

Synthesis, Structure, Chemical Bonding, and Magnetism of the Series $RELiGe_2$ ($RE = La-Nd, Sm, Eu$)Svilen Bobev,* Tae-Soo You,[†] and Nian-Tzu Suen

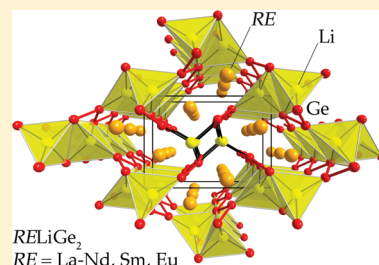
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S Supporting Information

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 $RELiGe_2$ ($RE = La-Nd, Sm, \text{ and } Eu$). The structures of these compounds have been established by single-crystal X-ray diffraction ($CaLiSi_2$ structure type, space group $Pnma$, $Z = 4$, Pearson symbol $oP16$). The chemical bonding within this atomic arrangement can be rationalized in terms of anionic germanium zigzag chains, conjoined via chains of edge-shared $LiGe_4$ tetrahedra and separated by rare-earth metal cations. The structure can also be viewed as an intergrowth of AlB_2 -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 $LaLiGe_2$ and $SmLiGe_2$, the remaining four $RELiGe_2$ phases exhibit Curie–Weiss paramagnetism above about 50 K. In the low temperature regime, the localized 4f electrons in $CeLiGe_2$, $PrLiGe_2$, and $SmLiGe_2$ order ferromagnetically, while antiferromagnetic ordering is observed for $NdLiGe_2$ and $EuLiGe_2$. The calculated effective magnetic moments confirm RE^{3+} ground states in all cases excluding $EuLiGe_2$, in which the magnetic response is consistent with Eu^{2+} 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.^{1–11} In addition to some relatively simple binaries,^{2,4,5} examples with more intricate bonding include the ternary RE_2InGe_2 ,¹ and $RE_{5-x}Mg_xGe_4$ ($1 \leq x \leq 2.3$) phases ($RE = \text{rare-earth metal}$),⁷ RE_2MgGe_2 ,¹¹ the homologous series $A_{2[n+m]}In_{2n+m}Ge_{2[n+m]}$ ($A = Ca, Sr, Eu, \text{ and } Yb$),⁸ $(Sr_{1-x}Ca_x)_5In_3Ge_6/(Eu_{1-x}Yb_x)_5In_3Ge_6$ ($x \approx 0.7$) and $(Sr_{1-x}Ca_x)_3In_2Ge_4/(Sr_{1-x}Yb_x)_3In_2Ge_4$ ($0.4 \leq x \leq 0.5$),¹⁰ among others. The Ge atoms in most of these structures are either dimerized into Ge dumbbells (formally $[Ge_2]^{6-}$) or “polymerized” into one-dimensional (1-D) chains (formally $^{1}_{\infty}[Ge_2]^{q-}$); the latter being an alternation of cis- and trans-Ge–Ge bonds with partial π -delocalization of the Ge 4p-orbitals (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 - Sr_2LiGe_3 ,¹² Eu_2LiGe_3 ,¹³ $A_2(Li_{1-x}Mg_x)_2Ge_3$ ($A = Sr, Eu; x \approx 0.5$),¹⁴ $ALiGe_2$ ($A = Sr, Ba$),¹⁵ $RELiGe_2$ ($RE = La-Nd, Sm, \text{ and } Eu$),¹⁶ 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 $ALi_{1-x}In_xGe_2$ ($0 \leq x \leq 0.1$) and $A_2(Li_{1-x}In_x)_2Ge_3$ ($x \approx 0.3$)

phases ($A = Sr, Ba, Eu$)⁹ 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 $RELiGe_2$ ($RE = La-Nd, Sm, \text{ and } Eu$) 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-ampoules. 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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Table 1. Selected Crystal Data and Structure Refinement Parameters for RELiGe₂ (RE = La–Nd, Sm, Eu)

formula	LaLiGe ₂	CeLiGe ₂	PrLiGe ₂	NdLiGe ₂	SmLiGe ₂	EuLiGe ₂
fw/g·mol ^{−1}	291.03	292.24	293.03	296.36	302.47	304.08
T/ °C				−73 ± 2		
radiation, wavelength				Mo–Kα, 0.71073 Å		
space group				Pnma (No. 62); Z = 4		
unit cell dimensions						
a/ Å	7.8401(12)	7.816(3)	7.7846(6)	7.773(3)	7.7638(5)	8.0735(7)
b/ Å	4.0061(6)	3.9721(15)	3.9509(3)	3.9361(14)	3.9014(3)	3.9730(3)
c/ Å	10.8755(17)	10.757(4)	10.6870(8)	10.644(4)	10.5243(7)	11.0099(9)
V/ Å ³	341.61(9)	333.9(2)	328.69(4)	325.6(2)	318.78(4)	352.5(3)
ρ _{calc} / g·cm ^{−3}	5.659	5.813	5.922	6.045	6.302	5.719
μ _{Mo Kα} / cm ^{−1}	294.63	309.78	324.47	337.3	365.93	341.63
final R indices ^a [I > 2σ(I)]	R ₁ = 0.0179	R ₁ = 0.0212	R ₁ = 0.0176	R ₁ = 0.0142	R ₁ = 0.0144	R ₁ = 0.0141
	wR ₂ = 0.0402	wR ₂ = 0.0453	wR ₂ = 0.0383	wR ₂ = 0.0345	wR ₂ = 0.0327	wR ₂ = 0.0295
final R indices ^a [all data]	R ₁ = 0.0220	R ₁ = 0.0249	R ₁ = 0.0197	R ₁ = 0.0148	R ₁ = 0.0153	R ₁ = 0.0129
	wR ₂ = 0.0413	wR ₂ = 0.0477	wR ₂ = 0.0390	wR ₂ = 0.0349	wR ₂ = 0.0331	wR ₂ = 0.0291
largest diff. peak and hole/ e [−] Å ^{−3}	1.002, −1.025	0.994, −1.037	1.007, −0.975	0.626, −0.745	0.732, −1.232	1.053, −0.678

^aR₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR₂ = $[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]^{1/2}$, and $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, $P = (F_o^2 + 2F_c^2)/3$; A and B are weight coefficients.

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.¹⁷ 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 containing La and Ce produced the purest products when they were slowly cooled down to 600 °C (rate of 10 °C/h) and then brought to room temperature by turning the furnace off. Under the same conditions the reactions containing Pr, Nd, and Eu generated mixtures of the “1-1-2” and the “2-2-3” phase (Ce₂Li₂Ge₃ structure type)¹⁸ with a small amount of elemental Ge remaining. The targeted “1-1-2” phase was obtained as single-phase material when the slow cooling step was extended to 300 °C. For all reactions, no additional annealing procedure was needed to improve crystallinity. All products appeared to be stable upon exposure to air and moisture for at least three weeks.

The undertaken elaborate synthetic efforts confirm earlier work (via arc-melting)¹⁶ that the RELiGe₂ series spans only the early/mid-early rare-earth metals La, Ce, Pr, Nd, and Sm (as well as the nominally divalent Eu and Yb). From the alkaline-earth metals, only Ca forms a compound with this structure,¹⁹ which suggests that the metal's atomic size is the decisive factor for the realization of this structure.

Caution! Mixtures of the above-discussed elements heated in Nb tubes to 1000 °C and higher temperatures could be dangerous. At these conditions, Nb and Ge could react, causing Li vapors (and molten metals) to leak into the silica tubes. Therefore, the latter must be made sufficiently long, so that one of the ends can be left protruding outside the furnace. In this way, should a leak occur, a condensation at the end of the silica tube would indicate that the furnace must be stopped immediately.

Crystal Structure Determination. All six compounds were characterized by both powder and single crystal X-ray diffraction. X-ray powder diffraction patterns were collected on a Rigaku MiniFlex powder diffractometer using Cu Kα radiation. The diffractometer was operated at room temperature. The data were gathered in θ – θ scans with a step size of 0.05° in the range of 10° ≤ 2θ ≤ 85° (rate 10 s/step). JADE 6.5 was used for data analysis, which indicated that the observed peaks' positions and intensities were in very good agreement with the simulated patterns.

Single-crystal X-ray diffraction experiments were carried out on a Bruker SMART CCD-based diffractometer. The diffractometer was operated at 200 K, attained through evaporating liquid nitrogen.

Monochromated Mo Kα₁ radiation (λ = 0.71073 Å) was used, and data collections were handled in batch runs at different ω and φ angles. Many crystals from each sample were selected and checked by rapid scans before the best ones were found. For the crystals chosen for further analysis, full spheres of intensity data were gathered in batch runs with frame width of 0.3° in ω and θ and data acquisition rate of 10 s/frame. The automated process was controlled by the Bruker SMART software;²⁰ the SAINT program²¹ was used for raw data reduction and extraction of the observed structure factors. Semi-empirical absorption correction based on equivalents was applied using SADABS.²² Intensity statistics and space group determination were done by the subprogram XPREP in the SHELXTL software package.²³ Subsequently, the structures were solved by direct methods and refined to convergence by full matrix least-squares methods on F². Refined parameters included the scale factors, the atomic positions with 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 STRUCTURE TIDY.²⁴ Important crystallographic data, atomic positions, selected interatomic distances, and thermal displacement 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 LaLiGe₂; CSD-423556 for CeLiGe₂; CSD-423557 for PrLiGe₂; CSD-423558 for NdLiGe₂; CSD-423559 for SmLiGe₂; and CSD-423560 for EuLiGe₂. The crystal structures of several REGe monogermanides, 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 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 carried out using either a Physical Property Measurement System (PPMS) or Magnetic Property Measurement System (MPMS) SQUID magnetometer, both by Quantum Design. The measurements were performed in the interval from 2 to 300 K in an applied magnetic field (H) of 100, 500, 1000, or 10000 Oe. The samples (typically 40–100 mg) were loaded in gel caps wrapped with Kapton tape. To ensure reproducibility, specimens from at least two

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (U_{eq}^a) for $RE\text{LiGe}_2$ ($RE = \text{La} - \text{Nd}, \text{Sm}, \text{Eu}$)

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
LaLiGe ₂					
La	4c	0.1412(1)	1/4	0.3664(1)	0.007(1)
Li	4c	0.4953(16)	1/4	0.6141(10)	0.016(3)
Ge1	4c	0.1590(1)	1/4	0.6811(1)	0.008(1)
Ge2	4c	0.2174(1)	1/4	0.0700(1)	0.008(1)
CeLiGe ₂					
Ce	4c	0.1405(1)	1/4	0.3656(1)	0.007(1)
Li	4c	0.4928(16)	1/4	0.6106(12)	0.007(3)
Ge1	4c	0.1571(1)	1/4	0.6828(1)	0.008(1)
Ge2	4c	0.2218(1)	1/4	0.0689(1)	0.009(1)
PrLiGe ₂					
Pr	4c	0.1406(1)	1/4	0.3653(1)	0.006(1)
Li	4c	0.4924(14)	1/4	0.6092(10)	0.011(2)
Ge1	4c	0.1558(1)	1/4	0.6832(1)	0.007(1)
Ge2	4c	0.2232(1)	1/4	0.0682(1)	0.007(1)
NdLiGe ₂					
Nd	4c	0.1403(1)	1/4	0.3651(1)	0.006(1)
Li	4c	0.4916(11)	1/4	0.6097(8)	0.011(2)
Ge1	4c	0.1547(1)	1/4	0.6838(1)	0.006(1)
Ge2	4c	0.2243(1)	1/4	0.0673(1)	0.007(1)
SmLiGe ₂					
Sm	4c	0.1394(3)	1/4	0.3642(1)	0.008(1)
Li	4c	0.4876(12)	1/4	0.6076(9)	0.013(2)
Ge1	4c	0.1530(1)	1/4	0.6852(1)	0.009(1)
Ge2	4c	0.2277(1)	1/4	0.0658(1)	0.009(1)
EuLiGe ₂					
Eu	4c	0.1358(1)	1/4	0.3658(1)	0.009(1)
Li	4c	0.4973(12)	1/4	0.6130(8)	0.018(2)
Ge1	4c	0.1659(1)	1/4	0.6776(1)	0.009(1)
Ge2	4c	0.2244(1)	1/4	0.0666(1)	0.009(1)

^a U_{ij} is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

different reaction batches were measured. The derived net effective moments are listed in Table 4.

Table 4. Relevant Parameters Derived from Linear Fits of the Inverse Susceptibility $\chi(T)^{-1}$ in the Range from 100–300 K for $RE\text{LiGe}_2$ ($RE = \text{La} - \text{Nd}, \text{Sm}, \text{Eu}$)

compounds	magnetic ordering	$[J(J+1)]^{1/2}$	$\mu_{\text{eff}} (\mu_B)$	θ_p (K)	T_C (K)	T_N (K)
LaLiGe ₂	Pauli paramagnetic	0	0			
CeLiGe ₂	FM	2.54	2.78	15(1)	11(1)	
PrLiGe ₂	FM	3.58	3.82	41(1)	18(1)	
NdLiGe ₂	AFM	3.62	3.74	13(1)	9(1)	13(1)
SmLiGe ₂ ^a	FM	0.84	0.7	10(1)	22(1)	5(1)
EuLiGe ₂	AFM	7.94	8.07	−4(1)		26(1)

^aThe net effective moment for Sm^{3+} in SmLiGe_2 is derived by a non-linear fit to the modified Curie–Weiss law.

Computational Details. Tight-binding, linear muffin-tin orbital (TB-LMTO) calculations were carried out in the atomic sphere approximation (ASA) using the LMTO47 program.²⁵ Exchange and correlation were treated by the local density approximation (LDA).²⁶ All relativistic effects except spin–orbit coupling were taken into account by using a scalar relativistic approximation. In the ASA method, space is filled with overlapping Wigner–Seitz (WS) atomic spheres.²⁷ The symmetry of the potential is considered spherical inside each WS sphere, and a combined correction is used to take into account the overlapping part. The radii of WS spheres were obtained by requiring that the overlapping potential be the best possible approximation to the full potential, and were determined by an automatic procedure. This overlap should not be too large because the error in kinetic energy introduced by the combined correction is proportional to the fourth power of the relative sphere overlap. No empty spheres were used. The WS radii are as follows: for LaLiGe_2 , La = 2.18 Å, Ge1 = 1.48 Å, Ge2 = 1.48 Å, and Li = 1.52 Å; for EuLiGe_2 , Eu = 2.23 Å, Ge1 = 1.44 Å, Ge2 = 1.44 Å, and Li = 1.59 Å. The basis sets included 6s, 6p, 5d, and 4f orbitals for La; 6s, 6p, 5d, and 6f orbitals for Eu; 4s, 4p, and 4d orbitals for Ge; and 2s, 2p, and 3d orbitals for Li. The La 6p, Eu 6p, Ge 4d, and Li 2p and 3d orbitals

Table 3. Important Interatomic Distances (Å) for $RE\text{LiGe}_2$ ($RE = \text{La} - \text{Nd}, \text{Sm}, \text{Eu}$)

LaLiGe ₂		CeLiGe ₂		PrLiGe ₂	
atomic pair	distance	atomic pair	distance	atomic pair	distance
Ge1–Ge2 (×2)	2.5318(8)	Ge1–Ge2 (×2)	2.5180(10)	Ge1–Ge2 (×2)	2.5109(7)
Li–Ge1	2.582(14)	Li–Ge1	2.563(13)	Li–Ge1	2.561(12)
Li–Ge2	2.643(10)	Li–Ge2	2.632(13)	Li–Ge2	2.615(12)
La–Ge1 (×2)	3.1335(8)	Ce–Ge1 (×2)	3.1034(11)	Pr–Ge1 (×2)	3.0812(7)
La–Ge1 (×2)	3.2454(8)	Ce–Ge1 (×2)	3.2111(11)	Pr–Ge1 (×2)	3.1944(7)
La–Ge2 (×2)	3.1847(7)	Ce–Ge2 (×2)	3.1435(11)	Pr–Ge2 (×2)	3.1183(6)
La–Ge2	3.2788(10)	Ce–Ge2	3.2546(15)	Pr–Ge2	3.2410(8)
La–La (×2)	4.0061(6)	Ce–Ce (×2)	3.9721(15)	Pr–Pr (×2)	3.9509(3)
La–La (×2)	4.1661(7)	Ce–Ce (×2)	4.1389(11)	Pr–Pr (×2)	4.1199(5)
NdLiGe ₂		SmLiGe ₂		EuLiGe ₂	
atomic pair	distance	atomic pair	distance	atomic pair	distance
Ge1–Ge2 (×2)	2.5088(8)	Ge1–Ge2 (×2)	2.4986(5)	Ge1–Ge2 (×2)	2.4948(5)
Li–Ge1	2.537(9)	Li–Ge1	2.531(10)	Li–Ge1	2.678(9)
Li–Ge2	2.611(9)	Li–Ge2	2.606(6)	Li–Ge2	2.697(9)
Nd–Ge1 (×2)	3.0659(9)	Sm–Ge1 (×2)	3.0376(5)	Eu–Ge1 (×2)	3.1791(5)
Nd–Ge1 (×2)	3.1839(8)	Sm–Ge1 (×2)	3.1553(5)	Eu–Ge1 (×2)	3.2865(5)
Nd–Ge2 (×2)	3.1007(8)	Sm–Ge2 (×2)	3.0608(5)	Eu–Ge2 (×2)	3.1793(4)
Nd–Ge2	3.2359(13)	Sm–Ge2	3.2152(7)	Eu–Ge2	3.3709(6)
Nd–Nd (×2)	3.9361(14)	Sm–Sm (×2)	3.9014(3)	Eu–Eu (×2)	3.9730(3)
Nd–Nd (×2)	4.1084(10)	Sm–Sm (×2)	4.0813(4)	Eu–Eu (×2)	4.1818(4)

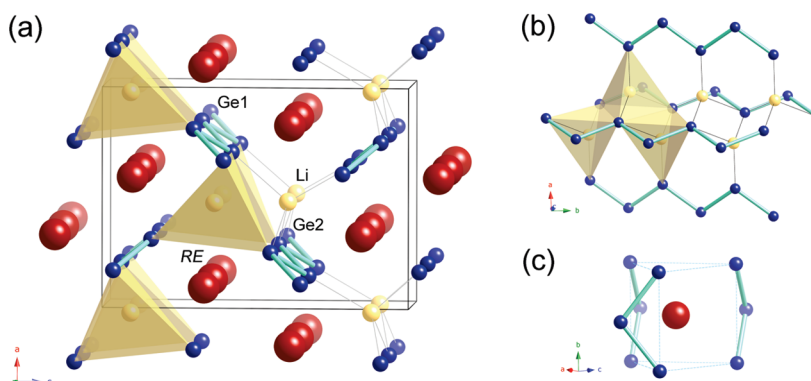


Figure 1. (a) Combined polyhedral and ball-and-stick representations of the orthorhombic structure of $RELiGe_2$ ($RE = La-Nd, Sm, \text{ and } Eu$). The unit cell is outlined. The RE atoms are shown as dark-red spheres, and the Ge atoms are drawn as blue spheres. The Li atoms (in yellow) are shown as the centers of translucent $LiGe_4$ tetrahedra or as yellow spheres connected to four neighboring Ge atoms. The ${}^1_{\infty}[Ge_2]$ chains are emphasized. (b) Expanded view of the ${}^1_{\infty}[Ge_2]$ chains and the edge-sharing mode of the $LiGe_4$ tetrahedra. (c) Expanded view of the coordination polyhedron of the RE atoms.

were treated by the Löwdin downfolding technique;²⁷ 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)²⁸ 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 $RELiGe_2$ ($RE = La-Nd, Sm, \text{ and } Eu$) phases have been identified previously from their powder X-ray diffraction patterns¹⁶ as crystallizing with the $CaLiSi_2$ structure type¹⁹ (space group $Pnma$; Pearson code $oP16$).²⁹ 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 ${}^1_{\infty}[Ge_2]$ chain. These 1-D polyanions propagate parallel to the crystallographic b -axis and are linked together via chains of edge-shared $LiGe_4$ -tetrahedra, also running in the same direction. Emphasizing the covalency of the $Li-Ge$ bonding, the structure can also be rationalized as a polyanionic ${}^3_{\infty}[LiGe_2]$ network, with rare-earth metal cations residing in the channels within it.

Besides the title $RELiGe_2$ ($RE = La-Nd, Sm, Eu$) compounds and $YbLiGe_2$,³⁰ other rare-earth metal lithium germanides with similar formula exist, such as $EuLi_{0.9}In_{0.1}Ge_2$.⁹ However, the topology of the ${}^1_{\infty}[Ge_2]$ 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,⁹ the “1-1-2” phases can be considered as derivatives of the hypothetical $REGe_2$ compounds (AlB_2 structure type). This idea is schematically represented in Figure 2, where the honeycomb ${}^2_{\infty}[Ge_2]$ layers in the parent AlB_2 -type structure are “cut” to either zigzag (*trans-trans*) or *cis-trans* ${}^1_{\infty}[Ge_2]$ chains by cleaving selected $Ge-Ge$ bonds. This imaginary process can account for the polymorphic

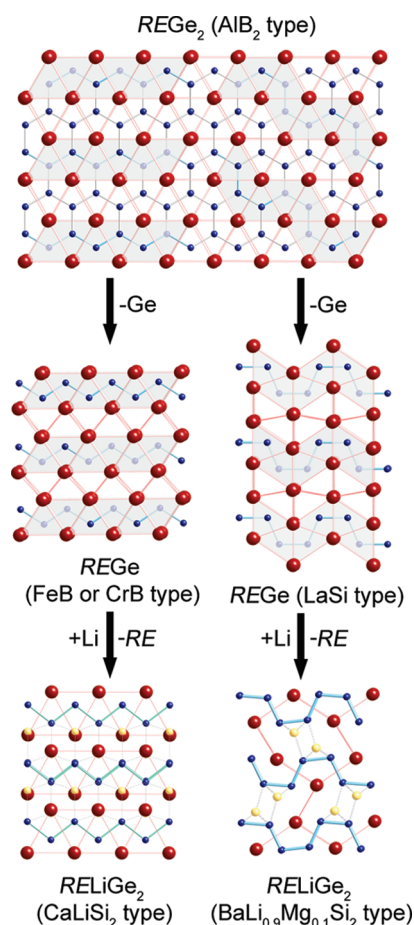


Figure 2. Schematic representation of the structural relationship between the hypothetical $REGe_2$ ($RE = La-Nd, Sm \text{ and } Eu$) compounds with the AlB_2 structure type and the corresponding $REGe$ monogermanides (FeB , CrB , or $LaSi$ structure types). A formal substitution of $1/2$ of the RE atoms in the latter structures with Li yields two different $RELiGe_2$ structures, with different ${}^1_{\infty}[Ge_2]$ 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.

structures of the monogermanides $REGe$ (FeB , CrB , or $LaSi$ structure types).³¹ In the next step, a “substitution” of $1/2$ of

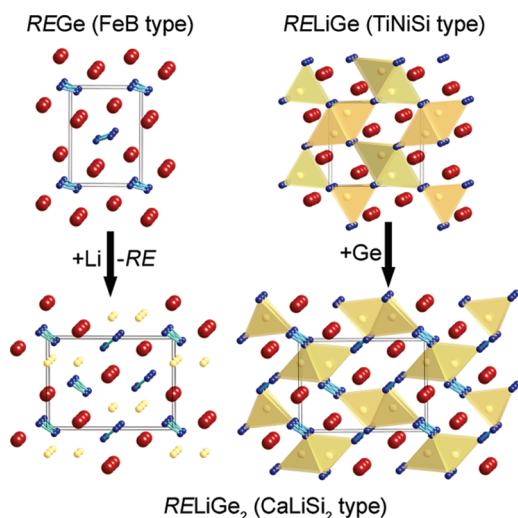


Figure 3. Schematic representation of the structural relationship between the $REGe$ (FeB structure type), $RELiGe$ (TiNiSi structure type), and the title $RELiGe_2$ compounds (CaLiGe₂ structure type). The three structures have the same extended symmetry and share the positions of the RE atoms. See text for details.

the rare-earth metals atoms with Li in the structure of each monogermanide yields the two different “1-1-2” structures.

The topological relation of the structure of $RELiGe_2$ ($RE = \text{La–Nd, Sm, and Eu}$) to that of the $REGe$ phases ($RE = \text{La–Pr}$)³¹ crystallizing with the FeB structure type is useful to note and is schematically presented in Figure 3. The same illustration also shows that the $RELiGe_2$ compounds can be considered as close relatives of the hypothetical $RELiGe$ germanides with the TiNiSi structure type³² (aka SrMgSi): a simple “insertion” of another germanium atom and an appropriate resizing of the unit cell accounts for the above-mentioned polyanionic ${}^{\infty}[\text{LiGe}_2]$ 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 $RELiGe_2$ 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 $REGe$ with the CrB structure type, with polymorphic transitions between the two for the middle members of the 4f-block.³¹ This phenomenology has been attributed to the lanthanide contraction and the decreasing size of the rare-earth metals. Indeed, we observe that as the atomic sizes of the lanthanides gradually decreases from La to Sm ($r_{\text{La}} = 1.69 \text{ \AA}$, $r_{\text{Ce}} = 1.65 \text{ \AA}$, $r_{\text{Pr}} = 1.64 \text{ \AA}$, $r_{\text{Nd}} = 1.63 \text{ \AA}$, and $r_{\text{Sm}} = 1.62 \text{ \AA}$),³³ the lattice parameters monotonically decrease (Table 1). These changes in the unit cell constants correlate with the refined Ge–Ge distances in the ${}^{\infty}[\text{Ge}_2]$ chains, which show a gradual decrease from 2.5318(8) Å for LaLiGe₂ to 2.4986(5) Å for SmLiGe₂, respectively (Table 3). The corresponding Ge–Ge–Ge angles decreases as well from 104.58(3)° to 102.67(3)° for LaLiGe₂ and SmLiGe₂, respectively.

The unit cell volume for EuLiGe₂ is larger than the rest because of the existence of europium as Eu(II), which results in the enlarged atomic radius ($r_{\text{Eu}} = 1.85 \text{ \AA}$).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 EuLiGe₂ is the shortest of all, 2.4948(5) Å. Such bond length compares well with those

reported for other compounds with polyene-like ${}^{\infty}[\text{Ge}_2]$ chains, such as $\alpha\text{-Sr}_2\text{LiGe}_3$,¹² Eu_2LiGe_3 ,¹³ $\text{A}_2(\text{Li}_{1-x}\text{Mg}_x)_2\text{Ge}_3$ ($A = \text{Sr, Eu}$),¹⁴ ALiGe_2 ($A = \text{Sr, Ba}$),¹⁵ and $\text{ALi}_{1-x}\text{In}_x\text{Ge}_2$ and $\text{A}_2(\text{Li}_{1-x}\text{In}_x)_2\text{Ge}_3$ ($A = \text{Sr, Ba, Eu}$).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 CaGe_2 ($d_{\text{Ge–Ge}} = 2.5417(7)–2.5513(7) \text{ \AA}$),⁵ and EuGe_2 ($d_{\text{Ge–Ge}} = 2.564(4) \text{ \AA}$),³⁴ in the $[\text{Ge}_4]$ clusters in BaGe_2 and K_4Ge_4 (average $d_{\text{Ge–Ge}} = 2.55–2.56 \text{ \AA}$),³⁵ and in the $[\text{Ge}_2]$ dumbbells in Ca_5Ge_3 ($d_{\text{Ge–Ge}} = 2.575(1) \text{ \AA}$),³⁶ among many others.

We must also note that similar zigzag ${}^{\infty}[\text{Ge}_2]$ chains are present in all $REGe$ 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 LaGe HT-polymorph (FeB-type), and refined its structure; the hereby determined Ge–Ge distance is 2.676(1) Å, not 2.509 Å as in the literature.³¹ Large discrepancies were also found for DyGe ($d_{\text{Ge–Ge}} = 2.678(3) \text{ \AA}$, instead of the published 2.546 Å³¹); and TmGe ($d_{\text{Ge–Ge}} = 2.639(3) \text{ \AA}$ instead of the published 2.571 Å³¹). For detailed crystallographic data on $REGe$, 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 $RELiGe_2$ are significantly shorter than the Ge–Ge distances in the corresponding $REGe$ 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 $RELiGe_2$ versus $REGe$ ($=RE_2Ge_2$) 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 $[\text{RE}^{3+}][\text{Li}^+][\text{Ge}^{2-}]_2$, whereby 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 CaGe (e.g., $\text{Ca}^{2+}\text{Ge}^{2-}$)³⁸ and EuGe (e.g., $\text{Eu}^{2+}\text{Ge}^{2-}$).³⁹ However, the formal electron count for the remaining $REGe$ phases with RE^{3+} cations yields a more reduced germanium state (viz., $\text{RE}^{3+}\text{Ge}^{3-}$) series. In contrast, EuLiGe_2 with Eu^{2+} instead of Eu^{3+} will require a formulation $[\text{Eu}^{2+}][\text{Li}^+][\text{Ge}^{1.5-}]_2$ (also valid in the cases of CaLiGe_2 ¹⁹ and YbLiGe_2 ³⁰), that is, a partial double bond character of the Ge–Ge interactions and some conjugation of the Ge π^* orbitals along the chain must be considered. The shortest Ge–Ge distance in EuLiGe_2 , which are isostructural (but not isoelectronic) to the $RELiGe_2$ compounds containing trivalent cations was already noted; another example confirming this line of thinking is the fact that CaLiGe_2 (formally $[\text{Ca}^{2+}][\text{Li}^+][\text{Ge}^{1.5-}]_2$)¹⁹ and YbLiGe_2 (formally $[\text{Yb}^{2+}][\text{Li}^+][\text{Ge}^{1.5-}]_2$)³⁰ also have very short Ge–Ge bonds of 2.490(2) Å and 2.476(2) Å, respectively. Comparing those to LaLiGe_2 ($d_{\text{Ge–Ge}} = 2.5318(8) \text{ \AA}$; formally $[\text{La}^{3+}][\text{Li}^+][\text{Ge}^{2-}]_2$) and CeLiGe_2 ($d_{\text{Ge–Ge}} = 2.518(1) \text{ \AA}$; formally $[\text{Ce}^{3+}][\text{Li}^+][\text{Ge}^{2-}]_2$) is instructive since the corresponding Pauling single-bond radii are very close and “size” effects could be ruled out: $r_{\text{Ca}} = 1.74 \text{ \AA}$, $r_{\text{Yb}} = 1.70 \text{ \AA}$, $r_{\text{La}} = 1.69 \text{ \AA}$, and $r_{\text{Ce}} = 1.65 \text{ \AA}$.³³

The “special” role of lithium in these structures must be briefly discussed too. As mentioned already, here and in some

earlier publications,^{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 ${}^3[\text{LiGe}_2]_{\infty}$ 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 ($r_{\text{Li}} = 1.225$ Å; $r_{\text{Ge}} = 1.242$ Å),³³ and compare well with those reported for other lithium germanides, such as Eu_2LiGe_3 ,¹³ $\text{A}_2(\text{Li}_{1-x}\text{Mg}_x)_2\text{Ge}_3$ ($\text{A} = \text{Sr}, \text{Eu}; x \approx 0.5$),¹⁴ and ALiGe_2 ($\text{A} = \text{Sr}, \text{Ba}$),¹⁵ $\text{Ce}_2\text{Li}_2\text{Ge}_3$,¹⁸ and $\text{ALi}_{1-x}\text{In}_x\text{Ge}_2$ ($0 \leq x \leq 0.1$) and $\text{A}_2(\text{Li}_{1-x}\text{In}_x)_2\text{Ge}_3$ ($x \approx 0.3$) ($\text{A} = \text{Sr}, \text{Ba}, \text{Eu}$).⁹ The shortest Li–RE distances are greater than 3.5 Å.

The larger lanthanide atoms reside in the “channels” of the ${}^3[\text{LiGe}_2]_{\infty}$ 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.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 ($\text{RE} = \text{La}–\text{Sm}$) and the 11 ve^- system with divalent cations ($\text{Ca}, \text{Eu}, \text{and Yb}$), respectively. In addition, a model structure of EuLiGe_2 adopting the $\text{BaLi}_{0.9}\text{Mg}_{0.1}\text{Si}_2$ -type structure was also taken in consideration to compare the energetic stability of the cis–trans versus trans–trans ${}^2[\text{Ge}_2]_{\infty}$ 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

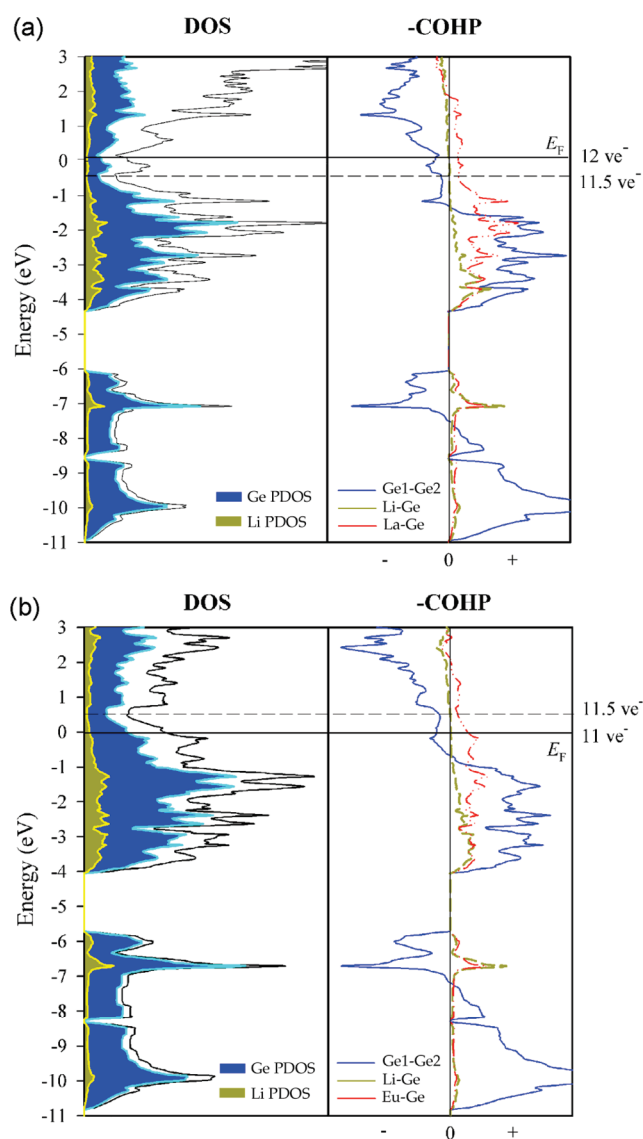


Figure 4. (a) Calculated DOS and COHP of LaLiGe_2 . (b) Calculated DOS and COHP of EuLiGe_2 . The total DOS and the partial DOS are plotted on the same energy scale. The actual Fermi level (E_{F}) is chosen as the energy reference at 0 eV and drawn as a solid line; estimated Fermi level for different valence electron counts are shown with dashed lines.

antibonding valence band of 4p of Ge together with a bonding valence band of 2s of Li between 6 and 8.5 eV 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 ${}^3[\text{LiGe}_2]_{\infty}$ 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

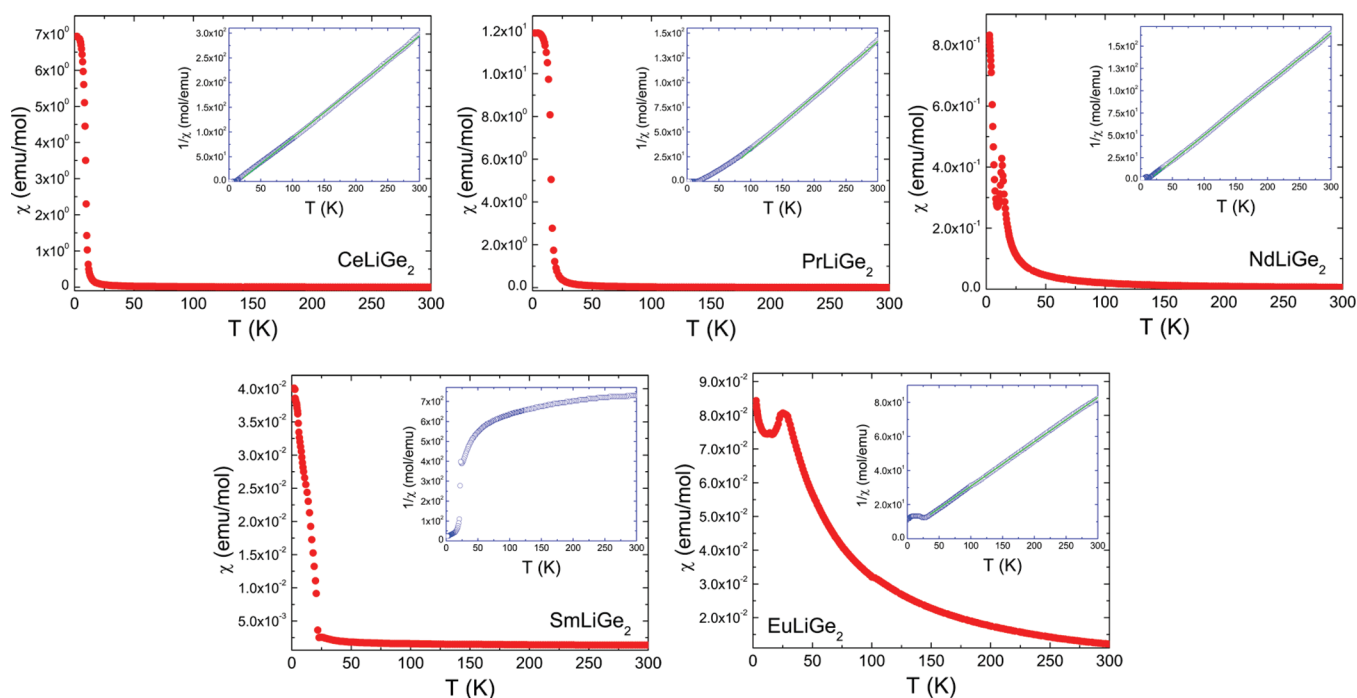


Figure 5. Temperature dependence of the magnetic susceptibility of $RELiGe_2$ ($RE = \text{Ce–Nd, Sm and Eu}$). Inset: Inverse susceptibility vs temperature with linear fits to the Curie–Weiss law.

DOS, which is presented in the Supporting Information section clearly rules out such a hypothesis: spin polarization leaves the Ge orbitals (main contributors near the Fermi level) untouched since essentially there is no exchange splitting. Another possibility is that this feature indicates electronic instability, therefore, we checked if another structure, which would be more stable from an electronic structural viewpoint can be adopted by EuLiGe_2 . A logical choice here was EuLiGe_2 (“extrapolated” from $\text{EuLi}_{0.91(1)}\text{In}_{0.09}\text{Ge}_2$)⁹ with the $\text{BaLi}_{0.9}\text{Mg}_{0.1}\text{Si}_2$ -structure type, whose structure features cis–trans chains. All the details are given in the Supporting Information; we just note that the calculation parameters, WS radii of each atom, number of k -points, and the volume of unit cells, were kept identical to those employed for the already discussed calculation of EuLiGe_2 with the CaLiSi_2 -structure type (zigzag chains). According to the results, the total electronic energy of the structure with the cis–trans chains is higher (by 971 meV/unit cell) than the structure with zigzag chains, rendering this supposition unreasonable.

COHP analyses of the LaLiGe_2 (12 ve^-) and EuLiGe_2 (11 ve^-) compounds reveal several interesting features as well. The Ge–Ge bonding in both cases has an antibonding character at E_F , which is easily understood following the in-depth analysis by Mudring and Corbett (the case study of Ca_3Ge_3).³⁶ However, we note that the antibonding character is smaller in EuLiGe_2 than in LaLiGe_2 , which can be clearly seen from the relatively less populated π^* states in EuLiGe_2 compared to LaLiGe_2 (Figure 4). Furthermore, the integrated crystal orbital Hamilton population (COHP) values—the ICOHP in EuLiGe_2 is 2.86 eV/cell, compared to 2.50 eV/cell in LaLiGe_2 . Such differences can also be correlated to the relatively shorter Ge–Ge distance in EuLiGe_2 ($d_{\text{Ge–Ge}} = 2.4948(5) \text{ \AA}$) versus LaLiGe_2 ($d_{\text{Ge–Ge}} = 2.5318(8) \text{ \AA}$), respectively. This means that a partial double-bond character should be ascribed to the Ge–Ge bonding.

The antibonding character of the Ge–Ge bonds in both LaLiGe_2 and EuLiGe_2 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 $RELiGe_2$ ($RE = \text{Ce–Nd, Sm and Eu}$) 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, CeLiGe_2 , PrLiGe_2 , NdLiGe_2 , and SmLiGe_2 display paramagnetic behavior that follows the Curie–Weiss law $\chi(T) = C/(T - \theta_p)$,⁴⁰ where C is the Curie constant ($N_A \mu_{\text{eff}}^2 / 3k_B T$) and θ_p is the Weiss temperature. The calculated effective magnetic moments (Table 4) are close to the theoretical values of RE^{3+} ($RE = \text{Ce–Nd}$),⁴⁰ as expected, which indicates magnetic ground states from 4f-electron origin. A Pauli-like paramagnetic ground state exists for LaLiGe_2 , since the La^{3+} ion has no 4f electrons. The SmLiGe_2 specimen shows typical Van Vleck paramagnetism⁴¹ in the high temperature range; in this instance, the significant contribution of the temperature independent term (χ_o) to the molar susceptibility requires a nonlinear fit to the modified Curie–Weiss law, $\chi_m(T) = \chi_o + C/(T - \theta_p)$,⁴¹ to calculate the effective moment for Sm^{3+} . The effective moment determined for the EuLiGe_2 sample ($8.07 \mu_B$) is on par with the free-ion value for Eu^{2+} ($7.94 \mu_B$),⁴¹ corroborating the earlier discussions on the crystal and electronic structure.

In the low temperature regime, all compounds in this series (excluding LaLiGe_2) undergo magnetic ordering: both CeLiGe_2 and PrLiGe_2 ⁴² enter into ferromagnetic states (FM) with T_C of

about 11 and 18 K, respectively. The data on NdLiGe₂ show a clear cusp-like feature in both the FC and ZFC magnetization curves, which indicate the onset of antiferromagnetic ordering (AFM) with Néel 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 NdLiGe₂ (Table 4) also suggests ferromagnetic ordering. The behavior of SmLiGe₂ in the low temperature regime is also complicated: from the FC data it appears that the unpaired electrons of the Sm³⁺ ions align in a ferromagnetic fashion with T_C 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 EuLiGe₂ indicates a straightforward antiferromagnet with a Néel 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)⁴⁰ and the monotonically decreased distance between the RE metal atoms on moving across the series.

■ ASSOCIATED CONTENT

■ 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 EuLiGe₂ with the BaLi_{0.9}Mg_{0.1}Si₂-structure type; results from spin-polarized calculations; table with integrated COHP for selected interactions; plots with $\chi(T)$ for RELiGe₂ (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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