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Research paper

Understanding the Electronic Transition of Normal Spinel Structure of Co3O4 Using GGA+U Calculations

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Abstract

The normal spinel cobalt oxide Co3O4 is considered as a magnetic semiconducting material comprising of cobalt ions with two oxidation states of Co2+ and Co3+. Density Functional Theory (DFT) calculation are employed to generate the structural, electronic and optical properties using Generalized Gradient Approximation (GGA) function. The Perdew-Burke-Ernzerh for solids (PBEsol) exchange-correlation functional approach successfully predict the semiconductor behaviour of Co3O4 but severely underestimates the band gap in relation to the experimental value. The GGA+U is performed in order to treat the Co-3d states and achieve the band gap of 1.26eV which agrees with the experimental results. For optical studies, here we unveil the predicted three assumed electron transition occurring in Co3O4 for O(2p)→Co2+(t2g), O(2p)→Co3+(eg) and Co3+(t2g)→Co2+(t2g).

Keywords: *Generalized Gradient Approximation (GGA); Hubbard U; Co3O4; Electronic Properties; Optical Properties*

1. Introduction

The intriguing physical properties, high capacitance (~3650 Fg-1), excellent chemical behaviour, cost-effective and environmental friendliness of Co3O4 has drawn extensive research interests. This is due to the many potential applications as electrodes, such as a catalyst for oxygen evolution and oxygen reduction [1], sensors [2], Li-ion batteries [3] and supercapacitors [4 - 5]. From a theoretical point of view, the cubic crystalline structure of Co3O4 (Fd3m) is a challenging material because of two distinct Co sites due to two oxidation states of Co2+ and Co3+. This two-formula-unit face-centered-cubic material (FCC) can be expressed as AB2O4 (A: tetrahedral, B: octahedral). The tetrahedral sites, (A) occupied by high spin (HS) Co2+ (d7) ions and octahedral sites (B) occupied by low spin (LS) Co3+ (d6) ions. Experimentally, the Co2+ ion has a magnetic moment of 3.0 μB while Co3+ is non-magnetic. The magnetic properties are governed by Co2+ ion due to unoccupied state in t2g orbital according to its electronic configuration t32g(↑)t02g(↓)e2g(↑)e2g(↓) while, Co3+ ion

completely filled the t2g level [6]. The electronic configuration of Co3+ is t32g(↓) t32g(↑)e0g(↑)e0g(↓). Various experimental methods and theoretical studies have been conducted to provide a better understanding of the electronic and optical properties [7 – 9] of this material, which constitute different interpretations of optical absorption spectrum related to its electron transition.

Three assumed electron transition is said to occur; including p and d orbital (Figure 1): two pathways from ligand O(2p) to metal charge transfer of cobalt cations (LMCT), transition between two metal to metal with different cobalt oxidation states (MMCT), and one d-d ligand field excitation within each of the Co2+ and Co3+ cations. According to Marten et al. [9] by using spectroscopy ellipsometry, the optical transition in Co3O4 obtained at 0.80, 1.60, 2.65, and 4.40 eV are pertaining to electronic transition of Co2+→Co3. As time elapsed, Kim and Park [10] have proposed more details of the three optical transition located at 1.65, 2.40 and 2.80 eV from dielectric function result corresponding to Co3+(t2g)→Co2+(t2g), O(2p)→Co2+(t2g), and O(2p)→Co3+(eg) respectively. However, Xu et al. [11] has disagreed with previous work and proposed another energy level performed by first principle studies (DFT) using GGA-PBE exchange-correlation. The variation of the different perceptions of charge transition in Co3O4 has led to the present work explained from a theoretical view.

Thus, in this work, we present the structural parameters, band structures, the density of states (DOS) and optical studies (dielectric function) by first principle calculation in normal spinel

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Co3O4. The purpose of the study is to go beyond understanding of pure Co3O4 based on optical absorption.

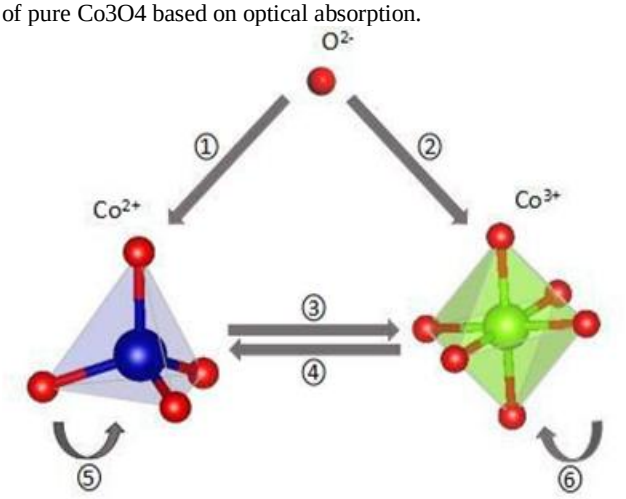


Figure 1 Types of charge transition, (1,2) ligand to metal chargetransfer, (3,4) metal to metal charge transfer, (5,6) d-d intraband transition

2. Method and Calculation Details

All the calculations have been carried out by spin-polarized quantum mechanical calculation within scalar relativistic treatment by using density functional theory (DFT) as implemented in the Cambridge Serial Total Energy Package (CASTEP) program package in Material Studio of Accelrys Inc [12]. Periodic DFT calculations were treated within the Kohn-Sham schemes of the local density approximation by Ceperley and Alder [13] as parameterized by Perdew and Zunger [14] (LDA-CAPZ) and semi-local generalized gradient approximation (GGA) exchange-correlation functional of the Perdew-Wang91 [15] (PW91), Perdew-Burke-Ernzerh (PBE) [16] and for solids [17] (PBEsol) for all geometry optimizations. The calculation proceeded with the GGA-PBEsol functional due to better description of structure than others. The plane-wave basis with a kinetic energy cutoff of 380eV and the Monkhorst-Pack grid with 6x6x6 k-point mesh to obtain well-converged sampling of the Brillouin zone.

The electronic minimization parameter of the total energy/atom convergence tolerance was 5.0x10-6eV. Ultrasoft pseudopotentials were employed where valence electron include O 2s, 2p, and Co 3d states. The highly correlated 3d orbitals of Co has to be corrected by performing the calculation using DFT+U. The Hubbard U values performed by single U is 3.5 eV resulting in the same region with the experimental value. As such, the chosen values of U is 3.5 eV.

3. Results and Discussion

Structural Properties

Co3O4 is classified as normal cubic spinel structure with the space group of (227 Fd3m). The relaxed structure of the cubic is shown in Figure 2. Two oxidation states occur in Co3O4 which are divalent (Co2+) and trivalent (Co3+) possessed due to tetrahedral and octahedral structure respectively. The divalent ions with AO4 coordination exhibit in a high-spin (HS) state coupling with four neighbours of the same kind via the antiferromagnetic (AFM) ordering. Otherwise, the trivalent ions adopt a low-spin (LS) state. The lattice parameters optimized with different functionals are compared in Table 1. In general, the results of Co3O4 calculated using the LDA-CAPZ functional underestimates all the lattice parameters, while the GGA functional overestimates them. Among the tested functionals, GGA-PBEsol shows the best agreement with the crystallographic parameters with percentage difference of less than ~1%. The optimized structure with lattice constant, Co-O bond length and magnetic moment values are presented in Table 2.

Table 1: Calculated lattice parameters and cell volumes of normal spinel Co3O4 local functional LDA-CAPZ and semi-local functional GGA-PBE, GGA-PW91 and GGA-PBEsol in comparison with the experimental values and other theoretical work. Values in the parentheses represent the percentage difference from available experimental data in references.

Material	Method	Lattice Parameter, a (Å)	Volume (Å^3)
Co_3O_4	GGA-PBE	8.197	550.727
		(1.61%)[a]	(4.91%)[a]
		(1.40%)[b]	(4.24%)[c]
		(1.89%)[c]	
	GGA-PW91	8.186	548.562
		(1.48%)[a]	(4.50%)[a]
		(1.26%)[b]	(3.83%)[c]
		(1.75%)[c]	
	GGA-PBEsol	8.087	528.984
		(0.25%)[a]	(0.77%)[a]
		(0.04%)[b]	(0.13%)[c]
		(0.04%)[c]	
	LDA-CAPZ	7.991	510.418
		(-0.93%)[a]	(-2.76%)[a]
		(-1.14%)[b]	(-3.39%)[c]
		(-0.66%)[c]	
	Experimental		
	Ref.[18] [a]	8.084	528.320
	Ref.[19][b]	8.080	
	Ref.[8][c]	-	529.600
	Theory		
	GGA-PBE [20][d]	8.190	549.35
	GGA-PBE [21][e]	8.110	-
	GGA-PBE [11][f]	8.084	-

[a]X-Ray diffraction analysis samples by spray pyrolysis technique
[b]X-Ray diffraction analysis samples prepared by thermal decomposition
[c]X-Ray diffraction analysis at low pressure (0GPa < P< 17GPa)
[d]Quantum Espresso package using norm conserving pseudopotential
[e]VASP code program
[f]Dmol3 program with double-numerical basis with polarization functions (DNP)

Table 2: Details on calculated data for Co3O4 as given by PBE and PBE+U calculation

	PBE	PBE+U
Lattice constant (a=b=c)	8.087	8.136
Volume (A^3)	528.98	538.65
Distance Co^{2+}-O^{2-}	1.92	1.95
Distance Co^{3+}-O^{2-}	1.93	1.93
Magnetic moment Co^{2+} (μB)	2.37	2.66
Magnetic moment Co^{3+} (μB)	0.00	0.00

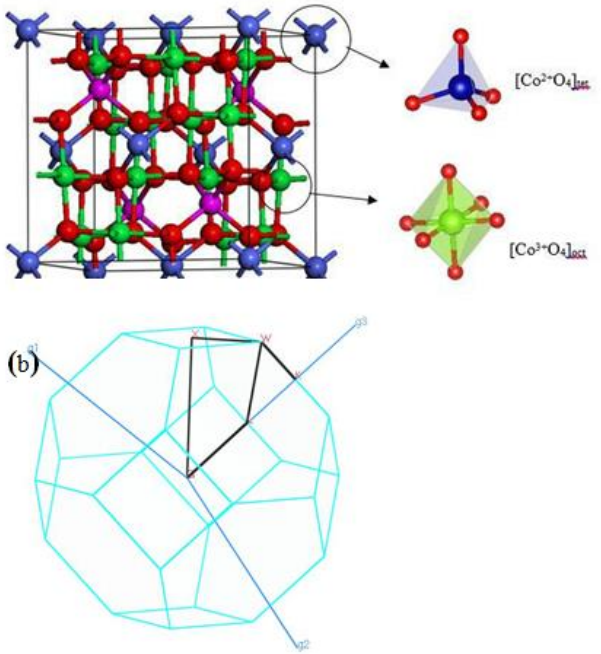


Figure 2 : Crystal structure of (a) cubic (Fd3m) with two inequivalent Co ions, Co2+ with tetrahedrally coordinated oxygen and Co3+ with octahedrally coordinated oxygen (polyhedron). (b) The high symmetry points within the Brillouin zone in primitive cell

4. Electronic and Magnetic Properties

Using the PBEsol functional, the electronic band structure was calculated along various symmetry points applied on the lattice structure within Brillouin zone at the point W(0.500, 0.250, 0.750), L(0.500, 0.500, 0.500), G(0.000, 0.000, 0.000), X(0.500, 0.000, 0.500), and K(0.375, 0.375, 0.750) as demonstrated in Figure 3. The GGA-PBEsol approach results in minimum band gap of 0.11eV predicted for Co3O4, which severely underestimates the band gap values in semiconductor reported to be comparable to the experimental result obtained in the range of 1-1.9 eV [7][22]. In order to obtain a valid band gap, Hubbard U is included to treat the Co-3d states [15]. The PBE+U method using single U=3.5eV for Co2+ and Co3+ respectively gives a minimum band gap of 1.26 eV, which is in agreement with the experimental data and previous calculation performed using other exchange-correlation potentials as stated in Table 3. The inclusion of Hubbard U parameter might correct the band gap, which is an ad-hoc correction scheme and significantly ……. Co d and O 2p states hybridize strongly [23].

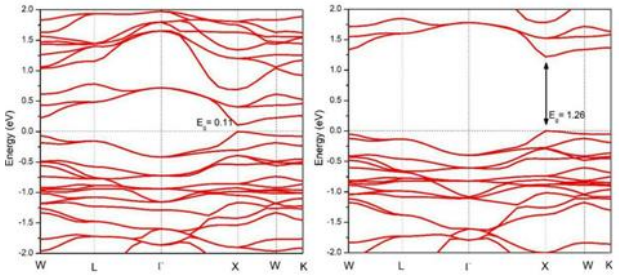


Figure 3 Calculated total band structures for Co_3O^4 obtained by (a) PBE and (b) PBE+U functional with U=3.5 for both Co^{2+} and Co^{3+}. Fermi energy is set to 0

Table 3 Comparison of calculated and experimental values of the band gap (eV) of Co3O4

	Direct		Indirect	
	X→X	Γ→ Γ	Γ→X	X→Γ
This study	1.26	2.22	1.77	1.61
Calculated GGA-PBE+U				
Ref [24]	1.23	1.67	1.51	-
Ref [25]	1.96	3.25	2.41	2.81
Experimental				
Ref [22]	1.60		2.10	

Figure 4 clearly shows the essential notions of partial density of states (PDOS) of Co3O4. PDOS are represented with spin polarization for the majority and minority spin states, namely, spin up and spin down respectively. For the Co2+ ions, it can be seen that the majority spin d states are split between the eg states (-5.5eV) and t2g states (-2.5eV). The filled minority spin eg states are situated at the top of valence band while unoccupied minority t2g states dominate at the bottom of the CB at (+2eV). However, Co3+ PDOS demonstrated it is almost symmetrical with respect to the majority and minority spin states. The Co3+ t2g states are concentrated at the top of the VB about (-1eV). The crystal field effect is nicely described by PDOS calculations (Figure 5). By referring to 'A' point (-5eV), hybridization occurred through oxygen with the tetrahedral Co2+ 3d states. While at point 'B', for Co3O4 coupling between the octahedral Co 3d states with O 2p results in a significant amount of oxygen p based CB at +3eV. From PDOS analysis, Xu et al described the electronic transition bands but they reported the transition of Co3+(t2g)→Co2+(t 2g) for the 3.3eV absorption to be larger than experimental (1.65eV). In this study, optical studies conducted will show comparable results with the experimental result.

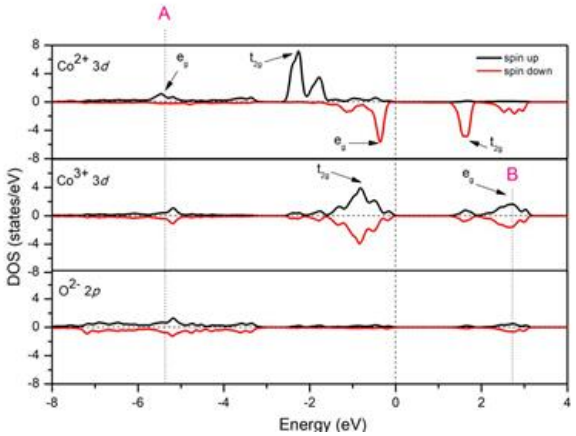


Figure 4 The projected DOS of Co3O4 with references valence band maximum set at 0Ev

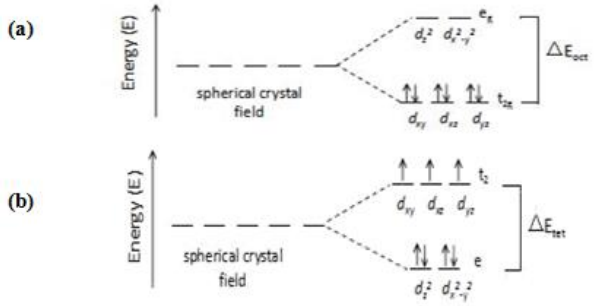


Figure 5 Schematic view of crystal field splitting of Co-3d states in Co3O4

5. Optical Studies

The optical properties of matter can be described by the complex dielectric function ε(ω), which presents the linear response of the system to an external electromagnetic field with a small wave vector. It can be expressed as

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

The imaginary part of the dielectric function $\varepsilon_2(\omega)$ is calculated by the sum of all possible direct transitions from the occupied to unoccupied states over the Brillouin zone [26].

The imaginary part $\varepsilon_2(\omega)$ can be calculated from the electronic structure based on the DOS given;

$$\varepsilon_2 = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\left\langle \psi_k^c \left| \hat{u}r \right| \psi_k^v \right\rangle\right|^2 \delta(E_k^c - E_k^v - E)$$

Wherein e refers to electron charge, and ψ^c and ψ^v are the CB and VB wave functions at k, respectively. The real and imaginary dielectric functions are linked by the Kramer–Kronig relation, which is used to calculate the real part $\varepsilon_1(\omega)$ of the dielectric function derived from $\varepsilon_1(\omega)$ by the Kramers–Kronig transformation.

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega'\varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$

The resulting dielectric function ε is shown in Figure 6 as compared with experimental result in inset graph. As can be seen, Figure 6 (b), is focused on the imaginary dielectric function (ε_2) where the experimental result demonstrated two clear peaks located at 1.65eV and 2.80eV while the calculated spectrum obtained three peaks. It is predicted that, at 1.13eV the transition could be due to Co^{3+} (↓) $t_{2g} \rightarrow Co^{2+}$(↓) t_{2g}. In this report, the transition which occurred could be by direct dipole-forbidden d-d transitions. These transitions (forbidden in the presence of perfect spherical symmetry) become allowed due to crystal-field splitting in the cubic spinel structure and due to hybridization of the oxygen 2p states with the cobalt 3d states [27][9]. Peaks at 2.15 and 2.63eV can be attributed to the ligand to metal transition between O2*p* and Co^{2+}/Co^{3+} 3d states. Due to larger oscillator strength of p-d type excitation, these transitions are orders of magnitude stronger than d-d type transition.

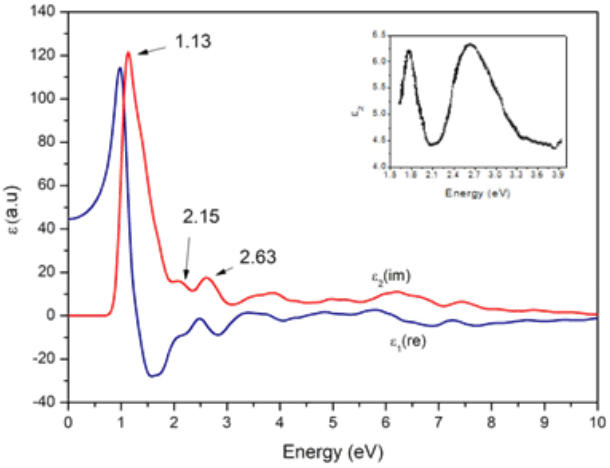


Figure 3 Imaginary parts of the dielectric function of Co3O4 normal spinel (a) calculated and (b) inset experimental result [10]

6. Conclusion

In this study, we have reported the electronic, optical and magnetic properties of the spinel compound Co3O4. We employed density functional theory at GGA-PBEsol + U approach to resolving the long-standing problem of the correct band gap and electronic structure for this material. In agreement with experimental results, the computed band gap 1.26eV is obtained by using the U parameter of 3.5eV for both Co2+ and Co3+. The calculation of imaginary part of the dielectric function (ε2) which is related to the absorption spectrum of Co3O4 accounts for the charge transfer to be due to direct dipole-forbidden d-d transitions between Co 3d. In this approach, the calculation predicted that the crystal field splitting at both octahedral and tetrahedral sites are of the same magnitude.

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