FP-LAPW investigation of mechanical and thermodynamic properties of Na$_2$X (X = S and Se) under pressure and temperature effects

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Structural, elastic and thermodynamic properties of sodium chalcogenides (Na$_2$X, X = S, Se) have been calculated using FP-APW+lo method. The ground state lattice parameter, bulk moduli have been obtained. The Zener anisotropy factor, Poisson’s ratio, shear modulus, Young’s modulus, have also been calculated. The calculated structural and elastic constants are in good agreement with the available data. We also determined the thermodynamic properties, such as heat capacities $C_V$ and $C_P$, thermal expansion $\alpha$, entropy $S$, and Debye temperature $\Theta_D$, at various pressures and temperatures for Na$_2$X compounds. The elastic constants under high pressure and temperature are also calculated and elaborated.

Keywords: sodium chalcogenides; FP-LAPW; GGA; structural properties; elastic constants; thermodynamic properties

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1. Introduction

The alkali metal chalcogenides Na$_2$X (X = S, Se) constitute a crystalline family that has shown great technological usefulness in devices requiring high ionic conductivity [1–3] and large fundamental energy band gaps. Apart from being used in power sources, fuel cells, gas-detectors and ultra violet space technology devices [4–6], these ionic compounds also play an important role in the development of photocathodes, in supporting catalytic reactions and enhancing oxidation of semiconductor surfaces [7–14].

At room temperature these compounds crystallize into a stable anti-CaF$_2$ (anti-fluorite) structure type [15, 16] (space group no. 225). The CaF$_2$ (calcium fluoride) compound has a basic crystalline structure that consists of face-centered cubic packing of Ca cations, with F anions located in all Ca tetrahedrals. In contrast, the amorphous to the CaF$_2$ structure, in which positions of the cations and anions have been exchanged, is known as an anti-fluorite type structure. In the Na$_2$X (X = S, Se) compounds, the metal atoms (Na) are located at (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) and the atoms (X) are located at (0, 0, 0). These compounds are subjects of many experimental and theoretical works, focusing on structural phase transformation [17–22] and electronic properties [23–27]. The electronic band structure of these materials at ambient conditions was discussed [25] using the self-consistent pseudo-potential method. Alay-e-Abbas et al. [23, 24] have studied electronic density of states of Na$_2$Se in the framework of density functional theory. They also predicted optical properties and discussed complex dielectric function, absorption coefficient, refractive index and reflectivity for a wide range of phonon energy.

The elastic constants determine the response of a crystal to the external forces, and obviously play an important role in determining the strength of the...
materials with respect to the changes in the external macroscopic variables, such as pressure and temperature effects. Elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature, and Grüneisen parameter. Most importantly, knowledge of the elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internal strain, sound velocities, and fracture toughness. For more than ten years, the elastic constants of Na$_2$S and Na$_2$Se compounds have been determined experimentally by elastic neutron scattering at low temperature [28, 29]. Lichanot et al. [30] and Bührer and Bill [1] have calculated the elastic constant for Na$_2$S compound by linear combination of atomic orbitals (LCAO) method and the shell model. Besides, Kalarasse and Bennecer [31] have used the first principle pseudo-potential method in the framework of the density functional theory [31–33] to obtain the ground state properties and applied linear response techniques [34, 35] to calculate the elastic constants, phonon spectra and related quantities. We, therefore, thought deeply to perform these calculations in the framework of the full potential augmented plane wave plus local orbitals (FP-APW+lo) method to study the structural, elastic and thermodynamic properties of Na$_2$S, Na$_2$Se in the anti-fluorite phase under high pressures and temperature, in order to provide reference data for the experimentalist and to complete the exciting theoretical work on this fascinating class of materials.

The paper is organized as follows. In the section two we give a brief description of computational methodology employed in this study. Section three deals with the results and their discussion, whereas in section four we summarize conclusions drawn from our study.

2. Computational methods

In this study, DFT calculations were completed using FP-LAPW+lo scheme of calculations [36–38] as realized in WIEN2k computational package [39]. This method has proven to be one of the most accurate methods for the computation of the electronic structure of solids within DFT [40–45]. In this scheme of calculations APW+lo basis set is incorporated to represent the electronic band structure for all atoms as well as corresponding orbitals. Correspondingly, computational time is considerably shortened as convergence criteria are met professionally at lesser value of R$_{MT}$K$_{max}$. Moreover, no shape approximation is imposed for charge density as well as potential. To deal with semi-core states, local orbital extensions are mixed up. To perform calculations, a simulated crystal unit cell is partitioned into non-touching muffin tin (MT) spheres as well as interstitial space. To attain the best criterion of convergence for energy eigenvalues, in the interstitial space, wave functions are expanded into plane-waves taking a cutoff value of R$_{MT}$K$_{max} = 9$, whereas R$_{MT}$ stands for muffin tin (atomic sphere) radii and K$_{max}$ is used for the largest value of K vector used to expand the plane-waves. The values of R$_{MT}$, i.e. 2.1 a.u. for Na, 2.2 a.u. for S and 2.8 a.u. for Se were used. Inside the muffin tin spheres, valence wave functions were expanded equal to l$_{max} = 10$, while the value of G$_{max} = 12$ was taken into account for the Fourier expansion of the charge density. For the exchange-correlation energy functional, we employed parameterized generalized gradient approximation implemented by Wu and Cohen [46] (WC-GGA). Brillouin zone (BZ) integration was performed by employing tetrahedron technique. For a suitable set of special k-points, 9 × 9 × 9 Monkhorst-Pack sampling was used to calculate the total energy. In our calculations the valence electrons were treated within the scalar relativistic limit, whereas core electrons were dealt fully relativistically.

To investigate the thermodynamic properties of Na$_2$X compounds, we here applied the quasi-harmonic Debye model implemented in the Gibbs program [47]. This model allows determination of all thermodynamic quantities from the calculated energy-volume points. For the calculations, the non-equilibrium Gibbs function $G^*$ was used:

$$G^*(V,P,T) = E(V) + PV + A_{vib}(\Theta(V), T)$$  (1)
here $E(V)$ is the total energy per unit cell, $P(V)$ is the constant hydrostatic pressure condition, $\Theta$ is the Debye temperature and $A_{\text{vib}}$ is the vibrational Helmholtz free energy. According to quasiharmonic Debye model of phonon density of states, $A_{\text{vib}}$ as in [47, 48] is described as follows:

$$A_{\text{vib}}(\Theta, T) = 7nk_BT \left[ \frac{9\Theta}{8T} + 3\ln(1 - e^{-\Theta/T}) \right] - D(\Theta/T)$$  \hspace{1cm} (2)

where $n$ is the number of atoms per formula unit, $k_B$ is the Boltzmann’s constant, and $D(\Theta/T)$ represents the Debye integral. For an isotropic solid, $\Theta$ is expressed as in [47, 48]:

$$\Theta = \frac{\hbar}{K}[6\pi^2V^{1/2}n]^{1/3}f(\sigma)\sqrt{\frac{B_S}{M}}$$  \hspace{1cm} (3)

$\Theta$ is the Debye temperature, $M$ is the mass of per formula unit, $\sigma$ is Poisson ratio and $B_S$ is the adiabatic bulk modulus that is approximated as:

$$B_S \approx B(V) = V \frac{d^2E(V)}{dV^2}$$  \hspace{1cm} (4)

where $f(\nu)$ is defined as:

$$f(\nu) = \left\{ 3 \left[ \frac{2(1 + \nu)}{3(1 - 2\nu)} \right]^{3/2} + \left( \frac{1 + \nu}{3(1 - \nu)} \right)^{3/2} \right\}^{-1/3}$$  \hspace{1cm} (5)

Details of the values of $f(\nu)$ and $B_S$ are given in various references [50–53] and $\nu$ is taken as 0.25 [50]. Therefore, the non-equilibrium $G^*$ is a function of $V, P$, and $T$. It is minimized with respect to $V$:

$$\left( \frac{\partial G^*(V, P, T)}{\partial V} \right)_{P, T} = 0$$  \hspace{1cm} (6)

By solving equation 6, we obtain the EOS $V(P, T)$. The isothermal bulk modulus $B_T$, the heat capacity at constant volume $C_V$, the heat capacity at constant pressure $C_P$ and the thermal expansion coefficient $\alpha$ are given by:

$$B_T(P, T) = V \left( \frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right)_{P, T}$$  \hspace{1cm} (7)

$$C_V = 3nk_B \left[ 4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right]$$  \hspace{1cm} (8)

$$C_P = C_V(1 + \alpha \gamma T)$$  \hspace{1cm} (9)

$$\alpha = \frac{\gamma C_V}{B_T V}$$  \hspace{1cm} (10)

$$S = nk_B[4D(\Theta/T) - 3\ln(1 - e^{-\Theta/T})]$$  \hspace{1cm} (11)

Here, $\gamma$ is the Grüneisen parameter which is defined as follows:

$$\gamma = -\frac{d\ln(\Theta(V))}{d\ln V}$$  \hspace{1cm} (12)

3. Results and discussion

3.1. Structural properties

While calculating structural properties of Na2S and Na2Se crystals in anti-CaF2 structure type, volume optimization was performed using WC-GGA exchange-correlation functional. Equilibrium lattice constants ($a_0$), total energies ($E_0$), bulk modulus ($B_0$) and its pressure derivatives ($B_0'$) were calculated by fitting Murnaghan equation of state [54] to the total energy versus volume curve. The total energy versus volume curve for sodium chalcogenides (viz. Na2X, X = S, Se) are shown in Fig. 1. Table 1 summarizes our calculated structural parameters (lattice constants, bulk modulus and its pressure derivative) of Na2S and Na2Se at ambient pressure. Our calculated lattice constant for Na2S and Na2Se is 6.5223 Å and 6.7756 Å, respectively. This result accords well with the experimental and theoretical ones. However, for the results of B0 and B0', we find that there is good agreement between our results and the results calculated with other theories. The temperature effect on the lattice parameters of Na2S and Na2Se compounds is displayed in Fig. 2. It can be seen that the lattice parameters increase linearly with increasing of temperature. The rate of increase is almost zero from $T = 0$ to 100 K and becomes very moderate for $T > 100$ K. On the other hand, as the pressure increases, the lattice parameter decreases at a given temperature. Generally speaking, the lattice constant increases as the
temperature increases, and decreases as the pressure increases. The calculated equilibrium primitive cell volume $V$ at zero pressure and room temperature is 468.10 Å$^3$ and 524.79 Å$^3$ for Na$_2$S and Na$_2$Se, respectively. The relationship between the bulk modulus $B_0$ and temperature at different pressures is shown in Fig. 3. At temperatures lower than 100 K, $B_0$ remains almost constant because of the small change in volume of the primitive cell. At temperatures higher than 100 K up to 1000 K, $B_0$ decreases with $T$ at a given pressure which indicates that the rapid volume variation causes the bulk modulus to decrease rapidly, while it increases with $P$ at a given temperature. It shows that the effect of increasing pressure on Na$_2$S and Na$_2$Se is the same as decreasing its temperature.

Fig. 1. Total energy as a function of volume for Na$_2$S and Na$_2$Se calculated with GGA.

Fig. 2. The variation of the primitive cell volume as a function of temperature at different pressures of Na$_2$S and Na$_2$Se.

### 3.2. Thermodynamic properties

Using the quasi-harmonic Debye model, the thermal EOS and thermodynamic properties of Na$_2$X (X = S, Se) with anti-CaF$_2$ phase compounds were investigated below the melting point (up to 1000 K), where the quasi-harmonic approximation remains fully valid. The pressure effect was studied in the range from 0 to 30 GPa.

The heat capacity is an important parameter of the condensed matter. It does not only provide a fundamental insight into the vibrational properties but is also mandatory for many applications. At intermediate temperatures, temperature dependence of the heat capacity $C_V$ is governed by the vibrations of atoms and could be determined only experimentally for a long time past [55]. Fig. 4 and Fig. 5 show the calculated specific heats at a constant volume $C_V$ and a constant pressure $C_P$ of Na$_2$S and Na$_2$Se. At low temperatures, the shapes of the curves of $C_V$ and $C_P$ are similar. As known, the increase of heat capacity with $T^3$ at low temperatures is due to the harmonic approximation of the...
Table 1. Calculated lattice constant $a_0$ (Å), bulk modulus $B_0$ (GPa), its first pressure derivatives $B'_0$ for Na$_2$S and Na$_2$Se, compared to the experimental data and previous theoretical calculations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Present work</th>
<th>Other calculations</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S</td>
<td>$a_0$</td>
<td>6.5223</td>
<td>6.526$^a$</td>
</tr>
<tr>
<td></td>
<td>$B_0$</td>
<td>28.3643</td>
<td>49.00$^b$</td>
</tr>
<tr>
<td></td>
<td>$B'_0$</td>
<td>4.0502</td>
<td>4.30$^o$</td>
</tr>
<tr>
<td>Na$_2$Se</td>
<td>$a_0$</td>
<td>6.7756</td>
<td>6.823$^n$</td>
</tr>
<tr>
<td></td>
<td>$B_0$</td>
<td>25.2718</td>
<td>30.70</td>
</tr>
<tr>
<td></td>
<td>$B'_0$</td>
<td>4.2571</td>
<td>4.15$^o$</td>
</tr>
</tbody>
</table>

$^a$[15], $^b$[29], $^c$[26], $^d$[20], $^e$[62], $^f$[64], $^g$[65], $^h$[66], $^i$[67], $^j$[23], $^k$[68], $^l$[69], $^m$[31], $^n$[70].

Debye model. However, at high temperatures, when $T > 600$ K, $C_V$ converges to a near-constant value, which is in agreement with Dulong-Petit law. However, $C_p$ tends to be linear with temperature. Our calculated values of $C_V$ at zero-pressure and 300 K are 70.48 and 72.41 (J·mol$^{-1}$·K$^{-1}$) for Na$_2$S and Na$_2$Se, respectively.
Fig. 5. Temperature dependence of heat capacity of Na$_2$S and Na$_2$Se at a constant pressure ($C_P$).

Variations of the thermal expansion coefficient $\alpha$ with temperature at 0, 10, 20, and 30 GPa are shown in Fig. 6. It is seen that for a given temperature, $\alpha$ decreases with an increase of pressure and becomes small at higher pressures. On the other hand, it is clear that $\alpha$ also increases exponentially at lower temperatures ($T < 250$ K) and starts to increase linearly at higher temperatures ($T > 300$ K). The temperature dependence of $\alpha$ is very small at high temperature but the variation increases linearly with temperature. At $P = 0$ GPa and $T = 300$ K, the values of $\alpha$ for Na$_2$S, Na$_2$Se are $12.25 \times 10^{-5}$, $12.48 \times 10^{-5}$ K, respectively.

The Debye temperature ($\Theta_D$) is an important parameter characteristic of the thermal properties of solids. It is the temperature above which the crystal behaves classically, because the thermal vibrations become more important than the quantum effects. The variation of the Debye temperature as a function of pressure and temperature is plotted in Fig. 8. At temperatures less than 100 K, the values of $\Theta_D$ remain constant; above 100 K, $\Theta_D$ decreases linearly with increasing of temperature. The Debye temperatures $\Theta_D$ of the Na$_2$X compounds at the temperature of 300 K are higher than those at 1000 K, which shows that the vibration frequency of the particles in Na chalcogens: Na$_2$S and Na$_2$Se changes with the pressure and temperature.
Calculated values of $\Theta_D$ for Na$_2$S and Na$_2$Se at zero pressure and zero temperature were found to be equal to 342.62 and 258.94 K, respectively. Therefore, $\Theta_D$ decreases in the order Na$_2$S < Na$_2$Se. The volume dependence of the Debye temperature $\Theta_D$ is shown in Fig. 9 at some fixed temperatures and the quasi-harmonic approximation, which introduces the temperature dependence through the volume. It is noted that as the volume $V$ increases, the value of the Debye temperature decreases. The relatively small effect of temperature on the Debye temperature can be explained by the small effect on the volume changes. It is observed that for a constant temperature, the Debye temperature of the herein studied materials increases almost linearly with a decrease of the volume.

### 3.3. Elastic properties

Knowledge of elastic constants of materials is essential for better understanding of their properties. From practical viewpoint, the elastic constants describe the linear response of a material to external forces. Some basic mechanical properties can be derived from the elastic constants, such as the bulk modulus, Young’s modulus, shear modulus, Poisson’s ratio, which play an important role in determining the strength of the materials. From a fundamental viewpoint, the elastic constants are related to various essential solid-state properties, such as interatomic potentials, equation of state, structural stability, phonon spectra, which are linked thermodynamically to the specific heat, thermal expansion, Debye temperature, melting point, and Grüneisen parameter. In our case, these compounds have a cubic symmetry, hence, only three independent elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ should be calculated. The elastic constants $C_{ij}$ are obtained by calculating the total energy as a function of volume conserving strains using Mehl
The variation of the Debye temperature as a function of volume at different pressures of Na$_2$S and Na$_2$Se.

The Zener anisotropy factor $A$, Poisson’s ratio $\sigma$, shear modulus $G$, and Young’s modulus $E$, which are the most interesting elastic properties for applications, are often measured for polycrystalline materials when investigating their hardness. These quantities are calculated in terms of the elastic constants $C_{ij}$, using the following relations [57]:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}$$  (13)

$$\sigma = \frac{1}{2} \left( \frac{B - \frac{2}{3}G}{B + \frac{1}{3}G} \right)$$  (14)

$$E = \frac{9BG_H}{3B + G_H}$$  (15)

where $B = (C_{11} + 2C_{12})/3$ is the bulk modulus and $G = (G_V + G_R)/2$ is the isotropic shear modulus, $G_V$ is the Voigt’s shear modulus corresponding to the upper bound of $G$ values and $G_R$ is the Reuss’s shear modulus corresponding to the lower bound of $G$ values; they can be written as [58]:

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5}$$  (16)

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}$$  (17)

The calculated relative quantities of elastic properties are listed in Table 3. As can be seen from the Table 3, the Na$_2$S and Na$_2$Se compounds are considered as isotropic materials. Poisson’s ratio provides more information about the characteristics of the bonding forces than any other elastic constants. 0.25 and 0.5 are the lower and the upper limits for central force solids. The calculated Poisson ratio of Na$_2$S and Na$_2$Se is very close to 0.22, 0.23, respectively, which means that Na$_2$S and Na$_2$Se are with predominantly central interatomic forces [59]. The bulk modulus $B_0$ represents the resistance to fracture, while the shear modulus $G$ represents the resistance to plastic deformation [60]. A high Pugh’s $B/G$ ratio is associated with ductility, whereas a low value corresponds to the brittle nature. The critical value which separates ductile and brittle material is 1.75; i.e. if $B/G > 1.75$, the material behaves in a ductile manner; otherwise the material behaves in a brittle manner [61]. The calculated results for our materials Na$_2$S, Na$_2$Se are 1.46 and 1.58, respectively, so they can be classified as brittle at ambient conditions.

We further studied the high-pressure elastic behavior of Na$_2$S and Na$_2$Se by computing the second-order elastic constants and their variation.
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Table 2. Calculated elastic constants (in GPa) for Na$_2$S and Na$_2$Se in anti-CaF$_2$ structure.

<table>
<thead>
<tr>
<th>Material Parameters</th>
<th>Present work</th>
<th>Other calculations</th>
<th>Experimental</th>
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<tbody>
<tr>
<td>Na$_2$S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>53.94</td>
<td>64.4$^a$ 58.4$^b$</td>
<td>61.36$^l$ 62.8$^m$</td>
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<tr>
<td>$C_{12}$</td>
<td>15.50</td>
<td>21.7$^c$ 13.6$^d$</td>
<td>20.28$^f$ 21.7$^m$</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>19.00</td>
<td>17.9$^e$ 20.0$^e$</td>
<td>21.42$^f$ 22.9$^m$</td>
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<td>$C_{11}$</td>
<td>46.09</td>
<td>50.84$^o$</td>
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<td>$C_{12}$</td>
<td>14.01</td>
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</tr>
<tr>
<td>$C_{44}$</td>
<td>15.28</td>
<td>17.17$^o$ 22.86$^o$</td>
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</table>

$^a$[30], $^c$[1], $^d$[28], $^f$[63], $^m$[68], $^o$[31].

with pressure as shown in Fig. 10. The elastic constant $C_{11}$ represents the elasticity in length, which changes with longitudinal strain. The elastic constants $C_{12}$ and $C_{44}$ are related to the elasticity in shape. It can be seen that $C_{11}$ and $C_{12}$ increase linearly with pressure. $C_{11}$ and $C_{12}$ are more sensitive to the change in pressure compared to $C_{44}$.

Fig. 10. Pressure dependence of the elastic constants ($C_{11}$, $C_{12}$ and $C_{44}$) of Na$_2$S and Na$_2$Se.

In order to study the temperature dependence of the elastic properties of these compounds, we have focused our study on the temperature range from 0 to 1000 K. The temperature variations of the isothermal elastic constants $C_{ij}^T$ for Na$_2$X compounds are presented in Fig. 11. We can observe that the elastic constants: $C_{11}^T$ and $C_{12}^T$ decrease slightly when the temperature is enhanced. However, we have found almost constant behavior of $C_{44}^T$ versus temperature. The variation of $C_{11}^T$ and $C_{12}^T$ with temperature is found to be larger as compared with $C_{44}^T$ which is related to the elasticity in shape (connected with shear constant). It is known that a longitudinal strain produces a change in volume without a change in shape, and from that we can conclude that the change in volume is related to the temperature and, thus, it produces some changes in $C_{11}^T$ and $C_{12}^T$. On the other hand, a transverse strain or shearing causes a change in shape without a change in volume. Thus, $C_{44}^T$ is less sensitive to temperature.

4. Conclusion

In the present work, first principles calculations have been used to study the structural, elastic and thermodynamic properties of anti-CaF$_2$ type compounds, Na$_2$X, X = S, Se. The calculations indicate that the obtained values of equilibrium lattice constant, $a_0$ and bulk modulus, $B_0$ are in good agreement with available theoretical and experimental studies. Furthermore, the elastic constants are in reasonable agreement with available data and indicate that these compounds are stable against elastic deformations and demonstrate that the Na$_2$S and Na$_2$Se in anti-CaF$_2$ phase keep dynamic
Table 3. Calculated Zener anisotropy factor A, Poisson’s ratio $\nu$, bulk modulus B (in GPa), shear modulus G (in GPa), Young’s modulus E (in GPa).

<table>
<thead>
<tr>
<th>Material</th>
<th>Reference</th>
<th>B</th>
<th>G</th>
<th>E</th>
<th>A</th>
<th>B/G</th>
<th>$\nu$</th>
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<td>19.34</td>
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<td>0.22</td>
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<td>0.22$^a$</td>
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<td>GGA</td>
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<td></td>
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<td>[63].</td>
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Fig. 11. Temperature dependence of the elastic constants ($C_{11}$, $C_{12}$ and $C_{44}$) of Na$_2$S and Na$_2$Se.

We have also calculated and presented the thermodynamic quantities, elastic constants $C_{ij}$ and interrelated quantities under high pressure and temperature. The thermal contribution to the elastic constants is very significant, and in the range of 0 to 1000 K, the values of the SOEC are changing remarkably.

Acknowledgements

Y.A. would like to acknowledge University Malaysia Perlis for Grant No. 9007-00111 and TWAS-Italy for the full support of his visit to JUST-Jordan under TWAS-UNESCO Associateship.

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Received 2014-11-29
Accepted 2015-03-14