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First principle study on the elastic and thermodynamic properties of TiB_2 crystal under high temperature*

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This paper predicts the elastic and thermodynamic characteristics of TiB_2 crystal through the method of density functional theory within the generalized gradient approximation (GGA). The five independent elastic constants (C_{ij}), the bulk modulus (B_0), the dependence of bulk modulus (B_0) on temperature T and pressure P and the coefficient of thermal expansion ($\alpha_{\rm L}$) at various temperatures have been evaluated and discussed. According to calculation, the bulk modulus will increase with increasing pressure while decrease with the increasing temperature. The coefficient of thermal expansion is consistent with the famous Grüneisen's law when the temperature is not too high. The obtained results agree well with the experimental and other theoretical results.

Keywords: titanium diboride, density functional calculations, bulk modulus, coefficient of heat expansion

PACC: 7430E, 6220D, 6550, 6410

1. Introduction

Titanium diboride (TiB_2) is well known as a ceramic material with relatively high strength and durability as characterized by high melting point (about 3500 K), strong hardness (about 25 GPa at room temperature), high strength to density ratio, strong wear resistance, low electrical resistivity and excellent chemical inertness.[1,2] These characteristics make it a potential candidate for several high-performance applications, in cutting tools, electrodes and wear-resistant components. Especially in recent years, some composite materials on TiB_2 have become one of the hot research topics because of its perfect properties.[3,4] But most these researches mainly focused on the electronic structure and neglected the studies on the elastic and thermodynamic characteristics. However, the researches about elastic and thermodynamic properties of TiB_2 will give much precise knowledge and provide theoretic guide for the industrial application of TiB_2 crystals.

Lots of research works have been done on TiB_2 crystals. However, only a few of them paid attention to the thermodynamic properties and the behaviours under ambient pressure and temperature. It is well known that the specific knowledge about material plays an important role in devices design and industrial application. For example, to improve the wear-resisting ability of materials, we can grow ultrahard film on the substrate materials. One of the important factors we should consider during this processing is the match of heat expansion for both two kinds of materials. In addition, we also need the knowledge about the physical properties of the material under different temperatures and pressures. In our paper, we will employ the method of density functional theory (DFT) to study the properties of TiB_2 under different temperatures and pressures. Especially, for the first time, we will give the information about the heat expansion coefficient of TiB_2 crystal at different environments by DFT.

2. Methods

The calculations are based on the DFT[5] within the generalized gradient approximation (GGA)[6] using ultrasoft pseudopotential and plane wave ba-

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sis sets[7,8] implemented in the VASP code. The plane wave cutoff is 400 eV for structural optimization and 470 eV for static electronic structural calculation. Brillouin zone sampling is preformed on a grid of $21 \times 21 \times 21$ Monkhorst–Pack special points and the self-consistent convergence of the total energy is at 1×10^{-6} eV/atom. The bulk unit cell lattice vectors and atomic coordinates of TiB_2 were relaxed at a series of fixed volumes by optimizing both the forces and stresses. The obtained energies were fitted with the third-order Birch–Murnaghan equation of state (EOS)[9] to give the equilibrium volume and the minimum energy.

In order to calculate the elastic coefficients, some defined strains should be loaded to the crystals. Because the internal energy $E(V, \{\delta_i\})$ of crystal under a specified strain can be expressed by expanding the internal energy $E(V)$ of the deformed crystal with respect to the strain tensor, the equation with Voigt notation can be expressed as follows:[10]

$$E(V, \delta_i) = E(V) + V \sum_{i=1}^{6} \sigma_i \delta_i + \frac{1}{2} V \sum_{i,j=1}^{6} C_{ij} \delta_i \delta_j + \dots .$$

For hexagonal crystal, there are five independent elastic coefficients (Named C_{11}, C_{12}, C_{13}, C_{33} and C_{44}), which can be determined by five sets of strains. Finally, we can determine the dependence of the resulting change in energies by applying different deformations to the equilibrium lattice of the hexagon unit cell and get the elastic constants. For this calculation, up to eight strains, which are from –0.012 to 0.012 in step of 0.003, are loaded to the crystal to determine every elastic coefficient.

3. Results and discussion

The crystallization of TiB_2 occurs in the AlB_2 structure, space group $P6/mmm$, with one titanium at the origin and two boron atoms at the site 2d (1/3, 2/3, 1/2), as shown in Fig.1.

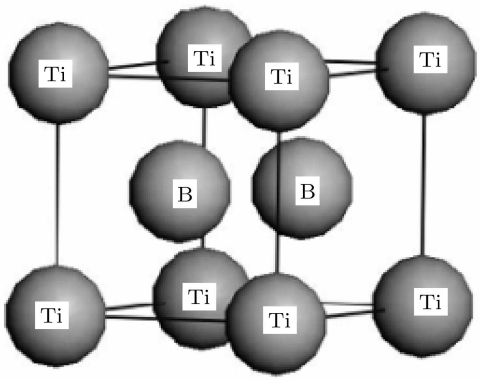


Fig.1. Schematic view of TiB_2 unit cell.

According to our calculation, the equilibrium lattice parameters a and c are about 0.30315 nm and 0.3238 nm, respectively, which agree well with the experimental values ($a = 0.3030$ nm, $c = 0.3232$ nm).[11] The calculated Debye limit temperature (θ_D) is about 1023.4 K at $T = 0$ K and $P = 0$ GPa, which agrees well with the other experimental results about 1005.6 K (neutron scattering method)[12] and 1024.0 K (Mössbauer experiments)[12] and other theoretical results about 1033.7 K[12] and 988.3 K.[13] The results of the elastic constants are shown in Table 1.

The anisotropic factor[14] can be defined as: $A = 2C_{44}/(C_{11} - C_{12})$. According to our calculation, the A is about 0.90, which consists with the experimental and other theoretical results,[15–17] as shown in Table 1. Thus, the TiB_2 is close to isotropic, because the value of $A = 1$ represents completely elastic isotropy, while values smaller or greater than 1 measure the degree of elastic anisotropy.

Table 1. Calculated elastic constants C_{ij} (in GPa) and bulk modulus (in GPa) in Voig and Reuss approximation (namely B_V, B_R, respectively) and anisotropic factor (A) for TiB_2 at $P = 0$ GPa and $T = 0$ K.

methods	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B_V/B_R	A
experimental[15]	660	48	93	432	260	247/240	0.85
theoretical[16]	650	79	100	443	256	256/249	0.89
theoretical[A]	777*		83	568	—	273/270	—
theoretical[B]	730*		78	572	—	260/260	—
this work	646.5	76.5	110	452	255	260/255	0.90

[*] $C_{11} + C_{12}$

[A] DFT with *ab initio* norm-conserving pseudopotentials in the local density approximation (LDA) for the exchange–correlation contribution to the energy.[17]

[B] The same as in note A, but in the GGA.[17]

In order to obtain the macroscopic mechanical parameters of TiB_2, we also calculated the bulk modulus (B) using two kinds of methods: Voigt (V)[18] and Reuss (R),[19] the formulations are listed as follows:

$$B_{\rm V} = \frac{2}{9}\left(C_{11} + C_{12} + \frac{C_{33}}{2} + 2C_{13}\right), \quad (1)$$

$$B_{\rm R} = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}. \quad (2)$$

The results are listed in Table 1. According to our calculation, both the values of $B_{\rm V}$ and $B_{\rm R}$ are slightly larger than the experimental results, which can be partly attributed to the fact that the theoretical values are got at $T = 0\,{\rm K}$ while the experimental values usually got at $T = 300\,{\rm K}$.

In order to investigate dependence of bulk modulus B on the temperature T and pressure P we apply the quasi-harmonic Debye model method[20] by which the thermodynamic properties of MgB_2,[21,22] GaAs[23] and AlB_2[24] have been researched successfully. The zero pressure bulk modulus B_0 is determined by fitting the calculated energy–volume (E–V) data points to Birch–Murnaghan EOS:[9]

$$\begin{aligned}&\Delta E(V)\\ &= E - E_0\\ &= B_0 V_0\left[\frac{V_{\rm n}}{B_0'} + \frac{1}{1 - B_0'} + \frac{V_{\rm n}^{1-B_0'}}{B_0'(B_0' - 1)}\right], \end{aligned} \quad (3)$$

where E_0 is the equilibrium energy. The pressure P versus the normalized volume $V_{\rm n}(V_{\rm n} = V/V_0$, where V_0 is the equilibrium volume at zero pressure) is obtained through the following relationship:

$$P = -\frac{{\rm d}E}{{\rm d}V} = \frac{B_0}{B_0'}\left[V_n^{-B_0'} - 1\right]. \quad (4)$$

Besides, the bulk modulus B is also investigated under various pressures and temperatures using the quasi-harmonic Debye model. In the quasi-harmonic Debye model, the non-equilibrium Gibbs energy of the crystal phase $G^*(V; P, T)$ of TiB_2 can be written as[25]

$$G^*(V; P, T) = E(V) + PV + A_{\rm Vib}(V; T), \quad (5)$$

where $E(V)$ is the total energy per unit cell, the second term, PV, corresponds to the constant hydrostatic pressure condition, the third term, $A_{\rm vib}$, is the vibrational Helmholtz free energy, which can be written as[26,27]

$$\begin{aligned}&A_{\rm vib}(\Theta_{\rm D}; T)\\ &= nkT\left[\frac{9}{8}\frac{\Theta_{\rm D}}{T} + 3\ln(1 - {\rm e}^{-\Theta_{\rm D}/T}) - D(\Theta_{\rm D}/T)\right], \end{aligned} \quad (6)$$

where $\Theta_{\rm D}$ is the Debye temperature, $D(\Theta_{\rm D}/T)$ represents the Debye integral, n is the number of atoms per formula unit. By solving the following equation:

$$\left(\frac{\partial G^*(V; P, T)}{\partial V}\right)_{P,T} = 0, \quad (7)$$

one could obtain the isothermal bulk modulus B

$$B_{(P,T)} = V\left(\frac{\partial^2 G^*(V; P, T)}{\partial V^2}\right)_{P,T}. \quad (8)$$

We now investigate the dependence of bulk modulus B on temperature T and pressure P. The relations of the bulk modulus B as a function of temperature T up to 2000 K are plotted in Fig.2. The calculated values of bulk modulus B_0 are 247 GPa, 231 GPa and 210 GPa at $T = 20$°C, 500°C and 1000°C, respectively,

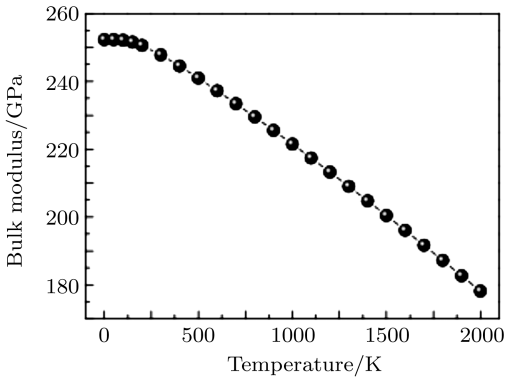


Fig.2. The bulk modulus B_0 as a function of temperature T at $P = 0\,{\rm GPa}$.

which agree well with experimental results reported by Munro,[28] as shown in Table 2. In addition, we find from Fig.2 that B_0 nearly keeps constant when $T < 300\,{\rm K}$, the lattice parameters a and c also nearly keep constant, which also results in constant volume V of TiB_2 crystal. When $T > 300\,{\rm K}$, the bulk modulus B decreases obviously with the increase of T, which indicates that the cell volume changes rapidly. It is the rapid variation of volume which makes the rapid decrease of bulk modulus B_0. By fitting the $B_0 - T$ data points to third-order polynomial, we obtain the following relationship:

$$\begin{aligned}B_0 \;=\; &253.702 - 1.701\times10^{-2}T - 1.935\times10^{-5}T^2\\ &+4.551\times10^{-9}T^3, \quad \text{for} \quad T < 2000\,{\rm K}. \end{aligned} \quad (9)$$

Table 2. The experimental/theoretical values of bulk modulus and coefficient of heat expansion at different temperatures.

temperature/ K	bulk modulus/GPa		coefficient of heat expansion/10^{-6} K^{-1}			
	experimental[A]	present work	experimental[B]			this work[C]
			α_a	α_c	α_m	α_L ($\alpha_V/3$)
293	240	245	6.4	9.2	7.4	7.0
773	234	231	7.0	9.8	7.9	9.6
1273	228	214	7.7	10.4	8.6	11.5
1473	—	202	7.9	10.6	8.8	12.0
1773	—	189	8.3	11.0	9.2	13.0

[A] Relative standard uncertainly is 24%.[24]
[B] Relative standard uncertainly for α_a, α_c and α_m is 7%, 5% and 6%, respectively.[28]
[C] We have assumed the coefficient of linear expansion α_L and the coefficient of cubical expansion α_V satisfies the equation: $\alpha_L = \alpha_V/3$.

In addition, the relationship between bulk modulus B and pressure P at different temperatures T = 300, 1000 and 2000 K is plotted in Fig.3. It can be seen from Fig.3 that the relationships between bulk modulus B and pressure P are nearly linear at various temperatures. The bulk modulus B will increase with the increase of pressure P, while decrease with the increase of temperature T. Such results can be attributed to the fact that the effect of increasing pressure is same as decreasing temperature on the materials.

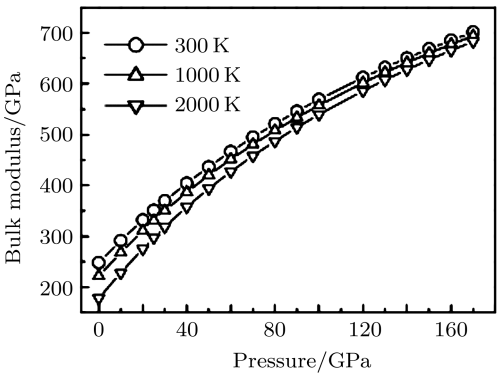


Fig.3. The bulk modulus B_0 as a function of pressure P at different temperature T.

The problem of thermal expansion is another key question which should be paid attention to during the producing process of composite materials. According to the Grüneisen's approximate EOS:

$$P = -\frac{\mathrm{d}U}{\mathrm{d}V} + \gamma\frac{\bar{E}}{V}, \tag{10}$$

where P is the external pressure, for solid state materials, the pressure P usually can be ignored in atmosphere, U and V are the inner energy and volume of the crystal, respectively, $\bar{E}$ is the mean vibrational energy, γ is the Grüneisen parameter, which can be deduced from the Mei–Grüneisen equation:[20]

$$P - P_{\mathrm{static}} = \gamma\frac{U}{V}. \tag{11}$$

Finally, the coefficient of cubical expansion α_V can be written as

$$\alpha_V = \frac{\gamma C_V}{B_T V}, \tag{12}$$

where C_V is the heat capacity at constant volume and B_T is the isothermal bulk modulus. As we all know, the coefficient of linear expansion α_L and coefficient of cubical expansion α_V are satisfied with the equation

$$\alpha_L = \frac{1}{3}\alpha_V. \tag{13}$$

According to above analysis, it is reasonable to assume that the thermal expansion is isotropic for TiB_2 crystal. So we can obtain the coefficient of linear expansion at different temperatures, as shown in Fig.4 and our results are consistent with the experimental results reported by Munro.[28] In addition, it can be also seen from Fig.4 that there is a knee point (about 500 K) when the heat expansion coefficient changes with increasing temperature. The rate of slope between the coefficient of linear expansion (α_L) and temperature (T) is significantly greater before the knee point than that after the knee point. According to our calculation, the parameters of γ, B_T and V change slightly (γ and V increase while the B_T decreases) when the temperature is no more than about 700 K, thus, the coefficient of linear expansion α_L mainly depends on the heat capacity C_V. As a result, there is approximately linear relationship between α_V and C_V at lower

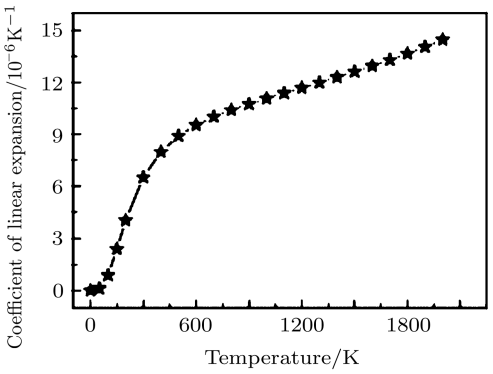


Fig.4. The dependence of the coefficient of linear expansion $\alpha_{\rm L}$ on the temperature T.

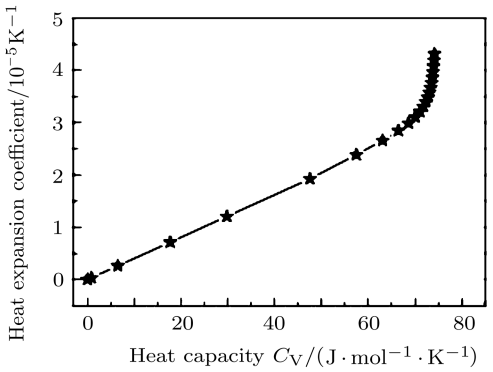


Fig.5. The dependence of the coefficient of bulk expansion $\alpha_{\rm V}$ on the heat capacity $C_{\rm V}$.

temperature, as shown in Fig.5. In addition, as we all know, the $C_{\rm v}$ will reach the classical limit value and nearly keeps constant at high temperature. As a consequence, the coefficient of linear expansion $\alpha_{\rm L}$ will increase dramatically with the slow increase of the heat capacity $C_{\rm V}$ at high temperature, as shown in Fig.5.

4. Conclusion

We have employed the method of DFT and investigated the elastic characteristics of TiB_2 crystals. The five independent elastic constants and the dependence of bulk modulus on pressure and temperature have been obtained. We find that the bulk modulus will increase with the increase of pressure while decrease with the increase of temperature. In addition, we have investigated the dependence of the heat expansion coefficient $\alpha_{\rm L}$ on temperature. We also find that the expansion coefficient $\alpha_{\rm L}$ is approximately proportional to heat capacity $C_{\rm V}$ when the temperature is no more than 700 K. Our results are consistent with the other experimental and other theoretical results.

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