High pressure behaviour of heavy rare earth mono antimonides

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Abstract. We have investigated theoretically the high-pressure structural phase transition and cohesive properties of two heavy rare earth mono antimonides (RESb; RE = Dy and Lu) by using two body interionic potential with necessary modifications to include the effect of Coulomb screening by the delocalized 4f electrons of the RE ion. The peculiar properties of these compounds have been interpreted in terms of the hybridization of f electrons with the conduction band and strong mixing of f states of RE ion with the p orbital of neighboring pnictogen ion. These compounds exhibit first order crystallographic phase transition from their NaCl (B₁) phase to CsCl (B₂) phase at 23.6 GPa and 25.4 GPa respectively. The bulk modulii of RESb compounds are obtained from the P-V curve fitted by the Birch equation of state. We also calculated the RE-RE distance as a function of pressure. Elastic properties of these compounds have also been studied and their second order elastic constants are calculated.

1. Introduction
The rare earth compounds, which crystallize in the NaCl (B₁) structure, have been extensively studied in the last decades. These compounds display numerous polymorphic structure and properties, which can be interpreted in terms of mix valence or valence fluctuations that comes from partially filled f electron orbital of rare earth ion [1]. These partially filled f-electron shells of the lanthanide ions are highly delocalized and therefore interact strongly with the lattice. Such behaviour has been interpreted in terms of promotion of 4f electron of rare earth ion to the 5d conduction band and the mixing of f states with the p states of the neighbouring ion. So far as the structural properties are concerned, many theoretical [2, 3] as well as experimental [4] researches have been carried out. Several pnictides of lanthanide group, which crystallize in NaCl (B₁) crystal structure, have been investigated by using high-pressure X-ray diffraction technique [5] and reported to undergo either to CsCl (B₂) or body centered tetragonal (BCT) structure. The electronic structures of Ce and Nd mono pnictides (GdX, X= N, P, As, Sb, Bi) are known to exhibit unusual electric and magnetic [6, 7] phenomena. The high pressure form of lighter lanthanide antimonides (RESb, RE=La,Ce, Pr and Nd) is reported to be body centered tetragonal [8] whereas the structure of middle RESb (RE=Sm, Gd and Tb) is unknown. The heavier RESb (RE= Dy, Ho, Er, Tm and Lu) show B₁- B₂ phase transition [9].

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In the present paper we have investigated the high-pressure structural phase transition, cohesive and elastic properties of the two rare earth antimonides RESb (RE=Lu and Dy) and explain the salient features of the experimental observations reported by Shirotani et.al [4,9] from their high-pressure X-ray diffraction experiments. For this purpose we use an interionic potential model, proposed in our earlier papers [10], for the REY type mono pnictides. This potential includes the effect of f-electron screening on the Coulomb interactions between the ions, through a modified ionic charge parameter. We examine first the suitability of this potential to predict the NaCl to CsCl structure transformation in this group of RESb compounds. We also use this potential to calculate the phase transition pressures, relative volume changes, and variations of nearest and next nearest neighbour distances with pressure.

2. Method of calculation
The inter-ionic potential for RESb compounds in the framework of the rigid ion model are expressed as:

\[ U(r) = \sum_{ij} \frac{Z_{me}^2 e^2}{r_{ij}} + \sum_{ij} b_{ij} \exp \left[ \frac{r_i + r_j - r_{ij}}{\rho_{ij}} \right] + \sum_{ij} C_{ij} r_{ij}^{12} + \sum_{ij} D_{ij} r_{ij}^{8} \]  

(1)

which includes the long-range Coulomb interaction (first term), Hafemesiter and Flygare (HF) form of short range repulsive (second term) and van der Waals multipoles interactions (third and fourth terms). \( Z_{me} \) is the modified ionic charge and parametrically includes the effect of the Coulomb screening by the delocalized f-electrons. \( \beta_{ij} \) are the Pauling coefficients. \( b \) and \( p \) are short range parameters, which can be determined from the equilibrium condition. Thermodynamically, a phase transition is said to occur when change in the structural details of the phase are caused by variation of the free energy. The stability of a particular structure is decided by the minima of the Gibbs energy [10]. In our calculation, the lattice energies for \( B_1 \) and \( B_2 \) phases are uniquely defined in terms of the atomic co-ordination as:

\[ U_{B_1}(r) = -\alpha_{M} e^2 Z_{me}^2 \rho_{M} + 6\phi_{ij}(r) + 6\phi_{ij}(r) \]

(2)

\[ U_{B_2}(r) = -\alpha_{M} e^2 Z_{me}^2 \rho_{M} + 8\phi_{ij}(r) + 3\phi_{ij}(r) \]

(3)

Here \( r \) and \( r' \) are nearest neighbour (nn) separation corresponding to NaCl and CsCl structure, respectively \( \alpha_{M} \) and \( \alpha'_{M} \) are the Madelung constants for NaCl and CsCl structures, respectively. The short range potentials for both the phases between the ions are written as:

\[ \phi_{ij}(r) = b_{ij} \exp \left[ \frac{-r_{ij}}{\rho_{ij}} \right] - C_{ij} r_{ij}^{12} - D_{ij} r_{ij}^{8} \]  

(4)

3. Result and discussion
The required crystal properties and calculated model parameters for the interionic potential are given in table 1. The structural properties of RESb compounds have been investigated at high pressure using the methodology outlined above. We have predicted the structural stability by calculating the cohesive energy in NaCl and CsCl structures for both the compounds and found that the NaCl structure possesses minimum energy and thus most stable at ambient pressure. Under compression the interionic distance changes causing more and more overlapping of orbitals. The decreasing trend of \( Z_{me}^2 \) across the series from DySb to LuSb, is the direct consequence of delocalization of f electrons. The delocalization is usually accompanied by the first order phase transition, thus the structural phase transition properties are mainly governed by the change in the electronic structure of rare earth ion. The bulk modulii of DySb and LuSb have been evaluated by fitting the experimental curve data to the Birch’s equation of state [11]. A least square fit to the data gives the experimental bulk moduli of these compounds. The bulk moduli are presented in table 1.
The values of $B_0$ for LuSb and DySb have been used to calculate the model parameters. We have computed the structural phase transition pressure following the technique of minimization of Gibb’s free energies.

The equation of state for RESb compounds have been calculated up to various pressure ranges and plotted in figure 1 and compared with available experimental results [9, 4]. We report 23.6 and 25.4 GPa as phase transition pressure along with 6.8% and 6.2% volume collapse for DySb and LuSb respectively. The % volume collapse is reported to 3% [9] for DySb where as our calculated result for % volume collapse is 6.8%, which over estimates the measured ones. The experimental value of % volume collapse for LuSb is not available, so we could not compare our results with the experimental value. Nevertheless, our calculated phase transition pressures agree well with the experiments [9, 4].

Figure 2 shows the RE-RE and RE-Sb distance at high pressure. In figure 3(a), the Dy-Sb distance in NaCl structure is 3.08Å at ambient pressure. This distance is slightly shorter than the sum of atomic radius of Dy (1.77Å) and the covalent radius of Sb (1.38 Å), longer than the sum of covalent radii of Dy (1.59 Å) and Sb (1.38 Å). Thus the chemical bond between Dy and Sb atoms has the covalent character. At phase transition pressure the Dy-Dy distance suddenly decreases, where as the Dy-Sb distance increases and reaches to its ambient pressure value. These changes in the interionic distances may be due to the change in the coordination number at phase transition. The Dy-Sb distances in the CsCl type structure almost agree with the sum of the atomic radius of RE and covalent radius of Sb. The same analysis is done for LuSb. In the present work, the second order elastic constants have been calculated from the method outlined by Singh [12] by making use of model parameters for rare earth pnictides and presented in table 2. Since we use two-body interaction potential between the ions, the calculated values of $C_{12}$ and $C_{44}$ are equal.

### Table 1- Input crystal data and modal parameters for the RESb compounds.

| Solids | Input parameters | Output parameters |
|--------|------------------|-------------------|
|        | $r_0$ (Å)        | $B_0$ (GPa)       | $Z_m^2$ ($\times 10^{19}$) | $b$ (Å) | $\rho$ (Å) | Phase transition pressure (GPa) | Relative Volume change (%) |
| DySb   | 3.08$^a$         | 64.15$^a$        | 2.80                         | 5.139   | 0.278       | 23.6                        | 6.8                      |
| LuSb   | 3.02$^b$         | 53 ± 4$^b$       | 2.30                         | 3.826   | 0.276       | >22$^a$                     | 3.0$^a$                  |

$^a$Ref. [9]  
$^b$Ref. [4]

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The equation of state for RESb compounds have been calculated up to various pressure ranges and plotted in figure 1 and compared with available experimental results [9, 4]. We report 23.6 and 25.4 GPa as phase transition pressure along with 6.8% and 6.2% volume collapse for DySb and LuSb respectively. The % volume collapse is reported to 3% [9] for DySb where as our calculated result for % volume collapse is 6.8%, which over estimates the measured ones. The experimental value of % volume collapse for LuSb is not available, so we could not compare our results with the experimental value. Nevertheless, our calculated phase transition pressures agree well with the experiments [9, 4].

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Table 2 - Elastic constants and bulk moduli of RESb compounds.

| Solids | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{44}$ (GPa) | $B_0$ (GPa) |
|--------|----------------|----------------|----------------|-------------|
| DySb   | 141.74         | 25.86          | 26.22          | 64.49       |
| LuSb   | 122.77         | 23.14          | 23.34          | 56.35       |

$^a$Ref. [9]  
$^b$Ref. [4]

4. Conclusion
In conclusion we have presented the detailed structural and elastic properties of two heavy rare earth mono pnictides (LuSb and DySb) by using a two body potential model. Both the RESb are found to undergo a phase transition from their initial NaCl phase to CsCl phase. The calculated phase transition pressure and compression curve for both the compounds show a good agreement with the experiment. We have predicted the partially covalent nature of bonds in these compounds. The elastic constants of these compounds are calculated.

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