Four constant potential function of amorphous selenium and evaluation of its thermodynamic and acoustic properties

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Abstract. Litov and Anderson after various considerations suggested a four constant potential function for a-Se as well as a-As$_2$S$_3$. Hence we also used a four constant potential function with the sole purpose of applying this potential function to obtain several acoustic, thermodynamic and other properties. We calculated several acoustic properties of a-Se like second order elastic constants (SOECs), their pressure derivatives, the longitudinal and transverse Grüneisen constant by two different methods, phonon frequencies, absorption band position through the use of Nath–Smith–Delaunay's equation, and the thermodynamic properties like heat capacity, bulk modulus, thermal Grüneisen constant, the pressure derivative of the bulk modulus $(\mathrm{d}K_T/\mathrm{d}P = C_1)$, the pressure derivative of C_1 which is related to Anderson–Grüneisen parameter, pressure derivative of Grüneisen constant namely γ'_g which is related to second Grüneisen constant, characteristics of phonon frequencies, potential energy function through the use of fitted parameters and third order elastic constants. Finally we calculated K_T at the reduced density of $\rho/\rho_0 = 1.1$. K_T is obtained from the potential function with the fitted parameters. In all the above cases the calculated values are found to be in good agreement with experiment wherever available. In this connection it is important to point out that we eliminated 'C' a constant in the potential function using the equilibrium condition as was done by Litov *et al* in a-Se and Gerlich *et al* in the case of a-As$_2$S$_3$ as all amorphous substances are isotropic as mentioned by several authors. We contemplate to calculate several other properties for a-Se and a-As$_2$S$_3$ and present them at a later stage.

Keywords. Second order elastic constant (SOECs); pressure derivative of elastic constants; longitudinal, transverse and thermal Grüneisen constant; absorption band position; heat capacity; bulk modulus; pressure derivative of Grüneisen constant; characteristics of phonon frequencies; potential energy characteristics; third order elastic constants (TOECs).

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1. Introduction

Selenium is a technologically important substance because of its semiconducting [1] and photoelectric properties [2]. Because of these reasons, extensive investigations have been made to understand its properties [3–9]. Of these references, ref. [5] is a classical piece of work. According to Andonov [5, 10] and others it occurs in three important crystaline forms, hexagonal and monoclinic forms and it is found [5, 10] that γ-Se with hexagonal prototype is very stable. Andonov [5] gives an excellent description of a-Se. However one should not confuse crystalline forms with amorphous forms of Se, since this paper is

on a-Se. Extensive description of the properties of amorphous substances is given by Elliott [6]. It consists of hexagonal rings and chains. The fact that $C_{33} \gg C_{11}$ indicates that atoms in the chains are strongly bound whereas the interaction between the chains is of Van der Walls type [7]. According to Martin *et al* [11] the application of hydrostatic pressure promotes transfer of electrons from the intra-chain bonding orbitals to bonding states between chains take place and can bring about a change in the relative charge distribution between inter-chain and intra-chain bonds and hence the force constants change with pressure [11]. Further, the studies of McCann and Cartz [12] clearly predicts a phase transformation at about 130 kbar when the non-bonding orbitals overlap with anti-bonding states at different chains and this causes the weakening of the interchain bond. Hence the simple Lennard–Jones type of potential function cannot predict the various properties theoretically. Therefore one has to add an additional term of Born type. This leads one to add another term to get theoretically several properties of a-Se. Martin *et al* [13] suggested the necessity to add some more terms as the simple bireciprocal functions fails to give experimental results correctly and several others also [3, 5] used an extra term. Like others [3, 5], we also added an exponential term $-e^{-\lambda R/R_0}$ to the Lennard Jones type of potential function. Here R_0 is the interchain distance under equilibrium conditions. The interchain distance according to various workers varies from 3.5 Å–3.8 Å [14, 15] and is nearer to Van der Walls diameters of 4.0 Å [5].

Litov and Anderson [7] did considerable experimental work on a-Se and used a four constant potential function. They experimentally studied the elastic constants and used the very well-known condition of equilibrium [16] to eliminate one of the constants of the potential function.

In the present theoretical investigation we used exactly the same type of potential function and eliminated one of the constants as was done by Litov and Anderson [7]. The method of using the equilibrium condition is very well-known since the times of Born [16] to eliminate an unknown constant. Litov *et al* [5] and the present authors did the same thing. In the present investigations we theoretically obtained pressure derivatives of SOECs by two different methods and calculated the pressure derivative of bulk modulus as well as the second pressure derivative of bulk modulus and hence the evaluation of γ'_g the pressure derivative of the Grüneisen constant, the absorption band position and various other thermodynamic and acoustic properties. Thus our motto is not to change the potential function but to see how well it works for predicting the acoustic, thermodynamic and other properties and also to compute the dispersion curves of ω_L and ω_T with the wave vector. Here ω_L is the longitudinal and ω_T is the transverse frequencies.

2. Theory

2.1

We write the potential function for a-Se following Litov and Anderson [7] as

$$\phi_{(R)} = A\left(\frac{R_0}{R}\right)^m - B\left(\frac{R_0}{R}\right)^n - C\,e^{-(2R/R_0)}. \tag{1}$$

Here a-Se stands for amorphous selenium.

Further A, B, C, n, m and λ are potential energy constants. For convenience we assume $m = 12$ and $n = 6$ as was done by many others [16, 7]. If we have to determine these constants also we require more data. However as was done by Litov and Anderson [7] we also assume 12 and 6 as stated above for m and n respectively [16, 17]. They [7] eliminated C [3, 7] by using the equilibrium condition. This of course is a very well known procedure [16, 17]. This is especially true for all amorphous substances. Thus from equation (1) we eliminate C as was done by Litov and Anderson [7] by using the equilibrium condition that $(d\phi/dR)_{R=R_0} = 0$ and obtain

$$C = \frac{(mA - nB)e^{\lambda}}{\lambda}. \tag{2}$$

This was also done by Litov and Anderson in all their investigations [3, 7]. As is well known the bulk modulus K_T is given by

$$K_T = V\left(\frac{d^2\phi}{dV^2}\right) = \left(\frac{d^2\phi}{dV^2}\right)V \tag{3}$$

which can be rewritten for amorphous substances as [16]

$$K_T = \frac{N}{9V}\left[R^2 \frac{d^2\phi}{dR^2}\right]_{R=R_0}. \tag{4}$$

We define a dimensionless quantity,

$$\rho/\rho_0 = V_0/V = 1/v = (R_0/R)^3,$$

where we assumed along with others [3, 7, 17] that for amorphous substances $V \propto R^3$ [3]. From equations (1), (3) and (4) we get

$$K_T = \frac{N}{9V_0}\left[156A\left(\frac{1}{v}\right)^4 - 42B\left(\frac{1}{v}\right)^2 - (12A - 6B)\lambda v^{2/3}e^{\lambda}(1 - v^{1/3})\right]. \tag{5}$$

Here V_0 is the volume of a-Se under a pressure of one atmosphere. At this stage it is important to discuss the nature of the roots of equation (1). If we have just two terms on the right hand side and with $m = 12$ and $n = 6$ we will have 12 roots but with the addition of an exponential term it becomes transcendental type of equation and there will be several roots and therefore one has to choose the best possible set of constants A, B and λ to give the maximum number of properties in agreement with that of experimental results. The values chosen for $m = 12$ and $n = 6$ is just optional so as to minimise numerical calculations. We choose three experimental values of K_T at 0, 10, and 15 kbar and extensive computational search was made so as to obtain the correct set of properties in agreement with experiment and the best set of parametes were found to be $A = -0.5290 \times 10^{-12}$ erg, $B = +0.7203 \times 10^{-12}$ erg and $\lambda = 14.6364$. Hence we get $(mA - nB) = -10.5726 \times 10^{-12}$ with the assumed values of n and m with these set of parameters we find that at $V_c/V_0 = X_c = 1.45$ the bulk modulus $K_T = 0$ because of the occurence of a phase transition. The experimental value is 1.5 as was obtained by McCann and Cartz [12] in their x-ray analysis data. Now we want to say a few words about the parameters of equation (1). From the fitted parameters with three experimental values of K_T and chosen values of m and n the first two terms are attractive in nature

while $-C\,\mathrm{e}^{-(\lambda R/R_0)}$ is positive and hence repulsive. There is absolutely nothing wrong in having two attractive terms and one repulsive term namely $-C\,\mathrm{e}^{-(\lambda R/R_0)}$. An extensive discussion can be found where two attractive forces exists as in the case of methyl fluoride [16]. Thus $m = 12$ and $n = 6$ are just chosen values and hence the fitted values give the first two terms as attractive while third term which is an exponential term namely $-C\,\mathrm{e}^{-\lambda R/R_0}$ as repulsive. This is just a fit with three K_T values and the set values A, B and λ are not unique. In what follows we give very large number of properties calculated with these parameters. However the potential function with these parameters give exactly the same type of potential function as obtained by Litov and Anderson [7] as it should, since they also form another set of parameters. It may further be pointed out that in the case of simple alkali metals one has to use two repulsive terms as was done by Bardeen [18]. Reed and Gubins [19] give an extensive discussion on various types of potential functions. In fact the third term $-C\,\mathrm{e}^{(\lambda R/R_0)}$ which is repulsive is more quantum mechanically acceptable than any bireciprocal function [17].

2.2 *Evaluation of certain acoustic properties of a-Se with the use of equation* (1)

Bhatia and Singh (BS) defined two quantities β and δ as

$$\beta = \frac{\rho_w R^2}{2M}\left[\frac{1}{R}\frac{\mathrm{d}\phi}{\mathrm{d}R}\right]_{R=R_0} \tag{6}$$

and

$$\delta = \frac{\rho_w R_0^3}{2M}\left[\frac{\mathrm{d}}{\mathrm{d}R}\left(\frac{1}{R}\frac{\mathrm{d}\phi}{\mathrm{d}R}\right)\right]_{R=R_0}. \tag{7}$$

Here M is the mass of the atom, ρ_w is the weight density and R is the distance between two nearest chains while R_0 is its equilibrium value. Since we are dealing with a-Se $(\mathrm{d}\phi/\mathrm{d}R)_{R=R_0} = 0$, and hence $\beta = 0$ as can be seen from equation (6) and δ is given by

$$\delta = \frac{\rho_w R_0^2}{2M}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}R^2}\right)_{R=R_0} \tag{8}$$

vide equation (7).

It has been shown [20] that

$$C_{11} = n_c[\tfrac{1}{3}\beta + \tfrac{1}{5}\delta] + K_e, \tag{9}$$

$$C_{44} = n_c[\tfrac{1}{3}\beta + \tfrac{1}{15}\delta]. \tag{10}$$

Here K_e is the electronic bulk modulus and is equal to zero for a-Se, since it is a semiconductor and n_c is the number of nearest neighbours.

From (9) and (10) we get

$$\left(\frac{\mathrm{d}C_{11}}{\mathrm{d}P}\right)_T = \frac{1}{5}\,n_c\left(\frac{\mathrm{d}\delta}{\mathrm{d}P}\right)_T, \tag{11}$$

$$\left(\frac{\mathrm{d}C_{44}}{\mathrm{d}P}\right) = \frac{1}{15}\,n_c\left(\frac{\mathrm{d}\delta}{\mathrm{d}P}\right)_T. \tag{12}$$

From equation (7) it can be easily shown that

$$\frac{d\delta}{dP} = \frac{2}{3K_T} - \frac{\rho_w R_0^3}{6K_T M}\left(\frac{d^3\phi}{dR^3}\right)_{R=R_0}.$$ (13)

In the derivation of equation (13) it is assumed as was done by Gerlich *et al* [3] that in amorphous substances, the volume $V \propto R^3$ unlike in crystalline Se. From equation (1) we can easily get

$$\left(\frac{d^3\phi}{dR^3}\right) = \frac{m(m+1)(m+2)}{R^3}\left(\frac{R}{R_0}\right)^{-m} + \frac{Bn(n+1)(n+2)}{R^3}\left(\frac{R}{R_0}\right)^{-n}$$

$$+ \left(\frac{mA - Bn}{R_0^3}\right)\lambda^2 e^{[1-(R/R_0)]\lambda}.$$ (14)

Using equations (11) to (14) we can calculate (dC_{11}/dP) and (dC_{44}/dP). It was shown [21, 22] using Schofields equation [23] that

$$\left(\frac{dC_{11}}{dP}\right)_T = \frac{C_{11}}{K_T} + 1.8(C_1^T - 1),$$ (15)

$$\left(\frac{dC_{44}}{dP}\right)_T = \frac{C_{44}}{K_T} + 0.6(C_1^T - 1).$$ (16)

It was shown that [24]

$$C_1^{L,T} = 2\gamma_g^{L,T} + \tfrac{1}{3}.$$ (17)

This equation is a generalization by the well known Debye's equation,

$$C_1 = 2\gamma_g^{th} + \tfrac{1}{3}.$$

Here γ_g^L and γ_g^T are the longitudinal and transverse Grüneisen constants for a-Se. It is also possible to calculate the same from Bhatia–Singh (BS) parameters [22].

For isotropic substances like a-Se they are shown to be (22)

$$\frac{dC_{11}}{dP} = \frac{n_c}{K_T}\left[\frac{\delta}{45} + \frac{2\gamma_g^L \delta}{5}\right],$$ (18)

$$\frac{dC_{44}}{dP} = \frac{n_c}{K_T}\left[\frac{-0.6}{9} + \frac{2\gamma_g^T \delta}{15}\right].$$ (19)

We used the value of 2 for n_c, the number of nearest neighbours [25].

2.3 *Evaluation of $C_1 \equiv (dK_T/dP)_T$ and $C_1' = (dC_1/dP)_T$ from the potential energy (vide equation (1)) function*

Since we have the potential energy constants, we can easily evaluate the pressure derivative of bulk modulus C_1. Thus from equation (5) we get

$$C_1 = \frac{dK_T}{dP} \equiv \frac{1}{3} - \frac{NR_0^3}{27K_TV}\left(\frac{d^3\phi}{dR^3}\right)_{R=R_0}.$$

(20)

Using the potential parameters we get $C_1 = 6.95$ while the experimental value is 8.0 [7]. This can be considered as good agreement. From the value of C_1 we can easily obtain $C_1' \equiv (dC_1/dP)$ from (14) and (20). Thus the final expression for C_1' after a little bit of algebra can be obtained as

$$C_1' = \frac{1}{K_T}\left[\frac{NR_0^3}{27K_TV_0}\left\{C_1\phi'''(R) + \frac{R_0}{3}\phi''''(R)\right\}\right].$$

(21)

The fourth derivative can be obtained from equation (14). Equation (21) can be rearranged to give

$$C_1' = \frac{1}{K_T}\left[\frac{32760NA}{81K_TV_0} - \frac{3024NB}{81K_TV_0} - \frac{C\lambda^4N}{81K_TV_0}e^{-\lambda} - C_1^2 + \frac{C_1}{3}\right].$$

(22)

Here N is Avagadros number and V_0 is molar volume and is equal to $18.45\,\text{cc/gm}$ atom. The value obtained for $C_1' = 0.118\,(\text{kbar})^{-1}$ (and hence $\gamma_g' = 0.059$ vide equation (17). This is a small value and unless one is very sure of the accuracy of the results the calculations can be of great help. This is related to Anderson Grüneisens parameter [26].

Another simple method of calculating γ_g' is from the well known equation namely

$$\gamma_g = -\frac{a}{6}\left[\frac{\phi'''(R)}{\phi''(R)}\right]_{R=R_0}.$$

(23)

Here as pointed earlier, a is the interatomic distance between two Seatoms [5] in the same chain

$$\gamma_g^{th} = -\frac{1}{6}a[\phi'''(R)(\phi''(R))^{-1}]_{R=R_0},$$

(24)

$$\frac{d\gamma_g^{th}}{dP} = -\frac{1}{6}a\left[\frac{\phi''''(R)}{\phi''(R)} - \left(\frac{\phi'''(R)}{\phi''(R)}\right)^2\right]_{R=R_0}\left(\frac{dR}{dP}\right)_{R=R_0}.$$

(25)

We assume as done by Gerlich *et al* and others [3, 5, 7] $V \propto R^3$. Hence by chain rule and assuming that the bond length is not effected by pressure we get,

$$\frac{dR}{dP} \equiv \frac{dR}{dV}\frac{dV}{dP}$$

(26)

and

$$\frac{dV}{dR} = \frac{3V}{R}.$$

(27)

Therefore

$$dR/dP = -R/3K_T.$$

(28)

Substituting and simplyfing we get

$$\gamma'_g = -\frac{1}{6}a\left[-\frac{\phi''''(R)R}{\phi''(R)3K_T} + \frac{R}{3K_T}\left(\frac{\phi'''(R)}{\phi''(R)}\right)^2\right]_{R=R_0},$$ (29)

$$\gamma'_g = \frac{a}{K_T}\left[\frac{\phi''''(R)}{\phi''(R)}\frac{R_0}{18} - \frac{2R_0a^2}{36a^2} - \left(\frac{\phi'''(R)}{\phi''(R)}\right)^2\right].$$ (30)

Using the values of A, B, λ with $C = ((mA - nB)/\lambda)\,e^{+\lambda}$ we get $\gamma'_g = +0.085\,(\text{kbar})^{-1}$. We used $a = 2.32\,\text{Å}$ (5), while the value obtained from equation (22) is $0.06\,(\text{kbar})^{-1}$. These values can be considered as good since the values are very small and any small experimental error will cause this discrepancy.

2.4 *Evaluation of the band absorption position and bulk modulus*

From the calculated values of SOECs obtained from the potential function (vide equations (9) and (10) it is possible to calculate the absorption band position using Nath–Smith De-Launay's equation [27] which is given by

$$\frac{8A_1[A_1 + 8C_{11} - 16C_{44}]}{[3A_1 - 8C_{11} + 16C_{11}^2]} = 1,$$ (31)

where

$$A_1 = \omega^2 M/2a.$$ (32)

Here $a = 2.32\,\text{Å}$ and is the nearest neighbour distance [28,5] between two a-Se atoms in the same chain and ω is the absorption frequency. We evaluate the band absorption position since $(1/\lambda) = \omega/2\pi C_0$. Here C_0 is the velocity of light. We can obtain the bulk modulus from equation (31) and (32). Thus differentiating equations (31) and (32) with respect to pressure and rearranging we get

$$\left\{8\left(\frac{dC_{11}}{dP}\right)[3A_1 - 8C_{11} + 16C_{12}] + 16\left(\frac{dC_{12}}{dP}\right)(8C_{11} - 16C_{12} - A_1)\right\}$$

$$\times (A_1 - 24C_{11} + 16C_{12})^{-1} = \frac{A_1}{K_T}[2\gamma_g^{el} + \tfrac{1}{3}].$$ (33)

Here

$$\gamma_g^{el} = (\gamma_g^L + 2\gamma_g^T)/3$$ (34)

which is the elastic Grüneisen constant.

Here for an amorphous substance like Se which is isotropic we assume

$$\left(\frac{dC_{12}}{dP}\right) = \left(\frac{dC_{11}}{dP}\right) - 2\left(\frac{dC_{44}}{dP}\right)$$

and using the calculated values of (dC_{11}/dP) etc. from equations (11) and (12) we can calculate K_T from equation (33). The value obtained under 1 atm pressure is 87 kbar while the experimental value is 91 kbar. This calculation forms a self consistent check on the potential energy parameters used along with various other equations in obtaining the band position and bulk modulus.

2.5 *Computation of thermal Grüneisen parameter*

From the potential function it is possible to calculate the thermal Grüneisen constant γ_g^{th} and is given by the well known equation [29]

$$\gamma_g^{th} = -\frac{1}{6} a \left[\frac{\phi'''(R)}{\phi''(R)} \right]_{R=R_0}.$$

Here R_0 is the interchain distance which is the van der Waals diameter and is equal to 4.0 Å [7]. The value obtained is given in table 3.

Another method of calculating γ_g^{th} is as follows. We have from equation (1)

$$\frac{d^2\phi(R)}{dR^2} = \phi''(R) = \frac{Am(m+1)R_0^m}{R^{m+2}} - \frac{Bn(n+1)R_0^n}{R^{n+2}} - \frac{C\lambda^2}{R_0^2} e^{-\lambda R/R_0}. \tag{35}$$

We may point out that $[\phi''(R)]_{R=R_0}$ can be treated as the force constant and using this value the heat capacity of a-Se was evaluated which gives a value in excellent agreement with experiment. Hence we have

$$\omega^2 = \left[\frac{\phi''(R)}{M} \right]_{R=R_0}. \tag{36}$$

Here M is the atomic mass and ω is the frequency.

$$2\ln\omega = \ln[-\phi''(R)] - \ln M \tag{37}$$

$$2\left(\frac{\partial \ln\omega}{\partial \ln V} \right) = \frac{\partial \ln[\phi''(R)]}{\partial \ln V}.$$

By definition

$$\left(\frac{\partial \ln\omega}{\partial \ln V} \right) = -\gamma_g^{th}. \tag{38}$$

Hence from equation (37) we get,

$$-2\gamma_g^{th} = \frac{\partial \ln[\phi''(R)]}{\partial \ln V}, \tag{39}$$

$$\frac{\partial \ln\phi''(R)}{\partial V} = -(m+2)\frac{\partial \ln R}{\partial V} - (n+2)\frac{\partial \ln R}{\partial V} + \frac{\lambda}{R_0}\frac{dR}{dV}. \tag{40}$$

Multiplying by V and simplifying with $m = 12$, $n = 6$, and $\lambda = 14.6364$ we get

$$2\gamma_g^{th} = -22 \frac{dR}{dV} \times \frac{V}{R} + \frac{\lambda V}{R_0}\frac{dR}{dV}. \tag{41}$$

We assume along with Gerlich *et al* [3, 6, 7] that $V \propto R^3$ and hence we finally get

$$2\gamma_g = \frac{22}{3} - \frac{\lambda}{3}. \tag{42}$$

Therefore we get $\gamma_g^{th} = 1.23$ while the experimental value is 1.0 and the value obtained from equation (24) is 1.38. Equation (42) is the result of the approximation that $V \propto R^3$ so as to obtain a numerical value. Since the result is good the approximation can be

justified. Thus it can be considered that the various values of γ_g are in good agreement with experiment obtained by different methods.

2.6 *Calculation of phonon frequency from the potential function*

We can calculate the phonon frequencies using Bhatia–Singh's method [20]. The equations for longitudinal and transverse phonon frequencies of Bhatia and Singh are given by [20]

$$\rho_w \omega_L^2 = \frac{2n_c}{a^2}(\beta_0 + \delta I_2) + \frac{K_e K_{TF}[G(Kr_s)]^2}{K^2 + K_{TF}^2 \, \tilde{g}(R)}, \tag{43}$$

$$\rho_w \omega_T^2 = \frac{2n_c}{a^2}[\beta I_0 + 0.5\delta(I_0 - I_2)]. \tag{44}$$

Here n_c is the number of nearest neighbours, K_e is the electronic bulk modulus, K_{TF} the Thomas–Fermi screening length, $G(Kr_s)$ is the shape factor and the rest of the symbols have their usual significances [22]. The electronic bulk modulus for a semiconducting substance like a-Se K_e is zero. Hence we do not want to further delineate regarding the second term in equation (43). The terms I_0 and I_2 are defined as

$$I_0 = 1 - \frac{\sin x}{x}, \tag{45}$$

$$I_2 = \frac{1}{3} - \left[\frac{1}{x} - \frac{2}{x^3}\right]\sin x - \frac{2\cos x}{x^2} \tag{46}$$

and

$$x = ka. \tag{47}$$

The calculated phonon frequencies of $w_L(K)$ and $w_T(K)$ are shown in figure 1.
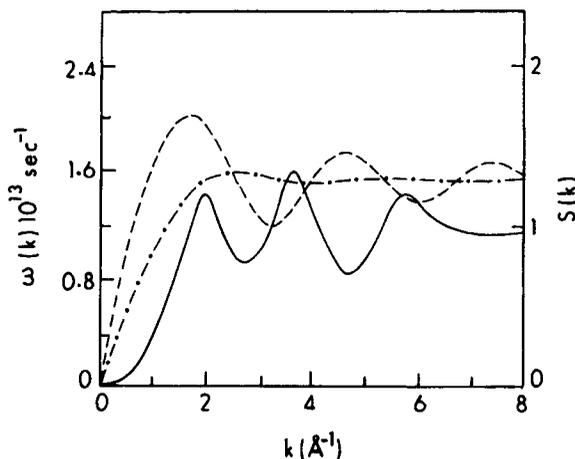

Figure 1. Phonon frequencies of a-Se as obtained from the potential function. (– – – –) Longitudinal and (—·—·—) transverse phonon frequencies. Structure factor is also included by (———) line.

2.7 Calculation of third order elastic constants (TOECs)

There are no experimental values of TOECs and hence the theoretical values become important. We use the equations of Rao and Venkatesh [30], Thurston [31] and Shiren [32]. These are given by

$$\frac{C_{111}}{C_{11}} = -\left[5 + \frac{C_{11}}{K_T}(C_1 - 1)\right], \tag{48}$$

$$\frac{dC_{11}}{dP} = C'_{11} = -\frac{1}{3K_T}(C_{111} + 2C_{112}), \tag{49}$$

$$C'_{44} = -\frac{1}{3K_T}(C_{144} + 2C_{166}), \tag{50}$$

$$C'_{12} = -\frac{1}{3K_T}(C_{112} + C_{123}). \tag{51}$$

In order to calculate C_{166} we use Shiren's [31] non-linear parameters for $\langle 100 \rangle$ and $\langle 110 \rangle$ directions and

$$K = 3 + \frac{C_{111}}{C_{11}}, \tag{52}$$

$$K = 3 + \frac{1}{\alpha_1}[1/2C_{111} + 1.5C_{112} + 6C_{166}], \tag{53}$$

where

$$\alpha_1 = C_{11} + C_{12} + 2C_{44} \tag{54}$$

and K is Shiren's constant.

Here for a-Se since no direction can be fixed as it is isotropic [5, 6, 8, 9] we assume that equations (52) to (54) are applicable in the calculation of K. Thus from equation (52) to (54) we calculate C_{456} through the well known equation [9]

$$C_{166} = C_{144} + 2C_{456}. \tag{55}$$

In this connection it may be emphasized that for isotropic substances there are only three independent TOECs. However, for completeness we have calculated all the six TOECs. In order to check the veracity of the calculated TOEC we use Birch equation [33] to calculate C_1 the pressure variation of bulk modulus which is given by

$$C_1 = \left(\frac{dK_T}{dP}\right)_T = -\frac{1}{9}[C_{111} + 6C_{112} + 2C_{123}]. \tag{56}$$

The calculated value is 9.9 while the experimental value is 8.0 [7]. The agreement can be considered as fair.

2.8 Calculation of head capacity of a-Se with the present potential function parameters

We have from equation (1)

$$\phi''(R) = \frac{d^2\phi}{dR^2} = \frac{Am(m+1)}{R_0^2}\left(\frac{R_0}{R}\right)^m - \frac{B_n(n+1)}{R_0^2}\left(\frac{R_0}{R}\right)^n - \frac{e^{-\lambda(R/R_0)\lambda^2}}{R_0^2}.$$

Substituting the values of A, B and λ along with assumed values of m and n as was done by Litov and Anderson [7] whose procedure was followed totally in determining the value of $C = (10.5726/\lambda)\,\mathrm{e}^{+\lambda} \times 10^{-12}$ erg we get,

$$\phi''(R_0) = \frac{24.60}{R_0^2} \times 10^{-12}. \tag{57}$$

As stated earlier $\phi''(R)$ can be treated as a force constant and hence we get

$$\omega^2 = \frac{\phi''(R)}{M}.$$

We get $\omega = 1.2376 \times 10^{13}\,\mathrm{sec}^{-1}$ with $R_0 = 4.0\,\mathring{A}$ since we are calculating C_v at room temperature. We used Einstein's equation which is given by [34]

$$C_v = \frac{3Ry^2\mathrm{e}^y}{\left(\mathrm{e}^y - 1\right)^2}. \tag{58}$$

Here

$$y = \frac{\hbar\omega}{K_B T}, \tag{59}$$

where the symbols have their usual significances.

The calculated value of C_v with the parameters necessary for evaluating $\phi''(R_0)$ is $5.95\,\mathrm{cal}/^\circ\mathrm{K}$ gm-atom while the experimental value is $5.83\,\mathrm{cal}/^\circ\mathrm{K}$ gm-atom [10], the agreement being excellent.

3. Results and discussion

A large number of properties of a-Se isotropic substance have been evaluated using the method of Litov and Anderson [7]. Even very complex amorphous substances have been treated as isotropic and it is extremely difficult to give the large number of available references. Since the potential function is a inverse 12th and 6th power of R with a Born exponential term added to it, the set of roots are not unique, neither there is anything unphysical in having either two repulsive or two attractive terms [35, 16, 19]. It is a fit with experimentally observed bulk moduli at different pressures with chosen values of m and n. It is very much gratifying to note that very large number of properties can be produced in excellent agreement with experiment.

Table 1. SOECs calculated by different methods.

Elastic moduli	Calc. values in GPA		Expt. (in GPA)	Equations used	Ref.
	From P. F.	From low k values of phonon freq.			
C_{11}	15.4	15.4	17.0	9, 43	Page 202 of ref. [4]
C_{44}	5.3	5.2	5.0	10, 44	

P.F. = Potential function.

Table 2. Several calculated properties of a-Se with the potential function.

Property	Calc. values	Expt. values	Equations used	Ref.
dC_{11}/dP	15.2	14.0	11	[4, 24]
dC_{44}/dP	3.3	2.7	12	[4]
$\gamma_g^L(S)^*$	2.9	3.5	15, 17	[4, 22]
$\gamma_g^T(S)^*$	2.7	3.0	16, 17	[4, 22]
$\gamma_g^L(B-S)^*$	4.2	3.5	18	[22, 21]
$\gamma_g^T(B-S)^*$	3.3	3.0	19	[21, 22]
A_1	579.4 (GPA)	—	32	
C_v	5.95 (cal/°K gm atom)	583 (cal/°K gm atom)	61	[34]
$1/\lambda$	240 cm^{-1}	254 cm^{-1}	32	[6]
K_T	8.7 (GPA)	9.1 GPA	33, 34	[7]

*S = From Schofield's equations, B–S= Bhatia–Singh's parameters.

Table 3. Thermal Gruneisen's constant γ_g^{th}.

γ_g^{th} value Calc.	γ_g^{th} Expt.	Equations used	Ref. for expt. value
1.38	0.96	24	[26]
1.23		42	[26]

Table 4. Calculated values of C_1' and γ_g'.

C_1'	γ_g'	Equations used
0.170	0.085	30
0.118	0.059	22

$C_1 = 2\gamma_g'$ (vide equation 17).

We present in table 1, C_{11} and C_{44} and they are in very good agreement with that of Brassington *et al* [9].

We present in table 2 a very large number of calculated properties and compared the same with experimental values wherever possible. Sometimes the same property has been calculated by different methods. Thus we calculated γ_g^{th} by different methods. They are given in table 3. We also calculated $\gamma_g' = (d\gamma_g^{th}/dP)_T$ by two different methods. γ_g' is important in the calculation of Anderson–Gruneisen parameter [26]. It is also useful in the evaluation of second Gruneisen constant and in the estimation of $C_1' = dC_1/dP = d^2 K_T/dP^2$. In fact we can easily see that $C_1' = 2\gamma_g'$ from equation (17). The calculated values of C_1' are given in table 4. Extensive discussion on the application of γ_g' is given by Rao *et al* [26] and also by Perrin *et al* [36]. We give in figure 1 the phonon frequencies computed through Bhatia–Singh's equations. The phonon frequency characteristics are given in table 5. In table 1 we also give the elastic constants obtained from the slope of the phonon frequencies at low values of k. The agreement between experiment and theoretical values of elastic constants can be considered as very good.

Table 5. Characteristics of phonon frequencies (vide figure 1).

	Position		Peak height in 10^{13} sec^{-1}	
	From P.F.	From E.C.	From P.F.	From E.C.
ω_L	1.78 Å^{-1}	1.80 Å^{-1}	2.01	1.90
ω_T	2.50 Å^{-1}	2.46 Å^{-1}	1.59	1.50

P.F. = Potential function; E.C. = Elastic constants.
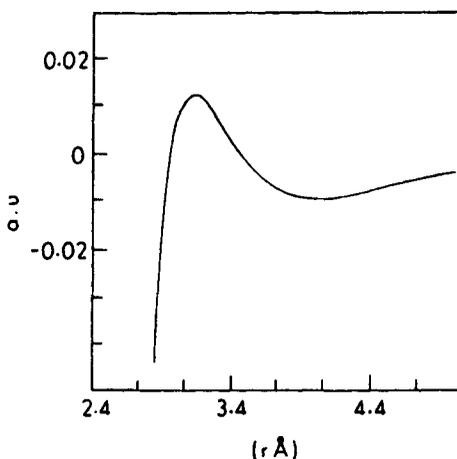
Figure 2. Potential function of a-Se.

Table 6. Potential energy characteristics.

Potential energy	Calculated	Litov and Anderson [7]
Maximum position	3.2 Å	3.29 Å
Value	0.013 a.u.	–
Minimum position	4.0 Å	4.0 Å
Value	−0.0097 a.u.	–

We show in figure 2 the potential function obtained with our parameters. It may be observed from table 6 that the potential function obtained by Litov and Anderson [7] is in excellent and exact agreement with ours, thus proving that the set of parameters are not unique. Very large number of properties calculated presently are found to be in very good agreement with experimental values.

We have given in table 7 the TOECs calculated through equations (48) to (54). From the calculated TOECs we computed $C_1 = (dK_T/dP)_T$ through Birch equation (56) and the value is found to be 9.9 while the experimental value 8.0 and this can be considered as a fair agreement.

The values of TOECs show the same trend as in the case of a-AS$_2$S$_3$ and a-As. Thus C_{144} is positive [9, 37] while C_{144} in a-polysyrene and a pyrex glass it is negative [37]. (Here a stands for amorphous.)

Table 7. Calculated TOECs.

TOECs	Values in GPA
C_{111}	−228.0
C_{112}	−64.8
C_{123}	−105.2
C_{144}	+6.9
C_{166}	−40.3
C_{456}	−23.6

Another important property which can be obtained from the potential function is the heat capacity with the aid of the potential parameters. The agreement between calculated value and the experiment is excellent. We would like to point out that by using equation (5) we calculate K_T at $\rho/\rho_0 = 1.1 = V_0/V \equiv 1/v$. Substituting the value of 1.1 for $1/v$ we obtain a value of 139 kbar for k_T while the experimental value is 149 kbar. This again shows the veracity of the parameters. Several other acoustic and optic properties can be calculated which will be presented later on along with various other substances. Thus we have calculated extensively both acoustic and thermodynamic properties and the agreement in most of the cases is very good and this gives credence to the potential parameters which produce exactly the same type of potential function as obtained by Litov and Anderson [7].

Acknowledgements

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