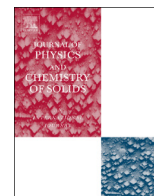




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journal homepage: www.elsevier.com/locate/jpcsDensity functional theory study on the magnetic properties of Co_3O_4 with normal spinel structure

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ABSTRACT

The magnetic properties of Co_3O_4 with a normal spinel structure were investigated via the full potential linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT). The exchange and correlation effects between electrons were treated with a standard generalized gradient approximation (GGA) from Perdew–Burke–Ernzerhof (PBE), as a function of the on-site Coulomb U term, the GGA–PBE+ U method, and a B3PW91 hybrid functional with different Hartree–Fock exchange admixtures. We calculated all of these exchange–correlation (XC) functionals both with and without spin–orbit coupling (SOC). The objective for these calculations was to predict the ground-state magnetic structure of Co_3O_4 crystal using different XC functionals and to investigate the influence that SOC had on these results. All of our calculations confirmed that the collinear antiferromagnetic (AFM) order was energetically more favorable than the ferromagnetic (FM) one, which agrees with experimental findings. This conclusion was not influenced by the XC functional type employed or whether the spin–orbit effect was used. Thus, the present work does not confirm the recent DFT plane wave pseudopotential results that when including spin–orbit effects, the calculations determined that the collinear FM state had lower energy than the AFM one.

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1. Introduction

Tricobalt tetraoxide (Co_3O_4) with a cubic normal spinel structure is an important semiconductor magnetic material because of its various technological applications and, in particular, its potential photocatalytic activity [1–3]. The normal spinel structure can be expressed as $(\text{A})[\text{B}]_2\text{O}_4$ with A and B denoting the divalent (Co^{2+}) and trivalent (Co^{3+}) cations, respectively, and the parentheses and square brackets represent the tetrahedral and octahedral sites, respectively [4]. The ground-state magnetic structure for Co_3O_4 has been experimentally studied using different methods and techniques [4–7]. These studies found that the Co_3O_4 magnetic structure is due to a collinear antiferromagnetic (AFM) ordering ($T_N \sim 40$ K) of the spins at the A site. Co^{2+} ions have a high-spin state ($S=3/2$ and configuration $e_g^4 t_{2g}^3$), while Co^{3+} ions possess a low-spin state ($S=0$ and configuration $t_{2g}^6 e_g^0$). The Co^{2+} ion has a magnetic moment of $3.26 \mu_B$, which is slightly greater than the spin-only value of $3.0 \mu_B$ due to the small contribution from spin–orbit coupling (SOC). More recently, Ikedo et al. [8]

suggested the possible formation of an incommensurate AFM ordering below 30 K based on their experimental results.

Theoretical studies of the electronic and magnetic properties of Co_3O_4 based on density functional theory (DFT) [9,10] calculations using different exchange–correlation (XC) functional schemes and basis sets have been performed [11–16]. However, divergent values (see Table 1) were recently obtained for the exchange coupling between Co^{2+} ion nearest-neighbors (J_1) by Cheng et al. [13] and Singh et al. [15] using the same GGA–PBE+ U XC functional, which prevented the DFT calculations from predicting the true ground-state magnetic structure for this compound. In these last two works, the authors employed the same plane wave pseudopotential method using different computational packages: Quantum Espresso [17] and VASP [18,19], respectively. Furthermore, Singh et al. [15] performed the first DFT calculations including SOC because it is considered important for describing the magnetic properties of Co_3O_4 compounds, and their results for both GGA–PBE and GGA–PBE+ U XC functionals indicated that the ferromagnetic (FM) state is more stable than AFM one. However, this result completely contradicts the experimental findings [4–7].

Calculations based on DFT employing the standard local density approximation (LDA) or a generalized gradient approximation (GGA) for XC functionals are known in the literature not to adequately describe the magnetic and electronic structure of materials containing partially occupied d- or f-states [20,21]. However, it

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Table 1
Nearest-neighbor exchange interaction (J_1) of Co_3O_4 calculated by different XC functionals with SOC either switched off (SOC-off) or switched on (SOC-on), spin and orbital magnetic moments for Co^{2+} ions for Co_3O_4 in the AFM state ($\mu_{\text{Co}^{2+}}^{\text{AFM}}$).

XC functionals		J_1 (μeV)		$\mu_{\text{Co}^{2+}}^{\text{AFM}}$ ($\mu_{\text{B}}/\text{atom}$)	
		SOC-off	SOC-on	Spin	Orbital
PBE	This work	-3.6	-4.1	2.22	0.12
	Singh et al. [15]	-2.2	> 0	2.28	0.16
	Cheng et al. [13]	-2.5		2.64	
Hybrid ^a	This work	-6.5	-6.3	2.43	0.13
	Singh et al. [15]	-1.4		2.66	
	Cheng et al. [13]	-5.0		2.90	
PBE+ U^b	This work	-1.1	-4.3	2.42	0.15
	Singh et al. [15]	-0.2	> 0	2.71	0.20
	Cheng et al. [13]	+0.1		2.84	
	Experimental		-0.6 ^c	3.02 ^d	0.24 ^d

^a $\alpha=0.13$ in this work and in Singh et al. [15] but 0.25 in Cheng et al. [13].

^b $U=4.4$ eV for Co^{2+} ions and $U=6.7$ eV for Co^{3+} ions in all three studies.

^c Reference [6].

^d Reference [4].

expected that other schemes, either LDA+ U (GGA+ U) [22,23] or hybrid functionals (PBE0, HSE06 or B3PW91) [24–28], overcome these problems. However, these facts were not observed in the results of Cheng et al. [13] and Singh et al. [15]. Another interesting fact observed in this last work was that the SOC calculations inverted the sign of J_1 . Thus, is valuable calculated again the magnetic properties of Co_3O_4 compound using DFT+SOC calculations for different XC functionals employing another computational method. For instance, the full potential linearized augmented plane wave (FP-LAPW) method, that has proven to be one of the most accurate methods for the computation of the electronic structure of crystalline solids within of the DFT [29,30].

This work performed a systematic DFT study of the collinear AFM- and FM-states for Co_3O_4 with a normal spinel structure using the FP-LAPW method and different XC functionals (GGA+PBE+ U [23], B3PW91 [28], and GGA+PBE [31]). The various α (from 0.05 to 0.20) and U (with $3.0\text{eV} \leq U \leq 6.7\text{eV}$) values associated the B3PW91 and PBE+ U XC functional features, respectively, were tested. In these calculations, both the AFM- and FM-states in Co_3O_4 were simulated in a twofold manner for all three XC functionals. For the first calculations, the SOC was not accounted, while the second calculations had the SOC switched on. The aims of these calculations were: (1) to predict which magnetic state (AFM or FM) is energetically more favorable for Co_3O_4 and (2) to investigate the influence of the SOC on these results, as reported by Singh et al. [15]. All of our calculations confirmed that the AFM state should be the ground-state magnetic configuration for Co_3O_4 with normal spinel structure independent of the employed XC functional, which did not depend on accounting for the SOC. Thus, the present results do not corroborate the previous DFT+SOC plane wave pseudopotential calculations [15], but confirm the experimental predictions [4–7].

2. Method and calculation details

All calculations were performed via the FP-LAPW method [29,30], which is based on DFT [9,10] and embodied in the WIEN2k computer code [32]. This method expands the electronic wave functions, charge densities, and crystal potentials as spherical harmonics within non-overlapping spheres centered at each nuclear position (atomic spheres) and as plane waves in the rest of

the space (the interstitial region). The atomic sphere radii were 1.87 for Co and 1.66 for O (in atomic units). Within the atomic spheres, the partial waves were expanded up to $l_{\text{max}}=12$, while the number of plane waves in the interstitial region was limited by a cut-off at $K_{\text{max}}=8.0/R_{\text{MT}}$. The augmented plane waves were used as the basis set. The charge density was Fourier-expanded up to $G_{\text{max}}=14$, and an $8 \times 8 \times 8$ k-point grid was used to obtain a well-converged sampling in the Brillouin zone (as in previous DFT calculations [13,15]). The Co 3s, 3p, 3d and 4s electronic states and the O 2s and 2p electronic states were considered valence states. The spin-orbit coupling accounted for via a second variation procedure using scalar-relativistic eigenfunctions as the basis set [30,33].

The exchange and correlation effects were treated using the standard GGA parametrized per Perdew–Burke–Ernzerhof (GGA+PBE) [31], GGA+PBE+ U [23] scheme and B3PW91 hybrid functional [28]. In the B3PW91 hybrid functional, a fraction, α , of the semilocal (SL) exchange energy is replaced by the Hartree–Fock (HF) exchange energy, i.e., $E_{\text{xc}}^{\text{hybrid}}=E_{\text{xc}}^{\text{SL}}+\alpha(E_{\text{x}}^{\text{HF}}-E_{\text{x}}^{\text{SL}})$. α is only applied inside the atomic sphere and to a select set of partially occupied electronic states (Co 3d-states in our case) that are treated poorly by semilocal functionals (e.g., GGA+PBE) [27,34]. In this work, values of $\alpha=0.05, 0.10, 0.13, 0.15$ and 0.20 were verified. The GGA+PBE+ U method applies an on-site Coulombic repulsion parameter, U , to partially filled d- or f-shells. This study used a GGA+PBE+ U approach from Czyzyk and Sawatzky [20] that is more appropriate for weakly correlated systems as suggested for Co_3O_4 [4]. Three different sets of U values were used: (1) $U=3.0$ and 4.4 eV for Co^{2+} and Co^{3+} ions, respectively; (2) $U=4.4$ and 6.7 eV for Co^{2+} and Co^{3+} ions, respectively; and (3) $U=3.0$ eV for both Co^{2+} and Co^{3+} ions. These U values were used during previous DFT calculations [13,15,16].

The FM and AFM magnetic orderings for Co_3O_4 with normal spinel structure were simulated based on the last two paragraphs using parameters from the experimental crystal structure ($a=8.065$ Å, $u=0.388$ and space group F-43m) [4]. The AFM configuration was simulated based on this face-centered-cubic unit cell which has two nonequivalent crystallographic Co^{2+} sites. These nearest Co^{2+} ions neighbors had their magnetic moments in opposite direction (see Table 2 in Ref. [4]). The AFM- and FM-states and the different XC functionals (PBE, B3PW91 and PBE+ U) were calculated both with and without spin-orbit coupling (SOC). The self-consistent calculations for all systems studied in this work were performed to the same level of precision and successfully converged within the energy precision of 10^{-5} Ry.

3. Results and discussion

The nearest-neighbors exchange interaction (J_1) between Co^{2+} ions in Co_3O_4 with the normal spinel structure was calculated to compare to previous theoretical [13,15] and experimental studies [4,6]. Based on the Heisenberg spin Hamiltonian model, J_1 can be expressed as

$$J_1 = \frac{1}{2} \cdot \frac{1}{4} \cdot \frac{1}{S^2} (E_{\text{AFM}} - E_{\text{FM}}) \quad (1)$$

where $S=3/2$, and E_{AFM} and E_{FM} are the total Co_3O_4 energies simulated with AFM- and FM-ordering, respectively. $J_1 < 0$ and $J_1 > 0$ were assumed for the AFM and FM interactions, respectively. This model was adopted in the last works to study the magnetic interactions of Co_3O_4 compounds [4,6,13,15].

Table 1 compares the computed J_1 values from different studies based on DFT calculations when the SOC is switched off (SOC-off) or on (SOC-on), and the predicted experimental J_1 value. Additionally, the contribution of the spin and orbital moments from

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