Thermal, Magnetic, Electronic and Superconducting Properties of Rare-Earth Metal Pentagermanides REGe5 (RE = La, Nd, Sm, Gd) and Synthesis of TbGe5

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Thermal, Magnetic, Electronic and Superconducting Properties of Rare-Earth Metal Pentagermanides REGe5 (RE = La, Nd, Sm, Gd) and Synthesis of TbGe5

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<td>Complete List of Authors:</td>
<td>Meier, Katrin; MPI CPfs, Chemical Metals Science Cardoso-Gil, Raul; MPI CPfs, Chemical Metals Science Schnelle, Walter; MPI CPfs, Chemical Metals Science Rosner, Helge; MPI CPfs, Chemical Metals Science Burkhardt, Ulrich; MPI CPfs, Chemical Metals Science Schwarz, Ulrich; MPI CPfs, Chemical Metals Science</td>
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Keywords: terbium; germanium, high-pressure synthesis; rare-earth metal germanides; physical properties

A series of isotypic rare-earth metal pentagermanides including the new compound TbGe₅ have been prepared by high-pressure synthesis. They crystallize in the orthorhombic space group Immm (No. 71; \(a = 395.70(9)\) pm; \(b = 611.1(2)\) pm and \(c = 983.6(3)\) pm for TbGe₅). The crystal structure is isotypic to LaGe₅ and consists of puckered germanium slabs which sandwich a second germanium species and the rare-earth metal atoms. At ambient pressure, the thermal decomposition of the phases \(\text{REGe}_5\) \((\text{RE} = \text{La, Nd, Sm, Gd, Tb})\) proceeds via discrete intermediate steps into \(\text{Ge}(\text{F}8)\) and thermodynamically-stable germanium-poorer phases.

The investigated compounds \(\text{REGe}_5\) are paramagnetic metallic conductors which order antiferromagnetically at low temperatures. Specific heat measurements reveal that the superconducting state of \(\text{LaGe}_5\) below \(T_c = 7.1(1)\) K is characterized by a critical field of \(\mu_0H_c2 = 0.2\) T and weak electron-phonon coupling. Density-functional based band-structure calculations yield a very similar electronic structure for all the isotypic \(\text{REGe}_5\) compounds. Besides a slight increase in the width of the valence band for smaller \(\text{RE}\) atoms, only minor differences are found for the two different Ge environments.

Fig. 1. Crystal structure of pentagermanides \(\text{REGe}_5\) \((\text{RE} = \text{La, Ce, Pr, Nd, Sm, Gd})\). Ge1 atoms form three short contacts within corrugated layers. Two longer contacts to Ge2 complete the 3+2 coordination. Between the two-dimensional units the species Ge2 is coordinated by eight Ge1 atoms and the metal atoms centre larger voids of the germanium network.

Thermal stability and decomposition of the new compound at ambient pressure is discussed in comparison to results for isotypic atomic patterns. The unusual columnar alignment of the metal atoms in the phases \(\text{REGe}_5\) motivated a consequent theoretical and experimental study of the magnetic, electrical and superconducting properties.

Introduction

Compounds of an electropositive metal and an element of group 14 often comprise covalent substructures of the post-transition element in which electron count and number of covalent bonds are strictly interrelated by the 8–9 rule. Thus, four-bonded silicon and germanium atoms are formally uncharged, i.e., \((4b)\text{Si}^0\) and \((4b)\text{Ge}^0\). Despite an excess of electrons, some binary high-pressure phases of silicon like \(M[(4b)\text{Si}^0]_2\) \(2e^-\) \((M = \text{Ca, Sr, Ba; Eu})\) [1–5] form four covalent bonds per framework atom. In germanides, a transfer of electrons typically induces defects in the germanium partial structure, a formation of lone-pairs [6] and a decrease of the homonuclear coordination number.

Aiming to substantially expand the coordination environment of the tetrel atoms and, thus, to modify the physical properties, high-pressure high-temperature synthesis has emerged as a powerful and versatile tool. Experiments yielded binary compounds \(\text{REGe}_5\) \((\text{RE} = \text{La, Ce, Pr, Nd, Sm, Gd})\) [5, 7–10]) in which two different types of germanium atoms are coordinated by five and eight neighbours within the framework, respectively (Fig. 1).

Here we report the high-pressure high-temperature synthesis of \(\text{TbGe}_5\), a new member of the isotypic series with the hitherto smallest embedded rare-earth metal.
Results and Discussion

Synthesis
The synthesis experiments reveal that TbGe\textsubscript{3} forms only in a narrow \( P, T \) window around 8.3(5) GPa and 820 K. Variation of pressure by \( \pm 1 \) GPa or temperature by \( \pm 100 \) K suppresses completely the formation of the high-pressure phase as evidenced by subsequent X-ray powder diffraction measurements. Thus, the parameter window to synthesize the terbium compound is even narrower than that of recently prepared GdGe\textsubscript{3} \cite{[9]}. A metallographic investigation of a polished sample of the reaction products after high-pressure high-temperature synthesis evidences the new germanium-rich compound as the main component (Fig. 2). Energy-dispersive X-ray spectroscopy of this major constituent reveals a ratio Tb : Ge of 1 : 4.90(5) in good agreement with a composition TbGe\textsubscript{3}. Besides, small amounts of germanium and a phase with a composition close to TbGe\textsubscript{2.1} are present.

Crystal Structure
The powder X-ray diffraction diagram of TbGe\textsubscript{3} is characterized by a high background and a low signal to noise ratio (Fig. 3) indicating a small size of the crystalline domains. An increase of the annealing time during the synthesis from 9 h to 45 h at 820 K did not improve the quality of the diffraction data. In agreement with the findings from a metallographic analysis, additional lines evidence the presence of Ge(cF8) and a small amount of a phase with a hitherto unknown crystal structure.

Indexing of the powder diffraction peaks of the new compound on the basis of an orthorhombic body centred lattice results in unit cell parameters of \( a = 395.70(9) \) pm, \( b = 611.1(2) \) pm, \( c = 983.6(3) \) pm. On the basis of the powder diffraction intensities, the terbium compound is identified as isotypic to LaGe\textsubscript{3}. Due to the poor quality of the crystalline powder and the resulting diffraction data, the parameter refinement using complete diffraction profiles was performed in a successive manner in order to reduce the number of free parameters in each least squares cycle. Applying these limitations, the atomic coordinates converge to Tb (0, 0, 0); \( U_{iso} = 0.0046(6) \), Ge1 (0.5, 0.2970(3), 0.8314(2)); \( U_{iso} = 0.0082(5) \), Ge2 (0, 0.5, 0); \( U_{iso} = 0.010(1) \) resulting in interatomic distances which are close to those of the other isotypic germanides.

Closer inspection of the refinement results evidences a difference in the displacement parameters of the crystallographically distinct germanium atoms which has also been observed for other members of this rather unusual atomic pattern. Since refinements of the diffraction data of TbGe\textsubscript{3} are hampered by the high background and the low signal to noise ratio, a more detailed investigation of this issue was performed with powder X-ray diffraction diagrams of the isotypic compound SmGe\textsubscript{3} which were measured with synchrotron radiation. In order to search for local deviations from the average symmetry, a disorder model with a split position for Ge2 was refined in space group \textit{I4mm} (Tab. 1). The finding that the \( U_{iso} \) parameters of the germanium atoms become the same within estimated experimental error is taken as an indication for a thermal displacement rather than a partial occupation of the eight-fold coordinated position. A dynamic effect is also consistent with the specific heat measurements (see below). Consequently, a decrease of symmetry by using the space groups \textit{Imm2}, \textit{I222}, and \textit{I2/m1} does not result in an improvement with respect to the residuals or the magnitude of the displacement parameters.

<table>
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<tr>
<th>Atom</th>
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<th>( z )</th>
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<td>2d</td>
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<td>0</td>
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<td>0.0078(4)</td>
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\( a \) The site occupancy factor of the position is fixed to 0.25.

In the previously known binary terbium germanium compounds, a wide variety of Ge species covering isolated
atoms, one-bonded Ge in dumbbells, two-bonded Ge in chains and rings as well as nets of three-bonded Ge are observed [11–22]. In Tb$_2$Ge$_4$ (Er$_3$Ge$_4$ type) a square-planar coordinated type of four-bonded germanium is present. In short, despite a wide variety of structural motifs, the number of homonuclear neighbours has an upper limit of four in the previously characterized compounds. Thus, TbGe$_3$ is the first binary compound in the system Tb–Ge in which the number of homonuclear neighbours of germanium exceeds four.

**Thermal Stability**

A systematic study on thermal properties of compounds REGe$_5$ (RE = La, Nd, Sm, Gd, Tb) reveals that all the synthesized pentagermanides exhibit exothermic decompositions at ambient pressure (Fig. 4). The disintegrations proceed via intermediate phases into germanium-poorer compounds which are stable at ambient conditions, i.e., REGe$_{2-\delta}$ (RE = La, Nd, Sm and Gd) or TbGe$_3$ and Ge(cF8).

![Fig. 4. DSC measurements of pentagermanides REGe$_5$ for increasing temperatures between 298 K and 1473 K.](image)

The finding of intermediate phases is confirmed by in-situ powder X-ray diffraction data of the compounds NdGe$_5$ (Fig. 5) and SmGe$_5$. In agreement with the prolonged holding time of the experiment, the formation of Ge(cF8) due to the disintegration of NdGe$_5$ is observed already at 513 K. The similarity of the diffraction diagrams of NdGe$_5$ and the first germanium-poorer phase NdGe$_{5-x}$ (diagram measured at 563 K) is consistent with the assumption that the latter is a defect variety of the starting compound. At 598 K, this germanium-poorer phase decomposes into NdGe$_{2-\delta}$ and Ge(cF8). Further temperature increase induces a significant growth of the crystalline domains (see pattern at 823 K). Diffraction data measured at 298 K evidence that the formed phases NdGe$_{2-\delta}$ and Ge(cF8) remain stable upon cooling to ambient temperature.

Despite the formation of different final products, the thermal decomposition of the pentagermanides REGe$_5$ exhibits a systematic decrease of the onset temperature with increasing atomic number of the metal atom (Fig. 4). Since the stability of a certain crystal structure motif is, among other factors, influenced by the geometric features of the constituents, the decomposition temperature was investigated as a function of the radius of the metal atom (Fig. 6). The descent can be described by a linear fit in good approximation clearly indicating that the stability of the structural pattern decreases monotonously with the size of the metal ions in the investigated series.

**Electronic Structure**

To study the electronic structure of compounds REGe$_5$ on a microscopic level, especially the change regarding the exchange of the RE atoms and the role of the two different Ge environments for the crystal chemistry, band structure calculations within the density-functional theory were carried out. As a representative result, the electronic densities of states (DOS) for LaGe$_5$ and TbGe$_5$ are shown in the upper panel of Fig. 7. For LaGe$_5$, our results are in good agreement with earlier calculations [7]. In general, apart
from a change of the position of the narrow 4f band complex, the DOS for isotypic compounds \( \text{REGe}_5 \) is very similar. The main difference is a systematic, slight broadening of the valence band by about 0.6 eV going from \( \text{LaGe}_5 \) to \( \text{TbGe}_5 \). This is caused by an increasing Ge–Ge overlap related to the smaller cell volume due to the lanthanide contraction [23]. The states at the Fermi level \( E_F \) originate mainly from Ge 4p electrons. Although we obtain a stable magnetic solution for all compounds except \( \text{LaGe}_5 \), the Ge states are essentially unpolarized. This results in a very similar DOS(\( E_F \)) between 2.4 and 2.6 states per eV and unit cell for all \( \text{REGe}_5 \) systems, corresponding to a bare electronic \( \gamma_0 \) between 5.65 and 6.13 mJ mol\(^{-1} \) K\(^{-2} \) (see specific heat measurements below).

The lower panel of Fig. 7 shows the partial DOS for the two different Ge sites in \( \text{TbGe}_5 \). They are very similar despite the rather different crystallographic environments (five and eight homonuclear contacts for Ge(1) and Ge(2), respectively). This similarity holds for all pentagermanides of the investigated metals \( \text{RE} \). An explicit population analysis exhibits a difference of 0.09 additional electrons at the Ge(2) site for \( \text{TbGe}_5 \) (only 0.01 for \( \text{LaGe}_5 \)). Thus, a simple model for the charge transfer between the metal atoms \( \text{RE} \) and the different Ge sites as suggested earlier [7] is not confirmed by our calculations. We rather obtain a picture of a Ge(4) "polyanion" with considerable covalent interactions with the included \( \text{RE} \) constituents, typical for intermetallic systems. According to the electronic structure calculations, the intermetallic character of the compound is also in line with the absence of any indication of a lone pair at the Ge! Site which would be presumably directed towards the channels filled with \( \text{RE} \) atoms.

**Transport Properties**

The electrical resistivity \( \rho(T) \) of the compounds \( \text{REGe}_5 \) (Fig. 8) is typically metallic with room temperature values \( \rho(300 \text{ K}) \) of 43 – 72 \( \mu\Omega \) cm. Inflections in \( \rho(T) \) are visible for \( \text{SmGe}_5 \), \( \text{GdGe}_5 \) and \( \text{TbGe}_5 \) which are due to the reduced scattering of the charge carriers in the magnetically ordered phases (see below). The residual resistivity of the \( \text{LaGe}_5 \) sample is 2.8 \( \mu\Omega \) cm (residual resistance ratio \( \approx 15 \)), indicating a good crystalline sample quality for a high-pressure synthesis. Zero resistance is observed at 7.1 K, in agreement with the magnetic shielding data (see below). The residual resistivity (16 \( \mu\Omega \) cm) of the \( \text{TbGe}_5 \) sample is significantly higher than that of the other samples.

The thermal conductivity of the three tested \( \text{REGe}_5 \) samples (\( \text{RE} = \text{Nd, Sm, Gd, Tb} \)) is estimated to be of the order 8 – 13 W K\(^{-1} \) m\(^{-1} \) at 300 K. Below 100 K it decreases rapidly. The Seebeck coefficient at room temperature ranges between –1.5 and –2.5 mV K\(^{-1} \) and is surprisingly small for a compound with such a high germanium content. The small value as well as the relatively low resistivities indicates typical intermetallic behaviour of the compounds.

**Magnetic Properties**

The magnetic susceptibilities \( \chi(T) = M/H \) of \( \text{NdGe}_5, \text{GdGe}_5 \), and \( \text{TbGe}_5 \) follow a Curie-Weiss law at high temperatures (Fig. 9). From fits to the data above 100 K the following effective paramagnetic moments and paramagnetic Weiss temperatures are obtained: \( \text{NdGe}_5, \mu_{eq} = 3.69 \mu_B, \theta_B = -36.9 \text{ K} \) (the effective moment being in agreement with
earlier data [8]; GdGe₅, \( \mu_{\text{c}} = 8.28 \mu_B \), \( \theta_p = -43.4 \) K; TbGe₅, \( \mu_{\text{c}} = 9.79 \mu_B \), \( \theta_p = -25.9 \) K. SmGe₅ displays van-Vleck-type paramagnetism, as reported previously [8]. From the slope of the experimental susceptibility data above 300 K the typical minimum of \( \chi(T) \) for Sm\(^{3+} \) compounds is expected to occur just above 400 K (the maximum temperature of our measurement). The observed paramagnetic behaviours are in good agreement with the presence of rare-earth ions in the oxidation state +3 with respective Hund’s rule ground multiplets: NdGe₅, \( ^{4}S_{3/2} \), \( \mu_{\text{free}} = 3.62 \mu_B \); SmGe₅, \( ^{4}S_{5/2} \), (see above); GdGe₅, \( ^{8}S_{7/2} \), \( \mu_{\text{free}} = 7.94 \mu_B \); TbGe₅, \( ^{5}F_{6} \), \( \mu_{\text{free}} = 9.72 \mu_B \). At low temperatures kinks in \( \chi(T) \) due to antiferromagnetic ordering of the rare-earth moments are observed (Fig. 10, NdGe₅; \( T_N = 5.7 \) K (not detected earlier [8]); SmGe₅; \( T_N \approx 10 \) K (cf. 10.4 K [8]); GdGe₅; \( T_N \approx 29 \) K; TbGe₅; \( T_N \approx 41 \) K).

LaGe₅ is a Pauli paramagnet with pronounced temperature dependence. Only at the lowest temperatures a second paramagnetic contribution with Brillouin behaviour due to minor paramagnetic impurities becomes evident. Thus, at elevated temperatures mostly Pauli paramagnetism is observed which is temperature-dependent due to a strongly structured DOS at the Fermi level. The strong decrease of the susceptibility with increasing temperature is consistent with the steep decrease of the calculated DOS right above the Fermi level (Fig. 7). Taking into account the Curie-paramagnetic “tail” we extrapolate a value of \( \chi(T \to 0) \) of \( +135(30) \times 10^{-6} \) emu/mol. With the sum of the diamagnetic core contributions \( -55 \times 10^{-6} \) emu/mol a Pauli-paramagnetism \( \chi_p(T \to 0) \) of \( +190(30) \times 10^{-6} \) emu/mol is derived. This value corresponds to a \( \gamma \) of 13.9 mJ mol\(^{-1} \) K\(^{-2} \) consistent with the value for \( \gamma_{\text{exp}} \) extracted from the specific heat data.

In a low field (\( \mu_0 H = 1 \) mT) a sharp transition to the superconducting state is observed between 6.95 K and 7.15 K (shielding signal 10% / 90%) in accordance to earlier data (\( T_c = 7.0 \) K [7]). However, besides low-field susceptibility and zero-field resistivity no superconducting data have been reported. For our sample, the volume susceptibility \( \chi_{\text{vol,zfc}} \) measured after zero-field cooling indicates that the shielding is complete (\( \chi_{\text{cal}} \) is 137% of \(-1/4\pi \) due to the neglected demagnetization correction). The field-cooling Meissner effect is very small (only 5% of \(-1/4\pi \)) as often observed experimentally for type-II superconductors due to strong flux line pinning.

**Specific Heat and Superconductivity of LaGe₅**
The specific heat capacity of the investigated REGe₅ compounds is plotted in \( c_{p}/T \) representation in Fig. 11. Clear anomalies indicating antiferromagnetic long-range ordering are visible at the Néel temperatures. For NdGe₅ the anomaly at \( T_N \) has a typical \( \lambda \)-shape. At a temperature \( T_{N2} \) a sharp kink in \( c_p(T) \) probably indicates a spin-reordering transition. For SmGe₅, GdGe₅ and TbGe₅ the anomalies at \( T_N \) are more similar to a mean-field transition, i.e., step-like. Moreover, in GdGe₅ a double transition of unknown origin is visible. The specific heat of the compounds REGe₅ consists of the terms \( c_p(T) = c_{\text{ph}} + c_{\text{el}} + c_{\text{mag}} \). In LaGe₅ the only contributions are the phonon \( c_{\text{ph}}(T) \) and conduction electron \( c_{\text{el}}(T) \) terms (for their determination see below), thus \( c_p(T) \) of LaGe₅ in the normal state may serve as a reference for the respective contributions in the “magnetic” REGe₅ compounds assuming that \( c_p(\text{REGe}_5) = c_{\text{el}}(\text{LaGe}_5) \). The phonon terms \( c_{\text{ph}}(\text{RE Ge}_5) \) are calculated from \( c_{\text{ph}}(\text{La Ge}_5) \) (see below) by a scaling to the equivalent Debye temperature \( \theta_D(T) \) with the square root of the molar mass ratio of the compounds (see Ref. [24]).

After subtraction of the phonon and electronic terms the magnetic specific heats \( c_{\text{mag}}(T) \) are obtained. The magnetic entropies \( S_{\text{mag}}(T) \) are calculated by integration of \( c_{\text{mag}}(T) \). It is found that \( T_{N,\text{cal}} \) (the critical temperature of the peak) and \( T_{N,\text{cal}} \) are 5.5 K and 0.57 R for NdGe₅ and 9.5 K and 0.54 R for SmGe₅, indicating that the crystal field ground state of these ions are Kramers doublets (expected entropy \( \approx R \ln 2 \) [25]). For GdGe₅ we find 1.94 R indicating the expected entropy \( R \ln 8 \) well above \( T_N \). As typical for Gd\(^{3+} \) compounds we observe a hump-like anomaly well below \( T_N \) which is due to the highly degenerate ground state of this ion. For TbGe₅ an anomaly of 1.48 R is observed at \( T_{N,\text{cal}} = 41 \) K, which may indicate that the ordering TbGe₅ involves 6 out of a total of 13 singlet levels [25]. The specific heat of LaGe₅ for various magnetic fields is displayed in Fig. 12. The superconducting transition step centred at \( T_c(H = 0) = 6.80(2) \) K is already broad for zero magnetic field which is probably due to chemical
inhomogeneity of the sample. With increasing field the transition broadens further. For fields $\mu_B H \gtrsim 200$ mT the specific heats below $T_c(0)$ become indistinguishable, thus for these fields the material is in the normal state.

A fit to these data in the range 2.3 K to 8.2 K requires besides the electronic Sommerfeld term $\gamma T$ a phonon contribution beyond the simplest Debye $T^3$ model. We have tried both the harmonic lattice approximation $c_{ph} = \beta T^3 + \delta T^5 + ...$ and a combination of a Debye and an Einstein term $c_{ph} = \beta T^3 + \varepsilon E(T/\theta_E)$ in which $E$ is the Einstein function and $\theta_E$ represents the characteristic phonon frequency $h\omega_0/k_B$ [24]. Regarding the least-squares deviation the latter model is far superior to the first. The resulting parameters are $\gamma_{exp} = 11.39(3)$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 4.76(2) \times 10^{-5}$ J mol$^{-1}$ K$^{-4}$ corresponding to an initial Debye temperature $\theta_D(0) = 290$ K for 6 atoms, and a relatively small contribution $\varepsilon = 6.94(4)$ J mol$^{-1}$ K$^{-1}$, and $\theta_E = 74.8(7)$ K. The “spectral weight” $\varepsilon$ of the Einstein term has to be compared to the gas constant $R = N_A k_B$ expected for one vibrational degree of freedom. $\delta R = 1$ signifies that the Einstein term is due to the weak bonding of one atom (per formula unit) in only one space direction, viz. the Ge(2) atom within the rigid channels along the $a$ axis formed by the Ge(1) atoms. This correlates well with the powder X-ray diffraction refinements (see above) and especially the large anisotropic displacement parameter $U_{11}$ of the Ge(2) atom as reported earlier [7].

After subtraction of the phonon specific heat $c_{ph}(T)$ the superconducting electronic term $c_{el}(T)$ can be compared with the predictions of the BCS theory (weak electron-phonon coupling limit) and the phenomenological two-fluid model (suitable for strong $e$-ph coupling) [26]. In the least-squares deviation the fit with the BCS model (including a Gaussian smearing of the transition) is superior by a factor of two to the two-fluid model indicating weak $e$-ph coupling. A midpoint $T_{c,\text{med}} = 6.80(2)$ K and a reduced specific heat jump $\Delta c_{\text{el}}/T_c = 17.0(2)$ mJ mol$^{-1}$ K$^{-2}$ are obtained. The ratio $\Delta c_{\text{el}}/T_c = 1.493$ is slightly higher than for the weak-coupling BCS limit (1.426). The experimental value agrees also with that derived from $\Delta c_{\text{el}}/T_c = 1.426(1 + 53 \ln(x/3)/x^2)$ with $x = \theta_D/T_c$ [27] giving 1.536.

By using the McMillan formula $\ln(1.45 T_c/\theta_D) = -1.04(1 + \lambda)(1 - \mu(1 + 0.62\lambda))$ we can estimate an electron-phonon coupling parameter $\lambda$ of 0.76 when assuming a typical value for the Coulomb pseudopotential $\mu$ of 0.15. This value of $\lambda$ correlates well with the calculated interval derived from the Sommerfeld coefficient $\gamma_{el}$ in the band structure calculation (see above): $\gamma_{exp} = \gamma_{el} \times (1 + \lambda)$ resulting in 0.85 $\leq \lambda \leq$ 0.95. In agreement with the magnetic susceptibility results (see above), the normal state $\gamma_{el}$ corresponds to a Pauli susceptibility $\chi_p$ of approximately $156 \times 10^{-6}$ emu/mol.

From the observed pinning and the behaviour of the specific heat step in magnetic fields LaGe$_5$ is a type-II superconductor. Due to the broad transition steps in fields the determination of the midpoint of the transitions, $T_{c,\text{med}}(\mu_B H)$, is only possible for fields $\lesssim 50$ mT. The slope $d\mu_B H_c(0)/dT$ thus determined is $-25$ mT/K which yields an upper critical field $\mu_B H_c(0)$ of only 120 mT using the (dirty-limit) WHH extrapolation $\mu_B H_c(0) = -0.693 T_c(0) \mu_B dH_c/dT$ [28]. Taking the onset temperatures $T_{c,\text{on}}(\mu_B H)$ of the transitions for the same fields we obtain $d\mu_B H_c/dT = -52$ mT/K and a $\mu_B H_c(0) = 260$ mT. This would be however the value for a hypothetical homogeneous LaGe$_{5-x}$ sample with the optimum $T_c$ of 7.3 K. Actually, we observe that $c_{ph}(T)$ is independent from field above $\mu_B H \gtrsim 200$ mT and $T > 1.8$ K, thus the average $\mu_B H_c(1.8)$ K is about 200 mT.

**Summary**

The new compound TbGe$_5$ can be prepared by high-pressure high-temperature synthesis at 8.3(5) GPa and 820(50) K. At ambient pressure, the decomposition temperature of the metastable high-pressure phases REGe$_5$ ($RE = La, Nd, Sm, Gd, Tb$) decreases linearly with increasing atomic number of the metal atoms indicating that the stability of the structural pattern decreases with the size of the metal ions. Band structure calculations reveal a very similar electronic structure of the studied compounds apart from the 4f configuration and slight changes of the valence band-width due to different radii of the metal atoms. The different germanium environments cause only minor differences of the occupied Ge valence states.

The temperature dependences of the magnetic susceptibility indicate the oxidation state +3 for the rare-earth metals in REGe$_5$ ($RE = La, Nd, Sm, Gd, Tb$) and magnetic ordering of the moments between 5.7 K ($NdGe_5$) and 41 K (TbGe$_5$). LaGe$_5$ is a type II superconductor with weak electron-phonon coupling and a $T_c$ of 7.1 K. The analysis of the phonon specific heat contribution evidences a low-frequency Einstein mode which is attributed to an anomalous one-dimensional vibration of the eightfold coordinated atom Ge2 in the structural pattern. This finding is consistent with a pronounced dynamic displacement as indicated by refinements of X-ray diffraction data.

**Experimental Section**

Preparation and sample handling was performed in glove boxes (argon atmosphere, $p(\text{H}_2\text{O}) \leq 0.1$ ppm; $p(\text{O}_2) \leq 0.1$ ppm). The precursor samples with a nominal composition Tb:Ge:Se = 1:5 (TbGe$_5$+Ge) were prepared by arc melting of elemental terbium (Lamprecht, 99.99 % metals basis) and germanium (Chempur 99.999 %). High-pressure and high-temperature conditions were realized by means of an octahedral multianvil press described earlier [29]. Pressure and temperature calibration is performed prior to the experiments by in-situ monitoring of the resistance.
changes of bismuth [30] and by runs using a thermocouple, respectively. As crucible material hexagonal boron nitride was used. For determining the stability field of TbGe$_5$ experiments were performed in a parameter field around the formation conditions, i.e., at pressures of 8 GPa, 8.3 GPa and 9 GPa and temperatures of 720 K, 820 K and 920 K for 540 min. The high-temperature high-pressure treatment was followed by quenching to ambient temperature before decomposition.

 Differential Scanning Calorimetry (DSC) was performed with a Netzsch DSC 449 apparatus in Al$_2$O$_3$ crucibles in the temperature range from 295 K to 1473 K with a heating rate of 10 K / min. X-Ray powder diffraction data were collected in transmission employing Cu K$_\alpha$ ($\lambda = 1.54056$ Å) radiation. An internal LaB$_6$ standard ($\alpha = 4.15962(1)$ Å) was added before placing the mixture between two Mylar foils. For lattice parameters refinement a set of 25 reflections was used. Crystallographic calculations were performed with the program package WinCSD [31]. High-temperature measurements are realized with a STOE-STADIP-MP, Ge-Monochromator, Debye-Scherrer geometry and a linear position sensitive detector using heating rates of 10 K / min and a holding time for diffraction measurements of 170 min.

 The quality of the prepared samples is independently examined by optical metallography followed by a verification of the chemical composition using a Philips XL30 scanning electron microscope (EDXS system) with an integrated EDXS system. X-Ray powder diffraction data were collected in transmission using a Philips XL30 scanning electron microscope employing Cu K$_\alpha$ ($\lambda = 1.54056$ Å) radiation. An internal LaB$_6$ standard ($\alpha = 4.15962(1)$ Å) was added before placing the mixture between two Mylar foils. For lattice parameters refinement a set of 25 reflections was used. Crystallographic calculations were performed with the program package WinCSD [31]. High-temperature measurements are realized with a STOE-STADIP-MP, Ge-Monochromator, Debye-Scherrer geometry and a linear position sensitive detector using heating rates of 10 K / min and a holding time for diffraction measurements of 170 min.

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