J. Phys.: Condens. Matter 29, 035401 Supplementary data **(2017)**

First-principles phase diagram calculations for the rocksalt-structure quasibinary systems TiN-ZrN, TiN-HfN and ZrN-HfN

Z. T. Y. Liu[1], B. P. Burton[2], S. V. Khare[1*], D. Gall[3]

[1]Department of Physics, University of Toledo, Toledo, OH 43606, USA

[2]Materials Measurement Laboratory, Metallurgy Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA

[3]Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

*Corresponding author: sanjay.khare@utoledo.edu

Supplementary data

A. Crystal Orbital Hamilton Populations analyses

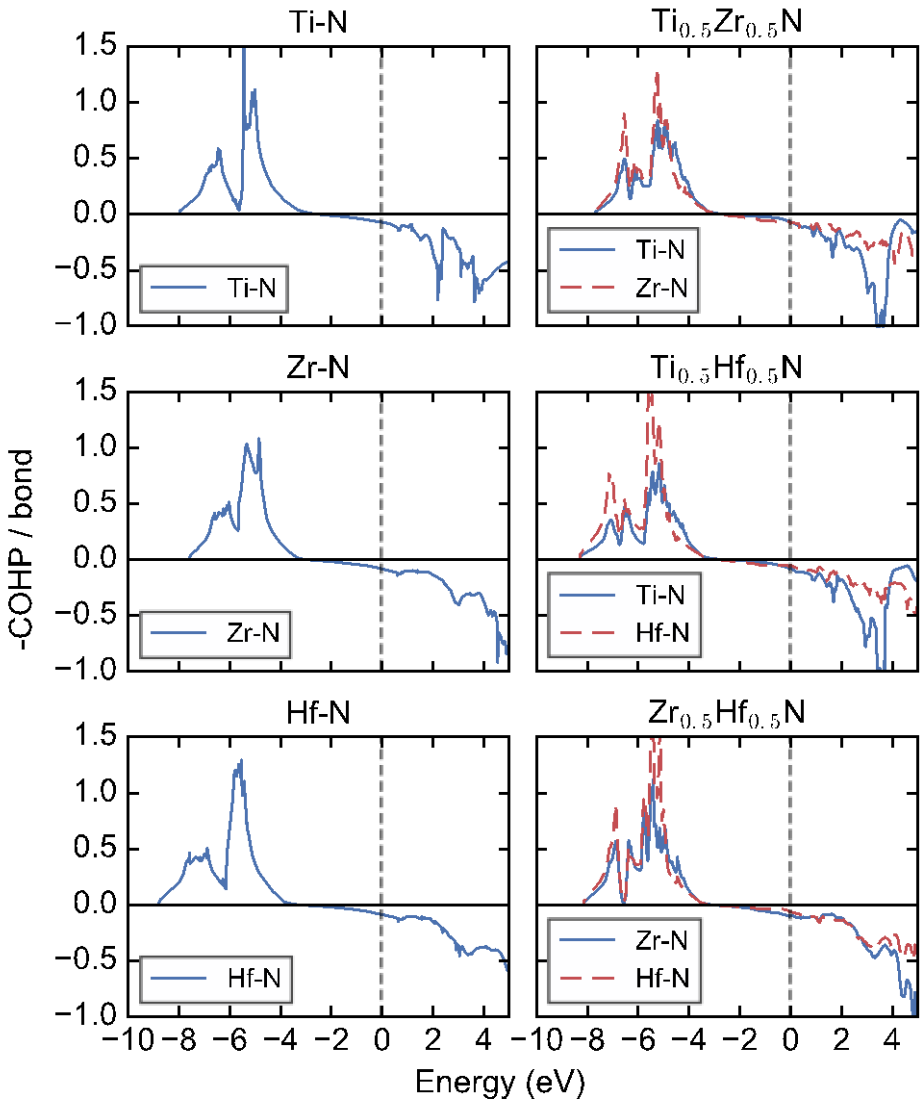

Figure S1 The COHP of various bonds in TiN, ZrN, HfN and three solid solutions with composition $A_{0.5}B_{0.5}N$ where *A* and *B* are transition metals. This quantity is inversely plotted because negative values of COHP stand for bonding, while positive for anti-bonding. The Fermi energy is set to 0 for each case.

We studied various bonds of the end members and one structure with a composition of $A_{0.5}B_{0.5}N$, where *A* and *B* are transition metals in each system, by the projected Crystal Orbital Hamilton Populations (COHP)[1] using the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER 2.0.0)[2–4] program. No symmetry constraints were imposed, extra empty bands were included, and appropriate basis functions were chosen to be physically consistent[5]. We used the new pbeVaspFit2015 basis set for all elements[4]. Negative COHP values signify bonding, and positive values indicate anti-bonding. In Figure S1 we observe the similarity of the Ti-N, Zr-N and Hf-N bonds, featuring majorly bonding states below the Fermi energy level (E_F). Furthermore,

there is a slightly anti-bonding slope (-COHP below 0) at E_F. In Table S1 bond lengths and integrated COHPs up to E_F of the end member and solid solutions are provided. The integrated COHP up to E_F is a measurement of bond strength, and generally, the more negative its value is, the stronger the bond. The differences between the quantity of bonds in the solid solution and end members are also provided. We notice minimal changes in both quantities, and do not find them indicative enough for the difference in formation energy (ΔE_f) behaviors, between $Ti_{1-x}Zr_xN$, $Ti_{1-x}Hf_xN$ ($\Delta E_f > 0$) and $Zr_{1-x}Hf_xN$ ($\Delta E_f < 0$).

Table S1 Lengths (d) and integrated COHPs up to the Fermi energy of metal-nitrogen (M-N) bonds in TiN, ZrN, HfN and three solid solutions with composition $A_{0.5}B_{0.5}N$ where *A* and *B* are transition metals. Differences between the solid solutions and the end members are also provided. Spilling stands for the unpartitioned remainder of the wave-function.

	d (Å)		Integrated COHP (eV)		Spilling (%)
	M-N		M-N		
TiN	2.12		-3.09		4.8
ZrN	2.30		-3.18		4.1
HfN	2.27		-3.27		6.4
	A-N	B-N	A-N	B-N	
$Ti_{0.5}Zr_{0.5}N$	2.17	2.26	-2.76	-3.46	4.1
$Ti_{0.5}Hf_{0.5}N$	2.18	2.22	-2.66	-3.62	4.8
$Zr_{0.5}Hf_{0.5}N$	2.32	2.25	-2.99	-3.43	4.7
	Difference from bonds in end members				
	A-N	B-N	A-N	B-N	
$Ti_{0.5}Zr_{0.5}N$	0.05	-0.03	0.33	-0.28	
$Ti_{0.5}Hf_{0.5}N$	0.06	-0.04	0.43	-0.35	
$Zr_{0.5}Hf_{0.5}N$	0.02	-0.02	0.20	-0.16	

B. Cluster expansions and phase diagrams

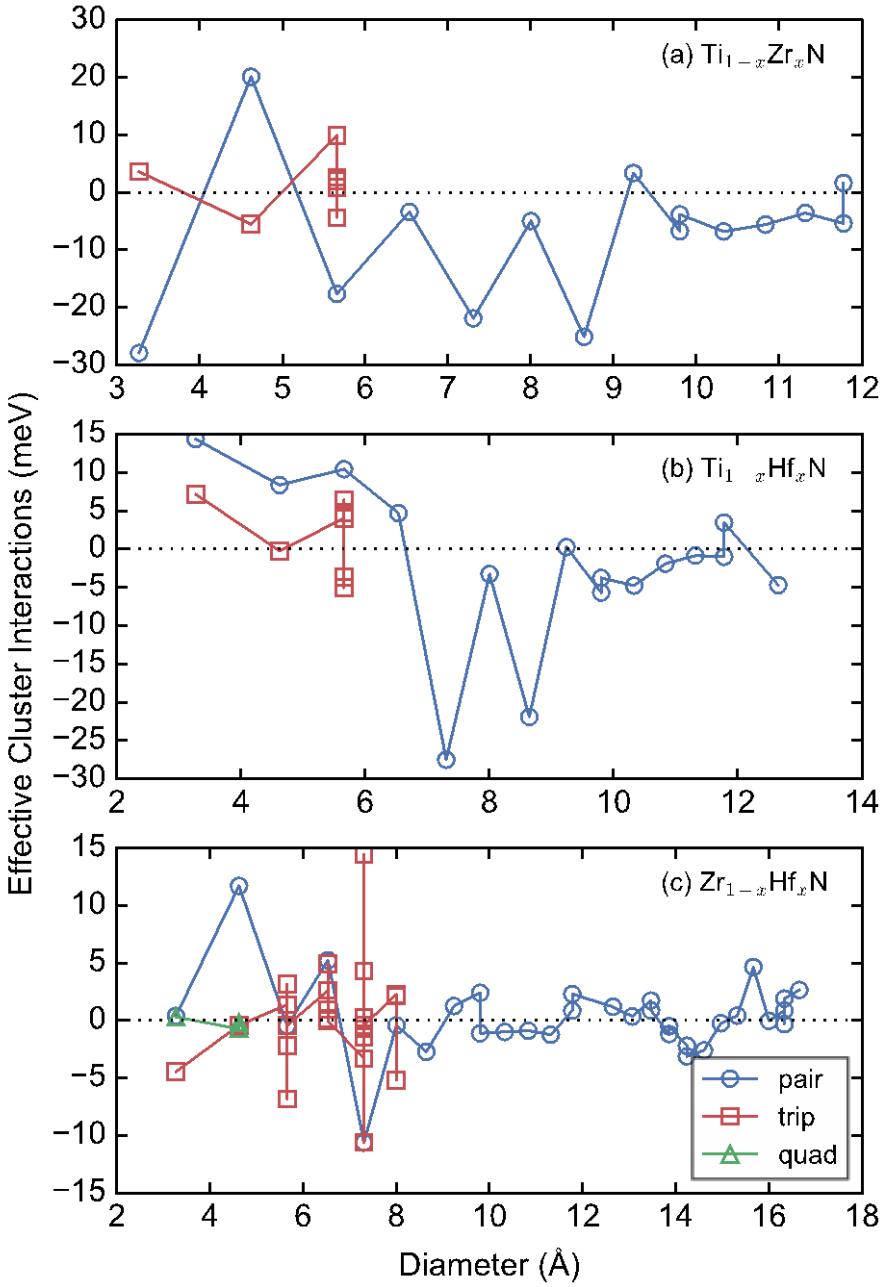

Figure S2 Effective cluster interactions (ECIs) of (a) $Ti_{1-x}Zr_xN$, (b) $Ti_{1-x}Hf_xN$ and (c) $Zr_{1-x}Hf_xN$. ECI values have been multiplied by their multiplicities. Blue circles, red squares and green triangles indicate pair, triplet and quadruplet interactions. Connecting lines are a guide to the eye.

Table S2 Cluster sets and effective cluster interactions (ECIs) of the $Ti_{1-x}Zr_xN$, $Ti_{1-x}Hf_xN$ and $Zr_{1-x}Hf_xN$ systems.

Type	Index	Diameter (Å)	Multiplicity	Coordinates	ECI [$Ti_{1-x}Zr_xN$] (meV)	ECI [$Ti_{1-x}Hf_xN$] (meV)	ECI [$Zr_{1-x}Hf_xN$] (meV)
empty	1	0.000	1		108.019	33.993	-9.363

point	1	0.000	1	[[1.0, 1.0, 1.0]]	-9.574	-13.743	-0.292
pair	1	3.267	6	[[1.0, 1.0, 1.0], [1.5, 1.0, 1.5]]	-4.658	2.394	0.067
pair	2	4.620	3	[[1.0, 1.0, 1.0], [0.0, 1.0, 1.0]]	6.713	2.786	3.905
pair	3	5.658	12	[[1.0, 1.0, 1.0], [0.0, 0.5, 1.5]]	-1.471	0.869	-0.038
pair	4	6.534	6	[[1.0, 1.0, 1.0], [0.0, 0.0, 1.0]]	-0.565	0.780	0.875
pair	5	7.305	12	[[1.0, 1.0, 1.0], [-0.5, 1.0, 1.5]]	-1.825	-2.292	-0.885
pair	6	8.002	4	[[1.0, 1.0, 1.0], [0.0, 2.0, 2.0]]	-1.245	-0.815	-0.103
pair	7	8.643	24	[[1.0, 1.0, 1.0], [-0.5, 1.5, 0.0]]	-1.047	-0.913	-0.113
pair	8	9.240	3	[[1.0, 1.0, 1.0], [1.0, 1.0, 3.0]]	1.129	0.088	0.419
pair	9	9.801	12	[[1.0, 1.0, 1.0], [0.5, 0.5, 3.0]]	-0.561	-0.473	0.201
pair	10	9.801	6	[[1.0, 1.0, 1.0], [-0.5, -0.5, 1.0]]	-0.637	-0.628	-0.185
pair	11	10.331	12	[[1.0, 1.0, 1.0], [-1.0, 1.0, 2.0]]	-0.565	-0.398	-0.082
pair	12	10.835	12	[[1.0, 1.0, 1.0], [-0.5, -0.5, 2.0]]	-0.466	-0.159	-0.073
pair	13	11.317	12	[[1.0, 1.0, 1.0], [-1.0, 0.0, 2.0]]	-0.298	-0.072	-0.103
pair	14	11.779	24	[[1.0, 1.0, 1.0], [-0.5, 0.5, 3.0]]	-0.224	-0.042	0.036
pair	15	11.779	12	[[1.0, 1.0, 1.0], [-1.5, 0.5, 1.0]]	0.137	0.289	0.192
pair	16	12.652	24	[[1.0, 1.0, 1.0], [-1.5, 0.0, 0.5]]		-0.196	0.050
pair	17	13.067	6	[[1.0, 1.0, 1.0], [1.0, 3.0, 3.0]]			0.060
pair	18	13.469	12	[[1.0, 1.0, 1.0], [-0.5, -0.5, 3.0]]			0.145
pair	19	13.469	12	[[1.0, 1.0, 1.0], [-1.5, -0.5, 1.0]]			0.073

pair	20	13.860	12	[[1.0, 1.0, 1.0], [0.0, 3.0, 3.0]]			-0.098
pair	21	13.860	3	[[1.0, 1.0, 1.0], [-2.0, 1.0, 1.0]]			-0.164
pair	22	14.240	12	[[1.0, 1.0, 1.0], [-2.0, 0.5, 0.5]]			-0.182
pair	23	14.240	24	[[1.0, 1.0, 1.0], [-1.5, -0.5, 2.0]]			-0.130
pair	24	14.610	12	[[1.0, 1.0, 1.0], [-2.0, 0.0, 1.0]]			-0.216
pair	25	14.971	24	[[1.0, 1.0, 1.0], [0.5, 3.5, 3.0]]			-0.010
pair	26	15.323	12	[[1.0, 1.0, 1.0], [2.0, 4.0, 2.0]]			0.036
pair	27	15.667	24	[[1.0, 1.0, 1.0], [-0.5, 1.5, 4.0]]			0.194
pair	28	16.004	4	[[1.0, 1.0, 1.0], [-1.0, -1.0, 3.0]]			-0.007
pair	29	16.334	24	[[1.0, 1.0, 1.0], [3.0, 3.5, -0.5]]			0.036
pair	30	16.334	6	[[1.0, 1.0, 1.0], [-1.5, -1.5, 1.0]]			-0.052
pair	31	16.334	12	[[1.0, 1.0, 1.0], [-2.5, 0.5, 1.0]]			0.159
pair	32	16.658	12	[[1.0, 1.0, 1.0], [-1.0, 1.0, 4.0]]			0.222
trip	1	3.267	8	[[1.0, 1.0, 1.0], [1.5, 1.0, 1.5], [1.0, 1.5, 1.5]]	0.450	0.895	-0.556
trip	2	4.620	12	[[1.0, 1.0, 1.0], [0.5, 0.5, 1.0], [0.0, 1.0, 1.0]]	-0.460	-0.020	-0.034
trip	3	5.658	24	[[1.0, 1.0, 1.0], [0.5, 0.5, 1.0], [0.0, 0.5, 1.5]]	0.415	0.167	0.058
trip	4	5.658	24	[[1.0, 1.0, 1.0], [1.0, 0.5, 1.5], [0.0, 0.5, 1.5]]	-0.182	-0.210	-0.092

trip	5	5.658	24	[[1.0, 1.0, 1.0], [0.5, 1.0, 0.5], [0.0, 0.5, 1.5]]	0.039	-0.152	-0.285
trip	6	5.658	24	[[1.0, 1.0, 1.0], [1.0, 0.0, 1.0], [0.0, 0.5, 1.5]]	0.108	0.269	0.132
trip	7	5.658	8	[[1.0, 1.0, 1.0], [0.5, 0.0, 0.5], [0.0, 0.5, 1.5]]	0.251	0.590	-0.053
trip	8	6.534	6	[[1.0, 1.0, 1.0], [0.5, 0.5, 1.0], [0.0, 0.0, 1.0]]			0.439
trip	9	6.534	48	[[1.0, 1.0, 1.0], [0.5, 1.0, 1.5], [0.0, 0.0, 1.0]]			0.103
trip	10	6.534	12	[[1.0, 1.0, 1.0], [0.0, 1.0, 1.0], [0.0, 0.0, 1.0]]			0.013
trip	11	6.534	12	[[1.0, 1.0, 1.0], [0.5, 0.5, 2.0], [0.0, 0.0, 1.0]]			0.079
trip	12	6.534	8	[[1.0, 1.0, 1.0], [0.0, 1.0, 2.0], [0.0, 0.0, 1.0]]			-0.003
trip	13	7.305	24	[[1.0, 1.0, 1.0], [1.0, 1.5, 1.5], [-0.5, 1.0, 1.5]]			-0.138
trip	14	7.305	48	[[1.0, 1.0, 1.0], [0.5, 0.5, 1.0], [-0.5, 1.0, 1.5]]			0.301
trip	15	7.305	24	[[1.0, 1.0, 1.0], [0.5, 1.0, 1.5], [-0.5, 1.0, 1.5]]			0.179
trip	16	7.305	24	[[1.0, 1.0, 1.0], [0.5, 1.0, 0.5], [-0.5, 1.0, 1.5]]			0.011
trip	17	7.305	12	[[1.0, 1.0, 1.0], [1.0, 1.0, 2.0], [-0.5, 1.0, 1.5]]			-0.120
trip	18	7.305	48	[[1.0, 1.0, 1.0], [0.5, 0.0, 1.5], [-0.5, 1.0, 1.5]]			-0.221

trip	19	7.305	48	[[1.0, 1.0, 1.0], [0.5, 0.5, 2.0], [-0.5, 1.0, 1.5]]	-0.015
trip	20	7.305	12	[[1.0, 1.0, 1.0], [0.0, 1.0, 0.0], [-0.5, 1.0, 1.5]]	-0.034
trip	21	8.002	24	[[1.0, 1.0, 1.0], [1.0, 1.5, 1.5], [0.0, 2.0, 2.0]]	0.095
trip	22	8.002	24	[[1.0, 1.0, 1.0], [0.0, 1.0, 1.0], [0.0, 2.0, 2.0]]	0.088
trip	23	8.002	48	[[1.0, 1.0, 1.0], [0.0, 0.5, 1.5], [0.0, 2.0, 2.0]]	-0.108
quad	1	3.267	2	[[1.0, 1.0, 1.0], [1.5, 1.5, 1.0], [1.5, 1.0, 1.5], [1.0, 1.5, 1.5]]	0.153
quad	2	4.620	12	[[1.0, 1.0, 1.0], [0.5, 1.0, 1.5], [0.5, 0.5, 1.0], [0.0, 1.0, 1.0]]	-0.060
quad	3	4.620	3	[[1.0, 1.0, 1.0], [0.5, 1.5, 1.0], [0.5, 0.5, 1.0], [0.0, 1.0, 1.0]]	-0.059

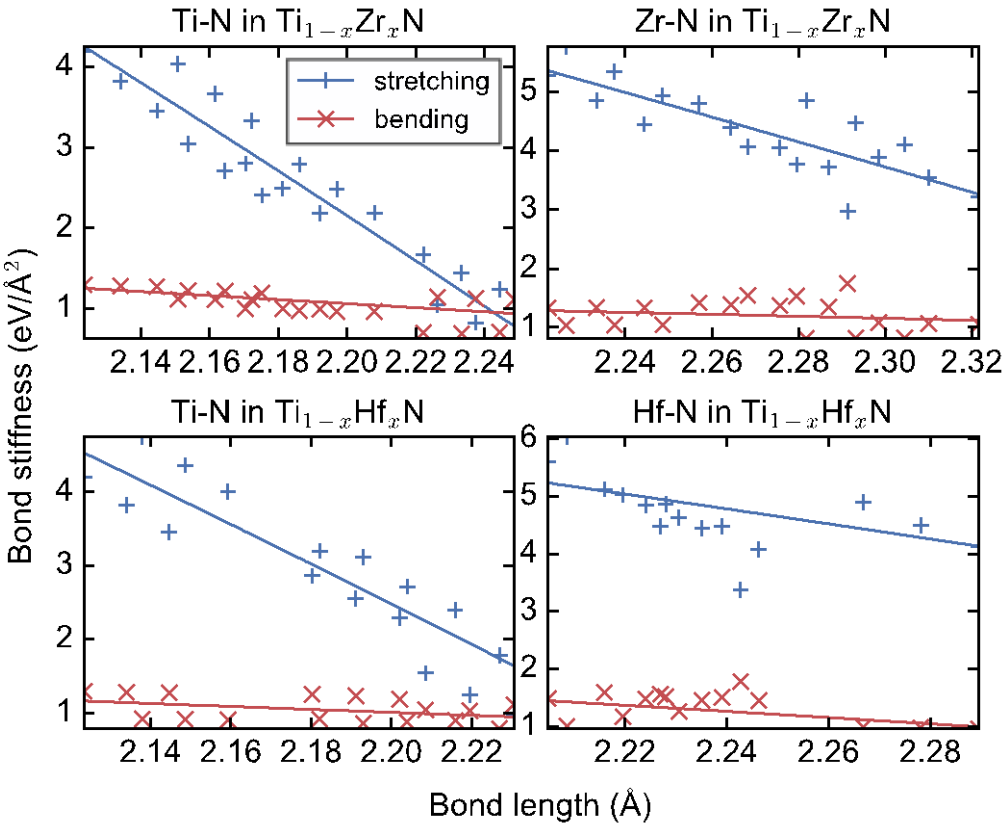

Figure S3 Nearest neighbor stretching and bending stiffness constants versus bond lengths of various bonds in $Ti_{1-x}Zr_xN$ and $Ti_{1-x}Hf_xN$. Blue "+" and red "×" crosses indicate stretching and bending terms respectively. Lines are linear fits, which were used in the calculations of the vibrational contributions to the free energy.

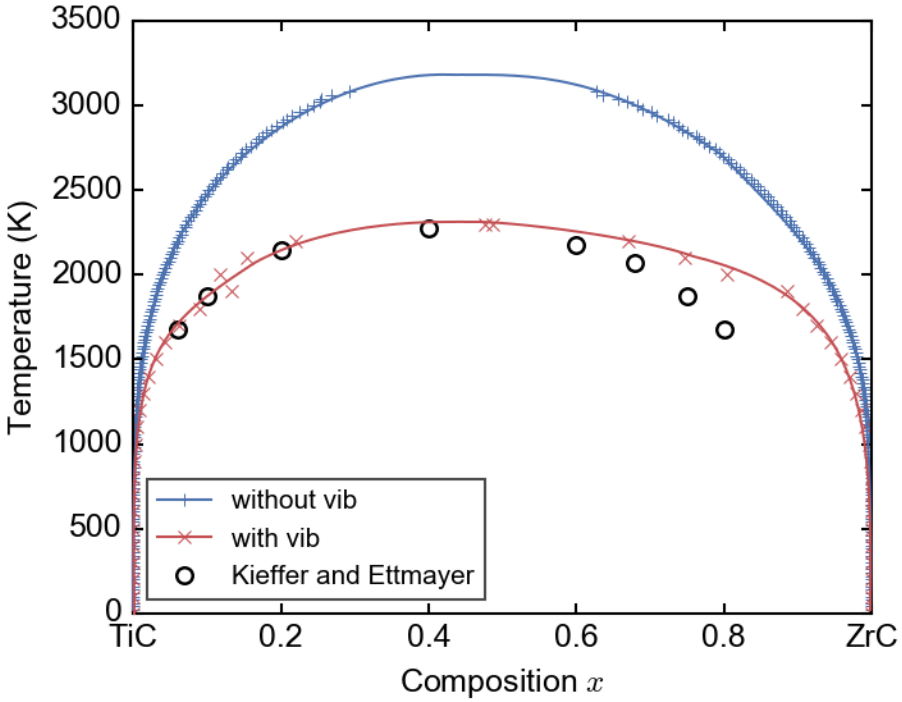

Figure S4 The calculated phase diagram of $Ti_{1-x}Zr_xC$. Small crosses are raw data points, and curves are smooth interpolations and extrapolations. Blue + and red × correspond to the results without and with the vibrational contributions. Black hollow circles are experimental data[6].

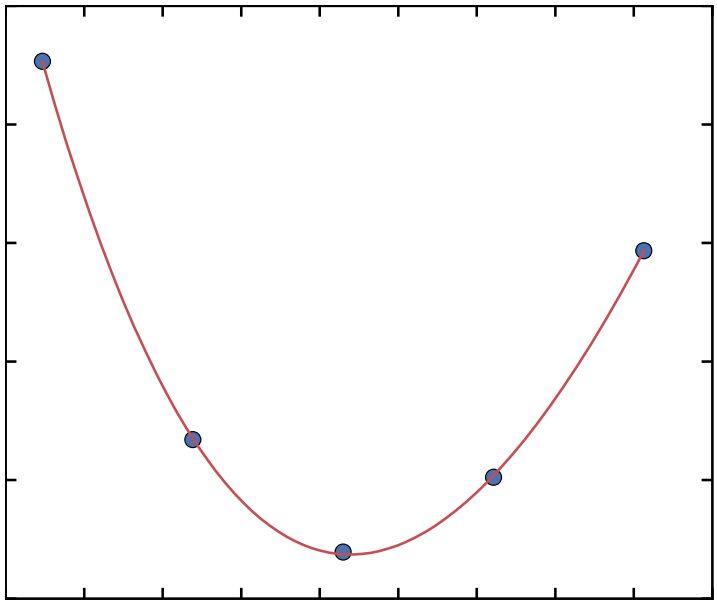

Figure S5 The equation of state (EOS) of TiN. It takes more energy to contract rather than expand by the same amount from the equilibrium volume.

C. Mechanical properties

Table S3 Elastic constants C_{11}, C_{12}, C_{44}, bulk moduli (B), shear moduli (G), Pugh's ratios (k), Poisson's ratios (ν) and Vickers hardnesses (H_V) of the SQS's of $Ti_{1-x}Zr_xN$, $Ti_{1-x}Hf_xN$ and $Zr_{1-x}Hf_xN$.

	x	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	B (GPa)	G (GPa)	k	ν	H_V (GPa)
	0	518	130	166	259	177	0.68	0.22	23.2
	Ref.[a]	554	131	169					
	0.25	515	114	144	248	164	0.66	0.23	21.3
	Ref.[a]	526	126	148					
$Ti_{1-x}Zr_xN$	0.5	498	115	132	242	153	0.63	0.24	19.3
	Ref.[a]	513	120	136					
	0.75	496	104	125	235	149	0.64	0.24	19.1
	Ref.[a]	505	118	127					
	1	497	112	123	240	147	0.61	0.25	18.1
	Ref.[a]	504	116	120					
	0	518	130	166	259	177	0.68	0.22	23.2
	0.25	531	114	147	253	169	0.67	0.23	22.0
$Ti_{1-x}Hf_xN$	0.5	518	114	137	249	160	0.64	0.24	20.2
	0.75	535	107	129	250	158	0.63	0.24	19.7
	1	536	103	124	247	155	0.63	0.24	19.3
	0	496	111	123	240	147	0.61	0.24	18.1
	0.25	520	100	121	240	151	0.63	0.24	19.1
$Zr_{1-x}Hf_xN$	0.5	533	106	122	248	153	0.62	0.24	18.8
	0.75	549	103	123	251	156	0.62	0.24	19.2
	1	536	103	124	247	155	0.63	0.24	19.3

[a] FLAPW-GGA from Ref. [7]

References

1. Dronskowski, R. & Blochl, P. E. Crystal Orbital Hamilton Populations (COHP) - Energy-Resolved Visualization of Chemical Bonding in Solids Based on Density-Functional Calculations. *J. Phys. Chem.* **97,** 8617–8624 (1993).
2. Deringer, V. L., Tchougreeff, A. L. & Dronskowski, R. Crystal Orbital Hamilton Population (COHP) Analysis As Projected from Plane-Wave Basis Sets. *J. Phys. Chem. A* **115,** 5461–5466 (2011).
3. Maintz, S., Deringer, V. L., Tchougreeff, A. L. & Dronskowski, R. Analytic Projection From Plane-Wave and PAW Wavefunctions and Application to Chemical-Bonding Analysis in Solids. *J. Comput. Chem.* **34,** 2557–2567 (2013).
4. Crystal Orbital Hamilton Populations: The Official Reference Page. Available at: http://cohp.de/.
5. Liu, Z. T. Y., Gall, D. & Khare, S. V. Electronic and bonding analysis of hardness

in pyrite-type transition-metal pernitrides. *Phys. Rev. B* **90,** 134102 (2014).

6. Kieffer, R. & Ettmayer, P. Principles and Latest Developments in the Field of Metallic and Nonmetallic Hard Materials. *Angew. Chemie Int. Ed. English* **9,** 926–936 (1970).
7. Abadias, G., Ivashchenko, V. I., Belliard, L. & Djemia, P. Structure, phase stability and elastic properties in the Ti1-xZrxN thin-film system: Experimental and computational studies. *Acta Mater.* **60,** 5601–5614 (2012).