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Temperature variation in direct and indirect band gaps of β -CdIn₂Se₄

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Abstract. Samples of CdIn₂Se₄ were produced by the melt-and-anneal technique, annealing at 500 °C giving samples of the β -structure. Measurements of optical absorption were carried out in the temperature range 20–300 K and the data analysed to give values of the indirect and direct gap, E_{0I} and E_{0D} , respectively, at each temperature. The variations in E_{0I} and E_{0D} with temperature were fitted to a simplified Manoogian–Leclerc equation and the fitted coefficients used to give values of $(dE_0/dT)_1$, due to electron–phonon interaction, and $(dE_0/dT)_2$, due to lattice dilation, for each gap. Hence the values were determined for the deformation potentials of the valence and conduction bands.

1. Introduction

A wide range of ternary semiconducting compounds have been studied in recent years, with emphasis on the II–IV–V₂ and I–III–VI₂ compounds which have an adamantine structure. A third class of ternary compounds which have received considerable attention are the II–III₂–VI₄ compounds, which again have an adamantine structure but are defect structures with only three of every four cation sites occupied. CdIn₂Se₄, which is a member of this class and which has possible applications in device technology, has been studied in some detail. This compound was first studied crystallographically by Hahn *et al* [1] using an x-ray powder method, and it was reported that the pseudocubic unit cell had space group symmetry P $\bar{4}2m$ with $a = c = 5.81$ Å. Later work by Koval *et al* [2], using single crystals grown by a chemical transport method, showed the occurrence of two forms of CdIn₂Se₄, an α -type as described by Hahn *et al* and a β -type shown to be tetragonal with space group P $\bar{4}$ and lattice parameter values of $a = 5.815$ Å and $c = 2a = 11.63$ Å. Work by Przedmojski and Palosz [3] showed that crystals with $c = 4a$ could also be produced by chemical transport growth. Mocharnyuk *et al* [4] investigated the T - x phase diagram and order–disorder transitions in the Cd(Ga_{1-x}In_x)₂Se₄ system and showed that for CdIn₂Se₄ an ordering transition (labelled by them $\alpha \rightarrow \alpha'$) occurs at about 260 °C, where the lower-temperature form has the P $\bar{4}$ structure and the higher-temperature form is zincblende. The melting point was found to be about 930 °C.

Measurement of optical absorption and of photoconductivity [2, 5, 6] were made to investigate the band gaps of both forms of CdIn₂Se₄, and it was shown that for both cases

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the lowest gap was indirect with a direct gap of slightly larger energy value. Initially [5] it was assumed that the occurrence of two such gaps was due to transitions from the valence band maximum to two different conduction band minima, as is observed in various III–V compounds, etc. However, calculations by Baldereschi *et al* [7] and by Chizhikov *et al* [8] using pseudopotential models indicated that for both structures the minimum of the conduction band is at the Γ point but that for the valence band, in addition to a local maximum at the Γ point, a slightly higher maximum is present at the A point in the Brillouin zone of the α -form and at the N point for the β -form of the compound.

In the various optical measurements, values of the energy gaps have been determined at room temperature, liquid-nitrogen temperature and liquid-helium temperature and linear temperature coefficients estimated for the various gaps [5]. In the present work, measurements of optical absorption have been made on β -CdIn₂Se₄ to determine in more detail the variation in the two gaps with temperature in the range 20–300 K. These variations have been fitted to the equation of Manoogian and Leclerc [9] and the resulting parameters used to calculate values of the deformation potential.

2. Preparation and characterisation of materials

The present work was the initial part of a programme to investigate the properties and behaviour of the alloy system Cd_{1–x}Mn_xIn₂Se₄. Since all the alloys were being prepared by the melt-and-anneal technique, the compound CdIn₂Se₄ was made in this way also. Each 1.5 g was made from appropriate amounts of high-purity elements by sealing the elements under vacuum in a small quartz ampoule and melting at 1150 °C. The ampoule was then annealed at 500 °C for 1 month and finally cooled to room temperature in the furnace. With the furnace current switched off, the cooling from 500 °C to room temperature required about 4–5 h. Each sample was then x-rayed using the Guinier powder technique with Mo K α radiation.

The x-ray photograph of CdIn₂Se₄ indicated that the sample was in good single-phase condition. Analysis showed that the main structure lines corresponded to an apparently cubic zincblende structure. However, weak ordering lines indicated that the structure was pseudocubic tetragonal with $c/a = 2.00$. The weaker structure lines, i.e. those with h and k even, l doubly even and $h + k + l/2$ singly even, were not observed. All lines observed satisfied the condition that $h + k + l$ is even. These results indicate that the CdIn₂Se₄ produced here was the β -type with space group $I\bar{4}$ and lattice parameters $a = 0.5808$ nm and $c = 2a$. These data are in good agreement with those of Koval *et al* [2]. A differential thermal analysis run on the CdIn₂Se₄ gave a melting point value of 925 °C in reasonable agreement with the value obtained by Mocharnyuk *et al* [4].

3. Optical absorption data: measurement and analysis

Optical energy gap values were determined using measurements of optical absorption as described previously [10]. Slices cut from the sample ingot were polished to thickness d in the range 50–150 μm and were used for standard transmission measurements. The variations in I_0 , the incident intensity, and I_t , the transmitted intensity, as a function of photon energy $h\nu$ were determined as a continuous curve on a chart recorder. Thus values of $\ln(I_0/I_t)/d$ were determined as a continuous function of $h\nu$. The optical

samples were mounted in a Cryodyne 215C cryocooler so that the temperature could be controlled at any value in the range 15–300 K. Curves of $\ln(I_0/I_t)/d$ as a function of $h\nu$ were determined at 11 temperatures in that range.

If interference effects within the sample may be ignored (which is the case in the present work because of the thickness of the sample), then the transmitted intensity is given by

$$I_t = [I_0(1 - R)^2(1 + k^2/n^2) \exp(-\alpha_0 d)]/[1 - R^2 \exp(-2\alpha_0 d)] \quad (1)$$

where R is the reflection coefficient and α_0 , n and k are the absorption coefficient, refractive index and extinction coefficient of the material, respectively. The value of $R^2 \exp(-2\alpha_0 d)$ is much less than unity for all cases considered here and k is much less than n near the absorption edge. Thus to a good approximation

$$I_t = I_0(1 - R)^2 \exp(-\alpha_0 d). \quad (2)$$

R varies by little in the wavelength range concerned [11, p 157] and so the factor $(1 - R)^2$ may be treated as a constant to a good approximation. Hence,

$$\ln(I_0/I_t)/d = \alpha_0 - C \quad (3)$$

where C is a constant independent of wavelength. There will be background absorption and scattering, etc, and this can be combined with C and the sum labelled α_B . The absorption coefficient α_0 will consist of contributions from both the indirect and the direct band-gap transitions, labelled α_1 and α_D , respectively. If $\ln(I_0/I_t)/d$ is for convenience labelled α , then equation (3) becomes

$$\alpha = \alpha_1 + \alpha_D + \alpha_B.$$

The values of α_1 and α_D can be used to give values of the energy gaps E_1 and E_D . The theory of interband optical absorption [12] shows that at the absorption edge the absorption coefficient α_j varies with the photon energy $h\nu$ according to the expression

$$\alpha_j h\nu = A(h\nu - E_{0j})^N \quad (4)$$

where A is a constant and N is a number which characterises the transition process, being $\frac{1}{2}$ for direct allowed and 2 for indirect allowed transitions.

Since the values of α_D and α_1 become appreciable at energies close to the corresponding energy gaps E_{0D} and E_{0I} , it is possible to determine separate contributions by extrapolation from lower-energy values. Thus in figure 1, for a typical case of $T = 100$ K, the variation in α with $h\nu$ is given. For $h\nu < 1.45$ eV, the value of α is clearly that of α_B and these values have been linearly extrapolated to give effective α_B -values at higher $h\nu$. Thus values of $\alpha_D + \alpha_1$ were determined as $\alpha - \alpha_B$. Within the energy range between E_{0I} and E_{0D} , the value of α_D will be negligible and hence in that range $\alpha_1 = \alpha - \alpha_B$. For an indirect gap the relation $\alpha_1 h\nu = A_1(E_{0I} - h\nu)^2$ applies as indicated above. Hence, in figure 2, values of $(\alpha_1 h\nu)^{1/2}$ are plotted against $h\nu$. In the range $1.48 \text{ eV} \leq h\nu \leq 1.58 \text{ eV}$, the graph is reasonably linear and has been extrapolated to $(\alpha_1 h\nu)^{1/2} = 0$ to give a value for E_{0I} of 1.450 eV. For $h\nu > 1.58$ eV, the curve of $(\alpha_1 h\nu)^{1/2}$ rises above the linear extrapolation because of the contribution of α_D . In this range, the value of α_1 can be obtained from the linear extrapolation and hence $\alpha_D = \alpha - \alpha_B - \alpha_1$. For the direct-gap case, as seen above $\alpha_D h\nu = A_D(E_{0D} - h\nu)^{1/2}$ and so, in figure 3, values are plotted of $(\alpha_D h\nu)^2$ versus $h\nu$. There is some scatter in the experimental values and α_D saturates above $h\nu \approx 1.66$ eV, but a reasonable straight line can be drawn through the points below 1.66 eV and this line gives a value for E_{0D} of

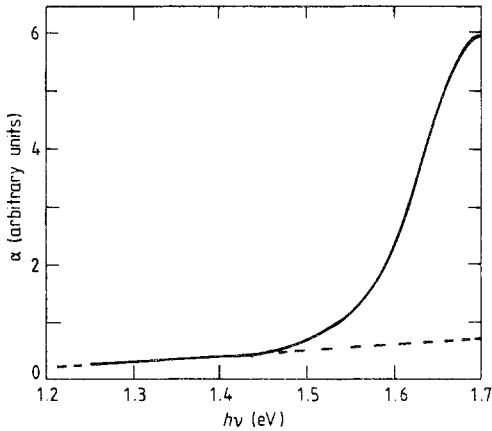


Figure 1. Variation in total absorption coefficient α with photon energy $h\nu$ at $T = 100$ K.

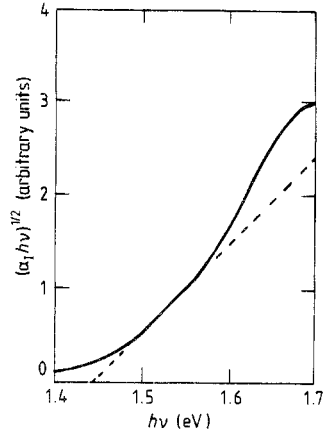


Figure 2. Variation in $(\alpha_1 h\nu)^{1/2}$ with photon energy $h\nu$ at $T = 100$ K.

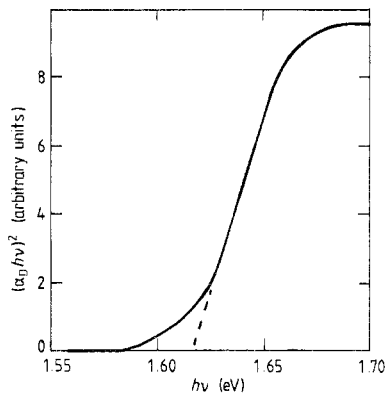


Figure 3. Variation in $(\alpha_D h\nu)^2$ with photon energy $h\nu$ at $T = 100$ K.

1.619 eV. The same method of analysis was used for the data at other temperatures and the resulting variations in E_{0I} and E_{0D} with temperature are shown in figure 4. The scatter of the points in figure 4 indicates that the probable relative error in the values of E_{0I} and E_{0D} does not exceed ± 0.005 eV. The absolute error in the energy gaps may be larger than this, but that will not affect the analysis which follows.

It has been shown [12] for a range of semiconductor compounds and alloys that the variation in the energy gap with temperature can be well represented by a simplified Manoogian–Leclerc equation of the form

$$E_0(0) - E_0(T) = UT^{2/3} + V\varphi[(\coth \varphi)/2T - 1] \quad (5)$$

where U , V and φ are constants independent of T . As shown by Manoogian and Leclerc [9], the main contribution to the change in E_0 is from the $V\varphi$ dynamic term, the $UT^{2/3}$ static term contributing only a small fraction over most of the temperature range. In the present case, the two band-gap variations will need separate equations, with appropriate

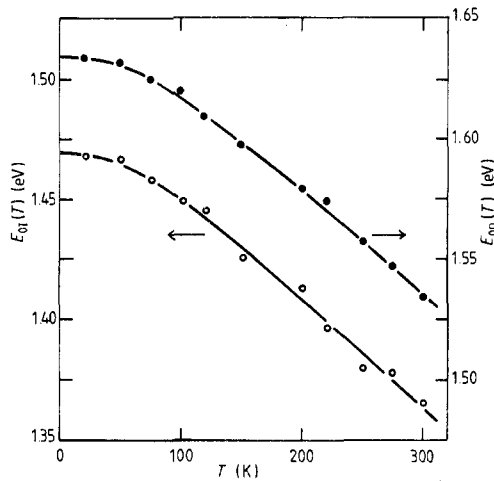


Figure 4. Variation in the indirect energy gap E_{0I} (○) and direct energy gap E_{0D} (●) with temperature T : —, lines fitted with Manoogian–Leclerc equation.

values of $E_0(0)$, U and V to be determined for each case, but φ , which is related to the phonon energy distribution in the material, should be the same in both cases. Thus it was necessary to determine by least-squares fitting the values of φ , $E_{0D}(0)$, U_D , V_D , $E_{0I}(0)$, U_I and V_I which gave the best overall fit to the two sets of data. Fitting in this way gave the following values for the various parameters: $\varphi = 190$ K, $E_{0D}(0) = 1.635$ eV, $U_D = 1.143 \times 10^{-4}$ eV K^{-2/3}, $V_D = 2.184 \times 10^{-4}$ eV K⁻¹, $E_{0I} = 1.470$ eV, $U_I = 2.712 \times 10^{-4}$ eV K^{-2/3} and $V_I = 2.202 \times 10^{-4}$ eV K⁻¹.

The resulting lines of E_0 versus T are shown in figure 4. The room-temperature values obtained were $E_{0I}(300\text{ K}) = 1.365$ eV and $E_{0D}(300\text{ K}) = 1.534$ eV. These are to be compared with values in the literature of 1.48 eV and 1.64 eV [5] (however, it is not clear whether these values are for the α - or β -phase) and 1.30 eV and 1.49 eV [2]. As seen from figure 4, above 150 K the variation in E_0 with T can be taken as linear within the limits of experimental error. A linear temperature coefficient of band gap has been quoted [3, 8] and Trykozko [5] gives $dE_0/dT = -5.5 \times 10^{-4}$ eV K⁻¹ for the direct gap of the α -phase based on measurements at room temperature and liquid-nitrogen temperature. If linear fits are made to the present E_0 data between 150 and 300 K in figure 4, the resulting values of dE_0/dT are

$$dE_{0D}/dT = -4.25 \times 10^{-4} \text{ eV K}^{-1} \quad dE_{0I}/dT = -4.37 \times 10^{-4} \text{ eV K}^{-1}.$$

The relative temperature variations in E_{0D} and E_{0I} show any change occurring with temperature in the shape of the valence band. The value of $E_{0D} - E_{0I}$ changes from 0.165 eV at 0 K to 0.172 eV at 300 K, a small variation which is comparable with the experimental error in the measurements of E_0 .

4. Deformation potential values

It has been shown [13] that the electron–phonon interaction in the effectively linear range of E_0 variation with T can be written

$$(dE_0/dT)_1 = -(8/9\pi)(3/4\pi)^{1/3} (k_B \Omega^{2/3} / h^2 M v^2) (m_h C_h^2 + m_e C_e^2) \quad (6)$$

where M and Ω are, respectively, the mass and volume of the unit cell, v is the velocity

of sound in the material, m_h and m_e are, respectively, the hole and electron effective masses, and C_h and C_e are, respectively, the valence and conduction band deformation potentials. The lattice dilation term is related to the deformation potentials [14] by

$$(dE_0/dT)_2 = 2\alpha_L(C_h + C_e) \quad (7)$$

where α_L is the thermal expansion coefficient of the lattice. Quintero *et al* [15] have used equations (6) and (7) to make estimates of the deformation potentials of the $\text{CuGa}(\text{S}_2\text{Se}_{1-z})_2$ alloys. Here it is proposed that a similar analysis can be made with the present CdIn_2Se_4 data using the parameters U and V of the Manooogian–Leclerc equation to give values for the two temperature coefficients of E_0 .

As indicated above, in equation (5) the term $UT^{2/3}$ is the dilation term while the term in V is the dynamic term. Thus the dynamic term can be used to give $(dE_0/dT)_1$, and the dilation term to give $(dE_0/dT)_2$, i.e.

$$(dE_0/dT)_2 = -\frac{2}{3}UT^{-1/3} \quad (8)$$

$$(dE_0/dT)_1 = -V\varphi^2/2T^2 \operatorname{cosech}^2(\varphi/2T). \quad (9)$$

It is seen that, in equations (8) and (9), $(dE_0/dT)_1$ and $(dE_0/dT)_2$ vary to some extent with T . Taking the range 150–300 K over which the variation in E_0 is effectively linear and using the values of U , V and φ given above, the following values are obtained: for the direct gap,

$$\begin{aligned} (dE_0/dT)_1 &= -3.83 \times 10^{-4} \text{ eV K}^{-1} \\ (dE_0/dT)_1 &= -4.22 \times 10^{-4} \text{ eV K}^{-1} \\ (dE_0/dT)_2 &= -1.43 \times 10^{-5} \text{ eV K}^{-1} \\ (dE_0/dT)_2 &= -1.14 \times 10^{-5} \text{ eV K}^{-1} \end{aligned} \quad \text{at} \begin{cases} 150 \text{ K} \\ 300 \text{ K} \end{cases}$$

and, for the indirect gap,

$$\begin{aligned} (dE_0/dT)_1 &= -3.86 \times 10^{-4} \text{ eV K}^{-1} \\ (dE_0/dT)_1 &= -4.25 \times 10^{-4} \text{ eV K}^{-1} \\ (dE_0/dT)_2 &= -3.40 \times 10^{-5} \text{ eV K}^{-1} \\ (dE_0/dT)_2 &= -2.70 \times 10^{-5} \text{ eV K}^{-1} \end{aligned} \quad \text{at} \begin{cases} 150 \text{ K} \\ 300 \text{ K} \end{cases}$$

Taking mean values of these limits to represent the values for this range of T gives the following: for the direct gap

$$(dE_0/dT)_1 = -4.03 \times 10^{-4} \text{ eV K}^{-1} \quad (dE_0/dT)_2 = -1.29 \times 10^{-5} \text{ eV K}^{-1}$$

and, for the indirect gap,

$$(dE_0/dT)_1 = -4.06 \times 10^{-4} \text{ eV K}^{-1} \quad (dE_0/dT)_2 = -3.05 \times 10^{-5} \text{ eV K}^{-1}.$$

Thus these values give total temperature coefficients dE_0/dT in this temperature range of $-4.16 \times 10^{-4} \text{ eV K}^{-1}$ for the direct gap and $-4.37 \times 10^{-4} \text{ eV K}^{-1}$ for the indirect gap, in reasonable agreement with the values given above from the slopes of the E_0 versus T curves.

In order to use these data to calculate C_e and C_h it is necessary to know values for ν , m_e , m_h and α_L in equations (6) and (7). Koval *et al* [16] give $m_e = 0.16m_0$ (m_0 is the free-electron mass) while the data of Mocharnyuk *et al* [4] gives $\alpha_a = \alpha_c = 1.0 \times 10^{-5} \text{ K}^{-1}$ for

the a and c axes of CuIn₂Se₄. Hence α_L , which can be taken as $(2\alpha_a + \alpha_c)/3$, also has a value of $1.0 \times 10^{-5} \text{ K}^{-1}$. No values are available for m_h and ν for the case of CuIn₂Se₄. Thus m_h has been taken as m_0 , which is usually a reasonable approximation for m_h , while ν has been assumed to be the same value as for CuGaSe₂, i.e. $\nu = 2.33 \times 10^5 \text{ cm s}^{-1}$ [15].

Using the above values, equations (6) and (7) can be solved for C_e and C_h . When this is done, two solutions are possible. For the direct gap, either $C_e = -16.2$ and $C_h = +15.5$ or $C_e = +15.1$ and $C_h = -15.7$ while, for the indirect gap, $C_e = -17.0$ and $C_h = +15.5$ or $C_e = +14.3$ and $C_h = -15.9$ (all in units of electronvolts per unit dilation). In all cases, C_e and C_h have opposite signs, indicating that under any given stress the conduction band minimum and the valence band maxima move in the same direction. The magnitude of $|C_e| - |C_h|$ is in all cases small compared with the values for CuInSe₂ and similar chalcopyrite structures [15] and is effectively within the range of experimental uncertainty for C_e and C_h .

5. Discussion

The x-ray results show that samples produced by annealing at 500 °C and then slowly cooling to room temperature have the β -form, i.e. tetragonal $I\bar{4}$. This is consistent with the data of Mocharnyuk *et al* [4]. However, the room-temperature values of the two energy gaps were somewhat higher than those determined for the β -phase by Koval *et al* [2].

Values of both energy gaps, E_{0D} and E_{0I} , were measured in the temperature range 20–300 K, and it was found that both sets of data could be well fitted to a Manoogian–Leclerc form (equation (5)) with a single φ -value of 190 K. In this fitting, good values could be obtained for V_D and V_I but, since the contributions of the U -terms are relatively small, the values of U_D and U_I were less certain and varied appreciably with variation in φ .

The Manoogian–Leclerc parameters U and V represent the static and dynamic parts of the E_0 variation [9], respectively, and so have been used here to give the lattice dilation and electron–phonon interaction terms. Hence values were determined for the deformation potential C_e of the conduction band and the deformation potential C_h of the valence band. The values determined for these parameters were similar in magnitude to those found for other ternary compounds such as the chalcopyrites [15], but the difference between the magnitudes for C_e and C_h was small and significantly less than the chalcopyrite values. However, since C_e and C_h have opposite signs, this difference is determined mainly by equation (7) which contains $(dE_0/dT)_2$. From equation (8), $(dE_0/dT)_2$ depends upon U , which is small and, as indicated above, is sensitive to the value taken for φ . $(dE_0/dT)_2$ also depends upon α_L , so that the value determined for $C_e + C_h$ will be inversely proportional to the value assumed for α_L . The value of α_L determined from the data of Mocharnyuk *et al* [4] was $1.0 \times 10^{-5} \text{ K}^{-1}$ which is very similar to the value for the chalcopyrite CuGaSe₂ [15]. It appears unlikely to be smaller than this. The magnitudes of C_e and C_h are mainly determined by equation (6). Most of the parameters of this equation are better known, so that the magnitude of values found should be reasonably good.

The two gaps, direct and indirect, must involve

(a) one conduction band minimum and two valence band maxima as proposed from theoretical calculations [7, 8] or

(b) two conduction band minima and one valence band maximum as originally assumed [5].

For case (a) the C_c -values for direct and indirect gaps should be identical, while for case (b) the corresponding values C_h -values should be the same. The present results would tend to favour (b) but, as indicated above, the differences are too small to allow any definite conclusion to be drawn.

Acknowledgments

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