Lattice Dynamics of Diamond

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Abstract

A phenomenological model has been developed for zinc blende structure and diamond structure crystals. Both types of crystals are covalent and tetrahedrally bonded. The model developed in the present work is an extended valence force field model which takes into account the short-range valence force interactions between bonded atoms and central interaction between non-bonded atoms. The model also incorporates the long-range coulombic interaction for zinc-blende structure crystal which are partially ionic in bonding. The extended valence force model has been applied to lattice vibration of diamond to obtain the theoretical values of phonon dispersion curves along three principal symmetry directions and Debye characteristic temperatures at different temperatures. The calculated results are compared with the available experimental values with satisfactory agreement.

Keywords: Phenomenological model, covalent bonding, specific heats, Debye characteristic temperature.

Introduction

Diamond is an elemental semiconductor which is entirely different from other elemental semiconductors of diamond structure. The study of diamond has been made extensively both experimentally and theoretically. Earlier Pandey and Dayal[1] and Singh and Dayal[2] have reported the lattice dynamics of diamond. Patel[3] et al also reported the lattice dynamics of diamond applying BKM for phonon dispersion curves along different symmetry directions. Bashnov[4] et al studied the lattice dynamics of diamond structure crystal using Keating's valence force field. In recent years some studies[5-6] have been made on the different aspects of lattice dynamics of diamond and diamond structure elemental semiconductors. Recently some studies[7-10] have been reported on lattice dynamics and other properties of tetrahedrally bonded elemental and binary semiconducting crystals.

In present lattice dynamical model of diamond structure crystals the valence force field model has extended to include the central interaction between non-bonded atoms up to second neighbors for short-range interactions. In addition to this the bond-bending, bond-stretching and interactions between bond-stretching internal coordinates are considered for short-range interaction between atoms. The extended valence force field model is developed for the zinc-blende crystals which are partially ionic and takes into account the coulombic interaction. The model is modified for the diamond structure elemental semiconductor crystals which are predominantly covalent and the ionicity is almost negligible. The extended valence force field is physically realistic for such covalent elemental semiconductor crystals.

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 extended valence force field (EVFF) takes into account the interaction between non-bonded atoms of the crystal in accordance with the modification of Urey-Bradley[11]. The changes in the bond-length and bond-angles during vibration are called internal coordinates, following the method of Wilson[12] et al, the valence internal coordinates are transformed into atomic displacement coordinates of the crystal as reported by Singh and Roy[13]. 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

$$V = \frac{1}{2}\sum_{j=1}^{4} K_r \left(\delta r_{ij}\right)^2 + \frac{1}{2}\sum_{l=1}^{12} K'_r \left(\delta r_{il}\right)^2 + \frac{1}{2}\sum_{k=1}^{12} K''_r \left(\delta r_{ik}\right)^2$$
$$+ \frac{1}{2}\sum_{\theta_{jik}=1}^{4} K'_\theta \left(\delta\theta_{jik}\right)^2 + \frac{1}{2}\sum_{\theta_{ijl}=1}^{4} K''_\theta \left(\delta\theta_{ijl}\right)^2 + \frac{1}{2}\sum_{r_{ij}=1}^{4} K_{rr} \left(\delta r_{ij}\right)\left(\delta r_{ik}\right)$$

(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

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

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

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

In equation (3) $D_{\alpha\beta}\binom{q}{\sigma\sigma'}$ 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 diamond 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 $K_r' = K_r''$, $K_\theta' = K_\theta'' = K_\theta$

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 extended valence force field model (EVFF) are obtained for diamond lattice.

$$D_{xx}(q,11) = \frac{1}{m}\left[\frac{4}{3}K_r - \frac{2}{3}K_{rr} + 4K_r' + \frac{28}{3}\frac{K_\theta}{r_0^2} + \frac{8}{3}\frac{K_\theta}{r_0^2}\cos\pi q_y \cos\pi q_z \right.$$
$$\left. - \left(2K_r' + \frac{2}{3}\frac{K_\theta}{r_0^2}(\cos\pi q_x \cos\pi q_z + \cos\pi q_x \cos\pi q_y)\right) \right] \tag{4}$$

$$D_{xy}(q,11) = \frac{1}{m}\left[\left(2K_r' + \frac{2}{3}\frac{K_\theta}{r_0^2}\right)\sin\pi q_x \sin\pi q_y + \frac{4}{3}\frac{K_\theta}{r_0^2}i\sin\pi q_z \right.$$

$$\left. (\cos\pi q_x - \cos\pi q_y) \right] \tag{5}$$

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

$$D_{xy}(q,22) = \frac{1}{m}\left[2K_r' + \frac{2}{3}\frac{K_\theta}{r_0^2}\sin\pi q_x \sin\pi q_y - \frac{4}{3}\frac{K_\theta}{r_0^2}i\sin\pi q_z \right.$$

$$\left. (\sin\pi q_x - \sin\pi q_y) \right] \tag{7}$$

$$D_{xx}(q,12) = -\frac{1}{m}\left[\left(\frac{4}{3}K_r + \frac{2}{3}K_{rr} - \frac{32}{3}\frac{K_\theta}{r_0^2}\right) \right.$$
$$\left. \left(\cos\frac{\pi q_x}{2}\cos\frac{\pi q_y}{2}\cos\frac{\pi q_z}{2} - i\sin\frac{\pi q_x}{2}\sin\frac{\pi q_y}{2}\sin\frac{\pi q_z}{2}\right) \right] \tag{8}$$

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

Here r_0 is the chemical bond length and 'a' is half lattice constant, other elements of the determinantal matrix $D_{\alpha\beta}(q,\sigma\sigma')$ 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.

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

Elastic constants: Taking into account the contribution from coupling coefficients, the following expression 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 diamond are obtained with the help of the expression of the longitudinal and transverse optic phonons at zone center 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 expression are

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

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

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

From these expression, we have

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

and

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

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 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 diamond crystal are given in the table-1.

Table-1

Input Physical data	Model parameters in units of 10^4 dynes cm⁻¹
$\nu_{LO}(\Gamma) = 39.975\,THz$	$K_r = -14.309212$
$\nu_{LO}(X) = 35.52\,THz$	$K_r' = 3.577303$
$\nu_{TO}(X) = 32.16\,THz$	$K_{rr} = -76.067446$
2a (lattice constant) = 3.5668×10^{-8} cm	$K_\theta = 2.935913$
m(mass) = 19.9366×10^{-34} gm	

Results and Discussion

Phonon dispersion curves for diamond: Warren[14] et al measured the phonon frequencies in symmetry directions. Robertson[15] et al reported the first order Raman spectra of diamond. The one phonon infrared spectra of diamond have been studied experimentally by Smith and Hardy[16]. The precise data on second order Raman spectra for diamond are made available by Solin and Ramdas[17].

The phonon dispersion curves along different symmetry directions have been obtained on the basis of extended volume force field approximation by solving the secular equation utilizing the values of model parameters given in table. The phonon dispersion curves along symmetry directions [100], [110] and [111] are shown in Figure-1. The experimental points due to Warren[14] et al have also been shown in figure. The computed results are in excellent agreement with the experimental values. In view of the small number of force parameters used in the present work, the EVFF model describes satisfactorily the phonon dispersion results obtained experimentally.

Specific Heat and Debye Characteristic Temperatures of Diamond: Following the theory of specific heat of solids by Born and Von Karman[18] the atomic specific heat at constant volume is given by

$$C_V = 3NR\sum_\nu E(\nu)g(\nu) \qquad (14)$$

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) is the frequency distribution function and E(ν) is the Einstein function given by

$$E(\nu) = \frac{(h\nu)^2 \exp(h\nu/KT)}{\exp(h\nu/KT^{-1})^2} \qquad (15)$$

For the calculation of Debye characteristic temperature θ_D at various temperatures, the values of C_V is computed first with the help of equation (14). θ_D/T values corresponding the different computed values of C_V are obtained from $C_V - \theta_D/T$ table[19]. Having a theoretical values of θ_D/T obtained in this way, θ_D is obtained at various temperatures.

The vibrational frequencies of diamond for 48 wave vectors are computed employing the EVFF model. The frequency distribution function g(ν) is obtained from computed values of phonon frequencies. The computed values of g(ν) are used in calculating the specific heats at different temperatures for diamond crystal.

The computed results of Debye characteristic temperatures for diamond in the present work are given in figure-2. The experimental values of Pitzer[20] are also given in the figure. The theoretical results agree satisfactory at low temperatures. However, there is a divergence from experimental results at higher temperatures. This is mainly due to the harmonic approximation adopted in the calculation of the vibrational potential energy of atoms of the crystal. The calculated results may be improved if anharmonic vibration is considered in the development of this lattice dynamical model. But our results compare well with the results of Pandey and Dayal[1]. Noteworthy feature of EVFF model lies in the fact that it involves small number of parameters, the evaluation of which

does not take help of the measured values of elastic constants. Notwithstanding, the model explains satisfactorily the phonon dispersion curves and Debye characteristic temperatures.
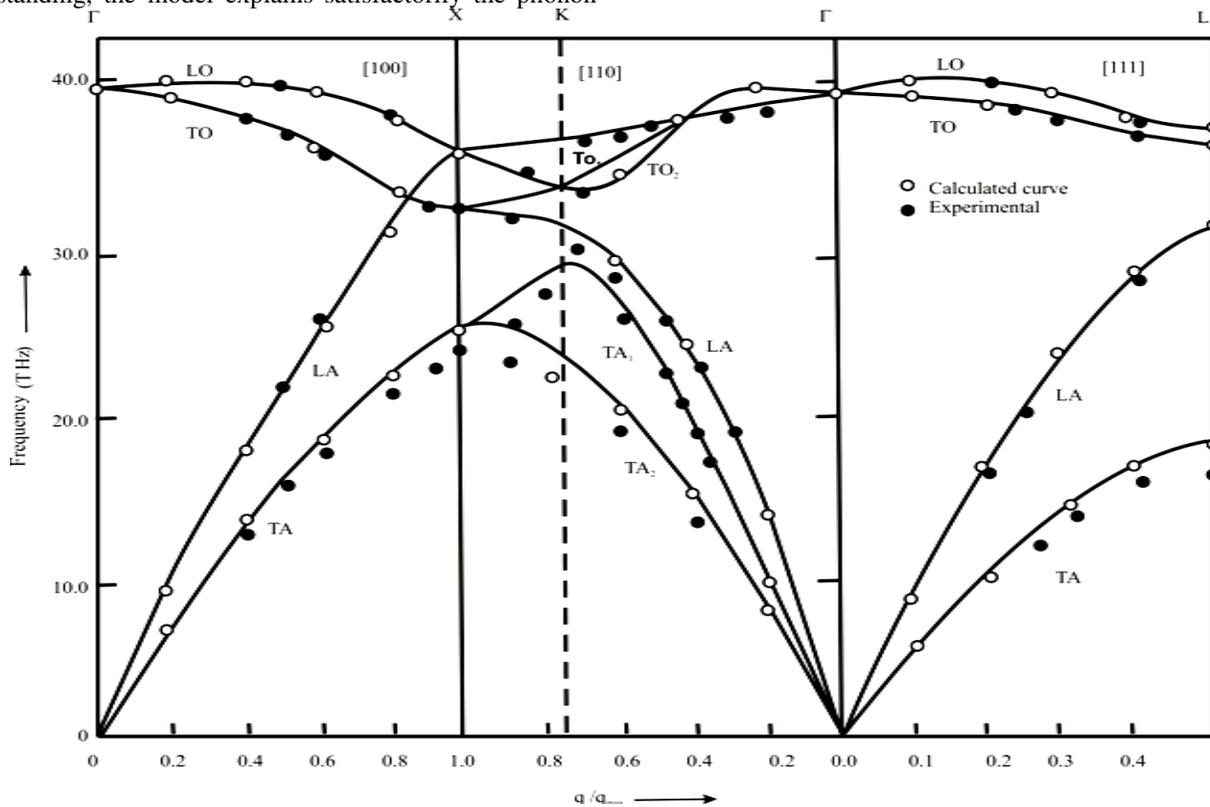
Figure-1
Phonon dispersion curves of diamond along symmetry directions. Solid circles (•) represent the experimental results (Ref.14)
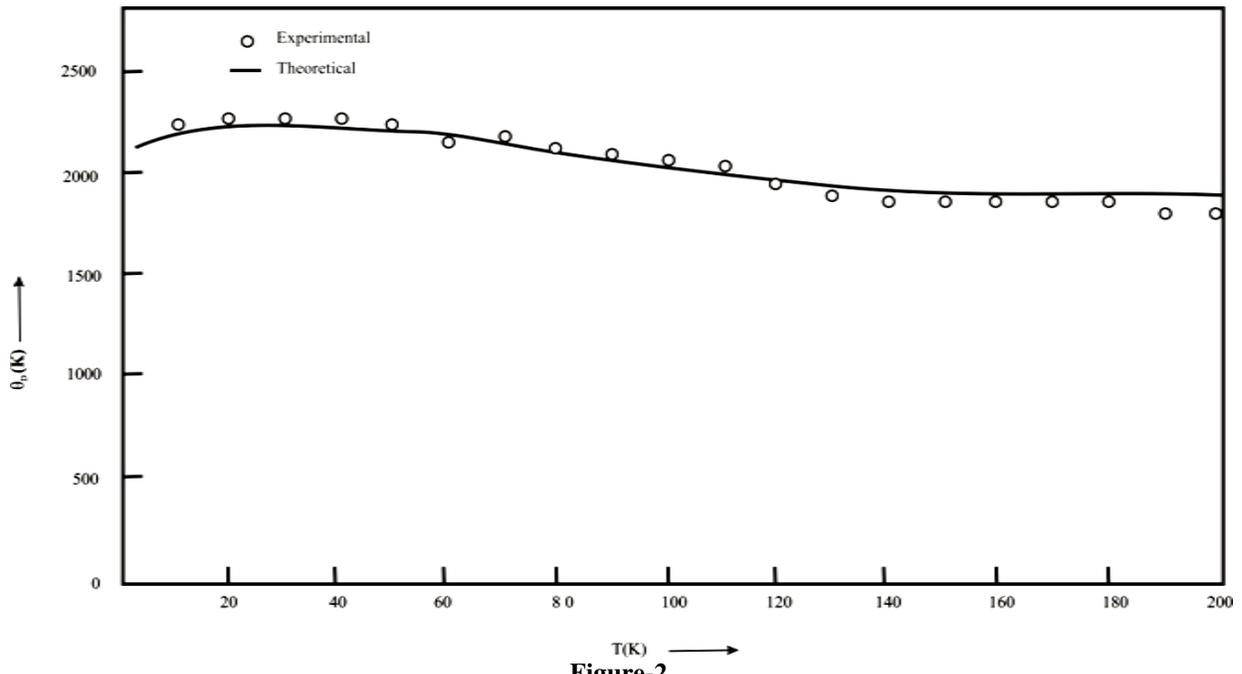
Figure-2
(θ_D-T) curve for diamond. Circles represent the experimental results (Ref.20)

Conclusion

The extended valence force field (EVFF) developed for the tetrahedrally bonded elemental and binary semiconductors has been found to explain satisfactorily the experimental results of phonon dispersion curves, specific heats and Debye characteristic temperatures of diamond. It is significant the present lattice dynamical model developed for elemental semiconductors does not require the use of the values of elastic constants for the evaluation of model parameters.

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