Short-Range Order in High-Entropy Alloys: First Principles Theory and Atomistic Modelling

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Introduction

Short-range order (SRO) in multicomponent alloys can affect a variety of material properties. An understanding of the nature of order and how it emerges is essential to guide material design.

We can:

– Use a linear response theory to calculate atomic SRO *ab initio* and infer order-disorder transitions directly.

– Extract interactions in real space.

– Run atomistic simulations to understand nature of order.

As a case study, looked at an Ni-based family of high-entropy alloys which form on an fcc lattice(1).

High-entropy alloys:

– First examples synthesised in 2004 (4, 5).

– Multiple metals combined in roughly equal ratios.

– Simple, close-packed structures: fcc, bcc, hcp.

– Single-phase solid solution stabilised by configurational entropy:

$$-\beta^{-1}\sum_{i\alpha} c_{i\alpha}\log c_{i\alpha} \tag{1}$$

Theory

Linear Response

– Mean-field free energy based on ensemble-averaged site-occupancies, $\{\bar{c}_{i\alpha}\}$(2):

$$\Omega = -\beta^{-1}\sum_{i\alpha} c_{i\alpha}\log c_{i\alpha} - {\sum_{i\alpha}}' \nu_{i\alpha}c_{i\alpha} + \langle\Omega_{\mathsf{el}}\rangle_0[\{c_{i\alpha}\}] \tag{2}$$

– Impose perturbation about homogeneous reference state, $c_{i\alpha} = c_\alpha + \Delta c_{i\alpha}$.

– Change in free energy due to perturbation written:

$$\delta\Omega = \frac{1}{2}\sum_{i,j}\sum_{\alpha,\alpha'}\Delta\bar{c}_{i\alpha}[\beta^{-1}C^{-1}_{\alpha,\alpha'} - S^{(2)}_{i\alpha,j\alpha'}]\Delta\bar{c}_{j\alpha'}, \quad \text{where} \quad C^{-1}_{\alpha\alpha'} = \frac{\delta_{\alpha\alpha'}}{c_\alpha}, \quad -\frac{\partial^2\langle\Omega_{\mathsf{el}}\rangle_0}{\partial\bar{c}_{i\alpha}\partial\bar{c}_{j\alpha'}} \equiv S^{(2)}_{i\alpha;j\alpha'}. \tag{3}$$

Term in square brackets referred to as 'chemical stability matrix'.

– Assess which perturbations are energetically favourable to find dominant correlations.

– Convenient to perform analysis in reciprocal space, writing $\Delta c_\alpha(\mathbf{k})$.

Atomistic Modelling

– Bragg-Williams Hamiltonian for atomistic modelling:

$$H(\{\xi_{i\alpha}\}) = \sum_{i,j}\sum_{\alpha,\alpha'} V_{i\alpha;j\alpha'}\xi_{i\alpha}\xi_{j\alpha'} + \sum_{i\alpha}\nu_{i\alpha}\xi_{i\alpha} \tag{4}$$

– Metropolis Monte Carlo with Kawasaki dynamics(3). Measure specific heat capacity (SHC) and SRO parameters.

Results

Linear Response Analysis

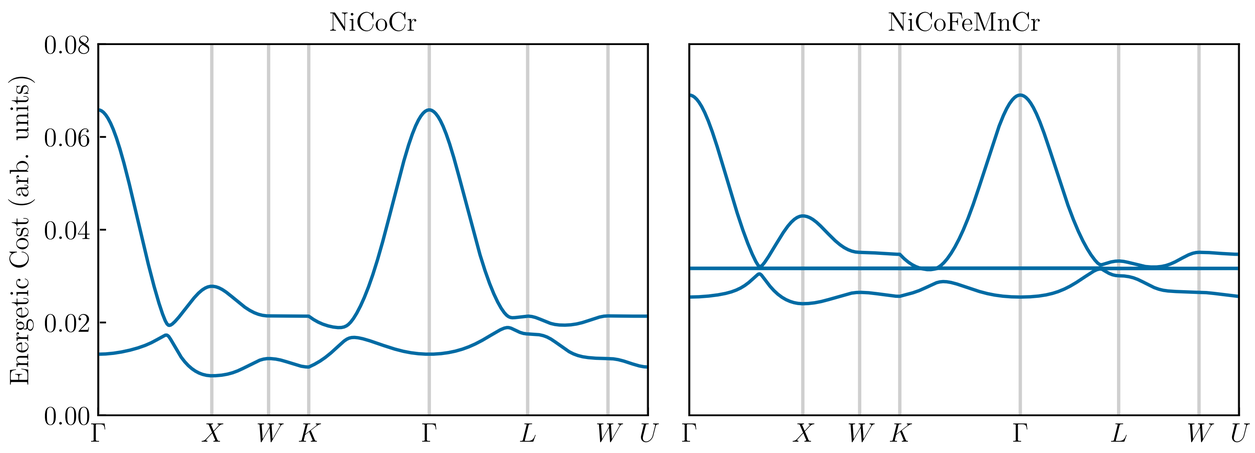

Fig. 1: Eigenvalues of the chemical stability matrix around the irreducible Brillouin zone for NiCoCr and NiCoFeMnCr. Fe and Mn introduce flat modes, associated with weak ordering tendencies, and drive up predicted ordering temperatures.

– NiCoCr:

  – Dominant mode: $\mathbf{k} = \{0, 0, 1\}$, $\Delta c_{i\alpha} = (-0.035, -0.689, 0.724)$.

  – Ordering temperature: $T = 606$K.

  – Describes ordering into alternating Co-rich, Cr-deficient/Co-deficient, Cr-rich layers.

– NiCoFeMnCr:

  – Dominant mode: $\mathbf{k} = \{0, 0, 1\}$, $\Delta c_{i\alpha} = (0.033, -0.685, -0.082, 0.011, 0.723)$.

  – Ordering temperature: $T = 281$K.

Monte Carlo Simulations

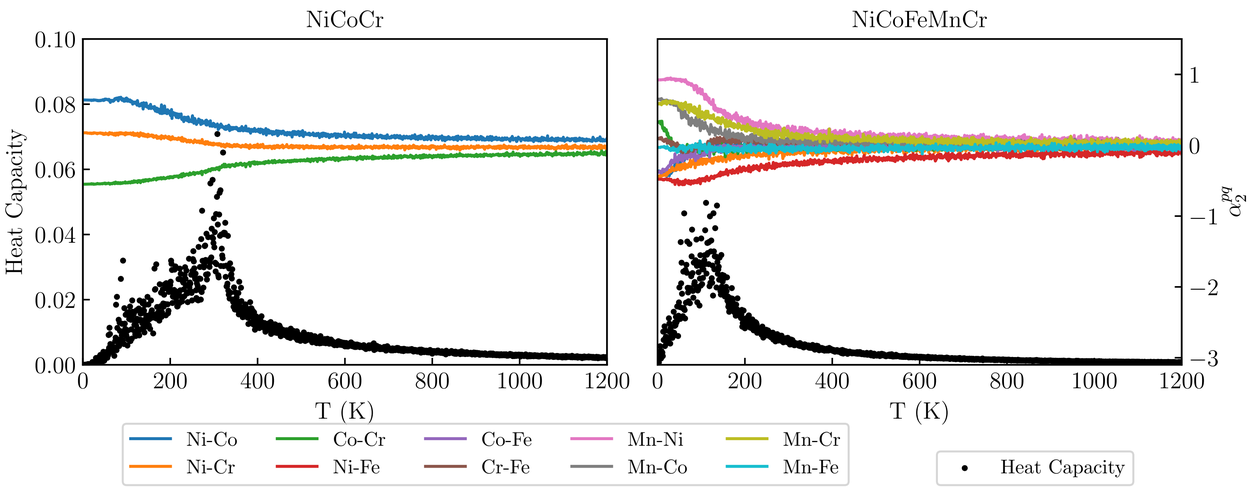

Fig. 2: Warren-Cowley SRO parameters and specific heat capacity as a function of temperature for NiCoCr and NiCoFeMnCr. SRO and the predicted ordering temperature are seen to be markedly reduced with increasing number of components.

– Co-Cr pairs clearly favoured in ternary NiCoCr.

– Greater number of components drives down transition temperature.

Visualisations

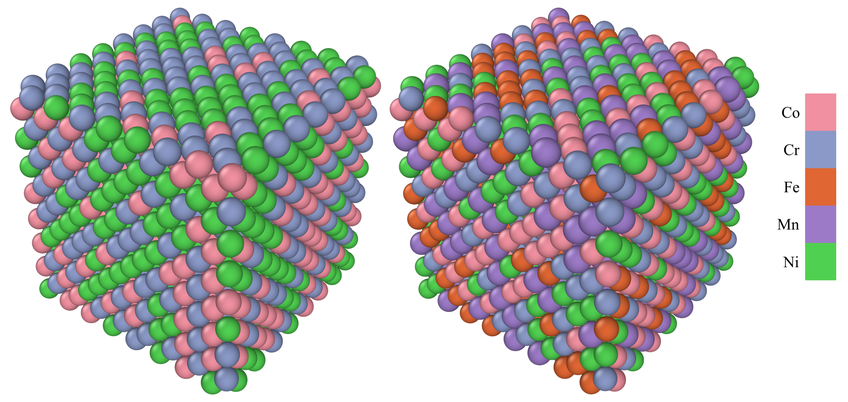

Fig. 3: Equilibrated configurations at 300K for a supercell of 2048 atoms for NiCoCr and NiCoFeMnCr. Solid solution remains disordered at this temperature.

Conclusions

– Dominant correlations are between Co and Cr.

– Fe, Mn, interact weakly and dilute the Ni-Co-Cr interactions, stabilising the solid solution.

– Interactions extend beyond nearest neighbour distance.

– Interactions are poorly approximated as pseudobinary.

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References

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