Addressing Disorder

Modelling Alloys and Magnetic Materials Across Length Scales

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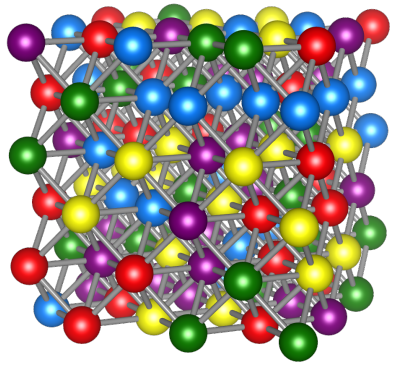
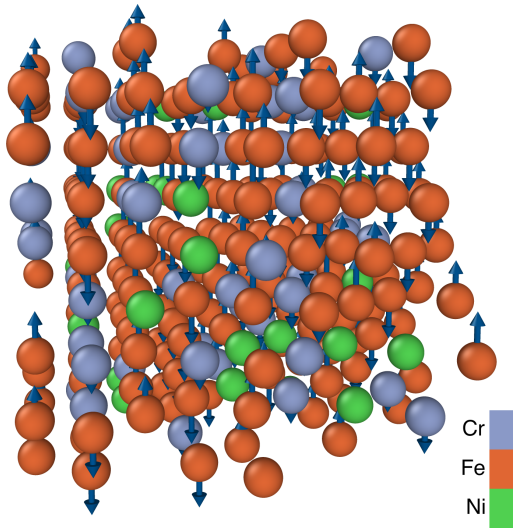


Talk Plan

1. Background and Motivation
   - 1.1 (Multicomponent) Alloys
   - 1.2 Magnetic Materials
   - 1.3 Modelling Challenges
2. Three Stories:
   - 2.1 High-Entropy Alloys: Phase Stability[1,2]
   - 2.2 Permanent Magnets: Thermal effects[3,4]
   - 2.3 Machine-Learned Interatomic Potentials[5]
3. Summary and Outlook



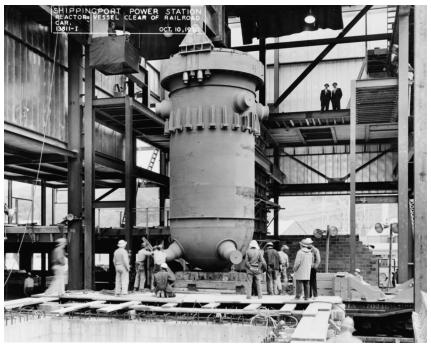
[1] Woodgate, Staunton, Phys. Rev. Mater. **7**, 013801 (2023).
[2] Woodgate, Staunton, J. Appl. Phys. **135**, 135106 (2024).
[3] Woodgate, Patrick, Lewis, Staunton, J. Appl. Phys. **134**, 163905 (2023).
[4] Woodgate, Lewis, Staunton, npj Comput. Mater. **10** 271 (2024).
[5] Shenoy, Woodgate, Staunton *et al.*, Phys. Rev. Mater. **8** 033804 (2024).

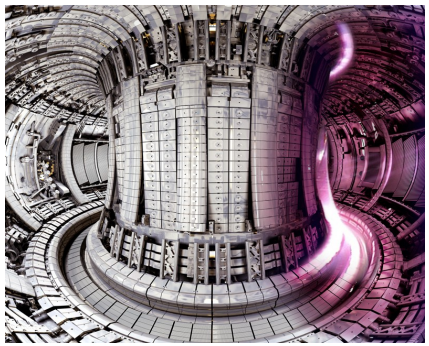
Background and Motivation

Alloys: Why Are We Interested?

So many of the materials around us are alloys.

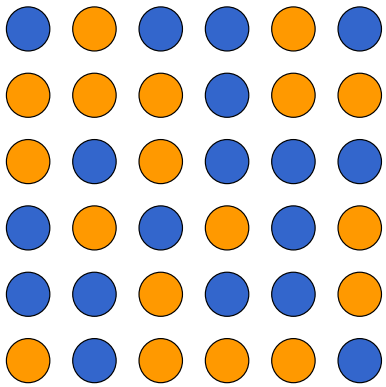
- Entire periods of human prehistory classified by use of alloys: 'Bronze Age', 'Iron Age'.
- Structural (steels, aluminium-based, titanium-based).
- Corrosion resistance (stainless steels).
- Magnetic (transformer cores, permanent magnets, magnetostrictive materials).
- Semiconductors (Band-gap tuning).



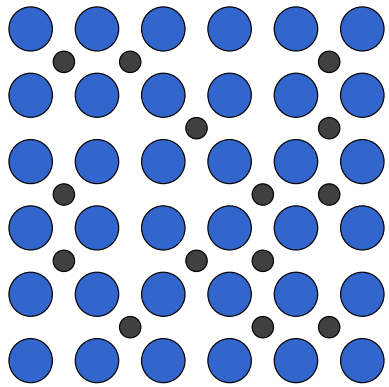


Atomic Arrangements: Substitutional *vs* Interstitial

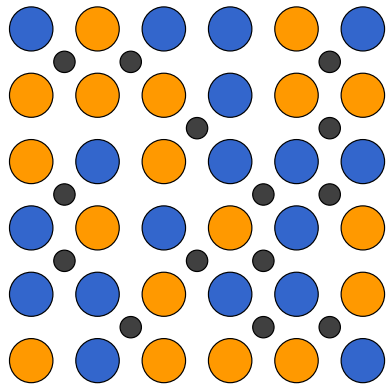
- Alloy: mixture of two or more (typically metallic) elements.
- Can be 'substitutional' or 'interstitial' (or both):
  - Substitutional: alloying atoms positioned randomly 'sharing' same lattice—they 'substitute' for one another. *E.g.* Cu + Au.
  - Interstitial: (smaller) alloying atoms squeeze into gaps—they sit at 'interstices'. *E.g.* Fe + C.
- Today: only worry about substitutional alloys.



Substitutional



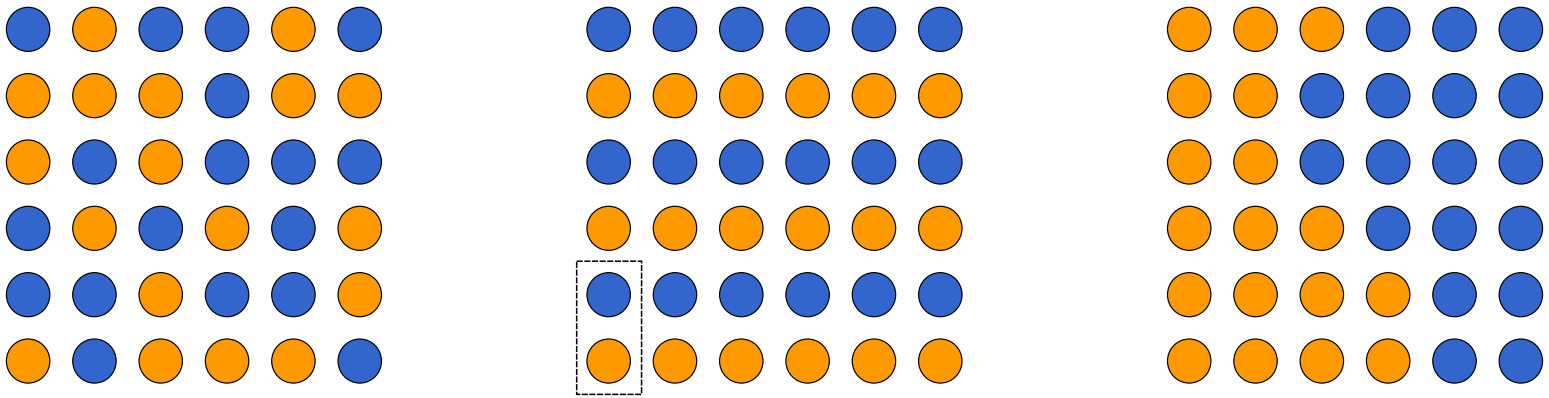
Interstitial



Both

Atomic Arrangements: Phase Diagrams

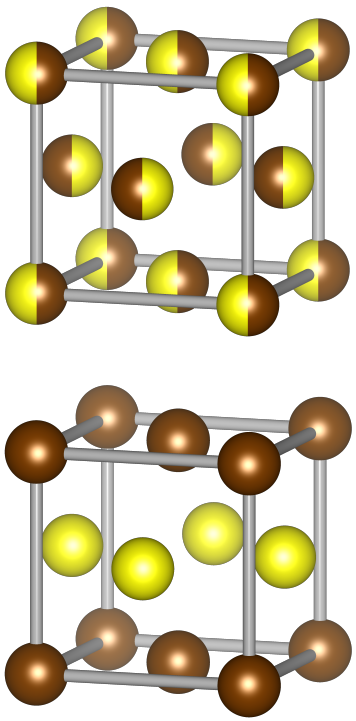
- Also need to consider how atoms are arranged.
- Do I have a 'solid solution', an 'intermetallic', or 'phase segregation', depending on processing conditions:
  1. Solid solution: random distribution of atoms.
  2. Intermetallic: repeating arrangement of atoms.
  3. Phase segregation: different elements stay separate.
- Today: will talk about modelling this for multicomponent alloys.

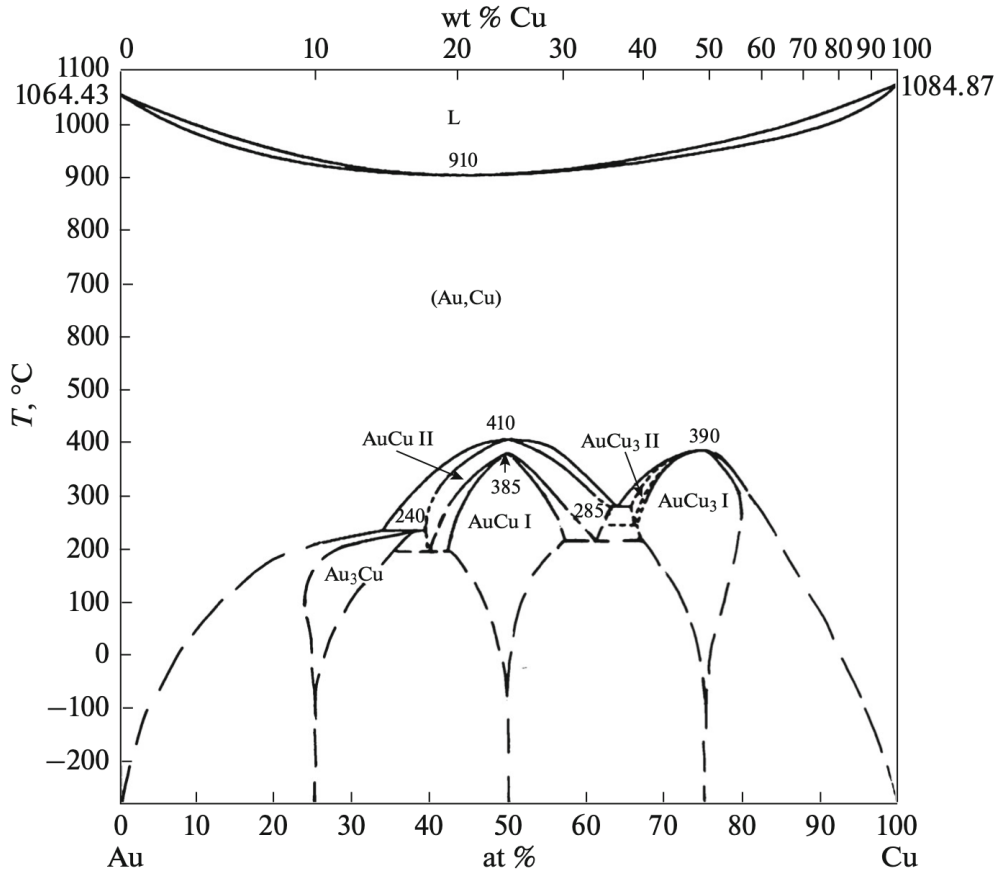


Solid Solution Intermetallic Segregation

Alloy Phase Diagram Example

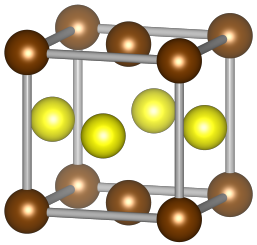
CuAu—3*d* Transition Metal + 5*d* Transition Metal.

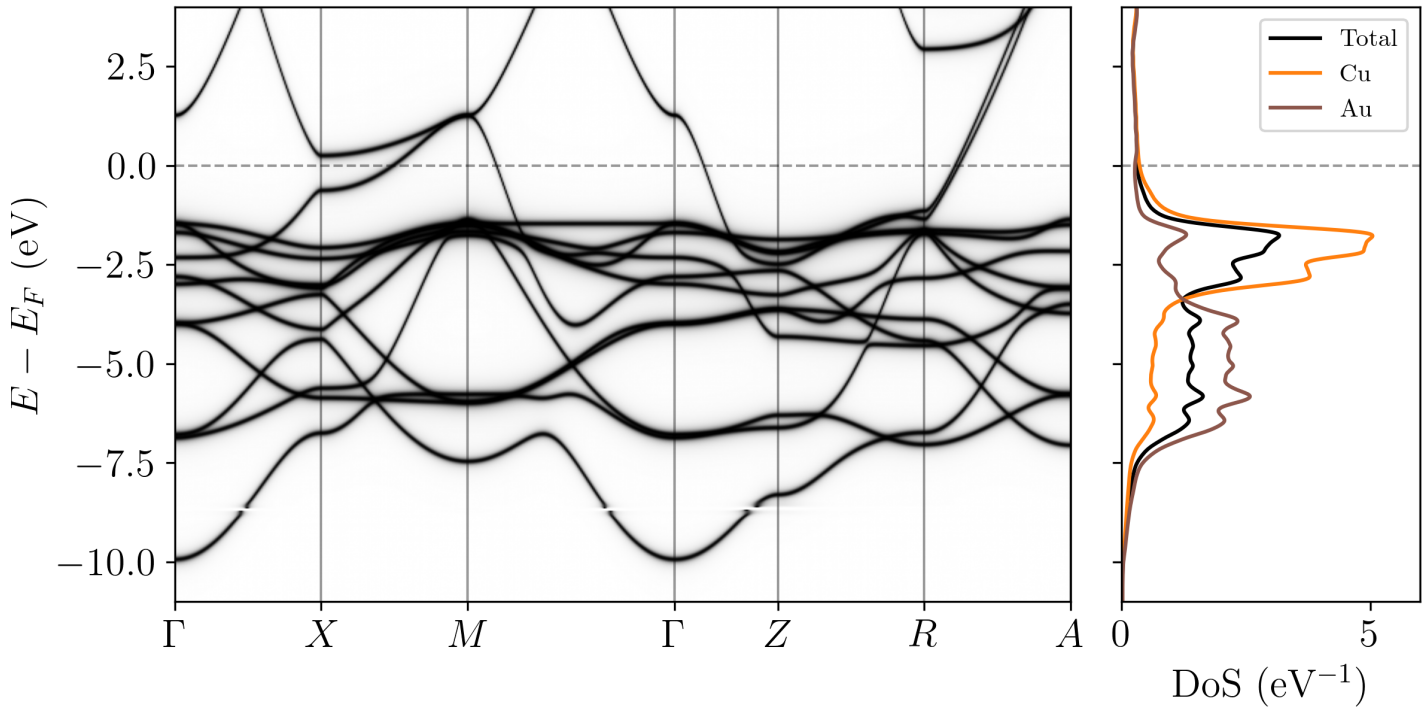




CuAu: Intermetallic ($L1_0$) Phase

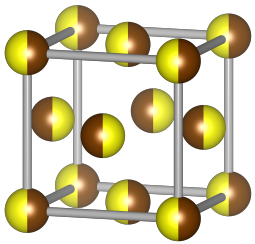
DFT Energy: -278894.253269 eV

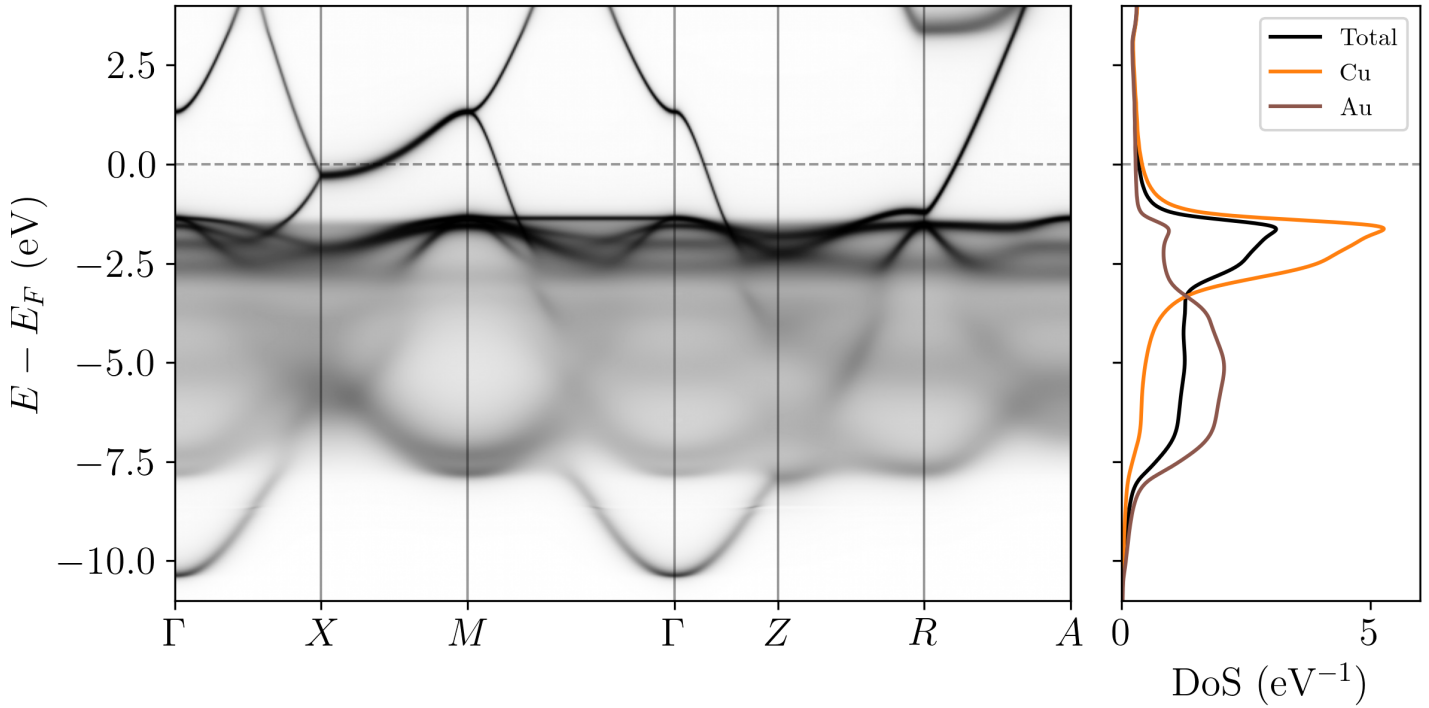




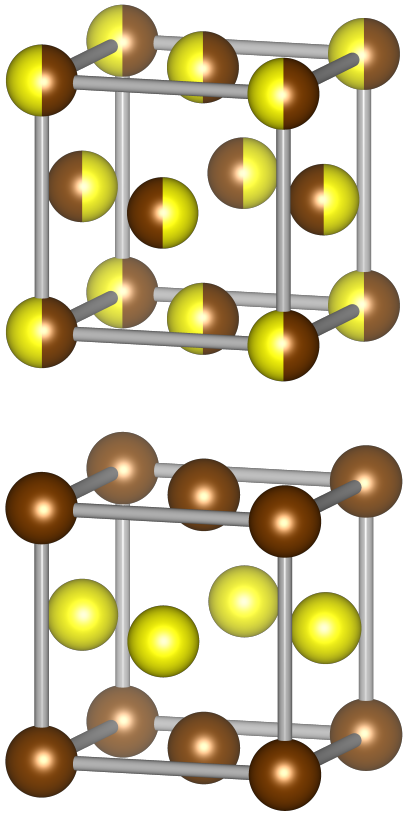
CuAu: Disordered (A1) Phase

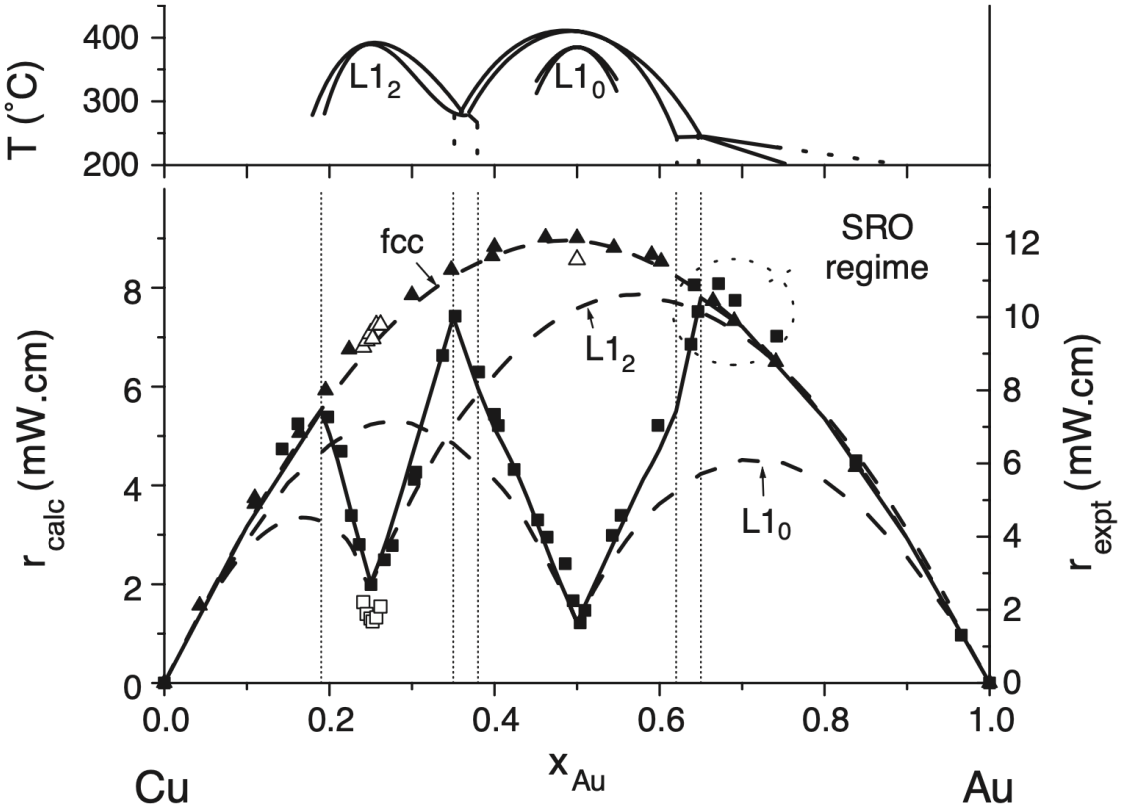
DFT Energy: -278894.077583 eV (Change of $+0.176$ eV/atom.)





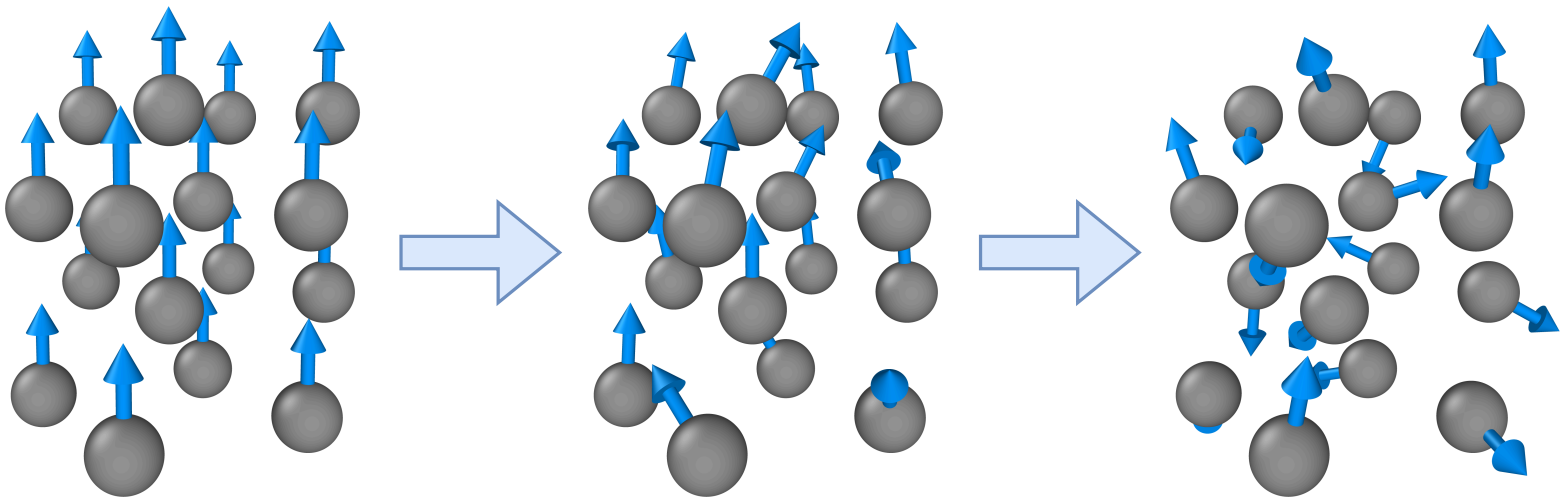
Example of Property Affected: Residual Resistivity





Magnetic Materials

- Magnetic moments, most generally:
  - Hund's rules $\rightarrow$ unpaired electrons.
  - Net spin polarisation (usually) localised around atoms.
  - Interactions between moments originate from 'sea' of electrons.
- Magnetism introduces a new degree of freedom



$T = 0$
$m = 1$

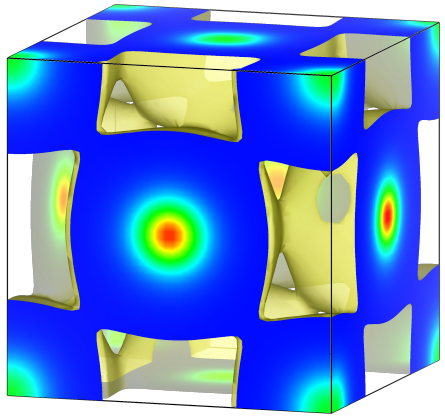
$0 < T < T_C$
$0 < m < 1$

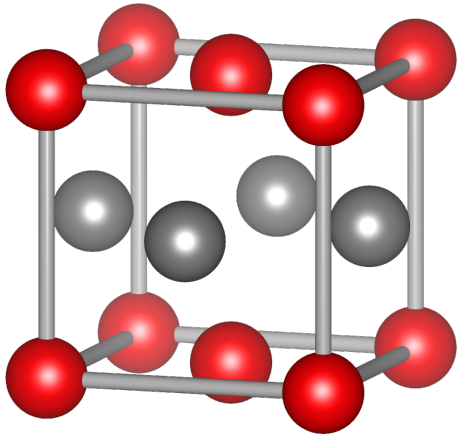
$T > T_C$
$m = 0$

Modelling 'Real' Materials

For me, three main 'lines of attack':

1. Density functional theory (DFT).
   - Sub-atomic length scale—ions and electrons.
   - (Approximately) solve the electronic many-body problem.
   - Learn about electronic structure.
2. Interatomic potentials, atomistic models.
   - Atomic length scale—ions and electrons.
   - Learn about forces, energies.
3. Statistical physics.
   - Recover bulk, equillibrium properties.

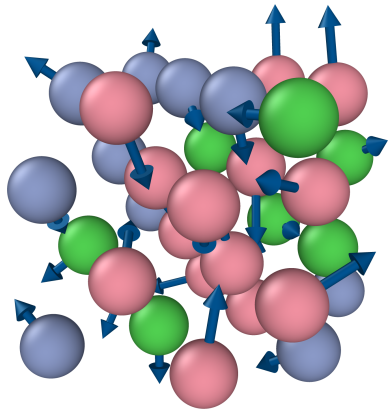


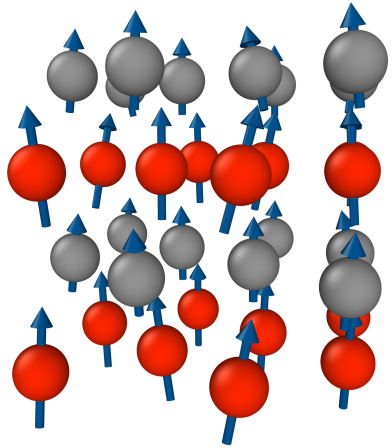


Disorder Presents Modelling Challenges

1. Compositional disorder—alloys.
   - Solid solution—no meaningful primitive unit cell.
   - How to handle elements at arbitrary concentrations?
2. Magnetic disorder—finite temperature.
   - Again, broken translational symmetry.
   - Non-collinear spin arrangements?

In a magnetic alloy, we need to worry about both of these aspects!





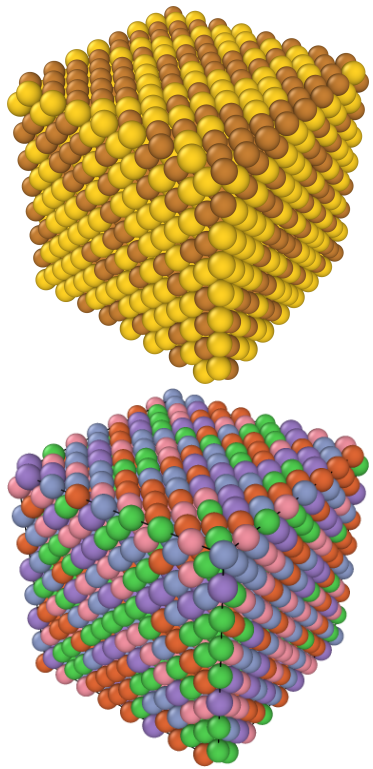
Story 1: Phase Equilibria in High-Entropy Alloys

High-Entropy Alloys: Background

- 'High-Entropy' Alloy
  - First reported in 2004.
  - Sufficiently many elements (4+) in right concentrations (near-equiatomic) that 'entropy of mixing',

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

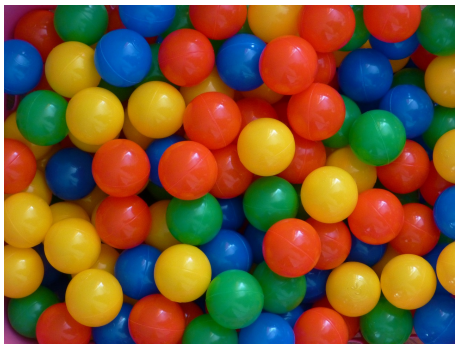
    makes 'significant' contribution to free energy.
  - Often superior physical properties for applications.
  - Of fundamental physical interest, too.
- Question: How do atoms preferentially arrange themselves at a given temperature?



High-Entropy Alloys: Phase Equilibria

Two options:

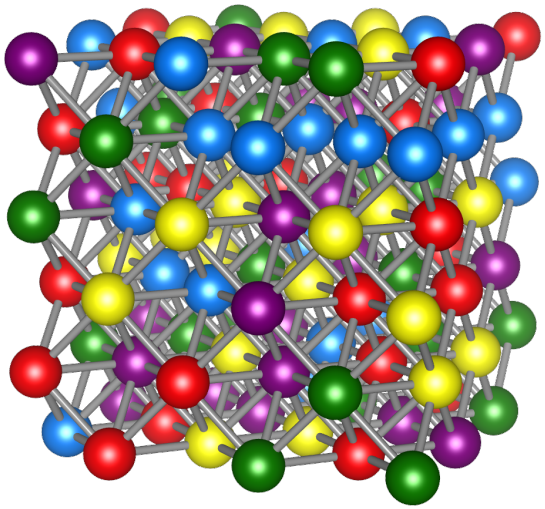
1. 'Ballpit' option:
   - Some kind of sampling algorithm on supercell (e.g. Metropolis Monte Carlo) to determine equilibria.
   - Get energies from DFT calculations, or cluster expansion, or interatomic potential.
2. 'Beachball' option:
   - Start from fully disordered system and assess the energetic cost of small chemical fluctuations.

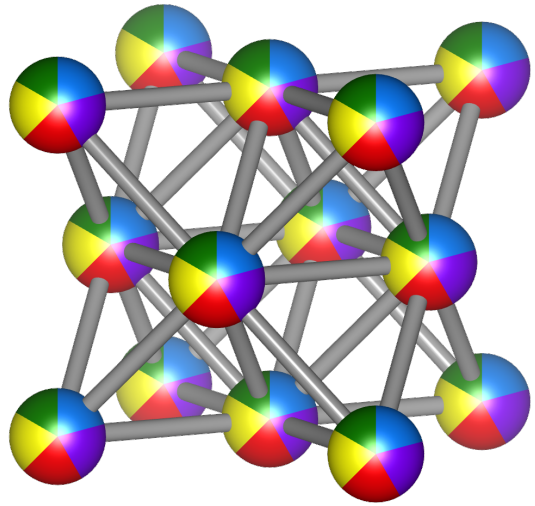


Our Approach: Beachball Option

We start by describing the internal energy of the disordered alloy:

- Do this using the 'coherent potential approximation' (CPA).
- Computationally cheap while accurately capturing many features of disordered phase.
- Folklore: gets 'better' the more disordered the system is.

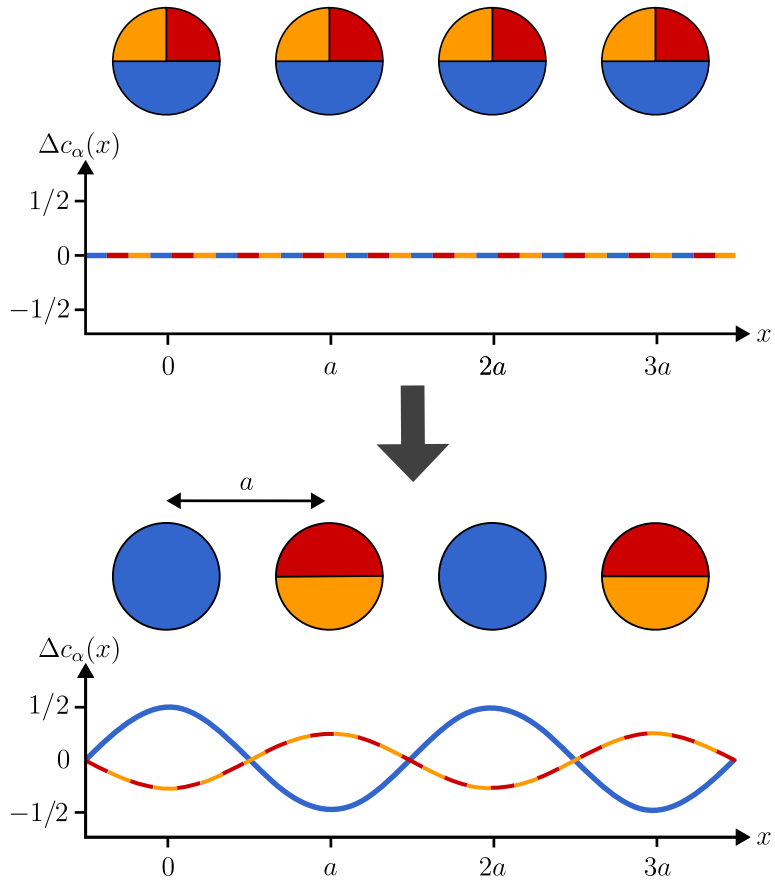




Concentration Waves: Describing Fluctuations

$$k = \frac{\pi}{a},\ \eta_\alpha = \frac{1}{\sqrt{2}}(1, -1)$$

- How to represent chemical fluctuations compactly and meaningfully?
  Concentration waves.
- Illustrative, 1D example.
- Alloy $S^{(2)}$ theory[6] tells me energetic cost of these fluctuations (in 3D!) using DFT and CPA.



[6] Woodgate, Staunton, Physical Review B **105**, 115124 (2022).
[7] Khan, Staunton, Stocks, Physical Review B **93** 054206 (2015)

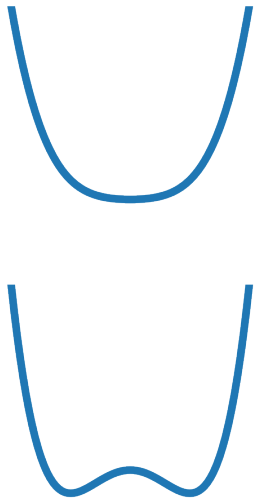
Alloys: Inferring Ordering—Landau Theory

- Write down (approximate) free energy,

$$G = TS - \mu N + U$$

$$G = \beta^{-1} \sum_{i\alpha} c_{i\alpha} \log c_{i\alpha} - \sum_{i\alpha}{}' \nu_{i\alpha} c_{i\alpha} + \langle \Omega_{\mathrm{el}} \rangle_0 [\{c_{i\alpha}\}],$$

and evaluate its derivative(s)[3].



- At some temperature, derivative will go negative—infer an ordering here.
- Actually, in our case, is eigenvalue of Hessian—eigenvector tells me about ordering.

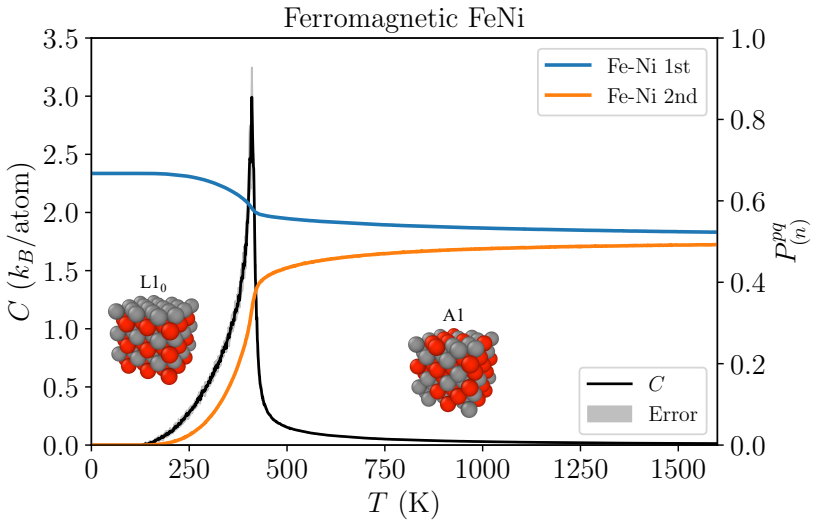
[6] Woodgate, Staunton, Physical Review B **105**, 115124 (2022).

Alloys: Inferring Ordering—Monte Carlo Simulation

- Conveniently, can also map derivatives of internal energy back to a simple, pairwise form of alloy internal energy:

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

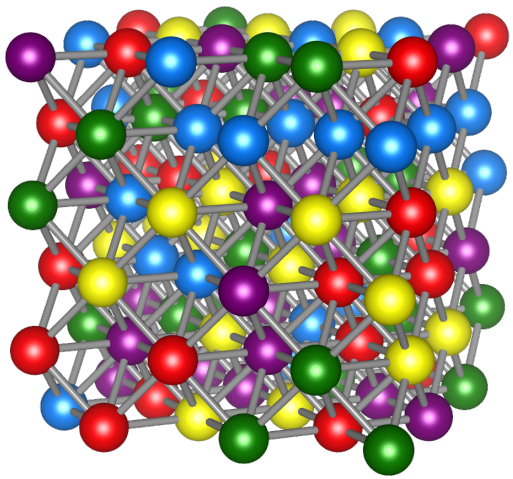
- Can then use sampling techniques to fully explore phase space.

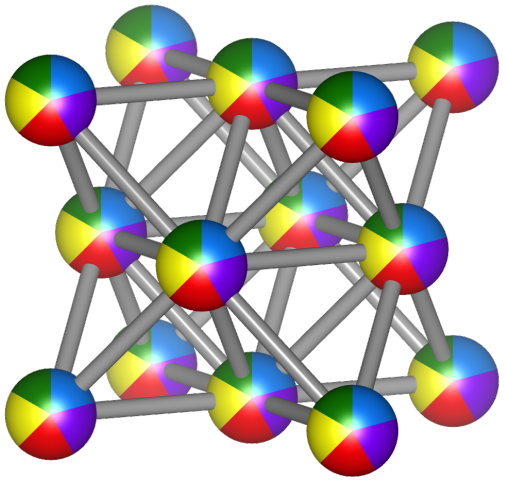


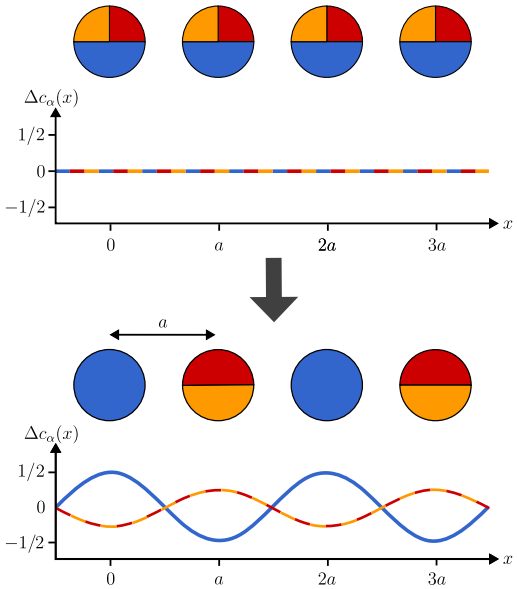
[6] Woodgate, Staunton, Physical Review B **105**, 115124 (2022).

Alloy Phase Stability Overview

Disordered Alloy → Effective medium → Concentration waves





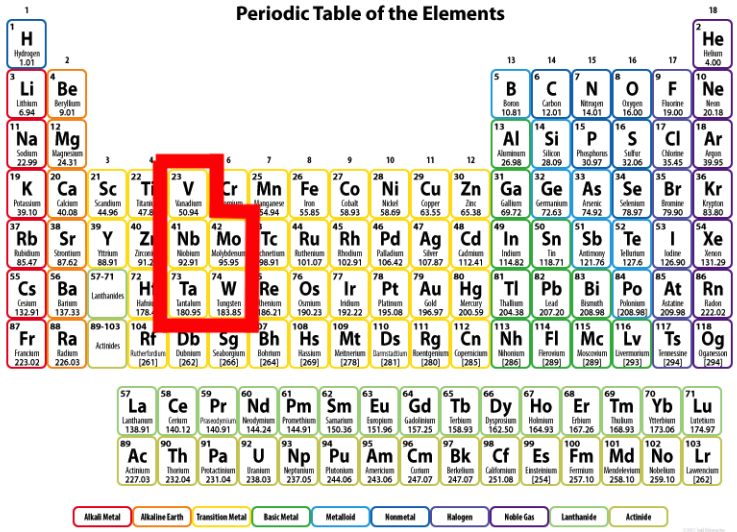


[1]Woodgate, Staunton, Physical Review Materials **7**, 013801 (2023).
[2]Woodgate, Staunton, Journal of Applied Physics **135**, 135106 (2024).
[6]Woodgate, Staunton, Physical Review B **105**, 115124 (2022).
[8]Woodgate *et al.*, npj Computational Materials **10**, 271 (2024)
[9]Woodgate *et al.*, Physical Review Materials **7**, 053801 (2023).

Application: Refractory HEAs

Refractory High-Entropy Alloys: Context

- Prototypical BCC HEAs.
- Typically V, Nb, Mo, Ta, W.

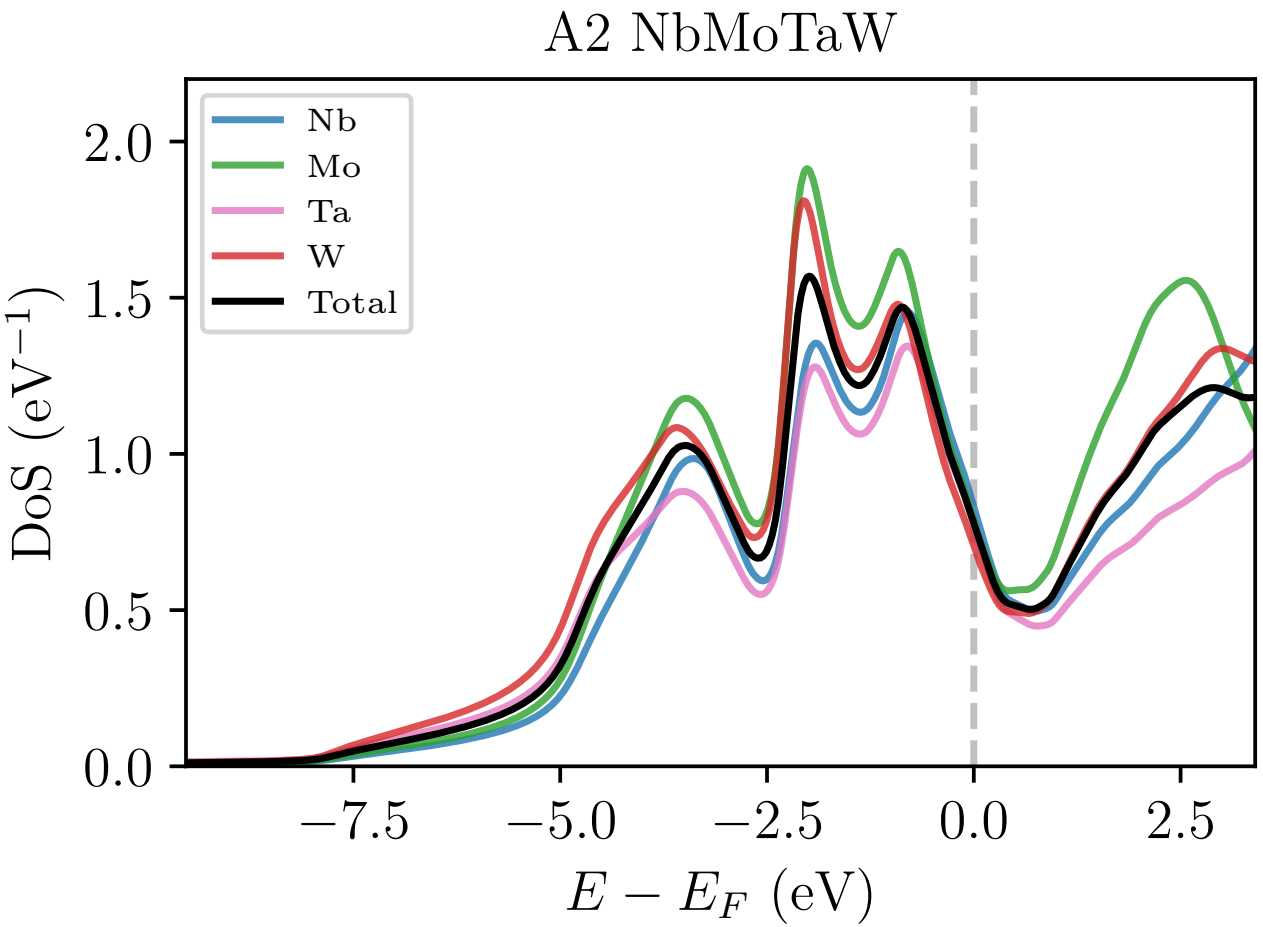


- Of interest for high-T, high-radiation applications.
- Focus on 4-component NbMoTaW.

[1] Woodgate, Staunton, Physical Review Materials **7**, 013801 (2023).
[2] Woodgate, Staunton, Journal of Applied Physics **135**, 135106 (2024).

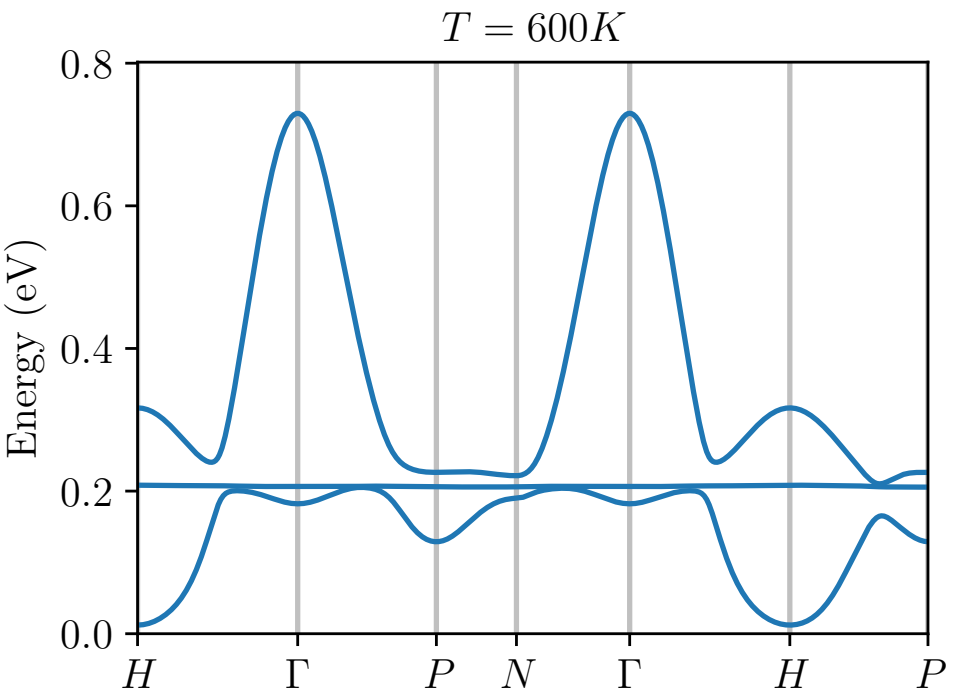
Refractory High-Entropy Alloys: Electronic Structure

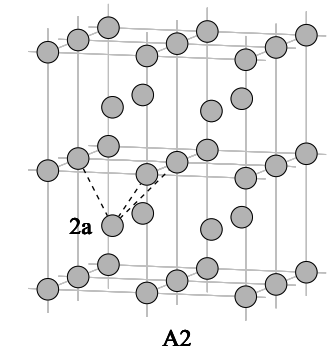
Electronic density of states around E_F within KKR-CPA.

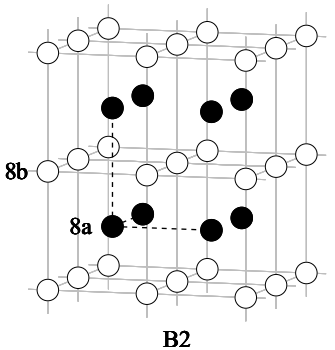


Refractory High-Entropy Alloys: Landau Theory

Minimum at H indicates B2-like ordering. Calculated $T_{ord} = 559$ K, $\eta_\alpha = (-0.42, 0.57, -0.57, 0.42)$.

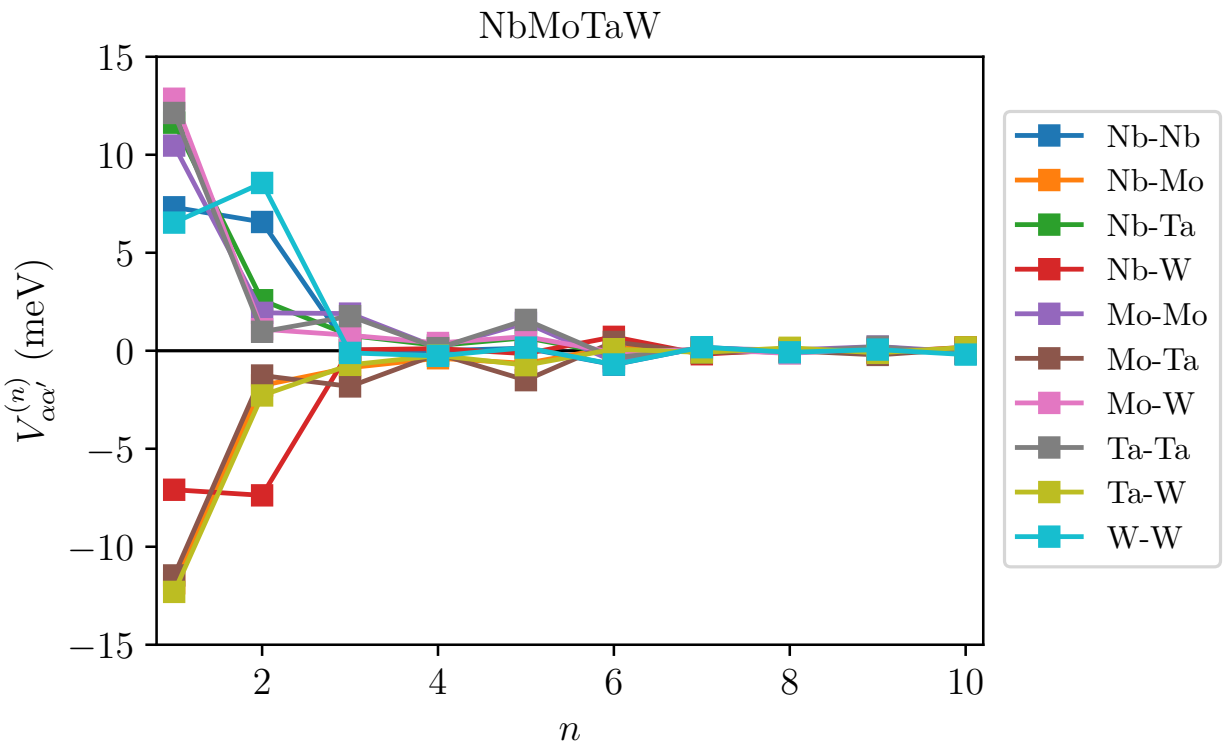


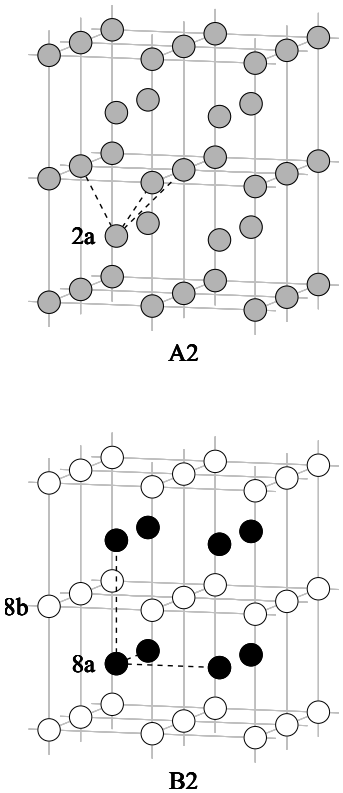




[1] Woodgate, Staunton, Physical Review Materials **7**, 013801 (2023).
[2] Woodgate, Staunton, Journal of Applied Physics **135**, 135106 (2024).

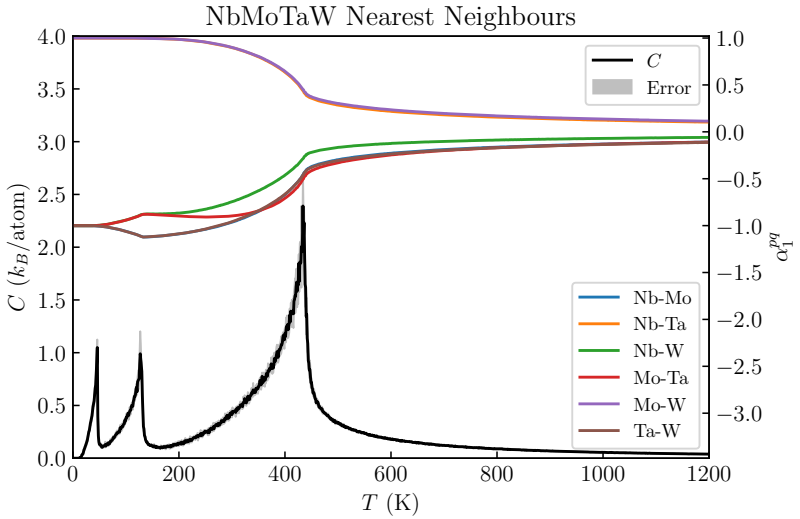
Refractory High-Entropy Alloys: Effective Pair Interactions

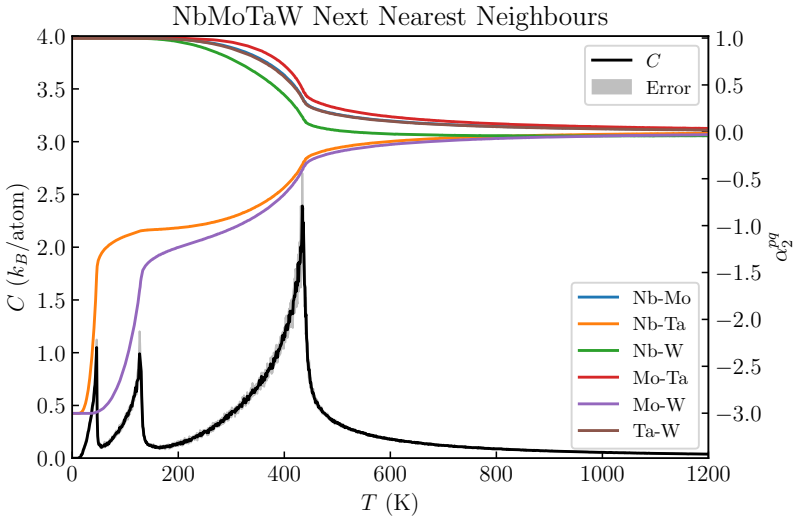


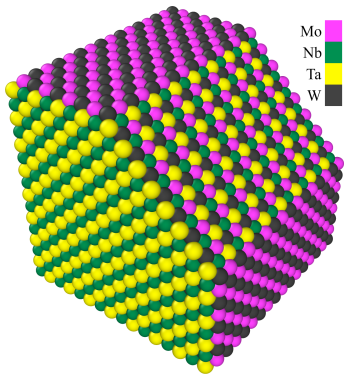


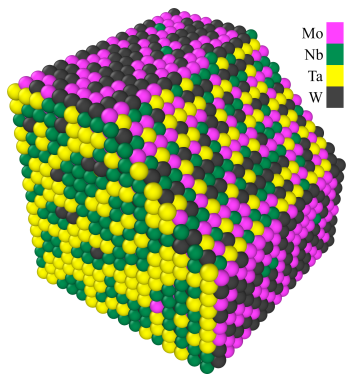
[1] Woodgate, Staunton, Physical Review Materials **7**, 013801 (2023).
[2] Woodgate, Staunton, Journal of Applied Physics **135**, 135106 (2024).

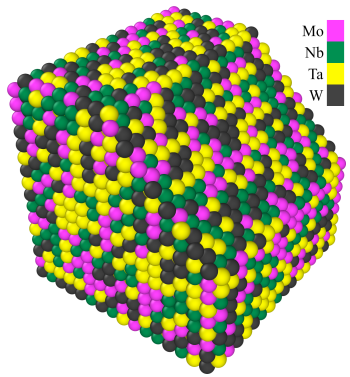
Refractory High-Entropy Alloys: Monte Carlo Simulation







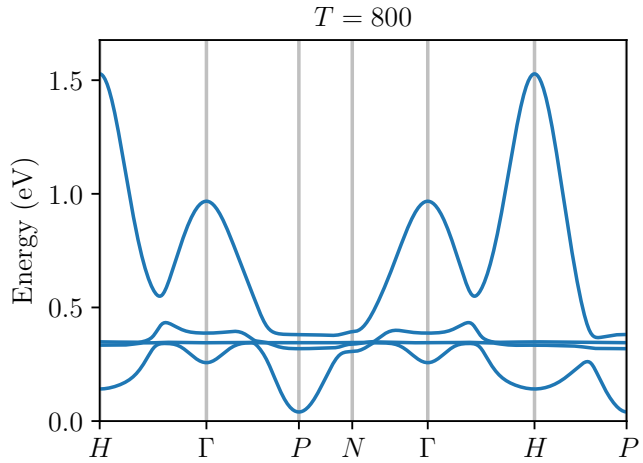


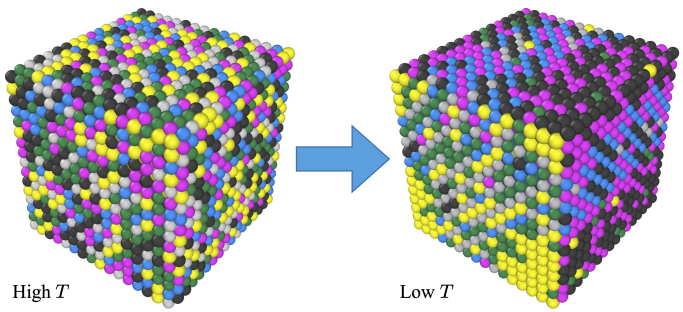


[1] Woodgate, Staunton, Physical Review Materials **7**, 013801 (2023).
[2] Woodgate, Staunton, Journal of Applied Physics **135**, 135106 (2024).

Refractory High-Entropy Alloys: Addition of V and Ti

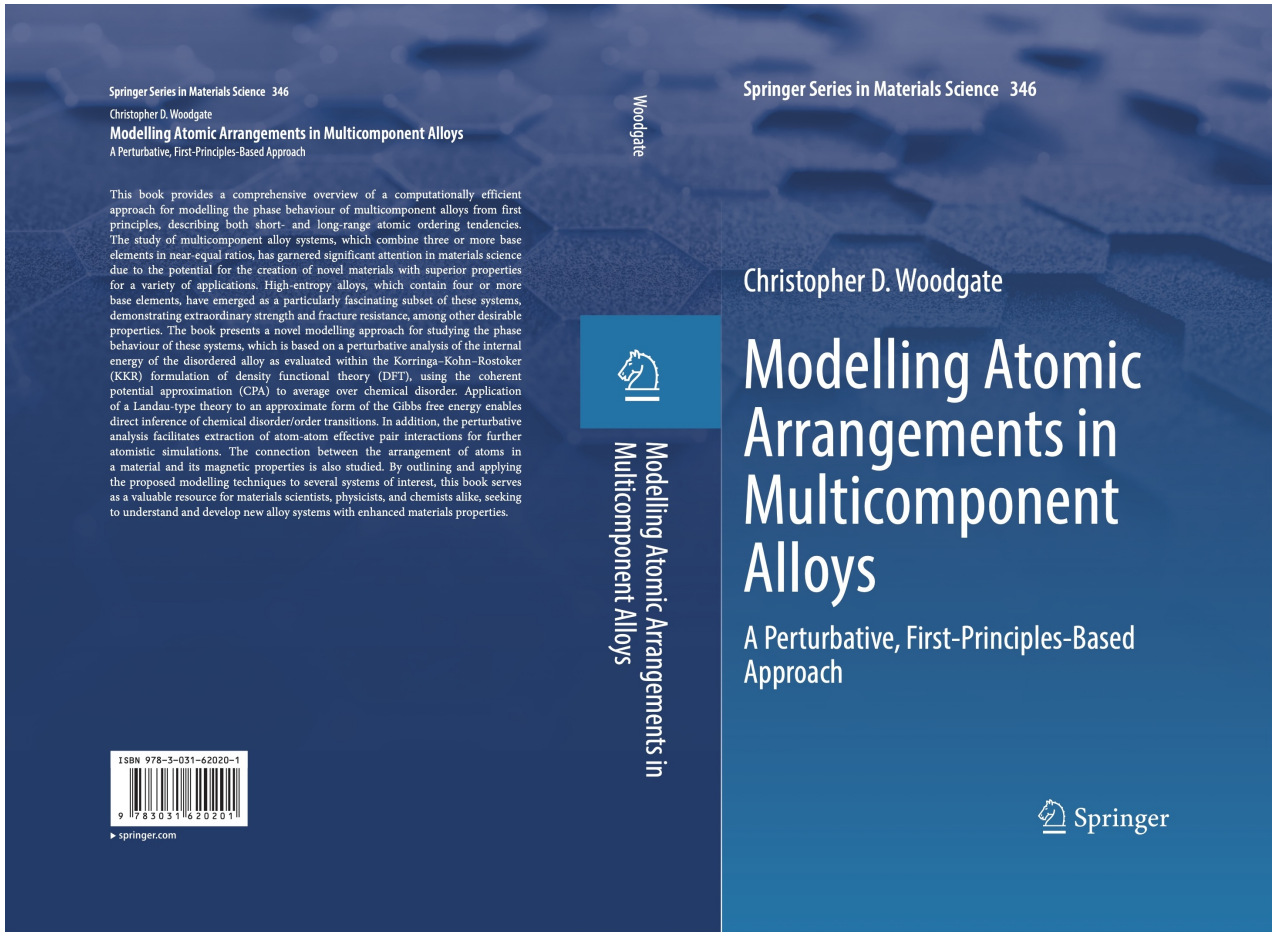
- Addition of V:
  - Charge transfer/bandwidth difference between $3d$ and $4d/5d$ elements drives B32 ordering.
- Addition of Ti (to improve ductility)[2]
  - B32-like ordering tendencies mixed with increased propensity for phase segregation.





[1] Woodgate, Staunton, Physical Review Materials **7**, 013801 (2023).
[2] Woodgate, Staunton, Journal of Applied Physics **135**, 135106 (2024).

More Information? Book



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

Take-Home

Story 1: Concentration Waves in High-Entropy Alloys

Concentration waves provide a powerful tool for exploring HEA phase space.

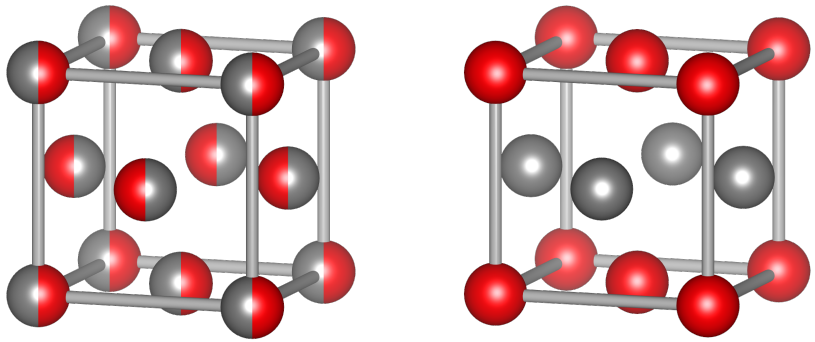
Story 2: Finite Temperature Effects in Magnets

Permanent Magnets: Why Do We Care?

- 'Hard' permanent magnet: resists being demagnetised.
- Particularly important for 'green' technologies.
- Currently heavily reliant on rare-earth elements, Nd, Sm, ...
- Seeking alternative materials to diversity supply chain and fill current capability 'gap'.

$L1_0$ FeNi: A Potential 'Gap' Magnet?

- Case for $L1_0$ FeNi (tetrataenite)[7]:
  - Theoretical $|BH|_{max}$ of 335 kJm^{-3}.
  - Good high-T performance[1]. Curie temperature $T_C > 830\ K$.
- BUT currently challenging to synthesise:
  - As cast, get disordered (A1) structure.
  - Need ordered $L1_0$ phase for hard magnetic properties.
- Can modelling help address this challenge?

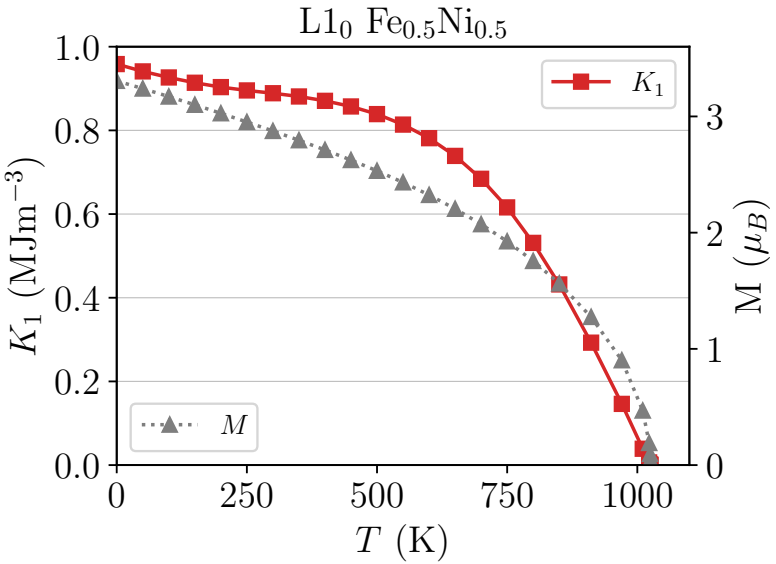


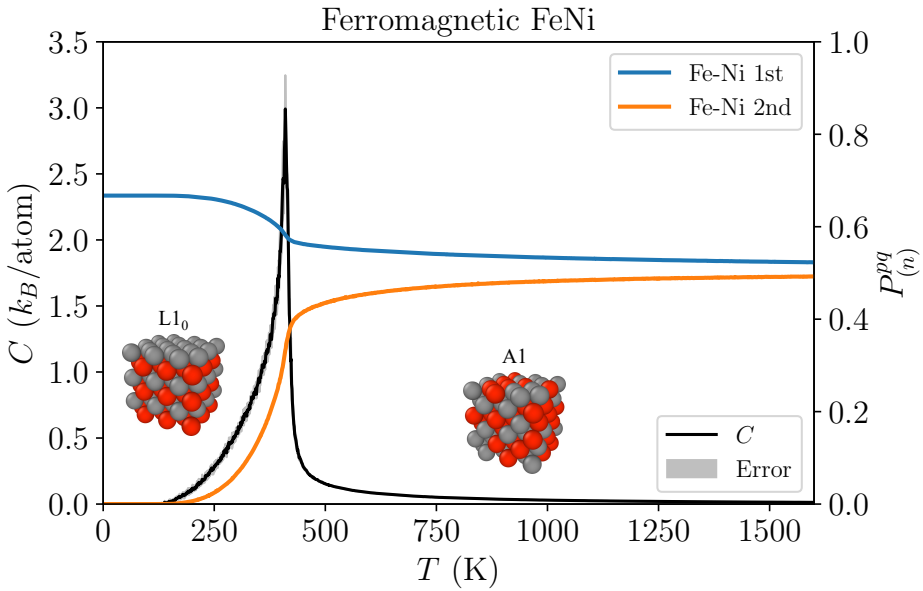
[1]Woodgate, *et al.*, J. Appl. Phys. **134**, 163905 (2023).

[11]Lewis *et al.*, J. Phys.: Condens. Matter **26** 064213 (2014).

$L1_0$ FeNi: Temperature Dependence of Anisotropy

- Modelled the temperature dependence of magnetic properties[3].





- Have also worked on controlling atomic 'layering'[4].

[3] Woodgate, Patrick, Lewis, Staunton, J. Appl. Phys. **134**, 163905 (2023).
[4] Woodgate, Lewis, Staunton, npj Comput. Mater. **10** 271 (2024).

Take-Home

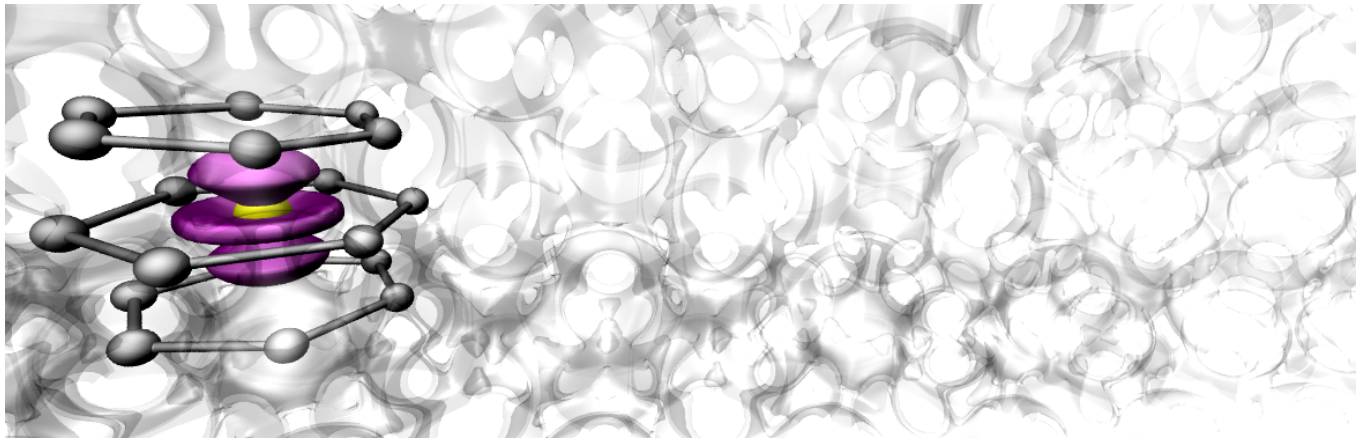
Story 2: $L1_0$ FeNi

Need to incorporate both magnetic and compositional disorder to compare with experiment.

Story 3: MLIPs for Alloys

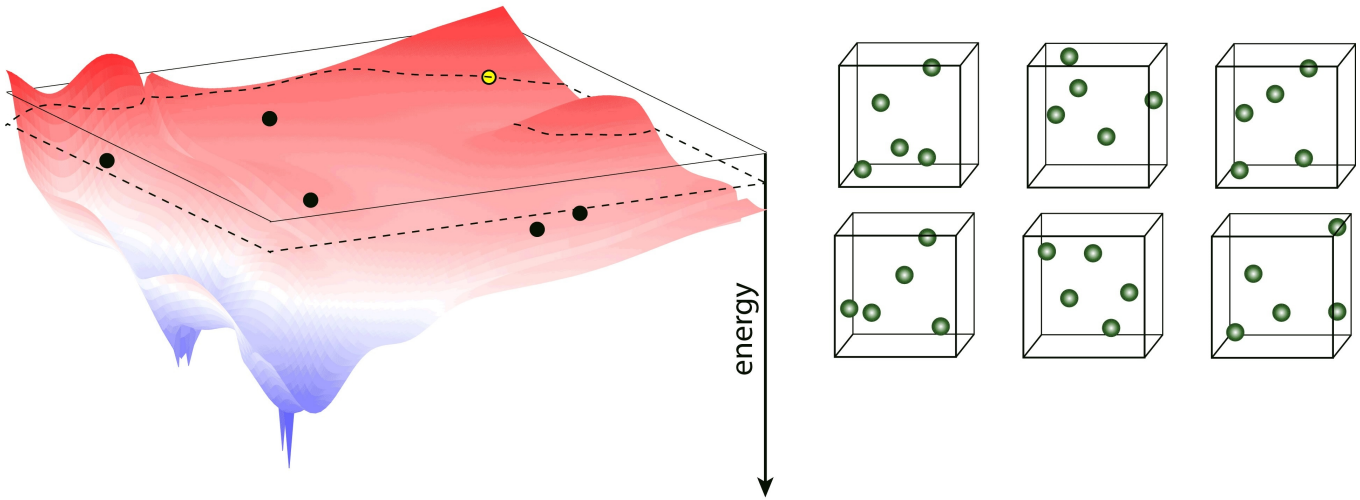
DFT is *great*, but 'expensive'

- DFT $\rightarrow$ learn about materials with QM accuracy.
- Can get forces, energies, magnetic moments, *etc.*
- But calculations are expensive to run for large systems.
  - Usually $O(N^3)$ scaling.
  - 'Linear scaling' methods have higher base cost.
- One 'single point' calculation on a largeish supercell?
  $\sim$1000 core hours.



Do we always need to do DFT?

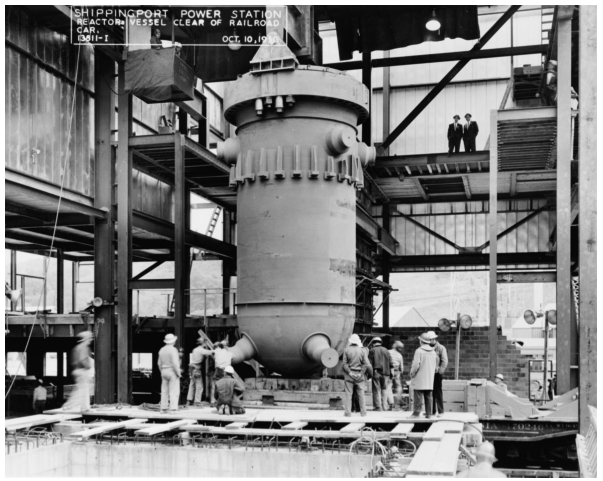
- In most studies, we examine many 'similar' atomic configurations.
- Forces/energies should vary smoothly between configurations.
- Q: Can we 'learn' this unknown 'potential energy surface'?
- A: Yes, many established ways of doing do.



[12] Image credit: Livia Bartok-Partay, University of Warwick

Example: Stainless Steel, Fe_7Cr_2Ni

- End goal: study failure of material, which requires long length/time scales.
- We developed a Gaussian Approximation Potential (GAP).
- Incorporated magnetic degree of freedom on Fe atoms—'Spin GAP'.



PHYSICAL REVIEW MATERIALS **8**, 033804 (2024)

Collinear-spin machine learned interatomic potential for Fe_7Cr_2Ni alloy

Lakshmi Shenoy[1,*] Christopher D. Woodgate[2] Julie B. Staunton[2] Albert P. Bartók[1,2] Charlotte S. Becquart[3] Christophe Domain[4] and James R. Kermode[1]

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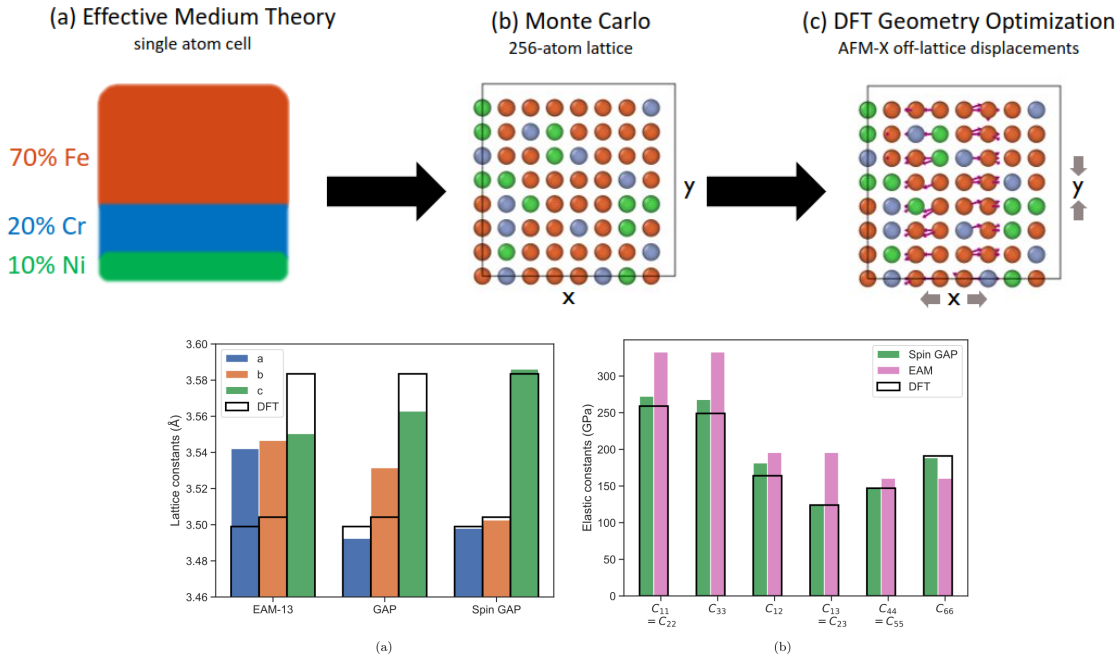
[5]Shenoy, Woodgate, Staunton *et al.*, Phys. Rev. Mater. **8** 033804 (2024).

Model is as accurate as DFT with much-reduced cost

- Can model elastic properties, vacancies, short-range order, . . .



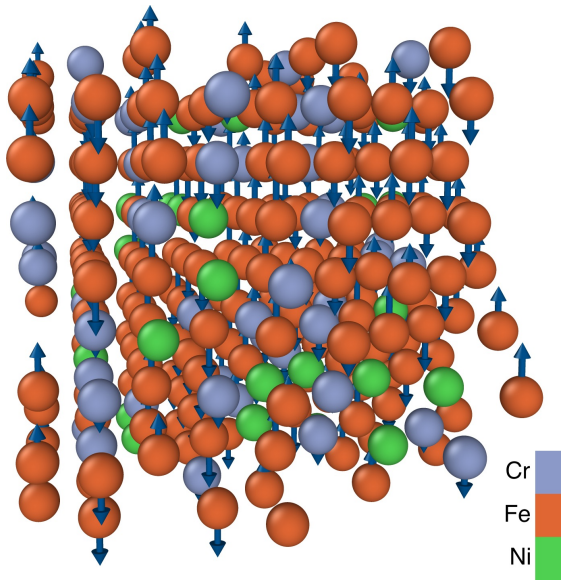


FIG. 4. (a) Lattice constants (a), (b), (c) averaged over 400 configurations predicted by EAM, GAP, and spin GAP for the AFM state,

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

Take-Home

Story 3: Machine-Learning for Materials Modelling

Machine-learned interatomic potentials can help us model magnetic materials accurately at reduced cost.

Summary and Outlook

Summary

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Concentration waves provide a powerful tool for exploring HEA phase space.

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Story 3: Machine-Learning for Materials Modelling

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