

# Structural Stabilities and Elastic Constants of EuX (X = O, S, Se, and Te) Compounds at High Pressure

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The structural stabilities, elastic properties and charge transfers of EuX (X = O, S, Se, Te) compounds as a function of pressure are investigated extensively using first-principles calculations. The ground-state parameters, such as lattice constants, bulk modulus are predicted and compared with the available data, our results are satisfactory. The calculated phase transition pressures from the NaCl-type (*B1*) structure to the CsCl-type (*B2*) structure for EuX (X = O, S, Se, Te) also accord with the experiments. Particularly, the elastic constants of EuX (X = O, S, Se, Te) under zero pressure and high pressure are simulated appropriately for the first time via density functional theory. The softening behaviors of the elastic shear modulus  $C_{44}$  under pressure for the *B1* phase of EuX (X = O, S, Se, Te) are captured, which should be responsible for the pressure-induced structural phase transition in the EuX system. It is also suggested that the softening behavior might be induced partly by the  $p \rightarrow d$  and  $f \rightarrow d$  electron transfers of Eu atom under pressure. In addition, the aggregate elastic modulus ( $B$ ,  $G$ ,  $E$ ), Poisson's ratio ( $\sigma$ ), Debye temperature  $\Theta_D$  are also successfully obtained for both *B1* and *B2* phases of EuX.

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## 1. Introduction

Europium monochalcogenides EuX (X = O, Se, S, Te) possess the striking diversities in the structural, electronic, optical and magnetic properties, they can be used as magneto-optical modulators or as magnetic field activated electronic switches [1] or as fast, light beam addressable memory systems in computers. These EuX compounds crystallize in cubic NaCl (*B1*)-type structures at ambient pressure and lattice parameter  $a$  increases when X varies from O to Te [2, 3]. With increasing pressure, they were found to undergo a structural transition from the NaCl (*B1*)-type structure to the CsCl- (*B2*) structure in experiments, but the transition pressure decreases when X varies from O to Te [3, 4]. Interestingly before the structure transition, these compounds are expected to undergo an insulator-metal transition accompanied by the valence change from 2+ state towards 3+ state; although the change was observed only in the case of EuO [5]. On the other hand, EuO and EuS are ferromagnetic; while EuSe has a complex magnetic structure at low temperatures, and EuTe is antiferromagnetic [6]. In term of these wide physical properties and the realistic or potential applications, it is not surprising that these europium monochalcogenides EuX (X = O, Se, S, Te) have drawn the renewed attentions both experimentally and theoretically in magnetism, high-pressure phase transition, electronic, optical and elastic properties [7].

We focus on the interesting theoretical works. In classical molecular-dynamics simulations, Islam and Shah-datullah [8] simulated the elastic, optical, vibrational and thermodynamic properties of EuO and EuS with the relatively simple interionic potential model in 1994. In 2008–2009, Gour et al. [9–11] investigated the pressure-induced phase transitions and elastic properties of EuX (X = O, S, Se, Te) using three-body interaction potential (TBIP) approach. In first-principles calculations, the electronic, elastic (EuS, EuSe and EuTe) and magnetic properties as well as pressure-induced phase transitions of EuX (X = O, S, Se, Te) were investigated in the recent years using the tight-binding linear muffin-tin orbital method within the local-density approximation (LDA) [12–14] and the full-potential linear muffin-tin orbital (FP-LMTO) method within the LDA scheme [15], also LDA+U and GGA+U schemes [7] as well as the full-potential linearized-augmented plane wave (FP-LAPW) scheme in the frame of the generalized gradient approximation (GGA) [16]. The obtained transition pressures from these different methods were similar and were in reasonable agreement with the experimental data [3, 4] except for one or two cases. But it is found that the obtained elastic constants from the different classical molecular-dynamics simulations [8–11] and the different first-principles calculations [12–17] were not in good consistence, some were not in agreement with the experimental results [3, 4]. Particularly and confusedly, the obtained elastic constants in 2007 with the FP-LMTO method in the LDA scheme [15] and in 2011 with the FP-LAPW scheme in the frame of the GGA [16] deviated from the experimental data [3, 4] far away; the recent An et al. [17] calculations for EuO and EuS using the

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projector augmented plane-wave (PAW) method also did not agree well with the experimental data [3, 4].

Thus the main aim of this paper is to explore the elastic properties of EuX (X = O, S, Se, Te) compounds under zero and high pressure to provide a comparative and complementary study via density functional theory. From the drawn elastic constants, we will analyze their mechanical stabilities and draw some important physical quantities, such as Poisson's ratio  $\sigma$ , Debye temperature  $\Theta_D$ , and so on. The structure phase transition and electron or charge transfers under high pressure for these compounds are also calculated and compared with the available data. The paper is organized as follows. In Sect. 2, we give the brief descriptions of theoretical methods. The results and discussions of these studies are presented in Sect. 3. A summary can be found in the last section.

## 2. Theoretical methods

We calculated the electronic structures of EuX (X = O, S, Se, Te) compounds using the plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) code [18], together with the generalized gradient approximation (GGA-PBE) [19] for the exchange-correlation function. The Kohn–Sham equation was solved by means of the ultrasoft pseudopotentials introduced by Vanderbilt [20]. Pseudoatomic calculations were performed for Eu  $4f^7 5s^2 5p^6 6s^2$ , O  $2s^2 2p^4$ , S  $3s^2 3p^4$ , Se  $4s^2 4p^4$  and Te  $5s^2 5p^4$ . A plane-wave basis set with energy cut-off 450 eV was applied. For the Brillouin zone sampling, we used  $10 \times 10 \times 10$  (110 *K*-points) and  $15 \times 15 \times 15$  (120 *K*-points) Monkhorst–Pack meshes for *B1* and *B2* structures, respectively. The self-consistent convergence of the total energy was  $10^{-6}$  eV/atom. A full optimization of the unit cell structure for each target external pressure was performed using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique [21].

The elastic constants of EuX were calculated via the static finite strain technique. The maximum strain amplitude was set from  $-0.003$  to  $0.003$  with the step of  $0.001$ , all forces on atoms were converged to less than  $0.006$  eV/Å for every case. These parameters can ensure that our calculations in the studied pressure range were converged. Once elastic constants are obtained, the average bulk modulus *B*, shear modulus *G*, and so on can be drawn from elastic constants [22].

## 3. Results and discussions

### 3.1. Structure and structure stability under zero and high pressure

The experimental data about the structures of EuX (X = O, S, Se, Te) [2, 23–27] were used as initial input. In our calculations, only spin polarized (ferromagnetic) case was considered since the previous theoretical works [12–14] have shown that the magnetic phase is obviously

more stable than the nonmagnetic phase in those compounds. We optimized the lattice geometry and ionic positions to get their fully stable geometry structures. No constraints were imposed; the ionic positions and lattice parameters were optimized simultaneously. Through the method, we can obtain the equilibrium lattice parameters and the corresponding primitive cell volume, equilibrium energy and enthalpy at arbitrary pressure for the *B1* or *B2* structural EuX. To get the zero pressure bulk modulus and its pressure derivative, we optimized the *B1* and *B2* geometry structures in the pressure range from  $-8$  GPa to  $50$  GPa. A series of equilibrium cell volumes (from  $1.3V_0$  to  $0.6V_0$ , where  $V_0$  is zero-pressure equilibrium primitive cell volume) and the corresponding equilibrium energy were drawn. Then, these *V*–*E* data were fit to the third-order Birch–Murnaghan equation of state (EOS) [28]:

$$P = \frac{3}{2}B_0 \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4}(B'_0 - 4) \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}, \quad (1)$$

where  $B_0$  is the zero pressure bulk modulus, and  $B'_0$  is the first derivative of the bulk modulus; they can be obtained from the fitting.

The obtained structural parameters, zero pressure bulk modulus and its pressure derivative, magnetic moments are presented in Table I, together with the available experimental and other theoretical data. It is seen that the lattice constants *a* for the *B1* and *B2* structures are in good agreement with the experimental data [2, 23–26]; furthermore the presented results are apparently closer to the experimental data than other theoretical results [12–16]. The calculated magnetic moments are also consistent with the available data. The obtained bulk modulus for the *B1* phase are a little underestimated. When X varies from O to Te, the bulk modulus of EuX in the *B1* structure decreases while the magnetic moment keeps almost constant. The bulk modulus for the *B2* phase is slightly bigger than that of the *B1* phase, and also decreases when X varies from O to Te. In contrast to the current results, Singh et al. [12–14] obtained a much larger bulk modulus for the *B2* phase using the FP-LMTO method within the LDA scheme; furthermore, their data showed that the bulk modulus of the *B2* phase keeps almost constant when X varies from O to Te. So Singh et al. may have some problems for their estimations in the bulk modulus of the *B2* phase. For the magnetic moments in the *B1* and *B2* phases, the current calculations show they are almost equal, as is consistent with the results of Singh et al. [12–14].

The structural phase stability is determined by the calculation of the Gibbs free energy (*G*) [29] for the two phases, given by  $G = E_{\text{tot}} + PV - TS$ . Since the theoretical calculations are performed at 0 K, the Gibbs free energy becomes equal to the enthalpy,  $H = E_{\text{tot}} + PV$ . For a given pressure, a stable structure is one for which

the enthalpy has its lowest value. In our cases, as shown in Figs. 1–4, before transition pressure ( $P_t$ ) the  $B1$  phase has lower enthalpy and hence a stable structure for every  $\text{EuX}$ , which is consistent with the experiments [3, 4]; but after the transition pressure, the enthalpy of the  $B2$  phase becomes lower and hence the  $B2$  phase becomes the stable phase. At the transition pressure, the en-

thalpies for the two structures are equal. The calculated transition pressures from  $B1$  to  $B2$  are about 49, 22, 18, 13.5 GPa for  $\text{EuO}$ ,  $\text{EuS}$ ,  $\text{EuSe}$ ,  $\text{EuTe}$ , respectively. These transition pressures as well as the corresponding changes of volume collapses at transition points are in reasonable agreement with the experimental data and other theoretical results shown in Table II.

TABLE I

Lattice constants  $a$  [Å], magnet moments [ $\mu_B$ ] in per formula unit, bulk modulus [GPa] and its pressure derivative for  $\text{EuX}$  ( $X = \text{O}, \text{S}, \text{Se}, \text{Te}$ ) at 0 GPa and 0 K.

				$a$	$B$	$B'$	$\mu$
EuO	$B1$	theory	present	3.63	–	–	6.96
		exp.	others	3.635 <sup>[23]</sup>	95 <sup>[7]</sup> 118 <sup>[4]</sup> , 91 <sup>[26]</sup>	3.33 <sup>[7]</sup> 2.2 <sup>[4]</sup>	
EuS	$B1$	theory	present	3.118	–	–	7.12
		theory	present	4.226	47	4.19	7.00
			others	4.034 <sup>[13]</sup> , 3.945 <sup>[15]</sup> , 3.87 <sup>[16]</sup>	57 <sup>[7]</sup> , 68 <sup>[13]</sup> , 77 <sup>[15]</sup> , 87 <sup>[16]</sup>	2.7 <sup>[7]</sup> , 3.79 <sup>[15]</sup> , 3.9 <sup>[16]</sup>	6.96 <sup>[13]</sup>
		exp.		4.213 <sup>[24]</sup>	61 ± 5 <sup>[3]</sup>		
EuSe	$B2$	theory	present	3.626	53	4.19	7.13
		theory	present	3.38 <sup>[15]</sup> , 3.36 <sup>[16]</sup>	101.19 <sup>[13]</sup> , 71.19 <sup>[15]</sup> , 86.3 <sup>[16]</sup>	4.55 <sup>[15]</sup> , 3.77 <sup>[16]</sup>	6.99 <sup>[13]</sup>
		others		4.364	41.5	4.089	7.00
		theory	present	4.232 <sup>[12]</sup> , 4.115 <sup>[15]</sup> , 4.04 <sup>[16]</sup>	51 <sup>[7]</sup> , 52 <sup>[12]</sup> , 66 <sup>[15]</sup> , 73.4 <sup>[16]</sup>	2.6 <sup>[7]</sup> , 3.96 <sup>[15]</sup> , 4.6 <sup>[16]</sup>	6.95 <sup>[12]</sup>
		exp.		4.368 <sup>[25]</sup>	52 ± 5 <sup>[26]</sup>		
EuTe	$B2$	theory	present	3.75	45.28	4.375	7.02
		theory	present	3.54 <sup>[15]</sup> , 3.52 <sup>[16]</sup>	101.73 <sup>[12]</sup> , 59.71 <sup>[15]</sup> , 75.2 <sup>[16]</sup>	4.51 <sup>[15]</sup> , 4.56 <sup>[16]</sup>	6.98 <sup>[12]</sup>
		others		4.684	32.5	4.091	7.000
		theory	present	4.529 <sup>[14]</sup> , 4.341 <sup>[1]</sup>	38 <sup>[7]</sup> , 42.1 <sup>[14]</sup> , 53.4 <sup>[16]</sup>	2.6 <sup>[7]</sup> , 4.1 <sup>[16]</sup>	6.99 <sup>[14]</sup>
		exp.		4.661 <sup>[2]</sup>	40 ± 5 <sup>[3]</sup>		
		theory	present	4.042	36.5	3.837	7.06
		others		3.76 <sup>[16]</sup>	101.7 <sup>[14]</sup> , 53.6 <sup>[16]</sup>	4.06 <sup>[16]</sup>	6.99 <sup>[14]</sup>

<sup>[7]</sup> Using FP-LMTO within GGA+U scheme. <sup>[12–14]</sup> Using the tight-binding LMTO (TB-LMTO) method within the LDA.

<sup>[15]</sup> Using FP-LMTO within LDA scheme. <sup>[16]</sup> Using the FP-LAPW scheme in the frame of the GGA.

TABLE II

Transition pressure  $P_t$  [GPa] and the corresponding volume collapses at 0 K for  $\text{EuX}$  ( $X = \text{O}, \text{S}, \text{Se}, \text{Te}$ ).

EuX	Transition pressure $P_t$				Volume collapses [%]			
		theory		exp.	theory			exp.
		present	others		present	others		
EuO	$B1 \rightarrow B2$	49	44 <sup>[7]</sup> , 36 <sup>[9]</sup> ,	47 <sup>[4]</sup>	8.9	7.7 <sup>[9]</sup>		6.5 <sup>[3]</sup>
EuS	$B1 \rightarrow B2$	22	20 <sup>[7]</sup> , 21 <sup>[13]</sup> , 27 <sup>[15]</sup> , 48.6 <sup>[16]</sup> , 20 <sup>[11]</sup>	22 <sup>[3]</sup>	8.7	14.5 <sup>[13]</sup> , 11.2 <sup>[15]</sup> , 6.6 <sup>[16]</sup> , 12 <sup>[11]</sup>		12.5 <sup>[3]</sup>
EuSe	$B1 \rightarrow B2$	18	14 <sup>[7]</sup> , 9.5 <sup>[12]</sup> , 24 <sup>[15]</sup> , 8.9 <sup>[16]</sup> , 15 <sup>[11]</sup>	15 <sup>[3]</sup>	8.4	10.5 <sup>[15]</sup> , 6.1 <sup>[16]</sup> , 9.5 <sup>[11]</sup>		12.8 <sup>[3]</sup>
EuTe	$B1 \rightarrow B2$	13.5	12 <sup>[7]</sup> , 9.9 <sup>[14]</sup> , 17.4 <sup>[16]</sup> , 10.5 <sup>[10]</sup>	11 <sup>[3]</sup>	7.9	8.23 <sup>[14]</sup> , 7.7 <sup>[16]</sup> , 8.8 <sup>[10]</sup>		11.6 <sup>[2]</sup>

<sup>[7]</sup> Using FP-LMTO within GGA+U scheme. <sup>[12–14]</sup> Using the TB-LMTO method within the LDA. <sup>[15]</sup> Using FP-LMTO within LDA scheme. <sup>[16]</sup> Using the FP-LAPW scheme in the frame of the GGA. <sup>[9–11]</sup> Using the classical molecular-dynamics simulations with TBIP approach.

### 3.2. Elastic properties

Elastic constant may be the most important mechanical quantity in that the elastic constants of a solid re-

late to various fundamental solid state properties such as interatomic potentials, equation of state, phonon spectra [30]. Most importantly, knowledge of elastic stiffness

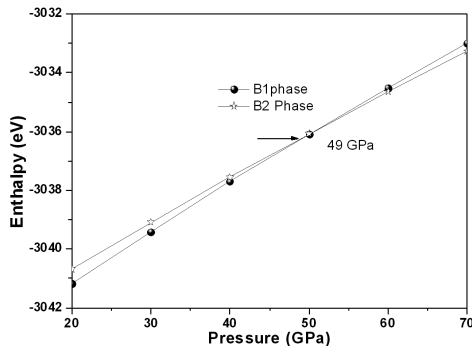


Fig. 1. Enthalpy as a function of pressure for the *B1* and *B2* structural EuO at 0 K.

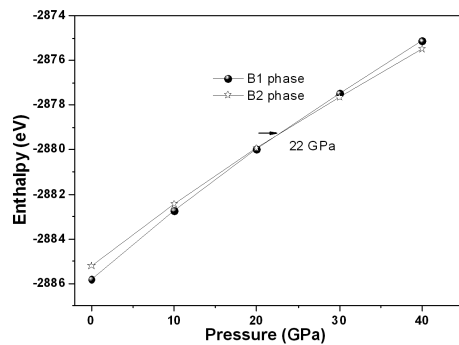


Fig. 2. Enthalpy as a function of pressure for the *B1* and *B2* structural EuS at 0 K.

coefficients is essential for many practical applications related to the mechanical properties of a solid. Elastic properties are also linked thermodynamically to the specific heat, thermal expansion, the Debye temperature, melting point, and the Grüneisen parameter. But the different theoretical methods presented the apparent different results for these EuX compounds mentioned in the above introduction part, and the different experiments also reported the different results (for EuS [31, 32]). Thus it is necessary to provide a comparison and reference for the elastic constants of these compounds.

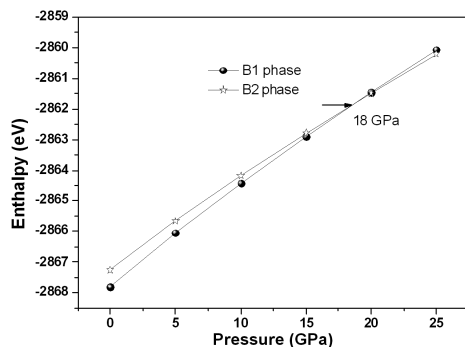


Fig. 3. Enthalpy as a function of pressure for the *B1* and *B2* structural EuSe at 0 K.

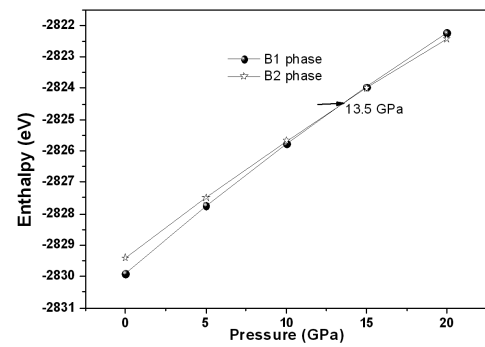


Fig. 4. Enthalpy as a function of pressure for the *B1* and *B2* structural EuTe at 0 K.

The simulated elastic constants with CASTEP-GGA at zero pressure and high pressure for *B1* phase are listed in Table III (EuO and EuS) and Table IV (EuSe and EuTe) together with the available data [8–11, 15, 16, 31–34]. The obtained elastic constants at zero pressure and zero temperature for every EuX compound are in good agreement with the experimental data. Some small discrepancies may be the fact that the theoretical calculations were done at 0 K whereas the experimental results were obtained at room temperature. For the other theoretical results, both Rached et al. [15] and the recent Charifi et al. [16] calculations with first-principles deviated from the experimental data far away and An et al. [17] calculations for EuO and EuS also did not agree well with the experimental data.

Some results of molecular-dynamics simulations also deviated from obviously the experimental data. For example, Gour et al. [9–11] overestimated  $C_{11}$  (EuO) about 46%, and underestimated  $C_{11}$  (EuTe) and  $C_{44}$  (EuTe) about 32% and 57%, respectively. Generally our results are closer to the experimental values when the present results are compared with those of the classical molecular-dynamics simulations [9–11].

With increasing pressure,  $C_{11}$  and  $C_{12}$  for EuO, EuS, EuSe present almost linear increase, while  $C_{44}$  presents linear decrease. The change ratio  $dC_{ij}/dP$  is basically consistent with that of Islam and Shahdatullah [8]. For EuS, the theoretical results are not in good agreement with the experimental data [32], especially for  $C_{44}$ . However, all theoretical calculations [8–11] showed that  $C_{44}$  decreases with increasing pressure for the *B1* phase of EuX ( $X = O, S, Se$ ), but Benbattouche et al. experiment [32] showed the contrary changing tendency for  $C_{44}$  (EuS). So the more experimental works under pressure are needed. For EuTe, the pressure dependences of  $C_{12}$  and  $C_{44}$  present irregular tendencies in our calculation. One possible reason was the approximation of magnetism; EuTe is antiferromagnetic, but the simulation was carried out in the case of ferromagnetic structure like in some other simulations [12–14].

Elastic constants [GPa] of *B1* structural EuO and EuS under pressure [GPa] as well as the pressure derivative of elastic constants at 0 K.

TABLE III

$P$	EuO	$C_{11}$	$C_{12}$	$C_{44}$	$P$	EuS	$C_{11}$	$C_{12}$	$C_{44}$
0	present	177	43	54	0	present	118	13	26
	MD <sup>[8]</sup>	192	49	54		FP-LMTO (LDA) <sup>[15]</sup>	211	10.5	174
	MD <sup>[9]</sup>	251	55	52		FP-LAPW (GGA) <sup>[16]</sup>	227	16	31.8
	VASP-PAW (GGA) <sup>[17]</sup>	189	62	78		VASP-PAW (GGA) <sup>[17]</sup>	147	24	39
						MD <sup>[8]</sup>	117	17	26
						MD <sup>[9]</sup>	113	26	24
						MD <sup>[10]</sup>	113	26	11
10	exp. <sup>[31]</sup>	192	42	54	10	exp. <sup>[31]</sup>	115	36	26
						exp. <sup>[32]</sup>	131	11	27
							220	20	25
							301	23	20
							405	31	19
							486	36	15
							568	45	11
20		376	74	51	20		301	23	20
30		458	87	48	30		405	31	19
40		542	103	44	40		486	36	15
50		695	120	39	50		568	45	11
60		694	128	35	60		673	74	8
$dC_{ij}/dp$	present	8.62	1.41	-0.31	$dC_{ij}/dp$	present	9	0.64	-0.3
	others <sup>[8]</sup>	8.94	1.45	-0.55		others <sup>[8]</sup>	10	1.5	-0.54
						exp. <sup>[31]</sup>	10.3	4.2	0.22

TABLE IV

Elastic constants [GPa] of *B1* structural EuSe and EuTe under pressure as well as the pressure derivative of elastic constants at 0 K.

$P$ [GPa]	EuSe	$C_{11}$	$C_{12}$	$C_{44}$	$P$ [GPa]	EuTe	$C_{11}$	$C_{12}$	$C_{44}$	
0	present	110	14	24	0	present	94	14	18	
	FP-LMTO (LDA) <sup>[15]</sup>	185	7	183						
	FP-LAPW (GGA) <sup>[16]</sup>	213	3.6	30		FP-LAPW (GGA) <sup>[16]</sup>	163.5	-1.6	8.8	
	MD <sup>[11]</sup>	118	27	18		MD <sup>[10]</sup>	64	23	7	
	MD <sup>[33]</sup>	166	24	27		MD <sup>[33]</sup>	104	10.4	18.7	
	exp. <sup>[34]</sup>	116	12	23		exp. <sup>[34]</sup>	93.6	7	16	
5		153	10	18	5		142	12	17	
10		214	19	23	10		167	7	9	
15		261	22	22	15		238	12	11	
20		301	23	20	20		291	19	13	
25		347	26	18	25		320	15	6	
30		407	37	16	30		350	15	0.8	
$dC_{ij}/dp$	present	2.7	1.64	-0.33						

The calculated average bulk modulus  $B$ , shear modulus  $G$ , the Debye temperature  $\Theta_D$ , Young's modulus  $E$ , and Poisson's ratio  $\sigma$  at zero pressure and high pressure for the *B1* structural EuX ( $X = O, S, Se, Te$ ) are listed in Table V. The obtained zero-pressure bulk modulus for these compounds accord with the experimental data shown in Table I, this lends another support in the validity of the current elastic constant calculations. The

Debye temperature  $\Theta_D$  for EuO and EuS at 0 K and 0 GPa are also in good consistency with the theoretical data of Islam and Shahdatullah [8] and the data from the measurement of heat capacity [31]. So the Debye temperature  $\Theta_D$  for EuSe and EuTe should be predicted appropriately, while Charifi et al. [16] apparently overestimated the Debye temperature of EuX ( $X = S, Se, Te$ ).

TABLE V

Bulk modulus  $B$  [GPa], shear modulus  $G$  [GPa], Young's modulus  $E$  [GPa], the Poisson ratio  $\sigma$  and Debye temperature  $\Theta_D$  [K], of  $B1$  structural EuX ( $X = O, S, Se, Te$ ) under pressure  $P$  (GPa) at 0 K.

	$P$ [GPa]		$B$	$G$	$E$	$\sigma$	$\Theta_D$
EuO	0	present	87	59	144	0.225	343
		others					348 <sup>[8]</sup> , 353 <sup>[31]</sup>
EuS	50	present	311	99	268	0.356	432
	0	present	48	36	83	0.209	270
EuSe	20	others					265 <sup>[8]</sup> , 262 <sup>[31]</sup>
		Charifi et al. <sup>[16]</sup>	87	61.3	148.8	0.21	371
	present	123	53	140	0.309	328	
	0	present	46	31	77	0.219	235
EuTe	20	Charifi et al. <sup>[16]</sup>	73	60	141	0.18	335
		present	115	49	128	0.314	282
	0	present	40	24	62	0.245	197
	15	Charifi et al. <sup>[16]</sup>	53	38.3	92.7	0.21	252
		present	87	34	91	0.32	224

TABLE VI

Elastic constants [GPa], bulk modulus  $B$  [GPa], shear modulus  $G$  [GPa], Young's modulus  $E$  [GPa], the Poisson's ratio  $\sigma$  and the Debye temperature  $\Theta_D$  [K], of  $B2$  structural EuX ( $X = O, S, Se, Te$ ) at 0 GPa and 0 K.

		$C_{11}$	$C_{12}$	$C_{44}$	$B$	$G$	$E$	$\sigma$	$\Theta_D$
EuO	present	272	4.7	-3	94	23	64	0.38	216
EuS	present	145	5.4	5.5	52	20	53	0.33	204
	Charifi et al. <sup>[16]</sup>	142	57.2	-38.5	86	-6.2	-18.9	0.54	0.0068
EuSe	present	136	7.7	7	50	21	53.8	0.32	187
	Charifi et al. <sup>[16]</sup>	143.6	41	-3.3	74	18.5	51.4	0.39	292
EuTe	present	98	8	6	38	15	40	0.32	153
	Charifi et al. <sup>[16]</sup>	115	22.3	11.9	52	25	66.6	0.29	324

TABLE VII

Charge transfer circumstances on the  $B1$  structural EuX ( $X = O, S, Se, Te$ ) at 0 K and 0 GPa. Positive sign means losing electrons; negative sign means getting electrons.

Compounds	EuO		EuS		EuSe		EuTe	
atom	Eu	O	Eu	S	Eu	Se	Eu	Te
charge	0.75	-0.75	0.63	-0.63	0.29	-0.29	0.01	-0.01

From the calculated elastic constants, the analysis of elastic stability under pressure is interesting because the elastic instability under pressure may be related to the pressure-induced transition regardless of the first-order or second-order phase transition [35]. As is known, for a cubic crystal, the elastic or mechanical stability under isotropic pressure is judged from the following conditions [36]:

$$\tilde{C}_{44} > 0, \quad \tilde{C}_{11} > |\tilde{C}_{12}|, \quad \tilde{C}_{11} + 2\tilde{C}_{12} > 0, \quad (2)$$

where

$$\begin{aligned} \tilde{C}_{\alpha\alpha} &= c_{\alpha\alpha} - P(\alpha = 1, 4), \quad \tilde{C}_{12} = c_{12} + P, \\ \tilde{C}_{13} &= c_{13} + P. \end{aligned} \quad (3)$$

The elastic constants in Table III and IV satisfy all of these conditions at zero pressure. Therefore, the cubic

$B1$  structure for EuX is mechanical stable at zero pressure. But the calculated  $\tilde{C}_{44}$  decreases with increasing pressure, so the condition  $\tilde{C}_{44} > 0$  cannot be satisfied after some pressure. The theoretical critical pressures for EuO, EuS, EuSe, EuTe are about 45, 22, 20, 10 GPa respectively, which are very near the corresponding phase transition pressures (47, 22, 15, 11 GPa, respectively). Thus the elastic instability should be responsible for the pressure-induced phase transition in the EuX system. On the other hand, a softening behavior of the elastic shear modulus  $C_{44}$  in cubic crystals usually means a reduction in the corresponding force constant which in turn is connected to the softening behavior of phonon. For example, in the case of NaH (NaH belongs to  $B1$  structure at ambient conditions, and has the similar structural transition

under pressure to EuX (X = O, S, Se, Te), the softening behaviors of both  $C_{44}$  and transverse acoustic (TA) phonon mode were predicted [37]. Furthermore, the corresponding authors suggested that the TA phonon softening behavior, instead of  $C_{44}$  shear modulus instability, is mainly responsible for the pressure-induced structural phase transition of NaH because the phonon instabilities occur at points away from the center of the Brillouin zone (BZ) and appear before the materials become unstable according to elastic stability criteria. In fact, the softening behaviors of the TA phonon modes for these europium chalcogenides have been captured theoretically by Sakalle et al. [38]. However, which one should be mainly responsible for the pressure-induced structural phase transition between the softening behavior of  $C_{44}$  and the softening behavior of the TA phonon mode is unknown in the EuX (X = O, S, Se, Te) system. Therefore, further experimental and theoretical works are desired.

At 0 GPa, the elastic constants and other some physical quantities for the  $B2$  phase of EuX (X = O, S, Se, Te) are also presented in Table VI together with the recent Charifi et al. [16] results. It is seen that our results and Charifi et al. results still have the large differences, and our results may be more reasonable and provide the better references for the future investigations since there are no experimental studies at present.

### 3.3. Electron transfers

For these europium chalcogenides, ionic interactions are expected to be predominant in the literature [8]. The charge transfers between Eu and X should be obvious. At zero pressure and zero temperature, the electron or charge transfers for EuX (X = O, S, Se, Te) are shown in Table VII (the relative value in the population analysis of charge is more meaningful than the absolute value). It is seen that the charge actually transfers from Eu atom to X atom. But the charge transfer decreases when X varies from O to Te, because of the decreasing electronegativity. This implies that the ionic bonding character of EuX should weaken when X varies from O to Te.

TABLE VIII

The charge populations on  $s$ ,  $p$ ,  $d$ ,  $f$  orbitals under zero pressure and high pressure [GPa] for the Eu atom of  $B1$  structural EuO.

$P$ [GPa]	$s$	$p$	$d$	$f$
0	2.24	6.19	0.88	6.93
10	2.23	6.15	0.97	6.91
20	2.23	6.12	1.04	6.89
30	2.22	6.09	1.10	6.87
40	2.22	6.07	1.16	6.86
50	2.21	6.05	1.20	6.84

On the other hand, in Table VIII, it is noted that the electrons on the  $p$  and  $f$  orbitals of Eu atom also decrease while the electrons on  $d$  orbital increase obviously under pressure; the  $p \rightarrow d$  and  $f \rightarrow d$  electron transfers of Eu

atom occur continuously under pressure (taking EuO as an example, other EuX has similar consequence). Further, it is suggested that the softening behaviors of the shear modulus  $C_{44}$  and TA phonon mode in the EuX system might be induced in part by the  $p \rightarrow d$  and  $f \rightarrow d$  electron transfers of Eu atom under pressure; the  $p \rightarrow d$  and  $f \rightarrow d$  electron transfers also might be responsible for the pressure-induced structural phase transition in the EuX system.

## 4. Conclusions

In the paper, the structures, structural stabilities, elastic properties and charge transfers of EuX (X = O, S, Se, Te) compounds under pressure have been investigated extensively using the first-principles plane-wave pseudopotential density functional theory method with the ultrasoft pseudopotential scheme in the frame of the GGA correction. The ground-state parameters, such as lattice constants, bulk modulus and its pressure derivative for  $B1$  and  $B2$  structures were predicted and compared with the available experimental and theoretical data. The obtained phase transition pressures from the NaCl-type ( $B1$ ) structure to the CsCl-type ( $B2$ ) structure for EuX (X = O, S, Se, Te) are 49, 22, 18, 13.5 GPa, respectively, which are in good agreement with the experimental data. Especially, we have appropriately and systematically predicted the elastic constants of EuX (X = O, S, Se, Te) under zero pressure and high pressure via density functional theory. From the obtained elastic constants, we have analyzed their mechanical stabilities; some important physical quantities, such as the aggregate elastic modulus ( $B$ ,  $G$ ,  $E$ ), the Poisson ratio ( $\sigma$ ), the Debye temperature  $\Theta_D$  were also successfully drawn for both  $B1$  and  $B2$  phases of EuX. The softening behaviors of the elastic shear modulus  $C_{44}$  or elastic instabilities under pressure in the  $B1$  phase of EuX (X = O, S, Se, Te) are captured, which should be responsible for the pressure-induced structural phase transition in the EuX system. It is also suggested that the softening behavior might be induced partly by the  $p \rightarrow d$  and  $f \rightarrow d$  electron transfers of Eu atom under pressure.

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