Analysis of equations of state and temperature dependence of thermal expansivity and bulk modulus for silicon

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Abstract. In the present paper an attempt has been made for the comparative study of different equations of state for silicon (Phase-1, cubic diamond structure) in the pressure range of 0-11 GPa. We compare the results of different equations of state (EOS) with available experimental data. The Kwon and Kim EOS is found to give far better agreement with the available experimental data. Results obtained by Poirier-Tarantola, Vinet, Tait and Suzuki’s equations of state are not giving satisfactory agreement with the available experimental data. In the present study simple methods based on thermodynamic functions are presented to investigate the temperature dependence of thermal expansivity and bulk modulus for silicon. The results are reported for silicon. The calculated values of thermal expansivity are in good agreement with experimental data.

1. Introduction
Compression behaviour of the diamond-type semiconductors has been a topic of experimental and theoretical study for a long time [1, 2]. Large amount of theoretical [3-5] and experimental work [6-9] have been devoted to the high pressure studies of Group IV element silicon. Angilella G.G.N [10] et.al have summarized some studies, both theoretical and experimental, relating to x-ray diffraction for diamond –lattice semiconductors under compression. Silicon undergoes a series of structure phase transition with pressure: cubic diamond [CD] to β-Sn, to simple hexagonal, to hexagonal closed packed, to face centred cubic [11]. Since the CD phase has the lowest minimum total energy, it is the most stable phase of silicon at ambient pressure [11].

Studies on equations of state [EOS] are very useful to understand the high pressure behaviour of silicon. In the present paper we report the analysis of equations of state for the CD-phase of silicon in the pressure range of 0-11 GPa. Attempt has been made to identify the better equation of state that gives satisfactory agreement with the available experimental data. In the present study simple methods based on thermodynamic functions are presented to investigate the temperature dependence of thermal expansivity and bulk modulus for the CD phase of silicon.
2. Method of analysis

2.1. Equations of state

We consider a number of equations of state representing the relationship between pressure and volume at a fixed temperature. These are briefly described as follows along with the basic assumptions implied in their derivations.

Kwon and Kim [12, 13] presented the following method for the determination of equation of state

\[ \frac{dP}{dV} = \frac{B}{P_0 V_0} \]  

(1)

Or,

\[ V - V_0 = \frac{P - P_0}{B_0} \]  

(2)

Where, \( P_0 \) is the atmospheric pressure referred as zero, \( V_0 \) and \( B_0 \) are the volume and isothermal bulk modulus at zero pressure. Equation (2) thus gives,

\[ P = B_0 \left( 1 - \frac{V}{V_0} \right) \]  

(3)

Equation (3) seems to be very simple for the determination of pressure (P) at different values of compression \( (V/V_0) \) [12, 13] in a number of papers.

A theoretical method based on thermodynamic analysis for EOS has also been presented by Kumar [14]. The form of Shankar EOS is written as follows:

\[ \exp \left( \frac{A}{1 - \frac{V}{V_0}} \right) \]  

(4)

The derivation of equation (4) is based on the volume dependence of Anderson-Gruneisen parameter \( \delta_T \) as proposed by Anderson et.al [15] in the following form,

\[ \frac{\delta_T}{V_0} + 1 = A \]  

(5)

Where A is the parameter equal to \( \delta_T^0 + 1 \). Here, it should be mentioned that if we take \( \delta_T \) is independent of V, equation (4) becomes identical to the well known Murnaghan EOS [12]. It has also been discussed in the literature [15] that for some solids \( \delta_T = B_0' \), the first order pressure derivative of bulk modulus. If we consider this idea and determine \( A = B_0' + 1 \) then the form of equation (4) resembles with so called Tait equation of state as quoted by MacDonald [16]. Tait equation [17] which is widely used in recent literature for studying P-V data is given as,

\[ \frac{\Delta V}{V_0} = \frac{1}{B_0' + 1} \ln(1 + \beta P) \]  

(6)

Here, \( \beta = (B_0' + 1)/B_0 \)

Vinet et.al [18] have proposed a new universal equation of state [UEOS] which is found to be extensive use for all kinds of solids subjected to high pressure.

Vinet UEOS is written as follows

\[ P = 3(1 - x)B_0 \exp\left[ \frac{\eta(1 - x)}{x^2} \right] \]  

(7)

Where, \( x = (V/V_0)^{1/3} \) and \( \eta = 3/2(B_0' - 1) \)

The natural strain equation of state developed by Poirier-Tarantola EOS [19] reads as follows.
The EOS based on the Suzuki’s theory of thermal expansivity reads as follows [20]

\[
P = B_0 \left[ \ln \frac{V}{V_0} + \frac{(B_0 - 2)}{2} \left( \ln \frac{V}{V_0} \right)^2 \right]
\] (8)

2.2. Temperature dependence of thermal expansivity

Following the approximation given by Anderson et.al [21-23], that the product of the coefficient of volume thermal expansion [\(\alpha\)] and the isothermal bulk modulus [B] remains constant under the effect of temperature (T). We can write;

\[
\alpha B = \text{const}
\] (10)

\[
\alpha \left( \frac{dB}{dT} \right)_p + B \left( \frac{d\alpha}{dT} \right)_p = 0
\] (11)

Which gives,

\[
\delta_T = -\frac{1}{\alpha B} \left( \frac{dB}{dT} \right)_p = \frac{1}{\alpha} \left( \frac{d\alpha}{dT} \right)_p
\] (12)

Where, \(\alpha\) is defined as,

\[
\alpha = \frac{1}{V} \left( \frac{dV}{dT} \right)_p
\] (13)

Using equations (12) and (13) we get,

\[
\delta_T = \frac{V}{\alpha} \left( \frac{\partial \alpha}{\partial V} \right)_p
\] (14)

At constant pressure integration of equation (14) gives,

\[
\left( \frac{\alpha}{\alpha_0} \right) = \left( \frac{V}{V_0} \right)^{\delta_T}
\] (15)

Now equation (12) can be written as,

\[
\delta_T = \frac{1}{\alpha^2} \left( \frac{d\alpha}{dT} \right)_p
\] (16)

The integration of equation (16) gives,

\[
\frac{\alpha}{\alpha_0} = \left[ 1 - \alpha_0 \delta_T (T - T_0) \right]^{-1}
\] (17)

Equation (17) gives directly the values of \(\alpha\) at required temperature and thus does not require the knowledge of \(V/V_0\) as a function of temperature.

2.3. Temperature dependence of bulk modulus

The isothermal Anderson-Gruneisen parameter \(\delta_T\) is defined as:

\[
\delta_T = -\frac{1}{\alpha B} \left( \frac{dB}{dT} \right)_p
\] (18)

From equations (13) and (18) we get,
Thus at constant pressure we get,
\[ \frac{d\delta_T}{B} = -\frac{dV}{V} \]  
(20)

Integrating equation (20) within the limits \( B = B_0 \) at \( V = V_0 \), assuming \( \delta_T \) constant, we get
\[ \frac{B}{B_0} = \left( \frac{V}{V_0} \right)^{-\delta_T} \]  
(21)

This equation may be used to calculate \( B \) at different temperatures provided that \( V/V_0 \) versus \( T \) are known. At constant pressure equation (18) may be rewritten as,
\[ \frac{dB}{dT} = -(\alpha B \delta_T) \]  
(22)

Integrating equation (22) gives,
\[ \int_{B_0}^{B} dB = -(\alpha_0 B_0 \delta_T) \int_{T_0}^{T} dT \]  
(23)
\[ \frac{B}{B_0} = \left[ 1 - \alpha_0 \delta_T (T - T_0) \right] \]  
(24)

This equation (24) is based on the assumption that \((\alpha B \delta_T)\) is a constant under the effect of temperature. We make the use of equation (24) to calculate \( B \) at different temperatures.

### 3. Results and Discussion

The input parameters required for present calculations are compiled from literature [24]. The values of \( B_0, B'_0 \) and \( \alpha_0 \) are taken as 97.8 GPa, 4.1 and \( 8.76\times10^{-6} \) K\(^{-1} \) respectively. The isothermal Anderson-Gruneisen parameter for silicon is 3.11 [15]. The results for silicon based on the various EOS for pressure \( (P) \) versus compression \( (V/V_0) \) are given in Figure 1 along with the experimental data. It is found that the results obtained by Kwon-Kim equation are in very good agreement with the X-ray diffraction data [25]. A good agreement between theory and experiment demonstrates the validity of simple form of the Kwon-Kim EOS, applicable for the entire range of pressure, from atmospheric pressure up to the structural transition pressure of Silicon. The results obtained by Poirier-Tarantola, Vinet, Suzuki and Tait EOSs are not giving satisfactory agreement with the available experimental data [25]. The results of temperature dependence of thermal expansivity based on equation (17) are reported in Figure 2. The calculated values of thermal expansivity are in good agreement with available experimental data [24]. Equation (17) gives directly the values of \( \alpha \) at required temperature and thus does not require the knowledge of \( V/V_0 \) as a function of temperature. Thus it is clear that application of equation (17) is simpler as compared with equation (15). The results of pressure dependence of bulk modulus obtained using equation (24) are shown in Figure 3 in the absence of experimental data. These results may be of some interest to the researchers engaged in the experimental work.
Figure 1. Compression behaviour of silicon using different EOS models along with available experimental data.

Figure 2. Comparison of predicted values of thermal expansivity at different temperatures through equation (17) with the experimental data.
Figure 3. Predicated values of bulk modulus of silicon at different temperature through equation (24).

4. References

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