

DISSERTATION

RELATIONSHIP BETWEEN ELECTRONIC STRUCTURE, PHASE STABILITY AND
MECHANICAL PROPERTIES IN THE TRANSITION METAL CARBIDES, NITRIDES AND
CARBO-NITRIDES

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ABSTRACT

RELATIONSHIP BETWEEN ELECTRONIC STRUCTURE, PHASE STABILITY AND MECHANICAL PROPERTIES IN THE TRANSITION METAL CARBIDES, NITRIDES AND CARBO-NITRIDES

The transition-metal carbides (TMCs), nitrides (TMNs) and carbo-nitrides (TMCNs) make up a class of hard materials whose melting temperatures generally exceed 3000 K. These refractory ceramics, generally referred to as ultra-high-temperature ceramics (UHTCs), are naturally of interest for a range of extreme environment applications, from nuclear power generation to hypersonic flight. The carbides of the Group IV and Group V transition metals—Ti, Zr, Hf, V, Nb and Ta—are of particular interest, since some of these materials are claimed to possess the highest melting temperatures among all known compounds; some are found to exceed 4000 K. The Group IV and Group V TMCs generally share the same rocksalt (NaCl) crystal structure and covalent-metallic bonding character; furthermore, they all exhibit large rocksalt phase homogeneity ranges, with structural vacancies accommodating off-stoichiometry. Yet they exhibit surprisingly varied hardness behaviors: some, like TiC, are seen to lose hardness with decreasing carbon content; others, like TaC, are found to increase in hardness. Additionally, alloying of the rocksalt carbides and nitrides has been claimed to produce optimized melting temperatures and hardnesses. This work seeks to develop computational models to describe the hardness behavior of the TMCs, TMNs and TMCNs, with a focus particularly on dislocations—the low-temperature carriers of plastic deformation. This work will also investigate the electronic mechanisms underpinning the anomalous hardness behaviors in these materials, seeking to provide plausible explanations centered on the chemical bonds within these crystalline solids.

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Chapter 1

Introduction

The carbides, nitrides and carbonitrides of the transition metals comprise a class of ceramic materials with highly varied and interesting properties. Generally selected for their high hardness and exceptional melting temperatures, these refractory ceramics serve as excellent candidate materials for wear-resistant coatings in extreme high-temperature environments. For applications such as hypersonic flight, where travel at speeds between Mach 5 and Mach 25 are desired, these properties make the transition-metal carbides (TMCs), nitrides (TMNs) and carbo-nitrides (TMCNs) highly desirable for sharp leading edges; likewise, the TMCs and TMNs show promise as heat shielding materials for re-entry vehicles in spacecraft. At lower temperatures, the high hardness (and thus wear resistance) and relatively low cost of materials like TiC, TiN, and TiCN make them ideal for hard coatings on cutting tools; cemented composites such as WC-Co are commonly used as inserts for machining tools, allowing for enhanced fracture toughness in addition to high wear resistance. Furthermore, the TMCs, TMNs and TMCNs show a vast array of other appealing properties. They are generally electrical conductors, and many undergo a superconducting transition at very low temperatures. The TMCs and TMNs are also interstitial compounds, typically having B1 (rocksalt) structures with interpenetrating face-centered cubic (FCC) sub-lattices of metal and non-metal atoms. They generally exhibit large B1 phase homogeneity ranges, with off-stoichiometry being accommodated by structural vacancies on the metal or nonmetal sublattices, and are thus often represented by the general chemical formula MX_y —M being a transition metal species, X being a nonmetal species, and y representing the nonmetal-to-metal atom ratio. The compositional flexibility of these compounds presents an array of opportunities for material design: some of the TMCs and TMNs display enhanced hardness, toughness, or melting temperature at specific compositions, possibly allowing for detailed tailoring of mechanical properties; furthermore, the presence of vacancy ordering in some of these materials at specific compositions within the rocksalt-phase

region may have significant effects on mechanical characteristics, non-metal atom diffusion rates, and electrical and thermal properties.

Compounding this array of intriguing characteristics is the fact that most of the rocksalt TMCs and TMNs have very high solubility with one another, allowing for the creation of TMCNs and mixed transition-metal carbides (MTMCs). Since the Group IV and Group V TMCs and TMNs display varied thermal and mechanical behaviors within their respective B1 homogeneity ranges, this raises the possibility of very precise design of ultra-high-temperature ceramics (UHTCs) via alloying. Prior work on ZrC-TaC, HfC-TaC, and HfC-HfN alloys, for example, has shown these materials to possess maxima in melting temperature (ZrC-TaC and HfC-TaC) and shear modulus (HfC-HfN) at intermediate compositions. Hence, by substitution of atoms on the metal and/or nonmetal sublattices, it may be possible to achieve performance greater than any of the constituent binary or ternary compounds; this is precisely the motivation for the increasingly popular study of high-entropy carbides (HECs) and nitrides (HENs), which seek to enhance specific mechanical and/or thermal properties via alloying of five or more binary TMCs or TMNs.

In the interest of learning how to better exploit these fascinating and versatile materials, this work will focus on developing computational models of intrinsic hardness in the TMCs, TMNs and TMCNs. First-principles simulation and hierarchical modeling will be used to generate predictions of mechanical properties for this family of materials, focusing particularly on dislocation mobility as a predictor of hardness and slip plane preference. We will also explore the underlying electronic mechanisms which determine these characteristics, aiming to generate a more comprehensive understanding of the effect of off-stoichiometry and alloying on the mechanical properties of the Group IV and Group V transition-metal carbides, nitrides and carbonitrides.

Chapter 2

Motivation

2.1 Engineering Interest in Transition-Metal Carbides and Nitrides

There remains in many engineering fields a pressing need for more capable materials. Novel materials with high hardness, high corrosion and oxidation resistance, good toughness and high melting temperatures are desired for use as hard coatings [1], cutting tools [2], armor materials [3, 4] and heat shielding materials. This latter case in particular has spurred interest in the carbides, nitrides and borides of the transition metals; many of these are ultra-refractory materials, possessing melting temperatures in excess of 3000°C [5] and thus serve as good candidate materials for extreme high-temperature environments. Specifically, ultra-high-temperature ceramics (UHTCs) show great promise for applications in hypersonic vehicle construction [6–8], where very sharp leading edge geometries are favored [9] and friction from contact with atmospheric air at speeds greater than Mach 5 can generate leading edge temperatures well above 2000°C [10].

The carbides, nitrides and borides of the Group IV and Group V transition metals comprise some of the best candidate materials for these applications; specifically within the transition-metal carbides (TMCs) and transition-metal nitrides (TMNs), materials such as ZrC, HfC, HfN, and TaC exhibit good mechanical properties and exceptional melting temperatures. Unsurprisingly, these materials share the same combination of metallic and covalent bonding; they all have a strong metallic character and are electrically conductive, and are thus often referred to as the "hard metals." Many of these materials—all of the Group IV and Group V TMCs, and the Group IV TMNs—also share stable rocksalt (NaCl), or B1, phases around the stoichiometric composition $MX_{1.0}$. The B1 crystal structure, shown in Figure 2.1, consists of two inter-penetrating face-centered cubic (FCC) lattices, one containing metal (M) atoms and the other containing non-metal (X) atoms. Furthermore, the rocksalt carbides and nitrides (TiC, ZrC, HfC, VC, NbC, TaC, TiN,

ZrN and HfN) are all predicted to exhibit large homogeneity ranges for the B1 structure [11–18], with significant off-stoichiometry being accommodated by structural vacancies on either the metal or nonmetal sublattice. Computed phase diagrams for the IVB and VB TMCs (Figure 2.2) and IVB TMNs (Figure 2.3) are reproduced in this text from a variety of sources, with the rocksalt-phase region highlighted in blue. The broad B1 phase stability seen in these compounds gives rise to fascinating variations in mechanical, electrical and thermal properties at different non-metal-to-metal atom ratios, raising the possibility of detailed design of these materials via alterations to stoichiometry. Much of the interest in the TMCs and TMNs stems from the promise of precise tailoring of properties via composition and processing, which can (at least in principle) be used to optimize properties such as hardness, toughness and melting temperature. In hafnium carbide, HfC_y , for example, a possible sub-stoichiometric maximum melting temperature has been observed in the range $0.9 < y < 1.0$ [19–22], and a recent study claimed $\text{HfC}_{0.98}$ to have the highest melting temperature of any known compound [23].

The structural and bonding similarities between the Group IV and Group V TMCs and the Group IV TMNs also give rise to high mutual solubility within this class of materials [24], and mixing of the B1-structured transition-metal ceramics has been explored in some detail. The transition-metal carbonitrides (TMCNs) are, generally speaking, an example of this: they consist of solid solutions of a transition metal’s carbide and its nitride (*e.g.* the titanium carbonitrides, $\text{TiC}_{1-y}\text{N}_y$, which are solid solutions of B1 TiC and B1 TiN). In these materials, mixing is accomplished by substitutions on the non-metal sub-lattice, while the metal lattice remains the same. Much prior work has been dedicated to exploring the effects of carbonitride composition on properties such as elastic moduli [25], hardness [25, 26] and melting temperature [27]. In addition to mixing via substitution on the non-metal sub-lattice, alloying of carbides via metal-atom substitutions has also been explored for decades. Early work on the ZrC-TaC system discovered an elevated melting temperature around the $\text{Zr}_{0.2}\text{Ta}_{0.8}\text{C}$ composition, exceeding the melting temperatures of both ZrC and TaC [28]. Subsequent investigation supported this result, and also identified a maximum hardness at an intermediate composition in the $\text{Zr}_{1-y}\text{Ta}_y\text{C}$ system [29]. Experimental

studies have also indicated exceptional melting temperatures in the HfC-TaC system [21, 23, 28], often exceeding 4000 K; some of these works have suggested that the maximum melting temperature in this system is achieved at an intermediate composition (a solid solution of HfC and TaC). Recent *ab-initio* modeling has supported these findings, predicting elevated melting temperatures in the hafnium carbo-nitrides, $\text{HfC}_{1-y}\text{N}_y$ and in the hafnium-tantalum carbides, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ [27].

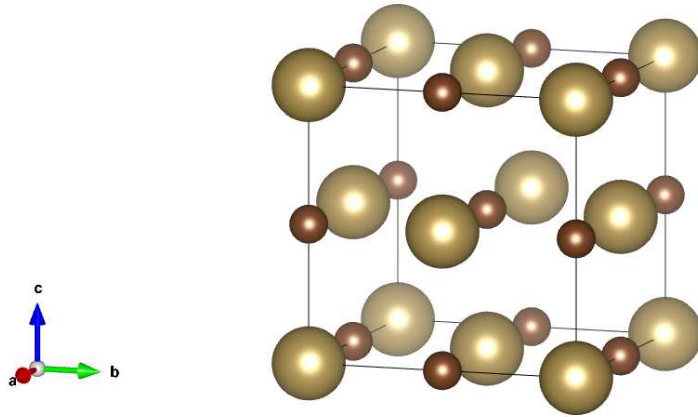


Figure 2.1: Representative model of the rocksalt (B1) crystal structure, formed from two inter-penetrating FCC lattices containing atoms of unlike type. Large gold-colored spheres represent metal (in this case, tantalum) atoms, while the smaller brown spheres represent non-metal (in this case, carbon) atoms. Image generated using VESTA [30].

At elevated temperatures—above roughly $0.5T_m$ —the carbides and nitrides behave similarly to metals, exhibiting significant plasticity under an applied load. At room temperature, however, most of these materials are quite hard and brittle. The Group IV carbides in particular are known to exhibit essentially negligible plasticity in tensile, bending and indentation tests; the Group V carbides and the Group IV nitrides are seen to behave in a more "ductile" manner, but still possess high hardness and tend to crack during indentation. Specifically on the topic of indentation hardness, several of these compounds are seen to have maximum hardnesses at sub-stoichiometric compositions, *i.e.* with some nonzero concentration of structural vacancies on the non-metal sublattice; furthermore, ordering of these vacancies into super-structures has been claimed to have

non-negligible effects on measured hardness [31, 32]. The phase diagrams for the IVB and VB TMCs (Figure 2.2) predicted by Gusev [11] show that all of the cubic carbides are expected to form vacancy-ordered phases at low temperatures.

2.2 The Anomalous Hardness of Tantalum Carbides

The tantalum carbides, generally described by the chemical formula TaC_y , have been materials of interest for roughly a century [34] in various engineering fields. Owing to its good low-temperature hardness and exceptional melting temperature [35], TaC_y has been investigated extensively as a candidate material for hard coatings, in applications ranging from hypersonic flight [36] to power electronics [37, 38].

In his 1963 survey of properties of TaC_y , Santoro [39] observed "anomalous" variation in some properties with respect to carbon content. Specifically, the hardness was both seen to rise with some loss of carbon, achieving maximum values at compositions between $y = 0.8$ and $y = 1.0$; corresponding minima were found in both the ultimate tensile strength and the transverse rupture strength. This alone is an interesting observation: as Santoro pointed out, maximum values of strength and hardness could be reasonably expected to coincide, at least for materials with appreciable plasticity. Prior measurements [40] by Kieffer and Kolbl (1949), Foster *et al.* (1950), and Hinnüber (1950) assumed a stoichiometric composition, and only collected data for this composition; likewise, Mierson and Umanskii (1953) assumed a composition of $\text{TaC}_{1.0}$. Only the later work of Samsonov and Rukina (1957) tracked the hardness of TaC_y over a large composition range; these measurements showed a roughly linear decline in hardness with decreasing y within the domain $0.4 < y < 1.0$. Comparison of Santoro's results with previous experiments can be seen in Figure 2.5. Another investigation, carried out in 1966 by Steinitz [41], indicated a roughly linear increase in the hardness of TaC_y with decreasing y in the region $0.80 < y < 0.95$ —a trend essentially opposite to that reported by Samsonov and Rukina [42].

These results, along with those of subsequent investigations carried out by Ramqvist (1968) [43, 44] and Rempel *et al.* (1993) [45], were aggregated by Gusev *et al.* [24] and are shown in

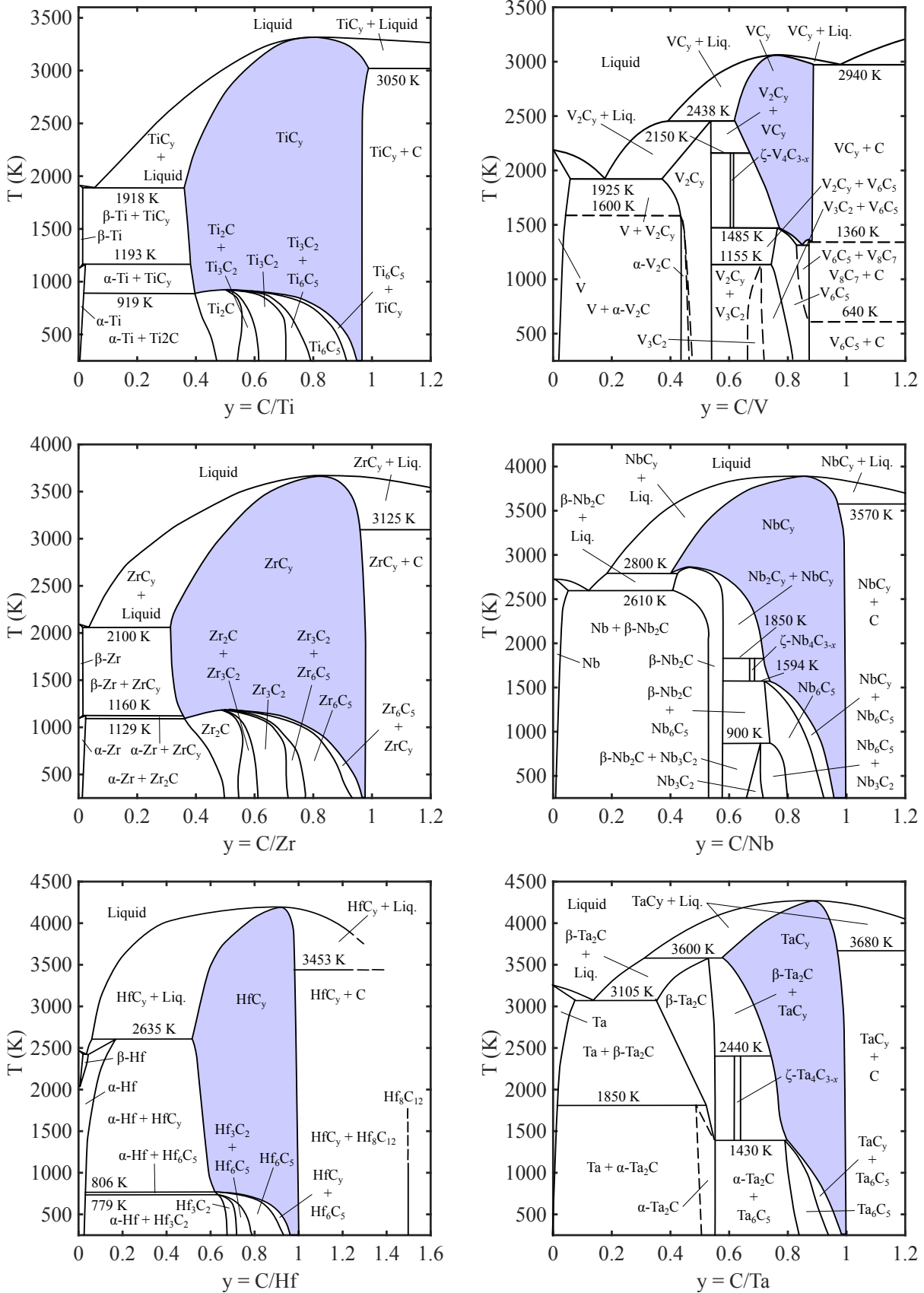


Figure 2.2: Binary phase diagrams computed by Gusev *et al.* (2000) [11] for the IVB and VB TMCs.

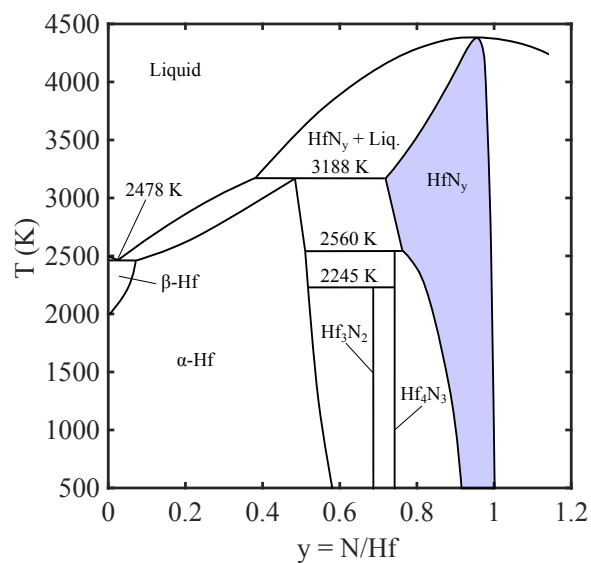
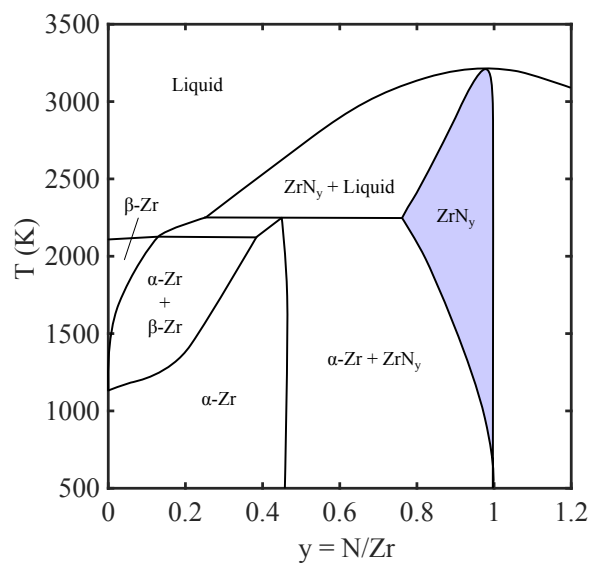
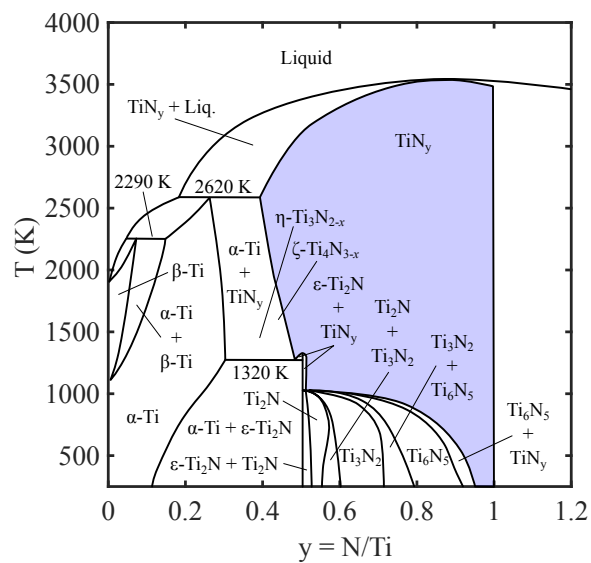


Figure 2.3: Binary phase diagrams computed for the IVB TMNs: TiN_y [11], ZrN_y [16], and HfN_y [14].

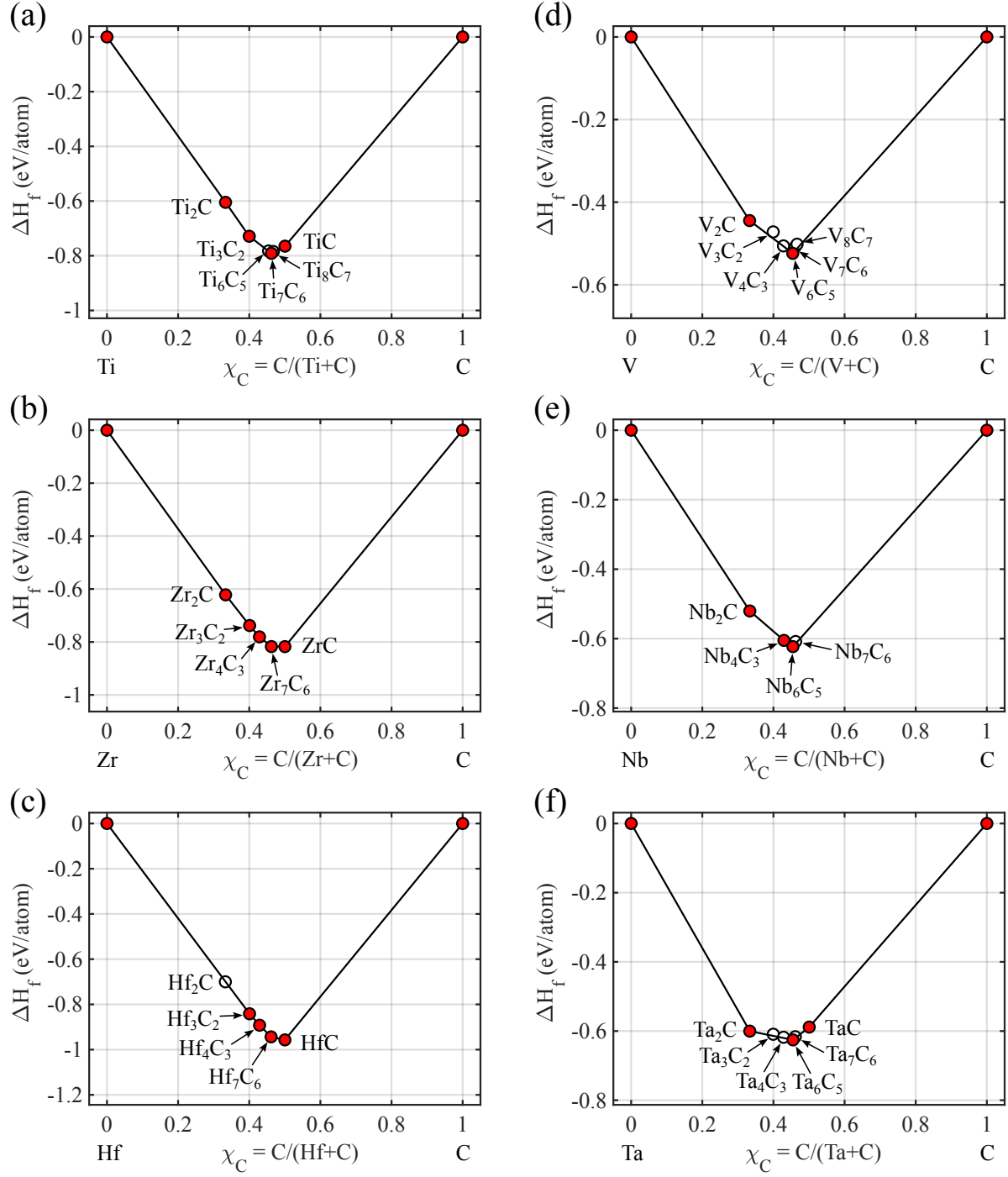


Figure 2.4: DFT-computed convex hull constructions for the Group IV and Group V TMCs: (a) TiC_y , (b) ZrC_y , (c) HfC_y , (d) VC_y , (e) NbC_y and (f) TaC_y . Filled red markers indicate stable phases, while unfilled markers indicate meta-stable phases lying close to the convex hull. Data taken from Yu *et al.* (2016) [33].

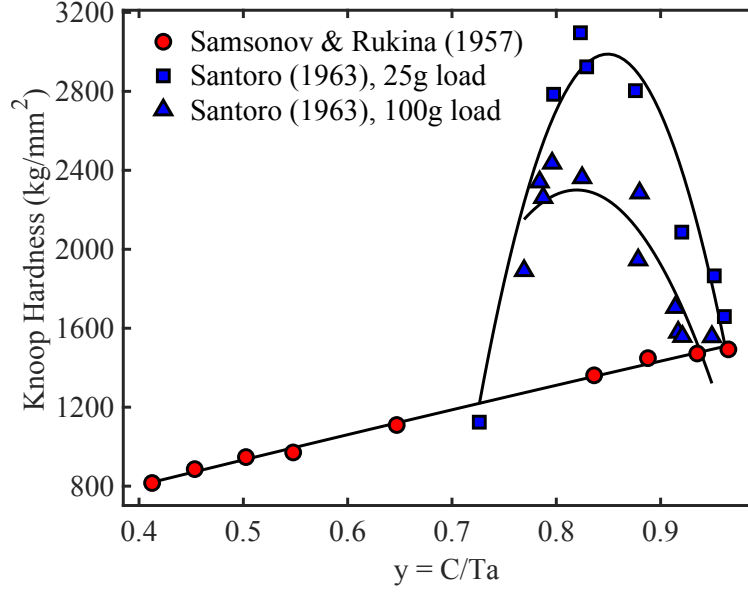


Figure 2.5: The 'anomalous' sub-stoichiometric maximum hardness observed in TaC_y by Santoro [39], compared to the earlier results of Samsonov and Rukina [42]. Second-order polynomial (*i.e.*, quadratic) fits are shown for each dataset, illustrating the qualitative difference in behavior reported in the two experiments.

Figure 2.6. Taken together, the results of these different experiments indicate a fairly unambiguous "anomalous" behavior in the hardness of TaC_y , although the magnitude of the sub-stoichiometric hardness increase and the exact composition at which it occurs are not obvious from these data. What can be reasonably concluded is that the sub-stoichiometric peak hardness of TaC_y is reliably observed in experiments. Looking at the aggregated data of Gusev *et al.* more broadly, the trends observed in these works indicate very different behaviors in the IVB and VB carbides. In the IVB TMCs, loss of carbon content yields a monotonic and roughly linear decrease in indentation hardness; in the VB TMCs, the trends are more disparate and less intuitive. TaC_y , according to the various included datasets, displays an anomalous sub-stoichiometric peak around $y \approx 0.84$. NbC_y , while exhibiting the same diminished hardness near the stoichiometric composition $y = 1$, does not feature an obvious sub-stoichiometric maximum hardness; rather, loss of carbon in NbC_y seems to produce a monotonic increase in hardness until the boundary of its rocksalt homogeneity range is reached at $y \approx 0.75$. Since the homogeneity range of VC_y is much smaller, a comparison with the other carbides is more difficult to make; between $y \approx 0.57$ and $y \approx 0.88$, loss of hardness results in a reduction in hardness similar to that seen in the IVB carbides. This behavior can be

taken to be consistent with either that of the IVB TMCs, or that of TaC_y , depending on one's interpretation. Adding further intrigue to the problem of 'anomalous' hardness is the behavior of the IVB TMNs—also shown in Figure 2.6—which are generally seen to behave similarly to the VB TMCs; this will be explored further in Section 2.3.

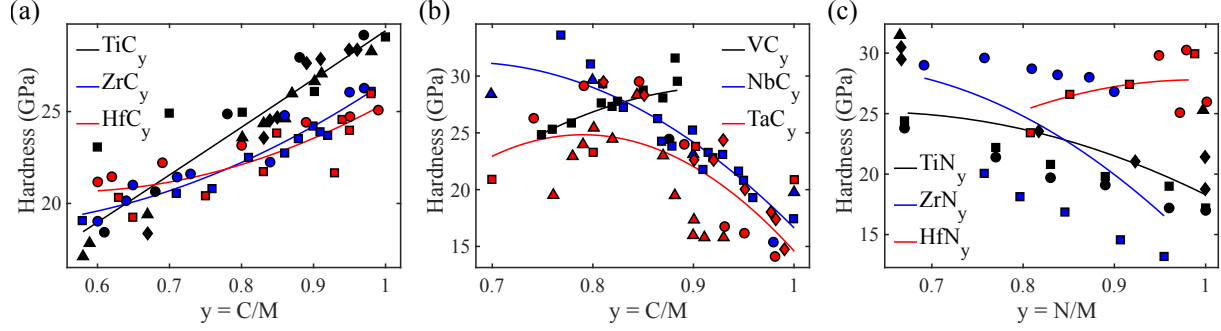


Figure 2.6: Measured hardness as a function of carbon content in the rocksalt-structured TMCs and TMNs: TiC_y [43,45], ZrC_y [43], HfC_y [43], VC_y [44], NbC_y [44,45], TaC_y [39,44,45], TiN_y [46–48], ZrN_y [25,49] and HfN_y [50,51]. Figure published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

But why do these compounds, with their shared rocksalt structure and metallic-covalent bonding character, behave so differently? A number of plausible explanations for the disparate hardness trends have been proposed. Prior works on the topic have leant on arguments regarding increased cohesive energy, bond stiffness, phase transitions, vacancy-ordering effects, changes in porosity, and changes in slip plane preference. The evidence available for each of these candidate mechanisms will be discussed below.

2.2.1 Cohesive Energy

A naïvely compelling explanation stems from a possible increase in the cohesive energy of some of the carbides with some loss of carbon content; that is, if these materials see some increase in cohesive energy (*i.e.*, larger enthalpy of formation) at lower carbon-to-metal ratios, then they can be expected to exhibit greater overall bond strength, and therefore will offer greater resistance to indentation. Materials scientist John J. Gilman likened the motion of a dislocation in a crystal to a chemical reaction [53], and sought to model it as such. In this view, the core of a dislocation in

a covalent material like SiC can be seen to consist of a line of broken silicon-carbon bonds. Thus, as a dislocation kink moves, a silicon-carbon bond ahead of the kink is broken, and a new one is formed behind it; the reaction can be modeled via the substitution equation:



with C and C' indicating that the carbon atoms participating in the initial and final covalent bonds are not the same. A schematic illustration of this is shown in Figure 2.7, outlining the reaction coordinate system between 0 (starting state) and w (final state). The unstable intermediate position (the transition state) is located at $w/2$. It should be noted that, in this work, Gilman takes issue with the more conventional Peierls-Nabarro model (discussed in greater detail in Section 2.6), which generally predicts very high kink mobilities and thus neglects resistance to kink propagation as a rate-limiting factor for dislocation motion. In contrast, Gilman identifies the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as the quantity of interest; this selection is made because the HOMO can be taken to represent a bonding state, whereas the LUMO is taken to be an anti-bonding state. Thus, as the carbon atom moves toward the $(\text{CSiC}')^*$ transition state at $w/2$, the original Si-C bond changes from bonding to anti-bonding; the final Si-C bond changes from anti-bonding to bonding. The energy difference, $\Delta\epsilon$, between the bonding energy ϵ_b and the anti-bonding energy ϵ_a is the HOMO-LUMO gap, meaning that the HOMO-LUMO gap is thus essential in determining the height of the energy barrier and the maximum value of the restorative force ($\propto \frac{\partial\epsilon}{\partial x}$). Unlike the sinusoidal restorative force assumed in the Peierls-Nabarro model, Gilman's formulation produces a discontinuity in the restorative force at the transition state; this is attributed to the broken symmetry of molecular orbitals at the center of the kink.

In SiC (and, in fact, in the B1 TMCs and TMNs) $w = b$, where b is the dislocation Burgers vector magnitude; assuming a parabolic form for the energy curve, Gilman derives a maximum force equal to $2\Delta\epsilon/b$. This force acts on an area equal to half the area bounded by the initial and final kink boundaries, since the model assumes that the maximum restorative force occurs when

the C atom has moved to the $w/2$ position. Given the hexagonal symmetry of the slip plane, this should produce an area given by

$$A = \frac{1}{2}b^2 \sin \frac{\pi}{3} = \frac{1}{2}b^2 \frac{\sqrt{3}}{2} = \frac{\sqrt{3}}{4}b^2 \quad (2.1)$$

However, Gilman arrives at an area equal to $b^2/2$; the reasoning behind this is not clearly stated in the article. Nonetheless, this finding produces a theoretical shear stress equal to

$$\tau = \frac{4\Delta\epsilon}{b^3} \quad (2.2)$$

and produces plausible estimates for the shear strength of SiC.

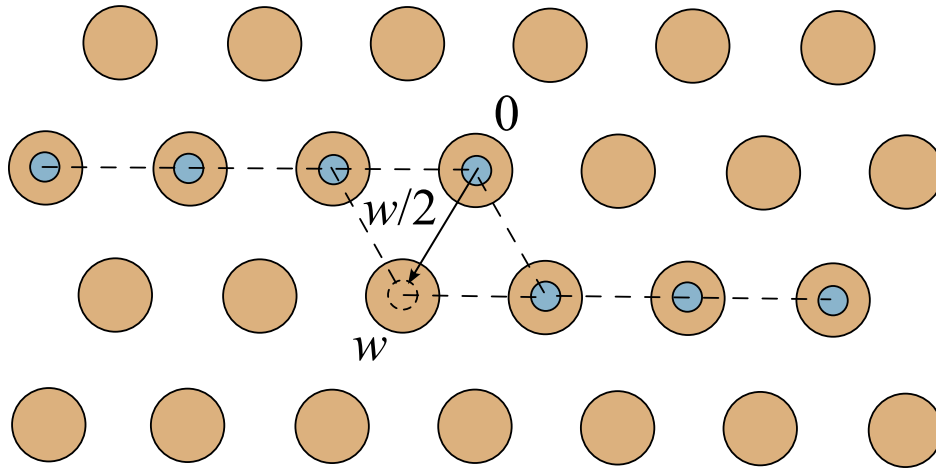


Figure 2.7: Schematic illustration of dislocation kink propagation in SiC, viewed perpendicular to the glide plane. The reaction coordinate ranges from 0 to w , with the unstable (highest-energy) point being located at $w/2$.

For the transition-metal carbides, though, this approach encounters a serious complication: though the carbides contain a great deal of covalent bonding, they have a significant metallic character, and thus do not have a defined HOMO-LUMO gap. Thus it becomes necessary to offer a different explanation. Gilman proposes that a simple model for the hardness of these "hard metals" may be obtained simply by examining the excess cohesive energy associated with "metal-metalloid interactions" which must be exceeded in order to move a dislocation [54]. This gives rise

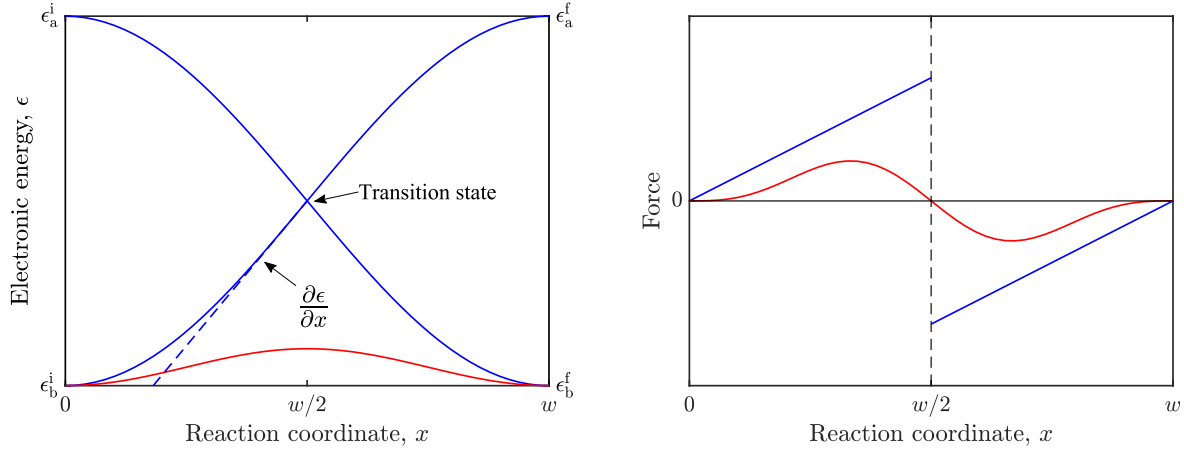


Figure 2.8: Energy correlation diagram (left) for kink propagation reaction proposed by Gilman [53], showing the shift in bonding (ϵ_b) and anti-bonding (ϵ_a) energy contributions as the C atom is displaced between 0 and w . The restorative force (right) associated with this energy change shows a discontinuity at the unstable point $w/2$. The kink propagation reaction model behavior is indicated in blue, with the sinusoidal Peierls-Nabarro (PN) energy and restorative force shown in red for comparison.

to a straightforward correlation with the Burgers vector magnitude and the formation enthalpy:

$$H_V \approx \frac{\alpha_G \Delta H_f}{b^3}, \quad (2.3)$$

where the leading coefficient α_G is the Gilman factor, confusingly equal to either 2 or 3 depending on the time of publication. Gilman's 2005 article in *Materials Science and Engineering A* provides some clarification, stating that the local bonding at the mid-glide position ($u = b/2$) is reduced essentially to zero. In this case, the work performed by the applied shear stress, τ , is taken to be τb^3 , and the resistance is equated to the energy required to fully break the local bonds; this latter quantity is the formation enthalpy ΔH_f . Work-energy equivalence then gives

$$\tau \approx \frac{\Delta H_f}{b^3}. \quad (2.4)$$

Gilman further argued that a leading coefficient of 2 converts the shear stress into a compressive stress, and that a value of $\alpha_G = 3$ converts it into a hardness number [55]. The precise logic behind this decision is not entirely clear; in this 2005 article, Gilman chose a leading coefficient value of

3; in his 1996 article, published in the same journal, he selected a value of $\alpha_G = 2$. Further complicating this model is the option of the author to express ΔH_f in units of kJ/mol; this can have different meanings depending on the value of y in the chemical formula TiC_y , for example, as off-stoichiometry will change the number of moles of atoms present in each mole of formula units. Thus, it is probably most reasonable to take α_G to be a fitting parameter, whose value can be tweaked to obtain optimal correlation between theory and experiment, rather than as a physically significant constant determined from first-principles considerations. It should be further noted that this represents a charitable view of Gilman's model, giving it as much flexibility as possible in relating chemical (energetic) and mechanical properties in the "hard metals."

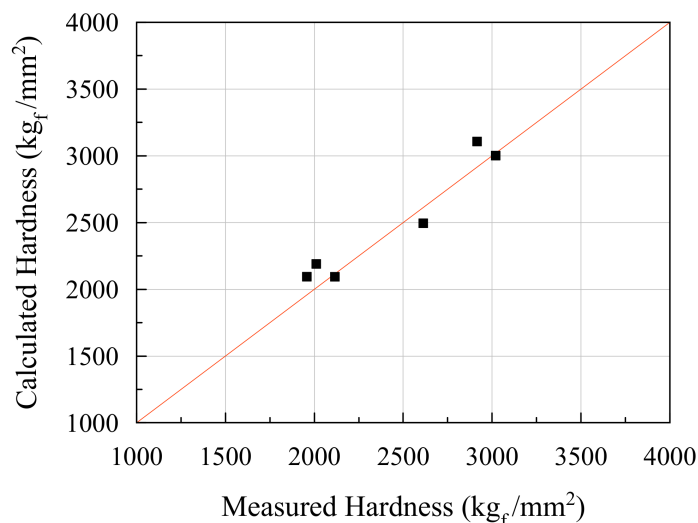


Figure 2.9: Published correlation between measured and computed indentation hardness of IVB and VB TMCs, according to Gilman's enthalpy-based model [55].

In any case, Gilman's model has yet to be applied to sub-stoichiometric carbides; it is possible that such an analysis would reveal a peak in computed hardness (arising from a peak in the enthalpy of formation) in TaC_y at some composition $y < 1.0$, which would do a great deal to explain the anomalous hardness trend. But is there any indication of a sub-stoichiometric maximum in the formation enthalpy of TaC_y ? In fact, Ramqvist (1969) [56] compared shifts in the inner electron binding energy (an indicator of charge transfer, computed relative to the binding energy

seen in the pure metals) to formation enthalpy data aggregated from prior experiments [57–61]. The ΔH_f data actually do present the possibility for "anomalous" trends in the cohesive energies of the B1 monocarbides: while the formation enthalpies of TiC_y and VC_y exhibit fairly unambiguous declines with loss of carbon content, the trends seen in NbC_y and TaC_y are far less obvious. Furthermore, it could be claimed that both NbC_y and TaC_y actually see increased ΔH_f with some loss of carbon content, although the large spread in nominal values (as well as the very large error bars) make it difficult to draw any concrete conclusions. In light of these confounding details, the trendlines indicated by Ramqvist (seen in Figure 2.10) do look a bit spurious—perhaps an attempt by the author to reconcile these findings with his own previous hardness measurements [43,44]—but nonetheless it is certainly possible that NbC_y and TaC_y exhibit sub-stoichiometric maxima in their cohesive energies.

There is actually reason to suspect something to this effect: prior work has speculatively attributed differences in the properties of the Group IV and Group V TMCs to optimal filling of molecular orbitals in the B1 crystal structure. These arguments depend on the notion of valence-electron concentration (VEC), or the number of valence electrons present per unit volume in the material. Since the cubic TMCs have similar lattice constants, this quantity is commonly expressed in dimensions of electrons per formula unit (f.u.) or per unit cell. This concept is paired with ligand-field (LF) theory, wherein atomic d -orbitals split into non-degenerate energy levels in the presence of an applied electric field, such as in a crystalline solid. A more detailed explanation of this theory will be given in Section 2.5, but for now it will suffice to point out that population of the lower-energy states by valence electrons will lower the energy of the compound—contributing to bonding—while the occupation of higher-energy electronic states will increase the compound's energy and form an anti-bonding state. Thus, changes in VEC within a given crystal structure may dramatically alter the occupation of anti-bonding states, resulting in alterations to the net bonding contribution of the occupied states to the band energy.

In a recent computational study, Liang *et al.* (2021) indicated a maximum (magnitude) energy of formation at a VEC of about 8 electrons/f.u. in the rocksalt-structured carbides [62]. These

authors attributed the increased formation energy at this VEC to the optimal filling of molecular orbitals; bonding (lower-energy) e_g states are derived from the metal d_{z^2} and $d_{x^2-y^2}$ orbitals, whereas the anti-bonding (higher-energy) t_{2g} states are derived from the atomic d_{xy} , d_{yz} and d_{zx} orbitals. Comparing rocksalt HfC and TaC, they observe features in the electron density-of-states (DoS) that indicate similar occupation of bonding e_g states (which hybridize with the C-2p and C-2s atomic orbitals) in both compounds. However, the DoS indicates significant occupation of the t_{2g} states just below the Fermi level in TaC—a feature which is absent in HfC. Since these are considered anti-bonding states, Liang *et al.* conclude that increasing VEC from 8 electrons/f.u. to 9 electrons/f.u. in the rocksalt structure populates higher-energy states, and thus reduces the net bonding contribution of the occupied states to the band energy. Two things to note about this work, though, are that (1) the bonding/antibonding character the authors claim is the reverse of that claimed in most work (*i.e.*, the t_{2g} states are typically assumed to be lower-energy), and that (2) the more detailed bonding analysis performed in this work did not actually indicate any additional occupation of bonding states due to the additional electrons.

Some prior experimental work on the carbides also points to a VEC-based change in cohesive energy. Vinitskii (1972) [63] computed the extent of charge transfer from the metal atoms to the carbon atoms in the transition-metal carbides, using the data collected by Ramqvist (1969) [64]. The calculated electron configurations for TiC, ZrC, HfC, VC, NbC and TaC are shown in Table 2.1; these data show that the charge transfer to the carbon atoms is relatively constant across all of the cubic carbides, and that the additional valence electron (per f.u.) present in the VB TMCs occupies states formed from hybridized metal-atom orbitals. Vinitskii even argued that, due to the increased occupation of t_{2g} states in the VB TMCs, the overall bonding state would be less energetically favorable than in the IVB TMCs. Furthermore, this work claimed that the IVB TMCs possessed sub-optimal occupation of the t_{2g} states, implying that the optimal occupation of bonding states (and thus the highest net bonding contribution to the band energy, *i.e.* the greatest bond strength) would occur at some intermediate VEC between 8 and 9 electrons/f.u. This is somewhat at odds with the findings of Liang *et al.*, which indicated greatest favorability at a VEC

of 8 electrons/f.u., but would be in good agreement with a cohesive-energy-based explanation for the sub-stoichiometric peak hardness of TaC_y : the maximum hardness in TaC_y is generally claimed to appear around $y \approx 0.84$, or at a VEC of about 8.4 electrons/f.u.

Table 2.1: Charge transfer and valence electron configuration data computed for the Group IV and Group V TMCs by Vinitskii [63]. Charge transfer data taken from prior work by Ramqvist [64].

Carbide	ΔE (eV) [64]	Δq ($-e$) [64]	C config.	Me config.
TiC	-3.3	0.40	$s^2p^{2.4}$	$se_g^2t_{2g}^{0.6}$
ZrC	-3.7	0.45	$s^2p^{2.45}$	$se_g^2t_{2g}^{0.55}$
HfC	-4.0	0.48	$s^2p^{2.48}$	$se_g^2t_{2g}^{0.52}$
VC	-2.6	0.32	$s^2p^{2.32}$	$se_g^2t_{2g}^{1.68}$
NbC	-2.9	0.35	$s^2p^{2.35}$	$se_g^2t_{2g}^{1.65}$
TaC	-2.9	0.35	$s^2p^{2.35}$	$se_g^2t_{2g}^{1.65}$

2.2.2 Elastic Stiffness

Closely related to the cohesive energy argument is an argument arising from the stiffness of bonds within a crystalline solid. Even if the carbides do not possess enhanced cohesive energies at sub-stoichiometric compositions, might they still contain stiffer bonds? And, furthermore, might the bonds in particular directions (*e.g.* the cubic shear modulus C_{44} in the C_{ij} stiffness matrix) be stiffened at reduced carbon contents? The correlation between materials' hardness and stiffness has been observed for some time. Teter [65] demonstrated that both the bulk modulus and the shear modulus of a material can be used to predict its hardness, Figure 2.11, with the shear modulus being a more reliable predictor than the bulk modulus. This is intuitive on some level: stiffer materials, generally possessing stronger interatomic bonds, may be expected to resist plastic deformation to a greater degree, since plastic deformation involves the straining, breaking, and re-forming of interatomic bonds. While this view may be simplistic—it ignores anisotropy in slip resistance, as well as the fact that elastic stiffness characterizes resistance to small, reversible deformations—it has proven effective for predicting some general hardness trends. Furthermore, within the IVB

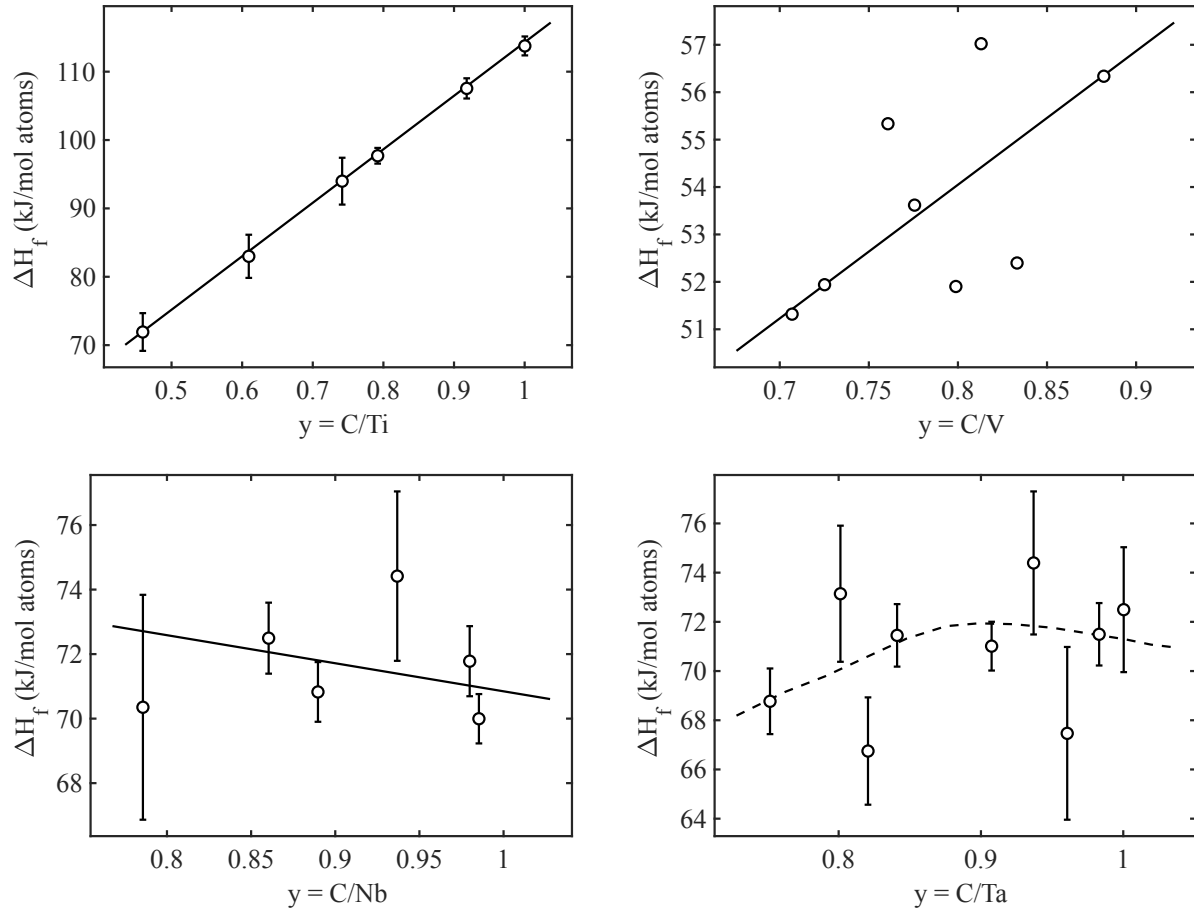


Figure 2.10: Enthalpy of formation as a function of carbon content in selected TMCs, as measured by Ramqvist [56].

and VB TMCs, large variations in the compliance of the bonding network should not be expected, since these carbides all have large rocksalt-phase homogeneity ranges; thus, variations in elastic stiffness among the carbides may be attributed primarily to variation in average bond strength, or, alternatively, spatial density of interatomic bonds.

It should be noted that some prior computational work has claimed maximum stiffnesses in B1 carbides and carbo-nitrides at specific VEC values. Jhi *et al.* (1999) [67] claimed maxima in the DFT-computed C_{44} moduli in the HfC-HfN, ZrC-NbC and TiC-TiN pseudo-binary systems, at VEC values between 8.2 electrons/f.u. and 8.6 electrons/f.u. Subsequently, Liang *et al.* (2021) [62] computed DFT elastic constants for a wide range of carbides; this work found maxima in elastic moduli at a VEC of 9 electrons/f.u. in the B1 structure. Both of these works pointed to optimal

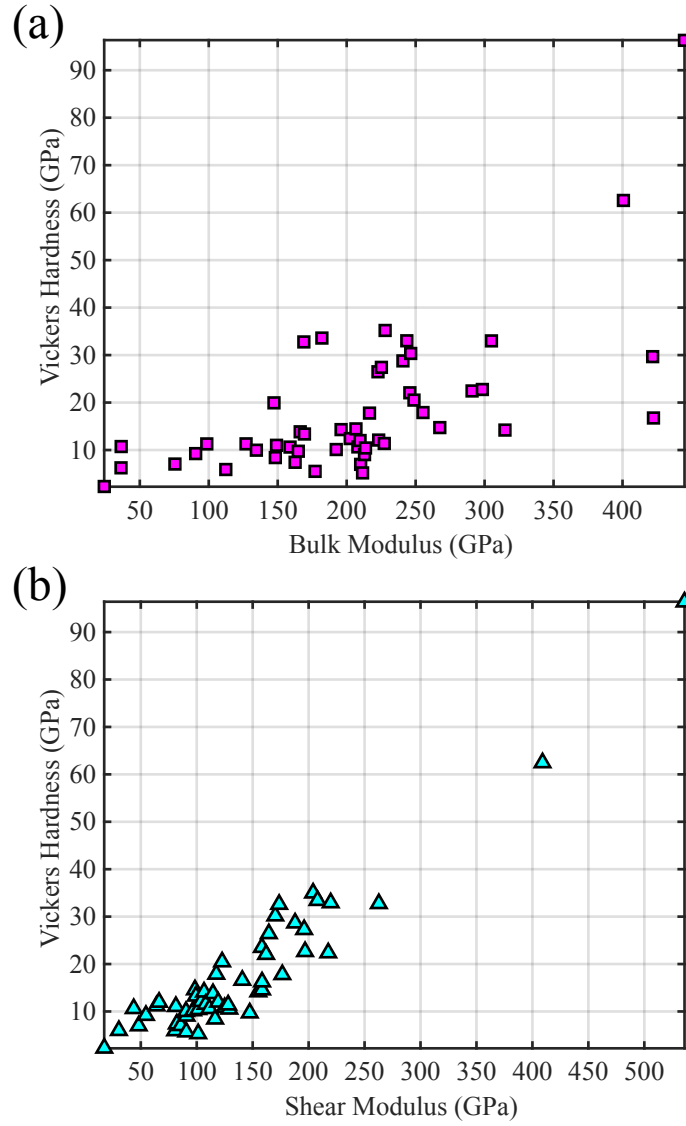


Figure 2.11: Correlation of Vickers hardness with (a) bulk moduli and (b) shear moduli for various materials [65].

Table 2.2: DFT-computed elastic moduli for rocksalt-structured Group IV and Group V transition-metal carbides, taken from Yu *et al.* [66]. All stiffness values are in GPa. The Young’s modulus, E , and the Hill averaged shear modulus, G , were not reported for the stoichiometric ($y = 1.0$) carbides in this work.

Elastic constant	TiC _y	ZrC _y	HfC _y	VC _y	NbC _y	TaC _y
$y = 1.0$						
C_{11}	546	490	540	669	644	737
C_{12}	133	112	112	152	129	141
C_{44}	162	147	171	186	166	175
G						
B	270	238	253	332	302	340
E						
$y = 0.96875$						
C_{11}	541	484	535	663	628	709
C_{12}	127	108	110	143	133	147
C_{44}	162	146	170	184	162	169
G	179	161	184	211	192	207
B	265	234	252	317	287	337
E	438	394	445	518	474	515
$y = 0.875$						
C_{11}	520	460	508	640	608	684
C_{12}	117	104	107	138	126	147
C_{44}	154	139	162	170	153	157
G	171	153	176	199	181	195
B	252	223	223	305	287	337
E	419	374	425	490	452	488
$y = 0.75$						
C_{11}	470	403	464	557	512	579
C_{12}	113	105	101	164	150	172
C_{44}	118	105	131	107	109	116
G	139	120	149	139	134	147
B	233	204	223	285	270	308
E	348	301	366	359	345	380

filling of molecular orbitals by the valence electrons, an idea which will be discussed in greater detail in following sections. In these studies, however, nonstoichiometry was not considered; that is, the structures used for their calculations contained no vacancies. We would naïvely expect the presence of non-metal vacancies to produce reductions in the stiffness of the lattice, since the

density of bonds in the bonding network is being reduced; changes in VEC due to changes in stoichiometry should not meaningfully offset the loss of bond density.

Naturally, then, we should expect maxima in the elastic stiffnesses of the Group IV and Group V TMCs at the stoichiometric TMCs; that is, they should all exhibit some elastic softening as carbon atoms are removed from the non-metal sub-lattice. Prior *ab-initio* investigation of this phenomenon by Yu *et al.* (2015) broadly supports this intuition [66]. This work computed the cubic elastic moduli C_{11} , C_{12} and C_{44} , and from these quantities derived the Hill averaged shear modulus for a polycrystalline aggregate [68, 69]:

$$G = \frac{1}{2}(G_V + G_R) \quad (2.5)$$

where G_V and G_R are the Voigt [70] and Reuss [71] shear moduli, respectively given by

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (2.6)$$

$$G_R = 5 \frac{C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (2.7)$$

These moduli, along with the Young's modulus E and the bulk modulus B for sub-stoichiometric compositions, are shown in Table 2.2; the data generally show diminished elastic stiffness with loss of carbon content for the Group IV and Group V TMCs, including TaC_y . A clearer illustration of these trends can be seen in Figure 2.12, which shows the decline in the computed G values for all of the carbides. Based on the correlation identified by Teter, we would expect this to be the best indicator of hardness among the various elastic constants. The normalized values—normalized by the stoichiometric ($y = 1.0$) shear moduli to easily identify any sub-stoichiometric increase that may occur—show with even greater clarity that reduction in carbon content produces a reduction in the polycrystalline shear modulus in each of the Group IV and Group V TMCs, including TaC_y .

But more can be done to examine whether a sub-stoichiometric hardness is predictable from the elastic moduli. Beyond a simple correlation with the polycrystalline shear modulus, prior

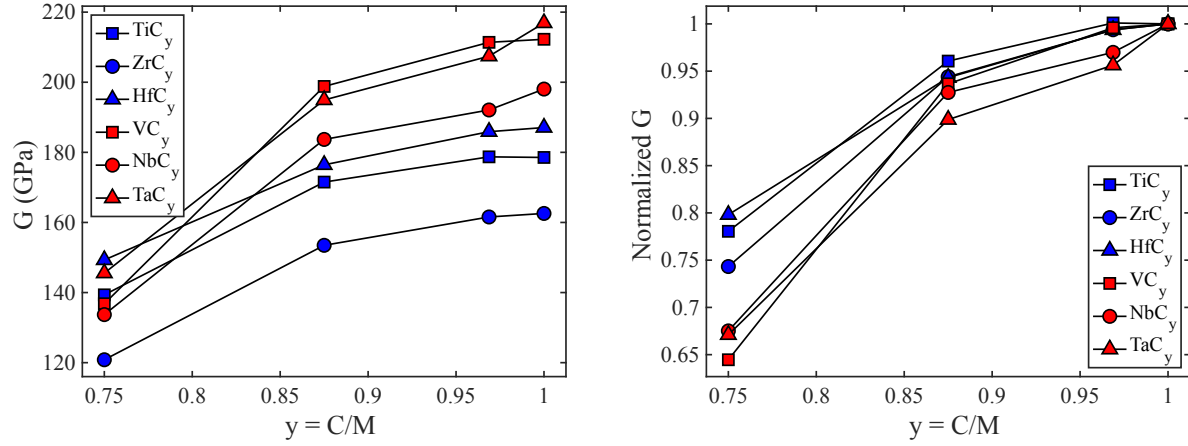


Figure 2.12: (a) Computed polycrystalline shear moduli for the Group IV and Group V TMCs, and (b) these same elastic moduli normalized by the values at the stoichiometric ($y = 1.0$) composition. Data taken from Yu *et al.* (2015) [66].

researchers have posited that the hardness may better correlate with the Pugh's modulus [72], which is given by

$$k = G/B \quad (2.8)$$

Conveniently, the Voigt and Reuss estimates for the bulk modulus are the same:

$$B_V = B_R = B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (2.9)$$

and so B can also be considered the average bulk modulus. Expanding on the Pugh's modulus correlation, Chen *et al.* (2011) derived a stiffness-based hardness model whereby the Vickers hardness could be estimated:

$$H_V \propto Gk^2 \quad (2.10)$$

This correlation was subsequently parameterized using a large sampling of hardness and stiffness values for different compounds [73], producing the following fit:

$$H_V = 2(k^2G)^{0.585} - 3 \quad (2.11)$$

This model was applied to the Group IV and Group V TMCs by Yu *et al.*, using the computed shear and bulk moduli discussed above; the results can be seen in Figure 2.13. As is evident from these data, TaC_y is not predicted to exhibit a sub-stoichiometric peak hardness; neither is NbC_y , the only carbide among the Group IV and Group V TMCs reported to show hardness behavior similar to that of TaC_y . Both materials appear to decrease monotonically in hardness with loss of carbon content. The only carbides which show even a modest increase in H for $y < 1.0$ are TiC_y and VC_y , neither of which are seen in experiment to exhibit an "anomalous" sub-stoichiometric hardness. TiC_y , firstly, exhibits a monotonic (and, in fact, almost perfectly linear) decline in hardness with decreasing y . Since VC phase separates into $\text{V}_8\text{C}_7 + \text{C}$ at carbon contents greater than $y \approx 0.88$, we can only draw good experimental conclusions regarding the range $0.50 < x < 0.88$; however, within this domain of compositions, VC_y seems to behave just like TiC_y . Thus, the model presented by Chen *et al.*, while perhaps valid over a wide range of materials, does not accurately reproduce the experimental hardness trends observed in the Group IV and Group V TMCs. For TaC_y , specifically, the trends computed by Yu *et. al* indicate the presence of no sub-stoichiometric maximum hardness, at least not one arising from increased stiffness of the bonding network.

More recent computational investigation by Gusev (2022) [74] into the elastic moduli of disordered TaC_y demonstrated essentially monotonic decline in the C_{11} , C_{12} and C_{44} stiffnesses with decreasing y within the interval $0.7 < y < 1.0$. It could be claimed from this work that there are sub-stoichiometric maxima in the C_{44} modulus (between $y = 0.96$ and $y = 0.97$), the shear modulus G (between $y = 0.96$ and $y = 0.97$), and the Pugh's modulus $k = G/B$ (between $y = 0.93$ and $y = 0.95$). However, these maxima are very modest, showing almost negligible deviation from the stoichiometric values. The following approximations were generated from the DFT data:

$$C_{11}(y) = C_{11}(y = 1)[1.89031y - 0.85992y^2] \pm 10.0\text{GPa} \quad (2.12)$$

$$C_{12}(y) = C_{12}(x = 1)[1.89031y - 0.85992y^2] \pm 5.0\text{GPa} \quad (2.13)$$

$$C_{44}(y) = C_{44}(y = 1)[-4.78732 + 12.03181y - 6.2246y^2] \pm 5.0\text{GPa} \quad (2.14)$$

And these fitted curves were used to compute theoretical hardness values using the correlation of Chen *et al.* described by Equation 2.11. The theoretical hardness fit then shows a (modest) sub-stoichiometric increase, rising from $H_V(y = 1.0) \approx 25\text{GPa}$ to a maximum value of $H_V(y \approx 0.95) \approx 26\text{GPa}$. Compared with the magnitudes of the sub-stoichiometric hardness increase reported in other literature, this seems far too small a change; furthermore, the curve-fitting scheme used for the C_{44} modulus appears to exaggerate the "anomalous" maxima in the elastic constants. Gusev also aggregated experimental data in this work, compiling bulk and shear moduli [75–81] for TaC_y . The trends seen in these (nominal) data support a small decline in B with decreasing y over the range $0.85 < y < 1.0$, and in G over the range $0.90 < y < 1.0$, but the error bars are large enough that any interpretation of the change in B and G within these composition ranges is spurious.

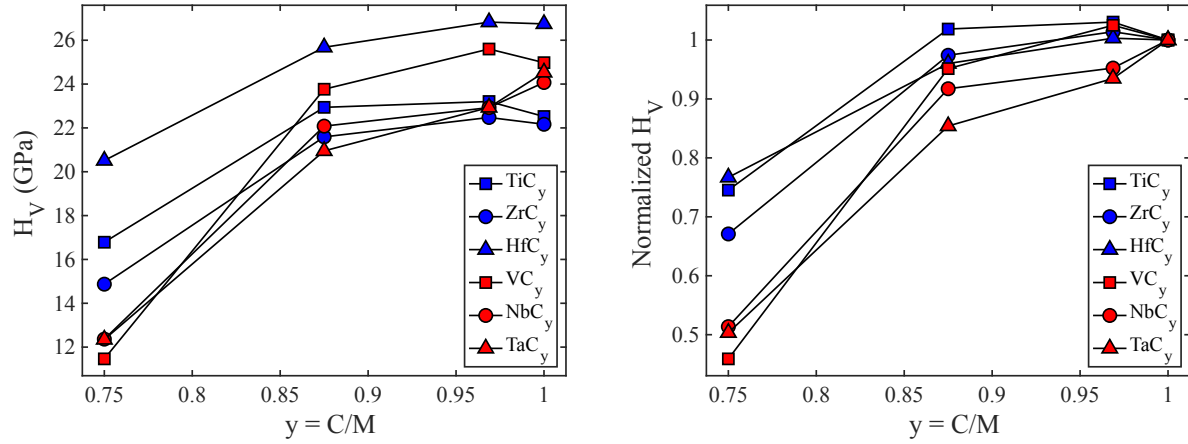


Figure 2.13: (a) Estimated hardnesses for the Group IV and Group V TMCs, computed from elastic stiffnesses; (b) the same predicted hardnesses normalized by the values at the stoichiometric ($y = 1.0$) composition. Data taken from Yu *et al.* (2015) [66].

2.2.3 Vacancy-Ordering Effects

Some prior work has attributed the anomalous hardness behavior of the Group IV and Group V TMCs to the presence of vacancy-ordered phases at sub-stoichiometric compositions, and not without reason. Ordering has been repeatedly observed in the cubic carbides at sub-stoichiometric

carbon contents, and (as seen in Section 2.1) all of the carbides are computationally predicted to contain vacancy-ordered phases at low temperatures. Electron bombardment of VC_y by Venables and Lye [82] in 1969 indicated the presence of a vacancy-ordered phase at a nominal composition close to V_6C_5 , and subsequent work by Billingham, Bell and Lewis [83] has identified two distinct ordered phases (nominally V_6C_5 and V_8C_7). Furthermore, Hiraga [84] has identified long-range ordered V_6C_5 structures consisting of enantiomorphic (anti-phase) domains. The spacing of these vacancy-ordered domains was found to be approximately 11 nearest-neighbor spacings, indicating a very high density of anti-phase boundaries in the material.

Transmission electron diffraction analysis of $\text{NbC}_{0.84}$ and $\text{TaC}_{0.83}$ single crystals grown by Venables and Myerhoff [85] revealed only weak vacancy ordering in the as-grown samples. Upon annealing and slow cooling through the expected disorder-order transition temperature, $\text{NbC}_{0.84}$ exhibited significantly increased vacancy ordering, and vacancy-ordered domains could be resolved via bright-field transmission electron microscopy (TEM) in the annealed samples. In $\text{TaC}_{0.83}$, however, annealing and cooling produced little difference in ordering, leading the authors to estimate a disorder-order transition temperature far lower in TaC than in NbC; the transition to ordering would then occur in a temperature range wherein carbon diffusion rates are low, meaning that excessive annealing times would be required to produce significant long-range vacancy ordering.

As in the rocksalt transition-metal carbides generally, sub-stoichiometry in TaC_y is accommodated by the presence of carbon vacancies on the nonmetal sub-lattice. This contributes to a fairly wide homogeneity range of the B1 crystal structure across different values of the carbon-to-metal ratio, y . At low temperatures (relative to the very high melting temperatures seen in TaC_y , of course), it has been claimed that long-range ordering of these carbon vacancies exists; furthermore, vacancy-ordering effects are often cited as explanations for variations in mechanical properties over different carbon contents. Prior computational work has also demonstrated the energetic favorability of carbon vacancy ordering in all of the Group IV and Group V transition-metal carbides. In TaC_y , specifically, Yu *et al.* [86] identified three stable ordered structures: TaC ($\text{Fm}\bar{3}\text{m}$), Ta_4C_3 ($\text{R}\bar{3}\text{m}$), and Ta_2C ($\text{P}\bar{3}\text{m}1$). Two additional structures, Ta_6C_5 ($\text{C}2/\text{m}$, $\text{C}2/\text{c}$ and $\text{R}\bar{3}\text{m}$ all having the

same enthalpy of formation) and Ta_3C_2 ($\text{R}\bar{3}\text{m}$), were found to lie near the convex hull, making them meta-stable phases. In a subsequent analysis by the same authors [33], the stable phases for TaC_y were determined to be Ta_2C , Ta_6C_5 , and TaC ; Ta_3C_2 , Ta_4C_3 , and a novel Ta_7C_6 ordered phase were found to be meta-stable. In both works, the stable and meta-stable phases within the range $0.75 < y < 1.0$ were found to be vacancy-ordered derivatives of the B1 structure, consistent with the B1 phase homogeneity ranges discussed in Section 2.1.

It has been suggested that ordering of these structural carbon vacancies in B1 TaC_y may contribute to the 'anomalous' sub-stoichiometric hardness maximum, via a mechanism similar to grain boundary strengthening. Hardening of a polycrystalline material via grain refinement is a very well-known phenomenon, with the most widely used phenomenological model being that of Hall [87] and Petch [88]:

$$\sigma_y = \sigma_\infty + k_{\text{HP}}d^{-1/2},$$

where σ_y is the material's yield strength, σ_∞ is the 'intrinsic' strength of the material, with infinitely large grains (*i.e.* no grain boundaries), d is the average grain diameter, and the parameter k_{HP} is the Hall-Petch slope. Thus, as the grain structure of the material is refined—or, equivalently, the spatial density of grain boundaries is increased—the boundary-strengthening term $k_{\text{HP}}d^{-1/2}$ grows, and the overall yield strength rises. Furthermore, there exists a well-known correlation between yield strength, σ_y , and hardness, H , established by Tabor [89]: $H = c\sigma_y$, where c is a constant known as the Tabor factor. Using this relation, the Hall-Petch model can be used to produce estimates of hardness:

$$H = H_\infty + k_{\text{HP}}d^{-1/2},$$

where H_∞ is the indentation hardness absent any boundary hardening effects. Here, the Tabor factor has simply been absorbed into the constant k_{HP} , since it is essentially a fitting parameter. It should also be noted that the above equation is not necessarily a good approximation, since the Tabor relation presupposes that the material does not undergo significant work hardening, *i.e.* that the work-hardening effect is small compared to the intrinsic strength of the material. This

is probably not a realistic assumption in the context of an indentation event, since considerable irreversible deformation—facilitated by dislocation nucleation and movement—is likely to occur. These objections aside, however, the Hall-Petch model may prove a good analogy for the proposed mechanism of hardness enhancement in the transition-metal carbides.

Hannink and Murray (1972) [32] posited that regions of uniform vacancy-ordering (ordering domains) could behave analogously to grains, and that the boundaries between ordering domains can similarly arrest dislocation motion. This work specifically highlighted the sub-stoichiometric $\text{VC}_{0.84}$, which (as discussed in the preceding paragraphs) has been shown to readily form regions of vacancy-ordered V_6C_5 . This vacancy-ordered phase is characterized by a hexagonal super-lattice of carbon vacancies superimposed on the host rocksalt structure. The super-lattice of vacancies is oriented with its basal plane on a $\{111\}_{B1}$ plane, meaning that the axis of the super-lattice is oriented along a $\langle 111 \rangle_{B1}$ direction. Figure 2.14 shows a "quasi-molecule" of the vacancy-ordered M_6C_5 phase, pictured within a conventional unit cell of the cubic host lattice. Since the vacancy super-lattice may have its axis along any $\langle 111 \rangle_{B1}$ direction, this naturally gives rise to ordering domains: as the carbide is cooled through the order-disorder transition temperature, regions of the ordered M_6C_5 phase will nucleate throughout the crystal and begin to grow. The domains will be randomly oriented along any of the four $\langle 111 \rangle_{B1}$ directions in the crystal. Given enough annealing time, the ordering domains will eventually grow together, forming anti-phase boundaries where they meet. These anti-phase boundaries might be expected to produce a similar effect to grain boundaries in a polycrystal, arresting dislocations that attempt to glide from one domain to another and causing dislocation pile-up.

To test this, Hannink and Murray synthesized various samples of $\text{VC}_{0.84}$ using a floating-zone technique and cooled them at different rates: 0.8 °C/s, 9.5 °C/s, 62.5 °C/s and 225 °C/s. As might be expected, faster cooling was seen to produce much finer ordering domains (see Figure 2.15); additionally, slower cooling also increased the number of dislocations visible in the specimens. The authors attributed this difference in dislocation density to the slow growth of ordering domains, wherein the misfit between the ordered V_6C_5 domain and the surrounding disordered

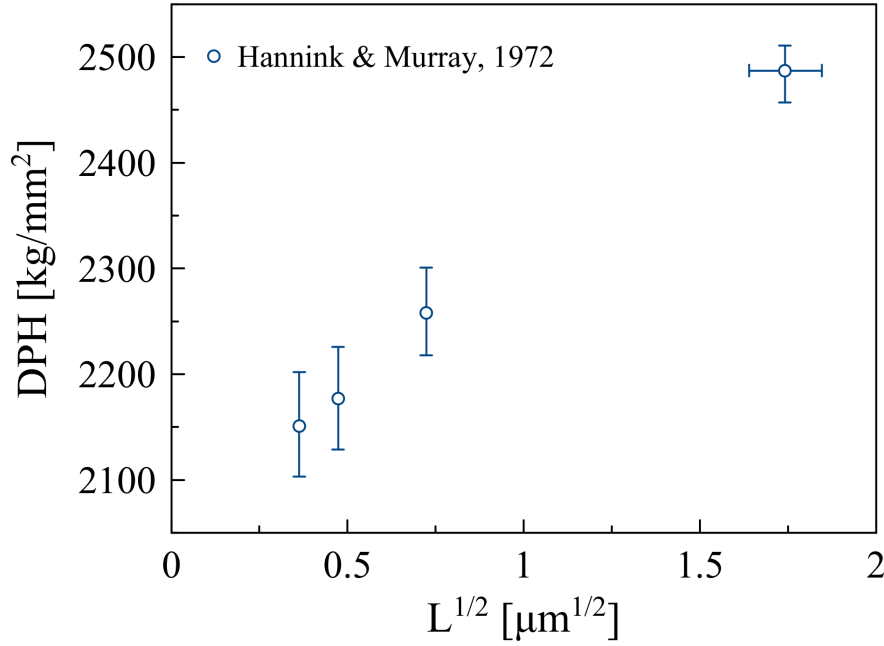


Figure 2.14: Illustration of vacancy-ordered M_6C_5 phases, showing different quasi-molecule stacking sequences: (a) monoclinic C2/m , (b) trigonal P3_1 and monoclinic (C2); (d) Orientation of quasi-molecule relative to conventional B1 unit cell. Image published by Gusev *et al.* [24].

$\text{VC}_{0.84}$ crystal would cause dislocations to nucleate. In the faster-cooled samples, where many ordered domains nucleate in quick succession, the authors argue that the amount of domain growth is insufficient to produce such large numbers of dislocations before the domains intersect. In any case, the mean-average axial domain sizes and measured hardnesses were used to parameterize a Hall-Petch model, arriving at $k_{\text{HP}} = 0.37\text{kg/mm}^{3/2}$ and $H_{\infty} = 2080\text{kg/mm}^2$. The data shown in Figure 2.15 show good agreement with the proposed Hall-Petch behavior, indicating that something akin to grain boundary hardening is likely taking place in the V_6C_5 specimens. The indents reported in this work lend further credence to this explanation: in addition to the $\langle 100 \rangle$ cracks due to cleavage, their indents contained cracks along $\langle 110 \rangle$ directions. The authors reported that the $\langle 100 \rangle$ cracks generally appeared as the indenter was withdrawn from the sample, and therefore attributed them to cleavage on the $\{100\}$ planes; the $\langle 110 \rangle$ cracks, in contrast, were seen to form during indentation, and were attributed to dislocation pile-up at the intersection of different $\{111\}$ planes. Furthermore, the authors of this work etched their indented samples in an attempt to deter-

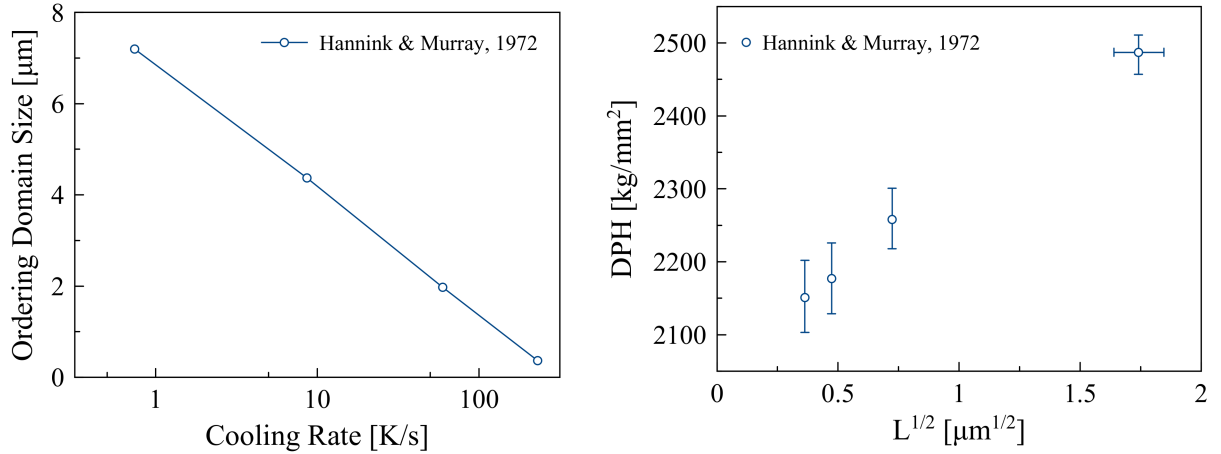


Figure 2.15: (a) Effect of cooling rate on the average ordering domain size in vacancy-ordered V_6C_5 ; (b) effect of average ordering domain size on the indentation hardness of V_6C_5 . Figure taken from Hannink and Murray (1972) [32].

mine the preferred slip plane; though this was unsuccessful, a large number of dislocations were indicated by the etching.

This work raises an interesting point: in vacancy-ordered V_6C_5 , this experiment offers plenty of evidence for the existence and movement of dislocations. The results also agree well with a Hall-Petch model, lending support to the idea of a boundary-hardening phenomenon arising from ordering in sub-stoichiometric VC_y . However, another possible contribution to the increased hardness of the domain-refined samples could be a very low dislocation density. With such small ordering domains, it is possible that—arguments regarding dislocation mobility and pile-up aside—there is simply not a sufficient number of dislocations present to facilitate plastic deformation. Sticking to boundary hardening effects, though, the authors note that each ordering domain has one unique $\{111\}$ plane—its basal plane, perpendicular to its axis—and that slip anisotropy within each domain may arise from the different types of $\{111\}$ planes present. This, the authors argue, would contribute to dislocation pile-up, since slip resistance could change dramatically at an anti-phase boundary even if the dislocation remains on the same crystallographic plane within the B1 host lattice.

To our knowledge, no similar experimental analysis has been performed on either TaC_y or NbC_y , making it difficult to draw any real conclusions regarding vacancy-ordered domain refinement and the "anomalous" rise in hardness of sub-stoichiometric NbC_y and TaC_y . Frustratingly, VC_y is the only carbide among the Group V TMCs which does not show an anomalous hardness—either due to lack of phase homogeneity in the relevant composition range, or due to other factors. However, other prior work exists which may leave us more or less skeptical of the vacancy-ordering hypothesis regarding the "anomalous" hardness.

Specifically, prior to any speculation on the *effects* of vacancy ordering in TaC_y , the actual *prevalence* of vacancy ordered phases must be considered. Even though *ab-initio* calculations at 0K indicate thermodynamic stability of vacancy-ordered and stacking-fault-formed phases [33, 86], there may be significant kinetic barriers (*e.g.* low rates of carbon diffusion) to forming any meaningful degree of long-range vacancy ordering as a TaC_y sample is cooled below the order-disorder transition temperature.

Furthermore, Gusev *et al.* (1996) [90] and Lipatnikov and Rempel (2005) [91] have identified incommensurate ordered phases in TaC_y via neutron diffraction. These vacancy-ordered structures were observed near the Ta_6C_5 composition, in the range $0.79 < y < 0.89$. This structure has greatly reduced symmetry when compared with the commensurate M_6C_5 phases shown in Figure 2.14; while every second $\{111\}$ plane in the carbon sub-lattice is fully populated in the commensurate structure, only every eighteenth $\{111\}$ non-metal plane is fully populated in this commensurate phase. In the former of the two works mentioned above, though, the authors point out that the ordering domains observed via diffraction were estimated to be quite small, and that tantalum carbides appear not to form an ideal long-range ordered structure even after thorough annealing (1600 K for 5 hours) and slow cooling (0.16 K/min). This suggests that TaC_y likely does not vacancy-order as readily as some of the other TMCs—notably VC_y —and thus casts doubt on the notion that long-range vacancy-ordering effects are responsible for its ‘anomalous’ hardness. Since prior experiments wherein the ‘anomalous’ hardness was observed were not explicitly searching for vacancy ordering (and thus did not adopt such rigorous annealing and slow-cooling

schedules), it seems unlikely that significant long-range vacancy ordering was present in those samples.

2.2.4 Slip Anisotropy and Slip Plane Preference

Another possibility is that the IVB and VB TMCs exhibit different hardness behaviors simply due to differences in intrinsic slip behavior; that is, the behavior of dislocations may differ among the TMCs without any defects being present to inhibit dislocation motion. Perhaps some of the carbides have generally greater lattice resistance to dislocation motion than others, or perhaps this is only true on specific crystallographic planes. Firstly, though, the evidence for dislocation plasticity in these materials must be reviewed.

As will be discussed in detail in the following paragraphs, indentation and bend testing often reveal evidence of dislocation plasticity, with the degree of deformation prior to fracture varying wildly among the carbides. As the B1 crystal is essentially a FCC lattice with a more complex basis, the anticipated Burgers vector is the nearest-neighbor displacement within either FCC sublattice—that is, the $\frac{a}{2}\langle 110 \rangle_{B1}$. This is consistent with ionic compounds possessing the same structure (*e.g.*, the prototype compound, NaCl), though the slip behavior is not necessarily the same. Much early work on the carbides assumes that, since they are hard materials comprised of metal and nonmetal species, their candidate slip systems must include the $\frac{a}{2}\langle 110 \rangle\{100\}_{B1}$ and $\frac{a}{2}\langle 110 \rangle\{110\}_{B1}$. This is a reasonable supposition for an ionic—or primarily ionic—compound, as slip on both the $\{100\}_{B1}$ and $\{110\}_{B1}$ planes conserves charge: sectioning of the crystal along these planes produces free surfaces with equal numbers of metal and nonmetal atoms. And indeed, the fracture behavior of the TMCs does seem to broadly comport with this assumption, as these compounds are overwhelmingly found to favor cleavage fracture on the expected $\{100\}_{B1}$ planes. However, due to the significant metallic character of the rocksalt carbides (they are all electrical conductors, after all, with no electronic band gaps [66, 86, 92, 93]), other work has sometimes indicated slip on the $\frac{a}{2}\langle 110 \rangle\{111\}_{B1}$ systems as well. This makes sense, as this is the dominant slip system in FCC metals; since the TMCs have an interesting blend of ionic, covalent and metallic

bond characters, it is possible that different carbides—or, for that matter, carbides with different carbon contents—may prefer different slip systems.

In some early work on the hardness of carbides, Williams and Schaal (1962) [94] had observed dislocation structures in TiC_y and found evidence of dislocation slip in some deformed specimens. In room-temperature three-point bending tests, $\text{TiC}_{0.94}$ and $\text{TiC}_{0.96}$ were seen to crack along the $\{100\}$ planes, exhibiting essentially no plasticity; etching after failure revealed no evidence of dislocation motion. At higher temperatures (between 800 °C and 1100 °C), slip was observed to occur either on the $\{110\}$ or $\{111\}$ planes. The exact slip plane could not be established with certainty, since etch pits on a $\{100\}$ surface from dislocations on $\{110\}$ and $\{111\}$ will be identically oriented. Later, Breval (1981) confirmed the probable low-temperature slip systems to be $\langle 110 \rangle \{110\}$ and $\langle 110 \rangle \{100\}$, with fracture and cleavage along $\{100\}$ dominating over plasticity. At elevated temperatures, Breval also noted the emergence of the $\{111\}$ planes as the dominant slip system [95].

Knoop and Vickers indentation of TaC_y by Rowcliffe and Warren (1970) [96] characterized the hardness behavior of the material with different y by indenting at various locations along a partially-decarburized sample. The authors noted a maximum hardness at about $y = 0.83$, which is consistent with the findings of previous investigations. These indentations were performed on a $\{100\}$ face of the sample for easy identification of active slip planes. The authors also etched the samples subsequent to indentation, revealing extensive evidence of dislocation plasticity around the indent. In addition to cracks along $\langle 100 \rangle$ directions around the indent, the Vickers indents revealed dislocation slip patterns in the $\langle 110 \rangle$ directions, indicating either $\{110\}$ or $\{111\}$ slip. This result was bolstered by follow-up work by Rowcliffe and Hollox (1971), which observed $\{111\}$ slip in TaC while HfC only showed slip on $\{110\}$ [97]; this subsequent investigation also revealed (relatively) extensive plastic deformation in TaC prior to cracking, whereas HfC exhibited very little evidence of dislocation slip.

Expanding on these findings, experimental investigations into the slip behavior of the cubic TMCs have been conducted using hardness anisotropy (HA) since the mid-1960s. Prior work

by Brookes *et al.* [98] established that, during indentation of a crystalline material, the measured hardness varies greatly depending on the orientation of the indenter relative to the crystal lattice; furthermore, materials with shared crystal structures and dominant slip systems exhibit similar trends in HA, and so determinations of active slip systems can be made based on the indenter orientations at which hardness minima occur. In the cubic carbides, an investigation by Rowcliffe and Hollox (1971) [76] used HA measurements to determine the dominant slip systems in $\text{TiC}_{0.8}$, $\text{VC}_{0.84}$, $\text{HfC}_{0.98}$ and $\text{TaC}_{0.96}$. This work claimed $\{110\}$ to be the preferred slip plane for $\text{TiC}_{0.8}$, $\text{HfC}_{0.98}$ and $\text{VC}_{0.84}$, while $\text{TaC}_{0.96}$ was seen to slip primarily on $\{111\}$. This already hints at some intriguing behavior for TaC_y , indicating that its generally higher plasticity near the stoichiometric ($y = 1$) limit may be caused—at least in part—by some difference in intrinsic slip behavior as compared to the other TMCs. As it happens, the intrigue deepens further, since these authors also partially decarburized some of their tantalum carbide samples and indented them; in stark contrast to the nearly-stoichiometric $\text{TaC}_{0.96}$, the decarburized sample exhibited slip on the $\{110\}$ planes. Hence, it is possible that some transition from $\{111\}$ slip dominance to $\{110\}$ slip dominance in TaC_y occurs as y decreases. It is also worth noting that, while the vanadium carbide used for this work was seen to slip on $\{110\}$, it was also significantly sub-stoichiometric ($y = 0.84$); this leaves room for the possibility of similar slip behaviors within the Group V TMCs, although testing would be essentially impossible due to the phase separation of VC_y into V_8C_7 and graphite beyond $y \approx 0.88$. An additional complication is the fact that no composition information was reported for the decarburized $\text{TaC}_{0.96}$, so it is possible that these samples were outside the B1 phase homogeneity range.

In a subsequent investigation by Hannink *et al.* (1972), hardness anisotropy measurements were made for titanium carbide ($\text{TiC}_{0.96}$), zirconium carbide ($\text{ZrC}_{0.94}$), vanadium carbide ($\text{VC}_{0.83}$) and niobium carbide ($\text{NbC}_{0.87}$). The Group IV carbides, $\text{TiC}_{0.96}$ and $\text{ZrC}_{0.94}$, were both found to slip on the $\{110\}$ planes; the Group V carbides, $\text{VC}_{0.83}$ and $\text{NbC}_{0.87}$, were seen to slip on both $\{110\}$ and $\{111\}$ planes. Interestingly, on the $\{110\}$ planes, NbC was found to be softer in $\langle 100 \rangle$ than $\langle 110 \rangle$ [99]. Taken together, these results may indicate a profound difference in slip behavior

between the Group IV and Group V TMCs: while the Group IV TMCs were not seen to slip on $\{111\}$ at low temperatures, the Group V TMCs appear to slip readily on $\{111\}$ even at room temperature. This result disagrees somewhat with the prior claims about TiC_y , since $\{100\}$ was not identified as an active slip system by Hannink *et al.*. Further confounding this work is the fact that the Group IV TMCs tested were very nearly stoichiometric, while the Group V TMCs were significantly sub-stoichiometric. With VC_y this is unavoidable due to the thermodynamic instability of $\text{VC}_{1.0}$, but $\text{NbC}_{1.0}$ has been identified as thermodynamically stable. Thus it is not possible to discern from this work whether NbC_y would display a transition between $\{111\}$ and $\{110\}$ slip dominance with changes in y , as was suggested for TaC_y in the preceding paragraph.

Building on the work of Hannink *et al.*, Morgan and Lewis (1974) [100] carried out additional HA tests on Nb_6C_5 . This experiment determined that, while both $\{110\}$ and $\{111\}$ slip systems were active, the resolved shear strength on the $\{111\}$ was lower than on the $\{110\}$. Thus, experimental HA measurements at low temperatures seem to strongly indicate $\{111\}$ slip in NbC_y , at least at relatively high y . This finding challenges the results of Rowcliffe and Hollox [76] discussed above, at least in the sense that it does not support a transition to $\{110\}$ slip in all of the Group V TMCs; the extent to which these results are in conflict unfortunately depends a great deal on one's interpretation, for reasons discussed above.

Unfortunately, since hardness is not a material property *per se*—merely arising from a combination of geometric and material properties of a sample—it is difficult to directly compare the results of various experiments. This obstacle to convenient aggregation of data is compounded by the fact that many indentation experiments do not fully characterize their samples for porosity, grain size, phase composition, nominal non-metal-to-metal ratio, etc. There is hope, though, beyond simply undertaking the expensive and tedious process of attempting to replicate these experiments under more consistent conditions. Computational approaches offer researchers an opportunity to probe the properties of the carbides at different compositions using a very repeatable methodology. It is lamentable that accurate direct simulations of dislocation slip are not (yet) possible for

the cubic carbides (see Section 2.6 for a more detailed explanation), but many possible indicators of dislocation slip can still be extracted from simulations using DFT.

One useful piece of information which can be produced with relative ease from either *ab-initio* or atomistic simulation is a material's resistance to rigid shear. That is, the energy penalty associated with translating one half of a crystal relative to the other can be expediently computed by simply dividing the crystal in two—along the expected dislocation glide plane—and displacing one half by some uniform slip u in the anticipated slip direction. If several u values are sampled between the unsheared configuration and an equivalent energy minimum, then a generalized stacking-fault (GSF) energy curve is produced. A significant amount of work has focused on computing GSF energies for FCC metals, which slip along $\langle 110 \rangle \{111\}$, in an attempt to understand how dislocations in these materials behave. First-principles calculations by Wu *et al.* (2010) have shown that, while the $\langle 110 \rangle \{111\}$ GSF energy curves are vaguely sinusoidal, the $\langle 112 \rangle \{111\}$ curves show a metastable point at $u = \frac{1}{6} \langle 112 \rangle \{111\}$ for all of the FCC metals tested (Ni, Rh, Cu, Ag, Au, Ir, Pt, Al, Pd and Pb) [101]. This is consistent with the findings of other *ab-initio* investigations [102], as well as those of atomistic simulations [103]. The meta-stable point on the $\langle 112 \rangle \{111\}$ GSF energy curve is referred to as the intrinsic stacking-fault (ISF), and the energy barrier separating the unsheared ($u = 0$) configuration and the ISF is known as the unstable stacking-fault (USF). These GSF energy curve features are important due to the propensity of perfect dislocations on the $\{111\}$ planes in FCC metals to dissociate into Shockley partial dislocations; for example, a perfect edge dislocation with a Burgers vector $b = \frac{a}{2} \langle 110 \rangle$ will tend to dissociate into a pair of dislocations with $b_p = \frac{a}{6} \langle 112 \rangle$ and mixed edge-screw character:

$$\frac{a}{2} \langle 110 \rangle \{111\} \longrightarrow \frac{a}{6} \langle 112 \rangle \{111\} + \frac{a}{6} \langle 112 \rangle \{111\} \quad (2.15)$$

Here, a represents the conventional lattice constant. Note that this dissociation reaction conserves Burgers vector, but alters the shape of the dislocation quite dramatically.

In their *ab-initio* study on HfC and TaC, De Leon *et al.* [104] found that TaC contained a metastable ISF at the $u = \frac{a}{6} \langle 112 \rangle \{111\}$ location along the $\langle 112 \rangle \{111\}$ GSF energy curve; no

such metastable point was present on the same curve in HfC. The authors postulated that the extra valence electron in TaC stabilizes the ISF by providing some degree of charge delocalization and allowing bonds to rotate. This would then hold true for NbC and VC as well, as the metal atoms in both carbides also contribute an additional valence electron; in fact, the supplemental material from De Leon *et al.* shows all of the Group V TMCs—VC, NbC and TaC—to possess distinct ISF and USF points on the $\langle 112 \rangle \{111\}$ GSF energy curve, whereas the Group IV TMCs—TiC, ZrC and HfC—all lack a meta-stable ISF. Subsequent work by Yu *et al.* confirmed this finding, demonstrating that the rocksalt TMCs demonstrate very uniform behavior (in terms of GSF energy curve morphology) within each transition metal group. Yu *et al.* also extended the investigation to the rocksalt TMNs, yielding some very interesting results. The Group IV TMNs—TiN, ZrN and HfN—showed high levels of similarity to the Group V TMCs, with obvious ISF and USF points on the $\langle 112 \rangle \{111\}$ curves. This alone raises an interesting question regarding the effect of VEC on slip plane preference, as the primary difference between the Group IV and Group V transition metals is the presence of an additional valence electron per atom in the group V metals. Since all of the cubic TMCs have the same rocksalt structure, the effect of this additional electron can be directly observed: the Group IV TMCs have a VEC of 8 electrons per B1 formula unit (f.u.), while the Group V TMCs have 9 electrons/f.u.—as do the Group IV TMNs. Although the additional electron (per f.u.) is supplied by the metal atom in the Group V TMCs and by the non-metal atom in the Group IV TMNs, the effect seems to be largely the same, bolstering the arguments often made for VEC as a primary determinant of hardness behavior. It should be noted, though, that the ISF energies are considerably higher in the Group V TMNs than in the Group IV TMCs, possibly hinting at a lower degree of charge de-localization if the extra VEC is due to non-metal atom substitution rather than metal atom substitution. The work of Yu *et al.* also surveyed the Group V TMNs—VN, NbN and TaN—finding that the ISF configuration in the B1 structure was actually stable relative to the un-faulted configuration; since an ISF in the B1 crystal changes the coordination environment from octahedral to trigonal prismatic, this finding essentially implies an energetic preference for the B_h structure at low temperatures.

Taken together, though, these findings strongly indicate fundamental differences in dislocation slip behavior in the carbides and nitrides, possibly based on VEC. In any case, the possibility of $\{111\}$ slip in some of these materials (and not in others) would have enormous implications for hardness, since the $\{111\}$ planes in the B1 crystal are sufficient to satisfy the von Mises general plasticity criterion, whereas the $\{110\}$ alone cannot.

2.3 Mechanical Behavior of Rocksalt Carbides and Nitrides

In addition to the cubic carbides, the IVB and VB TMNs are of great interest. The IVB TMNs have rocksalt crystal structures; furthermore, TiN_y [17, 18], ZrN_y [16] and HfN_y [14, 15] are all predicted to exhibit sizeable homogeneity ranges for the B1 phase. As in the carbides, nonstoichiometry is accommodated by structural vacancies on the metal or non-metal sub-lattices.

These materials are of scientific interest largely due to their similarity to the VB TMCs: they have the same structure, the same bonding character, and the same nominal VEC (9 electrons/f.u., at the stoichiometric composition). Additionally, like the Group V TMCs, they have been seen to exhibit considerable plasticity in indentation tests. Egeland *et al.* (2011) [105] observed considerable dislocation density under an indent in ZrN , as well as pile-up of material around the indenter; these features indicate that dislocation plasticity plays a significant role in the behavior of ZrN , similar to NbC and TaC . Even more interesting is the earlier observation by Andrievskii (1981) that ZrN_y increases in hardness with decreasing y in the composition range $0.7 < y < 1.0$, even as the Young's modulus E declines on the same interval [25].

Indentation experiments by Lengauer in 1992 also pointed to an "anomalous" sub-stoichiometric hardness in TiN_y , with the hardness initially increasing as y decreases from 1.0 to about 0.65 before falling again as y falls to about 0.50 [46]. This is somewhat consistent with the findings of Saoula *et al.* (2009), who observed a peak hardness at about 40 at.% N ($y \approx 0.67$) in TiN_y thin films [48]. Though the compositions at which the sub-stoichiometric hardness maxima are seen in these two works differ, they nonetheless both indicated "optimized" hardness at N/Ti ratios between 0.5 and 1.0.

Prior experimental work by Politis and Rejman (1978) showed that rocksalt NbN_y and TaN_y exhibited steep increases in hardness with decreasing y within the domain $0.75 < y < 0.98$. This work reported the B1 homogeneity ranges to be $0.80 < y < 0.98$ for NbN_y , and $0.75 < y < 0.98$ for TaN_y . Subsequent investigation by Lengauer and Ettmayer (1986) [106] confirmed this finding, observing a significant increase in hardness in NbN_y as y was decreased from 1.0 to 0.92. Lengauer and Ettmayer (1985) also found that VN_y exhibited depressed hardness values near the stoichiometric composition, with the hardness dropping by over 50% as y increased from 0.75 to 1.0 [107].

It should be noted that the VB TMNs are not expected to have stable B1 structures at low temperatures. An *ab-initio* investigation by Weinberger *et al.* (2017) predicted the B_h structure to have the lowest energy in VN and NbN; this same work predicted TaN to have either a B_h structure or a ϵ -TaN structure, with the two having nearly equal formation energies [108]. Despite this, the B1 structure in the VB TMNs is claimed to form at higher temperatures and can be "frozen in" by quenching to room temperature [106].

2.4 Mixing Effects in Rocksalt Carbides and Nitrides

The rocksalt carbides and nitrides are generally found to have high solubility with one another. As with the arguments covered in Section 2.2.1 and Section 2.2.2 of this text, the interest in carbide and nitride mixing generally hinges on the concept of optimizing bonding in the rocksalt crystal structure via changes in VEC. Alloying different carbides and nitrides changes the VEC by introducing substitutional defects with greater or fewer valence electrons than the original atoms. This research has been popularized recently by the development of high-entropy alloys (HEAs) and high-entropy ceramics (HECs), which consist of roughly equiatomic solid mixtures of five or more principal components.

An early study by Agte and Alterthum (1930) on carbide mixing indicated the presence of an elevated melting temperature in ZrC-TaC solid solutions at an intermediate composition [28] near $\text{Zr}_{0.2}\text{Ta}_{0.8}\text{C}$. Subsequent work by Shaffer *et al.* [29] in 1961 reproduced this increase in melting

temperature. Also noted in the latter work was a maximum indentation hardness at the $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{C}$ composition, exhibiting a hardness ($2290 \text{ kg}_f/\text{mm}^2$) in excess of either that of TaC ($886 \text{ kg}_f/\text{mm}^2$) or ZrC ($1831 \text{ kg}_f/\text{mm}^2$). It should be noted that $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{C}$ has a nominal VEC of 8.2 electrons/f.u., close to the VEC at which the sub-stoichiometric hardness maximum is claimed to occur in TaC_y .

Holleck (1986) [1] also suggested hardness maxima at intermediate compositions in $\text{Ti}_{1-y}\text{Hf}_y\text{C}$, $\text{V}_{1-y}\text{Nb}_y\text{C}$, $\text{V}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{Nb}_y\text{C}$ mixtures, although no actual data appears to be referenced for this claim. If substantiated, these trends would be intriguing—each the terminal compounds for each mixture have the same VEC, so arguments from increased stiffness or cohesive energy would seem not to apply. Rather, these trends would likely be entirely attributable to changes in dislocation mobility, with mechanisms such as precipitation hardening or solid-solution strengthening contributing to the excess hardnesses.

Andrievskii (1981), in studying carbide-nitride mixing, observed $(\text{TiC})_{1-y}(\text{ZrN})_y$ to exhibit a peak hardness at approximately $y = 0.20$. This corresponds to a VEC of 8.2 electrons/f.u., putting this in reasonable agreement with claims of "optimized" hardness properties of rocksalt TMCs and TMNs in this VEC range. However, this study also included data on the $(\text{TiC})_{1-y}(\text{HfN})_y$ system, wherein hardness was seen to decline monotonically with increasing y [25].

Yang (2000) experimental hardness tests (nano-hardness and micro-hardness). Monotonic decline with increasing y in $\text{TiC}_{1-y}\text{N}_y$. Same trend but with depressed H values in sub-stoichiometric $\text{Ti}(\text{C}_{1-y}\text{N}_y)_{0.81}$; more pronounced hardness reduction on TiC end than TiN end. Possible anomalous hardness (non-constant slope) in $\text{ZrC}_{1-y}\text{N}_y$. Maximum hardness in $\text{HfC}_{1-y}\text{N}_y$ at approximately the $\text{HfC}_{0.60}\text{N}_{0.40}$ composition (VEC=8.4) [26].

Some computational work has also indicated that binary mixing of carbides might produce superior properties, as compared to the properties of the terminal compounds. Jhi *et al.* (1999) tracked the "cubic shear modulus" C_{44} across different compositions within the HfC-HfN, ZrC-NbC, and TiC-TiN pseudo-binary systems. Maxima in DFT-computed C_{44} were identified at intermediate compositions for all three systems: at a valence electron concentration of about 8.3

electrons/f.u. in $\text{HfC}_y\text{N}_{1-y}$, around 8.5 electrons/f.u. in $\text{Zr}_y\text{Nb}_{1-y}\text{C}$, and around 8.4 electrons/f.u. in $\text{TiC}_y\text{N}_{1-y}$ [67].

Using first-principles calculations, Hong and van de Walle (2015) [27] predicted a maximum melting temperature in the $\text{Hf}_{1-y}\text{Ta}_y\text{C}_{0.88}$ system: the melting temperature of $\text{Hf}_{0.75}\text{Ta}_{0.25}\text{C}_{0.88}$ ($T_m = 3920 \pm 16$ K) was found to exceed that of the terminal compounds, HfC ($T_m = 3842 \pm 25$ K) and $\text{TaC}_{0.88}$ ($T_m = 3830 \pm 24$ K). However, this work predicted a higher maximum melting temperature in the $\text{HfC}_{x-y}\text{N}_y$ system, with x being some number between 0.5 and 1.0 (to denote a sub-stoichiometric non-metal-to-metal ratio) and y being less than or equal to x . This work found $T_m = 4141 \pm 21$ K at the composition $\text{HfC}_{0.56}\text{N}_{0.38}$, claimed as the highest known melting temperature for any compound. Interestingly, Hong and van de Walle also predicted an elevated melting temperature in a sub-stoichiometric hafnium-tantalum-carbo-nitride, $\text{Hf}_{0.75}\text{Ta}_{0.25}\text{C}_{0.56}\text{N}_{0.25}$, with $T_m = 3980 \pm 13$ K.

More recently, Liang *et al.* (2021) conducted an extensive investigation into mixed-transition-metal carbides (MTMCs) [62]. Using DFT calculations, these authors modeled various MTMCs in both the rocksalt (B1) and α -WC (B_h) structures in order to identify "optimal" VEC values for each coordination environment. The B1 MTMCs ($\text{Sc}_{1-y}\text{Ti}_y\text{C}$, $\text{Ti}_{1-y}\text{V}_y\text{C}$, $\text{V}_{1-y}\text{Cr}_y\text{C}$, $\text{Y}_{1-y}\text{Zr}_y\text{C}$, $\text{Zr}_{1-y}\text{Nb}_y\text{C}$, $\text{Nb}_{1-y}\text{Mo}_y\text{C}$, $\text{Lu}_{1-y}\text{Hf}_y\text{C}$, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$) spanned a range of VECs from 7 electrons/f.u. to 10 electrons/f.u.; the B_h MTMCs ($\text{Sc}_{1-y}\text{Ti}_y\text{C}$, $\text{Ti}_{1-y}\text{V}_y\text{C}$, $\text{V}_{1-y}\text{Cr}_y\text{C}$, $\text{Cr}_{1-y}\text{Mn}_y\text{C}$, $\text{Mn}_{1-y}\text{Fe}_y\text{C}$, $\text{Y}_{1-y}\text{Zr}_y\text{C}$, $\text{Zr}_{1-y}\text{Nb}_y\text{C}$, $\text{Nb}_{1-y}\text{Mo}_y\text{C}$, $\text{Mo}_{1-y}\text{Tc}_y\text{C}$, $\text{Tc}_{1-y}\text{Ru}_y\text{C}$, $\text{Lu}_{1-y}\text{Hf}_y\text{C}$, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$, Ta_{1-y}WC , W_{1-y}ReC and $\text{Re}_{1-y}\text{Os}_y\text{C}$) had between 7 electrons/f.u. and 12 electrons/f.u. Compositions determined by $y = 0.00, 0.25, 0.50, 0.75$ and 1.00 were used, offering a reasonably dense sampling of VEC values. The bulk moduli in the B1 MTMCs were seen to increase monotonically with increasing VEC from 7 electrons/f.u. to 10 electrons/f.u., whereas the B_h MTMCs exhibited very modest maxima in B at approximately 11 electrons/f.u. Both structures showed distinct maxima in the shear modulus G —at approximately 9 electrons/f.u. in the B1 MTMCs, and about 10.25 electrons/f.u. in the B_h MTMCs. Using these elastic properties, theoretical hardnesses were computed according to the shear modulus correlation developed by Teter [65] (discussed in Section

2.2.2):

$$H = 0.1769G - 2.899 \quad (2.16)$$

Since this is simply a linear regression with the shear modulus, the trends in the theoretical H values are the same as those seen in the G values. Nonetheless, this work does lend some credence to the idea of VEC optimization in the B1 and B_h structures. The underlying mechanism proposed by Liang *et al.*, as discussed in Section 2.2.1, is optimal filling of molecular orbitals. As VEC increases in the B1 structure, the additional valence electrons initially occupy bonding (e_g) states, but further increases in VEC begin to populate anti-bonding (t_{2g}) states, leading to a decline in the net bond strength of the material. The same could be expected to occur in the B_h structure as well, but with the "optimal" bonding occurring at a different VEC, owing to the different coordination environments present in the two structures.

2.5 Electronic structure and Bonding in Transition-Metal Carbides, Nitrides and Carbo-Nitrides

To understand the claims made regarding VEC optimization in the rocksalt carbides and nitrides, a brief digression into ligand-field (LF) theory will be helpful. LF theory is essentially a combination of crystal-field (CF) theory and molecular orbital (MO) theory. CF theory essentially seeks to model the splitting of atomic orbitals (d -orbitals, in our case) into non-degenerate energy states in the presence of an external electric field. In a spherically-symmetric applied field, the energetically-degenerate d -orbitals are uniformly elevated in energy; in a non-symmetrical external field (*e.g.* an octahedral environment), these orbitals become non-degenerate. Figure 2.16 offers a concise visual representation of this concept.

The case of the octahedrally-symmetric applied field is naturally the most applicable to our materials, since atoms are octahedrally coordinated in the NaCl structure. CF theory denotes the lower-energy states, formed from the d_{xy} , d_{yz} and d_{zx} orbitals, as the t_{2g} states; the higher-energy states, formed from the $d_{x^2-y^2}$ and d_{z^2} orbitals, are called the e_g states. The energetic spacing Δ

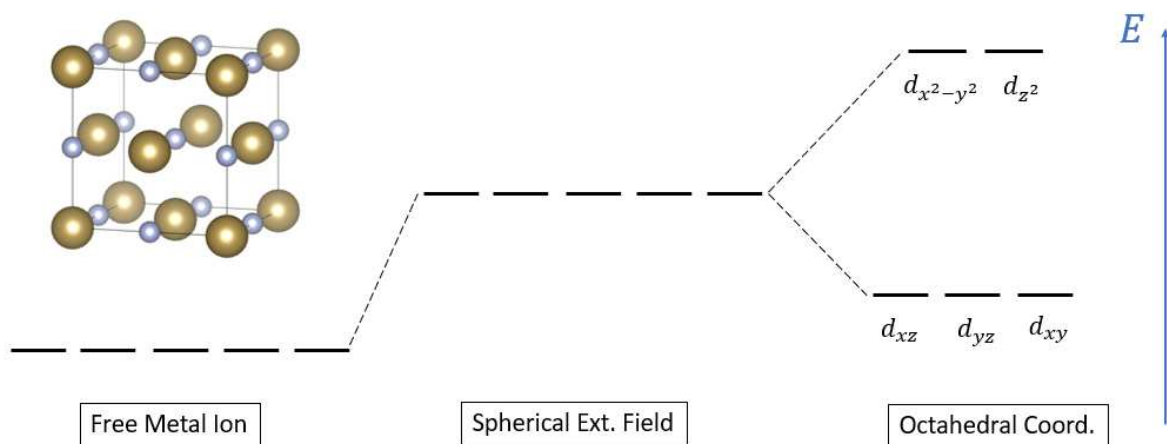


Figure 2.16: Schematic illustration of atomic d -orbital splitting in an external electric field, per crystal-field theory.

between these energy levels depends on the strength of the applied electric field. In the presence of a weak-field ligand, Δ is small, and the t_{2g} and e_g can be populated according to the Pauli exclusion principle (Figure 2.17). In the case of a strong-field ligand, though, Δ is too large for d -electrons to populate the d -orbitals in this manner; instead, they must all populate the lower-energy t_{2g} states (Figure 2.18). In either case, the deviation in energy of the t_{2g} and e_g from the energy of the original energy of the un-split d -orbitals in an octahedral applied field is

$$\Delta_{t_{2g}} = \frac{2}{5} \Delta \quad (2.17)$$

$$\Delta_{e_g} = \frac{3}{5} \Delta \quad (2.18)$$

This allows for the calculation of the crystal-field stabilization energy (CFSE), which represents the energy decrease of the electrons due to orbital splitting. If $n_{t_{2g}}$ and n_{e_g} are the number of electrons occupying the stabilizing (t_{2g}) and destabilizing (e_g) states, respectively, then the CFSE is given by

$$\text{CFSE} = n_{t_{2g}} \Delta_{t_{2g}} - n_{e_g} \Delta_{e_g} \quad (2.19)$$

Thus, in the case of the weak-field ligand in Figure 2.17, the CFSE evaluates to zero, giving no stabilization due to the presence of the external field. With the strong-field ligand in Figure 2.18,

the CFSE evaluates to 2Δ , indicating an energy change of -2Δ when compared to the un-split orbitals. In this latter case, the splitting of the d -orbitals yields a significant stabilization of the d -electrons.

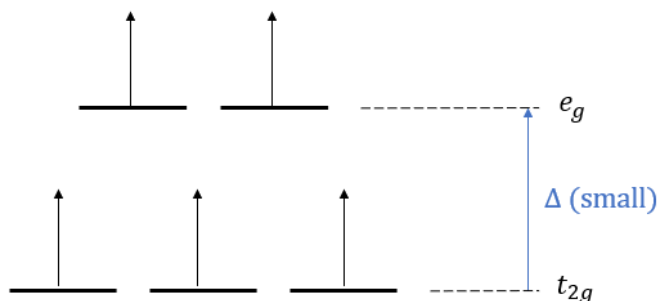


Figure 2.17: Splitting of atomic d -orbitals in the presence of a weak-field ligand.

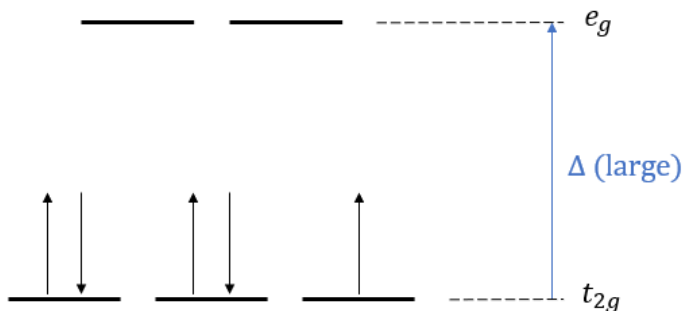


Figure 2.18: Splitting of atomic d -orbitals in the presence of a strong-field ligand.

The other part of LF theory is molecular orbital theory, which essentially relies on the construction of molecular orbitals via linear combination of atomic orbitals (LCAO). In the quantum-mechanical formulation, each valence electron "orbiting" a nucleus (to borrow slightly from the

classical conception) possesses its own wave-function, Ψ . Solving the Schrödinger equation,

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \quad (2.20)$$

for the hydrogen atom gives the shapes of the atomic orbitals. The molecular orbitals, then, are formed from the overlapping wave-functions of the atomic orbitals, *i.e.* the constructive or destructive interference of the atomic electrons' wave-functions. Hence the j th molecular orbital Φ_j is said to be a superposition of its n constituent atomic orbitals Ψ_i :

$$\Phi_j = \sum_{i=1}^n c_{ij} \Psi_i, \quad (2.21)$$

where c_{ij} are constant coefficients determined via the Schrödinger equation. Building upon this reasoning, LF theory combines the principles of CF theory and MO theory to classify bonding and anti-bonding interactions between atoms in a metal-ligand complex. Per LF theory, the primary types of bonds created in such a complex are σ -bonds and π -bonds; each has different symmetry, and thus different contribution to bonding or anti-bonding interactions dependent on the coordination environment. In σ -bonds, each ligand atom donates an electron pair to the metal atom—specifically, to the metal atom's $d_{x^2-y^2}$ and d_{z^2} orbitals—leading to the creation of six bonding MOs and six anti-bonding MOs. In π -bonding, two possible scenarios exist: ligand-to-metal π -bonding, where ligand p -orbitals donate electrons to the metal d_{xy} , d_{yz} and d_{xz} orbitals, and metal-to-ligand π -bonding, where the electrons are transferred in the opposite direction. Ligand-to-metal π -bonding generally results in a lower CFSE than metal-to-ligand π -bonding, contributing less stability to the bonded complex.

Dronskowski and Bloechl (1993) [109] formulated a quantity known as the crystal orbital Hamilton population (COHP), which allows the electron density of states (DoS) to be partitioned into individual interactions between neighboring atoms. This is a helpful theoretical tool for identifying and characterizing bonds, particularly for covalent compounds. In this work, the authors

constructed the one-electron wave-function ψ_j for the j^{th} band index in a crystalline solid:

$$|\psi_j\rangle = \sum_{RL} |\chi_{RL}\rangle u_{RL,j} \quad (2.22)$$

where R denotes the atomic site and $L \equiv lm$ represents the angular momentum quantum numbers. The mixing coefficients $u_{RL,j}$ are the eigenvectors. Note that this double summation accounts for all the atomic positions within the unit cell, and for all atomic orbitals at each position. Assuming the wave-functions to be orthogonal, this gives

$$\delta_{jj'} = \langle \psi_j | \psi_{j'} \rangle = \sum_{RL} \sum_{R'L'} u_{RL,j}^* S_{RL,R'L'} u_{R'L',j'}, \quad (2.23)$$

where $S_{RL,R'L'} \equiv \langle \chi_{RL} | \chi_{R'L'} \rangle$ is the overlap matrix. Here, the notation R' , L' , j' , etc. indicates interactions across different atomic positions, atomic orbitals, and one-electron wave-functions, etc. The authors then present the one-electron problem:

$$\sum_{R'L'} \{ H_{RL,R'L'} - \epsilon_j S_{RL,R'L'} \} u_{R'L',j} = 0 \quad (2.24)$$

with the one-electron energies being given by the eigenvalues of the above problem. The Hamiltonian in this equation is given by

$$H_{RL,R'L'} \equiv \langle \chi_{RL} | \hat{H} | \chi_{R'L'} \rangle \quad (2.25)$$

Some further manipulation, and the application of orthogonality gives

$$\sum_{RL} \sum_{R'L'} u_{RL,j}^* H_{RL,R'L'} u_{R'L',j} = \epsilon_j \delta_{jj'} \quad (2.26)$$

The band-structure energy is defined as

$$E_{\text{band}} \equiv \sum_j f_j \epsilon_j = \int^{\epsilon_F} d\epsilon \sum_j f_j \epsilon_j \delta(\epsilon_j - \epsilon), \quad (2.27)$$

where $0 \leq f_j \leq 2$ are the occupation numbers of the bands. This can be coupled with Equation 2.26 to give

$$\begin{aligned}
\sum_j f_j \epsilon_j \delta(\epsilon_j - \epsilon) &= \sum_j f_j \sum_{RL} \sum_{R'L'} u_{RL,j}^* H_{RL,R'L'} u_{R'L',j} \delta(\epsilon_j - \epsilon) \\
&= \sum_{RL} \sum_{R'L'} H_{RL,R'L'} \sum_j f_j u_{RL,j}^* H_{RL,R'L'} u_{R'L',j} \delta(\epsilon_j - \epsilon) \\
&= \sum_{RL} \sum_{R'L'} H_{RL,R'L'} N(\epsilon)
\end{aligned} \tag{2.28}$$

where $N(\epsilon)$ is the electron density-of-states (DoS). The quantity inside the summation is then named the crystal orbital Hamilton population (COHP):

$$\text{COHP}_{RL,R'L'}(\epsilon) = H_{RL,R'L'} N_{RL,R'L'}(\epsilon) \tag{2.29}$$

which is essentially the sum of these pair contributions to the electron band structure energy. Dronskowski and Bloechl also derived an expression for the cohesive energy:

$$\begin{aligned}
E_{\text{coh.}} &= \int^{\epsilon_F} \sum_{RL} \sum_{\neq R'L'} \text{Re}\{H_{RL,R'L'} N_{RL,R'L'}(\epsilon)\} \\
&\quad + \int^{\epsilon_F} d\epsilon_F \sum_{RL} H_{RL,R'L'} N_{RL,R'L'}(\epsilon) \\
&\quad - \sum_R \sum_i f_i^R \epsilon_i^R \\
&\quad + \Delta E_{\text{el.}}\{n(\vec{r})\} \\
&\quad + \Delta E_{\text{xc}}\{n(\vec{r})\} \\
&\quad + \sum_R \sum_{\neq R'} \frac{Z_R Z_{R'}}{|\vec{R} - \vec{R}'|}
\end{aligned} \tag{2.30}$$

The first term is referred to as the off-site COHP, or the COHP due to the occupation of overlapping orbitals from different atoms; the second term is the on-site COHP, arising from the interactions between orbitals of the same atom.

Subsequent development of this theory [110] led to the creation of the Local Orbital Basis-Suite Toward Electronic-structure Reconstruction (LOBSTER) software [111, 112], which allows for the calculation of COOP, COHP and other quantities from the outputs of *ab-initio* software programs such as VASP. This allows for deeper and more detailed analysis than the more common electron DoS can provide: LOBSTER can be used to resolve the DoS onto specific MOs from specific atom pairs, and the COHP analysis allows for direct comparison of different inter-atomic interactions. The contribution of particular atomic orbital overlaps to the overall band energy can then be computed, potentially giving useful insights into the mechanisms by which bonding and anti-bonding interactions contribute to the stability of different coordination environments in the cubic carbides and nitrides.

2.6 Modeling Dislocation Mobility

Since the introduction of dislocation theory, attempts have been made to elucidate the role of dislocations in determining the strength and hardness of crystals. The existence of dislocations was initially only speculative, inferred as a solution to irreconcilable disagreements between theories of plastic deformation and actual tests. A model proposed by Frenkel in 1926 [113] sought to predict the shear strength of a crystal by estimating the amplitude of the restorative force when one half of the crystal is rigidly translated relative to the other half, with the half-spaces being separated by the slip plane. The spatially-periodic restorative force is represented as a sinusoid, yielding the theoretical shear stress:

$$\tau = \frac{\mu \Delta x}{2\pi a} \sin \frac{2\pi x}{\Delta x}, \quad (2.31)$$

where μ is the isotropic shear modulus, Δx is the spacing of atoms in the direction of the applied shear stress, a is the spacing of atomic planes perpendicular to the applied stress, and x is the displacement coordinate (*i.e.* the registry between the upper and lower half-spaces of the crystal). The theoretical shear strength is then given by the maximum value of the periodic shear stress:

$$\tau_{\text{th.}} = \frac{\mu \Delta x}{2\pi a} \quad (2.32)$$

Estimates generated using this model are generally on the order of 0.2μ , while experimentally-observed shear strengths for metals may be anywhere from $10^{-8}\mu$ to $10^{-4}\mu$. In order to address this, Taylor proposed a mechanism in 1934 whereby one-dimensional crystallographic defects—dislocations—could be moved under an applied shear stress, facilitating plastic deformation without requiring rigid slip of an entire plane of atoms over another [114, 115]. The movement of dislocations could thus be expected to accommodate irreversible deformations at much lower applied shear stresses, since the movement of a dislocation core requires far less distortion of the crystal than the mechanism proposed by Frenkel.

Subsequent to this development, Peierls (1940) introduced a framework for estimating the size of a dislocation core and the stress required to move the dislocation [116]; this model, as acknowledged in the work, was far too sensitive to simplifying assumptions and arbitrary constants. Nonetheless, it provided a very mathematically useful view of a dislocation: rather than being a discrete defect located at some particular position x_0 along the slip coordinate on the slip plane, the dislocation was instead a spatial distribution of "misfit" (or, equivalently, "disregistry" or "slip") between the upper and lower half-spaces of the crystal. This slip distribution, $u(x)$, is essentially a continuous distribution of infinitesimal dislocations such that

$$\frac{du(x)}{dx} = \rho(x) \quad (2.33)$$

where x is the coordinate in the slip direction (relative to the dislocation center-of-mass position x_0 , and $\rho(x)$ is the dislocation density. From Burgers vector conservation, it is necessary that

$$\int_{-\infty}^{+\infty} \rho(x) dx = \int_{-\infty}^{+\infty} \frac{du(x)}{dx} dx = b \quad (2.34)$$

where b is the magnitude of the dislocation's Burgers vector. The later work of Nabarro (1947) formalized the Peierls-Nabarro (PN) model [117] in its application to an "edge-type" dislocation [118] in a simple cubic lattice. The birds-eye view of the PN model is that the motion of the dislocation is contingent on competing factors contributing to the total dislocation energy: (1) the

work performed by the applied shear stress, (2) the energetic penalty to elastically deforming the upper and lower half-spaces of the crystal, and (3) the energetic penalty associated with misfit (disregistry) between the upper and lower half-spaces. This gives the total energy as a functional of the slip distribution $u(x)$:

$$E[u(x)] = E_{\text{elastic}} + E_{\text{misfit}} - W_{\text{stress}} \quad (2.35)$$

The first term, the elastic energy associated with the presence of a dislocation line at $x = x'$ is:

$$E_{\text{elastic}}[u(x)] = -K \int \int \rho(x) \rho(x') \ln|x - x'| dx dx', \quad (2.36)$$

where the pre-logarithmic energy factor K arises from the elastic constants in an isotropic solid with shear modulus μ and Poisson's ratio ν . For an edge and screw dislocation, respectively, this factor is given by

$$K_e = \frac{\mu}{4\pi(1 + \nu)} \quad (2.37)$$

$$K_s = \frac{\mu}{4\pi} \quad (2.38)$$

A competing energy contribution is the misfit energy due to the local misfit between the upper and lower half-spaces at each position x :

$$E_{\text{misfit}}[u(x)] = \int \gamma[u(x)] dx \quad (2.39)$$

The original PN model incorporated a sinusoidal restorative force:

$$F[u(x)] = \frac{d\gamma[u(x)]}{du} = \tau_{\text{max}} \sin \frac{2\pi u(x)}{b}, \quad (2.40)$$

where τ_{max} is the maximum value of the restorative force, equal to the rigid ideal shear stress (RISS). This form naturally assumes a sinusoidal misfit potential $\gamma[u(x)]$, which is not very physically realistic, but this selection does allow for the derivation of a fairly simple analytical solution.

Subsequently, a more detailed formulation of the misfit energy was developed [119] to use the generalized stacking-fault (GSF) energy as the misfit potential. This choice removes some of the arbitrariness of the sinusoidal model (since $\tau_{\max}$ is now the maximum slope of the GSF energy curve, and thus has real physical significance), but it does render an analytical solution practically unfeasible. Consequently, use of the GSF energy as the misfit potential necessitates the use of numerical methods. Finally, the work performed by the applied stress is given by

$$W_{\text{stress}}[u(x), \tau] = -\tau \int x' \rho(x') dx' \quad (2.41)$$

As many prior works have noted, this model is far from a perfect representation of a dislocation, even considering the case of a dislocation in an otherwise-perfect crystal. Specifically, the PN model tends to underestimate lattice friction somewhat dramatically in metals, as compared to experimental measurements; furthermore, the PN model struggles to predict the behavior of narrow-core dislocations, such as those seen in covalent crystals [120]. Bulatov and Kaxiras (1997) [121] accordingly produced a solution to this problem: rather than sampling the continuous disregistry $u(x)$ with a mesh of arbitrary density along the slip direction x , the misfit distribution could be sampled discretely to reflect the discrete nature of the lattice. The sampling was chosen to occur at intervals of $\Delta x = a'$, where a' is the spacing of atomic planes perpendicular to the slip direction. This alteration to the basic PN model gives rise to the semi-discrete variational Peierls-Nabarro (SVPN) model; though the disregistry is still fundamentally considered to be a continuous distribution according to the theory, the discretization into lattice spacings provides (perhaps) a more realistic description of the lattice. To start, the dislocation density is redefined as

$$\rho_i = \frac{u_i - u_{i-1}}{x_i - x_{i-1}}, \quad (2.42)$$

which yields a discretized elastic energy given by

$$E_{\text{elastic}} = K \sum_{ij} \chi_{ij} \rho_i \rho_j, \quad (2.43)$$

where

$$\chi_{ij} = \frac{3}{2}\phi_{i,i-1}\phi_{j,j-1} + \psi_{i-1,j-1} + \psi_{i,j} + \phi_{i,j-1} + \phi_{j,i-1}, \quad (2.44)$$

$$\phi_{i,j} = x_i - x_j, \quad (2.45)$$

$$\psi_{i,j} = \frac{1}{2}\phi_{i,j}^2 \ln|\phi_{i,j}|, \quad (2.46)$$

The misfit potential can also be sampled discretely, yielding

$$E_{\text{misfit}} = \Delta x \sum_i \gamma(u_i), \quad (2.47)$$

where Δx is chosen to be the spacing between atomic planes in the slip direction along x . The discretized work performed by the applied stress is

$$W_{\text{stress}}[u(x), \tau] = -\tau \sum_i \frac{x_i^2 - x_{i-1}^2}{2} \rho_i \quad (2.48)$$

An SVPN model was recently implemented by Liu *et al.* (2016) to determine Peierls stresses in FCC metals [122]; the model used in this work was anisotropic, eschewing the pre-logarithmic energy factor K for the anisotropic Stroh [123] tensor H :

$$E_{\text{elastic}} = \sum_{i,j=1}^N \chi_{ij} [H_{11}\rho_1(x_i)\rho_1(x_j) + H_{33}\rho_3(x_i)\rho_3(x_j) + 2H_{13}\rho_1(x_i)\rho_3(x_j)] \quad (2.49)$$

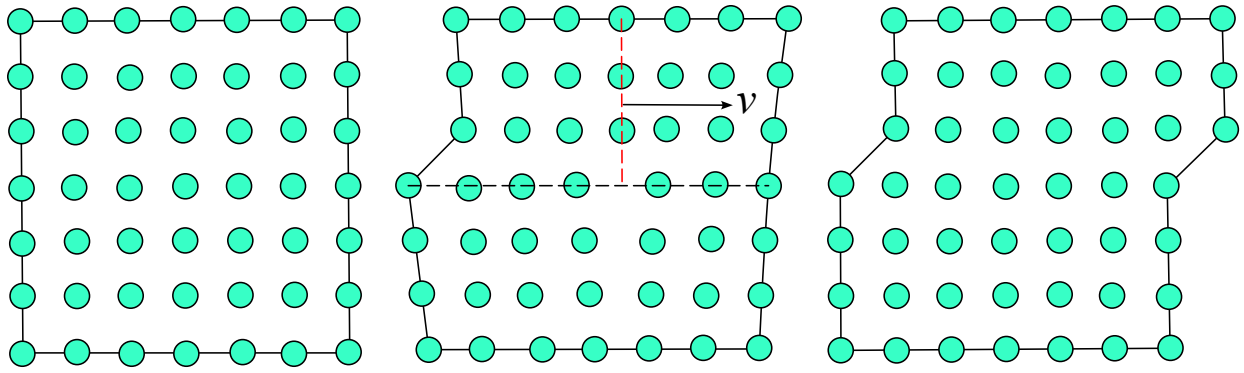
where χ_{ij} was defined the same way as in the work of Bulatov and Kaxiras. This simulation was subsequently modified to incorporate a non-local gradient term [124] in order to more accurately model FCC metals, but the parameterization of this term required molecular dynamics (MD) simulation of the unstressed dislocation core; this is easy to do for metals, but not for other materials for which reliable MD inter-atomic potentials may not exist.

On this point, why deal with semi-continuum hierarchical models at all? Why not just simulate dislocation motion directly to better understand the carbides and nitrides? Firstly, MD simulations in programs such as the Large-scale Atomistic/Molecular Massively Parallel Simulator

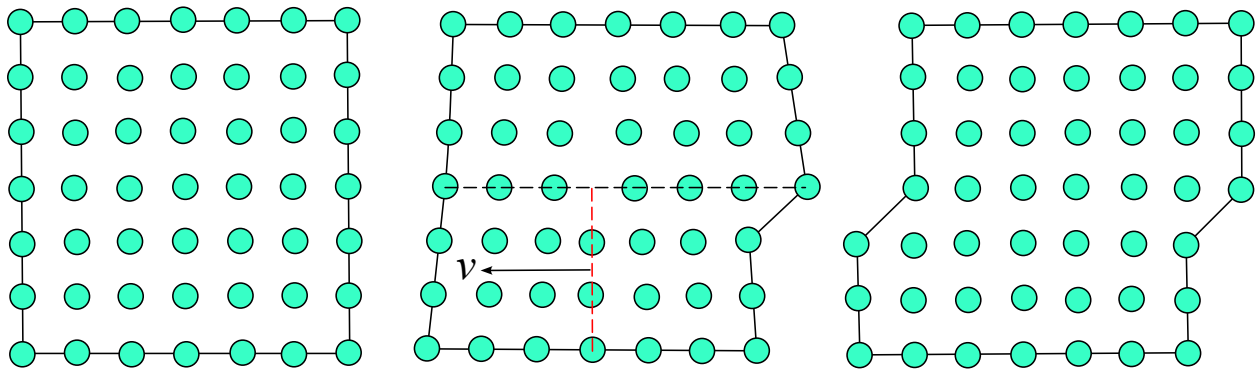
(LAMMPS) [125] have been used successfully to model dislocations in metals [126] and obtain Peierls stress estimates [127]. However, many metals in MD have reasonably good inter-atomic potentials available (*e.g.* embedded-atom metal, or EAM, potentials); these do not exist for the carbides and nitrides. DFT calculations construct interatomic forces by explicitly modeling electrons using one-electron wave-functions—thereby computing the spatial charge density distribution, and assuming the system energy to have a functional relationship to the charge density—obviating the need for something like an EAM potential. Instead, each species of atom present in a simulation cell in a program such as VASP has an associated pseudo-potential, meaning that the interactions of atoms in the system are built up from the individual atoms’ electron wave-functions. In MD, however, no electrons are explicitly modeled. Instead, general inter-atomic interactions must be parameterized; this is tricky for materials comprised of very unlike atom types—tantalum and carbon, for example—and is further complicated by the fact that, for the carbides and nitrides, we wish to investigate mixing and vacancy effects. Thus, we desire the ability to accurately model inter-atomic interactions in these materials even when we substitute or simply remove atoms. Though some attempts are being made to create inter-atomic potentials for MD simulation of these ceramics, at present it is not suitable for the purposes of dislocation modeling.

But DFT calculations, as mentioned above, *are* capable of accurately predicting energies and inter-atomic forces in these materials. So why not directly simulate dislocations in DFT? The primary obstacle is computational expense. Due to the periodic boundary conditions in DFT, a simulation cell containing, for example, a positive edge dislocation will also have to contain a negative edge dislocation so that the top and bottom boundaries of the cell are identical. This means that a single dislocation cannot effectively be modeled independently. Furthermore, each dislocation in the cell will interact with its periodic replicas—both to either side of the simulation cell, and above and below. These considerations, taken together, require a very large simulation cell in order to limit dislocation interactions. A computationally inexpensive way of enlarging the unit cell in a program like VASP is to create vacuum gaps around the simulated portion of the crystal—limiting defect interactions by simply moving the defects further away [128] without

increasing the number of atoms. However, in the case of dislocations, the creation of free surfaces will necessarily alter the dislocations' behavior, since dislocations can nucleate and annihilate at free surfaces. The other option, simply enlarging the unit cell, requires the simulation of huge numbers of atoms; this can rapidly increase the computational expense of the simulation, rendering this approach impractical.



Positive edge dislocation



Negative edge dislocation

Figure 2.19: Schematic illustration of plastic deformation via movement of a positive (top) or negative (bottom) dislocation in a simple cubic crystal, per the model devised by Taylor [114]. Note the opposite directions of travel indicated for an identical applied shear stress. Dislocation glide planes are denoted by dashed black lines, and the extra half-plane of atoms forming in each case is indicated with a red dashed line.

Chapter 3

Research Questions

All of the information discussed in the preceding sections leads us to ask a few meaningful questions about these interesting and useful materials. Why do some, but not all, of the substoichiometric TMCs and TMNs exhibit such unintuitive hardness behaviors? Furthermore, will the alloyed carbides and nitrides behave the same way within an intermediate VEC range? And, finally, can we interrogate a possible mechanism for this behavior using, among other first-principles tools, a detailed analysis of these materials' electronic structure? This section will address these questions scientifically, using them to formulate hypotheses and propose testing procedures.

3.1 Anomalous Hardness of the Tantalum Carbides

3.1.1 Scientific Question

Why does the hardness of tantalum carbide, TaC_y , increase with some loss of carbon content (*i.e.* with some reduction in the density of the covalent bonding network within the crystal)?

3.1.2 Hypothesis

I hypothesize that the anomalous hardness of TaC_y will not be seen to arise from intrinsic slip resistance. That is, decreasing y on the interval $0.83 < y < 1.0$ will produce diminished lattice friction (measured by the Peierls stress) on the dominant slip planes; furthermore, I expect that the same trend will be observed in TiC_y , which will serve as our prototypical Group IV TMC.

3.1.3 Proposed Hypothesis Testing

In order to rule out intrinsic slip resistance as a mechanism of the anomalous hardness, we will need to see how (if at all) the "lattice friction" experienced by dislocations on the most probable slip planes varies with changes in carbon content. Specifically, we want to see how the Peierls stresses on the $\{110\}$ and $\{111\}$ planes—the most probable slip planes indicated by literature on

the carbides—changes in TaC_y and TiC_y on the interval $0.83 < y < 1.0$. If, as expected per my hypothesis, the Peierls stresses in both materials decline with loss of carbon content, then we can conclude that the anomalous hardness does not arise from some change in intrinsic slip resistance; in this case, it could possibly arise from extrinsic hardening mechanisms—porosity changes, dislocation interactions with other defects, grain boundary hardening, etc. Should the Peierls stresses in TaC_y and TiC_y both be constant or increasing on $0.83 < y < 1.0$, then we shall conclude that the hardness behavior of both materials is governed by extrinsic mechanisms, since the intrinsic slip resistance in this case will not explain the observed behavior of either material. It is possible, though, that the intrinsic slip resistance will vary differently with loss of carbon content in TaC_y and TiC_y ; in this case, we might reject our hypothesis and necessarily consider the "lattice friction" to be a possible mechanism for the anomalous hardness behavior of TaC_y .

To this end, we will construct a Peierls-Nabarro (PN) dislocation model in TaC_y , along the lines of PN models discussed in detail in Section 2.6, and use it to estimate Peierls stresses at various compositions within $0.83 < y < 1.0$. To accurately model TaC_y at different y , we will need the following material data: Burgers vector magnitudes (derivable from the B1 lattice constants), elastic stiffnesses (C_{11} , C_{12} and C_{44}), and misfit potentials. Since reliable experimental data are not available at various compositions, we will use DFT-computed quantities to parameterize the PN model. To estimate the trends in B1 lattice constants with loss of carbon content, a series of special quasi-random structures (SQSs) will be used, each consisting of a $2 \times 2 \times 2$ repetition of the conventional B1 unit cell with "randomly" distributed vacancies on the non-metal sub-lattice. Each of these structures will be relaxed in VASP to determine the lattice constant. Elastic constants will be computed in VASP using these same structures; the use of SQSs is intended to neglect any effects of vacancy ordering on the stiffness (and stiffness isotropy) of the material at sub-stoichiometric compositions. Misfit potentials for stoichiometric and sub-stoichiometric compositions will be approximated by generalized stacking-fault (GSF) energies obtained in VASP; full parameterization of the Peierls-Nabarro model will require computation of GSF energy curves for uniform slip in the $\langle 110 \rangle \{110\}$, $\langle 112 \rangle \{111\}$ and $\langle 112 \rangle \{111\}$ directions, since dislocations will be modeled on the

$\{110\}$ and $\{111\}$ crystallographic planes—the slip planes most often claimed in experimental investigations. This analysis will be conducted in identical fashion for a IVB TMC, TiC_y , to reveal any disparate effects the loss of carbon content may have on the two carbides.

3.2 Effects of Metal and Non-Metal Atom Substitutions on the Slip Behavior of the Cubic Carbides, Nitrides and Carbo-nitrides

3.2.1 Scientific Question

What changes in intrinsic slip resistance will arise from substitutional defects on the metal and non-metal sublattices of the cubic TMCs, TMNs and TMCNs? Furthermore, will increasing VEC (within the range from 8 electrons/f.u. to 9 electrons/f.u.) by means of metal-atom substitutions (*e.g.* $\text{Hf}_{1-y}\text{Ta}_y\text{C}$) and, alternatively, non-metal-atom substitutions (*e.g.* $\text{HfC}_{1-y}\text{N}_y$) produce the same changes in Peierls stress? In other words, will all rocksalt TMCs, TMNs or TMCNs with a given VEC exhibit the same slip plane preference, as determined by the lowest-Peierls-stress slip planes?

3.2.2 Hypothesis

I hypothesize that increasing VEC on the interval between 8 electrons/f.u. and 9 electrons/f.u. in the B1 MTMCs, MTMNs and TMCNs will produce a change in preferred (lower Peierls stress) slip system from $\{110\}_{\text{B1}}$ to $\{111\}_{\text{B1}}$; furthermore, I anticipate that this change will occur somewhere between 8.3 and 8.6 electrons/f.u., since this is the approximate location of the maximum hardness observed in prior studies. I hypothesize that this will occur irrespective of the type of substitutional defects used to produce a given VEC.

3.2.3 Proposed Hypothesis Testing

Testing of this hypothesis will follow much the same procedure as the testing approach discussed in Section 3.1.3. The same SVPN modeling approach will be used to produce Peierls stress estimates for dislocations on the most probable slip planes in these materials—the {110} and {111} planes—and predict the dominant slip system at various compositions (*i.e.* various VECs). This analysis will first focus on the sub-stoichiometric Group IV and Group V carbides and nitrides (ZrC_y , HfC_y , VC_y , NbC_y , TiN_y , ZrN_y , HfN_y , VN_y , NbN_y and TaN_y), in the interest of determining whether the same {110} and {111} Peierls stress trends appear over the same VEC range in these different materials. Subsequently, this analysis will be extended to the mixed-transition-metal carbides $\text{Ti}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$ in order to see the effect of VEC tailoring via metal atom substitutions on dislocation mobility; the carbo-nitride system $\text{HfC}_{1-y}\text{N}_y$ will be modeled to see the effect of mixing on the non-metal sub-lattice. Naturally, the testing of this hypothesis will entail the generation of a great deal of *ab-initio* material data—lattice constants, elastic moduli and GSF energy curves for various non-metal-to-metal atom ratios; along the way, trends in these values will be examined, and possible indicators of slip plane preference (USF energies, ISF energies, rigid ideal shear stresses, polycrystalline shear moduli, etc.) will be analyzed.

3.3 Electronic Mechanism of ISF Stabilization in the VB TMCs and IVB TMNs

3.3.1 Scientific Question

What electronic mechanism gradually stabilizes the intrinsic stacking-fault with increasing VEC in the rocksalt carbides and nitrides? Does the increased stability of the B_h structure relative to the $B1$ structure with increasing VEC (between 8 and 10 electrons/f.u.) arise from different metal-atom *d*-orbital splitting in the different coordination environments?

3.3.2 Hypothesis

I hypothesize that increasing VEC in the B1 structure (ranging from 8 electrons/f.u. to 10 electrons/f.u.) will further populate molecular orbitals—comprised of overlapping metal-atom d -orbitals—that lower the band structure energy of the B_h structure while having little effect on the net bonding interactions in the B1 structure. I expect this difference to arise from different splitting of metal-atom d -orbitals in the octahedral (B1) and trigonal prismatic (B_h) coordination environments. Furthermore, I expect that the metal-non-metal interactions (arising from metal d -orbital interactions with non-metal p -orbitals) will not be significantly affected by the presence of additional electrons in the higher-VEC compounds; these additional electrons will be seen to participate in d - d bonding interactions, reducing the band structure energy by a significantly greater amount in the B_h structure than in the B1 structure. This will be seen to contribute to the meta-stable ISF at intermediate VEC (*e.g.* TaC, with a VEC of 9 electrons/f.u.) and a stable ISF at higher VEC (*e.g.* WC, with a VEC of 10 electrons/f.u.).

3.3.3 Proposed Hypothesis Testing

To investigate the effect of VEC on the net bonding contribution of atomic d -orbital overlaps in the B1 and B_h structures, we can make use of the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) software package described in Section 2.5. This computational tool will provide crystal orbital Hamilton population (COHP) analysis of the TMCs, TMNs and TMCNs, allowing us to observe the specific population-weighted orbital overlap contribution to the overall band structure energy. Essentially, this will allow us to see the energies of particular hybrid states—for example, those formed from overlapping d_{xy} , d_{xz} and d_{yz} atomic orbitals—and classify these interactions as bonding, non-bonding or anti-bonding. This will allow us to determine, firstly, whether the claims about d -orbital splitting into e_g and t_{2g} levels are true: by breaking down the COHP into specific d -orbital overlaps, we will be able to observe the energies of the hybrid states, either supporting or challenging the conventional view of d -orbital splitting in an octahedral coordination environment. This analysis will also be performed for trigonal-

prismatically-coordinated structures, giving detailed information about the effect of each environment on the metal atoms' d -orbitals. Secondly, we will examine the population of these orbitals in a range of compounds—sub-stoichiometric carbides and nitrides, as well as mixed-metal carbides and carbo-nitrides—to determine whether increasing VEC actually increases the bonding contribution of particular metal-metal interactions to the band energy. This analysis will be applied to both vacancy-containing structures and substitutional alloys in order to observe changes in the p - d and d - d COHPs adjacent to each type of defect. This will give us precise information regarding how vacancies and substitutions actually alter the population of specific molecular orbitals (and thereby alter the band structure energy), allowing us to either refute or fail to refute our hypothesis regarding the additional d - d bonding interactions present in the B_h structure at higher VEC.

Chapter 4

Findings

The hypothesis testing outlined in Chapter 3 has been performed. A great deal of investigation into the mechanical and electronic properties of the cubic carbides, nitrides and carbo-nitrides has been done; additionally, some inquiry into the effects of metal and non-metal atom mixing in the TMCs and TMNs has taken place. Our findings, detailed in the many following sections, (1) propose a mechanism for the anomalous hardness of the tantalum carbides, (2) address questions concerning alloying effects, and (3) delve into detailed electronic structure analysis to identify underlying mechanisms for the disparate mechanical behaviors of these materials.

4.1 On the Anomalous Hardness of TaC_y

4.1.1 Bond Strength and Cohesive Energy

An initial investigation into the effect of composition on the formation enthalpy of the Group IV and Group V TMCs has been performed, in order to see whether or not TaC_y displays any sort of anomalous behavior. Formation energies for various metal carbide phases, M_xC_y , were calculated from VASP-computed total energies:

$$\Delta E_f^{\text{M}_x\text{C}_y} = \frac{E_{\text{M}_x\text{C}_y} - xE_{\text{M}} - yE_{\text{C}}}{x + y}, \quad (4.1)$$

where the M reference state was either hexagonal close-packed (HCP) or body-centered cubic (BCC), depending on the species of transition metal, and the C reference state was graphite. Since these calculations were carried out at zero external pressure, these internal energy changes are equivalent to enthalpy changes; thus, $\Delta H_f = \Delta E_f$. The phases investigated were M_2C , M_3C_2 , M_4C_3 , M_6C_5 and MC. These formation enthalpy estimates were used to compute theoretical hardnesses for all of the Group IV and Group V TMCs, using Gilman's derived model discussed in Section 2.2.1. The results, shown in 4.1, do not clearly indicate any anomalous behavior in TaC_y .

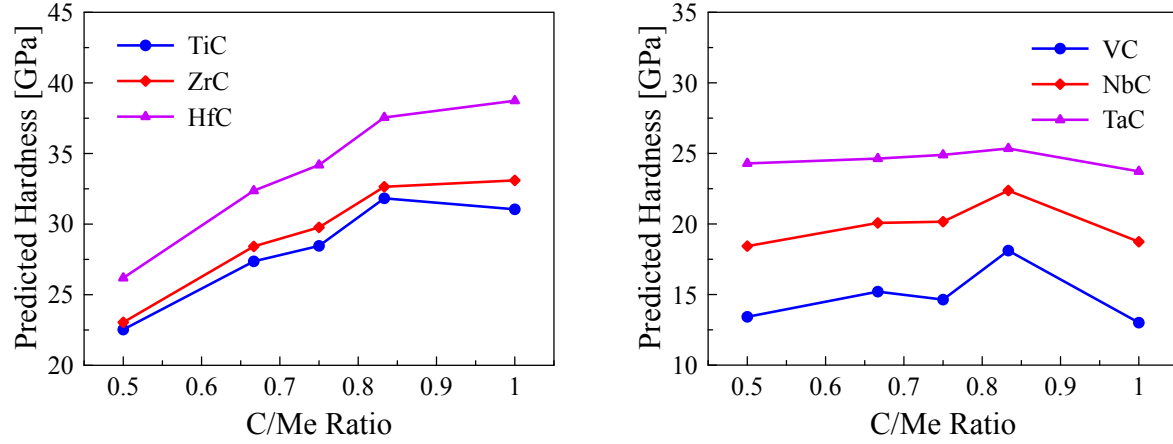


Figure 4.1: Calculated hardnesses for the Group IV and Group V TMCs, per the formation enthalpy correlation proposed by Gilman [53, 55].

In the Group IV carbides, the trends actually do somewhat resemble experimental results, with hardness generally declining in TiC_y , ZrC_y and HfC_y with decreasing y . In the Group V TMCs, though, little variation is seen across the whole composition range; TaC_y is predicted to show almost no variation in hardness across this composition range, when in experiment TaC_y shows the most variation. It should be noted that VC_y , NbC_y and TaC_y are predicted to show modest increases in hardness in the M_6C_5 phase, as compared to the MC phase; however, the change in hardness is very moderate. Furthermore, TiC_y is predicted to show a sub-stoichiometric increase in hardness greater than that predicted for TaC_y ; this result represents a problem for this model, since TiC_y is not seen to exhibit a sub-stoichiometric hardness maximum in experiment.

As discussed in Section 2.2.2, it is possible that a correlation between hardness and elastic stiffness will better describe the disparate hardness behaviors of the carbides. To examine the effect of carbon vacancy concentration on the average bond strength within the tantalum carbides, elastic moduli have been computed for TaC_y at various y . A selection of "disordered" quasi-random structures have been used in these calculations, with the aim of accounting for any potential ordering effects on the stiffness of the sub-stoichiometric carbides; these quasi-random structures are shown in Figure 4.2. The computed cubic elastic stiffnesses— C_{11} , C_{12} and C_{44} —are shown in Figure 4.3, along with the Hill average shear modulus values derived from these quantities.

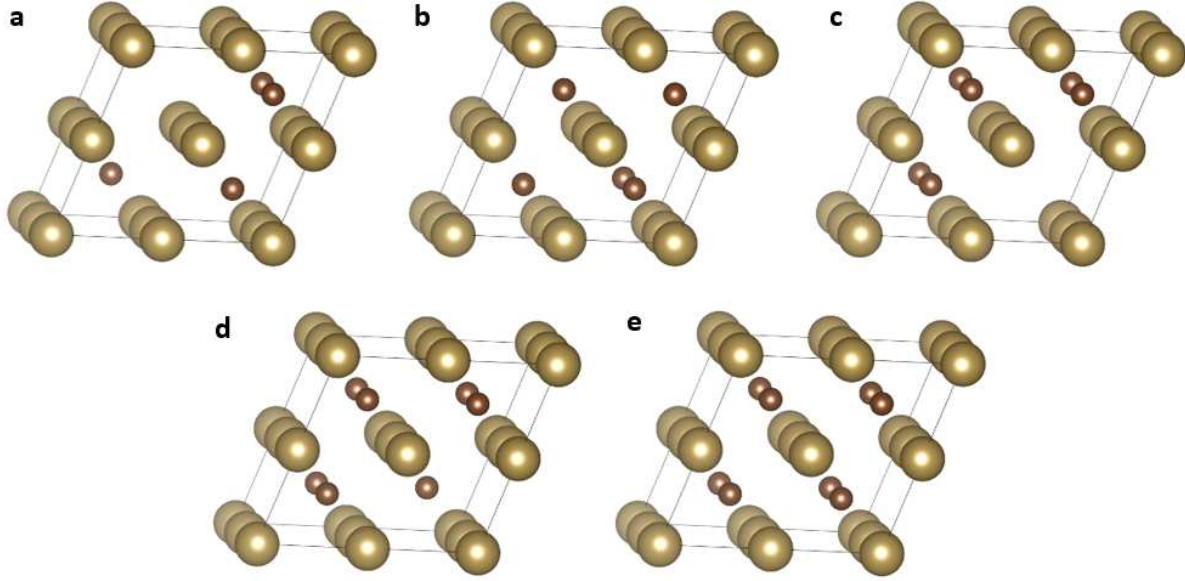


Figure 4.2: 16-atom TaC_y SQSs used for VASP elastic modulus calculations. Images taken from work by Watkins *et al.* [129].

Ultimately, TiC_y and TaC_y exhibit very similar variations in stiffness with carbon content, with moduli generally declining as y decreases. In TaC_y , interestingly, the C_{12} modulus is seen to rise with decreasing y below $y = 0.875$, but this seems to have no effect on G . These results are quite similar to the more limited dataset published by Yu *et al.* [66]. Since the shear modulus may not perfectly correlate with hardness, though, we used the Chen correlation model (discussed in Section 2.2.2) to compute theoretical hardnesses using both shear and bulk moduli for our carbides of interest. The results, seen in Figure 4.4, show nearly identical trends for the two carbides—providing no evidence for a stiffness-driven anomalous hardness in TaC_y .

4.1.2 Vacancy-Ordering Effects

A limited investigation into the effect of ordering domain size has been carried out. Specifically, the data presented by Hannink and Murray [32] for V_6C_5 was used to independently generate a Hall-Petch relationship. As noted in Section 2.2.3, the original authors published a Hall-Petch slope, k_{HP} , of $0.37 \text{ kg/mm}^{3/2}$ and a boundary-free hardness, H_∞ , of 2080 kg/mm^2 . From our parameterization of the Hall-Petch model, however, we found a very different slope: $k_{\text{HP}} = 7.67$

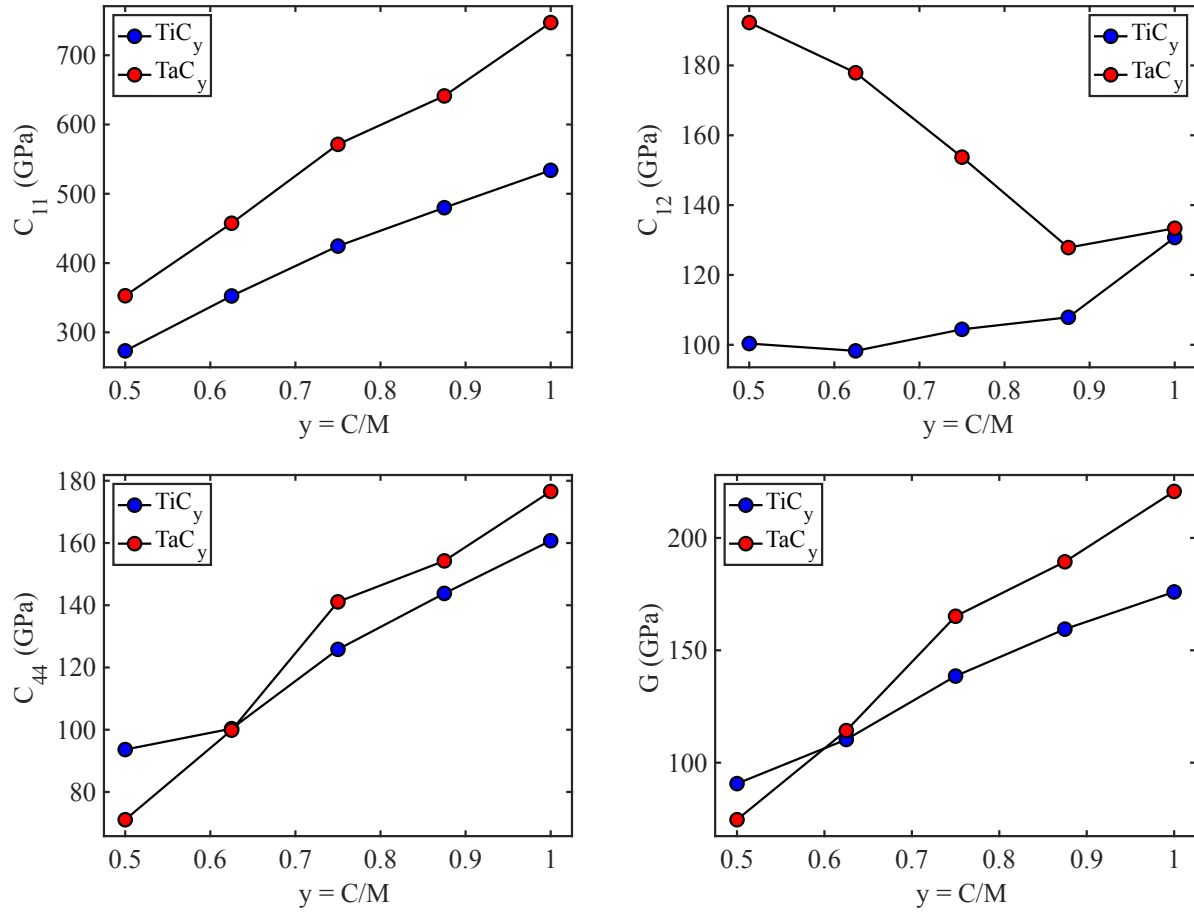


Figure 4.3: Trends in DFT-computed elastic constants in TiC_y and TaC_y , including the derived Hill average shear modulus for a polycrystalline aggregate. Data taken from Watkins *et al.* [129].

$\text{kg/mm}^{3/2} = 2.38 \times 10^6 \text{ N/m}^{3/2}$. Our intercept value, though, was $H_\infty = 2068 \text{ kg/mm}^{3/2} = 2.02 \times 10^{10} \text{ N/m}^2 = 20.2 \text{ GPa}$. The reason for the slope disagreement between our fit and the original published result is unclear. Nonetheless, we used this fit to estimate the average ordering domain size required to produce a given hardness change in the carbides.

This model was developed for VC_y , and without detailed experimental data for TaC_y and NbC_y , it is difficult to know how similar the Hall-Petch effect may be in these latter materials. However, we can use our parameterized model to estimate the required domain size to produce the "anomalous" sub-stoichiometric hardness increases seen in NbC_y and TaC_y . In both of these carbides, the hardness is seen experimentally to increase by about 15 GPa between $y = 1.0$ and $y = 0.80$. Using our Hall-Petch relationship, this corresponds to an ordering domain size of about $0.02 \mu\text{m}$,

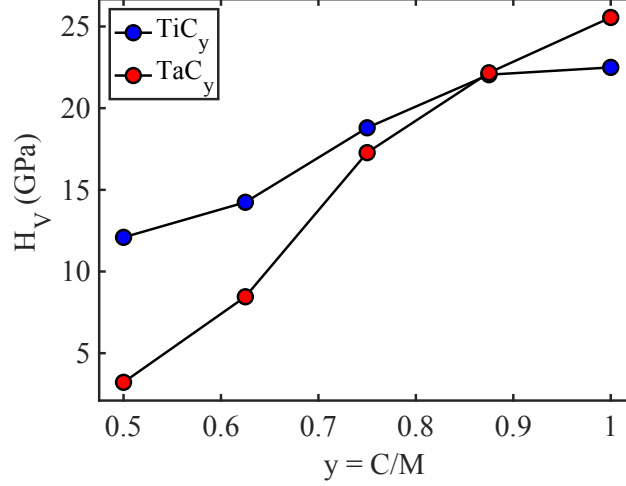


Figure 4.4: Trends in computed hardness values in TiC_y (blue circle markers) and TaC_y (red diamond markers), obtained using the hardness-stiffness correlation developed by Chen *et al.* [73]. Data taken from Watkins *et al.* [129].

or about 20 nm. If TaC_y and NbC_y are supposed to behave like VC_y with respect to ordering domain formation, then this would require a cooling rate in excess of 200 K/s in addition to sufficient annealing to produce long-range ordering. Given the apparent difficulty in forming long-range vacancy ordering in TaC_y (see Section 2.2.3), it thus seems unlikely that vacancy-ordered domain refinement would be a governing mechanism for the sub-stoichiometric hardness increases seen in NbC_y and TaC_y .

4.1.3 Generalized Stacking-Fault Energies

From the DFT-computed GSF energy curves, TiC_y and TaC_y exhibit remarkably different behaviors with loss of carbon content. The stoichiometric (B1 MC) curves produced in this work generally exhibit good agreement with those computed by Yu *et al.* [92], showing a meta-stable ISF at the geometrically expected location ($u_{(112)} = b\sqrt{3}/3$) in TaC and no meta-stable ISF in TiC. In the novel sub-stoichiometric (C2/m M_6C_5) GSF energy curves, a surprising change occurs. The GSF energies in Ti_6C_5 are generally depressed, as compared to those of TiC, with essentially no change in GSF energy curve morphology; in Ta_6C_5 , the energy values exhibit only modest changes overall, but with a huge (nearly threefold) increase in ISF energy. This result is highly intriguing, as it suggests a greatly increased energetic penalty for dissociation of dislocations on $\{111\}_{B1}$

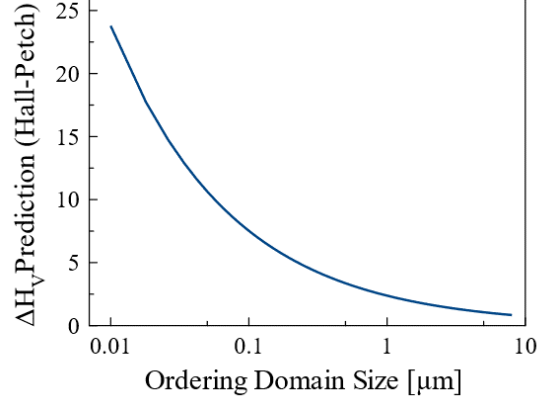


Figure 4.5: Hardness change associated with ordering domain refinement in V_6C_5 , per a Hall-Petch model parameterized using data collected by Hannink and Murray [32].

planes in TaC_y with loss of carbon content. This in turn gives some indication that dislocations on the $\{111\}_{B1}$ planes may lose mobility as y decreases, possibly facilitating a transition to $\{110\}_{B1}$ slip dominance at sub-stoichiometric compositions. That no meta-stable ISF ever appears in TiC_y suggests that this material will undergo no change in slip plane preference; based on the experimental findings discussed in Section 2.2.4, it is likely that dislocation mobility will be highest on $\{110\}_{B1}$ over the entire sampled range of y values.

Because the gradient of the GSF energy with respect to disregistry, $d\gamma/du$, is generally equivalent to the force seeking to restore the undeformed geometry of the crystal, the rigid ideal shear strength (RISS) is commonly used as a predictor of slip resistance in a material. The RISS in the i^{th} slip direction on the j^{th} crystallographic plane is given by

$$\tau_{\langle i \rangle \{ j \}} = \max\{d\gamma_{\langle i \rangle \{ j \}}/du\}, \quad (4.2)$$

offering a quick estimate for the stress required to move a dislocation. Though this quantity is often (inappropriately) used as an estimate for the Peierls stress, it more realistically represents the stress required to rigidly translate one plane of atoms over another toward an equivalent energy minimum. Thus, the RISS generally overestimates the Peierls stress considerably—sometimes by orders of magnitude—and does not accurately describe the behavior of dislocations on a given

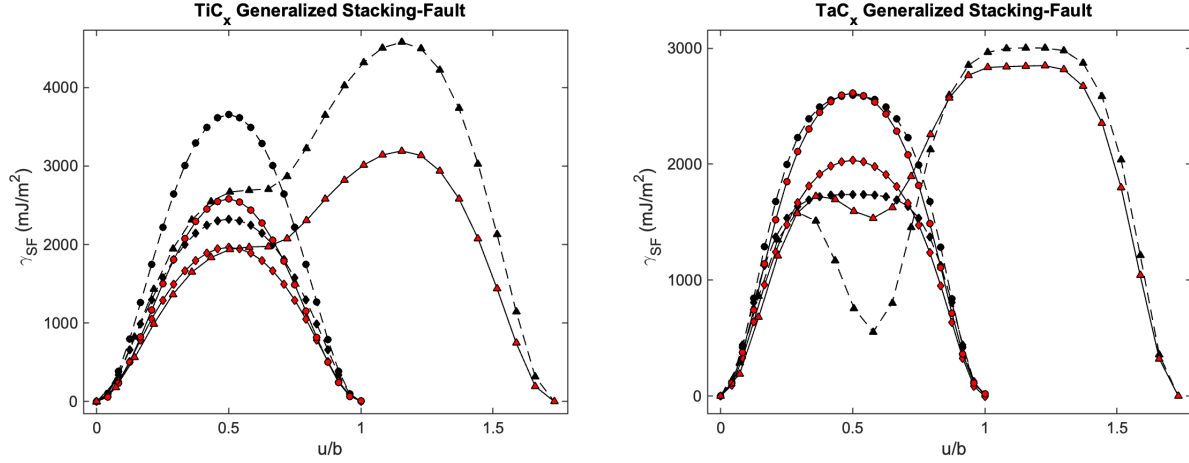


Figure 4.6: Stacking-fault energy curves for TiC_x and TaC_x . Dashed lines with black markers denote the stoichiometric B1 MC phase, while solid lines with red markers denote the sub-stoichiometric C2/m M_6C_5 phase. Slip in $\langle 110 \rangle \{110\}$ is indicated by diamond markers; $\langle 110 \rangle \{111\}$ slip is indicated by circle markers; $\langle 112 \rangle \{111\}$ slip is indicated by triangle markers.

crystallographic plane. Nonetheless, RISS estimates may be useful in comparing materials with similar GSF energy curve morphology; after all, a steeper GSF energy curve (all else being equal) can be reasonably expected to produce a higher Peierls stress.

For this reason, the unstable stacking-fault energy γ_{USF} is also of interest: even if a low-energy meta-stable ISF is present, a high-energy USF may prevent the dislocation core from ever spreading to the ISF location. In the $\langle 112 \rangle \{111\}$ GSF energy curves that contain metastable ISFs, the ISF and USF appear as a local minimum and a local maximum, respectively. However, in the curves lacking metastable ISFs, no local minimum or maximum is evident; instead, the two distinct points merge into a single inflection point. Sampling of the geometrically-expected locations ($u = b\sqrt{3}/6$ for the USF, and $u = b\sqrt{3}/3$ for the ISF) is therefore not wholly appropriate for comparing features of these curves. Rather, these features should be located via the slope and curvature of the GSF energy curves; these derivatives are easily approximated by finite-difference:

$$\gamma'_i = \left. \frac{d\gamma}{du} \right|_{u=u_i} \approx \frac{\gamma_{i+1} - \gamma_{i-1}}{u_{i+1} - u_{i-1}} = \frac{\gamma_{i+1} - \gamma_{i-1}}{2\Delta u} \quad (4.3)$$

$$\gamma''_i = \left. \frac{d^2\gamma}{du^2} \right|_{u=u_i} \approx \frac{\gamma'_{i+1} - \gamma'_{i-1}}{u_{i+1} - u_{i-1}} = \frac{1}{2\Delta u} \frac{(\gamma_{i+2} - \gamma_i) - (\gamma_i - \gamma_{i-2})}{2\Delta u} = \frac{\gamma_{i+2} - 2\gamma_i + \gamma_{i-2}}{4\Delta u^2} \quad (4.4)$$

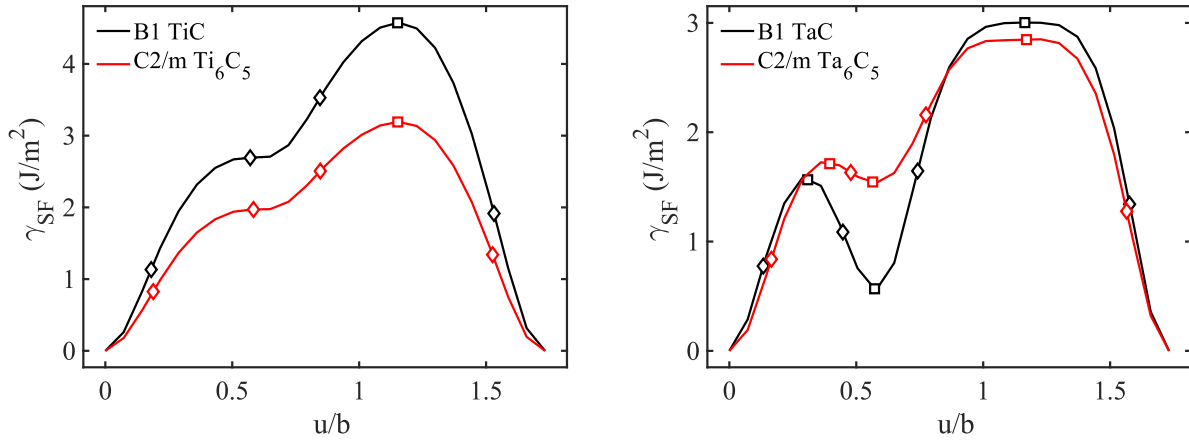


Figure 4.7: Identified local extrema (square markers) and inflection points (diamond markers) on the $\langle 112 \rangle \{111\}$ GSF energy curves for stoichiometric and sub-stoichiometric TiC_y and TaC_y .

This approach allows for more precise description of the GSF energy curve morphology. As seen in 4.7, no local minima or maxima are present in the TiC_y curves—save for the very large peak at $u \approx 1.15b$, which will never be visited by a dislocation core under any normal conditions. In TaC_y , though, the ISF and USF are clearly identified as local extrema for both compositions. Furthermore, while the ISF is present at almost exactly the same location ($u \approx 0.5720b$ in TaC, and $u \approx 0.5647b$ in Ta_6C_5), the USF changes position quite dramatically. The unstable point in TaC occurs at $u \approx 0.3086b$, whereas in Ta_6C_5 it has moved to $u \approx 0.3955b$; this suggests that, as the VEC in TaC_y is reduced, the USF and ISF begin to merge into the single inflection point seen in the curves for the IVB TMCs, similar to the result observed by Smith *et al.* [93] in the $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ system.

The equilibrium stacking-fault width $w_{\text{eq.}}$ in the absence of an applied shear stress can be expected to vary inversely with the ISF energy γ_{ISF} ; that is, a lower ISF energy should produce a wider stacking-fault. A convenient equation for this is presented by Cai and Nix [130]:

$$w_{\text{eq.}} = \frac{1}{\gamma_{\text{ISF}}} \left[\frac{\mu b_e^2}{2\pi(1-\nu)} - \frac{\mu b_s^2}{2\pi} \right], \quad (4.5)$$

where μ and ν are the isotropic shear modulus and Poisson's ratio, respectively, and b_e and b_s are the edge and screw components of the Burgers vector for the dissociated dislocation. Though this

Table 4.1: Characteristics of GSF energy curves which may indicate slip plane preference in the sub-stoichiometric carbides TiC_y and TaC_y .

	B1 TiC	C2/m Ti_6C_5	B1 TaC	C2/m Ta_6C_5
b (Å)	3.067	3.059	3.164	3.148
γ_{ISF} (mJ/m ²)	2692	1970	568	1545
γ_{USF} (mJ/m ²)	2692	1970	1565	1712
$\gamma_{\text{ISF}}/\gamma_{\text{USF}}$	1.000	1.000	0.3628	0.9023
$\tau_{\langle 110 \rangle \{110\}}$ (GPa)	25.86	21.69	27.75	24.16
$\tau_{\langle 110 \rangle \{111\}}$ (GPa)	38.01	26.77	33.91	30.41
$\tau_{\langle 112 \rangle \{111\}}$ (GPa)	27.64	19.40	25.10	23.17

equation incorporates a good number of simplifying assumptions, it offers a convenient way to estimate the wideness of dislocations on planes where they may dissociate.

In the interest of better understanding the effects of short- and long-range ordering of vacancies on the GSF energy curves in the M_6C_5 crystal, a study has been carried out on the selective filling of structural vacancies in Ta_6C_5 . The positions of carbon vacancies within the C2/m Ta_6C_5 crystal are indicated in 4.8, along with the corresponding $\langle 112 \rangle \{111\}$ GSF energy curve for each carbon atom replacement. Since the simulation cell used in this work contains three carbon atoms per non-metal $\{111\}_{B1}$ layer—one of them being replaced with a vacancy in the sparsely-populated non-metal layers—the filling of a carbon vacancy in any layer fully populates that layer with atoms via VASP’s periodic boundary conditions. The stacking-fault is formed on the $\{111\}_{B1}$ layer denoted as L3; unsurprisingly, it is the elimination of the L3 carbon vacancies which exhibits the most pronounced effect on the GSF energy curve. With the repopulation of this plane with carbon atoms, the ISF energy falls from 1545 mJ/m² to 601 mJ/m², nearly recovering the B1 TaC value. What may be surprising, given some of the grandiose claims made regarding vacancy-ordering effects in the carbides, is that the filling of carbon vacancies in planes adjacent to the slip plane (L3 being closest to the stacking-fault) has a modest effect on the ISF energy. Indeed, the repopulation of non-metal planes anywhere other than directly adjacent to the stacking-fault seems to have very little impact on the morphology of the GSF energy curve as a whole. The implication of this

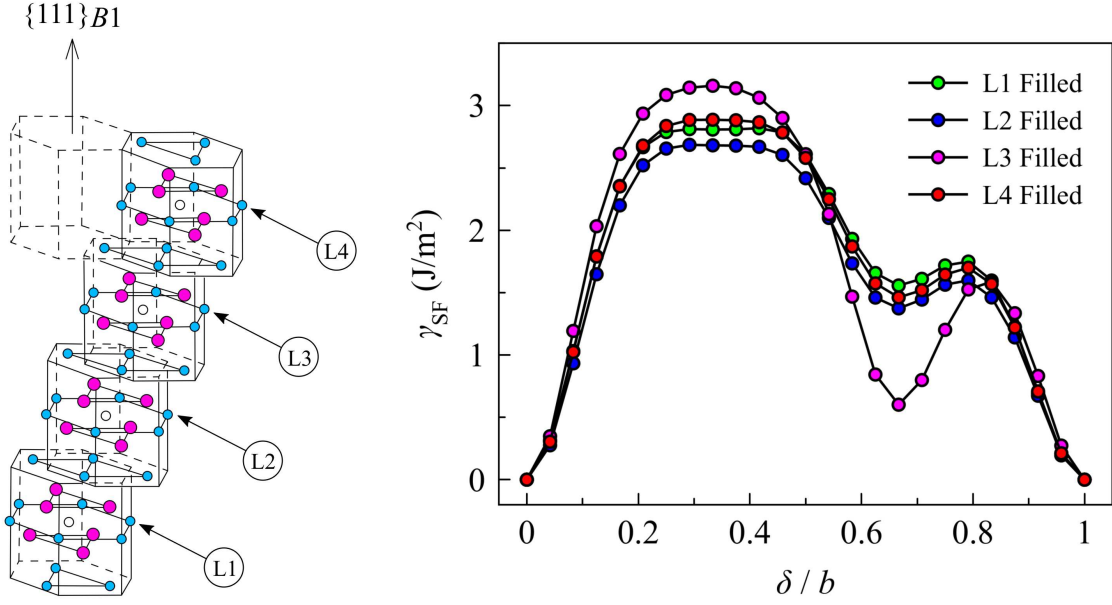


Figure 4.8: Effect of selective filling of carbon vacancies on the stacking-fault energies seen in sub-stoichiometric TaC_y . Images taken from work by Watkins *et al.* [129].

finding is that the particular ordering of carbon vacancies in the crystal plays only a minor role in determining the slip resistance of the crystal; rather, the presence of carbon vacancies on particular crystallographic planes may have a dramatic effect on the mobility of dislocations on those planes. Thus, at least in the Ta_6C_5 structure used for this investigation, the effect of vacancies appears to be highly localized.

In addition to selective vacancy filling, the effect of the particular in-plane ordering of vacancies on the GSF energy curves must be investigated. To this end, we also identified the non-degenerate $\{110\}$ and $\{111\}$ crystallographic planes in our selected $\text{C2/m } \text{M}_6\text{C}_5$ structure. Within the $\{111\}$ family of planes, shown in Figure 4.9, all four planes show unique ordering of vacancies, so $\langle 110 \rangle \{111\}$ and $\langle 112 \rangle \{111\}$ GSF energy curves were computed for each. Within the $\{110\}$ family of planes, however, some of these planes are degenerate—that is, they show identical ordering of atoms and vacancies (see Figure 4.10. Specifically, the (011) and $(10\bar{1})$ planes are degenerate, and the (101) and $(01\bar{1})$ are likewise indistinguishable from one another. Thus, of all the $\{110\}$ planes, only the (110) , $(01\bar{1})$ and $(1\bar{1}0)$ planes were modeled. It is important to note, though, that two of these crystallographic planes do not show the nominal stoichiometry of the compound:

the $(\bar{1}\bar{1}1)$ and the (110) . The $(\bar{1}\bar{1}1)$ plane shows 1/3 of the carbon atoms to be missing, while the (110) plane is missing 1/2 of its carbon atoms. Globally, the M_6C_5 compound is missing 1/6 of the carbon atoms present in the stoichiometric B1 structure, so there are necessarily different choices of $(\bar{1}\bar{1}1)$ and (110) sections in the M_6C_5 crystal. The situation for each of these is slightly different, since the $\{111\}$ planes alternate between metal and non-metal composition, whereas every $\{110\}$ plane contains both metal and non-metal atoms. The non-metal $(\bar{1}\bar{1}1)$ planes, specifically, alternate between fully-populated (no carbon vacancies) and sparsely-populated (1/3 of carbon atoms replaced by vacancies) close-packed planes; these we have chosen to label as the $(\bar{1}\bar{1}1)(f)$ and the $(\bar{1}\bar{1}1)(s)$ planes, respectively. Similarly, every third (110) plane has 1/2 of its carbon atoms replaced by vacancies, while the other two (110) planes in each 3-plane period contain no vacancies. In the same pattern as before, we have opted to call these "filled" and "sparse" planes the $(110)(f)$ and $(110)(s)$, respectively.

We computed GSF energy curves for these possible slip systems as well. The GSF energy curves for $\langle 110 \rangle \{111\}$ and $\langle 112 \rangle \{111\}$, shown in Figure 4.11, show relatively little variation in morphology across the different $\{111\}$ planes. Notably, the GSF energies in Ti_6C_5 scale exactly with carbon content. The $(\bar{1}\bar{1}1)(f)$, which contains no carbon vacancies adjacent the slip plane, has the highest GSF energies; the (111) and $(\bar{1}\bar{1}1)$, in which 1/6 of the carbon atoms are missing, have generally lower GSF energies; finally, the $(\bar{1}\bar{1}1)(s)$, which is missing 1/3 of its carbon atoms, has the lowest GSF energies. No meaningful differences in GSF energy curve morphology are evident within the $\{111\}$ family of planes in Ti_6C_5 . In Ta_6C_5 , similarly, all $\{111\}$ planes have generally the same GSF energy curve morphology; furthermore, the ISF energies are virtually identical across all $\{111\}$. The main difference—and the only difference likely relevant for intrinsic slip resistance—is that the USF energies for both the $\langle 110 \rangle \{111\}$ and $\langle 112 \rangle \{111\}$ energy curves are seen to rise appreciably with carbon content. As such, we might expect the $(\bar{1}\bar{1}1)(s)$ plane, with the lowest USF energies on both curves, to exhibit the lowest intrinsic slip resistance; the $(\bar{1}\bar{1}1)(f)$, with the highest USF energies, might be expected to have the highest Peierls stress, with the other $\{111\}$ planes showing intermediate behavior. In the $\{110\}$ slip planes, we see much the same pattern:

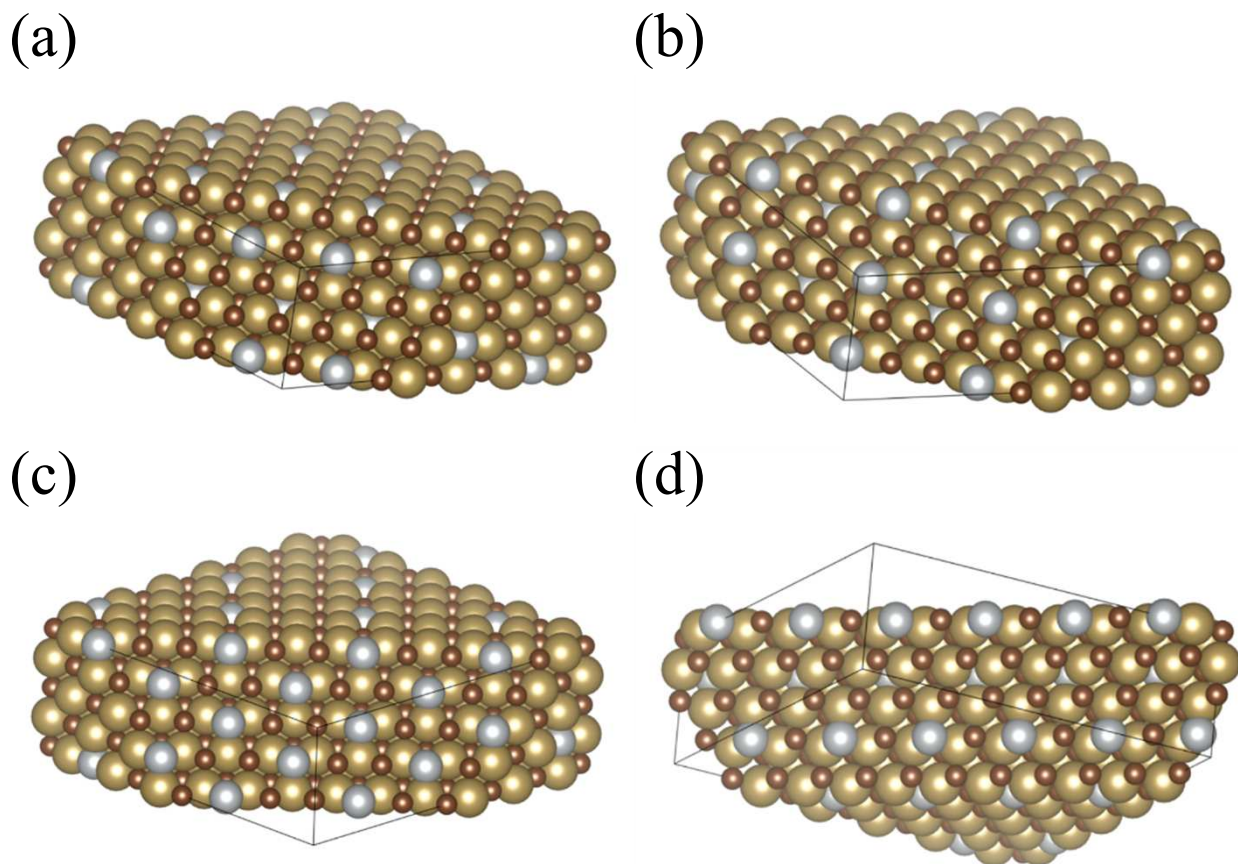
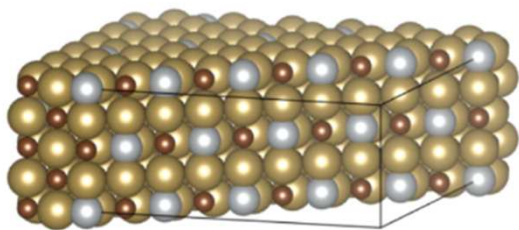
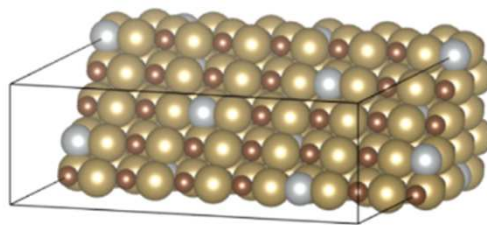


Figure 4.9: $\{111\}$ crystallographic planes in the $C2/m$ M_6C_5 structure: (a) (111) , (b) $(\bar{1}\bar{1}1)$, (c) $(1\bar{1}\bar{1})$ and (d) $(11\bar{1})$. Shown as sections of a $2 \times 2 \times 6$ repetition of conventional B1 unit cells, with the hexagonal superlattice of carbon vacancies indicated with silver markers. Image taken from work by Watkins *et al.* [129].

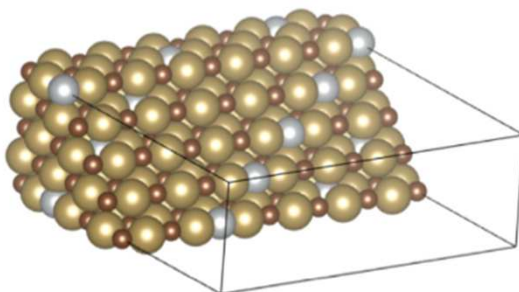
(a)



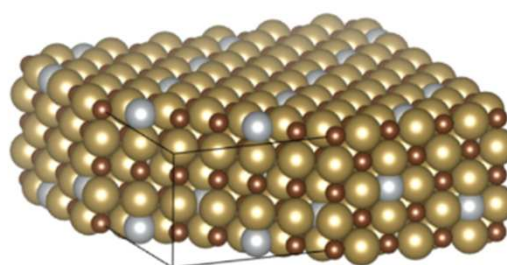
(b)



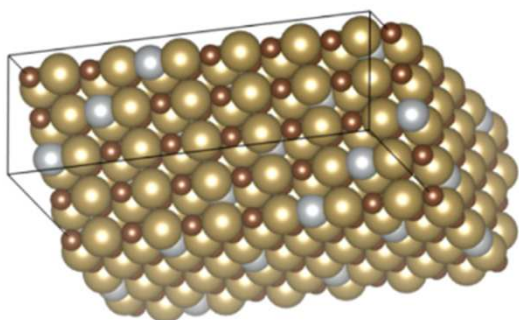
(c)



(d)



(e)



(f)

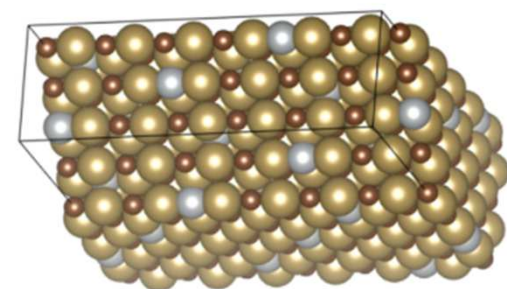


Figure 4.10: $\{110\}$ crystallographic planes in the C2/m M_6C_5 structure: (a) (110), (b) (101), (c) (011), (d) ($\bar{1}\bar{1}0$), (e) ($10\bar{1}$) and (f) ($01\bar{1}$). Image taken from work by Watkins *et al.* [129].

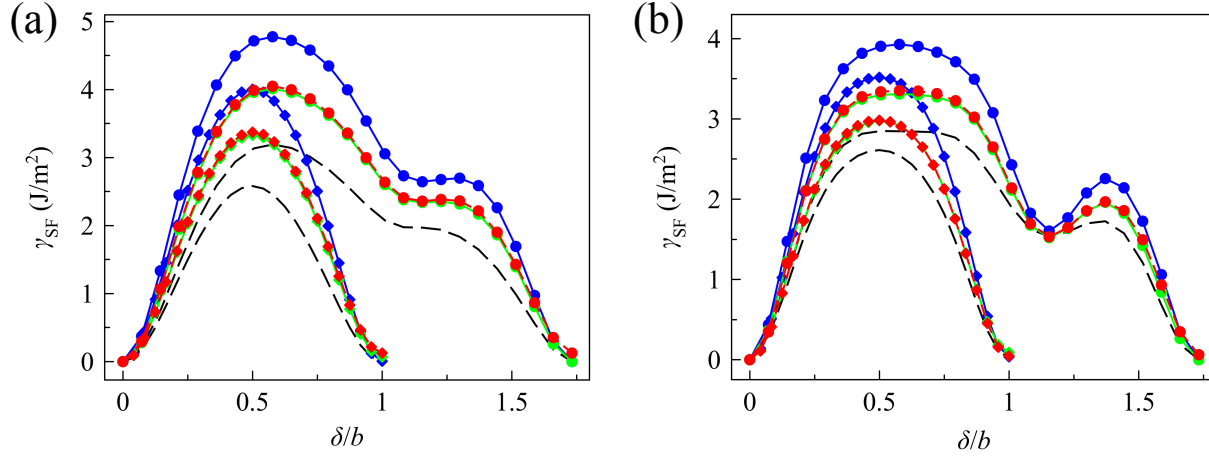


Figure 4.11: Generalized stacking-fault energy curves for non-degenerate $\{111\}_{B1}$ slip planes in (a) Ti_6C_5 and (b) Ta_6C_5 . GSF energy curves for slip in $\langle 110 \rangle$ and $\langle 112 \rangle$ directions are indicated by diamond and circle markers, respectively. Blue markers denote the $(1\bar{1}1)(f)$ plane, green markers denote the (111) plane, and red markers denote the $(\bar{1}11)$ plane. The primary slip plane used in this investigation, the $(1\bar{1}1)(s)$, is represented with dashed black lines for comparison. Image taken from work by Watkins *et al.* [129].

both in Ti_6C_5 and Ta_6C_5 , increased concentration of vacancies adjacent the slip plane appears to depress GSF energies—most importantly, the USF energy at the midway point on the $\langle 110 \rangle \{110\}$ GSF energy curve. In the stoichiometric compounds, $\text{TiC}_{1.0}$ and $\text{TaC}_{1.0}$, no carbon vacancies are present, and so all planes within each family are identical.

4.1.4 Slip System Preference in TaC_y

A semi-discrete variational Peierls-Nabarro model has been created as described in Section 2.6, incorporating discrete sampling of the lattice at the locations of atomic planes. This SVPN implementation takes several inputs: the B1 lattice constant a_0 ; the elastic moduli C_{11} , C_{12} and C_{44} ; and the generalized stacking-fault energies γ_{SF} . A simple illustration of the model's general workflow can be found in Figure 4.13. Each of the input quantities is imported as a collection of values taken from VASP simulations with different carbon-to-metal atom ratios; for each composition y_i (associated with the chemical formula TaC_{y_i} , for instance) simulated in the SVPN model, these input properties are linearly interpolated within the provided datasets. The interpolated $a_0(y_i)$ is then used to compute the Burgers vector magnitude b , and the interpolated C_{ij} and γ_{SF} values are used to compute the elastic energy (Equation 2.49) and misfit energy (Equation 2.47), respectively.

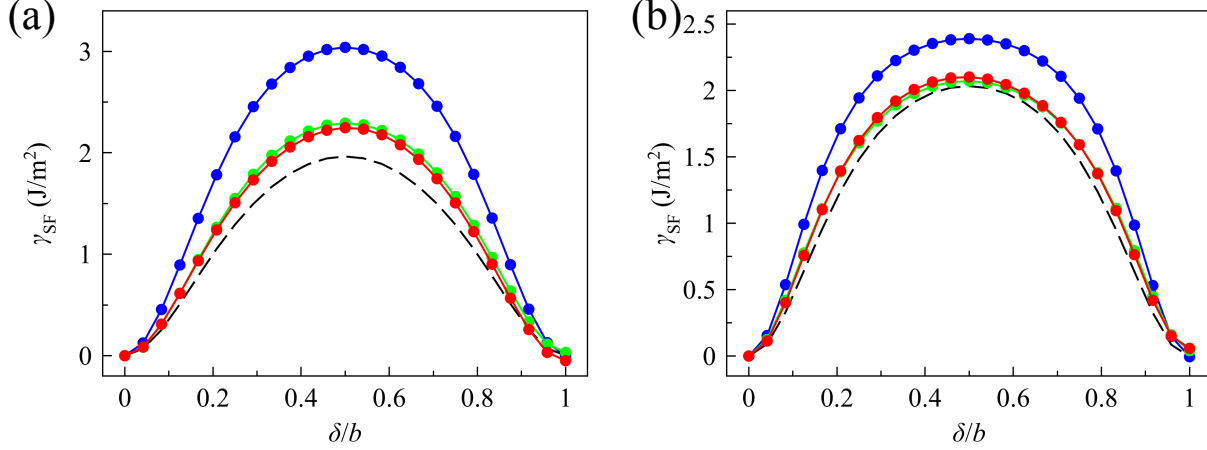


Figure 4.12: Generalized stacking-fault energy curves for $\langle 110 \rangle$ slip on non-degenerate $\{110\}_{B1}$ slip planes in (a) Ti_6C_5 and (b) Ta_6C_5 . The $(110)f$ slip planes are shown in blue, the $(01\bar{1})$ are shown in green, and the $(1\bar{1}0)$ are shown in red. The primary $\{110\}$ slip plane used in this investigation, the $(110)s$, are indicated by dashed black lines for comparison. Image taken from work by Watkins *et al.* [129].

The lattice discretization distance Δx in the slip direction $\hat{x}$ was chosen to be one nearest-neighbor separation—equal to b , or $\frac{a}{2}\langle 110 \rangle\{110\}_{B1}$, in the rocksalt crystal structure—in order to accurately reflect the spacing of atomic planes. A simulation volume of $N\Delta x \times N\Delta x$, with $N = 200$ was used in order to ensure that interactions between the simulation cell boundaries and the dislocation could be neglected. This was necessary because of the enforced boundary conditions on the slip distribution $u(x)$: $u_1(x = -N\Delta x/2) = 0$, $u_1(x = N\Delta x/2) = 1$, $u_2(x = -N\Delta x/2) = 0$, and $u_2(x = N\Delta x/2) = 0$. These boundary conditions were chosen to reflect an edge dislocation with a possible screw component—that is, allowing for possible formation of partial dislocations.

Minimization of the total energy is performed by a steepest-descent algorithm, wherein the next iteration's slip distribution $\mathbf{u}^{k+1}$ is computed from the current slip distribution $\mathbf{u}^k$ according to

$$\mathbf{u}_{k+1} = \mathbf{u}^k - \alpha \nabla \mathbf{u}^k \quad (4.6)$$

where $\nabla \mathbf{u}^k$ is the gradient of the total energy—approximated as the linear combination of central-finite-difference derivatives of each energy term with respect to x —and α is a scaling constant, chosen for fast and reliable convergence. Energy minimization proceeded until the magnitude of the change in the slip distribution between steps was less than a cutoff value, chosen to be $10^{-6}b$.

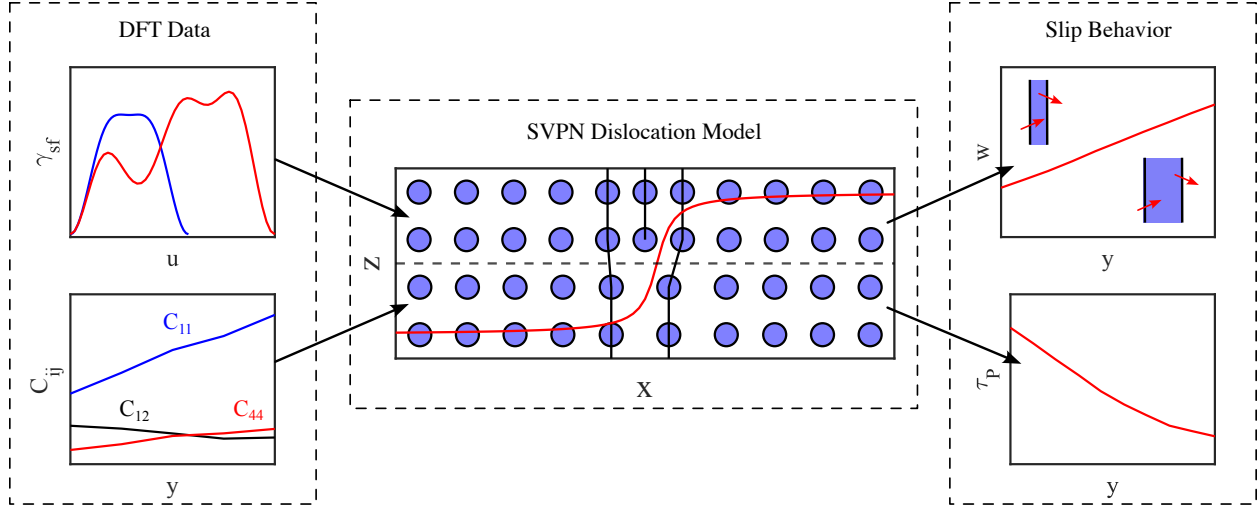


Figure 4.13: Schematic representation of semi-discrete Peierls-Nabarro (SVPN) model workflow, with DFT-computed quantities taken as inputs and slip distributions and Peierls stresses and produced as outputs. Figure taken from work by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

Mathematically, this stopping condition is expressed as

$$|\mathbf{u}^{k+1} - \mathbf{u}^k| < 10^{-6}b \quad (4.7)$$

Estimation of Peierls stress was not performed direction within the SVPN model, since the model is essentially a static simulation. Rather, at the end of each simulation, the dislocation center-of-mass (CoM) position was estimated as the midpoint between $x_{0.25}$ and $x_{0.75}$, chosen such that

$$u_1(x_{0.25}) = 0.25b \quad (4.8)$$

$$u_1(x_{0.75}) = 0.75b \quad (4.9)$$

When, after energy minimization within the SVPN, the dislocation CoM was displaced by more than $1.0b$ —indicating the dislocation core’s displacement into an adjacent energy minimum—the Peierls stress was considered to have been exceeded. Estimation of Peierls stresses was expedited using a bisection routine, with a termination accuracy of ± 20 MPa.

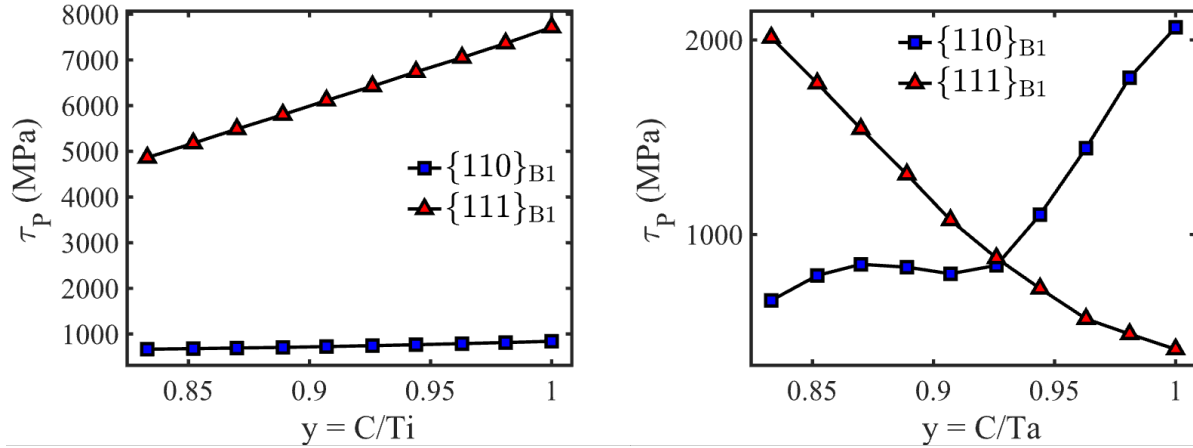


Figure 4.14: SVPN-generated Peierls stress estimates for TiC_y and TaC_y on $0.83 < y < 1.0$. Note the very high $\{111\}$ Peierls stresses over the whole composition range for TiC_y , which indicate lack of $\{111\}$ slip availability; in TaC_y , $\{111\}$ Peierls stresses are seen to be low at high y values (above $y = 0.875$ or so), indicating that $\{111\}$ slip systems will be active at near-stoichiometric compositions. Data taken from work by Watkins *et al.* [129].

The results of these simulations can be seen in Figure 4.14, which compares Peierls stresses on $\{111\}$ and $\{110\}$ planes in TiC_y and TaC_y . In TiC_y , our prototypical IVB TMC, τ_P is seen to decline on both planes as y decreases; more importantly, the Peierls stress on (111) is nearly an order of magnitude higher than on (110). This not only indicates that intrinsic slip resistance is likely to decrease with loss of carbon content, but also that only slip on the $\{110\}$ crystallographic planes will occur within the sampled range of compositions. TaC_y , on the other hand, exhibits very different behavior: as y decreases, the Peierls stress on (110) is generally seen to decrease; at the same time, the Peierls stress on (111) shows the opposite trend, increasing dramatically as carbon content falls. In fact, at $y = 1.0$, the (111) plane shows substantially lower τ_P than does the (110) plane, whereas the opposite is true at $y = 0.83$. This suggests that, at the stoichiometric composition, $\{111\}$ slip may be favored over $\{110\}$ slip in TaC_y . As y decreases, then, the (110) and (111) Peierls stresses approach one another, indicating that both slip planes would be active; as y decreases further, though, the rising Peierls stress on (111) may render it unavailable for slip, effectively leaving only (110) slip. Crucially, the $\{110\}$ planes alone do not contain enough independent slip systems to satisfy the von Mises criterion for general plasticity, whereas the $\{111\}$

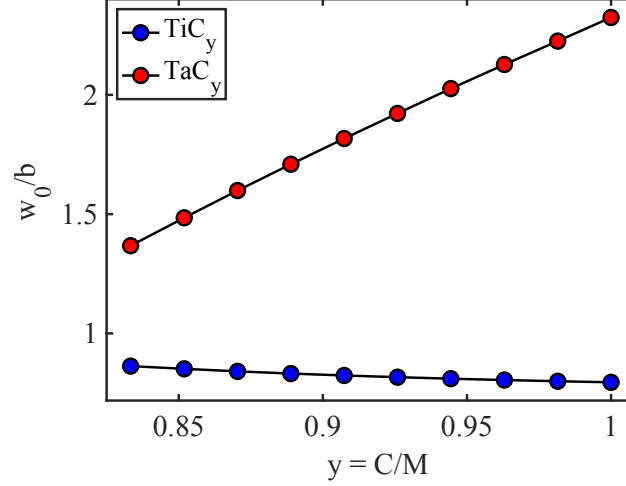


Figure 4.15: SVPN-generated stacking-fault width estimates for TiC_y and TaC_y on $0.83 < y < 1.0$. In TiC_y , the dislocation widths are very small, indicating negligible dissociation of the original edge dislocation; furthermore, the dislocation is seen to widen slightly with loss of carbon content. In TaC_y , the opposite is true: the dislocation is very wide at the stoichiometric composition, and is seen to narrow significantly with loss of carbon content. Data taken from work by Watkins *et al.* [129].

planes do. Thus, if $\{111\}$ slip is not available at lower y in TaC_y due to high lattice resistance, we would expect the material to exhibit more brittle behavior and higher hardness.

Additionally, we have computed dislocation core widths on the $\{111\}$ planes for TiC_y and TaC_y over the same composition range, in the interest of observing whether these dislocations do narrow in TaC_y with loss of carbon content. Indeed, as seen in Figure 4.15, the dislocations in TiC_y are very narrow (well below $1b$) over the entire sampled range of compositions; this is likely the cause of their high computed Peierls stresses. In $\text{TaC}_{1.0}$, the dislocations are initially quite wide—about $2.5b$ —and narrow dramatically with decreasing y , falling to about $1.25b$ at $\text{TaC}_{0.83}$. This suggests that, perhaps due to the increase in ISF energy at lower y , the dislocations on $\{111\}$ in TaC_y are less able to dissociate, leading to narrower slip distributions and higher Peierls stresses. At the very least, these results imply that the differences in hardness between TiC_y and TaC_y arise as a result of changes in intrinsic slip resistance; this offers a strong challenge to the hypothesis put forward in Section 3.1.2.

In order to gain a more comprehensive view of intrinsic slip resistance in TaC_y and TiC_y , we also computed Peierls stresses on the other $\{110\}$ and $\{111\}$ slip planes described in Section 4.1.3;

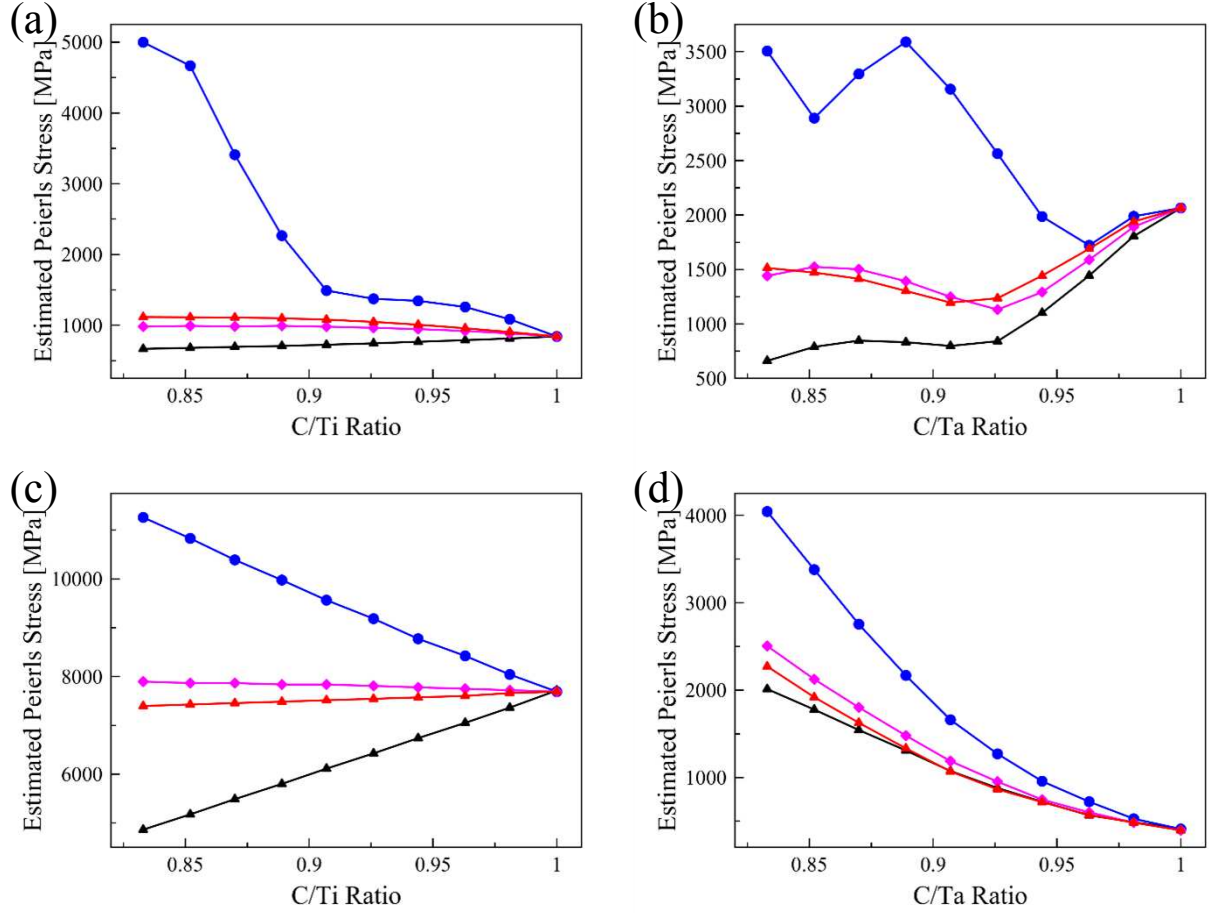


Figure 4.16: Computed Peierls stresses for (a) the $\{110\}$ planes in TiC_y , (b) the $\{110\}$ planes in TaC_y , (c) the $\{111\}$ planes in TiC_y and (d) $\{111\}$ planes in TaC_y . In the $\{110\}$ plots, black markers indicate the $(110)(s)$ slip planes, blue markers represent the $(110)(f)$ planes, magenta markers represent the $(1\bar{1}0)$ planes, and red markers indicate the $(01\bar{1})$ planes. In the $\{111\}$ plots, black markers denote the $(1\bar{1}\bar{1})(s)$ planes, blue markers indicate the $(1\bar{1}\bar{1})(f)$ planes, magenta markers indicate (111) planes, and red markers denote the $(\bar{1}11)$ slip planes. Figure published previously by Watkins *et al.* [129].

the results can be seen in Figure 4.16. These results indicate that, as expected from the GSF energy curves, intrinsic slip resistance is highest on the planes that contain no carbon vacancies; likewise, the Peierls stresses are lowest on planes with the highest concentration of carbon vacancies. On the whole, though, the SVPN-computed lattice friction estimates strongly indicate high mobility (neglecting extrinsic hardening mechanisms) on the $\{111\}$ planes in TaC_y at higher y , whereas the Peierls stresses on $\{111\}$ in TiC_y are extremely high over the whole sampled range of y values. These findings imply that we can refute our first hypothesis—the intrinsic slip resistance cannot be dismissed as a possible driving mechanism of the anomalous hardness of TaC_y .

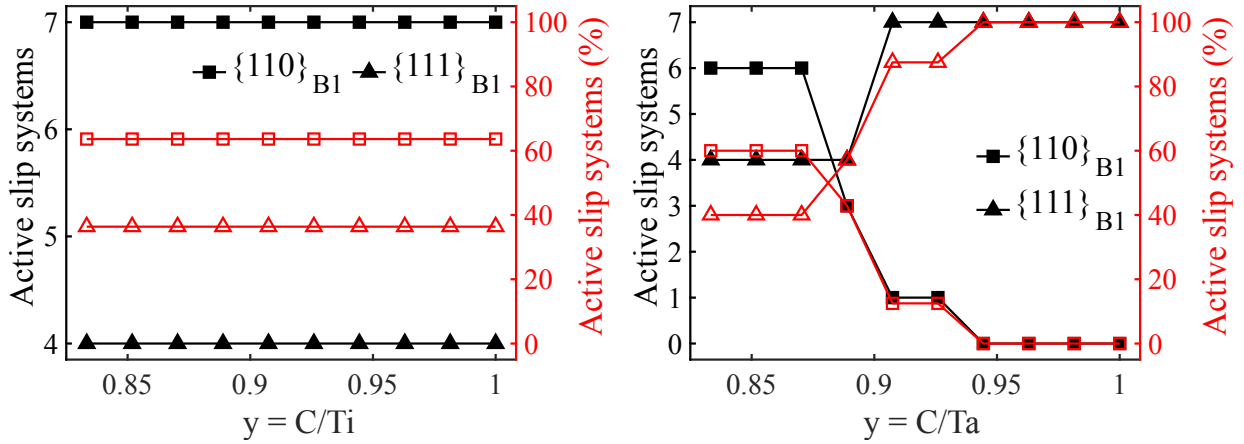


Figure 4.17: Slip systems found to be necessary for a general state of plasticity in titanium and tantalum carbides with varied carbon content.

Experimental validation has been obtained for the intriguing suggestions of this computational approach. Our collaborators at the University of Alabama—Dr. Gregory B. Thompson and C. Haas Blacksher—have synthesized tantalum carbide samples and investigated their mechanical properties; these findings will be further explored in Section 4.1.6, after a bit more elaboration on the theoretical consequences of the SVPN results in the following section.

4.1.5 Effective Peierls Stress Trends

Building upon the findings discussed in the previous section, further consideration has been given as to the nature of plastic deformation during an indentation event. Specifically, it is generally not the case that a single slip system or slip plane is responsible for deformation; rather, not knowing the orientation of the indented grain relative to the indenter, it is necessary to consider a generalized state of deformation. In this case, per the von Mises criterion, there must be at least five independent elements within the strain tensor; in a crystalline solid, this requires the activation of five or more linearly independent slip systems within the material. Accordingly, the different $\langle 110 \rangle \{110\}_{B1}$ and $\langle 110 \rangle \{111\}_{B1}$ slip systems were ranked in order of ascending SVPN-computed Peierls stress, τ_P^i . Starting with only the lowest- τ_P slip system, additional systems were activated until five linearly independent combinations of slip directions and plane normals were included.

The combination of slip planes necessary for generalized plasticity in the titanium and tantalum carbides are shown in Figure 4.17, illustrating the dominance of $\{110\}_{B1}$ slip at all carbon contents in TiC_y and a transition in preference from $\{111\}_{B1}$ slip to $\{110\}_{B1}$ slip in TaC_y as y decreases.

Subsequently, the *effective* Peierls stress—that is, the stress required to achieve *generalized* plasticity—was taken to be the Peierls stress of the lowest-mobility slip system among those necessary for generalized plasticity:

$$\tau_P^{\text{eff}} = \max\{\tau_P^i\} \quad (4.10)$$

This effective Peierls stress is thus the estimated resistance to generalized deformation by means of dislocation slip alone, and in the absence of any additional hardening effects. As discussed in Section 2.2.4, though, indentation experiments have shown the carbides—IVB and VB alike—to nucleate enormous numbers of dislocations in the immediate vicinity of the indenter tip [93]; these dense forests of dislocations will inevitably lead to non-negligible strain-hardening effects within the region of greatest interest to this investigation. As such, strain-hardening effects have been included in the model using the Kuhlmann-Wilsdorf theory [131], yielding estimates for the critical resolved shear stress required for a generalized state of plastic deformation:

$$\tau_{\text{CRSS}} = \tau_P^{\text{eff}} + \Delta\tau = \max\{\tau_P^i\} + \beta Gb\sqrt{\rho}, \quad (4.11)$$

where ρ is the estimated dislocation density.

The τ_P^{eff} estimates, shown in Figure 4.18, indicate substantial differences in behavior between the titanium and tantalum carbides. As y is decreased on $y \in [\frac{5}{6}, 1]$, the titanium carbides exhibit an intuitive reduction in τ_P^{eff} . The tantalum carbides, in contrast, display a remarkable increase in τ_P^{eff} as y decreases. Shown for comparison are estimates for τ_{CRSS} with a significant strain hardening contribution, the effect of which diminishes slightly with decreasing y due to reduced elastic stiffnesses and Burgers vector magnitudes. The relatively high dislocation density, $\rho = 3 \times 10^{15} \text{ m}^{-2}$, is extrapolated from experimental estimates generated by Smith *et al.* for HfC and TaC [93]. Unlike the proposed mechanisms discussed in preceding sections, these trends in

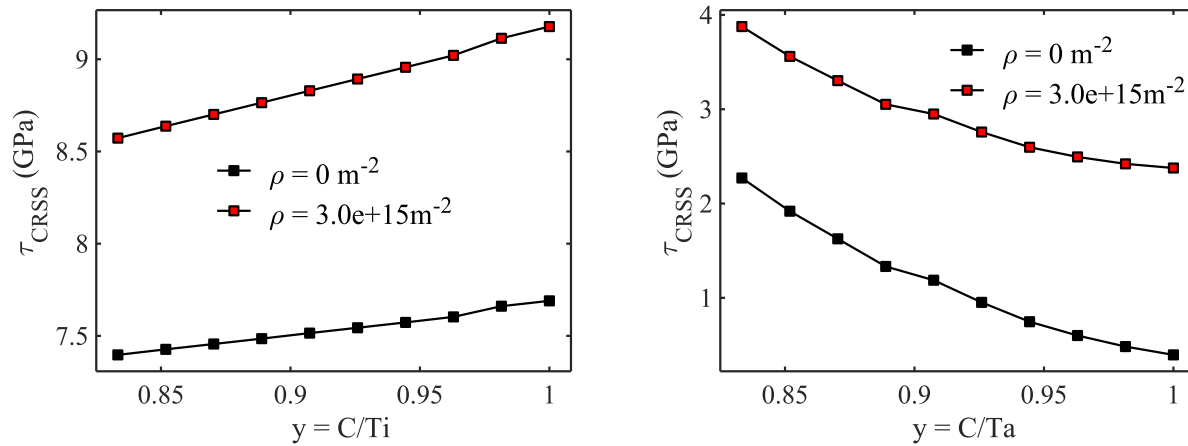


Figure 4.18: Effective Peierls stress estimates for TiC_y and TaC_y , with and without strain hardening contributions. Taken from work by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

dislocation mobility actually provide a promising explanation for the unusual hardness behavior of the tantalum carbides: as carbon content decreases, the material’s resistance to general plastic deformation increases substantially, presumably resulting in a far greater indentation hardness at substoichiometric compositions. Moreover, no such phenomenon is observed in our representative ‘non-anomalous’ carbide, TiC_y .

4.1.6 Experimental validation

Given the conclusions of the preceding section, we should expect to see an ‘anomalous’ hardness peak in TaC_y only when there is sufficient dislocation plasticity under indentation. That is, though trends in intrinsic slip resistance might suggest a significant hardening as carbon content is lost, this would only be observed in samples where extrinsic hardening factors are minor contributors to the measured hardness. And, in fact, we have an experimental demonstration that this is the case.

As part of the work published in *Nature Communications* in 2024, our experimental collaborators at the University of Alabama—Dr. Gregory B. Thompson’s research group—synthesized and indented tantalum carbide samples at varied carbon contents; both bulk samples and thin films were synthesized, characterized and tested for mechanical properties. In a somewhat serendipitous

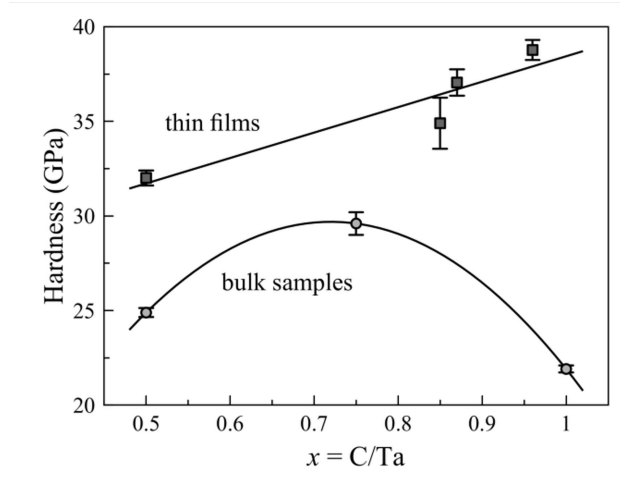


Figure 4.19: Hardness measurements taken from bulk and thin-film TaC_y samples, showing ‘anomalous’ hardness in the bulk samples but not in the thin films. Taken from work by Watkins *et al.* [129].

development, the thin films (prepared via sputtering) were synthesized with a nanocrystalline grain structure: the average grain size in the thin films was only 21.5 nm, as compared to 14.7 μm in the bulk samples. Thus we might expect to see considerable plasticity in the near-stoichiometric bulk TaC samples—at least, if our predictions regarding dislocation mobility are correct—since the grains are large enough to facilitate considerable dislocation motion. In the thin films, though, the density of grain boundaries is such that not much dislocation plasticity can be expected; even if the *intrinsic* resistance to dislocation slip is low, there are substantial *extrinsic* barriers to dislocation motion. In fact, the average grain size is so low that there may not be many dislocations present within each grain.

Indeed, the results shown in Figure 4.19 bolster the conclusions drawn from our computational efforts: in the bulk samples, we see a pronounced ‘anomalous’ hardness at a substoichiometric composition, while no such anomaly is present in the thin films. Furthermore, the bulk samples show considerable evidence of plasticity surrounding the indent (see Figure 4.20, with obvious pile-up being visible in the SEM image of the indented surface. The bulk samples also show little cracking, implying that dislocation plasticity is sufficient to accommodate the strain imposed on the grain by the intrusion of the indenter. In the thin films, a completely different behavior is evident, with extensive cracking and no discernible pile-up or sink-in around the indent. Thus

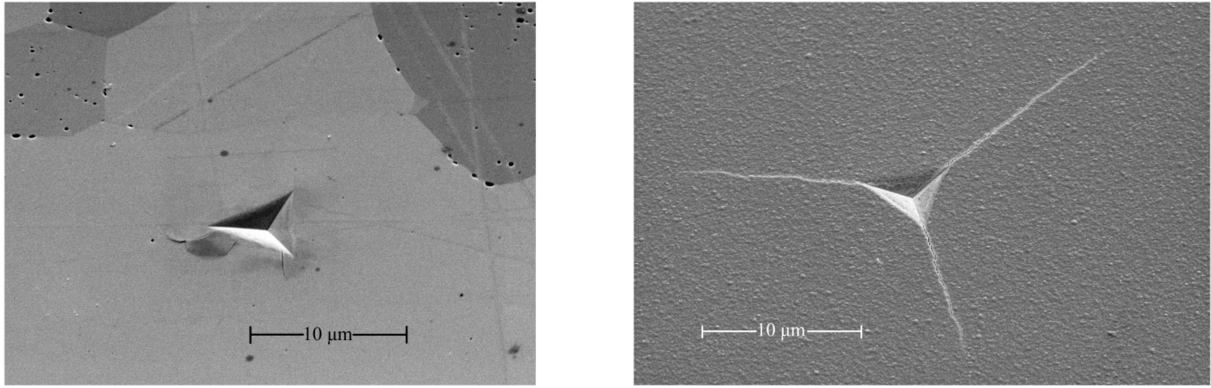


Figure 4.20: Indented samples of bulk TaC (left) and thin-film TaC_{0.96} (right), imaged using SEM. Note the evidence of considerable plasticity and little cracking in the bulk sample, whereas the thin film appears to exhibit only cracking. Images published previously by Watkins *et al.* [129].

it is reasonable to conclude that the bulk samples facilitated considerable dislocation plasticity, while dislocation plasticity was essentially absent in the films. This result is heartening, since it is consistent with the expectation that dislocation mechanics are responsible for the ‘anomalous’ hardness: in the samples with little or no dislocation plasticity, no substoichiometric increase is observed. Consequently, the thin films’ behavior more closely resembles that of TiC_y, which this work predicts to have very high *intrinsic* resistance to dislocation motion.

4.1.7 Plasticity-Fracture Competition

The findings presented in the preceding section outline a compelling case for the ‘anomalous’ hardness increase in TaC_y as y decreases on $y \in [\frac{5}{6}, 1]$, but do not necessarily indicate a subsequent reduction in hardness with further carbon loss. In fact, further investigation into rocksalt-structured tantalum carbides at lower carbon contents shows no such trend. We computed γ_{SF} curves for $\langle 112 \rangle \{111\}_{\text{B1}}$ slip in TaC_y with $y = 1$, $y = \frac{5}{6}$ and $y = \frac{2}{3}$ (slip plane structures for each shown in Figure 4.21) in order to determine whether dislocation slip may be easier at lower carbon contents; the results, shown in Figure 4.22, actually suggest that further reduction of carbon content produces an even greater elevation in stacking-fault energies. In other words, the TaC_y crystal’s resistance to shear on $\{111\}_{\text{B1}}$ planes continues to increase as more carbon is removed, as a consequence of

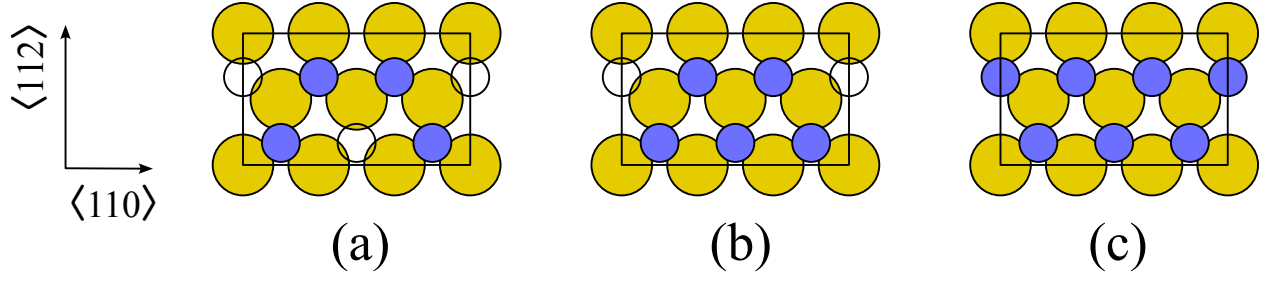


Figure 4.21: Slip plane compositions used for γ_{SF} calculations in (a) Ta_3C_2 , (b) Ta_6C_5 , and (c) TaC . Sections taken from VASP simulation cells, seen along a $\langle 111 \rangle_{\text{B1}}$ direction. Figure published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

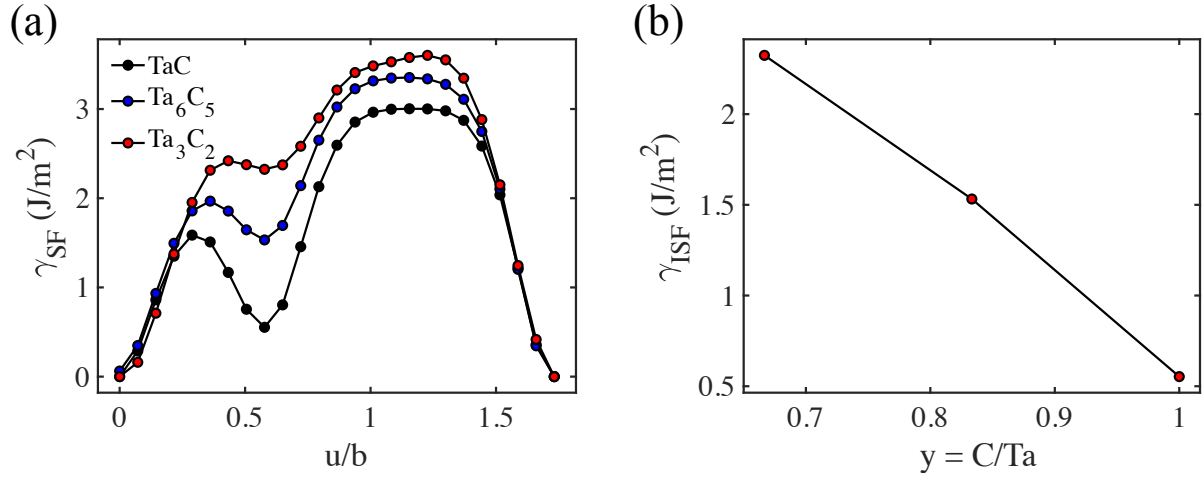


Figure 4.22: (a) DFT-computed γ_{SF} for slip along $\langle 112 \rangle \{111\}_{\text{B1}}$ in TaC_y at different carbon contents. (b) Variation in computed γ_{ISF} with carbon content in TaC_y . Figures published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

both increased RISS and increased γ_{ISF} . These features have the effect of increasing dislocations' resistance to rigid translation across $\{111\}_{\text{B1}}$ planes, as well as encouraging narrower dislocation cores by making stacking-fault formation energetically costly. This is compounded by the fact that the elastic stiffness of TaC_y declines monotonically with substoichiometry (as discussed in Section 4.1.1), which also has the effect of narrowing dislocation cores per the Peierls-Nabarro model.

In order to fully address the problem of 'anomalous' hardness in TaC_y , then, we proposed a competition between distinct failure modes. Although the stress required to move dislocations may indeed increase monotonically with carbon loss in the tantalum carbides, this does not necessarily translate into an increase in hardness, so long as we are willing to abandon the assumption that dislocation mobility is the *governing* mechanism of indentation hardness at all carbon contents.

Considering that the TMCs and TMNs are hard ceramic materials, dislocation slip is not the only mechanism by which they may fail under indentation; on the contrary, as discussed in Section 2.2.4, the IVB TMCs in particular often exhibit cracking prior to the occurrence of significant plasticity. The promise of fracture as a competing failure mode is bolstered by recent computational work by Hossain *et al.* [132], which indicates that the cleavage energy, γ_c , of tantalum carbide has both a high degree of anisotropy and a significant dependence on carbon content. The significance of this prior work is that the work of fracture in a simple Griffith [133] model is equal to the cleavage energy for a case of pure intragranular fracture.

This is also a naïvely plausible explanation for the oft-reported ‘anomalous’ hardness phenomenon: if dislocation mobility is essentially only *generally* high in TaC_y at higher y , then dislocation plasticity could be expected to dominate hardness behavior only within this regime. In other words, the low dislocation mobility seen in significantly substoichiometric TaC_y (and in TiC_y at all y) raises the possibility of fracture as a dominant failure mechanism during indentation in these compounds. Thus one might expect to see a nonlinear ‘anomaly’ in the $H_V(y)$ trend in TaC_y , signaling the transition from one failure mode to the other, and no such transition in TiC_y , wherein dislocation plasticity likely never dominates.

To test this hypothesis, models must be developed (or acquired from elsewhere) which allow us to generate hardness estimates for different carbides at different carbon contents using quantities readily estimable from DFT calculations. Hardness not being a material property, and being dependent on myriad geometric, material and structural variables, we look first to analytic models that explicitly assume particular governing mechanisms. For determinations of hardness from dislocation plasticity, a modification can be made of the influential model developed by Nix and Gao [134] to represent the indentation size effect:

$$H = H_0 \sqrt{1 + \frac{h^*}{h}}, \quad (4.12)$$

where H is hardness measurement for a given indentation depth h , and H_0 is essentially a converged hardness estimate for some large indentation depth ($h \rightarrow \infty$). The parameter h^* is a

characteristic length scale given by

$$h^* = \frac{b}{2} \left(9\alpha \sin \theta \frac{G}{H_0} \right)^2, \quad (4.13)$$

where b is the Burgers vector magnitude, G is the shear modulus, θ is the indenter tip angle (equal to 136° in the case of a Vickers indenter), and α is a constant whose value is often chosen to be $\frac{1}{2}$. In order to make this analytic framework helpful for the present work, however, we need to connect the converged hardness, H_0 , to something we can readily compute via our numerical modeling approach. To this end, we draw upon the Tabor relation [89], which relates a material's hardness to its compressive yield stress:

$$H = 3\sigma \quad (4.14)$$

The compressive yield stress σ is then related to the flow stress τ by $\sigma = \sqrt{3}\tau$; this allows us to actually implement this model using quantities we have already estimated, as the computed τ_{CRSS} values essentially estimate the flow stress—the resistance of the material to dislocation slip for a given *general* stress state, with some extrinsic (strain hardening) considerations. Thus we arrive at a workable analytic estimate for the indentation-depth-dependent Vickers hardness as a function of quantities obtainable from our hierarchical modeling approach:

$$H_V^p = 3\sqrt{3}\tau_{\text{CRSS}} \sqrt{1 + \frac{b}{2h} \left(9\alpha \sin \theta \frac{G}{3\sqrt{3}\tau_{\text{CRSS}}} \right)^2}, \quad (4.15)$$

where the ‘p’ superscript denotes the model’s reliance on dislocation plasticity as the governing mechanism of indentation hardness.

The plasticity model being sufficiently developed, we then seek a means of estimating hardness from fracture resistance. This is a somewhat more difficult task, as fewer attempts have been made to connect indentation hardness to work of fracture (the relevant quantity most readily obtainable from DFT calculations). A promising avenue appears in the form of prior efforts to reliably deter-

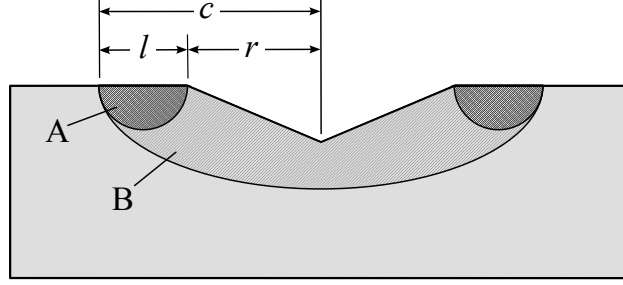


Figure 4.23: Idealized crack geometry for both (A) Palmqvist and (B) radial-median cracks surrounding an indent. Figures published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

mine fracture toughness from indentation experiments. These approaches seek to develop models which can robustly and repeatably compute fracture toughness based on measured hardness, indentation size, and crack length. Many different models of this sort have been developed, each drawing on assumptions about crack geometry in order to estimate the total energy dissipation due to cracking. Two commonly assumed crack types are Palmqvist (corner) cracks and radial-median (half-penny-like) cracks; these geometries are illustrated in Figure 4.23. These crack geometries being significantly different, the fracture toughness models derived from their expected propagation differ accordingly. For the case of Palmqvist cracks [135], the fracture toughness is estimated as

$$K_{IC} = \chi \sqrt{\frac{HP}{4l}}, \quad (4.16)$$

where H is the measured hardness, P the indentation load, and l the average length of Palmqvist cracks at the indent corners. In this case, the leading constant χ is equal 8.89×10^{-2} for a Vickers indenter. Alternatively, for a ‘well-developed’ radial-median crack, the toughness is given by

$$K_{IC} = \chi P c^{-3/2}, \quad (4.17)$$

where c is the half-length of a crack spanning the indent (again, see Figure 4.23 for clarification). In this latter case, χ is given by $\chi = \xi(E/H)^m$, where E is the Young’s modulus, ξ is a geometry-dependent constant generally chosen to lie between 0.012 and 0.020 for a Vickers indent [136], and the exponent m is usually set equal to either 2/5 or 1/2 [136, 137].

Which of these models is appropriate is ultimately dependent on the actual behavior of the material, and so (lamentably, from the perspective of the computational researcher) we must turn to experiments to determine the form of our model. There are essentially two features of the experimental dataset to examine: (1) the size of the cracks—which are often only observable from the indented surface—relative to the indent size, and (2) the relationship between the crack size and the applied load. The former criterion produces a boundary between the two crack regimes at $c/r = 2.5$, or $l/r = 1.5$, where r is equal to the indent half-diagonal length, $d/2$. Note that the boundary values for c/r and l/r are equivalent because of the relationship shown in Figure 4.23, which gives $l = c - r$. For the latter criterion, criterion (2), there are two theoretical relationships between the applied load and the resultant crack size. For cracks within the Palmqvist regime,

$$l = \alpha P, \quad (4.18)$$

with α being a constant. Within the radial-median regime,

$$c = \beta P^n, \quad (4.19)$$

where β is a constant and the exponent n is often found to be approximately $2/3$ [136].

So, with this in mind, which is correct for our purposes? As part of a broader study of the cubic carbides and nitrides (the results of which are enumerated in greater detail in Section 4.2.3), we collaborated with Dr. Gregory B. Thompson’s research group at the University of Alabama to obtain experimental parameters. Dr. Alyssa Stubbers, working as a postdoctoral researcher there, prepared and indented samples of representative IVB and VB TMCs—HfC and TaC—so that we might gain some insight into the load-crack-size relationship.

To this end, we were provided with indentation loads, indent diagonal lengths, and crack lengths. The crack lengths were measured from the indent corners, as they can generally be seen to propagate from the indent corners in Figure 4.24. This does not necessarily assume Palmqvist crack geometry, though; per the idealized crack geometries shown in Figure 4.23, this experimen-

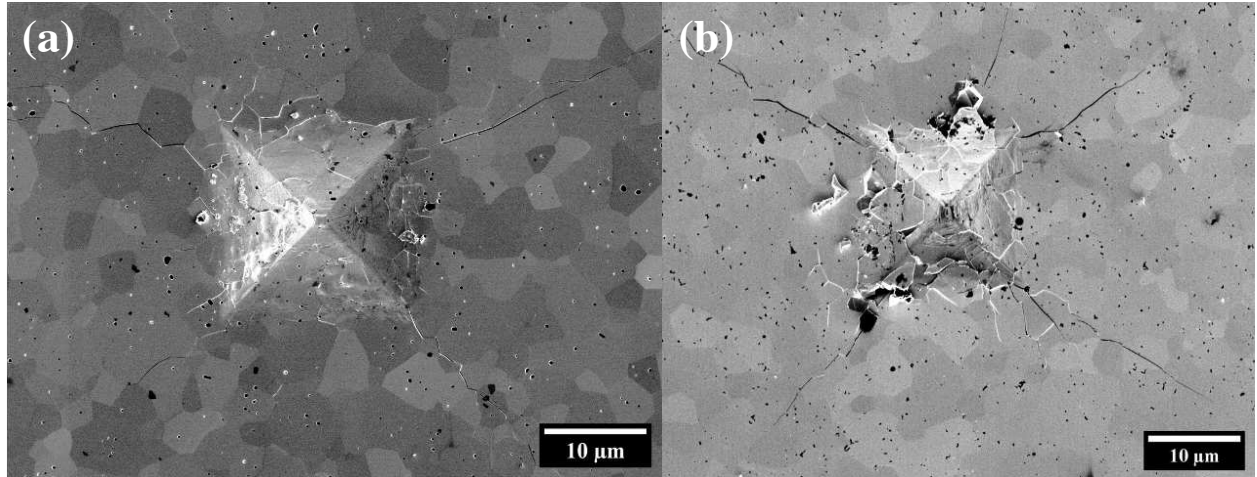


Figure 4.24: Samples of HfC and TaC prepared and indented by Dr. Gregory B. Thompson and Dr. Alyssa Stubbers at the University of Alabama. Figures published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

tal data can be characterized either as corner cracks of length l or as radial-median cracks of length c , as both appear similar from the indented surface. The selection is then made primarily by means of an examination of the load-dependence of the crack sizes. Figure 4.25 shows computed average crack sizes, both l and c , with linear fits included. The linear fits do not appear to represent the data particularly well, even though, per the same Figure, the cracks do appear to be marginally within the Palmqvist regime.

An alternative power-law fit for each material's dataset is shown in Figure 4.26, and appears to represent the data more accurately. The fitting parameters β and n were computed for both the HfC data and the TaC data, yielding $\beta_{\text{HfC}} = 2.37$, $\beta_{\text{TaC}} = 2.23$, $n_{\text{HfC}} = 0.56$, and $n_{\text{TaC}} = 0.65$. These exponents are somewhat low compared to the oft-stated value of $2/3$, but the load-dependence of the crack size is clearly better represented by a power-law fit than by a linear one. Thus, despite the marginal crack size relative to the indent size, we elected to model the cracks in our materials as radial-median cracks of size c .

Naturally, then, we selected Equation 4.17 as the starting point for our analytical approach. Rearranging this toughness relationship for a radial-median crack, we can obtain an expression for

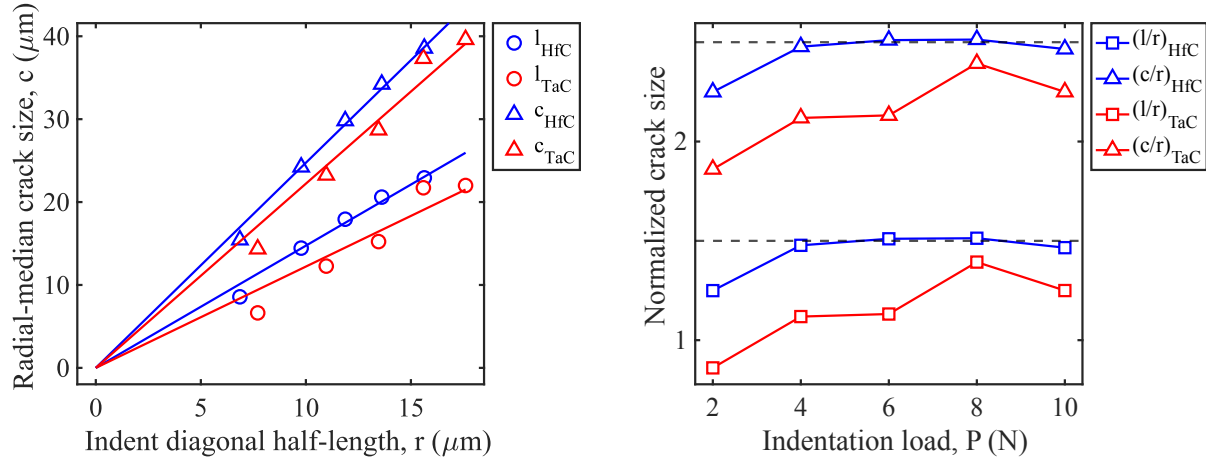


Figure 4.25: Crack sizes measured for various indentation loads in HfC and TaC samples, represented as both corner (Palmqvist) cracks of size l and as radial-median (half-penny-like) cracks of size c . Included $c(P)$ and $l(P)$ fits are linear. Also shown are normalized crack sizes, again represented as both geometries, relative to the conventional boundary separating the Palmqvist and radial-median regimes. All data provided by Dr. Alyssa Stubbers from the University of Alabama.

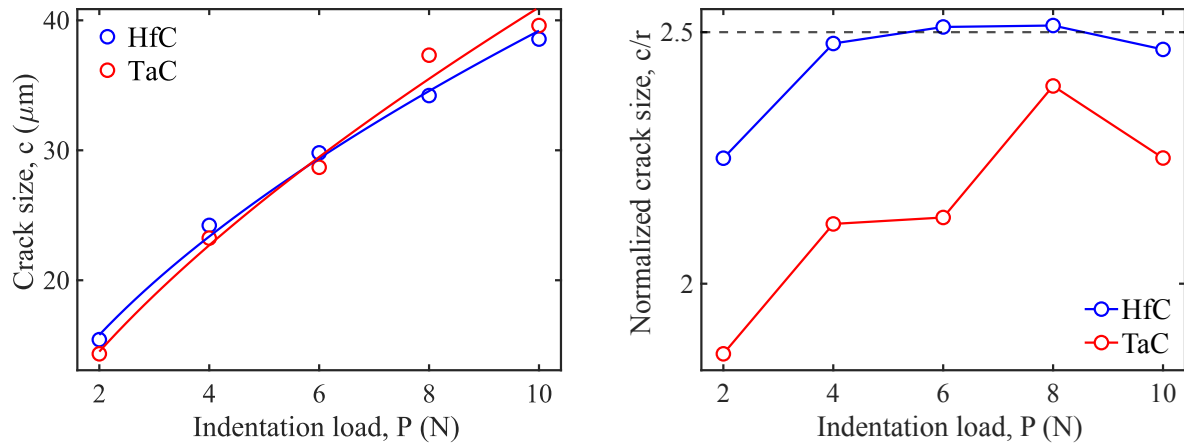


Figure 4.26: Power-law fits for $c(r)$, showing better agreement with data than the linear fits provided in Figure 4.25. Also included are normalized radial-median crack sizes, showing crack development to be marginal between the Palmqvist and radial-median regimes. All data provided by Dr. Alyssa Stubbers at the University of Alabama and published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

the applied load as a function of the other variables:

$$P = \frac{K_{IC}}{\chi} c^{3/2} \quad (4.20)$$

Then, using the ideal brittle fracture criterion of Griffith [133],

$$K_{IC} = \eta \sqrt{2\gamma E}, \quad (4.21)$$

where γ is the energy of each free surface created by the (intragranular) fracture and η is a scaling factor used to obtain better agreement between DFT predictions and experimental fracture toughness estimates (more information on this parameterization is provided in Appendix C), we have

$$P = \frac{\eta \sqrt{2\gamma E}}{\chi} c^{3/2} \quad (4.22)$$

As a quick check, we can examine the form of this analytic model. The indentation load varies directly with elastic stiffness, cleavage energy and crack length, all of which would be expected to increase the required load as they increase. The hardness is then given by the basic Vickers formulation:

$$H_V = \frac{2 \sin \theta / 2P}{4r^2}, \quad (4.23)$$

where θ is again the indenter tip angle, and r is the indent diagonal half-length after the indenter is withdrawn. Combining Equation 4.23 with Equation 4.22 then yields

$$H_V^c = \frac{2 \sin \theta / 2P}{4r^2} \frac{\eta \sqrt{2\gamma E}}{\chi} c^{3/2} \quad (4.24)$$

Again, more information regarding parameter selection for this model can be found in Appendix C.

In any case, we now have two semi-analytical models of hardness: one dependent on resistance to dislocation slip, one dependent on resistance to crack propagation, and both readily parameter-

ized by available computed and measured quantities. Using both models, load-depth and hardness-depth curves were computed for both of our representative carbides at varied carbon contents. Figure 4.27 shows the load-depth, or $P(h)$, curves for stoichiometric and substoichiometric TiC_y and TaC_y . In the titanium carbides, little change is observed as carbon content is varied: at both visualized compositions, plasticity and $\{100\}_{\text{B1}}$ fracture are competitive for small indent depths, with fracture becoming overwhelmingly dominant for larger indents. In stoichiometric TaC , we see entirely different behavior: dislocation slip appears to be preferred over both $\{111\}_{\text{B1}}$ and $\{100\}_{\text{B1}}$ fracture, even for quite large indent depths; the implication is that considerable plasticity can be expected to occur under indentation prior to the onset of cracking. In substoichiometric Ta_6C_5 , however, the behavior has shifted closer to that of TiC_y , with plasticity and $\{100\}_{\text{B1}}$ fracture competing closely for small indents and fracture eventually overtaking plasticity as the preferred failure mechanism for larger indents.

The hardness-depth, $H(h)$, curves tell much the same story, with very limited plasticity and fairly rapid onset of cracking in TiC_y at both sampled y . In TaC_y , the $H(h)$ curves indicate extensive plasticity under the indenter at $y = 1$; at lower carbon content, plasticity is more limited, and the onset of cracking more rapid; however, these results do still suggest that Ta_6C_5 may be prone to undergo more plastic deformation than Ti_6C_5 prior to fracture.

Finally, an examination of the evolution of the hardness of each compound with respect to varied carbon content can be made using the results visualized in Figure 4.29. These data are taken from the largest modeled indent depth (around $7 \mu\text{m}$) at each sampled composition, aiming to represent each material's response to indentation in the large-indent limit. Two primary observations can immediately be made regarding these findings. First, a single failure mechanism—fracture—appears to dominate the behavior of TiC_y over the entire range $y \in [\frac{5}{6}, 1]$, whereas in TaC_y there is a transition from plasticity dominance to fracture dominance at a composition near $y = 0.87$. Note that, of course, the precise location of this peak may depend on the exact parameterization of each model, almost certainly evolving in response to changes in the assumed dislocation density, crack size, etc. The second observation is that, assuming the dominant mechanism to essentially

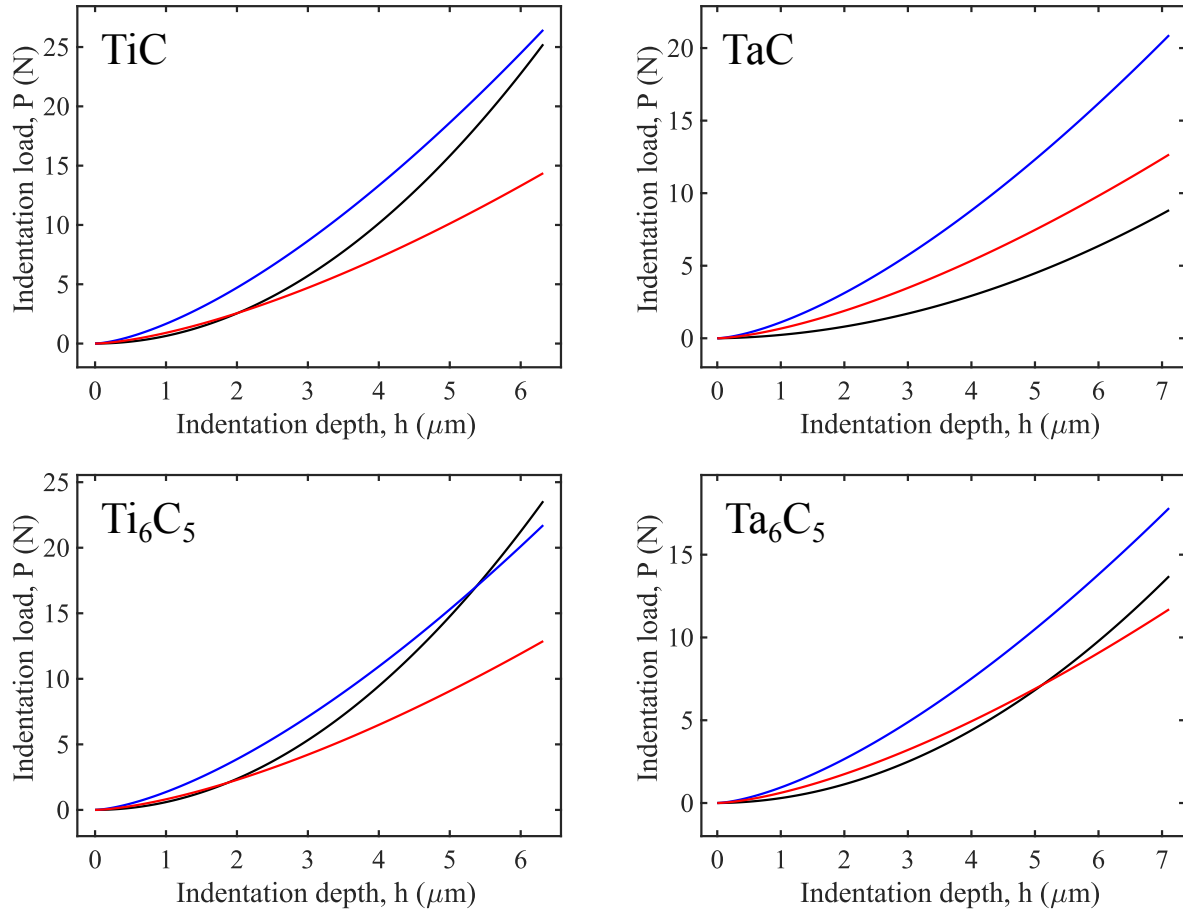


Figure 4.27: Computed load-depth curves for titanium and tantalum carbides, according models regulated by dislocation slip (black lines), cleavage cracking on $\{100\}_{B1}$ (red lines), and cleavage cracking on $\{111\}_{B1}$ (blue lines). All data published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

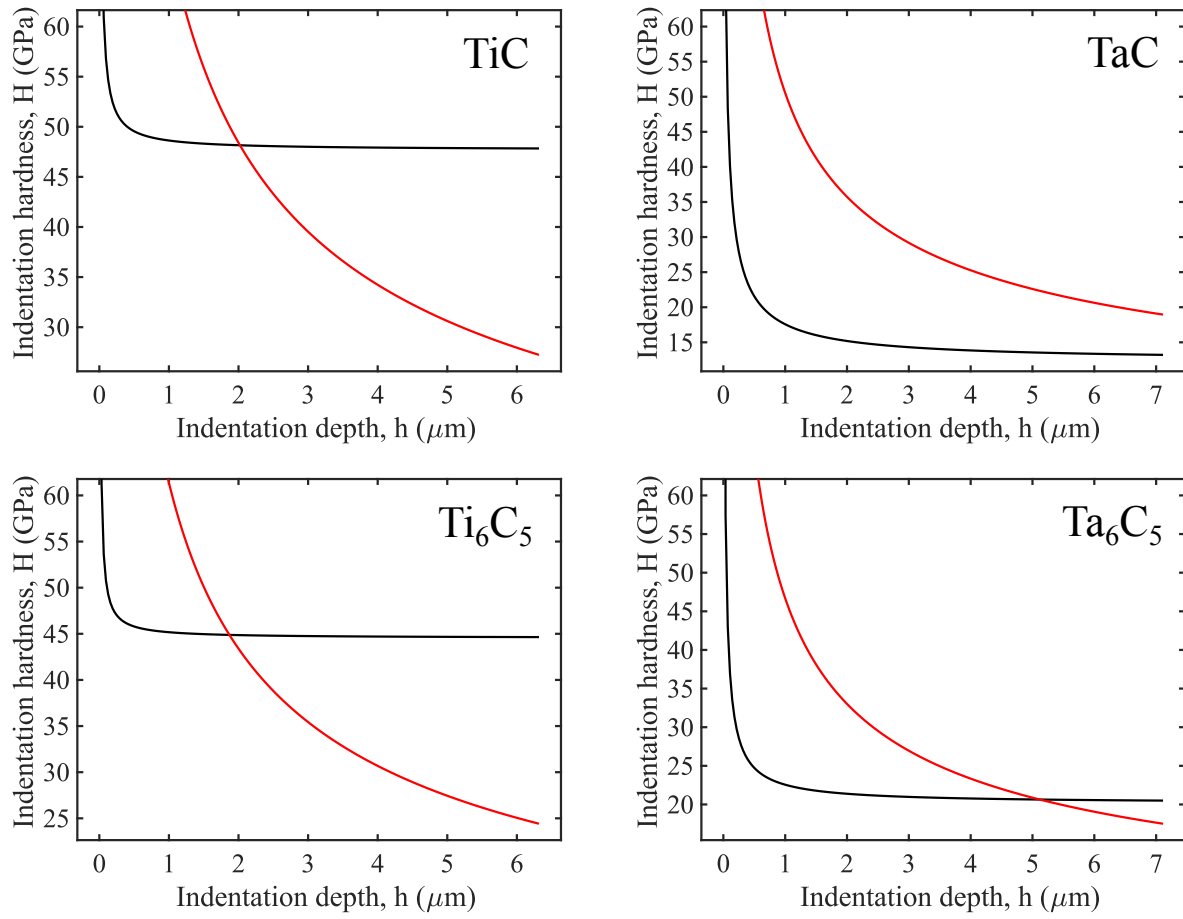


Figure 4.28: Computed load-depth curves for titanium and tantalum carbides, according models regulated by dislocation slip (black lines), cleavage cracking on $\{100\}_{\text{B1}}$ (red lines), and cleavage cracking on $\{111\}_{\text{B1}}$ (blue lines). All data published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

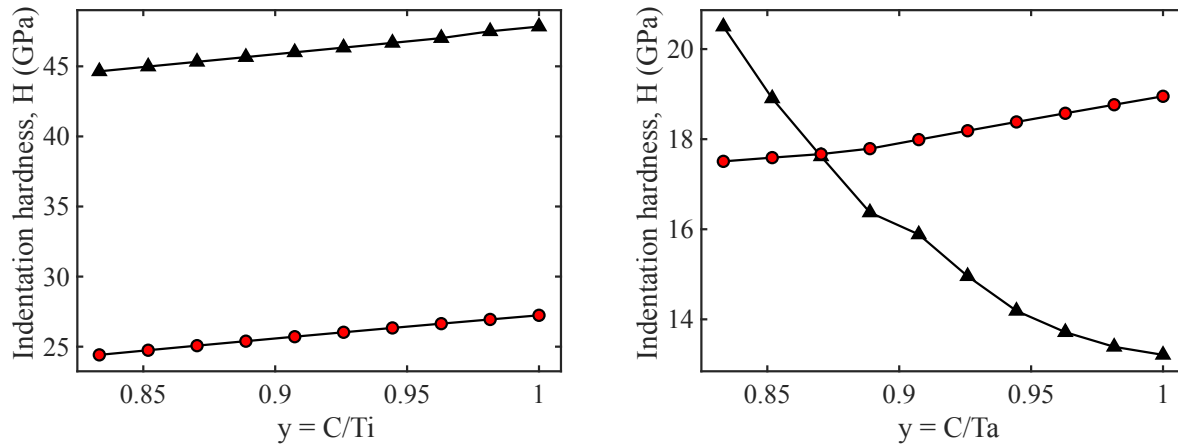


Figure 4.29: Computed hardness-composition trends according models regulated by dislocation slip (black markers), cleavage cracking on $\{100\}_{B1}$ (red markers). All data published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

govern each material’s response to indentation at each composition, we find that the hardness of TiC_y declines monotonically with loss of carbon content, whereas the hardness of TaC_y sees an initial (and significant) increase in hardness prior to the transition to cracking-dominated behavior. That is, the transition between plasticity and fracture as the governing failure mechanism marks a substoichiometric maximum hardness—precisely what is seen in experiment.

This finding is intriguing for a few reasons. First and foremost, unlike prior efforts to properly characterize the ‘anomalous’ hardness of tantalum carbides, this approach actually does explain the initial increase in hardness as y starts to decrease in TaC_y . Previous explanations, hinging on formation enthalpy or elastic stiffness, almost universally fail even to reproduce this initial apparent strengthening under indentation. And, furthermore, this is not terribly surprising: these arguments, which ultimately boil down to examination of trends in overall or average bond strength in the material, generally ignore highly relevant information regarding dislocations and their resistance to movement through the lattice. It is true that bond strength and stiffness will affect dislocations—their core structures, their mobility, etc.—but the ease (or lack thereof) with which atoms can be locally rearranged to extend or move a dislocation cannot be ignored. Prior work on generalized stacking-fault energies in the carbides was well founded, but in this present work we have actually demonstrated that the ‘anomalous’ hardness increase in the substoichiometric tantalum carbides

can be predicted from dislocation mobility arguments, and particularly from a consideration of slip system preference and requirements for generalized plastic deformation. The other innovation of this work is that we have demonstrated the possibility of the ‘anomalous’ hardness peak arising as a consequence of competition between different modes of failure during indentation. Previous works, varied though their fundamental explanations may be, seek to identify a hardness increase (with some loss of carbon content) followed by a peak hardness and then a decline in hardness (with further loss of carbon content), all due to a single governing mechanism. What we have proposed, and indeed demonstrated, is that a competition between fracture and dislocation plasticity can actually account for the presence of the substoichiometric hardness peak. This is made more compelling by the fact that the model presented in this work is really quite simplistic: it incorporates no additional extrinsic hardening or softening mechanisms, such as grain structure or porosity, and it could likely be improved in the future by the production of more detailed and material-specific experimental data for parameterization.

On the whole, though, the work discussed in this and the preceding sections does help us answer our first major research question. Enthalpy of formation, ordering domain refinement, and elastic stiffness optimization in substoichiometric tantalum carbides cannot be used to predict an ‘anomalous’ hardness trend. In contrast, this trend can be predicted from dislocation mobility and slip plane preference, meaning that fundamental differences in dislocation slip behavior between TaC_y and other carbides (*e.g.*, TiC_y) cannot be ruled out as the primary mechanism of ‘anomalous’ hardness in the tantalum carbides.

4.2 On the Slip Behavior of the Cubic Carbides and Nitrides

As outlined in the Research Proposal, we seek to examine the trends in mechanical behavior in all of the rocksalt carbides and nitrides; accordingly, the approach outlined in the previous section has been extended to these compounds as well. Furthermore, mixed systems (*i.e.*, carbonitrides and alloyed carbides) have been investigated in order to more comprehensively characterize the

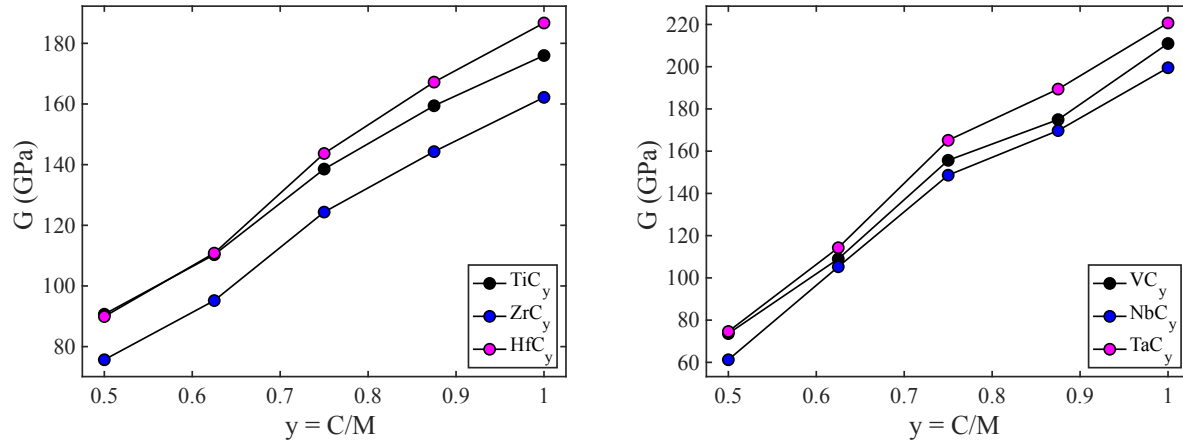


Figure 4.30: Hill averaged polycrystalline shear moduli for the IVB (left) and VB (right) TMCs.

effect of VEC on plasticity in this class of materials. The following sections detail the findings for different predictors of indentation hardness in the TMCs, TMNs, MTMCs, and TMCNs.

4.2.1 Elastic Stiffness Trends

Just as with the specific cases of the tantalum carbides discussed in the preceding sections, we seek to determine whether the hardness behavior of the substoichiometric carbides and nitrides is broadly explainable by changes in elastic stiffness alone. In other words, can elastic stiffness account for the ‘anomalous’ hardness behaviors reported for many of these compounds, or will some other explanation be required? This section will detail our findings as to the computed and derived elastic stiffnesses for all of the cubic TMCs and TMNs, as well as Vickers hardness predictions drawn therefrom. As a further inquiry, we will discuss whether the results suggest any differences between VEC modification via substoichiometry and VEC modification via alloying (metal or nonmetal substitution).

Substoichiometric Transition-Metal Carbides and Nitrides

While emphasis was placed on our findings regarding the elastic stiffnesses of TiC_y and TaC_y in Section 4.1.1, we performed this same analysis for all of the IVB and VB TMCs: TiC_y , ZrC_y , HfC_y , VC_y , NbC_y and TaC_y . Detailed results (C_{11} , C_{12} , C_{44} , and all derived quantities) have been

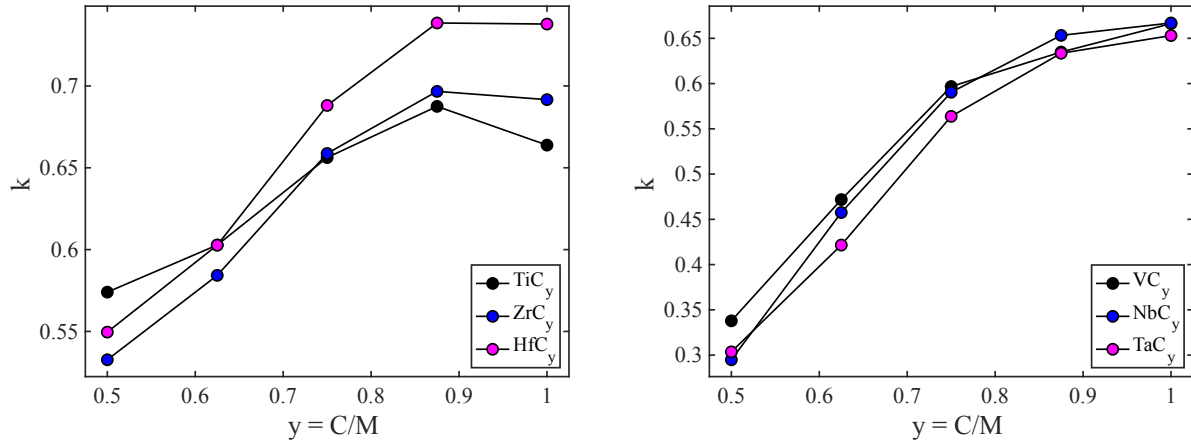


Figure 4.31: Computed Pugh's modulus, $k = G/B$, for the IVB (left) and VB (right) TMCs.

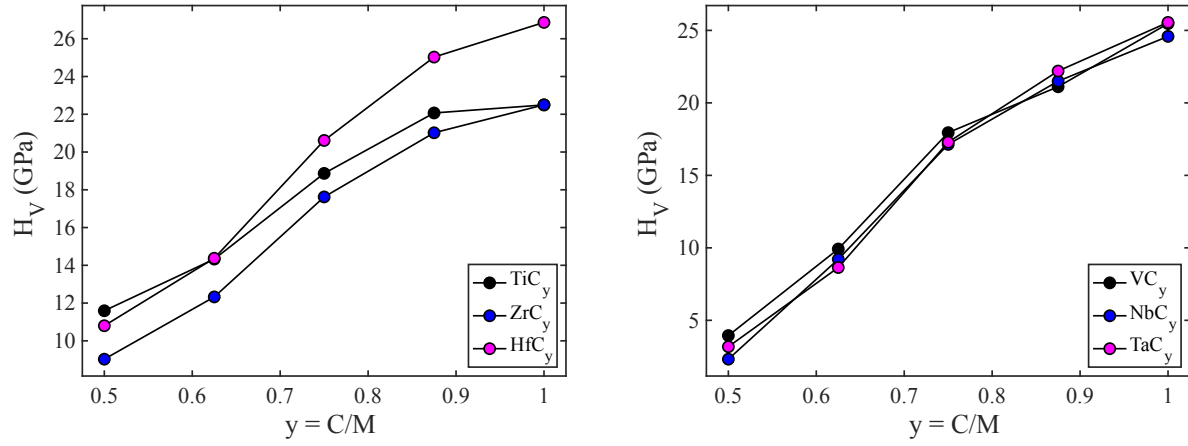


Figure 4.32: Theoretical hardness values for all of the IVB and VB TMCs, obtained using the elastic stiffness correlation developed by Chen *et al.* [73].

sequestered to Appendix A in the interest of brevity, but they generally indicate a relative uniformity of elastic stiffness behavior in all of the cubic monocarbides, MC_y . The cubic stiffnesses C_{11} , C_{12} and C_{44} are broadly seen to decline with decreasing y in all of the IVB and VB carbides, with the exception of C_{12} ; this particular stiffness is seen to increase slightly at lower y in HfC_y , and to increase more significantly at lower y in all of the VB TMCs. The effect of this is that C_{12} exceeds C_{44} at lower y ; this is true in all of the cubic carbides, per the present work, but C_{12} is seen to overtake C_{44} more quickly (*i.e.*, with less carbon depletion) in the VB TMCs than in the IVB TMCs. This cross-over seems to correspond to a small slope discontinuity in the derived polycrystalline shear moduli, as the discontinuity's position within the modeled y range matches the composition at which C_{12} first exceeds C_{44} in each compound.

Examining the shear moduli themselves, we might hope to draw some conclusions about possible slip resistance (and thus hardness) trends in the substoichiometric carbides. The C_{44} stiffness, often described as the cubic shear modulus, is seen to decline monotonically with loss of carbon content in all of the IVB and VB TMCs, giving no suggestion of a hardness anomaly in any of these materials. Furthermore, the derived polycrystalline shear moduli— G_V , G_R , and G —mirror this behavior in all of the carbides, declining monotonically with loss of carbon content even in the ‘anomalous’ carbides NbC_y and TaC_y . As a quick summary of these findings, the Hill averaged shear moduli for the IVB and VB TMCs are compiled in Figure 4.30. The polycrystalline bulk modulus B is also found to decline monotonically—and roughly linearly—with loss of carbon content in all of the carbides, giving no indication of anomalies in the G/B ratio, or Pugh’s modulus k , of any of the carbides. These results, shown in Figure 4.31, only show a substoichiometric maximum in the IVB TMCs, particularly TiC_y and ZrC_y .

Since the hardness correlation of Chen *et al.* [73] directly relates k to the Vicker’s hardness, H_V , this trend produces very modest substoichiometric maximum hardness in TiC_y , though this peak is absent from ZrC_y and HfC_y . More generally, though, the hardness predictions shown in Figure 4.32, anticipate a general decline in hardness with loss of carbon content for all of the IVB and VB carbides. As expected based on some of the prior work covered in Section 2.2.2, the elastic

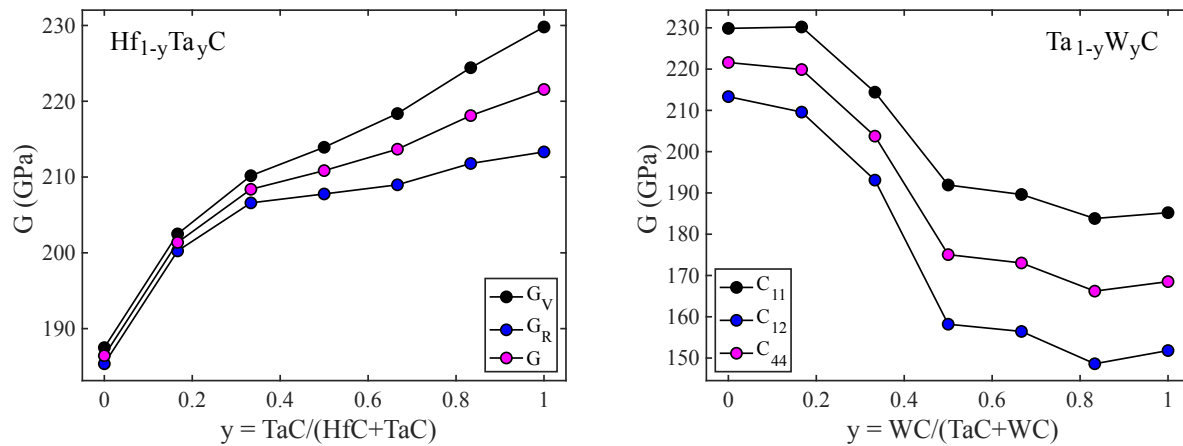


Figure 4.33: Computed polycrystalline shear modulus estimates for selected alloyed carbides: $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$.

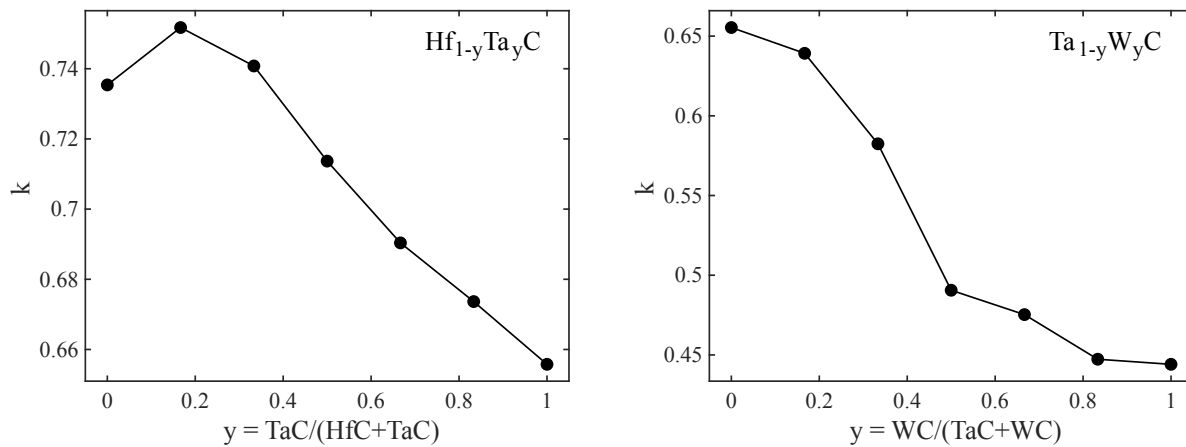


Figure 4.34: Pugh's modulus estimates computed for selected alloyed carbides: $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$.

stiffness trends do not offer a compelling explanation for the disparate hardness trends seen in the TMCs; bond stiffness is likely not the driving mechanism behind these varied hardness behaviors. In fact, in addition to failing to predict the anomalous hardness trends of NbC_y and TaC_y , the stiffness-correlated hardness estimates predict a remarkable uniformity of hardness behavior in the substoichiometric carbides—a finding very much at odds with experimental observations of these materials.

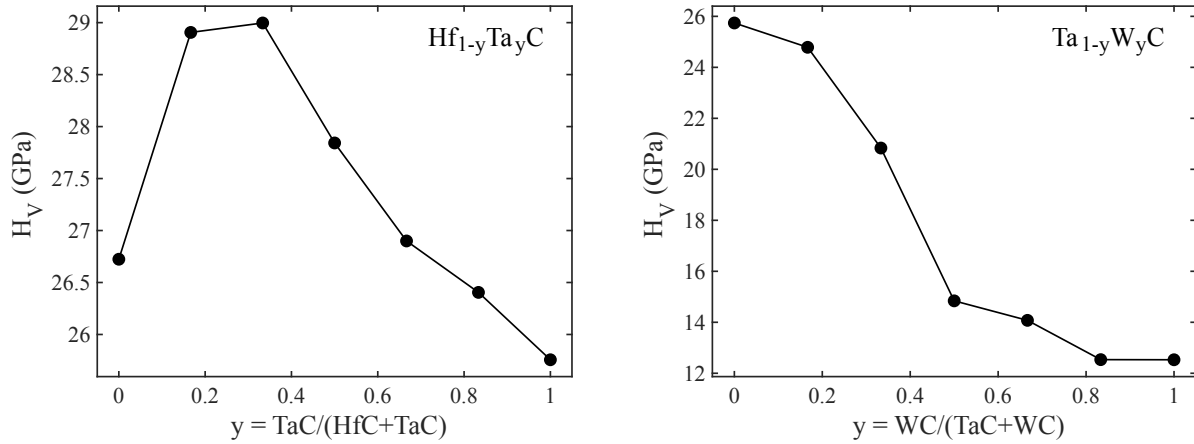


Figure 4.35: Computed hardness estimates for selected alloyed carbides, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$, per the correlation model of Chen *et al.* [73].

Mixed Transition-Metal Carbides

In addition to substoichiometry effects (*i.e.*, the presence of nonmetal vacancies) on elastic stiffness, we have examined the effects of alloying (*i.e.*, substitution of metal or nonmetal atoms) within a few pseudo-binary systems of interest. The mixed carbides $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$ have been modeled using much the same approach described for the individual carbides and nitrides; also included in our study are the carbonitrides $\text{TiC}_{1-y}\text{N}_y$ and $\text{HfC}_{1-y}\text{N}_y$, which will be discussed in detail in Section 4.2.1.

In the alloyed carbides, we see very different trends in elastic stiffnesses, which is unsurprising for two reasons. Firstly, these alloyed systems occupy different VEC ranges: $\text{VEC} \in [8, 9]$ in $\text{Hf}_{1-y}\text{Ta}_y\text{C}$, and $\text{VEC} \in [9, 10]$ in $\text{Ta}_{1-y}\text{W}_y\text{C}$; secondly, the terminal compound WC in the latter alloy is not B1-phase-stable at low temperatures. Thus we would naturally expect these two alloys to exhibit different elastic behaviors, and we might expect some more unusual behaviors in the rocksalt-structured TaC-WC alloys.

The cubic elastic stiffnesses computed for $\text{Hf}_{1-y}\text{Ta}_y\text{C}$, which are shown in Figure A.10, appear to vary roughly linearly with y , with both C_{11} and C_{12} increasing as VEC increases. In the C_{44} stiffness, though, we find very similar magnitudes in both of the terminal compounds, with a modest intermediate-composition maximum at around $y = 0.3$. This may suggest an enhanced

hardness at a hafnium-rich intermediate composition, as has been suggested by prior work on the elastic stiffness of compounds within this system. This is not reflected in the polycrystalline shear moduli, shown in Figure 4.33, which are seen to increase monotonically with increasing VEC; however, the Pugh's modulus, $k = G/B$, shown in Figure 4.34, does show a maximum value around $y = 0.2$. Correspondingly, Vickers hardness predictions according to the model of Chen *et al.* [73] suggest a modest peak hardness at a composition near $\text{Hf}_{0.33}\text{Ta}_{0.67}\text{C}$. This predicted hardness enhancement, exceeding the hardness of the terminal compounds by about 2.5–3 GPa, may suggest an ‘anomalous’ hardness behavior in the HfC-TaC system, as seen in some of the substoichiometric carbides and nitrides occupying the same VEC range; however, since this prediction wholly ignores plasticity, the findings presented in following sections may again be at odds with those derived from stiffness-hardness correlations. Indeed, there is some reason to doubt these predictions, as they anticipate very similar Vickers hardnesses for the terminal compounds, HfC and TaC; from experiment, we know that stoichiometric TaC typically exhibits a markedly lower hardness than stoichiometric HfC.

Unsurprisingly, the stiffnesses computed for $\text{Ta}_{1-y}\text{W}_y\text{C}$ (see Figure A.11) exhibit quite different trends from those computed for the HfC-TaC alloys. Unlike in the latter system, the C_{11} stiffness is seen to change very little with y ; while C_{12} is still seen to show a slight, roughly linear increase with y , the trend in C_{44} is the opposite: as y increases, C_{44} actually sees a significant decline, even dropping below C_{12} at around $y = 0.33$. There is also a slight slope discontinuity in C_{44} around the composition for an equiatomic mix (*i.e.*, TaWC_2); this is reflected in the polycrystalline shear moduli shown in Figure 4.33. These shear moduli are seen to decline significantly with increasing y , though the rate of decline is reduced in the W-rich compounds. The computed Pugh's modulus estimates (see Figure 4.34) show a fairly steep and monotonic decline with increasing VEC, and this is reflected in the correlated hardness estimates shown in Figure 4.35.

Transition-Metal Carbonitrides

Unlike in the other systems examined thus far (with the exception of $\text{Hf}_{1-y}\text{Ta}_y\text{C}$), the elastic moduli computed for the modeled pseudo-binary TMCN systems— $\text{TiC}_{1-y}\text{N}_y$ (Figure 4.37),

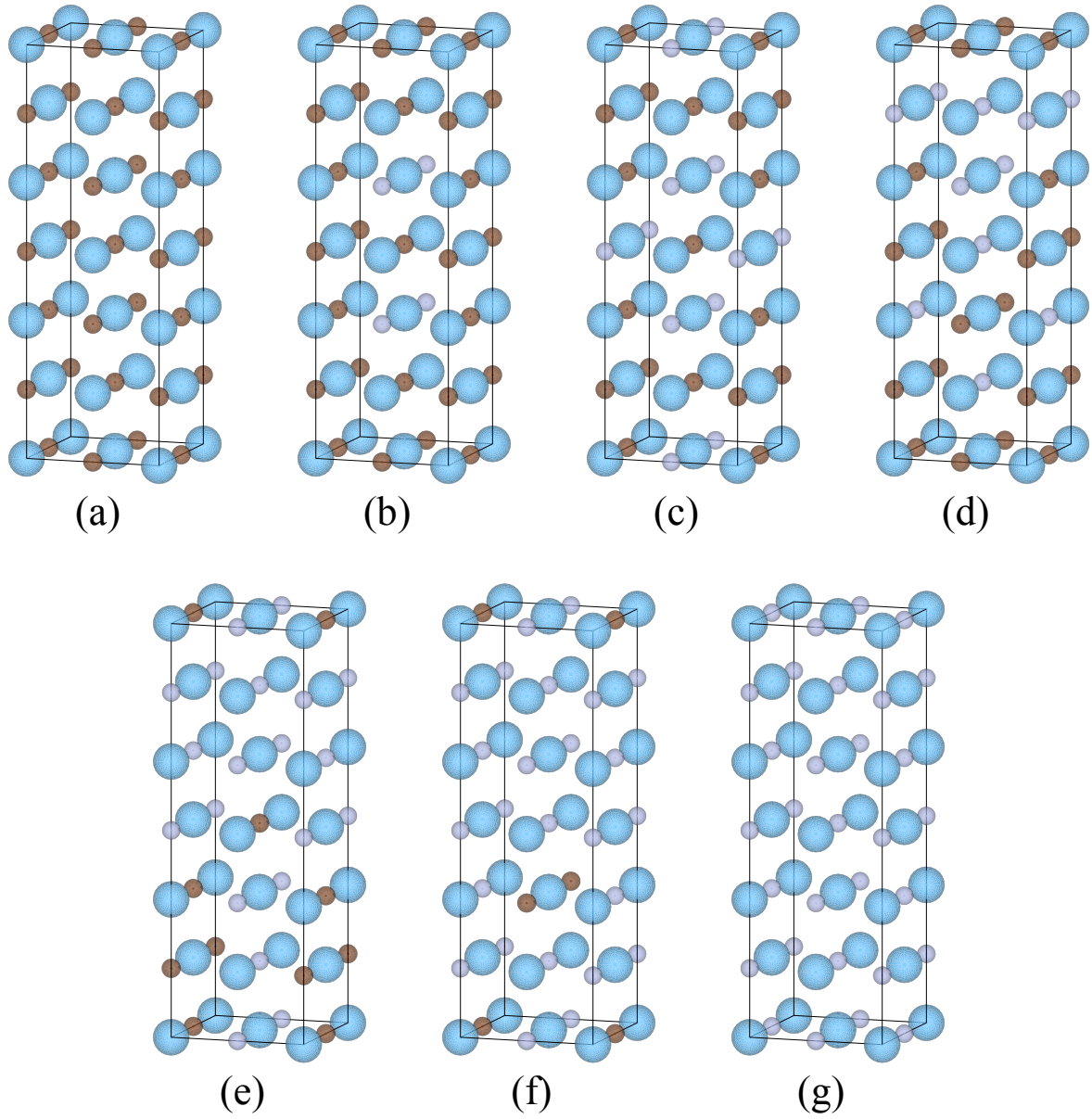


Figure 4.36: VASP simulation cells used for computing C_{ij} in $\text{TiC}_{1-y}\text{N}_y$: (a) TiC , (b) $\text{Ti}_6\text{C}_5\text{N}$, (c) $\text{Ti}_3\text{C}_2\text{N}$, (d) Ti_2CN , (e) Ti_3CN_2 , (f) Ti_6CN_5 , and (g) TiN . Structures rendered in VESTA [30], with large blue spheres representing Ti atoms, small brown spheres representing C atoms, and small blue spheres representing N atoms.

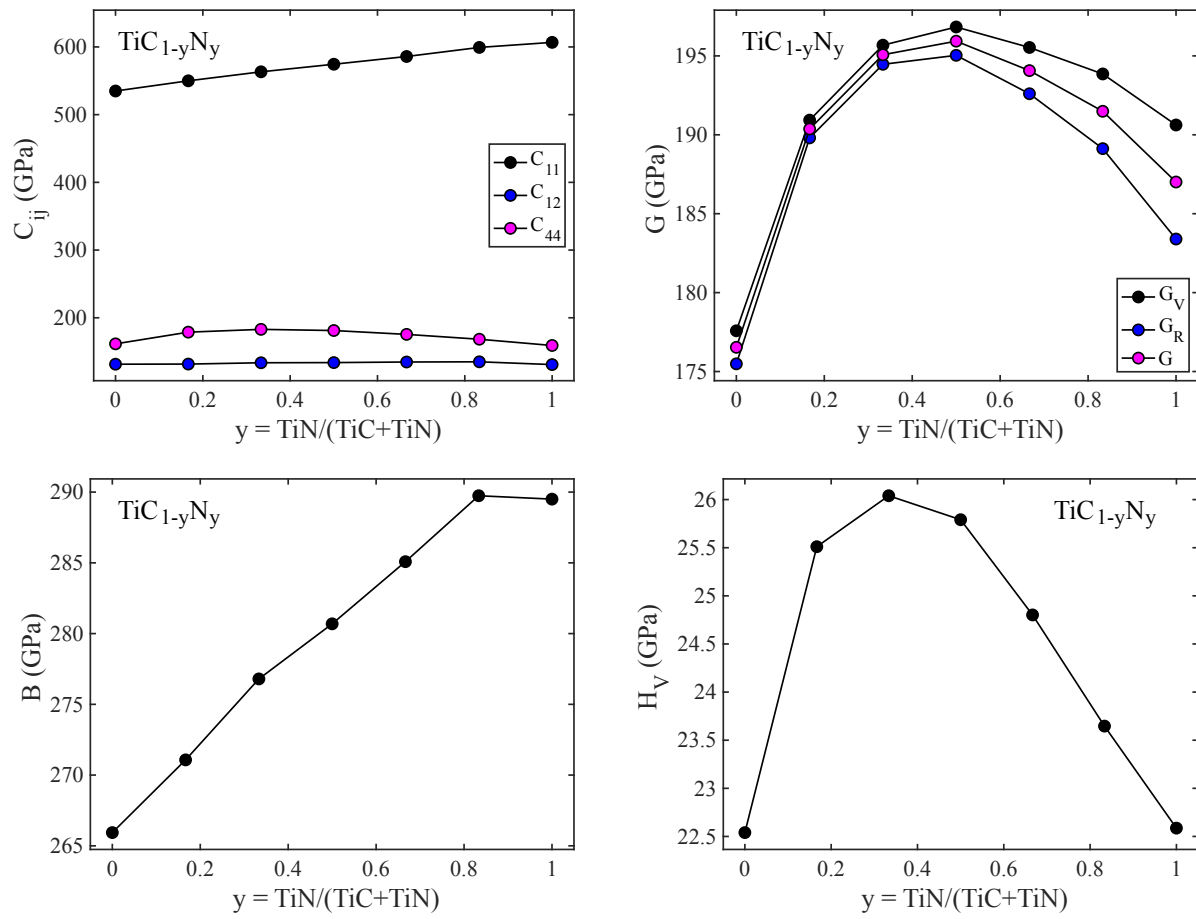


Figure 4.37: VASP-computed cubic elastic stiffnesses, derived moduli and theoretical hardness for rocksalt-structured titanium carbonitrides, $\text{TiC}_{1-y}\text{N}_y$.

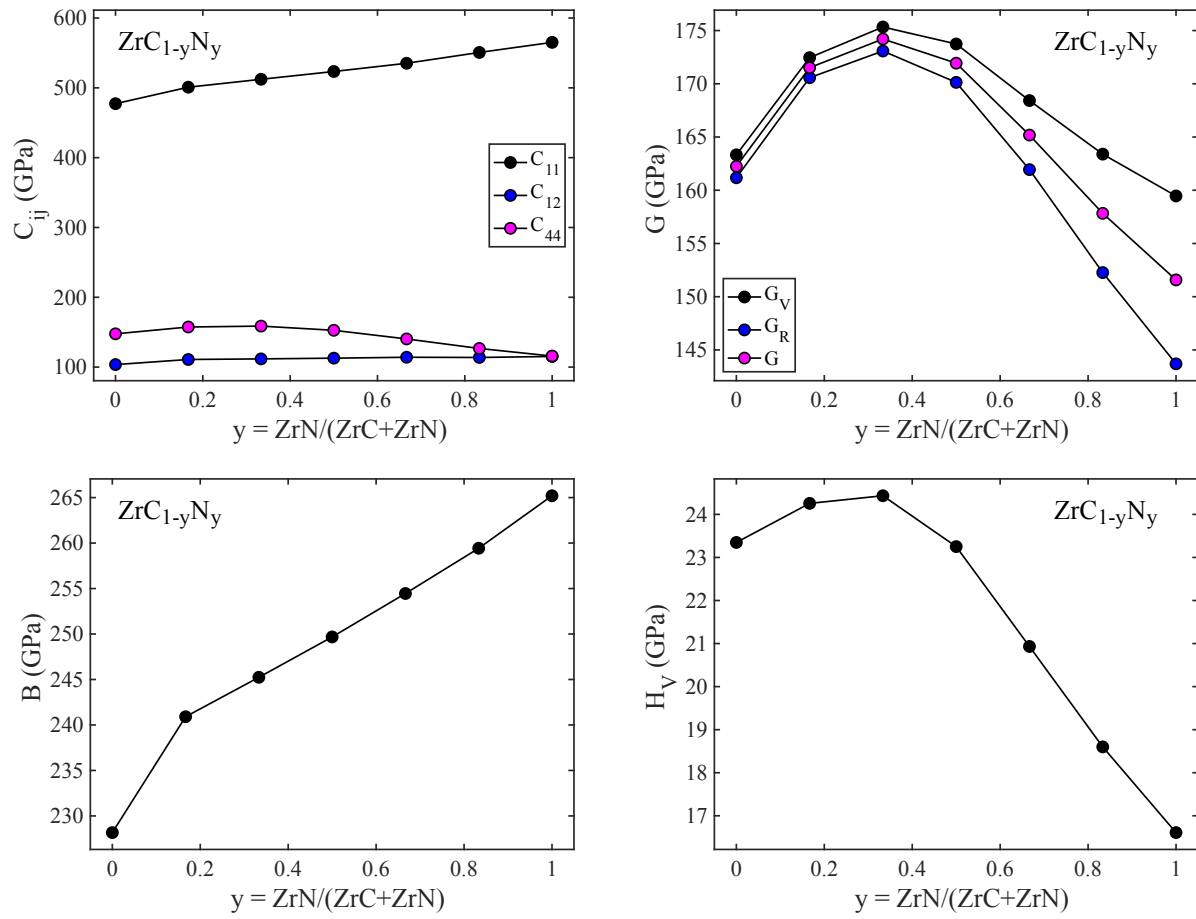


Figure 4.38: VASP-computed cubic elastic stiffnesses, derived moduli and theoretical hardness for rocksalt-structured zirconium carbonitrides, $\text{ZrC}_{1-y}\text{N}_y$.

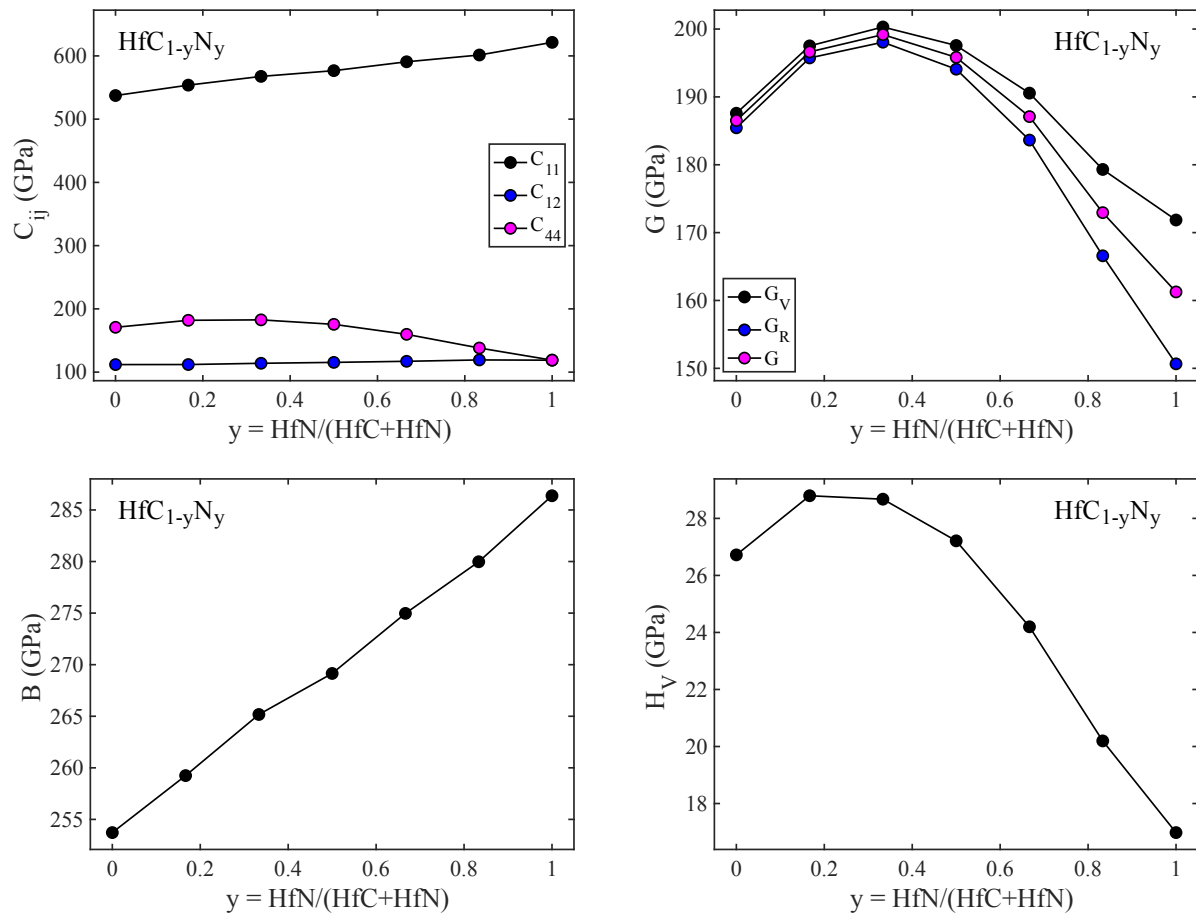


Figure 4.39: VASP-computed cubic elastic stiffnesses, derived moduli and theoretical hardness for rocksalt-structured hafnium carbonitrides, $\text{HfC}_{1-y}\text{N}_y$.

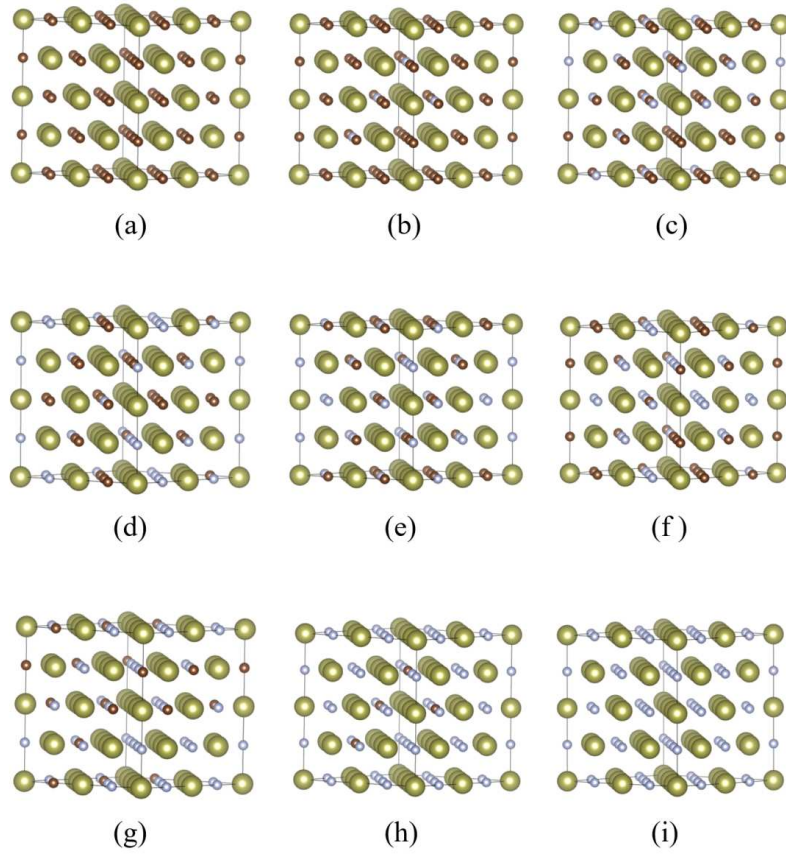


Figure 4.40: Special quasi-random structures used for calculation of formation enthalpies and elastic moduli in the disordered rocksalt hafnium carbonitrides: (a) HfC, (b) HfC_{0.875}N_{0.125}, (c) HfC_{0.75}N_{0.25}, (d) HfC_{0.625}N_{0.375}, (e) HfC_{0.50}N_{0.50}, (f) HfC_{0.375}N_{0.625}, (g) HfC_{0.25}N_{0.75}, (h) HfC_{0.125}N_{0.875}, and (i) HfN. These super-cells are based on a $2 \times 2 \times 2$ repetition of the B1 conventional unit cell, with the different compositions accommodated by random nonmetal-atom substitutions. Figure published previously by Watkins *et al.* [138].

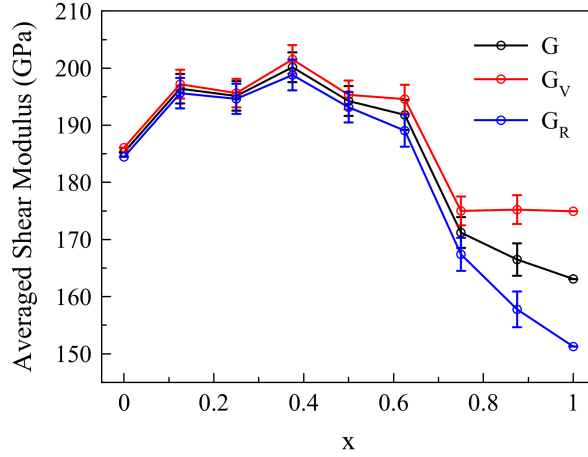


Figure 4.41: Comparison of average shear moduli calculated from DFT-computed C_{11} , C_{12} and C_{44} stiffnesses in the $\text{HfC}_{1-y}\text{N}_y$ system. Figure published previously by Watkins *et al.* [138].

$\text{ZrC}_{1-y}\text{N}_y$ (Figure 4.38), and $\text{HfC}_{1-y}\text{N}_y$ (Figure 4.39)—actually *do* suggest enhanced stiffness at intermediate compositions. All three systems demonstrate considerable increases in C_{11} with increasing y , and fairly negligible changes in C_{12} over the same domain, with both of these trends being roughly linear. The intriguing difference seen in these TMCNs—as opposed to the substoichiometric TMCs and TMNs—is that the cubic shear modulus C_{44} exhibits a modest maximum value at an intermediate y value. This is reflected in the computed polycrystalline shear modulus estimates, which peak around $y = 0.5$ in $\text{TiC}_{1-y}\text{N}_y$ and around $y = 0.3$ in $\text{ZrC}_{1-y}\text{N}_y$ and $\text{HfC}_{1-y}\text{N}_y$; the bulk modulus estimates are, unsurprisingly, quite linear in all three systems. Most interestingly, though, the Vickers hardness predictions made using the correlation model of Chen *et al.* [73], which indeed show maxima at intermediate compositions. These hardness maxima are somewhat modest (around 2-3 GPa), but are nonetheless consistent with prior work on these material systems. Again, these predictions may differ starkly from those made using models which consider dislocation plasticity—as was found to be the case in our more limited discussion of the ‘anomalous’ hardness of TaC_y —but that possibly will be explored in detail in succeeding sections of this manuscript.

As it happens, we have modeled the $\text{HfC}_{1-y}\text{N}_y$ system in this very capacity twice—once for this inquiry, inclusive of the other MTMCs and TMCNs, and once for our general *ab-initio* in-

vestigation into the HfC-HfN pseudo-binary system published in *Open Ceramics* in 2023. In that latter work, we used an array of quasi-random structures, shown in Figure 4.40, to compute elastic moduli for various non-ordered hafnium carbo-nitrides at different compositions. The computed Reuss, Voigt and Hill average shear moduli for these compounds are shown in Figure 4.41, indicating a maximum shear modulus at approximately the $\text{HfC}_{0.6}\text{N}_{0.4}$ composition. This implies a peak shear modulus corresponding to a VEC of about 8.4 electrons/f.u., consistent with the findings of Jhi *et al.* [67] mentioned in Section 2.2.2.

4.2.2 Stacking-Fault Energies

Substoichiometric Transition-Metal Carbides and Nitrides

As anticipated, the computed GSF energy curves for the stoichiometric IVB and VB TMCs (see Figures 4.42 and 4.43) look very similar to those published by Yu *et al.* [92]: all of the IVB TMCs show an inflection point on the $\langle 112 \rangle \{111\}$ GSF energy curve, with no metastable or unstable points present, while all of the VB TMCs exhibit well-defined ISF and USF locations on the same curve. The M_6C_5 carbides also generally share features within their respective groups. Like TiC_y , ZrC_y and HfC_y exhibit a general depression of GSF energies with reduced carbon content, but with essentially no modification of the overall shapes of the energy curves. NbC_y and VC_y , like TaC_y , show modest changes in GSF energy values overall, but all of the VB TMCs exhibit a dramatic increase in ISF energy at the sub-stoichiometric composition. The USF energies increase as well, and the positions of the ISF and USF appear to draw together with reduced y —perhaps an indication that they will merge into an inflection point with further loss of carbon. These results suggest that the Peierls stress trends on $\{111\}$ and $\{110\}$ will look very similar within each group of carbides; that is, the IVB TMCs will likely exhibit very high intrinsic slip resistance on $\{111\}$, while the VB TMCs will likely show low Peierls stresses on $\{111\}$ at higher carbon contents.

These results are somewhat unsurprising in light of findings from prior work (see Section 2.2.4), which generally indicates a remarkable uniformity of stacking-fault energy curve morphology within each group of (stoichiometric) carbides. What the present work shows is that

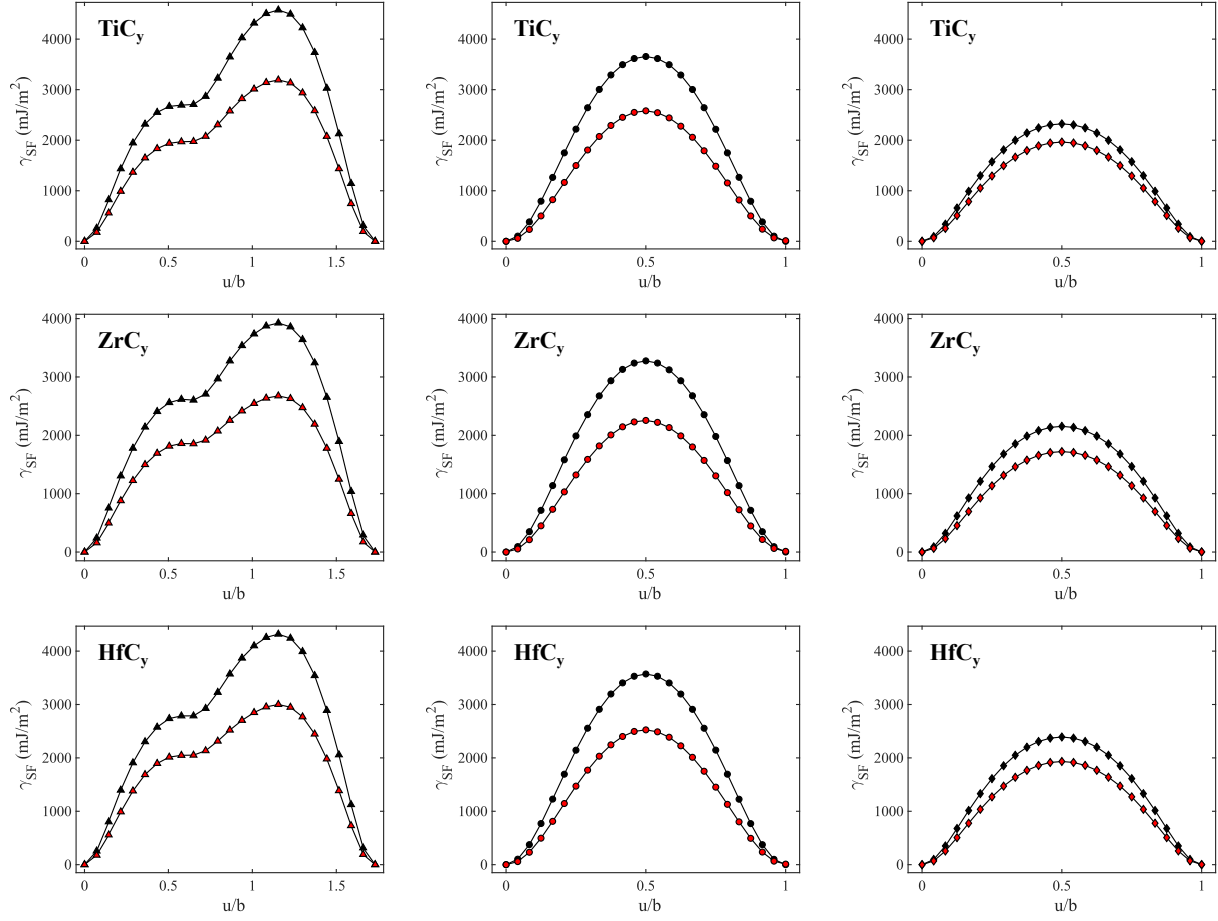


Figure 4.42: DFT-computed GSF energy curves for the IVB TMCs: TiC_y , ZrC_y , and HfC_y . Black lines and markers denote the stoichiometric (B1 MC) phase, while red lines and markers denote the sub-stoichiometric ($\text{C2/m M}_6\text{C}_5$) phase. Slip in $\langle 110 \rangle \{110\}_{\text{B1}}$ is indicated by *diamond* markers; $\langle 110 \rangle \{111\}_{\text{B1}}$ slip is indicated by *circle* markers; $\langle 112 \rangle \{111\}_{\text{B1}}$ slip is indicated by *triangle* markers. Taken from Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

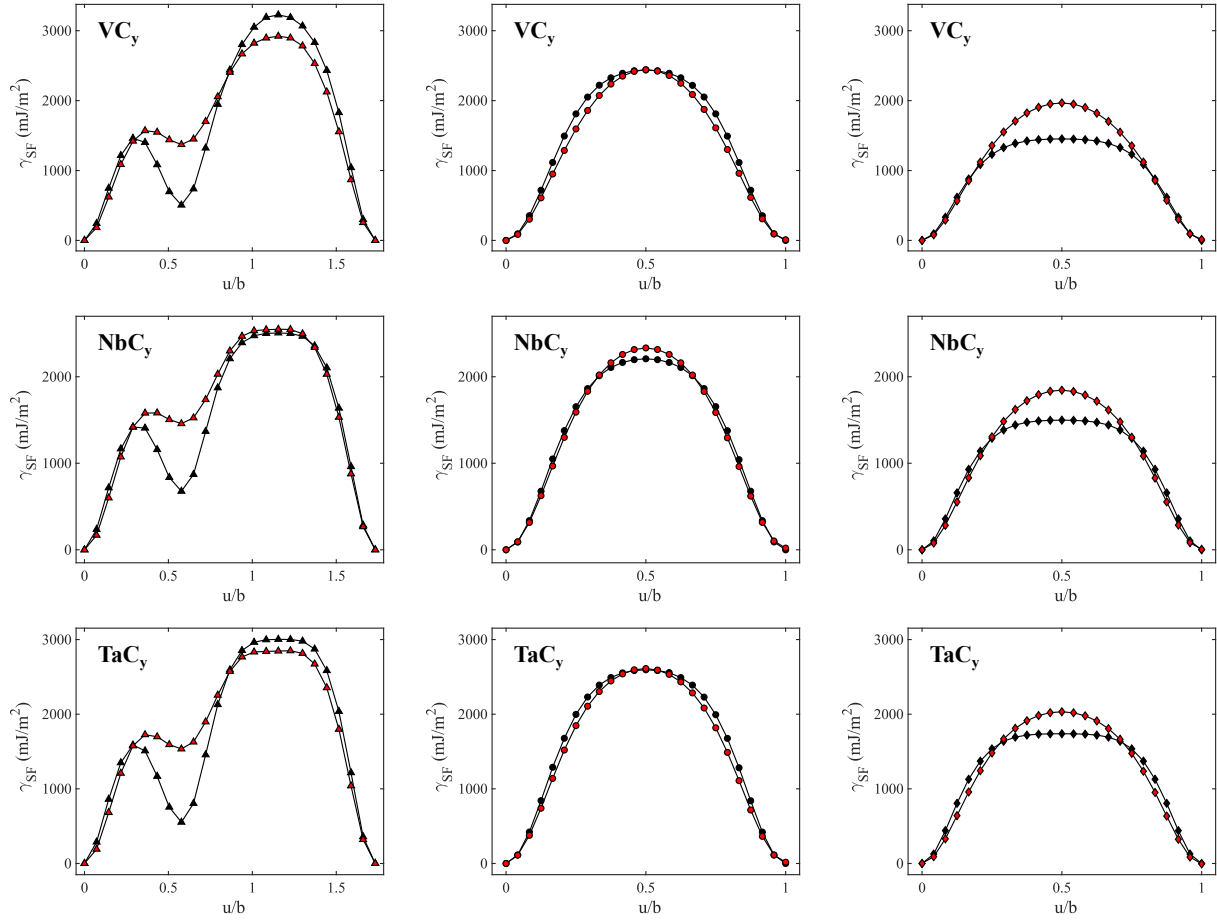


Figure 4.43: DFT-computed GSF energy curves for the VB TMCs: VC_y , NbC_y , and TaC_y . Black lines and markers denote the stoichiometric (B1 MC) phase, while red lines and markers denote the sub-stoichiometric ($\text{C2/m M}_6\text{C}_5$) phase. Slip in $\langle 110 \rangle \{110\}_{\text{B1}}$ is indicated by *diamond* markers; $\langle 110 \rangle \{111\}_{\text{B1}}$ slip is indicated by *circle* markers; $\langle 112 \rangle \{111\}_{\text{B1}}$ slip is indicated by *triangle* markers. Taken from Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

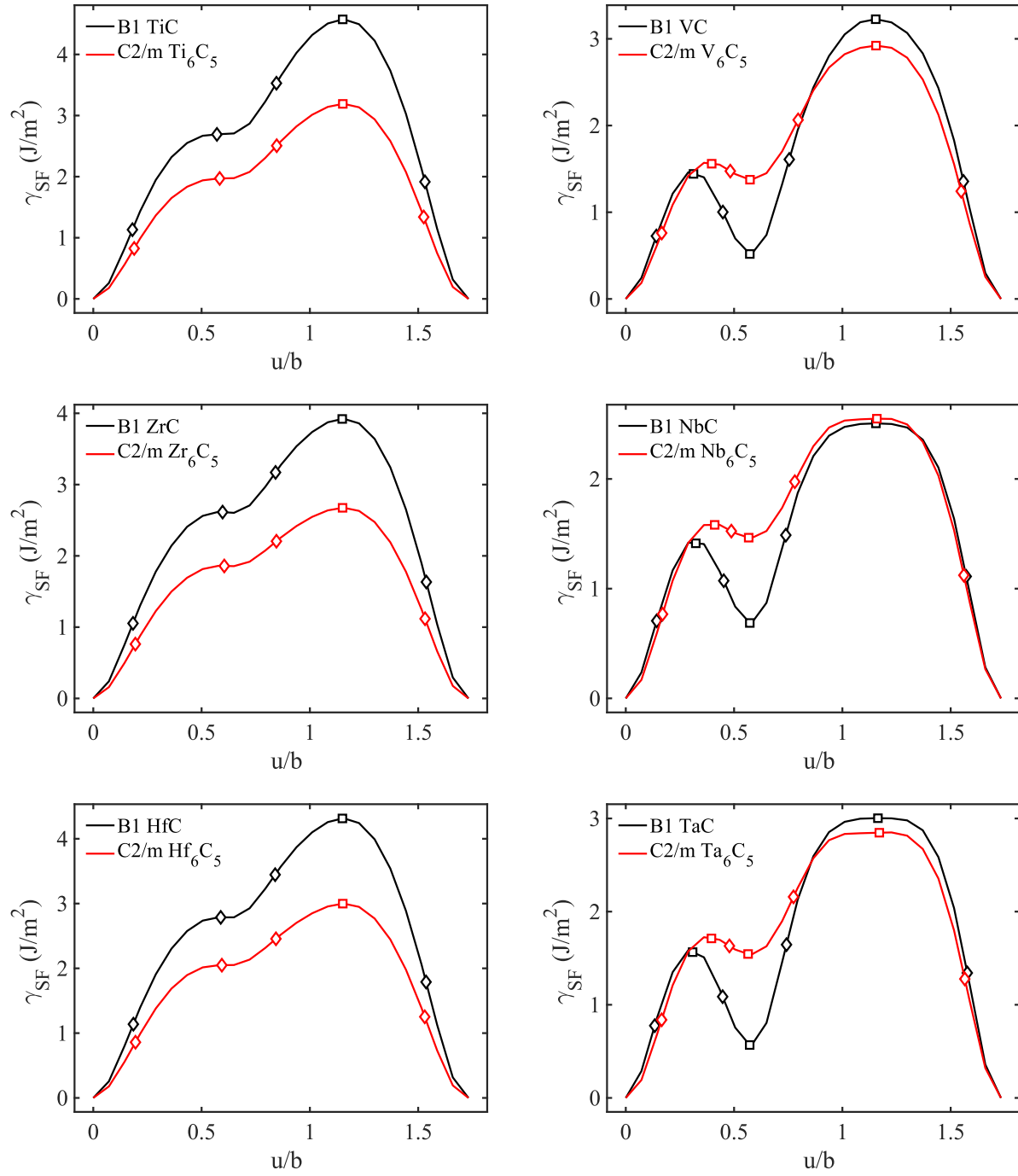


Figure 4.44: Identification of local extrema (square markers) and inflection points (diamond markers) on $\langle 112 \rangle \{111\}_{B1}$ GSF energy curves for the IVB and VB TMCs. Black lines and markers denote the stoichiometric (B1 MC) phase, while red lines and markers denote the sub-stoichiometric (C2/m M_6C_5) phase. Results for HfC_y and TaC_y previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

the changes in γ_{SF} magnitudes and curve morphologies seen in TiC_y and TaC_y are indeed representative of these materials' respective groups of carbides: as VEC is decreased via removal of nonmetal atoms, the IVB TMCs tend to suffer a general reduction in stacking-fault energies, whereas the VB TMCs see a fairly localized increase in γ_{SF} , particularly in the area of the intrinsic stacking fault. It should be further noted that the behavior of the IVB TMCs is the behavior one would naïvely expect for all of the cubic carbides and nitrides, since leaving vacancies in the lattice could reasonably be expected to lessen the lattice's resistance to deformation (by virtue of leaving fewer interatomic bonds to break and re-form via rigid slip). That the VB TMCs do not undergo this general diminishing of γ_{SF} is alone quite interesting, suggesting no significant decrease in τ_{RISS} at lower carbon contents; as indicated by our earlier findings regarding TaC_y , though, the dramatic increase in γ_{ISF} seen in all of the VB TMCs will likely serve to substantially increase Peierls stresses at substoichiometric compositions.

In the interest of thoroughness, we have modeled the same non-equivalent slip systems in all of the IVB and VB TMCs that were discussed in Section 4.1.3 for Ti_6C_5 and Ta_6C_5 . The results of this study, shown in Figures 4.45 and 4.46, show relatively little variation between the distinguishable slip systems in each material. In general, the 'filled' slip systems—those wherein no carbon vacancies are present immediately adjacent to the slip plane—show somewhat elevated stacking-fault energies when compared to the partially carbon-depleted systems; the only exception to this trend is VC_y , which has a somewhat depressed γ_{ISF} in the non-carbon-depleted $\langle 112 \rangle \{111\}_{\text{B1}}$ energy curve. As an aside, VC_y being an outlier in this—or any—capacity is not terribly surprising, as the vanadium carbides are known to exhibit many behaviors dissimilar to those of the other TMCs, even the other VB TMCs.

Turning our attention to the IVB TMNs, Figure 4.48, we see a great many similarities to the VB TMCs. Compared to the stoichiometric IVB TMNs, the substoichiometric IVB TMNs have substantially elevated intrinsic stacking-fault energies, indicating a reduced propensity to form stacking faults on $\{111\}_{\text{B1}}$ crystallographic planes. The γ_{ISF} values, interestingly, are extremely similar to those seen in the VB TMCs; also interesting to note is that this then represents a more

modest elevation in γ_{ISF} than we see in the VB TMCs, since γ_{ISF} is higher in the stoichiometric IVB TMNs than in the stoichiometric VB TMCS. One feature of the IVB TMN γ_{SF} curves not seen in any of the IVB or VB TMCs is the appearance of a metastable aligned stacking fault (ASF) as the size of the metal atoms increases. The energy of this point, γ_{ASF} , represents a local maximum in TiN_y , but becomes a metastable local minimum in both ZrN_y and HfN_y . This metastable ASF is also seen in the curves computed for the VB TMNs (see Figure 4.49), although in VN_y this appears true only for one of the four inequivalent $\langle 112 \rangle \{111\}_{\text{B1}}$ slip systems. More importantly, though, the ISF is again seen to increase in energy with decreasing VEC in the VB TMNs; while the ISF is actually a stable point in the stoichiometric VB TMNs (having $\gamma_{\text{ISF}} < 0$), nitrogen loss appears to render the ISF metastable in all but one of the $\langle 112 \rangle \{111\}_{\text{B1}}$ slip systems modeled for each material. That is, at a slightly substoichiometric composition, an octahedral atomic coordination environment is slightly favored to a trigonal prismatic one.

We have also computed GSF energies for a number of mixed HfC-HfN mixtures, hoping to observe changes in GSF curve morphology with varied VEC. As seen in Figure 4.53, the $\langle 112 \rangle \{111\}$ GSF energy curves show the emergence of a meta-stable ISF with increasing VEC. Corresponding to this change is an appreciable increase in theoretical stacking-fault widths on $\{111\}$, computed using Equation 4.5. This strongly suggests that intrinsic slip resistance on $\{111\}$ will decline significantly with increased VEC in the HfC-HfN system, similar to the difference observed between the IVB and VB TMCs.

Preliminary investigation into the slip behavior of some the mixed-transition-metal carbides (MTMCs) has been performed. Upon computing stacking-fault energy curves on $\{111\}$ in the $\text{Ti}_{1-y}\text{Ta}_y\text{C}$ system, we found the metastable ISF to emerge with increasing VEC; the VEC is seen to increase linearly with y within this pseudo-binary alloy, rising from 8 to 9 electrons/f.u. Looking at TaC-WC alloying, we observe the ISF energy to fall rapidly with increasing VEC, ultimately dropping to a negative value and indicating greater stability in the B_h structure as compared to the B1. Generalized stacking-fault energies for these two systems are shown together in Figure 4.51.

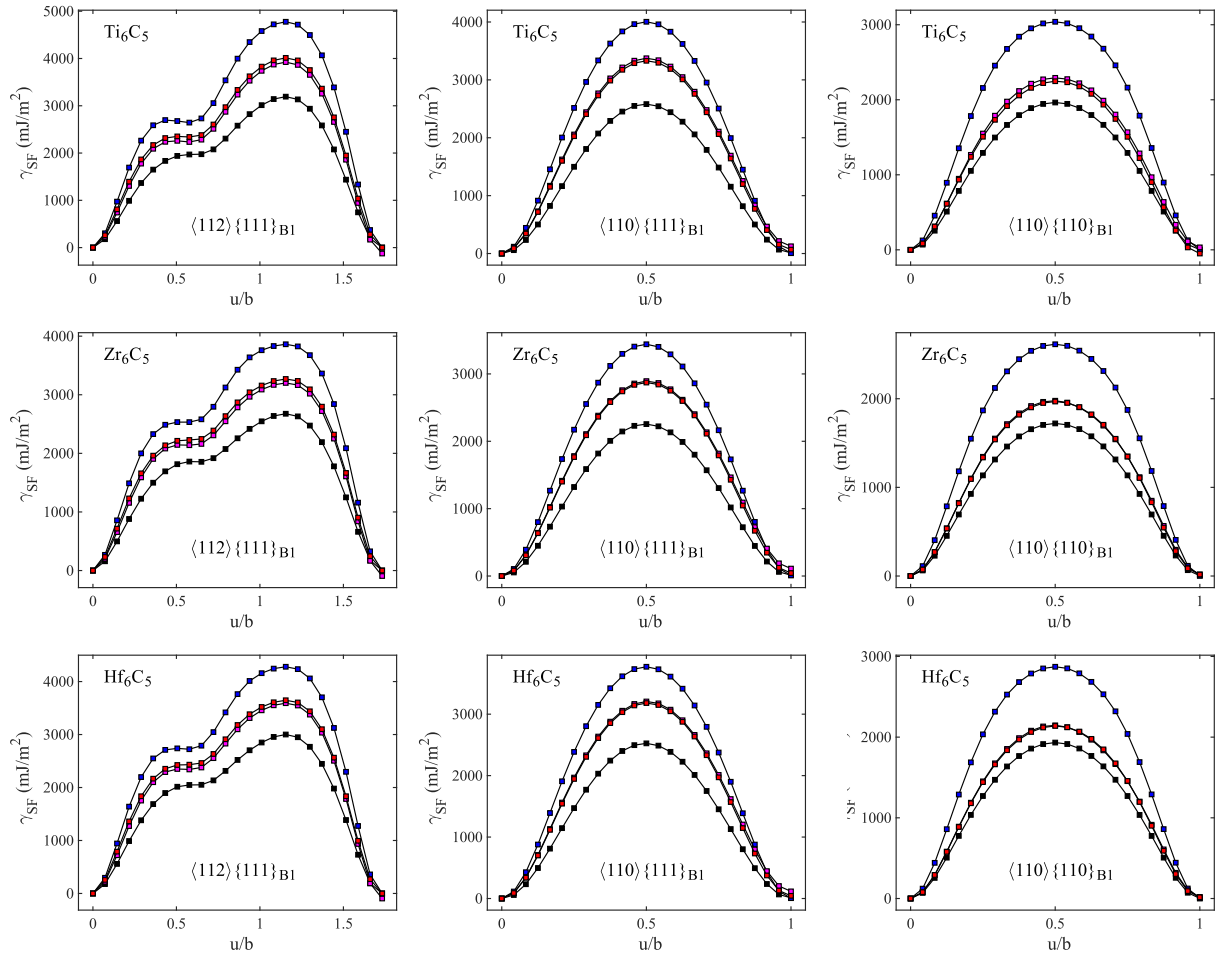


Figure 4.45: DFT-computed generalized stacking-fault energy curves for substoichiometric IVB TMCs: Ti_6C_5 , Zr_6C_5 , and Hf_6C_5 . Taken from Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

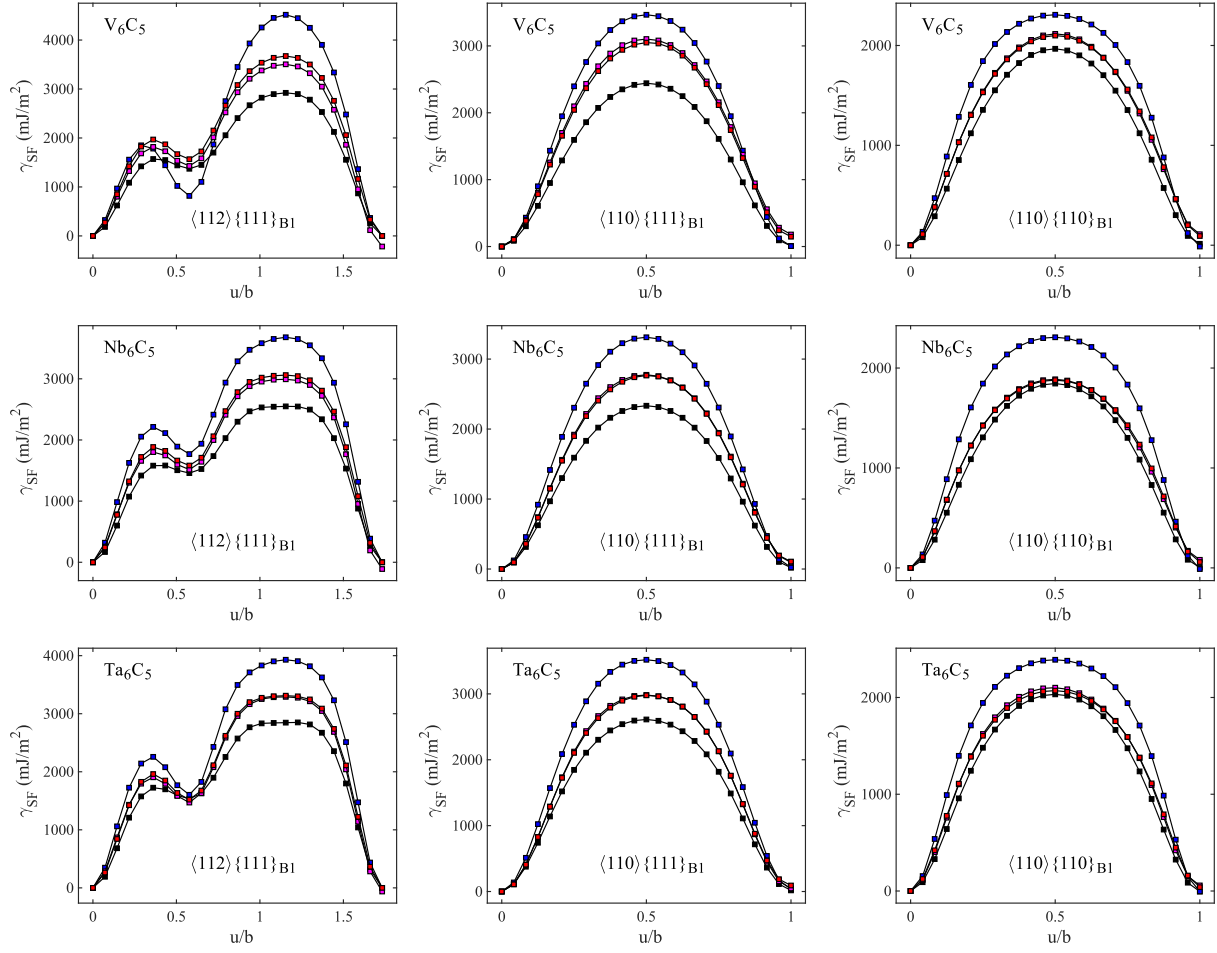


Figure 4.46: DFT-computed generalized stacking-fault energy curves for substoichiometric VB TMCs: V_6C_5 , Nb_6C_5 , and Ta_6C_5 . Taken from Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

Table 4.2: Characteristics of GSF energy curves in the IVB TMCs which may indicate their slip plane preference. All data published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

	TiC	Ti ₆ C ₅	ZrC	Zr ₆ C ₅	HfC	Hf ₆ C ₅
b (Å)	3.067	3.059	3.340	3.342	3.286	3.284
γ_{ISF} (mJ/m ²)	2691	1970	2614	1858	2787	2049
γ_{USF} (mJ/m ²)	2691	1970	2614	1858	2787	2049
$\gamma_{\text{ISF}}/\gamma_{\text{USF}}$	1.000	1.000	1.000	1.000	1.000	1.000
$\tau_{\{110\}\{110\}}$ (GPa)	25.96	21.72	24.15	18.94	26.47	21.21
$\tau_{\{110\}\{111\}}$ (GPa)	38.16	26.81	34.72	23.44	36.65	26.20
$\tau_{\{112\}\{111\}}$ (GPa)	27.75	19.43	24.94	17.34	26.90	19.56

Table 4.3: Characteristics of GSF energy curves in the VB TMCs which may indicate their slip plane preference. All data published previously by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

	VC	V ₆ C ₅	NbC	Nb ₆ C ₅	TaC	Ta ₆ C ₅
b (Å)	2.938	2.926	3.186	3.175	3.164	3.148
γ_{ISF} (mJ/m ²)	518	1375	687	1465	567	1545
γ_{USF} (mJ/m ²)	1442	1560	1413	1582	1565	1712
$\gamma_{\text{ISF}}/\gamma_{\text{USF}}$	0.359	0.882	0.486	0.926	0.363	0.902
$\tau_{\{110\}\{110\}}$ (GPa)	22.35	22.55	23.65	21.93	28.75	24.90
$\tau_{\{110\}\{111\}}$ (GPa)	31.27	26.85	29.29	26.93	35.12	31.35
$\tau_{\{112\}\{111\}}$ (GPa)	22.92	21.08	21.82	21.48	25.99	23.88

Mixed Transition-Metal Carbides

Much of our discussion up to this point has revolved around differences in stacking-fault energies within TMCs and TMNs at different levels of carbon or nitrogen depletion, with the underlying assumption being that the depletion of these compounds of valence electrons, by means of substoichiometry, is of importance in determining the stacking-fault energies. In principle, this reduction in VEC should produce quite similar effects, irrespective of how it is achieved, within the B1 TMCs and TMNs; thus, we turn our attention in this section to the effects of alloying on γ_{SF} in the carbides.

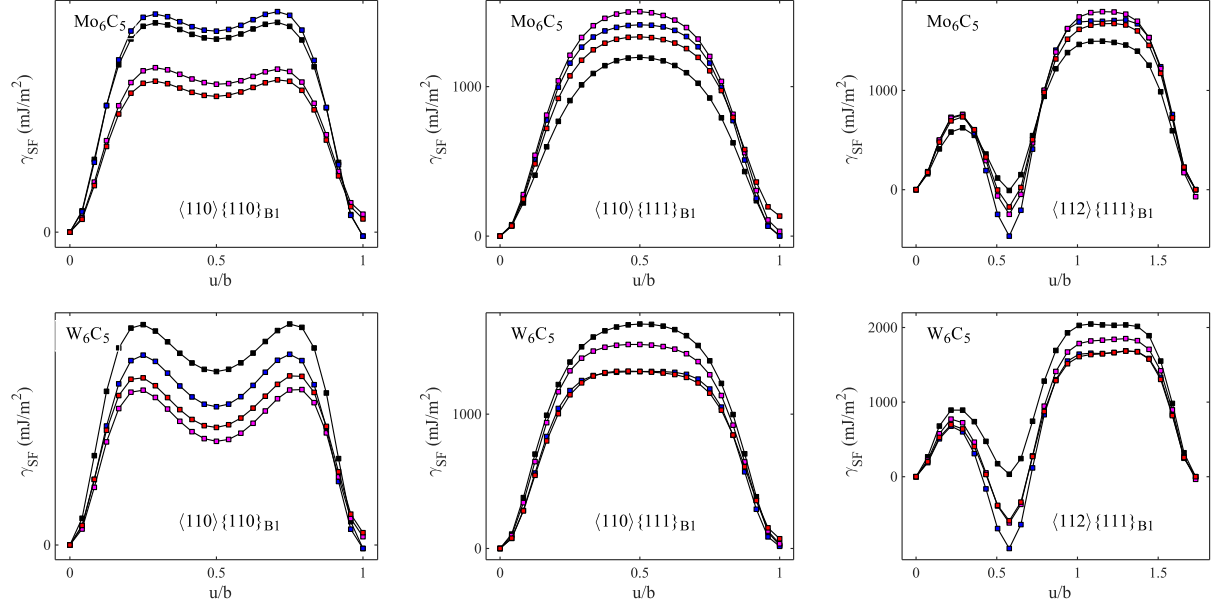


Figure 4.47: DFT-computed generalized stacking-fault energy curves for substoichiometric VIB TMCs: Mo_6C_5 and W_6C_5 .

Our first system of interest, the HfC-TaC system, has been the subject of study in some previous work, both experimental and computational (see Section 2.2.4). The alloyed carbides $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ span the range $\text{VEC} \in [8, 9] e^-/\text{f.u.}$, making them appealing for examining the hypothesis that VEC tailoring by means of metal substitution will have a similar effect to VEC tailoring via substoichiometry. As before, our primary interest is in the evolution of the intrinsic stacking-fault energy, γ_{ISF} , as VEC increases. Accordingly, γ_{SF} curves were generated for slip along $\langle 110 \rangle \{110\}_{\text{B1}}$, $\langle 110 \rangle \{111\}_{\text{B1}}$ and $\langle 112 \rangle \{111\}_{\text{B1}}$; this modeling was performed for three intermediate compositions: Hf_2TaC_3 , HfTaC_2 , and HfTa_2C_3 . Looking at the curves shown in figure 4.50, we see general agreement with the prior results of Smith *et al.* [93]. In the case of $\langle 110 \rangle \{110\}_{\text{B1}}$ slip, the intermediate-composition curves are near-perfectly linearly interpolated between the corresponding data for the terminal compounds, HfC and TaC. This alone may suggest a relatively smooth Peierls stress evolution between the terminal compounds, though variations in the elastic moduli may render this prediction incorrect. The peak energy, γ_{USF} , is significantly higher in the HfC-rich alloys, but the slope of the curve (and therefore the restorative force resisting slip, per the Peierls-Nabarro model) is greater in the TaC-rich compounds; thus, we might suspect Peierls stresses for

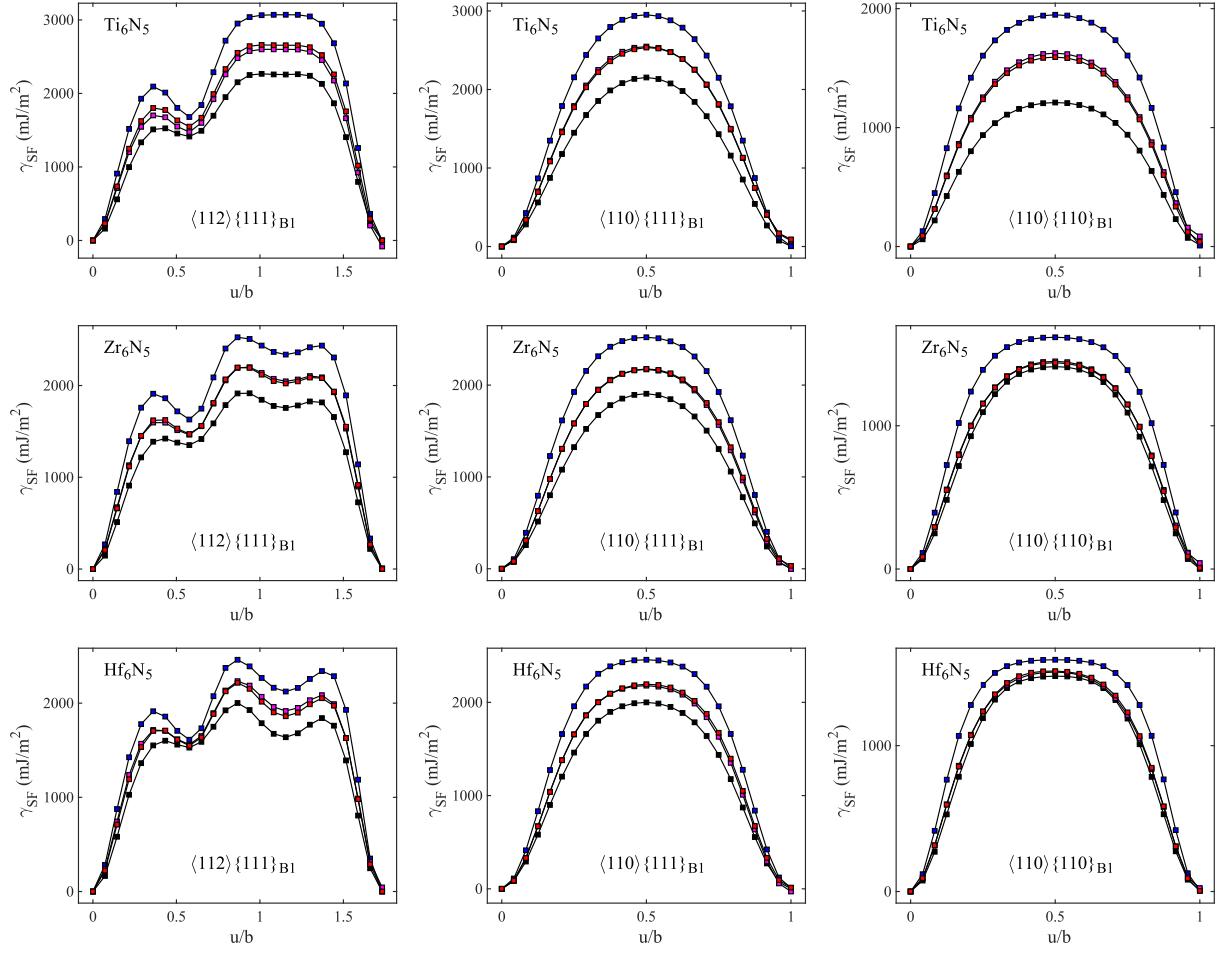


Figure 4.48: DFT-computed generalized stacking-fault energy curves for substoichiometric IVB TMNs: Ti_6N_5 , Zr_6N_5 , and Hf_6N_5 . Taken from Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

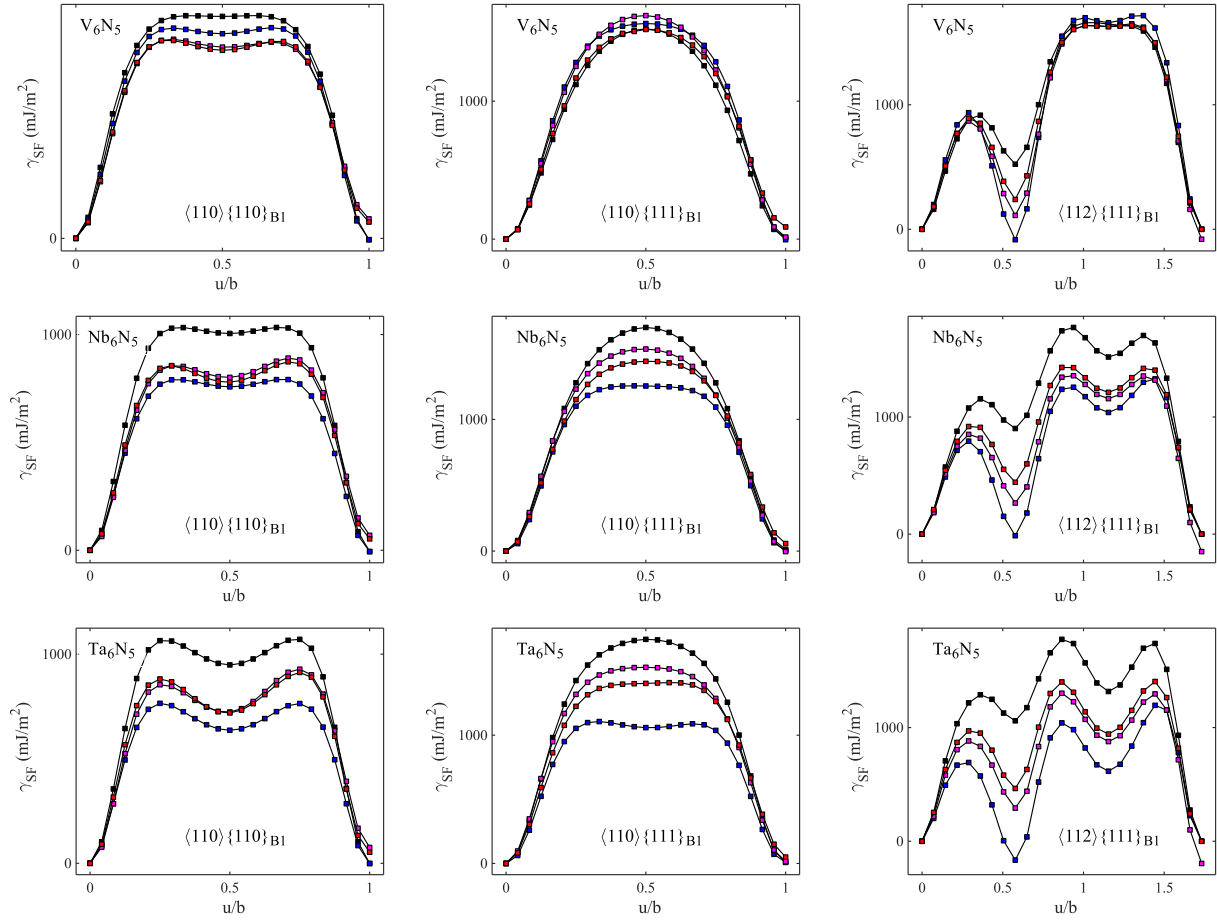


Figure 4.49: DFT-computed generalized stacking-fault energy curves for substoichiometric VB TMNs: V_6N_5 , Nb_6N_5 , and Ta_6N_5 .

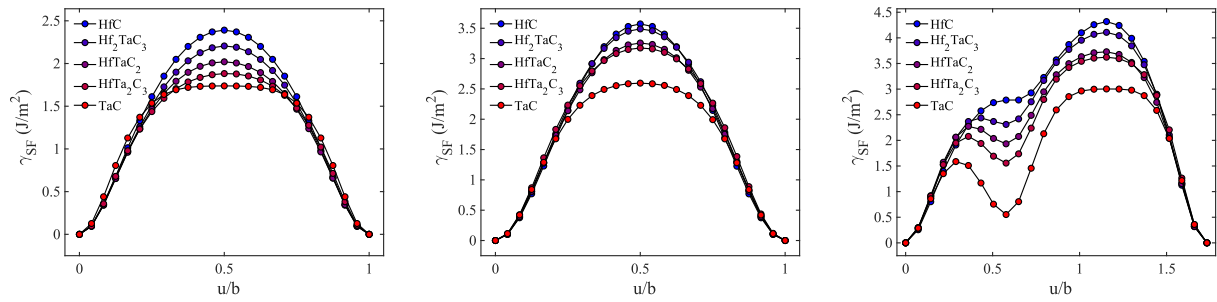


Figure 4.50: Stacking-fault energy curves computed for (left) $\langle 110 \rangle \{110\}_{B1}$, (middle) $\langle 110 \rangle \{111\}_{B1}$, and (right) $\langle 112 \rangle \{111\}_{B1}$ slip in the alloyed hafnium-tantalum carbides, $Hf_{1-y}Ta_yC$.

$\langle 110 \rangle \{110\}_{B1}$ slip to be greater on the higher-VEC end of the composition domain. This would be consistent with the SVPN results obtained for the terminal compounds, which will be discussed in Section 4.2.3.

The γ_{SF} curves for slip on $\{111\}_{B1}$ planes are, naturally, of greater interest, as they offer insight as to whether easy $\{111\}_{B1}$ slip will be available in $Hf_{1-y}Ta_yC$ at intermediate y ; as stated before, this is a crucial determinant as to whether the material can be expected to exhibit significant plasticity under indentation, as the $\{111\}_{B1}$ planes are independently capable of satisfying the von Mises criterion for a general state of plastic strain. Looking again at Figure 4.50, the stacking-fault energies for both slip directions are roughly interpolated between those of the terminal compounds, although not quite as smoothly as in the $\langle 110 \rangle \{110\}_{B1}$ curves. The fluctuation likely arises from the particular ordering of substitutional atoms within the simulation cells, as different representative volumes were used to achieve each stoichiometric ratio. Nonetheless, the γ_{ISF} values transition fairly smoothly between the terminal compounds—not quite linearly, but with a smooth, monotonic decrease as y (and thus VEC) increases. This is again consistent with prior work, and ultimately consistent with the notion that VEC is a primary determinant of both the energy and stability of intrinsic stacking-faults in the B1 structure; furthermore, these results suggest increasing preference for $\{111\}_{B1}$ slip as VEC is increased via alloying within the HfC-TaC system.

These same indicators for slip plane preference were also generated for the TiC-TaC and TaC-WC system, in the interest of tracking changes in γ_{SF} magnitudes and curve morphologies over the whole range $VEC \in [8, 10] e^-/f.u.$ for the stoichiometric B1 carbides. As seen in Figure 4.51, these datasets can be concatenated (at the mutual terminal compound TaC) in order to demonstrate a remarkably smooth transition in stacking-fault energies across the whole range of alloys. As in the $Hf_{1-y}Ta_yC$ system, the γ_{SF} for slip on $\langle 110 \rangle \{111\}_{B1}$ in $Ti_{1-y}Ta_yC$ generally decline as y increases; this trend continues in the $Ta_{1-y}W_yC$ system, with WC having significantly lower stacking-fault energies than TaC. This trend is accompanied by a gradual change in γ_{SF} curve morphology, with the roughly sinusoidal curve of TiC transitioning into more of a flat-topped (*i.e.*, truncated) si-

nusoidal shape in TaC before developing a slight positive concavity at the midpoint ($\delta/b = \frac{1}{2}$) position in WC. The curves for $\langle 112 \rangle \{111\}_{B1}$ slip are even more interesting, demonstrating the same smooth reduction in γ_{SF} with increasing VEC. An examination of the curve morphology shows a steady divergence of the unstable and intrinsic stacking-fault energies as VEC increases; from the initial inflection point seen in the $\langle 112 \rangle \{111\}_{B1}$ energy curve for TiC, one can see the distinct local minimum and maximum— γ_{ISF} and γ_{USF} —appear with even a slight increase in VEC: they are well-differentiated even in Ti_2TaC_3 , which has a VEC of only $8.3 e^-/f.u.$ As VEC rises, both γ_{ISF} and γ_{USF} decrease quite rapidly, hinting at a substantial decrease in intrinsic slip resistance on $\{111\}_{B1}$ planes as higher-valency metal atoms are substituted for lower-valency ones. The decline in γ_{USF} alone signals a decrease in slip resistance—as it corresponds to a reduction in the rigid ideal shear stress, τ_{RISS} —but the more rapid decline in γ_{ISF} increases the stability of stacking faults on $\{111\}_{B1}$, presumably contributing to far more glissile dislocation structures.

Looking at the trend in ISF energies (Figure 4.52), we find a roughly linear decline with increasing VEC, with γ_{ISF} passing through 0 mJ/m^2 at a VEC of about $9.2 e^-/f.u.$ This indicates a steady stabilization of the ISF with increasing VEC, resulting in an energetic preference for the trigonal prismatic coordination environment over the octahedral one at VECs above 9.2 electrons/f.u. This is unsurprising, as the stable phase for stoichiometric tungsten carbide is (naturally) the α -WC structure, or the B_h structure. Thus we might theoretically expect the drop in stacking-fault energy to produce substantially wider stacking-faults when examined using our Peierls-Nabarro model; past the point wherein γ_{ISF} becomes negative, we would expect to see very wide stacking-faults, with the theoretically infinite w_0 being confined somewhat in our model by both the restorative force (which varies with γ_{USF}) and the boundary conditions of the limited simulation volume. But, in an infinite crystal, the equilibrium separation distance between the Shockley partial dislocations would be infinite, as increasing the stacking-fault width would always be energetically favorable. It is interesting to note that this framing of the process—propagation of the stacking-fault as a localized phase change to B_h —is consistent with our general interest in the energetic differences between the atomic coordination environments found in the $B1$ and B_h structures.

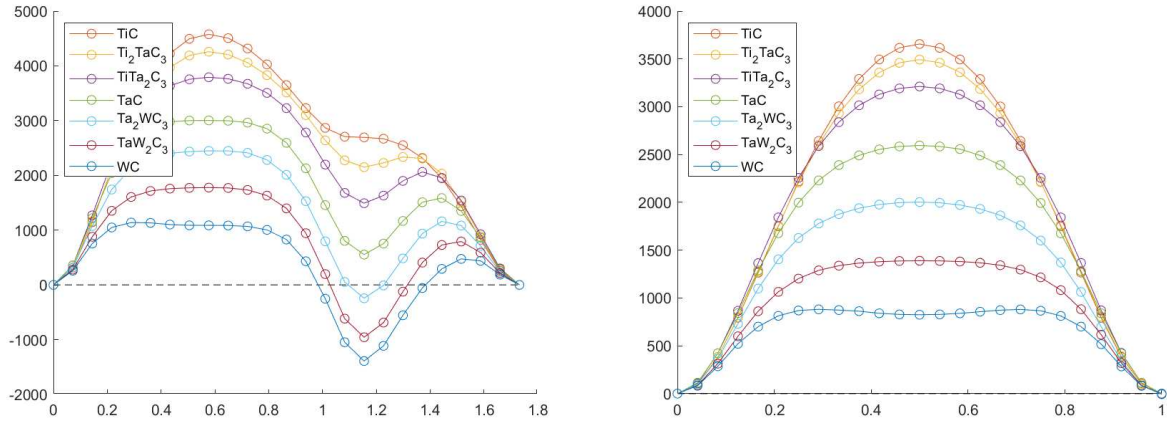


Figure 4.51: Generalized stacking-fault energies computed for the alloyed carbides $\text{Ti}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$. Shown on the left are GSF energy curves for $\langle 110 \rangle \{111\}$ slip, and shown on the right are curves for $\langle 112 \rangle \{111\}$ slip.

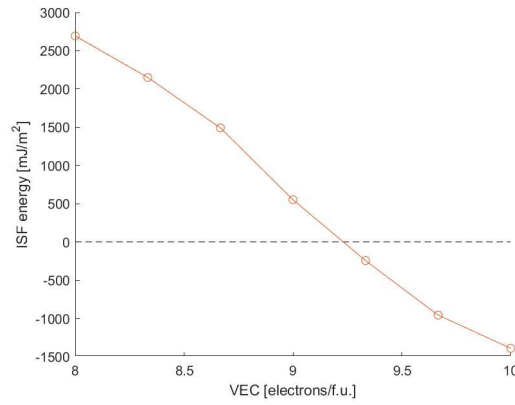


Figure 4.52: Variation in ISF energy with VEC in the alloyed carbides $\text{Ti}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ta}_{1-y}\text{W}_y\text{C}$. Note the roughly linear decline in ISF energy with increasing VEC, resulting in the stabilization of the B_h phase relative to the B_1 phase at VECs above approximately $9.2 e^-/\text{f.u.}$

Transition-Metal Carbonitrides

A study of the DFT-computed stacking-fault energy curves for our selected carbonitride systems yields fairly intuitive results, when considered in light of the findings discussed in the previous section. In both the ZrC-ZrN and HfC-HfN pseudo-binary systems, it is readily apparent that the γ_{SF} curves at intermediate compositions roughly interpolate between the corresponding γ_{SF} curves of the terminal compounds. Furthermore, increasing y in both $\text{ZrC}_{1-y}\text{N}_y$ and $\text{HfC}_{1-y}\text{N}_y$ —which, of course, increases VEC from 8 to 9 $e^-/\text{f.u.}$ —causes a rapid differentiation of local extrema from the original inflection point on the $\langle 112 \rangle \{ 111 \}_{\text{B1}}$ energy curve. Just as in the $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ and $\text{Ti}_{1-y}\text{Ta}_y\text{C}$ systems, which occupy the same VEC range, we see a steady decline in the intrinsic stacking-fault energy; compared to the alloyed carbide systems, though, the drop in γ_{ISF} is not as severe—the ISF energy is on the order of 1 J/m² in the IVB TMNs, as compared to around 500 mJ/m² in the VB TMCs. This may suggest a less significant reduction in intrinsic slip resistance with increasing VEC in the carbonitrides than in the alloyed carbides, but the interesting variations in elastic stiffnesses discussed in Section 4.2.1 will ultimately also influence our estimated Peierls stresses.

4.2.3 Dislocation Mobility and Slip Plane Preference

Using precisely the approach established in Section 4.1.7, we have sought to predict the intrinsic—that is, from ‘lattice friction’ alone—resistance to dislocation slip in compounds from all of the categories previously discussed. Accordingly, this section will enumerate our findings for rocksalt-structured carbides, nitrides, and carbonitrides, examining the effects of VEC alteration by means of nonmetal depletion, metal substitution and nonmetal substitution on the availability of dislocation slip on different crystallographic planes.

Substoichiometric Transition-Metal Carbides and Nitrides

Alongside the specific results for TiC_y and TaC_y discussed in Section 4.1.7, we have extended our analysis to all of the IVB and VB TMCs, as well as to the IVB TMNs. The VB TMNs will

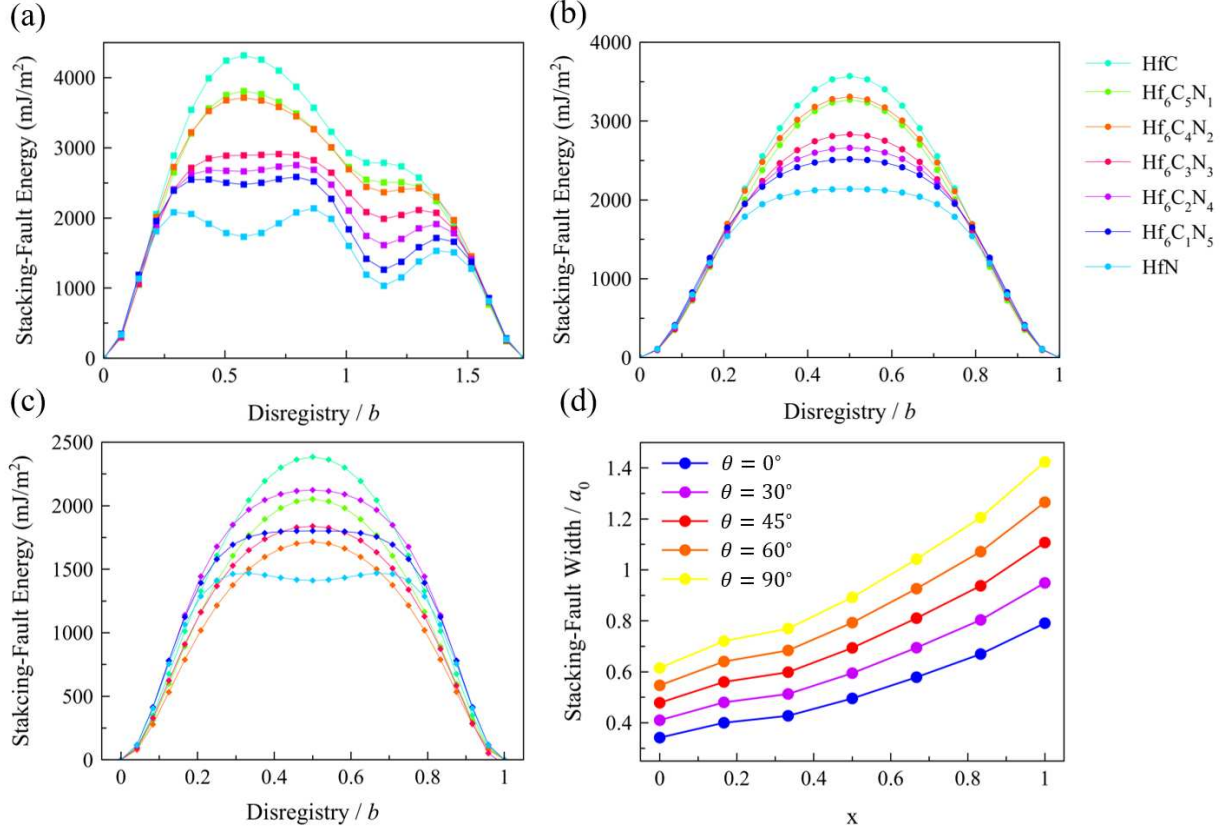


Figure 4.53: Generalized stacking-fault energies in the HfC-HfN pseudo-binary system: (a) $\langle 112 \rangle \{111\}$, (b) $\langle 110 \rangle \{110\}$ and (c) $\langle 110 \rangle \{111\}$; (d) theoretical stacking-fault widths in the HfC_{1-y}N_y system, evaluated for different dislocation characters. For the stacking-fault widths, $\theta = 0^\circ$ represents a screw dislocation and $\theta = 90^\circ$ represents an edge dislocation. Figure published previously by Watkins *et al.* [138].

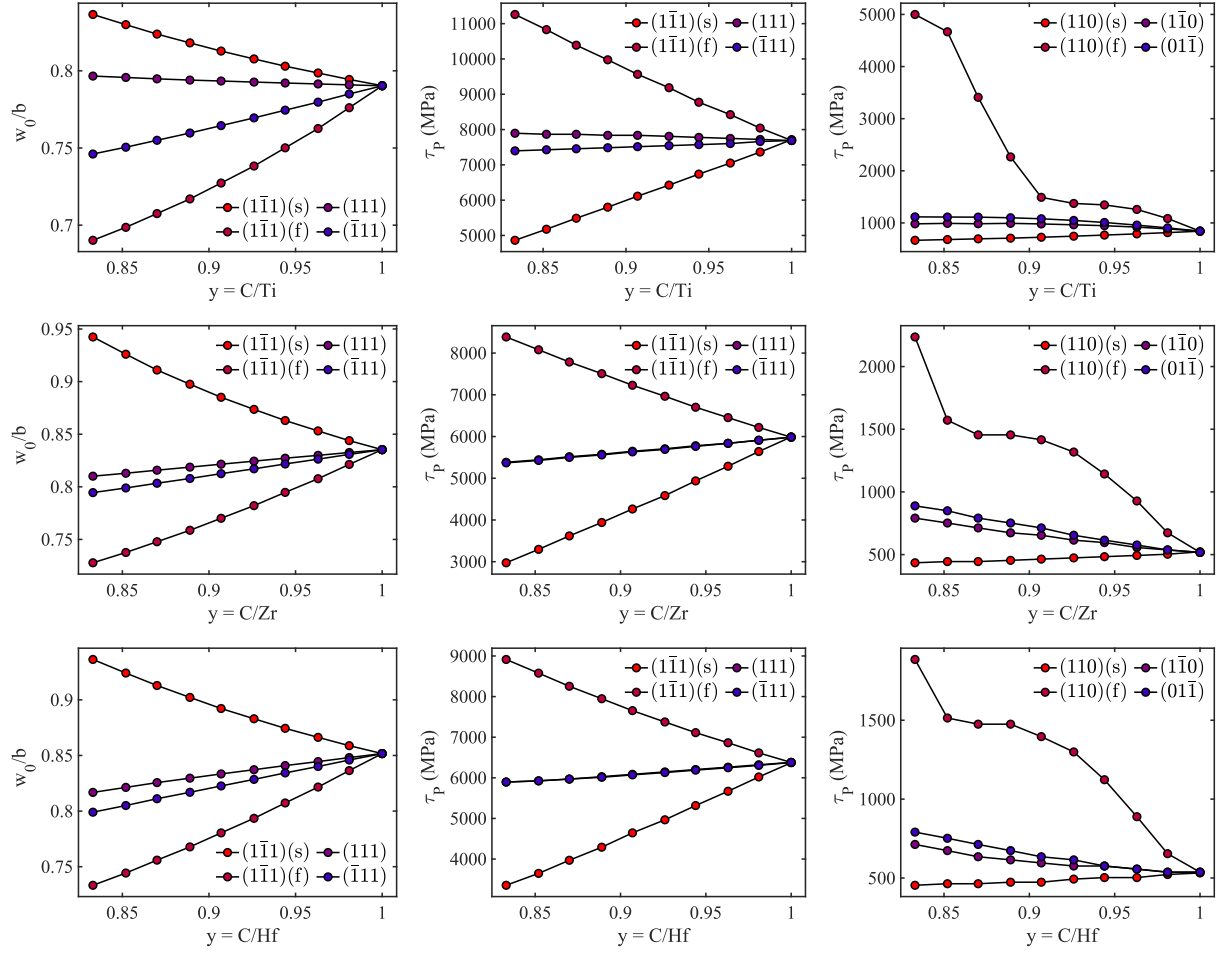


Figure 4.54: SVPN-generated Peierls stress estimates for $\langle 112 \rangle \{111\}_{B1}$, $\langle 110 \rangle \{111\}_{B1}$, and $\langle 110 \rangle \{110\}_{B1}$ slip in the IVB TMCs as a function of carbon content.

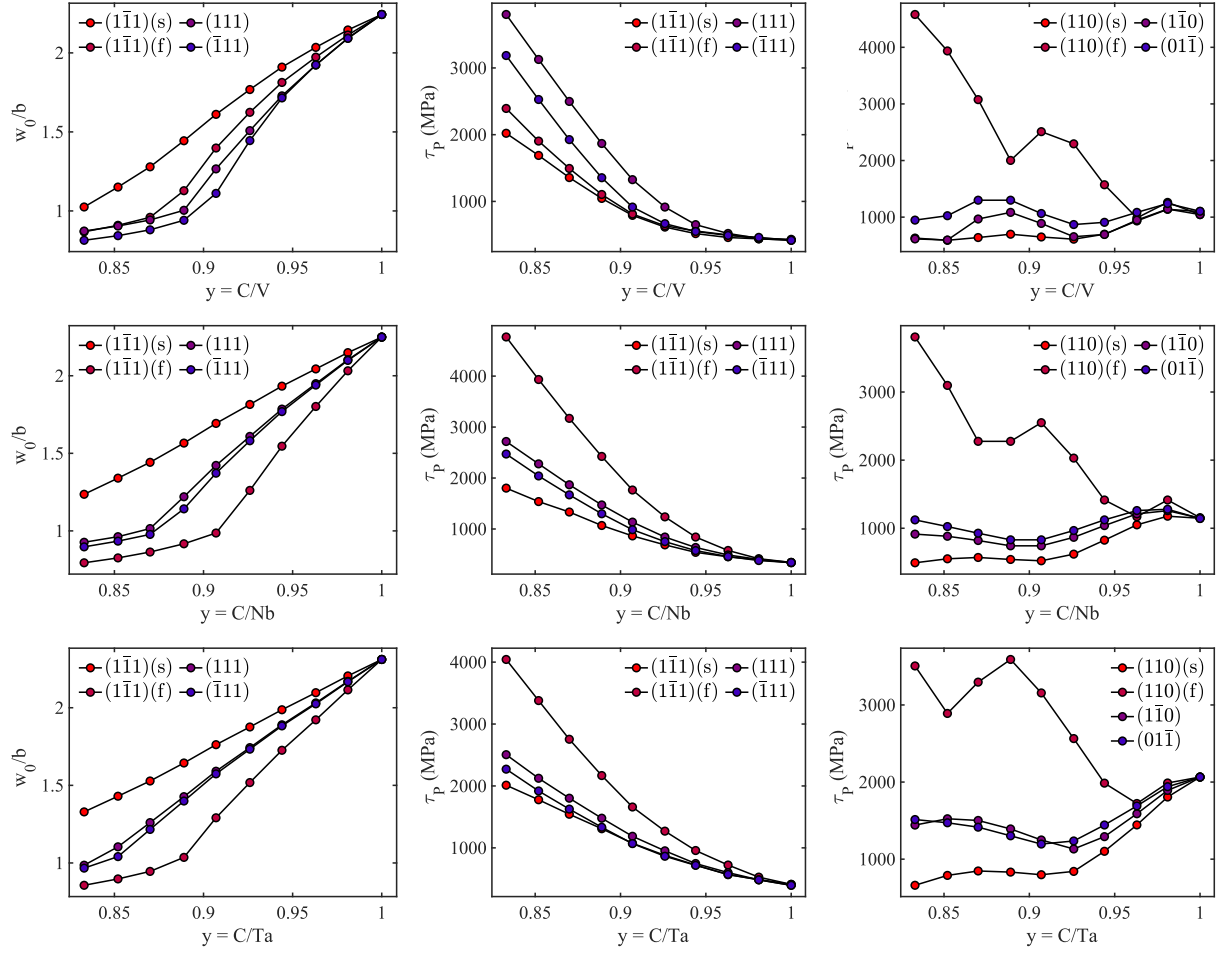


Figure 4.55: SVPN-generated Peierls stress estimates for $\langle 112 \rangle \{111\}_{B1}$, $\langle 110 \rangle \{111\}_{B1}$, and $\langle 110 \rangle \{110\}_{B1}$ slip in the VB TMCs as a function of carbon content.

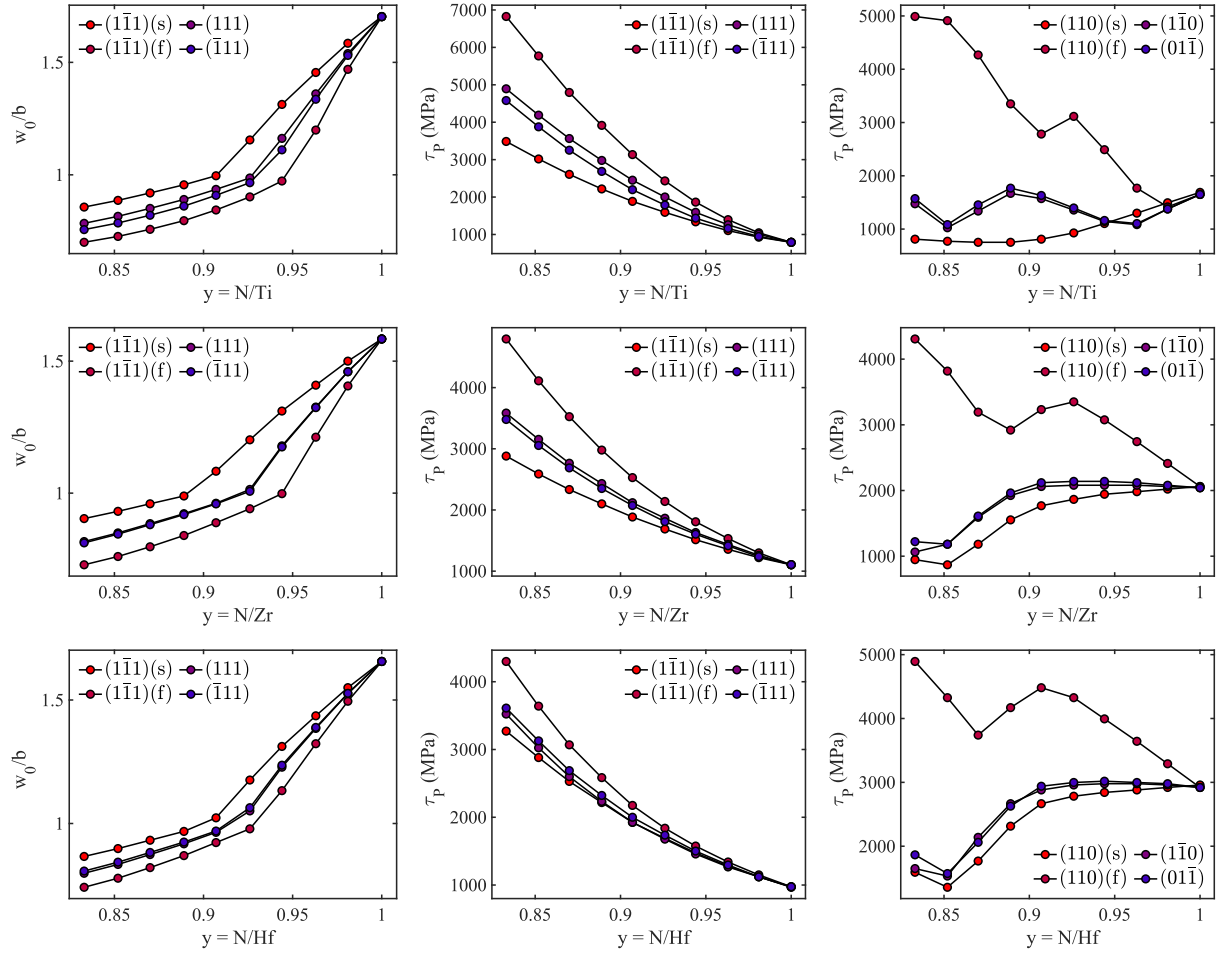


Figure 4.56: SVPN-generated Peierls stress estimates for $\langle 112 \rangle \{111\}_{\text{B1}}$, $\langle 110 \rangle \{111\}_{\text{B1}}$, and $\langle 110 \rangle \{110\}_{\text{B1}}$ slip in the IVB TMNs as a function of carbon content.

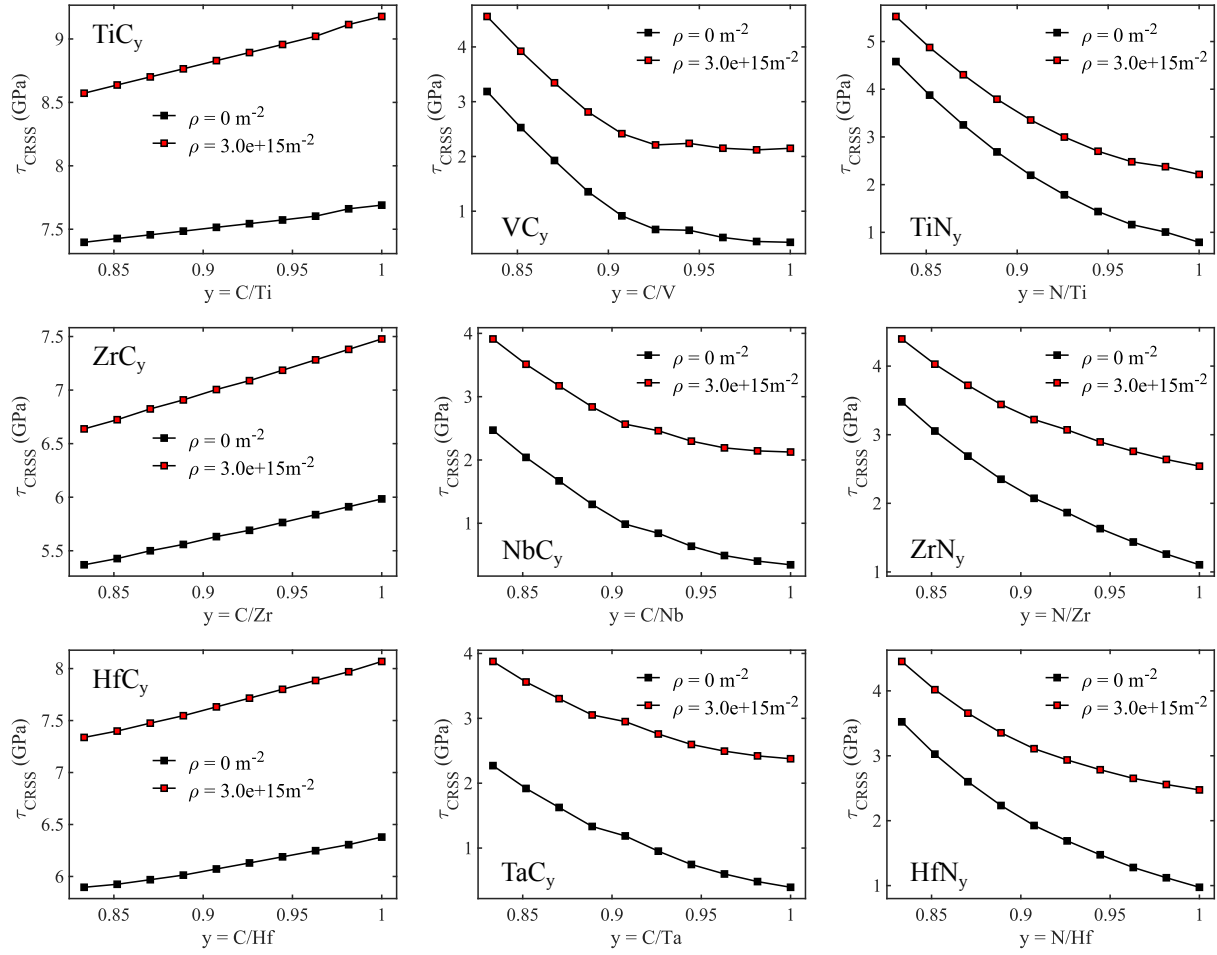


Figure 4.57: Computed effective Peierls stress, $\tau_{\text{P}}^{\text{eff}}$, estimates for rocksalt-structured carbides and nitrides. Critical resolved shear stress, τ_{CRSS} , includes strain hardening effects based on estimated dislocation density immediately below the indenter tip.

also be discussed in this section, with the caveat that those materials are generally not found to be B1-phase-stable.

In brief, our findings unsurprisingly indicate great similarity of slip behavior within each group of materials. The IVB TMCs, like TiC_y , all exhibit very high Peierls stresses on their $\{111\}_{\text{B1}}$ slip planes; furthermore, this high Peierls stress is only significantly impacted by carbon content on particular $\{111\}_{\text{B1}}$ planes, per the data included in Figure 4.54. Just as before, this is seen to arise from the fact that not all $\{111\}_{\text{B1}}$ planes in our C2/m structure have the nominal carbon content of the system. In the carbon-rich planes, τ_{P} is seen to rise with loss of carbon content, whereas in the carbon-depleted planes, τ_{P} decreases with decreasing y . It is interesting to note that, in the planes that have the nominal carbon content, the Peierls stress is affected relatively little by changes in composition. Also note the unstressed dislocation widths, which are quite small (less than one Burgers vector magnitude) in all of the IVB TMCs and at all carbon contents. This likely contributes to the relatively low mobility of dislocations on the $\{111\}_{\text{B1}}$ planes. In any case, the $\{110\}_{\text{B1}}$ Peierls stresses are generally significantly lower than those computed for the $\{111\}_{\text{B1}}$ planes, indicating a uniform preference for slip on $\{110\}_{\text{B1}}$ in the IVB TMCs. This is consistent with much of the experimental literature, which generally supports $\{110\}_{\text{B1}}$ slip at room temperature. In light of the von Mises criterion for general plasticity, though, we would expect some of the $\{111\}_{\text{B1}}$ planes to be active during an indentation event, so the *effective* Peierls stresses will likely be quite high—again, this is consistent with the observation of very high hardness in these compounds.

Similarly, the results obtained from the SVPN model for the VB TMCs are generally consistent with those previously presented for TaC_y . In all of these carbides— VC_y , NbC_y and TaC_y —the unstressed width of dislocations on $\{111\}_{\text{B1}}$ planes is typically high at the stoichiometric composition; specifically, dislocations on $\{111\}_{\text{B1}}$ planes in the stoichiometric VB TMCs are about three times wider than equivalent dislocations in the IVB TMCs, indicating greater separation of the Shockley partials bounding the stacking faults. Correspondingly, we can see in Figure 4.55 that the Peierls stress estimates for slip on $\{111\}_{\text{B1}}$ planes are low at the stoichiometric composition $y = 1$; *i.e.*,

the dislocations are highly mobile. As carbon is removed, we see a rapid decline in stacking-fault width, along with a corresponding rise in Peierls stress. Thus the mobility of dislocations on $\{111\}_{B1}$ planes is seen to lower significantly at lower carbon contents, presumably contributing to a significant increase in hardness. On the $\{110\}_{B1}$ planes, Peierls stresses decline with loss of carbon content, though the magnitude of the decline is not very large. The notable exception is the non-carbon-depleted (*i.e.*, ‘filled’) slip planes, which actually see some increase in τ_P as the global carbon content drops.

Taken together, these results are quite interesting: the IVB TMCs, with their nominal VEC of $8 e^-/\text{f.u.}$, display very high Peierls stresses on $\{111\}_{B1}$ planes, whereas the VB TMCs, nominally having $9 e^-/\text{f.u.}$, exhibit high mobility of dislocations on those same planes. Moreover, as carbon content is removed, the VB TMCs show a considerable decline in dislocation mobility on the $\{111\}_{B1}$ planes, increasing the favorability of $\{110\}_{B1}$ slip as their VEC decreases. This finding offers compelling evidence for VEC indeed being a strong determinant for mechanical properties in the cubic carbides, albeit not for the reason most often suggested by previous research. Most prior work, as discussed earlier in this manuscript, focuses on hardness enhancement by means of elastic stiffening; our results suggest that, even though decreasing VEC in the VB TMCs causes *elastic* weakening, concurrent changes in stacking-fault energies actually cause significant *plastic* strengthening. Further support for the importance of VEC can be drawn from the results discussed in Section 4.2.2, which illustrate that the γ_{SF} —and specifically γ_{ISF} —are impacted similarly by changes in VEC regardless of how those VEC changes arise.

If this conjecture is correct, we should expect to see the IVB TMNs behave rather like the VB TMCs, owing to their shared nominal VEC. And, indeed, an examination of the results contained in Figure 4.56 reveals this to be the case. Just as in the VB TMCs, the IVB TMNs exhibit wide dislocations on $\{111\}_{B1}$ planes at $y = 1$; reduction of nitrogen content narrows these dislocations rapidly, resulting in a dramatic loss of dislocation mobility on these slip planes. Furthermore, the narrowing of these dislocations appears to occur more rapidly with decreasing y in the IVB TMNs than in the VB TMCs: the loss of each N atom removes five valence electrons from the material,

as opposed to 4 valence electrons for each lost C atom, meaning that substoichiometry in the IVB TMNs decreases VEC faster than in the VB TMCs. Also of interest are the values of w_0 and τ_P at the $y = 1$, which show lower dislocation width and lower dislocation mobility than in the stoichiometric VB carbides. This is consistent with the results presented in Section 4.2.2, and with the more limited results of Yu *et al.* [92], which show the IVB TMNs to have substantially higher ISF energies than the VB TMCs.

The significance of these findings is succinctly conveyed in Figure 4.57, which shows the effective Peierls stresses, τ_P^{eff} , and critical resolved shear stresses, τ_{CRSS} , for all of these compounds. The IVB TMCs (again, with a shared nominal VEC of $8 e^-/\text{f.u.}$) all undergo a monotonic decline in effective slip resistance with loss of carbon content; the VB TMCs and IVB TMNs (sharing a nominal VEC of $9 e^-/\text{f.u.}$) all exhibit a dramatic increase in slip resistance as nonmetal atom content decreases. Thus, out of all of these compounds, we might expect only the stoichiometric VB TMCs and IVB TMNs to have low indentation hardness. The IVB TMCs, and all of the other substoichiometric carbides and nitrides shown in Figure 4.57, are predicted to have very high resistance to (general) dislocation plasticity, and thus might be expected to exhibit high indentation hardness. This would be consistent, for the most part, with experimental observation of these materials, as discussed in Section 2.2.

Consistent with the general methodology used for hardness predictions in TiC_y and TaC_y , we also computed load-depth curves, hardness-depth curves, and hardness-composition curves for all of these materials. For use in the fracture model, cleavage energies were computed for all of the cubic carbides and nitrides by our colleague Yuchen Huang; these data are included in Figure C.3 in Appendix C. All other material data were computed as part of this present work, and in fact have been presented almost in their entirety in the preceding sections of this manuscript.

The cleavage energies, γ_c , estimated for the carbides and nitrides do not offer great insight into these materials' mechanical behaviors on their own, but they are interesting enough to discuss in brief. In all of the cubic TMCs and TMNs, and at all nonmetal-to-metal atom ratios, γ_c is found to be far lower on $\{100\}_{\text{B1}}$ than on $\{111\}_{\text{B1}}$, indicating that (intragranular) crack propagation along

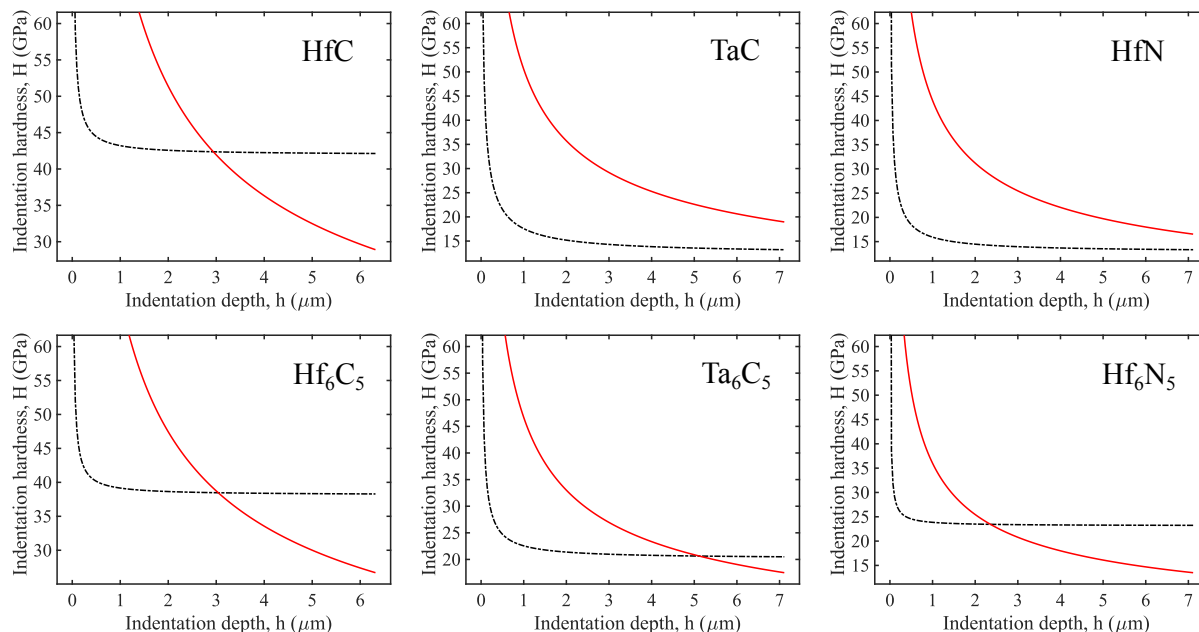


Figure 4.58: Computed hardness-depth curves for representative compounds: a IVB TMC (HfC_y), a VB TMC (TaC_y), and a IVB TMN (HfN_y). Results are shown for both the plasticity model (black lines), which depends on dislocation slip resistance, and for the fracture model (red lines), which depends on intragranular (cleavage) cracking along $\{100\}_{\text{B1}}$ planes.

$\{100\}_{\text{B1}}$ planes will always dominate. The cleavage energies are relatively similar in magnitude for all of the cubic carbides and nitrides, though a noticeable decrease occurs between the IVB TMCs and the VB TMCs, and a further decrease is seen as we move from the VB TMCs to the IVB TMNs. This suggests that cleavage cracking becomes more energetically favorable as VEC increases, due to variations in both stoichiometry and valency.

The question of how to properly parameterize the load-crack-size relationship, $P(c)$, naturally pertains to this extension of the plasticity-fracture modeling approach to the nitrides. Following from our earlier discussion of this same issue (refer to Section 4.1.7), the available experimental data for HfC was used to parameterize the fracture model for all IVB TMCs; the TaC data was used to do the same for the VB TMCs, and, since the IVB TMNs seem to behave like the VB TMCs in a great many other respects, we opted to use the TaC data to model the IVB TMNs as well. We did manage to procure experimental indentation data for a single sample of HfN (though only for one applied load, regrettably) from our experimental collaborators at the University of Alabama; this

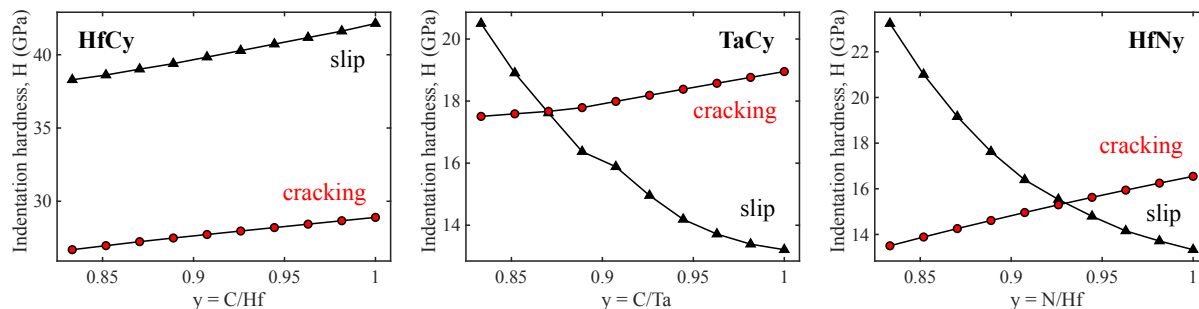


Figure 4.59: Computed hardness estimates, shown as a function of composition, for representative compounds: a IVB TMC (HfC_y), a VB TMC (TaC_y), and a IVB TMN (HfN_y). Results are shown for both the plasticity model (black markers), which depends on dislocation slip resistance, and for the fracture model (red markers).

data indicated behavior somewhat consistent with that of TaC, but it is difficult to draw conclusions from such limited testing. In any case, it was deemed best to parameterize the IVB TMN cracking models using $P(c)$ data from TaC since a far more complete dataset was available.

In any case, the representative hardness-depth curves are included in Figure 4.58; a more complete set of $H(h)$ curves (Figures D.4, D.5, and D.6) and $P(h)$ curves (Figures D.1, D.2, and D.3) for all of these cubic compounds can be found in Appendix D. The results, perhaps unsurprisingly, indicate once again a remarkable uniformity of behavior within each group of carbides or nitrides. Within the IVB TMCs, represented in Figure 4.58 by HfC_y, the hardness predicted by the fracture model is seen to drop below that predicted by the plasticity model at a certain indentation depth, indicating that fracture comes to dominate the hardness behavior. This is true in both stoichiometric HfC and substoichiometric Hf₆C₅. In stoichiometric TaC, and indeed in stoichiometric HfN, this is not the case: within the range of indent depths modeled in this work (up to about 7 μm), fracture never overtakes dislocation plasticity as the governing mechanism of hardness. That is, in TaC and HfN, the hardness predicted from dislocation slip resistance is always lower than that predicted from fracture toughness, and so these materials are likely to exhibit considerable plasticity under indentation prior to cracking. This is no longer so in the substoichiometric compounds Ta₆C₅ and Hf₆N₅, where we see behavior far more akin to that of HfC_y: as indent size grows, the hardness

predicted from cracking, H_V^c , quickly drops below that predicted from plasticity, H_V^p , suggesting that little irreversible deformation will occur prior to the onset of cracking.

These findings are illustrated more clearly in Figure 4.59, which shows hardness estimates as a function of nonmetal atom content for the same three representative materials. Here we can clearly see that in HfC_y , and in HfC_y alone, resistance to slip is always too high for plasticity to dominate, and thus fracture is the dominant failure mechanism under indentation at all sampled y . In the other compounds, this is only true at lower y : when depleted of nonmetal atoms, and consequently reduced in VEC, TaC_y and HfN_y are also prone to accommodate indentation via cracking. However, at higher y , these compounds are capable of accommodating irreversible deformation via dislocation plasticity, owing to their highly mobile dislocations on $\{111\}_{\text{B1}}$ planes. Thus, while the governing mechanism of hardness in HfC_y prescribes a gradual decline in H_V with loss of carbon content, both TaC_y and HfN_y see an initial *increase* in hardness, followed by a subsequent decrease as a transition to cracking-dominated failure at some substoichiometric y . Examination of these same results for all of the cubic carbides and nitrides, contained in Figure D.7, shows these trends to hold for all compounds within each group. The IVB carbides are expected to exhibit brittle behavior at all carbon contents, preferring fracture to slip and therefore undergoing monotonic, roughly linear declines in hardness with loss of carbon content. The VB TMCs and IVB TMNs, in contrast, exhibit a transition from plasticity-dominated behavior to fracture-dominated behavior at some $y < 1$, resulting in an ‘anomalous’ peak hardness at the transition point.

Mixed Transition-Metal Carbides

Repetition of the now-familiar plasticity-fracture-comparison approach yields somewhat unsurprising results for the mixed hafnium-tantalum carbides, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$. But first, a note on methodology. As discussed in Section 4.1.7, parameterization of the fracture model for each group of materials depends (regrettably, from the theorist’s point of view) on experimental observations of the load-crack-size relationship; *i.e.*, the $P(c)$ or $P(l)$ relationship. While the experimental data provided by our collaborator, Alyssa Stubbers, allows for separate parameterization of IVB TMCs (using the HfC data) and VB TMCs (using the TaC data), it is not quite so clear what to do about

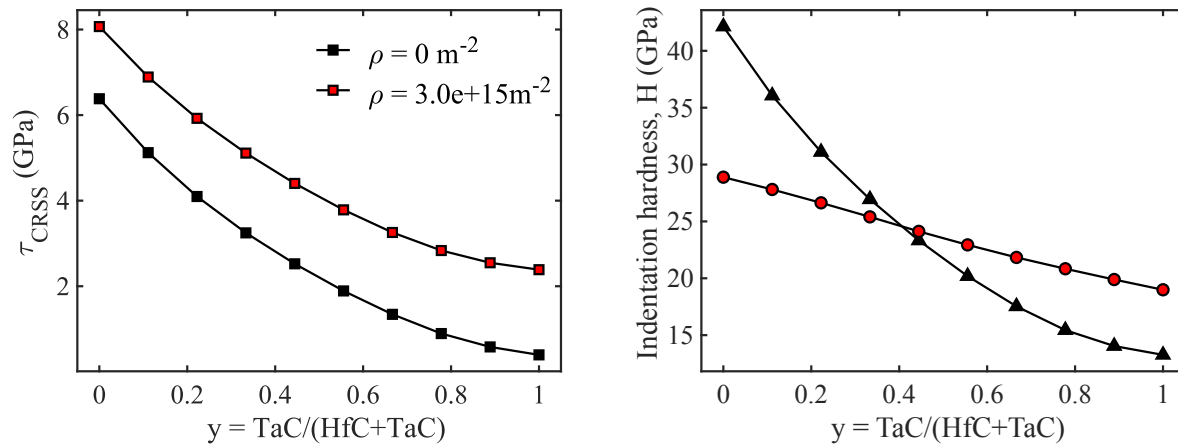


Figure 4.60: Computed critical resolved shear stress, τ_{CRSS} , and theoretical Vickers hardness estimates for the alloyed hafnium-tantalum carbides, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$.

the other compounds. As was mentioned in the previous section, the IVB TMNs were modeled using the experimental data for TaC, since the IVB TMNs and the VB TMCs generally behave quite similarly to each other. In the case of the hafnium-tantalum carbides, though, we would have reason to suspect that each terminal compound will behave according to its own experimental parameterization—in fact, this must be the case, as we have already modeled both HfC and TaC. In order to maintain consistency with our previous modeling effort, then, we opted to interpolate the crack sizes linearly between those of the terminal compounds, and thereby obtained estimates for $c(h)$ at the intermediate compositions.

Using this approach, we obtained the results shown in Figure 4.60, which indicate a fairly intuitive transition from the fracture-dominated behavior of HfC at $y = 0$ to the plasticity-dominated behavior of TaC at $y = 1$. As expected per our hypothesis, increasing VEC on $\text{VEC} \in [8, 9]$ $e^-/\text{f.u.}$ results in increasing availability of generalized plasticity—arising from dramatically reduced Peierls stresses on $\{111\}_{\text{B1}}$ planes, which in turn arise from increased energetic favorability of stacking faults—and eventually causes a transition from fracture dominance to slip dominance at a VEC of around $8.4 e^-/\text{f.u.}$ Though our modeling approach does not seem to suggest a maximum hardness at this composition, as some prior work has presumed, it is interesting to note that the overall hardness trend is reasonably consistent with the experimental findings of Smith *et*

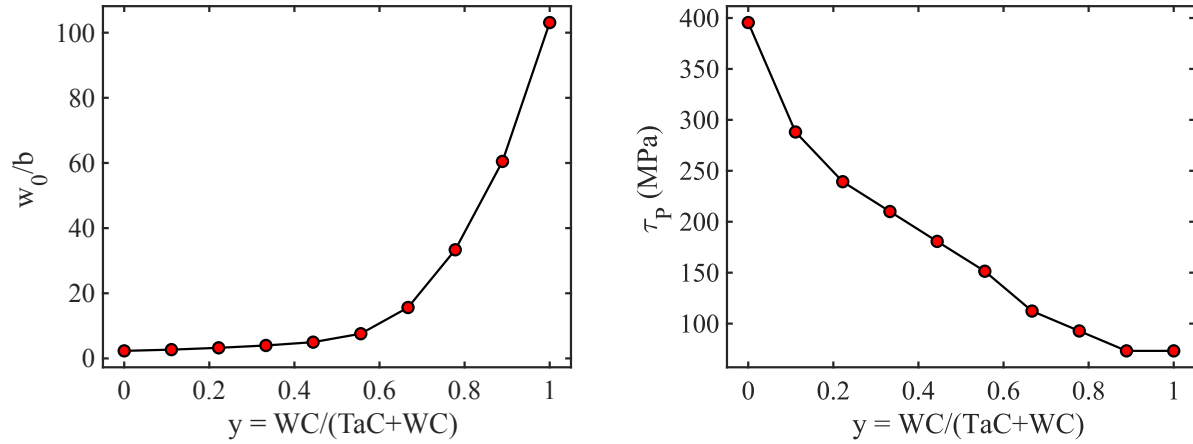


Figure 4.61: SVPN-computed stacking-fault widths and Peierls stresses on $\{111\}_{B1}$ planes in the alloyed tantalum-tungsten carbides, $Ta_{1-y}W_yC$.

al. [93]. This is not too surprising, as dislocation densities estimated from the findings of this same previous work were used to parameterize the plasticity model, but it is nonetheless satisfying to see some agreement with experimental results. Furthermore, although the data of Smith *et al.* has been used to claim an peak hardness at some intermediate-composition HfC-TaC alloy, the error bars on these experimental data are so large as to render such a claim spurious.

We have also modeled the tantalum-tungsten carbides, $Ta_{1-y}W_yC$, in order to examine the effects of VEC modification over the domain $VEC \in [9, 10] e^-/\text{f.u.}$ Unlike in the HfC-TaC system, which develops a metastable ISF as VEC increases, the TaC-WC system develops a *stable* ISF at higher y ; this is because WC is not thermodynamically stable in the rocksalt structure at low temperatures, instead preferring the trigonal prismatic coordination environment of the B_h structure. Thus we would expect very wide stacking faults—essentially phase-transforming the entire slip plane, if the simulation were performed with an infinitely large modeling volume—and correspondingly very low Peierls stresses on $\{111\}_{B1}$ planes. And, indeed, the SVPN model results in Figure 4.61 show that, as y increases, the equilibrium stacking-fault width w_0 increases from around $2b$ to over 100 Burgers vector magnitudes: in essence, the slip plane is undergoing a local phase transformation from the octahedral coordination of the $B1$ structure to the B_h , limited only by interactions with the boundaries of the simulation volume (which is $200b \times 200b$). Concurrent

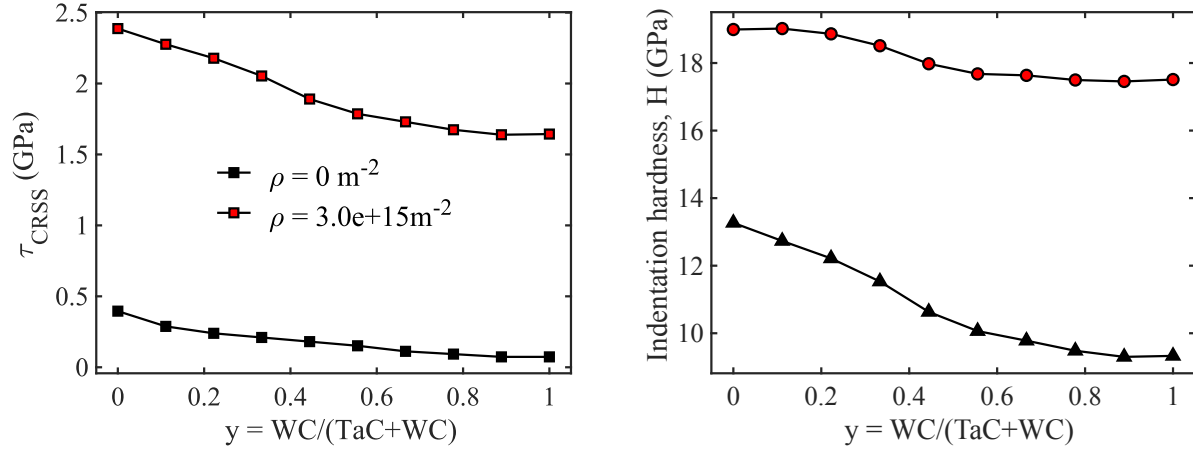


Figure 4.62: Computed critical resolved shear stress, τ_{CRSS} , and theoretical Vickers hardness estimates for the alloyed tantalum-tungsten carbides, $\text{Ta}_{1-y}\text{W}_y\text{C}$.

with this change is a precipitous decline in Peierls stress (also shown in Figure 4.61), from the already-low slip resistance of TaC to only about 70 MPa in B1 WC.

This evolution is also seen in the effective Peierls stresses and CRSS estimates in Figure 4.62. As VEC increases from 9 to 10 $e^-/\text{f.u.}$, the stress required for general plastic deformation decreases dramatically, and the corresponding Hardness estimates are low over the whole composition range. Unsurprisingly, then, dislocation plasticity is predicted to dominate the hardness behavior of the tantalum-tungsten carbides at all modeled compositions—intragranular fracture never becomes energetically competitive due to the extremely high dislocation mobility.

Transition-Metal Carbonitrides

The hafnium carbonitrides, $\text{HfC}_{1-y}\text{N}_y$, were modeled in exactly the same way as the hafnium-tantalum carbides discussed in the previous section. The cracking behavior of HfC was parameterized using experimental HfC data, while HfN was parameterized using data from TaC; intermediate compositions used a $c(h)$ interpolated linearly between the terminal compounds' data. The results, shown in Figure 4.63, display behavior quite similar to that of our representative alloyed carbide system, with the brittle, cracking-dominated behavior of HfC ultimately giving way to the more locally plastic behavior of HfN as VEC increases. The transition appears to occur at a slightly

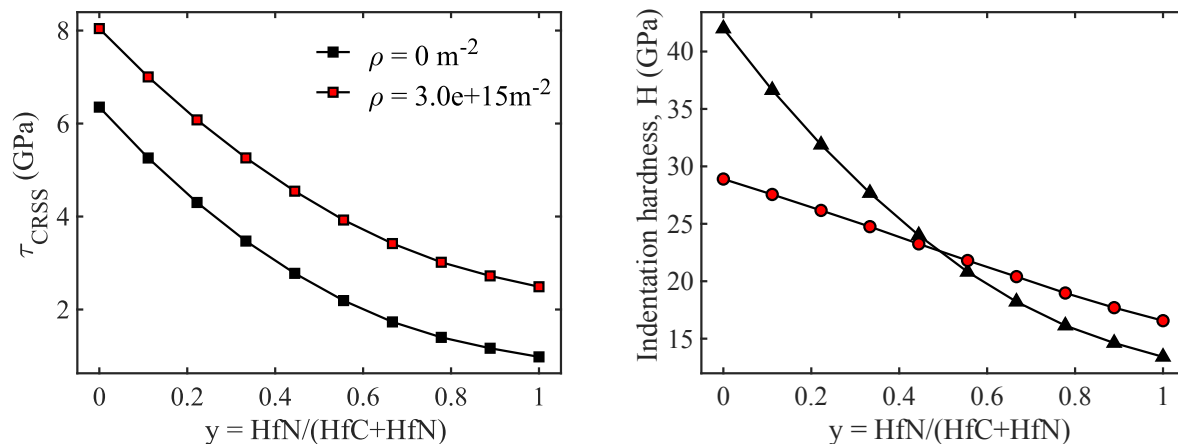


Figure 4.63: Computed critical resolved shear stress, τ_{CRSS} , and theoretical Vickers hardness estimates for the hafnium carbonitrides, $\text{HfC}_{1-y}\text{N}_y$.

higher VEC in this system, with plasticity overtaking fracture as the dominant failure mechanism at compositions where VEC exceeds approximately $8.5 e^-/\text{f.u.}$

Though this finding is likely, at this point in our discussion, not surprising in the least, it is nonetheless a crucial part of our analysis. Our work thus far on the substoichiometric TMCs and TMNs, alloyed TMCs, and TMCNs does a great deal to address one of our main research questions: do VEC alterations via substoichiometry, nonmetal atom substitution, and metal atom substitution have meaningfully different effects on predicted mechanical properties? From our work thus far, it appears that the answer to this question is no. That is, the same changes in mechanical behavior—specifically, the material’s resistance to localized plastic deformation—seem to occur within the same VEC range irrespective of how VEC tailoring is achieved.

4.3 Electronic Structure of the TMCs, TMNs and TMCNs

In order to gain insights into the stabilization of stacking faults at higher VEC in the cubic TMCs and TMNs, detailed electronic structure analyses have been performed on a multitude of these materials. Per the hypothesis laid out in the Research Proposal, it was anticipated that there would be discernible differences in the contributions of different atomic orbitals (AOs) to the band structure energy between the un-faulted (B_1) and faulted (B_h) structures across a range of VEC

values. It was furthermore proposed that the B_h structure would be stabilized relative to the B₁ at higher VEC as the band structure energy was reduced by means of bonding *d*-AO overlaps between metal atoms, and that the nature of the metal-nonmetal interactions would not meaningfully change with increasing VEC. In other words, it was expected that the B_h structure would become favorable at higher VEC due to increased metal-metal bonding interactions.

The following sections will detail our findings from the electronic structure analysis, ranging from basic electronic density-of-states (DoS) to highly detailed orbital-wise band structure energy contributions; this document will detail results for a wide range of cubic TMCs and TMNs at various VEC, and will additionally investigate trends in band structure energy contributions in substoichiometric TMCs and TMNs.

4.3.1 Stoichiometric Transition-Metal Carbides and Nitrides

Metal-Metal and Metal-Nonmetal Interactions

The electronic DoS plots for the TMCs and TMNs (see Appendix E) do not reveal much beyond what is already known about these compounds. All of the IVB, VB and VIB TMCs, and the IVB and VB TMNs, exhibit continuous DoS through the Fermi level, ϵ_F , indicating that they are electrical conductors. The metal-nonmetal (M-X) interaction plots show reasonably well-defined peaks, meaning that assignment of energy levels to particular interactions may not be too difficult. Unfortunately, the metal-metal (M-M) interactions do not generally have well-defined peaks, so the possibility of readily assigning energies to different atom pair (or AO pair) interactions is somewhat more distant. While inconvenient, this is not necessarily an obstacle to our answering our research question—after all, the electronic DoS on its own reveals relatively little about the character and strength of different bonding (or antibonding, for that matter) interactions within the material. Rather, software such as the Local Orbital Basis Suite Toward Electronic-structure Reconstruction (LOBSTER) package can be used to obtain far more information by means of resolving the site-projected DoS (the pDoS) onto the expected spherical harmonics (AOs expected per the hydrogen atom model) at each site. This analysis can be used to procure information such

as partial charges and population analyses, and (more importantly) to partition the pDoS into bonding and antibonding interactions—either by electron charge (COOP) or by band structure energy contribution (COHP). Moreover, these quantities can be integrated from the lower energy bound of DoS calculation—ideally equal to $-\infty$, but of course this is not the case in practice—to give some impression of the net bonding/antibonding contribution of various atom-atom interactions or AO-AO overlaps.

The LOBSTER-computed pCOOP results are somewhat more interesting than the DoS. Data for the rocksalt-structured IVB and VB TMCs, shown in Figures E.5 and E.6, reveal very similar-looking distributions, indicating very similar bonding overall. The results for the IVB and VB TMNs, shown in Figure E.7 and E.8, likewise indicate great similarity between all of the B1 nitrides. What is superficially interesting about these results is that the TMCs and TMNs are more similar to themselves than to one another despite the variation in VEC within each collection of compounds. In the carbides, the bonding peaks (pCOOP values greater than zero) are well-differentiated, with a large bimodal peak occurring just below the Fermi level and a smaller monomodal peak situated around 10 eV below the Fermi level. The nitrides show a similar bimodal peak—further below the Fermi level than in the carbides, since the addition of electrons in the B1 structure essentially has the effect of raising the Fermi level—with the smaller peak being absent within the 15 eV energy range sampled below the Fermi level. It should be noted that in the VB TMCs, and in the IVB and VB TMNs, both the M-M and M-X interactions transition from bonding to antibonding below the Fermi level, whereas in the IVB TMCs this transition only occurs above ϵ_F . This could indicate a slight reduction in overall bond strength in the VB TMCs and IVB and VB TMNs, though from these results the difference seems slight.

More informative than a simple pCOOP analysis of the B1 structure is a comparison against the same series of compounds modeled in the B_h structure. The B_h carbide and nitride pCOOP results—shown in Figures E.9, E.10, E.11 and E.11, and summarized with selected compounds in Figures 4.65, 4.67, 4.66 and 4.68—all clearly show the same peaks, just shifted vertically according to the number of valence electrons. Interestingly, the similarity in pCOOP distribution morphology

within the B_h -structured TMCs and TMNs seems to be greater than that seen in the B1-structured compounds. A sharp, narrow pCOOP peak is present near ϵ_F in all of the B_h TMCs and TMNs; the positive value of this peak indicates that it is a bonding interaction, and as VEC increases in the B_h structure this peak can be seen to drop below the Fermi level. The significance of this observation is that, in the IVB TMCs, this bonding AO overlap is unoccupied in the ground state, whereas it is occupied in all of the other compounds (the VB TMCs, IVB TMNs and VB TMNs). The raising of the Fermi level to populate this bonding state at higher VEC may have the effect of stabilizing the B_h structure relative to the B1, since no discernible change in bonding/antibonding character can be readily inferred from the B1 pCOOP/IpCOOP alone.

To know whether the differences discussed in the preceding paragraph really have a discernible impact on the relative stability of the B1 and B_h phases, the LOBSTER-computed pCOHP (and IpCOHP) may be examined. As discussed in Section 2.5, this weighting of the pDoS actually partitions the band structure energy, rather than the electron charge, into bonding and antibonding contributions, with the caveat that the sign convention is opposite that of the pCOOP/IpCOOP. The pCOHP results for the B1 compounds (seen in Figures E.13, E.14, E.15 and E.16) shows the same general collection of peaks, intuitively shifted down relative to the Fermi level as the VEC increases; likewise, the B_h compounds appear to have roughly the same pCOHP distribution, again shifted relative to ϵ_F with variations in VEC (see Figures E.17, E.18, E.19 and E.20). This is illustrated more clearly in Figures 4.69 and 4.70, which show pCOHP data for selected compounds with $VEC \in [8, 10] e^-/\text{f.u.}$ in both atomic coordination environments. In the B1 structure, this Fermi level shift causes the occupation of a small, diffuse M-M bonding interaction—partially compensated by a M-X antibonding interaction—as VEC rises. Since the increase in bonding interactions between the metal atoms outstrips the growth of the antibonding interactions between metal and nonmetal atoms, this contributes to a general increase in covalent bond strength in the B1 structure at higher VEC. This is contrary to the hypothesis put forward by researchers decades ago (see Section 2.2), which posits that increasing VEC in the rocksalt structure results in the population of antibonding states (with no change in bonding state occupation) and thereby mechanically

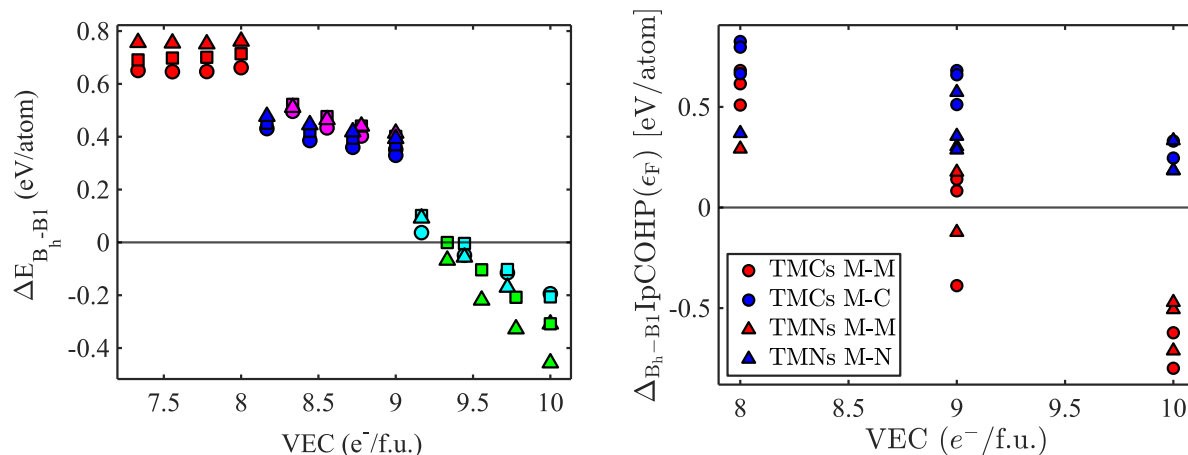


Figure 4.64: Comparison of trends in (left) structural energy differences and (right) $\text{IpCOHP}(\epsilon_F)$ between B1- and B_h -structured carbides and nitrides. In the left figure, red markers denote IVB TMCs, magenta markers denote VB TMCs, blue markers denote IVB TMNs, cyan markers denote VB TMNs, and green markers denote VIB TMCs. In the right figure, data are separated into metal-metal (M-M) and metal-nonmetal (M-X) interactions.

weakens the crystal. Nonetheless, the trend can be seen clearly in the included IpCOHP plots: as increasing VEC raises the Fermi level, a slight decline in M-X bonding interactions is outstripped by a marked increase in M-M bonding interactions, indicating overall higher bond strength.

The pCOHP distributions for the B_h structure are even more revealing. Just as with the pCOOP results discussed earlier, there is a large peak—with a bonding character, indicated in this case by its negative value—near ϵ_F in all of the carbides and nitrides. In the IVB TMCs ($\text{VEC} = 8 e^-/\text{f.u.}$), this peak is completely above the Fermi level, indicating that it will be unoccupied in the ground state. In the VB TMCs and IVB TMNs ($\text{VEC} = 9 e^-/\text{f.u.}$), the peak is almost perfectly centered on ϵ_F , and in the VB TMNs ($\text{VEC} = 10 e^-/\text{f.u.}$) the peak is seen to fall completely below the Fermi level. In other words, raising ϵ_F by means of increasing VEC in the B_h TMCs and TMNs has the effect of populating a significant bonding interaction between metal atoms; this is only slightly mitigated by a small increase in antibonding interactions between the metal and nonmetal atoms.

These findings are intriguing for a number of reasons. First and foremost is that the oft-proposed loss of bond strength in the B1 TMCs and TMNs at higher VEC is not indicated by the pCOOP and pCOHP analyses. Second is that the overall bond strength—as seen in the reduc-

tion in band structure energy—actually appears to *increase* non-negligibly in both the B1 and B_h structures as the Fermi level rises. These findings, taken together, suggest that changes in mechanical properties in these materials arise not from a general weakening or strengthening of bonds within the crystal, but rather from an evolving energetic competition between two different atomic coordination environments. Furthermore, this implication superficially bolsters our general claim that the differences in mechanical behavior among the carbides and nitrides arise from dislocation mechanics, since the energetic competition between the octahedral (B1) and trigonal prismatic (B_h) coordination environments is most immediately relevant to a discussion of stacking-fault energies.

In fact, an aggregation of DFT-computed structural energy differences, ΔE_{B_h-B1} can be seen in Figure 4.64; these data show a trend much like that observed in our much-discussed γ_{ISF} values, with ΔE_{B_h-B1} appearing to decline rapidly with increasing VEC. Similar to γ_{ISF} trend shown in Figure 4.52, the structural energy difference drops below zero at some VEC between 9 and 9.5 $e^-/\text{f.u.}$, indicating a shift toward B_h phase stability at higher VEC. Also shown in Figure 4.64 are aggregated differences in $\text{IpCOHP}(\epsilon_F)$ computed for various carbides and nitrides; these data indicate a very similar trend. Keep in mind that for Δ_{B_h-B1} , a positive value indicates a net antibonding difference, equivalent to a higher band structure energy in the B_h structure. This being stated, the data shown in Figure 4.64 show a reduction in energetic preference for the B1 structure as VEC increases, again transitioning to a preference for the B_h structure beyond about 9 $e^-/\text{f.u.}$ Furthermore, these data are separated into metal-metal (M-M) and metal-nonmetal (M-X) interaction differences, clearly illustrating that, based on M-X interactions alone, the B1 structure is always preferred; that is, the B1 structure always has greater net bonding M-X interactions than the B_h structure. As VEC increases, though, the M-M interactions trend toward a preference for trigonal prismatic coordination, producing stronger M-M bonding in the B_h structure at VEC greater than 9 $e^-/\text{f.u.}$ Thus, when both M-M and M-X interactions are considered, the energetic preference for the octahedral coordination environment of the B1 structure declines with increasing VEC, leading to the stabilization of intrinsic stacking faults as the trigonal prismatic coordination environment becomes more favorable.

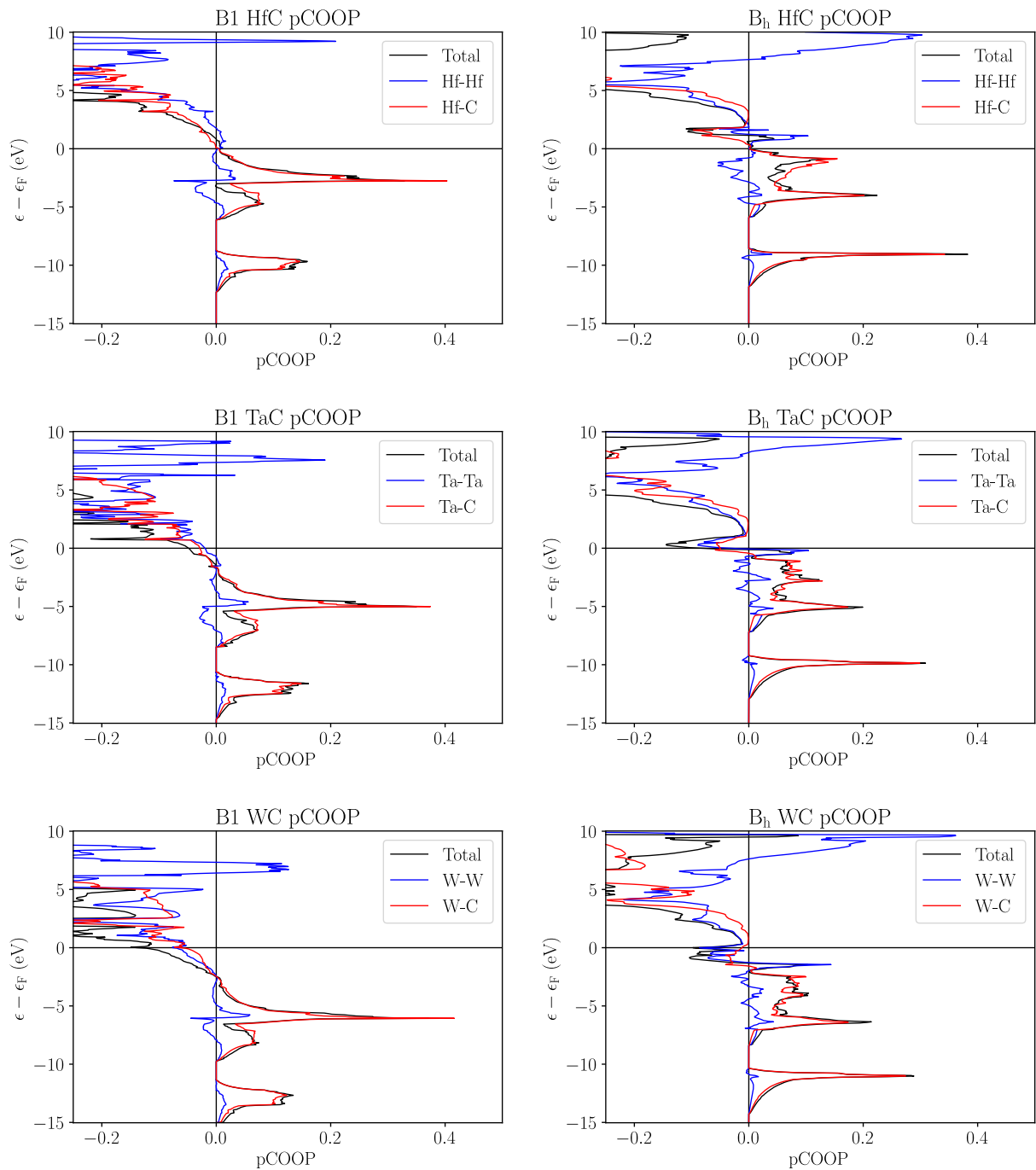


Figure 4.65: Computed pCOOP for selected TMCs: HfC (VEC= $8 e^-/\text{f.u.}$), TaC (VEC= $9 e^-/\text{f.u.}$), and WC (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant pCOOP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

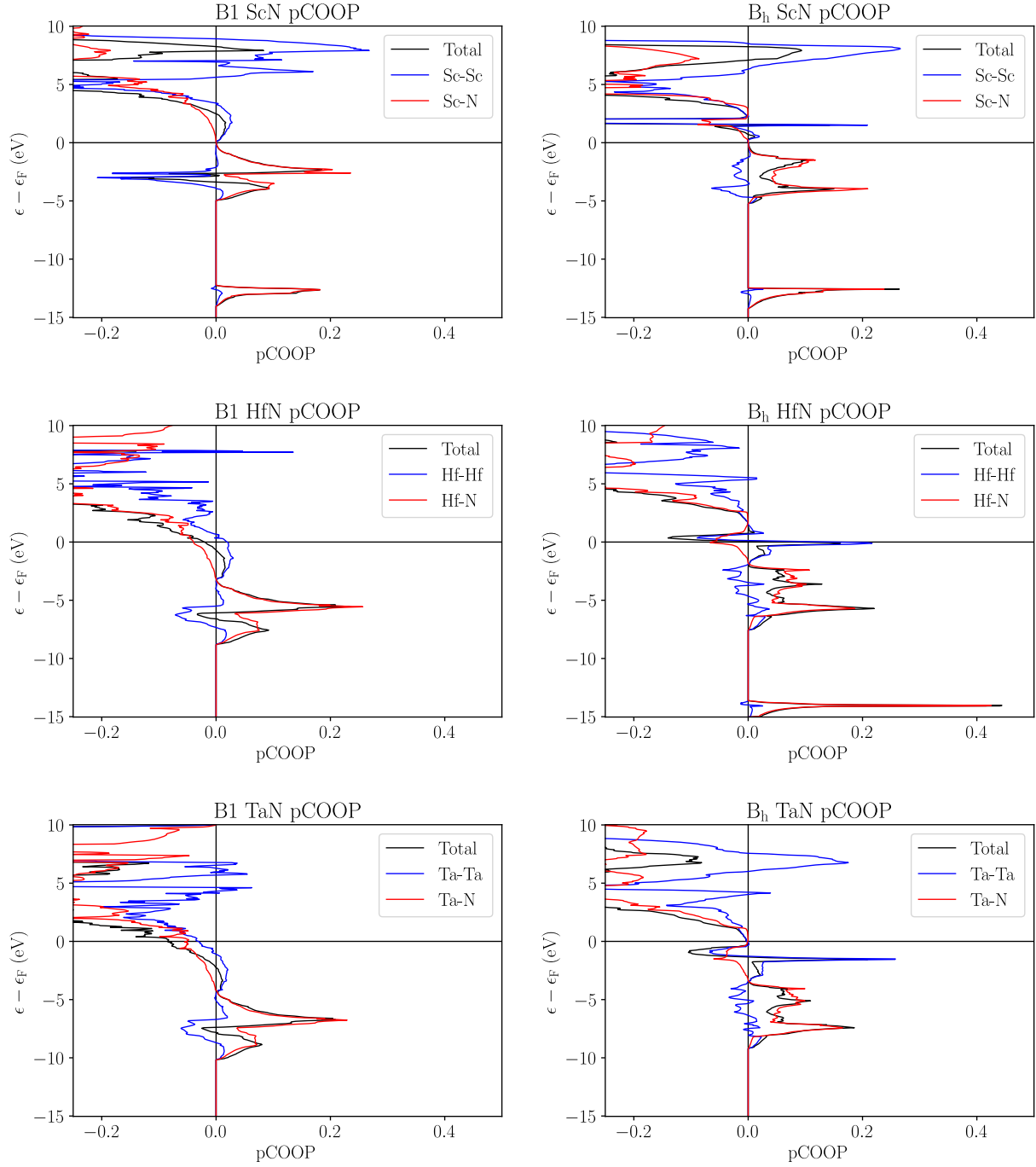


Figure 4.66: Computed pCOOP for selected TMNs: ScN (VEC= $8 e^-/\text{f.u.}$), HfN (VEC= $9 e^-/\text{f.u.}$), and TaN (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant pCOOP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

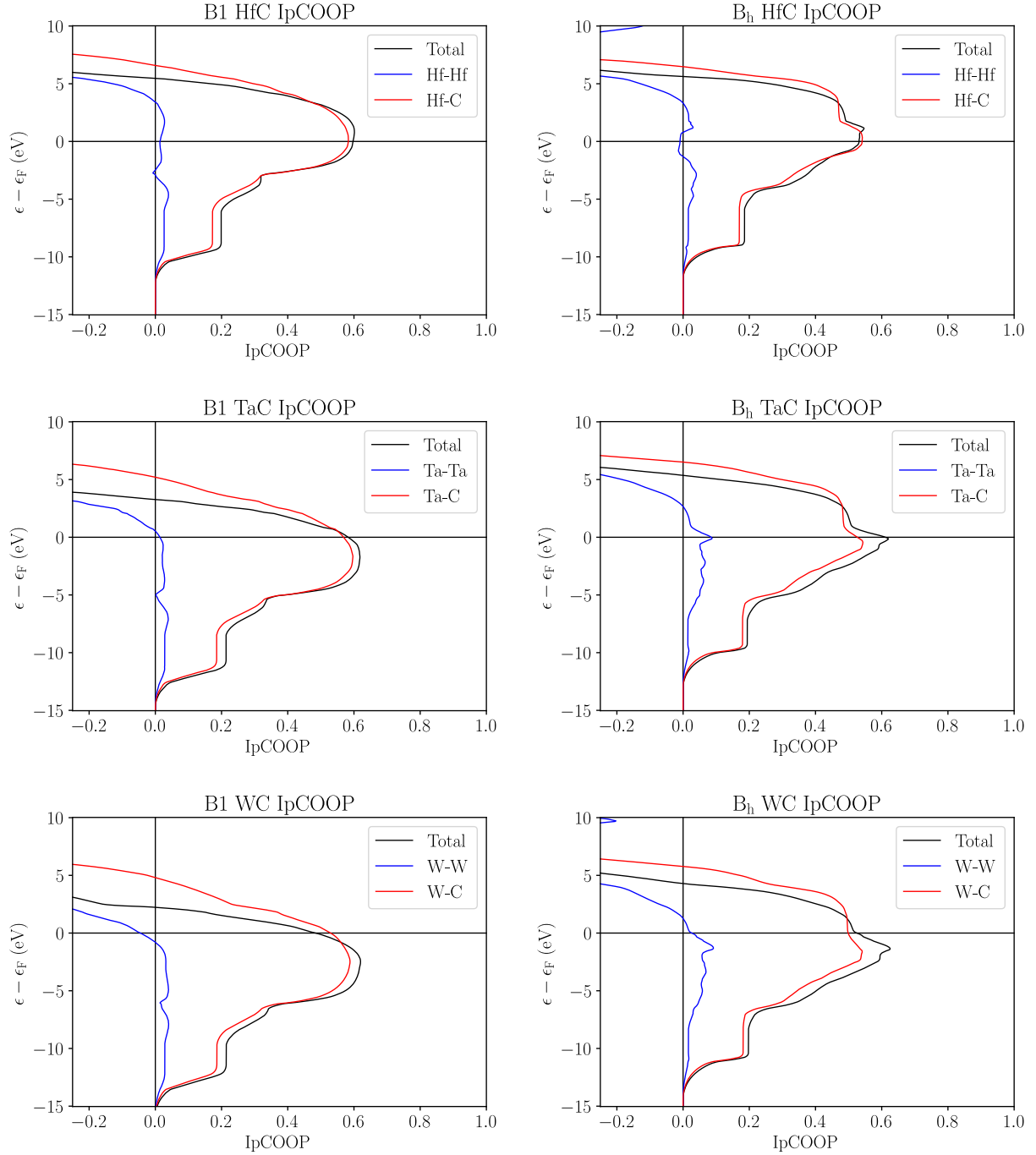


Figure 4.67: Computed IpCOOP for selected TMCs: HfC (VEC= $8 e^-/\text{f.u.}$), TaC (VEC= $9 e^-/\text{f.u.}$), and WC (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant IpCOOP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

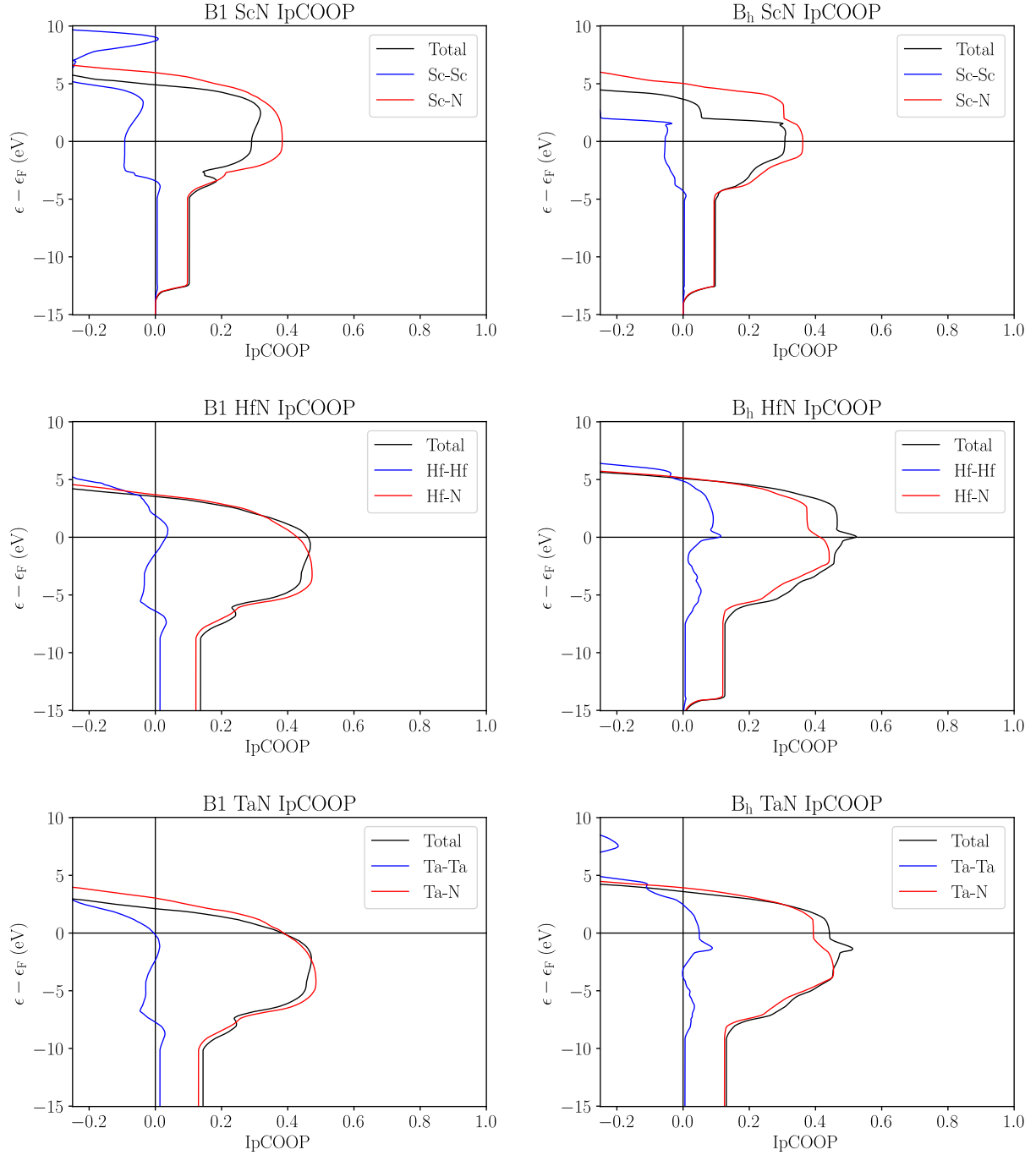


Figure 4.68: Computed IpCOOP for selected TMNs: ScN (VEC= $8 e^-/\text{f.u.}$), HfN (VEC= $9 e^-/\text{f.u.}$), and TaN (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant IpCOOP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

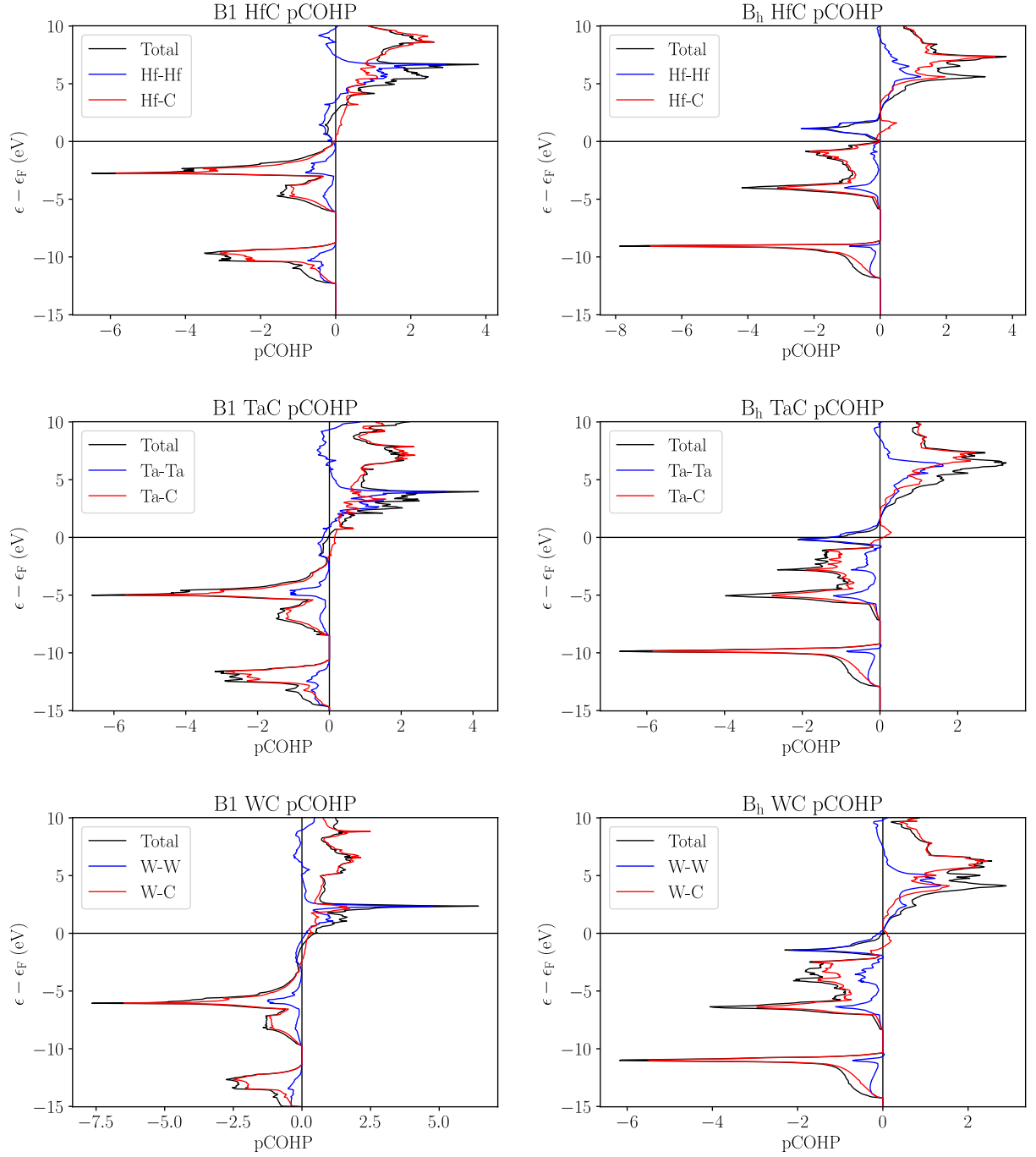


Figure 4.69: Computed pCOHP for selected TMCs: HfC (VEC= $8 e^-/\text{f.u.}$), TaC (VEC= $9 e^-/\text{f.u.}$), and WC (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant pCOHP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

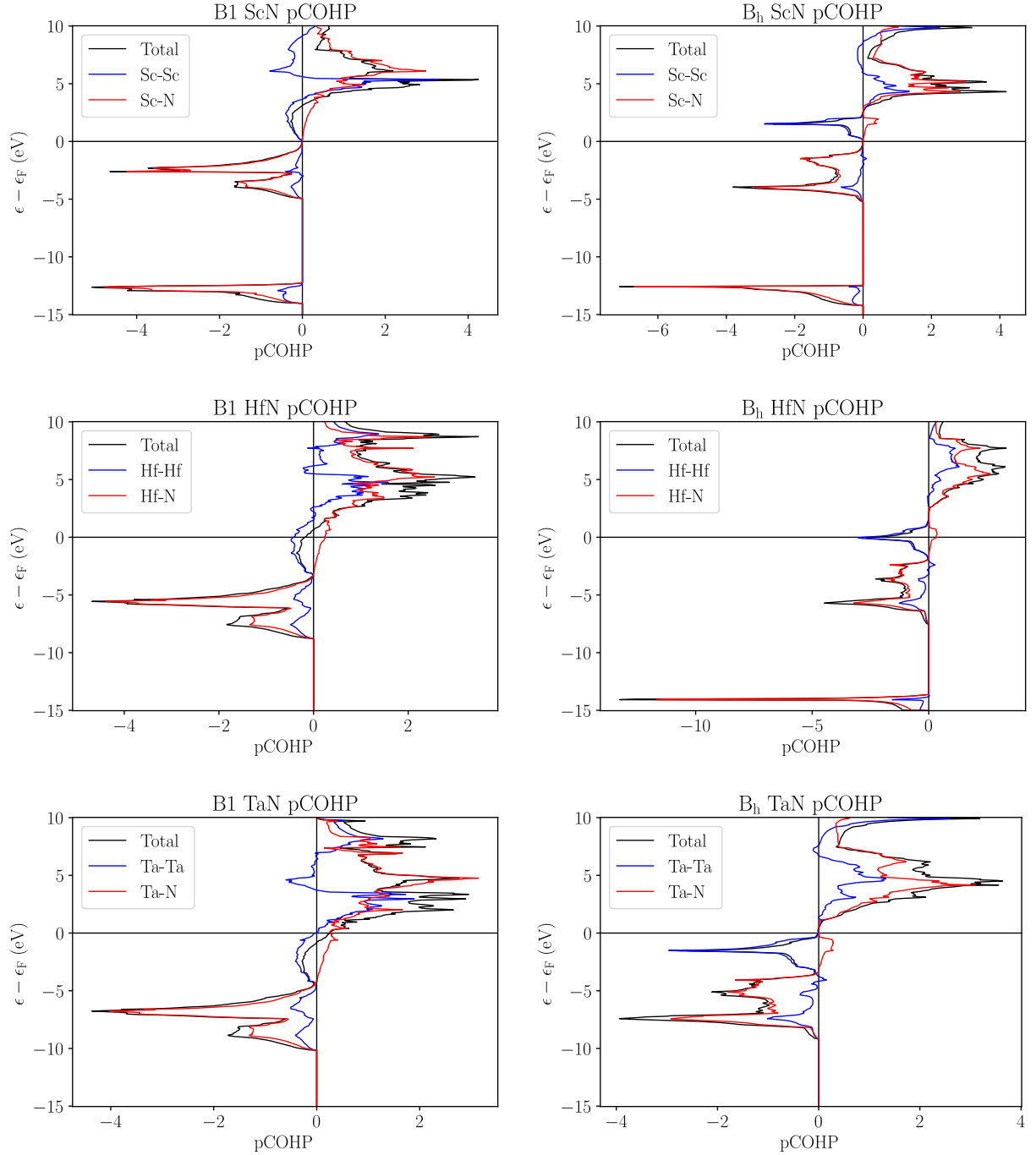


Figure 4.70: Computed pCOHP for selected TMNs: ScN (VEC= $8 e^-/\text{f.u.}$), HfN (VEC= $9 e^-/\text{f.u.}$), and TaN (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant pCOHP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

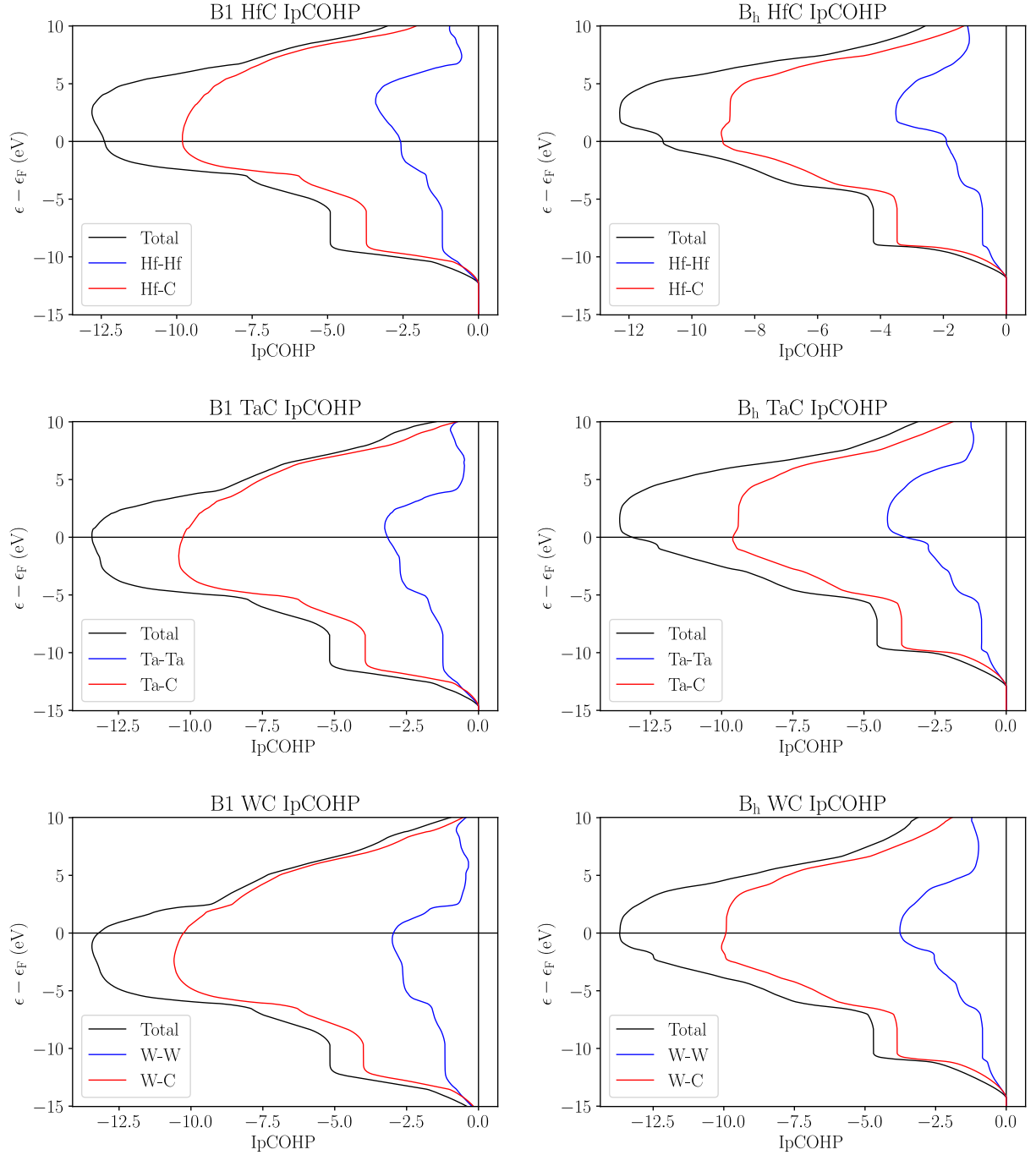


Figure 4.71: Computed IpCOHP for selected TMCs: HfC (VEC= $8 e^-/\text{f.u.}$), TaC (VEC= $9 e^-/\text{f.u.}$), and WC (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant IpCOHP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

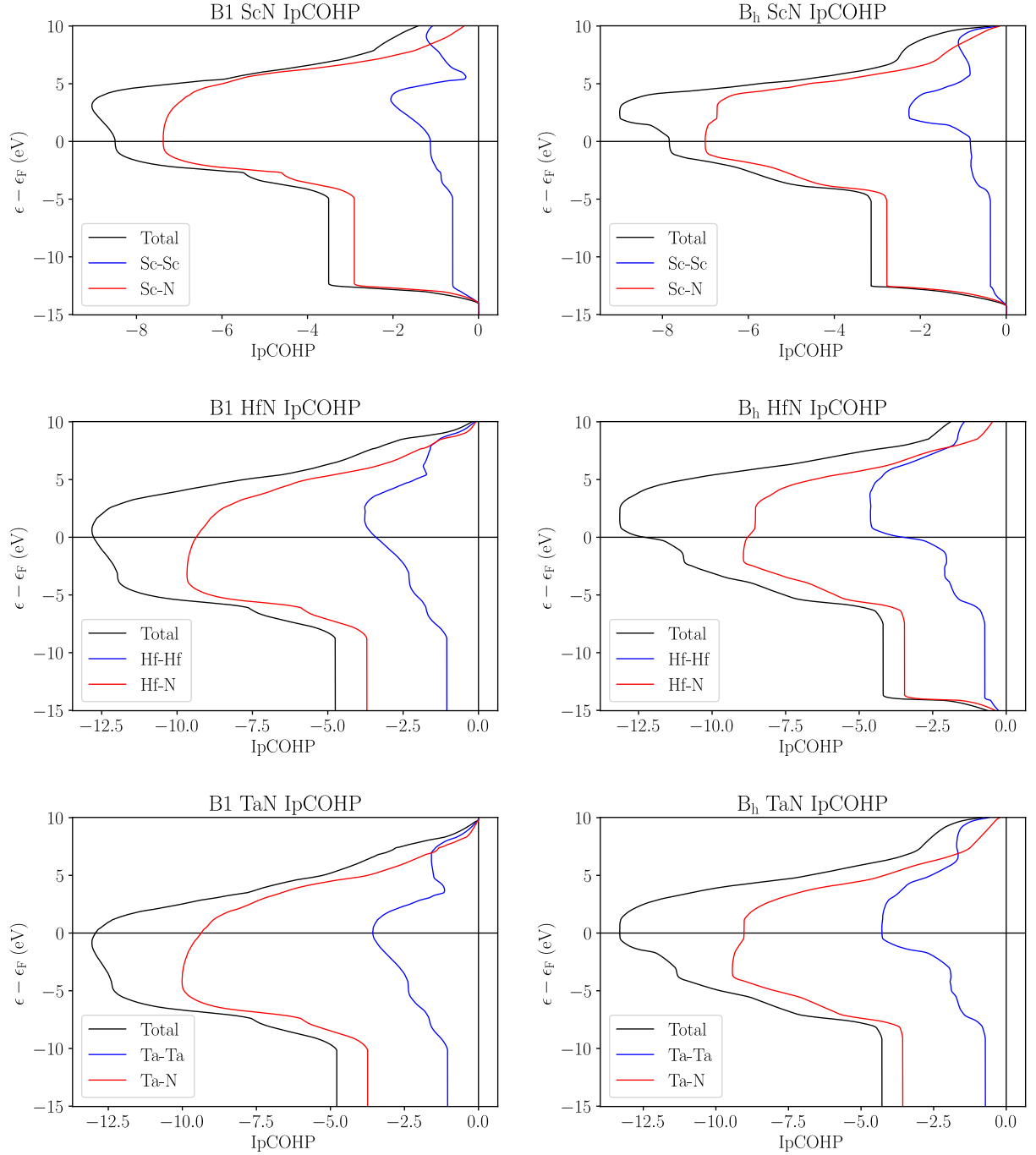


Figure 4.72: Computed IpCOHP for selected TMNs: ScN (VEC= $8 e^-/\text{f.u.}$), HfN (VEC= $9 e^-/\text{f.u.}$), and TaN (VEC= $10 e^-/\text{f.u.}$). Both B1 and B_h structures exhibit relatively constant IpCOHP distribution, only shifted downward relative to the Fermi level as valence electrons are added.

Orbital-Specific Bonding Analysis

More detailed information on the contribution of particular AOs to bonding and antibonding MOs is readily obtained from LOBSTER using the *orbitalwise* tag in the *lobsterin* input file. In the interest of brevity, orbital-decomposed pCOOP and pCOHP curves for the various carbides and nitrides will be relegated to one of the many appendices that accompany this manuscript. More succinct (and informative) are comparisons of these quantities integrated up to the Fermi level. Integrating the pCOHP from the lower energy bound to ϵ_F yields the $\text{IpCOHP}(\epsilon_F)$ value, which gives a reasonable estimate for the covalent bond strength within the material.

Estimates for $\text{IpCOHP}(\epsilon_F)$ in B1-structured carbides can be found in Figures 4.73, 4.74, 4.75, and 4.76, decomposed into contributions from MOs composed of specific AO overlaps. In the octahedral coordination environment of the B1 structure, the degenerate *d*-AOs of the metal atoms split into energetically non-degenerate e_g and t_{2g} states; these states interact with one another, and with the metal *s*-AOs, nonmetal *s*-AOs, and nonmetal *p*-AOs. Looking at Figures 4.73, 4.74, 4.75, and 4.76, we can see that the $\text{IpCOHP}(\epsilon_F)$ breakdowns look remarkably similar for all of the IVB TMCs, VB TMCs, IVB TMNs and VB TMNs. In fact, the only real variation seen among these compounds is that the $\text{IpCOHP}(\epsilon_F)$ values generally become more negative (*i.e.*, the net bond strength tends to increase) with atomic size within each group of compounds. But the notable finding from these results is that there are no fundamental differences in the bonding character of the B1-structured carbides and nitrides. This is perhaps unsurprising in light of our much earlier findings regarding formation enthalpies and elastic stiffnesses, but it nonetheless conflicts with the conventional position that bond strength (and therefore some given mechanical property) is somehow ‘optimized’ within some particular VEC range in the rocksalt structure.

Looking at the results for B_h -structured TMCs and TMNs, we actually do see some interesting deviations. In the IVB carbides—and *only* in the IVB carbides—we actually see the emergence of antibonding states arising from particular *d*-AO overlaps. These are the interactions between the metal d_{odd} -AOs and the $d_{\text{even,LE}}$ -AOs, and are seen to produce a non-negligible antibonding MO which decreases the overall energetic favorability of M-M interactions in the IVB TMCs.

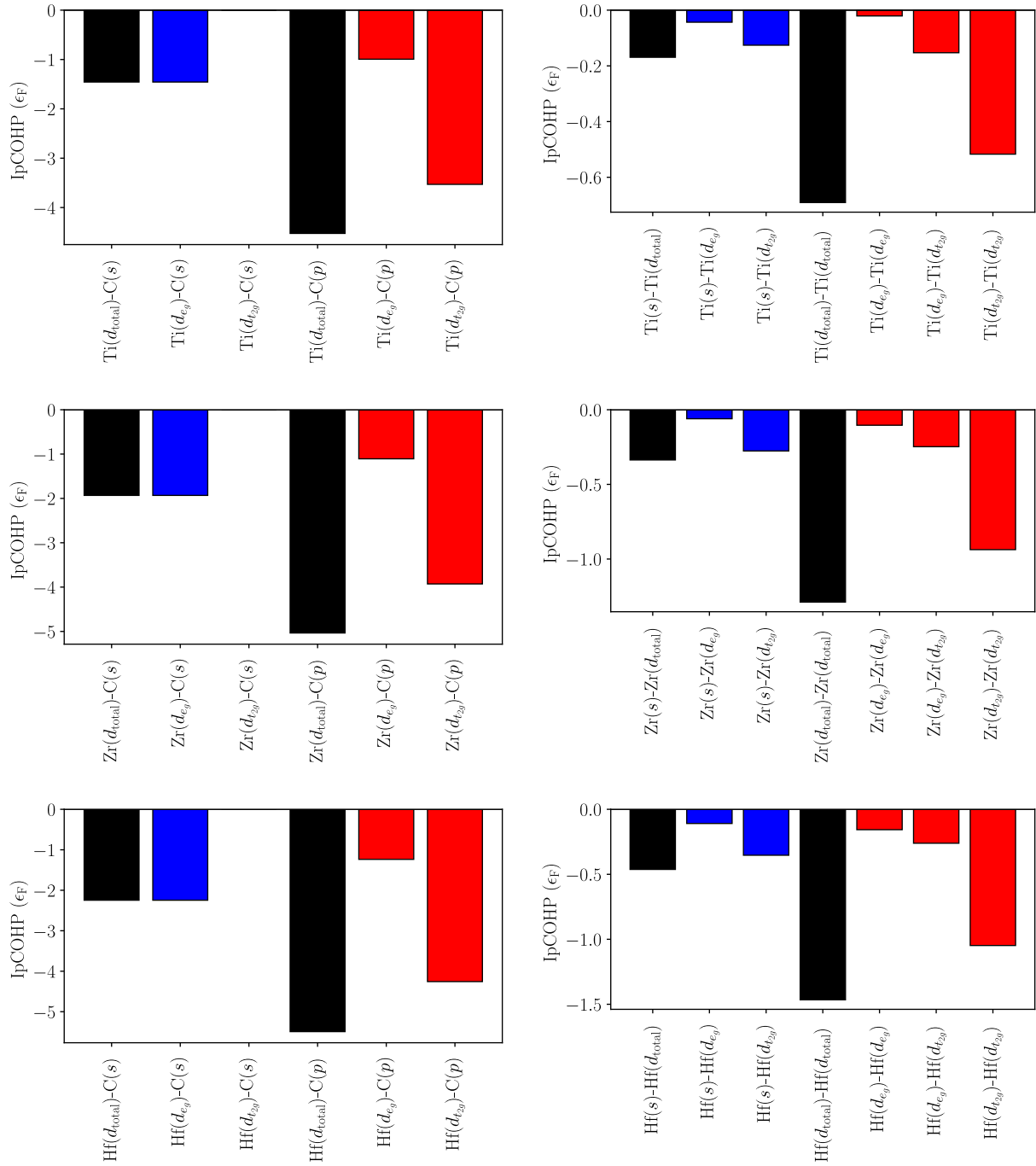


Figure 4.73: Computed $\text{IpCOHP}(\epsilon_F)$ for B1-structured IVB TMCs.

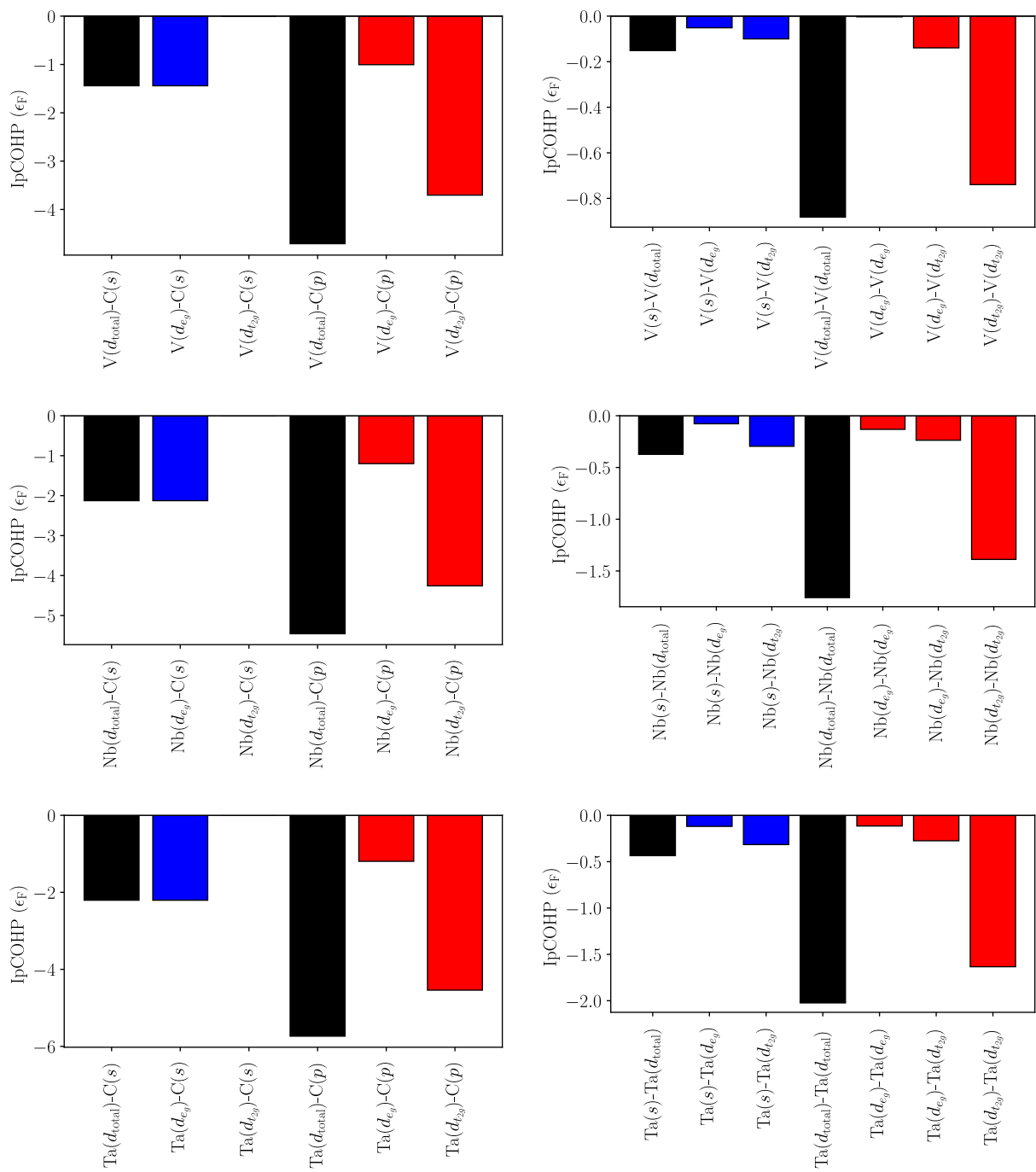


Figure 4.74: Computed $\text{IpCOHP}(\epsilon_F)$ for B1-structured VB TMCs.

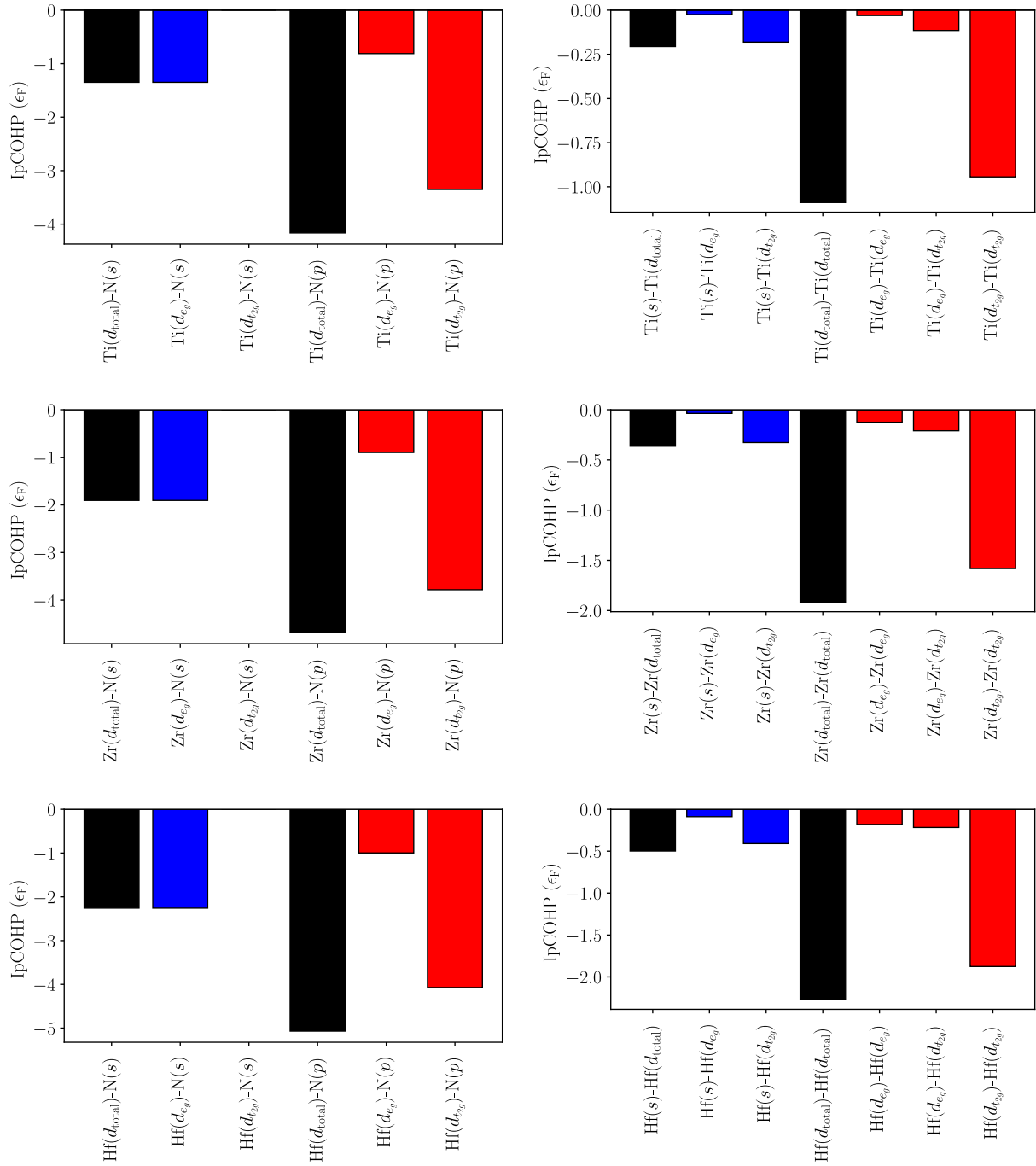


Figure 4.75: Computed $\text{IpCOHP}(\epsilon_F)$ for B1-structured IVB TMNs.

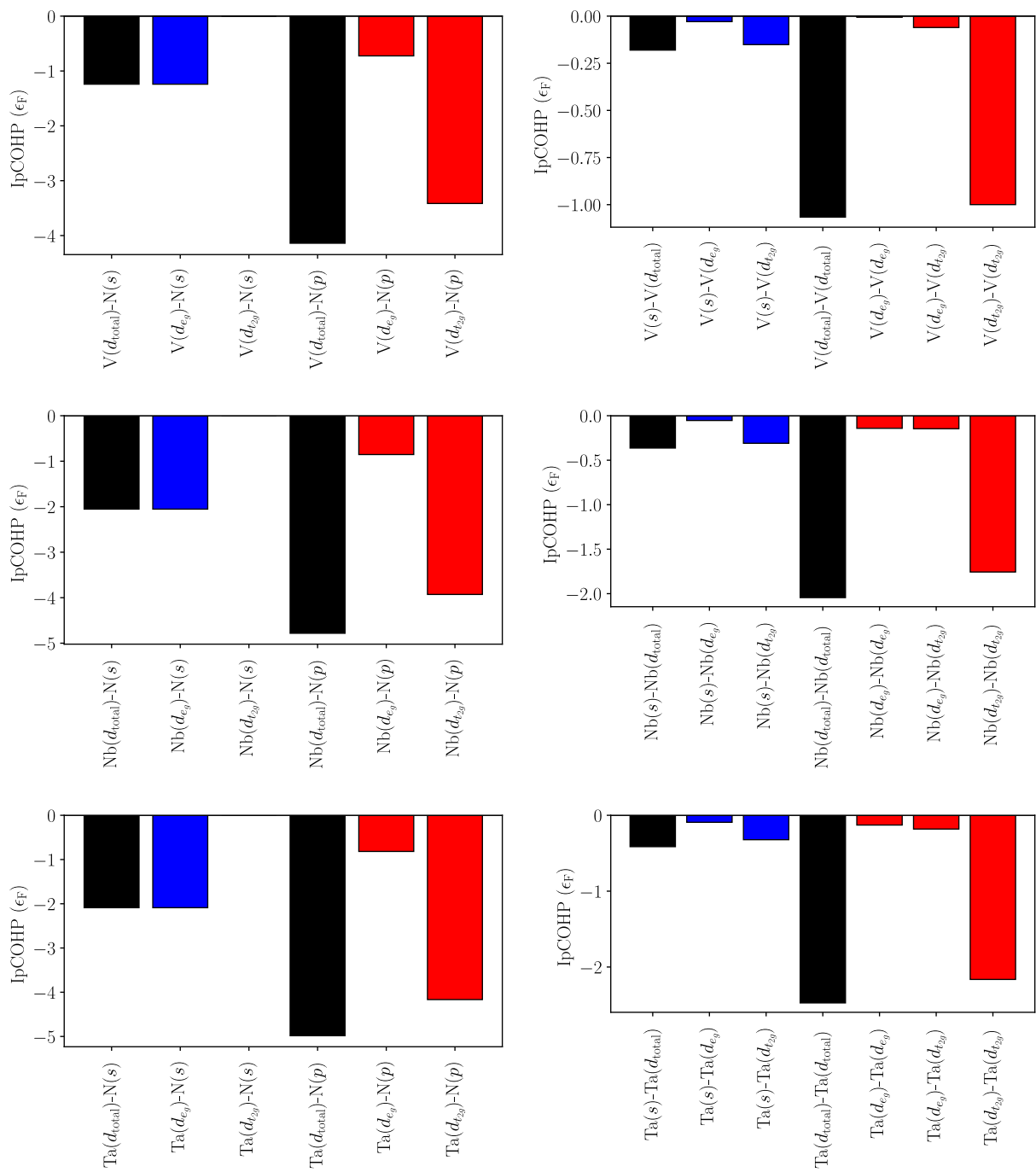


Figure 4.76: Computed $\text{IpCOHP}(\epsilon_F)$ for B1-structured VB TMNs.

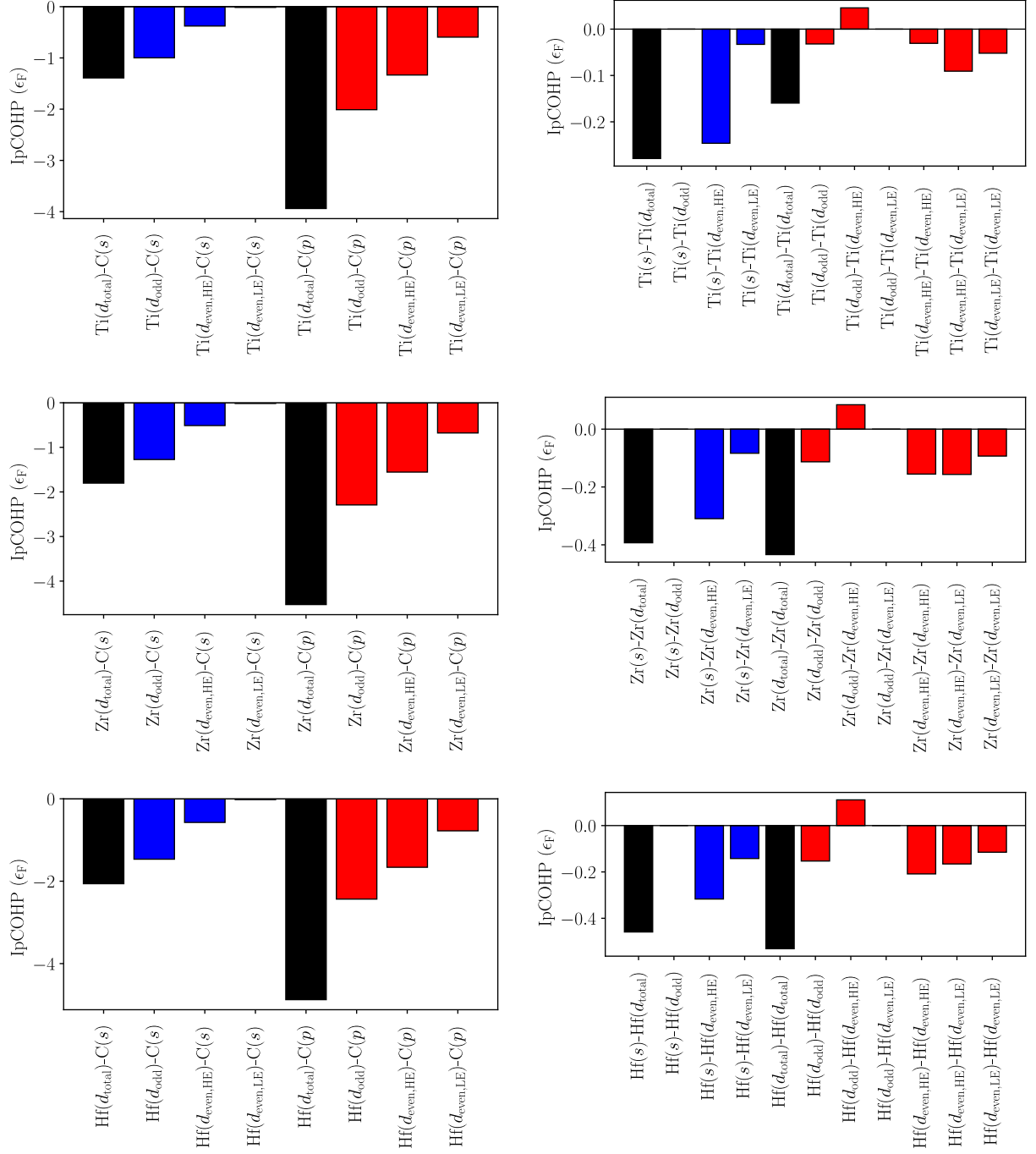


Figure 4.77: Computed $\text{IpCOHP}(\epsilon_F)$ for B_h -structured IVB TMCs.

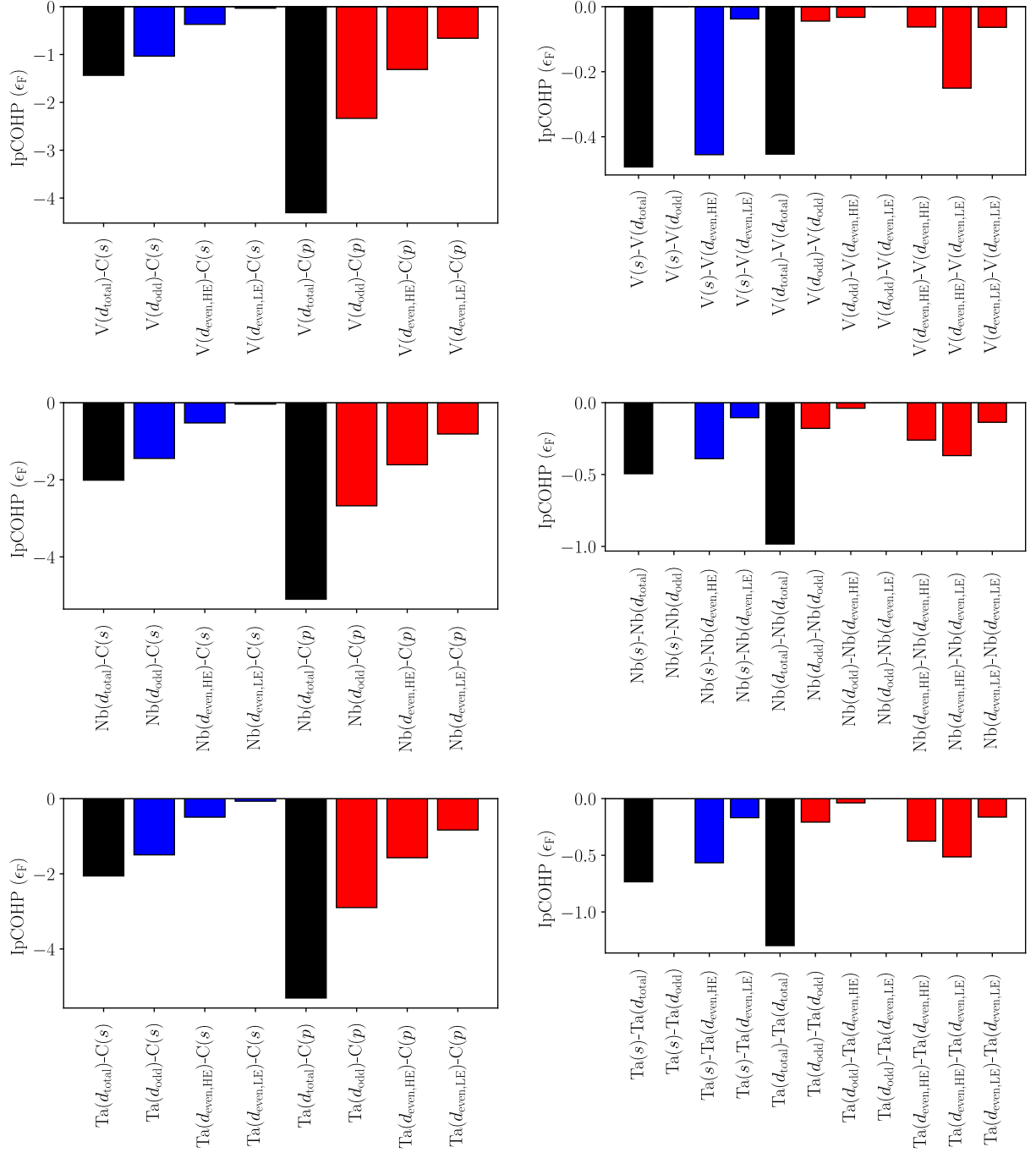


Figure 4.78: Computed $\text{IpCOHP}(\epsilon_F)$ for B_h -structured VB TMCs.

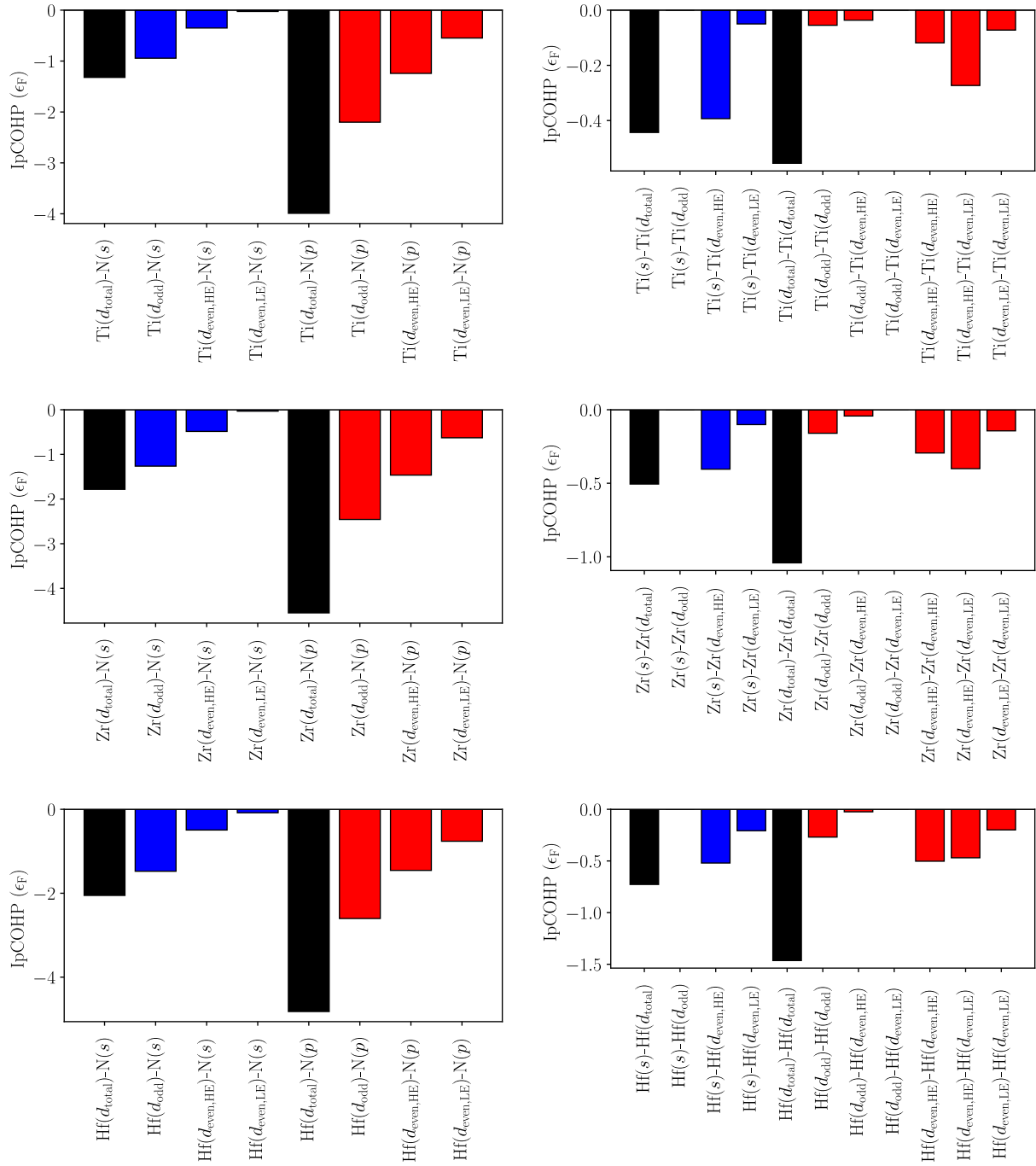


Figure 4.79: Computed $\text{IpCOHP}(\epsilon_F)$ for B_h -structured IVB TMNs.

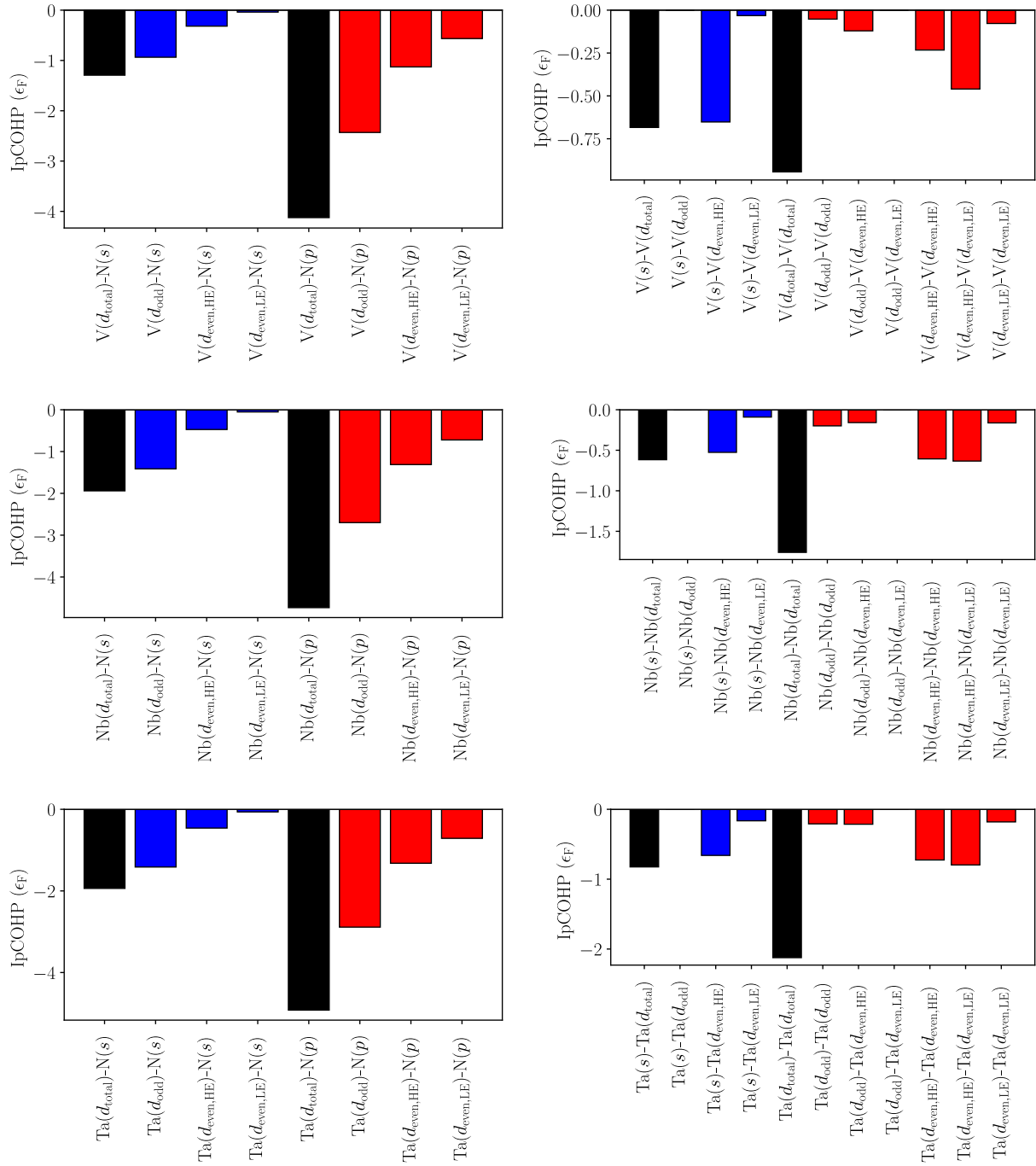


Figure 4.80: Computed $\text{IpCOHP}(\epsilon_F)$ for B_h -structured VB TMNs.

In the VB TMCs and IVB TMNs, which have a higher VEC, this feature is absent: the $d_{\text{odd-}}$ $d_{\text{even,LE}}$ interactions now have a very small bonding contribution. Likewise, in the VB TMNs, which have even higher VEC, we can see these MOs increase in their contribution to the net bonding interactions between metal atoms in these B_h -structured compounds. These findings add essential context to the results from the B1-structured TMCs and TMNs, giving us insight into the underlying causes of the γ_{ISF} trends discussed earlier in this manuscript: in short, increasing VEC affects the bonding character of the B1 structure surprisingly little, whereas it leads to a significant increase in net bonding interactions between metal atoms in the B_h structure, increasing the latter phases's relative stability compared to the former phase. Thus the stabilization of the intrinsic stacking fault in the B1-structured TMCs and TMNs at higher VEC arises from changes in the bonding character of the B_h structure, not in that of the B1 structure.

4.3.2 Substoichiometric IVB and VB Transition-Metal Carbides

Analysis of the bonding and anti-bonding electronic states has also been conducted for the stoichiometric and sub-stoichiometric IVB and VB TMCs: TiC_y , ZrC_y , HfC_y , VC_y , and TaC_y . Just as with the hafnium carbonitrides, the $-\text{IpCOHP}(\epsilon_F)$ values have been computed across a range of compositions. In this case, however, an effort has been made to compare the known stable structures of each carbide with a selection of 'disordered' quasi-random structures. For NbC_y , the quasi-random structures are still being simulated, but modeling of the ordered structures is complete. The initial approach to modeling these materials involves calculation of the crystal orbital Hamilton populations (COHPs), which give a Hamiltonian-weighted breakdown of specific atomic orbital overlaps to the overall band structure energy (see Section 2.5 for details). Using the LOBSTER toolkit, we have computed COHPs for the carbides and integrated them up to the Fermi level; this gives a good idea of how individual interaction types (metal-metal, metal-carbon and carbon-carbon) contribute bonding or anti-bonding states. Prior to a deeper analysis of specific orbital overlaps, this gives some idea as to the general contribution of each type of interatomic bond to the stability of the crystal.

In the IVB carbides, the changes in $-\text{IpCOHP}(\epsilon_F)$ with loss of carbon content are intuitive. That is, the net bonding contribution to the band energy declines slightly, with the reduction in net metal-carbon bonding interactions driving this. At the same time, the net bonding contribution of metal-metal interactions to the band energy rises somewhat with loss of carbon content—consistent with the idea that these compounds take on a more metallic character as carbon is lost—but the increase is not enough to compensate for the reduced metal-carbon bonding. These results imply that the overall bond strength in the Group IV TMCs does decline with loss of carbon content. It should be noted that the carbon-carbon net bonding contribution is negligible over the whole composition range $0.50 < y < 1.0$.

In the tantalum carbides, though, a very interesting trend emerges: comparing the stable ordered structures to the quasi-random structures, the (dominant) tantalum-carbon and (negligible) carbon-carbon overlaps show nearly identical trends across the selected range of carbon contents. However, as y drops below about 0.80, a sudden increase is seen in the net bonding atomic orbital overlap between the tantalum atoms. Furthermore, this increase in bonding contribution between the metal atoms does not appear to come at the expense of metal-carbon bonding: the trend in metal-carbon bonding interactions seems totally unchanged, even throughout the region of "enhanced" metal-metal bonding.

It is unlikely that ordering of carbon vacancies plays much of a role in producing this intriguing trend: throughout the shown domain where the B1-ordered TaC_y structures dominate—from $y = 1$ to roughly $y = 0.8$ —there is no discernible difference between the vacancy-ordered and non-vacancy-ordered structures. The increase in metal-metal net bonding interactions occurs at the transition from B1-ordered stable structures to the stacking-fault-formed phases. These phases— Ta_4C_3 , Ta_3C_2 , and Ta_2C —feature stacking-faults between close-packed tantalum planes, meaning that the stoichiometry is essentially accommodated by the deletion of entire planes of carbon atoms. Between these planes of metal atoms, metal-metal bonding will naturally dominate; furthermore, the inter-planar spacing is reduced by the presence of the stacking-fault, leading to stronger inter-

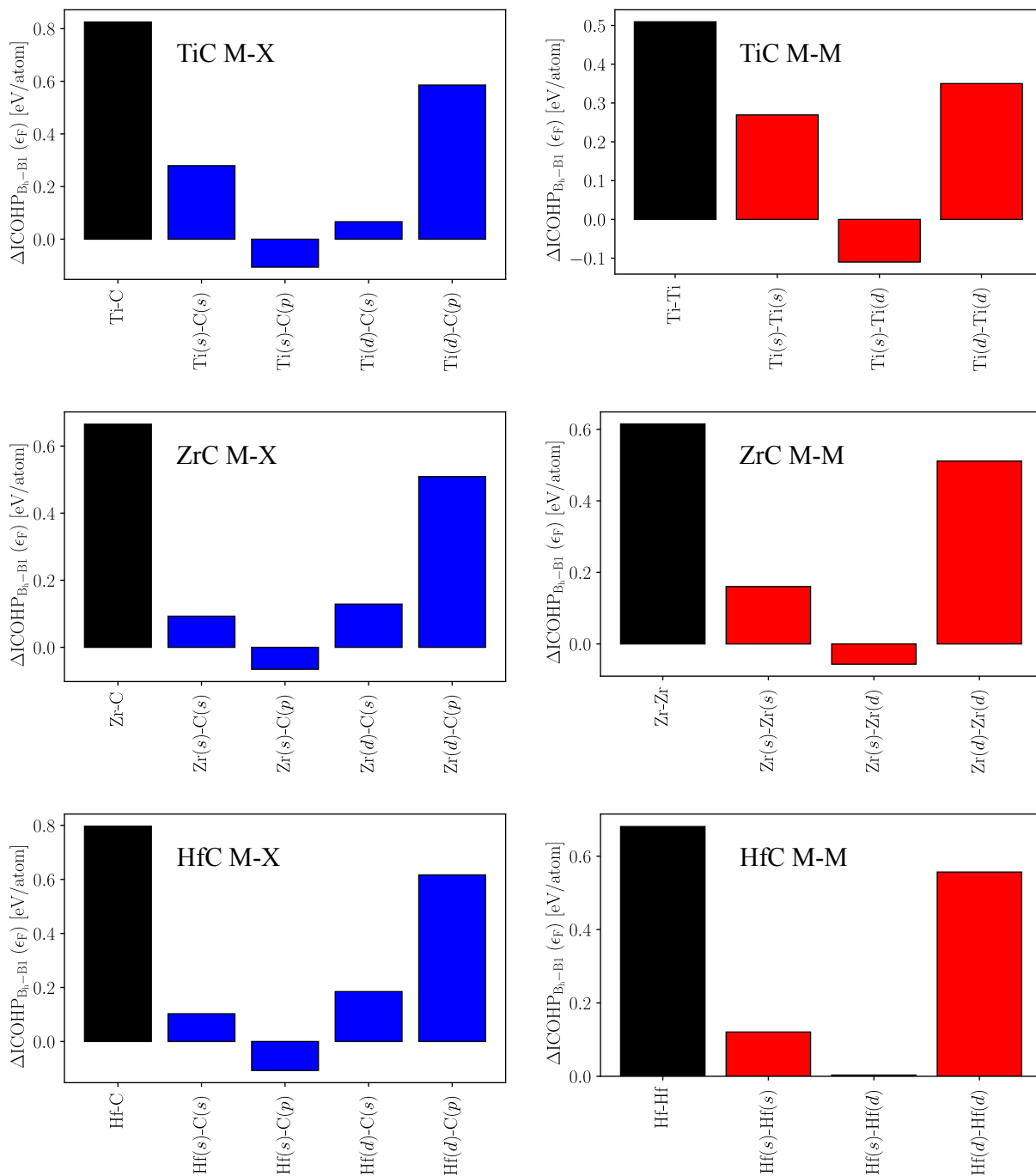


Figure 4.81: Computed difference in $-\text{IpCOHP}$ between B_h and $B1$ structures for the IVB TMCs: TiC (top row), ZrC (middle row), and HfC (bottom row). Data are separated into metal-nonmetal (M-X, left column) and metal-metal (M-M, right column) interaction types.

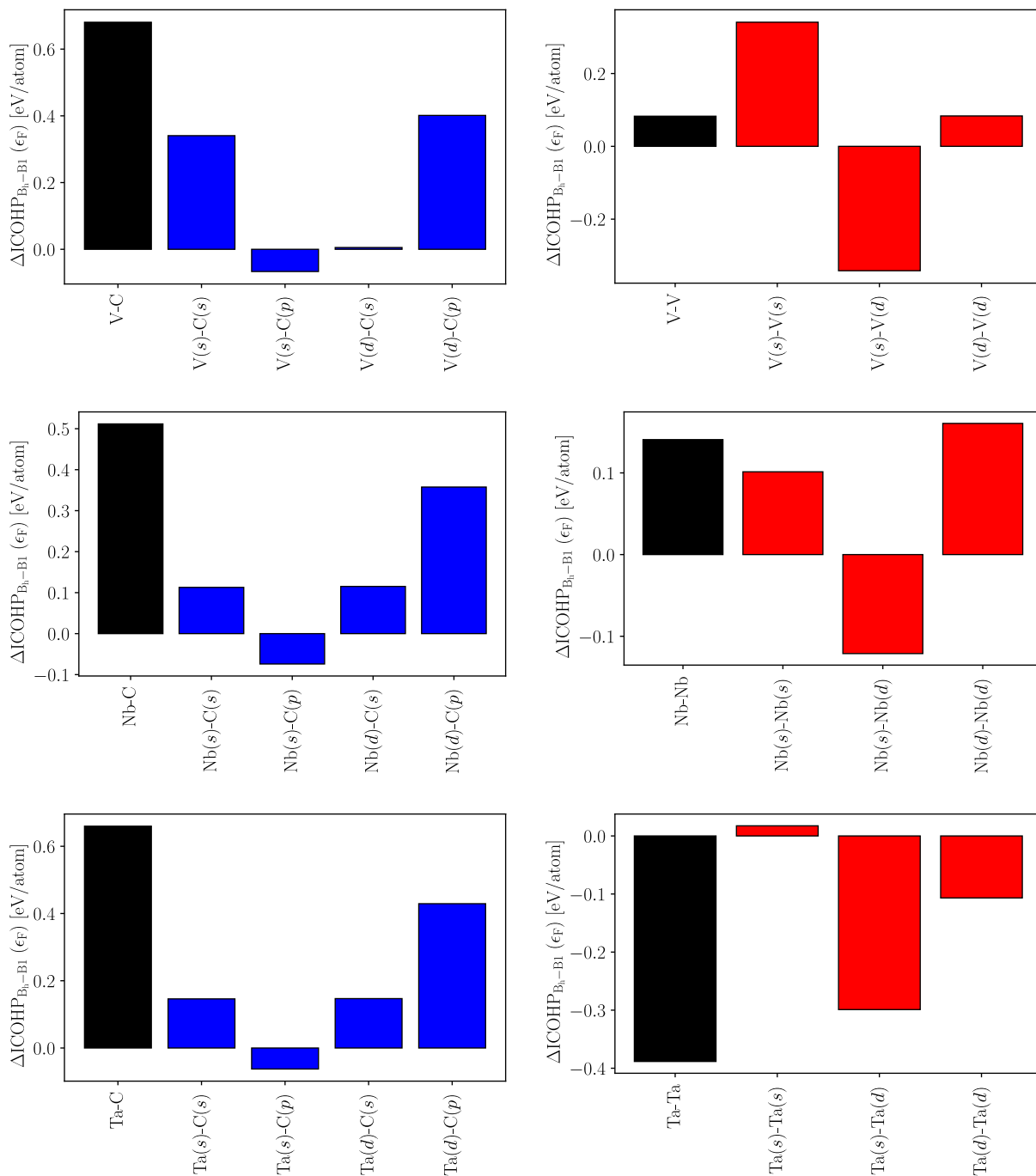


Figure 4.82: Computed difference in $-\text{IpCOHP}$ between B_h and $B1$ structures for the VB TMCs: VC (top row), NbC (middle row), and TaC (bottom row). Data are separated into metal-nonmetal (M-X, left column) and metal-metal (M-M, right column) interaction types.

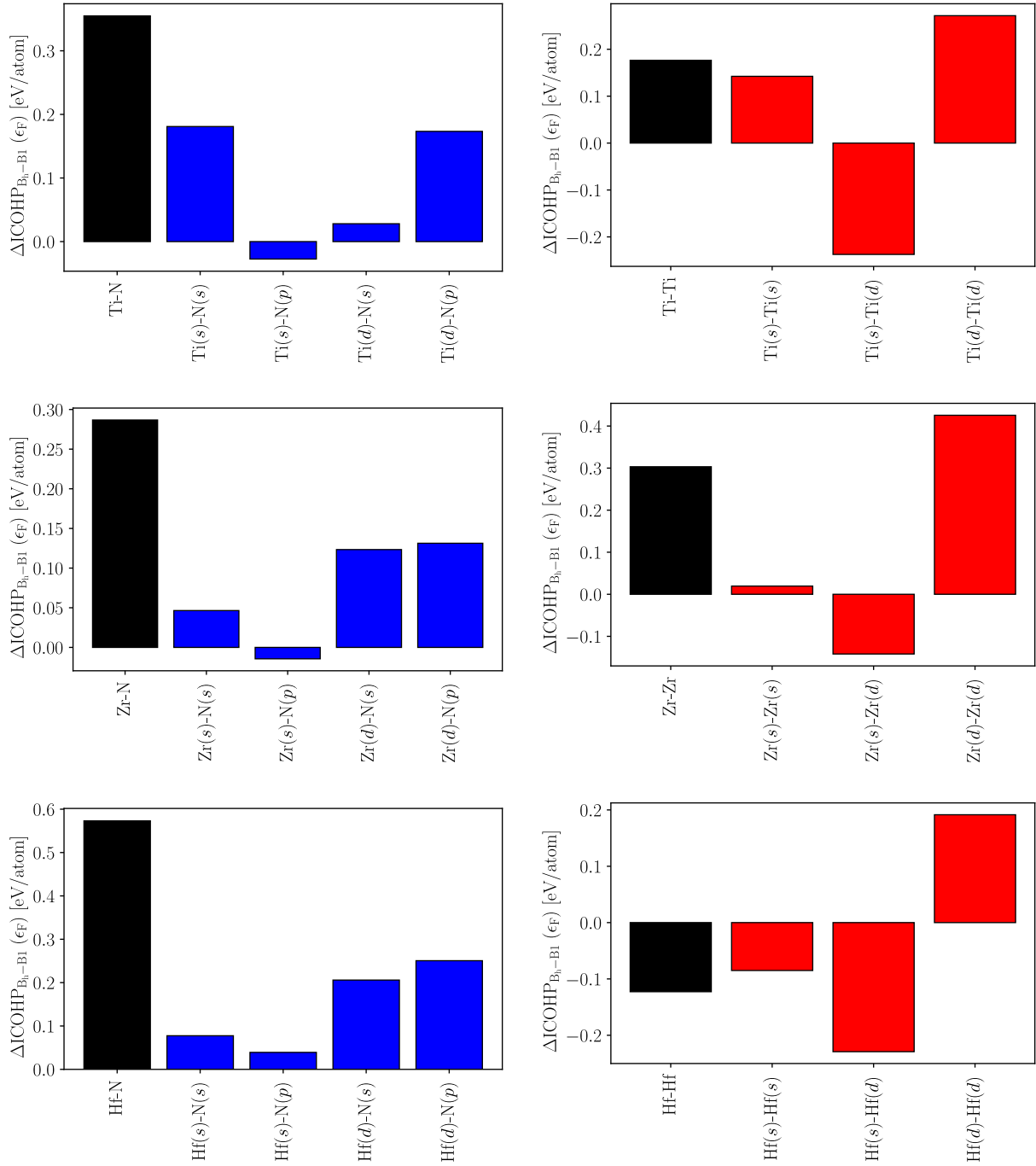


Figure 4.83: Computed difference in $-\text{IpCOHP}$ between B_h and $B1$ structures for the IVB TMNs: TiN (top row), ZrN (middle row), and HfN (bottom row). Data are separated into metal-nonmetal (M-X, left column) and metal-metal (M-M, right column) interaction types.

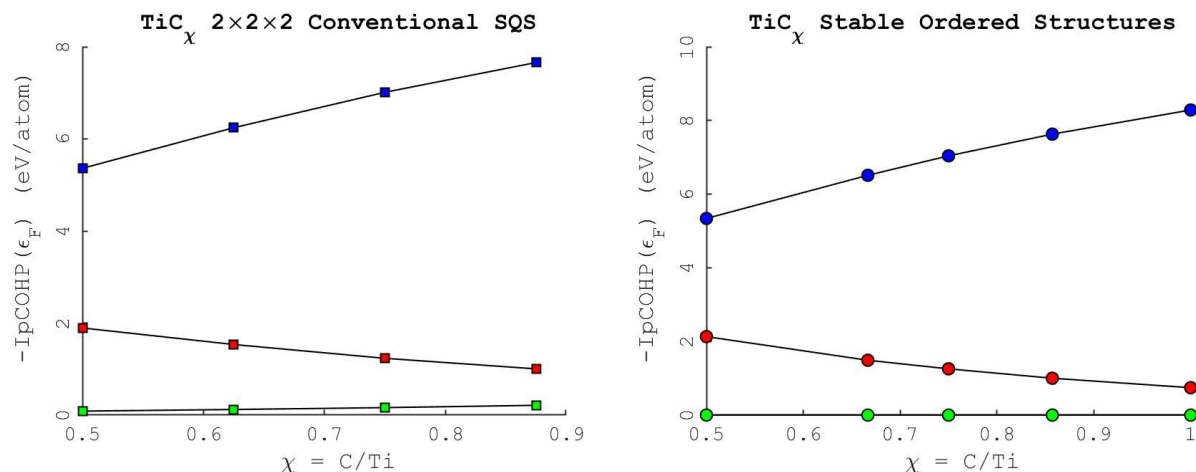


Figure 4.84: LOBSTER-computed $-\text{IpCOHP}(\epsilon_F)$ values for quasi-random structures ($\text{TiC}_{0.5}$, $\text{TiC}_{0.625}$, $\text{TiC}_{0.75}$ and $\text{TiC}_{0.875}$) and vacancy-ordered phases (Ti_2C , Ti_3C_2 , Ti_4C_3 , Ti_7C_6 and TiC). Square markers denote SQS data, while circle markers indicate ordered phases. Shown for each type of structure are the metal-metal (red), metal-carbon (blue) and carbon-carbon (green) net bonding interactions.

actions between those planes. This likely accounts, at least in part, for the oft-cited increase in fracture toughness observed in the ζ -phases of TaC_y .

Additionally, DoS and COHP data have been computed for all of the rocksalt nitrides— TiN_y , ZrN_y , HfN_y , VN_y , NbN_y and TaN_y —and analysis of this data is expected to be completed prior to the end of the summer. Furthermore, in the TMCs and TMNs, we have begun investigating the contribution of specific atomic orbital overlaps in the interest of testing the third hypothesis proposed in the research proposal. LOBSTER allows for orbital-wise breakdown of COHP information, allowing us to both visually and numerically represent the bonding and anti-bonding contribution of the p - d and d - d overlaps. Once this work is complete, we will also investigate the changes in bonding around vacancies and substitutional atoms in an attempt to characterize in detail the effect that these defects have on the stability of the $B1$ and B_h structures. This analysis will be performed for all compounds discussed in this section, covering TMCs, TMNs, MTMCs and TMCNs.

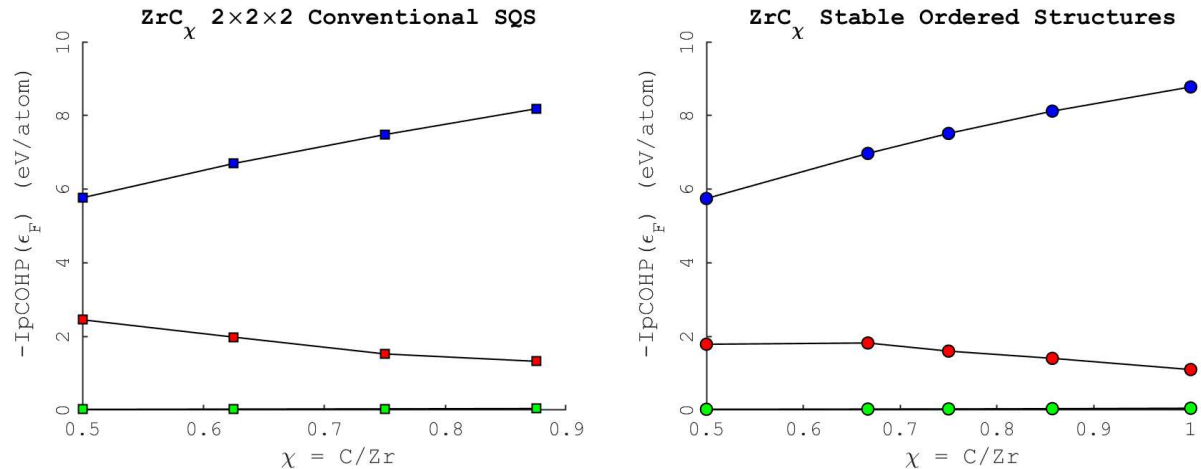


Figure 4.85: LOBSTER-computed $-\text{IpCOHP}(\epsilon_F)$ values for quasi-random structures ($\text{ZrC}_{0.5}$, $\text{ZrC}_{0.625}$, $\text{ZrC}_{0.75}$ and $\text{ZrC}_{0.875}$) and vacancy-ordered phases (Zr_2C , Zr_3C_2 , Zr_4C_3 , Zr_7C_6 and ZrC). Square markers denote SQS data, while circle markers indicate ordered phases. Shown for each type of structure are the metal-metal (red), metal-carbon (blue) and carbon-carbon (green) net bonding interactions.

4.4 Summary and Conclusions

Taken together, the findings discussed in this manuscript offer a reasonably comprehensive explanation for the highly disparate hardness behaviors seen in the cubic transition-metal carbides and nitrides. Specifically, these results illustrate that arguments from elastic stiffness generally fail to accurately predict the hardness of these unusual compounds, whereas a more nuanced dislocation-focused approach can produce meaningful qualitative predictions that generally agree with experimental observations.

In summary, the DFT-computed elastic moduli presented for the substoichiometric TMCs and TMNs indicate declining stiffness with loss of nonmetal atom content, consequently predicting declining hardness at lower y . The exceptions to this trend are the VB TMNs (which, recall, have higher VEC and are not typically B1-phase-stable at low temperatures), which show increasing shear moduli (and, consequently, increasing predicted hardness) at lower nitrogen content. None of the substoichiometric carbides or nitrides are predicted to exhibit ‘anomalous’ hardness maxima. The Peierls-Nabarro model results, in contrast, do anticipate increasing hardness with loss of nonmetal atom content in all of these compounds, owing to the pronounced increase in intrinsic stacking-fault energy (γ_{ISF} as VEC is reduced by substoichiometry. Thus, while substoichiometry

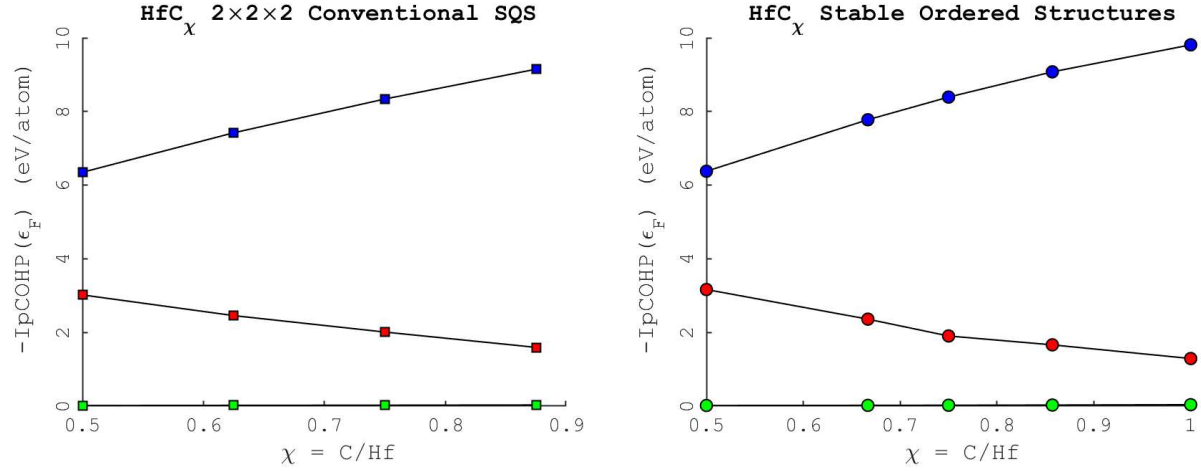


Figure 4.86: LOBSTER-computed $-\text{IpCOHP}(\epsilon_F)$ values for quasi-random structures ($\text{HfC}_{0.5}$, $\text{HfC}_{0.625}$, $\text{HfC}_{0.75}$ and $\text{HfC}_{0.875}$) and vacancy-ordered phases (Hf_2C , Hf_3C_2 , Hf_4C_3 , Hf_7C_6 and HfC). Square markers denote SQS data, while circle markers indicate ordered phases. Shown for each type of structure are the metal-metal (red), metal-carbon (blue) and carbon-carbon (green) net bonding interactions.

generally leads to *elastic* softening, a dislocation-centered approach reveals a significant *inelastic* hardening at lower VEC. Building upon this result, the hardness ‘anomaly’ seen in the VB TMCs and IVB TMNs is predicted to arise from a competition between dislocation plasticity—which becomes more and more difficult as VEC declines—and fracture, which becomes easier at lower VEC.

This produces two main conclusions: (1) the ‘anomalous’ hardness increase seen in some of the substoichiometric TMCs and TMNs can be predicted from dislocation mobility, and (2) the subsequent decline can be predicted from an energetic competition between dislocation slip and intragranular fracture. The alloyed carbide $\text{Hf}_{1-y}\text{Ta}_y\text{C}$ and the IVB carbonitrides— $\text{TiC}_{1-y}\text{N}_y$, $\text{ZrC}_{1-y}\text{N}_y$, and $\text{HfC}_{1-y}\text{N}_y$ —do show ‘anomalous’ hardness maxima, as predicted from the elastic stiffnesses, but these maxima do not appear in our predictions from dislocation mobility or fracture resistance. This is because the cleavage energies are generally higher in the lower-VEC terminal compounds, meaning that in these systems the resistance to fracture tends to increase with reduction in VEC. Importantly, there could still be ‘anomalous’ hardness trends in experiment, since our model neglects differences microstructural differences which may be present between different compositions in real experiments. Nonetheless, these results holistically make the case that hard-

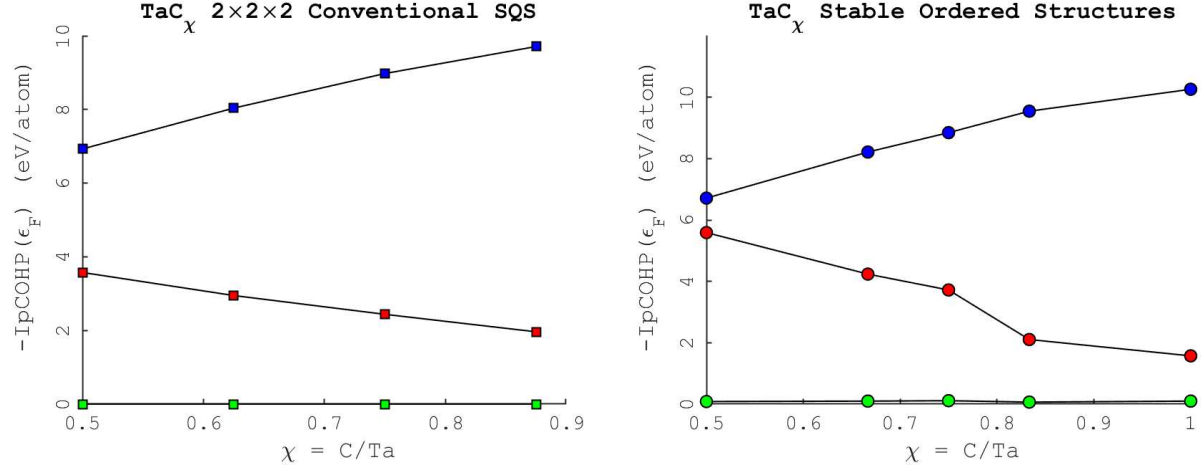


Figure 4.87: LOBSTER-computed $-\text{IpCOHP}(\epsilon_F)$ values for quasi-random structures ($\text{TaC}_{0.5}$, $\text{TiC}_{0.625}$, $\text{TiC}_{0.75}$ and $\text{TaC}_{0.875}$) and vacancy-ordered phases (Ta_2C , Ta_3C_2 , $\zeta\text{-Ta}_4\text{C}_3$, Ta_6C_5 and TaC). Square markers denote SQS data, while circle markers indicate ordered phases. Shown for each type of structure are the metal-metal (red), metal-carbon (blue) and carbon-carbon (green) net bonding interactions.

ness behaviors in these materials are (somewhat unsurprisingly) not governed by differences in elastic stiffness, but by fundamental differences in dislocation structure and mobility; furthermore, we have developed a compelling argument against ‘anomalous’ hardness peaks arising from variation in a single mechanical property, be it elastic stiffness, formation enthalpy, fracture resistance or dislocation mobility. Rather, the oft-observed changes in the slope of the $H_V(y)$ curve (most often reported for TaC_y) arise from competition between multiple modes of irreversible deformation.

The marked differences in hardness behavior between these otherwise-similar compounds is thus explainable primarily in terms of dislocation slip resistance, which is in turn seen to arise from differences in γ_{ISF} . But why do these differences in stacking-fault energies exist? In summary, we assert that they result from differing energetic preferences for octahedral atomic coordination environments (as seen in the B_1 crystal structure) over trigonal prismatic coordination environments (as seen in the B_h structure). That is, while increasing VEC has relatively little effect on the bonding/antibonding character (as determined from the $\text{IpCOHP}(\epsilon_F)$ values obtained from LOBSTER), the extra valence electrons present in higher-VEC compounds have the effect of strengthening the metal-metal bonding interactions and ultimately stabilizing the B_h phase relative to the B_1 phase.

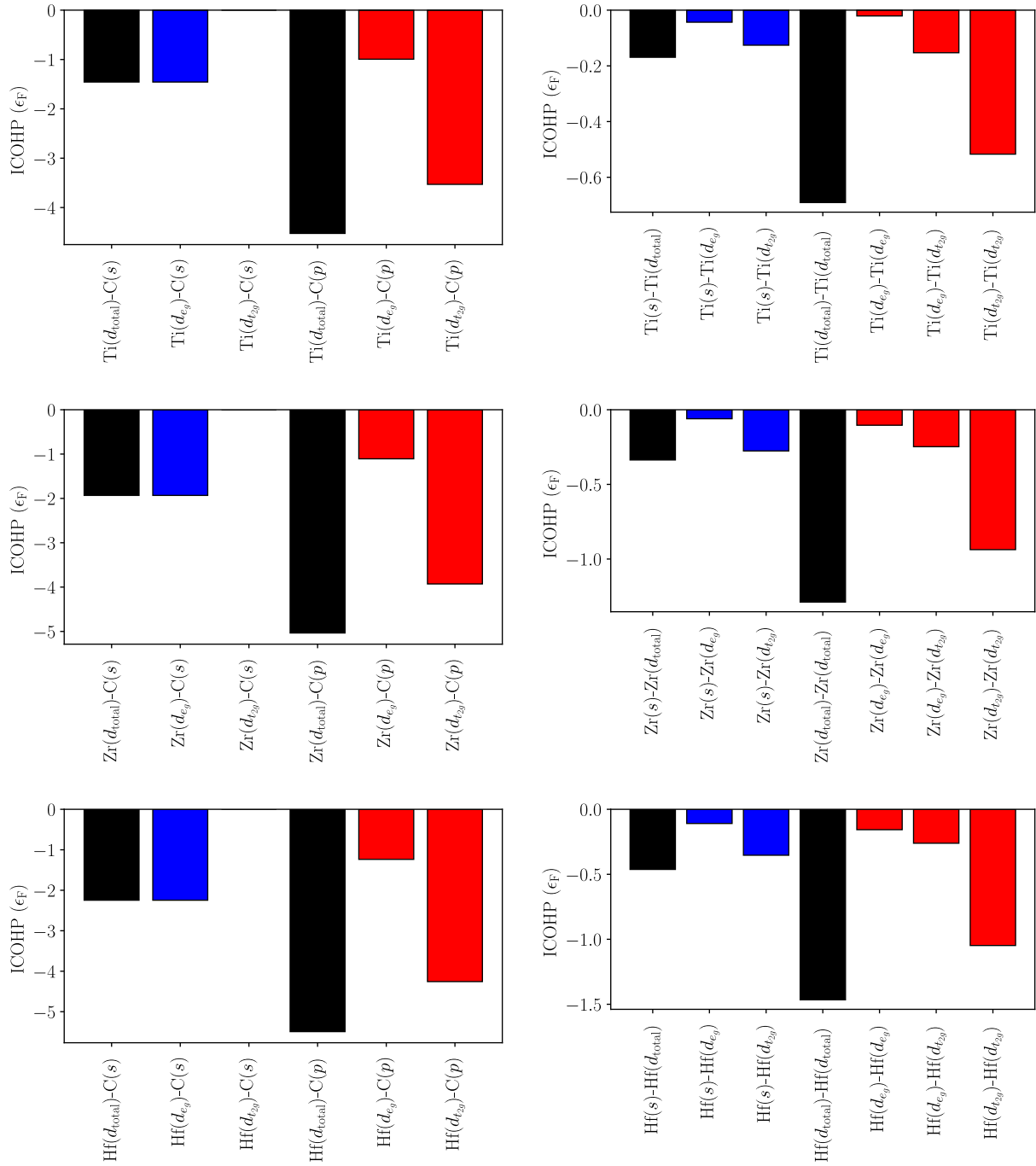


Figure 4.88: Orbital-wise pCOHP, integrated up to the Fermi level, for B1-structured IVB TMCs: TiC, ZrC, and HfC. Separated into metal-carbon (left column) and metal-metal (right column) interactions.

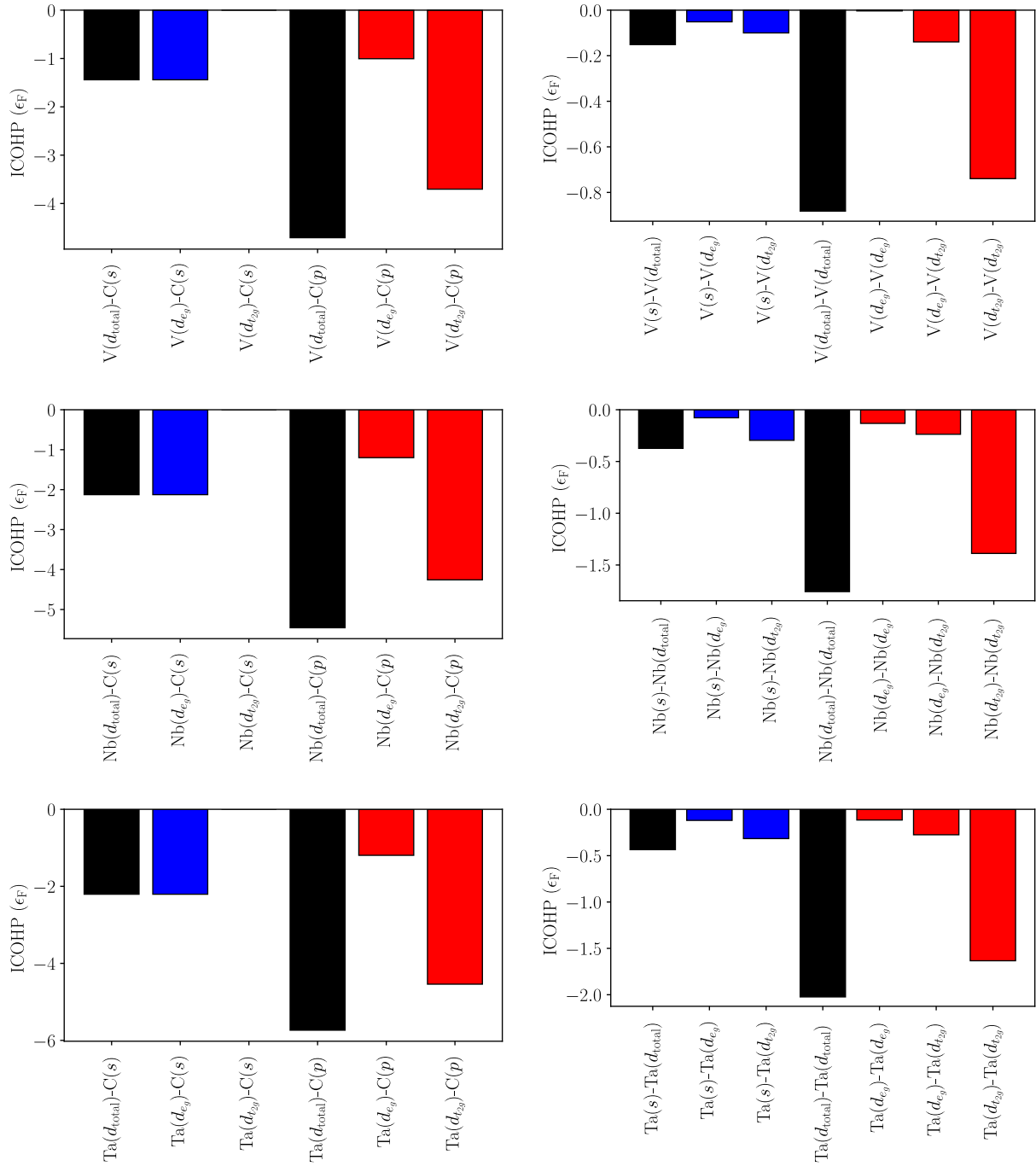


Figure 4.89: Orbital-wise pCOHP, integrated up to the Fermi level, for B1-structured VB TMCs: VC, NbC, and TaC. Separated into metal-carbon (left column) and metal-metal (right column) interactions.

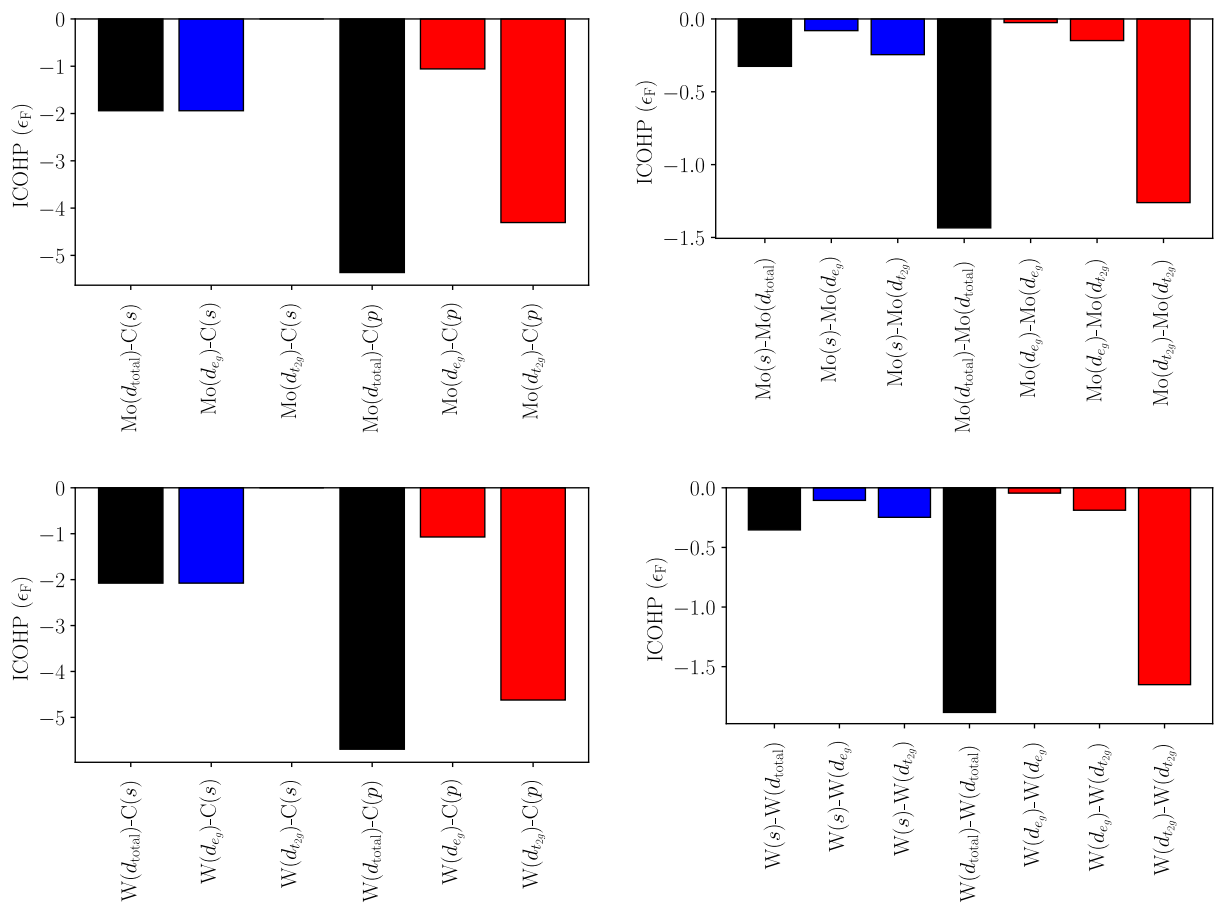


Figure 4.90: Orbital-wise pCOHP, integrated up to the Fermi level, for B1-structured VIB TMCs: MoC and WC. Separated into metal-carbon (left column) and metal-metal (right column) interactions.

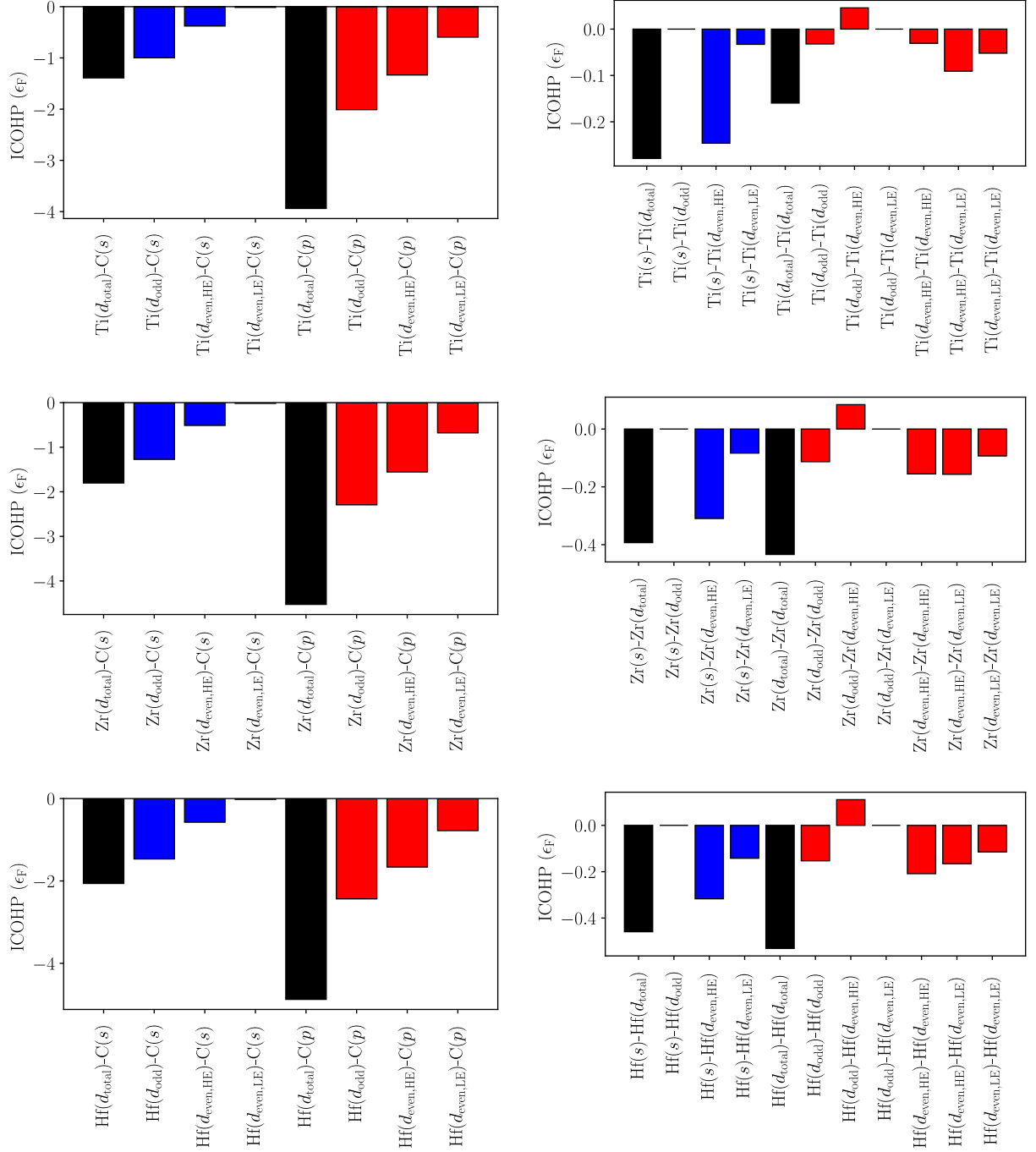


Figure 4.91: Orbital-wise pCOHP, integrated up to the Fermi level, for B_h -structured IVB TMCs: TiC, ZrC, and HfC. Separated into metal-carbon (left column) and metal-metal (right column) interactions.

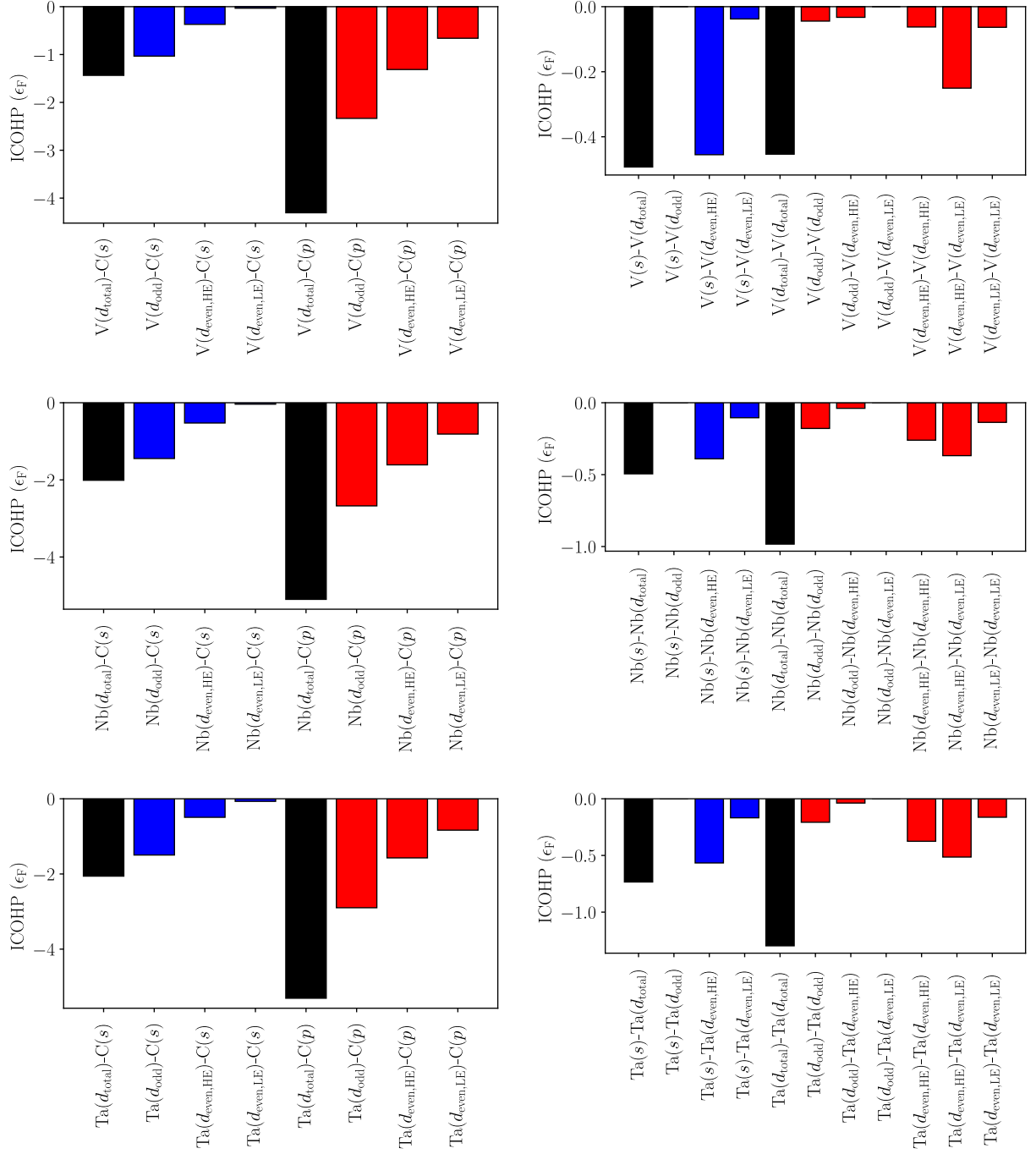


Figure 4.92: Orbital-wise pCOHP, integrated up to the Fermi level, for B_h-structured VB TMCs: VC, NbC, and TaC. Separated into metal-carbon (left column) and metal-metal (right column) interactions.

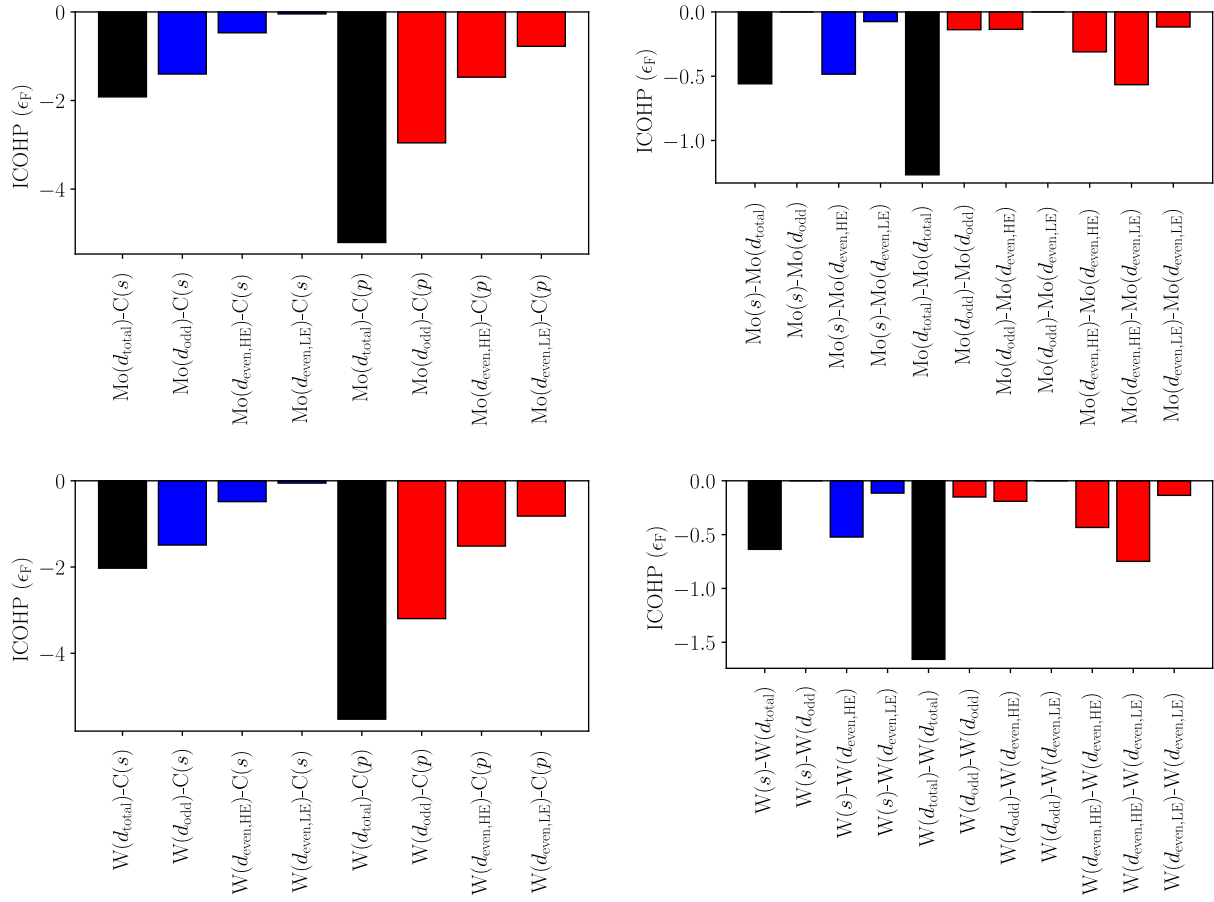


Figure 4.93: Orbital-wise pCOHP, integrated up to the Fermi level, for B_h -structured VIB TMCs: MoC and WC. Separated into metal-carbon (left column) and metal-metal (right column) interactions.

Thus we have, in essence, a basic explanation for the disparate hardness behaviors commonly seen among the cubic carbides and nitrides. As VEC increases—via stoichiometry tailoring or via substitution—the strengthening of net metal-metal bonding in the B_h leads to energetic favorability of this phase compared to the B1 phase; this, in turn, reduces the energetic cost of forming stacking faults, which leads to more glissile dislocations on the planes most necessary for generalized plasticity (the $\{111\}_{B1}$ planes) and producing lower hardness and increased plasticity under indentation.

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Appendix A

Additional Information on Elastic Stiffness

Calculations

This appendix contains additional results from elastic stiffness calculations omitted from the main text in the interest of brevity. The results, as discussed in the main text of this document, generally increase elastic softening (and correspondingly lower predicted hardness) with substoichiometry, though this trend is reversed in the higher-VEC compounds (*e.g.*, the VB TMNs). The alloyed hafnium-tantalum carbides, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$, show a modest increase in predicted hardness at an intermediate composition, whereas the mixed tantalum-tungsten carbides, $\text{Ta}_{1-y}\text{W}_y\text{C}$, show a decline in predicted hardness consistent with the trends seen in the VB TMNs.

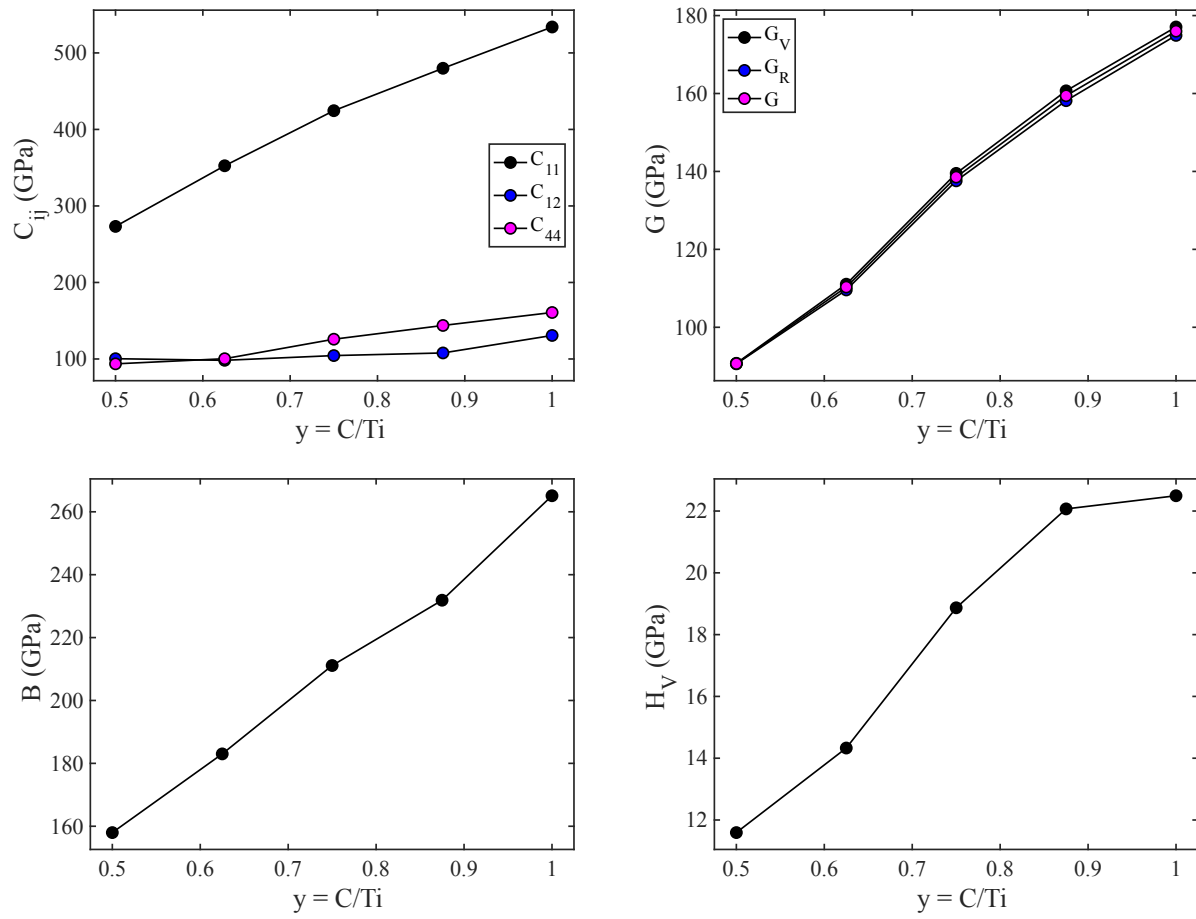


Figure A.1: VASP-computed cubic elastic moduli for rocksalt-structured titanium carbides, TiC_y .

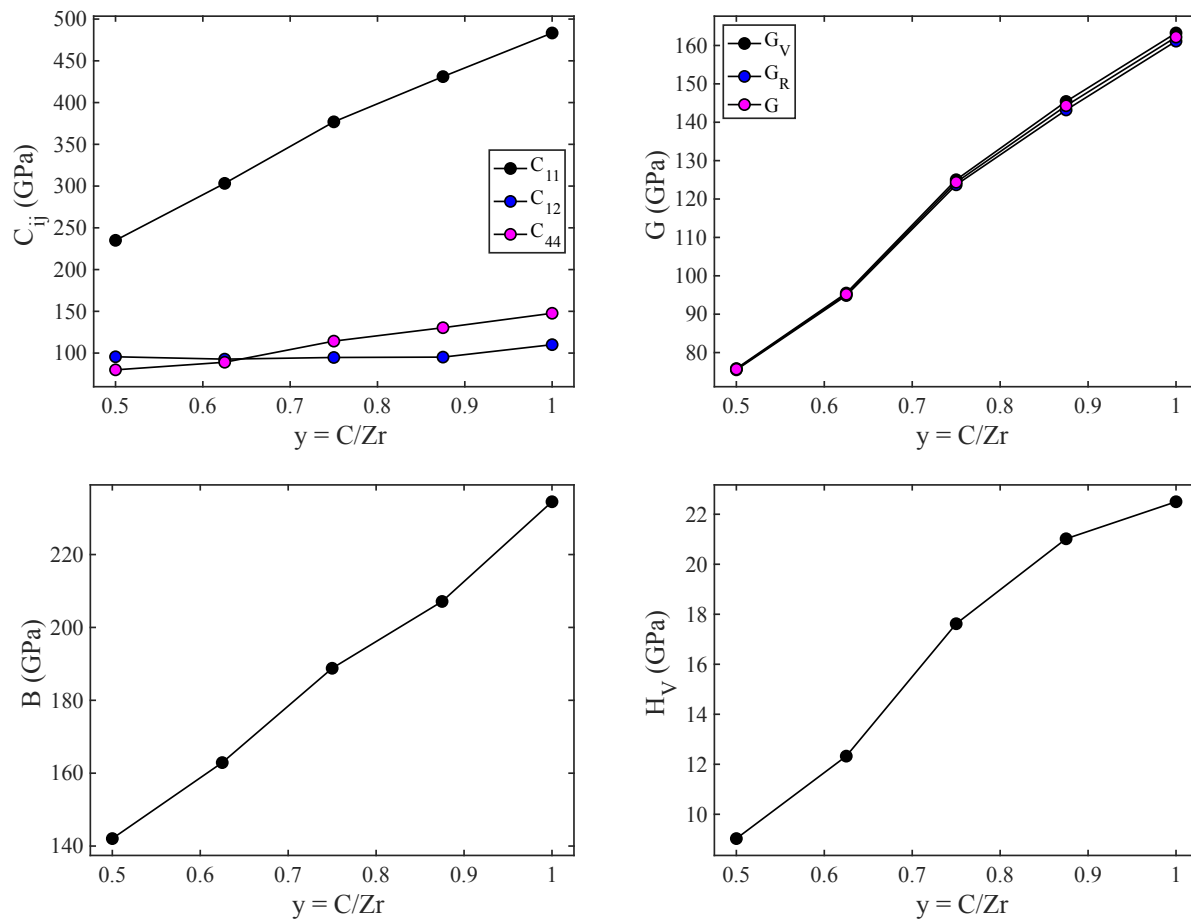


Figure A.2: VASP-computed cubic elastic moduli for rocksalt-structured zirconium carbides, ZrC_y .

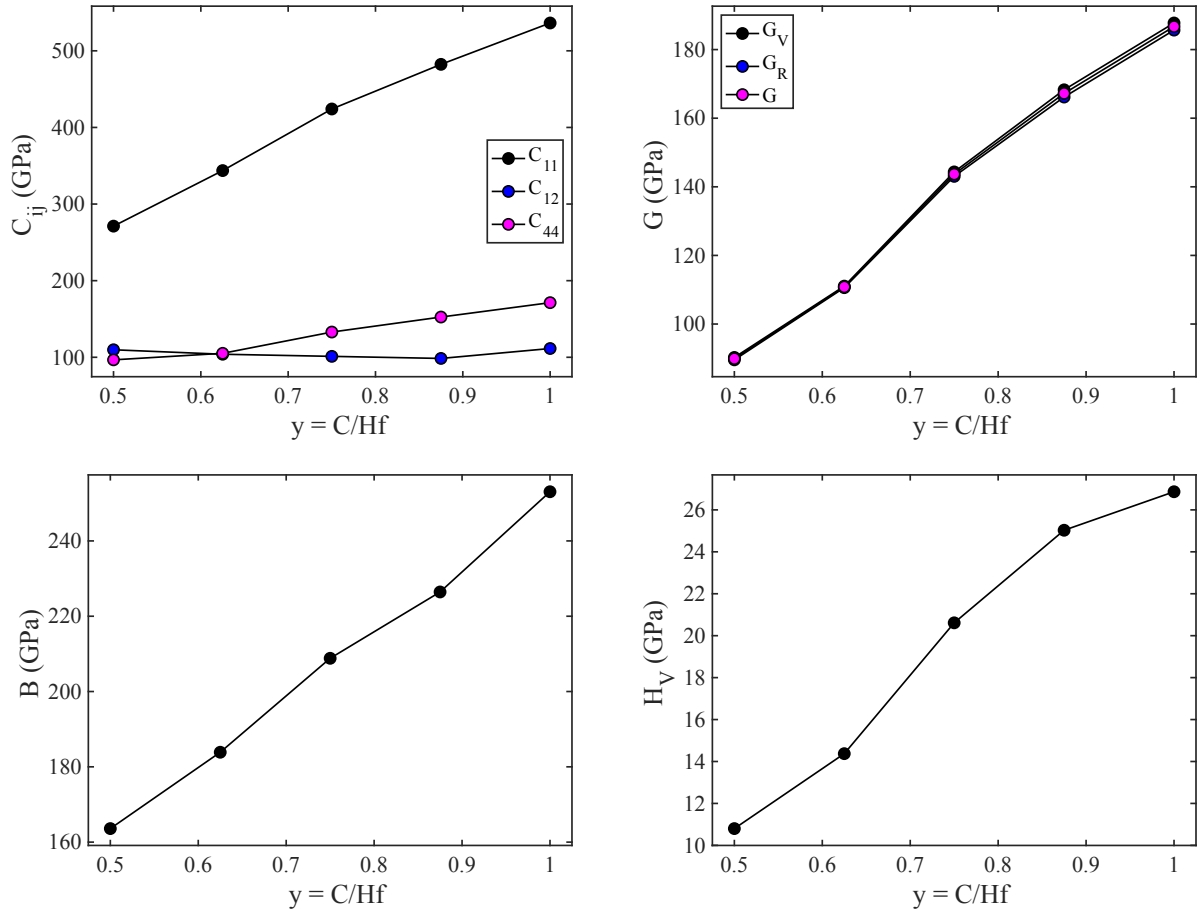


Figure A.3: VASP-computed cubic elastic moduli for rocksalt-structured hafnium carbides, HfC_y .

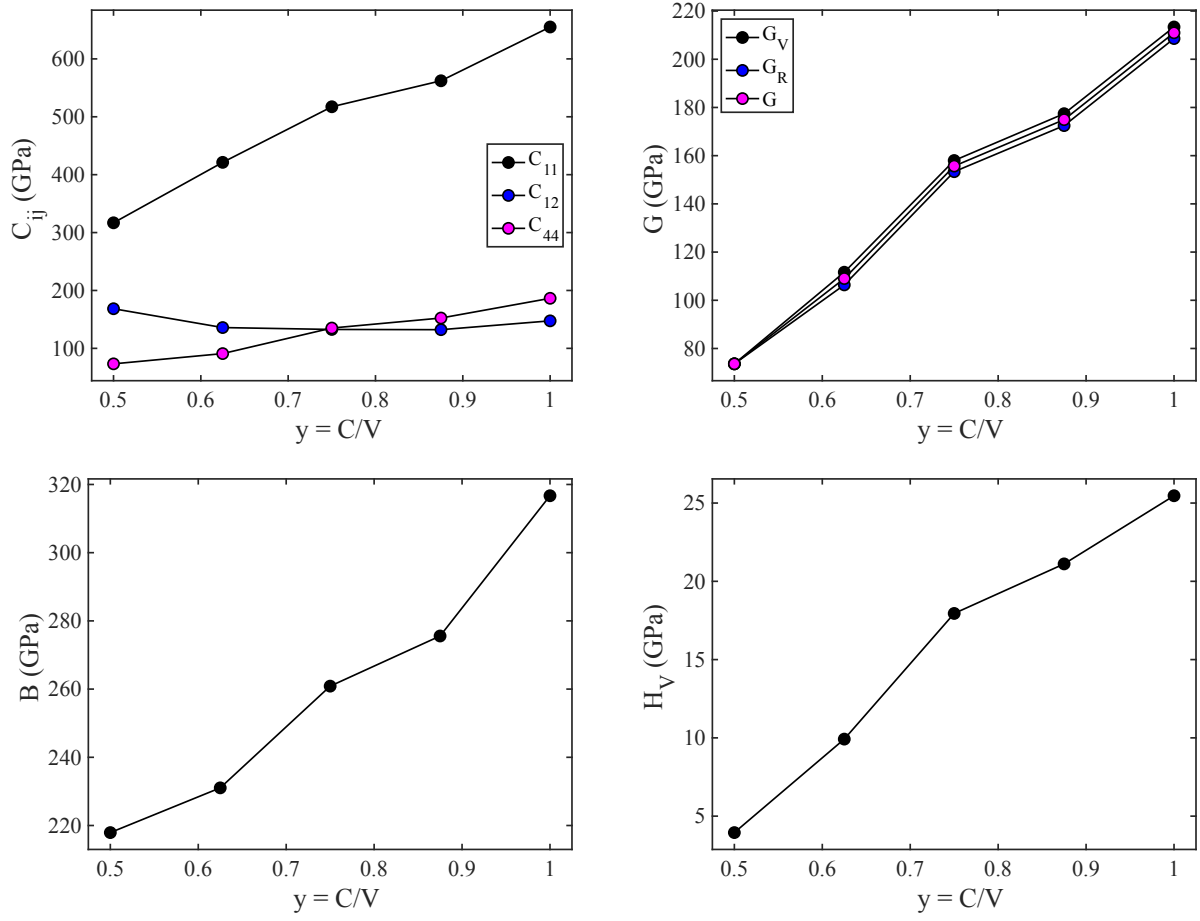


Figure A.4: VASP-computed cubic elastic moduli for rocksalt-structured vanadium carbides, VC_y .

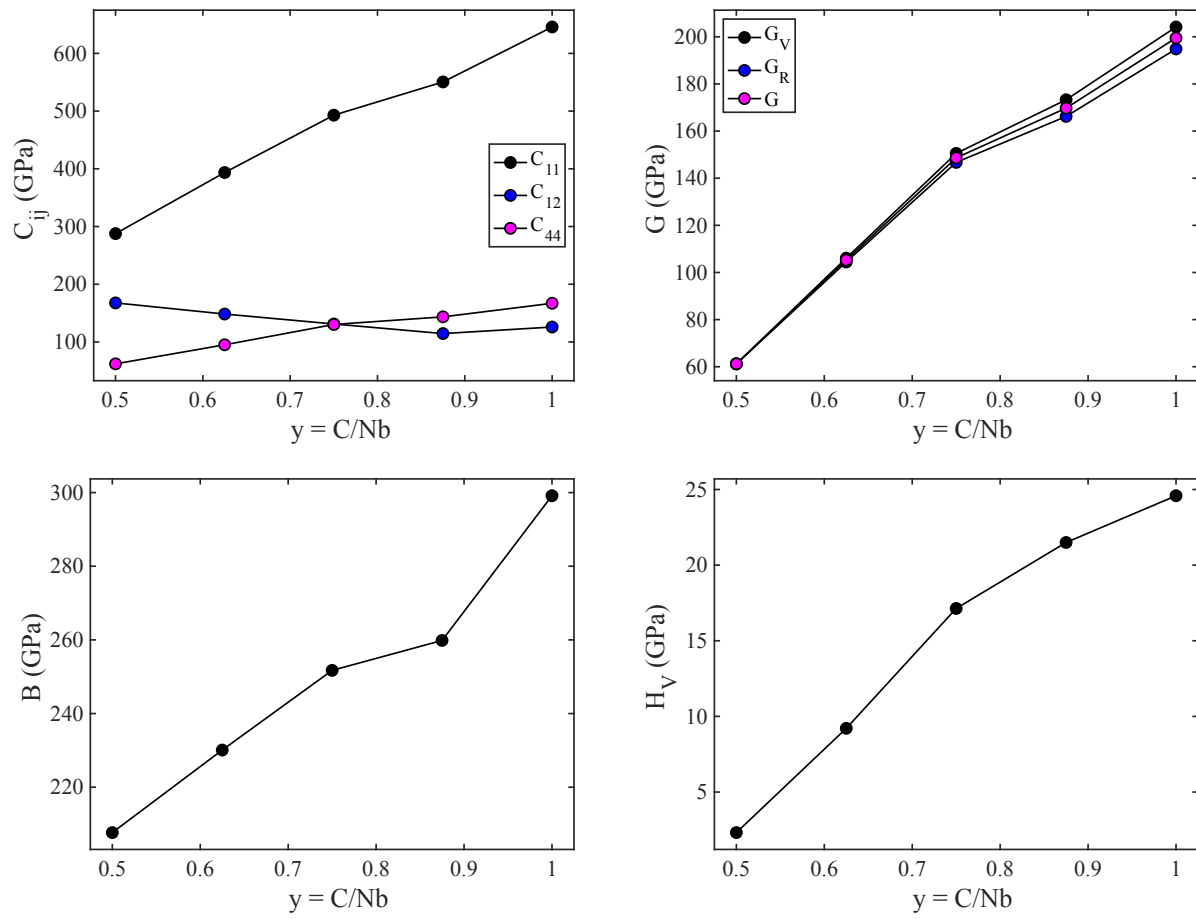


Figure A.5: VASP-computed cubic elastic moduli for rocksalt-structured niobium carbides, NbC_y .

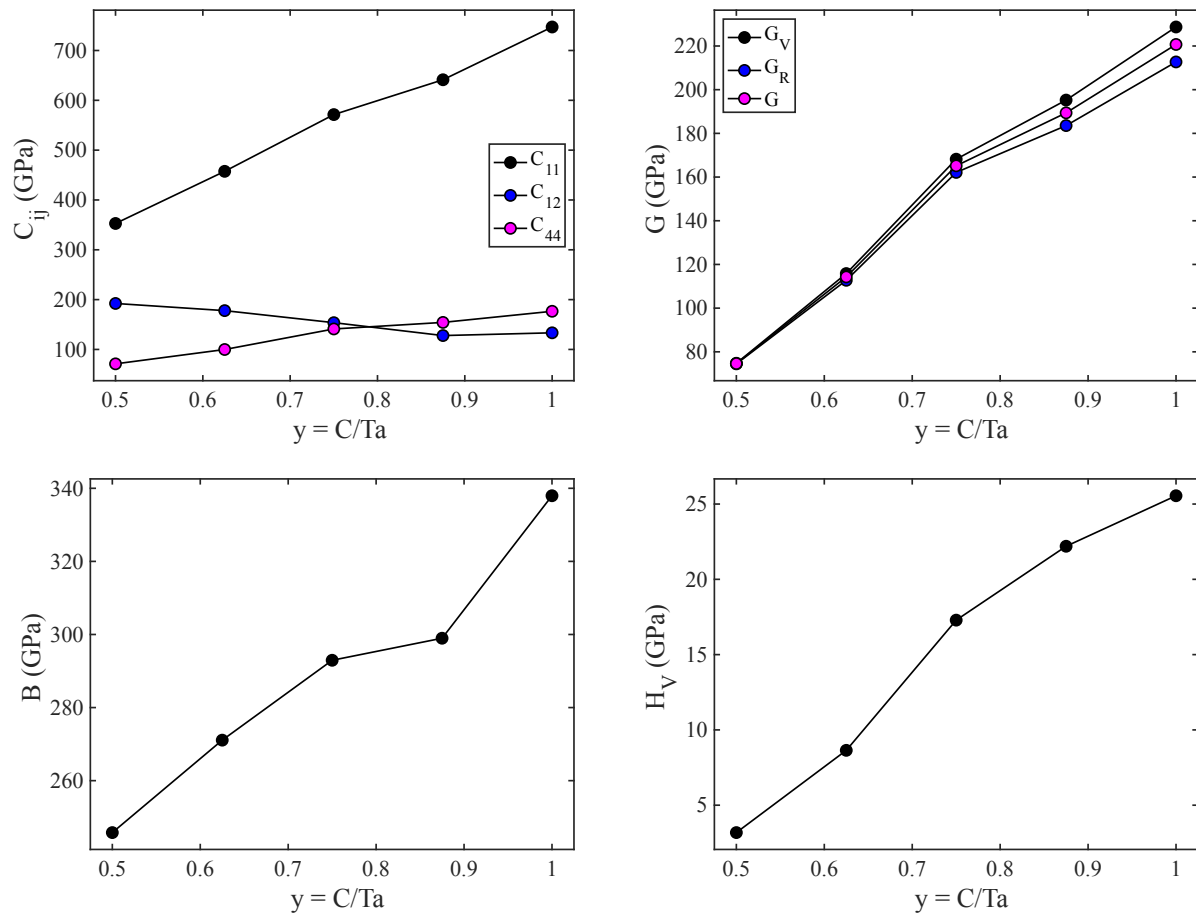


Figure A.6: VASP-computed cubic elastic moduli for rocksalt-structured tantalum carbides, TaC_y .

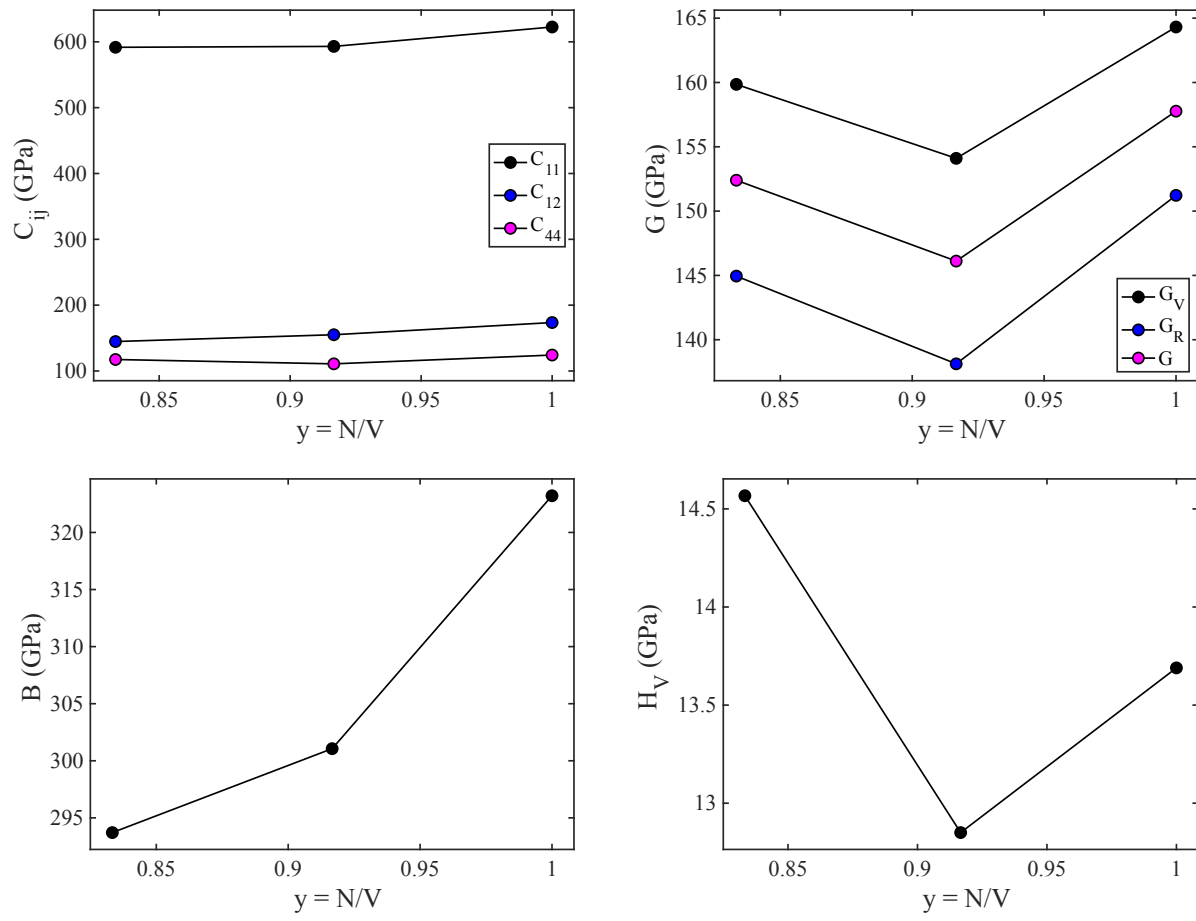


Figure A.7: VASP-computed cubic elastic moduli for rocksalt-structured niobium nitrides, VN_y .

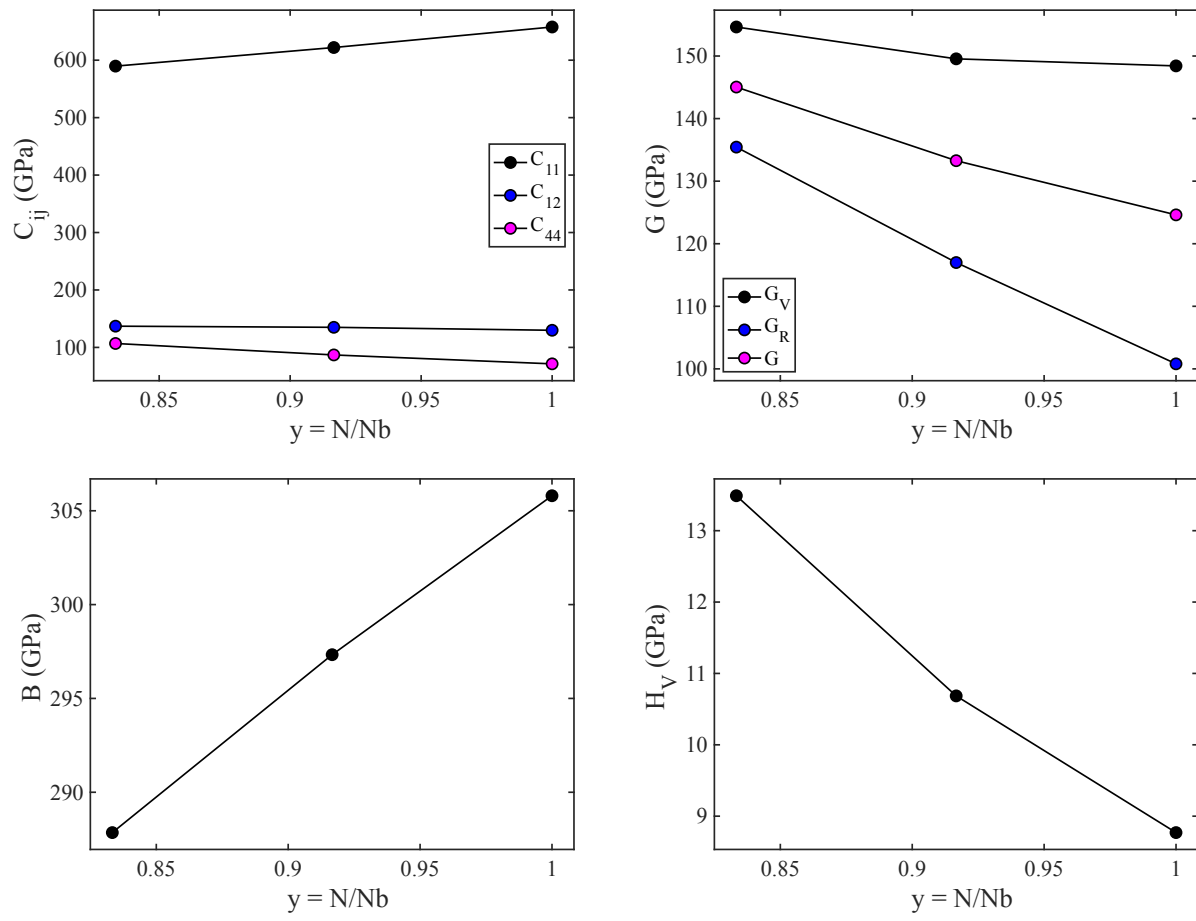


Figure A.8: VASP-computed cubic elastic moduli for rocksalt-structured niobium nitrides, NbN_y .

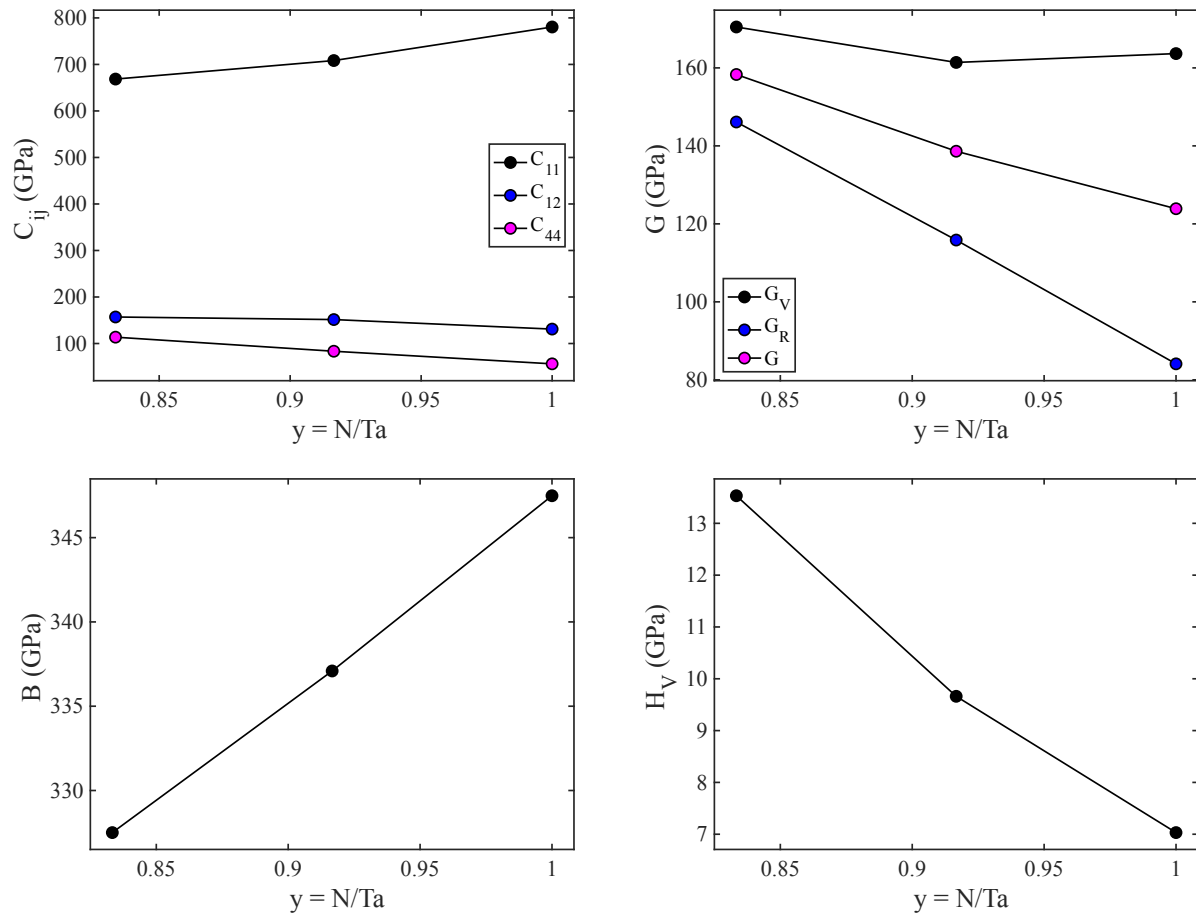


Figure A.9: VASP-computed cubic elastic moduli for rocksalt-structured tantalum nitrides, TaN_y .

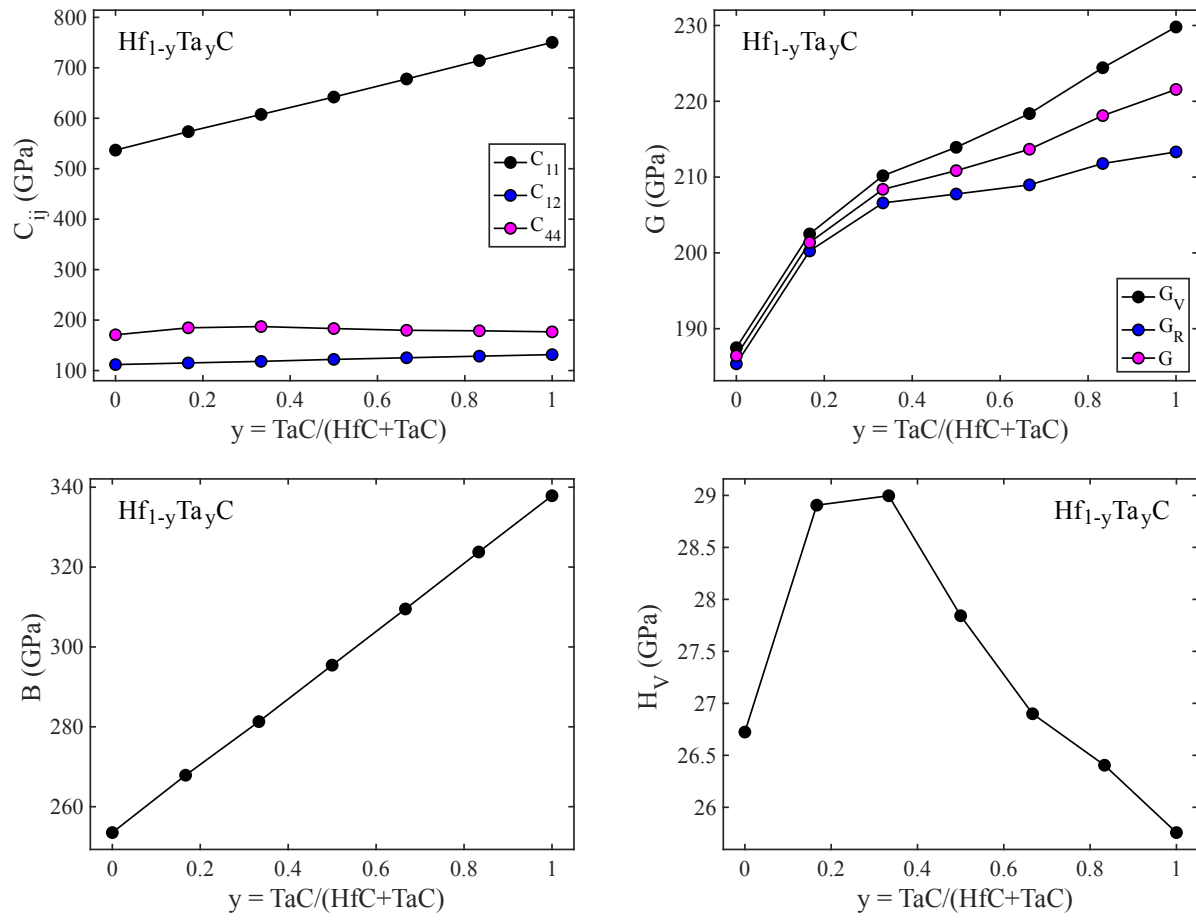


Figure A.10: DFT-computed cubic elastic stiffnesses for the B1-structured hafnium-tantalum carbide alloys, $\text{Hf}_{1-y}\text{Ta}_y\text{C}$.

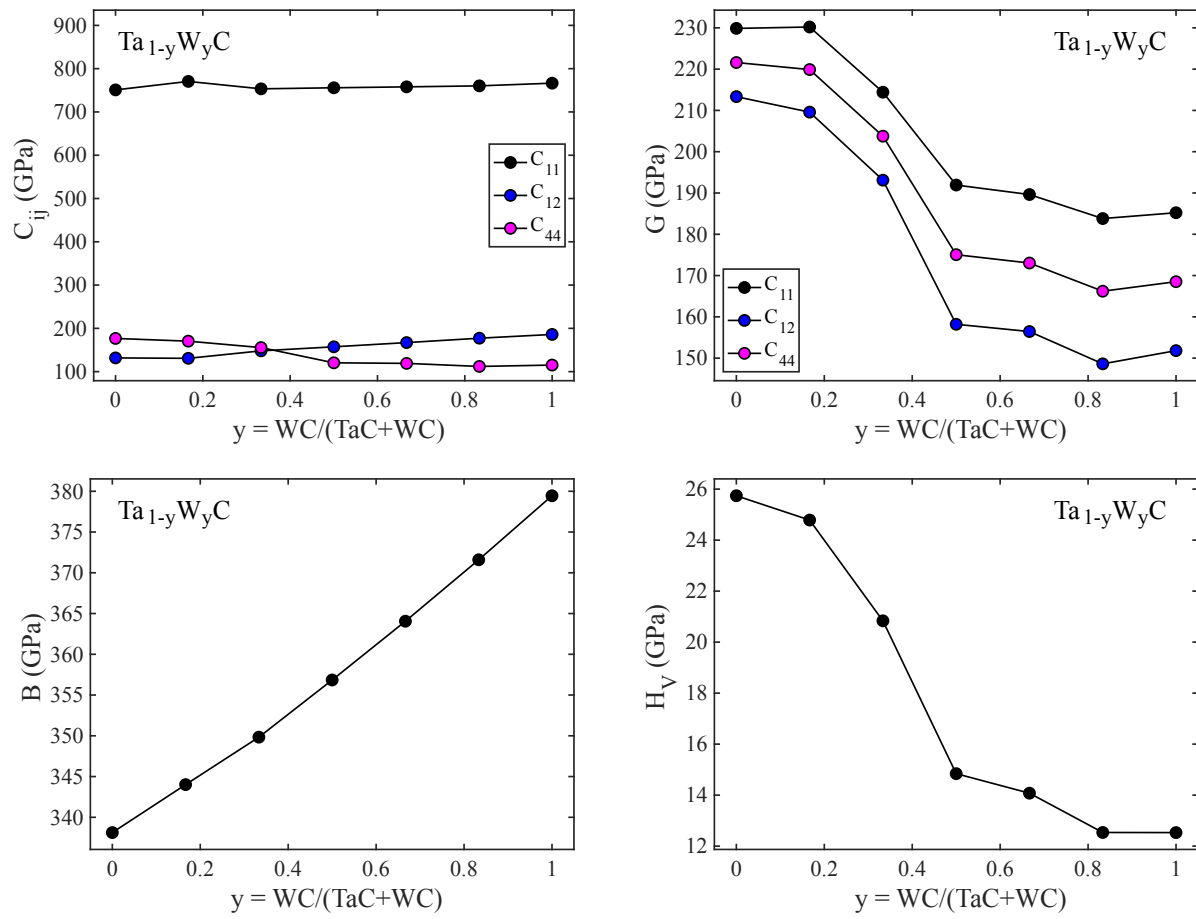


Figure A.11: DFT-computed cubic elastic stiffnesses for the B1-structured tantalum-tungsten carbide alloys, $\text{Ta}_{1-y}\text{W}_y\text{C}$.

Appendix B

Additional Stacking-Fault Energy Results

Included in this Appendix are additional stacking-fault energy results omitted from the main text of the Dissertation for the sake of brevity. Information in this section is not necessary for the reader to understand the primary findings of this work overall, but are included in the interest of completeness.

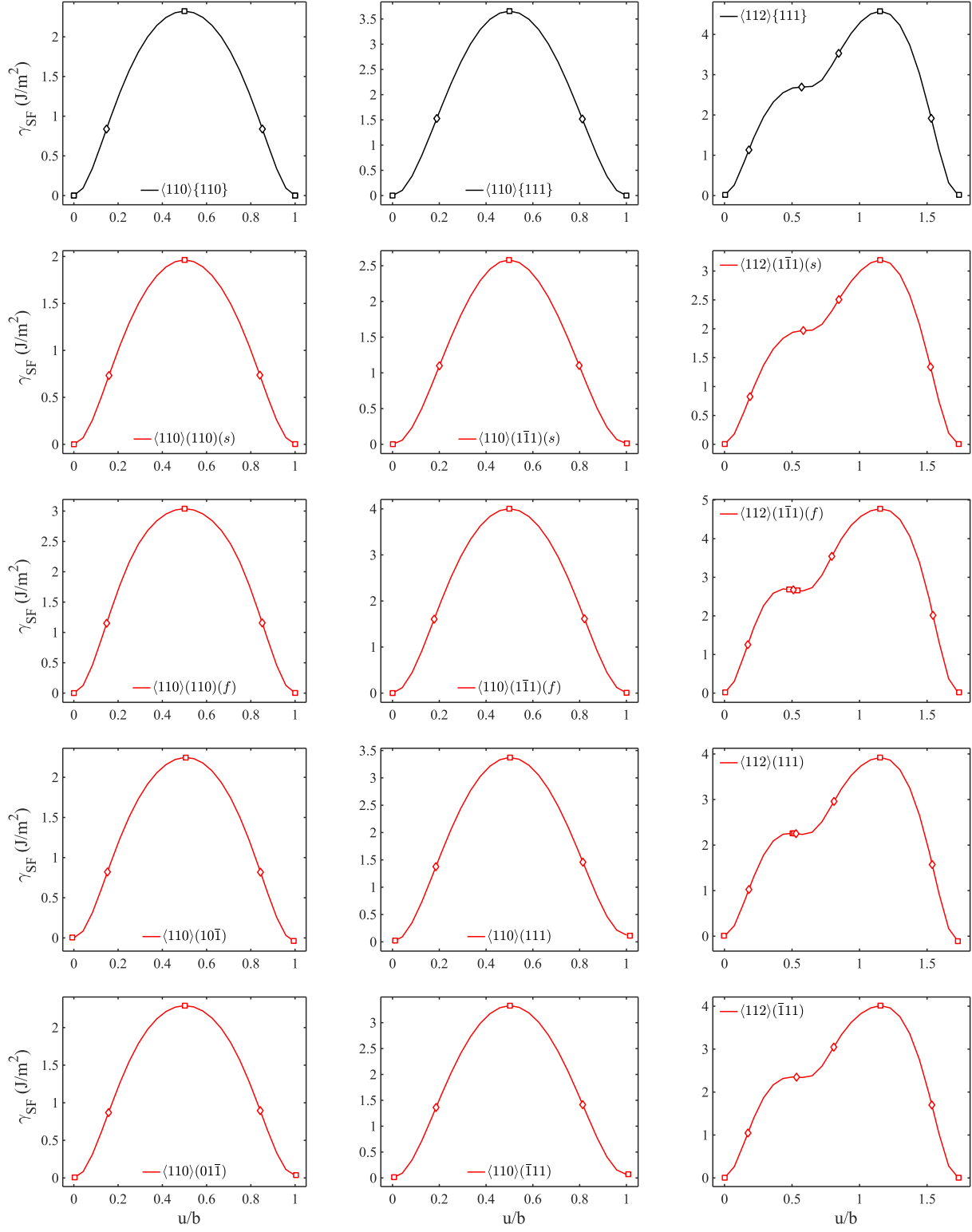


Figure B.1: Feature identification for all computed γ_{SF} curves in TiC (black) and Ti₆C₅ (red).

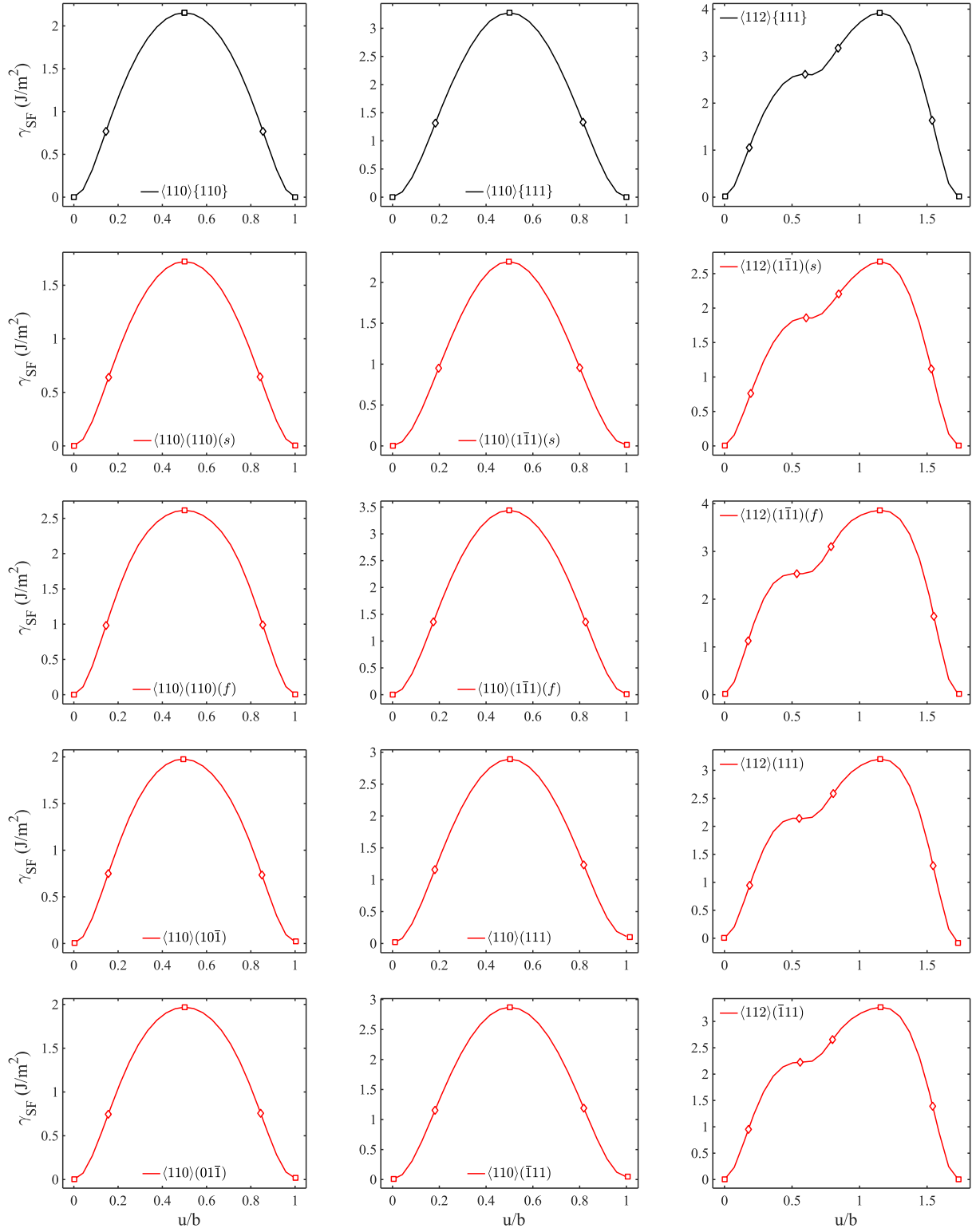


Figure B.2: Feature identification for all computed γ_{SF} curves in ZrC (black) and Zr_6C_5 (red).

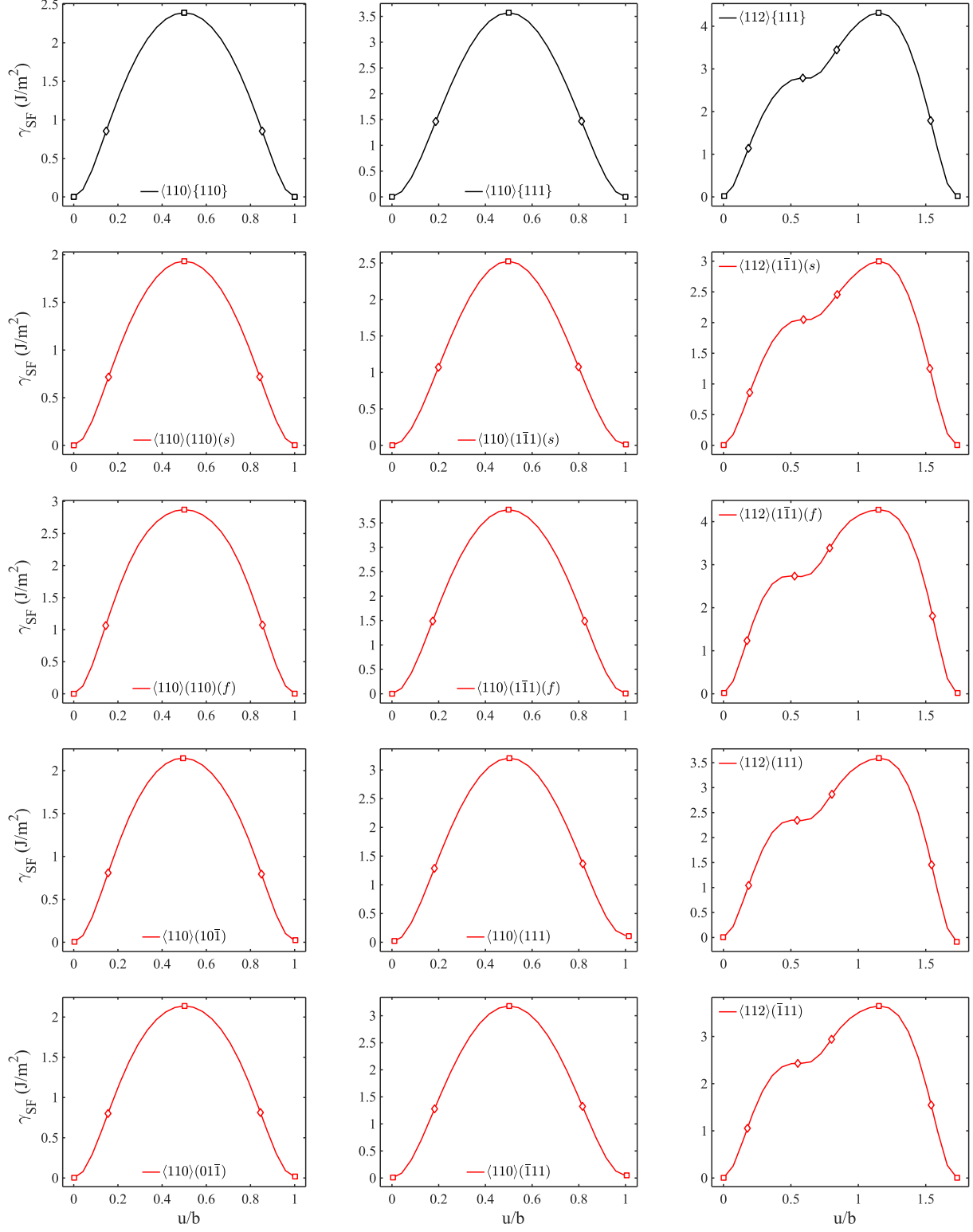
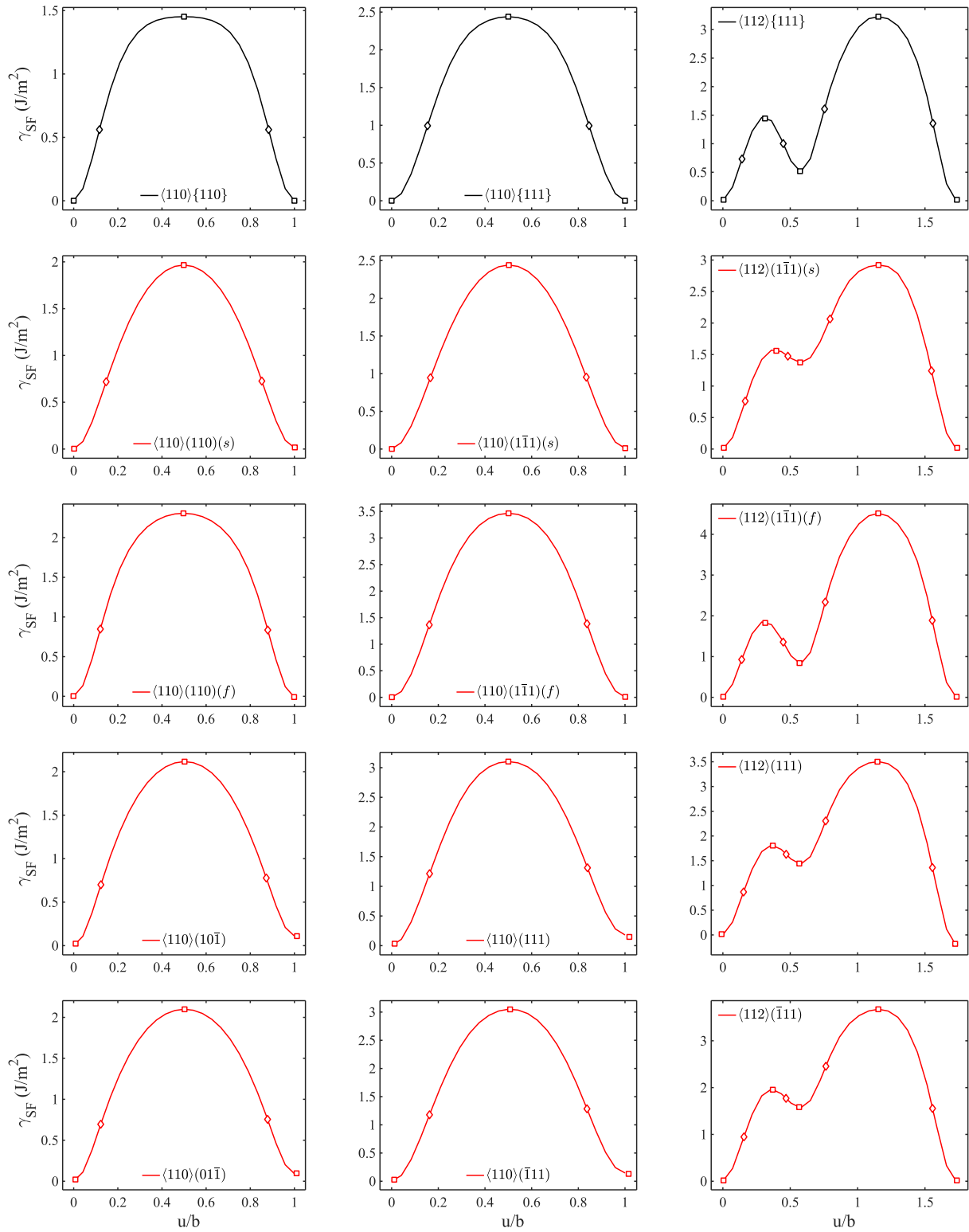


Figure B.3: Feature identification for all computed γ_{SF} curves in HfC (black) and Hf₆C₅ (red).



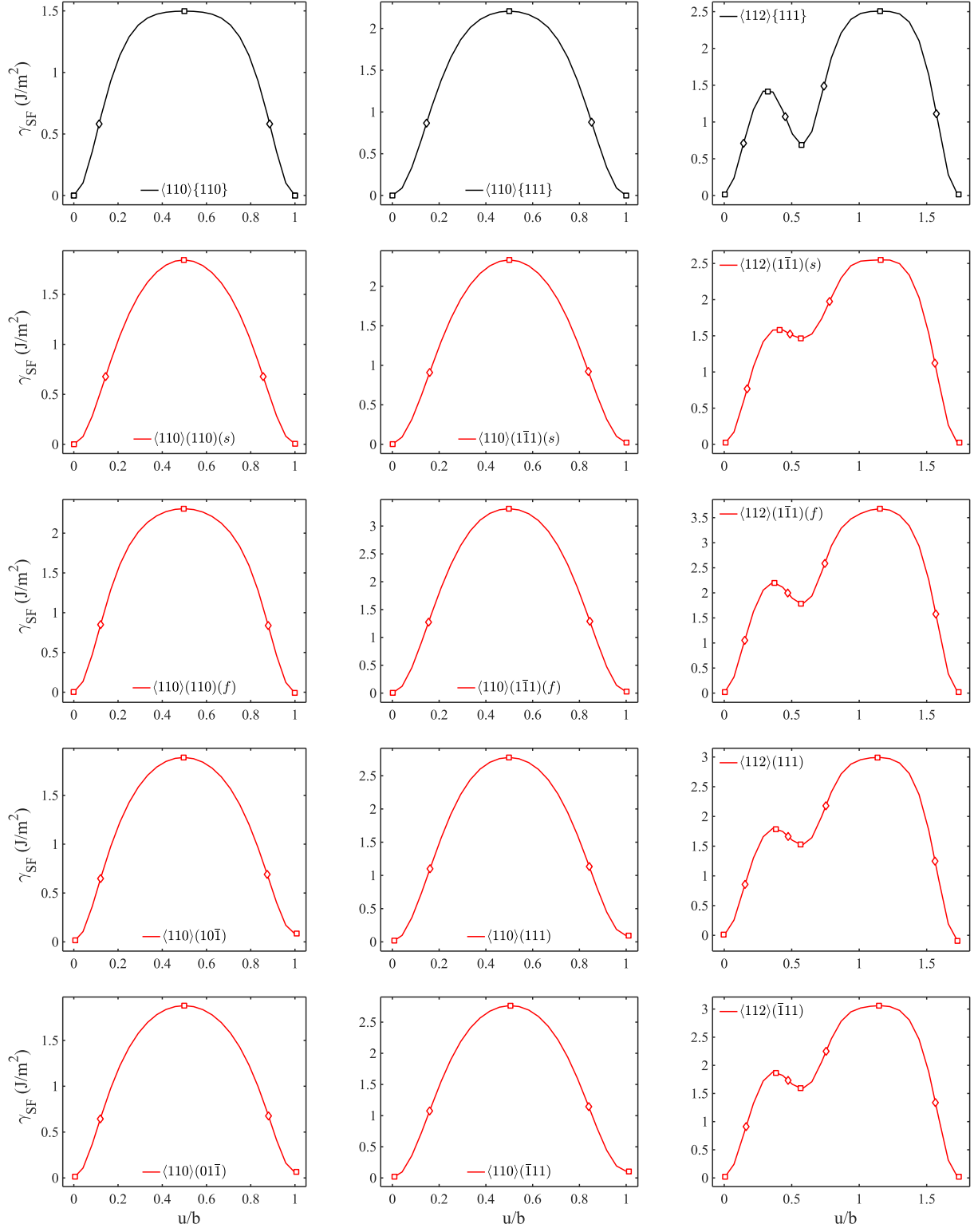


Figure B.5: Feature identification for all computed γ_{SF} curves in NbC (black) and Nb₆C₅ (red).

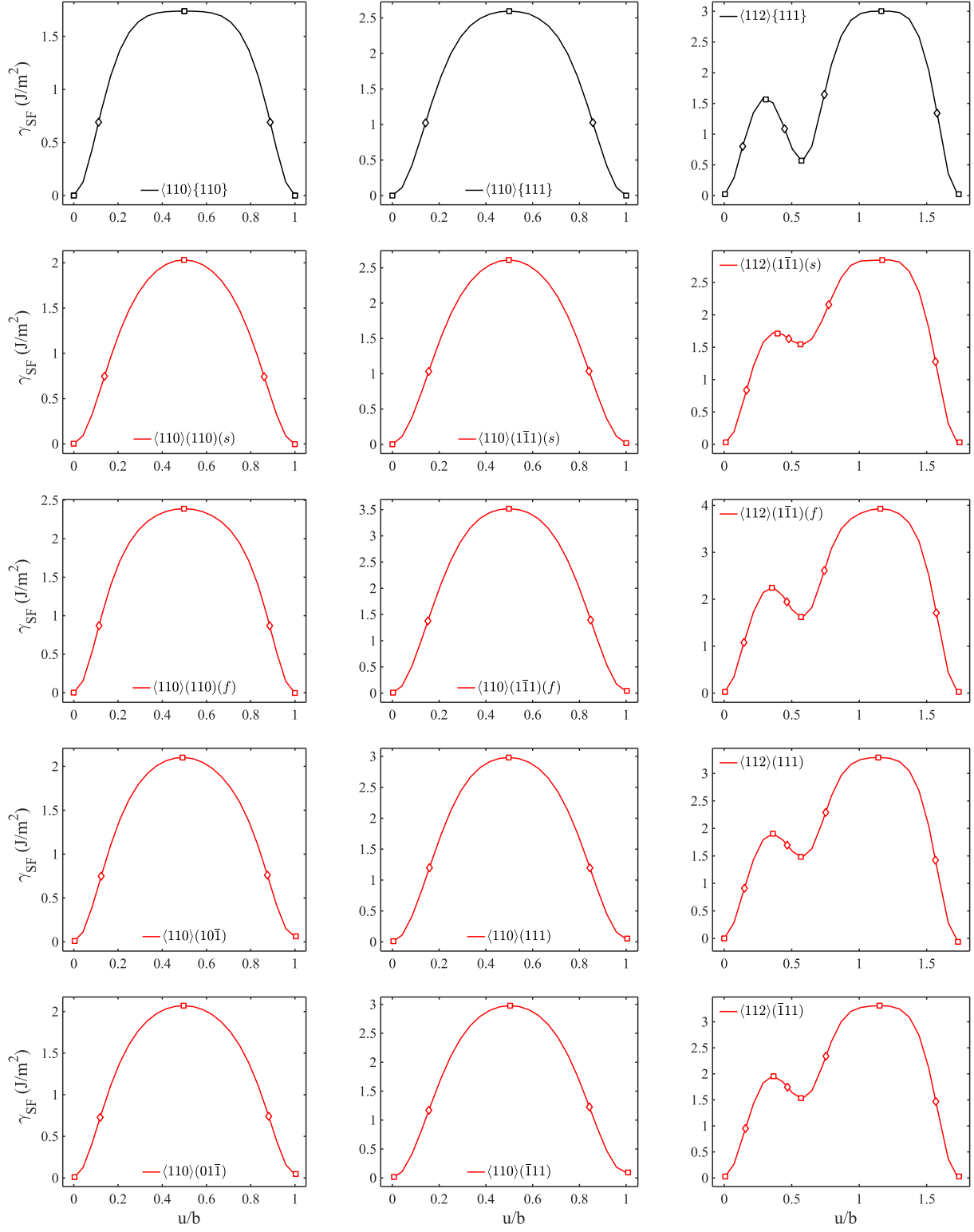


Figure B.6: Feature identification for all computed γ_{SF} curves in TaC (black) and Ta₆C₅ (red).

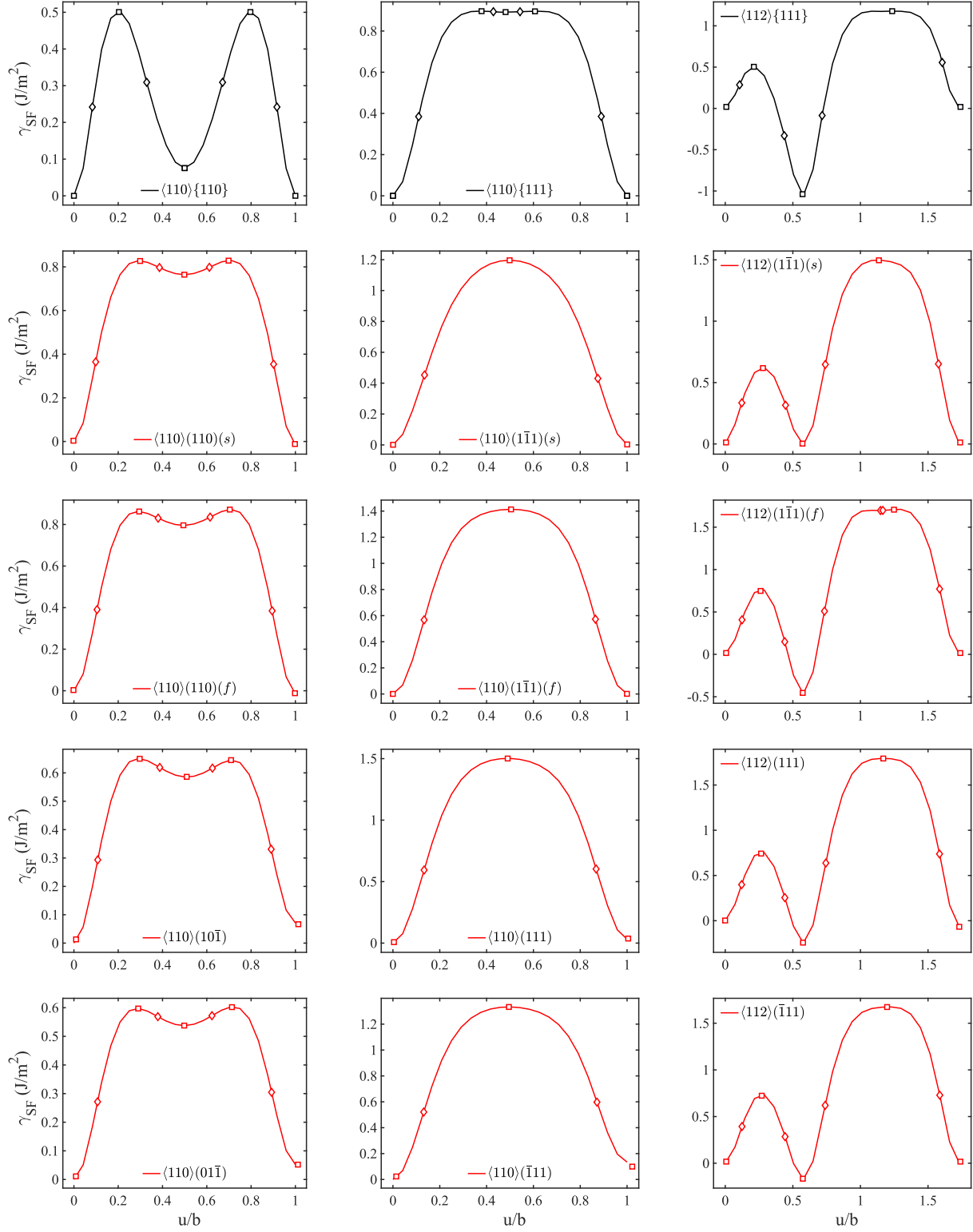


Figure B.7: Feature identification for all computed γ_{SF} curves in MoC (black) and Mo₆C₅ (red).

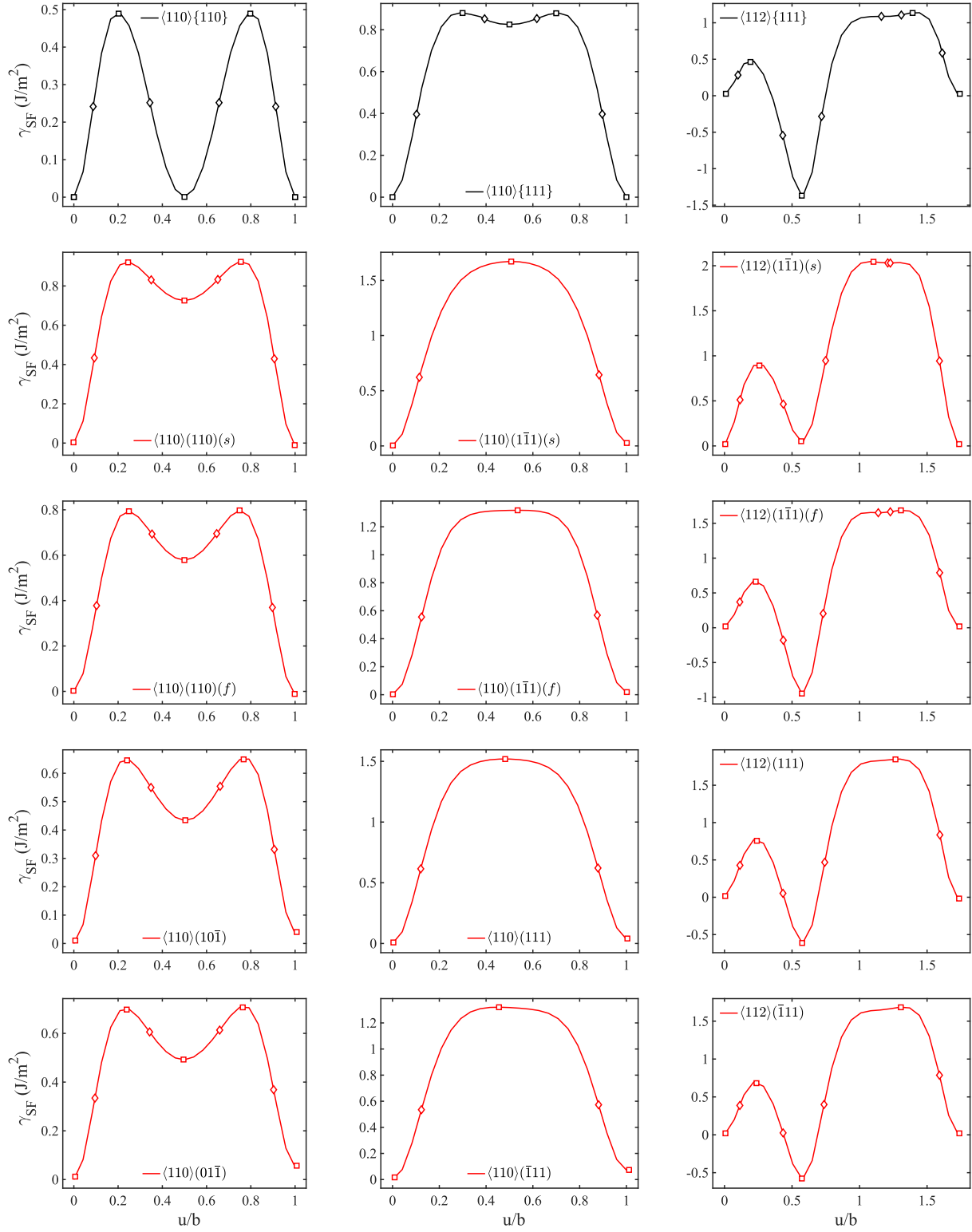


Figure B.8: Feature identification for all computed γ_{SF} curves in WC (black) and W_6C_5 (red).

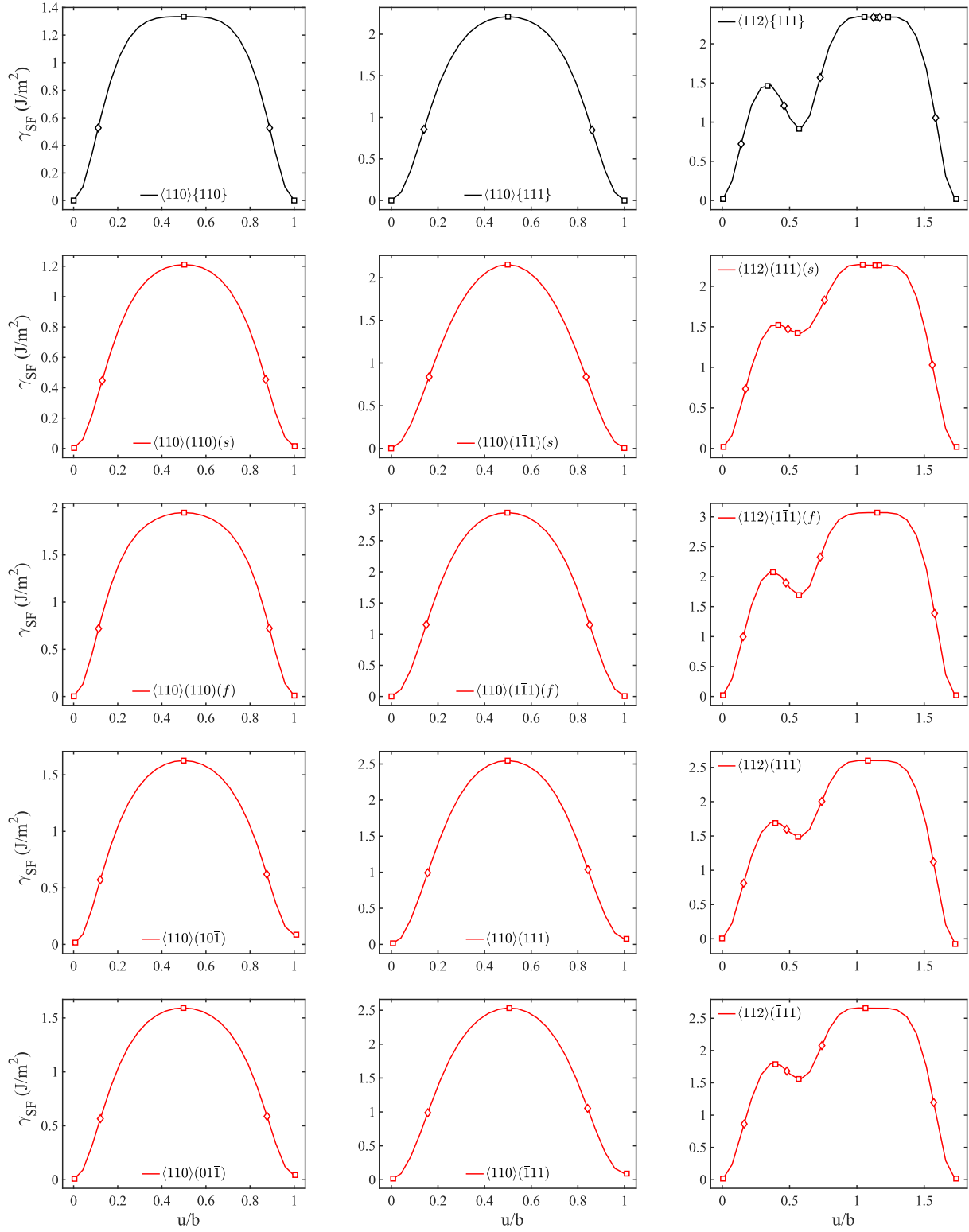


Figure B.9: Feature identification for all computed γ_{SF} curves in TiN (black) and Ti₆N₅ (red).

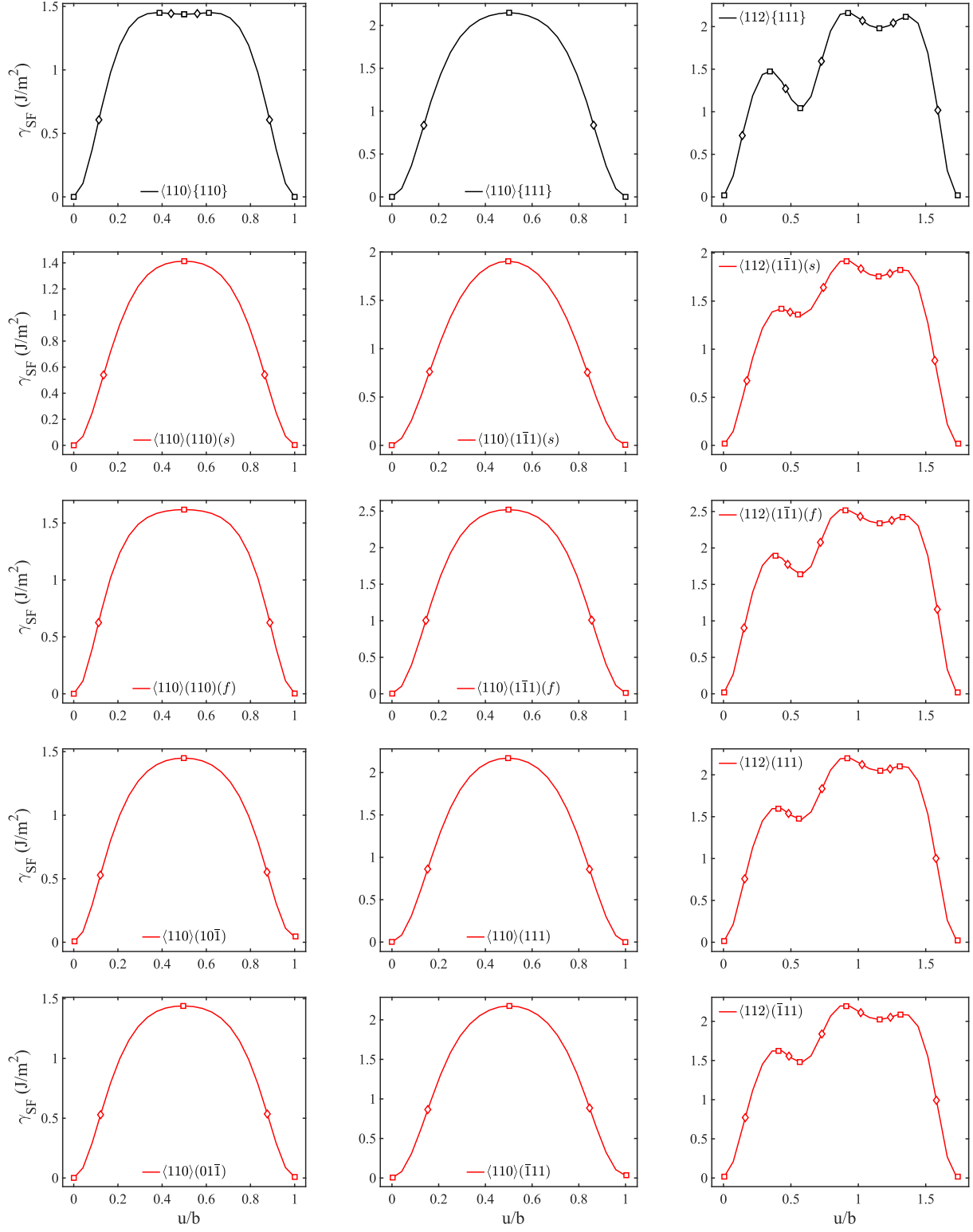


Figure B.10: Feature identification for all computed γ_{SF} curves in ZrN (black) and Zr₆N₅ (red).

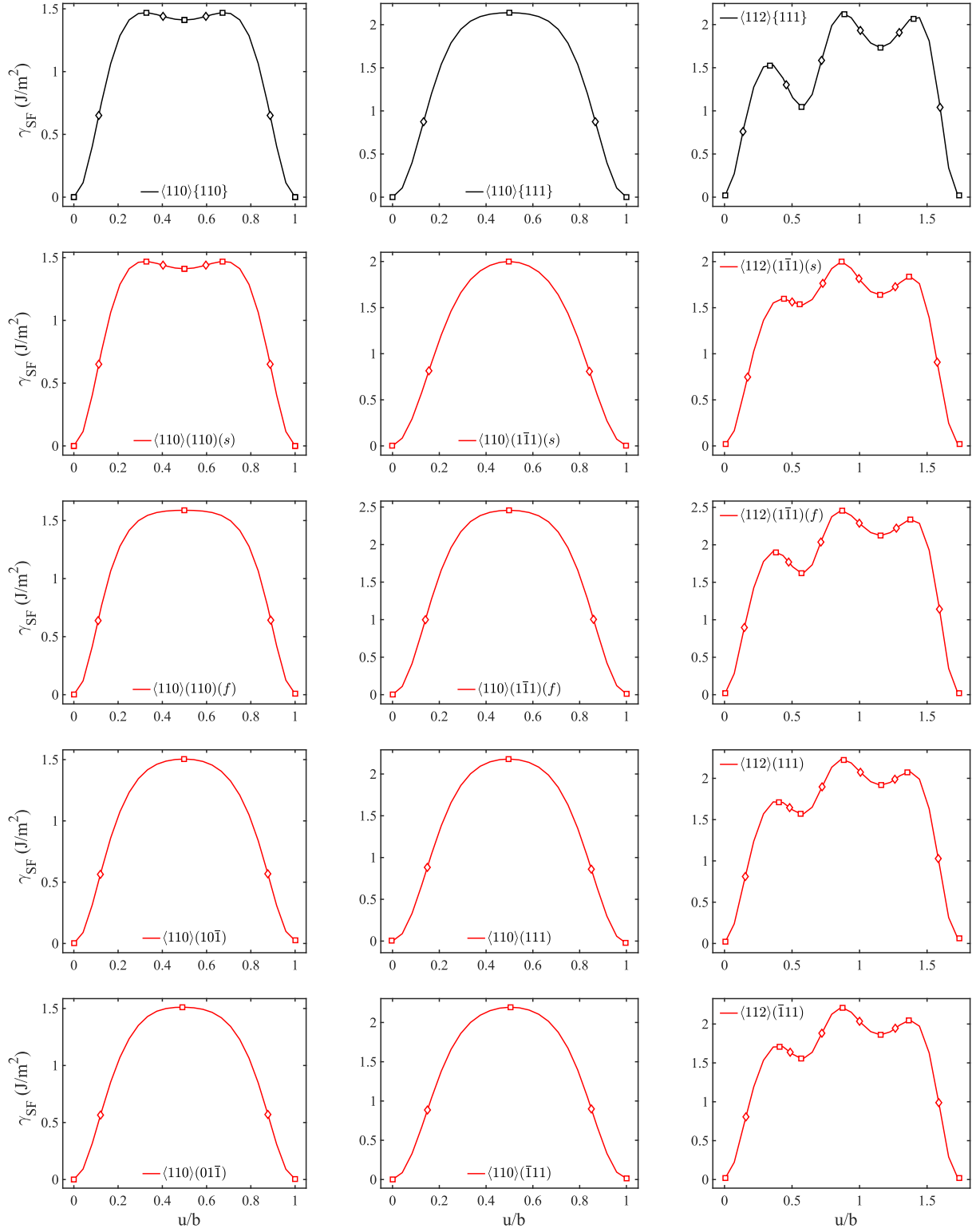


Figure B.11: Feature identification for all computed γ_{SF} curves in HfN (black) and Hf₆N₅ (red).

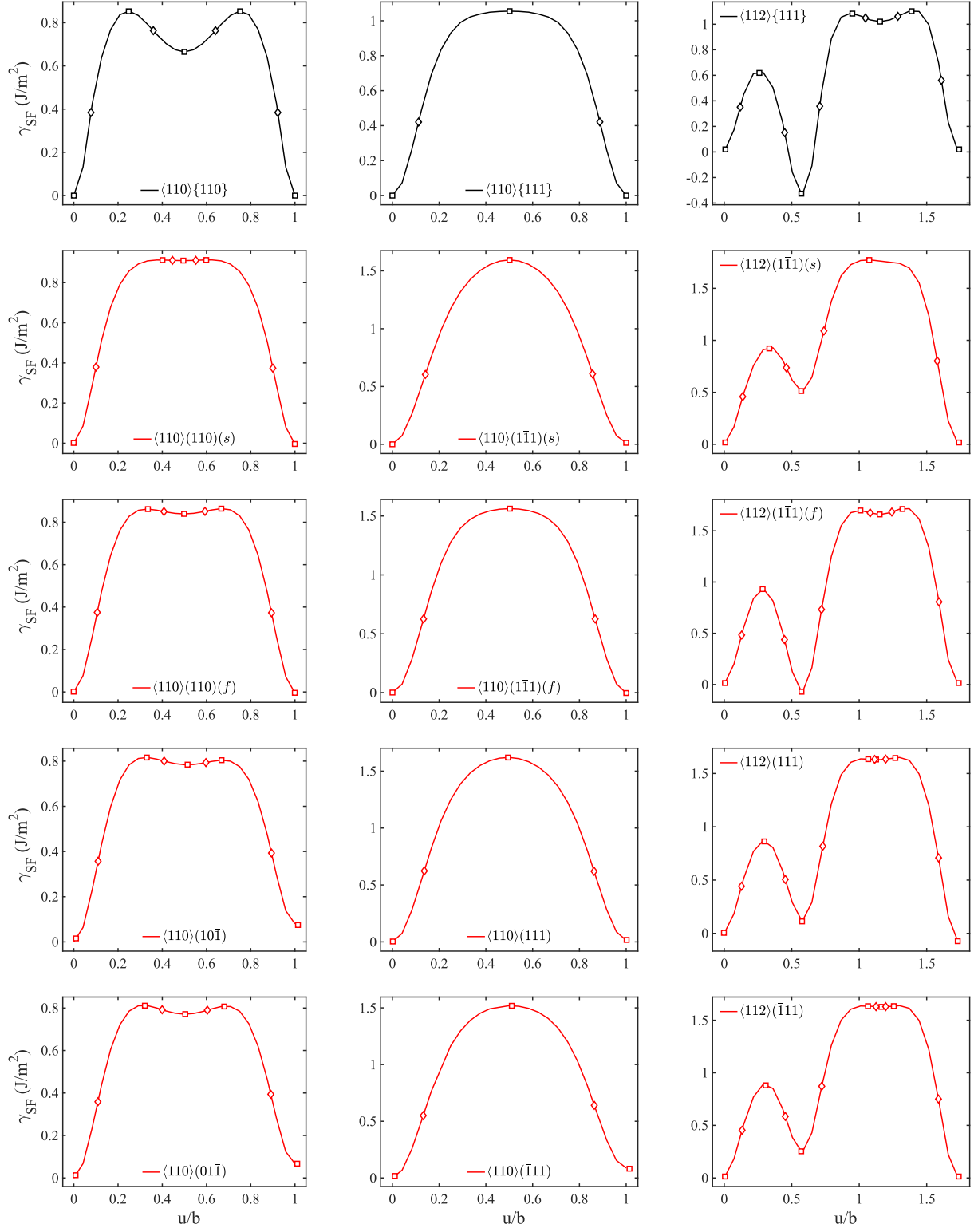


Figure B.12: Feature identification for all computed γ_{SF} curves in VN (black) and V₆N₅ (red).

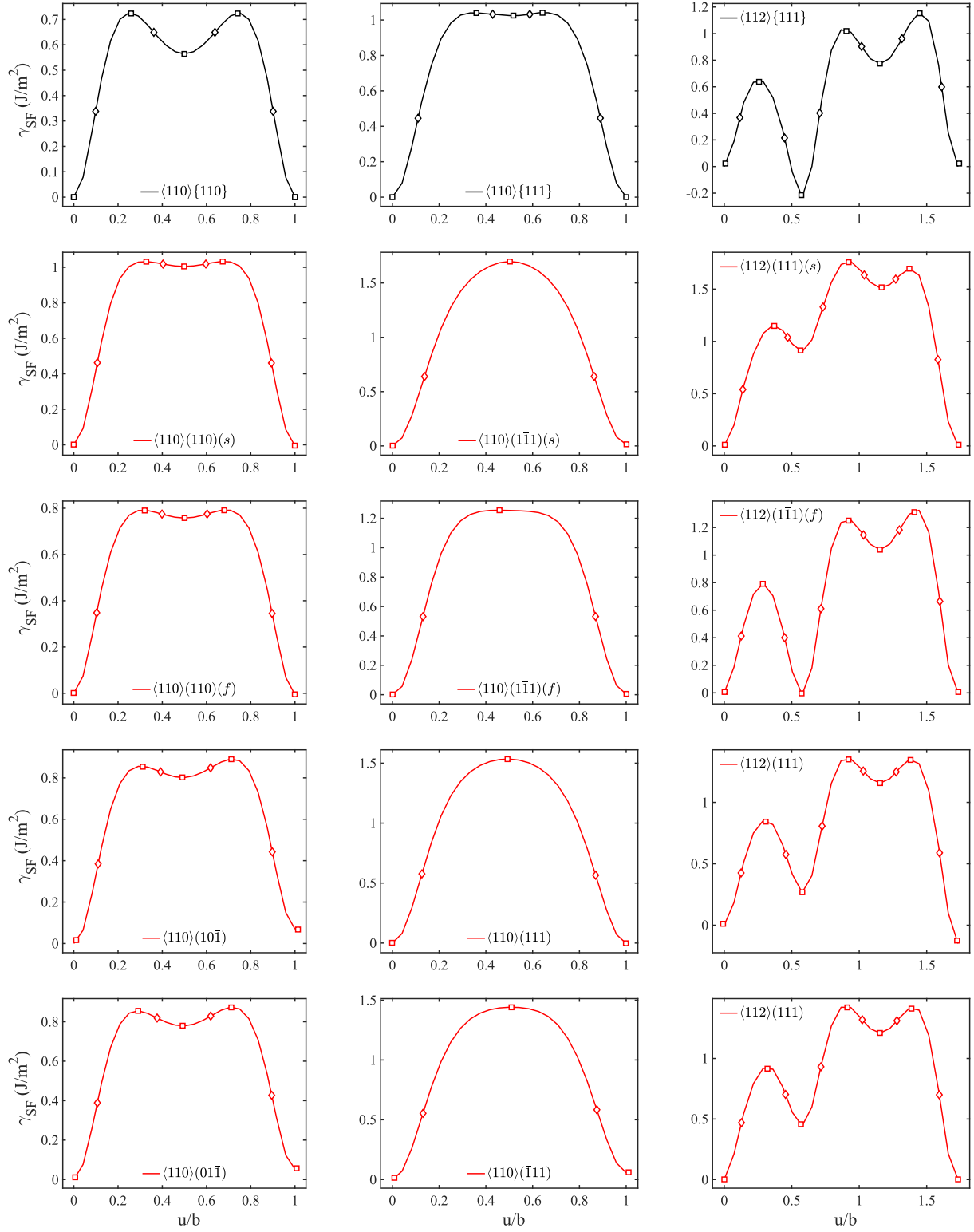


Figure B.13: Feature identification for all computed γ_{SF} curves in NbN (black) and Nb₆N₅ (red).

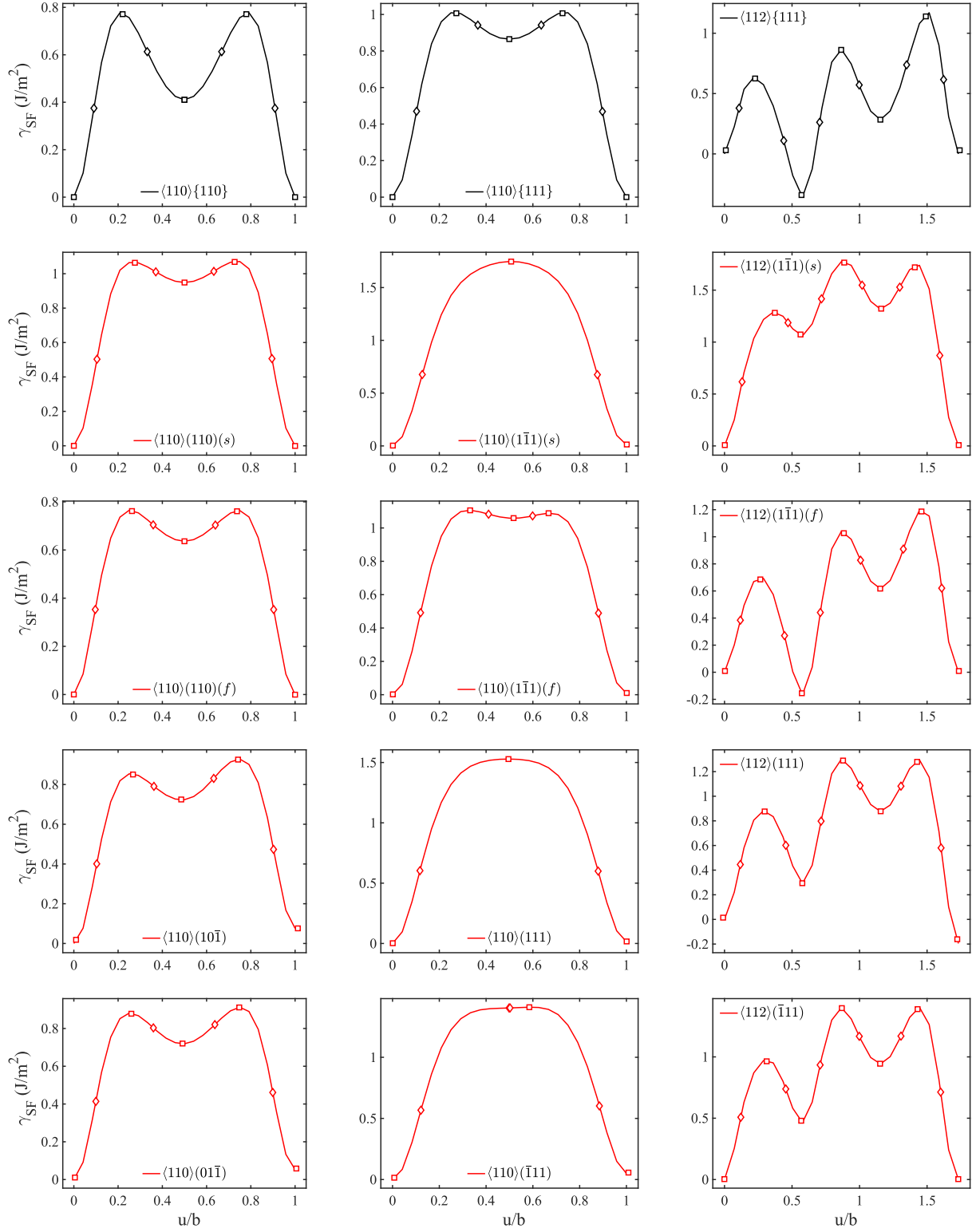


Figure B.14: Feature identification for all computed γ_{SF} curves in TaN (black) and Ta₆N₅ (red).

Appendix C

Additional Information on the Fracture Model of Hardness

As was covered in Section 4.1.7, the analytical formulation of our cracking-based hardness model was drawn from prior work seeking to determine fracture toughness from indentation tests. Based on the arguments presented in Section 4.1.7, we elected to use the relationship of Lawn and Fuller [136, 139], which was subsequently popularized by Niihara [140]; this ultimately yielded a model of the form

$$H_V^c = \frac{2 \sin \theta / 2P}{4r^2} \frac{\eta \sqrt{2\gamma E}}{\chi} c^{3/2}, \quad (\text{C.1})$$

which contains a number of parameters whose selection should be addressed in greater detail. The first, χ , is given by the Lawn-Fuller model as

$$\chi = \xi(E/H)^m, \quad (\text{C.2})$$

where E/H is the ratio of the polycrystalline Young's modulus to the measured hardness. While both E and H are conventionally both measured from the indentation experiments themselves, the data we received did not contain consistent elastic modulus measurements. Accordingly, we opted to use the polycrystalline Young's modulus computed from our DFT-derived elastic stiffnesses. For each modeled material, E and H were selected according to the material's VEC group—HfC data for the IVB TMCs, and TaC data for the VB TMCs and IVB TMNs. Consistent with earlier literature using the Lawn-Fuller model, the phenomenological parameters ξ and m were chosen to be 0.012 and 0.5, respectively.

We also sought to choose the coefficient η in order to secure reasonable toughness estimates for use in our model. This was deemed necessary due to the somewhat controversial nature of toughness determinations by indentation: though expedient, the indentation methodology suffers

from a well-documented lack of reproducibility. That is, the measured toughness depends greatly on the particular methodology used, as well as on the characteristics of the samples used to make the toughness determinations. Furthermore, since experimental indentation-toughness experiments often use polycrystalline samples—rather than single crystals, as generally assumed by the analytic models—and so predictions from purely intragranular fracture (*i.e.*, cleavage) will require some adjustment to match experimental toughness data. From our first-principles study, we have

$$K_{\text{IC}}^{\text{DFT}} = \sqrt{2\gamma(y)E(y)}, \quad (\text{C.3})$$

where y is the composition coordinate, typically equal to the nonmetal-to-metal atom ratio. We then sought to develop the scaling constant η by comparing our DFT-computed toughness estimates to experiment. It was decided that the experimental data should be collected for HfC—as it is harder and more ideally brittle than TaC, and therefore likely behaves more like our first-principles approach would predict—and at the stoichiometric composition $y = 1$. The experimental HfC fracture toughness data chosen for the η parameterization was that of Demirskyi *et al.* [141], which relied on bending of a single-edge-notched beam (SENB)—an approach generally held to be more reliable and reproducible than determinations of K_{IC} by indentation. The parameter η is then given by

$$\eta = \frac{K_{\text{IC}}^{\text{HfC(SENB)}}}{K_{\text{IC}}^{\text{HfC(DFT)}}} = \frac{K_{\text{IC}}^{\text{HfC(SENB)}}}{\sqrt{2\gamma^{\text{HfC(DFT)}}E^{\text{HfC(DFT)}}}} \quad (\text{C.4})$$

The toughness estimate from Demirskyi *et al.* is approximately $K_{\text{IC}}^{\text{HfC(SENB)}} = 2.2 \pm 0.4 \text{ MPa}\sqrt{\text{m}}$, giving a nominal η of about 1.75.

Obviously, this model accepts as inputs the Griffith work of fracture, 2γ , which is equal in the case of pure intragranular fracture to the cleavage energy, γ_c . The cleavage energy values themselves were computed by our colleague, Yuchen Huang, for use in the fracture-based hardness model and considering the possibility of cleavage fracture on both $\{111\}_{\text{B1}}$ and $\{100\}_{\text{B1}}$ planes. Carbon depletion of cleavage planes of both types can be seen in Figures C.1 and C.2, illustrating the VASP simulation cells used for these calculations.

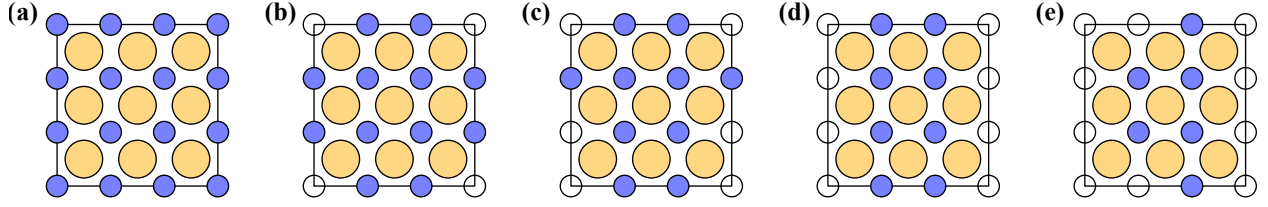


Figure C.1: Illustration of $\{100\}_{B1}$ surfaces used for cleavage energy calculations. Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

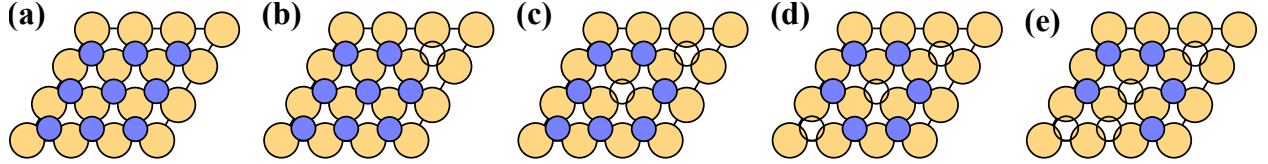


Figure C.2: Illustration of $\{111\}_{B1}$ surfaces used for cleavage energy calculations. Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

The results, shown in Figure C.3, indicate remarkably similar trends in all of the modeled carbides and nitrides. Cleavage on $\{100\}_{B1}$ planes is preferred at all compositions in all of these materials, with γ_c on these planes increasing slightly with decreasing y . On the $\{111\}_{B1}$ planes, γ_c is generally very high, and is seen to decrease significantly as y decreases. One trend that is readily identified within these data is that cleavage energies seem to decline in general at higher VEC: the computed γ_c , particularly on the $\{111\}_{B1}$ planes, are noticeably lower in the VB TMCs and IVB TMNs than in the IVB TMCs.

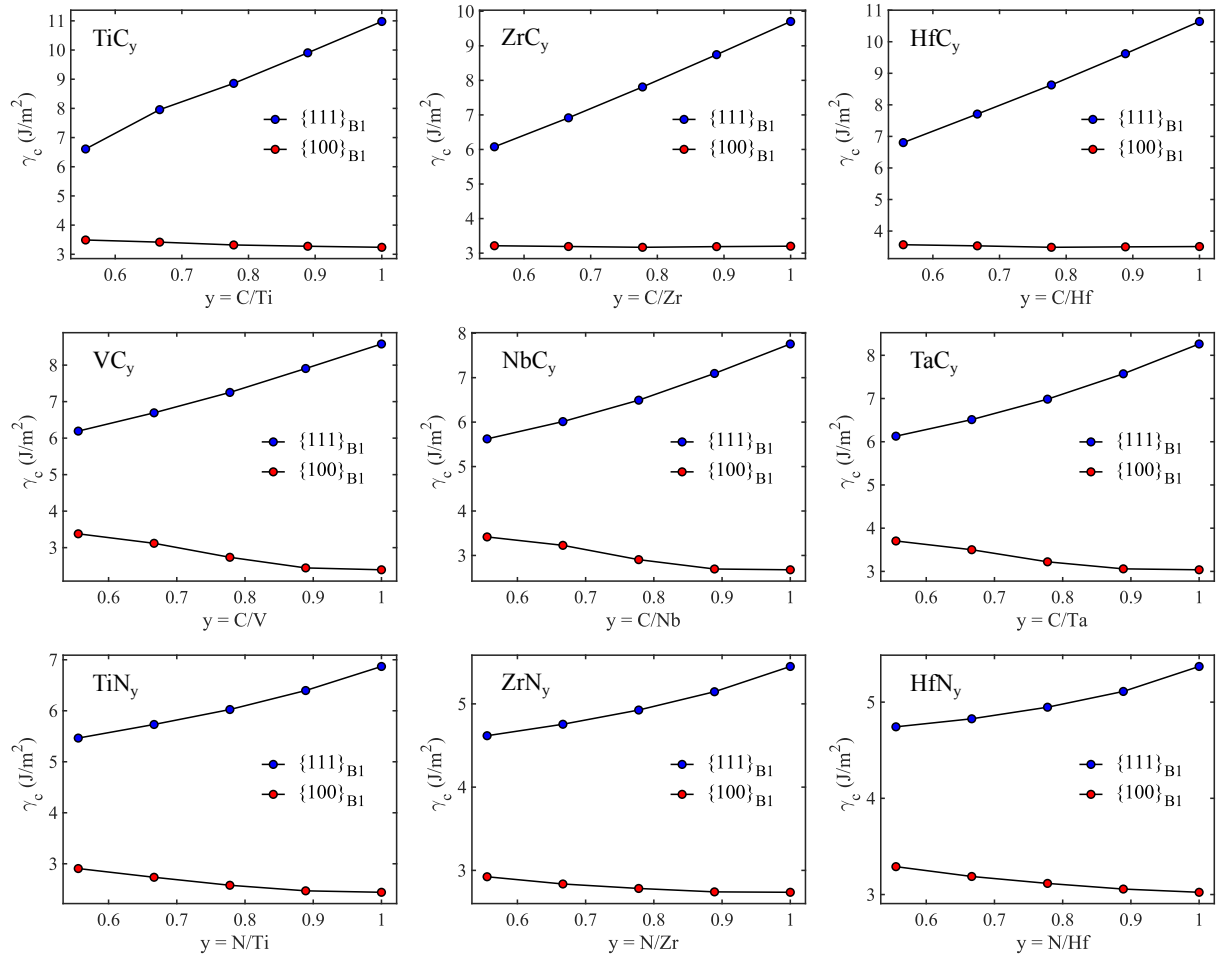


Figure C.3: Cleavage energies on $\{100\}_{\text{B1}}$ and $\{111\}_{\text{B1}}$ crystallographic planes at various nonmetal-to-metal atom ratios for the IVB TMCs, the VB TMCs and the IVB TMNs. All data generated by Yuchen Huang and previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

Appendix D

Additional Findings from Plasticity-Fracture Model

In addition to the summarized results published in the main text of this manuscript, we have computed load-depth, hardness-depth, and hardness-composition curves for all of the cubic carbides and nitrides using both the plasticity-regulated hardness model and the fracture-regulated hardness model.

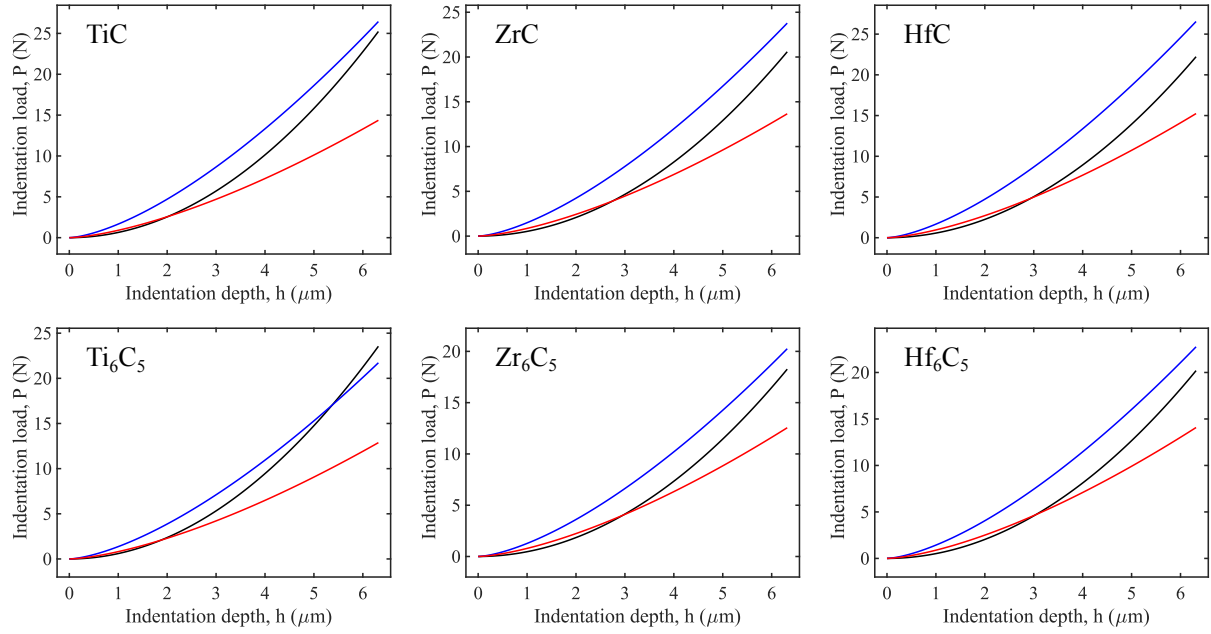


Figure D.1: Load-depth curves computed for stoichiometric and substoichiometric IVB TMCs. Predictions are shown for failure governed by dislocation plasticity (black lines), intragranular cracking along $\{100\}_{\text{B1}}$ (red lines), and intragranular cracking along $\{111\}_{\text{B1}}$ (blue lines). Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

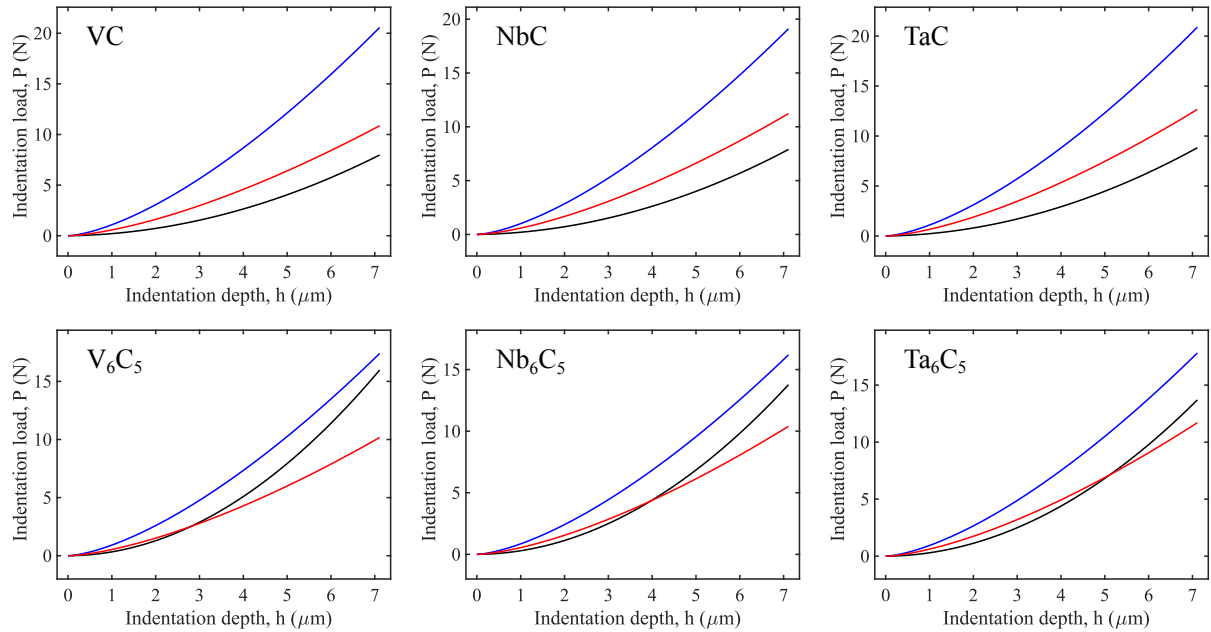


Figure D.2: Load-depth curves computed for stoichiometric and substoichiometric VB TMCs. Predictions are shown for failure governed by dislocation plasticity (black lines), intragranular cracking along $\{100\}_{\text{B1}}$ (red lines), and intragranular cracking along $\{111\}_{\text{B1}}$ (blue lines). Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

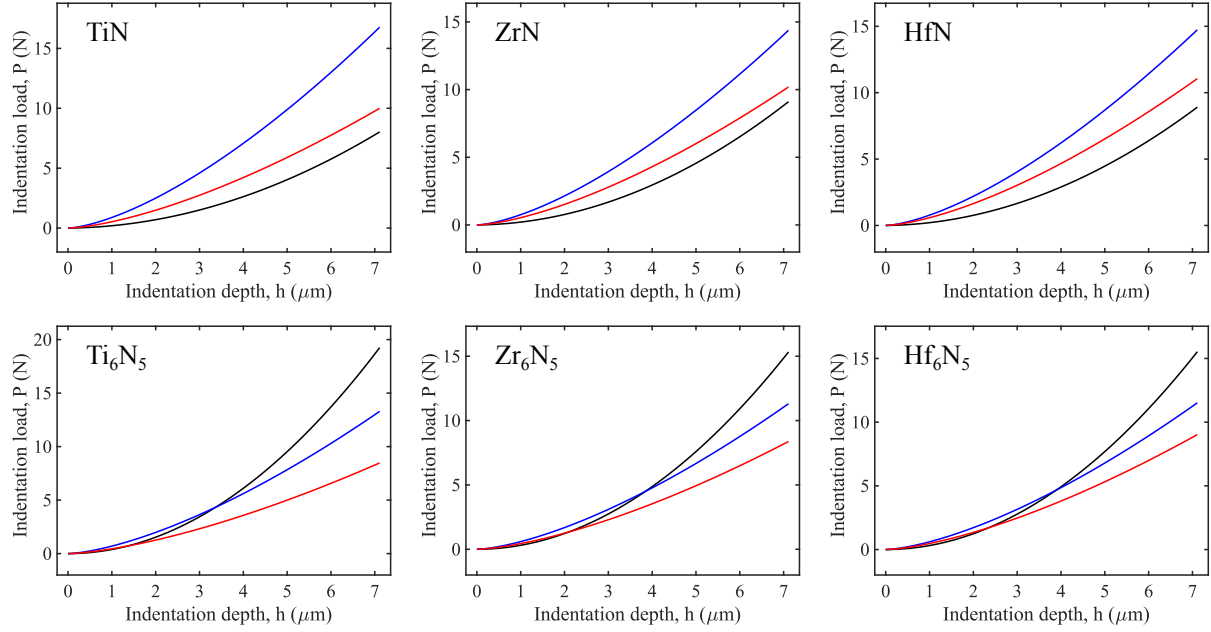


Figure D.3: Load-depth curves computed for stoichiometric and substoichiometric IVB TMNs. Predictions are shown for failure governed by dislocation plasticity (black lines), intragranular cracking along $\{100\}_{B1}$ (red lines), and intragranular cracking along $\{111\}_{B1}$ (blue lines). Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

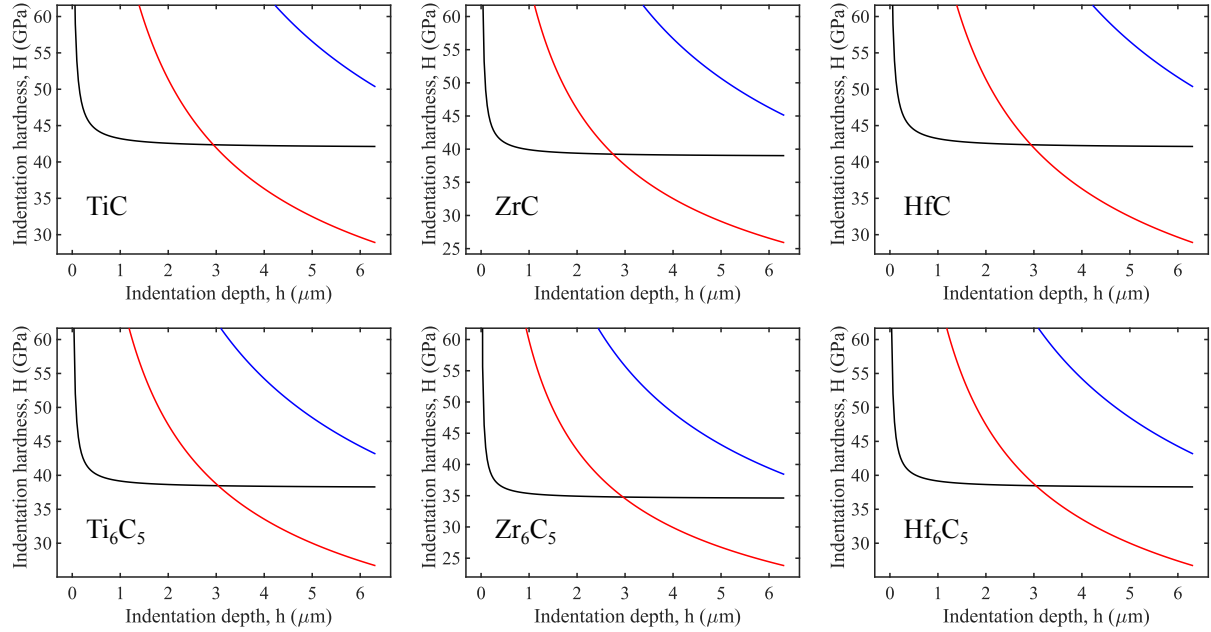


Figure D.4: Hardness-depth curves computed for stoichiometric and substoichiometric IVB TMCs. Predictions are shown for failure governed by dislocation plasticity (black lines), intragranular cracking along $\{100\}_{B1}$ (red lines), and intragranular cracking along $\{111\}_{B1}$ (blue lines). Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

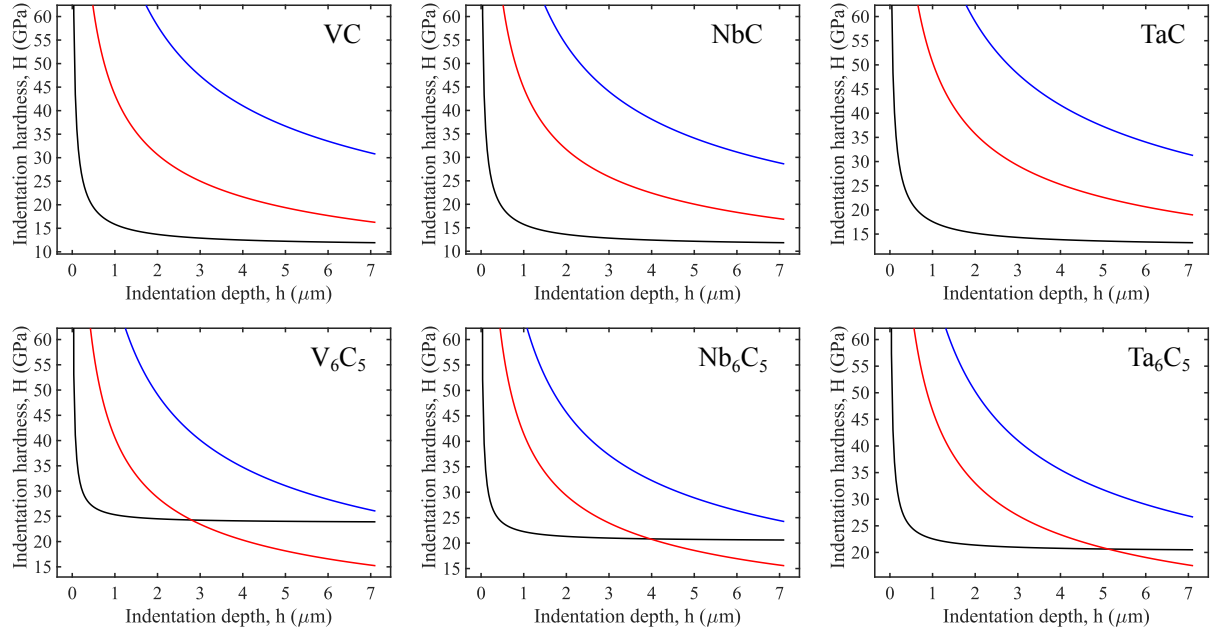


Figure D.5: Hardness-depth curves computed for stoichiometric and substoichiometric VB TMCs. Predictions are shown for failure governed by dislocation plasticity (black lines), intragranular cracking along $\{100\}_{B1}$ (red lines), and intragranular cracking along $\{111\}_{B1}$ (blue lines). Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

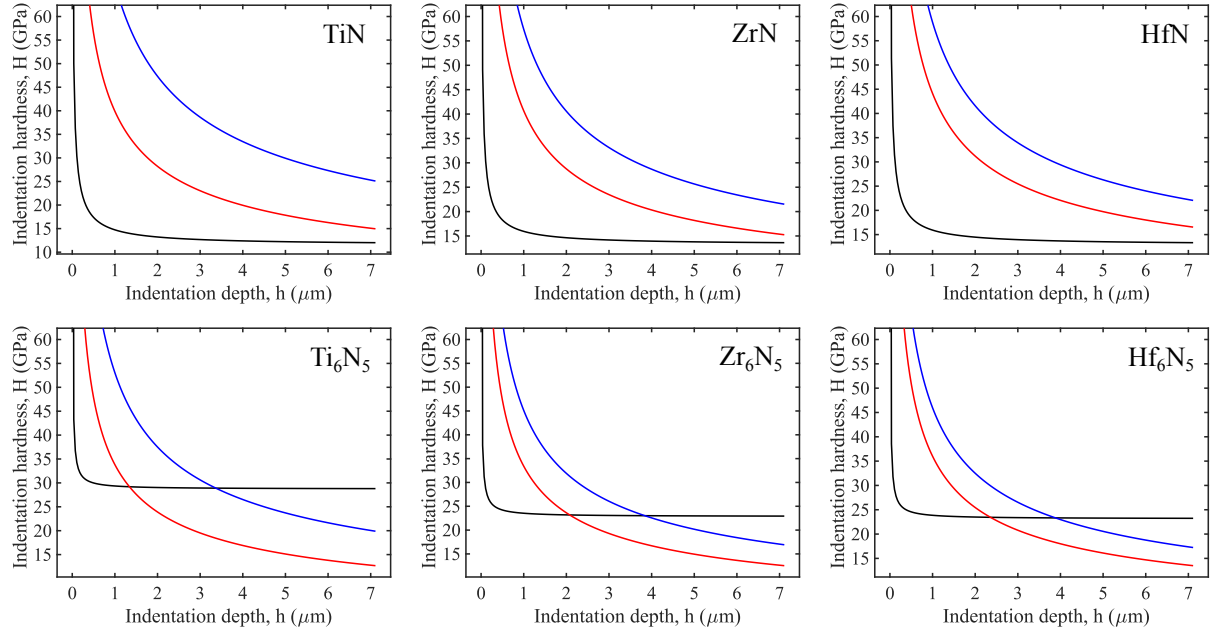


Figure D.6: Hardness-depth curves computed for stoichiometric and substoichiometric IVB TMNs. Predictions are shown for failure governed by dislocation plasticity (black lines), intragranular cracking along $\{100\}_{B1}$ (red lines), and intragranular cracking along $\{111\}_{B1}$ (blue lines). Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

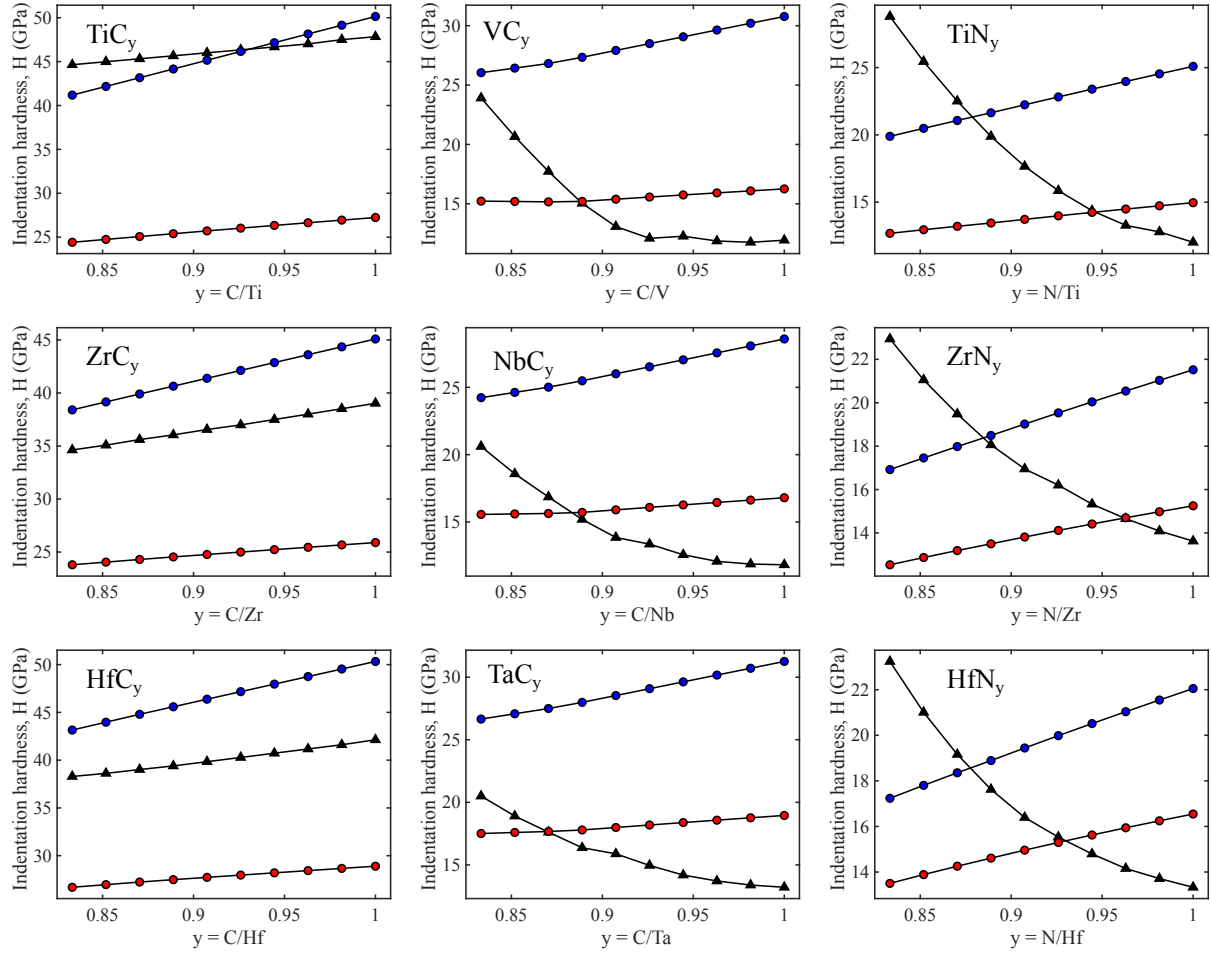


Figure D.7: Composition dependence of hardness computed for stoichiometric and substoichiometric cubic TMCs and TMNs. Predictions are shown for failure governed by dislocation plasticity (black markers), intragranular cracking along $\{100\}_{B1}$ (red markers), and intragranular cracking along $\{111\}_{B1}$ (blue markers). Previously published by Watkins *et al.* [52]. ©2025 Elsevier. All rights reserved.

Appendix E

Additional pCOOP, pCOHP and COBI Results

This appendix includes additional electronic structure analysis omitted from the main text of the Dissertation for the sake of brevity. The density-of-states (DoS), pCOOP, IpCOOP, pCOHP and IpCOHP results are generally consistent within each VEC-grouped class of carbides and nitrides, and therefore do not change the conclusions drawn in the main text, but are included here in the interest of completeness.

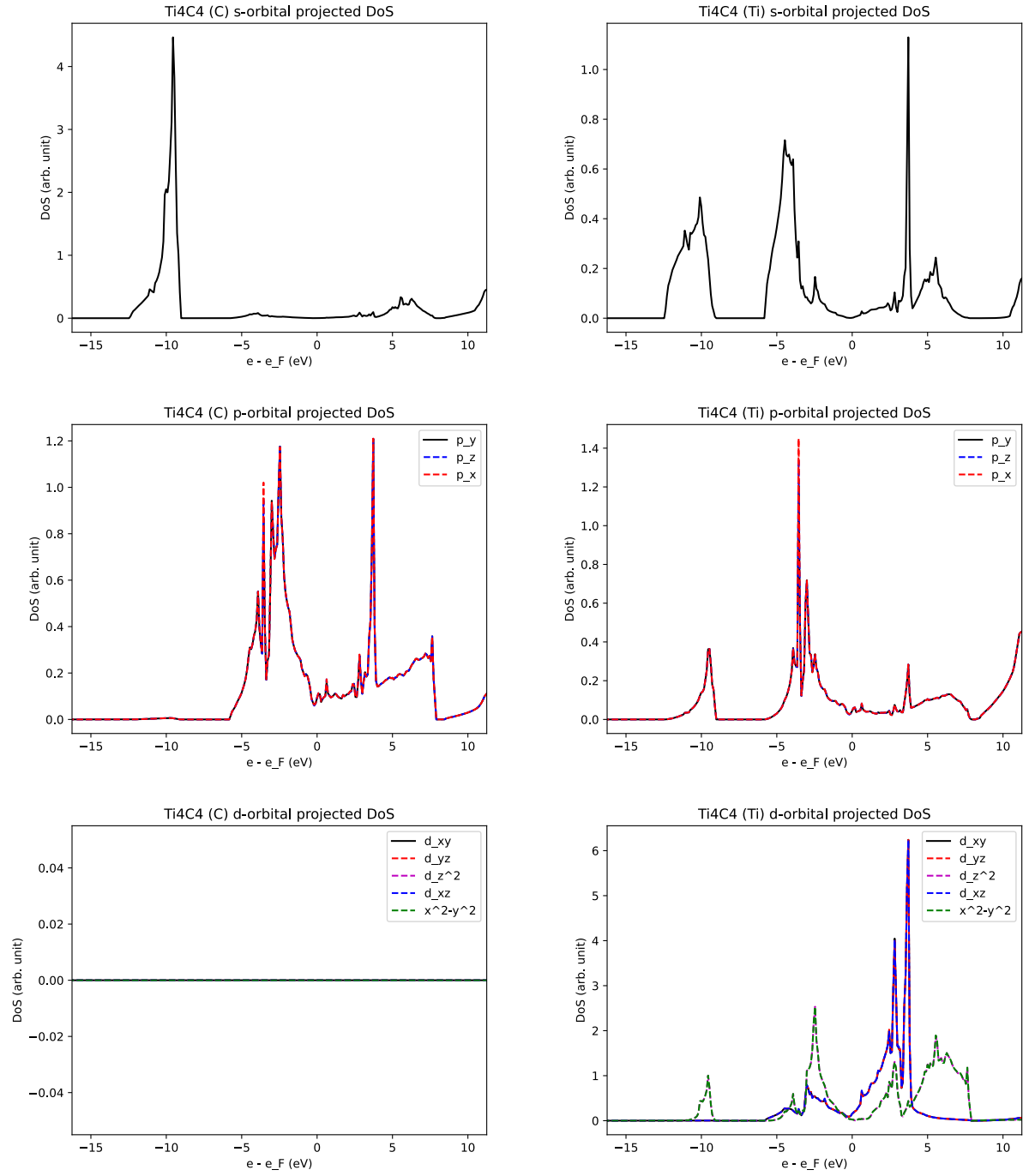


Figure E.1: Orbital-projected DoS for B1-structured TiC

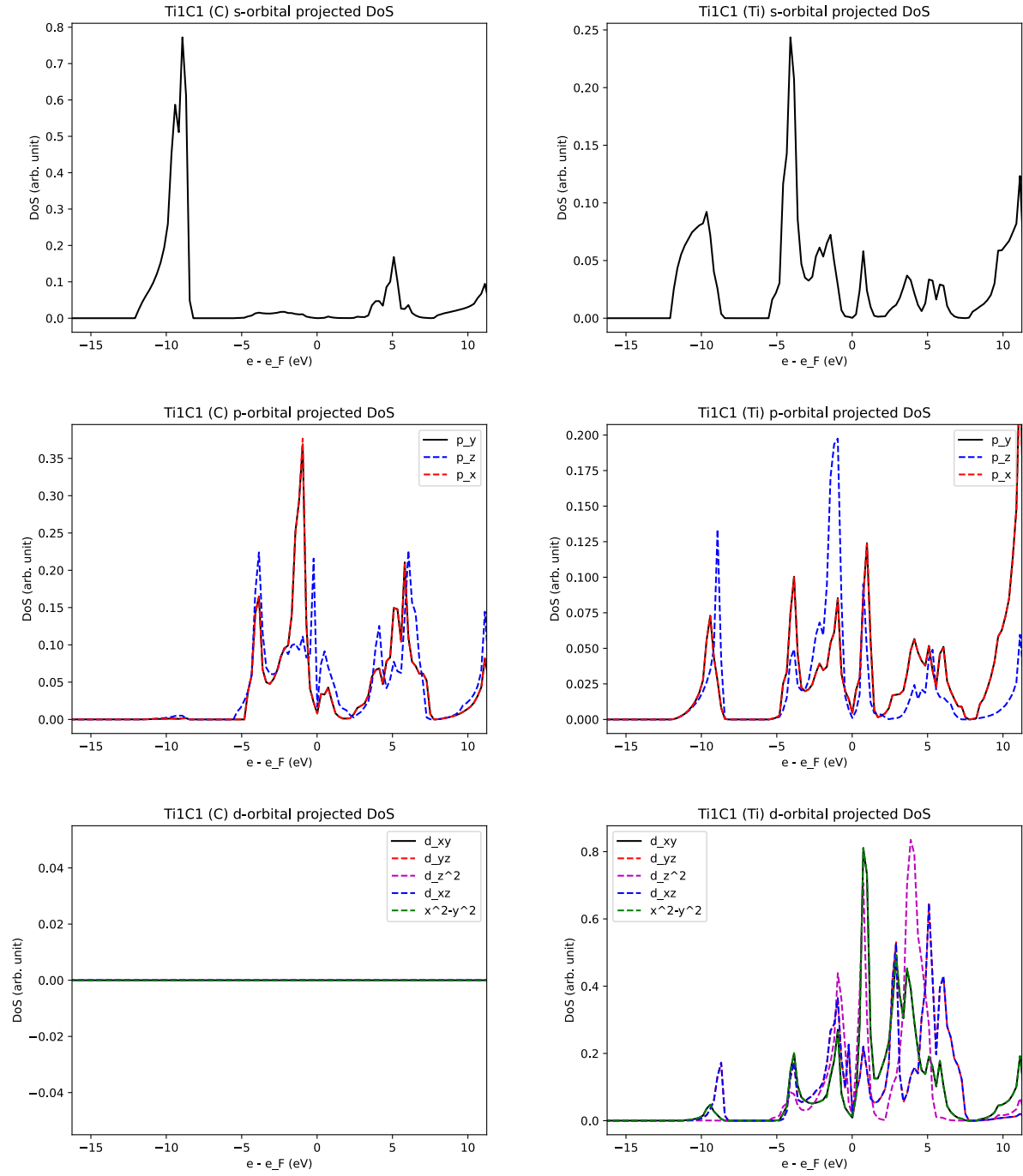


Figure E.2: Orbital-projected DoS for B_h -structured TiC

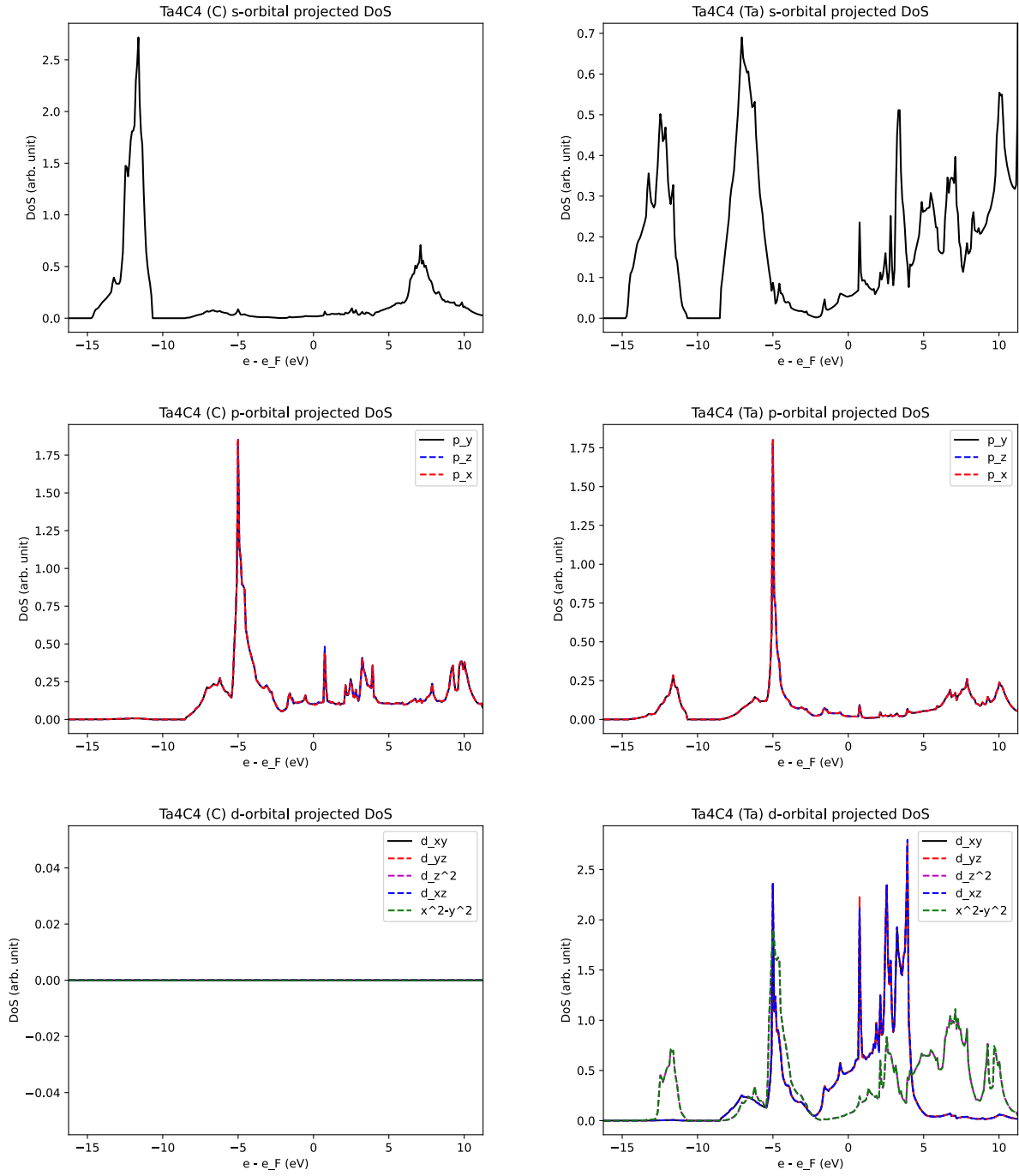


Figure E.3: Orbital-projected DoS for B1-structured TaC

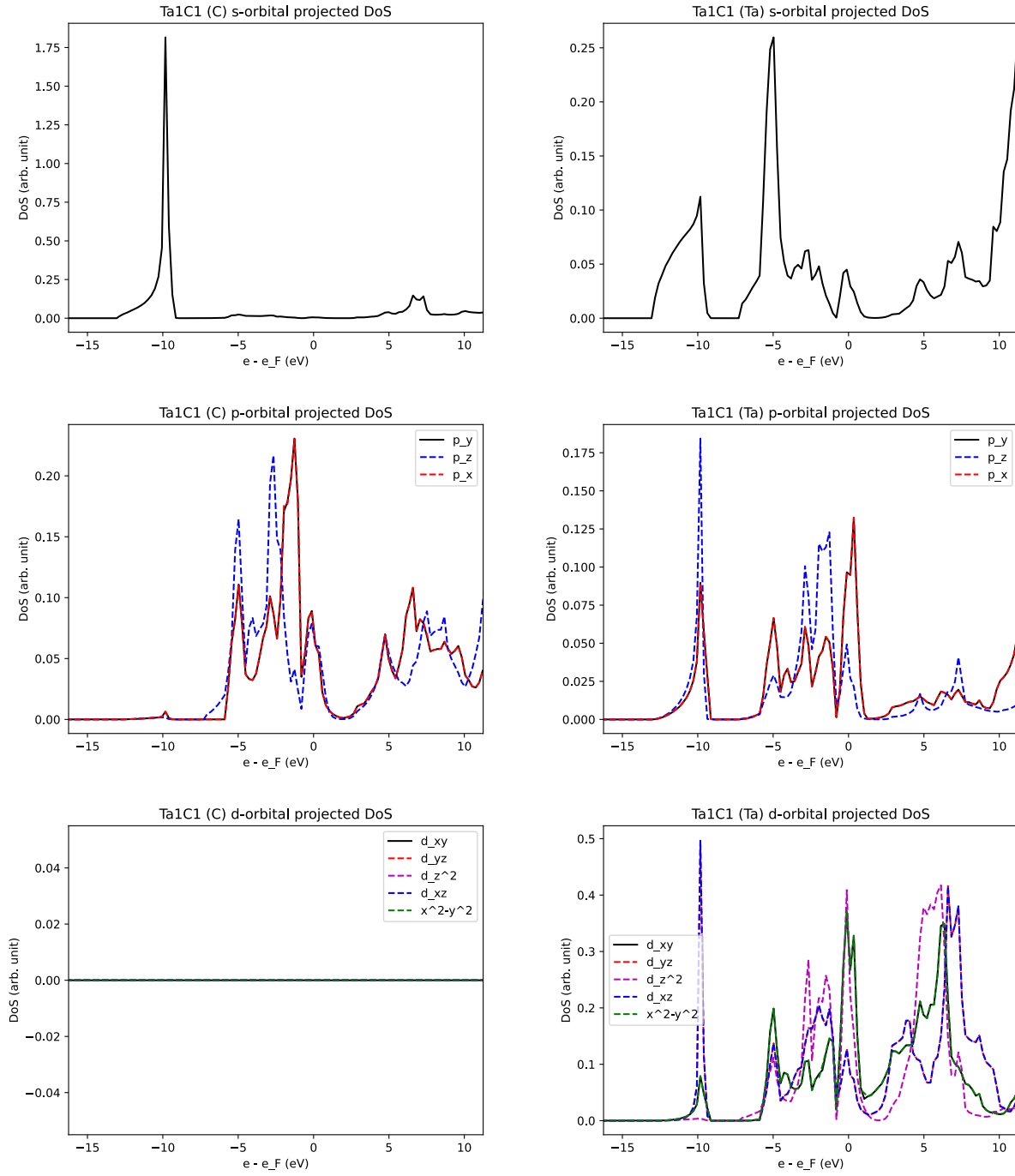


Figure E.4: Orbital-projected DoS for B_h -structured TaC

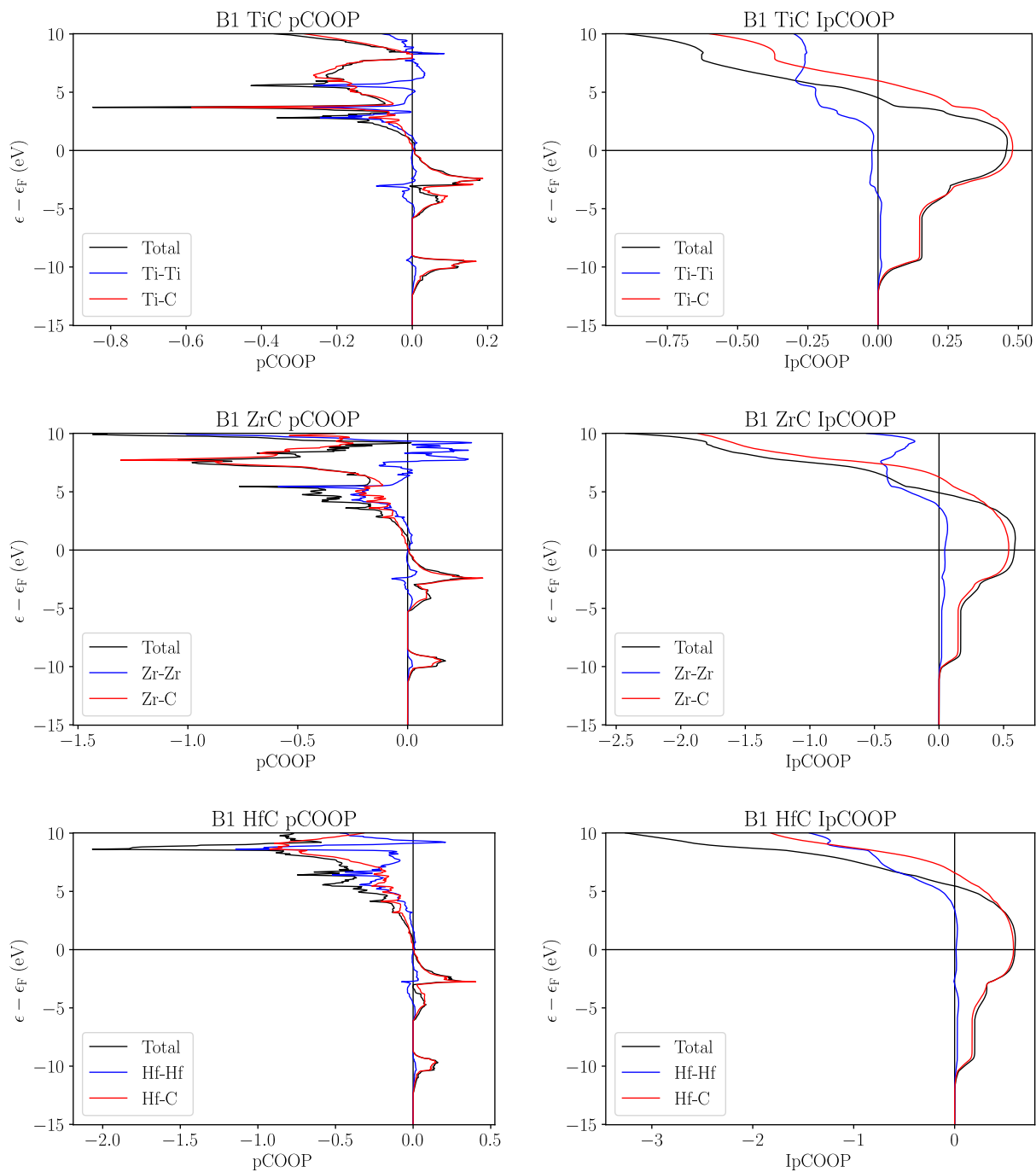


Figure E.5: Computed pCOOP for stoichiometric B1-structured IVB TMCs: TiC, ZrC and HfC. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

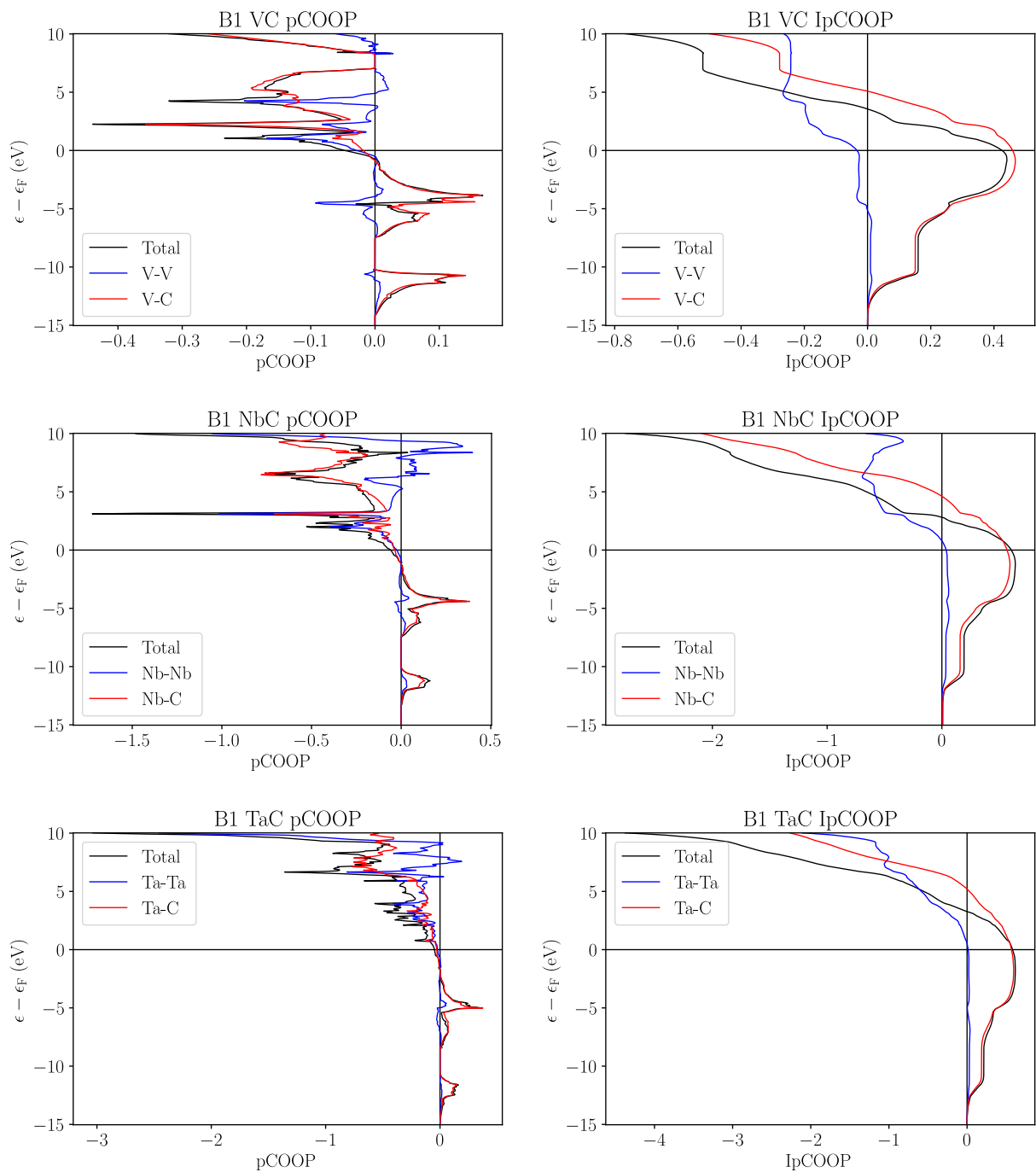


Figure E.6: Computed pCOOP for stoichiometric B1-structured VB TMCs: VC, NbC and TaC. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

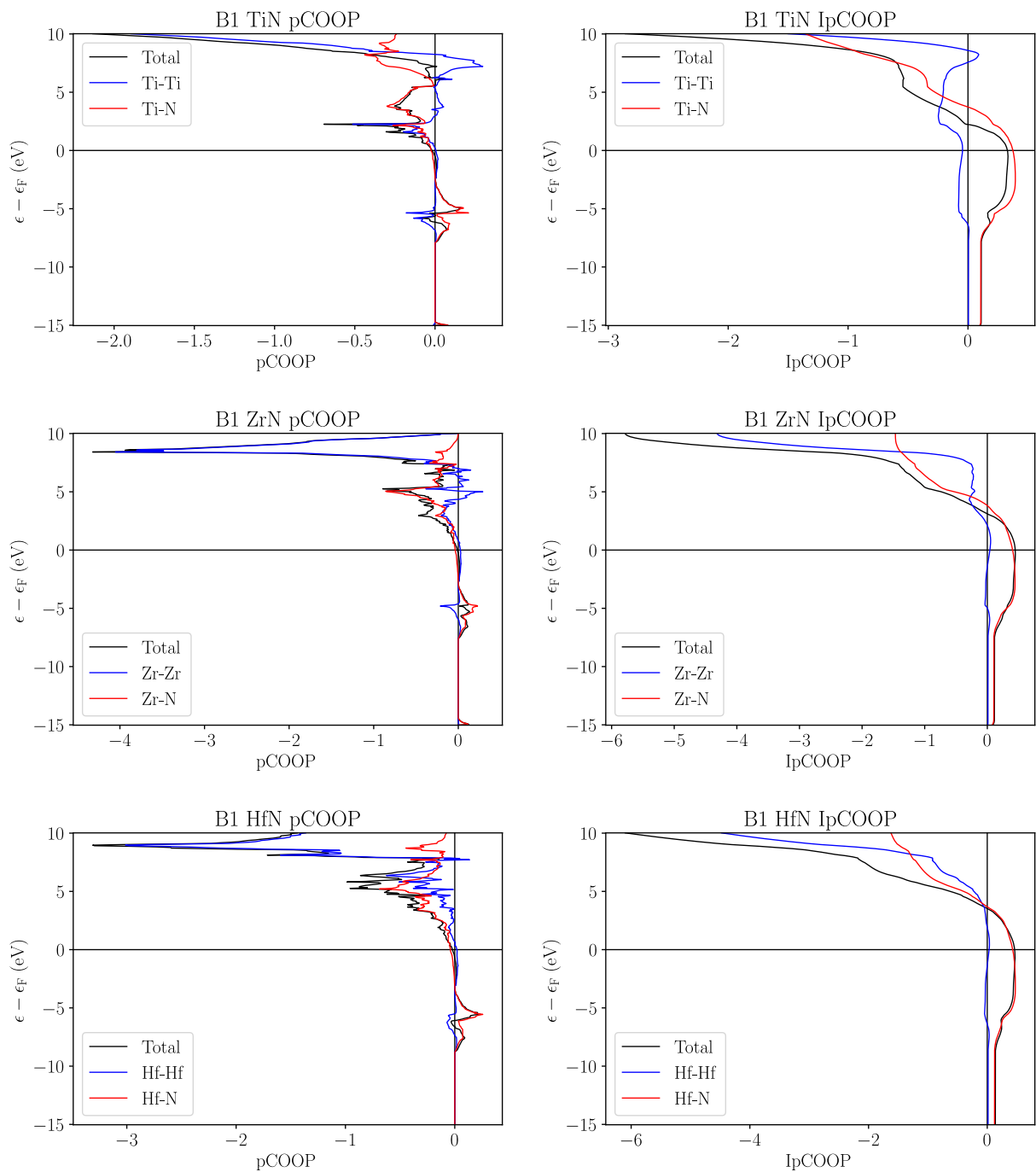


Figure E.7: Computed pCOOP for stoichiometric B1-structured IVB TMNs: TiN, ZrN and HfN. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

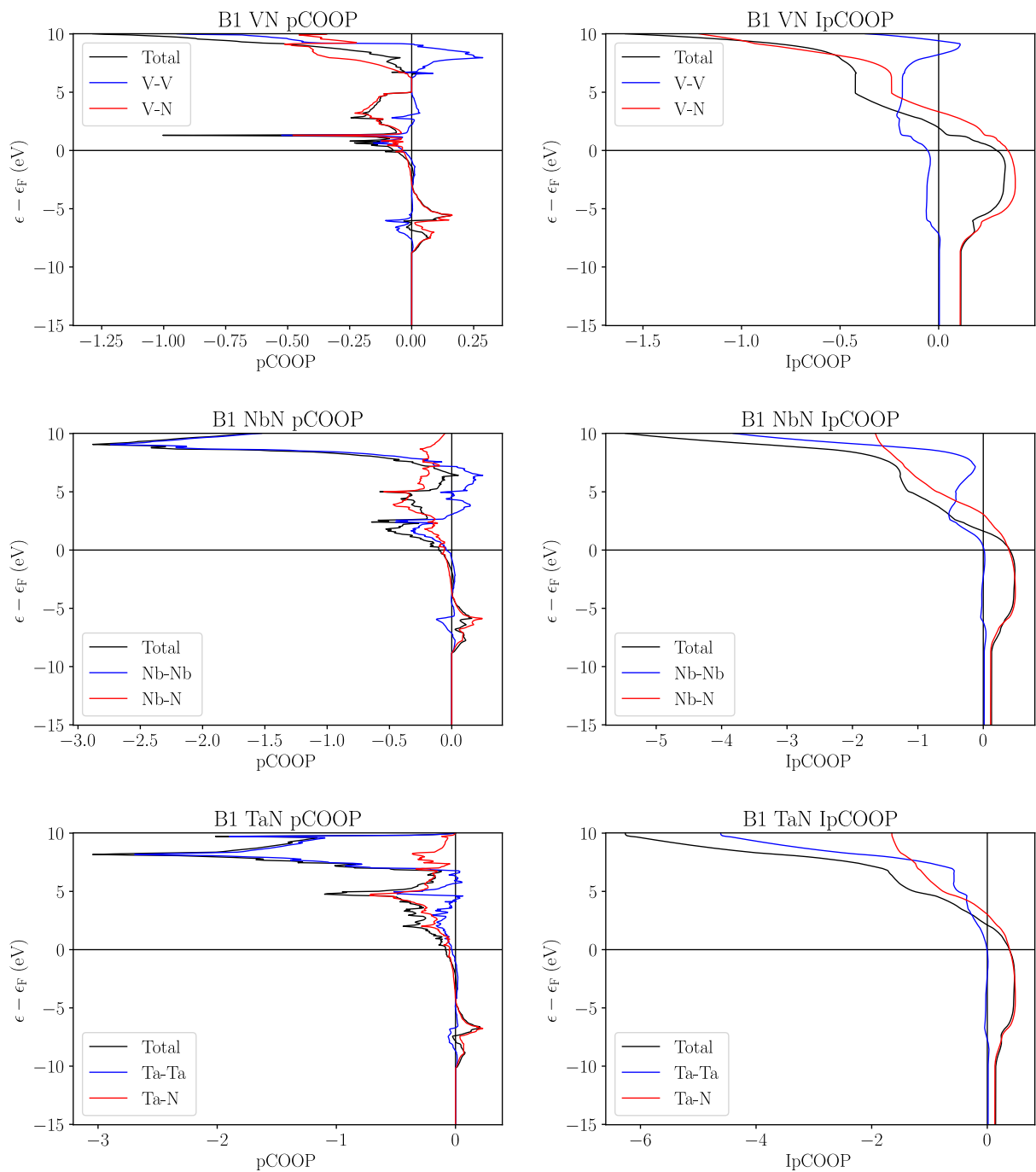


Figure E.8: Computed pCOOP for stoichiometric B1-structured VB TMNs: VN, NbN and TaN. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

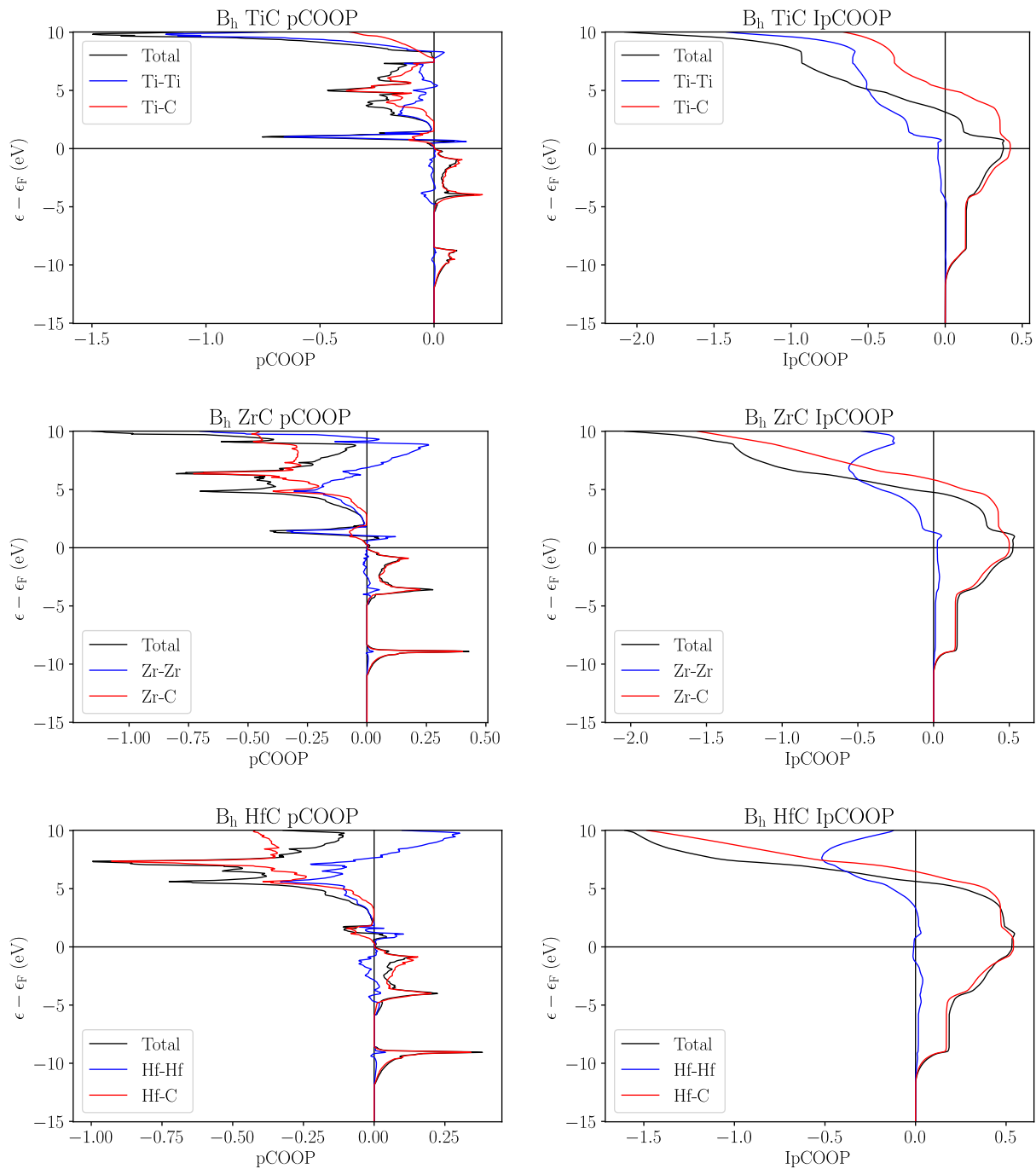


Figure E.9: Computed pCOOP for stoichiometric B_h -structured IVB TMCs: TiC, ZrC and HfC. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

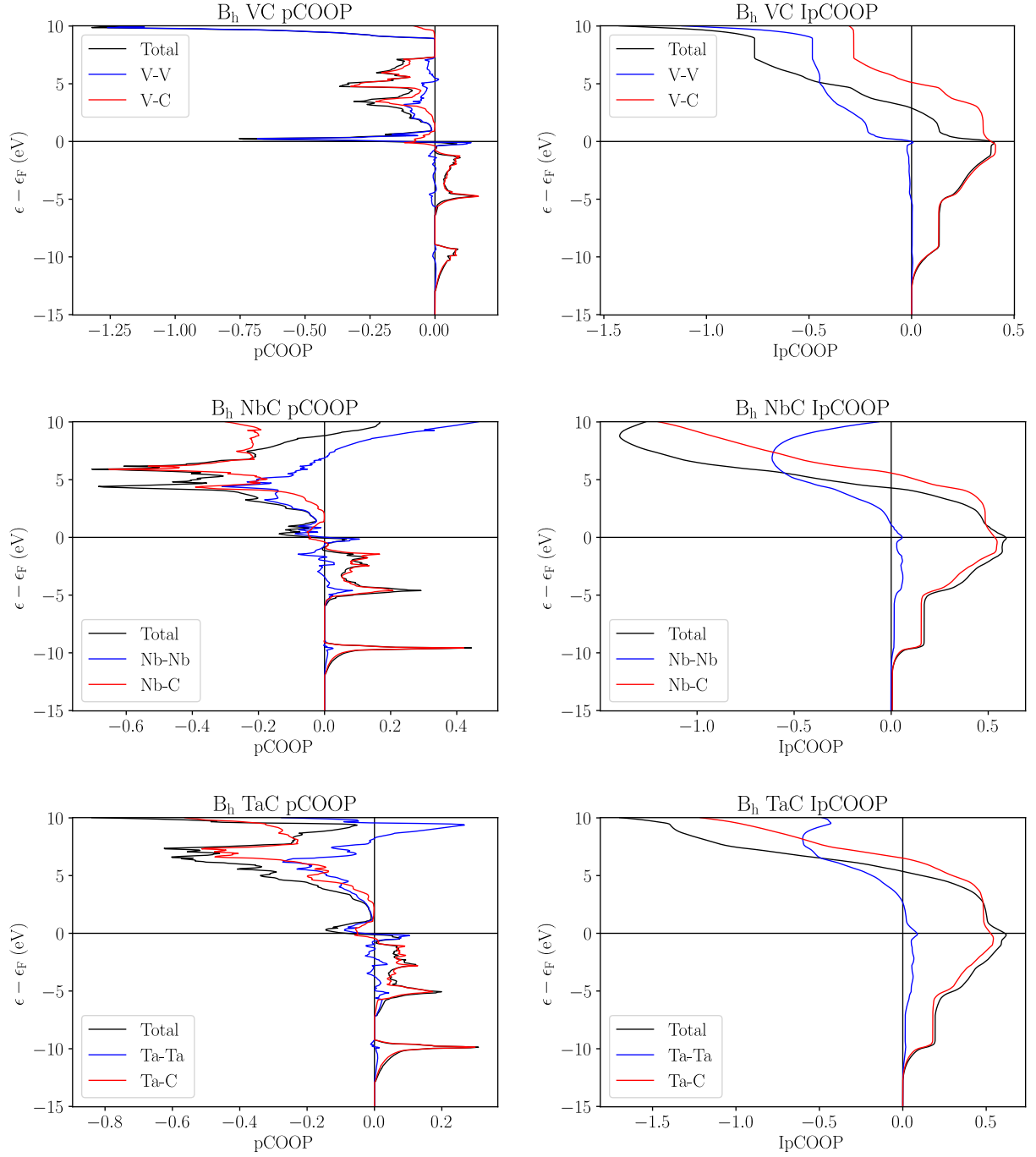


Figure E.10: Computed pCOOP for stoichiometric B_h -structured VB TMCs: VC, NbC and TaC. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

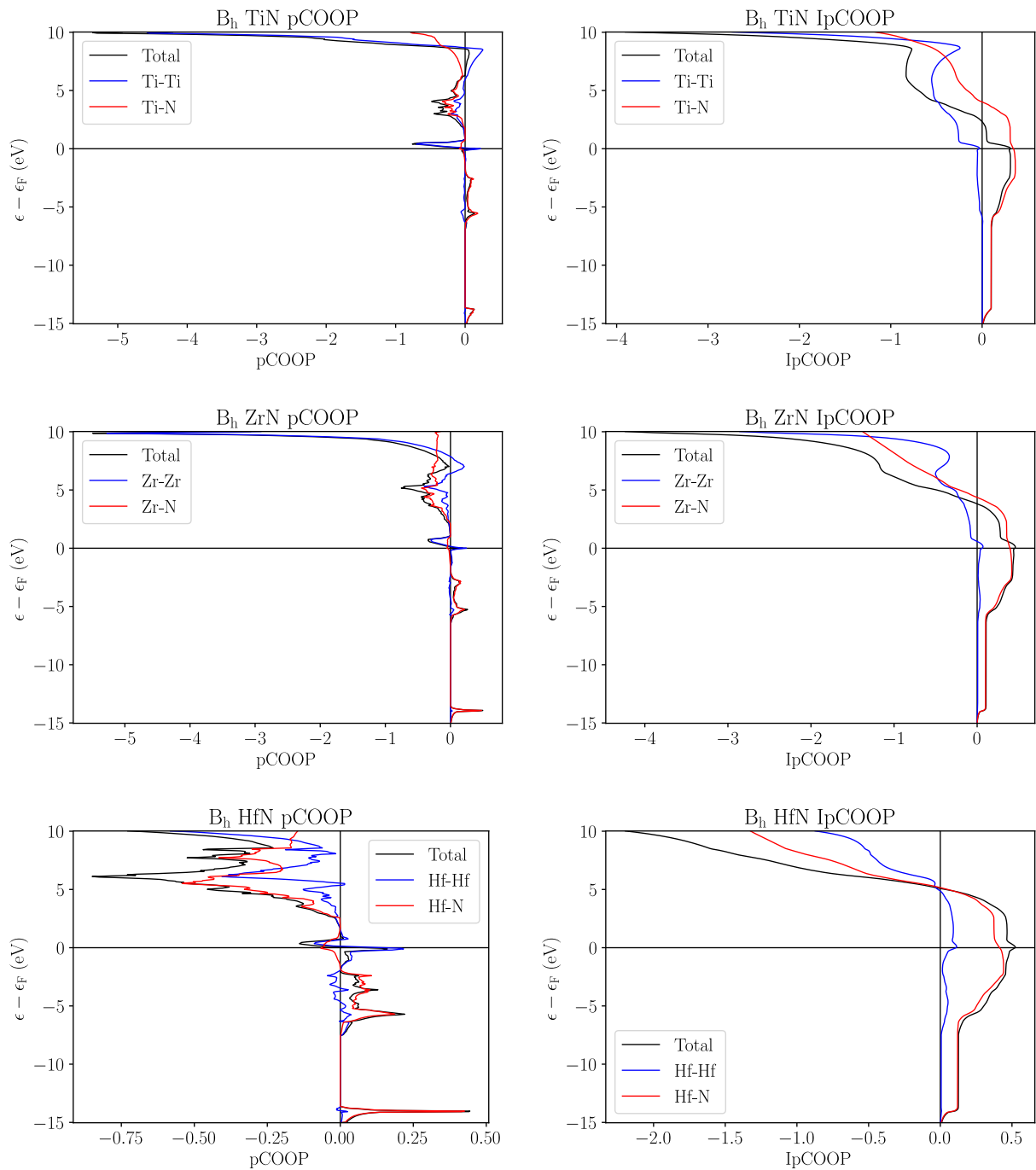


Figure E.11: Computed pCOOP for stoichiometric B_h -structured IVB TMNs: TiN, ZrN and HfN. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

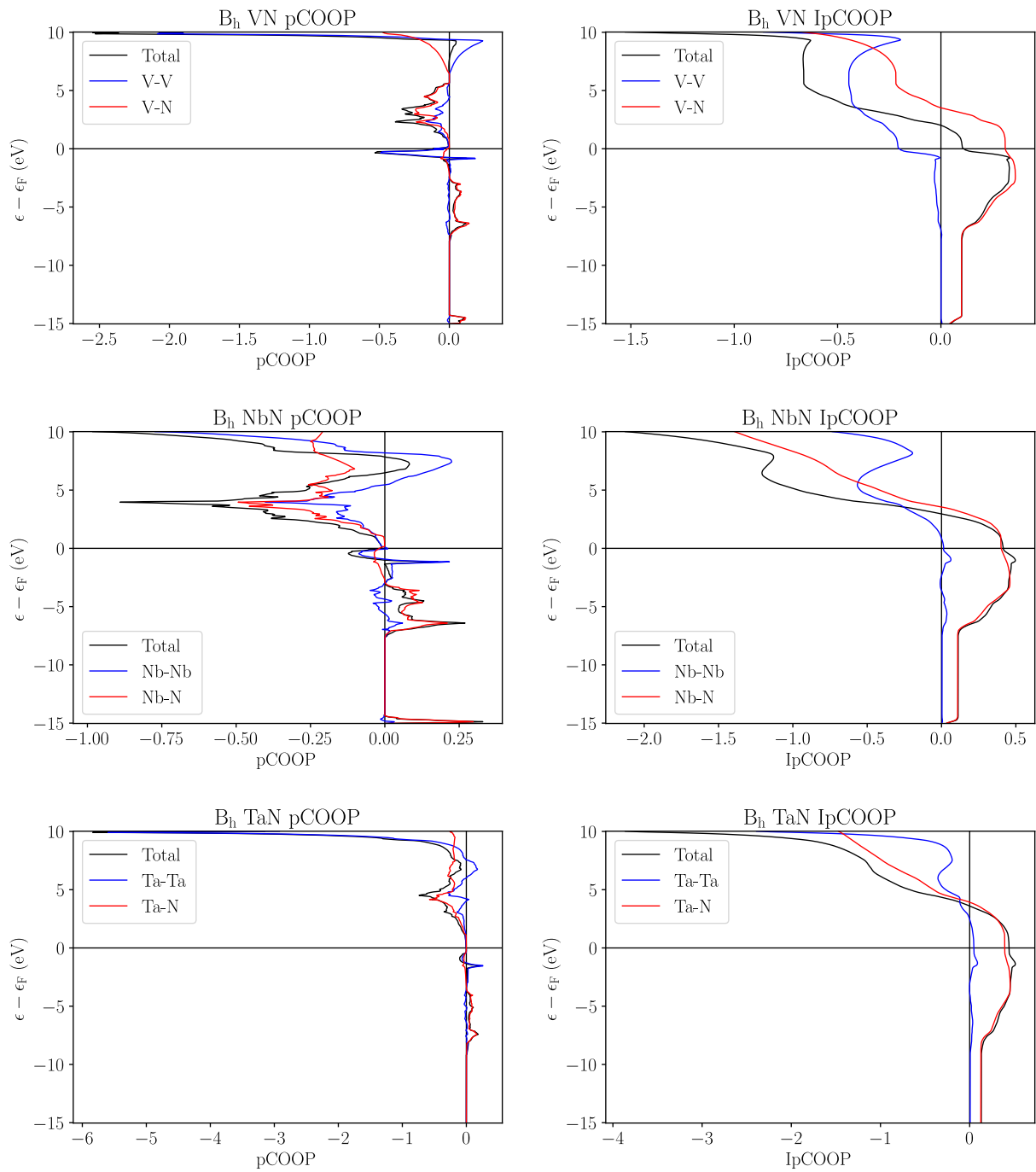


Figure E.12: Computed pCOOP for stoichiometric B_h -structured VB TMNs: VN, NbN and TaN. Positive values indicate bonding interactions, while negative values indicate antibonding interactions.

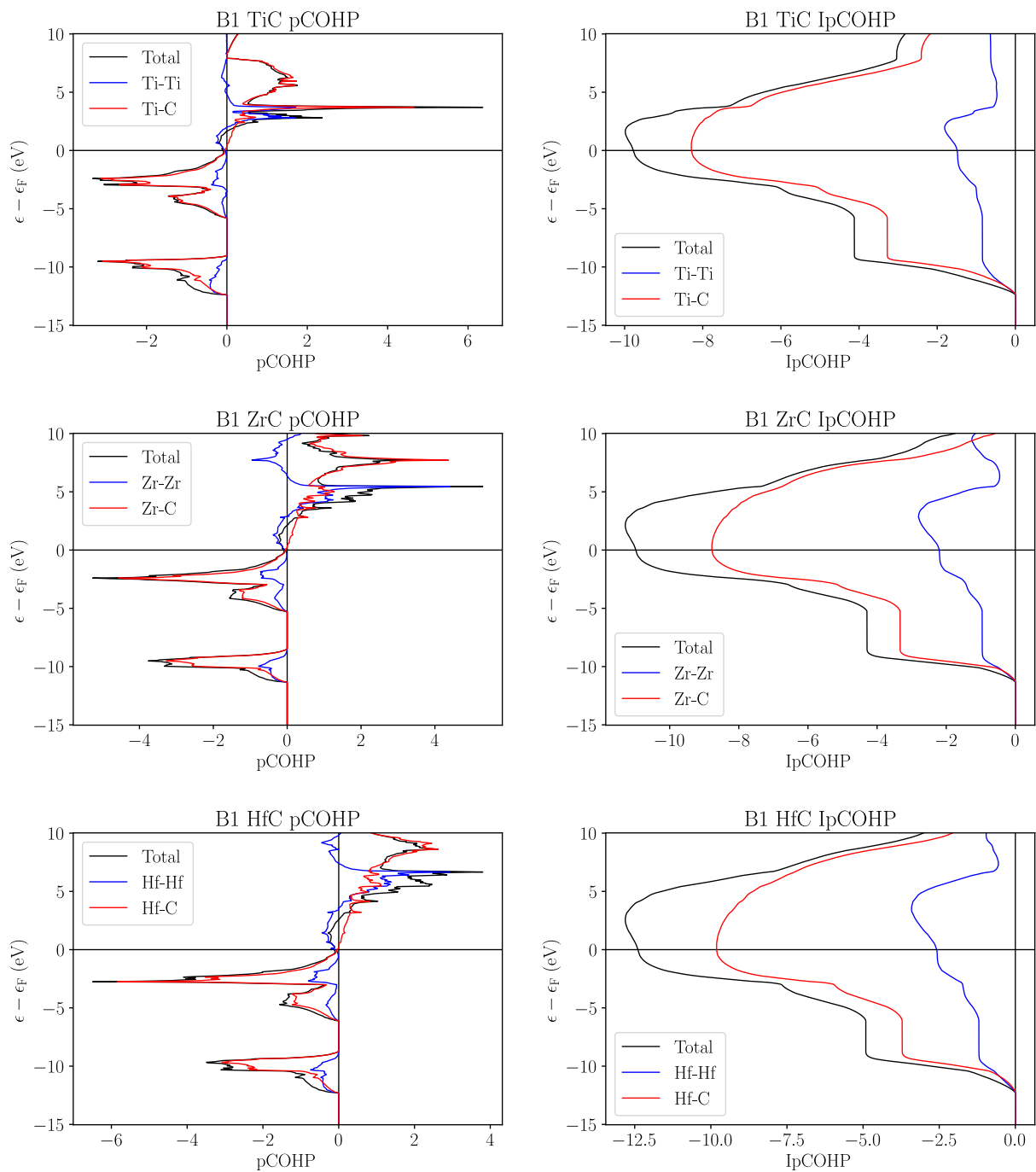


Figure E.13: Computed pCOHP for stoichiometric B1-structured IVB TMCs: TiC, ZrC and HfC. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

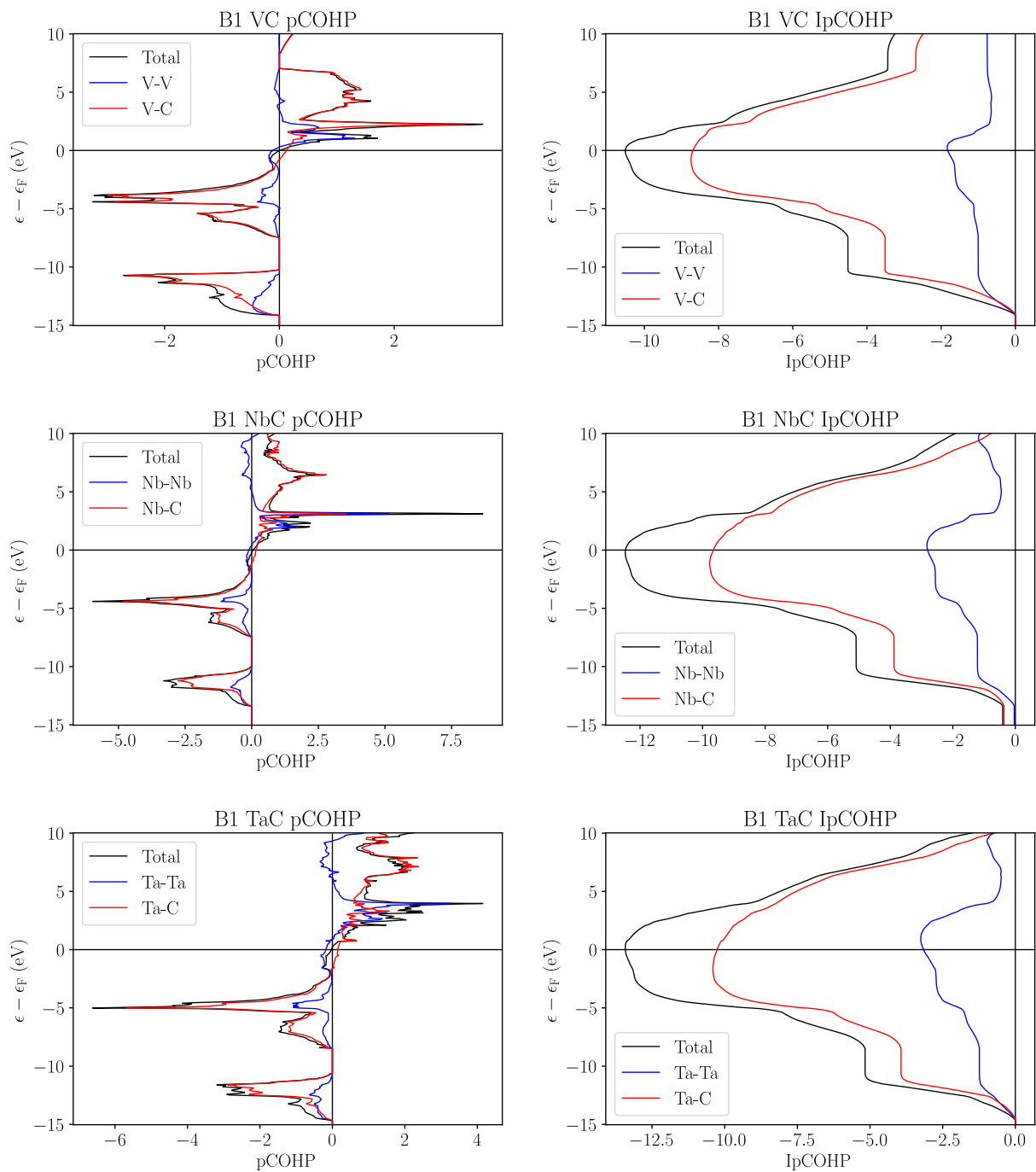


Figure E.14: Computed pCOHP for stoichiometric B1-structured VB TMCs: VC, NbC and TaC. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

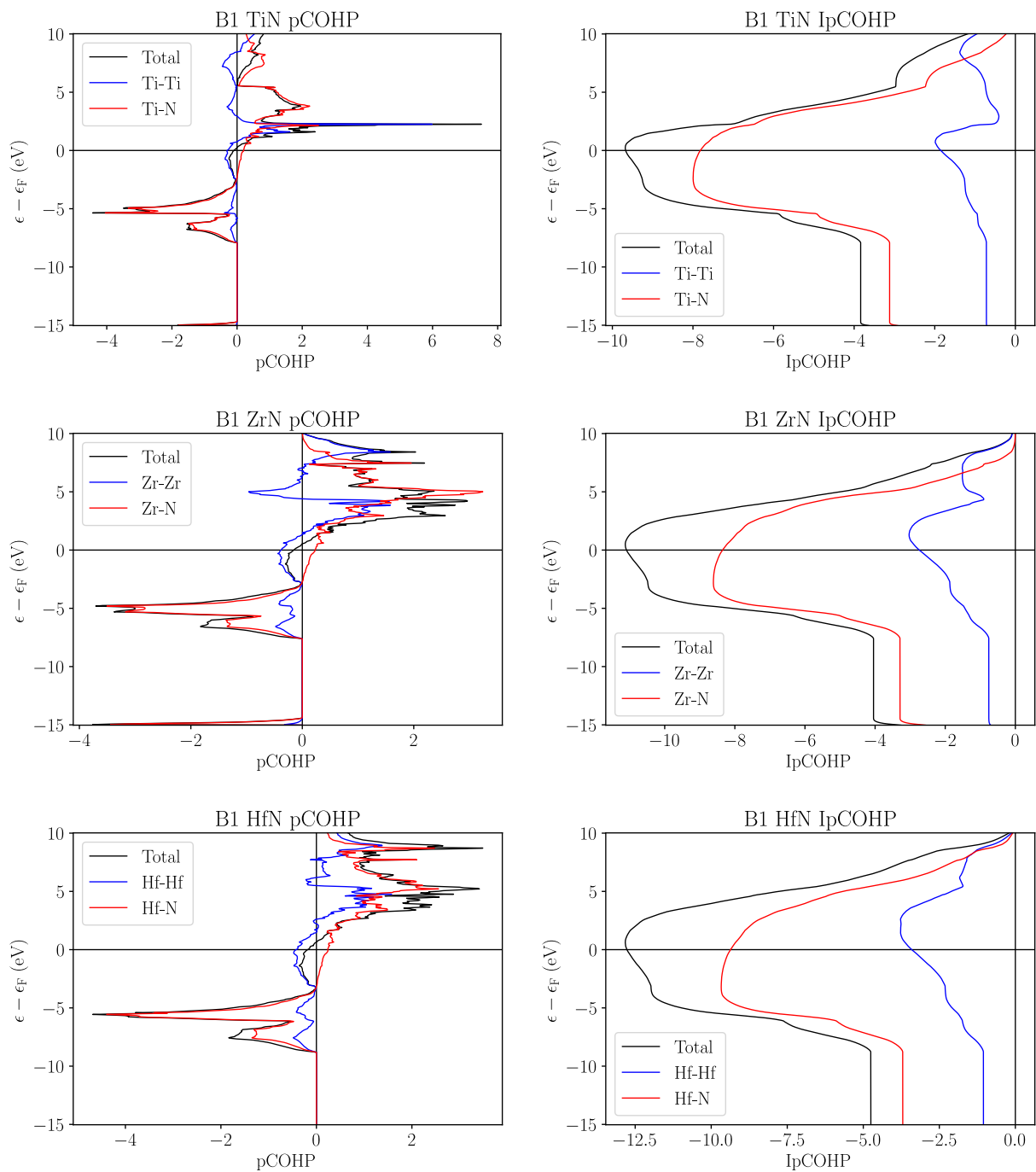


Figure E.15: Computed pCOHP for stoichiometric B1-structured IVB TMNs: TiN, ZrN and HfN. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

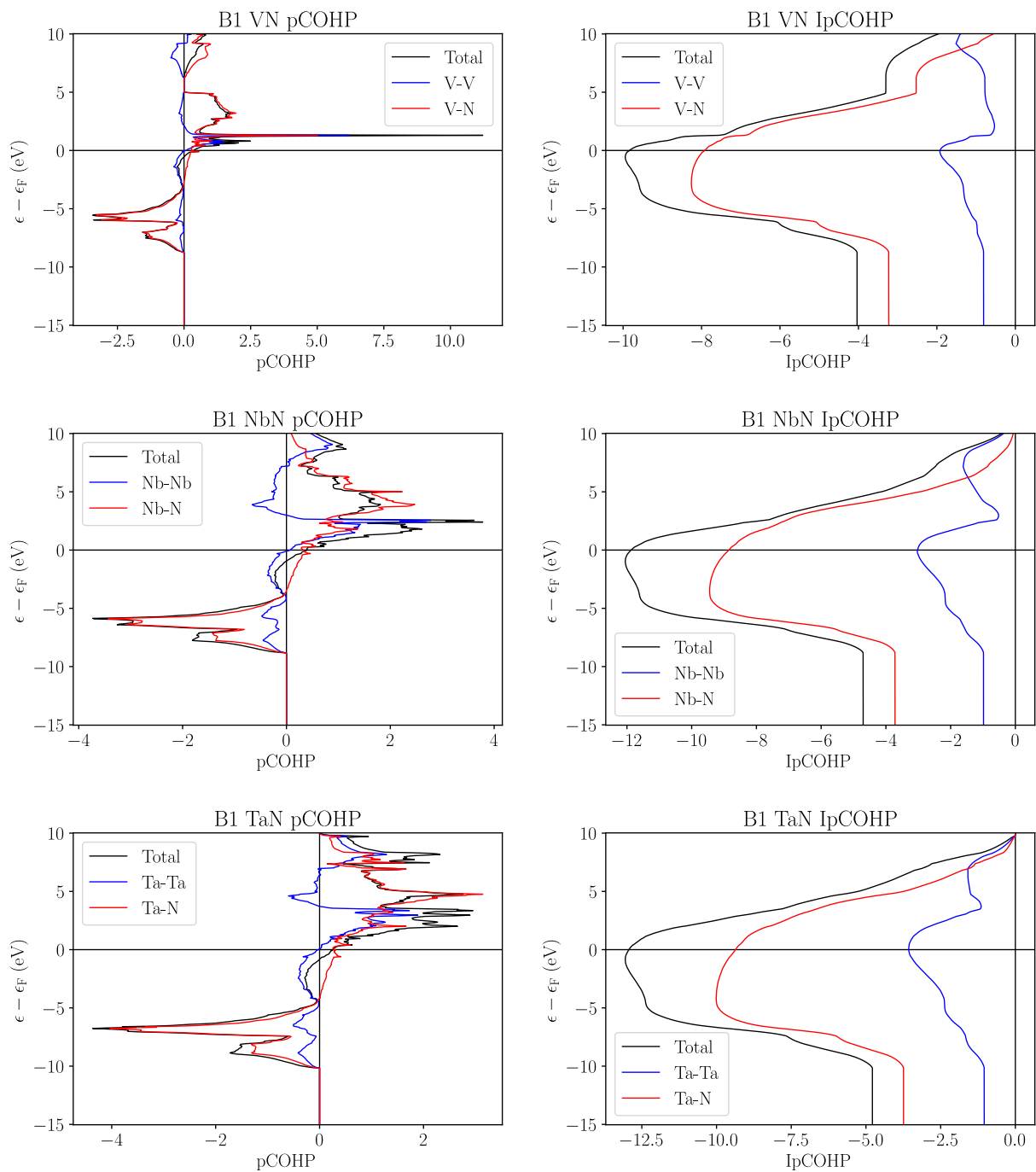


Figure E.16: Computed pCOHP for stoichiometric B1-structured VB TMNs: VN, NbN and TaN. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

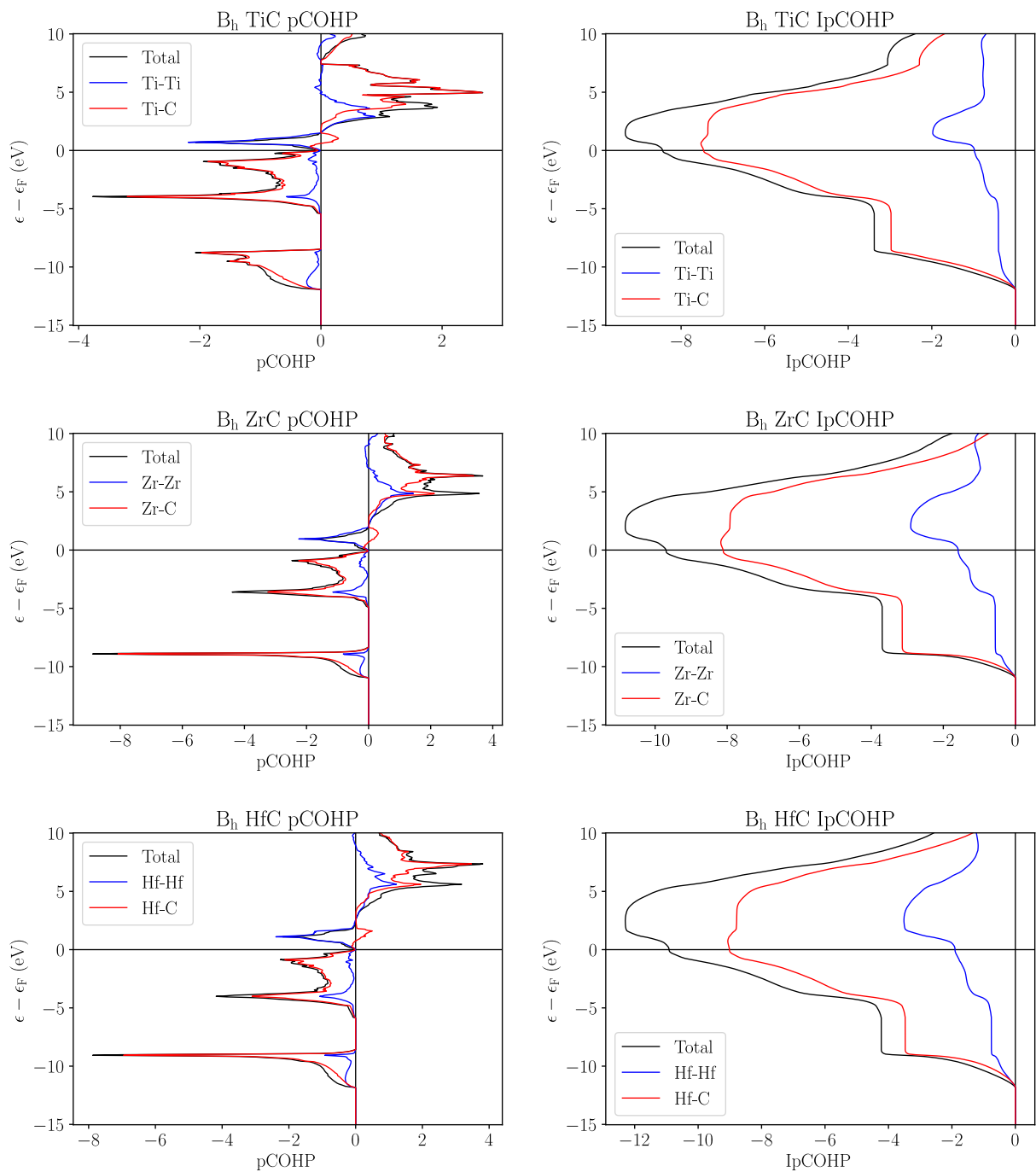


Figure E.17: Computed pCOHP for stoichiometric B_h -structured IVB TMCs: TiC, ZrC and HfC. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

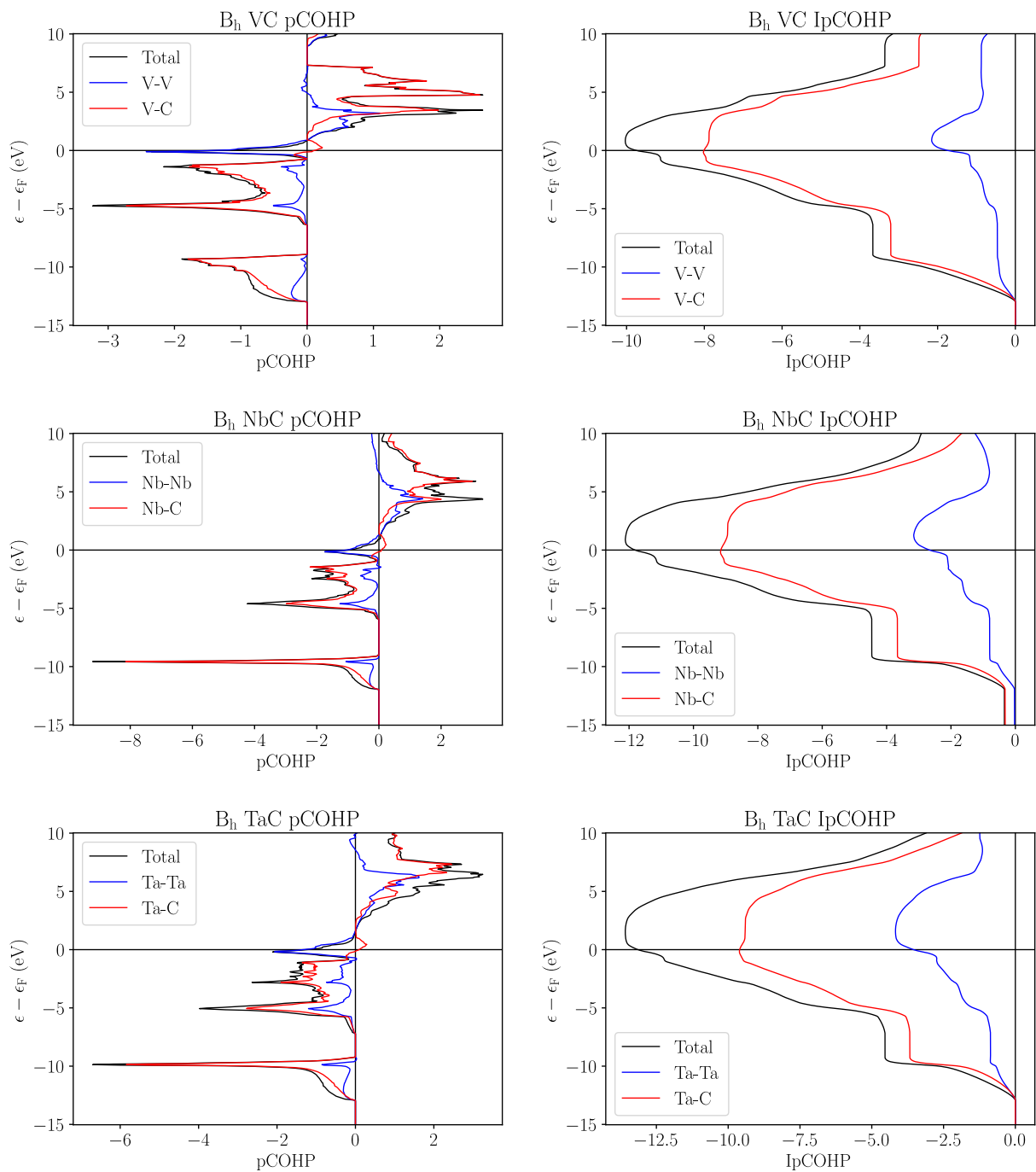


Figure E.18: Computed pCOHP for stoichiometric B_h -structured VB TMCs: VC, NbC and TaC. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

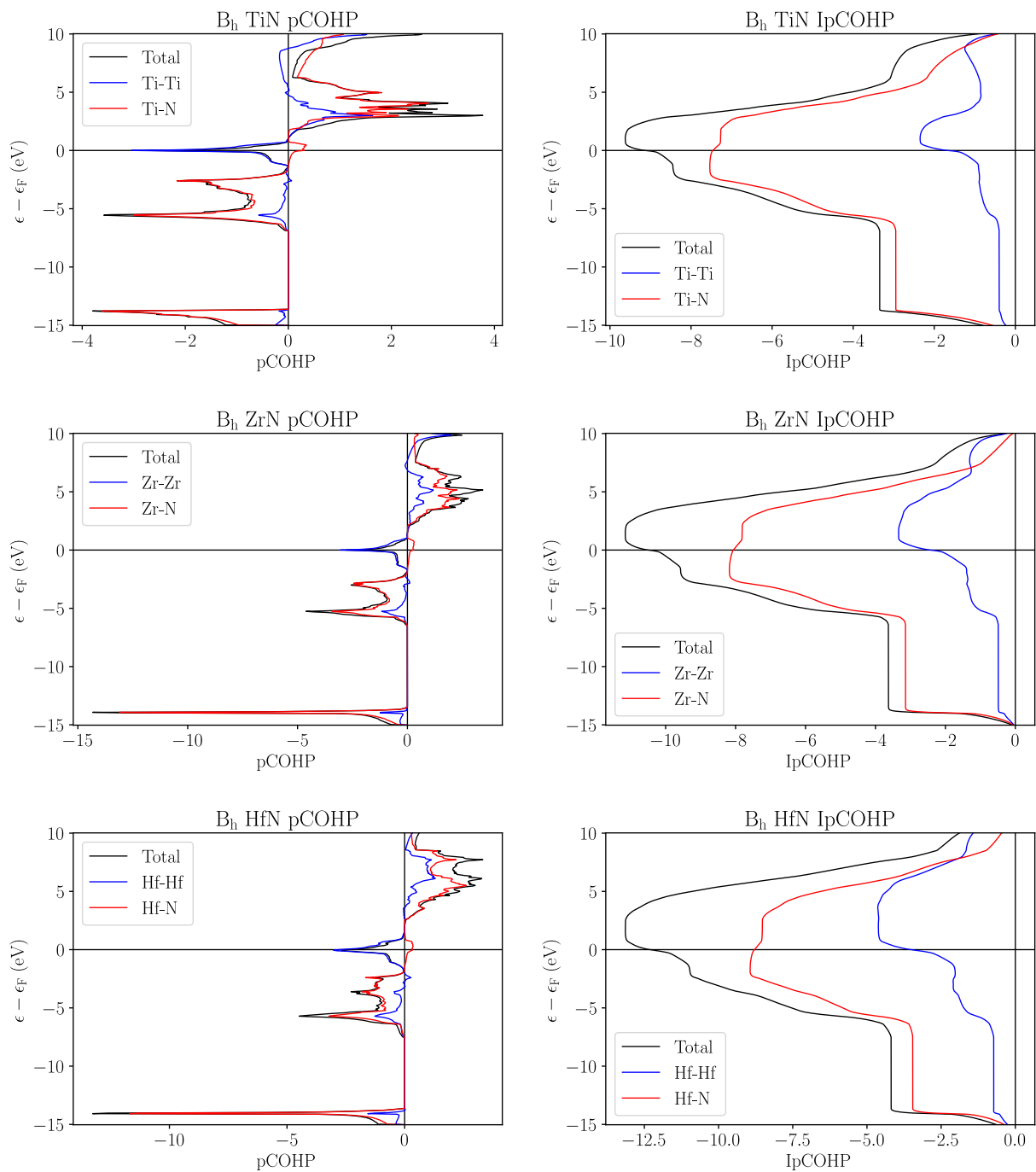


Figure E.19: Computed pCOHP for stoichiometric B_h -structured IVB TMNs: TiN, ZrN and HfN. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

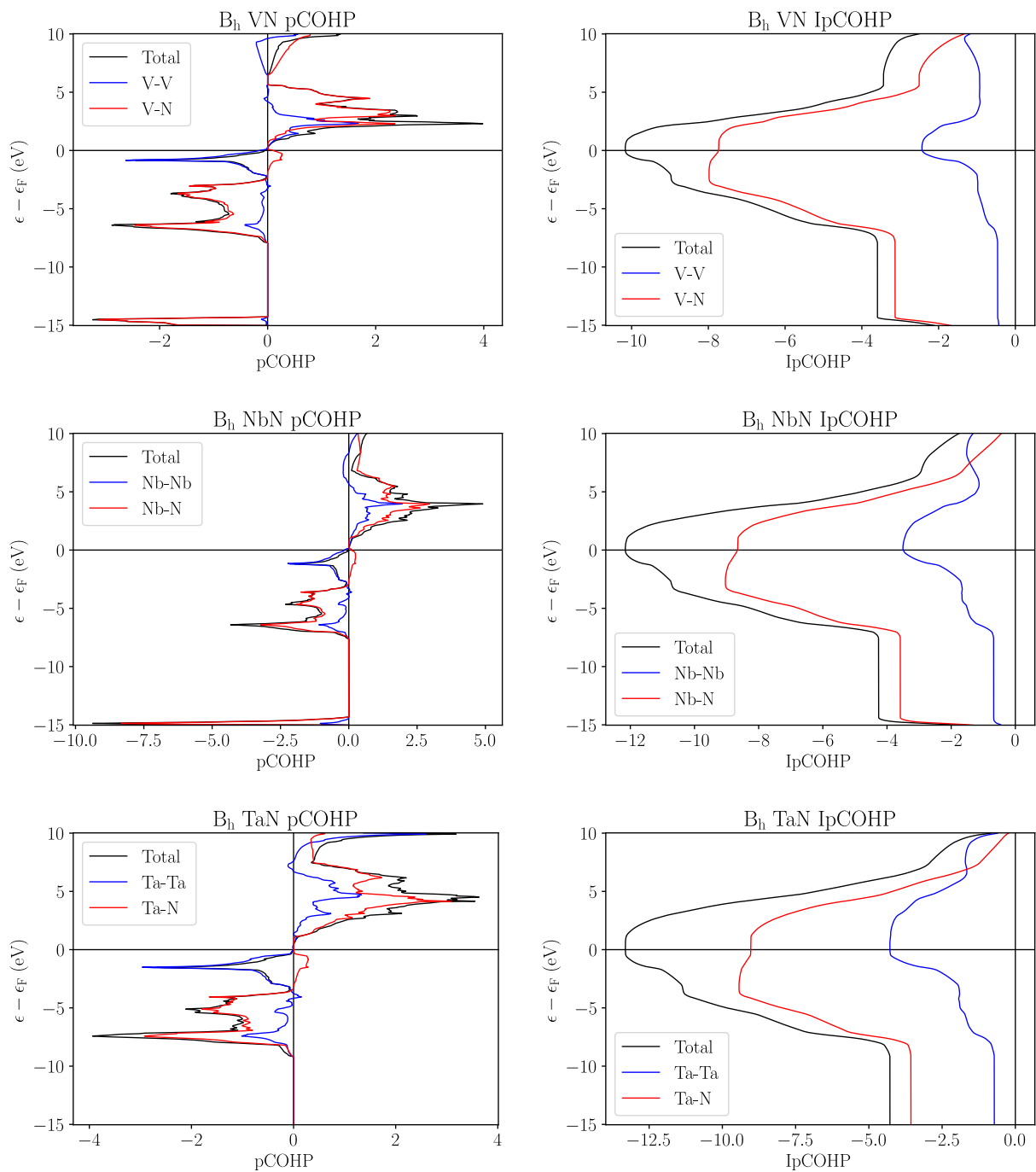


Figure E.20: Computed pCOHP for stoichiometric B_h -structured VB TMNs: VN, NbN and TaN. Negative values indicate bonding interactions, while positive values indicate antibonding interactions.

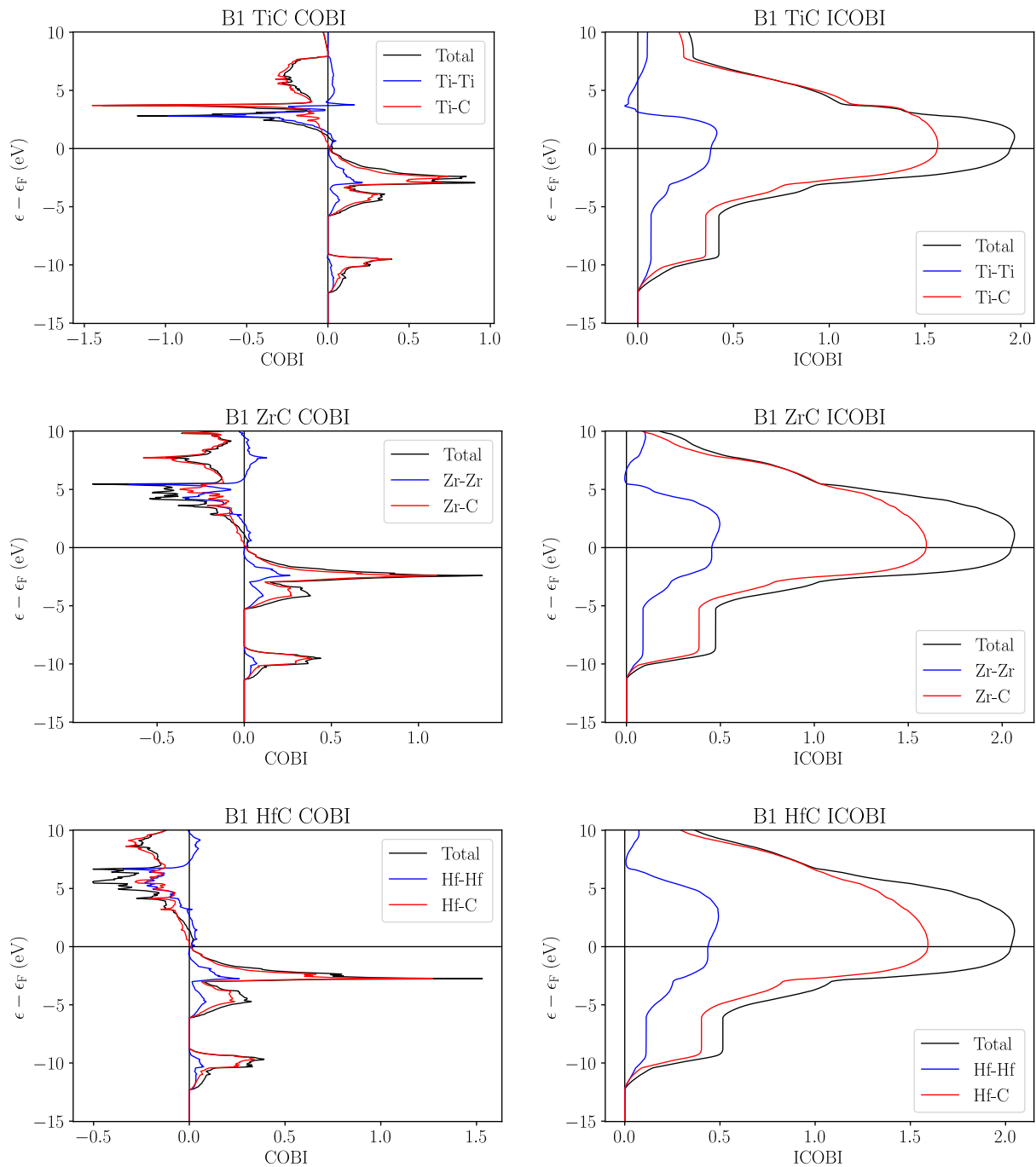


Figure E.21: Computed COBI for IVB TMCs.

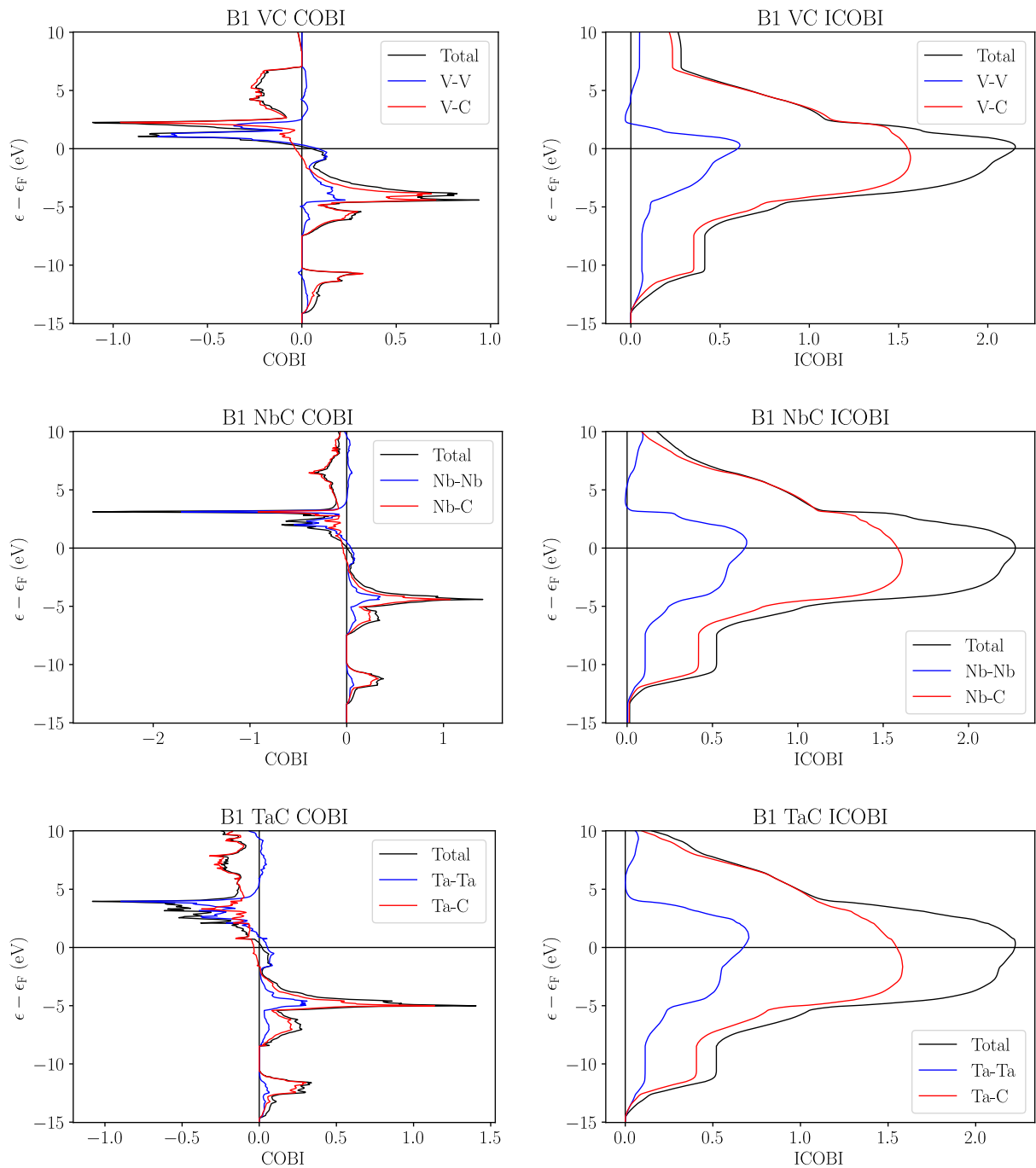


Figure E.22: Computed COBI for VB TMCs.

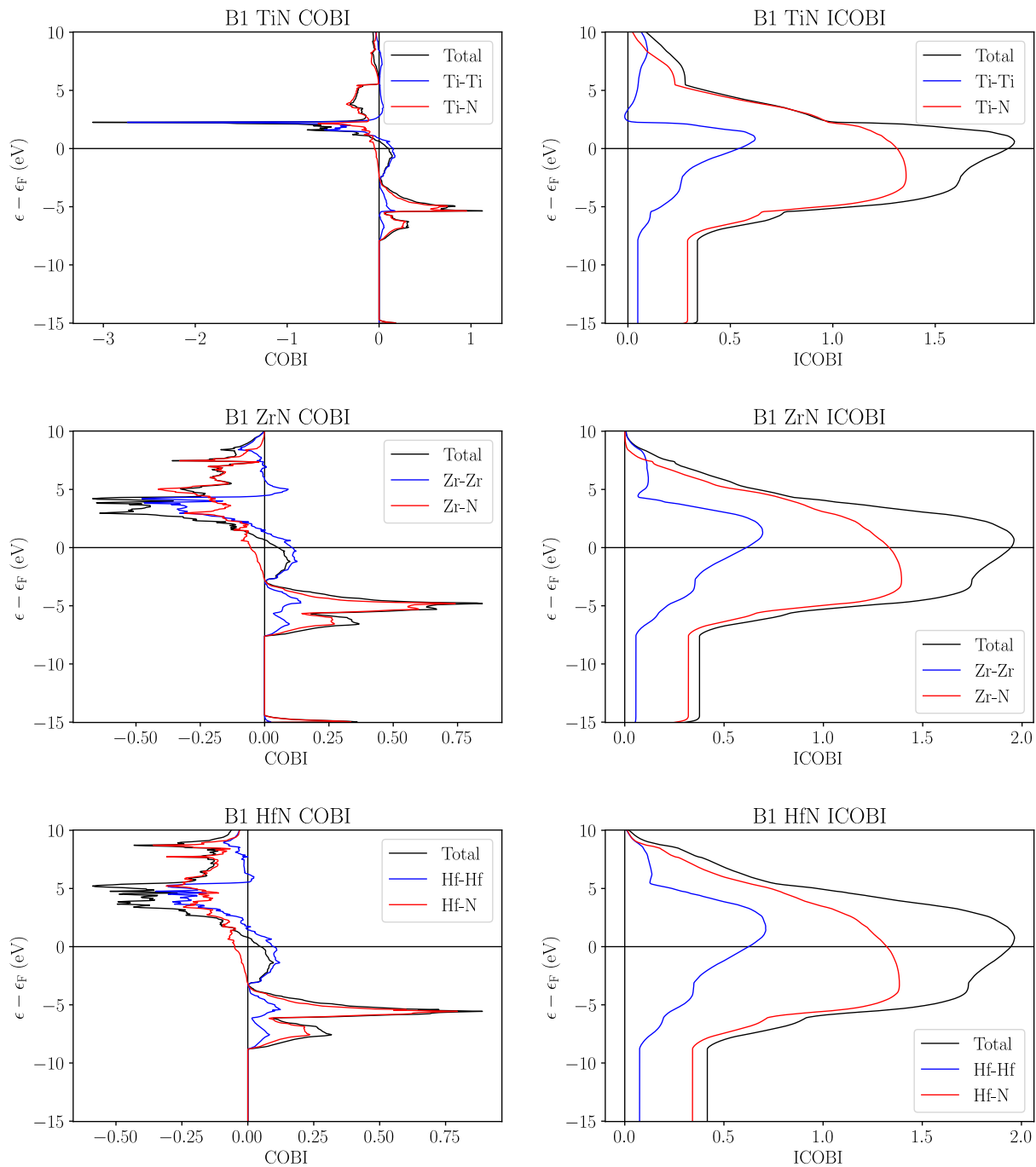


Figure E.23: Computed COBI for IVB TMNs.

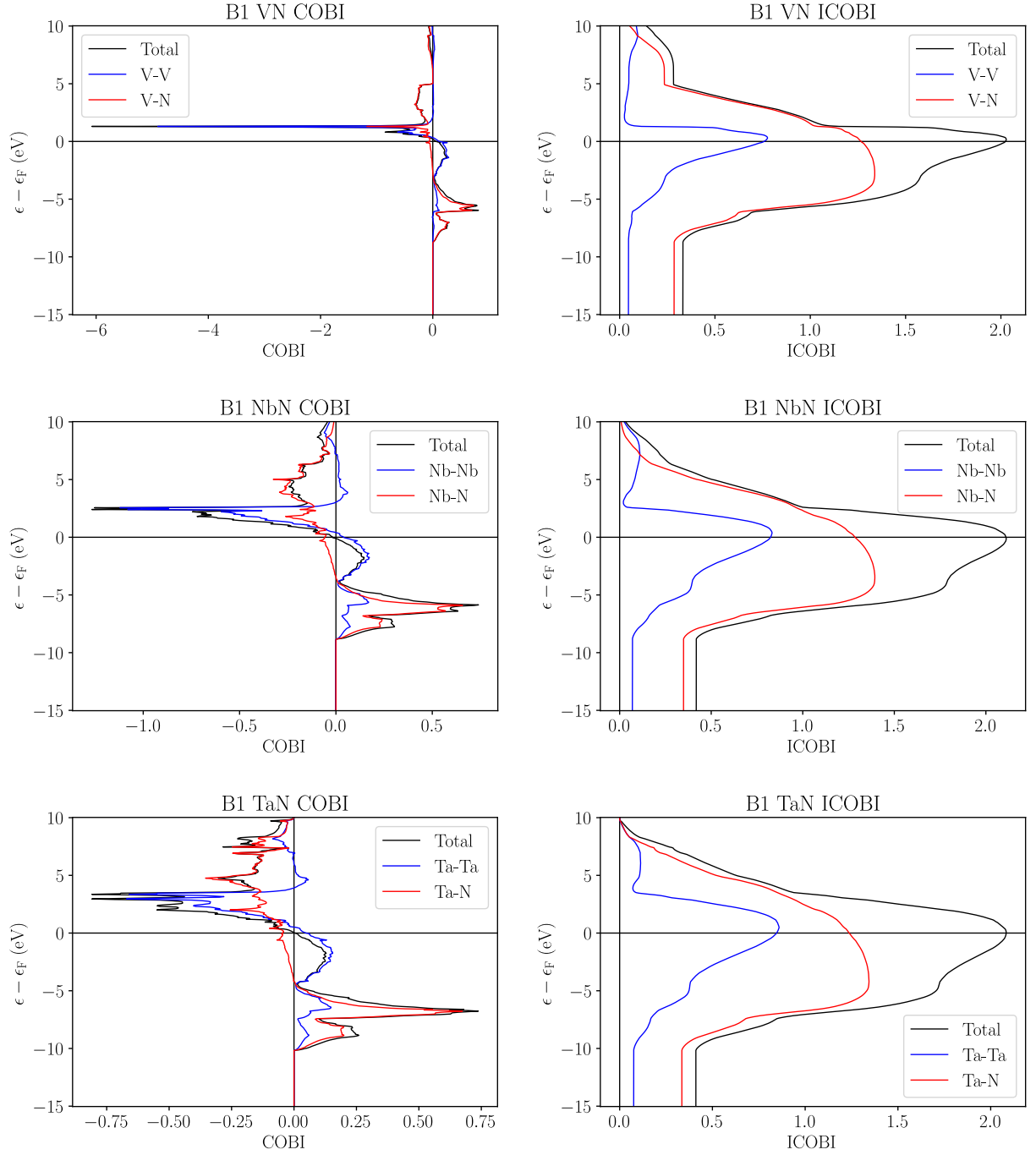


Figure E.24: Computed COBI for VB TMNs.

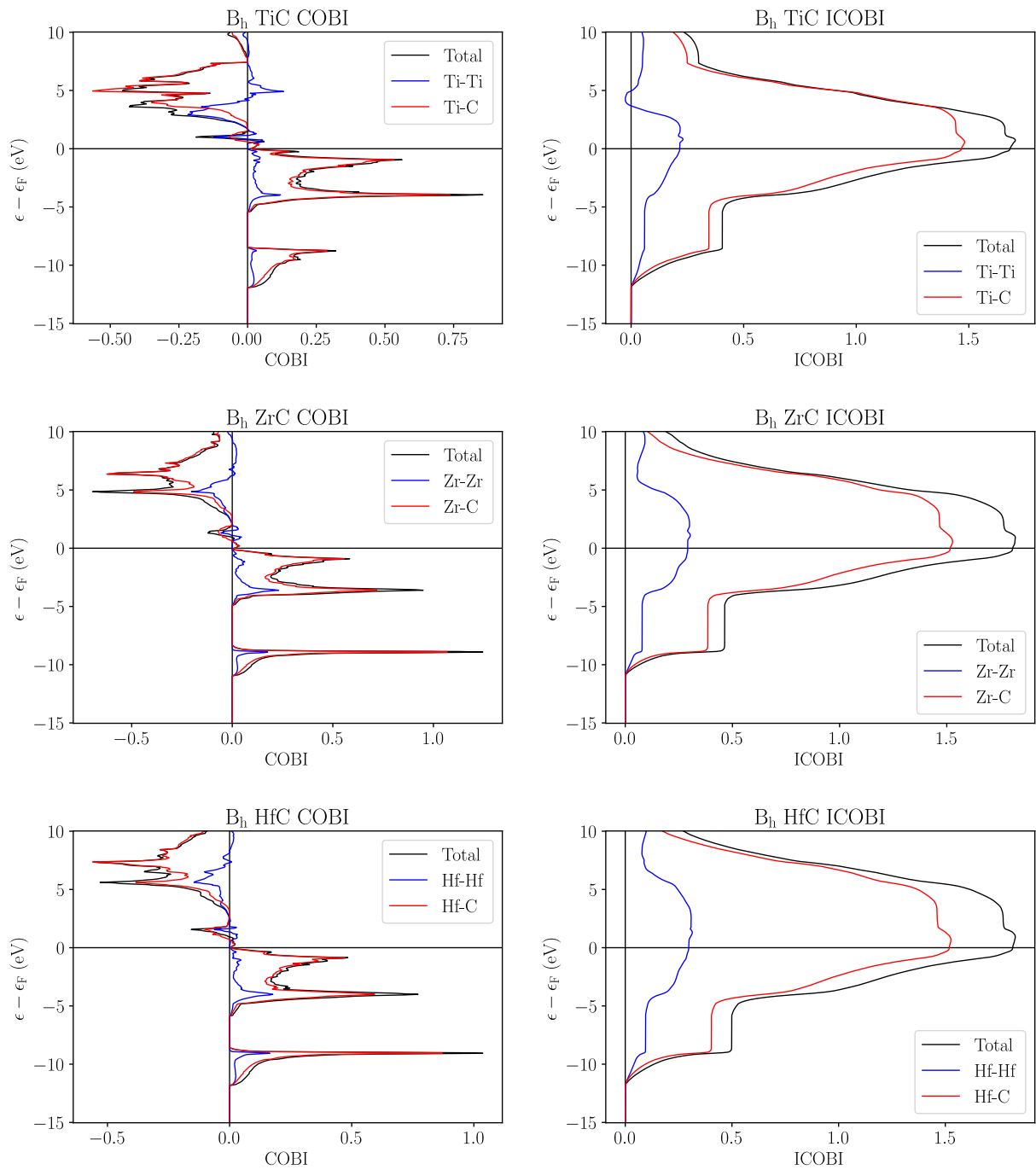


Figure E.25: Computed COBI for IVB TMCs.

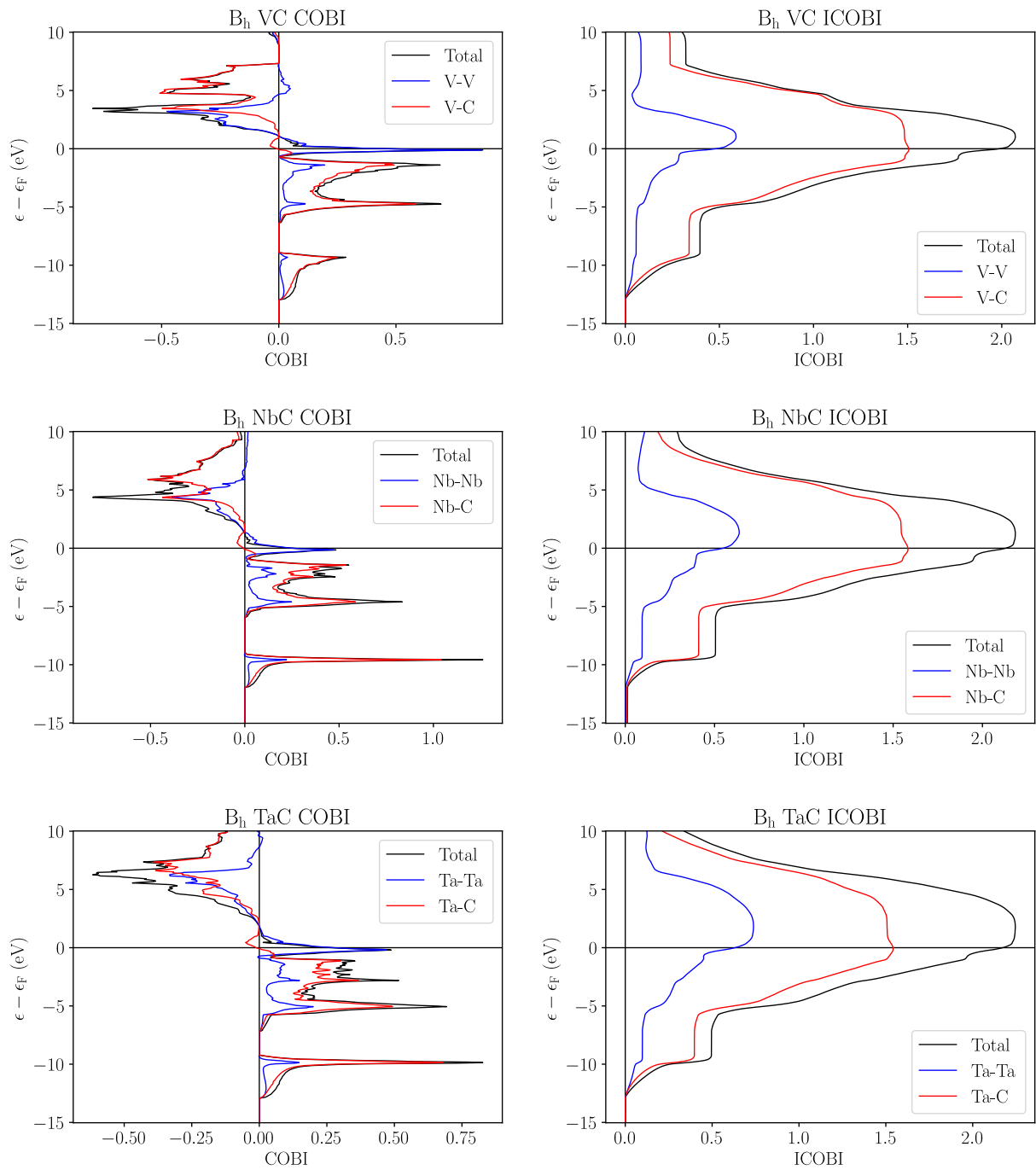


Figure E.26: Computed COBI for VB TMCs.

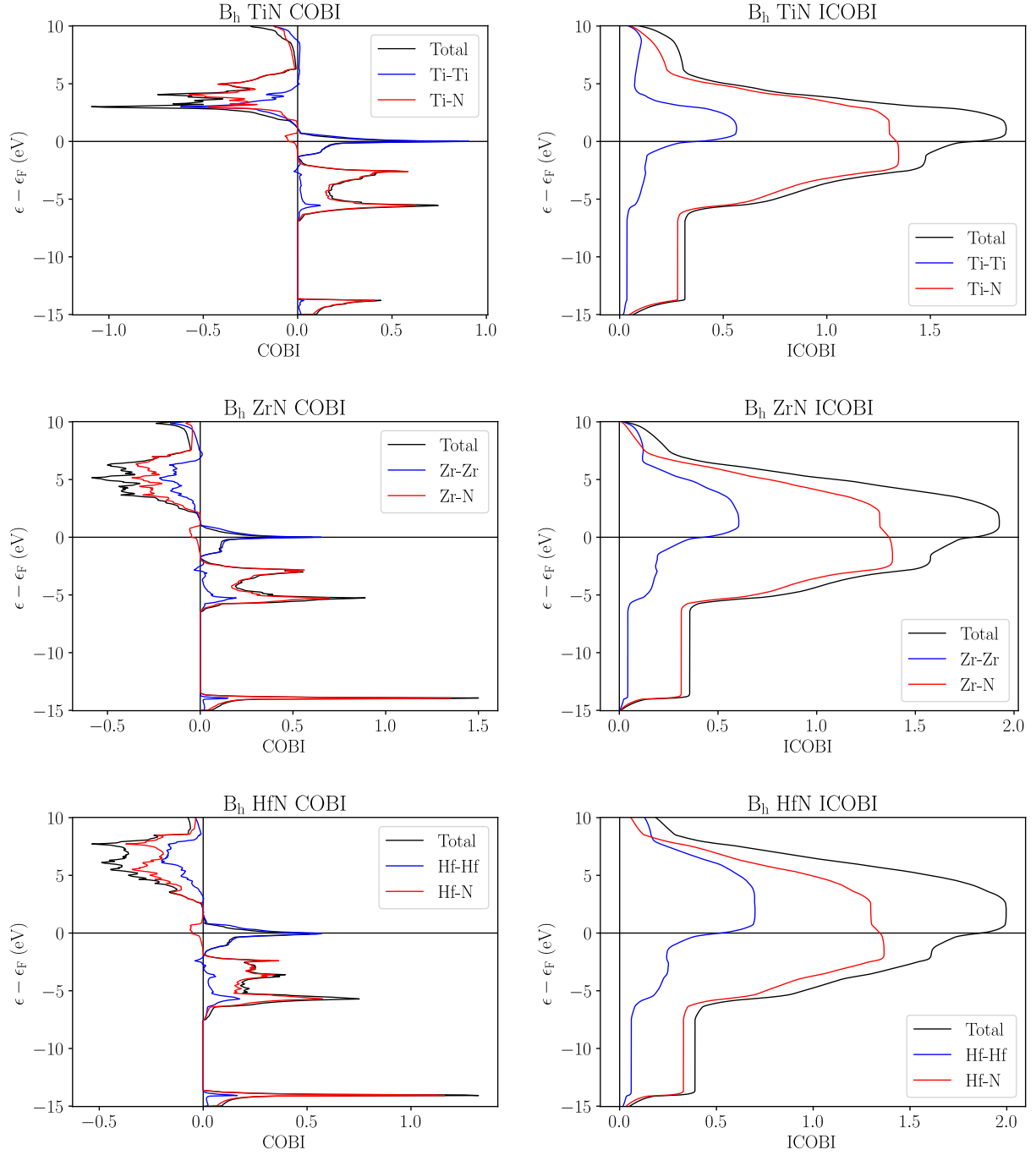


Figure E.27: Computed COBI for IVB TMNs.

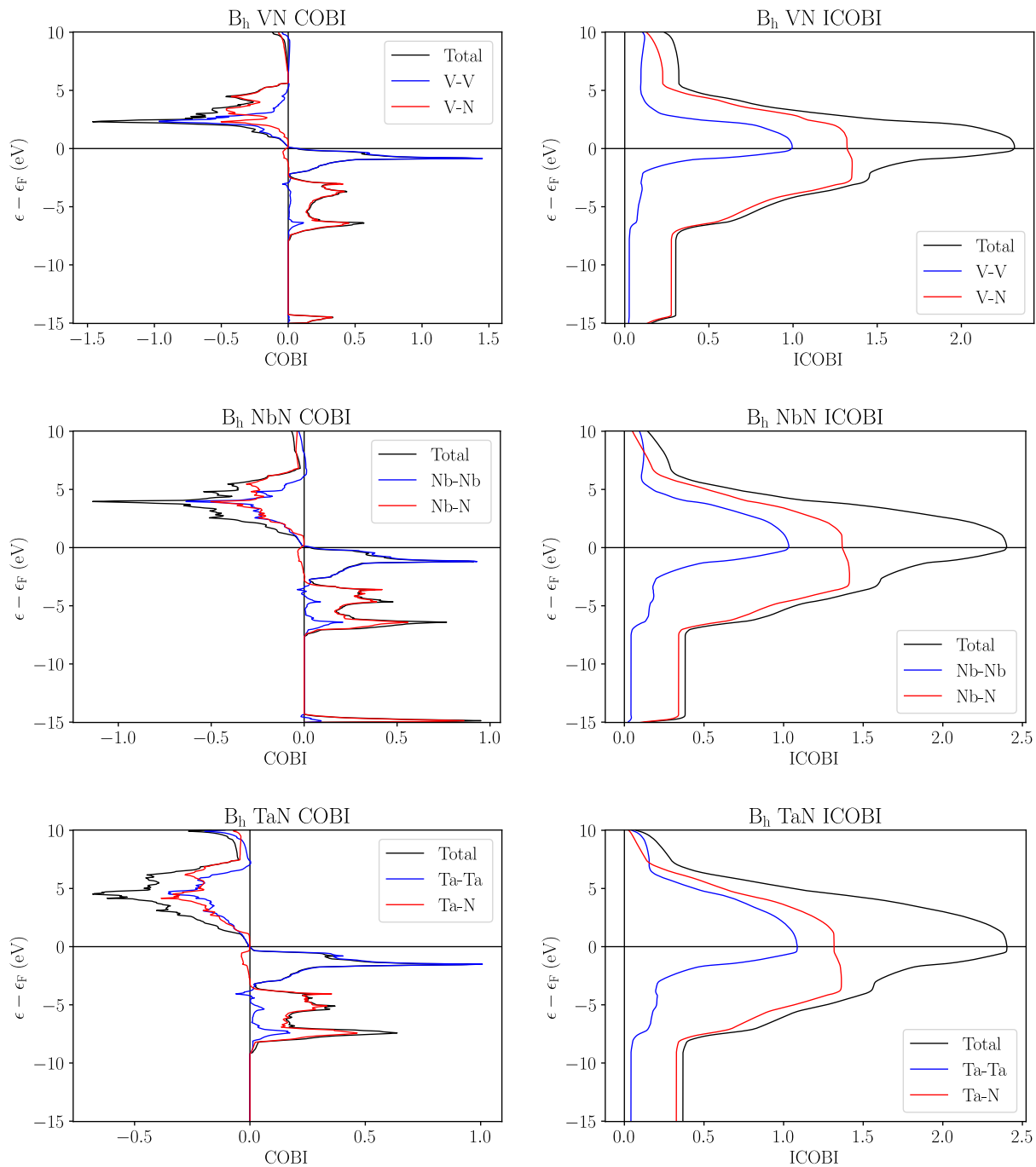


Figure E.28: Computed COBI for VB TMNs.

Appendix F

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