

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

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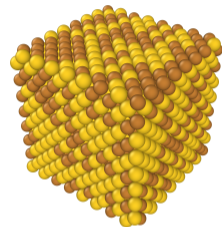


Our Description

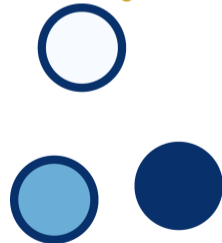
- ▶ On lattice.
- ▶ Specify configuration by $\{\xi_{i\alpha}\}$.
- ▶ Interested in the *average* value of these:

$$c_{i\alpha} \equiv \langle \xi_{i\alpha} \rangle.$$

- ▶ High temperature, homogeneous: $c_{i\alpha} = c_{\alpha}$.
- ▶ Perturb homogeneous state $c_{i\alpha} = c_{\alpha} + \delta c_{i\alpha}$ and see what favourable correlations are.

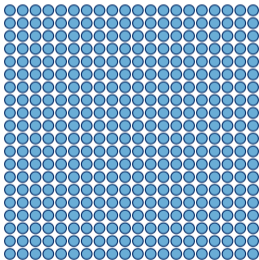


(1)

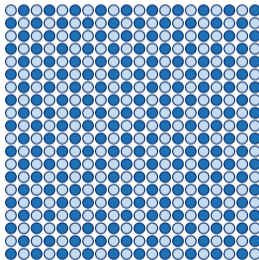


Concentration Waves

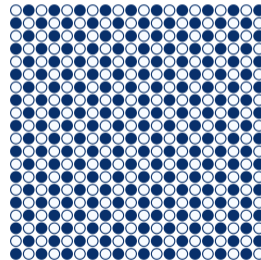
$$c_{i\alpha} = c_\alpha + \eta_\alpha \frac{1}{2} \left(e^{i\mathbf{q}\cdot\mathbf{R}_i} + e^{-i\mathbf{q}\cdot\mathbf{R}_i} \right), \quad \mathbf{q} = \left(\frac{1}{2}, \frac{1}{2} \right). \quad (2)$$



$$\eta = (0, 0)$$



$$\eta = (0.25, -0.25)$$



$$\eta = (0.5, -0.5)$$

Energetics

- ▶ Evaluate cost of fluctuations *ab initio* via DFT, using KKR-CPA and a linear response theory^{ab}.
- ▶ Mean-field free energy:

$$G = \beta^{-1} \sum_{i\alpha} c_{i\alpha} \log c_{i\alpha} - \sum_{i\alpha} \nu_{i\alpha} c_{i\alpha} + \langle \Omega_{\text{el}} \rangle_0[\{c_{i\alpha}\}] \quad (3)$$

- ▶ Important quantity:

$$S_{i\alpha; j\alpha'}^{(2)} \equiv \frac{\partial^2 \langle \Omega_{\text{el}} \rangle_0}{\partial c_{i\alpha} \partial c_{j\alpha'}} \rightsquigarrow \Psi_{\alpha\alpha'}^{-1}(\mathbf{q}) \quad (4)$$

^aS. N. Khan, J. B. Staunton, G. M. Stocks, Phys. Rev. B **93** 054206 (2016)

^bB. L. Gyorffy, G. M. Stocks, Phys. Rev. Lett. **50**, 374 (1983)

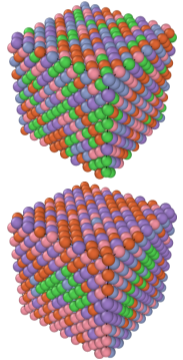


Energetics

- ▶ Bragg-Williams Hamiltonian for atomistic modelling:

$$H(\{\xi_{i\alpha}\}) = \frac{1}{2} \sum_{\substack{i\alpha \\ j\alpha'}} V_{i\alpha;j\alpha'} \xi_{i\alpha} \xi_{j\beta} + \sum_{i\alpha} \nu_{i\alpha} \xi_{i\alpha}. \quad (5)$$

- ▶ If H as above, $V_{i\alpha;j\alpha'}$ are *exactly* $-S_{i\alpha;j\alpha'}^{(2)}$.



Cantor-Wu Alloys

- ▶ Prototypical FCC high entropy alloy is the “Cantor alloy” - NiCoFeMnCr.

Periodic Table of the Elements

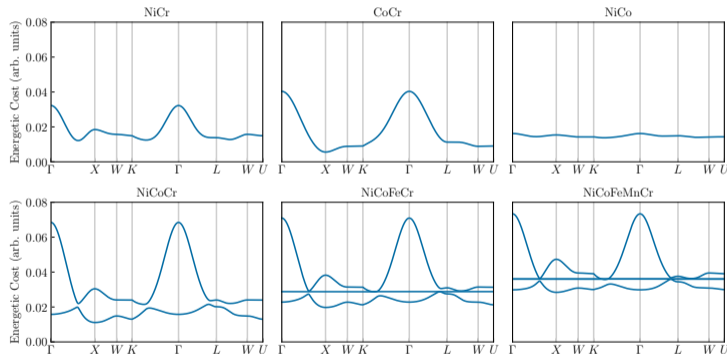
1																	18								
H Hydrogen 1.01																	He Helium 4.00								
3	4											5	6	7	8	9	10	11	12	13	14	15	16	17	18
Li Lithium 6.94	Be Beryllium 9.01											B Boron 10.81	C Carbon 12.01	N Nitrogen 14.01	O Oxygen 16.00	F Fluorine 18.99	Ne Neon 20.18							Ar Argon 39.95	
11	12											13	14	15	16	17	18							18	
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							Ar Argon 39.95	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36							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 78.97	Br Bromine 79.90	Kr Krypton 83.80							Kr Krypton 83.80	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54							54	
Rb Rubidium 85.47	Sr Strontium 87.62	Y Yttrium 88.91	Zr Zirconium 91.22	Nb Niobium 92.91	Mo Molybdenum 95.95	Tc Technetium 98.91	Ru Ruthenium 101.07	Rh Rhodium 102.91	Pd Palladium 106.42	Ag Silver 107.87	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							Xe Xenon 131.29	
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86							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 207.20	Bi Bismuth 208.98	Po Polonium 209	At Astatine 210	Rn Radon 222.02							Rn Radon 222.02
87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118							118	
Fr Francium 223.02	Ra Radium 226.03	Actinides		Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (265)	Mt Meitnerium (268)	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)							Og Oganesson (294)

- ▶ At what temperature will order emerge? What is the nature of order?
- ▶ We looked at a series of three Cantor-Wu alloys: NiCoCr, NiCoFeCr, NiCoFeMnCr, along with some binary subsystems¹.

¹C. D. Woodgate, J. B. Staunton, Phys. Rev. B **105** 115124 (2022)

Linear Response

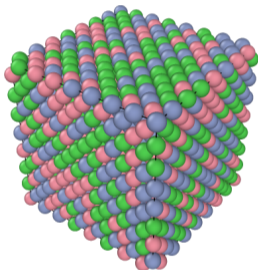
Eigenvalues of $\Psi_{\alpha\alpha'}^{-1}(\mathbf{q})$ around IBZ at 1200K.



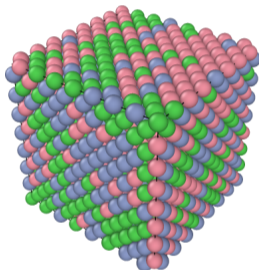
C. D. Woodgate, J. B. Staunton, Phys. Rev. B **105** 115124 (2022)

Atomistic Simulations

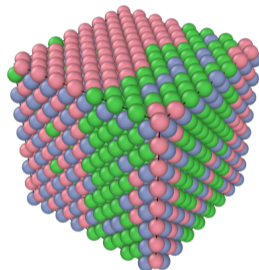
NiCoCr



1000K



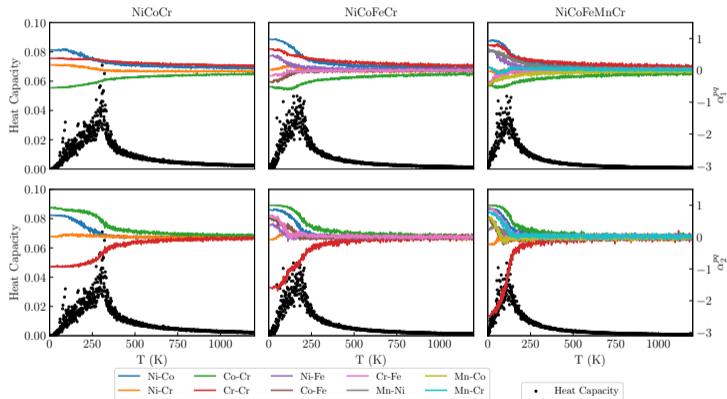
300K



50K

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Atomistic Simulations



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Summary

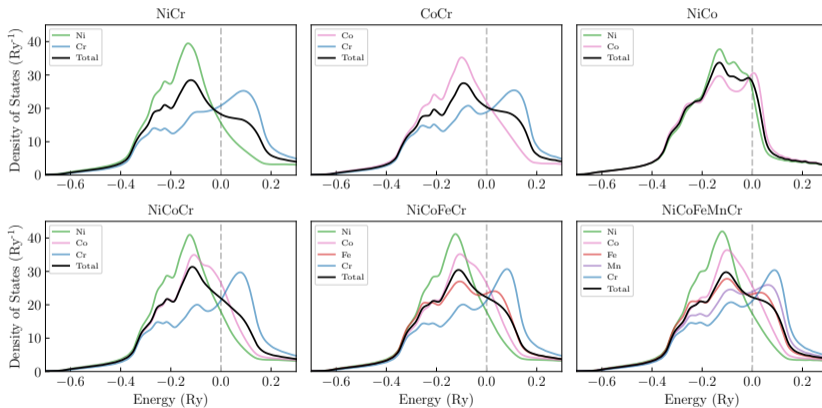
- ▶ SRO dominated by Co-Cr and Cr-Cr correlations.
- ▶ Fe, Mn, serve a diluting effect and stabilise solid solution.
- ▶ Predicted ordering temperatures are low, consistent with experiment.
- ▶ **Method obtains results comparable with conventional techniques for a fraction of the computational cost.**

Acknowledgements

- ▶ I am funded by a studentship in the UK EPSRC-supported CDT in Modelling of Heterogeneous Systems at the University of Warwick, UK. warwick.ac.uk/hetsys
- ▶ Work was also supported by EPSRC grants as part of the PRETAMAG project.



Density of States



Linear Response

System	k -vector	δc_1	δc_2	δc_3	δc_4	δc_5	T_{order} (K)
NiCr	(0, 0, 0.6)	0.70711	-0.70711				200
CoCr	(0, 0, 1)	0.70711	-0.70711				793
NiCo	(0, 0.6, 0.6)	0.70711	-0.70711				83
NiCoCr	(0, 0, 1)	-0.034613	-0.68916	0.72378			606
NiCoFeCr	(0, 0, 1)	0.013671	-0.68858	-0.048489	0.72340		404
NiCoFeMnCr	(0, 0, 1)	0.033024	-0.68516	-0.081509	0.010666	0.72298	281

Fitting to Pairwise Interaction

We approximate the true interaction by fitting to a Bragg-Williams-like Hamiltonian. That is, we approximate the *ab initio* data by $V_{\alpha\beta}(\mathbf{q})$, where

$$V_{\alpha\beta}(\mathbf{q}) = V_{\alpha\beta}^0 + V_{\alpha\beta}^1 \left(\sum_{\{\mathbf{R}_i\}_1} e^{i\mathbf{q}\cdot\mathbf{R}_i} \right) + \dots + V_{\alpha\beta}^N \left(\sum_{\{\mathbf{R}_i\}_N} e^{i\mathbf{q}\cdot\mathbf{R}_i} \right), \quad (6)$$

a constant plus a nearest-neighbour term, next-nearest neighbour term, etc.

Pairwise Interactions

$V_{\alpha\beta}^{(1)}$	Ni	Co
Ni	0.023	-0.023
Co	-0.023	0.023

$V_{\alpha\beta}^{(1)}$	Ni	Cr
Ni	0.199	-0.199
Cr	-0.199	0.199

$V_{\alpha\beta}^{(1)}$	Co	Cr
Co	1.026	-1.026
Cr	-1.026	1.026

$V_{\alpha\beta}^{(1)}$	Ni	Co	Cr
Ni	-0.218	0.682	-0.465
Co	0.682	0.672	-1.351
Cr	-0.465	-1.351	1.813

Pairwise Interactions

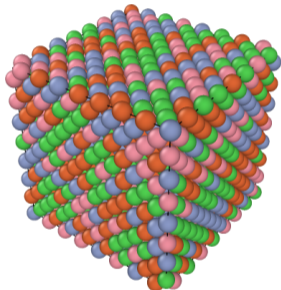
$V_{\alpha\beta}^{(1)}$	Ni	Co	Fe	Cr
Ni	-0.338	0.606	0.097	-0.367
Co	0.606	0.656	-0.049	-1.213
Fe	0.097	-0.049	-0.019	-0.029
Cr	-0.367	-1.213	-0.029	1.609

$V_{\alpha\beta}^{(2)}$	Ni	Co	Fe	Cr
Ni	0.316	0.058	-0.061	-0.313
Co	0.058	0.005	-0.007	-0.057
Fe	-0.061	-0.007	-0.010	0.058
Cr	-0.313	-0.057	0.058	0.312

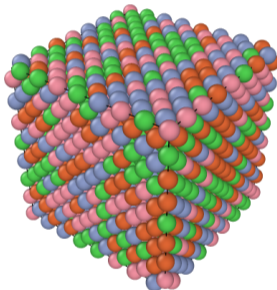
$V_{\alpha\beta}^{(3)}$	Ni	Co	Fe	Cr
Ni	0.002	0.090	0.008	-0.100
Co	0.090	0.053	-0.009	-0.135
Fe	0.008	-0.009	-0.002	0.003
Cr	-0.100	-0.135	0.003	0.232

Atomistic Simulations

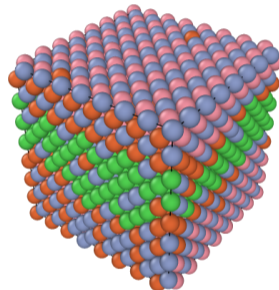
NiCoFeCr



1000K



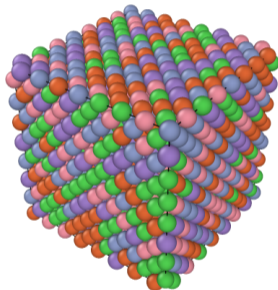
300K



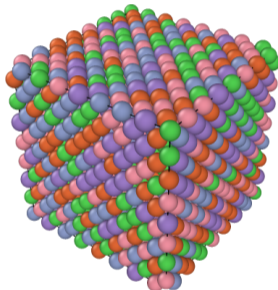
50K

Atomistic Simulations

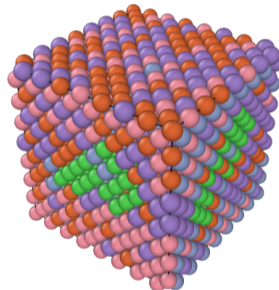
NiCoFeMnCr



1000K



300K



50K

Ab Initio Theory

- ▶ Expand free energy around homogeneous reference state:

$$\begin{aligned}\Omega(\{\bar{c}_{i\alpha}\}) &= \Omega(\{c_\alpha\}) + \sum_{i\alpha} \left. \frac{\partial \Omega}{\partial \bar{c}_{i\alpha}} \right|_{\{c_\alpha\}} \Delta \bar{c}_{i\alpha} \\ &+ \frac{1}{2} \sum_{i\alpha; j\alpha'} \left. \frac{\partial^2 \Omega}{\partial \bar{c}_{i\alpha} \partial \bar{c}_{j\alpha'}} \right|_{\{c_\alpha\}} \Delta \bar{c}_{i\alpha} \Delta \bar{c}_{j\alpha'} + \dots\end{aligned}\quad (7)$$

Ab Initio Theory

- ▶ Important bit is second-order term.

$$\delta\Omega = \frac{1}{2} \sum_{i,j} \sum_{\alpha,\alpha'} \Delta\bar{c}_{i\alpha} [\beta^{-1} C_{\alpha,\alpha'}^{-1} - S_{i\alpha;j\alpha'}^{(2)}] \Delta\bar{c}_{j\alpha'}, \quad (8)$$

where $-\frac{\partial^2 \langle \Omega_{el} \rangle_0}{\partial \bar{c}_{i\alpha} \partial \bar{c}_{j\alpha'}} \equiv S_{i\alpha;j\alpha'}^{(2)}$, and $C_{\alpha\alpha'}^{-1} = \frac{\delta_{\alpha\alpha'}}{c_\alpha}$.

Ab Initio Theory

- ▶ Or, in reciprocal space,

$$\delta\Omega = \frac{1}{2} \sum_{\mathbf{k}} \sum_{\alpha, \alpha'} \Delta\bar{c}_{\alpha}(\mathbf{k}) [\beta^{-1} C_{\alpha\alpha'}^{-1} - S_{\alpha\alpha'}^{(2)}(\mathbf{k})] \Delta\bar{c}_{\alpha'}(\mathbf{k}). \quad (9)$$