



J dependence in the LSDA+*U* treatment of noncollinear magnets

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We re-examine the commonly used density-functional theory plus Hubbard *U* (DFT+*U*) method for the case of noncollinear magnets. While many studies neglect to explicitly include the exchange-correction parameter *J*, or consider its exact value to be unimportant, here we show that in the case of noncollinear magnetism calculations the *J* parameter can strongly affect the magnetic ground state. We illustrate the strong *J* dependence of magnetic canting and magnetocrystalline anisotropy by calculating trends in the magnetic lithium orthophosphate family LiMPO₄ (*M*=Fe and Ni) and difluorite family MF₂ (*M*=Mn, Fe, Co, and Ni). Our results can be readily understood by expanding the usual DFT+*U* equations within the spinor scheme, in which the *J* parameter acts directly on the off-diagonal components which determine the spin canting.

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Density-functional theory (DFT) within the local-density (LDA) and generalized gradient (GGA) approximations is widely used to describe a large variety of materials with good accuracy. The LDA and GGA functionals often fail, however, to correctly reproduce the properties of strongly correlated materials containing *d* and *f* electrons. The LDA+*U* approach—in which a Hubbard *U* repulsion term is added to the LDA functional for selected orbitals—was introduced in response to this problem and often improves drastically over the LDA or GGA. Indeed, it provides a good description of the electronic properties of a range of exotic magnetic materials, such as the Mott insulator KCuF₃ (Ref. 1) and the metallic oxide LaNiO₂.²

Two main LDA+*U* schemes are in widespread use today. The Dudarev³ approach in which an isotropic screened on-site Coulomb interaction $U_{eff}=U-J$ is added and the Liechtenstein¹ approach in which the *U* and exchange (*J*) parameters are treated separately. The Dudarev approach is equivalent to the Liechtenstein approach with $J=0$.⁴ Both the effect of the choice of LDA+*U* scheme on the orbital occupation and subsequent properties like the electronic band gap,^{5,6} as well as the dependence of the magnetic properties on the value of *U* and *J*,^{7,8} have been analyzed. There has been no previous systematic study, however, of the effect of the *J* parameter of the Liechtenstein approach in noncollinear magnetic materials. Here we show that neither the approach of not explicitly considering the *J* parameter (as in the Dudarev implementation) nor the assumption that its importance is borderline—a common approximation is to use $J \approx 10\% U$ without careful testing—within the Liechtenstein implementation are justified in the case of noncollinear magnets. We demonstrate that in the case of noncollinear antiferromagnets, the choice of *J* can strongly change the amplitude of the spin canting angle (LiNiPO₄) or even modify the easy axis of the system (LiFePO₄ and FeF₂), with consequent drastic effects on the magnetic susceptibilities and magneto-electric responses.

First we remind the reader how the *U* and *J* parameters appear in the usual collinear spin (local spin density approximation) LSDA+*U* formalism. The LSDA+*U* reformulation

of the LSDA Hamiltonian is usually written as

$$H_{\text{LSDA}+U} = H_{\text{LSDA}} + H_U \quad (1)$$

with

$$H_U^\sigma = \sum_{m_1, m_2} P_{m_1, m_2} V_{m_2, m_1}^\sigma, \quad (2)$$

where *P* is the projection operator, σ is the spin index, and (on a given atomic site)

$$V_{m_2, m_1}^{\uparrow(\downarrow)} = \sum_{3,4} (V_{1,3,2,4}^{ee} - U\delta_{1,2} - V_{1,3,4,2}^{ee} + J\delta_{1,2}) n_{3,4}^{\uparrow(\downarrow)} + (V_{1,3,2,4}^{ee} - U\delta_{1,2}) n_{3,4}^{\downarrow(\uparrow)} + \frac{1}{2}(U - J)\delta_{1,2}. \quad (3)$$

Here $V_{1,3,2,4}^{ee} = \langle m_1, m_3 | V_{m_1, m_3, m_2, m_4}^{ee} | m_2, m_4 \rangle$ are the elements of the screened Coulomb interaction, which can be viewed as the sum of Hartree (direct) contributions $V_{1,3,2,4}^{ee}$ and Fock (exchange) contributions $V_{1,3,4,2}^{ee}$ and $n_{i,j}^\sigma$ are the *d*-orbital occupancies.

In the case of noncollinear magnetism, the formalism is extended and the density is expressed in a two-component spinor formulation

$$\rho = \begin{pmatrix} \rho^{\uparrow\uparrow} & \rho^{\uparrow\downarrow} \\ \rho^{\downarrow\uparrow} & \rho^{\downarrow\downarrow} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} n + m_z & m_x - im_y \\ m_x + im_y & n - m_z \end{pmatrix}, \quad (4)$$

where *n* is the charge density and m_α the magnetization density along the α direction ($\alpha=x, y, z$). Using the double counting proposed by Bultmark *et al.*,⁸ the LSDA+*U* potential is then also expressed in the two-component spin space as

$$V_{i,j} = \begin{pmatrix} V_{i,j}^{\uparrow\uparrow} & V_{i,j}^{\uparrow\downarrow} \\ V_{i,j}^{\downarrow\uparrow} & V_{i,j}^{\downarrow\downarrow} \end{pmatrix}, \quad (5)$$

where $V^{\uparrow\uparrow}$ and $V^{\downarrow\downarrow}$ are equal to Eq. (3) and

$$V_{m_2, m_1}^{\uparrow(\downarrow)\uparrow(\downarrow)} = \sum_{3,4} (-V_{1,3,4,2}^{ee} + J\delta_{1,2}) n_{3,4}^{\uparrow(\downarrow)\uparrow(\downarrow)}. \quad (6)$$

TABLE I. Experimental cell parameters (\AA) used in the simulations of LiMPO_4 phosphates and MF_2 difluorites.

	a	b	c	Ref.
LiFePO_4	10.332	6.010	4.692	12
LiNiPO_4	10.032	5.854	4.677	13
NiF_2	4.650	4.650	3.084	14
FeF_2	4.700	4.700	3.310	15
MnF_2	4.650	4.650	3.084	16
CoF_2	4.695	4.695	3.179	17

For collinear magnets, only $V^{\uparrow\uparrow}$ and $V^{\downarrow\downarrow}$ [Eq. (3)] are relevant since $n^{\uparrow\downarrow}$ and $n^{\downarrow\uparrow}$ are equal to zero and J affects the potential mainly through an effective $U-J$. However, in the case of noncollinear magnetism, the $n^{\uparrow\downarrow}$ and $n^{\downarrow\uparrow}$ and hence the $V^{\uparrow\downarrow}$ and $V^{\downarrow\uparrow}$ [Eq. (6)] are nonzero. Then it is clear from Eq. (6) that J acts explicitly on the off-diagonal potential components.

Next, we show the effect of the choice of J parameter in the family of lithium orthophosphates, LiMPO_4 ($M=\text{Ni}$ and Fe) and in the family of difluorites MF_2 ($M=\text{Mn}$, Co , Fe , and Ni). The orthophosphates crystallize in the orthorhombic $Pnma$ space group with C -type antiferromagnetic (AFM) order. The difluorites crystallize in the tetragonal $P4_2/mnm$ rutile structure with AFM order. We performed calculations within the Liechtenstein approach of the LSDA+ U as implemented in the VASP code⁹⁻¹¹ with U and J corrections applied to the $3d$ orbitals of the M cations. We performed all calculations (both relaxations of the ionic positions and calculations of the subsequent properties) for spin-polarized configurations with spin-orbit coupling explicitly taken into account. In each case we relaxed the atomic positions until the residual forces on each atom were lower than $10 \mu\text{eV}/\text{\AA}$. The volume and cell shape were held fixed at the experimental values as reported in Table I. We found good convergence of the noncollinear spin ground state with a cutoff energy of 500 eV on the plane-wave expansion and a k -point grid of $2 \times 4 \times 4$ for the orthophosphates and $4 \times 4 \times 6$ for the difluorites.

First, we focus on LiNiPO_4 , which is known experimentally to be C -type AFM, with an easy axis along the c direction and a small A -type AFM canting of the spins along the a direction ($C_z A_x$ ground state with $mm'm$ magnetic point group).¹⁸ Performing calculations within the LSDA+ U method with $J=0$, we find that we correctly reproduce the $C_z A_x$ ground state with a rather small U sensitivity of the magnetocrystalline anisotropy energy (MCAE) and the spin canting; this finding is consistent with a previous report using the GGA functional.¹⁹ However, our calculated canting angle of 1.6° for $U=5$ eV and $J=0$ eV severely underestimates the experimental value of 7.8° .¹⁸ In Fig. 1(a) we show the evolution of the canting angle with J at $U=5$ eV. We find that the canting angle is extremely sensitive to the value of J —in fact it is $\propto J^3$ —changing from 1.6° at $J=0$ eV to 7.8° at $J=1.7$ eV. To reproduce the experimental value of the canting angle we need to use the surprisingly large J value for Ni^{2+} of 1.7 eV.²⁰ The dependence of the canting angle on J is consistent with Eq. (6), as the off-diagonal

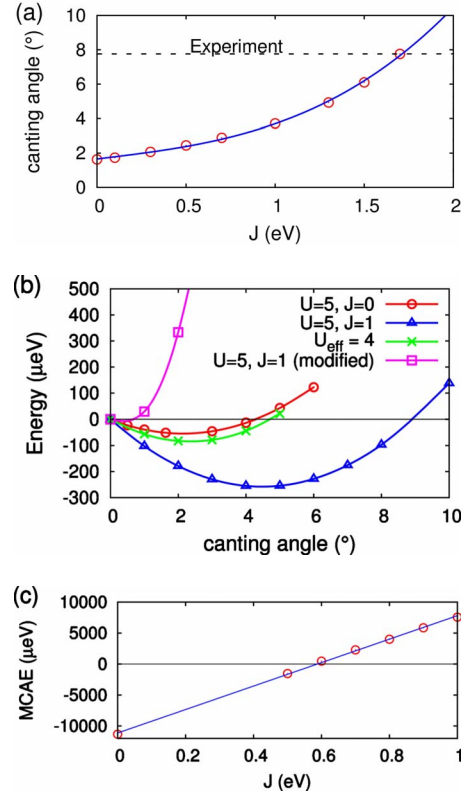


FIG. 1. (Color online) (a) Calculated LSDA+ U canting angle of LiNiPO_4 versus J for $U=5$ eV. The experimental value of the canting angle is equal to 7.8° (Ref. 18). (b) Energy versus canting angle in LiNiPO_4 for $U=5$ eV and $J=0$ eV (red circles), $U=5$ eV and $J=1$ eV (blue triangles), $U_{\text{eff}}=4$ eV (green crosses), and $U=5$ eV and $J=1$ eV but by fixing $J=0$ eV in Eq. (6) (pink squares). The zero-energy reference is chosen at zero canting angle. (c) MCAE between the a and b orientations of the magnetic moments of LiFePO_4 . The experimental b orientations is taken as energy reference.

elements $n^{\uparrow\downarrow}$ and $n^{\downarrow\uparrow}$ are nonzero when the spins cant away from the easy axis.

In Fig. 1(b) we report the energy versus the canting angle in LiNiPO_4 for $U=5$ eV and different values of J . We see that as J is increased from $J=0$ eV to $J=1$ eV (red circles and blue triangles) the minimum of the energy shifts to larger canting angle with a stronger gain of energy with respect to the uncanted reference. When performing the same calculation with $U_{\text{eff}}=4$ eV (green crosses in Fig. 1) we obtain results that are very similar to the case $U=5$ eV and $J=0$ eV, which is formally equivalent to the Dudarev approach with $U_{\text{eff}}=5$ eV. These comparisons confirm that varying U has a minimal effect on the canting angle in LiNiPO_4 and also that the use of the Liechtenstein treatment of J is extremely important. To further confirm the direct relationship between the spin canting and the J parameter, we performed the same calculations with $U=5$ eV and $J=1$ eV but we artificially fixed $J=0$ eV only in Eq. (6) [pink squares in Fig. 1(b)]. We clearly see that the energy versus canting angle is strongly affected by this modification and, in fact, the canting is almost removed.

Similar J dependence of the canting angle was also re-

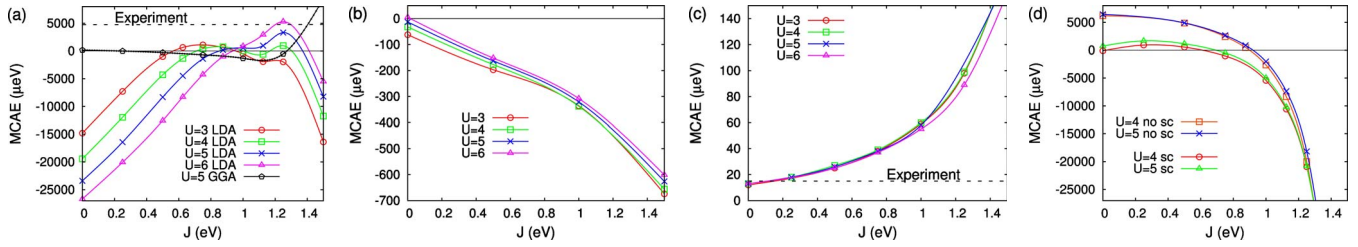


FIG. 2. (Color online) Magnetocrystalline anisotropy energy versus the J parameter of (a) FeF_2 (experimental value from Ref. 22), (b) NiF_2 , (c) MnF_2 (experimental value from Ref. 23), and (d) CoF_2 (“sc” are calculations with Co semicores while “no sc” are calculations without Co semicores). The MCAE reported here is the energy between the a and c orientations of the spins, the energy of the c orientation is taken as reference.

ported previously for Ni^{2+} in BaNiF_4 ;²¹ in Ref. 21 it was found that at $U=5$ eV, the canting varies from 2° to 3° when J is varied from 0 to 1 eV. In both LiNiPO_4 and BaNiF_4 the Ni ion is divalent, with a d^8 configuration, and octahedrally coordinated. To investigate the generality of this behavior, we next consider the case of the canted-spin antiferromagnet NiF_2 , in which the Ni ion is in the same coordination environment as in BaNiF_4 . Experimentally, NiF_2 has the spins aligned preferentially in the plane perpendicular to the c axis with a slight canting from antiparallel alignment by an estimated $\sim 0.5^\circ$ at low temperatures.¹⁴ Performing LSDA+ U calculations at the experimental volume and with $U=5$ eV and $J=0$ eV we indeed obtain the easy axis perpendicular to the c axis and a small canting of 0.3° , in excellent agreement with the experiments. In contrast to the case of LiNiPO_4 , however, we find that the amplitude of the canting angle is almost insensitive to the value of J with just a small tendency to be reduced when J increased. This insensitivity of the canting angle to the value of J in NiF_2 can be understood from the fact that in this compound the magnetism is almost collinear, and therefore the off-diagonal elements of the occupation matrix, $n^{\uparrow\downarrow}$ and $n^{\downarrow\uparrow}$, are close to zero. Inspection of Eq. (3) then shows that the effect of J is reduced largely to the diagonal part of the potential where the U parameter is dominant.

To summarize our findings for the Ni-based compounds, in cases where the experimental canting is large (2° – 3°) we find a strong J dependence of the canting angle, which increases with increasing J ; when the canting is weak experimentally the J dependence is much weaker. We note that at the LSDA relaxed volume, in LiNiPO_4 we obtain a reduction in the volume of 5.65% with respect to the experimental value which corresponds to an equivalent hydrostatic pressure of 6.2 GPa. At this smaller volume the canting angle is enhanced (2.7° at $U=5$ eV and $J=0$ eV). As reported in Ref. 24 the increase in the canting angle can enhance the magnetoelectric response in LiNiPO_4 , playing with pressure can then be a possibility to tune the magnetoelectric response.

Next we analyze the effect of J on the behavior on the corresponding divalent iron compounds. We begin with LiFePO_4 , which is known experimentally to be a C -type AFM with an easy axis along the b direction and no observed canting of the spins^{25,26} (C_y ground state with mmm' magnetic point group). Our calculations within the LSDA+ U functional at the commonly used values of $U=4$ eV and J

$=0$ eV for Fe^{2+} yield the correct C -type AFM order but find the easy axis incorrectly along the a direction. Now we switch to $J \neq 0$ eV and report in Fig. 1(c) the MCAE between the b and a directions, calculated by turning all the spins homogeneously from the C_y to the C_x direction. We find that the MCAE is approximately linear with J but with rather dramatic qualitative dependence: while at $J=0$ eV the easy axis is along the a direction (negative MCAE) the MCAE is almost reduced to zero around $J=0.5$ eV and the easy axis changes to the b direction for $J \geq 0.5$ eV (positive MCAE). To reproduce the experimental easy axis (C_y) a value of J greater than 0.58 eV is required. In the cases where the correct easy axis is reproduced (C_y) we do not observe any canting of the spins, in agreement with the experimental magnetic point group mmm' .

As a second example with Fe^{2+} , we analyze the effect of J on the MCAE of FeF_2 . Experimentally FeF_2 is known to have its spin magnetization parallel to the tetragonal c axis with a rather large MCAE of about $+4800 \mu\text{eV}$.^{27,28} In Fig. 2(a) we report the LSDA+ U MCAE energies with respect to J at four different values of U (3, 4, 5, and 6 eV). All the calculations with $J=0$ eV give the wrong easy axis (spins are perpendicular to c) with a huge error in the MCA energy (MCAE from $-16\,000$ to $-26\,000 \mu\text{eV}$ for U going from 3 to 6 eV). Increasing the value of J in the range of 0–0.5 eV has the tendency to strongly reduce this error with a linear increase in the MCAE with J as we found above for LiFePO_4 . However, beyond $J \approx 0.5$ the increase in the MCAE is reduced and the evolution becomes more complex with the appearance of two maxima before a drastic decrease beyond $J \approx 1.3$ eV. The correct easy axis (MCAE > 0) is only obtained for a very small range of U and J values, and the amplitude of the MCAE is correct over an even smaller range. This J dependence of the MCAE is again consistent with Eqs. (3)–(6). From Eq. (4) it is clear that when changing the orientation of the spins from the z axis to the x or y axis the off-diagonal parts of Eq. (4) become nonzero resulting in a direct effect of J on the MCAE from Eq. (6).

We also performed the same analysis of the MCAE for NiF_2 [Fig. 2(b)], MnF_2 [Fig. 2(c)] and CoF_2 [Fig. 2(d)]. MnF_2 and CoF_2 have the same easy axis as FeF_2 while NiF_2 has its easy axis perpendicular to the c direction. The easy axis is well reproduced for all three compounds at $J=0$ eV. As for FeF_2 , the amplitudes of the MCAE depend strongly on J but with a completely different trend in each compound. For MnF_2 and FeF_2 the experimental value can be repro-

duced by adjusting the values of U and J . In the case of CoF_2 and NiF_2 no experimental values are available. For CoF_2 we also performed calculations with and without Co semicore states [Fig. 2(d)] and find a strong difference in the magnitude of the MCAE for the two cases. For FeF_2 we also performed calculations within the GGA functional [black pentagons in Fig. 2(a)] and obtained a completely different J dependence than those calculated with the LDA functional. These comparisons illustrate the difficulty of extracting a general rule about the J dependence of the MCAE.

Our results reveal a problem with the predictability of the LSDA+ U method for noncollinear magnetic materials. A strong dependence of the MCAE and spin canting angles on the values of U and particularly J that are used in the calculation. Since properties such as magnetostriction, piezomagnetic response, magnetoelectric response, and exchange bias coupling are directly related to MCAEs and spin canting, it is of primary importance to reproduce these quantities accurately. At the moment, the most reliable, although not entirely satisfactory, option appears to be a fine tuning of the U

and J parameters by adjustment to reproduce experimentally measured anisotropies and canting angles; there is some evidence to suggest that properties such as magnetoelectric responses are then in turn well reproduced.²⁴ Future studies might explore methodologies for self-consistent calculation of the J parameter or the predictions of new descriptions of the exchange and correlation such as the hybrid functionals.²⁹ On the flip side, it is clear that noncollinear magnetic systems provide a challenging case for testing the correctness of new exchange-correlation functionals within the density-functional formalism.

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