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The Temperature Dependence of the Energy Gap of $CdGeP_2$ Semiconductor

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ABSTRACT

The theoretical method of Fan and shockly-Bardeen is used to calculate the temperature dependence of the energy gap in the temperature range (300 – 425 K) for the ternary semiconducting compound $CdGeP_2$. The results are (1.63-1.71)±00.01 eV in the temperature range mentioned above and they are in good agreement with those of the reported experimental work. The temperature variation of ΔEg and Eg were discussed in terms of the effects of the electron - phonon interaction and the lattice dilation . The effect of the lattice expansion is larger than that of the lattice vibration, but both effects , for this compound , are found to be linear with T for the temperature range investigated

The empirical relation of (Varshni, Ravindra - Srivastava and Seehra – Sehra) is also used to calculate Eg versus T. It gives good results in comparison with the reported experimental work , as well as with the calculated results.

Keywords; Semiconductors, $CdGeP_3$, Energy gap, Lattice vibration Lattice dilation

* Part of his M.Sc. Thesis.

Introduction

The ternary semiconductor $CdGeP_2$ belongs to II-IV-V_2 group compounds and is tetrahedrally bonded like the (In + GaP) binary system, crystallising in the chalcopyrite structure, space group $I\,4\,2\,d$ [1]. The cell dimensions are a = 5.741 A^O, and C = 10.775 A^O, [2].

Previous researchers have investigated the electrical and band structure properties of this compound . The electroreflectance measurements showed that the compound $CdGeP_2$ has a direct energy gap equal to (1.72 *eV*)[3]. However, different room temperature values have been reported in the range of (1.67 *eV*) to (1.8 *eV*) [3,4].

The calculation methods of Fan and Shockly-Bardeen have been used successfully in a wide range of chalcopyrite compounds[5]. Also empirical relations of Varshni [6], Ravindra-Srivastava[7] and Seehra-Seehra were used successfully in calculating the temperature dependence of Eg for most semiconductors such as Si, Ge, binary and ternary compounds[5,8].

The aim of this work is to calculate the temperature dependence of energy gap for $CdGeP_2$ by using the empirical relations and comparing the results with that of the reported experimental work.

11- Methods of Calculation

11-1: Fan`s and Shockly Barddeen method

According to Fan[9] and Shockly - Bardeen[10] the electron - phonon interaction and the lattice dilation of the crystal have their effects in producing a shift in the energy gap in semiconductors. They have used this method to calculate the temperature dependence of Eg for Si and Ge [9]. However, this method was used succussfully for calculating the temperature dependece in the ternary semiconducting compound $ZnGeP_2$ [11].

The change in the energy of the electron-lattice interaction due to the lattice distortion is, to the first approximation proportional to the displacement of ions in the lattice. The vibrations of the ions can be analyzed into normal modes and can be specified by a set of quantum numbers n and a wave number q. When only few states are occupied in semiconductors, the energy gap can be represented by:

$$Eg(T) \quad Eg(0) + \Delta Eg \quad \ldots\ldots\ldots\ldots (1)$$

were Eg (0) is the difference in the crystal potential, for the undistorted lattice, due to the transfer of an electron from a state (k_t, v) to a state (k_b, c) ; That is,

$$Eg(0) = Eg(k_b, c) - Eg(k_t, v) \ldots\ldots\ldots\ldots (2)$$

While ΔEg is the difference between the values of the energy gap at temperatures (T)K and (0) K. The change in the energy of the electron -lattice interaction in the crystal which accompanies such excitation, and the lattice distortion caused by vibration due to temperature, can be given by the second order perturbation method , which gives [12];

$$(\frac{dEg}{dT})_{LV} = -\frac{4}{g\pi}(\frac{3}{2}\pi)^{1/3}\frac{k_o\Omega}{Mh^2u^2}[m_c^* C_c^2 + m_v^* C_v^2] \quad \ldots\ldots\ldots\ldots\ldots(3)$$

Where k_o is the Boltzman constant, is the unit cell volume which is defined by the lattice constants a, b and c as:

$\Omega = axb.c$,

M is the twice mean atomic mass, which is due to the form of the lattice vibration [12], 'and u is the speed of sound waves in the crystal . More details can be found elsewhere [5].

Equation (3) however is suitable for the intrinsic temperature range.[13], in which the parameters Cc and Cv can be estimated from the carrier mobility. Since the data used in this work were from samples of impure and n-type conductivity and not intrinsic in the investigated temperature [14], then Cv can be neglected, while the parameter Cc can be estimated from the relation of the lattice scattering of the carrier mobility as [15,16].

$$C_c = \frac{2(2\pi)^{1/2} e\hbar^4 Mu^2}{3\Omega(k_o)^{3/2} m^{*5/2} \mu T^{3/2}} \quad \ldots\ldots\ldots(4)$$

Where e is the electron charge and is the mobility of electrons.

In order to perform the total calculation of Eg versus T, the effect of lattice dilation should also be added to the electron phonon interaction effect . This effect is given by shockly and Bardeen [10,5] as:

$$(\frac{dEg}{dT})_\beta = \frac{2}{3} C_c \beta \ldots\ldots(5)$$

Where â is from the coefficients of volume expansion, which can be calculated from the temperature dependence of the principal linear thermal expansion along the "a" and "c" axes as J_a and J_c ,respectively, in the form

$$\beta = 2\alpha_a + \alpha_c \ldots\ldots(6)$$

By summing eq. (3) and (5) , the total Eg dependence on temperature is:

$$(\frac{dEg}{dT})_{Total} = (\frac{dEg}{dT})_{LV} + (\frac{dEg}{dT})_\beta \ldots\ldots\ldots(7)$$

II-II Empirical methods for calculating the temperature dependence of Eg:

A:Varshni`s formula

Vasileff[17] considered the shift of the band edge through electron phonon interaction. Adams pointed out that Vasileff's theory fails for most semiconductors, however he agrees with Vasileff's conclusions on the temperature dependence of the band edge . These calculations led Varshni[18] to suggest that the linear temperature dependence of Eg is due to the lattice dilation effect which occures only at high temperature, and the electron - phonon interaction effect which contributes as T^2 for $T<<\theta_D$ and as T for $T>>\theta_D$ Combining these variations the relation becomes as [6].

$$Eg(T) = Eg(0) - \frac{\alpha T^2}{T+\varphi} \quad \ldots\ldots\ldots(8)$$

Where $Eg\ (T)$ is the energy gap at temperature T which may be direct or indirect, $Eg\ (0)$ is the energy gap at (0)K, φ is an empirical constant and might approximately be the (0)K Debye temperature.

B:Ravinra and Srivastava formula

Ravindra and Srivastava[7] have shown the variation of the energy gap with temperature in semiconductors is given by:

$$Eg(T) = Eg(0) - \frac{(2.25x10^{-5}\theta_D - 4.275x10^{-3})T^2}{5(T - 5\theta_D - 1135)} \quad \ldots\ldots\ldots(9)$$

Where θ_D and T are in K, and the numbers in the above formula are determined by using the standard procedures of the curve fitting

C: Seehra and Seehra formula :

The following empirical relation has been proposed by Seehra and Seehra [8];

$$Eg\ (T) = Eg\ (O) + aT + bT^2 \quad \ldots\ldots\ldots(10)$$

Where the constant a and b, are determined by plotting $Eg\ (T) - Eg\ (0)$

$$\frac{Eg(t) - Eg(0)}{T} versus \quad T \quad \ldots\ldots(11)$$

In 1979 Seehra and Seehra have attributed the (b T^2) term to the electron - phonon interaction while the (a T) term associated with the lattice dilation.

III- Results and Analysis

The effective mass of carriers m^* in semiconductors is an important parameter in calculating the temperature coefficients of Eg (eqn. 4). The temperature dependence of effective mass was calculated from magneto-optical measurements through the relation *[Pankove 1971]*

$$m_r^* = \frac{1}{2}\left(\frac{1}{\Delta Eg}\right)e\hbar B \qquad \ldots\ldots\ldots(12)$$

where B is the magnetic field intensity, whose value was 0.7 Tesla. The results for m_r^* are shown in fig. (1) . However, the details are given elsewhere [14].

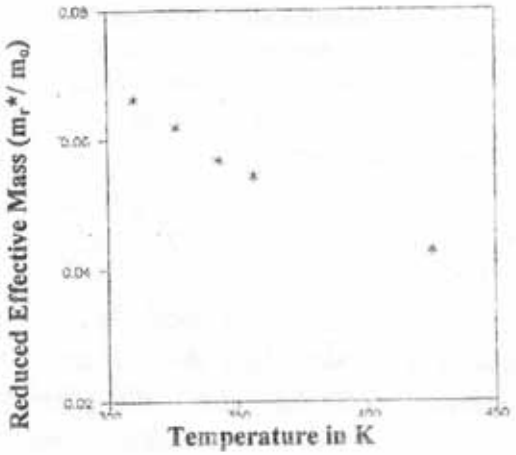

Fig.(1):Temperature dependence of the effective mass of carries for $CdGeP_2$.

The sample was a single crystal grown by using a Tin Solution method. This method however , has been used successfully for a high temperature melting point compounds in which contains a volatile components [20].

The average sound velocity u which is also an important parameter, can be calculated from the expression [21];

$$u = \left(\frac{k_o\theta_D}{\hbar}\right)\left(\frac{\bar{v}}{6\pi^2}\right)^{1/3} \qquad \ldots\ldots\ldots(13)$$

Where $\bar{v}$ is the average atomic volume[22], and èD is the Debay temperature . The room temperature values of $\bar{v}$ and èD are equal to 2.609x10-23 Cm3 and 324 K, respectively. These values give an average sound velocity in CdGeP2 equal to (3.229 x 103) m/sec. The atomic volume is calculated from the relation $\bar{v} = \bar{M}/\rho$ where $\bar{M}$ is the average atomic mass and ρ is the density and have the values of (73.25 a.m..u.) and 4.66 g/cm^3[22], respectively . The coefficient of volume expansion β which was calculated from relation (6) is equal to (18.2 x 10-6K-1), however, the change in ‰ due to â in this calculation was found to be too small and was neglected . The room temperature value of ‰ is equal to (355.1341 x 10-30 m3) and was used in the persent work.

The temperature dependence of Eg calculated from Fan and shockly Bardeen relations equ(1) is shown in fig. (2) .

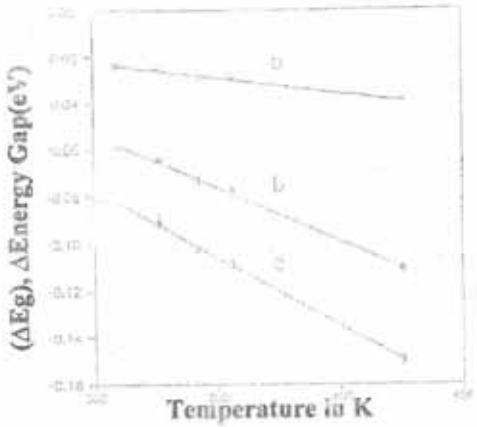

Fig.(2): ΔEg verus T of $CdGeP_2$ compound from fan and Shockly-Bardeen method.
(a)Effect of lattice vibration.
(b) Effect of lattice expansion.
(c) The total effect

This figure shows that ΔEg increases when the temperature is raised due to electron - phonon interaction as shown in curve (a). This effect, which depends on the scattering of carriers by lattice vibrations is described by equations (3) and (4). This figure also shows the effect of lattice dilation (b) which is large in comparison to that of the lattice vibration (a) and their combined effect is shown in *C*. However, in other semiconductors the lattice dilation effect has been shown to be smaller than that of the lattice vibration [8,11 and 12].

Fig. (3) shows different results of Eg versus *T* for different samples. The experimental results (curves 1 and 2) represent two samples of different carrier concentrations[14], while the calculated curves are from Fan's and shockly - Bardeen equation (curve 3), Varshni (curve 6) and Seehra - Seehra (curve 5) empirical relations are in good agreement with the experimental data (curves 1 and 2) Ravindra and Srivastava formula gave a higher values for *Eg* (curve 4) Comparing to the reported experimental values (curves 1 and 2) This could explain that, this formula has been derived from a more pure semiconductors than samples (1) and (2). However, a heavy doped and impure semiconductors are always those crystals which are grown by using solution method . [20,24].

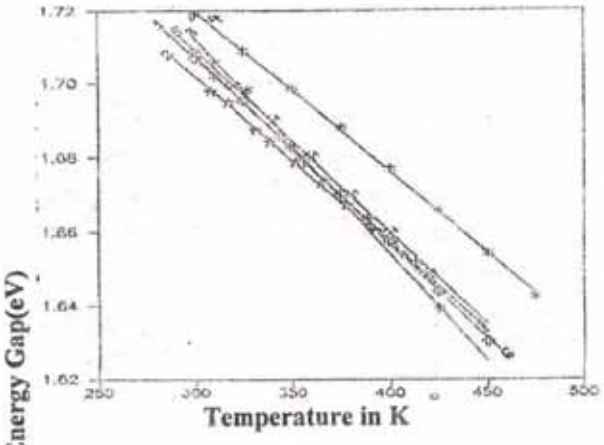

Fig.(3):Eg versus temperature of $CdGeP_2$ compound

(1)From experimental work (sample No.1)
(2) From experimental work (sample No.1)
(3) From Fan and Shockly vardden method.
(4) From Ravindra and Srivastava wquatioa.
(5) From Seehra - Seehra equation.
(6) From Varshni equation.

IV - Conclusions

The method of Fan and shockly-Bardeen is applicable for calculating the temperature dependence of Eg for the ternary semiconducting compound $CdGeP_2$ and the results showed good agreement with experimental work. The effect of the lattice vibration on the temperature variation of *Eg* is smaller than the lattice expansion of this compound

Empirical relations of Varshni and Seehra - Seehra gave better fitting with the experimental results than the Ravindra - Srivastava relation.

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وەستانی بۆشاییيە وزە لەسەر پلەی گەرمی لە نیمچە گەیاندی (CdGeP2) دا.

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پوختە

ڕێگای تیۆری (فان و شۆکلی - باردن) بەکارهات بۆ دۆزینەوەی کاتێکردنی پلەی گەرمی لەسەر بۆشاییە وزە Eg لە پلەکانی گەرمی (300-425 K) لە نیمچە گەیەنەری سیانی (CdGeP2) دا. لە ئەنجامدا بڕیە بۆشاییە وزە لەو پلە گەرمیانەی سەرەوەدا 0.01 ± (1.71 مەتا 1.63) ئەلێکترۆفۆلت بوو وەباشیش هاوشێوە بوو لەگەڵ ئەنجامی تاقیکاریەکاندا. گۆڕانی Eg،Δ Eg لەگەڵ گەرمی دا بەپێی کارلێکی ئەلیکترۆن- فۆنۆن و هەروەها کشانی تۆڕی هاتە گفتوگۆکردن. لە ئەنجامدا دەرکەوت کاریگەری کشانی تۆڕی زیاترە لە لەرەی تۆڕی، بەڵام هەردوو کاریگەریەکە بیندران کە بە شێوەیەکی هێڵی دەگۆڕێن لەگەڵ گۆڕانی پلەی گەرمی لێکۆڵدراوا.

هەروەها پەیوەندیە کردتریەکانی (فارشنی، ڕافیندار ، سریڤاس ، ستافاوە سیهرا) بەکارهێنرا بۆ ژمێرەکردنی گۆڕانی Eg لەگەڵ T دا. بە پێی بەرازردکردنی لەگەڵ ئیشە تاقیگەریە ڕاپۆرت کراوەکان و ئەنجامە ژمێریاریەکان. دەرکەوت کە ئەنجامێکی باشی بەدەستەوە داوە.

الاعتماد الحراري لفجوة الطاقة للشبه الموصل الثلاثي (CdGeP2)

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الخلاصة

استخدمت طريقة فان شوكلي- باردن النظرية لحساب الاعتماد الحراري لفجوة الطاقة للمدى الحراري (300-425 K) للمركب الشبه الموصل الثلاثي (CdGeP2) و النتائج هي : Ev ±0.01 (1.71 - 1.63) في مدى درجات الحرارة المبينة اعلاه و هذه متفقة بشكل جيد مع نتائج الاعمال التجريبية المنشورة. تم مناقشة تغير Eg،Δ Eg مع درجة الحرارة معتمدا على تاثير تفاعل الكترون- فونون و كذلك التمدد الشبيكي. و وجد بان كلاهما تتغير خطيا في مدى درجات الحرارة الكبينة اعلاه.

استخدمت كذلك العلاقات التجريبية لـ (فارشيني ، رافيندرا ،سريفاستاغا و كذلك سيهرا) لحساب تغير Eg مع T . هذه اعطت نتئج جيدة مقارنة مع النتائج التجريبية المنشورة.

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