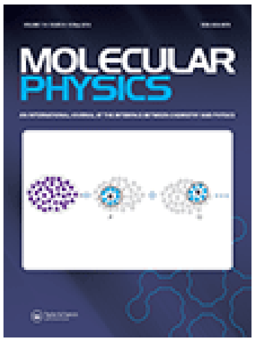

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RESEARCH ARTICLE

Structures and energetics of Be_nGe_n ($n = 1$–5) and $Be_{2n}Ge_n$ ($n = 1$–4) clusters

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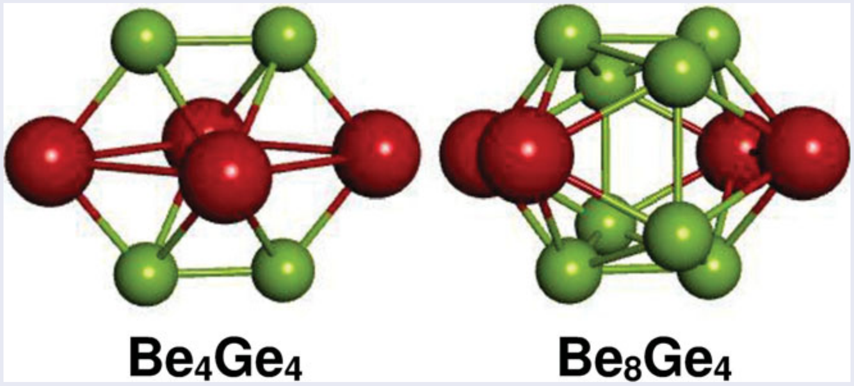
ABSTRACT
Cluster geometries and energies of Be_nGe_n ($n = 1$–5) and $Be_{2n}Ge_n$ ($n = 1$–4) have been examined in theoretical electronic structure calculations. Structure optimisations were carried out using DFT B3LYP/6-31G(2df) and the energies of the optimum geometries were ordered in QCISD(T) calculations. Be and Ge bond to each other and to other atoms of their own kind, creating a great variety of low-energy clusters in a variety of structural types. Comparisons of the germanide clusters with previously explored silicide and carbide structures reveal some structural similarities, but the germanides have much more in common with the beryllium silicides than with the carbides. However, germanide clusters show a greater tendency to form cage-like structures with potential in technological applications.



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Beryllium germanide; germanium clusters; density functional theory

1. Introduction

Clusters of germanium atoms are of interest as possible sources of materials with new electronic and structural properties. Theoretical study of small Ge clusters began early [1], and they continue to be important [2–5]. Pure germanium clusters containing up to 25 atoms has been well characterised. Among the smallest clusters, Ge_3 is an isosceles triangle (C_{2v}) with bond length 2.40 Å and apex angle of 84.9°, the Ge_4 cluster is a D_{2h} rhombus with Ge–Ge distances larger than Ge_3, Ge_5 is a trigonal bipyramid, Ge_6 a distorted octahedron, and the most stable geometries for Ge_7, Ge_8, and Ge_9 are pentagonal bipyramid, capped pentagonal bipyramid and bicapped pentagonal bipyramid, respectively [4,5]. More recently, the study of doped clusters has begun, primarily as potential sources of new nanostructures. Doping with Li has, in fact, been shown to permit formation of incipient nanowires [6–10].

A variety of theoretical and experimental explorations of germanium nanostructures have been recently published, including metal- and nonmetal-doped clusters [11–13], nanowires [14] and germanium–organics combinations [15]. Cage clusters, in which transition metals, Be, B, Al, and nonmetal dopants are encapsulated by Ge atoms, have been examined [11,16]. A single atom of Be added to small Ge clusters can lead to Be@Ge_8, a Ge_8 cage with an endohedral Be [17,18]. King *et al.* [19], in density functional theoretical (DFT) calculations, have explored Be@Ge_{10} cage clusters and shown that Be stabilises the cluster. Uţă and King [18] studied 6-, 7- and 8-Ge cage clusters through DFT to examine the smallest Ge cluster size capable of encapsulating a Be atom. They found that the lowest energy structures of the Ge_8 clusters possess an enclosed Be, but that the most stable forms of smaller clusters do not. Hung and coworkers [17]

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studied by DFT pathways both the exohedral and endohedral $BeGe_8$. They found Be–Ge bonding to be covalent and that Be is hypervalent in the complexes, assisted by back-donation of electrons from Ge.

The present study is grounded in previous examinations of beryllium silicides and carbides [20–22] and motivated by the need to understand stability, bonding and structure in germanide clusters per se and in comparison to the other group clusters. Hitherto, cluster studies have concentrated on germanium as the structural element, with no studies of clusters in which the number of Be atoms is equal to or greater than Ge. Therefore, we explore this realm by examining small low-energy clusters formed by beryllium and germanium combined in equal proportions (Be_nGe_n) or containing twice beryllium atoms than germaniums ($Be_{2n}Ge_n$). The study extends prior examinations of beryllium carbides [22], silicides [20] and larger beryllium silicide cage clusters [21], and it may identify trends in cluster type, bonding and stability for the carbon group clusters with beryllium.

The study of small beryllium carbide clusters [22] revealed great structural variety owing to the capacity of carbon to form multiple bonds and planar pentagons and hexagons. In contrast, the silicide clusters [20] displayed fewer structures, with no Si–Si multiple bonds, but low-energy silicide cluster structures were still found among the low-energy types of carbides. Carbon is capable of forming stable cage clusters, whereas silicon can form cages only with endohedral Si atoms [23]. However, combination of Si with Be was found to yield several stable cage clusters, $Be_{12}Si_8$, $Be_{24}Si_8$ and $Be_{20}Si_{12}$ [21], the latter a symmetrical Be_{20} dodecahedron with each face capped by a Si atom. The principal motifs from which the large cage structures were constructed were identified in the study of small Be–Si clusters [20].

The present study, though it examines structures found in previous studies, is focused upon Be_nGe_n ($n = 1$–5) and $Be_{2n}Ge_n$ ($n = 1$–4) clusters and aims to identify as many of the most stable isomers of each as possible. The analysis of a large fraction of the lowest energy clusters may identify essential elements of stability and structural motifs useful in synthesising larger clusters. Comparison of the results of the present with the former studies on silicides [20] and carbides [22] may offer additional structural insight.

2. Methods

Starting geometries for optimisation of the smaller clusters were taken from stable geometries of the individual atomic clusters [4,5,24], of beryllium carbides reported in previous studies [22], of Be_nSi_n and $Be_{2n}Si_n$ clusters [20] and of variations on the foregoing. Extensive potential surface searches were performed using DFT Monte Carlo simulated annealing (DFT-MCSA). In simulated annealing [25], the temperature is gradually lowered to ‘freeze’ the system in a minimum energy configuration. Lowering the temperature slowly enough yields the global minimum; more rapid annealing locates local minima. In DFT-MCSA [26], geometries are Monte Carlo sampled, and the energy at each step is evaluated in a DFT calculation. Final geometries and harmonic frequencies were obtained in B3LYP/6-31G(2df) optimisations. B3LYP contains Becke’s [27] three-parameter exchange functional and the correlation functional of Lee, Yang and Parr [28]. Calculations were done with Gaussian09 [29].

In previous work on beryllium silicide clusters [20], energies were ordered in G3XMP2 [30] calculations. Gaussian-n theory employs a QCISD(T)/6-31G* single-point calculation at the optimised geometry as the principal correlation energy correction. The present study replaces the multistep G3XMP2 process with a two-step estimation of the energy ordering via a single-point QCISD(T)/6-31G(2df) evaluated at the B3LYP/6-31G(2df) geometry. This is a time-saving approach, considering the more than 100 energy evaluations to be done, though it assumes that the 6-31G(2df) basis adequately describes the germanide clusters.

3. Results and discussion

Tables 1–7 list the calculated ground-state B3LYP/6-31G(2df) and QCISD(T)/6-31G(2df) energies of clusters and selected interatomic distances, while Figures 1–7 depict low-energy structures of each isomer. The three rightmost columns of the Tables show, respectively, cluster atomisation energies, atomisation energies divided by number of atoms less one, and the QCISD(T) energy of each structure relative to the most stable. In each Figure, germanium atoms are depicted as larger and darker in colour, and berylliums smaller and lighter in colour. We discuss the clusters ordered by *n*, the number of germanium atoms.

BeGe and Be_2Ge. BeGe has a spin triplet ground state (see Table 1) at the QCISD(T)/6-31G(2df) level with bond length 2.14 Å. A singlet lies 0.77 eV (17.82 kcal/mol) above the ground state and a quintet somewhat higher. The ground states of BeC and BeSi are also $^3\Sigma^-$ with bond lengths of 1.67 [20] and 2.12 Å [22], respectively, so the germanide geometry is similar to that of the silicide.

Three Be_2Ge structures were found (Figure 1), with Isomer A being a nearly equilateral triangle, the lowest in energy. Be_2C and Be_2Si [20,22] also have low-energy $^1A_1$

Table 1. Energies and minimum distances of BeGe, Be_2Ge and Be_2Ge_2 clusters. Column contents are described in the text.

Species	State	B3-LYP[a]	QCISD(T)[a]	d(Ge–Ge)	d(Ge–Be)	d(Be–Be)	E^b_{At}	$E_{At}/(N-1)^b$	ΔE^b_{Rel}
BeGe									
	$^3\Sigma^-$	– 2089.83668	– 2088.14923		2.140		54.90	54.90	0.00
	$^1\Sigma^+$	– 2089.80659	– 2088.12084		2.140		37.08	37.08	17.82
	$^5\Sigma^-$	– 2089.79474	– 2088.11274		2.134		32.00	32.00	22.90
Be_2Ge									
A	$^1A_1$	– 2104.57963	– 2102.83377		2.066	2.122	99.15	49.57	0.00
A	$^3B_1$	– 2104.58127	– 2102.82746		2.177	2.055	95.19	47.60	3.96
B	$^3\Sigma^+$	– 2104.54261	– 2102.79550		2.107	2.114	75.13	37.57	24.01
C	$^5\Sigma_u^+$	– 2104.54490	– 2102.79187		2.135	4.270	72.86	36.43	26.29
B	$^5\Sigma^+$	– 2104.53244	– 2102.78330		2.125	2.085	67.48	33.74	31.67
B	$^1\Sigma^+$	– 2104.51935	– 2102.77009		2.123	2.069	59.19	29.60	39.96
C	$^1\Sigma_g$	– 2104.49431	– 2102.74627		1.910	3.821	44.24	22.12	54.90
Be_2Ge_2									
A	^1A	– 4179.84886	– 4176.47378	2.987	2.088	2.919	219.81	73.27	0.00
B	^1A	– 4179.83497	– 4176.46179	2.795	2.217	1.868	212.28	70.76	7.53
B	$^3A'$	– 4179.83399	– 4176.45672	2.979	2.159	2.120	209.11	69.70	10.70
C	^1A	– 4179.82902	– 4176.45410	2.294	2.207	2.010	207.46	69.15	12.35
A	^3A	– 4179.81320	– 4176.43160	2.855	2.211	3.377	193.34	64.45	26.47
A	^5A	– 4179.79552	– 4176.41937	3.988	2.251	2.089	185.67	61.89	34.14
B	$^5A'$	– 4179.78134	– 4176.40491	2.679	2.238	2.614	176.59	58.86	43.22
D	$^1\Sigma^+$	– 4179.77003	– 4176.39401	2.188	2.001	2.050	169.76	56.59	50.05
E	$^5\Sigma^+$	– 4179.74105	– 4176.36423	6.397	2.171	2.055	151.07	50.36	68.74
E	$^1\Sigma^+$	– 4179.71629	– 4176.35840	6.458	2.220	2.018	147.41	49.14	72.40
D	$^3\Sigma^+$	– 4179.77763	– 4176.35588	2.229	2.144	2.116	145.82	48.61	73.99
E	$^3\Sigma^+_g$	– 4179.74750	– 4176.35197	6.566	2.243	2.080	143.38	47.79	76.44
D	$^5\Sigma^g$	– 4179.73491	– 4176.32480	2.431	2.138	2.102	126.32	42.11	93.49

[a] Energies in atomic units.
[b] Energies in kcal/mol. Distances in angstroms.

triangular structures. At the B3LYP level, the triplet is the more stable, also the case with Be_2Si. Second in order of energy is isomer B triplet, a Ge–Be–Be linear structure and only 0.1 eV (2.28 kcal/mol) above the triplet, is the linear isomer C with the germanium atom between the berylliums at a distance of 2.135 Å, larger than the Be–Ge distances of isomers A and B. For each isomer, the singlet, triplet, and quintet states are near in energy (Table 1). The linear structures are similar to those of Be_2C [22], with the Be–C distance significantly smaller than the Be–Ge but with Be–Be about the same. Some charge transfer is seen in Be_2Ge; about one-quarter of an electron charge is transferred from Ge to the Be atoms. The magnitude of charge transferred is about the same as that seen in Be_2Si

Table 2. Energies and minimum distances of Be_4Ge_2 clusters. Column contents are described in the text.

Species	State	B3-LYP[a]	QCISD(T)[a]	d(Ge–Ge)	d(Ge–Be)	d(Be–Be)	E^b_{At}	$E_{At}/(N-1)^b$	ΔE^b_{Rel}
A	$^1A'$	– 4209.35405	– 4205.86024	3.387	2.138	2.006	319.22	63.84	0.00
B	^1A	– 4209.34299	– 4205.85256	2.504	2.094	2.016	314.40	62.88	4.82
C	^1A	– 4209.34148	– 4205.85152	3.332	2.146	1.961	313.75	62.75	5.47
D	^3A	– 4209.33424	– 4205.84489	3.207	2.208	2.147	309.59	61.92	9.64
A	$^3A''$	– 4209.33556	– 4205.83959	2.976	2.099	1.966	306.26	61.25	12.96
E	^1A	– 4209.32488	– 4205.83871	3.107	2.217	1.948	305.71	61.14	13.51
C	^3A	– 4209.33017	– 4205.83760	3.044	2.200	2.063	305.01	61.00	14.21
D	^1A	– 4209.31444	– 4205.82799	3.223	2.189	2.094	298.99	59.80	20.24
F	$^1A'$	– 4209.32377	– 4205.82527	2.471	2.136	1.933	297.28	59.46	21.95
B	^3A	– 4209.31558	– 4205.82469	2.398	2.281	2.002	296.91	59.38	22.31
D	^5A	– 4209.30810	– 4205.81701	3.542	2.282	1.966	292.10	58.42	27.13
G	^1A	– 4209.31172	– 4205.80966	2.537	2.029	2.011	287.48	57.50	31.74
A	$^5A'$	– 4209.30529	– 4205.80859	3.828	2.165	2.038	286.81	57.36	32.41
E	^5A	– 4209.29529	– 4205.80513	2.935	2.214	2.041	284.64	56.93	34.58
C	^5A	– 4209.29980	– 4205.80162	4.240	2.205	1.909	282.44	56.49	36.79
G	^3A	– 4209.31151	– 4205.79576	2.583	2.045	1.918	278.76	55.75	40.46
B	^5A	– 4209.27708	– 4205.76750	2.591	2.270	2.140	261.03	52.21	58.20

[a] Energies in atomic units.
[b] Energies in kcal/mol. Distances in angstroms.

Table 3. Energies and minimum distances of Be_3Ge_3 clusters. Column contents are described in the text.

Species	State	B3-LYP[a]	QCISD(T)[a]	*d*(Ge–Ge)	*d*(Ge–Be)	*d*(Be–Be)	E_{At}^b	$E_{At}/(N-1)^b$	ΔE_{Rel}^b
A	$^1A_1$	– 6269.86852	– 6264.82125	2.596	2.154	2.250	399.10	79.82	0.00
B	^1A	– 6269.86742	– 6264.81450	2.284	2.154	1.980	394.87	78.97	4.23
C	^1A	– 6269.86064	– 6264.80640	2.431	2.077	2.007	389.79	77.96	9.31
D	^1A	– 6269.85805	– 6264.80482	2.404	2.080	1.979	388.80	77.76	10.30
E	^1A	– 6269.85824	– 6264.80467	2.949	2.171	2.150	388.70	77.74	10.40
F	^1A	– 6269.85844	– 6264.80455	2.493	2.128	1.970	388.63	77.73	10.48
A	^3A	– 6269.85561	– 6264.80139	2.504	2.190	2.034	386.64	77.33	12.46
G	$^1A'$	– 6269.85280	– 6264.79907	2.419	2.129	1.965	385.19	77.04	13.92
E	^3A	– 6269.84802	– 6264.79554	2.630	2.182	2.062	382.98	76.60	16.13
H	^3A	– 6269.84718	– 6264.79218	2.695	2.145	2.034	380.86	76.17	18.24
H	^1A	– 6269.83817	– 6264.78730	2.526	2.152	2.024	377.81	75.56	21.30
G	$^3A'$	– 6269.83944	– 6264.78016	2.444	2.181	1.979	373.32	74.66	25.78
I	^1A	– 6269.82638	– 6264.76960	2.616	2.077	3.045	366.69	73.34	32.41
A	$^5A_1$	– 6269.81916	– 6264.76840	2.640	2.232	2.093	365.94	73.19	33.16
I	^3A	– 6269.82720	– 6264.76775	2.832	2.115	2.239	365.54	73.11	33.57
B	^5A	– 6269.81772	– 6264.76096	2.679	2.137	2.039	361.27	72.25	37.83
H	^5A	– 6269.79735	– 6264.74060	2.558	2.197	1.981	348.49	69.70	50.61

[a] Energies in atomic units.
[b] Energies in kcal/mol. Distances in angstroms.

[20] though opposite in direction, while a much smaller effect was found in Be_2C [22].

Be_2Ge_2. The global minimum energy structure (Figure 1, Isomer A) is a singlet of D_{2h} symmetry; a rhombus of alternating Be and Ge. The structure is similar to the most stable isomer of Be_2Si_2. In Be_2C_2, the most stable cluster more closely resembles isomer C in Figure 1, probably stabilised by the presence of a C–C triple bond. A triplet lies more than 25 kcal/mol above the ground state, with similar geometry though with shortened Ge–Ge distances and elongated Be–Ge bond. These structures are similar to those found for Be_2Si_2 and Be_2C_2 although not in the same energy order. The only nonplanar isomer (Figure 1, isomer B) resembles a distorted tetrahedron displaying the shortest Be–Be bond noted in this study (1.87 Å), even shorter than that of tetrahedral Be_4 (2.03 Å) [24]. The Be–Be distances in structures B and C are similar for the germanide and silicide analogues. Isomer B was not found among the carbides; in fact, no three-dimensional structures for

Table 4. Energies and minimum distances of Be_6Ge_3 clusters. Column contents are described in the text.

Species	State	B3-LYP[a]	QCISD(T)[a]	*d*(Ge–Ge)	*d*(Ge–Be)	*d*(Be–Be)	E_{At}^b	$E_{At}/(N-1)^b$	ΔE_{Rel}^b
A	^1A	– 6314.17809	– 6308.95613	2.652	2.114	1.953	582.86	72.86	0.00
B	$^1A'$	– 6314.17748	– 6308.95155	3.972	2.258	2.010	579.98	72.50	2.88
C	^1A	– 6314.17356	– 6308.94848	2.704	2.169	1.971	578.05	72.26	4.81
D	^1A	– 6314.16155	– 6308.94053	2.674	2.111	1.991	573.07	71.63	9.79
E	^3A	– 6314.15500	– 6308.92937	2.586	2.157	1.988	566.06	70.76	16.80
A	^3A	– 6314.14832	– 6308.92084	2.691	2.115	1.963	560.71	70.09	22.15
F	^3A	– 6314.14327	– 6308.91722	2.735	2.127	2.006	558.44	69.80	24.42
G	^1A	– 6314.13490	– 6308.91499	2.513	2.171	1.946	557.04	69.63	25.82
H	^1A	– 6314.13492	– 6308.91348	2.429	2.178	1.933	556.09	69.51	26.77
H	^3A	– 6314.13321	– 6308.90845	2.402	2.212	1.965	552.93	69.12	29.92
D	^3A	– 6314.13727	– 6308.90788	2.806	2.104	2.037	552.58	69.07	30.28
B	$^5A'$	– 6314.12724	– 6308.90397	3.784	2.235	2.040	550.13	68.77	32.73
C	^5A	– 6314.11786	– 6308.89516	2.545	2.199	1.988	544.60	68.07	38.26
I	^1A	– 6314.12219	– 6308.89495	2.671	2.099	1.898	544.46	68.06	38.39
H	^5A	– 6314.11219	– 6308.88626	2.416	2.170	1.986	539.01	67.38	43.84
A	^5A	– 6314.10699	– 6308.88270	2.690	2.162	1.980	536.78	67.10	46.08
I	^5A	– 6314.10134	– 6308.87634	2.691	2.145	1.974	532.79	66.60	50.07
G	^5A	– 6314.09700	– 6308.87145	2.439	2.185	1.990	529.72	66.21	53.14
E	^5A	– 6314.09667	– 6308.86896	2.513	2.229	2.061	528.16	66.02	54.70
D	^5A	– 6314.09376	– 6308.86777	2.710	2.146	2.017	527.41	65.93	55.45
J	^1A	– 6314.09148	– 6308.84860	2.535	2.066	1.998	515.38	64.42	67.48
J	^3A	– 6314.06704	– 6308.82068	2.549	2.060	2.022	497.86	62.23	85.00

[a] Energies in atomic units.
[b] Energies in kcal/mol. Distances in angstroms.

Table 5. Energies and minimum distances of Be_4Ge_4 clusters. Column contents are described in the text.

Species	State	B3-LYP[a]	QCISD(T)[a]	d(Ge–Ge)	d(Ge–Be)	d(Be–Be)	E^{b}_{At}	$E_{At}/(N-1)^{b}$	ΔE^{b}_{Rel}
A	^1A	– 8359.93421	– 8353.21146	2.685	2.126	1.962	605.22	86.46	0.00
B	^1A	– 8359.93489	– 8353.21006	2.715	2.168	2.050	604.34	86.33	0.88
C	^1A	– 8359.92193	– 8353.19640	2.652	2.164	1.972	595.77	85.11	9.45
D	^1A	– 8359.91952	– 8353.19225	2.423	2.166	1.980	593.17	84.74	12.05
E	^1A	– 8359.92090	– 8353.19088	2.290	2.058	2.022	592.31	84.62	12.91
F	^1A	– 8359.91399	– 8353.18938	2.557	2.134	1.939	591.37	84.48	13.86
G	$^3B_3$	– 8359.91708	– 8353.18871	2.467	2.179	2.080	590.95	84.42	14.28
C	^3A	– 8359.91740	– 8353.18844	2.671	2.132	1.991	590.78	84.40	14.44
F	^3A	– 8359.91404	– 8353.18768	2.691	2.112	1.998	590.30	84.33	14.92
G	^1A	– 8359.91073	– 8353.18579	2.505	2.175	1.998	589.11	84.16	16.11
H	^1A	– 8359.91191	– 8353.18513	2.434	2.164	2.052	588.70	84.10	16.52
B	^3A	– 8359.90974	– 8353.17665	2.812	2.079	2.291	583.38	83.34	21.85
I	^1A	– 8359.90267	– 8353.17579	2.515	2.235	1.917	582.84	83.26	22.39
D	^3A	– 8359.90570	– 8353.17565	2.510	2.149	2.016	582.75	83.25	22.47
I	^3A	– 8359.89543	– 8353.16607	2.528	2.183	2.026	576.74	82.39	28.48
H	^3A	– 8359.89230	– 8353.16238	2.505	2.153	1.982	574.42	82.06	30.80
J	^1A	– 8359.87897	– 8353.15663	2.649	2.213	2.006	570.81	81.54	34.41
K	^1A	– 8359.87994	– 8353.15355	2.413	2.170	1.941	568.89	81.27	36.34
E	^3A	– 8359.88019	– 8353.14711	2.312	2.143	1.917	564.84	80.69	40.38
C	^5A	– 8359.87270	– 8353.14416	2.680	2.118	2.092	562.99	80.43	42.23
A	^3A	– 8359.88407	– 8353.14111	2.662	2.132	1.967	561.07	80.15	44.15
K	^3A	– 8359.87031	– 8353.13942	2.479	2.187	2.009	560.02	80.00	45.21
D	^5A	– 8359.85895	– 8353.12976	2.504	2.151	2.018	553.95	79.14	51.27
L	^1A	– 8359.87297	– 8353.12913	2.607	2.036	2.176	553.56	79.08	51.67
F	^5A	– 8359.85393	– 8353.12148	2.624	2.112	1.986	548.76	78.39	56.47
H	^5A	– 8359.84811	– 8353.11851	2.476	2.168	2.027	546.89	78.13	58.33
I	^5A	– 8359.82608	– 8353.09972	2.443	2.151	1.955	535.10	76.44	70.12
K	^5A	– 8359.82671	– 8353.09477	2.439	2.217	2.026	532.00	76.00	73.23

[a] Energies in atomic units.
[b] Energies in kcal/mol. Distances in angstroms.

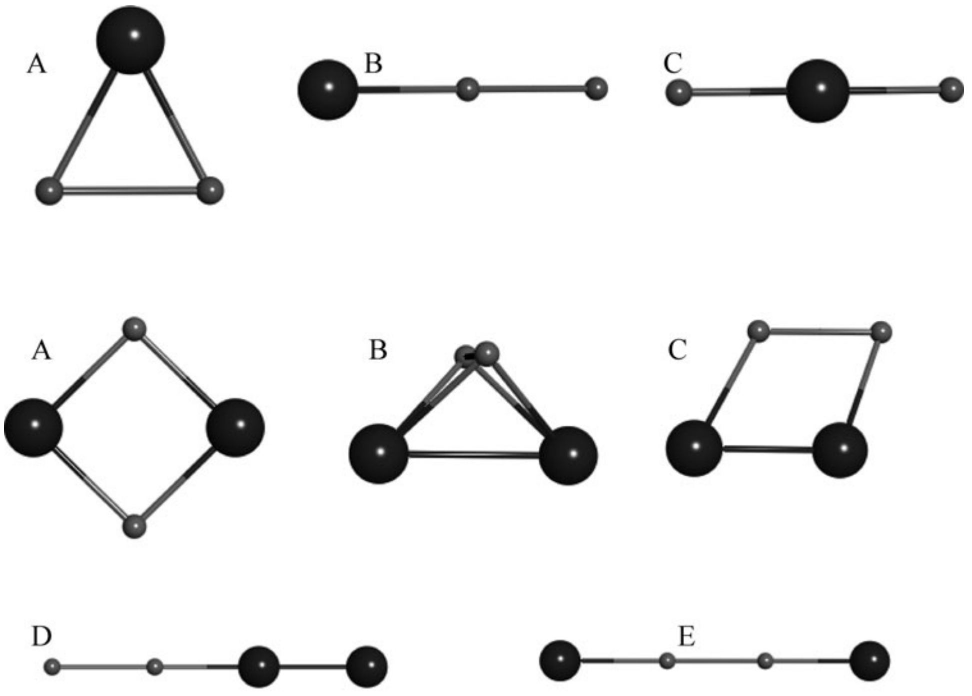

Figure 1. B3LYP/6-31G(2df)-optimised structures of Be_2Ge and Be_2Ge_2. Germanium atoms are larger and in darker colour; beryllium atoms are smaller and lighter in colour.

Table 6. Energies and minimum distances of Be_8Ge_4 clusters. Column contents are described in the text.

Species	State	B3-LYP[a]	QCISD(T)[a]	*d*(Ge–Ge)	*d*(Ge–Be)	*d*(Be–Be)	$E^{\mathrm{b}}_{\mathrm{At}}$	$E_{\mathrm{At}}/(N-1)^{\mathrm{b}}$	$\Delta E^{\mathrm{b}}_{\mathrm{Rel}}$
A	$^1A'$	– 8418.99773	– 8412.04287	2.578	2.240	2.027	840.75	76.43	0.00
B	^1A	– 8418.99651	– 8412.03469	3.786	2.148	2.118	835.61	75.96	5.13
C	^1A	– 8418.98915	– 8412.03216	2.746	2.064	2.048	834.03	75.82	6.72
D	^1A	– 8418.98692	– 8412.02915	2.847	2.101	2.030	832.14	75.65	8.61
B	^3A	– 8418.98861	– 8412.02644	3.694	2.127	2.092	830.44	75.49	10.31
E	^1A	– 8418.97631	– 8412.02020	2.676	2.125	2.051	826.52	75.14	14.22
D	^3A	– 8418.97669	– 8412.01842	2.883	2.084	2.041	825.41	75.04	15.34
F	^1A	– 8418.97780	– 8412.01678	3.542	2.218	2.003	824.38	74.94	16.37
C	^3A	– 8418.97614	– 8412.01644	2.803	2.062	2.056	824.16	74.92	16.58
G	^1A	– 8418.96747	– 8412.01070	2.415	2.104	2.000	820.56	74.60	20.19
H	^3A	– 8418.96888	– 8412.00836	2.593	2.211	2.058	819.09	74.46	21.65
H	^1A	– 8418.95655	– 8412.00144	2.535	2.116	1.998	814.75	74.07	26.00
I	^3A	– 8418.95696	– 8411.99772	2.676	2.133	1.972	812.42	73.86	28.33
G	^3A	– 8418.94691	– 8411.98787	2.443	2.129	2.005	806.23	73.29	34.51
J	^1A	– 8418.93820	– 8411.98312	2.612	2.064	1.951	803.26	73.02	37.49
I	^1A	– 8418.94204	– 8411.98134	2.646	2.065	1.969	802.14	72.92	38.61
B	^5A	– 8418.93738	– 8411.97862	3.566	2.158	2.023	800.43	72.77	40.32
C	^5A	– 8418.93464	– 8411.97481	2.751	2.080	1.998	798.04	72.55	42.71
J	^3A	– 8418.93429	– 8411.97417	2.697	2.102	1.950	797.64	72.51	43.11
D	^5A	– 8418.93439	– 8411.97226	3.733	2.112	2.087	796.44	72.40	44.31
F	^5A	– 8418.92692	– 8411.96724	3.504	2.213	2.078	793.29	72.12	47.46
E	^5A	– 8418.91775	– 8411.96073	2.686	2.157	2.030	789.20	71.75	51.54
K	^1A	– 8418.91358	– 8411.95890	2.427	2.125	1.908	788.06	71.64	52.69
H	^5A	– 8418.91804	– 8411.95835	2.420	2.233	2.049	787.71	71.61	53.04
K	^3A	– 8418.91074	– 8411.95407	2.551	2.130	1.964	785.02	71.37	55.72
G	^5A	– 8418.91224	– 8411.95360	2.471	2.168	1.999	784.73	71.34	56.02
I	^5A	– 8418.90744	– 8411.95134	2.575	2.170	1.972	783.31	71.21	57.44
L	^1A	– 8418.89529	– 8411.94059	2.715	2.172	1.967	776.56	70.60	64.18
J	^5A	– 8418.89564	– 8411.93741	2.676	2.109	1.932	774.57	70.42	66.17
K	^5A	– 8418.88044	– 8411.92576	2.519	2.140	1.985	767.26	69.75	73.49
E	^3A	– 8418.96349	– 8411.91891	2.620	2.176	1.996	762.96	69.36	77.78

[a] Energies in atomic units.
[b] Energies in kcal/mol. Distances in angstroms.

Be_2C_2 were found. Relatively higher in energy are two linear structures D and E. Linear structures were not explored for Be_2Si_2, but in Be_2C_2, there are three, and they are also high-lying.

Be_4Ge_2. Seven interesting, symmetric structures of Be_4Ge_2 were identified. Low-lying isomer A (Figure 2) possesses C_s symmetry, a Be_3Ge_2 almost-regular pentagonal pyramid. This beryllium-capped pentagonal

Table 7. Energies and minimum distances of Be_5Ge_5 clusters. Column contents are described in the text.

Species	State	B3-LYP[a]	QCISD(T)[a]	*d*(Ge–Ge)	*d*(Ge–Be)	*d*(Be–Be)	$E^{\mathrm{b}}_{\mathrm{At}}$	$E_{\mathrm{At}}/(N-1)^{\mathrm{b}}$	$\Delta E^{\mathrm{b}}_{\mathrm{Rel}}$
A	^1A	– 10,449.96913	– 10,441.56627	2.569	2.144	2.105	789.12	87.68	0.00
B	^1A	– 10,449.94520	– 10,441.54291	2.511	2.109	2.113	774.46	86.05	14.66
C	^1A	– 10,449.94620	– 10,441.54102	2.701	2.113	2.034	773.28	85.92	15.84
D	^1A	– 10,449.94202	– 10,441.53888	2.536	2.066	1.954	771.94	85.77	17.19
E	^1A	– 10,449.94290	– 10,441.53828	2.593	2.078	1.956	771.56	85.73	17.56
B	^3A	– 10,449.93467	– 10,441.52889	2.601	2.162	2.052	765.66	85.07	23.46
C	^3A	– 10,449.92927	– 10,441.52274	2.506	2.129	2.083	761.81	84.65	27.32
E	^3A	– 10,449.92770	– 10,441.52025	2.666	2.076	1.962	760.25	84.47	28.88
D	^3A	– 10,449.91789	– 10,441.51485	2.558	2.154	1.993	756.85	84.09	32.27
E	^5A	– 10,449.91701	– 10,441.51418	2.691	2.145	1.974	756.44	84.05	32.69
B	^5A	– 10,449.91146	– 10,441.50531	2.548	2.132	2.120	750.87	83.43	38.25
C	^5A	– 10,449.89951	– 10,441.49626	2.508	2.158	2.11	745.19	82.80	43.93
D	^5A	– 10,449.89736	– 10,441.49116	2.455	2.184	2.082	741.99	82.44	47.13
F	^1A	– 10,449.91265	– 10,441.48915	2.284	2.079	2.049	740.73	82.30	48.39
F	^3A	– 10,449.89842	– 10,441.46840	2.303	2.084	2.061	727.71	80.86	61.42
F	^5A	– 10,449.85425	– 10,441.42764	2.371	2.09	2.075	702.13	78.01	86.99

[a] Energies in atomic units.
[b] Energies in kcal/mol. Distances in angstroms.

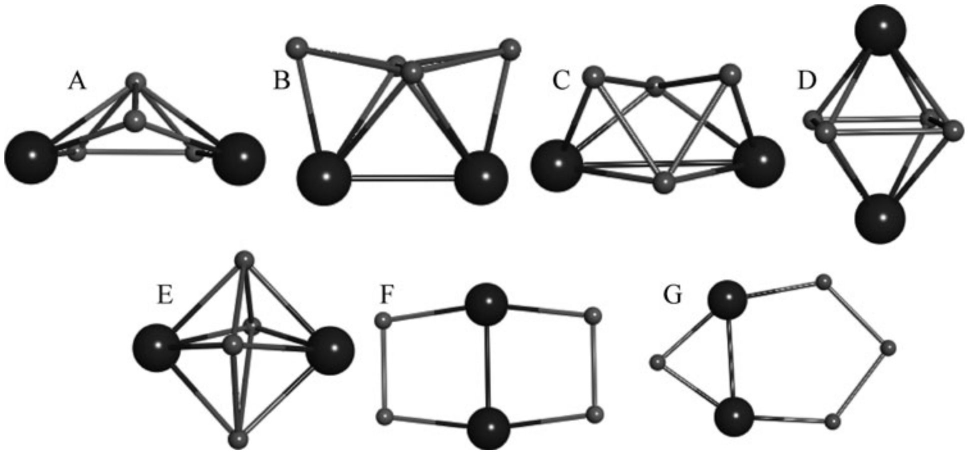

Figure 2. Optimised structures of low-energy Be_4Ge_2 clusters.

structure is also the low-energy form of Be_6 [24] and Be_4Si_2. Structure B, next in energy, is a bent rhombus of berylliums above a pair of germaniums, forming a bicapped tetrahedron with overall C_{2v} symmetry. Be–Be and Be–Ge distances are similar while Ge–Ge is longer. Isomer C is similar to B with the rhombus of berylliums warped into a more compact tetrahedron. D and E follow in energy; both are square bipyramids with the germanium atoms at the apices and the berylliums forming the square base of the pyramids. Both possess D_{2h} symmetry, but *D* is elongated along the Ge–Ge axis.

There is a close analogy between isomers A–D of Be_4Ge_2 and the four isomers identified for Be_4Si_2. The forms of the isomers and their energy ordering correspond, and in each case, all four isomers lie within 12 kcal/mol of each other, and their bond lengths and angles are similar. Analogous clusters are to be found among the 13 isomers identified for Be_4C_2; however, the energy order is quite different. Among Be_4C_2 clusters, structures that are planar or partly so and which display strong C–C bonding lie relatively lower in energy.

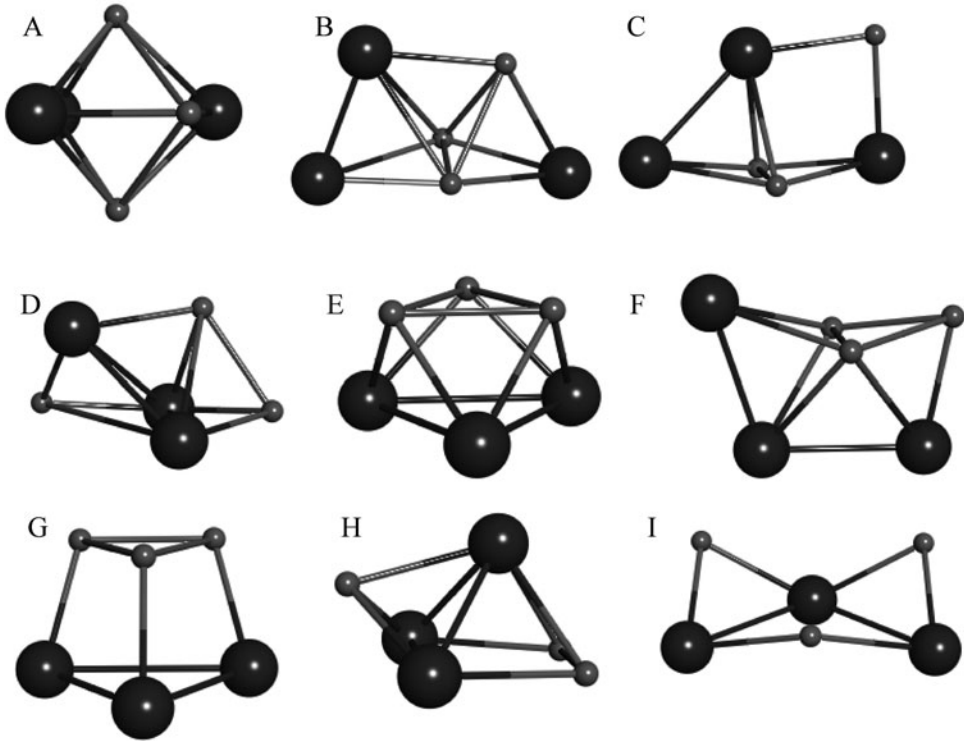

Figure 3. Optimised structures of low-energy Be_3Ge_3 clusters.

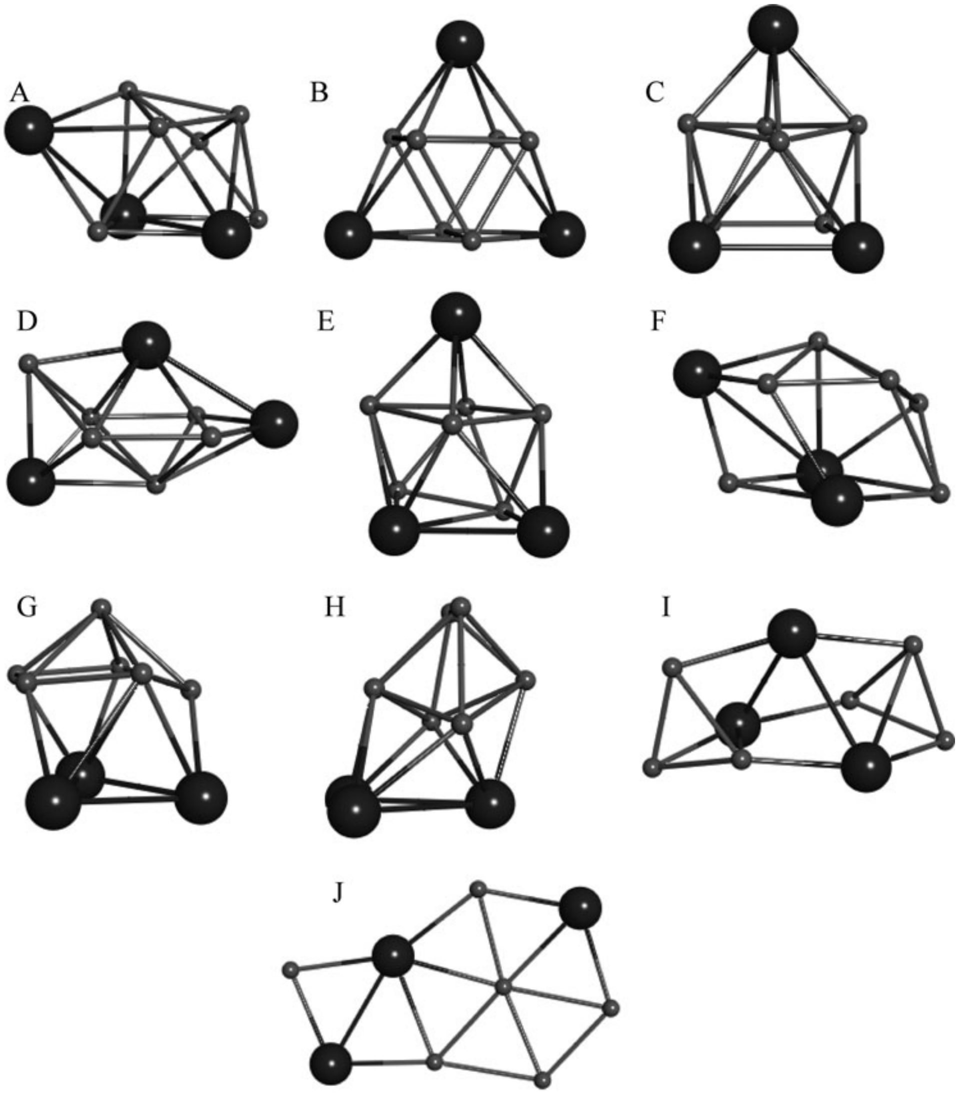

Figure 4. Optimised structures of low-energy Be_6Ge_3 clusters.

Be_3Ge_3 and Be_6Ge_3. Nine isomers of Be_3Ge_3 were optimised, the most stable being six of them within 11 kcal/mol of each other. The global minimum energy cluster (Figure 3) is a slightly distorted octahedron, three atoms of each type forming triangles that intersect at right angles. The structure closely resembles the global minimum of Be_3Si_3 [20], though Ge–Ge distances are longer than Si–Si. This cluster type is also observed in Be_3C_3 [22], but it is a relatively high-energy structure. Isomers B and C are irregular, asymmetrical cage-like structures. One kcal/mol above C lie the more symmetrical D–F isomers, within one kcal/mol of each other in energy but with distinct geometries. Isomers B, D, and F are bicapped tetrahedrons. Structure E is particularly interesting, formed by triangles, respectively, of Ge and Be, stacked as a trigonal antiprism. It is a relatively expanded structure; Ge–Ge is 2.95 Å and Be–Be 2.15 Å. Higher energy structure G has geometry similar to that of E, but the triangles arranged to form a prism. Structures A, E and G of Be_3Ge_3 have analogues among the Be_3C_3 and Be_3Si_3 isomers.

Ten Be_6Ge_3 clusters (Figure 4) were found. The lowest energy structure A consists of an irregular square prism capped with a beryllium; it has one degree 6 vertex occupied by a germanium and four degree 4 vertices, forming a 9-vertex *isocloso* structure as it is named in polyhedral borane chemistry [31]. Isomer B is a trigonal prism of berylliums tricapped with germanium atoms, whereas structure C is a capped square antiprism. Each is in the ^1A state and all are within 6 kcal/mol in energy. Isomers B and C exhibit higher symmetry than A, but the three of them have similar Be–Be distances. Clusters A and B are similar to the two most stable clusters of Be_6C_3 and Be_6Si_3. The energy order is followed in the carbides and

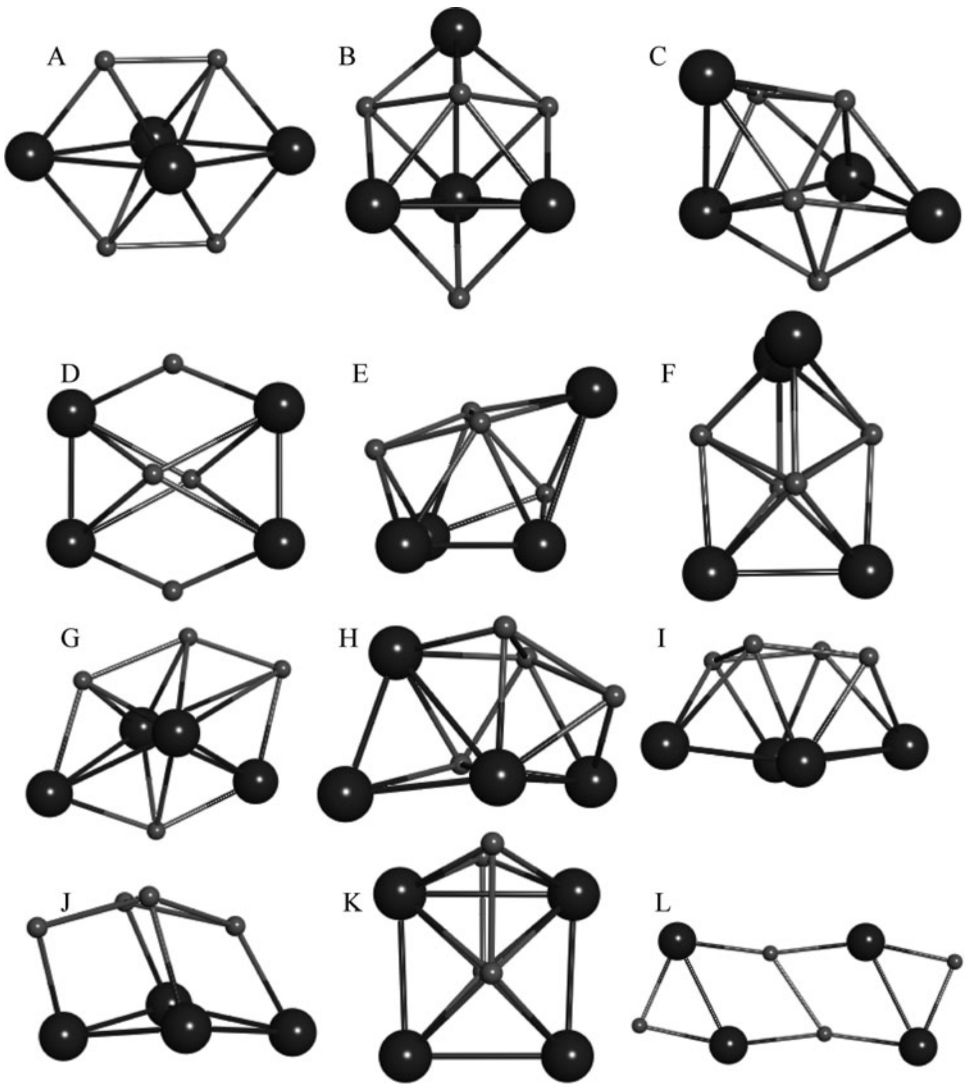

Figure 5. Optimised structures of low-energy Be_4Ge_4 clusters.

reversed in the silicides. Among both the Be_3Ge_3 and the Be_6Ge_3 clusters, substantial transfer of charge from Ge to Be is seen, as much as three-quarters of an electron charge in some isomers. Charge transfer of this magnitude was also observed in the silicide clusters [20] and, given the electron-deficiency of the 2p-subshell of Be, it is likely a source of stabilisation of the three-dimensional clusters.

Be_4Ge_4 and Be_8Ge_4. Twelve low-lying structures of Be_4Ge_4 are presented in Figure 5. The one planar structure, isomer L, is the highest in energy. Structures A and B are less than 1 kcal/mol apart in energy and both have a ground ^1A state. Isomer A is symmetrical, a Ge square bridged top and bottom by two Be, yielding a hexagonal bipyramid. Isomer B is also a cage hollow structure that can be seen as interlocking triangular pyramids of, respectively, Ge and Be, forming a bicapped octahedron. Neither Be_4Si_4 nor Be_4C_4 present structures with these geometries. However, less than 10 kcal/mol above the global minimum is isomer C, resembling a bisdisphenoid structure which does have a counterpart among the Be_4Si_4 isomers. Structure D is also a symmetrical hexagonal bipyramid as A, but with beryllium atoms at the apices. Five of the seven Be_4Si_4 structures identified were found to have counterparts among the clusters of Be_4C_4, yet only structure C of Be_4Ge_4 has a counterpart in the Be_4Si_4 series and there are none among Be_4C_4 structures. Though the differences in atomic size and electronic structure between Ge and C might be expected to lead to great differences among their beryllium clusters, the differences between the clusters of Ge and Si with Be are more surprising, given the generally close correspondence between them in some of their sets of clusters.

In the Be_8Ge_4 global minimum energy cluster, the atoms are arranged at the vertices of a nearly regular icosahedron with D_{2h} symmetry, also the low-energy structure of Be_8Si_4. The structure appears among the

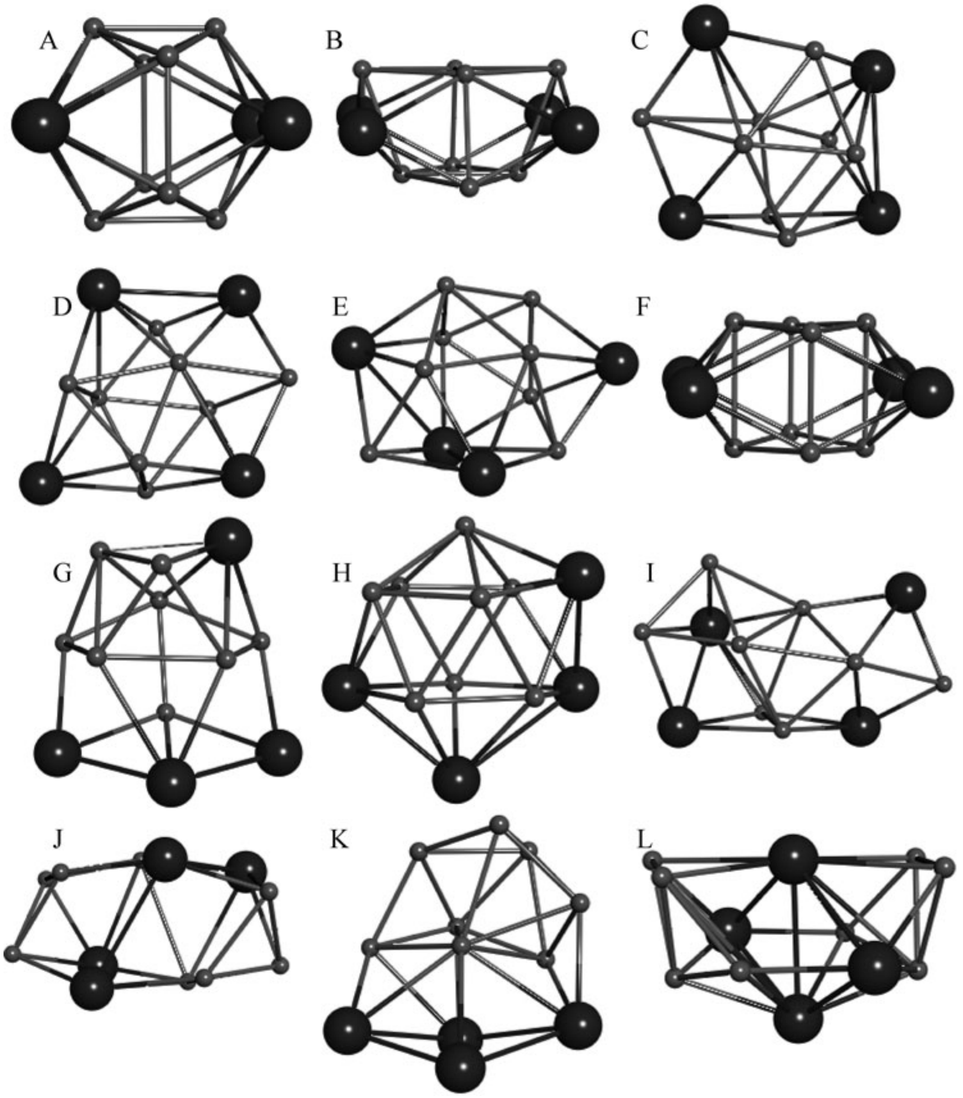

Figure 6. Optimised structures of low-energy Be_8Ge_4 clusters.

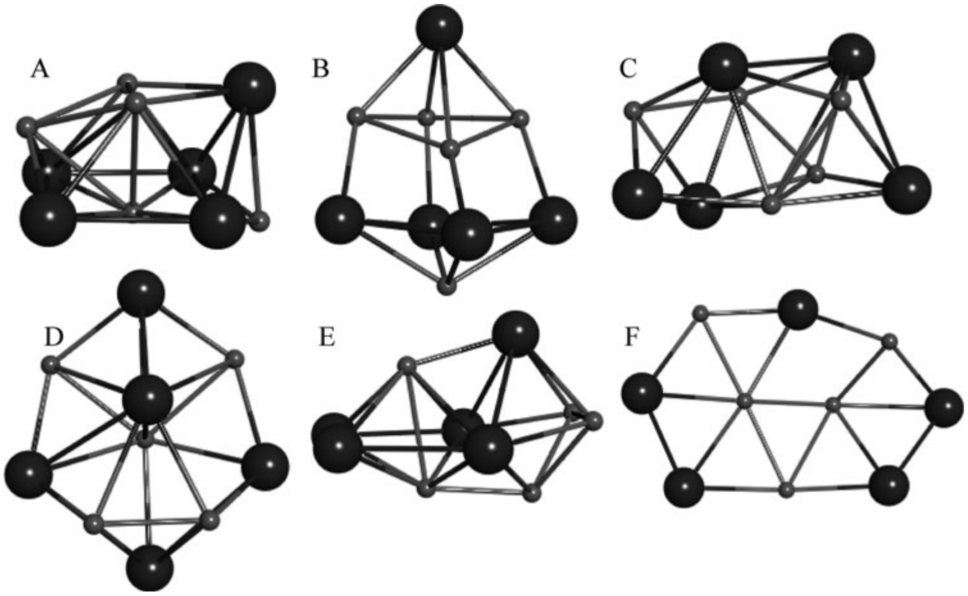

Figure 7. Optimised structures of low-energy Be_5Ge_5 clusters.

isomers of Be_8C_4 but is of relatively high energy. Be_8Ge_4 isomers B and F are variants of the minimum energy cluster. The four low-energy isomers of Be_8Ge_4, all in singlet states, lie within 10 kcal/mol of each other in energy. The same statement is true of Be_8Si_4, but in Be_8C_4 the global minimum energy isomer is some 16 kcal/mol below the next-lowest-energy isomer.

Among the six Be_8Si_4 clusters optimised, only one, a D_{2d} structure next in energy to the minimum, does not appear among the Be_8Ge_4 clusters. Be_8Si_4 isomer C is similar to Be_8Ge_4 isomers C and D, Be_8Si_4 isomer D is similar to Be_8Ge_4 isomer J and isomers E and F correspond to Be_8Ge_4 isomers G and E, respectively. The correspondence between the clusters of Be_8C_4 and those of either Be_8Ge_4 or Be_8Si_4 is less straightforward, owing to the preference in Be_8C_4 for structures in which C–C multiple bonds occur. The two low-energy Be_8Ge_4 isomers feature Be_8 square prisms with four Ge face caps. The same feature is seen in the low-energy isomers of Be_8Si_4 but not among the clusters of Be_8C_4. Planar clusters or moieties are not present among the germanides, silicides or carbides.

Be_5Ge_5. Six stable isomers were found, the same number as were identified for Be_5Si_5. All the Be_5Ge_5 isomers are in the ^1A ground state, and only the highest energy structure F is planar. Fifteen structures were identified for Be_5C_5. None of the Be_5Ge_5 and Be_5Si_5 clusters are of high symmetry while several striking structures of Be_5C_5 were found, symmetrical and featuring extensive C–Be–C bridging. Similarities among the three sets of clusters do however present themselves. The low-energy structure of Be_5Ge_5 has a counterpart in the second-lowest-energy Be_5C_5 structure. Be_5Ge_5 isomer C is closely related to Be_5C_5 isomer D and to the low-energy isomer of Be_5Si_5. Be_5Ge_5 structure D is similar to one of the isomers of Be_5Si_5 and to the high-energy isomer I of Be_5C_5.

Cluster energetics. The stability of each cluster as an atom is added can be estimated from the atomisation energies divided by $N_{\text{atoms}} - 1$. This stability alternates between the Be_nGe_n and the $Be_{2n}Ge_n$ clusters, being greater for the 1:1 clusters than for the 2:1 counterparts with the same number of Ge atoms. This result may be explained from the fact that each Ge contributes twice the number of valence electrons to each cluster as does each Be. This allows the 1:1 clusters to potentially form more bonds per atom. This behaviour is also seen in the silicides and carbides; however, germanium clusters exhibit higher $E_{\text{atomisation}}/(N_{\text{atoms}} - 1)$ values than silicides and significantly lower values than carbides. For each type of cluster (1:1 or 2:1), stability per atom increases with cluster size. However, the stability increment is greater for the smaller clusters with a tendency to decrease as the cluster size increases. This behaviour is to be expected as the incremental increase should approach zero as cluster sizes approach the bulk solid.

4. Conclusions

The small beryllium germanide clusters examined in this study have much more in common with the beryllium silicides [20] than with the carbides [22]. Be–Ge, Be–Si and Be–Be bonds are similar in length, a fact that allows the germanides and silicides to form clusters of similar form and almost the symmetry of pure Be clusters [24], most often in singlet ground states. The germanides and silicides generally display some significant transfer of electrons in the bonding, from Ge or Si to Be. Charge transfer stabilises moieties within the clusters in which Ge or Si act as capping atoms on a face of Be atoms. Such formations are important in forming stable silicide cage clusters [21], and it is therefore to be expected that similar germanide cages will also form. Furthermore, in some clusters, Ge is found to transfer more charge to electron-deficient Be than does Si, and may therefore stabilise clusters with the face-capping feature more than does Si. The carbides, on the other hand, show multiple bonding among C atoms, a greater tendency to planar structures, more triplet ground states and more nearly pure covalent bonding. C does not act to cap Be faces; the C–Be bond length is too short for such structural motifs to develop.

The cluster stability measured as $E_{\text{atomisation}}/(N_{\text{atoms}} - 1)$, is greater for the 1:1 Be:Ge clusters than for the 2:1, a result that may arise from the fact that each Ge contributes with more valence electrons to each cluster than Be does, allowing clusters with lower Be:Ge ratio potentially to form more bonds per atom. In general, the highest atomisation energies for similar clusters are found in the carbides, followed by the germanides, and the silicides display the lowest. The reason the germanides are generally more stable than the silicides likely resides in the ability of Ge to donate more charge to the Be atoms than does Si. Whether this property also leads to improved stability of beryllium germanide cage clusters is a question worthy of inquiry, but it is clear from the results presented here that Be_nGe_n and $Be_{2n}Ge_n$ clusters have the potential to produce interesting cage-like structures.

Disclosure statement

No potential conflict of interest was reported by the authors.

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