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Correlating structure and orbital occupation with the stability and mechanical properties of 3d transition metal carbides

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Table S1: Calculated lattice parameters (a_{calc}) for all 3d transition metal carbides (TMCs) in the zincblende structure (ZB), rocksalt structure (RS) [1], and cesium chloride structure (CsCl). Experimental data, where available, is listed in parenthesis for comparison. The mechanical and dynamical stability of each compound are also presented. "MS/MU" correspond to the mechanically stable/unstable and "DS/DU" correspond to the dynamically stable/unstable.

Compound	Zincblende		Rocksalt		Cesium chloride	
	a_{calc} (Å)	Stability	a_{calc} (Å)	Stability	a_{calc} (Å)	Stability
ScC	5.08	MU, DU	4.69 4.72[E, b]	MS, DS	2.87	MU, DU
TiC	4.73 4.74[T, a]	MS, DS	4.33 4.33[E, c]	MS, DS	2.71 2.72[T, a]	MU, DU
VC	4.52	MS, DS	4.16 4.18[E, d]	MS, DS	2.60	MU, DU
CrC	4.39	MS, DS	4.07 4.03[E, e]	MS, DS	2.52	MS, DU
MnC	4.31	MS, DS	4.05	MS, DU	2.49	MS, DU
FeC	4.26	MS, DS	3.99	MS, DU	2.46	MU, DU
CoC	4.28	MS, DS	4.00	MS, DU	2.50	MU, DU
NiC	4.35	MS, DU	4.07	MS, DU	2.54	MU, DU
CuC	4.50	MU, DU	4.23	MS, DU	2.64	MU, DU
ZnC	4.69	MS, DS	4.40	MS, DS	2.76	MU, DU

[a]: Ref.[2], [b]: Ref. [3], [c]: Ref.[4], [d]: Ref.[5], [e]: Ref. [6], [E]: Experimental value, [T]: Computed value

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Table S2: Elastic constants (C_{11}, C_{12}, C_{44}), and mechanical stability of 3d transitional metal carbides (TMCs) in zincblende (ZB), rocksalt (RS), and cesium chloride (CsCl) structures. The mechanical and the dynamical stability of each compound are also presented; "MS/MU" indicates mechanically stable/unstable and "DS/DU" correspond to the dynamically stable/unstable.

TMCs	C_{11} (GPa)			C_{12} (GPa)			C_{44} (GPa)			Stability		
	ZB	RS	CsCl	ZB	RS	CsCl	ZB	RS	CsCl	ZB	RS	CsCl
ScC	85.6	298.1	103.2	107.0	82.9	175.6	23.9	61.6	-132.7	MU, DU	MS, DS	MU, DU
TiC	193.8	517.2	11.0	151.1	120.4	325.2	59.5	173.8	-342.0	MS, DS	MS, DS	MU, DU
VC	289.3	625.3	438.2	164.9	145.5	213.0	60.3	165.7	-65.3	MS, DS	MS, DS	MU, DU
CrC	301.3	621.4	665.9	194.7	179.7	161.4	25.4	138.5	109.5	MS, DS	MS, DS	MS, DU
MnC	306.3	578.7	756.3	210.8	210.8	143.6	42.3	21.6	46.3	MS, DS	MS, DU	MS, DU
FeC	342.9	589.4	769.9	208.7	205.8	132.3	65.3	77.6	-28.2	MS, DS	MS, DU	MU, DU
CoC	307.9	530.6	558.6	204.0	195.5	170.1	62.1	49.2	-19.2	MS, DS	MS, DU	MU, DU
NiC	201.1	319.5	362.4	200.0	223.5	162.6	24.1	67.8	-38.1	MS, DU	MS, DU	MU, DU
CuC	147.3	240.1	222.6	150.8	153.3	160.2	19.0	20.5	-38.0	MU, DU	MS, DU	MU, DU
ZnC	117.4	225.7	128.4	107.4	101.9	143.7	25.2	41.7	-40	MS, DS	MS, DS	MU, DU

Table S3: Calculated bulk modulus (B), shear modulus (G), Cauchy's pressure (P_c), Poisson's ratio (ν), Pugh's ratio (κ), and Vickers's hardness (H_V) of stable 3d transition metal carbides (TMCs) in the zincblende (ZB) and rocksalt (RS) structures. Instability is denoted by "U". As all TMCs are unstable in the cesium chloride structure (CsCl), the corresponding values are not presented.

TMCs	B (GPa)		G (GPa)		P_c		ν		κ		H_V (GPa)	
	ZB	RS	ZB	RS	ZB	RS	ZB	RS	ZB	RS	ZB	RS
ScC	U	153.8 154.8[E, a]	U	77.2	U	21.5	U	0.29	U	0.50	U	9.10
TiC	164.9	251.8 240.0 [E, b]	39.5	183.3	91.6	-53.5	0.39	0.21	0.24	0.73	2.44	25.66
VC	206.1	303.7 302.0 [T, c]	61.0	192.2	104.7	-20.4	0.37	0.24	0.30	0.63	4.23	22.63
CrC	229.1	326.4	34.3	167.1	167.3	41.4	0.43	0.28	0.15	0.51	1.30	16.11
MnC	241.9	U	44.4	U	168.5	U	0.41	U	0.18	U	1.97	U
FeC	252.9	U	66.1	U	143.5	U	0.38	U	0.26	U	3.88	U
CoC	237.8	U	57.8	U	141.9	U	0.39	U	0.24	U	3.26	U
ZnC	109.3	142.4	13.4	48.9	82.1	60.2	0.44	0.35	0.12	0.34	0.53	4.28

[a]: Ref.[7], [b]: Ref. [8], [c]: Ref. [9], [E]: Experimental value, [T]: Computed value

Table S4: Electronegativity (χ) [10] of the transition metals and Bader charge transfer (q_{tran}) from the metal to the carbon atom in zincblende (ZB), rocksalt (RS), and cesium chloride (CsCl) structure.

Compound	q_{tran}-ZB	q_{tran}-RS	q_{tran}-CsCl	Electronegativity (χ)
ScC	1.59	1.64	1.56	1.20
TiC	1.69	1.66	1.43	1.32
VC	1.49	1.52	1.26	1.45
CrC	1.25	1.29	1.09	1.56
MnC	1.08	1.11	0.90	1.60
FeC	0.79	0.88	0.70	1.64
CoC	0.66	0.78	0.65	1.70
NiC	0.63	0.75	0.61	1.75
CuC	0.64	0.73	0.63	1.75
ZnC	0.83	0.90	0.86	1.66

Table S5: Cohesive energy per atom (ΔE_{coh}) in eV of the transition-metal carbides in zincblende (ZB), rocksalt (RS), and cesium chloride (CsCl) structure. The Experimental value is from Ref [11].

Compound	ZB	RS	CsCl	Exp.
ScC	5.73	6.34	5.79	6.35
TiC	7.01	7.71	6.53	7.23
VC	6.63	7.18	6.34	7.01
CrC	5.61	5.95	5.43	5.86
MnC	5.53	5.63	5.28	5.21
FeC	6.21	6.08	5.72	5.74
CoC	6.15	5.91	5.47	5.76
NiC	5.67	5.50	5.15	5.58
CuC	4.17	4.16	3.97	
ZnC	2.90	2.93	2.65	

Table S6: Calculated formation Energy per atom (ΔE_F) in eV of the transition-metal carbides in zincblende (ZB), rocksalt (RS), cesium chloride (CsCl), and wurtzite structure.

Compound	ZB	RS	CsCl	Wurtzite
ScC	0.44	-0.17	0.37	0.09
TiC	-0.17	-0.83	0.35	-0.57
VC	0.13	-0.42	0.42	-0.34
CrC	0.51	0.16	0.68	0.05
MnC	0.44	0.33	0.70	0.19
FeC	0.43	0.56	0.92	0.45
CoC	0.57	0.80	1.24	0.67
NiC	0.93	1.10	1.44	0.94
CuC	1.70	1.71	1.90	2.14
ZnC	1.67	1.64	1.92	1.59

Table S7: Integrated Projected Crystal Orbital Hamiltonian Populations (ipCOHP) in eV of the transition-metal carbides in zincblende (ZB) and rocksalt (RS). M and C correspond to metal and carbon respectively.

Compound	ZB			RS		
	M-M	M-C	C-C	M-M	M-C	C-C
ScC	0.019	1.398	0.037	-0.007	1.223	0.048
TiC	0.103	2.235	0.079	0.008	1.546	0.034
VC	0.054	2.108	0.151	0.038	1.292	0.078
CrC	0.161	2.071	0.145	0.114	1.211	0.071
MnC	0.154	2.131	0.163	0.095	1.189	0.090
FeC	0.134	2.042	0.159	0.0761	1.217	0.106
CoC	0.109	1.987	0.124	0.057	1.073	0.131
NiC	0.081	2.023	0.154	0.044	1.091	0.140

CuC	0.056	1.679	0.199	0.031	1.142	0.142
ZnC	0.023	1.398	0.220	-0.016	0.889	0.083

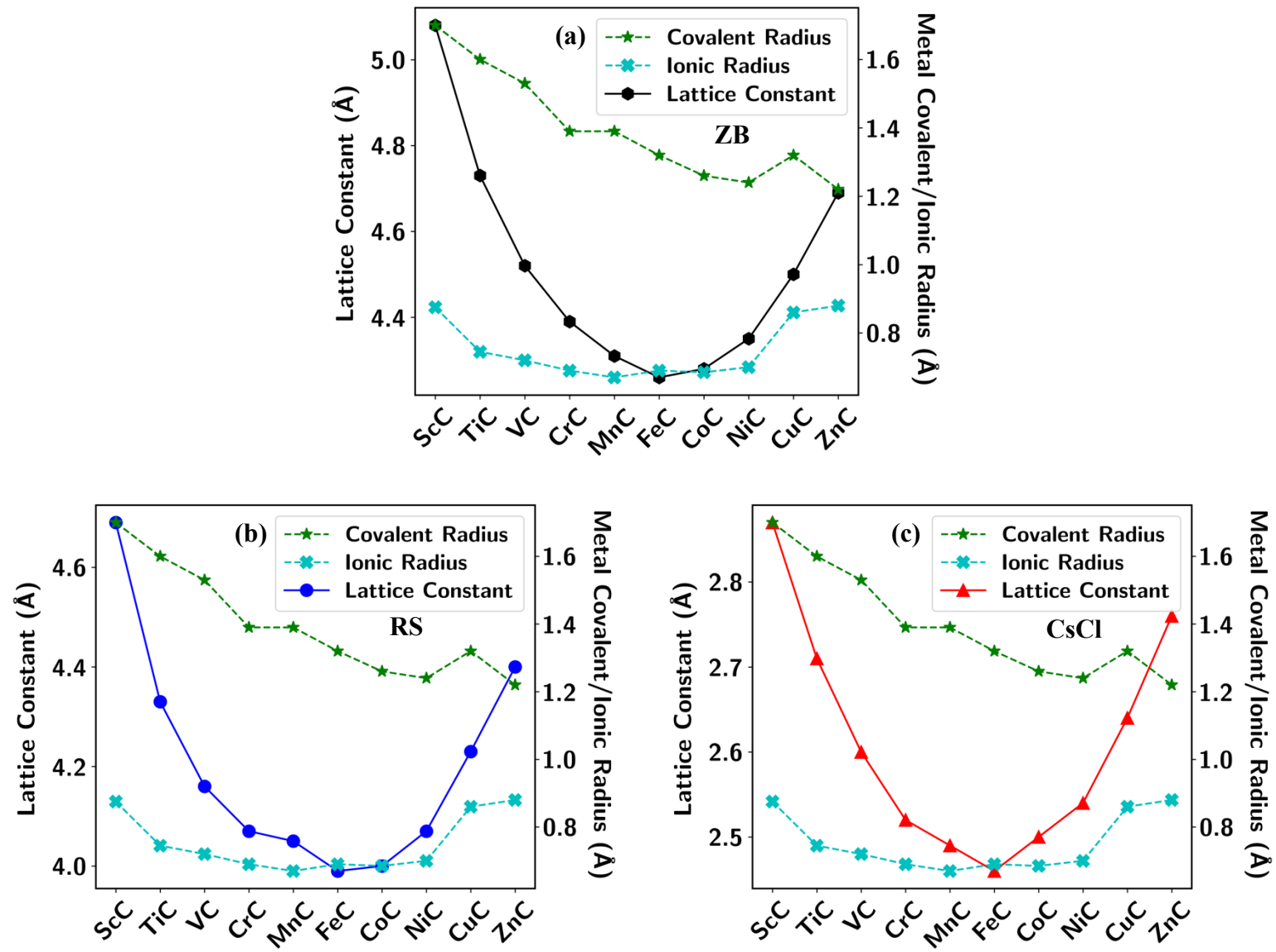

Figure S1: Correlation between calculated lattice constants of the 3d TMCs with ionic and metal covalent radius [12] for zincblende (ZB) (a), rocksalt (RS) (b) [1], and cesium chloride (CsCl) (c) structures.

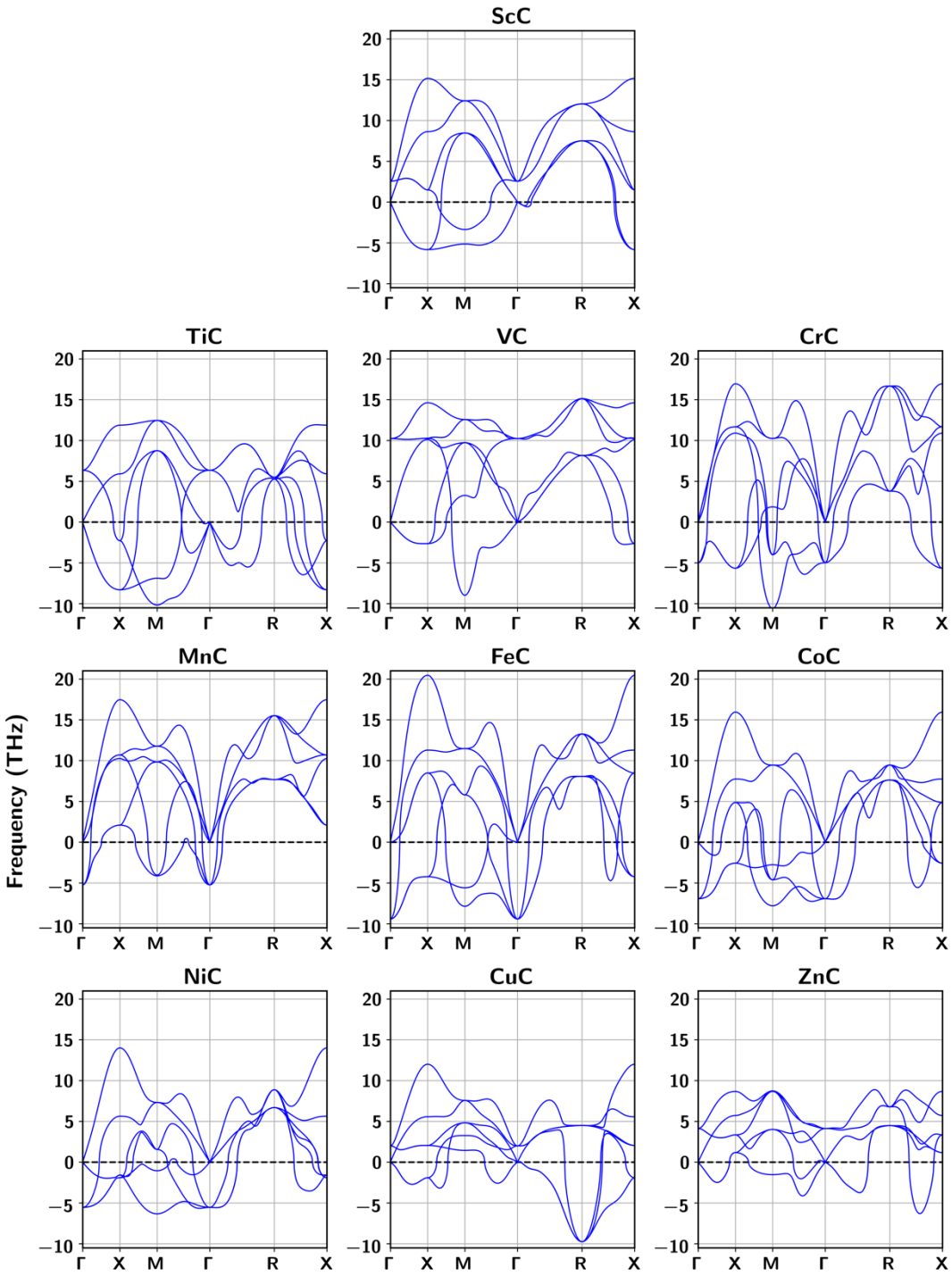

Figure S2: Phonon dispersion curves of 3*d* TMCs in cesium chloride (CsCl) structures calculated within the quasiharmonic approximation.

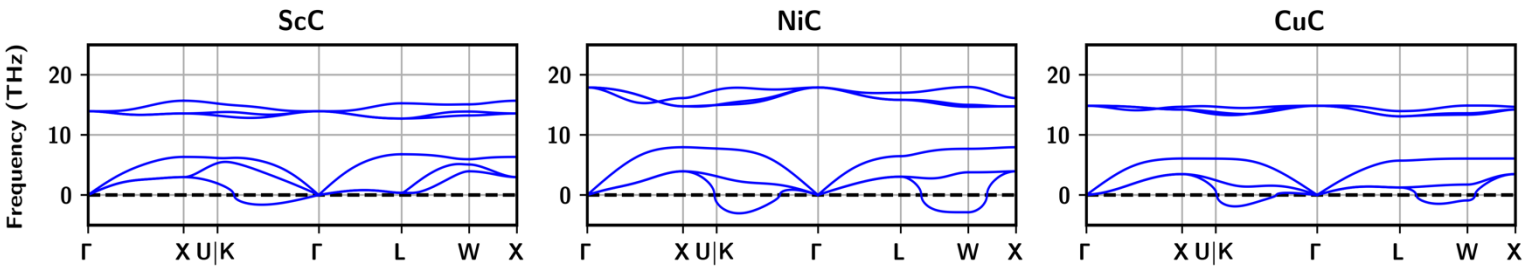

Figure S3: Phonon dispersion curves of the 3*d* TMCs in zincblende (ZB) structures which were found to be dynamically unstable in the harmonic approximation.

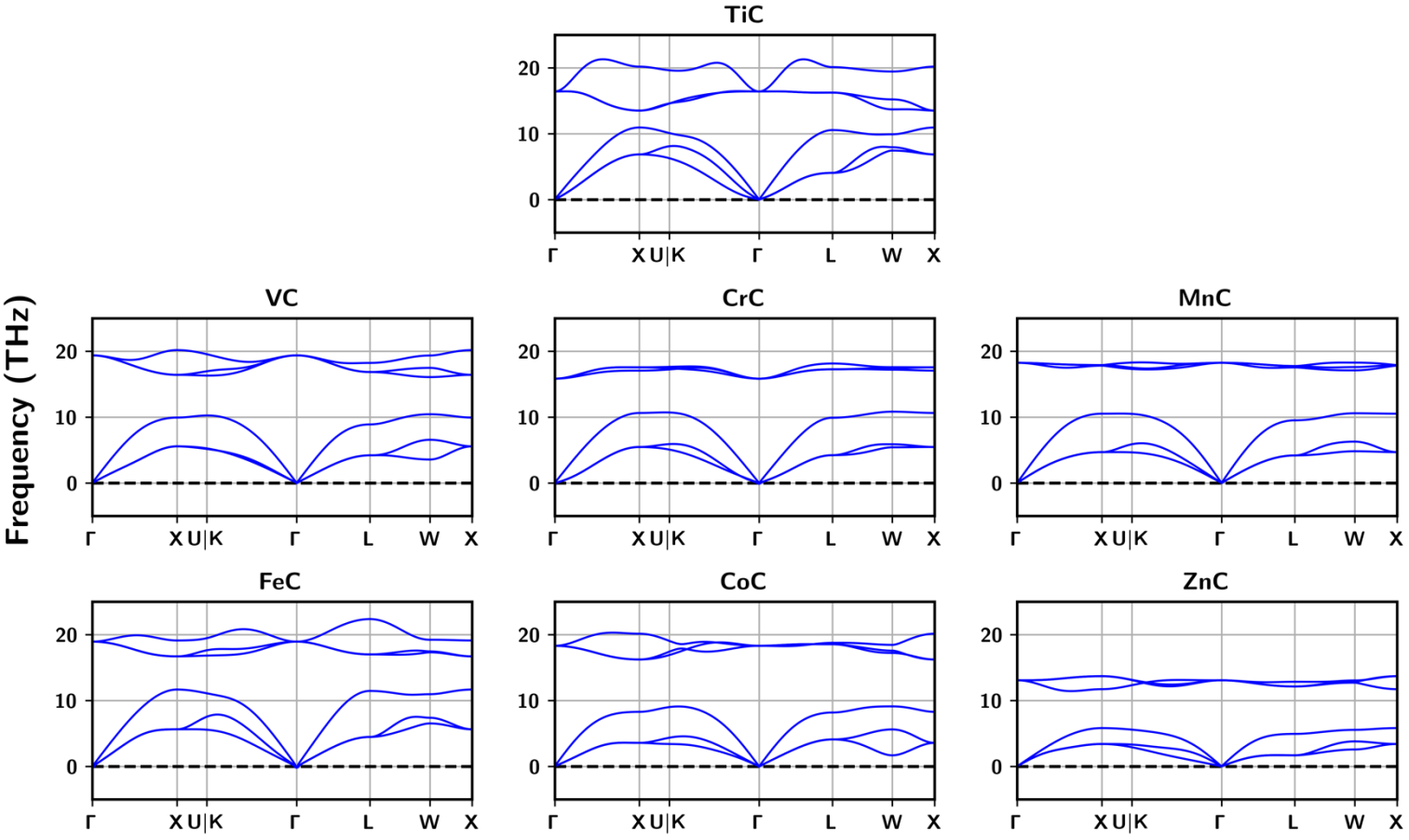

Figure S4: Phonon dispersion curves, calculated in the quasiharmonic approximation, for those 3*d* TMCs in zincblende (ZB) structures which were found to be dynamically stable.

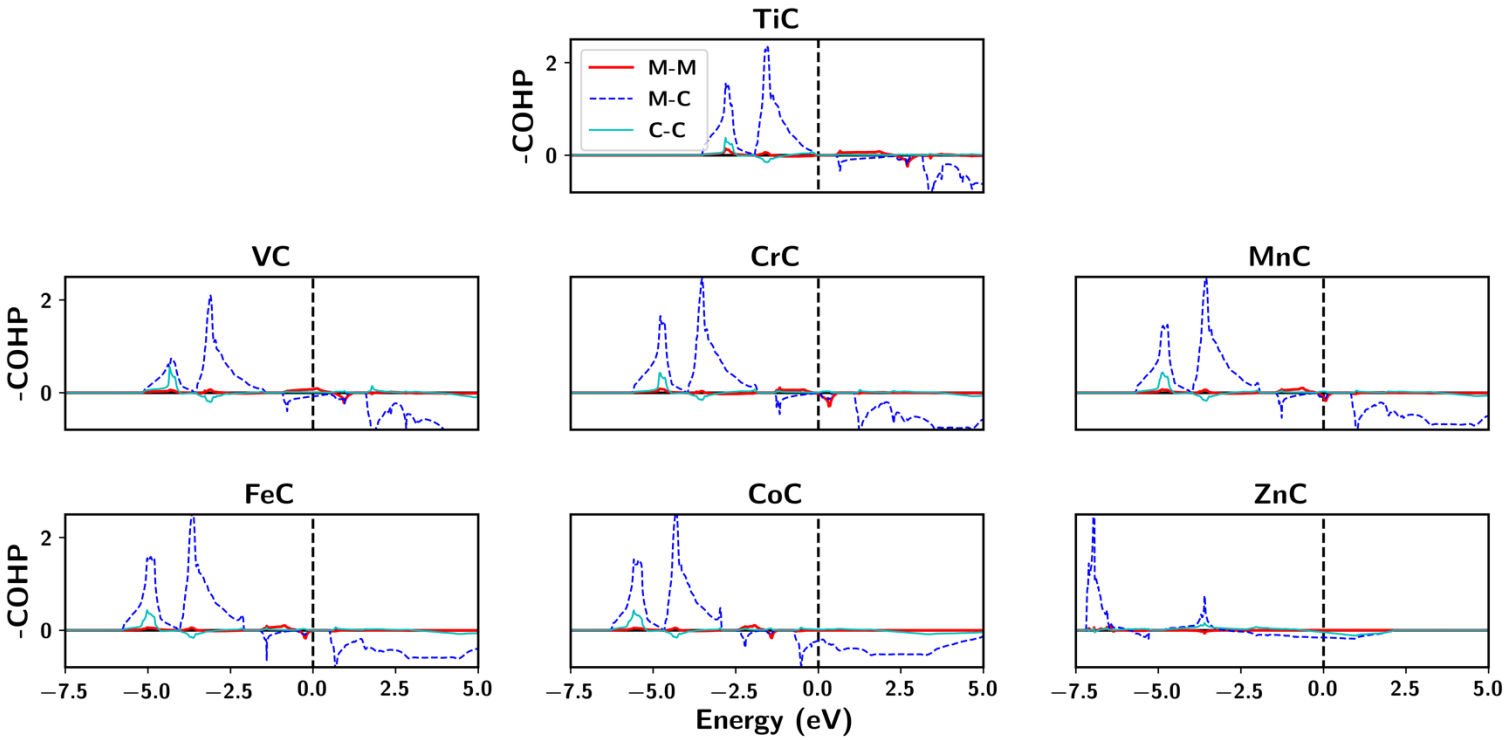
TiC
VC
CrC
MnC
FeC
CoC
ZnC
M-M
M-C
C-C
-COHP
2
0
−7.5
−5.0
−2.5
0.0
2.5
5.0
Energy (eV)

Figure S5: -Crystal Orbital Hamiltonian Populations (-COHP) of stable individual bonding pairs, metal-carbon (M-C), metal-metal (M-M), and carbon-carbon (C-C), in zincblende (ZB) structures are shown. Positive values represent bonding states, whereas negative values represent anti-bonding states. The Fermi level is set to 0 eV.

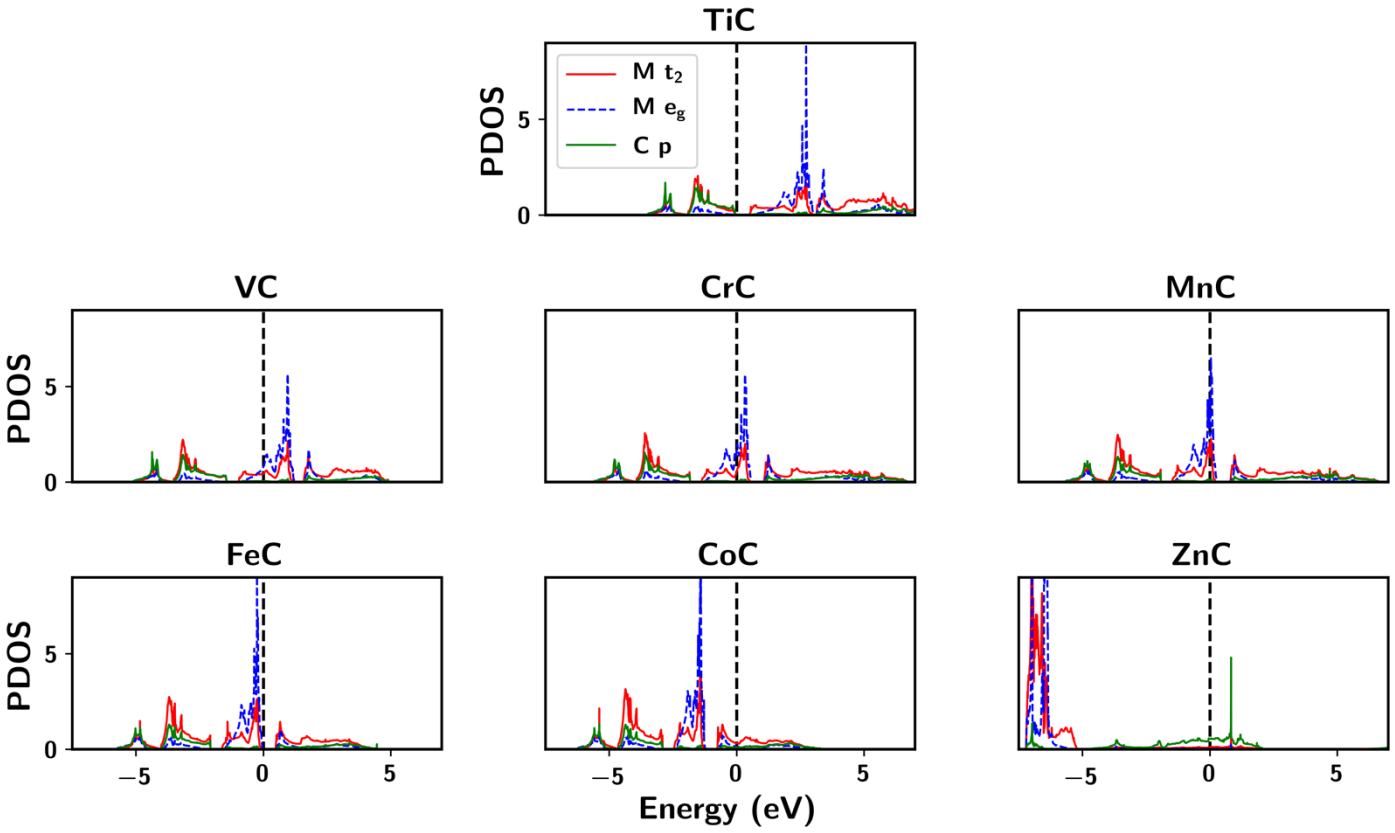

Figure S6: Projected density of states (PDOS) of stable 3*d* transitional metal carbides in zincblende (ZB) structures. Metal (M) 3*d* t_2 and e_g densities, as well as C *p* densities, are shown.

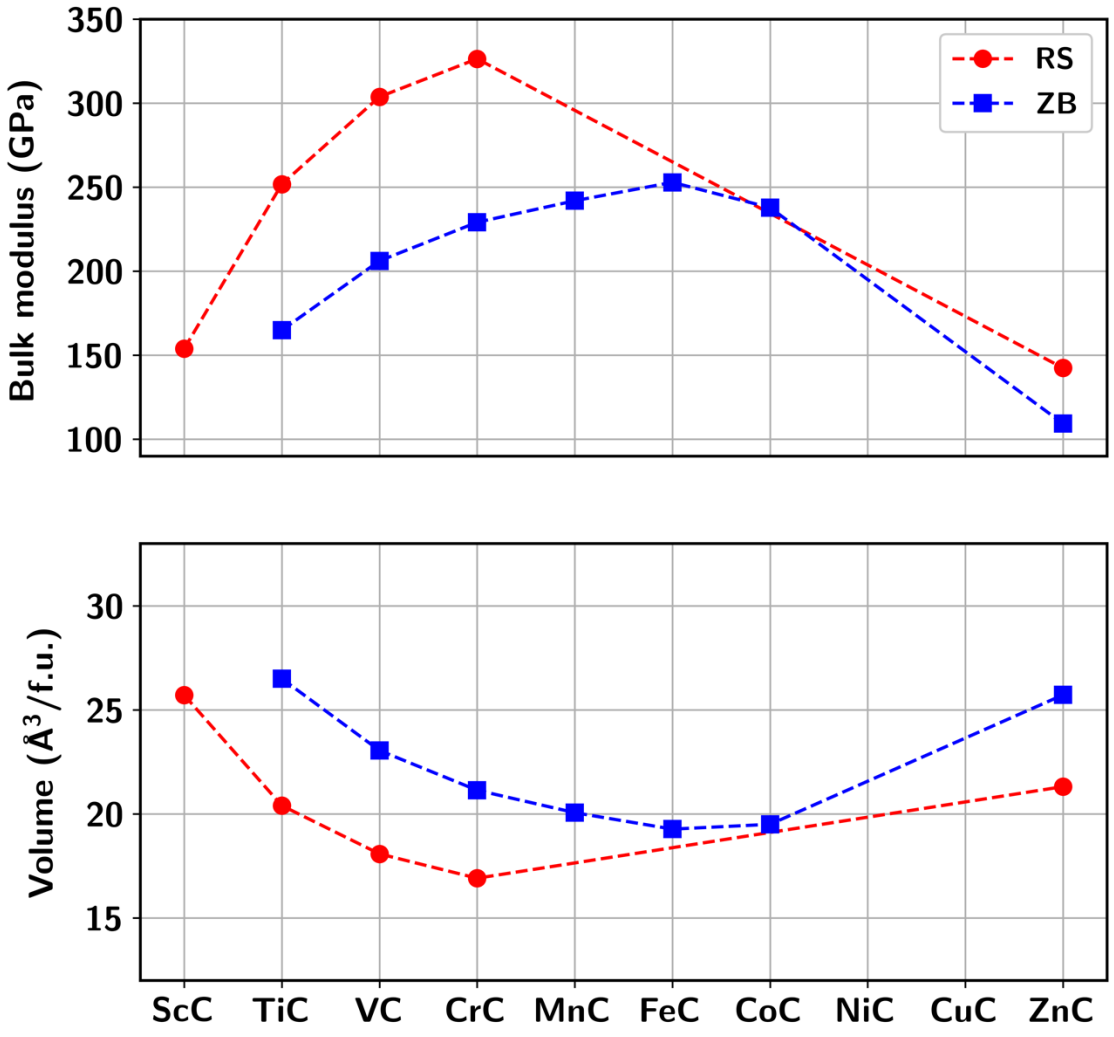

Figure S7: Plot showing anti-correlation of calculated equilibrium cell volume (V) and bulk modulus (B) of 3d TMCs in rocksalt (RS) and zincblende (ZB) structures. Markers represent calculated values, whereas lines represent interpolations plotted to highlight general trends.

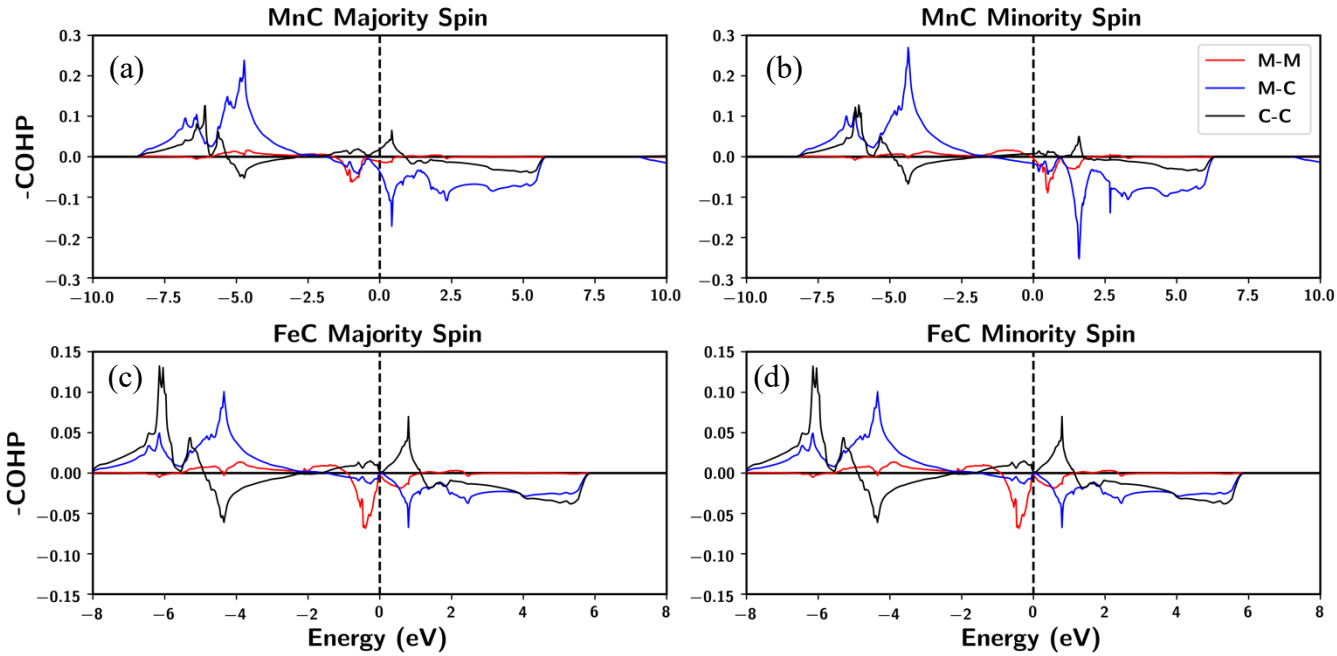

Figure S8: -Crystal Orbital Hamiltonian Populations (-COHP) of MnC (a and b) and FeC (c and d) individual bonding pairs, metal-carbon (M-C), metal-metal (M-M), and carbon-carbon (C-C), in rocksalt (RS) structures are shown. Positive values represent bonding states, whereas negative values represent anti-bonding states. The Fermi level is set to 0 eV.

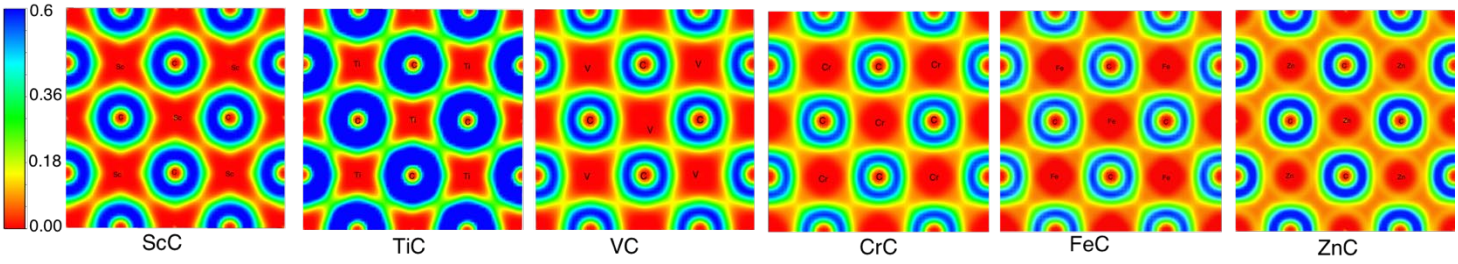

Figure S9: Electron localization function of stable/metastable 3d transition metal carbides in rocksalt (RS) structure.

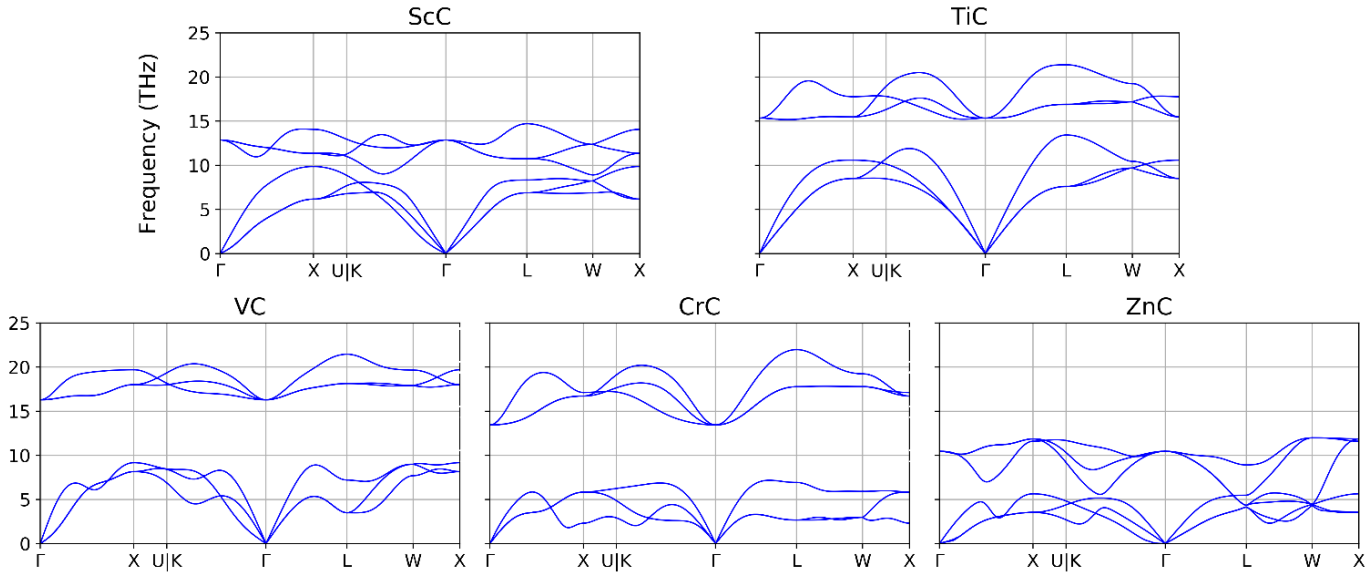

Figure S10: Phonon dispersion curves, calculated within the framework of the harmonic approximation, of the 3*d* TMCs which are found to be dynamically stable in rocksalt (RS) structure from Ref. [1], i.e., no imaginary frequencies exist, at zero temperature and zero applied pressure.

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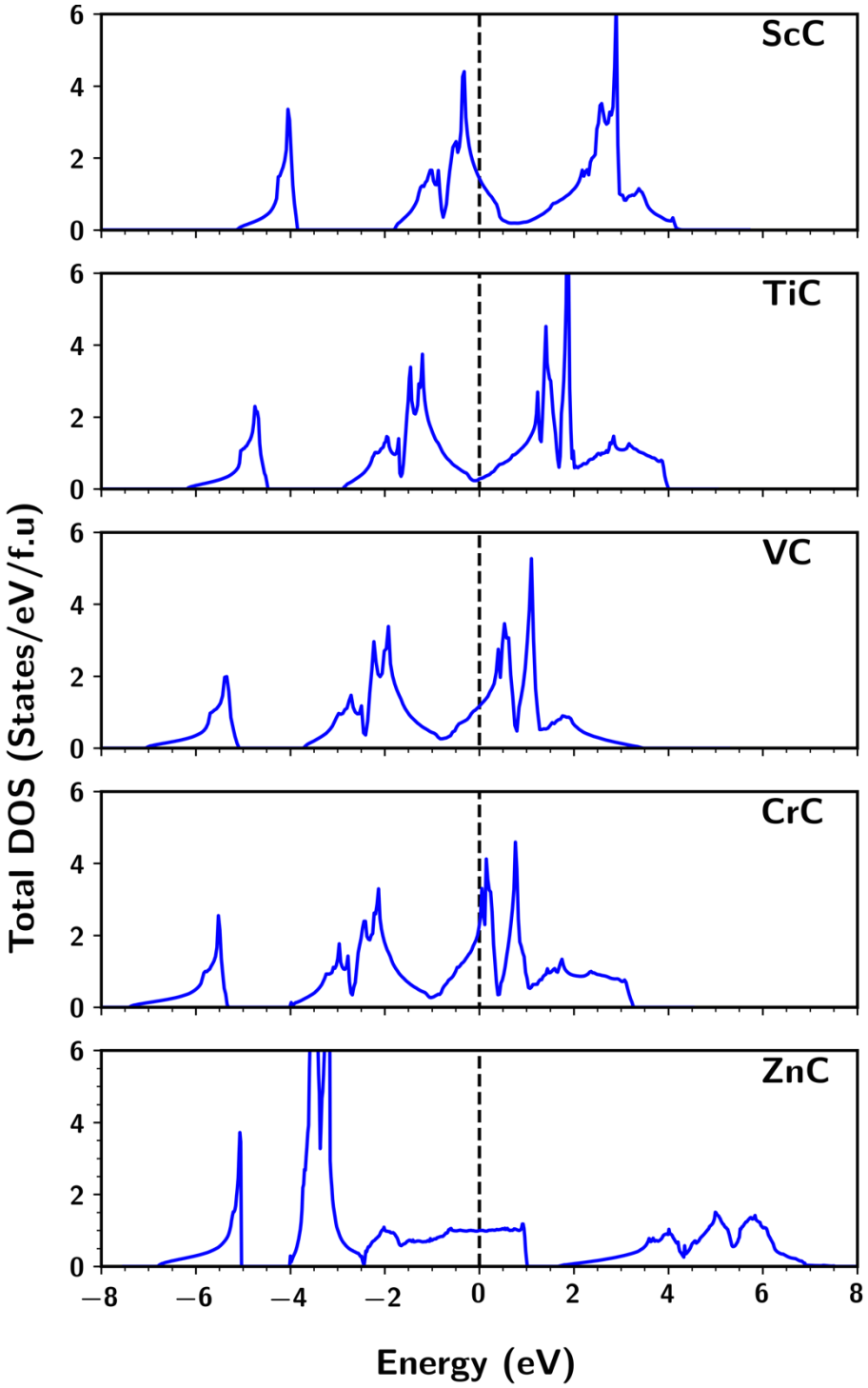

Figure S11: Total density of states (TDOS) per formula unit of stable 3d transition metal carbides in rocksalt (RS) structure. Fermi energy is set to 0 eV in each panel.

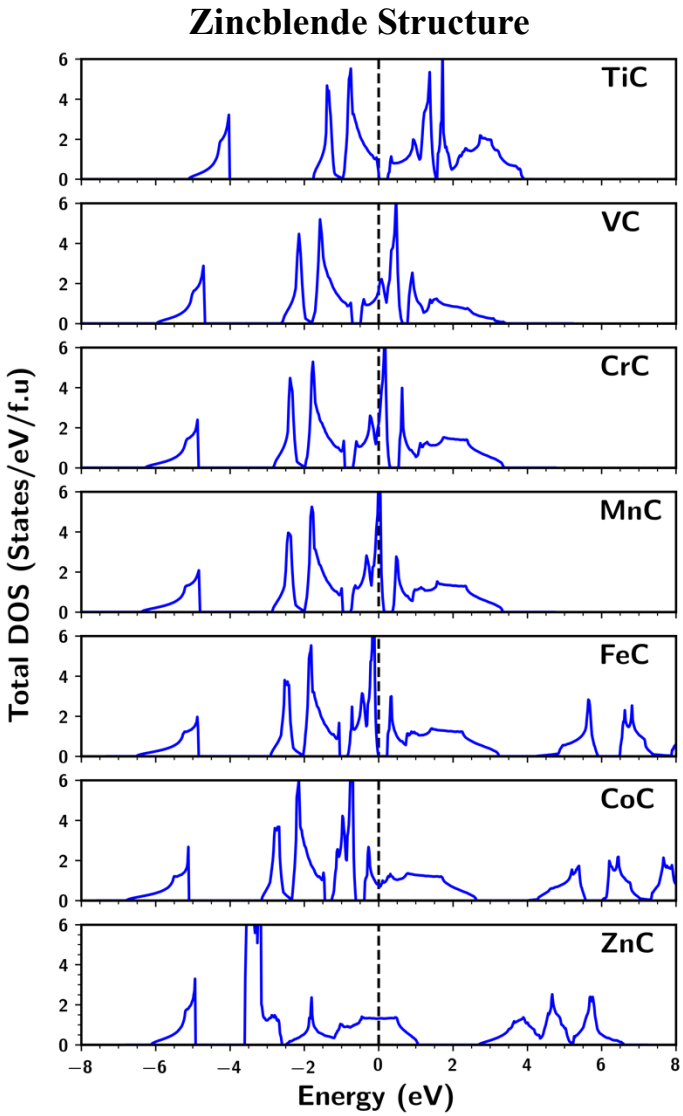

Figure S12: Total density of states (TDOS) per formula unit of the stable 3d transition metal carbides in zincblende structure. Fermi energy is set to zero in each panel.

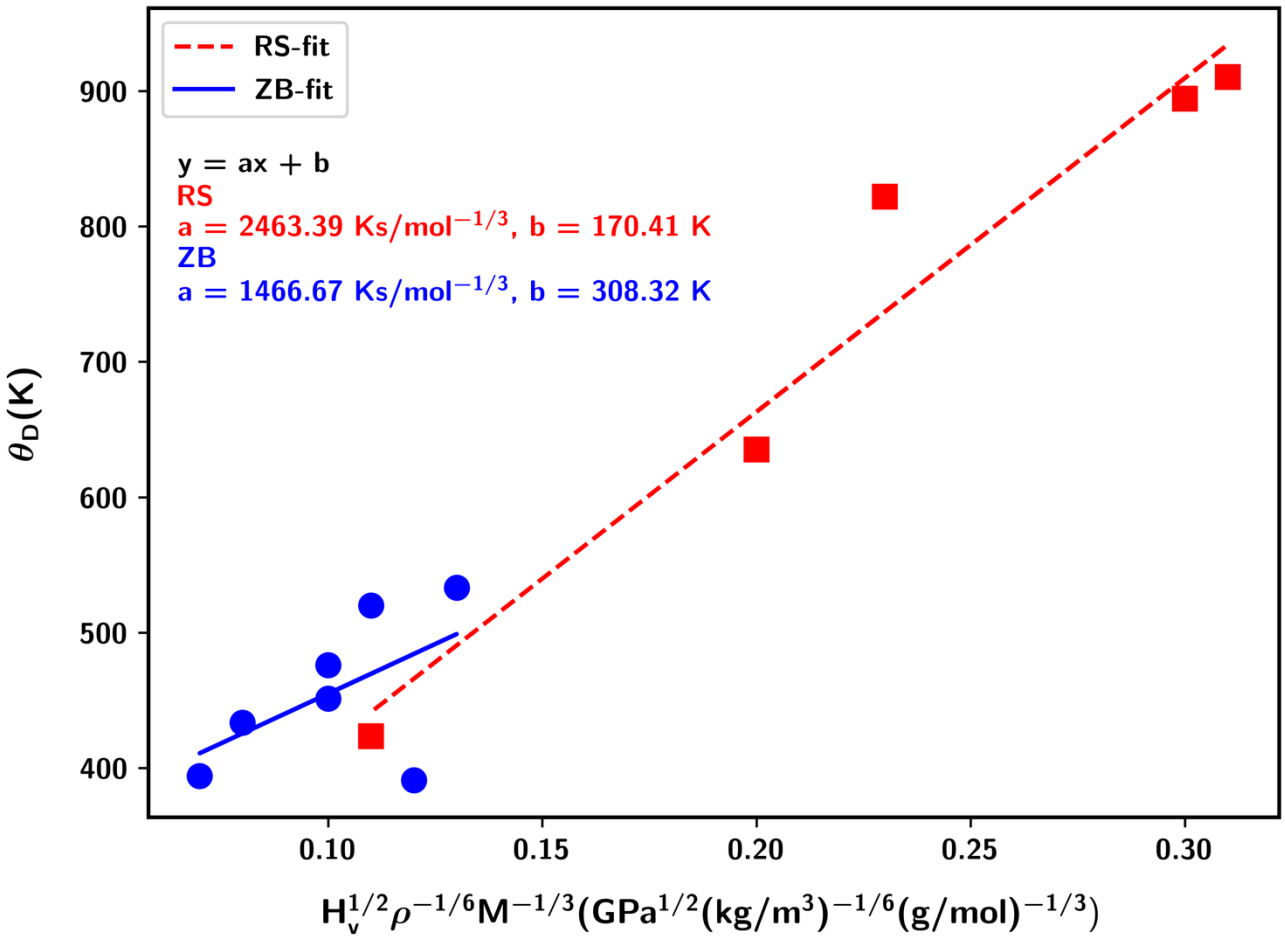

Figure S13: Computed Debye temperature (θ_D) versus Vickers hardness (H_{VA}) of stable 3d TMCs in rocksalt (RS) and zincblende (ZB) structures. Linear fits to the data for RS (dashed line) and ZB (solid line) and their fitting coefficients are also displayed.

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