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# Cohesive Energy of Chalcogenide and Pnictide Based Ternary Tetrahedral Semiconductors

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**_Abstract_**

*There is a great amount of interest in tertiary chalcopyrite semiconductors because of the potential uses they have in the field of optoelectronics. These applications include solar energy converters, detectors, light emitting diodes (LED), and non-linear optical devices (NLO). There are variety of ZnS Zinc blende types of superstructures in which one of the types is called chalcopyrite semiconductor. This study is based on the characteristics of the chalcopyrite semiconductor. So, we demonstrate an expression that relates the cohesive energy i.e. Ecoh in kcal / mol for this chalcopyrite semiconductors with the multiplication of ionic charges as well as nearest neighbor distance i.e. d (Å). We plot a log-log scale with respect to the nearest neighbour distance d (Å ) and the cohesive energy of variety of these material compounds and we get a linear connection. However, when the ionic charge product of the compounds is taken into consideration, the cohesive energy of these compounds falls on separate straight lines. A decent arrangement has been established between the experimental against the calculated values of the given cohesive energy for* $A B C_2$ *as well as* $A B C_2$ *chalcopyrite semiconductors.*

**Keywords:** Cohesive energy, bond length, chalocopyrites, tetrahedral semiconductors, optoelectronics.

## INTRODUCTION

Chalcogens are these three elements namely Sulfur, Selenium and Tellurium while the term chalcogenide is more frequently used for the compound form of sulfides, selenides, tellurides, etc. For e.g. ZnS, ZnSe and ZnTe are Zn-chalcogenide group members. Chalcogenide semiconductors are known to be as functional materials. Chalcogenides are compounds comprising one or more chalcogen elements. It is typically signified as ($P_aX_b$), P is Group III, IV, V element, or transition metal element in addition to X that is S, Se, Te. Chalcogenide compounds are pertinent in numerous extents for instance photovoltaic, photocatalyst, optoelectronics, sensors, fuel cell, and battery. Chalcogenides demonstrate huge IR transmission as well as large reflective index, with extensive applications in catalyst machineries & detecting, sensing devices. One aspect of chemical bonding that may be utilised to forecast a number of other important characteristics is cohesive energy. The stability, bond strength, and boiling temperatures of molecules can all be predicted using cohesive energy. It is also a helpful tool for comprehending how compounds behave in different phases. Using its magnitude, we can determine a solid's stability and chemical reactivity. Because of the difference in cohesive energies between different possible structures, the quantity ultimately determines the structure. Solid state theory has been developed using semi-empirical molecular orbitals. Chalcogenide and pnictides chalcopyrites itself was known many years before semi-conduction in the elements was discovered. Numerous interactions of non-linear frequency mixing as well as the

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optoelectronic devices have been verified using the chalcopyrite semiconductors [ 1, 2]. Due to appropriate energy band-gap, nonlinear coefficient, and birefringence, chalcopyrite crystals are valuable design parameters [3]. As a result of this last property, chalcopyrite’s especially suitable for nonlinear laser devices [4]. which cover a wide range of electromagnetic spectrums from UV to IR through visible spectrums. Parametric oscillation, sum mixing, second harmonic generation, and difference frequency generation are a few examples. Chalcopyrite is also of essential relevance as a non-cubic ternary analogue of the well-known binary zinc blende. Chalcopyrites become anisotropic, however, because there are two types of bonds present. The high birefringence and nonlinear susceptibility of these materials make them highly valuable for effective phase matching and second harmonic generation. Many scientists have lately become aware of these semiconductors' electrical, mechanical, elastic, and optical capabilities. Because the experimental process is difficult, expensive, and difficult to obtain accurate structural, mechanical, and optical property values, and because such a method has always been the most difficult to calculate due to its long process, complicated computational methods, and approximations, researchers switched to theoretical techniques for figuring out material characteristics. The importance of theoretical computations based on empirical connections in material research has grown during the last few years. Solid-state computations are increasingly based on empirical relations. By computing or simulating many properties of materials instead of conducting traditional experiments, researchers can investigate many properties of materials. Even though empirical relationships could not yield quite precise outcomes for every particular substance, they are nevertheless very helpful in a lot of situations. Researchers can calculate useful properties with simple empirical relations, and often trends are evident as a result. Then, a variety of empirical ideas can be applied, including plasmon energy, ionicity, valence, and electronegativity [5-8]. Chemical bonds are directly associated with these concepts as they describe and classify a number of fundamental qualities of solids and molecules. Valence electrons have an impact on alterations in an atom's crystallographic environment. In most cases, when the wave function of outer electrons changes, there is a shift in charge within the valence shell that influences how the electrons in the shell interact, valence shell, and core. A variation in the inner electron's binding energy results in an alteration in the absorption boundary.

Solid-state ionic charge theory has been used by Verma and co-authors [9-13] to calculate electronic, mechanical, and optical properties. This is due to the fact that the valence electron number of metals, which varies when they form compounds, determines their ionic charge. Thus, we reasoned that it would be interesting to consider a different theory for the cohesive energy of chalcopyrite organised solids.

## THEORY, RESULTS AND DISCUSSION

As stated by Sohn et al. [14]. the cohesive energy (Ecoh) for each unit cell is the total of the Madelung energies and the Morse potential.

$$\text{Ecoh is equivalent to } \{ - (AZ\,e/r) + N\,D\,e \;-2\,N\,D\,e \} \qquad (1)$$

Here, the Madelung constant is denoted by A, bond energy by D, and N is bond count in a unit cell approximates Born-Mayer type cohesive energy without the last term, equivalent to the potential for Morse attraction energy attracted to a new equilibrium position d (nearest neighbour distance) in Morse potential. Based on equation (1), The group IV crystals' cohesive energy consisting only of the Morse potential can be determined as b:

$$\text{Ecoh (IV)} = N\,D\,e \;-2\,N\,D\,e \qquad (2)$$

whereas N is equal to 4. The cohesive energy per volume unit of the cell, V is correlated with the bulk modulus K:

$$K = V\,( dr / dV )\,( d\,\text{Ecoh}/ dr )_{r = rc} \qquad (3)$$

We derive the constant with the covalent bond length from equations (2) and (3):

$$\beta = (2\sqrt{3}\, r_c K / D] \quad (4)$$

An empirical relationship between cohesive energy and closest neighbour, separated by d, has been proposed by Aresti et al [15]. They claim that the following relation can be used to express cohesive energy.

$$Ecoh = Ecoh\ (IV) – K\ (d, R)\ \{1 - \Sigma\ Ecoh\ (i) / Ecoh\ (IV)\ \} \quad (5)$$

The cohesive energy of fully covalent crystals is represented by $E_{coh}$ (IV), and the parameter K (d, R) = Ecoh (IV) – k(R)♦d (BX)/d now depends on d and R

$$.k(R) = C\ e \quad (6)$$

where Z = Z(A) + Z(B), the atomic numbers of atoms A and B, and C, the constant, are dependent upon the rows

Solid-state compounds' cohesive energy value has been determined by a number of theoretical approaches recently [16-18]. In terms of interatomic distance, Schlosser [19, 20]. examined the trends in cohesive energy in the rock salt structure,

$$Ecoh\ \ = constant /d \quad (7)$$

Despite a linear relationship between, cohesive energy and the distance to the closest neighbour when plotted against ionic charge product, chalcopyrite semiconductors fall on different straight lines, which is presented in Fig. 1. Observations of cohesive energy versus nearest neighbour distance indicate that chalcogenide chalcopyrites lie closely parallel to pnictide chalcopyrites. By using their ionic charges, ternary tetrahedrally coordinated semiconductors can be evaluated for their cohesive energy. It is possible to in regard to ionic charges, extend relation (7) in order to increase the degree of agreement between theoretical and experimental evidence for cohesive energy of compounds made of chalcopyrite,

$$Ecoh\ \ = constant / (Z_1 Z_2\, Z_3)\ d \quad (8)$$

where the A, B, and $C_2$ values are, respectively, $Z_1$, $Z_2$, and $Z_3$.. The value of constant for chalcopyrite crystals is 4000.

All experimental cohesive energy values in this picture are derived from reference [15].

It has been reported in reference [21]. that chalcopyrite compounds exhibit detailed ionic charges. Copper has valency one in all chalcopyrite compounds, and gallium, aluminium, and indium have always had valency three, according to Ballal et al. [21]. Thus The compounds' valence structures can be expressed as A B $C_2$ (A = Cu, Ag; B = Al, Ga, In; C = S, Se, Te) and A B $C_2$ (B = Si, Ge, Sn; C = P, As; A = Zn, Cd). Consequently, the ionic product charge is 6 for A B $C_2$ and 24 for A B $C_2$ .. d BC and d AC are anion-cation distances. are determined by the renowned fact that each anion in chalcopyrites has four (two + two) anion bonds, while each cation has four equal anion bonds. distinct cation bonds. The formula for calculating the chalcopyrites of A B $C_2$ and A B $C_2$ is (d AC + d BC) / 2, where d denotes the average closest neighbour’s distance in this relationship. Using equation (8) cohesive energy for chalcopyrite semiconductors have been computed. Table 1 presents the findings. It is observed that the assessed values of cohesive energy by the numbers given by earlier researchers do not accord as much as our hypothesised connection does with the experimental data. For instance, cohesive energy values deviate from experimental data by Cu $GaSe_2$—3.5%, Cu $GaTe_2$—2%, Cu $InSe_2$—9%, Cu In $Te_2$—2.6%, Ag Ga $Te_2$—0.7%, Zn Si $P_2$—0.3%, Zn Sn $As_2$—1.5% and Cd Si $P_2$—6% in the present investigation. Overall, these findings imply that the suggested approach is feasible and can be a helpful reference for determining and forecasting the cohesive energies of ternary chalcopyrite semiconductors.

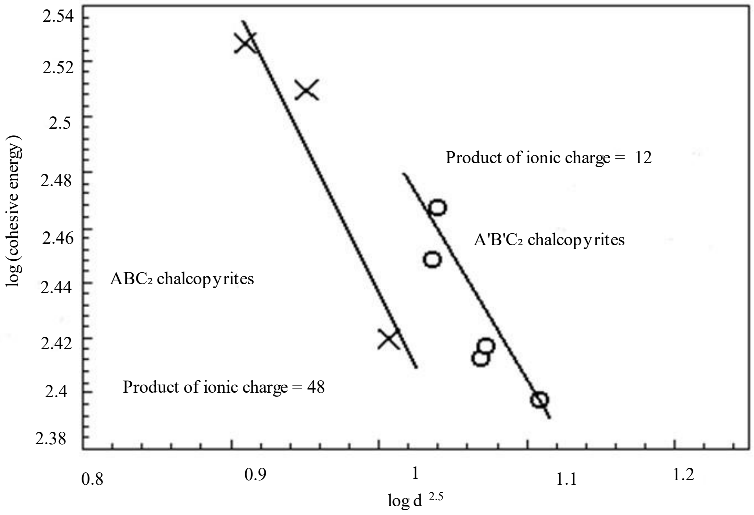

**Figure 1.** In the plot of log (Ecoh in kcal/mol) and log d , $A B C_2$ chalcopyrites lay along a line that is almost in line with the parallel for $A B C_2$ chalcopyrites, which is depending upon the product of ionic charges

**Table 1.** The cohesive energy ($E_{coh}$ in kcal/mol) values for the semiconductors $A\ B\ C_2$ and $A\ B\ C_2$ are shown in this table. The semiconductors $A\ B\ C_2$ have an ionic charge product of $(Z_1 Z_2 Z_3) = 12$, whereas $A\ B\ C_2$ semiconductors have $(Z_1 Z_2 Z_3) = 48$.

| **Solids** | **d (Å)** | **Experimental [15]** | **This work** |
|---|---|---|---|
| Cu Ga $S_2$ | 2.30 | | 388.9 |
| Cu Ga $Se_2$ | 2.42 | 330.4 ± 13.8 | 342.5 |
| Cu Ga $Te_2$ | 2.60 | 280.3 ± 4.8 | 286.2 |
| Cu Al $S_2$ | 2.29 | | 393.2 |
| Cu Al $Se_2$ | 2.40 | | 349.6 |
| Cu Al $Te_2$ | 2.58 | | 291.8 |
| Ag Al $S_2$ | 2.40 | | 349.6 |
| Ag Al $Se_2$ | 2.51 | | 312.6 |
| Ag Al $Te_2$ | 2.68 | | 265.3 |
| Cu In $S_2$ | 2.40 | | 349.6 |
| Cu In $Se_2$ | 2.51 | 341.2 ± 9.3 | 312.6 |
| Cu In $Te_2$ | 2.68 | 258.3 ± 11.3 | 265.3 |
| Ag In $S_2$ | 2.49 | | 318.9 |

| | | | |
|---|---|---|---|
| Ag In $Se_2$ | 2.61 | 292.5 ± 9.2 | 283.5 |
| Ag In $Te_2$ | 2.78 | 249.5 ± 10.2 | 242.1 |
| Ag Ga $S_2$ | 2.42 | | 342.5 |
| Ag Ga $Se_2$ | 2.53 | 348.7 ± 20.7 | 306.5 |
| Ag Ga $Te_2$ | 2.69 | 261.0 ± 3.7 | 262.9 |
| Cd Si $P_2$ | 2.40 | 323.4 ± 11.8 | 304.4 |
| Cd Ge $P_2$ | 2.44 | | 292.05 |
| Cd Sn $P_2$ | 2.54 | | 264.2 |
| Zn Si $P_2$ | 2.31 | 336.0 | 334.9 |
| Zn Ge $P_2$ | 2.35 | | 320.8 |
| Zn Sn $P_2$ | 2.45 | | 289.1 |
| Cd Si $As_2$ | 2.49 | | 277.6 |
| Cd Ge $As_2$ | 2.53 | | 266.8 |
| Zn Si $As_2$ | 2.41 | | 301.2 |
| Zn Ge $As_2$ | 2.44 | | 292.05 |
| Zn Sn $As_2$ | 2.53 | 262.9 ± 7.6 | 266.8 |
| Cd Sn $As_2$ | 2.62 | | 244.4 |

## CONCLUSION

Any compound's electrical, optical, and mechanical properties must be calculated by taking in the product of its ionic charges. First Fig. displays the data points for A B $C_2$ semiconductors are nearly parallel to A B $C_2$ those for semiconductors, indicating that ionic binding dominates. In addition, the suggested empirical relation is more generalized and easier to understand than previous empirical relations [14-20]. and values are more in agreement with experiments. Through the use of the nearest neighbour distance and the ionic product charges, materials, we were able to ascertain the cohesive energy, also known as Ecoh in kcal/mol, which is the ground-state characteristic of the chalcopyrite crystals. Because of this, it is possible to make predictions about the physical properties of metallic and semi-conductive substances based on the ionic charge of those substances.

## REFERENCES

1. Kumari J, Tomar S, Sukhendra, Choudhary B L, Rani U and Verma A S, Fundamental Physical Properties of LiInS2 and LiInSe2 Chalcopyrite Structured Solids. *East European Journal of Physics*, 2021; (3),62-9.
2. Kumari J, Singh C, Choudhary B L and Verma A S, First-principles study for physical properties and stability of Li based chalcopyrite semiconductors Reliable for green energy sources. *Physics and Chemistry of Solid State*,2022; 23(4), 728-40.
3. Kumari J, Singh C, Agrawal R, Choudhary B L and Verma A S , Structural, electronic and thermoelectric properties of LiAlX2 (X=S and Se) chalcopyrites promising for thermoelectric power generators. *Chalcogenide Letters*,2023; 20(1), 73-83.
4. Sukkabot W, Electronic structures and optical properties of doped $CuInTe_2$ chalcopyrite materials density functional calculations. *Philosophical Magazine*, 2021; 101(19), 2157- 68.
5. Janicek P, Kucek V, Kasparova J, Plechacek T, Cernoskova E, Benes L, Munzar M, and Drasar C, Study of Indium Non-stoichiometry in CuInTe2 and Its Effects on the Thermoelectric Properties. *Journal of Electronic Materials*, 2019; 48(4), 2112-19.
6. Liu K, Ji M, Li H, and Xu C, Calculation of energy band and optical properties of CuInTe2 with doping. *Integrated Ferroel*ectrics,2019; 197(1), 33-42.
7. Hamid M, Fadaam S A, Mohammed L A, and Hussein B H, Influence of addition (Mn) on enhance efficiency of (CuInTe2) photovoltaic cell. *Eurasian Chemico-Technological Journal*, 2019; 21(1), 183-5.

8. Singh R, Akram S V, Gehlot A, Buddhi D, Priyadarshi N, and Twala B, Energy System 4.0: Digitalization of the Energy Sector with Inclination towards Sustainability, *Sensors*, 2022; 22(17), 6619-53.
9. Verma A S and Bhardwaj S R, Correlation between ionic charge and ground-state properties in rocksalt and zinc blende structured solids. *Journal of Physics Condensed Matter*, 2006; 18 (37), 8603.
10. Verma A S and Bhardwaj S R, Correlation between ionic charge and the mechanical properties of complex structured solids. *Journal of Physics Condensed Matter*, 2007; 19 (2), 026213.
11. Verma A S and Bhardwaj S R, Electronic and optical properties of zinc blende and complex crystal Structure solids. *physica status solidi (b)*,2006; 243 (15), 4025-34.
12. Verma A S and Sharma D, Dielectric constants of AIBIIIC2VI and AIIBIVC2V chalcopyrite semiconductors. *Physica Scripta*, 2007; 76, 22-7.
13. Verma A S, Kumar A and Bhardwaj S R, Correlation between ionic charge and the lattice constant of cubic perovskite solids. *physica status solidi (b)*,2008; 245(8), 1520-6.
14. Sohn S H, Hyun D G, Noma M, Hosomi S and Hamakawa Y, Crytal Growth J, Effective charges in II–VI semiconductors. *Journal of Crystal Growth*,1992; 117(1-4), 907-12.
15. Aresti A, Garbato L and Rucci A, Some cohesive energy features of tetrahedral semiconductors. *Journal of Physics and Chemistry of Solids*, 1984; 45 (3), 361-5.
16. Liu L M, Wang S Q and Ye H Q, First-principles study of the effect of hydrogen on the metal–ceramic interface. *Journal of Physics Condensed Matter*,2005; 17(35), 5335-9.
17. Haglund J, Grimvall G, Jarlborg T and Guillermet A F , Band structure and cohesive properties of 3d-transition-metal carbides and nitrides with the NaCl-type structure. *Physical Review B (Condensed Matter)*,1991; 43 (18), 14400-8.
18. Mota R C, Costa S C, Pizani P S and Rino J P, Molecular dynamics simulation of the structural and dynamical properties of crystalline BaO. *Physical Review B*, 2005; 71 (22), 224114.
19. Schlosser H, Cohesive energy-lattice constant and bulk modulus-lattice constant relationships: Alkali halides, Ag halides, Tl halides. *Journal of Physics and Chemistry of Solids*, 1992; 53(6), 855-6.
20. Schlosser H, Cohesive Energy–Lattice Constant Relationship. *physica status solidi* (b), 1993; 179(1), k1-k3.
21. Ballal M M and Mande C, X-ray spectroscopic study of some chalcopyrites, *Journal of Physics C Solid State Physics*,1978; 11(4), 837.