Modelling noncollinear spin structure in YNiO₃ perovskite: a GGA+U APW approach

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Abstract. In this work we compute the magnetic spin structure of the YNiO₃ perovskite using the noncollinear APW implementation of WIEN2K. We compare LDA+U, GGA+U results to experimental results and find an improvement in comparison to previous theoretical work supposing an antiferromagnetic collinear alignment of the magnetic momenta.

1. Introduction

The perovskite system \( RNiO_3 \) (where \( R \) is a trivalent rare earth) is a very attractive family of compounds around which intense research activity has been recently developed, see [1-3] for instance. This family of materials is particularly interesting because it exhibits structural and metal-insulator phase transitions around room temperature, especially when doped with some rare earths. This allows for instance to modulate the amount of infrared radiation transmitted as a function of temperature, with potential applications in defense (infrared stealth) or building (smart windows which let heat in winter and out in summer).

In this work we will compute \textit{ab initio} the magnetic structure of \( YNiO_3 \). Due to nonmagnetic character of \( Y \), the magnetic properties of the \( Ni \) lattice can be studied in \( YNiO_3 \) without interference with other magnetic species.

Magnetic properties of transition metals compounds, especially oxides, have become a subject of intensive research, both from the experimental and theoretical point of view. One of the most challenging and interesting aspects of that field is the subtle interplay between magnetic ordering and geometric structure. Finite size effects and a reduced dimensionality often lead to a significantly different magnetic behavior.

Noncollinear magnetism is manifested in a wide variety of substances. Those compounds can be ferromagnetic (FM), where the spins are aligned in parallel directions; antiferromagnetic (AFM), where the spins are antiparallel; or noncollinear, where the spins are not parallel and may be disordered. Noncollinear magnetism can arise naturally due to geometric frustration of AFM interactions. Other effects also giving rise to noncollinear magnetism include magnetic anisotropy,
which arises due to a parallel direction of magnetization. Finally, the competition between exchange interaction and magnetic anisotropy also contributes to noncollinear magnetism [4].

In this paper we study the noncollinear spin structure of this nickelate and compare it to experimental data. This structure can serve as a benchmark to check previous computations restricting to collinear configurations.

2. Previous results

2.1. Experimental facts

At high temperatures, \( YNiO_3 \) is orthorhombic and metallic but below \( T_{MI} = 582K \) it changes to a monoclinic insulator due to a charge disproportionation \( 2Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+} \), that develops at the opening of the gap. Crystallographic studies combining X-ray diffraction and neutron diffraction [5] have shown the presence of two alternating \( NiO_6 \) octahedra, with expanded \( Ni \) and contracted \( Ni \) octahedra. \( YNiO_3 \) systems contains four \( Ni \) ions in its crystallographic unit cells and each locates on the inversion center. Four \( Ni \) sites are labeled as \( Ni (\frac{1}{2},0,0) \), \( Ni (0,\frac{1}{2},0) \), \( Ni (0,0,\frac{1}{2}) \), \( Ni (0,\frac{1}{2},\frac{1}{2}) \). In \( YNiO_3 \), no symmetry operations transfer a position \( Ni (\frac{1}{2},0,0) \) or \( Ni (0,\frac{1}{2},0) \) to that of \( Ni (0,0,\frac{1}{2}) \) or \( Ni (0,\frac{1}{2},\frac{1}{2}) \). Therefore, there are two inequivalent positions of \( Ni \) ions in \( YNiO_3 \). The structure of \( YNiO_3 \) is shown on Fig. 1 and Fig. 2 (graphics were generated by \( XCrySDen \) [6]).

Fig. 1.: Unit cell of \( YNiO_3 \) (obtained by \( XCrySDen \) [6]).
Finally, we shall focus on the magnetic structure. The experimentally observed magnetic moments are $\pm 1.4 \mu_B$ for $Ni^{2+}$ ions and $\pm 0.7 \mu_B$ for $Ni^{4+}$ ions [5]. The charge disproportionation is mainly due to the crystal field effect. $YNiO_3$ are antiferromagnetic insulators in their low temperature phases. The spin alignment in these two nickelates is quite unique one such that the symmetrical coexistence of ferro- and antiferromagnetic couplings along the three pseudocubic axes:

$$\cdots Ni \uparrow - O - Ni \uparrow - O - Ni \downarrow - O - Ni \downarrow \cdots$$

In $YNiO_3$, the charge disproportionation $2Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+}$ and the symmetrical coexistence of ferro- and antiferromagnetic couplings are observed, though the $Ni^{4+}$ ions have small magnetic moments.

2.2. Previous theoretical work

Previous work on the present class of materials has been performed using typically the LSDA+U approach in an antiferromagnetic setting, using a supercell, and the LMTO-ASA approximation. This calculation results in a band structure with insulating and metallic characteristics for monoclinic and orthorhombic phases, respectively [7,8] with gap $E_g = 1.03 eV$ for the insulating phase. This corresponds more or less to experimental results [3] obtained on closely related compounds, exhibiting however some dispersion due to the measuring method (four points methods or optical methods). In those works, however, the magnetic moments for one of the nickel species come out as zero, in contradiction with experimental results. Some authors have also studied the effect of cell parameters on the conducting characteristics of related materials in order to understand thin film or pressure effects, or optimized the oxygen positions within the LDA or LDA+U picture, getting magnetic momenta closer to experimental results of [5].

3. Theoretical choices

An essential difference between collinear and noncollinear magnetism is that the latter lacks a global spin quantization axis. In the case of noncollinear magnetism a solution is to follow Von Barth and Hedin [10] formulation of DFT and Kohn-Sham equations: adopt the spinor formalism and work with $2 \times 2$ matrixes for the operators as done in [11,12] for instance.
3.1. Noncollinear Density Functional Theory
The one-electron Hamiltonian-like Kohn-Sham operator for magnetic systems can be approximated
from Dirac’s equation in the non relativistic case by:
\[
h_i = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}} + \mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}} + \zeta \hat{L} \cdot \vec{I},
\]
where the scalar product $\mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}}$ expresses the interaction of spins with effective magnetic field,
$\zeta \hat{L} \cdot \vec{I}$ express the spin-orbit coupling.
In this case, the Schrödinger-like equation appears as:
\[
h \begin{pmatrix} \psi_{i1} \\ \psi_{i2} \end{pmatrix} = \varepsilon_i \begin{pmatrix} \psi_{i1} \\ \psi_{i2} \end{pmatrix},
\]
where the one-electron Kohn-Sham wavefunction is a 2–component vector (spinor): $\psi_{i1}$ – spin up component, $\psi_{i2}$ – spin down component.
Effective potential is sum of external and exchange-correlation potential:
$V_{\text{eff}} = V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}},$
where $V_{\text{H}}$ is the Hartree potential.
Effective magnetic field is sum of external and exchange-correlation fields:
$\vec{B}_{\text{eff}} = \vec{B}_{\text{ext}} + \vec{B}_{\text{xc}}.$
In the density functional formalism, the exchange-correlation potential and magnetic exchange-correlation vector field are defined as functional derivatives:
$\n = \frac{\partial E_{\text{xc}}}{\partial n} \hat{m},$
and
$\bar{B}_{\text{xc}} = \frac{\partial E_{\text{xc}}}{\partial \bar{m}} \hat{m},$
where $n$ is the a spin density and $\bar{m}$ is a charge densities vector.
In a noncollinear case $\bar{m}$ varies in space. Furthermore, all three components of the scalar products
$\mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}}$ have to be taken into account. Note that $\sigma_z = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ and the potential matrix is of the form:
$\hat{V} = V_{\text{eff}} I + \bar{B}_{\text{eff}} \vec{\sigma} = \begin{pmatrix} V_{\text{eff}} + \mu_B B_z & \mu_B \left( i B_x - i B_y \right) \\ \mu_B \left( i B_x + i B_y \right) & V_{\text{eff}} - \mu_B B_z \end{pmatrix}.$

The diagonalization can not be performed for up and down spins, separately. The total matrix in spin space ($2 \times 2$) must be setup and locally diagonalized. In this case, complex basis functions are necessary.

We can write the Schrödinger-like equation as:
\[
\begin{pmatrix} -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}} + \mu_B B_z + ... \\ \mu_B \left( i B_x + i B_y \right) \end{pmatrix} \begin{pmatrix} \psi_{i1} \\ \psi_{i2} \end{pmatrix} = \varepsilon_i \psi_i.
\]
Here we have noncollinear magnetic moment and solutions can be non-pure spinors:
$\psi_i = \begin{pmatrix} \psi_{i1} \\ \psi_{i2} \end{pmatrix}, \psi_{i1}, \psi_{i2} \neq 0.$
The local spin density matrix in a noncollinear system has the form:
\[
\rho_{\alpha\beta} = \frac{1}{2} n_i^\alpha + a m_i + \frac{1}{2} \left( n_i^\alpha + m_i - n_i^\beta - m_i \right). 
\]

The space dependent spin density matrix contains all the information necessary to describe the magnetic state of the considered material. In a collinear calculation, \( m_i \) and \( m_i \) are zero, thus \( \rho_{\alpha\beta} \) is diagonal. In the non magnetic case \( m_i \) is zero thus \( \uparrow \uparrow \) and \( \downarrow \downarrow \) parts are the same [12]. Magnetic moments are estimated as the quantum mechanical average over all electrons summed up in a sphere of arbitrary radius centered around each atom.

### 3.2. Numerical choices

*Mainten* calculations were performed by the WIEN2k and WIENncm program package [13,14], based on the density functional theory in the local density approximation (LDA) and the generalized-gradient approximation (GGA), and on-site U corrections. In this case, we can note that for instance the presumably faster. QuantumESPRESSO pseudopotential program package has not been used because noncollinear calculations can not be combined with LDA+U. However, WIEN2k and WIENncm program packages work perfectly in this case, although quite slowly because all electrons are taken into account. The interest of WIEN2k consists in the high accuracy of the results and the capacity to compute effects linked to the core electrons, such as NMR or Mössbauer parameters. Calculations were based on the crystallography parameters reported by Alonso and al [5,15]: monoclinic space group \( P2_1/n \), \( a = 9.7875 \text{ bohr} \), \( b = 10.4224 \text{ bohr} \), \( c = 14.0152 \text{ bohr} \), \( \beta = 90.081 \text{ } \). It is interesting to note that the \( P2_1/n \) symmetry there are two crystallographically independent \( Ni \) positions (\( Ni(\text{c}) \) and \( Ni(\text{c}) \)), as well as three nonequivalent oxygen atoms (\( O_{\text{c}} \), \( O_{\text{c}} \) and \( O_{\text{i}} \)) all in general (\( x,y,z \)) positions. Parameters used in the calculation are presented in Table 1:

| Atom | Site | \( x \) | \( y \) | \( z \) |
|------|------|------|------|------|
| Y    | 4e   | 0.9816(2) | 0.0729(1) | 0.2502(4) |
| Ni(1)| 2d   | 0.5  | 0    | 0    |
| Ni(2)| 2c   | 0.5  | 0    | 0.5  |
| O(1) | 4e   | 0.0998(3) | 0.4705(3) | 0.2457(5) |
| O(2) | 4e   | 0.6973(7) | 0.3080(7) | 0.0467(5) |
| O(3) | 4e   | 0.1882(6) | 0.2038(7) | 0.9465(5) |

In addition, we adopted in the calculations: lattice type: \( P \), number of inequivalent atoms in unit cell: 12, number of equivalent atoms: 2 for \( Y \), 1 for \( Ni \), 2 for \( O \), number of radial mesh points: 781, first radial mesh point: \( R_0 = 0.000010000 \) for \( Y \), \( R_0 = 0.000050000 \) for \( Ni \), \( R_0 = 0.000100000 \) for \( O \), atomic sphere radius: \( RMT = 2.23000 \) for \( Y \), \( RMT = 1.89000 \) for \( Ni \) (the same radius used to compute the magnetic momenta), \( RMT = 1.68000 \) for \( O \).

We asked for simultaneous charge convergence to 0.00001 units and force convergence to 1.0mRy/bohr. SCF was run with \( RK_{\text{max}} = 6 \) and 8 k-points in irreducible Brillouin zone.

In order to describe the strong electronic correlation of the material, we use as other authors a phenomenological on-site Hubbard like correction within the LDA+U or GGA+U formalism. [12-14]. The values of \( U \) and \( J \) were fixed close to received value from the literature for this family of compounds, namely at \( U = 5eV \) and \( J = 0eV \). We could check after the SCF a resulting estimated \( U \) of 4.7 eV, so that the procedure is almost self-coherent. A trial doubling of the number of k-points in the irreducible Brillouin zone did not change this result significantly, so we kept it at 8 to limit
computational time. All the calculations were performed on the 10 core Linux computational cluster of LPEC laboratory.

4. Results and discussion
Results are summarized on Table 2, where we compare the results of using the LDA+U and GGA+U methods as implemented in the WIENncm package:

Table 2. Magnetic moments on nickel atoms in YNiO$_3$.

| Ions  | Experiment | LDA+U | GGA+U |
|-------|------------|-------|-------|
| $Ni^{2+}$ | ±1.4$\mu_B$ | ±1.6$\mu_B$ | ±1.6$\mu_B$ |
| $Ni^{4+}$ | ±0.7$\mu_B$ | ±0.2$\mu_B$ | ±0.8$\mu_B$ |

Experimental data from Ref. 5.

Analyzing the results, it can be concluded, that the results closer to experiments are given by the GGA+U method, which is not surprising due to the fact that GGA+U has been developed to depend explicitly on the gradient of the density in addition to the density itself. However, the LDA+U method is the least computationally demanding approach.

One can note that the results are better than the ones of [15], which were using an AFM collinear modeling of the system with a large supercell, and could only reproduce the momenta of one of the nickel species ($Ni^{2+}$), finding a null momentum for the other species, and closer to experiment than the ones of [9] which find momenta of 1.25 and 0.28 $\mu_B$.

Alltogether, the magnetic structure of YNiO$_3$ that we computed can be observed on Fig. 3 and 4.

Fig. 3. Magnetic unit cell of YNiO$_3$ (obtained by struct2x).
The compounds can be ferromagnetic (FM), where the spins are aligned in parallel directions; antiferromagnetic (AFM), where the spins are antiparallel. This system is noncollinear, where the spins are not parallel and are partially disordered.

In large distorting perovskite such as $\text{YNiO}_3$, the charge disproportionation $2\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+}$ occurs. The charge ordering mechanism can explain the stabilization of the local magnetic moments around each nickel site.

5. Conclusion

In summary, we have studied the magnetic properties of the Ni lattice in the insulator $\text{YNiO}_3$. The GGA+U calculations gives the best results for magnetic moments, close to experimental results and improving previous studies supposing antiferromagnetic collinear order. Further work could be done to study the effects of cell distortion on the magnetic order, to simulate epitaxied thin films effects or pressure effects; a fully self-consistent GGA+U procedure could also be tried. The whole family of compounds could be studied and compared to experimental results for the Nd substitution for instance where experimentalists using resonant soft x-ray diffraction also suspect a noncollinear spin structure [16].

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