Overview
Technologically or scientifically interesting alloys have multiple components and sublattices. As a result, N-component alloys have "complex" ordering with up to (N-1) phase transitions and arrive at the ground-state from an infinite number of possible high-temperature, partially-ordered phases. Predicting the N→1 transitions, their electronic origin, and the short-range order (SRO) and long-range order (LRO) at fixed composition in alloys, is crucial for interpreting experiment and for materials design. Using both classical and electronic density-functional-theory (DFT) methods [1], a thermodynamic theory of ordering is possible based upon electronic structure and energetic, multiple-scattering (KKR) theory, in particular [2].

Why are alloys complex?
N-component alloys have an infinity of choices for ordering [3], e.g., site occupations in ternary (N=3) hcp BCAB alloy, with k(111) SRO peak has N→1 (or 2) phase transitions.

Thermodynamic Theory of Ordering from Combined Classical and Electronic DFT
The thermodynamic average Grand Potential of an alloy can be written in terms of (non-)interaction contributions as:
\[ \Omega = \Omega_{\text{fun}} + \Omega_{\text{int}} \]

where \( \Omega_{\text{fun}} \) is the functional of total electronic free energy.

Using a cluster-based average Non-Local CPA [5], we have derived an analytic expression for the N→N symmetry, which requires numerical implementation and testing.

The original theory [5] has been implemented for tested the DOS for 1-D square-well potential, and not the integrated DOS. We are implementing the NL-CPA within our existing KKR-CPA (3-D) code, which will then be basis for SRO calculations.

2. Extension to Multisublattice Case
We have extend the KKR-CPA (single-site) theory for the multicomponent alloy. The above equations generalize with more than two supercells (1) that designate the interacting sublattices having species \( \alpha \) and \( \beta \), except that the Brillouin zone is that given by the partially-ordered symmetry.

However, the mean-field thermodynamic approximation is potentially more severe for multi-component case. Here we present the calculated SRO and correlation energy given by \( S^2(q) \) for fully-disordered bcc Cu3AlZn.

3. Using Better Thermodynamic Mean-Field Approximations for Improved T
We are extending the KKR-CPA-based SRO formula to improve the self-energies correction by summing all cyclic diagrams to O(1/Z), where Z is the number of neighbor. These correction maintain required intensity sum rules (as with mean-spherical model and Onsager) but renormalize the pair-correlation in k-dependent manner. Recently these correlations have been called the Ring approximation [7], where they have been tested for lattice-gas and near-neighbor Ising model.

Example of the effect of summing cyclic diagrams [7]: 1-D Ising model (\( T_c \) in units of \( k_B T \))

- Exact: MFT
- NL-CPA
- MFT-cyclic
- MFT

We are currently testing a multiparameter version of this approach to assess its validity and usefulness.

Future
• Complete and test KKR-NL-CPA for electronic-structure.
- Test "cyclic" corrections for multi-component Ising case.
- Validate the analyticity of the derived analytic expression for the NL-CPA integrated DOS, which is required for thermodynamics (probably by 1-D model Hamiltonian).
- Combine the three for NL-CPA calculations of SRO.
- Address numerical issues required to implement either CPA or NL-CPA into usable and extensible code.

Acknowledgements
We are grateful to Mark Jarrell for useful conversations regarding applying DFT concepts within KKR, and Derwyn Rawlons and Julia Staurton for initial discussion on the derivation of integrated density of states within NL-CPA. S. Ghosh is supported under DOE DE-FG02-03ER46406.

References