

Pressure-induced phase transition and stability of EuO and EuS with NaCl structure

ATUL GOUR^{1,*}, SADHNA SINGH¹, R K SINGH^{2,4} and M SINGH³

¹Physics Department, Barkatullah University, Hoshangabad Road, Bhopal 462 026, India

²Institute of Professional and Scientific Studies and Research, Chaudhary Devi Lal University, Sirsa 125 055, India

³Govt. SPSPG College, Bareth Road, Ganjbasoda, Vidhisa 464 221, India

⁴Present address: MATS University, MATS Tower, Pagariya Complex, Pandri, Raipur 492 002, India

*Corresponding author. E-mail: atul_gour@rediffmail.com

MS received 5 January 2008; revised 27 February 2008; accepted 12 March 2008

Abstract. We have predicted the phase transition pressures and corresponding relative volume changes of EuO and EuS having NaCl-type structure under high pressure using three-body interaction potential (TBIP) approach. In addition, the conditions for relative stability in terms of modified Born criterion has been checked. Our calculated results of phase transitions, volume collapses and elastic behaviour of these compounds are found to be close to the experimental results. This shows that the inclusion of three-body interaction effects makes the present model suitable for high pressure studies.

Keywords. High pressure; phase transition, three-body interaction.

PACS Nos 61.50.Ks; 61.50.Lt; 61.66.-f; 62.20; 64

1. Introduction

Most rare-earth monochalcogenides (REX, RE=Ce and Eu and X=O, Se, S, Te) show NaCl(B_1) to CsCl(B_2) structural phase transition and have attracted both experimental and theoretical workers. The presence of 4f-electron in these compounds is mainly responsible for these peculiar physical properties. They show metallic nature when the rare earth ion is in trivalent state and semi-conducting in case of divalent state [1]. Studies on pressure–volume relationship for divalent rare-earth chalcogenides have been extensively done by high-pressure X-ray diffraction technique. EuO shows an electronic transition at 30 GPa and then it shows a structural transition ($B_1 \rightarrow B_2$) at 40 GPa.

Also, EuS exhibits $B_1 \rightarrow B_2$ structural phase transition around 20 GPa [2]. Looking at the interesting properties of these compounds and the fact that no study has been done using three-body interaction [3], it is pertinent to apply three-body

interaction potential (TBIP) approach in these EuX compounds. The importance of three-body interactions in potential model to improve the results has also been emphasized by others like Sims *et al* [4].

2. Potential model and methods of calculations

It is well-known that the application of pressure on crystals results in change in its volume which leads to an increased charge transfer (or three-body interaction effects) due to deformation of the overlapping electron shells of the adjacent ions. This overlapping leads to the transfer of charge and this transferred charge interacts with charges, leading to many-body interactions (MBI). The dominant part of MBI is three-body interactions [3]. The TBI parameter $f(r)$ is dependent on the nearest-neighbour distance (r) as

$$f(r) = f_0 \exp(-r/\rho). \quad (1)$$

These effects have been incorporated in the Gibbs free energy ($G = U + PV - TS$) as a function of pressure (P). 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 energies for rock salt (B_1 , real) and CsCl (B_2 , hypothetical) structures are given by

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1}, \quad (2)$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2}, \quad (3)$$

where V_{B_1} ($=2.00r^3$) and V_{B_2} ($=1.54r^3$) are the unit cell volumes for B_1 and B_2 phases respectively. The first terms in the energies (2) and (3) are lattice energies for B_1 and B_2 structures and they are expressed as

$$\begin{aligned} U_{B_1}(r) = & [-(\alpha_m z^2 e^2)/r] - [(12\alpha_m z e^2 f(r))/r] \\ & + 6b\beta_{ij} \exp[(r_i + r_j - r)/\rho] \\ & + 6b\beta_{ii} \exp[(2r_i - 1.41r)/\rho] + 6b\beta_{jj} \exp[2r_j - 1.41r)/\rho] \\ & - \{(C_{ij}r^{-6} + D_{ij}r^{-8})\} + (0.5)h\langle\omega^2\rangle_{B_1}^{1/2}, \end{aligned} \quad (4)$$

$$\begin{aligned} U_{B_2}(r') = & [-(\alpha'_m z^2 e^2/r')] - [(16\alpha'_m z e^2 f(r'))/r'] \\ & + 8b\beta_{ij} \exp[(r_i + r_j - r')/\rho] \\ & + 3b\beta_{ii} \exp[(2r_i - 1.154r')/\rho] + 3b\beta_{jj} \exp[2r_j - 1.154r')/\rho] \\ & - \{(C'_{ij}r'^{-6} + D'_{ij}r'^{-8})\} + (0.5)h\langle\omega^2\rangle_{B_2}^{1/2}. \end{aligned} \quad (5)$$

Here, ze is the ionic charge, $r_i(r_j)$ is the ionic radii of $i(j)$ ions, ρ is the range parameter, b is the hardness parameter, C_{ij} and D_{ij} are the van der Waals coefficients from dipole-dipole and dipole-quadrupole interactions, $r(r')$ is the interionic separation for $B_1(B_2)$ phases β_{ij} is the Pauling coefficient.

The effective interionic potential described for NaCl [B_1] and CsCl [B_2] structures contain three model parameters ρ, b and $f(r)$, namely range, hardness parameter and three-body interaction parameter which is calculated by the equilibrium conditions $[d(U)/dr]_{r=r_0} = 0$ and $[d^2U/dr^2] = 9kr_0B_T$.

These lattice energies consist of long-range Coulomb energy (first term), three-body interactions [3] corresponding to the nearest-neighbour separation $r(r')$ for $B_1(B_2)$ phases (second term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential (i, j) ions (third term) and extended up to the second neighbour ions (fourth and fifth terms) [5], vdW interaction (sixth term) [6] and last term indicates zero point effect [7] term in eqs (4) and (5). Zero point energy effects have also been included in the interaction potential model which is the lowest possible energy that the compound may possess even at absolute zero temperature.

Now, in the last term $\langle\omega^2\rangle^{1/2}$ as the mean-square frequency is related to the Debye temperature (Θ_D) as

$$\langle\omega^2\rangle^{1/2} = k\Theta_D/h. \quad (6)$$

Here Θ_D can be expressed by the well-known Blackman's formula described in [7].

$$\Theta_D = (h/k)\sqrt{[(5r_0B_t)/\mu]}, \quad (7)$$

where B_t and μ are the bulk modulus and the reduced mass of the compounds respectively.

To understand elastic properties of these compounds, we have followed the expressions of Shanker *et al* [8] for calculating second-order elastic constants (SOEC), (C_{11}, C_{12} and C_{44}) and their pressure derivatives at 0 K. The expression for SOE constants are as follows:

$$C_{11} = e^2/4r_0^4[-5.112z\{z + 12f(r)\} + A_1 + (A_2 + B_2)/2 + 9.30z(rdf/dr)], \quad (8)$$

$$C_{12} = e^2/4r_0^4[1.391z\{z + 12f(r)\} + (A_2 - B_2)/4 + 9.30z(rdf/dr)], \quad (9)$$

$$C_{44} = e^2/4r_0^4[2.556z\{z + 12f(r)\} + B_1 + (A_2 + 3B_2)/4]. \quad (10)$$

In eqs (8)–(10), first term represents the long-range Coulomb interaction, second term represents the contribution due to TBIP and the remaining contributes overlap repulsion expressed in terms of the short-range parameters (A_1, B_1) and (A_2, B_2) for the nearest-neighbour (nn) and next nearest-neighbour (nnn) ions.

3. Results and discussion

We have followed the technique of minimization of $U_{B_1}(r)$ and $U_{B_2}(r')$ at different pressures in order to obtain the interionic separations r and r' corresponding to B_1

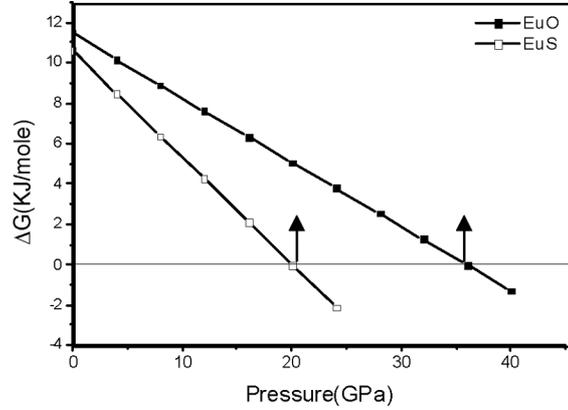


Figure 1. Variation of Gibbs free energy differences ΔG with pressure. The line with solid boxes and empty boxes indicate the Gibbs free energy differences for EuO and EuS.

Table 1. Ionic radii r_i , r_j , interionic separation r_0 and range ρ are given in (\AA).

Compounds	Input parameters				Model parameters		
	r_i	r_j	r_0	B_T (GPa)	b (10^{-19} J)	ρ	$f(r)$
EuO	1.17 ^b	1.41 ^b	2.57 ^a	113 ^a	2.47	0.4	-0.0165
EuS	1.17 ^b	1.82 ^b	2.985 ^b	61 ^b	1.75	0.46	-0.013

^aRef. [2], ^bref. [11].

and B_2 phases. Input and model parameters are well tabulated in table 1. Now $\Delta G = (G_{B_2}(r) - G_{B_1}(r'))$, are plotted against pressure (P) as shown in figure 1 for EuO and EuS. The phase transition pressure (P_t) is the pressure at which ΔG approaches zero. We have also computed the relative volume changes $V(P)/V(0)$ and plotted them against pressure as depicted in figures 2a,b for EuO and EuS. It is clear from figures 2a,b that phase transition $B_1 \rightarrow B_2$ occurs at about 36 GPa and 20 GPa for EuO and EuS respectively and the calculated volume collapses from TBIP model is 7.7% for EuO and 12.5% for EuS which are close to experimental values and shown in table 2. It is clear from table 3 that C_{11} and C_{12} increase with pressure while C_{44} decreases with pressure. As a result of this, C_L and C_S also increase with pressure.

Vukceвич [9] followed the Born high pressure stability criterion for ionic crystal according to which the stable phase of a crystal is one in which the shear elastic constant C_{44} is small and positive. Also, C_{44} decreases up to P_t but the phase transition to the B_2 structure takes place before C_{44} reaches zero. Demarest *et al* [10] proposed a slight modification of the above criterion that a phase transition takes place when the ratio C_{44}/B_T reaches a critical value between 0.14 and 0.2. From table 3 and figure 3, it is clear that we have obtained exactly the same trends as reported by Demarest *et al* [10].

Stability of EuO and EuS with NaCl structure

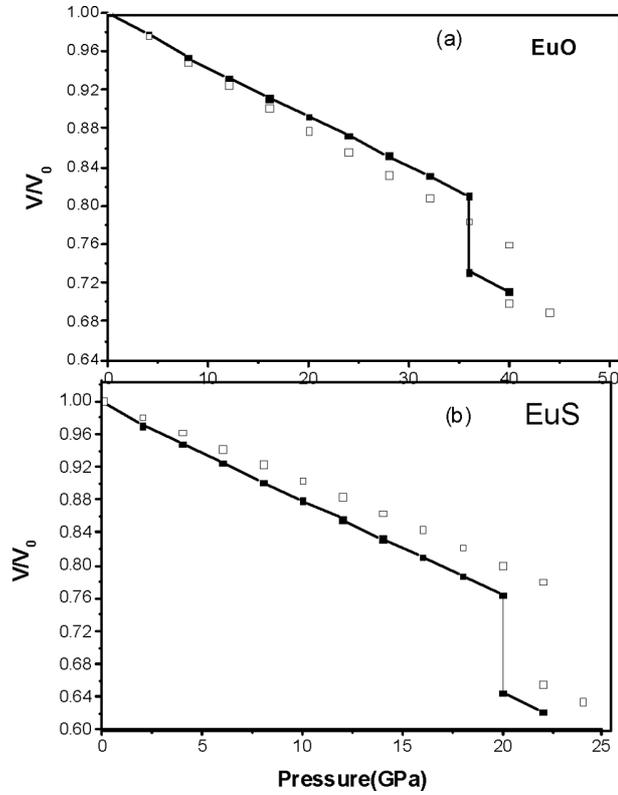


Figure 2. Relative volume change against pressure for (a) EuO and (b) EuS. The lines with solid boxes are the present values and the empty boxes are the experimental values [2].

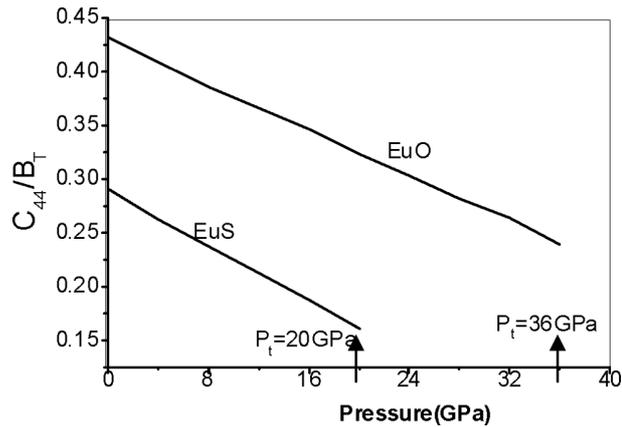


Figure 3. Variation of C_{44}/B_T with pressure up to phase transition pressure P_t .

Table 2. Calculated transition pressures and volume collapses.

Compounds	Transition	Transition pressure (GPa)		Volume collapses	
		Present	Exp.	Present	Exp.
EuO	$B_1 \rightarrow B_2$	36	(40) ^a	7.7%	(6.5%) ^a
EuS	$B_1 \rightarrow B_2$	20	(21.5) ^a	12%	(12.5%) ^a

^aRef. [2].**Table 3.** Calculated elastic constants and their combinations (GPa) at zero pressure and at phase transition pressure P_t .

Compounds	Pressure	C_{11}	C_{12}	C_{44}	C_{44}/B_T	$C_S = \frac{1}{2}(C_{11} - C_{12})$	$C_L = \frac{1}{2}(C_{11} + C_{12} + C_{44})$
EuO	0	251	55	52	0.433	98	205
	36	466	75	31.21	0.152	195	330.7
EuS	0	113.5	26	24	0.290	43	93.5
	20	253.8	52.6	21.65	0.181	100.6	153.2

On the basis of the above work, it is concluded that the TBIP approach is adequately suitable for the prediction of $B_1 \rightarrow B_2$ phase transition pressures, associated volume collapses and relative stability in RE-monochalcogenides.

References

- [1] F Hullinger, in: *Handbook of physics and chemistry of rare earths* edited by K A Gschneidner and L Eyring (North Holland Publ. Co., Amsterdam, 1979) vol. 4, p. 153
- [2] A Jayaraman, A K Singh, A Chatterjee and S Usha Devi, *Phys. Rev.* **B9**, 2513 (1974)
- [3] R K Singh, *Phys. Rep.* **85**, 259 (1982)
- [4] C E Sims, G D Barrera and N L Allan, *Phys. Rev.* **B57**, 11164 (1998)
- [5] W Hafemeister and W H Flygare, *J. Chem. Phys.* **43**, 795 (1965)
- [6] W Cochran, *Crit. Rev. Sol. St. Sci.* **2**, 1 (1971)
- [7] R K Singh, D K Neb and S P Sanyal, *J. Phys.* **C16**, 3409 (1983)
- [8] J Shanker, V C Jain and J P Singh, *Phys. Rev.* **B22**, 1083 (1980)
- [9] M R Vukcevic, *Phys. Stat. Sol. (b)* **54**, 435 (1972)
- [10] H Demarest, R Otto and O L Anderson, *High pressure research applications in geophysics* edited by M H Mangham and S I Akimoto (Academic Press, New York, 1977) pp. 281-301
- [11] R Lide, *CRC handbook of chemistry and physics*, 82nd ed (CRC Press, New York, 2002)