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Thermodynamic properties of UB_6 under high temperature and pressure

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First-principles calculations of the crystal structure of the uranium hexaboride (UB_6) have been carried out the plane-wave pseudopotential density functional theory method. The quasi-harmonic Debye model is applied to the study of the thermal and vibrational effects. The structural parameters, heat capacities, thermal expansions, Grüneisen parameters and Debye temperatures dependence on the temperature and pressure are obtained in the whole pressure range from 0 to 45 GPa and temperature range from 0 to 1000 K.

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1. Introduction

A compounds including boron element have been used many research fields [1] and they have a variety of interesting physical properties such as high hardness [2-4], magnetism (ferromagnetism) [5], low work function [6], high melting point [7] etc. Recently, N. Singh et all have been investigated the electronic structure and optical properties of rare-earth hexaborides RB_6 (R=La, Ce, Pr, Nd, Sm, Eu, Gd) by using first-principle techniques [8]. Single crystals of pure and carbon-substituted divalent hexaborides EuB_6 and YbB_6 have been prepared by the Al flux method by J. M. Tarascon et al. [9]. S. F. Matar et al. have been studied the electronic structures of uranium borides including diborides, tetraborides, hexaborides and dodecaborides from local spin-density functional calculations [10].

LaB_6 which a member of hexaboride family is used as thermionic electron emitters and this compound is metallic and becomes superconducting at T_c=0.45 K [11]. However, uranium hexaboride (UB_6) has same structure with LaB_6, and in this present work its thermodynamic properties such as heat capacity, thermal expansion, Grüneisen parameter and Debye temperature are studied in detail. UB_6 has Pm3m space group. And its crystal structure consists of boron octahedrons (B_6) and uranium atoms localized to interstitial space of octahedrons [12].

2. Theory and calculation details

We studied thermodynamic properties of UB_6 hexaboride by using CASTEP simulation package [13] based on density functional theory. The Vanderbilt ultrasoft pseudopotential [14] was used in this study. Exchange-correlation effects were taken into account using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [15]. The plane wave cut-off energy of 500 eV was employed. The valance electrons configuration considered in this study were including $5f^3$ $6s^2$ $6p^6$ $6d^1$ $7s^2$ for U and $2s^2$ $2p^1$ for B. k-point meshes of 10×10×10 were generated by using Monkhorst-Pack scheme [16]. Ultra-fine setup of software package was chosen in the calculations, namely, all calculations were converged when the maximum ionic Hellman-Feynman force was below 0.01 eV/Å, maximum displacement between cycles was below 5.0×10^{-4} Å, maximum energy change was below 5.0×10^{-6} eV/atom, and maximum stress was below 0.02 GPa. Additionally, spin polarization effects were not considered in the calculations.

To obtain the thermodynamic properties of UB_6, quasi-harmonic Debye model [17, 18] is used and in this model, non-equilibrium Gibbs function $G^*(V;P,T)$ as follows:

$$G^*(V;P,T) = E(V) + PV + A_{vib}(\theta(V);T) \qquad (1)$$

where $E(V)$ is total energy of unit-cell, $\theta(V)$ is the Debye temperature, A_{vib} is vibrational Helmholtz free energy expressed as

$$A_{vib}(\theta;T) = nKT\left[\frac{9}{8}\frac{\theta}{T} + 3ln\left(1 - e^{-\theta/T}\right) - D\left(\frac{\theta}{T}\right)\right] \qquad (2)$$

Here, n is the number of atoms per formula unit. $D(\theta/T)$ is Debye integral given as

$$D(y) = \frac{3}{y^3}\int_0^y \frac{x^3}{e^x-1}dx \qquad (3)$$

and θ is expressed as

$$\theta = \frac{\hbar}{k}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma)\sqrt{\frac{B_s}{M}} \qquad (4)$$

for an isotropic solid. Where M is the molecular mass per formula unit, B_s is adiabatic bulk modulus and σ is Poisson ratio. For UB_6, M=302.89 a.m.u and σ=0.26 However, $f(\sigma)$ function is expressed as

$$f(\sigma) = \left\{3\left[2\left(\frac{2}{3}\frac{1+\sigma}{1-2\sigma}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2}\right]^{-1}\right\}^{1/3} \qquad (5)$$

Then, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume V as follows:

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{P,T} = 0 \tag{6}$$

By solving Eg.(6), the isothermal bulk modulus is found to be

$$B_T(P,T) = -V\left(\frac{\partial P}{\partial V}\right) = V\left(\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\right)_{P,T} \tag{7}$$

However, other thermodynamic properties such as heat capacity at constant volume (C_V), heat capacity at constant pressure C_P, thermal expansion (α) and Grüneisen parameter (γ) are respectively represented as

$$C_V = 3nk\left[4D(\theta/T) - \frac{3\theta/T}{e^{\theta/T}-1}\right] \tag{8}$$

$$\alpha = \frac{\gamma C_V}{B_T V} \tag{9}$$

$$C_P = C_V(1 + \alpha\gamma T) \tag{10}$$

$$\gamma = -\frac{d\ln\theta(V)}{d\ln V}$$

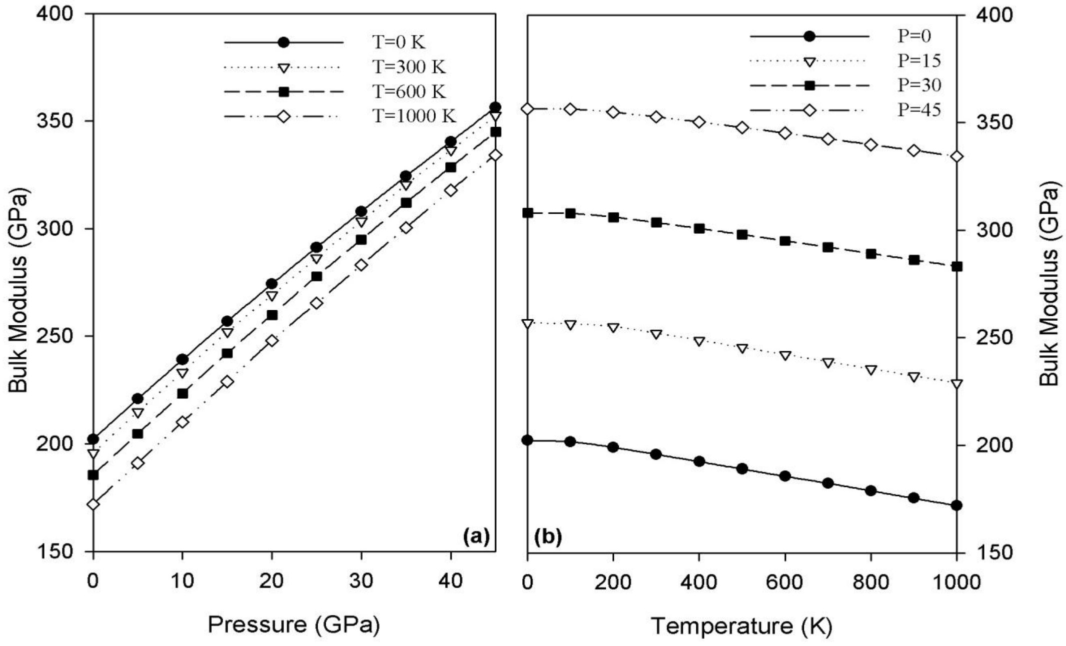

Fig. 1. Pressure (a) and temperature (b) dependence of the isothermal bulk modulus for UB_6..

3. Results and discussion

UB_6 hexagonal crystal structure is consist of octahedrons and boron chains of two-atoms. The space group of this structure is Pm3m and lattice parameter was calculated by Matar et al. as a = 4.112 Å [10]. The calculated lattice parameter in this work as a= 4.157 Å. It is seen that the calculated values are in good agreement with another theoretical calculation. In order to investigate the behaviors of structure under high pressure, hydrostatic pressure is applied to UB_6 on the 0-45 GPa interval by step of 5 GPa. We show the relations of the bulk modulus as a function of temperature T up to 1000 K at P=0, 15, 30 and 45 GPa in Fig. 1. Isothermal bulk modulus increases at the constant temperature with increasing pressure, this case is shown in Fig. 1 a. It seen that in Fig. 1 b, isothermal bulk modulus decreases at the constant pressure when temperature is increased.

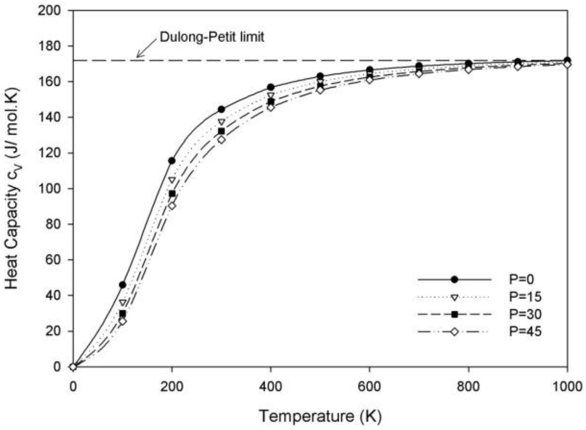

Fig. 2. Temperature dependence of the heat capacity (c_V) at different pressure for UB_6.

In Fig. 2, we explain to change of the heat capacity at constant volume (C_v) according as temperature at the constant pressure in the 0-45 GPa interval. At low temperature, heat capacity at constant volume(C_v) is very small and at high temperature approaches a constant value. The values follow the debye model at low temperature (C_v (T)~T^3) and the classical behavior (C_v (T) ~3R for mono atomic solids) is found at sufficient high temperatures, obeying Dulong and Petit's Rule. Fig. 2 illustrate that the heat capacity increases with the temperature at the same pressure and decreases with the pressure at the same temperature, the influences of the temperature on the heat capacity are much more significant than that of the pressure on it.

We presented the thermal expansion coefficient α with temperature and pressure for UB_6 in Fig. 3. Our calculated thermal expansion coefficient at 1000 K and 0 GPa is about 4.612×10^{-5} K^{-1}. The thermal expansion coefficient of diamond is ≈ 4.5×10^{-6} K^{-1} [19]. From Fig. 3(a), thermal expansion coefficient α is very high at low pressure and when pressure is increased this value decreases almost exponentially. The thermal expansion coefficient α increases at high temperature values and when pressure is increased this value decreases. In Fig. 3(b), the effects of pressure on the thermal expansion coefficient α are very small at low temperatures; the effects are increasingly obvious as the temperature increases. As pressure increases, the thermal expansion coefficient α increases slowly [20].

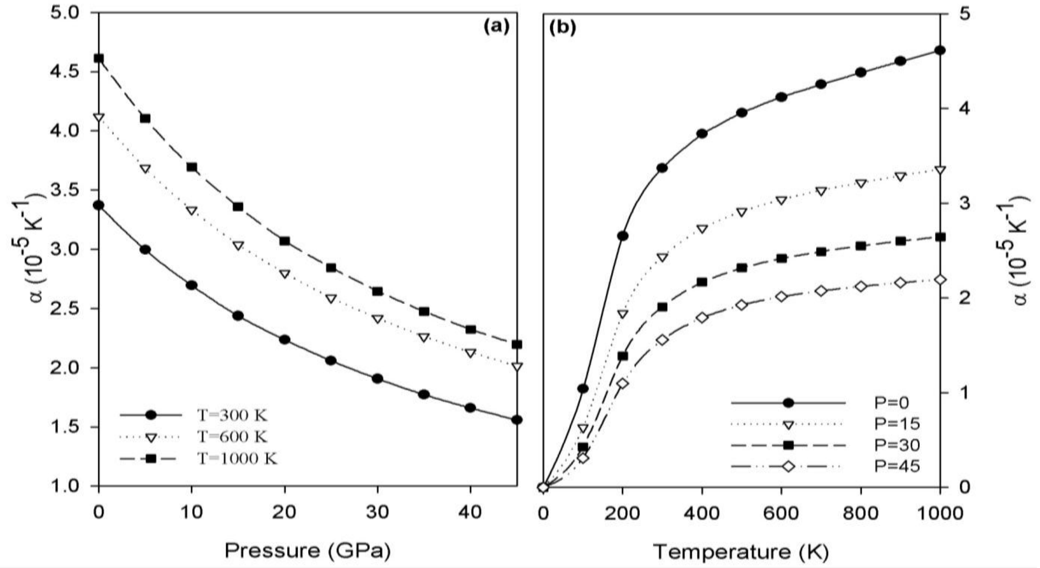

Fig. 3. Pressure (a) and temperature (b) dependence of the thermal expansion coefficient (α) for UB_6.

The calculated properties at different temperatures are very sensitive to the vibrational modes [20]. In the quasi-harmonic Debye model, Debye temperature and Grüneisen parameter are two important parameter. In Table 2 are listed the Debye temperatures and Grüneisen parameters. At the constant temperature, as pressure increases, Debye temperature increases and Grüneisen parameter decreases. However, at the constant pressure, as temperature increases, Debye temperature decreases and Grüneisen parameter increases.

Table 2. The calculated Debye temperature and Grüneisen parameter of UB_6. under pressure at different temperatures.

T (K)	P (GPa)	0	15	30	45
300	θ	597.41	670.40	728.66	779.01
	γ	1.774	1.616	1.503	1.414
600	θ	585.15	660.82	721.45	772.98
	γ	1.801	1.636	1.516	1.424
1000	θ	566.63	646.63	710.38	763.73
	γ	1.843	1.666	1.537	1.440

4. Conclusions

First-principles calculations of the crystal structure of the Uranium hexaboride (UB_6) have been carried out the plane-wave pseudopotential density functional theory. The thermodynamic properties including the equation of state, the isothermal bulk modulus, the Debye temperature, the heat capacity, thermal expansion and grüneisen parameter are predicted using the quasi-harmonic Debye model.

We showed that isothermal bulk modulus increases at the constant temperature with increasing pressure. And isothermal bulk modulus decreases at the constant pressure when temperature is increased. At low temperature, heat capacity at constant volume (C_v) is very small and at high temperature approaches a constant value. The thermal expansion coefficient α is very high at low pressure and when pressure is increased this value decreases almost exponentially. At the constant temperature as pressure increases, Debye temperature increases and Grüneisen parameter decreases.

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