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# Electronic Properties of Bonds in $A^IB^{III}C^{VI}_2$ Chalcopyrite Semiconductors

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**Abstract** In this paper a new approach utilizing the concept of plasma oscillations theory of solids has been applied to investigate the electronic properties such as homopolar gap ($E_h$), heteropolar or ionic gap ($E_c$), average energy gap ($E_g$), bond ionicity ($f_i$) and electronic susceptibility ($\chi_e$) for the chemical bonds (A-C and B-C) in complex structured $A^IB^{III}C^{VI}_2$ ternary chalcopyrite crystals. We have presented the expressions relating the electronic properties for these chalcopyrite crystals with plasmon energy ($\hbar\omega_p$). The homopolar gap ($E_h$), heteropolar gap ($E_c$), average energy gap ($E_g$), bond ionicity ($f_i$)and electronic susceptibility ($\chi_e$)of the bonds in these semiconductors exhibit a linear relationship when plotted on a log-log scale against the valence electron plasmon energy, which lies on the straight line. The calculated values of $E_h$, $E_c$, $E_g$, $f_i$ and $\chi_e$ have been compared with the available theoretical values reported by several workers so far. A fairly good agreement has been obtained between them.

***Keywords:*** *A. Ternary chalcopyrites, D. Electronic properties, D. Optical properties*

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## 1. Introduction

The ternary $A^IB^{III}C^{VI}_2$semiconductors, which crystallize in the chalcopyrite structure with a tetrahedral space group I42d having four formula units in each unit cell, have received much attention in a recent year [1,2,3].They form a large group of semiconducting materials with diverse optical, electrical and structural properties [4,5]. Ternary chalcopyrite compounds appear to be promising candidates for solar-cells applications, light emitting diodes, nonlinear optics and optical frequency conversion applications in solid state based tunable laser systems. These chalcopyrite semiconductors have potentially significant advantages over dye lasers because of their easier operation and the potential for more compact devices. The energy gaps and other dielectric properties, electronic and electrical properties have been studied by several workers [6-11]. There have been many types of theoretical approaches to the calculation of energy gaps and the ionicity of the chemical bond in this family of compounds. The first approach for simple binary compounds was given by Pauling [12] based on thermo-chemical effects and electro-negativity. Phillips and Van-Vechten's [8,9,10] have defined the average energy gap in terms of homopolaror covalent and heteropolar or ionic parts using spectroscopic definitions and the one-electron model originally suggested by Penn [13].This theory of Phillips and Van-Vechten [8,9,10] has been extended to multiband and complex crystals by Levine [11], Neumann [7] and several other workers [14,15,16] including the effect of d-electrons. Coulson et al [17] have used the LCAO-MO approximation to calculate these energy gaps.

Many researchers [18-25] have developed various theories and calculate the micro-hardness, heat of formation, bulk modulus, cohesive energy, Debye temperature, melting temperature, refractive index, homopolar gap, ionic gap, average energy gap and ionicity for zinc blende, rock-salt and complex structured semiconductors. Recently, the authors [26,27,28] have proposed a simple model based on the valence electron plasmon energies of solids for the calculation of electronic, mechanical and optical properties such as electronic polarizability, bulk modulus, cohesive energy, energy gaps and refractive index of wurtzite, zinc-blende and rock-salt structured binary solids. It is now well established that the plasmon energy of a metal changes when it undergoes a chemical combination and forms a compound. This is due to fact that the plasmon energy depends upon the number of valence electrons, which changes when a metal forms a compound. Therefore we thought it would be of interest to give an alternative explanation for the homopolar gap ($E_h$), heteropolar gaps ($E_c$), average energy gaps ($E_g$), bond ionicity ($f_i$) and electronic susceptibility ($\chi_e$) of the bonds ($A^I$-$C^{VI}$ and $B^{III}$-$C^{VI}$) in $A^IB^{III}C^{VI}_2$chalcopyrite crystals. The values obtained for these parameters are in fairly good agreement with the values reported by earlier researchers. Our method turns out to be widely applicable.

The purpose of this work is to obtain electronic properties of A-C and B-C bonds in$A^IB^{III}C^{VI}_2$ class of chalcopyrite semiconductors using the plasma oscillations theory of solids. The present investigations are organized as follows: the theoretical concept is given in Section 2

and we present the discussion and simulation results for electronic properties of A-C and B-C bonds in $A^{I}B^{III}C^{VI}_2$ type chalcopyrite crystals in this Section also. Finally, the conclusion is given in the last Section 3.

## 2. Theory, Results and Discussion

According to the Phillips and Van-Vechten's [PVV] theory [8,9,10], the values of average energy gap ($E_g$) or Penn gap ($E_P$), homopolar gap ($E_h$) and ionic gap ($E_c$) for a binary compound semiconductors (AC) with tetrahedral coordination are given by-

$$E_{g,AC}^2 = E_{h,AC}^2 + E_{c,AC}^2 \quad (1)$$

where

$$E_h = ar_{AC}^{-2.5} \quad (2)$$

$$E_{c,AC} = be^2\begin{bmatrix}(Z_A / r_A)\\ +(Z_C / r_C)\end{bmatrix}\exp[-K_s(r_A + r_C)/2] \quad (3)$$

$$f_{i,AC} = E_{c,AC}^2 / E_{g,AC}^2 \quad (4)$$

In above relations (2)-(3), a and b are constants, $r_{AC}$ is the inter-atomic distance between A and C atoms, $Z_A$ and $Z_C$ and $r_A$, $r_C$ are the valence numbers and covalent radii of A and C atoms respectively. $K_s$ is the Thomas–Fermi Screening parameter for the free electron gas with a density of four electrons per atomic volume and b is the adjustable parameter which depends upon the co-ordination number of a compounds [11] and is given by $b=0.089N_c^2$.The most generalized form of the above equations has been discussed by Levine [11] in detail. The equations given by Levine reduce to those of PVV when only one type of bond is present in the crystal.

The physical meaning of equation (3) is that $E_c$is given by the difference between the Screened Coulomb Potentials of atoms A and B having core charges $Z_A$ and $Z_B$. These potentials are to be evaluated at the covalent radii $r_{AC}$. Only a small part of the electrons are in the bond, the rest screen the ion cores, reducing their charge by the Thomas-Fermi Screening Factor $e^{-K_s(r_A+r_C)/2}$, which affects the chemical trend in a compound. This screening factor, as well as the bond length, is related to the effective number of free electrons in the valence band. Thus, there must be some correlation between the physical process, which involves the ionic contribution $E_c$to the average energy gap ($E_g$) and the plasmon energy ($\hbar\omega_p$) of a compound. A detailed study for plasmon energies of chalcopyrite has been presented in refs. [23,24].

Previously, Verma et al [25] have shown that the heteropolar gaps ($E_c$), average energy gap ($E_g$), bond ionicity ($f_i$) and dielectric constant ($\varepsilon_\infty$) of $A^{I}B^{III}C_2{}^{VI}$chalcopyrite semiconductors can be expressed in terms of the product of ionic charge and nearest neighbor distance d (in $A^0$) by the following form-

$$E_c = A/(Z_1Z_2)^V d^2 \quad (5)$$

$$E_g = A^*/(Z_1Z_2)^{V^*} d^{2.12} \quad (6)$$

where A, V, A* and V* are the constants, which depends upon the crystal structure. This is due to fact that, the ionic charge depends on the number of valence electrons and plasmon energy also depends on the number of valence electrons, which changes, when a metal forms a compound. The heteropolar gap ($E_c$), average energy gap ($E_g$), bond ionicity ($f_i$) and electronic susceptibility ($\chi_e$) ofthe bonds in these semiconductors exhibit a linear relationship when plotted on a log-log scale against the valence electron plasmon energy ($\hbar\omega_p$) of the compounds ,which are presented in Figure 1-Figure 10. We observed that in the plot of $E_h$, $E_c$, $E_g$, $f_i$ and $\chi_e$ versus $\hbar\omega_p$; the semiconducting chalcopyrite lies on the straight line. From Figure 1-Figure 10, it is quite obvious that the homopolar gap ($E_h$), heteropolar gap ($E_c$) and average energy gap ($E_g$) trends in these compounds increase with increasing plasmon energy and the bond ionicity ($f_i$) and electronic susceptibility ($\chi_e$) of A-C and B-C bonds decreases with increases in plasmon energy of these compounds.

Recently, In our previous work [26,27,28], we proposed simple empirical relations for the optical, electronic, static and dynamical properties such as bulk modulus (B), cohesive energy ($E_{coh}$), refractive index (n), polarizability ($\alpha_e$), heteropolar gaps ($E_c$), average -

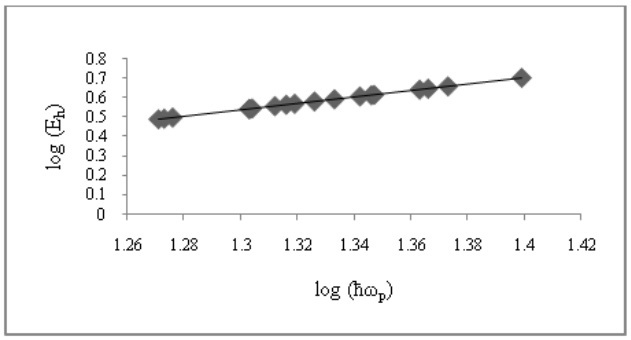


**Figure 1.** Plot of homopolar gap versus plasmon energy of A-C bond in $A^{I}B^{III}C^{VI}_2$ chalcopyrites

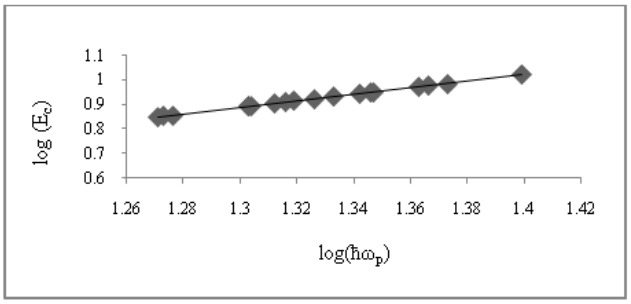


**Figure 2.** Plot of heteropolar gap versus plasmon energy of A-C bond in $A^{I}B^{III}C^{VI}_2$ chalcopyrites

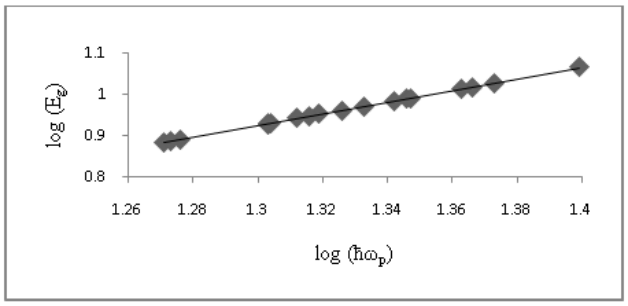


**Figure 3.** Plot of average energy gap versus plasmon energy of A-C bond in $A^{I}B^{III}C^{VI}_2$ chalcopyrites

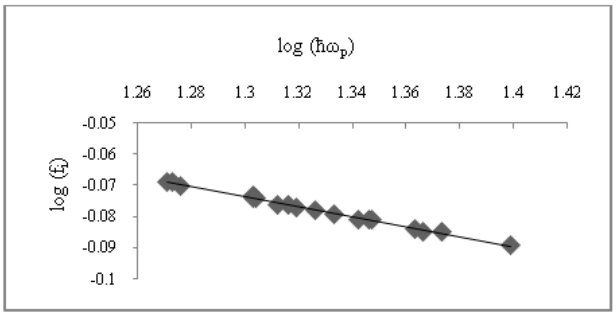


**Figure 4.** Plot of bond ionicity versus plasmon energy of A-C bond in $A^{I}B^{III}C^{VI}_{2}$ chalcopyrites

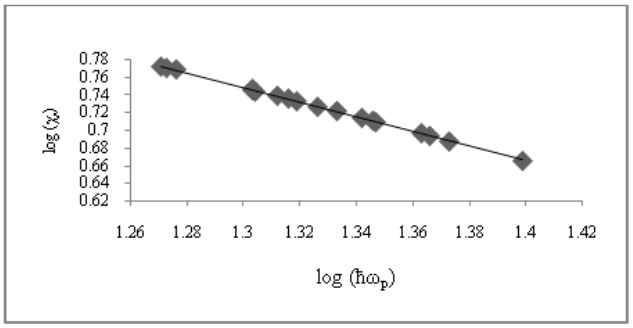


**Figure 5.** Plot of electronic susceptibility versus plasmon energy of A-C bond in $A^{I}B^{III}C^{VI}_{2}$ chalcopyrites

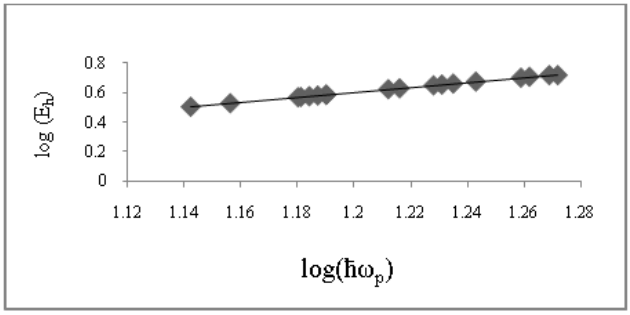


**Figure 6.** Plot of homopolar gap versus plasmon energy of B-C bond in $A^{I}B^{III}C^{VI}_{2}$ chalcopyrites

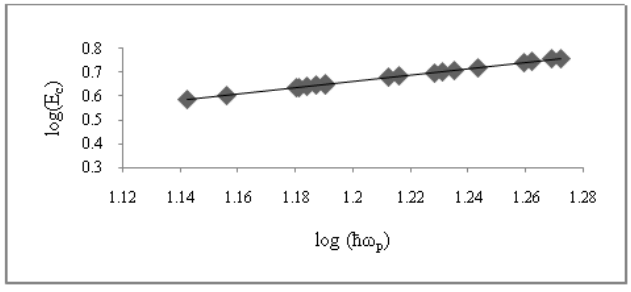


**Figure 7.** Plot of heteropolar gap versus plasmon energy of B-C bond in $A^{I}B^{III}C^{VI}_{2}$ chalcopyrites

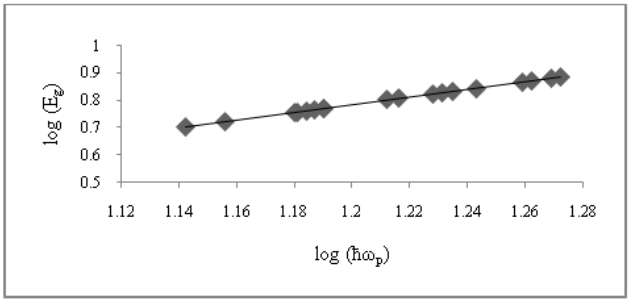


**Figure 8.** Plot of average energy gap versus plasmon energy of B-C bond in $A^{I}B^{III}C^{VI}_{2}$ chalcopyrites

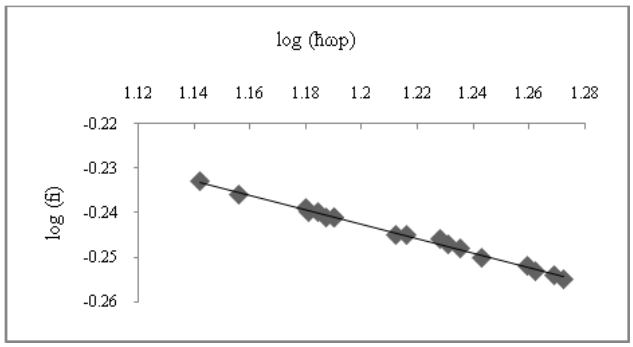


**Figure 9.** Plot of bond ionicity versus plasmon energy of B-C bond in $A^{I}B^{III}C^{VI}_{2}$ chalcopyrites

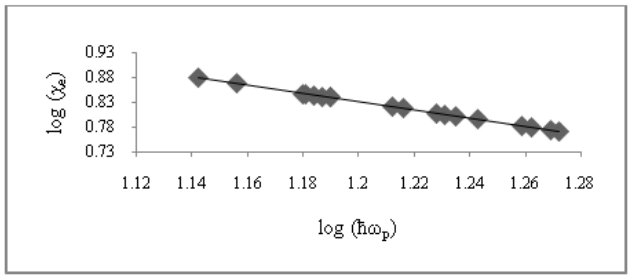


**Figure 10.** Plot of electronic susceptibility versus plasmon energy of B-C bond in $A^{I}B^{III}C^{VI}_{2}$ chalcopyrites

energy gap ($E_g$), crystal ionicity ($f_i$) and optical susceptibility ($\chi_o$) of zinc blende, wurtizite and rock-salt structured binary solids in term of plasmon energy ($\hbar\omega_p$) by the following relations-

$$E_g = M\left(\hbar\omega_p\right)^N \tag{7}$$

$$\chi_o = M^*\left(\hbar\omega_p\right)^{-N^*} \tag{8}$$

where M, N, $M^*$ and $N^*$ are the constants, which depends upon the various type of crystal structure. Using this idea to get better agreement with the theoretical values for the homopolar gap ($E_h$), ionic gap ($E_c$), average energy gap ($E_g$), crystal ionicity ($f_i$) and electronic susceptibility ($\chi_e$) of bonds in $A^{I}B^{III}C^{VI}_{2}$ ternary chalcopyrite semiconductors may be written in terms of plasmon energy $\hbar\omega_p$, (in eV) as-

$$E_h = D\left(\hbar\omega_p\right)^{1.666} \tag{9}$$

$$E_c = S(\hbar\omega_p)^{1.333} \tag{10}$$

$$E_g = D^*\left(\hbar\omega_p\right)^{1.413} \tag{11}$$

$$f_i = S^*\left(\hbar\omega_p\right)^{-0.16} \tag{12}$$

$$\chi_e = D^{\dagger}\left(\hbar\omega_p\right)^{-0.826} \tag{13}$$

where D, S, $D^*$, $S^*$and $D^{\dagger}$are constants for these ternary chalcopyrite crystals, which depends upon the various type of bondsin a compound semiconductors and are presented in Table 1. In above expressions the valence electron plasmon energy of different type of the bonds has been taken from ref. [25]. A detailed discussion of electronic properties of these materials has been given

elsewhere [8,9,10,18,19,20,22,25,29] and will not be presented here. Using Eqs. (9)-(13), the homopolar gap ($E_h$), heteropolar or ionic gap ($E_c$), average energy gap ($E_g$), crystal ionicity ($f_i$) and electronic susceptibility ($\chi_e$) for A-C and B-C bonds in these materials has been calculated. The results are presented in Table 2 & Table 3. The calculated values are in excellent agreement with the theoretical values reported by several workers so far. In the present model, the electronic properties such as homopolar gap ($E_h$), heteropolar or ionic gap ($E_c$), average energy gap ($E_g$), bond ionicity ($f_i$)and electronic susceptibility ($\chi_e$) for the chemical bonds in complex structured $A^IB^{III}C^{VI}_2$ ternary chalcopyritescan be calculated by the plasmon energy as input parameter alone.

**Table 1. In this table, we present the values of the constants for A-C and B-C bonds in $A^IB^{III}C^{VI}_2$ semiconductors, which are used in relations (9)-(13)**

| Constants | D | S | $D^*$ | $S^*$ | $D^\dagger$ |
|---|---|---|---|---|---|
| A-C bond | 0.0235 | 0.1432 | 0.1227 | 1.361 | 66.42 |
| B-C bond | 0.0400 | 0.1156 | 0.1226 | 0.889 | 66.53 |

**Table 2. Properties of the $A^I$-$C^{VI}$ bond in $A^IB^{III}C_2^{VI}$ chalcopyrites**

| Comp. | Energy gaps (in eV) | | | | | | | | Bond Ionicity | | | Electronic Susceptibility | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Homopolar gap | | Heteropolar gap | | | Average energy gap | | | | | | | | |
| | $E_{h[Our]}$ | $E_{h[11]}$ | $E_{c[Our]}$ | $E_{c[25]}$ | $E_{c[11]}$ | $E_{g[Our]}$ | $E_{g[25]}$ | $E_{g[11]}$ | $f_{i[Our]}$ | $f_{i[25]}$ | $f_{i[11]}$ | $\chi_{e[Our]}$ | $\chi_{e[25]}$ | $\chi_{e[7]}$ |
| $CuAlS_2$ | 5.071 | | 10.518 | 10.565 | | 11.663 | 11.719 | | 0.813 | 0.813 | | 4.633 | 4.591 | 4.78 |
| $CuAlSe_2$ | 4.505 | | 9.482 | 9.460 | | 10.449 | 10.425 | | 0.823 | 0.824 | | 4.942 | 4.966 | 5.42 |
| $CuAlTe_2$ | 3.854 | | 8.214 | 8.196 | | 8.974 | 8.954 | | 0.837 | 0.838 | | 5.402 | 5.427 | 7.73 |
| $CuGaS_2$ | 5.010 | 4.91 | 9.697 | 9.699 | 9.95 | 10.701 | 10.704 | 10.964 | 0.821 | 0.821 | 0.825 | 4.874 | 4.872 | 4.83 |
| $CuGaSe_2$ | 4.446 | 4.50 | 8.913 | 8.936 | 7.87 | 9.785 | 9.813 | 8.888 | 0.829 | 0.829 | 0.784 | 5.135 | 5.107 | 6.00 |
| $CuGaTe_2$ | 3.721 | | 8.132 | 8.133 | | 8.879 | 8.881 | | 0.838 | 0.839 | | 5.435 | 5.434 | 5.65 |
| $CuInS_2$ | 4.249 | 4.16 | 8.942 | 8.936 | 8.52 | 9.819 | 9.813 | 9.617 | 0.824 | 0.829 | 0.785 | 5.125 | 5.132 | 5.22 |
| $CuInSe_2$ | 3.842 | | 9.389 | 9.382 | | 10.341 | 10.334 | | 0.829 | 0.824 | | 4.972 | 4.980 | 6.38 |
| $CuInTe_2$ | 3.376 | | 7.853 | 7.830 | | 8.556 | 8.531 | | 0.842 | 0.842 | | 5.554 | 5.588 | 7.45 |
| $AgAlS_2$ | 5.211 | | 8.571 | 8.587 | | 9.388 | 9.408 | | 0.833 | 0.833 | | 5.261 | 5.240 | 4.02 |
| $AgAlSe_2$ | 4.713 | | 7.813 | 7.830 | | 8.510 | 8.531 | | 0.842 | 0.842 | | 5.572 | 5.546 | 4.65 |
| $AgAlTe_2$ | 3.809 | | 7.092 | 7.117 | | 7.679 | 7.710 | | 0.852 | 0.852 | | 5.917 | 5.871 | 6.02 |
| $AgGaS_2$ | 5.211 | 4.90 | 8.394 | 8.388 | 9.87 | 9.183 | 9.177 | 10.600 | 0.835 | 0.835 | 0.867 | 5.330 | 5.337 | 3.83 |
| $AgGaSe_2$ | 4.572 | 4.43 | 7.823 | 7.830 | 8.56 | 8.522 | 8.531 | 9.275 | 0.842 | 0.842 | 0.852 | 5.567 | 5.557 | 4.78 |
| $AgGaTe_2$ | 3.703 | | 7.204 | 7.220 | | 7.809 | 7.829 | | 0.850 | 0.851 | | 5.859 | 5.831 | 5.07 |
| $AgInS_2$ | 4.189 | | 8.807 | 8.794 | | 9.663 | 9.648 | | 0.830 | 0.831 | | 5.173 | 5.190 | 4.02 |
| $AgInSe_2$ | 3.761 | 3.83 | 8.033 | 8.010 | 8.15 | 8.764 | 8.739 | 8.862 | 0.839 | 0.840 | 0.846 | 5.477 | 5.510 | 4.64 |
| $AgInTe_2$ | 3.193 | | 7.126 | 7.117 | | 7.720 | 7.710 | | 0.852 | 0.852 | | 5.899 | 5.915 | 6.02 |

**Table-3. Properties of the $B^{III}$-$C^{VI}$ bond in $A^IB^{III}C_2^{VI}$ chalcopyrites**

| Comp. | Energy gaps (in eV) | | | | | | | | Bond Ionicity | | | Electronic Susceptibility | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Homopolar gap | | Heteropolar gap | | | Average energy gap | | | | | | | | |
| | $E_{h[Our]}$ | $E_{h[11]}$ | $E_{c[Our]}$ | $E_{c[25]}$ | $E_{c[11]}$ | $E_{g[Our]}$ | $E_{g[25]}$ | $E_{g[11]}$ | $f_{i[Our]}$ | $f_{i[25]}$ | $f_{i[11]}$ | $\chi_{e[Our]}$ | $\chi_{e[25]}$ | $\chi_{e[7]}$ |
| $CuAlS_2$ | 5.066 | | 5.567 | 5.584 | | 7.450 | 7.471 | | 0.558 | 0.559 | | 6.030 | 5.997 | 4.26 |
| $CuAlSe_2$ | 4.450 | | 5.064 | 5.084 | | 6.738 | 6.764 | | 0.565 | 0.565 | | 6.391 | 6.347 | 4.76 |
| $CuAlTe_2$ | 3.719 | | 4.470 | 4.469 | | 5.904 | 5.899 | | 0.573 | 0.574 | | 6.905 | 6.920 | 7.19 |
| $CuGaS_2$ | 4.577 | 4.58 | 5.513 | 5.536 | 5.60 | 7.374 | 7.402 | 7.45 | 0.559 | 0.559 | 0.565 | 6.063 | 6.021 | 5.59 |
| $CuGaSe_2$ | 4.118 | 4.13 | 5.011 | 5.001 | 5.10 | 6.663 | 6.646 | 6.80 | 0.567 | 0.566 | 0.563 | 6.433 | 6.471 | 6.80 |
| $CuGaTe_2$ | 3.673 | | 4.346 | 4.366 | | 5.731 | 5.755 | | 0.575 | 0.576 | | 7.026 | 6.971 | 9.17 |
| $CuInS_2$ | 4.136 | 4.46 | 4.833 | 4.839 | 5.49 | 6.413 | 6.419 | 6.39 | 0.568 | 0.569 | 0.636 | 6.579 | 6.570 | 6.02 |
| $CuInSe_2$ | 4.396 | | 4.459 | 4.469 | | 5.888 | 5.899 | | 0.574 | 0.574 | | 6.916 | 6.984 | 7.30 |
| $CuInTe_2$ | 3.516 | | 4.321 | 4.017 | | 5.276 | 5.269 | | 0.581 | 0.581 | | 7.374 | 7.399 | 9.35 |
| $AgAlS_2$ | 3.922 | | 5.735 | 5.734 | | 7.688 | 7.683 | | 0.556 | 0.557 | | 5.917 | 5.929 | 4.26 |
| $AgAlSe_2$ | 3.499 | | 5.251 | 5.258 | | 7.002 | 7.009 | | 0.562 | 0.563 | | 6.249 | 6.241 | 4.76 |
| $AgAlTe_2$ | 3.095 | | 4.428 | 4.434 | | 5.845 | 5.850 | | 0.574 | 0.575 | | 6.946 | 6.937 | 7.19 |
| $AgGaS_2$ | 3.821 | 3.87 | 5.690 | 5.683 | 5.64 | 7.625 | 7.611 | 7.47 | 0.557 | 0.558 | 0.570 | 5.946 | 5.971 | 5.59 |
| $AgGaSe_2$ | 3.499 | 3.57 | 5.124 | 5.127 | 5.02 | 6.824 | 6.824 | 6.70 | 0.564 | 0.565 | 0.561 | 6.345 | 6.348 | 6.80 |
| $AgGaTe_2$ | 3.157 | | 4.329 | 4.332 | | 5.706 | 5.708 | | 0.576 | 0.576 | | 7.044 | 7.044 | 9.17 |
| $AgInS_2$ | 4.058 | | 4.778 | 4.800 | | 6.335 | 6.364 | | 0.569 | 0.569 | | 6.626 | 6.571 | 6.02 |
| $AgInSe_2$ | 3.617 | 3.48 | 4.383 | 4.400 | 4.71 | 5.782 | 5.802 | 6.70 | 0.575 | 0.575 | 0.604 | 6.990 | 9.646 | 7.30 |
| $AgInTe_2$ | 3.114 | | 3.845 | 3.844 | | 5.032 | 5.029 | | 0.584 | 0.584 | | 7.580 | 7.596 | 9.35 |

## 3. Conclusion

From the above results and discussions obtained by using the proposed approach, it is quite obvious that the parameters such as homopolar gap ($E_h$), heteropolar gap ($E_c$), average energy gap ($E_g$),bond ionicity ($f_i$) and electronic susceptibility ($\chi_e$) of the chemical bonds in complex structured $A^IB^{III}C^{VI}_2$ ternary chalcopyrite semiconductors reflecting the electronic properties and

can be expressed in terms of plasmon energies of these materials, which is definitely a surprising phenomenon and need further investigation of the reason. The calculated values of these parameters are presented in Table 2 & Table 3. From Figure 1-Figure 10, we observe that the homopolar gap, heteropolar gap, and average energy gap of these bonds are directly related to the plasmon energy and bond ionicity and electronic susceptibility is inversely related to it. We note that the investigated values of these parameters by our proposed empirical relations are in close agreement with available theoretical values reported by previous researchers. The various evaluated parameters show a systemic trend and are consistent with the available theoretical values reported so far, which proves the validity of the proposed approach. It is also note worthy that the proposed empirical relations are simpler and widely applicable since we have been reasonably successful in calculating these parameters using the plasmon energy of the materials. It is natural to say that this model can easily be extended to rock-salt and zinc-blende structured crystals for which the work is in progress and will be appearing in forthcoming papers. Hence it is possible to predict the order of electronic properties of ternary chalcopyrite compounds from their plasmon energies.

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