Compositional order in the Cantor-Wu high entropy alloys via *ab initio* theory and atomistic modelling

This is the supplementary materials accompanying the main text. The details involved in the main text will be explicitly addressed here.

I. WORKFLOW

To move from potentials describing the electronic structure of the alloy to atomistic modelling involves a number of steps. The workflow we used can be summarised as follows:

1. Generate self-consistent potentials via a Density Functional Theory (DFT) calculation using the Korringa-Kohn-Rostoker (KKR) method and the Coherent Potential Approximation (CPA).

2. Use these self-consistent potentials to compute the short-range order (SRO) parameters in reciprocal space *ab initio* via our implementation of the linear response theory outlined in the main text. From the SRO parameters, reconstruct the chemical stability matrix and search for the temperature and point in reciprocal space where the lowest eigenvalue passes through zero. Here we infer an order/disorder transition with the leading correlations described by the associated mode k_0 and eigenvector.

3. Take $S^{(2)}_{\alpha\beta}(\mathbf{k})$ and fit to a real-space interaction. To this end we choose to model the interaction as consisting of nearest neighbour, next-nearest neighbour, etc. This generates our $V_{i\alpha;j\beta}$ to use in atomistic modelling.

4. Perform Monte Carlo simulations using the computed interchange parameters, $V_{i\alpha;j\beta}$ to explore the phase space both above and below our estimated transition temperature.

II. INTERCHANGE PARAMETERS

Interchange parameters up to fourth neighbour distance for all six systems considered in the main text are tabulated below. These are the interactions which were used for our Monte Carlo simulations.

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

$V_{\alpha\beta}^{(2)}$	Ni	Co
Ni	0.031	-0.031
Co	-0.031	0.031

$V_{\alpha\beta}^{(3)}$	Ni	Co
Ni	0.001	-0.001
Co	-0.001	0.001

$V_{\alpha\beta}^{(4)}$	Ni	Co
Ni	0.035	-0.035
Co	-0.035	0.035

TABLE I: Fitted interchange parameters up to fourth neighbour distance for NiCo. All values are quoted in mRy.

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

$V_{\alpha\beta}^{(2)}$	Co	Cr
Co	0.109	-0.109
Cr	-0.109	0.109

$V_{\alpha\beta}^{(3)}$	Co	Cr
Co	0.100	-0.100
Cr	-0.100	0.100

$V_{\alpha\beta}^{(4)}$	Co	Cr
Co	-0.069	0.069
Cr	0.069	-0.069

TABLE II: Fitted interchange parameters up to fourth neighbour distance for CoCr. All values are quoted in mRy.

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

$V_{\alpha\beta}^{(2)}$	Ni	Cr
Ni	0.313	-0.313
Cr	-0.313	0.313

$V_{\alpha\beta}^{(3)}$	Ni	Cr
Ni	0.123	-0.123
Cr	-0.123	0.123

$V_{\alpha\beta}^{(4)}$	Ni	Cr
Ni	0.128	-0.128
Cr	-0.128	0.128

TABLE III: Fitted interchange parameters up to fourth neighbour distance for NiCr. All values are quoted in mRy.

$V^{(1)}_{\alpha\beta}$	Ni	Co	Cr
Ni	-0.218	0.682	-0.465
Co	0.682	0.673	-1.351
Cr	-0.465	-1.351	1.813

$V^{(2)}_{\alpha\beta}$	Ni	Co	Cr
Ni	0.266	0.032	-0.296
Co	0.032	0.004	-0.035
Cr	-0.296	-0.035	0.330

$V^{(3)}_{\alpha\beta}$	Ni	Co	Cr
Ni	0.021	0.099	-0.120
Co	0.099	0.052	-0.151
Cr	-0.120	-0.151	0.270

$V^{(4)}_{\alpha\beta}$	Ni	Co	Cr
Ni	0.239	-0.005	-0.232
Co	-0.005	-0.050	0.056
Cr	-0.232	0.056	0.175

TABLE IV: Fitted interchange parameters up to fourth neighbour distance for NiCoCr. All values are quoted in mRy.

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

$V^{(4)}_{\alpha\beta}$	Ni	Co	Fe	Cr
Ni	0.255	0.006	-0.032	-0.229
Co	0.006	-0.046	-0.001	0.041
Fe	-0.032	-0.001	0.003	0.030
Cr	-0.229	0.041	0.030	0.158

TABLE V: Fitted interchange parameters up to fourth neighbour distance for NiCoFeCr. All values are quoted in mRy.

$V^{(1)}_{\alpha\beta}$	Ni	Co	Fe	Mn	Cr
Ni	-0.464	0.528	0.097	0.183	-0.344
Co	0.528	0.701	0.063	-0.282	-1.010
Fe	0.097	0.063	0.002	-0.048	-0.114
Mn	0.183	-0.282	-0.048	-0.067	0.214
Cr	-0.344	-1.010	-0.114	0.214	1.253

$V^{(2)}_{\alpha\beta}$	Ni	Co	Fe	Mn	Cr
Ni	0.435	0.129	-0.016	-0.229	-0.319
Co	0.129	0.036	0.001	-0.070	-0.096
Fe	-0.016	0.001	-0.000	0.008	0.008
Mn	-0.229	-0.070	0.008	0.121	0.171
Cr	-0.319	-0.096	0.008	0.171	0.235

$V^{(3)}_{\alpha\beta}$	Ni	Co	Fe	Mn	Cr
Ni	0.007	0.092	0.014	-0.009	-0.104
Co	0.092	0.062	0.006	-0.047	-0.112
Fe	0.014	0.006	0.000	-0.007	-0.013
Mn	-0.009	-0.047	-0.007	0.007	0.056
Cr	-0.104	-0.112	-0.013	0.056	0.173

$V^{(4)}_{\alpha\beta}$	Ni	Co	Fe	Mn	Cr
Ni	0.296	0.027	-0.003	-0.138	-0.182
Co	0.027	-0.040	-0.002	-0.010	0.025
Fe	-0.003	-0.002	-0.000	0.001	0.004
Mn	-0.138	-0.010	0.001	0.064	0.083
Cr	-0.182	0.025	0.004	0.083	0.070

TABLE VI: Fitted interchange parameters up to fourth neighbour distance for NiCoFeMnCr. All values are quoted in mRy.