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Elastic and thermodynamic properties of c-BN from first-principles calculations*

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The elastic constants and thermodynamic properties of c-BN are calculated using the first-principles plane wave method with the relativistic analytic pseudopotential of the Hartwigen, Goedecker and Hutter (HGH) type in the frame of local density approximation and using the quasi-harmonic Debye model, separately. Moreover, the dependences of the normalized volume V/V_0 on pressure P, as well as the bulk modulus B, the thermal expansion α, and the heat capacity C_V on pressure P and temperature T are also successfully obtained.

Keywords: elastic constants, thermodynamic properties, local density approximation, c-BN

PACC: 6220D, 6740K, 7115M, 7470E

1. Introduction

In the binary boron-nitride system, four crystalline polymorphs are known as well as some amorphous modifications. Cubic boron nitride (c-BN) is the most important form and is the second hardest material after diamond. Therefore, c-BN has been utilized in industrial application as cutting tools and abrasives.[1,2] The compound crystallizes in a zinc blende structure which closely resembles that of diamond, each atom being tetragonally linked to four neighbouring boron or nitrogen atoms by strong covalent bonds. Charge accumulates strongly between the atoms due to the strong interatomic overlap of s and p orbitals.[3] Moreover, because of its wide band gap ($E_g \approx 6.6\,\mathrm{eV}$) and good thermal conductivity, c-BN also has the potential for the high-temperature and high-power electronic applications.[1] Therefore it is of great interest to physicists in experimental[4−10] and theoretical[11−19] investigations.

Earlier work[4] indicated hexagonal BN (h-BN) to be the stable phase under ambient conditions while cubic BN (c-BN) and wurtzite BN (w-BN) were synthesized from h-BN at high temperature and high pressure. Later, experiments[5−7] revealed more information with improved accuracy about the characteristics of c-BN. It was found that c-BN was thermodynamically stable at ambient environment and h-BN became stable only at high temperatures $T =$ 900–1500 °C. The equilibrium phase boundary between h-BN and c-BN was determined at 3–6 GPa and 1200 °C–2200 °C.[8] Despite these studies, the structural phase and its thermodynamic stability of c-BN under high temperature and high pressure remain unresolved.

On the other hand, elastic properties are related to equations of state (EOS), phonon spectra, specific heat, thermal expansion, Debye temperature, Grüneisen parameter, and so on. The knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internal strain, sound velocities, and fracture toughness.[20] To date, several theoretical methods have been applied successfully to the calculation of the elastic constants of c-BN, such as the full-potential augmented plane waves plus local orbitals method (FP-APW+lo),[11] the molecular dynamics simulation method (MD),[12−14] the full-potential linear muffin-tin orbital method (FP-LMTO),[15] and the tight-binding method (TB).[16]

In the present work, we investigate the elastic constants and the thermodynamic properties of c-BN by

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using a first-principles plane wave method in the frame of local density approximation (LDA). The results obtained are in good agreement with the available experimental results and those obtained by other theoretical methods. In Section 2, we make a brief review of the theoretical method. The calculated results with some discussion are presented in Section 3.

2. Theoretical method

2.1. Total energy electronic structure calculations

We use a first-principles plane wave method with the norm-conserving relativistic analytic pseudopotential of Hartwigen, Goedecker and Hutter (HGH) type, based on Gaussian projector functions[21] within density functional theory (DFT)[22,23] in the frame of local density approximation (LDA). The HGH-type pseudopotential requires about ten parameters.[23] The kinetic energy cut-off criterion of 55 Rydberg is employed to obtain the convergence of 10^{-5}. The total energy and the ground state wave functions are calculated on a $10 \times 10 \times 10$ k-point mesh. The Perdew–Zunger–Ceperley–Alder functional is employed for the exchange–correlation functional. Applying the method, we have successfully investigated the electron–phonon coupling constant, the elastic constants and the thermodynamic properties of superconducting MgB_2.[24−26]

The energy–volume (E–V) curve can be obtained by fitting the calculated E–V data to the Vinet EOS,[27] which connects the pressure–volume relationship through

$$\ln\left[\frac{Px^2}{3(1-x)}\right] = \ln B_0 + a(1-x),\ x = \left(\frac{V}{V_0}\right)^{1/3}, \quad (1)$$

where $V_0 = V(0,T)$ is the zero-pressure equilibrium volume, derived by integration of the thermodynamic definition of the thermal expansion coefficient $\alpha(T) = V^{-1}\partial V/\partial T$,

$$V(0,T) = V(0,0)\exp\int_0^T \alpha(T)\mathrm{d}T, \quad (2)$$

$\ln B_0$ and $a = 3(B_0' - 1)/2$ are the fitting parameters. $B_T(P,T)$, $B_T'(P,T)$, and $B_T''(P,T)$ are given by

$$B_T = -x^{-2}B_0 \mathrm{e}^{a(1-x)} f(x), \quad (3)$$

$$B_T' = \left(\frac{\partial B_T}{\partial P}\right)_T = \frac{1}{3}\left[(ax+2) - x\frac{f'(x)}{f(x)}\right], \quad (4)$$

$$B_T'' = \left(\frac{\partial^2 B_T}{\partial P^2}\right)_T = \frac{x}{9B_T}\left\{x\frac{f''(x)}{f(x)} - a + \frac{f'(x)}{f(x)}\left[1 - x\frac{f''(x)}{f(x)}\right]\right\}, \quad (5)$$

where $f(x) = x - 2 - ax(1-x)$.

2.2. Elastic constants

The elastic constants are calculated as the second derivatives of the internal energy with respect to the strain tensor. Recently, we have calculated the elastic constants of MgB_2[25,28] using the theoretical method proposed by Sin'ko and Smirnov.[29] Only a brief description of this method is made as follows.

Consider a cubic crystal compressed by the isotropic pressure P to the density $\rho_1 = 1/V1$ (where V_1 is the distorted volume from the lattice distortion ε_{ij}). Small homogeneous deformation of this crystal takes every Bravais lattice point $\boldsymbol{R}$ of the undistorted lattice to a new position $\boldsymbol{R}'$ in the strained lattice

$$R_i' = \sum_j (\delta_{ij} + \varepsilon_{ij})R_j. \quad (6)$$

For a homogeneous strain, the parameters ε_{ij} are simply constants, independent of $\boldsymbol{R}$, where the subscripts i and j indicate the Cartesian components, δ_{ij} is the Kronecker delta. Expand the internal energy per unit mass of the crystal

$$E(\rho_1, \{\eta_{mn}\}) = E(\rho_1) + \frac{1}{\rho_1}\left(\sum_{ij} T_{ij}\eta_{ij} + \frac{1}{2}\sum_{ijkl} C_{ijkl}\eta_{ij}\eta_{kl} + \cdots\right), \tag{7}$$

where

$$\eta_{ij} = \varepsilon_{ij} + \frac{1}{2}\sum_k \varepsilon_{ik}\varepsilon_{kj}, \tag{8}$$

$$T_{ij} = \rho_1 \frac{\partial E(\rho_1, \{\eta_{mn}\})}{\partial \eta_{ij}}\Big|_{\{\eta_{mn}=0\}}, \tag{9}$$

$$C_{ijkl} = \rho_1 \frac{\partial^2 E(\rho_1, \{\eta_{mn}\})}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_{\{\eta_{mn}=0\}}. \tag{10}$$

Here T_{ij} stands for the components of the stress tensor before deformation, C_{ijkl} are the elastic constants of the crystal at an arbitrary isotropic pressure P. Equation (6) represents the energy of the strained crystal in the case of full relaxation of atom positions within the distorted Bravais lattice.

To calculate the ab initio elastic constants, the deformation parameters are usually specified in the form

$$\varepsilon_{ij} = s_{ij}\gamma + e_{ij}\gamma^2 + \cdots. \tag{11}$$

Then, Eq.(7) can be written as follows

$$E(\rho_1, \{\eta_{mn}\}) = E(\rho_1) + A\gamma + \frac{D}{2}\gamma^2 + \cdots, \tag{12}$$

where

$$A = -\frac{P}{\rho_1}\sum_i s_{ii}, \tag{13}$$

$$D = \frac{1}{\rho_1}\sum_{ijkl} C_{ijkl}s_{ij}s_{kl} - \frac{2P}{\rho_1}\sum_{ik}\left(e_{ik}\delta_{ik} + \frac{{s_{ik}}^2}{2}\right). \tag{14}$$

The linear equation for the elastic constants C_{ijkl} is then given by

$$\sum_{ijkl} C_{ijkl}s_{ij}s_{kl} = 2P\sum_{ik}\left(e_{ik}\delta_{ik} + \frac{{s_{ik}}^2}{2}\right) + \rho_1 \frac{\partial^2 E(\rho_1, \gamma)}{\partial \gamma^2}\Big|_{\gamma=0}. \tag{15}$$

Using the symmetry properties of matrices $\hat{\varepsilon}$ and $\hat{C}$, one can rewrite Eq.(15) as

$$\sum_{\alpha\beta} \xi_\alpha\xi_\beta C_{\alpha\beta}s_\alpha s_\beta = 2P\sum_\alpha (2-\xi_\alpha)e_\alpha + P\sum_\alpha \xi_\alpha {s_\alpha}^2 + \rho_1 \frac{\partial^2 E(\rho_1, \gamma)}{\partial \gamma^2}\Big|_{\gamma=0}. \tag{16}$$

2.3. Thermodynamic properties

The quasi-harmonic Debye model,[30] in which the phononic effects are considered, has been successfully applied to the investigation of the thermodynamic properties of MgB_2[26] and GaAs.[31] In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of

$$G^*(V; P, T) = E(V) + PV + A_{\rm vib}(\Theta(V); T), \tag{17}$$

where $\Theta(V)$ is the Debye temperature, and the vibrational term $A_{\rm vib}$ can be written as[32,33]

$$A_{\rm vib}(\Theta; T) = nk_{\rm B}T\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln\left(1 - {\rm e}^{-\Theta/T}\right) - D(\Theta/T)\right], \tag{18}$$

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

$$\Theta = \frac{\eta}{k_{\rm B}} \left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma) \sqrt{\frac{B_{\rm s}}{M}}, \qquad (19)$$

where M is the molecular mass per formula unit, $B_{\rm s}$ is the adiabatic bulk modulus approximated by the static compressibility[30]

$$B_{\rm s} \simeq B(V) = V \left(\frac{{\rm d}^2 E(V)}{{\rm d}V^2}\right). \qquad (20)$$

In Eq.(19) $f(\sigma)$ is given by Refs.[34,35]. Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume V

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{P,T} = 0. \qquad (21)$$

By solving Eq.(21), one can obtain the thermal EOS $V(P,T)$. Here, electronic excitation at $T \neq 0$ is not considered. The isothermal bulk modulus B_T, the heat capacity C_V and the thermal expansion coefficient α are given by[35]

$$B_T(P,T) = V \left(\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\right)_{P,T}, \qquad (22)$$

$$C_V = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{{\rm e}^{\Theta/T} - 1}\right], \qquad (23)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \qquad (24)$$

where γ is the Grüneisen parameter, which is defined as

$$\gamma = -\frac{{\rm d}(\ln \Theta(V))}{{\rm d}(\ln V)}. \qquad (25)$$

Through the quasi-harmonic Debye model, one can calculate the thermodynamic quantities of any temperatures and pressures of c-BN from the calculated energy–volume point at $T = 0$ and $P = 0$.

3. Results and discussion

First of all, a series of different lattice constant a for the c-BN are set to calculate the total energy E and the corresponding primitive cell volume V, and then a least-square fit of these energy–volume $(E - V)$ data is made to the Vinet EOS.[27] The obtained equilibrium lattice constant, bulk modulus and its pressure derivative are listed in Table 1. The agreement between our results, the experimental data[9] and the other theoretical results[11,12,17–19] is good.

Table 1. The lattice constants (Å), bulk modulus (GPa) and its pressure derivatives of c-BN at zero pressure and zero temperature, compared with the experimental data and other theoretical results.

	Present calculations	Other calculations	Experiments
a	3.604	3.584,[11] 3.658,[12] 3.599,[17] 3.593,[18] 3.633 (3.583),[19]	3.615[9]
B_0	403.25	401.7,[11] 377,[12] 379,[17] 395,[18] 369 (401),[19]	369–400[9]
B_0'	4.02	3.661,[11] 3.81,[12] 2.5,[17] 3.65,[18] 3.00 (3.96),[19]	4.00[9]

To determine the elastic constants of c-BN, we use the three independent strains listed in Table 2.

Table 2. The strains used to calculate the elastic constants of c-BN. In the second column, all the unlisted elements of strain tensors are set to zero.

Strains	Distortion	$\rho_1 \frac{\partial^2 E(\rho_1,\gamma)}{\partial \gamma^2}\Big\vert_{\gamma=0}$
1	$\varepsilon_{11} = \varepsilon_{22} = \gamma$	$2(C_{11} + C_{12})$
2	$\varepsilon_{13} = \varepsilon_{31} = \gamma$	$4C_{44}$
3	$\varepsilon_{11} = \gamma$	C_{11}

All these stains are not volume-conserving. The atomic positions are optimized at all strains. For each strain, a number of small values of γ are taken to calculate the total energies E for the strained crystal structure. The calculated $E - \gamma$ points are then fitted to a second-order polynomial $E(\rho_1, \gamma)$, and the third-order derivatives of $E(\rho_1, \gamma)$ with respect to γ are easily obtained. The calculated elastic constants, the experimental data and the other theoretical results are listed in Table 3. Obviously, the results are consistent with the experimental data[10] and those by others[11,14,15] except for those by Moon and his co-worker[12,13] and Talwar.[16]

Table 3. The elastic constants C_{ij} (in GPa) of c-BN at $T = 0$ and $P = 0$.

Elastic constants	C_{11}	C_{12}	C_{44}
Present work	838	184	489
FP-APW+lo[11]	834	189.5	494.7
Empirical MD[12]	605[a]	263[a]	443[a]
Empirical MD[13]	774[a]	179[a]	433[a]
ab initio MD[14]	819	195	475
FP- LMTO[15]	837	182	493
TB[16]	990	441	394
Experiments[10]	820	190	480

[a]Elastic constants of c-BN at $T = 300\,{\rm K}$

We now investigate the thermodynamic properties of c-BN. All the calculations are implemented through the GIBBS program proposed by Blanco, Francisco and Luaña.[30] In Fig.1, we present the normalized volume–pressure diagrams of c-BN at 300, 600 and 900 K, obtained from the thermal EOS $V(P,T)$.

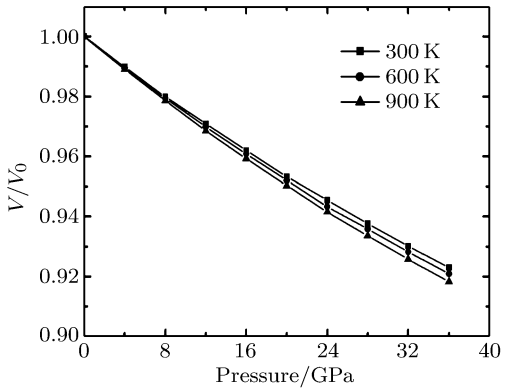


Fig.1. The normalized volume V/V_0–P diagrams of c-BN at $T = 300$, 600 and 900K.

It is noted that as the pressure P increases, the relative volume V/V_0 decreases at a given temperature. From Eq.(22), we have $B_0 = 382.94$ GPa, consistent with the experimental data[9] and other theoretical results.[11,12,17–19] The relationship between the bulk modulus B and pressure P at different temperatures are shown in Fig.2. These results indicate that B increases with P at a given temperature and decreases with T at a given pressure. It shows the fact that the effect of increasing pressure on c-BN is the same as decreasing its temperature.

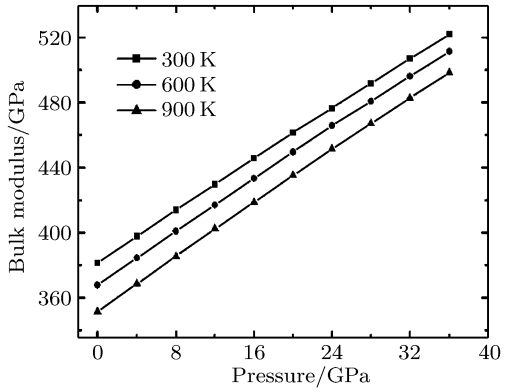


Fig.2. The relationships between bulk modulus B and pressure P at temperatures of 300, 600 and 900 K.

The variations of the thermal expansion α with temperature and pressure are shown in Fig.3. We note that at zero pressure α increases exponentially with T at low temperatures and gradually approaches to a linear increase at high temperatures. As the pressure increases, the increase of α with temperature becomes smaller, especially at higher temperatures. At a given temperature, α decreases monotonically with the increase of pressure. It is shown from Fig.3 that the temperature dependence of α is a little great at higher temperatures and higher pressures.

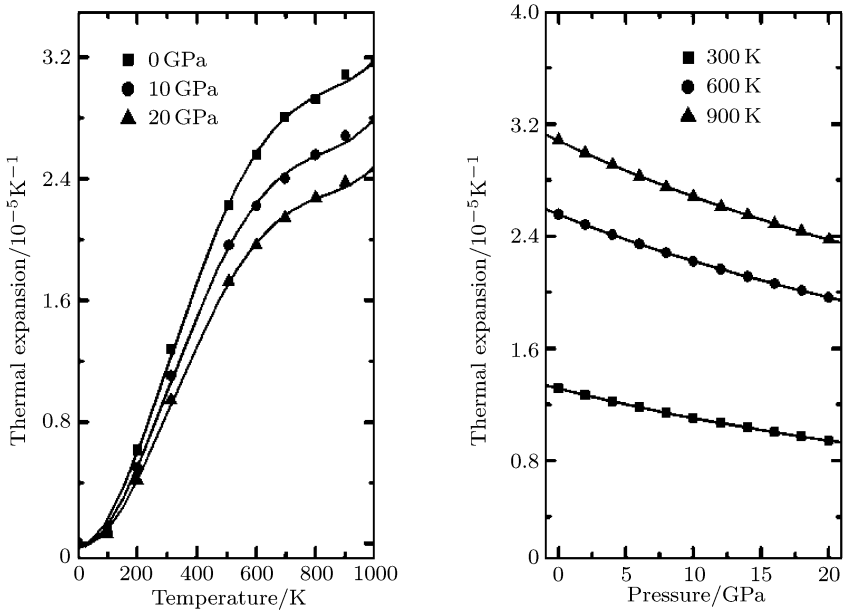


Fig.3. The thermal expansion versus temperature and pressure for c-BN.

Finally, the heat capacities of the c-BN are plotted in Fig.4 at pressures of 0 and 20 GPa. It is found that when $T < 1000$ K, the heat capacity C_V is dependent on both temperature T and pressure P. This is due to the anharmonic approximations. However, at higher temperatures and higher pressures, the anharmonic effect on heat capacity C_V is suppressed, and C_V is close to the Dulong-Petit limit $3k_{\rm B}$ ($\approx 49.90 \rm J{\cdot}mol^{-1}{\cdot}K^{-1}$), which is common to all solids at high temperatures.

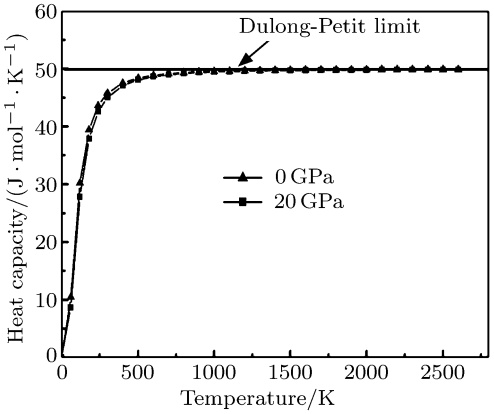


Fig.4. The heat capacity of the c-BN versus temperatures at different pressures.

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