and the concentration \( x \) of excess Nickel, which offers a new way to determine \( x \) precisely. In fact the accurate determination of \( x \) was overlooked for a long time. If new techniques \([13]\) permit now to determine the proportion of extra Ni ions with a reasonable accuracy, one should certainly be more careful about older results for stoichiometric \( \text{LiNiO}_2 \), which very likely concern samples with a non zero effective value of \( x \).

Moreover, Bajpai et al. \([13]\) have recently reported the coexistence of ordered and random phases in the same sample, the proportion of each phase depending on the heat treatment during elaboration. The coexistence of two distinct phases may very well explain the anomaly observed at 240 K in the ac susceptibility of some samples, a point currently investigated \([29]\).

Finally, the antiferromagnetic nature of \( J_{\|} \) implies 2D magnetic frustration because the Ni planes have a trigonal symmetry. The magnetic properties of the system at very low temperatures (\( T < |J_{\|}| \) would thus probably be better described in a 2D model with a random distribution of quenched spins due to the intra-plane coupling. We plan to investigate this point in the near future.

*e-mail: celest@matop.u-3mrs.fr

[1] L. D Dyer, B. S. Jr. Borie and G. P. Smith, J. Am. Chem. Soc. 20, 1499 (1954)
[2] J. B. Goodenough, D. J. Wicham and W. J. Croft, J. Phys. Chem. Sol. 5, 107 (1958)
[3] A. Rougier, C. Delmas and G. Chouteau, J. Phys. Chem. Sol. 57, 1101 (1996) and A. Rougier, Phd Thesis, Université de Bordeaux (1995).
[4] C. Delmas, J.P. Pérès, A. Rougier, A. Demourges, F. Weill, A. Chadwick, M. Broussely, F. Pertonn, Ph. Benssan and P. Willmann, J. Pow. Sources 68, 120 (1997)
[5] G. Dutta, A. Manthiram, J. B. Goodenough and J. C. Grienier, J. Sol. Sta. Chem. 96, 123 (1992)
[6] J. B. Goodenough, D. J. Wicham and W. J. Croft, J. Appl. Phys. 29, 382 (1958)
[7] V. W. Bronger, H. Bade and W. Klemm, Z. Anorg. Allg. Chem. 333, 188 (1964)
[8] W. Li, J. N. Reimers and J. R. Dahn, Phys. Rev. B 46, 3236 (1992) and Phys. Rev. B 49, 826 (1994)
[9] K. Hirakawa, H. Kadowaki and K. Ubukoshi, J. Phys. Soc. Jap. 9, 3526 (1985)
FIG. 1. Perspective view of the Li$_{1-x}$Ni$_{1+x}$O$_2$ structure.

FIG. 2. (a) Positions of the Nickel and Lithium ions in the LiNiO$_2$ structure (Oxygen ions are not represented). The presence of an extra Ni ion in a (111)$_{Li}$ plane induces the formation of a seven-ion Ni cluster and alters the 2D behavior expected for stoichiometric LiNiO$_2$. (b) Depending on the sign of $J_{\perp}$, the two possible relative spin orientations are sketched.

FIG. 3. Temperature variation of the magnetization for five samples of the Li$_{1-x}$Ni$_{1+x}$O$_2$ family.

FIG. 4. Plot of the in-phase component of $\chi_{ac}$ for the $x = 0.02$, $x = 0.14$ and $x = 0.20$ samples ($f = 10$ kHz, $h_{ac} = 3$ Oe).

FIG. 5. Magnetic moment measured at $T = 4.3$ K and $B = 2$ T as a function of the extra Nickel concentration. Squares represent our experimental data and diamonds are taken from Ref. [3]. The full line corresponds to the maximum saturation $M_s$. The dashed and dotted lines correspond to calculated magnetizations for the different cases of intra-plane exchange interactions as defined in section III: respectively $M_1$ ($J_{\parallel} \geq 0$) and $M_2$ ($J_{\parallel} < 0$).

FIG. 6. A spatial configuration of magnetic Ni ions in Li$_{0.98}$Ni$_{1.02}$O$_2$. Lithium and Oxygen atoms are omitted for clarity. Grey spheres correspond to Ni ions belonging to ferromagnetic clusters, white ones to other Ni ions. In the lower left-hand corner, one can see a cluster containing more than one extra Nickel.

FIG. 7. Reduced magnetization of Li$_{1-x}$Ni$_{1+x}$O$_2$ for $x = 0.02$, 0.14 and 0.2, measured under an external field $B = 5$ T. Full lines and symbols represent respectively experimental and numerical results.

FIG. 8. Magnetic ordering temperature $T_0$, deduced from magnetization curves, as a function of $x$. Open diamonds correspond to numerical results, black circles to experimental ones.

FIG. 9. Reduced magnetization of Li$_{0.86}$Ni$_{1.14}$O$_2$ calculated for an applied field $B = 5$ T, an antiferromagnetic coupling $J_{\perp} = 110$ K, and intra-plane coupling $J_{\parallel} = 1$ K, 0 K, $-1$ K, $-2$ K and $-3$ K.
$J > 0$
$J_\perp > 0$
$J'_\perp < 0$
$J'_\perp < 0$
B=2T

- $x=0.2$
- $x=0.14$
- $x=0.02$
