Data Assessments for the ALLEE Project

M. Schick, K. Hack

GTT Workshop, Herzogenrath
June 29th – Julyst 2016

Outline:

The binary system Al-Zr:

- $C_p(T)$-curves of Al_3Zr & AlZr (Neumann-Kopp)
- Refinement of the Neumann-Kopp approach and comparison to exp. data
- Optimisation of the binary system Al-Zr using improved c_p functions

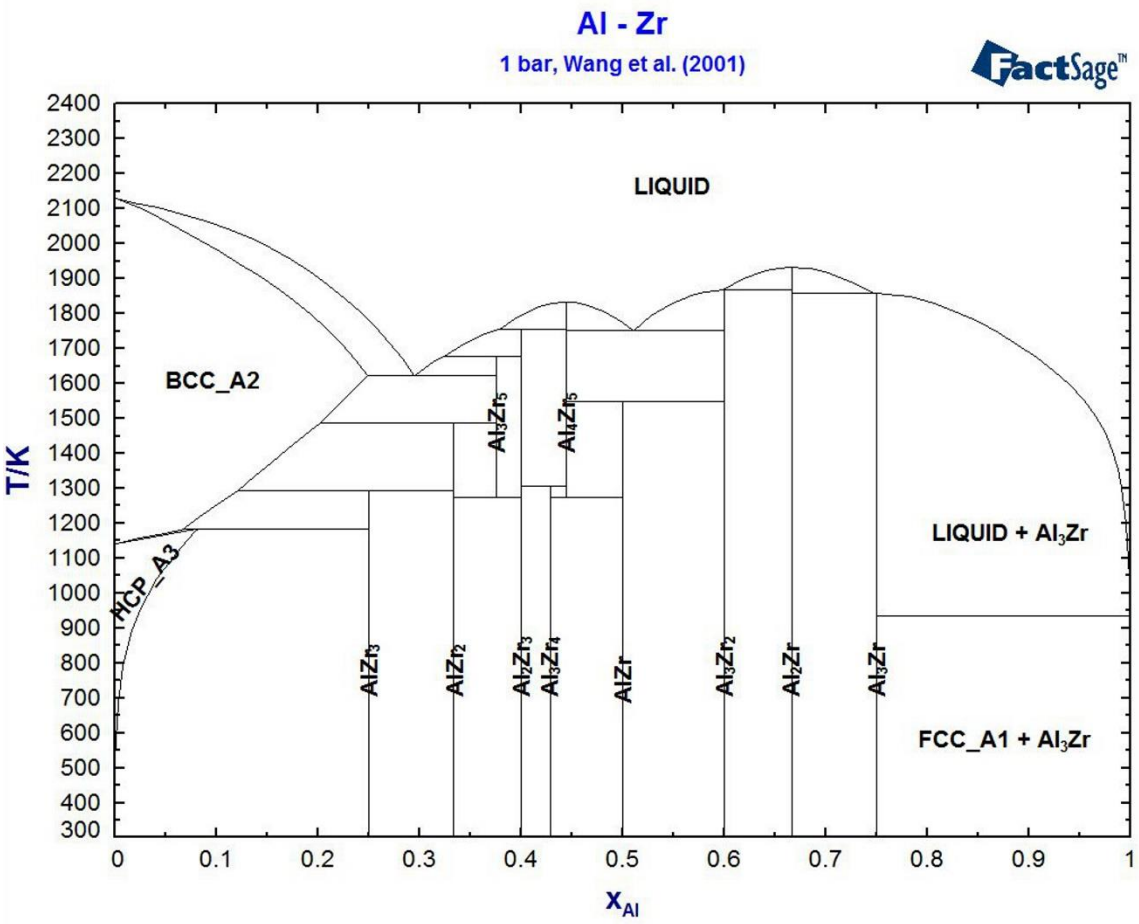
Refinement procedure applied to further compounds

- Al_3Ni, "$Al_{13}Fe_4$" and "$Al_{10}Fe_3Ni$"

Evaluation of recent publication by Q. Zhao et al.[1]:
Influences of Fe, Si and homogenization on electrical conductivity and mechanical properties of dilute Al-Mg-Si alloy

[1]Q. Zhao, Z. Qian, X. Cui, Y. Wu, X. Liu, JALCOM 666 (2016) 50

The binary system Al-Zr:



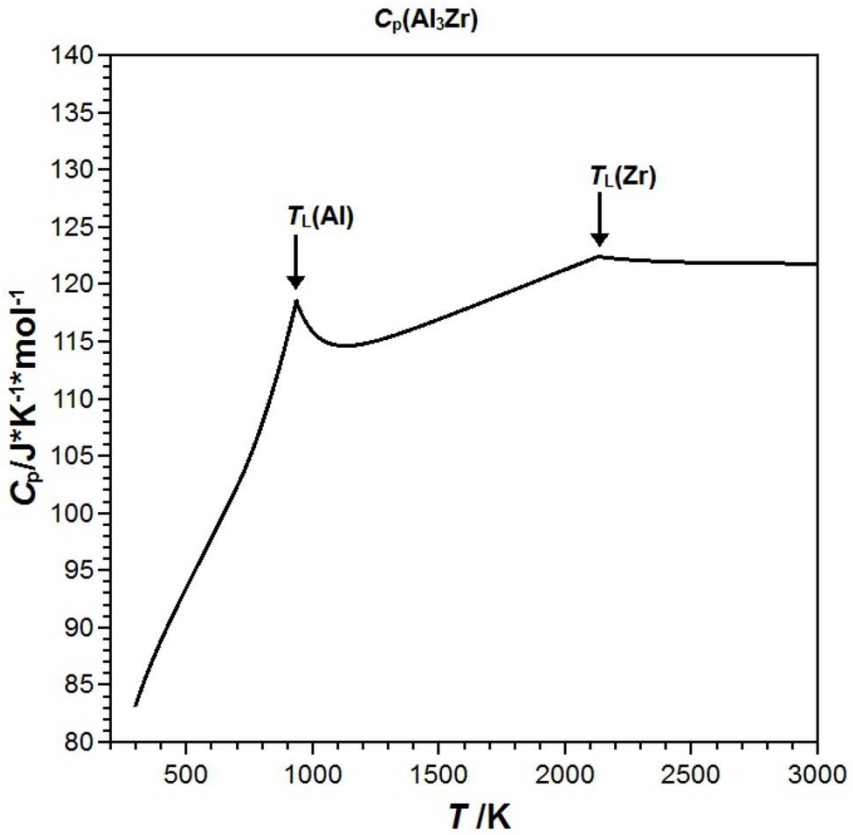
new thermodynamic assessment for binary Al-Zr from literature:

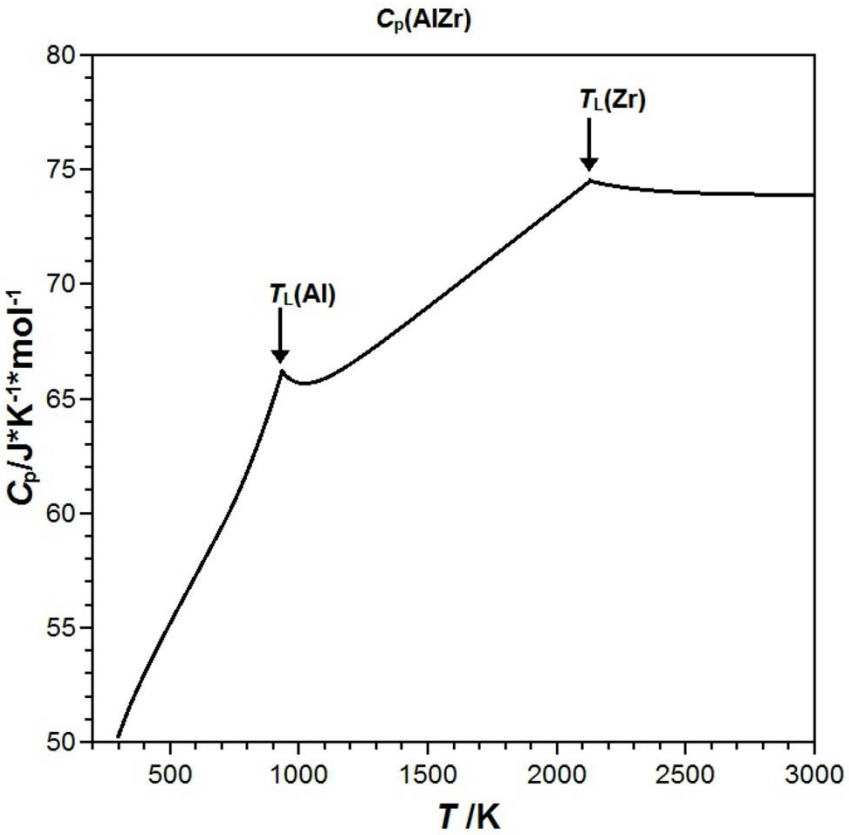
T. Wang, Z. Jin, J.-C. Zhao, Journal of Phase Equilibria 22(5) (2001) 544

10 stoichiometric compounds, $c_p(T)$ curves obtained with Neumann-Kopp approach

The binary system Al-Zr:

$c_p(T)$ curves, examples (Al_3Zr, AlZr) :





melting points of pure elements ⇒ artefacts in c_p curves

Refinement of Neumann-Kopp:

if no further data available:

procedure of refinement

1. refit c_p-curve with (standard) polynomial function:

$$c_p = a_0 + a_1 \cdot T + a_2 \cdot T^{-2} + a_3 \cdot T^2 + \left(a_4 \cdot T^3\right)$$

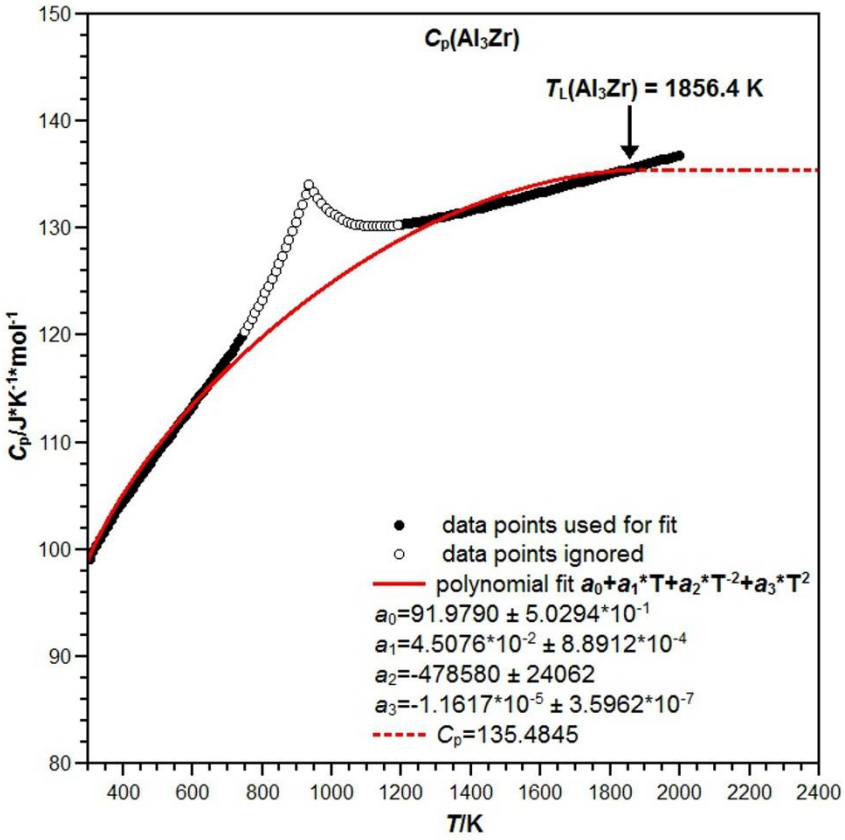
2. recalculate melting temp. (peritectic temp.) of compound (optimisation of ΔH_f^{298} and S^{298})

3. recalculate invariant equilibria where compound is involved

Refinement of Neumann-Kopp:

C_p refit for Al_3Zr:

melting temperature: T_L =1856.4 K (Wang et al., N-K C_p)



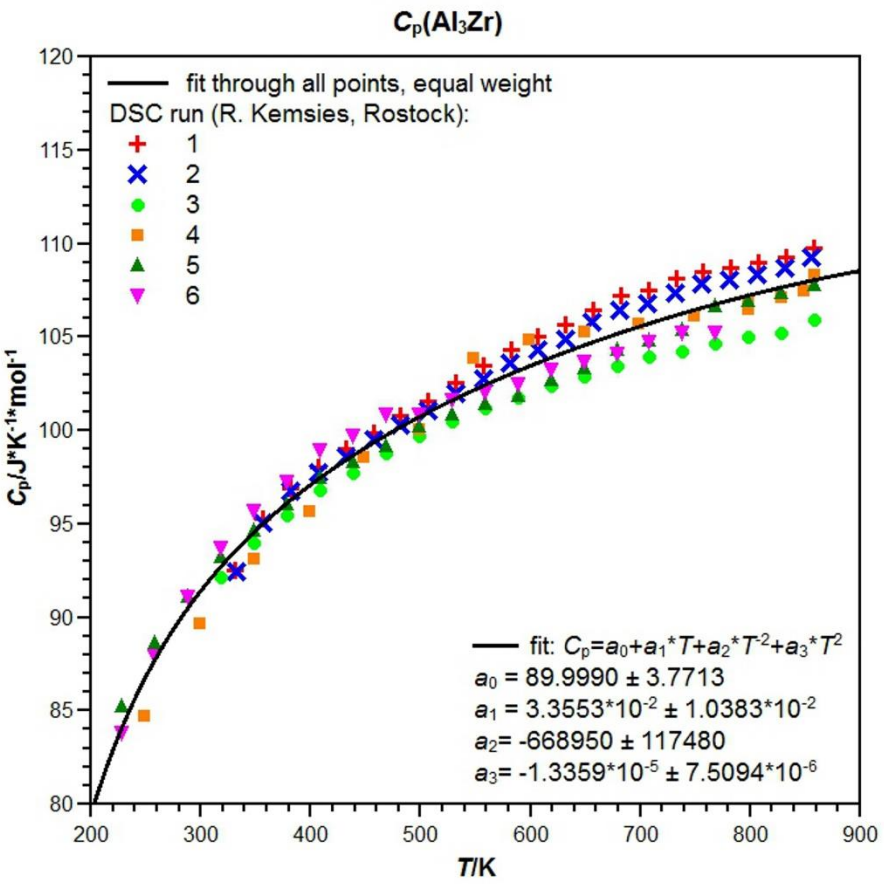
2 temperature ranges for C_p:

polynomial function 298.15 K – T_L

C_p = const. for $T > T_L$

Experimental data for C_p:

C_p measurements for Al_3Zr by R. Kemsies, Rostock:



exp. data fitted nicely by standard polynomial function for C_p, but:

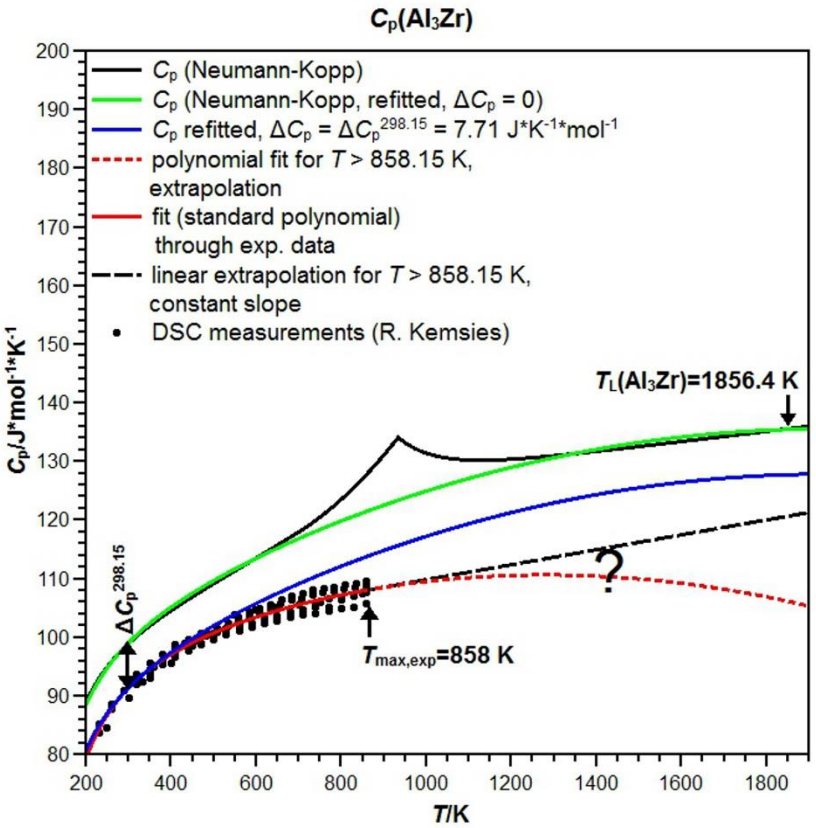
maximum temperature for exp. data quite low (T_{max} = 858 K),

melting temperature rather high (T_L =1856.4 K)

no exp. data in the range between 858 –1856 K !

Experimental data for C_p:

comparison between simple and refined Neumann-Kopp approach, and experimental data for $C_p(Al_3Zr)$



problem:
no exp. data available in the range between 858 –1856 K !

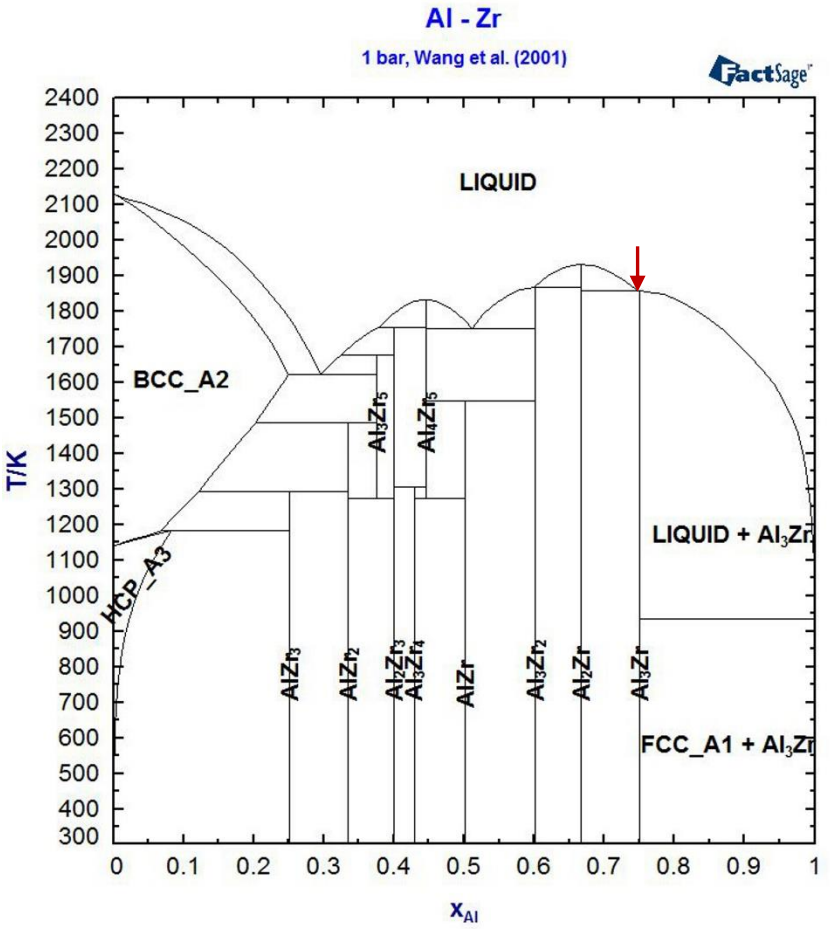
possible way:
linear extrapolation of $C_p(T)$ curve with constant slope

$$\left(\frac{dC_p}{dT}\right) = \left(\frac{dC_p}{dT}\right)_{T=298.15} = \text{const.}$$

another possible way:
use of *ab-initio data* (planned)

Optimisation:

optimisation of ΔH_f^{298} and S^{298} for refitted function $C_p(T)$:



⇒ match melting temperature

⇒ match invariant equilibria, where Al_3Zr is involved

with $C_p(T)$, ΔH_f^{298}, S^{298} fixed
⇒ Gibbs energy is defined !

Optimisation:

Comparison of invariant equilibria involving Al_3Zr:

inv. equilibrium	*T/K (Wang et al.)*	*T/K (after opt.)*
Liquid ⇆ Al_2Zr + Al_3Zr	1856.2	1857.7
Liquid ⇆ Al_3Zr	1856.4	1858.6
Liquid + Al_3Zr ⇆ FCC_A1	933.8	933.8

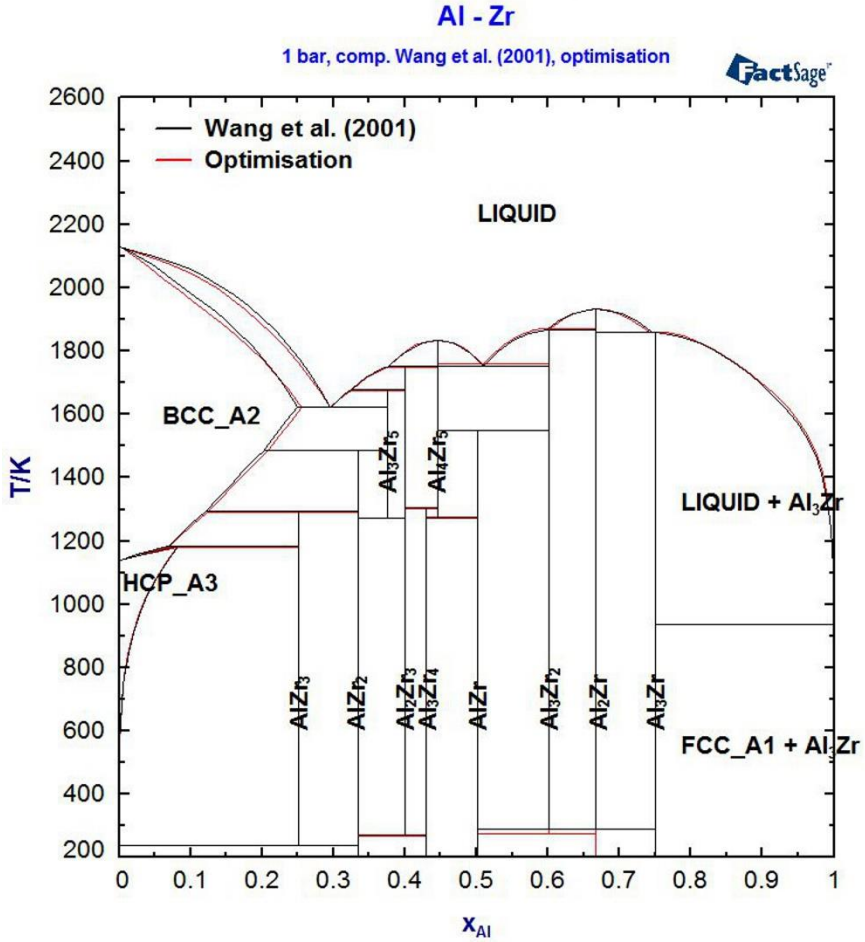
Comparison of ΔH_f^{298} values for Al_3Zr[1] and Al_2Zr[1]:

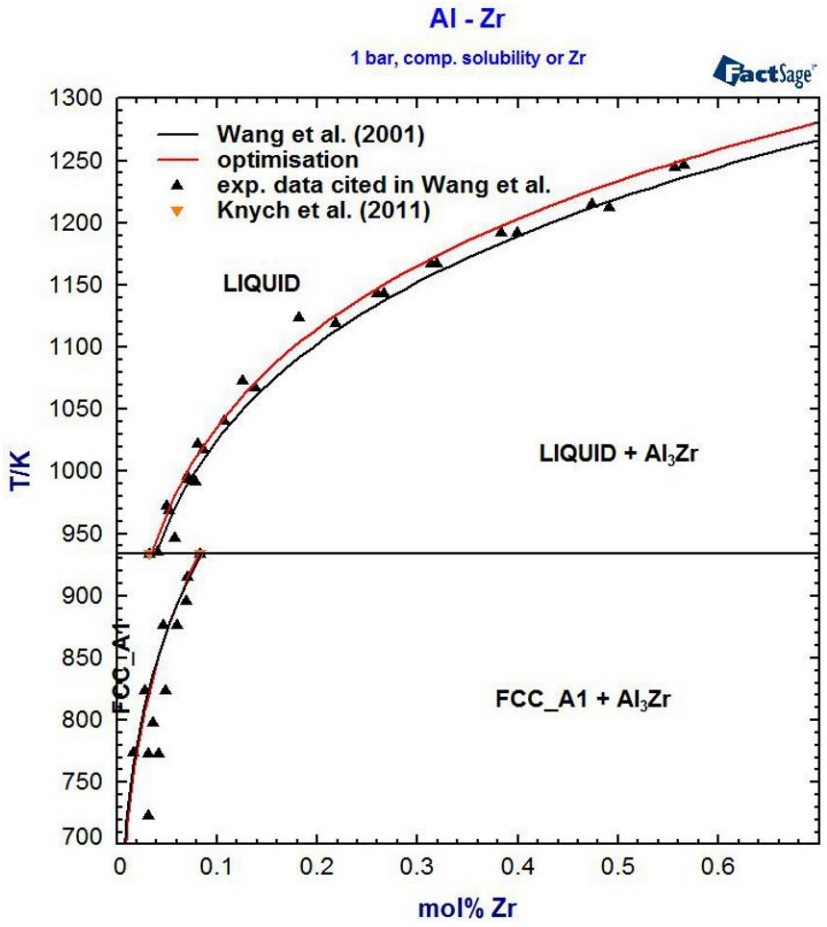
compound	optimised	Colinet[1]		
	*kJ*mol(at)$^{-1}$*	*VASP*	*DSC*	*Calomtr.*
Al_3Zr	-47.5	-46.97	-48.4	-44.4
Al_2Zr	-55.3	-52.02	-52.1	-49.0

[1]New literature: C. Colinet, J.-C. Tedenac, Calphad 54 (2016)6

Optimisation:

binary system Al-Zr optimised with improved $c_p(Al_3Zr)$ and solubility of Zr in Al(fcc) and LIQUID[2]

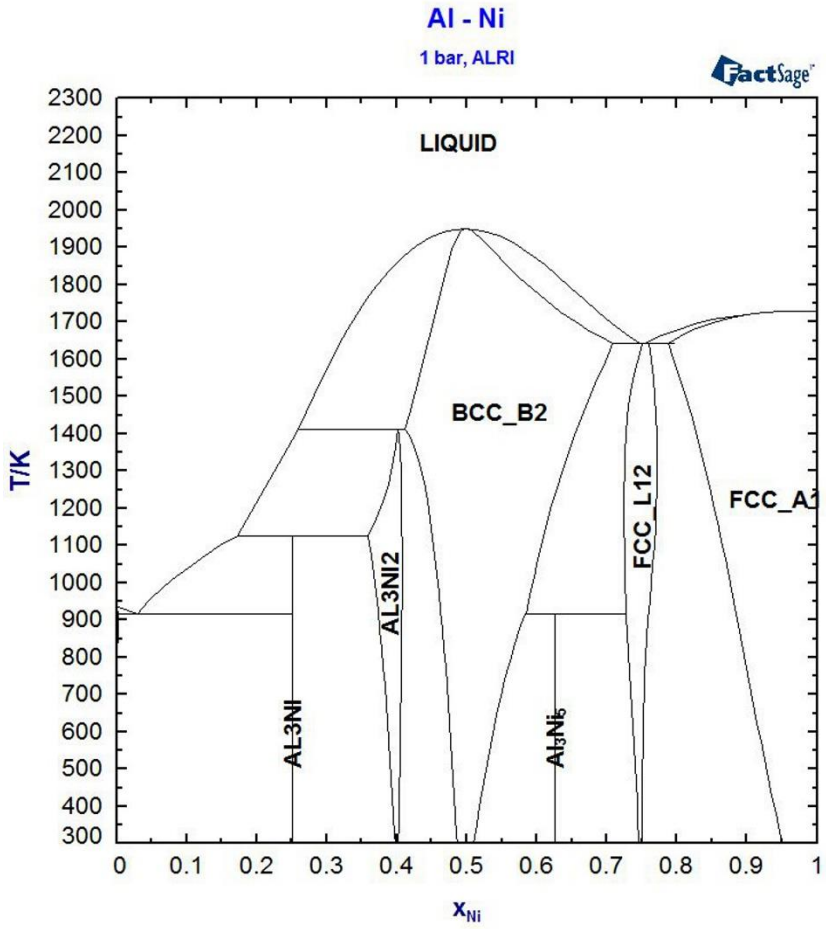




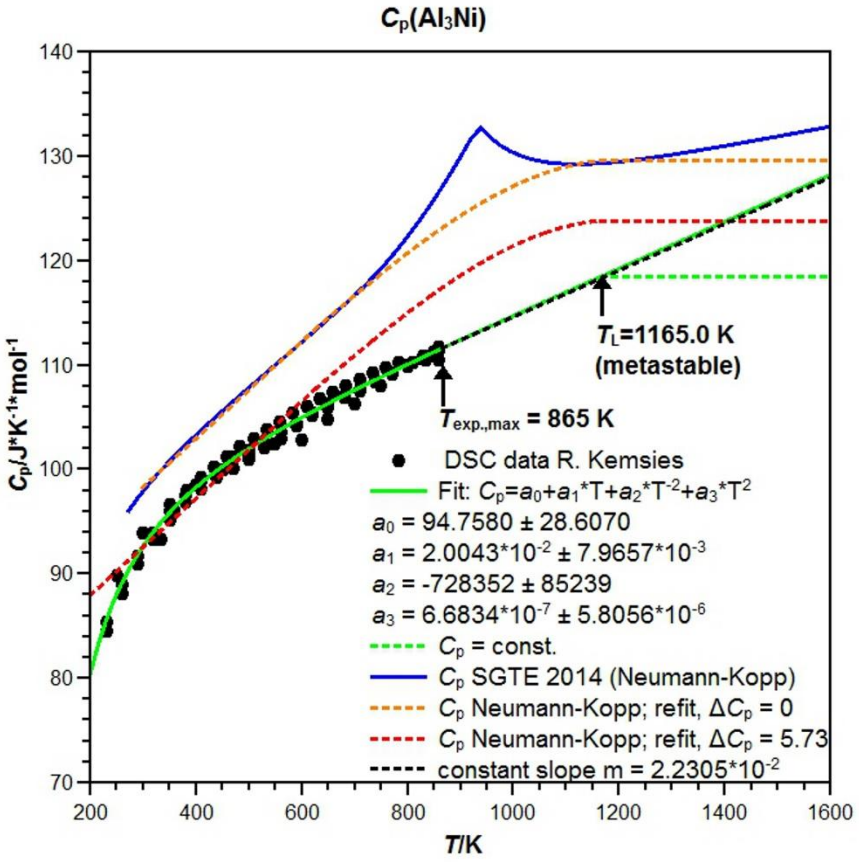
[2]T. Knych et al., Archives Met. Mater. 56(3) (2011) 685

The binary system Al-Ni:

binary phase diagram:

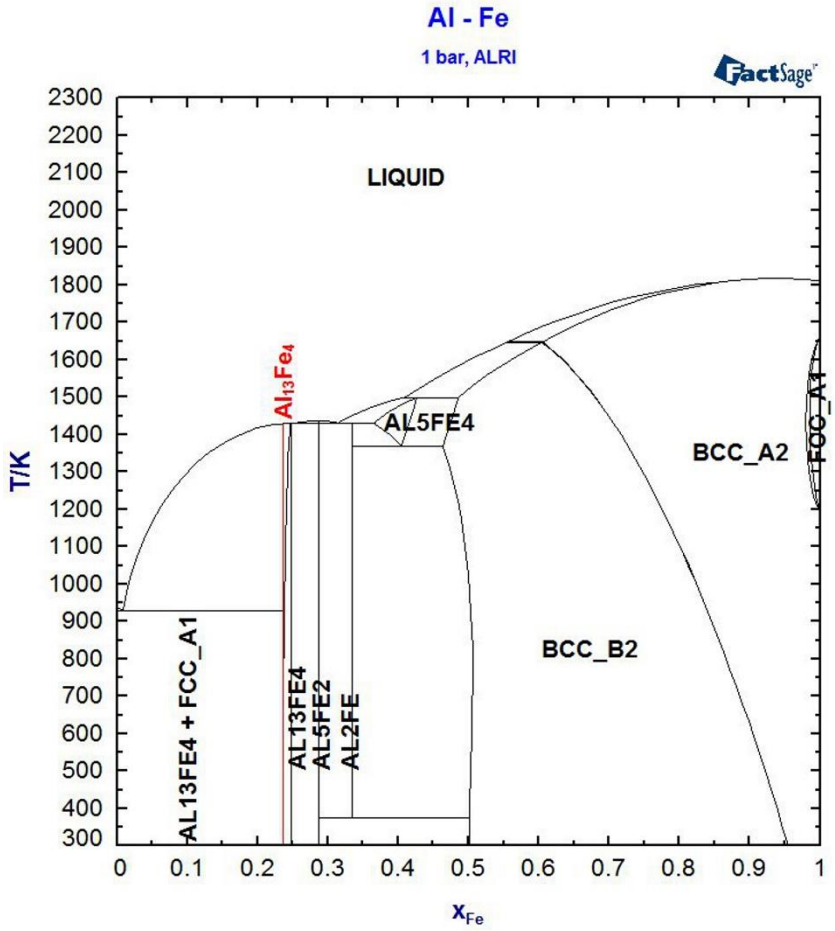


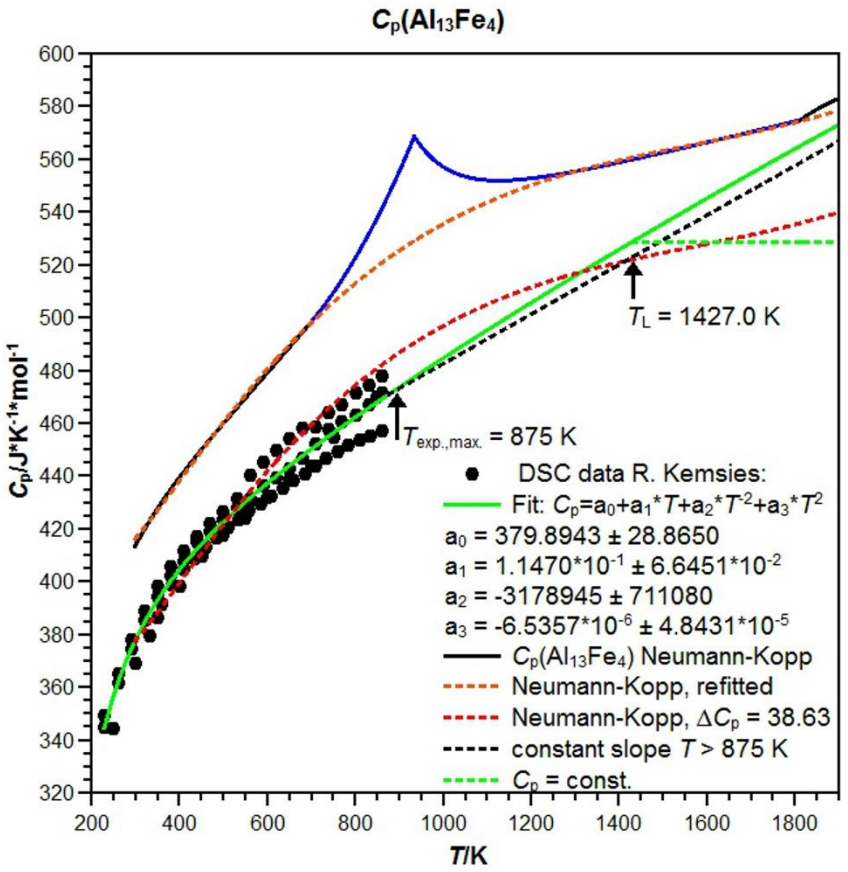
heat capacity $c_p(Al_3Ni)$:



The binary system Al-Fe:

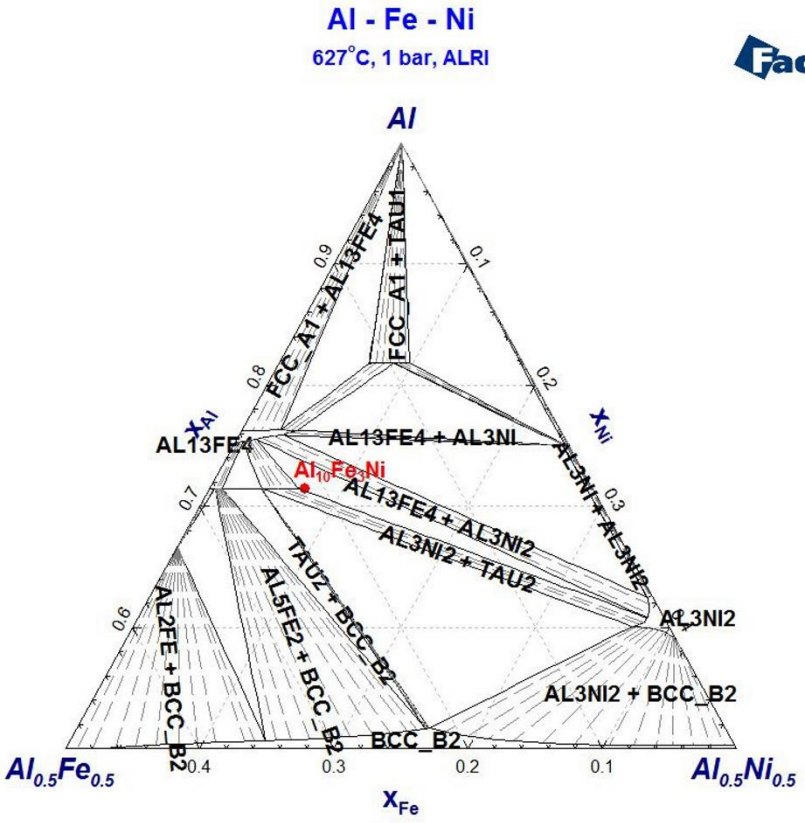
AL13FE4 is non-stoichiometric (solution phase), modelled $(Al)_{32}(Fe)_{12}(Al,Va)_7$

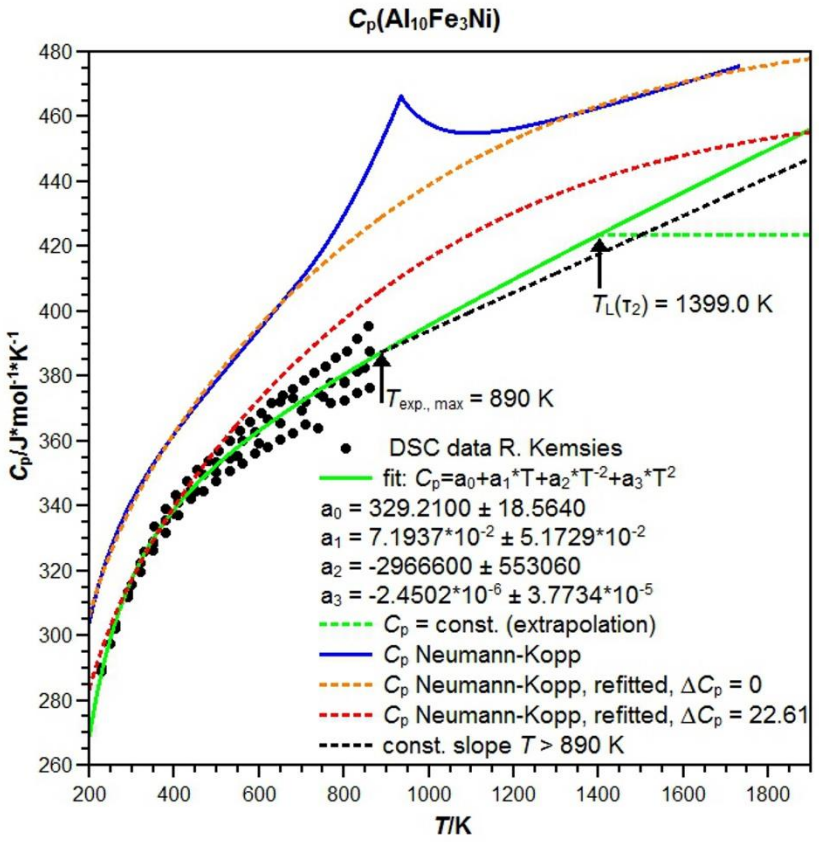




The ternary compound $Al_{10}Fe_3Ni$:

composition $Al_{10}Fe_3Ni$ corresponds to non-stoichiometric phase $\tau_2 = Al_5(Fe,Ni)_2$ (line compound) in Al-Fe-Ni





Data assessment: Fe in Al-Mg-Si:

Publication found recently:

Influences of Fe, Si and homogenization on electrical conductivity and mechanical properties of dilute Al-Mg-Si alloy
Q. Zhao, Z. Qian, X. Cui, Y. Wu, X. Liu, JALCOM 666 (2016) 50

⇒ Of interest: influence of Fe on the solubility of Si in Al(fcc) and LIQUID

⇒ Authors argue:
ternary eutectic phase α-Al_8Fe_2Si is formed upon solidification, which leads to improved electrical & mechanical properties

Data assessment: Fe in Al-Mg-Si:

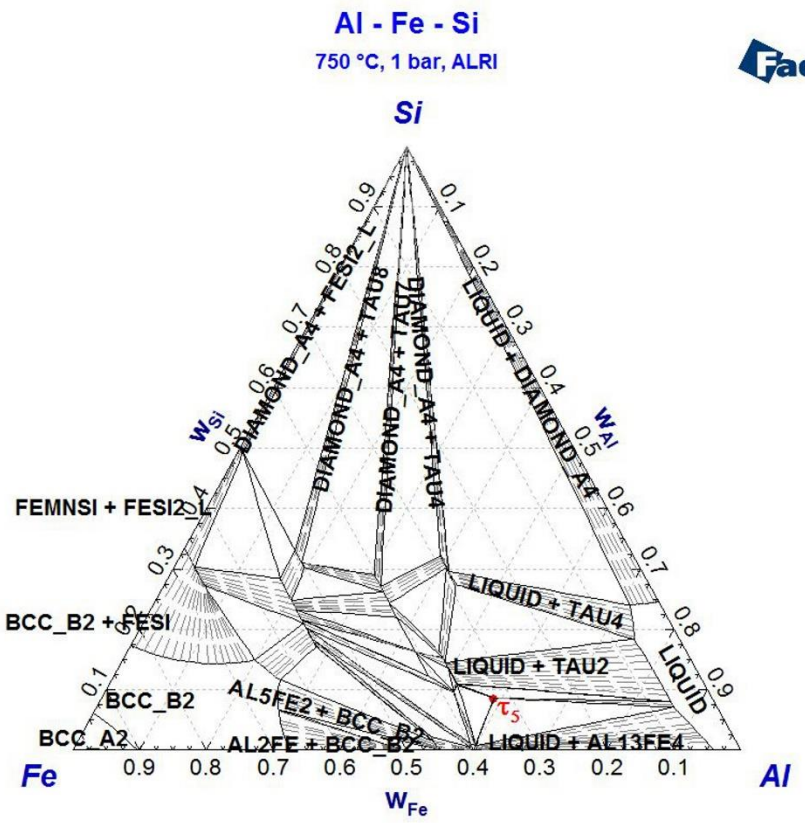
Sample preparation:

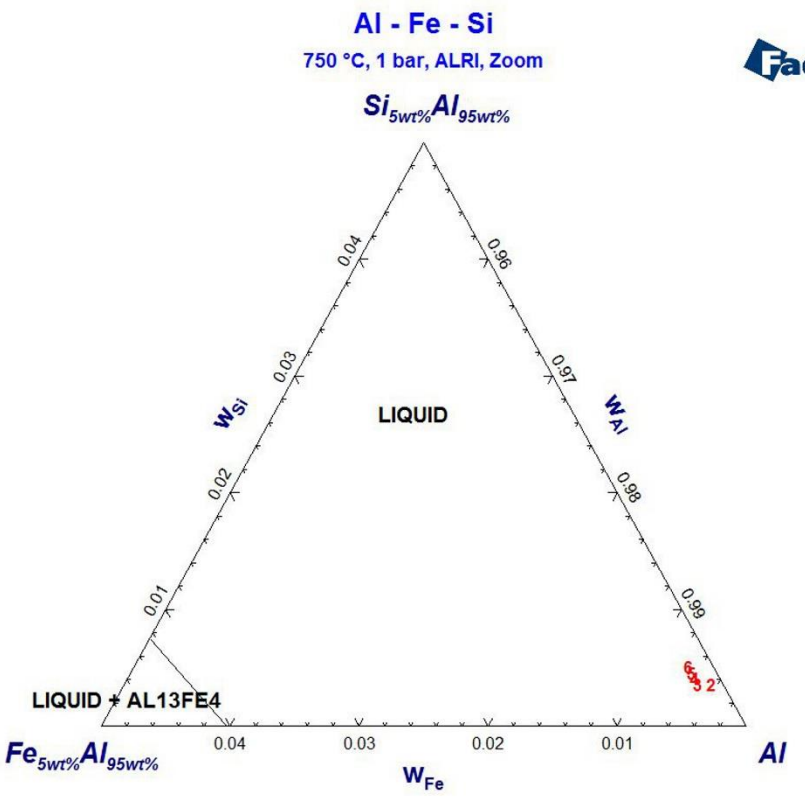
1. melting together pure elements, T = 750°C
2. T = 720°C, 10 min., slag removing
3. casting, mould temp. (200°C), solidification
4. heating T = 510°C, 2h, quenching (water)
5. "Ageing": T =175°C, 9h, cooling (air)
6. "homogenisation", $T \approx T_L^{Al}$ (660°C), time ?

sample	w_{Al}	w_{Fe}	w_{Mg}	w_{Si}
1	0.9915	0.0000	0.0050	0.0035
2	0.9905	0.0010	0.0050	0.0035
3	0.9895	0.0020	0.0050	0.0035
4	0.9890	0.0020	0.0050	0.0040
5	0.9885	0.0020	0.0050	0.0045
6	0.9880	0.0020	0.0050	0.0050

Data assessment: Fe in Al-Mg-Si:

ternary eutectic phase α-Al_8Fe_2Si ($\cong \tau_5$) is stable at T = 750°C

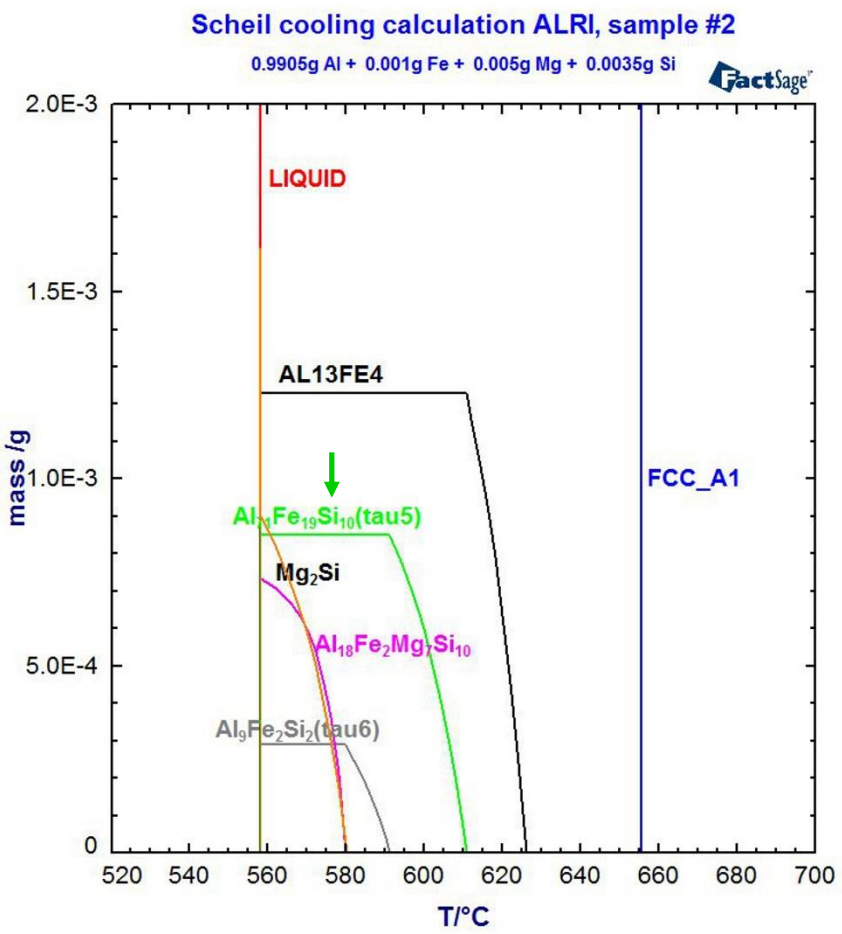


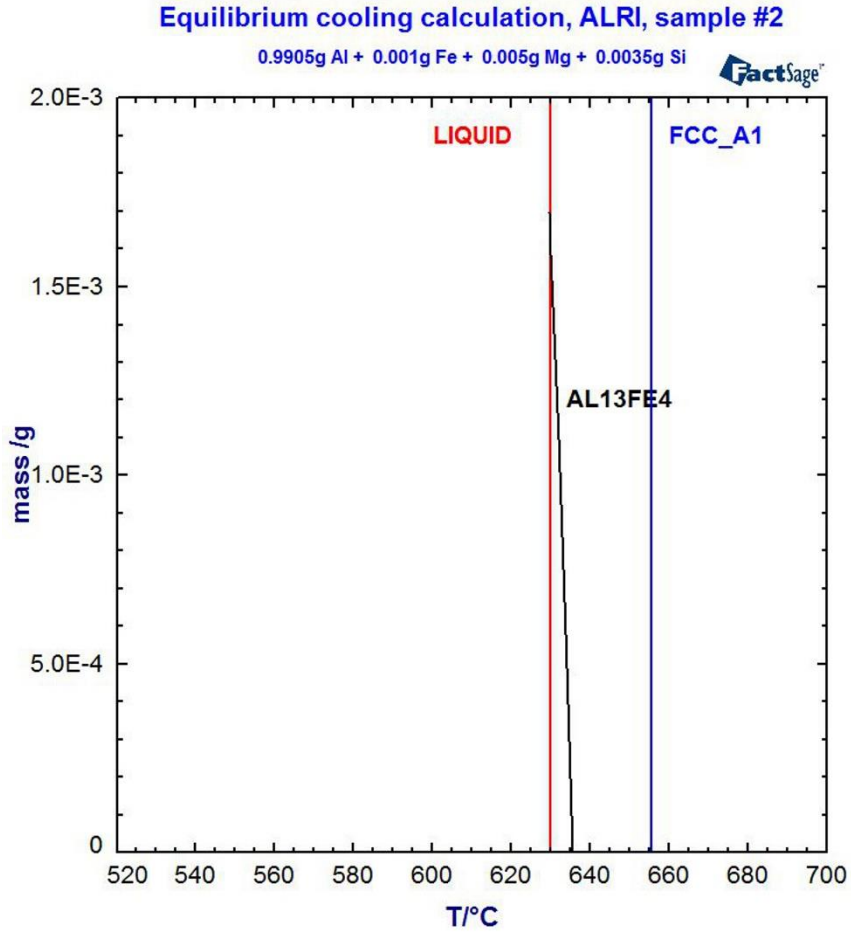


compositions: samples 2-6, sample 1: Fe free

Data assessment: Fe in Al-Mg-Si:

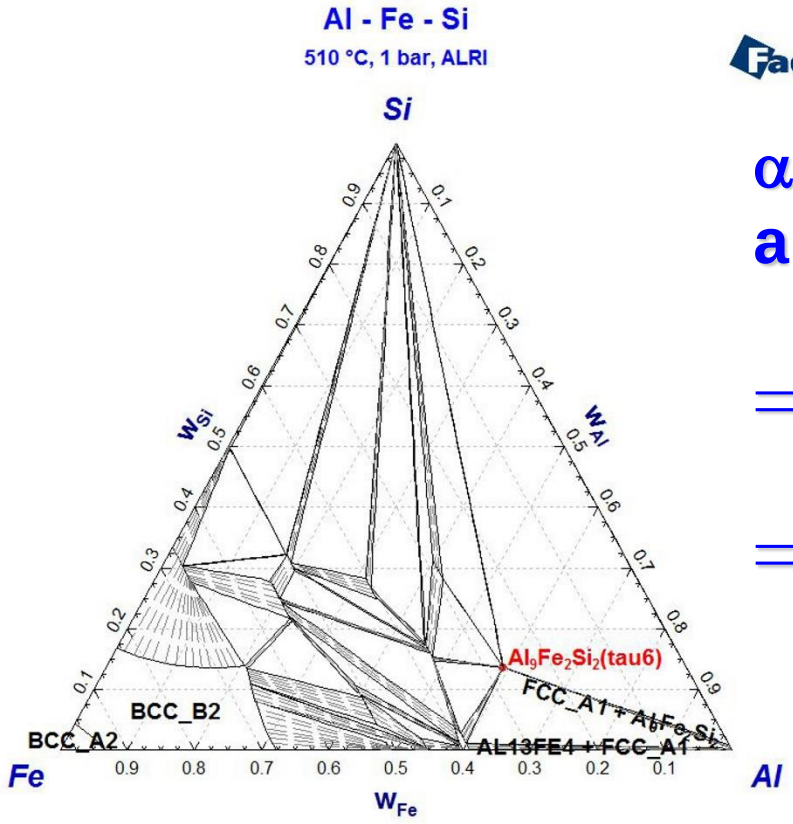
does α-Al_8Fe_2Si ($\cong \tau_5$) form during casting & solidification?





Data assessment: Fe in Al-Mg-Si:

Annealing at *T* = 510°C:



FactSage™

α-Al_8Fe_2Si ($\cong \tau_5$) is not stable any more $\Rightarrow$ $Al_9Fe_2Si_2$ ($\cong \tau_6$) !

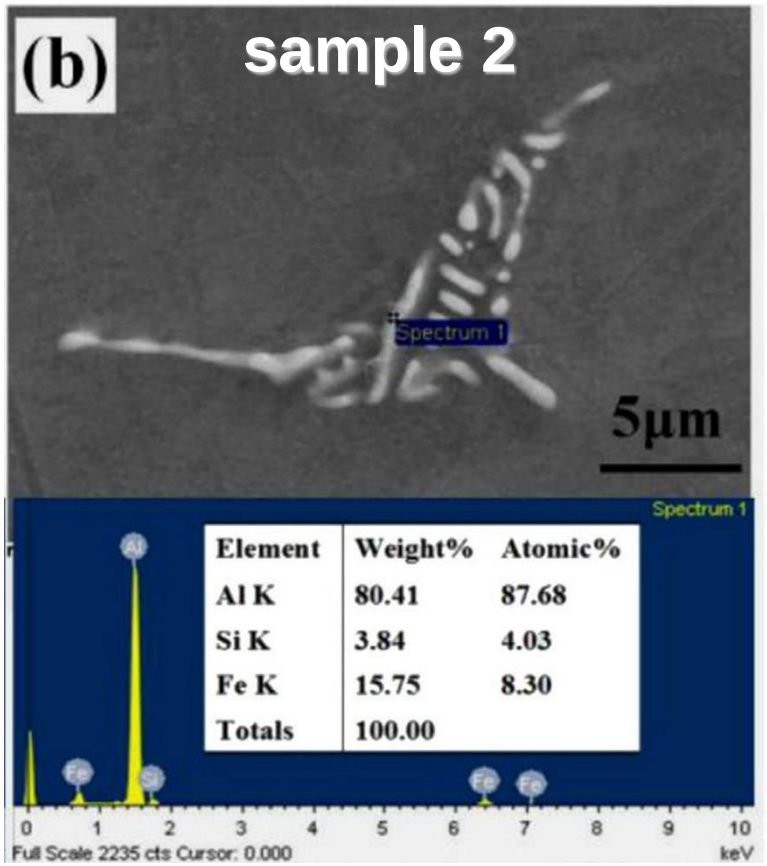
$\Rightarrow$ upon annealing τ_5 may react to form stable phases

$\Rightarrow$ sample compositions in three phase region:

DIAMOND_A4 + FCC_A1 + τ_6

Data assessment: Fe in Al-Mg-Si:

The authors want to prove formation of phase α-Al_8Fe_2Si by EDS:



composition of phase α-Al_8Fe_2Si according to formula:

	Al	*Fe*	*Si*
mole%	72.73	18.18	9.10
weight%	60.69	31.40	7.90

none of the EDS analyses matches nominal composition !

$\Rightarrow$ no experimental proof for existence of α-Al_8Fe_2Si

Thanks for your attention !