

Higher Order Elastic Constants of Thorium Monochalcogenides

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Abstract. We have predicted the anharmonic elastic properties of thorium chalcogenides (ThS and ThSe) having NaCl-type structure under high temperature (100–1000 K) using Born-Mayer repulsive potentials and the long- and short-range interaction approach. Taking the nearest neighbour distance and hardness parameter as the input data second and third order elastic constants were computed at various temperatures. The significance of these properties in predicting the elastic behaviour of Th compounds has been discussed.

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1 Introduction

The rare earth chalcogenide compounds have been intensively studied because of their interesting physical properties including complex magnetic structures, pressure induced insulator-metal transitions, anomalous valence fluctuations, *etc.* In this work we explore the high temperature behavior of the Th chalcogenides by the theory. Density functional calculations are performed to compare basic theoretical predictions with the literature. For these compounds no high-temperature results on elasticity have been reported previously. The objective of the present work is to investigate the temperature dependence of the second and third order elastic constants of the Thorium monochalcogenides (ThS and ThSe), for which there are no experimental results available. Elastic constants are derived from well known force shell model with long- and short-range interactions.

The Uranium monochalcogenides crystallize in simple NaCl structure at normal pressure and room temperature and have been extensively studied in recent years, both experimentally and theoretically [1-7]. The corresponding Thorium compounds having the same structure except for ThTe which crystallizes in the CsCl structure, are comparatively less explored so far. In the case of Uranium

chalcogenides, the lattice parameters, elastic and phonon properties are strongly related to the localized state of the 5f electrons of the Uranium ion [3]. On the other hand, Thorium has essentially no 5f electrons, therefore, a comparison of the elastic and phonon properties of the Uranium and Thorium compounds should give some information on the influence of the 5f electrons and the type of bonding in these compounds. The high pressure structural behaviour, equation of state and electronic structure calculation of Thorium compounds have received some importance in the recent years [7-8]. It has been observed from high pressure X-ray diffraction studies that Thorium nitride does not show any phase change up to 47 GPa unlike its Uranium counterpart [9]. Another anomaly is also observed in the case of Thorium telluride (ThTe) which crystallizes in CsCl (B2) structure at ambient condition, while Uranium telluride (UTe) undergoes a B1(NaCl) to B2(CsCl) structural transition at high pressure. A remarkable feature in the case of bulk modulus scaling shows that the B_0 is inversely proportional to the power -1.85 of VO for Thorium monochalcogenides while this value lies between -5/3 for the Uranium mononictides and -2 for the Uranium monochalcogenides [9-10]. Electronic structures of ThAs and ThSb at high pressure calculated from first principle tight binding have also recently been reported [8]. No other first principle or model calculations to understand the physical properties of these compounds are available so far. Motivated by the above facts and some of our earlier works on the anharmonic properties and high temperature behaviour of several compounds [11-15], in this work, we are reporting the high temperature elastic properties of Thorium compounds by using simple Born-Mayer repulsive potential approach [14]. In the present paper, we report for the first time the results on elastic properties of Thorium compounds (ThS and ThTe) using theoretical models relevant to the present system, namely, force shell model [14] which has been found to explain the anharmonic properties in various types of compounds [16-20] successfully. The present study will also be helpful in making qualitative understanding of elastic behaviour in this group of solids. In the absence of any measured data on the elastic properties at higher temperature, comparison cannot be made.

The rest of the paper is organized as follows. In Section 2 we discuss the computational details of our work. The calculated higher order elastic constants as well as the theoretical results for these properties are presented in Section 3, and the conclusions are given in Section 4.

2 Formulation

The elastic energy density for a crystal of a cubic symmetry can be expanded up to quartic terms as shown below [14]:

$$\begin{aligned}
 U_0 &= U_2 + U_3 + U_4 \\
 &= \frac{1}{2!} C_{ijkl} x_{ij} x_{kl} + \frac{1}{3!} C_{ijklmn} x_{ij} x_{kl} x_{mn} + \frac{1}{4!} C_{ijklmnpq} x_{ij} x_{kl} x_{mn} x_{pq},
 \end{aligned} \tag{1}$$

where C_{ijkl} and C_{ijklmn} are the second and third order elastic constants in tensorial form; x_{ij} are the Lagrangian strain components; C_{IJ} and C_{IJK} are the SOECs and TOECs in Brugger's definition and Voigt notations. The SOECs and TOECs are as given below:

$$\begin{aligned}
 C_{ijkl} &= C_{IJ} = \left. \frac{\partial^2 U}{\partial x_{ij} \partial x_{kl}} \right|_{x=0} \quad \text{and} \\
 C_{ijklmn} &= C_{IJK} = \left. \frac{\partial^3 U}{\partial x_{ij} \partial x_{kl} \partial x_{mn}} \right|_{x=0}
 \end{aligned} \tag{2}$$

An elastic constant consists of two parts as follows:

$$C_{IJ} = C_{IJ}^0 + C_{IJ}^{\text{vib}} \quad \text{and} \quad C_{IJK} = C_{IJK}^0 + C_{IJK}^{\text{vib}}. \tag{3}$$

The first part is the strain derivative of the internal energy U_0 and it is known as "static" elastic constant and the second part is the strain derivative of the vibrational free energy U^{vib} and is called "vibrational" elastic constant. The superscript "0" has been introduced to emphasize that the static elastic constants correspond to 0 K. By adding the vibrational elastic constants to the static elastic constants, one may get SOECs and TOECs at any temperature for FCC crystals. The general expressions for these properties have been reported in literature [14], and, therefore, are not repeated in this paper.

3 Evaluation

The brief introduction of formulation is given in the preceding Section 2. The whole evaluation is based on the assumption that the crystal structure of the material does not change when temperature varies up to the melting point. Using the concept of nearest-neighbour distance and hardness parameter [14], the elastic constants and pressure derivatives for NaCl-type Thorium monochalcogenides are evaluated at different temperatures (from 100 to 1000K) using the formulation and shown in Figures 1 and 2. The comparison has also been made for some elastic properties for these crystals with available theoretical data [21] and presented in Table 1.

4 Results and Discussions

Experimental as well as theoretical work on different aspects of anharmonic properties for several compounds has been reported in the recent years [12-18]. Though compendiums of elastic constant data for several compounds exist, they are restricted to temperatures at or near room temperature. Current problems in material science often require values of elastic constants at elevated temperatures. The chalcogenides have attracted a lot of interest due to their complex physical and chemical characteristics [1-10]. However, no results are available on temperature dependent anharmonic properties of Thorium monochalcogenides (ThS, and ThSe), *viz.* second and third order elastic constants (SOECs and TOECs) *etc.*, which are very important to explain the microstructure and other related physical properties of these crystals. Therefore, in the present work, temperature dependence of second and third order elastic constants has been studied in the temperature range of 100–1000 K.

We have calculated the SOECs and TOECs for Thorium compounds (ThS and

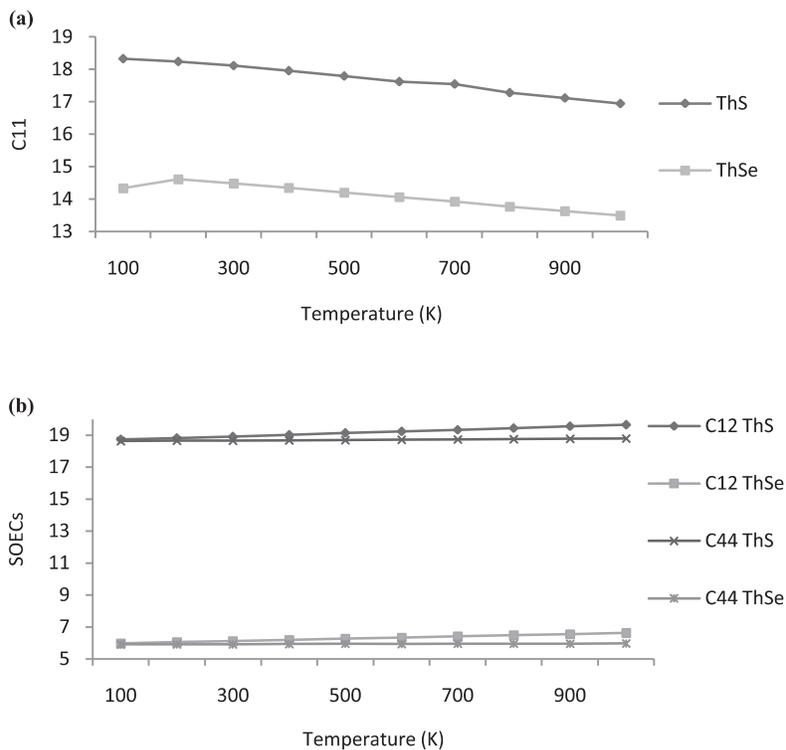


Figure 1. Temperature variation of SOECs (10^{10}N/m^2).

ThSe) in high temperature range (100-1000K) using nearest neighbor distance and hardness parameter as input data and the results are listed in Table 1 and in Figures 1 and 2. It is obvious from Table 1 that there are three independent SOECs at room temperature. One may state that all the SOECs are positive in nature. From Table 1, it is also clear that there are six TOECs at room temperature. It is clear from Figure 1, that the second order elastic constant C_{11} decreases with temperature, while the C_{12} and C_{44} increases, as expected [11,14]. Similar arguments are in general applicable to all other rare earth compounds [21]. For the sake of comparison, we have tabulated the calculated data of ThS and ThSe compounds obtained from literature [21] in Table 1. At the room temperature, the results obtained from the present study for Thorium chalcogenide

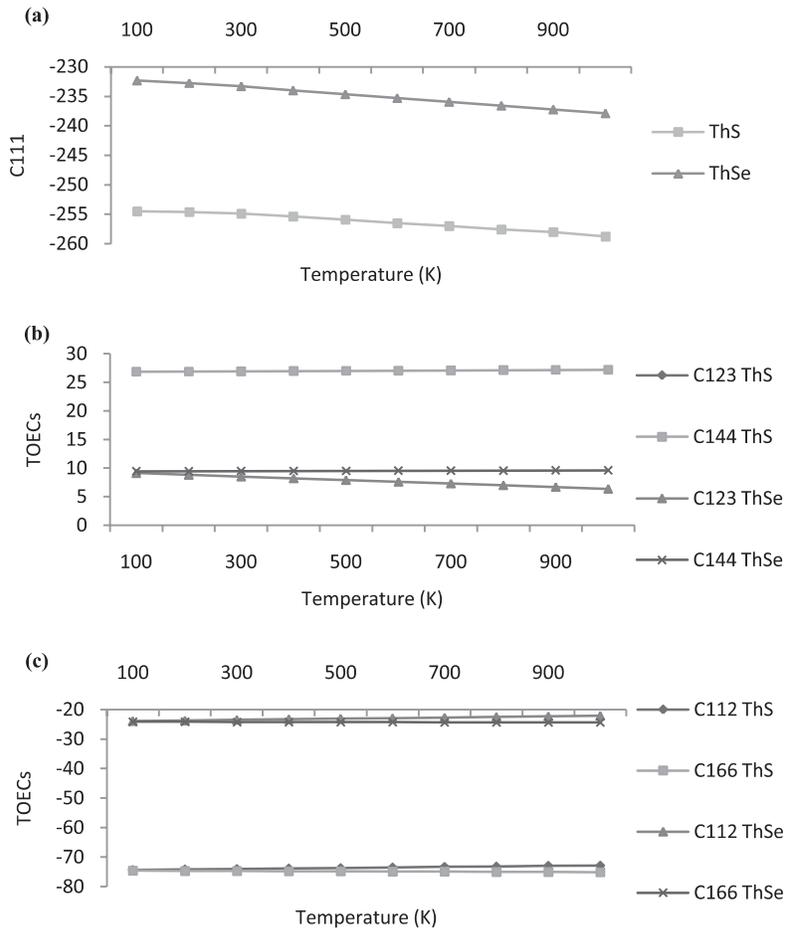


Figure 2. Temperature variation of TOECs (10^{10} N/m^2).

Table 1. Comparison data of SOECs and TOECs (in 10^{11} dyne/cm²) at 300 K for Thorium chalcogenides (data from [21] in GPa).

Crystal	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}	Ref.
ThS	18.11	18.92	18.66	-254.90	-74.00	26.07	26.91	-74.68	2.67	Present [21]
	30.76	5.01	5.01							
ThSe	14.48	6.12	5.92	-233.30	-23.52	8.49	9.46	-24.20	9.40	Present [21]
	28.30	4.35	4.35							

compounds are quite similar. However, these results differ considerably for ThS. This can be ascribed to the inclusion of the effect of linear expansion coefficient in the later model. The agreement is satisfactory for C_{12} and C_{44} in ThSe. This disagreement between the comparison values of SOECs for some of the compounds studied may be because we have derived our expressions assuming that the overlap repulsion is significant only up to the level of next nearest neighbours. Furthermore, other approaches for obtaining elastic moduli can be used at one temperature only, while our approach is simple and can be used for obtaining the temperature dependence of the elastic constants over a wide temperature range. Our approach is very simple, it involves only two basic parameters; the nearest neighbour distance (r) and the hardness parameter (q). In the case of ThS, the variation of SOECs is quite similar to that of ThSe, but gradually decreases for C_{11} . A similar conclusion can also be drawn in the case of TOECs curves for ThS and ThSe (Figure 2). This shows that similar behavior has been observed in the former class of solids [11-15].

The temperature variations of third order elastic constants for chalcogenides of Thorium are presented in Figures 2(a-c). The values of C_{123} , C_{144} and C_{456} are positive and are not affected by the inclusion of second-nearest-neighbour interaction to any significant extent suggesting that they are not sensitive to the short-range interaction, whereas other constants C_{111} , C_{112} and C_{i66} which come out negative show a substantial change and are most sensitive to this interaction. Among the calculated TOECs of three materials, C_{111} 's are larger in their absolute values and an order of magnitude larger than the SOECs. Magnitudes of other TOECs are markedly smaller than those of C_{111} . The values of TOECs increase when temperature is increased. This behaviour is similar to that observed for NaCl-structured solids [14]. Thus our study also proves the previous work. The temperature variation of TOECs could prove useful in studies of various anharmonic properties of ionic solids in general.

As previously stated, there is at present no experimental information regarding the temperature variation of elastic constants available for the Thorium chalcogenides, however, the elastic constants of these solids are of roughly the same magnitude [14-17] and the same variations as those calculated for the other chalcogenide compounds [11] having NaCl-structure, which can be taken as an

indirect check on our calculated elastic constant values. The available literature [11-15] shows that the present model has been most extensively used for studying the lattice properties of various kinds of solids. The versatility of our model is further witnessed from its successful applications [16-20]. It may thus be concluded that the “deformation-mechanism” generally provides much better interpretation of the crystal properties. Our whole theoretical approach can be applied to the evaluation of related parameters to study the anharmonic and microstructural properties of Thorium chalcogenides. The higher order elastic constants are strongly related to other anharmonic properties; such as thermal expansion, thermo-elastic constants and thermal conductivity, *etc.* [14]. This treatment gave the possibility to understand the temperature dependences of elastic constants, as well as to secure more exact values of parameters for characterizing the material. This paper presents for the first time the results of systematic calculations of the second and third order elastic constants at high temperatures for Th chalcogenides. This study will be useful in characterization of the material and it will give a clear picture of elastic behaviour in these compounds and we emphasize the need of measurements of the complete elastic properties to support the present results.

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