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Decoupling of orbital and spin degrees of freedom in  $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$ 

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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  $\text{NaNiO}_2$ , 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  $\text{LiNiO}_2$ , does not take place in these layered compounds with  $\sim 90^\circ$  super-exchange bonds. We also discuss the relevance of the O crystal field splitting induced by the trigonal distortion, in generating AFM in-plane Ni-Ni interactions.

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The interplay between orbital and spin degrees of freedom in transition metal (TM) oxides can yield 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  $\text{LiNiO}_2$ , indeed clearly observed in isomorphic and isoelectronic  $\text{NaNiO}_2$  [2, 3, 4], is especially puzzling. Recently there have been attempts to explain these curious different behaviours, but the situation is still unsettled. Most 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  $\text{LiNiO}_2$  inhibits the stabilization of a 3D magnetic ordering. Here, our synthesis and study of intermediate  $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$  compounds shows that the macroscopic Jahn-Teller (JT) transition observed in  $\text{NaNiO}_2$  can be killed by a small amount of Li replacing Na ions. Paradoxically, the magnetic properties exhibited by Li doped  $\text{NaNiO}_2$  remain very close to those displayed by the pure  $\text{NaNiO}_2$ . Our experimental observations support previous analysis [10] and recent theoretical calculations [11] showing that, in the  $\sim 90^\circ$  TM-O-TM systems, orbitals and spins are essentially decoupled. Departure from the ideal  $90^\circ$  angle, contribution from extra overlappings [9] or crystal field splitting effects [12] have been invoked to strengthen the coupling between spins and orbitals in these systems, but the results reported here indicate that those hypothesis are not appropriate in the case of  $\text{LiNiO}_2$ .

The  $\alpha\text{-NaFeO}_2$  structure of  $\text{LiNiO}_2$  has planes of Ni magnetic ions arranged in a triangular network. No

long range magnetic ordering has been reported for this compound. The  $\text{Ni}^{3+}$  ions are in the low spin configuration ( $t_{2g}^6 e_g^1$ ) with  $s=1/2$  on the doubly degenerate  $e_g$  level. The Goodenough-Kanamori-Anderson rules yield ferromagnetic (FM) spin exchange couplings between nearest-neighbour Ni ions in the same plane. The measured Curie-Weiss temperature indicates the predominance of FM interactions. Interestingly, it has been recently pointed out [12] that the trigonal crystal field splitting of the  $\text{O}2p$  orbitals could induce also antiferromagnetic (AFM) exchange integrals in the Ni planes. That would give a microscopic foundation for the coexistence of intra-layer FM and AFM couplings in  $\text{LiNiO}_2$ , as considered by some authors [9, 13]. Concerning the orbital occupation, no JT transition is observed.

On the other hand,  $\text{NaNiO}_2$  undergoes a cooperative JT ordering of the  $\text{Ni}^{3+}$  ions at 480K reducing its symmetry from rhombohedral to monoclinic. It presents a long range AFM order below 20K [2, 3]. It has been then speculated that a different oxygen crystal field splitting would inhibit these AFM in plane Ni-Ni interactions in  $\text{NaNiO}_2$ , yielding its different magnetic properties [12].

We perform here a crystallographic and magnetic study of  $\text{LiNiO}_2$ ,  $\text{NaNiO}_2$  and the new  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  [14]. Our main point is that samples with this intermediate composition do not undergo the JT transition of  $\text{NaNiO}_2$ , but keep a rhombohedral structure like  $\text{LiNiO}_2$  even at low temperature. In spite of this fact, they achieve the long range magnetic ordering of  $\text{NaNiO}_2$ . This shows the decoupling between orbital and spins for these oxides with  $\sim 90^\circ$  bonds. Furthermore, the quan-

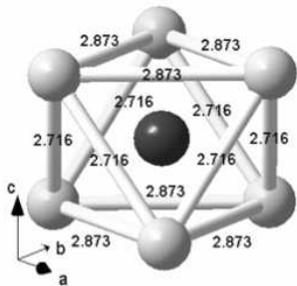


FIG. 1: the trigonal distorted  $\text{NiO}_6$  octahedra in  $\text{LiNiO}_2$  with O-O distances.

tification of the trigonal distortion in these 3 compounds also allow us to discuss its relevance in generating in-plane AFM interactions in  $\text{LiNiO}_2$ , conjectured to suppress the magnetic ordering [12].

The products were obtained by classical high-temperature solid-state reaction. They were synthesized from  $\text{Na}_2\text{O}_2$ , NiO and  $\text{LiOH}\cdot\text{H}_2\text{O}$  powders. The starting materials were mixed in an argon atmosphere with a 10% excess of (Na+Li) to account for volatilization losses. The mixture was heated under flowing oxygen at  $680^\circ\text{C}$  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 Fullprof software [15].

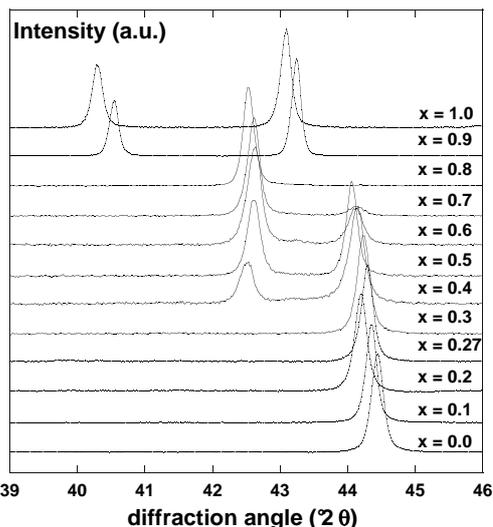


FIG. 2: x-ray diffractograms as a function of the nominal composition  $\text{Li}_{1-x}\text{Na}_x\text{NiO}_2$ .

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

	$\text{LiNiO}_2$	$\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$	$\text{NaNiO}_2$
space group	R3m	R3m	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 ( $^\circ$ )	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

It is not possible to synthesize single phase samples for arbitrary Li/Na ratio. As shown in Fig.2 and reported by Matsumura et al.[14], the  $\text{LiNiO}_2/\text{NaNiO}_2$  phase diagram contains 3 different single phase solid solution regions, in between which, two phase mixtures are observed. For  $x \leq 0.3$ , the R3m  $\alpha$ - $\text{NaFeO}_2$  structure type of  $\text{LiNiO}_2$  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  $\text{NaNiO}_2$  is observed, with substitution of  $\text{Li}^+$  for  $\text{Na}^+$  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 concentration range about  $x \approx 0.8$ , a new rhombohedral phase (RI phase) is obtained, which has the same structural arrangement as  $\text{LiNiO}_2$ , but quite different cell parameters: the c/a ratio is  $\approx 5.24$  instead of  $\approx 4.94$  for  $\text{LiNiO}_2$ . The exact cationic composition of this phase found both by Rietveld refinement of the x-ray data and atomic absorption is  $\text{Li}_{0.30(1)}\text{Na}_{0.70(1)}$ . No 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  $\text{LiNiO}_2$  and not like  $\text{NaNiO}_2$ .

To better understand the magnetism of these compounds, it is interesting to compare the structural arrangements of the  $\text{NiO}_2$  octahedral layers (Table I). The R3m  $\text{LiNiO}_2$  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  $\text{NiO}_2$  edge-shared octahedral layers separated by  $\text{Li}^+$  cations planes. This is accompanied by a trigonal distortion of the  $\text{NiO}_6$  octahedra brought about by the difference of charge and size between  $\text{Li}^+$  and  $\text{Ni}^{3+}$  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 linking oxygen anions from the plane above and below the Ni cation, called  $d(\text{O-O})_c$ , become shorter ( $\approx 2.72\text{\AA}$ ) than those in the  $ab$  plane,  $d(\text{O-O})_{ab}$  ( $\approx 2.87\text{\AA}$ ). At the same time, the O-Ni-O angles between oxygen anions from the same plane above or below the Ni cation opens to  $93.2^\circ$ , while the ones between oxygen anions from the two planes close down to  $86.8^\circ$ . This distortion can be characterized by the ratio  $\gamma = d(\text{O-O})_c/d(\text{O-O})_{ab}$ , and is 0.945 for  $\text{LiNiO}_2$ .

Although the structural arrangement is the same for  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$ , the interatomic distances and angles are markedly modified because of the steric effect due to the large size difference between  $\text{Na}^+$  and  $\text{Li}^+$  cations (ionic radius= $1.02\text{\AA}$  and  $0.76\text{\AA}$ ). Due to charge balance, the 6 Ni-O distances are almost unchanged ( $1.98\text{\AA}$ ), but the 2 O-O distances and angles defined above become  $\approx 2.94\text{\AA}$ ,  $2.64\text{\AA}$ ,  $96.1^\circ$  and  $83.9^\circ$ , respectively.  $\gamma = 0.899$ , indicates a much stronger trigonal distortion than for  $\text{LiNiO}_2$ .

Very similar Ni-O and O-O distances and O-Ni-O angles can be calculated in the isostructural high temperature form of  $\text{NaNiO}_2$  from the NPD data of Chappel et al. [4] (at 565K: Ni-O :  $6 \times 1.98\text{\AA}$ ; O-O :  $6 \times 2.96\text{\AA}$ ,  $6 \times 2.63\text{\AA}$ ,  $\gamma = 0.899$  ; O-Ni-O :  $6 \times 96.8^\circ$ ,  $6 \times 83.2^\circ$ ). At room temperature, in the monoclinic phase, the  $\text{NiO}_6$  octahedra become JT distorted: 4 Ni-O distances become shorter ( $1.93\text{\AA}$ ) and 2 longer ( $2.17\text{\AA}$ ). The average O-O distances become  $d(\text{O-O})_c \approx 2.72(0.1)\text{\AA}$ , and  $d(\text{O-O})_{ab} \approx 2.96(0.1)\text{\AA}$ , and the average O-Ni-O angles  $\approx 95^\circ$  and  $\approx 85^\circ$ . The same ratio can still be used to evaluate the trigonal distortion:  $\gamma = 0.919$ . By comparing these values with those of  $(\text{Li}_{0.3}\text{Na}_{0.7})\text{NiO}_2$ , one can conclude that in monoclinic  $\text{NaNiO}_2$ , the JT distortion is superimposed on the trigonal one without markedly changing the amplitude of the latter.

Having in mind that  $\text{NaNiO}_2$  undergoes a collective JT transition, while  $\text{LiNiO}_2$  as well as  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  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 ( $\approx 2.1\mu_B$ ) while it is smaller in the orbitally ordered phase of  $\text{NaNiO}_2$  ( $1.85\mu_B$ ). Deviation from the free electron value ( $1.75\mu_B$ ) is enhanced in the orbital ordered phase reflecting the importance of the orbital contribution to the  $\text{Ni}^{3+}$  magnetic moment.

The 3 compounds show a maximum in the susceptibility at low temperature: 20K for  $\text{NaNiO}_2$ , 25K for  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  and 9K for  $\text{LiNiO}_2$ . In fact,  $\text{LiNiO}_2$  is never stoichiometric: the exact formula be-

ing  $\text{Li}_{1-\epsilon}\text{Ni}_{1+\epsilon}\text{O}_2$  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 yielding instead spin glass behaviour [16]. In  $\text{NaNiO}_2$  and  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  which are stoichiometric (no Ni ions are present in the Na/Li planes), the field dependence of the magnetization at 4K indicates long range magnetic order for both compositions (Figs.4a and b).  $\text{NaNiO}_2$  is considered as an A type antiferromagnet with FM Ni layers coupled AF below  $T_N \approx 20\text{K}$  [2, 3, 4]. However our NPD measurements failed to detect such a simple magnetic structure, in spite of the adequate sensitivity of the D1B spectrometer. A careful analysis of the magnetization data 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 an A type antiferromagnet ( $H_{c0}$ , and  $H_{sat}$ ) [17]. The same behaviour is observed in  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$ , with  $H_{c0}$ ,  $H_{c1}$  lowered and  $H_{sat}$  enhanced (Table I). Similarly no magnetic diffraction peak was detected by NPD. So, we can conclude that both  $\text{NaNiO}_2$  and  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  undergo the same long range magnetic transition, this is the relevant point for our discussion concerning the decoupling of the orbital and spin degrees of freedom in these systems.

In a first approach, this common magnetic structure can still be described 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 [17]. Table I yields all these measured and calculated quantities. Note the significant decrease of  $H_A$ : while  $\text{NaNiO}_2$  is an easy plane antiferromagnet,  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  is more isotropic. This can be well explained by the presence or absence of orbital order in these compounds: the magneto-crystalline anisotropy

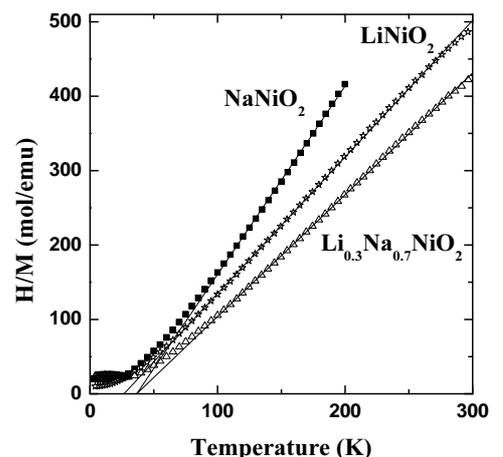


FIG. 3: inverse of the susceptibility vs temperature, showing the Curie-Weiss behaviour.

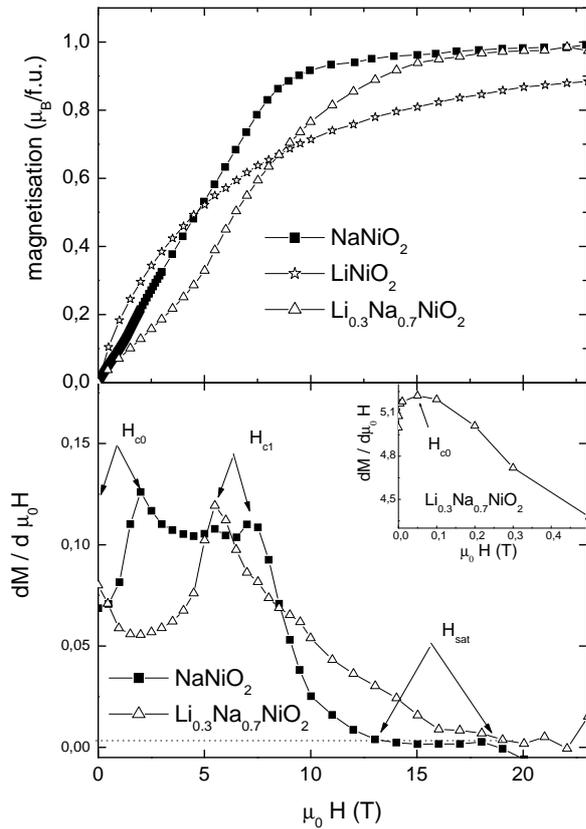


FIG. 4: field dependence (top) and field derivative of the magnetization (bottom) at 4K, showing the 3 characteristics fields. Inset: blow up of the low field results for  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$ .

arises from spin-orbit coupling; in  $\text{NaNiO}_2$  orbital order insures the presence of preferred orientations for the magnetic moment, whereas in  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  the disordered orbital occupancy gives rise to isotropic probability for the spins orientation. From  $H_E$  we deduce the AF interaction  $J_{AF}$ :  $-1.3\text{K}$  for  $\text{NaNiO}_2$  and  $-1.9\text{K}$  for  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$ . Using also the Curie-Weiss temperature, we calculate the FM interaction  $J_F$ :  $+13.3\text{K}$  for the

former,  $+15.2\text{K}$  for the latter. Both interactions increase slightly from  $\text{NaNiO}_2$  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  $\sim 90^\circ$  Ni-O-Ni in-plane bonds explained before.

To summarize, while  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  and  $\text{NaNiO}_2$  have very different orbital ground state, they present a similar magnetic ground state with similar exchange energies. The orbital contribution can only be seen in the value of the magnetic moment and the anisotropy field associated with  $\text{Ni}^{3+}$  ions. Although we cannot conclude about the orbital occupation in the Li containing compounds,  $\text{NaNiO}_2$  can most probably be the spin model for the magnetic ground state of pure  $\text{LiNiO}_2$  [16]. The exact magnetic structure of  $\text{NaNiO}_2$ , most likely a modulated one derived from the A-type antiferromagnet, remains to be determined but this is out of the scope of this paper. In the calculation of Daré et al.[12] a large enough trigonal distortion can generate AFM interactions in the Ni planes in addition to the FM interactions. This parameter has been quantified in our structural analysis:  $\text{LiNiO}_2$  has the lowest trigonal distortion ( $\gamma = 0.945$ ) compared to  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  (0.899) and to  $\text{NaNiO}_2$  (0.89 for the high temperature orthorhombic phase, 0.92 for the monoclinic phase). Then this mechanism should lead to a stronger AF contribution in  $\text{NaNiO}_2$  and  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  than in  $\text{LiNiO}_2$  while the opposite occurs according to the measured Curie-Weiss temperatures (Table I).

In conclusion, this crystallographic and magnetic study shows that the intermediate compound  $\text{Li}_{0.3}\text{Na}_{0.7}\text{NiO}_2$  has the same magnetic behaviour as  $\text{NaNiO}_2$  while its orbital behaviour is different: like  $\text{LiNiO}_2$  it does not undergo a collective Jahn-Teller transition. So, these experimental results establish that the orbital and spin degrees of freedom are decoupled in these systems.

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