First-principles concentration-wave approach to predict incipient order in high-entropy alloys: case of Ti0.25 CrFeNiAlx

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Abstract
High-temperature disordered multi-component alloys, including high-entropy alloys, experience either segregation or partially-ordered phases to reach low-temperature phases. For Ti0.25CrFeNiAlx (0 ≤ x ≤ 1), experiments suggest a partially-ordered B2 phase, whereas CALculation of PHAse Diagrams (CALPHAD) predicts a region of L21+B2 coexistence. We employ first-principles KKR-CPA to assess stability of phases with arbitrary order and a KKR-CPA linear-response theory to predict atomic short-range order (SRO) in the disorder phase that reveals the competing long-range ordered (LRO) phases in a given Bravais lattice. The favorable SRO provides a specific concentration-waves (site occupation probabilities and partially-ordered unit cells) and estimated energy gains that can then be assess directly by KKR-CPA formation enthalpies. Our results are in good agreement with experiments and CALPHAD in Al-poor regions (x ≤ 0.75) and with CALPHAD in Al-rich region (1 ≥ x > 0.75). Our first-principles KKR-CPA and SRO-based concentration-wave analysis is shown to be a powerful and fast method to assess competing LRO phases in complex solid-solution alloys, and our results suggests more careful experiments in Al-rich region are needed.

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First-principles concentration-wave approach to predict incipient order in high-entropy alloys: case of Ti$_{0.25}$CrFeNiAl$_x$

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High-temperature disordered multi-component alloys, including high-entropy alloys, experience either segregation or partially-ordered phases to reach low-temperature phases. For Ti$_{0.25}$CrFeNiAl$_x$ ($0 \leq x \leq 1$), experiments suggest a partially-ordered B2 phase, whereas CALPHAD (CALPHAD) predicts a region of L2$_1$+B2 coexistence. We employ first-principles KKR-CPA to assess stability of phases with arbitrary order and a KKR-CPA linear-response theory to predict atomic short-range order (SRO) in the disorder phase that reveals the competing long-range ordered (LRO) phases in a given Bravais lattice. The favorable SRO provides a specific concentration-waves (site occupation probabilities and partially-ordered unit cells) and estimated energy gains that can then be assessed directly by KKR-CPA formation enthalpies. Our results are in good agreement with experiments and CALPHAD in Al-poor regions ($x \leq 0.75$) and with CALPHAD in Al-rich region ($1 \geq x > 0.75$). Our first-principles KKR-CPA and SRO-based concentration-wave analysis is shown to be a powerful and fast method to assess competing LRO phases in complex solid-solution alloys, and our results suggest more careful experiments in Al-rich region are needed.

I. INTRODUCTION

Multi-principal-element alloys (MPEAs), of which high-entropy alloys (HEAs) are a subset, has established a new paradigm in alloy design with key fundamental science questions and opened up a vast unexplored composition space that has lead to the discovery of novel alloys with unusual properties.$^{2,12}$ Short-range order (SRO) is one such key property in complex solid-solution alloys (CSAs), which, nonetheless, remains less explored in MPEAs.$^{13,20}$ In CSAs, the site-pairwise correlation between atoms is given by the Warren-Cowley SRO parameters defined with respect to the diffraction lattice, as found in diffuse-scattering measurements, and, in partially or fully-ordered alloys, two distant atoms are connected by non-zero LRO correlations, dictated by LRO parameters.$^{22,23}$ By controlling SRO and LRO, the processing of advanced materials can be manipulated.$^{24}$ Therefore, prediction and understanding of SRO in MPEAs is of great importance. Although SRO can be determined (in principle) experimentally from the diffuse-scattering intensities measured in reciprocal space using X-ray, neutron, or electron diffraction,$^{25,26}$ depending on the differences of atomic scattering factors. However, the electronic or microscopic origin of SRO cannot be determined from such experiments. Therefore, the calculation of diffuse intensities in high-temperature CSAs based on electronic density-functional theory (DFT) methods and the subsequent connection of those intensities to its origin(s) can provide a fundamental understanding of the experimental data and phase instabilities.$^{13}$

Generally, SRO assessed in high-temperature, homogeneously disordered CSA is not biased by an a priori choice of partial LRO structures (unit cells), which may be a problem with more traditional total-energy methods.$^{14,15}$ Singh et al.$^{16,17}$presented a DFT-based KKR-CPA thermodynamic linear-response theory (a first-principles Landau theory) that predicts all SRO pairs simultaneous (as done for displacement modes, i.e. phonons) and provides the incipient ordering in MPEAs.$^{18}$ The SRO yields the eigenvectors (chemical modes) and the maximum temperature for the most unstable mode(s) in the CSA, i.e., the spinodal temperature ($T_{sp}$), with respect to the formation of short-wavelength composition waves that characterizes potential ordered structures, i.e., site-probabilities are modulated with a wave-like periodicity.$^{25,26}$ Besides specifying SRO, a great strength of the concentration-wave approach is predicting various competing sub-lattice occupation probabilities for partial LRO phases, which can then be used to assess directly the stabilities of low-temperature competing phases with respect to random alloy.

Here, KKR-CPA formation enthalpies and SRO are predicted to assess HEA Ti$_{0.25}$CrFeNiAl$_x$ ($x$ in mole-fractions). Our first-principles results for $x \leq 0.75$ compare well with the experiments of Liu et al.$^{25}$ both show A2 as the most stable phase. However, CALPHAD suggests competing B2 and L2$_1$ phases in the Al-rich regions ($1 \geq x > 0.75$). We use the KKR-CPA linear-response calculated SRO and then, based on the analytically formulated concentration-wave site occupations, establish potential competing partially-ordered unit cells and use KKR-CPA to compare directly the partially-ordered states relative to the disordered phase. We find agreement with the CALPHAD for $x > 0.75$, predicting competing B2 and L2$_1$ phases, suggesting more careful experiments are needed.
II. COMPUTATIONAL METHOD

DFT-based KKR-CPA is a Green’s function electronic-structure approach to permit charge self-consistency and configurational averaging to be done concomitantly (averaged Green’s functions are related directly to observables). Our KKR-CPA code handles core electrons relativistically and semi-core and valence electronic scalar-relativistically (no spin-orbit terms) and the coherent potential approximation (CPA) is used to handle chemical disorder and its configurational averaging. The LibXC library is used to include generalized gradient approximation as the exchange-correlation functional. A variational potential zero $v_0$ is used to yield kinetic energies and dispersions near those of full-potential methods. The Atomic Sphere Approximation (ASA) is used to represent each Voronoi polyhedra (VP) site in the unit cell but we enforce periodic boundary conditions and use integration over the VP spatial integrals for unit cell charge distributions. For self-consistent densities, a 20 (complex) energy point Gauss-Legendre semi-circular contour integration is employed. Brillouin zone (BZ) is sampled using Monkhorst-Pack k-point method with $12 \times 12 \times 12(6)$ for A1,A2 (A3) meshes. We used 300 k-points in the irreducible-BZ to visualize dispersion along symmetry lines and chose $L_{max}=3$ spherical-harmonic basis.

Chemical SRO and Concentration-waves: Formally, the Warren-Cowley SRO parameters (pair-correlations), i.e., $\alpha_{\mu\nu}(k;T)$ in Laue units for atom types $\mu$, $\nu$, are defined relative to average x-ray scattering lattice, as atomic displacements sum to zero on average (by symmetry, for each spatial direction). In second-order variation of DFT free-energy (linear-response) of the concentration, the SRO parameters [in Laue units] are analytically found for any arbitrary MPEA at given temperature (T) with elemental (site) concentration $\{c_{\mu}\}$ to be given by

$$\begin{align*}
[\alpha^{-1}(k;T)]_{\mu\nu} &= C_{\mu\nu} - (k_B T)^{-1} c_{\mu} (\delta_{\mu \nu} - c_{\nu}) S^{(2)}_{\mu\nu}(k;T),
\end{align*}$$

where $k_B$ is the Boltzmann constant and $C_{\mu\nu}$ is a composition-only constant matrix element. The pairwise interaction energy $S^{(2)}_{\mu\nu}(k;T)$ is the chemical stability matrix in linear-response (a symmetric, thermodynamically average functional) referenced to the homogeneous MPEA which reflects the free-energy cost for all pair fluctuations of site concentrations with a specific periodicity (wavevector $k$). This $S^{(2)}_{\mu\nu}(k;T)$ reveals the unstable (Fourier) modes with order vector $k_0$ (or clustering if $k_0 = (000)$) and identifies the origin and associated energy cost for the modes.

The most unstable SRO mode has the largest peak occurring at wavevector $k_0$ for a specific $\mu - \nu$ pair in $\alpha_{\mu\nu}(k_0;T > T_{sp})$. An absolute instability to $k_0$ mode occurs below the spinodal temperature $T_{sp}$ defined where $[\alpha^{-1}](k_0;T_{sp})_{\mu\nu} = 0$. The normal modes at $T_{sp}$ are the eigenvectors of $S^{(2)}(k_0, T > T_{sp})$ driving divergence in SRO. The free energy cost to establish one of these modes vanishes at $T_{sp}$. Above $T_{sp}$, all eigenvalues remains positive, costing energy to disordered state for substantiating concentration modulations. Below $T_{sp}$, the critical eigenvalue establishes the anticipated probability distribution.

Once the normal modes of eigenvectors that drive divergence in SRO (Eq. 1) are determined, the vector of occupational probabilities ($n(r)$) of atoms to occupy specific sites in a given crystal structure, i.e., the concentration-waves for partially ordered unit cell or superlattice, can be written as

$$\begin{align*}
n(r) &= c(r) + \sum_{s,\sigma} \eta_s^\sigma (T) \nu_s \sum_j \gamma_\sigma (k_{jes}) e^{i \mathbf{k}_s \cdot \mathbf{r}}.
\end{align*}$$

Here, $c(r)$ is an $N - 1$-component vector in site occupation probabilities (for $N$ element alloy) in the Bravais lattice of the MPEA homogeneous reference state, whereas $n(r)$ depends on the type of order and real-space site coordinates. The sum $s$ runs over the “stars” (in-equivalent $k$ that define the order), $j_s$ (equivalent $k_j$ in the $s$th-star), and $\sigma$ (eigenvector branch of the free-energy quadric). The other quantities are LRO parameter $\eta_s^\sigma (T)$ for the $\sigma$th branch and $s$ star; $\nu_s$ is $N - 1$-component vector of the normal concentration mode of chemical fluctuation stability matrix for the $\sigma$th branch; and the symmetry coefficient $\gamma_\sigma (k_{jes})$ determined by normalization condition and geometry. See Ref. 19 for more details and examples. The bottom line is that Eq. 2 represents the possible competing types of ordered superlattices (symmetry broken order) that are incipient in the chemical SRO for a fixed Bravais lattice. Each of the anticipated partially- or fully-ordered cells can be assessed using KKR-CPA formation enthalpies relative to the disordered phase.

III. RESULTS AND DISCUSSION

Liu et al. recently reported experimental observations on quinary Ti$_{0.25}$CrFeNiAl$_2$ alloys and found A2 as the stable phase throughout the Al composition range, i.e., $x = 0 - 1$ mole fraction (or 0 – 23.5 at.%) for the KKR-CPA calculated phase stability plot versus Al content. Fig. 1 shows A2 as the most stable phase for $x \leq 3.25$. Over the full Al composition range, A1 is the stable phase from 3.25 mole fraction and beyond. The initial increase in A1% further stabilizes the A2 phase (until 40%Al), i.e., Al plays the role of A2-phase stabilizer, which is in agreement with the experiments and CALPHAD.

To understand the effect of chemical disorder by Al-doping on A2-Ti$_{0.25}$CrFeNiAl$_2$, we calculate Bloch-spectral function (BSF) using KKR-CPA based electronic structure approach for $x=0$, and $x=1.0$ cases as shown in Fig. 2. The BSF is the generalization of ordered band structure, when disorder is present. On adding Al to Ti$_{0.25}$CrFeNi, the BSF is smeared out near the Fermi energy (EF) due to increased disordered scattering. The disorder broadening of the BSF can directly be related
to the inverse of the electron mean free path.\textsuperscript{19} Increased k-space smearing at $E_F$ indicates a decrease in electron mean-free path for Fig. 2(b) compared to Fig. 2(a). The shift in dispersion in Fig. 2(b) compared to Fig. 2(a) is clearly visible at low energies, i.e., below $E_F$. The Al doping enhances disorder and lowers bonding states, which stabilizes the A2 phase as also shown in Fig. 2.

For near equiatomic HEA ($x=1.0$ Al mole-fraction), the negative formation energy indicates the favorability for the mixing of alloying elements.

The configurational entropy, dominated by point-entropy $S_{pt} = k_B \sum_{\mu=1}^{N} c_\mu \ln c_\mu$ ($S_{pt} = -k_B \ln N$ for $c_\mu = 1/N$), is a key factor for the formation of single-phase MP\AE s. Point entropy increases with increasing number of alloying components, which suppresses the formation of intermetallic phases\textsuperscript{18,19} unless enthalpically dominated by favorable chemical interactions amongst pairs of atoms, which grows as $N(N - 1) \sim N^2$. Empirically literature suggests a threshold of $S_{pt} \sim 1.5R$ for an operational definition of high-entropy alloy (assuming fully random solid solution).\textsuperscript{23} While $S_{pt}$ in A2 Ti$_{0.25}$CrFeNiAl$_x$ is large, a strong magnetic phase also has a significant contribution, see Table I.

For solid solutions, we estimate the chemical entropy by $S_{pt}$ and the magnetic entropy by $\Delta S_{mag} = c_\mu \ln(1 + \mu_\nu)$, here $\mu_\nu$ are the magnetic moment of $\nu^{th}$ element in units of gas constant (R) \cite{Boltzman}. As the SRO is dictated mostly by the electronic-structure of the alloy, the electronic origins of the observed ordering tendencies in Ti$_{0.25}$CrFeNiAl$_x$ can be determined, i.e., all the competing effects (e.g., band-filling, Fermi-surface nesting, atomic size, and charge transfer) can be assessed\textsuperscript{19,41}. To reveal the ordering behavior of Ti$_{0.25}$CrFeNiAl$_x$ and find out the plausible reasons for disagreement between experiments and CALPHAD, we chose four sets of alloys, i.e., $x = 0.25, 0.50, 0.75, 1.00$, permitting a one-to-one comparison to experimental composition range of Liu et al.\textsuperscript{37} As the SRO is dictated mostly by the electronic-structure of the alloy, the electronic origins of the observed ordering tendencies in Ti$_{0.25}$CrFeNiAl$_x$ can be determined, i.e., all the competing effects (e.g., band-filling, Fermi-surface nesting, atomic size, and charge transfer) can be assessed\textsuperscript{19,41}.

We present Ti$_{0.25}$CrFeNiAl$_{0.5}$ ($x = 0.5$) to exemplify the predictive capability of the SRO and concentration-wave approach. In Fig. 3 we plot the interchange energies $S_{\mu\nu}^{(2)}$ (b) and SRO (a) at 1.15 of the calculated $T_{sp}$ (794 K). As $\alpha^{-1}(\mathbf{k} = \mathbf{H}; T)|_{\mu\nu}$ vanishes at $T_{sp}$, the SRO diverges at $k_0 = \mathbf{H} = (111)$, indicating B2-type (CsCl) ordering instability. At $T_{sp}$, the Al-Fe pair drives the instability, whereas Al-Ni pair is the most dominant SRO. Clearly, $\alpha_{\mu\nu}(\mathbf{H})$ has a dominant SRO peak for Al-Ni pair (followed by Al-Fe and Ti-Ni); however, the instability in $S^{(2)}$ is driven by Al-Fe pairs (followed by Al-Cr). This odd (but correct) result occurs due the probability sum rule and the matrix-inverse relating $\alpha_{\mu\nu}(\mathbf{k})$ with $S_{\mu\nu}^{(2)}(\mathbf{k})$.\textsuperscript{17,18,41,42}

The instability at $\mathbf{H}$ in A2-Ti$_{0.25}$CrFeNiAl$_{0.50}$ occurs when (at least) one of the eigenvalues of the correlation

TABLE I. The chemical, magnetic and total entropy contribution in units of gas constant (R), considering $k_B=1$.

| $x_{Al}$ | $S_{mix}$ | $S_{mag}$ | $S_{total}$ |
|----------|-----------|-----------|-------------|
| 0.25     | 1.40      | 0.22      | 1.62        |
| 0.50     | 1.48      | 0.19      | 1.67        |
| 0.75     | 1.51      | 0.17      | 1.68        |
| 1.00     | 1.52      | 0.15      | 1.67        |
matrix is maximum, i.e., inverse of the corresponding pair-correlation component of the correlation matrix vanishes. The relative polarization of concentration waves is represented by the eigenvector corresponding to the vanishing eigenvalue of aforementioned correlation matrix in the Gibbs space. We extract the eigenvector corresponding to \( \mathbf{H} \) and \( \mathbf{P} \) for \( \text{Ti}_{0.25}\text{CrFeNiAl}_{0.50} \) at \( T_{sp} \) to analyze the B2 and L2₁ type ordering. The eigenvectors at \( T_{sp} \) helps determine the LRO parameters to solve the concentration-wave Eq. (2) for occupation probabilities [19].

Using disordered state information of elemental composition, structure factor, instability vector and eigenvector (at \( T_{sp} \)), the concentration-wave (probability \( n(\mathbf{r}) \)) for \( \text{A2-Ti}_{0.25}\text{CrFeNiAl}_{0.50} \) can be written as (using Ni as the ‘host’ arbitrarily):

\[
\begin{bmatrix}
  n^{A1}(\mathbf{r}) \\
  n^{Cr}(\mathbf{r}) \\
  n^{Fe}(\mathbf{r}) \\
  n^{Ti}(\mathbf{r})
\end{bmatrix} =
\begin{bmatrix}
  0.133 \\
  0.269 \\
  0.269 \\
  0.050
\end{bmatrix} + \eta_{B2} \frac{1}{2} \begin{bmatrix}
  +1.167 \\
  +0.027 \\
  −0.521 \\
  +0.271
\end{bmatrix} e^{i(111) \cdot \mathbf{r}},
\tag{3}
\]

where \( \eta_{B2} \) is the LRO parameter for B2-order, which is used for occupation probability determination for B2 sublattices at \( T = T_{sp} \), i.e., \( a=(000) \) or \( b=(\frac{1}{2} \frac{1}{2} \frac{1}{2}) \). With sum rules \( \sum_{\alpha=1}^{N} c_{\alpha} = \sum_{\alpha=1}^{N} n_{\alpha}(\mathbf{r}) = 1 \), \( n^{Ni}(\mathbf{r}) \) is obtained.

Upon ordering the A2 lattice splits into two simple-cubic sublattices with ordering vector \( \{111\} \). Here, the maximum possible LRO corresponds to Al at sublattice \( \{\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \), i.e., occupation probability of Al vanishes and \( n^{Al} = 0 \). With \( n^{Al} = 0 \), Eq. (3) (righthand side for Al occupation) simplifies to \( 0.133 − 0.5 \times 1.167 \times \eta_{B2} = 0 \). As the alloy cannot have negative probabilities, the maximum LRO parameter is \( \eta_{B2} = 0.22794 \) and corresponds to unstable \( k_{0} = \{111\} \) and to sublattice \( \{\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \). The occupation probabilities \( n(\mathbf{r}) \) for sublattices \( \{000\} \) and \( \{\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \) calculated using the maximum allowable LRO are \((0.26600, 0.27208, 0.20962, 0.08089, 0.17141) \) and \((0.26592, 0.32838, 0.01911, 0.38659) \), respectively. The calculated occupations probabilities from first-principles SRO theory shows that in symmetry-breaking process, i.e., on ordering Al breaks the symmetry of A2 lattice and preferentially occupies the cube corner. The Al probability vanishes at one of sublattice, i.e., \( \{\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \). This way \( \text{Al}_{0.50}\text{CrFeNiTi}_{0.25} \) partially orders into B2 superstructure, where partially-ordered B2 phase has lower energy than A2 phase, where the energy gain from partial ordering to this state \( \Delta E_{B2-A2}^{B2} \) is given by the KKR-CPA total energy difference from disordered A2 and partially-ordered B2 (site probabilities given by Eq. (3)), i.e., \( \Delta E_{B2-A2}^{B2} = E_{B2}^{A2} − E_{A2} = −3.48 \) mRy. The partially-ordered energetics is very sensitive to order parameter and sublattice occupations. Thus, care must be taken in calculating occupation probabilities such that sum rules are obeyed. The B2 phase is stabilized with respect to A2 phase using similar calculations for \( x = 0.75 \) and 1, yielding KKR-CPA \( \Delta E_{B2-A2}^{B2} \) of 2.98 mRy and 8.33 mRy, respectively.

As we have already discussed, A2 can order into different lower symmetry structures in going from high-temperature (disorder) phase to low-temperature (partially-ordered) phases. At first, on lowering temperature A2 lattice shows regions of B2 superstructure by lowering symmetry along \( \{111\} \). Further lowering the temperature can further break the A2 symmetry along \( \{111\} \) (secondary ordering) and may order into L2₁ superstructure depending on the material characteristics.

The A2 to B2 transition is second-order and specified by one LRO parameter, while L2₁ is controlled by two: \( \eta_{1} \) and \( \eta_{2} \). Our KKR-CPA linear-response predicts SRO, which yield second-order transitions, but often dictate the expected first-order. However, first-order transitions have a discontinuous \( \eta(T) \) versus \( T \), requiring a thermodynamic simulation to predict directly. L2₁ occurs due to secondary-ordering, a qualitative prediction can be made if we deliberately break the symmetry of \( \text{Ti}_{0.25}\text{CrFeNiAl}_{0.50} \) along \( \{\frac{111}{2}\} \) in presence of \( \{111\} \) wavevector using the eigenvectors calculated in primary transition, i.e., in A2-B2 ordering. L2₁ is represented by a concentration-wave with vector \( n(\mathbf{r}) \)

\[
\begin{bmatrix}
  n^{A1}(\mathbf{r}) \\
  n^{Cr}(\mathbf{r}) \\
  n^{Fe}(\mathbf{r}) \\
  n^{Ti}(\mathbf{r})
\end{bmatrix} =
\begin{bmatrix}
  0.2375 \\
  0.2375 \\
  0.2375 \\
  0.0500
\end{bmatrix} + \frac{\eta_{B2}}{2} \begin{bmatrix}
  +1.167 \\
  +0.027 \\
  −0.521 \\
  +0.271
\end{bmatrix} \times \{\frac{\eta_{1}}{4} e^{2\pi i k_{1} \cdot \mathbf{r}} \}
\tag{4}
\]

with \( k_{1} = \{111\} \) and \( k_{2} = \{\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \) at \( T = T_{sp} \). The last term reflects the additional L2₁ ordering over B2 order, enriching minority components along \( \{\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \).
It is convenient to describe A2 lattice with L2\(_1\) ordering with the help of the four interpenetrating FCC sublattices: \((000)\), \((\frac{1}{2} \frac{1}{2} \frac{1}{2})\), \((\frac{1}{4} \frac{1}{4} \frac{1}{4})\) and \((\frac{3}{4} \frac{3}{4} \frac{3}{4})\), with twice the cubic lattice parameter of A2 phase. The maximum LRO \(\eta_1\) and \(\eta_2\) correspond to the lattice \((\frac{1}{2} \frac{1}{2} \frac{1}{2})\) and \((\frac{1}{4} \frac{1}{4} \frac{1}{4})\) for which ‘Al’ site probability vanishes first, i.e., \(n_{Al}^{A2} = 0\) and \(0.133 - \frac{1}{2} \times 1.167 \times \eta_1(T) = 0\) and \(0.133 - 0.25 \times 1.167 \times \eta_2(T) = 0\) at \(T = T_{sp}\). The resulting LRO parameters are \(\eta_1 = 0.45587\) and \(\eta_2 = 0.32235\) for sub-lattices \((\frac{1}{2} \frac{1}{2} \frac{1}{2})\) and \((\frac{1}{4} \frac{1}{4} \frac{1}{4})\), respectively, for unstable wavevector \(\mathbf{k}_0 = (111) + (\frac{1}{2} \frac{1}{2} \frac{1}{2})\) at \(T = T_{sp}\).

With a non-stoichiometric \(\text{Al}_{0.50}\text{CrFeNiTi}_{0.25}\) the above probabilities lead to a partially-ordered \(\text{L}_2\) state. The calculated KKR-CPA energy gain is \(E^{\text{L}_2} - E^{\text{A}_2} = 10.14\) mRy for partially-ordered \(\text{L}_2\) phase with respect to A2 phase, and \(E^{\text{B}_2} - E^{\text{A}_2} = 6.64\) mRy relative to B2 phase, i.e., \(E^{\text{L}_2} - E^{\text{B}_2} = 3.48\) mRy. For \(\text{Ti}_{0.25}\text{CrFeNiAl}_{1.2}\), we also found that \(\text{L}_1\) phase is stabilized with respect to A2 and B2 by \(E^{\text{A}_2} - E^{\text{B}_2} = 2.98\) mRy and \(E^{\text{B}_2} - E^{\text{A}_2} = 2.49\) mRy for \(x = 0.75\); and, for \(x = 1\), by \(E^{\text{L}_2} - E^{\text{B}_2} = 8.33\) mRy and \(E^{\text{B}_2} - E^{\text{L}_2} = 6.11\) mRy. The spinodal decomposition temperature occurs at \(T_{sp} = (794; 1802; 1190)\) K for \(x = (0.50; 0.75; 1)\), respectively. The increase in Al content increases stability with disorder, i.e., disorder phase remains stable over larger temperature range.

In alloys, the instability occur at the spinodal temperature but mixture still remains homogeneous. For homogeneous fluctuations, we can write from linear-response approach the change to the free-energy in terms of concentration fluctuations and pair-correlation function evaluated at the point of instability. The estimated change in energy, \(\delta E^{X - A_2}\), can be written \((5)\) as:

\[
\delta E^{X - A_2} = \frac{1}{2} \sum_{j \neq \beta} \sum_{\alpha \neq \beta} S_{\alpha \beta}^{(2)}(\mathbf{k}_{j,\alpha}; T) \delta c_{\alpha j}^{(2)}(\mathbf{k}_{j,\beta}) \delta c_{\beta j}^{(2)}(\mathbf{k}_{j,\alpha}),
\]

where \(X\) is superlattice order for any \(\mathbf{k}_{j,\alpha}\) instability with \(\delta c_{\alpha j}(\mathbf{k}_{j,\beta})\) associated concentration changes, respectively. This ‘back-of-the-envelope’ calculation uses the pair-interchange energies to estimate directly the energy gain for particular ordering without additional calculations beyond the SRO. In Table I the SRO-estimated B2 energy gain is \(\delta E^{B_2 - A_2}\) \((\mathbf{k}_{j,\alpha} = \mathbf{H} = (111))\) for \(x = (0.50; 0.75; 1)\) and it shows the same trend as from direct KKR-CPA calculations. It is clear that the SRO estimate give robust trends without additional calculations.

![A2-B2-L21](image)

**FIG. 4.** (Color online) Unit cell of high-symmetry (disorder) A2 lattice (left) in MPEA, which, upon cooling, lowers symmetry to a partially-ordered superstructure, e.g., B2 (middle), and at low temperature to L2\(_1\) (right). Sites: 1 A (black), 3 B (red), 1 C (yellow), 3D (blue), 3 E (brown), 1 F (purple), 3 G (green) and 1 F (orange), i.e., 8-sites (16-atoms).

### TABLE II. For \(\text{Ti}_{0.25}\text{CrFeNiAl}_{1}\) we show the B2-A2 energy difference from SRO \((\delta E_{\text{SRO}})\) which compares well with a direct KKR-CPA energy difference \((\Delta E)\) using the ASA or a better integration over VP for charges.\(^{[1]}\)

| \(x\) | \(\delta E_{\text{SRO}}\) | \(\Delta E^{\text{B}_2 - \text{A}_2}\) (mRy) | \(\Delta E^{\text{L}_2 - \text{A}_2}\) (mRy) | \(\Delta E_{\text{VP}}\) |
|---|---|---|---|---|
| 0.50 | -5.03 | -3.48 | -3.26 |
| 0.75 | -4.23 | -2.98 | -2.70 |
| 1.00 | -9.43 | -8.33 | -7.88 |
perfectly ordered. In a MPEA, as temperature is lowered, the B2 phase can only be partially-ordered, then B2 phase breaks symmetry along (111) to a Heusler-type superstructures, e.g., DO3 (AB3) or L21 (ABC2).

IV. CONCLUSION

For arbitrary MPEAs, we presented a first-principles KKR-CPA methods for calculating the relative stability and the atomic short-range order (SRO) via thermodynamic linear-response theory (all pair correlations obtained simultaneously) using the electronic-structure of the homogeneous alloy as a reference state. The SRO gives detailed information on the unstable ordering modes inherent in the MPEA and their origins.

From a concentration-wave analysis of the SRO, we presented a fast assessment of the probability distributions for all possible low-temperature competing partially-ordered states for a MPEA in a given Bravais lattice, which directly provides the partially- or fully-ordered unit cells for all competing states. With the relevant competing states identified, we can make an estimate of energy gain for each structure from the SRO parameters (a ‘back-of-the-envelope’ estimate that gives correct trends), or we can use the partially-ordered unit cells directly in the KKR-CPA to obtain quantitative results for energy difference between all competing states.

We exemplify the stability, electronic-dispersion, and the Warren-Cowley SRO parameter for Ti0.25CrFeNiAl0.75. Our direct KKR-CPA total-energy calculations showed that increasing Al content stabilizes A2 phase up to 2 mole-fraction, and then above 3 mole fraction A1 phase becomes stable. The KKR-CPA-based SRO calculations with a concentration-wave analysis predicts competing B2 and L21 phases in the Al-rich region, which is in good agreement with CALPHAD study of Liu et al. that has competing B2 and L21 phases in the Al rich-region (0.75 to 1 mole fraction). Our combined first-principle analysis of stability and SRO provides a robust predictive tool for guide to experiments in assessing the design and properties of complex alloy systems.

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