Supplementary Information for the paper entitled *"Investigation of superconductivity in compressed vanadium hydrides"*

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Supplementary Information Methods

Here is some details of ELocR (Crystal Structure Analysis by Evolutional Local Random Computational Method) code, which have been illustrated by Y. Li *et al.* before.[1] It is a code for crystal structural prediction combined with *ab initio* energy calculational codes, e.g. VASP, and a special evolutional strategy, and is developing by our group. The method can predict the stable or metastable structures for a given compound when the chemical compositions and external conditions (e.g. pressure) are given. In the first generation, the unit cell is established and restricted by cell volume, cell angles, and axis lengths to the target values. Atoms or atomic groups are distributed uniformly and randomly but must satisfy the criteria of bond length or distance between atoms in the unit cell. The *ab initio* code is utilized in relaxing the configurations to the energetically preferred optimized structure. Subsequently, a certain amount of optimized structures with typical character, for example higher symmetry, lower energy etc. are adopted as the seeds for next generations. Then part of atoms are deviated from the original positions by certain operations, e.g. dandelion operation, and meet certain distribution, e.g. Gaussian distribution. Meanwhile, the structural diversity are enhanced by the adopting of a proportion of configurations mentioned in the first generation. Duplicated the steps described above until the convergence of energy and symmetry have been reached. In addition, the reliability of ELocR has been checked in some reported works.[1,2,3] In the works exploring K_2S and SnH_8,[1,2] the structures predicted by ELocR agree well with that obtained from the well-known USPEX,[4] and the X-ray powder diffractograms of $P6_3/mmc$ (K_2S) we calculated coincide well with reported experiment observation.[1] When performing the research on Ta-H compound, $C222$ (Ta_2H) and $C2$ (Ta_5H) have been predicted by ELocR, and our calculations based on the $C222$ (Ta_2H) and $C2$ (Ta_5H) agree well with the experimentally reported XRD patterns.[3]
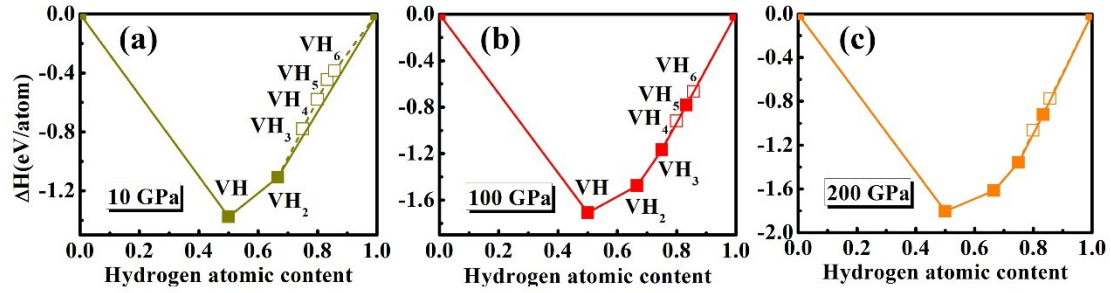
Fig. S1 Calculated formation enthalpies of various vanadium hydrides with respect to V and solid H_2 at (a) 10 GPa, (b) 100 GPa, (c) 200 GPa. Solid symbols indicate that the hydrides are stable at corresponding pressures, while the open signs represent the metastable ones.
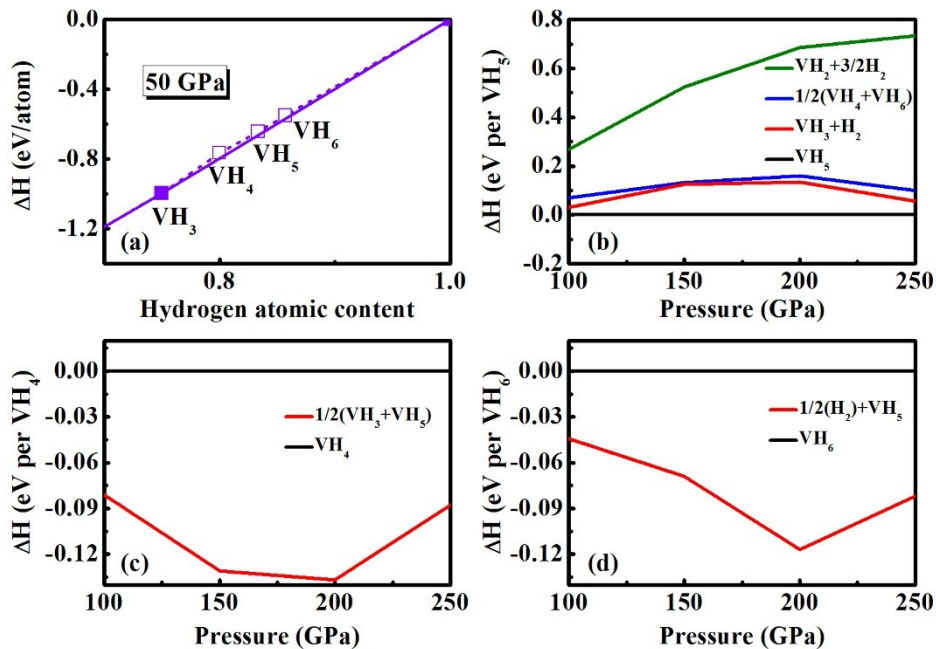

Fig. S2 (a) Magnification of convex hull at 50 GPa. (b, c, d) The formation enthalpies of VH_4, VH_5, VH_6 relative to the adjacent stoichiometries in the pressure ranges of 100 ~ 250 GPa.
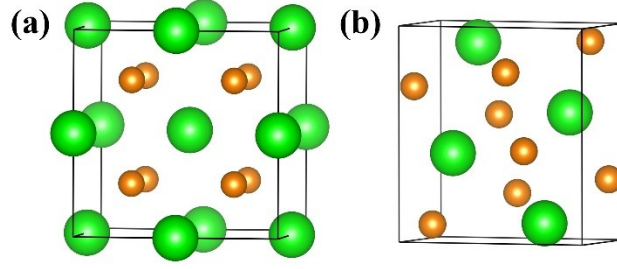
Fig. S3 Crystal structures of VH$_2$. (a) *Fm-3m* at 10 GPa, (b) *Pnma* at 100 GPa. Golden and green spheres denote H and V atoms. The two phases of VH$_2$ we predict here, is consistent with previous works[5].
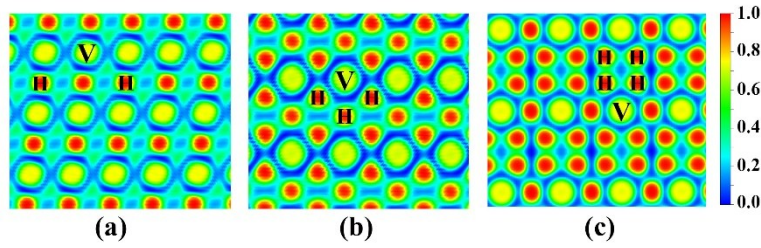

Fig. S4 Electron localization function (ELF) maps of different phases at 150 GPa. (a) *R-3m* (VH), (b) *Fm-3m* (VH$_3$), and (c) *P6/mmm* (VH$_5$).
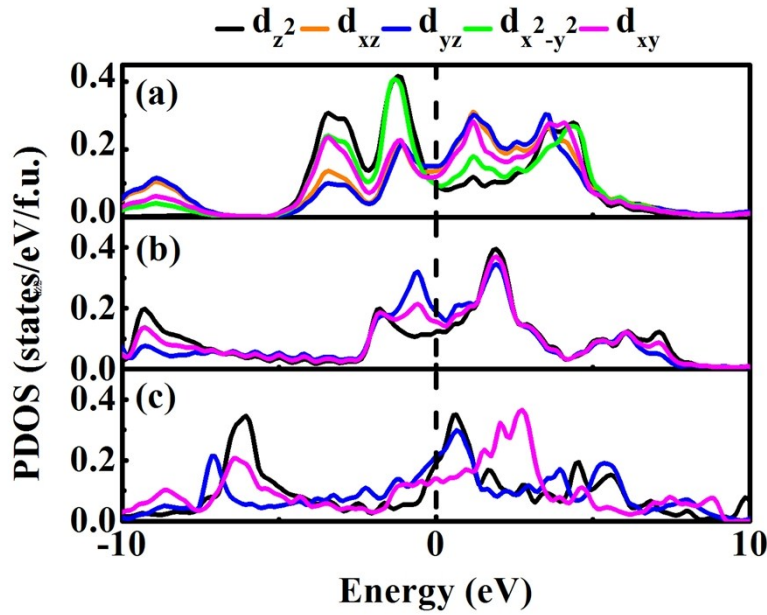

Fig. S5 Projected density of states of decomposed V-3d orbitals (V-d_{z^2}, V-d_{xz}, V-d_{yz}, V-$d_{x^2-y^2}$, V-d_{xy}) at 150 GPa. (a) *R-3m* (VH), (b) *Fm-3m* (VH$_3$), and (c) *P6/mmm* (VH$_5$).

Table S1 Detailed structural information of the V-H compounds predicted at high pressure.

Phase	Pressure (GPa)	Lattice Parameters (Å, °)	Atomic coordinates			
$R\text{-}3m$ (VH)	150	$a=b=c=2.375$	H(1b)	-0.500	-0.500	-0.500
		$\alpha=\beta=\gamma=65.81$	V(1a)	-1.000	0.000	-1.000
$Fmmm$ (VH$_3$)	100	$a=7.373$	H(16l)	-0.874	-0.750	0.750
		$b=5.518$	H(8h)	-0.500	-0.321	0.500
		$c=5.692$	H(8g)	-0.888	-0.500	0.500
		$\alpha=\beta=\gamma=90.00$	H(16n)	-0.699	-0.500	0.647
			V(8e)	-0.250	-0.250	0.000
			V(8i)	-0.500	-0.500	0.739
$Fm\text{-}3m$ (VH$_3$)	150	$a=b=c=3.800$	H(4b)	-0.500	-0.500	-0.500
		$\alpha=\beta=\gamma=90.00$	H(8c)	-0.250	-0.250	-0.250
			V(4a)	0.000	0.000	0.000
$P6/mmm$ (VH$_5$)	150	$a=b=2.516$	H(4h)	0.333	0.667	0.220
		$c=3.217$	H(1a)	0.000	0.000	0.000
		$\alpha=\beta=90.00$	V(1b)	0.000	0.000	0.500
		$\gamma=120.00$				

Table S2 Comparison of nearest H-H separations in V-H compound and molecular H$_2$.

Phase	Pressure (GPa)	Shortest H-H separations in V-H compound	Shortest bonding H-H separations in H$_2$
$R\text{-}3m$ (VH)	150	2.36	0.74
	200	2.30	0.75
	250	2.26	0.75
$Fm\text{-}3m$ (VH$_3$)	150	1.63	0.74
	200	1.60	0.75
	250	1.57	0.75
$P6/mmm$ (VH$_5$)	150	1.41	0.74
	200	1.34	0.75
	250	1.29	0.75

Table S3 The remnant number of valence electrons on V and H atoms based on the Bader charge analysis in *R-3m* (VH), *Fm-3m* (VH$_3$), and *P6/mmm* (VH$_5$) at the pressure of 150 GPa. σ(e) represents the electrons transferred from V to H.

	Atom	Number of valence electrons	σ(e)
R-3m (VH)	V	12.4393	0.5607
	H1	1.5607	-0.5607
Fm-3m (VH$_3$)	V	11.8529	1.1471
	H1	1.4629	-0.4629
	H2	1.4623	-0.4623
	H3	1.2212	-0.2212
P6/mmm (VH$_5$)	V	12.0086	0.9914
	H1	1.2300	-0.2300
	H2	1.1970	-0.1970
	H3	1.1771	-0.1771
	H4	1.1837	-0.1837
	H5	1.2036	-0.2036

References

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