Unconventional Metal–Framework Interaction in MgSi₅

Julia-Maria Hübner, Wilder Carrillo-Cabrera, Yurii Prots, Matej Bobnar, Ulrich Schwarz,* and Yuri Grin

Abstract: The silicon-rich cage compound MgSi₅ was obtained by high-pressure high-temperature synthesis. Initial crystal structure determination by electron diffraction tomography provided the basis for phase analyses in the process of synthesis optimization, finally facilitating the growth of single crystals suitable for X-ray diffraction experiments. The crystal structure of MgSi₅ (space group Cmme, Pearson notation oS24, a = 4.4868(2) Å, b = 10.1066(5) Å, and c = 9.0753(4) Å) constitutes a new type of framework of four-bonded silicon atoms forming Si₁₅ cages enclosing the Mg atoms. Two types of smaller Si₈ cages remain empty. The atomic interactions are determined by two-center two-electron bonds within the silicon framework. In addition, there is evidence for multicenter Mg–Si bonding in the large cavities of the framework and for lone-pair-like interactions in the smaller empty voids.

Intermetallic framework compounds constitute fascinating inorganic phases, in which a majority of framework atoms enclose a minority of guest species. In recent years, this class of materials attracted significant interest in preparative solid-state chemistry and current basic materials science research because several members exhibit beneficial thermoelectric or superconducting properties. The structural organization covers a wide variety of compositions involving three-dimensional frameworks usually based on four-bonded tetrel atoms such as Si, Ge, or Sn. Generally, the connectivity of the network atoms is related to the electron count by the 8–N rule although silicon compounds may tolerate a certain electron excess. Typically, members of the alkaline, alkali-earth, or rare-earth metal groups act as cationic guest species. However, magnesium constitutes an exception as the metal tends to participate in the anionic network, for example, in TiNiSi-type CaMgSi or BaAl₄-type phases such as EuGa₄.[4] At ambient pressure, the binary system Mg–Si shows (anti-)fluorite-type MgSi₅ as the only phase,[5] and also ternary magnesium–silicon compounds tend to evade clathrate-like frameworks.[4–6] However, high-pressure synthesis techniques provide valuable tools for advancing the spectrum of accessible tetrel frameworks regarding network topology and chemical composition.[7,8]

Herein, we report on the synthesis, crystal structure, and chemical bonding of a silicon framework embedding cationic magnesium in a binary compound. MgSi₅ was obtained by high-pressure synthesis between 5(1) and 10(1) GPa upon heating to temperatures between 1173(120) K and 1373(150) K and quenching to room temperature before decompression. At normal pressure, the diamagnetic compound decomposed at 468(10) K (see Figures S1 and S2 in the Supporting Information). The new compound was first discovered by scanning electron microscopy (SEM) in form of domains in matrices of hp-Mg₂Si and (cF8)Si. Specimens suitable for selected area electron diffraction experiments were prepared by the focused ion beam (FIB) lift-out technique (Figure 1 and Figure S3). Manual electron diffraction tomography measurements yielded 354 reflections indicating the space group Cmme. Structure solution was performed using 142 symmetry-independent reflections (Tables S1 and S2).

---

Figure 1. a) Polished surface of the MgSi₅ sample (back-scattering electron scanning electron microscope image) with arrays of equally oriented domains of MgSi₅ (light gray), separated by thin Si layers (dark gray); black frames show the positions of the FIB cuts. b) Surface image after extracting the first FIB cut. c) Second FIB cut soldered to the copper holder. d) Transmission electron microscopy image of a FIB lamella (perpendicular to [001]) showing the area used for electron diffraction tomography (circle). The inset shows the aperture.

---

[4] M. Sc. J.-M. Hübner, Dr. W. Carrillo-Cabrera, Dr. Yu. Prots, Dr. M. Bobnar, Dr. U. Schwarz, Prof. Yu. Grin
Chemische Metallkunde
Max-Planck-Institut für Chemische Physik fester Stoffe
Nöthnitzer Straße 40, 01187 Dresden (Germany)
E-mail: schwarz@cpfs.mpg.de

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.201907432.

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.
The determination of basic crystallographic information and chemical composition set the stage for optimizing the synthesis conditions. Powder diffraction patterns with LaB₆ as an internal standard resulted in lattice parameters of \( a = 4.4868(2) \) Å, \( b = 10.1066(5) \) Å, and \( c = 9.0753(4) \) Å. The optimized synthesis produced ingots containing specimen of sufficient size and quality for single crystal X-ray diffraction. These were isolated from the crude product by leaching with 0.1M NaOH.

Structure refinement with single-crystal and powder X-ray diffraction data (Tables S3–S5) shows that MgSi₅ represents a new structure type (Pearson notation a324; Figure 2). The crystal structure can be described as a three-dimensional framework of four-bonded (4b) Si atoms with Si₁₅ cages centered by Mg atoms and empty Si₈ polyhedra (Figure 2a). The filled [MgSi₁₅] cages are stacked along [100] and form columns by sharing pentagonal faces (Figure 2b). The stacking sequence in MgSi₅ resembles that of LaSi₁₀ and bears pronounced similarity to the arrangement of MSi₁₈ polyhedra in the compounds MSi₆ (\( M = \text{Ca, Sr, Ba, Eu} \)). The space between the columns is filled by empty Si₈ polyhedra—strongly distorted rhombic antiprisms—of two kinds A and B (Figure 2a,c,d). The connected Si₆ boat rings of the type A cavities (Figure 2c) resemble the proposed atomic arrangement of carbon atoms in sp² hydrocarbon (2,2) nanotubes. The observed distances between 2.379(2) and 2.4742(8) Å between neighboring silicon atoms in MgSi₅ (Table S6) are longer than those observed in elemental Si (2.3516 Å).

According to the Zintl–Klemm concept and the \( 8-N \) rule, frameworks containing solely four-bonded tetrel atoms would not require additional electrons for stabilization. Thus, the electron balance of MgSi₅ with (4b)Si atoms may be written as \( \text{MgSi}_5 = [\text{Mg}^{2+}]_2[\text{Si}^0]_4 \times 2e^- \) with two excess electrons per formula unit. In a simple picture for a four-bonded silicon network with electron excess, the electronic density of states (DOS) below the Fermi level would consist of two ranges, which are dominated by s and p states of silicon, respectively, and above a pseudo-gap-like minimum, several anti-bonding states are populated. For example, Ba-containing clathrates show such a DOS pattern. In comparison to that situation, the calculated electronic DOS for MgSi₅ reveals distinct differences (Figure 3a). First, the Si-s- and Si-p-dominated regions below the Fermi level can still be recognized by the corresponding atomic contributions, but there is no marked separation like the gap found for Ba clathrates. Second, the Fermi level is located almost exactly in the center of a pseudo-gap, again in contrast to a typical clathrate-like DOS. Such a situation may arise if “anti-bonding” states change character because of lone-pair-like configurations (“non-bonding” states) or direct (multi-center) interactions between silicon and magnesium (bonding states). In line with this picture, the integration of the electronic DOS in the window between −0.62 eV (first dip in the DOS below \( E_F \)) and the Fermi level yielded quite precisely two electrons per formula unit. These findings of the DOS analysis were used as the starting point for a detailed study of the chemical bonding in MgSi₅ by positional-space quantum-chemical techniques.

The electron density of MgSi₅ reveals magnesium species with an almost spherical shape, which according to the quantum theory of atoms in molecules (QTAIM) indicates a mostly cationic character of the magnesium atoms (Figure 4). However, some characteristics of the distribution differ from that of typical cationic metal species, such as in clathrates. Despite the generally convex surface, we note here that the faces in the (100) plane are significantly flattened, which hints at a distinct covalence of the interactions between magnesium and silicon. The effective QTAIM charge of +1.6 for Mg is in good agreement with the large electronegativity difference between Mg and Si. The corresponding charges in other intermetallic compounds of magnesium amount to values between +1.28 and +1.59, the calculated results for Mg₁₋₋₂B₂ range from +1.4 to +1.6. The shapes of the silicon species are more polyhedral-like, and the flat contact faces between neighboring atoms are typical for non-polar covalent bonding. The silicon QTAIM atoms have charges between 0.0 and −0.6, revealing an unequal charge transfer from the magnesium to the silicon atoms.
The distribution of the electron localizability indicator (ELI-D) reveals the typical picture of four-bonded silicon atoms. The maxima visualized by the isosurface with ELI-D = 1.44 (Figure 5a–c) are located on or close to the bond lines between silicon atoms. Moreover, the corresponding basin populations of these attractors (Figure 5a) amount to values of around two electrons. The intersection of the atomic basins of magnesium with the bonding basins of the Si–Si bonds indicate only a small contribution of Mg to three-atom interactions, as suggested by the location of small parts of the Si–Si bonding basins within the atomic basin of Mg (Figure 5c). A new feature of the ELI-D appears in vicinity of the Si2 atoms within the cavity labeled B. The local ELI-D maximum reveals a lone-pair-like interaction between neighboring Si2 atoms in the (100) plane across the cavity. Although the population of 0.27 electrons for the according basin (light yellow in Figure 5b,c) is rather small, its presence is the first hint to additional interactions within the crystal structure. This is also suggested by an analysis of the electronic DOS.

In order to study this finding in more detail, the contributions of electrons in certain energy regions below the Fermi level were investigated by partial ELI-D (pELI-D).\[16\] The calculation for states with energies between $-0.62$ eV (first dip in the DOS below $E_F$; Figure 3a) up to the Fermi level shows main pELI-D contributions close to the lone-pair-like attractor of Si2 in cavity B, confirming that this interaction is supported by magnesium electrons, which stabilize the cavity (Figure 3b). Further local maxima are found on the bond lines between Mg and Si2 and Si3, revealing multi-center Mg–Si interactions within the large cavity of the framework. Finally, large values are also observed within cavity A. Although the pELI-D values are insufficiently high to form a local maximum, they still suggest a polar—or a lone-pair-like—interaction. Both silicon atoms Si2 and Si3 acting within the small cavities have larger negative charges than Si1, which does not interact in the voids. The calculated pELI-D for the next energy window between $-1.56$ eV and $-0.62$ eV (Figure 3c) reveals mainly contribu-
tions to Mg–Si1 and Si–Si bonding, characteristic for cage (clathrate-like) compounds.

In summary, the electronic structure of the silicon-rich cage compound MgSi5 exhibits distinct differences to typical intermetallic host–guest assemblies despite similar structural features. The calculated electronic density of states of MgSi5 reveals a clear pseudo-gap around the Fermi level. Chemical bonding is organized in form of conventional two-center two-electron bonds within the three-dimensional silicon framework. In addition, there is evidence for multi-atom bonding between framework and cage atoms in the large cavities as well as lone-pair-like interactions in the smaller empty voids of the framework.

**Experimental Section**

MgSi5 was obtained by high-pressure, high-temperature synthesis between 5(1) and 10(1) GPa upon heating to temperatures between 1173(120) K and 1373(150) K before quenching to ambient conditions (see the Supporting Information). Thin samples prepared from crude ingots by the focused ion beam (FIB) lift-out technique were investigated with transmission electron microscopy by means of selected area electron diffraction data for structure solution (see the Supporting Information). Refinements of X-ray diffraction data were performed with the crystallographic program package WinCSD. Electronic band structure calculations (Figure S4) and bonding analysis of MgSi5 were carried out using the experimental values of lattice parameters and atomic coordinates (Tables S3 and S4) employing the program package TB-LMTO-ASA (see the Supporting Information). Position-space analysis of the chemical bonding in MgSi5 was performed by means of the electron localizability approach (see the Supporting Information).

**Acknowledgements**

We thank Susann Leipe for supporting high-pressure syntheses, Marcus Schmidt and Susann Scharsach for DSC measurements, Ulrich Burkhardt, Sylvia Kostmann, and Petra Scheppan for metallographic characterizations as well as Gudrun Auffermann and Ulrike Schmidt for chemical analysis. Stimulating discussions with Frank R. Wagner are appreciated. J.-M.H. gratefully acknowledges support by the International Max Planck Research School for Chemistry and Physics of Quantum Materials.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** cage compounds · chemical bonding · high-pressure synthesis · magnesium · silicon

**How to cite:** Angew. Chem. Int. Ed. 2019, 58, 12914–12918

Angew. Chem. 2019, 131, 13046–13050

[1] a) M. Pouchard, C. Cros in The Physics and Chemistry of Inorganic Clathrates (Ed.: G. S. Nolas), Springer, Dordrecht, 2014, pp. 1 – 33; b) M. Baïtinger, B. Böhme, A. Ormeci, Yu. Grin in The Physics and Chemistry of Inorganic Clathrates (Ed.: G. S. Nolas), Springer, Dordrecht, 2014, pp. 55 – 64; c) C. Cros, M. Pouchard, P. Hagemüller, J. Solid State Chem. 1970, 2, 570–558; d) M. Beekman, G. S. Nolas, J. Mater. Chem. 2008, 18, 842–851; e) S. Yamanaka, Dalton Trans. 2010, 39, 1901–1915; f) A. V. Shevelkov, K. Kouviri, Struct. Bonding (Berlin) 2011, 139, 97–142; g) S. C. Peter, M. G. Kanatzidis, Z. Anorg. Allg. Chem. 2012, 638, 287–293; h) A. Iyo, I. Hase, K. Kawashima, S. Ishida, H.
