Creating Materials and Energy Solutions

Science of Multicomponent Alloys – a Roadmap for Theoretical and Experimental Research

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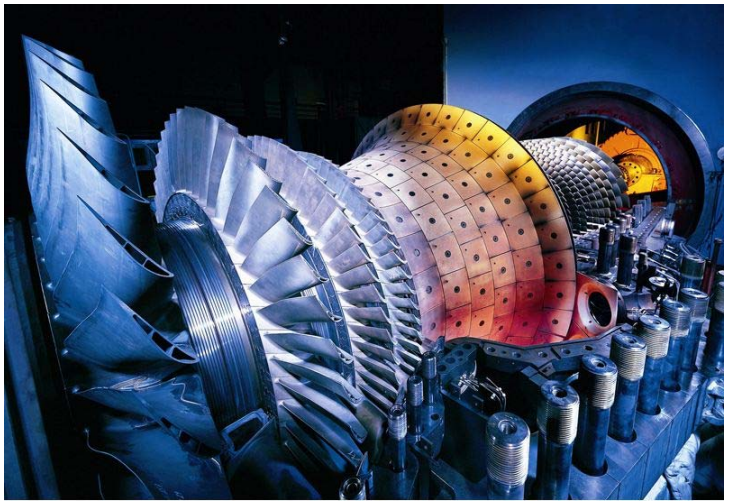
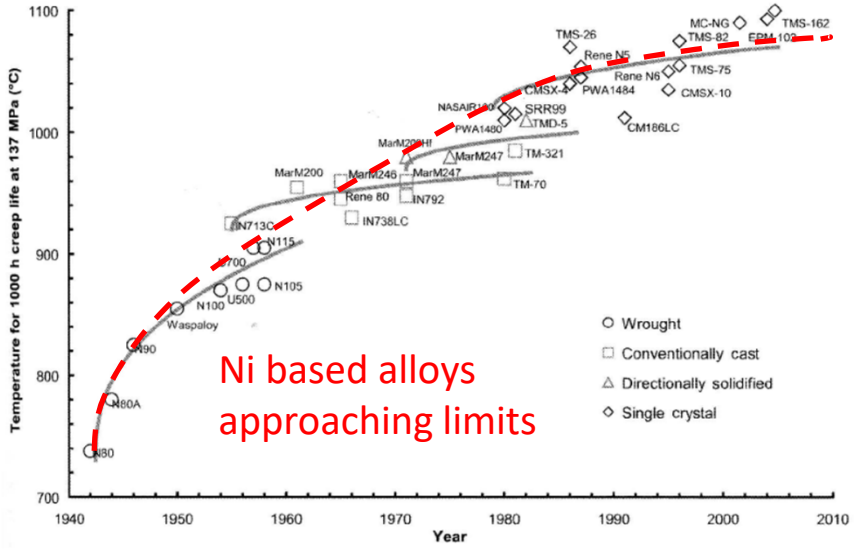
Alloy Design for Elevated Temperatures



Higher temperatures → Higher energy efficiencies

Challenges –

- High T oxidation
- Moisture
- Creep and high T deformation
- Toughness & manufacturability



Alloy architecture –

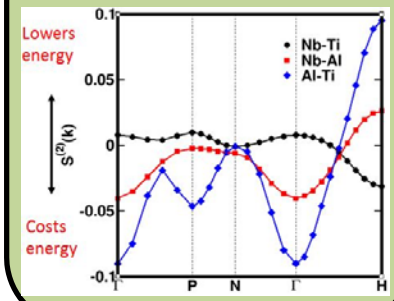
- Tough, solid solution matrix
- Strengthening Mechanisms
- Phase stability
- High Temperature Oxidation Resistance

High Entropy Alloys (HEAs) are rapidly emerging as candidate materials

Problem Definition and Approach

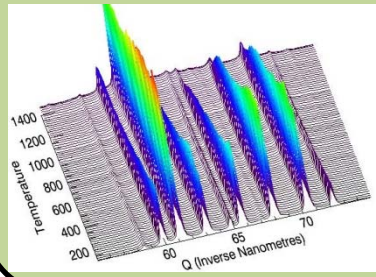
Grand Challenge: to speed the discovery and optimization of these chemically complex alloys and leverage our theoretical and experimental capabilities for assessing their long-term stability

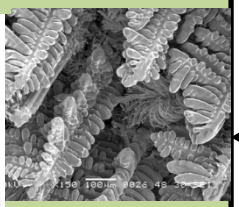
Theoretical tools (KKR-CPA)



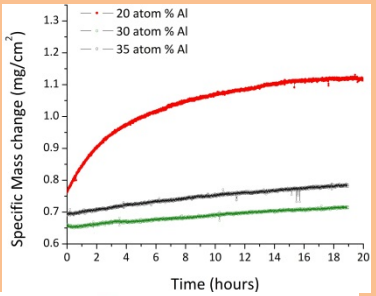
validation

Structural studies





Stability in harsh environments

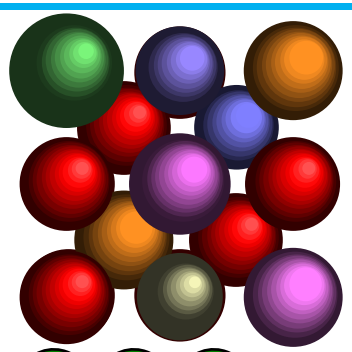


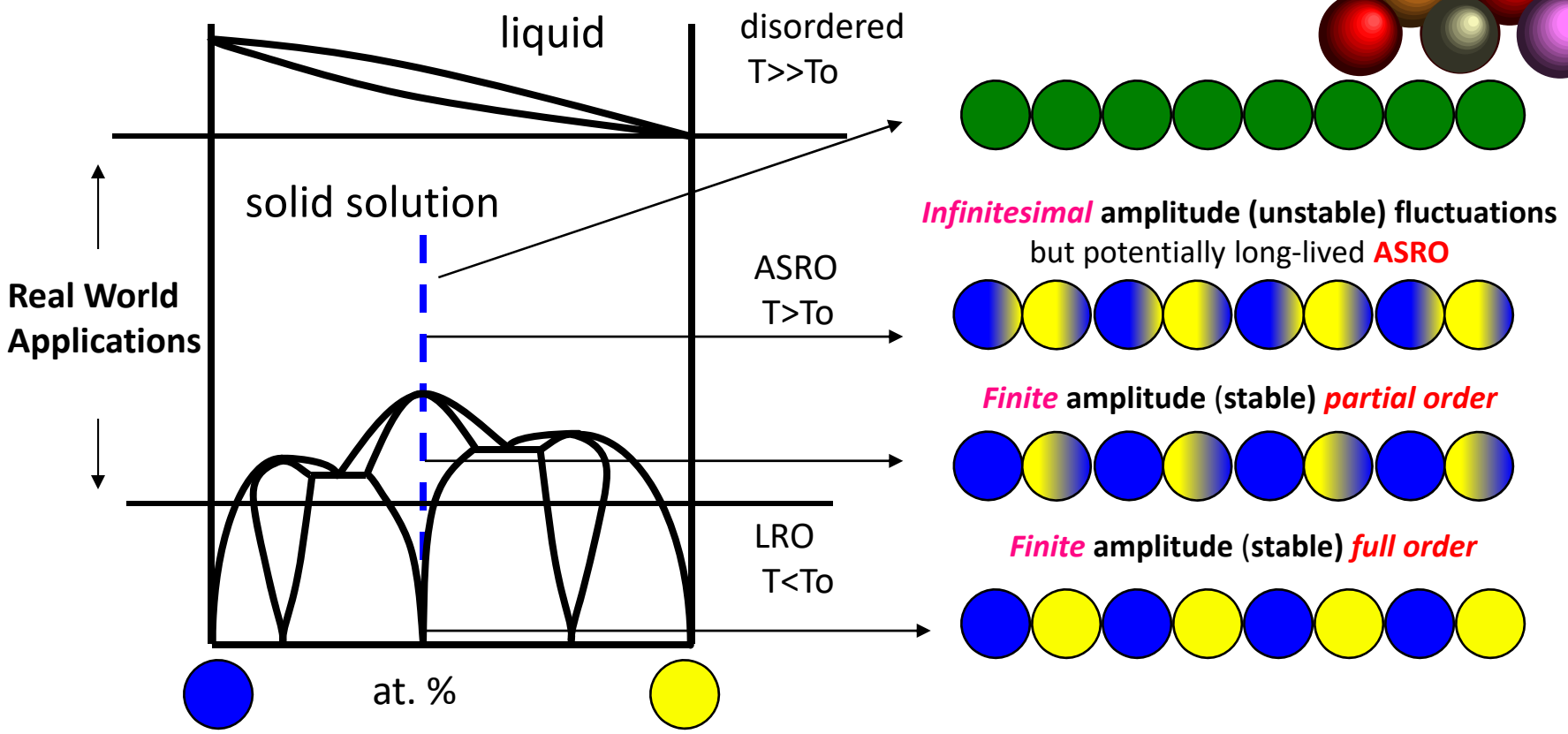
Processing

Theory will inform experiments on new chemistries while experiments will be used to validate models and access kinetics.

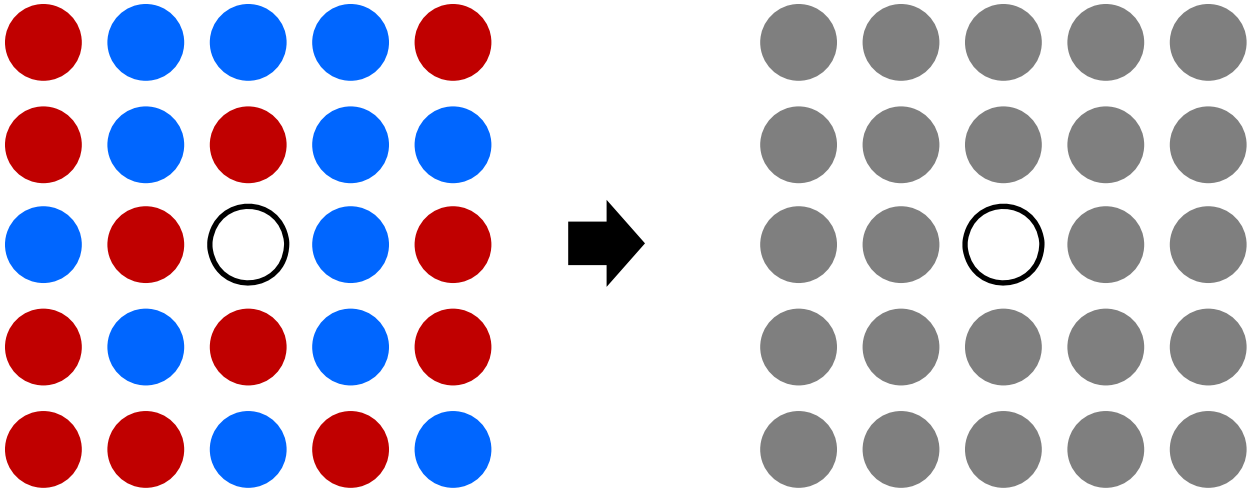
Challenges in Disordered Systems

- Experimental Measurement: quenched or annealed samples.
- Band calculations: not always related to experimentally assessed (thermal and off-stoichiometric effects).





Modeling Disordered Solids: Thermodynamics



Idea of CPA
(**C**oherent **P**otential **A**pproximation)

Velicky et. al., Phys Rev 165 (1968) 747

Direct calculation of energetics for Disordered/Partially-Ordered/ Ordered States

- DFT-based multi-sublattice KKR-CPA (configurational averaging)

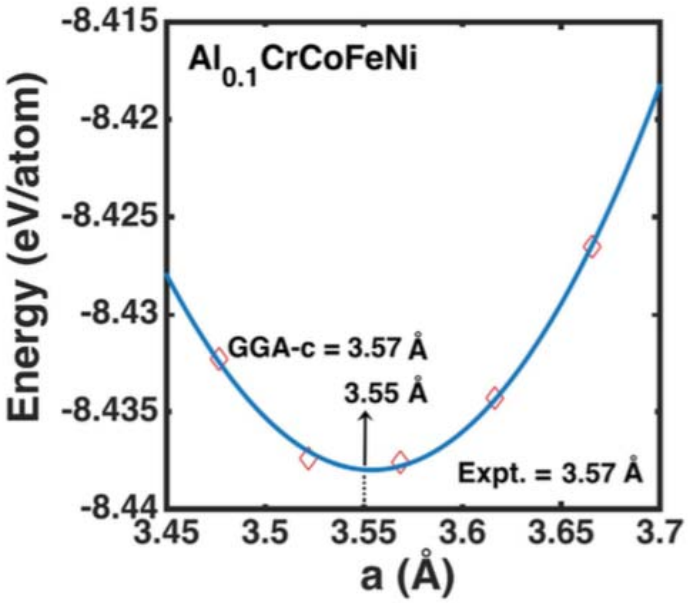
Thermodynamic Linear-Response calculations

- KKR-CPA based chemical or magnetic susceptibilities
- Directly calculate the energy associated with ASRO

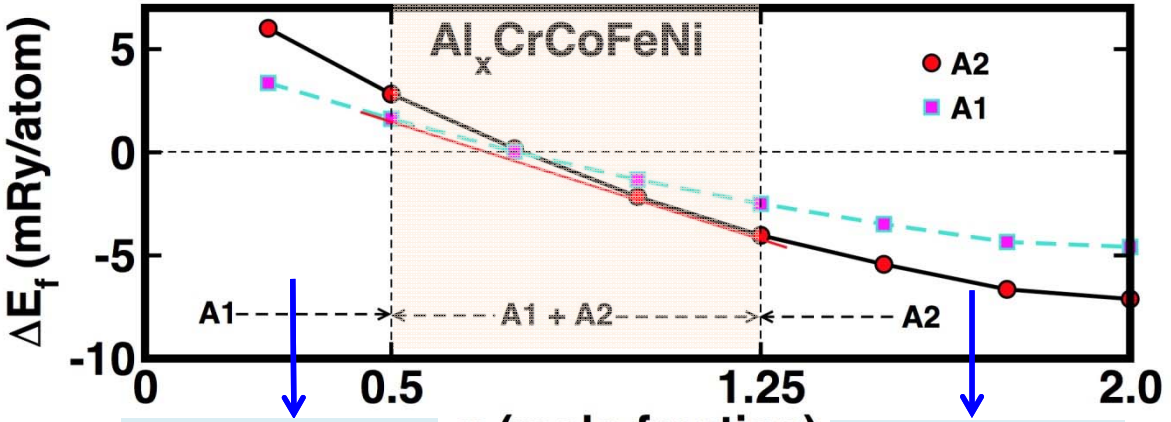
Concentrated Solid Solution Alloys

Near equiatomic **High Entropy Alloys** (N>4) are **entropically & enthalpically competing** stabilized solid solutions with potential for high strength and oxidation resistance.

A1 HEA structural



HEA relative global stability



SRO: Clustering **SRO: Ordering**

- ✓ Adding A1-Aluminum **promotes** A2 phase
- ✓ 'A1+A2' range *same* as in experiment

Liu et al., *J Alloys Compd*. **619**, 610 (2015)

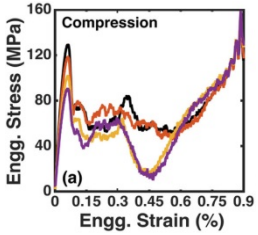
Global Stability & SRO in HEA: Singh, Smirnov, Johnson, *Phys. Rev. B* 91, 224204 (2015)
Mechanical Properties in HEA: Sharma et al., *Scientific Reports* **6**, 31028 (2016)

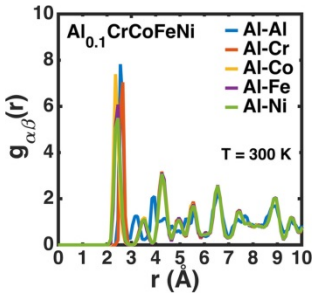
Opportunities and Challenges

Opportunities

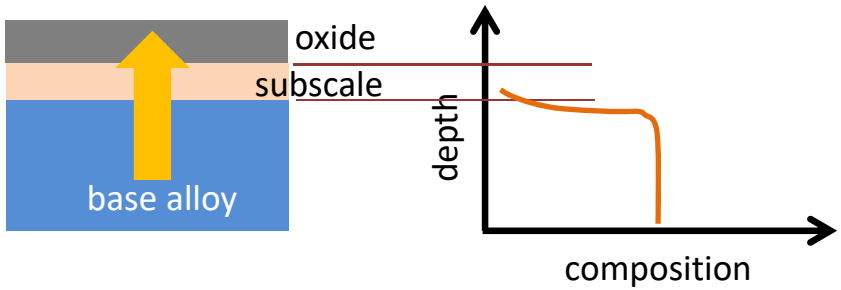
Manipulating SRO and MRO

- Promote clustering for enhanced strength or toughness





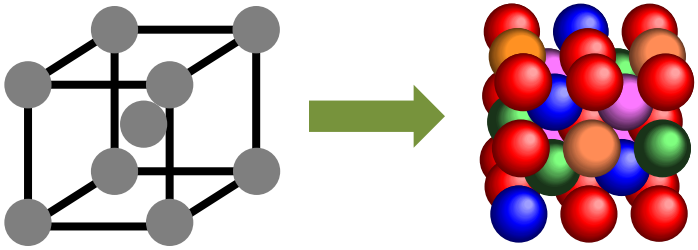
- **Enhanced diffusion of passivating elements**



Challenges

Requires accurate models

- **Typical DFT approach is expensive and introduces of artificial order**



- Need for capturing long spatial and length scales with these computations
- Need to capture system dynamics as a function of Temperature.

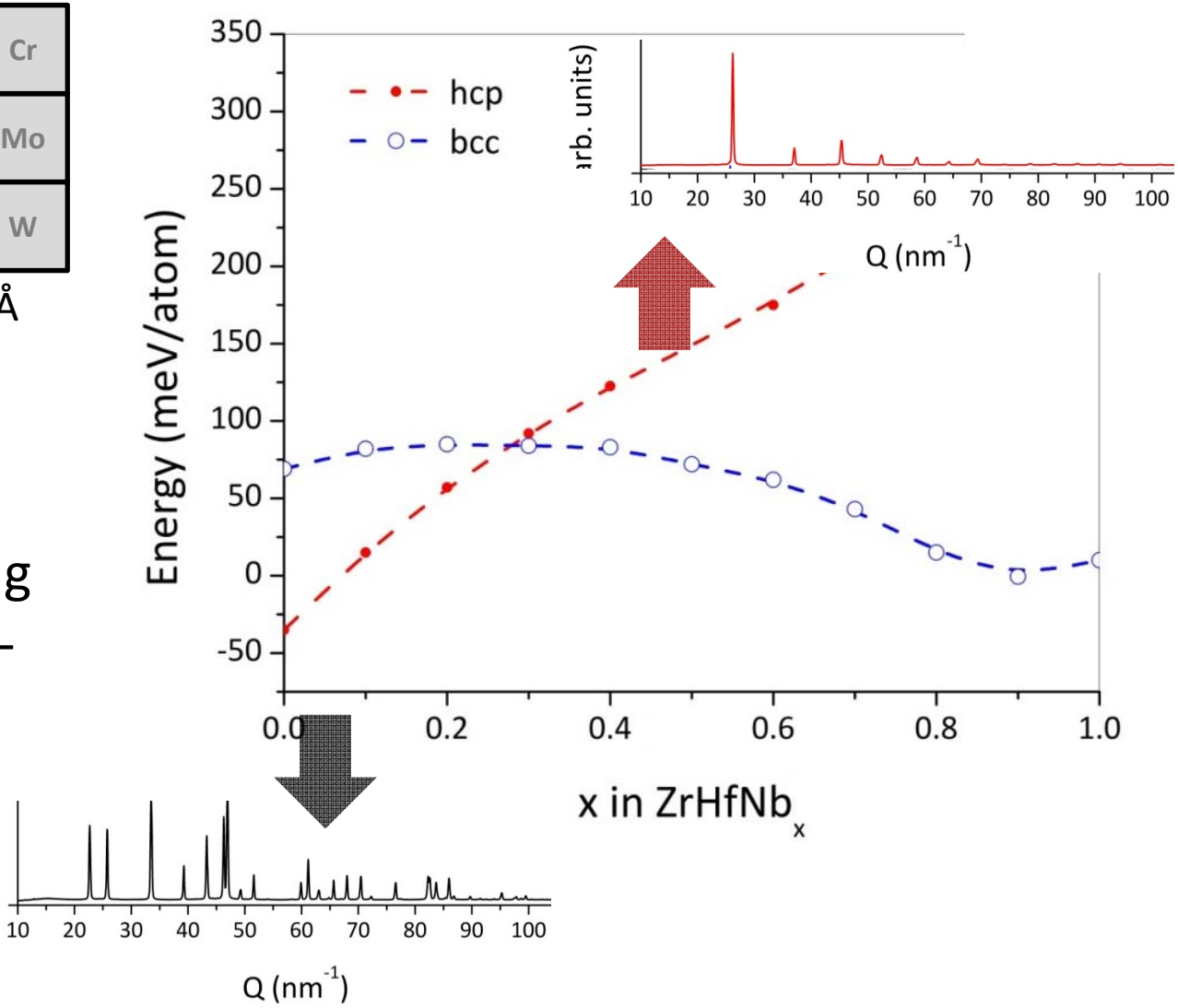
Model Systems

ZrHfNb

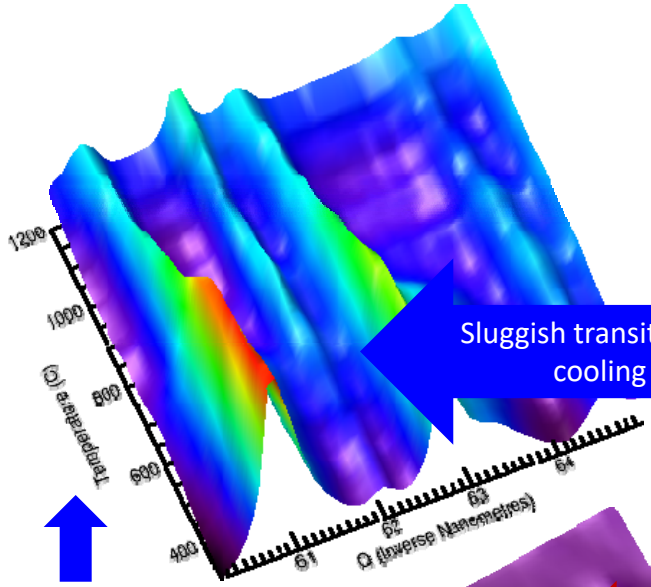
Sc	Ti	V	Cr
Y	**Zr**	**Nb**	Mo
La-Lu	**Hf**	Ta	W

1.55Å (hcp) 1.45Å (bcc)

Nb drives the ordering process towards hcp-bcc transition as a function of composition.



Phase selection in ZrHfNb alloys

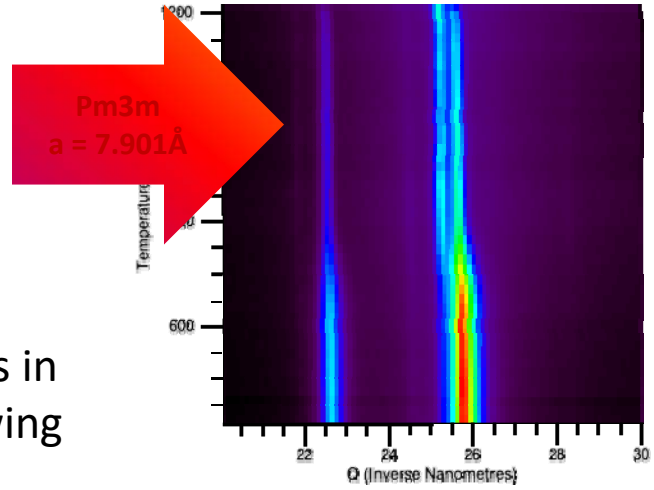


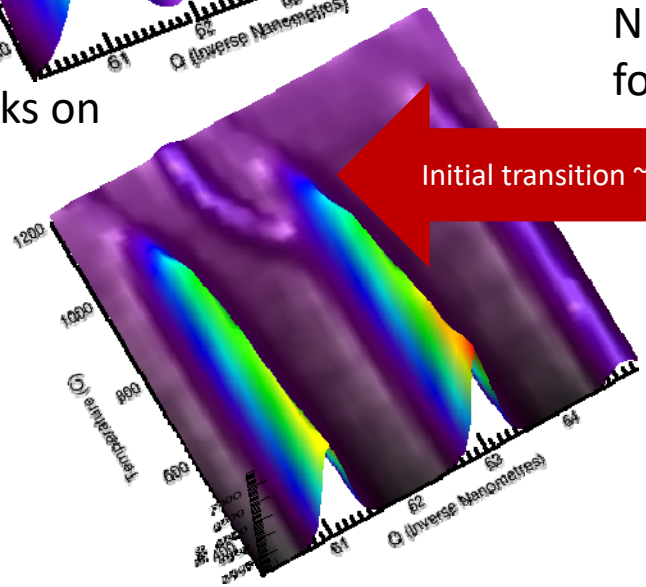
Sluggish transition on cooling

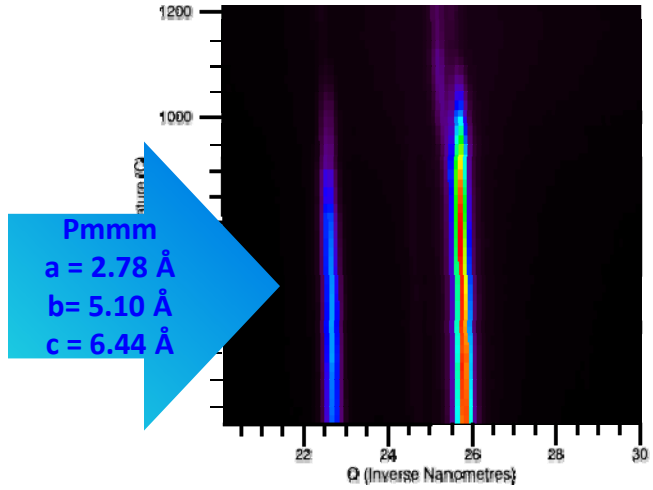
Broader peaks on cooling

Transition to a cubic phase is observed

In-situ experiments in line with CPA showing Nb promotes B2 formation



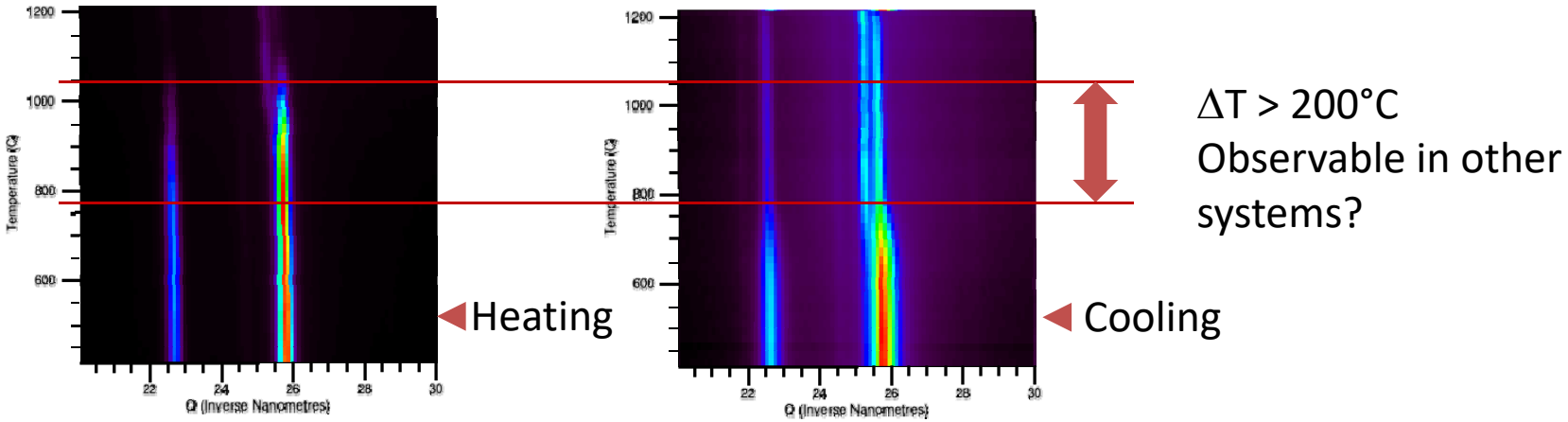




Critical Questions

Phase Stability

- How does the local ordering influence the phase transformation and its kinetics?
- Do we observe similar effects with Al?

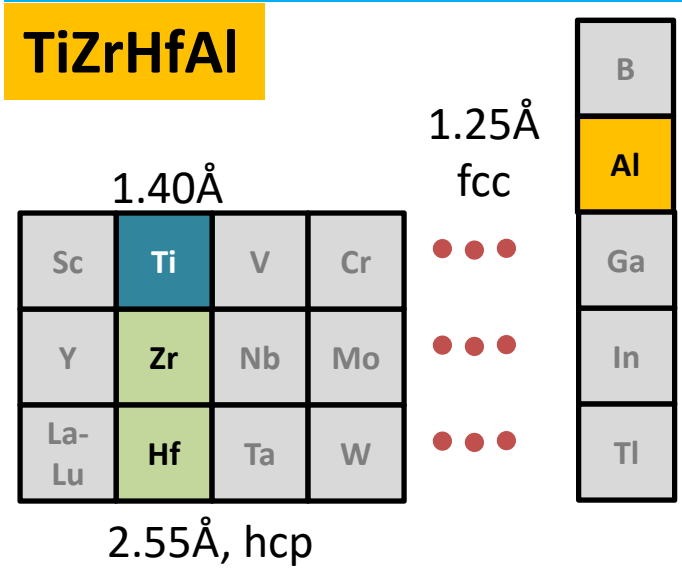


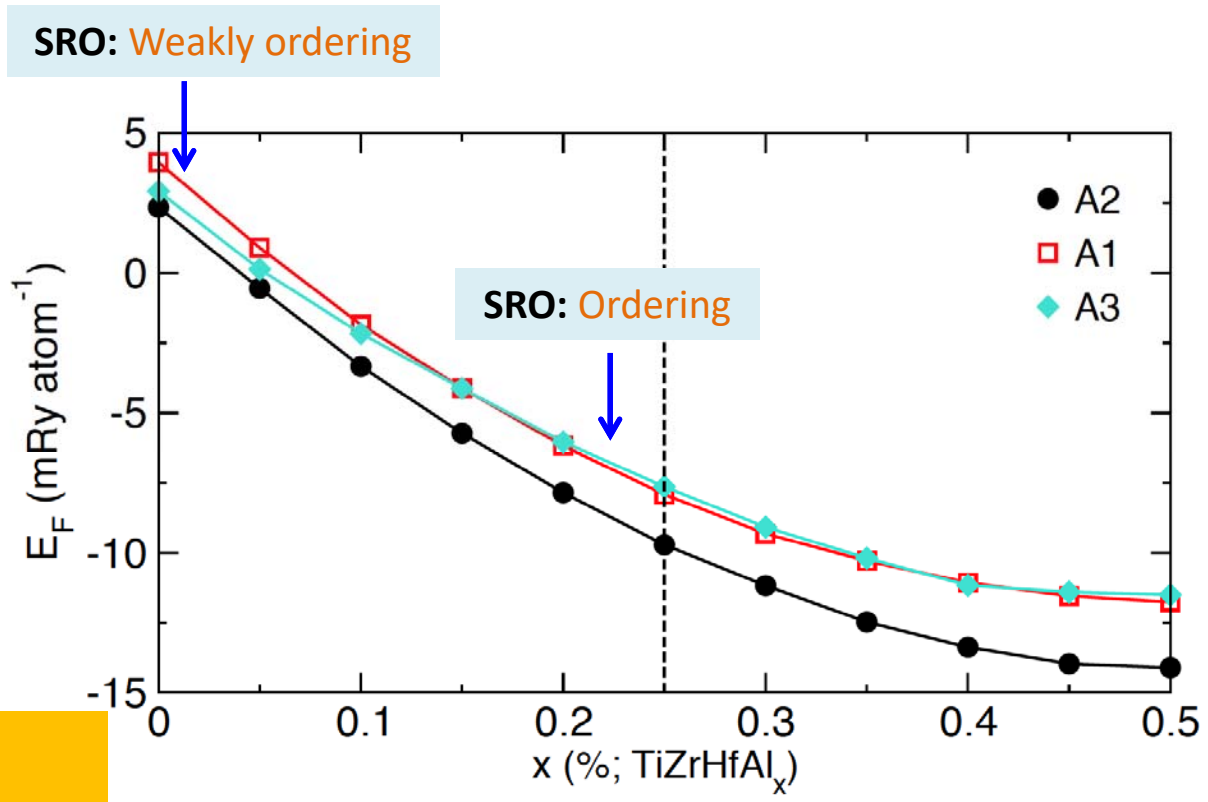
Oxidation

- Manipulate the local ordering kinetics by altering the chemistry to yield a microstructure with improved oxidation resistance.

Model systems

TiZrHfAl





Energetics prefer the A2 structure at higher Al content.

How does entropy intervene?

- ✓ Adding Aluminum **promotes** the A2 phase
- ✓ *A2 and A3 compete at low %Al, but A2 is lowest*

(A1: fcc; A2: bcc; A3: hcp)

SRO in High Entropy Alloys: $TiZrHfAl_{x=0.25}$

- ✓ KKR-CPA thermodynamic linear-response reveals SRO and its origins
- ✓ Eigenmodes of SRO (pair exchange energy $S^{(2)}$] reveal incipient LRO

Warren-Cowley SRO parameter:

- ✓ Ordering T_{sp} = 730 K
- ✓ SRO peak (from Hf-Al)
- ✓ Hf-Al & Zr-Al at H-point

Inverse WC SRO parameters

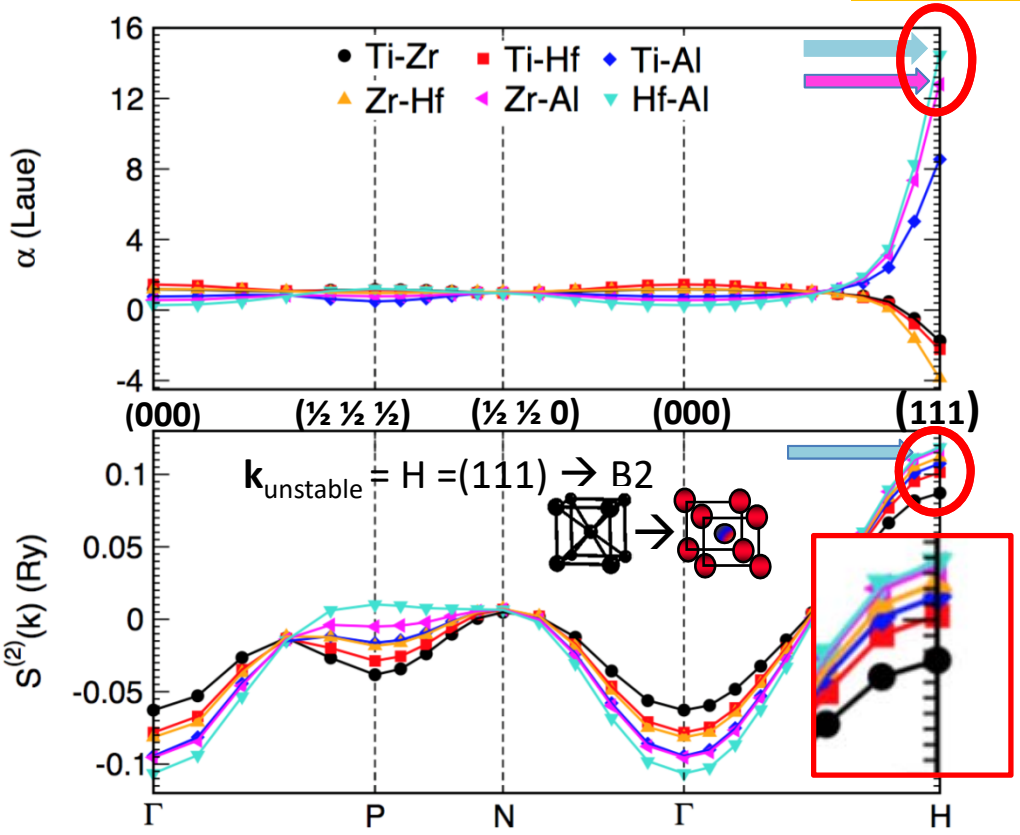
$$\alpha^{-1}_{\alpha\beta}(q;T) = \frac{\left(\delta_{\alpha\beta}c_\alpha^{-1} - c_{host}^{-1}\right) - (kT)^{-1} S^{(2)}_{\alpha\beta}(q;T)}{c_\alpha(\delta_{\alpha\beta} - c_\beta)}$$

Interchange energies

$S^{(2)}$ reveals unstable modes:

- ✓ Hf-Al and Zr-Al drive SRO,
- ✓ followed closely by Zr-Hf
- ✓ Albeit not true generally, pairs reflected in Warren-Cowley SRO

@ 1.15 T_{sp}



Global Stability & SRO in HEA: Singh, Smirnov, Johnson, *Phys. Rev. B* 91, 224204 (2015)
Mechanical Properties in HEA: Sharma et al., *Scientific Reports* **6**, 31028 (2016)

Incipient ordering in TiZrHfAl alloys

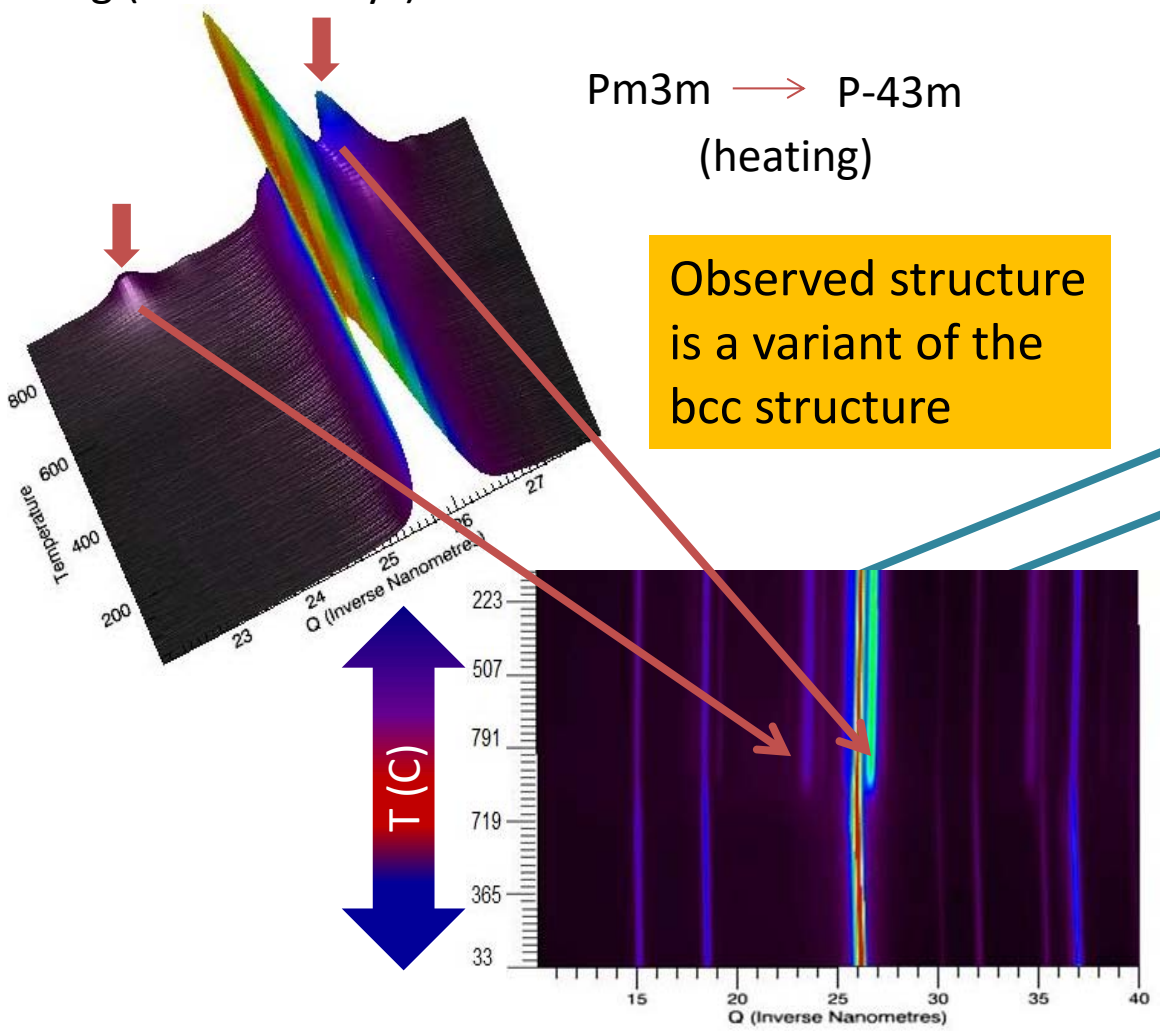
Heating (As-Cast alloys)

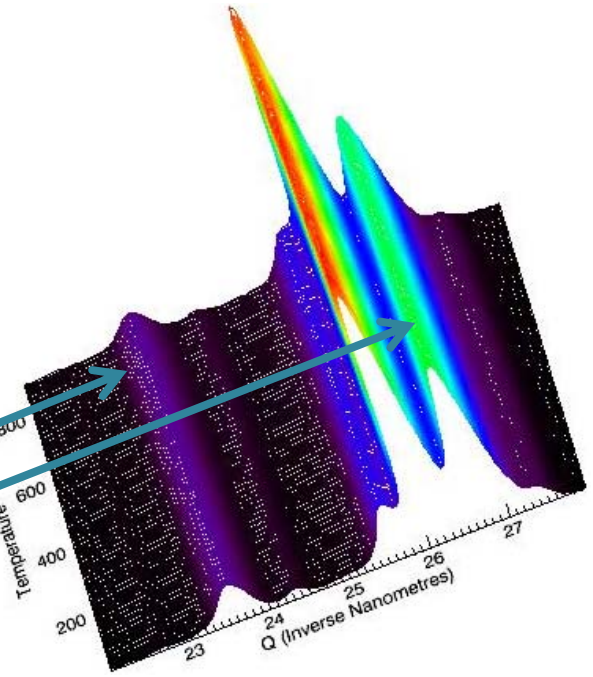
Cooling (As-Cast alloys)

Pm3m ⟶ P-43m

(heating)

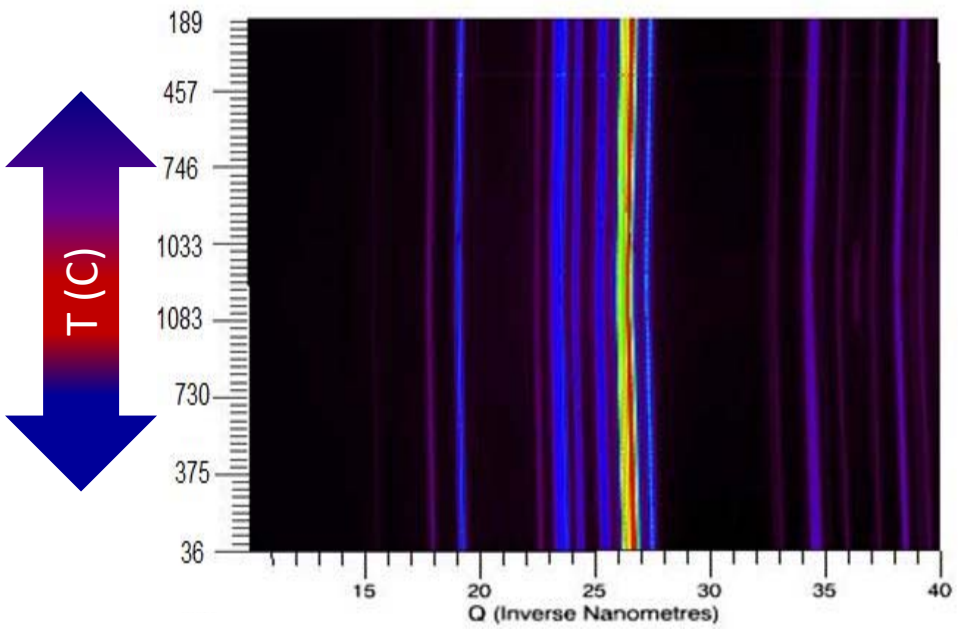
Observed structure is a variant of the bcc structure





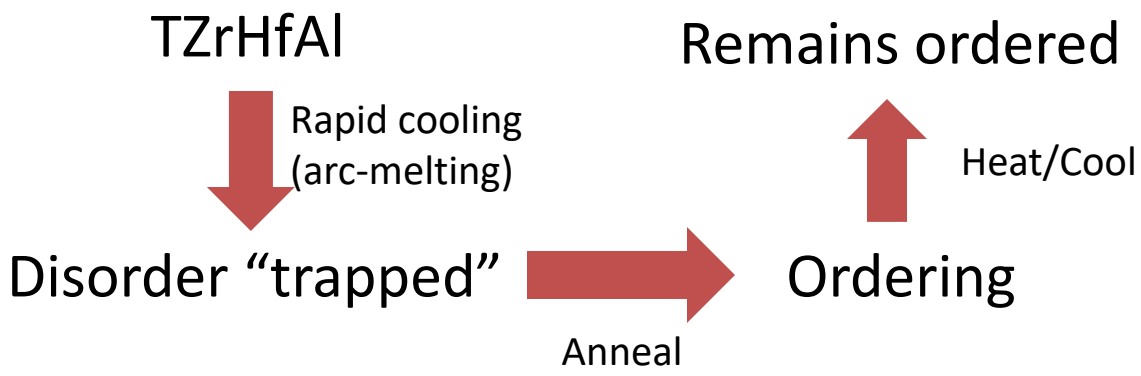
The ordered structure persists during cooling

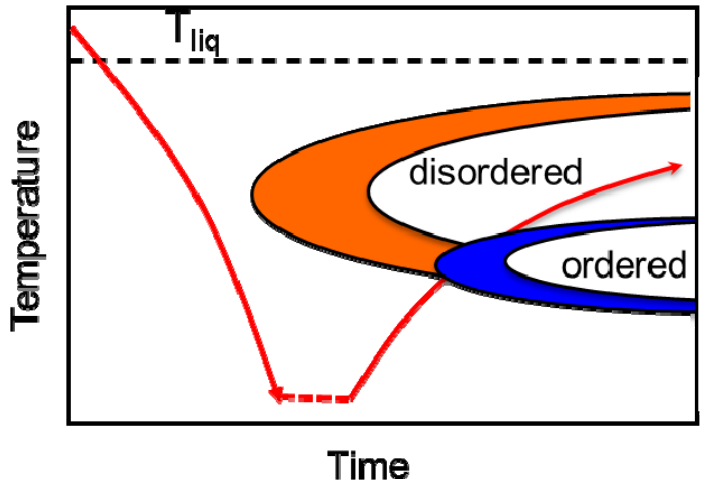
Incipient ordering in TiZrHfAl alloys



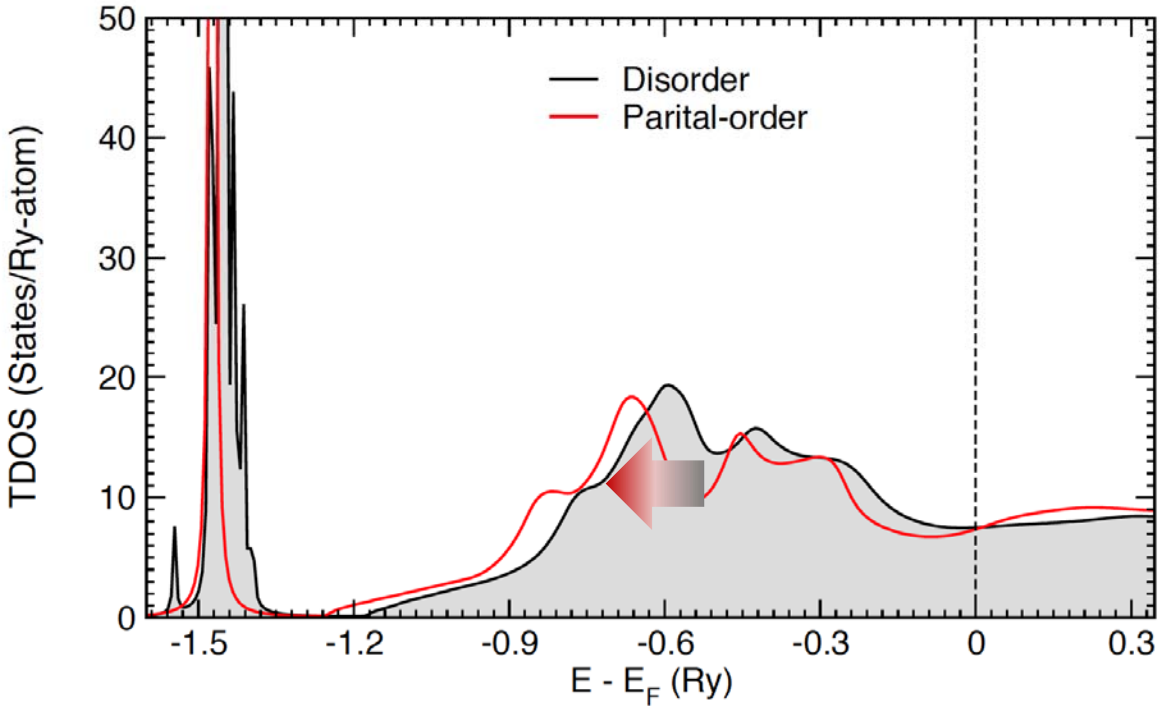
Alloys annealed at 1100°C does not exhibit the Temperature dependent transitions

Possibility of kinetically stabilized phases below certain critical T





Alloy Phase Stability for SRO/LRO: $TiZrHfAl_x$

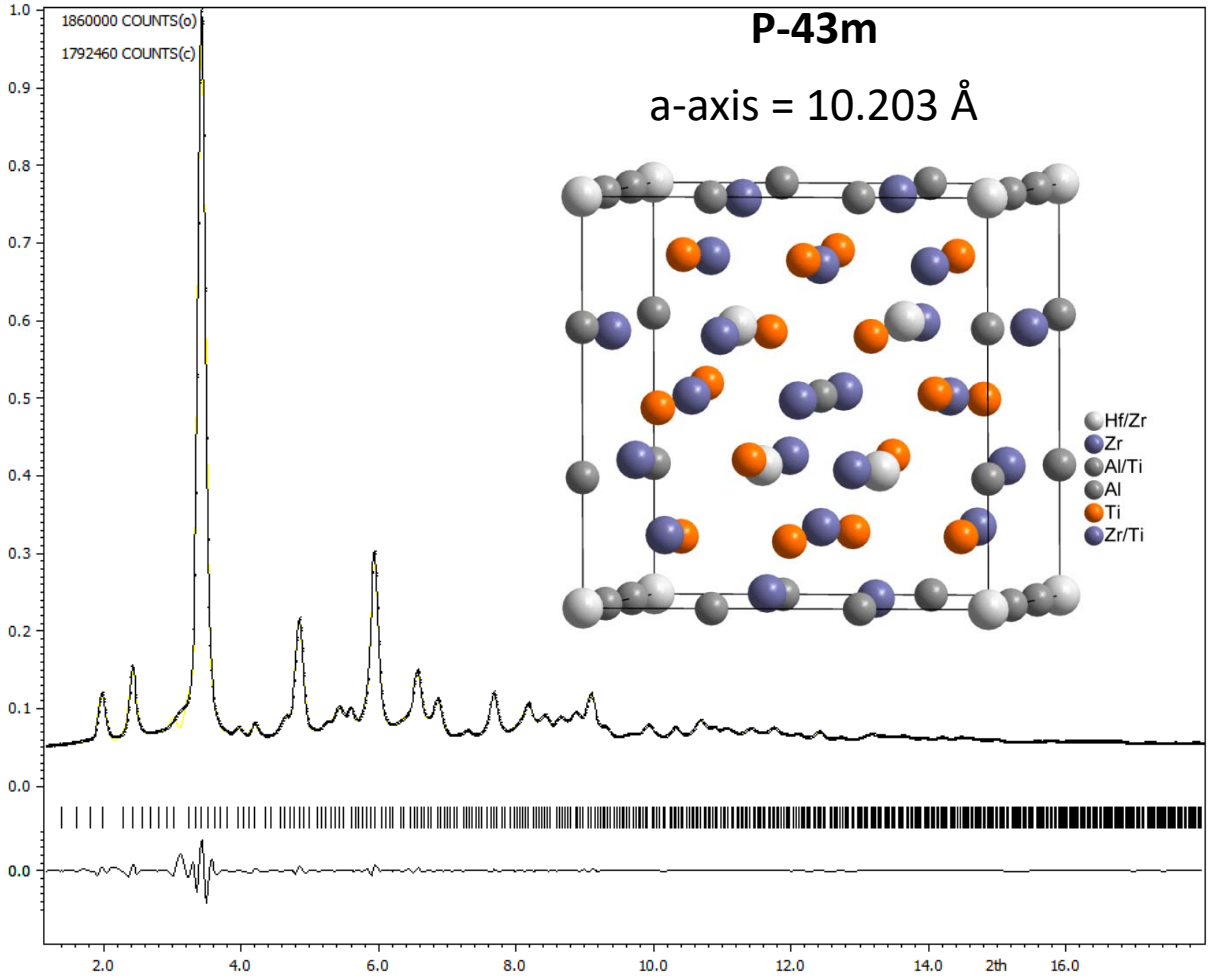


- Phase competition occurs between disordered and partially ordered structures.
- Small energy difference in these structures:

$E_{PO} - E_{DO} = -7$ mRy/atom

Electronic density of states favor the partially ordered structure, relative to the disordered structure.

Structure of TiZrHfAl alloys



Experiments

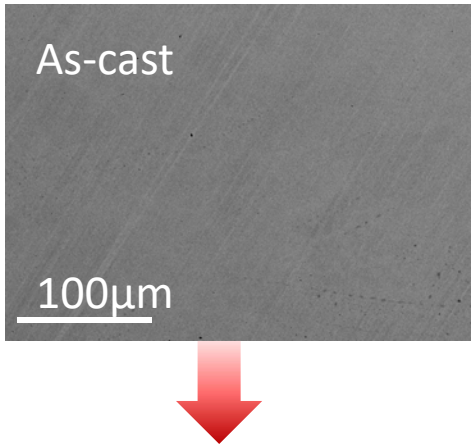
- TiZrHf hcp ss
- Al destabilizes hcp
  - γ-brasses
  - (bcc w/ vacancies)

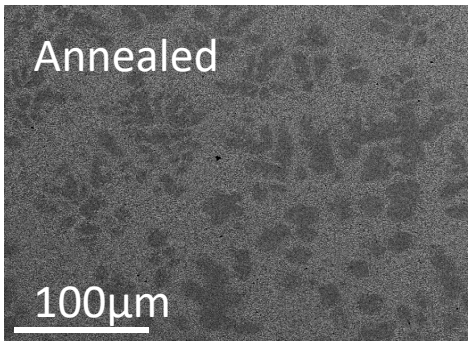
Simulations predicted

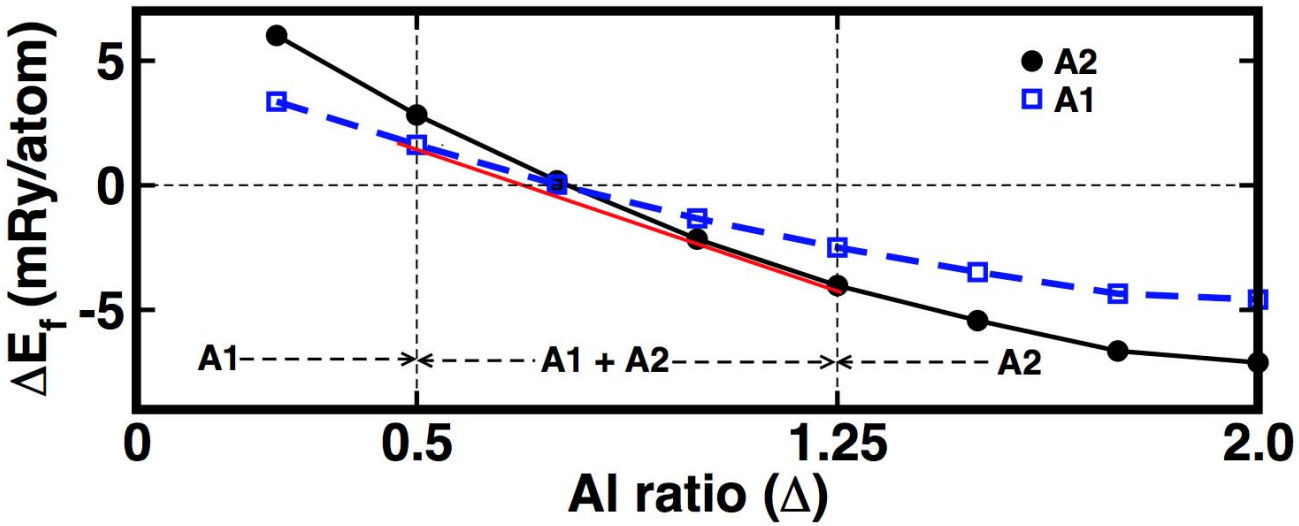
- TiZrHf hcp ss
- Al destabilizes hcp
  - To bcc

Model Systems

FeNiCoCrAl







- ✓ Reservoir of passivating elements
- ✓ Possibility of inducing phase transitions and microstructure control

Adding Al-stablizes BCC-phase in $Al_xCoCrFeNi$

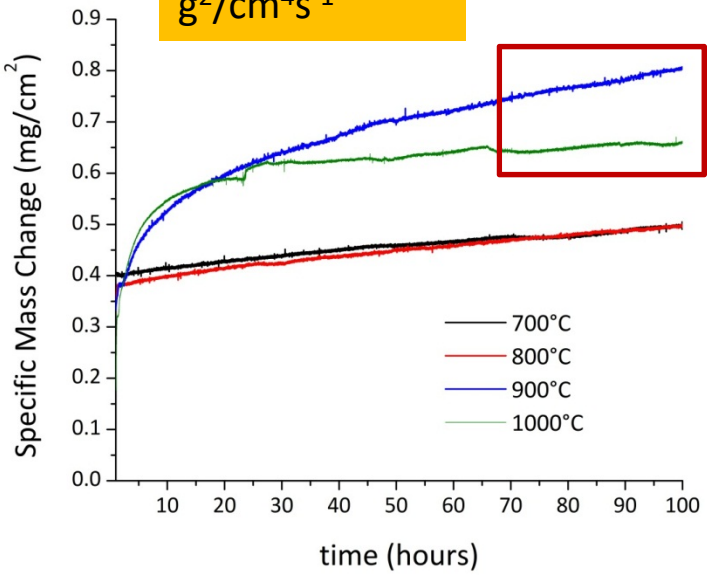
In agreement with Experiments.

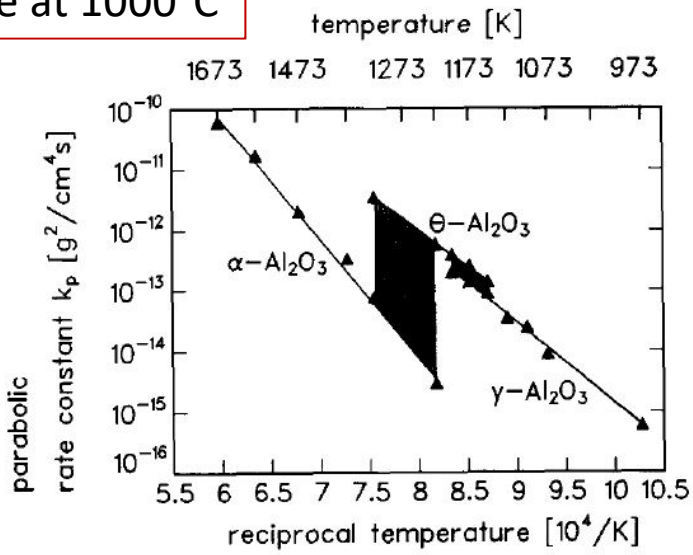
Singh, Smirnov, and Johnson, Phys. Rev.B **91**, 224204 (2015)

Effect of Temperature on Oxidation of FeNiCoCrAl

k_p^{1273K}
HEA: 1.6 x 10^{-12} g^2/cm^4s^{-1}

Better oxidation resistance at 1000°C



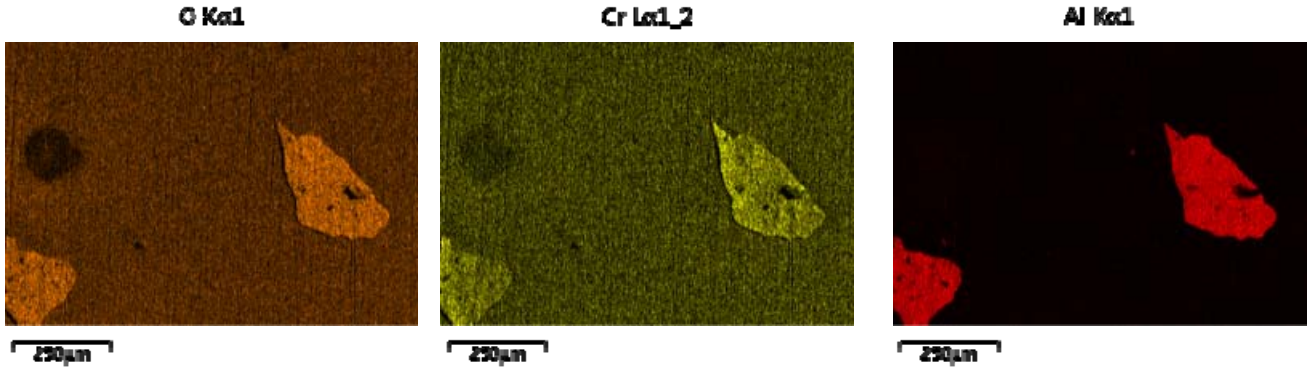


Brumm and Grabke, Corrosion Science 33 (1992) 1167

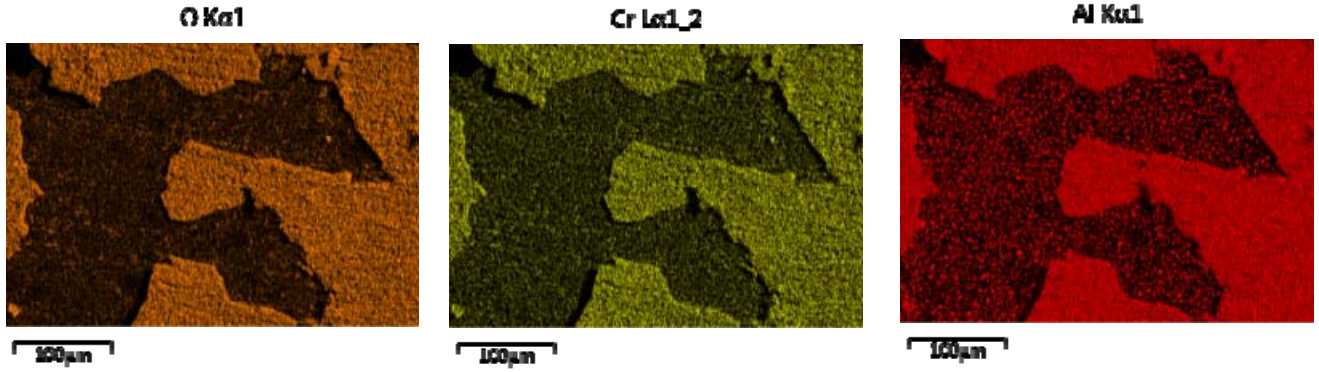
Phase	k_p ($g^2/cm^4.s$)	E_A (kJ/mol)
α-Al_2O_3	3.5 x 10^{-13}	231
θ-Al_2O_3	6.3 x 10^{-13}	382

θ-Al_2O_3 forms at lower temperatures, whereas, the external scale consists of α-Al_2O_3 at higher temperatures (>1000°C)

Evolution of the Oxide Scale in FeNiCoCrAl

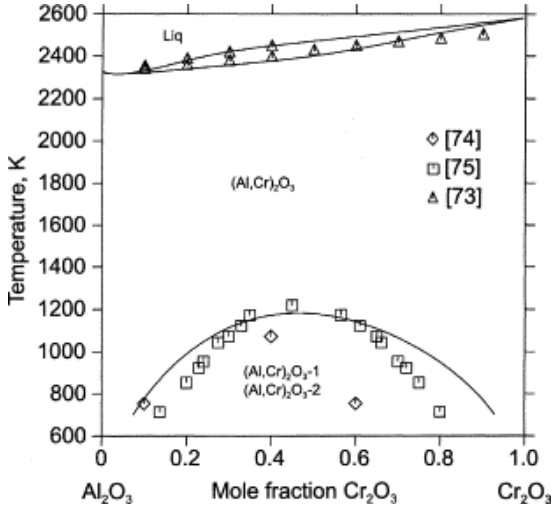


1 hour @ 1000°C

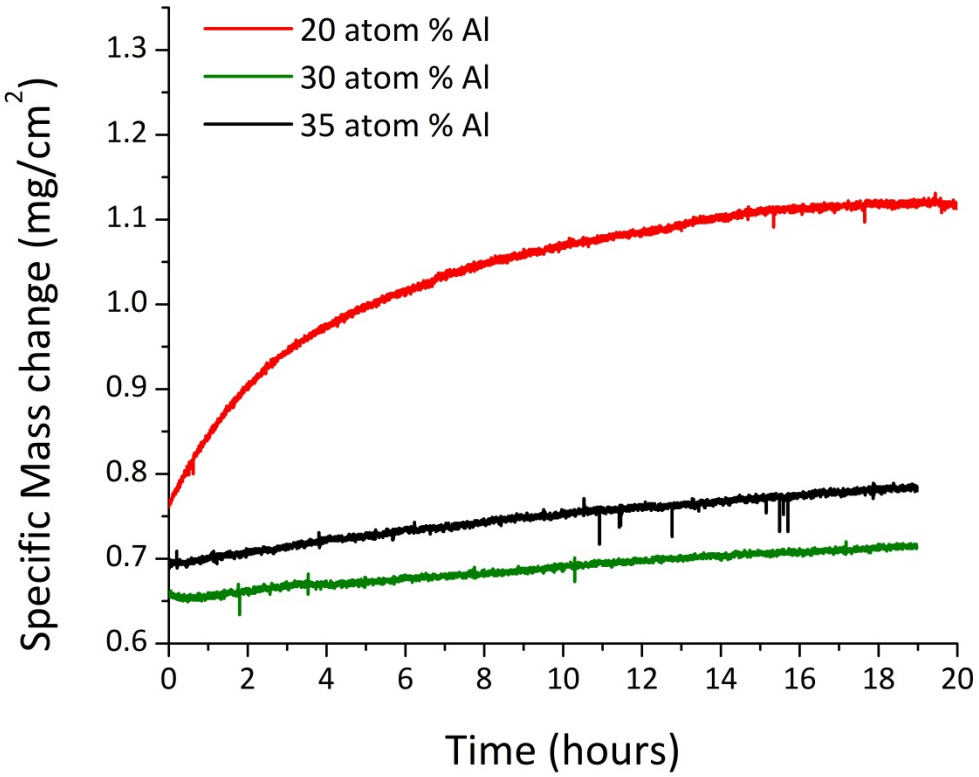


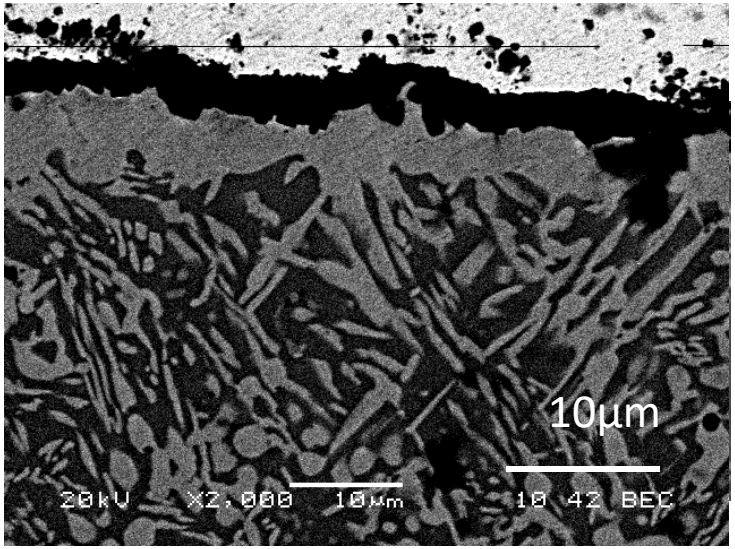
100 hours @ 1000°C

The initial oxide is rich in Cr content, and becomes Al rich with time.



Effect of Al:Cr ratio on Oxidation of FeNiCoCrAl

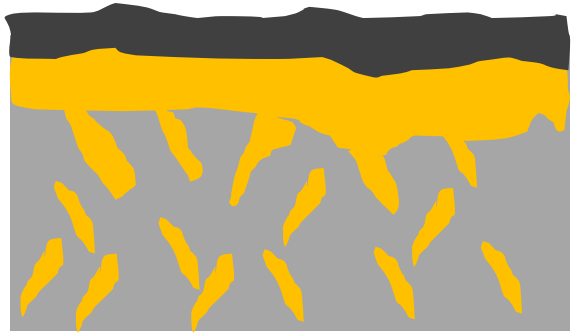




- Given the relatively low stability of chromia, increased Al content helps with oxidation.

- But the initial formation of Cr_2O_3 promotes the growth of Al_2O_3, hence extremely low Cr content may not be desirable either

Improving Oxidation Resistance



Oxide scale

Subscale (FeCr) rich – *governs Al diffusion/interlayer oxides*

Base Alloy –
(FeCr) rich + (AlNi) rich
(Both phases have similar Co content)

- How does Cr content affect the subscale thickness and composition?
- Can the distribution of (FeCr) rich phase be modified, via different processing routes, in order to tune the "accessibility" of Al to the external scale by modifying the subscale thicknesses?

The Kinetic Challenges

Kinetic Challenges

Kinetics of Oxidation

- How can we predict the oxidation kinetics as a function of T and comp?
- Can we design microstructures to optimize oxidation resistance?

Kinetics of Phase Transformations

- How do we rapidly assess the effect of time and Temperature on Phase Transformations and control the microstructures?
- Can the calculated T_{sp} in conjunction with activation energies predict the transition temperatures more accurately?

Proposed Work

- Work on the ZrHfNb and TiZrHfAl alloys indicate significant kinetic effects during phase transformations – including the possibility of kinetic stabilization of phases below a certain blocking Temperature ?

- Can these concepts be leveraged for modifying the microstructures of High Entropy Alloys, and eventually affect the oxidation resistance ?

Focus Areas for FY 2017-2018: *In-situ diffraction studies for rapid assessment of TTT diagrams for quinary Al and Cr containing alloys, and subsequently designing phase/microstructure assemblage by adjusting processing conditions for optimal oxidation resistance.*

General Summary

- Extension of the KKR-CPA approach to general lattices, i.e. *n* components, *n* sub-lattices.
- Combined KKR-CPA, ASRO and planar defect energies (with Suzuki effect) will guide the design of improved alloys, e.g., High-Entropy Alloys.
- Used *In-situ* synchrotron diffraction to determine the T range of stability
- Determined evolution of the oxide scale at elevated temperatures
- A combination of the theoretical tools and experimental work on kinetics of transformations and oxidation will guide the microstructural design of novel HEAs.

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