

## Study of Polarizability on EuO under High Pressure\*

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**Abstract:** We have investigated the pressure volume relationship, pressure induced structural phase transformation and elastic behaviour in Europium oxide (EuO) compound. We are using two different potential models (i) improved interaction potential model (IIPM) which includes Coulomb interaction, three body interaction, Polarizability effect and Overlap repulsive interactions. (ii) interaction potential model (IPM) which excluded Polarizability effect in the previous model. The EuO compound transformed from B1-B2 phase under pressure  $P_t = 40.5$  and equation of state shows volume collapse of 10.52%. The results are in good agreements with the available experimental data. The second order elastic constants and thermophysical properties like force constant, Debye temperature; Gruneisen parameter and ratio of thermal expansion to specific heat have also been computed at normal and high pressures.

**Keywords:** Rare earth compounds, Semiconductor, Phase transition, Elastic properties, Thermophysical properties, High pressure.

### 1. Introduction

The structural phase transition and elastic behaviour of rare earth chalcogenides such as EuO at high pressure have been investigated theoretically and experimentally in the last few decades because of their interesting optical, magnetic and electrical properties<sup>1-4</sup>. The study of europium oxide has received renewed attention because of their technological importance<sup>3-5</sup>. One obvious reason was the hope of using this magnetic semiconductor industrially, e.g. in the form of fast light beam addressable memory systems in computers, as magneto-optical modulator or as magnetic field activated electronic switches<sup>6</sup>. The various ways in which light interacts with matter (i.e. reflection, transmission, absorption, scattering, or emission) are of practical interest. The europium oxide is divalent compounds. It crystallizes in the face centred cubic NaCl structure

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to CsCl structural phase transition. The presence of 4f-electron in this compound is mainly responsible for these peculiar physical properties. Pressure induced phase transitions in EuO has also attracted the attention of many workers and hence a number of works has been reported on the pressure-volume relationship in this compound<sup>7-12</sup>. EuO shows an electronic transition at 30 GPa and then it shows a structural transition (B1-B2) at 40 GPa<sup>7</sup>.

In the present article, we have developed an improved interaction potential model (IIPM) and interaction potential model (IPM) which excluded Polarizability effect in the previous model to study the high pressure phase transition, elastic and thermo-physical properties of europium oxide.

## 2. Improved Interaction Potential Model

It is well known that pressure causes an increase in the overlap of adjacent ions in a crystal. Consequently, charge transfer<sup>13</sup> takes place between the overlapping electron shells. These transferred charges interact with all other charges of the lattice via Coulomb's law and gives rise to many body interactions, of which the most significant part is three body interaction (TBI)<sup>14</sup>. The increased effects of TBI, thus obtained, lead to an obvious necessity of their inclusion in the high pressure study of materials. A phase transition occurs when the solid becomes unstable under a given set of thermodynamic conditions. A phase of the solid is the most stable when its Gibbs free energy  $G(=U+PV-TS)$  is minimum. Here  $U$ , the internal energy at  $T=0K$ , corresponds to the cohesive energy due to mutual interaction of the ions;  $S$  is the vibrational entropy at absolute temperature  $T$ , and  $V$  is the unit Cell volume at pressure  $P$ . At  $T=0K$  the Gibbs free energies for rock salt (B1) and CsCl (B2) phases can be expressed as<sup>15</sup>

$$(2.1) \quad G_{BX}(r^X) = U_{BX}(r^X) + PV_{BX}(r^X),$$

$$(2.2) \quad U_{BX}(r) = \frac{-\alpha_M Z^2 e^2}{r^X} - \frac{12\alpha_M Z e^2 f_m(r)}{r^X} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^{X4}} + \\ 6b\beta_{ij} \exp[(r_i + r_j - r^X)/\rho] + 6b\beta_{ii} \exp[(2r_i - Y_X r^X)/\rho] \\ + 6b\beta_{jj} \exp[(2r_j - Y_X r^X)/\rho],$$

where  $X = 1, 2$  stand for Phase 1(B1) and Phase 2 (B2) and  $Y_X = 1.414, 1.154$ , for NaCl and CsCl structures respectively.

Here the first term is Coulomb energy, second term is three body interactions, third term is polarization energy, fourth term is overlap repulsive energy represent by Hafemeister and Flygare (Hf) type potential and extended up to the second neighbour ions.

### 3. Computational Method and Results

The input data and model parameters are given in Table 1. We have computed the phase transition pressure and associated volume collapses of europium oxide compound with IIPM which includes polarizability along with TBI. To further investigate the effect of polarizability we have computed phase transition pressure with using two models. Model I (without including polarizability) and Model II (with including polarizability). The results on phase transition and volume collapse are given in Table 2. The lattice energies  $U_{B1}(r)$  and  $U_{B2}(r')$  contain only three model parameters ( $b$ ,  $\rho$ ,  $f(r)$ ) hardness, range and three body parameter, which have been calculated by using input data given in Table 1 and have been computed from the knowledge of the bulk modulus and equilibrium conditions as described by earlier<sup>16</sup> using the self consistent method.

$$(3.1) \quad [dU(r)/dr]_{r=r_0} = 0,$$

$$(3.2) \quad B_r = \frac{e^2}{12r^4} [-4.66Z(Z + 12f(r)) + (A_1 + A_2) - 2(B_1 + B_2) + 27.9612Zrf'(r)].$$

As the stable phase is always associated with minimum of energy, we have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. We have minimized  $G_{B1}(r)$  and  $G_{B2}(r')$  given by Eqs.(2.1) at different pressures in order to obtain the interionic separations  $r$  and  $r'$  for B1 and B2 phases associated with minimum energies.  $\Delta G$  is very important factor in deciding phase transition pressure. We have plotted  $\Delta G$  against pressure to obtain the phase transition pressure ( $P_t$ ) at which  $\Delta G$  approaches zero. Here B1 and B2 are real and hypothetical phases before phase transition and B1 becomes hypothetical phase after phase transition while B2 becomes real. The phase transition pressures so obtained are presented in Table 2 and they are compared with the other's values. We have calculated the relative volumes ( $V(P) / V(0)$ ) and plotted them against pressures ( $P$ ) to obtain the equation of state for B1 and B2 phases. There is a sudden collapse in relative volume indicating the occurrence of first order phase transition.

## 4. Discussion

### 4.1 Phase transition Properties

As, the stable phase is associated with minimum free energy of the crystal, we have minimized the lattice energies in both the real and the hypothetical phases at ambient conditions corresponding to equilibrium interionic separation  $r$  ( $r'$ ) using the IIPM model parameters listed in Table 1. We have plotted the values of Gibbs free energy difference  $\Delta G$  against the pressure ( $P$ ) as shown in figs. 1 for EuO. The phase transition pressure ( $P_t$ ) is the pressure at which  $\Delta G$  approaches zero. At  $P_t$  these europium oxide undergo a (B1-B2) transition associated with a sudden collapse in volume showing a first order phase transition. The values of  $P_t$  computed by us are in good agreement with the experimental results<sup>7</sup> and better than those obtained by earlier workers<sup>11</sup>.  $\Delta G$  becomes negative beyond  $P_t$  predicting that at high pressure B2 phase is now thermodynamically and mechanically stable as compared to parent B1 phase.

We have also computed the relative volume changes  $V/V_0$  corresponding to the values of  $r$  and  $r'$  at different pressures and plotted them against the pressure in Figs. 2 for EuO. It is clear from Table 2 and Fig 2. That our calculated phase transition is 40.5 with volume collapses  $-\Delta V/V_0$  of 10.52 from our modified model I and for model II our calculated phase transition is 26.5 with volume collapses 12.48. Our computed values of  $P_t$  and volume collapse for Model I are in good agreement with the experimental results<sup>7</sup> and better than Gour et al<sup>11-13</sup>.

### 4.2 Elastic properties

To study the high pressure elastic behaviour of Europium oxide, we have calculated the value of second order elastic constants. It is clear that our calculated  $C_{11}$  are relatively large as compared to  $C_{12}$  and  $C_{44}$ . The elastic constant  $C_{11}$  represents elasticity in length. A longitudinal strain produces a change in  $C_{11}$ . The elastic constants  $C_{12}$  and  $C_{44}$  are related to the elasticity in shape, which is a shear constant. A transverse strain causes a change in shape without a change in volume.

### 4.3 Thermo physical properties

We have also computed the thermophysical properties of EuO compound, i.e., the ratio of thermal expansion coefficient to specific heat ( $\frac{\alpha_v}{C_v}$ ), Debye temperature ( $\theta_D$ ) and Gruneisen parameter ( $\gamma$ ) for this compound with the help of model parameters and the expressions reported

elsewhere<sup>17-18</sup>. These values are reported in Table 3 and can be compared with experimental result<sup>19</sup>.

Finally we can conclude that the improved interaction potential model I (IIPM) has yielded somewhat more realistic predictions of the phase transition and elastic behavior of europium oxide as compared to interaction potential model II (IPM).

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Table 1: Input data and model parameters

EuO (GPa)	Input parameters				model parameters		
	$r_j$ (Å)	$r_j$ (Å)	$r_0$ (Å)	$B_T$	$b$ ( $10^{-12}$ erg.)	$\rho$ (Å)	$f(r)$
Model I $113 \pm 5$ <sup>7</sup>	1.17	1.41	2.57		0.6214	0.240	-
Model II					0.0061		
					0.2764	0.240	-
					0.0099		

Table 2: Phase transition pressure (GPa) and volume collapse

EuO	Phase transition pressure		Volume collapse (%)	
	Model I II	Model II	Model I II	Model II
Present	40.5	26.5	10.52	12.48
Exp.	40 <sup>7</sup>		6.5	
Others	36 <sup>11</sup>		7.7	

Table 3: Second order elastic constants (GPa) and thermophysical properties

EuO	Present		Experimental	Others
	Model I II	Model II		
$C_{11}$	242.53	177.86	192.6 <sup>19</sup>	251 <sup>11</sup>
$C_{12}$	48.60	84.53	42.5 <sup>19</sup>	55 <sup>11</sup>
$C_{44}$	89.67		54.2 $\pm$ 13 <sup>19</sup>	52 <sup>11</sup>
$\alpha_v / C_v$ ( $10^{-3}$ )	77.53		-	-
$\theta_D$ (K)	0.508	1.015	350 <sup>20</sup>	348 <sup>19</sup>
$\gamma$	549.56			
	458.51			
	1.118	2.236	1.57 <sup>21</sup>	

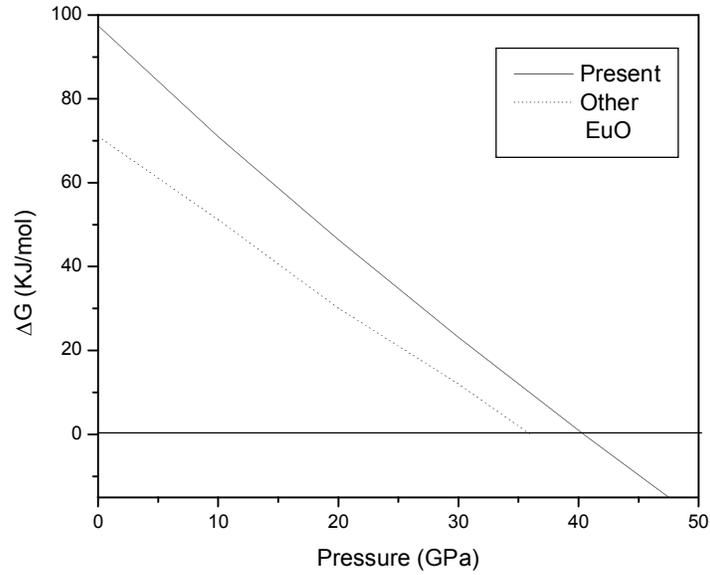


Fig 1. Variation of Gibbs free energy with pressure

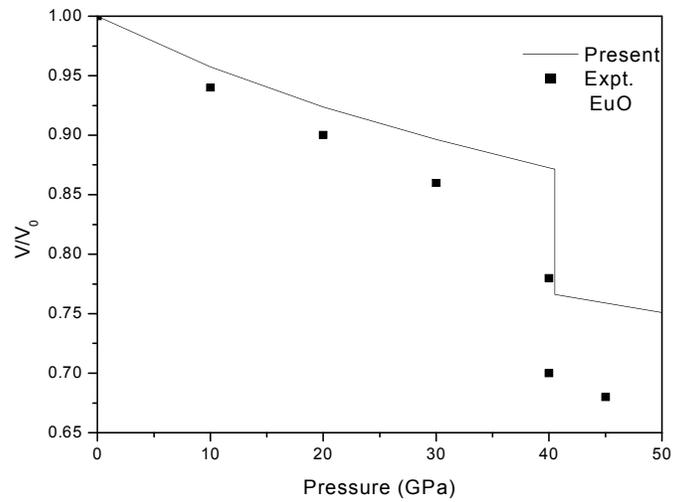


Fig 2. Variation of relative volume change with pressure

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