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Application of the statistical moment method to thermodynamic quantities of silicon

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Abstract

The lattice constants, thermal expansion coefficients, specific heats at constant volume and those at constant pressure, C_v and C_p , second cumulants, and Lindemann ratio are derived analytically for diamond cubic semiconductors, using the statistical moment method. The calculated thermodynamic quantities of the Si crystal are in good agreement with the experimental results. We also find the characteristic negative thermal expansion in the Si crystal at low temperatures.

1. Introduction

Semiconductor heterostructures and nanodevices are now of great importance in the modern semiconductor technologies [1–5]. However, some problems arise in conjunction with the thermal residual stresses and strain effects in the semiconductor nanodevices which are caused by the differences in the lattice constants and thermal expansion coefficients among the constituent elements. The strain effects are an important factor in determining, e.g., the band-edge potential profile for epitaxially grown quantum dots (Stranski–Krastanow mode) [6, 7]. The interface disorder, intermixing and phase separation, i.e., thermodynamic instabilities occurring in the semiconductor nano-systems, are also serious problems [4–7]. The present paper provides the explicit formulation of the thermodynamic quantities of the elemental semiconductors with the use of the statistical moment method [8–10], taking into account the anharmonicity effects of thermal lattice vibrations. The thermal expansion coefficients, elastic moduli, specific heats at constant volume and those at constant pressure, C_v and C_p , are derived analytically for diamond cubic semiconductors.

In addition to the standard thermodynamic quantities, we also discuss the Lindemann's criterion and Lindemann's ratio [11, 12], which have been widely used for predicting

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the melting temperature of solids. For this purpose, we derive the mean square relative displacements σ_j^2 of the thermal atomic vibrations, which are also the important ingredients in the theory of XAFS (x-ray-absorption fine structure) [13]. The mean square relative displacements σ_j^2 , also called second cumulants, are related to an attenuation of x-ray coherent scattering, caused by displacement of the atoms from their equilibrium positions (fluctuations in the interatomic distances). The XAFS technique is generally superior to the x-ray diffraction technique, because it provides us local atomic configurations, the species of atoms and their locations in crystals [13]. The numerical calculation results and the related discussions of the present study are given for the Si crystal.

2. Statistical moment method

For simplicity and clarity, we present the statistical moment method (SMM) formulation for the elemental semiconductors by assuming the interatomic potentials φ_{ij} between the constituent atoms. However, it is straightforward to extend our formulation to include the angle dependent many-body electronic potentials and also the first principles density functional theory, as will be done for some of the numerical calculations for Si crystals. (For the combined use of SMM formalism with the *ab initio* energetics beyond the pairwise potentials, we refer to our previous studies [9, 10].) Then, we start with the potential energy of the system given by

$$U = \frac{N}{2} \sum_i \varphi_{i0}(|\vec{r}_i + \vec{u}_i|), \quad (1)$$

where r_i is the equilibrium position of the i th atom, u_i its displacement, and φ_{i0} the effective interatomic potential between zeroth and i th atoms.

The atomic force acting on a central zeroth atom can be evaluated by taking derivatives of the interatomic potentials. We expand the potential energy $\varphi_{i0}(|r_i + u_i|)$ in terms of the atomic displacement u_i up to the fourth-order terms. When the zeroth central atom in the lattice is affected by a supplementary force [8–10] due to the thermal lattice vibration effects, a_β , the total force acting on it must be zero, and one can get the force balance relation as

$$\begin{aligned} \frac{1}{2} \sum_{i,\alpha} \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta}} \right)_{\text{eq}} \langle u_{i\alpha} \rangle_a + \frac{1}{4} \sum_{i,\alpha,\gamma} \left(\frac{\partial^3 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta} \partial u_{i\gamma}} \right)_{\text{eq}} \langle u_{i\alpha} u_{i\gamma} \rangle_a \\ + \frac{1}{12} \sum_{i,\alpha,\gamma,\eta} \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta} \partial u_{i\gamma} \partial u_{i\eta}} \right)_{\text{eq}} \langle u_{i\alpha} u_{i\gamma} u_{i\eta} \rangle_a - a_\beta = 0, \end{aligned} \quad (2)$$

where α , γ and η denote the Cartesian components of the lattice coordinates. The introduction of the supplementary force a_β due to thermal vibration effects is the essence of our SMM scheme. Using the statistical moment recurrence formula [8–10] one can get power moments of the atomic displacements and then derive the thermodynamic quantities of the crystal, taking into account the anharmonicity effects of the thermal lattice vibrations. The thermal averages of the atomic displacements $\langle u_{i\alpha} u_{i\gamma} \rangle_a$ and $\langle u_{i\alpha} u_{i\gamma} u_{i\eta} \rangle_a$, second and third order moments, can be expressed in terms of the first order moment $\langle u_{i\alpha} \rangle_a$ as

$$\langle u_{i\alpha} u_{i\gamma} \rangle_a = \langle u_{i\alpha} \rangle_a \langle u_{i\gamma} \rangle_a + \theta \frac{\partial \langle u_{i\alpha} \rangle_a}{\partial a_\gamma} + \frac{\hbar \delta_{\alpha\gamma}}{2m\omega} \coth\left(\frac{\hbar\omega}{2\theta}\right) - \frac{\theta \delta_{\alpha\gamma}}{m\omega^2}, \quad (3)$$

and

$$\begin{aligned} \langle u_{i\alpha} u_{i\gamma} u_{i\eta} \rangle_a = \langle u_{i\alpha} \rangle_a \langle u_{i\gamma} \rangle_a \langle u_{i\eta} \rangle_a + \theta P_{\alpha\gamma\eta} \langle u_{i\alpha} \rangle_a \frac{\partial \langle u_{i\gamma} \rangle_a}{\partial a_\eta} \\ + \theta^2 \frac{\partial^2 \langle u_{i\alpha} \rangle_a}{\partial a_\gamma \partial a_\eta} + \frac{\hbar \langle u_{i\eta} \rangle_a \delta_{\alpha\gamma}}{2m\omega} \coth\left(\frac{\hbar\omega}{2\theta}\right) - \theta \frac{\langle u_{i\eta} \rangle_a \delta_{\alpha\gamma}}{m\omega^2}, \end{aligned} \quad (4)$$

where $\theta = k_B T$ (k_B being the Boltzmann constant), and $P_{\alpha\gamma\eta}$ takes unity for $\alpha = \gamma = \eta$, and otherwise zero. Here, it is noted that correlations, i.e., deviations from the simple mean-field approximation in the second and third order moments, are treated exactly in the above equations (3) and (4), respectively [14]. This is one of the advantages of the present SMM scheme.

The above equation (2) is now transformed into the differential equation of the first order moment $\langle u_i \rangle_a$ as

$$\gamma\theta^2 \frac{d^2 y}{da^2} + 3\gamma\theta y \frac{dy}{da} + ky + \gamma \frac{\theta}{k} (x \coth x - 1)y + \beta\theta \frac{dy}{da} + \beta y^2 - a = 0, \quad (5)$$

where $y \equiv \langle u_i \rangle_a$ and $x = \hbar\omega/2\theta$. In the above equation (5), k , γ and β are defined by

$$k = \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{ix}^2} \right)_{\text{eq}} = m\omega^2, \quad (6)$$

$$\gamma = \frac{1}{12} \sum_i \left[\left(\frac{\partial^4 \varphi_{i0}}{\partial u_{ix}^4} \right)_{\text{eq}} + 6 \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{ix}^2 \partial u_{iy}^2} \right)_{\text{eq}} \right], \quad (7)$$

and

$$\beta = \frac{1}{2} \sum_i \left(\frac{\partial^3 \varphi_{i0}}{\partial u_{ix} \partial u_{iy} \partial u_{iz}} \right)_{\text{eq}}, \quad (8)$$

respectively. In deriving equation (5) we have imposed the symmetry criterion for the thermal averages in the diamond cubic lattice as

$$\langle u_{i\alpha} \rangle_a = \langle u_{i\gamma} \rangle_a = \langle u_{i\eta} \rangle_a \equiv \langle u_i \rangle_a. \quad (9)$$

Let us introduce the new variable y in the above equation (5)

$$y = y' - \frac{\beta}{3\gamma}. \quad (10)$$

Then, we have the new differential equation instead of equation (5)

$$\gamma\theta^2 \frac{d^2 y'}{da^{*2}} + 3\gamma\theta y' \frac{dy'}{da^*} + \gamma y'^3 + Ky' + \frac{\gamma\theta}{k} (x \coth x - 1)y' - a^* = 0, \quad (11)$$

where

$$K = k - \frac{\beta^2}{3\gamma}, \quad (12)$$

$$a^* = a - K^*, \quad (13)$$

and

$$K^* = \frac{\beta k}{\gamma} \left[\frac{2\beta^2}{27\gamma k} - \frac{1}{3} - \frac{\gamma\theta}{3k^2} (x \coth x - 1) \right]. \quad (14)$$

The nonlinear differential equation of equation (11) can be solved in the following manner: We expand the solution y' in terms of the 'force' a^* up to the second order as

$$y' = y'_0 + A_1 a^* + A_2 a^{*2}, \quad (15)$$

where A_1 and A_2 are the constants [8–10, 14]. Firstly, we get the solution of equation (11) in the low temperature limit ($T \rightarrow 0$ K) by solving the equation

$$\gamma y'^3 + Ky' + \frac{\hbar\omega\gamma}{2k} y' - a^* = 0. \quad (16)$$

Here, the relation $\gamma y'^3 \ll (K + \frac{\hbar\omega\gamma}{2k})y'$ is used and the solution is simply given by

$$y'_0 = B_1 \theta (x \coth x - 1) + B_2, \quad (17)$$

with

$$B_1 = \frac{\beta}{3k[k - \frac{\beta^2}{3\gamma} + \frac{\hbar\omega\gamma}{2k}]}, \quad (18a)$$

and

$$B_2 = \frac{k}{\gamma} \left[\frac{1}{3} - \frac{2\beta^2}{27\gamma k} \right] B_1. \quad (18b)$$

On the other hand, for higher temperatures, the relation $x \coth x \sim 1$ holds and equation (11) is reduced to

$$\gamma\theta^2 \frac{d^2 y'}{da^{*2}} + 3\gamma\theta y' \frac{dy'}{da^*} + \gamma y'^3 + Ky' - a^* = 0. \quad (19)$$

The above equation (19) is solved as

$$y'_0 = \sqrt{\frac{2\gamma\theta^2}{3K^3}} A, \quad (20)$$

with

$$A = \frac{\gamma^2\theta^2}{K^4} + \frac{\gamma^3\theta^3}{K^6} + \frac{\gamma^4\theta^4}{K^8}. \quad (21)$$

Here, y'_0 represents the atomic displacement for the case when the force a^* is zero. The general solution of equation (11) is solved as

$$\begin{aligned} y_0 = y|_{a=0} &= y'|_{a^*=-K^*} - \frac{\beta}{3\gamma} \\ &= y'_0 - \frac{\beta}{3\gamma} + \frac{1}{K} \left(1 + \frac{6\gamma^2\theta^2}{K^4} \right) \left[\frac{1}{3} + \frac{\gamma\theta}{3k^2} (x \coth x - 1) - \frac{2\beta^2}{27\gamma k} \right]. \end{aligned} \quad (22)$$

Then, we find the nearest-neighbour distance at temperature T as

$$r_1(T) = r_1(0) + y_0, \quad (23)$$

where $r_1(0)$ denotes the nearest-neighbour distance at the temperature 0 K. Using equation (23), the linear thermal expansion coefficient $\alpha(T)$ is given by the following formula:

$$\alpha(T) = \frac{k_B}{r_1(0)} \frac{dy_0}{d\theta}. \quad (24)$$

The Helmholtz free energy of our system can be derived from the Hamiltonian H of the following form:

$$H = H_0 - \lambda V, \quad (25)$$

where H_0 denotes the Hamiltonian of the harmonic approximation, λ the parameter and V the anharmonic vibrational contributions. Following exactly the general formula in the SMM formulation [8–10], one can get the free energy Ψ of the system as

$$\Psi(\lambda) = \Psi_0 - \int_0^\lambda \langle V \rangle_\lambda d\lambda, \quad (26)$$

where Ψ_0 is the free energy corresponding to the Hamiltonian H_0 , and $\langle V \rangle_\lambda$ the thermal average over the equilibrium ensemble with the Hamiltonian H . After a bit of algebra, one can find the Helmholtz free energy Ψ of the diamond cubic semiconductors in the following form:

$$\begin{aligned}
\Psi = & \frac{N}{2}U_0 + N\theta \sum_{q,j} \ln \left(2 \sinh \frac{\hbar\omega_j(q)}{2\theta} \right) + \frac{3N\theta^2}{k^2} \left\{ \gamma_2 x^2 \coth^2 x - \frac{2\gamma_1}{3} \left(1 + \frac{x \coth x}{2} \right) \right\} \\
& + \frac{3N\theta^2}{k^2} \left\{ \frac{4}{3} \gamma^2 x \coth x \left(1 + \frac{x \coth x}{2} \right) - 2(\gamma_1^2 + 2\gamma_1\gamma_2) \left(1 + \frac{x \coth x}{2} \right) \right. \\
& \times \left. (1 + x \coth x) \right\} + 3N\theta \left[\frac{\beta^2 k}{6K\gamma} - \frac{\beta^2}{6K\gamma} \right] + 3N\theta^2 \left[\frac{\beta}{K} \left(\frac{2\gamma}{3K^3} a_1 \right)^{1/2} - \frac{\beta^2 a_1}{9K^3} \right. \\
& \left. + \frac{\beta^2 k a_1}{9K^4} + \frac{\beta^2}{6K^2 k} (x \coth x - 1) \right], \quad (27)
\end{aligned}$$

where U_0 represents the sum of effective pair interaction energies and the second term gives the harmonic part of the free energy. Here, the lattice dynamical theory [15] is used for the harmonic part of the free energy Ψ_0 , second term of equation (27). The remaining terms in the above equation (27) represent the anharmonicity contributions of thermal lattice vibrations. γ_1 and γ_2 are the fourth order vibrational constants and are defined by

$$\gamma_1 = \frac{1}{48} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\alpha}^4} \right)_{\text{eq}}, \quad \text{and} \quad \gamma_2 = \frac{6}{48} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\alpha}^2 \partial u_{i\beta}^2} \right)_{\text{eq}}, \quad (28)$$

respectively. Here, it is noted that for the combined use of SMM formalism with the *ab initio* energetics the harmonic k and anharmonic β , γ_1 and γ_2 parameters are replaced by those expressions including the total energy E_0 per atom [9, 10], e.g.,

$$k = \frac{\partial^2 E_0}{\partial u_{ix}^2} \Big|_{\text{eq}}, \quad \text{and} \quad \beta = \sum_i \left[\frac{\partial^3 E_0}{\partial u_{ix} \partial u_{iy} \partial u_{iz}} \right]_{\text{eq}}.$$

The compressibility of the diamond cubic lattice can be derived from the Helmholtz free energy Ψ , and the isothermal compressibility χ_T is given by

$$\chi_T = \frac{3 \left(\frac{r_1(T)}{r_1(0)} \right)^3}{2P + \frac{r_1^2(T)}{3V} \left(\frac{\partial^2 \Psi}{\partial r_1^2} \right)_T} \quad (29)$$

where P and V denote the pressure and volume of the crystal, respectively. The isothermal compressibility χ_T is also expressed in an analytic form, but it is rather a lengthy expression and is not reproduced here. Furthermore, from the definition of the linear thermal expansion coefficient α , one obtains the following formula:

$$\alpha = \frac{k_B \chi_T}{3} \left(\frac{\partial P}{\partial \theta} \right)_V = - \frac{\sqrt{3} k_B \chi_T}{4r_2^2(T)} \frac{1}{3N} \frac{\partial^2 \Psi}{\partial \theta \partial r_1}. \quad (30)$$

This is equivalent to the expression of equation (24), but based on the free energy of the system.

On the other hand, the internal energy of the system is given by

$$\begin{aligned}
E = & \frac{N}{2}U_0 + N\theta \sum_{q,j} \frac{\hbar\omega_j(q)}{2\theta} \coth \left(\frac{\hbar\omega_j(q)}{2\theta} \right) \\
& + \frac{3N\theta^2}{k^2} \left\{ \gamma_2 x^2 \coth^2 x + \frac{\gamma_1}{3} \left(2 + \frac{x^2}{\sinh^2 x} \right) - 2\gamma_2 \frac{x^3 \coth x}{\sinh^2 x} \right\} \\
& - 3N\theta^2 \left\{ \frac{\beta}{K} \left(\frac{2\gamma}{3K^3} a_1 \right)^{1/2} - \frac{\beta^2 a_1}{9K^3} + \frac{\beta^2 k a_1}{9K^4} + \frac{\beta^2}{6K^2 k} (x \coth x - 1) \right\} \\
& - 3N\theta^2 \left\{ \left(\frac{-x \coth x}{2} + \frac{x^2}{2 \sinh^2 x} \right) \left[\frac{\beta}{2K} \left(\frac{2\gamma}{3K^3} \right)^{1/2} (a_1)^{-1/2} - \frac{\beta^2}{9K^3} \right. \right. \\
& \left. \left. + \frac{\beta^2 k}{9K^4} + \frac{\beta^2}{6K^2 k} \right] \right\}. \quad (31)
\end{aligned}$$

Then, the specific heat at constant volume C_v is obtained from the derivative of internal energy E with respect to the temperature T and is given by

$$\begin{aligned}
C_v = Nk_B \sum_{q,j} \frac{\hbar\omega_j(q)}{2\theta} \sinh^{-2} \frac{\hbar\omega_j(q)}{2\theta} \\
+ 3Nk_B \left\{ \frac{2\theta}{K^2} \left[\left(2\gamma_2 + \frac{\gamma_1}{3} \right) \frac{x^3 \coth x}{\sinh^2 x} + \frac{\gamma_1}{3} \left(1 + \frac{x^2}{\sinh^2 x} \right) \right. \right. \\
\left. \left. - \gamma_2 \left(\frac{x^4}{\sinh^4 x} + 2 \frac{x^4 \coth^2 x}{\sinh^2 x} \right) \right] \right\} + 3Nk_B \theta^2 \left[\frac{\beta}{2K} \left(\frac{2\gamma}{3K^3} \right)^{1/2} (a_1)^{-1/2} - \frac{\beta^2}{9K^3} \right. \\
\left. + \frac{\beta^2 k}{9K^4} + \frac{\beta^2}{3K^2 k} \right] \left(x \coth x - \frac{x^3 \coth x}{\sinh^2 x} \right) + 3Nk_B \theta^2 \left[\frac{\beta}{4K} \left(\frac{2\gamma}{3K^3} \right)^{1/2} (a_1)^{-3/2} \right] \\
\times \left(\frac{x \coth x}{2} - \frac{x^2}{2 \sinh^2 x} \right)^2 + 3Nk_B \theta^2 \left[\frac{-2\beta}{K} \left(\frac{2\gamma}{3K^3} a_1 \right)^{1/2} + \frac{2\beta^2 a_1}{9K^3} \right. \\
\left. - \frac{2\beta^2 k a_1}{9K^4} - \frac{\beta^2}{3K^2 k} (x \coth x - 1) \right]. \quad (32)
\end{aligned}$$

The specific heat at constant pressure C_p , the adiabatic compressibility χ_s , and isothermal bulk modulus B_T are determined from the well known thermodynamic relations

$$C_p = C_v + \frac{9TV\alpha^2}{\chi_T}, \quad \chi_s = \frac{C_v}{C_p} \chi_T, \quad \text{and} \quad B_T = \frac{1}{\chi_T}. \quad (33)$$

One can now apply the above formulae to calculate the thermodynamic quantities of diamond cubic semiconductors. The temperature dependence of the elastic moduli, specific heats and the linear thermal expansion coefficients are calculated self-consistently using the TB total energy scheme and *ab initio* density functional theory.

We now briefly discuss the Lindemann's criterion for melting transition of solids on the basis of the present SMM formalism. For this purpose, we firstly derive the root mean square relative displacements $\sigma_j^2(T)$ (second cumulants) in the diamond cubic lattice. (The second cumulant σ_j^2 is also an important factor in XAFS analysis since the thermal lattice vibrations influence sensitively the XAFS amplitudes through the Debye–Waller factor $e^{-w} \sim \exp(-2\sigma_j^2 k^2)$.) The root mean square relative displacements $\sigma_j^2(T)$ at the atomic site j around the central zeroth site are given by

$$\sigma_j^2(T) = \langle [(\vec{u}_j - \vec{u}_0) \vec{R}]^2 \rangle = \langle u_j^2 \rangle + \langle u_0^2 \rangle - 2\langle u_j u_0 \rangle. \quad (34)$$

Here, u_0 and u_j are the atomic displacements of zeroth and j th sites from their equilibrium positions. \vec{R} is a unit vector at the zeroth site pointing towards the j th site, and the brackets denote the thermal average. Using the exact moment formula of equation (3), we find the second moments $\langle u_j^2 \rangle$ and $\langle u_0^2 \rangle$. We assume that the correlation appearing in $\langle u_j u_0 \rangle$ is limited to the nearest-neighbour j th sites around the central zeroth site (small correlation length approximation) and use the decoupling scheme

$$\langle u_j u_0 \rangle \cong \langle u_j \rangle \langle u_0 \rangle. \quad (35)$$

Then, the second cumulant is given by

$$\sigma_j^2(T) = \frac{2\theta}{k} \left[x \coth x + \frac{2\gamma^2 \theta^2}{k^4} \left(1 + \frac{x \coth x}{2} \right) (1 + x \coth x) \right]. \quad (36)$$

Lindemann [12] has suggested that a solid melts when the ratio of the mean-square relative displacement to the square of the interatomic spacing r_1 exceeds a certain critical value. In

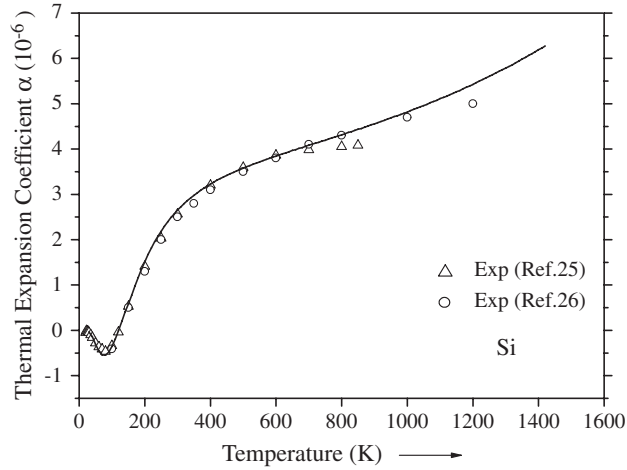


Figure 1. Thermal lattice expansion coefficients α of Si crystal.

terms of the mean square relative displacements σ_j^2 and the nearest-neighbour interatomic distance $r_1(T)$ at temperature T , the Lindemann ratio LR is given by

$$\text{LR}(T) = \frac{\sqrt{3\sigma_j^2(T)/2}}{r_1(T)}. \quad (37)$$

3. Results and discussions

The thermodynamic quantities of the Si crystal are calculated using the tight binding (TB) total energy calculation scheme [16, 17] as well as using the first principles density functional perturbation theory (DFPT) within the local density approximation (LDA) [18, 19]. For comparison, we also use the angular dependent empirical potentials [20–23]. For calculating the harmonic contributions of the thermodynamic quantities, we use the first principles DF theory, while the anharmonic contributions are evaluated with the use of the conventional TB theory. The harmonic contributions of the thermodynamic quantities are derived by applying the lattice dynamical model [15]. The dynamical matrix can be obtained directly from the *ab initio* density functional calculations or it can be derived from an expansion of the DFT total energy $U_{\text{static}}(\{R_i\})$ for any lattice parameter in an analytic form, which we need to know only up to second order in the atomic displacements [18, 19]. In order to attain a good accuracy, we choose 505 sampling points in a irreducible 1/48 part of the first Brillouin zone [24]. The anharmonic vibrational parameters β , γ_1 , and γ_2 can be evaluated efficiently and accurately by the TB theory for the thermodynamic quantities at higher temperatures, where the ‘Einstein’ approximation becomes sufficiently valid.

In figure 1, we present the linear thermal expansion coefficients of the Si crystal, calculated by the SMM formalism, together with the experimental results [25, 26]. Overall good agreements between the calculation and experimental results are obtained for a wide temperature range. The thermal expansion coefficients of elemental semiconductors like Si are one order of magnitude smaller than those of the ordinary metals and alloys [9, 10]. The smaller magnitudes of the thermal expansion coefficients are related to the inherent ‘anharmonicity’ of the thermal lattice vibrations, i.e., the smaller ratio of $\gamma_1\gamma_2/k^2$ of the Si crystal, compared to

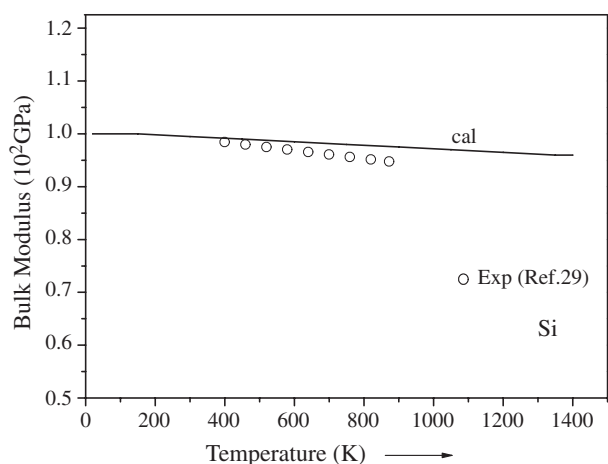


Figure 2. Temperature dependence of bulk modulus of Si crystal, in comparison with the experimental results.

those of metals and alloys. We have found a characteristic small negative thermal expansion of Si crystal at low temperatures as clearly seen in the figure. This negative thermal expansion arises from the peculiar temperature dependence of the bond stretching and bond bending force constants. The bond bending force constant of Si crystal is found to be an increasing function of the temperature, while the bond stretching force constant is a decreasing function of the temperature by the density functional calculations. Around 80 K the linear thermal expansion coefficient exhibits a minimum with a negative value, which reflects a contraction of the crystal compared to the zero-kelvin lattice spacing. This contraction reproduces well the expansion coefficients for lower temperatures as well as for higher temperatures. In our calculations, the atomic mass of silicon is taken to be $m = 28.08538$ and ‘isotopic effects’ [27, 28] of the thermal expansion as fully discussed in [27] and [28] are not considered here. (The natural composition of Si crystals is a mixture of different isotopes: 92.232% of ^{28}Si , 4.677% of ^{29}Si and 3.090% of ^{30}Si .)

In figure 2, we present the temperature dependence of the bulk modulus of the Si crystal by a solid line, in comparison with the experimental results (circles) [29]. The calculated bulk modulus of the Si crystal is a decreasing function of the temperature; and the decreasing rate is smaller than those of the metals and alloys. The smaller decreasing rate arises from the fact that the thermal expansion coefficients of the elemental semiconductors like Si are one order of magnitude smaller than those of the metals and alloys. Above 150 K, the decrease of bulk moduli of Si crystal with increasing temperature is fairly linear, and this tendency is in good agreement with the experimental results.

The calculated specific heats at constant volume C_v and those at constant pressure C_p are shown by solid curves in figure 3, in comparison with the experimental results. Below 400 K, there are no visible differences between C_v and C_p values of the Si crystal. The experimental specific heats C_p ($\text{cal K}^{-1} \text{mol}^{-1}$) are taken from [30] and [31], and they are given by a simple analytic function of the temperature. The calculated specific heats C_p at constant pressure become larger compared to those at the constant volume C_v for the higher temperature region. The differences between the specific heats C_p and C_v arise from the anharmonicity of thermal lattice vibrations, as given by equation (33). For comparison, we also present in figure 3 the specific heats C_p ($\cong C_v$) by a dashed curve calculated by using the harmonic Einstein

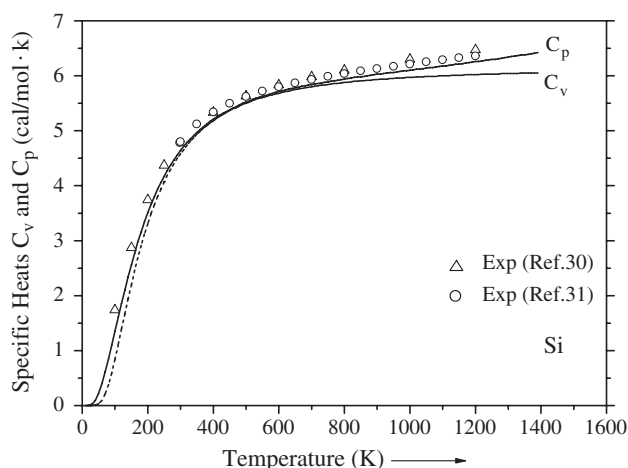


Figure 3. The specific heats C_v and C_p of the Si crystal, in units of $\text{cal mol}^{-1} \text{K}^{-1}$.

approximation, i.e., using the formula

$$C_v^0 = 3k_{\beta}x \sinh^{-2} x.$$

One can see in figure 3 that the harmonic Einstein approximation clearly underestimates the specific heats C_v and C_p at lower temperatures. This is the natural consequence of the fact that in the harmonic Einstein approximation only the single Einstein vibrational frequency is taken into account, and dispersion of vibrational frequencies (especially lower ones) is neglected. For the low-temperature region, the low-lying vibrational modes contribute significantly to the specific heats, and the neglect of the low-lying vibrational modes leads to underestimation of the specific heats.

The calculated bulk moduli B_T , second cumulants (mean square relative displacement), and Lindemann ratios LR are presented in tables 1. The Lindemann ratios are calculated as a function of temperature, and take values of about 0.069 at the experimental melting temperature 1685 K. This theoretical finding is in good agreement with the previous studies: Cartz [32] and Gilvarry [33] reformulated the Lindemann criterion utilizing the Debye and Waller theory of the temperature dependence of the mean-square amplitude of vibration, and showed that the amplitude attains a value of less than 10% of interatomic distances at melting. However, it must be noted that the Lindemann ‘constant’ is not strictly constant from one lattice type to another, and in spite of the partial success the physical relation between lattice instability and melting has not yet been clarified. In this respect, we point out that the more rigorous treatment for melting of solids can be developed by taking into account the anharmonicity of thermal lattice vibrations. A more complete theory based on the lattice instability has been proposed by Ida [34], taking into account the anharmonicity contribution to the thermal energy. Furthermore, it is also interesting to note that the crystal anharmonicity plays an important role even for the liquid–vapour phase transitions [35]. The present SMM anharmonicity theory can also be extended to treat the melting phase transition of solids and the detailed analysis is one of our subjects for future publications.

Summarizing the above mentioned calculations by the SMM formalism the analytic derivations are quite useful for the numerical calculations of the various thermodynamic quantities. The calculation results by empirical potentials are similar, in orders of magnitude, to the present calculations, but they are less satisfactory compared to the experimental results.

Table 1. Calculated thermodynamic quantities and Lindemann ratio of Si crystal.

T (K)	$\alpha(T)$ (10^{-6} K^{-1})	Exp. [26] (10^{-6} K^{-1})	B (10^2 GPa)	C_v ($\text{cal K}^{-1} \text{ mol}^{-1}$)	C_p ($\text{cal K}^{-1} \text{ mol}^{-1}$)	Exp. [30]	σ_j^2 (10^{-2} \AA^2)	LR
10		0.48×10^{-3}	1.011	0.000 02	0.000 02	—	0.2919	0.0348
50	-0.3051	-0.282	1.011	0.223 72	0.223 73	—	0.2919	0.0348
100	-0.3582	-0.330	1.011	1.351 86	1.351 89	1.74	0.2935	0.0348
150	0.5859	—	1.011	2.560 75	2.561 37	2.87	0.3034	0.0349
200	1.5120	1.406	1.010	3.504 17	3.505 18	3.74	0.3239	0.0352
250	2.1870	2.105	1.009	4.172 30	4.174 06	4.37	0.3523	0.0357
300	2.6550	2.616	1.008	4.637 12	4.640 10	—	0.3863	0.0365
350	2.9790	—	1.007	4.964 47	4.969 24	—	0.4239	0.0375
400	3.2310	3.253	1.006	5.200 10	5.207 45	5.33	0.4657	0.0387
500	3.5820	3.614	1.003	5.504 89	5.519 71	5.63	0.5513	0.0411
600	3.8430	3.842	1.000	5.685 05	5.711 27	5.83	0.6408	0.0437
700	4.0860	4.016	0.996	5.799 52	5.842 41	5.98	0.7352	0.0462
800	4.3110	4.151	0.992	5.877 38	5.941 32	6.1	0.8281	0.0488
900	4.5540	4.185	0.987	5.931 18	6.025 04	—	0.9250	0.0513
1000	4.8150	4.258	0.982	5.970 23	6.100 54	6.3	1.0181	0.0537
1100	5.1120	4.323	0.976	5.999 44	6.176 45	—	1.1152	0.0560
1200	5.4270	4.384	0.970	6.021 86	6.255 60	6.47	1.2119	0.0583

The empirical potentials are usually fitted to the ground state properties of materials derived from the first principles electronic structure calculations and/or the corresponding experimental results and it is difficult to include the temperature dependence of the potential parameters and electronic entropy effects which give the important contributions at higher temperatures in the thermodynamic quantities. We have found that anharmonic contributions play an important role in determining the thermodynamic quantities for a higher temperature region than the ‘Debye temperature’. The characteristic negative thermal expansions are also calculated for the Si crystal for the low temperature region as in the previous theoretical studies [12–14]. However, the present SMM calculations are in contradiction with the previous quasi-harmonic ones in the sense that the related thermodynamic quantities such as the specific heats and elastic constants are calculated simultaneously and self-consistently with the thermal lattice expansions including the anharmonicity effects contributions.

4. Conclusion

We have presented the SMM formulation for the thermodynamic quantities of diamond cubic semiconductors taking into account the higher order (fourth order) anharmonic vibrational terms in the Helmholtz free energy and derived the various thermodynamic quantities in closed analytic forms. The lattice constants, linear thermal expansion coefficients, specific heats at constant volume and those at constant pressure, C_v and C_p , second cumulants (mean-square relative displacements) and Lindemann ratio have been calculated successfully for the Si crystal. We have demonstrated the applicability of the ‘real space’ and analytic statistical moment method (SMM) for the thermodynamic calculations of the elemental semiconductors. Accordingly, we hope that the present SMM scheme will be used extensively for the atomistic structure and thermodynamic calculations of nanoscale materials as well.

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