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“Nanoscale Zippers” in Gd5(SixGe1-x)4: Symmetry and Chemical Influences on the Nanoscale Zipping Action

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“Nanoscale Zippers” in Gd5(Si_xGe_1-x)_4: Symmetry and Chemical Influences on the Nanoscale Zipping Action

Abstract
One critical parameter influencing the structural nature of the phase transitions in magnetocaloric materials Gd_5(Si_xGe_1-x)_4 is the Si/Ge ratio (x/1 − x), because transition temperatures and structures depend crucially on this value. In this study, single-crystal X-ray diffraction indicates that Si and Ge atoms are neither completely ordered nor randomly mixed among the three crystallographic sites for these elements in these structures. Ge atoms enrich the T sites linking the characteristic slabs in these structures, while Si atoms enrich the T sites within them. Decomposition of the total energy into site and bond energy terms provides a rationale for the observed distribution, which can be explained by symmetry and electronegativity arguments. For any composition in Gd_5(Si_xGe_1-x)_4, a structure map is presented that will allow for a rapid assessment of the specific structure type.

Disciplines
Materials Chemistry | Other Chemistry | Other Materials Science and Engineering | Physical Chemistry

Comments
“Nanoscale Zippers” in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$: Symmetry and Chemical Influences on the Nanoscale Zipping Action

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One critical parameter influencing the structural nature of the phase transitions in magnetocaloric materials Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ is the Si/Ge ratio ($x^4 - x$), because transition temperatures and structures depend crucially on this value. In this study, single-crystal X-ray diffraction indicates that Si and Ge atoms are neither completely ordered nor randomly mixed among the three crystallographic sites for these elements in these structures. Ge atoms enrich the T sites linking the characteristic slabs in these structures, while Si atoms enrich the T sites within them. Decomposition of the total energy into site and bond energy terms provides a rationale for the observed distribution, which can be explained by symmetry and electronegativity arguments. For any composition in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, a structure map is presented that will allow for a rapid assessment of the specific structure type.

Introduction

Aside from the fascinating magnetic and electrical properties discovered in the Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ system such as the giant magnetocaloric effect,¹ colossal magnetostriiction,² giant magnetoresistance,³ spontaneous voltage generation,⁴ and an unusual Hall effect,⁵ one structural feature of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ that has captured the attention of solid-state chemists is its remarkable ability to cleave or re-form the covalent bonds between pairs of (Si, Ge) atoms during the magnetically coupled, crystallographic phase transition for $x \leq 0.503$ in the vicinity of respective transition temperatures.⁶,⁷ Across these transitions, the distances between pairs of (Si, Ge) atoms change by ca. 0.9 Å. Since the making and breaking of covalent bonds are reminiscent of the closing and opening action of a zipper, Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ can be considered as “nanoscale zippers” in the solid state.⁸ The three “nanoscale zipper” structures observed in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ at room temperature are the Sm$_5$Ge$_4$-type¹⁰ (orthorhombic, Pnma, $0 \leq x \leq 0.3$), the Gd$_5$Si$_2$Ge$_2$-type¹¹ (monoclinic, P1121/a, 0.43 $\leq x \leq 0.503$), and the Gd$_5$Si$_1$-type¹¹ (orthorhombic, Pnma, 0 $\leq x \leq 0.3$).


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of chemical structure. Here we report single-crystal X-ray diffraction studies on the Ge-rich region of Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\))\(_4\), thereby monitoring any changes in atomic coordinates as well as Si/Ge occupation at each T site across the Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\))\(_4\) series. While compiling the cell parameter data in the Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\))\(_4\) system, we note that a simple plot of c/a ratio vs b/a ratio can effectively separate three known structure types in Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\))\(_4\). This plot can be used as a structure sorting map and will allow rapid assessment of the three structure types in the Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\))\(_4\) and its related systems.

### Experimental and Theoretical Methods

**Synthesis.** The Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\))\(_4\) samples, where x = 0, 0.11, 0.32, and 0.46, were prepared by arc-melting its constituent elements in an argon atmosphere on a water-cooled copper hearth. The starting materials were high purity Gd (99.99 wt %, Materials Preparation Center of the Ames Laboratory), Si (99.9999 wt %, CERAC, Inc.), and Ge (99.9999 wt %, CERAC, Inc.). Each alloy was remelted several times from both sides of the arc-melted button to ensure homogeneity. Single crystals were selected from the as-cast sample. Final products were analyzed using semiquantitative energy dispersive spectroscopy (EDS) attached to a scanning electron microscope (SEM). The differences between starting and measured sample compositions were within 3 at. %.

**X-ray Crystallography.** X-ray diffraction data were collected at 292 K using a Bruker CCD-1000, three-circle diffractometer with Mo K\(_\alpha\) radiation (\(\lambda = 0.71073 \, \text{Å}\)) and a detector-to-crystal distance of 5.08 cm on 2–3 crystal specimens for each composition. Data were collected in at least a quarter hemisphere and were harvested by collecting three sets of frames with 0.3 s exposure time of 20 frames. The range of 2\(\theta\) extended from 3.0 to 56.0\(^\circ\). The reflections were extracted from the frame data using the SMART program\(^{15}\) and then integrated using the SAINT program.\(^{15}\) Data were corrected for Lorentz and polarization effects. Absorption corrections using SADABS\(^{15}\) were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent reflections. Unit cell parameters were indexed by peaks obtained from 90 frames of reciprocal space images and then refined using all observed diffraction peaks after data integration. The structure solution was obtained by direct methods and refined by full-matrix least-squares refinement of \(F^2\) using the Bruker SHELXTL package.\(^{15}\) Table 1 lists crystallographic data.

<table>
<thead>
<tr>
<th>x</th>
<th>0</th>
<th>0.11</th>
<th>0.32</th>
<th>0.46</th>
</tr>
</thead>
<tbody>
<tr>
<td>param</td>
<td>0</td>
<td>0.11</td>
<td>0.32</td>
<td>0.46</td>
</tr>
<tr>
<td>crystal system</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>Pnma (No. 62)</td>
<td>Pnma (No. 62)</td>
<td>Pnma (No. 62)</td>
<td>P112(\tilde{a}) (No. 14)</td>
</tr>
<tr>
<td>a, Å</td>
<td>7.697(1)</td>
<td>7.689(1)</td>
<td>7.665(1)</td>
<td>7.587(1)</td>
</tr>
<tr>
<td>b, Å</td>
<td>14.831(1)</td>
<td>14.823(2)</td>
<td>14.809(2)</td>
<td>14.798(2)</td>
</tr>
<tr>
<td>c, Å</td>
<td>7.785(1)</td>
<td>7.777(1)</td>
<td>7.769(1)</td>
<td>7.790(3)</td>
</tr>
<tr>
<td>y, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(V, \text{Å}^3)</td>
<td>888.7(2)</td>
<td>886.4(2)</td>
<td>882.0(2)</td>
<td>872.2(2)</td>
</tr>
<tr>
<td>(R_1) [I &gt; 2(\sigma(I))]</td>
<td>0.0287</td>
<td>0.0597</td>
<td>0.0421</td>
<td>0.0419</td>
</tr>
<tr>
<td>w(R_2) [I &gt; 2(\sigma(I))]</td>
<td>0.0739</td>
<td>0.2042</td>
<td>0.1064</td>
<td>0.0754</td>
</tr>
<tr>
<td>(R_1) (all data)</td>
<td>0.0394</td>
<td>0.0641</td>
<td>0.0540</td>
<td>0.0836</td>
</tr>
<tr>
<td>w(R_2) (all data)</td>
<td>0.0828</td>
<td>0.2077</td>
<td>0.1128</td>
<td>0.0829</td>
</tr>
</tbody>
</table>

(13) For example, one can generate a series of Gd\(_3\)Si\(_4\)Ge\(_4\) type structures with a stoichiometry of Gd\(_3\)(Si\(_{1-x}\)Ge\(_x\))\(_4\) in various ways. Some examples are Gd\(_3\)(Si\(_{1-x}\)Ge\(_x\))\(_4\), Gd\(_3\)(Si\(_{1-x}\)Ge\(_x\))\(_4\) and Gd\(_3\)(Si\(_{1-x}\)Ge\(_x\))\(_4\) and its related systems.
(14) X-ray single-crystal diffraction is far superior to X-ray powder diffraction to determine the occupation in mixed atomic sites. Although there are powder refinements reported on various Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\))\(_4\), all of these refinements were based on the assumption that all T sites are occupied by statistical mixtures of Si and Ge atoms. See ref 9d and the following: Morellon, L.; Blasco, J.; Algarabel, P. A.; Ibarra, M. R. Phys. Rev. 2000, B62, 1022.
“Nanoscale Zippers” in Gd₅(Si₁₋ₓGeₓ)₄

Results and Discussion

Table 2. Positional Coordinates, Site Occupancies, and Isotropic Displacement Parameters for Gd₅(Si₁₋ₓGeₓ)₄ at 292 K

<table>
<thead>
<tr>
<th>x</th>
<th>y/a</th>
<th>z/b</th>
<th>z/c</th>
<th>occ</th>
<th>Ueq</th>
<th>Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11</td>
<td>Gd₁</td>
<td>0.97585(10)</td>
<td>0.39988(5)</td>
<td>0.17788(10)</td>
<td>1</td>
<td>0.0077(3)</td>
</tr>
<tr>
<td>Gd₂</td>
<td>0.62314(9)</td>
<td>0.38328(5)</td>
<td>0.8351(9)</td>
<td>1</td>
<td>0.0065(3)</td>
<td></td>
</tr>
<tr>
<td>Gd₃</td>
<td>0.20949(13)</td>
<td>3/4</td>
<td>0.49913(13)</td>
<td>1</td>
<td>0.0058(4)</td>
<td></td>
</tr>
<tr>
<td>T₁</td>
<td>0.78241(19)</td>
<td>0.45610(11)</td>
<td>0.5329(2)</td>
<td>1</td>
<td>0.0072(4)</td>
<td></td>
</tr>
<tr>
<td>T₂</td>
<td>0.0823(3)</td>
<td>3/4</td>
<td>0.1129(3)</td>
<td>1</td>
<td>0.0073(6)</td>
<td></td>
</tr>
<tr>
<td>T₃</td>
<td>0.3261(3)</td>
<td>3/4</td>
<td>0.8653(3)</td>
<td>1</td>
<td>0.0071(6)</td>
<td></td>
</tr>
<tr>
<td>0.46</td>
<td>Gd₁A</td>
<td>0.99423(13)</td>
<td>0.40126(8)</td>
<td>0.18074(13)</td>
<td>1</td>
<td>0.0092(3)</td>
</tr>
<tr>
<td>Gd₁B</td>
<td>0.98277(13)</td>
<td>0.90111(8)</td>
<td>0.81812(13)</td>
<td>1</td>
<td>0.0101(3)</td>
<td></td>
</tr>
<tr>
<td>Gd₂A</td>
<td>0.64324(13)</td>
<td>0.38121(7)</td>
<td>0.83679(13)</td>
<td>1</td>
<td>0.0089(3)</td>
<td></td>
</tr>
<tr>
<td>Gd₂B</td>
<td>0.32985(13)</td>
<td>0.87798(7)</td>
<td>0.17734(13)</td>
<td>1</td>
<td>0.0089(3)</td>
<td></td>
</tr>
<tr>
<td>Gd₃</td>
<td>0.17551(15)</td>
<td>0.74650(8)</td>
<td>0.50549(13)</td>
<td>1</td>
<td>0.0092(3)</td>
<td></td>
</tr>
<tr>
<td>T₁A</td>
<td>0.7935(4)</td>
<td>0.4572(2)</td>
<td>0.5362(4)</td>
<td>1</td>
<td>0.0071(6)</td>
<td></td>
</tr>
<tr>
<td>T₁B</td>
<td>0.1548(4)</td>
<td>0.9593(2)</td>
<td>0.4704(4)</td>
<td>1</td>
<td>0.0077(6)</td>
<td></td>
</tr>
<tr>
<td>T₂</td>
<td>0.0475(4)</td>
<td>0.7513(3)</td>
<td>0.1084(4)</td>
<td>1</td>
<td>0.0115(13)</td>
<td></td>
</tr>
<tr>
<td>T₃</td>
<td>0.2923(4)</td>
<td>0.7517(2)</td>
<td>0.8686(4)</td>
<td>1</td>
<td>0.0085(11)</td>
<td></td>
</tr>
</tbody>
</table>

All T₁, T₂, and T₃ atomic sites are fully occupied with Si and Ge atoms. Only Ge occupations are listed. Anisotropic thermal displacement parameters can be received from the authors upon request.

Electronic Structure Calculations. Tight-binding, linear muffin-tin orbital (TB-LMTO) electronic band structure calculations in the atomic sphere approximation (ASA) were carried out for various models of Gd₅Si₄Ge₂ (discussed in a subsequent section) using the LMTO47 program. Exchange and correlation were treated in a local density approximation. All relativistic effects except spin–orbit coupling were taken into account using a scalar relativistic approximation. The radii of the Wigner–Seitz (WS) spheres were obtained by requiring the overlapping potential to be the best possible approximation to the full potential according to an automatic procedure—no empty spheres were necessary. The WS radii determined by this procedure for the atoms in Gd₅Si₄Ge₂ are 1.847 Å for Gd, 1.541 Å for the T₁ position, and 1.505 Å for the T₂ and T₃ positions. The basis set included Gd 6s, 6p, and 5d orbitals, Si 3s, 3p, and 3d orbitals, and Ge 4s, 4p, and 4d orbitals. The Gd 4f orbitals were treated as core functions with seven valence electrons. Furthermore, the Si 3d and Ge 4d orbitals were treated by the Löwdin downfolding technique.

The k-space integrations to determine the total valence electron energies and crystal Hamiltonian orbital populations (COHP) were performed by the tetrahedron method using between 32 and 50 k-points in the irreducible wedges of the appropriate unit cells.

Results and Discussion

Structures. At room temperature, the Gd₅(Si₁₋ₓGeₓ)₄ structures adopt the orthorhombic Sm₅Ge₄-type for x = 0, 0.11, and 0.32 and the monoclinic Gd₅Si₄Ge₂-type for x = 0.46 (Figure 1). Low-temperature structures, i.e., below the corresponding transition temperatures, are all of the Gd₅Si₄Ge₂-type. One notable point is that coordinates of the individual atomic sites do not change significantly in a given structure.
type as can be seen in Table 2, regardless of the Si content. This cannot be seen easily in previous X-ray powder diffraction patterns. As mentioned in the Introduction, the critical difference between the Sm$_3$Ge$_2$-type and the Gd$_5$Si$_2$-Ge$_2$-type is how the $\alpha$-[Gd$_3$T$_2$] slabs are connected: either by dimers or nonbonded, isolated “monomers”. Figure 1 shows two kinds of T–T dimers, e.g., T$_2$–T$_3$ dimers in the slabs and T$_1$–T$_1$ dimers between the slabs. The T$_2$–T$_3$ interatomic distances are slightly dependent on the Si/Ge ratio and range from 2.63 to 2.68 Å as the Ge content increases, which are ca. 5% longer than similar distances in other tetrelide compounds containing 3-stage nets of metals, e.g., the U$_5$Si$_2$-type, the Sm$_3$Ge$_2$-type, and the Cr$_5$B$_3$-type tetrelides. Some examples include 2.525(3) Å for Gd$_5$Mg$_2$Ge$_2$, 2.513(3) Å for Gd$_5$In$_2$Ge$_2$, 2.537(2) Å for La$_5$In$_2$Ge$_2$, 2.620(6) Å for Ho$_5$Ge$_2$, 2.5292(3) Å for Sr$_5$Si$_2$, 2.530(4) Å for Sr$_5$Si$_2$Ge$_2$, 2.471(6) Å for Sr$_5$Si$_2$Ge$_2$O$_{13}$, and 2.474(4) Å for Sr$_5$Si$_3$. On the other hand, in Gd$_5$(Si$_{0.46}$Ge$_{0.54}$)$_4$, as the Si content increases, it is remarkable to see that half of the monomers (T$_1$–T$_1$: 3.5–3.6 Å) in the Sm$_3$Ge$_2$-type becomes dimers (T$_1$A–T$_1$A: 2.5–2.7 Å) in the Gd$_5$Si$_2$Ge$_2$-type while the other half remains as monomers (T$_1$B–T$_1$B: 3.5–3.6 Å). Therefore, the inter slab distance between (Si,Ge)–(Si,Ge) pairs can be viewed as a signature for distinguishing the three structure types, i.e., 2.6 Å for the Gd$_5$Si$_2$-type, 2.6 and 3.5 Å for the Gd$_5$Si$_2$Ge$_2$-type, and 3.5 Å for the Sm$_3$Ge$_2$-type. The structural transition from the Sm$_3$Ge$_2$-type to the Gd$_5$Si$_2$Ge$_2$-type is a rare example of a sequential reduction–oxidation reaction in the solid state.\(^\text{(19)}\)

Si/Ge Occupation and Bond Breaking. Figure 2 illustrates the Ge occupation in each T site in Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ as a function of x. The Si and Ge atoms occupy each T site in a nonstatistical fashion as was already seen in Gd$_5$Si$_2$Ge$_2$. Model (I) space group $Pnma$ contains 100% Ge on T$_1$ sites and 100% Si on both T$_2$ and T$_3$ sites; models (IIa) $(P112/$_a$)$, (IIb) $(P2_1ma)$, and (IIc) $(Pn2_1_a)$ have 50% Si and 50% Ge on the T$_1$ sites, Ge on the T$_2$ sites, and Si on the T$_3$ sites; model (III) has 100% Si on T$_1$ sites and 100% Ge on both T$_2$ and T$_3$ sites. For all model (I) structures, the T$_2$–T$_3$ dimers are heteronuclear. Model (IIa) contains 50% Si–Si and 50% Ge–Ge dimers at the T$_1$–T$_1$ positions, whereas models (IIb,c) involve only heteronuclear Si–Ge dimers at the T$_1$–T$_1$ sites. Table 3 summarizes important results from the TB–LMTO–ASA calculations relevant to the coloring of Si and Ge in Gd$_5$Si$_2$Ge$_2$. Model (I) is most energetically stable, followed by (IIa–c) (ca. 0.069 eV/formula unit) and (III) (0.088 eV/formula unit). The lowest energy model (I) shows the trend found in our diffraction experiments, as this model has Ge atoms between the slabs in the T$_1$ positions and Si atoms within the slabs in the T$_2$ and T$_3$ sites. However, we do not see a complete segregation of Ge and Si in any diffraction experiment on Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$, which can be attributed to the entropy component of the free energy. For the Gd$_5$Si$_2$Ge$_2$ example, the free energy can be approximated by the following expression:

\[
A(T) = E(\psi_f|\psi_f) + TS(\psi_f|\psi_f) + TS(\psi_f|\psi_f)
\]

Here $f_1$, $f_2$, and $f_3$ represent the fractions of models I–III.
constituting the total system (therefore, \( f_1 + f_{II} + f_{III} = 1 \)) and \( f_{II} \) and \( f_{III} \) represent the total energies of models II and III relative to model I (i.e., \( f_I = 0 \)). Due to the constraint on the fractions of each model, the free energy, \( A(T) \), can be plotted as a contour map with respect to two fractions, \( f_1 \) and \( f_{II} \). Figure 3 illustrates these plots for a calculation at low temperature (\( T = 500 \) K) and at high temperature (\( T = 2000 \) K). At high temperature, the minimum free energy value occurs for the fractions \( f_1 = 0.40, f_{II} = 0.31, \) and \( f_{III} = 0.29 \), which gives the T1 site occupancy as \( f_{Ge} = 0.56 \) and \( f_{Si} = 0.44 \). This result is in excellent agreement with experiment. At the lower temperature, we find the minimum value for \( f_1 = 0.59, f_{II} = 0.11, \) and \( f_{III} = 0.30 \), which gives the T1 site occupancy as \( f_{Ge} = 0.70 \) and \( f_{Si} = 0.30 \).

When electronic energies are calculated using a tight-binding scheme, the contribution from the valence electrons to these energies can be divided into two terms: a site energy term; a bond energy term. Within the TB–LMTO–ASA method, we can examine the contribution from the bond energy term by calculating the crystal orbital Hamiltonian population (integrated COHP values). The results for T1–T1 and T2–T3 dimers as well as for Gd–Ge and Gd–Si pairs are summarized in Table 3. Note that there is

---

**Table 3. TB–LMTO–ASA Results from Five Different Structural Models of Gd\(_2\)Si\(_2\)Ge\(_2\)**

<table>
<thead>
<tr>
<th>Model</th>
<th>I</th>
<th>IIa</th>
<th>IIb</th>
<th>IIc</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>tot. energy, eV</td>
<td>0</td>
<td>0.069</td>
<td>0.069</td>
<td>0.069</td>
<td>0.088</td>
</tr>
</tbody>
</table>

The orbital energies used in the calculation of site energy terms are as follows: Ge, \( \epsilon_{Ge} = -0.737 \) eV, \( \epsilon_{p} = -0.310 \) eV, \( \epsilon_{d} = -0.294 \) eV; Si, \( \epsilon_{Si} = -0.662 \) eV, \( \epsilon_{p} = -0.304 \) eV, \( \epsilon_{S} = -0.295 \) eV. The specific orbital energies for Gd are available from the author. Values in boldface indicate the lowest value.

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The competition between the site energy and the bond energy can be seen in structures such as LnAl\(_{2}\)Si\(_{2}\) (0.75 \( \leq x \leq 2 \)) and AEZn\(_2\)Al\(_2\) (\( Ln = La–Tb; AE = Ca, Sr, Ba \); Sec: Miller, G. J.; Lee, C.-S.; Choe, W. *Highlights in Inorganic Chemistry*; Meyer, G., Naumann, D., Wesemann, L., Eds.: Wiley-VCH: Weinheim, Germany, 2002; p 21.)
Therefore, the Gd$_5$Si$_4$-type structures of Gd$_5$Ge$_4$ prefer to have Ge, the more electronegative atom of the two, in T1 sites. The electronegativity difference between Si and Ge manifests itself through the valence atomic orbital energies: $\varepsilon_{4s}(\text{Ge}) < \varepsilon_{3s}(\text{Si})$ and $\varepsilon_{3p}(\text{Ge}) > \varepsilon_{3p}(\text{Si})$ (see Table 3).

How this Gd$_5$(Si$_{1-\lambda}$Ge$_\lambda$)$_4$ series can tolerate such severe changes in T1–T1 bonding still remains as a puzzle despite recent theoretical efforts. Nevertheless, a simple orbital rationale provides an important clue on why only T1–T1 dimers break rather than T2–T3 dimers during the GdSi$_4$-type (LT) → Gd$_5$Si$_2$Ge$_2$-type (RT) transition (see Figure 4). In the GdSi$_4$-type, the coordination environment surrounding each T1–T1 dimer has approximately “$C_{2h}$” ($2/m$) symmetry, which allows orbital mixing between $\sigma_p$ and $\pi^\ast$ (both gerade) or $\sigma$ and $\sigma^\ast$ (both ungerade) molecular orbitals of the dimers. In contrast, the T2–T3 dimers in the slabs of the Gd$_5$Si$_4$-type has “$D_{2h}$” (mmm) symmetry. In this case no mixing is allowed among $\sigma_p$, $\pi$, $\pi^\ast$, and $\sigma^\ast$ orbitals. It is the symmetry-allowed mixing between the $\pi$ and $\sigma^\ast$ molecular orbitals of the T1–T1 dimers that leads to lower integrated COHP values for these interactions as compared to the T2–T3 bonds. Valence s–p orbital hybridization also contributes to the bond breaking phenomena in Gd$_5$(Si$_{1-\lambda}$Ge$_\lambda$)$_4$, and this effect is tied to the distribution of Si and Ge atoms among the T1, T2, and T3 sites. Since $\Delta_{\sigma p}(\text{Ge}) > \Delta_{\sigma p}(\text{Si})$ ($\Delta_{\sigma p} = \varepsilon_{\sigma p} - \varepsilon_{\pi}$), there is greater s–p orbital hybridization in Si than in Ge, which makes the Si–Si $\sigma^\ast$ orbital high in energy and reduces its symmetry-allowed mixing with the $\pi$ orbital for the T1–T1 dimers. Therefore, Ge–Ge dimers will have a greater tendency to break during the phase transitions.

**Structure Map.** While compiling the lattice parameter data for various Gd$_5$(Si$_{1-\lambda}$Ge$_\lambda$)$_4$, we note that the $b/a$ ratio vs $c/a$ ratio plot can be a simple but powerful structure sorting map in this particular series. Kotur and co-workers$^{30}$ tried plotting a map on the basis of $a/b$ and $a/c$ ratios to distinguish binary Ln$_3$X$_4$ structures (Ln = lanthanides and Pu; X = Si, Ge).


“Nanoscale Zippers” in Gd₅(Si₁₋ₓGeₓ)₄

Figure 5. Structure map for 32 room-temperature structures of Gd₅(Si₁₋ₓGeₓ)₄ using the lattice parameter ratios b/a and c/a.6,7,9b,d Each point corresponds to a different value of x, and the three regions are correspondingly labeled.

Ge, Sn, Pb, Rh, Ir, Pt, Au) for a broad spectrum of compounds, but they observed that the separation between different structure types is not evident. Within this specific system, such a map is effective and allows structural characterization on the basis of lattice constant determinations alone. Figure 5 illustrates the b/a ratio vs c/a ratio plot for 32 samples of the Gd₅(Si₁₋ₓGeₓ)₄ series, which shows the three structure types to be well separated. The b/a and c/a ratios are parameters to determine whether the lattice changes are isotropic or not. The most evident change in cell parameters occurs along the a direction. For example, the a parameter for Gd₅Ge₄ is about 3% greater than for Gd₅Si₄. This effect is due to the fact that T–T covalent bond formation or separation occurs parallel to the a direction. Whenever the two-dimensional ∞[Gd₅T₄] slabs are connected by (Si,Ge)–(Si,Ge) dimers, the c/a ratio increases. Therefore, the most dimer-rich structure type, Gd₅Si₄, has the highest c/a ratio. In contrast, the relative change in the b or c lengths is quite small, compared to a direction. The lattice parameter b of Gd₅Ge₄ is 0.6% greater than for Gd₅Si₄ while the lattice parameter c for Gd₅Ge₄ is 0.5% greater than for Gd₅Si₄. Although the difference in relative changes between the b and c direction is miniscule, it does help to separate the three structures as shown in Figure 5. The structure map shown here works especially well when the compounds are in the same series, like Gd₅(Si₁₋ₓGeₓ)₄.

Recently we have found a new Ln₅T₄ series, Gd₅(GaₓGe₁₋ₓ)₄.12d One of its members, Gd₅GaGe₃, demonstrates an intermediate, orthorhombic structure between the Sm₅Ge₄-type and Gd₅Si₄-type, thereby opening up a new possibility of a new Ln₅T₄ series that can continuously vary the bond distance of the T₁–T₁ dimers between the slabs and allows us to study the relationship between the magnetic properties and the dimer separation between the slabs.32

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Supporting Information Available: An X-ray crystallographic file, in CIF format, containing information for Gd₅(Si₁₋ₓGeₓ)₄, where x = 0, 0.11, 0.32, and 0.46, is available free of charge via the Internet at http://pubs.acs.org.

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(31) The cell parameters are from refs 9b,d and the current single crystal work. For the cell parameter b in monoclinic system, \( b' = b \cos(\beta - 90^\circ) \) is used instead because \( b' \) corresponds to \( b \) in the orthorhombic system, which also indicates the thickness of two \( \frac{1}{2}[\text{Gd}_5\text{T}_4] \) slabs in the Gd₅(Si₁₋ₓGeₓ)₄ system.