FP-LMTO calculations of structural, elastic and electronic properties of CuS

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Abstract

The aim of this work is to study the structural, electronic and elastic properties of CuS. For this, we use the full-potential linear muffin-tin orbital (FP-LMTO) method in the framework of density-functional theory (DFT). The exchange and correlation energy is described in the generalized gradient approximation (GGA) using Perdew-Wang parameterization. We have investigated the effect of composition on structural properties such as lattice constants, bulk modulus and band gap. We report the results concerning the variation of the gaps and crossover of the direct, indirect band gap and bowing. Finally, a reasonable agreement is found from the comparison of our results with other theoretical calculations.

Keywords: CuS, FP-LMTO, Electronic Properties, elastic properties,

Introduction:

Copper sulfide compounds have been applied in various technologies, including solar cell devices, nonlinear optical materials, lithium ion batteries, nanometer scale switches, and gas sensors[1–2]. Covellite has a complex structure consisting of alternating layers of planar CuS3 triangles and CuS4 tetrahedrons with S–S bonds (Fig 1). Several experimental and theoretical studies have been carried out in an attempt to understand its electronic structure and the nature of the chemical bonding. Evans and Konnert[3] refined the crystal structure of CuS (Fig 1); they confirmed the structure solved by Oftedal[5] in 1932 with S–S bond length of 2.07(4) Å. At room temperature, the crystal structure has hexagonal symmetry and at $T = 55$ K the system spontaneously undergoes a transition from a hexagonal structure to a lower symmetry orthorhombic structure. To a good approximation, the transition amounts to sliding the Cu2-S2 plane with respect to the Cu1-S1 plane by 0.2 Å, and the two neighboring Cu2-S2 planes by 0.1 Å with respect to each other, in the same direction. The bond lengths change very little, one of the three Cu2-S2 bonds shortens by 0.04 Å, and the S2-S2 bonds lengthens by 0.05 Å, and all other bonds remain essentially unchanged. Note that such transitions are quite uncommon for metals, but rather characteristic of insulating Jahn-Teller systems. Transport properties are hardly sensitive to this transition.

Fig 1. Covellite hexagonal unit cell (CuS). Wyckoff positions are: Cu(1) in 2d (1/3, 2/3, 3/4); Cu(2) in 4f (1/3, 2/3, zCu(2)); S(1) in 2c (1/3, 2/3, 1/4); and S(2) in 4e (0.00, 0.00, zS(2)). Blue and yellow spheres are copper and sulfur atoms, respectively.

2. Method of Calculations

The calculations reported here were carried out using the ab-initio full-potential linear muffin-tin orbital (FP-LMTO) method[5] as employed in the Lmtart code[6] has been applied to perform first-principles total energy calculations. The exchange and correlation potential were calculated using the generalized approximation (GGA)[6]. In this method, the space is divided in the IR regions, the Fourier series represent the basic function. In side on MT spheres, the basic set is treated as a linear combination of radial functions times spherical harmonic.

The charge density and the potential are represented inside the muffin-tin sphere radius
(MTS) by spherical harmonics up to $l_{\text{max}}=6$. The integrals over the Brillouin zone are performed up to 35 special $k$-points for binary compounds. The MTS radius for each atomic position is taken to be different for each composition. We point out that the use of the full-potential calculation ensures that the calculation is not completely independent of the choice of sphere radii. Both plane waves cut-off are varied to ensure the total energy convergence. The values of the sphere radii (MTS) number of plane waves (NPLW), used in our calculation are summarized in Table 1.

Table 1: atomic positions energy cut-off (in Ry) and the muffin-tin radius (RMT) (in a.u.) chosen and used in calculation for binary CuS

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic positions</th>
<th>$E_{\text{cut total}}$(ry)</th>
<th>RMT (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>1/3 2/3 0.75</td>
<td>8216.58</td>
<td>2.939</td>
</tr>
<tr>
<td>Cu2</td>
<td>1/3 2/3 0.107</td>
<td></td>
<td>2.939</td>
</tr>
<tr>
<td>S1</td>
<td>1/3 2/3 0.25</td>
<td></td>
<td>2.373</td>
</tr>
<tr>
<td>S2</td>
<td>0.0 0.0 0.06</td>
<td></td>
<td>2.373</td>
</tr>
</tbody>
</table>

Results and Discussions

3.1 Structural Properties

At room temperature, covellite structure belongs to P63/mmc (194) space group (hexagonal symmetry) with $Z = 6$ per unit cell. The structural properties of CuS binary compounds by means of the full-potential LMTO method are calculated. We have started our FP-LMTO calculations of the structural properties with the hexagonal structure for CuS and let the calculation forces move the atoms to their equilibrium positions. We have chosen the basic atomic positions shown in Table 1. For the considered structures, we have performed the structural optimization take two steps, the first step is calculating the total energies for different $c/a$ parameters values with a constant volume, the second step is calculating the total energies for different volume $V_0$ with a constant $c/a$ parameter around the of CuS binary compounds.

The calculated total energies are fitted to the Murnaghan’s equation of state [21] to determine the ground state properties such as the equilibrium lattice constant $a$ and the bulk modulus $B$. Our results are summarized in Table 2 together with those of other ab-initio calculations and experimental works. that also contains results of previous calculations as well as the available experimental data. The obtained lattice constants for compound is in good agreement with experimental data and other ab-initio calculations.

Table 2: Comparison between our calculation of the equilibrium lattice constant, with the experimental values and other calculations for CuS compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>$a$(A)</th>
<th>$b/a$(A)</th>
<th>$c/a$(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>Present work</td>
<td>3.97</td>
<td>1.0</td>
<td>4.1277</td>
</tr>
<tr>
<td></td>
<td>Exp [9]</td>
<td>3.793</td>
<td>1.0</td>
<td>4.3081</td>
</tr>
<tr>
<td></td>
<td>Other Theo</td>
<td>3.807</td>
<td>1.0</td>
<td>4.3330</td>
</tr>
<tr>
<td></td>
<td>[11-10]</td>
<td>3.793</td>
<td>1.0</td>
<td>4.331</td>
</tr>
</tbody>
</table>

3.2 Elastic Properties

In the field of elasticity, the stresses are related by Hooke's law which involves the coefficients of elasticity of the material. The determination of elastic constants requires knowledge of the curvature energy in function of the stress for selected strains of the cell unit.

For an Hexagonal system it there's five independent elastic constants $C_{11}$, $C_{12}$, $C_{33}$, $C_{31}$, $C_{44}$.
and $C_{66}[13]$ with $C_{22} = \frac{1}{2}(C_{11} - C_{12})$. The condition for the elastic stability [12] is:

$$C_{44} \geq 0, \quad C_{11} - C_{12} \geq 0, \quad C_{11} + C_{12} + C_{33} \geq 0, \quad C_{11} + C_{12} + C_{33} \geq 0.$$

The knowledge of the elastic constants allows us to calculate the bulk modulus

$$B = \frac{1}{2} \left[ \frac{2}{9} (C_{11} + C_{12} + 2C_{33} + \frac{2}{3}C_{31}) \right]^{1/2},$$

and further, the calculated isotropic bulk moduli $B$ and shear moduli $G$ allow us to obtain the Young's moduli $Y$ and the Poisson's ratio $\nu$ as:

$$Y = \frac{9BG}{3B + G}, \quad \nu = \frac{(3B - 2G)}{2(3B + G)}.$$

The figs 3 show the variation of total energy in function constraint for the CuS material hexagonal structure for determining the elastic constants $C_{11}, C_{12}, C_{33}, C_{31}$ and $C_{44}$ using the GGA approximation.

According to table it is clear that the coefficient $A$ is near the unit for allowing us to say that this compound is an isotropic material. In other way, the $B/G$ for our material ratio is less than a critical values 1.75 that separate the compounds in brittle $<1.75<ductile$ [12] which classifies our material in brittle material.
Table(3) the elastic constant, bulk modulus B, shear modulus G, young modulus E and Poisson coefficient (all in Gpa).

<table>
<thead>
<tr>
<th>C_{11}</th>
<th>C_{12}</th>
<th>C_{13}</th>
<th>C_{66}</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.73</td>
<td>16.81</td>
<td>20.08</td>
<td>9.75</td>
</tr>
<tr>
<td>B</td>
<td>G</td>
<td>E</td>
<td>\nu</td>
</tr>
<tr>
<td>12.24</td>
<td>9.46</td>
<td>2.24</td>
<td>0.31</td>
</tr>
<tr>
<td>1.93</td>
<td>2.37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The condition on the mechanical stability criteria for our material CuS is satisfied that show the stability of our materials in this structure against elastic deformations.

3.3. Electronic properties

To complete this study, we conducted density of states (DOS) (Fig.5) and band structure. The Fermi level EF corresponds to the origin of the energy. We calculated the energy bands of the course materials using FP-LMTO method with GGA approximation. We have plotted in fig(4) the band structure of CuS along the symmetry points. The calculation of the energy bands shows that there are three sets almost parabolic bands, whenever degenerate at point A and we note that the maximum of the valence band in the \Gamma points, at the same points noted that the minimum of the conduction band and at the \Gamma point therefore it is a direct energy gap. Our calculation are summarized in Table 4.

Table(4) Energy gap values of CuS in the Hexagonal structure

<table>
<thead>
<tr>
<th>compound</th>
<th>method</th>
<th>Energy band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>Our calcul</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>FP-LAPW[10]</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>Exp [14]</td>
<td>1.2-2.7</td>
</tr>
</tbody>
</table>

The obtained result for compound is in good agreement with experimental data and other ab-initio calculations.

The density of states (DOS) is an important physical quantity for understanding of the physical properties of materials. Most of transport properties are determined on the basis of knowledge of the density of states.

From fig (5) it is clear the existence of four distinct regions separated by gaps for CuS compounds. The first region is located about -4.8 eV and -2, 2 eV below the Fermi level. This region is dominated mainly by the P and S states. The second region to about -2.1 and 1.2 is composed entirely of d stat of copper with a small hybrid withP state of sulfur. Just above this band, there is another region between 2,029 eV and 8 eV is dominated mainly by the P state copper. Below the Fermi level, the bands valences are dominated by S and P states of Copper and d the states of sulfur with low p-d hybridization. This indicates the strong covalent behavior between atoms of copper and sulfur. Conduction bands are dominated mainly by the d states of copper.

Conclusion

In conclusion, The objective of this work was to study the structural, electronic and elastic proprieties of CuS materiel. The latter has a special interest in solar cell technology applications. This study is carried out by the FP-LMTO method under the density functional theory DFT implemented in code Mstudio Mindlab using generalized gradient approximation (GGA). The most significant findings are as follows:
For structural proprieties we find the lattice parameters a and c are in good agreement over experimental values.

For elastic proprieties all elastic constants are calculated and checking mechanical stability criteria for our compounds. We clearly see that our results are in good agreement with those calculated or previously measured. From the elastic constants values obtained the CuS are classified as isotropic and brittle materials.

For electronic proprieties the band structures calculated for CuS compound indicate the presence of a direct gap at the high symmetry point Γ with 0.1 eV. For the density of stat (DOS) it was reported statements of the contributions of each part of bands, and we showed the nature of the liaison of our compound using the charge density for the [110] plane. We also concluded that the bonds in the CuS compound are mixed type(covalent-ionic)

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