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Investigation of silicon sublattice substitution within (Al,Si)$_3$Zr intermetallics via DFT simulations

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Abstract. Aluminum alloys commonly contain Si as an impurity or alloying element. The energetic behavior of Si within multiple compounds and solutions is incorporated inside thermochemical packages, such as FactSage. This tool allows determining the Si partitioning within complex multiphasic systems. Recent experimental research suggests that Si can be found within Al$_3$Zr-based intermetallics. Nevertheless, current FactSage databases do not consider the potential substitution of Si within the Al$_3$Zr-D0$_{23}$ solid solution. In this work, Si substitution within the (Al,Si)$_3$Zr-D0$_{23}$ phase was investigated by means of first-principles calculations. Replacement of Al atoms by Si resulted in a negative enthalpy of mixing, indicating that Si substitution is energetically enabled. The density of states (DOS) for both a Si-diluted (Al,Si)$_3$Zr and a non-Si-doped (Al$_3$Zr) simulation cells were analyzed. It is shown that (even in dilution), Si significantly impacts the electronic structure of the Al$_3$Zr-D0$_{23}$ structure. Specifically, the presence of Si localizes electrons in the p orbital of Al, and increases the DOS of the d_{xy}, d_{xz}, and d_{yz} sub-orbitals of Zr at low energies. Thus, yielding a coupled effect that stabilizes the D0$_{23}$ intermetallic. These findings are a benchmark for the future integration of a Si-based end-member within the Al$_3$Zr-D0$_{23}$ solid solution of FactSage databases.

Keywords: Al$_3$Zr, Si-substitution, DFT, enthalpy of mixing, density of states

1. Introduction

The energetic description of peritectic phases such as the Al$_3$Zr intermetallic is highly important for aluminum alloy design [1]. In complex systems (i.e. with multiple alloying elements), these intermetallics precipitate as ordered multicomponent solid solutions upon solidification. The substitution of compatible elements within Al$_3$Zr intermetallics can be thermodynamically described using Gibbs free energy models, such as the Compound Energy Formalism (CEF)[2]. These models can be integrated into self-consistent databases of computational thermochemistry packages. To construct these models, mixing parameters are required. As an example, the heat of mixing can be obtained by *in-situ* synthesis [3] for specific stability ranges (as a function of the concentration, temperature, or pressure) of a given phase. Nowadays, the enthalpy of mixing between end-members making up a phase (e.g. using the CEF approach) can be

obtained using computational quantum mechanics methods. For instance, Density Functional Theory (DFT) calculations are broadly employed to describe stable and meta-stable phases [4, 5]. Computational-based methods are at the core of the next generation of thermodynamic models [6]. Ultimately, these tools allow a constant updating of thermochemical databases, which is a critical aspect to study new alloys. For casting, thermochemistry is employed for two main purposes: on the one hand, the precipitation of desired primary phases can be easily anticipated by calculating isoplethal cross-sections as a function of temperature and with variations in the alloying elements. On the other side, the formation of secondary phases can be approximated by performing Scheil-Gulliver Cooling calculations [7]. Micro-segregation inside phases can also be predicted with the Scheil-Gulliver technique. Constant improvement on thermochemical databases are therefore required to properly describe the solidification of aluminium alloys.

Recent experimental observations indicate that Si can be found in Al_3Zr-based intermetallics. As an example, Salloum-Abou-Jaoude *et al.* [8] reported the presence of $Al_3(Zr_{1-x-y}, Ti_x, Si_y)$ intermetallics at the core of α-grains of AA6082 Direct Chill (DC)-cast billets. In an independent work, Jo *et al.* [9] indicated that Si can substitute Al sites in the complex $(Al,Si)_3(Zr,Ni,Fe)$ $D0_{23}$-like intermetallic, which was observed in the Al-14Si-3Cu-4.5Ni alloy. These findings, coupled with numerical tests, are required to model Si occupancy within the $D0_{23}$ solution of FactSage [10]. Other thermochemical-software developers can benefit from these results if Si has not been yet included in their $D0_{23}$ solution models, which is the case of the $(Al, Li, Mg)_3(Hf, Sc, Ti, Zr)$-$D0_{23}$ phase model in the Al-based Alloy Database (TCAL8) of Thermo-Calc [11].

In this work, the energetic description of the partially ordered $(Al,Si)_3Zr$-$D0_{23}$ solid solutions is carried out using DFT calculations. Supercells of Al_3Zr, Si_3Zr, and $(Al,Si)_3Zr$ (Si/Al-diluted) of the pseudo-binary solution are generated and equilibrated. Results are later integrated into an enthalpy of the mixing model derived from the partial enthalpies of infinite dilution. Following an equivalent methodology (i.e. with an infinite dilution approach), the lattice parameters of the tetragonal phase are calculated. Finally, the electronic density of states (DOS) of a Si-doped structure is analyzed and compared to a non-Si-doped Al_3Zr-$D0_{23}$ structure. The effect of the dopant (Si) on the electronic distribution of the p orbital of Al, and the d orbital of Zr are discussed.

2. Methodology

The Vienna ab initio Simulation Package (VASP) [12, 13, 14, 15] was used to execute plane wave Density Functional Theory (DFT) calculations to estimate the enthalpy of mixing of the $(Al,Si)_3Zr$-$D0_{23}$ solid solution. Pseudopotentials built with the projector-augmented wave (PAW) approach [16, 17] were utilized for Si, Al and Zr. The exchange-correlation functionals were described through the generalized gradient approximation (GGA) [18, 19]. Convergence in the cell volume and energy was accomplished with a cut-off energy of 520 eV. Sampling of the Brillouin zone was conducted using the Monkhorst-Pack scheme with a $7 \times 7 \times 2$ k-point mesh for the $D0_{23}$ configurations. An accuracy of more than 0.01 meV in the system's energy was achieved by using a Gaussian smearing parameter σ of 0.02 eV. The convergence criterion for self-consistent field (SCF) electronic calculations was 1×10^{-5} and 0.02 eV/Å for ionic relaxation loop. The total energy was estimated in the NPT statistical ensemble, i.e the atomic positions, the equilibrium lattice, cell shape and cell volume were allowed to be relaxed. Each simulation box contained 128 atoms. Al and Si were randomly substituted to generate the pseudo-binary $D0_{23}$-based configurations. According to the methodology reported by Sluiter & Kawazoe [20], the corresponding solution enthalpies ($\Delta h_{soln}^{\text{Al-rich}}$ and $\Delta h_{soln}^{\text{Si-rich}}$) can be computed as:

$$\Delta h_{soln}^{\text{Al-rich}} = \left[\frac{\partial \Delta h_{mix}}{\partial x} \right]_{x=0} \qquad \Delta h_{soln}^{\text{Si-rich}} = -\left[\frac{\partial \Delta h_{mix}}{\partial x} \right]_{x=1} \qquad (1)$$

The molar enthalpy of mixing (Δh_{mix}) can be approximated as follows [20]:

$$\Delta h_{mix} \approx \Delta h_{soln}^{\text{Si-rich}} x^2 (1-x) + \Delta h_{soln}^{\text{Al-rich}} x(1-x)^2 \tag{2}$$

x stands for the Si substitional ration [Si/(Al+Si)] within the $(Al_{1-x},Si_x)_3Zr$ pseudo-binary solid solution. In an equivalent manner, variations in the lattice parameters (Δa and Δc) were computed using infinite dilution approximations: $\Delta a \approx \Delta a_{soln}^{\text{Si-rich}} x^2(1-x) + \Delta a_{soln}^{\text{Al-rich}} x(1-x)^2$ and $\Delta c \approx c_{soln}^{\text{Si-rich}} x^2(1-x) + \Delta c_{soln}^{\text{Al-rich}} x(1-x)^2$, respectively. Where:

$$\Delta a_{soln}^{\text{Al-rich}} = \left[\frac{\partial a}{\partial x}\right]_{x=0} \qquad \Delta a_{soln}^{\text{Si-rich}} = -\left[\frac{\partial a}{\partial x}\right]_{x=1} \tag{3}$$

$$\Delta c_{soln}^{\text{Al-rich}} = \left[\frac{\partial c}{\partial x}\right]_{x=0} \qquad \Delta c_{soln}^{\text{Si-rich}} = -\left[\frac{\partial c}{\partial x}\right]_{x=1} \tag{4}$$

3. Results

The enthalpy of mixing for the $(Al_{1-x},Si_x)_3Zr$-D0$_{23}$ pseudo-binary solid solution is presented in Figure 1. Acceptance of Si atoms within Al sites lowers the energy of the intermetallic phase. The amount of Si added into an aluminum alloy will therefore impact the precipitation of this phase upon solidification. A fine-tuning accounting for this phenomenon is therefore required whether to promote or to suppress the formation of the D0$_{23}$ phase. This is particularly important for recycling, where Si (along with Cu and Fe) is one of the most critical alloying elements for the recovery and revaluation of aluminum alloys [21]. The enthalpy of mixing of the $(Al_{1-x},Si_x)_3Zr$-D0$_{23}$ solid solution modeled from the DFT calculations of the partial enthalpies (solid line in Figure 1) does not take into account the influence of the chemical ordering of the solid solution. Therefore the model exhibits different predictions than those using the Al:Al:Si:Zr and Al:Si:Si:Zr ordered compounds [22] (black squares in Figure 1). It is particularly interesting to note that the ordered configurations from [22] have a more negative enthalpy of mixing values than those predicted by the partial-enthalpy-based model. Those calculations hence show that the substitution of Al by Si has a stabilizing effect on the $(Al,Si)_3Zr$-$_{23}$ solid solution; and that the substitution is ordered [22]. Other elements play an important role in the stability of the D0$_{23}$ phase, such as Ti. Karpets *et al.* [23] have reported that only a fraction of Zr/(Zr+Ti)=0.1 is required to stabilize the D0$_{23}$ phase in equilibrium with the Al$_3$Ti-D0$_{22}$-based intermetallic for Al-Ti-Zr alloys. Another example is the case of V, whose substitution has already been studied by Han *et al.* [24]. Note that the substitution of Ti and V (among other elements) is already incorporated within the multi-component D0$_{23}$ solution model inside FactSage databases [10]. Nevertheless, acceptance of Si has not been integrated yet. As such, the enthalpy of mixing calculated in this work can be used to account for this event using the Compound Energy Formalism (CEF)[2]. Likewise, current experimental evidence of Si acceptance within the Al$_3$Zr phase [8, 9], coupled with additional experimental work, can be used to tune the thermodynamic model of this solid solution.

The evolution of the a and c lattice parameters is presented in Figure 2. The lattice constants for the reference Al$_3$Zr-D0$_{23}$ (no Si-doped) structure were a=4.012 Å and c=17.374 Å, which are consistent with the values reported the literature: a=4.015 Å and c=17.454 Å from Hu *et al.* [25]; a=4.018 Å and c=17.349 Å from Huang *et al.* [26]; a=4.008 Å and c=17.297 Å from Ghosh *et al.* [27]. On the other side, lattice parameters for the metastable Si$_3$Zr-D0$_{23}$ compound were a=3.691 Å and c=19.385 Å. The addition of Si within the solid solution decreased the a parameter, whereas the c constant was increased. Variations in both a and c parameters are necessary to quantify the lattice misfit of intermetallic phases with respect to the Al-FCC matrix [28]. For hyper-peritectic compositions, this information is useful to understand the grain refinement mechanisms [29]. In this case, precipitation of the α-Al is believed to be promoted by the phase coherency of the intermetallic and the Al-FCC [29]. Meaning that the
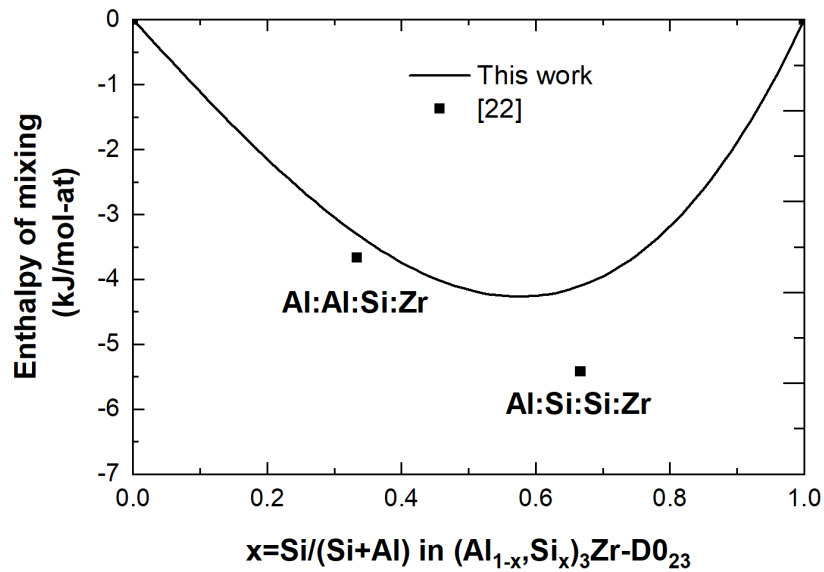
Figure 1. Enthalpy of mixing for the $(Al_{1-x},Si_x)_3Zr$ pseudo-binary solid solution at 0 K (solid line) compared to DFT-GGA data from Castillo-Sánchez *et al.* [22] (squares). For the latter, site occupancy is presented as A:B:C:D where A=4c, B=4c, C=4e and D=4e sites of the $D0_{23}$ structure
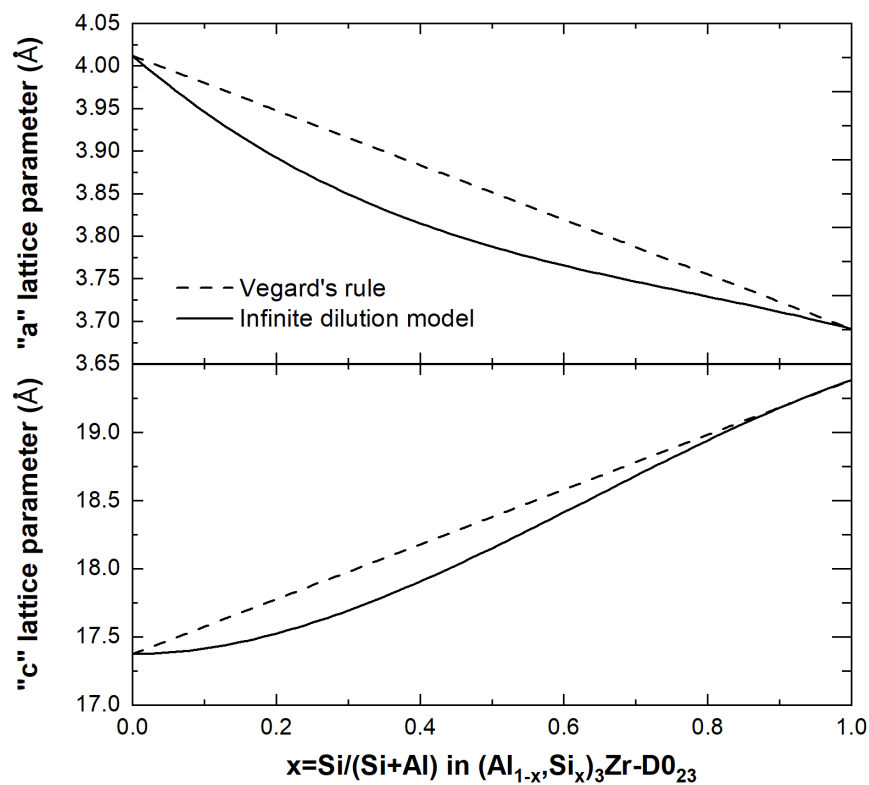
Figure 2. *a* and *b* lattice parameters of the $(Al_{1-x},Si_x)_3Zr$ pseudo-binary solid solution.

intermetallic phases can potentially act as nucleation sites [8]. Here, the complete pseudo-binary solid solution is presented. Nevertheless, experiments are required to correlate the variation of the lattice parameter according to the Si occupancy from the chemical analysis. For this case, crystallography orientation relationships can also be derived based on the lattice parameters of both Al-FCC and intermetallic phases. The lattice parameter of pure Al is reported as 4.046 Å from DFT calculations using the Generalized Gradient Approximation (GGA) [30]. In a rough manner, it can be observed that acceptance of Si increases the mismatch of a(Al-FCC)$|a$(D0$_{23}$) and $4a$(Al-FCC)$|c$(D0$_{23}$).

The stabilization effect of Si on the D0$_{23}$ phase has furthermore been studied from an electronic point of view. In the first place, the substitution of one atom of Si in an Al site of the D0$_{23}$ supercell (128 atoms) resulted in a considerable decrease of the Fermi energy ($E_{fermi}^{\text{Si-doped}}$-$E_{fermi}^{\text{Non-Si-doped}}$=-0.6875 eV). The total and partial density of states (DOS) of a reference Al$_3$Zr-D0$_{23}$ structure (non-Si-doped) and the Si-doped D0$_{23}$ simulation cell are displayed in Figures 3 and 4, respectively. At first glance, the total DOS is more populated at lower energy due to the presence of Si (Figure 3).
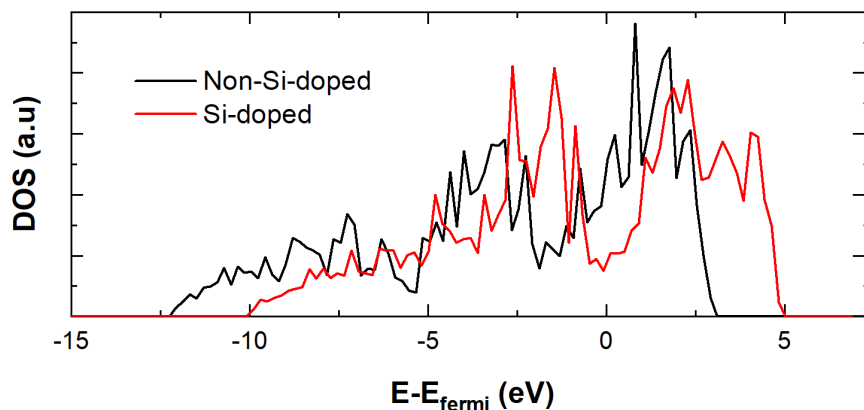

Figure 3. Total density of states (DOS) for a non-Si-doped Al$_3$Zr-D0$_{23}$ structure (black line), compared to and Si-doped [(Al,Si)$_3$Zr-D0$_{23}$] simulation cell.

Changes on the partial DOS of the p orbital of Al and the d orbital of Zr induced by the Si-sublattice substitution are reported in Figure 4. For the p orbital of Al, the electronic density of states increased at lowers energies when Si is incorporated. Consequently, electrons are localized at lower energy levels, which is characterized by the sharpening of the DOS at low energies and the flattened trend at higher energies. This is reflected in the strong Al-Si interactions promoting the stabilization of the D0$_{23}$ structure (for a Si-diluted scenario). Furthermore, DOS at low energies are also promoted for the d orbital of Zr (Figure 4). The p-suborbitals of Al adjusted in an equivalent manner; however, the d_{xy}, d_{xz}, and d_{yz} suborbital of Zr were the most altered (Figure 5). For such suborbitals, the addition of Si shifted the density of states to lower energy values when compared to the non-Si-doped structure. Thus, Zr also has an important role in the combined stability effect of the D0$_{23}$ phase induced by Si.
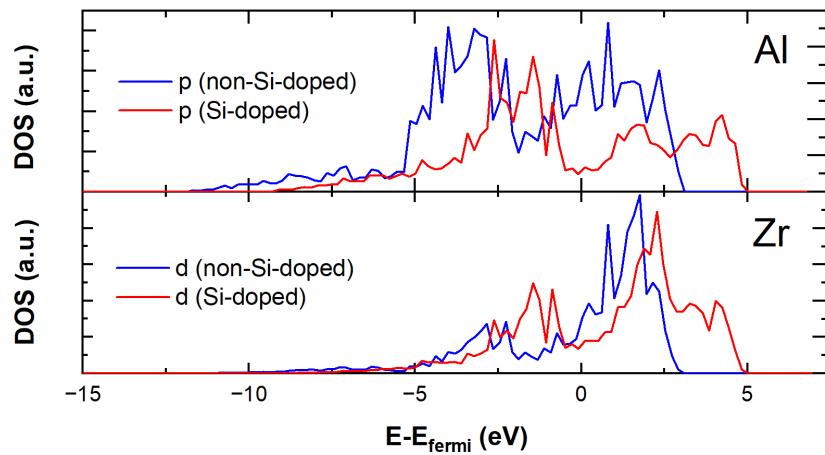
Figure 4. Partial density of states (DOS) for: p orbital of aluminium (top) and d orbital of Zirconium (bottom).
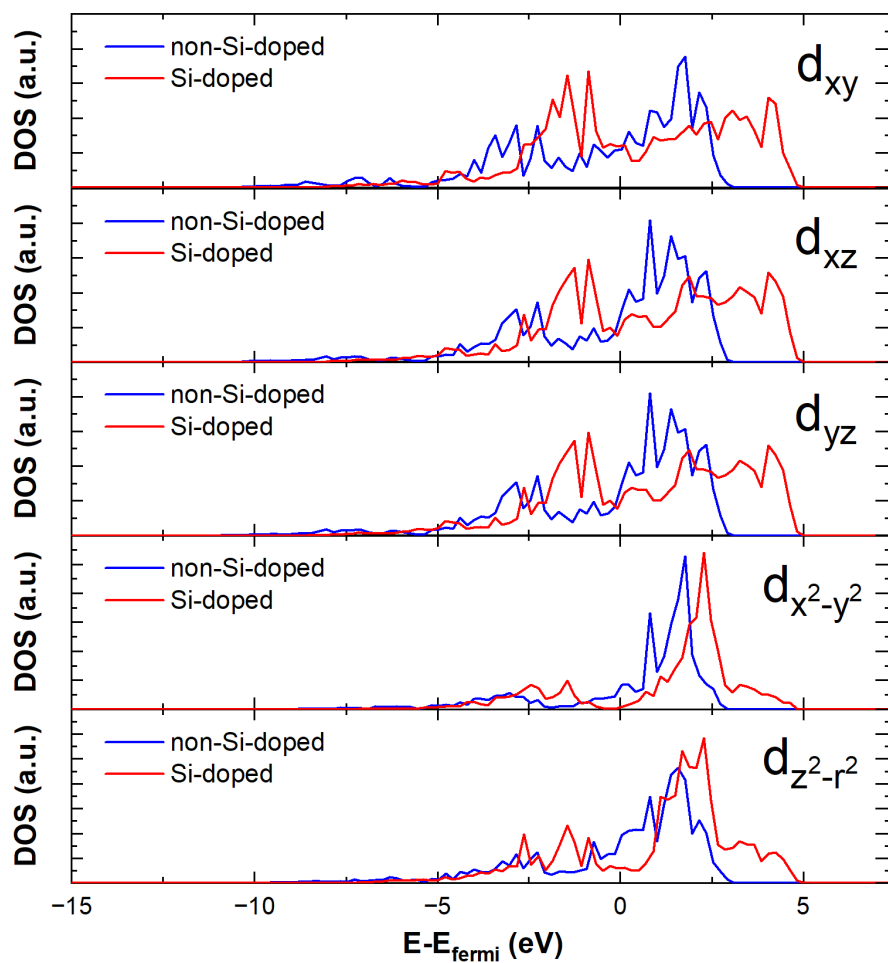
Figure 5. Density of states (DOS) of d-suborbitals of Zirconium.

4. Conclusion and perspectives

The enthalpy of mixing of the pseudo-binary $(Al,Si)_3Zr$-$D0_{23}$ solid solution was calculated using Density Functional Theory (DFT) calculations. Substitution of Si within Al sites of the $D0_{23}$-rooted intermetallic displayed a negative heat of mixing, indicating that such substitution is energetically favorable. The a lattice parameter decreases as Si is accepted into the tetragonal phase; the opposite is observed for the c lattice constant. Finally, the electronic density of states (DOS) for the p-orbital of Al and the d-orbital of Zr were evaluated for a Si-diluted scenario (one atom of Al replaced by Si in a 128-atom simulation cell). For both cases, the DOS was increased at low energies by the presence of Si, compared to a non-Si-doped simulation cell. The aforementioned implies that Al and Zr play an important role in the combined stabilization effect of Si on the $D0_{23}$ intermetallic. This is particularly achieved by the localization of electrons of the p-orbital of Al; and a noticeable increase on the DOS at low energies of the d_{xy}, d_{xz}, and d_{yz} sub-orbitals of Zr. These results are the basis for further integration of Si within the thermodynamic modeling of the Al_3Zr-$D0_{23}$-based solid solution inside FactSage databases.

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