

CHAPTER 4

ELECTRONIC BANDSTRUCTURE, THERMAL AND SUPERCONDUCTING PROPERTIES OF METALLIC CuS₂

4.1 INTRODUCTION

Transition metal dichalcogenides having the pyrite-type structure occur in the 3d series as the known mineral or synthetic compounds MnS₂ (hauerite), MnSe₂, FeS₂ (pyrite), CoS₂ and CoSe₂ (Bither et al 1968). The physical properties of pyrite structure CuX₂ compounds (X=S, Se, Te) under high pressure have been previously investigated by (Bither 1966). These authors reported for CuS₂ a metallic behaviour associated with a temperature independent susceptibility and superconductivity ($T_c < 2.4\text{K}$). Electron microscopy observations down to low temperatures ($T=10\text{K}$) show the occurrence of a charge density wave (CDW) (McMillan 1975) which could explain the physical properties of such systems. The Cu atoms in CuS₂ are monovalent and have a configuration very close to d^{10} as in all other Cu chalcogenides CuX₂ (X= S, Se, Te) (Folmer et al 1988). A lot of experimental work available for CuS₂, regarding the high-pressure structural phase transition (Folmer et al 1988, Krill et al 1976). However, theoretical investigation of electronic bandstructure and related characteristics is essential to understand the fundamental physical phenomena underlying their properties. Hence, computations have been carried out to study the ground state properties of CuS₂ using the tight-binding linear muffin-tin orbital method.



4.2 CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

The CuS_2 compound can only be obtained with the pyrite structure by high-pressure synthesis (Krill et al 1976). Space group of CuS_2 is $Pa-3$ (205) in cubic structure and $Pnmm$ (58) in orthorhombic structure. The band structure calculations for CuS_2 compound in both the structures have been carried out by using the tight-binding-linear-muffin-tin orbital method within the atomic sphere approximation (Andersen 1975, Andersen et al 1984). The density of states is calculated by the method of tetrahedron (Jepsen et al 1971). It is well known that the tight-binding linear muffin-tin orbital method works very well for high symmetry structures (Ravindran et al 1998). The ground-state properties were calculated for the lattice parameter that corresponds to the minimum of the electronic total energy. The Cubic and Orthorhombic structure of CuS_2 are shown in Figure 4.1- 4.2.

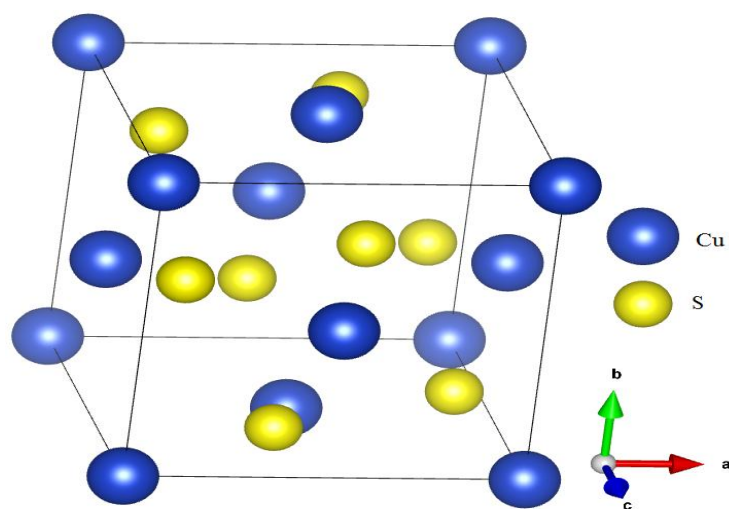


Figure 4.1 Cubic structure for CuS_2

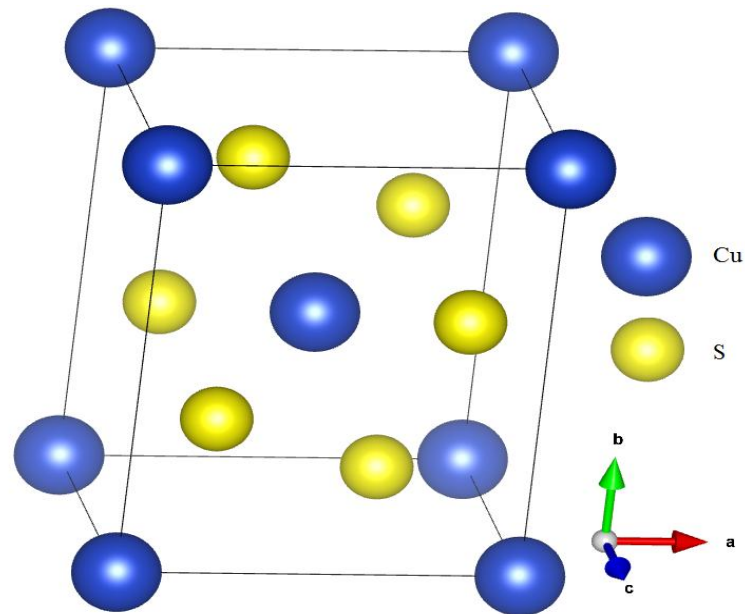


Figure 4.2 Orthorhombic structure for CuS_2

4.3 TOTAL ENERGY CALCULATION AND RELATED PROPERTIES

All the electronic properties such as the density of states and energy bands of cubic and orthorhombic phases of CuS_2 were computed for the equilibrium lattice parameters. For the equilibrium lattice parameter was obtained by minimizing the electronic total energy with respect to the cell volume. The plots of total energy as a function of cell volume for cubic and orthorhombic phases of CuS_2 are shown in Figure 4.3 - 4.5. This total energy curve was fitted to Murnaghan's equation of state (Murnaghan 1944). We found that in thermodynamical condition cubic phase is more stable. A comparison of the calculated and experimental (Bither et al 1968, Krill et al 1976, Arne Kjekshus et al 1979) lattice parameters of both phases of CuS_2 presented in Table 4.1 show a very good agreement between them.

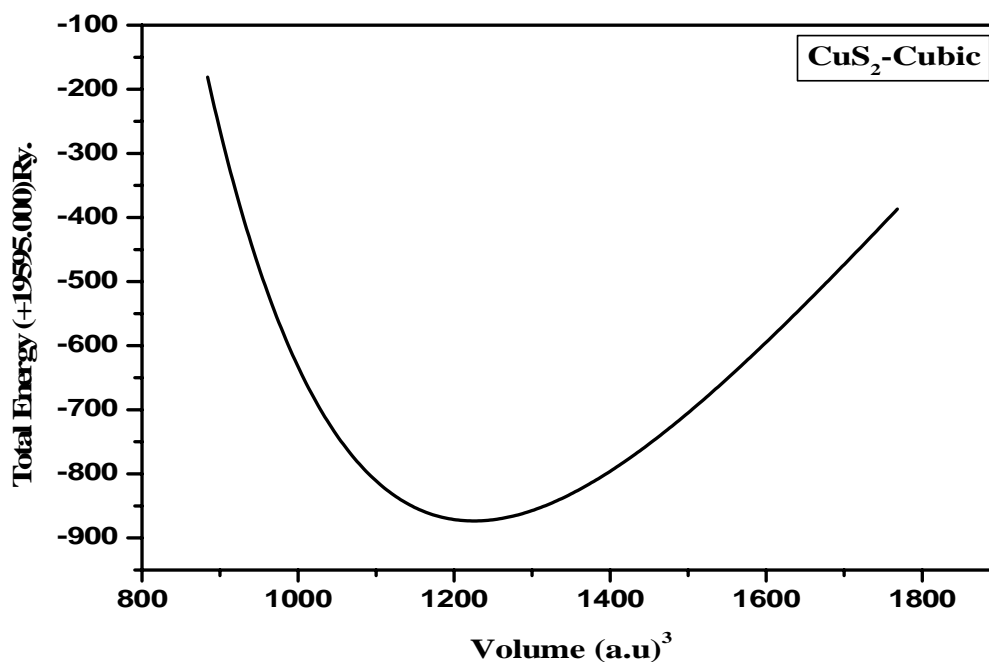


Figure 4.3 Variation of total energy (with reference to -19595.000Ry) with cell volume for Cubic structure of CuS₂

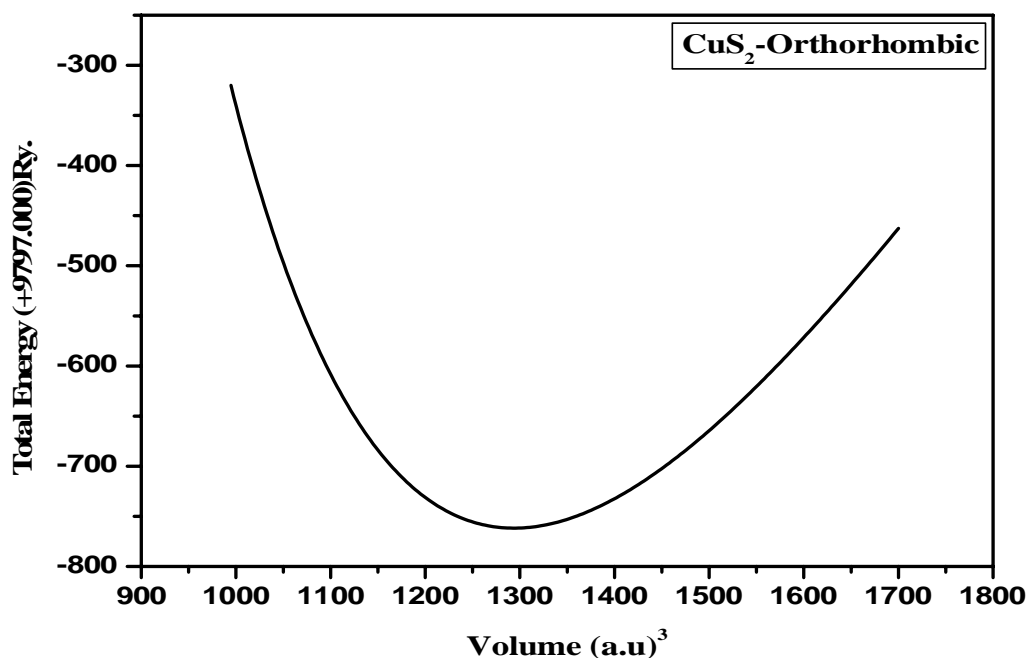


Figure 4.4 Variation of total energy (with reference to -9797.000Ry) with cell volume for Orthorhombic structure of CuS₂

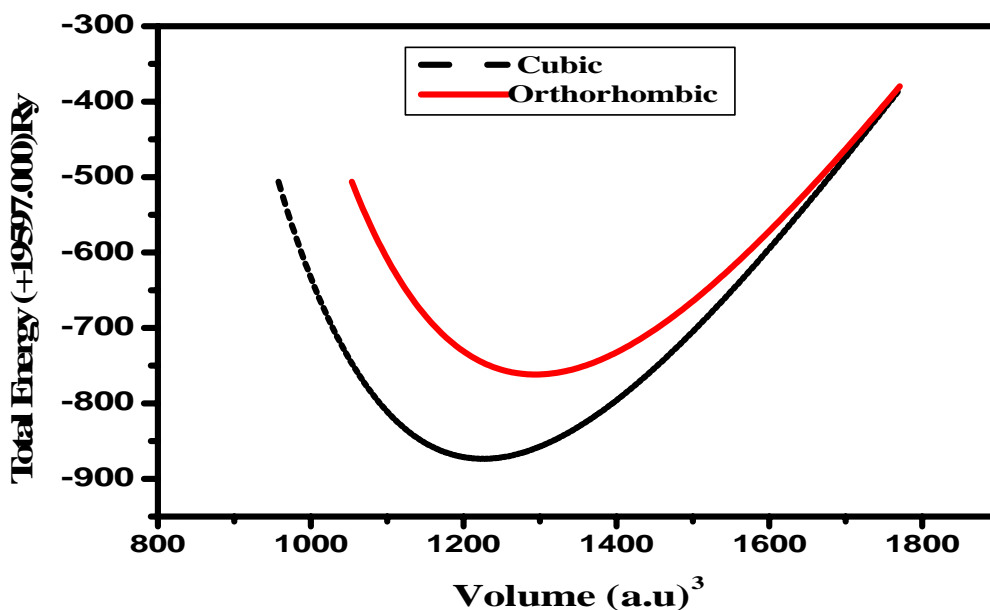


Figure 4.5 Variation of total energy (with reference to -19597.000Ry) with cell volume for CuS₂ in Cubic and Orthorhombic phases

Table 4.1 Lattice constant (Å) for CuS₂ in Cubic and Orthorhombic phases

CuS ₂	Lattice constant (Å)	
	Present	Experiment
Cubic	5.672	5.790 ^{a,b}
Orthorhombic	a=4.632	a=4.651 ^c
	b=5.774	b=5.793
	c=3.513	c=3.532

a = Bither et al 1968, b = Krill G et al 1976, c =Arne Kjekshus et al 1979

4.4 ELECTRONIC BAND STRUCTURE CALCULATIONS

The electronic bandstructures of cubic and orthorhombic phases of CuS₂ along the high symmetry directions of the Brillouin zone are displayed in Figure 4.6& 4.7. It is clearly evident in both phases of the material that

these p- bands dominate in their conduction. The Fermi energies of cubic and orthorhombic phases of CuS_2 are 0.6138Ry and 0.5762Ry, respectively.

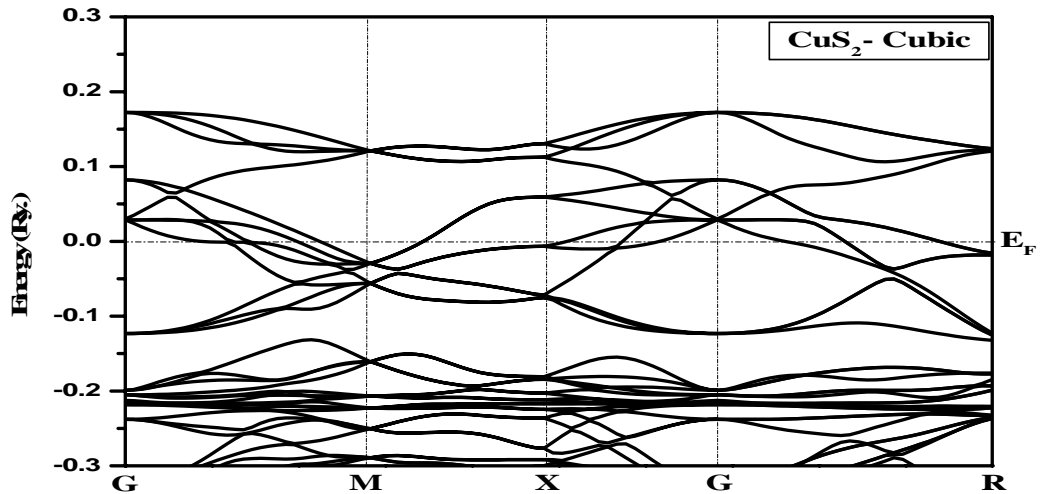


Figure 4.6 Energy band structure for Cubic structure of CuS_2

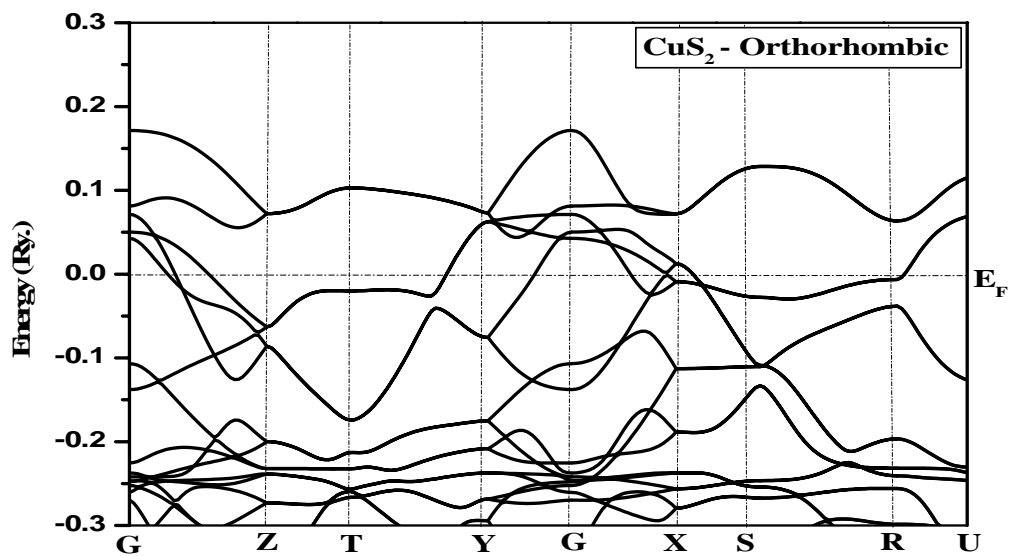


Figure 4.7 Energy band structure for Orthorhombic structure of CuS_2

4.5 ELECTRONIC DENSITY OF STATES

The total and partial DOS of cubic and orthorhombic phases of CuS_2 are presented in Figure 4.8 - 4.15. The high DOS around E_F is evidently due to the strong pile up of p- and d- states in both the phases of CuS_2 and it accounts for the structural stability. It is clearly seen that p- states of sulphur contribute predominantly at the Fermi level. The d- states of Cu also contribute a little at E_F . Thus the DOS at the Fermi level is almost exclusive of p- character. The total and partial DOS of cubic and orthorhombic phases of CuS_2 are presented in Table 4.2.

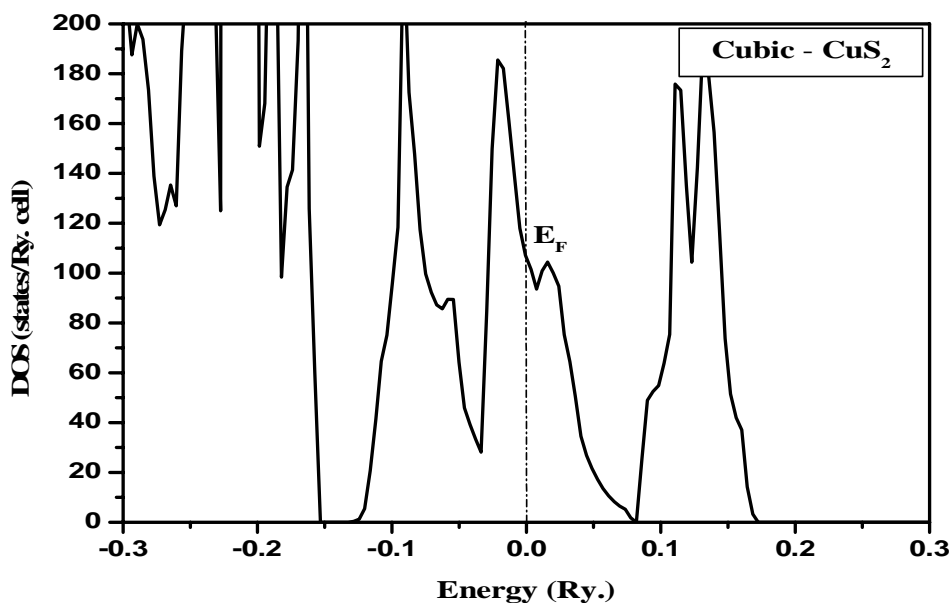


Figure 4.8 Total density of states for Cubic structure of CuS_2

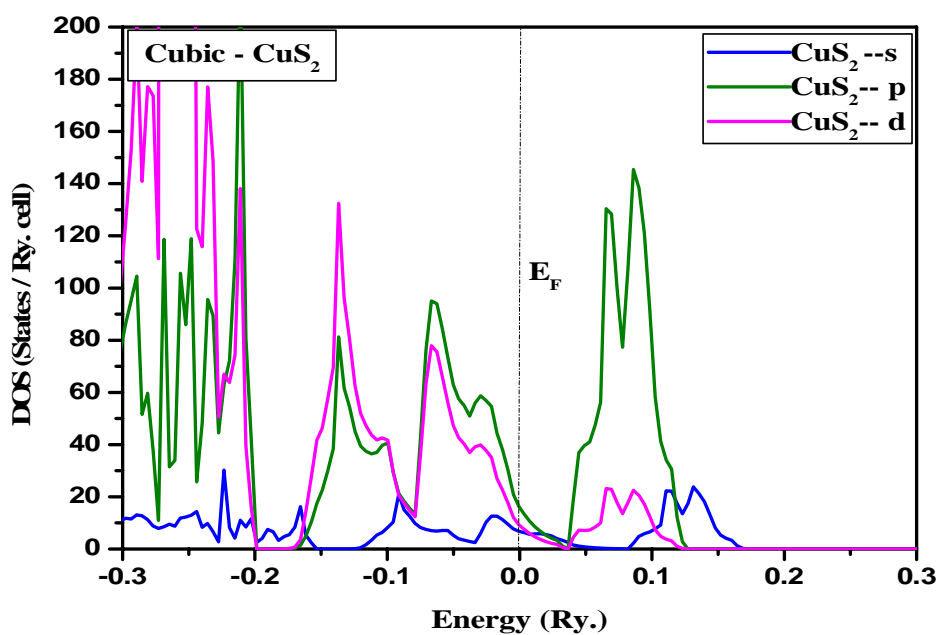


Figure 4.9 Partial density of states for Cubic structure of CuS_2

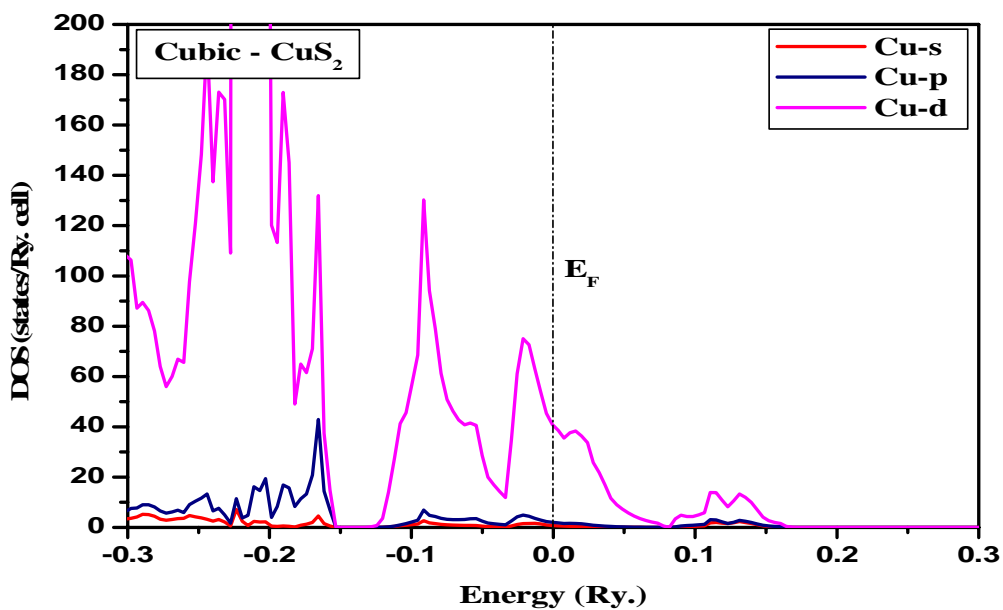


Figure 4.10 Partial density of states for Cu of Cubic structure of CuS_2

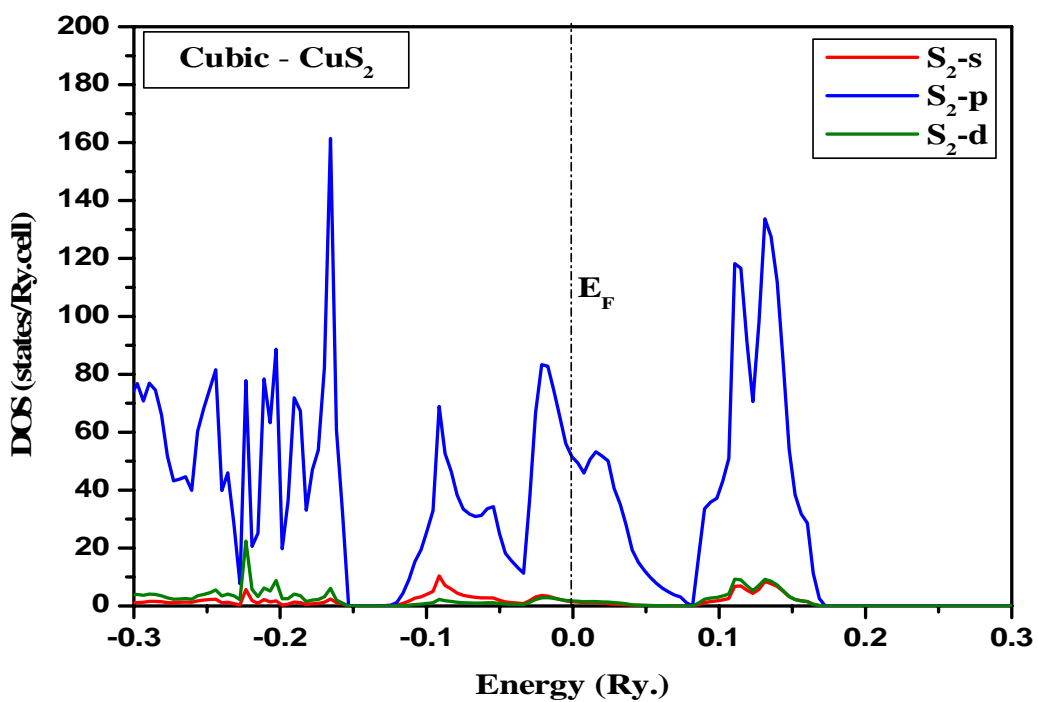


Figure 4.11 Partial density of states for S₂ of Cubic structure of CuS₂

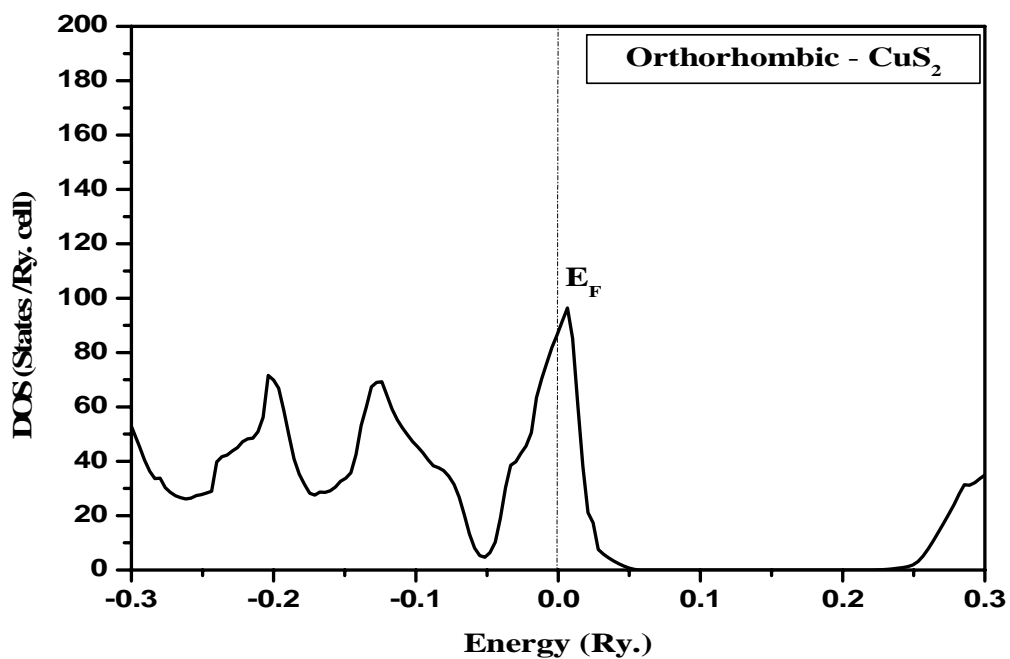


Figure 4.12 Total density of states for Orthorhombic structure of CuS₂

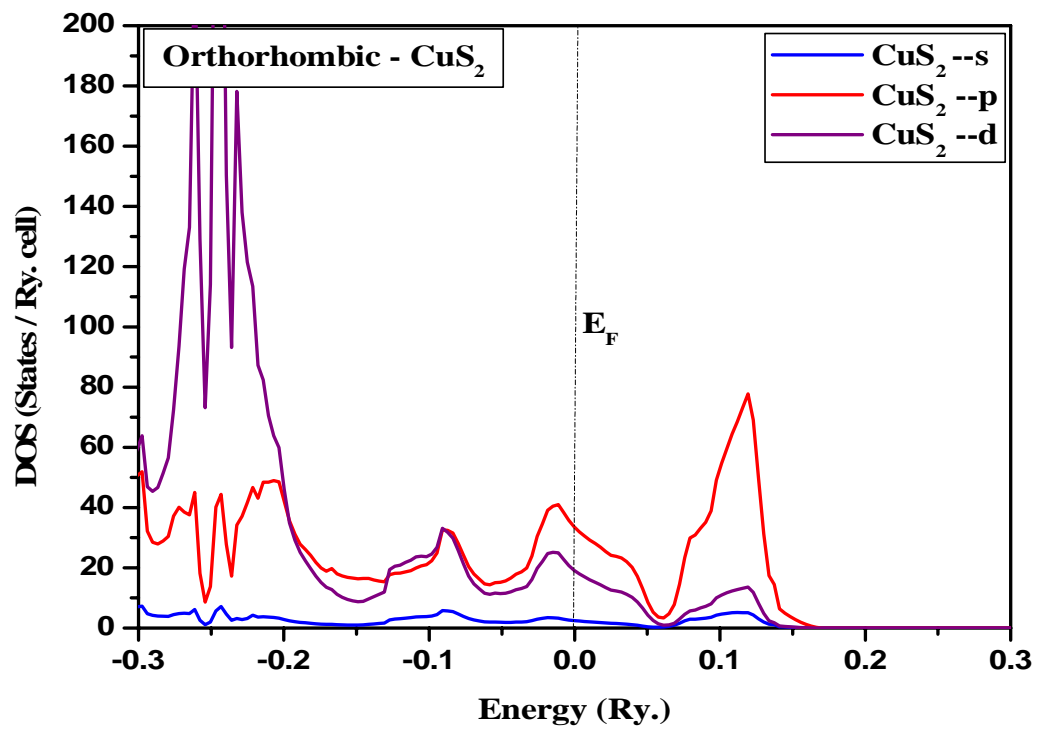


Figure 4.13 Partial density of states for Orthorhombic structure of CuS₂

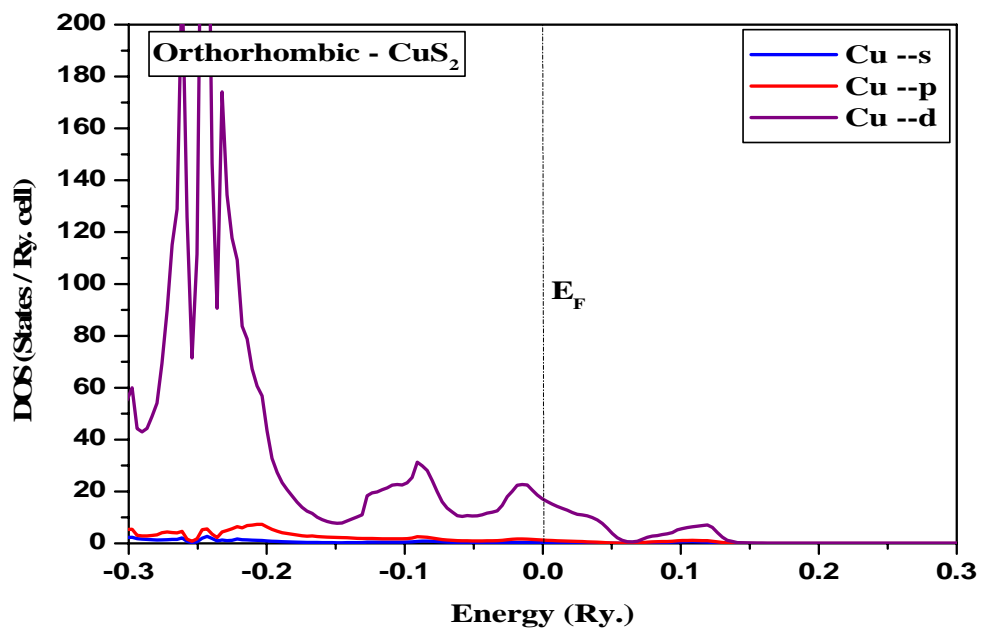


Figure 4.14 Partial density of states for Cu of Orthorhombic structure of CuS₂

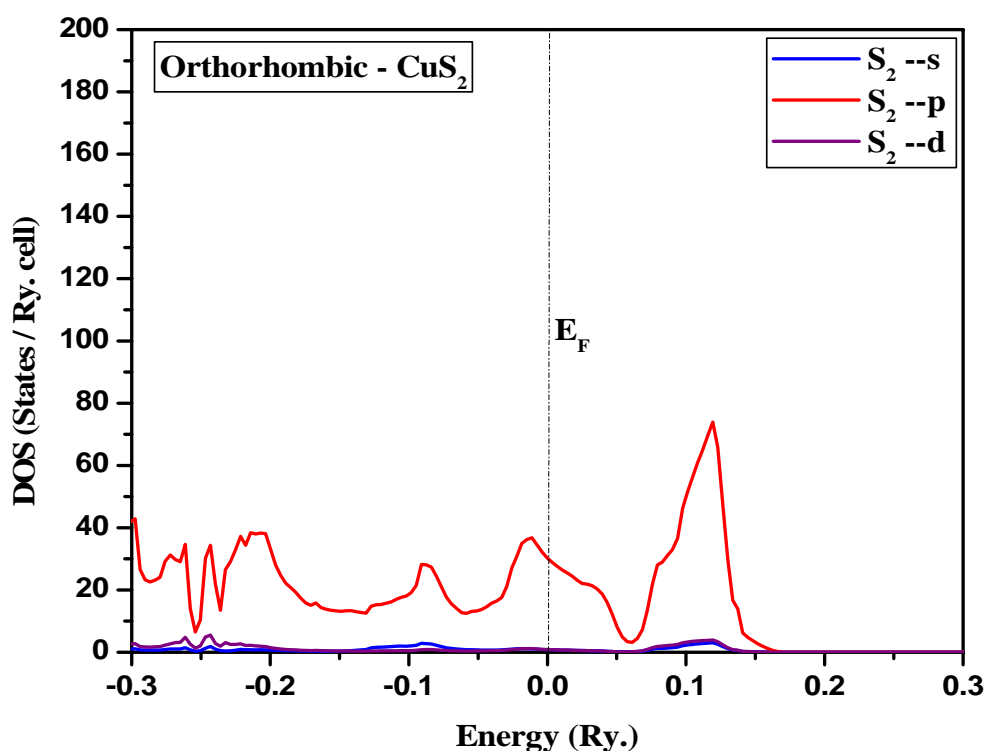


Figure 4.15 Partial density of states for S_2 of orthorhombic structure of CuS_2

Table 4.2 Electronic density of states at the Fermi energy in CuS_2 of various phases

Bands	Dos at E_F ((states/Ry)/atom)								
	Cubic				Orthorhombic				
	Cu	S_2	E	Total	Cu	S_2	E	E_1	Total
S	0.6254	1.3202	4.3402	6.2858	0.5392	2.9327	0.3204	1.3153	5.1076
P	1.8419	49.3002	3.7684	54.9105	1.0780	69.4305	0.7962	1.8144	73.1191
D	38.5859	1.6607	-	40.2466	6.8452	3.8381	1.2816	1.2432	13.2081

4.6 THERMAL PROPERTIES

The calculated and experimental values (Hiroaki Ueda et al 2002) of Θ_D and γ are presented in Table 4.3. The Debye temperature (Θ_D) (Debye 1912) and electronic specific heat coefficient (γ) (Dharmbir Singh 1999) are



important parameters that are closely related to the thermal properties of materials. To calculate the thermal properties of a vibrating Debye lattice, we have used the Debye-Gruneisen model (Debye 1912). In the present work, the calculated and experimental values of Θ_D and γ are presented in Table 4.3. The electronic specific heat coefficient (γ) is calculated using the Equation (3.53) the present theoretical estimate of γ agrees reasonably well with the experimental report (Hiroaki Ueda et al 2002) in the literature for CuS_2 .

Table 4.3 Equilibrium Wigner-seitz radii (r_0), Bulk moduli (B_0), Debye temperature (Θ_D) and Electronic specific heat coefficient (γ), for CuS_2 of various phases

CuS_2	r_0 (a.u)	B_0 (GPa)	Θ_D (K)		γ (mJmol ⁻¹ K ⁻²)	
			Present	Expt.	Present	Expt.
Cubic	2.0064	118.36	292	280 ^a	4.60	6.18 ^a
Orthorhombic	2.3298	115.38	308	-	4.75	-

a = Hiroaki Ueda et al 2002

4.7 SUPERCONDUCTING PROPERTIES

The electron-phonon coupling constant (λ) can be estimated, using the electronic band structure results from the relation (Equation 3.54). The superconducting transition temperature is calculated using Allen-Dynes formula (Allen et al 1975). The calculated and experimental values of λ and T_C are presented in Table 4.4. The values estimated by the present work for CuS_2 is agreeing well with the experimental values reported earlier (Hiroaki Ueda et al 2002, Bither et al 1966).



Table 4.4 Electron-phonon interaction constant (λ) and superconducting transition temperature (T_C) for Cubic structure of CuS_2

pyrite structure	λ	Tc (K)	
		Present	Experiment
CuS_2	0.32	1.04	1.50 ^a

a=Bither T A et al 1966

4.8 SUMMARY

The electronic bandstructure studies of CuS_2 compound in cubic and orthorhombic phases are carried out using the self-consistent tight binding linear muffin-tin orbital method. From the total energy calculations it can be seen that the cubic phase is more stable phase in thermo dynamical condition. The density of states at the Fermi energy is found to be strongly influenced by the p- states of sulphur, and, it is also evident in the band structure results. The calculated results are observed to be in good agreement with the available results existing in the literature. Estimation of the Debye temperature (Θ_D) and electronic specific heat coefficient (γ) have also been made for both the cubic and orthorhombic phase. The calculated value of T_C is observed to be in good agreement with the available experimental results existing in the literature. Thus the present studies have provided a better understanding of the fundamental electronic and superconducting properties of CuS_2 pyrite structure compound.

