Mechanical and Thermal Properties of Plutonium Monochalcogenides and Monopnictides

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***Abstract** – The mechanical and thermal properties of plutonium monochalcogenides and monopnictides are calculated using elastic constants and sound velocities, those have been derived from two body inter- ionic potential theory. We have calculated the Young's modulus (E), Poisson's ratio (v), anisotropy factors (A), bulk modulus to shear modulus ratio (B/G) for these compounds. The calculated values of Poisson's ratio show that the ionic contributions to the atomic bonding are dominant for these compounds. The B/G ratio indicates that, only PuS will behave in the brittle manner and other compounds will show the ductile nature. We have also calculated the sound velocities, Debye temperature (θ_D), Grüneisen parameter (ς), and lattice heat capacities (β) for these compounds.*
***Keywords**: Mechanical properties, Thermal properties, Debye temperature, Grüneisen parameter*

I. Introduction

In recent years, the investigation of the unusual electronic, magnetic, phase transition, mechanical and thermal properties of the monopnictides and monochalcogenides of the rare-earth elements with a NaCl (B1) structure has been an important and popular topic in condensed matter. These properties are related to their electronic structure where the 4f band is partially filled and extended valence states coexist in the same energy range. The plutonium monochalcogenides, PuX (X = S, Se, Te) and monopnictides, PuY (Y = As, Sb, Bi) all have unusual properties under pressure and all of them crystallize in NaCl (B1)-structure. These compounds undergo the first order structural phase transition from NaCl (B1)-structure to CsCl (B2)-structure at high pressure [1]. Amongst PuX and PuY compounds, PuS does not show any kind of phase transformation from its ambient NaCl structure up to 60 GPa [2], while PuSe [3] exhibits double phase change in the pressure range up to 47 GPa. Around 18 GPa, the B1 type structure undergoes a second order phase transition to a rhombohedral phase and finally it transforms to the B2 type structure around 35 GPa with a volume change of 11%. PuTe undergoes B1 to B2 transition between 15 and 19 GPa [4] with 9% volume reduction. In the mono-pnictides of plutonium, PuAs shows B1 to B2 transition around 35 GPa [5] while PuSb undergoes B1 to B2 transition at 18 GPa and B2 to tetragonal at 38 GPa [6] with 9% volume collapse for both phases. PuBi transforms into distorted B2 structure at 10 GPa with 12% volume change [7]. The electronic structure of Pu compounds have been investigated by Petit et al. [8] using SIC-LSD scheme within the Tight-Binding Linear-Muffin-Tin Orbitals (TB-LMTO) method [9]. In this investigation, the Pu f-electron manifold has been described in a mixed picture of localized and delocalized states. Their calculations have also shown that trivalent Pu^{3+} configuration is favored in most of the compounds, but valency transition has been encountered. A comparison of the properties of PuTe and SmTe [10] reveals that the former is a mixed valent compound. Shick et al. [11] have investigated the electronic structure of Pu chalcogenides by using the correlated band theory methods. Lee et al. [12] have computed the spectra of Pu chalcogenides and pnictides with dynamical mean field theory within the local density approximation (LDA+DMFT). They find the chalcogenides are mixed-valent materials with a strongly T-dependent low-energy density of states and a triplet of quasi particle peaks below the Fermi level. Only a few works have been devoted to the study of structural and electronic properties of this series of rare earth monochalcogenides and monopnictides.

Looking at the fact that these compounds are less explored, A systematic structural and elastic study of plutonium monochalcogenides (PuX: X = S, Se, Te) and plutonium monopnictides (PuY: Y = As, Sb, Bi) is reported by Srivastava et al. [13] from our group using the interionic potential theory with necessary modifications to the charge parameter. These compounds undergo B1 to B2 phase transitions at various pressures [13]. Our further interest in these compounds is motivated for their mechanical properties like anisotropy factor (A), Poisson's ratio (v), Young's modulus (E), shear modulus (G) and thermodynamic properties such as sound velocities, Debye temperature, Grüneisen parameter, and lattice heat capacities were also investigated.

II.   Method of Calculation

II.1.   Calculation of Mechanical Properties

The mechanical properties such as Shear and Young modulus, Poisson ratio, and anisotropic ratio are calculated using standard formulism as given in equations 1-4. The incorporation of second order elastic constants (SOEC) in the formalism is calculated using classical inter ionic potential theory [14]. The study of SOEC C_{11}, C_{12} and C_{44} and their pressure derivatives at 0K is quite important for understanding of the inter-atomic force in solids. The bulk modulus is derived from elastic constants as

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{1}$$

In addition another physical quantity, namely the anisotropic ratio A, defined as: $A=2C_{44}/(C_{11}-C_{12})$ has also been calculated. For an ideal isotropic system, A is unity and deviation from unity measures the amount of elastic anisotropy. The Poission's ratio, v is calculated using the relation:

$$v = \frac{3B - 2G}{2(3B + G)} \tag{2}$$

where, B is bulk modulus and G is average shear modulus. As per Hill [15] average shear modulus, G is defined as arithmetic mean of Voigt, G_V and Reuss, G_R values, which can be expressed in terms of elastic constants as:

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44})$$

and

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}} \tag{3}$$

The Young's modulus, E is calculated using the expression:

$$E = \frac{9BG}{3B + G} \tag{4}$$

II.2.   Calculation of Thermal Properties

The Debye temperature (θ_D) is an important thermal property of solids, which defines a demarcation line between quantum mechanical and classical behaviour of phonons. We have estimated Debye temperature of PuX and PuY compounds using the following expression [16, 17]:

$$\theta_D = \frac{h}{K_B}\left[\frac{3n}{4\pi V_a}\right]^{1/3} S_m \tag{5}$$

where h is a Plank`s constant, $K_B$ is Boltzmann`s constant and V_a is the atomic volume and S_m is average sound velocity.

III.   Results and Discussion

A study of the mechanical properties for materials is essential to understand the elasticity, stability, chemical bonds, cohesion, and stiffness of crystals and give important information concerning the nature of the forces operating in solids. The ground state properties of these compounds have been studied by Srivastava et al. [13] from our group; they have successfully calculated the equation of state, phase transition pressure, lattice parameters, bulk modulus, elastic constant and second order elastic constants of these compounds. Incorporating all the above parameters we have further investigated mechanical properties such as Young modulus (*E*), shear modulus (*G*), Poisson ratio (*v*), anisotropic ratio (*A*), and thermal properties such as sound velocities, Debye temperature (θ_D) for the PuX and PuY compounds which are given in Table I. We have estimated mechanical properties and Debye temperature of PuX and PuY compounds using the elastic constants and sound velocities. There is no data available for comparisons of our results.

The anisotropy factor, *A*, is a measure of the degree of elastic anisotropy in solids. The parameter *A* takes the value of 1 for a completely isotropic material. If the value of *A* is smaller or greater than 1 it shows the degree of elastic anisotropy. The calculated anisotropy factors for PuX, Y are smaller than 1 which indicates that these compounds have an elastically anisotropic character. The Poisson's ratio, *v*, is very important property for industrial applications. It is small (*v* = 0.1) for covalent materials, and it has a typical value of *v* = 0.25 for ionic materials [18]. Calculated *v* values are equal to 0.256, 0.269, 0.275, 0.268, 0.280, and 0.277 for PuS, PuSe, PuTe, PuAs, PuSb, and PuBi, respectively. It shows that, the ionic contributions to the atomic bonding are dominant for these compounds. The Young's modulus, *E*, which is the ratio of the tensile stress to the corresponding tensile strain, is required to provide information about the measure of the stiffness of the solids. The material is stiffer for the larger value of Young's modulus. The present values of Young's moduli

decrease from PuS to PuTe for chalcogenides and PuAs to PuBi for pnictides, which indicates that PuS is stiffer than PuSe and PuTe in the chacogenides and similarly PuAs is stiffer than PuSb and PuBi in the plutonium pnictides. We can also estimate the brittle/ductile behavior of these compounds using the calculated values of bulk modulus and shear modulus. According to the criterion, proposed by Pugh [19], a material is brittle if the *B/G* ratio is less than 1.75; otherwise it behaves in ductile manner. The present values of *B/G* are listed in the Table I, which indicate that, only PuS will behave in the brittle manner and other compounds will show the ductile nature.

TABLE I
MECHANICAL PROPERTIES OF PLUTONIUM CHALCOGENIDES AND PNICTIDES. SHEAR (*G*) AND YOUNG'S MODULUS (*E*) ARE IN GPA UNIT.

Solids	*G*	*E*	*v*	*A*	*B/G*
PuS	67.1	168.5	0.256	0.584	1.71
PuSe	50.3	127.7	0.269	0.386	1.83
PuTe	24.9	63.5	0.275	0.344	1.89
PuAs	36.7	93.1	0.268	0.394	1.82
PuSb	34.5	88.3	0.280	0.306	1.94
PuBi	32.5	83	0.277	0.315	1.91

The Debye temperature, θ_D, which is an important physical parameter, and Gruneisen parameter, ς, were calculated and the results are presented in Table II for PuX, Y compounds. Debye temperature, [16, 17] and Grüneisen parameter, [20] are sound velocity and mass density dependent, Grüneisen parameter is calculated using the expression:

$$\varsigma = \frac{9\left(V_L{}^2 - \frac{4V_S{}^2}{3}\right)}{2\left(V^2{}_L + 2V^2{}_S\right)}$$

The longitudinal, transverse and average sound velocity (S_L, S_T and S_m in m/s) have been calculated using their reported formulism. The Debye temperature is directly related to the average sound velocity. Thus greater the average sound velocity, greater is the Debye temperature. Furthermore, Debye temperature decreases from PuS to PuTe in chalcogenides and PuAs to PuBi in the plutonium pnictides. The Grüneisen parameter is the measure of anharmonicity. Greater the Grüneisen parameter, greater will be anharmonicity. In our case, Grüneisen parameter is equal for all the chalcogenides; thus, anharmonicity is equal in plutonium chalcogenides. Similarly, we find the ςlarge for PuAs in the pnictides; it means anharmonicity large in PuAs compound. We have also calculated the lattice heat capacities, *β*, which is calculated using the expressions given by:

$$\beta = \frac{12\pi^4 Rn}{5\theta_D^3}$$

where R is the molar gas constant and n is the total number of atoms per formula unit. The calculated values of lattice heat capacities are listed in Table II. To our knowledge, there is no previous experimental or theoretical data related to presented thermodynamic properties to compare our calculated results.

TABLE II
CALCULATED VALUES OF THE LONGITUDINAL, TRANSVERSE AND AVERAGE SOUND VELOCITY (S_L, S_T AND S_M IN M/S) AND DEBYE TEMPERATURE (θ_D IN K), GRÜNEISEN PARAMETER (ς) AND LATTICE HEAT CAPACITIES *β* (IN J/K⁴MOL) FOR PLUTONIUM CHALCOGENIDES AND PNICTIDES COMPOUNDS.

Solids	S_L	S_T	S_m	θ_D	ς	β
PuS	4413	2547	2828	298	1.50	2.93×10^{-4}
PuSe	3915	2260	2509	252	1.50	4.80×10^{-4}
PuTe	2859	1650	1832	173	1.50	1.49×10^{-3}
PuAs	3410	1969	2186	218	1.50	7.49×10^{-4}
PuSb	3481	2010	2231	208	1.49	8.51×10^{-4}
PuBi	3110	1795	1993	183	1.49	1.26×10^{-3}

IV. Conclusion

In conclusion, by using the formulism, we have calculated the mechanical and thermal properties of PuX and PuY compounds. The calculated elastic moduli showed that these compounds are mechanically stable and will behave as brittle material in B1 phase. In addition they exhibit almost similar anisotropy. The bulk modulus, elastic constants and Debye temperature are calculated successfully and trends are discussed.

Acknowledgements

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Authors Profile

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