Interlayer magnetic frustration in quasistoichiometric Li$_{1-x}$Ni$_{1+x}$O$_2$

E. Chappel, M. D. Núñez-Regueiro,* S. de Brion, and G. Chouteau

Grenoble High Magnetic Field Laboratory, MPI-FKF and CNRS, B.P. 166, 38042 Grenoble Cedex 9, France

V. Bianchi, D. Caurant, and N. Baffier

Laboratoire de Chimie Appliquée de l'Etat Solide, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 5, France

Susceptibility, high-field magnetization, and submillimeter-wave electron spin resonance measurements of layered quasistoichiometric Li$_{1-x}$Ni$_{1+x}$O$_2$ are reported and compared to isomorphic NaNiO$_2$. A mechanism of magnetic frustration induced by the excess Ni ions always present in the Li layers is proposed. We finally comment on the possible realization of an orbital liquid state in this controversial compound.

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Since its synthesis in 1958 by Goodenough *et al.*,[1] LiNiO$_2$ is a subject of continuous debate. Its ideal structure can be described as a packing of Li and NiO$_2$ slabs built up of edge sharing NiO$_6$ octahedra. Therefore, magnetic Ni^{3+} and nonmagnetic Li hexagonal planes alternate along the ⟨111⟩ direction, giving rise to a quasi-two-dimensional (quasi-2D) magnetic lattice. Detailed chemistry analysis of this compound has been motivated by its potential application in rechargeable batteries; this allowed us to overcome the initial disagreement between results from different groups due to the sensitivity of the physical properties to the sample preparation method. On the other hand, theoretical interest in this system comes from the interplay between different degrees of freedom: twofold orbital degeneracy of the Ni^{3+} ($t_{2g}^6 e_g^1$) ions and their eventual coupling to the $S=1/2$ spins, the effect of frustration in the triangular Ni lattice, and the elusive nature of the magnetic interactions. In spite of numerous studies and significant progress on these subjects,[2] the puzzling absence of both orbital and magnetic ordering, indeed clearly observed in isomorphic NaNiO$_2$,[3,4] remains a mystery. More recently, LiNiO$_2$ has been considered as the first realization of a quantum spin orbital liquid.[5–8]

Here we report measurements on well-characterized homogeneous Li$_{1-x}$Ni$_{1+x}$O$_2$. We study three samples, one of them being, to our knowledge, the closest one to stoichiometry reported up to now, and we compare their behavior to NaNiO$_2$. The overall results agree with a recent theoretical development[9] concerning the decoupling of the orbital and spin degrees of freedom, particular to these frustrated Jahn-Teller (JT) systems, and the always ferromagnetic (FM) sign of the intralayer Ni-Ni magnetic interactions. They also confirm the cluster model that we have proposed[10] to describe the dependence on the concentration x of different properties. Furthermore, we can conclude that most probably stoichiometric LiNiO$_2$ does not exist and that the clusters formed around the excess Ni^{2+} ions on Li planes are responsible for the peculiar behavior of this system. In fact, when the intrinsic weak antiferromagnetic (AF) interaction between adjacent Ni^{3+} layers, neglected in previous theoretical works,[9,10] is taken into account, the effective FM coupling induced by those clusters frustrates the AF stacking of the FM Ni planes, hindering the long-range 3D magnetic ordering observed in NaNiO$_2$ below 20 K.[3]

A detailed description of the synthesis conditions and of the structural characterization of our NaNiO$_2$ and [Li$_{1-x}^{1+}$Ni$_x^{2+}$][Ni$_x^{2+}$Ni$_{1-x}^{3+}$]O$_2$ samples has been given elsewhere.[3,11] The amount of extra Ni ions was determined by Rietveld refinement: $x=0.004$, 0.016, and 0.060 (± 0.002) in the latter system. The magnetic susceptibility measurements were performed on a superconducting quantum interference device (SQUID) magnetometer under 1 mT field, between 2 and 300 K, using pressed pellets. High magnetic fields up to 23 T were obtained using resistive magnets. Electron spin resonance (ESR) measurements were carried out at different frequencies and temperatures, using Gunn oscillators and Carcinotrons. The magnetic field (up to 12 T) was produced by a superconducting magnet.

Figure 1 reports the temperature dependence of the susceptibility M/H at 1 mT, showing the high quality of our Li$_{1-x}$Ni$_{1+x}$O$_2$ sample, $x=0.004$. The curve presents a cusp around $T_\chi=7.5$ K when heating after zero-field cooling (ZFC), whereas on field cooling (FC) M/H remains almost constant below T_χ. This is a typical spin-glass-like behavior.
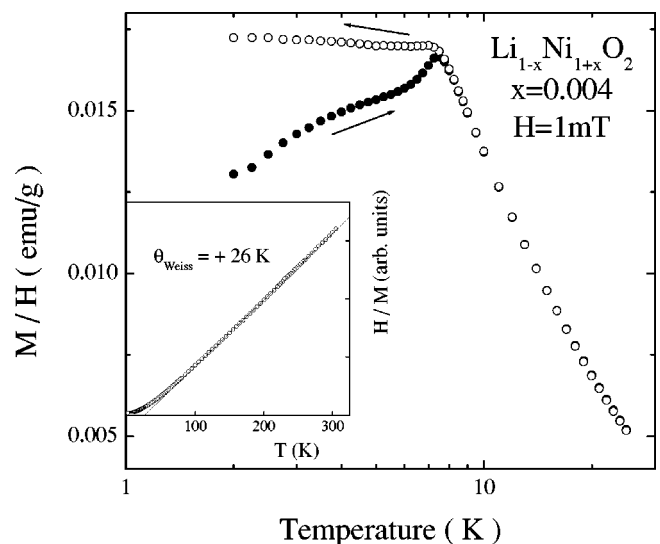

FIG. 1. Temperature dependence of M/H at 1 mT for Li$_{1-x}$Ni$_{1+x}$O$_2$, $x=0.004$. The open and solid circles correspond to measurements on FC and ZFC, respectively. Inset: H/M vs T at 1 mT for the same sample; the solid line shows the Curie-Weiss law.
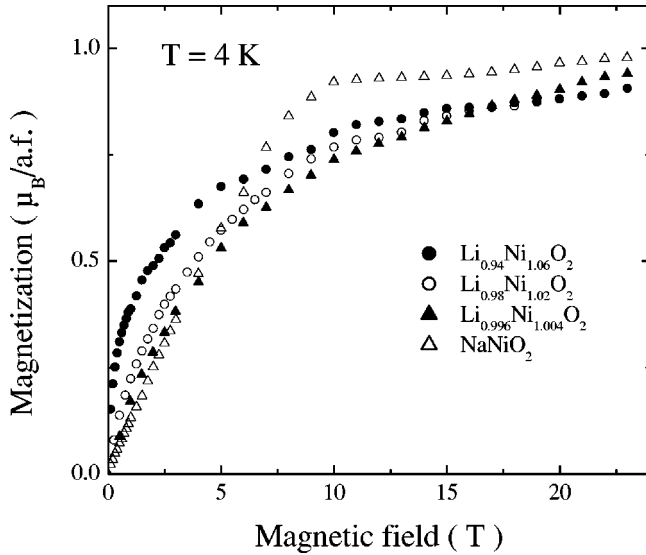
FIG. 2. Magnetization up to 23 T of $NaNiO_2$ and various quasistoichiometric $Li_{1-x}Ni_{1+x}O_2$ samples at 4 K.

FIG. 3. Low-temperature frequency dependence of the ESR spectrum width for $NaNiO_2$ (triangles) and $Li_{1-x}Ni_{1+x}O_2$, $x=0.004$ (circles), corresponding to the features A-B and A-C. Insets: typical spectra.

The inverse susceptibility H/M, shown in the inset of Fig. 1, can be fitted with a Curie-Weiss law between 70 and 300 K, with an effective moment $\mu_{eff}=2\mu_B$ and a Weiss temperature $\theta=+26$ K. These results are similar to those of Yamaura *et al.*[12] with $T_\chi=8.5$ K, $\mu_{eff}=1.91\mu_B$, and $\theta=+29.5$ K. The positive sign of θ indicates the predominance of FM interactions and the effective moment corresponds unambiguously to the low-spin state $(t_{2g}^6 e_g^1)$ of Ni^{3+} with $S=1/2$. It is interesting to point out that the most stoichiometric sample has the lowest Weiss temperature, the linear dependence of $\theta(x)$ for $x\rightarrow0$, making precise the concentration determined from Rietveld analysis.[11] This allows us to say that our $x\simeq0.004$ sample is the most diluted reported to date. The existence of a well-defined susceptibility peak is an indication of the homogeneity of the sample. Besides, if the Ni^{2+} ions were not distributed at random in the Li layers, this would lead to the formation of ferrimagnetic domains around them and to an additional anomaly at ~240 K in the susceptibility (only for mT fields), as clearly explained in Ref. 13.

Figure 2 shows the magnetization at 4 K of $NaNiO_2$ and $Li_{1-x}Ni_{1+x}O_2$ samples. The low-field curvature, the signature of ferrimagnetic clusters, vanishes when $x\rightarrow0$, approaching the linear behavior observed[3] for the A-type antiferromagnet $NaNiO_2$. For this compound, the saturation is reached at 10 T and the moment $1\mu_B/Ni$ agrees again with the low spin state of Ni^{3+}. For the $Li_{1-x}Ni_{1+x}O_2$ samples the saturation is almost achieved at 23 T and tends to $M_{sat}=(1-x)\mu(Ni^{3+})$.[10] The Ni^{2+} moments do not contribute in the latter formula since they are still AF coupled with almost zero magnetization, even at 23 T, following the Goodenough-Kanamori-Anderson (GKA) rules (Ni^{2+}-O-Ni^{3+} form 180° bonds). The high-field dependence of the magnetization of $Li_{1-x}Ni_{1+x}O_2$ samples confirms the presence of extra AF interactions, compared to $NaNiO_2$. Thus, the evolution of the magnetization curve with concentration x comes from ferrimagnetic clusters, created by these
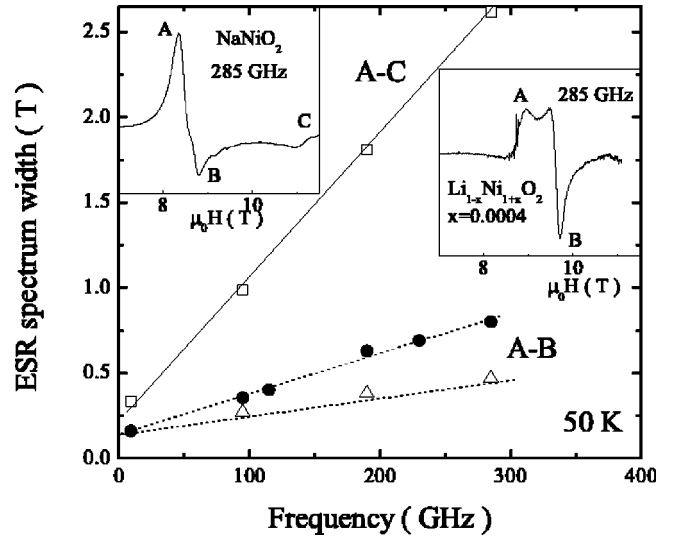
extra Ni^{2+} ions inducing AF couplings. Also the Arrot's plots at various temperatures in Ref. 11 are typical of an AF like $NaNiO_2$. In fact, the small number of clusters for this x cannot explain by itself such macroscopic AF behavior, strongly suggesting that, also in this case, there is an intrinsic weak AF interaction between adjacent Ni layers, ~1 K in $NaNiO_2$.[3]

Two different ESR studies have been already performed on diluted $Li_{1-x}Ni_{1+x}O_2$. As is well known, the main contribution to the ESR signal comes from the Ni^{3+} ions. Ohta *et al.*,[14] by measurements between 1.8 and 256 K, up to 370 GHz with pulsed magnetic fields, have shown the existence of two lines, already present at 86 K, which split progressively with further cooling. At 1.8 K, the frequency versus magnetic field diagram suggested the existence of an internal field, since the extrapolated lines did not cross the origin. Barra *et al.*[15] have performed similar ESR measurements at 73 and 246 GHz, interpreting the splitting of these two lines, observed below 130 K, in terms of anisotropic g factors with $g_\perp<g_\parallel$. Then, they proposed a dynamical JT effect of the Ni^{3+} ions, which becomes static below 130 K. Since $g_\perp<g_\parallel$, the occupied orbital should be $|d_{x^2-y^2}\rangle$, in contradiction with the extended x-ray absorption fine structure (EXAFS) study by Rougier *et al.*[16] In fact, these authors have shown the existence of elongated octahedra at 300 K, i.e., a local JT effect, favoring the occupation of the $|d_{3z^2-r^2}\rangle$ orbital. In isomorphic $NaNiO_2$ this orbital occupation has indeed been observed. In order to clarify this point we have undertaken a complete ESR study of the most stoichiometric sample which we compare with $NaNiO_2$, up to 285 GHz at various temperatures. Typical low-temperature spectra are shown in the inset of Fig. 3. In both systems the signal A-B is anisotropic with the splitting discussed above: this effect can be correlated with the deviation from the Curie-Weiss law, observed below ~70 K for both systems (inset Fig. 1 and Ref. 3), suggesting a magnetic origin. In contrast, the C
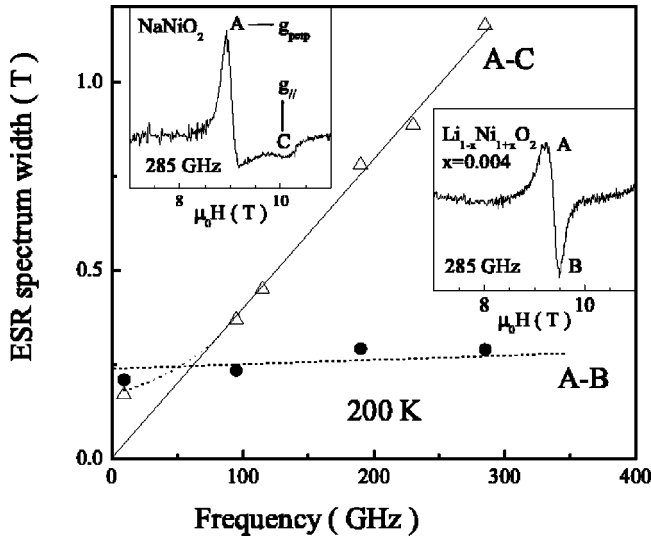
FIG. 4. Same as Fig. 3 at high temperature. Solid line: g anisotropy. Dashed line: intrinsic linewidths. Insets: typical spectra.

feature is only observed in $NaNiO_2$.

Figure 4 shows the same as Fig. 3 at $T = 200$ K, a temperature half lower than the temperature at which the JT distortion takes place for $NaNiO_2$ ($T_{JT} \simeq 480$ K). Even at the high frequencies (230–285 GHz) necessary to clearly separate the two g components in $NaNiO_2$ (features A and C), there is now a single line (feature A-B) for $Li_{1-x}Ni_{1+x}O_2$, yielding $g = 2.17$, and we do not see any splitting.

In $Li_{1-x}Ni_{1+x}O_2$ there are only 90° Ni-O-Ni paths within the same plane, while Ni^{2+} ions in the Li planes introduce 180° Ni-O-Ni bonds. Considering the GKA rules and fitting the high-temperature susceptibility as a function of the concentration x by a mean-field approach, we have shown[10] that the intralayer interactions are FM and the Ni-O-Ni couplings induced by the extra Ni^{2+} in Li layers are AF. Moreover, in order to obtain a good description of the whole data, it was necessary to take into account that the intralayer Ni^{3+}-O-Ni^{2+} (Ni^{2+} ions in the Ni^{3+} layers due to charge compensation) coupling J_{F1} is stronger than the Ni^{3+}-O-Ni^{3+} J_{F2} one, though ferrimagnetic clusters are formed: each Ni^{2+} ion in the Li plane connects six FM Ni ions (since the AF 180° Ni-O-Ni coupling applies twice), i.e., three in each of the two adjacent Ni layers. If also we consider the FM J_{F1} between Ni^{2+} and Ni^{3+} in the same Ni layer, then for $x = 1/12$ homogeneously distributed excess Ni^{2+} ions, all sites are coupled. This percolation threshold appears to be in agreement with experiments (see Fig. 2 in Ref. 10).

Since both intralayer interactions are FM, frustrated AF models in the triangular Ni layer, yielding a spin liquid,[17–19] are inappropriate for this system. Other works[5–8,20] proposed $LiNiO_2$ as an example of a quantum orbital spin liquid to explain both the absence of magnetic and orbital ordering. All these models assume a strong coupling between the orbital and spin degrees of freedom [so-called Kugel-Khomskii (KK) systems[21]]. Surprisingly, no author comments on the EXAFS results by Rougier *et al.*[16] showing the existence of two different Ni-O distances in quasistoichiometric
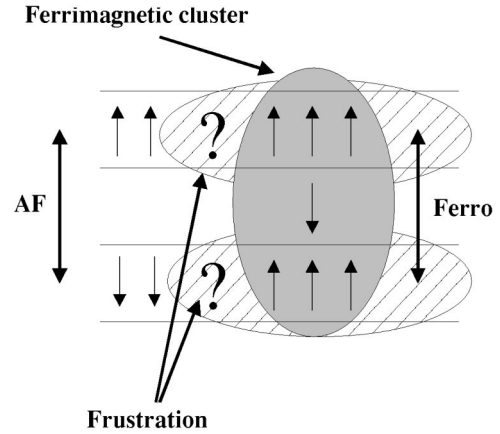

FIG. 5. Sketch of the magnetic frustration mechanism proposed here for quasistoichiometric $Li_{1-x}Ni_{1+x}O_2$. The effective FM interplane coupling, induced by extra Ni ions in the Li planes, hides the macroscopic magnetic ordering of $NaNiO_2$, which is driven by the weak AF interplane interaction.

$Li_{1-x}Ni_{1+x}O_2$, with four short and two long Ni-O bonds, as in $NaNiO_2$. Even if there is no macroscopic structural transition, this elongation of the NiO_6 octahedra occurs even at room temperature, and the local JT effect of the Ni^{3+} ions appears as the relevant process for the breakdown of orbital degeneracy. The KK rules concern cubic lattices with 180° bonds, and conclusions for these frustrated JT systems are different.[9] In fact, as we have first pointed out,[10] at 90° and independently of the orbital e_g occupation, the intralayer magnetic Ni-Ni coupling is always FM.

According to the experimental results and theoretical considerations discussed above, we propose here a new mechanism of magnetic frustration in diluted $Li_{1-x}Ni_{1+x}O_2$. The pure compound $LiNiO_2$, if it exists, would have the magnetic structure of $NaNiO_2$. The magnetization, susceptibility, and ESR measurements clearly show that the magnetic properties of $Li_{1-x}Ni_{1+x}O_2$ approach those of $NaNiO_2$ when the excess Ni concentration $x \rightarrow 0$. At low temperature, the weak AF interplane Ni-O-Li-O-Ni interaction of the $NaNiO_2$ type[3] should lead to an AF macrocopic order (AF alternation of adjacent FM Ni planes), in agreement with Arrott's plots and magnetization curves. However, it seems that the smaller size of the Li ions does not allow perfect stacking of the Na-Ni layers and that a Ni concentration of $x \neq 0$ always goes into the Li layers, inducing effective interplane Ni-Ni local FM couplings. Such competition of interactions leads to magnetic frustration, prevents the stabilization of long-range ordering, and explains the spin-glass behavior observed in quasistoichiometric $Li_{1-x}Ni_{1+x}O_2$ at low temperature, without the necessity of evoking a spin-liquid state. Figure 5 shows a sketch of this frustration mechanism. Assuming that spins around a cluster turn progressively like a magnetic wall, to finally adopt the AF stacking of $NaNiO_2$, an estimation of the number of perturbed spins by each additional Ni ion can be made. To simplify, in the case of a uniaxial crystal, the characteristic wall length is written

$$\delta_0 = a \sqrt{\frac{8H_E}{3H_A}}, \tag{1}$$

where a is the cell parameter, and H_E and H_A are the exchange and anisotropic fields, respectively.[22] Taking the characteristic field values obtained[3] for $NaNiO_2$ yields $\delta_0 = 6a$. In our hexagonal symmetry, up to sixth-neighbor spins are perturbed, i.e., ~ 60 spins per cluster. Therefore, less than 1% of excess Ni in the Li planes can induce complete magnetic disorder in $Li_{1-x}Ni_{1+x}O_2$.

EXAFS data indicate a JT elongation of the NiO_6 octahedra,[16] but this effect remains local: there is no macroscopic structural transition. It is noteworthy that the single ESR line at 200 K is not necessary in contradiction with EXAFS. For instance, a configuration with elongated octahedra in orthogonal directions $|d_{3z^2-r^2}\rangle$, $|d_{3x^2-r^2}\rangle$, and $|d_{3y^2-r^2}\rangle$ could explain both data. On the other hand, recent theoretical work[9] proposed that the high degeneracy of mean-field orbital ground state in the frustrated Ni lattice is lifted by quantum orbital fluctuations (Villain's order by disorder), which select particular ferro-orbital states, as observed in $NaNiO_2$. Then a weaker electron-lattice coupling, not enough for the stabilization of that ferro-orbital state, or even stronger orbital fluctuations going against it were invoked to explain the absence of a cooperative JT effect in $LiNiO_2$.

Finally, we would like to point out that the susceptibility anomaly at $T_{of} \simeq 400$ K reported by Reynaud et al.,[20] below which they claim that an orbitally frustrated state is established, is very weak and within experimental error ($\Delta\chi \sim 3$ $\times 10^{-5}$ cm^3/mol). Therefore, up to now, only the absence of a macroscopic structural distortion and the isotropic shape of the ESR line (Fig. 4) have been indications of this puzzling orbital state. Orbitals are much more difficult to measure than spins, and it will be a delicate task to distinguish between ordered chains in orthogonal directions, disordered or fluctuating orbitals. In any case this will not influence the magnetic behavior, which can be independently explained by the new frustration mechanism of Fig. 5. Small angle neutron measurements are in progress, in order to "see" these ferrimagnetic clusters.

In conclusion, from low and high magnetic field and ESR measurements on homogeneous quasistoichiometric $Li_{1-x}Ni_{1+x}O_2$, we have shown that the extra Ni ions always present in the Li planes induce magnetic frustration in the low-x limit, and this can explain the unusual magnetic properties. The splitting of the ESR lines below the temperature at which the susceptibility deviates from the Curie-Weiss law strongly suggests a magnetic origin. Instead, the single ESR line above this temperature, together with EXAFS data, indicates a peculiar orbital occupation with elongated octahedra.

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*Electronic address: nunezreg@polycnrs-gre.fr

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