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# B1–B2 structural phase transition and elastic properties of UX (X = S, Se, and Te) compounds at high pressure

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## Abstract

Pressure induced structural phase transformation and mechanical properties of NaCl-type (B1) to CsCl-type (B2) structure in uranium monochalcogenides (UX; X = S, Se, and Te) are presented. An effective interionic interaction potential is constructed, consisting of the long-range Coulomb and the Hafemeister and Flygare type short-range overlap repulsion extended up to the second-neighbour ions and the van der Waals (vdW) interaction. Particular attention is devoted to evaluate the vdW coefficients following the Slater–Kirkwood variational method, as both the ions are polarizable. Our calculated results have revealed reasonably good agreement with the available experimental data on the phase transition pressures ( $P_t = 81, 21, 13$  GPa) and the elastic properties of UX (X = S, Se, and Te). The equation of state curves (plotted between  $V(P)/V(0)$  and pressure) for both the NaCl-type (B1) and CsCl-type (B2) structures obtained by us are in fairly good agreement with the experimental results. The calculated values of the volume collapses ( $\Delta V(P)/V(0)$ ) are also closer to their observed data. The variations of the second- and third-order elastic constants with pressure have followed systematic trends, which are almost identical to those exhibited by the measured and observed data in other compounds of the NaCl-type structure family.

## 1. Introduction

The structural transformation which occurs under pressure in lanthanides, actinides and pnictides and many of their compounds, has attracted a wide attention as large changes of

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the bulk and electronic properties are then induced. The uranium monochalcogenides offer an attractive series for studying this phenomenon as these compounds have the simple cubic rock-salt structure and exhibit metallic conductivities and uranium is there in a trivalent state at atmospheric pressure [1, 2]. The majority of these compounds undergo the first order structural phase transition from the NaCl-type (B1) to the CsCl-type (B2) structure at high pressures.

The structural transformation associated with valence fluctuation at high pressure and displaying variance in valency is a striking feature of these compounds [3–5]. This behaviour is mainly related to the ‘f’ electrons of the rare-earth (RE) ion. Studies on electronic structure [4] reveal that both localized core-like and delocalized band-like ‘f’ electrons are responsible for the valence behaviour. The nature of f-orbital overlaps can be tuned in a controlled manner by changing the interatomic distance by applying external pressure [5]. The reasons mentioned as well the availability of high quality single crystals motivates us to investigate the structural phase transition and elastic properties of the f-electron based systems.

Bihan *et al* [6] performed x-ray diffraction measurements under pressure on uranium compounds with different pressure-transmitting media. US shows a phase transformation from its ambient NaCl structure (B1 phase) to CsCl type structure (B2 phase) around 80 GPa in a silicone oil pressure medium [6]. Gerward *et al* [7] have documented high-pressure structures, transition pressures and compressibilities for UX monochalcogenides. USe and UTe also transform from B1 to B2 phase at around 20 and 9 GPa [1], respectively. It is instructive to mention that the B1 to B2 transition is sluggish and the two phases are found to coexist in a large pressure range. This makes it difficult to determine a unique transition pressure. Compression–decompression also produces a pronounced hysteresis in the pressure–volume relation. In some cases, the B2 phase remains present even after the pressure has been completely released. Benedict has mentioned that the transition pressures range around 20–26 and 9–20 GPa for USe and UTe, respectively [1].

Furthermore, theoretical studies such as molecular dynamics of UX have been performed following the inelastic scattering of thermal neutrons [8]. Moreover, the change in magnetic ordering in response to hydrostatic pressure has interesting characteristics [9–12]. The experimental [1, 6–8] studies therefore pose a strong need to study the structural properties of UX compounds at high pressure, which can predict at least the extent of pressure one should generate to observe a structural phase transition and other related properties. In addition, the structural and elastic studies on lanthanum mono-chalcogenides [13] and other rare earth antimonide compounds [14] have further widened the scope of future theoretical and accurate experimental investigations of crystallographic phase transition from B1 to B2 in rare earth and actinide compounds. To the best of our knowledge there are no reports on the structural phase transition of uranium compounds using band structure calculations.

The investigations of structural, mechanical and vibrational properties of alloys under pressure are now routinely being performed by means of *ab initio* calculations. The accuracy of total energies obtained within the local density approximation is in many cases is sufficient to predict which structure, at a given pressure, has the lowest free energy, although most calculations still refer to zero temperature. Furthermore, comparing the free energies of various guessed crystal structures, *ab initio* molecular dynamics methods allow a better determination of the structures and understanding of transformation mechanisms, and performing the structural optimizations. However, with the rapid advancement of computational techniques, the nature of interatomic forces is still not properly interpreted for these materials and phenomenological lattice dynamical models, which take care of various interaction energies for determination of stable structure, have their own importance.

In the past, numerous efforts have been made to reveal the phase transition and anharmonic properties of solids by means of different forms of cohesion. Among the lattice models

which have been invoked so far to discuss the mechanical properties of several solids and alloys is the charge transfer approach [15], following Hafemeister and Flygare [16] type overlap repulsion extended up to second-neighbour ions besides short-range interactions. We refer to the pioneering work of Fumi and Tosi [17], who properly incorporate van der Waals interaction along with d–d and d–q interactions to reveal the cohesion in several ionic solids. In trying to understand the structural aspects, we admit that the vdW attractions [13, 14] are the cornerstone of lattice phenomenological models that is ignored in the first principles microscopic calculations.

The present investigations are organized as follows. Section 2 deals with the theory and supplies technical details to estimate the structural phase transition, volume collapse and pressure dependent elastic properties and support them by physical arguments. In section 3 we return to the details of the numerical analysis, and conclusions are presented in section 4.

## 2. Theory and method of calculation

The understanding of thermodynamical properties for uranium monochalcogenides needs the formulation of an effective interionic potential. The idea we have in mind follows: the change in force constants is small, the short-range interactions are effective up to the second-neighbour ions, and the atoms are held together with harmonic elastic forces without any internal strains within the crystal. The effective interionic interaction potential (EIoIP) is expressed as

$$U(r) = \sum_{ij} \frac{Z_m e^2}{r_{ij}} + \sum_{ij} b \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) + \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8}. \quad (1)$$

Here, long-range Coulomb interaction is represented by the first term; the second term corresponds to the Hafemeister and Flygare [16] form of short-range repulsive energies and the van der Waals multipoles are represented by the third and fourth terms, respectively. The symbols  $c_{ij}$  and  $d_{ij}$  are the van der Waals coefficients and  $\beta_{ij}$  are the Pauling coefficients, respectively.  $Z_m e$  is the modified ionic charge and parametrically includes the effect of Coulomb screening;  $b$  and  $\rho$  are short-range parameters. Henceforth, the effective interionic potential contains only three free parameters ( $Z_m$ ,  $b$  and  $\rho$ ), which can be determined from the crystal properties [18].

Thermodynamically, an isolated phase is stable only when its free energy is a minimum for the specified conditions (temperature or pressure). As the temperature or pressure or any other variable acting on the systems is altered, the Gibbs free energy changes smoothly and continuously. A phase transition is said to occur when the changes in structural details of the phase are caused by such variations of free energy and the uranium monochalcogenides transform from their initial B1 to B2 structure under pressure.

The structural phase stability of a particular structure is decided by the minima of Gibbs' free energy,  $G = U + PV - TS$ ;  $U$  is internal energy, which at 0 K corresponds to the cohesive energy;  $S$  is the vibrational entropy at absolute temperature  $T$ , pressure  $P$  and volume  $V$ . Since these theoretical calculations are performed at  $T = 0$  K, Gibbs' free energy becomes equal to the enthalpy,  $H = U + PV$ . For a given pressure, a stable structure is one for which thermodynamic potential ( $G$  or  $H$ ) has its lowest value. We have estimated the Gibbs' free energy for both the B1 and B2 phases.

The Gibbs' free energies  $G_{B1}(r) = U_{B1}(r) + 2Pr^3$  for the NaCl (B1) phase and  $G_{B2}(r') = U_{B2}(r') + [8/3\sqrt{3}]Pr'^3$  for the CsCl (B2) phase become equal at the phase-transition pressure  $P_t$  and at zero temperature, i.e.  $\Delta G (= G_{B1} - G_{B2})$ . Here,  $U_{B2}$  and  $U_{B1}$  represent

cohesive energies for B1 and B2 phases, and are

$$U_{B1}(r) = -1.7475 \frac{e^2 Z_m^2}{r} + 6V_{ij}(r) + 6V_{ii}(r) + 6V_{jj}(r), \quad (2)$$

$$U_{B2}(r') = -1.7627 \frac{e^2 Z_m^2}{r'} + 8V_{ij}(r') + 3V_{ii}(r') + 3V_{jj}(r'). \quad (3)$$

Here  $r$  and  $r'$  are nearest-neighbour (nn) separations corresponding to NaCl and CsCl phases, respectively.  $V(r)$  is the short-range overlap repulsive energy and is defined as

$$V_{ij}(r) = b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) - c_{ij}r_{ij}^{-6} - d_{ij}r_{ij}^{-8}; \quad i, j = 1, 2. \quad (4)$$

The last two terms in equation (4) are the van der Waals (vdW) energy due to dipole–dipole (d–d) and dipole–quadrupole (d–q) interactions. The study of the second-order elastic constants (SOECs) ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ) and their pressure derivatives at 0 K is quite important for understanding the nature of the interatomic forces in them. Since these elastic constants are functions of the first- and second-order derivatives of the short-range potentials, their calculations will provide a further check on the accuracy of short-range forces in these materials.

The potential (EIoIP) in equation (1) corresponds to a dynamical matrix in terms of force constants. The elements of the Coulomb interaction, the repulsive interaction matrix, are determined from the derivatives of EIoIP whose details are given elsewhere [15]. These are then obtained for B1 and B2 phases, and subjecting the dynamical matrix to the long-wavelength limit we find the expressions for the SOECs for the B1 phase as

$$C_{11} = \frac{e^2}{4r_0^4} \left[ -5.112Z_m^2 + A_1 + \frac{(A_2 + B_2)}{2} \right], \quad (5)$$

$$C_{12} = \frac{e^2}{4r_0^4} \left[ 0.226Z_m^2 - B_1 + \frac{(A_2 - 5B_2)}{4} \right], \quad (6)$$

$$C_{44} = \frac{e^2}{4r_0^4} \left[ 2.556Z_m^2 + B_1 + \frac{(A_2 + 3B_2)}{4} \right], \quad (7)$$

where  $(A_1, B_1)$  and  $(A_2, B_2)$  are the short-range parameters for the nearest and the next-nearest neighbours, respectively. These parameters are defined as

$$A_1 = \frac{4r_0^3}{e^2} \left[ \frac{d^2}{dr^2} V_{ij}(r) \right]_{r=r_0}, \quad (8)$$

$$A_2 = \frac{4(r_0\sqrt{2})^3}{e^2} \left[ \frac{d^2}{dr^2} V_{ii}(r) + \frac{d^2}{dr^2} V_{jj}(r) \right]_{r=r_0\sqrt{2}}, \quad (9)$$

$$B_1 = \frac{4r_0^2}{e^2} \left[ \frac{d}{dr} V_{ij}(r) \right]_{r=r_0}, \quad (10)$$

$$B_2 = \frac{4(r_0\sqrt{2})^2}{e^2} \left[ \frac{d}{dr} V_{ii}(r) + \frac{d}{dr} V_{jj}(r) \right]_{r=r_0\sqrt{2}}, \quad (11)$$

where  $V_{ij}(r)$  and  $V_{ii}(r)$  [ $V_{jj}(r)$ ] are the overlap potentials between the nearest and the next-nearest neighbours, respectively.  $r_0\sqrt{2}$  denotes the next-nearest-neighbour distance in the B1 phase.

In order to check the assumptions made for constructing the EIoIP, we have computed the phase transition pressures, the associated volume collapses and the mechanical behaviour of the UX ( $X = S, Se, \text{ and } Te$ ) chalcogenides. We shall now compute numerically the high-pressure phase transition and elastic properties for B1 phase in the next section.

**Table 1.** The values of van der Waals coefficients of UX compounds.  $c_{ij}$  ( $i, j = 1, 2$ ) (in units of  $10^{-60}$  erg cm<sup>6</sup>),  $d_{ij}$  ( $i, j = 1, 2$ ) (in units of  $10^{-76}$  erg cm<sup>8</sup>) and overall van der Waals coefficients ( $C, D$ ).

Compound	$c_{ii}$	$c_{ij}$	$c_{jj}$	$C$	$d_{ii}$	$d_{ij}$	$d_{jj}$	$D$
US	7.8	45.5	395.0	663.9	3.02	50.5	570.9	540.0
USe	8.4	75.6	1188.7	1579.9	3.02	101.9	2041.2	1444.3
UTe	8.38	89.8	1856.6	2277.3	3.02	142.67	3698.9	2357.8

**Table 2.** Crystal data and model parameters for UX compounds.

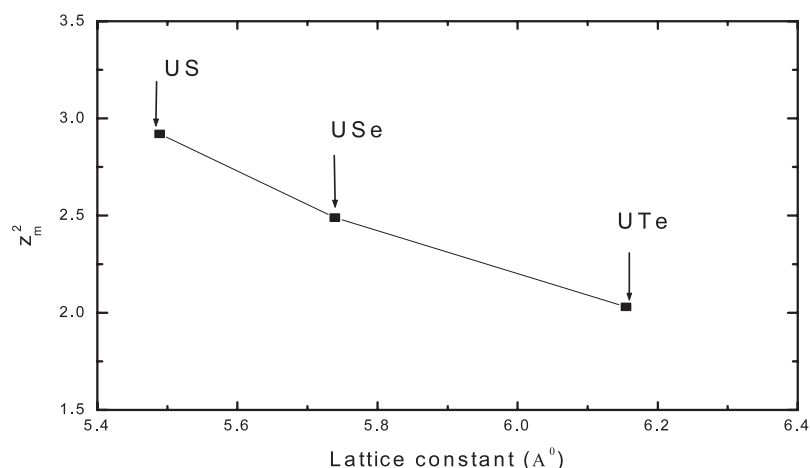
Compound	Material parameters				Model parameters		
	$r_i$ (Å)	$r_j$ (Å)	$a_0$ (Å)	$B_T$ (GPa)	$Z_m^2$	$b$ ( $10^{-12}$ erg)	$\rho$ ( $10^{-1}$ Å)
US	0.80	1.24	5.489 [20]	105 [1]	2.92	7.72	3.43
USe	0.80	1.30	5.744 [20]	74 [1]	2.49	9.728	3.32
UTe	0.80	1.30	6.155 [20]	48 [1]	2.03	9.82	4.03

### 3. Results and discussion

With application of high pressure, new crystal phases appear in materials and the relative stability of two crystal structures requires an extremely accurate prediction. Theoretical studies of cohesive, structural and vibrational properties of alloys under pressure are now accurately being performed by means of *ab initio* calculations. However, several empirical lattice models point out that the key for predicting relative structural energies is not absolute accuracy but to carefully incorporate the chemical trends in the atomic characteristics. It is true that phenomenological lattice models are interpretative rather than predictive of the stability of phases.

To discuss the stability of crystal structures and the pressure induced phase transition theoretically, it is essential to estimate the total free energy of crystals, which consists of ions and valence electrons. The contributions from the system of electrons to the total energy of the crystal are intimately connected with the mechanism of cohesion and interatomic bonding in the crystals. We need to determine the most stable structure at finite pressure and temperature; the thermodynamical potential as Gibbs' free energy,  $G = U + PV - TS$ , must be considered; the structure with lowest free energy is the most stable. However, it is difficult to minimize the free energy from randomly generated structures even with highly sophisticated computational techniques. To further simplify our calculations, the temperature has been set to zero, i.e., the entropy of the crystal is therefore ignored. It may be mentioned here that the contribution of temperature to free energy is small for the experimental data considered.

The effective interionic interaction potential is constructed in a hierarchical and easy generalizable manner. We have assessed such structural and elastic properties in an ordered way. For such purposes we have then three material parameters, namely, modified ionic charge, range, and hardness parameters ( $Z_m$ ,  $\rho$ , and  $b$ ). To estimate them, we first deduce the vdW coefficients from the Slater–Kirkwood variational method [19] and these are listed in table 1. Here, UX compounds are considered to be partially ionic. It is perhaps worth remarking that we have deduced the values of crystal dependent parameters, namely modified ionic charge ( $Z_m$ ), range ( $\rho$ ), and hardness ( $b$ ), from the knowledge of equilibrium distance and the bulk modulus following the equilibrium conditions [18]. The input data along with their relevant references and the model parameters for UX compounds are given in table 2.



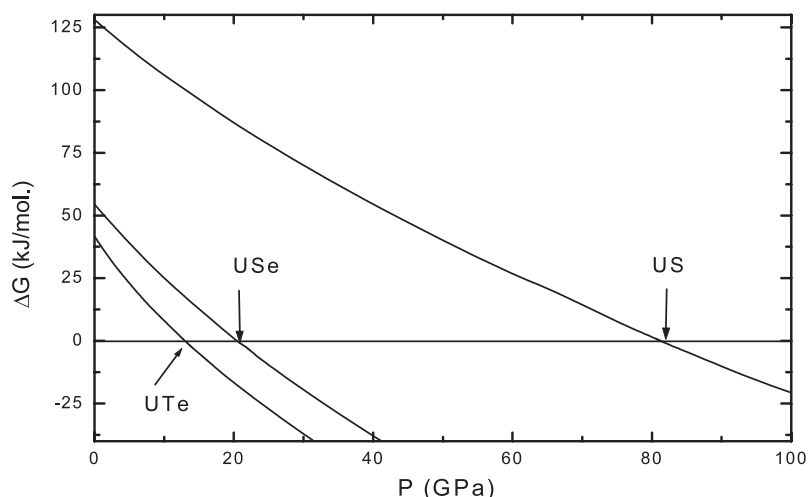
**Figure 1.** Variation of effective charge  $z_m^2$  with lattice constant for UX (X = S, Se, and Te) compounds.

Figure 1 shows the variation of modified ionic  $Z_m^2$  of UX compounds as a function of lattice constant ( $a$ ). It is inferred from the plot that the ionic charge parameters vary monotonically with lattice constant (Å) in UX. This can be readily understood by considering their electronic structure, f electrons and their hybridization with chalcogen p states (f-p hybridization). A linear trend in the ionic charge parameter is found in the series (US > USe > UTe) and interpreted in terms of competition between localization of the U 5f states and the f-p hybridization. Furthermore, the observed negative gradient of ionic charge parameter is also a direct consequence of a decreasing trend of variation in bulk modulus (see table 2). Our discussion of valency implies that there is a direct relationship between the difference in the number of the less well localized f electrons and the difference in energy between the two valence states. Similar results were earlier obtained for La monochalcogenides [13]. We appeal for the consistency of the results to be tested as a measure of the validity of these assumptions.

In an attempt to reveal the structural phase transition of the test materials, we minimize the Gibbs' free energies  $G_{B1}(r)$  and  $G_{B2}(r')$  for the equilibrium interatomic spacing ( $r_0$ ) and ( $r'_0$ ). The Gibbs' free energy difference  $\Delta G (=G_{B1}(r) - G_{B2}(r'))$  has been plotted as a function of pressure ( $P$ ) in figure 2 by using the interionic interaction potential discussed above for UX monochalcogenides. Let us summarize the results of the plots. The pressure corresponding to  $\Delta G$  approaching zero is the phase transition pressure ( $P_t$ ) (indicated by arrows in the figures).

It turns out that at zero pressure the B1 crystal phase is the thermodynamically and mechanically stable state of UX, which is in agreement with the experimental result, and it will remain stable until the pressure reaches a value of about 81 (US), 21 (USe) and 13 (UTe) GPa (transition pressure). At the transition pressure the thermodynamical potentials of both the phases are equal. As pressure increases, beyond the phase transition pressure ( $P_t$ ), the B2 phase becomes lower, and hence this phase becomes mechanically and thermodynamically stable (its  $\Delta G$  function value is more negative than that of B1 crystal).

At a pressure higher than the theoretical thermodynamic transition pressure, the B1 crystal becomes thermodynamically unstable while the B2 phase remains stable up to the greatest pressure studied. In UX compounds a crystallographic transition from B1 to B2 occurs. These results may be successfully compared with available experimental data [1, 6] and are tabulated in table 3. It is interesting to note that the transition pressure decreases from US to UTe, which is in agreement with the experimental result. It is noteworthy that there is a transfer of



**Figure 2.** Variation of Gibbs free energy difference with pressure.

**Table 3.** Calculated transition pressures and volume collapses in UX compounds.

Compounds	Transition pressure (GPa)	Volume collapse (%)
US	B1 → B2 81 (80 <sup>a</sup> )	4.7
USe	B1 → B2 21 (20 <sup>b</sup> )	7 (8 <sup>b</sup> )
UTe	B1 → B2 13 (9 <sup>b</sup> )	5.6 (8 <sup>b</sup> )

<sup>a</sup> The quantities are taken from experiment [6].

<sup>b</sup> The quantities are taken from experiment [1].

electrons from chalcogen *s* and *p*-like states to the U *f*-like states continuously under pressure, which must be responsible for the observed structural transformation.

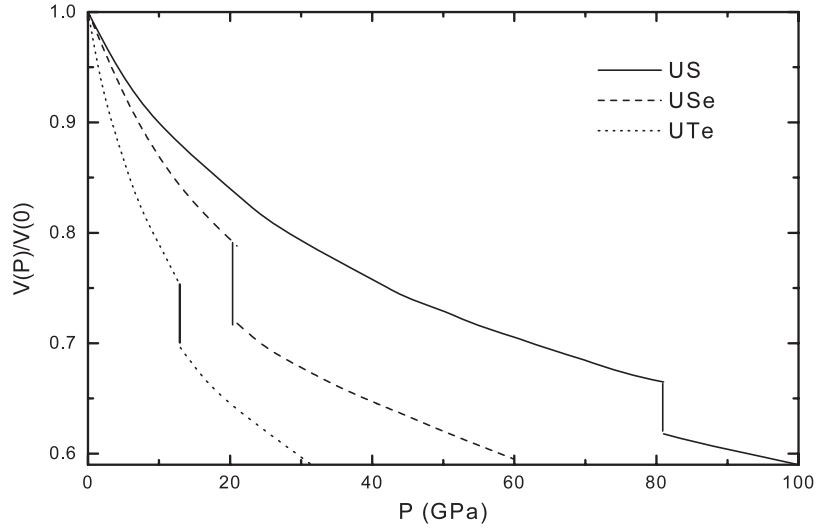
The pressure–volume relation of UX was determined from Murnaghan-type equation of state [18] that accounts for the values of the relative volumes  $V(P)/V(0)$  associated with various compressions as

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0}P\right)^{-1/B'} \quad (12)$$

where  $V_0$  is the cell volume at ambient conditions,  $B_0$  is the bulk modulus and  $B'$  its pressure derivative.

The estimated values of the pressure-dependent radii  $r(P)$  for both the structures (B1 and B2) have been used to compute the values of  $V(P)/V(0)$  and plot them against the pressure ( $P$ ) to depict the phase diagram illustrated in figure 3 for UX compounds. It is noticed from the plot that our approach has predicted correctly the relative stability of competitive crystal structures, as the values of  $\Delta G$  are positive. This is in agreement with the fact that a volume collapse occurs at the B1–B2 transition, and the U–U distances become smaller than the Hill limit [21], so the 5*f* bands can directly overlap and the *f* electrons are delocalized. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and their values are tabulated in table 3, which is in fairly good agreement with those revealed from experiments [1]. We must mention that the volume change during transition in USe is higher than that of US and Ute, which may also be possible due to the fractional valence change of the U ion during the structural transition.





**Figure 3.** Phase diagram of UX ( $X = S, Se, Te$ ).

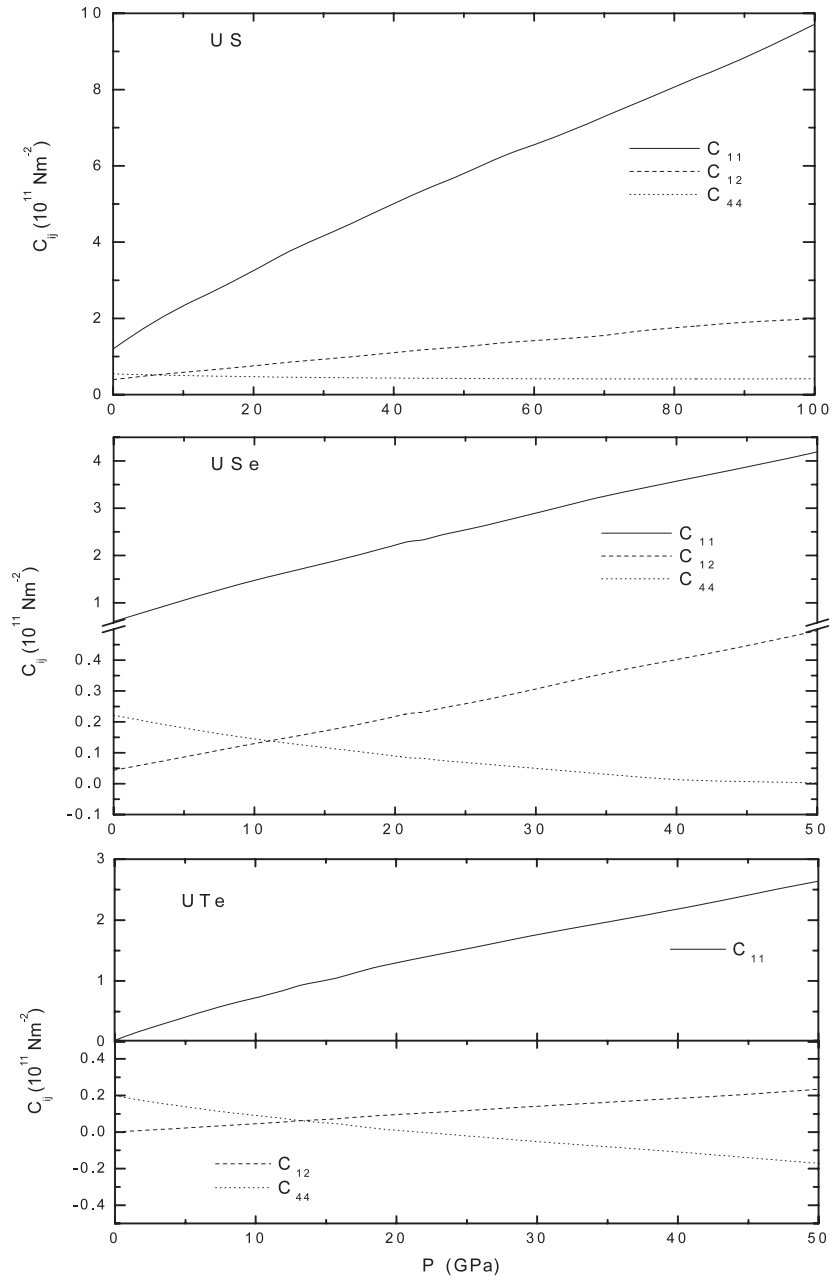
Finally, we shall briefly explain the slight differences of the observed values with the experimental values. It is very difficult at this stage to pinpoint the exact quantitative explanation for this disagreement. However, intuitively, one may argue for twofold reasons: these theoretical calculations are done at 0 K, whereas the experimental results are obtained at room temperature, and may be due to the uncertainties in the sphere radii chosen.

We further investigate the high-pressure elastic behaviour of these compounds, by computing the second-order elastic constants (SOECs) and their variation with pressure as shown in figure 4 for UX compounds. It is noticed that  $C_{44}$  decreases linearly with the increase of pressure away from zero at the phase transition pressures. In contrast, the value of  $C_{11}$  ( $C_{12}$ ) increases linearly with pressure. The above feature is quite similar to the earlier reported pressure dependence of elastic stiffness for PbTe and SnTe possessing the NaCl structure with B1 to B2 structural phase transition [22].

For better understanding, we plot the variation of the combination of SOEC elastic stiffnesses [ $C_L = (C_{11} + C_{12} + 2C_{44})/2$ ] and shear moduli [ $C_S = (C_{11} - C_{12})/2$ ] in figure 5 for UX. We observed that  $C_L$  and  $C_S$  increase linearly with increase in the pressure and in accordance with the first-order character of the transition for these compounds. The calculated values of second order elastic constants, bulk modulus ( $B_T$ ) and tetragonal moduli ( $C_S$ ) are given in table 4 and are also compared with various experimental techniques, i.e. neutron scattering [8, 23], ultrasonic techniques [24, 25], x-ray measurement [26] and other theoretical works [27]. It is true that the agreement between the theoretical and the experimental value of bulk modulus is not of the desired degree, but this may be because we have derived our expressions neglecting thermal effects and assuming the overlap repulsion significant only up to nearest neighbours.

The Born criterion for a lattice to be in the mechanically stable states is that the elastic energy density must be a positive definite quadratic function of strain. This requires that the principal minors (alternatively the eigenvalues) of the elastic constant matrix should all be positive. Further, the stability of a cubic crystal is expressed in terms of elastic constants as follow [13]:

$$B_T = (C_{11} + 2C_{12})/3 > 0, \quad (13)$$



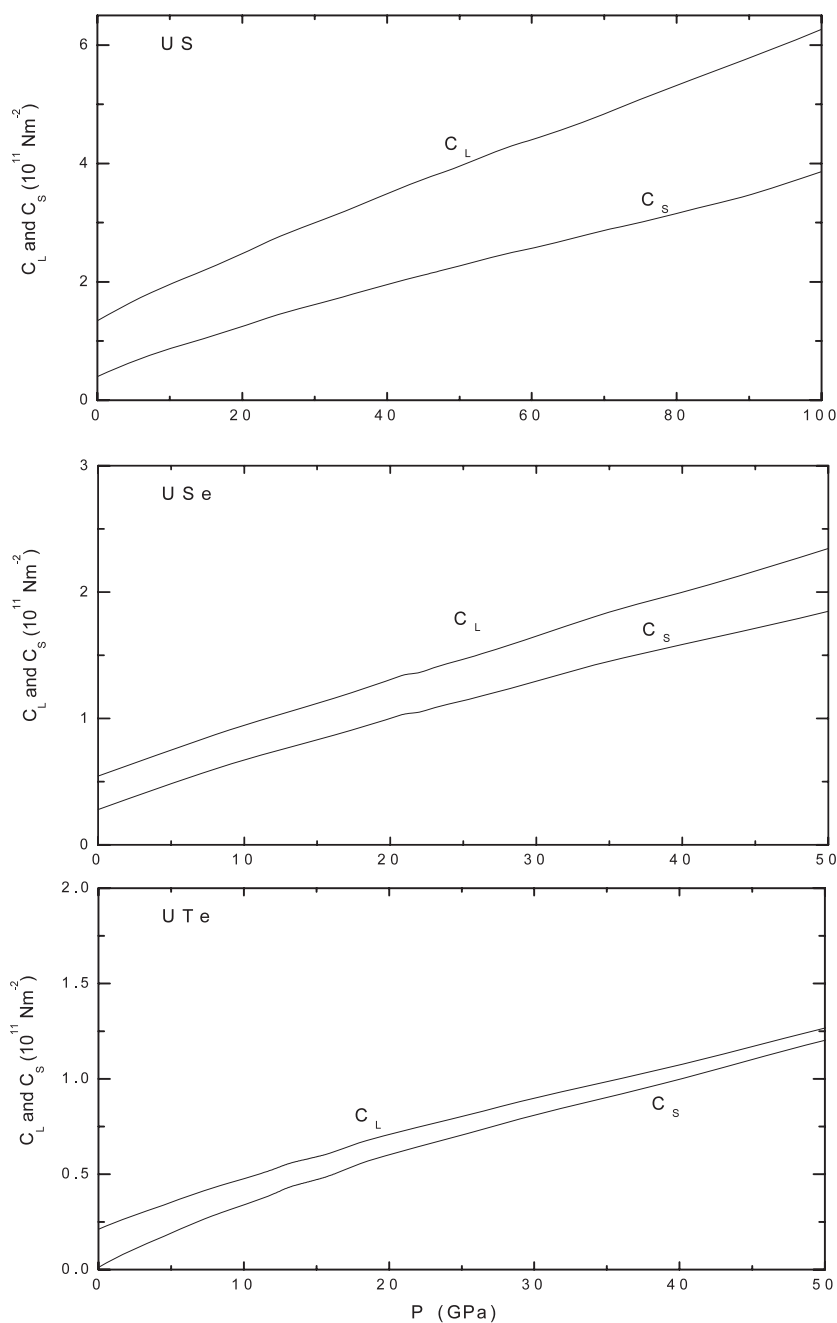
**Figure 4.** Variation of second-order elastic constants with pressure.

$$C_{44} > 0, \tag{14}$$

and

$$C_S = (C_{11} - C_{12})/2 > 0. \tag{15}$$

Here,  $C_{ij}$  are the conventional elastic constants and  $B_T$  is the bulk modulus. Estimated values of bulk modulus  $B_T = 6.6[2.3(0.07)] \times 10^{10} \text{ N m}^{-2}$ , shear moduli  $C_{44} = 5.5[2.2(1.9)] \times$



**Figure 5.** Variation of the combination of second order elastic constants with pressure.

$10^{10} \text{ N m}^{-2}$ , and tetragonal moduli,  $C_S = 4.0[2.8(0.1)] \times 10^{10} \text{ N m}^{-2}$ , well satisfied the above elastic stability criteria for US[Se(Te)] compounds. In passing we note that Vukcevic [28] proposed a high-pressure stability criterion for ionic crystals, combining mechanical stability with minimum energy conditions. In accordance, the stable phase of the crystal is one in which

**Table 4.** Second order elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ), bulk modulus ( $B_T$ ) and tetragonal moduli ( $C_S$ ) (in units of  $10^{10}$  N m $^{-2}$ ).

Compounds	$C_{11}$	$C_{12}$	$C_{44}$	$B_T$	$C_S$
US	11.9	3.9	5.5	6.6	4.0
	$24.5 \pm 1.4^a$	$0.4 \pm 0.7^a$	$2.1 \pm 0.1^a$	$8.4 \pm 0.6^a$	
	$30.17 \pm 0.39^b$	$1.32 \pm 0.73^b$	$1.693 \pm 0.019^b$	$10.7 \pm 0.8^b$	
	$30.5 \pm 1.5^c$		$1.72 \pm 0.05^c$	$9.2 \pm 0.9^d$	
			11.0 <sup>e</sup>		
USe	6.0	0.4	2.2	2.3	2.8
	$19.4 \pm 1.4^f$	$0.0 \pm 0.7^f$	$1.6 \pm 0.1^f$	$6.5 \pm 0.7^f$	
			9.4 <sup>e</sup>		
UTe	0.2	0.002	1.9	0.07	0.1
	$14.9 \pm 0.3^f$	$-2.0 \pm 0.4^f$	$1.13 \pm 0.04^f$	$3.4 \pm 0.6^f$	
	$14.34 \pm 0.36^b$		$1.20 \pm 0.02^b$	6.3 <sup>e</sup>	

<sup>a</sup> The quantities are taken from the neutron scattering experiment [23].

<sup>b</sup> The quantities are taken from the ultrasonic experiment [24].

<sup>c</sup> The quantities are taken from the ultrasonic experiment [25].

<sup>d</sup> The quantities are taken from the compressibility by x-ray experiment [26].

<sup>e</sup> The quantities are taken from band theoretical studies [27].

<sup>f</sup> The quantities are taken from the neutron scattering experiment [8].

the shear elastic constant  $C_{44}$  is nonzero (for mechanical stability) and which has the lowest potential energy among the mechanically stable lattices.

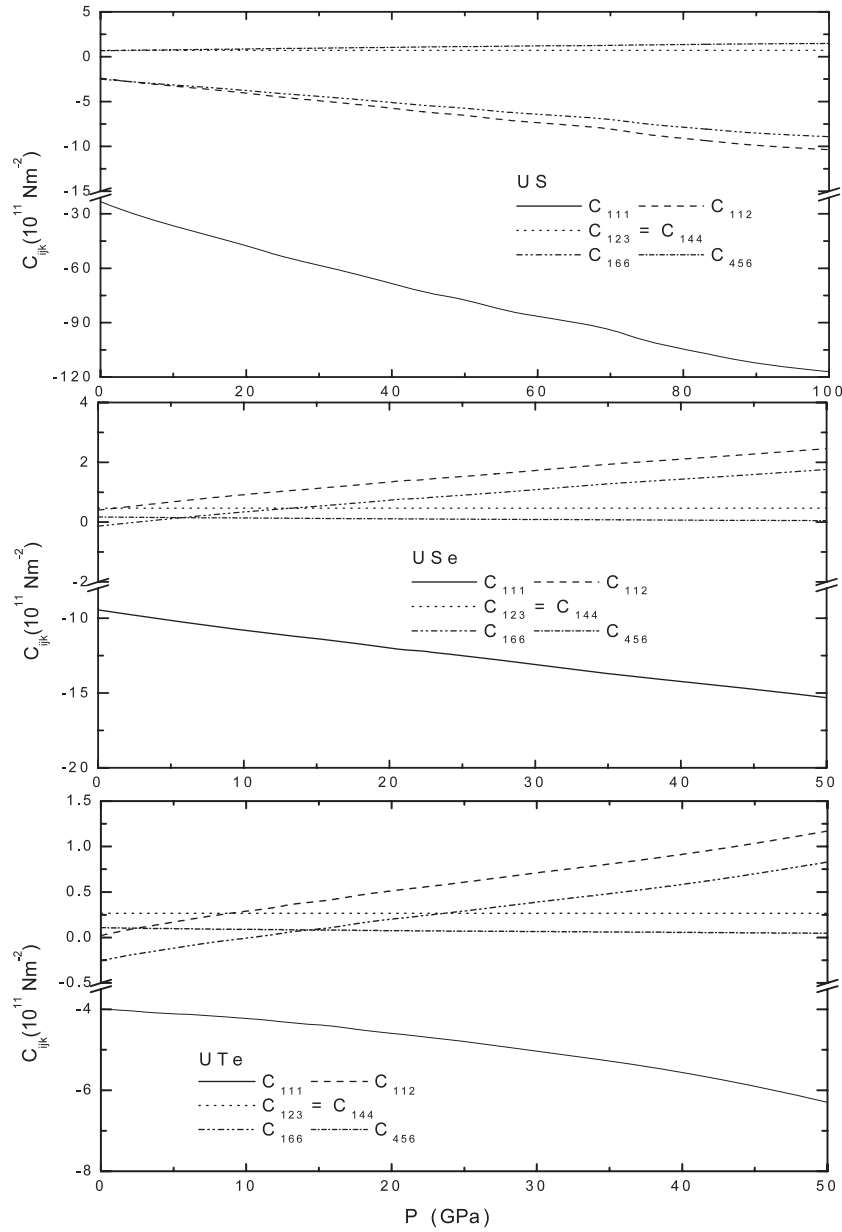
We may now concentrate our discussion on the elastic properties of uranium compounds within the framework of developed EIoIP. We have noticed that the shear elastic constant  $C_{44}$  is a very small quantity; the calculated value of  $[(4r_0/e^2)C_{44} - 0.556Z_m^2]$  is found to be a negative quantity so that  $(A_2 - B_2)$  is negative. This suggests that these terms belong to an attractive interaction and possibly arise due to the van der Waals energy. Based on this observation we suggest that the van der Waals energy converges quickly, but the overlap repulsion converges much more quickly.

The above fact implies that the second-nearest-neighbour forces are entirely due to the van der Waals interaction and the first-neighbour forces are the results of the overlap repulsion and the van der Waals attraction between the nearest neighbours. However, at high pressure the short-range forces for these compounds increase significantly, which, in turn, is responsible for change in the coordination number and phase transformation. Other than deriving the equation of states correctly from a model approach and then analysing the variation of short-range forces, at present we have no direct means to understand the interatomic forces at high pressure.

We also analyse the anharmonic properties of UX compounds by computing the third-order elastic constants (TOECs) and the pressure derivatives of SOECs at zero pressure [15]. The values of the pressure derivatives of SOECs ( $d\sigma/dP$ ,  $dB_T/dP$  and  $dC_{44}/dP$ ) for UX are listed in table 5. Also, the variation of TOECs with pressure is shown in figure 6. It can be seen that the variation of third order elastic constants with pressure points to the fact that the values of  $C_{111}$ ,  $C_{112}$ ,  $C_{123}$ ,  $C_{166}$ , and  $C_{456}$  are negative while that of  $C_{144}$  is positive as obtained from the effective interionic potential at zero pressure. Thus, we can say that in UX ( $X = S, Se, \text{ and } Te$ ) the developed EIoIP consistently explains the high pressure and elastic behaviour.

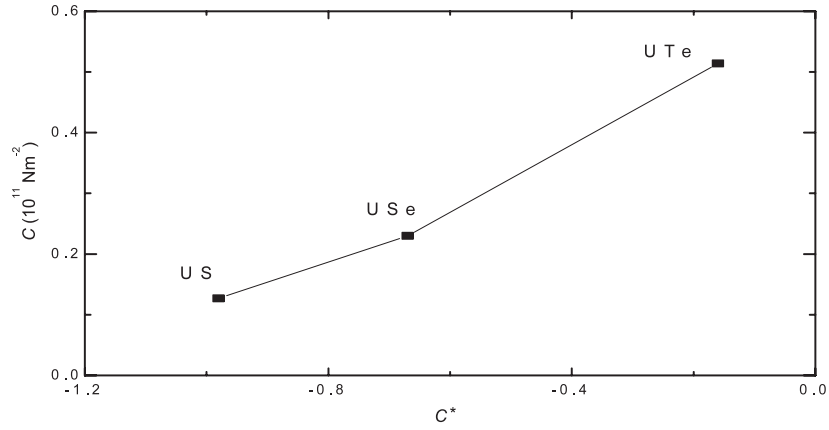
Apart from the phase transition and pressure dependence of SOECs, we also estimate the Debye temperature ( $\theta_D$ ) from the present approach. We define

$$\theta_D^3 = \frac{3.15}{8\pi} \left(\frac{h}{k_B}\right)^3 \left(\frac{r}{M}\right)^{\frac{3}{2}} (C_{11} - C_{12})^{\frac{1}{2}} (C_{11} + C_{12} + 2C_{44})^{\frac{1}{2}} C_{44}^{\frac{1}{2}}, \quad (16)$$



**Figure 6.** Variation of third-order elastic constants with pressure.

where  $M$  is the acoustic mass of the compound. Pressure-dependent elastic moduli may be expected to make the Debye temperature  $\theta_D$  pressure dependent. The calculated values of the Debye temperature at zero pressure are consistent with the reported data, 235 K (239 K [29],  $205 \pm 2.5$  K [30]), 150 K ( $172 \pm 2.3$  K [30]), and 126 K ( $124 \pm 2.5$  K [30]) for US, USe, and UTe, respectively. However, we do not claim the process to be rigorous, but a consistent agreement following EIoIP is obtained on Debye temperature as revealed from experiments and other work.



**Figure 7.** ‘Average’ elastic constant  $C$  as a function of Cauchy discrepancy  $C^*$  for UX compounds.

**Table 5.** Pressure derivative of bulk modulus ( $B_T$ ), shear modulus ( $C_{44}$ ), and tetragonal modulus ( $C_S$ ) for UX ( $X = S, Se, \text{ and } Te$ ).

Compounds	$dB_T/dP$	$dC_{44}/dP$	$dC_S/dP$
US	4.06	-0.5	6.57
USe	3.52	-0.57	2.07
UTe	2.96	-1.11	1.82

Usually, the Debye temperature is also a function of temperature, varies from technique to technique, and depends on the sample quality with a standard deviation of about 15 K. Thus, we see in fact that the Debye temperatures of the uranium monochalcogenides do exhibit a similar trend: a decrease in the crystal energy, phase transition pressure, and bulk modulus, an increase in the lattice constant, and a decrease in the Debye temperature. We comment that the high cohesive energies, high melting points, and extreme hardness of semiconducting chalcogenides generally are typical of covalently bonded systems. The rare earth monochalcogenides and alkaline earth monochalcogenides with rock-salt as crystal structure, on the other hand, are more typical for ionic crystals.

One can approximate that this result motivates the definition of an ‘average’ elastic constant as

$$C = \left( \frac{8\pi}{3.15} \right)^{\frac{2}{3}} \left( \frac{k_B}{h} \right)^2 \left( \frac{M}{r} \right) \theta_D^2, \quad (17)$$

which in turn is calculated from the Debye temperature, allowing us to correlate the Cauchy discrepancy in elastic constant following

$$C^* = \frac{C_{12} - C_{44}}{C_{12} + C_{44}}, \quad (18)$$

at zero pressure. Figure 7 shows the variation of the ‘average’ elastic constant ( $C$ ) with Cauchy discrepancy ( $C^*$ ) for UX compounds. It is worth mentioning that the diluted magnetic semiconductors with zinc-blende structure (B3–B1 structural phase transition) [31] and most of the body centred cubic transition metals show a positive Cauchy deviation  $C^*$ .

#### 4. Conclusion

Realistic description of structural and mechanical properties needs to take into account various interactive forces when the lattice is strained and their balance to attend the stable structure depending upon the ionic nature. We have therefore calculated the pressure induced structural and elastic properties of uranium monochalcogenes with stable rock-salt structures by considering various interionic interactions. To further simplify our calculations, the temperature has been set to zero so that the entropy of the crystal is therefore ignored. This is in the spirit of the fact that the contribution of temperature to the free energy is small for the experimental data is considered.

Obtained values of material parameters from the crystal data allow us to predict the phase transition pressure and associated volume collapses. The results of the lattice model calculations yield the phase transition pressure of 81, 21 and 13 GPa for US, USe and UTe monochalcogenides. For these three compounds excellent agreement is found with available data. The good agreement for both transition pressures and volume collapses shows that in the rock-salt phase the localized  $f^3$  U ions coexist with a partly occupied narrow  $f$  band, effectively describing an intermediate valent phase. The model's ability to predict realistic cohesive properties such as the equilibrium volume, the bulk modulus, its derivative with pressure, the relative stability of crystal structures, and transition pressures and volumes is exemplified in terms of the screening of the effective Coulomb potential through modified ionic charge ( $Z_m^2$ ).

For the disagreement in the elastic properties, intuitively, we may argue for the following reasons: these theoretical calculations are done at 0 K, whereas the experimental results are obtained at room temperature, may be due to the uncertainties in the ionic radii and by assuming the overlap repulsion significant only up to second-nearest neighbours. The lattice model calculation also supports the validity of the Born criterion. The second order elastic constants  $C_{11}$  and  $C_{12}$  increase with increase in pressure up to the phase transition pressure, that supports the high-pressure structural stability of UX compounds. Further,  $C_{44}$  decreases linearly with the increase of pressure and does not tend to zero at the phase transition pressures and is in accordance with the first-order character of the transition. Nevertheless, it has been found that this simple model as compared to sophisticated computational techniques may account for a considerable part of the available experimental and theoretical results for the high-pressure studies for uranium chalcogenides.

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