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Germanium(*cF*136): A New Crystalline Modification of Germanium with the Porous Clathrate-II Structure[**]

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Dedicated to Professor B. Eisenmann on the occasion of her 65th birthday

The structures of the elements are of particular beauty, owing to the usually high symmetry of their atomic arrangements. Therefore, the discovery of new modifications receives considerable attention far beyond the immediate field of research. One of the most outstanding recent contributions in this respect was the discovery of the fullerenes, which can be placed alongside diamond and graphite as new modifications of carbon. This pioneering work was awarded the Nobel Prize, but it was the capability to produce the fullerenes on a preparative scale that allowed the rapid expansion of this research area.[1,2] However, the discovery of new crystalline modifications of other elements at standard pressure has become rare; such discoveries have recently been restricted to the elements sulfur[3] and phosphorous, with the structure determination of red fibrous phosphorous being of particular interest.[4]

Recently, Guloy et al. presented a clathrate-II-analogous germanium structure that does not contain any guest atoms ("$\square_{24}Ge_{136}$", where □ represents a vacant guest-atom site within a cavity) and, hence, represents a new element modification, Ge(*cF*136) (the IUPAC nomenclature of elemental polymorphs includes the Pearson symbol; see below).[5] This rather astonishing result is of major importance, since nanostructured germanium (possibly in combination with silicon) offers a promising alternative to established materials in photovoltaics and in silicon-based optoelectronic building blocks.[6–9]

In addition to the well-known α form of germanium with the diamond structure (Ge-I, Ge(*cF*8)), several high-pressure modifications of germanium have been structurally characterized.[10] In Table 1, the germanium structures determined at atmospheric pressure and that of β-Ge at 120 kbar are compared. Under pressure, α-Ge transforms to the tetragonal, metallic β form (Ge-II, Ge(*tI*4), with the β-Sn structure). The application of even higher pressure followed by pressure release yields the γ-Ge (Ge-III, Ge(*tP*12)) and δ-Ge (Ge-IV, Ge(*cI*16)) modifications.[11,12] In the structures of both of these allotropes, the bond angles of the consistently fourfold-coordinated germanium atoms deviate considerably from the ideal tetrahedral angle. γ-Ge crystallizes in a three-dimensional structure of bent five- and seven-membered rings, whereas δ-Ge features six-membered rings. As expected, the atomic volume under standard conditions of these modifications is slightly smaller than that of α-Ge. Several other high-pressure modifications of germanium with even smaller atomic volumes are also known.[13]

In contrast, Ge(*cF*136) is a new crystalline modification at *atmospheric* pressure. Through a straightforward synthetic route, Ge(*cF*136) is obtained in good yield and in sufficient quantity to allow the characterization of its structure and the investigation of its electronic properties. The so-called *allo*-Ge modification, which was synthesized in the 1980s through another simple route, the topotactic reaction of $Li_{12}Ge_{12}$ with oxidizing agents, transforms into the 4H-Ge modification at 147 °C. Although the metrics of the unit cells are known, the structures of both *allo*-Ge and 4H-Ge could only be approximately described to date.[14]

In contrast, nanosized germanium particles can be produced reasonably well either by physical methods or by chemical routes, which have not yet been examined in detail.[15] The metal-

Table 1: Allotropic forms of germanium with known structures, as well as *allo*-Ge und 4H-Ge.

Allotrope (structure type)	Pearson symbol	Space group	Atomic volume [Å^3]	Bond lengths [Å]	Bond angles [°]
α-Ge, I (diamond)	*cF*8	$Fd\bar{3}m$	22.63	2.445	109.5
β-Ge, II (β-Sn)[a]	*tI*4	$I4_1/amd$	16.05	2.533–2.692	74.5–105.5
γ-Ge, III (ST12)	*tP*12	$P4_12_12/P4_32_12$	20.45	2.479–2.489	98–135
δ-Ge, IV (BC8)	*cI*16	$Ia\bar{3}$	20.71	2.421–2.469	99.0–117.6
ε-Ge, V (clathrate II)[b]	*cF*136	$Fd\bar{3}m$	25.88	2.435–2.492	106.1–119.9
allo-Ge[c]	*oP*128	$Pmc2_1$	24.06		
4H-Ge[d]	*hP*8	$P6_3mc$	22.58		

[a] At 120 kbar. [b] $a = 15.2115$ Å; Wyckoff positions and atomic parameters: 8*a* (7/8, 7/8, 7/8), 32*e* (0.7815, *x*, *x*), 96*c* (0.81667, *x*, 0.6296). [c] Severely disordered. [d] Indexed powder X-ray diffraction pattern.

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induced formation of germanium nanoparticles by chemical vapor deposition (CVD)[16,17] and by the recrystallization of thin films[18] has been described. CVD experiments with $Ge(C_6H_5)_2$ as the precursor[19] and the gold-induced decomposition of $Ge(C_6H_5)_2H_2$ in supercritical cyclohexane[16] led to the formation of nanowires. The reaction of Mg_2Ge with $GeCl_4$ yielded "mesostructured germanium with cubic pores",[20] whereas the oxidation of $[Ge_9]^{4-}$ Zintl ions in the presence of a surfactant led to "hexagonal nanoporous germanium".[21] However, an unambiguous structure determination has not yet been possible for either material, and contamination by oxygen or carbon could not be excluded.

The new Ge(*cF*136) modification was obtained in crystalline form through the oxidation of Zintl anions in an ionic liquid. The happenstance that the solvent used by Guloy et al., a 1:1 mixture of dodecyltrimethylammonium chloride and aluminum trichloride, also acts as an oxidizing agent for the Zintl anions was essential for the success of the synthesis. The oxidative coupling of $[Ge_9]^{4-}$ ions to form dimeric, oligomeric, and polymeric units has been investigated in detail previously. These ions form after the dissolution of binary phases with the nominal composition A_4Ge_9 (A = Na–Cs) in ethylenediamine. The structures of the A_4Ge_9 starting materials are only known for A = K and Cs;[22–24] Na_4Ge_9, which was used for the synthesis of Ge(*cF*136), has only been poorly characterized.

In addition to salts of the $[Ge_9]^{4-}$ and $[Ge_9]^{3-}$ ions,[25–27] the ethylenediamine solutions of the binary A_4Ge_9 phases also yielded salts of the dimeric $[Ge_9{-}Ge_9]^{6-}$ ion (Figure 1 a).[28–30] This dimeric unit could also be synthesized with dimethylformamide replacing ethylenediamine as the solvent.[31] The formation of dimers from $[Ge_9]^{4-}$ ions can be seen as the first step of an oxidative coupling reaction.

Further oxidation of the $[Ge_9]^{4-}$ ion formally leads to the "$[Ge_9]^{2-}$" ion, which could not yet be isolated, but could be stabilized in various ways: besides the trimeric $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$ and the tetrameric $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$ units (in which the "$[Ge_9]^{2-}$" ions are linked by pairs of single bonds),[32–35] a polymeric $^1_\infty[\{Ge_9\}_n]^{2n-}$ ion can be formed (Figure 1 b–d).[36,37] The monomeric "$[Ge_9]^{2-}$" ion is assumed to exist,[38] but the structural characterization of compounds that might contain the cluster has not been possible, owing to the pronounced disorder of the anion. The $[A(2.2.2\text{-crypt})]^+$ and $[A([18]\text{crown-6})]^+$ ions have been used almost exclusively as counterions for these polyanions. A continuation of the oxidative coupling could, in principal, lead to an uncharged layered structure built from Ge_9 units (Figure 1 e),[39] but no experimental proof of such a structure has yet been obtained.

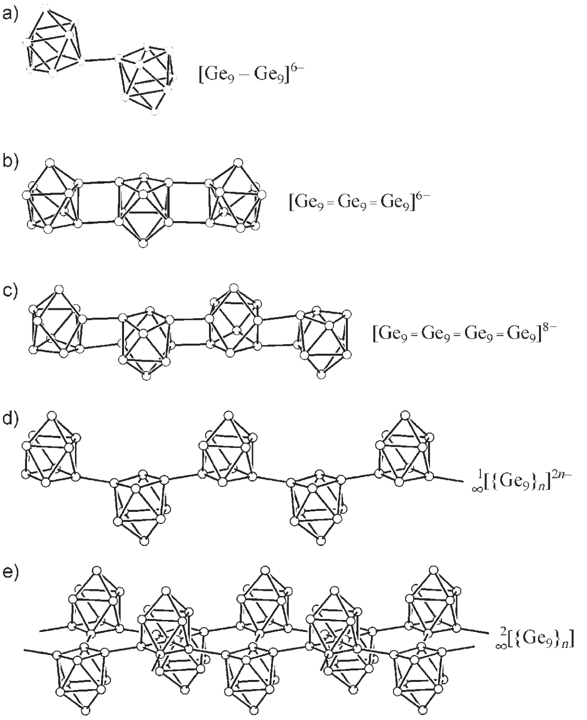

Figure 1. Structures of linked Ge_9 clusters. a) A $[Ge_9{-}Ge_9]^{6-}$ dimer. b) A $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$ trimer. c) A $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$ tetramer. d) A one-dimensional $^1_\infty[\{Ge_9\}_n]^{2n-}$ polymer. e) A hypothetical two-dimensional $^2_\infty[\{Ge_9\}_n]$ polymer.

The Ge(*cF*136) modification isolated by Guloy et al. crystallizes in the cubic clathrate-II structure. This structure can be derived from the zeolite ZSM-39 structure by replacing the $MO_{2/4}$ units (M = Al, Si) with Ge atoms. According to IUPAC, the nomenclature of elemental polymorphs includes the Pearson symbol, which designates the crystal family (for Ge(*cF*136), *c* = cubic) and type of centering (*F* = face-centered) of the Bravais lattice, as well as the number of atoms per unit cell (136). The three-dimensional structure of the new modification consists of two different kinds of germanium polyhedra, Ge_{20} pentagonal dodecahedra (pdod; Figure 2 a) and Ge_{28} hexakaidecahedra (hkad; Figure 2 d), which are linked by sharing pentagonal faces to form a

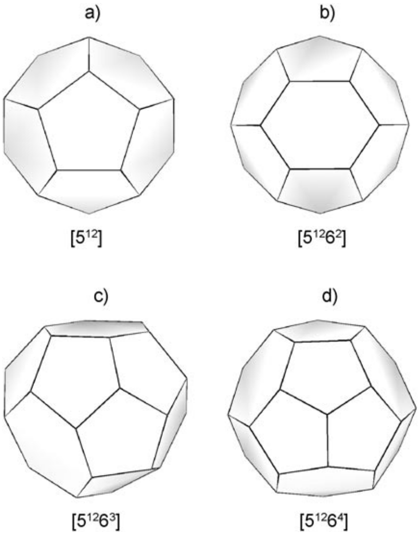

Figure 2. Polyhedral building blocks of the clathrate-I, -II, and -III structures. a) A pentagonal dodecahedron (pdod) with 20 atoms. b) A tetrakaidecahedron (tkad) with 24 atoms. c) A pentakaidecahedron (pkad) with 26 atoms. d) A hexakaidecahedron (hkad) with 28 atoms. The notation beneath the polyhedra indicates the number of pentagons and hexagons in each.

three-dimensional network of germanium atoms. The voids of various sizes formed by this arrangement are, in principal, capable of hosting Na^+ or Cs^+ ions,[40] but they are empty in Ge(*cF*136). The new allotrope crystallizes in the space group $Fd\bar{3}m$ (no. 227) with the unit-cell parameter $a = 15.2115$ Å.

The structure of Ge(*cF*136) was determined by powder X-ray diffraction and transmission electron microscopy. The absence of guest atoms was demonstrated by electron energy-loss (EEL) spectroscopy. As expected, the average atomic volume is bigger than that in any other element modification of germanium (Table 1). The modification is metastable with respect to the formation of α-Ge (transition temperature of 420 °C), and is diamagnetic and semiconducting (band gap of 0.6 eV).

The three-dimensional structure of Ge(*cF*136) (Figure 3 a) can be understood as a hierarchical variant of the cubic Laves phase $MgCu_2$ (Figure 3 c) in which each copper atom is replaced by a pdod and each magnesium atom is replaced by a hkad. Hence, the pdod (copper atoms) form layers equivalent to kagomé nets (Schläfli symbol 3.6.3.6; Figure 3 c,d), which are stacked along a body diagonal of the unit cell in an ABC sequence analogous to that of a cubic closest packing of atoms (Figure 3 a).[41,42] Two of these pdod layers are shown in Figure 3 b, viewed along the layers, and in Figure 3 e, viewed along a body diagonal. The layers are interconnected by further pdod (copper atoms) above the triangles of the kagomé layers (yellow polyhedra in Figure 3 a,b,e,f; yellow spheres in Figure 3 c). The hkad (purple polyhedra in Figure 3 a,f) are interconnected through their four hexagonal faces. They form a diamond-like three-dimensional structure analogous to the magnesium-atom network in $MgCu_2$ (purple spheres in Figure 3 c) and are situated above the hexagons of the kagomé net. The hkad share their pentagonal faces with pdod, leading to a complete space filling. The average interatomic distances are comparable to those in α-Ge. The shorter contacts are approximately 0.05 Å shorter than those in α-Ge; the longer contacts are comparable to those in the filled clathrate $Cs_8Na_{16}Ge_{136}$.[40]

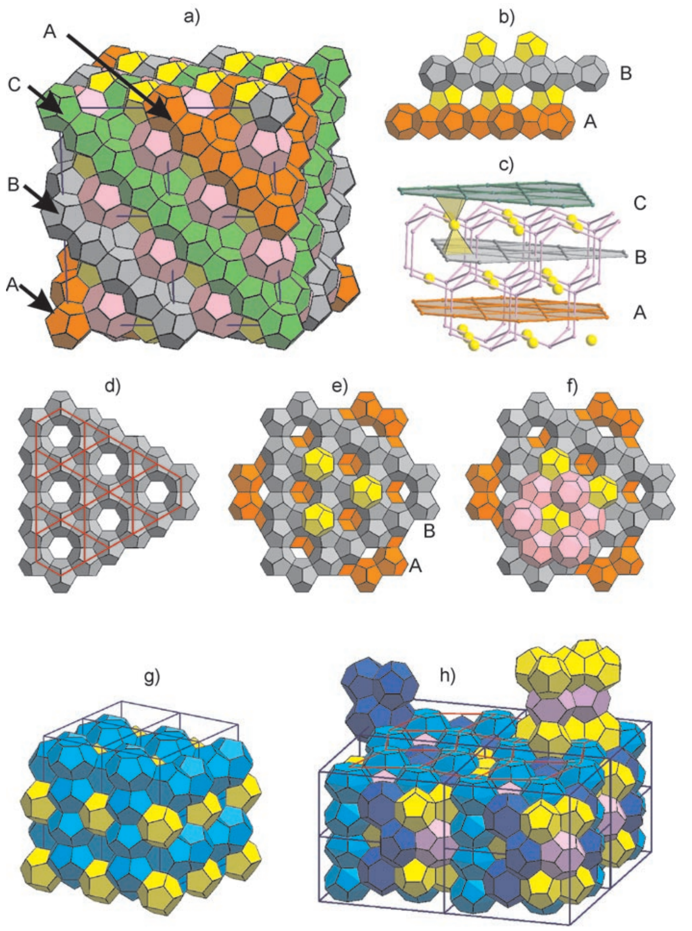

Figure 3. Clathrate structures. a) The clathrate-II structure (2×2×2 cell). Layers A (orange), B (gray), and C (green) of pdod are stacked along a body diagonal and are interconnected by additional pdod (yellow) and hkad (purple). b) Side view of layers A and B with connected pdod. c) Structure of the cubic Laves phase $MgCu_2$. Kagomé nets of copper atoms correspond to layers A (orange), B (gray), and C (green). The triangles of these nets are capped by additional copper atoms (yellow), forming vertex-sharing tetrahedra. The magnesium atoms form a diamond-like network (purple). d) A kagomé net of pdod (layer B) in the clathrate-II structure. e) Layer B from (d) with layer A and connected pdod (top view of (b)). f) The layers from (e) with additional hkad, which form a diamond-like network. g) The clathrate-I structure (2×2×2 cell). Strands of tkad (light blue) run orthogonally to one another, and the resulting voids are filled by pdod (yellow). h) The clathrate-III structure (2×2×2 cell). Strands of T1 tkad (light blue) form a rod packing of distorted squares and rhombi. The distorted-square channels are filled by edge-sharing tetrahedra of T2 tkad (dark blue). The rhombic channels are filled by a linear chain of alternating groups of five pdod (yellow) and two pkad (purple).

With the help of quantum-mechanical calculations, Nesper et al. demonstrated the relationship between hypothetical carbon modifications consisting of networks of four-bonded atoms and the frameworks of zeolites.[43] They found that the carbon frameworks derived from the structure types zeolite ZSM-23 (clathrate I), zeolite ZSM-39 (clathrate II), zeolite theta-1, melanophlogite, and bikitaite are energetically favored over C_{60}. The clathrate-II structure found for Ge(*cF*136) is the most stable structure for carbon after the diamond structure. The clathrate-I structure is slightly higher in energy than the clathrate-II structure.

In the clathrate-I structure, tetrakaidecahedra (tkad; Figure 2 b; light blue polyhedra in Figure 3 g) form one-dimensional strands by sharing hexagonal faces. Owing to the cubic symmetry, the strands run orthogonally to one another, and they interconnect by sharing pentagonal faces to form the three-dimensional structure, which is a hierarchical variant of the Cr_3Si type. The resulting voids are isolated from each other and have the shape of pdod (yellow polyhedra in Figure 3g).

The clathrate-III structure is another interesting framework for four-bonded atoms,[41,44] because it is made up of even smaller polyhedra. As in the clathrate-I structure, one type of tkad (T1; light blue polyhedra in Figure 3h) forms linear strands by sharing hexagonal faces. With respect to the centers of the hexagonal faces, a slightly distorted pattern of squares and rhombi results. The remaining canal-like voids are filled with different types of polyhedra. The quasifourfold voids contain chains of edge-sharing tetrahedra of a second type of tkad (T2; dark blue polyhedra in Figure 3h). The arrangement of tkads can be considered as a hierarchical defect variant of the SiS_2 structure type, in which the tkad replace the sulfur atoms. The T2 tkad share hexagonal faces, and the T1 and T2 tkad share pentagonal faces. The C_2-symmetrical canals of the rhombi are filled by chains consisting of alternating groups of five interconnected pdod (yellow polyhedra in Figure 3h) and units of two pentakaidecahedra (pkad; Figure 2c; purple polyhedra in Figure 3h). The pkad have three distorted hexagonal faces (with threefold pseudosymmetry), which are shared by the T2 tkad.

In general, the investigation of structure–property relationships in nanoscopic materials is complicated by the statistical size distribution of the particles and the often ill-defined chemical composition. However, the synthesis of a new crystalline germanium modification with zeolite-like voids from easily accessible precursors should lead to interesting post-synthetic chemistry, which might shed some light on structure–property relationships for this element. The structures presented herein might be feasible for modifications of silicon as well. An appropriate precursor containing nine-atom cluster anions is already known.[45,46]

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