Bull. Mater. Sci., Vol. 29, No. 1, February 2006, pp. 25–28. © Indian Academy of Sciences.

Pressure induced structural phase transition in SnS—An *ab initio* study

M RAJAGOPALAN*, G KALPANA and V PRIYAMVADHA
Department of Physics, Anna University, Chennai 600 025, India

MS received 21 June 2005; revised 16 November 2005

Abstract. The structural behaviour of SnS under pressure has been investigated by first principle density functional calculations of the total energy by the TB–LMTO approach. We find that SnS undergoes a structural phase transition from orthorhombic type to monoclinic type structure around 17 GPa which is in good agreement with the recent experimental study. In addition, the ground state properties are computed and compared with the available results.

Keywords. Electronic structure; high pressure; structural phase transition.

1. Introduction

The IV–VI compounds crystallize in several different crystal structures. The lead chalcogenides, PbS, PbSe and PbTe and also SnTe, adopt the NaCl structure. The compound, GeS, has an orthorhombic crystal structure. This structure consists of double layers of atoms, with each Ge atom coordinated by two S atoms in the plane of the layer and one additional S atom at a short distance perpendicular to this plane in the same double layer. The compounds, SnS and SnSe, form an intermediate case. These compounds have at low temperature the orthorhombic structure but at high temperature a more symmetric structure with space group, *Cmcm*. These layered semiconductors have been attracting the attention of scientists because of their potential application in optoelectronic devices (Shalvoy *et al* 1977; Trbojevic *et al* 1981; Subramanian *et al* 2001; Nabi *et al* 2003). They are also used in holographic recording systems (Parenteau and Carlone 1990). The electronic and optical properties of SnS and isostructural IV–VI semiconductors have been extensively studied by electron-energy-loss spectroscopy, photo emission spectroscopy and ellipsometry (Andersen and Morton 1945; Lambrss *et al* 1974; Otto *et al* 1977; Shalvoy *et al* 1977). Theoretical investigations by first principles calculations also have been reported (Taniguchi *et al* 1980; Ettema *et al* 1992). Experimental studies showed that SnS is a narrow gap semiconductor with an indirect gap of 1·07 eV and the direct gap is located at an energy of 1·3 eV. But the theoretical calculation gave the value of 1·19–1·6 eV for the indirect gap and 1·8 eV for the direct gap. In addition, the optical properties were also studied by optical, infrared and Raman spectroscopy (Lambrss *et al* 1974; Chandrasekar *et al* 1977; Yu *et al* 1993). The influence of high pressure and temperature on the band gap in SnS was studied by Parenteau and Carlone (1990) using optical absorption spectroscopy. They have observed that under pressure there is a reduction of both direct and indirect band gaps. Very recently, Ehm *et al* (2004) investigated the structural behaviour of SnS by angular dispersive synchrotron powder diffraction up to 38·5 GPa and they observed a structural transition from orthorhombic to monoclinic structure around 18·15 GPa. The motivation for the present work emerged from the above mentioned experimental work. This is achieved by performing the electronic structure and total energy calculation by means of the tight binding linear muffin–tin orbital method (TB–LMTO) within the density functional formalism.

2. Computational details

Tin sulfide crystallizes in the GeS (B16) type structure in space group, *Pnma*. Sn and S occupy the positions (0·1194, 0·25, 0·1198) and (0·8508, 0·25, 0·4793), respectively. The lattice parameters are taken from the experimental work (Ehm *et al* 2004). The tight binding linear muffin–tin orbital (TB–LMTO) method based on the local density approximation within the framework of density functional theory was used in the present work (Andersen 1975; Andersen and Jepsen 1984). The relativistic effect was taken into consideration in the scalar style, but the spin orbit coupling was neglected. The exchange correlation potential within the local density approximation is calculated using the parametrization scheme of von Barth and Hedin (1972). The Brillouin zone integration was done with tetrahedron method (Jepsen and Andersen 1971). The self consistency is obtained in the charge density with 1728 K

*Author for correspondence (mraja1948@yahoo.co.in)

points in the entire Brillouin zone. Without breaking the crystal symmetry, empty spheres are introduced to have close packing. The sphere radii are chosen in such a way that the maximum overlap between two different spheres is around 15% and charge flow is as per the electro negativity criterion.

3. Results and discussion

The electronic structure and the total energy of SnS which crystallize in the orthorhombic structure are obtained as a function of cell volume by performing the self consistent band structure calculation by TB–LMTO approach in a manner similar to our earlier work (Kalpana *et al* 1997; Rajagopalan and Sundareswari 2004). The total energies are fitted to equation of state (Birch 1978) to obtain the pressure volume relation and hence the bulk modulus. The values are presented in table 1. From the data, we can understand that the theoretically calculated lattice parameters differ from the experimental value by 1·5% and the value of bulk modulus is in good agreement with the reported experimental value. In order to look for the structural phase transition, the total energies are obtained as a function of cell volume in the monoclinic structure also. The total energy as a function of cell volume is presented in figure 1 for the two structure types. One observes that the total energies of the two structure types intersect at a critical volume indicating that SnS undergoes a structural phase transition. The transition pressure is obtained as the pressure at which the enthalpies of the two phases are identical. The calculated value of the transition pressure is 17 GPa with a volume collapse of 6·3% which is in good agreement with the recent experimental study (Ehm *et al* 2004) and given in table 2. The lattice parameters at the transition pressure are a = 11·55 Å, b = 3·741 Å, c = 7·373 Å and the bulk modulus is 76·28 GPa. The pressure volume curve is plotted and presented in figure 2.

Table 1. Comparison of experimental and theoretical values.

Lattice parameter (Å)	Present (TB–LMTO)	Experiment
a	11·0123	11·200 (2)
b	04·0370	3·987 (1)
c	04·2006	4·334 (1)
Bulk modulus (GPa)	39·55	36·6

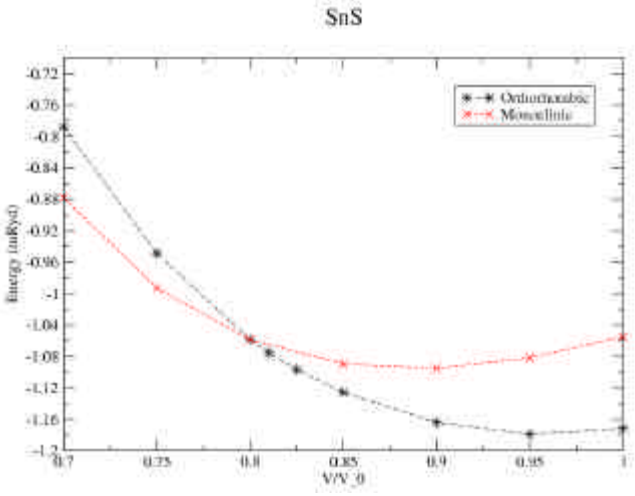

Figure 1. Total energy vs reduced volume.

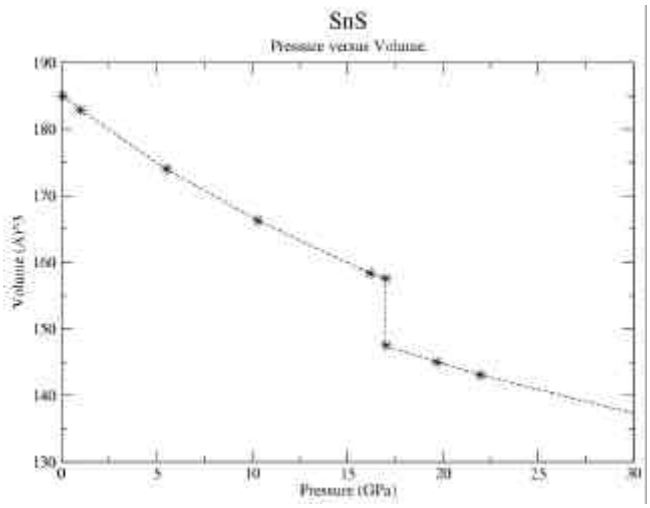

Figure 2. Pressure vs volume of SnS.

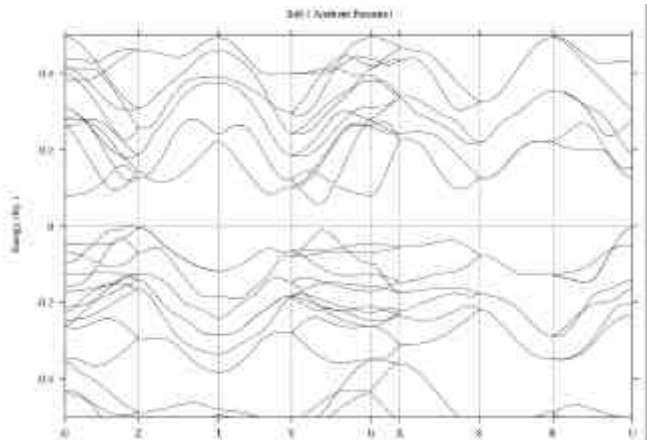

Figure 3. Energy band structure of SnS at ambient pressure.

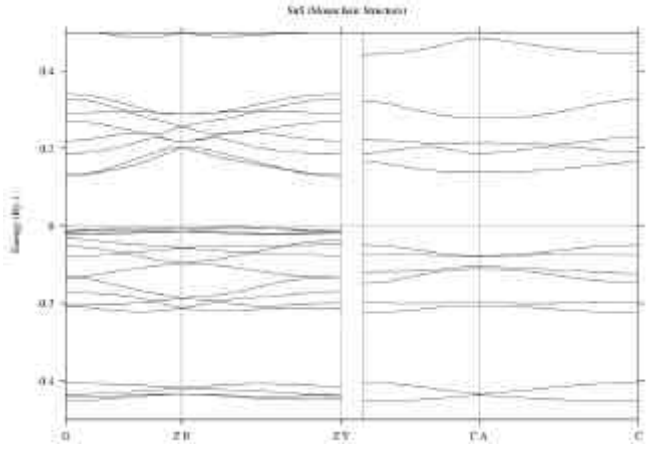

Figure 4. Energy band structure of SnS in the orthorhombic structure.

Table 2. Table indicating the volume collapse occurring in the phase transition from the orthorhombic to the monoclinic phase of SnS.

	Present	Experiment
Transition pressure (GPa)	17·0	18·1
V1 (B1)	147	
V2 (B2)	158	
Volume collapse (%)	6·3%	9·1%

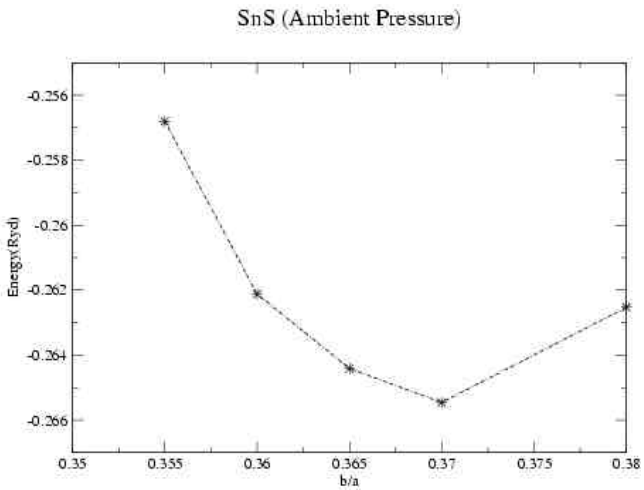

Figure 5. *b*/*a* vs energy(ryd).

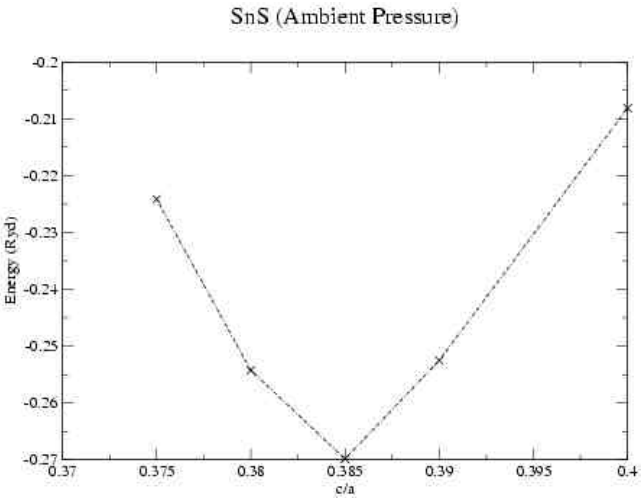

Figure 6. *c*/*a* vs energy(ryd).

The dispersion of energy bands for the selected directions in the Brillouin zone is shown in figure 3. The overall band profile is in agreement with those obtained by LSW method (Ettema *et al* 1992). The lowest band consisting mainly of sulfur 3*s* orbital are well separated from the other bands. These bands have nearly the same energy in the large part of the Brillouin zone. The bottom of the valence band consists of Sn 5*s* states for a large part. The bands in the middle of the valence band mostly consist of S 3*p* and Sn 5*p* states. The maximum of the valence band is not at *G* but the minimum of the conduction band is at *G*. There is an indirect gap between the valence band and the conduction band of 0·79 eV and the direct gap is 1·77 eV. When the compound, SnS, is compressed by reducing the cell volume, the band gap starts to reduce. The decrement of the direct gap is larger than the reduction of the indirect gap. This trend is also seen by Parenteau and Carlone (1990) in their experimental studies. As mentioned, the structural phase transition occurs around 17 GPa and SnS goes to monoclinic structure type. The band structure profile in this phase is also plotted and given in figure 4, *b*/*a* and *c*/*a* minimizations are given in figures 5 and 6, respectively. From the plot one observes that SnS is again a semiconductor with an indirect gap of 1·64 eV. Further compression in this structure increases the gap value.

4. Conclusions

We have studied the electronic structure of SnS in the orthorhombic and monoclinic structure types as a function of cell volume by first principles TB–LMTO approach. SnS is found to be a narrow gap semiconductor with an indirect gap. Application of pressure decreases the direct gap at a faster rate than indirect gap. At around 17 GPa, SnS undergoes a structural phase transition to monoclinic structure type with a volume collapse of 6·3% which is in good agreement with the experimental work (Ehm *et al* 2004). In the monoclinic phase also SnS is in the semiconducting state with an indirect gap of 1·64 eV. Further compression increases the band gap value.

Acknowledgement

One of the authors (MR) would like to thank the Max Planck Society and Prof. O K Andersen for the hospitality.

References

Andersen J S and Morton M O 1945 *Proc. R. Soc*. **A184** 83
Andersen O K 1975 *Phys. Rev*. **B12** 3060
Andersen O K and Jepsen O 1984 *Phys. Rev. Lett*. **53** 2571
Birch F 1978 *J. Geophys. Res*. **83** 1257
Chandrasekar H R, Humphreys R G, Zwick U and Cardona M 1977 *Phys. Rev*. **B14** 2177
Ehm L, Knorr K, Dera P, Krimmel A, Bouvier P and Mezouar 2004 *J. Phys. Cond. Matter* **16** 3545
Ettema A R H F, de Groot R A, Haas C and Turner T S 1992 *Phys. Rev*. **B46** 7363
Jepsen O and Andersen O K 1971 *Solid State Commun*. **9** 1763
Kalpana G, Palanivel B, Shammem Banu I B and Rajagopalan M 1997 *Phys. Rev*. **B56** 3532
Lambrss A P, Geraleas D and Economon N A 1974 *J. Phys. Chem. Solids* **35** 537

Nabi Z, Kellen A, Mecabih S, Khalfi A and Benosman N 2003 *Mater. Sci. Eng*. **B98** 104

Otto A, Ley L, Azoulay J, Grandke T, Eymard R, Braun W and Cardona M 1977 *Phys. Rev*. **B16** 4429

Parenteau M and Carlone C 1990 *Phys. Rev*. **B41** 5227

Rajagopalan M and Sundareswari M 2004 *J. Alloys and Compounds* **379** 8

Shalvoy R B, Fisher G B and Stoles P J 1977 *Phys. Rev.* **B15** 2021

Subramanian B, Sanjeeviraja C and Jayachandran M 2001 *Chem. Phys*. **71** 40

Taniguchi M, Johnson R L, Ghijsen L and Caudano R 1980 *Phys. Rev*. **B42** 3675

Trbojevic D, Nikelic P M, Perovic B and Cekic C 1981 *Appl. Phys. Lett*. **38** 362

von Barth U and Hedin L 1972 *J. Phys*. **C5** 1629

Yu L M, Degiovanni A, Thiry A, Ghijsen J and Caudano R 1993 *Phys. Rev.* **B47** 16222