Supplementary Information

SI.1. Structural Refinements

Full profile refinements of powder X-ray diffraction data for samples prepared using high pressure were performed using JANA2006. Peak positions for the majority phase in the $I4/mmm$ space group are marked by the top row of tics. The peak positions of the secondary phase, SrAlSi, is denoted by the lower row of tics in SrAl$_{3.5}$Si$_{0.5}$, SrAl$_3$Si, and SrAl$_{2.5}$Si$_{1.5}$ samples.
SI.2. Metallography

**Figure SI.2.1** Scanning electron microscopy of polished samples using the back scattered electron detector shows the presence of two secondary phases, identified as Sr(Al, Si)$_2$ by EDS (white spots), and Al (small black spots). The large black regions are the result of pullout during polishing and backfilling with epoxy.

**Figure SI.2.2** Optical microscopy images of polished samples taken in bright field mode.
SI.3 Nuclear Magnetic Resonance Spectroscopy

$^{27}$Al and $^{27}$Si nuclear magnetic resonance (NMR) was used to determine whether or not Si has a strong site preference, as this is not clear from powder X-ray diffraction. Figure 3a-b in the main text shows the $^{27}$Al frequency-sweep NMR spectra of SrAl$_4$ and tI$_{10}$–SrAl$_2$Si$_2$ as solid black curves. Having a nuclear spin of $5/2$, the $^{27}$Al spectra consist of the narrow signal arising from the central transition (-1/2 ↔ +1/2) and the specifically shaped broad background arising from the satellite transitions in the presence of the quadrupole interaction with the electric field gradient (EFG) [1]. All signals also include positive Knight shift due to the magnetic interaction of conduction electrons with the observed nuclei. Asymmetry of the central lines is a result of the second order quadrupole interaction and the anisotropy of the Knight shift.

Focusing on the central line, the results for SrAl$_4$ are consistent with a previous report by Pecher et al [2], in which the lower frequency signal was identified as belonging to 5-bonded Al$_2$ (4e site) and the high frequency signal to 4-bonded Al$_1$ (4d site). In contrast, the spectrum of tI$_{10}$–SrAl$_2$Si$_2$ exhibits a single, broader signal with a non-specific bell-shaped satellite background. The MAS result (at the spinning rate of 32 kHz), shown as the dotted black curve, indicates that this signal arises primarily from one crystallographic Al position. Figure SI.3.2 shows MAS measurements on tI$_{10}$–SrAl$_2$Si$_2$ performed with different spinning frequencies. The sidebands spread out slightly at high frequencies as expected. However, they do not appear to be positioned symmetrically due to the asymmetry of the isotropic peak. This asymmetry might be due to some disorder at the 4e position. Note: a tiny signal of the metallic Al impurity phase is observed at about 1640 ppm.

Likewise, $^{29}$Si MAS NMR spectroscopy (Figure S.I.3.b) of tI$_{10}$–SrAl$_2$Si$_2$ shows only one sharp signal, an indication of a single Si position. With the absence of a quadrupole coupling (nuclear spin $I = ½$), the $^{29}$Si signal is mostly affected by the Knight shift, a contact interaction between polarized conduction electrons and the nuclear spins, which is proportional to the DOS at Fermi level. tI$_{10}$–SrAl$_2$Si$_2$ shows much lower Knight shift compared with the SrAl$_3$Si sample, consistent with the former’s lower density of states at the Fermi level (see Figure S.I.4). The large broadness of the SrAl$_3$Si sample’s signal is an indication of the disorder of Al and Si which must be present even if Si occupies only the 4e site.
SI.4. Electronic structure calculations

Figure SI.4.1  Electronic density of states of SrAl$_4$, SrAl$_3$Si, and $tI10$-SrAl$_2$Si$_2$ in the ThCr$_2$Si$_2$-type structure and $hP5$-SrAl$_2$Si$_2$ in the CaAl$_2$Si$_2$-type structure were calculated using the FPLO code with the experimentally determined lattice parameters and atomic positions. The calculated electronic structures of the high pressure and ambient pressure compounds have significant density of states at the Fermi level, indicating metallic behavior. The clear pseudo-gap present in $hP5$-SrAl$_2$Si$_2$ becomes less pronounced as we proceed to $tI10$-SrAl$_2$Si$_2$, to SrAl$_3$Si, and finally to SrAl$_4$. Experimentally, the resistivity of $tI10$-SrAl$_2$Si$_2$ is found to be metal-like, consistent with calculations. $hP5$-SrAl$_2$Si$_2$ and SrAl$_4$ have both been previously reported to exhibit metal-like resistivity [3-5].
To investigate the site preference of Si, we used the virtual crystal approximation (VCA) in FPLO to compare the relaxed lattice constants of each SrAl_{2-x}Si_x composition with Si on the 4d (tetrahedral) vs. 4e (apical) sites. VCA assumes that at each disordered site there is a virtual atom that is an interpolation between Al and Si. It therefore neglects effects such as local distortions around atoms and therefore misses many of the finer details of disordered structures.

![Graphs showing lattice parameters and energy differences for SrAl_{2-x}Si_x compositions.]

**Figure S1.4.2.** VCA calculations were performed for each composition, with all of the Si assigned to either the tetrahedral (4d) or the apical (4e) site. Note that a constant value of \( z = 0.38 \) was used for the 4e site for all compositions. For each configuration, the relaxed lattice parameters were found by minimizing the total energy. When Si is assigned to the apical 4e site, the relaxed lattice parameters agree very well with the experimentally observed trend. If, in contrast, Si is assigned to the tetrahedral 4d site, the agreement is good at low Si concentrations, but diverges at high Si concentrations. The difference in energy, \( \Delta E = E_{\text{total,4e}} - E_{\text{total,4d}} \), confirms that the total energy when the lattice parameters are minimized is lower when Si is on the 4e position.
Details of LMTO calculations:
Because the calculation within the atomic sphere approximation (ASA) already includes corrections for neglected interstitial regions and partial waves of higher order [26] an addition of empty spheres was not necessary. The following radii of the atomic spheres were applied for the calculations: \( r\text{(Sr)} = 2.357 \, \text{Å}, \) \( r\text{(Al1)} = 1.560 \, \text{Å}, \) \( r\text{(Al2)} = 1.441 \, \text{Å} \) for \( \text{SrAl}_4; \) \( r\text{(Sr1)} = 2.431 \, \text{Å}, \) \( r\text{(Sr2)} = 2.391 \, \text{Å} \) for \( \text{SrAl}_4; \) \( r\text{(Al1)} = 2.445 \, \text{Å}, \) \( r\text{(Al3)} = r\text{(Al4)} = 1.450 \, \text{Å}, \) \( r\text{(Si1)} = r\text{(Si2)} = 1.342 \, \text{Å} \) for \( \text{SrAl}_3\text{Si}; \) \( r\text{(Sr1)} = 2.414 \, \text{Å}, \) \( r\text{(Sr2)} = 2.213 \, \text{Å}, \) \( r\text{(Al1)} = 1.435 \, \text{Å}, \) \( r\text{(Al2)} = 1.541 \, \text{Å}, \) \( r\text{(Al3)} = 1.441, \) \( r\text{(Si3)} = 1.554 \, \text{Å}, \) \( r\text{(Si1)} = 1.353 \, \text{Å}, \) \( r\text{(Si2)} = 1.352 \, \text{Å} \) for \( \text{SrAl}_{2.5}\text{Si}_{1.5}; \) \( r\text{(Sr)} = 2.324 \, \text{Å}, \) \( r\text{(Al)} = 1.447 \, \text{Å}, \) \( r\text{(Si)} = 1.469 \, \text{Å} \) for \( \text{SrAl}_2\text{Si}_2 \) and \( r\text{(Sr)} = 2.049 \, \text{Å}, \) \( r\text{(Al1)} = 2.343 \, \text{Å}, \) \( r\text{(Al)} = 1.434 \, \text{Å}, \) \( r\text{(Si)} = 1.456 \, \text{Å} \) for \( \text{hp-SrAl}_2\text{Si}_2. \) A basis set containing \( \text{Sr}(5s,4d), \text{Al}(3s,3p), \) \( \text{Si}(3s,3p) \) orbitals was employed with \( \text{Sr}(5p,4f), \text{Al}(3d), \text{Si}(3d) \) functions being down-folded.
The structural models for \( \text{SrAl}_4 \) and \( \text{hp-SrAl}_2\text{Si}_2 \) were taken from the experiment. For the intermediate compositions, the ordered models in the space group \( P4mm \) were used.

**SI.5 Superconductivity in SrAl\(_{2.5}\)Si\(_{1.5}\) and tI10-SrAl\(_2\)Si\(_2\)**

![Graph](image-url)

Figure SI.5.1 The upper critical field, \( \mu_0H_{c2} \), as a function of \( T_c \) is shown as open circles; the straight line is the linear extrapolation of \( \mu_0H_{c2}(T_c) \) to 0 K, and the full circles are the obtained WHH values of \( \mu_0H_{c2}(0) \). In red and green are the values obtained from the resistivity dropping to 90 \% and 10 \% of its value at 3 K. The linear extrapolation of \( \mu_0H_{c2}(T_c) \) to 0 K leads to the upper limit for \( \mu_0H_{c2}(0) \approx 844 \, \text{mT} \), while the Werthamer-Helfand-Hohenberg [6] extrapolation from the initial slope of the first five points gives \( \mu_0H_{c2}(0) \approx 506 \, \text{T} \). The real value of \( \mu_0H_{c2}(0) \) should lie in between these limits.
The magnetic susceptibilities of SrAl$_4$, SrAl$_{3.5}$Si$_{0.5}$, SrAl$_3$Si, SrAl$_{2.5}$Si$_{1.5}$ and t/10-SrAl$_2$Si$_2$ were measured in the external fields of $\mu_0H = 3.5$ and 7 T and when necessary extrapolated to infinite field to eliminate a saturated magnetization of a very small ferromagnetic impurity. In most cases, the susceptibilities above 100 K were modelled by a Curie-like behaviour plus a constant; otherwise small linear and quadratic contributions were added. The Curie-like upturns at the lowest temperatures are probably due to minor paramagnetic impurities. The constant contributions were taken as the extrapolated values of susceptibilities at $T = 0$ K, $\chi_0 = -3.8 \times 10^{-5}$, $-2.6 \times 10^{-5}$, $+2.1 \times 10^{-5}$, $-3.0 \times 10^{-5}$ and $-4.0 \times 10^{-5}$ emu mol$^{-1}$, respectively. By calculating diamagnetic contributions of Sr$^{2+}$ ion and covalently bonded Si and Al atoms [7], the measured Pauli susceptibilities are $\chi_P = +3.3 \times 10^{-5}$, $+4.5 \times 10^{-5}$, $+9.2 \times 10^{-5}$, $+4.1 \times 10^{-5}$ and $+3.1 \times 10^{-5}$ emu mol$^{-1}$, giving DOS$(E_F) = 1.0$, 1.4, 2.8, 1.3, 1.0 states/(eV f.u.), respectively.
Figure SI.5.3 Left) The low-temperature specific heat of the \(t/10\)-SrAl\(_2\)Si\(_2\) measured at the indicated magnetic fields. Right) The difference between the superconducting and normal-state specific heat, \(\Delta C_p = C_{pS} - C_{pN}\), for measured magnetic fields.

SI.6. Chemical bonding

Figure SI.6.1. ELI-D distributions in the (100) planes in SrAl\(_3\)Si (left) and SrAl\(_{2.5}\)Si\(_{1.5}\) (right) reveal the Si\(_2\)-Si\(_2\) and Al\(_2\)-Si\(_2\) interactions, respectively. Color code as in Figure 7 in the main article.

References:
