High-pressure chemistry of germanium

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At ambient pressure, the chemistry of silicon and germanium with metals of the alkaline-earth and rareearth metal groups is dominated by the occurrence of electron-precise Zintl phases. Application of highpressure high-temperature synthesis expands the range of available motifs significantly by giving access to phases with tetrel-rich compositions and sometimes surprising bonding properties.

The p-block semiconductors silicon and germanium form a variety of binary phases with elements of the alkaline, alkaline-earth or rare-earth metal groups. The tetrel atoms of the common ambient-pressure phases form covalent partial structures normally involving electron-precise electron balances so that the chemical bonding is typically within the scope of the Zintl-Klemm concept.

The considerable spectrum of conventional silicon and germanium motifs can be significantly enhanced by application high-pressure high-temperature of synthesis techniques, which have the potential to stabilize compounds with hitherto unrealized compositions. Some recent results [1,2] are discussed in the contribution on cage compounds (https://www1.cpfs.mpg.de:2443/CMS 03).

Successful syntheses in the last years evidence the formation of anionic frameworks by the p-block elements Si or Ge in the range of tetrel-rich compositions. Binary compounds with exclusively four-bonded framework atoms are characterized by the occurrence of excess electrons with respect to the 8-N rule, e.g., for compounds MTt_6 , the surplus may be indicated by the formula $M^{2+}[(4b)Tt_6^0] \times 2e$ (M = Ca, Sr, Ba; Tt = Si, Ge). However, in compounds like



Fig. 1: Crystal structure of $SrGe_{6-x}$ (x = 0.45). The germanium framework comprises interconnected germanium chains. One of these segments (emphasized in light red) contains defects which localize the excess electrons. Sr atoms are shown in yellow, Ge atoms red.

SrGe_{6-x} (see Fig. 1), the occurrence of defects works against the excess in the electron balance [3] as each vacancy is surrounded by four negatively charged atoms [(3b)Ge⁻] bearing free electron pairs, thus acting as electron traps. In the majority of cases, the vacancies are randomly distributed [4], but single crystals of the phase SrGe_{6-x} (x \approx 0.45) exhibit satellite reflections, which uncover incommensurate, but nevertheless periodic modulations of the vacancy pattern [5]. The incommensurate ordering requires methods of four-dimensional crystallography for crystal structure refinement.

An alternative reaction to the occurrence of excess electrons is adopted by the slightly germanium-richer phase $SrGe_6$ [6]. Here, the covalent germanium framework (Fig. 2) adapts to the electron balance by forming a unique framework pattern, which combines [(3b)Ge⁻] species with [(4b)Ge⁰] according to the formula $Sr^{2+}[(3b)Ge^{-}]_2[(4b)Ge^{0}]_4$. In accordance with



Fig. 2: Crystal structure of SrGe₆. The germanium framework is characterized by large voids occupied by Sr atoms (yellow). Four-bonded Ge atoms are shown in red, three-bonded Ge atoms are indicated in orange.



Fig. 3: Calculated density of states of $SrGe_6$. In response to the electron-precise composition, the Fermi level is located close to pronounced pseudo-gap.

the electron-precise balance, the calculated density of states (Fig. 3) reveals a pronounced pseudo-gap close to the Fermi level.

A frequent motif of one-dimensional polyanions are zig-zag chains of tetrel atoms, e.g., in the crystal structures of the CrB (TII) or FeB type. In contrast to the corresponding silicides, compounds MGe (M = Lu, Yb) have not been observed in the ambient-pressure phase diagrams of germanium and the rare-earth metals. Nevertheless, both compounds can be obtained at high-pressure high-temperature conditions (Fig. 4). The new high-pressure phase LuGe [7] fits well into the systematic relation between atomic volume and



Fig. 4: Volume per formula unit versus ionic radius (CN 6) of monogermanides RGe (R = rare-earth metal) of the FeB and CrB type. The new compounds LuGe and YbGe are located in the lower left of the diagram. Deviations of the systematic volume changes for R = Eu and Yb are attributed to the realization of oxidation states smaller than +3.

ionic radius of germanides *R*Ge (R = rare-earth metal). The deviation of YbGe is assigned to the deviation of the cationic metal radius from the value for Yb³⁺. This finding is taken as an indication for the realization of an oxidation state smaller than +3, which is in line with the earlier observed nonconformity of europium showing a similar behavior.

While the chain-like germanium anions fulfill the Zintl concept in combination with alkaline-earth metals with oxidation state +2, investigations of related segments in ternary compounds by means of theoretical methods reveal significant deviations from the formal 8-*N* picture because of polar-covalent interactions between anion and metal [8]. These unique bonding features are also confirmed for the new monogermanide LuGe by a recent study of the chemical bonding. In addition, the investigation using methods operating in direct space disclosed a novel type of bonding interaction of the lutetium cations [7] (https://www1.cpfs.mpg.de:2443/CMS_08).

Another type of one-dimensional building unit is found in the crystal structure of Mn_3Ge_5 [9]. The atomic arrangement is composed of two subsystems, one being a tetragonal arrangement of Mn atoms, which is combined with helical strings of Ge atoms (Fig. 5). However, bonding analysis (Fig. 6) in real space evidences a markedly different picture. The homoatomic distances of 3.0710(8) for Mn-Mn and 2.693(2) Å for Ge-Ge are significantly longer than the sum of the atomic radii. Instead, the heteroatomic Mn-Ge distances are within the range of the sum of the



Fig. 5: Atomic arrangements of Mn_3Ge_5 . The subsystems of the Mn (yellow) and Ge atoms (red) have separate identity periods in direction of the projection.



Fig. 6: Atomic interactions in Mn_3Ge_5 . Mn atoms are shown in white and greenish yellow, germanium in red. Two center interactions are indicated by grey lines, three center ones in orange.

atomic radii (1.24 Å for Mn and 1.23 Å for Ge) and reflect interactions, which involve two or three atoms.

A hitherto unique structural motif exceeding the scope of the 8-N rule is formed by the rare-earth metal trigermanide SmGe₃ [10]. The majority of reflections can be indexed on basis of a Cu₃Au-like motif, which resembles an ordered superstructure of an fcc pattern. However, weak superstructure reflections indicate a doubling of the lattice parameter. Crystal structure solution and refinement evidence that the enlarged unit cell grants an additional degree of freedom to the germanium atoms in form of a free positional parameter. The resulting subtle distortion (Fig. 7) with respect to the aristotype induces the formation of



Fig. 7: Atomic arrangements of SmGe₃. Sm is shown in yellow, Ge in brown. The short Ge-Ge distances are emphasized by grey lines.

slightly shorter Ge-Ge distances, which imply the formation of octahedral Ge₆ units.

External Cooperation Partners

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References

- [1]* Unconventional Metal-Framework Interaction in MgSi₅, J.-M. Hübner, W. Carrillo-Cabrera, Yu. Prots, M. Bobnar, U. Schwarz, and Yu. Grin, Angew. Chem. Int. Ed. 58 (2019) 12914, <u>doi.org/10.1002/anie.201907432</u>; Unkonventionelle Metall-Netzwerk Wechselwirkungen in MgSi₅, Angew. Chem. 131 (2019) 13046, <u>doi.org/10.1002/ange.201907432</u>
- [2]* In-cage interactions in the clathrate superconductor Sr₈Si₄₆, J.-M. Hübner, Yu. Prots, W. Schnelle, M. Bobnar, M. König, M. Baitinger, P. Simon, W. Carrillo-Cabrera, A. Ormeci, E. Svanidze, Yu. Grin, and U. Schwarz, Chem. Eur. J. 26 (2020) 830, <u>doi.org/10.1002/chem.201904170</u>
- [3]* Zintl defects in intermetallic clathrates, M. Baitinger, B. Böhme, F. R. Wagner, and U. Schwarz, Z. Anorg. Allg. Chem. 646 (2020) 1034, doi.org/10.1002/zaac.202000107
- [4] High pressure synthesis and transport properties of a new binary germanide, $SrGe_{6-\delta}$ ($\delta \cong 0.5$), with a cagelike structure, H. Fukuoka, S. Yamanaka, E. Matsuoka, and T. Takabatake, Inorg. Chem. **44** (2005) 1460.
- [5]* Modulated vacancy ordering in $SrGe_{6.x}$ ($x \approx 0.45$), U. Schwarz, R. Castillo, A. Wosylus, L. Akselrud, Yu. Prots, B. Wahl, T. Doert, M. Bobnar, and Yu. Grin, Z. Naturforsch. **74b** (2019) 137, <u>doi.org/10.1515/znb-2018-0200</u>
- [6]* The untypical high-pressure Zintl phase SrGe₆, U. Schwarz, R. Castillo, J.-M. Hübner, A. Wosylus, Yu. Prots, M. Bobnar, and Yu. Grin, Z. Naturforsch. 75b (2020) 209, <u>doi.org/10.1515/znb-2019-0197</u>
- [7]* "Excess" electrons in LuGe, R. Freccero, J.-M. Hübner, Yu. Prots, W. Schnelle, M. Schmidt, F. R. Wagner, U. Schwarz, and Yu. Grin, Angew. Chem. Int. Ed. 60 (2021) 6457, doi.org/10.1002/anie.202014284
- [8]* Polar-covalent bonding beyond the Zintl picture in intermetallic rare-earth germanides, R. Freccero, P. Solokha, S. De Negri, A. Saccone, Yu. Grin, and F. R. Wagner, Chem. Eur. J. 25 (2019) 6600.
- [9]* Structural, Magnetic and Thermoelectric Properties of hp-Mn₃Ge₅, R. Castillo, W. Schnelle, M. Bobnar, R. Cardoso-Gil, U. Schwarz, and Yu. Grin, Z. Anorg. Allg. Chem. 646 (2020) 256.
- [10]* High-pressure synthesis of SmGe₃, J.-M. Hübner, W. Carrillo-Cabrera, R. Cardoso Gil, P. Koželj, U. Burkhardt, M. Etter, L. Akselrud, Yu. Grin, and U. Schwarz, Z. Kristallogr. Cryst. Mater. 235 (2020) 233, <u>doi.org/10.1515/zkri-2020-0058</u>

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