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Temperature Variation of Optical Energy Gap and Deformation Potentials in AgInTe₂

By

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Values of the optical energy gap E_0 of AgInTe₂ as a function of temperature T in the range 10 to 300 K are obtained by optical absorption measurements. The variation of E_0 with T is fitted well by a Manoogian-Leclerc equation of the form $E_0(0) - E_0(T) = UT + V\varphi (\coth \varphi/2T - 1)$. Values of $(dE_0/dT)_1$, the electron-phonon interaction contribution to the variation of the energy gap with temperature, and $(dE_0/dT)_2$, the lattice dilation contribution, are obtained from the $V\varphi$ and U terms, respectively. From these values of $(dE_0/dT)_1$ and $(dE_0/dT)_2$, values are determined for the acoustic deformation potentials of the conduction band C_e and the valence band C_v .

Mit Hilfe optischer Absorptionsmessungen wird die optische Energielücke E_0 als Funktion der Temperatur T im Bereich von 10 bis 300 K ermittelt. Die Variation von E_0 mit T wird gut durch eine Manoogian-Leclerc-Gleichung der Form $E_0(0) - E_0(T) = UT + V\varphi (\coth \varphi/2T - 1)$ approximiert. Die Beiträge der Elektron-Phonon-Wechselwirkung, $(dE_0/dT)_1$, und der Gitterdilatation, $(dE_0/dT)_2$, werden aus den $V\varphi$ - bzw. U -Termen bestimmt. Aus diesen Werten von $(dE_0/dT)_1$ und $(dE_0/dT)_2$ werden die akustischen Deformationspotentiale des Leitungsbandes, C_e , und des Valenzbandes, C_v , erhalten.

1. Introduction

The chalcopyrite I–III–VI₂ compounds have received considerable attention [1, 2], both from their academic interest and also because of possible practical application in solar cell and photodiode technologies. One problem that arises in the necessary analysis of transport data for these materials is the discrepancy 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 Gonzales [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 mechanisms is not required in that case. Recently [5], it has been shown that values of deformation potentials can be obtained from the analysis of the variation of the energy gap E_0 with temperature in terms of the Manoogian-Leclerc equation [6]. In the present work, measurements of E_0 in the temperature range 10 to 300 K have been made for AgInTe₂ and these data are used to give values of the deformation potentials for the conduction and valence bands of the compound.

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2. Experimental Details

The AgInTe₂ samples used in the measurements were polycrystalline, produced by melting together appropriate weights of the elements and annealing. Slices were cut from the resulting ingot and polished down to a thickness d in the range 50 to 100 μm .

Values of the optical energy gap E_0 were determined using the optical absorption method described previously [7]. The variation of the incident intensity I_0 and the transmitted intensity I_t were determined as a function of photon energy $h\nu$. Thus values of $(\ln I_0/I_t)/d$ were determined as a function of $h\nu$ and were corrected by subtracting a background value so as to give values of the absorption coefficient α of the sample. The relation $\alpha h\nu = A(E_0 - h\nu)^{1/2}$ was then used to give a value for the optical energy gap E_0 . The samples were mounted in a Cryodyne 215C cryocooler so that the temperature could be controlled at any point in the range 15 to 300 K. Values of E_0 were determined at various temperatures in that range.

3. Results and Analysis

The measured variation of E_0 with T is shown in Fig. 1. As has been shown previously [5], data of this type can be well fitted by a simple Manoogian-Leclerc equation [6] of the form

$$E_0(0) - E_0(T) = UT^x + V\varphi \left[\coth \frac{\varphi}{2T} - 1 \right], \quad (1)$$

where the parameters U , V , φ , and x are independent of T . In this equation, the U term represents the lattice dilation contribution to the change in E_0 , while the V term represents the phonon contribution [6]. Thus as indicated previously [5], the two components of the energy gap variation with temperature can be related to the Manoogian parameters as follows. The component due to electron-phonon interaction, $(dE_0/dT)_1$, is given by

$$\left(\frac{dE_0}{dT} \right)_1 = - \frac{V\varphi^2}{2T^2} \operatorname{cosech}^2 \left(\frac{\varphi}{2T} \right), \quad (2)$$

while the dilation term due to thermal expansion of the lattice, $(dE_0/dT)_2$, has the value

$$\left(\frac{dE_0}{dT} \right)_2 = -xUT^{x-1}. \quad (3)$$

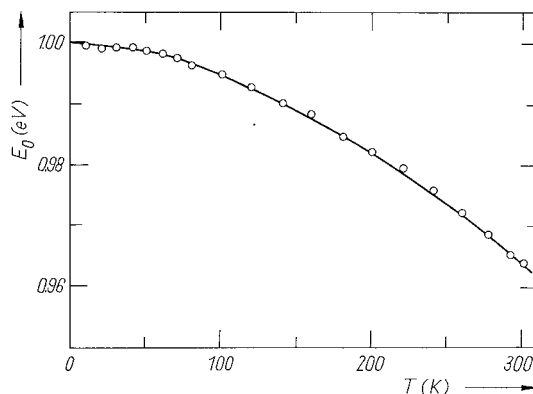


Fig. 1. Variation of energy gap E_0 with temperature for AgInTe₂. \circ experimental data, — curve fitted to the Manoogian-Leclerc equation

When fitting (1) to the E_0 versus T experimental data, in previous work (e.g. [8, 9]) it was assumed that $x = 2/3$. However, in the analysis of the optical absorption results for CuInTe_2 [5], it was shown that in order to obtain agreement between the values obtained from the variation of E_0 with T and those from the variation of E_0 with pressure, it was necessary to use a value of $x = 1$. Hence this value will be used in this analysis. Various values were assumed for φ and then the parameters determined from the fitting procedure, the final criterion for the overall best fit being minimum standard deviation. Fitting to the data in Fig. 1 in this way gave the following values for AgInTe_2 : $\varphi = 370$ K, $U = 3.929 \times 10^{-5}$ eV/K, $V = 7.849 \times 10^{-5}$ eV/K, and $E_0(0) = 1.0001$ eV. The resulting fitted curve is shown in Fig. 1.

With the above data, (2) and (3) can be used to give values for $(dE_0/dT)_1$ and $(dE_0/dT)_2$. With the value of T taken as 300 K, $(dE_0/dT)_1 = -1.385 \times 10^{-4}$ eV/K and $(dE_0/dT)_2 = -3.929 \times 10^{-5}$ eV/K. As seen from (3), with $x = 1$, $(dE_0/dT)_2$ is independent of T , but from (2), $(dE_0/dT)_1$ is still temperature dependent. However, with the present values it is found that $(dE_0/dT)_1$ varies by only 0.078%/K at 300 K. Thus the calculated values of both $(dE_0/dT)_1$ and $(dE_0/dT)_2$ are practically constant in this temperature region where the variation of E_0 with T is seen to be effectively linear.

4. Calculation of Deformation Potentials

The two temperature coefficients of the energy gap determined above 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 [10],

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

while for the lattice dilation contribution [11],

$$\left(\frac{dE_0}{dT}\right)_2 = 2\alpha_L(C_e + C_h), \quad (5)$$

where M and Ω are the mass and volume of the unit cell, respectively, v the velocity of sound in the material, m_e and m_h the electron and hole masses, respectively, and α_L the average thermal expansion coefficient of the material, which for I-III-VI₂ compounds is given by $\alpha_L = (2\alpha_a + \alpha_c)/3$, α_a and α_c being the thermal expansion coefficients along the x - and z -axes, respectively. In order to determine values of C_e and C_h from (4) and (5), it is necessary to know the values of these various parameters. From the lattice parameter values and structure (1), $M = 3.173 \times 10^{-21}$ g and $\Omega = 5.204 \times 10^{-22}$ cm³, and $\alpha_L = 8.72 \times 10^{-6}$ [12]. A value for v can be obtained from the Debye temperature θ_D which has the value of 155.9 K [13]. Thus $v = (k_B\theta_D/\hbar)(\Omega_1/6\pi^2)^{1/3}$, where Ω_1 is the mean volume per atom, giving $v = 1.670 \times 10^5$ cm/s.

There appear to be no values of m_e and m_h given in the literature, but values of these parameters can be estimated by using the Kildal equations [1, 14]. These relate the effective mass values to the energy differences between the conduction and the 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 the p - d

hybridization has been made by Yooder et al. [15], but it is not easy to obtain effective mass values from the resulting equations. However, Look and Manthuruthil [16] 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 d character occurring in the hybridized bands. The three energy gap values for AgInTe_2 have been determined from photoconductivity measurements as 1.00, 1.27, and 1.43 eV at 77 K [17], thus providing the energy values needed in the Kildal equations, while the values of the spin-orbit splitting A_{so} and the crystal-field splitting A_{cf} which are also needed can be obtained from these energy gap values [1], giving $A_{\text{so}} = 0.206$ eV and $A_{\text{cf}} = -0.316$ eV. The value of P^2 can be taken as 20 eV in these materials [1]. With regard to α , by combining the values from the photoconductivity measurements [17] with the results of the analysis of Yooder et al. [15], a value of 0.132 is obtained for $(1 - \alpha)$ [17], i.e. $\alpha = 0.868$. However, an alternative way of determining α is from the atomic spin-orbit splittings of the elements involved [15, 18], i.e.

$$A_{\text{so}} = \alpha A_{\text{so}}^{\text{p}} + (1 - \alpha) A_{\text{so}}^{\text{d}}, \quad (6)$$

where

$$A_{\text{so}}^{\text{p}} = G_{\text{p}} \left\{ \frac{1}{16} A_{\text{so}}^{\text{p}}(\text{Ag}) + \frac{3}{16} A_{\text{so}}^{\text{p}}(\text{In}) + \frac{3}{4} A_{\text{so}}^{\text{p}}(\text{Te}) \right\} \quad (7)$$

and

$$A_{\text{so}}^{\text{d}} = G_{\text{p}} A_{\text{so}}^{\text{d}}(\text{Ag}). \quad (8)$$

G_{p} being an enhancement factor, taken as 29/20 [18]. Use of the atomic A_{so} values given by Yooder et al. [15] gives α for AgInTe_2 as 0.562, a value appreciably different from that quoted above. Hence both values were separately used to give values of the deformation potentials.

With $\alpha = 0.868$, the Kildal analysis gives $m_{\text{e}} = 0.070$ and $m_{\text{h}} = 0.655$, while $\alpha = 0.562$ gives $m_{\text{e}} = 0.108$ and $m_{\text{h}} = 1.012$. These values of effective mass plus the other parameters listed above were substituted into (4) and (5). Since (4) is quadratic in C_{e} and C_{h} , two sets of solutions were obtained in each case. With $\alpha = 0.868$, either $C_{\text{e}} = -11.08$ and $C_{\text{h}} = +8.82$ or $C_{\text{e}} = +7.01$ and $C_{\text{h}} = -9.26$ eV/unit dilation. Assuming that in these materials $|C_{\text{e}}| > |C_{\text{h}}|$ [4, 19], the first solution was taken, i.e.

$$C_{\text{e}} = -11.08 \quad \text{and} \quad C_{\text{h}} = +8.82 \text{ eV/unit dilation.}$$

With $\alpha = 0.562$, the corresponding values of deformation potential are

$$C_{\text{e}} = -9.30 \quad \text{and} \quad C_{\text{h}} = +7.05 \text{ eV/unit dilation.}$$

The difference between these two sets of values is appreciably less than the discrepancies between various values quoted for other compounds previously.

5. Conclusions

It is seen that the analysis of the variation of E_0 with T by the Manoogian-Leclerc equation with $x = 1$ gives values of the thermal coefficients $(dE_0/dT)_1$ and $(dE_0/dT)_2$. These can be used to determine the acoustic deformation potentials C_{e} and C_{h} of the material, provided that values of the effective masses m_{e} and m_{h} can be obtained. In the case of AgInTe_2 , no experimental values appear to be available for these parameters, but estimates of the values were made using the Kildal relations [1, 14]. The uncertainty in these effective mass values

is the largest factor giving a resultant uncertainty in the values of C_e and C_h , which in the present case is at least 20%. However, no values of C_e and C_h have been given previously for AgInTe_2 , and the present values show good correlation with the values obtained previously for CuInTe_2 [5].

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