Electronic Structure and Optical Conductivity of $ZnCo_2O_4$ With PBE and TB-mBJ Potentials

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Abstract
We present the electronic and optical conductivity for $ZnCo_2O_4$ compound. The full-potential augmented plane plus local orbitals method based on the density functional theory is used within the PBE and TB-mBJ scheme. The optimized unit cell length a_0 and internal parameter u are in agreement with experimental data. The band gap obtained using TB-mBJ shows a significant improvement over PBE value and is close to the experimental data. Optical conductivity has been calculated for the energy range 0-14 eV.

Keywords
Electronic Structure, FPLAPW, Optical Conductivity, Spinel Oxides, TB-mBJ

I. Introduction

Spinels are crystalline solids which have general chemical formula $A^{II}B^{III}{}_2C^{VI}{}_4$ where the roman numerals indicate the appropriate column of the periodic table [1]. Generally, when C is Oxygen, the spinel compounds crystallize in the cubic spinel structure. Many of these compounds are wide band gap semiconductors which are transparent in the visible and infrared regions and thus are used as transparent conducting oxides (TCOs) in optoelectronic devices [2]. This has led to an extensive search for new TCO materials with higher transparency and conductivity.

The electronic structure methods, capable of accurately calculating the physical properties, are helpful in order to find new or better TCO materials. A well known example $ZnCo_2O_4$ has been studied theoretically [3] and experimentally. Dixit et al [4] found improved bandgap by TB-mBJ method over PBE method for $ZnCo_2O_4$. Samanta and Saini presented the electronic and optical properties with both PBE and TB-mbJ schemes and found that the latter more accurately explains the experimental results for $ZnCo_2O_4$ [14]. However, optical conductivity was not studied by PBE or mBJ to the best of our knowledge. Here, we present our theoretical results for $ZnCo_2O_4$, including the electronic structure and optical conductivity obtained with the full-potential augmented plane wave method using PBE and mBJ scheme.

II. Computational methods

The first principle calculations are performed by using the scalar relativistic version of the full- potential linearized augmented plane wave method [5-7], based on density functional theory [8], as implemented in WIEN2k package [9]. The exchange- correlation potential was calculated by the GGA based on Perdew et al [10], and TB-mBJ potential [11]. In the FP-LAPW method, the unit cell is divided into non-overlapping spheres centered at atomic sites (muffin- tin spheres) of radius R_{MT} and an interstitial region. The R_{MT} are taken to be 2, 1.95 and 1.68 (a.u.) for Zn, Co, and O respectively. The plane wave expansion of the wavefunction in the interstitial region was truncated at $R_{MT}K_{MAX}$=9. Self-consistency was obtained using 47 k-points in the Irreducible Brillouin Zone (IBZ). The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-4} Ry. The cut-off energy, which defines the separation of valence and core states, was chosen as -6 Ry.

III. Results and Discussions

$ZnCo_2O_4$ crystallizes in a cubic spinel structure with space group Fd-3m (#227) [2]. The Zn atoms are located at the Wyckoff positions, 8a (1/8, 1/8, 1/8) tetrahedral sites, while the Co atoms are located at the 16 d (1/2, 1/2, 1/2) octahedral sites and the oxygen atoms at 32e (u, u, u). The spinel crystal structure is characterized by the lattice parameter a0 and internal parameter u.

In this work we compared electronic structure and optical conductivity for $ZnCo_2O_4$ within PBE and TB-mBJ. Our calculated values of the lattice constant a0 and the internal parameter u with the available experimental and theoretical data are shown in Table 1. We obtained equilibrium lattice constants and internal parameter in good agreement with experimental values [12].

Table 1: Calculated Lattice Constant a_0 in Å, Internal Structure Parameters u, Compared With Experimental Data For $ZnCo_2O_4$.

	a_0	u
Present work	8.176	0.264
Experimental	8.104[a]	0.263[a]

[a]Reference [12].
[b]Reference [4].

The calculated band structures of $ZnCo_2O_4$ along the high symmetry directions using PBE and TB-mBJ potential are shown in Fig. 1(a) and Fig. 1(b). H Dixit et al [4] reported an indirect bandgap calculated with PBE and TB-mBJ. We obtained an indirect bandgap of 0.773 eV for PBE with Valence Band Maxima (VBM) occurring at X point and conduction band minima (CBM) located near X point and bandgap of 3.354 eV with VBM at K point and CBM near X point in Γ-X direction. We obtained four groups of band between -20 eV to 10 eV within each scheme. For PBE we get a group of bands from below -20 eV to -18.39 eV as shown in Fig. 1(a). We get a valence band group from -8.35 eV to the Fermi level. The conduction band approximately starts from 0.74 eV to 2.21 eV. The next higher group of bands starts from 2.75 eV to above 10 eV. For TB-mBJ there is a group of band from below -20 eV to -18.64 eV as shown in Fig. 1(b). The valence group of band starts from -6.67 eV upto the Fermi level. The conduction group of bands starts from 3.33 eV to 4.32 eV. The next upper group starts from 6.07 eV to above 10 eV.

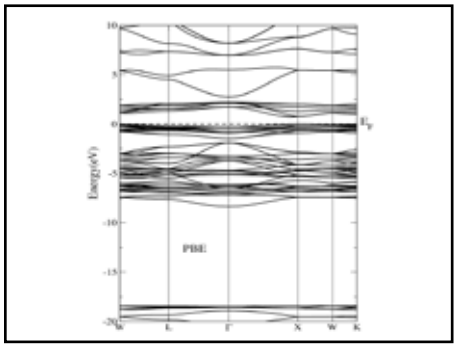

Fig. 1(a): Calculated Band Structure of $ZnCo_2O_4$ Using PBE Scheme

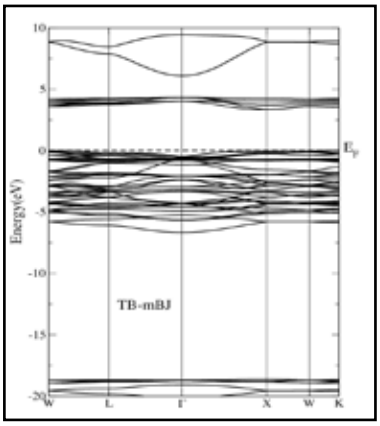

Fig. 1(b).Calculated Band Structure of $ZnCo_2O_4$ Using TB-mBJ Scheme

The indirect band gaps calculated with PBE and TB-mBJ along with experimental bandgaps are given in Table 2. The total and atomic site projected densities of states (DoS) is shown in Fig. 2. The Fermi level is set to zero. In both PBE and TB-mBJ calculations the DoS between -20 to -18 eV constitute mainly of O-s character. The upper valence band (UVB) constitutes mainly from Zn-d and Co-d orbitals.

Table 2: Calculated Indirect Bandgaps With PBE and TB-mBJ Along With Experimental Bandgaps For $ZnCo_2O_4$ (All in eV).

PBE		TB-mBJ		Experimental
Present	Others	Present	Others	
0.773	0.71[a]	3.354	3.36[a]	2.26[b], 2.63[c]

[a]Reference [4].
[b]Reference [12].
[c]Reference [13].

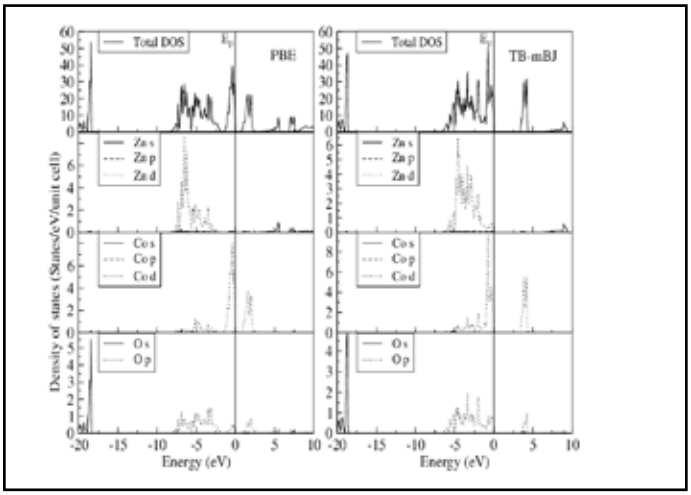

Fig. 2: Dos Plot For $ZnCo_2O_4$ Using PBE and TB-mBJ Method

The UVB also has slight O-p character. The lower energy range conduction band (LCB) contains mainly of Co-d and O-p States

Fig. 3 displays the optical conductivity using PBE and TB-mBJ potential. The first edge value of conductivity is at 0.068 eV for PBE and 0.31 eV for TB-mBJ. This is due to the increase in bandgap for TB-mBJ scheme compared to PBE scheme. The peaks in the optical conductivity in both PBE and TB-mBJ mainly arise from the occupied Zn-d and Co-d orbitals to unoccupied Co-d orbitals. There is a dip in optical conductivity at 2.5 eV and 10 eV in the PBE. This is due to the lack of energy states in the valence band at the above energies from the top of conduction band. The peaks for TB-mBJ in optical conductivity shift towards higher energy than the same for PBE. The shifting of the peaks towards higher energy in TB-mBJ is due to the shifting of conduction band minima towards higher energy in TB-mBJ scheme.

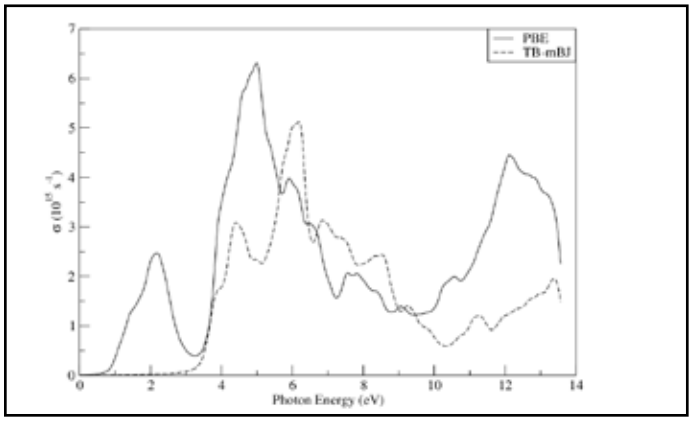

Fig. 3: Calculated Optical Conductivity Using PBE and TB-mBJ Scheme

IV. Conclusion

In this paper, using the PBE and TB-mBJ scheme, we have studied electronic properties and optical conductivity of $ZnCo_2O_4$. The energy bandgap calculated by TB-mBJ scheme shows a significant improvement over the PBE scheme and are closer to the experimental data. The optical conductivity is compared for PBE and TB-mBJ scheme and established the superiority of latter over former for calculating properties of $ZnCo_2O_4$.

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