

High Pressure Band Structure and Metallization in Zinc Sulphide

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Abstract The theoretical investigation of the electronic band structure, density of states and metallization of technologically important semiconductor zinc sulphide (ZnS) under high pressure is obtained using the full potential linear muffin-tin orbital (FP-LMTO) method. The ground state properties and band gap values are compared with the experimental results. Zinc sulphide becomes metal and superconductor under high pressure, but before this they undergo structural phase transition from zinc blende phase to rocksalt phase. The density of states at the Fermi level ($N(E_F)$) is enhanced as the pressure is further increased, which leads to the superconductivity in zinc sulphide. The non-occurrence of metallization and structural phase transition simultaneously in zinc sulphide is also confirmed.

Keywords Band Structure, Density of States and Metallization

Subject classification : PACS: 61.50.Ks; 71.15.Ap; 71.15.Fr; 71.20.Ps

1. Introduction

The electronic band structure study of crystalline materials play a basic role in condensed matter physics, because the better understanding of the various physical properties of solids mainly depend upon their and structure [1]. Currently there is lot of interest in the study of materials under high pressure. The physical properties of materials undergo a variety of changes when they are subjected to high pressure. This paper contains the details of the theoretical investigation of the electronic band structure, density of states and metallization of a semiconductor, ZnS under high pressure. Group II-VI compounds are widely investigated under normal and high pressures; since they act as photographic materials, solid electrolytes and liquid semiconductors [1]. The increase of pressure means the significant decrease in volume, which results in the change

of electronic states and crystal structure [3]. Subjecting zinc sulphide to high pressure induces structural phase transition, semiconductor - metal transition and superconducting transition at giga pascal (10^9 pascal = 1GPa) pressures [4]. It is felt that many important parameters are involved in these calculations and further theoretical studies are needed to improve the agreement with the experiment. In all the above studies, only very little information is provided about the high pressure band structure and density of states of ZnS [5]. In particular no work has been reported regarding the metallization of ZnS.

2. Computational Procedure

Table 1. Lattice constant(a), Pressure(P) and band gap (E_g) for different reduced volumes

V/V_0	a (a.u)	P (Mbar)	$E_g(P)$
1	5.4100	0	3.6856
0.9356	5.2987	14.20	3.3587
0.9	5.223	20.97	3.2650
0.8	5.022	56.08	2.8451
0.7	4.7568	96.37	1.5823
0.6254	4.6674	115.75	0
0.6	4.567	184.6	0
0.5	4.294	280.5	0
0.4	3.986	690.8	0
0.3	3.7649	1980.8	0

The band structures of ZnS corresponding to various pressures are obtained using the full potential linear muffin-tin orbital (FP-LMTO) method [2]. We have used FP-LMTO method with in generalized gradient approximation (GGA) [6] and exchange-correlation potential of Ceperley and Alder as parametrized by Perdew and Zunger [7]. The electronic configuration of Zn and S are [Ar] $3d^{10}4s^2$ ($Z = 30$) and [Ne] $3s^23p^4$ ($Z = 16$) respectively.

The valence electronic configurations chosen in our calculation are $3d^{10}4s^2$ for Zn and $3s^23p^4$ for S. There are 18 valence electrons contributing to the valence bands [2]. The final energy convergence is within 10^{-5} Ry. The calculated total energies are fitted to Murnaghan's equation of state (EOS), to determine the pressure derivative of bulk modulus B_0' [8]. The calculated values of pressure and lattice constant are given in Table.1.

3. Band Structure and Density of States

The relation connecting reduced volume and pressure of ZnS is given in Fig.1. Pressure increases with decreasing of reduced volume. The relation connecting reduced volume and lattice constant is given in Fig.2 Lattice constant decreases with decreasing reduced volume. The relation

connecting energy band gap and pressure is given in Fig.3. When pressure increases band gap decreases and reaches zero at metallization pressure [1]. The band structures and density of states of ZnS is computed (Figs.4 to 7) for various reduced volumes ranging from $V/V_0=1.0$ to 0.3 in steps of 0.05. Fermi level is indicated by dotted horizontal line. But here we have presented the band structures along the symmetry directions $\Gamma-X-W-L-\Gamma-K$ (Figs.4 and 5) corresponding to volume compressions $V/V_0=1.0$ and $V/V_0=0.6254$ for ZnS. At normal pressure, the single valence band, which is positioned at the bottom of the valence band arise from $3s^2$ electrons of S. The five bands nearer to the single band arise from $4p^6$ electrons of Zn and $3p^4$ electrons of S (Fig. 4). The three bands appearing below the Fermi level are due to the $4s^23d^4$ electrons of Zn (Fig.4).The empty conduction bands above the Fermi level are due to $3p, 3d$ states of Zn and S.

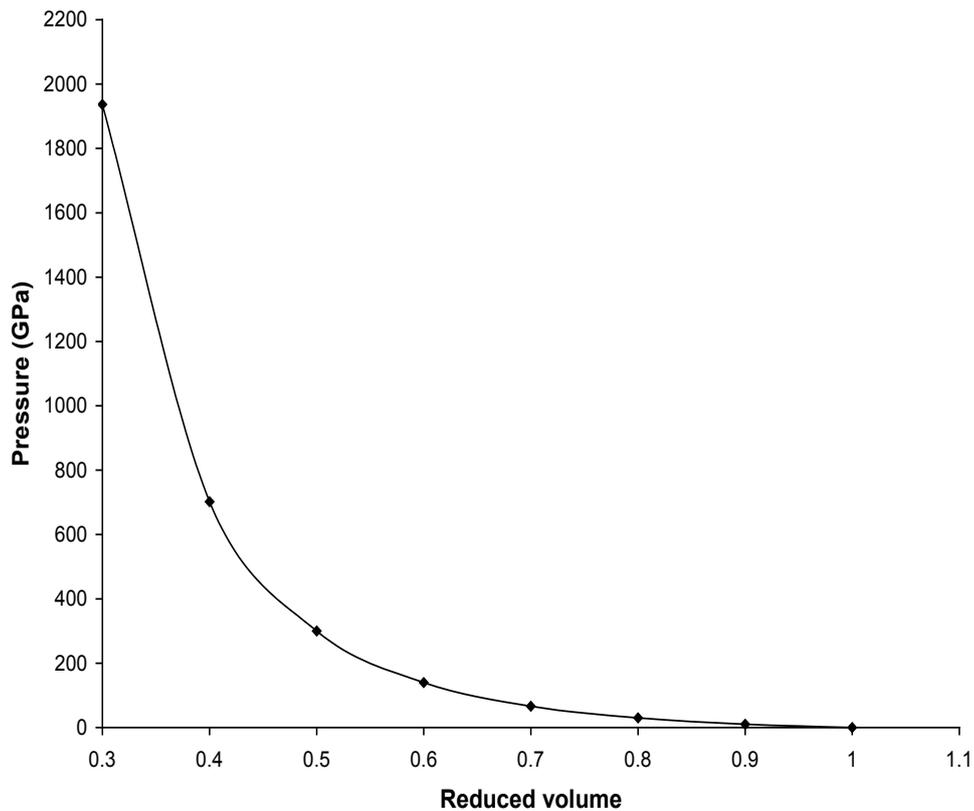


Figure 1. Relation connecting reduced volume and pressure of ZnS

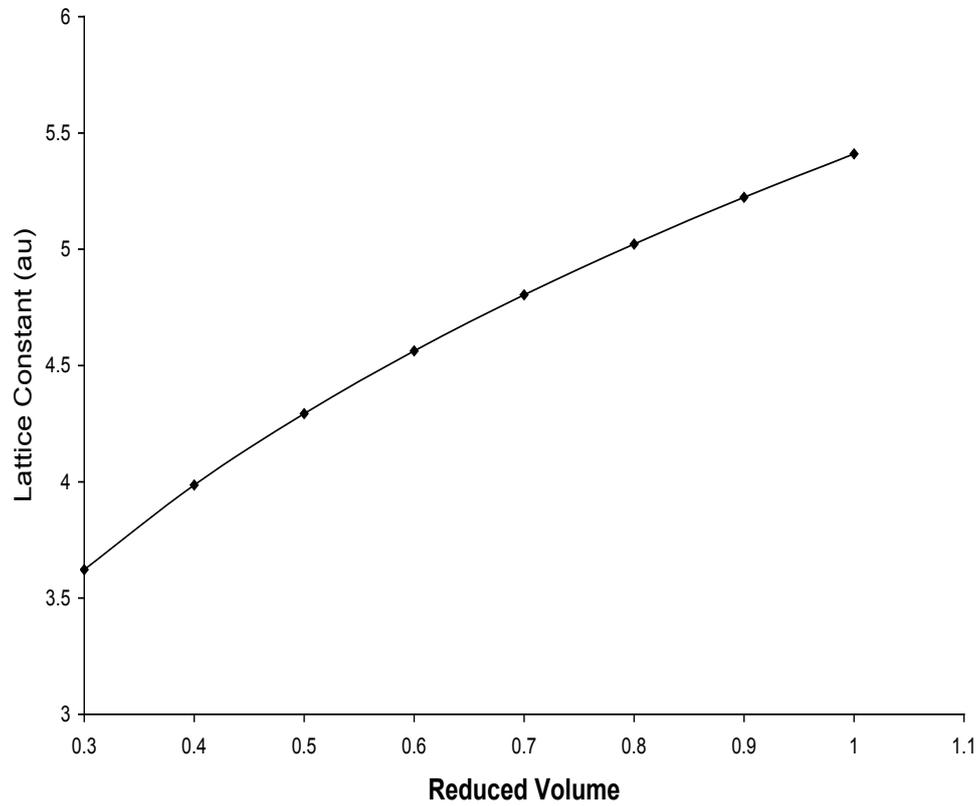


Figure 2. Relation connecting reduced volume and lattice constant of ZnS

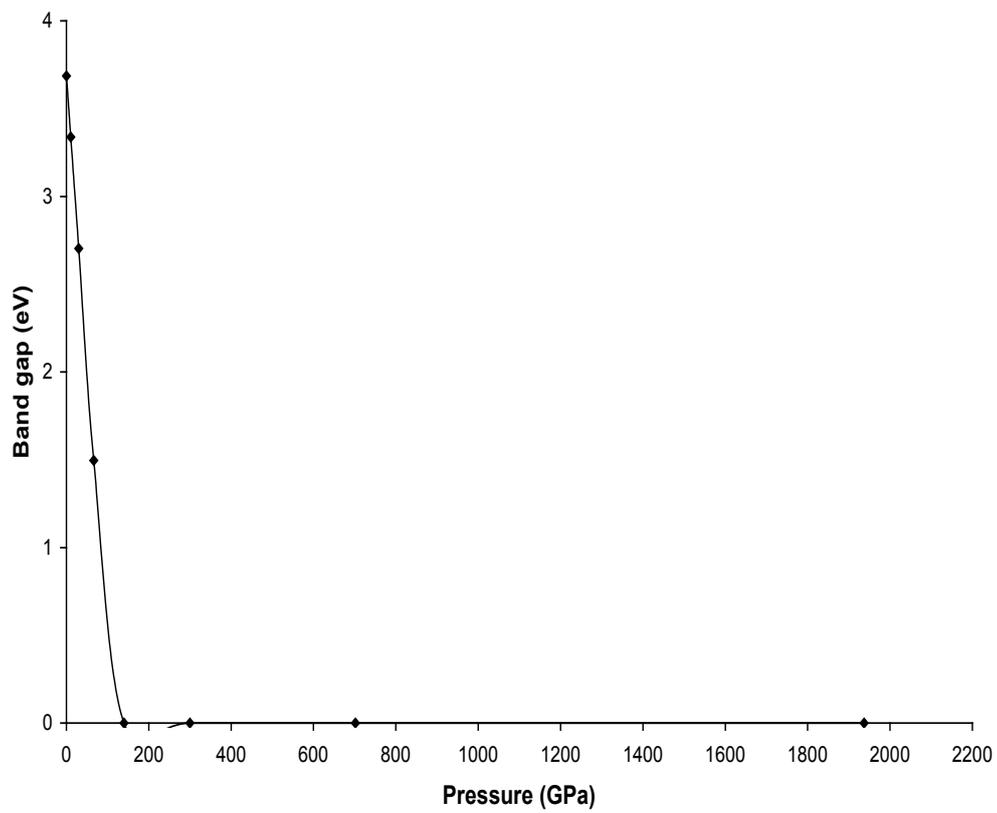


Figure 3. Relation connecting pressure and band gap of ZnS

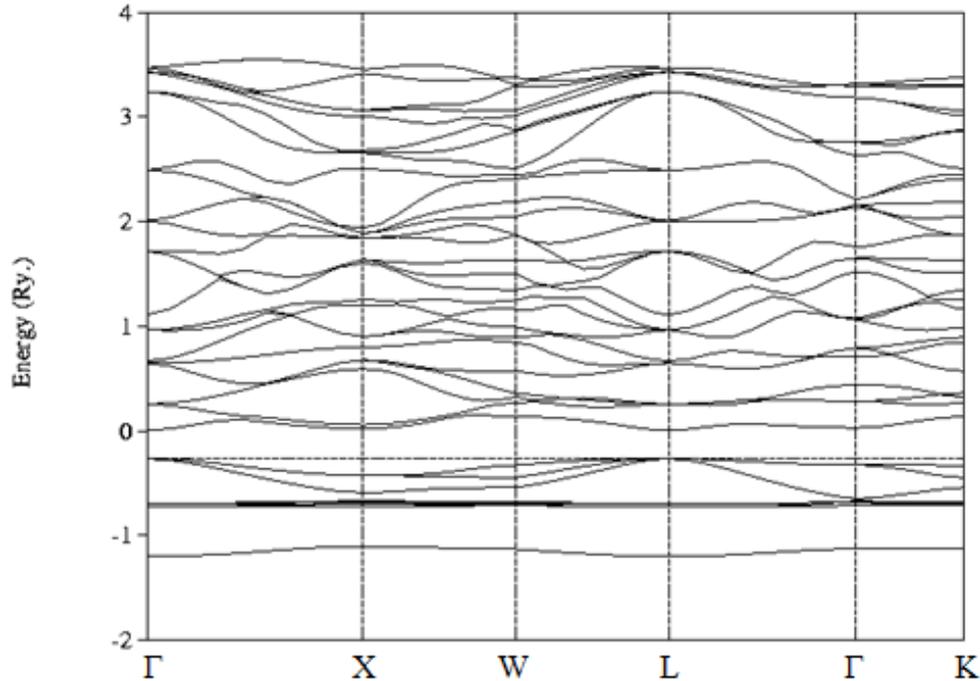


Figure 4. Band structure of ZnS at normal pressure

The characteristic features of ZnS band structure are similar to the previous calculations [1]. The fundamental energy gap is between the half-filled p like valence band due to sulphur and empty p like conduction band due to zinc. At normal pressure, the band gap of ZnS is direct (3.6856 eV) with top of the valence band in Γ point and the bottom of the conduction band in a Γ point (Fig. 4). The calculated band gap is in agreement with the experimental value than previous theoretical value (Table 2). As the pressure increases the width of the valence band and the empty conduction band get widened. These changes lead to the closing of the band gap under pressure (Fig. 5). The density of states (DOS) (states/Ry.) calculations for all the reduced volumes has been carried out but here we have given the DOS histograms of ZnS corresponding to normal pressure (Fig. 6) and metallization pressure (Fig. 7). At normal pressure (Fig. 6) the levels arising from $3s^2$ electrons of S give the short spike near the origin. The long spike near the Fermi energy is due to $4p^6 4s^2 3d^4$ electrons of Zn and $3p^4$ electrons of S. The short peaks above the Fermi energy E_F are due to the $3p$, $3d$ states of Zn and S.

Table 2. Equilibrium lattice constant (a_0), bulk modulus (B_0) and its pressure derivative (B_0'), Energy gap (E_g) of ZnS.

Ground State Properties	ZnS		
	Present study	Experiment [4]	Previous theory [3,5]
$a_0 \text{ \AA}$	5.410	5.423	5.385
$B_0 \text{ GPa}$	77	78.5	64.5
B_0'	4.86	4.237	3.339
$E_g \text{ eV (direct)}$	3.6856	3.82	3.35

The above normal pressure trend is changed under high pressure. The increase of pressure leads to the broadening of bands which results in the decrease of density of states value in most of the energy regions and increase in the width of the valence band and empty conduction band. When pressure increases the value of E_F increases whereas no density of states is available at the Fermi level up to metallization pressure. In Fig. 7, there are appreciable values of $N(E_F)$ for ZnS ($V/V_0 = 0.6254$) in ZnS structure, which indicate the occurrence of metallization in ZnS. Further increase in pressure leads to enhanced density of states at the Fermi level which induces super conductivity. In ZnS, metallization takes place by the indirect closure (Fig. 5) of band gap between valence band (at Γ -point) and conduction band (at X-point)[1]. The metallization volume of ZnS is $V/V_0 = 0.6254$, which corresponds to the pressure $P_M = 115.75$ GPa. The general features of high pressure band structure is similar to previous calculations [3,5]. From our calculation, in ZnS an indirect closure of band gap occurs.

The density of states histograms of ZnS at high pressure is given in Fig. 7. At this pressure ZnS is in cubic structure. From the histogram, it is seen that the heights of the spikes are considerably reduced when compared to Fig. 6. Reason is when pressure increased E_F increases whereas no density of states is available at the Fermi level up to metallization pressure. There are appreciable values for DOS at $V/V_0 = 0.6254$ (Fig. 7) indicating metallization in ZnS [1]. When pressure increases (reduced volume decreases) the value of the DOS at Fermi energy, $E_F(N(E_F))$ increases [5].

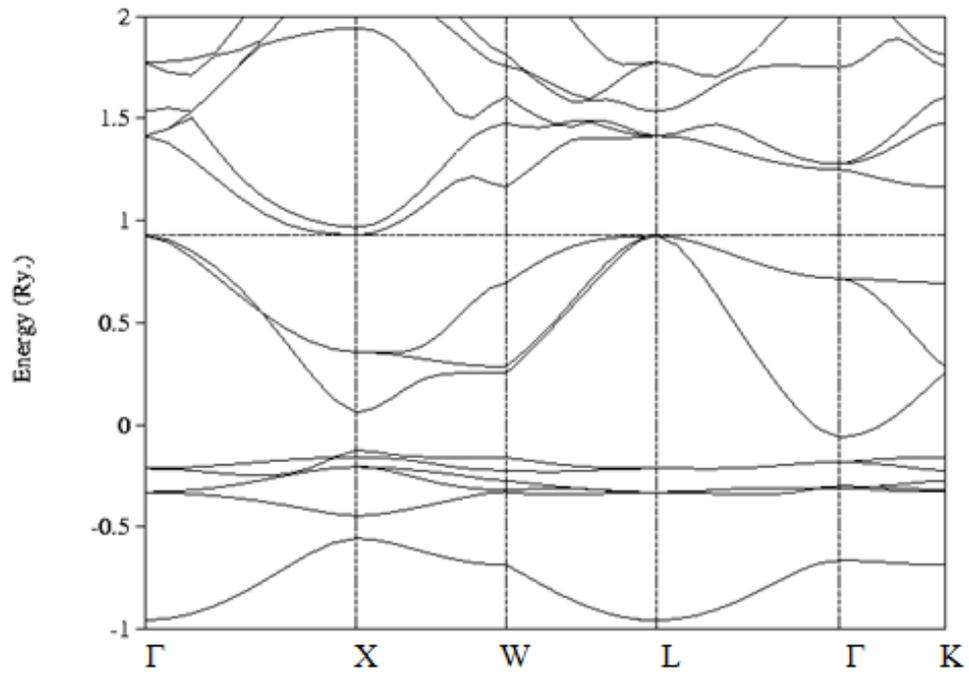


Figure 5. Band structure of ZnS at metallization pressure

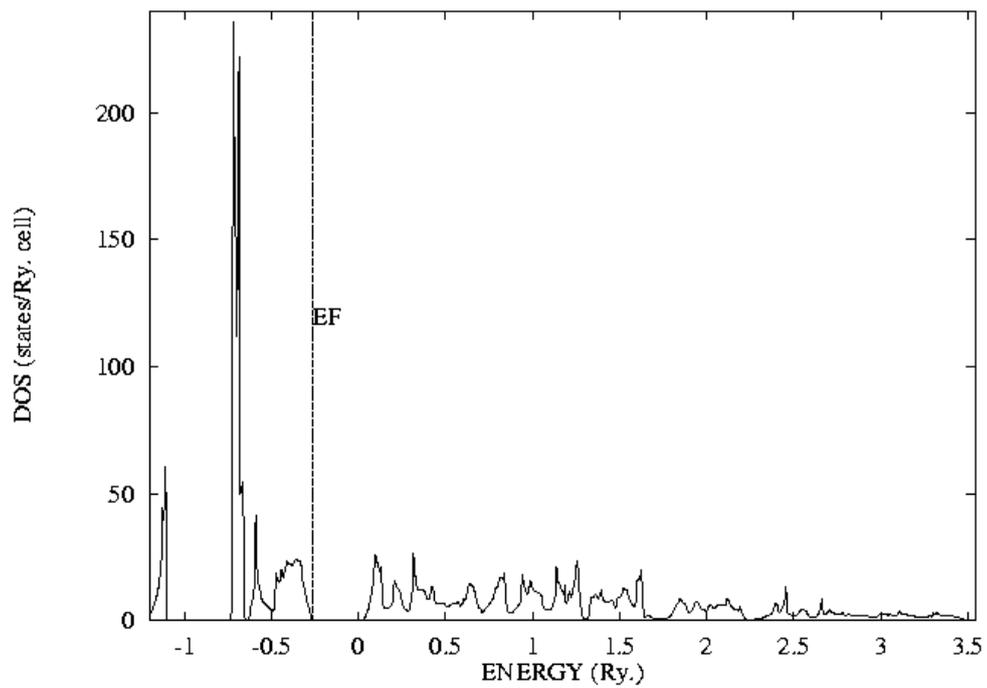


Figure 6. Density of states of ZnS at normal pressure

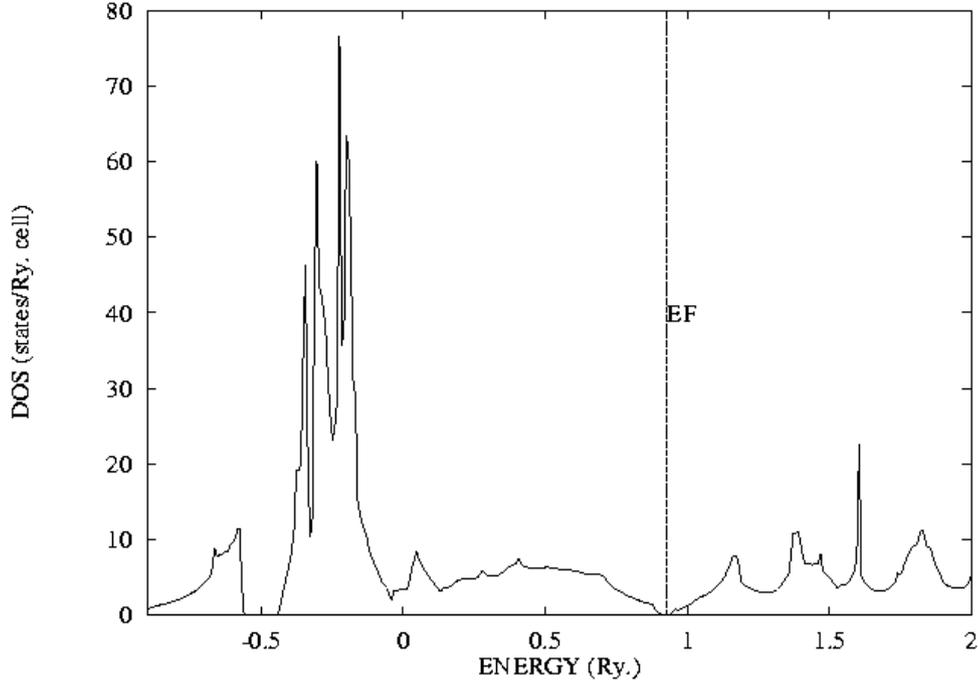


Figure 7. Density of states of ZnS at metallization pressure

4. Structural Phase Transition

The ground state properties of ZnS is studied from the total energies obtained from the FP-LMTO method [2]. The calculated total energies were fitted to Murnaghan's equation of state [1]

$$P = 1.5B_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left[1 + 0.75 \left(B_0^{-1} - 4 \right) \left\{ \left(\frac{V_0}{V} \right)^{2/3} - 1 \right\} \right]$$

To obtain the equilibrium lattice constant and other ground state properties. In Table.2, experimental and theoretical values of lattice constant and bulk modulus are compared, there is a close similarity between experiment [4] and theory[3] is obtained. The bulk modulus at normal pressure B_0 is a parameter of great physical significance in high pressure physics and few other thermo-physical properties. The value of B_0 is related to the electron density. The structure with highest B_0 will have low electron density and vice versa. Zinc sulphide becomes metal and superconductor under high pressure, but before this they undergo structural phase transition from zinc blende phase to rocksalt phase. Total energy versus reduced volume curve for ZnS is given in Fig.8. In this figure ZnS is stable up to $(V/V_0)_T = 0.9356$, further reduction of volume NaCl is the stable structure. In our calculation zinc blende phase to rocksalt phase transition occurs at 14.2 GPa corresponding phase transition volume $(V/V_0)_T = 0.9356$ (Table.3). Enthalpy versus Pressure curve for ZnS is given in Fig.9. In this figure

ZnS is stable upto $(P)_T = 14.2$.GPa, further increase of pressure NaCl is the stable structure. This value is good agreement with the experimental value of 15 GPa [4].

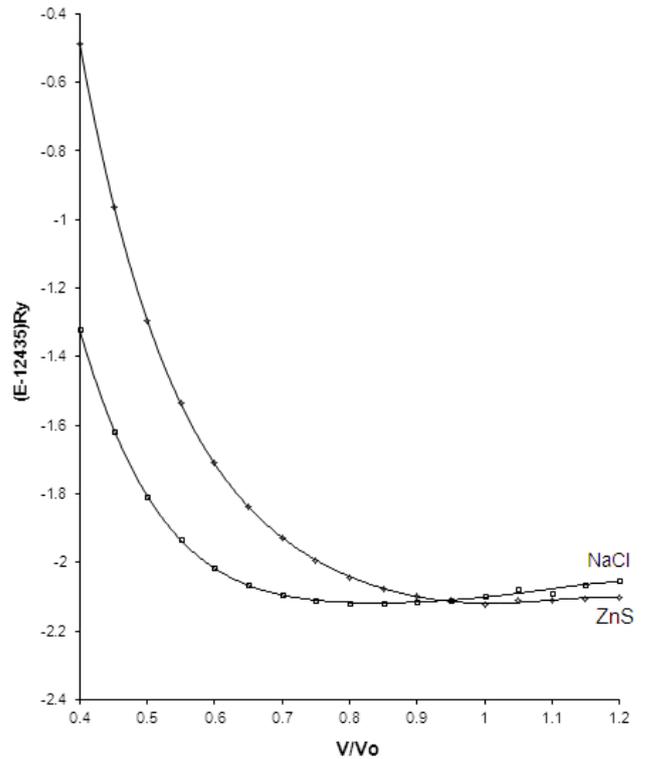


Figure 8. Total energy versus reduced volume curve for ZnS

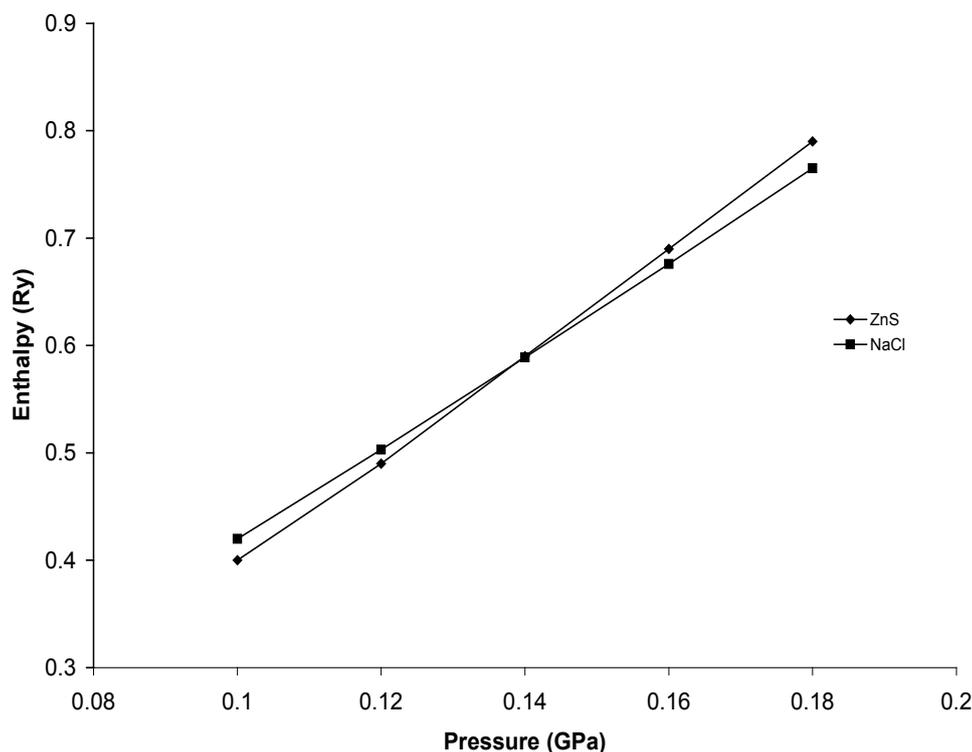


Figure 9. Enthalpy versus Pressure curve for ZnS

5. Metallization

Most of the metallization is associated with a structural transition from a low coordination non-metallic to a high coordination metallic phase[1]. At normal pressure, ZnS is a direct gap semiconductor. With increase of the pressure, the band gap decreases and at a particular pressure, there is a closing of the band gap. Similar to alkali halides, the electronic band structure calculations on ZnS suggest that metallization is due to the reordering of the energy bands with the empty p - like band (of Zn) dropping in energy and touching the top of the filled p - like band of S [1]. The band structure and density of states corresponding to metallization of ZnS is shown in Figs. 5 and 7 respectively. In ZnS, metallization takes place by the indirect closure (Fig.5) of band gap between valence band (at Γ -point) and conduction band (at X-point). The metallization volume is $V/V_0=0.6254$ (NaCl structure), and the corresponding pressure P_M is 115.75 GPa (Table.3). From Fig.7, it is seen that at high pressure the levels arising from different electrons produces the heights of the spikes considerably reduced when compared to Fig.5. Reason is when pressure increased E_F

increases whereas no density of states is available at the Fermi level up to metallization pressure.

Table 3. Structural phase transition and Metallization pressures

Group II-VI compound	Structural Phase Transition ZnS \rightarrow NaCl		Metallization	
	$(V/V_0)_T$	P_T (GPa)	$(V/V_0)_M$	P_M (GPa)
ZnS	0.9356	14.20	0.6254	115.75

6. Conclusions

The high pressure band structure and density of states of ZnS is investigated. The metallization reduced volume is $V/V_0=0.6254$ (NaCl structure), and the corresponding pressure P_M is 115.75 GPa. In our calculation zinc blende phase to rocksalt phase transition occurs at 14.2 Gpa. This value is good agreement with the experimental value of 15 Gpa [4].

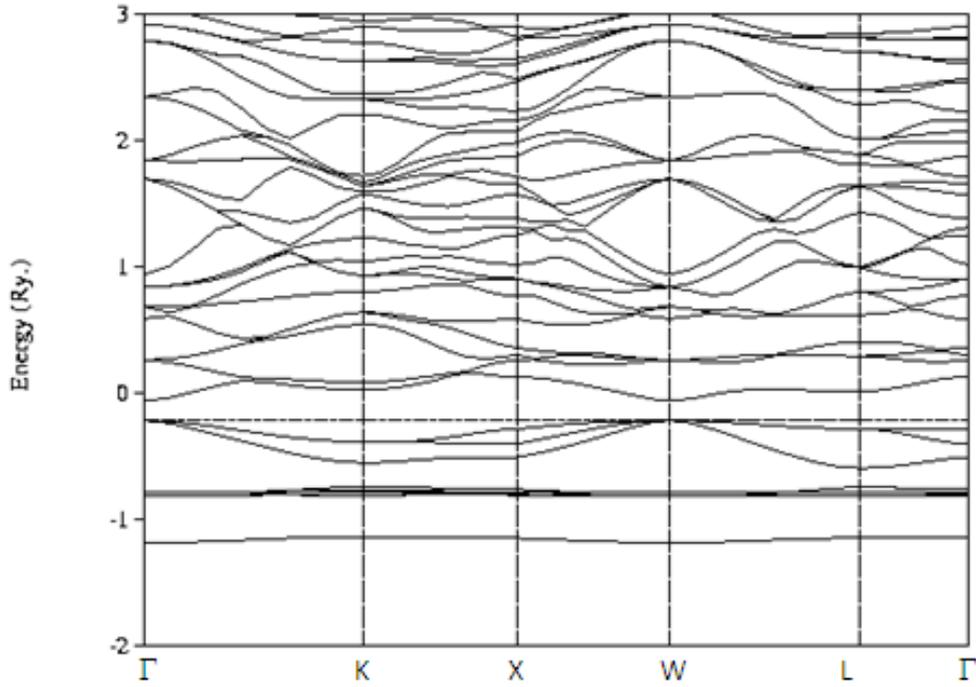


Figure 10. Band structure of ZnS at V/Vo=0.9(pressure= 20.97 GPa)

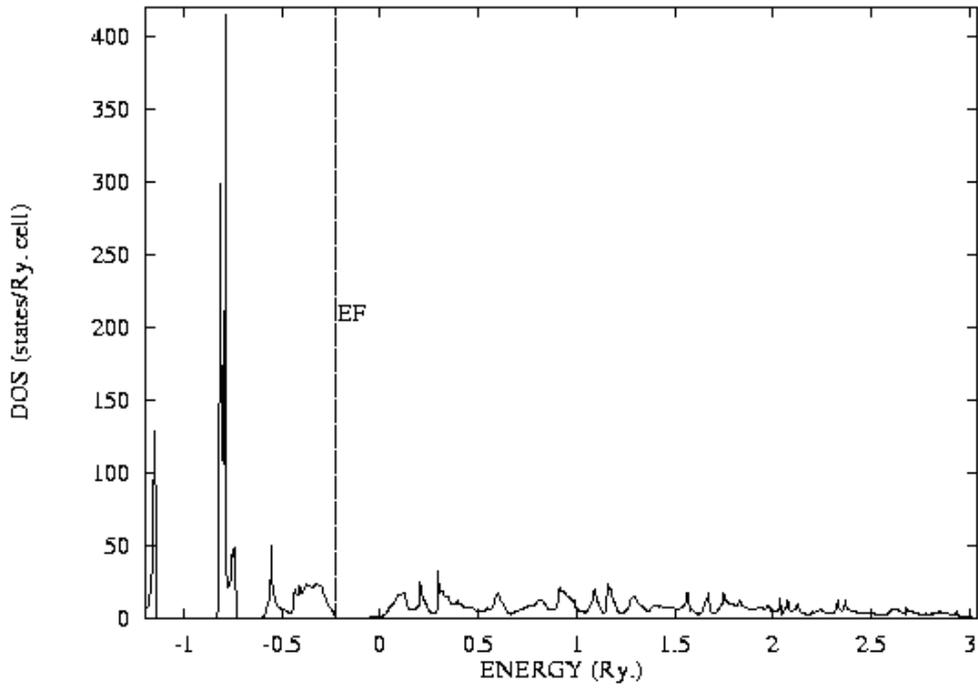


Figure 11. Density of states of ZnS at V/Vo=0.9(pressure= 20.97 GPa)

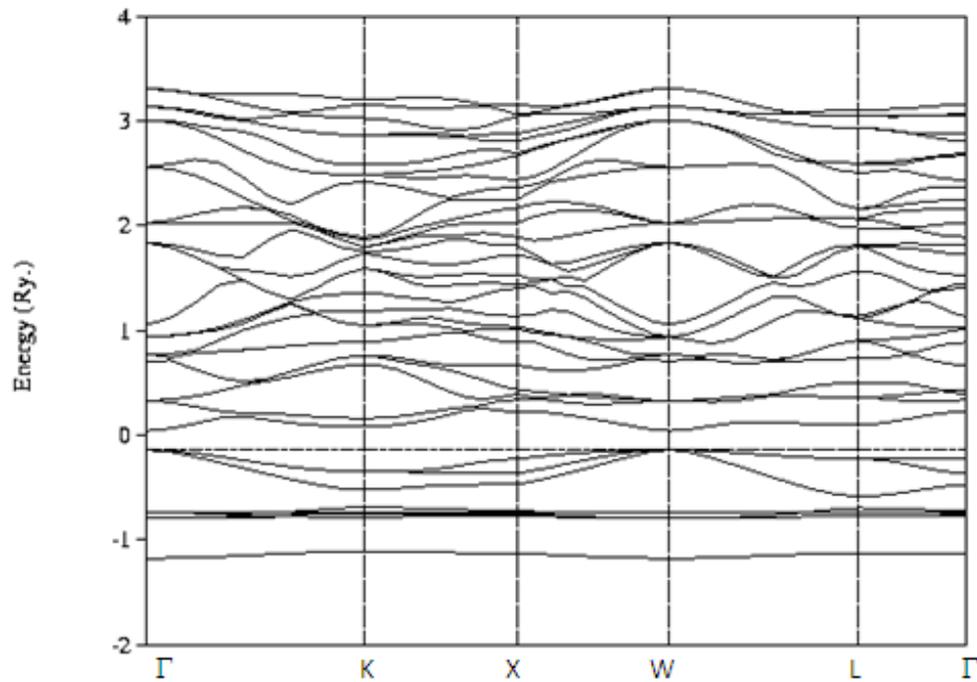


Figure 12. Band structure of ZnS at $V/V_0=0.8$ (pressure= 56.08GPa)

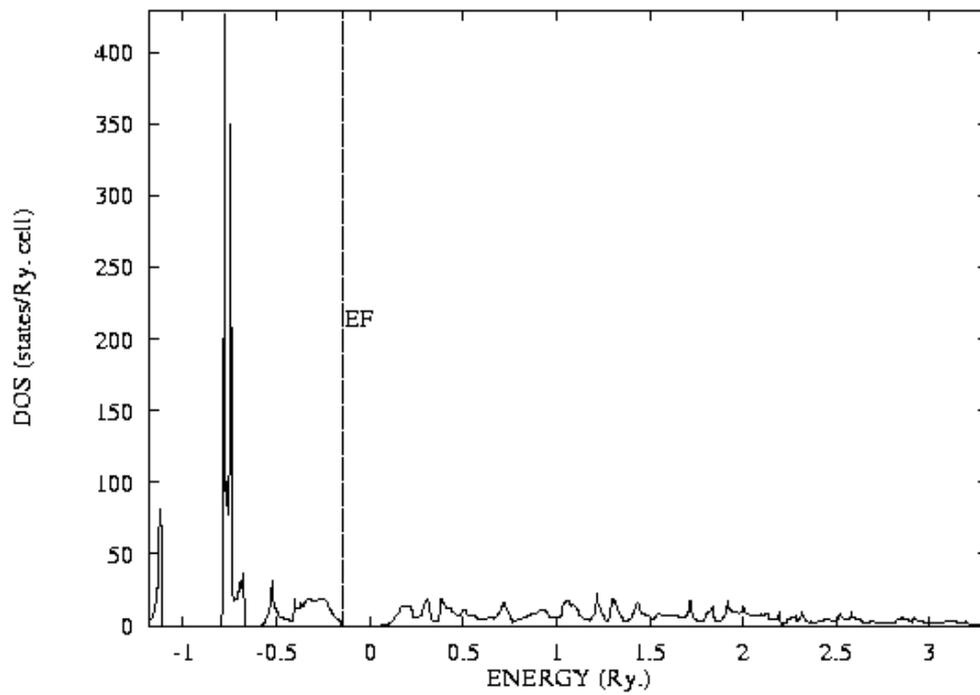


Figure 13. Density of states of ZnS at $V/V_0=0.8$ (pressure= 56.08GPa)

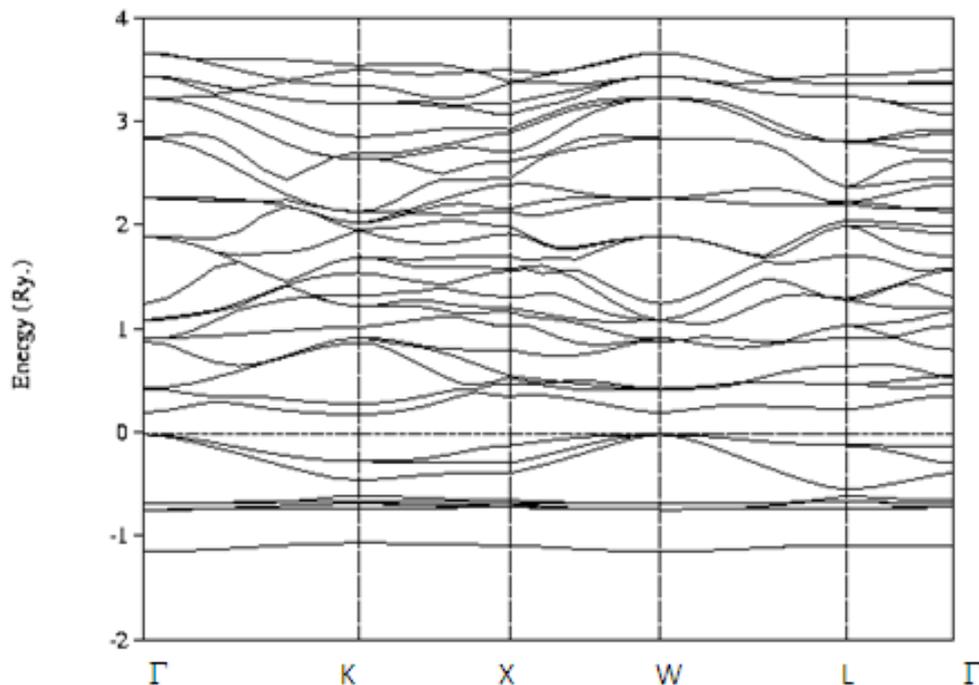


Figure 14. Band structure of ZnS at $V/V_o=0.7$ (pressure= 96.37GPa)

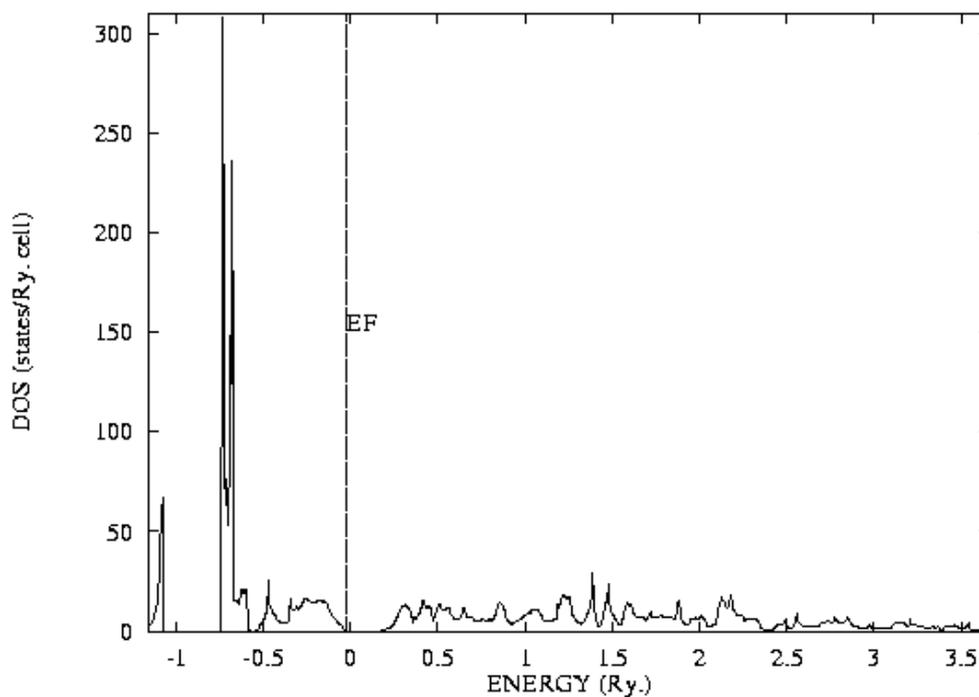


Figure 15. Density of states of ZnS at $V/V_o=0.7$ (pressure= 96.37GPa)

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