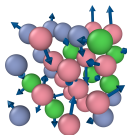


Modelling Atomic Arrangements in Multicomponent Alloys: A First-Principles-Based Approach

Christopher D. Woodgate

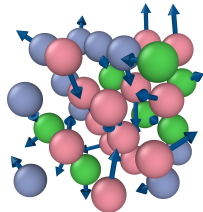
University of Warwick, Coventry, UK

Bristol Quantum Matter Seminar, 20th October 2023



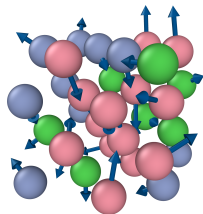


Talk Outline



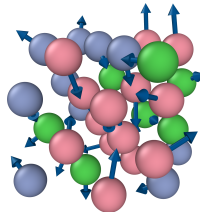
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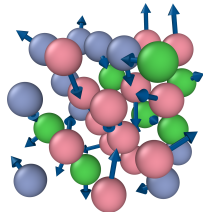
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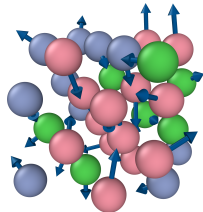
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- ▶ Outlook: where are we going?



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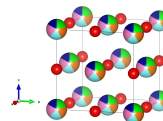
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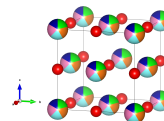
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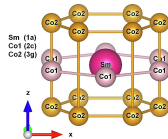
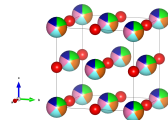
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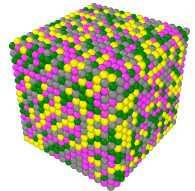


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 - ▶ 'High Entropy Magnets', e.g. $\text{SmCo}_5 \rightarrow \text{Sm}(\text{FeCoNi})_5$.

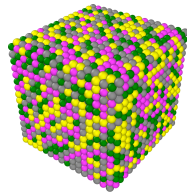


Focus on High-Entropy Alloys



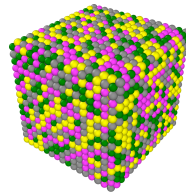
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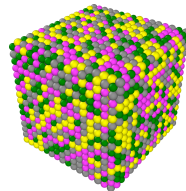
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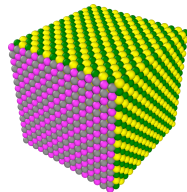
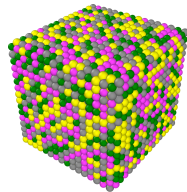
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- ▶ At what temperature will order emerge? What is the nature of order? Short-range? Long-range? Effect on materials properties?



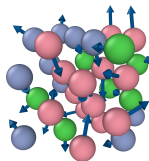
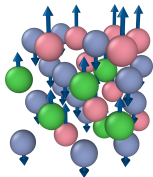
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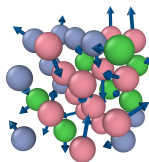
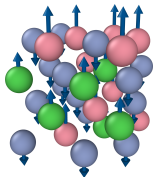
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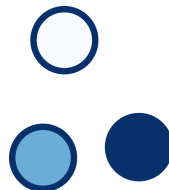
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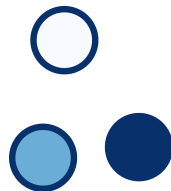
- ▶ Would like a *computationally efficient* modelling approach to assess phase stability. Can we do forward modelling?

Describing Atomic Configurations



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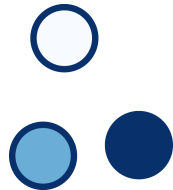
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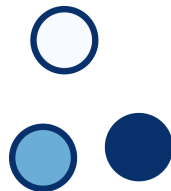
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- ▶ Above order-disorder transition temperature, these are *homogeneous*:

$$\lim_{T \rightarrow \infty} c_{i\alpha} = c_{\alpha}.$$



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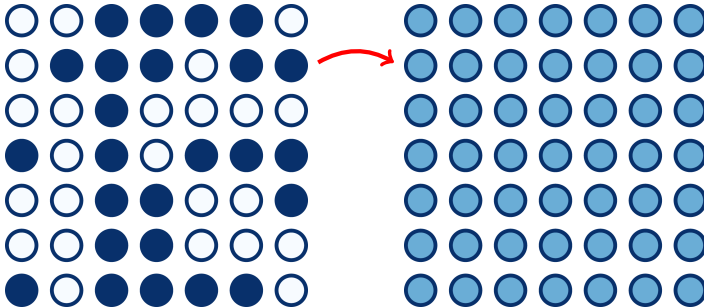
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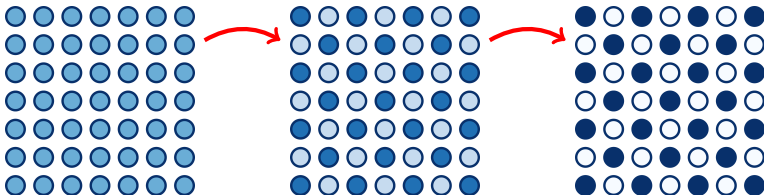
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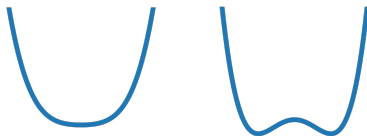
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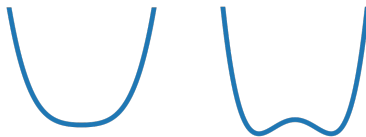
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- ▶ Assess energetic cost of perturbations to homogeneous reference state.
 - ▶ Infer both short-range order and phase stability.

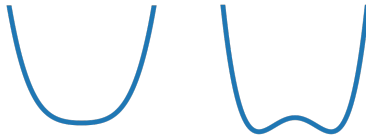


Landau Series Expansion



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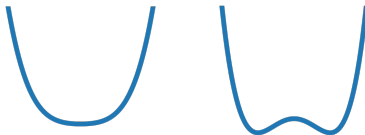
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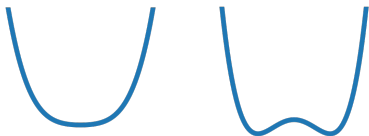
Landau Series Expansion

- ▶ For perturbation $c_{i\alpha} = c_\alpha + \Delta c_{i\alpha}$, want to know ΔF
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$$F[\{c_{i\alpha}\}] = F[\{c_\alpha\}] + \sum_{i\alpha} \left. \frac{\partial F}{\partial c_{i\alpha}} \right|_{\{c_\alpha\}} \Delta c_{i\alpha} + \frac{1}{2} \sum_{\substack{i\alpha \\ j\alpha'}} \left. \frac{\partial^2 F}{\partial c_{i\alpha} \partial c_{j\alpha'}} \right|_{\{c_\alpha\}} \Delta c_{i\alpha} \Delta c_{j\alpha'} + \dots$$



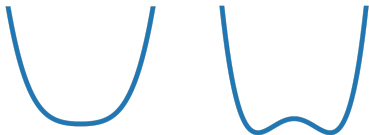
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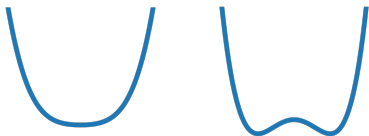
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- ▶ Or, in reciprocal space:

$$\Delta F = \frac{1}{2} \sum_{\mathbf{k}} \sum_{\alpha\alpha'} \Delta c_\alpha(\mathbf{k}) [\beta \Psi_{\alpha\alpha'}^{-1}(\mathbf{k})] \Delta c_{\alpha'}(\mathbf{k}) \quad (4)$$



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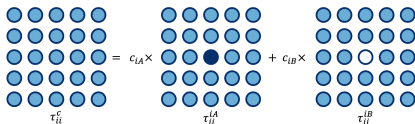
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- ▶ Third term more tricky.
- ▶ Can evaluate $\langle \Omega_{\text{el}} \rangle_0 [\{c_{\alpha}\}]$ within KKR formulation of DFT, using CPA to average over disorder.



Evaluating Free Energy and its derivatives

¹Khan, Staunton, Stocks, Phys. Rev. B **93** 054206 (2016)

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and

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*Science and Engineering Research Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD,
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(Received 18 June 1982)

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PACS numbers: 71.25.Mg, 71.10.+x, 71.25.Hc

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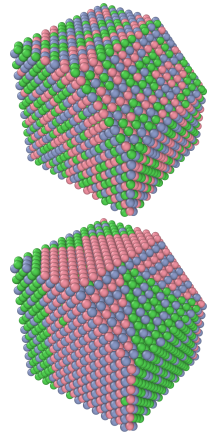
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- ▶ End result is quantity:

$$S_{i\alpha; j\alpha'}^{(2)} \equiv \frac{\partial^2 \langle \Omega_{el} \rangle_0}{\partial c_{i\alpha} \partial c_{j\alpha'}} \rightsquigarrow \Psi_{\alpha\alpha'}^{-1}(\mathbf{q})$$

¹Khan, Staunton, Stocks, Phys. Rev. B **93** 054206 (2016)

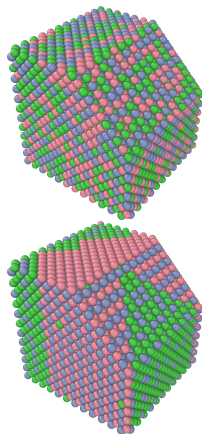
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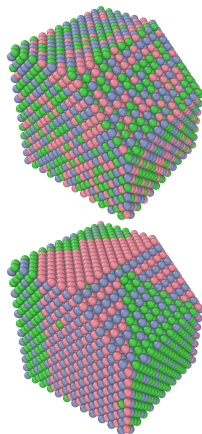


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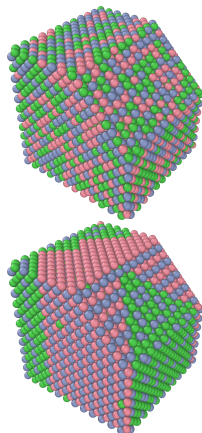


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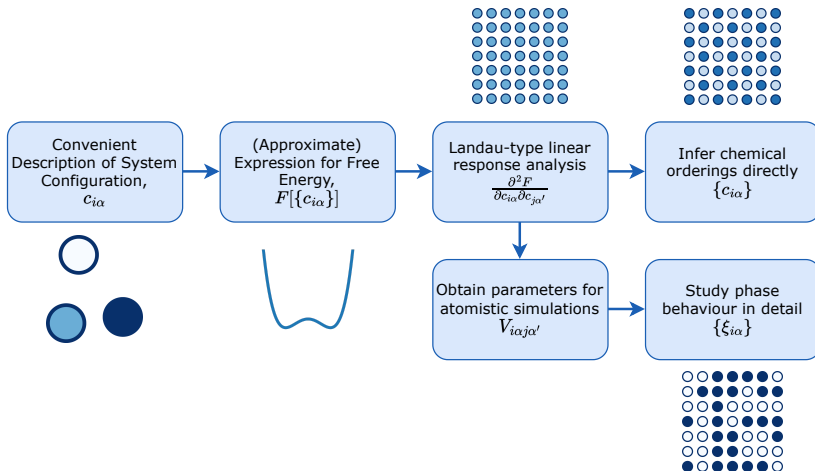
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- ▶ Study phase behaviour using, e.g. Monte Carlo simulations.



Workflow Summary



Refractory High-Entropy Alloys: Background

²Woodgate, Staunton, Phys. Rev. Mater. **7** 013801 (2023)

Refractory High-Entropy Alloys: Background

Periodic Table of the Elements

1																	18			
H																	He			
2	3											10	11	12	13	14	15	16	17	18
Li	Be											B	C	N	O	F	Ne			
4	5	6	7	8	9	10	11	12	13	14	15	16	17	18						
Na	Mg	Al	Si	P	S	Cl	Ar													
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	
Cs	Ba	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	
Fr	Ra	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og				

²Woodgate, Staunton, Phys. Rev. Mater. **7** 013801 (2023)

Refractory High-Entropy Alloys: Background

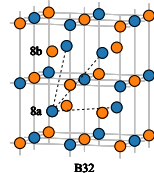
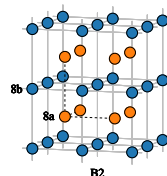
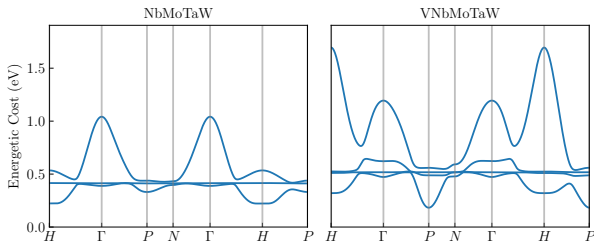
- ▶ First synthesised by Senkov around 2010.
- ▶ Excellent high-temperature performance, good radiation resistance.
- ▶ Previous studies of phase behaviour suggest interesting incipient ordering.

Periodic Table of the Elements

1																	18							
H																	He							
2	3											10	11	12	13	14	15	16	17	18				
Li	Be											B	C	N	O	F	Ne							
4	5											6	7	8	9	10	11	12	13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar							
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr							
39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe							
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90			
Cs	Ba	Lanthanides	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn							
87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122			
Fr	Ra	Actinides	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og							

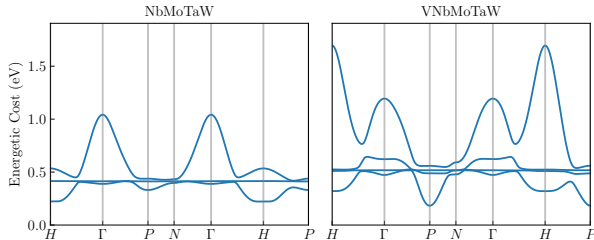
²Woodgate, Staunton, Phys. Rev. Mater. **7** 013801 (2023)

Refractory HEAs: Chemical Stability Matrices

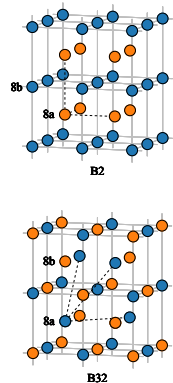


²Woodgate, Staunton, Phys. Rev. Mater. **7** 013801 (2023)

Refractory HEAs: Chemical Stability Matrices

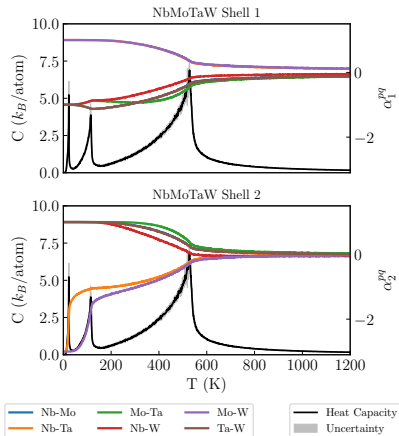
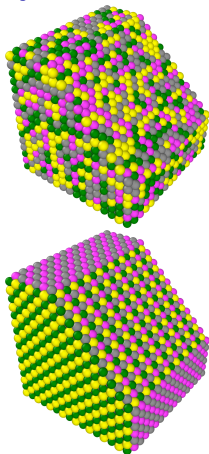


- ▶ NbMoTaW^2 : $T_{\text{ord}} = 559 \text{ K}$.
- ▶ VNbMoTaW^2 : $T_{\text{ord}} = 742 \text{ K}$.



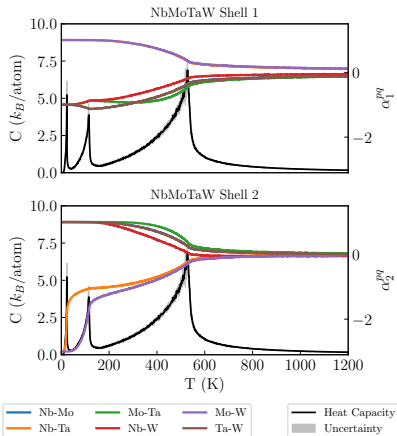
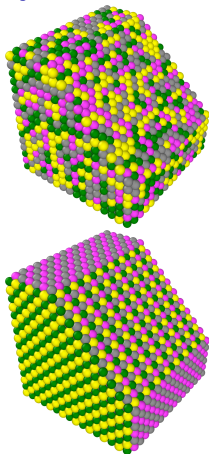
²Woodgate, Staunton, Phys. Rev. Mater. **7** 013801 (2023)

Refractory HEAs: Atomistic Modelling



²Woodgate, Staunton, Phys. Rev. Mater. **7** 013801 (2023)

Refractory HEAs: Atomistic Modelling



- NbMoTaW: predicted single-phase Heusler-like ground state².

²Woodgate, Staunton, Phys. Rev. Mater. **7** 013801 (2023)

Cantor Alloy & its Derivatives: Background

³Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022). (Editors' Suggestion.)

Cantor Alloy & its Derivatives: Background

Periodic Table of the Elements

The image shows a standard periodic table of elements. A red oval highlights the transition metal elements Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), and Copper (Cu) in the fourth row. The table includes element symbols, atomic numbers, and names.

1																	18				
H Hydrogen 1.01																	He Helium 4.00				
2	3	4											13	14	15	16	17	18			
Li Lithium 6.94	Be Beryllium 9.01											B Boron 10.81	C Carbon 12.01	N Nitrogen 14.01	O Oxygen 16.00	F Fluorine 18.99	Ne Neon 20.18				
9	10											31	32	33	34	35	36				
Na Sodium 22.99	Mg Magnesium 24.31											Al Aluminum 26.98	Si Silicon 28.09	P Phosphorus 30.97	S Sulfur 32.06	Cl Chlorine 35.45	Ar Argon 39.95				
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36				
K Potassium 39.10	Ca Calcium 40.08	Sc Scandium 44.96	Ti Titanium 47.88	V Vanadium 50.94	Cr Chromium 51.99	Mn Manganese 54.94	Fe Iron 55.85	Co Cobalt 58.93	Ni Nickel 58.69	Cu Copper 63.55	Zn Zinc 65.38	Ga Gallium 69.72	Ge Germanium 72.63	As Arsenic 74.92	Se Selenium 78.96	Br Bromine 79.90	Kr Krypton 83.80				
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54				
Rb Rubidium 85.47	Sr Strontium 87.62	Y Yttrium 88.91	Zr Zirconium 91.22	Nb Niobium 92.91	Mo Molybdenum 95.94	Tc Technetium 98.91	Ru Ruthenium 101.07	Rh Rhodium 101.07	Pd Palladium 106.37	Cd Cadmium 112.41	In Indium 114.82	Sn Tin 118.71	Sb Antimony 121.76	Te Tellurium 127.60	I Iodine 126.91	Xe Xenon 131.29					
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86				
Cs Cesium 132.91	Ba Barium 137.33	Lanthanides					Hf Hafnium 178.49	Ta Tantalum 180.95	W Tungsten 183.84	Re Rhenium 186.21	Os Osmium 190.23	Ir Iridium 192.22	Pt Platinum 195.08	Au Gold 196.97	Hg Mercury 200.59	Tl Thallium 204.38	Pb Lead 207.2	Bi Bismuth 208.98	Po Polonium (209)	At Astatine (210)	Rn Radon (222)
87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118				
Fr Francium (223)	Ra Radium (226)	Actinides			Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (264)	Hs Hassium (265)	Mt Meitnerium (266)	Ds Darmstadtium (271)	Rg Roentgenium (272)	Cn Copernicium (285)	Nh Nihonium (286)	Fl Flerovium (289)	Mc Moscovium (290)	Lv Livermorium (293)	Ts Tennessine (294)	Og Oganesson (294)		

³Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022). (Editors' Suggestion.)

Cantor Alloy & its Derivatives: Background

- ▶ First synthesised by Cantor around 2004.
- ▶ Prototypical fcc high-entropy alloys.
- ▶ Experimentally observed atomic short-range order.

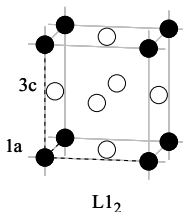
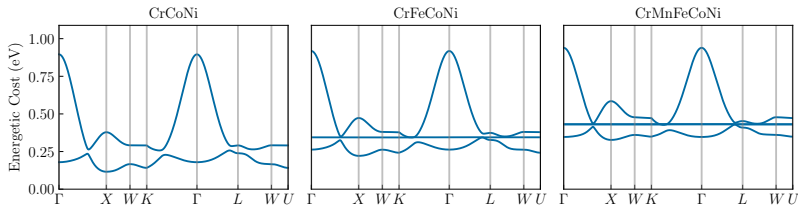
Periodic Table of the Elements

The image shows a standard periodic table of elements. A red circle highlights the elements Chromium (Cr), Manganese (Mn), Iron (Fe), and Nickel (Ni) in the fourth row, which are the primary components of the Cantor alloy. The table includes element symbols, names, atomic numbers, and atomic weights.

1																	18								
H Hydrogen 1.01																	He Helium 4.00								
2											13	14	15	16	17	18									
Li Lithium 6.94	Be Beryllium 9.01											B Boron 10.81	C Carbon 12.01	N Nitrogen 14.01	O Oxygen 16.00	F Fluorine 18.99	Ne Neon 20.18								
3											19	20					36								
Na Sodium 22.99	Mg Magnesium 24.31											Al Aluminum 26.98	Si Silicon 28.09	P Phosphorus 30.97	S Sulfur 32.06	Cl Chlorine 35.45	Ar Argon 39.95								
4											37	38	39	40					54						
K Potassium 39.10	Ca Calcium 40.08	Sc Scandium 44.96	Ti Titanium 47.88	V Vanadium 50.94	Cr Chromium 51.99	Mn Manganese 54.94	Fe Iron 55.85	Co Cobalt 58.93	Ni Nickel 58.69	Cu Copper 63.55	Zn Zinc 65.38	Ga Gallium 69.72	Ge Germanium 72.63	As Arsenic 74.92	Se Selenium 78.96	Br Bromine 79.90	Kr Krypton 83.80								
5											55	56	57	58					72						
Rb Rubidium 85.47	Sr Strontium 87.62	Y Yttrium 88.91	Zr Zirconium 91.22	Nb Niobium 92.91	Mo Molybdenum 95.94			Ru Ruthenium 101.07	Rh Rhodium 101.07	Pd Palladium 106.36	Cd Cadmium 112.41	In Indium 114.82	Sn Tin 118.71	Sb Antimony 121.76	Te Tellurium 127.60	I Iodine 126.90	Xe Xenon 131.29								
6											73	74	75	76	77	78	79	80					86		
Cs Cesium 132.91	Ba Barium 137.33	Lanthanides		Hf Hafnium 178.49	Ta Tantalum 180.95	W Tungsten 183.85	Re Rhenium 186.21	Os Osmium 190.23	Ir Iridium 192.22	Pt Platinum 195.08	Au Gold 196.97	Hg Mercury 200.59	Tl Thallium 204.38	Pb Lead 207.2	Bi Bismuth 208.98	Po Polonium (209)	At Astatine (210)	Rn Radon (222)							
7											87	88	89	90	91	92	93	94	95	96					102
Fr Francium (223)	Ra Radium (226)	Actinides		Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (277)	Mt Meitnerium (276)	Ds Darmstadtium (281)	Rg Roentgenium (281)	Cn Copernicium (285)	Nh Nihonium (286)	Fl Flerovium (289)	Mc Moscovium (290)	Lv Livermorium (293)	Ts Tennessine (294)	Og Oganesson (294)							

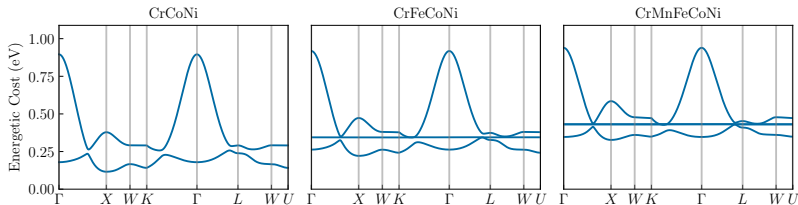
³Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022). (Editors' Suggestion.)

Cantor Alloy & its Derivatives: Chemical Stability Matrices

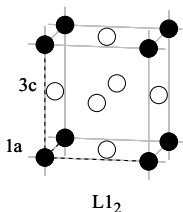


³Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022). (Editors' Suggestion.)

Cantor Alloy & its Derivatives: Chemical Stability Matrices

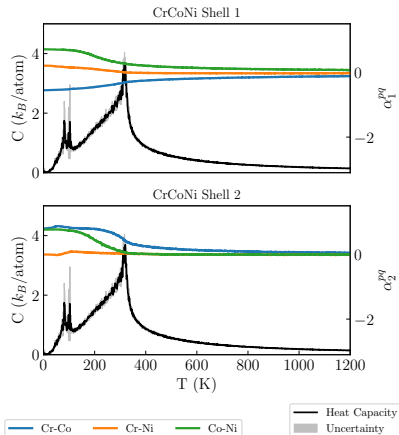
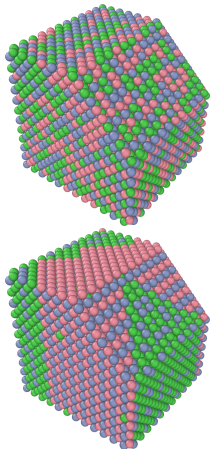


- ▶ CrCoNi^3 : $T_{\text{ord}} = 606 \text{ K}$.
- ▶ CrFeCoNi^3 : $T_{\text{ord}} = 404 \text{ K}$.
- ▶ CrMnFeCoNi^3 : $T_{\text{ord}} = 281 \text{ K}$.



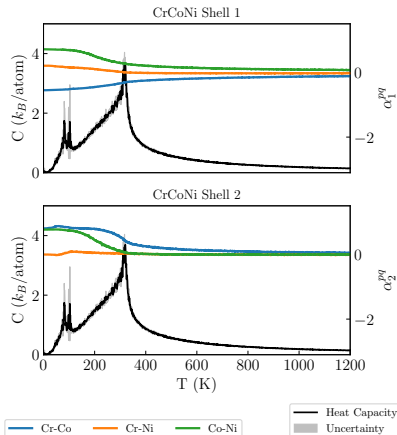
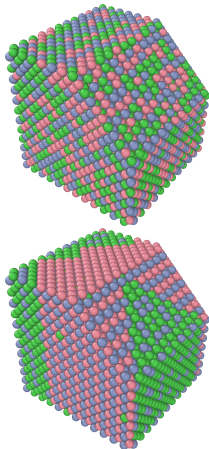
³Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022). (Editors' Suggestion.)

Cantor Alloy & its Derivatives: Atomistic Modelling



³Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022). (Editors' Suggestion.)

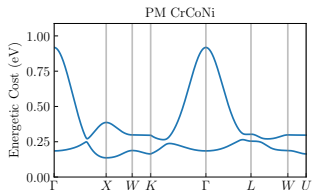
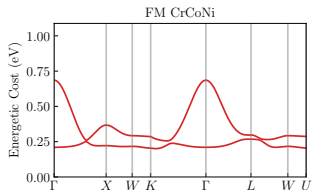
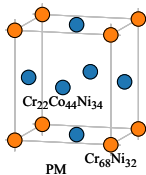
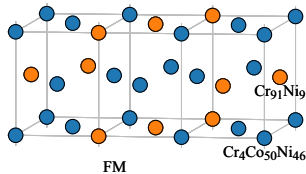
Cantor Alloy & its Derivatives: Atomistic Modelling



► No single-phase ground state³.

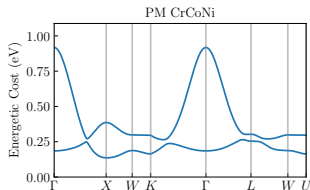
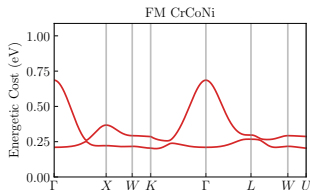
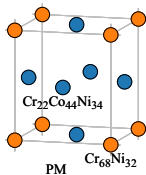
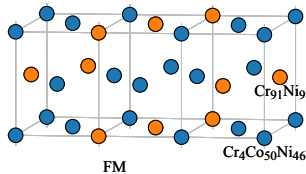
³Woodgate, Staunton, Phys. Rev. B **105** 115124 (2022). (Editors' Suggestion.)

Importance of the Magnetic State



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

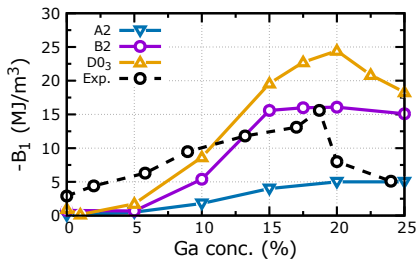
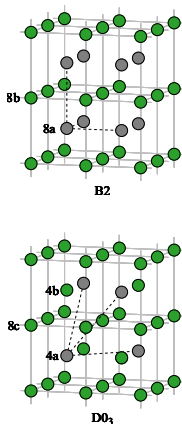
Importance of the Magnetic State



- Different magnetic state results in different orderings⁴.

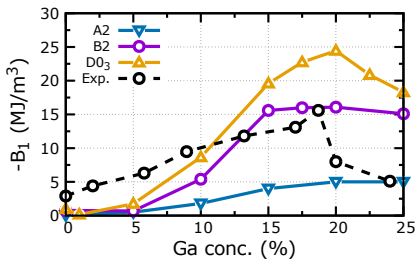
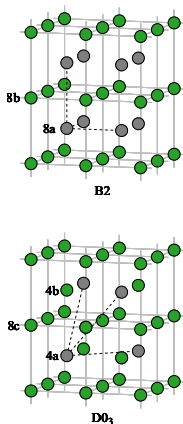
⁴Woodgate, Hedlund, Lewis, Staunton, Phys. Rev. Mater. **7** 053801 (2023)

Impact of atomic arrangements on magnetic properties



⁵Marchant, Woodgate, Patrick, Staunton, Phys. Rev. B **103**, 094414 (2021)

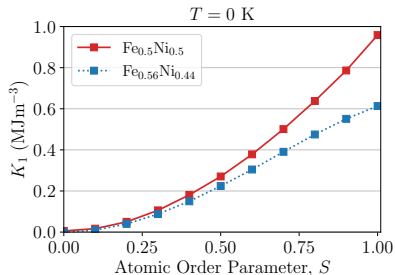
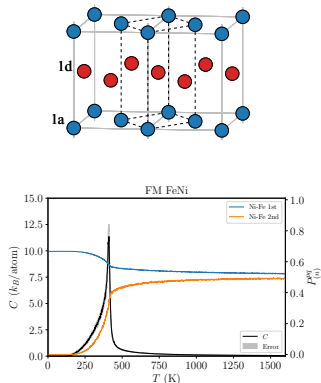
Impact of atomic arrangements on magnetic properties



► Atomic ordering affects magnetostriction⁵.

⁵Marchant, Woodgate, Patrick, Staunton, Phys. Rev. B **103**, 094414 (2021)

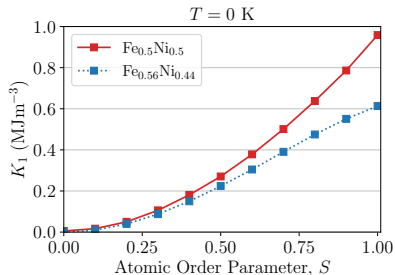
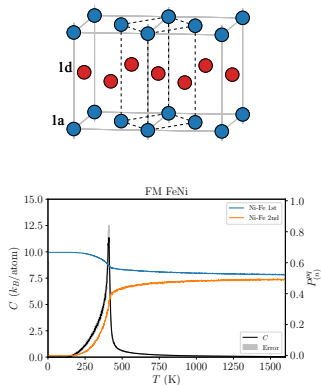
Impact of atomic arrangements on magnetic properties



⁶Woodgate, Patrick, Lewis, Staunton, [arXiv:2307.15470](https://arxiv.org/abs/2307.15470).

⁷Woodgate, Patrick, Lewis, Staunton, in preparation.

Impact of atomic arrangements on magnetic properties

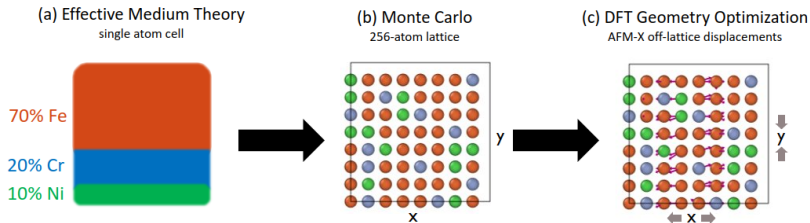


► Atomic ordering affects magnetic anisotropy^{6,7}.

⁶Woodgate, Patrick, Lewis, Staunton, [arXiv:2307.15470](https://arxiv.org/abs/2307.15470).

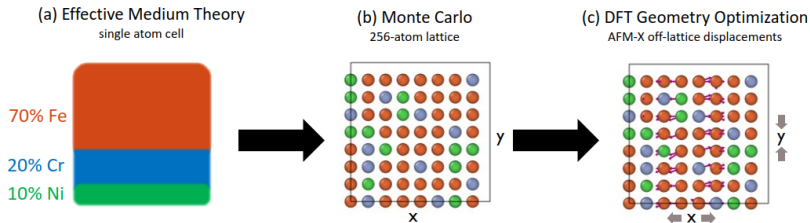
⁷Woodgate, Patrick, Lewis, Staunton, in preparation.

Feeding into Other Simulation Techniques



⁵Shenoy, Woodgate, *et al.*, [arXiv:2309.08689](https://arxiv.org/abs/2309.08689).

Feeding into Other Simulation Techniques



- ▶ Can use physically motivated configurations in training data for machine-learned interatomic potentials⁸.

⁵Shenoy, Woodgate, *et al.*, [arXiv:2309.08689](https://arxiv.org/abs/2309.08689).

Next Steps and Future Work

Next Steps and Future Work

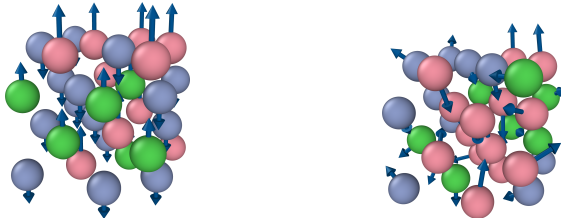
- ▶ Approach is highly computationally efficient. Materials discovery?

Next Steps and Future Work

- ▶ Approach is highly computationally efficient. Materials discovery?
- ▶ Feed into more sophisticated techniques, could we model impact of short-range order on physical properties of HEAs?.

Next Steps and Future Work

- ▶ Approach is highly computationally efficient. Materials discovery?
- ▶ Feed into more sophisticated techniques, could we model impact of short-range order on physical properties of HEAs?.
- ▶ Broaden approach to modelling general high-entropy oxides, carbides, etc.?.



Take-Home Messages

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Novel Approach For Modelling Atomic Arrangements in Alloys

Computationally efficient, DFT-based methodology predicts ordering and gives physical insight.

Take-Home Messages

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Can Study Impact on Materials Properties

Examples where atomic ordering impacts materials' magnetic properties.

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Computationally efficient, DFT-based methodology predicts ordering and gives physical insight.

Can Study Impact on Materials Properties

Examples where atomic ordering impacts materials' magnetic properties.

Interface with other techniques

Use physically motivated configurations in subsequent studies using other modelling techniques.

Acknowledgements

Funding

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



People

University of Warwick, UK

- ▶ Lakshmi Shenoy
- ▶ James R. Kermode
- ▶ Albert P. Bartók
- ▶ George A. Marchant
- ▶ Julie B. Staunton

Northeastern University, USA

- ▶ Laura H. Lewis
- ▶ Daniel Hedlund

University of Oxford, UK

- ▶ Christopher E. Patrick