Magnetism Matters: Modelling Atomic Arrangements in NiCoCr

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The Challenge

Modelling atomic arrangements in multicomponent alloys is difficult on account of the vast space of possible configurations to sample. In addition, for alloys containing mid- to late-3d elements, it is necessary to model the magnetic state appropriately.

Superb test case is given by NiCoCr, a ternary 'medium-entropy' alloy consisting of three elements which can exhibit interesting magnetic behaviours. At equiatomic composition, the material is near a quantum-critical point, and there is debate in the literature about how to model the material's magnetic state.

Medium- and High-entropy alloys:

– First examples synthesised in 2004 (3, 4).
– Multiple metals combined in roughly equal ratios.
– Simple, close-packed structures: fcc, bcc, hcp.
– Single-phase solid solution stabilised by configurational entropy:

$$-\beta^{-1}\sum_{i\alpha} c_{i\alpha}\log c_{i\alpha} \qquad (1)$$

Our Modelling Approach

Linear Response

– Mean-field free energy based on ensemble-averaged site-occupancies, $\{\bar{c}_{i\alpha}\}$(1, 2):

$$\Omega = -\beta^{-1}\sum_{i\alpha} c_{i\alpha}\log c_{i\alpha} - {\sum_{i\alpha}}' \nu_{i\alpha} c_{i\alpha} + \langle\Omega_{\text{el}}\rangle_0[\{c_{i\alpha}\}] \qquad (2)$$

– Impose perturbation about homogeneous reference state, $c_{i\alpha} = c_\alpha + \Delta c_{i\alpha}$.
– Change in free energy due to perturbation written:

$$\delta\Omega = \frac{1}{2}\sum_{i,j}\sum_{\alpha,\alpha'}\Delta\bar{c}_{i\alpha}[\beta^{-1}C^{-1}_{\alpha,\alpha'} - S^{(2)}_{i\alpha,j\alpha'}]\Delta\bar{c}_{j\alpha'}, \quad \text{where} \quad C^{-1}_{\alpha\alpha'} = \frac{\delta_{\alpha\alpha'}}{c_\alpha}, \quad -\frac{\partial^2\langle\Omega_{\text{el}}\rangle_0}{\partial\bar{c}_{i\alpha}\partial\bar{c}_{j\alpha'}} \equiv S^{(2)}_{i\alpha;j\alpha'}. \qquad (3)$$

Term in square brackets referred to as 'chemical stability matrix'.

– Assess which perturbations are energetically favourable to find dominant correlations.
– Convenient to perform analysis in reciprocal space, writing $\Delta c_\alpha(\mathbf{k})$.
– Derivatives of internal energy, $S^{(2)}_{i\alpha;j\alpha'}$, and description of atomic short-range order come from *ab initio* DFT analysis (1): can compare different magnetic states.

Atomistic Modelling

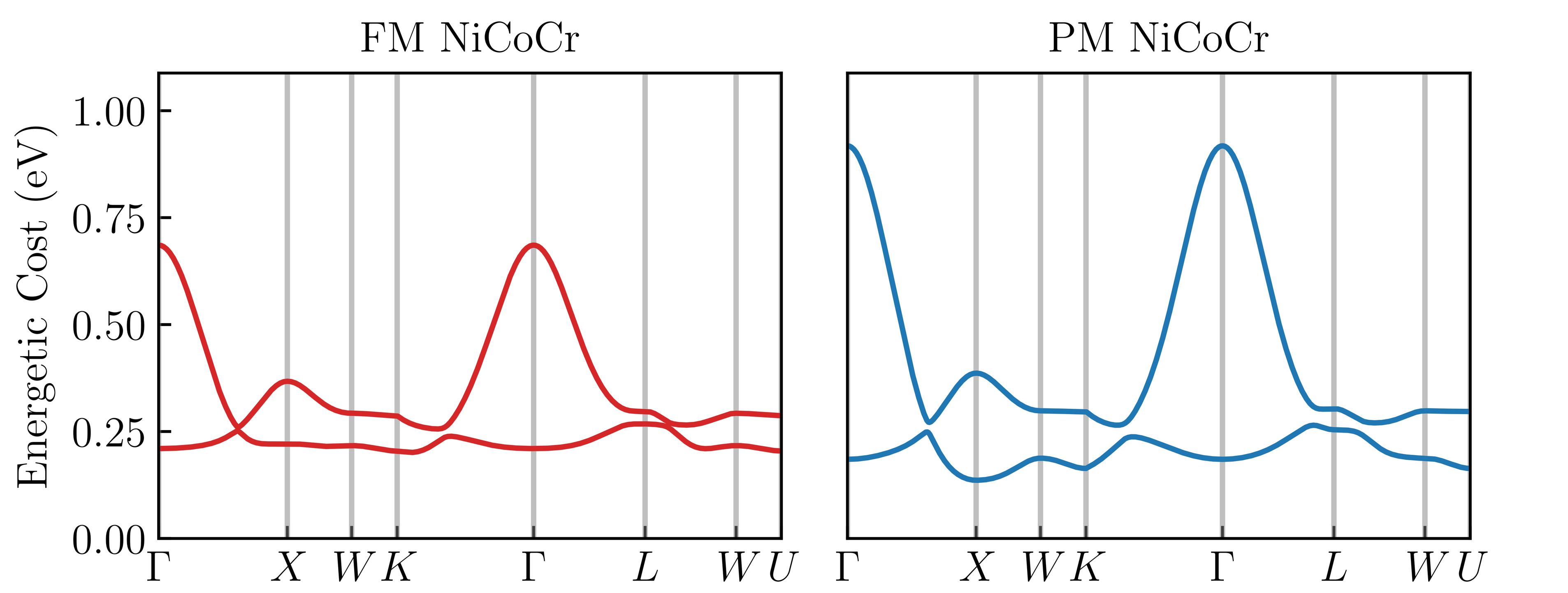
– Fit to a Bragg-Williams Hamiltonian for atomistic modelling:

$$H(\{\xi_{i\alpha}\}) = \sum_{i,j}\sum_{\alpha,\alpha'} V_{i\alpha;j\alpha'}\xi_{i\alpha}\xi_{j\alpha'} + \sum_{i\alpha}\nu_{i\alpha}\xi_{i\alpha} \qquad (4)$$

$\xi_{i\alpha}$ - does site i contain atom of species α?

Linear Response: Stability Analysis

Eigenvalues of Chemical Stability Matrix



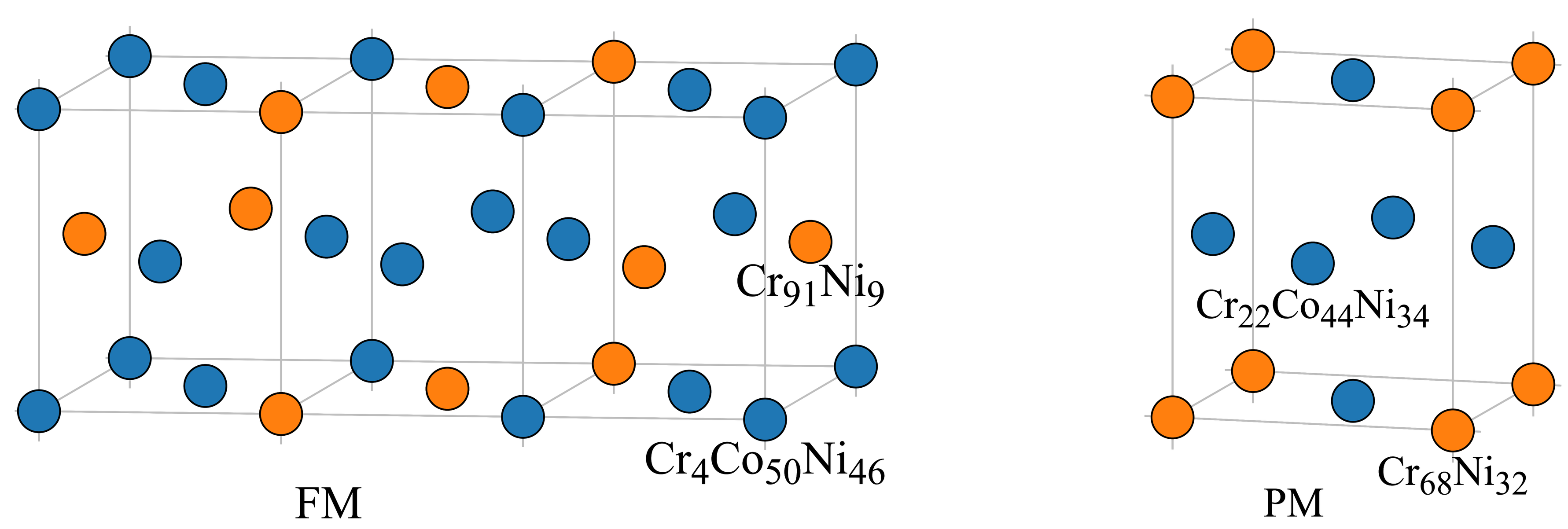
Eigenvalues of the chemical stability matrix around the irreducible Brillouin zone for NiCoCr in its ferrimagnetic ('FM') and paramagnetic ('PM') states, evaluated at T=1000 K. There is clear competition between minima at $\mathbf{k} = (0, 0, 1)$ $\mathbf{k} = (0, 2/3, 2/3)$

Ordering Temperatures

Magnetic State	T_{ord} (K)	$\mathbf{k}_{\text{ord}}$ $(2\pi/a)$	Δ Ni	Δ Co	Δ Cr
FM	252	$(0, 0, 1)$	−0.345	−0.468	0.813
PM	606	$(0, \frac{2}{3}, \frac{2}{3})$	−0.035	−0.689	0.724

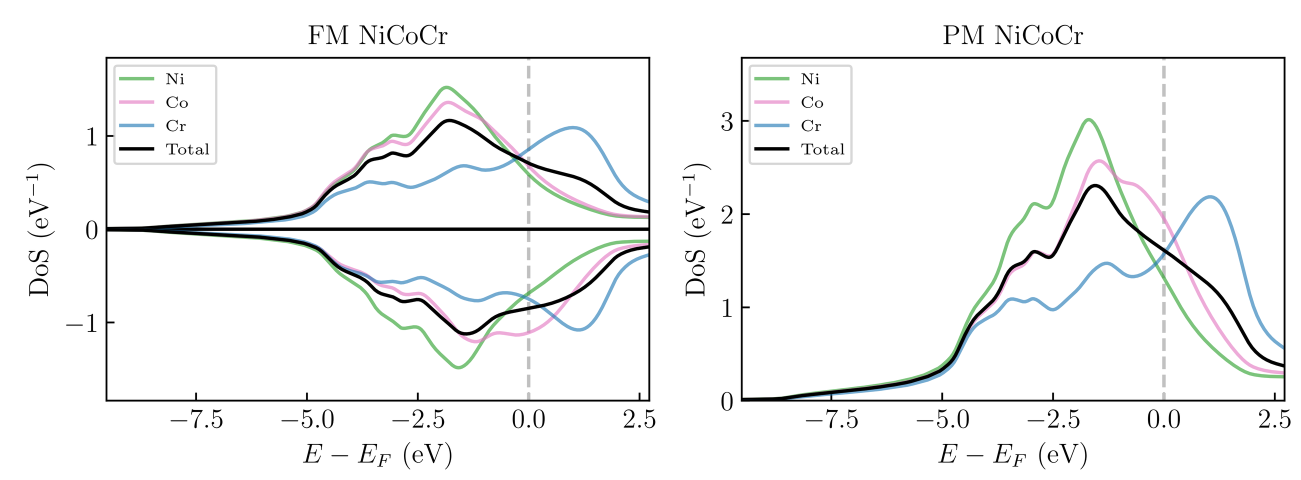
Predicted chemical ordering assuming a *ferrimagnetic* state is the $MoPt_2$ structure, versus $L1_2$ structure for paramagnetic state. Ordering temperature also changes dramatically.

Orderings Visualised



Visualisations of the predicted (partially) chemically ordered structures for both magnetic states. The nature of chemical order is unequivocally connected to the magnetic state of the material. This has significant implications for materials modelling.

Electronic Origins



All three of Ni, Co, and Cr, acquire magnetic moments, and this affects electronic structure, *i.e.* the 'glue' which drives chemical ordering. Effect most pronounced in majority spin channel.

Conclusions

– Correct treatment of magnetic state essential to modelling atomic arrangements and materials properties.
– Annealing some alloys in an applied magnetic field could alter nature of atomic arrangements.

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References

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