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Original Research Article

Metallization band structure and high pressure in zinc sulphide

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Abstract

In recent years there has been an increased interest in the effect of high pressure on materials. Geologists have probed the behavior of materials under pressure for learning the physico-chemistry of materials near the center of the earth. The physical, chemical and high Pressure properties of materials undergo a multiplicity of changes when they are subjected to pressure. The present study on electronic band structure, density of states, phase stability and structural changes of crystalline materials play a vital role in theoretical and Computational Physics as well as Chemical and Material Engineering, because the superior accepting of the various physical and chemical properties of solids for the most part depend upon their structure. The electronic band structure, density of states and metallization of scientifically important semiconductor ZnS under high pressure were obtained using the full potential linear muffin-tin orbital (FP-LMTO) method. The equilibrium lattice constant, bulk modulus and its pressure initiative and the phase transition pressure at which the compounds undergo structural phase transition from ZnS to NaCl are predicted from the total energy calculations. The non-occurrence of metallization and structural phase transition simultaneously in zinc sulphide is also confirmed.

Key Words: Band Structure, Metallization, Structural Transition, ZnS.

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INTRODUCTION

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 (109pascal = 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.

Calculation Procedure

able 1: Lattice constant (a), Pressure(P) and band gap (Eg) for different reduced volumes

V/Vo	*a* (a.u)	*P* (Mbar)	Eg(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] 3*d* 10 4*s* 2 (Z = 30) and [Ne] 3*s* 2 3*p* 4 (Z = 16) respectively. The valence electronic configurations chosen in our calculation are 3d 10 4s 2 for Zn and3s 2 3p 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 Bo'[8]. The calculated values of pressure and lattice constant are given in Table.1.

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 relationconnecting 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/Vo=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 Figs.4 and 5 corresponding to volume compressions V/Vo=1.0 and V/Vo=0.6254 for ZnS. At normal pressure, the single valence band, which is positioned at the bottom of the valence band arise from 3s2 electrons of S. The five bands nearer to the single band arise from 4p6 electrons of Zn and3p4 electrons of S (Fig. 4). The three bands appearing below the Fermi level are due to the 4s2 3d4 electrons of Zn (Fig.4).The empty conduction bands above the Fermi level are due to 3p, 3d states of Zn and S.

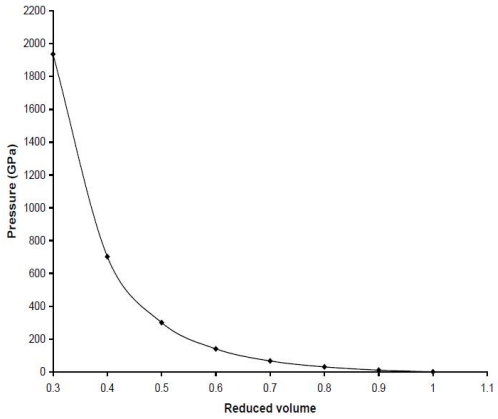

Figure 1: Relation connecting reduced volume and pressure of ZnS

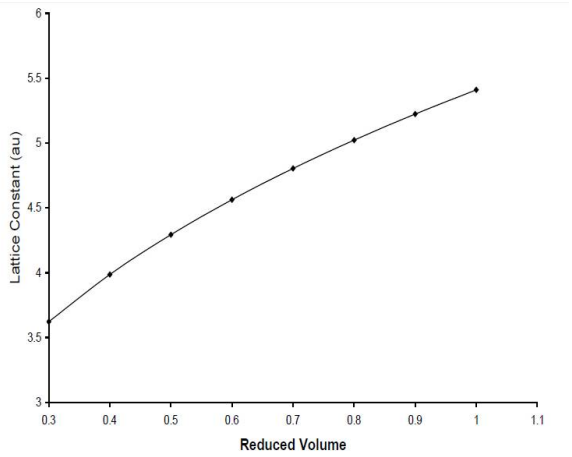

Figure 2: Relation connecting reduced volume and lattice constant of ZnS

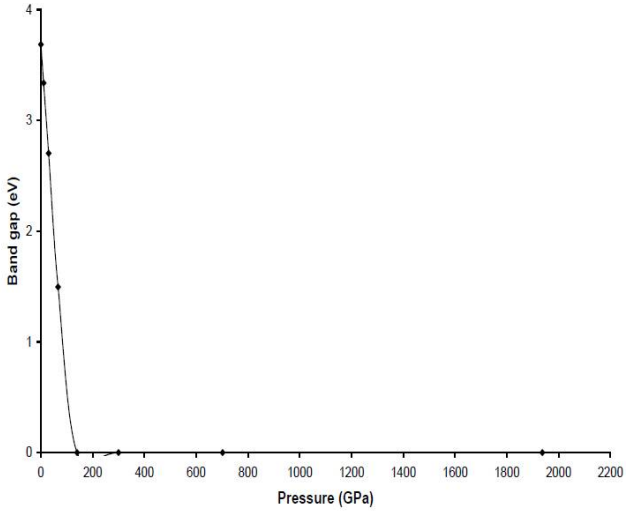

Figure 3: Relation connecting pressure and band gap of ZnS

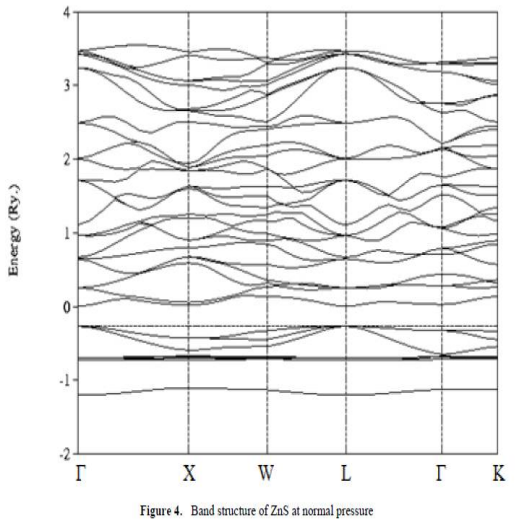

Figure 4. Band structure of ZnS at normal pressure

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 Γpoint 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 3s2 electrons of S give the short spike near the origin. The long spike near the Fermi energy is due to4p6 4s2 3d4 electrons of Zn and3p4 electrons of S. The short peaks above the Fermi energy EF are due to the 3p, 3d states of Zn and S.

Table 2: Equilibrium lattice constant (ao), bulk modulus (Bo) and its pressure derivative (Bo1), Energy gap (Eg) of ZnS

Ground State Properties	ZnS		
	Present study	Experiment [4]	Previous theory [3,5]
*ao*Å	5.410	5.423	5.385
*Bo*GPa	77	78.5	64.5
B1 0	4.86	4.237	3.339
*Eg*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 EF 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(EF) for ZnS (V/Vo =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/Vo =0.6254, which corresponds to the pressure PM=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.

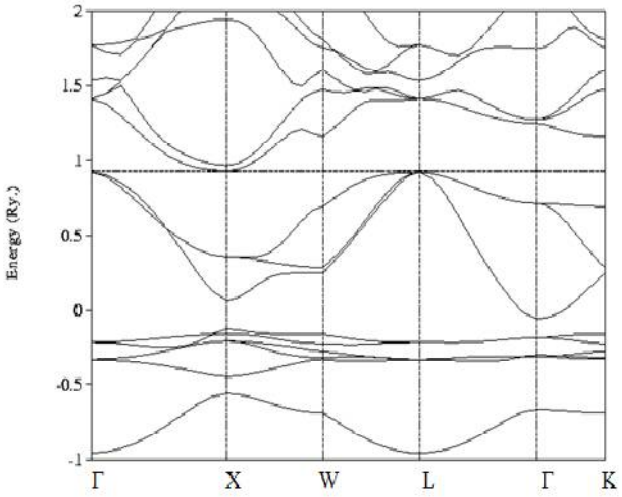

Figure 5: Band structure of ZnS at metallization pressure

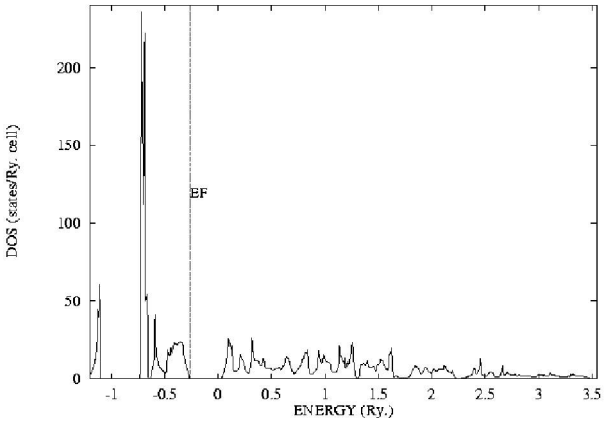

Figure 6: Density of states of ZnS at normal pressure

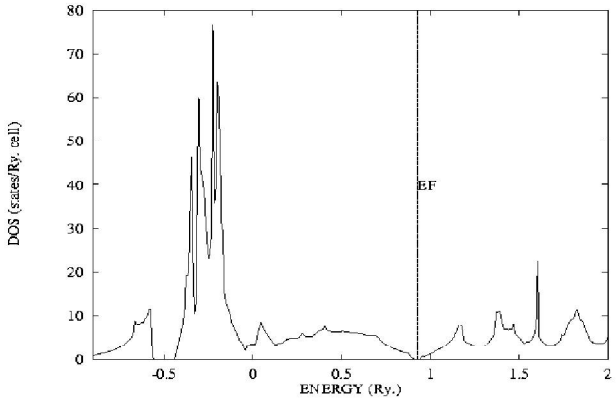

Figure 7: Density of states of ZnS at metallization pressure

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/Vo=0.6254 (NaCl structure), and the corresponding pressure PM 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 EF increases whereas no density of states is available at the Fermi level up to metallization pressure.

Table 3: Structural phase transition and Metallization pressures

GroupII-VIcompound	Structural Phase Transition ZnS→NaCl		Metallization	
	(V/Vo) T	*PT* (GPa)	*(V/VoM*	*PM*(GPa)
ZnS	0.9356	14.20	0.6254	115.75

CONCLUSIONS

The high pressure band structure and density of states of ZnS is investigated. The metallization reduced volume is V/Vo=0.6254 (NaCl structure), and the corresponding pressure PM 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].

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