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Magnetic structure of $Li_{1-x}Ni_{1+x}O_2$

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Abstract. We study the magnetic structure of layered $Li_{1-x}Ni_{1+x}O_2$ and propose a new scheme: the AF interaction between the excess Ni^{2+} in the Li layers and the Ni^{3+} ions in the Ni planes, gives rise to the formation of ferrimagnetic clusters, which control the physics of these systems. The values of the different interactions are estimated from a mean field calculation in the high temperature limit. For the small x samples studied here the method does not yield an accurate value of J_{AF}, but it is very sensitive to the intralayer interactions, allowing to conclude that they are ferromagnetic. The recent proposal of a quantum spin-orbital liquid in this system is discussed and the comparison with Jahn-Teller distorted $NaNiO_2$ is made.

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1 Introduction

The sign and the hierarchy of the magnetic interactions in $Li_{1-x}Ni_{1+x}O_2$ have been the subject of controversy for long, renewed recently by its promising properties for batteries. The system has been considered as a possible quantum spin liquid [1], a 2D frustrated antiferromagnet [2], a weakly coupled 2D Ising ferromagnet [3], a 2D Heisenberg ferromagnet [4], a spin glass [5, 6], as ferromagnetic (F) clusters within a frustrated antiferromagnetic (AF) matrix [7] and more recently, as the physical realisation of a quantum spin-orbital liquid [8-10]. It is now clear that some of these interpretations have been motivated by different samples, as the magnetic properties of $Li_{1-x}Ni_{1+x}O_2$ are extremely sensitive to the preparation conditions. Since this is also crucial for battery capacity, a great effort has been devoted to the synthesis and characterisation of the samples these last years. Therefore we are now in a better position to compare measurements from different groups in order to build a reliable theory.

Here, based on a systematic experimental study performed on carefully characterised samples [11], a new theoretical scheme is proposed: ferrimagnetic clusters are progressively formed and oriented with increasing x concentration. In the small x limit they induce frustration, going against the stabilisation of the long range magnetic order observed in the isomorphic compounds $NaNiO_2$ [12] and $LiFeO_2$ [13].

These materials crystallise in the rhombohedral structure ($R\bar{3}m$ space group). The Li/Ni ordering in the (111) planes of the FCC oxygen lattice leads to the ideal structure of $LiNiO_2$, which can also be described as a packing of NiO_2 slabs built up of edge sharing NiO_6 octahedra. Therefore Ni and Li hexagonal planes alternate [11], see Figure 1. In contrast with $NaNiO_2$ [12], the pure system cannot be synthesised, and extra Ni atoms are always present in the Li planes, leading to the $Li_{1-x}Ni_{1+x}O_2$ composition.

The Ni atoms in the Ni planes, coupled to O $2p$ states, appear as Ni^{3+} with $s = 1/2$ spins, the Li^{1+} atoms are not magnetic. The x Ni ions of the interslab space are divalent, inducing x Ni^{2+} ions with $s = 1$ in the Ni planes.

While the presence of extra Ni^{2+} ions in the lithium planes is well-detected by X-rays (Rietveld refinement method), neutron diffraction experiments performed on the samples that we will consider, showed that there was no Li ions in the Ni^{3+} planes for $x < 0.24$. Therefore for them, we can write the effective formula:

$$[Li^{+}_{1-x}Ni^{2+}_{x}]_{\mathrm{Light}}[Ni^{2+}_{x}Ni^{3+}_{1-x}]_{\mathrm{Heavy}}O_2 \qquad (1)$$

where the subscripts Light and Heavy correspond to the Li and Ni planes respectively.

2 Sign of the magnetic interactions

The signs of the magnetic interactions in $Li_{1-x}Ni_{1+x}O_2$ are very controversial. We have made an analysis considering the Goodenough-Kanamori-Anderson (GKA) rules [14] in order to predict the character of the different couplings and we have later looked for experimental indications of our hypothesis. The application of the GKA rules is simplified in this case by the fact that in both Ni^{3+}

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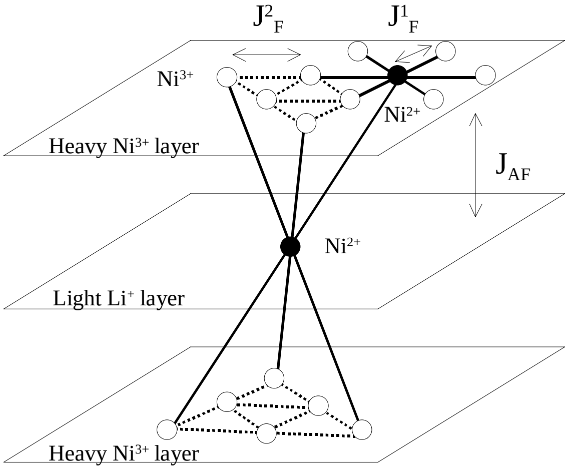

Fig. 1. Cluster model. Each Ni^{2+} in a Li layer correlates ferromagnetically 6 Ni ions (third nearest-neighbours in each plane). For electroneutrality one of them is in a Ni^{2+} state yielding a strong ferromagnetic interaction with the 6 nearest-neighbours Ni^{3+} around it. All Ni ions are in octahedral O environment, omitted for clarity. Interactions considered in the calculations are indicated.

and Ni^{2+} ions, all t_{2g} levels are doubly occupied, therefore there are no virtual excitations involving these orbitals. The first point to remark is that while in the Heavy (H) Ni layers there are only nearly 90° Ni(H)–O–Ni(H) couplings, the presence of Ni^{2+} ions in the Light (L) Li planes introduces straight 180° Ni(L)–O–Ni(H) interactions between layers. Taking this geometry and the relevant orbitals into account, our main conclusions are the following:

1) As shown in Figure 1, each additional Ni^{2+}(L) ion in a Li layer couples with six Ni(H) neighbours in the two adjacent Ni planes ($3 \times 2 = 6$ ions). Due to the 180° angle between the Ni^{3+}(H) and the Ni^{2+}(L) ions connected through the oxygen, the interaction Ni^{2+}(L)–O–Ni^{3+}(H) is AF: since virtual excitations involve the same O $2p$ orbital, the $s = 1/2$ and $s = 1$ spins of those ions will be antiparallel (in the semicovalent approach of Goodenough and Loeb [15], *i.e.* considering the $e_g sp^3$ hybrid in the latter case). Because of the 180° geometry there is also an AF coupling between two Ni^{2+} ions, one in the Li layer and the other induced for electroneutrality in the Ni plane. The AF contribution of the Ni^{2+}(L)–O–Ni^{2+}(H) bonds will be stronger (like in NiO) than that of the Ni^{2+}(L)–O–Ni^{3+}(H) bonds [15], but we will consider just an averaged interaction J_{AF}. This AF interlayer interaction will be later confirmed by the behaviour of the system with increasing Ni concentration x.

2) However, the fact that, in order to relate the two Ni(H) ions in adjacent Ni planes, the interlayer interaction J_{AF} applies twice, *i.e.* Ni^{3+}(H)–O–Ni^{2+}(L)–O–Ni^{3+}(H), makes the resulting coupling between Ni(H) ions in the two Ni planes F. This is in contrast with the case of $\mathrm{NaNiO_2}$, in which this effective coupling through the Na layer is AF.

3) In the Heavy planes, where the nearest neighbour (n.n.) Ni^{3+}(H) ions are connected through the oxygen forming a 90° angle, we cannot derive a conclusion from GKA rules: for this geometry, in which two O $2p$ orbitals are involved, the coupling Ni^{3+}(H)–O–Ni^{3+}(H) will be weaker but can have, in principle, both signs, F or AF. However, Hund's rule acting on the oxygen atom will favour a F interaction, J_{F}^2. Since in neutron experiments F peaks coincide with the lattice peaks, the absence of new magnetic peaks was first interpreted as a sign of spin liquid behaviour [1]. But if the intralayer coupling between Ni(H) sites is F there is no magnetic frustration in the triangular Ni planes. Also in $\mathrm{NaNiO_2}$ the intraplane interactions are F. In this stoichiometric compound the AF interaction between n.n. Ni^{3+}(H) planes, although weak, gives rise to a 3D A-type antiferromagnet, in which Ni(H) spin up and Ni(H) spin down planes alternate [12]. In the $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ compound the distance between adjacent Ni^{3+} planes is even shorter but this AF interaction is overcome by the stronger F interaction induced by the excess Ni^{2+} ions in the Li planes. This indirect frustration effect and the high value of the cluster magnetisation can be reasons to explain the difficulty in observing long range F ordering of the planes in this compound, without the necessity of invoking a spin liquid state. We will later come back to this point.

4) An important fact is the presence of x Ni^{2+}(H) ions in the Ni^{3+} planes, in order to achieve material electroneutrality. In this case, in which the number of electrons of the two Ni(H) ions connected by the 90° oxygen is different, the Ni^{3+}(H)–O–Ni^{2+}(H) F interaction will be stronger, and we will call it J_{F}^1. We will later see that this distinction between J_{F}^1 and J_{F}^2 is necessary to account for the experimental data.

3 Cluster model

Taking into account these interactions we propose now the following picture. As explained before, each Ni^{2+} ion in the Li plane connects ferromagnetically 6 Ni(H) ions in the Heavy planes: 3 on each adjacent Ni layer. Then for $x = 1/6$ homogeneously distributed Ni^{2+}(L) ions all sites are coupled. If we also consider the fact that, each Ni^{2+}(H) ion in the Ni plane has in turn a strong J_{F}^1 interaction with its 6 n.n. Ni^{3+}(H) in the same plane, this number is reduced to the half.

Therefore, at low temperature, there will be an increase of the magnetisation M_{C} following the formation of these ferrimagnetic clusters (indicated with a continuous line in Fig. 1) up to this critical value $x_{\mathrm{c}} = 1/12$, necessary to connect all sites:

$$M_{\mathrm{C}} = 11 x m_{\mathrm{Ni}^{3+}} \qquad \text{for} \qquad x < x_{\mathrm{c}} \tag{2}$$

for which M_{C} attains its maximum value. Instead, for $x > x_{\mathrm{c}}$ a decrease of M_{C} is predicted, due to the J_{AF} correlations of the excess Ni^{2+}(L)–O–Ni^{3+}(H) and Ni^{2+}(L)–O–Ni^{2+}(H) bonds:

$$M_{\mathrm{C}} = (1-x) m_{\mathrm{Ni}^{3+}} \qquad \text{for} \qquad x > x_{\mathrm{c}}. \tag{3}$$

This dependence is in fact experimentally observed and depicted in Figure 2. (For $x > 0.24$ there is a change in

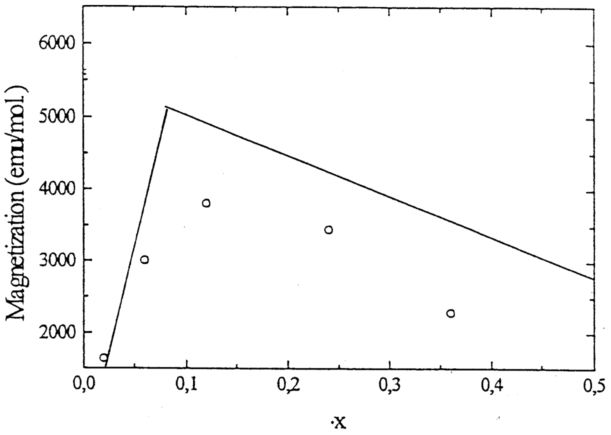

Fig. 2. Cluster magnetisation of the $Li_{1-x}Ni_{1+x}O_2$ family. Open dots: experimental data in an 11 T field at 4.2 K. Straight lines correspond to equations (2, 3).

the chemical structure – Li ions going into the Ni layers – and the model is not valid.) The faster increase of the experimental points probably indicates the polarization of the Ni sites due to the interaction between clusters, not considered in the simple expression given by equations (2, 3). However, the general behaviour is a clear confirmation the effective F coupling between Ni Heavy planes and of the AF nature of the 180° interlayer Ni(L)–O–Ni(H) bonds.

4 Hierarchy of the magnetic interactions

Considering these interactions as dominant and now that we have verified their signs, we can calculate the magnetic susceptibility χ in mean field approximation, in the diluted case (*i.e.* without interaction between clusters). Although a general calculation for all temperatures can be done, the high temperature limit will allow us to determine the magnitude of the different interactions. From the effective formula (Eq. (1)), we can write the molar magnetisation:

$$M_{\mathrm{T}} = (1-x)m_{\mathrm{Ni}^{3+},\mathrm{H}} + x m_{\mathrm{Ni}^{2+},\mathrm{H}} + x m_{\mathrm{Ni}^{2+},\mathrm{L}} \quad (4)$$

with:

$$m_{\mathrm{Ni}^{(i)},H_j} = c_i \frac{H_j}{T} \qquad c_i = \frac{N_A \mu_{\mathrm{B}}^2}{3k_{\mathrm{B}}} g_i^2 J_i(J_i+1) \quad (5)$$

where the local fields are $H_j = H_{\mathrm{H}}$ or H_{L} for the magnetic ions, in the Heavy Ni and Light Li planes respectively. For their calculation we will take into account the J_{F}^1 90° Ni^{2+}(H)–O–Ni^{3+}(H), J_{F}^2 90° Ni^{3+}(H)–O–Ni^{3+}(H) and the J_{AF} 180° Ni^{2+}(L)–O–Ni^{3+}(H) and 180° Ni^{2+}(L)–O–Ni^{2+}(H) interactions. The former will give rise to the average (weighted by the concentration) intralayer F α coupling, and the two last ones to the interlayer AF γ. We find:

$$\begin{aligned} H_{\mathrm{H}} &= H_0 - \gamma x m_{\mathrm{Ni}^{2+},\mathrm{L}} + \alpha x m_{\mathrm{Ni}^{2+},\mathrm{H}} \\ &\quad + \alpha(1-x) m_{\mathrm{Ni}^{3+},\mathrm{H}} \qquad (6) \\ H_{\mathrm{L}} &= H_0 - \gamma x m_{\mathrm{Ni}^{2+},\mathrm{H}} - \gamma(1-x) m_{\mathrm{Ni}^{3+},\mathrm{H}} \qquad (7) \end{aligned}$$

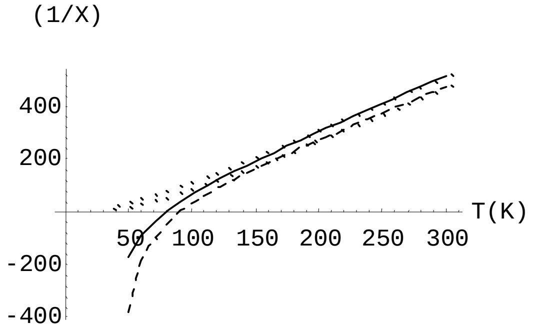

Fig. 3. χ^{-1} *vs.* T for $x_1 = 0.06$ (continuous) and $x_2 = 0.07$ (dashed line) concentrations. Dots: experimental points measured at 1 T. The calculation corresponds to equations (8, 9) and (10), parameters are given in the text.

in this limit the inverse susceptibility is:

$$\chi^{-1} = \frac{M_{\mathrm{T}}}{H_0} \approx T\left[x + \frac{\frac{3}{8}(1+\frac{5}{3}x)(1-x\frac{\gamma}{T})^2}{1-\frac{3}{8T}(1+\frac{5}{3}x)(\alpha + x\frac{\gamma^2}{T})}\right]^{-1} \quad (8)$$

in mol/emu units, where the averaged interactions are:

$$\begin{aligned} \gamma &= -6J_{\mathrm{AF}}\left[x\left(\frac{1-x}{c_{3+}} + \frac{x}{c_{2+}}\right) + 1\frac{x}{c_{2+}}\right]\frac{1}{2x} \\ &= -(11-5x)J_{\mathrm{AF}} \qquad (9) \end{aligned}$$

and distinguishing between J_{F}^1 and J_{F}^2:

$$\begin{aligned} \alpha &= 6\left\{J_{\mathrm{F}}^1\left[x(1-x)\left(\frac{1}{c_{2+}} + \frac{1}{c_{3+}}\right)\right]\right. \\ &\quad \left. + J_{\mathrm{F}}^2\left[\frac{(1-x)^2}{c_{3+}} + \frac{x^2}{c_{2+}}\right]\right\} \\ &= 2[11x(1-x)J_{\mathrm{F}}^1 + (8-16x+11x^2)J_{\mathrm{F}}^2]. \qquad (10) \end{aligned}$$

We point out the F interaction γ^2 induced by the excess x Ni^{2+} ions in the Li planes, which adds to the intraplane F interaction α, in the denominator of equation (8). From the high temperature limit of equation (8) we can determine the slope:

$$S = \frac{\mathrm{d}(\chi^{-1})}{\mathrm{d}T} \qquad \Rightarrow \qquad C_{\mathrm{eff}} = \frac{3+13x}{8} \quad (11)$$

i.e. the Curie constant C_{eff} just depends on the Ni^{2+}(L) concentration x, while the position of the straight line in the χ^{-1} *vs.* T plane is given by the interactions (see Fig. 3). The calculated expressions are only valid when the paramagnetic regime is attained. Although with increasing concentration x the slope S of the curves decreases, the corresponding Curie temperature T_{C} goes up. Fitting the slope for two samples we find: $x_1 = 0.06$ and $x_2 = 0.07$. These values are higher than those determined from initial Rieltveld analysis ($x_1 = 0.03$ and $x_2 = 0.05$), but this can be understood by a partial oxygen loss when heating the samples, which results in an increase of the Ni^{2+} concentration. For $Li_{1-x}Ni_{1+x}O_{2-\delta}$, equation (11) becomes:

$$C'_{\mathrm{eff}} = \frac{3+13x+10\delta}{8} \quad (12)$$

which allows to explain the concentrations derived from the high temperature susceptibility curves by an O deficiency of 3–4%, in agreement with latter thermogravimetric analysis, performed after all measurements.

For the determination of the magnitude of the interactions we have proceeded in the following way. We have first fitted the curves with equation (8), ignoring the different F intraplane interactions, *i.e.* considering $J_{\mathrm{F}}^1 = J_{\mathrm{F}}^2 = J_{\mathrm{F}}$, instead of equation (10). We found that it was not possible to fit correctly the experimental curves with the same parameter values but with $J_{\mathrm{AF}} = -15$ K and $J_{\mathrm{F}} = 11$ K for $x_1 = 0.06$ and $J_{\mathrm{F}} = 14$ K for $x_2 = 0.07$. As we have already mentioned the presence of Ni^{2+} ions in the Ni layers gives rise to strong 90° Ni^{2+}(H)–O–Ni^{3+}(H) F interactions, increasing the average α value with increasing x. Therefore, in order to describe the experimental data, it is necessary to distinguish between the J_{F}^1 and the weaker J_{F}^2 interactions between two Ni(H) ions. We have estimated this last interaction J_{F}^2 from a very diluted sample $x_0 \leq 0.01$ with a Curie-Weiss temperature $T_{\mathrm{C}}^0 \approx 26$ K [16]. Considering that in this case the small amount of Ni^{2+} ions can be neglected and that there is consequently, a weak AF interaction between adjacent Ni^{3+} planes mediated only by two O ions, $J_{\mathrm{AF}}^{'} \approx -2$ K (similar to the case of $\mathrm{NaNiO_2}$, Ref. [12]), we can derive $J_{\mathrm{F}}^2 \approx (T_{\mathrm{C}}^0/3) - J_{\mathrm{AF}}^{'} \approx 10$ K. Taking into account this value and equation (10) for the average α, we can now reproduce both curves with the same parameters $J_{\mathrm{F}}^1 = 30$ K, $J_{\mathrm{F}}^2 = 10$ K, $J_{\mathrm{AF}} = -15$ K as shown in Figure 3. The values obtained for the corresponding Curie temperatures $T_{\mathrm{C}}^{x_i}$ ($T_{\mathrm{C}}^1 = 40$ K and $T_{\mathrm{C}}^2 = 60$ K) are in very good agreement with experiment. The same hierarchy but with a higher J_{F}^1 value was obtained in reference [17] using approximate expressions for the low x concentration limit.

We have made more detailed calculations, distinguishing between the local fields H_{H}^3 and H_{H}^2 for the Ni^{3+}(H) and the Ni^{2+}(H) sites, but the differences in the results are not significant.

Previous mean field analysis by Azzoni *et al.* [18] neglected the Ni^{2+}/Li ratio in the lithium planes and the important difference between the J_{F}^1 and J_{F}^2 interactions. These authors have measured samples with large x concentrations, so comparison can be made only with the most diluted one, $x = 0.08$ in our notation. Although the obtained Curie temperature is higher than ours, suggesting that the paramagnetic regime was not reached (see also curve (c) in Fig. 2 of Ref. [18]), the values derived for the interactions are not very different, particularly for the small interlayer J_{AF} interaction. This is in contrast with the stronger value that they found for larger x samples. This paper had the merit of pointing out the crucial importance of the preparation method on the magnetic properties of the different samples of the $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ compound.

5 Interaction between clusters

When the concentration x increases, the clusters become closer and the fact that we are correlating sites already oriented will tend to increase the critical value x_{c}; we expect this effect not to be important for the cases that we consider. The correlation between clusters will orient larger domains of the sample without the application of a magnetic field, and a net moment must be observed for the critical concentration, even at $H = 0$. In fact, x_{c} can be interpreted as a percolation threshold which means that beyond it one can find at least one ferrimagnetic cluster with an infinite size. Other correlation effects seem not to be important for $x \leq 0.24$, value above which a chemical transition takes place and all the calculation breaks down.

6 Jahn-Teller effect and orbital occupation

$\mathrm{Ni}^{3+}(t_{2g}^6 e_g^1)$ is a well-known Jahn-Teller (JT) ion. This effect will split the two higher levels: for the oxygen tetrahedra elongated along the tetragonal axis the ground state will be $|3z^2 - r^2\rangle$, while for the compressed case it will be $|x^2 - y^2\rangle$. As expected, in the isomorphic compound $\mathrm{NaNiO_2}$ there is a macroscopic collective JT distortion: a uniform elongation is observed and the $|3z^2 - r^2\rangle$ is the lowest energy orbital for all Ni sites (F orbital ordering). In contrast, for $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ the absence of a macroscopic JT effect has been a mystery since its synthesis. However, EXAFS experiments indicate two different O–Ni distances (2 long bonds with $R = 2.09$ Å and 4 short bonds with $R = 1.91$ Å) due to the displacement of the O ions, *i.e.* a local JT effect favouring again the $|3z^2 - r^2\rangle$ state [19]. If this is the case, the orbital structure of $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ becomes similar to that of $\mathrm{NaNiO_2}$ with F orbital ordering and F magnetic intraplane interactions. But while in $\mathrm{NaNiO_2}$ there is a distortion of the triangular Ni lattice, no change of the Ni(H)–Ni(H) distance has been detected in $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ (although a very small one cannot be excluded) [19]. It is true that Na atoms are larger than Li atoms, so in that case ions can move more easily, but this is still a very puzzling problem.

The same result, *i.e.* 2 long O–Ni bonds and 4 short ones, has been derived from X-ray absorption (XAS) measurements [20]. Curiously, a $|x^2-y^2\rangle$ ground state has been found in high frequency electron spin resonance (ESR) experiments [11]. This disagreement must be clarified since this point is crucial to understand the role of the orbital degrees of freedom.

This absence of macroscopic JT effect in $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ has been recently interpreted as an example of a quantum spin orbital liquid. Because this system is more 3-dimensional than $\mathrm{NaNiO_2}$, quantum fluctuations between eventual degenerate ordered classical configurations become important and different orbitals fluctuate in the Ni sites, avoiding the stabilisation of the planar ferromagnetic state [8]. Another proposal [10] is that simply the frustration of the triangular lattice plays a role in preventing a staggered orbital ordering for double degenerate e_g orbitals, so there is a resonating state for the orbital degrees of freedom that yields fluctuating interactions, *i.e.* a quantum spin liquid. However, if both kinds of orbitals are alternatively occupied, the long and the short O-Ni bonds will be present in a different ratio than in the $\mathrm{NaNiO_2}$ case;

present EXAFS results [19] do not show this difference. On the other hand, we would like to point out that even if different e_g orbitals are occupied in $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$, the intraplane interactions between Ni(H) ions mediated by 90° oxygens, will be probably always F, although with different magnitudes. The positive values of the Curie temperature, even for the most diluted samples, seem to confirm this predominance of F interactions within the triangular Ni planes.

We believe that it is the frustration induced by the clusters, *i.e.* the strong effective F interaction (*via* the Ni^{2+} ions always present in the Li planes) competing with the AF interaction (*via* two oxygen ions when there is no Ni^{2+}(L) ion in the Li plane) between adjacent Ni planes, which goes against the long range magnetic ordering. While in NaNiO_2 this second interaction drives the AF stacking of the F Ni planes, in $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ it can be neglected compared to the strong effective F one. However, even if an orbital liquid is not necessary to explain why this system does not show magnetic order, we cannot exclude this state, since we still have no explanation for the non observation of a macroscopic JT effect.

7 Discussion

The intraplane interactions (J_F^1 and J_F^2) are ferromagnetic, they do not induce magnetic frustration in the triangular Ni lattice, therefore $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$ is not a quantum spin liquid, as it was proposed in reference [1]. The interplane interaction between Ni^{2+} ions in the Li planes and Ni^{3+} (or Ni^{2+}) ions in the heavy planes are AF in agreement with GKA rules and the measured M_C *vs.* x dependence (Eqs. (2, 3), Fig. 2). However these J_AF interactions yield an effective F coupling for the Ni(H) ions in adjacent Ni planes. The ferrimagnetic clusters formed in this way control the physics of this compound.

All these couplings have been incorporated in a cluster model which, treated in mean field approximation, allowed us to derive the magnitude of the magnetic interactions. The value of the interplane $J_\mathrm{AF} \approx -15$ K is significantly weaker than the interaction found in NiO [21]. Azzoni *et al.* [18] proposed that in the diluted regime this interlayer interaction is quenched by the diamagnetic Li layer. It would be important to have data in the paramagnetic regime for samples with higher x concentration, in order to precise the value of J_AF. In contrast, the curves are very sensitive to the intralayer interactions, which appear to be clearly ferromagnetic. The value of $J_\mathrm{F}^2 \approx 10$ K is in agreement with GKA predictions and $J_\mathrm{F}^1 \approx 30$ K much larger than J_F^2 is expected from the different number of electrons of connected Ni(H) ions in the same plane. Therefore, within this dilute limit, we can conclude:

$$|J_\mathrm{F}^1| > |J_\mathrm{AF}| > |J_\mathrm{F}^2|. \qquad (13)$$

We have tested that more detailed calculations do not change these results, and we believe that interactions between clusters do not modify this picture. This basic treatment of the problem conciliates the expected signs of the couplings with the observed magnetic behaviour. It remains the interesting question why the stoichiometric compound cannot be obtained.

We have recently performed magnetic measurements on a very pure compound ($x \leq 0.01$) [16] showing striking analogies with NaNiO_2. This questions the recent interpretation attributing to orbital disorder the absence of long range magnetic order in $\mathrm{Li}_{1-x}\mathrm{Ni}_{1+x}\mathrm{O}_2$, because this isomorphic compound orders below 20 K. However, it would be worthwhile to repeat EXAFS and ESR experiments on new improved samples in order to establish or rule out the realisation of an orbital liquid in this compound.

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