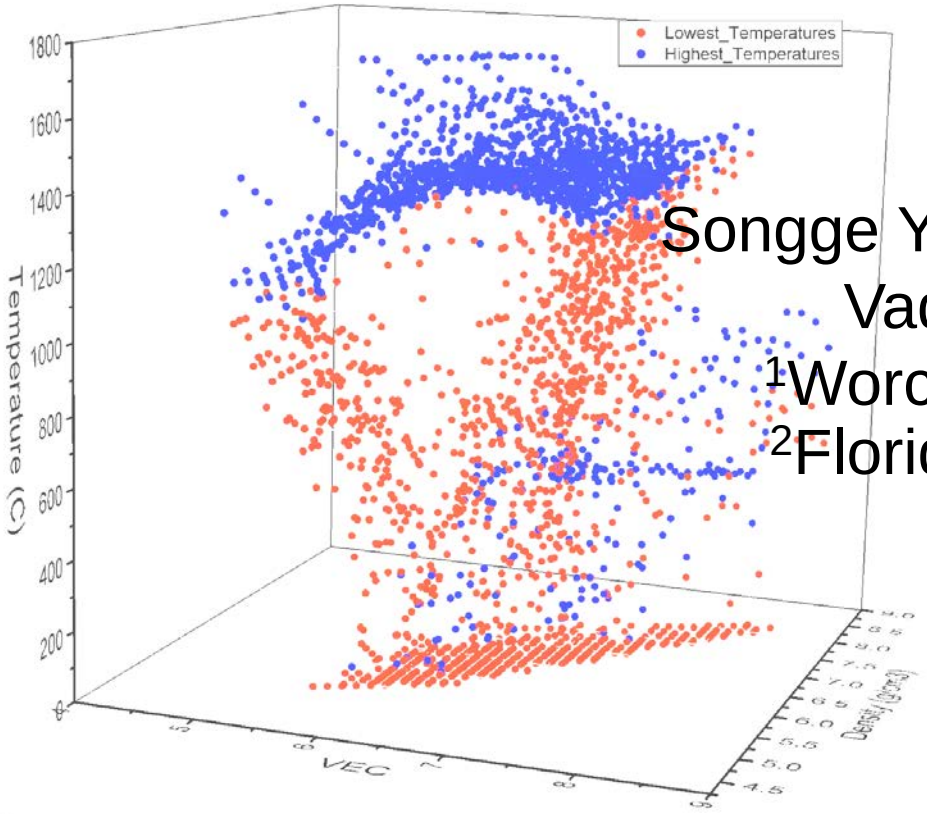
The Novel Hybrid Model of High Performance Structural Alloys Design for Fossil Energy Power Plants (FE-0030585)



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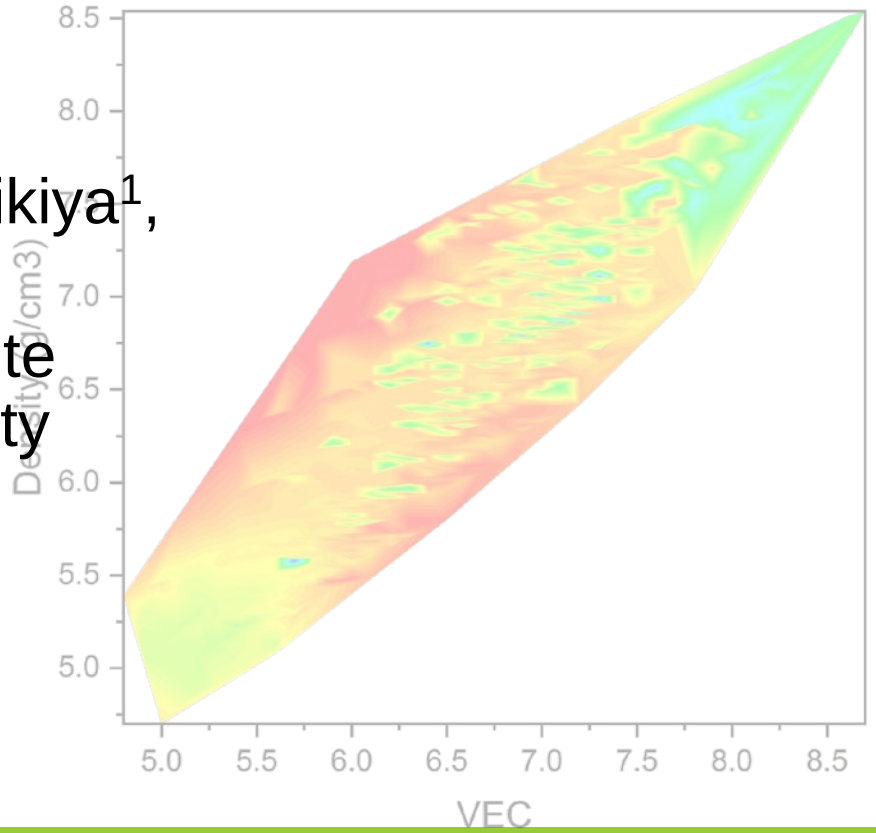
[2]Florida International University



Content

1. Introduction
2. Alloy design Approaches
3. Computational Details
4. Result and discussion

Objective/Vision

Develop a novel *modeling* approach, which can quickly design new high performance structural alloys for the application of FE power plants.

The long-term goal is to use the developed efficient hybrid computational model to predict the composition range of the new alloys with different elemental systems based on the specific application requirement.

In addition, new high performance structural alloys are to be designed based on the predictions from the model.

Current Challenges for Ab Initio

The prediction reliability of DFT simulations at elevated temperatures is still not comparable to which at 0K

Supercell is needed DFT calculations for HEA.

DFT is mainly limited to certain equimolar stoichiometries.

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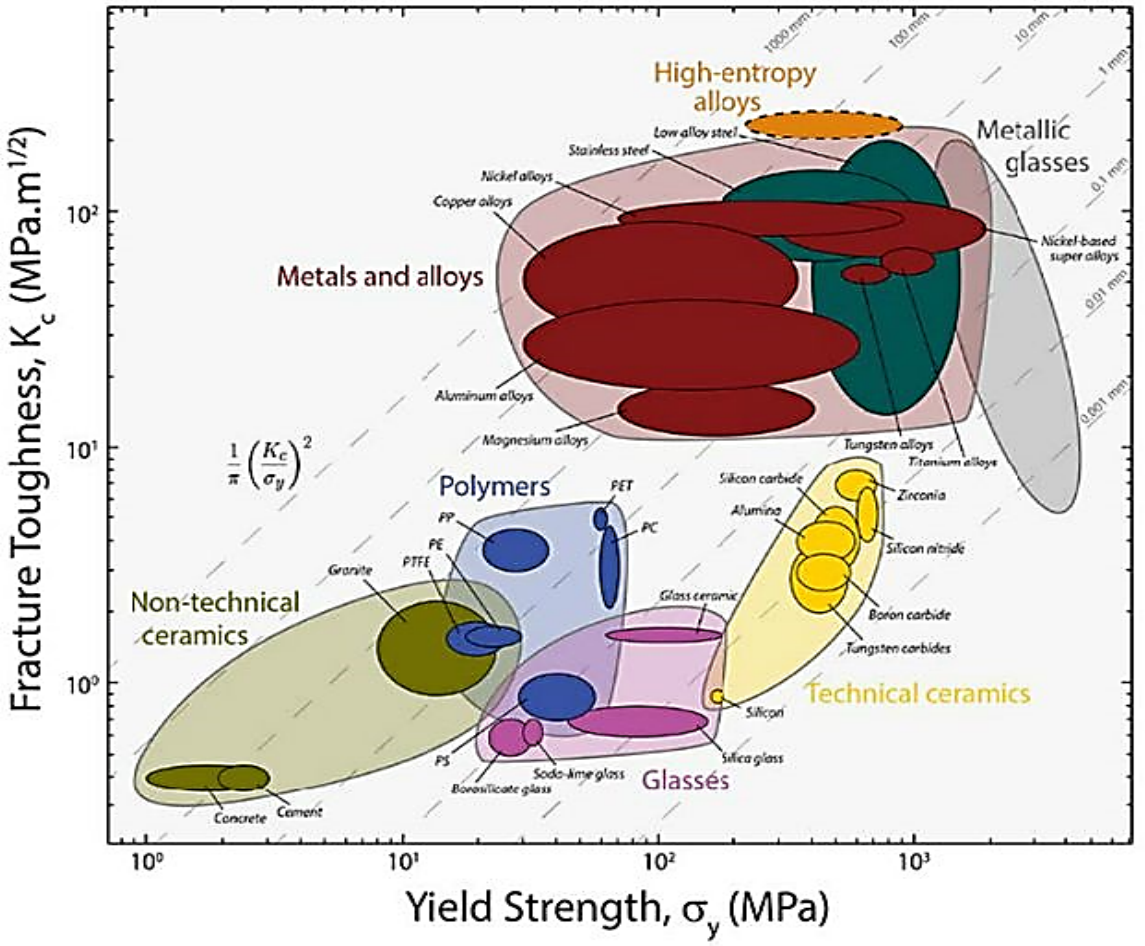
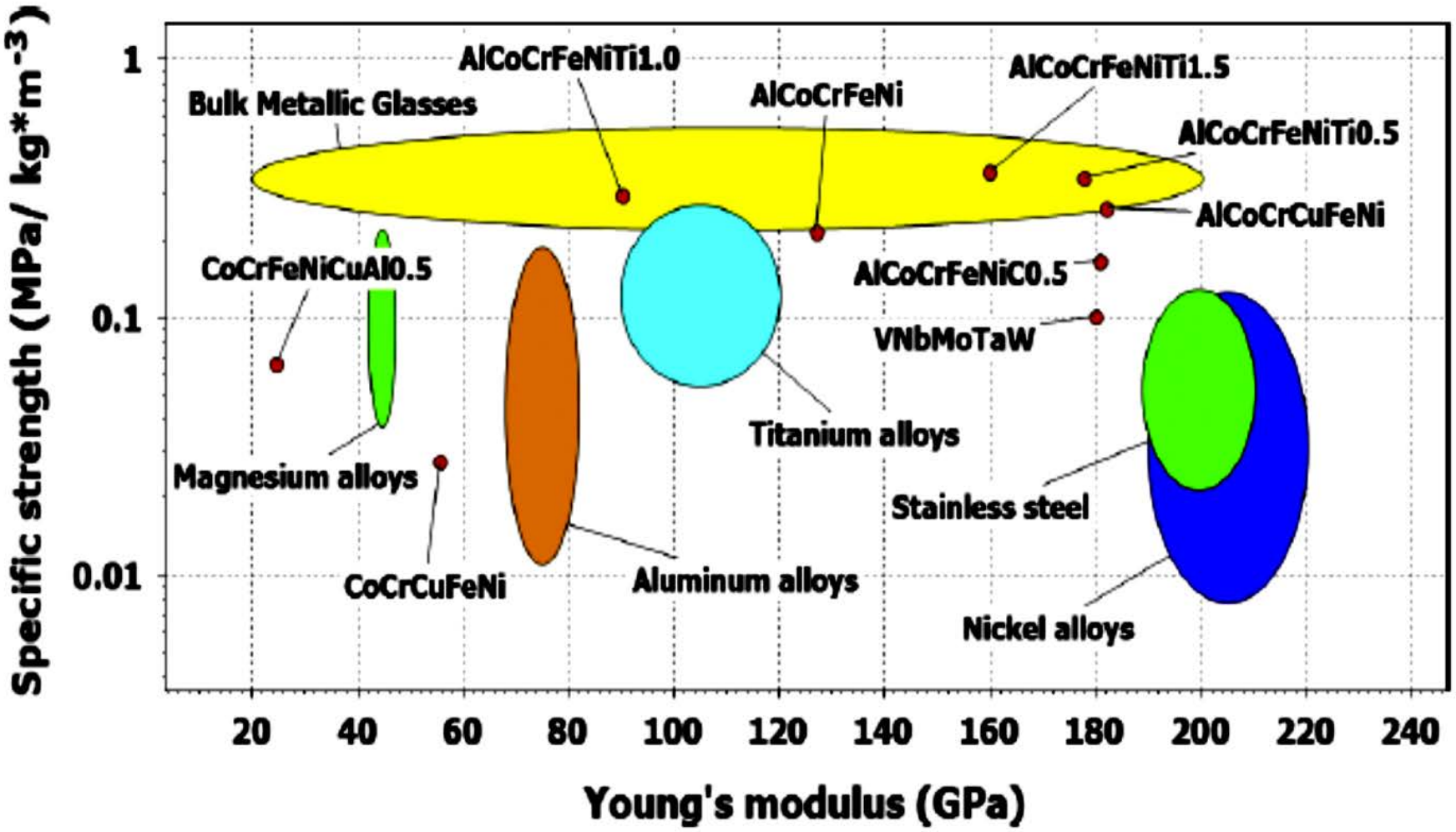
High entropy alloys

- High hardness and superb specific strength
- Superior mechanical performance at elevated temperatures
- Exceptional ductility and fracture toughness at cryogenic temperatures
- High wear resistance
- Significant resistance to corrosion and oxidation



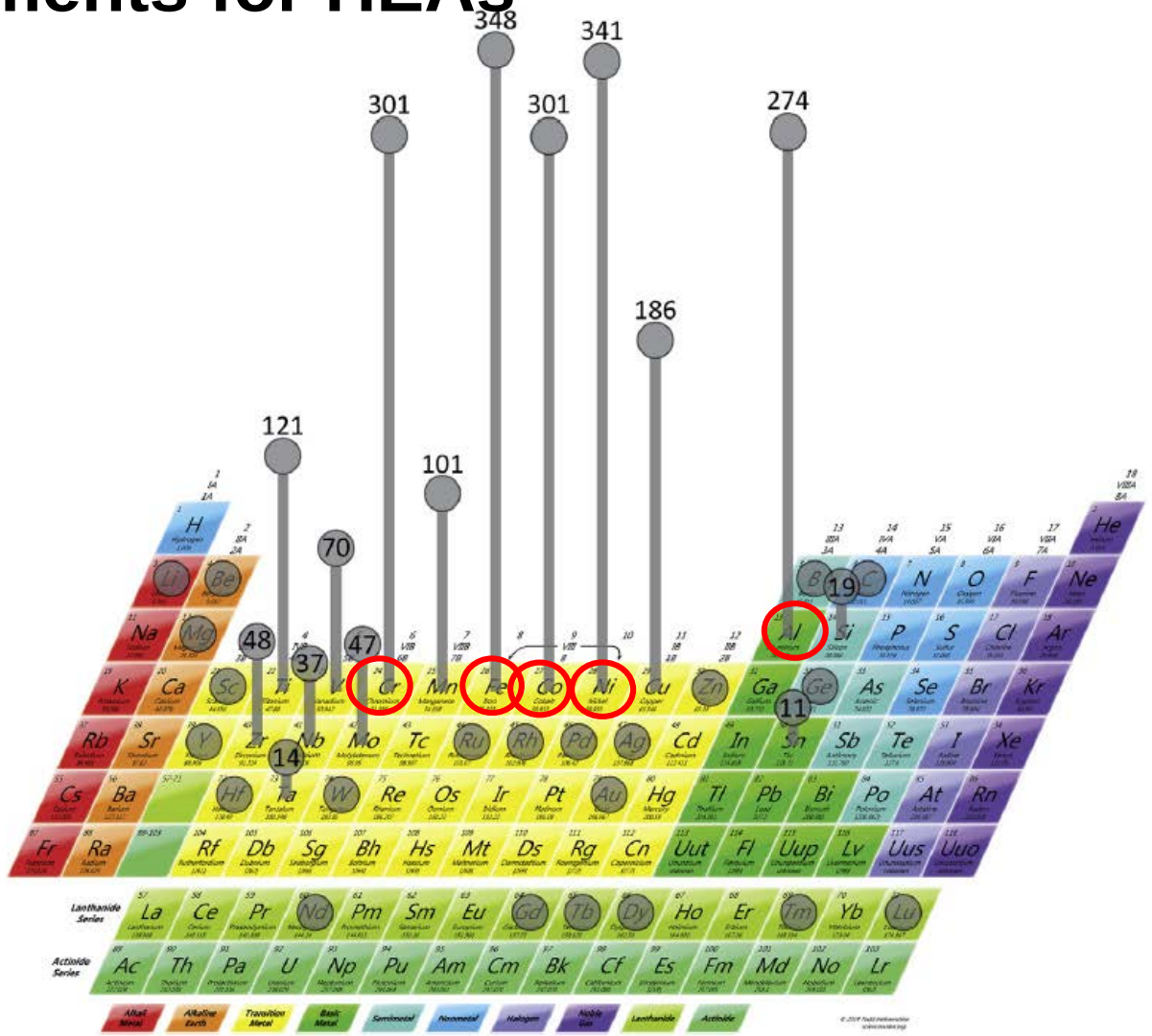
Ashby map showing fracture toughness vs. yield strength (Gludovatz et al.(2014))

Elastic Property of alloys



Specific-yield strength vs. Young's modulus: HEAs compared with other materials, particularly structural alloys. HEAs are among the materials with highest specific strength and with a wide range of Young's modulus

Target elements for HEAs

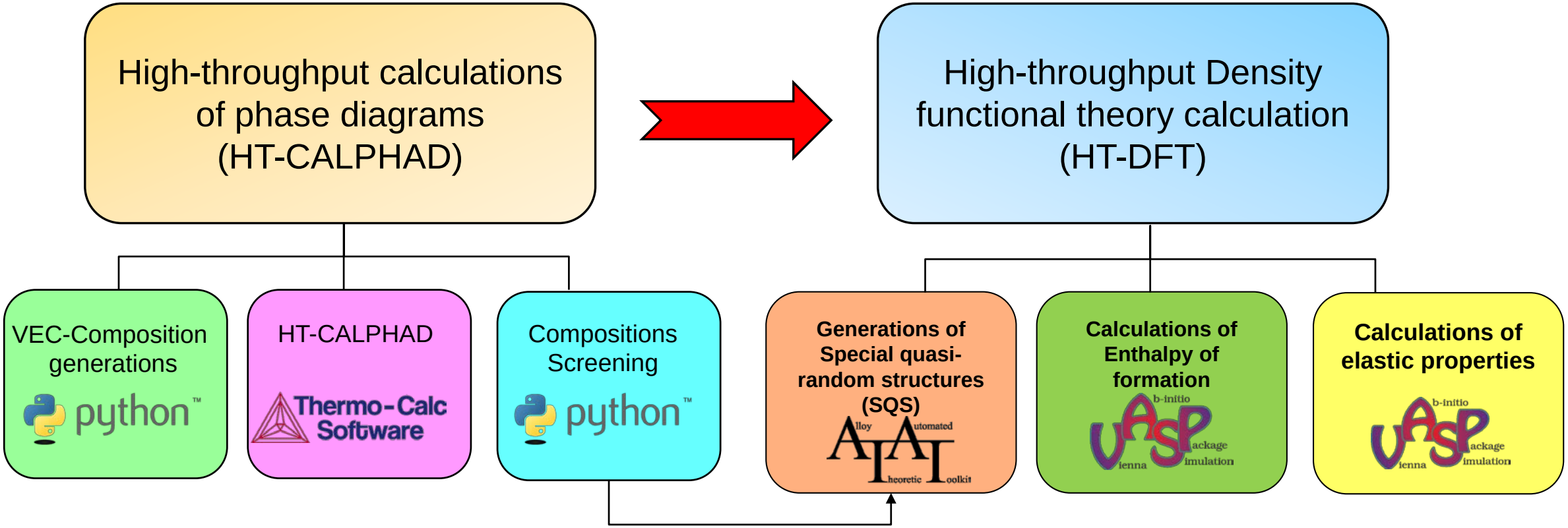


This study:

- Al
- Fe
- Cr
- Ni
- Co

The frequency with which elements are used in the 408 multi-principal element alloys (MPEAs). Al, Co, Cr, Cu, Fe, Mn, Ni and Ti are by far the most commonly used elements
[D.B. Miracle and O.N. Senkov (2017)].

Alloy Design Approaches



Good compositions screened by HT-CALPHAD would be used to generate SQS structures

Alloy Design Approaches

✓ ***HT-CALPHAD simulations***

Predictions of phase stability in the Al-Cr-Co-Fe-Ni system with the HEA thermodynamic database, down-selecting more than 3000 compositions(based on VEC phase stability criteria)

✓ ***Special quasi-random structure (SQS) generation:***

Binary, ternary and quaternary SQS structures for the random *FCC, BCC and HCP* alloys in Fe-Ni-Co-Cr system were generated using the Alloy-Theoretic Automated Toolkit (ATAT)

✓ ***DFT***

- Vienna ab initio simulation package (VASP)
- Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional
- Cutoff energy 520 eV (700 eV for elastic properties calculations)
- Monkhorst-Pack k-point meshes with density not less than 1000 pra (7000 pra for elastic properties calculations) (per-reciprocal-atom)

Phase formation rules in HEAs

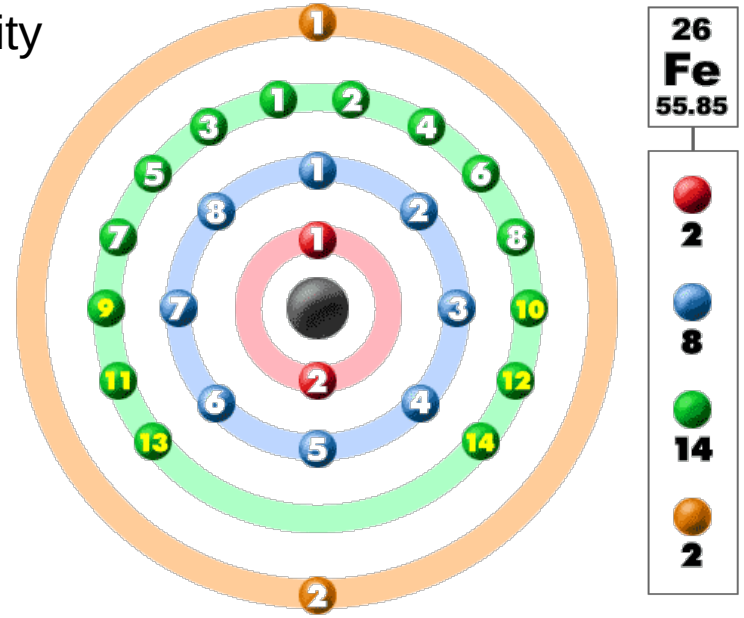
Hume-Rothery rules → **Valence electron concentration(VEC)**

Formation of solid solution：

1. Atomic size difference≤15%
2. Same crystal structure
3. Same valence
4. Similar electronegativity

Hume-Rothery electron concentration rule

Definite crystal structure will occur at a particular electron concentration



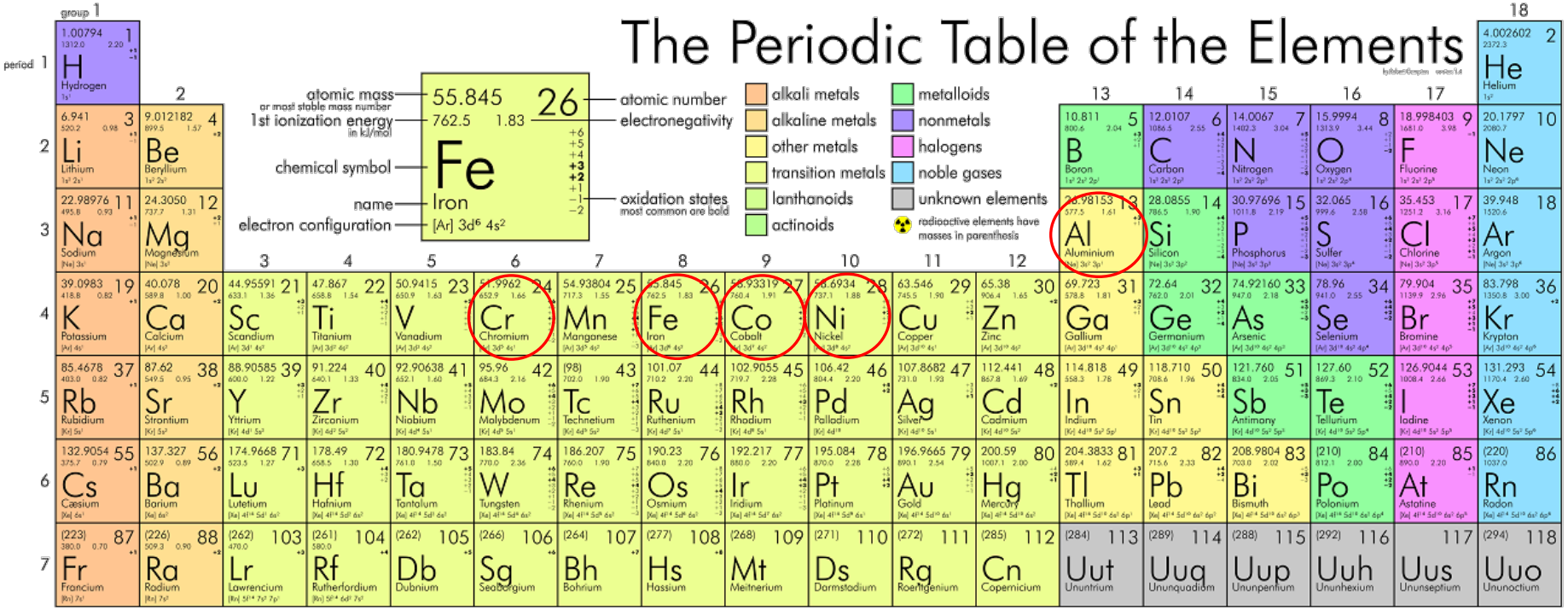
$Fe=1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

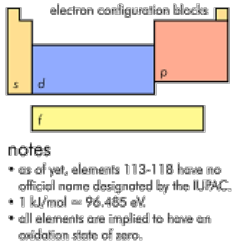
Valence electron concentration(VEC)

Reference: Mizutani U (2011) Hume-Rothery rules for structurally complex alloy phases. CRC Press, Boca Raton

Phase formation rules in HEAs

Hume-Rothery rules → **Valence electron concentration(VEC)**





$$VEC_{(sys)} = \sum_{i=1}^{n} C_i (VEC)_i$$

C_i :atomic percentage

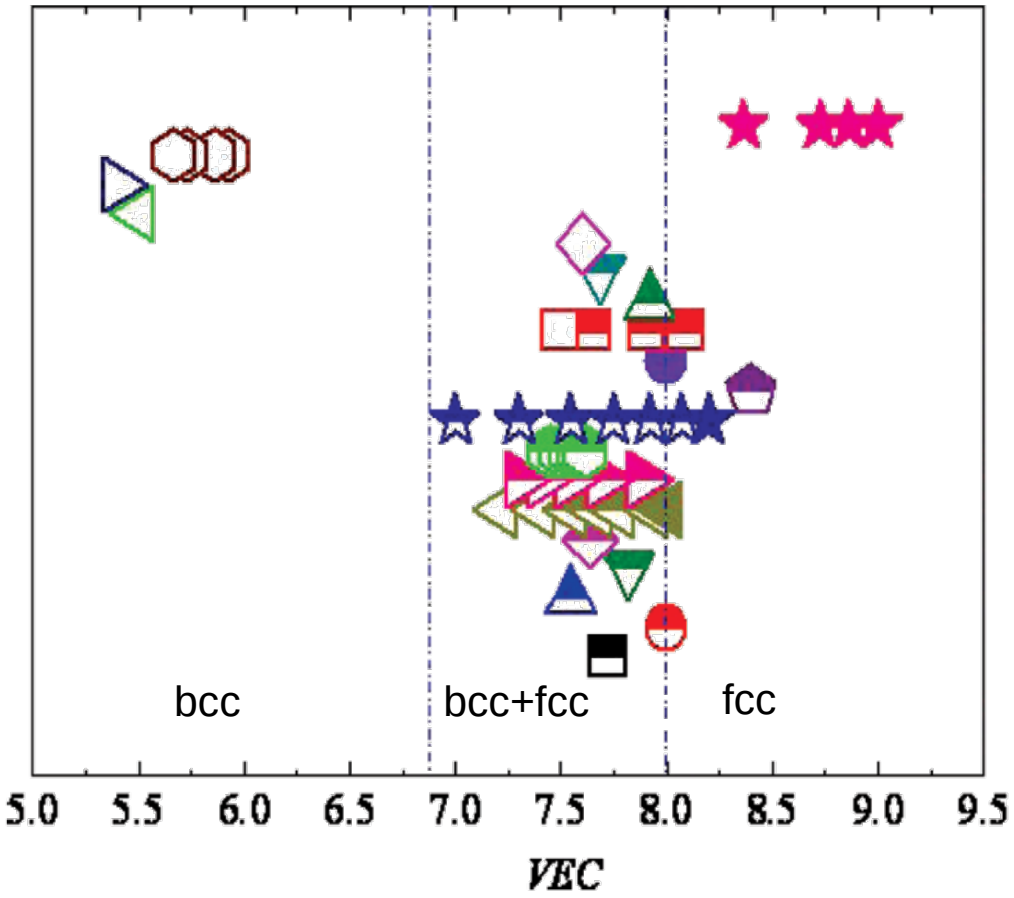
Al-Cr-Co-Fe-Ni system

$VEC = 3C_{Al} + 6C_{Cr} + 8C_{Fe} + 9C_{Co} + 10C_{Ni}$

$(VEC)_{Al} = 3$
$(VEC)_{Cr} = 6$
$(VEC)_{Fe} = 8$
$(VEC)_{Co} = 9$
$(VEC)_{Ni} = 10$

Reference: Guo S, Ng C, Lu J, et al. Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys[J]. Journal of applied physics, 2011, 109(10): 103505.

Impact of phase formation parameters on phase stabilities in HEAs



Main conclusions:

VEC < 6.87, BCC stable

6.87 ≤ VEC < 8, BCC+FCC stable

VEC ≥ 8, FCC stable

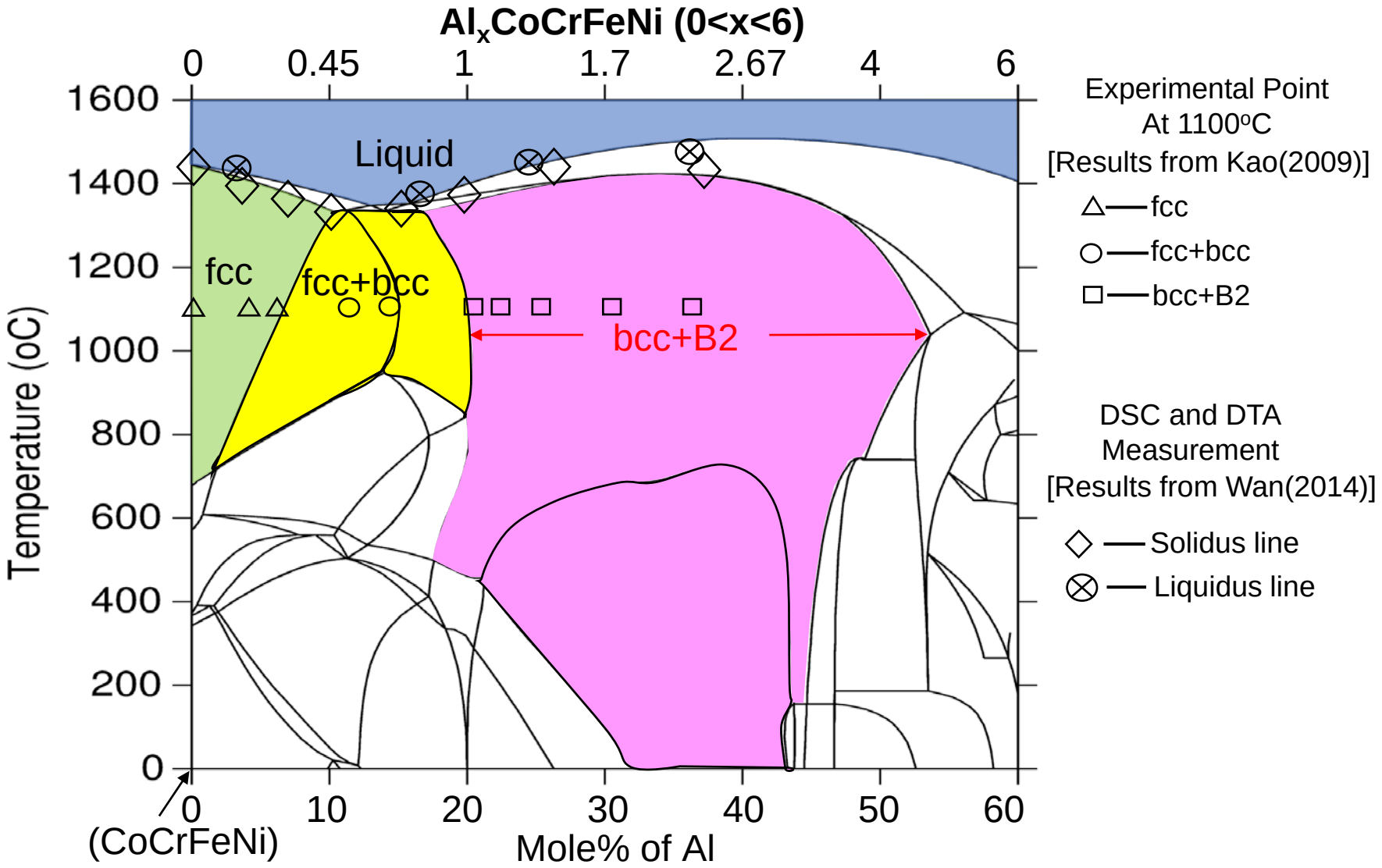
Problems:

Very limited experimental compositions

What is the role of temperature?

How does it work in real case?

Al-Cr-Co-Ni-Fe systems(transition from FCC to BCC)



Experimental Point
At 1100°C
[Results from Kao(2009)]

△—fcc

○—fcc+bcc

□—bcc+B2

DSC and DTA
Measurement
[Results from Wan(2014)]

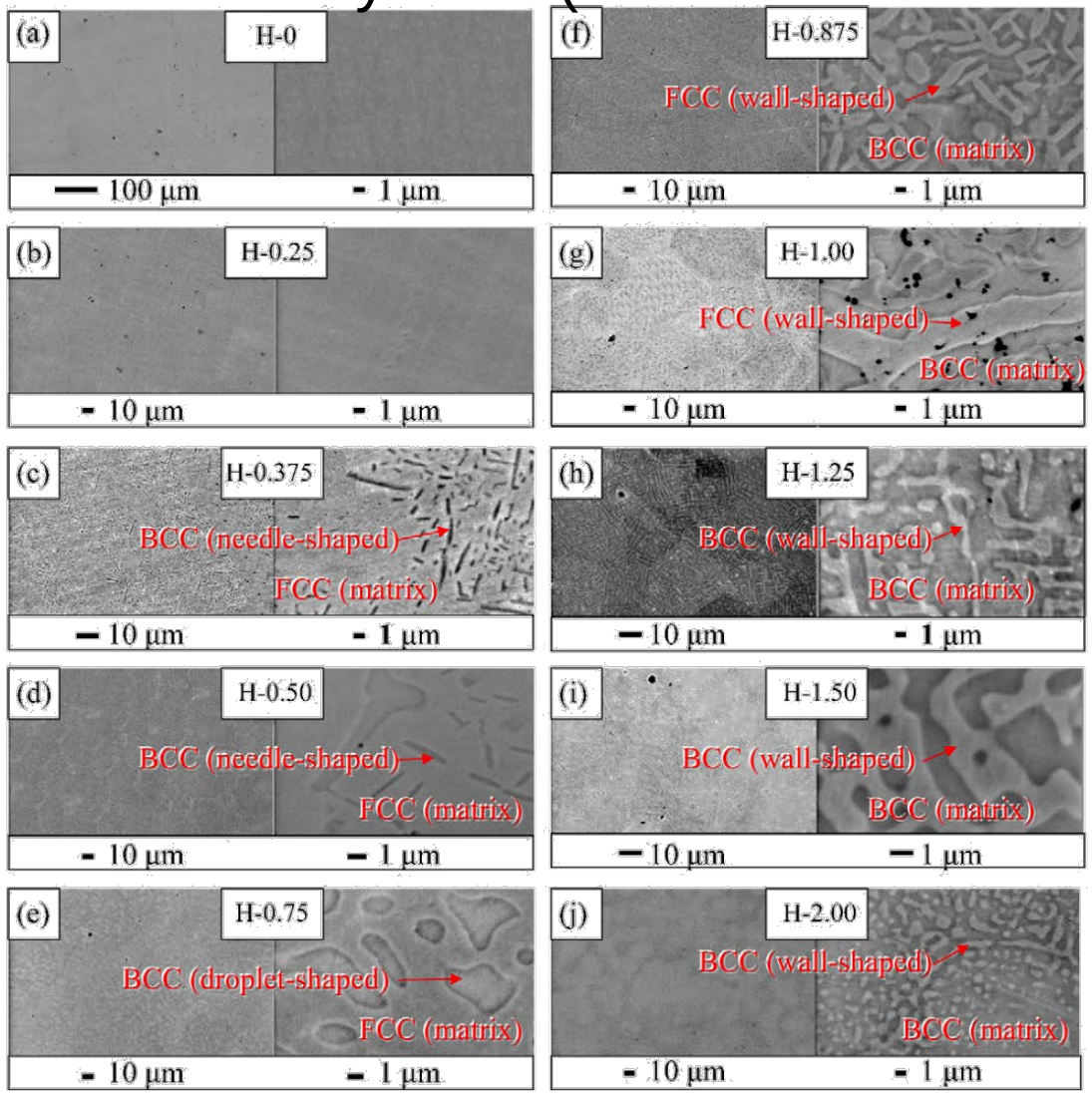
◇—Solidus line

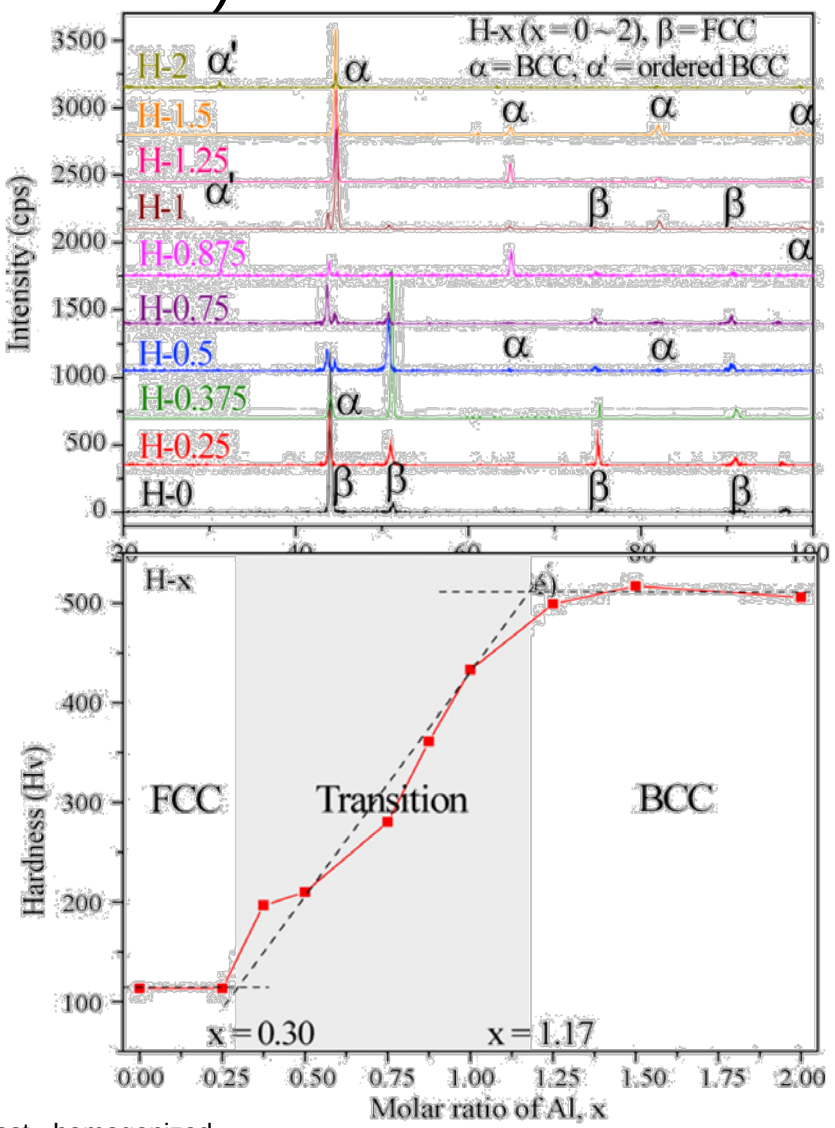
⊗—Liquidus line

VERY wide range of Al compositions to choose (20~53mol.%)-TCHEA3 13

References: Y.F Kao, T.J Chen, S.K Chen, J.W Ye. Microstructure and mechanical property of as-cast, -homogenized, and -deformed AlxCoCrFeNi (0≤x≤2) high-entropy alloys. Journal of Alloys and Compounds 488 (2009) 57–64

Al-Cr-Co-Ni-Fe systems(transition from FCC to BCC)



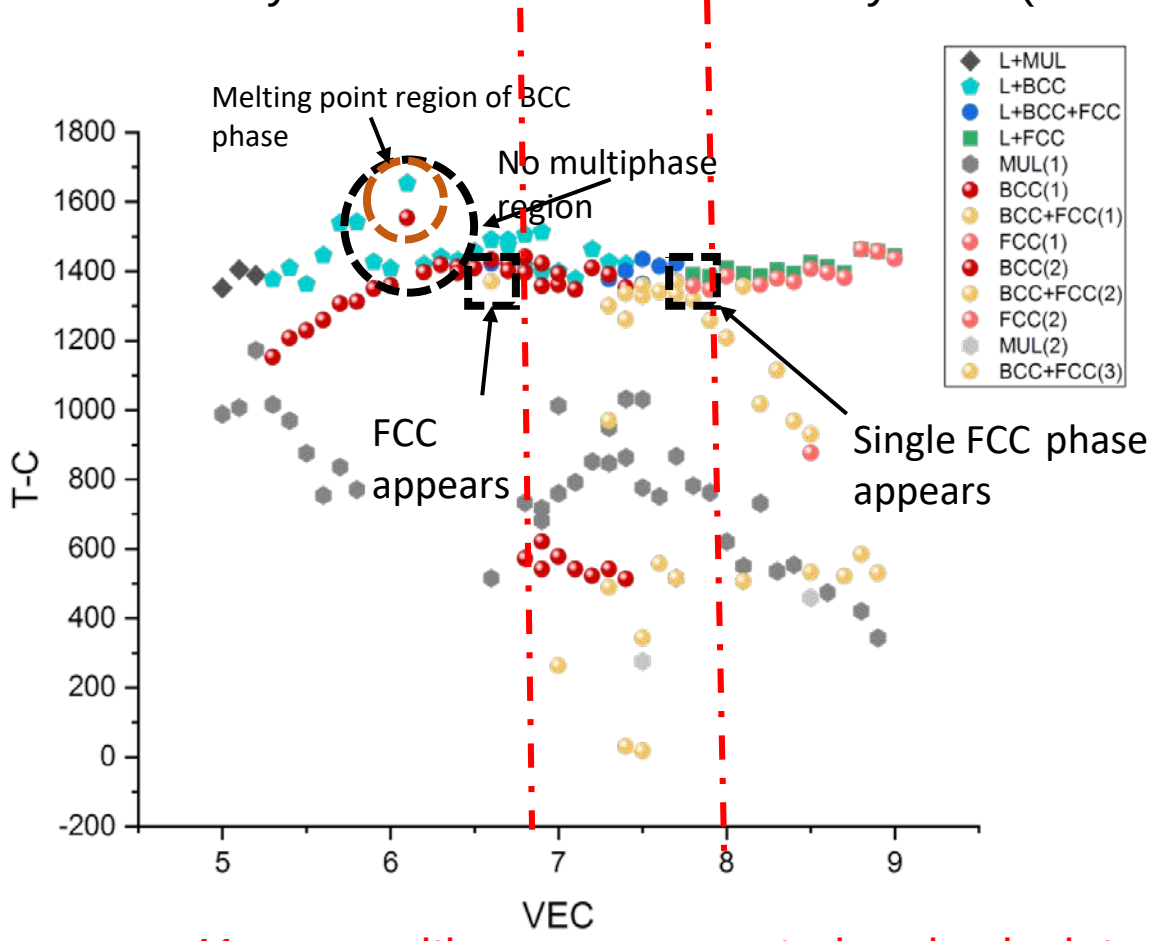


References: Y.F Kao, T.J Chen, S.K Chen, J.W Ye. Microstructure and mechanical property of as-cast, -homogenized, and -deformed AlxCoCrFeNi (0≤x≤2) high-entropy alloys. Journal of Alloys and Compounds 488 (2009) 57–64

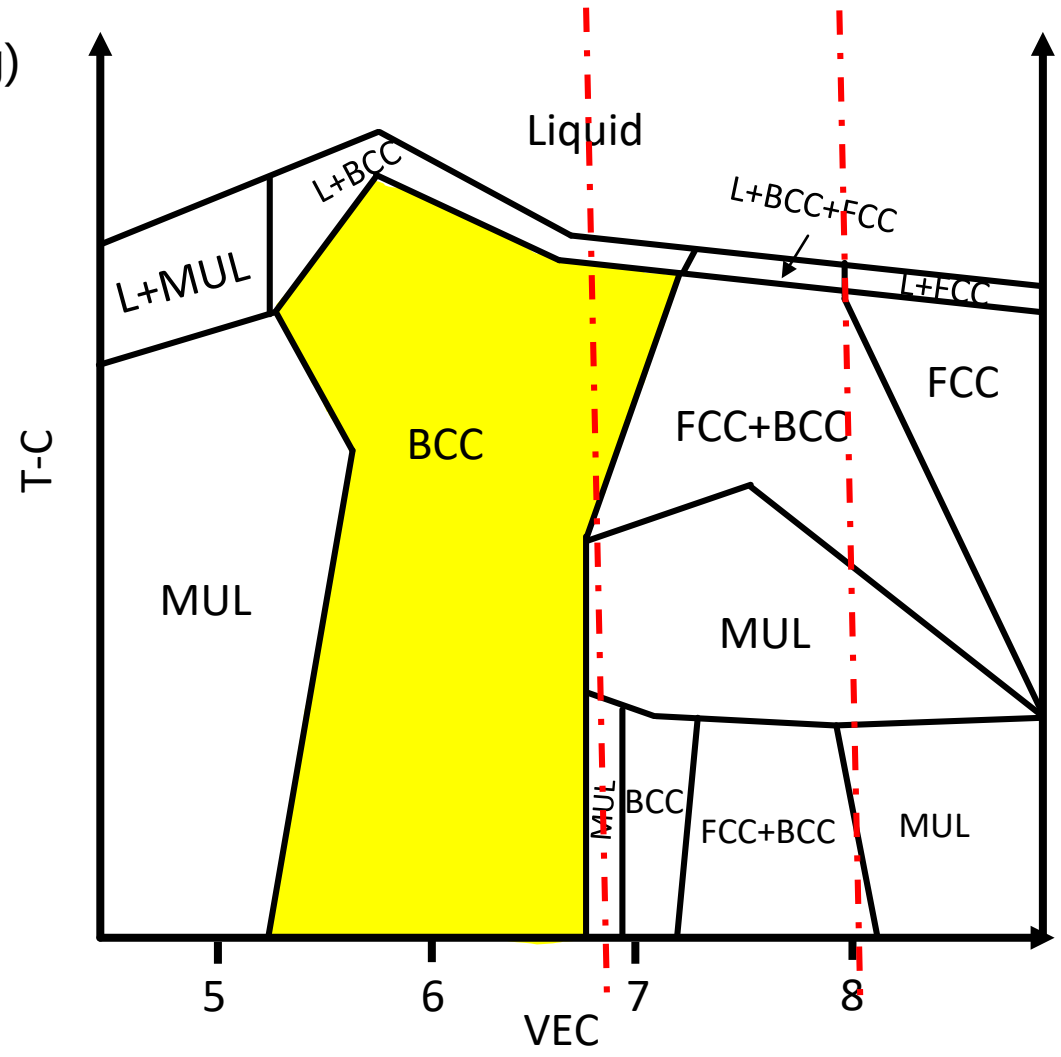
Result and discussion

1. HT-CALPHAD simulations

1.1 Preliminary results of Al-Cr-Co-Ni-Fe systems(2D screening)

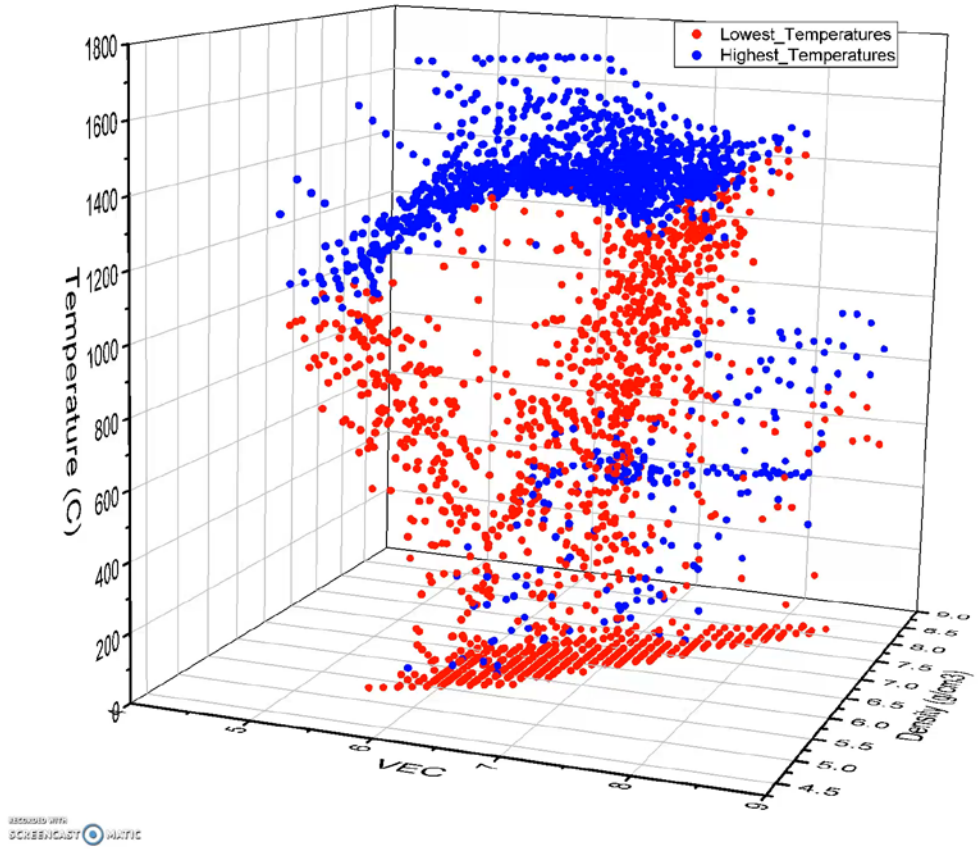


41 compositions are generated and calculated

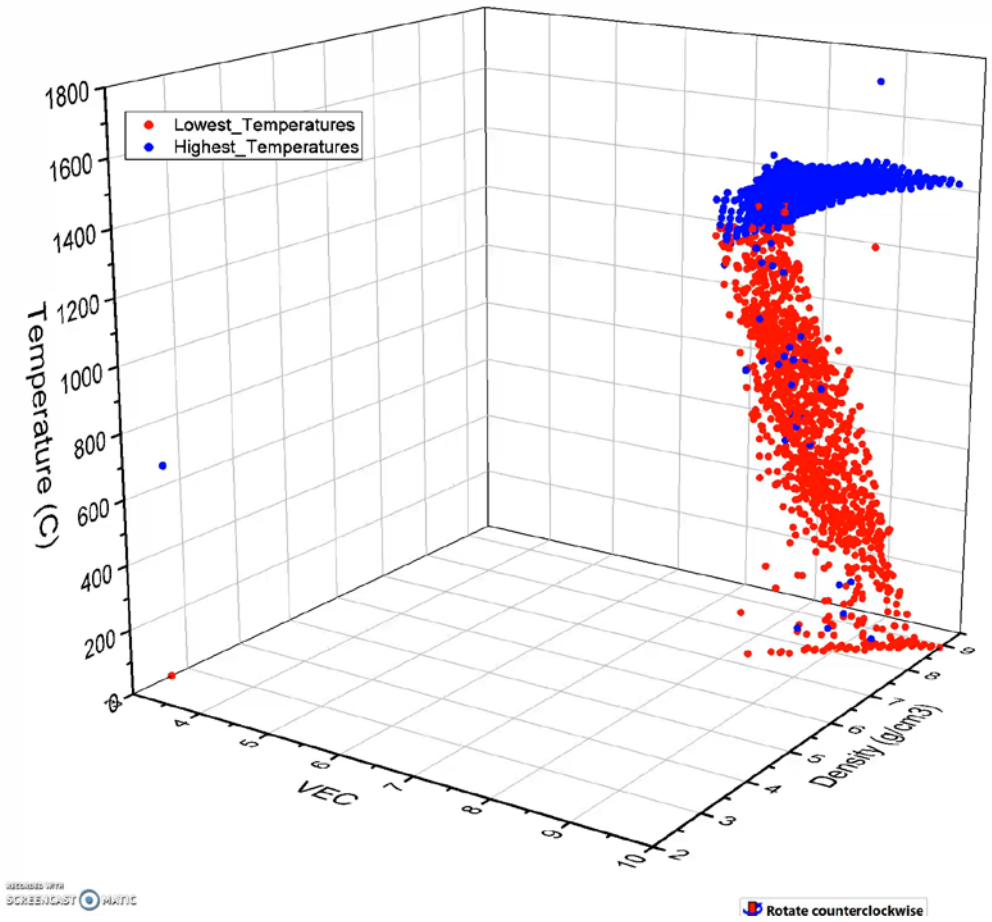


1. HT-CALPHAD simulations

1.2 Preliminary results of Al-Cr-Co-Ni-Fe systems(3D screening)



Temperature range of BCC phase

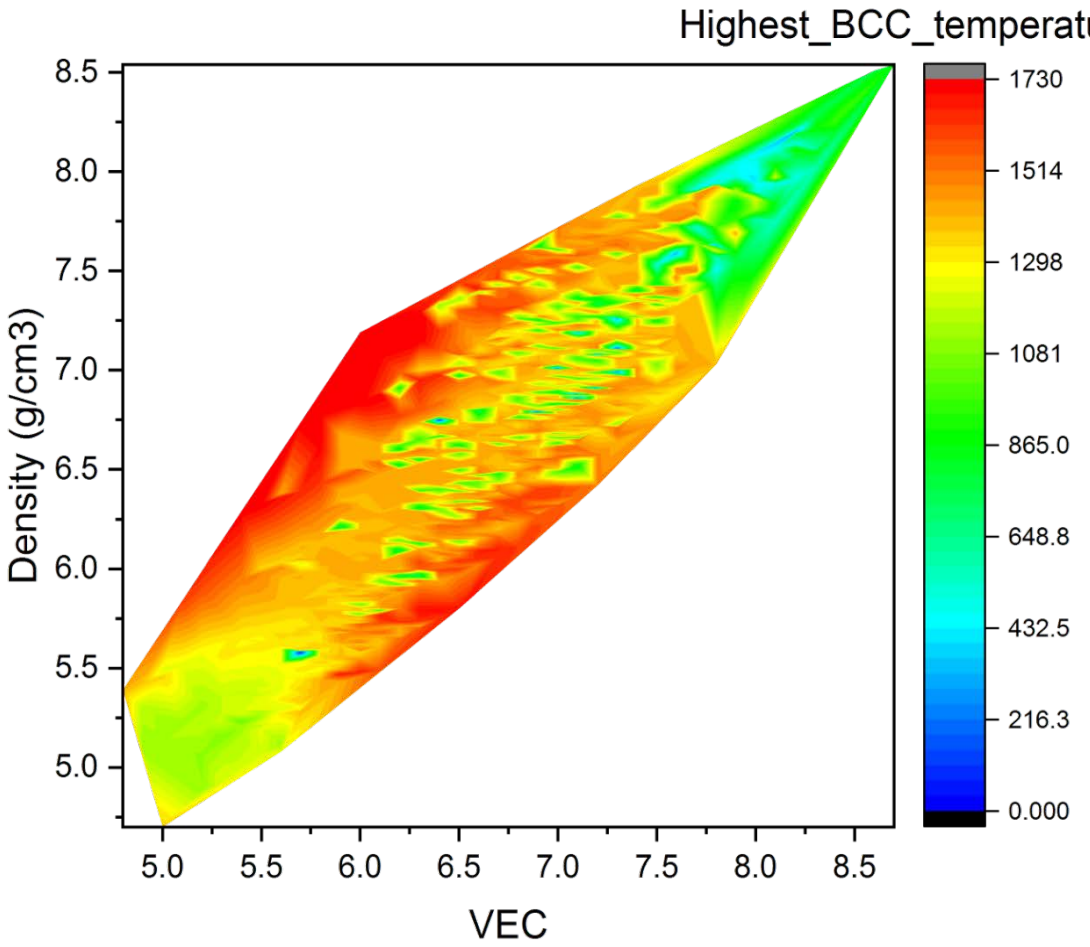


Temperature range of FCC phase

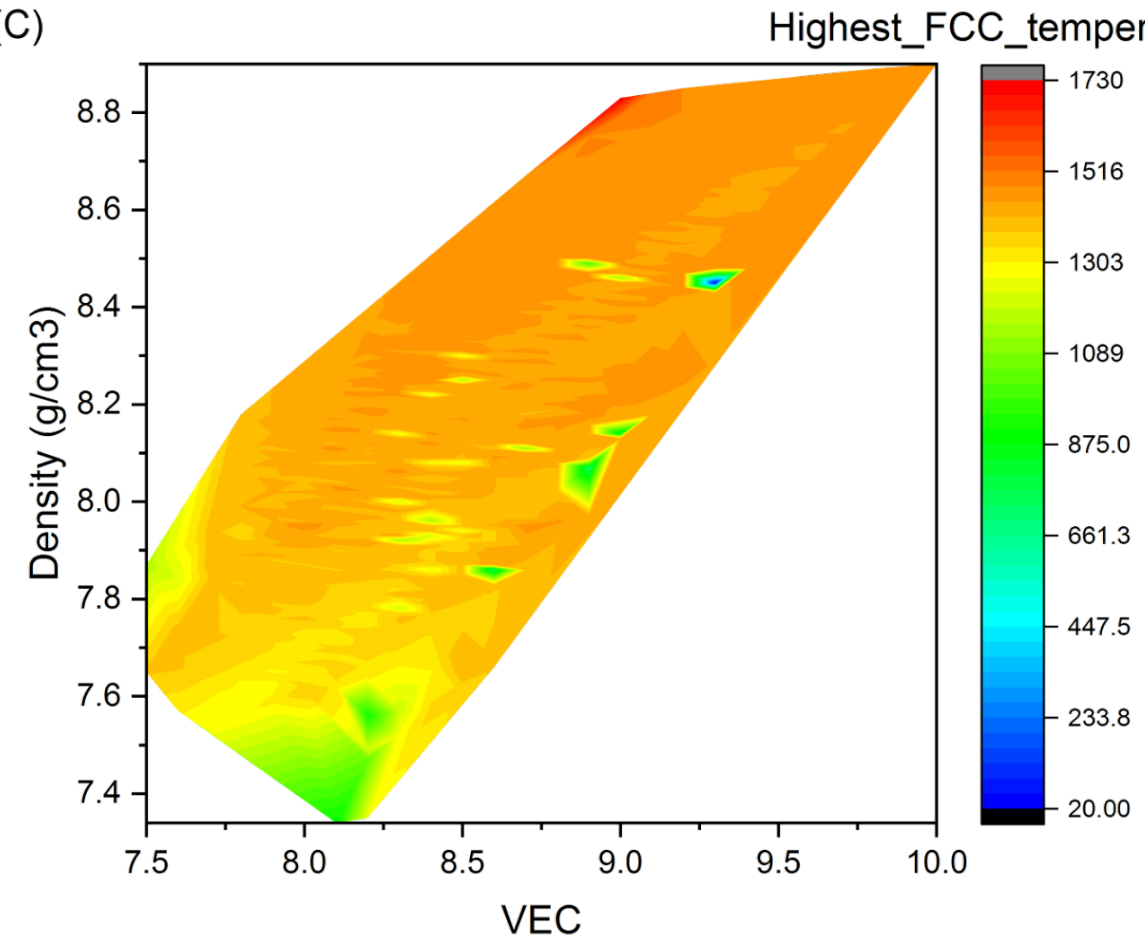
3312 VEC-Compositions are calculated

1. HT-CALPHAD simulations

1.2 Preliminary results of Al-Cr-Co-Ni-Fe systems(3D screening)



Temperature-density-VEC diagram of BCC phase



Temperature-density-VEC diagram of FCC phase

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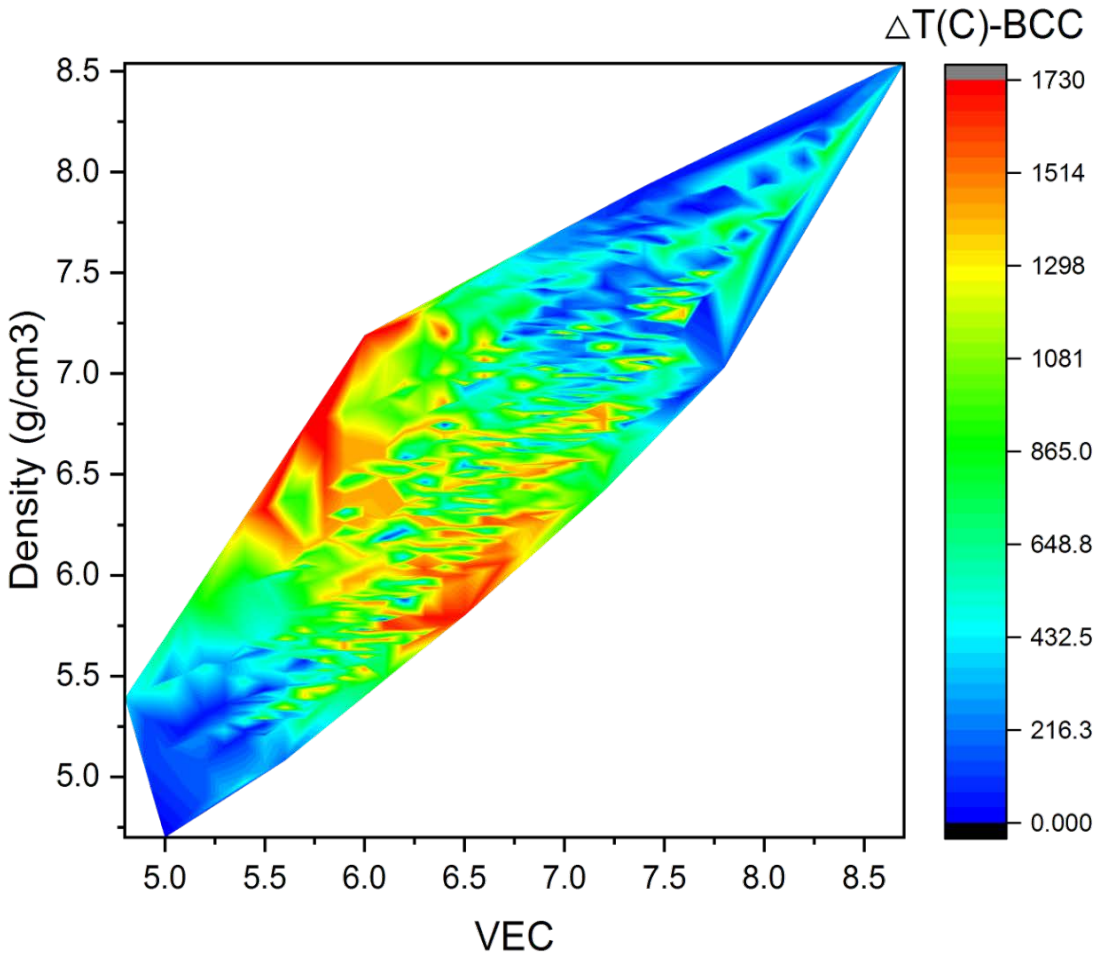
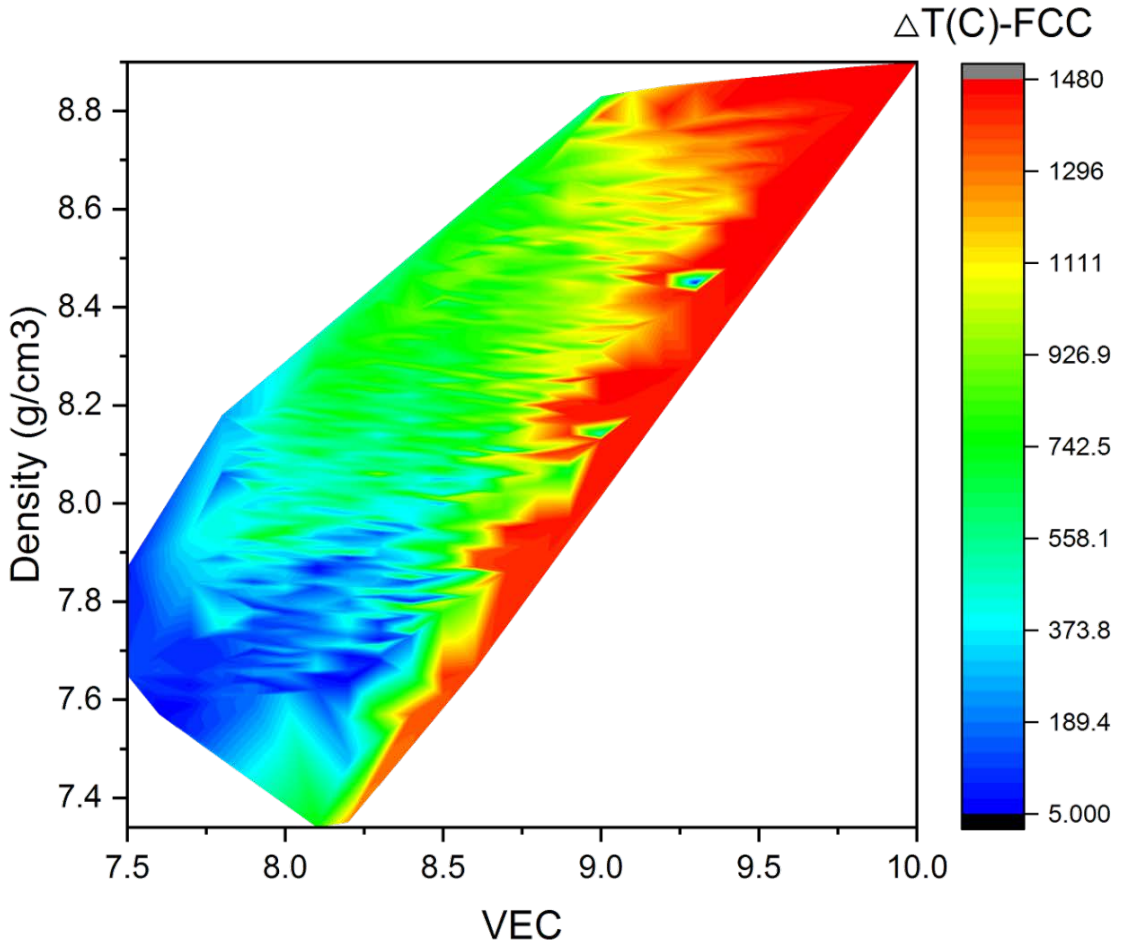


△T-density-VEC diagram of BCC phase

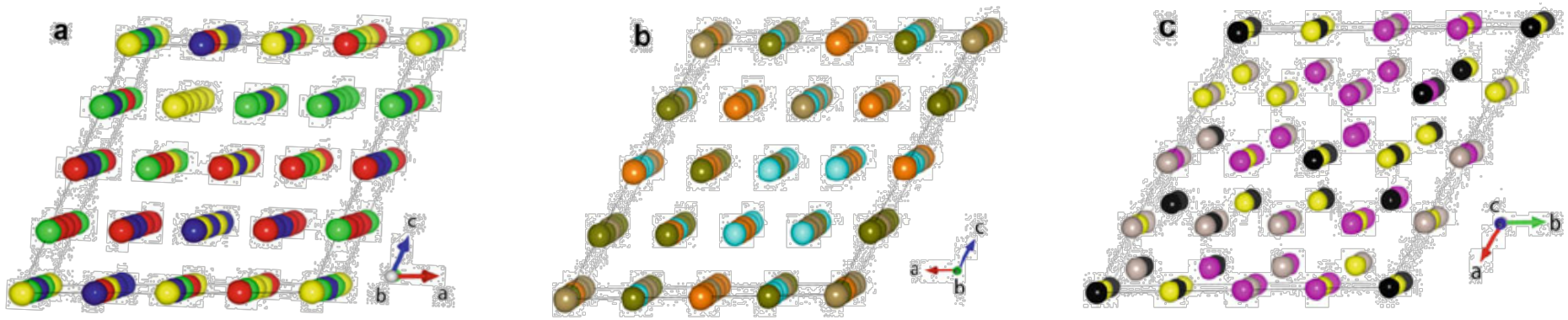


△T-density-VEC diagram of BCC phase

Special Quasi-random Structure

What is Special Quasi-random Structure(SQS)?

small-unit-cell periodic structures in random substitutional alloys



FCC *BCC* *HCP*

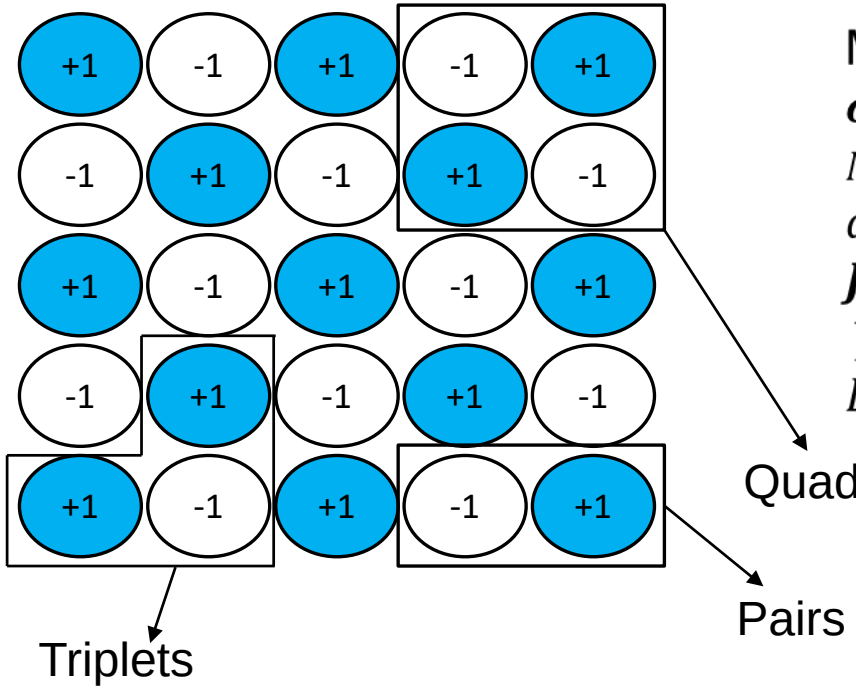
Fig. The input unrelaxed atomic structures of 64-atom quaternary SQS

Why do we introduce SQS concept?

SQS can be regarded as the best possible periodic unit cell representing a given random alloy.

SQS generation

1.Cluster Expansion



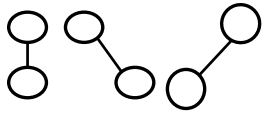
M = is the number of atomic sites in the parent (e.g. unit) cell
$\boldsymbol{\sigma}$ = configuration or structures
N_δ = number of configurations or structures
α = symmetrically distinct clusters
$\boldsymbol{J}_\alpha$ = effective cluster interaction
$\prod \alpha$ = Correlation matrix
$E(\boldsymbol{\sigma})$ = energy of configuration $\boldsymbol{\sigma}$

Random structures have lower energy of configuration!

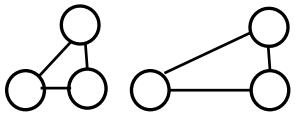
$$E(\sigma_1, \sigma_2, \sigma_3 \ldots \sigma_n) = \sum_\alpha m_\alpha J_\alpha \overline{\prod}_\alpha(\delta) = \sum_{\{ij\}} m_{ij} J_{ij} \delta i \delta j + \sum_{\{ijk\}} m_{ijk} J_{ijk} \delta i \delta j \delta k + \sum_{\{ijkl\}} m_{ijkl} J_{ijkl} \delta i \delta j \delta k \delta l + \cdots$$

$$\overline{\prod}_\alpha(\delta) = \frac{1}{N_\delta M_\alpha} \sum_{\beta \equiv \alpha} \prod \delta_i$$

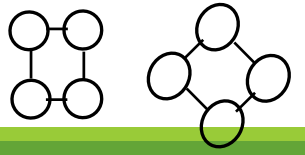
All of the pairs



All of the triplets

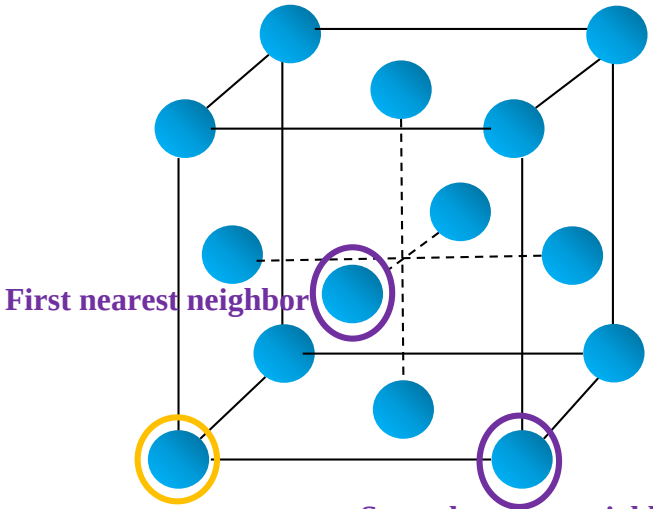


All of the quadruplets

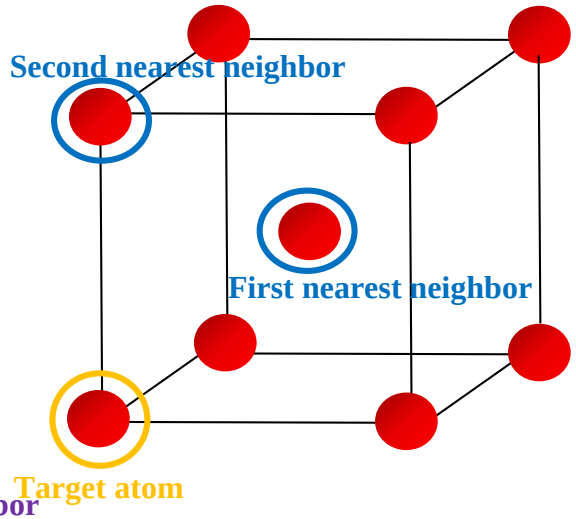


SQS generation

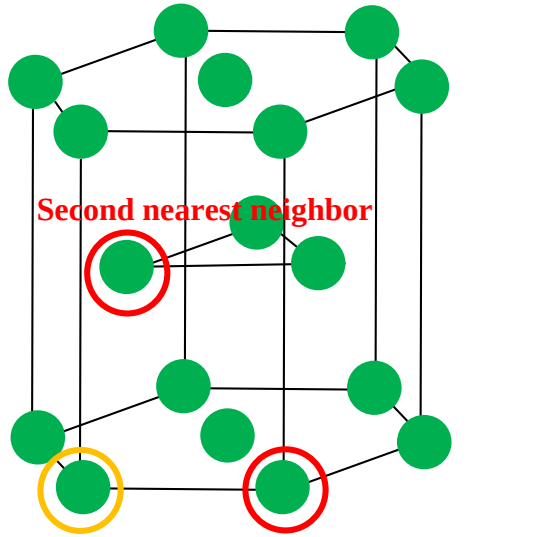
2.Correlation function



FCC



BCC



HCP

The more atoms match the correlation function, we could get more random SQS structures

Example: Fe3Ni(only consider pairs)

	ideal mismatch	SQS1	SQS2
$\prod_{2,1}$ =	0.25	0.25	0.25
$\prod_{2,2}$ =	0.25	0.25	0.25
$\prod_{2,3}$ =	0.25	0.25	0.458
$\prod_{2,4}$ =	0.25	0.25	0.333

SQS1 is more random than SQS2

Binary:

Substitutional model= $A_{1-x}B_x$

Ideal correlation mismatch = $\langle \bar{\Pi}_{k,m} \rangle_R = (2x-1)^k$

Number of points considered for cluster expansion

A=0.5 B=0.5 ideal mismatch=0

A=0.75 B=0.25 ideal mismatch=0.25

A=0.66 B=0.33 ideal mismatch=0.1111

2. Generated SQS structures

SQS structures:

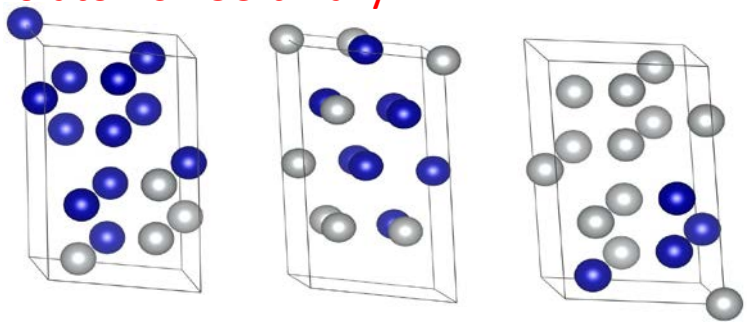
- ✓ 16 and 32 atoms per unit cell for binary systems
- ✓ 32 atoms per unit cell for ternary systems
- ✓ 32 and 64 atoms per unit cell for quaternary system
- ✓ 200 atoms per unit cell for quinary systems

Atomic arrangement tested:

Face Center Cubic structures(FCC)

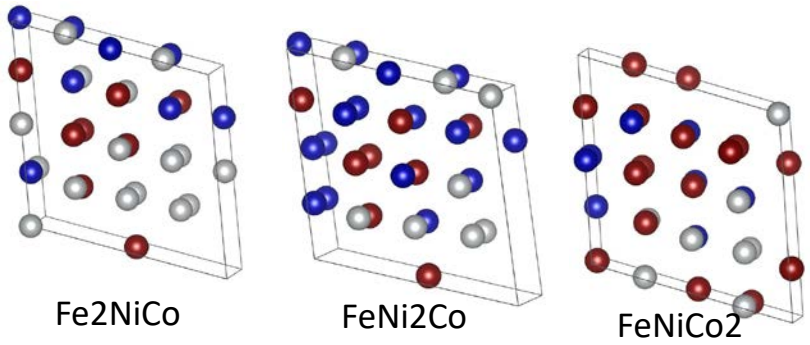
Body Center Cubic structures(BCC)

16 atoms FCC binary



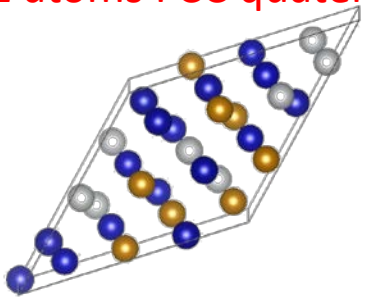
Fe0.25Ni0.75 Fe0.50Ni0.50 Fe0.75Ni0.25

32 atoms FCC ternary



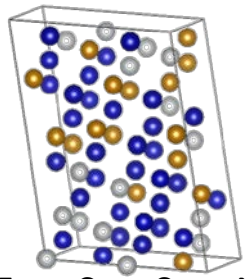
Fe2NiCo FeNi2Co FeNiCo2

32 atoms FCC quaternary



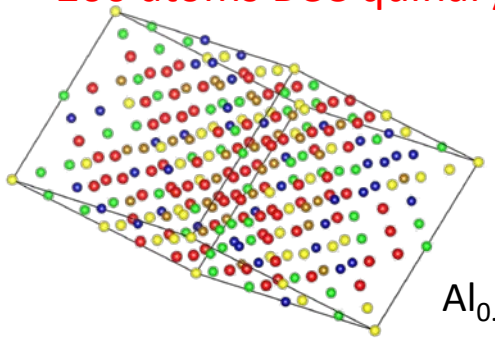
$Fe_{0.25}Cr_{0.25}Co_{0.25}Ni_{0.25}$

64 atoms FCC quaternary



$Fe_{0.25}Cr_{0.25}Co_{0.25}Ni_{0.25}$

200 atoms BCC quinary



$Al_{0.35}Fe_{0.15}Cr_{0.15}Co_{0.15}Ni_{0.2}$

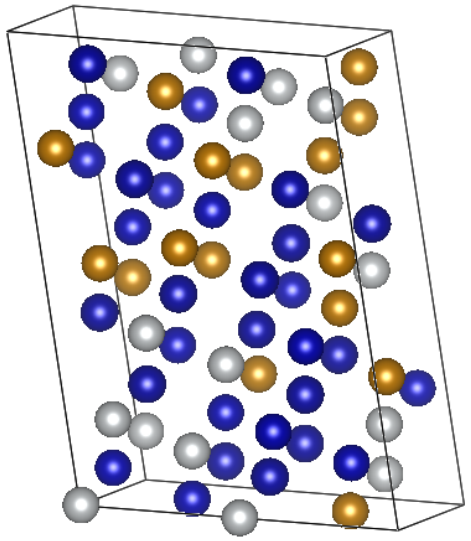
3. Elasticity constant(DFT calculation)

$Fe_{0.25}Ni_{0.25}Co_{0.25}Cr_{0.25}$ alloy

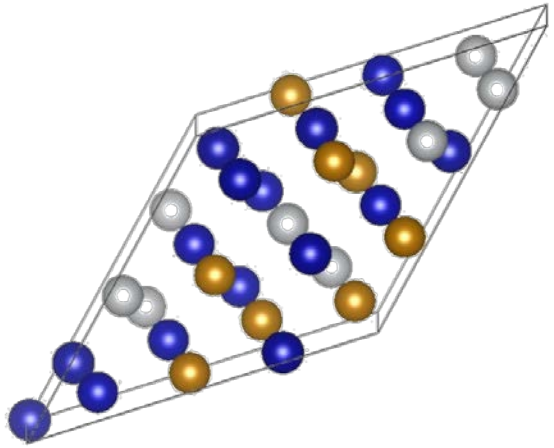
V, Å³/atom	Method	Reference
11.05	DFT	This work (64 atoms SQS)
11.09	DFT	This work (32 atoms SQS)
11.19	DFT	Gao et al. (2017)
11.27	EXP	Y.-F. Kao et al. (2009)
11.37	EXP	G. Laplanche et al. (2018)
11.57	EXP	B.Liu et al. (2016)

Average properties (numbers in parentheses are for 32 atoms SQS structure)

Averaging scheme	Bulk modulus, GPa	Young's modulus, GPa	Shear modulus, GPa	Poisson's ratio
Voigt	K_V = 167.0 (157.4)	E_V = 245.0 (247.4)	G_V = 97.6 (99.9)	v_V = 0.2554 (0.2380)
Reuss	K_R = 166.7 (155.89)	E_R = 201.1 (205.1)	G_R = 77.4 (80.1)	v_R = 0.2989 (0.2807)
Hill	K_H = 166.8 (156.62)	E_H = 223.4 (226.6)	G_H = 87.5 (90.0)	v_H = 0.2768 (0.2589)

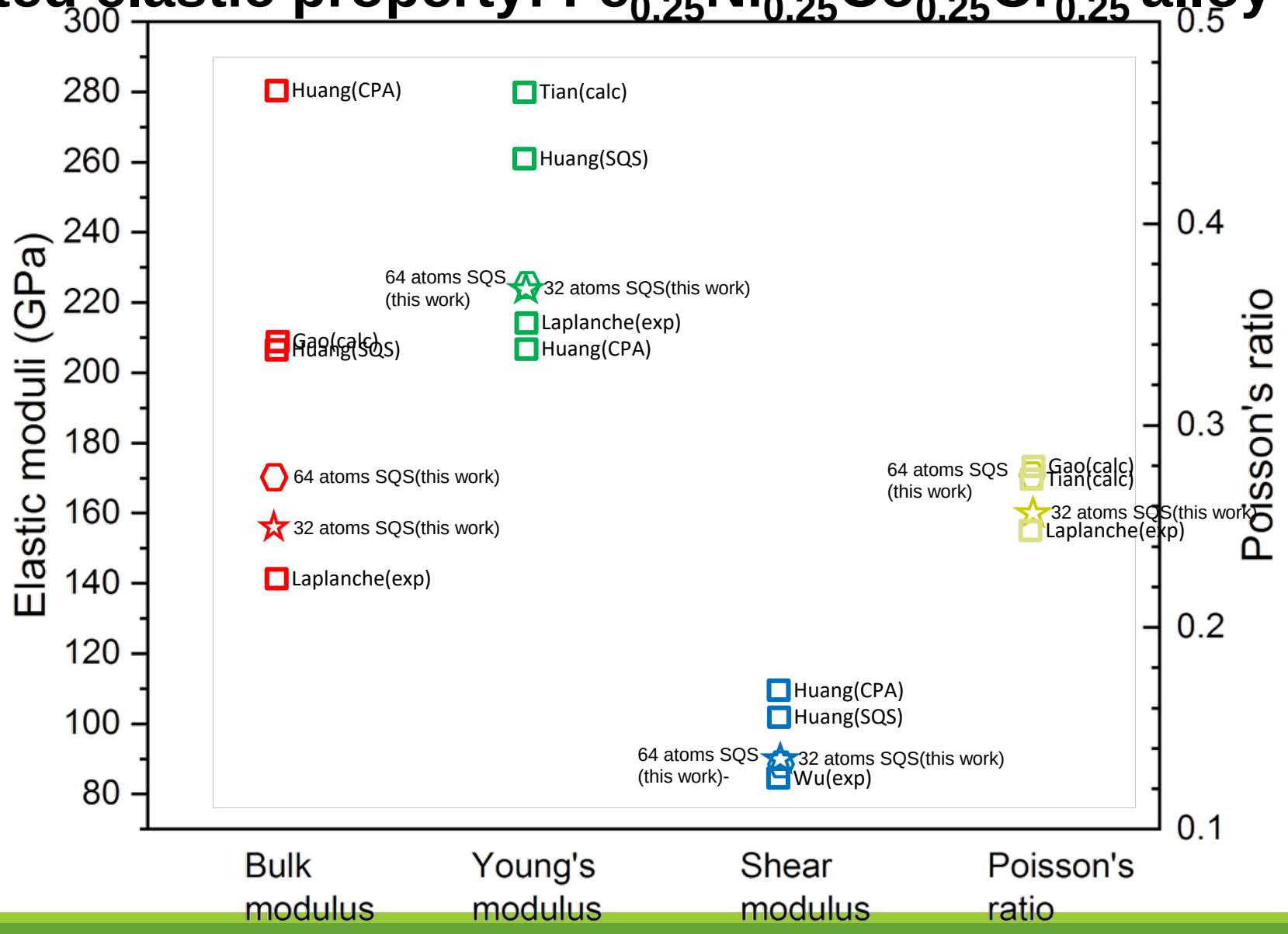


64 atoms SQS cell



32 atoms SQS cell

Calculated elastic property: $Fe_{0.25}Ni_{0.25}Co_{0.25}Cr_{0.25}$ alloy



Main Conclusions

1. The high-throughput CALPHAD approach shows the capability of the simulation of phase stability on Al-Cr-Co-Ni-Fe systems.
   - BCC structures have higher solidus temperatures and single phase temperature ranges when VEC is between 5.5 to 6.5
   - FCC structures have higher solidus temperatures and single phase temperature ranges when VEC is larger than 8.0
2. The calculated elastic properties of generated SQS structures show good agreement with the experimental data for the Fe-Ni-Cr-Co quaternary system.

Acknowledgment

Department of Energy (DOE)

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- Help from the program manager: Maria Reidpath

- *Collaborations on DFT: Dr. Michael Gao, Dr. Yi Wang*
- *Help from Computherm providing database*

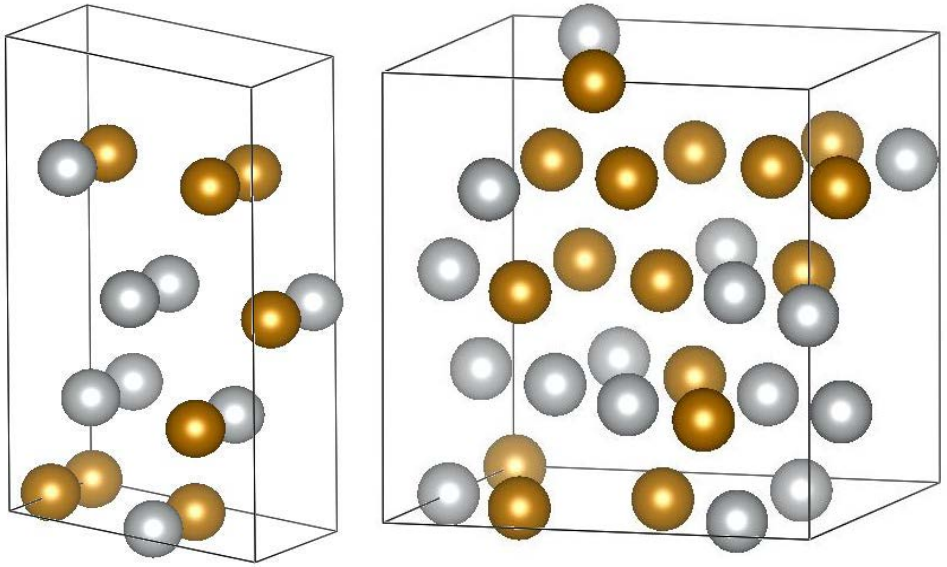
Thank you !

3. Enthalpy of formation(DFT calculation)

Fe-Ni system:16 atoms vs. 32 atoms per unit cell(FCC)

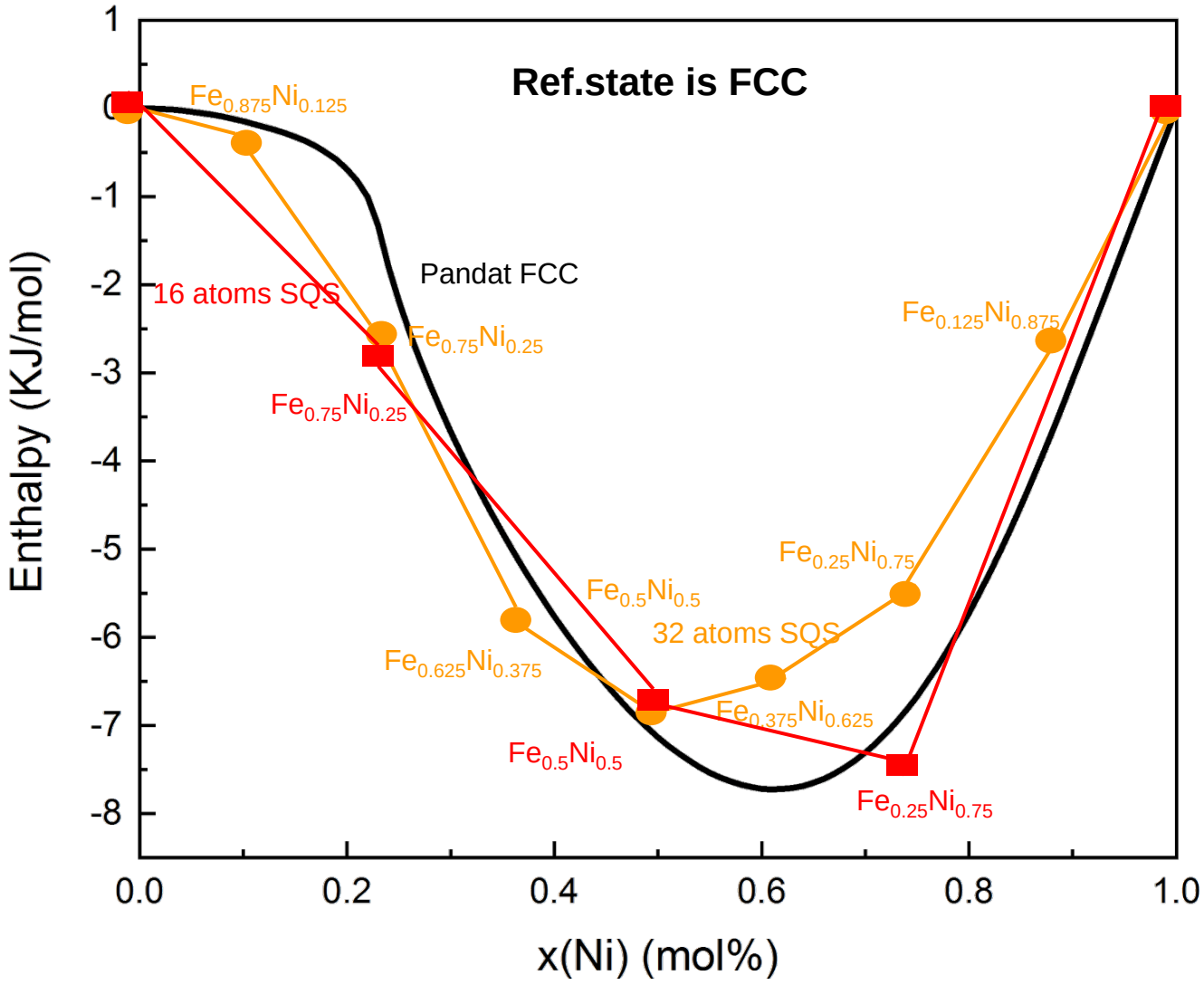
$$H = E(A_{1-x}B_x) - [(1-x)E(A) + xE(B)]$$

Enthalpy of Mixing; Energy of SQS structures; Energy of pure A; Energy of pure B



16 atoms unit cell

32 atoms unit cell



4. Elasticity constant(DFT calculation)

$$\delta = E\varepsilon \longrightarrow \begin{bmatrix} S_{11} \\ S_{22} \\ S_{33} \\ S_{23} \\ S_{13} \\ S_{12} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} E_{11} \\ E_{22} \\ E_{33} \\ 2E_{23} \\ 2E_{13} \\ 2E_{12} \end{bmatrix}$$

E——Green-Lagrange strain tensor

S——Calculated stress tensor

$\mathbf{C_{ij}}$——Elastic tensor

$\mathbf{s_{ij}}$——Compliance tensor

$$s_{ij} = C_{ij}^{-1}$$

Bulk modulus Voigt average(K_V)

$$9K_V = (C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31})$$

Bulk modulus Reuss average(K_R)

$$\frac{1}{K_R} = (s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{23} + s_{31})$$

Bulk modulus Hill average(K_H)

$$2K_H = (K_R + K_V)$$

Shear modulus Voigt average(G_V)

$$15G_V = (C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66})$$

Bulk modulus Reuss average(G_R)

$$\frac{15}{G_R} = 4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{23} + s_{31}) + +3(s_{44} + s_{55} + s_{66})$$

Bulk modulus Hill average(G_H)

$$2G_H = (G_R + G_V)$$

Young's modulus(E)

$$E = 2G(1 + \mu)$$

Poisson's modulus(μ)

$$\mu = (3K - 2G)/(6K + 2G)$$