Temperature-dependent mechanical properties of ZrC and HfC from first principles

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ABSTRACT

In order to gain insight into the effect of elevated temperature on the mechanical performance of zirconium carbide (ZrC) and hafnium carbide (HfC), their temperature-dependent elastic constants have been systematically studied. For both ZrC and HfC, isoentropic \( C_{11} \) gradually decreases with the increase in temperature, while the values of \( C_{44} \) and \( C_{12} \) of both are nearly temperature-independent. Temperature effects on modulus of elasticity, Poisson's ratio, elastic anisotropy, hardness, and fracture toughness are further explored and discussed. A good agreement is observed between the predicted isoentropic Young's modulus \( E \) and the available experiments for ZrC. Using quasistatic approximation can underestimate the decline rate of \( C_{11} \), bulk modulus \( B \), shear modulus \( G \), and Young's modulus \( E \) at high temperatures, especially above 298 K. This suggests the importance of the vibrational component of the free energy to calculate mechanical properties.

Introduction

Hypersonic vehicles, which travel at least five times faster than the speed of sound, represent the next frontier of aircraft. Developing new materials that can withstand ultrahigh temperatures (up to 3000 degrees Celsius), thermal shock, oxidation, and corrosion at such speeds is one of the formidable challenges for design. Ultrahigh-temperature ceramics (UHTCs), which exhibit a special combination of outstanding properties, such as exceptional hardness [1], high thermal conductivity [2], good wear resistance [3], good thermal shock resistance [4], and high melting point [1, 5–7], are promising candidate materials that can meet the above performance requirements. Among UHTCs, zirconium carbide (ZrC) and hafnium carbide (HfC) are receiving more and more attention, since they have extremely high melting points [7] (3845 ± 30 and 4255 ± 30 K for ZrC and HfC) due to their large heat of fusion [8] and also have good chemical inertness. The potential applications of ZrC and HfC go well beyond hypersonic flight. For example, both could be used as the thermal barrier coatings for gas turbines and ZrC is an ideal fuel-element cladding in nuclear reactors [9]. High
The experimental study on temperature-dependent elastic constants (TDEC) of ZrC is limited to the low temperature range (4.2–298 K) [10]. Elastic constants of ZrC and HfC at high temperatures are rarely reported, due to the experimental complexity of sample preparation and maintaining it at extreme temperatures. Based on density-functional theory (DFT) [11, 12], the present study is dedicated to a systematical investigation of the elastic constants and other mechanical properties of ZrC and HfC under a wide range of temperatures.

The elastic constant discussed in this paper refers to the second-order one, which describes the linear elastic stress–strain response and wave propagation in solids [13, 14]. Several theoretical approaches [15–21] have been proposed to study the TDEC of single crystals. These can mainly be classified into two categories: the empirical formula [15–18, 22, 23] and the method combining first-principles calculations with finite-strain continuum elasticity theory [24–26]. Since the applicability of the empirical models or formulas is limited to either some specific materials or to the cubic crystals, the latter method, which can be used for crystals with arbitrary symmetry, is the most commonly utilized technique in calculating TDEC. In this method, the elastic constants at a temperature are determined as the second-order strain derivatives of the Helmholtz free energy change induced by an applied strain. Generally, this energy under temperature can be obtained from three different methods: empirical Debye models [27, 28], lattice dynamics [29], and first-principles molecular dynamics [30]. Here, the widely used lattice dynamics method is considered.

Two methods of estimating the TDEC can be derived from the lattice dynamics [19, 20]. One is called the quasi-harmonic approximation (QHA), and the other is the quasi-static approximation (QSA). Both schemes are based on the quasi-harmonic description of the thermal expansion of the system. The former is a full quasi-harmonic one where the second energy derivatives with respect to strain are calculated in terms of the Helmholtz free energy $F$ and the latter is one where the second energy derivatives with respect to the strain are computed in terms of the purely static internal energy $E$. These two approaches will be described in the methods section. Compared with the QHA, the computational cost of QSA is much lower, but it is also more approximate. A recent theoretical report on ZrC [31] is calculated using QSA method due to its cheap cost. QSA method is also widely used for calculating the TDEC of other materials [32–36]. Therefore, another motivation of this study is to make a comparison between the QHA and QSA methods in estimating TDEC and other temperature-dependent mechanical properties.

### Methods

#### Temperature-dependent elastic constants

Based on finite-strain continuum elasticity theory [37], the internal energy $E(V)$ of a crystal under a general strain can be expressed in a Taylor series, as

\[
E(V) = E(V_0) + V_0 \sum_{m,n} \sigma_{mn} \epsilon_{mn} + \frac{V_0^2}{2!} \sum_{m,n,k,l} C_{mnkl}^S \sigma_{mn} \epsilon_{kl} + \cdots
\]

where $E(V_0)$ is the ground state energy, $V$ is the volume of the deformed crystal, $V_0$ is the volume of the unstrained crystal, $\sigma_{mn}$ are the elements of stress tensor, and $\epsilon_{mn}$ are those of strain tensor. Note that each strain corresponds to a different deformation tensor. Then, the second-order isentropic elastic constants $C_{mnkl}^S$ can be expressed as

\[
C_{mnkl}^S = \frac{\partial^2 E}{\partial \sigma_{mn} \partial \epsilon_{kl}}.
\]

This is the general equation to calculate the ground-state elastic constants from DFT. The Helmholtz free energy $F$ can also be expanded in terms of a Taylor series [26, 38, 39]

\[
F(V,T) = F(V_0,T) + V_0 \sum_{m,n} \sigma_{mn} \epsilon_{mn} + \frac{V_0^2}{2!} \sum_{m,n,k,l} C_{mnkl}^T \sigma_{mn} \epsilon_{kl} + \cdots
\]

where $T$ is the temperature. Thus, the second-order isothermal elastic constant $C_{mnkl}^T$ at a certain temperature is derived as
\[ C_{mnkl}^T = \frac{\partial^2 F}{\partial \epsilon_{mn} \partial \epsilon_{ij}}. \]

Note the Voigt notation \([38]\) is used for the tensor indices to write \(C_{mnkl}\) as \(C_{ij}\) in the subsequent discussion. In Eq. (4), \(F(T)\) is usually approximated by
\[
F(T) = E_s + F_d(T) + F_{vib}(T)
\]
where \(E_s\) is the energy of a static lattice at 0 K, \(F_d\) is the thermal electronic free-energy arising from electronic excitations, which can be determined integration over the electronic density of state through the Fermi–Dirac distribution \([40]\) (\(F_d\) is neglected in the following calculations, since the nonzero electronic density at the Fermi level of ZrC and HfC), and \(F_{vib}\) is the lattice vibrational energy contribution, which can be obtained by the partition function of lattice vibration.

In our work, the change of elastic properties at elevated temperatures is mainly caused by volume change due to thermal expansion. To calculate the elastic constants under temperature, one needs to perform three steps:

1. Apply compression and expansion with respect to the optimized structure (\(V_0\)) to obtain structures with different volumes. Then, a sets of distortions is applied to each volume with a small strain. For each volume, the elastic stiffness constants at any given temperature can be extracted by fitting the strain-volume, the elastic stiffness constants at any given applied to each volume with a small strain. For each
2. Using the first-principles quasi-harmonic approach to predict the temperature at which these volumes in the first step correspond to. (3) Based on the results from above two steps, the relationship between temperature and elastic constants is obtained using interpolation. This process of calculating TDEC is named as the quasi-harmonic approximation (QHA).

For simplicity of calculation, the contribution of vibrational free energy \(F_{vib}\) could be neglected in calculating the Helmholtz free energy [Eq. (5)] during step 1; this approximation is named as the quasi-static approximation (QSA).

Most elastic stiffness coefficients are measured by the resonance ultrasound spectroscopy, where elastic waves induced deformation in the crystal can be viewed as an isoentropic process. Therefore, to make direct comparison with the experimental elastic constants, \(C_{ij}^T\) need to be converted to \(C_{ij}\) (i.e., which are often measured). This can be achieved through the relationship [39],
\[
C_{ij}^T(T) = C_{ij}^T(0) + \frac{TV \lambda_i \lambda_j}{C_p}
\]
where \(C_p\) is the isochoric heat capacity and the coefficients \(\lambda\) are calculated as
\[
\lambda_i = -\sum_j \alpha_i C_{ij}^T(T)
\]
where \(\alpha_i\) is the thermal expansion tensor.

**Details of first-principles and phonon calculations**

These above three steps for calculating TDEC are implemented in the thermo_ps code \([41]\) combined with the ab initio DFT calculations \([11, 12]\). The latter was performed within the projector-augmented wave (PAW) pseudopotentials \([42, 43]\), as implemented in the QUANTUM ESPRESSO package \([44, 45]\). For the exchange and correlation terms in the electron–electron interaction, the generalized-gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) \([46]\) was used. The kinetic-energy cutoff for the plane wave basis set was chosen as 120 and 140 Ry for ZrC and HfC, respectively. k-point grids were based on 10 \times 10 \times 10 Monkhorst–Pack (MP) meshes. For Bril-louin zone integration, the first-order Methfessel–Paxton method \([47]\) was used with a smearing width of 0.02 Ry. These choices give a convergence in energy to less than 1 meV/atom. Density functional perturbation theory (DFPT) \([48]\) was used for phonon calculations, as (also) implemented within QUANTUM ESPRESSO. A \(4 \times 4 \times 4\) \(q\)-point mesh was used to produce the dynamical matrices for the phonon calculations.

**Results and discussions**

Both polycrystalline ZrC and HfC have an NaCl-type structure, as shown in Fig. 1. The calculated lattice parameter of ZrC and HfC is 4.710 and 4.633 Å, respectively, at ground state. As temperature increases to 298 K, the lattice parameter of ZrC is optimized as 4.724 Å and that of HfC is 4.646 Å, which agree well with the experimental data (4.693 Å for ZrC \([49]\) and 4.644 Å for HfC \([50]\)) at room temperature. There are three elastic constants \(C_{11}, C_{12}\), and \(C_{44}\) that need to be calculated for the cubic crystal structure. To simulate the thermal expansion, 17 different volumes are explored (compressed and expanded with respect
to \( V_0 \) in step 1 (in the “Methods” section), which is enough to enable the error bar for the calculated elastic constants at elevated temperature to be less than 1 GPa. For each volume, the sets of distortions were selected as \((\delta, \delta, \delta, 0, 0, 0)\), \((0, 0, \delta, 0, 0, 0)\), and \((0, 0, 0, \delta, \delta, \delta)\) to, respectively, calculate \( C_{11} - 2C_{12} \), \( C_{11} \), and \( C_{44} \) with a small strain \( \delta \) varying from -0.02 to 0.02 in steps of 0.005. One of volumes for ZrC is used as an example to illustrate this, see Figs. S1–S3 in Supplementary Materials.

Figure 2 shows the calculated Helmholtz energy densities against these strain curves for two selected volumes, which should correspond to two different temperatures. The exact values of the corresponding temperatures can be obtained from the first-principles quasiharmonic approach (as mentioned in step 2, in the “Methods” section). By fourth-order polynomial fitting the Helmholtz free energy densities to strain (see Fig. 2a–f), the second-order coefficient can be obtained and it equals to the corresponding elastic constants or linear combination of elastic constants. The elastic constants at other volumes can also be calculated in a similar way. For both ZrC (Fig. 2a–c) and HfC (Fig. 2d–f), it shows that the energy curve changes significantly with the increases of temperature and strain. The parabola at high temperatures is “wider” than that at low one, indicating the elastic constants become smaller. The difference between the line with filled dots for QHA and squares for QSA shows that the latter method can overestimate the value of Helmholtz free energy, which becomes greater at higher temperature.

Figure 3 shows the Helmholtz free energy at finite temperature for different crystal volumes, where the 17 volume points chosen were the same as those in step 1. These calculations were performed using the first-principles quasiharmonic approach (step 2, in the “Methods” section). The equilibrium volume at each temperature was determined by fitting the data to the Vinet equation of state [54]. Phonon dispersion curves of ZrC and HfC at different temperatures are shown in Fig. 4. There are no unstable branches with imaginary vibrational frequencies, indicating that the structures are dynamically stable at these temperatures. The Born elastic stability criteria [55, 56] for the cubic crystal system \((C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0, C_{44} > 0)\) were applied for checking the mechanical stability of ZrC and HfC. It can be seen that the temperature effect on phonon frequencies is discernible, they decrease as temperature increases since increasing the volume typically results in decreasing phonon frequencies.

The obtained volume coefficient of thermal expansion (\( \beta \)) as a function of temperature is displayed in Fig. 5a. It can be seen that the values of \( \beta \) for ZrC are overestimated by GGA when compared to the reported experimental data [49] (black dots in Fig. 5a). With temperature increasing, the change of thermal expansion coefficient with temperature for both ZrC and HfC is similar and exhibits dramatically increase with increasing temperature from 0 to 300 K and then the trend of increase turns out to be moderate, indicating that the thermal expansion coefficient is more sensitive to lower temperature. Compared with HfC, ZrC exhibits larger thermal expansion coefficient due to its slower decreasing rate of Helmholtz free energy as the temperature rises (shown in Fig. 3). The variation of vibrational entropy of ZrC and HfC with temperature is given in Fig. 5b. It is observed that the vibrational entropy of HfC is always higher than ZrC and the increasing rate of entropy for HfC is slowly higher than that of ZrC as the temperature increasing.

At 0 K, \( C_{12}^{\text{CS}} \) and \( C_{44}^{\text{CS}} \) of ZrC are 102.9 and 152.5 GPa, respectively, which reasonably agree with the experimental data [10] (98.4 GPa and 161.1 GPa) and calculation results [60] (103.5 GPa and 137.8 GPa [60]). For \( C_{11}^{\text{CS}} \), the value is in good agreement the pervious calculation result [60] (445.6 GPa) while slightly smaller than the corresponding experimental one [10] (480 GPa) at 0 K. For HfC (at 0 K), the calculated values of \( C_{11}^{\text{CS}}, C_{12}^{\text{CS}}, \) and \( C_{44}^{\text{CS}} \) are 500.9, 104.1, and 175.5 GPa, respectively. As temperature
increases to 298 K, $C_{11}^S$, $C_{12}^S$, and $C_{44}^S$ become 485.7, 104.1, and 174.4 GPa, respectively. These are in good agreement with the experimental values [61] $C_{11}^S=500$ GPa, $C_{44}^S=180$ GPa at 298 K ($C_{12}$ is not experimentally available).

As temperature increasing, the estimated $C_{ij}^S$ of ZrC and HfC and their corresponding isothermal elastic constants $C_{ij}^T$ are shown in Fig. 6. For some selected temperatures (0, 298, 900, 1500 and 2100 K), we also list the isothermal and isoentropic $C_{ij}$s of ZrC and HfC in Table 1, in comparison with the available experimental data [10]. Note that at 0 K, the elastic constant with and without considering zero point vibrational energies are also reported in Table 1. Although the diagonal elastic constant $C_{11}^S$ of ZrC under temperature is 7.4% underestimated compared with experimental result, this is within reasonable range since the elastic constants are known to be underestimated by using the PBE functional and
other functionals based on GGA by 5–10% [62–64].

The overall tendency of both ZrC and HfC is that all the calculated values of $C_{11}^S$ and $C_{44}^S$ decrease with increasing temperature and approach linearity at higher temperatures. There is a slight fluctuation of $C_{12}^S$ for both ZrC and HfC at finite temperature ($C_{12}^S$ slightly increases as temperature reaching to 1640 K for ZrC and 2000 K for HfC and then gradually decreases as the temperature increasing) in our QHA calculations. This anomaly of $C_{12}^S$ has also been reported in investigating the thermoelastic properties of fcc aluminum by using QHA [65]. One possible reason is that a small supercell size is used to calculate the strain-free energies.

In both cases of ZrC and HfC, the variations of $C_{12}^S$ and $C_{44}^S$ are found to be much smaller than that of $C_{11}^S$. The reason is that $C_{11}^S$ represents the stiffness against a longitudinal strain, which generates a change in volume without a change in shape. The volume change is highly related to the temperature. Meanwhile, the elastic and bonding nature is related to the electronic structures, such as the charge density [66].

With the volume increasing at elevated temperatures, the density of charge distribution decreases, resulting in the weak bonding between atoms and thus causes a large decrease in $C_{11}^S$. On the other hand, $C_{12}^S$ and $C_{44}^S$ are related to the deformation resistance to a transverse expansion (or shear strain), which causes a

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**Figure 3** Volume-dependent Helmholtz free energies of a ZrC and b HfC. Red lines connect the equilibrium volume with the minimum free energy at every temperature; the red crosses indicate the equilibrium volume at each temperature.

**Figure 4** Phonon dispersion relations of a ZrC and b HfC along high-symmetry directions over the Brillouin zone at several temperatures.
change in shape without a change in volume. Thus, $C_{12}^S$ and $C_{44}^S$ are less sensitive of temperature as compared with $C_{11}^S$.

As compared above with the elastic constant calculated within quasistatic approximation (QSA), the differences between the values of $C_{11}^S$, $C_{12}^S$, $C_{44}^S$ from QHA and QSA are quite small ($\sim 0.29$ GPa for $C_{11}^S$, 1.9 GPa for $C_{12}^S$, and 0.28 GPa for $C_{44}^S$) at 0 K. This small difference can mainly be attributed to the zero-point vibrational energy considered in the QHA method. With temperature increasing, especially the temperature beyond 298 K, the degree of decreasing rate of $C_{11}^S$ calculated from QHA is more prominent than the one calculated from QSA, indicating the quasistatic approach can underestimate the deteriorate rate of the $C_{11}^S$.

The temperature dependence of elastic moduli is extremely important for the strength of a material under high temperature and thermal shock properties. Based on the calculated isentropic $C_{ij}$ as a function of temperature, the isentropic elastic properties of polycrystalline ZrC and HfC, including bulk modulus $B$, shear modulus $G$, Young’s modulus $E$, and Poisson’s ratio $\nu$, can be evaluated under temperature using Voigt–Reuss–Hill approximation [51] (see Fig. 7). As expected, the overall observation is that temperature-dependent isentropic $B$, $G$, and $E$ decrease with increasing temperature. The temperature dependence of isentropic $E$ of ZrC obtained using the QHA approach is closer to the experimental result [52], as shown in Fig. 7c. The isentropic $B$, $G$, and $E$ (estimated from QHA) for both ZrC and HfC possess pronounced temperature softening of effect due to their particularly prominent decreasing of $C_{11}^S$ with the increase in temperature. The decreasing of $C_{11}^S$ of ZrC and HfC could be mainly attributed to their enhanced vibrational entropies caused by the thermal expansion (see Fig. 5a) for which the interatomic force constants is weakened as volume increases. Moreover, as the temperature increases, HfC exhibits the slightly higher increasing rate of entropy than that of ZrC (Fig. 5b), resulting the slightly higher decreasing rate of $B$ and $G$ for HfC than ZrC. Although the degradation rates of both $B$ and $G$ for HfC are slightly higher than ZrC, the temperature-dependent elastic moduli ($B$ and $G$) of HfC are always higher than ZrC because of its stronger covalent bond.

A comparison of $B$, $G$, and $E$ of both ZrC and HfC calculated using QHA and QSA reveals that the difference between the QHA and QSA is small below 250 K, while the decrease in $B$, $G$, and $E$ estimated from QHA is more significant than these from QSA above 250 K. For example, as the temperature increases from 298 to 2500 K, $B$, $G$, and $E$ of ZrC decrease by 38%, 30%, 32% according to the QHA method, whereas they only decrease by 25%, 16%, 18% from QSA. The value of $G/B$ ratio, which proposed by Pugh [67], represents the ratio of the resistance of cleavage to the energy of dislocation and can reflect the brittleness (ductility) of a material; a
material is deemed to be brittle if \( G/B < 0.57 \) and less than this indicates a ductile material [67]. At 298 K, the calculated isoentropic \( G/B \) ratio (from QHA) of ZrC and HfC is 0.74 and 0.78, respectively, indicating a behavior of brittleness and their brittle characteristic is enhanced at high temperatures based on the calculation.

All of the crystals are elastically anisotropic, which can cause for the emergence of microcracks [68]. Calculating and visualizing the elastic anisotropy is important for understanding such properties, and optimizing them for practical applications. Through analyzing the calculated temperature-dependent isoentropic \( C_{ij} \) (from QHA), the directional dependence of \( E \) and torsion shear modulus \( G_t \) for ZrC and HfC at several temperatures are displayed in Figs. 8 and 9, respectively. The degree of elastic anisotropy in a system can be reflected by observing the amount of deviation of the shape of these quantities from a sphere. As temperature increases, the extent of anisotropy of \( E \) and \( G_t \) for both ZrC and HfC increases. Within the same temperature range, the magnitudes

### Table 1: Elastic constants of ZrC and HfC at different temperatures calculated using QHA method

| Phase | Temp | Method | \( C_{11} \) | \( C_{44} \) | \( C_{12} \) | Phase | Temp | Method | \( C_{11} \) | \( C_{44} \) | \( C_{12} \) |
|-------|------|--------|-------------|-------------|-------------|-------|------|--------|-------------|-------------|-------------|
| ZrC   | 0    | Calc. \(^a\) | 460.8       | 153.7       | 102.9       | HfC   | 0    | Calc. \(^a\) | 512.5       | 177.4       | 104.1       |
|       |      | Calc. \(^b\) | 448.6       | 152.5       | 102.9       |       |      | Calc. \(^b\) | 509.9       | 175.5       | 104.1       |
|       | 298  | \( C_{11}^T \) | 434.9       | 152.0       | 102.5       | 298   | \( C_{11}^T \) | 485.7       | 174.4       | 104.1       |
|       |      | \( C_{11}^S \) | 437.0       | 152.0       | 104.7       |       |      | \( C_{11}^S \) | 488.0       | 174.4       | 106.4       |
|       |      | Expt.\(^c\) | 472.0       | 159.3       | 98.7        |       |      | Expt.\(^c\) | 482.0       | 168.3       | 103.8       |
|       | 900  | \( C_{11}^T \) | 386.5       | 149.6       | 100.4       | 900   | \( C_{11}^T \) | 436.3       | 169.8       | 103.3       |
|       |      | \( C_{11}^S \) | 394.8       | 149.6       | 108.7       |       |      | \( C_{11}^S \) | 444.7       | 169.8       | 111.7       |
|       | 1500 | \( C_{11}^T \) | 334.3       | 146.7       | 96.4        | 1500  | \( C_{11}^T \) | 383.5       | 164.5       | 100.7       |
|       |      | \( C_{11}^S \) | 348.8       | 146.7       | 110.8       |       |      | \( C_{11}^S \) | 398.2       | 164.5       | 115.4       |
|       | 2100 | \( C_{11}^T \) | 277.2       | 143.0       | 89.2        | 2100  | \( C_{11}^T \) | 326.4       | 158.9       | 95.8        |
|       |      | \( C_{11}^S \) | 297.4       | 143.1       | 109.5       |       |      | \( C_{11}^S \) | 347.0       | 158.9       | 116.6       |

\( C_{ij}^T \) and \( C_{ij}^S \) represent isothermal and isoentropic elastic constants, respectively

\(^a\)Without zero point vibrational energies

\(^b\)With zero point vibrational energies

\(^c\)Experiment [10]

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**Figure 6**: Temperature-dependent isoentropic (solid lines) and isothermal (dashed lines) elastic constants for a ZrC and b HfC. Also shown in a is experimental data [10] (green). The lines with filled and open symbols represent calculations by the QHA and QSA approaches, respectively.
of anisotropy of $E$ and $G_t$ for ZrC are larger than that of HfC.

Hardness of a materials is defined as its ability to resist plastic deformation, and fracture toughness $K_{IC}$ describes the resistance of a material against crack propagation [69]. The trend of both of these is important from an application standpoint. Based on the temperature-dependent isoentropic $C_{ij}$ (from QHA), temperature-dependent Vickers hardnesses can be predicted according to the Tian’s [57] and Mazhnik’s [58] models. Fracture toughness is estimated using Niu’s [59] and Mazhnik’s [58] ones. For both ZrC and HfC at 298 K, the hardnesses calculated from Chen’s model agree well with experimental results [53], though the ones calculated from Mazhnik’s model are a little bit lower. However, the experimentally tested hardness rapidly deteriorates with increasing temperature, while the calculated hardness, estimated from hardness models, drops mildly at elevated temperature (shown in Fig. 10a). Most likely, this indicates the inaccuracy of the current hardness models, in which the way of associating hardness with polycrystalline moduli (bulk and shear moduli as well as Pugh’s modulus ratio) has not reached the desired accuracy at elevated temperature. Another situation which is undesirable but
could occur in experiment is that the composition or the presence of oxides impurities of the sample might aggravate the deterioration of hardness as temperature increases [53, 70]. For example, oxides impurity, which is present at grain boundaries of Zr-based ceramics, can be softened at elevated
temperature, resulting the steep drop in its strength [70]. At 298 K, the calculated fracture toughnesses of ZrC and HfC from Niu’s model are 2.82 and 3.12 MPa m$^{1/2}$, respectively, and from Mazhnik’s model are 4.38 and 5.11 MPa m$^{1/2}$. Both decrease with increasing temperature, and the descending rate estimated from Mazhnik’s model is higher than that of from Niu’s one (e.g., $K_{IC}$ of ZrC decreases 33.6% from Mazhnik’s model and 23.4% from Niu’s one from 298 to 2000 K). Note that one should be careful about the capacity of using these models to predict the temperature-dependence though, since it might ignore behavior of crack propagation under temperature. Indeed, the mechanism controlling the changes in the hardness and fracture toughness of a material at high temperatures is actually more complex, and the current models to calculate them should be re-evaluated.

Conclusion

We predict the temperature-dependent isothermal and isentropic elastic constants for cubic ZrC and HfC over a wide range of temperature by combining first-principles calculations and continuous elastic theory. With increasing temperature, the isentropic $C_{11}$ gradually decreases, while $C_{44}$ and $C_{12}$ are virtually temperature independent. For both carbides, there are also apparent decreases in bulk modulus $B$, shear modulus $G$, and Young’s modulus $E$ at high temperatures. The temperature-dependent elastic properties of HfC are comparatively superior to those of ZrC. Besides, Young’s and the torsion shear moduli of both ZrC and HfC become substantially more anisotropic at high temperatures. The comparative study reveals that $C_{11}$, bulk modulus $B$, shear modulus $G$, and Young’s modulus $E$ are overestimated under high temperature within the quasistatic approximation. This suggests a surprising importance of the vibrational component of the free energy to calculate mechanical properties, even for systems such as these with heavy elements. In addition, the validity of using hardness and fracture toughness models to estimate their temperature-dependence was discussed. Since limited experimental data are available for the elastic constant of ZrC and HfC under high temperature, these results are expected to have important applications in applied physics, and also for future theoretical and computational work.

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