

Lattice dynamics of Germanium

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Abstract : The model employed in the theory of lattice dynamics based on any other phenomena is called the phenomenological model. The valence force field is employed in the vibrations of molecules in the fluid state this idea when applied in the solid-state vibration is called the valence force field. The present model developed for tetrahedrally bonded crystalline solids having zinc blende and diamond structure crystals. This phenomenological model in the present work is an extended valence force field model. The extended valence force field model had been applied to the lattice vibration of Germanium to obtain the theoretical values of the phonon dispersion curve along with three principal symmetry directions and Debye characteristic temperature at different temperatures. The calculated results are compared with the available experimental results.

Keywords :- Phenomenological model, Extended valence force field model, Phonon dispersion curve, Debye characteristic temperature.

I. INTRODUCTION

Germanium is the first element in the diamond series which has been studied experimentally and theoretically by various workers from as early as 1958. Brockhouse and Iyengar⁵ were the first to report the phonon dispersion relations along [100] and [111] directions on the basis of neutron scattering experiments. Later on, Brockhouse and Dasannacharya⁴ measured phonon frequency on some new wave vectors. The most complete and perfect data on germanium became available from the work of Nilsson and Nelin⁹. The two phonon infrared absorption spectra of this crystal have been studied by Fray et al¹³. The first order infrared spectra of germanium were measured by McFarlane et al⁸. Weinstein and Cardona³ have measured the second-order Raman spectra of germanium. 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 crystal to obtain the phonon dispersion curves and Debye characteristic temperatures. The agreement between experimental and theoretical results have been found to be satisfactorily good. The EVFF model applied to Diamond crystal is extended to describe the lattice dynamical properties of Germanium in the present work.

II. 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 considers the interaction between non-bonded atoms of the crystal in accordance with the modification of Urey-Bradley¹⁰. The changes in the bond-length and bond-angles during vibration are called internal coordinates. Following the method of Wilson et al⁷, the valence internal coordinates are transformed into atomic displacement coordinates of the crystal as reported by Singh and Roy¹⁴. 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

neighboring atoms except first and second neighbors 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

$$V = 1/2 \left(\sum_{j=1}^4 k_r (\delta r_{ij})^2 + \sum_{\ell=1}^{12} k'_r (\delta_{i\ell})^2 + \sum_{k=1}^{12} k''_r (\delta r_{jk}) + \sum_{\theta j i k=1}^4 k_\theta (\delta \theta_{jik})^2 \right. \\ \left. + \sum_{\theta i j \ell=1}^4 k'_\theta (\delta \theta_{ij\ell})^2 + \sum_{r i j=1}^4 k_{rr} (\delta r_{ij}) (\delta r_{ik}) \right) \tag{1}$$

In equation (1), *i* is the reference atom (one type) (1), *j* and *k* are two atoms (another type) 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.

In the case of Germanium lattice, the two atoms are similar. The force constant k'_r and k''_r are taken to be equal. Also k_θ and k'_θ are taken to be equal for similar reasons.

SECULAR EQUATION

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

$$\left| D_{\alpha\beta} \left(\vec{q} \right)_{\sigma\sigma'} - \omega^2 \delta_{\alpha\beta} \delta_{\sigma\sigma'} \right| = 0 \tag{2}$$

where, $D_{\alpha\beta} \left(\vec{q} \right)_{\sigma\sigma'}$ represents the elements of the dynamical matrix and ω is the circular frequency of the normal modes of the vibration. $\delta_{\alpha\beta}$ and $\delta_{kk'}$ are the usual Kronecker delta functions. The secular equation developed under valence force field approximation is solved along the symmetry direction [100], [110], [111] and [1ξ0] of the first Brillouin zone.

Elastic constants

The contributions 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.

$$C_{11} = \frac{1}{2a} \left(4k_r + \frac{1}{3} k_r - \frac{1}{6} k_{rr} + 4 \frac{\gamma}{r_0^2} \right) \tag{3}$$

$$C_{12} = \frac{1}{2a} \left(2k_r + \frac{1}{3} k_r - \frac{1}{6} k_{rr} - 2 \frac{\gamma}{r_0^2} \right) \tag{4}$$

$$C_{44} = \frac{1}{2a} \left(2k_r + \frac{1}{3} k_r - \frac{1}{6} k_{rr} + \frac{2}{3} \frac{\gamma}{r_0^2} - \frac{A^2}{B} \right) \tag{5}$$

where $A = - \left(\frac{2}{3} k_r - \frac{1}{3} k_{rr} - \frac{8}{3} \frac{\gamma}{r_0^2} \right)$

$$B = \frac{4}{3} k_r - \frac{2}{3} k_{rr} + \frac{32}{3} \frac{\gamma}{r_0^2}$$

Evaluation of model Parameters

The values of model parameters are obtained with the help of the expressions of frequencies of longitudinal and transverse optic phonons at zone centre and at the boundary of Brillouin zone along [100] direction. The expressions for LO(Γ), LO(X) and TO(X) as obtained in equation (6), (7) and (8) are

$$\frac{m}{2} \omega_{LO}^2(\Gamma) = \frac{4}{3} k_r - \frac{2}{3} k_{rr} + \frac{32}{3} \frac{\gamma}{r_o^2} \dots\dots\dots(6)$$

$$m \omega_{LO}^2(X) = \frac{4}{3} k_r - \frac{2}{3} k_{rr} + 8kr' + \frac{40}{3} \frac{\gamma}{r_o^2} \dots\dots\dots(7)$$

$$m \omega_{TO}^2(X) = \left(\frac{8}{3} k_r - \frac{4}{3} k_{rr} + 4k_r' + \frac{4}{3} \frac{\gamma}{r_o^2} \right) \dots\dots\dots(8)$$

From these expressions we have,

$$\frac{\gamma}{r_o^2} = \frac{3}{16} \left[\frac{1}{8} m \omega_{LO}^2(X) - \frac{1}{4} m \omega_{TO}^2(X) + \frac{3}{16} m \omega_{LO}^2(\Gamma) \right] \dots\dots\dots(9)$$

and

$$k_r' = \frac{1}{16} \left[\frac{15}{8} m \omega_{LO}^2(X) + \frac{1}{4} m \omega_{TO}^2(X) - \frac{19}{16} m \omega_{LO}^2(\Gamma) \right] \dots\dots\dots(10)$$

The parameter k_r is calculated by applying the equilibrium condition of the lattice. After obtaining the values of k_r , k_r' and $\frac{\gamma}{r^2}$, the value of k_{rr} is calculated from equation (10). It is significant to note that the valence force parameters have been evaluated without making use of the elastic constants C_{11} , C_{12} , and C_{44} of the crystals. The input physical data and calculated values of model parameters are given in Table 01 ji

Table-01 :Input physical data and calculated values of model parameters for germanium.

Input Physical Data	Model parameters in units of 10^4 dyne cm^{-1}
$\nu_{LO}(\Gamma) = 9.12$ THz	$k_r = -1.876336$
$\nu_{LO}(X) = 7.21$ THz	$k_r' = 0.469084$
$\nu_{TO}(X) = 8.26$ THz	$k_{rr} = -26.26348$
2a (lattice constant) = 5.65735×10^{-8} cm	$\frac{\gamma}{r_o^2} = 0.449778$
m (mass) = 120.553×10^{-24} gm	

III. RESULT AND DISCUSSION

Tubino et al¹², Soma and Morita¹⁵, Sinha and Zdetsis and Wang² reported the results for the phonon dispersion curve of germanium along with different symmetry directions. Soma et al¹⁵ presented the local Heine Abarenkov model potential for diamond-type crystals and got a good fit of the theoretical results with the observed data for phonon curves of germanium. Using 3D force constants Santiago-Perez et al⁶ calculated phonon dispersion curve for Ge which crystallizes in the diamond structure, and excellent agreement is found with the experimental data in [100] and [110] symmetry directions only.

The phonon dispersion curve of germanium has been calculated in the present work and shown in Fig.01 and 02. The calculated values of elastic constants and bulk modulus in the present work along with the experimental values are given in Table 02. Calculated elastic constants and bulk modulus by other workers are also given in Table 02 for the comparison.

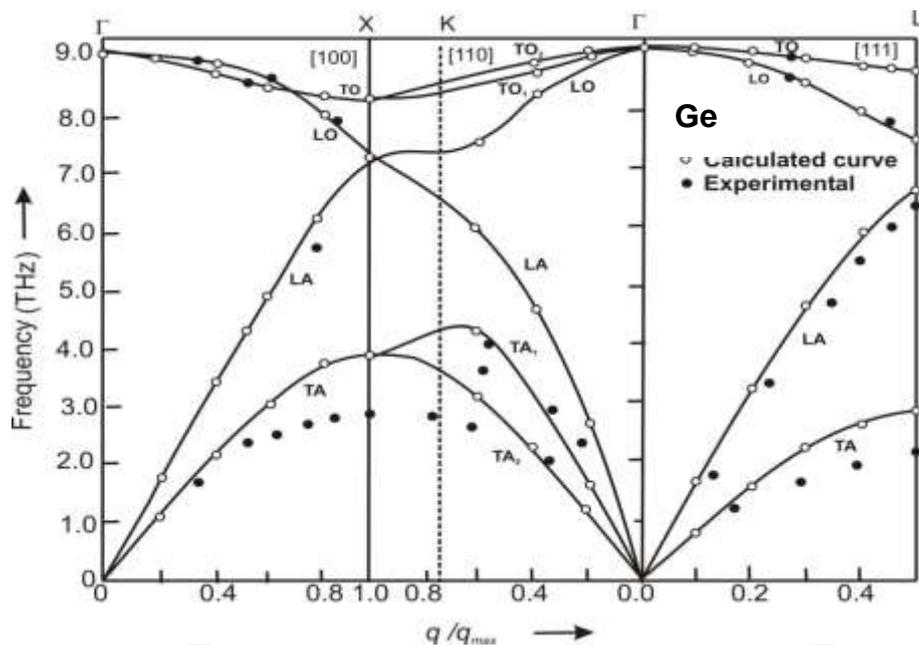


Fig-01 : Phonon dispersion curves of germanium along symmetry directions. Solid

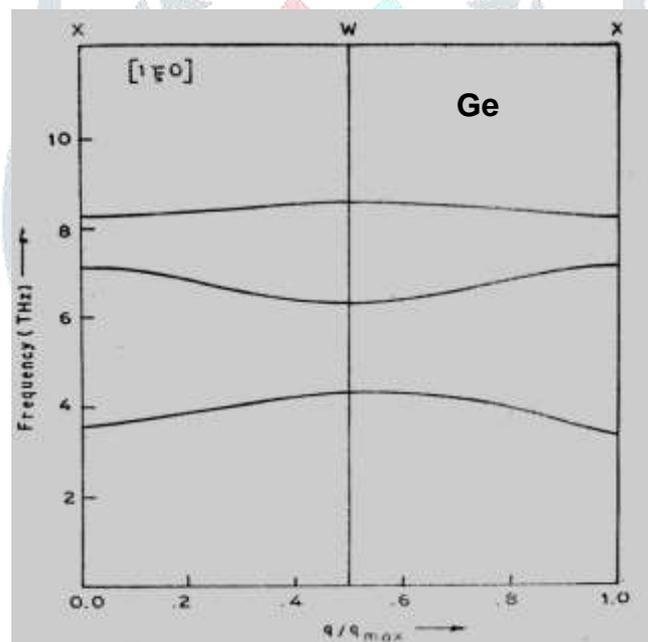


Fig-02 : Phonon dispersion curves of germanium along $[1\xi 0]$ direction.

The results obtained in the present work agree fairly well with the experimental values of Nilsson and Nelin⁹ shown in the figure. The agreement is poor for the transverse acoustic branch along $[100]$ direction. There is no experimental result for the phonon dispersion curve along $[110]$ and hence the comparison is not possible. However our results agree well with those of Tubino et al¹² along $[110]$ direction. In view of a simple four parameter model, the agreement is satisfactory. The calculated values C_{11} and C_{44} are in fair agreement with the experimental values but the value of C_{12} does not agree well with the experimental value. Our calculated value of C_{12} is found to be in agreement with the calculated values of Steif et al¹. The calculated value of bulk modulus is in agreement with the experimental value whereas the calculated value of Harrison and Sokel¹⁶ differ significantly from the experimental value.

Table-02 :Comparison of calculated values of elastic constants in units of 10^{12} dyne cm^{-2} and bulk modulus in 10^{12} erg/ cm^3 with the experimental values of germanium.

	Experimental values	Present calculated values	Calculated values (others)				
			a	b	c	d	e
C11	1.289	1.313	0.949	1.289			
C12	0.488	0.670	0.700	0.483			
C44	0.673	0.527	0.230	0.671	0.566	0.783	1.0
K	0.772	0.884					

Specific heat and Debye characteristic temperature of Germanium

According to born and Von Karman theory specific heat at constant volume is

$$C_v = 3NR \sum_v g(v) E(v) \quad \text{.....(11)}$$

where $N = 1/3 mn$

m = number of divisions in the first Brillouin zone

n = number of atoms in unit cell

R = Universal gas constant

$g(v)dv$ is the number of modes with frequencies lying between v and $v+ dv$. $g(v)$ is called the frequency distribution function for the solids. $E(v)$ is called the Einstein function defined by

$$E(v) = \frac{(\delta v)^2 \exp(\delta v / kT)}{\exp(\delta v / kT) - 1} \quad \text{.....(12)}$$

The vibrational frequencies for germanium for the 48 wave vectors have been computed. The frequency distribution function calculated for germanium using these vibrational frequencies are shown in Fig. 3. The specific heat at different temperatures have been computed with the help of frequency distribution function. The Debye characteristic temperature θ_D are calculated from the computed data of specific heat and are shown in Fig. 4 along with the experimental results. The calculated θ_{D-T} curves agree well with the experimental values of Flubacher and Leadbetter¹¹. The calculated values deviate from the experimental ones at high temperatures. Our results of Debye temperatures are almost same as those of Zdetsis and Wang².

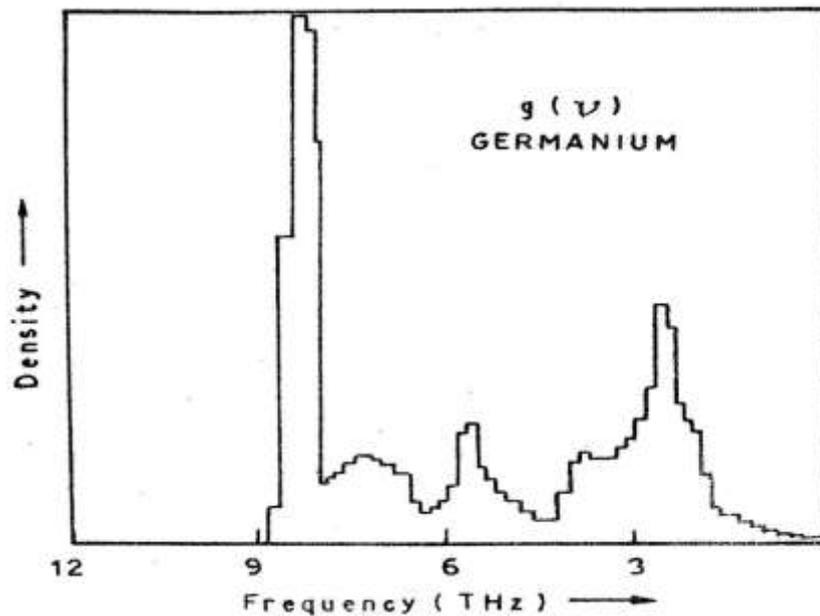


Fig. 3 : Frequency distribution for germanium.

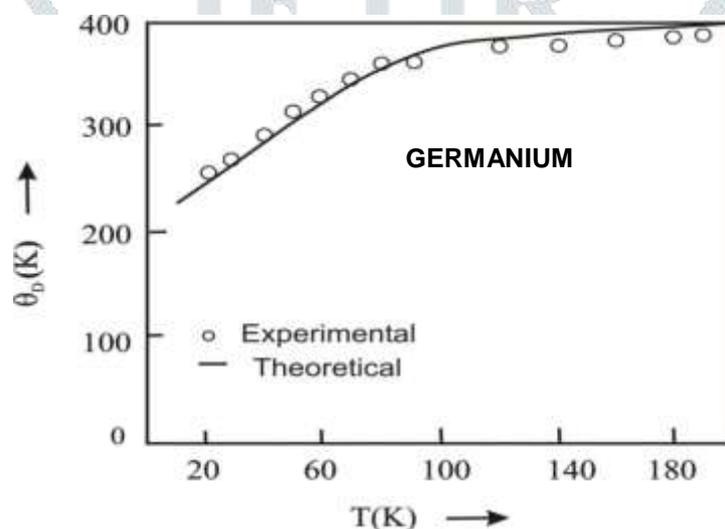


Fig.4 : θ_D versus temperature curve for germanium. Circles are experimental results.

Conclusion

The valence force field model developed in the present work is a simple rigid ion model involving only a smaller number of parameters compared to other workers. The results obtained for the phonon dispersion curves, specific heats at different temperatures and Debye characteristic temperature are compared with the available experimental observations of these properties by different workers. The comparison of the theoretical results with the available experimental values suggests significantly that the dynamical model explains satisfactorily the experimental observations. The minor variation in the case of specific heats and Debye characteristic temperature at high temperature is due to the limitations of the model.

The results obtained in the present work agree fairly well with the experimental values of Nilsson and Nelin⁹.

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