Planar spin exchange in LiNiO$_2$

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We study the planar spin exchange couplings in LiNiO$_2$ using a perturbative approach. We show that the inclusion of the trigonal crystal field splitting at the Oxygen sites leads to the appearance of antiferromagnetic exchange integrals in deviation from the Goodenough-Kanamori-Anderson rules for this 90 degree bond. That gives a microscopic foundation for the recently observed coexistence of ferromagnetic and antiferromagnetic couplings in the orbitally-frustrated state of LiNiO$_2$ (F. Reynaud et al, Phys. Rev. Lett. 86, 3638).

The compound LiNiO$_2$ which was first synthesized in 1958 [1] is known to be a good ionic conductor and therefore suitable as a material for rechargeable batteries. Despite its wide use as electrode material, its electronic and magnetic structures are not yet completely understood. Especially intriguing is the absence of any kind of long range magnetic or orbital order at low temperature even in the purest samples synthesized up to now. That is especially remarkable since the isostructural compound NaNiO$_2$ shows orbital order and a collective Jahn-Teller transition at $T_o = 480$ K from the trigonal high-temperature phase to the monoclinic low-temperature one, followed by an antiferromagnetic (AFM) order of ferromagnetic (FM) planes at the Néel temperature of $T_N = 20$ K [2, 3]. To explain the strange behavior of LiNiO$_2$ the proposal of an orbital liquid was pursued in terms of the SU(4) model [4, 5, 6]. There, a symmetry between orbital and spin degrees of freedom is assumed with equal amplitudes for the corresponding coupling terms. In reality, however, the energy scale for orbital interactions is one order of magnitude larger than those for spin exchange interactions as shown by experimental [3] and theoretical studies [9]. This is also indicated by the difference of those for spin exchange interactions as shown by experimental [3] and theoretical studies [9]. That gives a microscopic foundation for the recently observed coexistence of ferromagnetic and antiferromagnetic couplings in the orbitally-frustrated state of LiNiO$_2$ (F. Reynaud et al, Phys. Rev. Lett. 86, 3638).

The trigonal (rhombohedral) crystal structure $R3m$ of LiNiO$_2$ can be understood by starting from the cubic situation with oxygen and Ni/Li on the sites of the cubes, and with the cubic axes $\hat{x}$, $\hat{y}$, and $\hat{z}$. Perpendicular to the cube diagonal $z = \hat{x} + \hat{y} + \hat{z}$ in fig. 1 one finds alternating planes of Li, Ni, and O. The electronically active NiO$_2$ layer (see fig. 1) contains a triangular lattice of the magnetic Ni ions. The O$^{2-}$ ions have a completely filled 2p shell, whereas the Ni$^{3+}$ ion is in the low-spin electronic configuration $(t_{2g}^2 e_g^1)$ with spin 1/2 [3].

The trigonal distortion changes the bond angle from the ideal value of 90° to 94°, but the six neighbouring oxygens of Ni stay equivalent. Also the Ni $e_g$ orbitals remain degenerate, even in the trigonal crystal field. We now assume that we have some kind of orbital disorder that is frozen in for the triangular Ni lattice. The present knowledge does not conclusively predict in which way the orbital degeneracy is locally broken. Therefore, we have investigated two situations. The first case deals with orbitals that are oriented along the cubic axes: $d_{x^2-y^2}$ (0) and $d_{3z^2-r^2}$ (1). The second case chooses two complex combinations of the above orbitals that were predicted in Refs. [12, 13] and which have the advantage that they preserve the trigonal symmetry. We will now show that neglecting the crystal field splitting at the Oxygen sites one finds exclusively FM nearest neighbour exchange couplings. Due to the alternating stacking of Li and NiO$_2$ layers, however, one expects a considerable trigonal crystal field splitting of the O 2p orbitals (into one doublet and a singlet). That leads to the possibility of AFM exchange integrals in the Ni plane.

In the actual calculations we take the Hamiltonian in hole notation. The local part

$$H^0 = H^0_d + H^0_p$$

contains the Nickel contribution, which for one atom (omitting the site index) is given by

$$H^0_d = e_d \sum_m \hat{n}_{dm} + U_d \sum_m \hat{n}_{dm} \hat{n}_{dm} + \frac{U_d}{2} \sum_m \hat{n}_{dm} \hat{n}_{dm} - \frac{J_{Hd}}{2} \sum_m (2 \hat{S}_{dm} \hat{S}_{dm} + \frac{1}{2} \hat{n}_{dm} \hat{n}_{dm})$$

where $m$ and $\hat{m}$ stand for the two orthogonal $e_g$ orbitals. $U_d$ and $U_{di}$ are respectively the inter and intra-orbital Coulomb repulsions, which are equal when the Hund’s intra-atomic exchange $J_{Hd}$ is neglected. For an Oxygen atom
the local Hamiltonian is

\[ H_p^0 = \sum_n \epsilon_n \hat{n}_{pn} + U_p \sum_n \hat{n}_{pn\uparrow} \hat{n}_{pn\downarrow} + \frac{U_{pi}}{2} \sum_{n,n} \hat{n}_{pn} \hat{n}_{\bar{p}n} - \frac{J_{Hp}}{2} \sum_{n,n} \left( 2\hat{S}_{pn}\hat{S}_{\bar{p}n} + \frac{1}{2} \hat{n}_{pn} \hat{n}_{\bar{p}n} \right), \]

where \( n \) and \( \bar{n} \) are two of the three different 2p orbitals. \( U_p \) and \( U_{pi} \) are the intra and inter orbital Hubbard-like repulsions, respectively and \( J_{Hp} \) is the Hund’s exchange integral. It is well known for \( p \) as well as for \( e_g \) orbitals, using the definitions of \( U_i, U \) and \( J_H \) as Coulomb’s integrals, that one finds the general relation \( U_i = U - 2J_H \). However, the rotational symmetry at each site for degenerate orbitals demands an Hamiltonian of a more general form than the one used in eqs. (2, 3). One can keep the truncated parts as in eqs. (2, 3), but then one has to use instead the relation \( U_i = U - J_H \) to restore, in the case of degenerate orbitals, the invariance of the Hamiltonian under arbitrary rotation of the basis at each site.

The hopping term between Nickel and Oxygen involves the 6 O of the NiO$_6$ octahedra. Indexing the Ni site by \( x \), the Ni orbital by \( m \), the O site by \( i \), and the O orbital by \( n \), the hybridization part of the Hamiltonian reads

\[ H_{dp} = - \sum_{x,m,\sigma} \sum_{i,n} (t_{xm}^{\alpha\beta} p_{i\alpha\sigma}^\dagger d_{xm\sigma} + t_{ix}^{\alpha\beta} d_{xm\sigma}^\dagger p_{i\alpha\sigma}^\dagger), \]

where \( t_{ix}^{nm} = (t_{xi}^{mn})^* \). The hopping parameters are detailed below. Direct hopping between Ni is neglected. We evaluate the spin exchange between two Ni at the fourth-order in perturbation theory in the hopping parameters, looking for an effective Hamiltonian of the form

\[ H_{eff} = J_{mm'} \hat{S}_x \hat{S}_{x'}, \]

where \( m \) and \( m' \) are the orbital indices of the unpaired holes, \( x \) and \( x' \) the Nickel site labels. In hole representation, the 2p levels are empty, while there are three fermions per site in the \( e_g \) levels. If we neglect Hund’s local intra-orbital exchange \( J_{Hd} \) at Ni, we find in fourth-order perturbation theory the same processes that for the case of one fermion at each Ni site. To perform perturbation theory, we make no assumption about the orbital order, looking at all the possibilities for \( m \) and \( m' \), but we suppose that the orbital degree of freedom is frozen in the spin exchange process:
in the initial and final states the unpaired fermion on Ni is on the same \( m \) orbital. Neglecting \( J_{Hd} \), the result for the spin exchange is:

\[
J_{mm'} = \frac{4}{U_d} \left| \sum_n \frac{t_{mn}^m \bar{t}_{mn}^m}{\epsilon_n} \right|^2 \\
+ \frac{1}{\epsilon_n} \left( \frac{1}{\epsilon_n} + \frac{1}{\epsilon_n'} \right) \frac{1}{\epsilon_n + \epsilon_n' + U_p \delta_{nn'}} \\
+ \sum_n \frac{t_{mn}^m \bar{t}_{mn}^m}{\epsilon_n} \left( \frac{1}{\epsilon_n} + \frac{1}{\epsilon_n'} \right) \frac{1}{\epsilon_n + \epsilon_n' + U_p - J_{Hd}} \left( \frac{1}{\epsilon_n + \epsilon_n' + U_p + J_{Hd}} \right) \\
- \sum_n \frac{t_{mn}^m \bar{t}_{mn}^m}{\epsilon_n} \left( \frac{1}{\epsilon_n} + \frac{1}{\epsilon_n'} \right) \frac{1}{\epsilon_n + \epsilon_n' + U_p} \left( \frac{1}{\epsilon_n + \epsilon_n' + U_p + J_{Hd}} \right),
\]

where the energy needed to transfer a hole from Nickel to Oxygen is \( \epsilon_n = \epsilon_n - \epsilon_d - 2U_d \). For a Ni pair, sharing two Oxygen, 6 2p levels labelled by \( n \) are involved in the intermediate states. The sum on \( n \) enables to drop the Oxygen site index used in eq. (3), \( n \) and \( \bar{n} \) refer to two different orbitals of the same O site. The crystal field splitting at the Oxygen sites is taken into account through \( \epsilon_n = \Delta - \delta \) for two levels per Oxygen, and \( \epsilon_n = \Delta + \delta \) for the third one. The first term of eq. (4) implies a hopping of a hole from the first to the second Nickel; in the second process, the two holes jump to the same 2p orbital, or to two different Oxygen sites. The last two terms represent a process where the two holes meet on the same Oxygen, but on different orbitals, then the spin flip can act (fourth) or not (third). Including \( J_{Hd} \) one finds many additional terms involving spin-flip at the Ni sites. However these terms are typically smaller than the previous ones by factors of \( \frac{J_{Hd}}{U_d} \) or \( \frac{J_{Hd}}{\epsilon_n} \). We have explicitly checked that there is no qualitative change in the results when we add these terms for \( J_{Hd} \sim U_d/10 \).

Considering the exchange integrals for the usual \( e_g \) orbitals: \( d_{3z^2-r^2} \) (0) and \( d_{3z^2-r^2} \) (1) it can be seen from fig. 1 that not only the two Ni orbitals need to be specified, but also the particular Ni pair: this leads to 6 different spin exchange terms \( J_{00}, J_{01}, J_{01}, J_{01}, J_{11}, J_{11} \). The two degenerate 2p orbitals are labelled \( p_x \) and \( p_y \), the last one \( p_z \). In terms of the cubic \( p_x, p_y, \) and \( p_z \) orbitals they read

\[
p_x = \frac{1}{\sqrt{2}} (p_x - p_y), \quad (7a) \\
p_y = \frac{1}{\sqrt{6}} (p_x + p_y - 2p_z), \quad (7b) \\
p_z = \frac{1}{\sqrt{3}} (p_x + p_y + p_z) \quad (7c)
\]

The hopping parameters between the Nickel orbitals (0) and (1) and these Oxygen orbitals, depending on the O atom involved, can be obtained by linear combinations of the hopping integrals between the Ni orbitals and \( (p_x, p_y, p_z) \) which are specified in table I. An arabic index enables to distinguish between all the 6 Oxygen of the NiO\(_6\) octahedra, in correspondence with fig. 1.

The parameters \( U_d = 9.5 \) eV, \( U_p = 4.6 \) eV, and \( t_0 = 1.3 \) eV were taken from Ref. [16]. The charge transfer energy \( \Delta = 4 \) eV was roughly estimated from the difference of the centers of gravity of the 3d and 2p levels in a bandstructure.
calculation [17], which allows also to estimate the crystal field splitting $\delta$ from the bandwidth of the upper $3d_{eg}$ band. Namely, for $\delta = 0$ and only nearest neighbour hopping in the tight-binding Hamiltonian (eq. (4)), the bandwidth would be zero. We obtained a value for $\delta$ of about 1 eV, but we keep $\delta$ here as a parameter. The result for the different spin exchange couplings as a function of the crystal field splitting $\delta$ is presented in fig. 2. For $\delta = 0$, the only contribution to exchange is from $J_{Hp}$ ($J_{Hp} = U_p/10$). We used $U_{pi} = U_p - J_{Hp}$ (see above). A splitting of $|\delta| \approx 0.5$ eV can change the ferromagnetic character into an antiferromagnetic one for the exchange integrals $J_{\parallel 00}$, $J_{\perp 11}$, and $J_{\parallel 11}$. (The exchange coupling $J_{\perp 00}$ is identical to zero in the present approximation.) The exchange terms between different orbitals $J_{\perp 01}$ and $J_{\parallel 01}$ stay ferromagnetic (see Ref. [3]).

It seems as if an antiferromagnetic exchange integral between equal orbitals is in contradiction with the existence of ferromagnetic planes in NaNiO$_2$. One should keep in mind however that the low temperature phase of NaNiO$_2$ is not trigonal but has a large monoclinic distortion which leads to a different crystal field splitting at Oxygen. One could speculate that the monoclinic distortion in this compound can be described in our calculations by a reduced effective parameter $\delta_{eff}$ shifting all the exchange integrals into the ferromagnetic region.

At present there is no experimental indication for macroscopic Jahn-Teller distortions of the trigonal crystal structure of LiNiO$_2$ even at very low temperature. Therefore it is tempting to search for an orbitally-frustrated state in terms of orbitals that obey the trigonal crystal symmetry. For that purpose, noting that the $e_g$ stay degenerate, we can use instead of $d_{\tilde{x}^2-\tilde{y}^2}$ and $d_{3\tilde{z}^2-r^2}$ any linear and orthogonal combination of these two. The particular choice

\[
\begin{align*}
    d_\alpha & = \frac{1}{\sqrt{2}}(d_{\tilde{x}^2-\tilde{y}^2} + id_{3\tilde{z}^2-r^2}), \\
    d_\beta & = \frac{1}{\sqrt{2}}(d_{\tilde{x}^2-\tilde{y}^2} - id_{3\tilde{z}^2-r^2})
\end{align*}
\]

(8a) (8b)

corresponds to orbitals which satisfy the trigonal symmetry: under a rotation of $\frac{2\pi}{3}$ around the axis perpendicular to the Ni plane (fig. 1), these states are just changed by a phase factor. These complex orbitals were previously proposed for manganites [11, 12, 13]. It cannot be a priori excluded that also in LiNiO$_2$ one of these complex orbitals is preferred at each Ni site.

In terms of these new orbitals the calculations get simpler: there are only two different exchange integrals: $J_s = J_{\alpha\alpha} = J_{\beta\beta}$ and $J_d = J_{\alpha\beta}$, and there is no need to consider different Ni pairs, due to the trigonal symmetry. However
it is not possible to establish a simple link between these two new exchange terms, and the 6 previously studied: this is due to freezing the orbital degree of freedom in the calculation of the spin exchange. Using the transformation and the table one can easily specify the hopping for complex orbitals to be inserted in eq. (6).

The results are presented in fig. 3. At the same critical value as in fig. 2, the sign of \( J_d \) changes to an AFM coupling for large \( \delta \). But now, the effect is reversed in comparison to fig. 2 or Ref. [3], it is the exchange between different orbitals that becomes antiferromagnetic.

In the basis of complex orbitals, we can also consider the pseudospin exchange. Due to pseudospin anisotropy, there are many terms in the effective Hamiltonian involving the pseudospin operators. These terms are usually of the order of \( U_{p,t}/(\Delta^3(2\Delta + U_p)) \) for \( \delta = 0 \). This confirms that they are larger than the spin exchange terms characterized by \( J_{Hp} \). We have considered more in details the \( z \) component of the pseudospin exchange which corresponds to a term \( J_{Tz}^iT_{Tz}^j \) for a pair of Ni sites labelled by \( i \) and \( j \), with \( T^z = +(-)\frac{1}{2} \) depending of the orbital involved \( d_\alpha (d_\beta) \). We suppose that the spin degree of freedom is frozen at each site. Somewhat surprisingly when the Hund’s exchange term for Oxygen, as well as as the splitting of the \( 2p \) levels are neglected, we obtain that \( J_{Tz}^z = 0 \), indepently of the spins. That shows the highly anisotropic character of the pseudospin exchange. But one should note that this result is not in contradiction with the results from Mostovoy and Khomskii (who found a positive value for the orbital exchange) since they analysed the usual \( d_{3z^2-r^2} \) and \( d_{4z^2-r^2} \) orbitals which are eigenstates of the \( T^z \) pseudospin operators in the present basis. The pseudospin-rotational symmetry being not required as for spin, the result \( J_{Tz}^z = 0 \) does not rule out a pseudospin exchange along the others directions. The evaluation of other pseudospin-pseudospin or pseudospin-spin coupling terms will be detailed in a forthcoming paper using an alternative method with a direct diagonalization of the hopping part of the Hamiltonian which enables to evaluate the different terms in a more direct way.

In conclusion, we have shown that a proper inclusion of the trigonal crystal field splitting at the Oxygen sites of \( \text{LiNiO}_2 \) leads to a coexistence of AFM and FM couplings. Orientating the orbitals along the cubic axes we find AFM couplings between equal orbitals and FM couplings between different ones, which is at least in qualitative agreement with the analysis of Ref. [3]. Investigating the orbital symmetry breaking in \( \text{LiNiO}_2 \) in terms of complex orbitals is fascinating from the point of view of symmetry: one has only 2 orbitals and 2 different exchange couplings. Also in that case we found a coexistence of FM and AFM couplings which may explain the absence of magnetic long range order at low temperature in \( \text{LiNiO}_2 \). But the actual signs of exchange between different and equal orbitals are just reversed in comparison with the analysis of Ref. [3].

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