

AB-INITIO STUDY OF THE STRUCTURAL, ELECTRONIC AND ELASTIC PROPERTIES OF EuX (X = Se, Te) COMPOUNDS IN CUBIC STRUCTURES

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ABSTRACT

The structural, electronic and elastic properties of rare-earth monochalcogenides EuX (X=Se, Te) were investigated with the full-potential-linearized-augmented plane wave (FP-LAPW) based on density functional theory (DFT). The exchange-correlation term is treated using two approximations the generated gradient approximation (GGA) and the local density approximation (LDA). The structural parameters, such as the equilibrium lattice parameters, the bulk modulus B and its derivative B', the electronic properties (the band structure, the total density) and the elastic constants (C_{11} , C_{12} , C_{44}) of EuX compounds (X= Se, Te) are calculated in two phases: face-centered cubic structure type NaCl (B1) and the simple cubic structure CsCl type (B2) under ambient and high pressure. We also studied the structural phase transition between B1, B2. To determine this transition pressure, we calculated Gibbs energy $G = E + PV - TS$.

KEYWORDS: DFT, FP-LAPW, GGA, LDA, the band structure, phase transition.

NOMENCLATURE

Symbols :	C Elastic constants
G Gibbs energy	Greek symbols :
P Pressure (GPa)	σ Poisson 's ratio
V Volume	ϵ Stain tensor
T Temperature (K)	Subscripts :dices :
S Entropy	Max maximum
H Enthalpy	0 (V_0) volume of the unit cell

1. INTRODUCTION

Metals form an important class of technological materials that are exploited widely for their ductility and high electrical and thermal conductivities. The rare-earth monochalcogenides belong to this class. Electronic and optical properties of rare-earth monochalcogenides have long been a challenge to investigators; the chalcogenides and pnictides are difficult to fabricate into a single phase. During the last few years, frequent attempts have been made to understand the electronic properties of rare-earth compounds because of their interesting

semiconducting properties and various practical applications in the field of nonlinear optics, electro-optic components, glass making, grinding alloys, composites lasers, phosphors lasers, and electronics [1-2].

The rare-earth monochalcogenides XY (X= Eu, and Y= Se, Te) compounds crystallize in rock-salt structure but change to CsCl-type structure at high pressures (B2 phase) [3, 4, 5, 6]. The elastic constants are important technological properties of solids: they determine the behavior of materials under any arbitrary, but sufficiently small, loading.

In view of earlier studies, the high-pressure phase transition and the elastic constants have been investigated using a simple approach with a three or two body interaction potential [7–8] except for a few studies that used a sophisticated method. One study reported by Vaitheeswaran et al. [9, 10] who employed the tight-binding linear muffin orbital approach to density functional theory (DFT) within the local approximation to investigate the phase transition in lanthanum monochalcogenides and another one reported by Bouhemadou et al. [11] on the elastic constants of EuX(X= Se, and Te) at normal and under hydrostatic pressure using the method developed by Charpin. In addition, the study of the second-order elastic constants (C_{11} , C_{12} , and C_{44}) and their pressure derivatives at 0 K is quite important for understanding the nature of the inter-atomic forces. One can also directly obtain some useful information on the characteristics of bonding and the structural stability of a crystal.

We have used full-potential linearized-augmented plane wave (FP-LAPW) [12] based on the DFT [13] in WIEN2K code to investigate the high-pressure structural phase transition, electronic and the elastic constants of these compounds.

2. NUMERICAL SIMULATION

2.1 Total-Energy Calculation :

The calculations are performed using the FP-LAPW implemented in the WIEN2k computer package [14]. The essence of the method is: near an atomic nucleus the potential and wave functions are similar to those in an atom – they strongly varying but nearly spherical. However, between the atoms both the potential and wave functions are smoother [12]. Accordingly, space is divided into regions and different basis expansions are used in these regions. In this method, both the potential and charge density are treated without shape approximations and core electrons are treated in a relativistic way.

In our calculations, we used the generalized gradient approximation (GGA) for the exchange correlation potential [17]. The spherical harmonics inside nonoverlapping muffin-tin (MT) spheres surrounding the atoms are expanded up to $l_{\max}=10$. The MT radii are assumed to 2.5 atomic units (a.u.) for Eu, whereas a 2.5 (a.u.) is used for Se, and Te, respectively. The plane wave cut off of $k_{\max}=8/R_{\text{MT}}$ was chosen for the expansion of the wave function in the interstitial region for all the compounds EuY, where R_{MT} denotes the smallest atomic sphere radii and k_{\max} gives the magnitude of the largest k vector in the plane-wave expansion. Special k points were used in performing the Brillouin zone summations. The self-consistent iterations were performed until the convergence in the energy reached about 10^{-4} Ry.

2.2 Elastic Properties :

The knowledge of elastic constants of a solid provides access to an understanding of its mechanical properties for practical application in many fields. To obtain the elastic constants of these compounds with cubic structure, we have used a numerical first principles calculation by computing the components of the stress tensor e for small strains, using the method integrated in the WIEN2K code [14]. It is well-known that a cubic crystal has only three independent elastic constants.

The first equation involves calculating the bulk modulus (B), which is related to the elastic constants by [16] :

$$B = (C_{11} + 2C_{12}) / 3 \quad (1)$$

The shear modulus G of a cubic structure is given by :

$$G = (C_{11} - C_{12} + 3C_{44}) / 5 \quad (2)$$

Then, Young's modulus E and Poisson's ratio σ are:

$$\sigma = \frac{1}{2} + \left(1 - \frac{E}{3B}\right) \quad (3)$$

$$E = \frac{9BG}{3B+G} \quad (4)$$

3. RESULTS

3.1 Total-Energy Calculation, High-Pressure Structural Transformation and Electronic Properties

The total energy as a function of unit-cell volume around the equilibrium cell volume V_0 for EuX (X= Se, Te) compounds was calculated for each of the phases B1 and B2. The calculated total energies are fitted to Murnaghan's equation of state to obtain the ground-state properties [15]. The results are shown in Figure 1. The lowest energy is found in the B1 phase, the B2 structure is not favorable for the entire compound EuX (X= Se, Te), since the calculated energy is higher than that of B1 phase. From the graph 1, one can see that the rare-earth chalcogenides EuX (X= Se, Te) crystallize in NaCl phase (B1) at ambient pressure. They show a phase transformation from B1 to (B2) phase. The calculated structural parameter of EuX (X=Se, Te) phases are listed in. It is interesting to note that the lattice parameter increases when we move from EuSe to EuTe. On the other hand, the bulk modulus decreases from EuSe, to EuTe in both phases B1 and B2. High pressure, along with ambient-pressure studies on materials, can help with analyzing the nature of interaction around the atoms. It is found that under pressure; most of the rare-earth compounds undergo a first-order phase transition from the six-fold coordinate NaCl structure to the eightfold coordinate CsCl-type structure (B2). Thermodynamically, a phase transition occurs when changes 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 Gibbs energy [19]: $G = E +PV-TS$ Since the theoretical calculations are performed at 0 K, the free energy becomes equal to the enthalpy: $H= E + PV$.

At a given pressure, a stable structure is one for which the enthalpy has its lowest value and the transition pressure are calculated at which the enthalpies for the two phases are equal. The calculated phase transition pressures for these materials are summarized in Table 2, together with previous theoretical results. The application of pressure to the crystals causes the decrease in their volume, which in turn leads to an increased charge transfer due to the existence of the deformed charge between the overlapping electron shells of adjacent ions. We note that the pressure P_t increases when the chalcogen atom Se is replaced by Te (Figure 1, Figure 2). The energy study of the two phases shows that the lowest energy is in phase B1(NaCl) so that B1 is more stable than B2 phase (CsCl) because the calculated energy is above the phase B1. From the band structure and total state density EuX obtained by both approximations, we can see that the energy gap is zero in both phases B1 and B2. So these are metals (figure 3).

3.2 Elastic properties :

The elastic properties of a solid reflect the response of the interatomic forces between the atoms concerned to an applied stress. Since the bonding forces vary with crystallographic orientation, the elastic properties of metal single crystal may be highly anisotropic. In cubic materials, only three independent elastic constants are needed C_{11} , C_{12} , and C_{44} . So, the study of the second order elastic constants (C_{11} , C_{12} , C_{44}) and their pressure derivatives at 0 K is quite important for understanding the nature of the interatomic forces.

Hence, to determine these constants, we have used the method developed by Charpin and integrated by Mortada [18]. The obtained elastic constants of EuX (X= Se,Te) compounds at ambient and under pressure are listed and compared with available results in Table 3. To the best of our knowledge, no experimental value for the elastic constants of these compounds have appeared in literature, so our results for B2 phase can serve as a prediction for future investigation. It is clearly seen from Table 3 that the values of C_{12} are smaller than that of C_{11} and for the compound EuTe, the value of C_{12} is negative approximately -1.60 GPa. We note

that the elastic constants decrease with the chalcogen atom from Se to Te in EuX (X=Se, Te) compounds in B1 phase. From Table 3, we see that these elastic constants C_{ij} are decreased when we move from EuSe to EuTe in the two phases except C_{44} for the EuSe to EuTe in the high pressure phase B2. The Young's modulus E and Poisson's ratio ν are important in technological and engineering application [20]. Young's modulus is defined as the ratio of stress and strain when Hooke's Law holds. From Table 4, the Young's modulus in the Eu compound it is increased linearly. Also, we conclude that the stiffness of materials decreases with pressure. Our obtained values for Poisson's ratio varied from 0.17–0.28 in B1 phase, which is an indication that ionic bonds are presented [22]. However, in B2 phase ν is greater than 0.25, which indicates that the interatomic forces in B2 phase of XY (X= Eu, and Y=Se, Te) compounds are central forces [21].

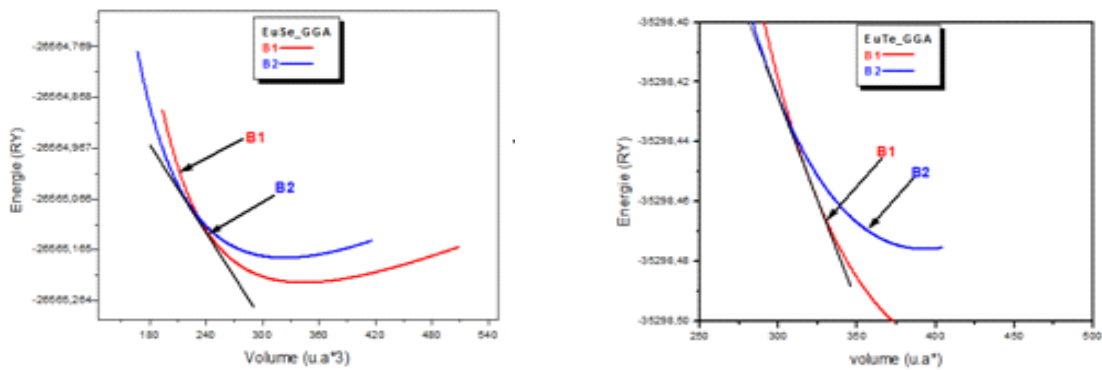


Figure 1 calculated ground-state energy versus optimized volume curves of B1 and B2 phases for EuX (X= Se, Te) compounds.

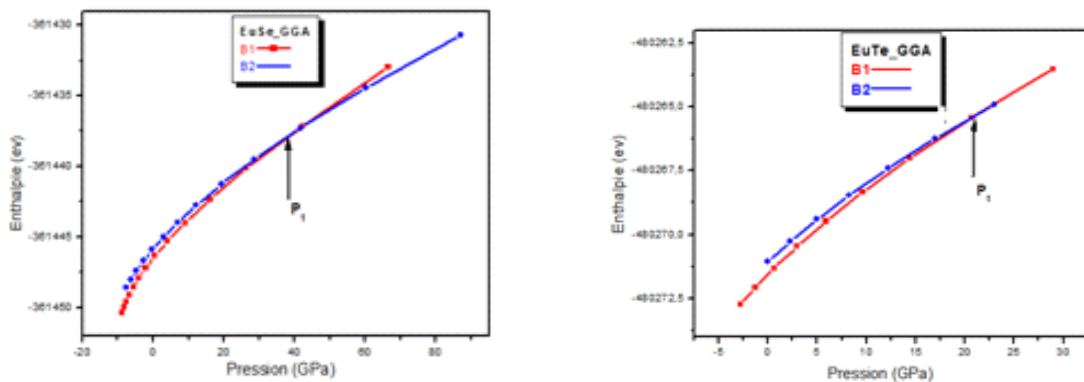


Figure 2 calculated pressure versus enthalpy of B1 and B2 phases for EuX (X= Se, Te) compounds and

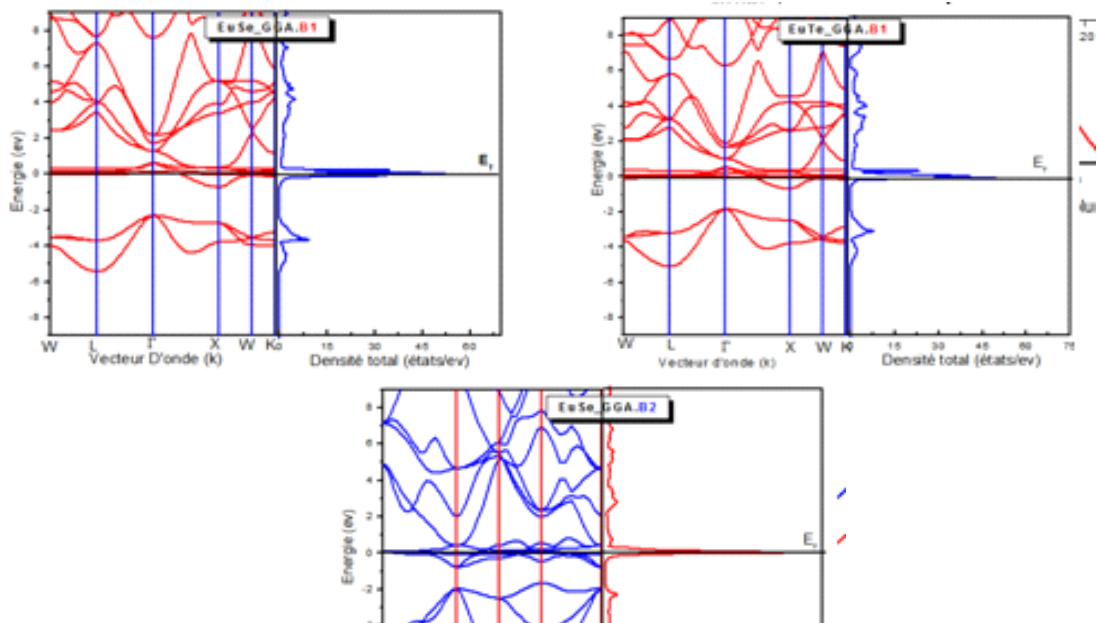


Figure 3 Band dispersion for EuX (X=Se, Te) calculated according to GGA.

Table 1 Calculated lattice constant a, bulk modulus B₀ and its pressure derivative B' for B1 and B2 phases XY (X= Eu and Y= Se, Te) compounds, compared with the available experimental and theoretical data.

B1phase						
	a (Å)		B ₀ (GPa)		B'	
	Present work	Theory +experiment	Present work	Theory +experiment	Present work	Theory +experiment
EuSe	5.72	----	73.4	---	4.6	---
EuTe	6.14	-----	53.4	---	4.1	----
B2phase						
	a (Å)		B ₀ (GPa)		B'	
	Present work	Theory +experiment	Present work	Theory +experiment	Present work	Theory +experiment
EuSe	3.52	---	75.2	---	4.56	---
EuTe	3.76	---	53.6	---	4.06	---

Table 2 Calculated values of phase transition pressures P_t, at phase transition pressures for EuSe, EuTe compounds.

B1 → B2			
	P _t (GPa)		
	Present work	Theory	experiment
EuSe	8.9	16 [5]	---
EuTe	17.4	-----	---

Table 3 Calculated elastic constants C_{ij} (GPa), for B1 and B2 phases of EuSe, EuTe compounds.

B1phase						
	C ₁₁		C ₁₂		C ₄₄	
	Present work	Theory	Present work	Theory	Present work	Theory
EuSe	213.1	80.5[5]	3.6	29.7[5]	30.06	35.6[5]
EuTe	163.5	-----	-1 .6	---	8.8	----
B2phase						
	C ₁₁		C ₁₂		C ₄₄	
	Present work	Theory	Present work	Theory	Present work	Theory
EuSe	143.6	---	41.0	---	-3.3	---
EuTe	115.3	---	22.3	---	11.9	---

Table 4 Calculated Young's modulus E (GPa), shear modulus G (GPa) and Poisson's ratio σ , (in GPa), for B1 and B2 phases of EuSe and EuTe compounds.

B1phase						
	E		G		Σ	
	Present work	Theory +experiment	Present work	Theory +experiment	Present work	Theory +experiment
EuSe	141,4	----	59,9	---	0,18	---
EuTe	92,7	-----	38,3	---	0,21	----
B2phase						
	E		G		Σ	
	Present work	Theory +experiment	Present work	Theory +experiment	Present work	Theory +experiment
EuSe	51,4	---	18,5	---	0,39	---
EuTe	66,6	---	25,8	---	0,29	---

4. CONCLUSIONS

The calculations were performed using the code wien2k [14] which is an implementation of the method FP-LAPW (full potential linearized augmented plane wave) based on DFT (functional density total). We used the approximation of the local density (LDA) and the gradient approximation (GGA) for the term of the exchange-correlation (XC). We deduced that these compounds are crystallized in phase B1; it is the more stable than in Phase B2 and the best approximation to calculate the structural property is the GGA approximation. Some basic physical properties, such as lattice constant, bulk modulus, second-order elastic constants (Cij), shear modulus, Young's modulus and Poisson's ratio constants are calculated. It is interesting to note that the lattice parameter increases when we move from EuSe to EuTe. On the other hand, the bulk modulus decreases from EuSe to EuTe with in both phases (B1 and B2). It is found that the pressure Pt decreases when the chalcogen atom Se is replaced by Te a for EuX (X=Se,Te) compounds. The same behavior is shown for the calculated elastic constants. They decrease with the chalcogen atom from Se to Te in B1 phase. We have also studied the ductility the brittleness and the stiffness of the compounds under consideration by analyzing the parameter Young's modulus. The effect of chalcogen atom on these properties is investigated. At the same time, it is found that the gap is zero in both phases which confirms that these are metals.

REFERENCES

- [1] O. P. Singh and V. P. Gupta, Phys. Status Solidi B 129, 153(1985).
- [2] K. G. Gschneidner, Rare Earth Alloys (D. Van Nostrand Co.Inc., Princeton, NJ, 1961).
- [3] J. M. Rooymans, Solid State Commun. 3, 421 (1965).
- [4] D. Varshney, N. Kaurav, P. Sharma, S. Shah, and R. K. Singh, Phys. Status Solidi B 241, 3179 (2004).
- [5] S. Singh, R. K. Singh, and A. Gour, Central Eur. J. Phys. 5, 576 (2007).
- [6] J. M. Le'ger, Physica B 190, 84 (1993).
- [7] V. Srivastava, A. K. Bandyapadhyay, P. K. Jha, and S. P.Sanyal, J. Phys. Chem. Solids 64, 907 (2003).

- [8] W. Bechenbaugh, J. Evers, G. Guntherodt, E. Kaldis, and P. Wachter, *Phys. Chem. Solids* 36, 239 (1975).
- [9] G. Vaitheeswaran, V.Kanchana, and M.Rajagopalan, *J. Phys. Chem. Solids* 64, 15 (2003).
- [10] G. Vaitheeswaran, V. Kanchana, S. Heathman, M. Idiri, T. Le Bihan, A. Svane, A. Delin, and B. Johansson, *Phys. Rev.* 75, 184108 (2007).
- [11] A. Bouhemadou, R.Khenata, and M.Maamache, *J.Mol. Struct.:THEOCHEM* 777, 5 (2006).
- [12] D. J. Sing, *Plane Waves, Pseudopotentials and the LAPW Method* (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994).
- [13] P. Hohenberg and W. Kohn, *Phys. Rev. B* 136, 864 (1964).
- [14] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K, an Augmented Plane Wave/Local orbitals program for calculating crystal properties* (Karlheinz Schwarz, Techn. Universita't, Wien, Austria, 2001), ISBN 633-9501031-1-2.
- [15] F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* 30, 244 (1944).
- [16] E. Schreiber, O. L. Anderson, and N. Soga, *Elastic Constants and Their Measurement* (McGraw-Hill, New York, 1973).
- [17] Z. Wu and R. Cohen, *Phys. Rev. B* 73, 235116 (2006). [18] Z. Charifi, H. Baaziz, F. El. Haj Hassan, and N. Bouarissa, *J. Phys.: Condens. Matter* 17, 4083 (2005).
- [19] M. Born and K. Huangin, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
- [20] F. Peng, D. Chen, and X. D. Yang, *Solid State Commun.* 149, 2135 (2009).
- [21] F. Chu, Y. He, D. J. Thome, and T. E. Mitchell, *Scr. Metall. Mater.* 33, 1295 (1995).
- [22] J. Haines, J. M. Leger, and G. Boquillon, *Annu. Rev. Mater. Res.* 31, 1 (2001).