

LATTICE VIBRATION AND LATTICE DILATION EFFECTS IN THE TEMPERATURE DEPENDENCE OF THE SILICON ENERGY GAP

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ABSTRACT

A theoretical calculation using potential scaled orthogonalized plane wave (PSOPW) method was used and implemented to predict the effect of lattice vibration and lattice dilation in the temperature dependence of the fundamental energy gap for Si. Through the calculation of the maximum of valence band and minimum of conduction band at different temperatures, the effect of temperature on the energy gap for lattice vibration (electron-phonon interaction), lattice dilation (thermal expansion) and total effect were calculated separately using the computer Pascal code PSOPW. The calculation for the temperature dependence of the band gaps predict the contribution of lattice vibration dependence of the energy gap is more than that of lattice dilation and the rate of change of valence band with temperature is more than that of the conduction band.

Keywords: Energy Gap; Energy band; LV; LD; LDV

INTRODUCTION

At present, semiconductors provide the materials basis for a number of well-established commercial technologies, as well as new cutting-edge classes of electronic and optoelectronic devices [1-3]. The energy bands of semiconductors exhibit considerable shifts with temperature, which are due to two effects. The first effect is attributed to the change of the energy of the electrons with volume and the second effect is due to the electron-phonon interaction (lattice vibration)[4-6]. Temperature leads to red shift of band gap which is an experimental evidence of the energy bands temperature dependence.

The purpose of the present work is to calculate theoretically the temperature dependence of the energy gap for Si semiconductor, and that is accomplished through calculating the dependence of bottom of the conduction band and the top of the valence band. To calculate E_g , one needs to calculate the minimum of conduction and the maximum of valence band which are the solutions of Schrodinger equation of one-electron in the periodic field of the crystal. To solve Schrodinger equation for a bulk crystal, one is obliged to rely on quantum mechanics, group theory and band theory approximations, the solution reveals the electronic structure of the crystal. The electronic structure of a material is usually defined as the complex of wave functions and (quasi) energies which are the solutions of the Schrodinger equation for the

electrons in that material. 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. The fundamental problem is to solve Schrodinger equation for the motion of an electron in such a potential. This potential certainly reflects the symmetry of the crystal. The most important approximation used in modern electronic structure calculations is the effective one particle approximation, which represents the electronic states of the whole crystal by “determinantal wave functions”; antisymmetrized products of one-electron functions. The behaviour of a system formed by

many electrons is studied by looking at the behaviour of one particular electron in an effective field. The effective field is the sum of the fields of the nuclei, the other electrons and possible external fields.

THEORY

(PSOPW) METHOD

To calculate band structure, which is the base of almost all the electronic properties of crystals, there are some of common methods employed in calculations of actual bands [7-9]. In the present work, the potential-scaled orthogonalized plane wave (PSOPW) method [10,11] was used, the method is a modification of orthogonalized plane wave (OPW) method [12], among various methods of band structure calculations that is used to calculate explicitly the eigenfunctions and energy eigenvalues for an electron in the periodic field of a crystal. The OPW method corresponds to expansion of the electronic states in terms of plane waves that are orthogonal to the atomic core states. The advantage of this method is the rapid convergence, that is, the number of plane waves required for performing electronic band structure calculations is less compared to using just plane waves. This is due to the fact that in the secular determinant, the off-diagonal elements are quite small and decrease very fast as the wave vector of the orthogonalized plane wave increases. Technically, most other electronic structure methods can be used to carry on such a task.

The PSOPW method is a modification of OPW in that it includes a scaling of the crystal potential without which the method is inconvenient to predict successively the effect of temperature on the energy gap. Obviously, the method constitutes as well the crystal potential attenuation due to lattice vibration [10]. The key element of a mixed basis set is that it is made up of two other basis sets having totally different mathematical character. Alternatively, one can also say the composing basis sets are generated by two different Hamiltonians. One part of the mixed basis set consists invariably of plane waves generated by a constant potential Hamiltonian. The other part is usually related to a Hamiltonian with a spherically symmetric potential which generates localized functions. This part is brought into cope with the singularities in the crystal potential introduced by the nuclei.

The theoretical backbone of present work is the OPW method modified by a potential

scale scheme and combined with Debye-Waller attenuation factors to calculate the temperature dependence energy gap of Si. To handle the calculation task, a computer code in Pascal, constructed initially for binary and ternary crystals [10,11], was modified and used to be applicable for Si crystal. The calculations were performed using modified code for the irreducible representations Γ and Δ (near X) to which the top of the valence band and bottom of the conduction band belong. The crystal wave functions have been symmetry-adapted to those irreducible representations only.

TEMPERATURE DEPENDENCE OF ENERGY GAP

It is well known that the band gap of semiconductors change noticeably with temperature in most experiments and applications. This is due to the change in band structure of crystals as temperature changes. There are two reasons (or effects) for this change of band structure with temperatures: the thermal expansion of the lattice, related to the change of the electron energies with the volume and the direct renormalization of band energies with the volume due to electron-phonon interaction [5,6]. The change of the band gap E_g with temperature can be written as:

$$\left(\frac{dE_g}{dT}\right)_{total} = \left(\frac{dE_g}{dT}\right)_{LD} + \left(\frac{dE_g}{dT}\right)_{LV} \quad (2.1)$$

The first term at the right hand side represents the contribution of the thermal-expansion effect, or what is often called the lattice dilation (LD) contribution, accounts for the effect of the change of lattice constant on the energy bands. LD effect is expected since the electronic energy bands are formed because of the overlapping of electronic wave functions, the extent of which is dependent upon the distances between neighbouring atoms (ions). The second term is the contribution of the electron-phonon interaction at constant volume, or which is often called lattice vibration (LV) contribution. The calculation of LD contribution, LV contribution and total effect of temperature LDV for Si was performed using potential scaled-OPW (PSOPW) method.

The top of VB is three-fold degenerate and belongs to the irreducible representation $^3\Gamma_{15}$. The bottom of CB is nondegenerate and belongs to the irreducible representation $^1\Delta_1$. So, present calculations are limited to those at the symmetry point Γ and Δ for finding solutions of the secular equation belonging to these irreducible representations only. The energy gap then is to be calculated as:

$$E_g = E_c^{^1\Delta_1} - E_v^{^3\Gamma_{15}} \quad (2.2)$$

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. At finite temperature, the energy of the electron is subject to change because of the interactions between electrons and phonons. The temperature dependence of a semiconductor band structure is obtained through temperature-dependent potential. The ionic potential seen by an electron is attenuated by a factor known as Debye-Waller factor which is a measure of thermal vibration of that ion. According to Brooks-Yu theory, at finite temperatures, the structure factor, at a given temperature T , is replaced by a temperature-dependent one given by [13,14]:

$$S_v(\mathbf{h}, T) = \exp(i\mathbf{h} \cdot \mathbf{R}_v) \exp[-W_v(\mathbf{h}, T)] \quad (2.3)$$

where $w_{v,(\mathbf{h}|, T)}$ is the Debye–Waller factor for the atom v at temperature T in Kelvins and is defined as:

$$W_v(\mathbf{h}, T) = \frac{1}{6} |\mathbf{h}|^2 \langle u_v^2 \rangle \quad (2.4)$$

where $\langle u_v^2 \rangle$ is the total mean–square displacement of the atom v from its equilibrium position at temperature T . The mean-square displacement is temperature dependent through its dependence on the phonon occupation number which obeys Bose–Einstein distribution law [15]. This amounts to replacing $w_{v,(\mathbf{h}|)}$ by a temperature–dependent:

$$V_v(\mathbf{h}, T) = V_v(\mathbf{h}) \exp\left[-\frac{1}{6} |\mathbf{h}|^2 \langle u_v^2 \rangle\right]; \quad (2.5)$$

The effect of the lattice vibration on the potential is considered through a potential attenuation as in Eq. (2.5), while the effect of lattice dilation contribution is taken into account through change of the lattice constant with temperature and considering the atoms to be rigid at their absolute zero temperature positions. On the other hand, when the total effect of temperature is required, both potential attenuation and changes in the lattice constant with temperature must be considered in the implementation of the OPW method. It is clear from above consideration that the effect of temperature on the crystal potential appears through Eq. (2.5) for lattice vibration contribution but the effect of interatomic distance on the potential is given by[10]:

$$V_c(d) = V_c^{(0)} \left(\frac{d_o}{d}\right)^2 \quad (2.6)$$

which means that the crystal potential decreases with an increase in interatomic, where $V_c^{(0)}$ is the crystal potential at absolute zero temperature when the interatomic distance is d_o , $V_c(d)$ and d are the crystal potential and equilibrium interatomic distance at a given temperature, respectively. For diamond and zinc blend lattice:

$$d = \frac{a}{4} |(1,1,1)|^{1/2} \quad (2.7)$$

Substituting Eq.(2.7) in Eq.(2.6), one gets:

$$V_c(d) = V_c^{(0)} \left(\frac{a_o}{a}\right)^2 \quad (2.8)$$

Where a_o and a are the lattice constants at absolute zero temperature and at a given

temperature, respectively. The calculation of LD–contribution and the total effect of temperature LDV on the energy gap were considered according to PSOPW method. In PSOPW method, the crystal potential is scaled through Eq.(2.8) for LD–contribution calculation, while, for calculation of total effect of temperature, the same scaling is performed in addition to the potential attenuation given by Eq.(2.5).

The effect of temperature on the band structure of a crystal can be calculated if sufficient values of lattice constant and total mean-square displacement at various given temperatures are known.

RESULTS AND DISCUSSION

LATTICE CONSTANT AND MEAN SQUARE ATOMIC DISPLACEMENT TEMPERATURE DEPENDENCE

The variation of lattice constant with temperature for semiconductors, starting from zero absolute temperature, is non-linear up to nearly 200K from which it is almost linear to and beyond room temperature [6]. The variation of lattice constant with temperature, in the linear region, is given by [16,17]:

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

Where $a(T)$ is lattice constant at temperature T and α is the linear thermal expansion coefficient at room temperature. Knowing that $a(300) = 5.431 \text{ \AA}$ [2,9] for Si, Eq. (3.1) was used to calculate the $a-T$ data for $\alpha = 3.73 \times 10^{-6} \text{ K}^{-1}$ [17] at $T=300\text{K}$, and the obtained values of lattice constant at various temperatures for Si are given in Table1.

Debye theory [18] was used to calculate the mean-square atomic displacements from equilibrium position at various temperatures. According to Debye theory, the motion of atoms in a simple crystal lattice containing N atoms is the superposition of $3N$ harmonic waves propagating in the material. In the approximation of Debye, the $3N$ waves have a frequency distributed quadratically between zero and a maximum frequency, $\nu_m = k_B \Theta_D / h$, where Θ_D is the Debye temperature, h is Planck's constant and k_B is Boltzmann's constant. Specifically, Debye theory predicts for the mean-square vibrational amplitude of an atom in a crystal the following expression [18]:

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

where

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

is the Debye integral, T is the crystal temperature and M_a is the mass of the vibrating atom. Once $\langle u^2 \rangle$ is known, the Debye-Waller exponent is easily calculated. Numerical method was used to calculate the mean-square atomic displacements for Si from equilibrium position at temperatures for which lattice constant values are

available. For completeness, the mean-square displacements $\langle u^2 \rangle$ are also given in Table1.

Table1: Lattice constant and mean-square atomic displacements from equilibrium position at various temperatures for Si calculated using linear thermal expansion coefficient [17] and Debye model [18]

T (K)	a (Å)	$\langle u^2 \rangle$ (in 10^{-16} cm ²)
50	-	0.006940
100	-	0.007720
150	-	0.008940
200	5.42897	0.010460
250	5.42999	0.012140
300	5.43100	0.013940
350	5.43201	0.015800
400	5.43303	0.017700
450	5.43404	0.019660
500	5.43505	0.021620
550	5.43606	0.023600
600	5.43708	0.025600
650	5.43809	0.027620
700	5.43910	0.029640

LATTICE DILATION CONTRIBUTION

The calculation of energy gap shift with temperature for the lattice dilation contribution was calculated by taking into account the lattice constant dependence on temperature. Thus, for each temperature value, the corresponding lattice constant was used in calculations with PSOPW without considering the Debye-Waller attenuation of atomic potentials, that is, at a given temperature each constituent atom is regarded to be fixed rigidly at their equilibrium positions. The calculations were performed first for the irreducible representation Δ which gives the energy eigenvalue of the bottom of the conduction band, then for the irreducible representation Γ which gives the energy eigenvalues of the top of the valence band. Afterwards, the energy gap was calculated as $E_g = E_c - E_v$ for that temperature. The same procedure was performed for all values of each and every lattice constant at various temperatures.

The calculated variation of E_c , E_v and E_g with temperature due to LD contribution are plotted in Figure 1(a,b, and c), respectively, which shows that E_v and E_c increase while E_g decreases as temperature increases and show a linear variation of E_c , E_v and E_g with temperature in the temperature range (200 K-400 K). Comparison between Figs. (1a) and (1b) reveals that the variation in E_v is nearly 6.685 meV as temperature increases from 200K to 400K while it is nearly 2.685 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. This implies that variation of E_c with temperature has less contribution to changes in E_g than the variation of E_v has. The temperature coefficient of the energy gap in the linear range due to LD contribution is:

$$\left(\frac{dE_g}{dT}\right)_{LD} = -0.2002 \times 10^{-4} \text{ eV/K}$$

This is close to results obtained by other workers [2,7-9,14].

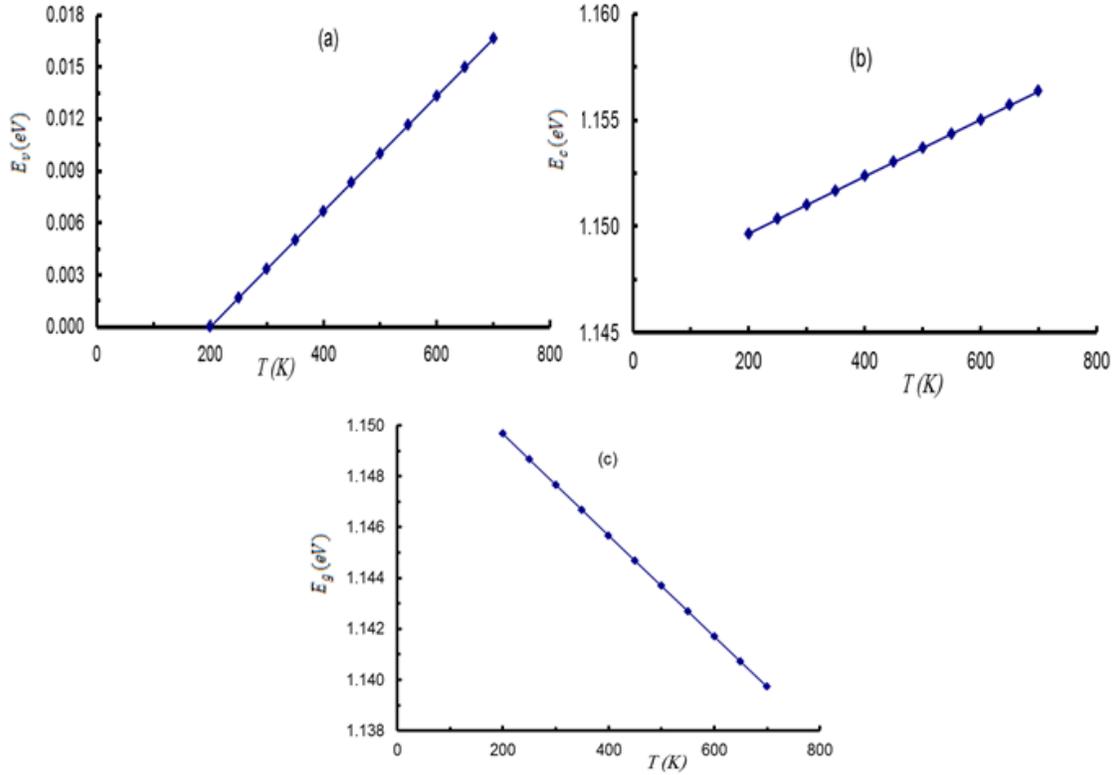


Figure 1: Lattice dilation contribution to the temperature dependence of the (a) top of the valence band, (b) bottom of the conduction band and (c) the energy gap

LATTICE VIBRATION CONTRIBUTION

The effect of lattice vibration or electron-phonon interaction calculated by adding Debye-Waller attenuation to the atomic potential for each constituent atoms at a constant volume, that is, a constant lattice constant. For each value of temperature the corresponding mean-square displacements of the constituent atoms were used to calculate the crystal potential attenuation. Similar to the case of LD contribution, calculations were performed for the irreducible representation Δ , then for Γ and from their results the energy gap was calculated. The temperature dependence of E_c , E_v and E_g due to LV contribution were calculated and are plotted in Figure 2 (a,b, and c), respectively. Comparison between Figs. (2a) and (2b) reveals that the variation in E_v is nearly 57.64 meV as temperature increases from 200K-400K while it is nearly 5.254

meV for E_c , that is, the effect of temperature change on the top of valence band is about 10 times greater than its effect on the bottom of conduction band. This implies that variation of E_c with temperature has less contribution to changes in E_g than the variation of E_v has. The temperature coefficient of the energy gap in the linear range due to LV contribution is:

$$\left(\frac{dE_g}{dT}\right)_{LV} = -2.5747 \times 10^{-4} \text{ eV/K}$$

Which is in good agreement with results obtained by other workers [2,7-9,14].

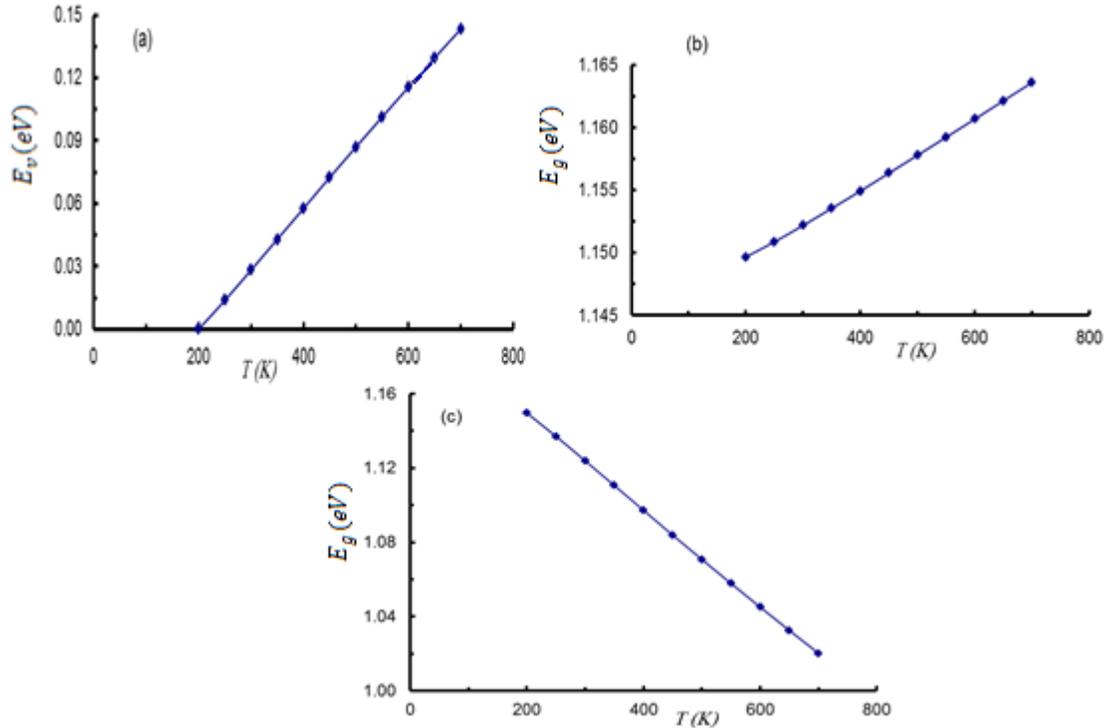


Figure 2: Lattice vibration contribution to the temperature dependence of the (a) top of the valence band, (b) bottom of the conduction band and (c) the energy gap

TOTAL EFFECT OF TEMPERATURE

The total effect of temperature, LDV contribution, was calculated by considering the change of lattice constant with temperature along with Debye-Waller attenuation. For a given temperature, the corresponding lattice constant and mean-square displacements of Table1 were taken into account. Comparison between Figs.(3a) and (3b) reveals that the variation in E_v is nearly 67.156 meV as temperature increases from 200K-400K while it is nearly 9.102 meV for E_c , that is, the effect of temperature change on the top of valence band is about 7 times greater than its effect on the bottom of conduction band. This implies that variation of E_c with temperature has less contribution to changes in E_g than the variation of E_v has. The results show that the energy gap at room temperature is

1.121 eV and the temperature coefficient of the energy gap in the linear range due to LDV contribution is:

$$\left(\frac{dE_g}{dT}\right)_{LDV} = -2.8669 \times 10^{-4} \text{ eV/K}$$

Which is in good agreement with results obtained by other workers [2,7-9,19].

The width of the energy gap decreases with temperature increase. In general, the energy gap-temperature dependence is slow and non-linear at low temperatures and becomes more rapid and linear as the room temperature is approached. The separate calculations of Deby-Waller (LV) and lattice-expansion (LD) effects show that the major part of the energy shift is caused by the lattice vibration effect, with only a small fraction caused by lattice expansion. Comparison between Figs. (1c, 2c, and 3c) shows that the contribution of LV to the changes of E_g with temperature within the linear range is greater than the LD contribution by a factor of 12.8, that is, the LV contribution is the most dominant and contributes to about 89% of the shift of E_g with temperature. This behaviour of E_g with temperature is consistent with many experimental evidences [2,3,19].

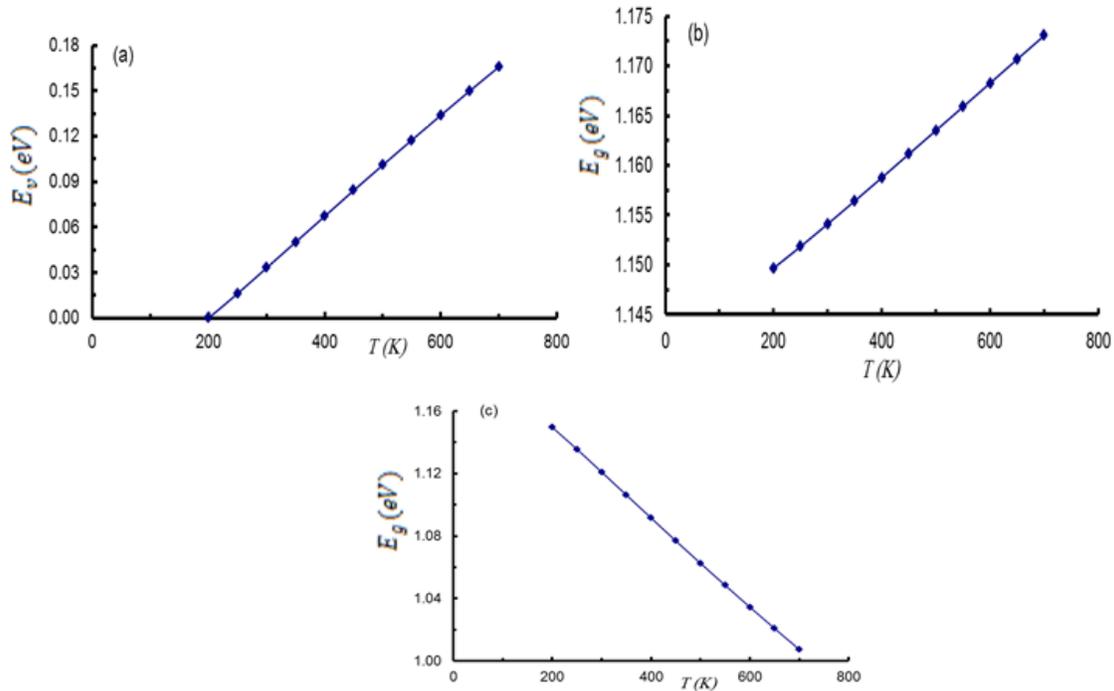


Figure 3: Total temperature dependence of the (a) top of the valence band, (b) bottom of the conduction band and (c) the energy gap

CONCLUSION

The results indicate that the energy gap-temperature dependence is linear in the temperature range (200K-400K) and the temperature coefficients in the linear region, due to lattice dilation and lattice vibration contributions as well as total temperature effect, were calculated and the results are in good agreement with those available from other works. The results show that the most important contribution to the energy gap-temperature dependence is the lattice vibration contribution. In the present work, as expected, the Deby-Waller contribution to the total effect of temperature is larger than the effect of lattice dilation with potential scaling. While the volume or dilation contribution has less contribution to the total temperature coefficient of the energy gap and its effect is to increase the temperature coefficients to the final values, that is, the total effect of temperature on energy gap.

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