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Theoretical elastic stiffness and thermodynamic properties of zirconium dodecaboride from first principles calculation

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ABSTRACT

The calculations based on density functional theory have been performed for the cubic zirconium dodecaboride (ZrB_{12}). Structural and elastic properties were obtained using Perdew–Burke–Enzerh (PBE) exchange- correlation functional. The lattice parameters and elastic constants at different pressures (0–30 GPa) have been calculated and total energies were used to determine the equation of state and free energy within the quasi-harmonic approximation. The agreement between the theoretical and experimental properties was found to be satisfactory. The thermodynamic properties including the normalized volume V/V_0, bulk modulus B, thermal expansion α, heat capacity C_P and C_V, Grüneisen constant γ and Debye temperature have been estimated at pressures from 0 to 50 GPa and temperatures from 0 to 2000 K, respectively. We anticipate that the calculated elastic and thermodynamic results can give an important reference especially to those not easy to be experimentally obtained.

1. Introduction

Metal dodecaborides (MB_{12}) materials are the subject of many scientific researches due to their interesting combination of excellent properties such as high-melting points, hardness, thermal and chemical stability. The clathrate-like rigid network composed of boron atoms make them serve as a paradigm for other cluster compounds such as fullerides or higher borides [1]. In the late 1960s, Matthias et al. [2] found that ZrB_{12} has the highest superconducting critical temperature ($T_c \approx 6$ K) in several of metal dodecaborides (M = Sc, Y, Zr, La, Lu, and Th). In order to understand its superconducting behavior, this compound has been widely studied in virtue of recent progress in growing large high quality single crystals of dodecaborides [3–8]. It was previously considered that the superconductivity in ZrB_{12} is directly connected with the vibrations of boron complexes [3]. Recently, the *ab initio* calculations and experimental research suggested that the quasilocal Zr vibrations are responsible for a considerable electron–phonon interaction and could take part in the formation of the superconducting state [9,10]. Furthermore, Zr electrons contribution to the electronic density of states at the Fermi level plays a key role in the negative pressure effect on T_c which is observed from magnetization measurements under pressure [11].

In addition, the structural and elastic properties of ZrB_{12} also deserve special attention. Grechnev et al. measured the elastic constants of transition metal dodecaborides with the high precision apparatus. They found that the bulk moduli of MB_{12} increase with increased filling of the conduction [11,12]. Recently, Escamilla et al. studied the structural and elastic properties of ZrB_{12} under pressure with density functional theory (DFT). The influences of pressure on Fermi level and electron–phonon coupling constant were especially concerned [13]. Korozlu et al. discussed the electronic and optical of MB_{12} based on the results of *ab initio* investigations with the local-density approximation (LDA) [14]. Simultaneously, the hardness and other elastic properties of MB_{12} under high pressure (0–50 GPa) were estimated with the generalized gradient approximation (GGA). The pressure tendency of hardness and elastic constants is attributed to combined interaction of bonding nature and the crystal structure [15].

There are some theoretical researches have been done on ZrB_{12}, however, most of them are focused on electronic structure, elastic constants and phonon dispersion. Few pay attention to the elastic stiffness and thermodynamic properties under high temperature and pressure, which are very important to extend our knowledge to material's performance under extremely severe environment. Therefore, it is necessary to examine the thermal and pressure influences on its elastic and thermodynamic properties. To address this interest, the first principles methods will be used to study the structural and elastic properties of ZrB_{12}. In addition, the thermodynamic properties of cubic ZrB_{12} are also investigated by using a quasi-harmonic Debye model. The outline of the article is as follows. Firstly, the brief description of the quasi-harmonic approximation and the computational details of our study are given in

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Section 2. Secondly, results for the structural, elastic and thermodynamic properties of ZrB_{12} are presented and discussed in Section 3. Finally, the conclusions are given.

2. Computational details

The electronic structure total energy calculations are implemented based on the DFT, the exchange and correlation potentials are treated within the GGA in the scheme of Perdew–Burke–Ernzerhof (PBE) [16] and the non-local ultrasoft pseudopotential is used to describe the interactions between electrons and the ion cores. The electronic wave functions are expanded in a plane wave basis set with energy cut-off 600 eV and the pseudo-atomic calculations are performed for Zr ($4s^2 4p^6 4d^2 5s^2$) and B ($2s^2 2p^1$), respectively. For the Brillouin-zone k-point sampling, we use the $10 \times 10 \times 10$ Monkhorst–Pack mesh, where the self-consistent convergence of the total energy is 5.0×10^{-7} eV/atom. The tolerances for the geometry optimization were: difference in total energy within 5×10^{-6} eV atom^{-1}, maximum ionic Hellmann-Feynman force within 0.01 eV Å^{-1}, maximum ionic displacement within 5×10^{-4} Å and maximum stress within 0.02 GPa. A primitive cell of ZrB_{12} with 13 atoms was used in all the first-principles calculations. The elastic coefficients were determined from first-principles calculation by applying a set of given homogeneous deformations with a finite value (the maximum strain amplitude of 0.003) and calculating the resulting stress with respect to optimizing the internal degrees of freedoms. All the total energy electronic structure calculations are implemented through the Cambridge Serial Total Energy Package (CASTEP) program [17].

To study the thermodynamic properties of the cubic ZrB_{12}, we apply the quasi-harmonic Debye model [18,19], in which the non-equilibrium Gibbs function $G^*(V;P,T)$ takes the form of:

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

where $E(V)$ is the total energy, PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and the vibrational Helmholtz free energy A_{vib} can be written as [20]:

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

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, Θ is expressed by [20]:

$$\Theta = \frac{\hbar}{k}(6\pi^2 V^{1/2} n)^{1/3} f(\sigma)\sqrt{\frac{B_S}{M}}$$

where M is the molecular mass per formula unit, σ is Poisson ratio. B_S is the adiabatic bulk modulus approximated by the static compressibility [18]:

$$B_S \approx B(V) = V\left[\frac{d^2E(V)}{dV^2}\right]$$

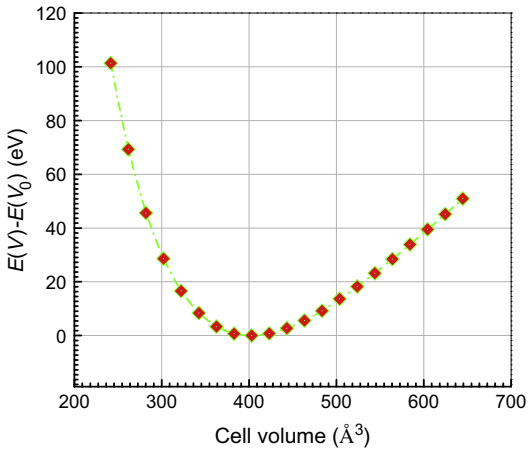

Fig. 1. Total lattice energy difference of ZrB_{12} as a function of cell volume.

Table 1
Lattice parameter (a, Å), boron parametric position (x), elastic constants (C_{ij}, GPa), bulk modulus (B, GPa), shear modulus (G, GPa), Young's modulus (E, GPa), Deby temperature (Θ_D, K), Poisson's ratio (σ) and Lamé constant (λ, GPa) of polycrystalline ZrB_{12} calculated with the Voigt, Reuss and Hill assumptions (labeled as subscript V, R and H) at different pressures (P).

P	a	x	C_{11}	C_{12}	C_{44}	$B_V = B_R = B_H$	G_V	G_R	G_H	E_H	λ_H	ν_H	Θ_D	B_H/G_H
0	7.3859	0.1609	412.6	141.3	244.4	231.7	200.9	185.1	193.0	453.1	103.1	0.174	1206	1.201
2.5	7.3597	0.1609	425.5	148.6	249.5	240.9	205.1	188.9	197.0	464.4	109.6	0.179	1217	1.223
5	7.3352	0.1609	433.8	155.1	253.6	248.0	207.9	191.0	199.4	471.8	115.0	0.183	1223	1.244
7.5	7.3113	0.1608	446.1	163.3	258.8	257.6	211.8	194.3	203.1	482.4	122.2	0.188	1232	1.268
10	7.2881	0.1608	457.0	171.2	262.8	266.5	214.8	196.8	205.8	491.0	129.3	0.193	1239	1.295
12.5	7.2662	0.1608	470.5	177.9	267.6	275.4	219.1	201.0	210.0	502.4	135.4	0.196	1250	1.311
15	7.2446	0.1608	481.7	185.5	270.4	284.2	221.5	203.3	212.4	510.1	142.7	0.201	1256	1.338
17.5	7.2239	0.1607	488.5	191.5	274.1	290.5	223.9	204.8	214.3	516.1	147.6	0.204	1261	1.356
20	7.2040	0.1608	500.0	200.1	279.8	300.1	227.9	207.8	217.8	526.2	154.8	0.208	1270	1.378
22.5	7.1846	0.1607	510.2	205.8	283.0	307.3	230.7	210.6	220.6	534.1	160.2	0.210	1276	1.393
25	7.1655	0.1607	518.1	212.0	285.2	314.0	232.3	212.0	222.2	539.3	165.9	0.214	1280	1.413
27.5	7.1470	0.1607	533.7	219.9	291.3	324.5	237.5	217.0	227.3	552.7	173.0	0.216	1293	1.428
30	7.1291	0.1607	551.8	234.8	299.2	340.5	242.9	220.8	231.9	566.9	185.9	0.223	1305	1.468
GGA [13]	7.3882	0.166	414.2	139.8	243.7	231.3	–	–	255.5	560.2	–	0.10	803–830 (0–10 Pa)	
GGA [14]	7.308–7.062		437.9–569.5	146.3–231.1	256.2–307.4	243.5–343.9			204.4–241.9	479.1–587.9		0.17–0.22		
LDA [15]	7.33					235.8								
LDA [9]	7.415	0.1606												
Exp. [9]	7.4077	0.1667												
Exp. [11]			443	129	265	234						0.226	1260	