First-principles investigation of the electronic, elastic and thermodynamic properties of VC under high pressure*

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An investigation of the electronic, elastic and thermodynamic properties of VC under high pressure has been conducted using first-principles calculations based on density functional theory (DFT) with the plane-wave basis set, as implemented in the CASTEP code. At elevated pressures, VC is predicted to undergo a structural transition from a relatively open NaCl-type structure to a more dense CsCl-type one. The predicted transition pressure is 520 GPa. The elastic constant, Debye temperature and heat capacity each as a function of pressure and/or temperature of VC are presented for the first time.

Keywords: high pressure, first-principles calculations, elastic property, phase transition

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1. Introduction

Transition-metal (TM) monocarbides and mononitrides, each with a simple rocksalt structure, have been studied because of their interesting physical and chemical properties. They are extremely hard and have high melting points, as well as metallic conductivities comparable to those of pure TMs. It is interesting that properties associated with covalent bonding are found in a system which displays a crystal structure normally associated with ionic bonding. These properties suggest that covalent, ionic and metallic bondings are present simultaneously. The curious behaviours of TM monocarbides and mononitrides make these materials very attractive from both fundamental and the technological viewpoints. In particular, TM monocarbides are increasingly being used in heterogeneous catalysis because they exhibit important advantages over bulk transition metals both in activity and selectivity.[1]

Häglund *et al.*[2] studied the bonding theory of transition-metal carbides and nitrides based on the total energy from *ab initio* electron-structure calculations. They confirmed that the bonding and antibonding states are formed by hybridized carbon p states and metal d states, and the nonbonding part of the electronic energy spectrum is dominated by metal d states. To investigate the electronic mechanism of hardness enhancement in TM carbonitrides, Jhi *et al.*[3] evaluated the shear modulus of various TM carbides and nitrides using *ab initio* pseudopotential calculations. Their results showed that the behaviours of these materials can be understood on a fundamental level in terms of their electronic band structures. Their unusual hardness originates from a particular band of σ bonding states between the non-metal p orbitals and the metal d orbitals, which strongly resists shearing strain or shape change. Filling of these states is completed at a valence-electron concentration of about 8.4, and any additional electrons go into a higher band that is unstable against shear deformation.

A study of the structural and the electronic properties of selected TMs and their carbides and nitrides was presented by Grossman *et al.*[4] using *ab initio* electronic structure computation techniques. A sys-

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tematic study of the bulk and the surface geometrical and electronic properties of a series of TM carbides was presented by Viñes *et al.*[5] using first-principles methods.

Das *et al.*[6] studied the systematics of the electronic structures of the carbides of the transition series Sc, Ti, V, Zr, Hf and the actinides U and Th using the tight-binding linear muffin-tin orbitals method. They predicted that there is the possibility of a transition to a CsCl structure under high pressure but did not present the transition pressure.

Trends found in the bulk electron-structural features of early TM carbides in the NaCl structure were presented by Vojvodic and Ruberto[7] through detailed and systematic density functional theory (DFT) study. The results showed that C atoms play two roles for the bonding in TMC, by their interactions with the TM atoms and with other C atoms, and that the dominating bond character lies in the ionic-covalent TM-C bond.

As stated above, different theoretical calculations of VC bulk electronic properties have been extensively compared and discussed. However, to our knowledge, there is no report on the pressure-induced structural transition of VC until now. Very few studies have been performed on the thermodynamic properties of VC. So, there is a need to investigate the elastic and thermodynamic properties of VC under simulated extreme working conditions.

In this work, an investigation of the electronic, elastic and thermodynamic properties of VC under high pressure is performed using first-principles calculations.

2. Computational details and theory

2.1. Computational details

Our first-principles calculations are performed with the CASTEP code in MS modeling based on the plane-wave basis set,[8] the ultrasoft pseudopotential for electron–ion interaction and the exchange correlation potential given by Perdew *et al.*[9] in the generalized gradient approximation (GGA) for electron–electron interaction. The typical configurations are $3s^2 3p^6 3d^3 4s^2$ and $2s^2 3p^2$ for V and C, respectively. Integrations in the Brillouin zone (BZ) are performed using special k points generated with 14×14×14 for the B1 and B2 structures, which makes the separation of the reciprocal space less than 0.02 Å^{-1} (1 Å=0.1 nm). One-electron valence states are expanded on a basis of plane waves with a cutoff energy of 700 eV in the electronic property calculations. Such parameters have been tested to be sufficient for convergence ($< 10^{-3}$ eV). During the structural optimization, the total energy is minimized by varying the cell parameters and atomic positions under the restriction of the given symmetry. In the geometrical optimization, all forces on atoms are converged to less than 0.001 eV/Å and the total stress tensor is reduced to the order of 0.005 GPa using finite basis-set corrections.[10]

2.2. Elastic properties

The elastic constants are defined by a Taylor expansion of the total energy $E(V,\delta)$ for the system with respect to a small strain δ of the lattice primitive cell volume V. The energy of a strained system is expressed as[11]

$$E(V,\delta) = E(V_0,\delta) + V_0\left[\sum_i \tau_i\xi_i\delta_i + \frac{1}{2}\sum_{ij} C_{ij}\delta_i\xi_i\delta_j\xi_j\right], \quad (1)$$

where $E(V_0,\delta)$ is the energy of the unstrained system with equilibrium volume V_0, τ_i is an element in the stress tensor, ξ_i and ξ_j are factors of the Voigt index.

2.3. Thermodynamic properties

In order to obtain the thermodynamic properties of VC, the quasi-harmonic Debye model[12] is introduced, in which the non-equilibrium Gibbs function $G^*(V;P,T)$ takes the form of

$$G^*(V;P,T) = E(V) + PV + A_{\rm Vib}[\Theta(V);T], \quad (2)$$

where $E(V)$ is the total energy per unit cell, $\Theta(V)$ is the Debye temperature and the vibrational Helmholtz free energy $A_{\rm Vib}(\Theta,T)$ can be written as[13–15]

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

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

$$\Theta = \frac{\hbar}{K}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma)\sqrt{\frac{B_{\rm S}}{M}}. \quad (4)$$

Here M is the molecular mass per formula unit, $B_{\rm S}$ the adiabatic bulk modulus, which can be approximated by the static compressibility

$$B_{\rm S} \cong B(V) = V\left(\frac{{\rm d}^2 E(V)}{{\rm d}V^2}\right), \quad (5)$$

and $f(\sigma)$ is given as[16]

$$f(\sigma) = \left\{3\left[2\left(\frac{2}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2}\right]^{-1}\right\}^{1/3}, \quad (6)$$

where σ is the Poisson ratio. 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 as

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

By solving Eq. (7), one can obtain the thermal equation of state $V(P,T)$. The isothermal bulk modulus is given in Ref. [12] as

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

Other thermodynamic properties, such as heat capacity at constant volume C_V, heat capacity at constant pressure C_P and thermal expansion α are, respectively, taken as

$$C_V = 3nk\left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{\mathrm{e}^{\Theta/T}-1}\right], \quad (9)$$

$$C_P = C_V(1+\alpha\gamma T), \quad (10)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (11)$$

where γ represents the Grüneisen parameter and is expressed as $\gamma = -(\mathrm{d}\ln\Theta(V)/\mathrm{d}\ln V)$.

3. Results and discussion

3.1. Electronic and structural properties

The total energy as a function of volume is calculated to determine the equilibrium volume and bulk modulus by parabolic fitting to a third Birch–Murnaghan equation of state.[17] The calculated equilibrium lattice constant and bulk modulus of VC in B1 and B2 structures are illustrated in Table 1. It can be clearly seen that the calculated structural parameters are in excellent agreement with other theoretical investigations[7,18] and experimental results.[19] Since the bulk modulus is inversely proportional to the bond length, the smaller atomic size of nitrogen and the shorter bond lengths make the bulk modulus larger and, consequently, the elastic constants, which in turn are related to hardness, are larger. For bulk modulus of VC–B1, the calculated results are consistent with experimental data[20] and previous theoretical results.[7,18]

Table 1. Calculated equilibrium lattice constant (a_0), energy gap (E_g) and bulk modulus (B) of VC, together with previous theoretical results and the available experimental data.

compound	a_0/Å	E_g/eV	B/GPa	B'
VC–B1	4.156, 4.164[a] 4.170[b], 4.163[c]	0	302, 290[a], 304[b], 303[d]	4.04
VC–B2	2.544	0	314	4.21

[a]Ref. [7], [b]Ref. [18], [c]Ref. [19], [d]Ref. [20].

Our computational approach is based on constant-pressure static quantum mechanical calculations at $T = 0$ K, so the relative stability behaviours of different structures can be deduced from the pressure dependence on enthalpy rather than on Gibbs free energy.[21–24] The calculation suggests that there is a transition from a B1 structure to a B2 structure, which is a second-order phase transition. The pressure corresponding to $\Delta H = H_{B2} - H_{B1}$ approaching zero is the transition pressure. The calculated transition pressure and volume collapse are 520 GPa and 4.6%, respectively.

3.2. Elastic properties

The elastic constants of solids provide a link between the mechanical and the dynamic properties and provide important information about the nature of the force action in a solid. In particular, they provide information about the stability and stiffness of materials. The total energy of the system depends on volume more strongly than on strain. In this work, the volume contribution to total energy can be eliminated using volume conserving strains. The systems are fully relaxed after each distortion in order to reach the equilibrium state with approximately zero force on all atoms.[25]

The calculated elastic constants of VC–B1 and VC–B2 at ambient pressure are listed in Table 2. Since there is no other report on the elastic constants of VC up to now, we could not compare our result with other results.

Table 2. Calculated elastic constants and values of Poisson ratio σ for VC–B1 and VC–B2 at ambient pressure.

compound	C_{11}	C_{12}	C_{44}	σ
VC–B1	629	144	194	0.21
VC–B2	302	264	–73	0.46

The traditional mechanical stability conditions of the elastic constants in cubic crystal are $C_{11}-C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11}+2C_{12} > 0$, $C_{12} < B < C_{11}$.[26] For VC–B1, the elastic constants satisfy these stability conditions, indicating that the VC–B1 structure

is a mechanically stable phase. For VC–B2, the elastic constants do not satisfy these stability conditions, indicating that the B2 phase is not a stable state at ambient pressure.

We further investigate the high-pressure elastic behaviour of VC–B1, by computing the second-order elastic constants (SOECs) and their variations with pressure, which are shown in Fig. 1. It is noticed that C_{11}, C_{12} and C_{44} increase linearly with an increase in pressure, while C_{11} is more sensitive to a change of pressure than C_{12} and C_{44}. The calculated bulk modulus B increases gradually as pressure increases, indicating that it becomes more and more difficult compress as pressure increases.

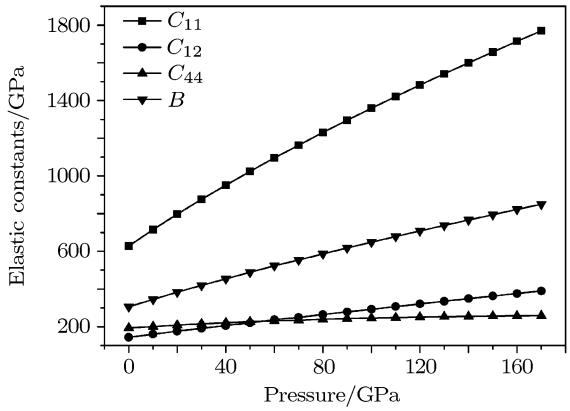


Fig. 1. Elastic constants of VC–B1 each as a function of pressure.

A simple relationship, which empirically links the plastic properties of materials with their elastic moduli, was proposed by Pugh.[27] The shear modulus G represents the resistance to plastic deformation, while B refers to the resistance to fracture.[28] A high B/G ratio is associated with ductility, whereas a low value corresponds to the brittle nature. The critical value which represents the delimitation between ductile and brittle materials is 1.75; i.e., if $B/G > 1.75$, the material behaves as being ductile; otherwise the material behaves as being brittle. Our results show that the B/G ratio is 1.38 for VC–B1 in ambient conditions, classifying it as brittle.

The elastic anisotropy of a crystal has an important application in engineering science since it is highly correlated to the possibility of inducing microcracks in materials.[29] The anisotropy factor $A = (2C_{44} + C_{12})/C_{11}$ has been evaluated to be able to provide an insight into the elastic anisotropy. For an isotropic crystal A equals 1, while any value smaller or larger than 1 indicates that the crystal is anisotropic. The magnitude of a deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. For VC–B1, A equals 0.85, indicating that it cannot be regarded as being elastical and isotropic.

3.3. Thermodynamic properties

The pressure and the temperature dependences of the isothermal bulk modulus for VC–B1 are shown in Fig. 2.

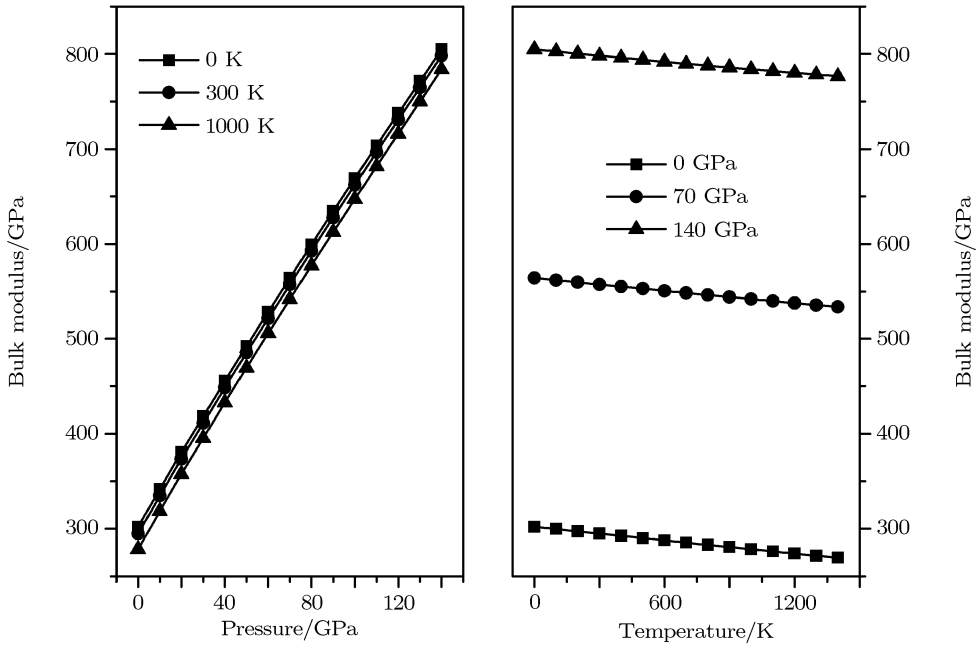


Fig. 2. Pressure and temperature dependences of the isothermal bulk modulus of VC–B1.

It is demonstrated that volume variation leads to a rapid decrease in the isothermal bulk modulus. These

results indicate that B increases with P increasing at a given temperature and decreases with T increasing at a given pressure. It shows that the effect of increasing pressure on VC–B1 is the same as that of decreasing temperature. However, the effect of temperature on the bulk modulus is less important than that of pressure.

The pressure and the temperature dependences of the Debye temperature for VC–B1 are shown in Fig. 3. It demonstrates that a dramatic variation in volume leads to a rapid decrease in Debye temperature. These results indicate that Debye temperature increases with P increasing at a given temperature and decreases with T increasing at a given pressure. It shows that the effect of increasing pressure on VC is the same as that of decreasing temperature. However, the effect of temperature on bulk modulus is less important than that of pressure.

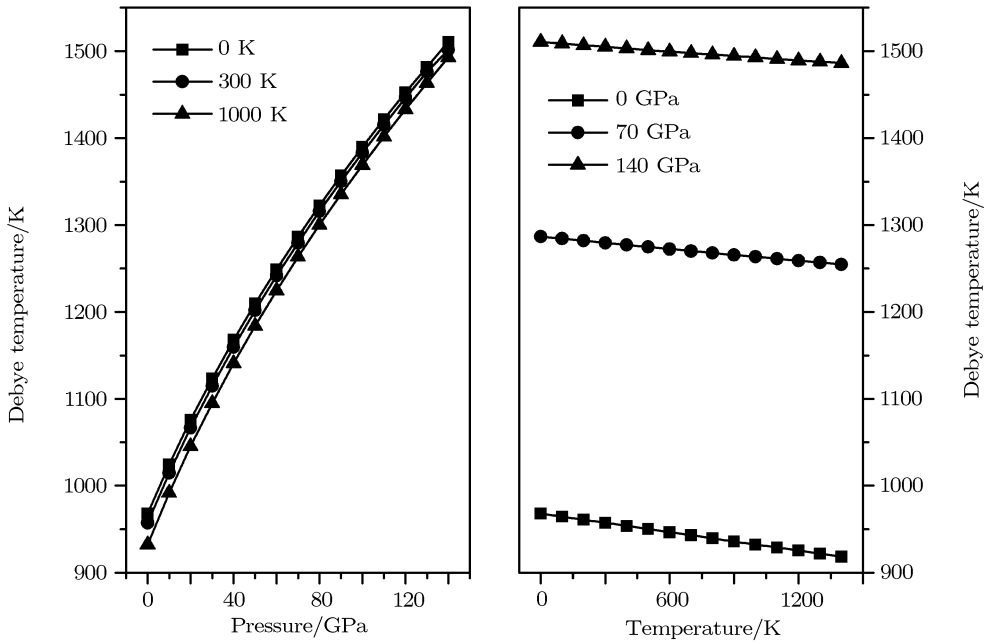


Fig. 3. Pressure and temperature dependences of Debye temperature of VC–B1.

Another thermodynamic parameter, heat capacity, is also very important. Through heat capacity C_V, one can obtain information about lattice vibrations, energy band structure, density of state, transition of phase of the solid, etc. In Fig. 4, the variation curves of the heat capacity of VC–B1 with T and P are presented. As $P = 0$ GPa, at sufficiently low temperatures ($T < 200$ K), C_V is proportional to $(T/\Theta_{\rm D})^3$. This is because only the long wavelength vibration modes of the lattice are populated and these modes could be approximated by treating the lattice as a continuum. However, at high temperatures ($T > \Theta_{\rm D}$), the anharmonic effect on C_V is suppressed and C_V is a constant $3R$ (R is the universal gas constant), which is in accordance with the law of Dulong and Petit. In this temperature range, maximum frequency lattice waves are populated and the energy difference is less than the heat kinetic energy kT. The energy difference can be ignored in order to fit classical statistical theory. These curves show that C_V has a quantum behaviour at low temperatures and classical behaviour at high temperatures.

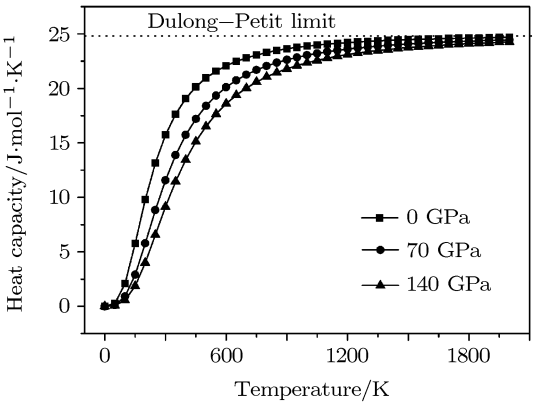


Fig. 4. Heat capacities of VC–B1 at various pressures and temperatures.

We further notice that pressure has less influence on heat capacity than temperature. The value of C_V becomes smaller and its changing trend becomes gentle and the range of agreement with Debye T^3 law becomes larger with an increase of pressure.

4. Conclusions

In this work, the electronic, elastic and thermodynamic properties of VC are studied using first-principles calculations. The calculated structural and elastic parameters accord well with the available experimental results and the previous theoretical data. It is predicted that a phase transition from a B1 structure to a B2 structure of VC occurs at a pressure of 520 GPa with volume collapse being 4.6%. The fundamental physical properties, such as elastic constants, Debye temperature and heat capacity, each as a function of pressure and/or temperature of VC, are reported.

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