Orbital Frustration at the Origin of the Magnetic Behavior in $LiNiO_2$

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We report on the ESR, magnetization, and magnetic susceptibility measurements performed over a large temperature range, from 1.5 to 750 K, on high-quality stoichiometric $LiNiO_2$. We find that this compound displays two distinct temperature regions where its magnetic behavior is anomalous. With the help of a statistical model based on the Kugel'-Khomskii Hamiltonian, we show that below $T_{of} \simeq 400$ K, an orbitally frustrated state characteristic of the triangular lattice is established. This then gives a solution to the long-standing controversial problem of the magnetic behavior in $LiNiO_2$.

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The problem of orbital degeneracy (OD) in transition-metal oxides has attracted considerable interest recently, due to its drastic effect on the magnetic, elastic, transport, and other properties of these compounds [1]. Among the most studied oxides exhibiting OD are manganites, vanadates, some titanates, and other systems. Here we discuss a new interesting aspect of OD: the frustration of degenerate orbitals, as applied to lithium nickel oxide.

Since $LiNiO_2$ was first studied as an ionic conductor [2], the magnetic properties of this layered compound have been reported in numerous publications but are still the subject of considerable controversy. Quantum spin liquid [3], spin glass [4–7], frustrated antiferromagnetism [4, 8–10], quantum disordered state without a spin gap [11], and other scenarios [12–20] have been claimed to be responsible for the magnetism of this material. Actually, interest in this compound stems essentially from two facts. First, following the suggestion by Anderson [21] that a resonating valence bond ground state may exist in a $S = 1/2$ Heisenberg triangular-lattice antiferromagnet, $LiNiO_2$ was proposed by Hirakawa *et al.* [3] as a potential physical realization of such a system. The second important feature, overlooked in earlier studies, is the unusual electronic state of Ni^{3+} ions. The strong crystal field acting on the nickel ions brings them in the low-spin state (t_{2g}^6, e_g^1; $S = 1/2$), with the two e_g levels being degenerate. Clearly, OD should play a crucial role in the magnetic properties of this compound [11,22,23]. However, no direct confirmation of this hypothesis exists yet.

In this paper we propose a novel scenario for $LiNiO_2$ based on an interplay between frustration on a triangular lattice and OD of Ni^{3+} ions. We show experimentally that an anomalous magnetic behavior occurs in two different temperature regions, which we interpret as the consequence of two distinct energy scales present in the system. The first one, of the order of hundreds of Kelvin, is related to the antiferro-orbital coupling between Ni^{3+} ions and leads to a frustrated distribution of Ni^{3+} orbitals. The second one, of the order of tens of Kelvin, is due to the spin-spin interactions between electrons in these frustrated Ni^{3+} orbitals, and drives the very unusual magnetic behavior at low temperatures. Our proposed scenario, which we confirm through a direct comparison between experimental data and simulation results, gives a coherent and natural explanation of this behavior.

High-quality powder samples of stoichiometric $LiNiO_2$ were prepared following the procedure described by Rougier *et al.* [24]. We studied these samples by X-band ($\nu = 9.45$ GHz) electron spin resonance (ESR), magnetization (up to 15 T) and dc-susceptibility measurements over a wide temperature range, from 1.5 to 750 K.

The ESR spectra have a symmetric shape at all temperatures and show no trace of any particular feature that would be representative of ferrimagnetic cluster formation or of any anisotropy. This is a first but clear indication that the samples studied in this paper are homogeneous and of good quality. We show in Fig. 1 the T dependence of the ESR linewidth, ΔH (half width at half maximum), of a typical sample of $LiNiO_2$ in the low-T regime. A huge increase of ΔH is noted when the temperature decreases below 50 K. This temperature, to which we shall refer below as T_m, quite naturally gives the scale of the magnetic interaction in $LiNiO_2$. Below $T \simeq 10$ K, ΔH tends to a saturation value of about 0.5 T. The inset of Fig. 1 shows the inverse of the spin susceptibility, $\chi^{-1}(T)$, deduced from the ESR spectra. As already reported earlier [5], $\chi(T)$ follows a Curie-Weiss behavior, $\chi = C/(T - \theta)$, down to about 80 K, with $\theta \simeq 35 \pm 5$ K. This low value of θ confirms that the sample studied is so close to stoichiometry that we may consider it as pure $LiNiO_2$ [5,11]. Bearing in mind

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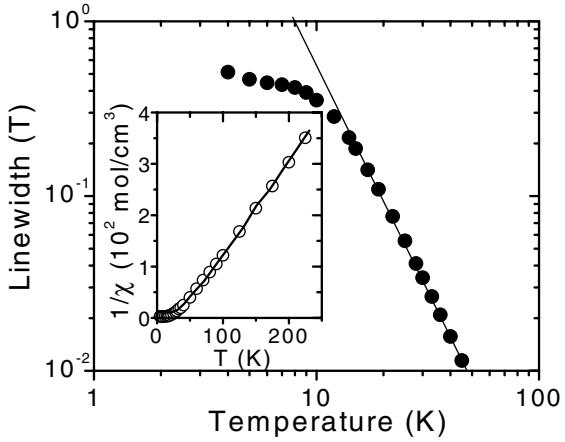

FIG. 1. Temperature dependence of the ESR linewidth, ΔH. The straight line is a fit to the law $\Delta H = AT^{-p}$ with $p = 2.65$. The inset shows the temperature dependence of the inverse of the spin susceptibility, $1/\chi$, as deduced from the ESR spectra. The circles and continuous line, respectively, represent experimental data and numerical simulations.

that θ represents the average sum of exchange interactions on an atomic site, the positive sign of θ implies that the dominant interactions are ferromagnetic (FM). However, the line broadening observed in Fig. 1 is rather indicative of strong antiferromagnetic (AF) fluctuations. Line narrowing would be expected if the interactions were purely ferromagnetic. Futhermore, between 13 and 50 K, ΔH can be fitted to the empirical formula $\Delta H = AT^{-p}$ with $p = 2.65$. Such an exponent value is known to be characteristic of AF materials having a strong 2D character [25]. Another important point is the tendency of the linewidth to saturate below 10 K. This constitutes strong evidence that the AF correlations do not propagate any longer below this temperature.

Figure 2 shows the magnetic moment, M, as a function of magnetic field, H. The curves deviate from linearity

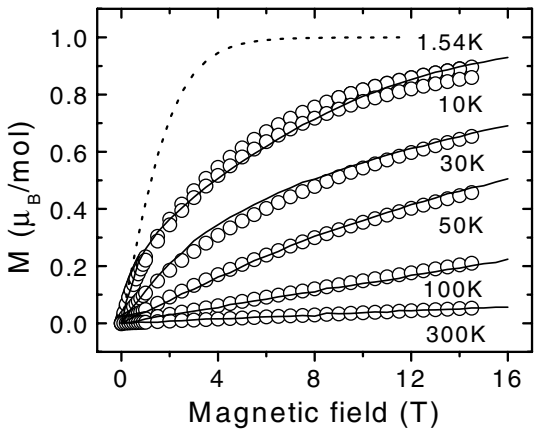

FIG. 2. Magnetic moment, M, as a function of magnetic field, H, up to 15 T. Circles: experimental data between 300 and 1.54 K; solid curves: simulation results; dotted curve: $M(H)$ calculated at 1.5 K using the Brillouin function.

below $T_m \simeq 50$ K, the same temperature below which the ESR linewidth was seen to markedly increase. At low temperatures, saturation is almost reached in fields of 15 T and, furthermore, below about 10 K, the temperature has hardly any effect on magnetization. Although the initial susceptibility increases with decreasing temperature in a manner reminiscent of a FM behavior, the $M(H)$ curve at the lowest temperature remains below what would be given by a Brillouin function. This confirms the existence of rather strong AF interactions along with ferromagnetism.

The second anomalous aspect of $LiNiO_2$ is found at high temperatures and plays a crucial role in understanding the magnetic properties of this compound. Figure 3a shows the results of the dc-susceptibility measurements, plotted in the form $(T + 10)\chi(T)$ between 300 and 750 K. The curve presents a weak anomaly at about 400 K. At higher temperatures, θ, which was found to be about 35 K from the low-T measurements, decreases to finally settle at the

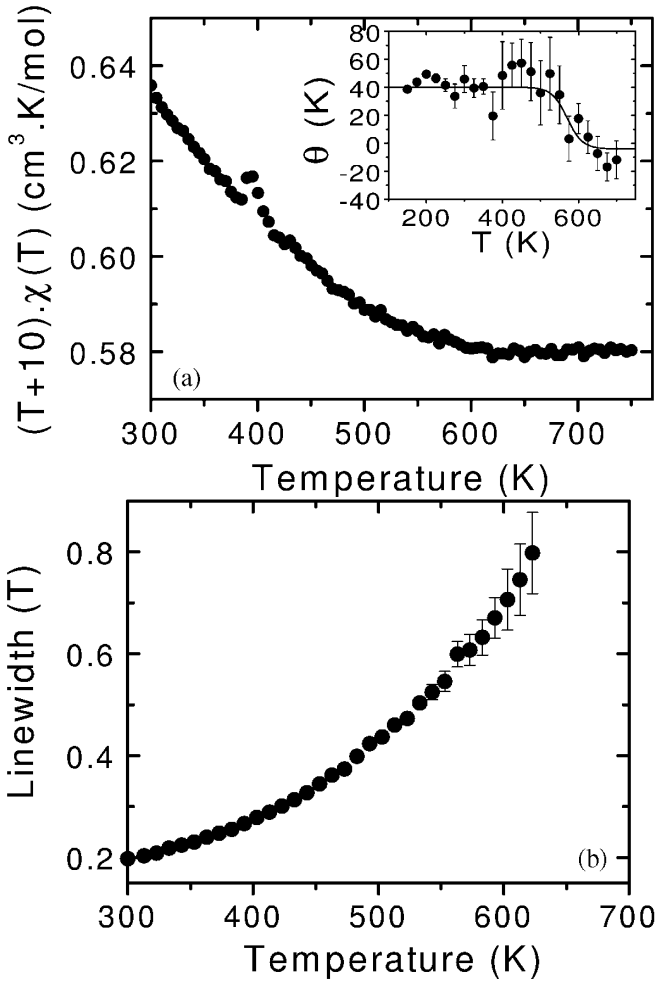

FIG. 3. (a) Results of dc-susceptibility measurements, plotted in the form $(T + 10)\chi(T)$. Note the plateau for $T > 600$ K. The inset shows the variation of θ with temperature; the line is a guide to the eye. (b) Temperature dependence of ΔH between 300 and 625 K.

negative value, $\theta = -10 \pm 5$ K, for $T \geqslant 600$ K. The inset of Fig. 3a details the variation of $\theta(T)$, as deduced from $\chi(T)$. Such a drastic change in θ is quite unusual and gives strong evidence for a concomitant modification of the Ni^{3+} orbital distribution in the NiO_2 layers. Additional support for this argument comes from the ESR data. Figure 3b presents the T dependence of ΔH, between 300 and 625 K. The divergence of ΔH above room temperature is quite in line with what is expected when, due to changes in the Ni^{3+} orbital distribution, strong fluctuations occur.

In order to explain this extremely rich and unusual magnetic behavior, we use the Kugel'-Khomskii (KK) spin-orbital model [1]. Derived from the two-band Hubbard Hamiltonian in the limit of a large Coulomb repulsion, this model has proven its efficiency to describe the interplay between magnetic and orbital ordering [26]. Here we rewrite the KK Hamiltonian in the following form:

$$H = \sum_{\langle i,j \rangle} \{ -J^o \tau_i \tau_j - \mathbf{s}_i \mathbf{s}_j [J_{so} \delta(\tau_i \tau_j - 1) + J_{do} \delta(\tau_i \tau_j + 1)] \}, \quad (1)$$

where the sum runs over nearest neighbor (NN) atoms and $\delta(\tau_i \tau_j \pm 1)$ is equal to 1, if $\tau_i \tau_j \pm 1 = 0$, and to 0 otherwise. As usual, $\mathbf{s}_i$ is the spin on atomic site i while the pseudospin, τ_i, is introduced to describe the orbital occupancy. The values $\tau_i = +1$ and $\tau_i = -1$, respectively, correspond to the two degenerate e_g orbitals of the Ni^{3+} ion, $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$. In the first term, J^o is the orbital coupling constant. J_{so} and J_{do} are the magnetic exchange constants between NN, with the same and with a different orbital occupancy, respectively. The spin-orbital model is here taken in its simplest form. First, we consider $\mathbf{s}_i$ as classical Ising spins. As a consequence, possible quantum effects at low temperatures cannot be described. Second, we do not distinguish between different relative orientations of the same orbital in the same site, as could be done by using a Potts model. Finally, we assume that the orbital coupling between two ions with the same orbital $\tau_i = \tau_j = 1$ is the same as the one between two ions with $\tau_i = \tau_j = -1$. These are rather crude approximations but we shall see that this minimal model is apparently able to capture the essential physics of the system, at least for temperatures greater than $\simeq 5$ K.

Recently, van den Bossche *et al.* [23] suggested that the SU(4) symmetry ($J_{so} = J_{do} = J^o$) could be at the origin of the magnetic properties of $LiNiO_2$. Our high-temperature experimental data presented above suggest that $|J^o| \gg |J_{so}|, |J_{do}|$. Therefore, we are here testing the relevance of the alternative SU(2) $*$ SU(2) symmetry in which the magnetic and orbital interactions have different orders of magnitude.

Concerning the sign of the orbital coupling, a ferro-orbital constant ($J^o > 0$) would lead to a structural ferro-distortive phase transition. This possibility is completely ruled out by the available x-ray data [27] so that we have to consider an antiferro-orbital coupling constant ($J^o < 0$). Since the Ni^{3+} ions form a triangular arrangement, we then expect *orbital frustration* to occur below a temperature T_{of} ($T_{of} = (3/2)|J^o|/k_B$, using the mean-field approximation) in a manner similar to the well-known AF-spin-frustration phenomenon. From the experimental results shown in Fig. 3, $T_{of} \simeq 400$ K, which gives $|J^o|/k_B \simeq 270$ K. The orbitally frustrated state may be described as a Wannier state (WS) [28]. A particular property of a WS is that three NN cannot have the same orbital occupancy. This is illustrated in Figs. 4a and 4b where we represent typical orbital distributions above and below T_{of}. It is evident that at high temperatures the probability to find a link between NN with a different orbital occupancy is $1/2$ and that this probability is $2/3$ in the WS. The mean-field values of θ are then given by

$$\theta_{ht} = (3J_{do} + 3J_{so})/k_B \quad \text{and} \quad \theta_{WS} = (4J_{do} + 2J_{so})/k_B, \quad (2)$$

where θ_{ht} and θ_{WS} denote the values in the high-temperature state and in the WS, respectively. The assumption of AF-orbital coupling, together with the experimentally inferred $\theta_{ht} = -10 \pm 5$ K and $\theta_{WS} = 35 \pm 5$ K, allows

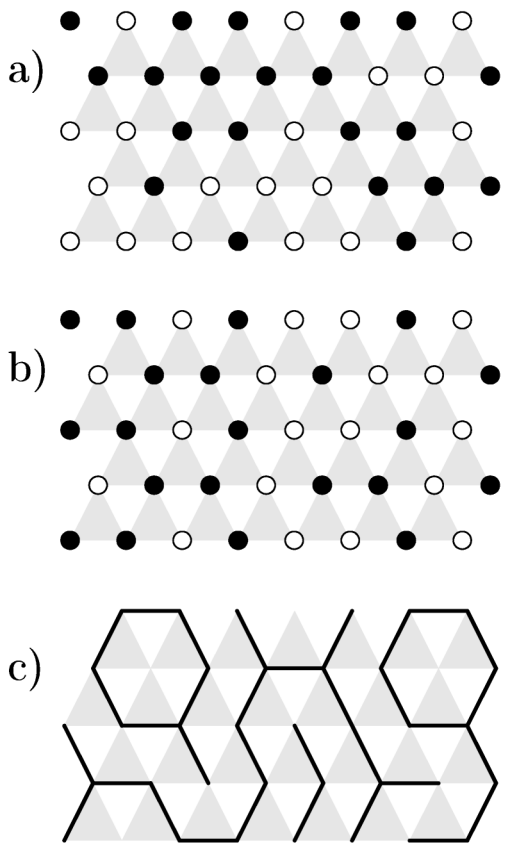

FIG. 4. Simulated distribution of orbitals at high (a) and low (b) temperatures. Filled and open circles distinguish between the two types of orbitals. (c) Satisfied FM links in the low-T Wannier state represented in (b).

us to determine the two magnetic coupling constants, J_{do} and J_{so}. We find a *FM exchange between NN with different orbitals* ($J_{do}/k_B = 18 \pm 6$ K) and an *AF one between NN with similar orbitals* ($J_{so}/k_B = -20 \pm 6$ K). It is interesting to note that this simple treatment of Hamiltonian (1) is sufficient for the qualitative understanding of the magnetic behavior of $LiNiO_2$ in a large temperature interval ($T > T_m$). It can also be shown that these values of J_{do} and J_{so} constitute the only combination of magnetic coupling constants that ensures the absence of a trivial long-range order, as indicated by the saturation of $\Delta H(T)$ at low temperatures (Fig. 1).

To test the ability of the model to describe the low-temperature magnetic properties, we have performed Monte Carlo (MC) simulations. The simulated system contains $N_i = 36 \times 36$ coplanar ions, and the classical Metropolis algorithm [29] is used. At each step both a spin and pseudospin are chosen randomly, and attempts to flip them are performed independently. A MC step consists of N_i such attempts. After a first run of 2×10^4 MC steps to ensure equilibrium, the magnetization and susceptibility are computed from uncorrelated configurations recorded during a second run of 5×10^4 MC steps. The best fit to the experimental results is obtained for $J_{do}/k_B = 21.0$ K and $J_{so}/k_B = -22.5$ K. Considering the simplicity of the model, the slight difference between these values and those deduced experimentally is not surprising. The good overall agreement found with the experimental data is rather satisfactory (Figs. 1 and 2) and allows us to interpret the magnetic behavior at intermediate and low temperatures. In the range $T_m < T < T_{of}$, the magnetic state is a paramagnetic one with $\theta > 0$. There are two-thirds of NN pairs with different orbitals and hence a majority of FM exchanges ($J_{do} > 0$) so that the system behaves as if approaching a FM transition. Since $|J_{so}| > |J_{do}|$, at lower temperatures the links between the NN having identical orbitals are preferably satisfied (see Fig. 4c), inducing AF-like fluctuations because $J_{so} < 0$. This situation finally leads to a *magnetically frustrated* state in $LiNiO_2$ at low temperatures.

To conclude, an important outcome of our experimental results is that there are two distinct energy scales characteristic of the magnetism of $LiNiO_2$, which correspond to the antiferro-orbital coupling between Ni^{3+} ions in the NiO_2 layers and to their spin-spin interactions. The adjunction of two facts, orbital degeneracy of the Ni^{3+} ions and their triangular arrangement, leads to the buildup of a Wannier orbitally frustrated state below $T_{of} \simeq 400$ K. This uncommon orbital state is at the origin of the observed low-T complex magnetic behavior of $LiNiO_2$.

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