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

NSF-DMR/ITR Workshop and Review

University of Illinois, 17-19 June 2004

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*supported by DOE

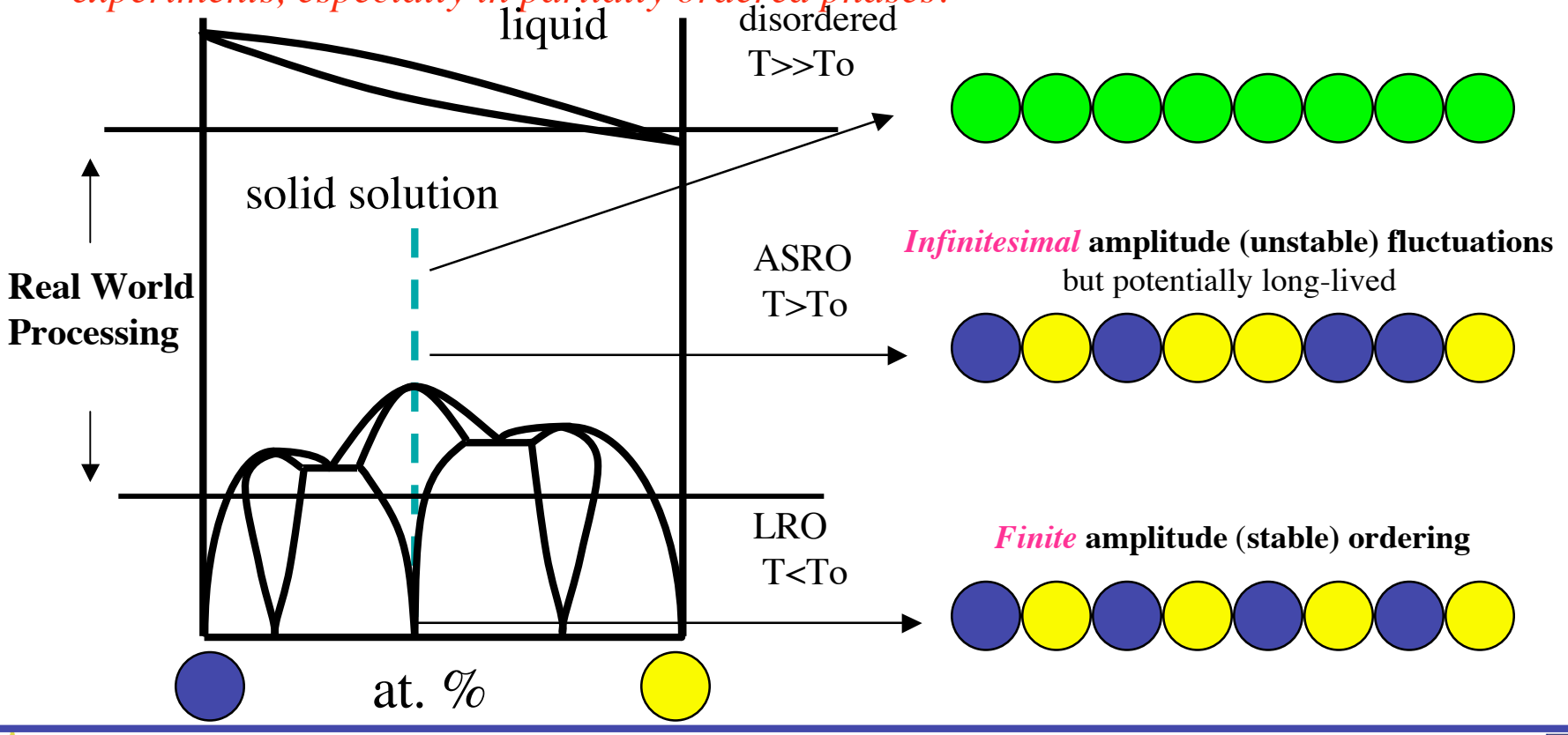
Funded by NSF DMR-0312448

From high to low T: Where do atoms go and why?

Characterization: Processing ⇒ Structure ⇒ Properties ⇒ Performance

- Measurement: quenched or annealed samples. *From what state? PM, FM, s.s.*
- Band calculations: not always related to assessed data *e.g., PRB* ***62****, R11917 (2000)*

Goal: Determine the ordering and its electronic origin for direct comparison/understand of experiments, especially in partially ordered phases?



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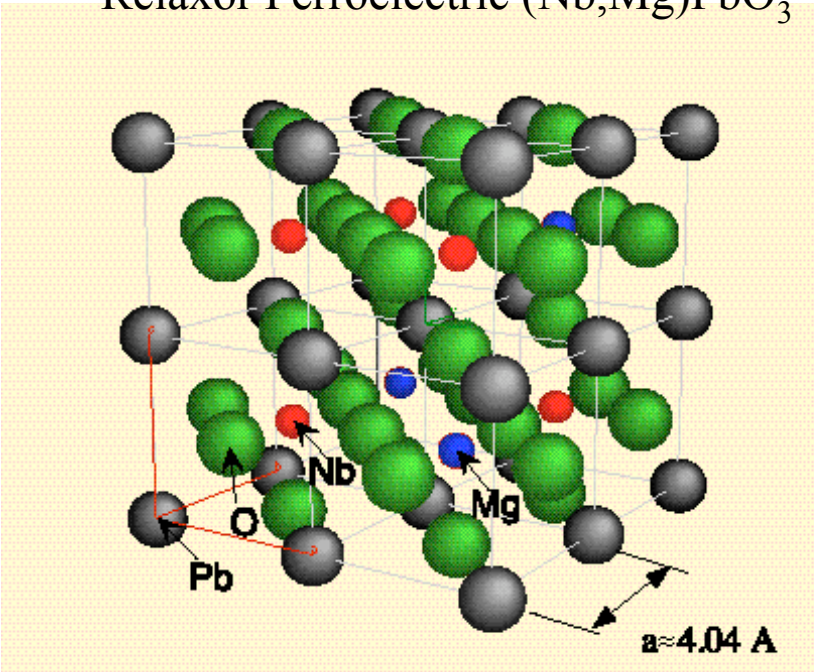
Alloys and Alloying Effects are Important

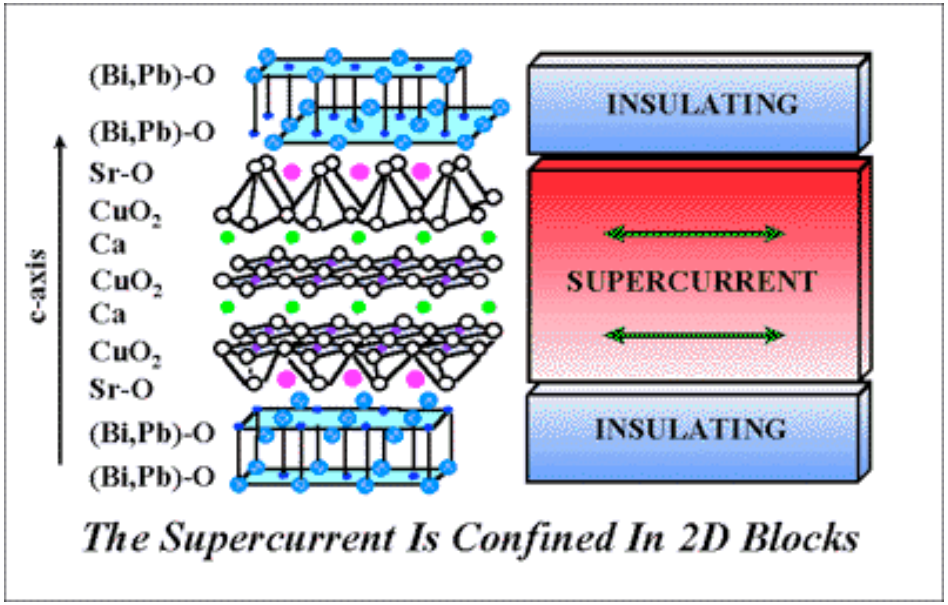
And involve…*disorder*, displacements, *ordering and clustering* (T-dependent effects)
Complex alloys are multicomponent and multisublattice and are the most interesting technologically and scientifically.

Relaxor Ferroelectric $(Nb,Mg)PbO_3$



Haydn Chen, UIUC (1999)

Bismuth 2223 filaments in a metal matrix



A commercial wire and tape (http://www.bicc-sc.com)

Multi-valency oxides that show "striped" phases: separation of magnetism and charge.

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Diffuse Scattering from *Fluctuations* in Disordered Alloy reveal the "*chemical ordering modes*" (analogs of phonon modes)

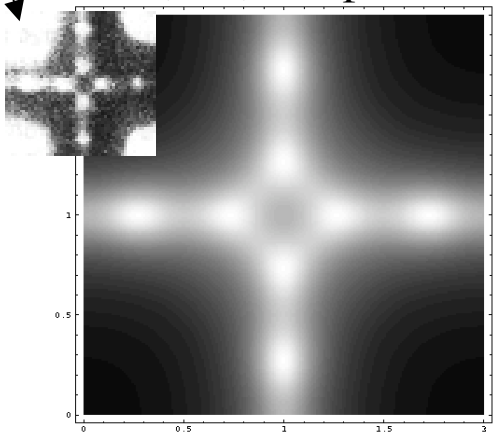
Ordering can be *commensurate* with underlying Bravais lattice

Ordering can be *incommensurate* due to electronically-induced modulations (e.g. long-period superstructures) and not just *symmetry* induced.

LEED on disordered $Ag_{75}Mg_{25}$

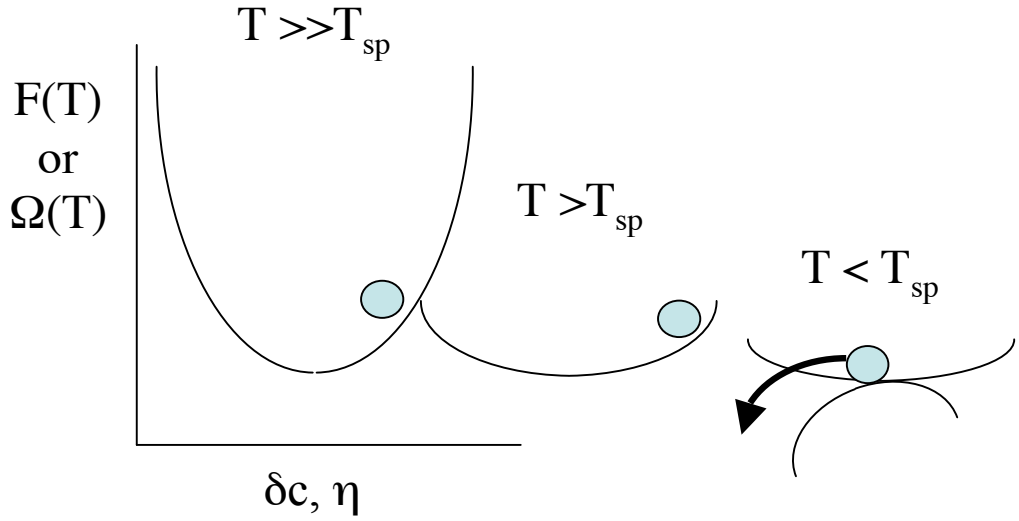
Ohshima and Watanabe Acta Crys. A33, 784 (1977)

(001) BZ plane



calculated $Ag_{75}Mg_{25}$

EEE Comput. Soc. Press., 103 (1994).



Unstable modes for N-component alloys depend on eigenvectors of stability matrix

$$\Delta\Omega^{ord-dis} = \frac{1}{2}\sum_{ij}\delta c_i^*\left[\frac{\delta^2 < \Omega >}{\delta c_i \delta c_j}\right]_{c_0}\delta c_j + K \Rightarrow \frac{1}{2}\sum_{\mathbf{k}} |\delta c_{\mathbf{k}}|^2 \alpha^{-1}(\mathbf{k};T) \sim \eta^2_{\mathbf{k}_{max}} \alpha^{-1}(\mathbf{k}_{max};T)$$

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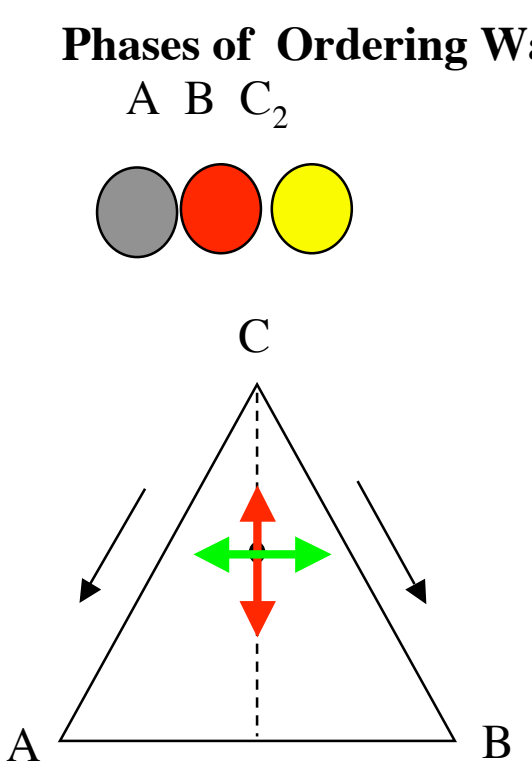
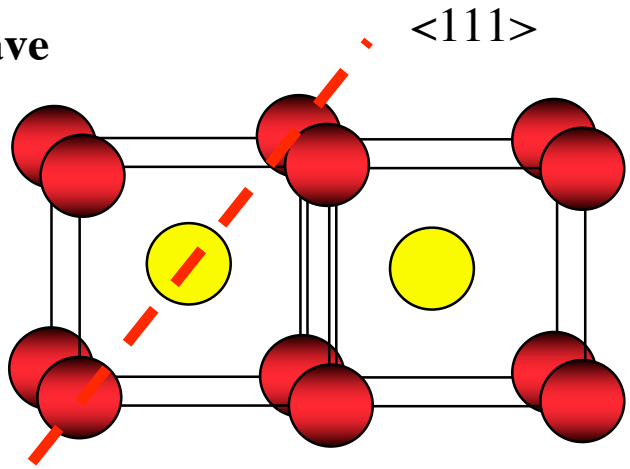
N-component alloys have an *infinity* of choices for ordering

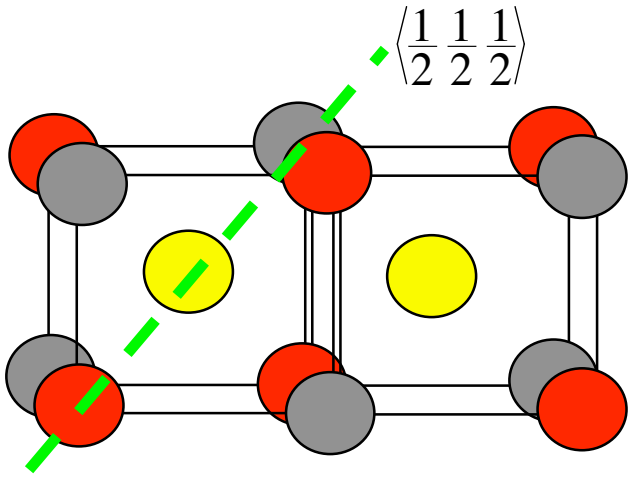
e.g., site occupations in ternary (N=3) bcc ABC_2 alloy with k=(111) SRO peak has N–1 (or 2) phase transitions: **disorder → partially LRO → fully LRO**





- Partially Ordered B2-phase

RED Phase: partially ordered
One of an infinity of orderings.
(A and B equally on sublattice I.)



- Ordered Huesler Phase

GREEN Phase:
Only one of many possible.

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Relevant Issues Experiment and Interpretation

• In complex alloys at high-temperature, thermodynamic equilibrium, the environment of a site responds by producing concentration and/or magnetic fluctuations tied to the underlying electronic density.

• Materials characterization (x-ray, neutron, and electron) experiments usually cannot uniquely determine the electronic "driving forces" responsible for ordering tendencies at the nanoscale in such materials.

• Interpretation of the diffuse scattering data and ordering many times rests on assumed models, which may or may not be valid.

These factors limit understanding of what controls ordering (electronic origins) and "intelligent" tailoring of a properties.

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Specific Topics to Address

For multicomponent and multisublattice alloys,

(1) How do you uniquely characterize the type of chemical ordering indicated by short-range order data?

(2) Can you determine origin for correlations/ordering?

(3) How do you correctly compare ordering energetics from usual T=0 K electronic-structure calculations with those assessed,say, from high-T scattering experiments.

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Classical DFT-based Thermodynamics

The thermodynamic average Grand Potential of an alloy can always be written in terms of (non-)interaction contributions (just like electronic DFT):

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

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

Just like diffuse-scattering experiments, look at *chemical ordering* fluctuations (or SRO), analogous to "phonon modes", which are unstable but potentially long-lived.

The classical DFT equations for SRO pair-correlations are EXACT, unless approximated!

$$\alpha^{-1}_{\alpha\beta}(\mathbf{q};T) = \frac{\left(\frac{\delta_{\alpha\beta}}{c_\alpha} - \frac{1}{c_{Host}}\right) - \beta S^{(2)}_{\alpha\beta}(\mathbf{q};T)}{c_\alpha(\delta_{\alpha\beta} - c_\beta)}$$

Looks like KCM, but it is not!

But need the curvature of electronic-based grand potential!
Not just any Mean-Field Approximation will do, for example.

$$S^{(2)}(q;T) = F.T.\left[\frac{\delta^2 < \Omega >}{\delta c_i \delta c_j}\right]_{c_0}$$

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Classical DFT-based Thermodynamics

Get thermodynamic average *electronic (DFT)* Grand Potential of an alloy (needed over all configurations allowed):

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

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

- Analytic expression for electronic GP within a given approximation.
  Good for any configurations (ordered version give Mermin's thm).

- BUT Need: analytic expression for <N> integrated DOS.

- From <N>cpa derived expression (old) and generalized to multi-component/sublattice for SRO (new).
(was/is the basis for KKR-CPA total energy now for disordered alloys)

Can we do better? Non-local CPA based on Dynamical MFT (new).

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Basic Idea: DFT-based Thermodynamics Linear-Response

• Use the high-T (most symmetric) state and find system-specific instabilities from electronic and configurational effects. FIND SRO.

• Can do thermodynamics based on electronic-structure due to separate times scales [atomic, 10^{-3} - 10^{12} secs)] and electronic (10^{-15} to 10^{-12} secs).

• Direct configurational averaging over electronic degrees of freedom using Gibbs relations based on analytic expression for <N> integrated DOS.

- *Coherent Potential Approximation* (CPA) using *KKR* method.
- *Nonl-Local CPA* via improved analytic <N>nl-cpa.
  - Linear-response to get *short-range order fluctuations*
  - Direct calculation of *structural energies vs. long-range order*

-Checking analyticity of <N>nl-cpa. (current)

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KKR-CPA results: precursor to Order in bcc Cu_2AuZn

unpublished

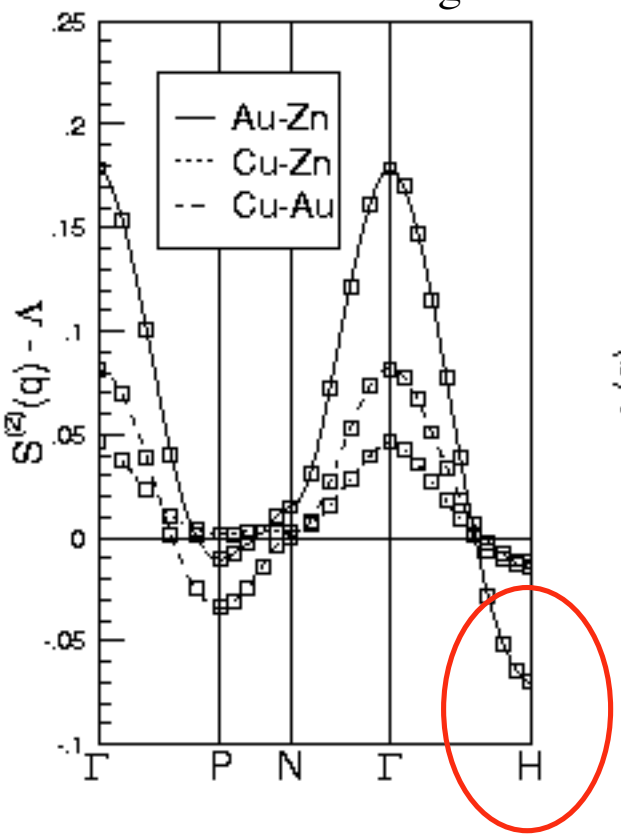
Relevant Ordering Waves
H=(100) or (111)
P=(1/2 1/2 1/2)

Expected Ordering
H= B2
H+P=Huesler

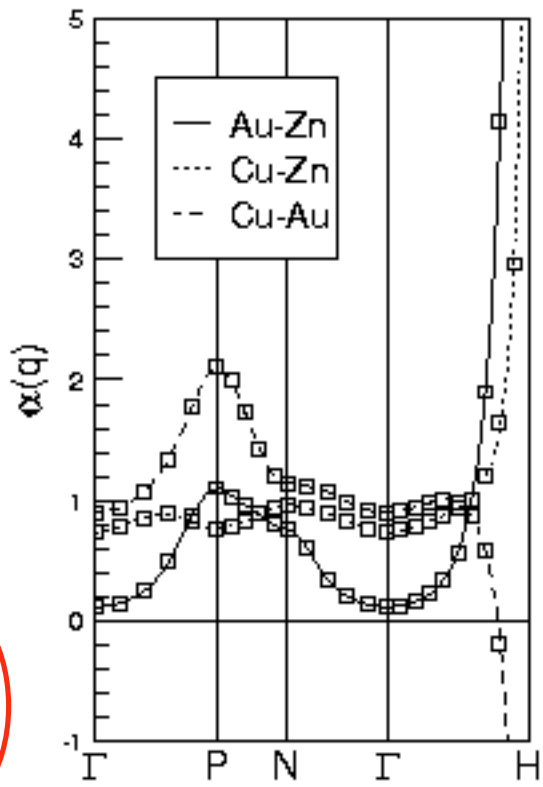
$S^{(2)}$ gives ΔE

Lower E
of alloys →

Correlation Energies



Calculated ASRO



SRO correct but temperature scale is sometime off, transition is ~40% in error!

…but MFT is not necessarily bad.

E.g., Temperature in NiPt
- Experiment Tc - 918 K
- full ASRO calculation T_{sp}= 905 K

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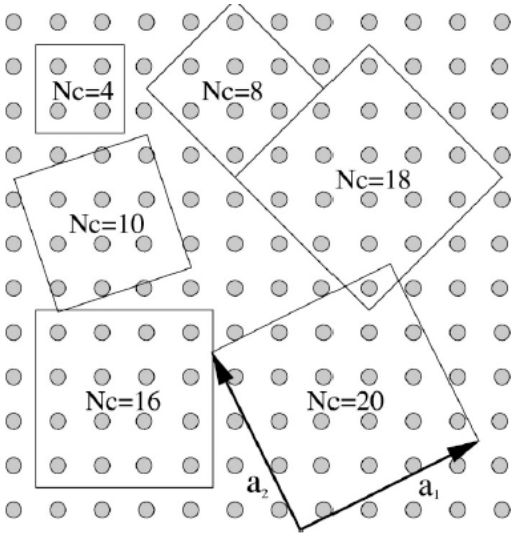
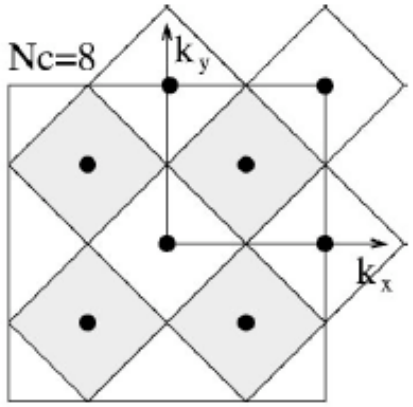
Use K-space Coarse-Graining Concepts from Dynamical Mean-Field Theory ==> NL-CPA

- The KKR version of Coarse-Grained DMFT is the NL-CPA
- Go beyond single-site configurational averaging by including local cluster configurations ….

- REQUIRES clluster chosen to conform to underlying pt-group symmetry
- and coarse-graining in K-Space.



Jarrell and Krishnamurthy Phys. Rev. B 63 125102



Implementing KKR-NL-CPA (current) improving e-DFT

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Improving MFT Statistical Mechanics

- Onsager Corrections included already (conserved intensity sum rule)
- But they are not k-depend corrections to self-correlation in SRO MF calculations.

- Now including summation of all Cyclic Diagrams to O(1/Z) from cumulant expansion, which is still MFT, but includes k-dependent renormalizations.

Effect of summing cyclic diagrams [R.V. Chepulskii, Phys. Rev. B 69, 134431-23 (2004); *ibid* 134432.]:

1-D Ising model	(T_c in units of kT/4J)		
	exact	MFT	MFT+cyclic
	0.0	1/2	0.22
2-D square lattice Ising model	(T_c in units of kT/4J)		
	exact	MFT	MFT+cyclic
	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**

Implementing Cyclic corrections in Multicomponents case (current) improving classical-DFT

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Summary: We can calculate and assess ordering and its origin in a system-dependent way

• Relevant to Materials characterization
(x-ray, neutron, and electron) experiments usually cannot uniquely determine the electronic "driving forces" responsible for ordering tendencies.

• Interpretation of the diffuse scattering data and ordering many times rests on assumed models, which may or may not be valid.

These factors limit understanding of what controls ordering (electronic origins) and "intelligent" tailoring of a properties.

We are progressing:
improving classical-DFT, needed for better T scales
improving e-DFT via NL-CPA (analytic), needed for correlated systems
Implementing KKR-NL-CPA in KKR-CPA code.

Future: **Developing needed numerical algorithms to calculate SRO on multi-sublattice version of theory.**

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