An averaged cluster approach to including chemical short range order in KKR-CPA

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The single-site Korringa-Kohn-Rostoker Coherent Potential Approximation (KKR-CPA) ignores short range ordering present in disordered metallic systems. In this paper, we establish a new technique to fix this shortcoming by embedding an averaged cluster that displays chemical short range order (SRO). The degree of SRO can be tuned by externally defined order parameters. The validity of this method is demonstrated by applying it to two alloy systems - the Cu0.5Zn0.5 body centered cubic (BCC) solid solution, and AlCrTiV, a four-element BCC high entropy alloy. We make the code available on the internet. Planned extensions to this work are discussed.

I. INTRODUCTION

The KKR-CPA method1–3 is heavily used to study the electronic structure of disordered systems. It is based on obtaining an effective medium, calculated using a single site approximation that mimics the ensemble average of the different configurations possible. CPA successfully predicts the total energy, the density of states, and other system properties of random alloys.4–7 One major shortcoming of the single site approximation is that it is unable to reproduce chemical ordering that may be present in the system. Short range ordering (SRO) can significantly impact the chemical and mechanical properties of a solid. For example, in the Ti-6Al alloy experiment confirms that SRO increases the nominal yield stress.8 In the CoCrNi medium entropy alloy, SRO increases the yield strength by approximately 25%, increases the nanoindentation hardness, and significantly affects the onset of plasticity.9 In α-brass, SRO can cause a change in the resistivity10 and increase the stacking fault energy.11

We wish to study the effects of SRO within the CPA framework. Modifications to the conventional CPA method are required in order to model chemical ordering. Early efforts include the molecular CPA (MCPA)12 method, where the crystal is divided into cells and each cell is treated like a “molecule”. The vibrational spectra of a one-dimensional isotopically disordered chain was successfully calculated using MCPA. For more complex systems, this method is difficult to implement. Gonis et al developed the Embedded Cluster Method (ECM-CPA)13,14 which embeds differently configured clusters of real atoms within a single-site CPA medium. The site-diagonal element of the Green’s Function (corresponding to the central atom of the cluster) is used for calculating system properties. This method was used to calculate the DOS for Ag0.5Pd0.5 binary by embedding multiple 13-atom clusters with various configurations (central atom plus 12 nearest neighbors). While this is an extremely powerful approach, it does not scale well with the number of configurations.

More recent methods include the Non-Local Coherent Potential Approximation (NLCPA)15–17, which is based on the Dynamical Cluster Approximation18 and involves finding a new effective medium, effective structure constant and a cluster-renormalized interactor that includes non-local effects. This is achieved by a self-consistent process where, for a fixed cluster size, all possible clusters are embedded and the impurity path operator is averaged to obtain the path operator for the NL-CPA medium. Unlike the Embedded Cluster approach, NL-CPA is fully self-consistent. This approach was used successfully to obtain the DOS of the Cu0.5Zn0.5 binary using two atom clusters.19,20,21 Marmodoro et al22 improved NL-CPA, making it applicable to multiple sublattices and complex geometries (MSNLCPA). Further improvements to the approach were proposed and applied to iron-based superconductor FeSe23. While NL-CPA has several desirable features, it is difficult to apply to systems that have a very large configuration space.

In the present work, we introduce the Cluster Averaged Coherent Potential Approximation (CA-CPA), that embeds a single “averaged” cluster containing SRO within the single site CPA medium. SRO is modelled by a set of pre-determined order parameters. Like ECM-CPA, our theory uses the diagonal element of the Green’s Function corresponding to the central atom of the cluster to calculate system properties. This approach does not require an ensemble of specific cluster configurations. It can be easily extended to high entropy alloy systems consisting of four or more chemical species. The paper is organized as follows. First we provide a brief introduction to the KKR method and the equations needed to embed a cluster in the CPA medium. We then introduce the formalism behind CA-CPA and compare it to NLCPA. We apply our method to calculate density of states and total energy of the Cu0.5Zn0.5 binary alloy and the AlCrTiV high entropy alloy. Both systems show B2 (CsCl) type ordering at low temperatures and A2 (BCC) type ordering at higher temperatures. We compare our results with single site CPA calculations to observe the effects of SRO. Finally we conclude with planned extensions to this work.

II. FORMALISM

The first principles electronic density functional theory (DFT) approach is based on solving a single
electron Schrödinger equation, called the Kohn-Sham equation \(^{22,23}\) (with \(\hbar = 1\) and \(m_e = \frac{1}{2}\)),
\[
[-\nabla^2 + V_{\text{eff}}(\rho(r))]\psi_i(r) = \epsilon_i\psi_i(r).
\]  
(1)

The Hamiltonian is a functional of the density, given by
\[
\rho(r) = \sum_{\epsilon_i \leq \epsilon_F} |\psi_i(r)|^2,
\]  
(2)

provided the Kohn-Sham orbital wave functions are orthonormal and the Fermi Energy \(\epsilon_F\) is known. The effective potential \(V_{\text{eff}}\) includes the Hartree potential, which describes the electronic coloumb repulsion, and the exchange-correlation (XC) functional. With the exception of the exchange-correlation functional, DFT is an exact theory. The XC functional is modelled using certain approximations. The local density approximation (LDA) \(^{22}\) assumes that the XC functional is only dependent on the local electron density, while the Generalized Gradient Approximation (GGA) \(^{24,25}\) assumes dependence on both local electron density and it’s gradient. In our work we choose to apply the GGA.

Solving the Kohn-Sham equation can be done in multiple ways. Because it is an eigenvalue equation, diagonalizing the Hamiltonian is a popular method of obtaining the required energy and wavefunctions. However, an alternate technique, called the KKR-Green’s Function Method can also be used.

A. KKR-Green’s Function Method

In the KKR method \(^{26,27}\), the system is divided into cells, each of which is centered around an atom. The one-electron effective potential \(V_{\text{eff}}\) is a sum of localized potentials, \(v_n\), within each cell. Specifically, for a cell \(n\) with volume \(\Omega_n\) whose center is the atomic site determined by position vector \(R_n\), the local potential is given by
\[
v_n(r_n) = \begin{cases} V_{\text{eff}}(r), & \text{if } r \in \Omega_n \\ 0, & \text{otherwise} \end{cases},
\]  
(3)

where \(r_n = r - R_n\). Consider each cell as an electron scattering center. The multiple scattering path matrix \(\tau_{nm}\) \(^{28}\), defined as the sum of all scattering processes that start from cell \(n\) and end at cell \(m\), becomes
\[
\tau_{nm}(\epsilon) = t_{nm}^{\epsilon} + t_{nm}^{\epsilon} \sum_{k \neq n} g^{nk}(\epsilon) \tau_{km}(\epsilon),
\]  
(4)

where \(t_{nm}^{\epsilon}\) represents the t-matrix of scattering center in cell \(n\) and \(g^{nk}(\epsilon)\) is the free electron propagator matrix that describes the propagation of a free electron with energy \(\epsilon\) from site \(n\) to site \(k\).

Calculating the multiple scattering path matrix is important because the Green’s function at a cell \(n\), given by \(G(r_n, r_n, \epsilon)\) can be written as \(^{29,30}\)
\[
G(r_n, r_n, \epsilon) = \sum_{LL'} Z_{LL'}^{n}(r_n, \epsilon)\tau_{LL'}^{nn}(\epsilon) Z_{LL'}^{*}(r_n, \epsilon) \\
- \sum_{L} Z_{L}^{n}(r_n, \epsilon)J_{L}^{nn}(r_n, \epsilon),
\]  
(5)

where \(L\) is a combination of orbital angular momentum quantum number \(l\) and magnetic quantum number \(m\). \(Z_{LL'}^{n}(r_n, \epsilon)\) and \(J_{L}^{nn}(r_n, \epsilon)\) represent the regular and irregular local solutions to Schrödinger’s equation in cell \(n\) with proper boundary conditions near \(r_n = 0\) and at the bounding sphere of cell \(n\), respectively. The complex conjugate, denoted by "*", in Eq. (5) only applies to the spherical harmonics contained in \(Z_{LL'}^{n}(r_n, \epsilon)\) and \(J_{L}^{nn}(r_n, \epsilon)\). The electron density associated with the valence states in cell \(n\) can be calculated from the Green’s Function by taking the imaginary part of the trace integrated in the valence energy band.
\[
\rho^{v}(r_n) = -\frac{1}{\pi} \text{Im} \text{Tr} \int_{\epsilon_{F}}^{T_{F}} G(r_n, r_n, \epsilon) \, d\epsilon
\]  
(6)

This means that calculation of the Kohn-Sham orbital wave functions is unnecessary in the KKR-Green’s Function Method. This is advantageous, as time-consuming operations like orthogonalizing and normalizing wave functions can be avoided.

B. Cluster Impurity Equations

In certain cases, the calculation of the multiple scattering path matrix (Eq. 4) can be simplified. For a single site CPA medium, all the cells have the same t-matrix, given by \(t_{\text{CPA}}(\epsilon)\). In such a system, the multiple scattering path matrix \(\tau_{\text{CPA}}(\epsilon)\) at a particular site \(n\) can be written as
\[
\tau_{\text{CPA}}^{nn}(\epsilon) = \frac{1}{\Omega_{BZ}} \int d^3k \left[ t_{\text{CPA}}^{-1}(\epsilon) - g(k, \epsilon) \right]^{-1},
\]  
(7)

where \(t_{\text{CPA}}\) represents the single-scattering t-matrix for the CPA medium and \(g(k, \epsilon)\) is the lattice Fourier transform of free electron propagator \(g^{nk}(\epsilon)\).

Another special case is a crystal with substitutional impurities. Consider the CPA Medium with an impurity at site \(n\). If the t-matrix at the impurity site is given by \(t_{\text{imp}}(\epsilon)\), it can be shown that the \(\tau_{\text{CPA}}^{nn}(\epsilon)\) at the impurity site is given by
\[
\tau_{\text{CPA}}^{nn}(\epsilon) = \left[ 1 + \tau_{\text{CPA}}^{nn}(\epsilon)t_{\text{CPA}}^{-1}(\epsilon) - \tau_{\text{CPA}}^{-1}(\epsilon) \right]^{-1} \tau_{\text{CPA}}^{nn}(\epsilon),
\]  
(8)

This idea can be extended to a cluster impurity in the CPA Medium. If we embed a cluster of size \(N_c\), \(\tau_{\text{CPA}}^{nn}(\epsilon)\) at impurity site \(n\) is given by
\[
\tau_{\text{CPA}}^{nn}(\epsilon) = \left[ 1 + \tau_{\text{CPA}}^{nn}(\epsilon) \left( t_{\text{CPA}}^{-1}(\epsilon) - \tau_{\text{CPA}}^{-1}(\epsilon) \right) \right]^{-1} \tau_{\text{CPA}}^{nn}(\epsilon).
\]  
(9)
Here the double underlined terms represent block matrices of size $N_c \times N_c$. The $(n, m)$ block of $\mathbf{\tau}_{\text{CPA}}(\epsilon)$ is given by

$$
\mathbf{\tau}_{nm\text{CPA}}(\epsilon) = \frac{1}{\Omega_{BZ}} \int d^3k \left[ \mathbf{t}_{\text{CPA}}^{-1}(\epsilon) - \mathbf{g}(k, \epsilon) \right]^{-1} e^{i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)},
$$

(10)

and $\mathbf{T}_{\text{CPA}}^{-1}(\epsilon)$ and $\mathbf{T}_{\text{CPA}}^{-1}(\epsilon)$ are block diagonal matrices defined as

$$
\left[ \mathbf{T}_{\text{CPA}}^{-1}(\epsilon) \right]_{nm} = t_{nm\text{CPA}}^{-1}(\epsilon) \delta_{nm}
$$

(11)

and

$$
\left[ \mathbf{T}_{\text{CPA}}^{-1}(\epsilon) \right]_{nm} = t_{n\text{CPA}}^{-1}(\epsilon) \delta_{nm}.
$$

(12)

$I_n$ refers to the impurity present at site $n$, and $t_{In}$ is the corresponding single scattering $t$-matrix.

### C. Averaged Cluster Embedding

The ECM-CPA method discussed in the introduction uses the equations defined in the above subsection to embed a cluster of real atoms in single site CPA Medium. Using this approach to study SRO would require embedding several real atom clusters, drawn from an ensemble of configurations weighted by the desired SRO. For large cluster sizes, and for systems that have more than two chemical species, this approach is highly inconvenient. Our idea is to embed clusters consisting of central atoms surrounded by “averaged” neighbor atoms. These neighbors atoms are an average of the chemical species present in the system, weighted by the chemical short-ranged order with single scattering t-matrix

$$
\mathbf{\bar{t}}_n(\epsilon) = \sum_b w_{ab} \mathbf{t}_b(\epsilon)
$$

(13)

for $a$, $b$ in the set of chemical species present. The SRO weights $w_{ab}$ are the fraction of neighbors of species $a$ that are species $b$. For a system that shows strong short range ordering, i.e. unlike neighbors are preferred, $w_{ab}$ approaches $1 - \delta_{ab}$ (taking $\delta_{ab}$ small). For the opposite case of short range clustering, where like neighbors are preferred, $w_{ab}$ approaches $\delta_{ab}$. In the limit of complete disorder, $w_{ab} = 1/N_s$, where $N_s$ is the number of chemical species present.

For a binary system with species $a$ and $b$, we can transform $w_{ab}$ to the well known Warren-Cowley SRO parameter

$$
\alpha_{ab} = 1 - 2w_{ab}.
$$

(14)

For $w_{ab} > 1/2$, $\alpha_{ab}$ becomes negative and approaches -1 as $w_{ab}$ approaches 1 corresponding to short range ordering. For $w_{ab} < 1/2$, $\alpha_{ab}$ is positive and approaches 1 as $w_{ab}$ approaches 0 corresponding to short range clustering. At $w_{ab} = 1/2$, $\alpha = 0$ corresponding to complete disorder.

To obtain the multiple scattering path matrix for an average cluster embedded in the CPA Medium, we use the cluster impurity equations defined in Section II.B. Consider a lattice for which a particular atom (the central atom) of species $a$ has $\gamma$ nearest neighbors. Then for $n, m \in \{1, 2, \cdots, \gamma\}$ we define the block-matrix $\mathbf{T}_{nm}(\epsilon)$ as

$$
\left[ \mathbf{T}_{nm}(\epsilon) \right]_{nm} = \begin{cases} t_{mn}(\epsilon) \delta_{nm}, & \text{if } n = 1 \\ t_{nm}(\epsilon) \delta_{nm}, & \text{otherwise}. \end{cases}
$$

(15)

Here $n = 1$ is the central atom and the remaining values of $n$ denote the neighbor atoms. Using the definition of $\mathbf{T}_{\text{CPA}}(\epsilon)$ from Eq. (12) and the block $\mathbf{\tau}_{nm\text{CPA}}$ from Eq. (10), we write the block $\mathbf{T}_{nm}$ for our averaged cluster embedded medium as

$$
\mathbf{T}_{nm}(\epsilon) = \left[ 1 + \mathbf{\tau}_{nm\text{CPA}}(\epsilon) \mathbf{T}_{nm}(\epsilon) \right]^{-1} \mathbf{T}_{nm\text{CPA}}(\epsilon).
$$

(16)

The (11) block $[\mathbf{T}_{nm}(\epsilon)]_{nm}$ corresponding to the central atom is used to calculate the Green’s Function [3], similar to the ECM-CPA approach. This method can be thought of as a modified ECM-CPA, where instead of embedding a cluster consisting of real atoms, a carefully constructed averaged cluster is embedded.

#### 1. Extension to Next Nearest Neighbors

In the above description the cluster size is limited to nearest neighbors, but the method can easily be extended to include longer ranged ordering. To include next nearest neighbors, a new type of “averaged” atom has to be defined using a new set of SRO parameters. For a central atom $a$, the next nearest neighbor average atom $\tilde{t}_a(\epsilon)$ can be defined as

$$
\tilde{t}_a(\epsilon) = \sum_b w_{ab}' \tilde{t}_b(\epsilon)
$$

(17)

Here $w_{ab}'$ represent the next nearest neighbor SRO parameters. The block $\mathbf{T}_{nm}(\epsilon)$ is now defined as

$$
\left[ \mathbf{T}_{nm}(\epsilon) \right]_{nm} = \begin{cases} t_{mn}(\epsilon) \delta_{nm}, & \text{if } n = 1 \\ t_{nm}(\epsilon) \delta_{nm}, & n \in \text{nearest neighbors} \\ t_{nm}(\epsilon) \delta_{nm}, & n \in \text{next nearest neighbors} \end{cases}
$$

(18)

The $\mathbf{T}_{nm}(\epsilon)$ matrix can then be obtained from $\mathbf{T}_{nm\text{CPA}}$.

If the neighbor atoms are chosen to be single site CPA $i.e.,$ if the block $\mathbf{T}_{nm}(\epsilon)$ is written as

$$
\left[ \mathbf{T}_{nm}(\epsilon) \right]_{nm} = \begin{cases} t_{mn}(\epsilon) \delta_{nm}, & \text{if } n = 1 \\ t_{nm}(\epsilon) \delta_{nm}, & \text{otherwise} \end{cases},
$$

(19)

it is easy to verify that equation (16) which represents the cluster $\mathbf{T}_{nm}(\epsilon)$ reduces to the single site $\mathbf{T}_{nm}(\epsilon)$, represented by equation (8). This is expected, because embedding a cluster with neighbor atoms as single site CPA is equivalent to embedding a single atom in the CPA Medium. An extension to include multipoint correlation functions is conceivable.
D. Comparison with NL-CPA

Other methods to include SRO in CPA were briefly discussed in the introduction of this paper. The most promising of these methods is the non-local NL-CPA. This section aims to highlight the difference between our cluster averaged CA-CPA and NL-CPA.

a. Effective Medium While NL-CPA obtains a new CPA medium and structure constant which contains non-local behavior, CA-CPA presently uses the single site CPA medium. The advantage of using the conventional CPA Medium is simplicity and computational efficiency, although at the cost of not being fully self-consistent. Future work will aim to make CA-CPA fully self-consistent.

b. Cluster Embedding In each NL-CPA iteration, the new effective medium is obtained by embedding and averaging over multiple real atom clusters.

\[
\langle \xi_{nm}^w(\epsilon) \rangle = \xi_{n,m}^{NL\text{-CPA}}(\epsilon)
\]

In contrast, CA-CPA only requires embedding a single cluster that is parametrized by the degree of SRO that we obtain from model or experiment. This is a significantly simpler approach as it is independent of the number of configurations and can be easily applied to multi-species high entropy alloys which may have a large configuration space.

III. RESULTS

To demonstrate Cluster Averaged CPA, we apply it to alloy systems with SRO at low temperatures. First we apply it to the Cu-Zn binary, a system whose SRO has been studied using both experimental and numerical techniques, including NL-CPA.

A. Cu-Zn

The Cu_{0.5}Zn_{0.5} BCC solid solution is a well-known example of a system that has an ordered BCC (B2) structure at low temperatures and transitions to a disordered BCC (A2) structure at approximately 750 K. This is a suitable system to test the Cluster Averaged CPA because the inclusion of SRO will have a noticeable effect on the total energy and electronic density of states.

1. Energy Analysis

As a first test we compare the energy obtained from single-site CPA with the energy obtained from Cluster Averaged CPA using different possible SRO parameters. Although there are four possible parameters for a binary,

![Energy Analysis Graph](image)

FIG. 1. Variation of the energy of Cu_{0.5}Zn_{0.5} with respect to the short range order parameter \( w = w_{CuCu} = w_{ZnZn} \) (using single site CPA energy as the reference level). \( w = 0 \) corresponds to complete short range ordering up to nearest neighbors while \( w = 1 \) corresponds to short range clustering up to nearest neighbors.

forcing the constraints \( w_{ab} = w_{ba} \) and \( \sum_b w_{ab} = 1 \) results in only a single independent SRO parameter \( w = w_{CuCu} = w_{ZnZn} \). Figure 1 shows the variation of energy with \( w \). The energy is lowest when \( w = 0 \), i.e., unlike neighbors are preferred, corresponding to a B2 type ordering as expected. At \( w = 0.5 \), the “averaged” neighbor atoms are an equal mix of like and unlike atoms. This is similar to a completely disordered state, and this explains why the energy at \( w = 0.5 \) closely matches the single site CPA energy (denoted by the red dashed line). Finally, as \( w \to 1 \), corresponding to the unphysical case of short range clustering, the system becomes increasingly unstable.

2. Density of States

As a second test we study the effect of SRO on the electronic density of states (DOS). As shown in Figure 2 when \( w = -1 \) the CA-CPA DOS better approximates the B2 DOS as compared to the single site CPA. The cluster embedding reduces the broadening of the single site CPA DOS. This is expected because the broadening is associated with disorder, and the Clustered Averaged CPA reduces the disorder in the system.

We can compare our results with the DOS calculated using NL-CPA. The main point of comparison is the size of the clusters embedded. Pair clusters were used in the NL-CPA study to obtain SRO. In our work, the DOS has been obtained by embedding a 15 atom cluster (central atom, 8 nearest and 6 next nearest neighbors). Due to the larger cluster size, the difference in SRO DOS and single-site CPA DOS is more pronounced in our work.
FIG. 2. Density of States for three different cases - the solid lines represent the pure B2 structure calculated using the KKR method, the dashed lines represent short range order up to next nearest neighbors using CA-CPA, and the dotted lines represent the A2 structure obtained from single site CPA.

B. AlCrTiV

The four-element AlCrTiV high entropy alloy displays B2 type ordering at low temperatures, with (Al, Cr) at one sublattice and (Ti, V) at the other. As temperature rises and disorder increases, the energy gap between A2 and B2 structure reduces. We use this test case to show that Cluster Averaged CPA scales well with the number of species present in the system and thus the number of possible configurations. For a 9 atom cluster (central atom plus 8 neighbors) in a 4 element random alloy, there are $4^9 = 262144$ configurations. Even though this number can be reduced by considering symmetry, it remains impractical to use any real atom cluster approach to study short range order in such a system. Using Cluster Averaged CPA opens the door to modelling short range order in high entropy alloys.

1. Energy Analysis

For a 4-element high entropy alloy, there are 6 independent SRO parameters, and hence it is difficult to study how the energy varies with all of these 6 parameters. Instead we focus on three possible orderings - (a) AlCr-type ordering, where Al and Cr share the same sublattice (and of course, Ti and V share the other). (b) AlTi-type ordering, where Al and Ti share the same sublattice. (c) AlV-type ordering, where Al and V share the same sublattice. Tables I, II and III contain the SRO parameters used for the three orderings. The energies of these three structures are presented in Figure 3. Here it can be seen that AlCr-type ordering has the lowest energy, which is the expected result.

2. Density of States

The individual stability of the three configurations studied can also be discerned from the density of states.

a. AlCr-type ordering Figure 4 shows the DOS for the disordered and the B2 ordered structure with Al and Cr on one sublattice. It can be seen that on the addition of SRO the DOS moves to the left, towards lower energies. Furthermore, the Fermi Energy has moved into the pseudogap. These observations indicate that this type of ordering has increased the stability of the system, which is the same conclusion derived from the energy analysis.

b. AlTi-type ordering Figure 5 shows the DOS for the disordered and the B2 ordered structure with Al and Ti on one sublattice. In this case, the opposite effect can be observed. The addition of SRO has shifted the DOS towards higher energies, and the Fermi Energy has moved away from the pseudogap. This type of ordering is unstable relative to the disordered structure.

c. AlV-type ordering Figure 6 shows the DOS for the disordered and the B2 ordered structure with Al and V at one sublattice. In this case, there is no appreciable movement of the DOS on the addition of SRO and no clear conclusion on stability can be obtained from this plot. The implication is that this type of ordering is not as stable as the AlCr-type (clear shift towards lower energies) and not as unstable as AlTi-type ordering (clear shift towards higher energies), which matches the energy analysis.

| w       | Al  | Cr  | Ti  | V  |
|---------|-----|-----|-----|----|
| Al      | 0   | 0   | 0.5 | 0.5|
| Cr      | 0   | 0   | 0.5 | 0.5|
| Ti      | 0.5 | 0.5 | 0   | 0  |
| V       | 0.5 | 0.5 | 0   | 0  |

TABLE I. SRO Parameters for B2 AlCr-type ordering
IV. CONCLUSION

We have introduced the Cluster Averaged Coherent Potential Approximation (CA-CPA) to include chemical short range order in the framework of KKR-CPA. This approach involves embedding a cluster consisting of "averaged" neighbor atoms constructed according to the SRO present in the system. The approach is independent of the number of configurations. It is simple to implement, and computationally efficient as only a single cluster per species needs to be embedded. The approach has been applied to a binary and a high entropy alloy, and the observations have been compared to existing results. Code is available on GitHub.

There are several possible extensions to this work that could improve its usefulness. Although the single site medium is obtained in a self-consistent manner, the cluster embedding is done non-self-consistently. Combining the simplicity of the average cluster embedding with a self-consistent iteration scheme for the CPA medium is the subject of current work.

The order parameters can be obtained in multiple ways. For binaries, there is only one independent SRO parameter. In such a case, it is not impractical to use a trial-and-error approach to find the SRO parameter that corresponds to the energy minimum. For more complex systems, this is less convenient, and experimental knowledge of SRO may be necessary to determine the order parameters. A third approach involves combining CA-CPA with a statistical physical method. Computer simulation can provide temperature-dependent predictions of short-range order parameters. The cluster variation method can order parameter-dependent energies from CA-CPA with a cluster expansion of the entropy to obtain the SRO parameters corresponding to the free energy minima across a temperature range. It would then

| TABLE II. SRO Parameters for B2 AlV-type ordering |
|-----------------|--------|-----------------|--------|-----------------|
|     w     | Al    | Cr    | Ti    | V    |
|----------|-------|-------|-------|------|
| Al       | 0     | 0.5   | 0.5   | 0    |
| Cr       | 0.5   | 0     | 0     | 0.5  |
| Ti       | 0.5   | 0     | 0     | 0.5  |
| V        | 0     | 0.5   | 0.5   | 0    |

| TABLE III. SRO Parameters for B2 AlTi-type ordering |
|-----------------|--------|-----------------|--------|-----------------|
|     w     | Al    | Cr    | Ti    | V    |
|----------|-------|-------|-------|------|
| Al       | 0     | 0.5   | 0.5   | 0    |
| Cr       | 0.5   | 0     | 0.5   | 0    |
| Ti       | 0     | 0.5   | 0     | 0.5  |
| V        | 0.5   | 0     | 0.5   | 0    |
be possible to calculate the transition temperature for systems that undergo an order-disorder transition.

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