Study of Electronic, Structural and Optical properties of Cadmium Sulfide (CdS) in Zinc-Blend and Wurtizite phase using DFT and DFT+U.

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Introduction:

Cadmium Chalcogenides are monochalcogenides have the formula CdX (X = S, Se, and Te). They typically crystallize in one of three motifs, ZB, WZ, and rock-salt (cubic) structures [1], and the experimentally stable crystal phase of CdS is WZ structure [2]. Farther more, the CdS can crystallize in either ZB crystal structure with space group F-43m or WZ crystal structure with $P6_3mc$ space group under ambient conditions [3]. The rock-salt structure is only observed under high pressure [4, 5]. Cadmium chalcogenides CdX (X= S, Se and Te) and their combinations are widely studied members of II-VI semiconductor family [6]. CdS is one of CdX and CdX compounds are the archetypal systems of the II-VI semiconductor [7]. Thin films are most auspicious for occupation in solar cells, photo electrochemical cells out of which axenic CdX have received intensive attention. Because their optical band gaps lies close to the range of optimum theoretically achievable energy conversion efficiency [8]. They can also be used in hetero-junctions, IR detectors, Lux meters, switching devices and Schottky barriers etc. Due to their potential applications, the II-VI compounds peculiarly are attracting a lot of attention in producing hetero-junction, photo-electrochemical, solar cells, optoelectronic devices, light emitting diodes and field effect transistor etc [9].

Objectives

- To study Electronic, structural and optical properties of CdS in zinc-blend phase and wurtizite phase within computational methods particularly using DFT and DFT+U.

Computational Methods

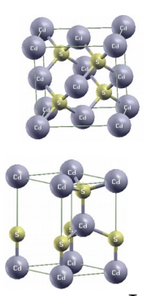
The physical (structural), Electronic and optical properties of CdS in both wz & zb phase was calculated using QUANTUM-ESPRESSO code in the frame work of the density functional theory. The interaction between core and valance electrons described using norm-conserving pseudopotentials (ncp) and Projector augmented-wave pseudopotential (paw) . The exchange-correlation effect in Kohn-Sham will treated by local density approximation (LDA) and generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE), hybrid functional approximation (PBE0) and Hubbard-correction(DFT+U). The evaluated band gap values using GGA and LDA were under-estimated compared to the experimental value. This problem was improved by ncp method within the hybrid functional approximation (PBE0) and using paw in DFT+U.

Results and Discussion

Structural properties of CdS

The equilibrium lattice constants of CdS in zb & wz phase were calculated using LDA, PBE, DFT+U and PBE0 approximation and summarized in table 1.

Table 1: Comparison of Calculated equilibrium Lattice constant of CdS with experimental and other theories.



This Work					References	
Phase	LDA	PBE	DFT+U	PBE0	Experimental	Theories
zb	a=5.819	a=5.979	a=5.847	a=5.983	a= 5.82[10], 5.80[11]	a = 5.81 [12] , 5.85 [13]
wz	a=4.158	a=4.226	a=4.37	a=4.160	a = 4.136 [10]	a = 4.097, c = 6.752 [12]
	c=6.752	c=6.863	c=7.10	c=6.756	c = 6.756	a = 4.160, c = 6.70 [13]

It shows that our calculations in accordance with LDA, PBE, DFT+U and PBE0 are in good agreement with the previous theoretical and experimental results. LDA underestimates the lattice constant by 1% whereas PBE overestimates it. Moreover, the graph of lattice constant versus total energy for CdS is displayed in Figure 1(a) and 1(b)

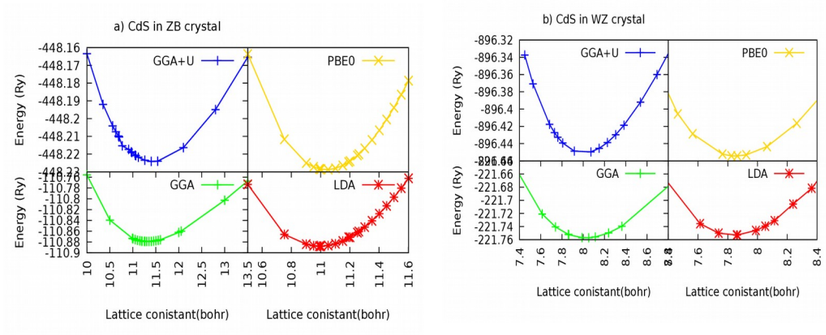


Figure 1: Total energy of CdS versus lattice constant
a) in ZB phase
b) in WZ phase.

Electronic properties of CdS

The electronic band structures of CdS in wz & zb are calculated along the high symmetry direction of the Brillouin zone and shown in figure 2(a) and 2(b). The band gap for all approximation: LDA, PBE, PBE + U, and PBE0 are calculated and demonstrated in table 2 and compared with the existing theoretical and experimental results.

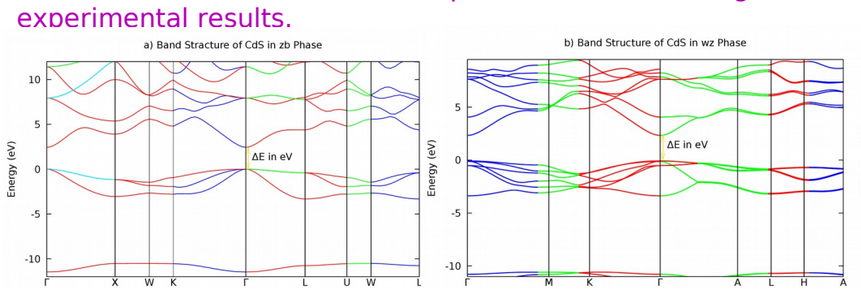


Figure 4: Plotted Band structure of CdS along high symmetry point
a) ZB phase
b) WZ phase.

Table 2 : Comparison of Calculated band gap of CdS with experimental and other theories.

This Work					References	
Phase	ΔE (LDA)	ΔE (PBE)	ΔE (DFT+U)	ΔE (PBE0)	Experimental	Other theories
zb	0.86	1.15	2.45	2.48	2,37[14], 2.58[15], 2.40[16]	1.37[17], 1.24[18], 0.94[19]
wz	0.88	1.17	2.41	2.47	2.48[20], 2.55[18] , 2.42 [21]	1.20[22], 1.15 [18], 0.72 [19]

From table 2 and figure 2 it is found that the results show that LDA and GGA severely under-estimate the band gap due to their poor approximation of exchange-correlation functional. However, the energy bandgap values obtained with respect to LDA+U and hybrid functional (PBE0) is in good agreement with the experimental value for both zb and wz phases.

Optical properties of CdS

The frequency-dependent real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric constant of zb- and wz-CdS compounds are computed using LDA, PBE & DFT+U approximation as shown in Figure 3. From the figure it is obseved that the dielectric functions of CdS in wz phase possess anisotropy in two directions in basal-plan and z-axis ($\varepsilon_{1x} = \varepsilon_{1y} \neq \varepsilon_{1z}$ and $\varepsilon_{2x} = \varepsilon_{2y} \neq \varepsilon_{2z}$). Moreover, the static dielectric constant ε(0) value is calculated using LDA, PBE and DFT+U approximations and compared with experimental value, for CdS crystals as shown in table 3

As seen in figure 4 we also calculated the refractive index, n(ω) of zb- and wz-CdS. In addition, the static refractive index n(0) for CdS in both zb and wz phase were calculated and summarized in table 4

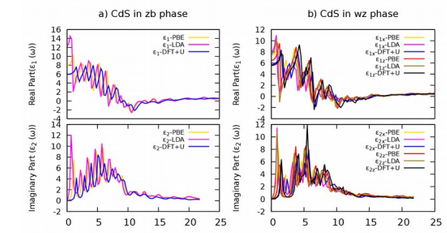


Figure 3: Real and imaginary parts of dielectric function for (a) zb-CdS and (b) wz-CdS.

Table 3 Comparison of calculated value of static dielectric constant for wz-CdS and for zb-CdS.

This Work					References
Phase	ε(0)	LDA	PBE	DFT+U	Experimental
zb	ε(0)	12.30	7.96	5.92	---
wz	ε1x(0)	8.13	7.64	5.72	---
	ε1z(0)	7.57	7.39	5.55	---

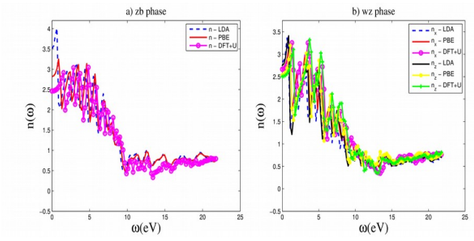


Figure 4: The refractive index, n(ω), for CdS (a) zb phase (b) wz phase.

Table 4 Comparision of calculated value with experimental and other theoretical value of static refractive index of CdS

This Work					References	
Phase	n(0)	LDA	PBE	DFT+U	Experimental	Theories
zb	n(0)	3.51	2.82	2.46	~2.529 [23]	~2.72[24]
wz	nxx(0)	2.82	2.70	2.66	--	--
	nzz(0)	2.75	2.54	2.50	--	--

Conclusion

The structural, electronic and Optical properties of zb- and wz-CdS are studied using DFT and DFT+U. The exchange correlation functional is approximated using LDA, GGA/PBE, GGA+U and PBE0. The lattice constants optimization was performed using LDA, PBE, DFT+U and PBE0 approximations and the obtained results are in good agreement with experimental. The band structure calculation was performed using LDA, PBE, DFT+U and PBE0 approximations. The results reveal that LDA and GGA under estimate the band gap due to their poor approximation of exchange-correlation functional. However, the Hubbard correction (DFT+U) and the hybrid functional approximation (PBE0) give a band gap value which is consistent with the experimental results. The calculation of real and imaginary part and static dielectric functions as well as refractive index of CdS were performed using LDA, PBE and DFT+U. However, DFT+U is in good agreement with experimental value.

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