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Optical energy gap values and deformation potentials in four Cu–III–VI₂ chalcopyrite compounds

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Abstract. Values of the optical energy gap E_o as a function of temperature T in the range 10 to 300 K were obtained by optical absorption and modulated reflectance measurements on samples of CuInSe₂, CuGaSe₂, CuInS₂ and CuGaS₂. The variations of E_o with T were fitted well by a Manoogian–Leclerc equation of the form $E_o(0, 0) - E_o(T, 0) = UT + V\varphi(\coth \varphi/2T - 1)$. Values of $(dE_o/dT)_1$, the electron–phonon interaction contribution to the variation of the energy gap with temperature and $(dE_o/dT)_S$, the static component, were obtained from the $V\varphi$ and U terms respectively. Comparison with values from the pressure coefficient dE_o/dP indicated that in addition to the lattice-dilation term $(dE_o/dT)_2$, $(dE_o/dT)_S$ contains a further contribution, labelled $(dE_o/dT)_3$, attributed to a change with temperature of the position coordinate u of the anions. From the values of $(dE_o/dT)_1$ and $(dE_o/dT)_2$, values were determined for the acoustic deformation potentials of the conduction band C_c and of the valence band C_v .

1. Introduction

The chalcopyrite I–III–VI₂ compounds have received considerable attention [1, 2], because of their academic interest and also their possible practical applications in solar cell and photodiode technologies. One problem that arises in the necessary analysis of transport data for these materials is the discrepancies found in the published values of deformation potentials. As indicated by Wasim [3], when these values are obtained from the analysis of mobility data, the discrepancies can be attributed to the different choices of the scattering mechanisms used in the analyses. Hence, Rincon and Gonzalez [4] suggested that more consistent values of deformation potentials may be obtained from the analysis of optical data, since a knowledge of the predominant scattering mechanism is not required in that case. The various chalcopyrite I–III–VI₂ compounds each have a direct allowed band gap E_o at $k = 0$, with values lying in the range $0.9 < E_o < 3.5$ eV [1].

Recently [5, 6], it has been shown that values of deformation potential can be obtained from the analysis of the variation of the energy gap E_o with temperature in terms of the Manoogian–Leclerc equation [7]. In the present work, values of E_o in the temperature range 10 to 300 K have been obtained for two chalcopyrite compounds

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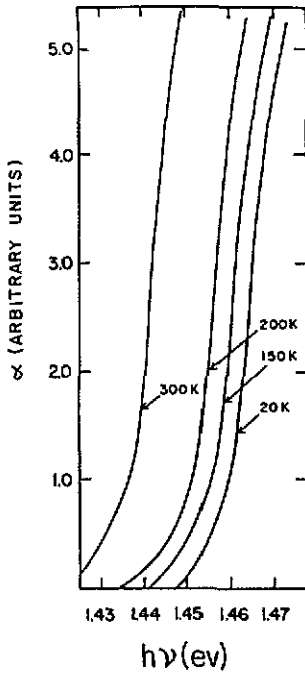


Figure 1. Variation of absorption coefficient α with photon energy $h\nu$ for CuInS_2 at the temperatures shown.

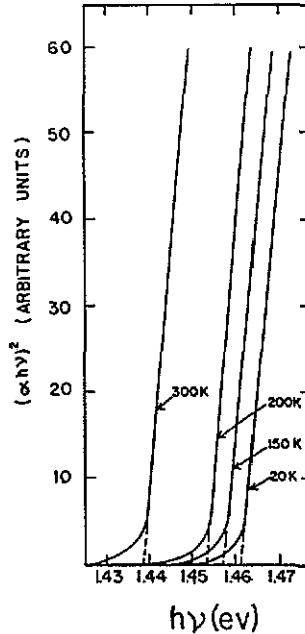


Figure 2. Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ for CuInS_2 at the temperatures shown.

CuInSe_2 and CuInS_2 , the values for CuGaSe_2 and CuGaS_2 having been published previously [8]. The data for all four compounds have been fitted with the Manoogian-Leclerc equation. The resulting parameters have then been compared with those from the variation of E_0 with pressure [4, 9], and values determined for the deformation potentials of the conduction and valence bands of each of the four compounds.

2. Experimental details

As indicated previously [8], the CuGaSe_2 and CuGaS_2 samples were grown by chemical vapour deposition and the values of the energy gap E_0 were determined by wavelength modulation reflectance measurements. These values have been used in the present analysis. The CuInSe_2 sample was grown by the Bridgman method, while the CuInS_2 was produced by the melt and anneal technique, the ingot being annealed for one month at 600 °C. The values of E_0 were determined in these cases by standard optical absorption measurements, described in detail previously [10]. Thus, slices of each ingot were cut and thinned down to give specimens suitable for the measurements. Values of $\ln(I_0/I_t)$, where I_0 is the incident intensity and I_t the transmitted intensity, were determined as a function of photon energy $h\nu$ at a number of temperatures in the range 10–300 K. These values were corrected by subtracting a background value to give values of the absorption coefficient α . Figure 1 shows the variation of α with $h\nu$ for some of the temperatures used for the CuInS_2 sample. As shown in Figure 2, for each temperature a graph of

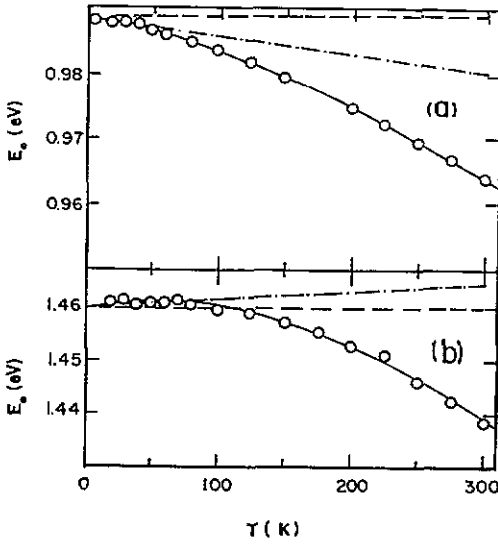


Figure 3. Variation of optical energy gap E_0 with temperature T for (a) CuInSe₂; and (b) CuInS₂. Open circles: experimental data; full curve: curve fitted to Manoogian-Leclerc equation; broken curve: value of $E_0(0, 0)$; chain curve: values of $E_0(0, 0) - UT$ for comparison purposes.

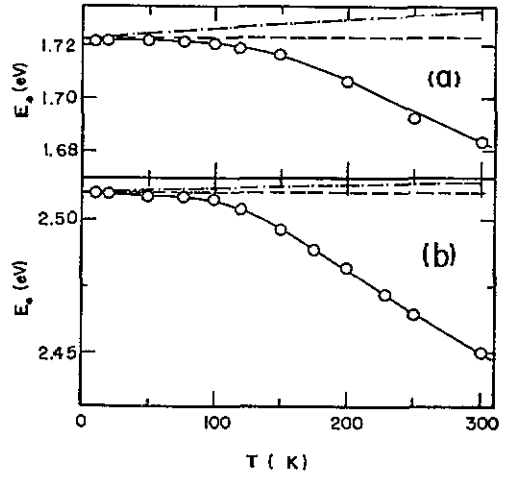


Figure 4. Variation of optical energy gap E_0 with temperature T for (a) CuGaSe₂ and (b) CuGaS₂. Open circles: experimental data; full curve: curve fitted to Manoogian-Leclerc equation; broken curve: value of $E_0(0, 0)$; chain curve: values of $E_0(0, 0) - UT$ for comparison purposes.

$(\alpha h\nu)^2$ was plotted against $h\nu$ and the linear region (i.e. above the tail) was extrapolated to $(\alpha h\nu)^2 = 0$ to give a value of the energy gap E_0 .

3. Results and discussion

The measured values of E_0 as a function of temperature T for each of the compounds are shown in figures 3 and 4. As has been shown previously [5, 6], these curves can be well fitted by a simple Manoogian-Leclerc equation of the form

$$E_0(0, 0) - E_0(T, 0) = UT^x + V\varphi(\coth \varphi/2T - 1) \tag{1}$$

where the parameters U , V , φ and x are constant and independent of T . Since the variation of E_0 with both T and pressure P is considered here, the energy gap has been written as $E_0(T, P)$. Thus, $E_0(300, 0)$ represents the value of E_0 at room temperature and atmospheric pressure. As was shown for the compounds CuInTe₂ and AgInTe₂ [5, 6], for these materials the best fit to the experimental data is obtained with $x = 1$, and that value will be used here. When fitting the E_0 against T data to (1), values need to be obtained for U , V , φ and $E_0(0, 0)$. In the initial analysis, various values were assumed for φ and then U , V and $E_0(0, 0)$ determined by a least squares fitting procedure, the final criterion for the overall best fit being minimum standard deviation. However, in some cases, with larger experimental scatter the standard deviation was not very sensitive to variation of φ around the optimum value. Since it was planned to try to correlate the final results for a set of these chalcopyrite compounds, it was necessary to find a consistent set of φ values.

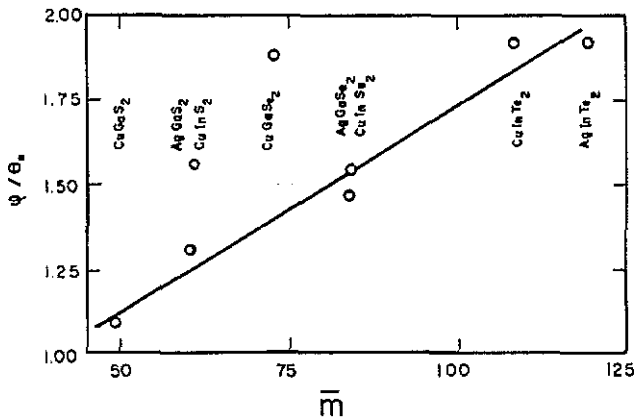


Figure 5. Variation of φ/θ_D , where θ_D is the Debye temperature, with mean atomic mass \bar{m} of the compound for various I-III-VI₂ compounds.

Table 1. The final values of φ , $E_o(0,0)$, U and V .

Compound	φ (K)	$E_o(0,0)$ (eV)	U (10^{-5} eV K ⁻¹)	V (10^{-5} eV k ⁻¹)
CuInSe ₂	320	0.989	+3.48	4.22
CuGaSe ₂	330	1.721	-3.69	15.04
CuInS ₂	340	1.460	-3.08	9.06
CuGaS ₂	350	2.5090	-1.623	20.54

It was indicated by Manoogian and Woolley [11] that the parameter φ in any given case is related to the Debye temperature θ_D for which values are available for these materials [4]. When the values of φ obtained for a range of I-III-VI₂ compounds were combined with the corresponding θ_D values, it was found that the value of φ/θ_D varied linearly, within the limits of experimental error, with the parameter \bar{m} , the average atomic mass of the atoms constituting the compound, as is shown in figure 5. However, since the estimated values of φ for two of the compounds considered here (CuGaSe₂ and CuInS₂) lay well off this line, it was chosen to use the values from the line in these cases. It is seen from the figures that the fit appears no worse in these cases than for the other materials. The final values for the various parameters of the four compounds are listed in table 1 and the resulting fitted curves are shown in figures 3 and 4. For these fitted curves, the standard deviation of the fit was, for each, in the range 0.8 – 3.4×10^{-4} eV. Since, as is seen from figures 3 and 4, the contribution of the U term is appreciably less than that of the V term, the probable error in U is correspondingly larger than that in V .

In (1), the U term represents the lattice dilation contribution to the change in E_o , while the V term represents the electron-phonon contribution [7]. Thus, as indicated previously [5], the two components of the energy gap variation with temperature can be related to the Manoogian parameter as follows. The component due to electron-phonon interaction $(dE_o/dT)_1$ is given by

Table 2. Values of $(dE_o/dT)_2$ as calculated from data given in the literature [4].

Compound	$(dE_o/dP)^a$ (10^{-11} eV Pa ⁻¹)	κ^a (10^{-11} Pa ⁻¹)	α_L^a (10^{-6} K ⁻¹)	$(dE_o/dT)_2$ (10^{-3} eV K ⁻¹)	$(dE_o/dT)_3$ (10^{-3} eV K ⁻¹)
CuInSe ₂	3.0	1.62	8.0	-3.93	+0.46
CuGaSe ₂	5.0	1.45	10.5	-10.90	+14.59
CuInS ₂	2.4	1.32	9.9	-5.40	+8.48
CuGaS ₂	4.0	1.04	8.9	-10.30	+11.92

^a See [4].

$$(dE_o/dT)_1 = -(V\varphi^2/2T^2) \operatorname{cosech}^2(\varphi/2T) \quad (2)$$

while the dilation term due to thermal expansion of the lattice $(dE_o/dT)_2$ has the value

$$(dE_o/dT)_2 = -U \quad (3)$$

The value of $(dE_o/dT)_2$ can also be obtained from the variation of E_o with P . Thus [12]

$$(dE_o/dT)_2 = -(3\alpha_L/\kappa)(dE_o/dP) \quad (4)$$

where κ is the compressibility and α_L the average thermal expansion coefficient of the material. In the case of CuInTe₂ [5], it was shown that the two values of $(dE_o/dT)_2$ obtained from the temperature and pressure variations showed good agreement. Since the pressure coefficients of E_o have been published for all four compounds considered here [4, 9], it is of interest to compare the pairs of values determined for $(dE_o/dT)_2$ in each case.

The values of (dE_o/dP) , κ and α_L for the four compounds, given in the literature [4], and the resulting values of $(dE_o/dT)_2$ are shown in table 2. From (3), these values of $(dE_o/dT)_2$ are to be compared with the values of $-U$ from table 1. In the case of CuInSe₂, the two values show fair agreement although the difference between the two values is somewhat bigger than in the case of CuInTe₂ [5]. However, for the other three compounds there is no agreement between the two values, in fact the two values obtained for $(dE_o/dT)_2$ have opposite sign in all three cases. It is clear that the behaviour for these three cases is very different from that for CuInTe₂, CuInSe₂ and AgInTe₂. It would appear that there is some mechanism that contributes to the change in E_o with temperature variation but not with pressure variation, or at least, the pressure variation has a smaller effect.

One factor which causes a change in E_o and which has been discussed by various works [13, 14], is a change in the position of the anions in the lattice. Jaffe and Zunger [13] have considered in some detail the effect on E_o of the anion displacement in CuInSe₂ caused by the resultant changes in p-d hybridization and bond lengths. Their calculations indicate that when the Se coordinate u is changed from the equilibrium value of 0.224 to the ideal value of 0.25, the band gap of CuInSe₂ increases by 0.47 eV, giving $(dE_o/du) = +18$ eV. For comparison, Paniutin *et al* [14] give values of (dE_o/du) of -3.0 eV for AgGaS₂ and $+0.04$ eV for AgGaSe₂. As indicated by Gonzalez and Rincon [12], such an effect will contribute to some extent to the values of dE_o/dP determined for the compounds. However, it is quite possible that the effect due to temperature change is appreciably bigger than that due to pressure. If the extra contribution above that of the pressure change is labelled $(dE_o/dT)_3$, it follows that the value obtained for

U in (1) is given by $-((dE_o/dT)_2 + (dE_o/dT)_3)$, i.e. the value of $(dE_o/dT)_2$ must be taken from (4) and

$$(dE_o/dT)_3 = -U - (dE_o/dT)_2 \quad (5)$$

The values of $(dE_o/dT)_3$ obtained from this relation are listed in table 2.

With $(dE_o/dT)_3$ being caused by changes of the parameter u with temperature, additional to those already contained in the (dE_o/dP) term, it is possible to write

$$(du/dT)_T = (dE_o/dT)_3 / (dE_o/du) \quad (6)$$

where $(du/dT)_T$ is the change in u given by this additional temperature effect. It is of interest to see what values of $(du/dT)_T$ are obtained from the values of $(dE_o/dT)_3$ given in table 2. In the case of CuInSe_2 , the value of $(dE_o/dT)_3$ is $+4.57 \times 10^{-6} \text{ eV K}^{-1}$ and $(dE_o/du) = 18 \text{ eV}$, which gives a value of $(du/dT)_T$ of $2.5 \times 10^{-7} \text{ K}^{-1}$. This change in u is too small to be detected with standard x-ray measurements. For CuGaSe_2 , CuGaS_2 and CuInS_2 , the values of $(dE_o/dT)_3$ are larger, lying in the range $+8$ to $+15 \times 10^{-5} \text{ eV K}^{-1}$, but no values of (dE_o/du) have been given in the literature. However taking $1 \times 10^{-4} \text{ eV K}^{-1}$ as a typical value for $(dE_o/dT)_3$, this gives values of $(du/dT)_T$ of $+5.6 \times 10^{-6}$, -3.3×10^{-5} and $+2.5 \times 10^{-3} \text{ K}^{-1}$ respectively for the three values of (dE_o/du) quoted above. The last of these values, which gives $\Delta u = u$ for $\Delta T \sim 100^\circ \text{C}$, is clearly too large, indicating that the value of $dE_o/du = +0.04 \text{ eV}$ does not apply in the present case. The other two values are small, and careful single-crystal x-ray work would be needed to detect them.

From (2), values of $(dE_o/dT)_1$ can be obtained from the data in table 1. For $T \times 300 \text{ K}$, these values are 7.69×10^{-5} , 2.72×10^{-4} , 1.63×10^{-4} and $3.67 \times 10^{-4} \text{ eV K}^{-1}$ for CuInSe_2 , CuGaSe_2 , CuInS_2 and CuGaS_2 respectively. As was seen in the case of CuInTe_2 and AgInTe_2 , although from (3) these values are temperature dependent, the temperature variation is quite small, being less than $0.1\% \text{ K}^{-1}$ at 300 K . Thus, the calculated values of both $(dE_o/dT)_1$ and $(dE_o/dT)_2$ are practically constant in this temperature range where the variation of E_o with T is seen to be effectively linear.

4. Calculation of deformation potentials

The temperature coefficients of the energy gap, $(dE_o/dT)_1$ and $(dE_o/dT)_2$, can be related to the deformation potentials of the conduction band, C_e , and the valence band, C_h . Thus, for the electron-phonon interaction [15],

$$(dE_o/dT)_1 = -(8/9\pi)(3/4\pi)^{1/3}(k_B\Omega^{2/3}/\hbar^2 Mv^2)(m_e C_e^2 + m_h C_h^2) \quad (7)$$

while for the lattice dilation contribution [12],

$$(dE_o/dT)_2 = 2\alpha_L(C_e + C_h) \quad (8)$$

where M and Ω are, respectively, the mass and volume of the unit cell, v is the velocity of sound in the material, m_e and m_h are respectively the electron and hole effective masses and α_L is the average thermal expansion coefficient of the material. In order to determine values of C_e and C_h from (3) and (4), it is necessary to know the values of these various parameters. From the structure and lattice parameter values (1), M and Ω can be determined, and values for α_L are listed by Rincon and Gonzalez [4]. The values of v are given by the relation $v = (k_B\theta_D/\hbar)(\Omega_1/6\pi^2)^{1/3}$ where Ω_1 is the mean volume per atom, i.e. $\Omega_1 = \Omega/16$. Values of m_h/m for each of the four compounds

Table 3. Various parameters for the four compounds.

Compound	M (10^{-21} gm)	Ω (10^{-22} cm ³)	θ_D (K) [4]	ν (10^5 cm s ⁻¹)	(m_h/m)	(m_e/m)	α [21]
CuInSe ₂	2.23	3.87	207	2.01	0.73 [16]	0.069	0.745
CuGaSe ₂	1.93	3.48	239	2.24	1.20 [17]	0.101	0.801
CuInS ₂	1.61	3.39	264	2.46	1.30 [18]	0.115	0.587
CuGaS ₂	1.31	3.00	320	2.85	0.69 [19]	0.162	0.646

considered here are given in the literature and are: for CuInSe₂, 0.73 [16]; for CuGaSe₂, 1.20 [17]; for CuInS₂, 1.30 [18]; and for CuGaS₂, 0.69 [19]. The values of these various parameters are listed in table 3.

There appear to be no values of m_e given in the literature, and so values of these parameters must be estimated by using the Kildal equations [20]. These relate the effective mass values to the energy differences between the conduction and three valence bands. However, one problem is that these equations were developed for the case of sp_3 wave-functions in a tetragonal system and do not take account of the p - d hybridization which occurs in the I-III-VI₂ compounds. A full analysis including the effects of p - d hybridization has been made by Yoodee *et al.* [21], but it is not easy to obtain effective mass values from the resulting equations. However, Look and Manthuruthil [18] pointed out that for these compounds, a good approximation is obtained if the matrix element P^2 in the Kildal equations is replaced by αP^2 , where $(1 - \alpha)$ is the fraction of the d character occurring in the hybridized bands. For each of the four compounds, the three energy gaps are given by Yoodee *et al.* [21] together with the values of α . The Kildal equations also contain the parameters Δ_{so} , the spin-orbit splitting, and Δ_{cf} , the crystal-field splitting, and values of these parameters can be obtained from the energy gap values [1]. Values for the various parameters needed for (7) are listed in table 3, the value of P^2 being taken as 20 eV [1].

Given the values listed in tables 2 and 3, it is possible to calculate values for the two deformation potentials for each of the compounds concerned. Since (4) is quadratic in C_e and C_h , two sets of solutions are obtained in each case. Since in these materials, it can be assumed that $|C_e| > |C_h|$ [4, 22], the solutions satisfying this condition have been taken here.

The resulting values of deformation potential (in eV/unit dilation) are:

CuInSe ₂	$C_e = -9.39$	$C_h = +6.93$
CuGaSe ₂	$C_e = -16.05$	$C_h = +10.88$
CuInS ₂	$C_e = -11.00$	$C_h = +8.27$
CuGaS ₂	$C_e = -22.51$	$C_h = +16.74$

In the determination of C_e and C_h , various parameters have been taken from the literature, and in most cases no probable error was given. Hence, it is difficult to give any values of probable error for the final values determined here. However, a systematic comparison of the values of C_e and C_h for a set of chalcopyrite compounds (to be published elsewhere) indicates that the relative errors in C_e and C_h probably do not exceed 20% in the worst case.

5. Conclusions

The results show that, as in previous cases, a good fit to the E_0 against T data can be obtained using the Manoogian–Leclerc equation with the parameter x taken as unity. Also, it is seen that the ratio of the parameter φ to the Debye temperature θ_D appears to vary linearly with the average atomic mass for a given type of compound, in this case chalcopyrite, so that an estimate can be made for the value of φ for other compounds of this structure.

For the case of CuInSe_2 , the value of $-U$ obtained from the fit to the E_0 against T data shows reasonable agreement with the value of $(dE_0/dT)_2$ determined from the pressure data, as was the case for CuInTe_2 [5], so that it is possible to use $-U$ as $(dE_0/dT)_2$ to determine values of C_c and C_b , as was done in the case of CuInTe_2 [5] and AgInTe_2 [6]. However, for the other three compounds, CuGaSe_2 , CuInS_2 and CuGaS_2 , the value of $-U$ does not even approximately satisfy this condition, and in fact $-U$ and $(dE_0/dT)_2$ have opposite sign. This indicates that, in addition to the lattice dilation term which is observed in the pressure variation measurements, there must be another effect contributing to the static part of the variation of E_0 with T , i.e. $-U = (dE_0/dT)_2 + (dE_0/dT)_3$. It is proposed here that this is the variation with temperature of the coordinate u of the anions, as discussed previously by Jaffe and Zunger [13]. From the values of (dE_0/du) given by Jaffe and Zunger and by Paniutin *et al* [14] and the present values of $(dE_0/dT)_3$, values of du/dT can be estimated. It is seen that the resulting changes of u with T are small but may be detectable with detailed x-ray single-crystal analysis.

Because of this extra temperature effect, it is seen that the suggestion that $(dE_0/dT)_1$ and $(dE_0/dT)_2$, and hence the values of C_c and C_b , can be determined from the temperature variation of E_0 with T is not valid for some of these chalcopyrite compounds. Thus, as shown previously for CuInTe_2 [5], and in the present case of CuInSe_2 , the value of (du/dT) is sufficiently small that it is possible to take $-U = (dE_0/dT)_2$, but for the other compounds considered here a value of $(dE_0/dT)_2$ from the pressure data is needed before values of the deformation potentials can be calculated.

The present analysis has so far been used to determine values of C_c and C_b for six of the I–III–VI₂ compounds. The correlation of these values plus those for other compounds of this type will be discussed elsewhere.

Acknowledgments

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