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First principles study on structural, phase transition and electronic structure of Zinc Sulfide (ZnS) within LDA, GGA and mBJ potential

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Abstract. An ab-initio calculation based on full potential linearised augmented plane wave method of density functional theory (DFT) within the localised density approximation (LDA), generalised gradient approximation (GGA) and modified Becke-Johnson (mBJ) for exchange correlation potential is performed to investigate the structural, phase transition and electronic structure of Zinc Sulfide (ZnS). A comparative study is performed for the three approximations and reveal that calculations within the GGA gives better structural stability and phase transition pressure of 17.6 GPa in reasonably close agreement to experimental results. The electronic structure calculation within mBJ predicts higher direct band gap of 3.5eV in comparison to LDA and GGA underestimated value. The trend in the accuracy of energy band gap calculation is found to be $LDA < GGA < mBJ$ -GGA. The electronic band structures are investigated using the total and partial density of states.

1. Introduction

Zinc Sulfide (ZnS) is an important semiconductor which has been a subject of great interest in the recent years due to its technological importance and scientific applications. Its wide and direct band gap makes it ideal for applications in solar cells, laser diodes, high-density optical memory and electronic image display [1,2]. Under ambient pressure conditions it crystallises in zinc blende (ZB) and wurzite (WZ) structure which transforms to a six-fold co-ordinated rock salt (RS) structure at high pressure. The electronic structure plays a significant role in understanding the electrical, optical and transport properties of a material. It helps in better interpretation of the solid state phenomena of a material. The structural and electronic properties of ZnS has been performed by many experimentalist and theorists using different methods but the variation in the theoretical results with experimental data has lead to various disagreements [3,4,5,6]. In order to sort out this discrepancy many methods with different approximation has been used by various theorists.

Recent developments in the computational simulations have resulted in a more systematic and precise study of the structural and electronic properties of a material from the first principle. The theoretical study of the structural and electronic properties of a material are generally performed within the local density approximation (LDA), generalised gradient approximation (GGA) and GW [7,8] but calculations within the LDA and GGA generally underestimates the energy band gap [9]. The best method for studying the energy band gap is the many perturbation theory within the GW approximation which give us very good results in comparison to experimental studies. But this method is computationally very expensive and time consuming. In 2009 Tran and Blah gave an alternative method for the energy band calculation [10] which is computationally cheap, less time consuming and equally effective by adding a potential known as the modified Becke-Johnson (mBJ) potential. The



mBJ potential within the Perdew-Burke-Ernzerhof (PBE)-GGA approximation performs energy band calculation similar to GW calculation giving us much improved results close to experimental studies and overcoming the underestimation problem within the LDA and GGA approximation.

2. Computational methods

The first principle study of ZnS calculation is performed using the first principle full potential linearized augmented plane wave (FP-LAPW) [11] method within the local density approximation (LDA), generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE-GGA) [12] and modified Becke-Johnson (mBJ) [13] potential within PBE-GGA under the framework of density functional theory (DFT) [14-16]. This method is used as it is one of the most accurate methods in electronic structure calculation of crystals. In this method, the lattice is divided into non-overlapping atomic spheres surrounding each atomic sites and an interstitial region [17]. Inside the muffin tin (MT) region, the potential is a product of radial function and spherical harmonics and expanded up to order $l = 10$. For the interstitial regions that are outside the muffin tin spheres, the potentials are expanded in plane waves. 8000 k-points are used for the integration part which reduces to 256 irreducible k-points inside the Brillouin zone. Convergence is obtained at $R_{MT}K_{max} = 9.0$ where R_{MT} is the atomic sphere radii and K_{max} gives the plane wave cut-off. All calculations are performed with the equilibrium lattice constants which are determined from the plot of the total energy against the unit cell volume by fitting to the Birch-Murnaghan equation of states [18]. The overall calculation is done with WIEN2K [19].

3. Results and discussion

The structural properties plays an important role in the study of solids as it provides detailed information about inter atomic binding forces in a material. The stable structure of ZnS is calculated by calculating the total energy and the corresponding primitive cell volume from series of different values of lattice constant and fitting it to the Birch Murnaghan equation of states. In figure 1 the energy versus volume curve of ZnS for both ZB and RS structure within (a) LDA and (b) GGA methods are given. From the figure we find that in both the calculations ZnS-ZB is more stable than ZnS-RS. A summary of the calculated structural parameters are compared with other experimental and theoretical studies and tabulated in table 1. From the table we find that our present work agrees well with other experimental and theoretical results and hence is used for further calculation of the phase transition and energy band gap.

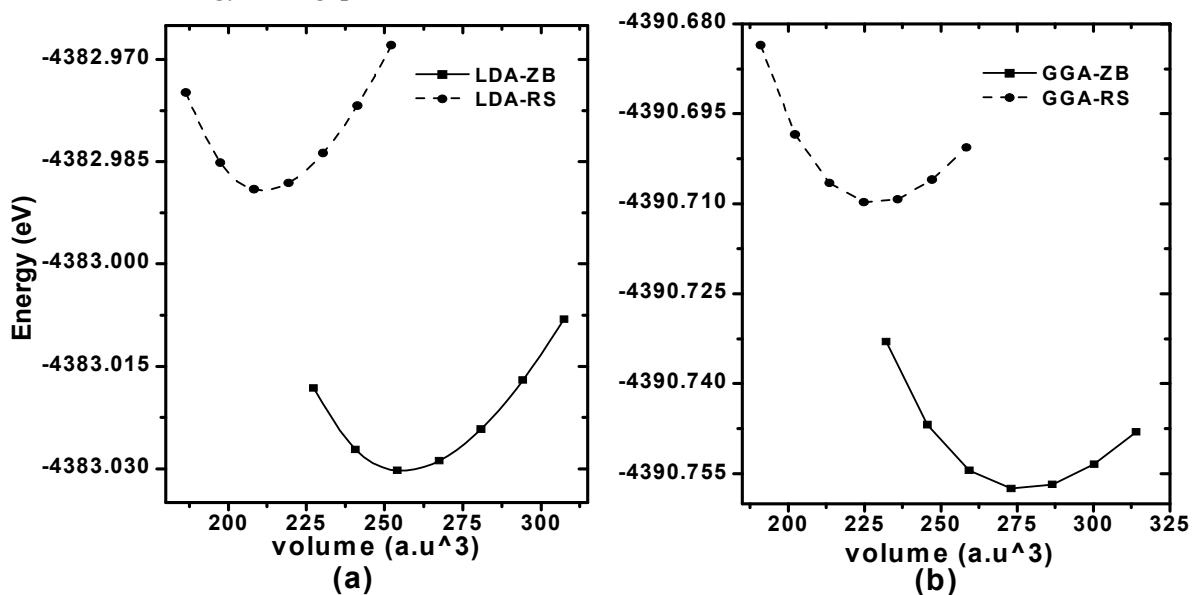


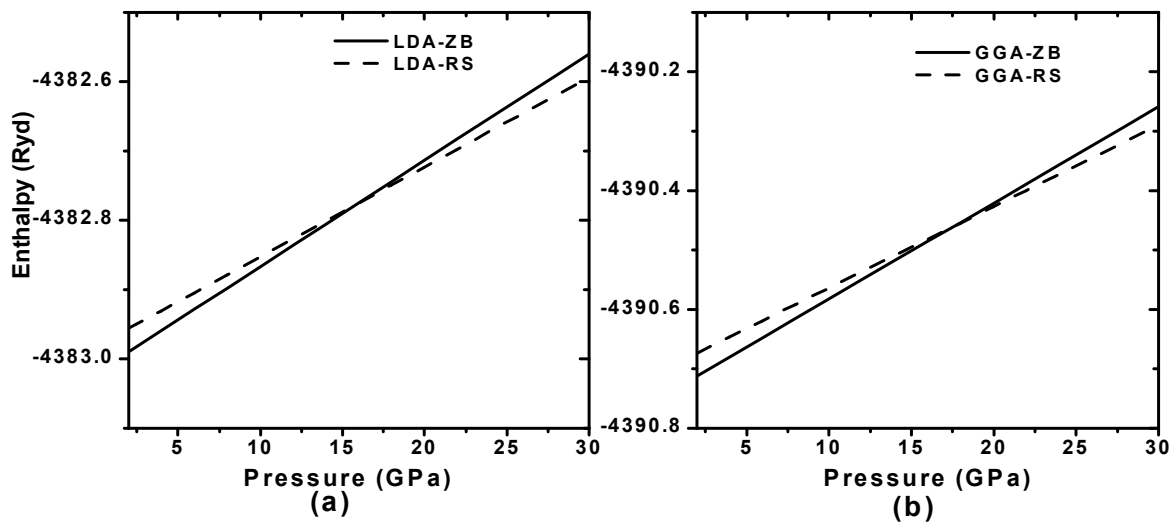
Figure 1. Total energy as a function of volume of ZnS-ZB and ZnS-RS within (a) LDA and (b) GGA.

Table 1. Experimental and calculated ground state structural parameters of ZnS

Structure	Ground state structural parameters	Present work		Experimental studies	Other theoretical calculations
		LDA	GGA		
ZB	a_0 (\AA)	5.336	5.475	5.412 ^a	5.328 ^b , 5.335 ^c ,
	B_0 (GPa)	88.88	71.51	75 ^a	5.342 ^d , 83.8 ^b , 83.70 ^c , 89.67 ^d
RS	a_0 (\AA)	5.004	5.135	--	5.066 ^e
	B_0 (GPa)	111.75	88.73	--	105.6 ^e

^aRef [4], ^bRef [5], ^cRef [20], ^dRef [21], ^eRef [6]

The structural, mechanical and physical properties of a material under pressure can be understood from the phase transition study. Generally the density functional calculation is performed at zero temperature conditions. Therefore the equal enthalpy condition, $H = E + PV$ including the pressure-volume effects is used for the structural phase transition calculations. In figure 2 the calculated enthalpy as a function of pressure is given within both (a) LDA and (b) GGA. From the figure we can see the crossing over of the enthalpy in both LDA and GGA methods indicating a phase transition between the two phases. Within the LDA, the structural transition pressure from the ZnS-ZB to ZnS-RS occurs at 15.9 GPa pressure while GGA shows a structural transition at 17.6 GPa pressure. Thus structural phase transition calculation within the GGA gives us results closer to the experimental study of 18.1 GPa pressure [22] and 16.9 GPa pressure [23] than the LDA.

**Figure 2.** Enthalpy as a function of pressure of ZnS-ZB and ZnS-RS within (a) LDA and (b) GGA.

ZnS crystallizes in the ZB structure under ambient pressure and RS structure at high pressure. We have therefore performed the electronic structure calculation at 0 GPa pressure within the LDA, GGA and mBJ-GGA for the ZB phase and shown in figure 3(a), 3(b) and 3(c) respectively. From the figures, we find that in all three cases the valance band maximum and the conduction band minimum are located at the middle of the brillion zone, Γ point indicating a direct band gap. However the energy band gap calculated within the LDA and GGA in figure 3(a) and 3(b) shows a band gap of 1.91 eV

and 1.98 eV respectively which is very low as compared to the experimental results of 3.6 eV [24,25,26] while in figure 3(c) the calculation within the mBJ-GGA shows a band gap of 3.5 eV which is very close to the experimental result. The reason for the mere difference in the calculation within the mBJ-GGA and experimental data is that the DFT calculation is performed at absolute temperature while the reported experimental data is at room temperature. One interesting point in the energy band gap calculation is the shifting of the conduction band maximum towards higher energy and wide opening of the band gaps. The order of the energy band gaps of ZnS in the three cases is $\text{LDA} < \text{GGA} < \text{mBJ-GGA}$. Also the gap between the lowest band and valance band minimum is found decreasing in the order $\text{LDA} > \text{GGA} > \text{mBJ-GGA}$. Thus the implementation of the mBJ-GGA overcomes the underestimation in the band gap calculation with LDA and GGA and gives us results closer to the experimental studies.

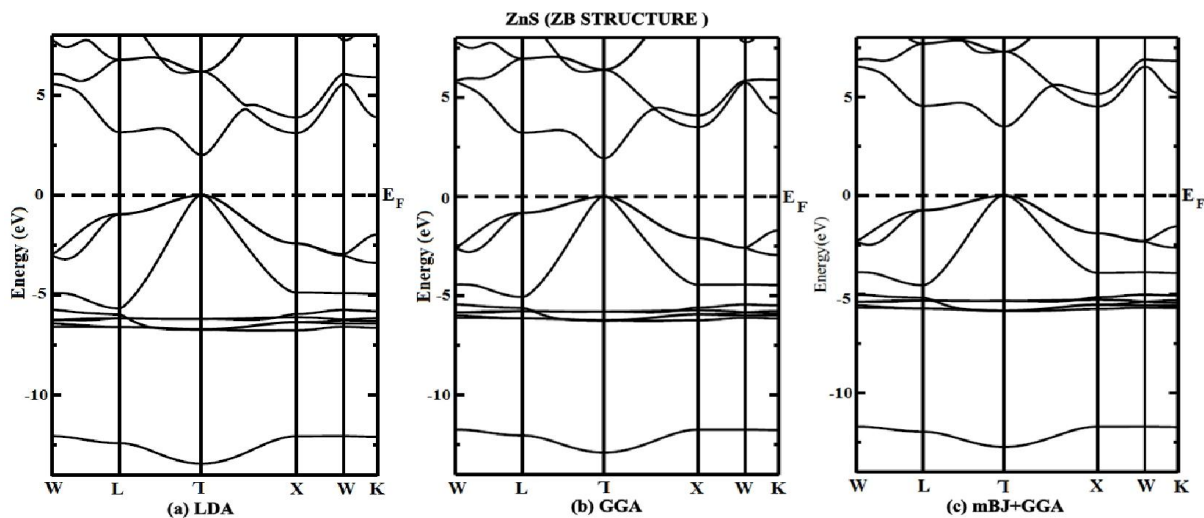


Figure 3. Energy band diagram of ZnS-ZB structure within (a) LDA, (b) GGA, (c) mBJ+GGA

The origin of the band structure is related to the corresponding density of states of the compound. For better understanding of the contribution of the states in the energy band gaps the total and partial density of states of ZnS-ZB within the LDA, GGA and mBJ-GGA at 0 GPa pressure is also studied and shown in figure 4(a), 4(b) and 4(c). From the total DOS study we find that the lowest band is mainly contributed by the s-state (S atom) and its contribution within the LDA, GGA as $\text{LDA} > \text{GGA} > \text{mBJ-GGA}$. The valance band is found to be mainly contributed by the d-state (Zn atom) whose contribution increases in the order $\text{LDA} > \text{GGA} > \text{mBJ-GGA}$. The increase in the intensity within the mBJ-GGA calculation leads to better treatment of the band structure than the LDA and GGA methods.

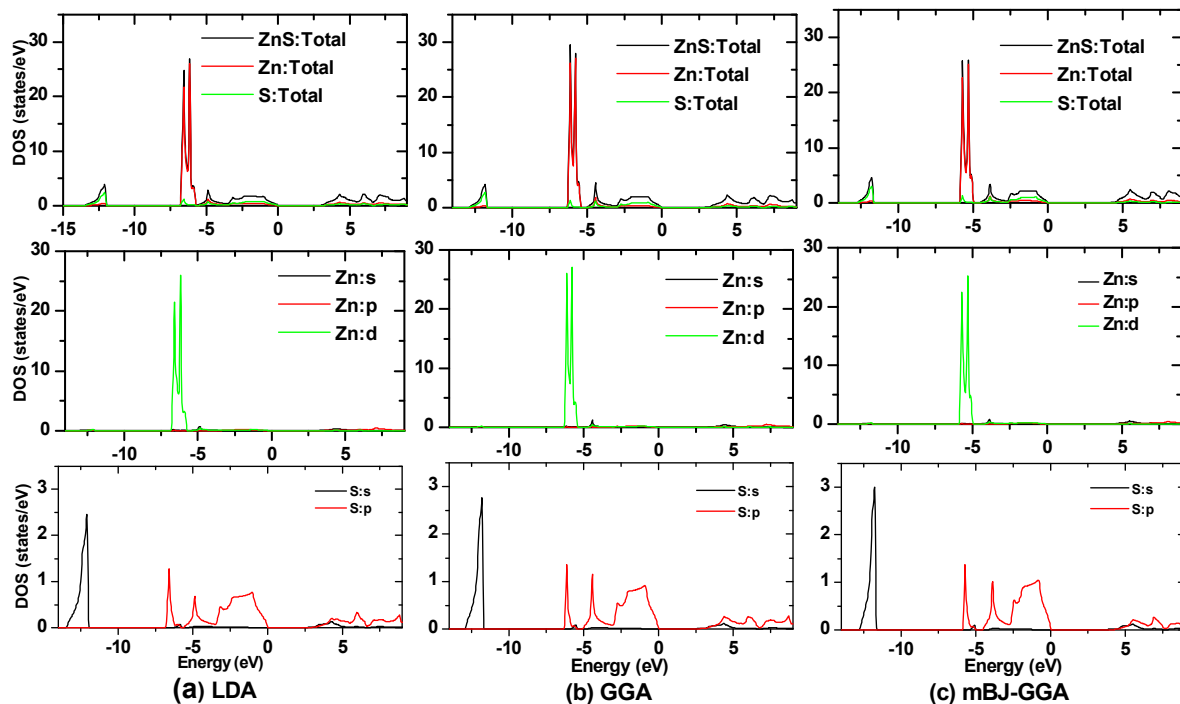


Figure 4. Total and Partial DOS of ZnS within (a) LDA, (b) GGA and (c) mBJ-GGA.

4. Conclusion

The structural parameters of ZnS-ZB and ZnS-RS are studied within the LDA and GGA. The structural phase transition from the ZB to RS phase calculated within the LDA occurs at 15.9 GPa pressure while within the GGA shows a structural phase transition at 17.6 GPa pressure which is closer to the experimental results. The energy band gap within LDA and GGA are 0.91 eV and 0.98 eV respectively while within mBJ-GGA, a band gap of 3.5 eV is shown. The LDA and GGA method underestimates the energy band gap while mBJ-GGA solves this discrepancy and gives us results very close to the experimental studies. Also the effective results provided by the mBJ-GGA method are found to be a result of the proper treatment of the electronic states. In conclusion, we find that the mBJ-GGA is a more effective tool for electronic structure calculation of ZnS and will validate its applications in optoelectronic devices.

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