Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Geometry Controls the stability of $FeSi_{14}$ Cluster

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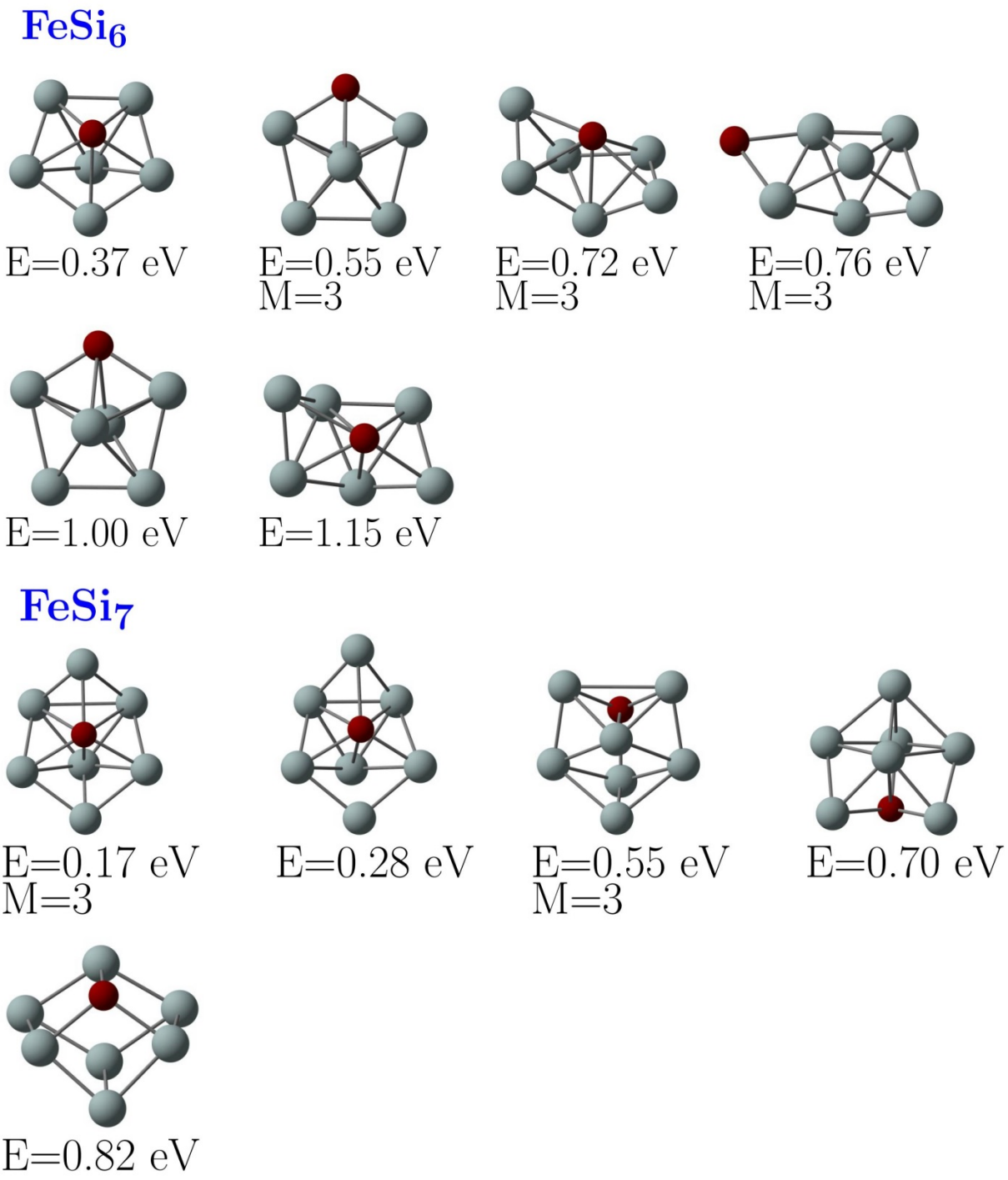

Fig. S1. (a) Higher energy isomers of $FeSi_n$ (n=6 and 7) clusters. Energy is given with respect to ground state structure. M stands for multiplicity (2S+1) of cluster.

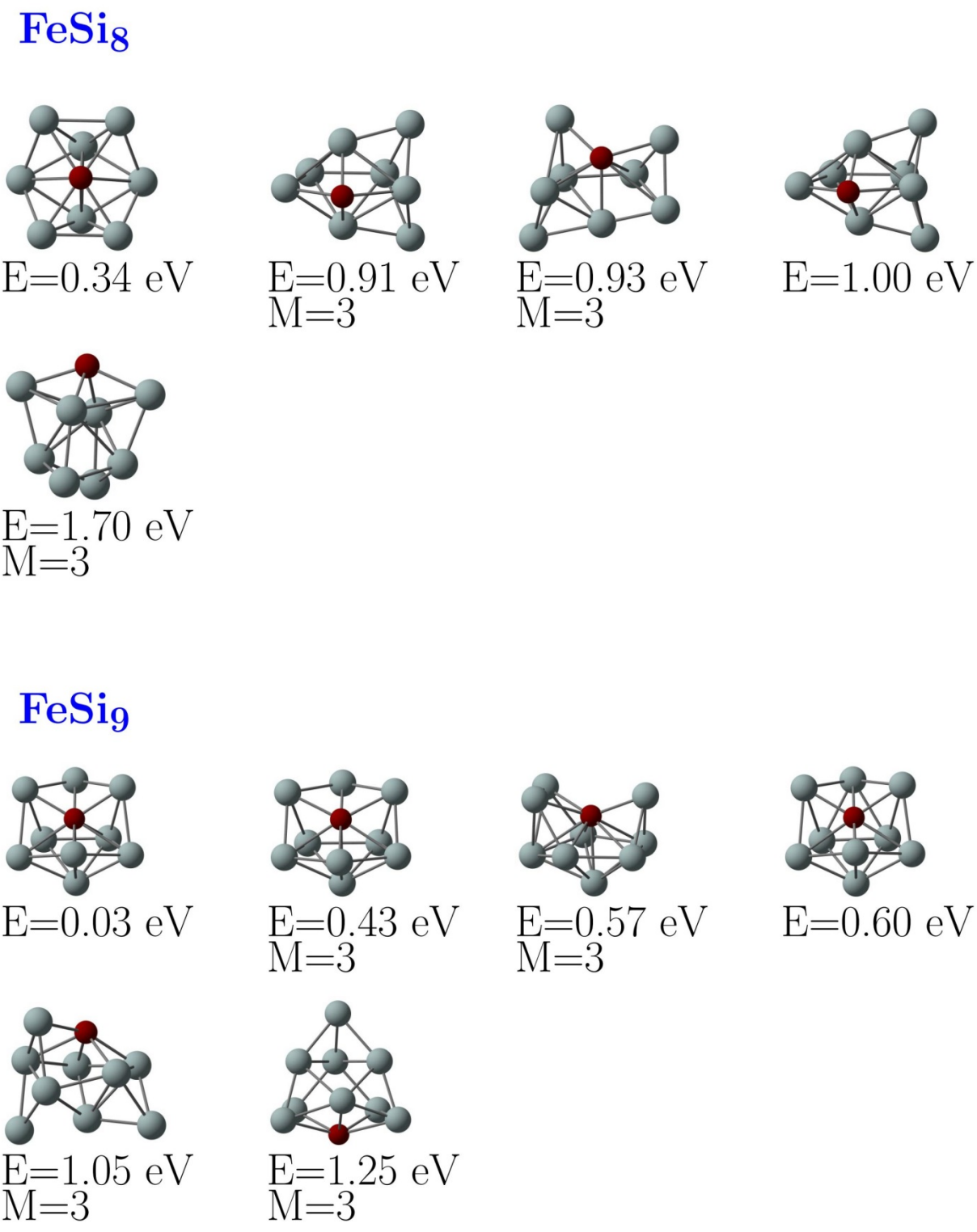

Fig. S1. (b) Higher energy isomers of $FeSi_n$ (n=8 and 9) clusters.

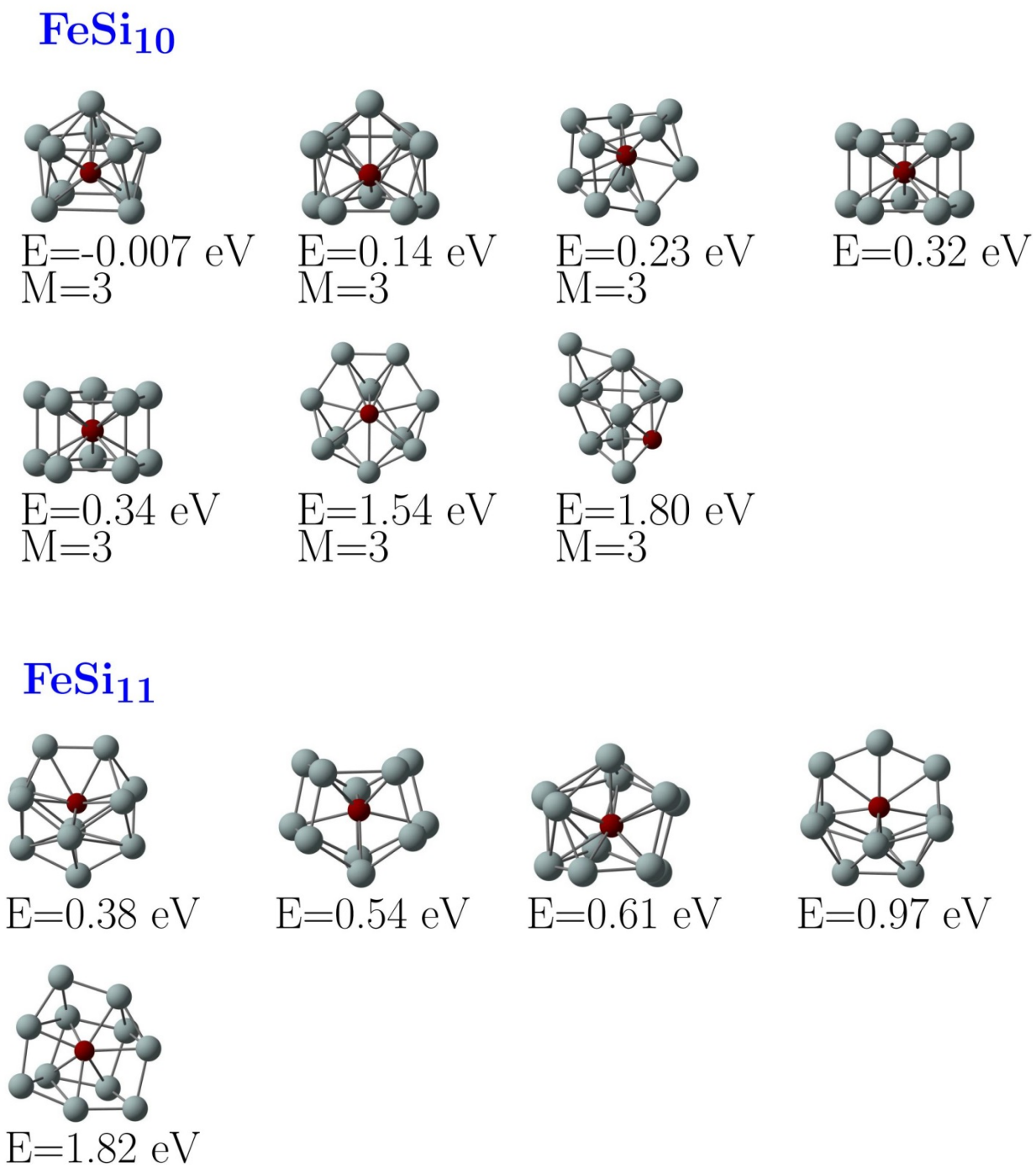

Fig. S1. (c) Higher energy isomers of $FeSi_n$ (n=10 and 11) clusters.

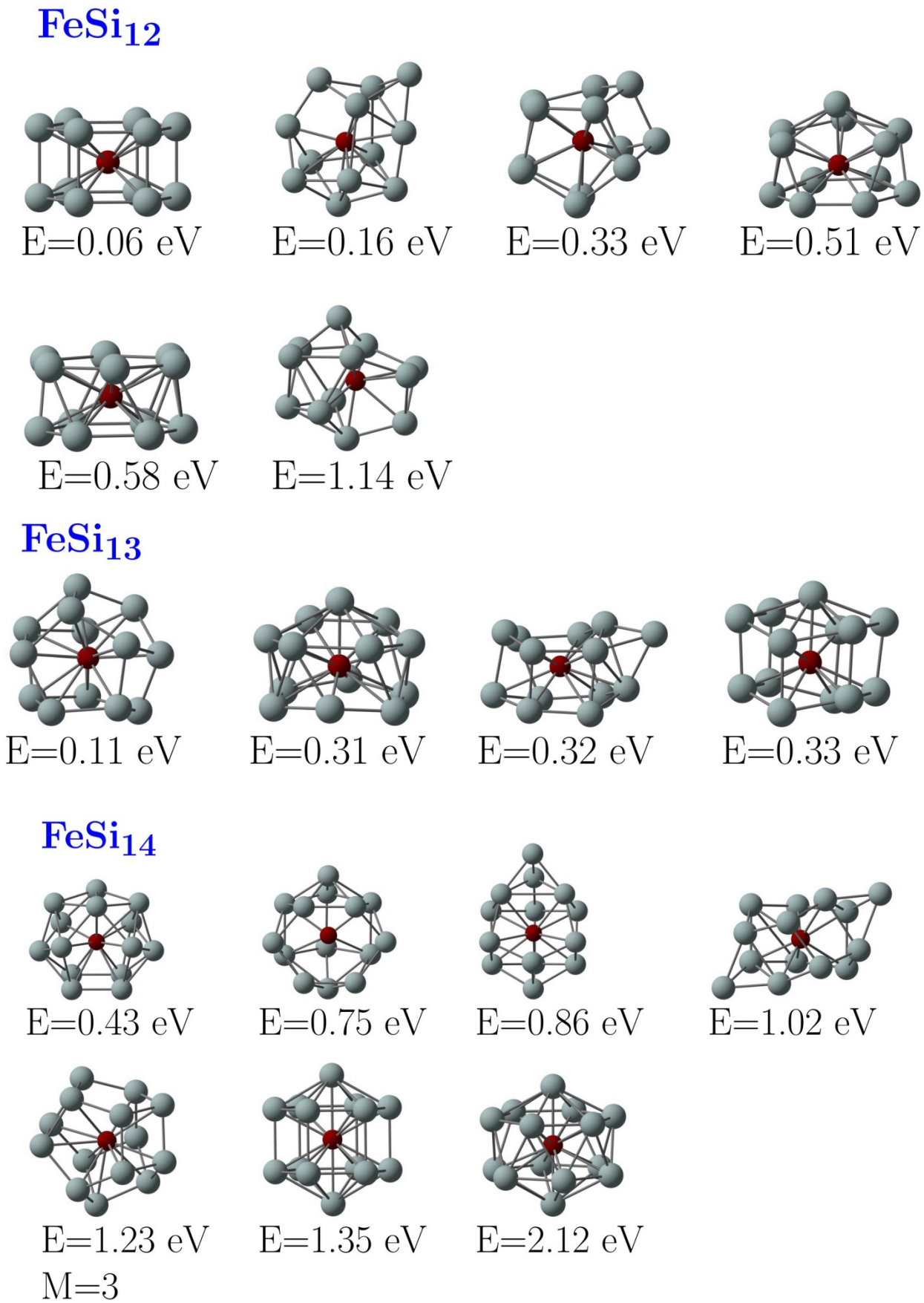

Fig. S1. (d) Higher energy isomers of $FeSi_n$ (n=12-14) clusters.

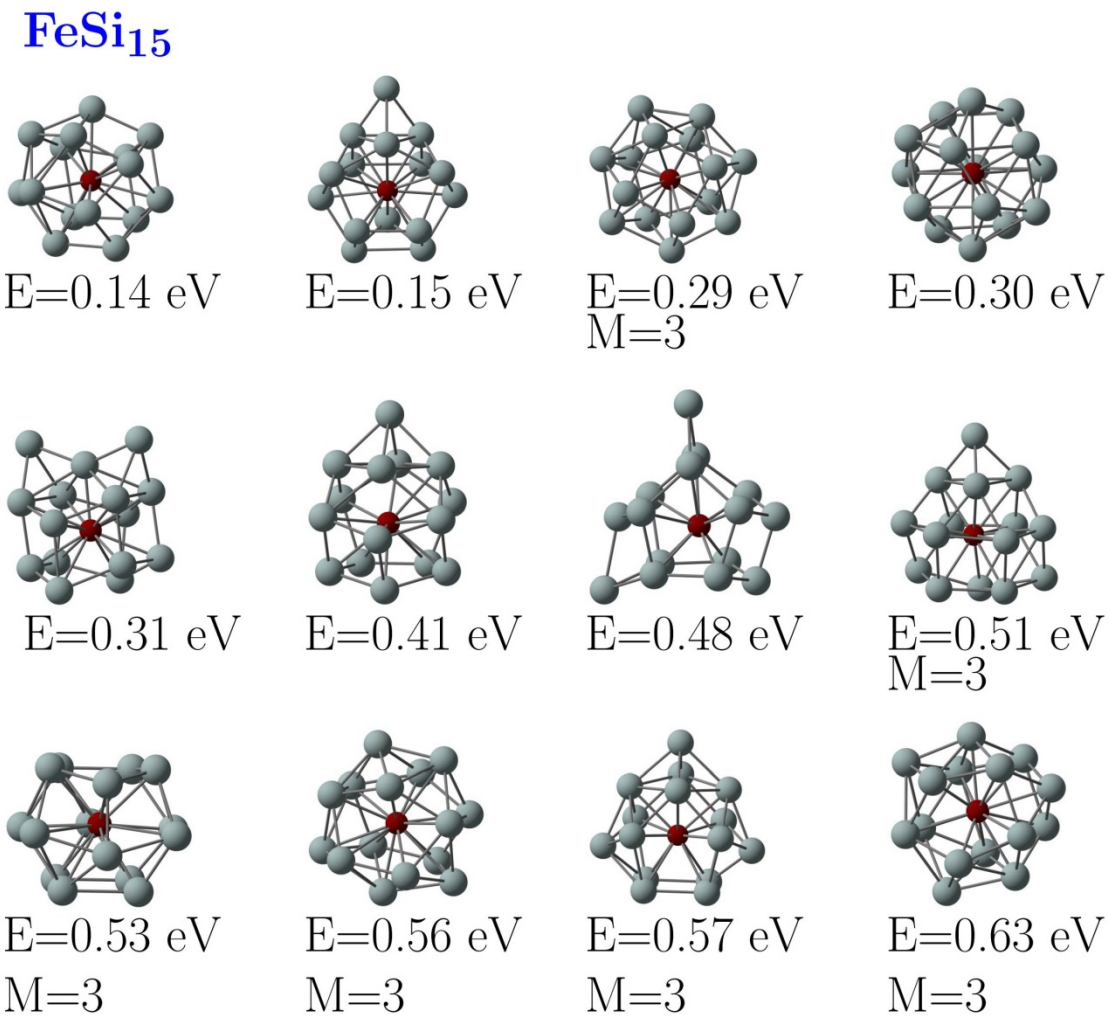

Fig. S1. (e) Higher energy isomers of $FeSi_{15}$ cluster.

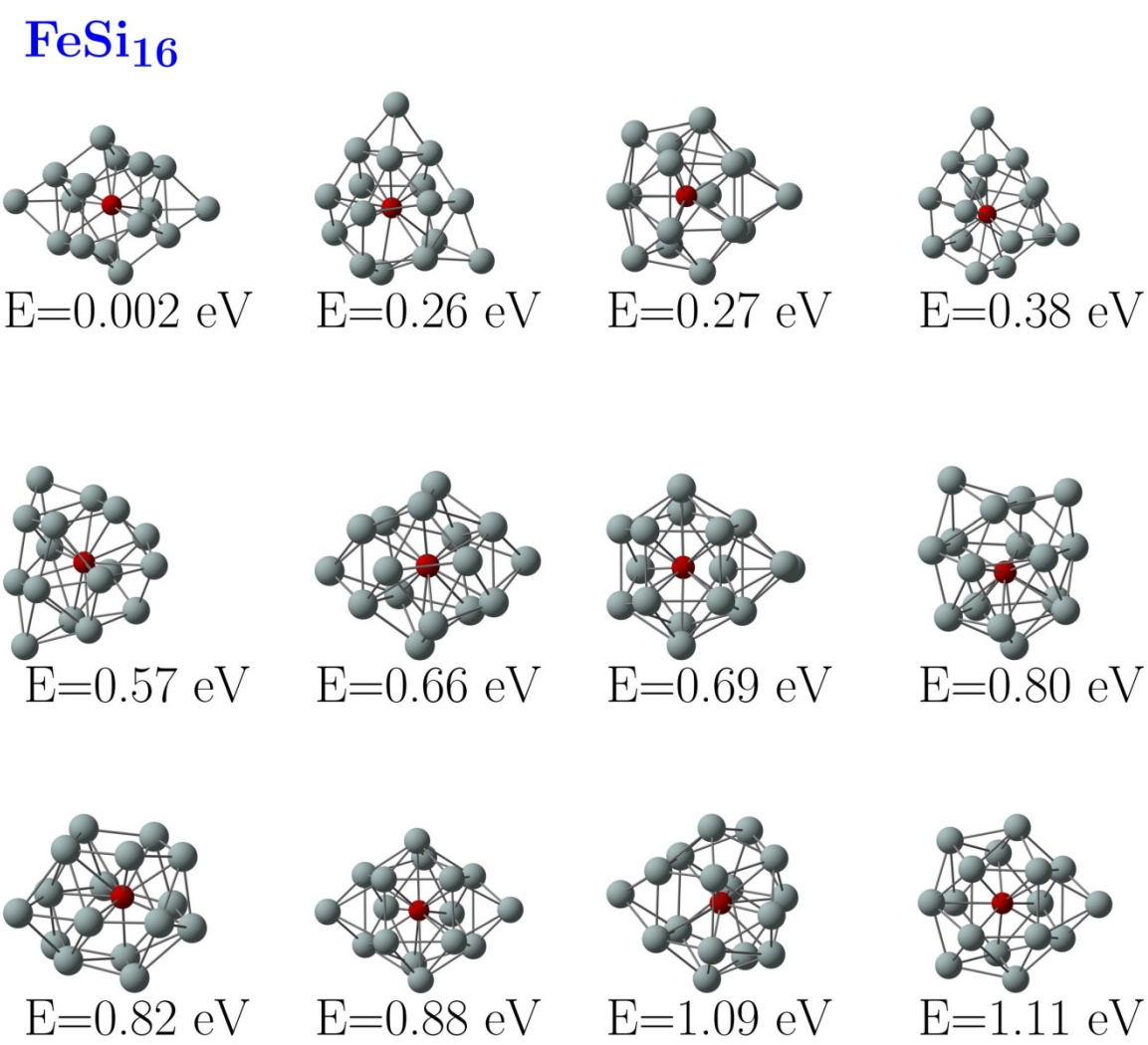

Fig. S1. (f) Higher energy isomers of $FeSi_{16}$ cluster.

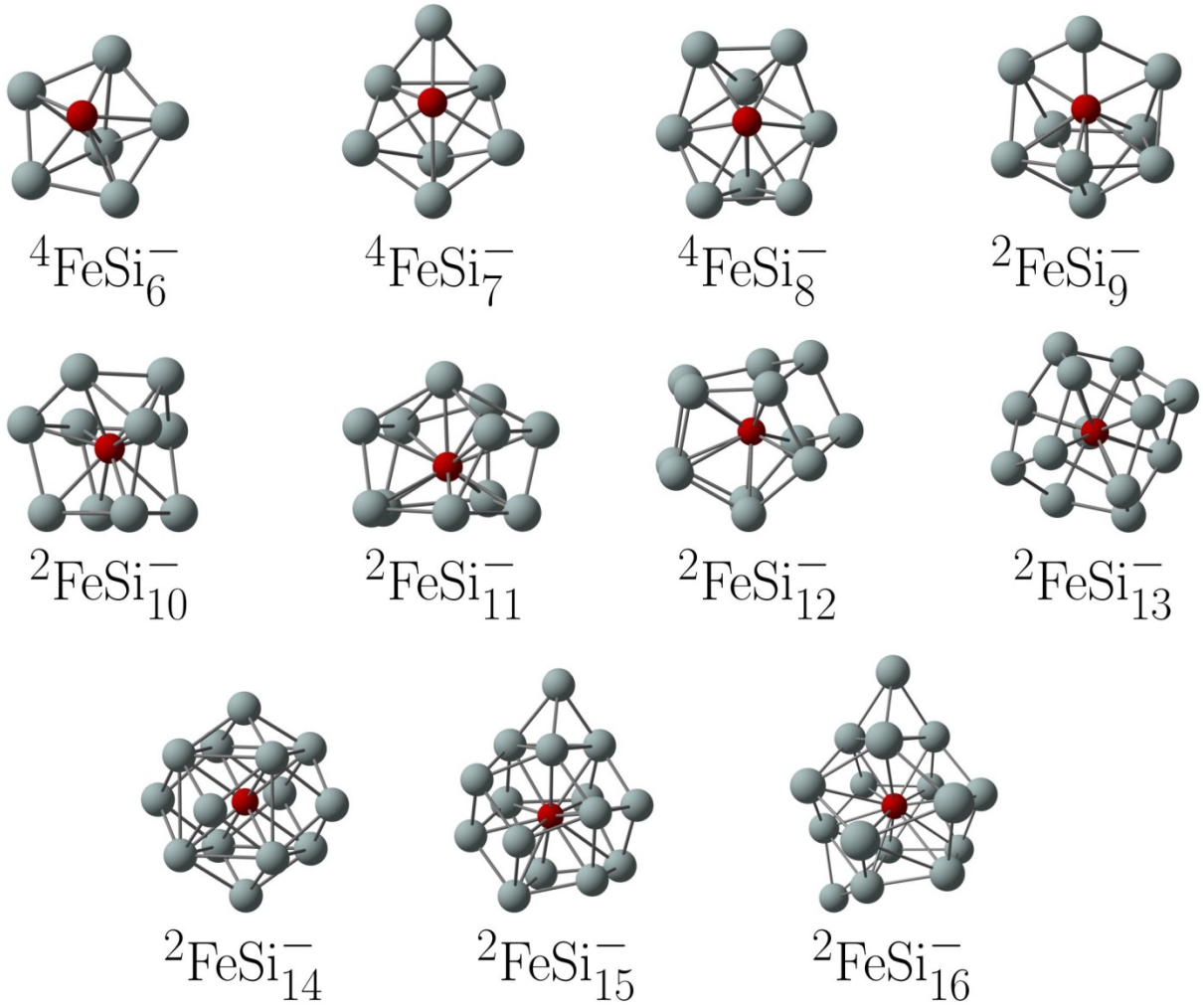

Fig. S2. Ground State Structures of $FeSi_n^-$ clusters.

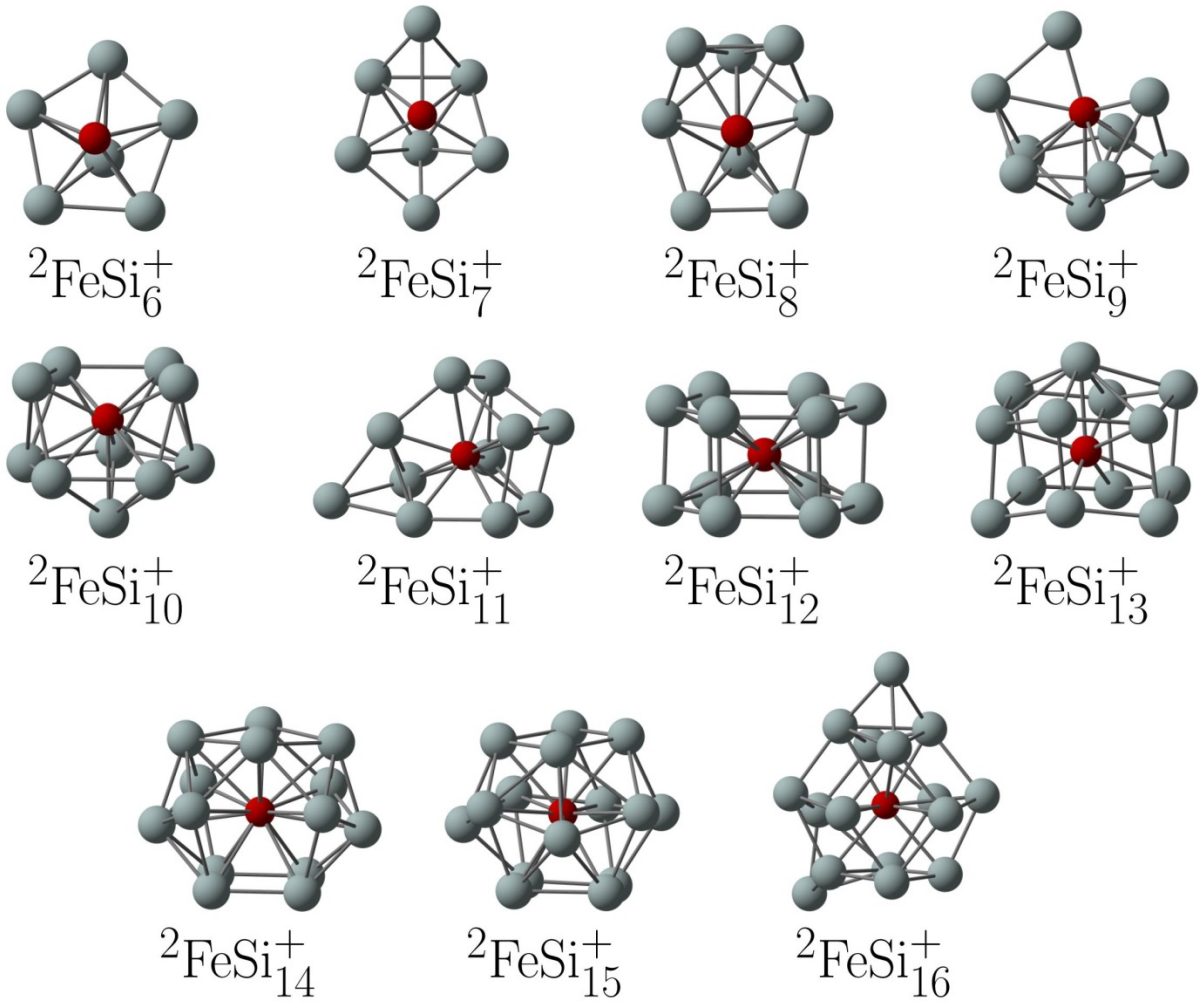

Fig. S3. Ground State Structures of $FeSi_n^+$ clusters.

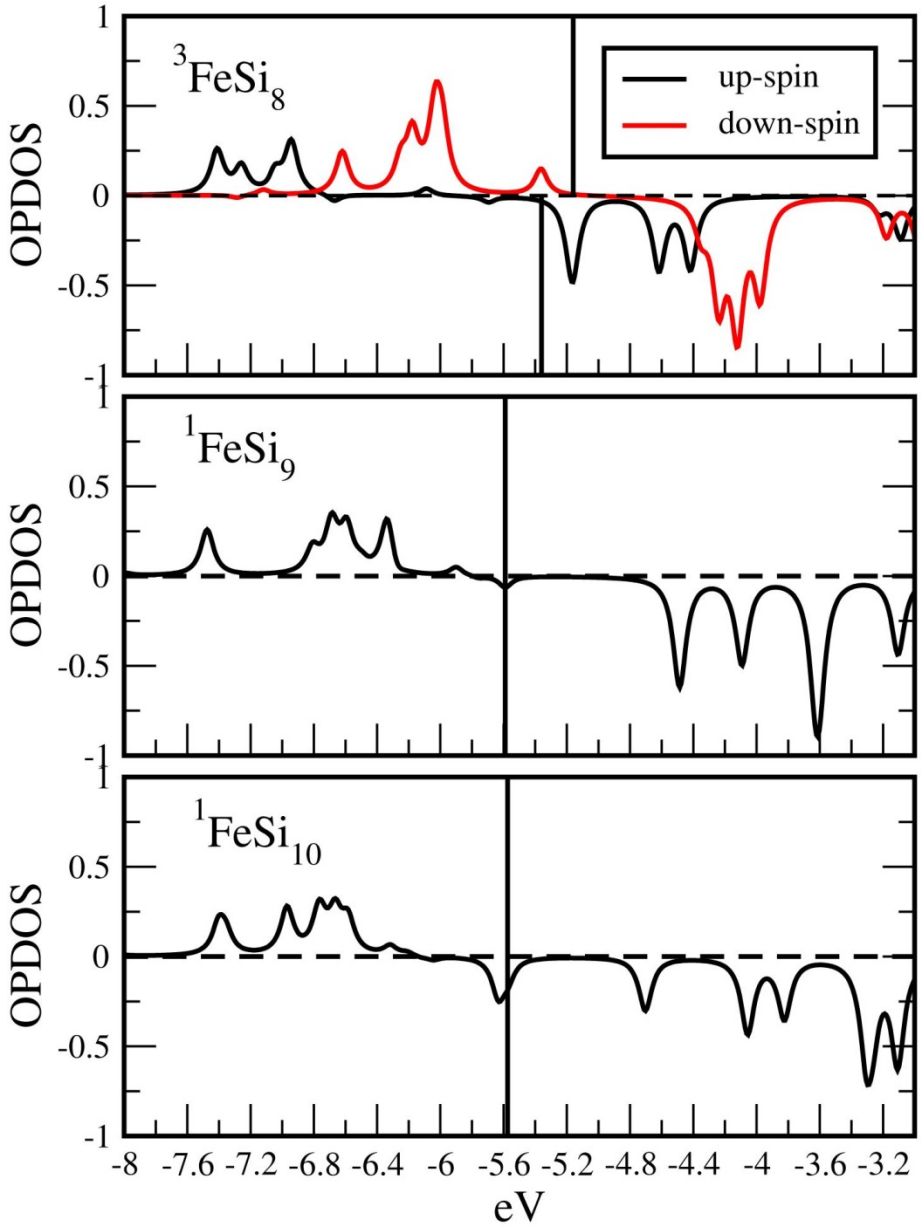

Fig. S4. The overlap partial density of states (OPDOS) between Fe d- and Si-p states for $FeSi_n$ (n=8-10) clusters

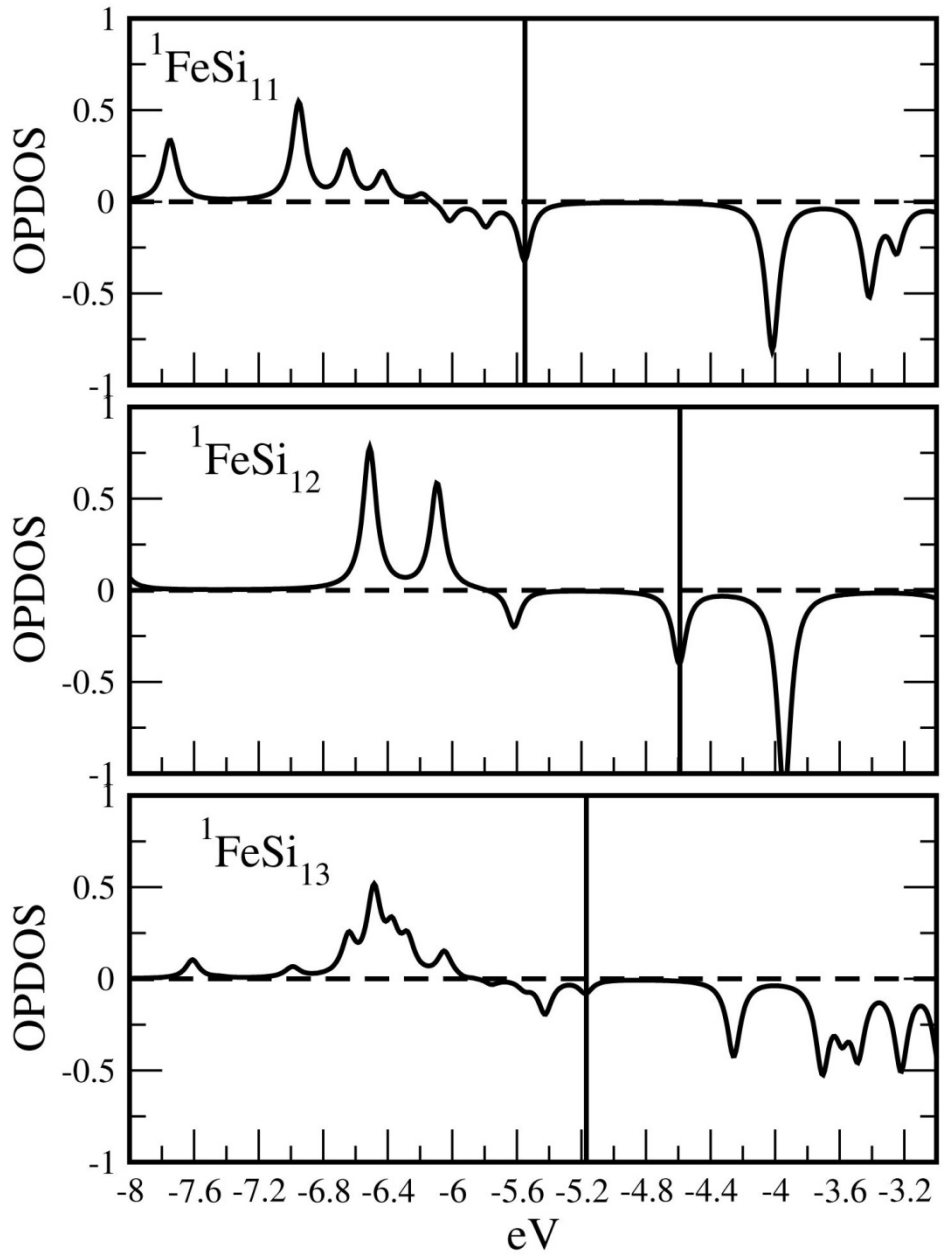

Fig. S5. The overlap partial density of states (OPDOS) between Fe d- and Si-p states for $FeSi_n$ (n=11-13) clusters.

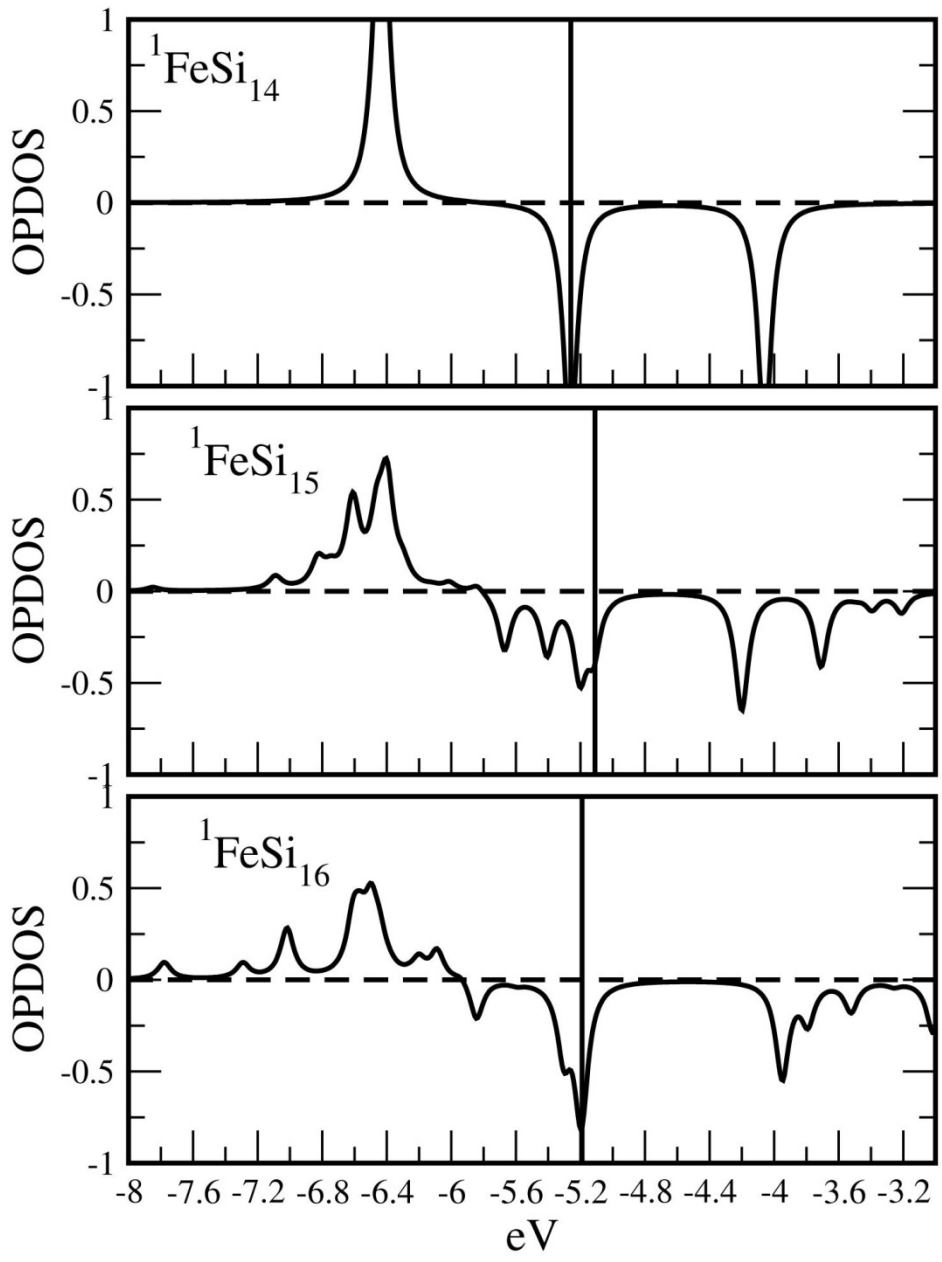

Fig. S6. The overlap partial density of states (OPDOS) between Fe d- and Si-p states for $FeSi_n$ (n=14-16) clusters.

Cartesian Coordinate(Å)of Ground State Structures of neutral $FeSi_n$(n=6-16)clusters

$FeSi_6$

```
7
XYZ
Si -0.020948 -1.640819  0.790278
Si  1.931175 -0.402536 -0.445166
Si  0.047191 -1.07824 -1.765714
Si -1.943594 -0.403763 -0.486007
Si -1.119247  0.625783  1.513221
Si  1.218964  0.500402  1.597145
Fe -0.067699  0.931604 -0.643958
```

$FeSi_7$

```
8
XYZ
Si  0.827946  1.558666  0.862566
Si -0.697046 -0.276624  1.545486
Si  2.535729  0.810364 -0.579524
Si  1.492946 -0.949884  0.582059
Si -0.372079 -1.898237 -0.608287
Si -2.298457 -0.509107 -0.315814
Fe  0.200749  0.238599 -1.140248
Si -1.307581  1.667957 -0.232995
```

$FeSi_8$

```
9
XYZ
Fe  0.002281 -0.391519 -0.746824
Si  0.002117  2.010606 -0.380473
Si  0.001307 -1.584923  1.380017
Si  2.021394  0.830551 -1.053986
Si  2.015513 -1.376972  0.010611
Si -2.016707  0.829956 -1.052723
Si -2.011947 -1.374178  0.011334
Si -1.253448  0.62753  1.348771
Si  1.2545  0.623374  1.342533
```

$FeSi_9$

```
10
XYZ
Fe -1.420391  1.582325 -0.335221
Si -2.136179  3.870943 -0.90038
Si  0.156507  3.459636 -0.602364
Si  0.508389  1.63626  0.955463
Si -1.782483  0.778716  1.615277
Si -3.460289  2.341438  0.441994
Si -0.921827  2.600147 -2.712189
Si  0.635906  1.104076 -1.529089
Si -3.147226  1.780576 -2.020173
Si -1.475137  0.030709 -2.028459
```

$FeSi_{10}$

```
11
XYZ
Fe  0.151894  0.107639  0.142314
Si -2.412417 -0.29779  0.180004
Si  2.248867 -0.901924  0.065206
Si -0.913016 -2.095288 -0.305786
Si  1.999616  1.462749 -0.157617
Si  0.015374  2.154664 -1.275842
Si  0.483031 -1.586106  1.643748
Si -1.073523  0.272976  2.115808
Si -0.072787  2.194181  1.107058
Si  0.826609 -1.461727 -1.81272
Si -1.09218  0.052796 -1.84453
```

$FeSi_{11}$

```
12
XYZ
Fe -1.198941  1.508793 -1.215254
Si -3.276805  1.427035 -0.184607
Si -2.129684  3.502501 -0.383246
Si  0.076551  2.901569  0.452382
Si  0.582896  0.565229 -0.007806
Si -1.592551 -0.400619  0.048416
Si -3.977207 -0.93089 -0.272706
Si -1.529218  3.485487 -2.74087
Si  0.640278  3.127621 -1.842613
Si  0.919363  0.837799 -2.403553
Si -2.696127  0.004424 -2.153908
Si -1.195655  1.214853 -3.548919
```

$FeSi_{12}$

```
13
XYZ
Fe -1.067133 -1.627899  0.245696
Si  1.595633 -2.083111 -0.334893
Si  0.889787 -0.612563  1.350989
Si -0.114861  0.933849 -0.163858
Si  0.152939 -0.792233 -1.731011
Si -0.936543 -0.632836  2.825489
Si -2.07372  0.472897  1.042554
Si -2.281166 -2.460091  2.223763
Si -3.733266 -1.172977  0.833574
Si -0.057657 -3.733633 -0.549979
Si -2.016593 -4.188664  0.658768
Si -3.02243 -2.641681 -0.853923
Si -1.195949 -2.617202 -2.32532
```

$FeSi_{13}$

```
14
XYZ
Fe -1.110956 -1.426822  0.064671
```

Si 1.363431 -1.927302 -0.051411
Si 0.682015 -0.344569 1.58287
Si 0.560103 0.511956 -0.601305
Si 0.366612 -1.210111 -2.263232
Si -1.539308 -0.394846 2.412451
Si -2.63867 0.679921 0.590927
Si -2.157924 -2.64099 2.284742
Si -3.633503 -1.389244 0.917038
Si 0.088961 -3.488454 -1.374754
Si -1.013972 -3.997051 0.732306
Si -2.976153 -3.154947 -0.457822
Si -1.871063 -2.018938 -2.265615
Si -1.635619 0.405391 -1.618552

$FeSi_{14}$

15
XYZ
Fe -1.075798 0.946164 -1.179414
Si -0.0667 0.943343 -3.578767
Si 1.361774 1.85429 -1.096787
Si 0.360638 -0.574937 0.368445
Si -1.067592 -1.482904 -2.11517
Si -2.515212 2.46945 -2.72474
Si -3.515857 0.041481 -1.264766
Si -2.083388 0.948646 1.221104
Si -1.085882 3.377438 -0.243161
Si -3.24587 2.297459 -0.419842
Si 1.09528 -0.404712 -1.933923
Si 0.192513 1.752311 1.020657
Si -0.188784 3.099441 -2.478549
Si -1.968003 -1.207026 0.119598
Si -2.343394 0.142753 -3.381695

$FeSi_{15}$

16
XYZ
Fe 0.013242 -0.052162 -0.061823
Si 0.807369 1.82569 1.487245
Si 2.60893 0.800631 0.188436
Si 1.928027 -1.303904 1.262677
Si -0.982924 -2.130406 1.239445
Si -2.652197 -0.690691 0.145934
Si -1.674783 1.12421 1.465978
Si 1.071073 1.719184 -1.505358
Si 1.907146 -0.930625 -1.434236
Si 0.798047 -2.823241 -0.33032
Si -1.123375 -1.789347 -1.456666
Si -1.796409 0.909376 -1.525778
Si -0.749555 2.650521 -0.215413
Si -0.457878 1.498019 3.563453
Si 0.031047 -0.049138 -2.760512
Si 0.13441 -0.557793 2.581221

$FeSi_{16}$

```
17
XYZ
Fe -0.496623  0.387088 -0.900522
Si -2.060748  2.420174 -0.255418
Si -0.456479  2.891648 -1.995546
Si  0.582625  2.538221  0.188018
Si -0.938307  1.336834  1.627078
Si  0.075326 -0.81378  1.272077
Si -2.545447 -0.28894  0.689569
Si  1.920224  0.60075 -0.169426
Si -1.354514 -2.130306 -0.309171
Si  2.51322 -1.367263  0.992518
Si  1.506648  1.434683 -2.335779
Si -2.956937  0.57399 -1.466336
Si  0.780828 -0.76201 -3.015535
Si -3.259305 -0.081952 -3.70956
Si -1.001579  0.968475 -3.3351
Si -1.517997 -1.369917 -2.569332
Si  0.975652 -1.786372 -0.863011
```

$FeSi_n$ clusters	HL gap (eV)	ΔSi (eV)	ΔFe (eV)	VIP (eV)	AIP (eV)	$FeSi_n^-$	
						ADE (eV)	VDE (eV)
$FeSi_6$	0.91		3.24	7.50	6.94	2.56	2.74
$FeSi_7$	0.63	4.31	3.14	7.08	6.74	2.66	2.83
$FeSi_8$	0.81	3.98	4.11	7.15	6.60	2.81	2.98
$FeSi_9$	1.10	4.73	4.49	7.58	7.42	2.76	2.84
$FeSi_{10}$	0.87	4.29	4.13	7.18	6.91	3.08	3.31
$FeSi_{11}$	1.53	4.43	5.49	7.37	7.23	2.53	3.19
$FeSi_{12}$	0.65	3.78	5.22	6.35	6.27	2.81	3.17
$FeSi_{13}$	0.92	3.84	5.59	7.05	6.49	2.84	3.13
$FeSi_{14}$	1.20	4.78	6.03	7.07	6.88	2.53	2.67
$FeSi_{15}$	0.91	3.90	5.79	7.00	6.60	2.73	2.86
$FeSi_{16}$	1.24	4.03	6.67	6.91	6.73	2.55	2.71

Tab. S1. The HL gap, Si binding energy, IP's and Fe embedding energy values of the $FeSi_n$ clusters. All the values are given in eV.

Cluster	Fe d-state Contribution (%)					
		d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
$^3FeSi_8$	Majority	82.60	82.37	92.30	81.07	80.38
	Minority	41.20	47.58	33.13	47.89	64.59
$^1FeSi_9$		62.32	66.33	66.63	71.19	59.32
$^1FeSi_{10}$		65.68	60.48	65.93	65.95	69.83
$^1FeSi_{11}$		66.71	64.50	62.41	64.98	68.94
$^1FeSi_{12}$		94.23	60.51	60.45	63.45	62.69
$^1FeSi_{13}$		64.23	65.19	64.51	66.98	63.28
$^1FeSi_{14}$		68.52	74.66	59.35	61.22	74.68
$^1FeSi_{15}$		64.06	71.68	69.34	61.22	64.72

Tab. S2. The Fe 3d-state contributions in the $FeSi_n$ clusters obtained from Mulliken population analysis. All the values are given in percentage.

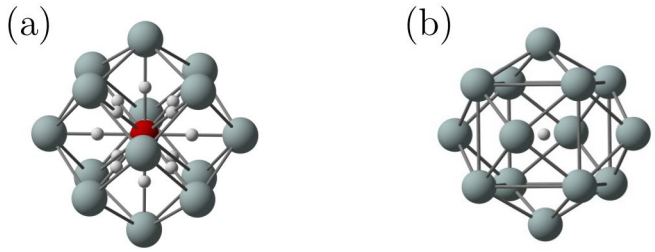

Fig. S7. (a) The (3,-1) bond critical points between Fe and Si in $FeSi_{14}$ (b) (3,3) cage critical point in Si_{14} cage.

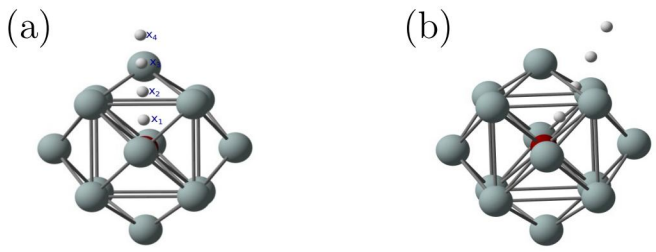

Fig. S8 (a) The positions of ghost atoms as indicated by white atoms in $FeSi_{14}$ (b) a different view.

$FeSi_{14}$	NICS (ppm)
X_1	-40.66
X_2	-73.16
X_3	-16.92
X_4	-2.67

Tab. S3. NICS values at various positions indicated in Fig. S8.