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

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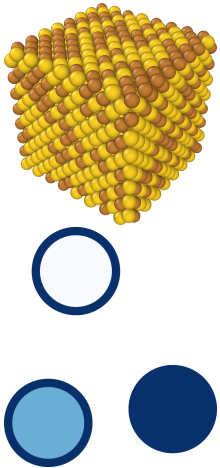
Our Description

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

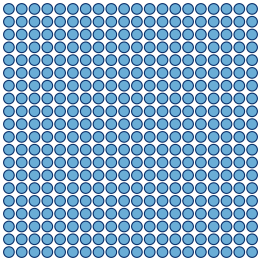
$$c_{i\alpha} \equiv \langle \xi_{i\alpha} \rangle. \tag{1}$$

- 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.

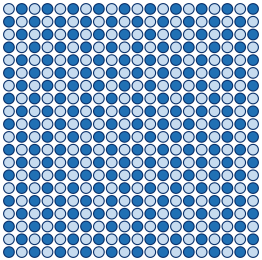


Concentration Waves

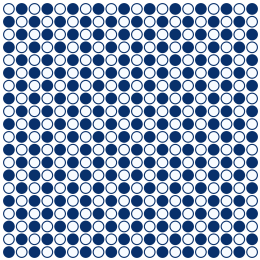
$$c_{i\alpha} = c_\alpha + \eta_\alpha \frac{1}{2}\left(e^{i\mathbf{q}\cdot\mathbf{R}_i} + e^{-i\mathbf{q}\cdot\mathbf{R}_i}\right), \quad \mathbf{q} = \left(\tfrac{1}{2}, \tfrac{1}{2}\right). \tag{2}$$



$\eta = (0, 0)$



$\eta = (0.25, -0.25)$

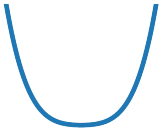


$\eta = (0.5, -0.5)$

Energetics

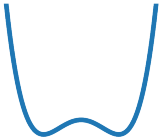
- Evaluate cost of fluctuations *ab initio* via DFT, using KKR-CPA and a linear response theory[ab].
- Mean-field free energy:

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



- Important quantity:

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



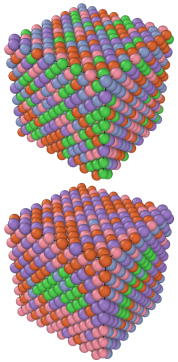
[a] S. N. Khan, J. B. Staunton, G. M. Stocks, Phys. Rev. B **93** 054206 (2016)
[b] B. L. Gyorffy, G. M. Stocks, Phys. Rev. Lett. **50**, 374 (1983)

Energetics

- Bragg-Williams Hamiltonian for atomistic modelling:

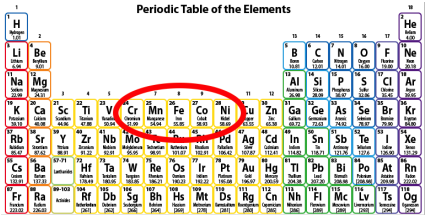
$$H(\{\xi_{i\alpha}\}) = \frac{1}{2}\sum_{\substack{i\alpha \\ j\alpha'}} V_{i\alpha;j\alpha'}\,\xi_{i\alpha}\xi_{j\beta} + \sum_{i\alpha}\nu_{i\alpha}\xi_{i\alpha}. \qquad (5)$$

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



Cantor-Wu Alloys

- Prototypical FCC high entropy alloy is the "Cantor alloy" - NiCoFeMnCr.

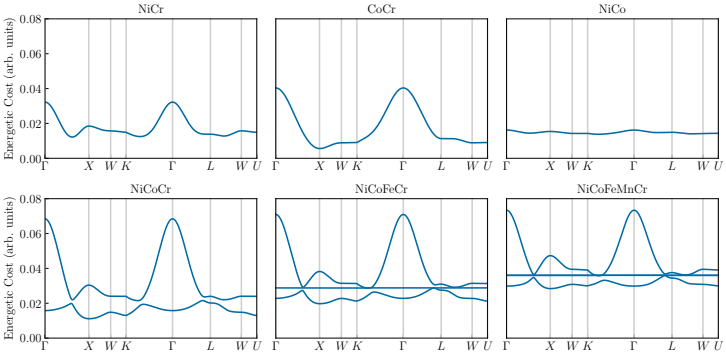


- At what temperature will order emerge? What is the nature of order?
- We looked at a series of three Cantor-Wu alloys: NiCoCr, NiCoFeCr, NiCoFeMnCr, along with some binary subsystems[1].

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

Linear Response

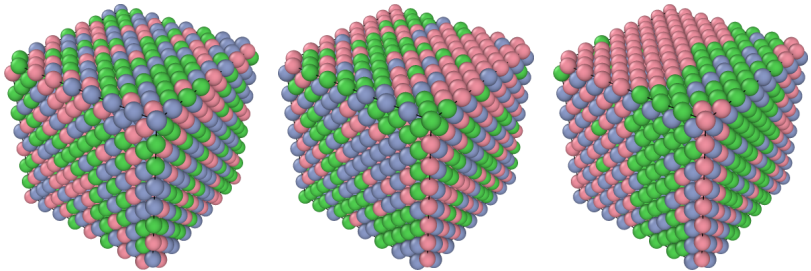
Eigenvalues of $\Psi^{-1}_{\alpha\alpha'}(\mathbf{q})$ around IBZ at 1200K.



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

Atomistic Simulations

NiCoCr



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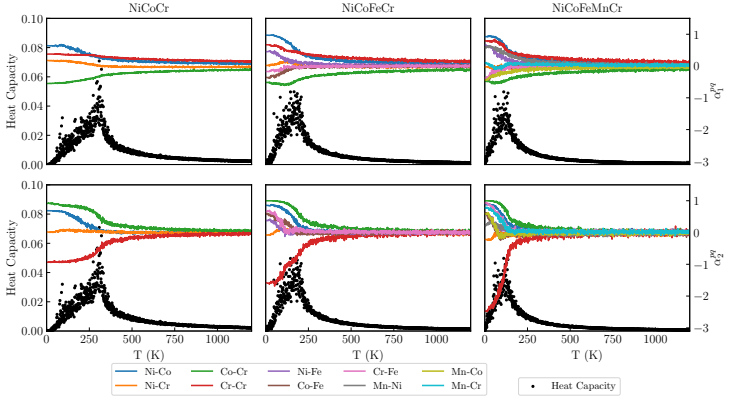
Atomistic Simulations



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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

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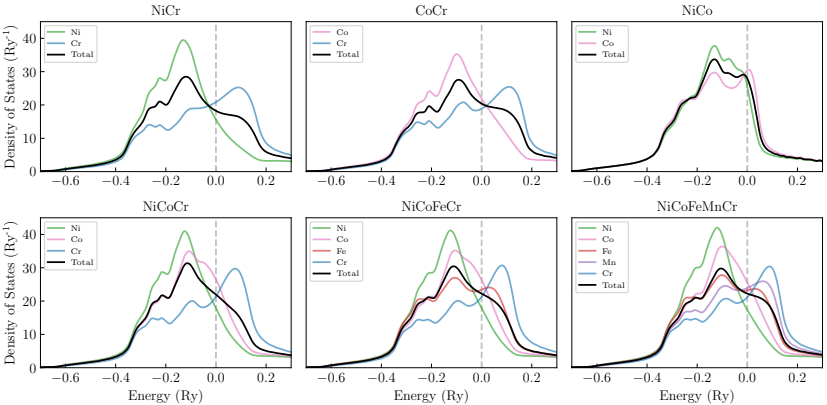
- Work was also supported by EPSRC grants as part of the PRETAMAG project.

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

$$V_{\alpha\beta}(\mathbf{q}) = V^0_{\alpha\beta} + V^1_{\alpha\beta}\left(\sum_{\{\mathbf{R}_i\}_1} e^{i\mathbf{q}\cdot\mathbf{R}_i}\right) + \cdots + V^N_{\alpha\beta}\left(\sum_{\{\mathbf{R}_i\}_N} e^{i\mathbf{q}\cdot\mathbf{R}_i}\right), \tag{6}$$

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

Pairwise Interactions

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

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

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

$V^{(1)}_{\alpha\beta}$	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

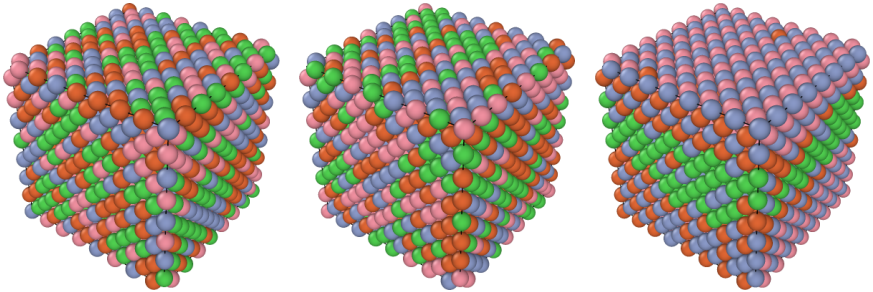
$V^{(1)}_{\alpha\beta}$	Ni	Co	Fe	Cr
Ni	-0.338	0.606	0.097	-0.367
Co	0.606	0.656	-0.049	-1.213
Fe	0.097	-0.049	-0.019	-0.029
Cr	-0.367	-1.213	-0.029	1.609

$V^{(2)}_{\alpha\beta}$	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

$V^{(3)}_{\alpha\beta}$	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

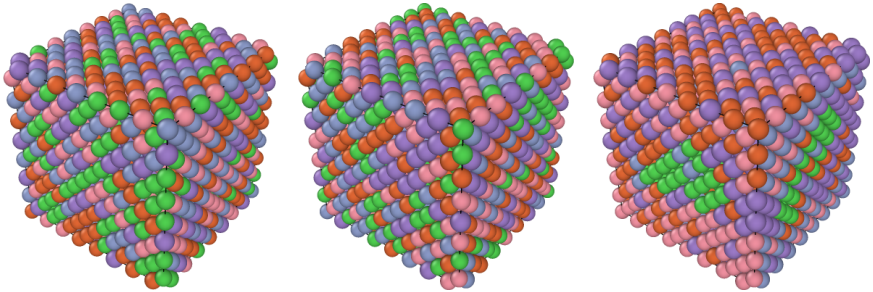
NiCoFeCr



1000K 300K 50K

Atomistic Simulations

NiCoFeMnCr



1000K 300K 50K

Ab Initio Theory

- Expand free energy around homogeneous reference state:

$$\Omega(\{\bar{c}_{i\alpha}\}) = \Omega(\{c_\alpha\}) + \sum_{i\alpha} \frac{\partial \Omega}{\partial \bar{c}_{i\alpha}}\bigg|_{\{c_\alpha\}} \Delta\bar{c}_{i\alpha} + \frac{1}{2} \sum_{i\alpha;j\alpha'} \frac{\partial^2 \Omega}{\partial \bar{c}_{i\alpha} \partial \bar{c}_{j\alpha'}}\bigg|_{\{c_\alpha\}} \Delta\bar{c}_{i\alpha} \Delta\bar{c}_{j\alpha'} + \ldots \tag{7}$$

Ab Initio Theory

- Important bit is second-order term.

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

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

Ab Initio Theory

- Or, in reciprocal space,

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