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Best Model for the calculation of Bulk Modulus of Ternary Chalcopyrites: A Comparative Study

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Abstract

There are a number of models proposed by different researchers for the calculation of Bulk Modulus of ternary chalcopyrites. In this work, we have used Microsoft excel data analysis tool and the Statistical Package for Social Science (SPSS) in order to identify the best model from the given models.

Keywords: Ternary Chalcopyrites, Bulk Modulus, SPSS analysis tool, Microsoft excel data analysis tool.

1. INTRODUCTION

Ternary chalcopyrites with general formula I-III-VI2 and II-IV-V2 have obtained considerable attention because of their potential applications in the areas of light emitting diodes, non-linear optics, photo voltaic devices and solar cells. The mixed crystals of these compounds are used for the fabrication of detectors, lasers and integrated optic devices such as filters, modulators, switches etc.

The bulk modulus of ternary chalcopyrite semiconductors represents the fundamental physical aspect that characterize their physio-mechanical properties. The applications of ternary chalcopyrite semiconductors as mechanical, electronic and optical devices are very much determined by the nature and magnitude of this elementary property. Bulk modulus of a material is defined as the property by virtue of which it resists to volume change when compressed.

Several researchers have proposed different theoretical models for calculating bulk modulus of ternary chalcopyrite semiconductors. But there is a need to know which one of these models that can give values of bulk modulus closest to the known values of bulk modulus.

In this work, a comparative study of the values of bulk modulus of ternary chalcopyrites semiconductors calculated from the theoretical models of different researchers with the experimental values are done. The Microsoft excel and Statistical Package for social science (SPSS) are used for the compression. The main goal of the analysis is to find out that which model gives values of bulk modulus closet to the experimental values.

2. THEORY

There are various theoretical models relating the bulk modulus of ternary chalcopyrite semiconductors. For cubic crystals, it is a critical single material characteristic to show hardness as recommended by theoretically as well as experimentally. Many theoretical approaches have been conveyed to estimate the bulk modulus of solids. By Murnaghan equation of state and his P-V relationship, using the pressure values, the bulk modulus can be easily calculated. The P-V relation of the Murnaghan equation of state is,

$$P = \frac{B}{B_0}\left[\left(\frac{V}{V_0}\right)^{B_0^1} - 1\right]$$

From the above equation we detect that,

$$dE = -PdV$$

By the definition of the bulk modulus of a solid material, Murnaghan proposed, the relation,

$$B_0 = -V\left(\frac{\partial P}{\partial V}\right)_T = -V(\frac{\partial^2 E}{\partial V^2})_T$$

Wang and Ye have suggested the linear fitting equation of bulk modulus of group IV and III-V zinc blende structure as,

$$B_0 = -\alpha + (\frac{\beta}{V_0})$$

where, α= -0.45118 and β= 0.22137 for group IV zinc blende phase and α= -0.32202 and β=0.19314 for III-V zinc blende phase.

For rock salt type crystalline compounds, Cohen has suggested the relation of isothermal bulk modulus in terms of nearest neighbor distance d (in A0) as,

$$B = 550d^{-3}$$

For zincblende solids, the following relation was proposed by Neumann,

$$B = 1761d^{-3.5}$$

Lam et al. using the local density formula and the Pseudo potential approach comprehended the relation for Bulk Modulus as,

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

where ΔZ = 1 for III – V and ΔZ =2 for II – VI type semiconductors.

Verma and Bhardwaj prolonged the Cohen's equation to:

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

where Z1 and Z2 are the ionic charges of the cations and anions respectively. Their numerical value of A is 0.75 and Z is 550 for rock salt like compounds and A is 0.2 and Z is 750 for zinc blende like compounds respectively.

Liu and Cohen have suggested the following relation for bulk modulus of binary crystalline materials,

$$B = \frac{\langle N_C \rangle}{4}(1971 - 221\lambda)d^{-3.5}$$

where Nc the bulk coordination number, λ is an empirical iconicity parameter and d is the bond

length. λ takes the value 0,1 and 2 for IV, II-VI and III-V semiconductors respectively, the correction factor of the bond ionicity, according to Meng et al. is,

$$\lambda = \frac{|G_A - G_B|}{2}$$

where GA and GB are the numbers of the group of elements- A & B in the periodic table. Meng et al. has proposed the formula for Bulk Modulus as,

$$B^{\mu} = \frac{N_C}{4}\frac{1971 - 221\lambda}{(d^{\mu})^{3.5}}$$

where λ is the correction factor of the bond ionicity, B^{μ} in GPa, d^{μ} in A^0 and Nc is the coordination number. For the group IV-IV compounds, λ =0, for III-V group compounds λ =1 and λ =2 for the II-VI group compounds.

In terms of discrete bond properties, Grima Gallardo projected a amendment of Cohen equation and predictable bulk modulus of I-III-V2 chalcopyrite compounds in terms of the electronic susceptibilities and bond length of different I-III and III-V bonds in I-III-V2 type ternary chalcopyrite compounds as,

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

where are electronic susceptibilities, λ=0.72 and $d = \frac{(d_{AC}+d_{BC})}{2}$.

Kumar et al. have calculated the bulk modulus of IV, III-V, II-VI, II-IV-V2 and I-III-VI2 semiconductors and projected an empirical relation for the bulk modulus of those compounds in terms of Plasmon energy. According to them, the bulk modulus of these semiconductors may be conveyed as,

$$\mathrm{B} = \mathrm{P}(\hbar \mathrm{w_p})^{2.333}$$

Where, P =0.109 and P =0.125 for I-III-VI2 and II-IV-V2 type chalcopyrites respectively.

Kumar et al. also amended the relation suggested by Plendl et al. between microhardness and bulk modulus as,

$$\mathrm{B} = \mathrm{kH} + \mathrm{g}$$

where *k* and *g* are constants. The value of k=16.88 and g =19.52 for I-IIIVI2.

Neumann has suggested the relation between bulk microhardness and Bulk Modulus in II-IV-V2 type chalcopyrite semiconductor materials as,

$$B = \frac{CV_0^{-K}H}{T_m}$$

where k and C are variable parameters.

Bearing in mind the ionic charge theory of solids, Verma and Bhardwaj has predicted the bulk modulus of ternary chalcopyrite materials from lattice thermal conductivity by the subsequent equation,

$$B = SK^{S+1}$$

where the value of S =0.375 and S =0.235 for I-III-VI2 and II-IV-V2 respectively.

Reddy et al. have interconnected bulk modulus with energy gap for chalcopyrite compounds, II-VI, III-V, II-IV-V2 and I-III-VI2 respectively. The empirical equation recommended by them may be conveyed as,

$$B = 13.89E_g + 46.90$$

Later on they have recommended a relation between bulk modulus and polarizability of the above compounds.

Gorai *et al*. have estimated bulk modulus from Plasmon energy by suggesting a linear relation between them. The empirical relation concerning bulk modulus and Plasmon energy recommended by them as,

$$B = a(\hbar w_p) - b$$

where a and b are constants and their numerical values are as a =10 GPa/eV and b =85 and 75 Pa for both ternary chalcopyrite's. Recently Al-Douri *et al*. has calculated the bulk modulus of III-V and II-VI semiconductors and proposed an empirical relation for the bulk modulus in terms of the lattice constants, transition pressure and charge density as,

$$B = [99 - (\lambda + 79)](10P_t)^{1/3}$$

where P_t is the transition pressure in GPa and λ is a parameter suitable for the group IV (λ =1), III-V (λ =5) and II-VI (λ=8) type semiconductors.

Gorai et. al. proposed the empirical relation for the calculation of ternary chalcopyrite as

$$B = \propto \left[\frac{\eta_{av}}{(\chi_A\chi_B)^{\frac{1}{4}} \ (\chi_C)^{1/2}}\right] + \beta$$

where $\alpha = -73.75$; $\beta = -91.00$ for $A^{I}B^{III}C_2^{VI}$ and $\alpha = 127.1$; $\beta = 162.56$ for $A^{II}B^{IV}C_2^{V}$ compounds.

Method of Analysis

The data in table 1 containing the values of the bulk modulus calculated from the models or relations stated above were analyzed using the SPSS analysis tool. Before carrying out the statistical analysis, the data were first tested for normality or non-normality. The reason for this test is to know the right statistical test i.e., parametric or non-parametric to use. So, homogeneity of variance test is used to test for non-normality i.e., to see if the variance across the data are homogeneous.

This is carried out in four steps as described below

(i) The ranking of the data was done i.e., the values of bulk modulus of each model or relations are ranked.

(ii) The mean values of bulk modulus of each model was found.

(iii) The absolute difference was computed i.e., $\left|$ Rank of values of bulk modulus of each model – Mean value of bulk modulus of each model $\right|$

(iv) The one-way analysis of variance (ANOVA) was done in order to see if there is any difference in the variance or the variance across the values of bulk modulus of each model is homogeneous. After computing the ANOVA, the significance value (p) for the variance across of 0.05, so, the null hypothesis (The variance across the data is homogeneous) was accepted.

The one-way ANOVA is a statistical test that is carried out on two or more samples or groups. The significance level (α) is a probability, with a value ranging from 0.01 to 1.00 and it is used to evaluate the significance of the sample result. The null hypothesis (H0) simply states that there is no difference between the two groups; using this term, one can define the p value to be the probability of observing a difference as large or larger than one observed if the null hypothesis were true. So, before carrying out any statistical test one usually set a threshold α value and traditionally or mostly the α value is set to 0.05. So, if, the null hypothesis (H0) is rejected and vice-versa.

After confirming that the data are non-normally distributed, the Friedman two way analysis of variance by ranks and Kendall's coefficient of concordance test were used to see if the

distribution of values of bulk modulus across the data were the same. Results are shown in table 2. Also, the Wilcoxon signed rank test was performed to test for the median difference between two related groups. Results are shown in table 3.

Table 1: Bulk modulus of I-III-VI2 and II-IV-V2 type ternary chalcopyrites

Compounds	Gorai et. al.	Kumar et. al.	H. Neumann	Experimental Values
$CuAlS_2$	88.01	84.02	96.8	94,99
$CuAlSe_2$	73.26	69.06	77.3	84
$CuAlTe_2$	45.23	54.68	57.2	
$CuGaS_2$	85.06	82.32	95.8	94,96,97
$CuGaSe_2$	69.57	69.67	76.6	71,94
$CuGaTe_2$	40.07	54.24	55.4	44
$CuInS_2$	80.63	71.73	84.4	75
$CuInSe_2$	63.67	61.49	68.4	48,53,62,72
$CuInTe_2$	32.70	48.74	50.6	36,45.4
$AgAlS_2$	83.58	73.19	79.9	
$AgAlSe_2$	68.10	56.02	65.0	
$AgAlTe_2$	37.86	56.02	48.8	
$AgGaS_2$	80.63	73.19	77.6	60,67,72,90
$AgGaSe_2$	64.41	62.15	63.8	59.8,65
$AgGaTe_2$	32.70	56.02	48.6	35.7,71.5,76.6
$AgInS_2$	76.21	71.52	71.60	
$AgInSe_2$	58.51	58.39	58.30	42
$AgInTe_2$	24.58	43.73	44.10	
$ZnSiP_2$	103.35	93.13	120.3	
$ZnGeP_2$	97.89	88.35	107.6	
$ZnSnP_2$	91.52	75.44	84.20	
$ZnSiAs_2$	84.24	81.22	93.40	
$ZnGeAs_2$	77.87	76.68	85.70	

$ZnSnAs_2$	**69.68**	**67.43**	**67**	
$CdSiP_2$	**96.98**	**82.88**	**97**	**97**
$CdGeP_2$	**91.52**	**75.10**	**86.4**	
$CdSnP_2$	**84.24**	**67.43**	**67.2**	
$CdSiAs_2$	**76.05**	**73.19**	**-**	
$CdGeAs_2$	**69.68**	**68.28**	**69.7**	
$CdSnAs_2$	**61.49**	**60.23**	**54.8**	

Table 2: Summary of the results of comparing known values with experimental values of bulk modulus

Sr. No.	Null Hypothesis	Test	Significance level (α)	p-value	Decision
1.	The distributions of Gorai et. al., Kumar et. al., and known values are the same	Related samples Friedman's analysis of variance by ranks	0.05	0.000	Reject the Null Hypothesis
2.	The distributions of Gorai et. al., Kumar et. al., and known values are the same	Related samples Kendall's Coefficient of concordance	0.05	0.000	Reject the Null Hypothesis

Table 3: Summary of the result of comparing known values with calculated values of Bulk modulus

Sr. No.	Null Hypothesis	Test	Significance level (α)	p-value	Decision

1.	The median of difference between Gorai et. al. and known values equals 0	Related samples Wilcoxon signed Rank test	0.05	0.716	Retain the Null Hypothesis
2.	The median of difference between Kumar et. al. and known values equals 0	Related samples Wilcoxon signed Rank test	0.05	0.056	Retain the Null Hypothesis
3.	The median of difference between Neumann and known values equals 0	Related samples Wilcoxon signed Rank test	0.05	0.287	Retain the null hypothesis

3. RESULT AND DISCUSSION

From table 2 the Friedman analysis of variance by ranks the distributions of values calculated from the models and known values are not the same, since the p-value is 0.000 which is below the significance level (α) set at 0.05. So, the null hypothesis was rejected indicating that the distributions are not the same. Also, from the Kendall's coefficient test, the distributions of values from the models and known values are not the same since the p-value is below the significance level (α) set at 0.05. So, the null hypothesis was rejected indicating that the distributions are not the same.

From table 3 the related samples Wilcoxon signed rank test shows that the median of differences between values calculated from models of Gorai et. al., Kumar et. al., H. Neuman and known values equals to zero since their p-values 0.716, 0.056, 0.287. So, the null hypothesis was accepted indicating that the median of differences between known values and values calculated from each of models are equal to zero.

CONCLUSION

So, using the appropriate statistical analysis tool in comparing the values of bulk modulus of ternary chalcopyrite semiconductors with their known values, results showed that the model of Gorai et. al. gave values closest to the known values.

REFERENCES

1. Shay J L, Wernic J H (1975) Ternary chalcopyrite semiconductors: Growth, Electronic properties and Applications, Pergamon press, Oxford, pp. 11,12 and 73.
2. Kazmerski, L. L. (1983). Ternary-compound thin-film solar cells. Nuovo Cimento D, 2(6), 2013-2028.
3. Deab S K & Zunger A, Ternary and multinary compounds,. Materials Research Soc Conf, Proc, (1987) (p. 37)
4. Zhu Y (2008) Applications of ternary chalcopyrite compounds, Functional Materials Letters.1239. 180, 676-681.
5. Ajay Kumar Sharma, Sanjay Kumar Goarai, "Heat of Formation of I-III-VI2 AND II-IV-V2 Type Ternary Chalcopyrites on the Basis of Optical Electronegativity," Journal of Multidimensional Research and Review (JMRR), Vol.1, Iss.2, pp.15-22, 2020.
6. Reddy, R. R., Ahammed, Y. N., Gopal, K. R., & Rao, T. V. R. (1998). Bulk modulus and electronic polarizability of compound and ternary chalcopyrite semiconductors. Infrared physics & technology, 39(1), 55-58.
7. Kumar, V., Prasad, G. M., & Chandra, D. (1996). Microhardness-Plasmon Energy-Bulk Modulus Relationship in Ternary Chalcopyrite Semiconductors. Crystal Research and Technology, 31(4), 501- 504.
8. Gorai, S. K., & Mahto, P. (2010). Plasmon energy, bulk modulus, electronic polarisability of AIBIIIC2VI & AIIBIVC2V ternary chalcopyrite semiconductors. Indian Journal of physics, 84(5), 587-592.
9. Meng, Q. B., Xiao, C. Y., Wu, Z. J., Feng, K. A., Lin, Z. D., & Zhang, S. Y. (1998). Bulk modulus of ternary chalcopyrite AIBIIIC2VI & AIIBIVC2V semiconductors. Solid state communications, 107(7), 369-371.
10. Reddy, R. R., Ahammed, Y. N., Gopal, K. R., & Raghuram, D. V. (1999). Bulk modulus and debye temperature of ternary chalcopyrite semiconductors.
11. Verma, A. S. (2013). Bulk modulus and hardness of chalcopyrite structured solids. Materials Chemistry and Physics, 139(1), 256-261.
12. Neumann, H. (1988). Microhardness scaling and bulk modulus-microhardness relationship in AII BIV C2V chalcopyrite compounds. Crystal research and technology, 23(1), 97-102.
13. Kumar, V., Shrivastava, A. K., & Jha, V. (2010). Bulk modulus and microhardness of tetrahedral semiconductors. Journal of Physics and Chemistry of Solids, 71(11), 1513-1520.

14. Verma, A. S. (2009). An empirical model for bulk modulus and cohesive energy of rocksalt-, zincblende- and chalcopyrite-structured solids. physica status solidi (b), 246(2), 345-353.
15. Rincon, C., Villareal, I., & Galindo, H. (1999). Microhardness-bulk modulus scaling and pressureinduced phase transformations in AIBIIIC2VI chalcopyrite compounds. Journal of applied physics, 86(4), 2355-2357.
16. Gorai, S. K., Parida, G., & Sharma, A. K. (2017). An Empirical Bulk Modulus of Ternary Chalcopyrite Structure Solids, Rasayan Journal of Chemistry, Volume- 10 (3), 751-758.
17. Łażewski, J., Neumann, H., Jochym, P. T., & Parlinski, K. (2003). Ab initio elasticity of chalcopyrites. Journal of applied physics, 93(7), 3789-3795.
18. Verma, A. S., Sharma, S., Bhandari, R., Sarkar, B. K., & Jindal, V. K. (2012). Elastic properties of chalcopyrite structured solids. Materials Chemistry and Physics, 132(2-3), 416-420.
19. Neumann, H. (1989). Trends in the microhardness of the CuBIIIC chalcopyrite compounds. Crystal Research and Technology, 24(8), 815-821.
20. Deus, P., & Schneider, H. A. (1983). Estimation of the debye temperature of diamond-like semiconducting compounds from bulk modul and microhardness. Crystal Research and Technology, 18(4), 491-500.
21. Kumar, V., Prasad, G. M., Chetal, A. R., & Chandra, D. (1996). Microhardness and bulk modulus of binary tetrahedral semiconductors. Journal of Physics and Chemistry of Solids, 57(4), 503-506.
22. Gorai, S. K., & Mahto, P. (2010). Plasmon energy, bulk modulus, electronic polarisability of AIBIIIC2VI & AIIBIVC2V ternary chalcopyrite semiconductors. Indian Journal of physics, 84(5), 587-592.
23. Ajay Kumar Sharma & Sanjay Kumar Goarai, "Electronic Susceptibility of I-III-VI2 and III-V-V2 type Ternary Chalcopyrite Semiconductors," Journal of Multidimensional Research and Review (JMRR), Vol.1, Iss.3, pp.61-67, 2020.
24. Sharma A.K, Goarai S.K, Prasad S.,(2020) Role of Ternary Chalcopyrites in enhancing Green Technologies and Innovations, Akshar Wangmay, SI(1), 208-210

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