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

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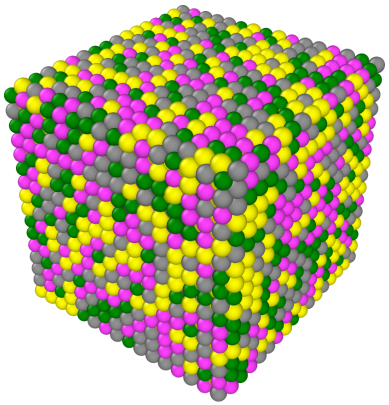
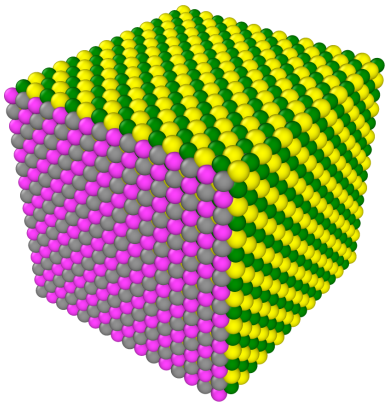
High Entropy Alloys

- High Entropy Alloy (HEA): *multiple* principle components.
- Solid solution stabilised by large "entropy of mixing"

$$TS = -k_B TN \sum_{\alpha} c_\alpha \log c_\alpha. \tag{1}$$

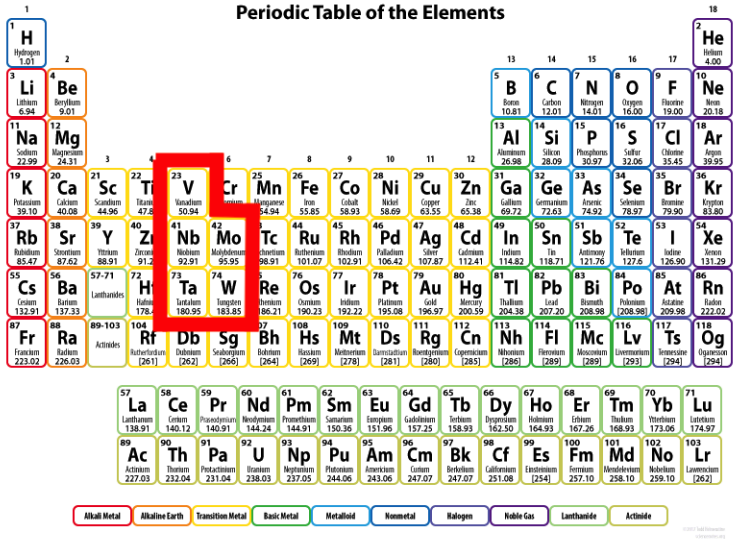




- At what temperature will order emerge? What is the nature of order? Is order beneficial or detrimental?

Refractory HEAs

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



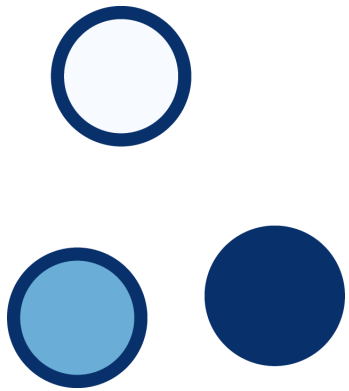
- Apply the modelling techniques used successfully on Ni-based HEAs[1] to refractory systems.

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

Our Description

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

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



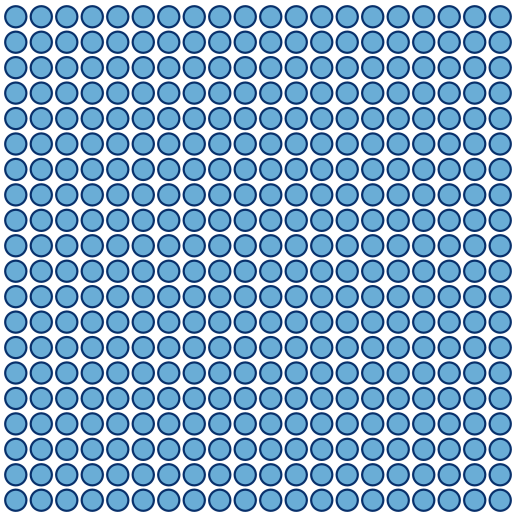
- Perturb high temperature, homogeneous state

$$c_{i\alpha} = c_{\alpha} + \delta c_{i\alpha}$$

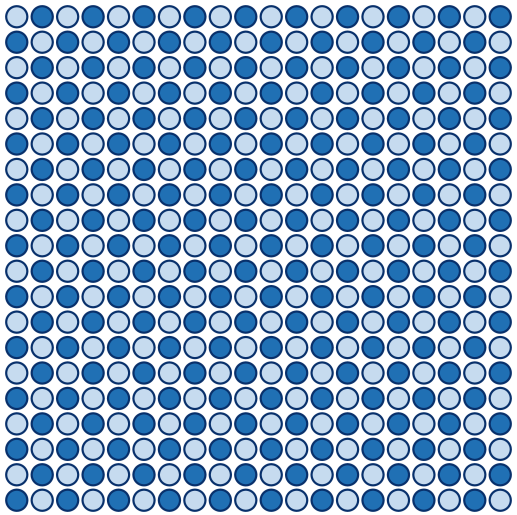
and see what favourable correlations are.

Concentration Waves

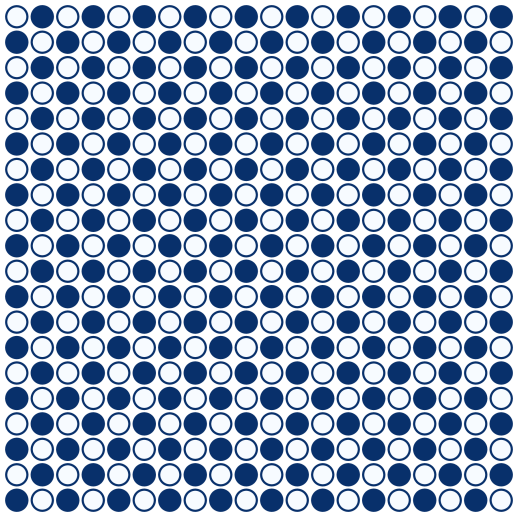
$$c_{i\alpha} = c_\alpha + \eta_\alpha \frac{1}{2}\left(e^{i\mathbf{q}\cdot\mathbf{R}_i} + e^{-i\mathbf{q}\cdot\mathbf{R}_i}\right), \quad \mathbf{q} = \left(\tfrac{1}{2}, \tfrac{1}{2}\right)$$



$\eta = (0, 0)$



$\eta = (0.25, -0.25)$

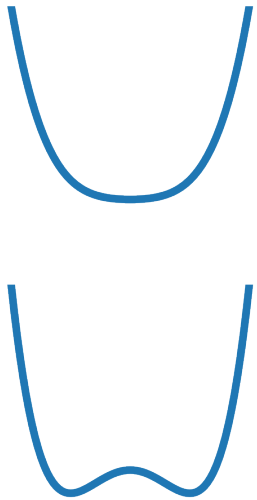


$\eta = (0.5, -0.5)$

Energetics

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

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



- Important quantities:

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

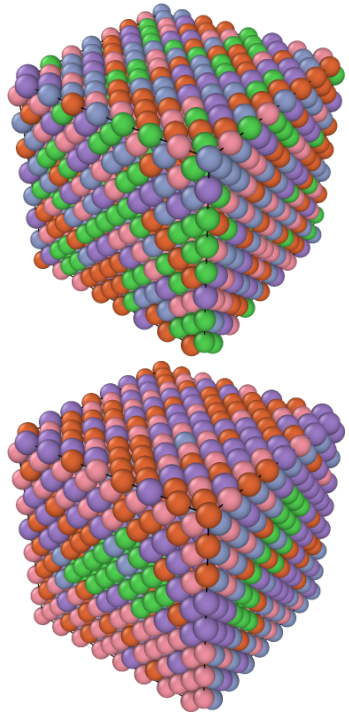
[a] Khan, Staunton, Stocks, Phys. Rev. B **93** 054206 (2016)
[b] Gyorffy, Stocks, Phys. Rev. Lett. **50**, 374 (1983)

Energetics

- Bragg-Williams Hamiltonian for atomistic modelling:

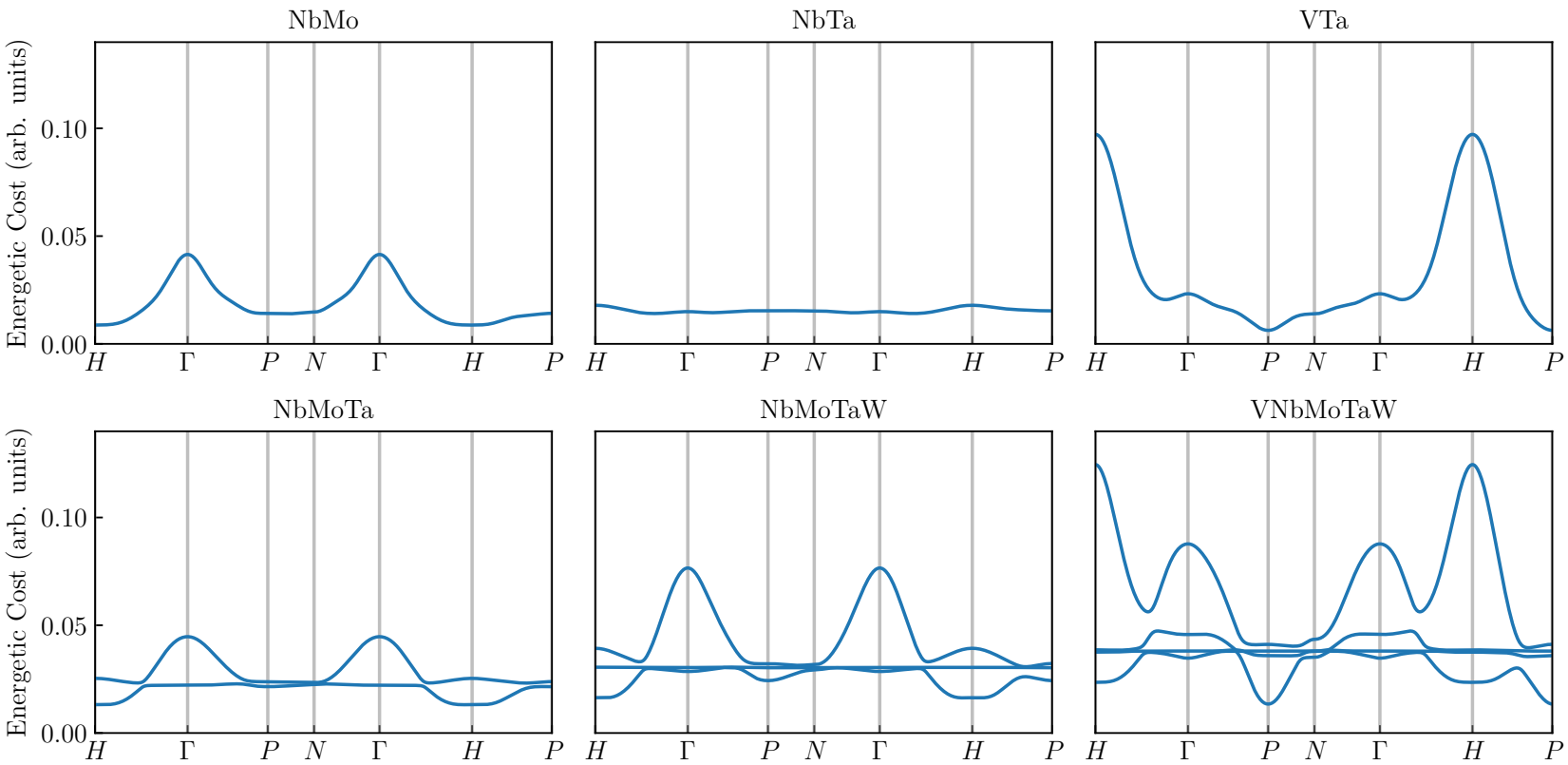
$$H(\{\xi_{i\alpha}\}) = \frac{1}{2}\sum_{\substack{i\alpha \\ j\alpha'}} V_{i\alpha;j\alpha'}\,\xi_{i\alpha}\xi_{j\beta} + \sum_{i\alpha}\nu_{i\alpha}\xi_{i\alpha}$$

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



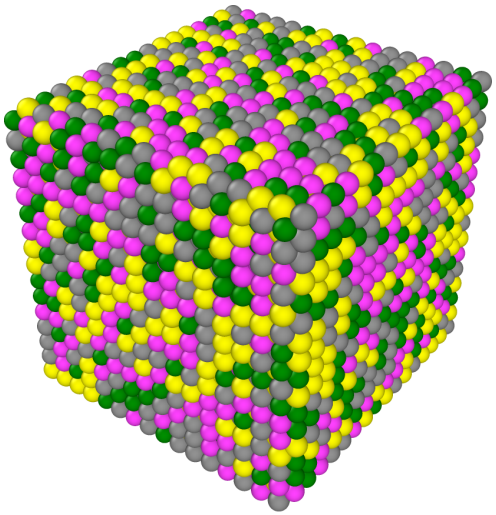
Linear Response

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

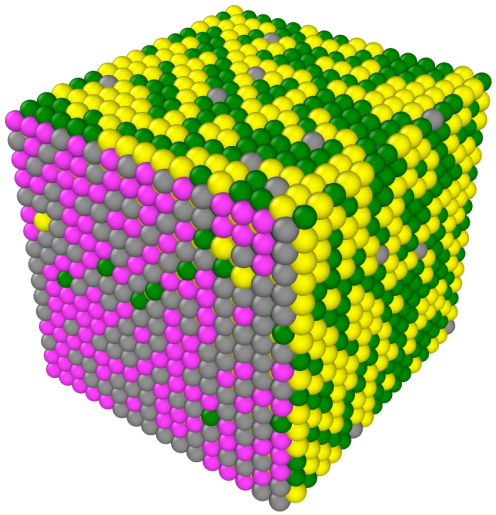


Atomistic Simulations

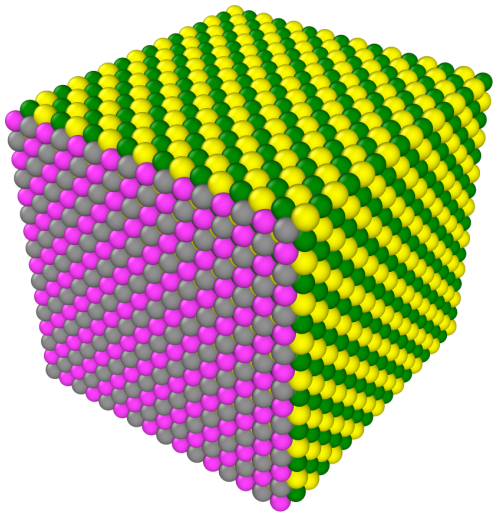
NbMoTaW



1200K

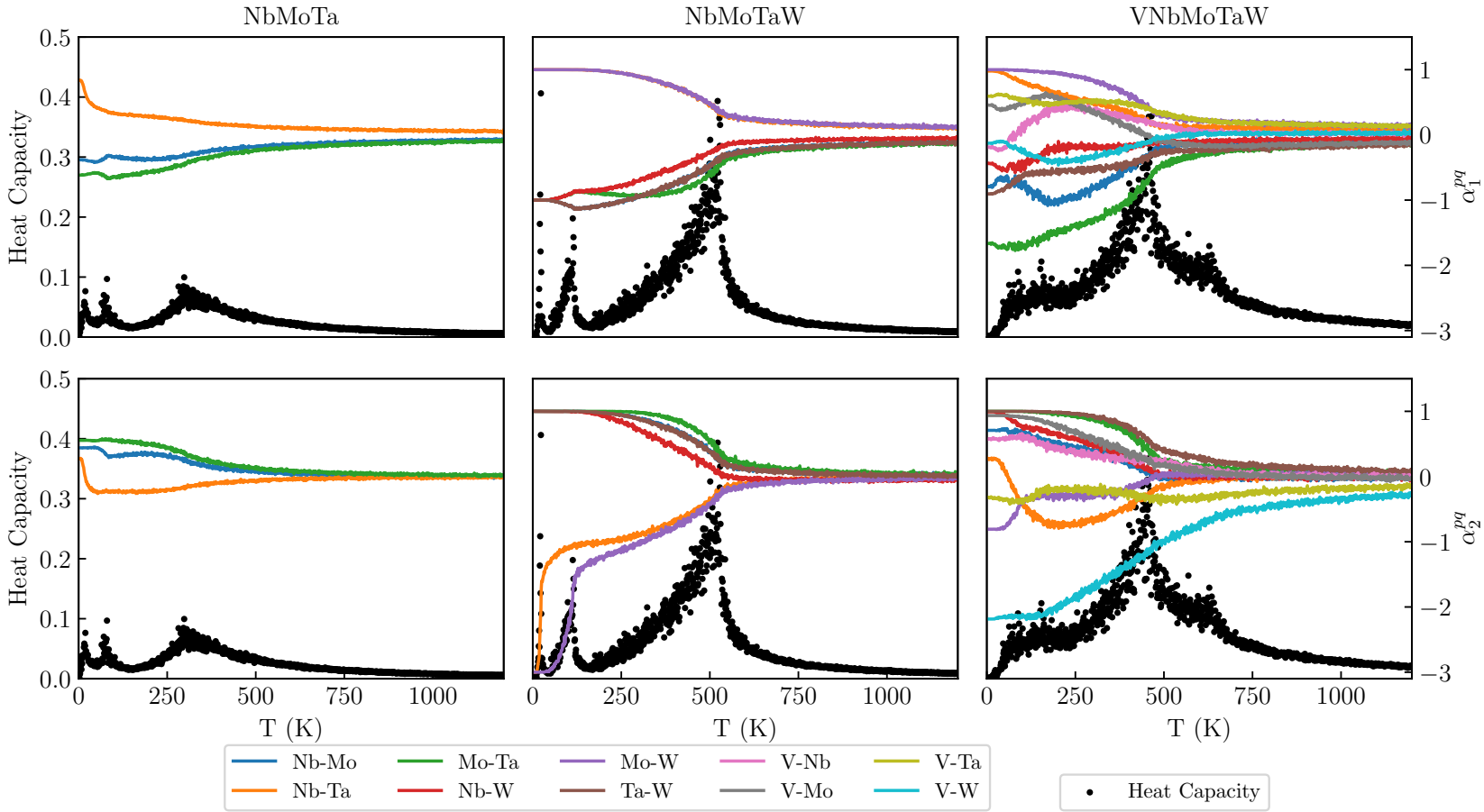


300K



10K

Atomistic Simulations



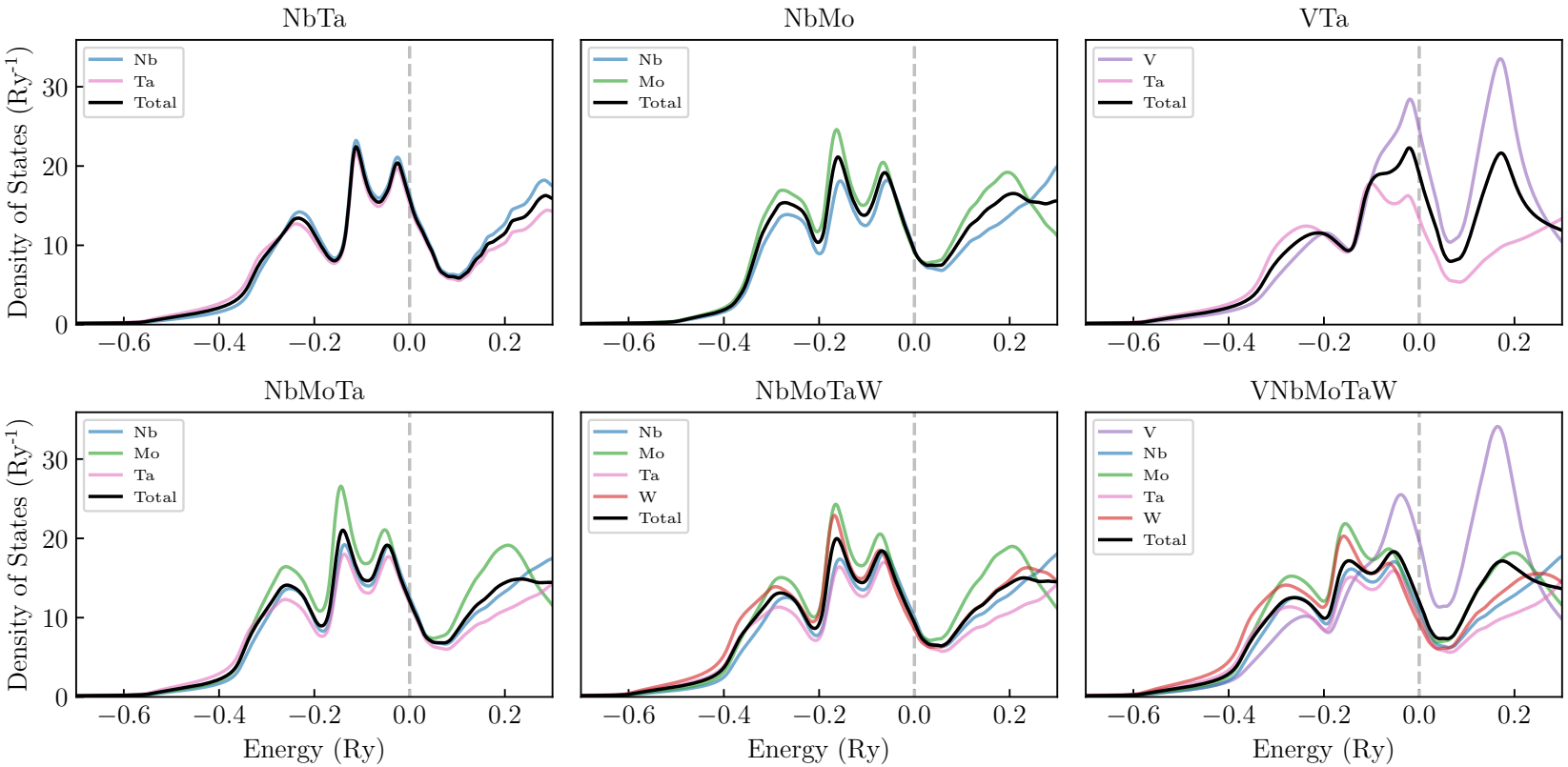
Summary

- B2-like ordering successfully predicted for NbMoTaW.
- SRO in VNbMoTaW dominated by V.
- Insight into physical origins of order.
- **Method obtains results comparable with conventional techniques for a fraction of the computational cost.**

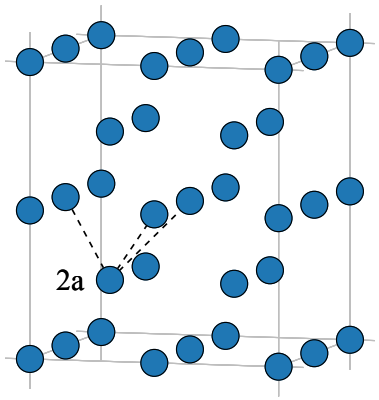
Acknowledgements

- 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

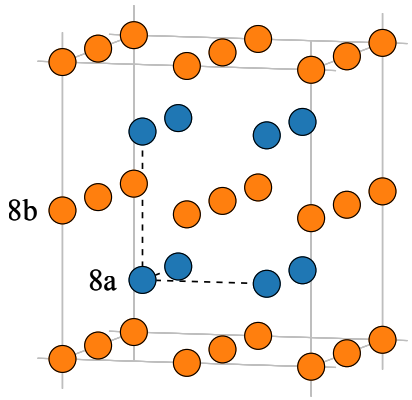
Density of States



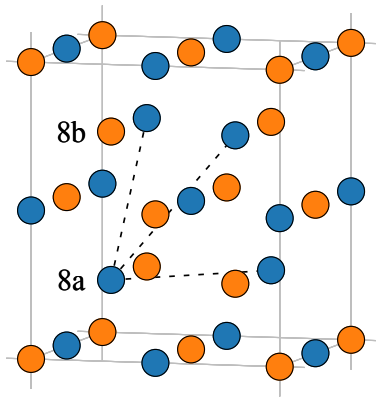
BCC Ordered Structures



A2



B2



B32

Linear Response

Material	$T_{\text{us}}(K)$	k_{us}	δc_1	δc_2	δc_3	δc_4	δc_5
NbMoTa	511	$\{0, 0, 1\}$	-0.406	0.816	-0.410		
NbMoTaW	559	$\{0, 0, 1\}$	-0.383	0.594	-0.595	0.383	
VNbMoTaW	742	$\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$	-0.824	0.012	0.085	0.252	0.500

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

$$V_{\alpha\beta}(\mathbf{q}) = V^0_{\alpha\beta} + V^1_{\alpha\beta}\left(\sum_{\{\mathbf{R}_i\}_1} e^{i\mathbf{q}\cdot\mathbf{R}_i}\right) + \cdots + V^N_{\alpha\beta}\left(\sum_{\{\mathbf{R}_i\}_N} e^{i\mathbf{q}\cdot\mathbf{R}_i}\right), \tag{2}$$

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

Ab Initio Theory

- Expand free energy around homogeneous reference state:

$$\Omega(\{\bar{c}_{i\alpha}\}) = \Omega(\{c_\alpha\}) + \sum_{i\alpha} \frac{\partial \Omega}{\partial \bar{c}_{i\alpha}}\Big|_{\{c_\alpha\}} \Delta\bar{c}_{i\alpha} + \frac{1}{2}\sum_{i\alpha;j\alpha'} \frac{\partial^2 \Omega}{\partial \bar{c}_{i\alpha}\partial \bar{c}_{j\alpha'}}\Big|_{\{c_\alpha\}} \Delta\bar{c}_{i\alpha}\Delta\bar{c}_{j\alpha'} + \ldots \quad (3)$$

Ab Initio Theory

- Important bit is second-order term.

$$\delta\Omega = \frac{1}{2}\sum_{i,j}\sum_{\alpha,\alpha'}\Delta\bar{c}_{i\alpha}[\beta^{-1}\,C^{-1}_{\alpha,\alpha'} - S^{(2)}_{i\alpha,j\alpha'}]\Delta\bar{c}_{j\alpha'}, \qquad (4)$$

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,

$$\delta\Omega = \frac{1}{2}\sum_{\mathbf{k}}\sum_{\alpha,\alpha'}\Delta\bar{c}_{\alpha}(\mathbf{k})[\beta^{-1}C^{-1}_{\alpha\alpha'} - S^{(2)}_{\alpha\alpha'}(\mathbf{k})]\Delta\bar{c}_{\alpha'}(\mathbf{k}). \qquad (5)$$