Supplementary Information

Discovery of a Silicon-based Ferrimagnetic Wheel Structure in $V_xSi_{12}^-$ (x = 1-3) Clusters: Photoelectron Spectroscopy and Density Functional Theory Investigation

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Table S1. On-site charge and on-site spin moment on V atoms and Si atoms (average values) in $V_xSi_{12}^-$ (x=1, 2, 3) clusters from Mulliken population analysis. The values from Hirshfeld analysis are given in the parenthesis for reference.

	Charge (e)		Spin (μ_B)	
	V	Si	V	Si
VSi_{12}^-	−0.466 (−0.108)	−0.044 (−0.074)	0 (0)	0 (0)
$V_2Si_{12}^-$	−0.459, −0.049 (−0.173, 0.078)	−0.041 (−0.075)	−0.192, 0.733 (−0.114, 0.589)	0.038 (0.044)
$V_3Si_{12}^-$	0.090, −0.641, 0.091 (0.094, −0.200, 0.094)	−0.045 (−0.082)	2.399, −0.600, 2.413 (2.038, −0.333, 2.051)	−0.018 (0.020)

Table S2. V-V, Si-V, and Si-Si bond lengths (Å) in $V_xSi_{12}^-$ (x=1, 2, 3) and V_3Si_{12} clusters (V_i denotes the interior V atom, V_s denotes the surface V atoms).

	V_i-V_s	Si-V_i	Si-V_s	Si-Si
VSi_{12}^-	–	2.643	–	2.357, 2.391
$V_2Si_{12}^-$	2.213	2.661	2.573, 2.740	2.441, 2.538
$V_3Si_{12}^-$	2.271	2.682	2.707	2.443, 2.547

Table S3. Cartesian coordinates (Å) for $V_xSi_{12}^-$ (x=1, 2, 3) clusters.

Atom	X	Y	Z
	VSi_{12}^-		
Si	1.1793	-1.1938	2.0287
Si	-1.2270	1.1279	2.0383
Si	1.1278	1.1963	2.0782
Si	-2.3953	1.1445	-0.0095
Si	2.3953	-1.1445	0.0095
Si	-1.1761	-1.2624	2.0111
Si	2.3247	1.2447	0.0478
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Si	1.2270	-1.1279	-2.0383
Si	1.1761	1.2624	-2.0111
Si	-1.1278	-1.1963	-2.0782
V	0	0	0
	$V_2Si_{12}^-$		
Si	0.6479	-1.1371	2.4099
Si	-0.7194	0.9655	2.3372
Si	1.7030	1.0387	1.7142
Si	-2.4544	0.8686	0.6470
Si	2.3145	-1.1985	0.6698
Si	-1.6445	-1.3180	1.6678
Si	2.4083	1.0121	-0.6113
Si	-2.2519	-1.2880	-0.7162
Si	-1.7562	1.0141	-1.6765
Si	1.7071	-1.1743	-1.7147
Si	0.6675	1.0855	-2.2967
Si	-0.5919	-1.0781	-2.4497
V	0	0	0
V	0.0546	-2.2121	-0.0397
	$V_3Si_{12}^-$		
Si	0.6280	-1.1315	2.3365
Si	-0.7031	1.0432	2.3579
Si	1.6794	1.1231	1.7630
Si	-2.4085	1.0346	0.6115
Si	2.3929	-1.0506	0.6500
Si	-1.7368	-1.1841	1.6644

Si	2.3561	1.1704	-0.5719
Si	-2.3405	-1.1423	-0.6895
Si	-1.7344	1.1032	-1.7229
Si	1.7911	-1.0395	-1.7048
Si	0.6498	1.1581	-2.3185
Si	-0.5734	-1.0771	-2.3751
V	-0.0543	2.2698	0.0392
V	0	0	0
V	0.0538	-2.2702	-0.0396

Table S4. Comparison of VDEs (eV) of $V_xSi_{12}^-$ (x=1, 2, 3) clusters from experiment and DFT calculations using PBE, RPBE and M06-L functional. DMol^3 program and DND basis set were used for PBE and RPBE, while Gaussian09 program and 6-311+G(d) basis set were used for PBE, M06-L, and M06.

Cluster	Expt. (eV)	PBE/DND	RPBE/DND	PBE/ 6-311+G(d)	M06-L/ 6-311+G(d)	M06/ 6-311+G(d)
VSi_{12}^-	3.82±0.08	3.94	3.89	3.86	3.79	3.82
$V_2Si_{12}^-$	3.66±0.08	3.75	3.72	3.69	3.67	3.81
$V_3Si_{12}^-$	2.59±0.08	2.54	2.53	2.51	2.49	2.54

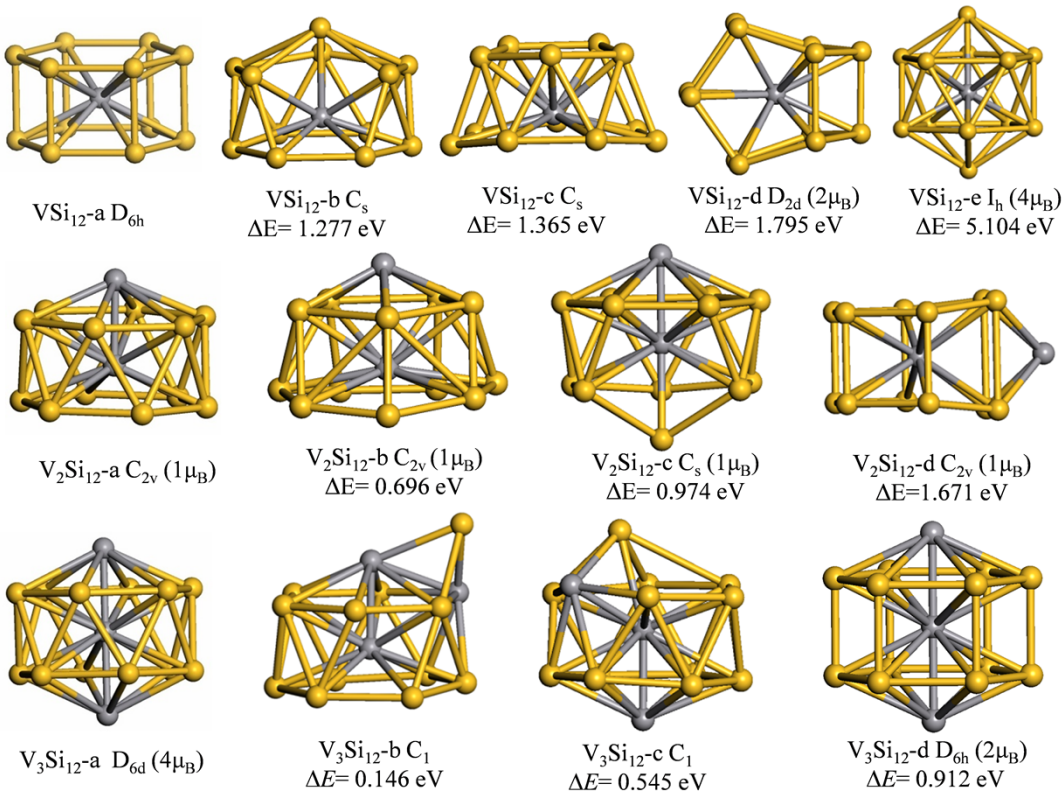

Figure S1. Low-lying isomer structures of $V_xSi_{12}^-$ (x=1, 2, 3) clusters. For each isomer, its energy difference to the ground state (a) is provided. For the magnetic clusters, their magnetic moments are given in parenthesis.

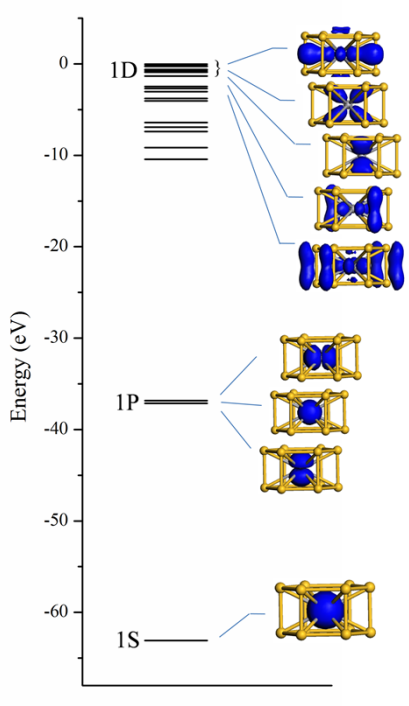

Figure S2. Energies and spatial distributions of selected molecular orbitals for VSi_{12}^- cluster, showing $1S^1P^31D^5$ electron shell.

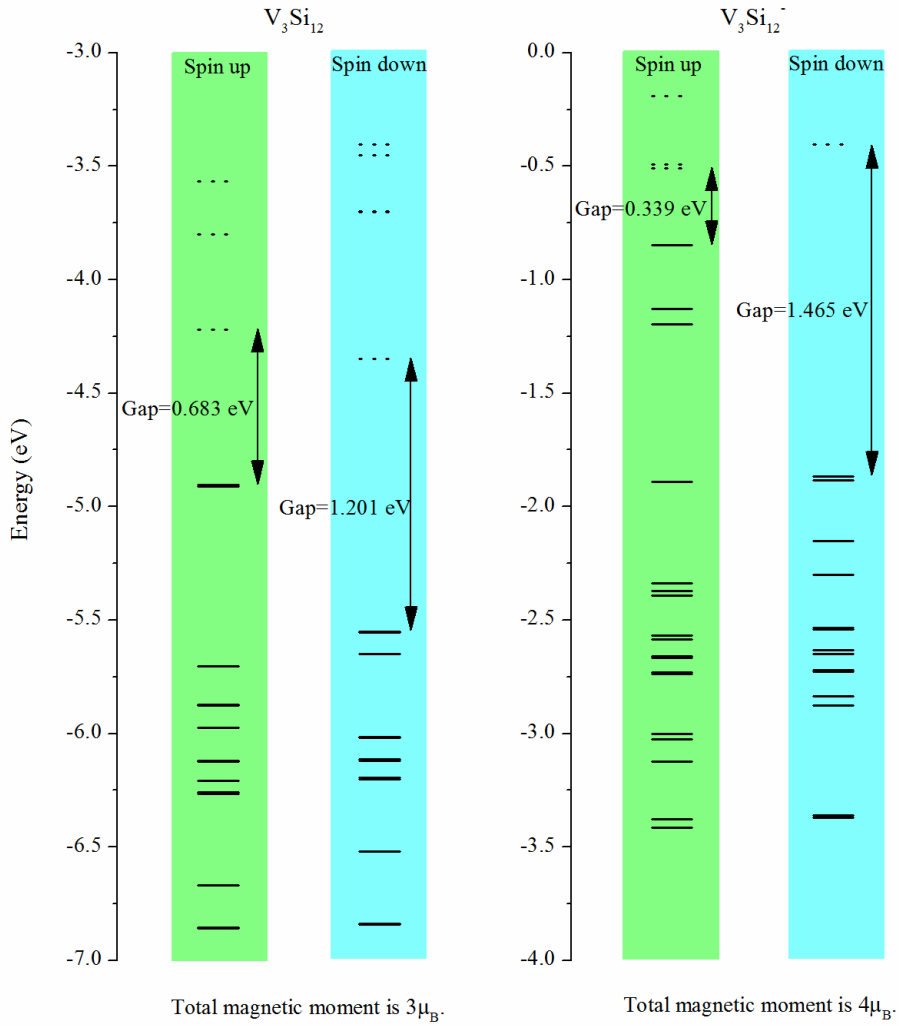

Figure S3. Spin-polarized energy levels for V_3Si_{12} and $V_3Si_{12}^-$ clusters. The solid lines are occupied levels and the dashed lines are unoccupied levels. A moderate HOMO-LUMO gap of 0.339 eV is obtained for the closed-shell $V_3Si_{12}^-$ cluster.

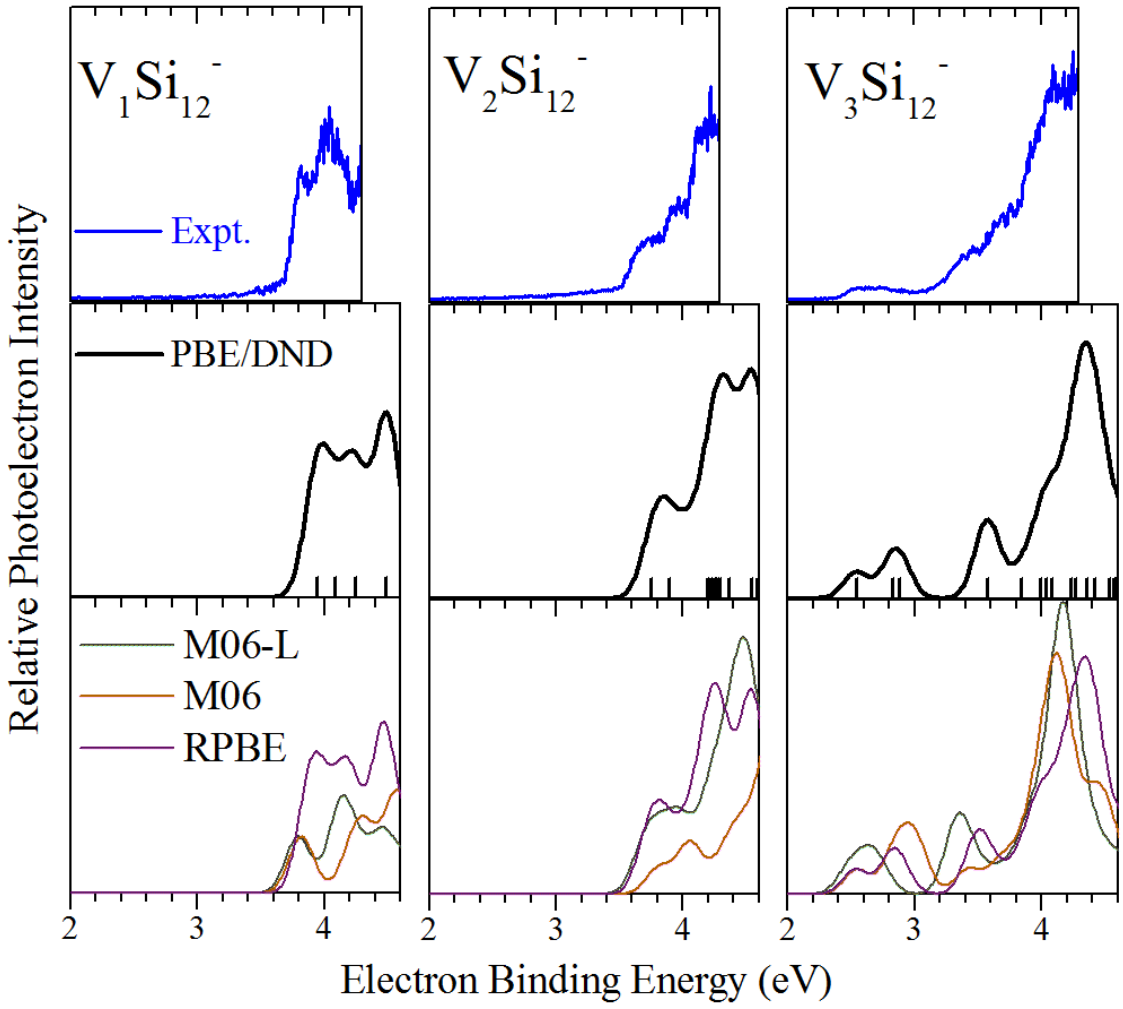

Figure S4. Comparison of photoelectron spectra of $V_xSi_{12}^-$ (x=1, 2, 3) clusters from experiment (upper panels) and DFT calculations using PBE/DND (middle panels), RPBE/DND (lower panels), M06/6-311+G(d) (lower panels), and M06-L/6-311+G(d) (lower panels). DMol^3 program was used for the PBE and RPBE functionals with DND basis set and Gaussian09 program was used for M06 and M06L functionals with 6-311+G(d) basis set. In the theoretical spectra, a uniform Gaussian broadening of 0.1 eV was chosen.