Theoretical studies on doubly and triply linked polymers of Ge_9 clusters

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Dedicated to M.C. (master of clustery) Mike Mingos.

Abstract

Experimental isolation of singly-bonded polymers of Ge_9, Sn_9 clusters and oligomers of doubly linked Ge_9 clusters encouraged us to explore other possibilities of polymerizing Ge_9 units. The electron counts in the reported oligomers are not consistent with simple ideas of localized intercluster bonding; demanding a detailed theoretical analysis. Band structure calculations suggest delocalized bonding with a charge requirement of 2− per Ge_9 unit for all polymeric doubly linked chains. DFT-based geometry optimization of model doubly linked polymers shows that one of the two possible forms is stable and has a band gap of ≈ 1.0 eV. A detailed bonding analysis of a theoretical model, Rb_4Ge_{18}, shows that the increased inter-polyhedral bond weakens the intra-polyhedral bonding. Ternary fusions are found to be generally unstable – for triple linkages the intrapolyhedral bonding is still further reduced; the polymers appear to be unstable towards dissociation into individual Ge_9 units.
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1. Introduction

The intertwined use of two simple paradigms – localization (e.g. Lewis structures) and delocalization (e.g. Hückel's and Wade's rules) [1] is a good way to approach interpreting chemical bonding. When it comes to describing molecules or extended structures in which there may be interactions between locally delocalized subsystems, things are less simple. Usually, such molecules are thought of in terms of localized bonds connecting delocalized units, a typical example being biphenyl. This works well for single bonds doing the joining, but when the linkages between aromatics or polyhedral clusters are themselves more complex, defying any localization schemes, things become complicated. Molecular orbital (MO) theory, inherently delocalized, is ideal for exploring these systems.

Deltahedral clusters, which are ubiquitous in borane compounds, are also a structural feature of some heavier

analogues of the carbon group [2]. Wade's skeletal electron counting rules, so useful in polyhedral boranes [3], can also be applied in a straightforward manner to clusters of the carbon family. Any group 14 atom, with one pair of its electrons in an out-pointing lone pair (E:), remains with two electrons available for skeletal bonding, isolobal to a B–H group. This results in very small charges (identical to the corresponding boron clusters) on these systems. Though the skeletal electron count is same as that of boranes, these ligand-free homoatomic clusters of group 14 differ from borane clusters in a subtle way. In boranes the MOs of the *exo*-B–H bonds lie low in energy and the frontier MOs are mostly of polyhedral nature, which makes them unreactive. On the contrary, the frontier MOs of group 14 clusters are mostly made up of the exohedral lone pairs, due to the absence of ligands. As a consequence, the reactivity of these molecules differs radically from that of boranes. These clusters are also of interest as potential building blocks of nano-scaled materials [4]. The most common among them so far are the nine-atom clusters, known to exist with different geometries and charges, E_9^{n-} $(n = 2–4)$ [5].

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Polymers made up of linked Group 14 E_9 units have come out of repeated efforts to functionalize the cluster [6]. The first polymer isolated involved a single bond linking two Ge_9 units, i.e. $[Ge_9–Ge_9]_\infty^{4-}$ [6]. Here the repeating unit actually consists of two Ge_9 clusters as each of these are placed in a *trans* manner. The synthesis of this polymer was preceded by the characterization of the corresponding molecular dimer $[Ge_9–Ge_9]^{6-}$ by the oxidation of a Ge_9 cluster [7]. The linkage of two (or more) Ge_9 units through a single bond formally involves the removal of electrons from the lone pairs of Ge, allowing *exo* bond formation [8,9]. In the singly linked dimer, the 6− charge can be easily rationalized in terms of a localized 2c–2e bond, and the *nido* characteristics for the individual Ge_9 unit (for which one would expect a Ge_9^{4-} electron count). Repeating the unit infinitely in one dimension leads to an average charge of 2− per Ge_9 unit as is indeed observed. But what happens when adjacent polyhedra are connected by two or more bonds?

The experimental characterization of doubly linked Ge_9 oligomers strongly suggests that stable polymers of the type, $[Ge_9{=}Ge_9]_\infty^{4-}$, may also emerge. Thus the trimer is reported to have a 6− charge [10] while the tetramer exists with an 8− charge [11,12]. These charges cannot be explained by any localized *exo*-bond formalism; a delocalized interpretation is needed [10]. In this paper, we investigate these systems systematically by starting with a dimer of doubly linked Ge_9 clusters (as yet unknown), and move on to polymeric chains using the dimers as building blocks. We also analyze the potential extension to triply linked systems.

2. Computational methods

Geometry optimizations of selected molecular systems are done with the GAUSSIAN-98 suite of programs [13], using Becke's exchange (B), Lee, Yang and Parr (LYP) correlation and within the hybrid functional (B3LYP) level [14], with a 6-31G* basis set [15]. Vibrational frequencies are also computed to ascertain the nature of stationary points. The energies of the MOs used in the correlation and interaction diagrams for molecules and their fragments are obtained from extended Hückel (eH) calculations using the YAeHMOP program [16]. Calculations on extended structures are done using the density functional theory based VASP program [17]. For geometry optimization the ultrasoft pseudopotentials based on the projector-augmented-wave (PAW) method is utilized [18]. The local density approximation (LDA) is used for the exchange and correlation potential [19]. A cut-off energy of 500 eV and an energy convergence of 1.0–07 eV atom^{-1} are used. For the crystal lattice, integration over the symmetrized Brillouin Zone is performed using the k-points generated via the Monkhost–Pack scheme [20]. A k-point separation of 0.04 Å^{-1} is uniformly employed for all the systems to generate the mesh. The geometry is well converged with respect to the plane-wave energy cutoff and k-point sampling. An eH based crystal orbital overlap populations (COOP) analysis [21] for atoms is carried out to analyze the bonding in these systems.

3. Monomers of Ge$_9$

There have been numerous studies of Ge_9 clusters, focusing on the varying geometries and electronic requirements of this molecule [5]. The most symmetric forms of Ge_9 are; a tricapped trigonal prism (D_{3h}) with a 2− charge [22] and a monocapped square antiprism (C_{4v}) with a 4− charge [23] (Fig. 1). These two geometries are related to each other through a single so-called *diamond-square* bond-forming/breaking process [24]. There are several Ge_9^{3-} clusters known, though crystallographic difficulties have precluded precise structure determination [25]. However, the trianionic species of Ge_9 have an h/e ratio closer to the D_{3h} form. There are also reports of less symmetric Ge_9 structures as well [5], we select the two highly symmetric forms (D_{3h} and C_{4v}) for our study as it makes the construction of infinite chains easier.

A Ge_9^{2-} polyhedron has 10 skeletal electron pairs. Since each Ge contributes one electron pair to the bonding, with the 2− charge we have $n + 1$ (n is the number of vertices, $n = 9$ here) bonding pairs. The molecule should then have a *closo* structure, according to Wade's rules. A Ge_9^{4-} has one additional electron pair; molecules with $(n + 2)$ electron pairs should, according to Wade's rules, have a *nido* skeleton. Indeed, the cluster is C_{4v}, i.e. a bond breaks upon reduction (diamond → square). Theoretical calculations at various levels of theory actually indicate that D_{3h} and C_{4v} isomers of Ge_9 are almost isoenergetic [26–28]; fluxional behavior has been observed for Sn_9^{4-} in the ^{119}Sn NMR characterization [29].

Before analyzing the polymerization it is useful to review the bonding relations between C_{4v} and D_{3h} geometries of Ge_9 clusters [5]. Fig. 1 gives a correlation of the MOs between the C_{4v} and D_{3h} symmetric Ge_9. The transformation of C_{4v} to D_{3h} geometry mostly involves the movement of the Ge atoms in the square face. One pair of diagonal atoms (marked by a dotted line in the figure) comes closer, to form a bond along the diagonal. This leads to a trigonal prism, while the other Ge pair originally in the square is pushed slightly up to the capping positions of the prism (see Fig. 1).

The MOs of the C_{4v} Ge_9 skeleton have been derived elsewhere [5]; they are shown at the left of Fig. 1. The important frontier orbitals are the HOMO e, a mixture of tangential and radial orbitals, and below it the radial a_1 orbital. The diamond-square transformation affects the three frontier MOs ($a_1 + e$) of the C_{4v} geometry; one of the orbitals in the degenerate HOMO is slightly stabilized and becomes degenerate with the MO derived from the non-degenerate a_1 in C_{4v} geometry, to give e' of D_{3h}. The other MO, which is antibonding in the region the new bond is formed, rises in energy and becomes the HOMO (a_2'') of the trigonal prismatic D_{3h} geometry, were it to have a 4− charge. This MO is antibonding along the prism height (h), and bonding along the basal edge (e).
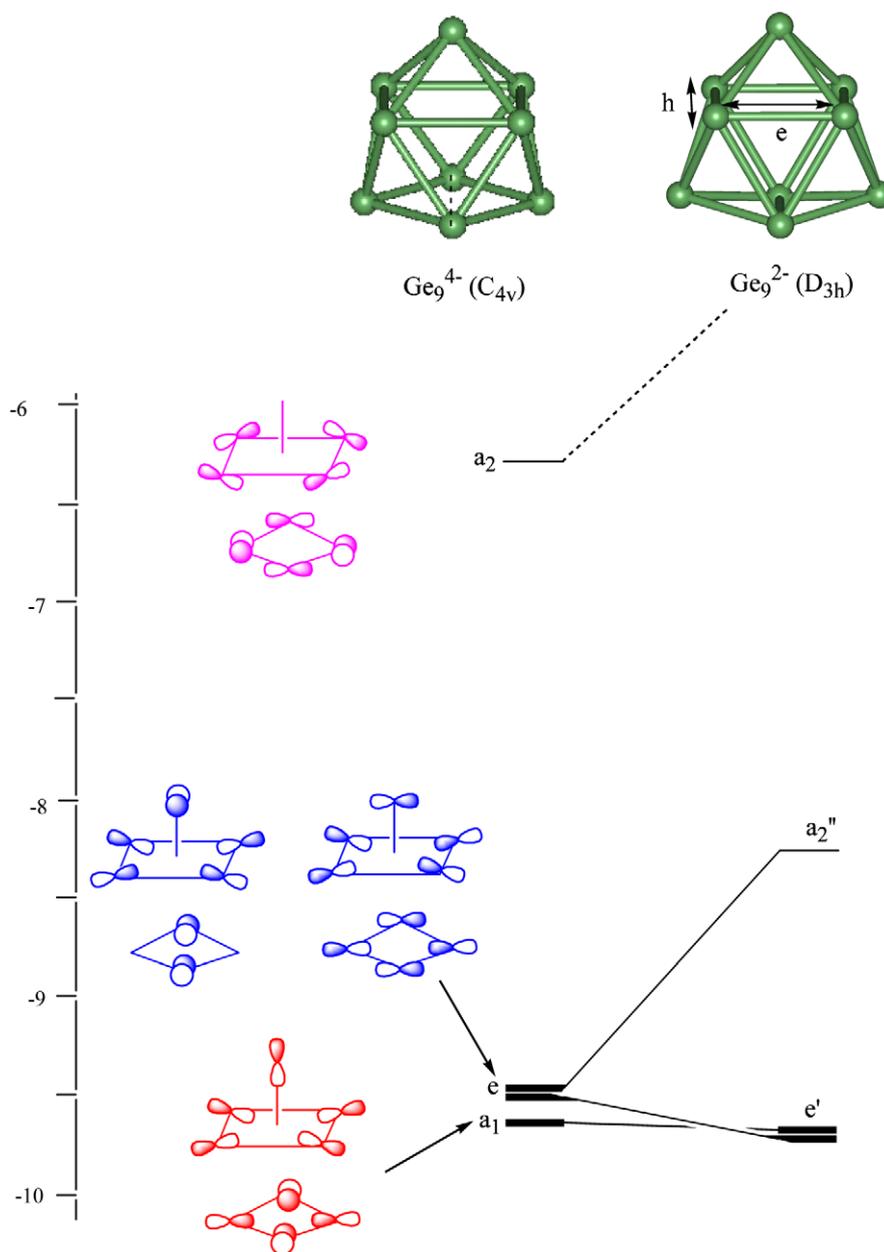
Fig. 1. A correlation diagram between the frontier MOs of Ge_9^{4-} (C_{4v}) and Ge_9^{2-} (D_{3h}).

Removal of electrons from this high-lying a_2'' MO to give Ge_9^{2-} decreases the prism height, h (the MO is antibonding in this region) and increases the basal edge separation, e (where the MO is bonding). Given the complexity of this structure, the h/e ratio is traditionally used to determine the electron count of the cluster [5].

4. Doubly linked dimers of Ge_9, [$Ge_9=Ge_9$]

Ge_9 units connected through two individual bonds between adjacent vertices have been isolated in trimeric and tetrameric forms [10–12]. The reduced overall charge on these trimers and tetramers suggests some delocalization throughout the compound. Assuming a 4– charge for a Ge_9 unit (as per Wade's count for a *nido* cluster), two of them together need an 8– charge. If two single bonds are formed between clusters, the dimer should be oxidized by 4 electrons, hence should exist as 4–.

Since the dimer is not experimentally characterized, we have explored it by theoretical calculations. The 4– charge requirement of the dimer is confirmed by eH calculations. Theoretically two isomers are possible for the dimer, with C_i and C_{2h} symmetries (Fig. 2). Similar to the monomers, these two are also related by a single *diamond-square* bond forming/breaking process. A comparison of Fig. 2a and b clearly shows the opening up of the *closo* skeleton to give a square face. This deformation also removes the C_2 axis; the reduction in symmetry follows.

DFT calculations show that the C_{2h} isomer is just 2.5 kcal/mol less stable than the C_i form. However, the

(a) Ge_{18}^{4-} (C_i, 17 cm^{-1})   **(b)** Ge_{18}^{4-} (C_{2h}, -26 cm^{-1})
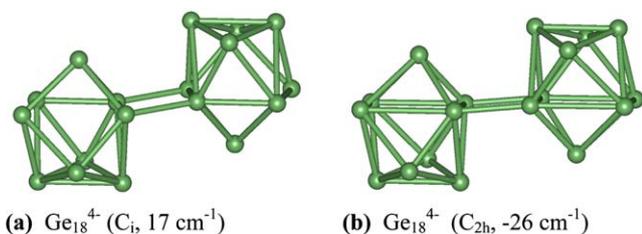
Fig. 2. The optimized geometries of (a) C_i and (b) C_{2h} isomers of Ge_{18}^{4-} with the lowest computed frequencies in the brackets.

C_{2h} structure, with two imaginary frequencies, is not a minimum on the potential energy surface. In general, stability calculations through a frequency analysis are difficult in these clusters, as there are many easy motions within each polyhedron. Because they are so close to each other in energy, we consider both structures as viable candidates for building up oligomers and the polymer.

We analyze the MOs of the C_{2h} symmetric Ge_{18}^{4-} system by interacting two Ge_9 fragments of D_{3h} symmetry; use of the C_{4v} monomer also gives similar results. Fig. 3 shows those frontier MOs which are affected by the forma-

tion of two single bonds between Ge_9 units. As expected, bonding and antibonding combinations are formed. Two of these, $3b_u$ and $1b_g$, are much destabilized. If these orbitals are vacated, there results a good HOMO–LUMO gap, and net bonding between the two component clusters, the net charge being 4− for the dimer.

Following this thinking [[(total charge required by n independent polyhedra) − (total number of electrons to be expelled on forming m single bonds) = (the net charge of the oligomer)], the trimer ($4 \times 3 - 2 \times 4 = 4$) and tetramer ($4 \times 4 - 2 \times 6 = 4$) also should exist with the same 4− charge. By the same reasoning, a polymer constructed from such a dimeric repeating unit should be neutral. But the trimer and tetramer are actually characterized experimentally with 6− and 8− charges, respectively, or 2− per Ge_9 cluster. The conflict between simple localized bonding supported by the orbital picture we just built up for the dimer, and the experimental findings of higher oligomers with a different electron count from that anticipated is what we must explore. Is the electronic requirement in an extended chain of Ge_{18} units neutral $[Ge_{18}]_\infty$ or charged $[Ge_{18}^{4-}]_\infty$?
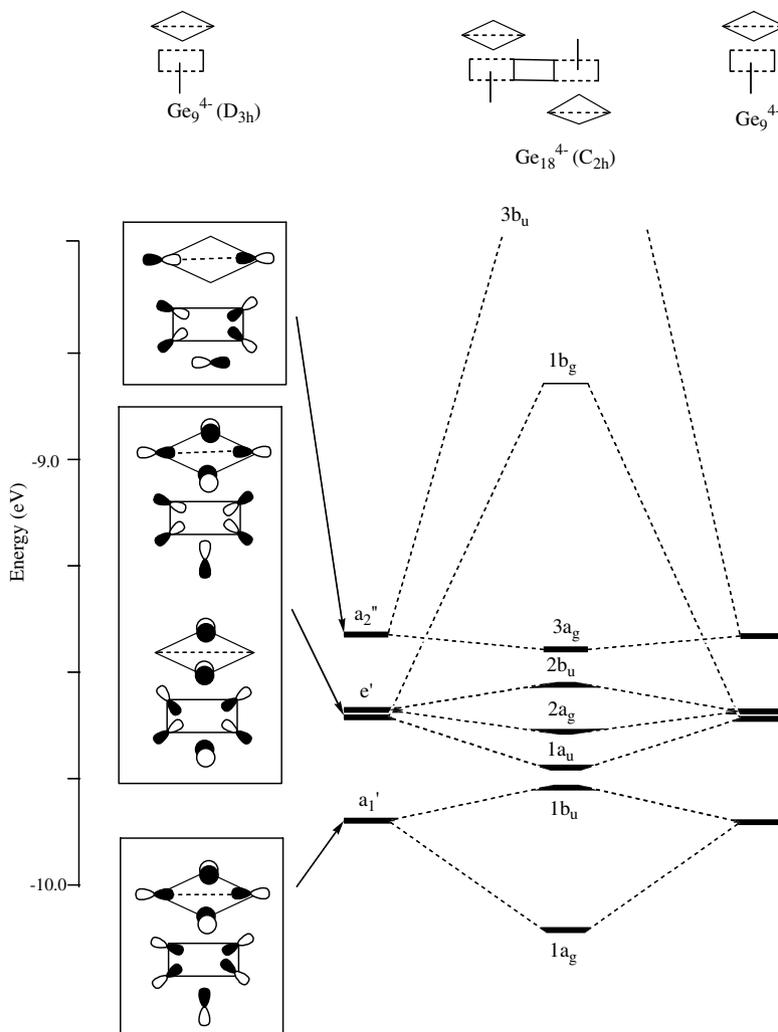
Fig. 3. The interaction between MOs of two Ge_9^{4-} units (C_{2h}) to give Ge_{18}^{4-} (D_{3h}) with two *exo*-single bonds.

5. Doubly linked polymer of Ge_9, $[Ge_9\!\!=\!\!Ge_9]_n$

An exploratory eH band calculation (not shown here) on a 1-D polymer (Fig. 4) features a substantial band gap at the charge of 4− per unit cell. A primitive cell with composition Rb_4Ge_{18} was then chosen for further geometry optimization using VASP. The choice of Rb as counterion is based on the presence of corresponding Ge_9 oligomers with Rb.

The geometry of Rb_4Ge_{18} is optimized in a monoclinic lattice; it has discrete 1-D chains of $=\![Ge_9\!\!=\!\!Ge_9]\!=$ running along the b axis and belongs to space group $P2_1/m$ (Fig. 5). The polymer was constructed using C_{2h} symmetry Ge_{18} units. A polymer with the C_i symmetric Ge_{18} unit starts out initially in a triclinic lattice, space group of $P\bar{1}$, but converges to a $P2_1/m$ structure.

The calculated bond lengths within the Ge_9 cluster are in the range 2.53–2.70 Å except for the prism height of 3.02 Å, which is typical for D_{3h} symmetric Ge_9 clusters and is consistent with its HOMO (see Fig. 1). Though the symmetry of the lattice allows the relaxation of individual Ge_9 units, which could lead to different bond lengths in alternate intercluster bonds, the converged geometry has a uniform bond length of 2.69 Å. The computed lattice parameters are $a = c = 8.69$ Å, $b = 11.27$ Å and $\alpha = \gamma = 90.0°$, $\beta = 96.3°$.

The band calculations, both eH and DFT, clearly point to 4− per two Ge_9 polyhedra as the magic electron count for this polymer. Where does the difference between this finding and simple localization ideas applied to the monomer and dimer (which would have led to a neutral Ge_{18} polymer) come from?

We begin an analysis with Fig. 6, which shows the eH band structure (Fig. 6a) of the Ge_{18}^{4-} 1-D sublattice of the optimized Rb_4Ge_{18}. A definite band gap of ≈ 1 eV is observed at the 4− charge per Ge_{18}. All bands are found to have a similar folding at X, characteristic of one-dimensional systems with a screw axis [30]. Fig. 6b gives the COOP of the bonds involved in the external linkage – one interpolyhedral [Ge(1)–Ge(2)] and another intrapolyhedral [Ge(1)–Ge(1′)].

The COOP shows that the interpolyhedral bonds are mostly bonding. Ge(1)–Ge(2) is bonding even in the region of −7.5 to −9.5 eV where there is only a single band running down from Γ to X of the Brillouin Zone (see Fig. 6).

The same band is folded back at −9.3 eV and continues, through some avoided crossings, to ∼−10.5 eV. A band with such great dispersion is unusual in complex structures.
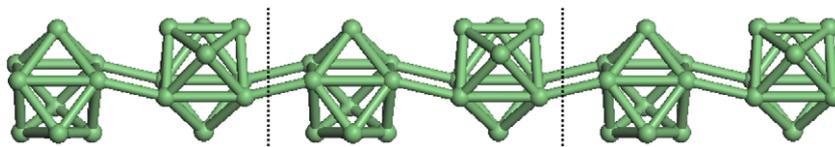
Fig. 5. The optimized 3-D lattice of Rb_4Ge_{18} consisting of discrete 1-D chains of doubly linked Ge_9 units.

The Ge(1)–Ge(1′), where both Ge atoms are exo-bonded with the same neighboring cluster, shows a negative COOP below the Fermi (see Fig. 6) where the highest occupied band lies. Among the frontier MOs of the dimer Ge_{18}^{4-}, only the $1a_u$–$1b_g$ pair has this feature (Fig. 7).

All the other frontier MOs have positive bonding interactions along this bond. Hence we take as a working hypothesis that the high dispersion band we see in Fig. 6 is descended from the $1a_u$–$1b_g$ pair. To understand what is going on, a schematic development of the polymer bands from the MOs of the dimer is shown in Fig. 8. The dimer levels are essentially two points in the development of the band.

If there were no mixing of bands, the system would have been metallic. But the MOs of like symmetry in the dimer do mix, sometimes strongly, which affects the distribution of energy levels in the extended system. For instance, the band arising from $3a_g$ is pushed up due to interaction with the lower-lying $2a_g$. Similarly the band evolving from $1b_g$ is pushed down from mixing with the $2b_g$ band arising from the LUMO + 1 of the dimer.

The net result is the opening up of a significant gap in the polymer for the same electron count per Ge_9 unit (2−) as in the dimer (the four lowest bands in Fig. 8 filled).

The dispersions of the bands drawn vary, depending on the extent of overlap between the monomeric units. While a rough picture of this can be obtained from Fig. 3 by looking at the energy separation of the bonding and antibonding MOs, the detailed outcome can be rationalized from calculated overlap values between the respective MOs

Fig. 4. A polymer of doubly linked Ge_9 with two Ge_9 units forming the unit cell.
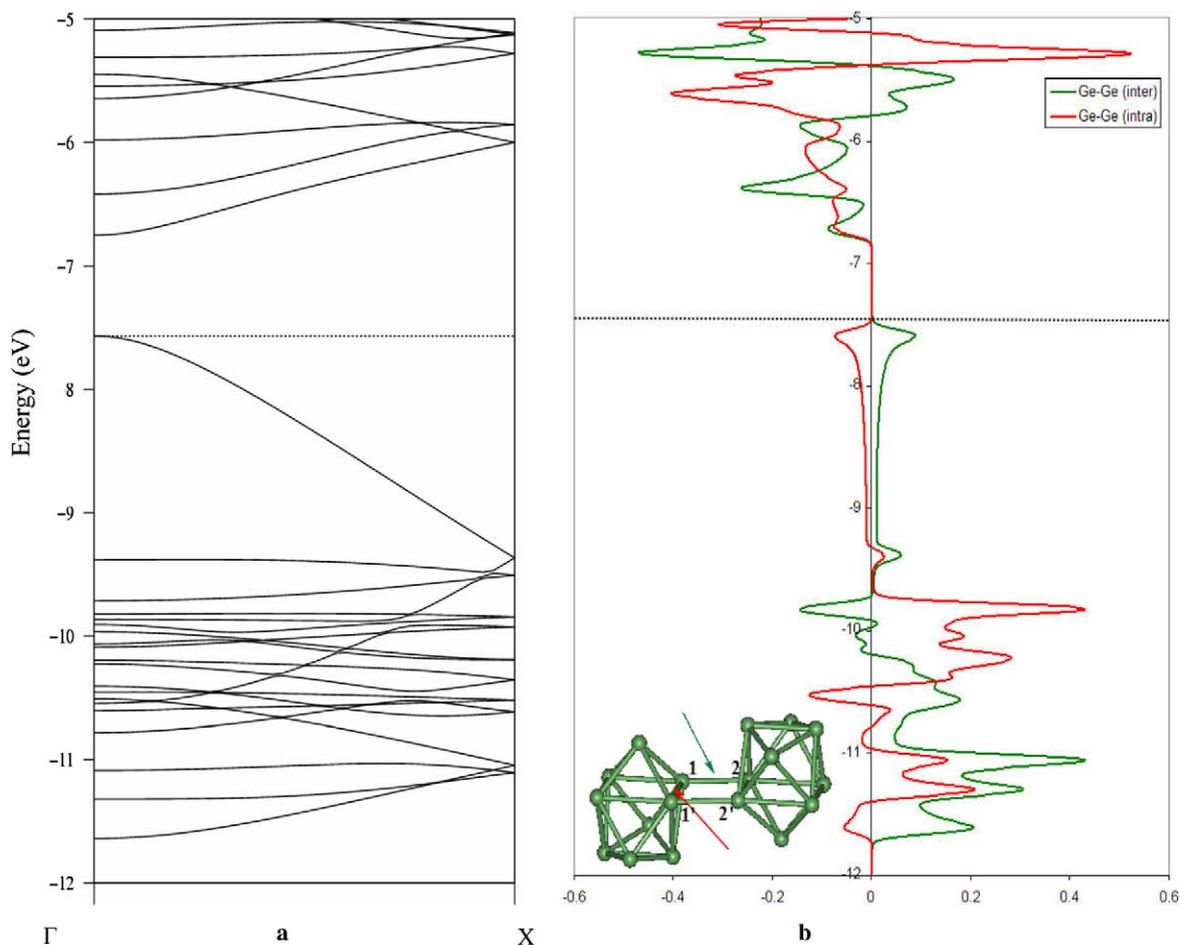
Fig. 6. (a) The band structure of the 1-D polymer containing Ge_{18} units. (b) The COOP between Ge atoms of two adjacent polyhedra forming the *exo*-bonds (Ge(1)–Ge(2) – green, inter) and between Ge atoms of the same polyhedra involved in the *exo*-bonding (Ge(1)–Ge(1′) – red, intra). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$1a_u$ $1b_g$
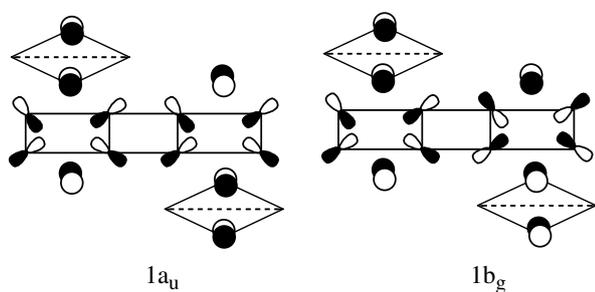
Fig. 7. The HOMO ($1a_u$) and the LUMO ($1b_g$) of the dimer which has antibonding interactions between intra-bonded Ge atoms.

(shown at the right-hand side of Fig. 8). The FMO overlap for the $2a_g$–$2b_u$ pair is only 0.01, so the band that arises from these dimer levels has the lowest dispersion, whereas for the $3a_g$–$3b_u$ pair, the overlap is highest with a value of 0.11. The bands arising from $1a_u$–$1b_g$ and $2a_u$–$2b_g$ pairs have medium dispersion with almost similar overlap values of 0.04 and 0.03, respectively. Since the band arising from $3a_g$, which is bonding between the Ge_9 clusters, is vacated in the polymer, replaced by a band arising from antibond-

ing $2b_g$, the interpolyhedral bond length in the polymer is increased (2.69 Å), when compared to that in the dimer (2.50 Å). The Ge(1)–Ge(1′) bond decreases in length (3.02 Å from 3.44 Å of the dimer), though it is weak when compared to the Ge_9^{4-} monomer (2.63 Å). As a whole, the mixing that we analyze forms bonds between Ge_{18} units at the expense of cluster bonding.

6. Triply linked polymers of Ge_9 $[Ge_9{\equiv}Ge_9]_n$

Though experimental realizations are not at hand, triply linked polymers are a natural extension. Sevov et al. have carried out eH calculations on some oligomers formed by eclipsed fusion of D_{3h} units which showed charges of 4− and 6− for its trimer and tetramer; a reduction of 2− charge compared to its corresponding doubly linked systems. But in an infinite chain of the respective systems the charge increment remains the same; i.e. 4− per dimer or 2− per Ge_9 unit [31]. Theoretically there are four possible fusion modes for Ge_9; eclipsed and staggered binding of both C_{4v} and D_{3h} symmetric Ge_9 units (see Fig. 9). An eclipsed stacking of C_{4v} symmetric Ge_9 units "bends" (see
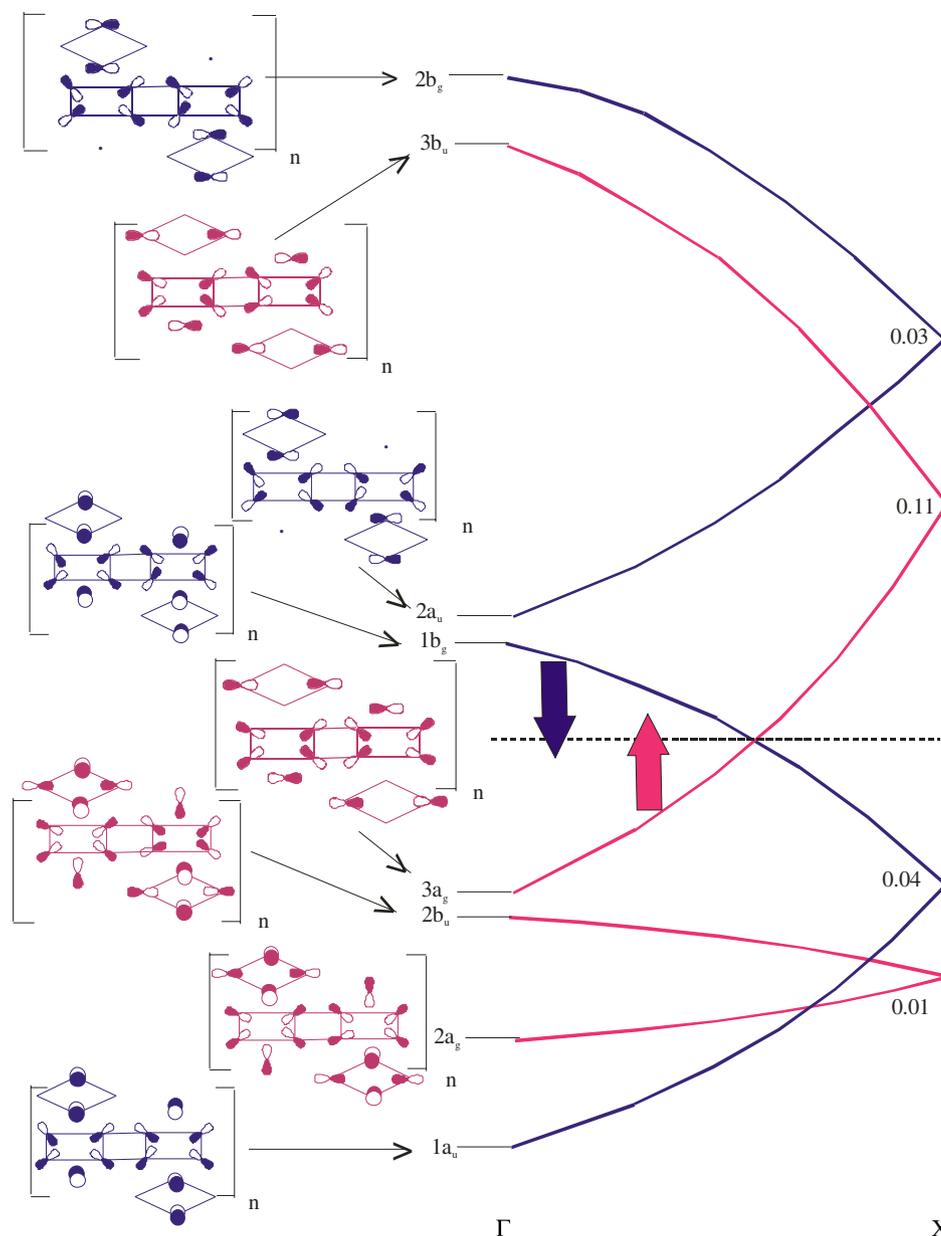
Fig. 8. A schematic band structure of 1-D –[Ge$_9$=Ge$_9$]– chains in the absence of mixing. The 3a$_g$ level goes up and 1b$_g$ comes down, in a critical mixing with other bands of the same symmetry, in the process opening up a gap at the Fermi level for a 2– charge per Ge$_9$ unit. Bands of different symmetry are colored differently. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 9a), and cannot be extended one-dimensionally. For an ideal geometry of Ge$_9$, the angle of bending is around 5°, and actually would complete a ring with around 72 Ge$_9$ units.

Guided by an eH calculation of the band structures, which suggest a charge requirement of 2– per Ge$_9$ in all cases, we tried optimizing a 3-D lattice containing discrete chains of Ge$_9$.

Though the band structure of Fig. 9c structure came out as that of a near zero band gap semiconductor by eH calculations, VASP failed to optimize the structure maintaining the same geometry. Instead it allowed the relaxation of Ge$_9$ units, which eventually break apart to give weakly interact-

ing Ge$_9$ units, separated from each other by a distance of ≈3.0 Å. The same was found to be the case with the geometry of Fig. 9d, though the eH calculation with the ideal geometry had a substantial gap of ≈2.0 eV. The packing in the 3-D lattice results in the same space group (*Pmma*) for both **c** and **d**. The structure in Fig. 9b on optimization tends to move towards a single bonded infinite chain of Ge$_9$ (breaking the other two *exo*-bonds), though convergence was not achieved. This single bonded polymer is different from the known one [7], in that the Ge$_9$ units are arranged in a *cis* fashion.

Similar to the doubly linked polymers, the charge requirement per Ge$_9$ unit of the various forms of ternary
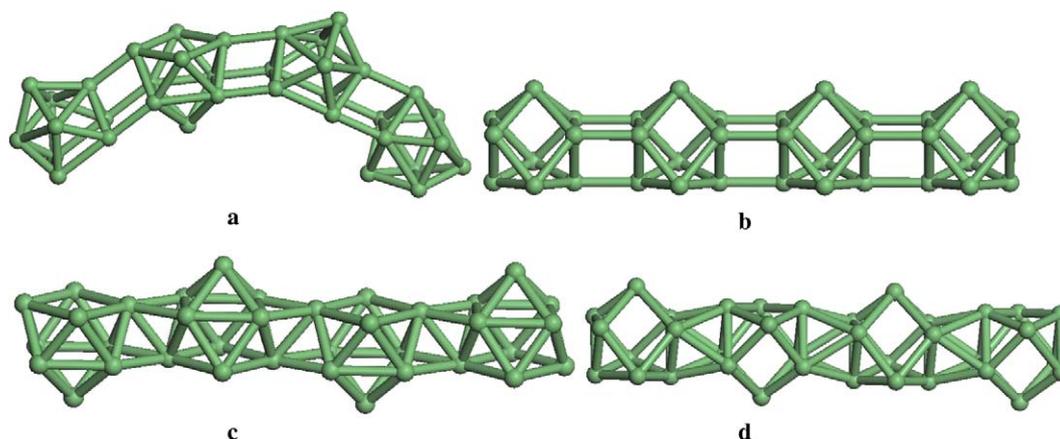
Fig. 9. Tetramers of triply linked Ge$_9$ clusters constructed from (a) C_{4v}, eclipsed; (b) D_{3h}, eclipsed; (c) C_{4v}, staggered; and (d) D_{3h}, staggered orientation.

fusions is 2-, based on an eH band structure calculation. The convergence problems and structural distortions we observed in our calculations are a definite sign of instability. We suspect that linking clusters through more than two bonds may not be favorable, because it necessitates a weakening of polyhedral bonding. Though some oligomers of ternary fusion may exist, a polymer is very unlikely.

7. Conclusions

A theoretical exploration of the various possibilities for extending Ge$_9$ clusters into a one-dimensional chain is carried out. With a singly-bonded polymer already known, we have examined theoretically a doubly linked system, which is found to be stabilized in the presence of Rb atoms. The band structure calculations indicate that Rb$_2$Ge$_9$ will be a semiconductor with a band gap of ≈1.0 eV. A detailed analysis shows that the bonding between polyhedra is formed at the expense of intrapolyhedral bonding. Since oligomers having this linkage are synthesized even upto four Ge$_9$ units, we strongly believe that the proposed polymer is a realistic prospect. Triply linked fusion of Ge$_9$ units in all possible conformations turns out to be unfavorable, presumably due to substantial weakening in the intrapolyhedral bonding.

Acknowledgment

References

[1] (a) E. Hückel, Z. Phys. 70 (1931) 204;
(b) K. Wade, Chem. Commun. (1971) 792.
[2] C.E. Housecroft, Cluster Molecules of p-Block Elements, Oxford University Press, Oxford, 1994.
[3] J. Casanova (Ed.), Borane, Carborane and Carbocation Continuum, Wiley, New York, 1998.
[4] L. Brus, Adv. Mater. 5 (1993) 286.
[5] T.F. Fässler, Coord. Chem. Rev. 215 (2001) 347.
[6] (a) A. Ugrinov, S.C. Sevov, J. Am. Chem. Soc. 124 (2002) 2442;
(b) A. Ugrinov, S.C. Sevov, J. Am. Chem. Soc. 125 (2003) 14059;
(c) A. Ugrinov, S.C. Sevov, Chem. Eur. J. 10 (2004) 3727.
[7] (a) C. Downie, J.-G. Mao, H. Parmar, A.M. Guloy, Inorg. Chem. 43 (2004) 1992;
(b) C.D. Downie, Z. Tang, A.M. Guloy, Angew. Chem., Int. Ed. 39 (2000) 338.
[8] (a) L. Xu, S.C. Sevov, J. Am. Chem. Soc. 121 (1999) 9245;
(b) R. Hauptmann, T.F. Fässler, Z. Kristallogr. NCS 218 (2003) 1.
[9] L. Yong, S.D. Hoffmann, T.F. Fässler, Z. Anorg. Allg. Chem. 631 (2005) 1149.
[10] A. Ungrinov, S.C. Sevov, J. Am. Chem. Soc. 124 (2002) 10990.
[11] A. Ungrinov, S.C. Sevov, Inorg. Chem. 42 (2003) 5789.
[12] L. Yong, S.D. Hoffmann, T.F. Fässler, Z. Anorg. Allg. Chem. 630 (2004) 1977.
[13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millan, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzales, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andreas, M. Head-Gordon, E.S. Reploge, J.A. Pople, GAUSSIAN-98, Revision A7, Gaussian, Inc., Pittsburg, PA, 1998.
[14] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(b) C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[15] W.J. Hehre, L. Radom, P.vR. Schleyer, J.A. Pople, Ab inito Molecular Orbital Theory, Wiley, New York, 1986.
[16] G.A. Landrum, W.V. Glassey, YAeHMOP 3.01 freely available at: <http://yaehmop.sourcefroge.net>.
[17] (a) P. Hohenberg, W. Kohn, Phys. Rev. A 136 (1964) 864;
(b) G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558;
(c) G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 558;
(d) G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[18] G. Kresse, J. Hafner, Phys. Rev. B 59 (1999) 1758.
[19] J.P. Purdew, Z. Zunger, Phys. Rev. B 23 (1981) 5048.
[20] H.J. Monkhost, J. Pack, Phys. Rev. B 13 (1976) 5188.
[21] R. Hughbanks, R. Hoffmann, J. Am. Chem. Soc. 105 (1983) 3528.
[22] H. Mercier, C. Belin, J. Chim. Phys. 86 (1989) 1643.
[23] H.G.v. Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding, M. Somer, Z. Anorg. Allg. Chem. 623 (1997) 1037.

[24] W.N. Lipscomb, Science (Washington, DC) 153 (1966) 373.
[25] T.F. Fässler, M. Hunziker, M. Spahr, H. Lueken, Z. Anorg. Allg. Chem. 626 (2000) 692.
[26] R.B. King, I. Silaghi-Dumitrescu, Inorg. Chem. 42 (2003) 6701.
[27] J.D. Corbett, P.A. Edwards, J. Am. Chem. Soc. 99 (1977) 3313.
[28] L.L. Lohr Jr., Inorg. Chem. 20 (1981) 4229.
[29] R.W. Rudolph, W.L. Wilson, F. Parker, R.C. Taylor, D.C. Young, J. Am. Chem. Soc. 100 (1978) 4629.
[30] R. Hoffmann, Solids and Surfaces, Wiley–VCH, New York, 1988.
[31] S.C. Sevov, private communication.