

Acoustic deformation potentials in $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ chalcopyrite semiconductors

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From the analysis of the variation of the energy gap with temperature and pressure in some $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ chalcopyrite compounds, valence- and conduction-band acoustic deformation potentials are calculated. It is found that both the valence- and conduction-band extrema move to higher energies on compression in these compounds. This should explain the small band-gap pressure and temperature coefficients observed in $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ chalcopyrite compounds relative to their binary analogs.

INTRODUCTION

The ternary $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ semiconducting compounds which crystallize in the chalcopyrite structure have received much attention in recent years.¹⁻³ In order to obtain information about some of the relevant electrical-transport parameters of these compounds, analysis of the variation of the carrier mobility with temperature, using the Mathiesen's approximation, has been made.⁴⁻⁸ However, difficulties arise in such analysis since the predominant scattering mechanisms of the charge carriers have not been completely identified in $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ compounds. In particular, large discrepancies exist in relation to the values of the acoustic deformation potentials obtained by several authors who have used different approaches to estimate the magnitude of the different scattering mechanisms.

An attempt has been made recently to analyze under a consistent criteria the mobility data for CuInSe_2 published by various authors.⁹ The results are satisfactory for hole-mobility data since practically all curves reported in the literature were adjusted with a valence-band deformation potential, $|C_h|$, of about 7.5 eV. On the contrary, depending of the sample, the conduction-band deformation potential, $|C_e|$, must be varied from 13 to 55 eV in order to adjust the electron-mobility data. This range of variation of $|C_e|$ seems to be very large and has not been explained satisfactorily to data.

In a recent paper, which analyzes the published data for the variation of the energy gap with temperature and pressure in CuInSe_2 , $|C_e|$ and $|C_h|$ were found to be 7.8 and 9.5 eV, respectively.¹¹ The result for $|C_h|$ confirms the value obtained in Ref. 10. However, $|C_e|$ is smaller than all the values reported in the literature. It has been suggested that this discrepancy can be explained if an additional scattering mechanism of the electrons, for example the electron-electron ($e-e$) scattering combined with polar-optical modes, is included in the theoretical adjustment of the electron-mobility data. This also indicates that if the influence of ($e-e$) scattering on the other scattering mechanism is not taken into account in the cal-

culations, the values of $|C_e|$ thus obtained must be overestimated.

In the present work, by analyzing the variation of the energy gap with temperature and pressure, C_e and C_h of the $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ compounds are obtained. Since in this analysis the knowledge of the predominant scattering mechanisms of the charge carriers is not required, the results are probably more reliable than those obtained up to data from the mobility data.

THEORY

The shift of the energy gap with temperature in a semiconductor is caused mainly by two contributing effects. The most important one is the electron-phonon interaction, which is given by¹²

$$(dE_g/dT)_1 = -(8/9\pi)(3/4\pi)^{1/3}(k_B V^{2/3}/h^2 M v^2) \times (m_h C_h^2 + m_e C_e^2), \quad (1)$$

where M and V are the mass and volume of the unit cell, respectively. v , the velocity of sound, can be estimated by using the formula $v = (k_B \Theta_D/h)(V/6\pi^2)^{1/3}$, Θ_D being the Debye temperature.

The second contribution to the shift in the energy gap is due to the thermal expansion of the lattice. This is given by¹³

$$(dE_g/dT)_2 = 2\alpha_L(C_h + C_e), \quad (2)$$

where α_L , the average thermal expansion coefficient, for $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ compounds is given by $\alpha_L = (2\alpha_a + \alpha_c)/3$, α_a and α_c being the thermal expansion coefficients of the lattice parameters a and c , respectively.

This contribution to the shift in the band gap can also be related to the variation of the energy gap with pressure by the expression¹³

$$(dE_g/dT)_2 = -(3\alpha_L/\kappa)dE_g/dP, \quad (3)$$

where κ is the compressibility of the crystal.

TABLE I. Calculated values of C_e and C_h for some $A^1B^{\text{III}}C_2^{\text{VI}}$ chalcopyrite compounds and parameters used in the calculation. Values of $|C_e|$ and $|C_h|$ reported in Refs. 3, 7, and 15 are indicated in parentheses.

Compound	$\frac{m_e^*}{m_0}$	$\frac{m_h^*}{m_0}$	α_L (10^{-6} K^{-1})	κ (10^{-11} Pa^{-1})	Θ_D (K)	dE_g/dT ($10^{-4} \text{ eV K}^{-1}$)	dE_g/dP ($10^{-11} \text{ eV Pa}^{-1}$)	C_e (eV per unit dilation)	C_h
CuInS ₂	0.16	1.30	9.9	1.32	264	-2.0	2.4	-10.3	7.6 (8.5) ^a
CuInSe ₂	0.09	0.73	8.0	1.62	207	-1.1	2.6	-9.5	7.1
CuInTe ₂	0.14	0.78	9.5	2.20	156	-2.4	2.2	-10.1 (11.4) ^b	8.6 (5.4) ^b
CuGaS ₂	0.13	0.69	8.9	1.04	320	-2.2	4.0	-15.5	9.0
CuGaSe ₂	0.14	1.20	10.5	1.45	239	-2.3	5.0	-11.9	6.8 (4.0) ^c
AgGaS ₂	0.23	0.72	3.7	1.43	259	-2.2	2.2	-13.0	10.7
AgGaSe ₂	0.17	0.73	6.7	1.74	156	-1.4	5.3	-8.5	4.0
AgInSe ₂	0.12	0.39	13.8	1.89	138	-1.5	2.7	-8.5	6.4

^aReference 3.

^bReference 15.

^cReference 7.

RESULTS AND DISCUSSION

Combining Eqs. (1), (2), and (3) with the experimental data for dE_g/dT ,¹⁴ dE_g/dP ,¹⁵ m_h and m_e ,¹⁶ α_L ,¹⁷ κ ,¹⁸ and Θ_D (Ref. 19) reported in the literature, C_h and C_e for some $A^1B^{\text{III}}C_2^{\text{VI}}$ compounds were determined. The results are listed in Table I. Whenever possible, values of $|C_h|$ and $|C_e|$ obtained from mobility data were also included in this table for comparison.

It can be observed that C_e and C_h have opposite signs for all the compounds studied and $|C_e| > |C_h|$. This indicated that the valence- and conduction-band extrema move in the same direction on compression and that the

relative shift of the conduction band is greater than that of the valence band. Thus, due to the fact that the band gap of these materials increases with pressure, it must be concluded that both band extrema move to higher energies on compression in these compounds. This also should explain the small band-gap pressure and temperature coefficients observed in these compounds relative to their binary analogs.

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