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Lattice Dynamics of Silicon

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ABSTRACT A phenomenological lattice dynamical model has been developed for the zinc-blende and diamond structure crystals. The model developed in the present work is an extended valence force field (EVFF) model which takes into account the short range valence force field interaction between bonded atoms and central interaction between non-bonded atoms. The model also incorporates the long-range coulombic interaction for zinc-blende crystals which are partially ionic in bonding. EVFF model is applied to lattice vibration of silicon to obtain the phonon dispersion curves, elastic constants, bulk modulus, Debye characteristic temperatures and phonon distribution function for silicon. The theoretical values are compared with the experimental results with satisfactory agreement.

KEYWORDS Extended valence force field (EVFF) model, phonon distribution function, Debye characteristic temperature, phenomenological models

INTRODUCTION

The knowledge of various prominent features of the phonon density of states spectrum of a solid is important for a general theoretical understanding and detailed quantitative description of its thermal as well as optical properties. Various theoretical efforts have been made in last decades to develop theoretical models for lattice vibrations to obtain the phonon density of states spectra for elemental semiconductor crystal of diamond structure. Giannozzi et al. [1] presented the phonon dispersions in Si and Ge semiconductors applying the density functional linear- response approach. Wei and Chou [2] investigated the full phonon spectrum for Si and Ge with the pseudo-potential method and the local density approximation without using linear-response theory. Tamura et al. [3] examined the propagation of acoustic phonons in silicon on the basis of a bond change model and effective force constant model consisting of only short range forces. Yin and Cohen [4] investigated theoretically lattice dynamics of silicon applying ab initio pseudo-potential theory. Fleszar and Resta [5] investigated the inter-planar and inter-atomic force constants in Si using adiabatic bond charge model. Bose et al. [6] presented the phonon dispersion curves for Si using de Launay [7] and Clark, Gazis and Wallis [8] models. Zdetsis and Wang [9] presented the theoretical data for elastic constants, phonon frequencies, specific heats and Debye characteristic temperatures for Si using Born and Von Karman [10] model. Lattice dynamical calculation of phonon scattering at ideal Si-Ge interfaces has been done by Zhao and Freund [11]. Powell et al. [12] applied the Tersoff bond-order potential energy model to obtain the elastic and dynamical properties of elemental semiconductors including Si and binary semiconducting crystals of III-V groups. In recent years some theoretical studies [13-16] have been reported on lattice dynamics and other properties of tetrahedrally bonded elemental and binary semiconductors.

In the present lattice dynamical model of diamond structure elemental semiconductor, this valence force field has been extended to include the central interaction between non-bonded atoms upto second neighbours for short range interaction. In addition to this, the bond-bending, bond-stretching and interaction between bond-stretching internal coordinates between adjacent bonds are considered for short-range interaction between atoms. This extended valence force field (EVFF) model is developed for the tetrahedrally bonded zinc-blende crystals which are partially ionic and it takes into account the long-range Coulomb interaction. The EVFF model is modified for the diamond structure elemental semiconductors which are predominantly covalent and the ionicity is almost negligible. This EVFF model is earlier applied to lattice dynamics of diamond [17] crystal to obtain the phonon dispersion curves and Debye characteristic temperatures. The agreement between experimental and theoretical results has been found to be satisfactorily good. The EVFF model applied to diamond crystal is extended to describe the lattice dynamical properties of silicon in the present work.

METHODOLOGY

The lattice dynamical model developed for the tetrahedrally bonded zinc-blende and diamond structure semiconducting crystals in the present work is a phenomenological model in the sense that vibrations of atoms and interactions between them have been taken just like the phenomenon of vibrations of atoms in molecules in the fluid phase. The molecular spectra are explained by taking bond-stretching force between valence atoms and the bending of valence angles. This is called a simple valence force field. In solids which are predominantly covalent, the interaction between valence bonds and valence angles are considered in the potential function of atoms in the unit-cell in the crystalline forms. The present EVFF model takes into account the interaction between non-bonded atoms of the crystal in accordance with the modification of Urey-Bradley [18]. The changes in the bond-length and bond-angles during vibration are called internal coordinates. Following the method of Wilson et al. [19], the valence internal coordinates are transformed into atomic displacement coordinates of the crystal as reported by Singh and Roy [20]. This transformation is employed in expressing the potential energy of the atoms of the unit cell in terms of the components of the displacements of atoms. In this model, the contribution to potential energy from other neighbouring atoms except first and second neighbours has been ignored because of the short-range character of the force-field.

The potential energy for short-range interactions of atoms of unit cell of tetrahedrally bonded semiconducting crystals having two types of atoms is given by

$$V=\frac{1}{2}\sum_{j=1}^{4}K_r\left(\delta r_{ij}\right)^2+\frac{1}{2}\sum_{l=1}^{12}K'_r\left(\delta r_{il}\right)^2$$

$$+\frac{1}{2}\sum_{k=1}^{12}K''_r\left(\delta r_{ik}\right)^2+\frac{1}{2}\sum_{\theta_{jik}=1}^{4}K'_\theta\left(\delta\theta_{jik}\right)^2$$

$$+\frac{1}{2}\sum_{\theta_{ijl}=1}^{4}K''_\theta\left(\delta\theta_{ijl}\right)^2+\frac{1}{2}\sum_{r_{ij}=1}^{4}K_{rr}\left(\delta r_{ij}\right)\left(\delta r_{ik}\right) \qquad (1)$$

In equation (1), *i* is the reference atom (one type) (1), *j* and *k* are two atoms (another types) bonded to *i*, and *l* is atom (type one) bonded to *j*. Also, in equation (1), we have

K_r = bond-stretching force constant,
K'_r = central force constant between non-bonded atoms of one type
K''_r = central force constant between non-bonded atoms of another type
K'_θ = bond-bending force constant for one type of bond-angle
K''_θ = the bond-bending force constant of another bond-angle
K_{rr} = the force constant for the interaction between adjacent bonds.

The components of the forces acting on the reference atoms of two types of the unit cell are obtained from the relation

$$\boldsymbol{F} = -grad\left(V\right) \tag{2}$$

SECULAR EQUATION

The secular equation of the lattice vibration of a lattice with a basis is written as

$$\left| D_{\alpha\beta}\begin{pmatrix} \boldsymbol{q} \\ \sigma\sigma' \end{pmatrix} - \omega^2 \delta_{\alpha\beta}\delta_{\sigma\sigma'} \right| = 0 \tag{3}$$

In equation (3), $D_{\alpha\beta}\begin{pmatrix} \boldsymbol{q} \\ \sigma\sigma' \end{pmatrix}$ are the elements of the dynamical matrix and $\delta_{\alpha\beta}, \delta_{\sigma\sigma'}$ are the Kronecker delta function.

To obtain the elements of the dynamical matrix for the short-range interaction, the components of the forces acting on the reference atoms by first and second neighbours are obtained. The internal coordinates are transformed into the atomic displacement coordinates. Taking help of this transformation and applying the equation (1) and equation (2), the elements of the dynamical matrix for short-range interaction are obtained.

The silicon and other crystals of diamond structure are predominantly covalent, the coulombic interaction is neglected. As there is only one type of atoms in such crystals, we have taken

$$K'_r = K''_r, \quad K'_\theta = K''_\theta = K_\theta$$

The first reference atom is designated as '1' and second reference atom is designated as '2'. Thus following elements of the short-range interaction matrix under EVFF model are obtained for silicon lattice:

$$D_{xx}\left(\boldsymbol{q},11\right) = \frac{1}{m}\left[\frac{4}{3}K_r - \frac{2}{3}K_{rr} + 4K'_r + \frac{28}{3}\frac{K_\theta}{r_0^2}\right.$$

$$+\frac{8}{3}\frac{K_\theta}{r_0^2}\cos\pi q_y \cos\pi q_z - \left(2K'_r + \frac{2}{3}\frac{K_\theta}{r_0^2}\right.$$

$$\left.\left(\cos\pi q_x \cos\pi q_z + \cos\pi q_x \cos\pi q_y\right)\right] \tag{4}$$

$$D_{xy}\left(\boldsymbol{q},11\right) = \frac{1}{m}\left[\left(2K'_r + \frac{2}{3}\frac{K_\theta}{r_0^2}\right)\sin\pi q_x \sin\pi q_y\right.$$

$$\left.+\frac{4}{3}\frac{K_\theta}{r_0^2} i \sin\pi q_z \left(\cos\pi q_x - \cos\pi q_y\right)\right] \tag{5}$$

$$D_{xx}\left(\boldsymbol{q},11\right) = D_{xx}\left(\boldsymbol{q},22\right) \tag{6}$$

$$D_{xy}\left(\boldsymbol{q},22\right) = \frac{1}{m}\left[2K'_r + \frac{2}{3}\frac{K_\theta}{r_0^2}\sin\pi q_x \sin\pi q_y\right.$$

$$\left.-\frac{4}{3}\frac{K_\theta}{r_0^2} i \sin\pi q_z \left(\sin\pi q_x - \sin\pi q_y\right)\right] \tag{7}$$

$$D_{xx}\left(\boldsymbol{q},12\right) = -\frac{1}{m}\left[\left(\frac{4}{3}K_r + \frac{2}{3}K_{rr} - \frac{32}{3}\frac{K_\theta}{r_0^2}\right)\right.$$

$$\left(\cos\frac{\pi q_x}{2}\cos\frac{\pi q_y}{2}\cos\frac{\pi q_z}{2} - i\sin\frac{\pi q_x}{2}\sin\frac{\pi q_y}{2}\sin\frac{\pi q_z}{2}\right)\Bigg] \qquad (8)$$

$$D_{xy}(\mathbf{q},12) = \frac{1}{m}\Bigg[\left(\frac{4}{3}K_r - \frac{2}{3}K_{rr} - \frac{16}{3}\frac{K_\theta}{r_0^2}\right)\left(\sin\frac{\pi q_x}{2}\sin\frac{\pi q_y}{2}\sin\frac{\pi q_z}{2} - i\cos\frac{\pi q_x}{2}\cos\frac{\pi q_y}{2}\cos\frac{\pi q_z}{2}\right)\Bigg] \qquad (9)$$

Here r_0 is the chemical bond length and 'a' is half lattice constant, other elements of the determinantal matrix $D_{\alpha\beta}(\boldsymbol{q},\sigma\sigma')$ can be obtained by circular permutation of the indices *x, y, z* where, α, β stands for *x*, *y* and *z*. The elements of the dynamical matrix obey the following relations.

$$D_{\alpha\beta}(\boldsymbol{q},11) = D^*_{\beta\alpha}(\boldsymbol{q},11),$$
$$D_{\alpha\beta}(\boldsymbol{q},22) = D^*_{\beta\alpha}(\boldsymbol{q},22),$$
$$D_{\alpha\beta}(\boldsymbol{q},12) = D_{\beta\alpha}(\boldsymbol{q},21)$$

ELASTIC CONSTANTS

Taking into account the contribution from coupling coefficients, the following expressions for three elastic constants C_{11}, C_{12} and C_{44} are obtained in terms of model parameters on solving the secular determinant for long waves for diamond structure crystals.

$$C_{11} = \frac{1}{2a}\left(4K_r' + \frac{1}{3}K_r - \frac{1}{6}K_{rr} + 4\frac{K_\theta}{r_0^2}\right)$$

$$C_{12} = \frac{1}{2a}\left(2K_r' + \frac{1}{3}K_r - \frac{1}{6}K_{rr} - 2\frac{K_\theta}{r_0^2}\right)$$

$$C_{44} = \frac{1}{2a}\left(2K_r' + \frac{1}{3}K_r - \frac{1}{6}K_{rr} + \frac{2}{3}\frac{K_\theta}{r_0^2} - \frac{A^2}{B}\right)$$

where,

$$A = -\left(\frac{2}{3}K_r - \frac{1}{3}K_{rr} - \frac{2}{3}\frac{K_\theta}{r_0^2}\right)$$

$$B = \frac{4}{3}K_r - \frac{2}{3}K_{rr} + \frac{32}{3}\frac{K_\theta}{r_0^2}$$

EVALUATION OF MODEL PARAMETERS

The values of EVFF model parameters for silicon are obtained with the help of the expressions of the longitudinal and transverse optical phonons at zone centre and at the zone boundary of Brillouin zone along [100] symmetry direction. The expressions for LO(Γ), LO(X) and TO(X) are obtained by solving the secular equation for zone centre (Γ) and zone boundary (X) along symmetry direction [100]. The expressions are

$$\frac{1}{2}m\omega_{LO}^2(\Gamma)=\frac{4}{3}K_r-\frac{2}{3}K_{rr}+\frac{32}{3}\frac{K_\theta}{r_0^2} \tag{10}$$

$$m\omega_{LO}^2(X)=\frac{4}{3}K_r-\frac{2}{3}K_{rr}+2K_r'+\frac{40}{3}\frac{K_\theta}{r_0^2} \tag{11}$$

$$m\omega_{TO}^2(X)=\frac{8}{3}K_r-\frac{4}{3}K_{rr}+4K_r'+\frac{4}{3}\frac{K_\theta}{r_0^2} \tag{12}$$

From these expressions, we have

$$\frac{K_\theta}{r_0^2}=\frac{2}{16}\left[\frac{1}{8}m\omega_{LO}^2(X)-\frac{1}{4}m\omega_{TO}^2(X)+\frac{2}{16}m\omega_{LO}^2(\Gamma)\right] \tag{13}$$

and

$$K_r'=\frac{1}{16}\left[\frac{15}{8}m\omega_{LO}^2(X)+\frac{1}{4}m\omega_{TO}^2(X)-\frac{19}{16}m\omega_{LO}^2(\Gamma)\right] \tag{14}$$

The parameter K_r is obtained applying the equilibrium condition of the lattice. After obtaining the values of K_r, K_r' and K_θ, the values of K_{rr} is calculated from equation (10). It is significant to note that the values of model parameters have been evaluated without taking use of the elastic constants, C_{11}, C_{12} and C_{44}. The values of model parameters and the input physical data for their evaluation for silicon crystal are given in the Table 1.

Table 1: Input physical data and calculated values of model parameters.

Input Physical data	**Model parameters in units of 10^4 dynes cm^{-1}**
$\nu_{LO}(\Gamma)$ = 15.53 THz	$K_r = -2.141340$
$\nu_{LO}(X)$ = 12.32 THz	$K'_r = 0.535335$
$\nu_{TO}(X)$ = 13.90 THz	$K_{rr} = -28.82433$
$2a$ (lattice constant) = 5.4307×10^{-8} cm	$K_\theta = 0.548956$
m(mass) = 46.629×10^{-24} gm	

RESULTS AND DISCUSSION

Phonon dispersion curves of silicon

The lattice dynamics of silicon has been studied theoretically and experimentally by various workers in the past. Dolling [21] reported the phonon dispersion results along three principal symmetry directions on the basis of his experiment. Palevski et al. [22] and Parker et al. [23] have reported the Raman frequency for silicon from their study of first-order Raman spectra of this crystal. One phonon and two-phonon infra-red spectra have been investigated by Angress et al. [24] and Balkanski [25] respectively. Temple and Hathaway [26] reported the second order Raman spectra experiment for phonon frequencies of silicon. Dolling [21] gave the theoretical descriptions of phonon dispersion curves of this crystal. Singh and Dayal [27], Solbrig [28], Tubino et al. [29], Zdetsis and Wang [9] and Soma and Marita [30] made theoretical studies of lattice dynamics of this crystal having good agreement with the experimental results.

The EVFF model developed for the diamond structure crystal has been applied to obtain the phonon dispersion curves for silicon in the present work. The phonon dispersion curves along the principal symmetry directions [100], [110] and [111] obtained for silicon have been presented in Figure 1. The agreement of the present result with the experimental values of Tubino et al. [29] is satisfactory. The model parameters used in the present calculations are shown in Table 1 along with the input physical data. The calculated values of elastic constants C_{11}, C_{12}, C_{44} and bulk modulus in the present work along with the experimental values are shown in Table 2. The calculated values of elastic constants by other workers are also shown for comparison. The bulk modulus calculated in the present work is found to be nearly twice the experimental value. Significantly our calculated value is exactly the same as obtained by Sokel and Harrison [31] calculated on the basis of linear combination of atomic orbitals (LCAO).

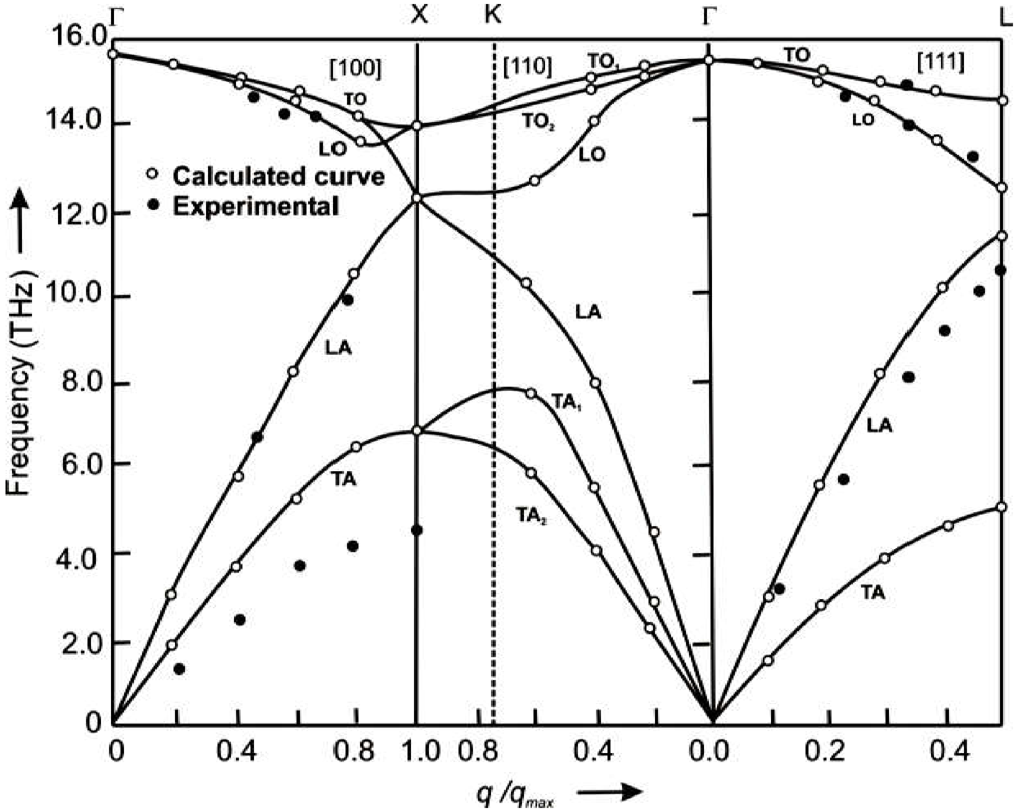

Figure 1: Phonon dispersion curves of silicon along symmetry directions. Solid circles represent the experimental results [29].

Table 2: Elastic constant in units of 10^{12} dyne cm^{-2} and bulk modulus in 10^{12} erg/cm^3

	Experimental values	Calculated values	Calculated values (others)			
			(34)	(35)	(31)	(31)
C_{11}	1.657	1.552	1.207	-	-	-
C_{12}	0.629	0.748	0.860	-	-	-
C_{44}	0.796	0.789	0.317	0.943	0.717	-
K	0.988	2.000	-	-	-	2.00

Specific heats and Debye characteristic temperatures of silicon

Following the theory of specific heat of solids by Born and Von Karman [10] the atomic specific heat at constant volume is given by

$$C_V = 3NR\sum_{\nu} E(\nu)g(\nu) \qquad (15)$$

Where N=*1/3mn*, *m* = number of divisions in the first Brillouin zone, *n* = number of atoms in the unit cell, *R* = universal gas constant, *g(ν)*= frequency distribution function and *E(ν)* is the Einstein function given by

$$E(\nu) = (h\nu)^2 \exp(h\nu/kT)/\exp(h\nu/kT)^2 \qquad (16)$$

For the calculation of Debye temperatures θ_D at various temperatures, the value of C_V is computed first with help of equation (15). θ_D/T values corresponding to computed values of C_V are obtained from ($C_V \sim \theta_D/T$) Table [32]. Having a theoretical value of θ_D/T obtained in this way, θ_D is obtained at various temperatures.

The vibration frequencies of silicon for 48 wave vectors are computed employing EVFF model developed in the present work. The frequency distribution function g(ν) is obtained from computed values of phonon frequencies. The computed values of *g(ν)* are utilized in obtaining the specific heats at different temperatures for silicon. The frequency distribution spectrum for silicon is shown in Figure 2.

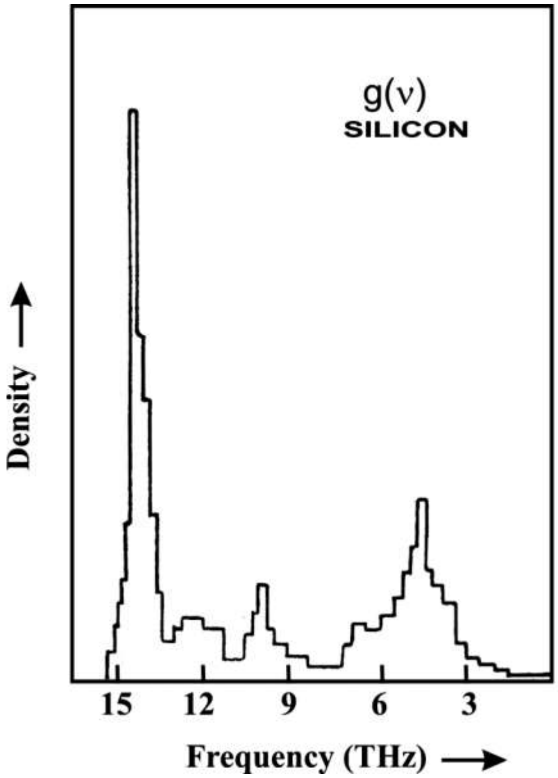

Figure 2: Frequency distribution spectra for silicon.

The computed results of Debye characteristic temperatures for silicon is given in Figure 3. The experimental results obtained by Flubacher and Leadbetter [33] are given in Figure 3 for comparison. The agreement between present theoretical results obtained on the basis of EVFF model and those obtained experimentally is fairly satisfactory with slight variation at high temperature. It is to be noted that the divergence of our results with the experimental ones is comparable with that of Zdetsis and Wang [9] obtained by applying BKM [10] using sixteen parameters. The deviations from experimental results at higher temperatures are mainly due to harmonic approximation adopted in the present theoretical model. Inclusion of anharmonic or quasi-harmonic factors in the development of the lattice dynamical model is expected to remove the divergence at higher temperatures. At higher temperatures anharmonocity becomes dominant. It is noteworthy that a simple four parameter EVFF model is successful in explaining the variation of θ_D with temperatures.

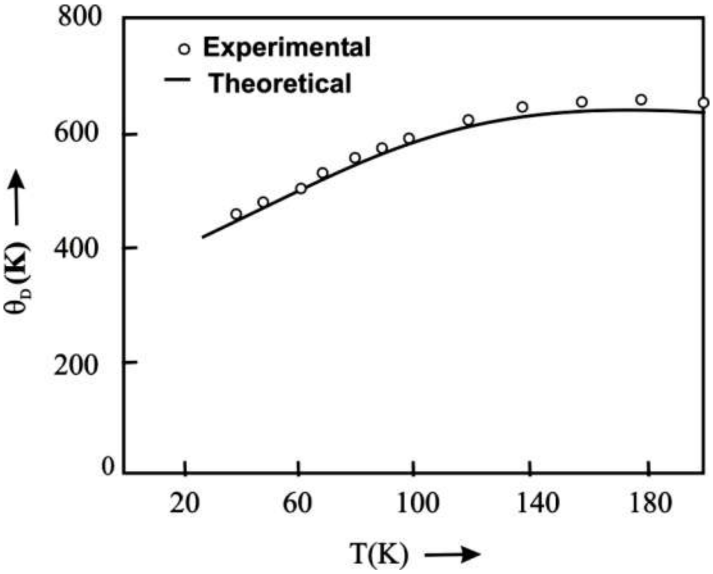

Figure 3: (θ_D~T) curve for silicon. Circles represent the experimental result [33].

CONCLUSIONS

The present EVFF model developed for the tetrahedrally bonded elemental and binary semiconducting crystals of diamond structure and zinc-blende structure respectively explains satisfactorily the experimental results of phonon dispersion curves, elastic constants, bulk modulus, and Debye characteristics temperatures of silicon. It is significant that the present model does not require the use of experimental values of elastic constants, yet it reproduces the elastic constants results almost same as the experimental values. The result obtained in the present work is expected to improve if interaction terms between bond-stretching and bond-bending internal coordinates are included in the model. Notwithstanding, the application of a simple four parameter EVFF model which theoretically explains the lattice vibration and thermal properties of silicon is an additional significant features of the present study.

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