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Thermodynamic Density-Functional Theory of Static and Dynamic Correlations in Complex Solids

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Overview

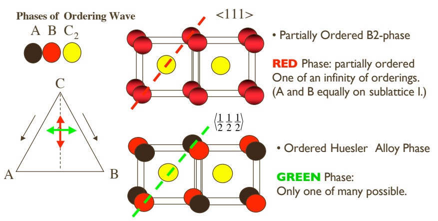
Technologically or scientifically interesting alloys have multiple components and sublattices. As a results, N-component alloys have "complex" ordering with up to (N-1) phase transitions and arrive at the ground-state from an *infinite* number of possible high-temperature, partially-ordered phases.

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 energetics, multiple-scattering (KKR) theory, in particular [2].

Why are alloys complex?

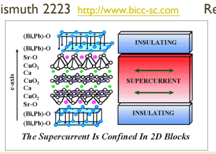
N-component alloys have an *infinity* of choices for ordering [3], e.g., site occupations in ternary (N=3) bcc ABC_2 alloy with k=(111) SRO peak has N–1 (or 2) phase transitions:

disorder → partially LRO → fully LRO

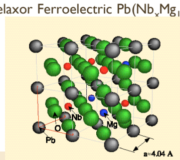


Mulitsublattice examples

Bismuth 2223 http://www.bicc-sc.com



Relaxor Ferroelectric $Pb(Nb_xMg_{1-x})O_3$



Goal

1. To improve the electronic DFT configurational averaging in (partially) disordered alloys (originally based on the single-site Coherent Potential Approximation) by including local, multi-site configurational effects in "systematically exact" manner via reciprocal-space *coarse-graining* concepts developed within dynamical mean-field theory [4].
2. To extend this DFT-based thermodynamic theory of ordering to general partially-ordered states (i.e., with multi-sublattice orderings) so as to compare directly to the k-space short-range order measured experimentally.
3. To improve the mean-field used within the exact classical DFT. In particular, to correct the atomic self-energies by summing **all** *cyclic diagrams* to O(1/Z), where Z is the number of neighbor. These correction maintain required intensity sum rules (violated in most mean-field theories) and renormalize correlation in k-dependent manner.

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:

$$<\Omega> = F_{non-\mathrm{int}} - <\Phi_{\mathrm{int}}> - \mu N_{atoms}$$

$$\text{where} \quad F_{non-\mathrm{int}} = -k_B T \sum_{\alpha=1}^{N} c_\alpha \ln c_\alpha$$

Diffuse scattering experiments on a disordered state reveal the *chemical ordering* fluctuations (or SRO), analogous to "phonon modes", which are unstable but potentially long-lived.

We study the linear-response to ordering about the (partial) disordered state, since the second-order terms give the SRO. The equations for SRO pair-correlations are EXACT!

$$\alpha^{-1}_{\alpha\beta}(\mathbf{q};T) = \frac{\left(\frac{\delta_{\alpha\beta}}{c_\alpha} - \frac{1}{c_{Host}}\right) - \beta S^{(2)}_{\alpha\beta}(\mathbf{q};T)}{c_\alpha(\delta_{\alpha\beta} - c_\beta)} \qquad S^{(2)}(q;T) = F.T.\left[\frac{\delta^2 <\Omega>}{\delta c_i \delta c_j}\right]_{c_0}$$

Approximations yield tractable solution, however, but these also lead to errors – in *temperature scale* (say, from using mean-field thermodynamics) or in *electronic energetics* (say, from using single-site, mean-field averaging).

Exact Electronic DFT Approach

The Gibbs' relation of particle number and chemical potential permits, in principle, a means to construct a electronic DFT for the (partially) disordered state. That is, with particle number related to the integrated (DOS) density of state N(E;μ),

$$<\mathrm{N}(\mu)> = -\frac{\partial <\Omega(T,V,\mu)>}{\partial \mu}$$

$$<\Omega(T,V,\mu)> = -\int d\mu <\mathrm{N}(\mu)> = -\int d\mu\, f(E-\mu) <\mathrm{N}(E;\mu)>$$

Given an analytic expression of the configurationally average N(E;μ), we may obtain an analytic expression for the grand potential for disordered, partially ordered, or fully ordered (Mermin's theorem) state.

1. Improved Electronic Configurational Averaging

In the single-site CPA, we obtain [2]

$$<\Omega(T,V,\mu)>_{ss-cpa} = -\int d\mu\, f(E-\mu) <\mathrm{N}(E;\mu)>_{ss-cpa}$$

the basis for KKR-CPA total energy calculations in use today, and has been implemented for homogenous disordered case [3] in ternary metallic alloys.

Recent ***coarse-graining*** concepts developed for Dynamical Mean-Field Theory [4] provides a means to go beyond single-site CPA [5] averaging over local, multi-site clusters compatible with point-group symmetry of the underlying Bravais lattice.

$$<\Omega(T,V,\mu)>_{nl-cpa} = -\int d\mu\, f(E-\mu) <\mathrm{N}(E;\mu)>_{nl-cpa}$$

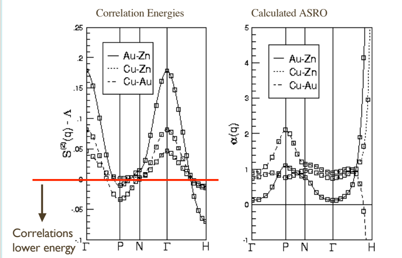
Using a cluster-based average *Non-Local* CPA [5], we have derived an *analytic* expression for the $<N>_{nl-cpa}$, which requires numerical implementation and testing.

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 a 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 two more superscripts (I,J) that designate the interacting sublattices having species α and β, 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 Cu_2AuZn.



Results

- Correlation energy leads to SRO peaks at k=(111) or H-point
- Secondary SRO at k=(0.5, 0.5,0.5) or P-point.
- These indicated high-T B2 and low-T Heulser transitions, as is observed (unpublished).
- Temperature scale is 50% in error.

We have employed the so-called *Onsager corrections* Λ, so intensity is conserved. Such correction provide good temperature scale in binary systems driven by formation energy, the temperature scale (e.g., fcc PdRh we obtained 1080 K and observed is 1050 K).

Potential Problem

For a ternary, for example, there are 3 pair-correlations that together must conserve intensity, potentially requiring k-dependent renormalization of intensities to get instability temperatures more correct. Need to improve mean-field thermodyamics to make still tractable with better T scale.

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 corrections 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]:

	exact	MFT	MFT+cyclic
1-D Ising model (T_c in units of kT/4J)			
	0.0	1/2	0.22
2-D square lattice Ising model (T_c in units of kT/4J)			
	0.57	1.0	**0.62**
3-D fcc Ising model (T_c in units of kT/4J)	"exact" (MC)	MFT	MFT+cyclic
	2.45	3.0	**2.41**

We are currently testing a multicomponent 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.

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