

Temperature Variation of Optical Energy Gap Values of the Compound CuGaTe_2

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Measurements of optical absorption in the temperature range 20 to 300K were made on polycrystalline samples of the compound CuGaTe_2 . These results were used to determine values of the optical energy gap E_g as a function of temperature T . The resulting curves of E_g vs T were fitted to a simplified Manogian-Leclerc equation and the fitted coefficients used to give values of (dE_g/dT) , and (d^2E_g/dT^2) , due to lattice dilation and electron-phonon contributions, respectively. Hence, the deformation potentials of the valence and conduction bands were estimated for the present compound.

Key words: CuGaTe_2 , energy gap, optical absorption

INTRODUCTION

The chalcopyrite I-III-VI₂ ($1\bar{4}2d$) compound semiconductors have received considerable attention,^{1,2} both from their academic interest and also because of possible practical application in solar cell, photodiode and nonlinear optic technologies. The CuGaTe_2 compound, which is a member of this class, has been studied in some detail by various authors. The phase diagram of this compound was studied by Belova³ and also by Congiu.⁴ The lattice thermal expansion in this material over the temperature range 80 to 650K was determined by Bodnar and Orlova.⁵ The specific heat and Debye temperature were reported by Bohmhammel et al.⁶ Hörig et al.⁷ investigated the electrical and optical properties using single crystal samples of this material. Neumann et al.⁸ studied the temperature dependence of the Hall coefficient of epitaxial layers of CuGaTe_2 on GaAs substrates. In spite of these studies, no accurate values of the absorption coefficient α , and hence of the optical energy gap E_g as a function of the temperature, have been given for this compound so far. Hence, in this work, measurements of optical absorption have been carried out on samples of the CuGaTe_2 compound to

determine accurate values of the fundamental optical energy gap E_g in the temperature range between 20 and 300K. The resulting E_g vs T curves have been used to estimate values of the valence and conduction band deformation potentials of the present compound.

PREPARATION AND CHARACTERIZATION OF MATERIALS

The present work was the initial part of a program to investigate the properties and behavior of the alloy system $\text{Cu}_{2(1-z)}\text{Mn}_z\text{Ga}_2\text{Te}_4$. Since all the alloys were being prepared by the melt and anneal technique, two samples of the compound CuGaTe_2 , i.e. $z = 0$, were made in this way also. In each case, the components of 1.5 g sample were sealed under vacuum in small quartz ampoules, melted together at 1150°C for about two hours and annealed to equilibrium at 600°C for one month. Then, the samples were finally either brine-quenched or slowly cooled to room temperature. Previous experience indicates that for this type of material, this procedure usually gives samples showing conditions corresponding to equilibrium near room temperature. Guinier x-ray powder photographs were taken of each sample to check their conditions before any measurement were made, and these showed that the samples were in good equilibrium conditions with the expected tetragonal structure. In each case, the

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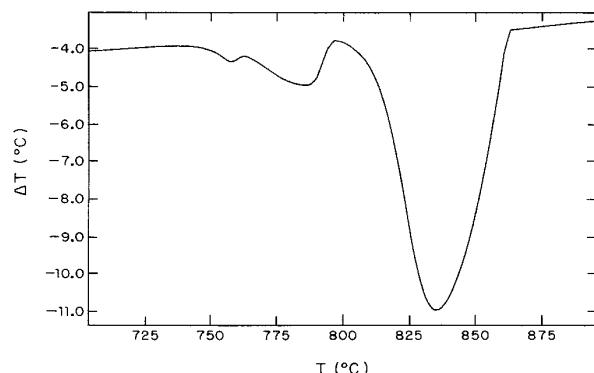


Fig. 1. DTA thermogram of the sample of CuGaTe_2 slowly cooled to room temperature.

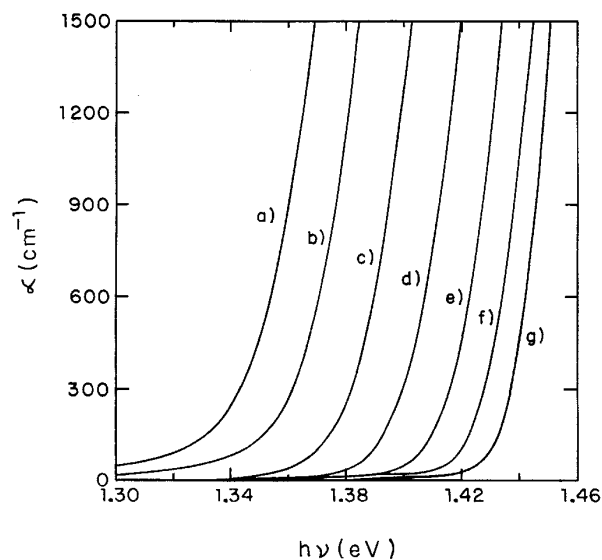


Fig. 2. Variation of absorption coefficient α with photon energy $h\nu$ for CuGaTe_2 , at the temperatures: (a) 300, (b) 250, (c) 200, (d) 150, (e) 100, (f) 60, and (g) 20K.

diffraction patterns were found to be very similar, and the lattice parameter values were calculated by using the usual least squares method together with all of the reflection lines. The values so obtained for the case of the slowly cooled sample were $a = 6.012\text{\AA}$ and $c = 11.906\text{\AA}$, with a standard deviation of the experimental points of $\sigma = \pm 1.38 \times 10^{-3}\text{\AA}$, these values are in good agreement with those reported earlier.^{5,7,9} Using Perkin Elmer DTA-7 equipment, differential thermal analysis runs were taken on each sample prepared, and again these were found to be alike. The DTA thermogram of the sample slowly cooled to room temperature is shown in Fig. 1, these results are in good agreement with those reported by Congiu et al.⁴ for CuGaTe_2 in the $\text{Cu}_2\text{Te-Ga}_2\text{Te}_3$ phase diagram.

OPTICAL ABSORPTION DATA: MEASUREMENTS AND ANALYSIS

The produced compounds were prepared for optical absorption measurements by the usual method. Slices

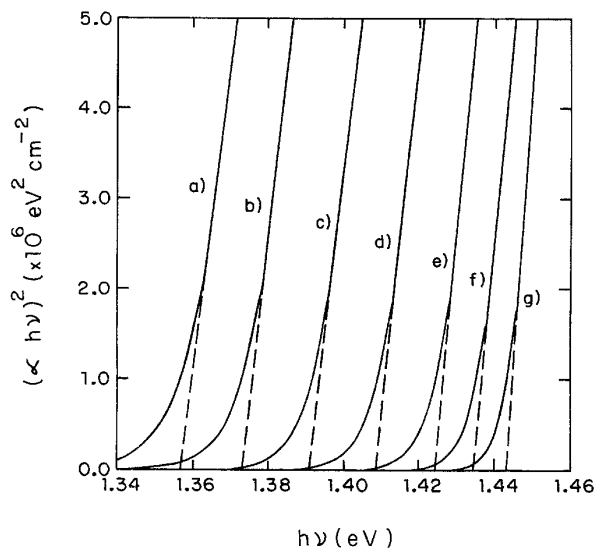


Fig. 3. Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ for CuGaTe_2 , at the temperatures: (a) 300, (b) 250, (c) 200, (d) 150, (e) 100, (f) 60, and (g) 20K.

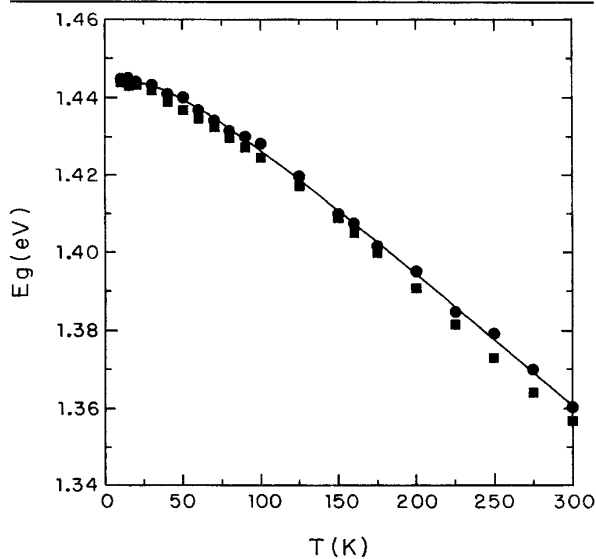


Fig. 4. Variation of optical energy gap E_g with temperature T for CuGaTe_2 . Full squares: data obtained from $(\alpha h\nu)^2 = 0$, full circles: data obtained from the continuum term of Eq. (1); full curve: curve fitted to Manogian-Leclerc equation.

cut from the sample ingot were polished down to give specimens suitable for standard transmission measurements. Values of $(1/d)\ln(I_0/I_t)$, where d is the thickness of the sample, I_0 is the incident intensity and I_t the transmitted intensity, were determined at room temperature, for each of the samples prepared, as a continuous function of photon energy $h\nu$. These values were corrected by subtracting a nearly constant background value to give values of the optical absorption coefficient α .

It was found that the obtained α vs $h\nu$ curves for both samples, grown using different cooling treat-

ments, were very similar. The sample slowly cooled to room temperature gave the sharpest x-ray diffraction lines, and hence this sample was selected for the optical absorption measurements as a function of temperature in the range 20–300K. The resulting α vs $h\nu$ curves at various temperatures, obtained as indicated above, are shown in Fig. 2.

As it has been shown that the fundamental energy gap E_g of these I-III-VI₂ compounds is direct,^{1,9} in the initial analysis, for each temperature, a graph of $(\alpha h\nu)^2$ was plotted against $h\nu$ and the linear region was extrapolated to $(\alpha h\nu)^2 = 0$ to give a value of the optical energy gap E_g . Typical sets of $(\alpha h\nu)^2$ vs $h\nu$ curves at various temperatures are shown in Fig. 3 for CuGaTe₂. The resulting values of E_g , obtained from the extrapolations of $(\alpha h\nu)^2 = 0$ as a function of the temperature T are shown in Fig. 4. However, in recently work, the optical absorption spectrum near the fundamental energy gap E_g of some II-VI, II-IV-V₂ and I-III-VI₂ compounds and their alloys^{10–12} has been analyzed using a relation which takes into account both the discrete and continuum contributions, respectively, given by,^{13,14}

$$\alpha(h\nu) = \alpha_0 \sum_n \frac{1}{n^3} \frac{(\Gamma_n/2)}{\left(h\nu - (E_g - R_0/n^2)\right)^2 + (\Gamma_n/2)^2} + C \left[\frac{\pi}{2} + \arctan\left(\frac{h\nu - E_g}{\Gamma_c/2}\right) \right] \quad (1)$$

where α_0 varies by little in the energy range concerned here, R_0 is the effective Rydberg of the exciton, $E_n = E_g - R_0/n^2$ are the energy values of the bound exciton states. Γ_n and Γ_c are the line width at half maximum of the Lorentzian and the width of the continuum excitors, respectively.

It is seen from the experimental data of α , shown in Fig. 2, that the discrete contribution to the absorption coefficient α is not observed for the present compound. This could be due to whether the quality the polycrystalline sample used, which would present several defects, etc., or to that because of the thermal broadening, occurring in this compound, the Γ_n values could be larger than the exciton binding energy so that the discrete term, i.e. the exciton peak, is not resolved here. Hence, the experimental curves of α vs $h\nu$, for each temperature, were fitted using the second term of Eq. (1) with C , Γ_c , and E_g treated as adjustable parameters. The values of C and Γ_c , determined as indicated above, were found to be independent of temperature, the mean values of these parameters being 624.5 cm⁻¹ and 10.6 meV, respectively. Examples of the fitted $\alpha(h\nu)$ spectra obtained at 300 and 20K are displayed in Fig. 5, and the resulting variation of E_g with T is shown in Fig. 4. It is observed in Fig. 4 that the values of $E_g(T)$ determined from the extrapolation of $(\alpha h\nu)^2$ to zero are very close to those obtained using the continuum term in Eq. (1). However, these present values of $E_g(T)$, determined either

from the extrapolation of $(\alpha h\nu)^2 = 0$ or the continuum term, are found to be about 100 meV higher than those reported in references.^{7,9} This disagreement could be due to the thickness of the samples used for the optical measurements. In the present case, specimens with thickness of about 30 μm were used for the optical transmission experiments giving, after the corresponding background correction, values of α up to about 1500 cm⁻¹, and curves of $\alpha(h\nu)$, at each temperature, with typical shapes of an absorption spectrum related to valence to conduction band transitions, i.e. with the fundamental optical energy gap E_g , of a semiconductor material. While in the work of Refs. 7 and 9 the optical absorption measurements were probably made on thicker samples, getting values of α only up to 500 cm⁻¹, which would represent the tail of the α vs $h\nu$ curve of the sample, yielding those lower values of E_g .

It has been shown for a range of semiconductor compounds and their alloys that the E_g vs T curves can be well fitted by a simple Manogian-Leclerc equation of the form^{15,16}

$$E_g(0) - E_g(T) = UT^x + V\theta[\coth(\theta/2T) - 1] \quad (2)$$

where $E_g(0)$ is the energy gap at $T = 0\text{K}$, and the

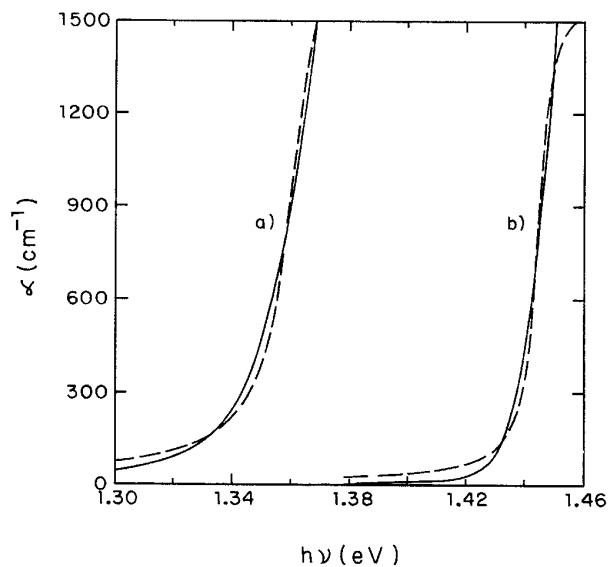


Fig. 5. Absorption spectra of the CuGaTe₂ compound at the temperatures: (a) 300, and (b) 20K. Full lines represent the experimental data. Theoretical absorption curves, obtained from the continuum term of Eq. (1), are represented as dashed lines.

Table I. The Fitted Values of $E_g(0)$, θ , U , and V Obtained Using the $E_g(T)$ Data Determined from the Second Term of Eq. (1)

| x | $E_g(0)$ (eV) | θ (K) | U (10 ⁻⁵ eV/K) | V (10 ⁻⁴ eV/K) | σ (10 ⁻³ eV) |
|-----|------------------|-----------------|--------------------------------|--------------------------------|-----------------------------------|
| 1 | 1.446 | 160.9 | 9.250 | 1.264 | 3.73 |

Note: σ is the standard deviation of the experimental points.

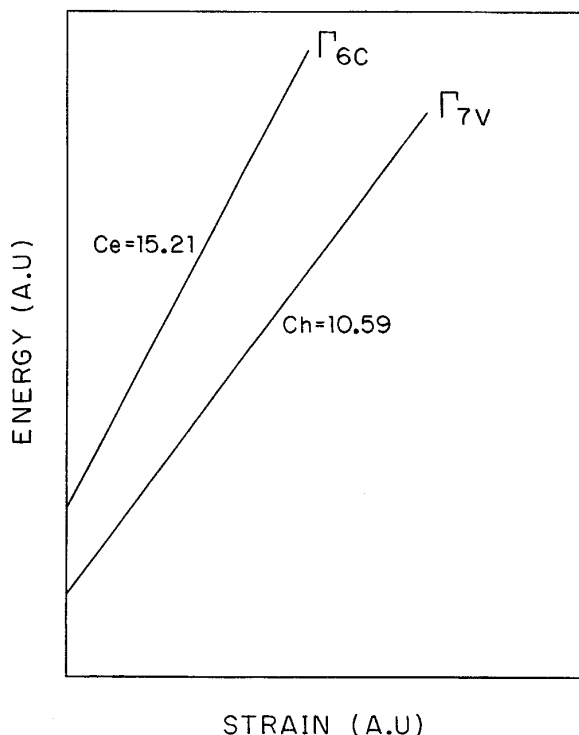


Fig. 6. Variations of the Γ_{6C} conduction and Γ_{7V} valence band energies as a function of strain for the CuGaTe₂ compound.

parameters x , θ , U , and V are constants and independent of temperature. The first term in Eq. (2) represents the effect of the lattice dilation and the second term represents the electron-phonon interaction. θ corresponds to the mean frequency of the entire phonon spectrum, and its value is of the order of the Debye temperature θ_D .¹⁵

When fitting Eq. (2) to the E_g vs T experimental data, in previous work (e.g. Refs. 16 and 17), it was assumed that $x = 2/3$. However, in the analysis of the optical energy gap data for CuInTe₂,¹⁸ it was found that a value of $x = 1$ was necessary to use in order to obtain agreement between the values obtained from the variation of E_g with T and those from the variation of E_g with pressure.

Hence, in the present analysis values of $x = 1$ and $2/3$ have been assumed, and then the parameters $E_g(0)$, θ , U , and V treated, in each case, as unknown parameters to be determined from the fitting procedure, the final criterion for the overall best fit being the minimum standard deviation. When this was done, it was found that, the fits to the $E_g(T)$ curves in Fig. 4 were, within the limits of experimental errors, very good. However, using the values of E_g vs T determined by using the continuum term of Eq. (1), with $x = 1$ in Eq. (2), gave the best fit to these experimental points. The values of $E_g(0)$, θ , U , and V obtained from fitting to the data indicated above, with $x = 1$, are listed in Table I, and the resulting fitted curve is shown in Fig. 4.

DEFORMATION POTENTIAL VALUES

Another point of interest here is to estimate values for the deformation potentials of the valence and conduction bands, C_h and C_e , respectively. These parameters can be related to the thermal coefficients of the energy gap. Thus, for the lattice dilation contribution,¹⁹

$$(dE_g/dT)_1 = 2\alpha_L(C_e + C_h) \quad (3)$$

while for the electron-phonon interaction,²⁰

$$(dE_g/dT)_2 = -(8/9\pi)(3/4\pi)^{1/3}(K_B\Omega^{2/3}/\hbar^2Mv^2) \times (m_e C_e^2 + m_h C_h^2) \quad (4)$$

where α_L is the average thermal expansion coefficient of the material. M and Ω are, respectively, the mass and volume of the unit cell, v is the sound velocity in the material, m_e and m_h are, respectively, the electron and hole effective masses. In previous work,¹⁶ Eq. (3) and Eq. (4) have been used to make estimates of the deformation potentials of the CuGa(S₂Se₁₋₂)₂ alloys. Here, it is proposed that a similar analysis can be made with the present E_g vs T data using the values of U and V of the Manoogian-Leclerc relation to give values for the temperature coefficients of E_g .

As indicated above, in Eq. (3) the term in U is the dilation contribution, while the term in V is the electron-phonon contribution. Thus, the dilation term can be used to give $(dE_g/dT)_1$, and the electron-phonon term to give $(dE_g/dT)_2$,

$$(dE_g/dT)_1 = -U \quad (5)$$

$$(dE_g/dT)_2 = -\sqrt{\theta^2/2T^2} \operatorname{cosech}^2(\theta/2T) \quad (6)$$

It is seen from the above equations that $(dE_g/dT)_2$ varies to some extent with T , while $(dE_g/dT)_1$ is independent of T . It is seen from Fig. 4 that in the range 150–300K, the variation of E_g with T is, within the limits of experimental errors, linear. Hence, the mean value of $(dE_g/dT)_2$, obtained in this temperature range from the values θ and V given in Table I, is used here.

In order to use these data to calculate C_e and C_h , it is necessary to know values of α_L , v , m_e , and m_h in Eq. (6) and Eq. (7). The average thermal expansion coefficient of the lattice parameters α_L , for CuGaTe₂ has been determined to be $10 \times 10^{-6} \text{ K}^{-1}$.⁵ A value of the sound velocity v in the material can be estimated from the Debye temperature θ_D , which has the value of 226K.⁶ It is to be noted that this value is in very good agreement with the value of 214.5K obtained from the relation $\theta_D = (4/3)\theta$, as suggested in Ref. 15, where θ is the value, determined from fitting the experimental data to Eq. (2), given in Table I. Thus, $v = (K_B\theta_D/\hbar)(\Omega/6\pi^2)^{1/3}$, where Ω is the mean volume per atom, giving $v = 2.271 \times 10^5 \text{ cm/s}$. The hole effective mass m_h of CuGaTe₂ has been found to lie between 1.16 and 1.45 m_0 .⁸ Hence, the mean value of $m_h = 1.30 m_0$ obtained from the above quoted values is used here. Since the electron effective mass for the present compound has not been reported, the value of m_e has been estimated as $0.12 m_0$, by using the Kildal's equations,²¹ as in Ref. 22 for some I-III-VI₂ compounds, which is a reason-

able approximation for m_e .

Using the above values, Eq. (3) and Eq. (4) can be solved for C_e and C_h . Since Eq. (4) is quadratic in C_e and C_h , two sets of solutions are obtained. However, in these I-III-VI₂ compounds, it can be assumed that $|C_e| > |C_h|$,¹⁶ the solution satisfying this condition has been taken here, i.e. $C_e = -15.21$ eV/unit dilation and $C_h = 10.59$ eV/unit dilation. It is seen that C_e and C_h have opposite signs, indicating that under any given stress the conduction band minimum and the valence band maximum move in the same direction on compression. This behavior is illustrated in Fig. 6 for the Γ_{6c} conduction and Γ_{7v} valence energy bands, respectively, and it is in agreement with the absolute deformation potentials calculated by Franceschetti et al. for the case of silicon (Si) semiconductor,²³ also this result is consistent with the fact that the value of dE_g/dP has been found to be positive for the I-III-VI₂ compounds.²⁵ The deformation potential of the energy gap, A_g , is given by $C_e + C_h$ which in the present case yields a value of -4.62 eV/unit dilation. It is interesting to note that the values of C_e , C_h , and A_g are in the range of the values obtained, from E_g vs T , E_g vs pressure data and as well as from mobility data, for the I-III-VI₂^{18,22,24,-26} and II-IV-V₂¹¹ chalcopyrite compounds and alloys.

CONCLUSIONS

The x-ray results show that the sample produced by annealing at 600°C and then slowly cooled to room temperature gives the sharpest diffraction lines. The DTA thermograms are in agreement with the phase diagram results reported by Congiu et al.⁴ and Quintero et al.⁹

The results show that that good fits of E_g against T data, determined by utilizing either the extrapolation of $(\alpha h\nu)^2 = 0$ or the continuum term, can be obtained using the Manoogian-Leclerc equation with $x = 2/3$ or 1. However, it is found that using the values of E_g vs T gotten from the continuum term, with the parameter x taken as unity, yields the best fit to the experimental points. The resulting fitted parameters can be used to determine values of the thermal coefficients $(dE_g/dT)_1$ and $(dE_g/dT)_2$, and hence values of C_e , C_h , and A_g estimated. In addition, when x is taken as 1 in the above analysis, the value of $(dE_g/dT)_1$ is found to be independent of temperature, which is to be expected in the range where E_g varies linearly with T . The values of C_e , C_h and A_g are found to lie in the range of the reported values for the I-III-VI₂ and II-IV-V₂ chalcopyrite materials. The main source of error in the values of C_e and C_h is probably due to uncertainty

in the values of v , m_e , and m_h . However, no values of C_e and C_h have been given previously for CuGaTe₂, and as indicated above the present estimated values show good correlation with the values obtained for the chalcopyrite materials.

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