

Pressure-induced phase transition and stability of LuSb with NaCl-type structure

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ABSTRACT

We have predicted the phase transition pressure and corresponding relative volume change of LuSb having NaCl type structure under high pressure using three body interaction potential approaches (TBIPA). The potential model is consisting of long range columbic, three body interaction forces, short range overlap repulsive forces operative up to next neighbor ions and short-range van der Waals interaction with zero point energy effects. We have obtained phase transition and relative volume change, which are in close agreement with experimental approach. Thus TBIPA is promising with respect to the prediction of transition pressure and stability of rare earth compounds.

Key words: Rare earth, phase transition, three body interaction.

INTRODUCTION

The Rare Earth (RE) monochalcogenides are the most interesting ionic solids, which have attracted attention due to its magnetic and electrical properties, they generally crystallize in NaCl-structure¹. They show metallic nature when the rare earth ion is in trivalent state and semi-conducting in case of divalent state.

The high-pressure electronic and structural phase transition of cerium pnictides are discussed by Svane *et al.*². The electronic and structural phase transition of LnSb (Ln = Lu, Dy, Er and Tm) are studied by Shirotani *et al.*^{3,4}, up to 40 GPa, they show the typical NaCl-CsCl ($B_1 \rightarrow B_2$) structural phase transition at high pressure, though the same transition is not observed in the heavier LnP and LnAs.

A survey of the literature reveals that although a large amount of experimental work has

been done but very scant attention has been paid to their theoretical understanding. Recently Sims *et al.*⁵ have studied phase transition in alkali halides and rare earth monochalcogenides, they have emphasized that the inclusion of many three body interactions is necessary for the improvements of results at high pressure. Motivated from this remark⁵, we thought it pertinent to investigate phase transition pressure and associated volume collapse for LuSb using three body interaction potential approach (TBIPA)^{6,7} incorporated with van der Waals (vdW) attraction due to dipole-dipole and dipole-quadrupole interaction effects⁸ and zero points effects⁹ within Hafemeister and Flagare approach¹⁰. The inclusion of vdW interaction seems essential as their effects are considerably important as per as the prediction of the relative stability of crystal structure. Thus, TBIPA including vdW interaction and zero point effects have been found adequately suitable for the prediction of transition pressure and relative volume change in case of Lu-monopnictides.

In the present paper, we also make our objective to reveal the an harmonic properties of LuSb by computing the pressure derivatives of second order constants (SOEC) and third order elastic (TOEC)¹¹. Also continuation we explore our efforts to check the stability of LuSb by using Born-criterion.

Potential model and method of calculation

Application of pressure on crystals result in change in its volume which leads to an increased charge transfer (or three-body interaction effects) due to the deformation of the overlapping electron shells of the adjacent ions. The three-body interaction arises when during lattice vibrations electron shells of neighboring with other charges, many body interactions (MBI) take place, the dominant part of MBI is three-body interaction⁶. The modified Columbic interaction due to three-body interaction is

$$\Phi_m(r_o) = [-\alpha_m Z^2 e^2 / r_o] [1 + (2n/Z)f(r)] \dots(1)$$

where α_m is the modeling constant, which is 1.7476 (1.7629) for NaCl (CsCl) structure solids and r_o is the equilibrium nn ion separation, $f(r)$ is the TBI parameter, n is the number of nearest neighbors, thus Columbic energy gets modified because of the presence of three body interaction (TBI) and is dependent on the nearest neighbor as

$$F(r) = f_o \exp (-r/\rho) \dots(2)$$

Also we have considered Zero point energy effects, which is the lowest possible energy that the compounds may possess and is the ground state energy of the compounds. At absolute zero, the energy of the compounds is $(\epsilon = (h\nu)/e^{(h\nu)/kT} - 1 + (h\nu)/2)$.

These effects have been incorporated in the 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 in the vibrational entropy at temperature T . At $T=0$ K and pressure P , the Gibbs free energies for rocks salt (B_1 , real) and CsCl (B_2 , hypothetical) structure are given by.

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} \dots(3)$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2} \dots(4)$$

With $V_{B_1} (=2.00r^3)$ and $V_{B_2} (=1.54 r^3)$ as the unit cell volumes for B_1 and B_2 phase respectively. The first terms in the energies (3) and (4) are lattice energies for B_1 and B_2 structures and they are expressed as:

$$U_{B_1}(r) = [-\alpha_m Z^2 e^2 / r] - [(12\alpha_m Z^2 e^2 f(r)) / r] + 6b \beta_{ij} \exp [(r_i + r_j - r) / \rho] + 6b \beta_{ij} \exp [(2r_i - 1.4r) / \rho] + 6b \beta_{ij} \exp [2r_j - 1.14r) / \rho] + \{C_{ij} r^{-6} + D_{ij} r^{-8}\} + (0.5)h <\omega^2>_{B_1}^{1/2} \dots(5)$$

$$U_{B_2}(r') = [-\alpha'_m Z^2 e^2 / r'] - [(16\alpha'_m Z^2 e^2 f(r')) / r'] + 8b \beta_{ij} \exp [(r_i + r_j - r') / \rho] + 3b \beta_{ij} \exp [(2r_i - 1.154r') / \rho] + 3b \beta_{ij} \exp [2r_j - 1.154r') / \rho] + \{C_{ij} r'^{-6} + D_{ij} r'^{-8}\} + (0.5)h <\omega^2>_{B_2}^{1/2} \dots(6)$$

Here, C_{ij} and D_{ij} are the Vander walls coefficients, b_{ij} are the Pauling coefficients, $r_i(r_j)$ are the ionic radii of $I(i)$ and $<\omega^2>^{1/2}$ as the mean-square frequency related to the Debye temperature (Θ) as

$$<\omega^2>^{1/2} = k \Theta_D / h \dots(7)$$

With k as the boltzman constant. Here D can be expressed by well known formula (Blackmann1935) formula

$$\Theta_D = (h/k) \sqrt{(5r_o B_1) / \mu} \dots(8)$$

With B_1 and μ as the bulk modulus and reduced mass of the compounds. These lattice energies consist of long-range Coulomb energy (first terms in eqns-5 and 6), three body interaction corresponding to the nearest neighbor separation r (r') (second terms in eqns-5 and 6) and energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential (third, fourth and fifth term in eqns-5 and 6) extended up to the second neighbor ions, vdW interaction (sixth term) and zero point effects (seventh term) in eqns-5 and 6.

To understand elastic properties of Lush we have calculated second order elastic (SOEC), (C_{11} C_{12} & C_{44}) and their pressure at 0 K, since these elastic constants are functions of first and second order derivatives of short range potential, so their calculations will provide knowledge about the effect of short range forces on these materials following Singh and Sharma^{6,11} and subjecting the dynamical matrix to the long-wave length limit, we obtain.

$$C_{11} = e^2 / 4r_o^4 [-5.112Z \{z + 12f(r)\} + A_1 + (A_2 + B_2) / 2] \dots(9)$$

$$C_{12} = e^2/4r_0^4 [0.266z \{z+12f(r)\} - B_1 + (A_2 - 5B_2)/4] \quad \dots(10)$$

$$C_{44} = e^2/4r_0^4 [2.566z \{z+12f(r)\} + B_1 + (A_2 + 3B_2)/4] \quad \dots(11)$$

$$\text{With } A_1 = 8 r_0^3 / e^2 [(b/\rho^2) \exp (r_1 + r_2 - r)/\rho]_{r=r_0} \quad \dots(12)$$

$$B_1 = 8 r_0^2 / e^2 [(-b/\rho) \exp (r_1 + r_2 - r)/\rho]_{r=r_0} \quad \dots(13)$$

$$A_2 = 16 r_0^3 / e^2 [(b/\rho^2) \{(1.5) e^{(2r_1 - r)/\rho} + (0.5) e^{(2r_2 - r)/\rho}\}]_{r=\sqrt{2}r_0} \quad \dots(14)$$

$$B_2 = 16 r_0^2 / e^2 [(-b/\rho^2) \{(1.5) e^{(2r_1 - r)/\rho} + (0.5) e^{(2r_2 - r)/\rho}\}]_{r=\sqrt{2}r_0} \quad \dots(15)$$

In equation (7 to 9), first term show the long-range coulomb interaction. The symbol (A_1 , B_1) and (A_2 , B_2) are the short range parameters for the nearest (nn) and next nearest(nnn), and these expression are given in equations 10 to 13 taken form¹¹

Furthermore we have computed the third order elastic constants (TOEC), their relevant expression are given below

$$C_{111} = L[37.5626z\{z+12f(r)\}+C_1-3A_1 + (C_2-3A_2-9B_2)/4 - 89.30z \{a(df/dr)_0\} + 13.980z \{a^2 d^2 r/dr\}_0]-3p]$$

$$C_{112} = L[-4.835 z\{z+12f(r)\}+(C_2-3A_2+3B_2)/4 - 18.64z \{a(df/dr)_0\} + 4.6603z \{a^2 \{d^2 r/dr\}_0\}]$$

$$C_{123} = L[2.7172z\{z+12f(r)\}+16.69z\{a(df/dr)_0\}]$$

$$C_{144} = L[2.7172z\{z+12f(r)\}+5.564z\{a(df/dr)_0\}]$$

$$C_{166} = L[-7.165z\{z+12f(r)\} - 2(B_1 + B_2) (C_2-3A_2-3B_2/8) + 5.564 \{a(df/dr)_0\}]$$

$$C_{144} = L[1.5522\{z+12f(r)\} - (B_1 + B_2) - p]$$

The suffix at a parenthesis indicates values of the quantities calculated in the equilibrium

condition with $L = (e^2/4a^2)$ and $p = -L [1.165z \{z+12f(r)\} + (B_1+B_2)]$.

RESULTS AND DISCUSSION

The input crystal properties of LuSb are present in Table 1. The equilibrium lattice constants in this series however do not differ much though the bulk moduli vary significantly. In order to obtain their model parameters [r , b , $f(r)$] namely range, hardness are three body parameter of the inter-ionic potential which is described in the preceding section for NaCl (B_1) and CsCl (B_2) phase we have used the equilibrium condition.

$$[dU/dr]_{r=r_0} = 0 \text{ and } [d^2U / dr^2] = 9Kr_0B_r \quad \dots(22)$$

Using the above equilibrium condition we have calculated the model parameters [b , p , $f(r)$], which are listed in Table-1. Now concisely we make an attempt to obtain inter-ionic separation r and r' respectively for B_1 and B_2 phase by minimization technique for U_{B1} and U_{B2} at different pressures. Now we have evaluated the corresponding $G_{B1}(r)$ and $G_{B2}(r')$ and their respective differences ΔG . Then we have plotted ΔG against (P) for LuSb in Fig.1. As the pressure increases ΔG decreases and approaches to zero at the phase transition pressure (P_t). The corresponding pressures at which ΔG approaches zero is the phase transition pressure and results from experiments are listed in Table-2. From Fig.1- its is clear that the phase transition pressure for LuSb from TBIPA is 28Gpa.

Furthermore, we now estimate the relative volume change with various high pressures as shown in Fig.2. The magnitude of relative volume change at the transition pressure for LuSb is 2%, which is fairly in good agreement with those revealed from experimental approach⁴. The second order elastic constant (SOEC) and their combination, C_L

Table -1: Input Crystal data and model parameters

Compounds	Input parameters			Model parameters			
	$r_i(A^0)$	$r_j(A^0)$	$r_0(A^0)$	$B_T(GPa)$	$b(10^{-19}J)$	$\rho(A^0)$	$f(r)$
LuSb	0.848	2.45	3.02 ^a	53 ^a	23.31	0.65	0.0163

^a references [4]

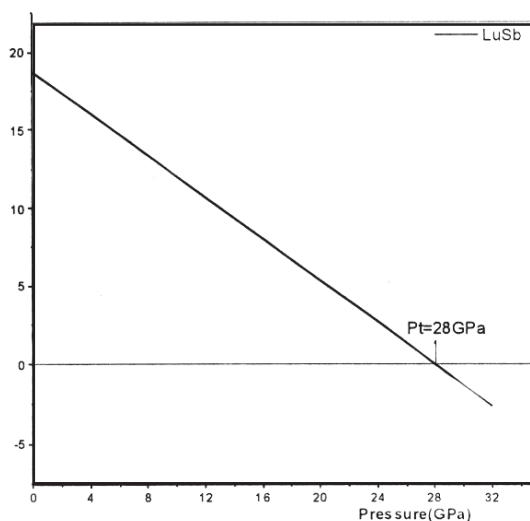


Fig. -1: Variation of Gibbs free energy differences ΔG (Kj/mol) against pressure for LuSb

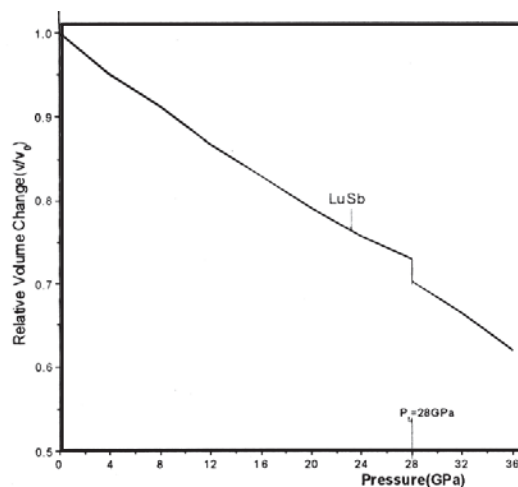


Fig. -2: Variation of relative volume change for LuSb with pressure

Table -2: Calculated transition pressure and volume collapses of LuSb
(The data given in parenthesis are experimental values)

Compounds	Transition	Trnsition Pressure (GPa)	Volume collapses
LuSb	$B_1 \rightarrow B_2$	28(33) ^a	2% (1%)

^areference [4]

Table -3: Calculated Elastic Constants and their combination of LuSb ($\times 10^{12}$ dyne/cm²)

Compounds	C_{11}	C_{12}	C_{44}	$C_S = \frac{1}{2} (C_{11} - C_{12})$ dyne/cm ²	$C_L = \frac{1}{2} (C_{11} + C_{12} + C_{44})$ dyne/cm ²
LuSb	0.895	0.28	0.92	0.35	0.68

Table -4: Calculated third order Elastic constants

Compounds	C_{111}	C_{112}	C_{123}	C_{144}	C_{456}	C_{166}
LuSb	-10.47	-3.94	0.168	0.205	-1.43	-0.027

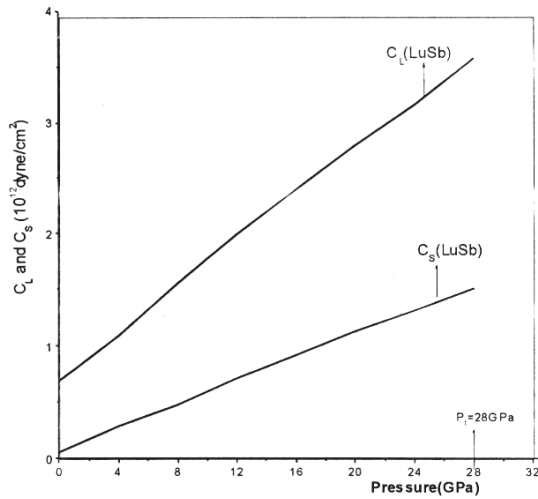


Fig. -3: Variation of C_L and C_S for LuSb with pressure

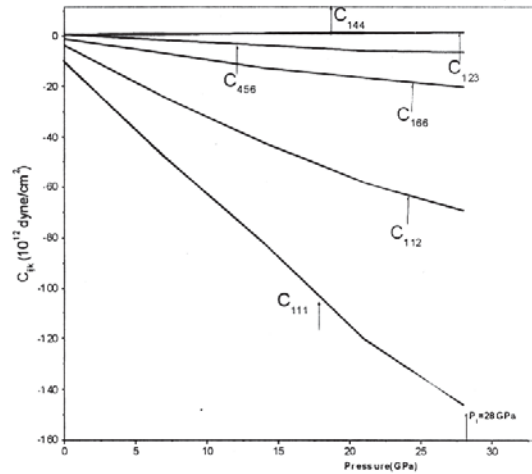


Fig. -4: Variation of third order elastic constants for LuSb with pressure

$= (C_{11} + C_{12} + 2C_{44})/2$ and $C_S = (C_{11} - C_{12})/2$ are calculated and are listed in Table 3. We note that C_L and C_S increase linearly with pressure and shows the same trends as PbTe and SnTe having ($B_1 \rightarrow B_2$) structural phase transition¹². Vukcevic¹³ also the high pressure stability criterion for ionic crystal, the stable phase of a crystal is one in which the shear elastic constant C_{44} is non-zero (for mechanical stability) and which has the lowest potential energy among the mechanically stable lattices. We then followed the criterion of Singh and Sharma^{6,11} for the stability of NaCl-type which include the stability criterion for such structure in terms of elastic constants as

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

The quantities C_{44} and C_S are the shear and tetragonal moduli of a Cubic crystal. Also estimated shear moduli of these compounds $C_{44} = (0.929) \times 10^{12}$ dynes/cm² and tetragonal moduli C_S

$= (0.305) \times 10^{12}$ dynes/cm² for LuSb which is well suited with the above elastic stability criterion for rare-earth monochalcogenides. Further TOEC with pressures as shown in Fig.-4. The values of C_{111} , C_{112} , C_{166} and C_{456} are negative and decreases with pressure and C_{144} , C_{123} are positive and increases with pressure. Experimentally studies on TOEC of the compound are yet not available, so comparability with experiments is not possible.

Moreover we conclude that during the crystallographic transition from NaCl to CsCl, the volume discontinuity in pressure-volume phase diagram identifies the same trends as the experimental approach, we also check the stability criterion for these compounds in terms of elastic constants. On the basis of above work, it is also concluded that the TBIPA approach including vdW interaction and zero point effects is more suitable for the prediction of $B_1 \rightarrow B_2$ phase transition pressures and associated volume collapses in Lu-monopnictides.

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