Supplementary Materials

for

The Origin of Anomalous Hydrogen Occupation in High Entropy Alloys

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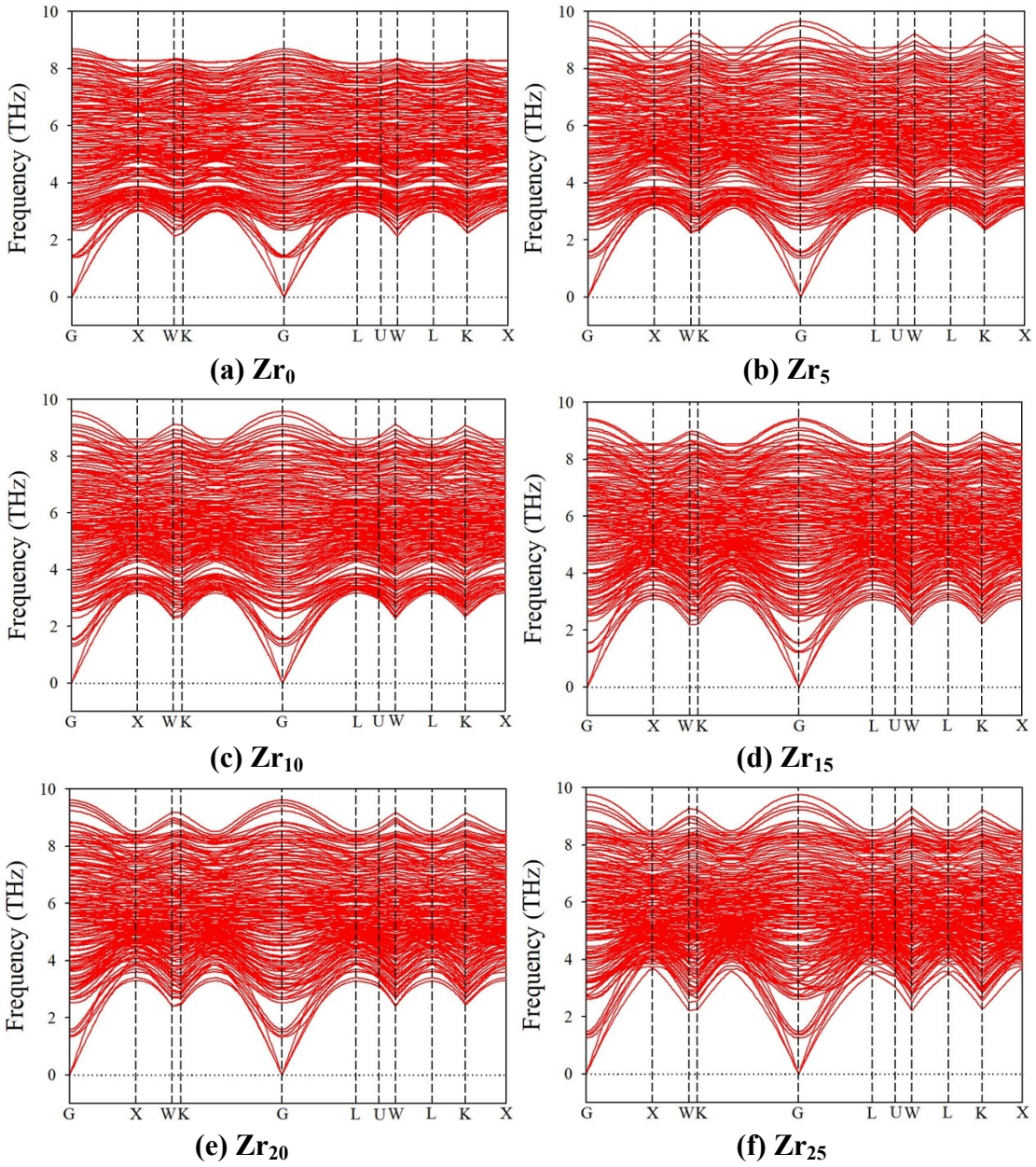
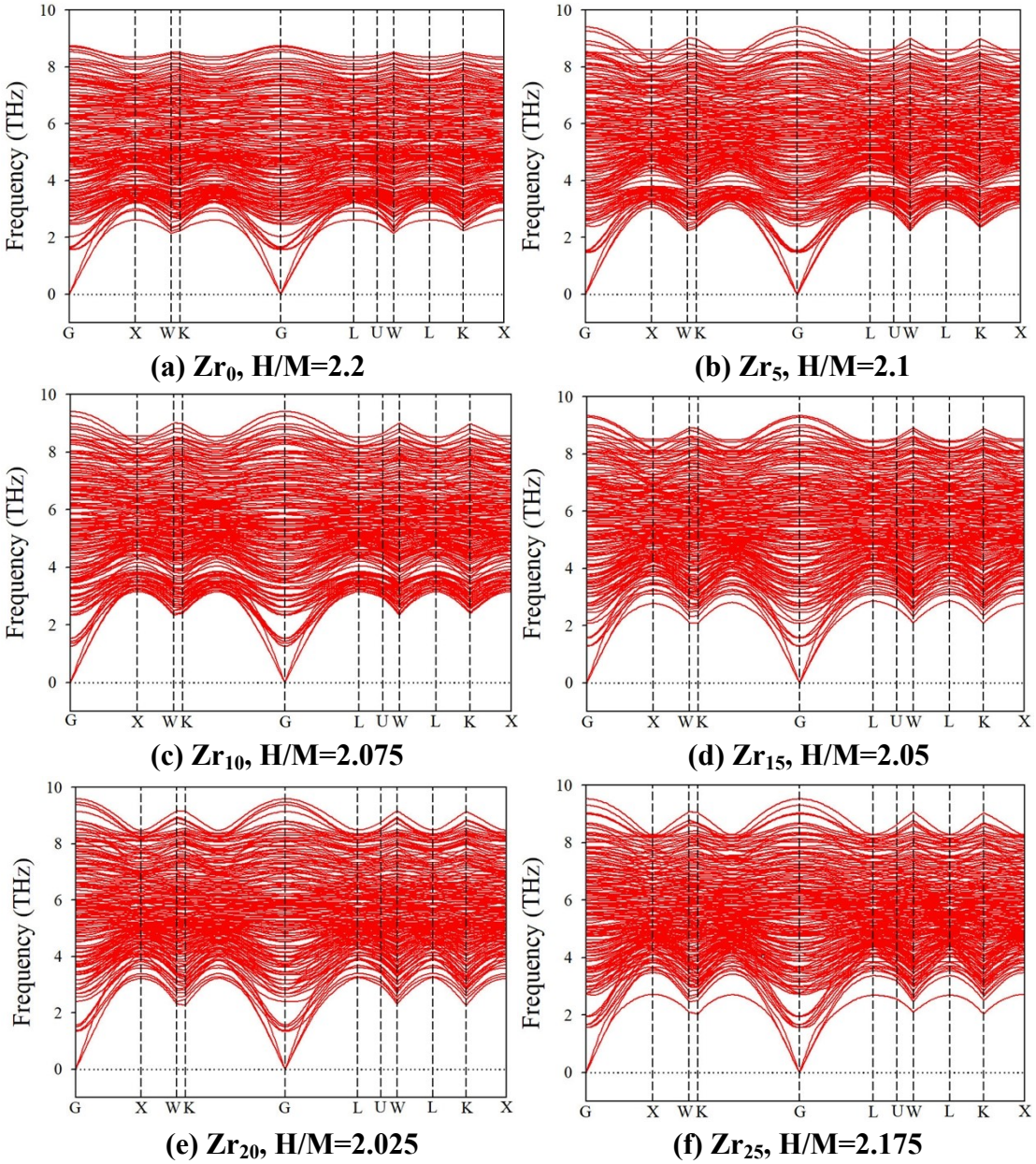
Supplementary Table S1. Elastic constants (C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55} and C_{66} in GPa) for $Ti_{25}V_{25}Nb_{25}Zr_xTa_{25-x}$ (Zr_x, x=0, 5, 10, 15, 20 and 25) hydrides. The considered H/M ratios for Zr_0, Zr_5, Zr_{10}, Zr_{15}, Zr_{20} and Zr_{25} are 2.2, 2.1, 2.075, 2.05, 2.025 and 2.175, respectively.

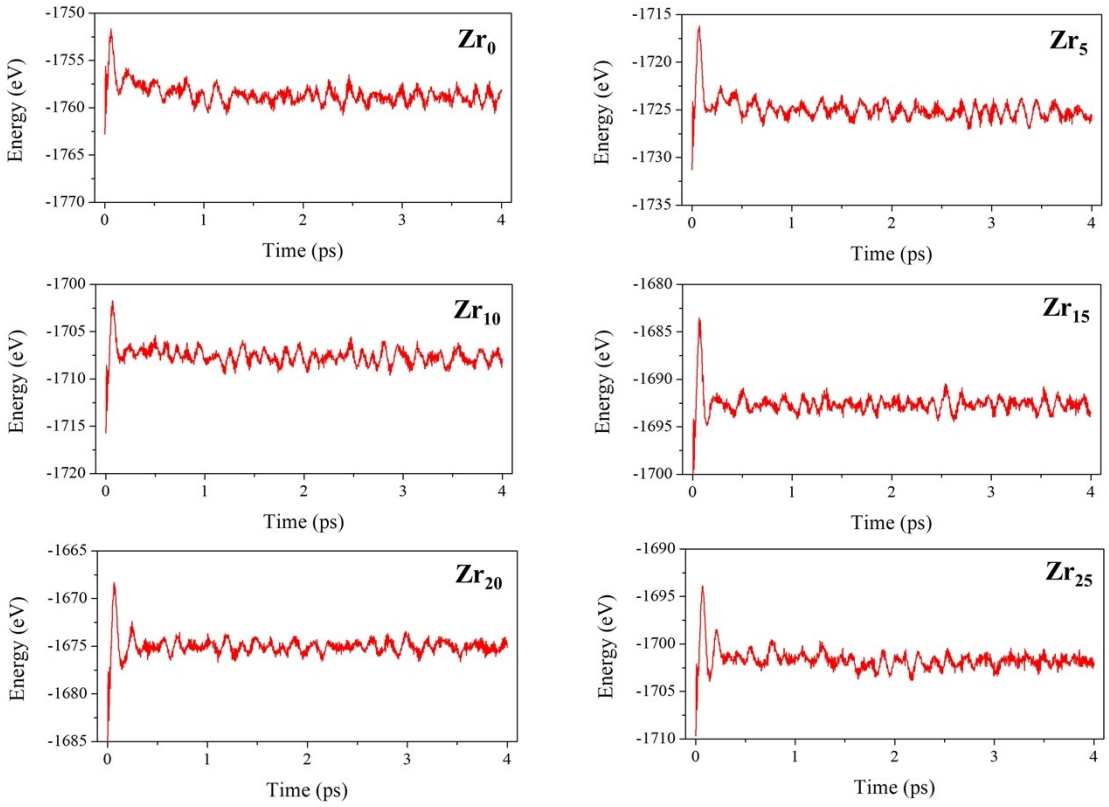
	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
Zr_0	282	115	123	277	138	235	102	79	113
Zr_5	253	130	131	265	129	230	89	86	90
Zr_{10}	245	131	130	244	134	220	73	78	79
Zr_{15}	223	136	138	229	132	209	59	56	68
Zr_{20}	224	133	132	236	124	210	60	69	69
Zr_{25}	224	125	123	232	127	209	74	56	87



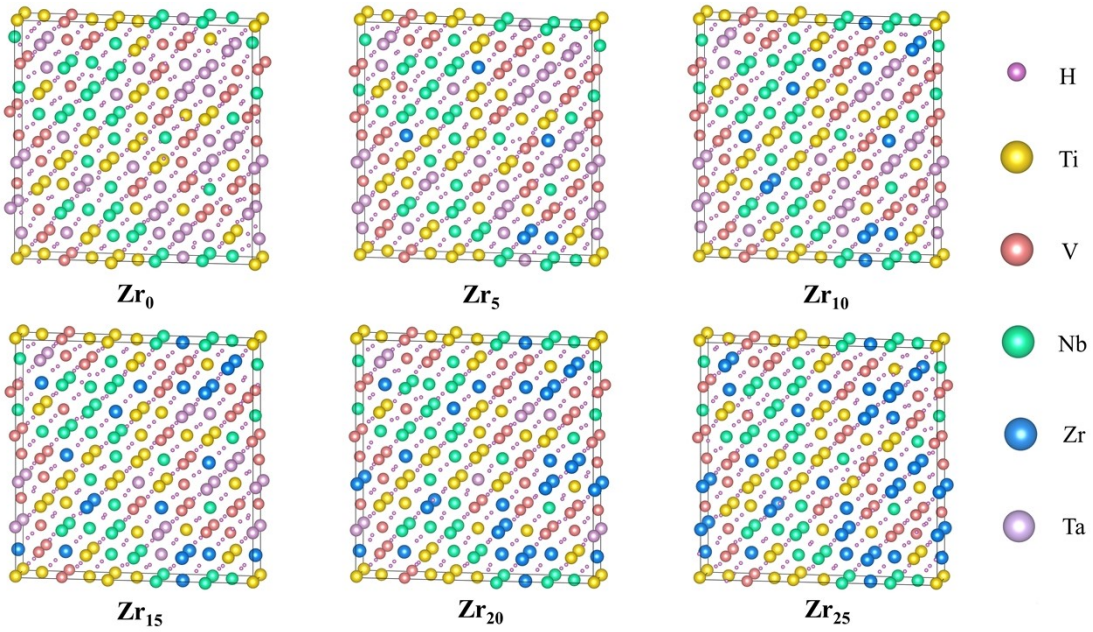
Supplementary Figure S1. Phonon spectra of (a) $Ti_{25}V_{25}Nb_{25}Ta_{25}$ (Zr_0), (b) $Ti_{25}V_{25}Nb_{25}Zr_5Ta_{20}$ (Zr_5), (c) $Ti_{25}V_{25}Nb_{25}Zr_{10}Ta_{15}$ (Zr_{10}), (d) $Ti_{25}V_{25}Nb_{25}Zr_{15}Ta_{10}$ (Zr_{15}), (e) $Ti_{25}V_{25}Nb_{25}Zr_{20}Ta_5$ (Zr_{20}) and (f) $Ti_{25}V_{25}Nb_{25}Zr_{25}$ (Zr_{25}) hydrides with H/M=2.



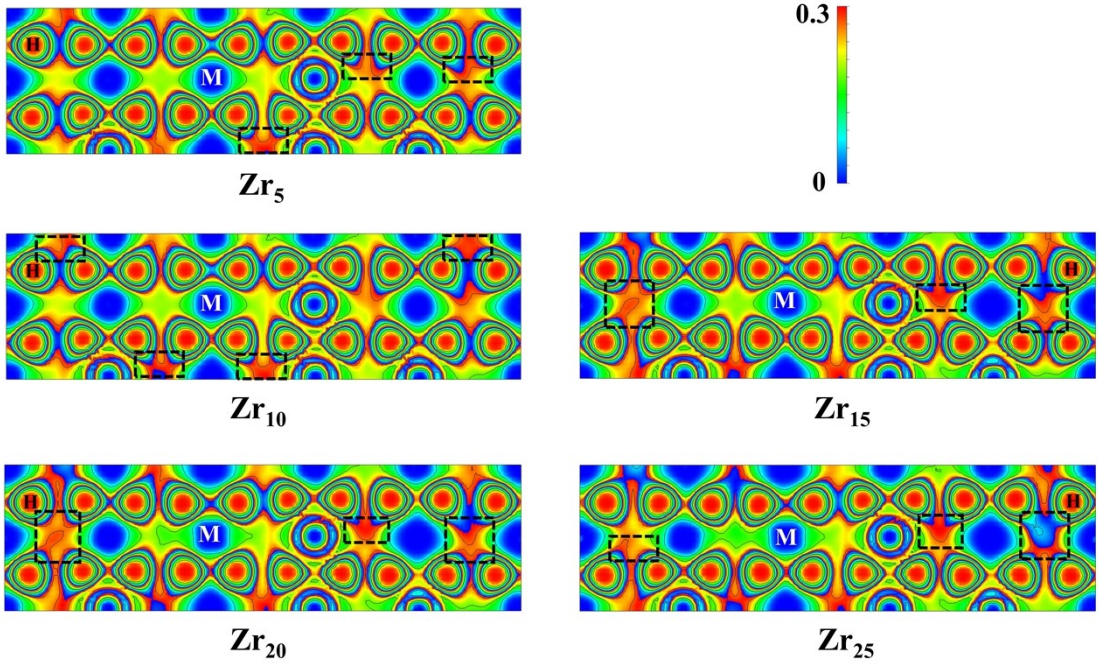
Supplementary Figure S2. Phonon spectra of (a) $Ti_{25}V_{25}Nb_{25}Ta_{25}$ (Zr_0) hydride with H/M=2.2; (b) $Ti_{25}V_{25}Nb_{25}Zr_5Ta_{20}$ (Zr_5) hydride with H/M=2.1; (c) $Ti_{25}V_{25}Nb_{25}Zr_{10}Ta_{15}$ (Zr_{10}) hydride with H/M=2.075; (d) $Ti_{25}V_{25}Nb_{25}Zr_{15}Ta_{10}$ (Zr_{15}) hydride with H/M=2.05; (e) $Ti_{25}V_{25}Nb_{25}Zr_{20}Ta_5$ (Zr_{20}) hydride with H/M=2.025; (f) $Ti_{25}V_{25}Nb_{25}Zr_{25}$ (Zr_{25}) hydride with H/M=2.175.



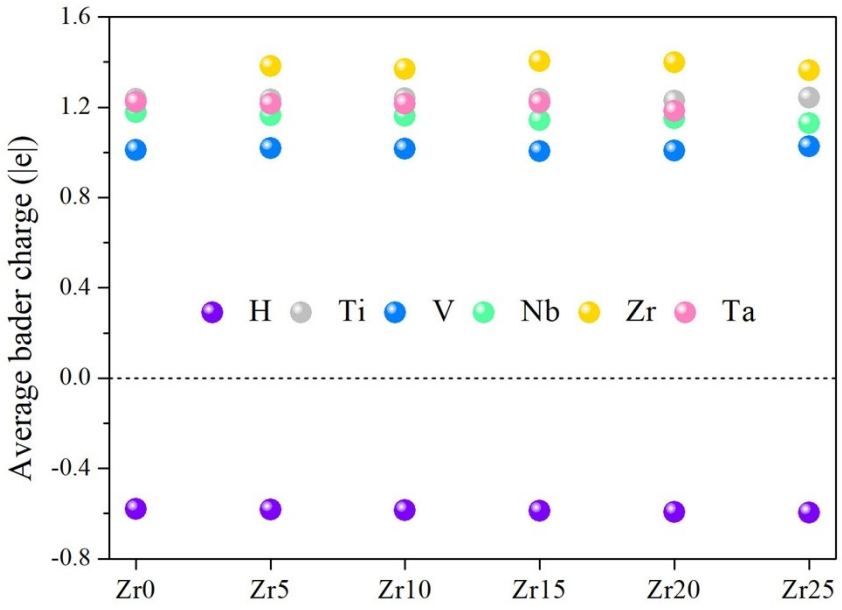
Supplementary Figure S3. Variation of the total energy with time for $Ti_{25}V_{25}Nb_{25}Zr_xTa_{25-x}$ (Zr_x, x=0, 5, 10, 15, 20 and 25) hydrides at 300 K. The considered H/M ratios for Zr_0, Zr_5, Zr_{10}, Zr_{15}, Zr_{20} and Zr_{25} are 2.2, 2.1, 2.075, 2.05, 2.025 and 2.175, respectively.



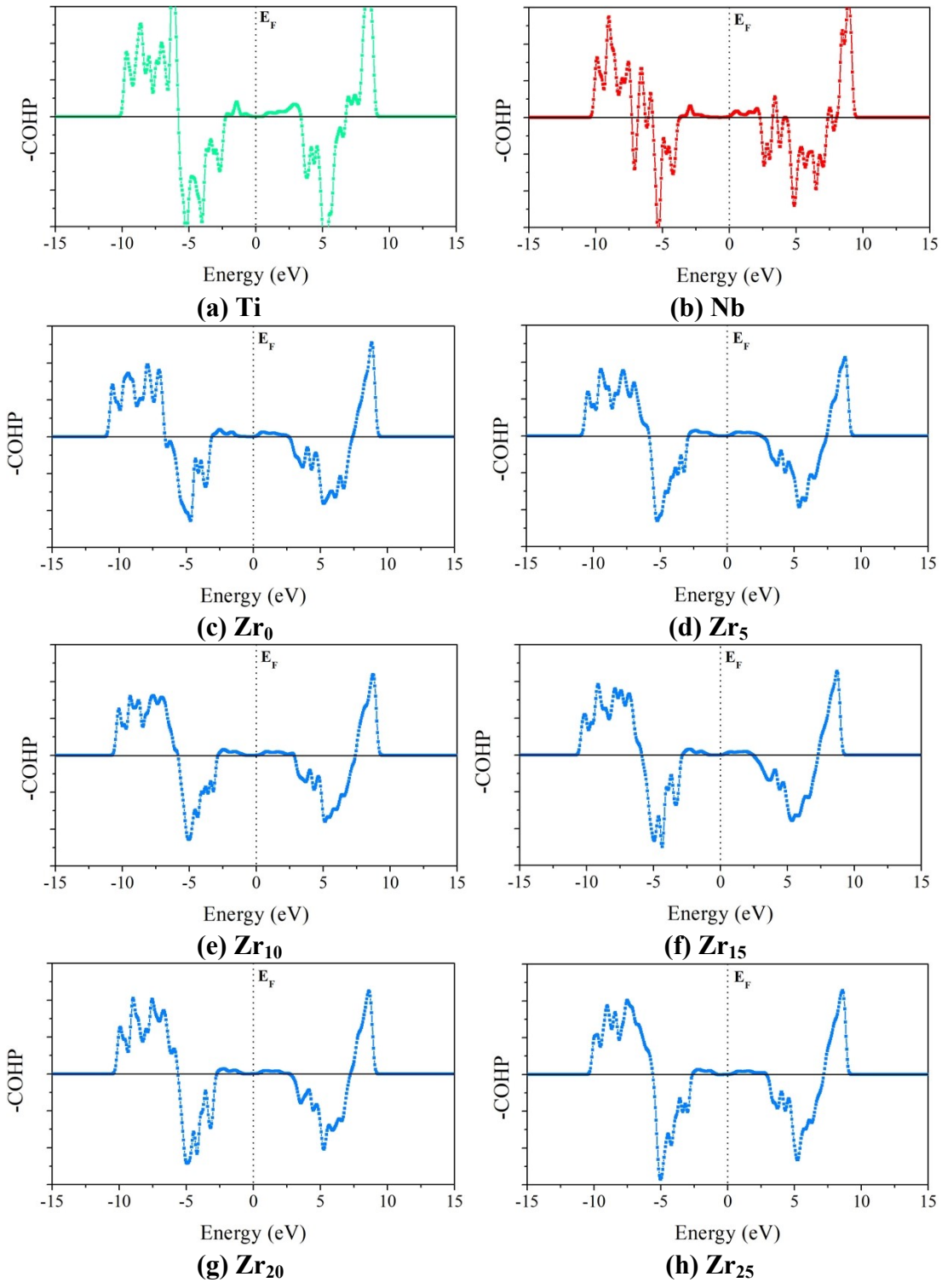
Supplementary Figure S4. Schematic view of the equilibrium structures for $Ti_{25}V_{25}Nb_{25}Zr_xTa_{25-x}$ (Zr_x, x=0, 5, 10, 15, 20 and 25) hydrides obtained from *ab initio* MD simulation at 300 K. The considered H/M ratios for Zr_0, Zr_5, Zr_{10}, Zr_{15}, Zr_{20} and Zr_{25} are 2.2, 2.1, 2.075, 2.05, 2.025 and 2.175, respectively.



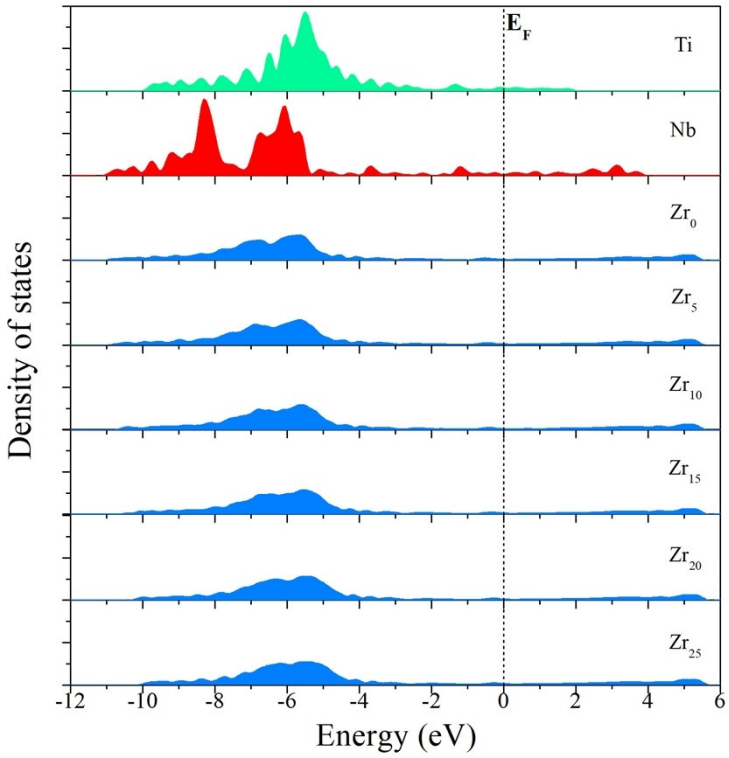
Supplementary Figure S5. Electron localization function (ELF) images of the (5 0 1) plane for $Ti_{25}V_{25}Nb_{25}Zr_xTa_{25-x}$ (Zr_x; x = 5, 10, 15, 20 and 25) hydrides with H/M=2. The symbols H and M represent hydrogen atoms and metal atoms, respectively. The polarizations of the electrons around the hydrogen in HEA hydrides are highlighted by the dashed rectangles.



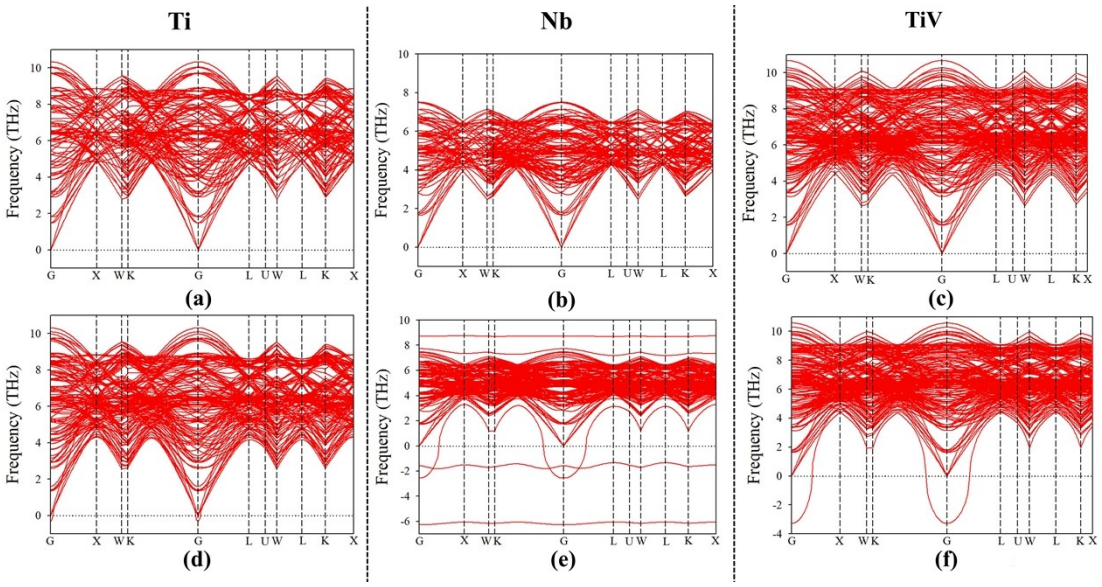
Supplementary Figure S6. The average Bader charge for different chemical elements in the $Ti_{25}V_{25}Nb_{25}Zr_xTa_{25-x}$ (Zr_x, x=0, 5, 10, 15, 20 and 25) hydrides with H/M=2.



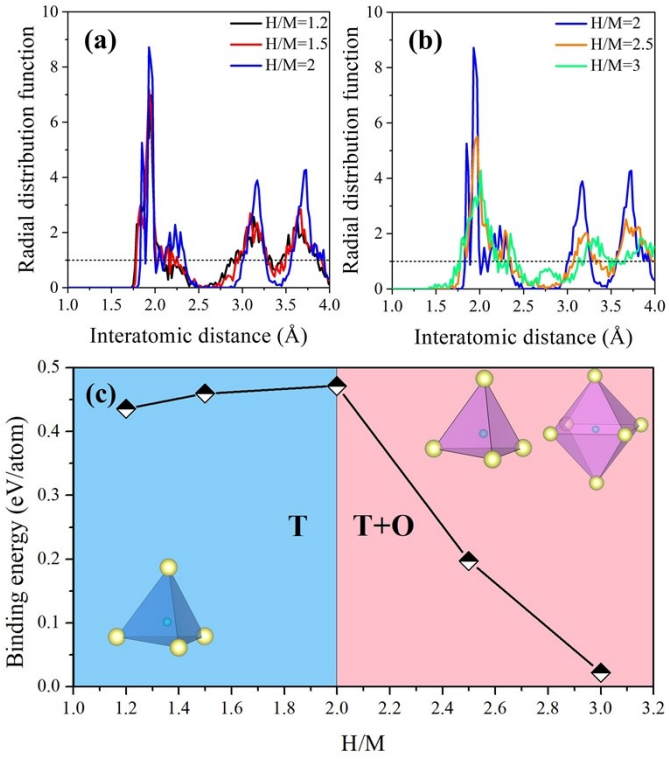
Supplementary Figure S7. The Crystal Orbital Hamilton Population (COHP) between hydrogen in pure Ti metal, pure Nb metal and $Ti_{25}V_{25}Nb_{25}Zr_xTa_{25-x}$ (Zr_x; x=0, 5, 10, 15, 20 and 25) hydrides with H/M=2. The Fermi level (E_F) is located at 0 eV.



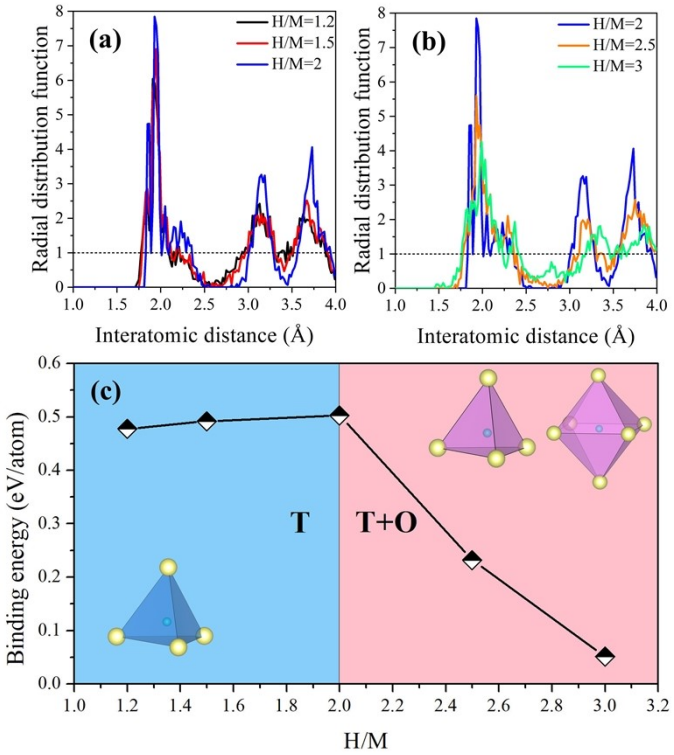
Supplementary Figure S8. The density of state (DOS) distribution of hydrogen in pure Ti metal, pure Nb metal and $Ti_{25}V_{25}Nb_{25}Zr_xTa_{25-x}$ (Zr_x; x=0, 5, 10, 15, 20 and 25) hydrides with H/M=2. The Fermi level (E_F) is located at 0 eV.



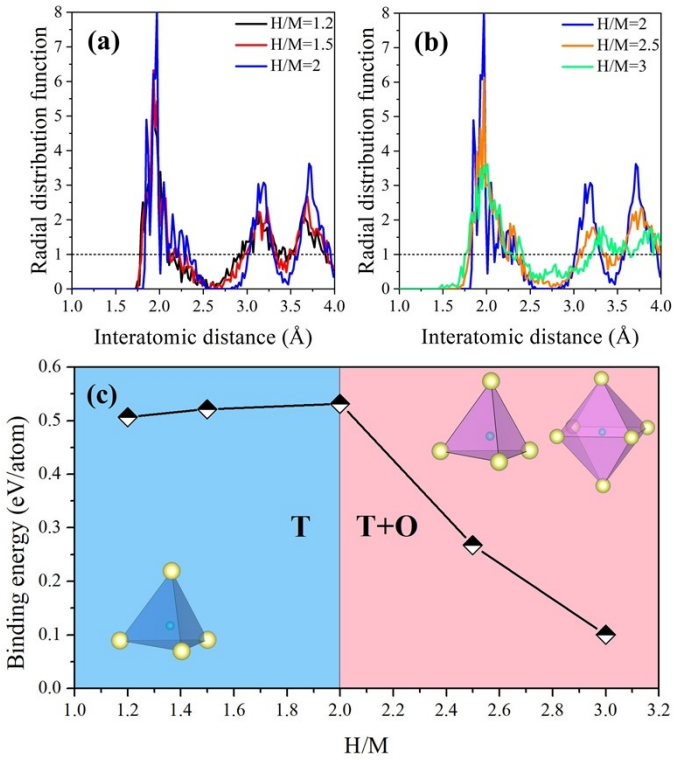
Supplementary Figure S9. The phonon spectra of Ti, Nb and TiV hydrides with (a-c) all tetrahedral sites occupied by hydrogen and (d-f) additional one octahedral site occupied by hydrogen.



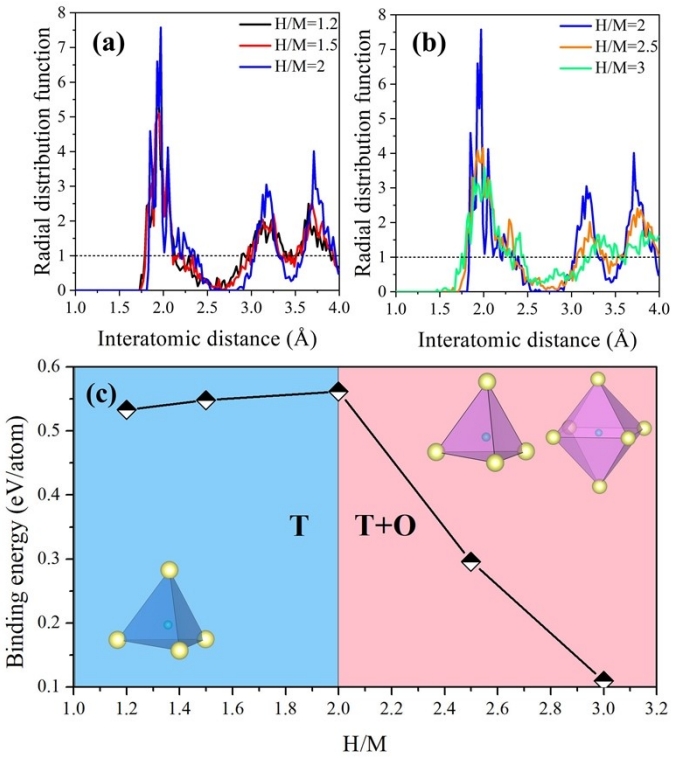
Supplementary Figure S10. Radial distribution functions between atoms for FCC $Ti_{25}V_{25}Nb_{25}Zr_5Ta_{20}$ (Zr_5) hydrides with (a) H/M=1.2, 1.5, 2 and (b) H/M=2, 2.5, 3; (c) The calculated binding energy as a function of hydrogen content for the FCC Zr_5 hydrides. The symbols T and O represent hydrogen occupying tetrahedral and octahedral sites in FCC Zr_5 hydrides, respectively.



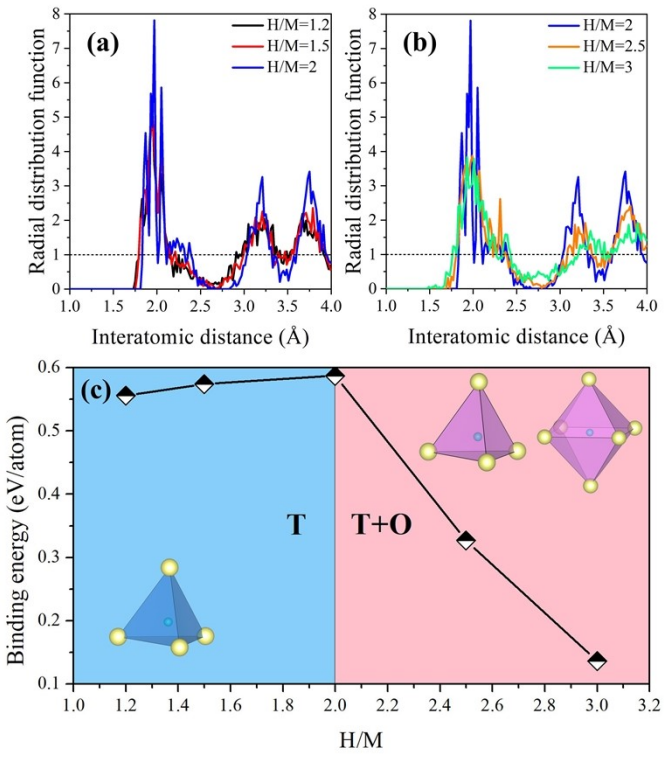
Supplementary Figure S11. Radial distribution functions between atoms for FCC $Ti_{25}V_{25}Nb_{25}Zr_{10}Ta_{15}$ (Zr_{10}) hydrides with (a) H/M=1.2, 1.5, 2 and (b) H/M=2, 2.5, 3; (c) The calculated binding energy as a function of hydrogen content for the FCC Zr_{10} hydrides. The symbols T and O represent hydrogen occupying tetrahedral and octahedral sites in FCC Zr_{10} hydrides, respectively.



Supplementary Figure S12. Radial distribution functions between atoms for FCC $Ti_{25}V_{25}Nb_{25}Zr_{15}Ta_{10}$ (Zr_{15}) hydrides with (a) H/M=1.2, 1.5, 2 and (b) H/M=2, 2.5, 3; (c) The calculated binding energy as a function of hydrogen content for the FCC Zr_{15} hydrides. The symbols T and O represent hydrogen occupying tetrahedral and octahedral sites in FCC Zr_{15} hydrides, respectively.



Supplementary Figure S13. Radial distribution functions between atoms for FCC $Ti_{25}V_{25}Nb_{25}Zr_{20}Ta_5$ (Zr_{20}) hydrides with (a) H/M=1.2, 1.5, 2 and (b) H/M=2, 2.5, 3; (c) The calculated binding energy as a function of hydrogen content for the FCC Zr_{20} hydrides. The symbols T and O represent hydrogen occupying tetrahedral and octahedral sites in FCC Zr_{20} hydrides, respectively.



Supplementary Figure S14. Radial distribution functions between atoms for FCC $Ti_{25}V_{25}Nb_{25}Zr_{25}$ (Zr_{25}) hydrides with (a) H/M=1.2, 1.5, 2 and (b) H/M=2, 2.5, 3; (c) The calculated binding energy as a function of hydrogen content for the FCC Zr_{25} hydrides. The symbols T and O represent hydrogen occupying tetrahedral and octahedral sites in FCC Zr_{25} hydrides, respectively.