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Prediction of super hardness in transition metal hexa-nitrides from density functional theory computations

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Table S1: Various interatomic distances in h-MN_6, where "S" denotes both mechanically and vibrationally stable material, "MS" denotes mechanically stable but vibrationally unstable material, "U" denotes unstable material in both ways. "p" denotes first nearest neighbor length from M to N in the first two opposite rings, "q" denotes second nearest neighbor length from M to N in the first two opposite rings, "r" denotes first nearest neighbor length from M to N in the second two opposite rings, "s" denotes distance between two M atoms in the same layer when viewed perpendicular to a-direction towards b-c plane, "t" denotes distance between two M atoms between two layers when viewed perpendicular to a-direction towards b-c plane, "u" denotes distance between two M atoms in the same layer when viewed perpendicular to b-direction towards a-c plane, and "v" denotes distance between two M atoms between two layers when viewed perpendicular to b-direction towards a-c plane.

D-block	Stability	Transition Metal (M)	Interatomic Distances (Å)								Coordination Number
			N-N	p	q	r	s	t	u	v	
5d	MS	Hf	1.43	2.52	3.05	2.39	3.98	3.98	3.98	4.89	6
	S	Ta	1.46	2.36	2.99	2.36	3.92	3.92	3.92	3.92	12
	S	W	1.46	2.31	2.93	2.32	3.87	3.87	3.87	3.87	12
	U	Re	1.46	2.31	2.95	2.35	3.89	3.89	3.89	4.71	12
	U	Os	1.45	2.13	2.78	2.93	4.38	4.38	4.38	5.02	6
	S	Ir	1.35	4.03	4.16	2.08	3.98	3.98	3.98	3.98	6
	MS	Pt	1.46	2.1	2.72	5.51	4.76	5.31	4.76	5.31	6
	MS	Au	1.34	4.3	4.33	2.34	4.23	4.23	4.23	4.23	6
	U	Hg	1.34	4.17	4.22	2.50	4.35	4.35	4.35	4.35	6
4d	MS	Y	1.36	3.35	3.51	2.44	4.16	4.16	4.16	5.53	6
	MS	Zr	1.37	4.18	4.37	2.24	4.19	4.19	4.19	4.19	6
	MS	Nb	1.45	2.37	2.98	2.37	3.92	3.92	3.92	4.77	12
	S	Mo	1.45	2.31	2.93	2.34	3.88	3.88	3.88	4.69	12
	U	Tc	1.45	2.22	2.86	2.53	4.03	4.03	4.03	4.77	6
	U	Ru	1.44	2.11	2.76	5.48	4.56	5.16	4.56	5.16	6
	MS	Rh	1.44	2.08	2.73	5.49	4.69	5.26	4.69	5.26	6

	MS	Pd	1.45	2.11	2.75	5.56	4.73	5.31	4.73	5.31	6
	MS	Ag	1.34	4.12	4.14	2.44	4.28	4.28	4.28	4.28	6
	MS	Cd	1.34	3.65	3.68	2.41	4.14	4.14	4.14	4.14	6
3d	MS	Sc	1.36	4.19	4.31	2.25	4.18	4.18	4.18	4.18	6
	MS	Ti	1.43	2.42	2.99	2.36	3.92	3.92	3.92	3.92	12
	S	V	1.36	3.91	4.12	2.04	3.94	3.94	3.94	3.94	6
	MS	Cr	1.46, 1.41	2.34	3.18	1.98	5.09	7.26	5.09	7.26	10
	S	Mn	1.35	3.8	3.98	1.97	3.84	3.84	3.84	3.84	6
	U	Fe	1.44	2.01	2.65	5.31	4.65	5.17	4.65	5.17	6
	S	Co	1.34	3.94	4.04	2.01	3.87	3.87	3.87	3.87	6
	U	Ni	1.45	1.95	2.59	5.7	5.42	5.84	5.42	5.84	6
	U	Cu	1.45	2.03	2.67	5.8	5.32	5.8	5.32	5.8	6
	S	Zn	1.35	4.1	4.1	2.21	4.07	4.07	4.07	4.07	6

Table S2: Lattice constants (a, c), formation energy (E_{form}) and elastic tensor (C_{ij}) for vibrationally unstable h-MN_6 compounds. S and U refer to mechanically stable and unstable materials respectively.

Group	M	a (Å)	c (Å)	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	E_{form} (eV)	Mechanical Stability
3	Sc	5.54	8.06	306	157	108	202	26	1.34	S
4	Ti	6.20	4.77	365	110	177	423	118	6.39	S
6	Cr	6.29	4.43	254	39	119	541	241	9.78	S
8	Fe	7.72	3.94	100	38	76	370	-8	9.74	U
10	Ni	9.12	3.79	-2080	-2117	-1782	-1237	20	9.21	U
11	Cu	8.92	3.99	-1903	-1949	-1785	-1434	24	10.31	U
3	Y	6.21	6.31	363	152	143	143	49	2.80	S
4	Zr	5.55	8.11	402	171	152	219	80	1.54	S
5	Nb	6.23	4.70	632	111	154	621	295	5.63	S
7	Tc	6.50	4.40	159	210	130	730	226	9.95	U
8	Ru	7.51	4.19	48	68	64	567	83	10.80	U
9	Rh	7.77	4.11	57	-8	25	464	47	10.39	S
10	Pd	7.83	4.16	136	67	73	349	30	10.70	S
11	Ag	5.88	7.82	153	82	70	117	36	6.75	S
12	Cd	5.99	6.83	258	128	103	201	60	6.40	S
4	Hf	6.29	4.92	427	206	201	336	74	4.48	S
7	Re	6.19	4.60	-44	-14	511	300	-265	10.35	U
8	Os	7.19	4.23	46	140	97	716	131	11.42	U
10	Pt	7.89	4.10	131	64	65	473	27	10.51	S
11	Au	5.59	8.20	160	128	82	143	16	7.64	S
12	Hg	5.98	7.95	92	111	59	93	30	7.36	U

Table S3: Bulk modulus (B), shear modulus (G), Young's modulus (E), Vickers hardness (H_v), Pugh's ratio (k), Poisson's ratio (ν), and Debye temperature (θ_D) for vibrationally unstable but mechanically stable h-MN_6 compounds.

Group	M	B (GPa)	G (GPa)	E (GPa)	H_v (GPa)	k	ν	θ_D (K)
3	Sc	167	48	133	4	0.29	0.37	622
4	Ti	228	118	302	13	0.52	0.28	902
6	Cr	161	156	354	32	0.97	0.13	998
3	Y	168	61	163	5	0.36	0.34	598
4	Zr	208	88	232	8	0.42	0.31	716
5	Nb	302	267	618	42	0.88	0.16	1155
9	Rh	49	51	113	15	1.03	0.12	513
10	Pd	108	41	110	4	0.38	0.33	473
11	Ag	95	35	93	4	0.37	0.34	436
12	Cd	152	62	164	6	0.41	0.32	567
4	Hf	265	89	240	6	0.34	0.35	566
10	Pt	110	44	117	5	0.40	0.32	404
11	Au	115	20	56	1	0.17	0.42	271

Table S4: Total magnetic moment found in the atomic orbitals in five h-MN_6.

Material	Magnetic Moment							
	Transition Metal				Nitrogen			Total in the Unit Cell
	s-orbital	p-orbital	d-orbital	Total	s-orbital	p-orbital	Total	
CoN_6	0.003	0.006	0.786	0.795	0.005	0.020	0.025	2.835
FeN_6	0.027	0.012	1.766	1.805	0.001	-0.037	-0.036	4.767
MnN_6	0.000	0.000	0.155	0.155	0.000	0.000	0.000	0.465
ScN_6	-0.001	0.002	0.014	0.015	0.002	0.043	0.045	0.855
VN_6	0.013	0.013	1.334	1.360	-0.004	-0.060	-0.064	2.928

Table S5: Lattice constant (a), elastic constants (C_{ij}), bulk modulus (B), shear modulus (G), Young's modulus (E), Vickers hardness (H_v), Pugh's ratio (k), Poisson's ratio (ν), formation energy (E_{form}) and Debye temperature (θ_D) for c-WN_6.

c-WN_6 properties	
a (Å)	5.20, 5.19[a]
C_{11} (GPa)	697, 687[a]
C_{12} (GPa)	39, 40[a]
C_{44} (GPa)	68, 50[a]
B (GPa)	258, 255.7[a]
G (GPa)	136, 117.3[a]
E (GPa)	347, 682.7[a]
H_v (GPa)	14, 10.1[a]
k	0.53
ν	0.28
E_{form}(eV)	1.50
θ_D (K)	713

[a]Theoretical Ref. [1]

Figure S1: Phonon DOS for both vibrationally and mechanically stable h-MN_6 materials in the order of increasing hardness from top to bottom.

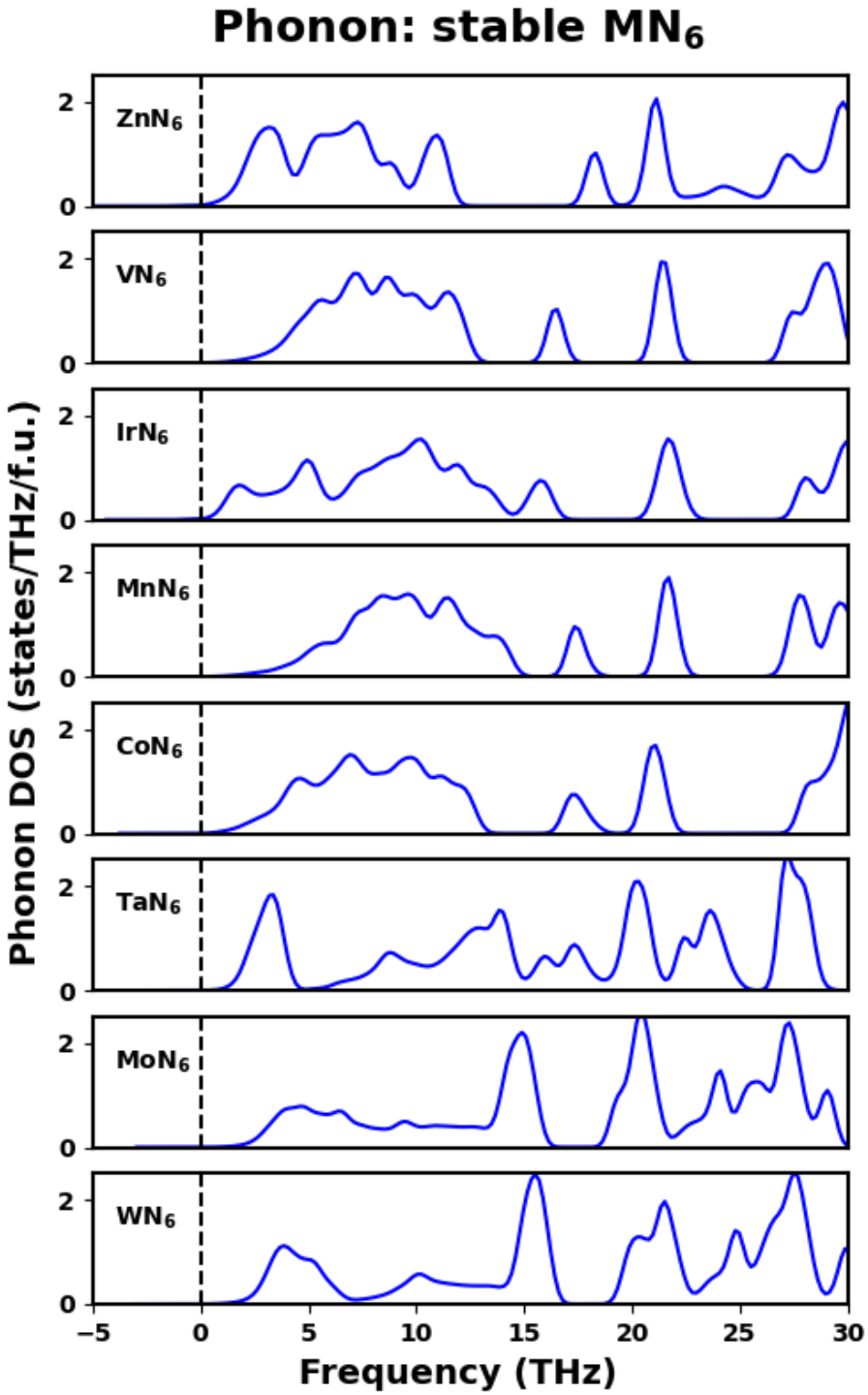


Figure S2: Phonon DOS for only mechanically stable h-MN_6 materials in the order of increasing hardness from top to bottom.

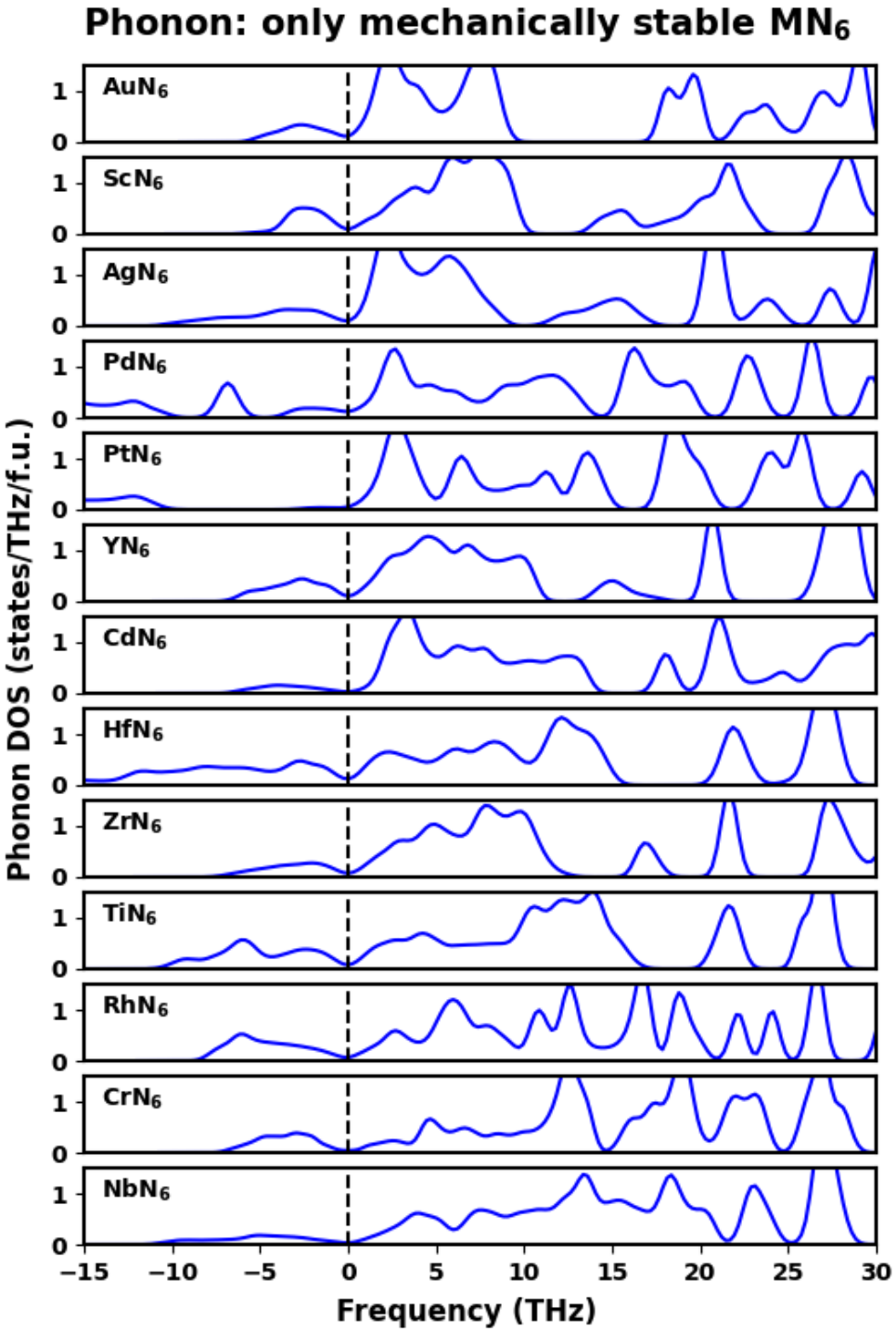


Figure S3: Phonon DOS for both vibrationally and mechanically unstable h-MN_6 materials.

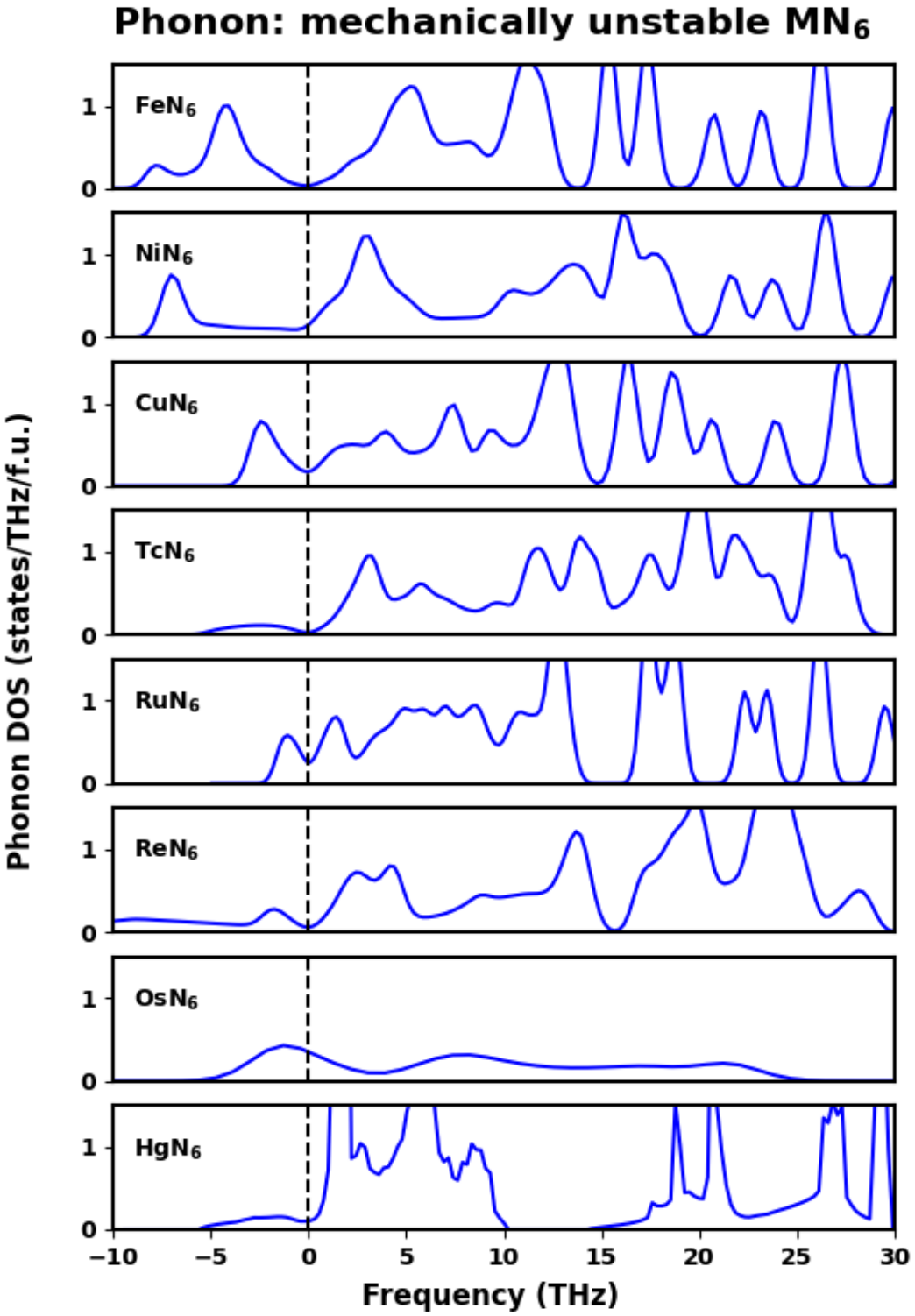


Figure S4: Debye temperature as a function of hardness for both vibrationally and mechanically stable h-MN_6.

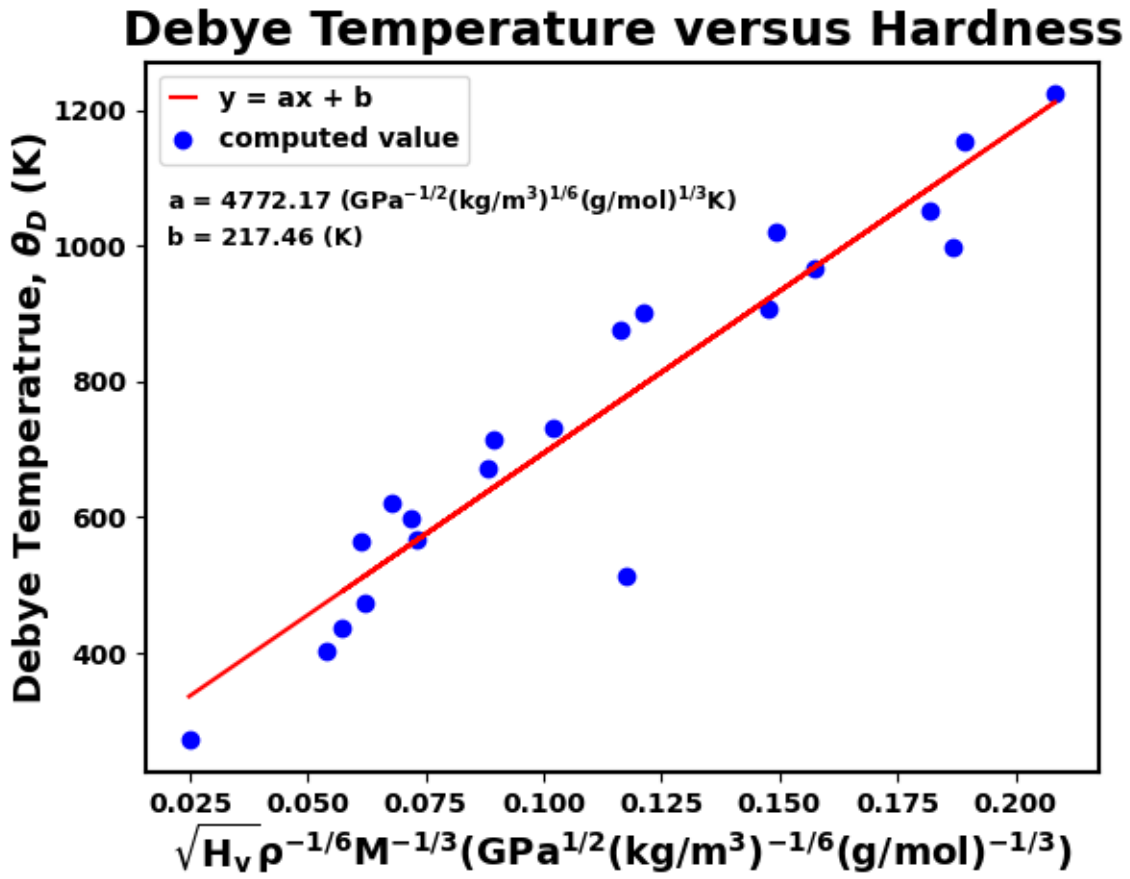


Figure S5: Electronic LDOS for both vibrationally and mechanically stable h-MN_6 materials in increasing order of hardness from top to bottom. The Fermi level is set at 0 eV.

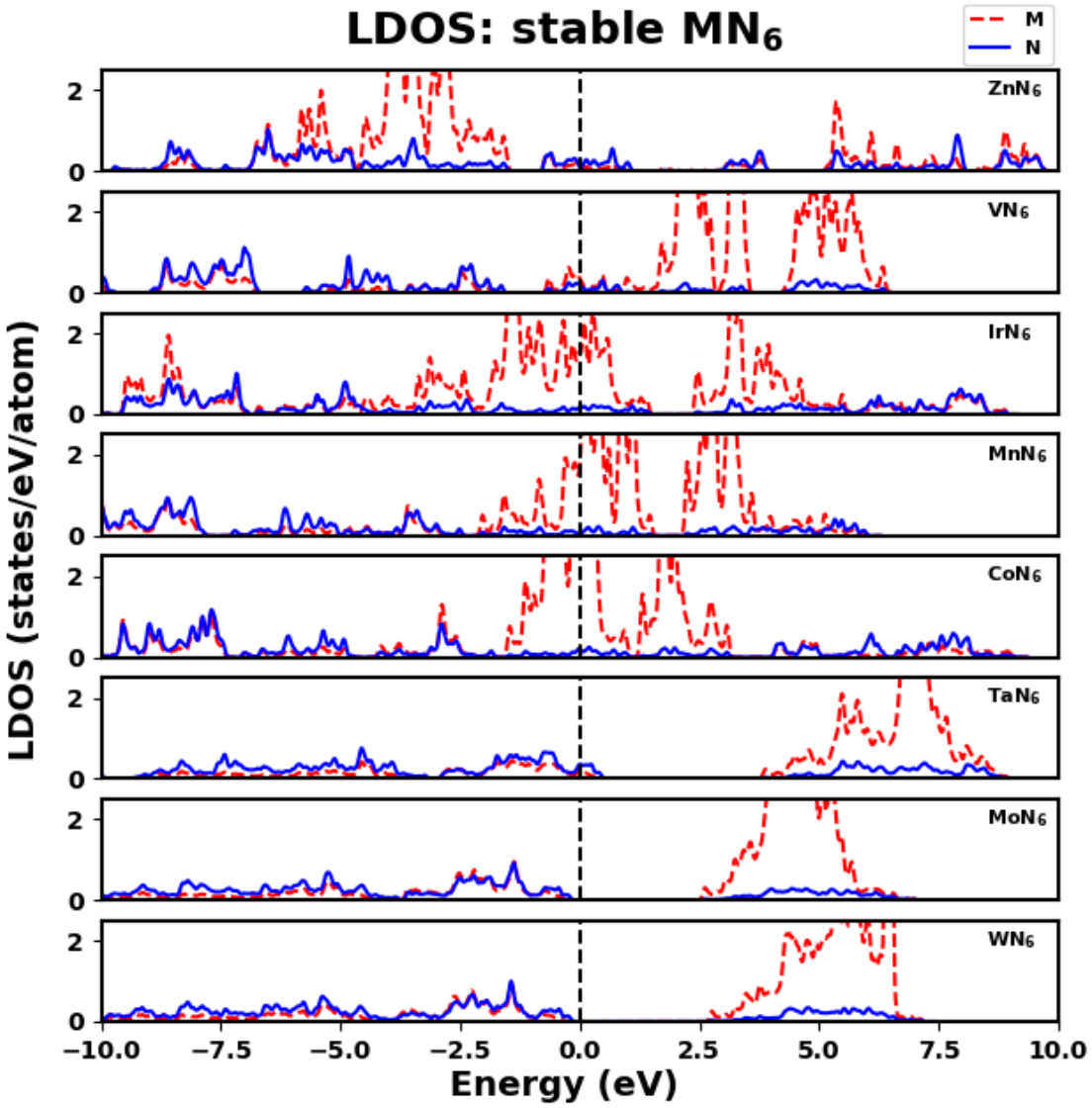


Figure S6: Electronic LDOS for only mechanically stable h-MN_6 material in increasing order of hardness from top to bottom. The Fermi level is set at 0 eV.

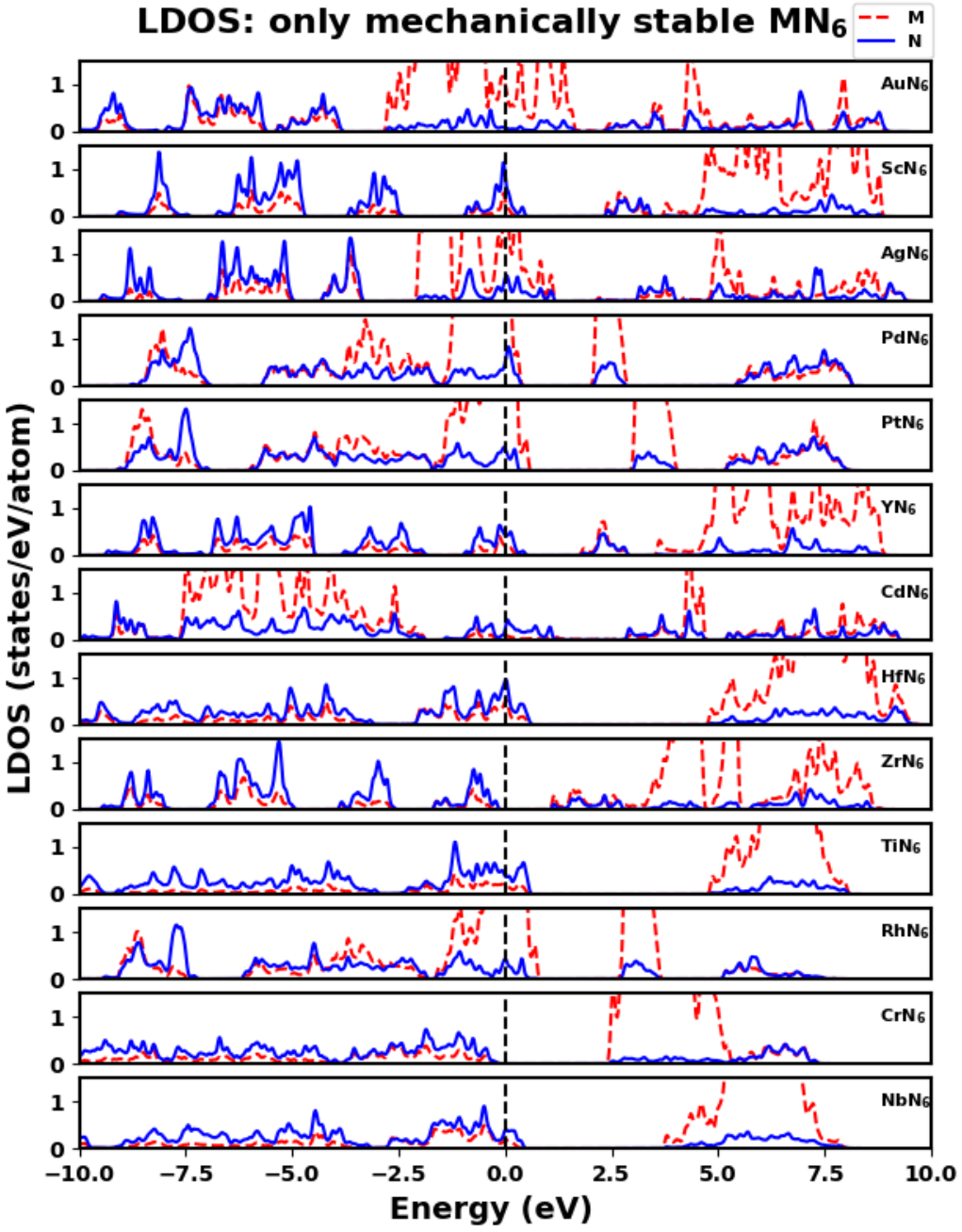


Figure S7: Electronic LDOS for both vibrationally and mechanically unstable h-MN_6 materials. The Fermi level is set at 0 eV.

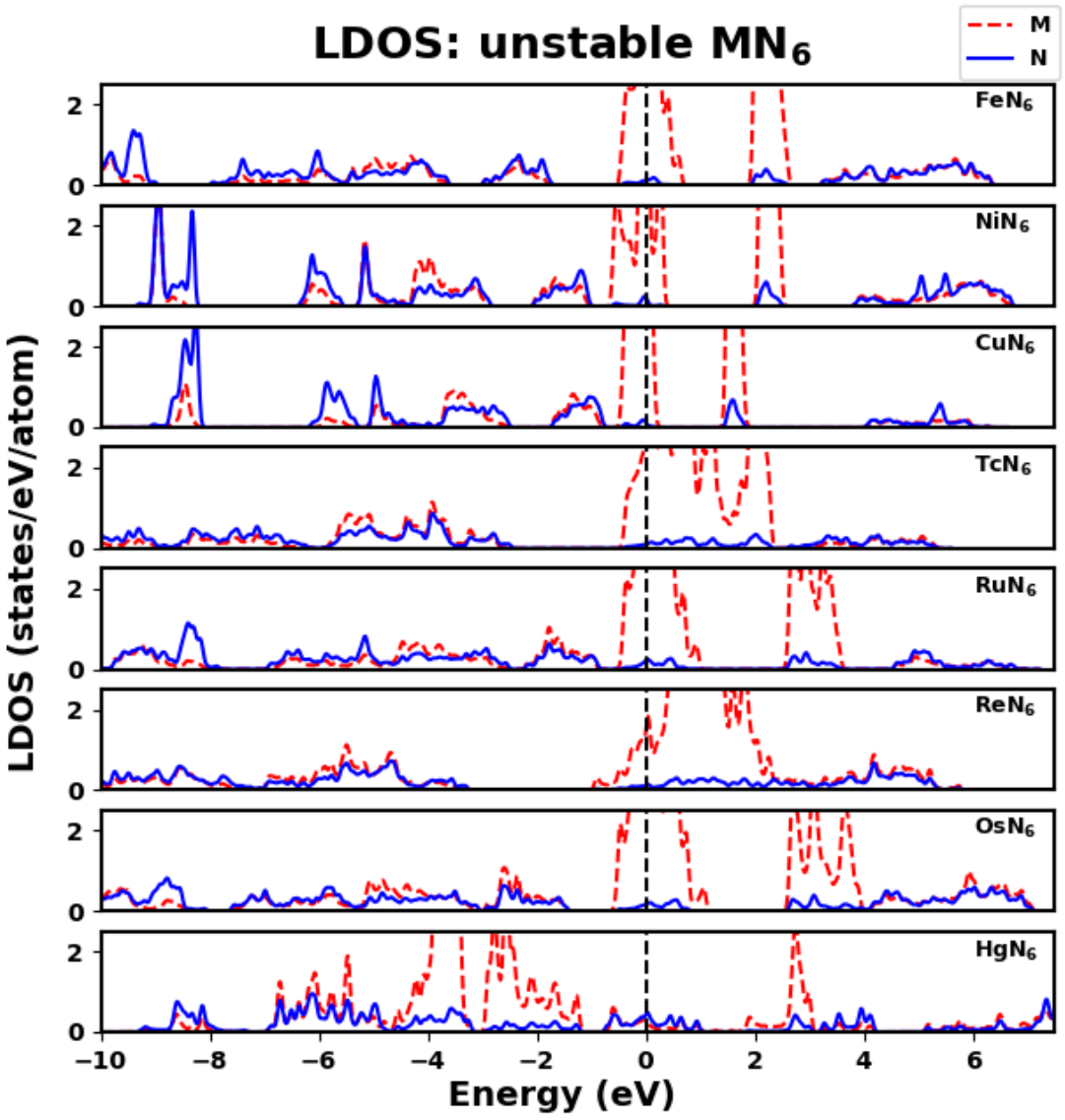


Figure S8: -pCOHP for both vibrationally and mechanically stable h-MN_6 materials in the order of increasing hardness from top to bottom. The Fermi level is set at 0 eV.

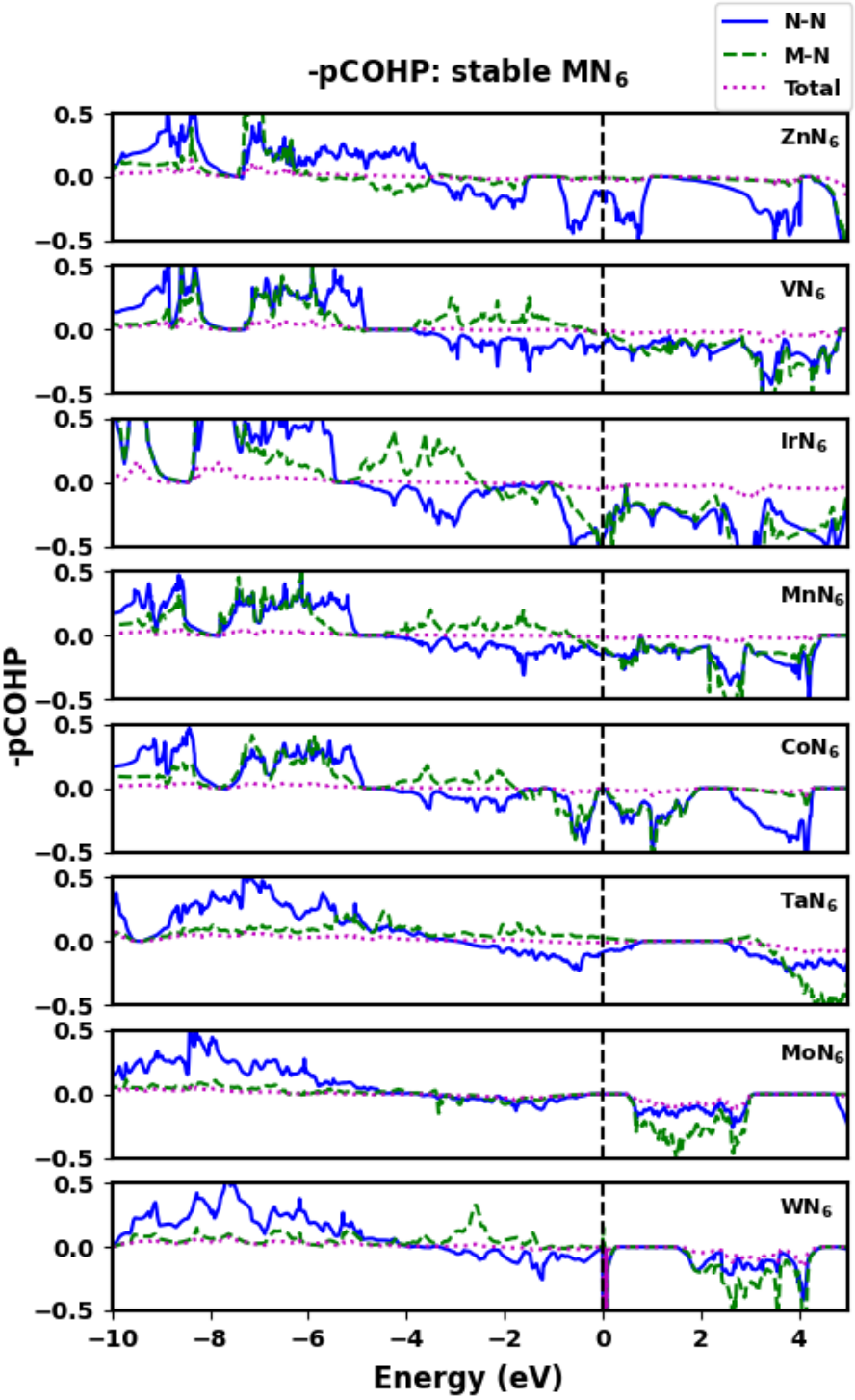


Figure S9: -pCOHP for only mechanically stable h-MN_6 materials in the order of increasing hardness from top to bottom. The Fermi level is set at 0 eV.

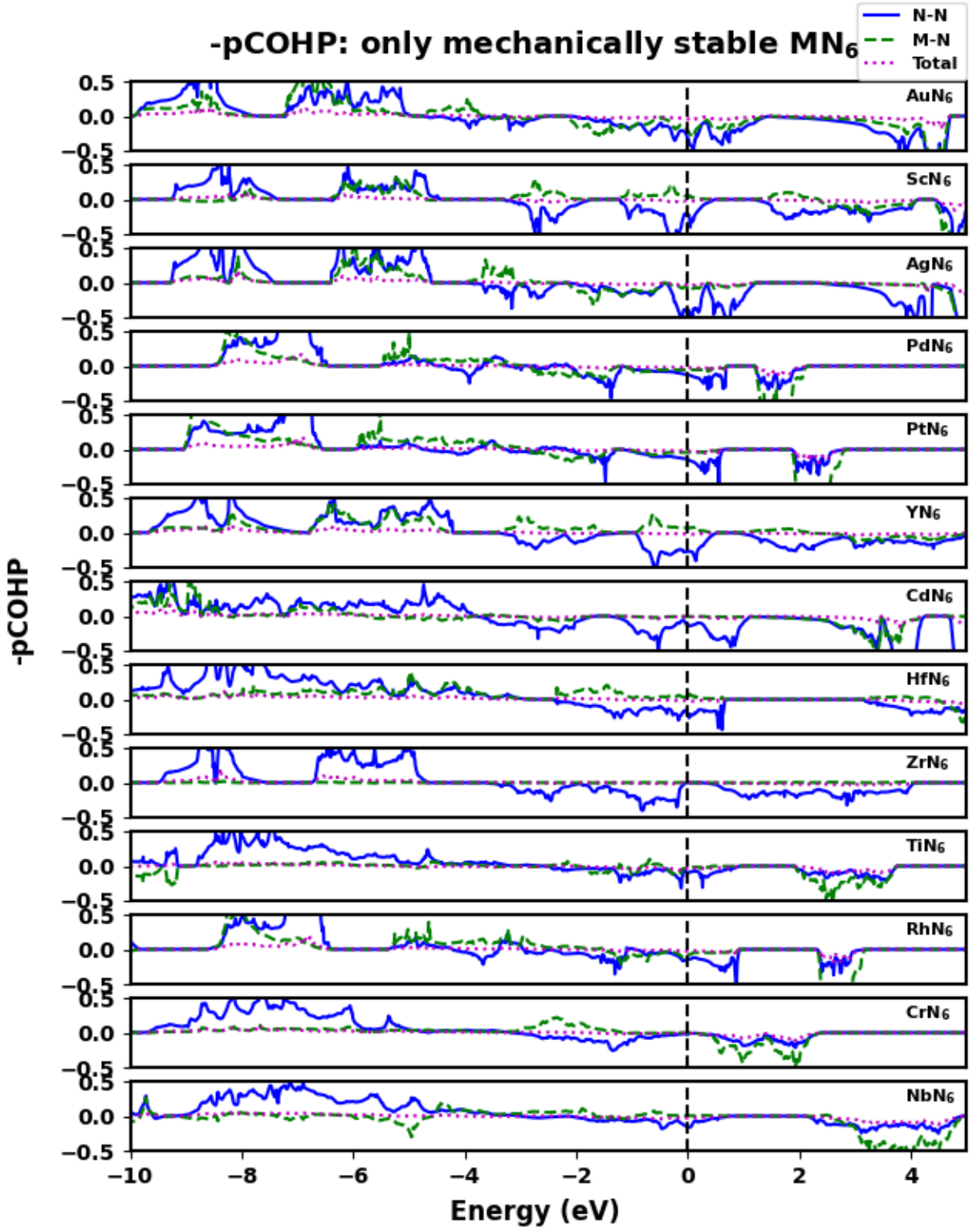


Figure S10: -pCOHP for both vibrationally and mechanically unstable h-MN_6 materials. The Fermi level is set at 0 eV.

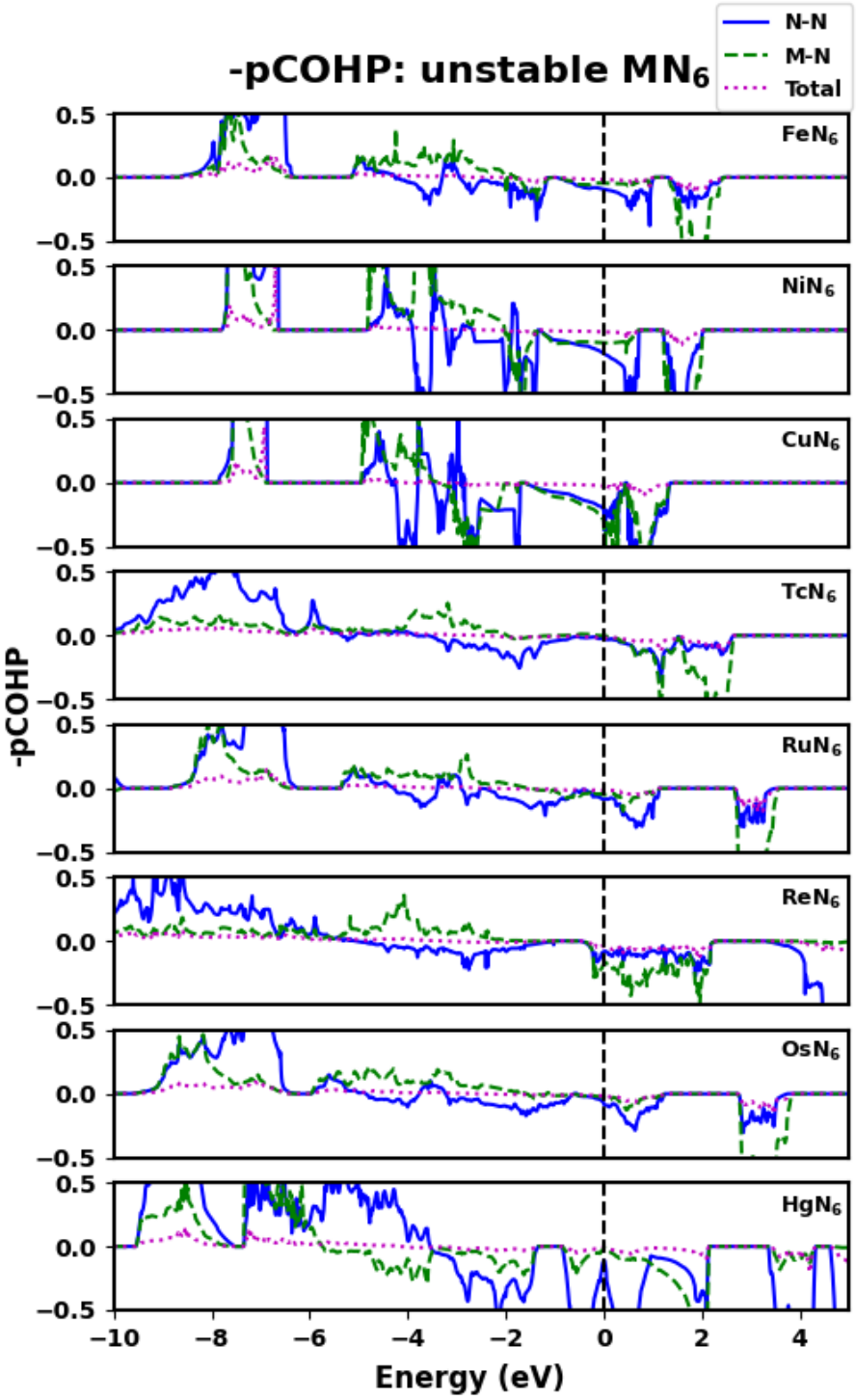


Figure S11-1: Electronic band structure for both vibrationally and mechanically stable h-MN_6 compounds. The Fermi level is set at 0 eV.

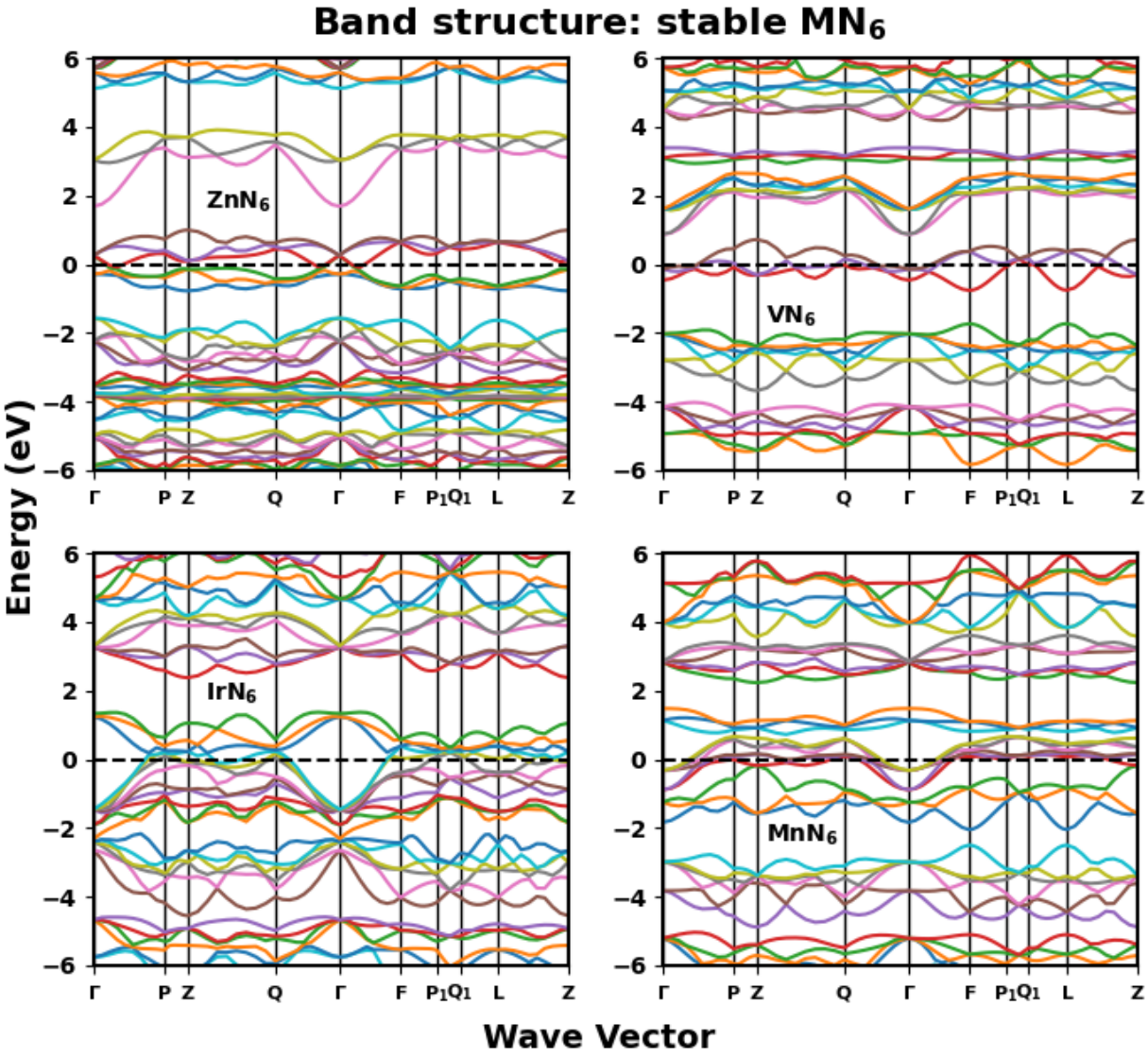


Figure S11-2: Electronic band structure for both vibrationally and mechanically stable h-MN_6 compounds. The Fermi level is set at 0 eV.

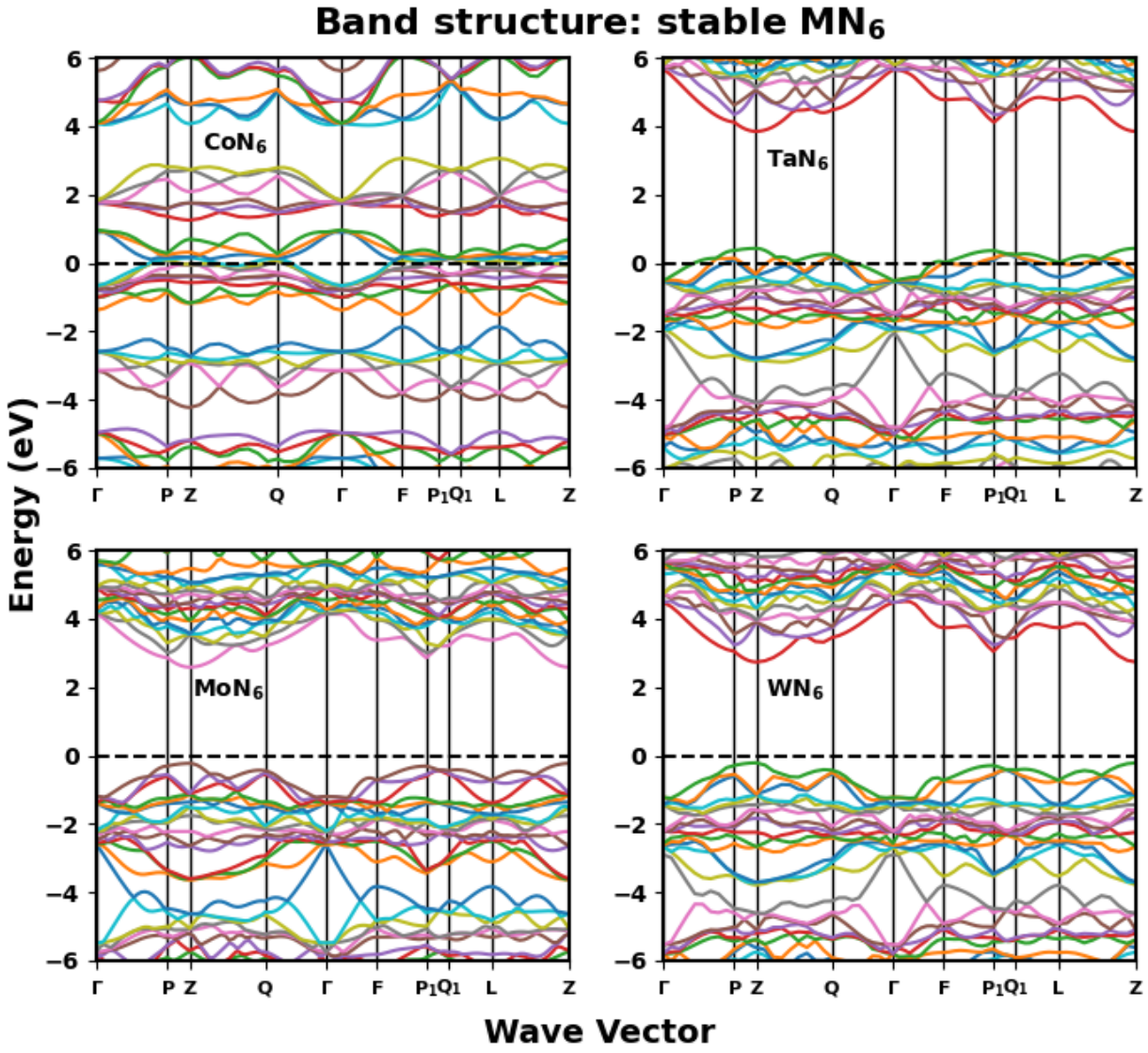


Figure S12-1: Electronic band structure for only mechanically stable h-MN_6 compounds. The Fermi level is set at 0 eV.

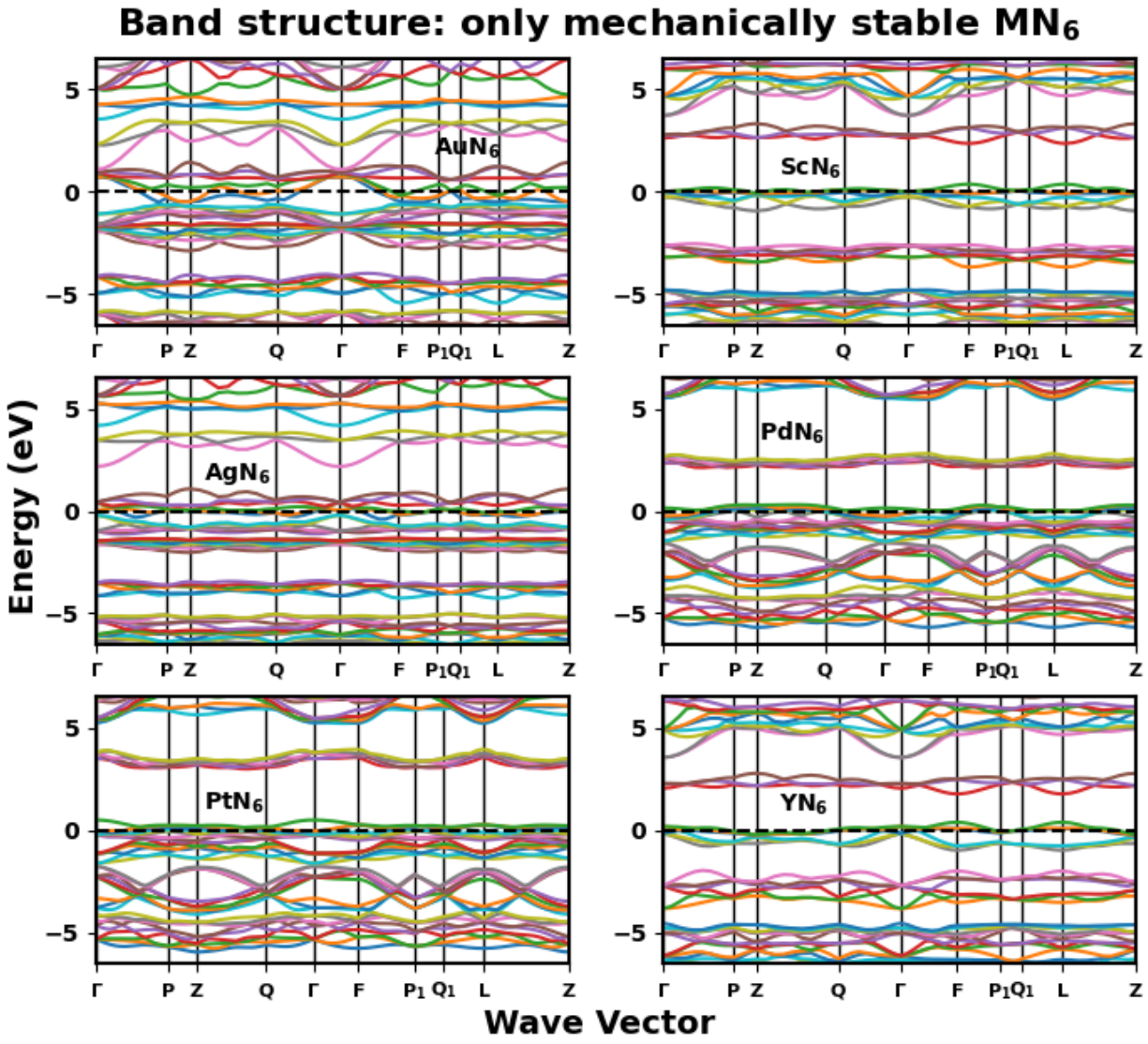


Figure S12-2: Electronic band structure for only mechanically stable h-MN_6 compounds. The Fermi level is set at 0 eV.

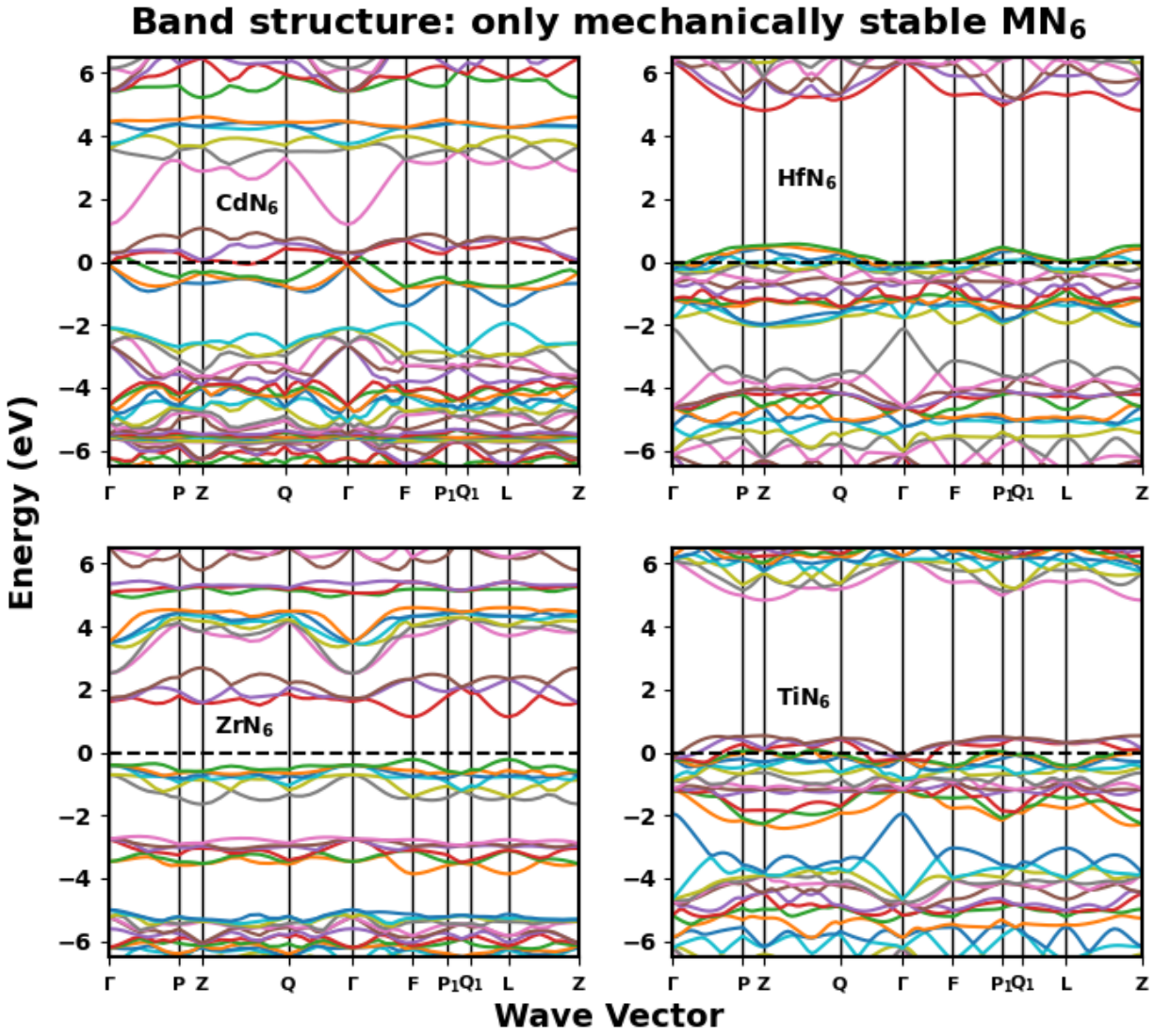


Figure S12-3: Electronic band structure for only mechanically stable h-MN_6 compounds. The Fermi level is set at 0 eV.

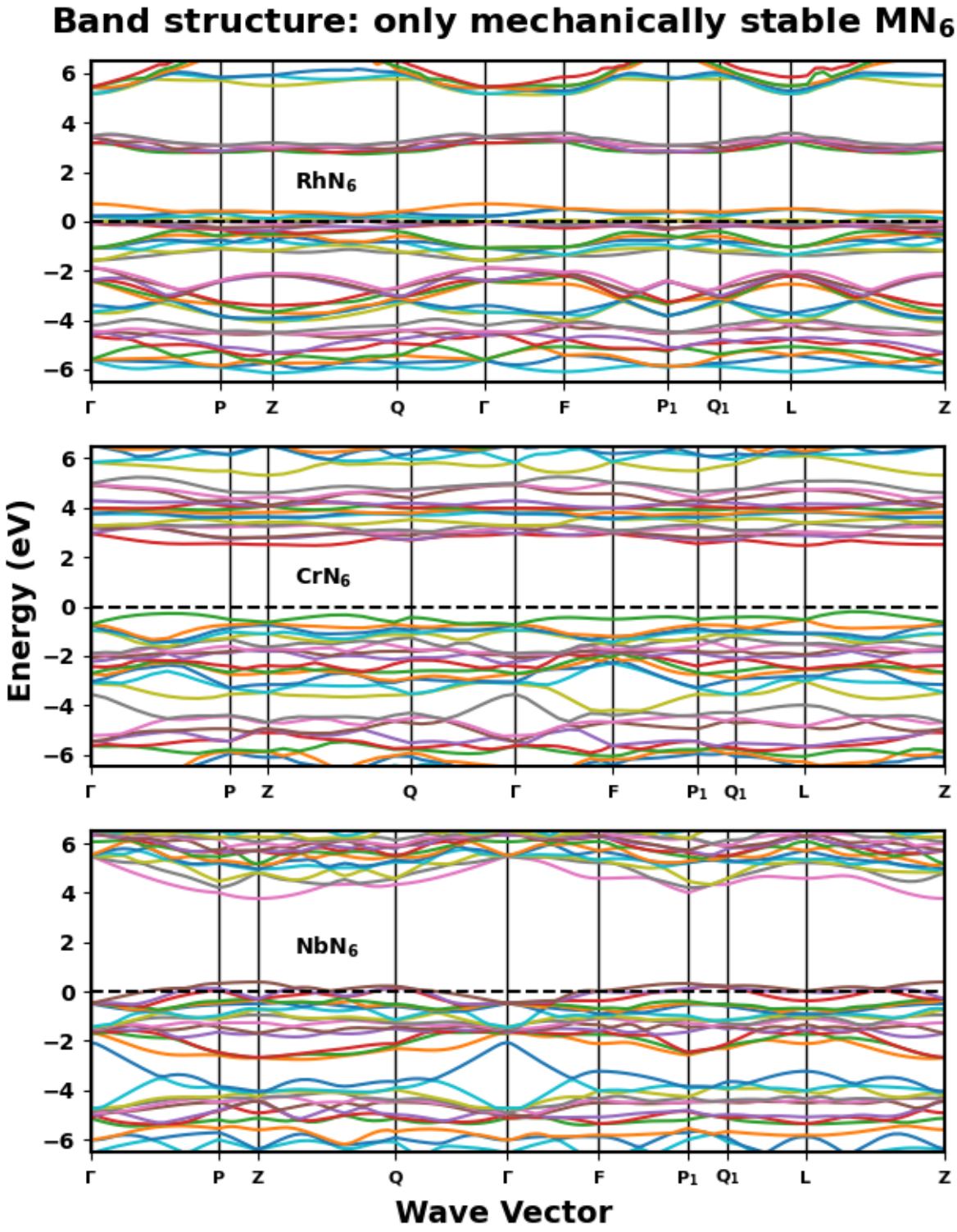


Figure S13-1: Electronic band structure for both vibrationally and mechanically unstable h-MN_6 compounds. Fermi level is set at 0 eV.

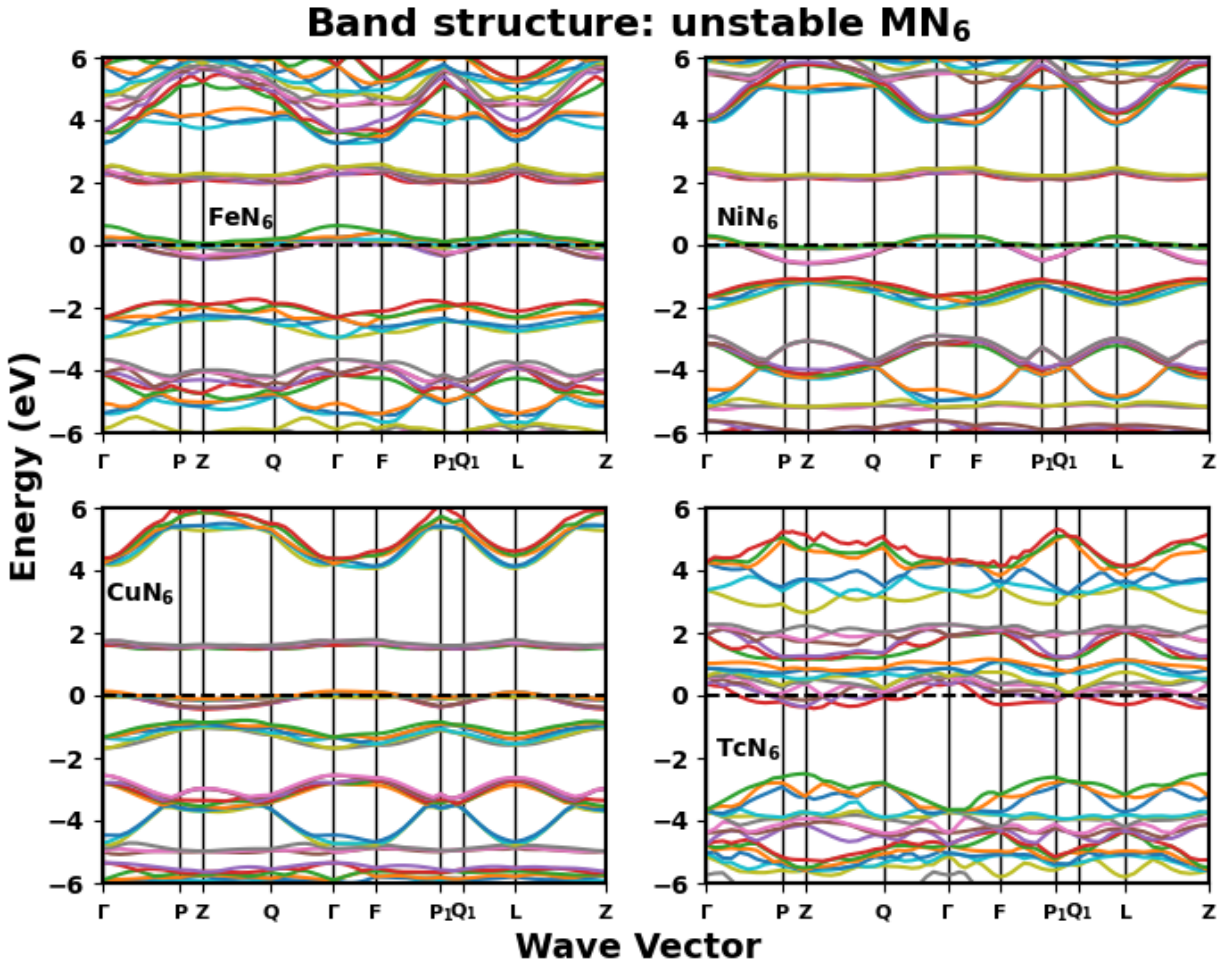


Figure S13-2: Electronic band structure for both vibrationally and mechanically unstable h-MN_6 compounds. Fermi level is set at 0 eV.

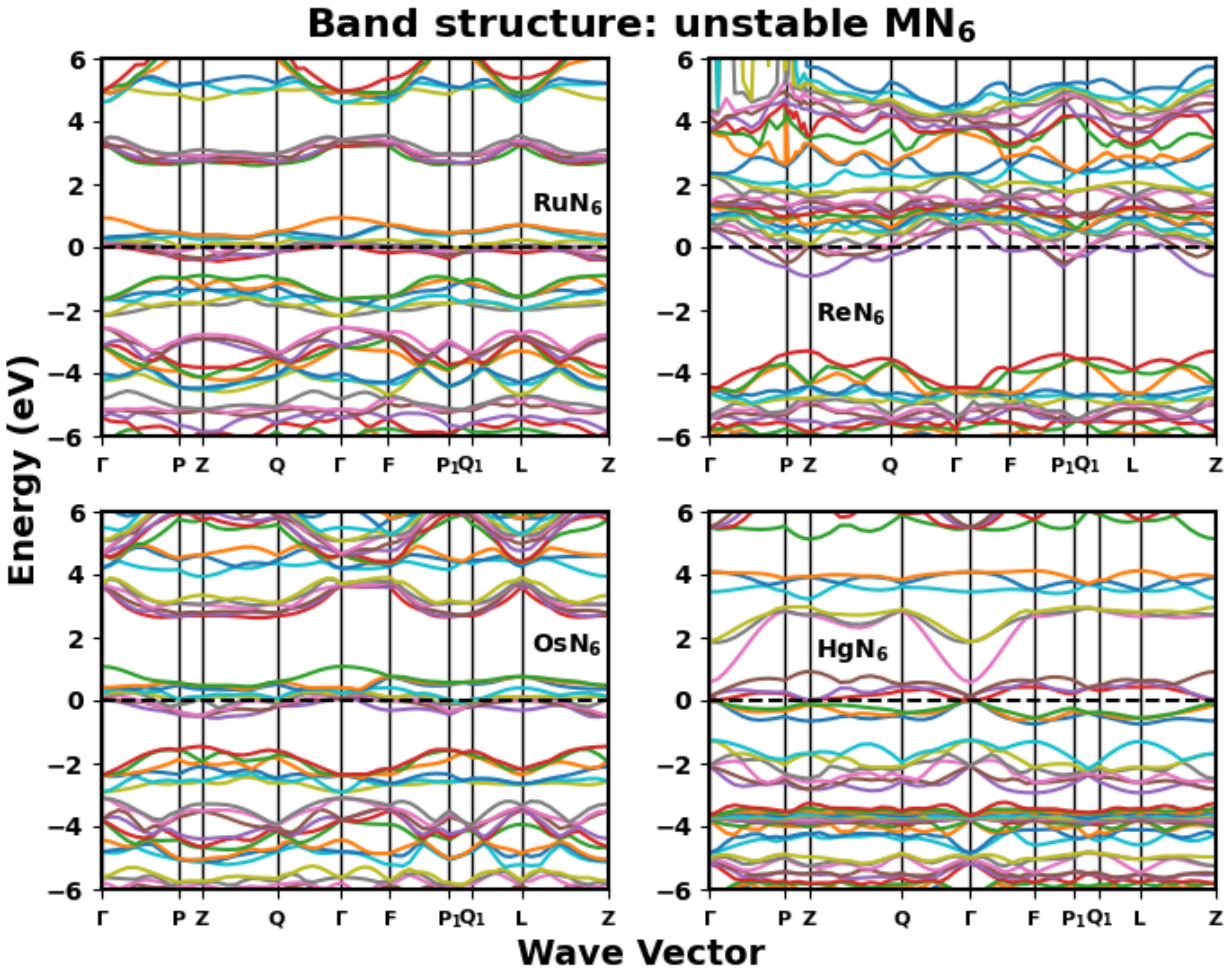


Figure S14: Phonon DOS per formula unit for h-WN_6 and c-WN_6 structures.

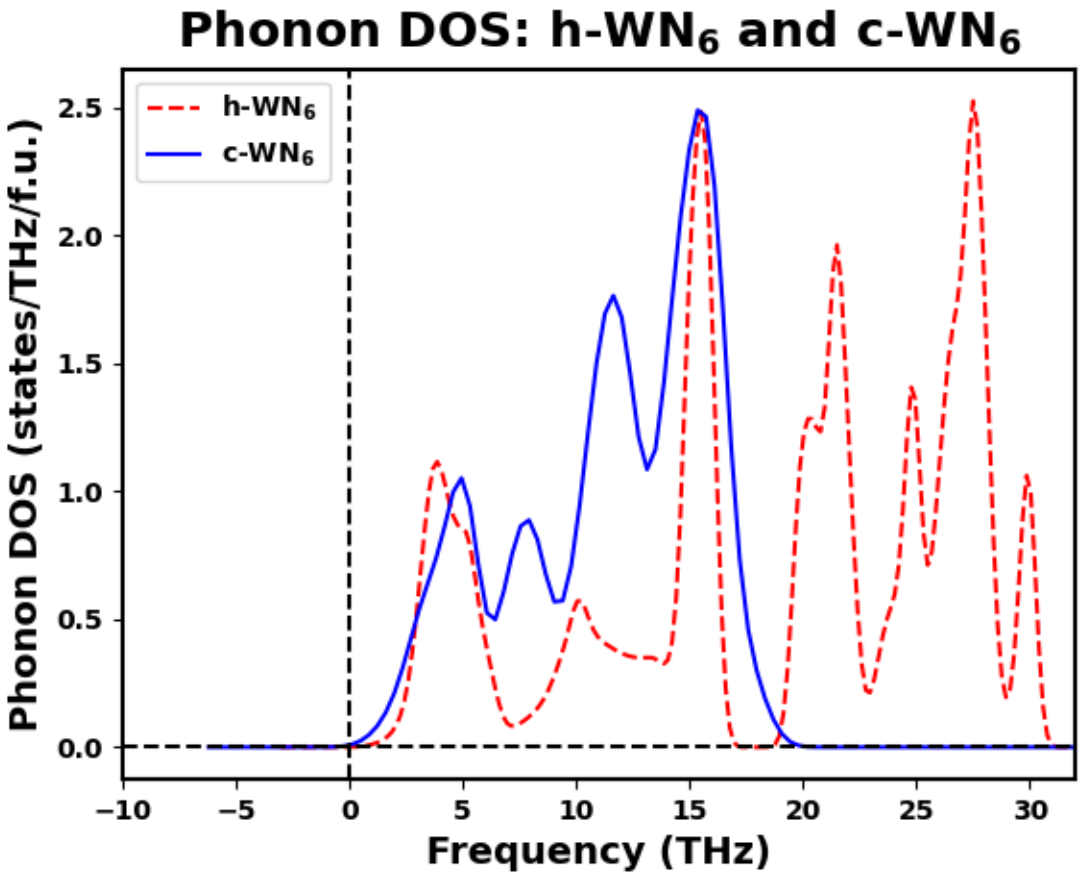


Figure S15: Electronic LDOS comparison of h-WN_6, h-ZnN_6, and c-WN_6 showing h-ZnN_6 and c-WN_6 have higher metallic density of states than nitrogen below the Fermi level. The Fermi level is set at 0 eV.

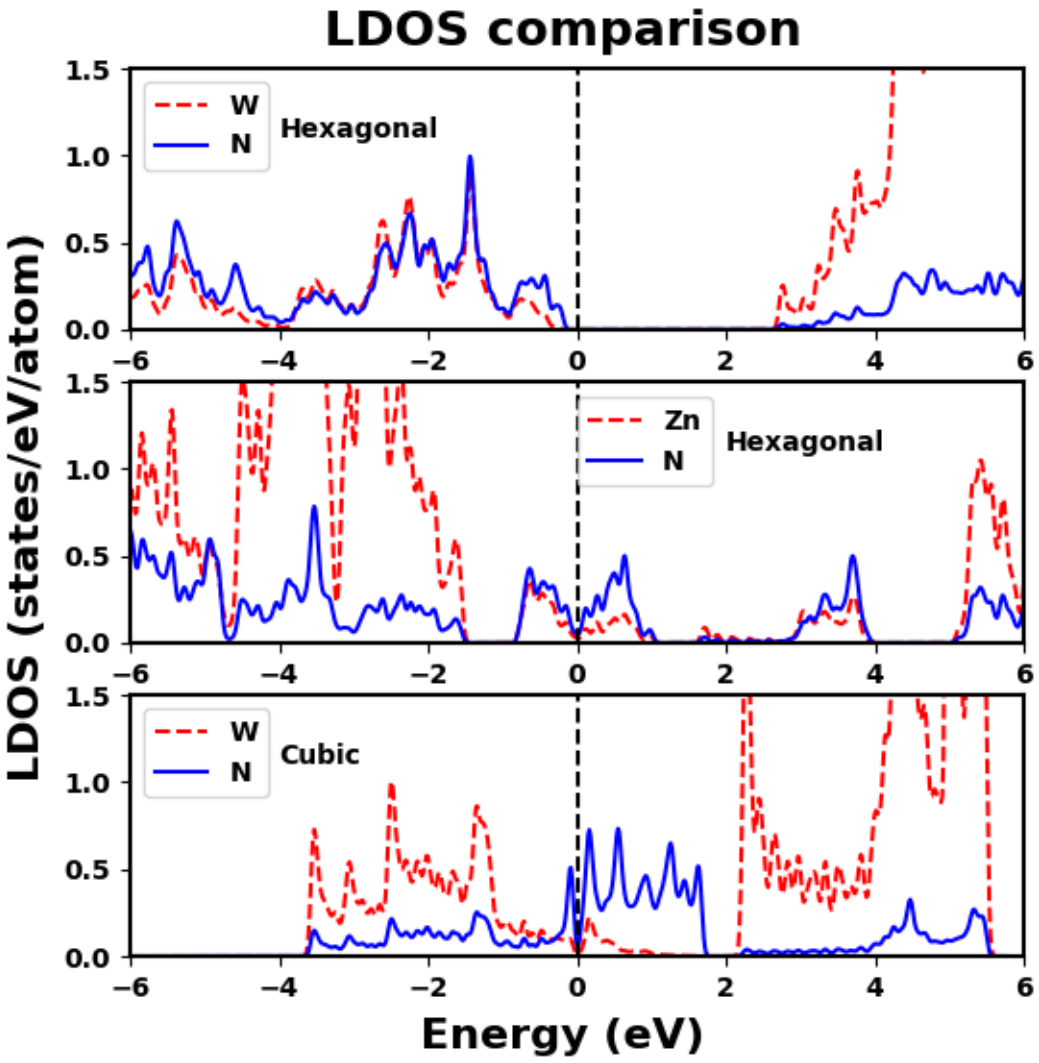
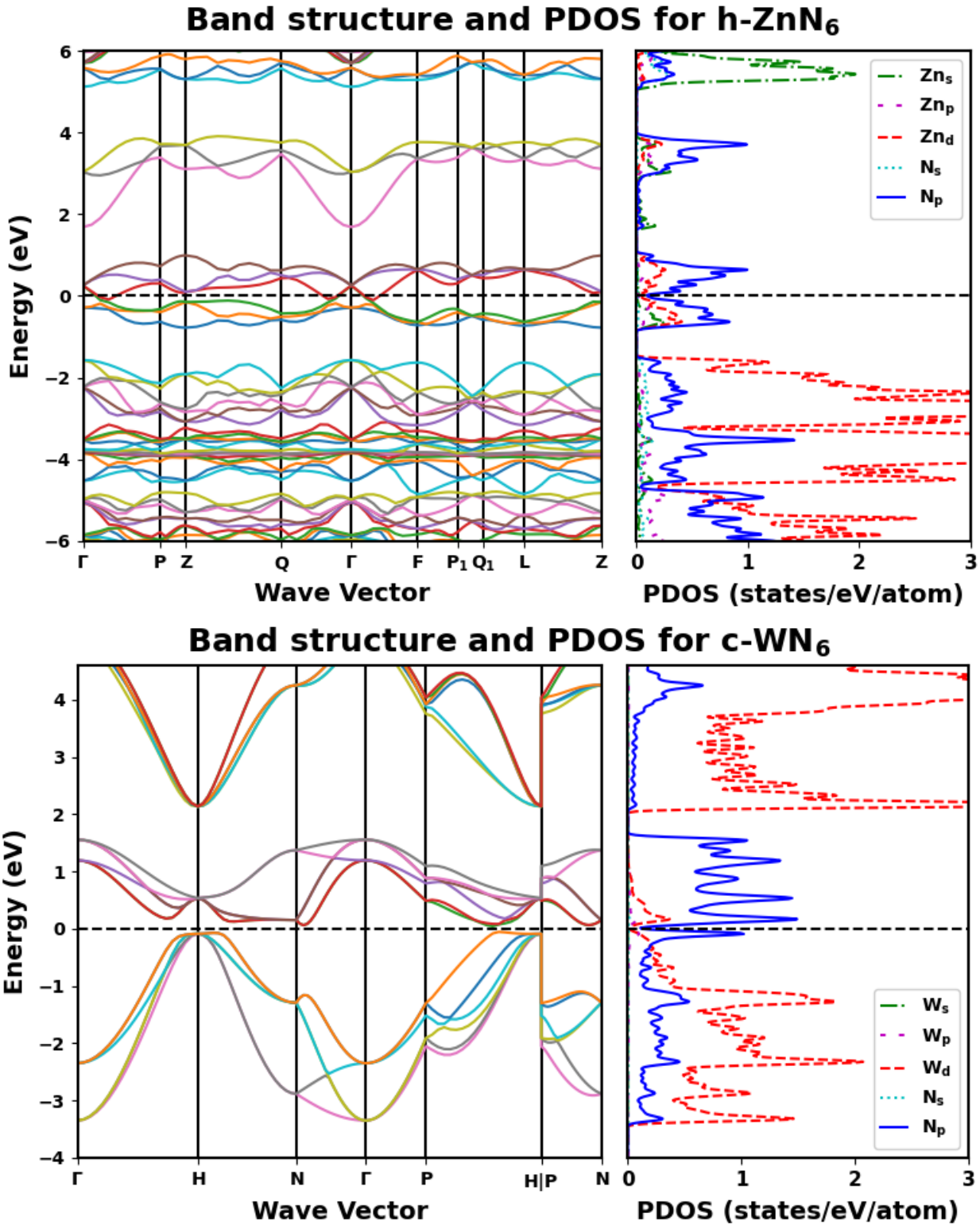


Figure S16: Electronic band structure and partial density of states for h-ZnN_6 and c-WN_6 structures. The Fermi level is set at 0 eV.



References

1. Li Qian, et al., *New multifunctional tungsten nitride with energetic N_6 and extreme hardness predicted from first principles.* EPL (Europhysics Letters), 2017. **118**(4): p. 46001p1-p5.