Using the Coherent Potential Approximation and DFT to Examine the Phase Behaviour of High-Entropy Alloys: Case Study of $Al_xCrFeCoNi$.

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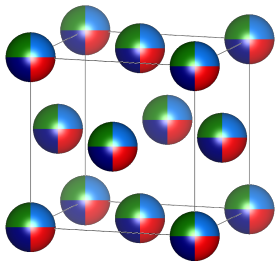
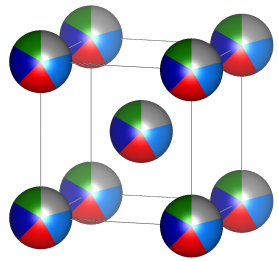
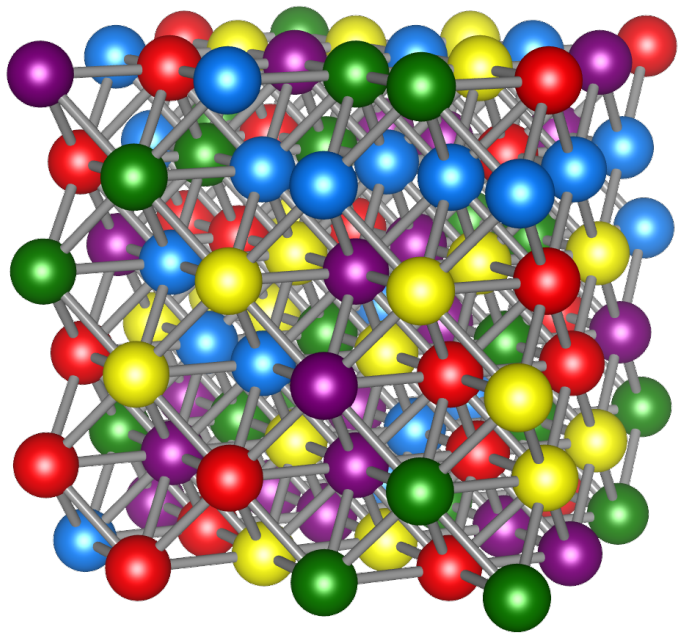




Talk Plan

Aim: demonstrate that perturbative analysis of CPA energy provides a powerful tool for exploring HEA phase space.



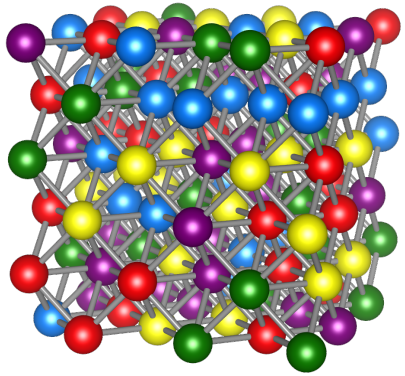
Context

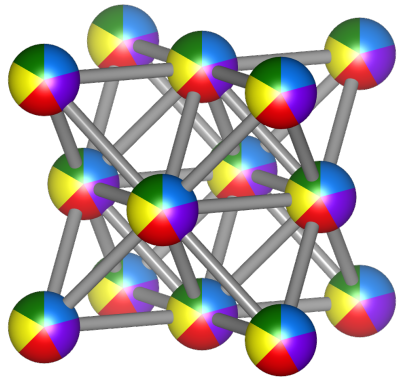
High-Entropy Alloys: Background

- Alloy
  - Mixture of multiple (usually) metallic elements.
  - Today's talk: *substitutional* alloys.
- 'High-Entropy' Alloy
  - First reported in 2004.
  - Sufficiently many elements (4+) in right concentrations (near-equiatomic) that 'entropy of mixing',

$$TS = -k_B T \sum_{\alpha} c_\alpha \log c_\alpha, \qquad (1)$$

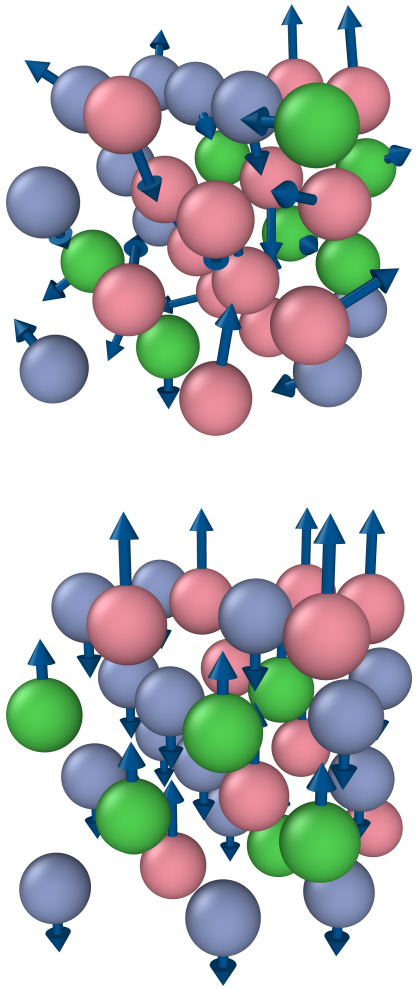
    makes 'significant' contribution to free energy.
  - Often superior physical properties for applications.
  - Of fundamental physical interest, too.





High-Entropy Alloys: Modelling Challenges

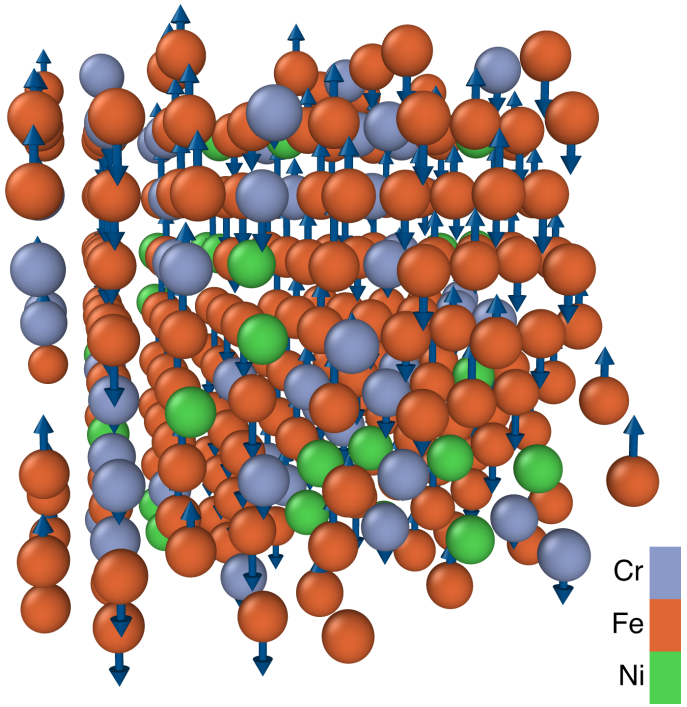
- Huge space of potential compositions, but most modelling results are specific to *one* particular composition.
- Even for one particular composition, need to inspect many possible atomic configurations.
- Magnetic elements: Fe, Mn, Ni, Co. Which magnetic state to model in DFT?



High-Entropy Materials: Modelling Solutions

Here, concerned with phase stability. A few options:

- 'Brute-force' DFT study: run DFT on many atomic configurations. *Hugely expensive*.
- Interatomic potentials, cluster expansions, MLIPs[1]. *Cheaper, but still need DFT training data.*
- Effective medium theories: average over disorder in a (clever) physically meaningful way. *Cheap!*



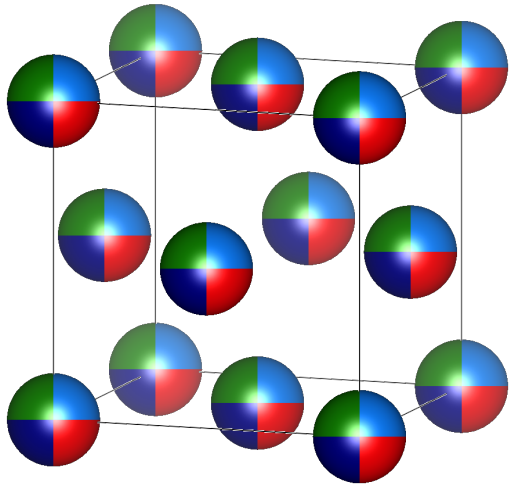
[1] Shenoy, Woodgate, *et al.*, Phys. Rev. Mater. **8** 033804 (2024).

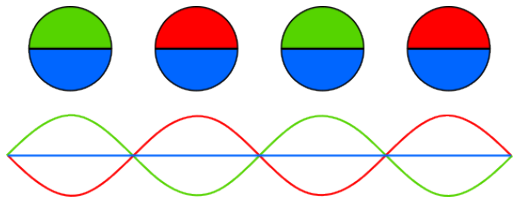
Modelling Approach

Our Description

Our approach uses the last option: an effective medium theory.

- Evaluate internal energy of fully disordered alloy within DFT using *Coherent Potential Approximation (CPA)*.
- Apply inhomogeneous chemical perturbation and assess energetic cost[2,3].
- Clever bit: do this using *concentration waves*, *i.e.* in **k**-space.





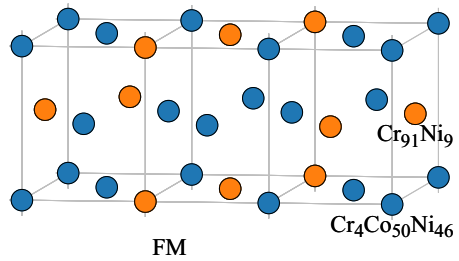
[2]Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022)
[3]Woodgate, Staunton, Phys. Rev. Mater **7** 013801 (2023)

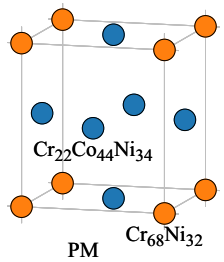
Inferring Orderings

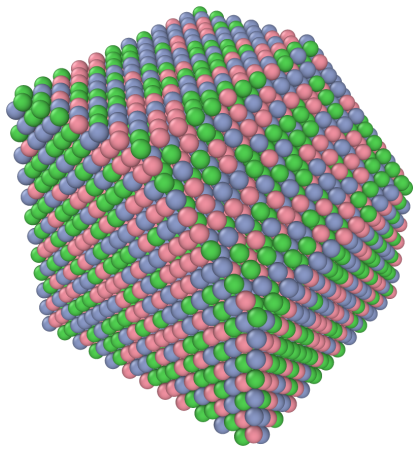
Two options:

- Option 1: infer orderings directly.
  - Perturbative analysis
    → Taylor expansion of Gibbs free energy.
    → Apply Landau theory.
- Option 2: lattice-based atomistic simulations.
  - Perturbative analysis
    → effective pair interactions.
    → Explore using *nested sampling*.

$$H(\{\xi_{i\alpha}\}) = \frac{1}{2} \sum_{\substack{i\alpha \\ j\alpha'}} V_{i\alpha;j\alpha'}\, \xi_{i\alpha}\xi_{j\beta}$$







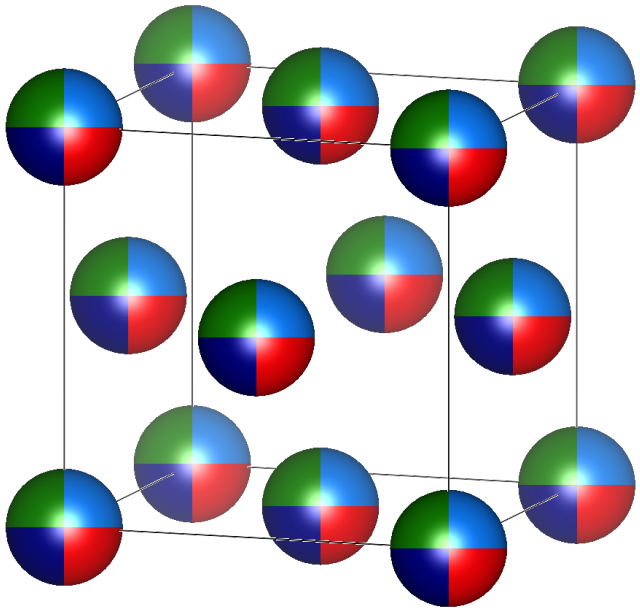
[4] Woodgate, Hedlund, Lewis, Staunton, Phys. Rev. Mater **7** 053801 (2023)

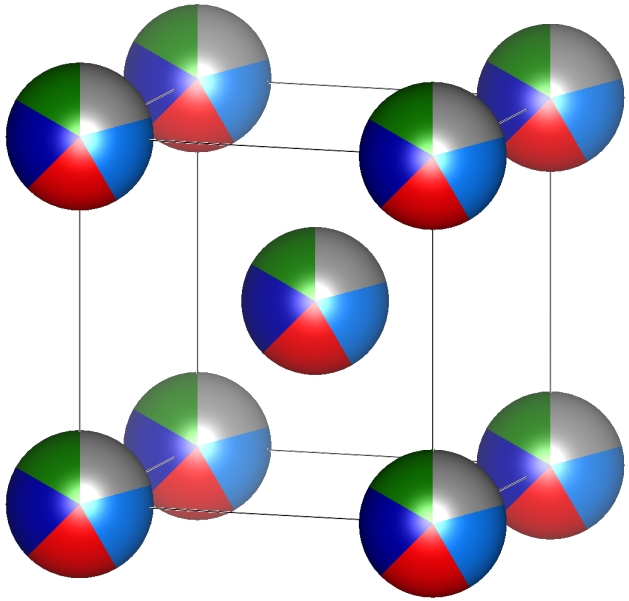
Successful Applications

- CrMnFeCoNi and derivatives.
  - C. D. Woodgate, J. B. Staunton, Phys. Rev. B **105** 115124 (2022).
- VNbMoTaW and derivatives.
  - C. D. Woodgate, J. B. Staunton, Phys. Rev. Mater. **7** 013801 (2023).
- Influence of Magnetism on Atomic Ordering.
  - C. D. Woodgate, D. Hedlund, L. H. Lewis, J. B. Staunton, Phys. Rev. Mater. **7**, 053801 (2023).
- Influence of Ti additions: Ti_xVNbMoTaW
  - C. D. Woodgate, J. B. Staunton, J Appl. Phys. **135** 135106 (2024).
- Al_xCrFeCoNi 'Superalloy'.
  - C. D. Woodgate, G. A. Marchant, L. B. Pártay, J. B. Staunton, arXiv:2404.01373.

Results

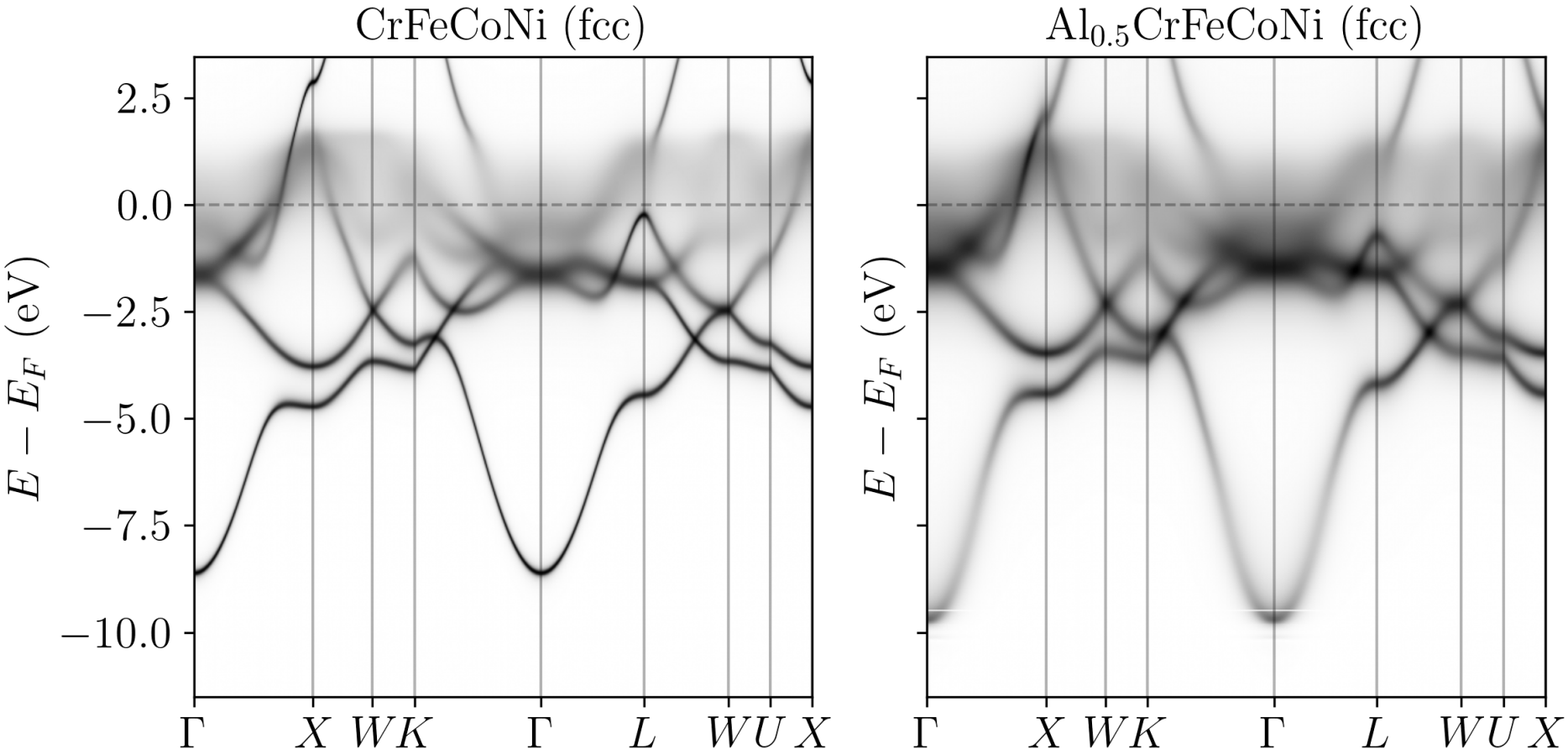
Case Study: $Al_xCrFeCoNi$





[5] Woodgate, Marchant, Pártay, Staunton, arXiv:2404.13173

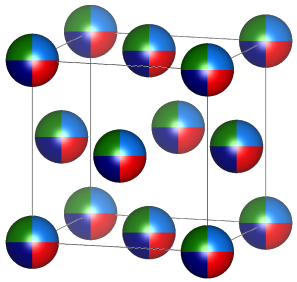
$Al_xCrFeCoNi$: Electronic Structure within CPA

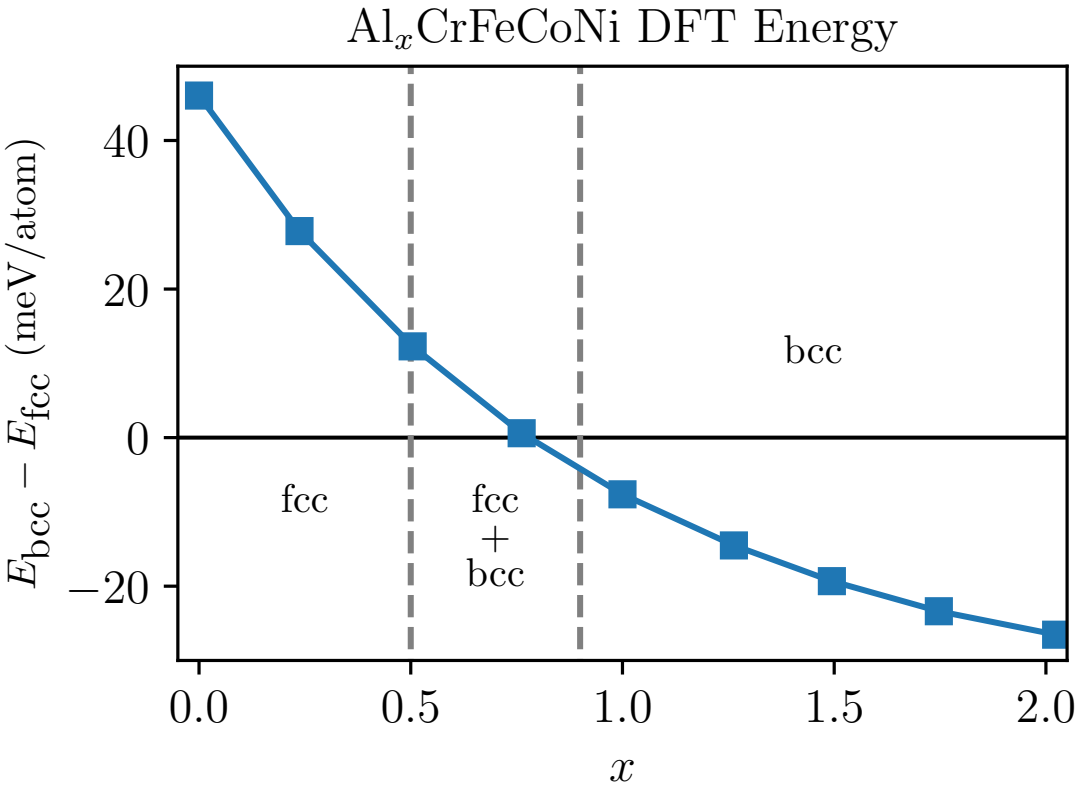


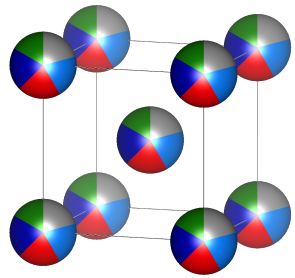
[5] Woodgate, Marchant, Pártay, Staunton, arXiv:2404.13173

$Al_xCrFeCoNi$: Underlying Lattice

Hutsepot

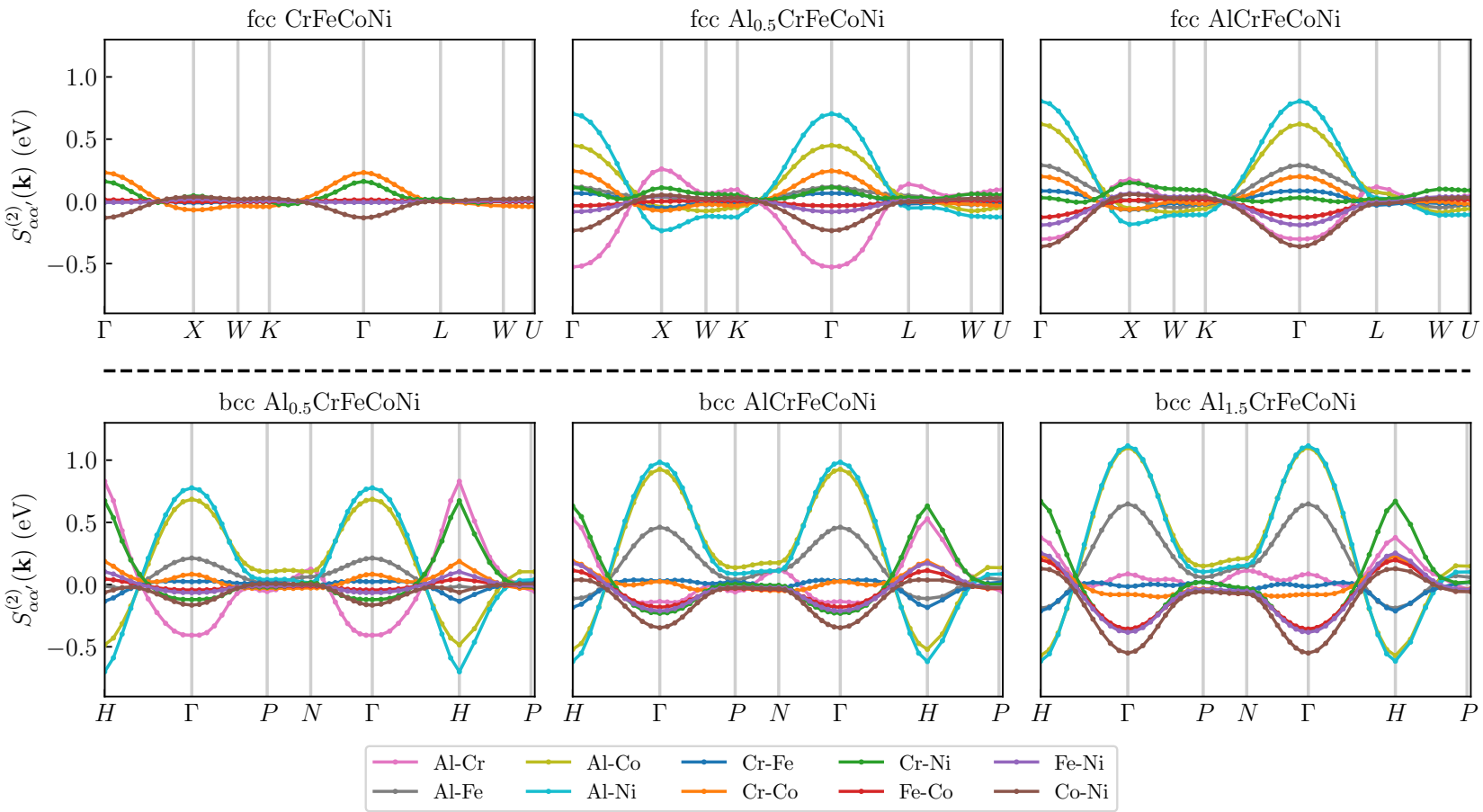






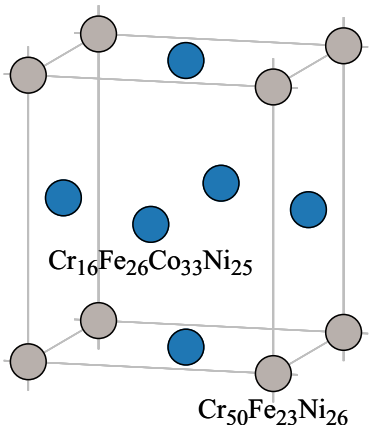
[5] Woodgate, Marchant, Pártay, Staunton, arXiv:2404.13173

$Al_xCrFeCoNi$: Perturbative Analysis

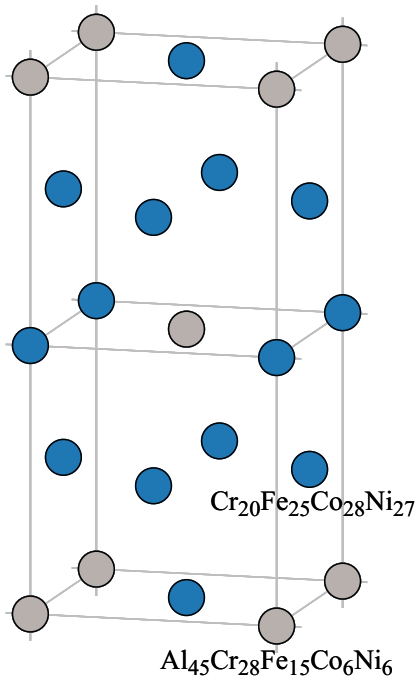


[5] Woodgate, Marchant, Pártay, Staunton, arXiv:2404.13173

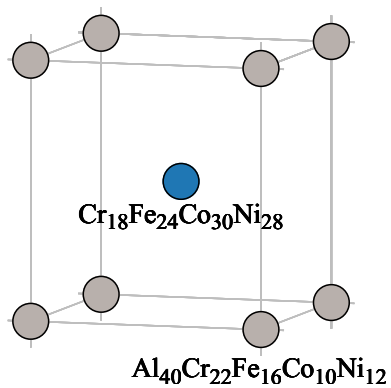
$Al_xCrFeCoNi$: Inferred Orderings



$x = 0$
$L1_2$



$x = 0.5$
$D0_{22}$



$x = 1$
B2

[5] Woodgate, Marchant, Pártay, Staunton, arXiv:2404.13173

$Al_xCrFeCoNi$: Ordering Temperatures

Lattice	Composition	T_{ord} (K)	$\mathbf{k}_{ord}$ $(2\pi/a)$	Structure
fcc	CrFeCoNi	380	(0,0,1)	$L1_2$
	$Al_{0.5}CrFeCoNi$	562	$(0,\frac{1}{2},1)$	$D0_{22}$
	AlCrFeCoNi	744	$(0,\frac{1}{2},1)$	$D0_{22}$
	$Al_{1.5}CrFeCoNi$	987	$(0,\frac{1}{2},1)$	$D0_{22}$
	$Al_2CrFeCoNi$	1082	(0,0,1)	$L1_2$
bcc	CrFeCoNi	488	(0,0,0)	Phase Seg.
	$Al_{0.5}CrFeCoNi$	1982	(0,0,1)	B2
	AlCrFeCoNi	3006	(0,0,1)	B2
	$Al_{1.5}CrFeCoNi$	3781	(0,0,1)	B2
	$Al_2CrFeCoNi$	4386	(0,0,1)	B2

High ordering temperatures consistent with experimental data.

[5] Woodgate, Marchant, Pártay, Staunton, arXiv:2404.13173

$Al_xCrFeCoNi$: Atomistic Modelling $\rightarrow$ Further Insight

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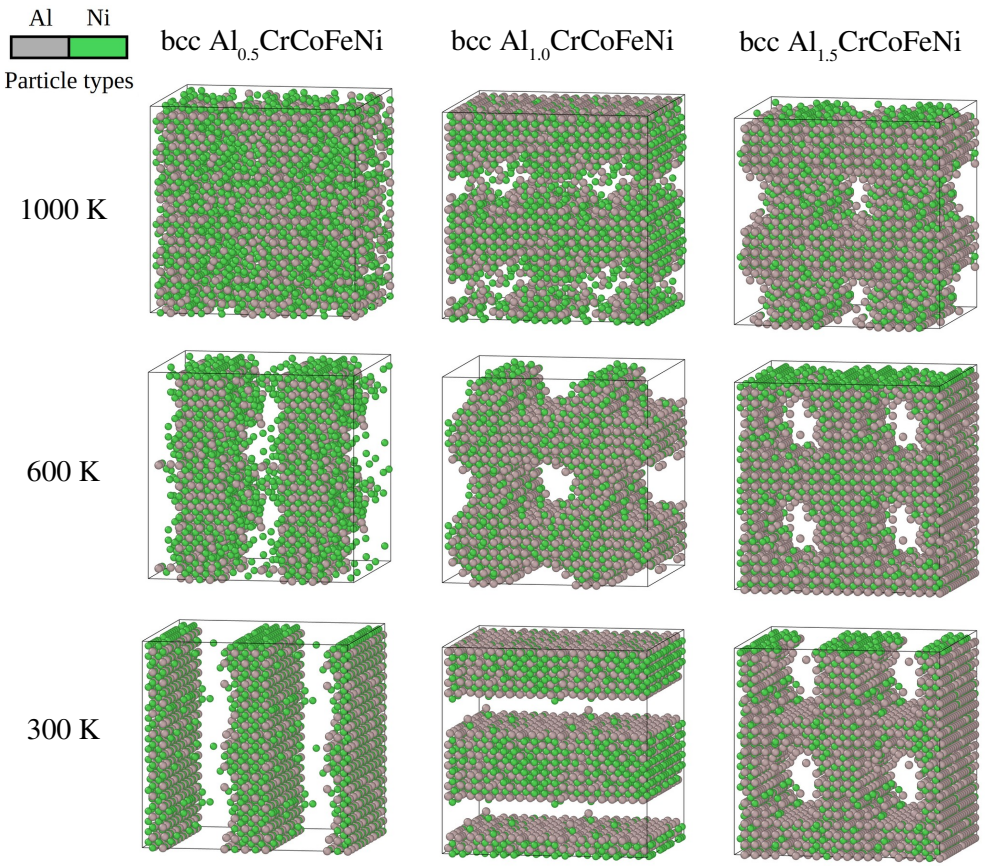


[5] Woodgate, Marchant, Pártay, Staunton, arXiv:2404.13173

Conclusions

Take-Home Messages

Coherent Potential Approximation (CPA)

CPA provides a *powerful* tool for modelling the electronic structure and internal energies of disordered, high-entropy systems for minimal computational cost.

Perturbative Analysis

Analysis of energetic cost of chemical fluctuations applied to homogeneous CPA medium can tell us about atomic ordering tendencies.

Superb Agreement with Experiment

For $\sim$ 1000 core-hours, can predict phase behaviour across range of compositions and temperatures.

Acknowledgements

Funding

- C.D.W. supported by a studentship within EPSRC-funded CDT: warwick.ac.uk/hetsys
- EPSRC (UK)

Upcoming Move

- C.D.W. will be moving to the University of Bristol (UK) from October.

Our paper: arXiv:2404.13173

People

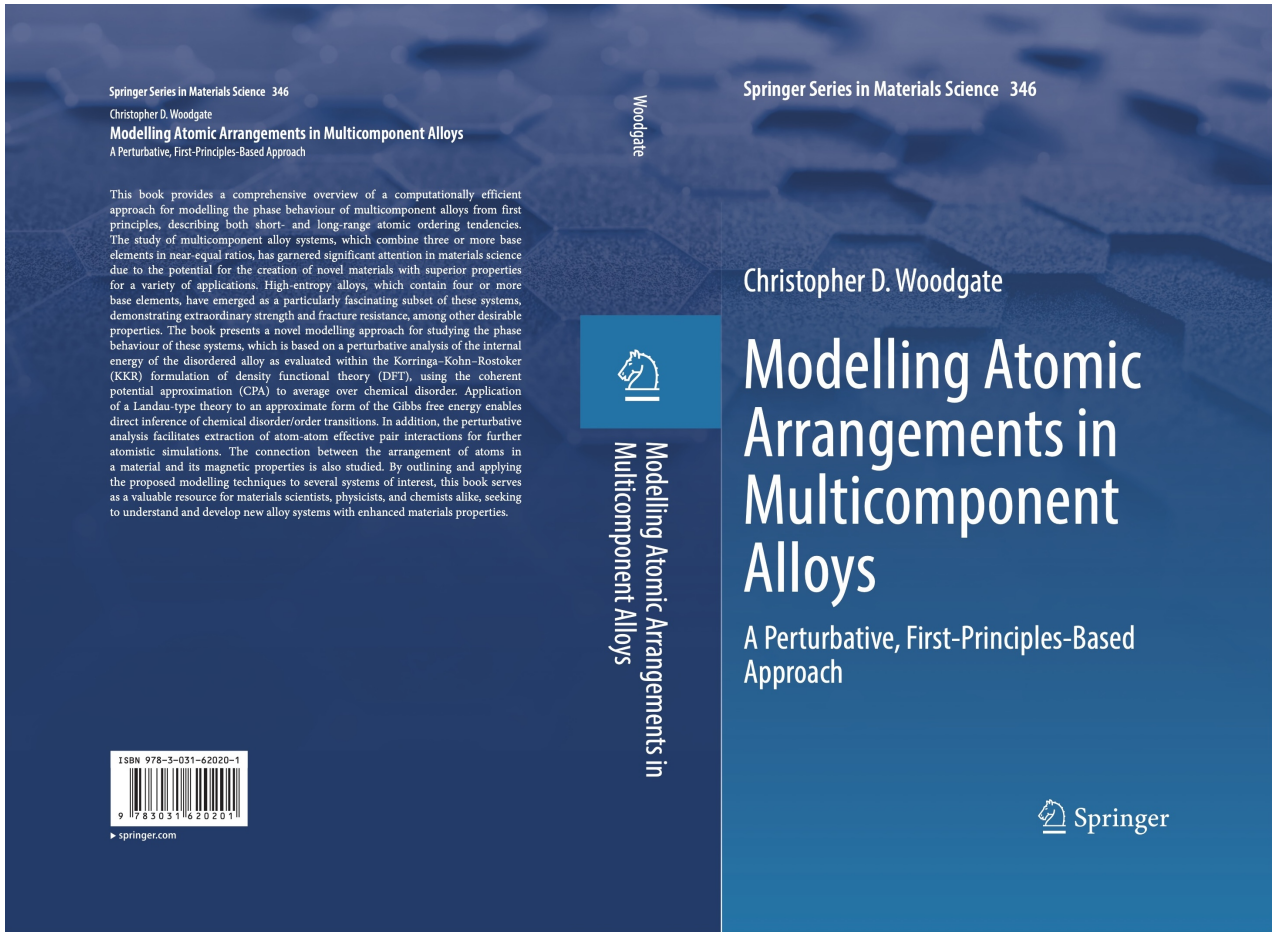
Department of Physics, University of Warwick, UK

- Christopher D. Woodgate
- George A. Marchant
- Julie B. Staunton

Department of Chemistry, University of Warwick, UK

- Livia B. Pártay

Recent Book:



[6] Woodgate, Springer Series in Materials Science, Vol. 346. (Springer Nature Switzerland, Cham, 2024).