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A S Verma and S R Bhardwaj

Department of Physics, BSA College, Mathura, 281004, India

E-mail: ajay_phy@rediffmail.com

Abstract

An empirical relationship previously introduced by the authors, relating the ground state properties such as bulk modulus and cohesive energy of rock-salt and zinc blende structured solids to the product of their ionic charges, is shown to be applicable with minor modifications to the more complex class of ternary chalcopyrite semiconductors. The bulk moduli of $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ chalcopyrite semiconductors exhibit a linear relationship when plotted on a log–log scale against the nearest neighbour distance d (Å), but fall on two straight lines according to the product of the ionic charge of the compounds. On the basis of this result a simple bulk modulus–microhardness relationship is proposed and used to estimate the microhardness of these semiconductors. We have applied the proposed relation to $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ chalcopyrite semiconductors and found a better agreement with experimental data than the values found by earlier researchers. The results for bulk modulus differ from the experimental ones by 0% ($CuAlS_2$), 0% ($CuGaSe_2$), 2% ($CuGaS_2$), 4.8% ($CuInSe_2$), 6% ($AgGaS_2$), 6.2% ($CdSiP_2$) and 0% ($CdGeAs_2$).

1. Introduction

During the last few years a number of theoretical calculations based on empirical relations have become an essential part of materials research. Because *ab initio* calculations are complex and require significant effort, the number of publications on empirical calculations has increased exponentially every year. Empirical relations have become widely recognized as the method of choice for computational solid-state studies. In modern high-speed computer techniques, this method allows researchers to investigate many structural and physical properties of materials by computation or simulation alone instead of traditional experiments. Empirical concepts such as valence, empirical radii, electronegativity and ionicity are then useful [1]. These concepts are directly associated with the character of the chemical bond and thus provide means for explaining and classifying many basic properties of molecules and solids. Recently [2–9], many theoretical applications have been reported for calculation of the mechanical and

optical properties of solid-state compounds. Compounds of the type $A^{II}B^{IV}C_2^V$ and $A^I B^{III} C_2^{VI}$ have attracted considerable attention because of their interesting semiconducting, electrical, structural, mechanical and optical properties. Compared to their binary analogues these compounds have higher energy gaps and lower melting points, and for this reason they are considered to be important in crystal growth studies and device applications. The ternary compounds are direct gap semiconductors with tetragonal chalcopyrite crystal structure. These material families are relevant in many fields including non-linear optics and optoelectronic and photovoltaic devices. The chalcopyrite structure is common to compounds with the chemical formulae $A^{II}B^{IV}C_2^V$ and $A^I B^{III} C_2^{VI}$. Structurally these compounds are derived from that of the binary sphalerite structure (III–V and II–VI) with a slight distortion. 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. Apart from this, the other important technological applications of these materials are in light emitting diodes, infrared detectors, infrared oscillations, lasers etc [9–17].

Many researchers [18–23] have developed various theories and calculated the microhardness, heat of formation, bulk modulus, dielectric constant, electronic polarizability and electronic susceptibility for chalcopyrite semiconductors. Recently the authors [24, 30] have proposed a simple model based on the product of the ionic charges of solids for the calculation of electronic and optical properties such as ionic (E_h) and average (E_g) energy gaps, crystal ionicity (f_i) and dielectric constant (ε_∞) for zinc blende and complex structured solids and ground state properties such as the bulk modulus and cohesive energy for various rock-salt and zinc blende structured solids. It is now well established that the ionic charge of a metal changes when it undergoes a chemical combination and forms a compound. This is due to the fact that the ionic charge depends on 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 bulk modulus of more complex classes of ternary chalcopyrite semiconductors. In this paper we extend the calculation of the bulk modulus reported earlier in the case of complex structured solids. The values found for these parameters are in better agreement with the values reported by earlier researchers.

2. Theoretical concepts

Anderson and Nafe [25] proposed an empirical relationship between bulk modulus B_0 at atmospheric pressure and specific volume V_0 of the form $B_0 \sim V_0^{-x}$. They found it to hold for a particular class of compounds; the value of x depends on the class of compounds. For alkali halides, fluorides, sulfides and tellurides they found x to be 1 and for oxide compounds x is close to 4.

Neumann [22] proposed an empirical relation for microhardness determination of $A^{II}B^{IV}C_2^V$ chalcopyrite compounds as given by

$$H = h T_m V_0^{-n} \tag{1}$$

where T_m is the melting temperature, V_0 is the unit cell volume and h is a function of the bond ionicity given as

$$h = h_0(1 - h_1 f_i)$$

where h_0, h_1 and n are constants.

Neumann [22] also proposed the bulk modulus–microhardness relationship in $A^{II}B^{IV}C_2^V$ chalcopyrite semiconductors as follows:

$$B = CV_0^{-k}H/T_m \tag{2}$$

where C and k are adjustable parameters. The relation of bulk moduli and geometrical properties of diamond and zinc blende solids was previously investigated by Cohen [27] and Lam *et al* [28]. Based on the Phillips and Van Vechten scheme [29] and theoretical analysis of bond geometry of covalent zinc blende solids, Cohen [27] proposed the following empirical relation:

$$B = (1971 - 220\lambda)d^{-3.5} \tag{3}$$

where λ is an empirical parameter which accounts for the effect of ionicity ($\lambda = 0$, 1, 2 for IV, III–V and II–VI compounds, respectively), d is the nearest neighbour distance in Å and B is in GPa. Lam *et al* [28] deduced an analytic relation of bulk moduli to lattice parameters within the local-density formalism and the pseudopotential approach:

$$B = 1971d^{-3.5} - 408(\Delta Z)^2 d^{-4} \tag{4}$$

where $\Delta Z = 1$ and 2 for III–V and II–VI semiconductors.

Gallardo [18] studied the bulk modulus of $A^{I}B^{III}C_2^{VI}$ chalcopyrite compounds and proposed a modification to Cohen's relation (3). According to this modification the bulk modulus may be expressed in terms of the average nearest neighbour distance and the electronic susceptibilities of different bonds by the following relation:

$$B = (1971 - 200\lambda)d^{-3.5} - |\chi_{AC} - \chi_{BC}|^{2.5} \tag{5}$$

where $\lambda = 0.72$, $d = (d_{AC} + d_{BC})/2$ and χ_{AC} and χ_{BC} are the electronic susceptibilities of the bonds.

In a previous work [30] we proposed a simple relation for ground state properties such as the bulk modulus and cohesive energy of rocksalt and zinc blende structured solids in terms of the product of ionic charges and nearest neighbour distance by the following relation

$$B = (Z_1 Z_2)^A N d^{-3} \tag{6}$$

where Z_1 and Z_2 are the ionic charges of the cation and anion, respectively, and A and N are constants which depend upon the crystal structure. Using this idea to get better agreement with experimental and theoretical data for the bulk modulus of $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^V$ chalcopyrite semiconductors equation (6) may be extended as

$$\text{Bulk modulus} = (Z_1 Z_2 Z_3)^S V d^{-5} \tag{7}$$

where Z_1, Z_2 and Z_3 are the ionic charges of A, B and C_2 respectively, and S and V are constants, which depend upon the crystal structure; they have values of 0.15 and 4056, respectively. A detailed study of the ionic charges of chalcopyrite compounds has been presented by Ballal and Mande [31]. According to Ballal and Mande [31], the valency of copper in all chalcopyrite compounds appears to be 1 and it is well known that gallium, aluminium and indium always have valency 3. Thus we can write the valence structures of the compounds as $A^+B^{3+}C_2^{2-}$ (A = Cu, Ag; B = Al, Ga, In; C = S, Se, Te) and $A^{2+}B^{4+}C_2^{3-}$ (A = Zn, Cd; B = Si, Ge, Sn; C = P, As). Therefore the product of the ionic charges 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 this relation 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 microhardness of these compounds is directly related to the values of the bulk modulus. Therefore, we have plotted a graph of
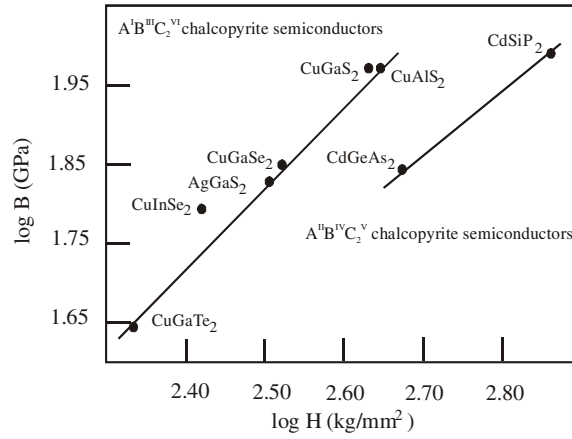
Figure 1. Plot of $\log B$ (GPa) against $\log H$ (kg mm^{-2}) for A^{I}B^{III}C$_2^{VI}$ and A^{II}B^{IV}C$_2^{V}$ chalcopyrite semiconductors. In the plots of $\log B$ and $\log H$, A^{I}B^{III}C$_2^{VI}$ chalcopyrites lie on a line nearly parallel to the line for A^{II}B^{IV}C$_2^{V}$ chalcopyrites. In this figure all data are taken from experimental results apart from CdSiP$_2$, which is a theoretical value [32].

experimental microhardness against bulk modulus, which is shown in figure 1 for the above series of compounds. From figure 1 it is quite obvious that the A^{I}B^{III}C$_2^{VI}$ and A^{II}B^{IV}C$_2^{V}$ chalcopyrites lie on two different straight lines. Thus the microhardness of these compounds may be evaluated by the following relation:

$$H = K B^{K+1} \tag{8}$$

where K is the adjustable parameter. The value of K if 0.5 and 0.59 for A^{I}B^{III}C$_2^{VI}$ and A^{II}B^{IV}C$_2^{V}$ chalcopyrites, respectively.

3. Results and discussion

The bulk modulus and microhardness are important mechanical properties of a material; bulk modulus defines its resistance to volume change when compressed. Both experimental and theoretical results suggest that the bulk modulus is a critical single material property to indicate hardness. Any change in the crystallographic environment of an atom is related to core electrons via the valence electrons. The change in wavefunction that occurs for the outer electrons usually means a displacement of electric charge in the valence shell so that the interaction between valence, shell and core electrons is changed. This leads to a change in binding energy of the inner electron and to a shift in the position of the absorption edge. The ionic charge of any compound depends on the valence electrons, and changes when a metal forms a compound. We have calculated the bulk modulus (B in GPa) and microhardness (H in kg mm^{-2}) for A^{I}B^{III}C$_2^{VI}$ and A^{II}B^{IV}C$_2^{V}$ chalcopyrite semiconductors using this idea. Although the properties of the A^{I}B^{III}C$_2^{VI}$ and A^{II}B^{IV}C$_2^{V}$ chalcopyrite semiconductors have been extensively investigated and some of these compounds have attracted attention for practical applications [11], knowledge of their mechanical properties such as microhardness and bulk modulus are rather incomplete. Experimental data are available for a few compounds for chalcopyrite series, A^{I}B^{III}C$_2^{VI}$ and A^{II}B^{IV}C$_2^{V}$, so there are many properties of the solid solution which have not been investigated. In [11] an analysis of the dependence of their chemical composition is given. In table 1, we present experimental microhardness values evaluated by Bodnar *et al* [33] and other experimental values [32] for the sake of comparison. There

Table 1. The values of bulk modulus (B in GPa) and microhardness (H in kg mm^{-2}) for the $A^IB^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^V$ chalcopyrite semiconductors.

Compounds	d (Å)	B_{exp} [26]	B_{theor} [18, 22]	$B_{This\ work}$	H_{exp} [32, 33]	H_{theor} [32]	$H_{This\ work}$
CuAlS$_2$	2.29	94	94	94	442	250, 261	456
CuAlSe$_2$	2.40		69	74	325, 210	226, 228	318
CuAlTe$_2$	2.58		45	52	182	255, 210	188
CuGaS$_2$	2.30	94, 96	93	92	430, 445	230, 245	441
CuGaSe$_2$	2.42	71	68	71	330, 197, 430, 435	197, 210	299
CuGaTe$_2$	2.60	44	43	50	215, 180, 360, 347	240, 185	177
CuInS$_2$	2.40		71	74	290, 231	140	318
CuInSe$_2$	2.51	62	54	59	260, 185, 251	160, 141	227
CuInTe$_2$	2.68		36	43	190, 152, 210	166, 140	141
AgAlS$_2$	2.40		73	74		145	318
AgAlSe$_2$	2.51		55	59	160	176, 135	227
AgAlTe$_2$	2.68		36	43	149	167, 142	141
AgGaS$_2$	2.42	67	70	71	320, 296	175, 130	299
AgGaSe$_2$	2.53		53	57	230, 143, 450, 310	158, 124	215
AgGaTe$_2$	2.69		35	42	135, 180, 260	166, 142	136
AgInS$_2$	2.49		56	62	200	80	244
AgInSe$_2$	2.61		42	49	127, 230, 187	102, 82	172
AgInTe$_2$	2.78		28	36	118, 190	116, 98	108
ZnSiP$_2$	2.31		120	110	1100	900	1039
ZnGeP$_2$	2.35		108	101	980	635	907
ZnSnP$_2$	2.45		84	82	650	530	651
ZnSiAs$_2$	2.41		93	89	920	820	742
ZnGeAs$_2$	2.44		86	84	680	630	677
ZnSnAs$_2$	2.53		67	70	455	430	507
CdSiP$_2$	2.40	97	97	91		730	769
CdGeP$_2$	2.44		86	84	565, 410	470	677
CdSnP$_2$	2.54		67	69		255	495
CdSiAs$_2$	2.49		77	76		615	577
CdGeAs$_2$	2.53	70	70	70	470	470	507
CdSnAs$_2$	2.62		55	59	350, 335	310	386

are many variations in the experimental data for microhardness for $A^IB^{III}C_2^{VI}$ compounds: for example, for CuAlSe$_2$ values of 325 and 210 have been given, for CuGaSe$_2$ values of 330, 197, 430 and 435, for CuInSe$_2$ values of 185, 260 and 251, for CuGaTe$_2$ values of 215, 180, 360 and 347, for CuInTe$_2$ values of 152, 210 and 190, for AgGaS$_2$ values of 296 and 320, for AgGaSe$_2$ values of 230, 310, 143 and 450, for AgInSe$_2$ values of 127, 230 and 187 and for AgGaTe$_2$ values of 135, 180 and 260. 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 $A^IB^{III}C_2^{VI}$ semiconductors are known to be anisotropic materials. Second, shifts of the composition of the compounds from stoichiometry greatly affect the values of microhardness.

In the present work it is shown that analogous relations exist for the ternary chalcopyrite semiconductors, which can be successfully employed to estimate the bulk modulus and microhardness from their ionic charges. We have plotted $\log B$ versus $\log d^5$ curves for $A^IB^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^V$ chalcopyrites, which are presented in figure 2, and we observe that in the plot of bulk modulus and nearest neighbour distance $A^IB^{III}C_2^{VI}$ chalcopyrites lie on a line nearly parallel to the line for $A^{II}B^{IV}C_2^V$ chalcopyrites. Similarly, we have plotted $\log B$ versus
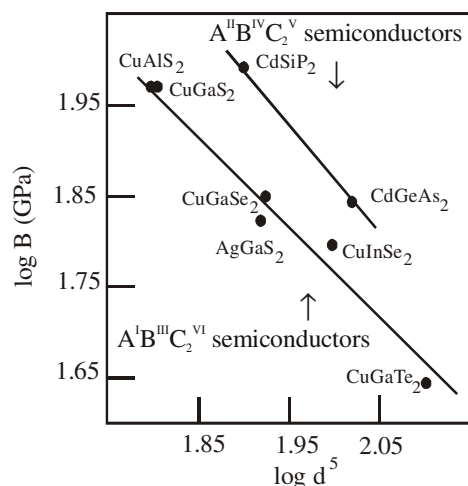
Figure 2. Plot of $\log B$ (bulk modulus) (GPa) against $\log d^5$ (d = interatomic distance) for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors. In the plots of $\log B$ and $\log d^5$, $A^I B^{III} C_2^{VI}$ chalcopyrites lie on a line nearly parallel to the line for $A^{II} B^{IV} C_2^V$ chalcopyrites. In this plot all data are taken from experimental results.

$\log H$ curve for $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrites, which is presented in figure 1, and we observe that in the plot of bulk modulus and microhardness $A^I B^{III} C_2^{VI}$ chalcopyrites lie on a line nearly parallel to the line for $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors, because microhardness is linearly related to bulk modulus and bulk modulus is linearly related to the product of ionic charges, so microhardness is also linearly related to the product of ionic charges. From these figures it is quite obvious that the bulk modulus and microhardness trends in these compounds decrease with increasing interatomic distance and fall on two straight lines according to the ionic charge product of these compounds.

The proposed empirical relations (7) and (8) have been applied to evaluate bulk modulus and microhardness values of $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ chalcopyrite semiconductors. The values are presented in table 1. We note that the values of bulk modulus and microhardness calculated from the our proposed relations are in closer agreement with the experimental data than the values reported thus far by previous researchers. For example, the results for bulk modulus differ from experimental by 0% ($CuAlS_2$), 0% ($CuGaSe_2$), 2% ($CuGaS_2$), 13.6% ($CuGaTe_2$), 4.8% ($CuInSe_2$), 6% ($AgGaS_2$), 6.2% ($CdSiP_2$) and 0% ($CdGeAs_2$) in the current study. These results show that our current method is quite reasonable and can give us a useful guide in calculating and predicting the bulk modulus of the more complex class of ternary chalcopyrite semiconductors.

4. Summary and conclusions

From the results and discussion obtained by using the proposed empirical relations, it is quite obvious that parameters such as bulk modulus and microhardness reflecting the mechanical properties can be expressed in terms of the product of ionic charges and nearest neighbour distance of these materials; this is a surprising phenomenon. The calculated values are presented in table 1. We come to the conclusion that the product of the ionic charges of any compound is key parameter for calculating the mechanical properties. Furthermore, we found that in the compounds investigated here, the bulk modulus 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 fall on two straight lines according to the ionic charge product of the compounds. From figure 2 we observe that the data points for $A^IB^{III}C_2^{VI}$ chalcopyrites lie on a line nearly parallel to the line for $A^{II}B^{IV}C_2^V$ chalcopyrites, and from figure 1 we observe that the data points for $A^IB^{III}C_2^{VI}$ chalcopyrites lie on a line nearly parallel to the line for $A^{II}B^{IV}C_2^V$ chalcopyrites, because microhardness is linearly related to bulk modulus. According to this idea we may evaluate all important properties of chalcopyrite semiconductors using their ionic charge and average nearest neighbour distance, which are basic parameters. Recently the authors [24, 30] have calculated the electronic and optical properties such as ionic (E_c) and average (E_g) energy gaps, crystal ionicity (f_i), dielectric constant (ε) and electronic susceptibility (χ) of zinc blende and complex structured solids and ground state properties such as bulk modulus and cohesive energy of rock salt and zinc blende structured solids from their product of ionic charges and nearest neighbour distance. In the present study we find that both bulk modulus and microhardness depend directly on the ionic charge of these compounds. Thus this theory can be easily extended to complex structured solids. An excellent agreement between our calculated values of bulk modulus and microhardness and the values reported by different researchers has been found. It is also note worthy that the proposed empirical relations are simple and widely applicable.

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