Eight-Connected Silicon

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Unusual Silicon Connectivities in the Binary Compounds $GdSi_5$, $CeSi_5$, and Ce_2Si_7**

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Covalent framework structures are a fascinating class of materials regarding both structural diversity[1] and physical properties.[2] Three-dimensional silicon networks in particular attract widespread attention owing to their potential thermoelectric applications and their superconducting properties. The emergence of these attractive physical features is frequently discussed in light of specific interactions between the anionic Group 14 element matrices and the filler cations.[3]

The connectivity of the silicon partial structure has an upper limit of four that is adopted by uncharged species Si^0 ($8-N$ rule). This situation corresponds to elemental silicon, which is four-connected under ambient conditions. A higher coordination number requires the continuous application of high pressure.[4]

With the aim of realizing an increased number of Si–Si contacts under ambient conditions, silicon-rich binary phases were synthesized at elevated pressures and then quenched. In the systems *RE*–Si (*RE* = Ce, Gd), hitherto unknown compounds with compositions *RE*/Si = 1:5 are obtained (Supporting Information, Figure S1). A second new cerium compound is observed for a ratio Ce/Si of 1:3.5. Syntheses at ambient pressure yields compositions $RESi_{2-x}$ (*RE* = Ce, Gd) as the silicon-richest phases.[5]

In the novel atomic arrangement of Ce_2Si_7,[6] three independent silicon atoms adopt coordination environments with four coplanar Si–Si contacts for Si1, five for Si3 in the form of a distorted square pyramid, and six for Si2 (Figure 1, top). This homonuclear coordination is complemented by four cerium atoms for each silicon species. The rare-earth metal atoms adopt a coordination number of 14 as in $[CeSi_{12}Ce_2]$.

In the structural pattern of $CeSi_5$ and $GdSi_5$[7] (Figure 1, bottom), Si1 forms three short homonulear distances and two longer contacts expand the connectivity to five. Atom Si2 forms eight of these long distances to Si1. The coordination is completed by three rare-earth metal atoms for Si1 and two for Si2. The lanthanoid atoms are coordinated by fourteen silicon atoms, corresponding to $[RESi1_{12}Si2_2]$. $CeSi_5$ and $GdSi_5$ are the first silicides adopting this structural pattern of the $LaGe_5$ type.[8]

To investigate the consequences of the unusual silicon connectivity, the interdependence of interatomic distances and coordination number, which is mainly due to Pauli repulsive forces, was evaluated. For this purpose, an empirical scaling given for binary compounds[9] is applied to the

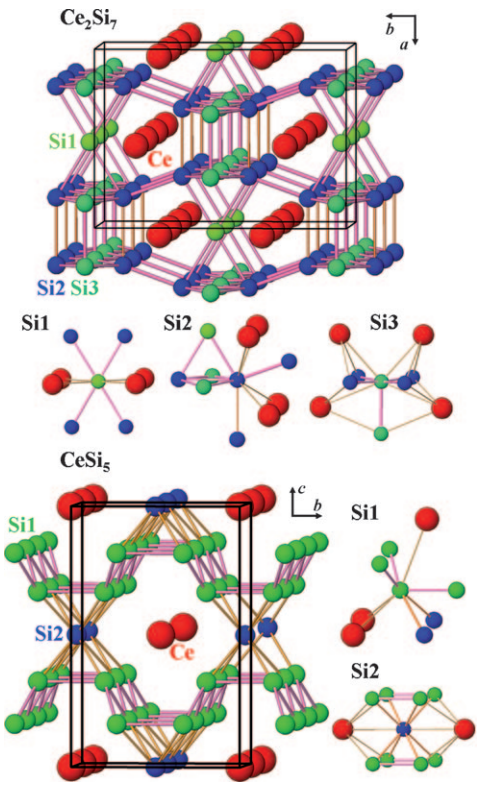

Figure 1. Atomic arrangement of Ce_2Si_7 (top) and $CeSi_5$ as well as $GdSi_5$ (bottom) and the coordination environments of the silicon atoms. Next-neighbor Si–Si distances are indicated by different colored lines: Ce_2Si_7, pink: Si1–Si2 256.77(8), Si2–Si2 249.6(1) and 263.9(1), Si2–Si3 260.42(5), Si3–Si3 251.2(2) pm; orange Si2–Si2 268.4(1) pm; Ce–Si 302.60(2)–322.34(6) pm. $CeSi_5$, pink: Si1–Si1 236.54(6), Si1–Si1 246.32(4) pm; orange: Si1–Si2 274.51(3) pm; Ce–Si 301.94(2)–326.75(5) pm. The coordination environments of the cerium atoms are shown in Figure 3. For details, see the Supporting Information, Tables S1a–S3c.

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connectivity CN_H in silicon networks. The calculated values follow the observed average distances in modifications of elemental silicon with four to eight next neighbors quite precisely (Figure 2).

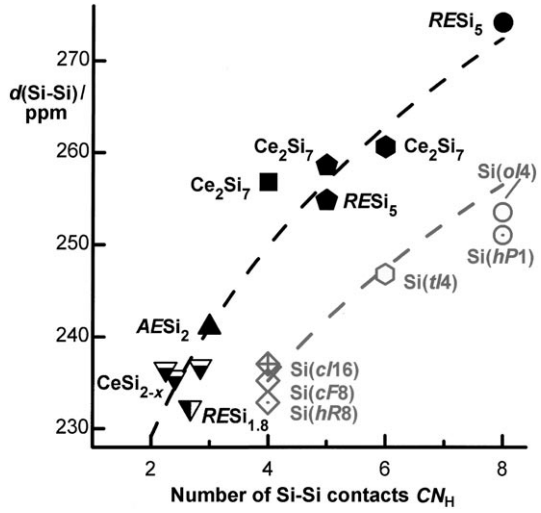

Figure 2. Connectivity of silicon CN_H and average interatomic distances d(Si–Si) [pm] in networks of binary compounds[10] and in modifications of the element.[4–7] The dashed curves are obtained by applying the scaling $d = d_{Ref}(CN_H/CN_{Ref})^{1/8}$.[9] A reference distance $d_{Ref} = 235.2$ pm is used for elemental silicon with $CN_{Ref} = 4$,[11] for networks of binary compounds with $CN_H = 3$, the value $d_{Ref} = 241$ pm corresponds to a weighted average for silicon environments in phase $AESi_2$ (AE = Ca, Sr, Ba).[12] The average connectivity of silicon in phases $RESi_{1.8}$ (RE = Ce, Gd) and $CeSi_{2-x}$ ($0.1 \le x \le 0.4$) is reduced below three owing to defects.[13]

This result motivated an analogous procedure for describing the Si–Si contacts in networks of binary compounds.[10] The calculated curve is in good agreement with the average value for homonuclear silicon contacts in alkaline-earth and rare-earth metal compounds (Figure 2). However, the interatomic Si–Si distance of 285.3 pm for eightfold connected silicon in compounds $ACSi_3$ ($AuCu_3$-type, AC = U, Np[10]) reveals that the validity of the scaling holds only for metal atoms adopting similar bonding scenarios.

The evidence for specific interactions between metal and framework atoms stimulated a study by quantum mechanical methods. The electronic density of states (DOS; Supporting Information, Figures S2, S3) computed within the LSDA + U scheme indicates metallic behavior for the compounds $RESi_5$ in agreement with the electrical resistivity data. In contrast to other silicon-rich high-pressure phases,[14] no pronounced pseudo gaps are found in the vicinity of the Fermi level. A closer inspection of the DOS yields a dominating contribution of Si 3s, 3p, and Ce 5d states to the valence band (Supporting Information, Figures S4, S5). Surprisingly, the Ce 5p semi-core states also provide a significant contribution.

An analysis of the chemical bonding in direct space was performed with the electron localizability indicator (ELI),[15] which is proportional to the charge required to form an electron pair (ELI-D). The spatial arrangement (topology) of the ELI reveals bonding interactions in systems with at least partially covalent bonding, for example in intermetallic compounds.

The distribution of the ELI around the Si1 atoms in $CeSi_5$ exhibits four maxima in the valence shell (Figure 3, top).

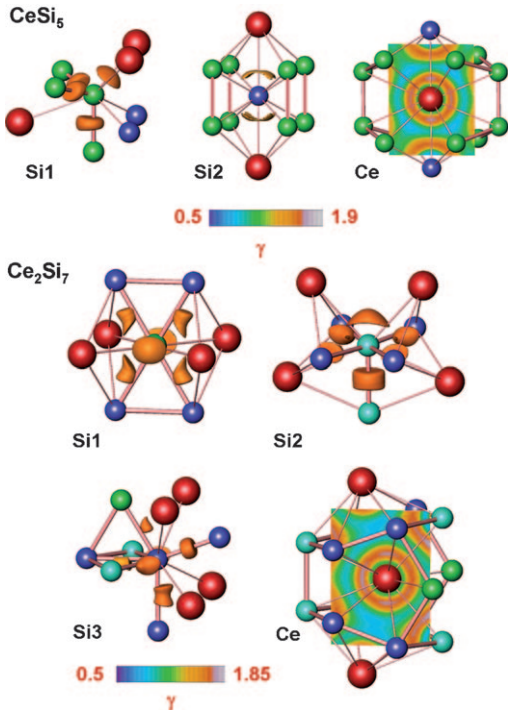

Figure 3. Electron localizability indicator in $CeSi_5$ and Ce_2Si_7. The shortest Si–Si distances are shown as pink lines. The color code of the atoms corresponds to that of Figure 1. For $CeSi_5$, the isosurface around Si1 shows four attractors; the topology of the isosurface around Si2 is consistent with multicenter bonding between the silicon framework and cerium. For Ce_2Si_7, the isosurfaces around Si1 visualize the formation of four bonds and two "lone-pair-like" attractors for Si1, the maxima around Si2 indicate six bonds and those around Si3 five bonds and a "lone pair" for Si3. The mapping of the ELI in the vicinity of the cerium atoms in both compounds clearly shows the structuring of its fifth shell (see text).

Three of these are located on the short Si1–Si1 contacts, indicating covalent two-center bonding within the corrugated silicon layers. The fourth maximum located within a triangle formed by Si1 and two cerium atoms appears similar to a stereochemically active electron pair and indicates cerium–silicon interactions. Despite relative short distances Si2–Si1, the ELI attractors are found close to the direction of the Ce–Si2 contacts. Regarding the participation of semi-core states in the chemical bonding, this finding indicates a multicenter interaction between the silicon and cerium atoms. A strong structuring of the fifth shell of cerium (Figure 3, top) gives additional evidence for a participation of the semi-core states or so-called penultimate shell in the chemical bonding.[16] The lack of spherical symmetry for the ELI distribution of Ce_2Si_7 (Figure 3, bottom) reveals similar directed multicenter bonding between network and filler atoms.

The structuring of the semi-core shell of the cerium atoms and the multicenter interactions are substantially different

from the bonding situation in electron-precise Zintl phases and electron-excessive cage compounds. In the latter, distinct maxima of the ELF are observed exclusively within the polyanionic network, indicating two-center bonding,[14] and the inner shells of the filler atoms retain spherical symmetry.

The different types of bonding in $CeSi_5$ are directly reflected by the pressure-induced structural changes. Although the volume decrease (Figure 4; Supporting Information, Table S4) is remarkably close to that of diamond-type silicon, Si(*cF*8), the binary silicide shows a pronounced anisotropy. The less-compressible axes *a* and *b* are oriented parallel to the layers that comprise two-center Si–Si interactions (Figure 3). The higher compressibility in the direction [001] is attributed to a lower rigidity of the multicenter Si–Ce bonds interconnecting the firm Si1 sheets into a three-dimensional network.

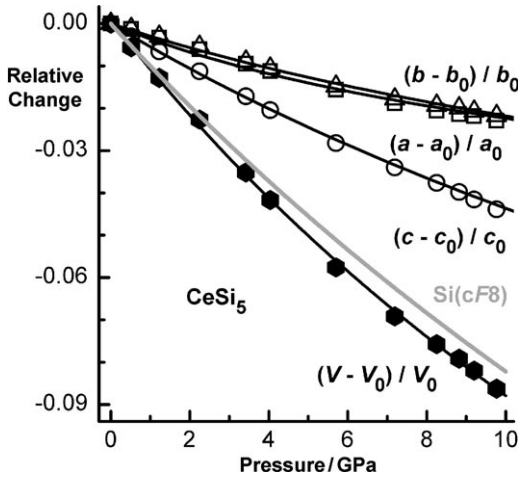

Figure 4. Relative changes in the volume and the lattice parameters of $CeSi_5$ as a function of pressure. Measured data are represented by symbols and fitted Murnaghan-type functions[17] as solid lines (Supporting Information, Tables S4, S5). The gray curve shows the volume change of diamond-type silicon Si(*cF*8) for comparison.

In agreement with the calculated density of states (Supporting Information, Figure S2), the room-temperature resistivity values ($GdSi_5$ 100 μΩ cm, $CeSi_5$ 140 μΩ cm, Ce_2Si_7 40 μΩ cm) and the temperature dependence of the resistivities $\rho(T)$ indicate metallic behavior (Supporting Information, Figure S6a and S6b, inset). The magnetic susceptibility $\chi(T)$ of $GdSi_5$ (Supporting Information, Figure S6b) yields an effective magnetic moment of 8.33 μ_B, which corresponds well to Gd^{3+} in the $4f^7$ configuration. The magnetic susceptibility of the cerium compounds (Supporting Information, Figure S6c) indicate Curie-like behavior at low temperatures, corresponding to only small effective magnetic moments ($CeSi_5$ μ_{eff}/f.u. = 0.22 μ_B; Ce_2Si_7 μ_{eff}/f.u. = 0.33 μ_B; f.u. = formula unit). On the basis of a static mixture Ce^{3+}/Ce^{4+} and a value $\mu_{free} = 2.54$ μ_B for Ce^{3+}, only small fractions of atoms with a $4f^1$ configuration would be present. However, an increase of the time resolution by means of X-ray absorption spectroscopy in the vicinity of the cerium L_{III} edge (Supporting Information, Figure S7) results in effective valences of 3.4(2) and 3.3(2) for $CeSi_5$ and Ce_2Si_7, respectively. These findings indicate rapidly fluctuating Ce^{3+}/Ce^{4+} states consistent with an intermediate cerium oxidation state in both compounds, and a description with localized configurations falls far short of explaining the electronic structure precisely.

In summary, the presented syntheses at extreme conditions open a route for realizing networks with unusual topologies and bonding situations for the Group 14 elements, which may be combined with the unique physical properties of rare earth metals. For the frameworks, a scaling of the interatomic distances with the number of Si–Si contacts is in good agreement with structural data of element modifications and binary silicides, but only quantum-mechanical calculations fully reveal the directed multicenter bonds between cerium and silicon atoms with contributions of the semi-core states of cerium. In short, the compounds $RESi_5$ (RE = Ce, Gd) and Ce_2Si_7 form a new class of binary silicides in addition to the well-known electron-precise Zintl phases and the smaller set of electron-excessive framework compounds.

Experimental Section

Synthesis of starting materials and sample handling (except high-pressure treatment) was performed in argon-filled glove boxes (H_2O and $O_2 \leq 0.5$ ppm). As reactants, we used mixtures $RESi_{2-x}$ (RE = Ce Ames 99.92%; Gd Lamprecht 99.9%) and Si(*cF*8) (Alpha Aesar, 99.9999%). For high-pressure syntheses, a Walker-type module[18] with boron nitride crucibles was used. After heating to 1400(140) K (Ce_2Si_7), 1100(110) K ($CeSi_5$), or 870(90) K ($GdSi_5$) for several hours at a pressure of 10(1) GPa, the metastable products (Supporting Information, Figure S8a,b) were quenched to room temperature before decompression. Ce_2Si_7 was obtained in form of small single crystals, and $GdSi_5$ as well as $CeSi_5$ in the form of crystalline powders.

Chemical analysis of three different samples containing mixtures of Ce_2Si_7 and $CeSi_5$ by the carrier-gas hot-extraction method revealed an average of 0.27(5) atom% oxygen, 0.6(4) atom% nitrogen, and 0.01(1) atom% hydrogen. Energy-dispersive X-ray spectroscopy (EDXS, Philips XL30 scanning electron microscope) of single-crystalline Ce_2Si_7 confirmed the presence of only silicon and cerium.

Lattice parameters were determined with the program package WinCSD,[19] and full-profile refinements were performed with WinCSD and GSAS.[20] High-pressure X-ray diffraction experiments were realized at ID09A of the ESRF ($\lambda = 40.11$ pm) using the diamond anvil cell technique, a 4:1 methanol/ethanol mixture as pressure medium, and ruby for pressure measurements.[21]

Samples for measurements of physical properties were polycrystalline pieces ($m < 10$ mg). The magnetization was measured from 1.8 K to 400 K in external fields $\mu_0 H$ between 0 T and 7 T in a SQUID magnetometer (MPMS XL-7, Quantum Design). The electrical resistance of $GdSi_5$ and Ce_2Si_7 was determined by a direct-current four-probe method (4 K–320 K), whilst that of the $CeSi_5$ sample was measured with alternating current (1.8 K–320 K) (PPMS, Quantum Design). Due to the irregular contact and sample geometry, the estimated inaccuracy of the electrical resistivity is ±30%.

Electronic structure-calculation and bonding analyses were carried out for $CeSi_5$ and Ce_2Si_7 using the TB-LMTO-ASA program package.[22,23] The Barth–Hedin exchange potential[24] was employed for the scalar relativistic LDA calculations. The following radii of the atomic spheres were applied for the spin-polarized calculations of $CeSi_5$: Ce 210.7, Si1 145.4, Si2 152.8 pm; for the calculations of Ce_2Si_7: Ce 198.6, Si1 153.5, Si2 145.2, Si3 146.2 pm. Basis sets: Ce(6s,5d,4f) and Si(3s,3p), Ce(6p) and Si(3d) functions downfolded. The electron localizability indicator (ELI)[15] was evaluated in the ELI-D representation.[25]

Electronic structure calculations that account for the strong correlations of the 4f electrons were performed using the full-potential non-orthogonal local-orbital minimum basis (FPLO) 9.00–34.[26] For the scalar-relativistic calculations within the local spin-density approximation (LSDA), the exchange and correlation potential of Perdew and Wang was chosen.[27] The strong correlations of the 4f electrons are treated in a mean-field-like approximation within the LSDA + U approach.[28] For the double-counting correction, we applied the fully-localized limit[29] with U values of between 6 eV and 10 eV; the resulting valence bands remain essentially unchanged, apart from the localized 4f states.

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[6] Ce_2Si_7: Space group *Cmmm*, $a = 708.93(7)$, $b = 996.44(7)$, $c = 448.68(4)$ pm, $Z = 2$, $R_{int} = 0.018$ for 350 unique reflections with $2\theta_{max} = 66.85°$, $R1 = 0.017$ for 19 refined parameters and 340 observed reflections with $I \geq 2\sigma$. Ce on 4*i* (0, 0.29620(2), 0), Si1 on 2*c* (0, $^1/_2$, $^1/_2$), Si2 on 8*q* (0.1893(1), 0.13244(9), $^1/_2$), Si3 on 4*g* (0.1772(2), 0, 0). For details, see the Supporting Information, Tables S1a–c.

[7] $CeSi_5$: Space group *Immm*, $a = 377.74(3)$, $b = 601.89(4)$, $c = 929.79(6)$ pm, $Z = 2$, $R_{wP} = 0.071$ and $R_P = 0.053$. Ce on 2*a* (0, 0, 0), Si1 on 8*l* ($^1/_2$, 0.30350(7), 0.82760(5)), Si2 on 2*d* (0, $^1/_2$, 0)). For details, see the Supporting Information, Tables S2a–c. $GdSi_5$: $a = 377.50(8)$, $b = 603.2(1)$, $c = 923.3(3)$ pm, $R_{wp} = 0.021$ and $R_P = 0.017$. Ce on 2*a* (0, 0, 0), Si1 on 8*l* ($^1/_2$, 0.3069(2), 0.8270(2)), Si2 on 2*d* (0, $^1/_2$, 0)). d(Si1–Si1) 233.0(2) pm, d(Si1–Si1) 246.1(2) pm, d(Si1–Si2) 273.3(1) pm; d(Gd–Si) between 301.60(5) and 323.6(2) pm. For details, see the Supporting Information, Tables S3a–c.

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