A theoretical study of the first-row transition metal doped germanium clusters $Ge_{14}M$

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Supplemental Information

In Figure S1, we present the geometries of the lowest-energy structures of the $Ge_{14}M$ (M = Sc – Zn) clusters, relative energy (eV), and spin state at B3PW91/6-311+G(d) level

In the Table S1, we display Electronic state (ES), point group (PG), average Ge-M bonding length (Å), sum of the covalent radii for Ge and M (r_{Ge} + r_M) (Å), the difference of average Ge-M bonding length and sum covalent radii $\Delta_{d\text{-}r}$ (Å), the coordination number of M (CN), electron configuration and natural charge of M of the most stable isomers of $Ge_{14}M$ (M = Sc – Zn) clusters.

For Table S2, we show relative energies of the **Ge_{14}V-A** and **Ge_{14}V-E** isomers at different functionals with the same basis set 6-311+G(d).

In the Table S3, we show relative energies of the **Ge_{14}Fe-A** and **Ge_{14}Fe-E** isomers at different functionals with the same basis set 6-311+G(d).

In the Table S4, we show average binding and embedded energies of the most stable isomers of $Ge_{14}M$ (M = Sc – Zn) clusters.

For Table S5, we display The Cartesian coordinates (Å) for the optimized structures of the most stable isomers of $Ge_{14}M$ (M = Sc – Zn) clusters as obtained using B3PW91/6-311+G(d).

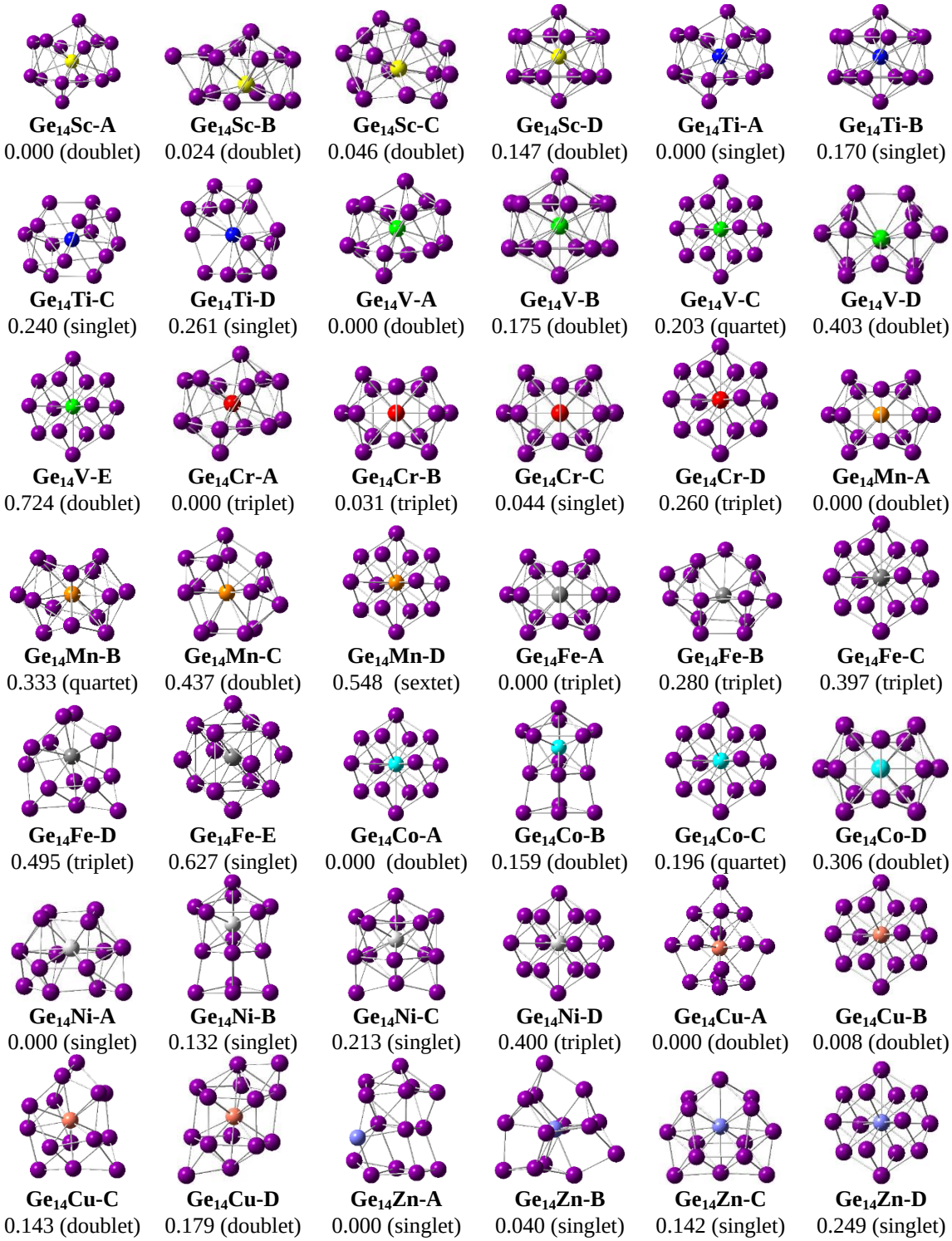

Figure S1. The lowest-energy structures of the $Ge_{14}M$ (M = Sc – Zn) clusters, relative energy (eV), and spin state at B3PW91/6-311+G(d) level.

Table S1. *Electronic state (ES), point group (PG), average Ge-M bonding length (Å), sum of the covalent radii for Ge and M ($r_{Ge} + r_M$) (Å), the difference of average Ge-M bonding length and sum covalent radii $\Delta_{d\text{-}r}$ (Å), the coordination number of M (CN), electron configuration and natural charge of M of the most stable isomers of $Ge_{14}M$ (M = Sc – Zn) clusters.*

Cluster	ES	PG	d_{TB}(Ge-M)	$r_{Ge}+r_M$	$\Delta_{d\text{-}r}$	CN	Electron configuration of M	Natural charge
$Ge_{14}Sc$	^2A	C_2	2.921	2.90	0.021	14	$[core]4s^{0.42}3d^{4.84}4p^{1.97}5s^{0.01}4d^{0.12}$	-4.342
$Ge_{14}Ti$	^1A	C_2	2.867	2.80	0.067	14	$[core]4s^{0.40}3d^{6.26}4p^{1.69}4d^{0.15}6s^{0.01}$	-4.514
$Ge_{14}V$	^2B	C_2	2.840	2.73	0.110	14	$[core]4s^{0.40}3d^{7.00}4p^{1.36}5s^{0.02}4d^{0.19}5p^{0.01}$	-3.972
$Ge_{14}Cr$	^3B	C_2	2.846	2.59	0.256	14	$[core]4s^{0.42}3d^{7.13}4p^{1.25}5s^{0.02}4d^{0.56}5p^{0.01}$	-3.384
$Ge_{14}Mn$	$^2A_1$	C_{2v}	2.844	2.59	0.254	14	$[core]4s^{0.43}3d^{7.50}4p^{1.23}5s^{0.02}4d^{0.43}5p^{0.02}$	-2.486
$Ge_{14}Fe$	$^3A_1$	C_{2v}	2.843	2.52	0.323	14	$[core]4s^{0.45}3d^{8.06}4p^{1.26}5s^{0.02}4d^{0.27}5p^{0.02}$	-2.086
$Ge_{14}Co$	$^2B_{1g}$	D_{4h}	2.788	2.46	0.328	14	$[core]4s^{0.47}3d^{8.83}4p^{1.33}5s^{0.02}4d^{0.14}5p^{0.02}$	-1.798
$Ge_{14}Ni$	^1A	C_2	2.672	2.44	0.232	12	$[core]4s^{0.46}3d^{9.70}4p^{1.39}4d^{0.02}5p^{0.02}6s^{0.02}$	-1.637
$Ge_{14}Cu$	$^2A'$	C_s	2.759	2.52	0.239	12	$[core]4s^{0.47}3d^{9.88}4p^{1.27}5s^{0.03}4d^{0.01}5p^{0.05}$	-0.699
$Ge_{14}Zn$	^1A	C_1	2.835	2.42	0.415	5	$[core]4s^{0.97}3d^{9.99}4p^{0.40}5p^{0.02}$	0.622

Table S2. *Relative energies of the **$Ge_{14}V$-A** and **$Ge_{14}V$-E** isomers at different functionals with the same basis set 6-311+G(d)*

Isomer	B3PW91	B3LYP	B3P86	M06-2X	PBE
$Ge_{14}V$-E	0.724	0.766	0.711	0.777	0.819
$Ge_{14}V$-A	0.000	0.000	0.000	0.000	0.000

Table S3. *Relative energies of the **$Ge_{14}Fe$-A** and **$Ge_{14}Fe$-E** isomers at different functionals with the same basis set 6-311+G(d).*

Isomer	B3LYP	B3P86	M06-2X	B3PW91
$Ge_{14}Fe$-E	0.820	0.529	1.760	0.627
$Ge_{14}Fe$-A	0.000	0.000	0.000	0.000

Table S4. *Average binding energy (a) and embedded energy (b) of the most stable isomers of $Ge_{14}M$ (M = Sc – Zn) clusters.*

a) Average binding energy, E_b (eV)		b) Embedded energy, E_e (eV)	
$Ge_{14}Sc$	3.096	$Ge_{14}Sc \rightarrow Ge_{14} + Sc$	3.553
$Ge_{14}Ti$	3.176	$Ge_{14}Ti \rightarrow Ge_{14} + Ti$	4.754
$Ge_{14}V$	3.129	$Ge_{14}V \rightarrow Ge_{14} + V$	4.042
$Ge_{14}Cr$	3.001	$Ge_{14}Cr \rightarrow Ge_{14} + Cr$	2.130
$Ge_{14}Mn$	3.018	$Ge_{14}Mn \rightarrow Ge_{14} + Mn$	2.376
$Ge_{14}Fe$	3.104	$Ge_{14}Fe \rightarrow Ge_{14} + Fe$	3.665
$Ge_{14}Co$	3.069	$Ge_{14}Co \rightarrow Ge_{14} + Co$	3.138
$Ge_{14}Ni$	3.095	$Ge_{14}Ni \rightarrow Ge_{14} + Ni$	3.532
$Ge_{14}Cu$	2.982	$Ge_{14}Cu \rightarrow Ge_{14} + Cu$	1.837
$Ge_{14}Zn$	2.875	$Ge_{14}Zn \rightarrow Ge_{14} + Zn$	0.234
Ge_{15}	3.061	$Ge_{15} \rightarrow Ge_{14} + Ge$	3.026

Table S5. *The Cartesian coordinates (Å) for the optimized structures of the most stable isomers of $Ge_{14}M$ (M = Sc – Zn) clusters as obtained using B3PW91/6-311+G(d)*

$Ge_{14}Sc$				$Ge_{14}Ti$			
Ge	1.776541	2.083586	-1.322031	Ge	0.843491	2.364599	-1.182546
Ge	2.296667	-0.539567	-1.777816	Ge	-2.902220	0.572567	0.639867
Ge	0.288345	-2.405613	-1.494591	Ge	-1.763688	1.952956	-1.335507
Ge	0.868915	2.418813	1.167903	Ge	-2.327365	-0.543033	-1.678288
Ge	1.205943	-0.168294	2.504678	Ge	-2.203574	-1.915740	0.550253
Ge	2.199699	-1.947307	0.492622	Ge	-0.320356	-2.323584	-1.446218
Ge	-2.296467	-0.548046	1.776711	Ge	2.204566	-1.914262	-0.550329
Ge	-0.280907	-2.408093	1.492664	Ge	2.902377	0.574218	-0.639389
Ge	-2.193133	-1.953278	-0.494844	Ge	0.321974	-2.324406	1.445016
Ge	-1.202012	-0.167080	-2.504739	Ge	2.327653	-0.541880	1.678716
Ge	-0.876833	2.417330	-1.164665	Ge	1.761777	1.953437	1.336074
Ge	-1.784893	2.076742	1.324114	Ge	-0.844548	2.365068	1.181771
Ge	-2.906956	0.563025	-0.600746	Ge	1.092254	-0.114620	-2.433756
Ge	2.905266	0.571161	0.599959	Ge	-1.092361	-0.115559	2.434134
Sc	-0.000267	0.010089	0.001189	Ti	0.000031	0.014893	0.000291
$Ge_{14}V$				$Ge_{14}Cr$			
Ge	2.312816	1.865211	-0.541457	Ge	1.686141	1.426371	-1.930705
Ge	0.205705	1.611565	-2.198661	Ge	-0.895251	1.159240	-2.279549
Ge	0.000000	2.741925	0.222582	Ge	2.290799	1.830016	0.545948
Ge	-0.929400	1.175233	2.204537	Ge	2.797695	-0.531322	-0.487028
Ge	-2.777429	0.502308	0.438709	Ge	0.000000	2.742645	-0.169863
Ge	-2.033658	0.306925	-2.036541	Ge	2.047419	-0.385865	2.024502
Ge	-1.720246	-1.434067	1.929388	Ge	-0.249578	-1.520603	2.280433
Ge	-2.312816	-1.865211	-0.541457	Ge	-2.797695	0.531322	-0.487028
Ge	2.033658	-0.306925	-2.036541	Ge	-2.290799	-1.830016	0.545948
Ge	1.720246	1.434067	1.929388	Ge	-1.686141	-1.426371	-1.930705
Ge	2.777429	-0.502308	0.438709	Ge	-2.047419	0.385865	2.024502
Ge	-0.205705	-1.611565	-2.198661	Ge	0.249578	1.520603	2.280433
Ge	0.929400	-1.175233	2.204537	Ge	0.895251	-1.159240	-2.279549
Ge	0.000000	-2.741925	0.222582	Ge	0.000000	-2.742645	-0.169863
V	0.000000	0.000000	-0.051636	Cr	0.000000	0.000000	0.043364
$Ge_{14}Mn$				$Ge_{14}Fe$			
Ge	0.000000	2.963288	0.529801	Ge	-1.284735	1.267442	2.079186
Ge	0.000000	2.221798	-1.959486	Ge	0.000000	-3.120579	0.530181
Ge	-1.319403	1.280030	2.110250	Ge	-1.284735	-1.267442	2.079186
Ge	-2.170241	1.822790	-0.332186	Ge	-2.154274	-1.803689	-0.305797
Ge	-1.319403	-1.280030	2.110250	Ge	0.000000	-2.179186	-1.874277
Ge	2.170241	1.822790	-0.332186	Ge	-1.497128	0.000000	-2.240926
Ge	1.475736	0.000000	-2.165244	Ge	0.000000	2.179186	-1.874277
Ge	1.319403	1.280030	2.110250	Ge	0.000000	3.120579	0.530181
Ge	2.170241	-1.822790	-0.332186	Ge	1.497128	0.000000	-2.240926
Ge	1.319403	-1.280030	2.110250	Ge	2.154274	1.803689	-0.305797
Ge	0.000000	-2.221798	-1.959486	Ge	1.284735	1.267442	2.079186
Ge	0.000000	-2.963288	0.529801	Ge	1.284735	-1.267442	2.079186
Ge	-1.475736	0.000000	-2.165244	Ge	-2.154274	1.803689	-0.305797
Ge	-2.170241	-1.822790	-0.332186	Ge	2.154274	-1.803689	-0.305797
Mn	0.000000	0.000000	0.099329	Fe	0.000000	0.000000	0.094144
$Ge_{14}Co$				$Ge_{14}Ni$			
Ge	1.563698	-1.563698	1.546598	Ge	-1.011176	1.284893	2.191536
Ge	1.563698	-1.563698	-1.546598	Ge	1.549945	1.463318	2.022748
Ge	-1.563698	-1.563698	1.546598	Ge	2.210341	1.307071	-0.385448
Ge	-1.563698	-1.563698	-1.546598	Ge	0.000000	2.863152	0.256814
Ge	1.563698	1.563698	1.546598	Ge	1.011176	-1.284893	2.191536
Ge	1.563698	1.563698	-1.546598	Ge	2.204512	-1.326141	-0.305819
Ge	-1.563698	1.563698	1.546598	Ge	0.000000	-2.863152	0.256814
Ge	-1.563698	1.563698	-1.546598	Ge	-1.549945	-1.463318	2.022748
Ge	0.000000	2.953679	0.000000	Ge	0.273610	-1.243933	-1.994471

Ge	0.000000	-2.953679	0.000000	Ge	-2.210341	-1.307071	-0.385448
Ge	-2.953679	0.000000	0.000000	Ge	-0.273610	1.243933	-1.994471
Ge	2.953679	0.000000	0.000000	Ge	-2.204512	1.326141	-0.305819
Ge	0.000000	0.000000	-2.813038	Ge	-1.439037	-3.084590	-1.926991
Ge	0.000000	0.000000	2.813038	Ge	1.439037	3.084590	-1.926991
Co	0.000000	0.000000	0.000000	Ni	0.000000	0.000000	0.323729
$Ge_{14}Cu$				$Ge_{14}Zn$			
Ge	-0.028735	0.057965	2.798196	Ge	2.769509	-1.467235	0.890149
Ge	-2.244297	-0.209501	1.487293	Ge	2.467235	1.012114	1.695528
Ge	-3.122276	-2.077390	0.000000	Ge	2.566846	2.696548	-0.296628
Ge	-0.570717	-2.491235	0.000000	Ge	0.219587	1.778437	-0.576116
Ge	1.221928	-1.656439	-1.487781	Ge	2.689246	0.439208	-1.224511
Ge	1.221928	-1.656439	1.487781	Ge	-1.900046	1.256187	-2.012431
Ge	3.289672	-1.731191	0.000000	Ge	-2.043045	2.210629	0.654795
Ge	-0.142748	3.168593	0.000000	Ge	-2.361888	0.032121	2.313390
Ge	-2.374468	1.764188	0.000000	Ge	-1.799649	-1.915733	0.630576
Ge	-2.244297	-0.209501	-1.487293	Ge	-2.168855	-1.420238	-1.956753
Ge	1.221928	1.963706	-1.687660	Ge	-3.395561	0.148139	-0.179489
Ge	1.221928	1.963706	1.687660	Ge	-0.005978	0.276516	1.520800
Ge	-0.028735	0.057965	-2.798196	Ge	2.344090	-1.972567	-1.606286
Ge	2.628810	0.756962	0.000000	Ge	0.101658	-0.773049	-1.079022
Cu	-0.055084	0.329500	0.000000	Zn	0.551308	-2.454481	1.307730