

Ab-initio Calculations, Debye-Wang model and Thermodynamic Modeling for the Short-Range Order and Crystal Chemistry Characterization of the τ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ Solid Solution

P. Lafaye^{a,*}, K. Poëti^a and J.-P. Harvey^a

^aCRCT- Polytechnique Montréal, Chem. Eng., Box 6079, Station Downtown, Montréal, Qc, Montréal, H3C 3A7, Canada

ARTICLE INFO

Keywords:

τ - $\text{Al}_2\text{Fe}_3\text{Si}_4$
Crystal chemistry
First-principles calculations
Debye model
Short-Range Order

ABSTRACT

This paper presents a comprehensive examination of the τ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution, investigating its crystal chemistry and short-range order. To do so, Density functional theory (DFT) calculations were performed, simulating partial substitutions of Al and Si on the four mixed sites of the structure. Our results indicate a negligible contribution from the SRO, allowing the Bragg-Williams approximation to be used to describe its crystal chemistry. Subsequently, systematic substitutions of Al and Si on all mixed sites generated a complete set of ordered structures, called end-members. The formation enthalpies, equation of state and elastic constants for each end-member were calculated, allowing the Gibbs free energy of the solid solution to be derived using the Debye-Wang model. On the basis of this new theoretical insights, a thermodynamic model was developed, predicting the Si occupancy factors in all the mixed sites of the structure at different temperatures, allowing the quantification of its chemical ordering.

1. Introduction

The urgent need to reduce the ecological impact of our economies, coupled with the growing scarcity of accessible resources, especially mining resources, has led to a heightened interest in the utilization of recycled aluminium alloys [1, 2, 3]. The adoption of recycled alloys presents a significant environmental advantage, as the remelting of aluminium alloys consumes only 5% of the energy required for primary aluminum production via electrolysis from bauxite [2, 4]. However, a notable challenge persists in current recycling processes, where the effective removal of certain impurities, notably iron (Fe) and silicon (Si), remains elusive [5, 6, 7]. These impurities accumulate with each recycling cycle, resulting in escalating concentrations. This accumulation poses significant technological hurdles, particularly in the deterioration of mechanical properties, attributed to the stabilization of brittle phases such as Al-Fe [8, 9, 10] or Al-Fe-Si phases [11, 12]. This problem is especially concerning for alloy series like 1xxx and 8xxx, where Fe and Si impurities pose severe limitations [2, 13]. However, even alloy series like 2xxx and 6xxx, which have relatively narrow composition limits for Fe and Si, are not immune to this challenge [2, 13]. To overcome these issues and extend the applicability of recycled aluminium alloys to these series, it becomes imperative to gain a deeper understanding of the thermodynamic behavior of these impurity stabilized phases and predict their precipitation tendencies.

In principle, phase equilibria in multiconstituent systems can be accurately predicted using the Compound Energy Formalism (CEF), a fundamental aspect of the Calphad method [14]. CEF relies on describing solid solutions by

considering the occupancy of various elements on distinct crystal sites, which can then be merged into sublattices (SL) based on comparable occupancies. However, obtaining accurate occupancy data is a persistent challenge in materials science, often missing in the literature. This gap arises from a combination of factors, including a lack of research interest and the inherent difficulty in conducting precise measurements or calculations. In the specific case of the Al-Fe-Si ternary system, the challenge is even greater. This system comprises 11 ternary intermetallic phases [15], all of them exhibiting virtually constant Fe content [15, 16]. Consequently, the homogeneity ranges of these phases are determined by the mixing of Al and Si. However, distinguishing Al and Si via traditional methods like X-ray diffraction is not feasible as their electron densities are almost identical (only 1 electron difference). Similarly, the neutron diffraction technique is ineffective since the Fermi lengths of Al and Si are relatively close ($b = 3.449$ fm for Al and $b = 4.149$ fm for Si). Only the complex technique of resonant diffraction, which employs anomalous dispersion, enables the differentiation of these elements but is challenging to implement. Faced with these experimental challenges, several authors have resorted to constructing SL models for Al-Fe-Si solutions solely based on phase diagrams [17, 18]. Regrettably, our research experience, exemplified in our study of the τ - $\text{Al}_9\text{Fe}_2\text{Si}_2$ phase [19] and other Al-based solid solutions [20, 21], reveals that such models often yield inadequate thermodynamic descriptions of phases, casting doubt on extrapolations to higher-order systems.

The primary objective of this paper is to comprehensively characterize the crystal chemistry of the τ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution ($Cmcm$ space group) over a wide range of composition and temperature. This phase is of particular interest due to its successive modeling as a stoichiometric compound (referred to as phase τ in [17]) or as an ideal

*Corresponding author

 paul.lafaye@polymtl.ca (P. Lafaye)

ORCID(s): 0000-0002-4576-689X (P. Lafaye)

solid solution [18]. These two models represent extremes in terms of chemical ordering, with the stoichiometric compound having zero configurational entropy and the ideal solid solution possessing maximum configurational entropy. To elucidate the ordering within this solution, we conducted a comprehensive analysis of the crystal structure and performed Density Functional Theory (DFT) calculations to estimate the Short-Range Order (SRO) contribution within the solution. Additionally, we performed DFT calculations of the formation enthalpies, elastic constants, and equations of state for all ordered structures resulting from Al and Si substitutions on the four mixed sites of the structure, referred to as end-members. These calculations served as input for a Debye-Wang model, enabling the determination of the isobaric heat capacity of each end-member and, ultimately, the derivation of their Gibbs free energies. These Gibbs energy values, in turn, were utilized for the thermodynamic modeling of the solution, allowing the Si occupancy on the Al/Si mixed sites of the structure to be computed.

2. Methodology

2.1. First-principles calculations

We conducted Density Functional Theory (DFT) calculations using the Vienna Ab initio Simulation Package (VASP) code [22]. To describe exchange-correlation effects, we employed the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation [23]. The calculations utilized a k-point grid of $14 \times 4 \times 5$ and a cut-off energy of 600 eV to ensure accurate representations of the electronic structure. Projector Augmented Wave (PAW) pseudopotentials were employed for the elemental species Al, Fe, and Si [24]. Given the magnetic properties of Fe, spin-polarized calculations were performed, involving the relaxation of lattice parameters and internal atomic positions to obtain equilibrium structures.

We calculated the total energy and formation enthalpy for a set of 16 end-members, each representing a distinct distribution of Al and Si atoms across the four non-equivalent mixed sites within the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ structure.

Moreover, in order to assess the contribution of short-range ordering (SRO) within the structure, configurations with partial Si substitution were generated. Specifically, the complete set of ${}^nC_k$ configurations corresponding to the distribution of k atoms of Si (and $n-k$ atoms of Al) among n atomic positions was considered. The generation of all these structures was automated using the FTCrystal software [25]. The SRO contribution was evaluated by comparing the formation enthalpy of these partially substituted structures with the linear combination of the formation enthalpy from the two adjacent end-members (representing the complete substitution of Al and Si on the considered sites).

One should note that for the calculation of the formation enthalpy of a given structure, the pure elements were considered in their respective standard states (Al in the face-centered cubic (fcc) structure, Fe in the body-centered cubic (bcc) structure, and Si in the A4 structure).

Detailed crystallographic information for this phase is provided in Table 1.

2.2. Heat capacity calculations

In this study, we calculated the isobaric heat capacities for each end-member of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution, from 0 K up to 1283 K, using the Debye method within the quasi-harmonic approximation (QHA) [26]. This involved fitting the total energy as a function of volume for each end-member to the Birch-Murnaghan equation of state. All calculations were conducted using the VASP software.

The Debye temperature for each end-member was determined using the Debye-Wang model [27] in its Slater form [28]. To assess the mechanical properties, we computed the elastic tensor for each end-member by applying 49 finite distortions to the crystal lattice. The mechanical stability of the end-members generated were evaluated through the Born stability conditions for an orthorhombic system [29]:

$$\begin{cases} C_{ii} > 0 & (i = 1, 4, 5, 6); \\ C_{11}C_{22} > C_{12}^2 \\ C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 \\ -C_{33}C_{12}^2 > 0 \end{cases} \quad (1)$$

Additionally, we evaluated the electronic contribution to the isobaric heat capacity for each end-member by analyzing the volume-dependent electronic Density of States (DOS) at the Fermi level [30].

2.3. Calculation of the occupancy factors

The Gibbs free energy of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ phase at a specific temperature can be calculated by utilizing Density Functional Theory (DFT) computations for the formation enthalpy and heat capacity of all the end-members constituting the solid solution by means of the CEF [14]. The Gibbs free energy of the solution is given by:

$$G^{\tau 8}(T) = \sum_{i,j,k,l=\text{Al,Si}} \left[y_i^{\text{Al}(1)} y_j^{\text{Al}(2)} y_k^{\text{Al}(3)} y_l^{\text{Al}(4)} \right] \cdot H_{ijkl}^{\tau 8} + RT \sum_i a^{\text{Al}(i)} \cdot \sum_{j=\text{Al,Si}} y_j^{\text{Al}(i)} \ln y_j^{\text{Al}(i)} \quad (2)$$

$y_j^{\text{Al}(i)}$ is the *sof* of the element j on site $\text{Al}(i)\text{L}$, $H_{ijkl}^{\text{for},\tau 8}$ is the enthalpy of formation of the considered *end-member*, R is the gas constant, $a^{\text{Al}(i)}$ is the multiplicity of site $\text{Al}(i)$. For readers seeking a more detailed understanding of this methodology, we invite them to explore our prior research where we extensively employ the CEF [31, 32].

3. Results and discussion

3.1. First-principles calculations

The structure of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ phase was initially determined by Yanson et al [33]. These authors established that this phase belongs to the orthorhombic crystal system with space group $Cmcm$. The lattice parameters are $a = 3.6687 \text{ \AA}$, $b = 12.3850 \text{ \AA}$, and $c = 10.1470 \text{ \AA}$. According

to their findings, this phase contains two Fe sites, one Al site, and three Si sites. However, the inherent challenge in distinguishing between Al and Si using X-ray diffraction arises due to their successive atomic numbers. Consequently, Yanson et al. proposed a crystallographic model that assumed no mixing between these elements. It's worth noting that the chemical composition derived from their model (8 atoms of Al and 16 atoms of Si per cell) falls beyond the recognized homogeneity range of the phase [15]. However, their work suggests that within the homogeneity range of the solution, the three sites labeled as Si must predominantly contain Si, while the site labeled as Al predominantly contains Al. These conclusions are exclusively applicable within the homogeneity range of the solution. In our study, we extend our investigation of the τ 8- $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution into a chemical composition range that extends from the Al-Fe binary system to the Si-Fe binary system. As a result, Yanson's labels for the mixed crystallographic sites are no longer relevant in this framework. To ensure clarity and consistency in our analysis, we have made an arbitrary decision to label all the mixed sites in the structure as Al. This choice simplifies our nomenclature and facilitates uniformity in our analysis. The crystallographic sites of the τ 8- $\text{Al}_2\text{Fe}_3\text{Si}_4$ phase, the Wyckoff positions and their coordinates are reported in the Table 1.

Site	Wyckoff position	x	y	z
Fe(1)	8f	0	0.1490	0.1254
Fe(2)	4c	0	0.3528	0.2500
Al(1)	8f	0	0.0575	0.6086
Al(2)	8f	0	0.3191	0.0150
Al(3)	4c	0	0.5448	0.2500
Al(4)	4c	0	0.7396	0.2500

Table 1: Crystal structure of the τ 8- $\text{Al}_2\text{Fe}_3\text{Si}_4$ phase.

The values of the total energies and enthalpies of formation for all the end-members of the τ 8- $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution are presented in Table 2.

Taking the end-members completely substituted by Al or Si as references (Fe:Al:Al:Al:Al and Fe:Si:Si:Si:Si end-members), we determine the enthalpy of mixing of the solid solution, as shown in Figure 1. In this Figure, the convex black line represents the *ground-state* of the solid solution, connecting the stable end-members at 0 K.

Several remarkable observations emerge from Figure 1. Firstly, we observe a minimum in the enthalpy of mixing at around -16 kJ/mol-at for $x = 0.5$ in $\text{Al}_{1-x}\text{Si}_x\text{Fe}_{0.333}$. This value stands out for its unusually high magnitude, revealing the exothermic nature of the solid solution. In addition, the other end-members of the solid solution exhibit significant energy differences compared to the *ground-state*, except for the end-members resulting from opposite substitutions on sites Al(3) and Al(4) (Al:Si:Si:Al - Al:Si:Al:Si or Si:Si:Si:Al - Si:Si:Al:Si), which show a more moderate energy difference. We can therefore expect the solid solution to exhibit a

Fe*	Site multiplicity				E_{tot} eV	ΔH_f kJ.mol-at ⁻¹
	Al(1)	Al(2)	Al(3)	Al(4)		
12	8	8	4	4		
Fe	Al	Al	Al	Al	-196.793	-21.538
Fe	Al	Al	Al	Si	-205.638	-29.880
Fe	Al	Al	Si	Al	-206.427	-31.996
Fe	Al	Al	Si	Si	-213.800	-36.393
Fe	Al	Si	Al	Al	-216.018	-42.340
Fe	Al	Si	Al	Si	-224.523	-49.773
Fe	Al	Si	Si	Al	-224.042	-48.483
Fe	Al	Si	Si	Si	-231.279	-52.517
Fe	Si	Al	Al	Al	-212.083	-31.794
Fe	Si	Al	Al	Si	-220.401	-38.724
Fe	Si	Al	Si	Al	-220.037	-37.749
Fe	Si	Al	Si	Si	-226.646	-40.098
Fe	Si	Si	Al	Al	-228.631	-45.418
Fe	Si	Si	Al	Si	-235.186	-47.625
Fe	Si	Si	Si	Al	-235.608	-48.758
Fe	Si	Si	Si	Si	-240.692	-47.021

Table 2: DFT calculated total energy (E_{tot}) and enthalpy of formation (ΔH_f) of the τ 8- $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution end-members. References are Al in *fcc* structure, Fe in *bcc* structure and Si in the *A4* structure. Fe* stands for Fe(1) and Fe(2) combined sites.

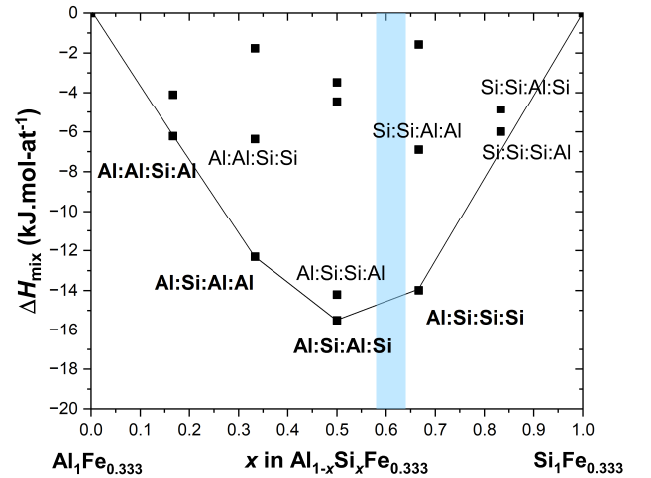


Figure 1: Mixing enthalpy of the τ 8- $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution calculated at 0 K. The blue band highlights the reported homogeneity range (i.e. stability range) of the phase. Stable end-members at 0 K are denoted in bold. End-member notation follows Table 1, with references $\text{Al}_1\text{Fe}_{0.333}$ and $\text{Si}_1\text{Fe}_{0.333}$.

relatively high level of chemical ordering over a wide range of temperatures.

The second and most interesting aspect of Figure 1 concerns the substitution of Al by Si in the composition range investigated. Specifically, for $x < 0.166$ (in $\text{Al}_{1-x}\text{Si}_x\text{Fe}_{0.333}$), the substitution of Al by Si is progressive on site Al(3). For

x between 0.166 and 0.333, the *ground-state* alternates between the end-members Al:Al:Si:Al and Al:Si:Al:Al, meaning that site Al(3) is progressively depleted from Si in favour of site Al(2). A complete reversal of the Si occupancy on sites Al(2) and Al(3) occurs from $x = 0.166$ to $x = 0.333$. This relatively unusual behaviour leads to homogeneity ranges described as irregular when observed experimentally [34]. The irregularity observed in our study occurs in the metastable domain of the solid solution and does not appear significant enough to qualify this solution as irregular. Moreover, although the end-member Al:Al:Si:Al is part of the *ground-state* of the solid solution, it shows minimal energy differences from the line formed by the Al:Si:Al:Al end-member. This observation suggests that for values of x less than 0.333 and for a finite temperature, the occupation of site Al(2) will be thermodynamically favoured at the expense of site Al(3) due to a greater contribution from its configurational entropy of mixing. Over the remaining composition range (x greater than 0.333), the substitution of Al by Si is strictly sequential, in the sense that Si cannot occupy several sites simultaneously. Indeed, the *ground-state* shows that Si substitutes for Al sequentially on sites Al(4), then Al(3), and finally Al(1). It is important to recall that the energy difference between the *ground-state* and the other end-members of the solid solution is relatively large (several kJ/mol-at). Consequently, outside the composition range of $0.166 < x < 0.333$, it is difficult to imagine how Si could substitute for Al on several sites simultaneously, at 0 K.

One final observation concerns the homogeneity range of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution, highlighted in blue in Figure 1. This range lies between the Al:Si:Al:Si and Al:Si:Si:Si end-members and therefore necessarily results from Al/Si substitution on the Al(3) site of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ structure. Notably, this observation invalidates the SL model used by Liu et al. [17], which postulates complete ordering in the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution.

The analysis of Figure 1 highlighted the sequential nature of the substitution of Al by Si, except for the composition range $0.166 < x < 0.333$ for which it cannot be excluded that both sites Al(2) and Al(3) are occupied by Si simultaneously. The characterisation of the short-range order (SRO) within the solution must therefore consider two distinct scenarios: firstly, the quantification of the SRO by considering each site individually, and secondly, the quantification of the SRO when Si partially occupies both sites Al(2) and Al(3) simultaneously.

The coordination polyhedra of the four Al sites within the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution structure are visually represented in Figure 2. In this illustration, the atomic positions of the Al(1), Al(2), Al(3), and Al(4) sites are distinguished by colors: blue, white, green, and yellow, respectively. This same color scheme extends to represent the coordination polyhedra of these sites. The analysis of these coordination polyhedra gives rise to a particularly interesting observation. The Al(3) and Al(4) sites have no atoms from the same

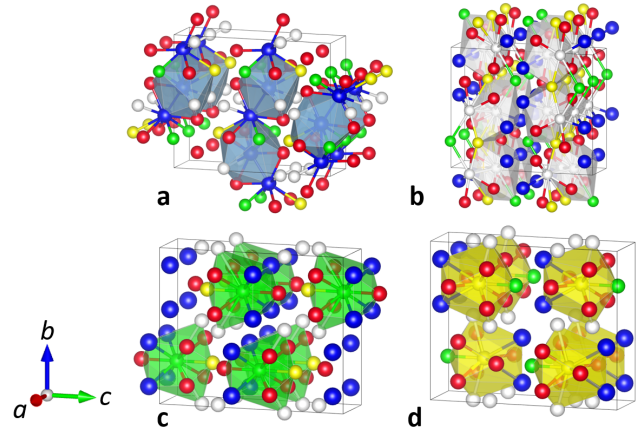


Figure 2: Coordination polyhedra for Al sites in the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ structure: (a) Al(1) in blue, (b) Al(2) in white, (c) Al(3) in green, and (d) Al(4) in yellow. Atomic positions are color-coded consistently with their respective coordination polyhedra.

site on their coordination polyhedra. In addition, the Al(1) and Al(2) sites have only two atoms from the same site on their coordination polyhedra (with coordination numbers of 11 and 12 respectively). This observation leads us to the important inference that the contribution of the SRO of each individual site may be negligible. To quantitatively assess this SRO contribution, the enthalpies of formation of partially substituted structures were calculated using DFT. Each Al site was addressed individually, with half of the site substituted by Si. All possible configurations corresponding to partial substitution with 50% Si have been generated *i.e.* 70 configurations for each of the Al(1) and Al(2) sites, and 6 configurations for each of the Al(3) and Al(4) sites. It is interesting to note that, for a given crystal site, the different partially substituted structures show very similar enthalpies of formation, with standard deviations below 0.2 kJ/mol-at for the Al(1) and Al(2) sites, and below 0.1 kJ/mol-at for the Al(3) and Al(4) sites. As a result, only the average value of the formation enthalpies of the partially substituted structures has been plotted in Figure 3 with the standard deviation shown by the error bars. The average formation enthalpy of the partially substituted structures for the Al(1), Al(2), Al(3) and Al(4) sites are shown in Figures 3 a), b), c) and d), respectively. The SRO contribution for each crystal site can thus be evaluated by comparing the average formation enthalpy of the partially substituted structures, shown in red, with the linear combination of the formation enthalpies of the adjacent end-members, shown in black in Figure 3. Notably, the deviation from the ideal mixing of Al and Si on sites Al(3) and Al(4) is virtually zero (deviation < 0.1 kJ/mol-at). For the Al(1) and Al(2) sites, although the SRO contribution is greater, the deviations from the ideal mixing are still relatively small, ± 0.4 kJ/mol-at. These results are in good agreement with our analysis of coordination polyhedra.

Finally, the simultaneous substitution of Si on both sites Al(2) and Al(3) was studied. To do this, we considered sites Al(2) and Al(3) as equivalent and generated all the

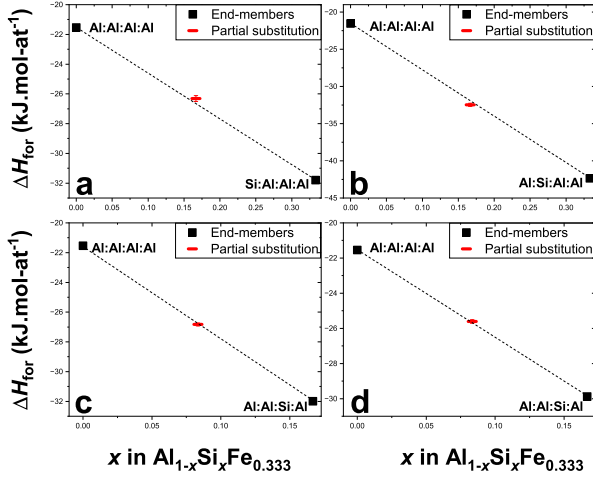


Figure 3: Average enthalpy of formation of all structures with 50% Si partial substitution on the crystal site a) Al(1), b) Al(2), c) Al(3), d) Al(4). The dotted line represents the enthalpy of formation resulting from ideal mixing on each crystal site of the structure

configurations with equal mole fractions of Al and Si, i.e. 924 configurations. We found that the formation enthalpies of all the structures studied were relatively close. In fact, the standard deviation of the enthalpies of the 924 structures is only 0.530 kJ/mol-at. Moreover, the mean value of the enthalpy of formation of these structures (-36.275 kJ/mol-at) is relatively close to the value of the ground-state at the same chemical composition (-37.168 kJ/mol-at), as shown in Figure 4. This shows that the SRO of the solution is low and can be neglected in this composition range.

Combining the results of the coordination polyhedra analysis and the DFT calculations of the partially substituted structures, we can conclude that the contribution of the SRO is minor and can be neglected. This validates the use of the Bragg-Williams approach implemented in the CEF [14] to characterise the crystal chemistry of the solid solution.

3.2. Debye-wang model and Thermodynamic modelling

The elastic tensor of each end-member of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution is presented in Table 3. All considered end-members meet Born's mechanical stability criteria [29], ensuring their mechanical stability. Combining these results with equations of state calculations allowed the determination of isobaric heat capacities for each end-member, from 0 K to 1283 K (solid solution decomposition temperature). Figure 5 illustrates the heat capacities between 298 K and 1283 K for all solid solution end-members, alongside the heat capacities approximated using the Kopp-Neumann rule [35] for the two extreme compositions ($x = 0$ and $x = 1$ in $\text{Al}_{1-x}\text{Si}_x\text{Fe}_{0.333}$). Detailed heat capacity functions for each end-member within the solid solution are provided

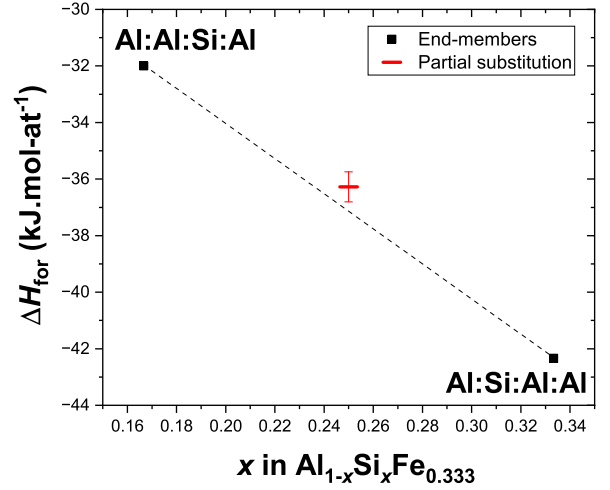


Figure 4: Average enthalpy of formation of all structures with 50% Si partial substitution on the crystal site Al(2) and Al(3). The vertical red bar represent the standard deviation of the formation enthalpy of the different structures. The dotted line represents the *ground-state* of the solid solution.

in Table 4, covering the temperature range from 298 K to 1283 K.

The widely used Kopp-Neumann approximation estimates a compound heat capacity as the compositional average of its pure elemental constituents. While straightforward, this approach proves unreliable in our study. Applying it would yield gradually varying heat capacities between those of the two end-members representing the extreme compositions ($x = 0$ and $x = 1$ in $\text{Al}_{1-x}\text{Si}_x\text{Fe}_{0.333}$). Notably, significant discrepancies are observed, especially for Al-rich and equal Al-Si content end-members. The Kopp-Neumann approximation tends to provide acceptable results only for some Si-rich end-members. This aligns with our prior study on the $\tau 6\text{-Al}_9\text{Fe}_2\text{Si}_2$ phase [19], cautioning against its application in characterizing crystal chemistry.

From the DFT calculations of the enthalpy of formation (see Table 2) and the heat capacity (see Table 4) of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution end-members, we determined the Si fraction on all the mixed sites within the structure at both 300 K and 1283 K, as illustrated in Figures 6 and 7, respectively.

Firstly, it is evident that a significant degree of ordering exists within the solid solution at 300 K, and this ordering persists up to 1283 K, which is the decomposition temperature of the solution. Notably, this ordering is characterized by the opposite Si fractions on the Al(1) and Al(2) sites: At all temperature, for $x = 0.5$ in $\text{Al}_{1-x}\text{Si}_x\text{Fe}_{0.333}$, the Al(1) site is entirely occupied by Al, while the Al(2) site is entirely occupied by Si. This observation is consistent with our initial remark following the analysis of Figure 1. Likewise, examination of Figures 6 and 7 reveals that the homogeneity range of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution,

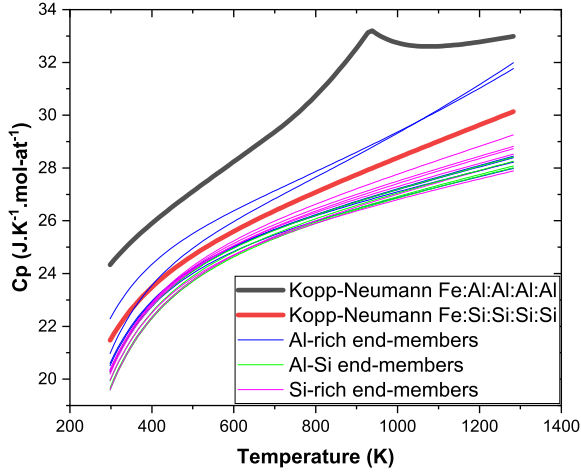


Figure 5: Isobaric heat capacities (C_p) of the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution end-members from 298 K to 1283 K. Al-rich end-members are shown in blue, Si-rich end-members in magenta, and those with equal Al and Si content in green. C_p values obtained using the Kopp-Neumann rule are reported for the two extreme end-members (the black and red curves stand for composition $x = 0$ and $x = 1$ in $\text{Al}_{1-x}\text{Si}_x\text{Fe}_{0.333}$, respectively).

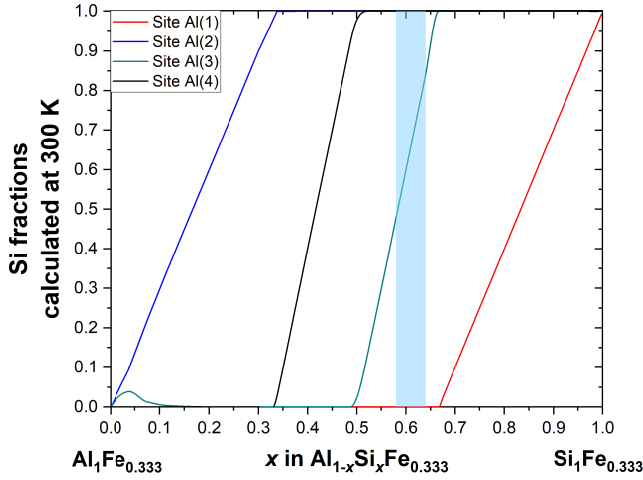


Figure 6: Si site occupation factors in the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution at 300 K. The blue band highlights the homogeneity range of the solid solution.

highlighted in blue, is defined by the mixing of Al and Si on site Al(3) at 300 K and on sites Al(3) and Al(4) at higher temperatures (1283 K). These findings reinforce our earlier conclusions regarding the homogeneity domain of the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solution and definitively invalidate the SL model presented by Liu et al. [17]. It can also be observed that the homogeneity range of the solution is characterized by

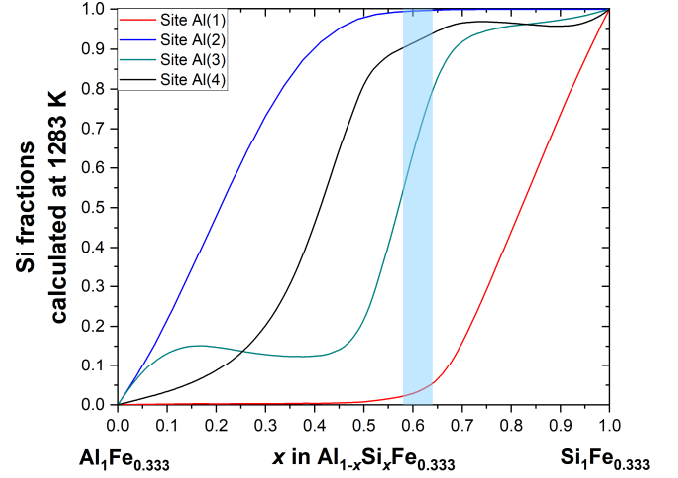


Figure 7: Si site occupation factors in the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution at 1283 K. The blue band highlights the homogeneity range of the solid solution.

a predominant Si occupation on the Al(2), Al(3), and Al(4) sites, while the Al(1) site remains virtually unoccupied by Si. These findings are in agreement with the conclusions of Yanson et al. [33]. Lastly, based on these new occupancy data, a potential simplification of the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution comes into view. This simplification would involve combining the Al(3) and Al(4) sites into a single sublattice (SL). Given the notably pronounced ordering observed at the Al(1) and Al(2) sites, no other simplification appears feasible.

The data obtained in this study not only enable the quantification of chemical ordering within the solid solution but also facilitate the evaluation of various SL models through the calculation of the configurational entropy of mixing. In Figure 8 we show the exact configurational entropy of the solid solution computed at 300 K and 1283 K, represented by the solid blue and red curves, respectively, labelled as '4-SL' in reference to the 4 sublattices required to describe the mixed sites of the structure (excluding the sublattice occupied solely by Fe). Additionally, Figure 8 depicts the configurational entropy at 300 K and 1283 K for the model involving the grouping of Al(3) and Al(4) sites in a single SL, illustrated by the dashed blue and red curves, respectively. The black dashed curve corresponds to the ideal mixing entropy, representing the model employed by Du et al [18].

This Figure illustrates the strong ordering observed in the solid solution at 300 K, which persists significantly across all temperatures. These findings align well with our initial assumptions drawn from the analysis presented in Figure 1. However, despite the substantial degree of ordering, it would be misleading to characterize this phase as a stoichiometric compound, as proposed by Liu et al [17]. Similarly,

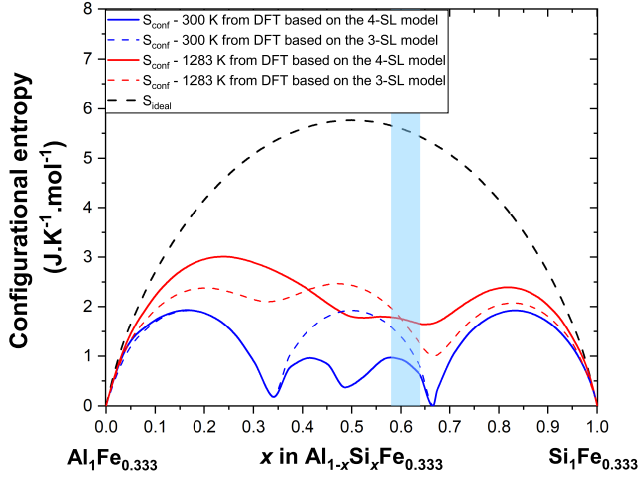


Figure 8: Configurational entropy of the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution at 300 K (blue) and 1283 K (red). Solid curves represent the exact crystal structure description, while dashed curves depict configurational entropy considering the merging of Al(3) and Al(4) sites into a single sublattice (SL). The black dashed curve represents the configurational entropy of an ideal solution.

the model by Du et al. [18], which treats this solution as ideal, is contradicted by our results. Additionally, the SL model tested in this study—merging the Al(3) and Al(4) sites into a single sublattice—proves inadequate for describing this solid solution. The simplification it offers seems too limited in relation to the deterioration in the configurational entropy of mixing description. Our results strongly support the relevance of the 4-SL model for accurately describing the mixed sites of the structure.

4. Conclusions

In this study, we conducted a detailed investigation of the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution, exploring its crystal chemistry through a combination of theoretical calculations and thermodynamic modelling. Our DFT calculations provided detailed information on the enthalpies of formation, elastic constants and equations of state of all the end-members of the solid solution, and also enabled us to calculate their isobaric heat capacities. In addition, by analysing the crystal structure of the solution and performing DFT calculations on partially substituted structures, we have shown that the contribution of short-range order (SRO) can be neglected, which validates the application of the Bragg-Williams approach to the study of the crystal chemistry of this solution.

Our results revealed significant chemical ordering within the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution, challenging previous models that treated it as stoichiometric or ideal. More specifically, the 4-SL model appeared to be the most relevant for an accurate representation of the thermodynamic stability of the solution.

This study not only provides valuable information on the limitations of existing models, but also greatly improves our understanding of the thermodynamic behaviour of the $\tau 8$ - $\text{Al}_2\text{Fe}_3\text{Si}_4$ solid solution.

5. Acknowledgement

This work was financially supported by the Professor Harvey Discovery Grant (RGPIN-2017-06168) (NSERC).

Funding support was obtained through the Alliance Grant (ALLRP 560998 - 20).

Compute Quebec and Compute Canada are thanked for supplying the intensive calculation tools.

References

- [1] T. G. Gutowski, S. Sahni, J. M. Allwood, M. F. Ashby, E. Worrell, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 371 (2013) 20120003.
- [2] D. Raabe, D. Ponge, P. J. Uggowitzer, M. Roscher, M. Paolantonio, C. Liu, H. Antrekowitsch, E. Kozeschnik, D. Seidmann, B. Gault, et al., Progress in materials science 128 (2022) 100947.
- [3] J. L. Cann, A. De Luca, D. C. Dunand, D. Dye, D. B. Miracle, H. S. Oh, E. A. Olivetti, T. M. Pollock, W. J. Poole, R. Yang, et al., Progress in Materials Science 117 (2021) 100722.
- [4] K. Daehn, R. Basuhi, J. Gregory, M. Berlinger, V. Somjit, E. A. Olivetti, Nature Reviews Materials 7 (2022) 275–294.
- [5] D. Ashkenazi, Technological Forecasting and Social Change 143 (2019) 101–113.
- [6] H. L. de Moraes, J. R. de Oliveira, D. C. R. Espinosa, J. A. S. Tenório, Materials transactions 47 (2006) 1731–1736.
- [7] G. Gaustad, E. Olivetti, R. Kirchain, Resources, Conservation and Recycling 58 (2012) 79–87.
- [8] D. Liang, P. Korgul, H. Jones, Acta materialia 44 (1996) 2999–3004.
- [9] J. Chen, R. Lengsdorf, H. Henein, D. Herlach, U. Dahlborg, M. Calvo-Dahlborg, Journal of alloys and compounds 556 (2013) 243–251.
- [10] P. R. Goulart, J. E. Spinelli, N. Cheung, A. Garcia, Materials Chemistry and Physics 119 (2010) 272–278.
- [11] T. Gao, Y. Wu, C. Li, X. Liu, Materials Letters 110 (2013) 191–194.
- [12] V. Srivastava, R. Mandal, S. Ojha, K. Venkateswarlu, Materials Science and Engineering: A 471 (2007) 38–49.
- [13] I. Polmear, Light alloys: from traditional alloys to nanocrystals, Elsevier, 2005.
- [14] M. Hillert, Journal of Alloys and Compounds 320 (2001) 161–176.
- [15] M. C. Marker, B. Skolyszewska-Kühberger, H. S. Effenberger, C. Schmetterer, K. W. Richter, Intermetallics 19 (2011) 1919–1929.
- [16] N. Krendelsberger, F. Weitzer, J. C. Schuster, Metallurgical and materials transactions A 38 (2007) 1681–1691.
- [17] Z.-K. Liu, Y. A. Chang, Metallurgical and Materials Transactions A 30 (1999) 1081–1095.
- [18] Y. Du, J. C. Schuster, Z.-K. Liu, R. Hu, P. Nash, W. Sun, W. Zhang, J. Wang, L. Zhang, C. Tang, et al., Intermetallics 16 (2008) 554–570.
- [19] P. Lafaye, M. D. Vo, J. Jofre, J.-P. Harvey, Physical Chemistry Chemical Physics 25 (2023) 20015–20025.
- [20] P. Lafaye, K. Oishi, M. Bourdon, J.-P. Harvey, Journal of Alloys and Compounds 920 (2022) 165779.
- [21] P. Lafaye, K. Oishi, J.-P. Harvey, Journal of Alloys and Compounds 944 (2023) 169054.
- [22] G. Kresse, J. Furthmüller, Physical review B 54 (1996) 11169.
- [23] J. P. Perdew, K. Burke, M. Ernzerhof, Physical review letters 77 (1996) 3865.
- [24] G. Kresse, D. Joubert, Physical review b 59 (1999) 1758.
- [25] K. Poëti, P. Lafaye, J. Jofre, K. Oishi, J.-P. Harvey, Calphad (to be submitted).
- [26] B. Fultz, Progress in Materials Science 55 (2010) 247–352.

- [27] Y. Wang, R. Ahuja, B. Johansson, International journal of quantum chemistry 96 (2004) 501–506.
- [28] J. C. Slater, Introduction to chemical physics, Read Books Ltd, 2011.
- [29] F. Mouhat, F.-X. Coudert, Physical review B 90 (2014) 224104.
- [30] A. Otero-de-la Roza, D. Abbasi-Pérez, V. Luaña, Computer Physics Communications 182 (2011) 2232–2248.
- [31] P. Lafaye, Developpement d’outils de modélisation thermodynamique pour la prediction de l’état metallurgique d’alliages a base zirconium, Ph.D. thesis, Université Paris-Est, 2017.
- [32] P. Lafaye, C. Toffolon-Masclet, J.-C. Crivello, J.-M. Joubert, Journal of Nuclear Materials 544 (2021) 152692.
- [33] T. I. Yanson, M. B. Manyako, O. I. Bodak, N. V. German, O. S. Zarechnyuk, R. Cerný, J. V. Pacheco, K. Yvon, Acta Crystallographica Section C: Crystal Structure Communications 52 (1996) 2964–2967.
- [34] J.-M. Joubert, M. Andasmas, J.-C. Crivello, Applied Sciences 5 (2015) 1570–1589.
- [35] H. Kopp, Philosophical Transactions of the Royal Society of London (1865) 71–202.

Site Multiplicity					Elastic constants (GPa)								
Fe*	Al(1)	Al(2)	Al(3)	Al(4)	C ₁₁	C ₁₂	C ₁₃	C ₂₂	C ₂₃	C ₃₃	C ₄₄	C ₅₅	C ₆₆
12	8	8	4	4									
Fe	Al	Al	Al	Al	208.3	89.4	107.6	243.3	50.7	197.3	109.4	48.1	79.6
Fe	Al	Al	Al	Si	214.1	112.6	94.9	291.0	47.7	278.3	143.2	98.0	119.7
Fe	Al	Al	Si	Al	210.3	105.3	85.7	287.4	79.1	296.8	125.1	101.0	120.4
Fe	Al	Al	Si	Si	248.4	117.8	110.2	318.6	48.8	281.1	141.2	89.7	119.4
Fe	Al	Si	Al	Al	258.3	109.3	110.4	301.4	63.7	303.0	141.4	108.1	127.5
Fe	Al	Si	Al	Si	330.9	107.2	91.4	330.1	61.8	336.7	139.4	119.7	130.7
Fe	Al	Si	Si	Al	322.6	100.4	88.5	340.9	67.9	327.6	140.3	112.4	124.9
Fe	Al	Si	Si	Si	368.0	116.2	90.7	350.9	60.2	345.8	129.5	121.2	119.5
Fe	Si	Al	Al	Al	252.6	102.4	105.5	324.6	45.1	290.9	137.3	77.4	107.4
Fe	Si	Al	Al	Si	322.3	103.9	85.1	352.0	44.8	330.3	139.0	97.1	108.7
Fe	Si	Al	Si	Al	297.4	109.1	90.0	349.9	53.4	319.3	132.4	82.5	113.3
Fe	Si	Al	Si	Si	345.6	120.7	84.3	366.3	43.8	339.0	126.6	97.0	102.0
Fe	Si	Si	Al	Al	308.7	131.6	107.3	318.5	46.0	345.5	135.4	102.0	115.2
Fe	Si	Si	Al	Si	342.8	137.3	117.1	345.3	39.1	341.9	121.3	111.8	103.2
Fe	Si	Si	Si	Al	284.7	137.7	113.9	361.2	71.7	348.9	126.7	104.2	124.6
Fe	Si	Si	Si	Si	336.0	139.1	114.0	375.5	72.3	355.4	103.0	108.1	107.2

Table 3: Elastic constants (GPa) of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution end-members calculated by DFT. Fe* stands for Fe(1) and Fe(2) combined sites. End-members notation follows Table 1.

Site Multiplicity					Heat capacity, Cp (J/K.mol-at.)			
Fe*	Al(1)	Al(2)	Al(3)	Al(4)	10	$10^{-3}T$	-10^5T^{-2}	$10^{-6}T^2$
12	8	8	4	4				
Fe	Al	Al	Al	Al	2.5609	1.0661	3.4769	3.0360
Fe	Al	Al	Al	Si	2.4095	3.0960	4.1564	0.1034
Fe	Al	Al	Si	Al	2.4160	3.2101	4.1064	0.2167
Fe	Al	Al	Si	Si	2.5532	0.6903	4.5161	3.5491
Fe	Al	Si	Al	Al	2.4051	3.4406	4.2800	0.1462
Fe	Al	Si	Al	Si	2.3743	3.7093	4.6666	-0.1269
Fe	Al	Si	Si	Al	2.3777	3.7034	4.6237	-0.1041
Fe	Al	Si	Si	Si	2.3784	3.6601	4.6888	0.0291
Fe	Si	Al	Al	Al	2.4143	3.3003	4.0252	0.0523
Fe	Si	Al	Al	Si	2.3909	3.5504	4.4760	0.0356
Fe	Si	Al	Si	Al	2.4048	3.4185	4.2865	0.1474
Fe	Si	Al	Si	Si	2.3908	3.4148	4.4045	-0.0822
Fe	Si	Si	Al	Al	2.4021	3.6245	4.3785	0.2000
Fe	Si	Si	Al	Si	2.4102	3.6709	4.3951	0.4294
Fe	Si	Si	Si	Al	2.4023	3.7972	4.3210	0.1133
Fe	Si	Si	Si	Si	2.4041	3.6130	4.2474	0.0633

Table 4: Isobaric heat capacities (Cp) of the $\tau 8\text{-Al}_2\text{Fe}_3\text{Si}_4$ solid solution end-members calculated from 298 K up to 1283 K. Fe* stands for Fe(1) and Fe(2) combined sites. End-members notation follows Table 1.