Electronic, elastic, and transport properties of alpha-type copper sulphide

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Abstract. . A full potential all-electron density functional method within generalised gradient approximation is used to investigate the electronic, elastic and transport structure of alpha-type copper sulphide. The electronic structure suggests a semimetallic material with a zero band gap. Elastic calculations suggest a hard material with the bulk to shear modulus ratio of 0.381. The transport properties were estimated using the Boltzmann transport approach. Electrical conductivity, Seebeck coefficient, and thermal conductivity suggest a potential p-type conductivity.

1. Introduction

Cu_2S is one of the copper sulphide forms referred to as chalcocite. Studies have shown that $Cu_{2-x}S$ exists in different crystallographic modifications, which are monoclinic, hexagonal, cubic and orthorhombic phase. Generally, monoclinic model the structure of α-chalcocite built on a hexagonal close packing of sulphur atoms with copper atoms basically in trigonal planar and contort tetrahedral coordination [1]. Monoclinic phase with a low-chalcocite (αCh) is stable between temperature 90 - 104°C, depending on the chemical composition of x's. Above 90°C, the hexagonal phase which is a high-chalcocite (βCh) is stable and when x is equal to zero, this phase is stable up to 435°C. Cubic phase, which is called digenite is stable between temperatures of 72 - 1130°C [2]. The crystal structure of digenite is based on an antifluorite-type sub-cell in which sulphur atoms form a cubic-close-packed framework [3]. The cubic structure of Cu_xS allows x to vary frequently from 1.8 to 2, that makes it to provides a great possibility to regularly examine the roles of chemical composition on the electrical and thermal transports in Cu_xS at elevated temperature, which are very important for understanding this non-toxic and earth-abundant Thermoelectric (TE) material [4]. Currently, different types of sulphides have attracted great attention in transport properties community due to the non-toxic and earth-abundant features of sulphur [4]. Cu_xS as one of the example with great potential on transport properties will be explored in this article [5].

2. Computational Method

The calculations are based on the ground state energies, first principle, linearized augmented plane waves + local orbitals of the density functional theory (DFT) [6]. The generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) revised for solids was used for the exchange correlation energy [6-7]. The all electron full-potential computational software which is called exciting was used [8]. Brillouin zone integrals projection of crystals were approximated using the method of Monkhorst and Pack, [8]. The energies were allowed to converge with respect to the k-points density (9 × 9 × 9) for density of state, band structure and elastic calculations. The transport coefficients with respect to the chemical potential at a constant temperature (300 K) were calculated using the full-potential all electron ab-initio calculations. These transport properties are based on the Boltzmann transport theory. In the calculations, only k-points with Eigen energies near the Fermi level were considered to contribute to the coefficients. In order to achieve a sufficient representation of the energy bands in this area, a fine extended k-points grid (40 x 40 x 40) near the Fermi level was adopted. The

optimized lattice constants for the alpha Cu_2S that were used during the calculation are a = b = c = 5.739 Å.

3. Results and Discussion

The electronic, elastic and transport properties of alpha Cu_2S were performed under room temperature. The electronic properties describe the state and behaviour of electrons in the material. For example, the electronic band structure and the density of state, which describes the state of the electrons in terms of their energy, E. Elastic properties determines the mechanical properties of the material. The transport properties assist with the understanding various interactions in electronic systems such as the Seebeck coefficient, electrical conductivity, thermal conductivity and the power factor.

3.1. Electronic Properties

The electronic structure of any material is important in order to understand the sub-atomic properties. This information is obtained from the calculated density of states (DOS) and band structure through the materials electron density.

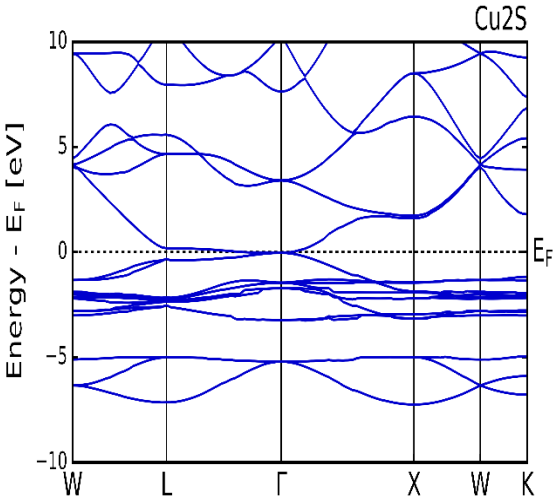

Figure 1. band structure of Cu_2S

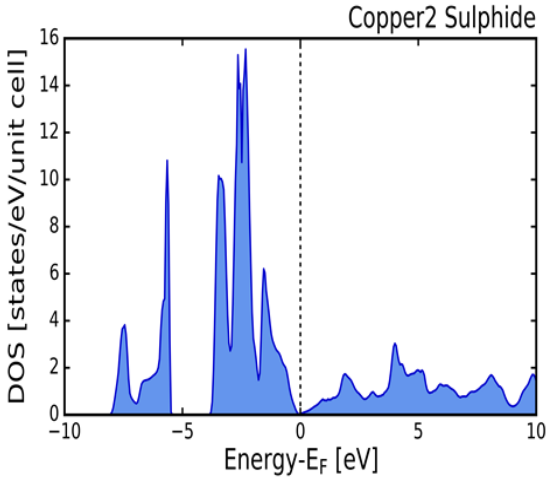

Figure 2. Density of states of Cu_2S

Figure 1 and 2, shows the calculated band structure and the total density of state of the alpha Cu_2S respectively. The band structure (Figure 1) shows that the material has a zero band gap which suggest a metallic behaviour. The top of valence band and the bottom of the conduction band touch one another from L to Γ points along the Fermi level. In figure 2, above the Fermi level, the DOS displays a mixture of deep level states possibly originating from the Cu and S electrons. At the Fermi level the overlap of orbitals maybe due to the Cu 3d-states mixing with S 4p-states. Below the Fermi level existence of s states for both Cu and S electrons are suggested. Also, the DOS shows that the nature of the valence band maximum (VBM) is widely Cu d-like. The results are in agreement with other theoretical calculations like those of Mazin [9] under DFT formalism within LDA approximation.

3.2. Elastic Properties

Systematically, the elastic properties of alpha Cu_2S were also computed. The calculations assist in understanding the stability, stiffness, ductility and anisotropy of the material. Young's modulus measures the stiffness of the materials, bulk modulus refers to the resistance to shape deformation, shear

modulus reflects the resistance against the shear deformation and Poisson's ratio will measure the ductility of the material [8]. There are three independent elastic constants in the cubic crystal structure, which are C_{11}; C_{12}, and C_{44}. These elastic constants were calculated using the ElaStic@exciting [9] interface, which can be used to obtain full elastic constants of any crystal systems.

TABLE I: Elastic constants (C_{11}; C_{12}; C_{44}), bulk modulus (B), Young's modulus (Y) shear modulus (G), all in GPa and Poisson's ratio (ν)

α-Cu_2S	C_{11}	C_{12}	C_{44}	B	Y	G	ν
This work (GPa)	64.349	75.477	23.442	71.767	63.421	23.442	0.381
Literature (GPa)				77.980(10)	65.413(11)	23.692 (10)	0.360 (11)

The elastic constants C_{11}, C_{12} and C_{44} assist in describing the mechanical hardness of the material with respect to deformation. The first two constants describe the crystal response to tension, while C_{44} describes the response to shear strain. Alpha Cu_2S is cubic; as such, the deformation stability needs to satisfy the following trend: $C_{11} > 0$; $C_{12} > 0$; $C_{11} - |C_{12}| > 0$ and $C_{44} > 0$ [110]. Most of the stability conditions are satisfied by our results accept one condition which is $C_{11} - |C_{12}| > 0$. In this study, $C_{11} - |C_{12}| < 0$ which does not satisfy the deformation stability of cubic. Because of this condition, it can be concluded that, the material alpha-Cu_2S is mechanically unstable and demonstrate some inhomogeneous character [10]. The Poisson's ratio (ν) is found to be a positive value of 0.381 which is between 0 and 0,5. This positive value of ν shows that when the Cu_2S compound can be stretched in one direction, and it tends to expand in the other two directions perpendicular to the direction of compression [12]. Mott *et al*. [13], explained that for incompressible material, the bulk modulus (B) is typically large compared to the shear modulus (G) and poison's ratio has to be close to 0.5. From this, it can be concluded that the material Cu_2S is incompressible [13]. The Young's modulus value suggests some form of inelasticity [14].

3.3. Transport Properties

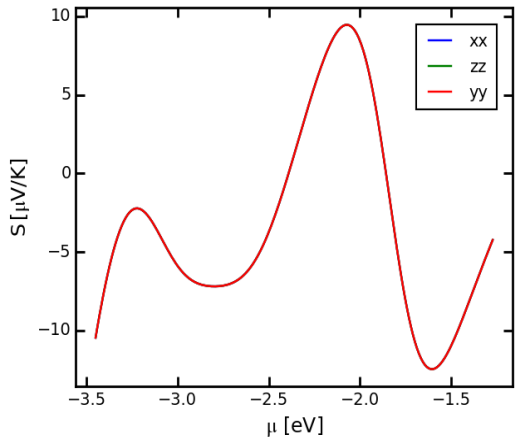

Figure 3. Seebeck coefficient vs chemical potential of Cu_2S at 300 K

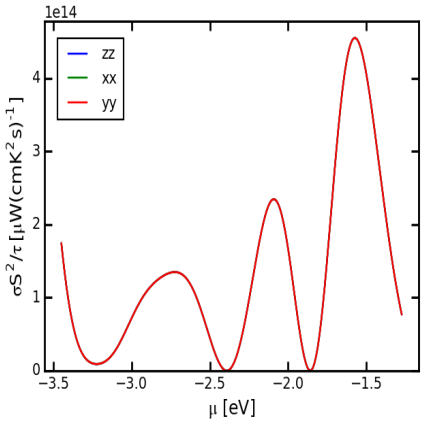

Figure 4. Power factor vs chemical chemical potential of Cu_2S at 300 K

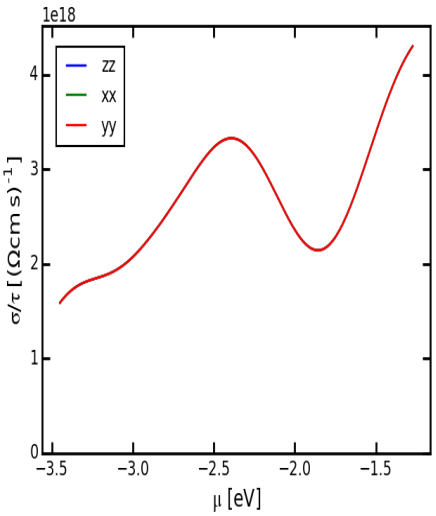

Figure 5. Electrical conductivity vs chemical potential at 300 K

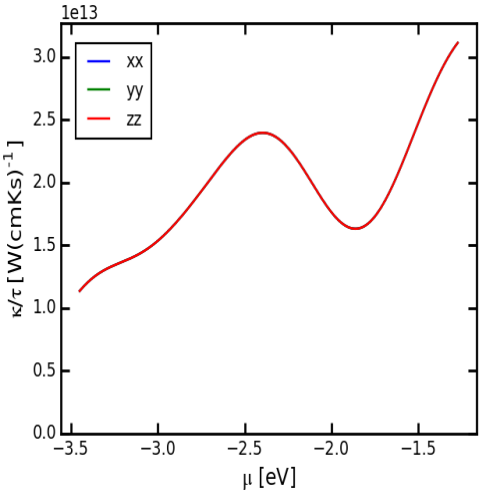

Figure 6. Thermal conductivity vs chemical potential at 300 K

The behaviour of the Seebeck coefficient (S) against the chemical potential (μ) is displayed in figure 3. Two visible positive maximum peaks can be observed at -2.0 and 9.0 μV/K. This behaviour is same for S_{xx}, S_{yy}, and S_{zz} and comparable to the experimental outcomes [15]. Narjis *et al*. [15] argued that the S on CuS possess two unequal positive peaks. The power factor per relaxation time ($\sigma S^2/\tau$) in figure 4, shows three peaks positively directed at 1.4, 2.4, and 4.8 W(cmK^{2}s)$^{-1}$. As with the Seebeck coefficient, the behaviour is the same in the x, y, and z-directions. The electrical and thermal conductivity per relaxation time plots vs μ are displayed in figure 5 and 6 respectively. Both curves display a similar behaviour relative to the changing chemical potential (μ). Electrical conductivity positive peaks are observed at around 3.1 and 4.1 (Ωcms)$^{-1}$. On the other hand, the thermal conductivity features positive values of 2.4 and 3.0 W(cmKs)$^{-1}$. Both the electrical and thermal conductivity peaks correspond with the chemical potential values of -2.4 and -1.3 eV respectively.

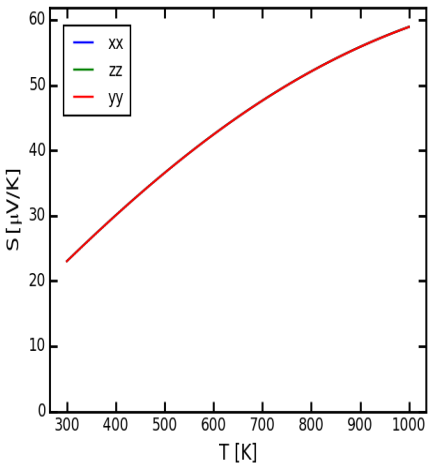

Figure 7. Seebeck coefficient vs temperature

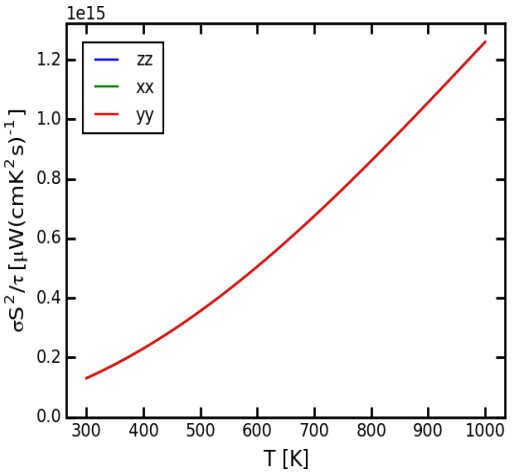

Figure 8. Power factor vs temperature

Figure 7 and 8 show the graphs of Seebeck coefficient and power factor against temperature respectively. Moreover, all values have a positive Seebeck coefficient indicating that the Cu_2S

compound is a p-type semiconductor. According to Narjis *et al*. [15], the positive values of Seebeck coefficient suggest that transport properties are dominated by holes, which are found in p-type materials. The highest measured Seebeck coefficient is about 59 μV/K at 1000 K, and the smallest is about 22 μV/K at 300 K. Both graphs increase with the increasing temperature. Figure 9 and 10 graphs represents electrical and thermal conductivity against temperature respectively. Electrical conductivity with increasing temperature suggest an almost linear behaviour with about 3.6 $(\Omega cms)^{-1}$ as the highest value. The thermal conductivity with increasing temperature suggest an exponential rise with about 1.8 $W(cmKs)^{-1}$ as the highest value.

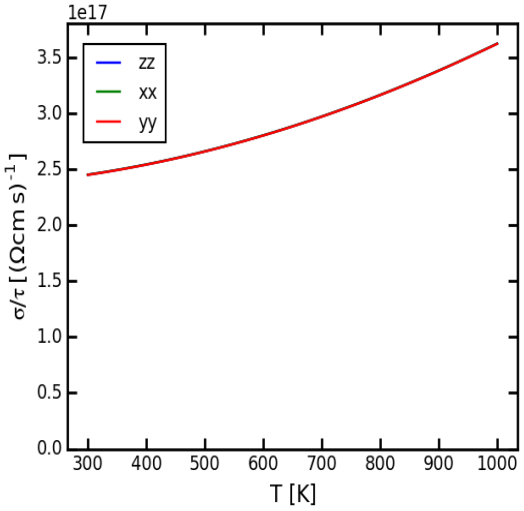

Figure 9. Electrical conductivity vs temperature

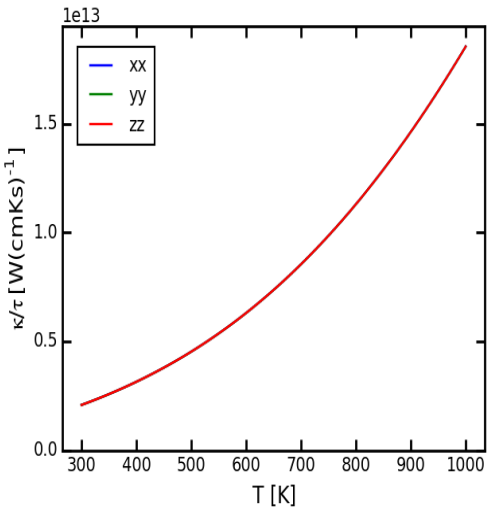

Figure 10. Thermal conductivity vs temperature

4. Conclusion

The electronic properties results are in agreement with previous studies, which shows that alpha copper sulphide is a semimetallic material with zero band gap. This zero band gap is attributed to the band structure geometry between the symmetry points L and Γ. Elastic constants show that the material is mechanically stable and it has a low shear modulus and high bulk modulus which are in agreement with previous studies. Transport properties of the material suggest a p-type conductivity. The power factor suggests a good thermoelectric material. The high positive Seebeck coefficient, the high electrical conductivity, and the low thermal conductivity accompanied by the power factor values above unify the required thermoelectric effect. This conduct is further corroborated by the little change of the electrical conductivity with temperature. The thermal conductivity demonstrates nearly linear whilst the power factor exponential rise with temperature.

References

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