

# Temperature dependence of the energy band gap of $\text{CuSi}_2\text{P}_3$ semiconductor using PSOPW method

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Theoretical formalism based on the orthogonalized plane wave method supplemented by a potential scaling scheme was used to predict the temperature dependence of energy gap of  $\text{CuSi}_2\text{P}_3$  semiconductor. A computer code in Pascal was used to perform the variation of fundamental energy gap with temperature in the range of 150 K to 800 K. The dependence of energy gap on temperature for lattice dilation contribution, lattice vibration contribution and total temperature effect were performed separately. The results revealed that, as temperature increases, the top of the valence band and the bottom of the conduction band increase, while the energy band gap decreases. Generally, at low temperatures, the energy gap varies slowly and exhibits a nonlinear dependence and approaches linearity as temperature increases. The calculated energy gap of  $\text{CuSi}_2\text{P}_3$  at  $T = 300$  K is 0.4155 eV. The temperature coefficients in the linear region due to lattice dilation contribution, lattice vibration contribution and total temperature effect were calculated as  $-1.101 \times 10^{-5}$  eV/K,  $-1.637 \times 10^{-4}$  eV/K and  $-1.7523 \times 10^{-4}$  eV/K, respectively. Also, the ratio of temperature coefficient of the energy gap due to LV contribution to its value and LD contribution in the linear region is equal to 14.868. That ratio is compared to those of  $\text{CuGe}_2\text{P}_3$  and III-V compounds, where those of the latter show a systematic change with  $E_g$ . Moreover, the  $E_g$  of all the compounds shows a quadratic dependence on the inverse of mean bond length.

Keywords:  $\text{CuSi}_2\text{P}_3$ ; ternary semiconductors; PSOPW; energy gap; Debye temperature

## 1. Introduction

From the point of view of basic science and solid state physics in particular, studies of semiconductor band structures have been central and fundamental. The knowledge of energy gap of semiconductors along with their temperature dependence is of considerable interest from both technological and theoretical points of view. The great interest in the properties of modern materials has led, in recent years, to an extensive and increasing search for new ternary and multinary compounds with tetrahedral structure. Theoretical and experimental efforts have been performed in order to understand the properties of ternary semiconductors, which provide a natural means of tuning the magnitude of the forbidden gap so as to optimize and widen the applications of semiconductor devices [1, 2]. Ternary semiconductors have opened a new

generation of device applications by increasing dramatically the possibilities for engineering the material properties. The band gap and the lattice parameter are among the most important physical parameters, since they are strongly connected with the operating wavelength of opto-electronic devices and also control the band offset and mismatching in different devices [3]. For this purpose, the dependence of the fundamental energy gap on temperature is of a particular importance. The effect of temperature can be estimated by computing the changes of the individual energy bands with temperature.

The (Si, Ge) phases adopt a diamond structure in which tetrahedral bonding around every atom is achieved by providing four electrons per atom [4, 5]. Similar bonding models are also realized in other semiconductors, such as II-VI and III-V [6]. There are also ternary phases with four electrons per atom and tetrahedral bonds, but now elements with a larger range of valences

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and different ratios can be combined to obtain the same electron count, e.g. II-IV-V<sub>2</sub> and I-IV<sub>2</sub>-V<sub>3</sub>. Among these ternary phases, CuSi<sub>2</sub>P<sub>3</sub> and CuGe<sub>2</sub>P<sub>3</sub>, discovered in 1961 [7], have bonding features similar to those of the (Si, Ge) alloys. Both CuSi<sub>2</sub>P<sub>3</sub> and CuGe<sub>2</sub>P<sub>3</sub> were found to adopt zinc blende structure with the Cu–Si or Cu–Ge atoms being mixed on one site. It has also been reported that alloying CuGe<sub>2</sub>P<sub>3</sub> with Ge yields the CuGe<sub>4</sub>P<sub>3</sub> phase with the same structure as CuGe<sub>2</sub>P<sub>3</sub> [8]. But in CuGe<sub>4</sub>P<sub>3</sub>, the Cu and P atoms have to be mixed on one site as opposed to the Cu–Ge mixture in CuGe<sub>2</sub>P<sub>3</sub>. Similarly, alloying CuSi<sub>2</sub>P<sub>3</sub> with Si has been reported to produce phases with a general formula of CuSi<sub>2+x</sub>P<sub>3</sub> (where x = 1, 2 and 3), but the atomic distribution was not established [9]. All phases, regardless of Si or Ge concentration, were found to adopt zinc blende structure. The Cu–Si–P and Cu–Ge–P phases may be very attractive in terms of thermoelectric properties and as statistical mixtures are likely to reduce their thermal conductivity. The presence of elements with different electronegativities may decrease the band gap, making these phosphides suitable for power generation at low temperatures. Omar et al. [10–12] have reported the Hall effect, conductivity, mobility, carrier concentration, energy gap, melting point, bond length, lattice parameter and thermal expansion as a part of elucidation of physical properties of these compounds. Recently, the authors studied the temperature dependence of the energy band gaps of Si, III-V and CuGe<sub>2</sub>P<sub>3</sub> semiconductors [13–15].

The energy bands of semiconductors exhibit considerable and large shifts with temperature. The shifts are due to two effects: the first effect is attributed to the change in the energy of the electrons with volume and the second effect is due to the electron-phonon interaction [16, 17]. The purpose of the present work is to calculate theoretically the temperature dependence of the fundamental energy gap of copper silicon phosphide CuSi<sub>2</sub>P<sub>3</sub> semiconductor, which has the zinc blende structure, with a space group F $\bar{4}3m$ , and belongs to the ternary normal tetrahedral structures of adamantine compounds [8, 13]. The temperature dependence

of the energy gap is determined once considering the lattice dilation only, then considering the lattice vibration only and lastly considering both for the total effect. In order to carry out the calculations, the computer code in Pascal PSOPW.pas was developed and used to simulate variation of energy gap with temperature in the range of 150 K to 800 K. The code was first written by Sami [13] for binary semiconductors and, afterwards, was modified by Abdullah [14] to suit ternaries.

## 2. The OPW method

The widely used term “band structure” commonly refers to the energy levels of electrons which move around in a three dimensional translational invariant system, for example a bulk crystal. In the band approximation, the problem reduces to solving the one-electron Schrödinger equation, in a.u.:

$$[-\nabla^2 + V(r)]\psi_i(k, r) = E_i(k)\psi_i(k, r) \quad (1)$$

where the crystal potential  $V(r)$  is invariant under all symmetry operations of the space group of the crystal.

In the present work, among various methods of band structure calculations, the potential-scaled orthogonalized plane wave (PSOPW) method [13–15] was used to calculate explicitly the eigenfunctions and energy eigenvalues of an electron in the periodic field of a crystal. The PSOPW method is a modification of orthogonalized plane wave (OPW) method [18]. The conceptual basis of OPW method is the expansion of electronic states in terms of plane waves that are orthogonal to the atomic core states. In OPW method, a valence or conduction state function  $\psi(k, r)$  of vector  $k$  is expanded in terms of OPWs:

$$\psi^\alpha(k, r) = \sum_j c(k_j) \chi^\alpha(k_j, r) \quad (2)$$

where  $k_j = k + h_j$ ;  $h_j$  being reciprocal lattice vectors including zero, and  $\chi^\alpha(k_j, r)$  are the plane waves orthogonalized to core states using Schmidt orthogonalization procedure [19]:

$$\chi_{kj}^\alpha \equiv \chi^\alpha(k_j, r) = W_{kj}^\alpha - \sum_c \langle \psi_c | W_{kj}^\alpha \rangle \psi_c \quad (3)$$

where  $W_{kj}^\alpha$  is a plane wave with  $k_j = k + h_j$ ,  $\psi_c$  are the core wave functions, whose eigenvalues  $E_c$  are known, and the summation runs over all core states. The index  $\alpha$  stands for the irreducible representation to which the state function belongs. Hence, the valence and conduction functions are:

$$\psi^\alpha(k, r) = \sum_j c_j (W_{kj}^\alpha - \sum_c \langle \psi_c | W_{kj}^\alpha \rangle \psi_c) \quad (4)$$

where the coefficients of expansion  $c_j \equiv c(k_j)$  as well as the eigenvalues  $E(k)$  are obtained by solving equation 1. With equation 2, the Schrödinger equation 1 yields the secular equation:

$$\langle \chi_{ki}^\alpha | H - E | \chi_{kj}^\alpha \rangle = 0 \quad (5)$$

In OPW method, the crystal potential,  $V(r)$  in equation 1, is approximated as a sum of atomic-like potentials:

$$V(r) = V(r + d_v) = \sum_v v(r + d_v) \quad (6)$$

where  $v(r + d_v)$  is the potential due to the ion at the lattice site  $d_v$ . The atomic-like potential is a sum of Coulomb potential and exchange potential [20].

The Hamiltonian matrix can be brought into block diagonalization where each block corresponds to an irreducible representation of a small group  $G_k$  [21]. This can be done by expanding the function in equation 2 in terms of linear combination of symmetry-adapted orthogonalized plane waves [13].

### 3. Temperature effect

The temperature effect on the energy bands of a semiconductor is a cumulative effect of thermal lattice expansion and electron-phonon interaction [22, 23], which are known as lattice dilation (LD) and lattice vibration (LV), respectively. The LV contribution is commonly referred to as Debye-Waller screening of the effective potential [17, 24]. Thus, the total change of the energy gap  $E_g$  with temperature is [16, 17]:

$$\left( \frac{dE_g}{dT} \right)_{total} = \left( \frac{dE_g}{dT} \right)_{LD} + \left( \frac{dE_g}{dT} \right)_{LV} \quad (7)$$

The one-electron theory of electronic energy band of a crystalline solid is based on the assumption that the crystal is perfect, which is true only at absolute zero degree temperature, where the structure factor is  $\exp(ih \cdot R_v)$ . According to Brooks-Yu theory, the structure factor at temperature  $T$  is given by [25, 26]:

$$S_v(h, T) = \exp(ih \cdot R_v) \exp[-W_v(|h|, T)] \quad (8)$$

where  $W_v(|h|, T)$  is the Debye-Waller factor of the  $v^{\text{th}}$  atom, located at  $R_v$ , and is given by:

$$W_v(|h|, T) = \frac{1}{6} |h|^2 \langle u_v^2 \rangle \quad (9)$$

where  $\langle u_v^2 \rangle$  is the total mean-square displacement of the  $v^{\text{th}}$  atom from its equilibrium position. The quantity  $\langle u_v^2 \rangle$  is temperature-dependent through its dependence on the phonon occupation number [27]. In band calculations, if the structure factors are considered to be  $\exp(ih \cdot R_v)$ , the atomic potentials must be temperature-dependent:

$$V_v(|h|, T) = V_v(|h|) \exp \left[ -\frac{1}{6} |h|^2 \langle u_v^2 \rangle \right]; \quad (10)$$

$v = 1, 2$  for zinc blende

Thus, at a finite temperature  $T$ , the ionic potential seen by an electron is attenuated by the Debye-Waller factor.

In LV calculations, the lattice constant is kept at its absolute zero temperature value while, in LD, the atoms are considered to be rigid at their absolute zero temperature positions. The total effect of temperature requires considering both lattice constant change and potential attenuation. The effect of temperature on the potential due to LV contribution is included in equation 10, while there is not any consideration of the effect of the change of lattice constant on the potential. To account for the change in lattice constant, the potential scaling scheme:

$$V_C(a) = V_C^{(0)} \left( \frac{a_0}{a} \right)^\eta; \eta = 2 \quad (11)$$

was proposed by Sami [13], where  $V_C^{(0)}$  is the crystal potential at temperature  $T = 0$  K, when the lattice constant is  $a_0$ , and  $V_C$  and  $a$  are the crystal potential and lattice constant at a given temperature,

respectively. In PSOPW method, the crystal potential in LD-contribution calculation is scaled according to equation 11, while, for total effect of temperature, the same scaling is performed in addition to the potential attenuation given by equation 10.

#### 4. Temperature dependence calculations

The temperature dependence of the valence band and conduction band and hence the energy band gap is implicit in the lattice constant and Debye-Waller factor. Thus, in calculations, it is sufficient to have values of the crystal lattice constant at different temperatures as well as the corresponding values of mean-square displacements from equilibrium positions for the constituent atoms. The calculations were performed according to the irreducible representations of the point group  $T_d$  of  $F\bar{4}3m$ . The results revealed that the fundamental energy gap is indirect and is given by:

$$E_g^{indirect} = E_c^{1X_1} - E_v^{3\Gamma_{15}} \quad (12)$$

where  $E_v^{3\Gamma_{15}}$  is the energy of the top of the valence band and  $E_c^{1X_1}$  is the energy of the bottom of the conduction band.

In the present work, for  $\text{CuSi}_2\text{P}_3$  semiconductor, the lattice constants at various temperatures were calculated from the linear thermal expansion coefficient [10, 28] and the mean-square atomic displacements from equilibrium position at various temperatures were calculated from the Debye theory [29].

For semiconductors, the variation of lattice constant with temperature starting from zero absolute temperature is nonlinear up to nearly 150 K from which it is almost linear to beyond room temperature [16]. In the linear region, the change of lattice constant with temperature is given by [10, 28]:

$$a(T_2) = a(T_1)[1 + \alpha(T_2 - T_1)] \quad (13)$$

where  $a(T_i)$  is the lattice constant at temperature  $T_i$  and  $\alpha$  is the linear thermal expansion coefficient at room temperature. Knowing that  $a = 5.2481 \text{ \AA}$  and  $\alpha = 5.35 \times 10^{-6} \text{ K}^{-1}$  at  $T = 300 \text{ K}$  [1, 10],

equation 13 was used to calculate the  $a - T$  data for  $\text{CuSi}_2\text{P}_3$  semiconductor, and the results are given in Table 1.

According to Debye theory, the mean-square vibrational amplitude of an atom in a crystal is given by [29, 30]:

$$\langle u^2 \rangle = \frac{3h^2T}{4\pi^2M_a k_B \Theta_D^2} \left[ \frac{1}{4} + \frac{T}{\Theta_D} \varphi\left(\frac{\Theta_D}{T}\right) \right] \quad (14)$$

where

$$\varphi(x) = \frac{1}{x} \int_0^x \frac{t}{\exp t - 1} dt, \quad x = \frac{\Theta_D}{T} \quad (15)$$

is the Debye integral,  $T$  is the crystal temperature,  $\Theta_D$  is the Debye temperature,  $h$  is Planck constant,  $k_B$  is Boltzmann constant and  $M_a$  is the mass of the vibrating atom.

In the present work, the Debye temperature for  $\text{CuSi}_2\text{P}_3$  was calculated from [31, 32]:

$$\Theta_D = c \left[ \frac{T_m}{M_a V^{2/3}} \right]^{1/2} \quad (16)$$

where  $T_m$  is the melting point,  $V$  equals to  $a^3/8$ , is the lattice volume,  $M_a$  is the atomic mass and  $c$  is a constant that has the same value for all compounds within a group. Knowing that the Debye temperature is 429 K for  $\text{CuGe}_2\text{P}_3$  and using the values of the parameters in equation 16 for  $\text{CuGe}_2\text{P}_3$  and  $\text{CuSi}_2\text{P}_3$  [1, 10, 33], the Debye temperature for  $\text{CuSi}_2\text{P}_3$  was obtained (Table 2).

#### 5. Results and analysis

In LD contribution calculation, for each temperature value, the corresponding lattice constant in Table 1 was used in the calculations without considering the Debye-Waller attenuation of atomic potentials. The calculated variation of  $E_v$ ,  $E_c$  and  $E_g$  with temperature due to LD contribution are plotted in Fig. 1, which shows that, as temperature increases,  $E_v$  and  $E_c$  increase while  $E_g$  decreases.

Fig. 1 implies that the dependence of the energy gap on temperature is very close to linearity in the temperature range of 200 K to 400 K. Comparison

Table 1. Lattice constants and mean-square atomic displacements from equilibrium position at various temperatures for CuSi<sub>2</sub>P<sub>3</sub> crystal calculated using equation 13 and equation 14, respectively.

T [K]	a [Å]	$\langle u^2 \rangle [10^{-16} \text{ cm}^2]$ for Cu/Si atoms	$\langle u^2 \rangle [10^{-16} \text{ cm}^2]$ for P atom
50	–	0.003758	0.005107
100	–	0.005426	0.00643
150	5.24379	0.007438	0.008233
200	5.24519	0.009574	0.010255
250	5.24660	0.011764	0.012384
300	5.24800	0.013982	0.014571
350	5.24940	0.016218	0.016793
400	5.25081	0.018464	0.019038
450	5.25221	0.020717	0.021299
500	5.25362	0.022976	0.02357
550	5.25502	0.025238	0.025849
600	5.25642	0.027503	0.028134
650	5.25783	0.029770	0.030424
700	5.25923	0.032039	0.032718
750	5.26063	0.034309	0.035015
800	5.26204	0.036580	0.037314

between Fig. 1a and Fig. 1b reveals that the effect of temperature change on the top of valence band is about 1.5 times greater than its effect on the bottom of conduction band; the variation in  $E_v$  is nearly 21.167 meV as temperature increases from 150 K to 800 K, while it is nearly 14.64 meV for  $E_c$ . The temperature coefficient of the energy band gap in the linear range of 200 K to 400 K due to LD contribution is  $-1.101 \times 10^{-5}$  eV/K.

The LV contribution to the temperature effect was calculated by taking into account the Debye-Waller attenuation of the potentials, while the lattice constant was considered unchanged with temperature. The temperature dependences of  $E_v$ ,  $E_c$  and  $E_g$  due to LV contribution were calculated and are plotted in Fig. 2 which, similar to the LD contribution, shows that  $E_v$  and  $E_c$  increase while  $E_g$  decreases as temperature increases.

Comparison between Fig. 2a and Fig. 2b reveals that the variation in  $E_v$  is nearly 163.33 meV as temperature increases from 150 K to 800 K, while it is nearly 68.96 meV for  $E_c$ , that is, the effect of temperature change on the top of valence band is about 2.5 times greater than its effect on

the bottom of conduction band. The temperature coefficient of the energy gap in the linear range of 200 K to 400 K due to LV contribution is  $-1.637 \times 10^{-4}$  eV/K.

The total effect of temperature, LDV contribution, was calculated by considering the change of lattice constant with temperature along with Debye-Waller attenuation. The calculated total temperature dependence of  $E_v$ ,  $E_c$  and  $E_g$  are plotted in Fig. 3 which also shows that, as temperature increases,  $E_v$  and  $E_c$  increase, while  $E_g$  decreases. Comparison between Fig. 3a and Fig. 3b shows that the effect of temperature change on  $E_v$ , similar to LV contribution, is nearly 2.5 times greater than its effect on  $E_c$ ; the variation in  $E_v$  is nearly 187.077 meV as temperature increases from 150 K to 800 K, while it is nearly 83.56 meV for  $E_c$ . This similarity to the LV case is obvious because the dominant contribution to the temperature effect is that of the LV. The calculated energy gap at room temperature for CuSi<sub>2</sub>P<sub>3</sub> and the temperature coefficient of the energy gap in the linear range of 200 K to 400 K due to LDV contribution are given in Table 3.



Table 2. Debye temperature for  $\text{CuSi}_2\text{P}_3$  compound calculated from the parameters in equation 16, which are also given.

Compound	Melting temperature $T_m$ [K]	Lattice constant $a$ [Å]	Mean atomic mass $M$ [a.u.]	Debye temperature $\Theta_D$ [K]
$\text{CuGe}_2\text{P}_3$	1103 [10]	5.3777 [33]	$\frac{1}{3}\text{Cu} + \frac{2}{3}\text{Ge} + \text{P} = 100.55$	429 [33]
$\text{CuSi}_2\text{P}_3$	1451 [10]	5.2480 [1, 33]	$\frac{1}{3}\text{Cu} + \frac{2}{3}\text{Si} + \text{P} = 70.88$	601 [This work]

Table 3. Energy gap, temperature coefficient of energy gap in the linear range and  $\alpha_{LV}/\alpha_{LD}$  for  $\text{CuSi}_2\text{P}_3$  compared with  $\text{CuGe}_2\text{P}_3$  [14] and some III-V compounds [13], all at room temperature.

Compound	Energy gap [eV]	$\frac{dE_g}{dT}$ [eV/K]	$\frac{\alpha_{LV}}{\alpha_{LD}}$
$\text{CuSi}_2\text{P}_3$	0.4155	$-1.7523 \times 10^{-4}$	14.868
$\text{CuGe}_2\text{P}_3$	0.2945	$-2.1946 \times 10^{-4}$	15.272
GaP	2.2659	$-3.7636 \times 10^{-4}$	13.676
GaAs	1.4368	$-3.4003 \times 10^{-4}$	7.7434
InP	1.3418	$-3.2972 \times 10^{-4}$	3.9860
GaSb	0.7525	$-3.7500 \times 10^{-4}$	1.5335
InAs	0.3631	$-3.2952 \times 10^{-4}$	2.1439

Comparison between Fig. 1 and Fig. 2 shows that LV contribution to the changes in  $E_v$ ,  $E_c$  and  $E_g$  is greater than that of LD; actually, by a factor of 7.7 for  $E_v$ , 4.7 for  $E_c$  and 14.4 for  $E_g$ . On the other hand, the temperature coefficient of the energy gap in the linear region, around  $T = 300$  K, due to LV contribution is greater than that due to LD contribution by a factor 14.868 and this factor is comparable with the same factors of  $\text{CuGe}_2\text{P}_3$  and GaP [13, 14] (Table 3). The LV contribution is greater because the effect of thermal agitation of the constituent atoms is much greater than that of thermal expansion of the lattice. Thermal expansion coefficients of the family of the groups I-IV<sub>2</sub>-V<sub>3</sub> and III-V compounds are of order of  $10^{-6} \text{ K}^{-1}$  which is true for most semiconductors [10]. The increase of valence and conduction band energies with temperature, which is observed in the present work, is implicit in the formation of the valence and conduction bands. Present results are consistent with the fact that an increase

in temperature causes lattice dilation and lattice vibration, where both result in a reduction of potential because of an increase in lattice constant for the former and the Debye-Waller attenuation for the latter as well as the potential scaling for lattice dilation and total effect of temperature.

Since both  $\text{CuSi}_2\text{P}_3$  and  $\text{CuGe}_2\text{P}_3$  compounds belong to the same group and have the same crystal structure and atomic distribution except that Ge is exchanged by Si, so any difference in electronic properties could be expected to be similar to that between Ge and Si. Accordingly, the ratio of the energy gaps  $[E_g(\text{Si})/E_g(\text{Ge})]$  could be approximately equal to that of  $[E_g(\text{CuSi}_2\text{P}_3)/E_g(\text{CuGe}_2\text{P}_3)]$ , that is:

$$\frac{E_g(\text{CuSi}_2\text{P}_3)}{E_g(\text{CuGe}_2\text{P}_3)} \cong \frac{E_g(\text{Si})}{E_g(\text{Ge})} \quad (17)$$

According to this relation the energy gap of 0.27 eV for  $\text{CuGe}_2\text{P}_3$  calculated from the experimental data [34] gives a value of 0.48 eV for  $\text{CuSi}_2\text{P}_3$ , which is 10 % higher than that obtained from the PSOPW method in this work.

Both compounds  $\text{CuSi}_2\text{P}_3$  and  $\text{CuGe}_2\text{P}_3$  are members of the ternary I-IV<sub>2</sub>-V<sub>3</sub> family and are direct analogues to binary III-V group compounds, which arises by the replacement of the III cations by Cu and Si (or Ge) atoms. Thus, the results of the present work can be compared with those of  $\text{CuGe}_2\text{P}_3$  and III-V compounds. For that purpose, the dependence of  $(\alpha_{LV}/\alpha_{LD})$  in the linear region (200 K to 400 K) on energy gap  $E_g$  at 300 K as well as on the reciprocal mean bond length  $(1/d_{\text{mean}})$  are considered as shown in Fig. 4 and Fig. 5. Values of  $(\alpha_{LV}/\alpha_{LD})$  for  $\text{CuSi}_2\text{P}_3$ ,  $\text{CuGe}_2\text{P}_3$  [14] and compounds from group III-V [13] are given in Table 3.

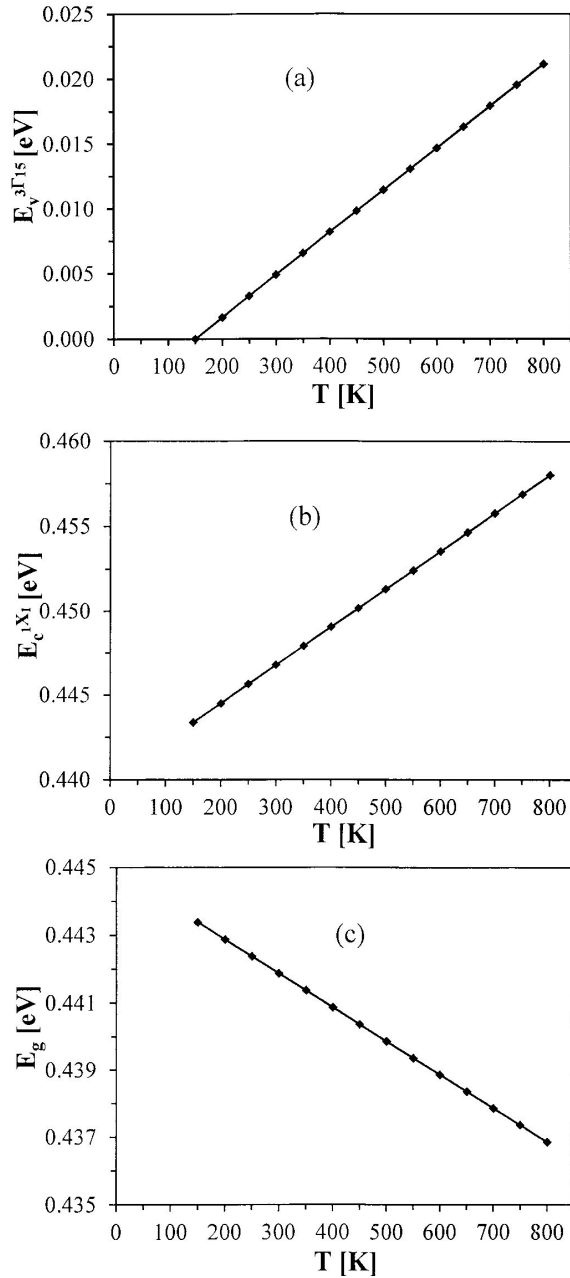


Fig. 1. Lattice dilation contribution to the temperature dependence of (a) top of the valence band, (b) bottom of the conduction band and (c) the energy gap for  $\text{CuSi}_2\text{P}_3$ .

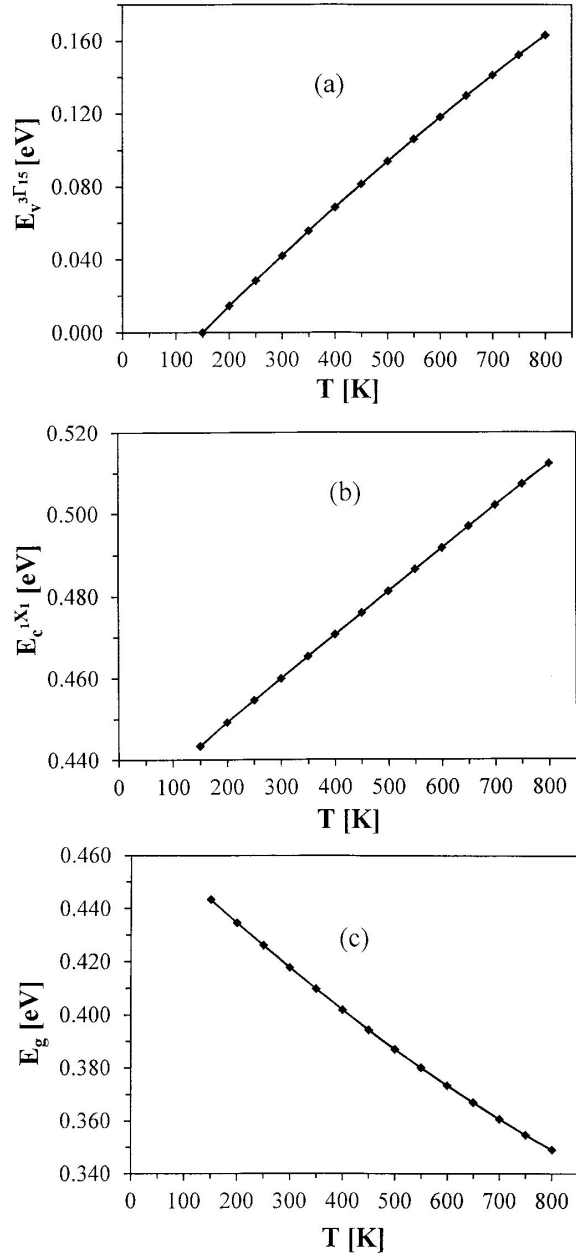


Fig. 2. Lattice vibration contribution to the temperature dependence of (a) top of the valence band, (b) bottom of the conduction band and (c) the energy gap for  $\text{CuSi}_2\text{P}_3$ .

The fitting relation obtained from Fig. 4 for III-V which is in the form  $E_g = 57572 \times (1/d_{\text{mean}})^{12.03}$  was modified to a form  $E_g = 9154 \times (1/d_{\text{mean}})^{12.28}$  with the assumption of being applicable to  $\text{CuGe}_2\text{P}_3$  since this ternary and  $\text{CuSi}_2\text{P}_3$

both belong to the same group compounds of I-IV<sub>2</sub>-V<sub>3</sub>. This relation is obtained by multiplying the x-axis values of  $(1/d_{\text{mean}})$  by a factor of 1.182. According to this form, an energy gap of 0.45 eV was obtained for  $\text{CuSi}_2\text{P}_3$ . This value

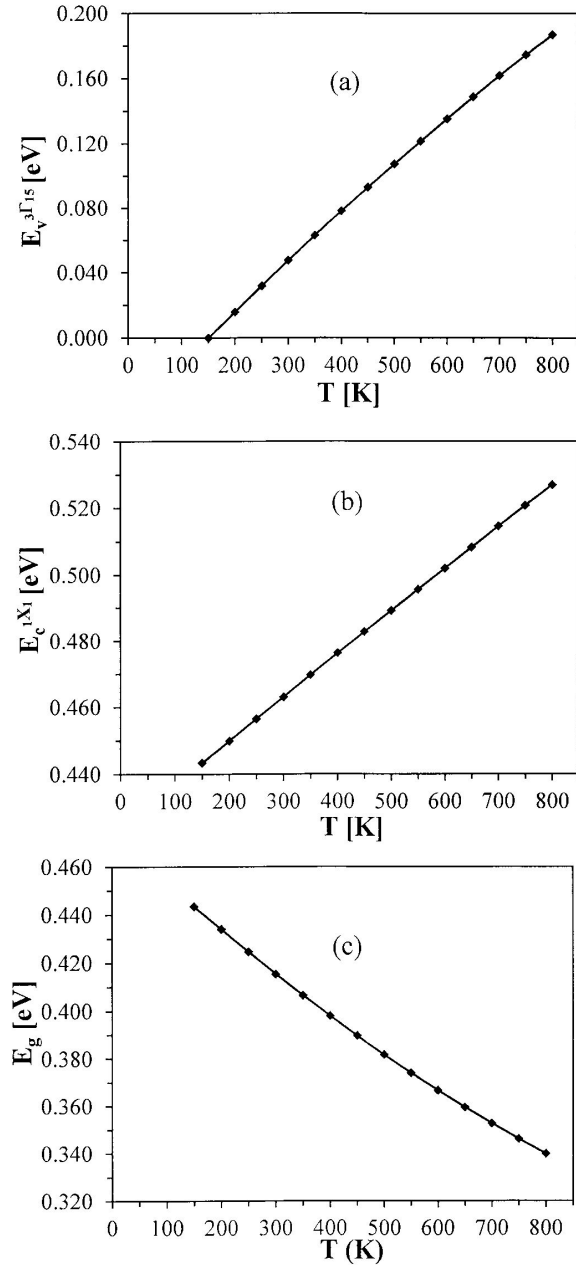


Fig. 3. Total temperature dependence of (a) top of the valence band, (b) bottom of the conduction band and (c) the energy gap for  $\text{CuSi}_2\text{P}_3$ .

is in the mid point between that obtained from equation 17 and that calculated by PSOPW method. To verify values of  $(\alpha_{LV}/\alpha_{LD})$  for  $\text{CuSi}_2\text{P}_3$ , the fitting curve relation to the binary compounds from III-V in the form of  $(\alpha_{LV}/\alpha_{LD}) = 3.802 \times E_g^{1.334}$  was

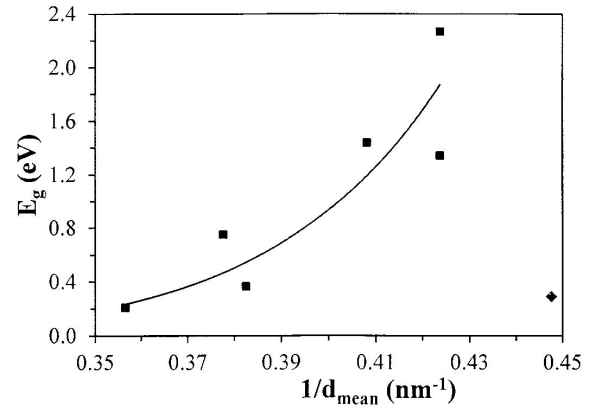


Fig. 4. Energy gap as a function of inverse mean bonding length for III-V and  $\text{CuGe}_2\text{P}_3$  compounds. The diamond shape circle point is for  $\text{CuGe}_2\text{P}_3$ .

modified to the form  $(\alpha_{LV}/\alpha_{LD}) = 82.11 \times E_g^{1.381}$  which is applicable to  $\text{CuGe}_2\text{P}_3$ . According to this relation, the  $E_g$  value of 0.45 eV for  $\text{CuSi}_2\text{P}_3$  obtained from Fig. 4 gives the ratio  $(\alpha_{LV}/\alpha_{LD})$  of 27 which is higher than that reported for  $\text{CuGe}_2\text{P}_3$ . The differences between the dependences for I-IV<sub>2</sub>-V<sub>3</sub> and III-V compounds in Fig. 4 and Fig. 5 are due to the differences between their ionicities, however the modifications to the empirical relations obtained from these two figures are dependent on the same principles explained in references [31, 35].

As  $\text{CuSi}_2\text{P}_3$  has not been so well studied, especially in zinc blende structure, experimentally measured energy gap and/or its change with temperature was not found. However, an energy gap related property for  $\text{CuSi}_2\text{P}_3$  can be compared to that of some III-V semiconductors. The calculated  $\alpha_{LD}/\alpha_{\text{total}}$  for  $\text{CuSi}_2\text{P}_3$  (equals to 0.0628 at 300 K with  $a = 5.248 \text{ \AA}$ ) compared with that of  $\text{CuGe}_2\text{P}_3$  (equals to 0.060 at 300 K with  $a = 5.377 \text{ \AA}$ ) [14] fits very well to the curve obtained from  $\alpha_{LD}/\alpha_{\text{total}}$  “temperature coefficient of lattice dilation contribution relative to its value due to the total effect of temperature on the energy gap” versus lattice constant for some III-V semiconductors [13] as shown in Fig. 6. This may be considered, to some extent, as a justification of the theoretical framework proposed in this work.



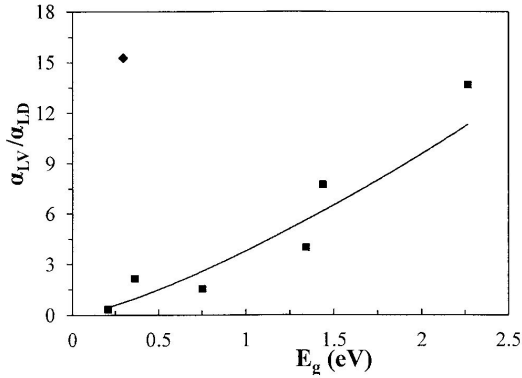


Fig. 5.  $\alpha_{LV}/\alpha_{LD}$  as a function of energy gap for III-V [13] and CuGe<sub>2</sub>P<sub>3</sub> compounds. The solid diamond shape point is for CuGe<sub>2</sub>P<sub>3</sub>.

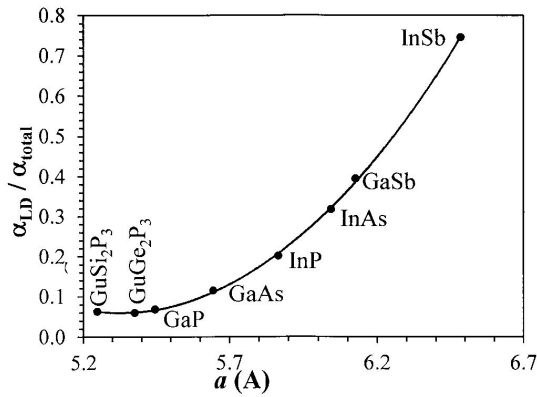


Fig. 6.  $\alpha_{LD}/\alpha_{total}$  of the energy gap as a function of lattice constant at  $T = 300$  K for some III-V semiconductors [13], CuGe<sub>2</sub>P<sub>3</sub> [14] and CuSi<sub>2</sub>P<sub>3</sub> in the present work. The solid line is a fit to the points for III-V compounds.

## 6. Conclusions

The theoretical calculation using OPW method with a potential scaling scheme (termed PSOPW method) is successful to predict the temperature dependence of the fundamental energy band gap of CuSi<sub>2</sub>P<sub>3</sub> zinc blende type semiconductor. The energy gap temperature dependence implies that variation of  $E_v$  with temperature has greater contribution to changes in the energy band gap than the variation of  $E_c$  has. The results of the temperature coefficients near  $T = 300$  K due to lattice dilation contribution and lattice vibration contribution as well as total effect of temperature show

that the most important contribution to the energy gap-temperature dependence is the lattice vibration contribution.

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