

First-Principle Calculations for Elastic and Thermodynamic Properties of Diamond*

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Abstract The elastic constants and thermodynamic properties of diamond are investigated by using the CRYSTAL03 program. The lattice parameters, the bulk modulus, the heat capacity, the Grüneisen parameter, and the Debye temperature are obtained. The results are in good agreement with the available experimental and theoretical data. Moreover, the relationship between V/V_0 and pressure, the elastic constants under high pressure are successfully obtained. Especially, the elastic constants of diamond under high pressure are firstly obtained theoretically. At the same time, the variations of the thermal expansion α with pressure P and temperature T are obtained systematically in the ranges of 0–870 GPa and 0–1600 K.

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1 Introduction

Diamond is a very important material in industrial application because of its excellent chemical and physical properties.^[1–15] It is the hardest material with the highest thermal conductivity (22 W/cm·K)^[2–5] and the lowest thermal expansion (1.05×10^{-6} K⁻¹).^[6] It is also the best electrical insulator (10^{16} $\Omega \cdot \text{cm}$).^[7] In addition, diamond has splendid electrical properties that have many applications in modern microelectronic devices for the reason of low dielectric constant and large band gap. For better use of it, some properties related to thermodynamic, mechanical and optical have been studied by special experiment and theory.^[8–11]

McSkimin *et al.*^[12] measured the elastic constants of diamond at 1 atm (1.01325×10^{-4} GPa) and 298 K early in 1972. Xie and Chen^[13] investigated its thermal expansion, bulk modulus, and phonon structure. Wang and Yang^[14] researched the phase transformation between diamond and graphite in preparation of diamonds by pulsed-laser induced liquid-solid interface reaction. Blumenau *et al.*^[15] obtained the theoretical values of bulk modulus and elastic constants with density-functional-based tight-binding (DFTB) method, and meanwhile, Wang *et al.*^[16] calculated the elastic properties of diamond by using plane-wave pseudopotential (PW-PP) method. In this work, we focus on the elastic and thermodynamic properties of diamond under high pressure by using CRYSTAL03 program^[17] and the quasi-harmonic Debye model.^[18] The results obtained are well consistent with the available experimental data and other theoretical values. In Sec. 2, we

will illuminate the computational theoretical method, and the results and some discussion are presented in Sec. 3.

2 Theoretical Methods

2.1 Total Energy Electronic Structure Calculations

In this work, the lattice parameter is calculated by the relation of energy and volume, and use the Monkhorst–Pack mesh with $8 \times 8 \times 8$ k -points. Calculations were performed with a development version of the periodic *ab initio* CRYSTAL03 program. Crystalline orbitals are represented as linear combinations of Bloch Functions (BF), and are evaluated over a regular three-dimensional mesh in reciprocal space. Each BF is built from local atomic orbitals (AO), which are contractions (linear combinations with constant coefficients) of Gaussian-type functions (GTF), each GTF being the product of a Gaussian times a real solid spherical harmonic. All electron basis sets have been used for C atoms. In order to obtain the elastic constants, we use two kinds of basis sets matching three functional forms, that is, 6-21G* modified basis set with B3PW,^[19–23] 6211 basis set with restricted closed shell Hartree–Fock Hamiltonian (RHF),^[24,25] and 6211 basis set with unrestricted open shell Hartree–Fock Hamiltonian (UHF).^[26]

For the ground state properties of cubic structure diamond, we set a series of lattice constant a to obtain the total energy E and the corresponding primitive cell volume V at $P = 0$ GPa and $T = 0$ K, and then the E - V

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curve can be obtained by fitting the E - V data to the natural strain EOS,^[27]

$$p = 3B_0 f_E (1 + f_E)^{5/2} \left(1 + \frac{3}{2}(B' - 4)f_E + \frac{3}{2} \left(B_0 B'' + (B' - 4)(B' - 3) + \frac{35}{9} \right) f_E^2 \right), \quad (1)$$

where f_E is written as

$$f_E = \frac{(V_0/V)^{2/3} - 1}{2}, \quad (2)$$

B_0 and B' are the zero pressure bulk modulus and its pressure derivative, respectively, B'' is the second derivative. They are given in terms of a_0 , a_1 , and a_2 , where a_0 , a_1 , and a_2 are the fitting parameters

$$B_0 = a_0, \quad (3)$$

$$B' = 4 + \frac{2a_1}{3B_0}, \quad (4)$$

$$B'' = \frac{(2a_2)/(3B_0) - B'(B' - 7) - (143/9)}{B_0}. \quad (5)$$

2.2 Elastic Properties

The elastic constants are the second derivatives of the energy density with respect to strain components^[28]

$$C_{ij} = \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j}, \quad (6)$$

where C_{ij} is the elastic constant, E is the unit cell energy, ε_i refers to the strain components expressed according to Voigt's notation with a single index ($i = 1, 2, 3, 4, 5, 6$), and V is the cell volume. Particular care is required in the selection of the computational parameters and of the points, where the energy is evaluated, in order to avoid large numerical errors in the fitting procedure. When the unit cell is deformed, the point group is reduced to a subgroup of the original point group. The new point group is automatically selected by the *CRYSTAL03* code. Off-diagonal (partial derivatives) elastic constants can be computed as linear combinations of single-variable energy curves. For the cubic structure diamond, C_{12} can be obtained from $B = (C_{11} + 2C_{12})/3$ and $(C_{11} - C_{12})$. Following the deformation of the unit cell, the internal relaxation of the atoms may be necessary (depending on the space group symmetry).

A Taylor expansion of the energy of the unit cell to the second order in the strain components yields^[29,30]

$$E(\varepsilon) = E(0) + \sum_i \frac{\partial E}{\partial \varepsilon_i} \varepsilon_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j. \quad (7)$$

If $E(0)$ refers to the equilibrium configuration the first derivative is zero, since there is no force on any atom in equilibrium. The elastic constants of the system can be obtained by evaluating the energy as a function of deformations of the unit cell parameters. The indices of the

non-zero element(s) (in the Voigt convention) of the matrix give the corresponding elastic constants.

To obtain the elastic constants of diamond under pressure, an elastic deformation of the lattice may be defined in terms of the γ strain tensors defined. The elastic constant is $(1/V)(\partial^2 E / \partial \gamma^2)|_{\gamma=0}$, where V is the volume of the primitive unit cell. We here apply three independent strains to each of these structures, which are given in Table 1. Strains 1–3 are not volume-conserving. We calculate the total energy of each strain for a number of small values of γ . These energies are then fitted to a polynomial in γ and the curvature of the energy versus γ curve was obtained.

Table 1 The strains used to calculate the elastic constants of diamond.

Strains	Parameters (unlisted: $\varepsilon_{ij} = 0$)	$\frac{1}{V} \frac{\partial^2 E}{\partial \gamma^2} \Big _{\gamma=0}$
1	$\varepsilon_{11} = \gamma, \varepsilon_{22} = -\gamma$	$2(C_{11} - C_{12}) - 4P$
2	$\varepsilon_{23} = \gamma, \varepsilon_{32} = \gamma$	$4C_{44} - 2P$
3	$\varepsilon_{11} = \varepsilon_{22} = \gamma$	$2(C_{11} + C_{12} - P)$

The bulk modulus B_0 and the shear modulus G are given by^[31]

$$B_0 = \frac{C_{11} + 2C_{12}}{3}, \quad (8)$$

$$G = \frac{G_V + G_R}{2}, \quad (9)$$

where $C = (C_{11} - C_{12})/2$, $G_V = (2C + 3C_{44})/5$, $G_R = 15 * (6/C + 9/C_{44})^{-1}$, G_V is the Voigt shear modulus and G_R is the Reuss shear modulus. For cubic crystals under pressure P , mechanical stability of crystals is judged by the following conditions,^[32]

$$\tilde{C}_{44} > 0, \quad \tilde{C}_{11} > |\tilde{C}_{12}|, \quad \tilde{C}_{11} + 2\tilde{C}_{12} > 0, \quad (10)$$

where $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P$ ($\alpha = 1, 4$), $\tilde{C}_{12} = C_{12} + P$.

An important parameter is the internal strain parameter ξ introduced by Kleinman,^[33] which describes the relative positions of the cation and anion sublattices under volume-conserving strain distortions, for which positions are not fixed by symmetry. The parameter ξ can be obtained from^[34,35]

$$\xi = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}}. \quad (11)$$

The shear anisotropic factors provide measures of the degrees of anisotropy in atomic bonding in different crystallographic planes. For a transversely isotropic material, the anisotropies in shear are given by^[36]

$$A_{\text{shear}} = \frac{2C_{44}}{C_{11} - C_{12}}. \quad (12)$$

2.3 Thermodynamic Properties

The thermodynamic properties of diamond are investigated by using the quasi-harmonic Debye model,^[18] in

which, the non-equilibrium Gibbs function $G^*(V; P, T)$ is taken in the form of

$$G^*(V; P, T) = E(V) + PV + A_{\text{vib}}(\Theta(V); T), \quad (13)$$

where $E(V)$ is the total energy, PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and the vibrational contribution A_{vib} can be written as^[37,38]

$$A_{\text{vib}}(\Theta; T) = nk_B T \left[\frac{9}{8} \frac{\Theta}{T} + 3 \ln(1 - e^{-\Theta/T}) - D\left(\frac{\Theta}{T}\right) \right], \quad (14)$$

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^[37]

$$\Theta_D = \frac{\hbar}{k_B} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_S}{M}}, \quad (15)$$

where M is the molecular mass per unit cell, B_S is the adiabatic bulk modulus, which can be approximated by the static compressibility^[39]

$$B_S \cong B(V) = V \left\{ \frac{d^2 E(V)}{dV^2} \right\}, \quad (16)$$

$f(\sigma)$ is given by Ref. [39],

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{2}{3} \frac{1+\sigma}{1-2\sigma} \right)^{3/2} + \left(\frac{1}{3} \frac{1+\sigma}{1-\sigma} \right)^{3/2} \right]^{-1} \right\}^{1/3}, \quad (17)$$

the Poisson σ is taken as 0.25.^[31] 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 ,

$$\left(\frac{\partial G^*(V; P, T)}{\partial V} \right)_{P,T} = 0. \quad (18)$$

By solving Eq. (18), one can get the thermal equation of state (EOS) $V(P, T)$. The isothermal bulk modulus B_T , the heat capacity C_V , and the thermal expansion coefficient α are given by^[17]

$$B_T(P, T) = V \left(\frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right)_{P,T}, \quad (19)$$

$$C_V = 3nk_B \left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{e^{\Theta/T}-1} \right], \quad (20)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (21)$$

where γ is the Grüneisen parameter, which is defined as

$$\gamma = - \frac{d \ln \Theta(V)}{d \ln V}. \quad (22)$$

Applying these methods described above, we have successfully investigated the thermodynamic properties of some materials.^[40–43]

3 Results and Discussion

The obtained lattice a , bulk modulus B_0 , and its pressure derivative B' for cubic structure diamond at $P = 0$ and $T = 0$ are listed in Table 2. We here choose three exchange-correlation Hamiltonian functionals for comparison, including the restricted closed shell Hhcartree–Fock functions (RHF), unrestricted open shell Hartree–Fock functions (UHF), and the B3PW form of density functional theory (DFT). It is found that the RHF and UHF obtain a very accurate lattice constant, compared with the experimental value, only less than 0.02%, and the B3PW form shows more than 0.1%. When we calculate the bulk modulus of diamond, the RHF and UHF do not have good results, but the B3PW has a good outcome. It suggests the B3PW be a reasonable choice for investigating the elastic constants of diamond.

For the cubic structure diamond, there are only three independent elastic constants, i.e. C_{11} , C_{12} , and C_{44} (because of the symmetry analysis, other parties are zero accordingly). In Table 1, we also list the obtained elastic constants, together with the experimental data^[12] and other theoretical results.^[15,16,44,45] Obviously, the results from B3PW are closer to the experimental data than those from RHF and UHF, and are in agreement with other theoretical results.

Table 2 Lattice constant a (Å), bulk modulus B_0 (GPa), and its pressure derivative B' , together with the experimental data and other theoretical results for diamond at 0 GPa and 0 K.

	a	B_0	B'	C_{11}	C_{12}	C_{44}	ξ	A_{shear}
Present (B3PW)	3.5707	442.8	3.43	1097.5	115.5	598.2	0.255	1.21
Present (RHF)	3.5663	508.7	3.58	1289	123	706	0.245	1.21
Present (UHF)	3.5663	508.7	3.58	1289	123	706	0.245	1.21
GAPSS ^a	3.5569	433		1043	128	534		
DFTB ^b		487		1116	172	608		
PW-PP ^c				1099.6	142.8	587.0		
PI MC ^d	3.5493	437						
Expt.	3.5665 ^e	442 ^f		1079 ^f	124 ^f	578 ^f		

^aRef. [44], ^bRef. [15], ^cRef. [16], ^dRef. [45], ^eRef. [46], ^fRef. [12]

In Fig. 1, we present the normalized volume-pressure diagrams of diamond at 0 K, 600 K, and 1500 K. We can see that, when the pressure P increases, the relative volume V/V_0 decreases at a given temperature, and the relative volume V/V_0 of higher temperature is less than that of lower temperature at the same pressure. On the other hand, the volume V decreases with the elevated pressure P , and decreases with the elevated temperature T .

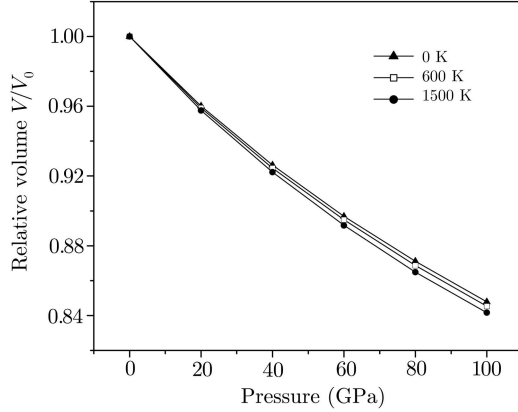


Fig. 1 Relative volume versus pressure of diamond at 0 K, 600 K, and 1500 K, respectively.

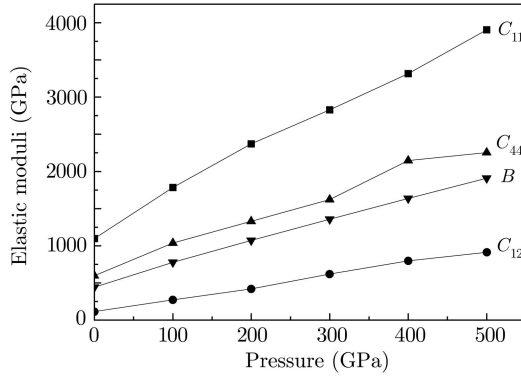


Fig. 2 Calculated pressure dependence of C_{ij} and B for diamond.

Table 3 Calculated lattice constant a (\AA), elastic constants C_{ij} (GPa), and elastic moduli B, B'_0 (GPa) of diamond under pressure (GPa) at 0 K.

P	a	C_{11}	C_{12}	C_{44}	B	B'
0	3.5707	1097.5	115.5	598.2	442.8	3.43
100	3.3798	1785	273	1037	777.1	3.02
200	3.2596	2371	421	1329	1071.7	2.89
300	3.1709	2829	620	1622	1357	2.81
400	3.1008	3315	796	2146	1635.8	2.76
500	3.0430	3905	911	2253	1909.4	2.71

In Table 3 and Fig. 2, we present the lattice constant, elastic constants, and bulk modulus of diamond under

high pressure. It is found that the variation of the elastic constants (C_{11} , C_{12} , and C_{44}) and the bulk modulus B is with respect to the variation of pressure. It is showed that the elastic constants and bulk modulus will linearly increase monotonously when pressure is enhanced, and according to the charts, our results accord with Eq. (10). Unfortunately, no experimental and theoretical data of elastic constants of diamond under high pressure are available for our comparison.

The heat capacity C_V , Debye temperature Θ , and Grüneisen constant γ of the cubic structure diamond at some temperatures T and pressures P are showed in Table 4. The Debye temperature is an important fundamental parameter and closely related to many physical properties of solids, such as specific heat and melting temperature. When below Debye temperature, quantum mechanical effects are very important in understanding the thermodynamic properties, while above Debye temperature quantum effects can be neglected. On the other hand, the Grüneisen parameter γ could describe the alteration in vibration of a crystal lattice based on the increase or decrease in volume as a result of temperature change. It has been widely used to characterize and extrapolate the thermodynamic properties of materials at high pressures and high temperatures. From Table 4, we find that along with the pressure increasing, the heat capacity and Grüneisen constant decrease gradually, but the Debye temperature is on the contrary trend in the constant temperature. From the point of view of temperature, when pressure is constant, the heat capacity and Grüneisen constant will increase along with the temperature increasing.

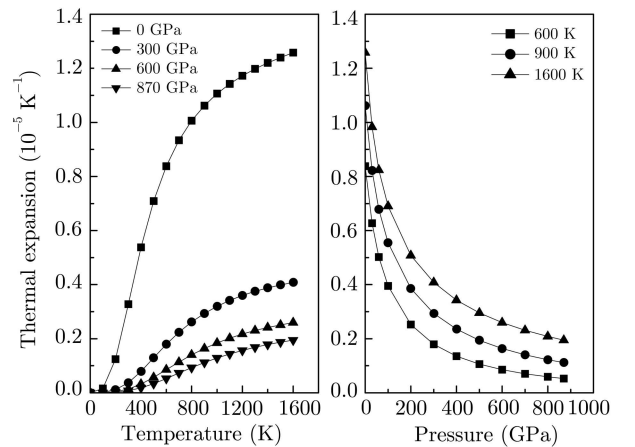


Fig. 3 Thermal expansion versus pressure and temperature for diamond.

The thermal expansion coefficients α are illustrated in Fig. 3. We find that for a given temperature, α decreases drastically with the increase of pressure and it is small at higher pressures. On the other hand, for a given pressure,

the thermal expansion coefficient α increases acutely before 800 K, and although increases after that, the thermal expansion coefficient α structure approaches to constant at high temperatures, which means that the temperature dependence of α is very small at high pressure and high temperature. We also calculate the linear thermal expansion parameters α_a in the intralayer and interlayer direc-

tions. Through the following equation at zero pressure

$$\alpha = \frac{(\Delta l / \Delta T)}{l_0} = \frac{1}{l_0} \left. \frac{\partial l}{\partial T} \right|_P, \quad (23)$$

where l represents the lattice constants a , we obtain $\alpha_a = 2.796 \times 10^{-6} \text{ K}^{-1}$ at room temperature. The experimental result is $\alpha_a = 1.05 \times 10^{-6} \text{ K}^{-1}$ at 300 K.^[6] Our result is appropriate on the order of magnitude.

Table 4 Heat capacity C_V ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), Debye temperature Θ (K), and Grüneisen constant γ of diamond at temperatures T (K) and pressures P (GPa).

T	P	0	100	200	300	400	500
0	C_V	0	0	0	0	0	0
	Θ	1816	2311	2669	2966	3221	3449
	γ	1.566	1.351	1.283	1.244	1.216	1.191
300	C_V	6.50	3.78	2.60	1.95	1.54	1.26
	Θ	1816	2310	2669	2966	3221	3449
	γ	1.567	1.351	1.283	1.244	1.216	1.191
600	C_V	16.45	13.12	10.95	9.36	8.16	7.20
	Θ	1811	2308	2667	2965	3220	3448
	γ	1.571	1.352	1.283	1.244	1.216	1.191
900	C_V	20.57	18.35	16.69	15.32	14.18	13.19
	Θ	1803	2303	2664	2963	3218	3446
	γ	1.576	1.353	1.284	1.245	1.216	1.191
1200	C_V	22.36	20.90	19.74	18.74	17.86	17.07
	Θ	1793	2297	2660	2959	3215	3443
	γ	1.583	1.355	1.285	1.245	1.216	1.192
1500	C_V	23.26	22.25	21.43	20.70	20.04	19.44
	Θ	1783	2291	2655	2954	3211	3440
	γ	1.591	1.356	1.285	1.246	1.217	1.192

4 Summary

In summary, the elastic and thermodynamic properties of the cubic structure diamond under pressure are investigated by using first-principles calculations. The lattice constant, bulk modulus, elastic constants of diamond are investigated. The calculated results are in excellent agreement with the available experimental data and other theoretical results. The normalized primitive volume V/V_0 on

pressure and temperature, the variations of the thermal expansion α and the heat capacity C_V with pressure P and temperature T , as well as the Grüneisen parameter-pressure-temperature (γ - P - T) relationships are obtained systematically. Especially, the elastic constants of diamond under high pressure are firstly obtained theoretically.

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