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First principles investigation of temperature and pressure dependent elastic properties of ZrC and ZrN using Debye–Gruneisen theory

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ABSTRACT

We investigated the effects of temperature and pressure on the elastic properties of ZrC and ZrN using first-principles calculations and quasi-harmonic Debye–Gruneisen theory. Three expressions, the Slater, Dugdale–MacDonald (DM), and free volume expressions, were employed in the Debye–Gruneisen theory to obtain the Gruneisen parameter, γ. The DM expression agreed well with the experimental measurements of the ZrN volume expansion. The volume expansion of ZrC, on the other hand, did not agree well with any expression investigated here. ZrC calculations, therefore, require a modified expression. Variations in the Debye temperature, the Gruneisen parameter, the bulk (B), shear (G), and Young's (E) moduli were calculated as a function of temperature and pressure. The temperature-dependent properties at room pressure agreed well with previous experimental results and other calculated results; however, the pressure effects at the various temperatures were not easily compared with the results from other experimental and computational results because their effects on the elastic properties of ZrC and ZrN remain largely unknown.

1. Introduction

Transition metal carbides and nitrides (TMCNs) are important materials for magnetic storage, cutting tools, and coating applications due to their excellent electronic, mechanical, chemical, and thermal properties [1,2]. The representative materials of the transition TMCNs are titanium- and zirconium-based carbides and nitrides. These materials have been widely used in not only structural applications but also in electronic devices [3–5]. A particular focus has been titanium- and zirconium-based carbides and nitrides, as used in rocket engine and nuclear reactor applications due to their excellent high-temperature properties [6].

Material properties under extreme conditions, such as high temperatures and pressures, are difficult to measure using experimental methods. However, these properties are becoming increasingly important with the development of modern technology. Therefore, many researchers have turned to theoretical calculations in seeking to estimate material properties under extreme conditions. For example, Cheng et al. calculated the elastic properties of ZrC and ZrN using first principles calculations [7]. In their calculation, they used strain–stress relations to obtain elastic constants at a temperature of absolute zero. Ivashchenko et al. investigated not only the elastic properties at absolute zero but also the electronic structure and mixing free energy of ZrC–ZrN and ZrC–TiC alloys [8]. In addition, Hao et al. calculated several properties of ZrC and ZrN under high pressures by using first principles calculations [9]. The authors employed a quasi-harmonic Debye model to obtain the effects of changing temperature and pressure on ZrC and ZrN, and reported the variations in bulk modulus and heat capacity with increasing temperature and pressure. Many other studies have performed calculations to determine the properties of TMCNs; however, few studies have investigated the effects of temperature and pressure on the elastic properties of TMCNs [9,10]. In particular, the effect of temperature on the elastic properties of TMCNs remains largely unknown.

In the present paper, we investigated the temperature and pressure dependent elastic properties of ZrC and ZrN using first-principle calculations and the Debye–Gruneisen theory [11,12]. The remainder of this paper is organized as follows. Section 2 briefly introduces the calculation methods, including the first-principle calculations at absolute zero temperature and the techniques for modeling anharmonic effects using the quasi-harmonic Debye–Gruneisen theory. Section 3 reports the temperature and pressure effects on the elastic properties of ZrC and ZrN. Finally, conclusions are presented in Section 4.

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2. Calculation

2.1. First-principle calculations and the elastic modulus

The Vienna ab initio simulation package (VASP) was used to calculate the elastic properties of ZrC and ZrN [13,14]. Exchange–correlation effects were treated in the framework of the generalized gradient approximation (GGA), proposed by Perdew and Wang [15]. Integration in the Brillouin zone was performed using the Monkhorst Pack 11 × 11 × 11 k-points for the given models. To improve the accuracy of the results, we employed a high-energy cutoff of 500 eV with an energy convergence of 0.01 eV/Å, and the tetrahedron method with Bloch corrections were used for the energy calculations. The effects of temperature and pressure on the elastic properties of ZrC and ZrN were calculated assuming NaCl-type (B1) structures for ZrC and ZrN. The bulk modulus and its pressure derivatives for ZrC and ZrN were obtained, assuming the zero temperature total energy (E) calculated with respect to the cell volume (V) using the VASP first-principle calculations. The Birch–Murnaghan equation of state with 5 parameters (BM5 EOS, Eq. (1)) was employed to fit the calculated E–V curves in the vicinity of the equilibrium volume [16].

$$E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2} + eV^{-8/3} \tag{1}$$

The bulk moduli from the E–V fittings were compared by considering the volume-conserving tetragonal and trigonal shear distortions from –3% to 3% per model to calculate the cubic elastic constants (C_{11}, C_{12}, and C_{44}) [17,18]. The calculated elastic constants were then used to obtain the elastic modulus using the Voigt–Reuss–Hill (VRH) method [19–21],

$$B_{\text{Voigt}} = \frac{C_{11} + 2C_{12}}{3}, \quad B_{\text{Reuss}} = (3S_{11} + 6S_{12})^{-1}, \quad B_{\text{VRH}} = \frac{B_{\text{Voigt}} + B_{\text{Reuss}}}{2}, \tag{2}$$

$$G_{\text{Voigt}} = \frac{C_{11} - C_{12} + C_{44}}{5}, \quad G_{\text{Reuss}} = 5(4S_{11} - 4S_{12} + 3S_{44})^{-1}, \quad G_{\text{VRH}} = \frac{G_{\text{Voigt}} + G_{\text{Reuss}}}{2}, \tag{3}$$

$$E_x = \frac{9B_xG_x}{G_x + 3B_x}, x = \text{Voight, Reuss and VRH}, \tag{4}$$

where B, G, and E are the bulk, shear, and Young's moduli, respectively, and S_{ij} is the compliance, which is the inverse matrix of the elastic constant matrix C_{ij},

$$S_{11} = (C_{11} + C_{12})/\{(C_{11} - C_{12})(C_{11} + 2C_{12})\}, \tag{5}$$

$$S_{12} = -C_{11}/\{(C_{11} - C_{12})(C_{11} + 2C_{12})\}, \tag{6}$$

$$S_{44} = 1/C_{44}. \tag{7}$$

2.2. Debye–Gruneisen theory

The equilibrium properties of ZrC and ZrN at finite temperatures were calculated using the Debye–Gruneisen theory. For a system at fixed temperature (T) and hydrostatic pressure (P), the equilibrium state is determined by minimizing the nonequilibrium Gibbs free energy of the relevant crystal. The nonequilibrium Gibbs free energy is expressed according to the following equation [22],

$$G^*(x, P, T) = E_{\text{tot}}(x) + PV(x) + A_{\text{tot}}(x, T), \tag{8}$$

where G^* is the nonequilibrium Gibbs free energy, x is the configuration vector, E_{tot} is the total energy in the first-principle calculations, $PV(x)$ determines the constant hydrostatic pressure conditions, and $A_{\text{tot}}(x,T)$ is the total Helmholtz free energy. The total Helmholtz free energy is given as:

$$A_{\text{tot}}(x, T) = E_D(x, T) - TS_D(x, T) + E_{\text{el}}(x, T) - TS_{\text{el}}(x, T), \tag{9}$$

where E_D and S_D are the internal energy and entropy of the Debye vibrational lattice, and E_{el} and S_{el} are the internal energy (Eqs. (10), (11)) and entropy of the electronic excitation (Eqs. (12), (13)), respectively.

$$E_D(x, T) = \frac{9}{8}Nk_B\theta_D + 3Nk_BTD\left(\frac{\theta_D}{T}\right) \tag{10}$$

$$S_D(x, T) = 3Nk_B\left\{\frac{4}{3}D\left(\frac{\theta_D}{T}\right) - \ln\left(1 - e^{-\frac{\theta_D}{T}}\right)\right\} \tag{11}$$

$$E_{\text{el}}(x, T) = N\int_0^{\infty} n(\varepsilon, x)f(\varepsilon)\varepsilon d\varepsilon - N\int_0^{\varepsilon F} n(\varepsilon, x)\varepsilon d\varepsilon \tag{12}$$

$$S_{\text{el}}(x, T) = Nk_B\int_0^{\infty} n(\varepsilon, x)f(\varepsilon)\ln f(\varepsilon) + (1 - f(\varepsilon))\ln(1 - f(\varepsilon))d\varepsilon \tag{13}$$

Here, D is the Debye integration, θ_D is the Debye temperature, N is the number of atoms, $n(\varepsilon, x)$ is the electronic density of states (DOS), $f(\varepsilon)$ is the Fermi–Dirac distribution, and k_B is the Boltzmann constant. The Debye–Gruneisen theory is valid in the vicinity of the equilibrium volume, and it agrees less well with experimental measurements at larger volumes corresponding to higher temperatures. We therefore employed three known expressions to describe the relation between the Debye temperature (θ_D) and the volume, proposed by Wang et al. [23]:

$$\gamma(V) = \frac{1}{3(\lambda - 1)} - \frac{v}{2}\frac{\partial^2\{PV^{(\frac{2}{3})(\lambda+1)}\}/\partial V^2}{\partial\{PV^{(\frac{2}{3})(\lambda+1)}\}/\partial V}, \tag{14}$$

$$\frac{\theta_D}{\theta_{D,o}} = \left(\frac{V_o}{V_T}\right)^{\gamma} \quad \gamma = \frac{\ln(\theta_D) - \ln(\theta_{D,o})}{\ln(V) - \ln(V_o)} \tag{15}$$

where $P(V) = -\frac{\partial E(V)}{\partial V}$ The values $\lambda = -1$, 0, and +1 indicate the Slater, Dugdale–MacDonald, and free volume expressions, respectively [24–26]. Integrating Eq. (15) from both sides and using Eq. (14) yields Eq. (16):

$$\theta_D(V) = k(v)\frac{\hbar}{k_B\sqrt{m}}(6\pi^2N)^{\frac{1}{3}}V^{\frac{2}{3}}\left\{-\frac{\partial P(V)}{\partial V} - \frac{2(\lambda + 1)}{3}\frac{P(V)}{V}\right\}^{\frac{1}{2}} \tag{16}$$

Depending on the target material, no expression may be valid over the whole temperature range; thus, we supplemented the three expressions ($\lambda = -1$, 0, and +1) for ZrN with the modified values ($\lambda = -0.5$ and -0.3) for ZrC.

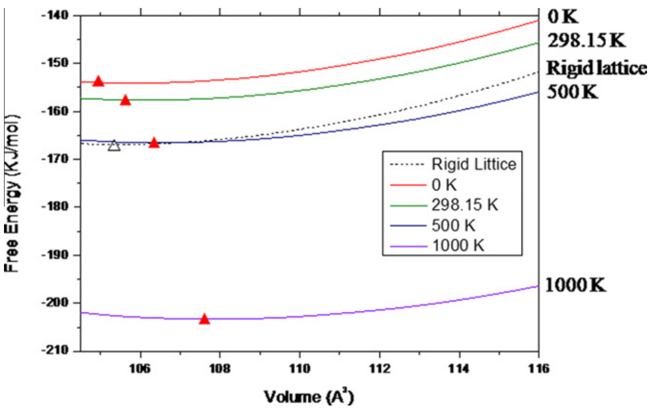

Fig. 1. Calculated free energy curves for ZrC at various temperatures using Slater's approximation. The dashed line indicates the rigid lattice energy from ab initio calculations. The triangles represent the positions of the energy minima.