First-principles investigation of the Al–Si–Sr ternary system: Ground state determination and mechanical properties

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\begin{abstract}
Twelve different ternary phases of the Al–Si–Sr system were characterized using first-principles calculations based on Density Functional Theory. Two different exchange correlation functionals were considered to extract its influence on the global results. In addition to the four phases (AlSiSr, Al\textsubscript{2}Si\textsubscript{2}Sr, Al\textsubscript{3}Si\textsubscript{2}Sr\textsubscript{3} and Al\textsubscript{4}Si\textsubscript{3}Sr\textsubscript{5}) reported for this system, we explored eight other ternary phases (Al\textsubscript{2}Si\textsubscript{2}Sr\textsubscript{3}, Al\textsubscript{2}Si\textsubscript{4}Sr\textsubscript{3}, Al\textsubscript{3}Si\textsubscript{2}Sr\textsubscript{5}, Al\textsubscript{5}Si\textsubscript{2}Sr\textsubscript{10}, Al\textsubscript{6}Si\textsubscript{2}Sr\textsubscript{14}, Al\textsubscript{8}Si\textsubscript{3}Sr\textsubscript{14} and Al\textsubscript{10}Si\textsubscript{4}Sr\textsubscript{14}) that have been reported in chemically analogous systems. The mechanical stability of the phases was determined through the analysis of the elastic constants, and the energetic stability was established using the calculated formation enthalpy. The thermodynamic and vibrational properties of the AlSiSr, Al\textsubscript{3}Si\textsubscript{2}Sr\textsubscript{3} and Al\textsubscript{4}Si\textsubscript{3}Sr\textsubscript{5} phases were studied considering the harmonic, quasi-harmonic as well as simple anharmonic corrections. All phases were found to be stable, except for the Al\textsubscript{8}Si\textsubscript{3}Sr\textsubscript{14} and Al\textsubscript{10}Si\textsubscript{4}Sr\textsubscript{14}. An isothermal section of the phase diagram was calculated at 0 K with the Thermocalc software, where it was found that the Al\textsubscript{2}Si\textsubscript{2}Sr\textsubscript{3} and Al\textsubscript{6}Si\textsubscript{2}Sr\textsubscript{14} phases belong to the ternary ground state. The surface energy sections show that the other phases are metastable with a $\Delta G_{0K}$ of 2 kJ/mol–atom, all stable and metastable phases show a metallic behavior and high compressibility.
\end{abstract}

\section{Introduction}

The Al–Si–Sr system is very important in the light-metal alloys industry. In Al–Si cast alloys, for example, strontium is used as a modifier of the Al–Si eutectic [1]. When small quantities of strontium (hundreds of ppm at most) are added to Al–Si eutectic alloys, the morphology of the silicon crystallites change dramatically, from an acicular to a fibrous morphology. This morphological change refines the microstructure, which in turn results in much better mechanical and structural properties [2]. Furthermore, recent work on Al–Mg alloys that use silicon as an alloying element, shows that strontium improves fatigue resistance at high temperatures [3–5]. Therefore, a deeper understanding of the Al–Si–Sr ternary system is important for the further development of these classes of light metal alloys, which have received considerable attention in recent years.

An in-depth study of the phase stability of the Al–Si–Sr ternary system is further justified by considering that several intermetallic compounds in this system are being studied for different applications: AlSiSr for its superconducting behavior [6,7], the non-stoichiometric SrAl\textsubscript{2} [8] for its potential as a hydrogen storage material and the Al\textsubscript{3}Si\textsubscript{2}Sr [9] and Al\textsubscript{10}Si\textsubscript{3}Sr\textsubscript{5} [10] phases for their thermoelectric properties. All of the previously mentioned phases have yet to be studied completely and outside of these compositions there is little theoretical or experimental information available.

Investigations on the phase stability of chemically-related systems suggest that it may be possible to find new intermetallic compounds in regions of the Al–Si–Sr phase diagram that are yet to be investigated in detail. Specifically, studies on the Al–Ge–Ba, Al–Ge–Ca, Al–Ge–Sr, and Al–Si–Mg systems report the existence of several ternary intermetallic phases that could also be stable in Al–Si–Sr. Table 1 shows the crystallographic information of eight intermetallic structures observed in the four systems already mentioned along with the structures reported for the Al–Si–Sr system. The structures with space group $P\text{--}6m2 \equiv p6/mmm$, $P\text{--}3m1$ and $Immm$ are present in Al–Si–Ca, Al–Ge–Ba, Al–Ge–Sr and Al–Si–Sr ternary systems [6,11–14] and have similar properties due to the affinity between the elements of the group IV and the rare-earth elements. The fact that these three structures are
structures were further investigated by considering mechanical on the formation enthalpy of these structures. The stability of these allowed us to determine whether any of these phases were unstable and thus not likely to form even under non-equilibrium conditions. Finally, for two intermetallic compounds metastable) that belong to the ternary ground state, we calculated the vibrational properties for the AlSiSr, Al2Si2Sr3 and Al2Si4Sr3 intermetallics. The discussion of the vibrational properties for the Al Si,Ge Y common to all these ternary systems suggests that structures with the same symmetry and stoichiometry may also be present in the Al–Si–Sr system.

The aim of this study is to investigate the possible existence of new phases in the Al–Si–Sr ternary system. In order to achieve this, we investigate the stability of those phases, considering both energetic and mechanical criteria. The energetic stability is evaluated considering the enthalpy of formation of the intermetallics calculated from first-principles at 0 K. In this case, there are no entropic contributions and the free energy simply corresponds to the enthalpy. This methodology was used in the case of the binary intermetallics of the Al–Sr [20] and Sr–Si [21] systems. In those cases as well as in this work, first-principles calculations were combined with the CALPHAD approach [22] to obtain the ground state and corresponding low-temperature phase diagram of the system. The phases under consideration include the known intermetallics in the Al–Si–Sr system, as well as those with the same symmetry observed in Al–X–Y (X = Si,Ge Y = Mg,Ca,Sr, Ba) systems (see Table 1). We report on the total energy calculations as well as on the formation enthalpy of these structures. The stability of these structures were further investigated by considering mechanical stability conditions in terms of the elastic tensor [23]. This analysis allowed us to determine whether any of these phases were unstable and thus not likely to form even under non-equilibrium (metastable) conditions. Finally, for two intermetallic compounds that belong to the ternary ground state, we calculated the vibrational and thermodynamic properties at finite temperatures.

The paper is organized as follows: Section 2 contains a description of the methodology used as well as the details of the first-principles calculations performed. The results and discussion of the stability and possible existence of new phases is presented in Section 3, as well as a detailed theoretical description of the stable intermetallics. The discussion of the vibrational properties for the AlSiSr, Al2Si2Sr3 and Al2Si4Sr3 intermetallics is presented in Section 4, and the conclusions of the paper are included in Section 5.

2. Methodology

2.1. Total energy calculations

The total energy calculations were performed within the framework of the Density Functional Theory [24], as implemented in the Vienna Ab Initio Simulation Package (VASP) [25,26]. Two approximations for the exchange correlation were considered: the Local Density Approximation (LDA) according to the Perdew–Zunger parameterization [27] and the Generalized Gradient Approximation (GGA) in the form of PW91 [28]. Wave functions were expanded in plane waves, using the Al:3s2 3p3, Si:3s2 3p2 and Sr:4s2 4p6 5s2 electronic configuration for the valence electrons described within the projector augmented-wave (PAW) pseudo-potentials formalism [29], implemented in the VASP package. The Brillouin zone integrations were performed using a Monkhorst-Pack mesh [30]. Full relaxations were realized by using the Methfessel–Paxton smearing method of order one [31] and a final self-consistent static calculation with the tetrahedron smearing method with Blöchl corrections [32]. To ensure the convergence in energy to better than 1 meV and 1 Kbar in pressure, we used an energy cut-off of 350 eV and a k-point grid sets according to Table 2.

2.2. Elastic constants calculations

The elastic constants of all the intermetallic compounds considered in this work were calculated using the efficient strain-stress method [33], where a set of strains \(\varepsilon = (\varepsilon_{11},\varepsilon_{22},\varepsilon_{33},\varepsilon_{12},\varepsilon_{23},\varepsilon_{31})\) is imposed on a crystal structure. If \(\mathbf{A}\) is the lattice vectors specified in Cartesian coordinates, \(x_{12},x_{23},x_{31}\) and \(x_{45},x_{56},x_{64}\) are the normal strains and the shear strains respectively. Then, the deformed lattice vectors are:

\[
\mathbf{x} = \mathbf{A} + \frac{\varepsilon_{11}}{2} \mathbf{x}_{11} + \frac{\varepsilon_{22}}{2} \mathbf{x}_{22} + \frac{\varepsilon_{33}}{2} \mathbf{x}_{33} + \varepsilon_{12} \mathbf{x}_{12} + \varepsilon_{23} \mathbf{x}_{23} + \varepsilon_{31} \mathbf{x}_{31},
\]

After the application of the strain, it is possible to obtain the set of stresses \(\sigma\), which result from the changes on the energy due to the deformation, which is obtained from the electronic structure calculations. Applying Hooke’s Law \((t = tC)\), if a n set of strains \(\varepsilon_{11} → \varepsilon_{11}'\) are applied, the result is n set of stresses \((t_{11} → t_{11}')\) which can be used to find the \(6 \times 6\) elastic constant matrix \((C)\) according to:

\[
\begin{pmatrix}
C_{11} & \ldots & C_{16} \\
\vdots & \ddots & \vdots \\
C_{61} & \ldots & C_{66}
\end{pmatrix} = \begin{pmatrix}
\varepsilon_{11} & \ldots & \varepsilon_{11'} \\
\vdots & \ddots & \vdots \\
\varepsilon_{61} & \ldots & \varepsilon_{66}
\end{pmatrix}^{-1} \begin{pmatrix}
t_{11} & \ldots & t_{11}' \\
\vdots & \ddots & \vdots \\
t_{61} & \ldots & t_{66}'
\end{pmatrix}
\]

The elements in the C tensor are written as \(C_{ij}\) according to the Voigt’s notation and the linearly independent sets of strains necessary to calculate the elastic constants can be written of the following way:

\[
\varepsilon = \begin{pmatrix}
x_{11} & 0 & 0 & 0 & 0 & 0 \\
0 & x_{22} & 0 & 0 & 0 & 0 \\
0 & 0 & x_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & x_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & x_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & x_{66}
\end{pmatrix}
\]

According to the symmetry of the structure, the minimum number of linearly independent sets of strains that can be used to determine the elastic constants are two for cubic, three for

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Pearson Symbol</th>
<th>Crystallographic information of the intermetallics phases in systems chemically analogous to Al–Si–Sr.</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td>AlSiSr</td>
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<td></td>
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<td>Al3Si4Sr</td>
</tr>
</tbody>
</table>

Table 1

<table>
<thead>
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<th>Phase</th>
<th>Mesh (k)</th>
<th>Phase</th>
<th>Mesh (k)</th>
</tr>
</thead>
<tbody>
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<td>AlSi2Sr</td>
<td>8 × 8 × 8</td>
</tr>
<tr>
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<td>15 × 15 × 9</td>
<td>Al2Si2Sr</td>
<td>8 × 8 × 4</td>
</tr>
<tr>
<td>Al2Si3Sr</td>
<td>12 × 12 × 12</td>
<td>Al2Si3Sr</td>
<td>4 × 5 × 15</td>
</tr>
<tr>
<td>Al2Si4Sr</td>
<td>4 × 4 × 4</td>
<td>Al2Si4Sr</td>
<td>6 × 6 × 6</td>
</tr>
<tr>
<td>Al3SiSr</td>
<td>6 × 15 × 4</td>
<td>Al3Si2Sr</td>
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<tr>
<td>Al3Si2Sr</td>
<td>12 × 12 × 9</td>
<td>Al3Si3Sr</td>
<td>9 × 9 × 12</td>
</tr>
</tbody>
</table>
hexagonal and rhombohedral, four for tetragonal, and six for orthorhombic, monoclinic, and triclinic structures.

2.3. Thermodynamic properties

Most thermodynamic properties at finite temperatures can be derived from the structural total free energy. In the present work, we consider the contributions to the total free energy coming from the electronic ($F_{ele}$) and the vibrational free energy ($F_{vib}$). The electronic part can be calculated according to the one-electron band approximation. This approximation is based on the self-consistent integration of the electronic density of states [34]:

$$F_{ele} = E_{ele} - T\sigma_{ele}$$  \hspace{1cm} (4)

$$F_{ele}(V, T) = \int \eta(\varepsilon, V)f\varepsilon \partial\varepsilon - \int \eta(\varepsilon, V)\varepsilon \partial\varepsilon$$  \hspace{1cm} (5)

$$S_{ele}(V, T) = -k_B \int \eta(\varepsilon, V)f\ln f + (1 - f)\ln(1 - f)\partial\eta$$  \hspace{1cm} (6)

$\eta(\varepsilon, V)$ is the electronic density of states and $f$ is the Fermi distribution function. $\eta$ is calculated self-consistently to ensure that at each temperature the total number of electrons is conserved.

The vibrational contributions to the free energy of the crystal ($F_{vib}$), as a function of temperature is calculated according to:

$$F_{vib}(T) = k_B T \int_0^\infty \ln \left[ 2 \sinh \left( \frac{h\varepsilon}{k_B T} \right) \right] \frac{g(\varepsilon)}{\partial}\varepsilon$$  \hspace{1cm} (7)

where $g(\varepsilon)$ is the phonon density of states. This function is usually obtained by two main different approaches: density functional perturbation theory [35] and the (direct) supercell approach [36]. In this work, we have used the latter method as implemented in the ATAT software package [37]. In this method, the force constants are obtained by calculating the interatomic forces—using the electronic structure code—resulting from finite atomic displacements from the equilibrium position. The force constants are used to obtain the dynamical matrix which is then diagonalized. In the harmonic approximation, the resulting eigenfrequencies correspond to the normal (independent) modes of oscillation of the crystal, while the eigenvectors correspond to the atomic displacements of the individual modes. The supercell method excludes the anharmonic effects due to phonon—phonon or electron—phonon interactions or higher other effects. In the present paper we evaluated the anharmonic effects originating from phonon—phonon interactions using the expression developed by Wallace and Callen [38]:

$$F_{anh} = A_2 T^2 + A_0 + A_2 T + \ldots$$  \hspace{1cm} (8)

Currently, we only are able to evaluate the first term of the expansion $A_2$ using information that can be derived directly from first-principles:

$$A_2 = \frac{3 k_B}{\Theta} [0.0078(\gamma) - 0.0154]$$  \hspace{1cm} (9)

where $\Theta$ corresponds to the harmonic Debye temperature and $\gamma$ corresponds to the Gruneisen parameter. We would like to point out that Eq. (9) was obtained from correlations between the Debye and Gruneisen values for crystals of different symmetries obtained by Wallace and Callen [38]. Eq. (9) is classical and therefore it cannot be applied at low temperatures. In order to obtain a valid expression for the anharmonic free energy over the entire temperature range, is necessary a better description of anharmonic free energy. Using thermodynamic perturbation theory [39] and the time-averaged internal energy at constant $T$ given by Einstein’s formula:

$$\langle E \rangle = \frac{1}{2} k_B \theta + \frac{k_B \theta}{\exp(\theta/T) - 1}$$  \hspace{1cm} (10)

is possible to evaluate the anharmonic free energy, considering a weakly anharmonic oscillator, symmetric potential and neglecting higher terms than proportional to $T^2$ according to (for more details see Ref [40]):

$$F_{anh} = (U - U_0)/T = \frac{3 n A_2}{6 k_B} \left[ \langle E \rangle^2 + 2 k_B C_V T^2 \right]$$  \hspace{1cm} (11)

$$F_{anh} = \eta k_B A_2 \frac{1}{4} \left[ \frac{\theta}{2} + \frac{\Theta}{\exp(\Theta/T) - 1} \right]^2$$

$$+ 2 k_B A_2 \frac{1}{4} \left( \frac{\theta}{2} \right)^2 \frac{\exp(\theta/T)}{\exp(\theta/T) - 1} \frac{1}{2} \frac{\exp(\theta/T)}{2} T^2$$  \hspace{1cm} (12)

Here, $\Theta$ corresponds to the high-temperature harmonic Debye temperature, defined as $\Theta = (\hbar/k_B)((S/p)/W)^{1/2}$. Eq. (12) is calculated at each volume considered in the quasi-harmonic correction, with the parameter $A_2$ calculated according to Eq. (9), with $\theta$ and $\gamma$ calculated directly from first-principles. The thermodynamic properties at finite temperatures can be calculated from the free energy now defined as:

$$F(V, T) = E_0 + k_B(V) + F_{vib}(V, T) + F_{ele}(V, T) + F_{anh}(V, T)$$  \hspace{1cm} (13)

3. Stability of the Al$_x$Si$_y$Sr$_{1-x-y}$ phases

3.1. Formation enthalpy

In order to discriminate the stability of the different phases in the Al–Si–Sr system, we first calculate their formation enthalpy. For the four ternary intermetallic phases reported in Ref. [14], the crystallographic information used as input for the calculations is consistent with the orthorhombic, monoclinic, and triclinic structures. We would like to note that in this case, the approximation for the calculation of the formation enthalpies does not influence the results in a significant manner. In fact, according to investigations by the authors on the Sr–Si system [21,41], we can suppose that the "true" formation enthalpy of these phases lies between the LDA and GGA approximations, as the former usually overestimates the cohesive energies while the latter one tends to underestimate them.

The formation enthalpy was calculated according to the following equation:

$$\Delta H_f^{Al_{x}Si_{y}Sr_{1-x-y}} = E^{Al_{x}Si_{y}Sr_{1-x-y}} - X E^{bcc} - Y E^{Dia} - A_4$$

where $E^{Al_{x}Si_{y}Sr_{1-x-y}}$, $E^{fcc}$, and $E^{Dia}$ are the energies of the pure elements in the more stable phase at 0 K and $E^{Al_{x}Si_{y}Sr_{1-x-y}}$ corresponds to the total energy of the intermetallic compound at 0 K. The energies of the structures are normalized by the number of atoms in their respective unit cell.
Table 3 shows that the formation enthalpy is negative for the four phases, demonstrating that these phases are energetically stable. In the case of the AlSiSr and Al$_2$Si$_2$Sr$_3$ phases, we notice a very negative formation enthalpy, which means that at low temperatures these phases are very likely to be always present in the phase diagram and must therefore belong to the ground state of the Al–Si–Sr system. In the present paper, we propose eight new phases that can belong to the Al–Si–Sr system, based on information from chemically analogous systems. Fig. 1 summarizes the crystallographic information of the intermetallics we have also included in this study. The initial symmetries and cell parameters of these phases in the Al–Si–Sr system were chosen according to

| Phase          | Unit cell | Space group | Pearson symbol |
|----------------|-----------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Al$_2$Si$_2$Sr$_3$ | ![Image](image1.png) | 71 | Immm | ol7 |
| Al$_2$Si$_3$Sr$_3$ | ![Image](image2.png) | 62 | Pnma | oP8 |
| Al$_2$Si$_4$Sr$_3$ | ![Image](image3.png) | 12 | C2/m | mC9 |
| Al$_2$Si$_7$Sr$_5$ | ![Image](image4.png) | 12 | C2/m | mC14 |
| AlSi$_6$Sr$_4$ | ![Image](image5.png) | 12 | C2/m | mC11 |
| Al$_3$Si$_7$Sr$_{10}$ | ![Image](image6.png) | 193 | P63/mmm | hP20 |
| Al$_6$Si$_9$Sr$_{10}$ | ![Image](image7.png) | 166 | R-3m | hR35 |
| Al$_{10}$Si$_{13}$Sr$_{20}$ | ![Image](image8.png) | 6 | Pm | mP39 |
| Al$_8$Si$_3$Sr$_{14}$ | ![Image](image9.png) | 148 | R-3 | hR35 |

Reference states: Fcc for Sr and Al, diamond cubic for Si.
prototype structures in those chemically-analogous systems (see Table 1).

The Al–Si–Sr ternary phases present interesting properties due to their crystalline structures. The main structural feature is that they contain a skeleton composed of Al–Si bonds, which is surrounded by strontium atoms. In this Al–Si skeleton the silicon atom may have different coordination number (two or four) while the aluminum atoms presents normal coordination number of three. The Al–Si bonds have an average of 2.46 ± 8 Å and the Si–Al–Si average angle is 116.5 ± 10°. The Sr–Sr distance can vary from 3.32 Å to 4.69 Å depending on the symmetry of the crystal structure.

All the new phases were fully relaxed in order to obtain the lowest energy structure and Table 4 shows the results for the optimized structures. The calculated cell parameters are similar to the prototype phases (see Table 1), with small differences due to different cations (Ca, Ba, Mg and Sr). The symmetry was conserved after the relaxation and the formation enthalpy is guaranteed when all \( E_{ij} \) values are positive and \( E_{ij} \) are significantly larger than \( E_{ij} \).

### 3.2. Mechanical stability

In order to determine if the new phases can exist at finite temperatures, it is necessary to establish their mechanical stability. A simple way to determine the limit of mechanical stability, is by knowing the strain energy \( (1/2C_{ijkl}e_{ij}) \) of a given crystal is always positive for all possible values of the set \( \{e_{ij}\} \) [38], according to:

\[
\Delta F = \frac{E_{ij} - E_0}{V_0} = \left(1 - \frac{V_0}{V_0}\right) P(V_0) + \frac{1}{2} \left(\sum_{ij} C_{ijkl} e_{ij}\right) + O\left(\left\{\frac{3}{3}, \frac{1}{1}\right\}\right)
\]

(15)

Where the crystal energy is a quadratic function of the strain, \( V_0 \) is the volume of the unstrained lattice, \( E_0 \) is the total minimum energy of the unstrained volume, \( P(V_0) \) is the pressure of the unstrained lattice and finally \( V \) is the volume of the strained lattice. The quadratic form of \((1/2C_{ijkl}e_{ij})\) imposes further restrictions on the elastic constants \( C_{ij} \) depending on the crystal structure, because it must be positive for all real values of strain. The mechanical stability conditions are shown in the Supplementary materials section.

Table 5 shows the calculated elastic constants for all the crystalline systems considered in this work. It can be seen that for all the phases the \( C_{ijkl} \) components of the strain tensor are positive. For the monoclinic phases, the values of the \( C_{ij} \) are close to zero. In the same manner, we appreciate small values of the \( C_{ij} \) and \( C_{ij} \) for the \( AlSiSr3 \) and \( AlSiSr14 \) phases, which means that there is a small distortion in their symmetry.

For the hexagonal phases, the stability conditions (see the Supplementary materials) are satisfied when \( C_{11}, C_{33} \) and \( C_{44} \) are positive and they are significantly larger than \( C_{12} \) and \( C_{13} \). We can see that for all hexagonal phases the \( C_{11}, C_{33} \) and \( C_{44} \) values are positive and at least two times larger than \( C_{12} \) or \( C_{13} \). Therefore, all hexagonal phases in the Al–Si–Sr are mechanically stable. In a similar fashion, for the orthorhombic phases the stability is guaranteed when all \( C_{ij} \) values are positive and \( C_{ij} \) are larger than 2 times \( C_{ij} \). Hence, the orthorhombic phases are also stable as shown in Table 5.

The case of the monoclinic phase happens to be more complex, owing to the fact that there are 13 independent elastic constants. However, we can summarize the stability conditions as follows: if the six elastic constants \( C_{11}, C_{22}, C_{33} \) are positive, coupled to the condition that \( C_{ij} \) are positive, mechanical stability is ensured. In particular, our calculation indicates that the monoclinic structure follows all those conditions, while \( C_{12}, C_{13}, C_{15}, C_{23} \) and \( C_{25} \) have small values and \( C_{ij} \) have large values. Therefore, we expect that \( AlSiSr3 \) and \( AlSiSr5 \) are both mechanically stable. For the \( AlSiSr4 \) phase we can appreciate that \( C_{33} \) values are larger than \( C_{44} \) and \( C_{66} \), which indicates that this phase is in the edge of being mechanical unstable.

For the \( AlSiSr8 \) phase, the small differences between the set of \( C_{11}, C_{22}, C_{33} \), \( C_{44}, C_{55}, C_{66} \) and \( C_{12}, C_{13}, C_{23} \) show that the structure is quite close to being cubic. The stability conditions are satisfied because \( C_{11}, C_{22}, C_{33} \), \( C_{44}, C_{55}, C_{66} \) and \( C_{12}, C_{13}, C_{23} \) are positive and \( C_{11}, C_{22}, C_{33} > C_{12}, C_{13}, C_{23} \).

Our analysis is able to discriminate the large variation in elastic behavior within the possibility of having most of our considered structures as elastically stable.

### 3.3. Ternary ground state

An important point in the analysis of phase stability is to know the ground state of the system since the presence or absence of a given phase from the ground state is determined by the relative stability of other phases, which in turn depends of the energy as a function of the composition. In the case of systems with more than two components, determination of the ground state happens...
to be quite complex. In this particular work, we determined the ground state by globally minimizing the free energy of the Al–Si–Sr system at 0 K, considering all the possible monoatomic, binary and ternary phases likely to take part in equilibria. The minimization was performed using the Thermocalc software [42] and the CALPHAD methodology [22]. According to this method, the energy difference between the Al–Si–Sr binary ground state, which actually corresponds to the SrSi phase, and the ternary ground state at 0 K is taken from the SGTE [43,44] database and the CALPHAD methodology [22]. According to this method, the Gibbs free energy—or Helmholtz free energy as in condensed phases—they are almost identical—for the stoichiometric compounds is written as:

$$\Delta H_m - H_{m, \text{SER}} = a \cdot b \cdot T + c \cdot T \cdot \ln(T) + \sum d_i \cdot T^i$$  \hspace{1cm} (16)$$

where the $\Delta H_m - H_{m, \text{SER}}$ is the Gibbs energy relative to a standard element reference state (SER), $H_{m, \text{SER}}$ is the enthalpy of the element in its stable state at the temperature of 298.15 K and the pressure of 1 bar, and $a, b, c$ and $d_i$ are model parameters fit to thermochemical properties. At 0 K only the parameter $a$ is important and it can be obtained from a first-principles calculation. The other important quantity is $H_{m, \text{SER}}$, which corresponds to the reference state of the element. In our case, it was necessary to change the reference state to 0 K according to:

$$H_{m, \text{SER}}(0 \text{ K}) = H_{m, \text{SER}}(298 \text{ K}) - \Delta H_{m, \text{SER}}$$  \hspace{1cm} (17)$$

The $H_{m, \text{SER}}(298 \text{ K})$ is taken from the SGTE [43,44] database and the $\Delta H_{m, \text{SER}}$ can be obtained following the same line as in Ref. [41]. The binary Gibbs energies were taken from reference [20] for the Al–Si system and [21] for the Sr–Si system. Fig. 2 shows the results of the calculated isothermal sections in both approximations. Only tree of the four phases reported belong to the ternary ground state as expected, because the formation enthalpy of the Al$_{16}$Si$_{30}$Sr$_8$ is much less negative than other phases.

The main difference between the LDA and GGA calculations is the fourth phase that belongs to the ternary ground state. In the case of the LDA approximation, the Al$_3$Si$_{16}$Sr$_8$ phase belongs to the ground state, while the GGA calculations indicate that Al$_3$Si$_{16}$Sr$_8$ belongs to the ground state instead. This difference is due to the phases present in the Al–Si binary ground state, which actually change depending on whether the LDA or GGA approximations are used [20]. In Fig. 2 it is possible to see that in the LDA approximation the Al$_3$Sr$_8$ phase belongs to the binary ground state while in the GGA approximation this is not the case.
between 2 and 4kJ/atom. In other words, the six phases in Fig. 3 (b) and (d) are metastable phases and their existence as equilibrium phases at finite temperatures depends on entropic contributions.

3.4. Electronic properties

In this section, we discuss the electronic properties for the Al–Si–Sr phases considered here, except for the AlSiSr phase, which has been widely studied [45–47]. The Al$_2$Si$_2$Sr phase has been recently discussed by some of the present authors [48], the Al$_{16}$Si$_{30}$Sr$_8$ where a more detailed study is required and is beyond the scope of this paper and the AlSi$_6$Sr$_4$ which is unstable as demonstrated previously in this paper.

We start by presenting the results of the total electronic density of states, as calculated by using the LDA approximation. Some specific calculations were performed with the PW-91 exchange correlation, but we do not see a significant difference with respect to the LDA approximation, which indicates that it is sufficient to...
Fig. 4. Partial and total density of state calculated by LDA approximation for different phases in the Al–Si–Sr systems.
investigate the results from only one exchange correlation approximation.

On the right hand side of Fig. 4, we show the phases with metallic behavior. For the Al2Si2Sr3 and Al6Si13Sr20 phases, there are \( p/C0 \) cross bands dominating the electronic conduction. For the Al2Si7Sr5 phase, the \( p \) and \( d \) orbitals are hybridized. However, for the Al3Si7Sr10 phase, which has more strontium than the previous ones, there is a partial hybridization between the \( p \) and \( d \) orbitals close to the Fermi level. At high energies there are more \( d \) states than \( p \), this is due to the aluminum increase.

On the left hand side of Fig. 4, we report the results for the phases with low density of states at the Fermi level. The Al2Si3Sr3 and Al2Si4Sr3 phases have a \( p–d \) cross bands and part of the \( s \) and \( p \) orbitals are hybridized. The increase of silicon in the Al2Si4Sr3 phase shows a decrease in the density of states at the Fermi level with respect to the Al2Si3Sr3 phase. This is because the increase of silicon creates more localized electrons between the \( Al/C0Si \) bonds.

The Al6Si9Sr10 and Al8Si3Sr14 phases have a semi-metallic behavior and in the first one it is also possible to see the \( p–d \) cross bands as in the other phases, but in this case only few states are available between the valence and conduction bands. The case of the Al2Si3Sr14 phase is totally different, because this structure is

<table>
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<th>Phase</th>
<th>Al</th>
<th>Si</th>
<th>Sr</th>
<th>% Sr</th>
<th>Sr:Al</th>
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<td>1.00:2.00</td>
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</tbody>
</table>

**Fig. 5.** Calculated formation thermodynamic properties of the AlSiSr phase (a) LDA (b) GGA. Har: harmonic approximation, Q-har: Quasi-harmonic approximation, Ele: Electronic free energy and Anh: anharmonic contribution.
conformed by small pyramids of aluminum inside a matrix of strontium and silicon (see Fig. 1). The density of states for this structure shows a very small gap at the Fermi level, where electrons on the valence band are mostly coming from $p$ orbitals from the aluminum atoms, while the contribution to the conduction band is mostly from $d$ orbitals of the strontium atoms. The above shows that the non-localized electron of aluminum cannot go freely between aluminum structures and therefore this phase is semi-metallic.

Table 6 shows the charge average calculated through a Bader-type analysis [49,50]. According to this table, in most phases, aluminum is a donor element, but for the Al$_2$Si$_3$Sr$_3$ phase there are few covalent bonds between silicon and aluminum. In the Al$_8$Si$_3$Sr$_{14}$ phase the aluminum behavior is different and the table shows a change of four which means that the aluminum atoms have covalent bonds between them and ionic bonds with the strontium atoms.

The chemistry of the silicon atoms depends on the concentration of aluminum: when the relation (Al%:Si%) is 1:1 ≤ $\xi$ ≤ 1.5, the Si–Al bonds have mostly ionic character and when the silicon concentration increases, the phase has more Si–Si bonds and the silicon atoms can have $sp$ and $sp^2$ hybridization.

4. Vibrational and thermodynamic properties of the AlSiSr, Al$_2$Si$_2$Sr$_3$ and Al$_2$Si$_4$Sr$_3$ phases

The vibrational properties of the AlSiSr phase has been studied in the past years [51,52] due to its superconducting behavior. We now discuss the formation thermodynamic properties of the AlSiSr, Al$_2$Si$_2$Sr$_3$ and Al$_2$Si$_4$Sr$_3$ phases.

Fig. 5 shows the formation enthalpy, entropy and free energy of the AlSiSr phase as a function of temperature. These thermodynamic properties were calculated by successively considering additional contributions to the total free energy. The $Q$ – $har$ and $Har$ + $Ele$ curves show that the electronic contribution are of the same magnitude as the quasi-harmonic contribution and these two account for almost 90% of the temperature dependence of the

![Fig. 6](image_url). Calculated formation thermodynamic properties of the Al$_2$Si$_3$Sr$_3$ phase (a) LDA (b) GGA. Har: harmonic approximation, $Q$-har: Quasi-harmonic approximation, Ele: Electronic free energy and Anh: anharmonic contribution.
thermodynamic properties of this structure. We can also notice that the formation entropy of this phase is negative, indicating a stiffening of the average interatomic bonds as Al, Si and Sr form AlSiSr. This is also in agreement with the exothermic formation enthalpy of this compound. Note, however, that the formation entropy is not very significant as it amounts to less than 0.25 k\(\text{B} \) and the formation free energy only increases by about 2 kJ/mol–atom over a 1000 K temperature range.

Fig. 6 shows the formation thermodynamic properties of the Al\(_2\)Si\(_2\)Sr\(_3\) phase. The figure shows that the behavior of this phase is very similar to AlSiSr, with the only difference that anharmonic effects seems to be even less significant in this case. The electronic free energy has the same strong contribution to the total free energy when compared to the harmonic and quasi-harmonic contributions. However, the formation entropy of this phase is much larger than that of AlSiSr and Al\(_2\)Si\(_4\)Sr\(_3\). This in turn increases the de-stabilization of this phase as temperature increases. This result is consistent with the observations on the pseudo-binary Sr–Al\(_2\)Si\(_2\)Sr phase diagram [53], which have shown that the Al\(_2\)Si\(_2\)Sr\(_3\) phase has a lower melting point than AlSiSr and Al\(_2\)Si\(_4\)Sr\(_3\).

Fig. 7 shows the formation thermodynamic properties of the Al\(_2\)Si\(_4\)Sr\(_3\) phase. Here, the main difference with the two previous cases is the large contribution to the free energy due to electronic degrees of freedom. The electronic free energy, along with the other contributions increase the formation enthalpy by more than 1 kJ/mol–atom as temperature increases. Given the fact that the formation enthalpy of this phase is rather close to that of AlSiSr and Al\(_2\)Si\(_2\)Sr\(_3\) and its formation entropy is less than that of Al\(_2\)Si\(_4\)Sr\(_3\) it is likely that Al\(_2\)Si\(_4\)Sr\(_3\) may become thermodynamically stable at large temperatures.

Fig. 8 shows the phonon dispersion for the three phases considered in this section. The phonon dispersion for the AlSiSr phase has been previously studied by other groups [45,46,54,55]. Our results are in good qualitative agreement with the reported calculations by Huang et al. [54,55], with the maximum frequency of the acoustic modes being approximately 3 THz and the maximum frequency of

![Graphs showing formation thermodynamic properties](image-url)
the optical modes being around 13–14 THz in both cases. As in the previous works [54,55], the acoustic modes are rather flat at the center of the Brillouin zone. For the other phases, to our knowledge the phonon dispersion curves have not been reported previously. The Al$_2$Si$_2$Sr$_3$ phase shows a gap between the TA acoustic modes and the optical modes. Another gap can be appreciated at even higher frequencies, suggesting that this phase may have lower transport properties than the other two. The last dispersion curve (Fig. 8 c) shows that the Al$_2$Si$_4$Sr$_3$ phase has high cross banding between the acoustic and optical modes. In all three cases there are no unstable modes in any region of the Brillouin zone, in agreement with the mechanical stability analysis presented above.

The summary of the results can be seen in the Table 7. The thermal expansion coefficients are lower than those of pure aluminum and strontium, although they are not as low as the thermal expansion coefficient of pure silicon. In the same way, the bulk modulus is much lower than that of pure aluminum and silicon, due to the sensitivity of strontium atoms to compression. Furthermore, the low Gruneisen parameter indicates that in all of these phases there is a weak dependence of the thermodynamic properties on temperature. This is corroborated by the formation free energy calculations for these structures, which increases only by 2–3 kJ/mol–atom over a 1000 K temperature range. Finally, the calculated heat capacities are very similar to the heat capacity of aluminum.

### 5. Summary and conclusions

We have studied, by using first-principles calculations, the structural, elastic and vibrational stability of a large set of Al$_x$Si$_y$Sr$_z$ alloys. It was demonstrated the possibility of the existence of new phases in the Al–Si–Sr system due to their energetic and mechanical stability, these results can be summarized as follows:

- In this work, the stability of twelve intermetallic compounds in the Al–Si–Sr system were studied. Four of these intermetallics have already been reported in the literature and eight of these structures have been reported in other chemically-analogous systems.
- The four reported phases were mechanically and energetically stable, while of the new phases only six were energetically stable. Virtually all the compounds studied were shown to be mechanically stable, with the only exception being the AlSi$_6$Sr$_4$ phase.
- The Al$_2$Si$_3$Sr$_3$, Al$_2$Si$_4$Sr$_3$, Al$_2$Si$_5$Sr$_5$, Al$_3$Si$_7$Sr$_{10}$, Al$_6$Si$_{13}$Sr$_{20}$ and Al$_8$Si$_{14}$Sr$_{14}$ intermetallics have an exothermic formation enthalpy. However, the stability of the phases is determined by the equilibrium conditions among all the phases in the ternary Al–Si–Sr system.
- The calculated ground state shows two new possible phases for the Al–Si–Sr ternary system with the other candidate phases being at best metastable with a $\Delta H^\text{f} = -7$–2–4 kJ/mol–atom.
- All the ternary intermetallics in the Al–Si–Sr system have metallic behavior with only the Al$_6$Si$_{14}$Sr$_{14}$ intermetallic having
a semi-metallic behavior. The $\text{Al}_2\text{Si}_2\text{Ge}_3$ and $\text{Al}_2\text{Si}_2\text{Sr}$ phases are metallic but with few states in the Fermi level.

- The vibrational and thermodynamic properties of the AlSiSr, $\text{Al}_2\text{Si}_2\text{Sr}$ and $\text{Al}_2\text{Si}_2\text{Sr}$ phases were studied considering the quasi-harmonic, anharmonic and electronic contribution to the free energy within the LDA and GGA approximations. These three phases show high electronic contribution to the free energy, this contribution are strong as the quasi-harmonic contribution. For the three phases we cannot appreciate significant changes when we employ the anharmonic contribution.

- The bulk modulus and the thermal expansion coefficients of the AlSiSr, $\text{Al}_2\text{Si}_2\text{Sr}$ and $\text{Al}_2\text{Si}_2\text{Sr}$ phases are low compared to the pure elements, while the heat capacity of the three is similar to the pure aluminum.

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Appendix: Supplementary material


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