“Excess” electrons in LuGe

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Abstract: The monogermanide LuGe is obtained via high-pressure high-temperature synthesis (5–15 GPa, 1023–1423 K). The crystal structure is solved from single-crystal X-ray diffraction data (structure type FeB, space group Pnma, a = 7.660(2) Å, b = 3.875(1) Å, and c = 5.715(2) Å, R₂ = 0.036 for 206 symmetry independent reflections). The analysis of chemical bonding applying quantum-chemical techniques in position space was performed. It revealed—beside the expected 2c-Ge-Ge bonds in the germanium polyanion—rather unexpected four-atomic bonds between lutetium atoms indicating the formation of a polycation by the excess electrons in the system Lu₄(2b)Ge²⁻ × e⁻. Despite the reduced VEC of 3.5, lutetium monogermanide is following the extended 8-N rule with the trend to form lutetium-lutetium bonds utilizing the electrons left after satisfying the bonding needs in the anionic Ge-Ge zigzag chain.

The structures of FeB[1] and α-TlI[2] first investigated in the 30ies, were considered as characteristic examples of “intermetallic” (FeB with trigonal prismatic coordination of the smaller boron atoms, CN = 9) or ionic (α-TlI as a distorted variant of the NaCl type) compounds. The later characterisation of the boride CrB³[3] revealed that the structural pattern of α-TlI is also well suitable for typical intermetallic compounds of elements with much lower difference in electronegativity. The discovery of the first monotetrelide—CaSi[4]—revealed, that the same structural pattern is compatible with covalent bonding in the chain anion of two-bonded silicon atoms plus its ionic interaction with the cations in accordance with the Zintl-Klemm concept: Ca⁺(2b)Si²⁻/[5–7] The subsequent finding of the monotetrelides YSi[8] or LaSi[9] evidenced that chains of two-bonded tetrel atoms can also form in presence of “excess” electrons, for example, Y⁺(2b)Si²⁻ × e⁻. Recent quantum chemical studies on LaₓMGeₓ (M = Li, Mg, Al, Zn, Cu, Ag, Pd) and YₓPdGeₓ comprising similar zig-zag chains revealed further significant deviations from the formal 8-N picture due to polar-covalent interactions.[10]

Systematic investigations going back to the 70ies revealed the new chain anion (2b)Si²⁻ in a second modification of LaSi[11] Strontium monosilicide with a new band-like anion of (2b)Si²⁻ and (3b)Si¹[12] completed the series of monotetrelides with rare-earth and alkaline metals compounds.[13] Thereby, high pressure-high temperature (HP-HT) preparation was found to be a very efficient tool for the preparation of new modifications of the members of this family and new intermetallic phases in general.[14,15] Among the monogerma-nides, the representatives of the heavy rare-earth metals are less studied. This was the reason to apply the HP-HT technique for the preparation of LuGe, which is not known in the published phase diagram.[16]

The product of the HT-HP preparation is brittle bulk with dark metallic luster. The compound is a high-pressure phase. By heating under ambient pressure up to 873 K, the structure keeps intact, but the lattice starts to lose one of the components, which leads to the marked reduction of the lattice parameters a = 7.735(1) Å, b = 3.8579(5) Å, c = 5.630(1) Å (cf. below). After further heating in a DSC apparatus up to 1023 or 1323 K, only the thermodynamically stable phases Lu₁₄Ge₄ and Lu₁₂Ge₁₀ are present in the sample, but no clear decomposition effect was detected. Further DSC experiment up to 1673 K reveals an endothermal effect at 1595(10) K corresponding to the peritectoid decomposition of Lu₁₄Ge₄ into Lu₅Ge₃ and Lu₁₂Ge₁₀, reported in the phase diagram.[16]

The powder X-ray diffraction pattern of LuGe is indexed in the orthorhombic system with a = 7.660(2) Å, b = 3.875(1) Å, and c = 5.715(2) Å. Further characterization of the crystal structure was performed on basis of single crystal diffraction data (crystallographic information is presented in Table S1 in the Supporting Information). Systematic extinctions yielded possible space groups Pnma and Pn2₁a, agreeing with the supposed structure of FeB type. The refinement in the centrosymmetric space group resulted in residuals R = 0.0360 and wR = 0.0455 denoting a sound agreement of structure model and data. The final atomic coordinates and displacement parameters are presented in Table S1, the anisotropic displacement parameters and interatomic distances can be found in Tables S2 and S3. The occupation factors of lutetium and germanium were refined to unity within the error margin, yielding the equiatomic composition LuGe. The composition Luₓ(3.5)Ge₄₋ₓ(3.5) found by EDXS measurements is in fair agreement (within 3 e.s.d.) with the results of the structure refinement.

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The new phase is isotypic to FeB.[1] In the crystal structure of LuGe, each lutetium atom possesses seven germanium and ten lutetium neighbors. Germanium is coordinated by two germanium and seven lutetium atoms (Table S3). The crystal structure is constituted by columns of triangular prisms \([\text{GeLu}_6]\) condensed along \([010]\) by rectangular faces (Figure 1, top).[27] Within these columns, zigzag chains of interconnected germanium atom run along the \([010]\) direction. The distances \(d(\text{Ge-Ge})\) amount to 2.594(2) Å, the distances \(d(\text{Lu-Ge})\) range between 2.897(1) and 3.168(3) Å, the shortest \(d(\text{Lu-Lu})\) amounts to 3.609(1) Å. The neighboring columns share edges along \([010]\). The space between the columns is filled by empty distorted tetrahedra \([\text{Lu}_4]\) and half-octahedra \([\text{Lu}_5]\) (Figure 1, bottom), which is also observed in the \(\alpha\)-TII- and LaSi-type monotetrelides. This is a more general feature of intermetallic compounds with trigonal-prismatic coordination.[18]

Other alkaline-earth and rare-earth metal monogerma-

nides crystallize in the structure types \(\alpha\)-TII, FeB, SrSi or LaSi, respectively. With the exception of the germanium-deficient compound \(\text{SrGe}_{0.76}\) adopting the SrSi-type structure, \([12]\) these structure types comprise Ge-Ge chains. The adaption of the structure and the chains itself upon implementation of different alkaline-earth and rare-earth metal atoms is illustrated by the examination of the average atomic volume \(V_\lambda\) (unit cell volume divided by number of atoms per unit cell) and the distances \(d(\text{Ge-Ge})\). While the atomic volume increases with the size of the cation (Figure 2), the chain distances \(d(\text{Ge-Ge})\) in the monogerma-
nides scatter strongly and are significantly longer than the contacts in elemental Ge (2.449 Å). The elongation of homoatomic contacts in mono-
tetrelides in comparison with the \(\alpha\)-modifications of the according elements was discussed in different ways. From the reconstructed electron density experiments on CaSi (structure type \(\alpha\)-TII), the elongated distances Si-Si (and the metallic behavior) are suggested to originate from the delocalized distribution of the valence electron density over the germanium chain, caused by partially covalent interactions of calcium with silicon.[19] Later quantum chemical calculation on this compound revealed, that the partial occupation of \(\pi^*\) orbitals (Si-Si bonds) reduces the charge transfer from Ca to Si and stabilizes the planarity of the Si chain.[19] cf. also Supporting Information S4. A similar marked reduction of the charge transfer was observed for LaGe (structure type FeB), caused by the participation of \(d\) electrons in the bonding according to \(\text{La}^{2+}(2b)\text{Ge}^{2-}\times e^-\). \([23]\)

The chains of two-bonded tetrel atoms \((2b)\text{Tt}\) are tradition-

ally well understood within the Zintl-Klemm concept in terms of the formal species \((2b)\text{Tt}^{-2}\). Being two-bonded, they need two additional electrons to fulfill the octet rule. This can be easily done in the binary monotetrelides \(\text{MTt}\) with \(\text{M}\) being an alkaline-earth metal.[5–7] In these compounds, the 1:1 composition is electronically balanced, e.g., \(\text{Ca}^{2+}(2b)\text{Ge}^{2-}\). Recently, this approach was found to be basically in agreement with the results of the reconstruction of electron density for CaSi from X-ray diffraction data.[19] However, the authors pointed out that the Ca-Si interaction cannot be considered as fully ionic. The situation becomes even more intriguing for the monogermanide LuGe, in which the cation can formally offer more than two valence electrons for bonding. The electronic balance \(\text{Lu}^{3+}(2b)\text{Ge}^{2-}\times e^-\) may be interpreted as an example of metallic behavior, where the excess electrons are filling Ge-Ge \(\pi\)-antibonding states above the pseudo gap. Another situation may appear, when the electronegativity of the cationic component allows to form homoatomic bonds employing excess electrons. Such a bonding situation may be adopted by gallium monoselenide (in a fully ionic represen-
tation) with a gallium di-cation: \([1b]\text{Ga}^{2+}[0b]\text{Se}^{2-}\]. In reality, the cation is not completely isolated, because of the
polar covalent interactions of gallium and selenium (insufficient electronegativity difference for ionic bonding). A further possibility for the bonding use of excess electrons is the formation of a lone pair at the cation, like in indium monobromide: \([\text{lpIn}^-]([\text{0bBr}^+]\text{]}\) (structure type \(\alpha\)-TII). In case of full transfer of three electrons from Lu to germanium one may expect also the formation of Ge dumbbells according to \([\text{La}^+][\text{(1b)Ge}^3^-]\). Such considerations were the starting point for the analysis of chemical bonding in LuGe applying quantum chemical techniques in position space.

The effective charges of the atomic species in LuGe were evaluated from the calculated electron density. First, the zero-flux surfaces in the gradient vector field of the electron density were determined. They form the boundaries of electron density basins which represent atomic regions within the framework of the Quantum Theory of Atoms in Molecules (QTAIM\(^{22}\)). Already the shapes of the QTAIM Lu atoms in LuGe reveal some characteristic features (Figure 3, top). Usually, the rare-earth metals atoms in the QTAIM representation in intermetallic compounds have close to spherical shapes including mostly the inner electronic shells. The spherical shape of the yttrium cation in the recently described crystal structure of \(\text{Y}_4\text{Be}_{33}\text{Pt}_{16}\)\(^{23}\) may serve as a characteristic example. In contrast, the shape of the Lu atoms in LuGe is far from spherical, indicating an appearance of rather unusual atomic interactions. The shape of the QTAIM Ge atoms is rather characteristic for a covalently bonded p-block atom: it has plane faces toward the neighboring germanium and slightly convex surfaces toward lutetium neighbours. Then the electron density was integrated in spatial regions, defined in QTAIM, and their electronic populations yield the QTAIM effective atomic charges. The obtained charge transfer of 1.34 electron per atom (Figure 3, top panel and Table S5) is rather low in comparison with the formal charges of \(+3\) and \(-3\) assumed for Lu and \((1b)\text{Ge}^3\) and suggests a smaller ionic contribution to the bonding in this compound in comparison with the expected one from the formal charges.

Further information about the atomic interactions was obtained by applying the electron localizability approach. The distribution of the electron localizability indicator (ELID) in the vicinity of the Lu nuclei (Figure 3, upper middle panel) deviates only slightly from a spherical one in the regions of the inner shells (structuring index \(\epsilon = 0.01\)^\(^{24}\)), indicating a rather small participation of the inner electrons in the bonding events. The last shell is not visible, agreeing with the charge transfer found within the QTAIM considerations. The four types of ELI-D attractors observed in the valence region visualize different components of bonding in LuGe. The first one (the basin is shown in yellow in Figure 3, bottom) represents homoatomic Ge-Ge bonding within the chain. The population of the bonding basin of 0.66 electrons is rather small (“1/3-bond”, cf. interatomic distances above). The large bonding basins above and below the Ge-chain plane (red and green in Figure 3) may be understood in first approximation as lone-pair-like for an isolated Ge chain. In LuGe, they are formed by contributions of one Ge and four Lu, that is, they illustrate five-atomic polar interactions (populations of 2.25 and 2.42 electrons, respectively). The next basin (orange in Figure 3, bottom; population 0.72 electrons) can be seen as a split part of a former lone-pair basin in the isolated chain and visualize the four atomic interaction GeLu, Quantitative evaluation of the basins above (using the criteria for the position-space characterization of the polar bonding\(^{25,26}\)) evidences that they have roughly equivalent lone-pair-on-
The calculation of partial ELI-D\[24\] using the states from the Ge-Ge zigzag chains (Ge-Ge bonds and “lone pairs” at Ge). The first two regions represent the bonding within the admixture of Ge-p states and contains ca. 4 electrons per unit cell. The third region reveals, that they contribute to the ELI-D distribution in the region of the 4a-Lu basin representing the lutetium-lutetium bonding. On the other hand, the same region is obviously defining the metallic behavior of LuGe, as this is confirmed by its diamagnetic behavior (Figure S10).

The bonding in LuGe can be summarized as covalently bonded zigzag chains of Ge atoms separated from the Lu environment by multi-atomic (four- and five-atomic) bonds (originating from the lone-pairs in an isolated chain). The lutetium atoms form four-atomic polycations by homoatomic interactions. In such way the bonding situation in LuGe is similar to that in GaSe: the interaction in the polycation is a four-atomic one in LuGe and two-atomic in the selenide; the germanium atoms form a chain polyanion, while isolated Se anion can be found in GaSe.

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**Conflict of interest**

The authors declare no conflict of interest.
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