Synthesis, Structure, Chemical Bonding, and Magnetism of the Series RELiGe₂ (RE = La–Nd, Sm, Eu)

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Supporting Information

ABSTRACT: This article focuses on the synthesis and the crystal chemistry of six members of a series of rare-earth metal based germanides with general formula RELiGe₂ (RE = La–Nd, Sm, and Eu). The structures of these compounds have been established by single-crystal X-ray diffraction (CaSi₂, structure type, space group Pmna, Z = 4, Pearson symbol P12₁). The chemical bonding within this atomic arrangement can be rationalized in terms of anionic germanium zigzag chains, conjoined via chains of edge-shared LiGe₄ tetrahedra and separated by rare-earth metal cations. The structure can also be viewed as an intergrowth of Al₇-like and TiNiSi-like fragments, or as the result of the replacement of 50% of the rare-earth metal atoms by lithium in the parent structure of the REGe monogermanides. Except for LaLiGe₂ and SmLiGe₂, the remaining four RELiGe₂ phases exhibit Curie–Weiss paramagnetism above about 50 K. In the low temperature regime, the localized 4f electrons in CeLiGe₂, PrLiGe₂, and SmLiGe₂ order ferromagnetically, while antiferromagnetic ordering is observed for NdLiGe₂ and EuLiGe₂. The calculated effective magnetic moments confirm RE³⁺ ground states in all cases excluding EuLiGe₂, in which the magnetic response is consistent with Eu²⁺ configuration (J = S = 7/2). The experimental results have been complemented by tight-binding linear muffin-tin orbital (TB-LMTO) band structure calculations.

INTRODUCTION

In the past several years, our group has successfully synthesized and characterized numerous types of rare-earth and/or alkaline-earth metal germanides with novel structures. In addition to some relatively simple binaries, examples with more intricate bonding include the ternary RE₄InGe₂₁ and RE₄Mg₂Ge₁² phases (RE = rare-earth metal), the homologous series A₂In₁₉Ge₁₉₂ₚₙ (A = Ca, Sr, Eu, and Yb)₈ (Sr₁₋₂Ca₉)₉InGe₄/(Eu₁₋₂Yb₉)₉InGe₄ (x = 0.7) and (Sr₁₋₂Ca₉)₉In₄Ge₁₂/(Sr₁₋₂Yb₉)₉In₄Ge₁₆ (0.4 ≤ x ≤ 0.5), among others. The Ge atoms in most of these structures are either dimerized into Ge dumbbells (formally [Ge₂]⁻) or “polymerized” into one-dimensional (1-D) chains (formally [Ge₄]⁻); the latter being an alternation of cis- and trans-Ge–Ge bonds with partial π-delocalization of the Ge π-bonds (hence the fractional formal charge on the 2-bonded germanium atoms). Surveying the recent literature, we found similar Ge chains in several, predominantly Li-containing compounds, such as α-Sr₂Li₅Ge₁₀, Eu₄Li₅Ge₁₀, Al₃(Al₃–Li₅)Ge₄ (A = Sr, Eu; x ≈ 0.5), Al₅Li₇Ge₂ (A = Sr, Ba), and Eu₅Li₇Ge₂ (RE = La–Nd, Sm, and Eu) to name a few. In all of these instances, the small size and the relatively high electronegativity of Li that is, its ability to form bonds with a partial covalent character, have been suggested as an explanation for the existence of such chains with varied electron count. Further studies on the Al₁₋₂In₃Ge₄ (0 ≤ x ≤ 0.1) and A₁₋₂Li₁₋₂In₃Ge₄ (x ≈ 0.3) phases (A = Sr, Ba, Eu) confirmed the above point, and demonstrated the potential for structural diversity brought up by the special characteristics of the Li metal.

In this article, we report more “lithium chemistry” within the realm of rare-earth metal based germanides by discussing the synthetic efforts and the single-crystal structures of the RELiGe₂ phases (RE = La–Nd, Sm, and Eu) phases, dubbed for short the “1-1-2” compounds. A short analysis of the bonding and the structural trends across the series is also presented. A theoretical treatment of the Ge–Ge bonding within the Ge chains, using the tight-binding linear muffin-tin orbital (LMTO) method, is discussed as well.

EXPERIMENTAL SECTION

Synthesis. All reactions were carried out in welded Nb-ampules. Because of the air-sensitivity of some of the starting materials (pure elements from Alfa or Aldrich (>99.9 wt %)), handling was done inside an argon-filled glovebox or under vacuum. Mixtures of the metals in the desired stoichiometric ratios (1:1:2) were loaded into Nb-tubes, which were then sealed by arc-melting under an argon atmosphere. To prevent oxidation upon heating to high temperature, the welded Nb-tubes were subsequently enclosed in fused silica tubes, which were then evacuated (below discharge) and flame-sealed.

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The reaction mixtures containing La, Ce, Pr, and Eu were heated in a tube furnace to 985 °C (rate of 200 °C/h), whereas those containing Nd and Sm were heated to 1085 °C at the same rate. The increase of the reaction temperature was deemed necessary because the melting points of Nd (1021 °C) and Sm (1074 °C) are higher than those of the rest of the early lanthanides. The silica ampules were slowly rotated several times at the melting temperature to ensure homogeneity. All reactions were kept at the maximum temperatures for 5 h, and then cooled at varied steps to ambient temperature (vide infra). The products of such reactions were typically small silver metallic crystals with irregular shapes. We note here that reactions conducted at higher temperatures could be dangerous. At these temperatures, handling the ampules in a glove box was necessary because the silica ampules are toxic.

### Table 1. Selected Crystal Data and Structure Refinement Parameters for $RE\text{LiGe}_2$ ($RE = \text{La–Nd, Sm, Eu}$)

<table>
<thead>
<tr>
<th>Formula</th>
<th>$f_w$/g mol$^{-1}$</th>
<th>$T_f$ °C</th>
<th>Δν</th>
<th>Radiation, wavelength</th>
<th>Space group</th>
<th>$a$/Å</th>
<th>$b$/Å</th>
<th>$c$/Å</th>
<th>$V$/Å$^3$</th>
<th>$\rho_{av}$/g cm$^{-3}$</th>
<th>$\mu_{iso}$/μm</th>
<th>Final R indices $^a$ [I &gt; 2σ(I)]</th>
<th>Largest diff. peak and hole/ e$^-$ Å$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaLiGe$_2$</td>
<td>291.03</td>
<td>−73 ± 2</td>
<td>Mo–Kα, 0.71073 Å</td>
<td>Pnma (No. 62), Z = 4</td>
<td>7.8401(12)</td>
<td>7.816(3)</td>
<td>7.7846(6)</td>
<td>7.773(3)</td>
<td>7.7638(5)</td>
<td>7.7638(5)</td>
<td>8073.5(7)</td>
<td>R$<em>{1}$ = 0.0179, R$</em>{1}$(all) = 0.0212</td>
<td></td>
</tr>
<tr>
<td>CeLiGe$_2$</td>
<td>292.24</td>
<td>−73 ± 2</td>
<td>Mo–Kα, 0.71073 Å</td>
<td>Pnma (No. 62), Z = 4</td>
<td>4.0061(6)</td>
<td>3.9721(15)</td>
<td>3.9509(3)</td>
<td>3.9361(14)</td>
<td>3.9014(3)</td>
<td>3.93730(3)</td>
<td>341.61(9)</td>
<td>339.3(2)</td>
<td>328.69(4)</td>
</tr>
<tr>
<td>PrLiGe$_2$</td>
<td>293.03</td>
<td>−73 ± 2</td>
<td>Mo–Kα, 0.71073 Å</td>
<td>Pnma (No. 62), Z = 4</td>
<td>10.8755(17)</td>
<td>10.757(4)</td>
<td>10.6680(7)</td>
<td>10.644(4)</td>
<td>10.5243(7)</td>
<td>11.0099(9)</td>
<td>341.61(9)</td>
<td>339.3(2)</td>
<td>328.69(4)</td>
</tr>
<tr>
<td>NdLiGe$_2$</td>
<td>296.36</td>
<td>−73 ± 2</td>
<td>Mo–Kα, 0.71073 Å</td>
<td>Pnma (No. 62), Z = 4</td>
<td>5.659</td>
<td>5.813</td>
<td>5.922</td>
<td>6.045</td>
<td>6.302</td>
<td>5.719</td>
<td>294.63</td>
<td>309.78</td>
<td>324.47</td>
</tr>
<tr>
<td>SmLiGe$_2$</td>
<td>302.47</td>
<td>−73 ± 2</td>
<td>Mo–Kα, 0.71073 Å</td>
<td>Pnma (No. 62), Z = 4</td>
<td>4.0361(6)</td>
<td>3.9217(15)</td>
<td>3.8914(3)</td>
<td>3.8631(14)</td>
<td>3.8214(3)</td>
<td>3.85730(3)</td>
<td>341.61(9)</td>
<td>339.3(2)</td>
<td>328.69(4)</td>
</tr>
<tr>
<td>EuLiGe$_2$</td>
<td>304.08</td>
<td>−73 ± 2</td>
<td>Mo–Kα, 0.71073 Å</td>
<td>Pnma (No. 62), Z = 4</td>
<td>7.8401(12)</td>
<td>7.816(3)</td>
<td>7.7846(6)</td>
<td>7.773(3)</td>
<td>7.7638(5)</td>
<td>7.7638(5)</td>
<td>8073.5(7)</td>
<td>R$<em>{1}$ = 0.0179, R$</em>{1}$(all) = 0.0212</td>
<td></td>
</tr>
</tbody>
</table>

The undertaken elaborate synthetic efforts confirm earlier work (via Table 1. Selected Crystal Data and Structure Refinement Parameters for $RE\text{LiGe}_2$ ($RE = \text{La–Nd, Sm, Eu}$)). The structure refinement parameters of the series are listed in Tables 1–3. CIFs are as follows: CSD-423561 for HT-LaGe (FeB structure type); CSD-4235555 for LaLiGe$_2$; CSD-4235565 for CeLiGe$_2$; CSD-4235577 for PrLiGe$_2$; CSD-4235588 for NdLiGe$_2$; and CSD-4235599 for EuLiGe$_2$. The crystal structures of several RE$_2$Ge$_2$ compounds have been deposited in the IUCr database (ICSD) appeared to have been inadequately established, were also reassessed as a part of this study; these details are provided as Supporting Information. The corresponding depository numbers are as follows: CSD-423561 for HT-LaGe (FeB structure type); CSD-423562 for LT-LaGe (LaSi structure type); CSD-423563 for EuGe; CSD-423564 for DyGe; CSD-423565 for ErGe; and CSD-423566 for TmGe, respectively.

### Magnetic Susceptibility Measurements

Field cooled (FC) and zero field cooled (ZFC) direct current ($dc$) magnetic susceptibility measurements were done by the subprogram XRCP in the SHELXTL software package. The structures were solved by direct methods and refined to convergence by full matrix least-squares methods. Refined parameters included the scale factors, the atomic positions, and anisotropic displacement parameters (excluding Li), and extinction coefficients (where applicable). The final difference Fourier maps in all six cases were featureless.

In the last refinement cycles, the atomic positions were standardized by employing the structure TIDY.24 Important crystallographic data, atomic positions, selected interatomic distances, and thermal parameters of the series are listed in Tables 1–3. CIFs have also been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de), depository numbers CSD-423555 for LaLiGe$_2$; CSD-4235565 for CeLiGe$_2$; CSD-4235577 for PrLiGe$_2$; CSD-4235588 for NdLiGe$_2$; and CSD-4235599 for SmLiGe$_2$ and CSD-4235600 for EuLiGe$_2$. The crystal structures of several RE$_2$Ge$_2$ compounds, which from a survey of the Inorganic Crystal Structure Database (ICSD) appeared to have been inadequately established, were also reassessed as a part of this study; these details are provided as Supporting Information. The corresponding depository numbers are as follows: CSD-423561 for HT-LaGe (FeB structure type); CSD-423562 for LT-LaGe (LaSi structure type); CSD-423563 for EuGe; CSD-423564 for DyGe; CSD-423565 for ErGe; and CSD-423566 for TmGe, respectively.

**Inorganic Chemistry**

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Table 3. Important Interatomic Distances (Å) for RELiGe2 (RE = La–Nd, Sm, Eu)

<table>
<thead>
<tr>
<th>atomic pair</th>
<th>distance</th>
<th>atomic pair</th>
<th>distance</th>
<th>atomic pair</th>
<th>distance</th>
<th>atomic pair</th>
<th>distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge1–Ge2 (x2)</td>
<td>2.5318(8)</td>
<td>Ge1–Ge2 (x2)</td>
<td>2.5180(10)</td>
<td>Ge1–Ge2 (x2)</td>
<td>2.5109(7)</td>
<td>Ge1–Ge2 (x2)</td>
<td>2.4986(5)</td>
</tr>
<tr>
<td>Li–Ge1</td>
<td>2.582(14)</td>
<td>Li–Ge1</td>
<td>2.563(13)</td>
<td>Li–Ge1</td>
<td>2.561(12)</td>
<td>Li–Ge1</td>
<td>2.531(10)</td>
</tr>
<tr>
<td>Li–Ge2</td>
<td>2.643(10)</td>
<td>Li–Ge2</td>
<td>2.632(13)</td>
<td>Li–Ge2</td>
<td>2.615(12)</td>
<td>Li–Ge2</td>
<td>2.606(6)</td>
</tr>
<tr>
<td>La–Ge1 (x2)</td>
<td>3.1335(8)</td>
<td>Ce–Ge1 (x2)</td>
<td>3.103(11)</td>
<td>Pr–Ge1 (x2)</td>
<td>3.0812(7)</td>
<td>Eu–Ge1 (x2)</td>
<td>3.0736(5)</td>
</tr>
<tr>
<td>La–Ge1 (x2)</td>
<td>3.245(8)</td>
<td>Ce–Ge1 (x2)</td>
<td>3.211(11)</td>
<td>Pr–Ge1 (x2)</td>
<td>3.1944(7)</td>
<td>Pr–Ge1 (x2)</td>
<td>3.183(5)</td>
</tr>
<tr>
<td>La–Ge2 (x2)</td>
<td>3.184(7)</td>
<td>Ce–Ge2 (x2)</td>
<td>3.1435(11)</td>
<td>Pr–Ge2</td>
<td>3.3180(6)</td>
<td>Pr–Pr (x2)</td>
<td>3.3240(8)</td>
</tr>
<tr>
<td>La–Ge2</td>
<td>3.2788(10)</td>
<td>Ce–Ge2</td>
<td>3.2548(15)</td>
<td>Pr–Pr (x2)</td>
<td>3.3909(3)</td>
<td>Pr–Pr (x2)</td>
<td>4.1199(5)</td>
</tr>
<tr>
<td>La–La (x2)</td>
<td>4.0061(6)</td>
<td>Ce–Ce (x2)</td>
<td>3.9721(15)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La–La (x2)</td>
<td>4.1661(7)</td>
<td>Ce–Ce (x2)</td>
<td>4.1389(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Relevant Parameters Derived from Linear Fits of the Inverse Susceptibility $\chi(T)^{-1}$ in the Range from 100–300 K for RELiGe2 (RE = La–Nd, Sm, Eu)

<table>
<thead>
<tr>
<th>compounds</th>
<th>magnetic ordering</th>
<th>$\mu_{\text{eff}}$ (μB)</th>
<th>$T_C$ (K)</th>
<th>$T_{\text{N}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaLiGe2</td>
<td>Pauli paramagnetic</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CeLiGe2</td>
<td>FM</td>
<td>2.54</td>
<td>2.78</td>
<td>15(1) 11(1)</td>
</tr>
<tr>
<td>PrLiGe2</td>
<td>FM</td>
<td>3.58</td>
<td>3.82</td>
<td>41(1) 18(1)</td>
</tr>
<tr>
<td>NdLiGe2</td>
<td>AFM</td>
<td>3.62</td>
<td>3.74</td>
<td>13(1) 13(1)</td>
</tr>
<tr>
<td>SmLiGe2</td>
<td>AFM</td>
<td>0.84</td>
<td>0.7</td>
<td>10(1) 5(1)</td>
</tr>
<tr>
<td>EuLiGe2</td>
<td>AFM</td>
<td>7.94</td>
<td>8.07</td>
<td>26(1)</td>
</tr>
</tbody>
</table>

The net effective moment for Sm3+ in SmLiGe2 is derived by a non-linear fit to the modified Curie–Weiss law.
were treated by the Löwdin downfolding technique; the Eu 4f wave functions were treated as core functions occupied by 7 electrons. This assigns the Eu atoms as formally Eu(II), which is consistent with the results of the magnetic susceptibility measurements. To evaluate various interatomic orbital interactions, the crystal orbital Hamilton populations (COHP) curves and the integrated COHP values (ICOHPs) were also calculated. The k-space integrations were conducted by the tetrahedron method, and the self-consistent charge density was obtained using 192 irreducible k-points in the Brillouin zone.

RESULTS AND DISCUSSION

Structure. The RELiGe₂ (RE = La–Nd, Sm, and Eu) phases have been identified previously from their powder X-ray diffraction patterns as crystallizing with the CaLiSi₂ structure type (space group Pnma; Pearson code oP 16). Our single-crystal work confirms this classification and for the first time provides accurate refinements of the atomic positions.

The structure, as seen in Figure 1, is not complicated, and can be readily described. The most prominent aspect of the structure is the zigzag \( \infty \) \([Ge₂]\) chain. These 1-D polyanions propagate parallel to the crystallographic \( b \)-axis and are linked together via chains of edge-shared LiGe₄ tetrahedra, also running in the same direction. Emphasizing the covalency of the Li–Ge bonding, the structure can also be rationalized as a polyanionic \( \infty \) \([LiGe₂]\) network, with rare-earth metal cations residing in the channels within it.

Besides the title RELiGe₂ (RE = La–Nd, Sm, Eu) compounds and YbLiGe₂, other rare-earth metal lithium germanides with similar formula exist, such as EuLi₀.₉In₀.₁Ge₂. However, the topology of the \( \infty \) \([Ge₂]\) chains in the structures in question is different: the former structure has chains with zigzag connectivity (i.e., Ge–Ge bonds alternating in trans-fashion), while the latter boasts a repeating unit of both the cis- and trans-conformations. The similarities and the differences between the two arrangements can be explained once their close connection to some other known structures is realized (Figure 2). More specifically, as described by us in a recent paper, the “1-1-2” phases can be considered as derivatives of the hypothetical REGe₂ compounds (AlB₂ structure type). This idea is schematically represented in Figure 2, where the honeycomb \( \infty \) \([Ge₂]\) layers in the parent AlB₂-type structure are “cut” to either zigzag (trans–trans) or cis–trans \( \infty \) \([Ge₂]\) chains by cleaving selected Ge–Ge bonds. This imaginary process can account for the polymorphic structures of the monogermanides REGe (FeB, CrB, or LaSi structure types). In the next step, a “substitution” of 1/2 of

Figure 1. (a) Combined polyhedral and ball-and-stick representations of the orthorhombic structure of RELiGe₂ (RE = La–Nd, Sm, and Eu). The unit cell is outlined. The RE atoms are shown as dark-red spheres, and the Ge atoms are drawn as blue spheres. The Li atoms (in yellow) are shown as the centers of translucent LiGe₄ tetrahedra or as yellow spheres connected to four neighboring Ge atoms. The \( \infty \) \([Ge₂]\) chains are emphasized. (b) Expanded view of the \( \infty \) \([Ge₂]\) chains and the edge-sharing mode of the LiGe₄ tetrahedra. (c) Expanded view of the coordination polyhedron of the RE atoms.

Figure 2. Schematic representation of the structural relationship between the hypothetical REGe₂ (RE = La–Nd, Sm and Eu) compounds with the AlB₂ structure type and the corresponding REGe monogermanides (FeB, CrB, or LaSi structure types). A formal substitution of 1/2 of the RE atoms in the latter structures with Li yields two different RELiGe₂ structures, with different \( \infty \) \([Ge₂]\) chains, either with zigzag connectivity (i.e., Ge–Ge bonds alternating in trans-fashion) or with a repeating unit of both the cis- and trans-conformations. See text for details.
The rare-earth metals atoms with Li in the structure of each monogermaine yields the two different "1-1-2" structures.

The topological relation of the structure of \( \text{RELiGe}_2 \) (\( \text{RE} = \text{La} \text{Nd}, \text{Sm}, \text{and} \text{Eu} \)) to that of the \( \text{REGe} \) phases (\( \text{RE} = \text{La} \text{P} \))\(^{32}\) crystallizing with the FeB structure type is useful to note and is schematically presented in Figure 3. The same illustration also shows that the \( \text{RELiGe}_2 \) compounds can be considered as close relatives of the hypothetical \( \text{RELiGe} \) germanides with the TiNiSi structure type\(^{32}\) (aka SrMgSi): a simple "insertion" of another germanium atom and an appropriate resizing of the unit cell accounts for the above-mentioned polyanionic \( \infty \) [Li12] network. Notably, the three depicted structures share not only the same arrangement of rare-earth metal atoms, but the same symmetry as well (Pnma).

The analogy with the FeB structure type can be used to rationalize the inability to extend the \( \text{RELiGe}_2 \) series beyond Eu (see Experimental Section). It is known that the FeB structure type is common among the early rare-earth metals, whereas the late rare-earth metals form \( \text{REGe} \) with the CrB structure type, with polymorphic transitions between the two for the middle rare-earth metals. Indeed, we observe that as the atomic radius of the rare-earth metals increases, the \( \text{RELiGe}_2 \) phases form with polymorphic transitions between the two for the middle rare-earth metals (see Table 1). These changes in the unit cell constants correlate with the refined Ge–Ge distances in the \( \text{RELiGe}_2 \) structure type, which show a gradual decrease from 2.5318(8) Å for \( \text{LaLiGe}_2 \) to 2.4986(5) Å for \( \text{SmLiGe}_2 \), and 2.4067(3) Å for \( \text{EuLiGe}_2 \) and \( \text{SmLiGe}_2 \), respectively (Table 3). The corresponding Ge–Ge–Ge angles decrease as well from 104.58(3)° to 102.67(3)° for \( \text{LaLiGe}_2 \) and \( \text{SmLiGe}_2 \), respectively.

The unit cell volume for \( \text{EuLiGe}_2 \) is larger than the rest because of the existence of europium as \( \text{Eu}^{(II)} \), which results in the enlarged atomic radius (\( r_{\text{Eu}} = 1.85 \) Å).\(^{33}\) However, the increased unit cell volume does not correspond to a longer Ge–Ge distance, as one could expect if the trends were followed. In fact, the Ge–Ge distance in \( \text{EuLiGe}_2 \) is the shortest of all, 2.4948(5) Å. Such bond length compares well with those reported for other compounds with polyene-like \( \infty \) [Ge1.5] chains, such as \( \alpha \)-SrLiGe\(_6\),\(^{12}\) EuLiGe\(_6\),\(^{13}\) \( \text{A}_2(\text{Li}_{0.8} \text{Mg}_{0.2})_4\text{Ge}_3 \) (A = Sr, Eu),\(^{14}\) \( \text{AlLiGe}_2 \) (A = Sr, Ba),\(^{15}\) and \( \text{AlLi}_{4-x}\text{Ne}_2 \text{Ge}_2 \) and \( \text{Al}_{2}(\text{Li}_{0.8} \text{In}_{0.2})_4\text{Ge}_3 \) (A = Sr, Ba, Eu).\(^{9}\) In all of the above cases, the Ge–Ge bonds in the chains are slightly shorter than what can be considered 2-center 2-electron Ge–Ge bonds. Some examples here include the Ge–Ge bonding in the puckered layers in \( \text{CaGe}_2 \) (\( d_{\text{Ge–Ge}} = 2.5417(7) \) Å),\(^{3} \) and \( \text{EuGe}_2 \) (\( d_{\text{Ge–Ge}} = 2.564(4) \) Å),\(^{34}\) in the \([\text{Ge}]_2\) clusters in \( \text{BaGe}_2 \) and \( \text{K}_2\text{Ge}_4 \) (average \( d_{\text{Ge–Ge}} = 2.55–2.56 \) Å),\(^{35}\) and in the \([\text{Ge}]_2\) dumbbells in \( \text{Ca}_3\text{Ge}_3 \) (\( d_{\text{Ge–Ge}} = 2.575(1) \) Å),\(^{36}\) among many others.

We must also note that similar zigzag \( \infty \) [Ge1.5] chains are present in all \( \text{REGe} \) phases (either FeB or CrB-type structures). However, the structures of many monogermanides appear inadequately studied and the published crystallographic data cannot be deemed reliable by today’s standards. For example, we repeated the synthesis of the \( \text{LaGe} \) HT-polymorph (FeB-type), and refined its structure; the hereby determined Ge–Ge distances in \( \text{EuLiGe}_2 \) is the shortest of all, Ge–Ge distances in the corresponding \( \text{REGe} \) phases (viz., EuGe2, \( d_{\text{Ge–Ge}} = 2.5417(7) \) Å, not 2.509 Å as in the literature).\(^{3} \) Large discrepancies were also found for \( \text{DyGe} \) (\( d_{\text{Ge–Ge}} = 2.56(4) \) Å, instead of the published 2.546 Å),\(^{31}\) and \( \text{EuGe}_2 \) (\( d_{\text{Ge–Ge}} = 2.639(3) \) Å instead of the published 2.571 Å).\(^{3} \) For detailed crystallographic data on \( \text{REGe} \), we refer the reader to the Supporting Information section. Because of these problems, a direct comparison of the structural trends among the monogermanides and the title compounds is hampered, although apparent correlations do exist. Most notably, it is clear that the refined Ge–Ge distances in all \( \text{RELiGe}_2 \) are significantly shorter than the Ge–Ge distances in the corresponding \( \text{REGe} \) monogermanides. These nuances of the Ge–Ge bonding are further discussed below and in the electronic calculation section.

The apparent contraction of the Ge–Ge bonds in \( \text{RELiGe}_2 \) versus \( \text{REGe} \) (\( =\text{RE}_2\text{Ge}_2 \)) series indicate an electronic effect at play here since the structural features in both families are subtly influenced by the available valence electrons. The simplest approach toward the electron count, the Zintl–Klemm formalism,\(^{37}\) calls for a formulation \([\text{RE}^3\text{Li}^+]\text{[Ge}^{2-}\text{]}\)\(_2\), where each 2-bonded Ge atom in the zigzag chain is assigned a formal charge 2− to satisfy the octet rule. Such an electron count is just like in \( \text{CaGe} \) (e.g., \( \text{Ca}^{2+} \text{Ge}^{-2} \)),\(^{38}\) and \( \text{EuGe} \) (e.g., \( \text{Eu}^{2+} \text{Ge}^{-2} \)).\(^{39}\) However, the formal electron count for the remaining \( \text{REGe} \) phases with \( \text{RE}^{3+} \) cations yields a more reduced germanium state (viz., \( \text{RE}^{2+} \text{Ge}^{-4} \)) series. In contrast, \( \text{EuLiGe}_2 \) with \( \text{Eu}^{2+} \) instead of \( \text{Eu}^{3+} \) will require a formulation \([\text{Eu}^{2+}\text{Li}^+]\text{[Ge}^{13-}\text{]}\)\(_2\) (also valid in the cases of \( \text{CaLiGe}_2 \) and \( \text{YbLiGe}_2 \)), that is, a partial double bond character of the Ge–Ge interactions and some conjugation of the Ge \( \pi \) orbitals along the chain must be considered. The shortest Ge–Ge distance in \( \text{EuLiGe}_2 \) is isostructural (but not isoelectronic) to the \( \text{RELiGe}_2 \) compounds containing trivalent cations was already noted; another example confirming this line of thinking is the fact that \( \text{CaLiGe}_2 \) (formally \( \text{Ca}^{2+}\text{[Li}^+]\text{[Ge}^{13-}\text{]}\)\(_2\))\(^{19}\) and \( \text{YbLiGe}_2 \) (formally \( \text{Yb}^{2+}\text{[Li}^+]\text{[Ge}^{13-}\text{]}\)\(_2\))\(^{20}\) also have very short Ge–Ge bonds of 2.490(2) Å and 2.476(2) Å, respectively. Comparing those to \( \text{LaLiGe}_2 \) (\( d_{\text{Ge–Ge}} = 2.5318(8) \) Å, formally \( \text{La}^{3+}\text{[Li}^+]\text{[Ge}^{15-}\text{]}\)\(_2\)), \( \text{CaMgGe}_2 \) (\( d_{\text{Ge–Ge}} = 2.518(1) \) Å, formally \( \text{Mg}^{2+}\text{[Li}^+]\text{[Ge}^{15-}\text{]}\)\(_2\)), and \( \text{CeLiGe}_2 \) (\( d_{\text{Ge–Ge}} = 2.518(1) \) Å, formally \( \text{Ce}^{3+}\text{[Li}^+]\text{[Ge}^{15-}\text{]}\)\(_2\)) is instructive since the corresponding Pauling single-bond radii are very close and "size" effects could be ruled out: \( r_{\text{Ca}} = 1.74 \) Å, \( r_{\text{Mg}} = 1.70 \) Å, \( r_{\text{La}} = 1.69 \) Å, and \( r_{\text{Ce}} = 1.65 \) Å.\(^{33}\) The "special" role of lithium in these structures must be briefly discussed too. As mentioned already, here and in some
earlier publications,\textsuperscript{9,10,12–14} the Li atoms can be regarded as both donors of valence electrons to the germanium chains, that is, as cations, and as participants in covalent interactions within the polyanionic $\infty$ [LiGe$_2$] network (the structural relationship to TiNiSi structure type; see Figure 3). A closer look at the coordination environment of the Li atoms supports both notions: Li atoms are found in distorted tetrahedra of Ge atoms at distances in the range 2.531(10)–2.697(9) Å. Each Li-centered tetrahedron is edge-shared with two neighboring tetrahedra, forming double-tetrahedral chains (Figure 1 and Figure 3). They propagate parallel to the c-axis and are further connected to four neighboring units (in the ab-plane) via zigzag Ge chains. The reported distances are slightly longer than the sum of the Pauling’s single-bond radii ($r_{Li} = 1.225$ Å; $r_{Ge} = 1.242$ Å),\textsuperscript{33} and compare well with those reported for other lithium germanides, such as Eu$_2$LiGe$_3$,\textsuperscript{13} A$_x$(Li$_{1-x}$Mg)$_2$Ge$_3$ ($A = Sr, Eu; x \approx 0.5$),\textsuperscript{14} and AlLiGe$_2$ ($A = Sr, Ba$).\textsuperscript{15} Ce$_2$Li$_x$Ge$_y$,\textsuperscript{16} and AlLi$_x$In$_{1-x}$Ge$_2$ ($0 \leq x \leq 0.1$) and A$_2$(Li$_{1-x}$In$_x$)$_2$Ge$_3$ ($x \approx 0.3$) ($A = Sr, Ba, Eu$).\textsuperscript{9} The shortest Li–RE distances are greater than 3.5 Å.

The larger lanthanide atoms reside in the “channels” of the $\infty$ [LiGe$_2$] network and are surrounded by nine Ge atoms located on three neighboring 1-D zigzag chains (Figure 1c). Such coordination polyhedron can be described as a trigonal prism formed by six Ge atoms located within less than 3.25 Å around the central atom, and three additional Ge atoms at distances of 3.28 to 3.42 Å, located in capping positions. The closest RE–RE contacts are on the order of 3.9–4.2 Å, much longer than the corresponding RE–RE contacts in the elemental crystal structures.\textsuperscript{29}

**Electronic Structure.** To access the electronic band structures and to investigate the chemical interactions influencing the structural stability and physical properties of the compounds of the RELiGe$_2$ series, TB-LMTO-ASA band structure calculations were carried out using local density approximation (LDA) on two observed and one hypothetical structure. In particular, two refined structures, that of LaLiGe$_2$ and EuLiGe$_2$, were used for the calculations of the 12 valence electron (ve) system with trivalent cations (La–Sm) and the 11 ve system with divalent cations (Ca, Eu, and Yb), respectively. In addition, a model structure of EuLiGe$_2$ adopting the BaLi$_x$Mg$_{0.5}$Si$_2$-type structure was also taken in consideration to compare the energetic stability of the cis–trans versus trans–cis $\infty$ [Ge$_2$] chains for systems with identical spatial and electronic characteristics. The results of these studies are presented with the corresponding density of states (DOS) and COHP curves; an analysis of the integrated crystal orbital Hamilton population (COHP) values is discussed as well.

Figure 4(a) shows DOS and COHP curves of LaLiGe$_2$. Overall total DOS (TDOS) displays significant mixing among valence orbitals of La, Li, and Ge, and the largest partial DOS (PDOS) contribution, of course, comes from Ge atoms because of the largest molar ratio in the given composition. Two deep pseudogaps are observed: one is almost at the Fermi level ($E_F$), which corresponds to 12 ve$^-$, and the other one is at about 0.4 eV below $E_F$, corresponding to 11.5 ve$^-$. The region below $E_F$ is mostly composed of contributions from Ge and Li, whereas the region above $E_F$ consists of mostly La 5d orbital contributions with some small admixture with Li and Ge. The occupied states below $E_F$ can be divided into three segments: (1) a bonding valence band of 2s of Li and 4s of Ge between about 9.5 and 11 eV below $E_F$; (2) a bonding and an antibonding valence band of 4p of Ge together with a bonding valence band of 2s of Li between 6 and 8.5 below $E_F$; and (3) a bonding valence band of 2s of Li, 4p of Ge, and 5d of La between about 0 and 4.5 eV below $E_F$. The Li PDOS displays a considerable participation in covalent interactions within the polyanionic $\infty$ [LiGe$_2$] network using 2s orbitals, providing additional evidence for the unique role the Li atoms play in the bonding, as already discussed.

TDOS and PDOS plots (Figure 4b) of EuLiGe$_2$ are similar, overall, to those of LaLiGe$_2$, including valence orbital mixing of Eu, Li, and Ge throughout all energy levels. However, unlike the system involving a trivalent rare-earth metal, which locates $E_F$ at the pseudogap, $E_F$ of EuLiGe$_2$ corresponding to 11 ve$^-$ is situated about 0.5 eV below a deep local minimum. In addition, TDOS at $E_F$ is relatively high. One could surmise that spin polarization and differences between the majority and minority spins cause an “anomaly”, but the corresponding spin-polarized
The antibonding character of the Ge–Ge bonds in both LaLiGe₂ and EuLiGe₂ is fully compensated by the relatively strong La–Ge1(Ge2) and Eu–Ge1(Ge2) bonding, which results in overall energetically favorable structures. The COHP curves for the Li–Ge1(Ge2) interactions show they are weaker than the Ge–Ge bonds and exhibit nearly nonbonding character in the proximity of the E_F.

**Magnetic Susceptibilities.** The temperature dependence of the molar magnetic susceptibilities ($\chi_m = M/H$) of all RELiGe₂ ($RE = Ce–Nd, Sm and Eu$) samples are presented in Figure 5. In all cases, polycrystalline specimens were used and $M$ was measured between 300 and 1.8 K in field cooling mode; a comparison of the temperature dependent magnetization data in field cooled (FC) and zero field cooled (ZFC) is provided as Supporting Information.

As seen from the figure, in the high temperature regime, CeLiGe₂, PrLiGe₂, NdLiGe₂, and SmLiGe₂ display paramagnetic behavior that follows the Curie–Weiss law $\chi(T) = C/(T - \theta_p)$, where $C$ is the Curie constant ($N_A \mu_B^2 / 3k_B T$) and $\theta_p$ is the Weiss temperature. The calculated effective magnetic moments (Table 4) are close to the theoretical values of $RE^{3+}$ ($RE = Ce–Nd$), as expected, which indicates magnetic ground states from 4f-electron origin. A Pauli-like paramagnetic ground state exists for LaLiGe₂ since the La³⁺ ion has no 4f electrons. The SmLiGe₂ specimen shows typical Van Vleck paramagnetism in the high temperature range; in this instance, the significant contribution of the temperature independent term ($\chi_0$) to the molar susceptibility requires a nonlinear fit to the modified Curie–Weiss law $\chi_m(T) = \chi_0 + C/(T - \theta_p)$, to calculate the effective moment for Sm³⁺. The effective moment determined for the EuLiGe₂ sample (8.07 $\mu_B$) is on par with the free-ion value for Eu²⁺ (7.94 $\mu_B$), corroborating the earlier discussions on the crystal and electronic structure.

In the low temperature regime, all compounds in this series (excluding LaLiGe₂) undergo magnetic ordering; both CeLiGe₂ and PrLiGe₂ enter into ferromagnetic states (FM) with $T_C$ of
about 11 and 18 K, respectively. The data on NdLiGe$_2$ show a clear cusp-like feature in both the FC and ZFC magnetization curves, which indicate the onset of antiferromagnetic ordering (AFM) with Ne"el temperature ($T_N$) of about 13 K. Below $T_N$, the susceptibility rises again, hinting at the possibility for a second transition, likely of a ferromagnetic type occurring at about 9 K. The positive Weiss constant of NdLiGe$_2$ (Table 4) also suggests ferromagnetic ordering. The behavior of SmLiGe$_2$ in the low temperature regime is also complicated: from the FC data it appears that the unpaired electrons of the Sm$^{3+}$ ions align in a ferromagnetic fashion with $T_N$ of about 22 K. However, the ZFC data reveal a peak at about 5 K, which is reminiscent of an antiferromagnetically ordered state, followed by a small jump of the susceptibility at $T_C$. The origin of these transitions is not fully understood yet. $\chi_m(T)$ of EuLiGe$_2$ indicates a straightforward antiferromagnet with a Ne"el temperature of about 26 K.

Comparing the magnetic ordering in this series with the closely related REGe monogermanides shows that the early ones (REGe, RE = Pr, Nd) are ordered ferromagnetically, while for the mid-to-late ones (REGe, RE = Tb–Tm), the magnetic ground state is antiferromagnetic. The magnetism in these compounds has been explained by the electrons-mediated coupling (RKKY theory) and the monotonically decreased distance between the RE metal atoms on moving across the series.

**ASSOCIATED CONTENT**

5 Supporting Information

A combined X-ray crystallographic file in CIF format, along with details on the reaccessed crystal structures of some REGe monogermanides; details on the electronic structure calculations of EuLiGe$_2$ with the BaLi$_2$Mg$_2$Si$_2$-structure type; results from spin-polarized calculations; table with integrated data it appears that the unpaired electrons of the Sm$^{3+}$ ions ($\chi(T)$ for RELiGe$_2$ ($RE =$ Ce–Nd, Sm and Eu) measured on FC and ZFC modes; a representative powder X-ray diffraction pattern matched with the calculated one. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**


(18) Pavlyuk, V. V.; Pecharskii, V. K.; Bodak, O. I.; Bruvskov, V. A.*Kristallografiya* 1988, 33, 46–50.


(20) SMART, NT; version 5.63; Bruker Analytical X-ray Systems, Madison, WI, 2003.


(22) SADABS; NT; version 2.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.


(42) The magnetic response for PrLiGe₂ in the ZFC measurement (Supporting Information), shows a cusp-like feature, which might suggest possible antiferromagnetic correlations in this compound as well.