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Electronic Supplementary Information

The Nature of the Electronic Ground State of M_2C (M= Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W) MXenes

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Table S1. Calculated HSE06 and PBE (in parenthesis) Bader charges (Q in a.u.) of metal and carbon atoms in M_2C (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W) using plane waves.

MXene	**Q(C)**	**Q(M)**
Ti_2C	-2.62 (-2.35)	1.31 (1.17)
Zr_2C	-2.44 (-2.16)	1.22 (1.08)
Hf_2C	-2.75 (-2.47)	1.37 (1.24)
V_2C	-2.22 (-2.04)	1.11 (1.02)
Nb_2C	-2.12 (1.92)	1.06 (0.96)
Ta_2C	-2.36 (-2.19)	1.18 (1.09)
Cr_2C	-1.84 (-1.66)	0.91 (0.83)
Mo_2C	-1.61 (-1.59)	0.80 (0.79)
W_2C	-1.57 (-1.43)	0.79 (0.72)

Table S2. Energy of the FM solutions relative to the NM (or closed-shell) one (ΔE_{FM-NM} in meV) of p(1×1) unit cell of M2C (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W) obtained from PBE, PBE0, and HSE06 functionals at the PBE optimized spin-polarized structures, as obtained with VASP and FHI-AIMS codes, the latter marked in italics. The negative sign indicates that the FM solution is more stable than the NM one. For diamagnetic MXenes the most stable FM solution is obtained by fixing the total number of unpaired electrons as described in the text.

MXene	PBE	PBE0	HSE06
Ti_2C[a]	-135	-488	-420
	-155	*-506*	*-417*
Zr_2C	-36	-339	-274
	20	*-281*	*-197*
Hf_2C	60	-191	-143
	79	*-189*	*-105*
V_2C[b]	769	151	128
	797	*189*	*222*
Nb_2C[b]	1462	1246	1220
	1497	*1286*	*1301*
Ta_2C[b]	2140	2134	2061
	2187	*2174*	*2177*
Cr_2C	-25	-1389	-1366
	-15	*-1238*	*-1122*
Mo_2C[c]	349	292	295
	395	*324*	*330*
W_2C[c]	812	883	841
	867	*1013*	*956*

[a] The values of Ti_2C from Ref. 45 of the main text have been also included to draw a clear and a wide picture of the influence of the metal atoms in these systems.

[b] Spin-polarized solution fixing two unpaired electrons per unit cell.

[c] Spin-polarized solution fixing one unpaired electron per unit cell.

Table S3. Energy of several FM solutions relative to the NM one (ΔE_{FM-NM} in meV, respectively) of $p(1\times1)$ unit cell of paramagnetic Cr_2C and diamagnetic M_2C (M= Mo, and W) obtained from PBE, PBE0, and HSE06 functionals, at the PBE optimized spin-polarized structures for the corresponding GS, as obtained with VASP and FHI-AIMS codes, the latter marked in italics. These solutions have been estimated fixing the total net spin density per unit cell consistent with the Bader charges.

	ΔE_{FM-NM}		
MXene	**PBE**	**PBE0**	**HSE06**
Cr_2C^a	2236	-1320	-1268
	2248	*-1218*	*-1008*
Cr_2C^b	875	-1182	-1190
	907	*-1098*	*-1011*
Cr_2C^c	72	-77	-67
	82	-45	-34
Mo_2C^a	6644	4806	4886
	6767	*4967*	*5171*
Mo_2C^b	3222	2194	2224
	3277	*2222*	*2350*
W_2C^a	9118	7904	7875
	9270	*8190*	*8395*
W_2C^b	4534	3882	3839
	4639	*4051*	*4150*

[a] Spin polarized solution fixing a value of 4 unpaired electrons per unit cell.

[b] Spin polarized solution fixing a value of 3 unpaired electrons per unit cell.

[c] Spin polarized solution fixing a value of 1 unpaired electron per unit cell.

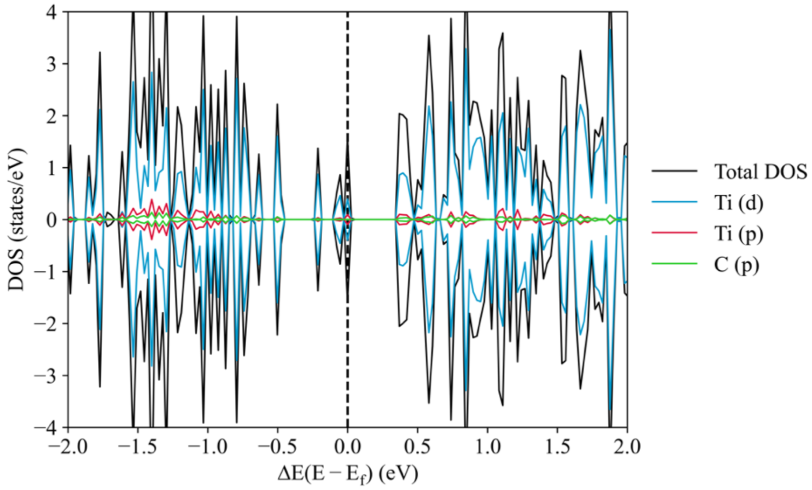
Table S4. Energy of AFM solutions relative to the FM one ($\Delta E_{AFM\text{-}FM}$ in meV) of p(1×1) unit cell of paramagnetic M_2C (M=Ti, Zr, Hf, and Cr) obtained from PBE, PBE0, and HSE06 functionals at the PBE optimized spin-polarized structures with (a) VASP and (b) FHI-AIMS codes. The negative sign indicates that the AFM solutions are more stable than the FM one.

MXene	PBE	PBE0	HSE06
Ti_2C[a]	-21	-99	-73
	-28	*-103*	*-73*
Zr_2C	-39	-90	-69
	0	*-128*	*-83*
Hf_2C	-63	-81	-60
	2	*-89*	*-58*
Cr_2C	45	-307	-263
	15	*-425*	*-342*

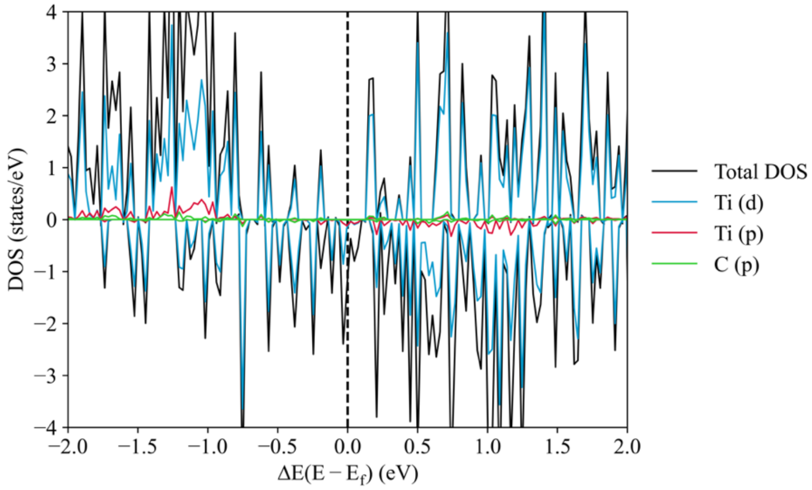
[a] The values of Ti_2C from Ref. 45 of the main text have been also included to draw a clear and a wide picture of the influence of the metal atoms in these systems.

Fig. S1. (a) AFM, (b) FM, and (c) NM projected DOS (in states/eV) for Ti_2C as obtained from calculations with the HSE06 functional at the PBE optimized $p(1\times1)$ unit cell. The energy is referenced to the Fermi level (in eV).

a)



b)



c)

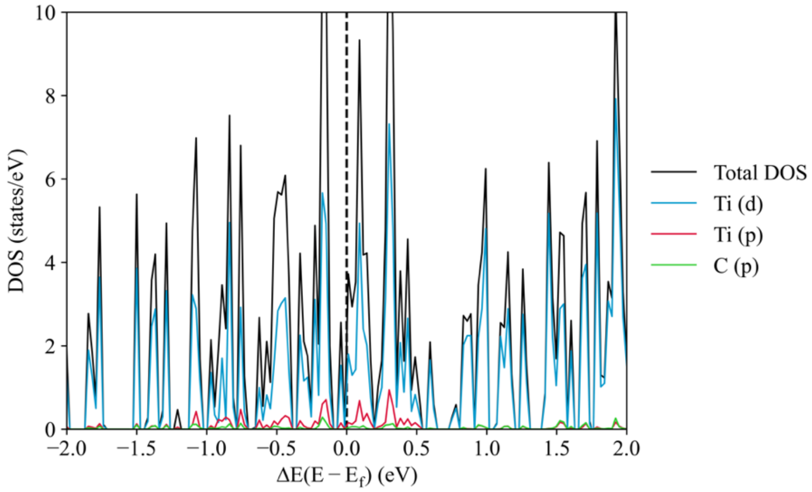
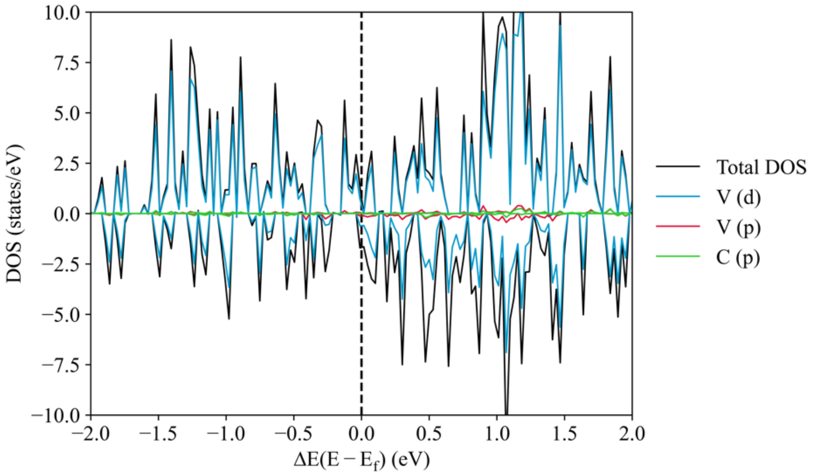


Fig. S2. (a) FM and (b) NM projected DOS (in states/eV) for V_2C as obtained from calculations with the HSE06 functional at the PBE optimized *p*(1×1) unit cell. The energy is referenced to the Fermi level (in eV).

a)



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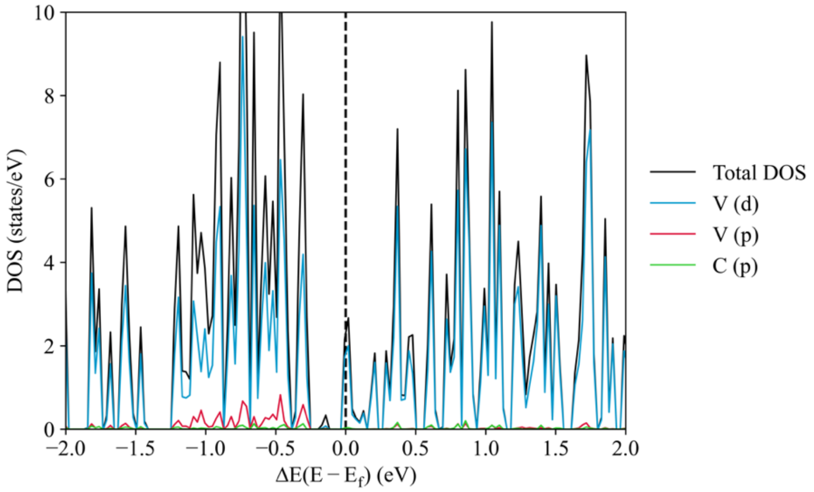


Fig. S3. (a) AFM, (b) FM, and (c) NM projected DOS (in states/eV) for Cr_2C as obtained from calculations with the HSE06 functional at the PBE optimized $p(1\times1)$ unit cell. The energy is referenced to the Fermi level (in eV).

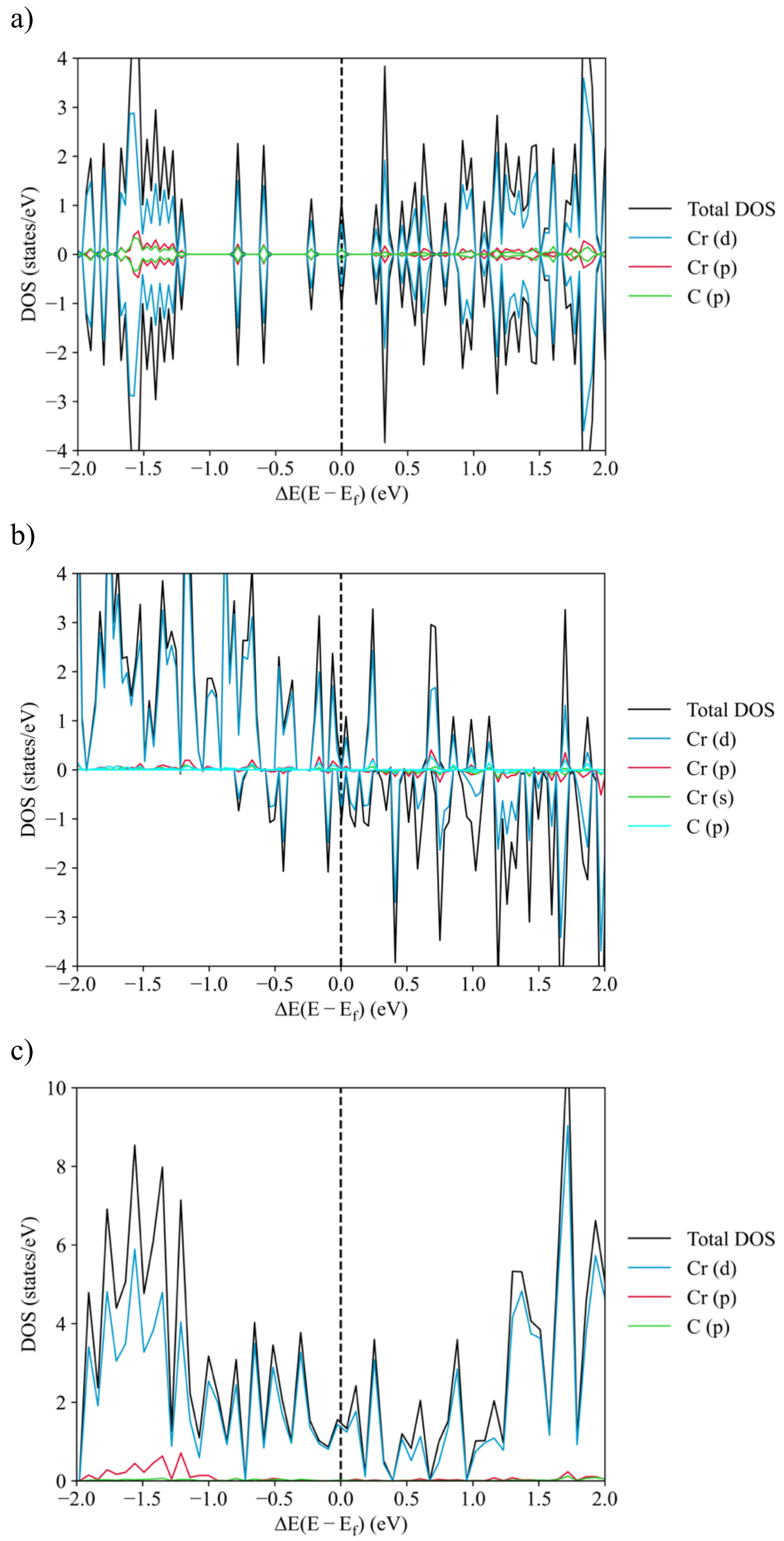


Fig. S4. (a) AFM, (b) FM, and (c) NM projected DOS (in states/eV) for Zr_2C as obtained from calculations with the HSE06 functional at the PBE optimized *p*(1×1) unit cell. The energy is referenced to the Fermi level (in eV).

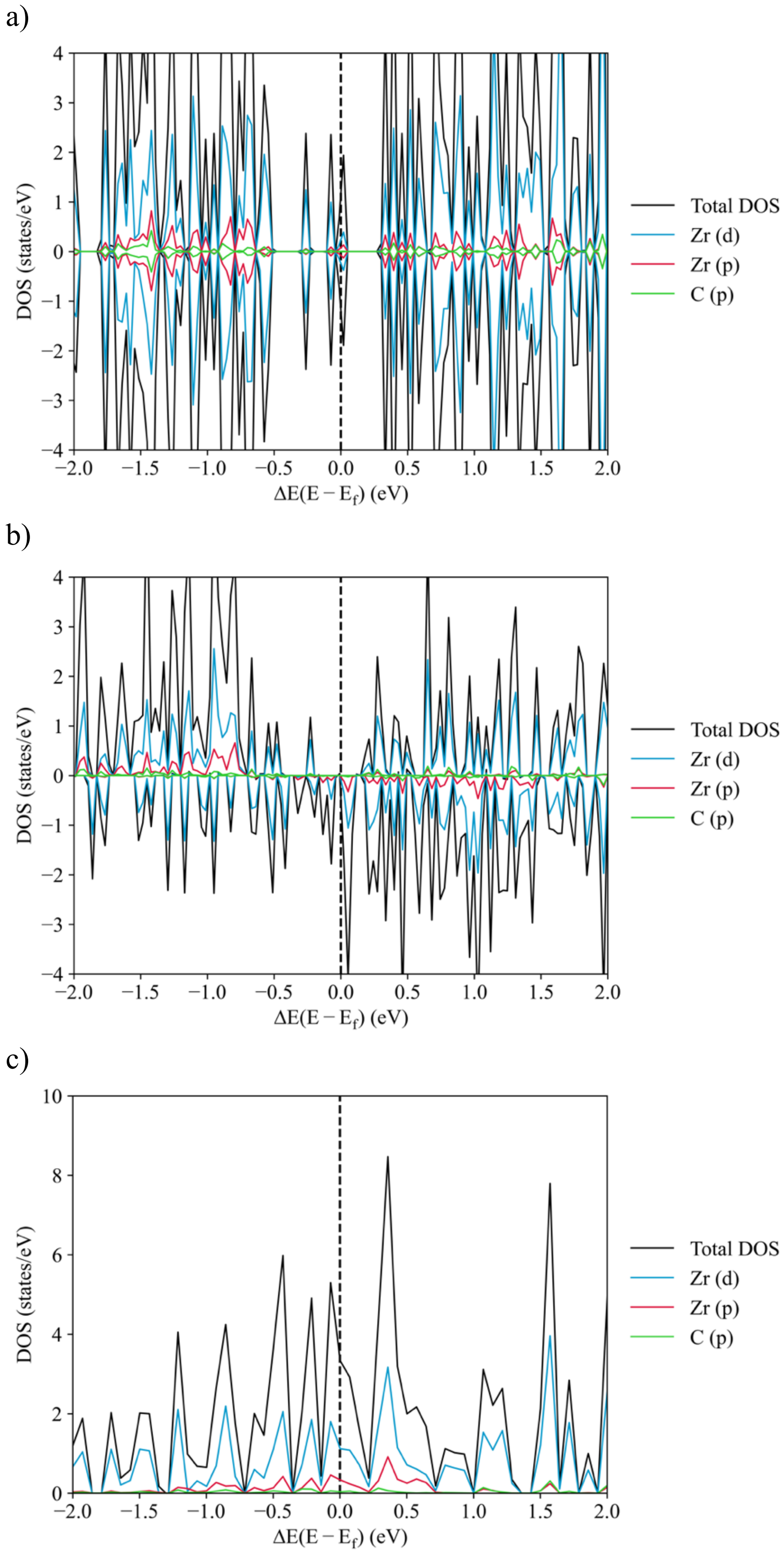
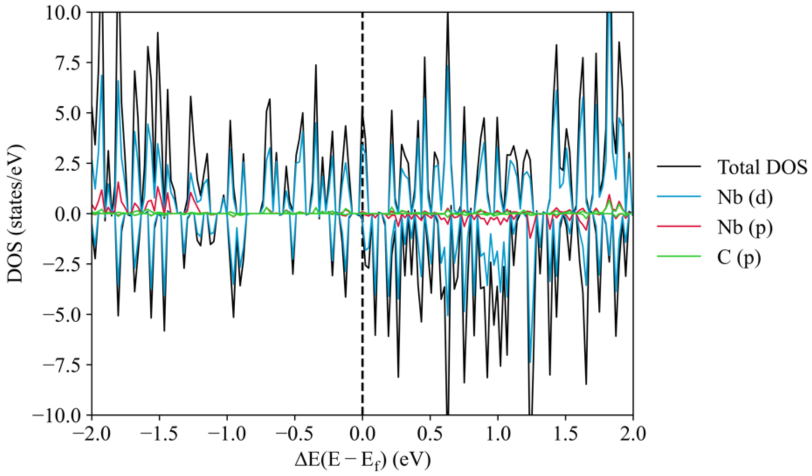


Fig. S5. (a) FM and (b) NM projected DOS (in states/eV) for Nb_2C as obtained from calculations with the HSE06 functional at the PBE optimized *p*(1×1) unit cell. The energy is referenced to the Fermi level (in eV).

a)



b)

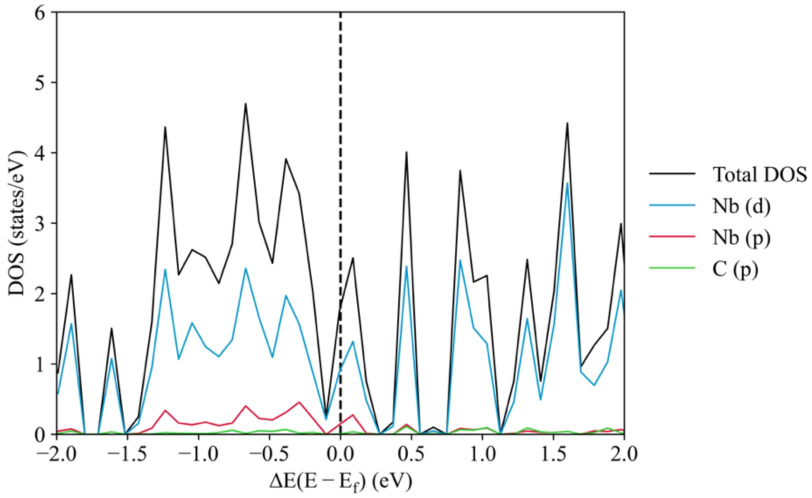
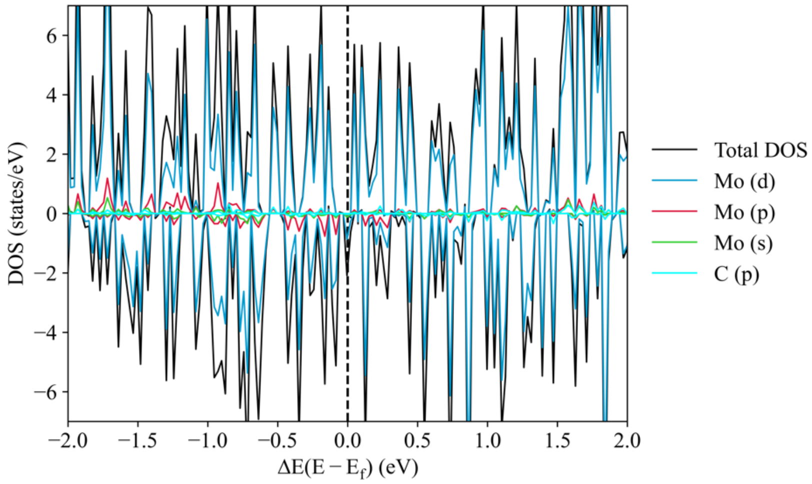


Fig. S6. (a) FM and (b) NM projected DOS (in states/eV) for Mo_2C as obtained from calculations with the HSE06 functional at the PBE optimized *p*(1×1) unit cell. The energy is referenced to the Fermi level (in eV).

a)



b)

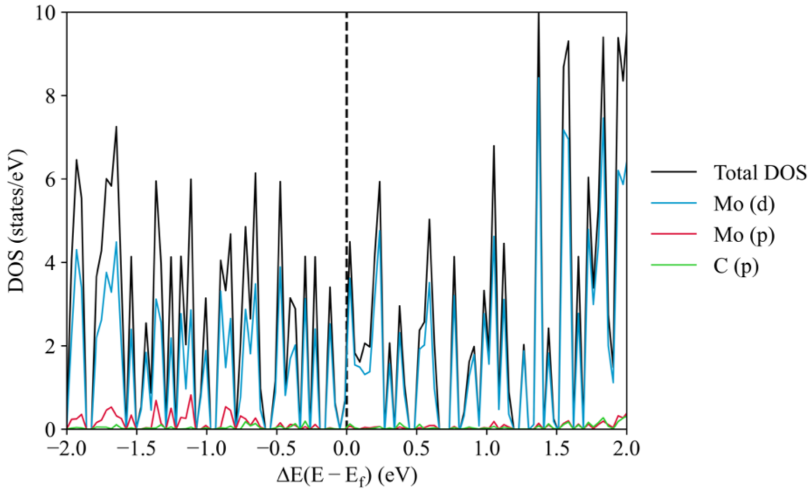
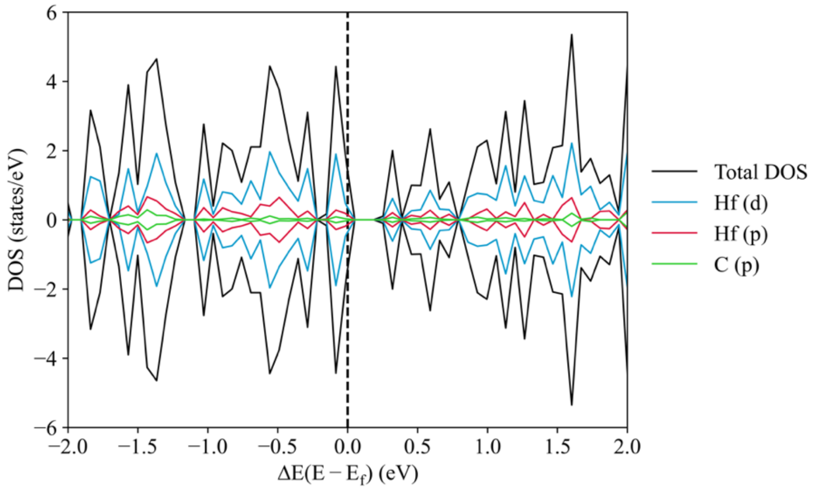
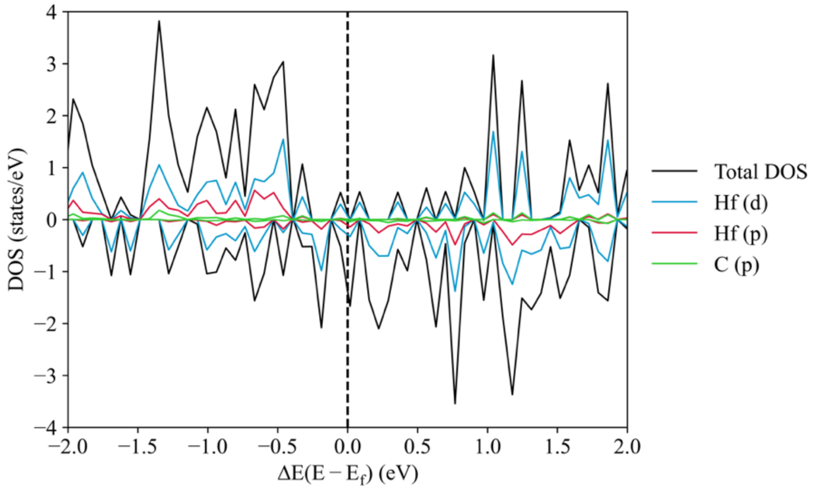


Fig. S7. (a) AFM, (b) FM, and (c) NM projected DOS (in states/eV) for Hf_2C as obtained from calculations with the HSE06 functional at the PBE optimized *p*(1×1) unit cell. The energy is referenced to the Fermi level (in eV).

a)



b)



c)

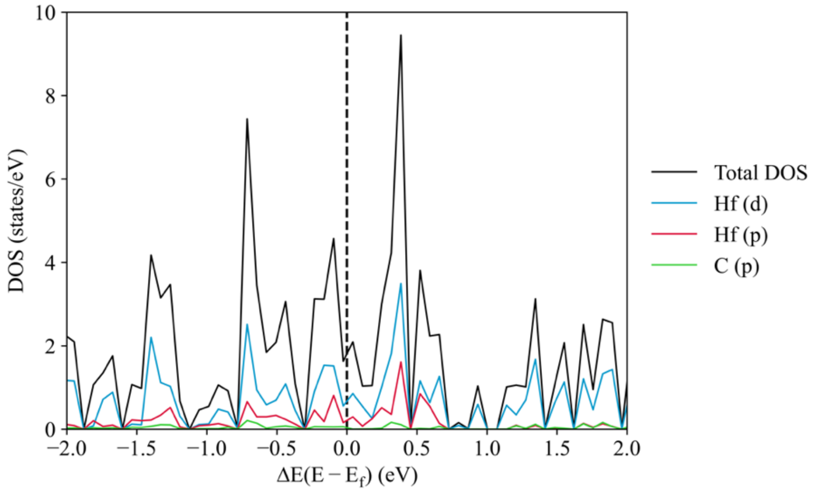
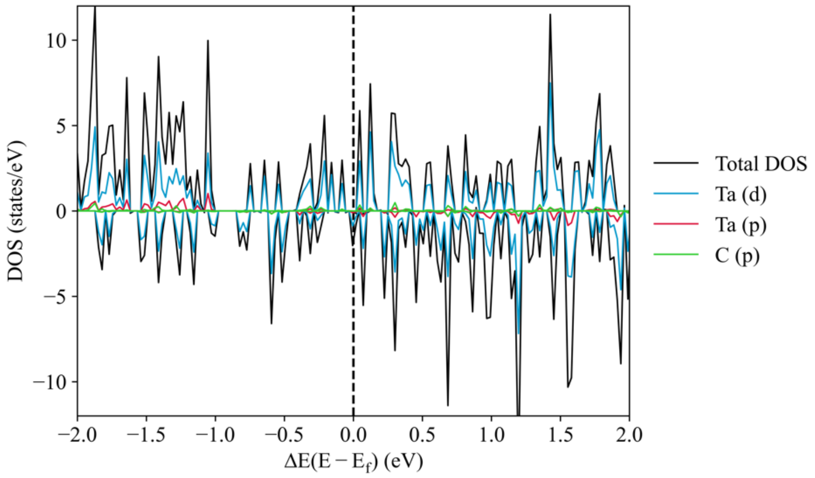


Fig. S8. (a) FM and (b) NM projected DOS (in states/eV) for Ta_2C as obtained from calculations with the HSE06 functional at the PBE optimized *p*(1×1) unit cell. The energy is referenced to the Fermi level (in eV).

a)



b)

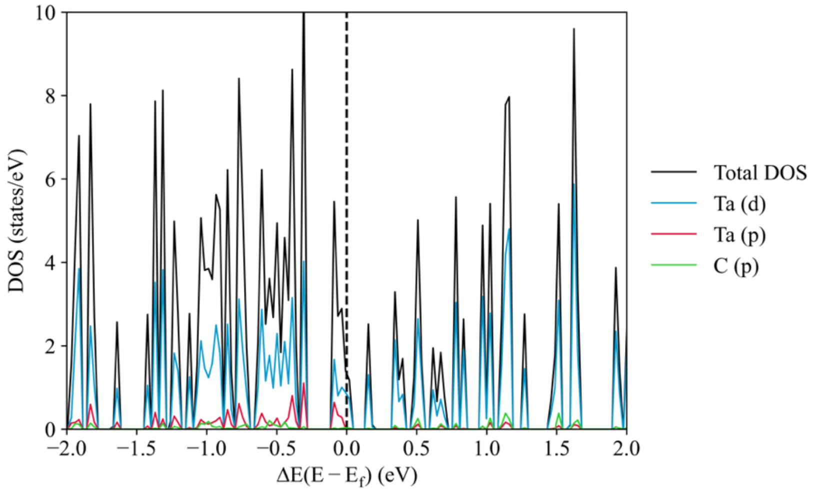


Fig. S9. (a) FM and (b) NM projected DOS (in states/eV) for W_2C as obtained from calculations with the HSE06 functional at the PBE optimized $p(1\times1)$ unit cell. The energy is referenced to the Fermi level (in eV).

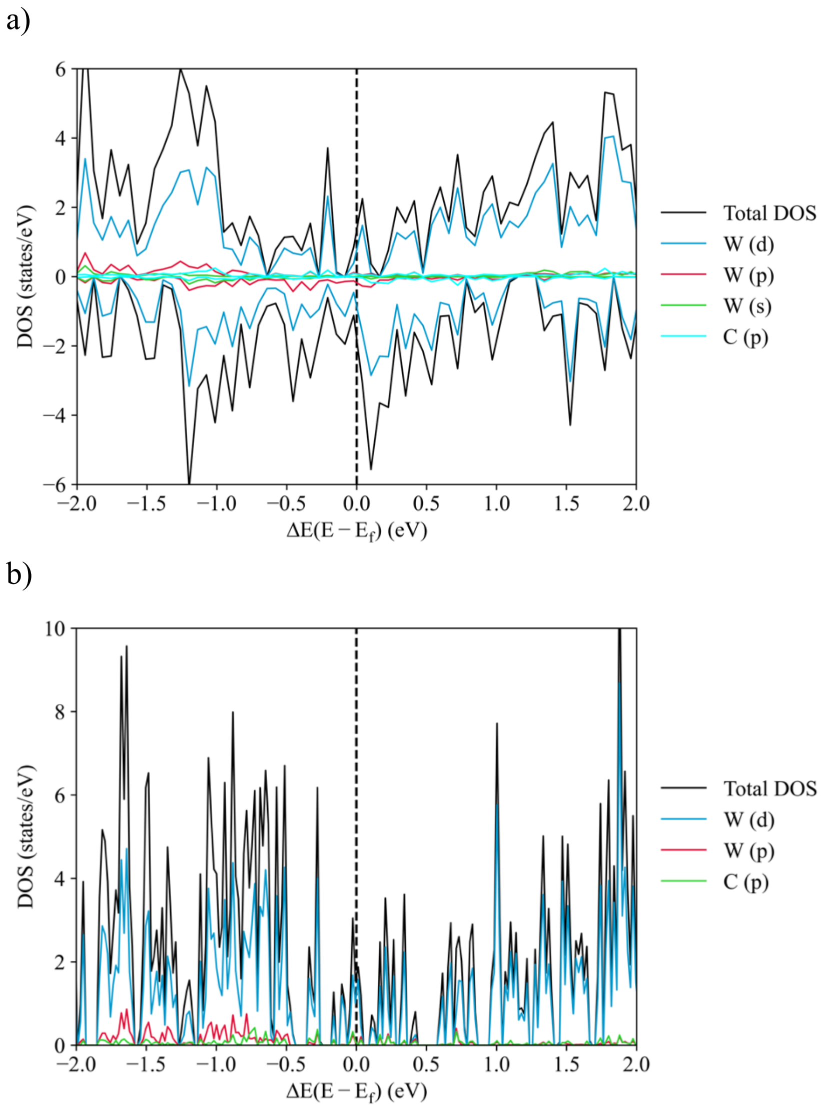


Fig. S10. Phonon dispersion of diamagnetic (left) and paramagnetic (right) solutions of Ti$_2$C as predicted from the calculations with the PBE functional.