The RELi$_x$Sn$_2$ ($RE$=La–Nd, Sm, and Gd; $0 \leq x < 1$) series revisited. Synthesis, crystal chemistry, and magnetic susceptibilities

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**A B S T R A C T**

This study is concerned with the ternary compounds RELi$_x$Sn$_2$ ($RE$=La–Nd, Sm, and Gd; $0 \leq x < 1$), which have been previously thought to be the stoichiometric RELiSn$_2$ phases. These materials crystallize with the base-centered orthorhombic space group Cmcm (No. 63), and can be formally assigned with the CeNiSi$_2$ structure type (Pearson symbol oC16). Our systematic single-crystal X-ray diffraction studies revealed substantial Li-deficiencies in all cases, with SmSn$_2$ (space group Cmcm, ZrGa$_2$ structure type, Pearson symbol oC12) and GdSn$_2$ (space group Cmcm, ZrSi$_2$ structure type, Pearson symbol oC12) being completely lithium-free. The structure refinements also uncovered positional disorder on the Sn site neighboring the vacancies. The Sn-disorder and the Li-deficiency correlate, and vary monotonically with the decreased size of the rare-earth atoms in the order $RE$=La–Nd. The SmSn$_2$ and GdSn$_2$ structures are devoid of any disorder. Temperature-dependent studies of the magnetic response of the title compounds are also presented and discussed.

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1. Introduction

In recent years, our research group has investigated in depth the ternary RE–Li–Ge systems, and we have already reported on the crystal chemistry and physical properties of a large variety of ternary compounds—these include RELiGe$_2$ ($RE$=La–Nd, Sm, and Eu) [1], RELi$_2$Ge$_3$, RELi$_4$Ge$_4$, RELi$_3$Ge$_6$, and RELi$_1$Li$_2$Ge$_6$ ($RE$=La–Nd, Sm), with the last four being members of the extended homologous series [REGe$_2$]$_n$[RELiGe]$_m$ [2,3]. Over the course of the structural work, we stipulated that the “electron shortages” in some of these structures are overcome via admixture of Li and Ge (on the Li site). Thus, to unequivocably establish such conjecture, our attention was focused on the possible existence of stannide analogs of RELi$_x$Ge$_4$ (2 [2]. As a result we successfully synthesized and characterized Ce$_3$Li$_{13.8}$Sn$_{3.1}$ (isotypic with Ce$_3$Li$_{13.95}$ Ge$_{4.05}$), where the magnitude of the Li–Sn substitution was much clearer [2]. Accidentally, the Ce–Li–Sn reaction also afforded CeLi$_{0.63}$Sn$_2$, a phase with unit cell parameters very close to those of the known compound CeLi$_{0.63}$Sn$_2$ (CeNiSi$_2$ structure type) [4,5], yet Li-deficient. With this respect, we note that Pavlyuk et al. [4], who explored initially the ternary RE–Li–Sn systems, identified the RELiSn$_2$ ($RE$=La–Nd, Sm, Gd–Tm, Lu) compounds from powder X-ray diffraction data (structure refined only for CeLiSn$_2$) [4]. The authors noted in their communication the existence of many non-stoichiometric RET$_x$X$_2$ ($0 < x < 1$; T stands for late transition metal, and X=Si, Ge, and Sn) [5], and alluded to the possibility for a wide homogeneity range in RELiSn$_2$ ternaries. Nonetheless, based on the variation of the unit cell parameters on going from La to Lu, and comparing the unit cell volumes with those of the corresponding binary phases RESn$_2$ (ZrSi$_2$ structure type) [6–8], presumed them all to be stoichiometric and isostructural with the CeNiSi$_2$ structure [5,9].

With this study, we carefully revise the crystal structures of the RELi$_x$Sn$_2$ ($RE$=La–Nd, $0 \leq x < 1$) compounds using single-crystal X-ray diffraction data. Interestingly, the structural data uncovered that the phase width, i.e., the partial occupation of the Li position is accompanied by a positional disorder on the next-nearest Sn neighbor. Consequently, the Sn1 positions are split into two distinct Sn1A and Sn1B sites, leading to intricate disorder. The Li off-stoichiometry and the concomitant Sn disorder mirror the lanthanide contraction, and on the basis of this work, we speculate that the crystal structures of RELi$_x$Sn$_2$ series has a “break-point” for $RE$=Sm, i.e., the Li uptake becomes diminutive. Thus, the major product of the Sm–Li–Sn reaction is the binary SmSn$_2$ phase, which is isotypic with NdSn$_2$ (ZrGa$_2$ structure type, space group Cmcm, Pearson symbol oC12) [5,10]. Similarly, the major product of the Gd–Li–Sn reaction is the binary GdSn$_2$ phase (ZrSi$_2$ structure type, space group Cmcm, Pearson symbol oC12) [5,11]. We present
and compare all structures and review the magnetic susceptibilities of these compounds, particularly in comparison with the previous work [4,7,8]. The electronic band structures, calculated with the aid of the TB-LMTO method [12] are also discussed.

2. Experimental

2.1. Synthesis

All starting materials and products of the present investigation were handled and stored inside an Argon-filled glove box atmosphere due to their sensitivity to oxygen and moisture. Polycrystalline samples were prepared using high purity (> 99.9 wt%) elements (RE=La–Nd, Sm and Gd; Li, Sn) purchased from Ames Labs, Alfa, or Aldrich and used as obtained except for Li, which was cleaned free of any dark surface with the aid of a blade. Weighed amounts (totaling ca. 500 mg) of the elements taken in the desired stoichiometric ratio (RE:Li:Sn = 3:4:4 initially, and then adjusted to 1:1:2 or 1:0.5:2) were filled into Nb tubes, which were arc welded under high-purity Argon gas. The elemental mixtures were then melted by slowly heating them in a high-frequency induction furnace up to 950–1000 °C. The heat treatment was done under residual pressure of 10⁻³ Torr. In all experiments, the temperature was initially raised to 600 °C within 3 h, an intermediate temperature which allows the melting of Sn and Li. The samples were homogenized at the maximum temperature for about 2–4 h, where $T_{\text{max}}$ = 950 °C was used for the RELi$_x$Sn$_y$ (RE=La–Pr) samples, and $T_{\text{max}}$ = 1000 °C for the NdLi$_x$Sn$_y$ specimen, respectively. After that the tubes were slowly cooled off at a rate of 5 °C/h for RELi$_x$Sn$_y$ (RE=La–Pr), and 10 °C/h for NdLi$_x$Sn$_y$, respectively.

The resulting bulk polycrystalline products were brought in the glove-box, ground using an agate mortar and pestle, and sealed again in Nb tubes for a subsequent heat-treatment following the above-mentioned procedure. After that, the sealed Nb tubes were placed in tube furnaces and annealed at 600 °C over 3–5 days, in order to grow suitable single crystals for the structure determination. The annealed samples were allowed to cool to room temperature by switching off the furnace. The experimental powder X-ray diffraction patterns of the RELi$_x$Sn$_y$ (RE=La–Nd) in comparison with the calculated patterns obtained from the single-crystal data revealed > 95 wt% purity of the target phases. Leftover Sn was detected as a minor impurity phase in all cases.

Here, we specifically note that single-crystals of SmSn$_2$ and GdSn$_2$ were first isolated from samples with nominal compositions Sml$_x$Sn$_y$ and GdLi$_x$Sn$_y$. For both samples, the temperature was raised to 950 °C over 2 h, equilibrated for 5 h, followed by a slow cooling (rate of 5 °C/h) to 600 °C, at which temperature the samples were annealed for 1 day. Thereafter, the furnace was switched off.

Besides the above-mentioned reaction schemes, another synthetic approach was also tried to establish the best route to the synthesis of the title compounds. Here, elemental Li and a pre-synthesized binary mixture with nominal composition RE$_3$Li$_2$ were mixed in equal molar ratios. The materials were loaded into Nb-tubes, which were subsequently encapsulated in fused silica tubes, and flame-sealed upon evacuation. The tubes were then slowly heated at 950 °C, dwelled at this temperature for 5 h and slowly cooled to 600 °C at a rate of 5 °C/h. Finally the samples were cooled to room temperature by switching off the furnace. The powder X-ray diffraction patterns of the as-synthesized samples revealed multi-component mixtures in all cases, although the targets were the major products. This method also confirmed that the $\text{RESn}_2$ “precursor” and the “final product” for the reactions involving Sm and Gd are the same.

**Caution!** Reactions at 950–1000 °C could be dangerous. At these conditions, the Nb tubes and Sn could react, causing Li vapors (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.

The crystals of the title compounds are dark grey, with metallic luster. They quickly decompose in air and must be handled with caution. For the purposes of collecting intensity data on the single-crystal diffractometer, the crystals were picked in the glove-box, and covered with Paratone-N oil—the latter was also used as a “glue” in the process of mounting the crystals on the tips of glass fibers.

2.2. Crystallographic studies

X-ray powder diffraction patterns were collected at room temperature on a Rigaku MiniFlex powder diffractometer using filtered CuKα radiation ($\lambda = 1.54056$ Å). The diffractometer was enclosed and operated inside a glove-box. The observed peak-positions and the peaks’ relative intensities, analyzed using the JADE 6.5 software package, matched well with those calculated from the single-crystal work. Samples exposed to air for a day lost their crystallinity, and the only Bragg peaks that could be indexed were those of elemental Sn.

Single-crystal X-ray diffraction data were collected on a Bruker SMART CCD-based diffractometer, employing monochromated MoKα radiation ($\lambda = 0.71073$ Å) generated from a sealed tube. The operating temperature was 200(2) K, maintained by a cold nitrogen stream. This method for handling the crystals alleviated the issue with their air-sensitivity. After ensuring the crystal quality, full spheres of data were collected in four major sections of frames with 0.4° steps in $\omega$ at different $\phi$ settings. The typical exposure time was 8–12 s per frame. The whole sphere in reciprocal space was covered up to ca. 56° in $\theta$. The Bruker SMART software package [13] was used to process and monitor the data collection. Data reduction and integration, as well as final unit cell refinements were performed using SAINT [14]. Empirical absorption corrections based on equivalent reflections were applied to all data using SADABS [15]. The subprogram XPREP in the SHEXLTL [16] software package was used to sort and merge the structure factors as well as to determine the space-group. The systematic extincts in all data sets proved consistency with the centrosymmetric space group Cmcm (excluding the data for SmSn$_2$, which showed no systematic absences for a $c$-glide and were merged in Cmmm). The structure was solved by direct method using SIR-92 [17] and refined against $F^2$ using SHEXL-97 [18] as implemented in WinGX [19].

As mentioned already, the crystal structure of CeLi$_x$Sn$_y$ compound was first established, and its atomic coordinates were used as starting model for the refinement of the remaining structures. The structure solution provided three independent crystallographic sites, two of them occupied by Sn1 and Sn2 atoms, and one by the Ce atoms. The Li atom was assigned on the basis of a peak in the difference Fourier map, distances, and chemical composition. Using these four atoms in the asymmetric unit (CeNiSi$_2$ structure type [5,9]), the first refinement cycles converged to unsatisfactory reliability factors $R_1 = 12\%$ and $wR_2 = 30\%$, with three times larger isotropic thermal parameters for the Sn1, Sn2 and Li atoms (ca. $2.4 \times 10^{-2}$ Å$^2$) when compared to that of the Ce atom, exhibiting a value of ca. $0.8 \times 10^{-2}$ Å$^2$. Such high atomic displacement parameters are unusual and may be suggestive of defects in the structure (or worse, wrongly assigned positions). More importantly, there was a high residual electron density in the difference Fourier map, indicated by a peak close to Sn1. Therefore, in the following trial refinements, the Sn1 site was described as a split position Sn1A and Sn1B, which lead to an overall improvement of the reliability indices
and no electron density leftover. Next, occupation factors (sof) of all atoms were checked—Ce and Sn2 did not deviate from full within 3σ, whereas the refinement with freed sof for the Li position revealed significant deficiency (ca. 30–40%). Since Sn1B and Li were both with fractional occupancies and at unrealistically close distance of ca. 2.0 Å, their site occupation factors were restrained to sum up to unity. This, and the constrain on the Sn1A and Sn1B split sites to vibrate with the same displacement parameter produced smoothly converging refinement to satisfactory $R_1$ = 2.8% and $wR_2$ = 7.8% indices, along with more uniform isotropic atomic displacement parameters. We note specifically here that all tested single-crystals isolated from the RELiSn2 (RE=La–Nd) series revealed the same defect structure and correlation between the refined sof of the Li and Sn1B positions. The distance between the two split positions was found to decrease from 0.498(5) Å to 0.409(1) Å for the Ce- and the Sn1B positions. The distance between the two split positions was found to decrease from 0.498(5) Å to 0.409(1) Å for the Ce- and the Nd-analogs, mirroring the decrease of unit cell volumes and the lanthanide contraction [20].

At this stage, it was clear that the originally proposed CeNiSi2 structure type cannot be an acceptable structural model, since split atomic positions (Sn1A and Sn1B) and Li deficiencies must be taken into account. We standardized the positional parameters using the STRUCTURE TIDY program [21] and refined all sited anisotropically (excluding the Li position). The remaining structures were refined using CeLiSn2 as a starting model, and all refinements proceeded smoothly. The final difference Fourier maps in all four cases were flat, with highest maxima and minima not larger than 1–2 e/Å³.

SmSn2 and GdSn2 structure determinations differed from the above in their own ways. SmSn2 was found to be isotopic with the binary stannides RELiSn2, which adopt the ZrGe2 structure type with the space group Cmcm [5,10] (also known as ThGe2 or UGe2 structure type [5]). The structural transformation can also be inferred from the “collapse” of the crystallographic b-axis between NdLi5Sn2 (x = 0.441(1), Table 1) and SmLi5Sn2 (x = 0; Table 2). Notice that we report SmSn2 as a binary compound, although the crystal came from a reaction containing Li, and there might be some small amount of Li in it; the crystals obtained from reactions between Sm and Sn only were not adequate for single-crystal work to assert this. We also note that the final difference Fourier map in this case has a small peak of ca. 3 e/Å³ located 0.8 Å away from Sm, but it was not possible to include it in any meaningful model for refinements.

The binary GdSn2 phase (space group Cmcm, Pearson symbol oC12) forms with the ZrSi2 structure type [5,11] and can be viewed as the Li-free version of the RELiSn2 structure. As such, there was no disorder found on any of the sites—the Sn1 site behaved as if it were a structure with a clear density. The empirical formula, LaLi0.69(1)Sn2, CeLi0.63(1)Sn2, PrLi0.56(1)Sn2, NdLi0.44(1)Sn2, respectively, was obtained from the analysis of the X-ray powder diffraction data. The space group, Cmcm, was confirmed by single-crystal X-ray diffraction measurements on crystals grown by the Bridgman method [22]. The orthorhombic lattice parameters are a = 4.4746(13) Å, b = 18.581(5) Å, and c = 4.4746(13) Å for LaLi0.69(1)Sn2, CeLi0.63(1)Sn2, PrLi0.56(1)Sn2, and NdLi0.44(1)Sn2, respectively. The unit cell volume is V = 315.98(17) Å³ for LaLi0.69(1)Sn2, V = 315.7(2) Å³ for CeLi0.63(1)Sn2, and V = 315.7(2) Å³ for PrLi0.56(1)Sn2, respectively. The crystal system of the compounds is orthorhombic, and the space group is Cmcm (No. 63).

### Table 1

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<td>a (Å)</td>
<td>4.5592(13)</td>
<td>4.5123(11)</td>
<td>4.4938(7)</td>
<td>4.4921(4)</td>
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<td>b (Å)</td>
<td>18.581(5)</td>
<td>18.234(4)</td>
<td>17.890(3)</td>
<td>17.3844(17)</td>
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<td>c (Å)</td>
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<td>4.4412(10)</td>
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<td>V (Å³)</td>
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<td>365.41(15)</td>
<td>355.76(9)</td>
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<td>20</td>
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<td>wR2 (I &gt; 2σ(I))</td>
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* R1 = \(|F_o|−|F_c|)/|F_o|\sum |F_o|; wR2 = \(\sum w|F_o|^2−|F_c|^2|/\sum w|F_o|^2\)½, where w = 1/\(|F_o|^2+(A P)^2+(B P)^2\); and P = (F² + 2F²)³. A, B—weight coefficients.

### Table 2

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<th>Empirical formula</th>
<th>SmSn2</th>
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<td>Cmcm (No. 63), 4</td>
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<td>b (Å)</td>
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<td>Refined parameters</td>
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<tr>
<td>R1 (I &gt; 2σ(I))</td>
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</table>

* R1 = \(|F_o|−|F_c|)/\sum |F_o|; wR2 = \(\sum w|F_o|^2−|F_c|^2|/\sum w|F_o|^2\)½, where w = 1/\(σ|F_o|^2+(A P)^2+(B P)^2\); and P = (F² + 2F²)³. A, B—weight coefficients.

3.2. Electronic structure calculations

The Stuttgart TB-LMTO 4.7 program [12,22] was used to calculate the band structure of an idealized, disorder-free LaLiSn2. The exchange and correlation terms were treated by the local density approximation (LDA) [23]. All relativistic effects except spin orbit coupling were taken into account by using a scalar relativistic approximation [24]. The symmetry of the potential was considered spherical inside each Wigner–Seitz (WS) sphere, and a
combined correlation was used to take into account the overlapping part. No empty spheres were needed to meet the minimum overlapping criteria. The radii of the WS spheres were determined by an automatic procedure and are as follows: La = 2.25 Å, Sm = 1.51–1.69 Å and Li = 1.25 Å. The basis sets included 6s, 6p, 5d and 4f orbitals for La; 5s, 5p and 5d orbitals for Sn; and 2s, 2p and 3d orbitals for Li. The La 6p and 4f, Sn 5d, and Li 2p and 3d orbitals were treated by the Löwdin downfolding technique [25]. The k-space integrations were done using the tetrahedron method [26], and the self-consistent charge density was obtained with 105 irreducible k-points in the Brillouin zone. The total and partial density of states (DOS), as well as the crystal orbital Hamilton populations (COHP) of selected interactions are presented.

### 2.4. Magnetic susceptibility measurements

The temperature dependent direct current (dc) magnetic susceptibility data were collected in a Quantum Design magnetic property measurement system (MPMS) SQUID magnetometer under applied magnetic fields of 1000–5000 Oe. Specimens from at least two different reaction batches were investigated to ensure the reproducibility of the magnetic data. Both field-cooled (FC) and zero-field cooled (ZFC) measurements were carried out in the temperature range of 1.8–300 K. The field dependent magnetization data were gathered at 1.8 K, with applied magnetic field varied between 0 and 70 kOe. All measurements were performed using approximately 50 mg of powdered sample, filled into custom designed sample holders for air-sensitive materials [27]. The holder contribution was subtracted from the raw magnetization data, which were subsequently converted to molar susceptibility.

### 3. Results and discussion

#### 3.1. Synthesis and chemical formulae

Two different synthetic approaches were used to establish the best route toward single-phase product of the RELiSn2 compounds. The
first method employed 1:1:2 mixtures of RE, Li and Sn—as suggested from the powder X-ray diffraction patterns, which are in excellent agreement with the simulations, the target materials can be produced in high yields. Nevertheless, there remain some minor impurity peaks that could not be assigned to a known phase. In all cases, the single-crystal structure refinements revealed a non-stoichiometric \( \text{RELi}_x\text{Sn}_2 \) (\( x \approx 0.4-0.7 \)), i.e., with Li deficient composition. This is in agreement with the literature, where among the many isostructural compounds \( MT_1X_2 \) (\( 0 < x \leq 1 \); \( M \) is an alkaline-earth or rare-earth metal, \( T \) stands for transition metal, and \( X = \text{Si, Ge, or Sn} \) [5], only very few are fully stoichiometric. Examples here include \( \text{BaCuSn}_2 \) [27], \( \text{SrCuSn}_2 \) [28], \( \text{CaNiGe}_2 \) [29], and \( \text{SrNiGe}_2 \) [30], while a relatively much larger number crystallize with significant amounts of vacancies at the \( T \) sub-lattice, especially among the stannides [31–33].

The above suggests that the \( \text{RELi}_x\text{Sn}_2 \) compounds inherently exist within a certain homogeneity range and may never form in the fully lithiated form. We acknowledge that the homogeneity range may be varied beyond the reported limits with the annealing temperature, which in our case is 600 °C (vs the 200 °C annealing temperature in the original study by Pavlyuk et al. [4]), but since the nominal compositions were Li-rich, we could argue that \( x_{\text{max}} \approx 0.7 \) as seen for \( \text{LaLi}_{0.65}\text{Sn}_2 \) represents the highest amount of Li uptake in this structure. The Li content \( x \) was found to decrease gradually (Table 1) with the decreasing the annealing temperature in the original study by Pavlyuk et al. [4]. Speciﬁcally, it has been reported that the \( b \)-axis is invariant of the size of the rare-earth metals, while the \( a \)- and \( c \)-axis marginally decrease across the series. Overall, the decrease of the unit cell volumes follows the lanthanide contraction, but the data as a whole is inconsistent with our ﬁndings—we report unit cell contraction in all three directions (Table 1). With the Sm-compound, the dependence of the unit cell volume on the lanthanide size abruptly changes slope, indicative of a structural change. The variation in the unit cell volumes between \( \text{SmSn}_2 \) and \( \text{GdSn}_2 \) is miniscule, because of yet another structural rearrangement (Table 2). From \( \text{GdSn}_2 \) on, the structure is retained until \( \text{LuSn}_2 \) (with the exception of \( \text{YbSn}_2 \) which does not exist) [6–8],

Fig. 1. (A) Projection of the crystal structure of \( \text{RELi}_x\text{Sn}_2 \) (\( \text{RE} = \text{La–Nd} \)) along the \( a \)-axis showing intergrowth sequences of \( \text{AlB}_2 \)-like and \( \text{PbO} \)-like slabs. (B) Top view along (0 1 0) of the planar square nets capped alternatively above and below with Li atoms. (C) Cutouts of the 1D \( \text{Sn1A} \) and \( \text{Sn1B} \) zigzag chains exhibiting different bond lengths and angles. (D) Coordination polyhedra for the \( \text{Sn1A} \) and \( \text{Sn1B} \) atoms.
whereby the unit cell axes/volumes decrease monotonically. This has been established by landelli and Palenzenza [6], and confirmed by the single-crystal structures of GdSn2 (Table 2) and LuSn2 (Supporting information).

The idealized, disorder-free structure can be articulated as intergrowth of AlB2- and PbO-like slabs [5]. The Sn1 atoms form 1\textsubscript{1/2}[Sn2] zigzag chain within a layer of fused trigonal prisms of RE, an arrangement which is the hallmark of the AlB\textsubscript{2} structure type [5]. The Sn1 and Sn2 atoms form PbO-like slabs, where each Sn atom is in a tetrahedral environment of Li atoms (Fig. 1A). The Li position shows occupational disorder, which correlates with the positional disorder involving the neighboring zigzag chain—the Sn1 site splits into two distinct Sn1A and Sn1B positions. A simultaneous occupation of Sn1A and Sn1B is not allowed due to the unphysical distance between them (ca. 0.4–0.5 Å). The same holds true for the Li and Sn1B positions (distance ca. 2.0–2.1 Å). Therefore, Li and Sn1B are treated as mutually exclusive.

If we consider the zigzag chain made of Sn1A only, the Sn1A–Sn1A distances vary between 2.683(3) and 2.641(8) Å, and the Sn1A–Sn1A–Sn1A angle ca. 113.2° (Fig. 1C), almost invariant of the unit cell contraction between LaLi\textsubscript{0.69(1)}Sn2 and NdLi\textsubscript{0.44(1)}Sn2. The Sn1B–Sn1B interatomic distances vary in the range 3.309(6)–3.165(2) Å, and the Sn1B–Sn1B–Sn1B angle decreases slightly from 88.3° (4°) to 85.09(2)° between the La- and Nd-analogs. The longer bonds and the more “kinked” topology of the Sn1B zigzag chain (i.e., no Li atom present) means that the Sn1B atom comes closer to its Sn2 neighbor from the square net, probably allowing some indirect interaction to compensate for the empty space [35].

The Sn1A atoms take the position near the center of trigonal prisms of RE atoms, having two Sn1A, and one Li atoms capping the rectangular faces (Fig. 1D). The Sn1A–Li distances are reasonable, ca. 2.6 Å, but shorter when compared to the sum of the covalent radii between the Li and Sn atoms (~2.9 Å) [34], which may be suggestive of much larger displacement of the Li atoms. Sn–Li distances as short as ca. 2.7 Å are reported in some binary compounds such as Li\textsubscript{17}Sn\textsubscript{4} [36], LiSn [37], and Li\textsubscript{2}Sn [38].

Concerning the Sn1A/Sn1B–RE distances, there appear to be no unphysically short contacts due to the disorder/offsetting of the Sn1 atom. The Sn1A–RE distances are distributed over the ranges 3.422(1)–3.320(2) Å and 3.541(3)–3.371(5) Å, respectively, on passing from LaLi\textsubscript{0.69(1)}Sn2 to NdLi\textsubscript{0.44(1)}Sn2 (Table 5). The corresponding Sn1B–RE distances fall in the intervals 3.281(1)–3.213(2) Å and 3.916(6)–3.686(6) Å, respectively. For comparison, the Sn2–RE contacts vary between 3.509(1) Å and 3.394(1) Å as the size of the rare-earth decreases from La to Nd within these structures.

The PbO-like slabs feature planar square nets of Sn2 atoms, capped above and below (alternatively) by the Li atoms (Fig. 1B) to form puckered [Li\textsubscript{2}Sn\textsubscript{4}] layers propagating along the ac-plane. Each Sn2 atom is coordinated by four other Sn2 atoms with Sn2–Sn2 distances ranging from 3.1941(6) Å to 3.1468(2) Å on going from the La- to the Nd-analog. These distances are considerably longer than the averaged Sn1A–Sn1A/Sn1B distance and the Sn–Sn distance in a-Sn (4 × 2.81 Å) [20]. These values match the contacts in the metallic β-Sn (4 × 3.02 Å and 2 × 3.18 Å) [20], suggesting weaker covalent interactions between the Sn2 atoms. Papanio and Hoffmann had analyzed in detail this scenario, dubbed as hypervalent bonding [35]—such configuration may favor a distortion leading to breaking or puckering of the Sn2 sheets. Interestingly, we found elongated anisotropic displacement parameters \(U_{22} \approx 2.3 \times 10^{-2} \text{Å}^2\) from averaging the \(U_{22}\) values in Table S1 in Supplementary information) for the Sn2 atoms suggesting a possible small Peierls distortion transforms these hypervalent square nets into classical structures with reduced dimensionality (such as closely spaced zigzag chains the ac-plane) [35]. However, there were no satellite reflections present in the gathered X-ray data, which could indicate superstructures or lowered symmetry due to ordering of the Li vacancies and/or breaking the \(\frac{1}{2}[\text{Sn}_2]\) square nets (a recent example of a modulated superstructure where this has been observed is the structurally related TbFe\textsubscript{3}Ge\textsubscript{5} [39]).

There are two distinct Sn2–Sn2–Sn2 angles, which are almost invariant of the unit cell metrics, and measure around 88.9° and 91.1°. The Li atom that caps the Sn layer is located at distances ca. 2.5–2.6 Å. These shortened distances attest for the “crowdedness” of the structure and help explain the gradual decrease of the Li content with the lanthanide contraction—likely, the “free volume” within the RESn2 sub-structure is not sufficient for a complete lithiation without additional structural distortion. To evaluate this hypothesis, we re-plotted the structure in a way that emphasizes the distribution, packing and connection of RE/Sn polyhedra, centered by the Li atoms (Fig. 2). Their volumes, as well as the volumes of the Voronoi cells were calculated with the aid of the NRCVAX software package [40]. As expected, between LaLi\textsubscript{0.69(1)}Sn2 and NdLi\textsubscript{0.44(1)}Sn2, the volumes of these partially filled trigonal prisms, were found to decrease from 62.96 Å\textsuperscript{3} to 57.66 Å\textsuperscript{3}, and the volumes of the Voronoi cells to decrease from 19.64 Å\textsuperscript{3} to 17.71 Å\textsuperscript{3}, respectively. These results are consistent with the observed reduction of the b-axis, and bolster the supposition that stoichiometric RELiSn2 phases, as reported in the literature [4], are unlikely, even with the very early lanthanides. Further, because of the quickly diminishing volumes, Li uptake falls off rapidly, and it is very plausible that RELiSn2 cannot be formed with the mid-to-late rare-earth metals; instead the Li-free RESn2 (RE=Gd–Lu) exist.

3.3. Structures of Sn2 and GdSn2

The RELiSn2 series appears to end with RE=Nd, and for RE=Sm, the same structure could not be realized. Instead, the binary SmSn2 phase (Fig. 3—ZrGa2 structure type, space group Cmcm, Pearson symbol oC\textsubscript{12}) [5,11] was formed. The nominally divalent Eu afforded only EuSn3 [41], and another, yet unidentified product, while for RE=Gd, the major product of the Gd–Li–Sn reaction was the binary GdSn3 phase (Fig. 4—ZrSn2 structure type, space group Cmcm, Pearson symbol oC\textsubscript{12}) [5,11].

SmSn2 had been previously reported from powder X-ray diffraction data as part of the study on the RESn\textsubscript{3}–Sn\textsubscript{2} homologous series by Rogl et al. [7]. GdSn2 had been previously identified, also from its powder X-ray diffraction pattern by Landelli and Palenzenza [6]. The unit cell volumes for SmSn2 and GdSn2 from the literature are in good, but not perfect agreement with ours (Table 2). Advances in the quality of rare-earth metals and/or differences in the diffraction equipment are among the most likely reasons for the observed discrepancies. Here, we re-evaluate the two structures on the basis of single-crystal work and provide more accurate atomic coordinates, displacement parameters, and distances.

The structure of SmSn2 is described by four crystallographically independent positions with different site symmetries (Table 4). The Sn1 atoms form \(\frac{1}{2}[\text{Sn}_2]\) zigzag chains along the a-axis (Fig. 3A). A cutout of the zigzag chain is shown in Fig. 3B. The Sn1–Sn1 distance of 3.035(2) Å is slightly smaller compared to the distance of 3.22 Å reported in the literature [7]. The Sn1–Sn1 angle of 93.823(5)° also differs from the reported angle (86.63°). The zigzag chains alternate with layers of \(\frac{1}{2}[\text{Sn}_2]\) square nets, which are formed by Sn2 and Sn3 atoms with Sn2–Sn3 distance of 3.1657 (7) Å. Note that because of the significant contraction of the b-axis, one might consider the zigzag chains and the square nets as “merged” with Sn1–Sn2 and Sn1–Sn3 distances of 3.682(1) Å and 3.651(1) Å (vertical separation between them of only 2.906 Å). Taking this into consideration, an alternative description of the structure emerges—layers of elongated, vertex-shared [Sn\textsubscript{6}] octahedra alternating with layers of Sn atoms. As discussed by Rogl and co-workers [7], this structure is an early member of the
REN Sn₃ homologous series, which starts with \( \text{RESn} \) (orthorhombically distorted CsCl structure type, \( n=1 \)) and ends with \( \text{RESn}_3 \) (AuCu₃ structure type, \( n=\infty \)), where the vertex-shared \([\text{Sn}6]\)-octahedra are extended in a 3D-structure. This crystal chemistry also bears resemblance with the perovskites, and with the layered structures of the Ruddleson–Popper phases [42].

We must also note that analysis of the anisotropic displacement parameters (\( U_{ij} \)) given in Supplementary information (Table S2) revealed that the \( U_{22} \) (2.24 \( \times 10^{-2} \) Å²) for Sn1, \( U_{33} \) (2.86 \( \times 10^{-2} \) Å²) for Sn2 and \( U_{11} \) (2.86 \( \times 10^{-2} \) Å²) for Sn3 are slightly enlarged, which induces a change from their ellipsoids shape-like to prolate ellipsoids directed towards (0 1 0), (0 0 1),
Sn1 distances in the isotypic LuSn2, also recalculated from powder data [6]. We can also compare the Sn1 distances (2.9683(5) Å, slightly shorter when compared to those (3.094 Å) reported from the early work [6]). The Sn1–Sn2 bond length within the zigzag chains (Fig. 4), aligned along the c-axis. The refined Sn1–Sn1 distances are 2.9683(5) Å, slightly shorter when compared to those (3.094 Å) calculated from powder data [6]. We can also compare the Sn1–Sn1 distances in the isotopic LuSn2, also refined from single-crystal data (2.959(1) Å, see Supporting information), which shows that the lanthanide contraction and the corresponding unit cell volume change has a small effect on the Sn1–Sn1 bonding. This also underscores the importance of refining structures, even when the work may appear redundant. This point is particularly well illustrated by comparing the Sn2–Sn2 bond length within the $\frac{2}{3}$[Sn2] square nets—refined value of 3.094(1) Å, vs 3.037 Å, reported from the early work [6] ($d_{Sn2-Sn2}=3.0323(8)$ Å in LuSn2, see Supporting information). The Sn2 bonds appear to be more sensitive to the volume change from GdSn2 to LuSn2, the planar square nets in the RELiSn2 (RE=La–Nd) series (Table 5) are even more expanded. The shortest Gd–Sn contacts occur between Gd and Sn1 and vary from 3.158(1) Å to 3.461(1) Å.

Last, we briefly compare the structures of GdSn2 and SmSn2. The basic building blocks here are nearly identical, the valence electron counts are the same. What are the differences? The Sn positions are nearly identical (CN 8, r(Gd3+)=1.193 Å, r(Th4+)=1.193 Å [44]), yet, in the ThSn2, the vertical separation between the zigzag chains and the square nets is almost 0.13 Å larger at 3.257 Å, in spite of the very similar Th–Sn and Gd–Sn distances. This "oxidation" of the square nets, where the formal electron counts change from the electronically saturated (Th4+)$\frac{1}{2}$[Sn2]$_{12}$ to (Gd3+)$\frac{1}{2}$[Sn2]$_{12}$ has already been discussed in the review by Papoian and Hoffmann [35] on hypervalent bonding in chains and sheets formed by the light and the heavy groups 14, 15 and 16 elements.

### 3.4. Electronic structure

Having just mentioned the valence electron count in GdSn2 and ThSn2 is a perfect way to begin the discussion on the electronic structure. Note that based on the formal charges, all Li-free RESn2 (RE=Gd–Lu) phases will have less than optimal electron count, since the ideal valence electron count for square sheet of Sn atoms is 6 e–/atom [35], and it cannot be met if the cation is a trivalent rare-earth metal (vide supra). This has been previously discussed elsewhere [35], and our tight-binding linear-muffin-tin-orbital (TB-LMTO-ASA) electronic structure calculations for LuSn2 (supporting information) confirm that the Fermi level is indeed located in a region of relatively high DOS. Just above it, a deep pseudo gap indicates that an electron-richer structure could be electronically more stable. This would be the case for an idealized LiLaSn2, where one more electron from the inserted Li atom restores the optimal valence electron count.

The TB-LMTO-ASA electronic structure calculations for a model LaLiSn2 (coordinates and unit cell dimensions from LaLi0.69(1)Sn2, with the occupancy of Li assumed to be full, and the Sn1 splitting neglected) confirm this reasoning. The plots of the computed interaction that overrides the apparent electronic instability of the structure (vide infra). Further evidence supporting this line of thinking comes from comparing the isosstructural, but not isoelectronic GdSn2 (11 valence electrons per formula unit) and ThSn2 (12 valence electrons per formula unit) [43]. Note that the ionic radii for the Gd3+ and Th4+ ions are nearly identical (CN 8, r(Gd3+)=1.193 Å, r(Th4+)=1.193 Å [44]), yet, in the ThSn2, the vertical separation between the zigzag chains and the square nets is almost 0.13 Å larger at 3.257 Å, in spite of the very similar Th–Sn and Gd–Sn distances. This "oxidation" of the square nets, where the formal electron counts change from the electronically saturated (Th4+)$\frac{1}{2}$[Sn2]$_{12}$ to (Gd3+)$\frac{1}{2}$[Sn2]$_{12}$ has already been discussed in the review by Papoian and Hoffmann [35] on hypervalent bonding in chains and sheets formed by the light and the heavy groups 14, 15 and 16 elements.
density of states (DOS) and the crystal orbital Hamilton populations (COHP) are shown in Fig. 5. In the total DOS diagram (Fig. 5 (a)), there is no band gap between the valence band and conduction band, which suggests the metallic behavior of LaLiSn₂. The Fermi level (solid line) is located in a region of relatively low DOS (pseudo gap), indicating favored electronic structure. The bands in the DOS curve can be separated into two energy ranges. Below the Fermi level from 0 eV to −4 eV, the contributions of the bands are mainly from La 5d and Sn 5p bands, where in the range from −5 eV to −10 eV, the major part of the DOS is from the Sn 5s band. In both energy ranges, significant overlapping of the bands from La, Li and Sn indicates strong bonding interactions between the atoms of these elements. This is a typical feature of the polar intermetallics, in which the covalency of the interaction between the atoms of these elements. This is a typical feature of the polar intermetallics, in which the covalency of the interaction between the atoms of these elements. This is a typical feature of the polar intermetallics, in which the covalency of the interaction between the atoms of these elements. This is a typical feature of the polar intermetallics, in which the covalency of the interaction between the atoms of these elements.

Fig. 5. (A) Calculated DOS diagrams for LaLiSn₂. The Fermi level is set as the energy reference at 0 eV. (B) Partial DOS curves for s, p, d bands of La. (C) Partial DOS curves for s, p bands of Sn. (D) Partial DOS curves for s, p bands of Li. (E) Integrated COHP curves of the La–Sn, Li–Sn, and Sn–Sn interactions. Since the “inverted” COHP values are plotted, the positive regions represent the bonding interactions, while the negative regions denote antibonding interactions.

3.5. Magnetism

Fig. 6 shows the temperature dependence of the molar magnetic susceptibility $\chi^{-1}(T)$ of the $\mbox{RELi}_x\mbox{Sn}_2$ ($\mbox{RE}=\mbox{Ce–Nd}$) series. As the temperature increase above 100 K, the $\chi^{-1}(T)$ plot follows well the Curie–Weiss law $\chi(T) = C/(T - \theta_p)$ [45], where $\theta_p$ is the paramagnetic Weiss temperature and $C$ is the Curie constant defined as $C = \mu_0 g^2 \mu_B^2 / 3 k_B$, where $\mu_0 = 4 \pi \times 10^{-7} \, \text{H m}^{-1}$ is the permeability of the vacuum, $\mu_B$ stands for the effective magnetic moment, and $k_B = 1.38 \times 10^{-23} \, \text{J K}^{-1}$ is the Boltzmann constant. The effective magnetic moments derived from the linear fits of the inverse susceptibility are 2.61 $\mu_B$ ($g(J(J+1))^{1/2} = 2.54 \mu_B$) for the Ce, 3.56 $\mu_B$ ($g(J(J+1))^{1/2} = 3.58 \mu_B$) for the Pr, and 3.61 $\mu_B$ ($g(J(J+1))^{1/2} = 3.62 \mu_B$) for the Nd-compound, respectively. As compared to the free-ion moments from the Hund’s rule [45] (given in parentheses, in which $g$ is the Landé factor and $J$ stands for the total angular momentum of the 4f-shell), the estimated effective magnetic moments are very close, indicating the well-localized nature of the 4f-electrons in all three cases. The numbers also confirm the expected 3+ ground states for Ce, Pr, and Nd.

The paramagnetic Weiss temperatures, $\theta_p$, for all samples were found to be positive and gradually decreasing from 12 K to 2 K on passing from CeLi0.63(1)Sn2 to PrLi0.56(1)Sn2 to NdLi0.44(1)Sn2. The positive values of $\theta_p$ for all three samples indicate that the magnetic interactions in the paramagnetic regime are of ferromagnetic type. These findings in part contradict the results from the original study by Pavlyuk et al. [4], where the Ce- and Pr-samples had negative Weiss temperatures ($\theta_p= -17 \, \text{K}$ and $\theta_p= -3 \, \text{K}$), while the Nd-analog had $\theta_p= -2 \, \text{K}$, matching our data. The earlier measurements did not allow for measurements at sufficiently low temperatures to capture the onset of spontaneous magnetic ordering, while others do—the magnetic ordering temperatures ($T_c$) calculated from the mid-point of jump in the $\chi(T)$ curves are close to 8–9 K for the Ce- and Pr-samples and almost 15 K for the Nd-sample. Fig. 6D displays the dependence of both $\theta_p$ and $T_c$ with the De Gennes factor $(g-1)^2J(J+1)$ [45], which clearly suggest that the magnetic response of these materials is not trivial. Further experimental data backing up this conjecture are the divergent ZFC and FC curves for PrLi0.56(1)Sn2, and NdLi0.44(1)Sn2 (see Supporting information), which could indicate metamagnetic behavior similar to that of PrSn2 (ZrGa2 type), which at low field appears to be an antiferromagnet like its PrSn2 counterpart [7], but at higher applied fields shows parallel alignments of the Pr-moments. We can also cite here the refinements from neutron diffraction for the binary phases with the heavy rare-earth metals RESn2 ($\mbox{RE}=\mbox{Tb–Tm}$) [8], which show the existence of sine-modulated magnetic structures undergoing successive transitions to collinear antiferromagnetically ordered states at lower temperatures. Given this level of complexity, we are preparing for field-dependent measurements, as well as ac-magnetometry and neutron diffraction investigations, which are needed to clarify the behavior of the RELiSn2 ($\mbox{RE}=\mbox{Ce–Nd}$) samples.

4. Conclusions

The crystal structures of the RELiSn2 ($\mbox{RE}=\mbox{La–Nd}$, Sm, Gd; $0 \leq x < 1$) compounds have been revised on the basis of single-crystal X-ray diffraction data. We have shown that these compounds crystallize with the defect CeNiS2 structure, within which
the Li positions feature significant deficiencies leading to a large displacement of the Li atoms along the $b$-axis. Consequently, the Li–Sn1 interactions are shortened, causing a split atomic position Sn1A and Sn1B. The Li deficiency and the refined occupation factor of the Sn1B atoms were found to increase monotonically with the decreasing size of the rare earth atoms. This led to intricate pattern of correlated disorders between these two atomic positions. The present study did not find any evidence for the existence of modulated superstructures, which might be possible for some compositions within the reported homogeneity range. Further investigations are awaited to clarify this behavior.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2013.12.010.

References


Fig. 6. Magnetic susceptibility vs temperature for polycrystalline CeLi0.63(1)Sn2 (A), PrLi0.56(1)Sn2 (B), and NdLi0.44(1)Sn2 (C). The inverse susceptibilities and how they vary with the temperature are also shown. Panel (D) shows the $T_C$ and $\theta_P$ variations with the deGennes factors for the 3 measured samples. ZFC and FC data are overlayed and the only places where divergence is observed are the data at the lowest temperature for PrLi0.56(1)Sn2 (B), and NdLi0.44(1)Sn2 (C). We refer the reader to the online Supporting Information for magnified views of the low temperature regions.