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On the Acoustic Deformation Potential of Some I-III-VI₂ Chalcopyrites and Their Mixed Versions



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Abstract

The valence band and conduction band acoustic deformation potentials of some I-III-VI₂ chalcopyrites and their mixed versions have been evaluated from the knowledge of the temperature dependence of the band gap dE_g/dT and pressure dependence of the band gap dE_g/dP and compared with the available reported values. Analysis of the results shows that the p-d hybridization is mainly responsible for the reduction of the values of the deformation potentials in these compounds and the same also throws some light on the electron-phonon contribution to the temperature dependence of band gap in these compounds, which is very important for understanding some physical processes taking place in these crystals.

Keywords: Chalcopyrite, Deformation Potential, Mixed Version, P-D Hybridization

Introduction

The dielectric properties of binary compounds can be explained by changing the cation or anion with the atoms belonging to the same column in the periodic table from the knowledge of the correlations¹⁻⁴ among the various useful parameters like band gap, crystal ionicity, effective charge and the band structure parameters of binary semiconductors and this helps in predicting the unknown dielectric properties of similar types of compounds. But the presence of plural kinds of cations in the unit cell of ternary and multinary compounds makes the evaluation process complicated, thus the correlation established in the binary compounds have not the same physical meaning when considering ternary and multinary compounds⁵.

The I-III-VI₂ ternary semiconducting compounds appear to be promising candidates for various technological applications like nonlinear optics, light emitting diodes, photovoltaic optical detectors and solar cells^{6,7,8}. For raising a device-use potentiality, further advancements are needed on growth methods controlling a degree of perfection, defects doping and also characterization of methods of those. Many studies have been carried out on the crystal growth, electrical, thermal dependence, pressure dependence and related properties but sufficient interpretation of the measured with the theory are not available yet. The advent of modern crystal growth technique like liquid phase epitaxy (LPE), vapour phase epitaxy (VPE), chemical vapour deposition (CVD), metallo-organic chemical vapour deposition (MOCVD) together with the highly sophisticated technique like molecular beam epitaxy (MBE) gave further impetus to the use of mixed crystals^{9,10} as the design parameters like lowest energy band gap, lattice parameters, thermal expansion coefficient, birefringence can be tailored to the desired value by changing the cationic/anionic concentration or both.

Temperature dependence of the band gap and electronic transitions give valuable informations about Fermion-Boson (electron-phonon) interaction and excitonic effect. The matrix elements for the interaction between carriers and acoustic phonons at band extreme of semiconductors can be evaluated from the deformation potentials for uniform strain. But the concept of absolute deformation potential for a uniform hydrostatic strain would correspond for the bottom of the conduction band, to the variation of the electron affinity with the strain and for the top of the valence band to that of ionizing potential. But the deformation potentials required to evaluate the electron-phonon interaction for phonons of wavelength much greater than the simple size, should be however bulk quantities independent of surface details. Further the knowledge of the band structure of these materials^{5,11} along with both

the temperature and pressure dependence property is of technological interest and we have reported here our studies on some I-III-VI₂ chalcopyrites and their mixed versions for evaluating the acoustic deformation potential of these compounds from a knowledge of temperature and pressure dependence of the band gap. Our work gain additional importance by the fact that it has been possible to evaluate the electron-phonon interaction whose knowledge is essential for determining the high field transport properties of the semiconductors. The dependence of the energy gap with pressure is related to the deformation potential¹² which measures the electronic energy states variation with lattice deformation. Again the electron-phonon interaction can be classified into a short range part i.e. potential deformation mechanism and a long range part called Frohlich interaction. And this later mechanism appears dominant in resonance Raman Scattering by the polar LO modes in mixed solution and enhancement of such a mechanism may be due to a potential fluctuation induced by intrinsic disorder and impurities. The knowledge of deformation potential^{13,14,15} (conduction band and valence band) is very important in assessing quantum confinement of holes and separately for electron in heterostructure. Again the hydrostatic deformation potential gives longitudinal electron-phonon interaction and is related to (i) the dc conductivity of the doped semiconductor and (ii) the changes in the lattice constant due to doping as well, thus making the evaluation of deformation potential very attractive as well as interesting.

Theory and Method of Evaluation

Measurements of the optical properties, mostly absorption of diamond and zinc blende semiconductors under hydrostatic pressure have been proved useful in identifying the symmetries of the lowest conduction bands. The changes of the energy levels with hydrostatic pressure occur because the interatomic distances decrease whereas the core can be regarded as essentially incompressible. The net result is a rearrangement of the valence wave function relative to the core functions, other words, a core shift. Bardeen and Shockley developed a deformation theory for the scattering of current carriers, in which lattice waves are considered to set up 'deformation potentials' with which the holes and electrons interact and established a relationship between conduction band deformation potential (C_e) and valence band deformation potential (C_h) and the mobilities of the two bands. From the shift of the energy gap with pressure it is possible to estimate the p-d hybridization contribution (and also p-d hybridization from the knowledge of (dE_g/dP)). Also it is possible to calculate the deformation potential for the valence-conduction band separation from the knowledge of dE_g/dP which is an easily measurable quantity and can provide useful information about the electronic band structure and optical properties of the compound.

The temperature dependence of energy gap in semiconductors are well known to be the combined effect of thermal expansion of the lattice and electron-phonon interaction mechanism^{16,17,18,19}. The knowledge of temperature dependence of the energy

gap²⁰ and broadening of the interband electronic transitions can give useful information about electron-phonon interactions, excitonic effects etc. An increase in temperature of a crystal leads to a red shift of the band gap and increase the line width, while a decrease in temperature of a crystal leads to a blue shift. The pressure dependence of the energy gap²¹ is very important like the temperature dependence of the same as the former is very useful for understanding the effect of pressure on the band structure of the crystal as well as interpreting the transport property measurements. Further, these two parameters help to evaluate the electron-phonon interaction term together with the deformation potentials associated with the conduction and valence band. We have evaluated the deformation potentials for some

I-III-VI₂ compounds following the method²² as well as their mixed versions by modifying the same accordingly.

The change of temperature in a semiconductor produces two effects—(i) thermal expansion of the lattice (ii) the change of band gap. Further the change of energy gap with temperature in a semiconductor arises due to (a) electron-phonon interaction i.e., $dE_g/dP|_{ep}$ and (b) thermal expansion of the lattice $dE_g/dP|_{TE}$

So,

$$dE_g/dP|_{total} = dE_g/dP|_{ep} + dE_g/dP|_{TE} \dots\dots\dots(1)$$

where

$$dE_g/dP|_{ep} = - (8/9\pi)(3/4)^{1/3}(k_B V^{2/3}/h^2 M v^2)(m_h C_h^2 + m_e C_e^2) \dots\dots\dots(2)$$

k_B , Boltzman constant, h , Plank constant, m_e and m_h the masses of electron and holes respectively, M , V , mass and volume of the unit cell, v , velocity of sound, C_e , conduction band deformation potential, C_h , valence band deformation potential.

The contribution to dE_g/dT due to thermal expansion of the lattice is given by (Moss 1959)

$$dE_g/dP|_{TE} = 2\alpha_L(C_e + C_h) \dots\dots\dots(3)$$

where α_L is the average thermal expansion coefficient of the crystal and is given by $\alpha_L = (2\alpha_a + \alpha_c)/3$ where α_a and α_c are the thermal expansion coefficient of a and c axis of the crystal respectively and a and c are the lattice parameters of the crystals, that due to electron-phonon interaction contribution by²³ as given by equation (2).

Further,

$$dE_g/dP|_{TE} = -(3\alpha_L/k)dE_g/dP \dots\dots\dots(4)$$

where k is the compressibility of the crystal and dE_g/dP the pressure dependence of the band gap of the crystal.

$$\text{Combining (3) and (4) yield } C_e + C_h = -(1.5/k)dE_g/dP \dots\dots\dots(5)$$

The values of α_L and k are known for the compounds considered here but the same is not true for the dE_g/dP values. And the values of dE_g/dP not known for the compounds (considered here) have been evaluated from a plot of downshift of dE_g/dP i.e., $\Delta[dE_g/dP|_{B.E.} - dE_g/dP|_{Ternary}]$ vs. percentage hybridization in figure (1) which is a new approach for this type of compounds, i.e. compounds containing noble metal.

In this case of I-III-VI₂ compounds, it is known that the noble metal d level appears quite unexpectedly higher energy region. In fact noble

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metal atoms (Cu, Ag) often are divalent in molecule which means that one of the 10 'd' electrons is participating in the bonding together with the 's' valence electron. It is also seen that the d level of the noble atom is nearly equal to the p level of the chalcogen, which forms the uppermost of the valence band of the II-VI compound. For the material studied here (usually for all the I-III-VI₂ compounds) the uppermost valence bands are derived from a combination of the anion p orbitals and the noble metal d orbitals while the conduction band is derived from s states of the cation. Because of the crystal field and spin-orbit splitting, it has been observed that the p-like and d-like states interact strongly in these materials leading to a reduction in the energy gap and this effect is known as p-d hybridization. From the knowledge of percentage hybridization of the compounds, it is possible to evaluate the downshift of dE_g/dP with respect to binary and ultimately for the compounds.

$$dE_g/dP|_{\text{downshift}} = dE_g/dP|_{\text{B.E.}} - dE_g/dP|_{\text{Ternary}}$$

So evaluating the $dE_g/dP|_{\text{downshift}}$ from figure (1) corresponding to the percentage hybridization of the compound and $dE_g/dP|_{\text{B.E.}}$, the parameter $dE_g/dP|_{\text{Ternary}}$ for the unknown compound can be found out and this appears a very useful method for evaluation of the pressure dependence of band gap of these type of compounds. Now from the knowledge of k and dE_g/dP , the sum of the conduction band and valence band deformation potentials (C_e and C_h) can be evaluated, whereas from the knowledge of α_L , k and dE_g/dT , it is possible to evaluate $dE_g/dT|_{\text{T.E}}$ i.e., thermal expansion contribution term to $dE_g/dT|_{\text{e.p.}}$. Using the relation (1) $dE_g/dT|_{\text{e.p.}}$ i.e. electron-phonon contribution to dE_g/dT can be calculated, as dE_g/dT for entire crystal i.e., $dE_g/dT|_{\text{Total}}$ is known. Now from the knowledge of $dE_g/dT|_{\text{e.p.}}$ and equation (2) and (5) it is possible to evaluate the values of conduction band deformation potential (C_h).

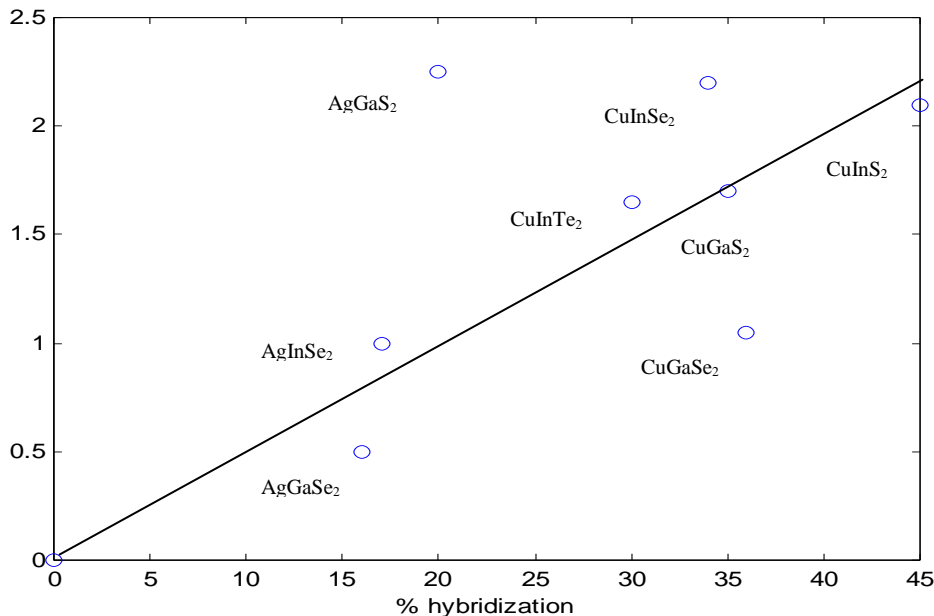


Fig 1: Plot of the downshift of the pressure dependence of the band gap of some I-III-VI₂ compounds relative to its binary equivalent as a function of percentage hybridization

Result and Discussions

We have evaluated C_e and C_h of some copper and silver chalcopyrites and their mixed versions and these have been shown in table 1 and table 2 respectively. And the results have been compared with the other reported values. The agreement is encouraging. The I-III-VI₂ chalcopyrite compounds draw special attention because of the presence of the d-electron, which cause the downshift of the band gap relative to the binary which is termed as p-d hybridization. The tetrahedral crystal field splits the five fold degenerate noble metal d- level into a three fold Γ_{15} and two fold Γ_{12} and these undergo further splitting due to spin-orbit interaction. The spin-orbit interaction also splits p-like Γ_{15} valence band state. And p-like and d-like Γ_{15} states interact strongly

in these materials and this interaction raises the top of valence band leading to a reduction in band gap²⁴. According to this picture, the application of pressure would promote a stronger overlap between the two Γ_{15} states because of the reduced lattice constants and cause a reduction of the energy gap with pressure. But the experimental results show the opposite trend. And this points to the conclusion that the bottom of the conduction band of ternary semiconductors must be rising with pressure at least as rapidly as the II-VI analogs but the effect is partially compensated by the opposite effect expected from the increase in p-d hybridization^{25,26}. This probably is one reason why the pressure induced energy gap shifts in II-VI compounds are larger.

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Analysis of C_e and C_h shows that C_e is -ve and C_h is +ve and $|C_e| > |C_h|$. Considering the magnitude i.e., $|C_e| > |C_h|$ it may be said that the valence band and the conduction band extreme move in the same direction on the compression and the relative shift of the conduction band is greater than that of valence band. This also confirms the experimental observation that the band gap of these materials increase with pressure $[(dE_g/dP) = +ve]$ and both band extreme move to higher energies on the application of pressure. Further p-d hybridization is playing a key role in both these²⁷ i.e., dE_g/dT and dE_g/dP . The variation of band gap with pressure in I-III-VI₂ compounds is also anomalous compared with that of their binary analogs. In the case of Cu-III-VI₂, the direct energy gap increases with increasing pressure, similar to the binary analogs, but the rate of change of E_g with pressure (dE_g/dP) is smaller. It has been suggested that the p-d hybridization of the uppermost valence bands of the I-III-VI₂ compounds is responsible for this anomaly. Recent results for the pressure dependence of the lattice parameters in

some I-III-VI₂ compounds by in situ high pressure X-ray studies seem to confirm this hypothesis.

The comparatively smaller values of C_e and C_h for Cu and Ag chalcopyrite may be explained due to p-d hybridization in I-III-VI₂ chalcopyrites because of presence of d-electrons in these. The effect of d-electrons on the band gap, the temperature dependence of the band gap, the pressure dependence of the band gap is an established fact and the same effect is again reflected in the values of conduction band deformation potential C_e and valence band deformation potential C_h thus pointing out the importance of the d-electron contributions to the various meaningful parameters characterizing the properties of solid. Further inspection of the results for the variation of C_e and C_h with concentration shows no bowing i.e., obeys Vegard's law, whereas bowing has been observed when one considers variation of band gap with concentration and this effect is more predominant in amalgamated type than persistence type.

Table 1
Acoustic Deformation Potential of Some I-III-VI₂ Chalcopyrite Compounds.

Compounds	$(dE_g/dT) \times 10^{-4} \text{ eV/K}$	$(dE_g/dT)_{T.E} \times 10^{-4} \text{ eV/K}$	$(dE_g/dT)_{c.p} \times 10^{-4} \text{ eV/K}$	$C_e \text{ eV}$	$C_h \text{ eV}$	$(C_e+C_h) \text{ eV}$
CuGaS ₂	-1.31	-1.03	-0.28	-15.08	9.3	-5.77
CuGaSe ₂	-2.45	-1.09	-1.36	-12.42	7.25	-5.17
AgGaS ₂	-1.86	-0.17	-1.69	-12.09	9.78	-2.31
CuGaTe ₂	-4.0	-0.44	-3.56	-19.26	16.84	-2.42
AgInS ₂	-2.65	-0.53	-2.12	-14.59	11.89	-2.70
CuAlS ₂	-1.11	-0.96	-0.15	-6.80	0.97	-5.83
CuAlSe ₂	-1.2	-1.15	-0.05	-4.27	-1.22	-5.49
AgGaTe ₂	-2.0	-0.10	-1.9	-14.58	11.96	-2.62

Table 2
Acoustic Deformation Potential of Some Mixed I-III-VI₂ Chalcopyrites

Compounds	Concentration	$(dE_g/dT) \times 10^{-4} \text{ eV/K}$	$(dE_g/dT)_{T.E} \times 10^{-4} \text{ eV/K}$	$(dE_g/dT)_{c.p} \times 10^{-4} \text{ eV/K}$	$C_e \text{ eV}$	$C_h \text{ eV}$	$(C_e+C_h) \text{ eV}$	Other reported results $(C_e+C_h) \text{ eV}$
CuGa(S _x S _{1-x}) ₂	x = 0.00	-2.20	-1.03	-1.17	-18.90	13.13	-5.77	-6.5 ^a , -4.4 ^b
	x = 0.25	-2.17	-1.04	-1.13	-13.96	8.38	-5.58	-
	x = 0.50	-2.20	-1.05	-1.15	-13.20	7.80	-5.40	-5.2 ^b
	x = 0.75	-2.39	-1.07	-1.32	-12.65	7.36	-5.29	-
	x = 1.00	-2.45	-1.09	-1.36	-12.42	7.25	-5.17	-5.11 ^a , -4.4 ^b
CuAl _x Ga _{1-x} S ₂	x = 0.00	-1.31	-1.03	-0.28	-15.08	9.30	-5.77	-6.5 ^a , -4.4 ^b
	x = 0.25	-1.25	-0.91	-0.34	-9.80	4.05	-5.78	-
	x = 0.50	-1.11	-0.92	-0.19	-7.94	2.14	-5.80	-
	x = 0.75	-1.11	-0.94	-0.17	-7.37	1.57	-5.80	-
	x = 1.00	-1.11	-0.96	-0.15	-6.80	0.97	-5.83	-
AgGa(S _x Se _{1-x}) ₂	x = 0.00	-1.40	-0.61	-0.79	-8.64	4.07	-4.57	-4.5 ^a
	x = 0.25	-1.60	-0.49	-1.11	-9.98	5.90	-4.08	-
	x = 0.50	-1.80	-0.40	-1.43	-11.16	7.60	-3.55	-
	x = 0.75	-2.00	-0.26	-1.74	-12.21	9.25	-2.96	-
	x = 1.00	-2.20	-0.17	-2.03	-13.09	10.78	-2.31	-2.3 ^a

For dE_g/dP :^{22,28,29}, For dE_g/dT :^{30,31}, For α :^{32,33}, For k :^{34,35}, For θ_D :^{36,37}
For ρ, α, c :³⁸, For m_e, m_h :²², For a :²², For b :³⁹

Conclusion

It is worth mentioning in this connection that very little information on the electron-phonon energy is available for ternary including their mixed versions and quaternary compounds as well a wide variety of hetero structures like quantum dots, super lattices

and multiple quantum well structures. So such a study will be of immense helpful for finding the same when evaluated from the deformation potential from some useful parameters characterizing the material but at the same time no knowledge of predominant

scattering mechanism is required and thus making the results more interesting and meaningful.

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