Prediction of stable hafnium carbides: Stoichiometries, mechanical properties, and electronic structure

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We have performed a search for stable compounds in the hafnium-carbon (Hf-C) system at ambient pressure using a variable-composition *ab initio* evolutionary algorithm implemented in the USPEX code. In addition to the well-known HfC, we predicted two additional thermodynamically stable compounds Hf_3C_2 and Hf_6C_5. The structure of Hf_6C_5 with space group $C2/m$ contains 22 atoms in the conventional cell, and this prediction revives the earlier proposal by Gusev and Rempel [Phys. Status Solidi A **135**, 15 (1993)]. The stable structure of Hf_3C_2 also has space group $C2/m$ and is more energetically favorable than the $Immm$, $P\bar{3}m1$, $P2$, and $C222_1$ structures put forward by Gusev and Rempel [Phys. Status Solidi A **135**, 15 (1993)]. The dynamical and mechanical stabilities of the newly predicted structures have been verified by calculations of their phonons and elastic constants. Structural vacancies are found in the ordered defective rock-salt-type HfC. Chemical bonding, band structure, and Bader charges are presented and are discussed. All three compounds are weak metals with increasing metallicity as the vacancy concentration increases. The mechanical properties of the hafnium carbides nonlinearly decrease with increasing vacancy concentration, indicating the defect tolerance of this refractory compound. It is, therefore, possible to tune the hardness, ductility, and electrical conductivity by varying the stoichiometry of the hafnium carbides.

I. INTRODUCTION

Hafnium carbides (HfCs), known as ultra-high-temperature ceramics, have attracted growing attention because of their unique features. These include extremely high melting temperature and hardness, high thermal and electrical conductivities, and chemical stability and make them promising advanced materials even in extreme thermal and chemical environments.[1–3]

Well-known HfC crystallizes in the NaCl-type structure (space group $Fm\bar{3}m$). Its elastic properties and phonon spectra have been studied experimentally,[4,5] and its structural, elastic, electronic, and phonon properties have been computed using first-principles methods.[6,7] However, according to the results of the theoretical calculation by Gusev and Rempel,[8] ordered stoichiometric phases Hf_3C_2 and Hf_6C_5 should exist with possible space groups $Immm$, $P\bar{3}m1$, $P2$, or $C222_1$ for Hf_3C_2 and $C2/m$, $P3_1$, or $C2$ for Hf_6C_5. Experimental synthesis and structure determination of these subtle ordered states encounter problems due to the lack of direct methods, such as x-ray or neutron diffraction. Gusev and Zyryanova[9] studied the order-disorder transition of the hafnium-carbon (Hf-C) system by measuring the magnetic susceptibility and confirmed the existence of Hf_3C_2 and the possible existence of Hf_6C_5.

Here we explore the stable compounds in the HfC system and their crystal structures at ambient pressure using the variable-composition *ab initio* evolutionary algorithm[10,11] and discuss their structures, elastic properties, and chemical bonding. In Sec. II, we describe the computational methods that were used in this paper. In Sec. III, we present the results—crystal structures, phonon spectra, elastic properties, and analysis of the electronic structure. Section IV presents the conclusions of this study.

II. COMPUTATIONAL METHODOLOGY

The prediction of stable compounds and their crystal structures was performed using the evolutionary algorithm implemented in the USPEX code.[12–14] This approach features global optimization with real-space representation and flexible physically motivated variation operators. For every candidate structure generated by USPEX, we use first-principles structural relaxation, based on density functional theory within the Perdew-Burke-Ernzerhof generalized gradient approximation functional for solids[15] as implemented in the VASP code.[16] The all-electron projector-augmented wave method[17] is used to generate pseudopotentials for Hf and C with the choices of the electronic configurations of $[Xe]6s^25d^2$ and $[He]2s^22p^2$, respectively. The plane-wave kinetic-energy cutoff is 900 eV, and the k-point mesh resolution in reciprocal space is $2\pi \times 0.06$ Å^{-1}. These settings enable excellent convergences of the energy differences, stress tensors, and structural parameters. Denser k-point meshes in reciprocal space with a resolution of $2\pi \times 0.04$ Å^{-1} are used for further property calculations. The calculations of the elastic properties, band structure, and density of states (DOS) were calculated by the VASP code. Phonon spectra were calculated by a direct method[18] as implemented in the PHONON code.[19,20] Some $2 \times 2 \times 2$ supercells

were used for the compounds with different stoichiometries. The phase stability of the compounds at finite temperatures up to 1600 K were investigated by quasiharmonic approximation. Bader charge analysis[21] was performed using the Bader charge analysis code.[22–24] The structures were visualized by VESTA.[25]

III. RESULTS AND DISCUSSIONS

A. Crystal structure prediction and structural properties

The variable-composition evolutionary algorithm[10,11] used in this paper is very effective in simultaneously predicting stable compositions and their structures for multicomponent systems. In our searches, we allowed all possible compositions in the Hf-C system with structures containing up to 30 atoms in the unit cell. The initial generation consisted of 120 structures, and all subsequent generations had 60 structures. Some 40% of new structures were produced by heredity, 20% were produced by soft mutation, 20% were produced by transmutation, and 20% were produced by a random symmetric structure generator. Stable structures and their compositions were determined using the convex hull construction: A compound is thermodynamically stable if the enthalpy of its decomposition into any other compounds is positive. For the computational intensity reason, zero-point energy (ZPE) is omitted for the systematic structural search. The convex hull can be reconstructed after phonon calculations for the selected thermodynamically stable phases, and meanwhile, their stability at finite temperatures can be considered.

In addition to rock-salt-type (B1) HfC ($Fm\bar{3}m$), we found two other compounds Hf_3C_2 and Hf_6C_5, both belonging to space group $C2/m$. The enthalpies of formation of the predicted structures are shown in Fig. 1. It can clearly be seen that HfC, Hf_6C_5, and Hf_3C_2 are thermodynamically stable compounds. Hf_2C ($R\bar{3}m$) is very close to the convex hull curve but lies above it, i.e., is a metastable phase. Transition-metal carbides often have numerous stable phases. For example, five titanium carbides have

FIG. 2. (Color online) The crystal structures of (a) HfC with one unit cell, (b) Hf_3C_2, and (c) Hf_6C_5 with two unit cells. The space groups for HfC, Hf_3C_2, and Hf_6C_5 are $Fm\bar{3}m$, $C2/m$, and $C2/m$, respectively. Carbon vacancies are shown in the green octahedra.

been reported[26–29] in the literature at ambient pressure, Ti_2C ($Fd\bar{3}m$), Ti_3C_2 ($C2/m$), Ti_8C_5 ($R\bar{3}m$), Ti_6C_5 ($C2/m$), and TiC ($Fm\bar{3}m$). However, hafnium carbides only have three thermodynamically stable polymorphs at ambient pressure from our systematic search using the USPEX code, i.e., Hf_3C_2 ($C2/m$), Hf_6C_5 ($C2/m$), and HfC ($Fm\bar{3}m$).

The crystal structures of Hf_3C_2 and Hf_6C_5 are shown in Fig. 2, and their crystallographic data and enthalpies of formation are listed in Table I. For comparison, we also present computational results for HfC in Table I. The enthalpies of formation without the ZPE correction are only about 0.02 eV/atom different from the ZPE-corrected energies and do not affect the final convex hull at 0 K. The structure of Hf_3C_2 has the space group $C2/m$ and 20 atoms in the conventional
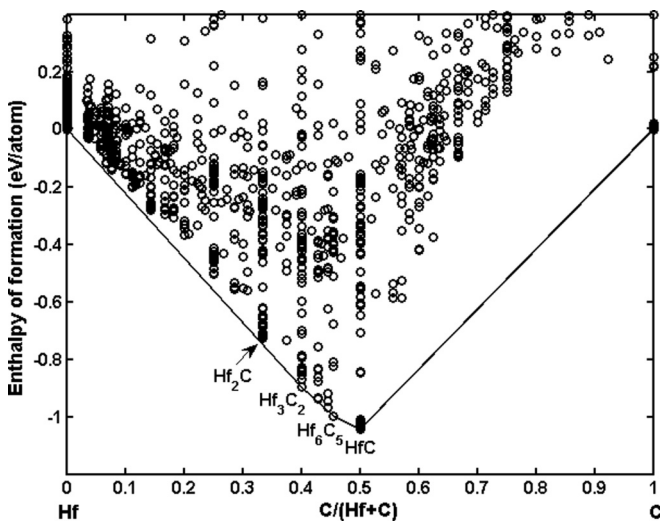

FIG. 1. Convex hull of the HfC system at ambient pressure. Circles denote different structures; those located on the convex hull are thermodynamically stable.
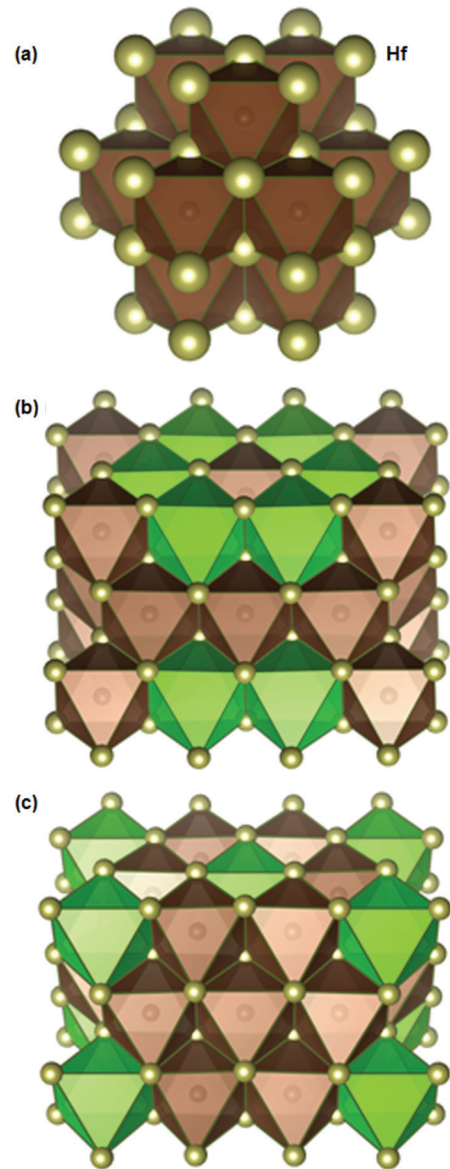
TABLE I. Crystallographic data and enthalpies of the formation of stable hafnium carbides and f.u. represents formula units.

Compound	Space group	Volume (Å³/f.u.)	Lattice constants (Å)	Atom position (Wyckoff position)	Enthalpy of formation (eV/atom)
Hf_3C_2	$C2/m$	73.02	$a = 5.642$	Hf(4i) (0.737,0.500,0.744)	-0.921[a]
			$b = 9.757$	Hf(8j) (0.248,0.161,0.264)	-0.898[b]
			$c = 5.636$	C(2a) (0.0,0.0,0.0,0.0)	
			$\beta = 109.70°$	C(2d) (0.0,0.5,0.5)	
				C(4h) (0.0,0.834,0.5)	
Hf_6C_5	$C2/m$	146.95	$a = 5.656$	Hf(4i) (0.739,0.000,0.260)	-1.015[a]
			$b = 9.748$	Hf(8j) (0.241,0.327,0.746)	-0.998[b]
			$c = 5.657$	C(4g) (0.0,0.333,0.0)	
			$\beta = 109.58°$	C(2d) (0.0,0.5,0.5)	
				C(4h) (0.0,0.832,0.5)	
HfC	$Fm\bar{3}m$	24.48	$a = 4.609$	Hf(4a) (0.0,0.00,0.00)	-1.057[a]
			$a = 4.637$ (Ref. 7)	C(4b) (0.5,0.5,0.5)	-1.045[b]
			$a = 4.639$ (Ref. 30)		

[a]With the ZPE correction.
[b]Without the ZPE correction.

unit cell [Fig. 2(b)]. Two more structures of Hf_3C_2 ($Immm$ and $P\bar{3}m1$) proposed by Gusev and Rempel[8] also were found during the structure search. However, their enthalpies are higher than that of $C2/m$, which is, therefore, more stable. The crystal structure of Hf_6C_5 is shown in Fig. 2(c). Its space group is also $C2/m$ with 22 atoms in the conventional unit cell, and its structural parameters are presented in Table I, which agree with the theoretical calculation of Gusev and Rempel.[8]

All stable hafnium carbides are strongly related structures and can be derived from the cubic rock-salt-type structure of HfC. HfC has a structure of cubic-packing hafnium atoms, and carbon atoms fill all octahedral voids [Fig. 2(a)], which is an ideal cubic rock-salt-type structure. The octahedra shown by the green color in Figs. 2(b) and 2(c) are empty, i.e., formed by six Hf atoms but without interstitial C atoms. In the Hf_3C_2 structure, only 2/3 of the carbon octahedral voids are filled (and 1/3 are vacant), and in Hf_6C_5, 5/6 are filled (and 1/6 are vacant). Both Hf_3C_2 and Hf_6C_5 structures are carbon-deficient ordered crystals in which the vacancies appear in every second octahedral layer with 1/3 of the in-layer octahedra occupied (Hf_3C_2) or 2/3 of the in-layer octahedra occupied (Hf_6C_5). Ordering of the vacancies in both cases lowers the symmetry from cubic ($Fm\bar{3}m$) to monoclinic ($C2/m$). Moreover, due to the vacancies, the coordination number of the Hf atoms varies in different systems: 6 in HfC, 5 in Hf_6C_5, and 4 in Hf_3C_2, whereas, in all these structures, carbon atoms invariably had the coordination number 6 (octahedral coordination). In this way, Hf_6C_5 and Hf_3C_2 can also be described as defective rock-salt-type structures.

It is instructive to look at molecular volumes (see Table I). The volumes per f.u. of Hf_3C_2 (73.02 Å³/f.u.), Hf_6C_5 (146.95 Å³/f.u.), and HfC (24.48 Å³/f.u.) correspond to a practically constant volume per Hf atom (24.34–24.48 Å³ per Hf atom). Figure 1 shows that the most prominent stable state is HfC. Hf_3C_2 and, especially, Hf_6C_5 will only be stable in a narrow range of chemical potentials in hafnium-rich conditions. This explains why HfC is well known from experiments, whereas, Hf_3C_2 and, especially, Hf_6C_5 are more elusive.

To verify the dynamical stability of the newly predicted Hf_3C_2 and Hf_6C_5, we computed their phonon dispersion and phonon density of states curves (Fig. 3). No imaginary phonon frequencies were found throughout the Brillouin zone, suggesting dynamical stability of these phases. Hf atoms
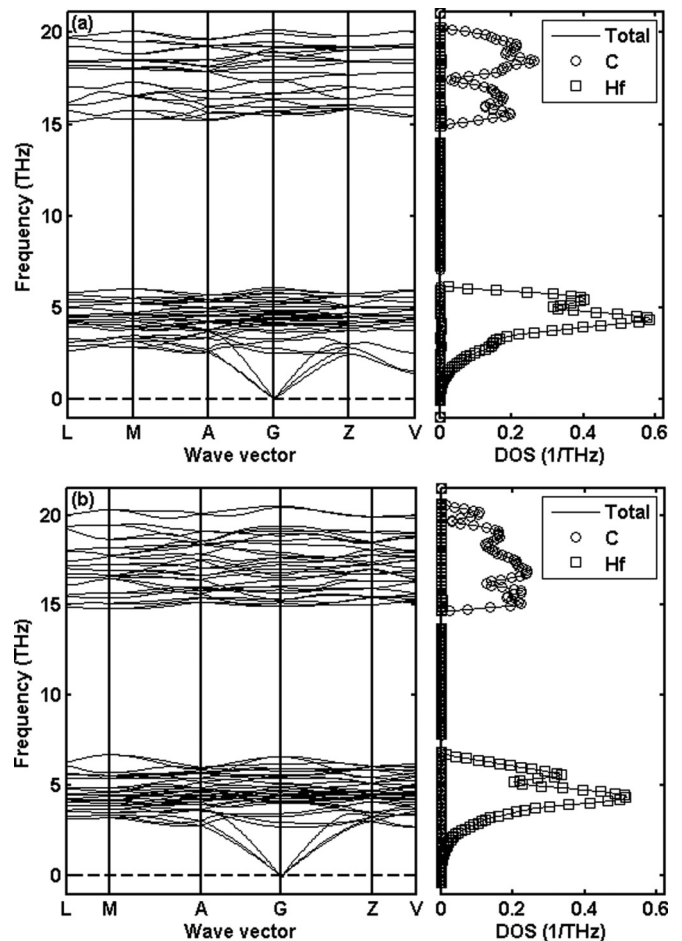

FIG. 3. Phonon dispersion and normalized density of states curves of (a) Hf_3C_2 and (b) Hf_6C_5 at ambient pressure.

TABLE II. Calculated elastic constants C_{ij}, the bulk modulus, shear modulus and hardness (GPa) of Hf_3C_2, Hf_6C_5, and HfC at the ground state, and some literature values of HfC.

Compound	Hf_3C_2	Hf_6C_5	HfC This paper	Calc.[36]	Expt.[37]	Expt.[4]
C_{11}	386	429	609	577	500	
C_{22}	404	462				
C_{33}	362	460				
C_{44}	125	184	183	171	180	
C_{55}	116	162				
C_{66}	131	185				
C_{12}	106	128	112	117		
C_{13}	113	130				
C_{16}	−8.6	4.2				
C_{23}	102	110				
C_{26}	4.4	26.7				
C_{36}	6.5	−18.1				
C_{45}	−9.1	22.1				
B_H	199	232	278	270		242
G_H	129	170	207	230		195
k^a	0.65	0.73	0.75			
H_V	17.74	24.92	29.08			

^{a}Pugh's ratio: $k = G_H/B_H$.

vibrate at the lower frequencies, whereas, C atoms vibrate at higher frequencies because the Hf atom is much heavier than the C atom. Hf_6C_5 has more carbon atoms in its unit cell than that of Hf_3C_2, so it has denser phonon dispersion curves in the C region, but there is not much difference in the Hf region. Using these phonon calculations, we estimated ZPE and vibrational entropy, and together with the configurational entropy of the ideal disorder, which yield a conclusion that above 1600 K, Hf_6C_5 might lose its thermodynamic stability.

B. Elastic properties

The elastic constants of a material describe its response to an applied stress or, conversely, the stress required to maintain a given deformation and can be used to evaluate the elastic properties. These properties are related directly to mechanical stability. The criteria of the mechanical stability of a monoclinic crystal are as follows:[31]

$$K_2 = \det|C_{ij}|, \quad i,j \leqslant 5, \quad K_2 > 0, \quad C_{44}C_{66} - C_{46}^2 > 0. \tag{1}$$

The calculated elastic constants of Hf_3C_2 and Hf_6C_5 at the ground state are listed in Table II. It is obvious that these criteria are satisfied, suggesting that Hf_3C_2 and Hf_6C_5 are mechanically stable.

The bulk modulus characterizes the response of a material-to-volume change $B = P/(\Delta V/V)$. P is the applied pressure, and ΔV is the volume change. The shear modulus characterizes the response to shear deformation $G = \tau/\gamma$. τ is the shear stress, and γ is the shear strain. The bulk modulus B and shear modulus G can be obtained from elastic constants,[32] and their values for Hf_3C_2 and Hf_6C_5 are presented in Table II. For comparison, the values of the elastic properties of HfC also are presented, and one can see good
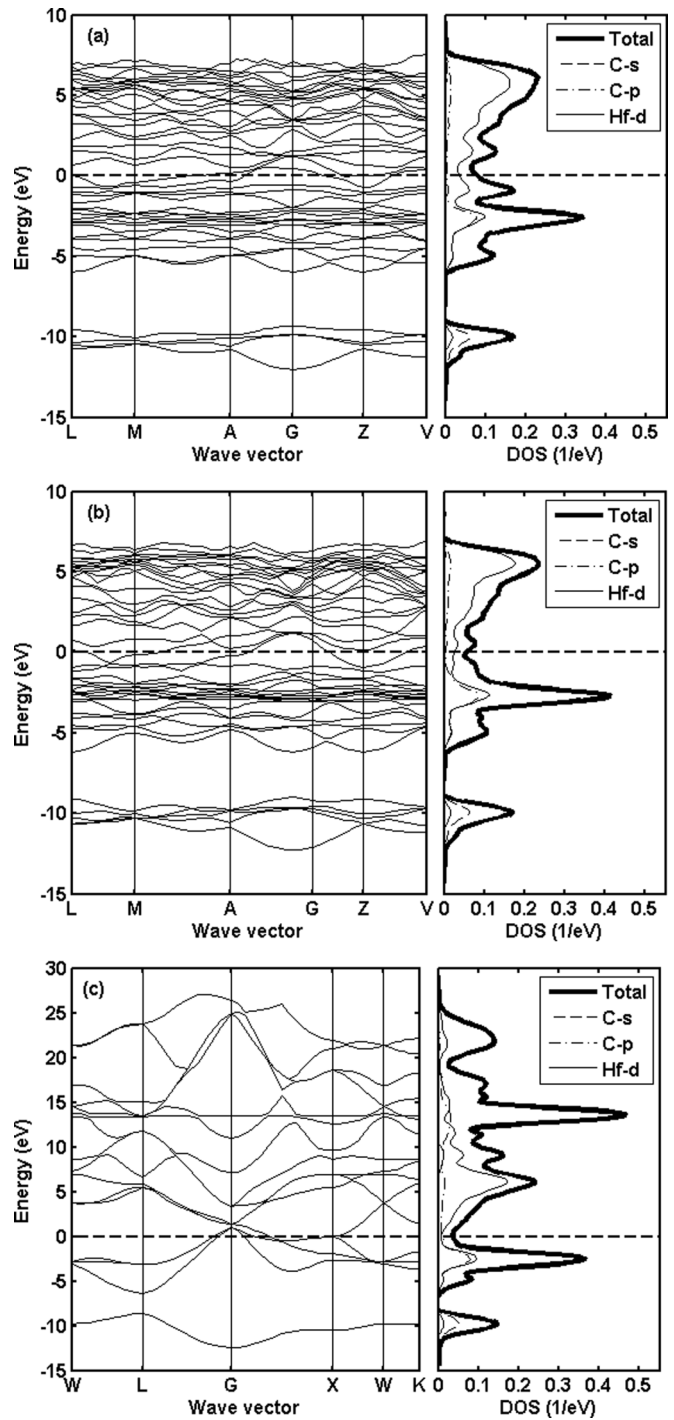

FIG. 4. The band structure and normalized density of states of (a) Hf_3C_2, (b) Hf_6C_5, and (c) HfC.

agreement with the reported data. The mechanical properties of the hafnium carbides nonlinearly decrease along with the vacancies increase, indicating the defect tolerance of this refractory compound. The Pugh ratios[33] of G/B of the three compounds decrease with increasing vacancy concentration, indicating increasingly ductile behavior. For brittle materials, G/B is >0.57, whereas, for the ductile ones, it is <0.57. According to Eq. (2),[34]

$$H_V = 2(k^2G)^{0.585} - 3, \tag{2}$$

the Vickers hardnesses of Hf_3C_2, Hf_6C_5, and HfC are 17.74, 24.92, and 29.08 GPa, respectively—lowering of the hardness from HfC to Hf_6C_5 to Hf_3C_2 is an expected consequence of the vacancies. This suggests the exciting possibility for tunable balance between hardness and ductility in hafnium carbides by changing the stoichiometry.[35]

C. Chemical bonding

The band structures and normalized DOS of these three compounds are shown in Fig. 4. All the stable hafnium carbides are weak metals as seen from the finite but small DOS at the Fermi level—3.83, 2.24, and 0.274 electrons/eV for Hf_3C_2, Hf_6C_5, and HfC, respectively. Taking into account the number of atoms in the primitive cells of Hf_3C_2, Hf_6C_5, and HfC, which were used in the calculations of the band structure and DOS, we see that the DOS at the Fermi level normalized per valence electron decreases as the number of vacancies decreases—from Hf_3C_2 (0.096 states/eV) to Hf_6C_5 (0.051 states/eV) and to HfC (0.034 states/eV). In all these three compounds, there are pronounced pseudogaps at the Fermi level, and bonding can be characterized as mixed metallic covalent. Indeed, orbital-projected DOS indicates strong hybridization of C-p and Hf-d valence states below the Fermi energy, i.e., the presence of significant covalency in all three compounds. Bader charge analysis shows that each Hf atom gives 1.702 electrons to each C atom in HfC. In the case of Hf_6C_5, Hf atoms contribute 1.526 ± 0.015 electrons/atom, and C atoms get 1.831 ± 0.017 electrons/atom. In the case of Hf_3C_2, Hf atoms contribute 1.268 ± 0.020 electrons/atom, and C atoms get 1.901 ± 0.043 electrons/atom. This, in agreement with the DOS, shows lower metallicity of HfC compared to that of Hf_6C_5 and Hf_3C_2. Thus, HfC could have the highest hardness and melting point among these three compounds.

IV. CONCLUSIONS

In this paper, we explored the possible stable compounds and structures in the Hf-C system at ambient pressure using the variable-composition evolutionary algorithm. Besides the well-known HfC ($Fm\bar{3}m$), two other stoichiometric compounds Hf_3C_2 ($C2/m$) and Hf_6C_5 ($C2/m$) are found. All three stable hafnium carbides have rock-salt-type structures: HfC with an ideal cubic structure without vacancies and defective rock-salt-type phases Hf_3C_2 and Hf_6C_5 with monoclinic symmetry ($C2/m$) due to ordering of carbon vacancies. Their elastic constants and phonon spectra verify their mechanical and dynamical stabilities. Finite-temperature investigation shows that Hf_6C_5 ($C2/m$) is thermodynamically unstable above 1600 K. All three compounds are weak metals with increasing metallicity as the vacancy concentration increases. We found significant covalency in all these weakly metallic compounds. The mechanical properties of the hafnium carbides nonlinearly decrease with increasing vacancy concentration, indicating the defect tolerance in these compounds. It is, therefore, possible to tune the hardness, ductility, and electrical conductivity by varying the stoichiometry of hafnium carbides.

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