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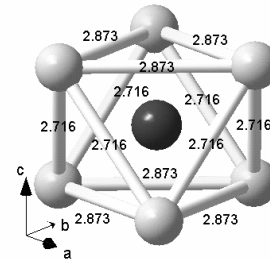
Decoupling of orbital and spin degrees of freedom in $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$ M. Holzapfel¹, S. de Brion, C. Darie², P. Bordet², G. Chouteau¹, P. Strobel², A. Sulpice³ and M. D. Núñez-Regueiro⁴¹*Grenoble High Field Magnetic Laboratory,
CNRS and MPI-FKF, BP 166, 38042 Grenoble, France*²*Laboratoire de Cristallographie, CNRS,
BP 166, 38042 Grenoble, France*³*Centre de Recherche sur les Très Basses Températures,
CNRS, BP 166, 38042 Grenoble, France*⁴*Laboratoire de Physique des Solides, Bâtiment 510,
Université Paris-Sud, 91405 Orsay, France*

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In the $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$ solid solutions three different single phase regions exist: for $x \geq 0.9$, for $x \approx 0.7$ and for $x \leq 0.3$. Although the intermediate compound does not show the cooperative Jahn-Teller transition of NaNiO_2 , its magnetic properties remain very similar with, in particular, the low temperature 3D magnetic ordering. Therefore, the strong coupling between orbital and spin degrees of freedom, characteristic of other oxides like perovskites, and usually invoked to explain the absence of both long-range orbital and magnetic ordering in LiNiO_2 , seems not to take place in these layered compounds with $\sim 90^\circ$ bonds. We also discuss the relevance of the O crystal field splitting induced by the trigonal distortion, in generating AFM Ni-Ni in-plane interactions.

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The interplay between orbital and spin degrees of freedom in transition metal (TM) oxides can yield very peculiar magnetic structures and so is a subject under active research [1]. In this context, the absence of both long-range magnetic and orbital ordering in layered LiNiO_2 , indeed clearly observed in isomorphous NaNiO_2 [2, 3, 4], is especially puzzling. Although, recently there have been several attempts to explain these curious different behaviours, the situation is still unsettled. Particularly, several models [5, 6, 7, 8, 9] assume an important coupling between the spin and orbital states, considering that frustration or the particular orbital ordering in the triangular lattice of LiNiO_2 inhibits the stabilization of the 3D magnetic ordering of NaNiO_2 . Here, the synthesis and study of intermediate $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$ compounds shows the contrary: the macroscopic Jahn-Teller (JT) transition observed in NaNiO_2 can be killed by a small amount of Li replacing Na ions, keeping however very similar magnetic properties. Our experimental observations support previous analysis [10] and recent theoretical calculations [11] showing that the physics of frustrated JT systems with 90° TM-O-TM bonds is different from those in materials with 180° bonds. Though usually ignored the different bond angle has important consequences: in contrast to the strong coupling in perovskites, in these $\sim 90^\circ$ systems orbitals and spins are essentially decoupled. Departure from the ideal 90° angle, contribution from other overlaps or crystal field splitting effects have been invoked [9, 12] to re-introduce the coupling between spins and orbitals in these systems, but the results reported here indicate that those hypothesis do not change this property.

The α - NaFeO_2 structure of LiNiO_2 contains planes ofFIG. 1: the trigonal distorted NiO_6 octahedra with O-O distances.

magnetic Ni ions arranged in a triangular network. The Ni^{3+} ions are in the low spin electronic configuration ($t_{2g}^6 e_g^1$) with a spin 1/2 on the doubly degenerate e_g level. Following the Goodenough-Kanamori-Anderson (GKA) rules, one finds only ferromagnetic (FM) spin exchange couplings between nearest-neighbour Ni ions in the same plane. However, it has been recently been pointed out [12] that the trigonal crystal field splitting of the $\text{O}2p$ orbitals (Fig.1), due to the alternating Li and Ni planes, could be significant, leading to the possibility of having also antiferromagnetic (AFM) exchange integrals in the Ni planes, in deviation from the GKA rules for these nearly 90° bonds. That would give a microscopic foundation for the coexistence of intra-layer FM and AFM couplings in LiNiO_2 , as considered by some authors [9, 13], inhibiting the initially expected AFM stacking of FM Ni planes of NaNiO_2 .

On the other hand, isostructural NaNiO_2 undergoes a cooperative JT ordering of the Ni^{3+} ions at 480K reducing its symmetry from rhombohedral to monoclinic. It has been then speculated that the different oxygen crystal

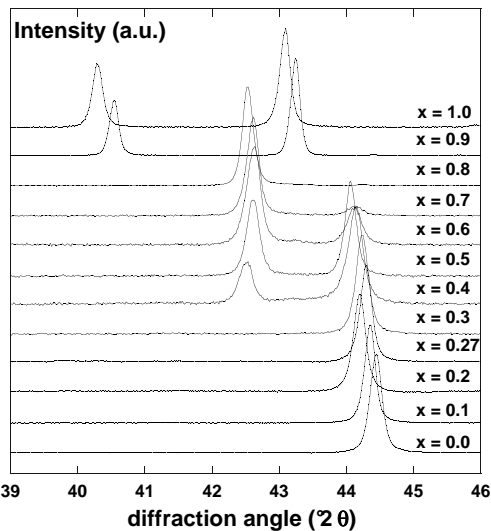


FIG. 2: x-ray diffractograms as a function of the nominal composition $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$.

field splitting would lead to the absence of these AFM in plane Ni-Ni interactions in the low-temperature phase of NaNiO_2 , yielding its different magnetic properties [12].

So in order to test the interplay between orbital and spin degrees of freedom, we perform here a detailed crystallographic and magnetic study of LiNiO_2 , NaNiO_2 and the new $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$ compound [14]. The interesting point is that samples with this intermediate composition do not undergo the JT transition of NaNiO_2 , but keep a rhombohedral structure like LiNiO_2 even at low temperature. The measurement of the trigonal distortion in these 3 compounds will also allow us to discuss the above argument, concerning its relevance in generating in-plane AFM interactions in LiNiO_2 , which in turn would inhibit the magnetic ordering [12].

The products were obtained by classical high-temperature solid-state reaction. They were synthesized from Na_2O_2 , NiO and $\text{LiOH}\cdot\text{H}_2\text{O}$. The starting materials were mixed in an argon atmosphere with a 10% excess of $(\text{Na}+\text{Li})$ to account for volatilisation losses. The mixture was heated under flowing oxygen at 680°C for 24h. Twelve samples with compositions $(\text{Li}_{1-x}\text{Na}_x)\text{NiO}_2$ with $0 \leq x \leq 1$ (x denotes the nominal Na content) were prepared. Their cationic compositions were analyzed by atomic absorption spectroscopy. The crystal structure was studied by x-ray powder diffraction (XPD). In order to detect possible magnetic ordering, neutron powder diffraction (NPD) data were collected down to 1.5K on the CRG-D1B instrument of the ILL. The x-ray and neutron diffractograms were refined by Rietveld technique using the WinPlotR suite [15].

It is not possible to synthesize single phase samples for arbitrary Li/Na ratio. As shown in Fig.2 and already

TABLE I: room temperature crystallographic and low temperature magnetic parameters for the three phases.

	LiNiO_2	$\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$	NaNiO_2
space group	R $\bar{3}m$	R $\bar{3}m$	C2/m
cell param.	a=2.8727(3) c=14.184(2)	a=2.9410(1) c=15.4082(1)	a=5.3208(3) b=2.8440(2) c=5.5818(4) $\beta=110.49(1)$
Na content	0.009(3)	0.698(4)	1.0
positional parameters	x(O)=0.24248(8)	x(O)=0.2324(2)	x(O)=0.282(2) z(O)=0.799(2)
R_{wp}, R_{Bragg}	3.91, 7.28	3.24, 6.6	3.78, 8.11
Ni-O (Å)	6x1.977	6x1.977	4x1.93, 2x2.17
O-O (Å)	6x2.716 6x2.873	6x2.644 6x2.941	4x3.02, 2x2.84 4x2.78, 2x2.60
O-Ni-O (°)	6x93.2 6x86.8	6x96.1 6x83.9	4x94.8, 2x95.1 4x85.2, 2x84.9
T_{CW}	+26K	+40K	+36K
T_N or T_{SG}	9K	25K	20K
H_{C0} at 4K		0.05T	1.8T
H_{C1}		5T	7T
H_{sat}	>23T	19T	13T
H_E		9.5T	6.5T
H_A		0.2mT	250mT

reported by Matsumura et al.[14], the $\text{LiNiO}_2/\text{NaNiO}_2$ phase diagram contains three different single phase solid solution regions, in between which, two phase mixtures are observed. For $x \leq 0.3$, the R $\bar{3}m$ α - NaFeO_2 structure type of LiNiO_2 is found (RII phase), where Li, Ni and O atoms occupy the 3a (0 0 0), 3b (0 0 1/2) and 6c (0 0 $z \approx 0.24$) positions, respectively. For $x \geq 0.9$, the monoclinic C2/m phase of NaNiO_2 is observed, with substitution of Li^+ for Na^+ ions. In this phase, the Na, Ni and O atoms occupy the 2d (0 1/2 1/2), 2a (0 0 0) and 4i ($x \approx 0.28$ 0 $z \approx 0.8$) positions. In a small domain about $x \approx 0.8$, a new rhombohedral phase (RI phase) is obtained, which has the same structural arrangement as LiNiO_2 , but quite different cell parameters: the c/a ratio is ≈ 5.24 instead of ≈ 4.94 for LiNiO_2 . The exact cationic composition of this phase found both by Rietveld refinement of the x-ray data and atomic absorption is $\text{Li}_{0.30(1)}\text{Na}_{0.70(1)}$. The Bragg reflexion widths are roughly the same throughout the whole composition range (Fig.2), which indicates a good sample homogeneity in the single phase regions. Neither magnetic diffraction peak and nor structural phase transition could be detected by NPD for $(\text{Li}_{0.3}\text{Na}_{0.7})\text{NiO}_2$ down to 1.5K. Therefore, this phase remains rhombohedral in this temperature range and does not undergo a cooperative JT ordering. In this respect, it behaves like LiNiO_2 rather than like NaNiO_2 .

To understand better the magnetism of these compounds, it is interesting to compare the structural arrangements of the NiO_2 octahedral layers. The R $\bar{3}m$ LiNiO_2 structure can be described by starting from the

F-centered cubic NiO structure and replacing every other Ni plane perpendicular to one of the 3-fold axes by a Li plane, forming NiO₂ edge-shared octahedral layers separated by Li⁺ cations planes. This is accompanied by a trigonal distortion of the NiO₆ octahedra brought about by the difference of charge and size between Li⁺ and Ni³⁺ cations. These octahedra are compressed along the c axis as shown in Fig.1. The six Ni-O distances remain equal ($\approx 1.98\text{\AA}$), but the six O-O distances perpendicular to the c-axis ($\approx 2.87\text{\AA}$) (which link oxygen anions from the plane above or below the Ni cation) become larger than the six other ones ($\approx 2.72\text{\AA}$) (which link one oxygen anion from the plane above to one from the plane below). At the same time, the O-Ni-O angles between oxygen anions from the same plane above or below the Ni cation opens to 93.2° , while the ones between oxygen anions from the two planes close down to 86.8° . This distortion can be characterized by the ratio between the two classes of O-O bonds, and is 0.945 for LiNiO₂.

Although the structural arrangement is the same for (Li_{0.3}Na_{0.7})NiO₂, the interatomic distances and angles are markedly modified because of the steric effect due to the large size difference between Na⁺ and Li⁺ cations (ionic radius=1.02Å and 0.76Å). Due to charge balance, the 6 Ni-O distances are almost unchanged (1.98Å), but the two O-O distances and angles defined above become $\approx 2.94\text{\AA}$, 2.64\AA , 96.1° and 83.9° , respectively. The O-O distance ratio thus becomes 0.899, indicating a much stronger trigonal distortion than for LiNiO₂.

Very similar Ni-O and O-O distances and O-Ni-O angles can be calculated in the isostructural high temperature form of NaNiO₂ from the NPD data of Chappel et al. [4] (at 565K: Ni-O : 6x1.98Å; O-O : 6x2.96Å, 6x2.63Å, ratio =0.899 ; O-Ni-O : 6x96.8°, 6x83.2°). At room temperature, in the monoclinic phase, the NiO₆ octahedra become JT distorted: 4 Ni-O distances become shorter (1.93Å) and 2 longer (2.17Å). The 6 O-O distances in the plane above or below the Ni cation become 4x3.02Å and 2x2.84Å (average 2.96(0.1)Å), the 6 other ones become 4x2.78Å and 2x2.60Å (average 2.72(0.1)Å). The O-Ni-O angles between oxygens of the same (above or below) plane are 4x94.8° and 2x95.1°, and between oxygens of different planes are 4x85.2° and 2x84.9°. The ratio of the average O-O distances given above can still be used to evaluate the trigonal distortion: one finds 0.919. By comparing these values with those of (Li_{0.3}Na_{0.7})NiO₂, one can conclude that in monoclinic NaNiO₂, the JT distortion is superimposed on the trigonal one without markedly changing the amplitude of the latter.

Having in mind that NaNiO₂ undergoes a collective JT transition, while LiNiO₂ as well as Li_{0.3}Na_{0.7}NiO₂ do not, we perform now a comparative study of their magnetic properties. The positive Curie-Weiss temperature for all of them (Fig.3 and Table I) reflects the predominance of FM interactions. The effective moment in all the high temperature orbitally disordered phases is nearly the same (close to $2\mu_B$) while it is smaller in the orbitally ordered phase of NaNiO₂. The 3 compounds

show a maximum in the susceptibility at low temperature: 20K for NaNiO₂, 25K for Li_{0.3}Na_{0.7}NiO₂ and 9K for LiNiO₂. In fact, LiNiO₂ is never stoichiometric: the exact formula being Li_{1- ϵ} Ni_{1+ ϵ} O₂ with extra Ni ions in the Li plane. This gives rise to frustrated magnetic interactions between the Ni planes and prevents any long range magnetic order[16] but giving rise to a spin glass behaviour. Instead, in NaNiO₂ and Li_{0.3}Na_{0.7}NiO₂ which are stoichiometric (no Ni ions are present in the Na/Li planes), the magnetization curves at 4K point towards an AF order (Fig.4a). NaNiO₂ is considered as an A type antiferromagnet with FM Ni layers coupled AF below T_N $\approx 20\text{K}$ [2, 3, 4]. However NPD measurements failed to detect such a simple magnetic structure. A careful analysis of the magnetization reveals indeed a more complex ordering: when taking its derivative as a function of the applied magnetic field (Fig.4b), clearly 3 characteristic fields are present: H_{c0} , H_{c1} and H_{sat} instead of 2 expected for a A type antiferromagnet. The same behaviour is observed in Li_{0.3}Na_{0.7}NiO₂, with H_{c0} , H_{c1} lowered and H_{sat} enhanced (TableI).

This common magnetic structure can still be described in a first approach, as an AF stacking of FM planes as previously proposed [2, 3, 4]. Then only H_{sat} and H_{c0} are relevant and we can estimate $H_{sat} \approx 2H_E$ and $H_{c0} = H_{sf} \approx \sqrt{2H_E H_A}$, where H_E is the AF exchange field (between the Ni layers) and H_A the anisotropy field which aligns the magnetic moment in a given direction. Table I yields all these measured and calculated quantities. Note the significant decrease of H_A : while NaNiO₂ is an uniaxial or easy plane antiferromagnet, Li_{0.3}Na_{0.7}NiO₂ is more of the Heisenberg type. This is well explained by the presence or absence of orbital order in these compounds: the anisotropy arises from spin-orbit coupling; in NaNiO₂, orbital order insures the presence of preferred orientations for the magnetic moment, whereas in Li_{0.3}Na_{0.7}NiO₂ the disordered orbital occupancy gives rise to isotropic probability for the spins orientation. From H_E we deduce the AF interaction J_{AF}: -1.3K for NaNiO₂ -1.9K for Li_{0.3}Na_{0.7}NiO₂.

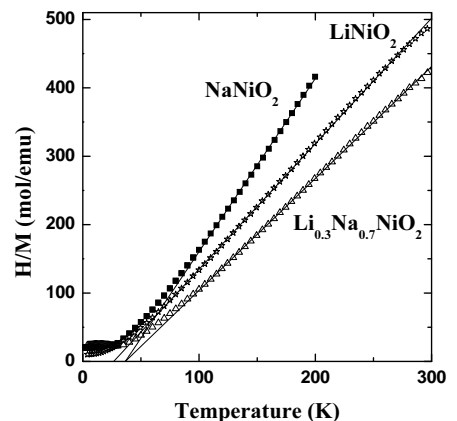


FIG. 3: inverse of the susceptibility vs temperature, showing the Curie-Weiss behaviour.

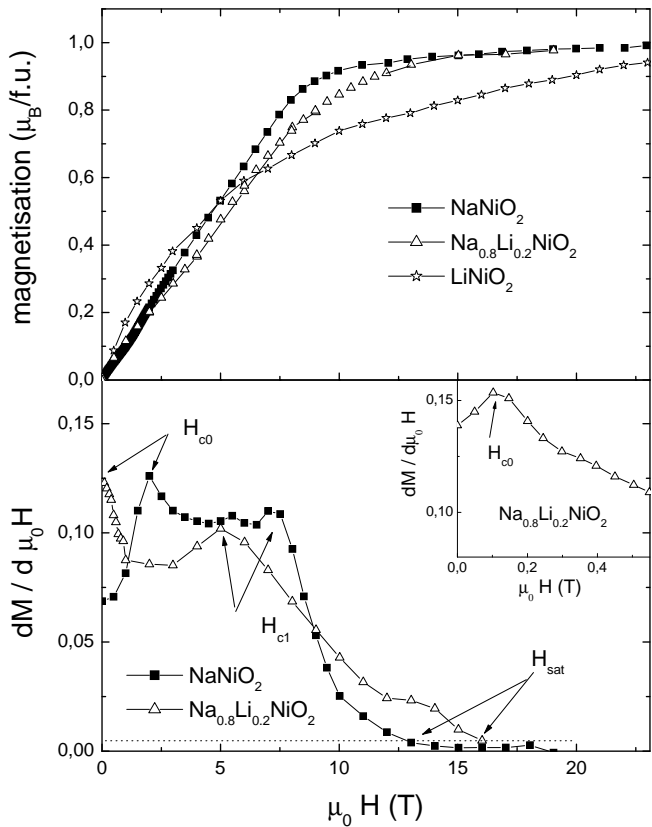


FIG. 4: field dependence (top) and field derivative of the magnetization (bottom) at 4K, showing the 3 characteristics fields. Inset: blow up of the low field results for $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$.

Using also the Curie-Weiss temperature, we calculate the FM interaction J_F : +13.3K for the former, +15.2K for the latter. Both interactions increase slightly from NaNiO_2 to $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$. J_{AF} arises from super-super-exchange Ni-O-O-Ni bonds across the Ni planes, and J_F from 90° Ni-O-Ni in-plane bonds explained before.

Recently, Daré et al.[12] have calculated the influence of the trigonal distortion on the exchange interaction in the Ni planes, via the crystal field seen by the oxygen atoms. For a large enough trigonal distortion, AFM interactions can be generated in the Ni planes in addition to (or instead of) the FM interactions expected for 90° Ni-O-Ni bonds. This parameter has been quantified in our structural analysis: LiNiO_2 has the lowest trigonal distortion (0.945) compared to $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$ (0.899) and to NaNiO_2 (0.89 for the high temperature orthorhombic phase, 0.92 for the monoclinic phase). Although in Daré et al. calculation [12] also the orbital occupation is crucial, if one should invoke only the magnitude of the trigonal distortion to conclude about the presence of these induced AFM interactions in the Ni plane for LiNiO_2 , they should be even more relevant for NaNiO_2 and $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$. This appears not be compatible with our magnetic results (see the corresponding Curie-Weiss temperatures).

The presence of the third critical field H_{c1} (Fig.4b) is definitely a signature that the magnetic order is more complex than the A type antiferromagnet: another interaction must be added. In the model of Daré et al. [12] in order to obtain simultaneously in-plane Ni FM and AFM interactions one has to include both e_g orbitals, $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$. But in NaNiO_2 only the former orbital is occupied, indicating a different origin. Our experimental results confirm that orbital and spin degrees of freedom are decoupled in these systems [10, 11]. Although we cannot conclude about the orbital occupation in the Li containing compounds, NaNiO_2 can most probably be the spin model for the magnetic ground state of pure LiNiO_2 .

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