

Thermodynamic properties of chalcogenide and pnictide ternary tetrahedral semiconductors

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In this paper, we present thermodynamic properties such as heat of formation, heat of fusion and entropy of fusion for chalcopyrite structured solids with the product of ionic charges and nearest neighbour distance d (Å). The heat of formation (ΔH_f) of these compounds exhibit a linear relationship when plotted on a log-log scale against the nearest neighbour distance d (Å), but fall on different straight lines according to the ionic charge product of the compounds. On the basis of this result two simple heat of formation (ΔH_f)—heat of fusion (ΔH^F), and heat of formation (ΔH_f)—entropy of fusion (ΔS^F), relationship are proposed and used to estimate the heat of fusion (ΔH^F) and entropy of fusion (ΔS^F) of these semiconductors. We have applied the proposed relation to $A^{II}B^{IV}C_2^V$ and $A^{III}B^{III}C_2^{VI}$ chalcopyrite semiconductor and found a better agreement with the experimental data than the values found by earlier researchers. The results for heat of formation differ from experimental values by the following amounts: 0.3% (CuGaSe₂), 6.7% (CuInSe₂), 5% (AgInSe₂), 5% (ZnGeP₂), 6% (ZnGeP₂), 0.4% (ZnSnP₂), 0.7% (ZnSiAs₂), 2.6% (ZnGeAs₂), 1.2% (ZnSnAs₂), 3.8% (CdGeP₂), 6.4% (CdGeAs₂), the results for heat of fusion differ from experimental values by the following amounts: 2.6% (CuGaS₂), 0.6% (CuInTe₂), 6% (ZnGeAs₂), 8.8% (ZnSiAs₂) and the results for entropy of fusion differ from experimental values by the following amounts: 6% (CuInSe₂), 8% (CdSiP₂).

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1. Introduction

Solid materials make up a large portion of the physical world around us and much of modern technology. Different solids have different properties and behaviors, so studying them is interesting. Solids can have very different properties, such as hardness, melting point, electrical conductivity, and elasticity. Studying these properties can help us to better understand materials and how they can be used. Many years before the discovery of semiconduction in elements, chalcopyrite itself was known. Various nonlinear frequency mixing interactions and optoelectronic devices have been demonstrated using the chalcopyrites [1, 2]. As a result of their useful design parameters, such as their nonlinear coefficient, appropriate energy band-gap, and birefringence, chalcopyrite crystals

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have been well established [3, 4]. Chalcopyrite crystals have also been used in a variety of applications, including solar cells, lasers, photodetectors, and optoelectronic devices. Additionally, chalcopyrite crystals are relatively inexpensive and easily available. The chalcopyrite structure is common to compounds of chemical formula $A^{II}B^{IV}C_2^V$ and $A^I B^{III} C_2^{VI}$. It is very difficult to prepare high quality crystals of these semiconductors as compared to binary $A^{II}B^{VI}$ and $A^{III}B^V$ semiconductors. These compounds are also of interest from the fundamental point of view since the chalcopyrite structure is the simplest, non cubic ternary analog of the well understood zinc blende. Therefore, like binary compounds they have a high non-linear susceptibility. However, because of the presence of two types of bonds in chalcopyrites they become anisotropic. This anisotropy gives rise to high birefringence. High non-linear susceptibility coupled with high birefringence in these compounds makes them very useful for efficient second harmonic generation and phase matching. Thus, it is necessary to study the thermodynamic properties such as heat of formation, heat of fusion and entropy of fusion of these semiconductors [4-8]. The heat of formation plays an important role in chemical bonding and crystal physics. The heats of fusion are of particular importance for the quantitative description of solid-liquid equilibrium. They also provide useful information about changes in the structural and binding states during the melting process.

Phillips and Van Vechten (PVV) [9] have redefined the concept of electronegativity and the calculated the heats of formation of a number of $A^N B^{8-N}$ tetrahedral semiconducting compounds. Later on, considerable amount of theoretical work has been made to extend the spectroscopic model of PVV of binary semiconductors to the ternary semiconductors ($A^I B^{III} C_2^{VI}$) [10-14]. However, in the case of $A^{II} B^{IV} C_2^V$ group of ternary semiconductors, the heat of formation has an intricate problem in experimental determination. Thus the theoretical model could not be established for $A^{II} B^{IV} C_2^V$ semiconductors due to lack of experimental data of critical point energies [13, 14]. For computational solid-state studies, empirical relations have become the method of choice. Various empirical concepts, such as electronegativity, ionicity, valence, and plasmon energy, can then be utilized [6, 8]. These concepts can be used to classify and group elements based on their properties. This helps to understand the physical and chemical behavior of elements and how they interact with one another. In addition to describing and classifying many basic properties of molecules and solids, these concepts are directly associated with the chemical bond.

With the aid of ionic charge theory of solids, Verma and co-authors [15-19] calculated the electronic, mechanical, and optical properties of rocksalt, zinc blende, and chalcopyrite crystals. The reason for this is that when a metal forms a compound, the number of valence electrons changes. In order to explain thermodynamic properties of chalcopyrite structured solids, we thought it would be interesting to give an alternative explanation.

2. Theoretical concepts

Numerous researchers [8, 20, 21] have discussed heat of formation in terms of electronegativity differences among atoms constituting the system. The heat of formation is a measure of the amount of energy released when a material is formed from its elements. It is an important property for understanding the thermodynamics of chemical reactions. It is also used to study the energy balance of materials. The following relation gives the energy of bond formation between atoms A and B, according to Pauling [8],

$$D_{AB} = \frac{1}{2} [D(A-A) + D(B-B) + 23 \sum (X_A - X_B)] \quad (1)$$

Here, $D(A-B)$, $D(A-A)$ and $D(B-B)$ are heteropolar bond $A-B$ and homopolar bond $A-A$ and $B-B$ energies respectively. Electro negativities of atoms A and B are X_A and X_B . Here is the value of standard heat of formation for the second term in equation (1):

$$-\Delta H_f = 23 \sum (X_A - X_B)^2 \quad (2)$$

Here \sum is taken over all the bonds in the compound. Several compounds semiconductors were investigated by Phillips [20, 21], and a modified relation was proposed

$$-\Delta H_f = 2 / 3 \times 23 \sum (X_A - X_B)^2 \quad (3)$$

Using nearest neighbour distance d_{R-X} , Mulokozi [22] proposes a relationship for the heats of formation of rare earth compounds. This relation can be used to express heat of formation, according to him,

$$-\Delta H_f = Ae^2 (\Delta X)^2 / d_{R-X} + C \quad (4)$$

In a series of rare earth compounds (where X does not vary) the partial charge ΔX will be constant (depending upon the electro negativity difference between the atoms R and X), e and A elementary charge, which are constants. Where C is covalent contribution. According to Mulokozi the value of $Ae^2 (\Delta X)^2$ and C depends upon cation.

A correlation between the heat of formation of binary compounds and the bond length was found by Phillips and Van Vechten [9],

$$\Delta H_f(AB) = \Delta H_o (d_{Ge} / d_{AB})^s D(AB)f_{iAB} \quad (5)$$

Here, d_{Ge} and d_{AB} are the bond length of germanium and the binary compound AB, respectively, f_{iAB} is the bond ionicity [23], and the $D(AB)$ is given by the relation [13, 23],

$$D(AB) = 1 - b\{2E_2(AB) / [E_o(AB) + E_1(AB)]\}^2 \quad (6)$$

where $E_o(AB)$ is the lowest direct energy gap, $E_1(AB)$ and $E_2(AB)$ are higher critical energies of the compound (AB), and $b = 0.0467$. The values of $E_o(AB)$, $E_1(AB)$ and $E_2(AB)$ can be either taken from the experimental reflectivity data or calculated theoretically using equations given by Van Vechten [24] and Neumann [13]. In equation (5), the values of scaling factor ΔH_o and the exponent's have been found by Phillips and Van Vechten [9] for two different sets of ΔH_o and s . For $s = 4$, $\Delta H_o = -300\text{kJ/mol}$ and $s = 3$, $\Delta H_o = -287\text{kJ/mol}$. Later on Neumann [13] has determined new empirical values of $\Delta H_o = -304\text{kJ/mol}$ and $s = 3.575$ using the experimental values of ΔH_f for binary ($A^{II}B^{VI}$ and $A^{III}B^V$) compounds reported in various references [10, 11], and taking the ionicities, critical point energies and bond lengths from Van Vechten [23, 24].

According to Kumar et al [6], the heat of formation of silicon semiconductors $A^{II}B^{IV}C_2^V$ and $A^{III}B^{VI}C_2^V$ can be calculated through the plasma oscillations theory of solids. According to them heat of formation ($-\Delta H_f$) of these semiconductors may be expressed as,

$$-\Delta H_f = A (\hbar\omega_p)^B \quad (7)$$

Here, A and B are constants and values are 0.3170 and 2.5310, respectively, for $A^{III}B^{VI}C_2^V$ semiconductors and 11.4136 and 1.1624, respectively, for $A^{II}B^{IV}C_2^V$ semiconductors.

In metals and compounds, the energy of a quantum of plasma oscillations of the valence electrons is given by the relation [6],

$$\hbar\omega_p = 28.8 \sqrt{(Z\sigma / W)} \quad (8)$$

where Z is the effective number of valence electrons taking part in the plasma oscillations, σ is the specific gravity and W is the molecular weight. Because, plasmon energy ($\hbar\omega_p$) depends on the number of valence electrons and ionic charge also depends on the number of valence electrons, which changes when a metal forms a compounds. Therefore, we thought it would be of interest to give an alternative explanation for heat of formation (ΔH_f) of chalcopyrite structured solids in terms of ionic charge.

In a previous work, Verma and co-authors [17] have proposed a simple relation for mechanical properties such as the bulk modulus and microhardness of chalcopyrite structured solids in terms of the product of ionic charges and nearest neighbour distance by the following relation,

$$\text{Bulk modulus (B)} = 4056 (Z_1 Z_2 Z_3)^{0.15} / d^5 \quad (9)$$

where Z_1 , Z_2 and Z_3 are the ionic charge on the A, B and C_2 respectively and d is the nearest neighbour distance in Å. Using this idea to get better agreement with experimental and theoretical data for the heat of formation ($-\Delta H_f$) of chalcopyrite semiconductors equation (9) may be extended as

$$-\Delta H_f = 5500 / (Z_1 Z_2 Z_3)^{0.08} d^3 \quad (10)$$

where Z_1 , Z_2 and Z_3 are the ionic charge on the A, B and C_2 respectively and d is the nearest neighbour distance in Å. A detailed study for ionic charges of chalcopyrite has been presented in reference [25]. According to M. M. Ballal et al [25], the valency of copper in all chalcopyrite compounds appears to be one and it is well known that gallium, aluminium and indium always have valency three. Thus we can write the valence structures of the compounds as $A^+ B^{3+} C_2^{2-}$ ($A = \text{Cu, Ag; B} = \text{Al, Ga, In; C} = \text{S, Se, Te}$) and $A^{2+} B^{4+} C_2^{3-}$ ($A = \text{Zn, Cd; B} = \text{Si, Ge, Sn; C} = \text{P, As}$). Therefore the product of ionic charge is 12 for $A^I B^{III} C_2^{VI}$ and 48 for $A^{II} B^{IV} C_2^V$. It is well known that in chalcopyrites each cation has four equal anion bonds but each anion has four (two + two) different cation bonds, this fact gives anion – cation distances d_{AC} and d_{BC} . In relation (10), d is average nearest neighbour distance and for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrites can be calculated by $(d_{AC} + d_{BC}) / 2$.

From the above study we are of the view that the heat of fusion and entropy of fusion of these compounds is inversely related to the values of the heat of formation. Therefore, we have plotted graph of experimental heat of fusion against heat of formation and entropy of fusion against heat of formation, which are shown in figure 1 and 2 for the above series of compounds.

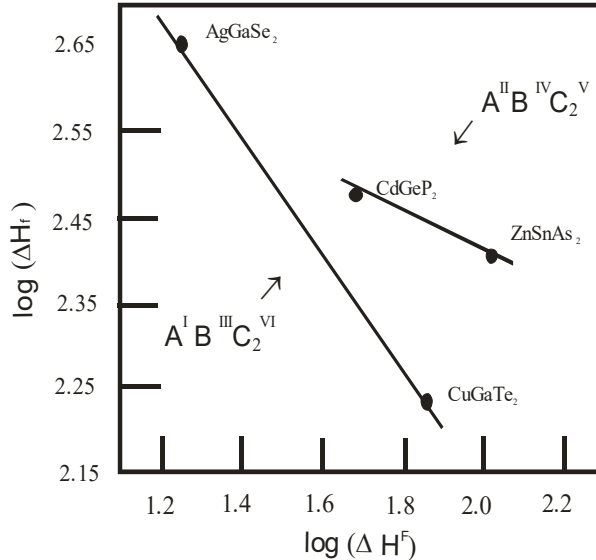


Fig. 1. Plot of $\log \Delta H_f$ (heat of formation in kJ/mol) against $\log \Delta H^F$ (ΔH^F = heat of fusion in kJ/mol) for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors. In the plots of $\log \Delta H_f$ and $\log \Delta H^F$, $A^I B^{III} C_2^{VI}$ chalcopyrites lie on line nearly parallel to the line for $A^{II} B^{IV} C_2^V$ chalcopyrites. In this plot all experimental data are taken from reference [5, 6].

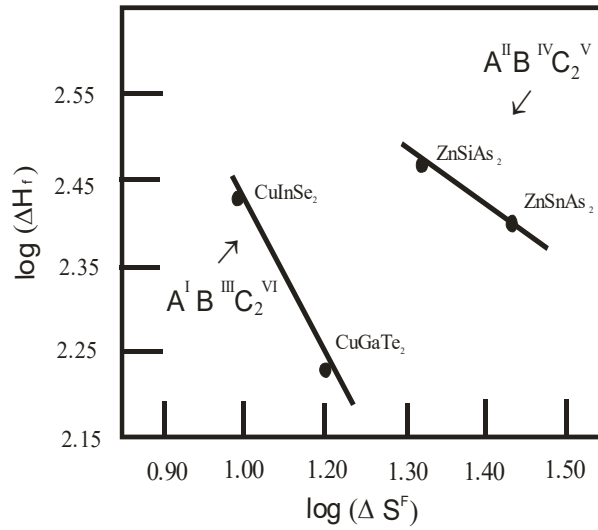


Fig. 2. Plot of $\log \Delta H_f$ (heat of formation in kJ/mol) against $\log \Delta S^F$ (ΔS^F = entropy of fusion in $J K^{-1} g\text{-atom}$) for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors. In the plots of $\log \Delta H_f$ and $\log \Delta S^F$, $A^I B^{III} C_2^{VI}$ chalcopyrites lie on line nearly parallel to the line for $A^{II} B^{IV} C_2^V$ chalcopyrites. In this plot all experimental data are taken from reference [5, 6].

From figure 1 and 2 it is quite obvious that the chalcopyrites lie on two different straight lines. Thus the heat of fusion and entropy of fusion of these compounds may be evaluated by the following relation:

$$-\Delta H^F = A / \sqrt{-\Delta H_f} \quad (11)$$

$$-\Delta S^F = V / \sqrt{-\Delta H_f} \quad (12)$$

where A and V are constants. The numerical value of A is 1000 and 1750 for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrites, respectively, and V is 175 and 300 for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrites respectively.

3. Results and discussion

Any change in the crystallographic environment of an atom is related to core electrons via the valence electrons. The valence electrons are responsible for determining the chemical and physical properties of an atom. This is why changes in the crystallographic environment of an atom can have a significant effect on its physical and chemical properties. When outer electrons' wavefunctions change, there is usually a displacement of electric charges in the valence shell, which alters the interaction between valence, shell, and core electrons. As a result, the inner electron's binding energy changes and the absorption edge shifts. The ionic charge of any compound depends on the valence electrons, and changes when a metal forms a compound. The compound formed usually has a positive charge if the metal has fewer electrons, and a negative charge if it has more electrons. The charge of the ions in the compound is determined by the number of electrons lost in the forming of the compound. We have calculated the heat of formation, heat of fusion and entropy of fusion for chalcopyrite semiconductors using this idea. Although the properties of the chalcopyrite semiconductors have been extensively investigated and some of these compounds have attracted attention for practical applications [26], knowledge of their thermodynamic properties such as heat of formation, heat of fusion and entropy of fusion are rather incomplete. Experimental data are available for a few compounds for chalcopyrite series, so there are many properties of the solid solution which have not been investigated. In table 1 and 2, we present experimental heat of

formation and heat and entropy of fusion values evaluated by earlier researchers [5, 6, 13, 27] for the sake of comparison. There are many variations in the experimental data for heat of fusion for these compounds: for example, for CuInS_2 values of 44.8 ± 6.7 and 40.0 ± 8.0 have been given, for CuFeS_2 values of 20.7 ± 3.1 and 47.3 ± 2.1 . It should be noted that there are a number of reasons for the wide variation in experimental results. First, the inconsistency of the results could be due to the experiments being carried out on polycrystalline samples, while $A^I B^{III} C_2^{VI}$ semiconductors are known to be anisotropic materials. Second, shifts of the composition of the compounds from stoichiometry greatly affect the values of heat of fusion.

In the present work it is shown that analogous relations exist for the ternary chalcopyrite semiconductors, which can be successfully employed to estimate the heat of formation, heat of fusion and entropy of fusion from their ionic charges. The heat of formation (ΔH_f) of chalcopyrite semiconductors exhibit a linear relationship when plotted against nearest-neighbour distance d (\AA), but fall on different straight lines according to the ionic charge product of the compounds, which is presented in figure 3. In figure 3, we observe that in the plot of experimental heat of formation (ΔH_f) and nearest neighbour distance, the $A^I B^{III} C_2^{VI}$ chalcopyrites lie on line nearly parallel to the line for $A^{II} B^{IV} C_2^V$ chalcopyrites. From the figure 3, it is quite obvious that the heat of formation (ΔH_f) trends in these compounds decreases with increases nearest neighbour distance and fall on straight lines according to the ionic charge product of the compounds. Similarly, we have plotted $\log \Delta H_f$ versus $\log \Delta S^F$ and $\log \Delta H_f$ versus $\log \Delta H^F$ curves for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrites, which are presented in figure 1 and 2, and we observe that in the plot of heat of formation Vs entropy of fusion and heat of formation Vs heat of fusion $A^I B^{III} C_2^{VI}$ chalcopyrites lie on a line nearly parallel to the line for $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors, because heat of fusion and entropy of fusion depend upon the heat of formation and heat of formation depend on the product of ionic charges, so heat of fusion and entropy of fusion are also depending on the product of ionic charges. From these figures 1 and 2, it is quite obvious that the heat of fusion and entropy of fusion trends in these compounds decrease with increasing heat of formation and fall on two straight lines according to the ionic charge product of these compounds. The values so obtained are presented in the following table 2.

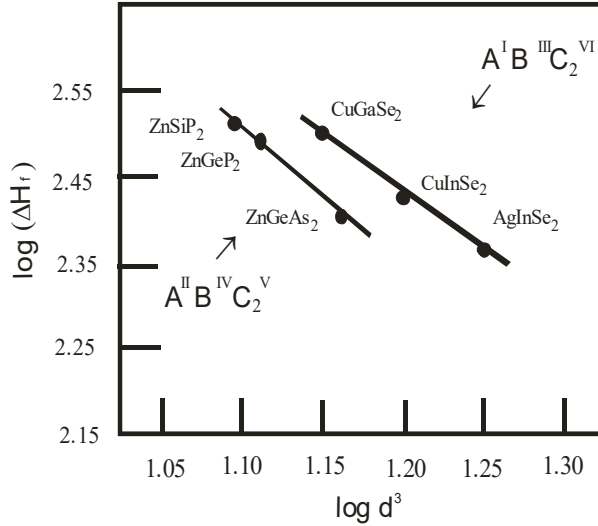


Fig. 3. Plot of $\log \Delta H_f$ (heat of formation in kJ/mol) against $\log d^3$ (d = nearest neighbour distance in \AA^3) for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors. In the plots of $\log \Delta H_f$ and $\log d^3$, $A^I B^{III} C_2^{VI}$ chalcopyrites lie on line nearly parallel to the line for $A^{II} B^{IV} C_2^V$ chalcopyrites. In this plot all experimental data are taken from reference [13, 27, 6].

The physical concept behind equation (10) is that the heat of formation (ΔH_f) is related to the crystal ionicity, energy gaps and plasmon energy of the crystals [14-17, 22]. The crystal ionicity, energy gaps also depends on the product of ionic charges [9-12]. Thus, there must be a correlation

between ΔH_f and product of ionic charges. The values so obtained are presented in the following table 1. The main advantage of equations (10), (11) and (12) are the simplicity of the formula, which does not require any experimental data except the nearest neighbour distance of $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrites. However, the previous models require the experimental values of E_o , E_1 , E_2 and f_i in addition to bond length of these semiconductors.

Table 1. In this table we have presented the values of heat of formation (ΔH_f in kJ/mol) for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ semiconductors. The value of product of ionic charge ($Z_1 Z_2 Z_3$) = 12 for $A^I B^{III} C_2^{VI}$ and ($Z_1 Z_2 Z_3$) = 48 for $A^{II} B^{IV} C_2^V$ semiconductors.

Solids	d (Å)	ΔH_f exp.[13,27]	ΔH_f [6]	ΔH_f [13]	ΔH_f [This work]
CuAlS ₂	2.29		427.9	463.8	375
CuAlSe ₂	2.40		345.9	389.9	326
CuAlTe ₂	2.58		268.5	285.4	263
CuGaS ₂	2.30		418.6	420.4	371
CuGaSe ₂	2.42	317	349.3	329.5	318
CuGaTe ₂	2.60	168	266.2	260.8	257
CuInS ₂	2.40		360.5	327.7	326
CuInSe ₂	2.51	267	305	263.5	285
CuInTe ₂	2.68	107	237.1	228.5	234
AgAlS ₂	2.40		365.6	417.9	326
AgAlSe ₂	2.51		308.6	361.3	285
AgAlTe ₂	2.68		275.7	279.9	234
AgGaS ₂	2.42		359.4	394.8	318
AgGaSe ₂	2.53	446	288.4	318.2	278
AgGaTe ₂	2.69	140	235.7	252.7	232
AgInS ₂	2.49		311.2	330.6	292
AgInSe ₂	2.61	242	262.9	268	254
AgInTe ₂	2.78	123	210.8	217.9	210
CuFeS ₂	2.30		424.2		371
ZnSiP ₂	2.31	312	307.8		327
ZnGeP ₂	2.35	293	299.8		311
ZnSnP ₂	2.45	275	277.1		274
ZnSiAs ₂	2.41	290	287.5		288
ZnGeAs ₂	2.44	271	279.4		278
ZnSnAs ₂	2.53	252	262		249
CdSiP ₂	2.40		290.4		292
CdGeP ₂	2.44	289	276.5		278
CdSnP ₂	2.54	270	262		246
CdSiAs ₂	2.49	290	273		261
CdGeAs ₂	2.53	266	263.7		249
CdSnAs ₂	2.62	247	247.7		224

Thus it is possible to predict the values of $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors from their ionic charge and nearest neighbour distance. We note that the evaluated values are in close agreement with the experimental and theoretical data as compared to the values reported by previous researchers so far. For example, the results for heat of formation differ from experimental values by the following amounts: 0.3% (CuGaSe₂), 6.7% (CuInSe₂), 5% (AgInSe₂), 5% (ZnGeP₂), 6% (ZnGeP₂), 0.4% (ZnSnP₂), 0.7% (ZnSiAs₂), 2.6% (ZnGeAs₂), 1.2% (ZnSnAs₂), 3.8% (CdGeP₂), 6.4% (CdGeAs₂), the results for heat of fusion differ from experimental values by the following amounts: 2.6% (CuGaS₂), 0.6% (CuInTe₂), 6% (ZnGeAs₂), 8.8% (ZnSiAs₂) and the results for entropy of fusion differ from experimental values by the following amounts: 6% (CuInSe₂), 8% (CdSiP₂) in the current study. We can use these results to calculate and predict the properties of more complicated classes of ternary chalcopyrite semiconductors using our current method.

Table 2. In this table we have presented the values of heat of fusion (ΔH^F in kJ/mol) and entropy of fusion (ΔS^F in $J K^{-1}g\text{-atom}$) for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ semiconductors.

Solids	ΔH_f	ΔH^F exp. [5]	ΔS^F exp. [5]	ΔH^F [This work]	ΔS^F [This work]
CuAlS ₂	375			51.6	9.04
CuAlSe ₂	326			55.4	9.69
CuAlTe ₂	263			61.7	10.8
CuGaS ₂	371	50.6±10.1	8.4±1.7	51.9	9.09
CuGaSe ₂	318			56.1	9.81
CuGaTe ₂	257	72.9±10.9	15.9±2.4	62.4	10.9
CuInS ₂	326	44.8±6.7, 40.0±8.0	8.2±1.2	55.4	9.69
CuInSe ₂	285	49.3±9.9	9.8±1.9	59.2	10.4
CuInTe ₂	234	65.0±9.7	15.5±2.3	65.4	11.4
AgAlS ₂	326			55.4	9.69
AgAlSe ₂	285			59.2	10.4
AgAlTe ₂	234			65.4	11.4
AgGaS ₂	318			56.1	9.81
AgGaSe ₂	278	17.4±2.6	3.9±0.6	60.0	10.5
AgGaTe ₂	232			65.7	11.5
AgInS ₂	292			58.5	10.2
AgInSe ₂	254			62.8	11.0
AgInTe ₂	210			69.0	12.1
CuFeS ₂	371	20.7±3.1, 47.3±2.1	4.3±0.7	51.9	9.09
ZnSiP ₂	327			96.8	16.6
ZnGeP ₂	311			99.2	17.0
ZnSnP ₂	274			105.7	18.1
ZnSiAs ₂	288	113.3±15.3	20.9±2.8	103.1	17.7
ZnGeAs ₂	278	111.7±19.0		105.0	18.0
ZnSnAs ₂	249		26.6±4.5	110.9	19.0
CdSiP ₂	292	92.7±13.9	16.3±2.4	102.4	17.6
CdGeP ₂	278	46.7±7.0	11.0±1.6	105.0	18.0
CdSnP ₂	246			111.6	19.1
CdSiAs ₂	261			108.3	18.6
CdGeAs ₂	249			110.9	19.0
CdSnAs ₂	224			116.9	20.0

4. Conclusions

In conclusion, the product of ionic charges of any compound is a very important parameter for calculating physical properties. We have found that the heat of formation of $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors exhibits a linear relationship, when plotted on a log-log scale against the average nearest neighbour distance d (Å), but falls on two straight lines according to the ionic charge product of the compounds. With the help of the proposed empirical relations, it is quite clear that the thermodynamic properties of these materials can be expressed in terms of their ionic charges and their nearest neighbour distance in terms of the heat of formation, heat and entropy of fusion. The calculated values are presented in tables 1, 2 and 3. The ionic charge and average nearest neighbour distance, which are basic parameters, can be used to evaluate the all-important properties of chalcopyrite semiconductors. According to the authors, the calculated values of thermodynamic properties agree very well with the values reported by other researchers. Furthermore, it is noteworthy that the empirical relationship proposed is simpler and more applicable to a wide range of situations. In a forthcoming paper, the model will be extended to rock salt and zinc blende crystals. The ionic charge of semi conducting and metallic compounds can predict their physical properties.

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