Structural phase stability of ThSb and ThAs under pressure

K VENKATASUBRAMANIAM, M RAJAGOPALAN,
B PALANIVEL[†] and G KALPANA^{*†}

Department of Physics, Anna University, Madras 600 025, India

[†]Department of Physics, Crescent Engineering College, Chennai 600 048, India

Abstract. The high-pressure behaviour of thorium mononpnictides is of considerable interest as these systems exhibit structural phase transitions under pressure. At ambient conditions these compounds crystallize in the NaCl-type (B1) structure. Experiments show that with the application of pressure these compounds transform to the CsCl-type (B2) structure. ThSb and ThAs are found to exhibit B1–B2 transition in the pressure range between 9–12 GPa and 1826 GPa respectively. In this work, we present the electronic and high-pressure behaviour of ThAs and ThSb performed using the tight-binding linear muffin–tin orbital method. The total energies within the atomic sphere approximation were calculated as a function of volume for both the B1 and B2 structures. The total energy calculations reveal that both ThSb and ThAs are stable in the B1 structure at ambient conditions and undergo structural transition to the B2 structure at pressures 78 and 240 kbar respectively, which are in good agreement with the experimental values. The calculated values of equilibrium lattice parameter and the transition pressure are found to be in good agreement with the experimental results.

Keywords. Electronic structure; high pressure; structural phase transition.

1. Introduction

Lanthanides from cerium on, successively fill the 4*f* shell until at lutetium the ‘*f*’ occupation is 4*f*¹⁴. Although practically there is no 5*f* occupancy at ambient pressure, the filling proceeds similar to the lanthanides, reaching 5*f*¹⁴ at lawrencium. At first sight one would thus expect a very similar evolution of the properties in general, and of the pressure behaviour in particular, along the two series.

However there are important differences. While the spatial extension of the 4*f* wave function around the nucleus in the lanthanide metals is relatively small, the 5*f* wave function interacts with 5*f* electrons of the neighbouring atoms. The 5*f* electrons of the actinide metals are itinerant or delocalized and participate in the metallic bonding. In contrast 4*f* electrons of lanthanides, the 5*f* electrons of americium and the heavier actinides are localized.

For high pressure behaviour of the compounds of ‘*f*’ elements, we are still much less advanced in systematic study and understanding than for the *f* elements themselves. The only group of compounds where systematic trends begin to emerge is for the B1 type structure and is the largest group of compounds formed by lanthanides and actinides. Nearly all 1:1 LnX and AnX compounds exhibit the NaCl-type (B1) structure. High pressure studies have only been reported for about 26 of the 121 known B1 type rare earth compounds. The proportion is higher for the actinides than for the lanthanides.

High pressure X-ray diffraction studies of uranium compounds have been carried out by Vedel *et al* (1986), Leger *et al* (1988), Gerward *et al* (1989) and Olsen *et al* (1990).

^{*} Author for correspondence

Very recently the high pressure behaviour of CmBi and UBi have been studied by Gensini *et al* (1993). The authors have shown from their studies that these compounds undergo a structural phase transition from B1 to B2 type, the transition is sluggish and is accompanied by a volume change in the range 8–12%. These features are similar to those of corresponding transitions in the alkali halides, indicating a common mechanism.

The aim of the present work is to study the structural phase transformation of the actinide compounds ThX ($X = N, P, S, As, Sb, Te$ and Se). For the compounds, such as As, Sb, Se and Te, the high pressure phase is generally of CsCl-type (B2) structure. In the B1 structure the ions have octahedral six-fold coordination whereas the B2 type structure is characterized by having both the ions in cubic eight-fold coordination. Geometrical considerations show that B1 structure is stable when the ratio of the cation to anion radius is between 0.41 and 0.73. A precise knowledge of the electronic structure of these compounds is not available. An attempt will be made in this direction by doing electronic structure calculation as a function of pressure. The method of calculation is briefly outlined in § 2 and the results are presented § 3.

2. Method of calculation

The energy bands of ThSb and ThAs have been obtained within the atomic sphere approximation (ASA) by means of the tight-binding linear muffin–tin orbital method (TBLMTO), which is the exact transformation of Andersen's (1975) linear muffin–tin orbitals to localized short-ranged orbitals or tight-binding orbitals. The exchange–correlation potential within the local density approximation is calculated using the parametrization scheme of von Barth and Hedin (1972). The most important relativistic corrections, namely Darwin's correction and the mass-velocity terms, were included while the spin orbit coupling term is neglected. The self consistent band structure calculations were carried out for 512-k points in the Brillouin zone and the density of states were obtained by the method of tetrahedra (Jepsen and Andersen 1971).

Under ambient conditions both ThSb and ThAs crystallizes in the NaCl-type structure (B1). It is well known that the LMTO method gives accurate results for the densely packed structures. Since B1 is a loosely packed structure, it becomes important for total energy calculations where the structural energy difference is only hundredths of a rydberg. Without breaking the crystal symmetry two equivalent empty spheres were included at the positions (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75), whereas the metal and non-metal occupies the positions (0, 0, 0) and (0.5, 0.5, 0.5). Apart from this, the combined correction terms were included which accounts for the nonspherical shape of the atomic cells, so that the errors in the LMTO method are minimized. We used minimal basis set consisting of *s*, *p*, *d* and *f* orbitals on metals, non-metal and empty sites.

In order to study the structural phase stability (Kalpana *et al* 1994) for each of the compounds, the total energies were computed for both B1 and B2 structures by changing the volume from $1.1 V_0$ to $0.7 V_0$, where V_0 is the experimental equilibrium volume (figure 1). The calculated total energies were fitted to the Birch–Murughan equation of state to obtain pressure–volume relation. The pressure is obtained by taking the volume derivative of the total energy. The bulk modulus is calculated from

Figure 1. The variation of total energy with volume for ThSb.

Figure 2. The variation of total energy with volume for ThAs.

the P–V relation. The structural phase stability is determined by calculating Gibb's free energy (G) for the two phases.

$$G = E_{\text{tot}} + PV - TS. \quad (1)$$

Table 1. Equilibrium lattice constant, transition pressure and volume reduction for ThSb and ThAs.

	ThSb (Expt.)	ThSb (TBLMTO)	ThAs (Expt.)	ThAs (TBLMTO)
$a(\text{B1})$ (a.u)	11.940	11.793	11.289	11.154
P_t (GPa)	9–12	7.8	18–26	24
$\Delta V/V_0$ (%)	9.0	9.76	10	8.8

Since the calculations are done at $T = 0$ K, the Gibb's free energy becomes equal to enthalpy (H)

$$H = E_{\text{tot}} + PV. \quad (2)$$

At a given pressure a stable structure is one for which the enthalpy has its lowest value and the transition pressures are calculated at which the enthalpies for the two phases are equal.

3. Results and discussion

Gerward *et al* (1989), from high pressure X-ray diffraction studies have shown that ThSb and ThAs undergo a pressure-induced structural transition from B1 to B2 in the pressure range between 9–12 GPa and 17–26 GPa with a volume collapse of 9 and 10% respectively. From the total energy calculations, we have estimated the equilibrium lattice parameter, transition pressure, bulk modulus and volume collapse for the above-mentioned compounds. They are presented in table 1, along with the experimental values. It can be seen from the table that the agreement between the theoretically calculated and the experimental values are good. Apart from this, the band profile and the total density of states are in agreement with the other reported works in the literature.

References

- Andersen O K 1975 *Phys. Rev.* **B12** 3060
 von Barth U and Hedin L 1972 *J. Phys.* **C5** 1629
 Gensini M, Haire R G, Benedict U, Benedict F and Hulliger F 1993 *Physica* **B190** 75
 Gerward L, Olsen J S, Benedict U, Dabos S, Luo J, Itie J P and Vogt O 1989 *High Press. Res.* **1** 235
 Jepsen O and Andersen O K 1971 *Solid State Commun.* **9** 1763
 Kalpana G, Palanivel B and Rajagopalan M 1994 *Phys. Rev.* **B50** 12318
 Leger J M, Vedel I, Redon A M, Rossat Mignod J and Vogt O 1988 *Solid State Commun.* **66** 1173
 Olsen J S, Gerward L, Benedict U and Itie J P 1990 *High Press. Res.* **2** 335
 Vedel I, Redon A M and Leger J M 1986 *Physica* **B144** 61