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Decoupling of orbital and spin degrees of freedom in $\mathbf{Li_{1-x}Na_xNiO_2}$

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In the $Li_{1-x}Na_xNiO_2$ solid solutions, three different single-phase regions exist: for $x \geqslant 0.9$, for $x \approx 0.7$, and for $x \leqslant 0.3$. Although the intermediate compound does not show the cooperative Jahn-Teller transition of $NaNiO_2$, its magnetic properties remain very similar, particularly with respect to the low-temperature three-dimensional 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 $LiNiO_2$, does not take place in these layered compounds with ~90° superexchange bonds. We also discuss the relevance of the O crystal-field splitting induced by the trigonal distortion in generating antiferromagnetic 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 thus 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 isomorphic and isoelectronic $NaNiO_2$,[2–4] is especially puzzling. Recently there have been attempts to explain these curious different behaviors, but the situation is still unsettled. Most models[5–9] 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 a three-dimensional magnetic ordering. Here, our synthesis and study of intermediate $Li_{1-x}Na_xNiO_2$ compounds shows that the macroscopic Jahn-Teller (JT) transition observed in $NaNiO_2$ can be eliminated by a small amount of Li replacing Na ions. Paradoxically, the magnetic properties exhibited by Li-doped $NaNiO_2$ remain very close to those displayed by the pure $NaNiO_2$. Our experimental observations support previous analysis[10] and recent theoretical calculations[11] showing that, in the ~90° TM-O-TM systems, orbitals and spins are essentially decoupled. Departure from the ideal 90° angle, and the 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 hypotheses are not appropriate in the case of $LiNiO_2$.

The α-$NaFeO_2$ structure of $LiNiO_2$ has planes of Ni magnetic ions arranged in a triangular network. No long-range magnetic ordering has been reported for this compound. The 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-neighbor 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 O 2p orbitals could also induce antiferromagnetic (AFM) exchange integrals in the Ni planes. That would give a microscopic foundation for the coexistence of intralayer FM and AFM couplings in $LiNiO_2$, as considered by some authors.[9,13] Concerning the orbital occupation, no JT transition is observed.

On the other hand, $NaNiO_2$ undergoes a cooperative JT ordering of the Ni^{3+} ions at 480 K, reducing its symmetry from rhombohedral to monoclinic. It presents a long-range AFM order below 20 K.[2,3] It has been speculated that a different oxygen crystal-field splitting would inhibit these AFM in-plane Ni-Ni interactions in $NaNiO_2$, yielding its different magnetic properties.[12]

We perform here a crystallographic and magnetic study of $LiNiO_2$, $NaNiO_2$, and $Li_{0.3}Na_{0.7}NiO_2$.[14] Our main 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. In spite of this fact, they achieve the long-range magnetic ordering of $NaNiO_2$. This shows the decoupling between orbital and spins for these oxides with ~90° bonds. Furthermore, the quantification of the trigonal distortion in these three compounds also allow us to discuss its relevance in generating in-plane AFM interactions in $LiNiO_2$, conjectured to suppress the magnetic ordering.[12]

The products were obtained by classical high-temperature solid-state reaction. They were synthesized from Na_2O_2, NiO, and $LiOH \cdot H_2O$ 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 °C for 24 h. Twelve samples with compositions $(Li_{1-x}Na_x)NiO_2$ with $0 \leqslant x \leqslant 1$ (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. In order to detect possible magnetic ordering, neutron powder diffraction (NPD) data were collected down to 1.5 K on the CRG-D1B instrument at the Institut Laue Langevin. The x-ray and neutron diffractograms were refined by the Rietveld technique using the FULLPROF software.[15]

It is not possible to synthesize single-phase samples for

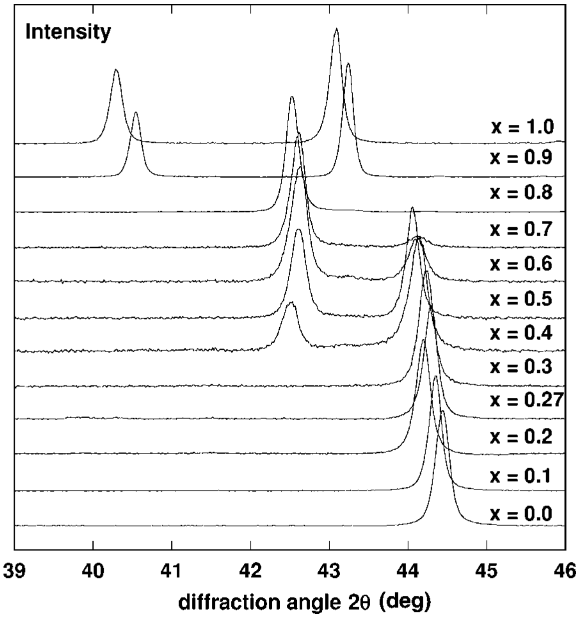

FIG. 1. X-ray diffractograms as a function of the nominal composition $Li_{1-x}Na_xNiO_2$.

arbitrary Li/Na ratios. As shown in Fig. 1 and reported by Matsumura *et al.*,[14] the $LiNiO_2/NaNiO_2$ phase diagram contains three different single-phase solid solution regions, in between which, two-phase mixtures are observed. For $x \leqslant 0.3$, 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 $x \geqslant 0.9$, 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 concentration range 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 $Li_{0.30(1)}Na_{0.70(1)}$. No structural phase transition could be detected by NPD for $(Li_{0.3}Na_{0.7})NiO_2$ down to 1.5 K. Therefore, this phase remains rhombohedral in this temperature range and does not undergo a cooperative JT ordering. In this respect, it behaves like $LiNiO_2$ and not like $NaNiO_2$.

To better understand the magnetism of these compounds, it is interesting to compare the structural arrangements of the NiO_2 octahedral layers (Table I). The $R\bar{3}m$ $LiNiO_2$ structure can be described by starting from the fcc NiO structure and replacing every other Ni plane perpendicular to one of the threefold axes by a Li plane, forming NiO_2 edge-shared octahedral layers separated by Li^+ planes. This is accompanied by a trigonal distortion of the NiO_6 octahedra brought about by the difference of charge and size between Li^+ and Ni^{3+} cations. These octahedra are compressed along the c axis as shown in Fig. 2. The six Ni-O distances remain equal ($\approx$1.98 Å), but the six O-O distances linking oxygen anions from the plane above and below the Ni cation, called d(O-O)$_c$, become shorter ($\approx$2.72 Å) than those in the ab

TABLE I. Room-temperature crystallographic and low-temperature magnetic parameters for the three phases.

	$LiNiO_2$	$Li_{0.3}Na_{0.7}NiO_2$	$NaNiO_2$
Space group	$R\bar{3}m$	$R\bar{3}m$	$C2/m$
Cell param.	$a=2.8727(3)$	$a=2.9410(1)$	$a=5.3208(3)$
	$c=14.184(2)$	$c=15.4082(1)$	$b=2.8440(2)$
			$c=5.5818(4)$
			$\beta=110.49(1)$
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)	6×1.977	6×1.977	4×1.93, 2×2.17
O-O (Å)	6×2.716	6×2.644	4×3.02, 2×2.84
	6×2.873	6×2.941	4×2.78, 2×2.60
O-Ni-O (°)	6×93.2	6×96.1	4×94.8, 2×95.1
	6×86.8	6×83.9	4×85.2, 2×84.9
T_{CW}	+26 K	+40 K	+36 K
T_N or T_{SG}	9 K	25 K	20 K
H_{C0} at 4 K		0.05 T	1.8 T
H_{C1}		5 T	7 T
H_{sat}	>23 T	19 T	13 T
H_E		9.5 T	6.5 T
H_A		0.2 mT	250 mT

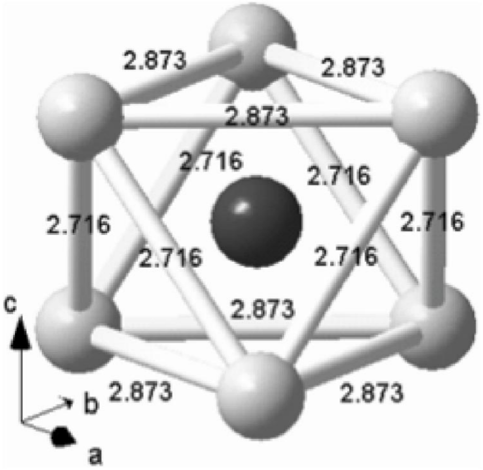

FIG. 2. Trigonal distorted NiO_6 octahedra in $LiNiO_2$ with O-O distances.

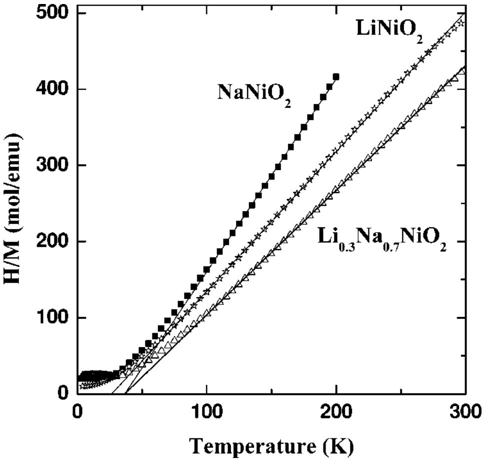

FIG. 3. Inverse of the susceptibility vs temperature, showing the Curie-Weiss behavior.

plane, $d(\text{O-O})_{ab}$ ($\approx$2.87 Å). 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 $\gamma = d(\text{O-O})_c / d(\text{O-O})_{ab}$, and is 0.945 for $LiNiO_2$. Although the structural arrangement is the same for $Li_{0.3}Na_{0.7}NiO_2$, 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 = 1.02 and 0.76 Å). Due to charge balance, the six Ni-O distances are almost unchanged (1.98 Å), but the two O-O distances and angles defined above become $\approx$2.94 Å, 2.64 Å, 96.1°, and 83.9°, respectively. $\gamma = 0.899$, indicates a much stronger trigonal distortion than for $LiNiO_2$.

Very similar Ni-O and O-O distances and O-Ni-O angles can be calculated in the isostructural high-temperature form of $NaNiO_2$ from the NPD data of Chappel *et al.*[4] (at 565 K: Ni-O: 6 × 1.98 Å; O-O: 6 × 2.96 Å, 6 × 2.63 Å, $\gamma = 0.899$; O-Ni-O: 6 × 96.8°, 6 × 83.2°). At room temperature, in the monoclinic phase, the NiO_6 octahedra become JT distorted: four Ni-O distances become shorter (1.93 Å) and two longer (2.17 Å). The average O-O distances become $d(\text{O-O})_c \simeq 2.72(0.1)$ Å and $d(\text{O-O})_{ab} \simeq 2.96(0.1)$ Å, and the average O-Ni-O angles $\simeq$95° and $\simeq$85°. The same ratio can still be used to evaluate the trigonal distortion: $\gamma = 0.919$. By comparing these values with those of $(Li_{0.3}Na_{0.7})NiO_2$, one can conclude that in monoclinic $NaNiO_2$, the JT distortion is superimposed on the trigonal one without markedly changing the amplitude of the latter.

Having in mind that $NaNiO_2$ undergoes a collective JT transition, while $LiNiO_2$ as well as $Li_{0.3}Na_{0.7}NiO_2$ do not, we perform now a comparative study of their magnetic properties. The positive Curie-Weiss temperature (TCW) 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 ($\simeq$2.1 μ_B), while it is smaller in the orbitally ordered phase of $NaNiO_2$ (1.85 μ_B). Deviation from the free electron value (1.75 μ_B) is enhanced in the orbital ordered phase reflecting the importance of the orbital contribution to the Ni^{3+} magnetic moment.

The three compounds show a maximum in the susceptibility at low temperature: 20 K for $NaNiO_2$, 25 K for $Li_{0.3}Na_{0.7}NiO_2$, and 9 K for $LiNiO_2$. In fact, $LiNiO_2$ is never stoichiometric: the exact formula being $Li_{1-\epsilon}Ni_{1+\epsilon}O_2$ wih 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 behavior.[16] In $NaNiO_2$ and $Li_{0.3}Na_{0.7}NiO_2$, which are stoichiometric (no Ni ions are present in the Na/Li planes), the field dependence of the magnetization at 4 K indicates long-range magnetic order for both compositions [Figs. 4(a) and 4(b)]. $NaNiO_2$ is considered as an A-type antiferromagnet with FM Ni layers coupled AF below $T_N \simeq 20$ K.[2–4] 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. 4(b)], clearly, three characteristic fields are present: H_{C0}, H_{C1}, and H_{sat} instead of two expected for an A-type antiferromagnet (H_{C0} and H_{sat}).[17] The same behavior is observed in $Li_{0.3}Na_{0.7}NiO_2$, with H_{C0}, H_{C1} lowered and H_{sat} enhanced (Table I). Similarly, no magnetic diffraction peak was detected by NPD. We can thus conclude that both $NaNiO_2$ and $Li_{0.3}Na_{0.7}NiO_2$ 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.[2–4] Only H_{sat} and H_{C0} are then relevant and we can estimate $H_{sat} \simeq 2H_E$ and $H_{C0} = H_{sf} \simeq \sqrt{2H_E H_A}$, where H_E is the AF exchange field (between the Ni layers) and H_A the anisotropy field that aligns the magnetic moments in a given direction.[17] Table I yields all these measured and calculated quantities. Note the significant decrease of H_A: while $NaNiO_2$ is an easy plane antiferromagnet, $Li_{0.3}Na_{0.7}NiO_2$ is more isotropic. This can be well explained by the presence or absence of orbital order in these compounds: the magneto-

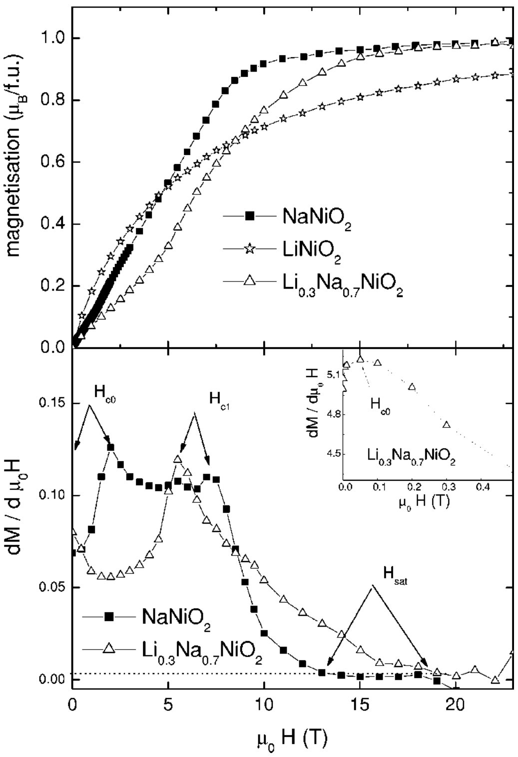

FIG. 4. Field dependence (top) and field derivative of the magnetization (bottom) at 4 K, showing the three characteristics fields. Inset: blow-up of the low field results for $Li_{0.3}Na_{0.7}NiO_2$.

crystalline anisotropy arises from spin-orbit coupling; in $NaNiO_2$ orbital order insures the presence of preferred orientations for the magnetic moment, whereas in $Li_{0.3}Na_{0.7}NiO_2$ 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 K for $NaNiO_2$ and −1.9 K for $Li_{0.3}Na_{0.7}NiO_2$. Using, in addition, the Curie-Weiss temperature, we calculate the FM interaction J_F: +13.3 K for the former, +15.2 K for the latter. Both interactions increase slightly from $NaNiO_2$ to $Li_{0.3}Na_{0.7}NiO_2$. J_{AF} arises from super-superexchange Ni-O-O-Ni bonds across the Ni planes, and J_F from ∼90° Ni-O-Ni in-plane bonds explained before.

To summarize, while $Li_{0.3}Na_{0.7}NiO_2$ and $NaNiO_2$ have very different orbital ground states, 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 Ni^{3+} ions. 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 $LiNiO_2$.[16] The exact magnetic structure of $NaNiO_2$, 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: $LiNiO_2$ has the lowest trigonal distortion ($\gamma = 0.945$) compared to $Li_{0.3}Na_{0.7}NiO_2$ (0.899) and to $NaNiO_2$ (0.89 for the high-temperature orthorhombic phase, 0.92 for the monoclinic phase). This mechanism should thus lead to a stronger AF contribution in $NaNiO_2$ and $Li_{0.3}Na_{0.7}NiO_2$ than in $LiNiO_2$, 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 $Li_{0.3}Na_{0.7}NiO_2$ has the same magnetic behavior as $NaNiO_2$ while its orbital behavior is different: like $LiNiO_2$, it does not undergo a collective Jahn-Teller transition. Thus these experimental results establish that the orbital and spin degrees of freedom are essentially decoupled in these systems.

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