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A New 3D Network of Four-Bonded Germanium: A Missing Link between Open and Dense**

Ulrich Schwarz*, Aron Wosylus, Bodo Böhme, Michael Baitinger, Michael Hanfland, and Yuri Grin

Solids comprising three-dimensional networks of mainly *p*-elements like intermetallic clathrates or substituted skutterudites are currently intensely investigated by solid state physicists and chemists aiming at the preparation of new materials with different property scales revealing novel combinations of physical characteristics [1, 2].

A large number of open framework structures is adopted by germanium. At ambient pressure, covalent interactions provide sufficiently high energy barriers to impede transformations so that phase formation becomes controlled kinetically, e.g., in allo-germanium Ge(*oP*128) and Ge(*hP*8) [3] as well as in Ge(*cF*136). This clathrate-II-type $\square_{24}\text{Ge}_{136}$ host assembly [4] persists at increasing temperatures up to 693 K, see Fig. 1. Two more germanium modifications, Ge(*tP*12) and Ge(*cI*16), can be generated by decompression [5, 6]. In all these allotropes, the four-bonded atoms adopt next-neighbour distances which are similar to those of diamond-type Ge(*cF*8).

Upon pressure increase, Ge(*cF*8) transforms above ten GPa (Fig. 1) into β -Sn-type Ge(*tI*4) with 4+2 coordination [7]. Above seventy five GPa, the so-called *Imma* phase Ge(*oI*4) [8] with a 4+2+2 coordination is formed. Around eighty GPa, hexagonal primitive Ge(*hP*1) [9] with coordination number 8 is stable. Upon further compression, Ge(*oC*16) adopts a crystal structure in which two types of atoms are coordinated by 10 and 11 neighbours, respectively [10]. This atomic pattern transforms at higher pressures into the hcp arrangement Ge(*hP*2) with coordination number 12 [10].

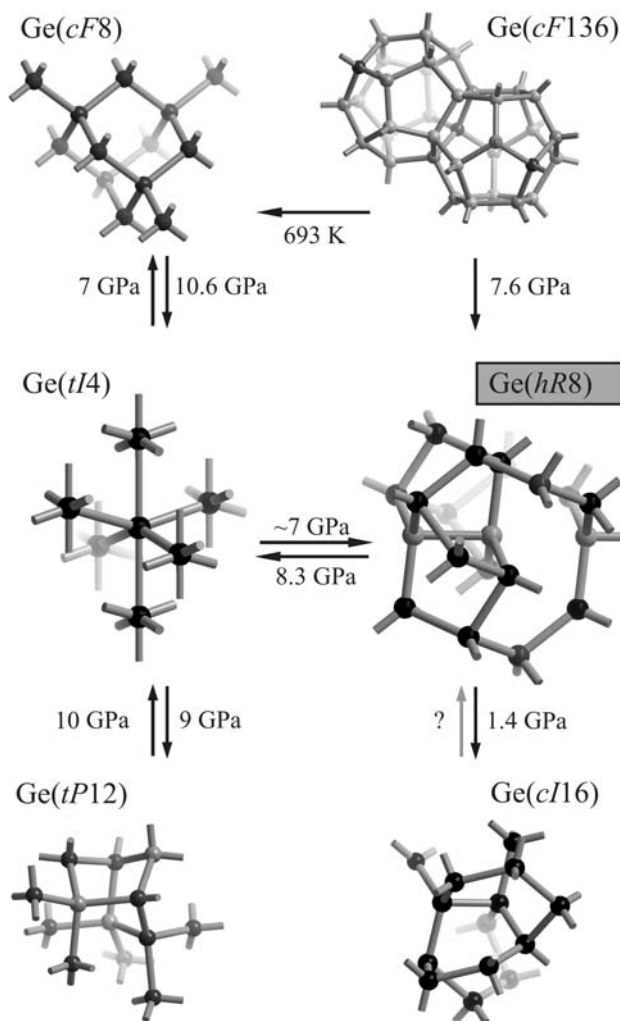


Fig. 1. Germanium frameworks in elemental crystal structures: The majority of modifications formed at moderate pressures are related to β -Sn-like Ge(*tI*4) or to the new allotrope Ge(*hR*8) rather than to diamond-like Ge(*cF*8). The name of the new phase is shaded grey.

The pressure-induced structural changes of the modification Ge(*cF*136) are so far unexplored. A sample of $\square_{24}\text{Ge}_{136}$ is synthesized by mild oxidation of $\text{Na}_{12}\text{Ge}_{17}$ with HCl [11]. In direction of increasing pressure, in-situ x-ray powder diffraction indicates a continuous compression of the clathrate between ambient pressure and 12.7(5) GPa (Fig. 2). In these experiments additional diffraction lines indicate a second, new phase at 7.6(5) GPa before a third, Ge(*tI*4)-type component starts to form at 8.3(5) GPa. Above 12.7(5) GPa the transformation into the Ge(*tI*4) pattern is completed. In direction of decreasing pressure, a mixture of the Ge(*tI*4) type and the new phase (formed at 9.8 GPa after several days) yields nearly pristine new diffraction patterns below approximately 6 GPa (Fig. 2). Pressure decrease to 1.4 GPa induces a further transition into mainly Ge(*cI*16). In these experiments, the phases may contain small amounts of hydrogen, oxygen and sodium from the starting material. In order to confirm the new phase unambiguously as a germanium allotrope, a second set of measurements is performed which starts with pure Ge(*tP*12). After formation of Ge(*tI*4), a stepwise pressure release down from 15.4 GPa induces the formation of the new allotrope Ge(*hR*8) mixed

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with Ge(*cF8*) and Ge(*tP12*) below 7 GPa (Fig. 2). The volume fraction of the phases as estimated from diffraction intensities corresponds to approximately 1:2:2 at 2.4 GPa.

Despite the pronounced differences of atomic volumes (Fig. 3), the compressibility as revealed by the bulk moduli of the clathrate Ge(*cF136*) [$B_0 = 76(6)$ GPa, $B_0' = 6(2)$] and the new modification Ge(*hR8*) [$B_0 = 73(3)$ GPa, $B_0' = 4$] are strikingly similar to the value of 75 GPa [12] for Ge(*cF8*).

The crystal structure of Ge(*hR8*) comprises a germanium network with two types of atoms. Typically, such an occupation of non-equivalent sites is correlated with a differentiation of the atomic coordination, e.g., in metals like Mn(*cI58*) [13], Ti(*hP3*) [14] or Ge(*oC16*) and isotypic phases [10, 15, 16] as well as in more complex high-pressure modifications [17, 18]. In Ge(*hR8*), both types of germanium atoms exhibit four neighbours, Ge1(Ge1)₁(Ge2)₃ and Ge2(Ge1)₁(Ge2)₃. Additionally, one germanium features a fifth contact with $d(\text{Ge1-Ge1}) = 3.24$ Å at 2.4 GPa. This expansion of the coordination sphere and the significantly reduced density of Ge(*hR8*) is reflected by an elongation of the next-neighbour distances with respect to Ge(*cF8*). The

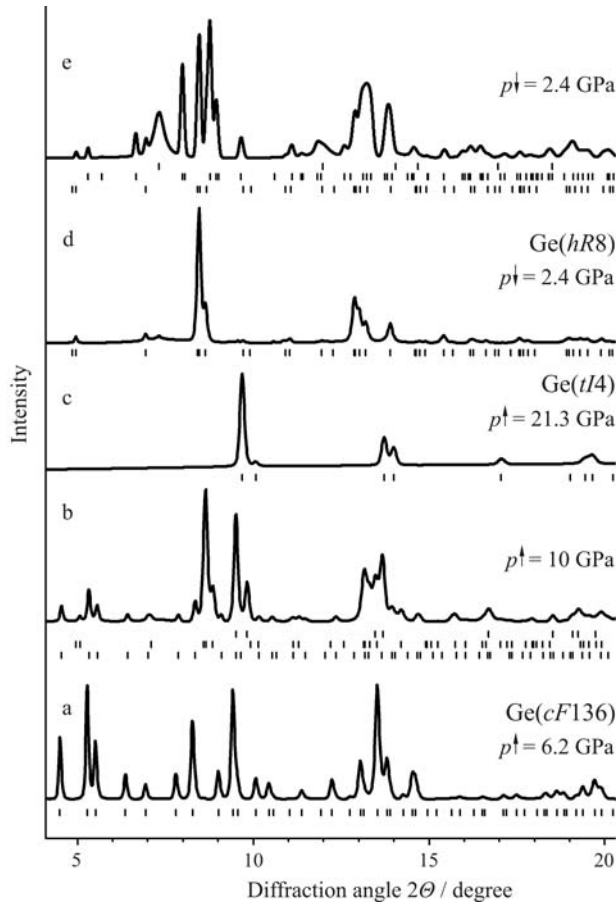


Fig. 2. X-ray powder diffraction patterns at elevated pressures. Upon pressure increase(↑), the starting material Ge(*cF136*) persists up to 7.6(5) GPa (a), a phase isotypic to Ge(*hR8*) coexists with clathrate and a β -Sn-type pattern between 8.3(5) GPa and 12.7(5) GPa (b). An arrangement isotypic to Ge(*tI4*) is stable at pressures exceeding 12.7(5) GPa (c). In direction of decreasing pressures (↓), the new phase is observed down to approximately 2 GPa (d). Taking Ge(*tP12*) as an educt, the new phase coexists with Ge(*cF8*) and Ge(*tP12*) upon decompression (e). Reflection positions are indicated by tick marks.

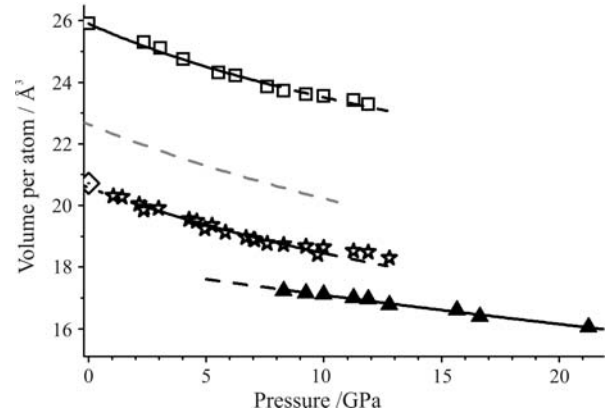


Fig. 3. Atomic volumes of germanium as a function pressure: Ge(*cI16*) (diamond, [5]), Ge(*cF136*) (open squares), β -Sn-type Ge(*tI4*) (triangles), Ge(*hR8*) (stars), diamond-type Ge(*cF8*) (dashed grey line, [10]). The structural phase transitions show in clearly discontinuous volume changes.

spatial organisation of the new allotrope may be derived from cubic Ge(*cI16*) [6] by symmetry reduction (*t4*, *translationsgleicher Übergang* of the order four [19]) and is isotypic to the high-pressure phase Si(*hR8*) [20].

While the distances of the Ge1–Ge2 and Ge2–Ge2 contacts change smoothly upon compression, a more distinct decrease is observed for the Ge1–Ge1 distances (Fig. 4). The

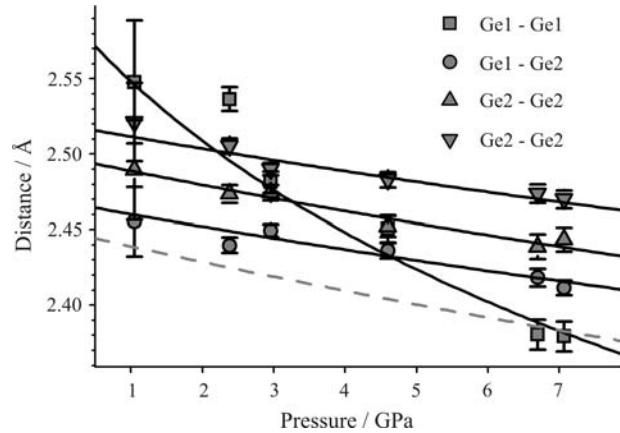


Fig. 4. Pressure dependence of interatomic distances in Ge(*hR8*). The calculated values for diamond-type Ge(*cF8*) are shown as a grey dashed line. Estimated standard deviations are shown as bars.

pronounced anisotropy of the compressibility suggests an alternative description of the atomic arrangement. The atoms Ge2 form spirals around a 3_1 screw axis, a substructure which is similar to elemental α -Te or α -Se, Te(*hP3*) and Se(*hP3*). These one-dimensional building units are linked by Ge2–Ge2 contacts into a 3D host network enclosing channels along the *c* axis. The other type of germanium guest atoms (Ge1) forms chains with alternating long and short distances in the resulting tubular voids (Fig. 5). A similar structural organization is observed in the tetragonal high-pressure modifications of K-III (Rb-IV) and Sb-II (Fig. 5) which exhibit incommensurate identity periods of the partial structures along the chain direction [17].

In order to investigate the implication of dissimilar interactions guest-guest, host-host and host-guest which may

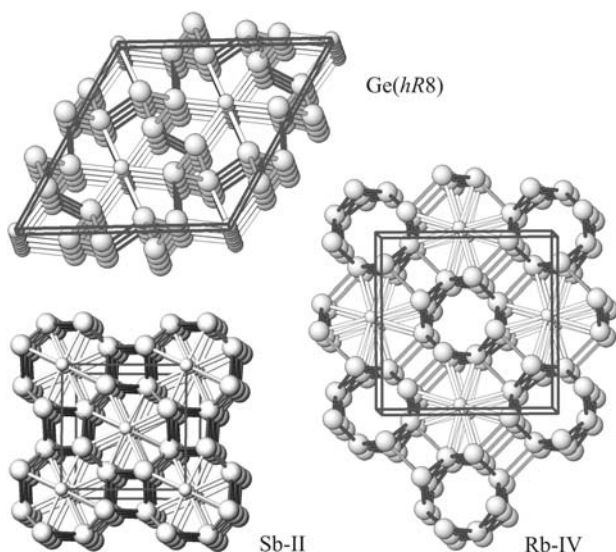


Fig. 5. Atomic arrangements in the crystal structures of Ge(*hR8*) (Ge1 – smaller, Ge2 – larger spheres), Sb-II and Rb-IV (K-III [17]; guest atoms smaller, host atoms – larger spheres). Crystallographic unit cells are indicated by grey lines. Projections are oriented along the *c* axes.

result from the special partitioning of the Ge(*hR8*) crystal structure, the chemical bonding is analyzed by means of the Electron Localizability Indicator (ELI [21]).

Despite the differences concerning interatomic distances within the germanium framework, each of the short Ge–Ge contacts in the crystal structure has its own attractor in ELI (Fig. 6). This finding clearly confirms the directional character of the bonding. The positioning of the four maxima around the Ge2 host atoms reflects a topological situation similar to that of Ge(*cF8*). Although the configuration of ELI around the guest-like Ge1 is different, an additional maximum on the longer Ge1–Ge1 contact is not observed. In other words, the Ge1 atom exhibits 3+1+1 next-neighbour contacts while forming four covalent bonds only.

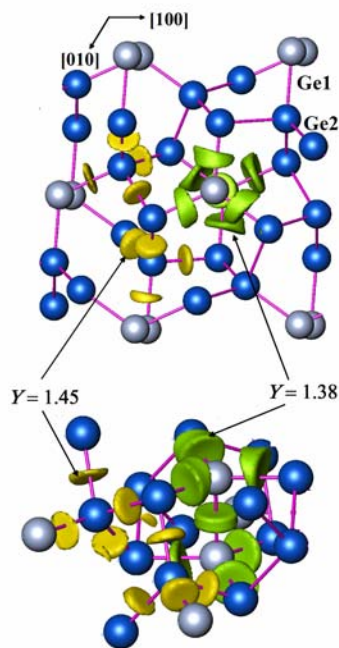


Fig. 6. Isosurfaces of the Electron Localizability Indicator for Ge(*hR8*): top: view along [001]; bottom: view along [010]. Maxima of ELI clearly reveal the four-bonded character of both types of germanium atoms.

As a summary, the structural organization of the new germanium allotrope bears some similarity to that of several recently described incommensurate high-pressure host-guest assemblies of elemental metals. However, both germanium atoms adopt the same bonding topology which results in equivalent interactions within and between the partial structures of Ge(*hR8*). The covalent character of the bonds interconnecting network (‘host’) and channel atoms (‘guest’) stabilizes the commensurate order of this arrangement.

Experimental Section

The prepared material with clathrate as a main phase contained traces of sodium (0.34 wt%), oxygen (1.1 wt%) and hydrogen (0.27 wt%). A detailed discussion of contaminations can be found in [4] and [22]. Ge(*tP12*) was synthesized from 99.9999 % semiconductor grade germanium in a multianvil device at 10(1) GPa and 1000(100) K. For the in-situ high-pressure experiments, powdered samples were placed in steel gaskets using a 4:1 methanol/ethanol mixture as a pressure transmitting medium. The diamond anvil cells for generating high-pressures had culet sizes of typically 0.4 mm. Pressures were determined by the ruby luminescence method [23].

X-ray powder diffraction measurements were performed at the undulator beamline ID 09A of the European Synchrotron Radiation Facility (ESRF, Grenoble). A bent Si(111) monochromator was used to select a radiation of $\lambda = 0.413$ Å from the white (pink) beam. During the exposures samples were oscillated by $\pm 3^\circ$ in order to enhance powder statistics. Intensity recording was performed with imaging plates. For calibration of detector distance and wavelength we used a standard silicon sample, Si(*cF8*). Integration of the two-dimensional diffraction intensities was performed with the Fit2d software [24]. The crystal structure was solved by using the data of isotopic Si(*hR8*) as starting values in the full profile refinements. In the least squares procedures performed with Fullprof [25] we fixed the isotropic displacement factor to $B_{\text{iso}} = 1 \text{ Å}^2$. In case of weak intensity contributions of phases, refinements were restricted to lattice parameter optimizations. Supplementary diffraction experiments were realized in Debye-Scherrer geometry with MoK α radiation.

The ambient pressure volume of Ge(*cF136*) was determined with CuK α_1 radiation using a focussing set-up (Huber Image Guinier Camera 670) and LaB $_6$ as an internal standard. Diffraction data up to 100° were evaluated with WinCSD [26]. Equations of state were obtained by least squares fits of Murnaghan-type functions to the experimental data [27].

Electronic structure calculation and bonding analysis was carried out using the TB-LMTO-ASA program package [28]. The Barth-Hedin exchange potential [29] was employed for the LDA calculations. The radial scalar-relativistic Dirac equation was solved to get the partial waves. The calculation within the atomic sphere approximation (ASA) included corrections for the neglect of interstitial regions and partial waves of higher order, an addition of empty spheres was necessary. The following radii of the atomic and empty spheres were applied: $r(\text{Ge1}) = 1.398 \text{ Å}$, $r(\text{Ge2}) = 1.398 \text{ Å}$, $r(\text{E1}) = 1.065 \text{ Å}$, $r(\text{E2}) = 1.024 \text{ Å}$. A basis set containing Ge(4*s*,4*p*) orbitals was employed for a self-consistent calculation with Ge(4*d*) functions being downfolded. The electron localizability indicator (ELI, Y) was evaluated according to [30] with an ELI module implemented within the TB-LMTO-ASA package. The topology of ELI was analyzed using the program Basin [31].

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- [1] G. A. Slack, *New materials and performance limits for thermoelectric cooling*, in: D. M. Rowe (Ed.), *Handbook of Thermoelectrics*, CRC press, Boca Raton, 1995, p. 407 (Chapter 34).
- [2] S. Paschen, W. Carrillo-Cabrera, A. Bentien, V. H. Tran, M. Baenitz, Yu. Grin, F. Steglich, *Phys. Rev. B* **2001**, *64*, 214404.
- [3] A. Grüttner, R. Nesper, H.G. von Schnering, *Angew. Chem.* **1982**, *94*, 933; *Angew. Chem. Int. Ed.* **1982**, *21*, 912;
- [4] A. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, Yu. Grin, *Nature* **2006**, *443*, 320.
- [5] F. P. Bundy and J. S. Kasper, *Science* **1963**, *139*, 340; C. H. Bates, F. Dacheille, and R. Roy, *Science* **1965**, *147*, 860; J. S. Kasper and S. M. Richards, *Acta Crystallogr.* **1964**, *17*, 752; A. Wosylus, Yu. Prots, W. Schnelle, M. Hanfland, U. Schwarz, *Z. Naturforsch.* **2008**, *63b*, 608.
- [6] R. J. Nemes, M. I. McMahon, N. G. Wright, D. R. Allen, and J. S. Loveday, *Phys. Rev. B* **1993**, *48*, 9883.
- [7] C. S. Menoni, J. Z. Hu, and I. L. Spain, *Phys. Rev. B* **1986**, *34*, 362.
- [8] R. J. Nemes, H. Liu, S. A. Belmonte, J. S. Loveday, M. I. McMahon, D. R. Allan, D. Häusermann, and M. Hanfland, *Phys. Rev. B* **1996**, *53*, R2907.
- [9] Y. K. Vohra, K. E. Brister, S. Desgreniers, A. L. Ruoff, K. J. Chang, and M. L. Cohen, *Phys. Rev. Lett.* **1986**, *56*, 1944.
- [10] K. Takemura, U. Schwarz, K. Syassen, M. Hanfland, N. E. Christensen, D. L. Novikov, I. Loa, *Phys. Rev. B* **2000**, *62*, 10603.
- [11] The synthesis was performed in analogy to the given reference with MgCl_2 and *n*-dodecyltrimethylammonium chloride as HCl source; B. Böhme, A. Guloy, Zh. Tang, W. Schnelle, U. Burkhardt, M. Baitinger, Yu. Grin, *J. Amer. Chem. Soc.* **2007**, *129*, 5348.
- [12] M. W. Guinan, D. J. Steinberg, *J. Phys. Chem. Solids* **1974**, *35*, 1501; K. A. Gschneidner, *Solid State Phys.* **1964**, *16*, 275.
- [13] F. M. Walters, C. Wells, *Trans. Amer. Soc. Met.* **1935**, *23*, 727; U. Zwicker, E. Jahn, K. Schuber, *Z. Metallkde* **1949**, *40*, 433; S. Setz, H. Nowotny, F. Benesovsky, *Monatshefte Chem.* **1968**, *99*, 730; J. A. Oberteuffer, J. A. Ibers, *Acta Crystallogr. B* **1970**, *26*, 1499; R. Benz, J. F. Elliott, J. Chipman, *Metall. Trans.* **1973**, *4*, 1449; A. Cely, L. E. Tergerius, T. Lundstöm, *J. Less Comm. Met.* **1978**, *61*, 193.
- [14] J. C. Jamieson, *Science* **1963**, *140*, 72.
- [15] U. Schwarz, K. Takemura, M. Hanfland, and K. Syassen, *Phys. Rev. Lett.* **1998**, *81*, 2711.
- [16] M. Hanfland, U. Schwarz, K. Syassen, K. Takemura, *Phys. Rev. Lett.* **1999**, *82* 1197; U. Schwarz, K. Syassen, A. Grzechnik, M. Hanfland, *Solid State Commun.* **1999**, *112*, 319.
- [17] U. Schwarz, L. Akselrud, H. Rosner, A. Ormeci, Yu. Grin, M. Hanfland, *Phys. Rev. B* **2003**, *67*, 214101; M.I. McMahon, R.J. Nemes, U. Schwarz, K. Syassen, *Phys. Rev. B.* **2006**, *74*, 140102.
- [18] For recent reviews, see U. Schwarz, *Z. Kristallogr.* **2004**, *219*, 376; M. I. McMahon, *Z. Kristallogr.* **2004**, *219*, 742; original contributions: U. Schwarz, A. Grzechnik, K. Syassen, I. Loa, M. Hanfland, *Phys. Rev. Lett.* **1999**, *83*, 4085; M. I. McMahon, S. Rekh, R. J. Nemes, *Phys. Rev. Lett.* **2001**, *87*, 055501; M. I. McMahon, T. Bovornratanaraks, D. R. Allen, S. A. Belmonte, R. J. Nemes, *Phys. Rev. B* **2000**, *61* 3135; R. J. Nemes, D. R. Allan, M. I. McMahon, S. A. Belmonte, *Phys. Rev. Lett.* **1999**, *83*, 4081; M. I. McMahon, O. Degtyareva, R. J. Nemes, *Phys. Rev. Lett.* **2000**, *85*, 4896; H. Fujihisa, Y. Akahama, H. Kawamura, Y. Gotoh, H. Yamawaki, M. Sakashita, S. Takeya, and K. Honda, *Phys. Rev. B* **2005**, *72*, 132103; M. I. McMahon, L. F. Lundegaard, C. Hejini, S. Falconi, R. J. Nemes, *Phys. Rev. B* **2006**, *73*, 134102.
- [19] H. Bärnighausen, *Math. Chem.* **9** (1980) 139.
- [20] R. O. Piltz, J. R. Maclean; S. J. Clark, G. J. Ackland; P. D. Hatton, *J. Crain, Phys. Rev. B* **1995**, *52*, 4072
- [21] M. Kohout, K. Pernal, F. R. Wagner, Yu. Grin, *Theor. Chem. Acc.*, **2004**, *112*, 453.
- [22] A recent NMR investigation of the silicon clathrate $\text{Cs}_8\text{Si}_{136}$ reveals that hydrogen is adsorbed at the surface and not incorporated into the bulk material; I. Veremchuck, F. Haarmann, T. Goebel, R. Ramlau, S. Hoffman, W. Schnelle, M. Baitinger, Yu. Grin, private communication.
- [23] G. J. Piermarini, S. Block, J. D. Barnett, R. A. Forman, *J. Appl. Phys.* **1975**, *46* 2774; H. K. Mao, P. M. Bell, J. W. Shaner, D. J. Steinberg, *J. Appl. Phys.* **1978**, *49*, 3276.
- [24] A. Hammersley, Computer program Fit2d, ESRF, Grenoble, 1996; A. P. Hammersley, S. O. Svenson, M. Hanfland, A. N. Fitch, D. Häusermann, *High Press. Res.* **1996**, *14*, 235-248.
- [25] J. Rodriguez-Carvajal, *Physica B* **1993**, *192*, 55.
- [26] L. G. Akselrud, P. Y. Zavalij, Yu. Grin, V. K. Pecharsky, B. Baumgartner, E. Wölfel, *Mat. Sci. Forum* **1993**, *133-136*, 335.
- [27] F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **1944**, *30* 244.
- [28] O. K. Andersen, *Phys. Rev. B*, **1975**, *12*, 3060; O. Jepsen, A. Burkhardt, O. K. Andersen, The TB-LMTO-ASA Program, Version 4.7. Max-Planck-Institut für Festkörperforschung, Stuttgart, **1999**.
- [29] U. Barth, L. Hedin, *J. Phys. C*, **1972**, *5*, 1629
- [30] M. Kohout, *Int. J. Quantum. Chem.* **2004**, *97*, 651.
- [31] M. Kohout, BASIN. Version 2.3. Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, **2001**.

A New Modification of Germanium

A New 3D Network of Four-Bonded Germanium: A Missing Link between Open and Dense**

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The new modification Ge(*hR8*) is obtained upon pressurizing of clathrate-type Ge(*cF136*) or controlled decompression of Ge(*tI4*)-type high-pressure phase. The atomic arrangement comprises four-bonded germanium atoms with a topological organization bearing remarkable similarity to high-pressure host-guest assemblies of other main-group elements.

