Thermodynamics of High-Entropy Alloys and Alloy Design

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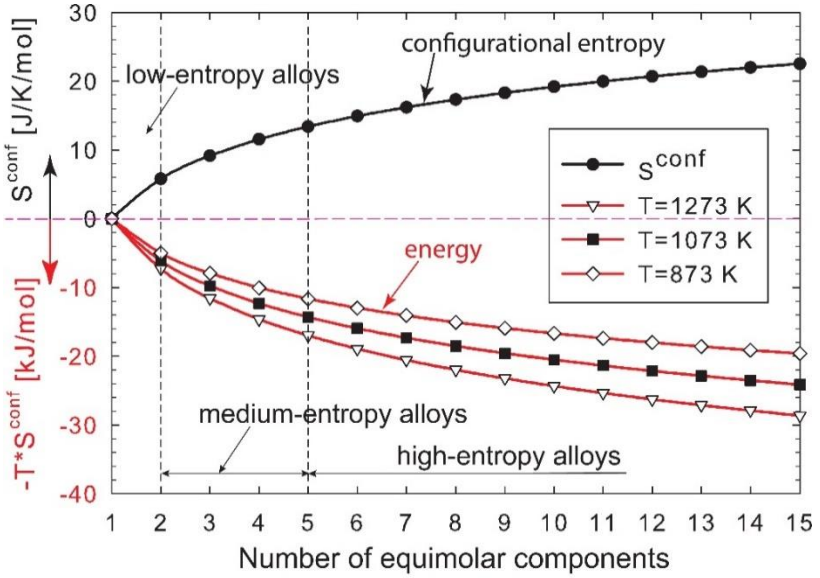
- Collaborators and colleagues: Peter K. Liaw's group (University of Tennessee), Chuan Zhang & Fan Zhang (CompuTherm), Chao Jiang (Idaho National Lab), Paul D. Jablonski, Martin Detrois, and Kyle Rozman (NETL), and many more.

High-Entropy Alloys and Four Core Effects

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta S_{mix}^{conf}\Big|_{\max} = R\ln N \quad \Delta S_{mix}^{conf}\Big|_{ideal} = -R\sum_{i=1}^{N} x_i \ln x_i$$

$$\Delta S_{mix} = \Delta S_{mix}^{conf} + \Delta S_{mix}^{el} + \Delta S_{mix}^{ph} + \Delta S_{mix}^{mag}$$



Two definitions by Professor Jien-Wei Yeh:

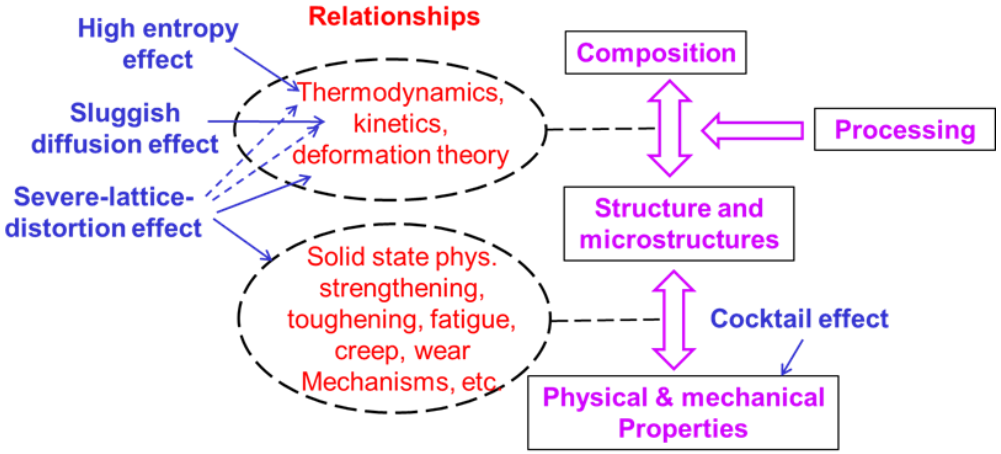
- One is based on composition. HEAs are preferentially defined as alloys containing at least five principal elements, each with an atomic percentage between 5% and 35%.
- The other is based on configurational entropy. HEAs are defined as alloys having configurational entropies at a random state larger than 1.5R, no matter they are single phase or multi-phase at room temperature.

Other names that are also used:

- Multi-principal-component alloys
- Compositionally complex alloys
- Solid-solution alloys
- Concentrated solid solution alloys

Four core effects:

- High entropy effect for thermodynamics
- Sluggish diffusion effect for kinetics
- Severe lattice distortion effect for structure
- Cocktail effect for properties



Reported Single-phase HEA Compositions

FCC	Refs.
CoCrFeNi	1
CoFeMnNi	2,3
CoCrMnNi	3
CoFeNiPd	4
CoCrFeMnNi	5
CoCrFeNiPd	6
$Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$	7

HCP	Refs.
CoFeReRu	22
MoPdRhRu	23
DyGdHoTbY	24
DyGdLuTbTm	24
DyGdLuTbY	25
$Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$	7

BCC	Refs.
AlNbTiV	8
HfNbTiZr	9
MoNbTaW	10,11
NbTaTiV	12
NbTiVZr	13
AlCrMoTiW	14
AlNbTaTiV	12
HfNbTaTiZr	15
HfNbTiVZr	16
MoNbTaVW	10,11
MoNbTaTiV	17
MoNbTiVZr	18
NbReTaTiV	17
MoNbReTaW	17
CrMoNbTaVW	19
HfNbTaTiVZr	20
MoNbTaTiVW	21
MoNbReTaVW	17
MoNbReTaTiVW	17

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Disordered HEA Formation Rules

1. **Enthalpy (ΔH_{mix}) versus atomic size difference (δ)**

$$\Delta H_{mix} = 4\sum_{i=1, i\neq j}^{N} \Delta H_{ij}^{mix} x_i x_j \qquad \delta = \sqrt{\sum_{i=1}^{N} x_i \left(1 - x_i / \sum_{j=1}^{N} x_j r_j\right)^2}$$

$\delta \leq 5$ or 6.6%
$-15 \leq \Delta H_{mix} \leq +5$ kJ/mol

2. **Ω–parameter**

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}$$

$\Omega > 1$ for solid solution

3. **Valence electron concentration (VEC)**

$$VEC = \sum_{i=1}^{N} x_i VEC_i$$

FCC if VEC > 8
BCC if VEC < 6.87
FCC + BCC if VEC in between

4. **Electronegativity difference ($\Delta\chi$)**

$$\Delta\chi = \sqrt{\sum_{i=1}^{N} x_i \left(\chi_i - \sum_{j=1}^{N} x_j \chi_j\right)}$$

5. **ϕ-parameter**

$$\phi = \frac{-R\sum_{i=1}^{N} x_i \ln x_i - |\sum_{i\neq j} 4H_{ij} x_i x_j| / T_m}{|S_E|}$$

$\phi \geq 20$

6. **Root mean square residual strain**

$$< \varepsilon^2 >^{1/2}$$

≤ 0.05

7. Gibbs free energy

$$\eta = \frac{T_{ann} \Delta S_{ideal}^{conf}}{|\Delta H_{ij}^{IM}|^{\max}}$$

$\eta > 1$

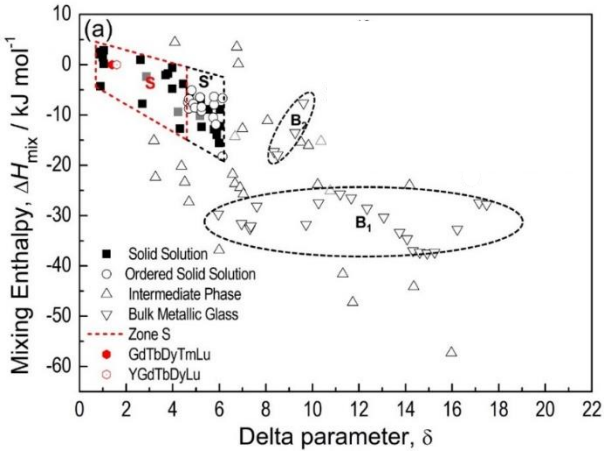
$$\kappa_1^{cr}(T) = 1 - \frac{T\Delta S_{mix}}{\Delta H_{mix}}(1 - \kappa_2) > \Delta H_{IM} / \Delta H_{mix}$$

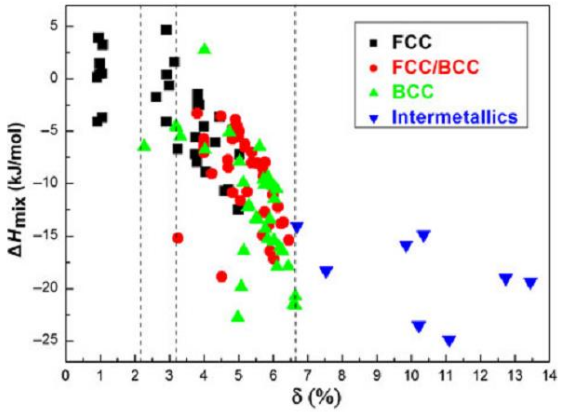
8. Elastic strain energy

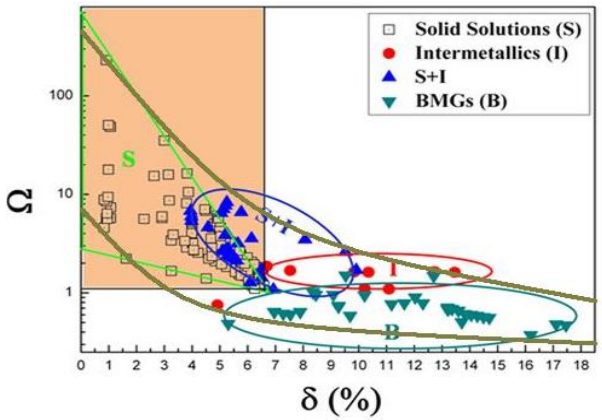
$$E_2 / E_0 = \sum_{j\geq i}^{N} \frac{c_i c_j \left|r_i + r_j - 2\bar{r}\right|^2}{4\left(\bar{r}\right)^2}$$

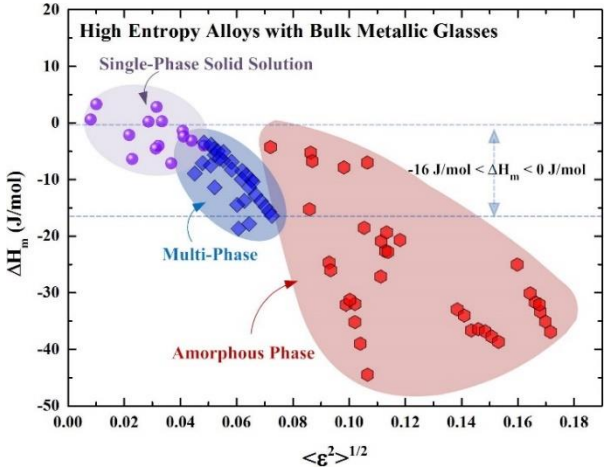
Disordered HEA Formation Rules

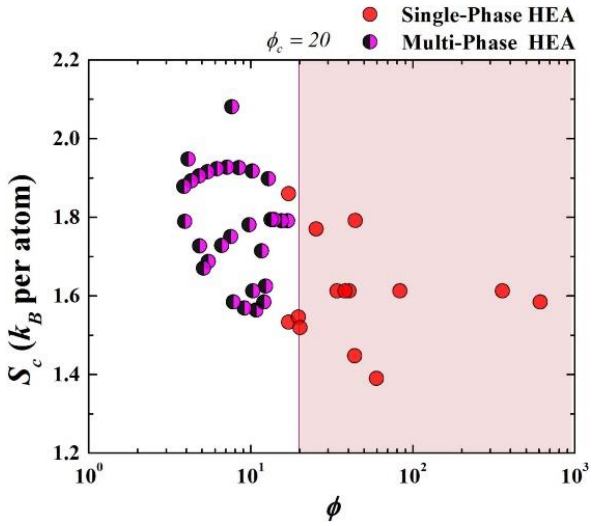
Literature review

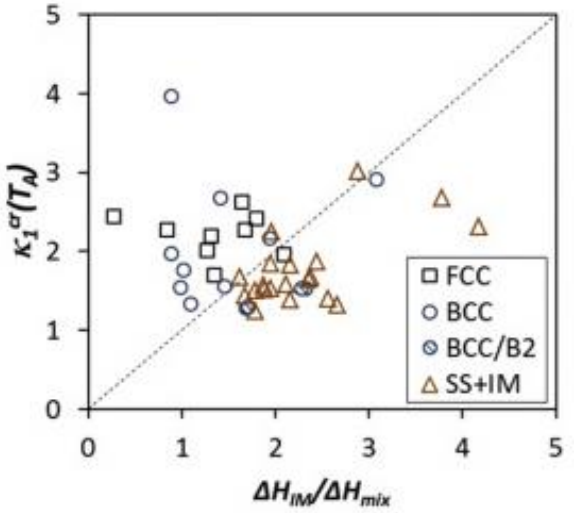




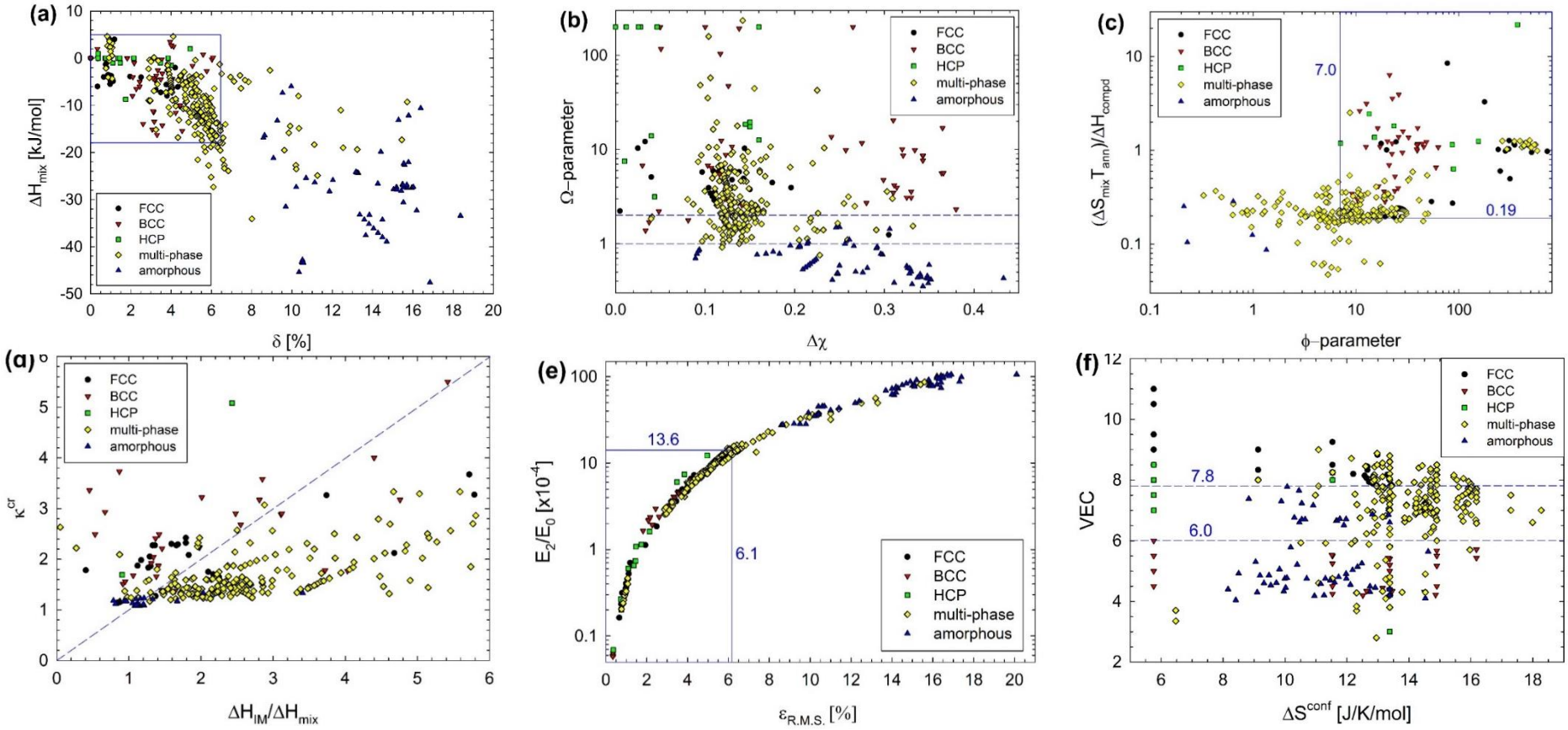








Reevaluate Disordered HEA Formation Rules



1) Most empirical thermo-physical parameters except $\Delta\chi$ are efficient in separating single-phase compositions from amorphous compositions, but they fail to separate single-phase compositions from multiphase compositions.
2) Considerable overlapping of single-phase compositions with multiphase compositions requires the development of new empirical parameters or methodologies that are stricter and more effective.

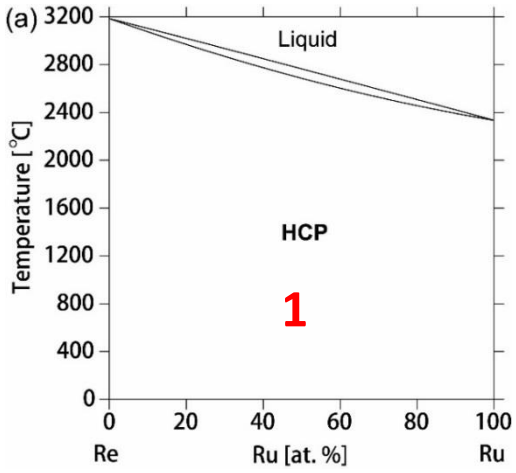
M.C. Gao, C. Zhang, P. Gao, F. Zhang, L.Z. Ouyang, M. Widom and J.A. Hawk, "Thermodynamics of Concentrated Solid Solution Alloys," Current Opinion of Solid State & Materials Science, 21 (2017) 238-251

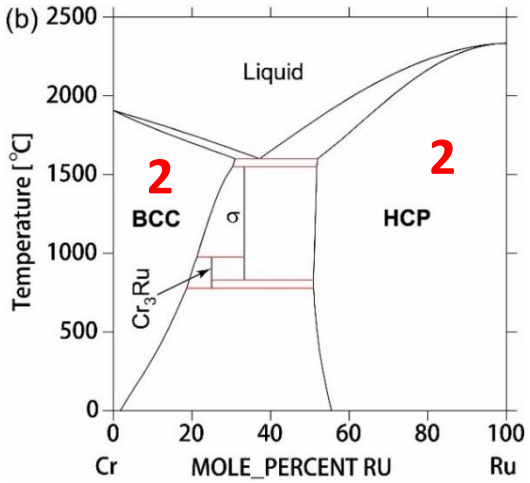
Our Searching Strategies

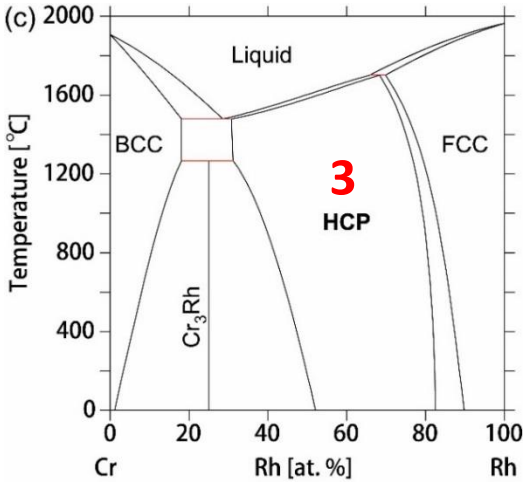
- **Inspection from existing binary/ternary phase diagrams**
  - Look for isomorphous or large solubility
- **Prediction from CALPHAD modeling**
  - The key is the database
- **Phase stability from density functional theory (DFT)**
- **Ab initio molecular dynamics (AIMD) simulations**
  - Avoid potent short-range order in the liquid
- **Experimental validations: casting and characterization**

Searching results

1. **Dy-Er-Gd-Ho-Lu-Sc-Sm-Tb-Tm-Y**
2. **Mo-Nb-Ta-Ti-V-W**
3. **Co-Os-Re-Ru**
4. **Ba-Ca-Eu-Sr-Yb**
5. **Co-Cr-Fe-Mn-Ni**
6. **Mo-Nb-Re-Ta-Ti-V-W**



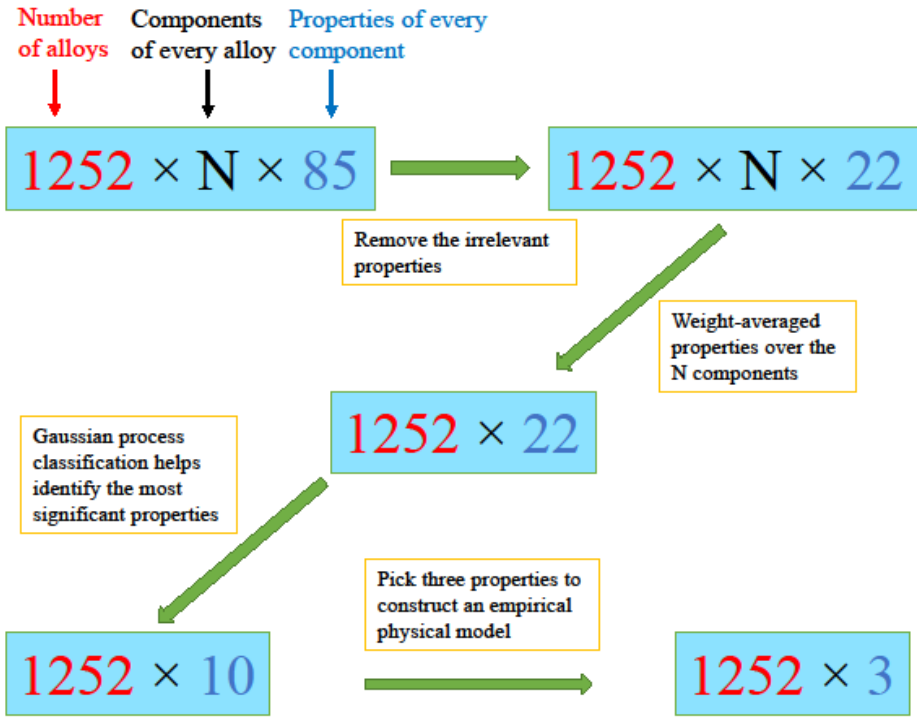


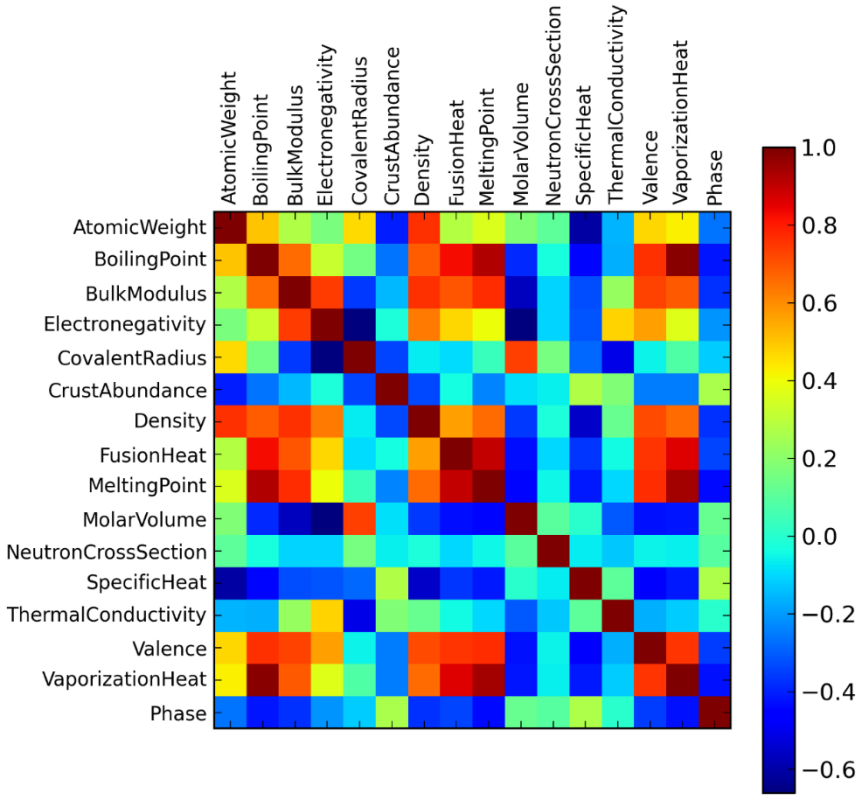


M.C. Gao, Chapter 11, "Design of High Entropy Alloys," High-Entropy Alloys: Fundamentals and Applications, eds. Gao, Yeh, Liaw, and Zhang, Springer, 2016.

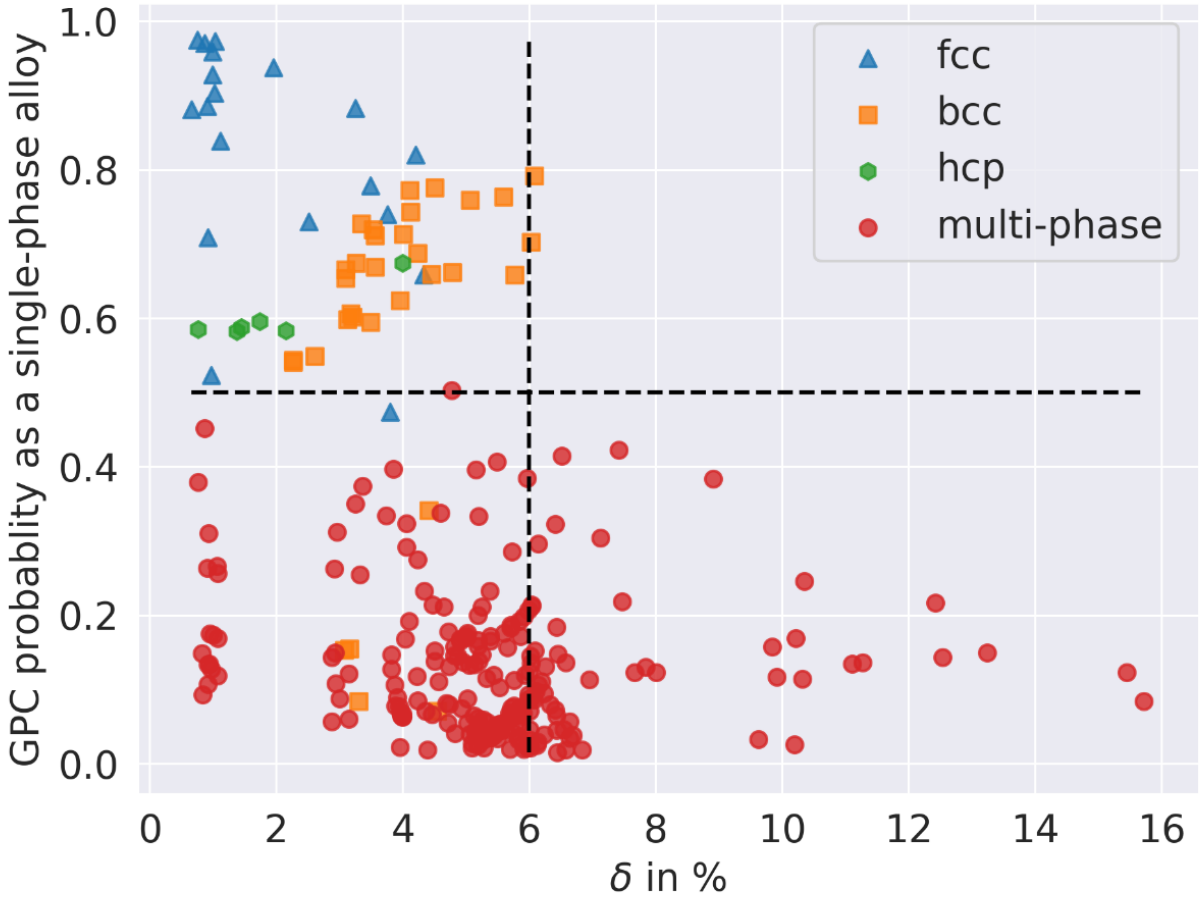
The machine-learning (ML) scenario

Gaussian Process Classification





ML prediction after learning half of 1252 multicomponent alloys



93% accuracy

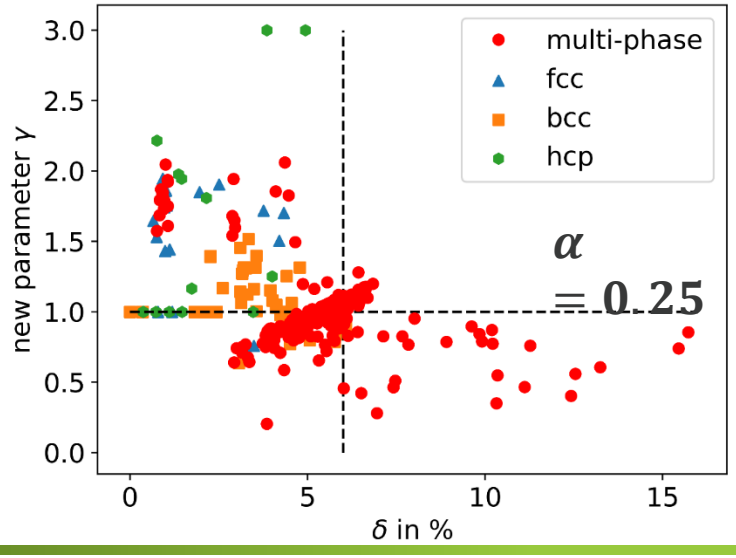
Z. Pei, J. Yin, J.A. Hawk, D.E. Alman, M.C. Gao, unpublished work, 2019

Propose a new rule based on ML

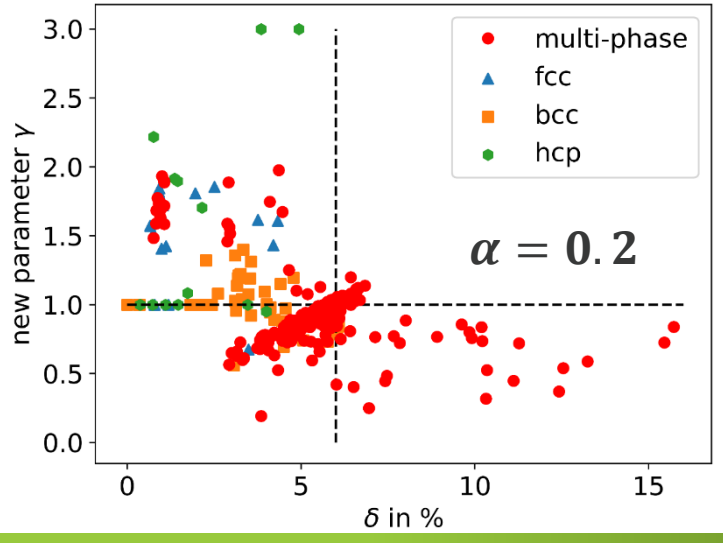
Three key quantities: bulk modulus, molar volume and melting temperature

- $\Delta G = \Delta H(< B >, < V >) - \alpha_1 < T_m > \alpha_2 S_{conf}$, $<>$ represents the average of a quantity;
- $$\gamma = \begin{cases} \dfrac{\Delta G_N}{\min(\Delta G_2)}, & \text{if } \min(\Delta G_2) < 0; \\ -\dfrac{\Delta G_N}{\min(\Delta G_2)}, & \text{if } \Delta G_N < 0 \text{ and } \min(\Delta G_2) > 0. \end{cases}$$
- New rule: $\gamma \geq 1$.

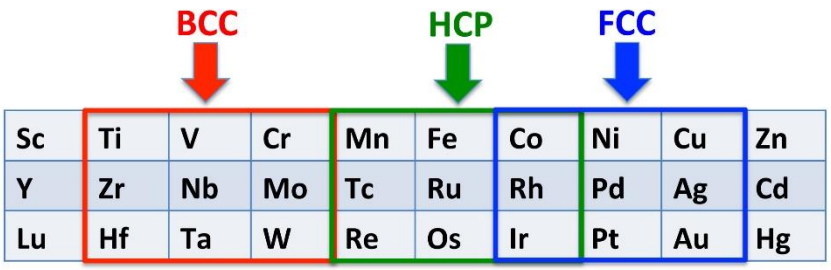
64% (75% jointly with delta parameter)



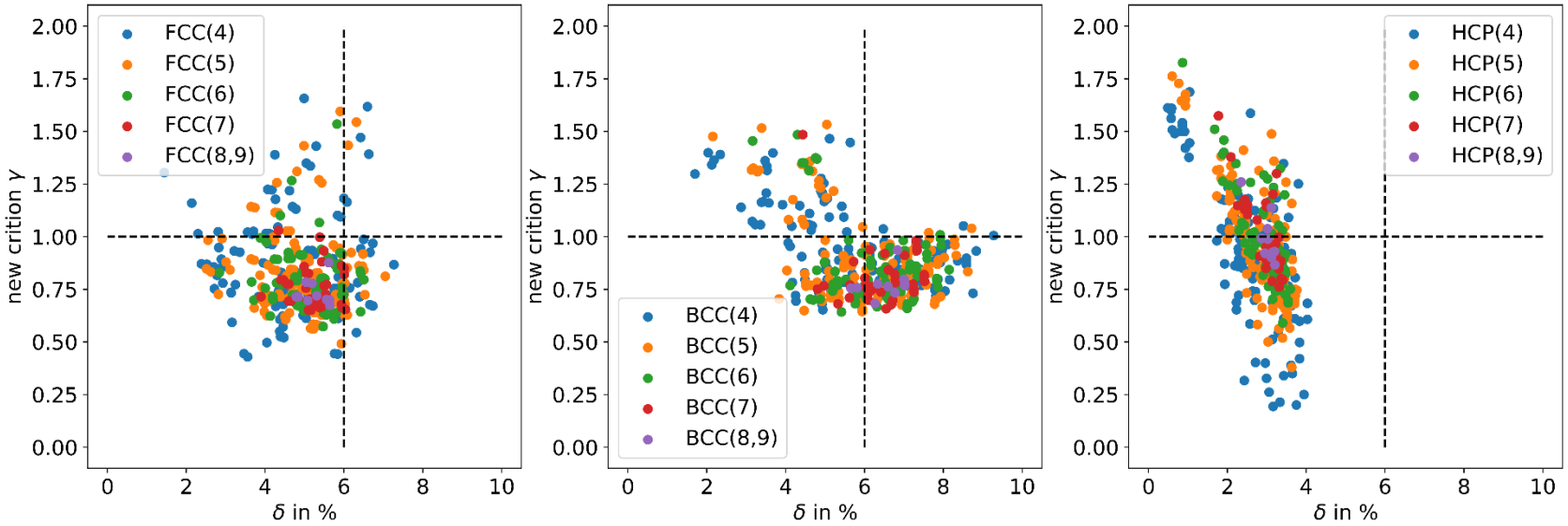
73% (81% jointly with delta parameter)



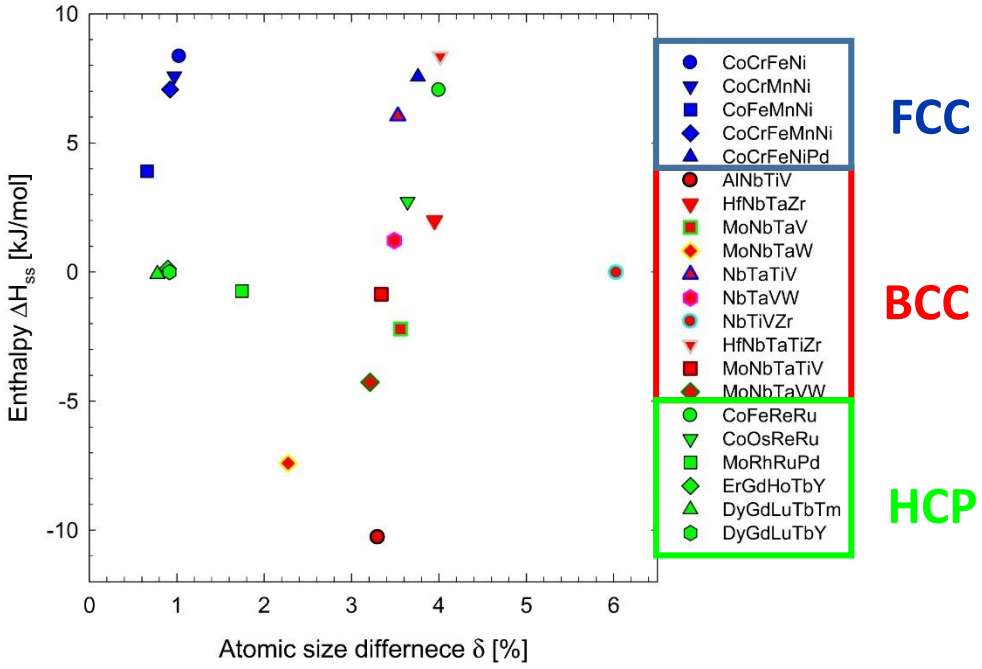
Application of the new rule



Group	new rule $\gamma \geq 1$	Calphad	consistency
FCC	5	5	100%
BCC	70	66	94%
HCP	1	0	0%
summary	76	71	94%



Z. Pei, J. Yin, J.A. Hawk, D.E. Alman, M.C. Gao, unpublished work, 2019



FCC

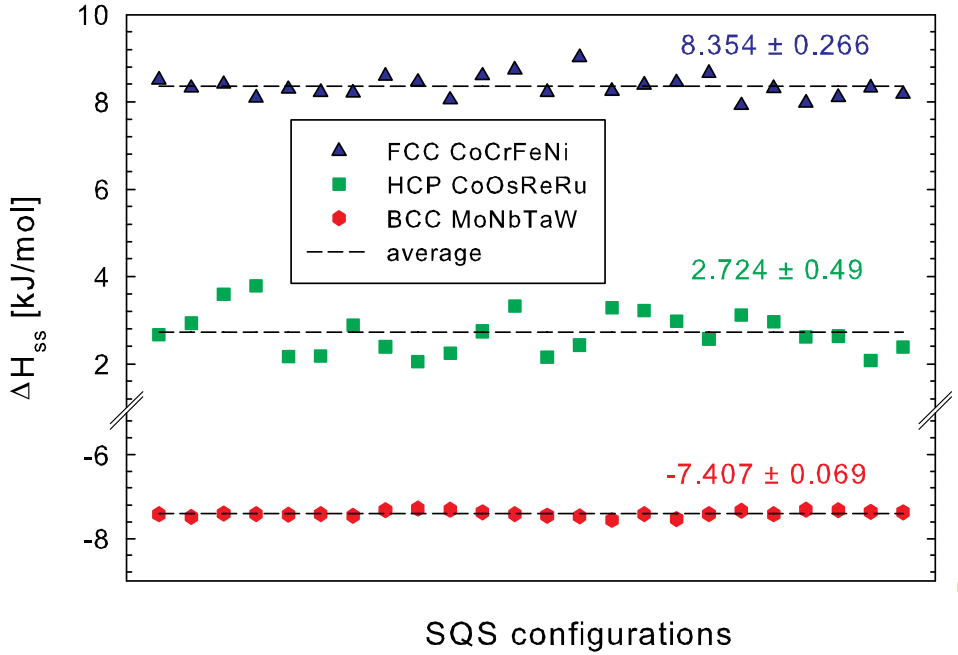
BCC

HCP

Enthalpy of Formation: DFT at T = 0 K

Top: Enthalpy of formation vs atomic size difference for reported single-phase HEAs with FCC, BCC and HCP structures.

Bottom: Enthalpy of formation as a function of atomic configurations of the quaternary FCC CoCrFeNi, BCC MoNbTaW and HCP CoOsReRu SQS.



Gao MC , Gao P, Hawk JA, Ouyang LZ, Alman DE, and Widom M, "Computational Modeling of High-Entropy Alloys: Structures, Thermodynamics and Elasticity", J. Mater. Res., 32 (2017) 3627-3641.

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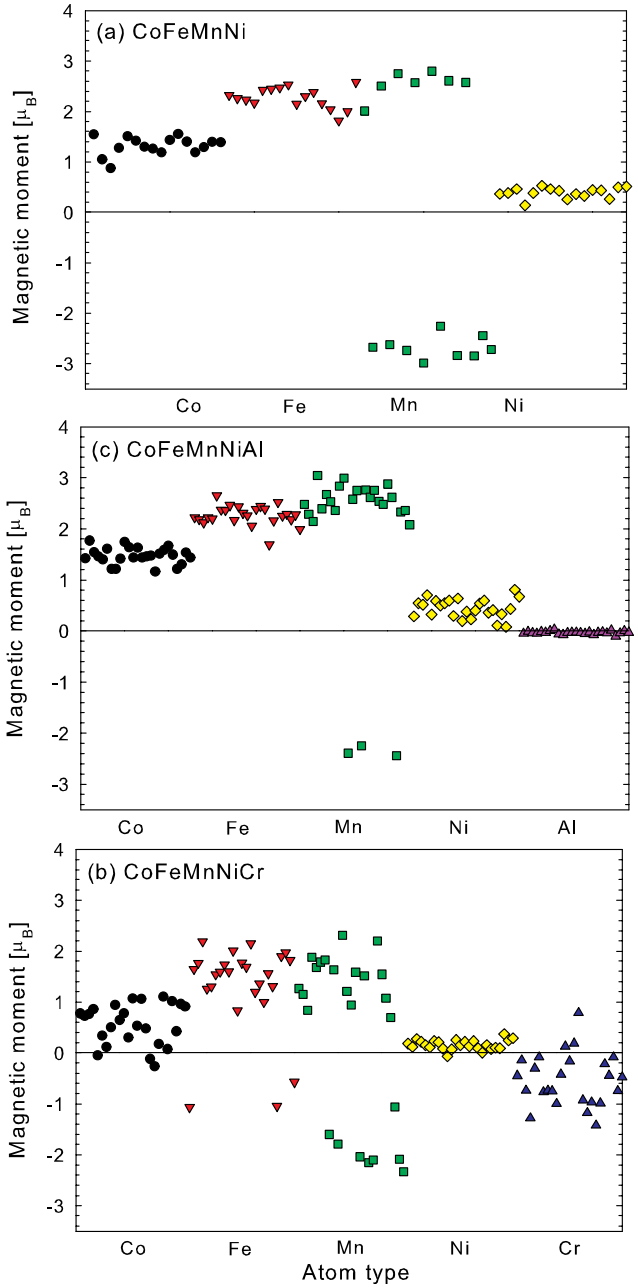
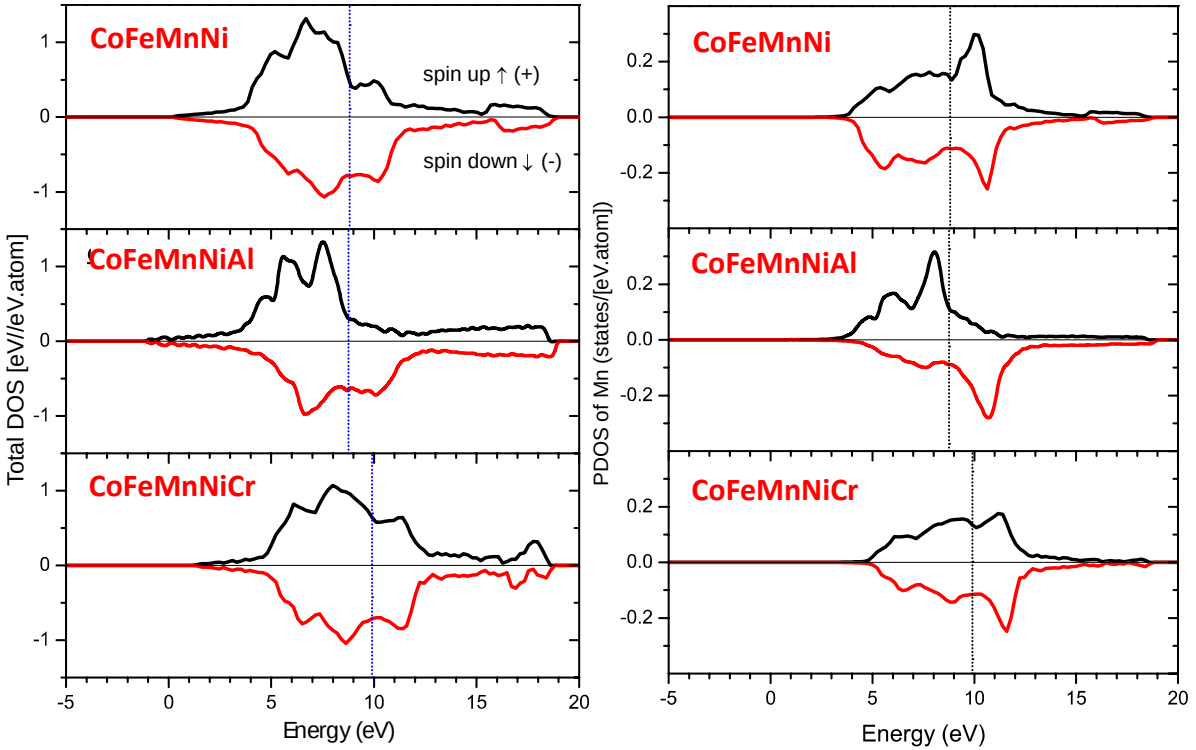
Magnetic Properties: CoFeMnNi-(Cr,Al)

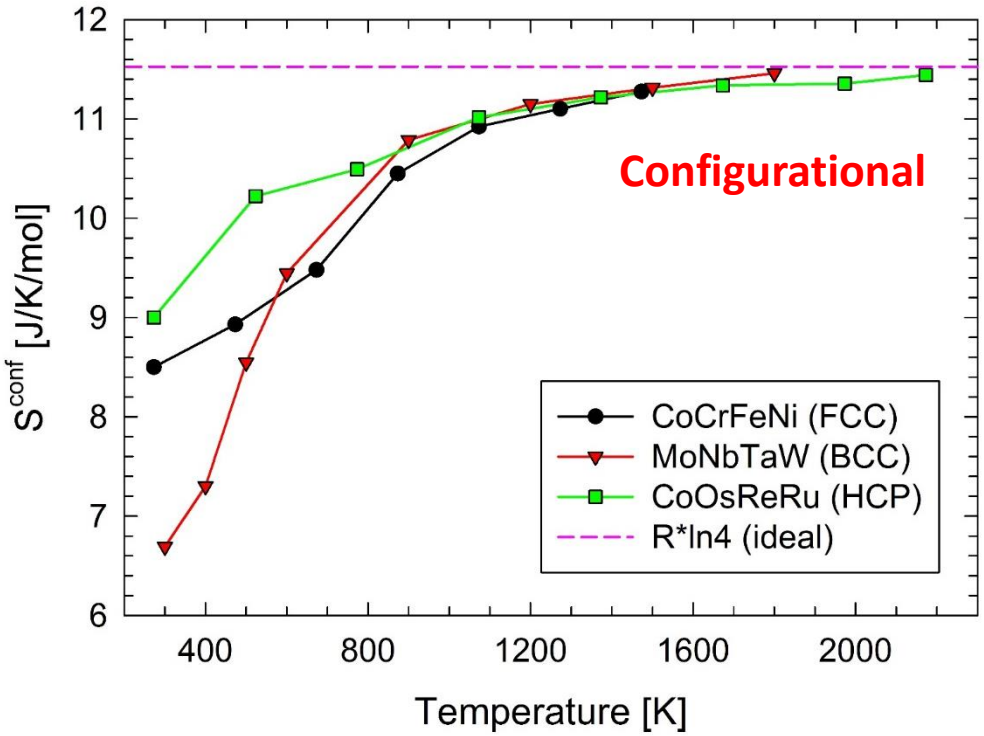


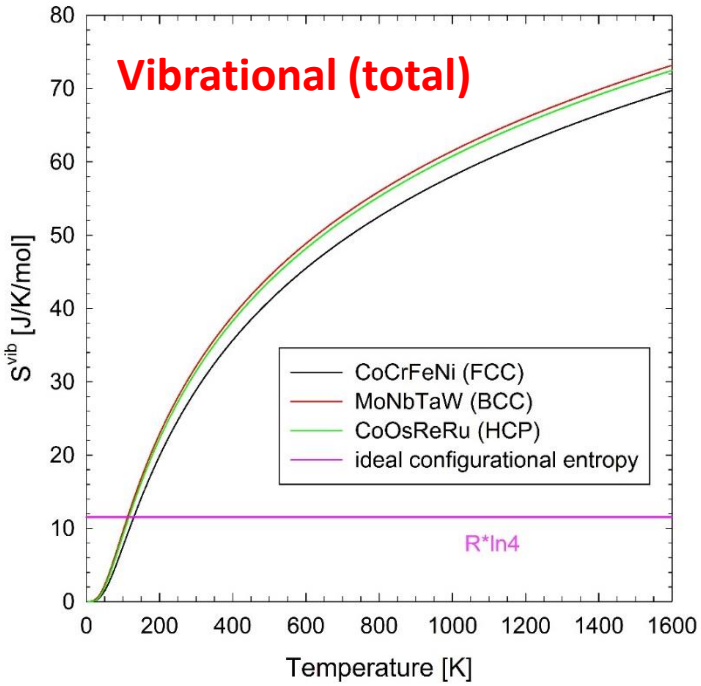


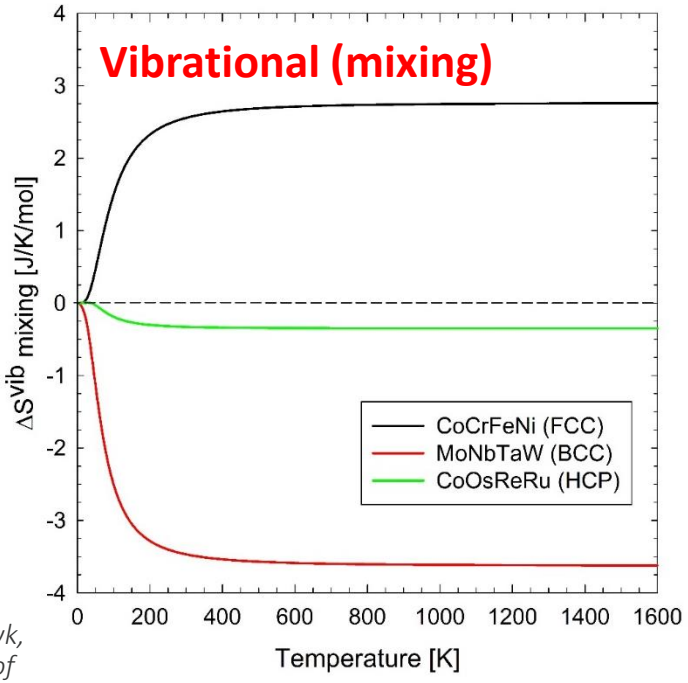
1) Antiferromagnetism of Mn atoms in CoFeMnNi is suppressed especially in BCC CoFeMnNiAl
2) Al changes the structure from FCC to BCC
3) Al changes the Fermi level and itinerant electron-spin coupling

Zuo TT, Gao MC, Ouyang LZ, Yang X, Cheng YQ, Zhao WL, Xia SQ, Feng R, Chen SY, Liaw PK, Hawk JA, and Zhang Y, "Structural and Magnetic Behaviors of CoFeMnNiX (X = Al, Ga, and Sn) High Entropy Alloys," Acta Mater., 130 (2017) 10-18

Configurational and Vibrational Entropies







- Total vibrational entropy is large and increases with increasing temperature.
- Vibrational entropy of mixing can be positive or negative.
- The magnitude of vibrational entropy is smaller than configurational entropy.
- Electronic entropy is negligible.

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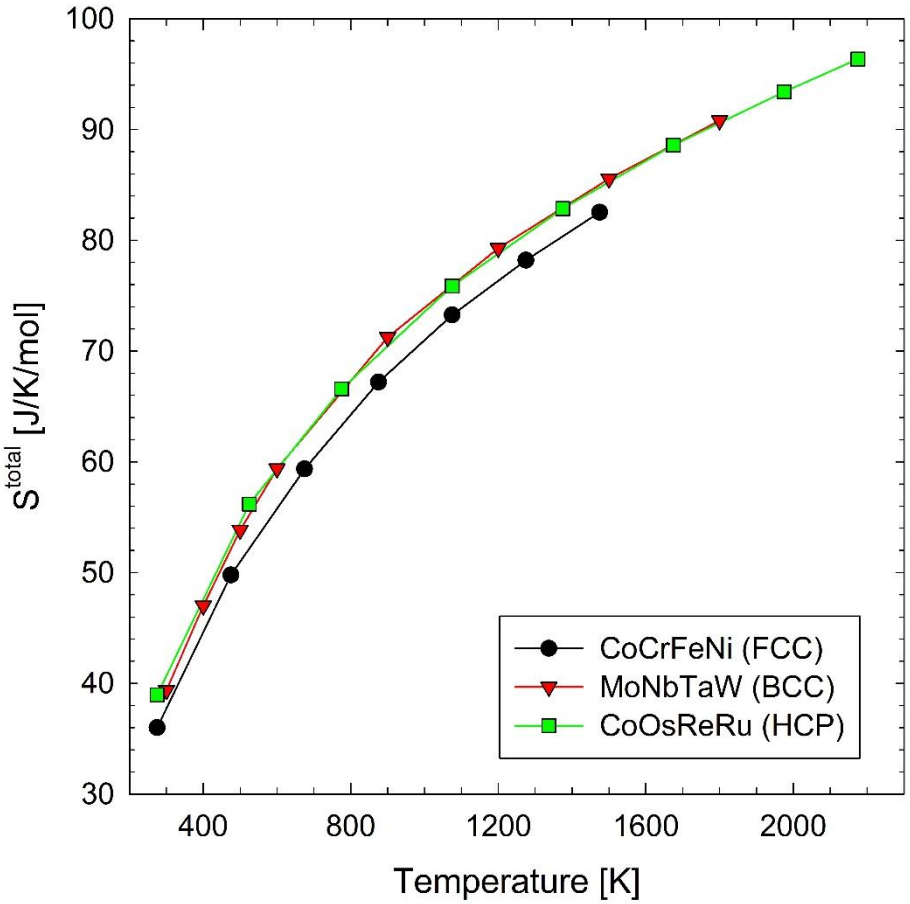
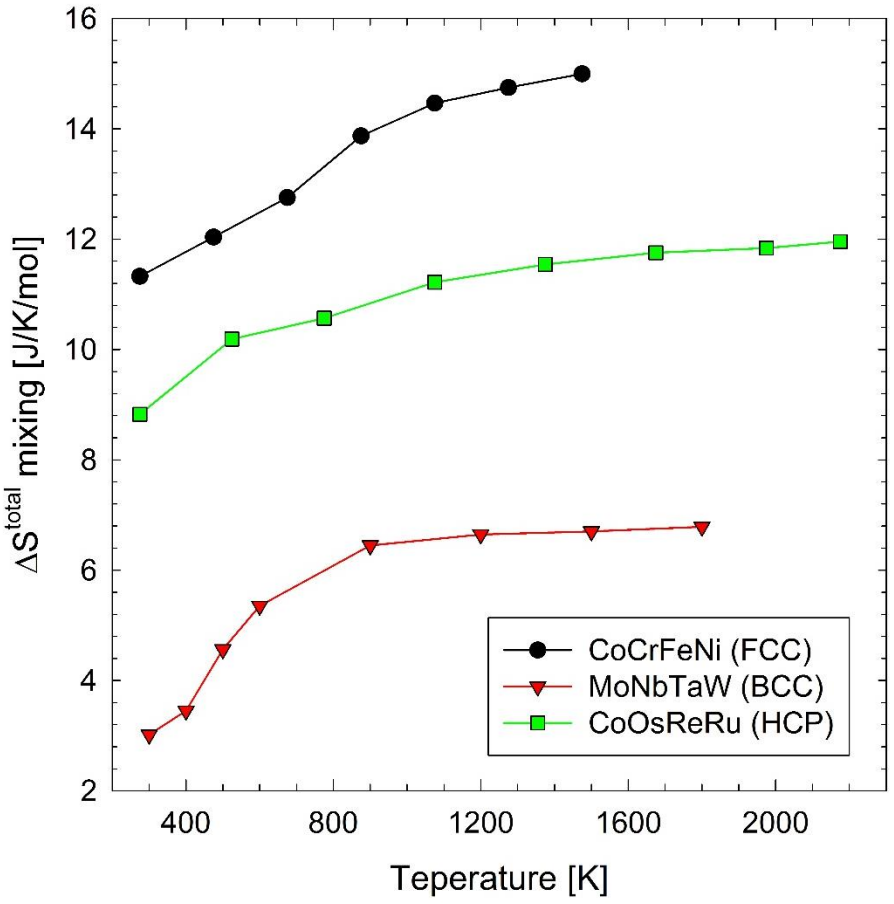
Total Entropy Properties

Total vs mixing

Total entropy



Total entropy of mixing



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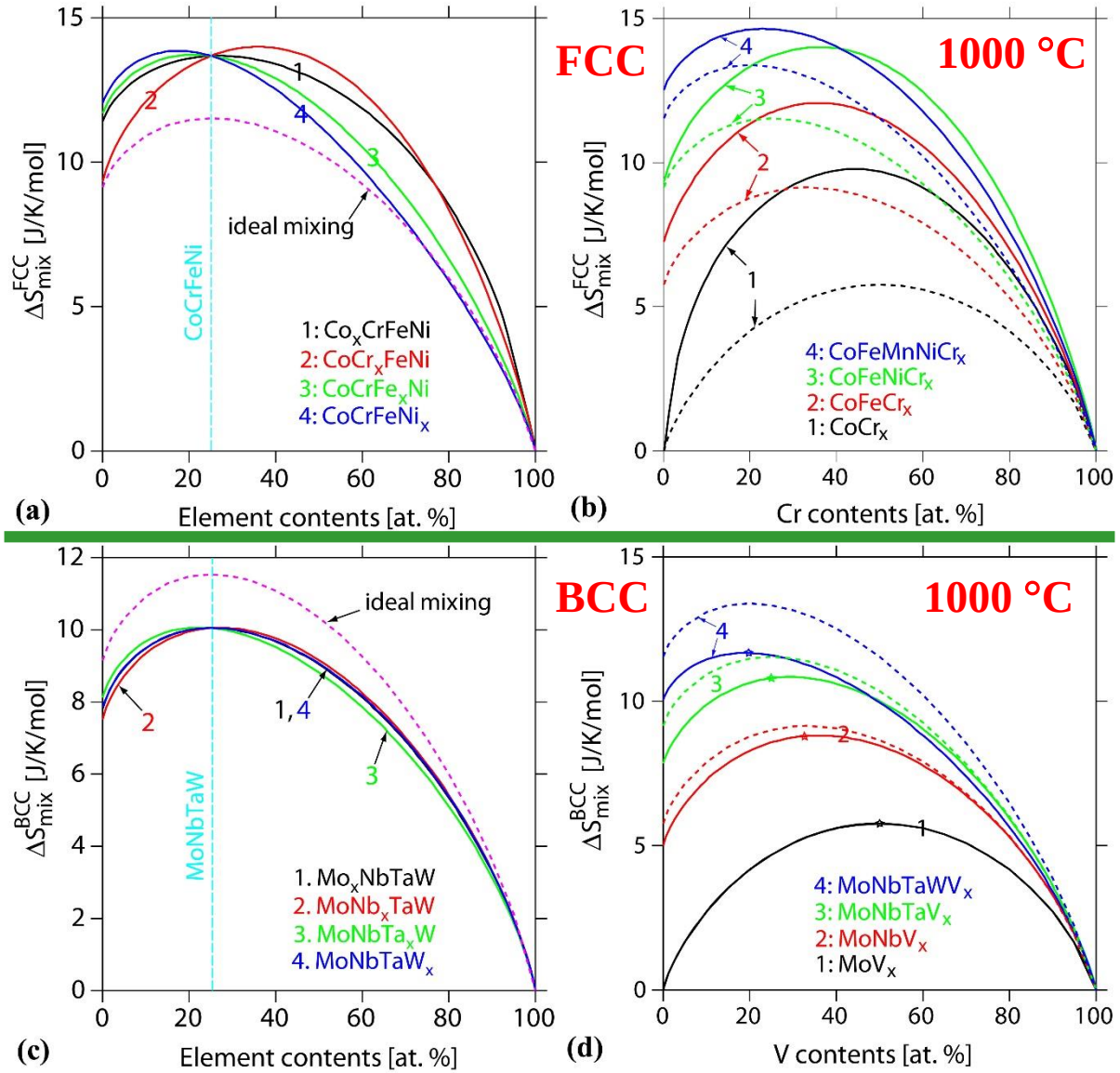
Excess Entropy: CALPHAD Modeling

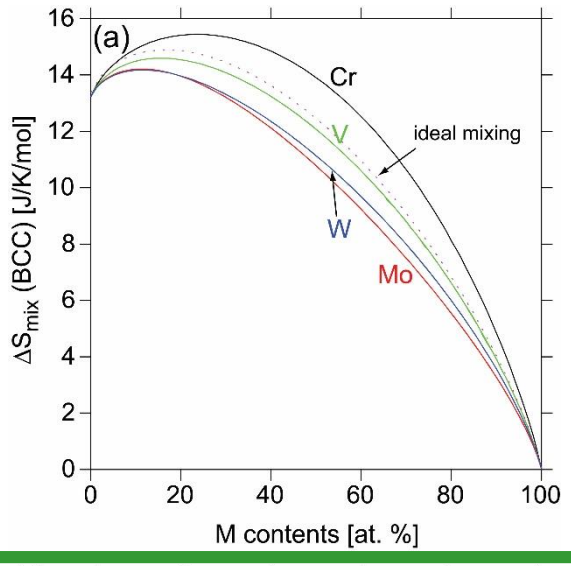


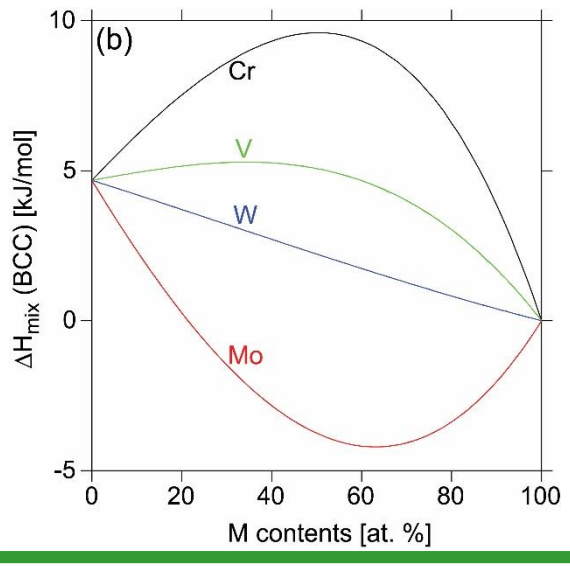
$$^{ex}S^{\varphi} = {}^{total}S^{\varphi} + R\sum_i x_i \ln x_i$$

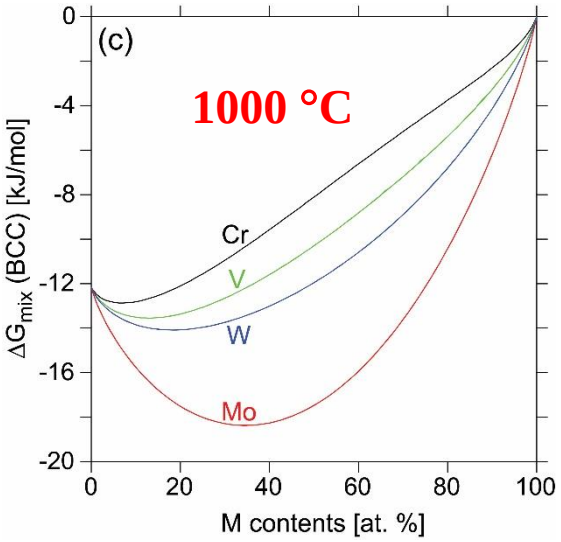
- Positive excess entropy in FCC phase in Co-Cr-Fe-Mn-Ni system, which may result from positive vibrational entropy of mixing.
- Negative excess entropy in BCC phase in Mo-Nb-Ta-Ti-V-W system, which may result from negative vibrational entropy of mixing.
- Maximum entropy of mixing may deviate from equimolar compositions.

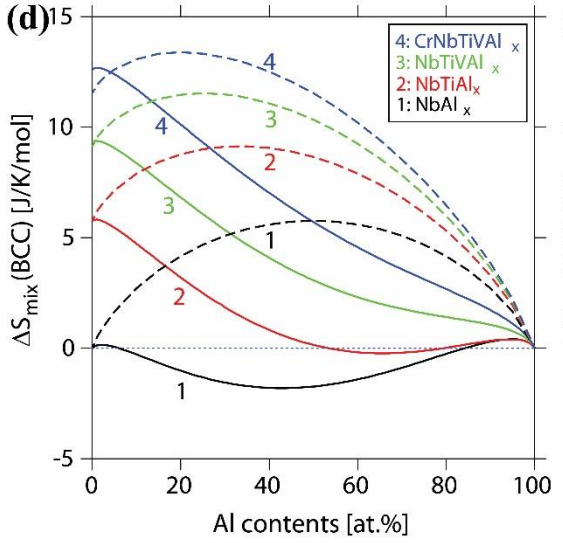
Gao MC , Gao P, Hawk JA, Ouyang LZ, Alman DE, and Widom M, "Computational Modeling of High-Entropy Alloys: Structures, Thermodynamics and Elasticity", J. Mater. Res., 32 (2017) 3627-3641.

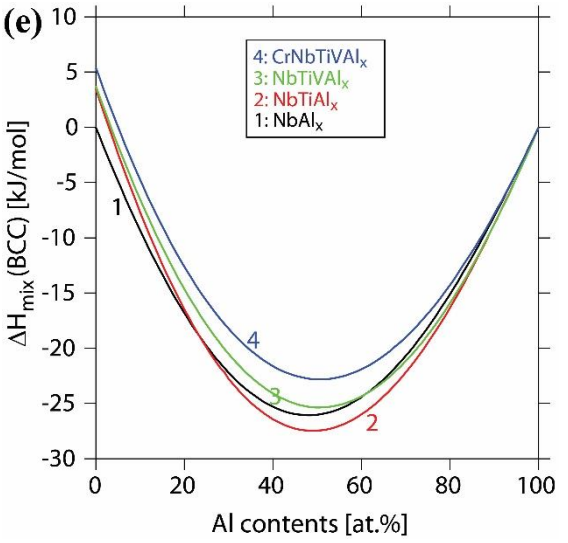
CALPHAD: Entropy vs Enthalpy

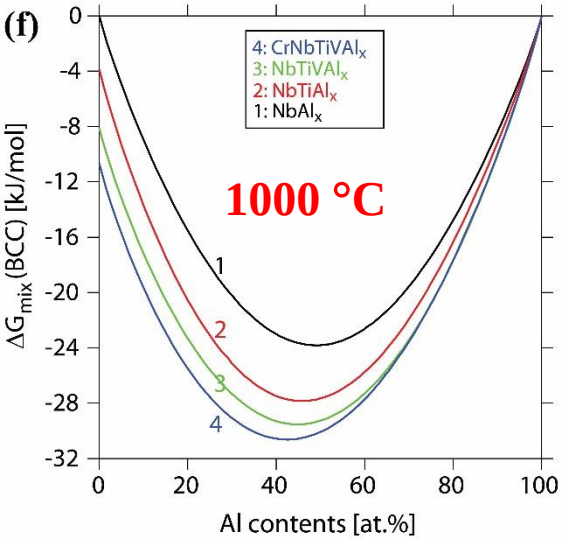






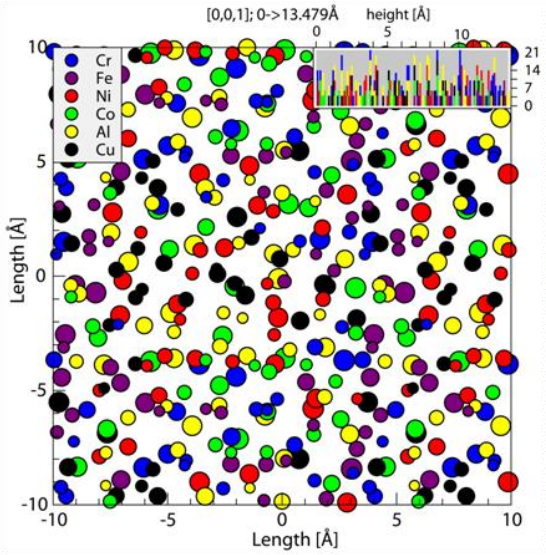


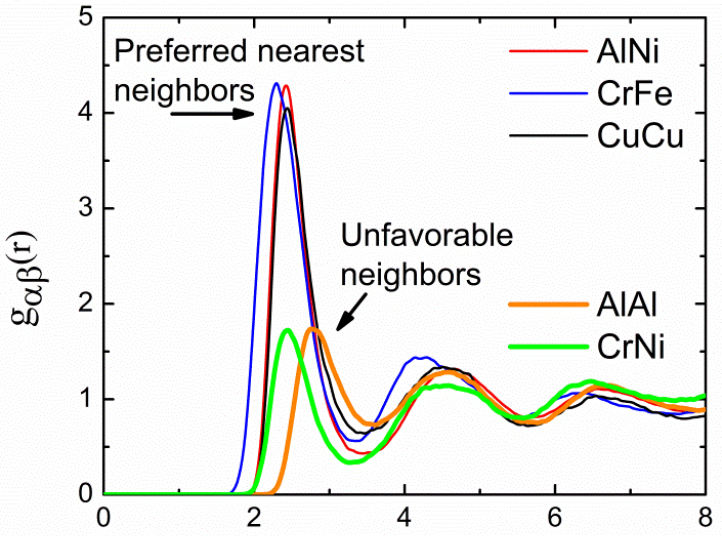




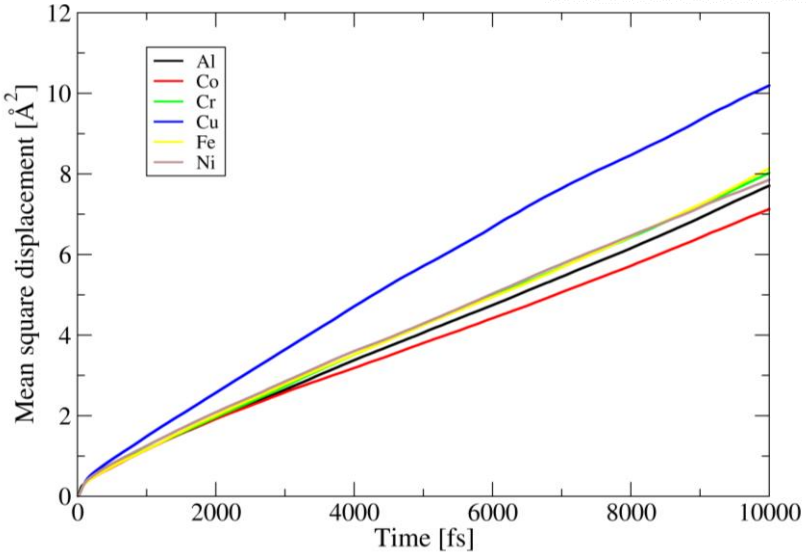
Gao et al., "Design of Refractory High-Entropy Alloys", JOM, 67 (2015) 2653. Rui et al., "Design of Light-Weight High-Entropy Alloys," Entropy 18 (2016) 333

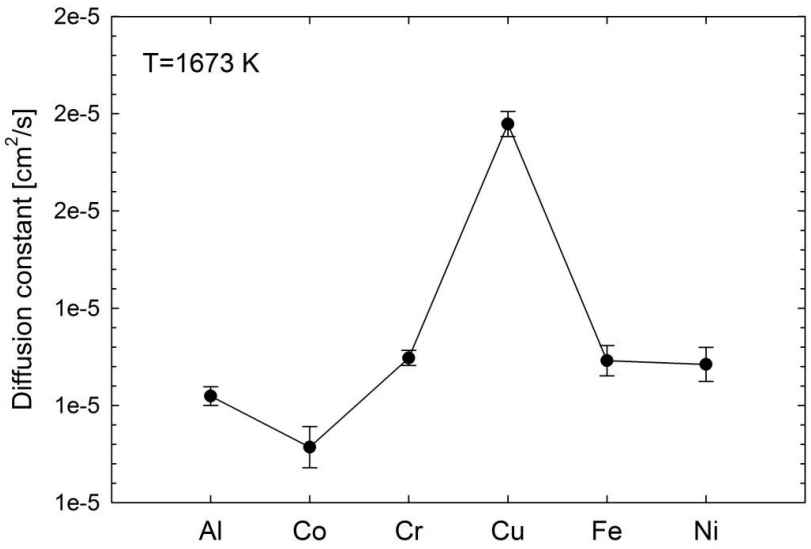
$Al_{1.25}CoCrCuFeMnNi$: AIMD





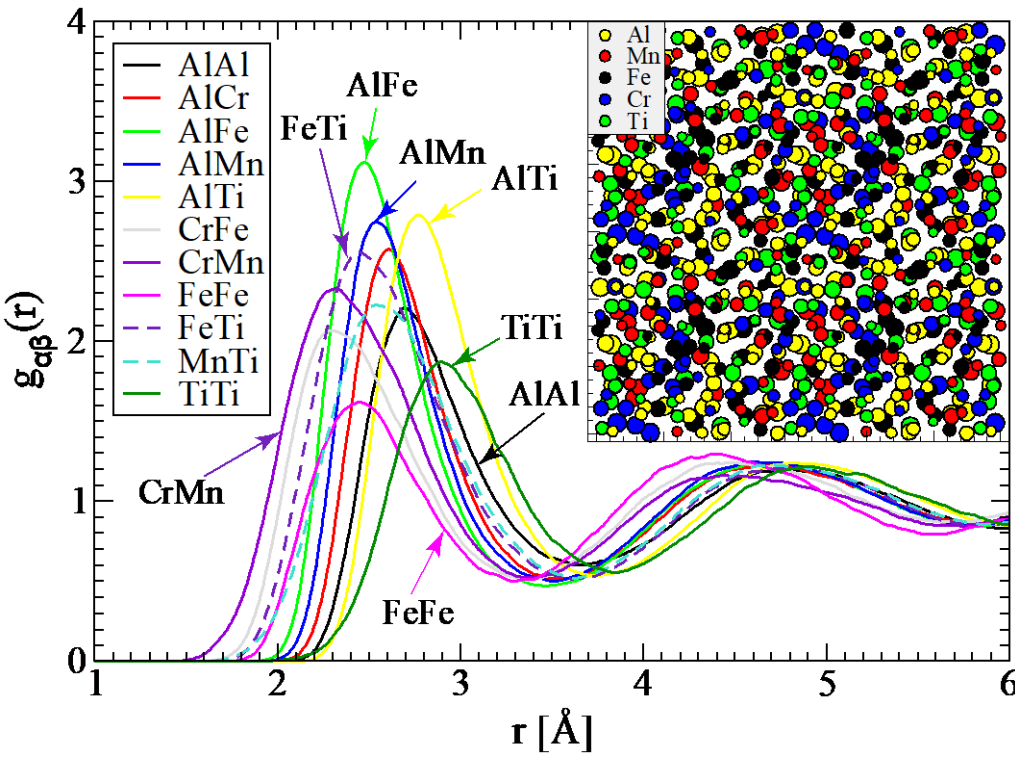
- Cu segregation exists in liquid.
- Cu has the fastest diffusion constant.
- Formation of Cu-rich FCC phase during solidification.

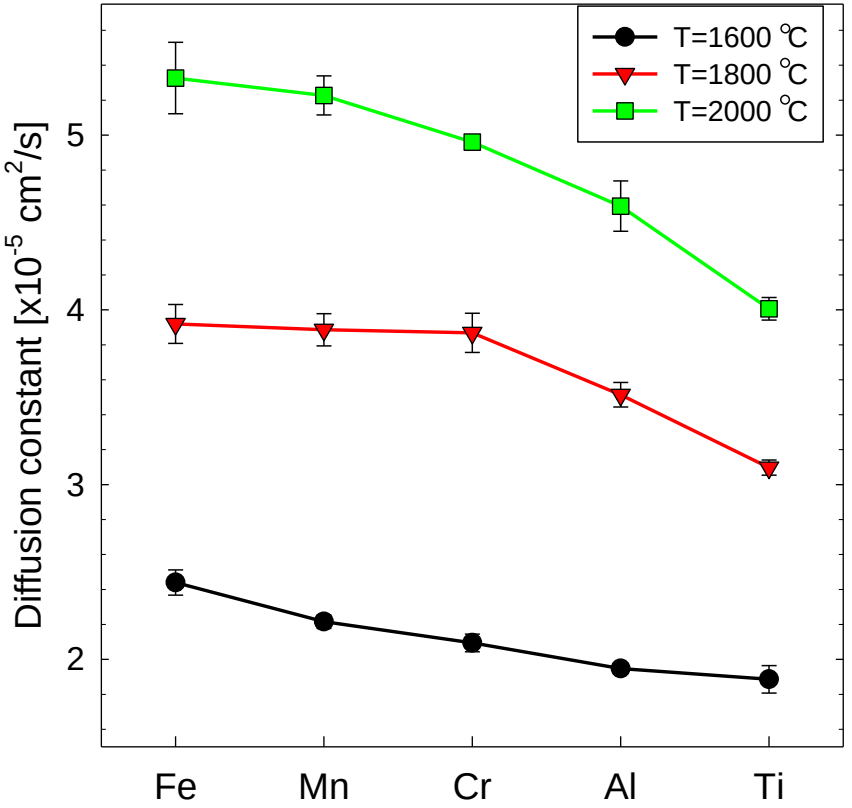




L.J. Santodonato, Y. Zhang, M. Feygenson, C. Parish, M.C. Gao, J.K.R. Weber, J.C. Neuefeind, Z. Tang, and P.K. Liaw, Nature Communication 6 (2015) 5964.

AIMD: $Al_{1.5}CrFeMnTi$ at 2073 K





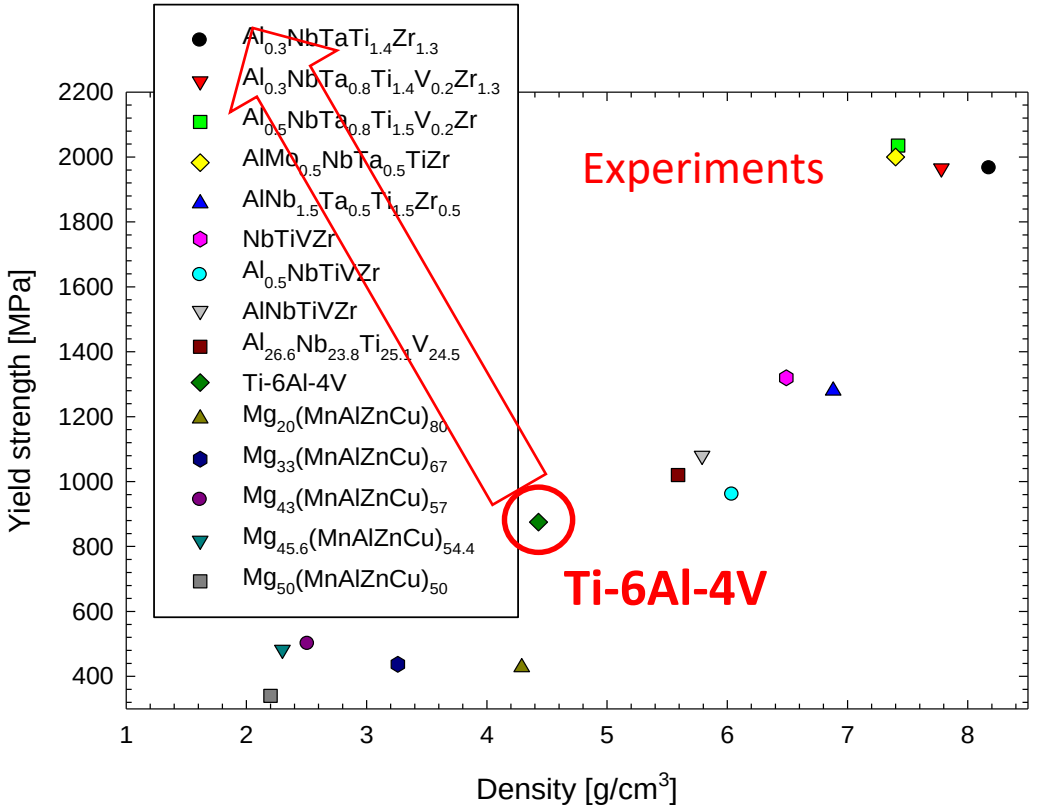
- Preferred correlations are AlFe, AlMn, AlTi, and FeTi pairs.
- Unfavorable correlations are FeFe, AlAl and TiTi pairs.

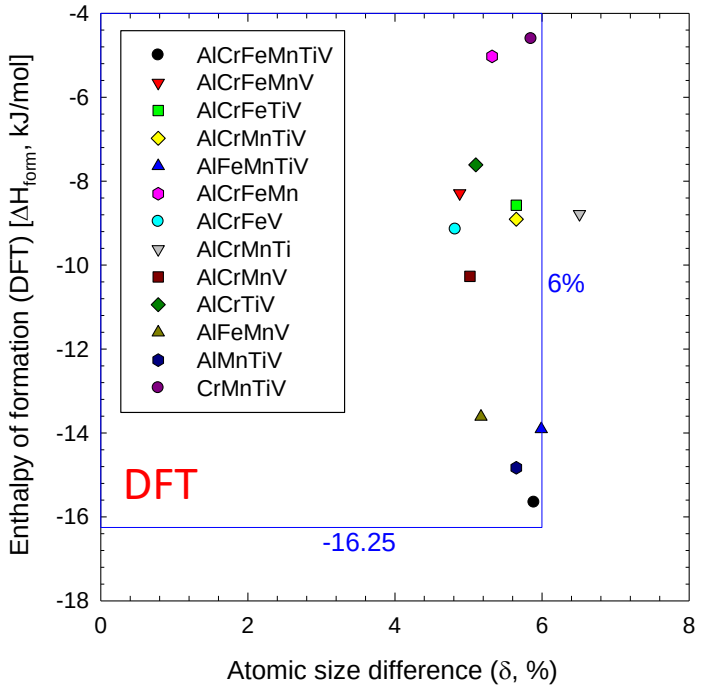
- Fe diffuses the fastest and Ti diffuses the slowest.
- Diffusivity follows the Arrhenius behavior.

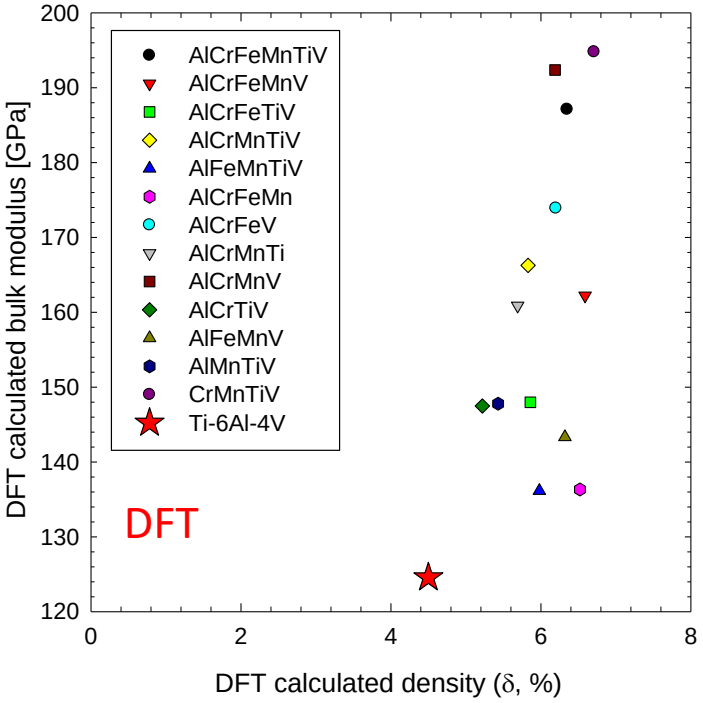
Feng R, Gao MC, Zhang C, Poplawsky JD, Guo W, Zhang F, Hawk JA, Neuefeind JC, Ren Y, and Liaw PK, "Phase Stability and Transformation in a Light-weight High-entropy Alloy," Acta Mater. 146 (2018) 280-293

Enthalpy and Bulk Modulus

DFT calculations: Al-Cr-Fe-Mn-Ti-V system







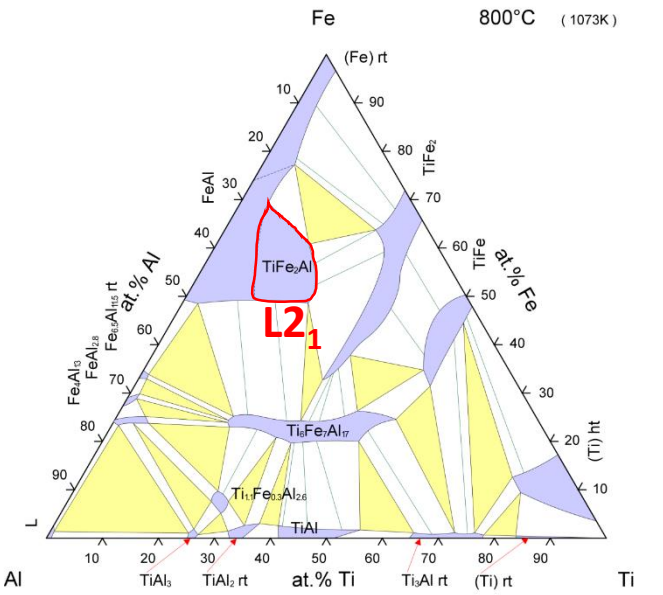
DFT predicts: strong attractive interaction and very negative enthalpy of formation and significantly larger bulk modulus than Ti-6Al-4V.

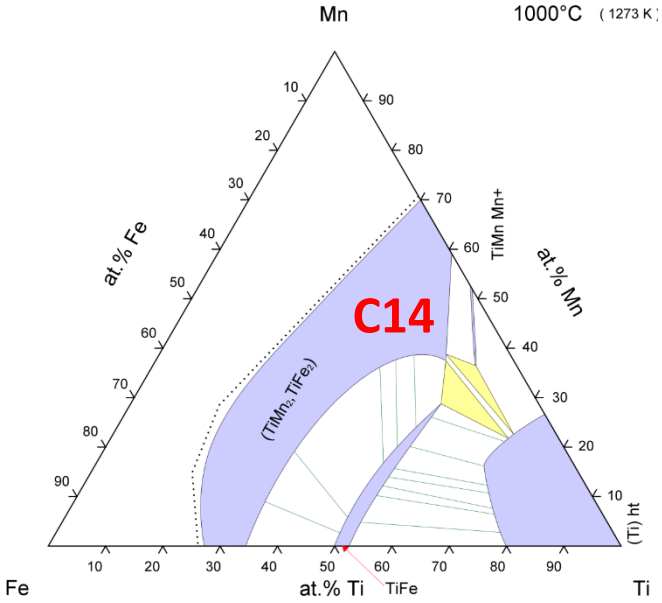
U.S. DEPARTMENT OF ENERGY

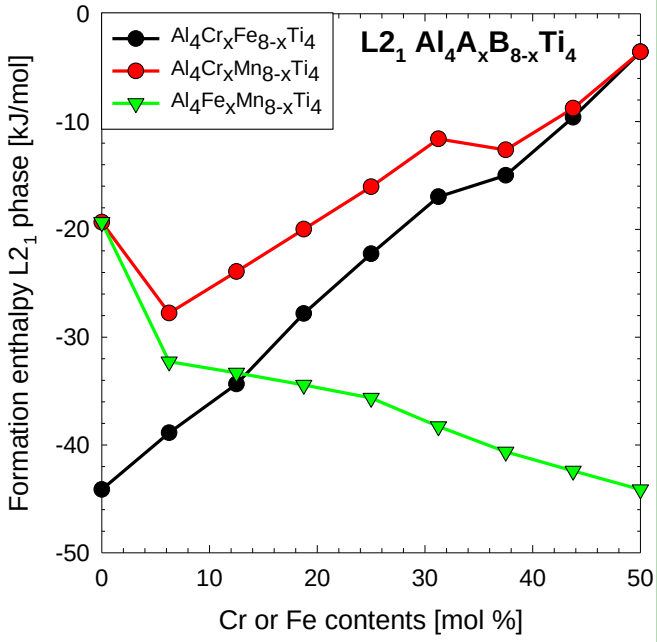
Gao MC, Hawk JA, and Alman DE, "High performance light-weight high-entropy alloys", US Non-provisional Patent Application No. 62/108566, filed on June 9, 2015

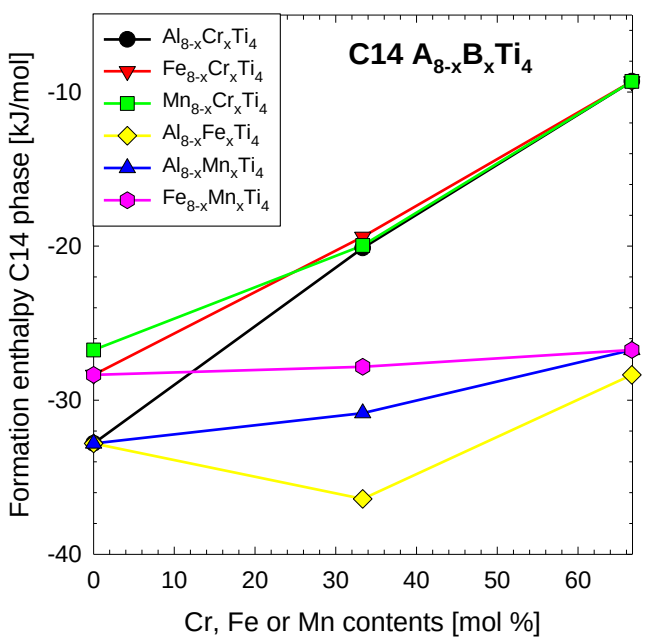
Enthalpy of Formation: $L2_1$ and C14

Al-Cr-Fe-Mn-Ti system: DFT calculations







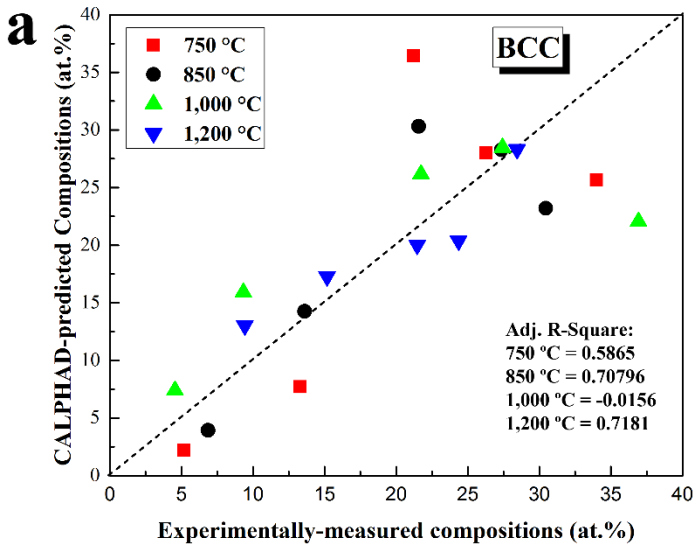


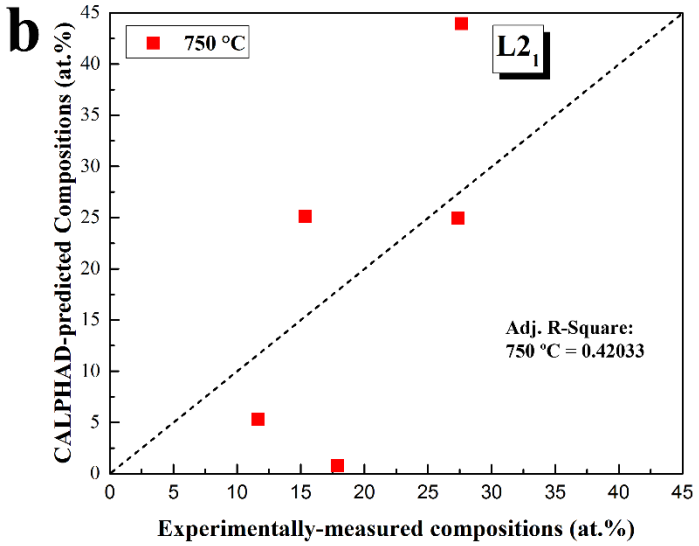
$L2_1$: Substitution in $AlFe_2Ti$ $L2_1$ increases the enthalpy

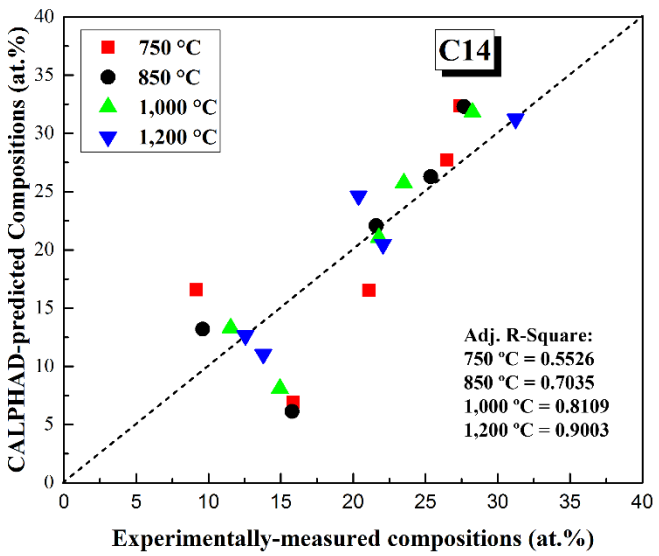
C14: $(AlFe)_2Ti$ has the lowest enthalpy; Al_2Ti has lower enthalpy than Fe_2Ti and Mn_2Ti

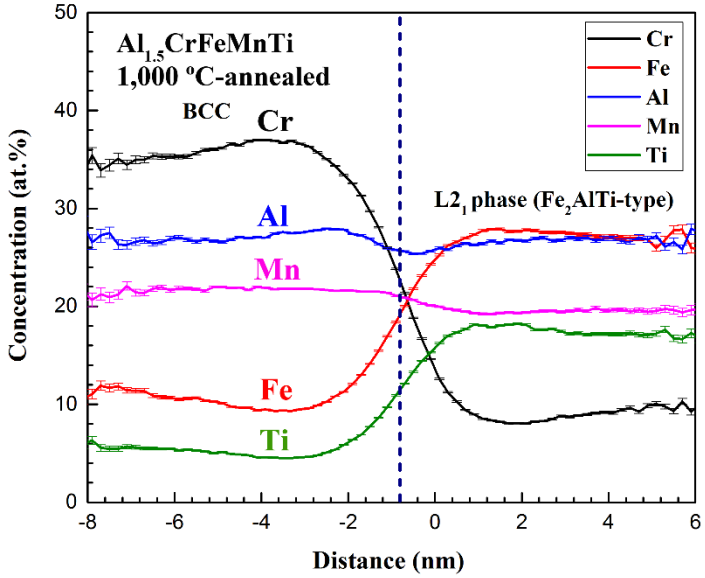
Feng R, Gao MC, Zhang C, Poplawsky JD, Guo W, Zhang F, Hawk JA, Neuefeind JC, Ren Y, and Liaw PK, "Phase Stability and Transformation in a Light-weight High-entropy Alloy," Acta Mater. 146 (2018) 280-293

Al-Cr-Fe-Mn-Ti: Phase Compositions



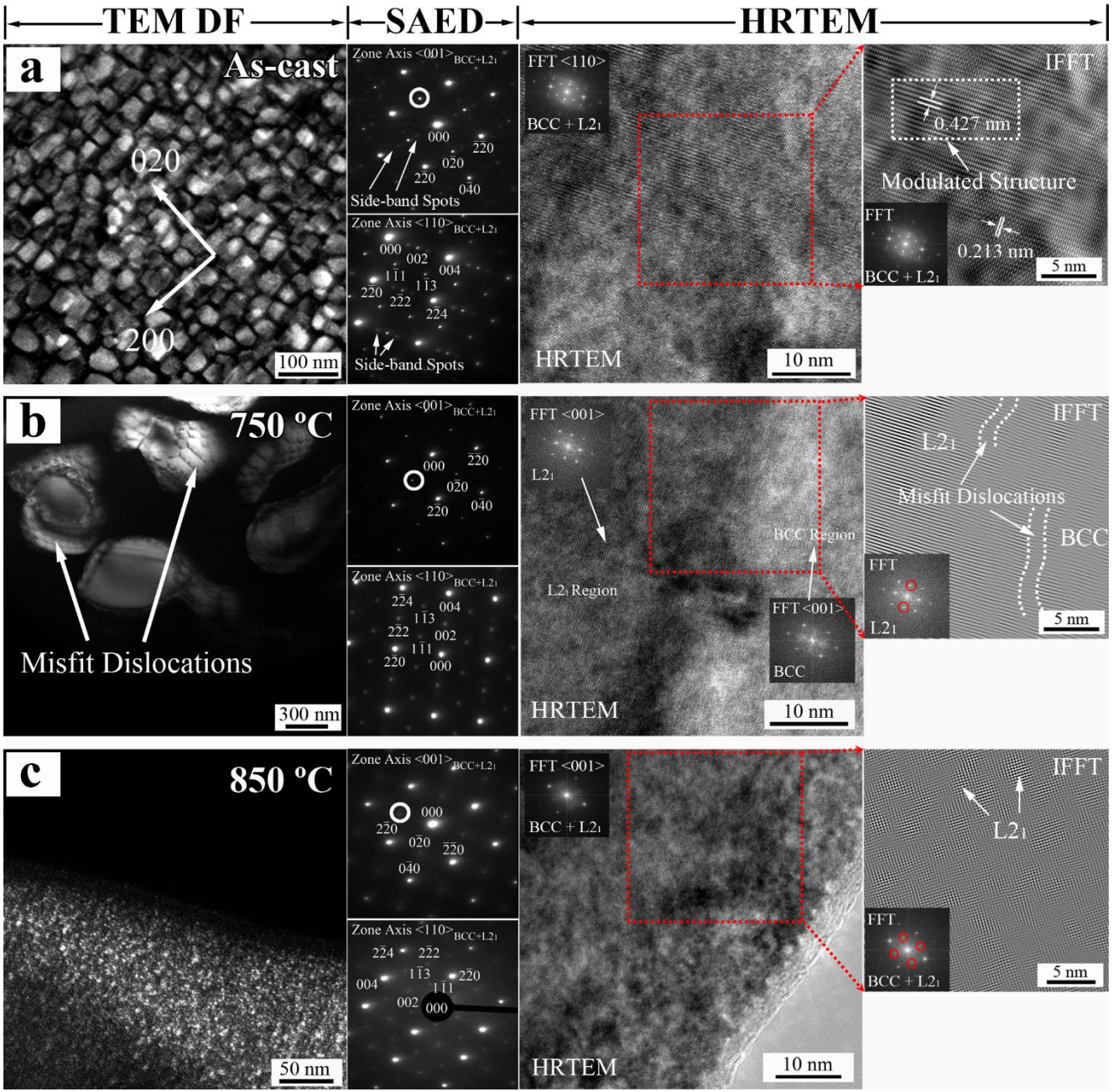






- BCC is rich in Cr.
- $L2_1$ is rich in Fe and Ti.
- C14 is rich in Ti and Fe.
- Agreement is acceptable between CALPHAD and experiments.

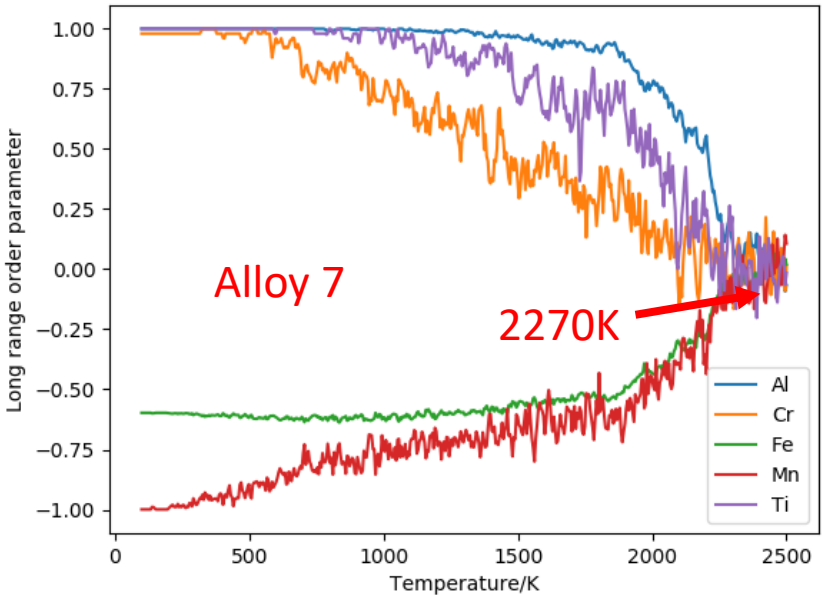
Feng R, Gao MC, Zhang C, Poplawsky JD, Guo W, Zhang F, Hawk JA, Neuefeind JC, Ren Y, and Liaw PK, "Phase Stability and Transformation in a Light-weight High-entropy Alloy," Acta Mater. 146 (2018) 280-293

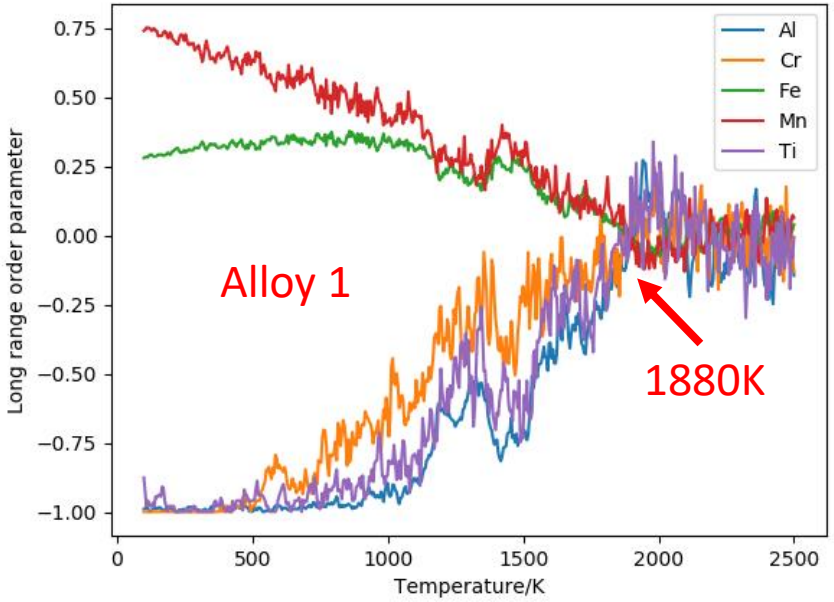


Precipitation of $L2_1$ Phase in $Al_{1.5}CrFeMnTi$

The size, shape, coherency, and spatial distribution of the $L2_1$ precipitates can be tuned through selected annealing treatments.

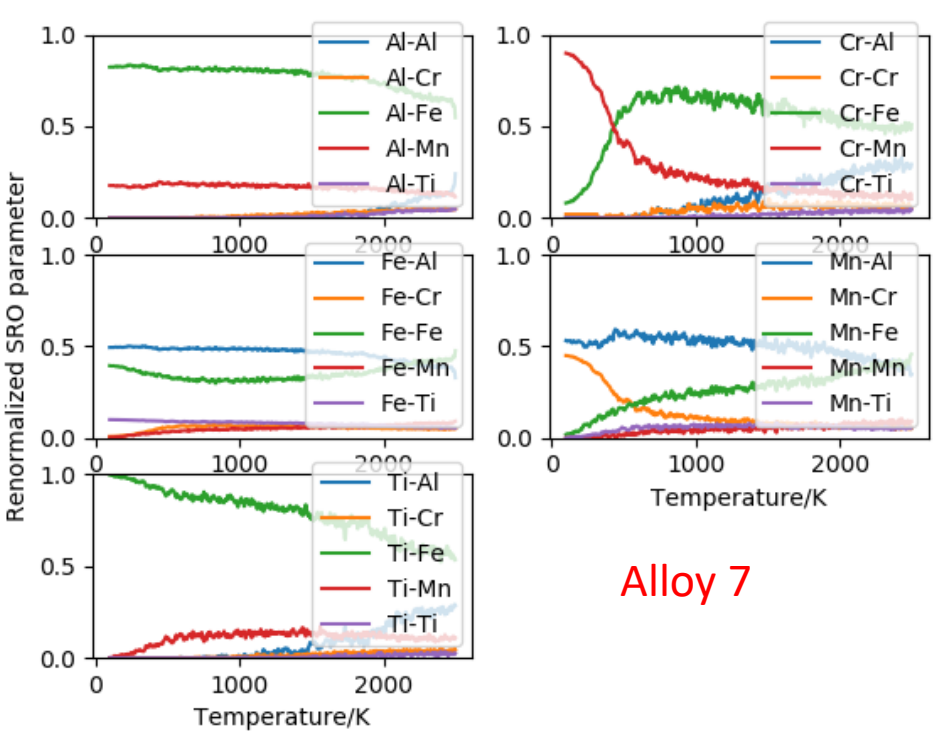
For alloy 7, the situation is similar except that the order-disorder transition takes place much later, ~2270K. The occupation of Fe, Al, Ti do not change until the temperature arrives at 1800K; so the LRO parameters of Cr and Mn changes in opposite directions.



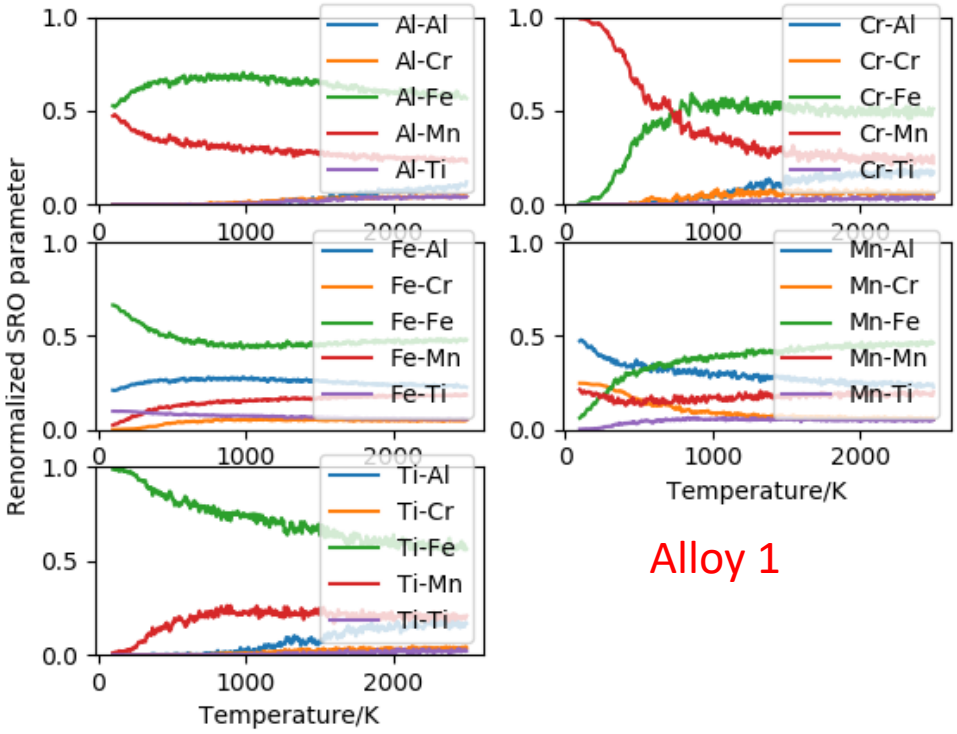


Z. Pei, J.A. Hawk, M.C. Gao, unpublished work, 2019

The renormalized SRO parameters for alloy7, which is similar to alloy 1 in trends. But the maximum changes take place at different temperatures due to the different concentrations.



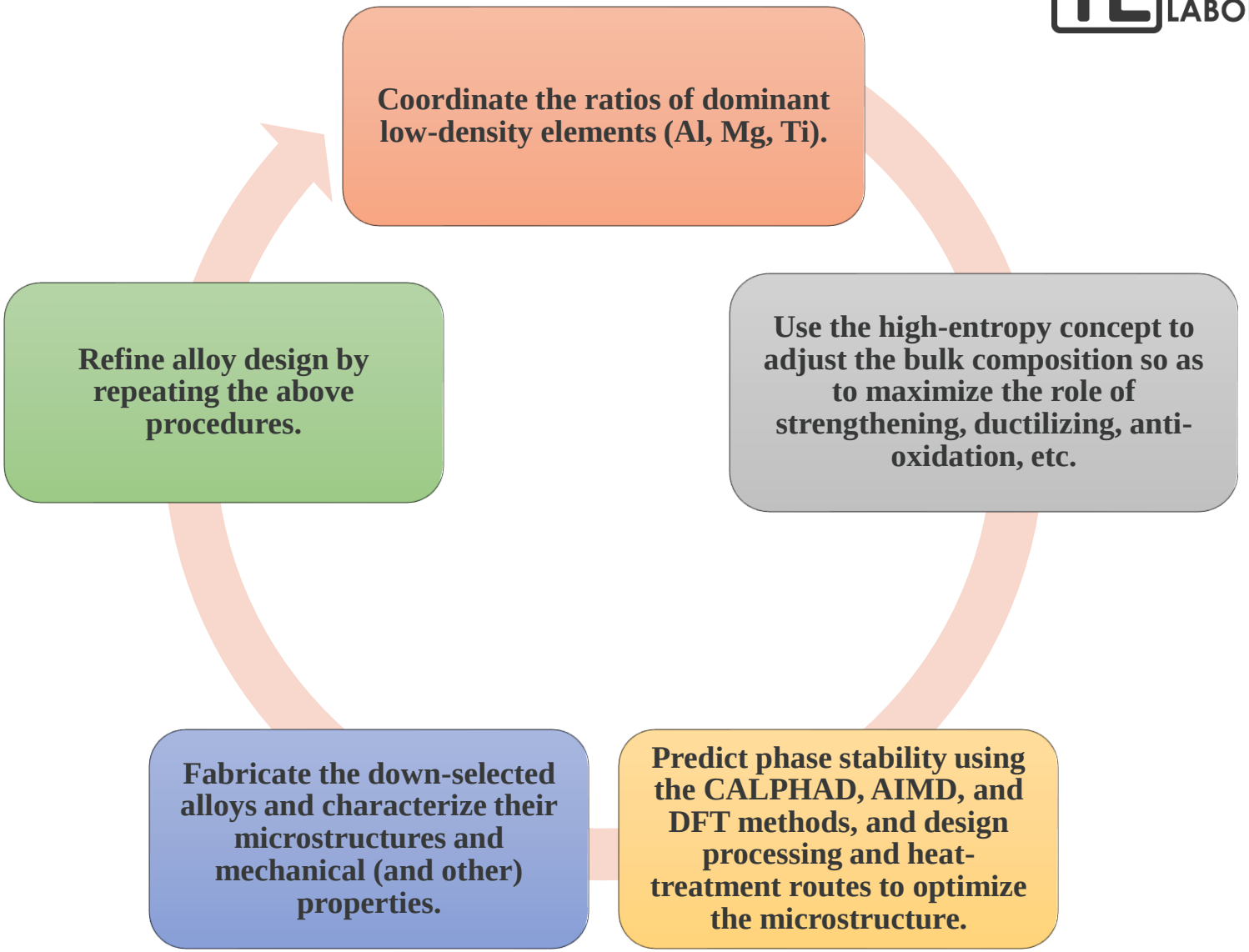
Alloy 7



Alloy 1

Z. Pei, J.A. Hawk, M.C. Gao, unpublished work, 2019

Perspectives of Alloy Design for Light-Weight HEAs



Feng R, Gao MC, Lee C, Mathes CM, Zuo T, Chen S, Hawk JA, Zhang Y, Liaw PK, Design of Light-Weight High-Entropy Alloys, Entropy 18(9) (2016) 333.

Summaries

- **Formation of single-phase high-entropy alloys**
  - Empirical rules cannot separate single-phase solid solution from multi-phase compositions effectively.
  - CALPHAD method is a much better tool in predicting HEA phase stability.
  - Machine learning (ML) and ML-inspired new empirical rule.
- **Entropy sources: DFT, MC/MD, and CALPHAD modeling**
  - FCC CoCrFeNi: Positive vibrational entropy of mixing ≈ positive excess entropy from CALPHAD.
  - BCC MoNbTaW: Negative vibrational entropy of mixing ≈ negative excess entropy from CALPHAD.
  - Electronic entropy of mixing is negligible for all three alloys studied.
  - Configurational entropy >> vibrational entropy of mixing >> electronic entropy of mixing.
  - Maximum entropy of mixing may deviate from equimolar compositions.
- **Light-weight high-entropy alloys**
  - DFT calculations were carried out to predict the enthalpy for substitution in $AlFe_2Ti$ $L2_1$ and $(Fe,Mn)_2Ti$ C14 Laves phases in Al-Cr-Fe-Mn-Ti system, and to predict density, enthalpy of formation and elastic properties of various equimolar light-weight HEAs in Al-Cr-Fe-Mn-Ti-V system with the BCC structure.
  - Metropolis Monte Carlo simulations predicted short-range order and long-range order transition.