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Formation of Nets of Corner-Shared Bicapped Gold Squares in SrAu₃Ge: How a BaAl₄-Type Derivative Reconciles Fewer Valence Electrons and the Origin of Its Uniaxial Negative Thermal Expansion

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Supporting Information

ABSTRACT: SrAu₃Ge was synthesized by direct fusion of the mixed elements at high temperature followed by annealing treatments, and its structure was determined by single crystal X-ray diffraction means in space group (Pearson symbol: tP10) P4/mnm, a = 6.264(1) Å, c = 5.5082(9) Å, Z = 2 at room temperature. The structure of SrAu₃Ge, a reapportioned 2 × √2 × 1 superstructure of CeMg₂Si₂ (P4/mnm), exhibits checkerboard nets of corner-shared bicapped Au squares (or corner-shared Au(Au₄/2)Ge octahedra), in which the apical Au–Ge pairs in adjoining nets are strongly interbonded in the c direction. This motif contrasts with that of the common BaAl₄ (P4/mnm) prototype in which Al squares in comparable layers are alternately monocapped by Al from the top or the bottom. Typical examples show valence electron counts (vec) between 12 and 16 for the BaAl₄ type and that for CeMg₂Si₂ is similar, 15. The special stability of SrAu₃Ge, with vec = 9, derives from significant relativistic contribution of the Au 5d¹⁰ states to Au–Ge bonding. These factors are also recognized in the marked redistribution of Au and Ge site occupancies from those in CeMg₂Si₂. SrAu₃Ge exhibits a pronounced uniaxial negative thermal expansion along c, with a coefficient of −1.57 versus 2.16 × 10⁻⁵ K⁻¹ in a and b. The reticulated Au₅Ge octahedral layers expand in the ab plane on heating, whereas the strong, interlayer Au–Ge bonds remain fixed.

INTRODUCTION

Our extended searches for new quasicrystals (QC) and their neighboring approximant crystals (AC) gave us a valuable bonus when we studied the Ca–Au–Ga system, not only an icosahedral QC and two conventional AC phases, but also the closely related 1/0 CaAu₃Ge (Pa₃, a = 9.10 Å). The latter is the structurally simplest cubic approximant and a mimic of icosahedral QC models. The structure features two interpenetrating networks of three-dimensional (slightly distorted) Penrose Tiles that are defined by electropositive Ca and by electronegative Au and Ga atoms, respectively.

To this point, we imagined that chemical and electronic tunings of other possible isotypic phases might serve as suitable starting points for chemical tunings to new QCs and high-order ACs, in parallel to the results with Mg₂Zn₁₁ type precursors. A check of the literature revealed that NaAu₃Si and NaAu₃Ge are the only phases isostructural with CaAu₃Ge; moreover, each has a neighboring Bergman type 1/1 AC (Na₅Au₁₃Si₁₉₂ and Na₆₀Au₇₆Ge₁₉₂) in their respective phase fields. These facts greatly encouraged us to seek other novel examples. Note also that this type of structure is not limited to the Au-rich compounds. The recent discovery of isostructural SrAu₃Ge by Sr2Au₃Sn and Sr3Au₈Sn₃, both with vec = 9, encourages us to seek other examples.

Our first explorations examined the Au-rich phases AeAu₃Tr with Ae = Ca, Sr, Ba, and Tr = Ge, Sn. These yielded exciting results, including not just the expected product CaAu₃Ge but also the unexpected Ca₄₂Au₄₃Sn₄ SrAu₃Ge, Sr₃Au₈Sn₃, and Ba₃Au₃Sn. The latter is the superstructure of CeMg₂Si₂ (P4/mnm), exhibits checkerboard nets of corner-shared bicapped Au squares (or corner-shared Au(Au₄/2)Ge octahedra), in which the apical Au–Ge pairs in adjoining nets are strongly interbonded in the c direction. This motif contrasts with that of the common BaAl₄ (P4/mnm) prototype in which Al squares in comparable layers are alternately monocapped by Al from the top or the bottom. Typical examples show valence electron counts (vec) between 12 and 16 for the BaAl₄ type and that for CeMg₂Si₂ is similar, 15. The special stability of SrAu₃Ge, with vec = 9, derives from significant relativistic contribution of the Au 5d¹⁰ states to Au–Ge bonding. These factors are also recognized in the marked redistribution of Au and Ge site occupancies from those in CeMg₂Si₂. SrAu₃Ge exhibits a pronounced uniaxial negative thermal expansion along c, with a coefficient of −1.57 versus 2.16 × 10⁻⁵ K⁻¹ in a and b. The reticulated Au₅Ge octahedral layers expand in the ab plane on heating, whereas the strong, interlayer Au–Ge bonds remain fixed.

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exploitation of other NTE materials, including a reinvestigation of CeMg$_2$S$_2$. The simple structure of SrAu$_3$Ge$_x$ with only four independent atoms in a unit cell, also may be a great playground for further study of NTE in theory.\textsuperscript{15}

\section*{EXPERIMENTAL SECTION}

\textbf{Synthesis.} All manipulations were performed in a N$_2$-filled glovebox (H$_2$O < 0.1 ppmv). Stoichiometric amounts of dendritic Sr pieces (99.95%, Alfa Aesar), with surfaces manually cleaned by a surgical blade, as-received Au particles (99.999%, Ames Lab), and Ge pieces (99.999%, Alfa Aesar) were welded-sealed into precleaned Ta containers ($\phi \approx$ 0.9 cm) under Ar. The containers were then enclosed in evacuated SiO$_2$ jackets (<10$^{-3}$ Torr). SrAu$_3$Ge was achieved in high yield (>85 vol%) by fusion of stoichiometric mixtures, ~400 mg in total, at 700 °C for 6 h, followed by cooling to 400 °C at a rate of 2 °C/h, annealing there for 6 d, and quenching into water. Reactions of SrAu$_3$Ge$_x$$_{-y}$(x = ± 0.5) yielded mixtures with Sr$_{1-x}$Sr$_{1+y}$Au$_3$Ge$_y$ and so forth as impurities, but the refined lattice parameters (below) indicated that the title phase was close to a line compound. SrAu$_3$Ge is stable in air at room temperature for extended periods, and down to 110 K (see below).

\textbf{Phase Analyses.} These were performed on the basis of powder diffraction data collected by a Huber 670 Guinier powder camera equipped with an area detector and Cu Ka$_1$ radiation ($\lambda = 1.540598$ Å). The detection limit of a second phase with this instrument and system is conservatively estimated to be about 5 vol% in equivalent scattering power. Phase identifications were done with the aid of calculations from PowderCell,\textsuperscript{16} and lattice parameters were refined with the aid of the program UnitCell\textsuperscript{17} from data for at least seven reflection peaks between 16 and 60° in 2θ that were distinguishable from peaks of other phases. The refined lattice parameters for SrAu$_3$Ge in Sr$_{1-x}$Sr$_{1+y}$Au$_3$Ge$_y$ products from reactions with x = −0.5, 0, and 0.5 fell in the range of a = 6.2749(4)–6.2829(4) Å; c = 5.5498(8)–5.4987(8) Å, with maximum differences of ~0.5 and ~3.5 σ in a and c, respectively. Thus, SrAu$_3$Ge appears to have an extremely small phase width.

\textbf{SEM-EDX.} Elemental compositions were determined via semi-quantitative energy-dispersive X-ray spectroscopy (EDX) on a JEOL 5910lv scanning electron microscope (SEM). Samples were mounted in epoxy, carefully polished, and then sputter-coated with a thin layer of graphite-monochromatized Mo K$_\alpha$ radiation ($\lambda$ = 1.209 nm). Samples were first scanned by means of backscattered electrons, through which different phases could be seen in regions with different darkenesses. Elemental proportions for selected single-phase areas were then measured. The average of four readings from a nominal Sr$_2$Ge sample was Sr/Au/Ge = 1:3.0(1):1.0(1) relative to the Sr content. These proportions are consistent with the more precise compositions refined from single crystal X-ray diffraction data.

\textbf{Structure Determination.} Selected single crystals were mounted on a Bruker APEX CCD single crystal diffractometer equipped with graphite-monochromatized Mo K$_\alpha$ radiation ($\lambda$ = 0.71069 Å) radiation. Intensity data were collected in a $\omega$ scan mode over 2θ = 7−57° and with exposures of 30 s per frame. Data sets at room temperature (295 K), 173 K, and 110 K were collected from the same crystal. The lattice parameters refined from all observed reflections were a = 6.2741(10) Å; c = 5.4944 (9) Å at 295 K; a = 6.2618 (10) Å; c = 5.5082 (9) Å at 173 K; and a = 6.2490 (9) Å; c = 5.5104 (8) Å at 110K. The reflections in all data sets were consistent with the primitive 4/m symmetry. Data integration, Lorentz polarization, and absorption corrections were performed with the aid of the subprogram SADABS. Systematic analyses in SHELXTL indicated two possible centric space groups for the first two data sets: P4/n and P4/nmm, but the former symmetry was excluded after additional mirror planes were suggested by the program Platon.\textsuperscript{19}

For the room temperature data, direct methods in the P4/nmm model yielded all four independent atom sites. Of these, three had suitable distances for Au/Ge–Au/Ge contacts, and one for Sr–Au/Ge contacts. Therefore, the former three were temporarily assigned to Au1–Au3 and the other, to Sr. Subsequent refinements converged at R1 ≈ 13.7%. At this stage, the isotropic displacement parameter for one of the three sites assigned to Au was about 7 times the average of the others (0.090 versus 0.013 Å$^2$), suggesting a site for Ge, a Au/Ge mixture, or with fractional occupancy. Assignment of Ge to this produced normal isotropic parameters (0.015–0.021 Å$^2$) for all atoms and a drastically decreased R1 (7.2%). The site occupancies were then separately refined, but all fell well within 1 σ of unity, that is, 0.99(4)–1.00(2). The composition calculated with such assignments was SrAu$_3$Ge, agreeing with the more approximate EDX data. The final refinements with anisotropic displacement parameters yielded R1 = 2.77%, wR2 = 5.74%, and GOF = 1.13 for 177 observed independent reflections. The maximum peak and hole in the difference map were 1.67 and −4.04 e/Å$^3$, respectively, both within 1.21 Å from Ge.

It should be noted that Au1 has the largest isotropic displacement parameters in the structure (0.022 Å$^2$), about 50% larger than the average for the other atoms. The anisotropic displacement parameters revealed that Au1 has elongated ellipsoids in the $ab$ plane (below). This feature is not the result of a wrong atom assignment (above), poor absorption corrections, or poor crystal quality inasmuch as another crystal yielded the same trend. Although such behavior might instead be attributed to an incipient phase transition, the feature remains unchanged after lower temperature X-ray diffraction analyses (below). Twinning in a P4/nm plane as a source of the behavior was ruled out inasmuch as the same dispositions remain on such a refinement. The presence of the additional mirror symmetry in P4/nmm was also established. Rather, the effects are caused by the special geometry of Au$_3$Ge octahedral clusters and the bonding between them, which will be discussed later.

The results for the 110 and 173 K data set are very similar to those of 295 K. As expected, the displacement parameters at lower temperatures are systemically smaller. The crystallographic data and structure refinements for all three temperatures are summarized in Table 1, and the refined positional and isotropic-equivalent displacement parameters, in Table 2. The anisotropic displacement parameters are also given in Table 3 to demonstrate the regularities of the system, and the important interatomic distances are listed in Table 4 together with corresponding −ICOHP values. Detailed crystallographic data are available in the cif outputs (Supporting Information).

\textbf{Electronic Structure Calculations.} The calculations were performed by means of the self-consistent, tight-binding, linear-muffin-tin-orbital (LMTO) method in the local density (LDA) and atomic sphere (ASA) approximations, within the framework of the DFT method.\textsuperscript{20–23} ASA radii were scaled at the limit of 18% maximum overlap between two neighboring atomic spheres, and no interstitial sphere was necessary. The ASA radii for Sr, Au1, Au2, and Ge were about 4.39, 2.89, 2.89, and 2.57 Å, respectively. Reciprocal space

\begin{table}[h]
\centering
\caption{Crystal and Structural Refinement Data for SrAu$_3$Ge at Different Temperatures}
\begin{tabular}{llll}
\hline
\textbf{temp} & 110 K & 173 K & 295 K \\
\hline
\textbf{Fw.} & 751.11 & 751.11 & 751.11 \\
\textbf{Space group, Z} & P4/nmm, 2 & P4/nmm, 2 & P4/nmm, 2 \\
\textbf{unit cell (Å)} & $a$ = 6.2490(9) & 6.264(1) & 6.274(1) \\
& $c$ = 5.5104(8) & 5.5082(9) & 5.4944(9) \\
\textbf{Vol. (Å$^3$)}, & 215.18(5) & 216.12(6) & 216.28(6) \\
$\langle g/cm^3\rangle$ & 11.593 & 11.542 & 11.533 \\
\textbf{data/restr./para.} & 175/0/14 & 174/0/13 & 177/0/13 \\
\textbf{GOF on F$^2$} & 1.209 & 1.223 & 1.128 \\
\textbf{R1/wR2 [1 > 2 σ(I)]} & 0.0214/0.0483 & 0.0223/0.0499 & 0.0277/0.0574 \\
\textbf{Ramd/σ(I)} & 0.0223/0.0485 & 0.0284/0.0511 & 0.0326/0.0560 \\
\textbf{diff. peak/hole (eÅ$^{-3}$)} & 1.96/−2.03 & 2.01/−1.97 & 1.67/−4.04 \\
\hline
\end{tabular}
\end{table}
relativistic effects were included in the calculations. The band structure defined as one-third of the trace of the orthogonalized

Table 4. Important Interatomic Distances (Å) at 110, 173, and 295 K

<table>
<thead>
<tr>
<th>bond</th>
<th>multi.</th>
<th>dist. (Å)</th>
<th>Δd (Å)</th>
<th>−ICOHP (eV/mol)</th>
<th>bond</th>
<th>multi.</th>
<th>dist. (Å)</th>
<th>Δd (Å)</th>
<th>−ICOHP (eV/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au1−Ge</td>
<td>4</td>
<td>2.559(1)</td>
<td>0.001(1)</td>
<td>2.35</td>
<td>Au2−Ge</td>
<td>4</td>
<td>2.558(1)</td>
<td>0.001(1)</td>
<td>2.35</td>
</tr>
<tr>
<td>Au1−Au2</td>
<td>4</td>
<td>2.8259(7)</td>
<td>-0.001(1)</td>
<td>1.28</td>
<td>Sr−Au1</td>
<td>8</td>
<td>3.1245(5)</td>
<td>0.009(1)</td>
<td>3.5310(4)</td>
</tr>
<tr>
<td>Au1−Au1</td>
<td>8</td>
<td>3.1319(5)</td>
<td>0.0125(7)</td>
<td>0.70</td>
<td>Sr−Au2</td>
<td>8</td>
<td>3.2786(5)</td>
<td>0.0125(7)</td>
<td>0.70</td>
</tr>
<tr>
<td>Au2−Ge</td>
<td>2</td>
<td>2.457(3)</td>
<td>-0.001(4)</td>
<td>2.96</td>
<td>Sr−Ge</td>
<td>8</td>
<td>3.450(1)</td>
<td>0.0125(7)</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The molecular orbital analyses for the Au4 square, the Au5Ge octahedron, and their combination were performed using the semiempirical extended-Hückel tight-binding (EHTB) method via CAESAR. The orbital energies (H0) and Slater exponents (ζ) employed in the calculation were: Au 6s, H0 = −10.92 eV, ζ1 = 2.602, c1 = 1.0; 6p, H0 = −5.35 eV, ζ1 = 2.584, c1 = 1.0; 5d, H0 = −11.076 eV, ζ1 = 6.163, c1 = 0.6851, ζ1 = 2.794, c1 = 0.5696. Ge 4s, H0 = −16.0 eV, ζ1 = 2.16, c1 = 1.0; 6p, H0 = −9.0 eV, ζ1 = 1.85, c1 = 1.0.

Results and Discussion

Structure. SrAu3Ge crystallizes in space group P4/nnm (Pearson symbol pI10), with a = √2a0, c = (1/2)c0, in which a0 and c0 denote the lattice parameters of the parent tetragonal BaAl4 (I4/mmm). This structure is isostructural with BaAu3Ge, the structure of which was recently reported without further comment. SrAu3Ge exhibits some close relationships with BaAl4 and its ordered ternary structure types (ThCr2Si2, CaBe2Ge2, and BaNiSn3) and particularly, the primitive CeMg2Si2 in terms of structural motifs. Nonetheless, SrAu3Ge is a notable electron-poor derivative of BaAl4 (P4/nnm) and its progeny, crystallographically, SrAu3Ge (Z = 2) is a reapportioned √2 × √2 × 1 superstructure of CeMg2Si2 (P4/mmm, Z = 1), in which Ce occupies the Wyckoff 1a (0 0 0), Mg occupies 2e (0 1/2 1/2), and Si occupies 2h (1/2 1/2 0) sites, as detailed in Figure 1. Although the conversion to SrAu3Ge reflects straightforward crystallographic relationships, the chemical alterations suggest major differences. The former Wyckoff 2h

Figure 1. The crystallographic and site relationships between SrAu3Ge and its parent CeMg2Si2. The chemical alternations between them are impressive (colored arrows).

Si site in P4/mmm gives rise to two 2c sites in P4/mnm that are now occupied by the contrasting Au2 and Ge, respectively, whereas the former 2e Mg site is converted to
Figure 2. Comparison of structural motifs among (a) SrAu₃Ge, (b) SrAu₂Ge₂ (ThCr₂Si₂ type), and (c) CeMg₃Si₃. Notice also the different unit cell proportions. Gold spheres represent Au; green, Ge; and red, Sr in (a) and (b) and Mg, Si, and Ge, respectively in (c).

4e Au₁ atoms. These redistributions of apparent atom polarities and, especially, the addition of 5d¹⁰ bonding contributions of gold are noteworthy (below). Even so, the space groups of both SrAu₂Ge and CeMg₃Si₃ are maximum Klassengleiche subgroups of that of BaAl₄ (I4/mmm).

Figure 2a shows the extended structure of SrAu₃Ge, with the unit cell outlined with solid black lines. The Au₁ atoms are equally spaced and form a two-dimensional basal square net at \( z = 1/2 \) (dashed). The last feature is a characteristic structural motif of the well-known BaAl₄ prototype and its subtypes, ThCr₂Si₂, CaBe₂Ge₂, and BaNi₅Si₃.¹¹ All BaAl₄ family members exhibit square pyramidal layers in which the basal square nets are alternately capped from above and below, as shown in Figure 2b for the equivalent ternary SrAu₂Ge₂ (ThCr₂Si₂-type).²⁹,³⁰ Such square pyramidal layers appear as checkerboards if the top-capped square nets are deemed as “black” and the bottom-capped as “white”, or vice versa. In comparison, the basal square nets in SrAu₃Ge show a different feature: one-half of the squares are trans-bicapped by apical Au₂ and Ge to form Au₂Ge octahedra, whereas the remaining squares lie opposite Sr cations. The two sets of squares again define a checkerboard pattern, similar to that in SrAu₂Ge₂, but the octahedra themselves generate a second-order checkerboard pattern in consideration of their “polar” character, as shown by the dashed red lines in Figure 3. This is the reason the lattice parameter \( a \) is increased to \( \sqrt{2} a_{\text{eq}} \).

The remarkable layers in SrAu₃Ge can also be viewed as corner-shared “polar” Au₄Ge octahedra with alternating trans-configurations along \( c \) (see Figures 2a and 3). In comparison, corner-shared Mg₄Si₂ octahedra in CeMg₃Si₃ are nonpolar (Figure 2c). In three dimensions, neighboring basal layers in the present example are interlinked through the apical-to-apical Au₂–Ge bonds, the shortest in the structure. This results in the formation of large cavities defined by 8 Au₁, 4 Au₂, and 4 Ge atoms that are customarily occupied by the counter-cationic Sr at \((1/2\,1/2\,0)\). Note that these cavities are exactly sandwiched by two empty squares in the basal layers in the \( c \) direction. In contrast, the parallel cavities in SrAu₂Ge₂ are sandwiched by two square pyramids, thus, adding two additional and more distant capping atoms around Sr and along \( c \), Figure 2b.

As listed in Table 4, the basal-to-apical contacts in SrAu₄Ge at room temperature are 2.835 (1) Å and 2.558 (1) Å for \( d_{\text{Au1–Au2}} \) and \( d_{\text{Au2–Ge}} \) respectively. The latter is \( \sim 0.07 \) Å less than the parallel interaction in SrAu₂Ge₂ (2.628 Å). However, the basal-to-basal distance \( d_{\text{Au1–Au1}} \) is about 0.04 Å larger than that in SrAu₂Ge₂. From another viewpoint, each (Au₁)₆Ge pyramid in SrAu₄Ge is relatively expanded in the \( a–b \) plane or compressed along \( c \) compared with that in SrAu₂Ge₂. The smaller intralayer distance within each octahedron, \( d_{\text{Au2–Ge}} = 3.038(4) \) Å, is one of the additional characteristics. The interlayer Au₂–Ge bond in SrAu₄Ge is, surprisingly, about 0.06 Å shorter than the interlayer Ge–Ge bond in SrAu₂Ge₂ (2.456(3) versus 2.494(4) Å). This distance is even about 0.1 Å less than the sum of the covalent radii of Au and Ge (Au, 1.36 Å; Ge, 1.20 Å) from Alvarez,³¹ a signature of strong covalent bonding. Nevertheless, slightly shorter Au–Ge bonds occur in the isolated molecular-like cluster (Au₄Ge₁₈)⁻ in the \( [\text{K(}[2.2.2]\text{crypt})]_{15}\text{[Au₄Ge₁₈]} \) salt, ~2.437–2.460 Å, in which the coordination number of gold is lower.³²

It should be noted that the basal Au₁ atoms in SrAu₄Ge always exhibit elongated anisotropic ellipsoids in the \( a–b \) plane. The same is true in the isostructural BaAu₄Ge, in which the larger cation also leads to further expansion of both \( d_{\text{Au1–Au1}} \) in the basal layers and the interlayer \( d_{\text{Au2–Ge}} \).²⁷ In contrast, no
atom in SrAu$_2$Ge$_2$ shows a particularly elongated displacement parameter (Supporting Information Table S1). We believe that the elongation of Au1 ellipsoids is associated with the compression of the octahedral layer (above) and that this could continue at higher temperatures assuming that the shortening of the intralayer distance $d_{\text{Au2-Ge}}$ remains. Whether a phase transition occurs at higher temperatures (>295 K) is beyond this study, but a future goal is to further characterize the negative thermal expansion property of SrAu$_3$Ge.

**Electronic Structure.** Figure 4a shows the total and projected densities-of-states (DOS) for each component in SrAu$_3$Ge at room temperature. The DOS below $-9.0$ eV are dominated by Ge 4s and Au 6s states, which generate the head-to-head $\sigma$ bonding. The large peaks between $-8.0$ and $-3.0$ eV are dominated by Au 5d states, together with some that originate from Au 6s, Ge 4p, and Sr 5s, 5p states (cf. Figure S1). The spiky character suggests complex interactions among these orbitals, including s–s, s–p, s–d, and p–p interactions of Au1–Ge and Au2–Ge, the s–s, s–p, s–d, p–p, p–d, and d–d interactions of Au1–Au1 and Au1–Au2, and those with Sr 5s and 5p. (For detailed orbital interactions, readers can refer to the eigenvectors given in Table S2.) The basal Au1 has larger contributions than Au2 below ca. $-4.5$ eV; in parallel, the contribution from apical Au2 exceeds that from Au1 in the region between $-4.5$ and $-2.0$ eV, Figure 4b. (Note that the influence of the 2:1 proportion for Au1:Au2 has been considered.) This fact is consistent with their different roles in the structure. On the other hand, the influence of Au 5d$^{10}$ on the Fermi surface is very small, as indicated by fatband analyses (Figure S2). Therefore, SrAu$_3$Ge might still be simply considered an s–p bonded compound in electron counting, as for other BaAl$_4$ derivatives, but the bonding is substantially perturbed by Au 5d$^{10}$ contributions at lower energies. As expected from the bond distances, the Au1–Ge, Au1–Au2, and Au2–Ge bonds show strong bonding character, Figure 4c. The bond indexes, evaluated as integrated $\pi$-COHP (–ICOHP) data, Table 4, indicate that the largest bond populations in SrAu$_3$Ge are Au2–Ge (2.96 eV/bond·mol), followed by the basal-to-apical Au1–Ge (2.35) and Au1–Au2 bond (1.28). Other interactions are at most one-fourth of the largest, although comparisons between different elements should not be taken too literally. These indicate that the Au$_5$Ge octahedra in SrAu$_3$Ge are strongly bonded units that form octahedral chains along c in the structure.

**Electron Counts in SrAu$_3$Ge, BaAl$_4$, and CeMg$_2$Si$_2$ Structures.** As shown in Figure 2, the structures of SrAu$_3$Ge and CeMg$_2$Si$_2$ are different from that of SrAu$_2$Ge$_2$ (and other BaAl$_4$-type ordered variants, viz. CaBe$_2$Ge$_2$ and BaNiSn$_3$), but all of these structural types have certain connections in terms of vec. The meaningful comparison among these 1:4 phases relies on the fact that they all exhibit common features of square nets. It is well-known that the normal BaAl$_4$ type phases (including its ordered variants) are optimized near 14 vec per formula unit, but this value is known to vary over ±2 because other factors (size, packing, bonding, etc.) also play pronounced roles in structural stabilization, for example, for CaAu$_2$Si$_2$ (12), CaAuAl$_3$ (12), RAl$_3$Ga$_2$ (R = rare-earth metal) (15), and SrAl$_2$Pb$_4$ (16). Zheng and Hoffmann have

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**Figure 4.** (a) The total and projected density-of-states (eV/formula) and integrated DOS (dotted) for SrAu$_3$Ge. (b) The difference in DOS for Au1 and Au2. (Note the correction for the Au1:Au2 = 2:1 proportion). (c) The crystal orbital Hamilton population (–COHP) data (eV/bond) for Au1–Au1 and Au1–Au2 bonds and (d) for Au1–Ge and both interlayer and intralayer Au2–Ge bonds in SrAu$_3$Ge. Dashed lines in (c) and (d) are integrated –COHP data for corresponding colored –COHP curves.
demonstrated by means of EHTB bonding analyses that the CeMg2Si2 type structure is predicted to be more stable than the BaAl4 type for typical analogues with large vec values (≥15); vice versa, BaAl4 structures are more stable than CeMg2Si2 at vec ≤ 15. Yet, no simple 1:4 phase has hitherto been reported in the lower vec region (<12). Rather, the La3Al11 type superstructures and other substoichiometric variants are often observed as effective ways to circumvent a low vec, for example, K3Hg11,35 Ca3Au8Ge3,13 and La3NiAl7.36 The only exception appears to be the recently reported isostructural BaAu3Ge.27 Apparently, the present structural model of SrAu3Ge, with 9 vec per formula (without counting the lower but nearby Au 5d10 in the valence shell) represents a preference for electron-poor phases, opposite to the related electron-rich CeMg2Si2 type and BaAl4. In other words, formation of corner-shared bicapped squares in SrAu3Ge and its supposed parent CeMg2Si2 rather than edge-shared square pyramids (in BaAl4 and its ordered variants) represent options for both electron-rich (vec ≥ 15) and electron-poor (≤12) 1:4 phases. (Tetravalent cation substitutions in or other variations of the singular CeMg2Si2 to reach the 16-electron version have evidently not been tried, or successfully so, anyway.)

To account for the vec preference for SrAu3Ge and to make a straightforward comparisons with BaAl4 and CeMg2Si2, we recall the rationale employed by Zheng and Hoffmann12 regarding the electronic structures of these two. That is, the electronic structures of BaAl4 and CeMg2Si2 types may be developed from two-dimensional layers of square nets that are differently capped by apical atoms. According to EHTB calculations, the electronic structure of a single layer in BaAl4 contains eight low-lying bands per four Al, with two of these localized on the apical Al. On stacking in three dimensions, the formation of interlayer bonds pushes one of these up as σ* band, thus, leaving seven bands in a strongly bonding region and nine in a strongly antibonding region. This is why and how a typical BaAl4 type phase is considered to be optimized at vec = 14. Similar analysis of the 15-electron CeMg2Si2 reveals five bands in a strongly bonding region, five in a nonbonding region, and six that are strongly antibonding. (cf. scheme 31 in ref 12). Thus, occupation of the first two groups yields a structural stabilization near vec of 20, whereas the observed 15-electron formation of interlayer bonds pushes one of these up as σ* orbital, is indistinguishable from the change of the lattice parameter of SrAu3Ge corresponding well to single crystal X-ray diffraction analyses, the unit cell of SrAu3Ge expands by 0.025(1) Å in the a and b axes (the basal square nets) and contracts 0.016 (1) Å in c on heating from 110 to 295 K (Table 1). The calculated coefficients19 of thermal expansion in a (b) and c are 2.16 × 10−5 K−1 and −1.57 × 10−5 K−1, respectively, indicating that SrAu3Ge exhibits a large uniaxial NTE along c. (For reference, the NTE coefficient for ZrW2O8 is similar, about −9 × 10−6 K−1 over 0.3–1050 K.14) As expected, such divergent lattice variations can result in a very small change in the unit cell volume, only ~0.51% from 110 to 295 K.

NTE behavior may be incurred by different mechanisms, for example, by rigid unit modes, varying electronic configurations, magnetic ordering, and conduction electron or vibrational effects.40 We believe that the NTE of SrAu3Ge is related to its particular geometry rather than other features. As a matter of fact, the anisotropic lattice changes in SrAu3Ge correspond well to the variations of related bond distances. That is, the in-plane Au1–Au1 distances in the basal square nets increase 0.0125(7) Å over the range studied, Table 3, one-half of the change of lattice parameter a. (Remember that each unit cell consists of 2 × 2 squares, Figure 2.) In the c direction, the 0.015(4) Å decrease of intralayer Au2−Ge distance within each octahedron, is indistinguishable from the change of the c lattice parameter, −0.016 (1) Å. In other words, the variation of the c lattice parameter is more germane to a compression of the octahedral layer than any shortening of the strong Au2–Ge interlayer bonds, which in fact shows negligible change (−0.001(4) Å) over the temperature range. A common NTE driving force is the so-called rigid unit mode, as observed in ZrW2O8p41 ScF3p42 and ReO3p43 in which the rigid structural units (e.g., octahedra) pivot or rock relative to each other to reduce the total volume. Although the Au4Ge octahedra in SrAu3Ge could presumably mimic similar pivot-and-rock motions (cf. Figure 2), in ZrW2O8p the observed NTE
along c and the expansion in ab plane of SrAu3Ge (on heating) are more analogous to the release of a “squeezed frog”. This change may be related to the different bond strengths within the Au,Ge octahedra, as suggested by the −ICOHP data in Table 4. That is, the weaker basal-to-basal bonding allows a more normal change with temperature, but the strong basal-to-apical bonds restrain atom motions along c. A uniaxial NTE effect is also observed in the hexagonal YbGaGe (P63/mmc) in which NTE in the ab plane and positive thermal expansion in c are apparently driven by the mixed Yb3+/Yb4+ valency.44

**FURTHER THOUGHTS**

As we know, the BaAl4 family represents one of the richest pools for technologically important materials in magnetic, heavy Fermion, and superconducting applications. The recent discovery of unconventional Fe-based superconductors45 rebooted interest in new superconductive examples among the BaAl4 type intermetallic compounds and their derivatives.46,47 The magnetically active Fe atoms in the structure of AFe2As2 (A = Ca, Sr, Ba) occupy the so-called basal sites only, whereas the nonmagnetic As atoms lie in the more strongly bonded apical sites. However, these phases do not show superconductivity without doping (at normal pressure). It is believed that magnetic fluctuations in close proximity to a very energetic antiferromagnetic state induce superconductivity.46,47 However, evidently no report regarding to the outcome of placing excess magnetically active centers on apical sites is available.

Apparently, a replacement of one-half of the apical atoms in BaAl4 type structure by transition metals would result in a large change in vec. Whether vec is increased or decreased depends on how the valence electrons of transition metals are counted. (Unfortunately, this is a still unsolved question.) For example, people may prefer eight for the valency of Fe, but in many cases, particularly in magnetic materials, −2.66 is the better value according to Pauling.48,49 Nevertheless, both counting schemes should predict whether a CeMg2Si2 or a SrAu3Ge type structure or unknown variants form if no superlattice or intergrowth structure occur. On the other hand, intergrowth structures of a SrAu3Ge-type phase and a magnetically active AFe2As2 (A = Ca, Sr, Ba) superconducting phase, if stable, could also be an interesting test of the influence of inter- and intralayer couplings on $T_c$.50

**CONCLUSIONS**

This work demonstrates that fascinating chemistries exist in electron-poor phase regions that are not limited to QC/ACs. Here, the structure and bonding of SrAu3Ge, a structural type for electron-poorer BaAl4 derivatives, has been examined. As a formal superstructure of CeMg2Si12, SrAu3Ge is vacancy-free and has a compact unit cell, comparable to that of BaAl4 and the additional influence of Au on the bonding would appear to be substantial. The structures of SrAu3Ge and CeMg2Si12 represent two distinctive extremites that are suitable for BaAl4 derivatives with smaller (≤10) or larger (>15) vec values. The present structure may shed new light on chemical tuning with other transition metals, our future work. For example, the quest to make new examples with similar octahedral layers but exhibiting CaBe2Ge2 and BaNiSn3-like ordering would be interesting. However, the choices of active metals and p-block metal combinations need additional considerations of orbital energies to meet the electronic structural requirements. In a more general sense, it has already become apparent that one-for-one substitutions of a single neighboring congener atom into a QC structure, or a prospect therefore, often leads to new and unexpected products that exhibit major changes in structure, as happened here.51,52 Both atom packing and electronic fits appear to be very dependent on size and probably on other factors we do not yet appreciate. SrAu3Ge shows large uniaxial NTE in c, whereas its basal a and b axes show positive responses. As a result, ~0.51% change in unit cell volume is found between 110 and 295 K, suggesting a nearly zero thermal expansion (ZTE) material. Although SrAu3Ge contains rigid octahedra, the NTE in SrAu3Ge is evidently related to a rare motion of the reticulated Au5Ge, in contrast to the pivot-and-rock motion as commonly seen in other NTE materials, for example, ZrW2O844,41 and SrF2.42 The uniaxial NTE behavior of SrAu3Ge may shed new light in the future design and exploitation of other NTE materials, including a reinvestigation of BaAu3Ge and CeMg2Si2. The unique NTE mechanism of SrAu3Ge may also be a great playground for further theoretical studies.15

**ASSOCIATED CONTENT**

§ Supporting Information

The anisotropic displacement parameters for SrAu3Ge in Table S1, the eigenvectors for Au1, Au2, and Ge bonding bands in SrAu3Ge (Table S2), the projected partial DOS data for SrAu3Ge, Figure S1, the Au 5d fatbands for SrAu3Ge. Figure S2, and the cif output. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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(30) The structure of SrAu2Ge2(1/31) was refined from single crystal diffraction data. The lattice parameters are \( a = 4.519(2) \) Å, \( c = 10.356(4) \) Å. Sr and Au occupy special Wyckoff 2a(0 0 0) and 4d(0 1/2 1/2) sites, respectively, and Ge occupies a 4e [0 0 0.3796(2)] site. These are consistent with the report in ref 30.
(39) A coefficient of thermal expansion is defined by the equation \( a = (1/L_0)(\Delta L/\Delta T) \), in which \( L \) is the instantaneous length, \( L_0 \) is an initial length, and \( \Delta L \) and \( \Delta T \) are changes in length referenced to the temperature at which \( L_0 \) is measured.