Indian Journal of Pure & Applied Physics
Vol. 52, October 2014, pp. 684-688

Phonon spectrum and thermal properties of mixed semiconducting compound $ZnS_{1-x}Se_x$

A K Kushwaha

Department of Physics, K N Govt P G College Gyanpur, Bhadohi 221304, India

E-mail: akkphys_bu@yahoo.com

Received 13 April 2013; revised 25 July 2013; accepted 17 January 2014

Phonon spectrum and thermal properties of mixed semiconducting compound $ZnS_{1-x}Se_x$ have been calculated by using a proposed three-body shell model (TBSM). This model incorporates the effect of three-body and short-range repulsive forces including second nearest neighbours, in addition to long-range Coulombic interactions in the frame work of rigid-shell model with both the ions polarizable. Using the above proposed model, the phonon dispersion relations, phonon density of states and Debye characteristic temperature have been calculated and plotted for the compound $ZnS_{1-x}Se_x$. The comparison of the theoretical results with the available experimental has been made along high symmetry directions. An overall good agreement between theoretical and experimental results has been found.

Keywords: Phonon spectrum, Semiconductor, Phonon, Density of states

1 Introduction

An accurate determination of phonon dispersion curves is important to study the physical properties of solids such as infrared, Raman and neutron diffraction spectra, specific heat, thermal expansion electron-phonon interaction and lattice thermal conduction. As a matter of fact, their understanding in terms of phonons is considered to be one of the most convincing pieces of evidence that our current quantum picture of solids is correct[1]. On the experimental side, Raman spectroscopy has been used to obtain the zone-center phonon frequencies of these materials. Investigations of their lattice vibrations were started early and are of interest because this material is the prototype of the important zinc-blende family of semiconductors.

The vibrational and thermodynamic properties of II-VI mixed semiconductor systems are widely studied in the recent years. $ZnS_{1-x}Se_x$ is one of them. $ZnS_{1-x}Se_x$ is promising solid solution for optoelectronic devices including waveguides and blue light emitting diodes. Zinc sulphide and zinc selenide both are wide gap II-VI compound semiconductors. These two compounds form a series of solid solution throughout the wide range of composition, with band-gap ranging from 2.78 eV in ZnSe to 3.79 eV in ZnS at 300K which is capable to emit visible luminescence. Vibrational and thermodynamical properties of mixed semiconductor $ZnS_{1-x}Se_x$ have been studied theoretically and experimentally by many researchers[2,3]. Despite of the interest in $ZnS_{1-x}Se_x$, several properties (like vibrational and thermodynamic ones) are at present poorly known.

Recently, Postnikov *et al*[4]. have calculated the vibrational properties of $Zn_{1-x}Be_xSe$ using *ab initio* technique in the sequence of density functional theory calculations. Postnikov *et al*[4]. have been using computer code[5] SIESTA which incorporates norm-conserving pseudopotentials in the combination with atom-centered strictly confined numerical basis functions[6,7]. They have constructed pseudopotentials along the Troullier-Martins[8] scheme. Oussaufi *et al*[9]. have calculated the elastic properties and the zone-centre phonon frequencies for zinc-blende structure compound $Sc_xGa_{1-x}N$ using an empirical pseudopotential method (EPM) under the virtual crystal approximation (VCA), combined with Harrison bond-orbital model. In which the EPM involves the fitting of the atomic form factors to experiment so as to reproduce as accurate as possible the observed gaps at selected points in the Brillouin zone. They have calculated the compositional variation of elastic constants, bulk modulus, shear modulus and optical phonon frequencies for $Sc_xGa_{1-x}N$. Very recently, Kushwaha *et al*[10]. have calculated only the phonon dispersion relations for $ZnS_{1-x}Se_x$ using three-body shell model.

In the present paper, the phonon dispersion relations, phonon density of states and Debye characteristics temperature for II-VI mixed semiconductor $ZnS_{1-x}Se_x$ using a three-body shell model proposed by Kushwaha *et al*[10]. have been studied.

2 Potential Model

The three-body shell model (TBSM) incorporates the effect of three-body and the short-range repulsive forces up to and including the second nearest neighbours, in addition to the long-range Coulombic interactions in the frame-work of rigid-shell model (RSM) due to Woods *et al*[11]. with both the ions polarizable. The general formulation of TBSM remains in the harmonic approximation can be derived from the work at Cochran and his collaborators[12] who have developed the frame work of RSM.

The lattice dynamical calculations are carried out by using a three-body shell model described in the literature[10]. According to Kushwaha[10], the harmonic potential energy per unit cell for zinc-blende structure compounds can be written as:

$$\phi = \phi^{SM} + \phi^{TB} \qquad \ldots(1)$$

where ϕ^{SM} and ϕ^{TB} are the potential energies of the binary crystal in the frame-work of RSM and three-body interaction, respectively.

The secular determinant, for determining the angular frequencies of vibration for the crystals may be obtained by solving the characteristic equation:

$$|D_{\alpha\beta}(\mathbf{q}, kk') - \omega^2\,\delta_{\alpha\beta}\,\delta_{kk'}| = 0 \qquad \ldots(2)$$

for various wave vectors $\mathbf{q}$ in the reciprocal space. The symbols $k, k' = 1,2$ represent the type of atoms in the unit cell and $D_{\alpha\beta}(\mathbf{q}, kk')$ are the elements of dynamical matrix.

2.1 Two-Body Short-Range Interaction

For the short-range non-Coulombic interaction, the potential energy of the zinc-blende structure ϕ using Taylor's series can be expressed as:

$$\Phi_1 = \sum_{lmn}\left[\frac{1}{r}\left(\frac{d\phi}{dr}\right)_{|r|=r_1}\left\{r^o_{lmn}(S_{lmn}-S_o)+\frac{1}{2}|S_{lmn}-S_o|^2\right\} + \frac{1}{2}\left\{\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi}{dr}\right)\right\}_{|r|=r_1}\left\{r^o_{lmn}\cdot(S_{lmn}-S_o)\right\}^2\right] \qquad \ldots(3)$$

where S_0 and S_{lmn} are the displacements of the central ion and its first neighbour ions from their normal positions, r_{lmn} represents the position coordinates of neighbouring ions in equilibrium. *l, m, n*, represent the direction cosines of the line joining the central ion and the nearest neighbours. $|r_1|$ is the nearest neighbour distance.

In the present work, the two-body short-range interactions between central ion and its first and second nearest neighbors, have been considered. Let A be the force constant corresponding to the second derivative of the potential energy in the above expression for the first nearest neighbour:

$$\frac{e^2}{V}A = \left.\frac{d^2\phi}{dr^2}\right|_{|r|=|r_1|} \qquad \ldots(4)$$

Similarly A_1, A_2 are the force constants for the second neighbours which includes two different types of similar atoms.

$$\frac{e^2}{V}A_1 = \left.\frac{d^2\phi}{dr^2}\right|_{|r|=|r_2} \quad (k,\ k) \text{ type of atoms} \qquad \ldots(5)$$

$$\frac{e^2}{V}A_2 = \left.\frac{d^2\phi}{dr^2}\right|_{|r|=|r_2} \quad (k',\ k') \text{ type of atoms} \qquad \ldots(6)$$

2.2 Three-Body Short-Range Interaction

The potential energy Φ_2 giving rise to the TBSM has been assumed to be of the form:

$$\Phi_2 = \frac{1}{2}\left(\frac{e^2}{a^3}\right)\gamma_\theta\,(\delta\theta)^2 \qquad \ldots(7)$$

where $\delta\theta$ is the change in the angle under consideration and γ_θ is the corresponding force constant. The term (e^2/a^3) is simply adjusted to keep force constants in units of (e^2/V), where e is the electronic charge and V $(= 2a^3)$ is the volume of the unit cell.

The change in the angle $(\delta\theta)$ is calculated geometrically as:

$$(\delta\theta) = \left[\frac{\left(\vec{S}_A - \vec{S}_O\right)\cdot\vec{\varepsilon}_{nA}}{|\vec{OA}|} + \frac{\left(\vec{S}_B - \vec{S}_O\right)\cdot\vec{\varepsilon}_{nB}}{|\vec{OB}|}\right] \qquad \ldots(8)$$

where $\vec{S_A}$, $\vec{S_O}$ and $\vec{S_B}$ are the displacement vectors of the respective atoms *A, O* and *B*. $\vec{\varepsilon_{nA}}$ and $\vec{\varepsilon_{nB}}$ are the unit vectors perpendicular to the vectors $\vec{OA}$ and $\vec{OB}$, respectively, and lying in the plane OAB (Fig. 1)

.

2.3 Long-Range Coulombic Interaction

For the Coulomb part, i.e., for Φ_3, the Coulombic contribution of all quantities has been calculated from the equation derived by Kellermann[13]. The potential function for the Coulombic part can be written as:

$$\Phi_3 = \frac{(Zk^{e})(Zk'^{e})}{|r|} \qquad \ldots(9)$$

where $\mathbf{r} = r^0(l',k') - r^0(l,k)$, $Z_k e$ and $Z_{k'} e$ are charges on the k^{th} and k'^{th} ions.

3 Green-Function Technique

We consider a zinc-blende lattice constituted by two interpenetrating sublattice numbered 1 and 2 and occupied by three types of atoms A, B and C in a way that corresponds to the situation in the mixed crystal $AB_{1-x}C_x$. The sublattice 1 is occupied by atoms of type A and sublattice 2 is occupied by atoms of the type B and C. If the occupancy of sublattice 2 is randomly distributed in such a way that the concentration of B is $(1-x)$ and that of C is x, then the situation is of homogeneous mixed crystal.

In a mixed crystal of the type $AB_{1-x}C_x$, we get the dynamical matrix for the mixed system $AB_{1-x}C_x$, of the similar type as given by Kutty[14].

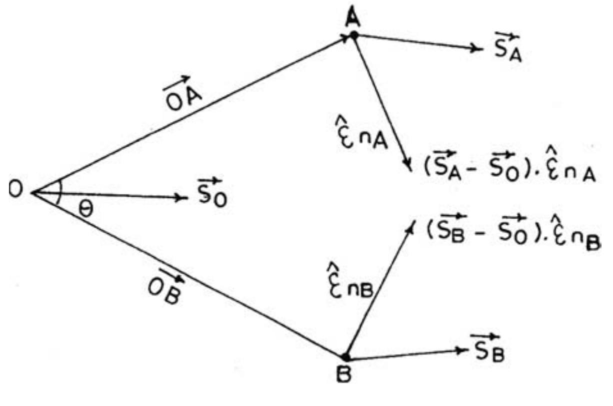

Fig. 1 — Geometrical interpretation of bond-bending interaction

$$\begin{vmatrix} D_{11} - m_A\omega^2 & (1-x)D_{12} & xD_{12} \\ (1-x)D^{\bullet}_{12} & (1-x)^2 D_{11} - m_B\omega^2 & x(1-x)D_{11} \\ xD^{\bullet}_{12} & x(1-x)D^{\bullet}_{11} & x^2(D_{11} - m_C\omega^2) \end{vmatrix} = 0 \qquad \ldots(10)$$

4 Thermal Properties

The vibrational frequencies are determined from the roots of the secular determinant for values of the wave vector corresponding to the non-equivalent points. Each frequency is assigned a statistical weight according to the number of similar points associated with it. When properly weighted, the vibrational spectra corresponding to these non-equivalent points will represent the complete vibration spectra for making use of Blackman's sampling technique[15].

For the sampling purpose, the entire frequency range is divided into a number of intervals of width $\Delta\nu = 0.1$THz and all the frequencies falling into these intervals are counted with their proper statistical weights and from these the histogram representing the frequency distribution $g(\nu)$ is prepared.

The lattice specific heat at constant volume (C_v), at temperature T is expressed as :

$$C_V = 3NK_B \int_0^{V_m} \frac{(hv/k_BT)^2 (e^{hv/k_BT}) g(v) dv (e^{hv/k_BT} - 1)^2}{\int_0^{V_m} g(v) dv} \qquad \ldots(11)$$

where v_m is the maximum frequency, N is the Avogadro's number, h is the Planck's constant and k_B is the Boltzmann constant. The Eq. (11) can be written in the form suitable for computational purpose as:

$$C_v = 3Nk_B \frac{\Sigma_v (hv/k_BT) g(v) dv}{\Sigma_v g(v) dv} \qquad \ldots(12)$$

where $E(hv/k_BT)$ is the Einstein function, defined by:

$$E(x) = x^2 \frac{\exp(x)}{[\exp(x) - 1]^2} \qquad \ldots(13)$$

where $x = (hv/k_BT)$. Also $\Sigma_v g(v) dv$ = total number of frequencies considered = 6000 for zinc-blende structure.

Hence Eq. (12) can be written for zinc-blende crystals as:

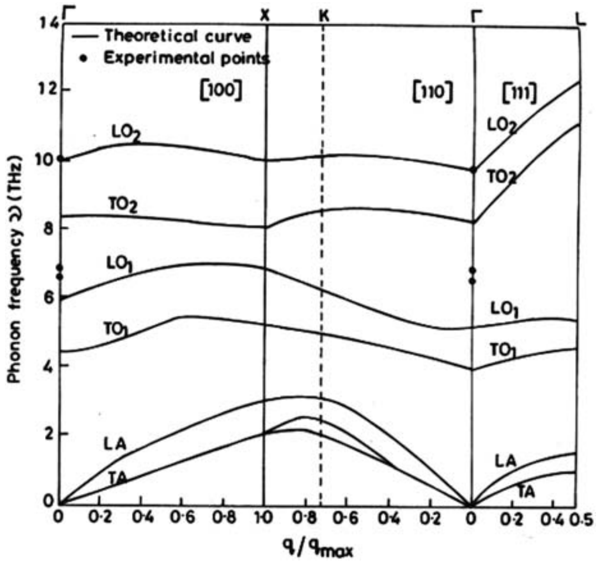

Fig. 2 — Phonon dispersion of $ZnS_{1-x}Se_x$ at $x = 0.2$

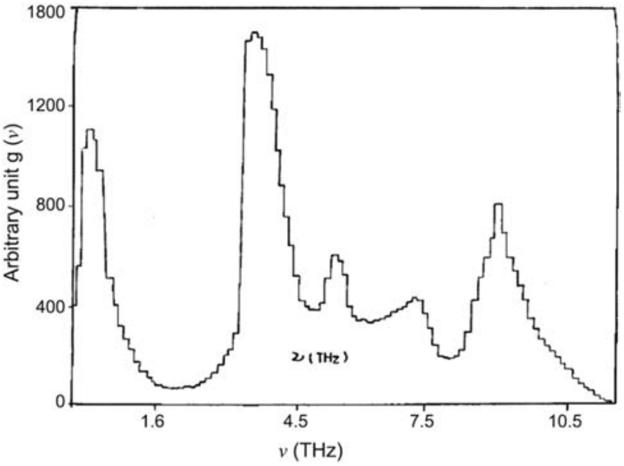

Fig. 3 — Phonon density of states for $ZnS_{1-x}Se_x$ at $x = 0.2$

$$C_v = \frac{3Nk_B}{6000} \Sigma_v E(x) g(v) dv$$

5 Results and Discussion

Our three-body shell model involved 11 parameters. These parameters are two-body short-range interaction (A, A_1, and A_2), three-body short-range interaction (γ_1, γ_2, and γ_3), electronic polarizability (α_1 and α_2), distortion polarizability (d_1 and d_2) and effective charge parameter (Z'). The ternary mixed zinc-blende crystal $ZnS_{1-x}Se_x$ resulted into two crystals at composition $x = 0$ and $x = 1$. These are called end members of the mixed crystal. We have solved the dynamical matrix at the zone-centre and the zone boundaries and found out the force parameters for the end members ZnS and ZnSe and the force parameters for $ZnS_{1-x}Se_x$ at $x = 0.2$ are evaluated using Vegard's law[16]. The calculated phonon dispersion relations are shown in Fig. 2 along with the high symmetry directions. The agreement between theoretical curves with experimental points is quite satisfactory.

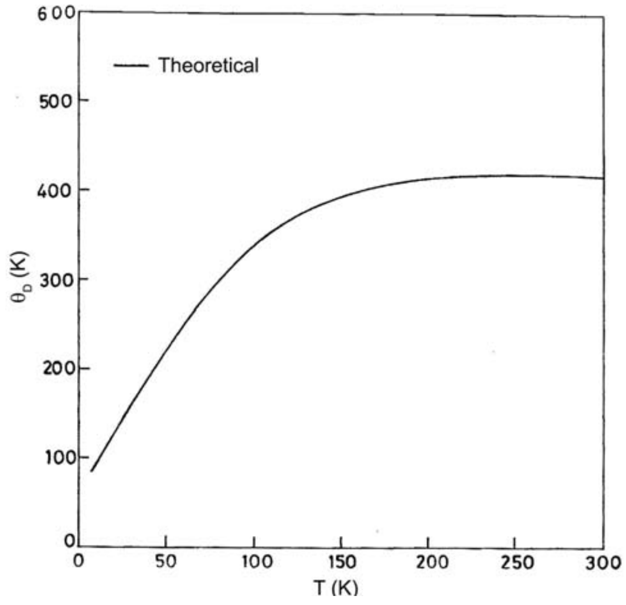

Fig. 4 — Debye characteristics for $ZnS_{1-x}Se_x$ at $x = 0.2$

The frequency distribution curves for $ZnS_{1-x}Se_x$ at $x = 0.2$ is shown in Fig. 3. Whole frequency spectrum is divided into steps of the order of $\Delta\nu = 0.1$ THz. In Fig. 3, the frequencies obtained at 0.3 THz and 3 THz are due to acoustic modes and the frequencies at 3.9 THz, 5.7 THz, 7.5THz and 9.3 THz are due to optic modes in $ZnS_{1-x}Se_x$.

For the calculation of Debye characteristic temperature θ_D at various temperatures, the calculated values of C_v from Eq. (12) at different temperatures (T) are taken and the corresponding values (θ_D/T) are determined from the calculated values of C_v and thus θ_D from temperature in the range 10-300 K are obtained. The calculated values of Debye characteristic temperature θ_D has been plotted as a function of temperature for $ZnS_{1-x}Se_x$ at $x = 0.2$ from 10-300 K, is shown in Fig. 4. Due to the lack of the availability of experimental results for specific heat variation in $ZnS_{1-x}Se_x$ system, we are unable to compare our theoretical results with the experimental results.

References

1 Baroni S, Gironcoli S de & Corso A D, *Rev Mod Phys*, 73 (2001) 515.

2 Brafman O, Chang I F, Lengyel G, Mitra S S & Carnall E, *Phys Rev Lett*, 19 (1967) 1120.

3 Schmeltzer D, Beserman R & Slamovits D, *Phys Rev B*, 22 (1980) 4038.

4 Postnikov A V, Pages O & Hugel J, *Phys Rev B*, 71 (2005) 115206.

5 Soler J M, Artacho E, Gale J D, Garcia A, Junquera J, Ordejon O & Portal D S, *J Phys C*, 14 (2002) 2745.

6 Portal D S, Artacho E & Soler J M, *J Phys C*, 8 (1996) 3859.

7 Qunquera J, Paz O, Portal D S & Artacho E, *Phys Rev B*, 64 (2001) 235111.

8 Troullier N & Tins J L, *Phys Rev B*, 43 (1991) 1993.

9 Oussaifi Y, Fredj A Ben, Debbichi M, Bouarissa N & Said M, *Semicond Sci Technol*, 22 (2007) 641.

10 Kushwaha A K, *Phys Lett A*, 372 (2008) 6145.

11 Woods A D B, Cochran W & Brockhouse B N, *Phys Rev*, (1960) 119.

12 R A Cowley, W Cochran, B N Brockhouse & A D B Woods, *Ibid* (1963) 131.

13 Kellermann E W, *Phil Trans Roy Soc A*, 238 (1940) 513.

14 Kutty A P J, *Solid State Commun*, 14 (1974) 213.

15 Blackman M, *Proc Roy Soc A*, 159 (1937) 416.

16 Vegard's L, *Skr Nor Vidensk Akad Oslo*, 12 (1947) 33.