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Phase transition in CeSe, EuSe and LaSe under high pressure

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Abstract: The high pressure phase transition and elastic behavior of rare earth monoselenides (CeSe, EuSe and LaSe) which crystallize in a NaCl-structure have been investigated using the three body interaction potential (TBIP) approach. These interactions arise due to the electron-shell deformation of the overlapping ions in crystals. The TBP model consists of a long range Coulomb, three body interactions and the short range overlap repulsive forces operative up to the second neighboring ions. The authors of this paper estimated the values of the phase transition pressure and the associated volume collapse to be closer than other calculations. Thus, the TBIP approach also promises to predict the phase transition pressure and pressure variations of elastic constants of lanthanide compounds.

Keywords: Phase transition, transition pressure, three body interaction, elastic constants, Gibbs free energy
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1 Introduction

The rare-earth monoselenides (REX), RE= Ce, Eu, La and X= Se which crystallize in an NaCl (B_1)-structure at ambient pressure, have been a topic of great interest because of their optical, magnetic and electrical properties [1, 2]. From the numerous RE-elements which are trivalent, the volume of the corresponding monoselenides shows an expected

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lanthanide contraction exhibiting metallic properties, e.g. LaSe demonstrates the electric resistivity at room temperature in the order of 250 $\mu\Omega$·cm [3]. The electronic and structural phase transition of cerium monopnictides at high pressure is described by Svane *et al.* [4].

Amongst cerium monopnictides, only CeP has been found to undergo a first order phase transition at about 10 GPa [5, 6] compared to CeAs, where a pressure-induced iso-structural valence change from 3^+ to 4^+ does not occur [7]. CeBi and CeTe have a relatively smaller bulk modulus which has been attributed to the volume dependent Kondo effect [8]. These compounds show a strong ionic character. CeSe shows a NaCl to CsCl ($B_1 \rightarrow B_2$) phase transition at about 20 GPa [6]. A theoretical study using a two body interaction approach of the CeSe compound, where the localized f-electron of the cerium ion screens the ionic charge, has been successfully done by Srivastava *et al.* [9]. EuSe has a discontinuous volume change at 14.5 GPa which is due to a transition from the NaCl to CsCl-type structure [10].

Furthermore, LaS shows a $B_1 \rightarrow B_2$ phase transition around 28 GPa in argon pressure medium [11]. Lu *et al.* [12] employed the local density approach (LDA) for LaS and SmS successfully, but this approach is inadequate to describe the localization of the f-electron in SmS. A tight binding linear muffin tin orbital (TBLMTO) approach [13] has been employed to accurately study, the theoretical high pressure behavior of rare earth monoselenides. Varshney *et al.* have recently employed two body interaction models which includes van der Waals attraction regarding the LaSe compound [14–16].

As lanthanides have interesting properties and the fact that no study has been conducted using the three body interactions, we thought it pertinent to apply a three body interaction potential approach [17] which has a more realistic potential than the two body potential. The importance of including three body interactions in a potential model to improve results has also been emphasized by Sims *et al.* [19] and W. Cochran [20].

In view of earlier studies [15–20], we decided to employ our three body interaction potential (TBIP) approach [17, 18] to study the high pressure behavior of CeSe, EuSe and LaSe. This TBIP includes the long range Coulomb, three body interactions and the short range overlap repulsive interaction operative up to the second neighboring ions within the Hafemeister and Flygare framework [21].

2 TBP Model and Method of Computations

The application of pressure on the crystals causes the decrease in their volume, which in turn leads to an increased charge transfer (or three-body interaction effects) due to the existence of the deformed (or exchange) charge between the overlapping electron shells of the adjacent ions. This overlapping leads to the transfer of charges which when interacts with another distant charge gives rise to many body interactions (MBI). The dominant part of MBI is three body interactions(TBI) [17]. To understand this mechanism, let us designate A, B, and C ions with positions (lk), *(l'k')* and *(l"k")* in an ionic crystal having an ionic charge ± Ze with l and k as the cell and basis indices as shown in Fig 1. Also, C is the nearest neighbor (nn) of ion A and separated by a distance $r = |r(lk, l'k')|$ and B is any distance ion a distance $|r(lk, l'k')|$ apart from A.

$$dq_k = \pm zef_k r(lk, l"k") = \pm zef_k(r). \tag{1}$$

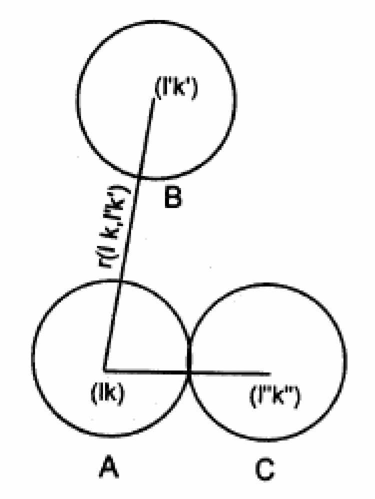

Fig. 1 Schematic representation of three body interactions model showing the three ions A, B and C with positions *(lk, l'k', l"k")*.

The occurrence of the above transferred charge leads to a modified charge of A (or C) as

$$z_m e = z_k e + nef_k r(lk, l"k") \cong z_k e[1 + (2n/z)f_k r(lk, l"k")]^{1/2}. \tag{2}$$

Here, n is the number of the nearest neighbor (nn) ions, e is the electronic charge, $f_k(r)$ is the interionic potential force and $[1 + (2n/z)f_k r(lk, l"k")]^{1/2}$ has been approximated as $[1 + (2n/z)f(r)]$. The expression for the modified Coulombic energy due to the three body potential (TBI) is

$$\Phi_m(r) = \Phi^c + \Phi^T, \tag{3}$$

$$\Phi_m(r) = [-\alpha_M z^2 e^2/r][1 + (2n/z)f(r)], \tag{4}$$

where α_M is the Madelung constant, which is 1.7476 (1.7629) for NaCl (CsCl) structure, r is the equilibrium nn ion separation and n is the number of nn ions, $f(r)$ is the TBI parameter and is dependent on the nearest neighbor ion distance as

$$f(r) = f_0 \exp(-r/\rho). \tag{5}$$

These TBP effects have been incorporated into Gibbs free energy ($G = U + PV - TS$). Here, U is the internal energy which at $T = 0$ K is equivalent to the lattice energy, S is the vibrational entropy at absolute temperature T. At $T = 0$ K and pressure P, the

Gibbs free energy for the rock salt (B_1,real) and CsCl (B_2, hypothetical) structures are given by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1}, \tag{6}$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2}, \tag{7}$$

with V_{B_1} ($= 2.00r^3$) and V_{B_2} ($= 1.54r'^3$) as the unit cell volumes for B_1 and B_2 phases respectively. Here r (r') is the interionic separation for NaCl (CsCl)-structures respectively. The first term in the Eqns. (6) and (7) are the lattice energies for B_1 and B_2 structures and they are expressed as:

$$\begin{aligned} U_{B_1}(r) = {} & [-(\alpha_M z^2 e^2)/r] - [(12\alpha_M z e^2 f(r))/r] + 6b\beta_{ij}\exp[(r_i + r_j - r)/\rho] \\ & + 6b\beta_{ii}\exp[(2r_i - 1.41r)/\rho] + 6b\beta_{jj}\exp[2r_j - 1.41r)/\rho], \end{aligned} \tag{8}$$

$$\begin{aligned} U_{B_2}(r') = {} & [-(\alpha'_M z^2 e^2)/r'] - [(16\alpha'_M z e^2 f(r'))/r'] + 8b\beta_{ij}\exp[(r_i + r_j - r')/\rho] \\ & + 3b\beta_{ii}\exp[(2r_i - 1.154r')/\rho] + 3b\beta_{jj}\exp[2r_j - 1.154r')/\rho]. \end{aligned} \tag{9}$$

Here r_i (r_j), ρ, b and β_{ij} are the ionic radii, range parameter, hardness parameter and Pauling coefficients of the compounds respectively. These lattice energies consist of the long-range Coulomb energy (first term in Eqns. (8) and (9)), and the three body interaction energy term which are expressed by the second term in Eqns. (8) and (9)). The energy due to the overlap repulsion extended up to the second neighboring are represented by Hafemeister and Flygare (HF) type potential [21].

To understand the elastic properties of these monoselenides, we have calculated the second order elastic constants (SOEC), (C_{11} C_{12} and C_{44}) and their pressure derivatives. Since these elastic constants are functions of first and second order derivatives of short range potential, their calculations will provide knowledge about the effect of short range forces on these materials. Following the procedure adopted by Singh [17] and his coworker Sharma [22], we can obtain the expressions of the SOEC as:

$$C_{11} = e^2/4r_0^4[-5.112z\{z + 12f(r)\} + A_1 + (A_2 + B_2)/2] \tag{10}$$

$$C_{12} = e^2/4r_0^4[0.226z\{z + 12f(r)\} - B_1 + (A_2 - 5B_2)/4] \tag{11}$$

$$C_{44} = e^2/4r_0^4[2.556z\{z + 12f(r)\} + B_1 + (A_2 + 3B_2)/4)] \tag{12}$$

Where,

$$A_1 = 8r_0^3/e^2[(b/\rho^2)\exp(r_1 + r_2 - r)/\rho]_{r=r_0} \tag{13}$$

$$B_1 = 8r_0^2/e^2[(-b/\rho r)\exp(r_1 + r_2 - r)/\rho]_{r=r_0} \tag{14}$$

$$A_2 = 16r_0^3/e^2[(b/\rho^2)\{(1.5)e^{(2r_1-r/\rho)} + (0.5)e^{(2r_2-r)/\rho}\}]_{r=\sqrt{2}r_0} \tag{15}$$

$$B_2 = 16r_0^2/e^2[(-b/\rho r)\{(1.5)e^{(2r_1-r/\rho)} + (0.5)e^{(2r_2-r)/\rho}\}]_{r=\sqrt{2}r_0} \tag{16}$$

The first and second terms in Eqns. (10–12) are the contributions from the long-range Coulomb and TBP and the remaining contributions from the short-range overlap repulsion expressed as short range parameters (A_1,B_1) and (A_2,B_2) due to the closest neighbor (nn) and next closest neighbor (nnn) interactions. Their values are obtained from the expressions defined by Singh and coworkers [17, 22] which use the values of b and ρ and whose determination procedure is describe below. Here r_0 is the inter-ionic separation at zero pressure.

3 Results and discussion

The input data on crystal properties of REX (RE=Ce, Eu and La) compounds are presented in Table 1. The values of the model parameters, $[\rho, b, f(r)]$ namely the range, hardness and TBIP parameter are evaluated from the knowledge of r_0, the bulk modulus and the Cauchy discrepancy $(C_{12} - C_{44})/(C_{12} + C_{44})$ for the NaCl-stucture and applying equilibrium.

$$[dU/dr]_{r=ro} = 0 \qquad \text{and} \qquad [d^2U/dr^2] = 9kr_0B_T \tag{17}$$

Table 1 Input Crystal data and model parameters of CeSe, EuSe and LaSe.

Compounds	Input data				Model parameters			
	r_i(Å)	r_j (Å)	r_0 (Å)	B_T (GPa)	b (10^{-19}J)	ρ (Å)	$f(r)$	f_0
CeSe	0.91[a]	1.82[d]	2.995[a]	76[a]	200.4	0.24	0.167	43881
EuSe	0.95[b]	1.82[d]	3.092[b]	52.6[b]	1.32	0.48	−0.020	12.54
LaSe	1.04[c]	1.82[d]	2.925[c]	97.7[c]	28.5	0.52	0.004	1.16

[a] [6] [b] [10] [c] [13] [d] [25]

Using the above equilibrium, we have calculated the model parameters $[\rho, bf(r)]$ and are listing them in Table 1; we are also using them to compute the values of $G_{B_1(r)}$ and $G_{B_2(r')}$ at $T = 0$ K and using minimization technique at different pressures. We have plotted the Gibbs free energy differences $\Delta G = (G_{B_1} - G_{B_2})$ against pressure (P) for CeSe, EuSe and LaSe as shown in Fig. 2. As the pressure is increased, ΔG decreases and approaches zero. The corresponding pressure at which G approaches zero is the phase transition pressure (P_t). From Fig. 2, it is evident that the phase transition pressure for CeSe is 18 GPa, EuSe is 15 GPa and LaSe is 12 GPa respectively. We point out that from the TBP approach, the estimated value of P_t is in good agreement with other experimental and theoretical works listed in Table 2.

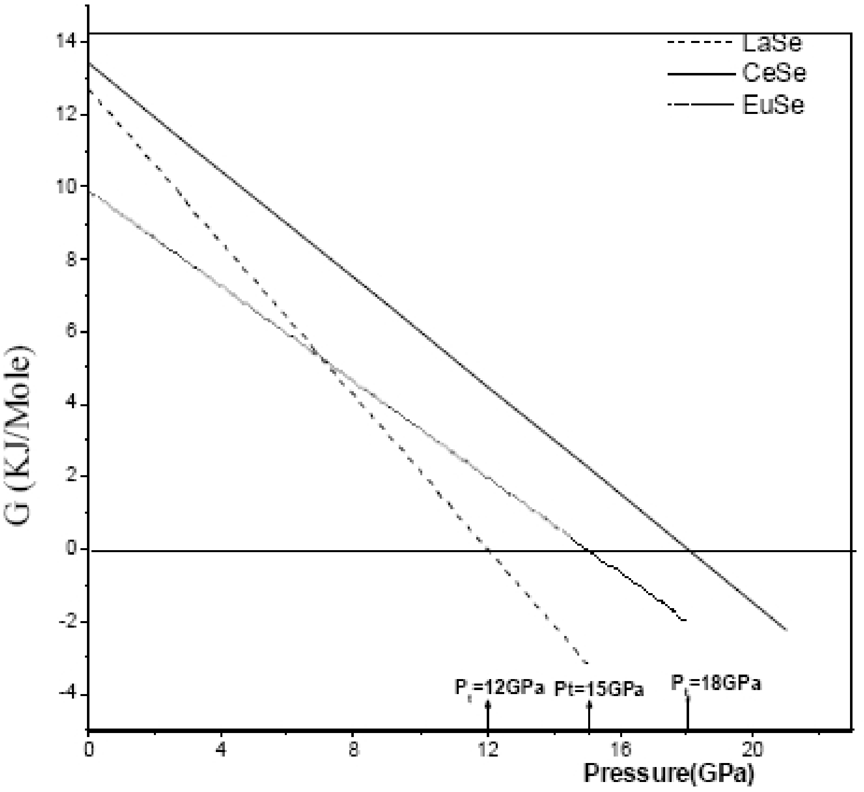

Fig. 2 Variation of Gibbs free energy differences ΔG (KJ/mol) against pressure P(GPa) for CeSe, EuSe and LaSe.

Table 2 Calculated transition pressures and volume collapses of CeSe, EuSe and LaSe.

Compounds	Transition	Transition Pressure(GPa)		Volume collapes	
		Theoretical	Exp. and others	Theoretical	Exp. and others
CeSe	$B_1 \rightarrow B_2$	18	$(20)^a$	8.9%	$(9)^a$ $(9)^b$
EuSe	$B_1 \rightarrow B_2$	16	$(14.5)^b$	14.1%	$(12.8)^c$
LaSe	$B_1 \rightarrow B_2$	12	$(12.7)^d$	8.8%	$(11)^d$ $(10.4)^e$

[a] [6] [b] [9] [c] [10] [d] [12] [e] [25]

Furthermore, we have estimated a relative volume change $[V(P)/V(0)]$ and have plotted it with various high pressures for CeSe, EuSe and LaSe depicted in Fig. 3. The magnitude of relative volume change at the transition pressure for CeSe, EuSe and LaSe lies at 8.9%, 14.1%, and 8.8% respectively. The second order elastic constants (SOEC) and their combination, $C_L = (C_{11} + C_{12} + 2C_{44})/2$ and $C_s = (C_{11} - C_{12})/2$ are calculated and listed in Table 3. We, noticed that C_L and C_s increased linearly with pressure as shown in Fig. 4. The present results are aligned with the first-order character of the transition for these compounds and they the above feature is similar to the earlier reported results for PbTe and SnTe [23].

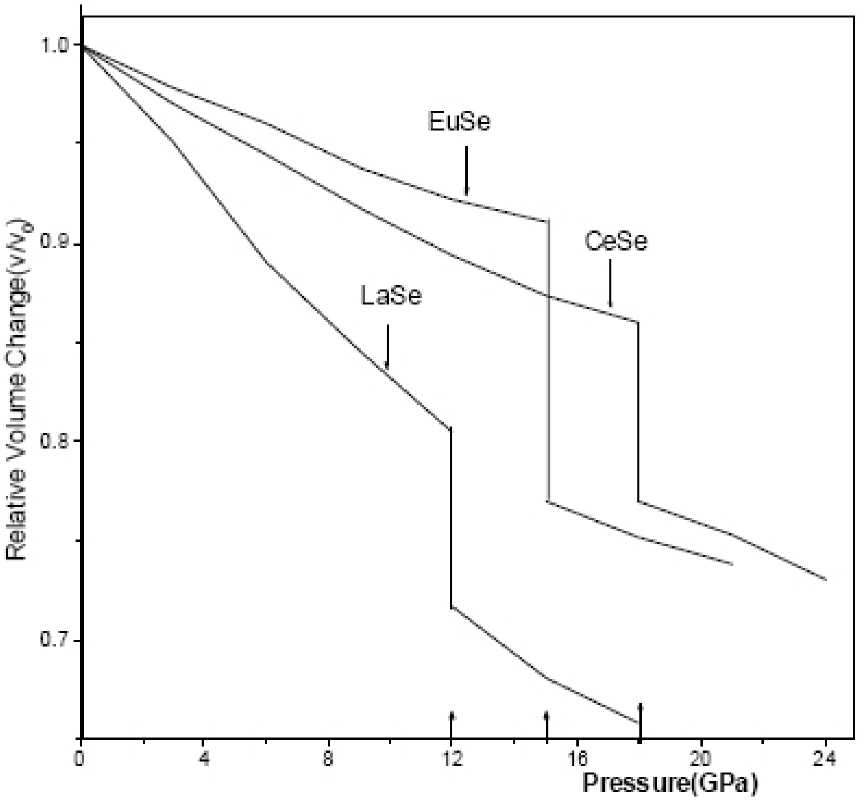

Fig. 3 Variation of relative volume change with pressure for CeSe, EuSe and LaSe.

Table 3 The calculated values of the elastic constants (10^{12} dyne/cm^{12}) of CeSe, EuSe and LaSe.

Compounds	C_{11}	C_{12}	C_{44}	$C_S = \frac{1}{2}(C_{11} - C_{12})$ $\times 10^{12}$ dyne/cm^2	$C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ $\times 10^{12}$ dyne/cm^2
CeSe	2.22	0.151	0.749	1.03	1.934
EuSe	0.805	0.297	0.356	0.204	0.857
LaSe	2.36	0.423	0.069	0.968	1.46

According to the Vukcevich [24], the stable phase of a crystal is one in which the shear elastic constant C_{44} is non-zero (for mechanical stability) and one of which has the lowest potential energy among the mechanically stable lattices. We have later on fol-lowed the Born criterion for a lattice to be mechanically stable which states that the elastic energy density must be a positive definite function of strain. This requires that the principal minors (the eigen values) of the elastic constant matrix should all be positive. Thus using the above stability, criterion for NaCl-stucture in terms of the elastic constants is as follows [17].

$$B_T = 1/3(C_{11} + 2C_{12}) > 0, C_{44} > 0 \qquad \text{and} \qquad C_S = (C_{11} - C_{12})/2 > 0 \tag{18}$$

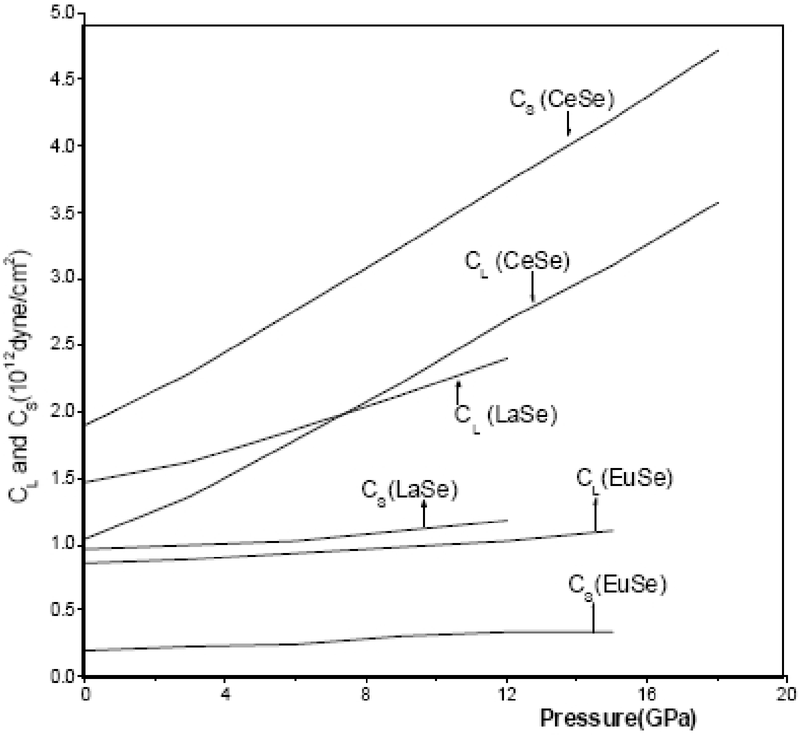

Fig. 4 Variation of combination of elastic constants for CeSe, EuSe and LaSe.

The C_{44} and C_S are the shear and tetragonal modulus of a cubic crystal. Also, the estimated shear moduli of these compounds are $C_{44} = (0.749) \times 10^{12}$ dynes/cm^2, $C_{44} = (0.356) \times 10^{12}$ dynes/cm^2 and $C_{44} = (0.069) \times 10^{12}$ dyne/cm^2 respectively and the tetragonal moduli for CeSe, EuSe and LaSe are $C_S = 1.03 \times 10^{12}$ dyne/cm^{12}, $C_S = 0.204 \times 10^{12}$ dyne/cm^{12} and $C_S = 0.968 \times 10^{12}$ dyne/cm^{12} respectively; these are well suited considering the above elastic stability criterion for REX compounds.

Finally, we may conclude that during the crystallographic transition from NaCl to CsCl, the volume discontinuity in the pressure-volume phase diagram, identifies the same trends as was exhibited by the experimental and other theoretical technique. We have also checked the stability criterion for these compounds in terms of the elastic constants. On the basis of an overall achievement, we may claim that the TBP approach is appropriately suitable for the description of the phase transition and elastic behavior under pressure in rare-earth monoselenides.

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