

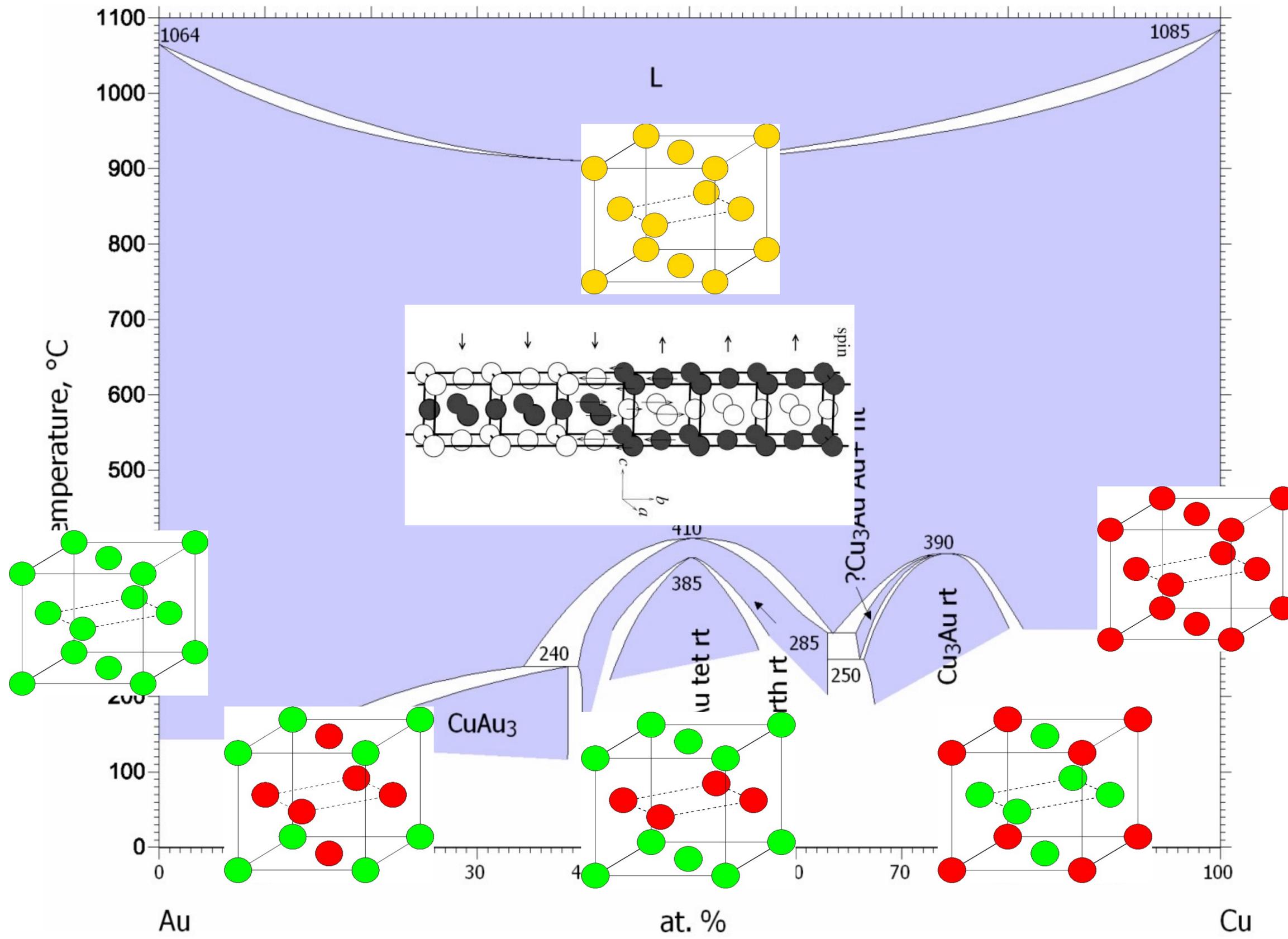
**GreenALM**

# Alloy properties by GreenALM

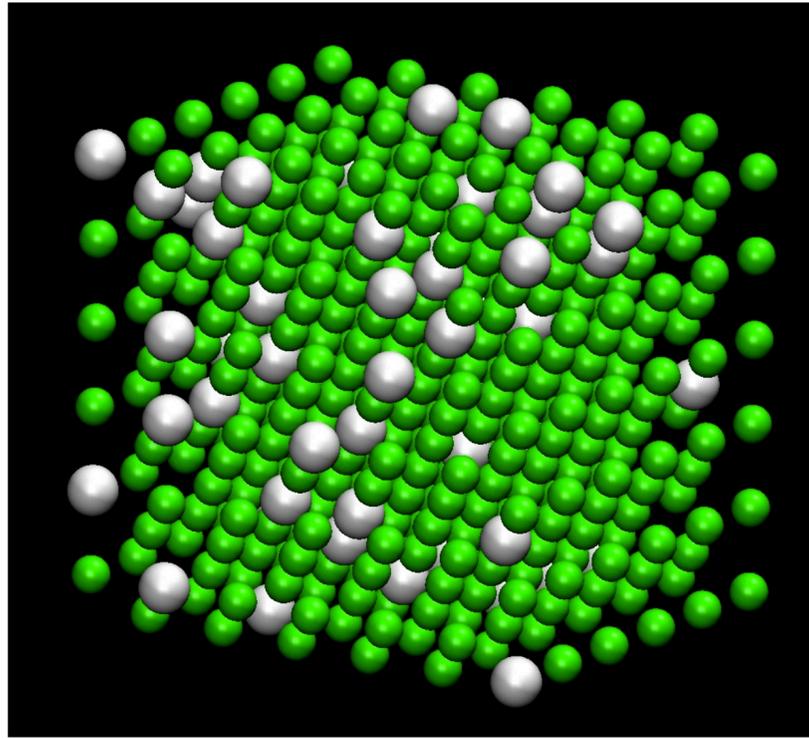
# Extra abilities by Green's CPA-based methods for alloy properties

1. Alloy conductivity (resistivity) can be obtained only by methods based on MST within CPA (or its extensions);
2. Effective interactions of Ising-type alloy configurational Hamiltonian (GPM,  $S^2$  formalism: both based on the CPA);
3. Magnetic exchange interactions in random alloys also in the magnetically disordered state;
4. Continuous concentration dependences of different properties: transport, elastic, thermodynamic,....
5. Easy access to (effective) chemical potentials (derivatives wrt concentration), including inhomogeneous system (surface alloys) also containing many alloy components.

# Cu-Au phase diagram



# The energy of an atomic alloy configuration



$$H_{conf} = \frac{1}{2} \sum_p \overset{\text{pairs}}{\tilde{V}_p^{(2)}} \sum_{i \neq j} \delta c_i \delta c_j + \frac{1}{3} \sum_t \overset{\text{triangles (of sites)}}{\tilde{V}_t^{(3)}} \sum_{i,j,k} \delta c_i \delta c_j \delta c_k + \dots$$

Concentration (spin-variable) fluctuations:

$$\delta c_i = c_i - c \quad (\delta \sigma_i = \sigma_i - \sigma)$$

Site occupation numbers:

$$c_i = \begin{cases} 1 & \text{if site } i \text{ is occupied by atom A} \\ 0 & \text{if it is occupied by atom B} \end{cases}$$

$V^{(n)}$  are effective cluster interactions, which should be determined in some way.

One (the least intelligent and in many cases quite “dangerous”) way is to use the so-called cluster expansion technique (given by the ATAT software, for instance).

The other one is (can be less accurate and missing some contributions) to use perturbation technique within CPA MST theory.

# Effective interactions from CPA electronic structure calculations: The generalized perturbation method (GPM)

It is an extremely powerful technique since

1) One should not guess if this interaction is important or not (like in the cluster expansion method): just calculate it.

2) The calculations are based on the electronic structure of a random alloy with a specific composition and at the given lattice parameter.

Thus, they correctly capture specific electronic effects, connecting, for instance, to the Fermi surface geometry and topology.

The latter are very important for many alloy systems.

3) It is possibly the only computationally affordable way to get interactions in inhomogeneous systems (at surfaces, interfaces and other defects)

# Cluster expansion method for Cu-Au

PHYSICAL REVIEW B

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## Cu-Au, Ag-Au, Cu-Ag, and Ni-Au intermetallics: First-principles study of temperature-composition phase diagrams and structures

V. Ozoliņš, C. Wolverton, and Alex Zunger

The mixed spaced cluster expansion (MSCE) is used for the representation configurational energy (with “constituent strain” interactions in reciprocal space).

30-35 ordered structures used in the calculations

Resulting real-space interactions:

J3-Q3 :  $V^{(3)}$

J4-L4:  $V^{(4)}$

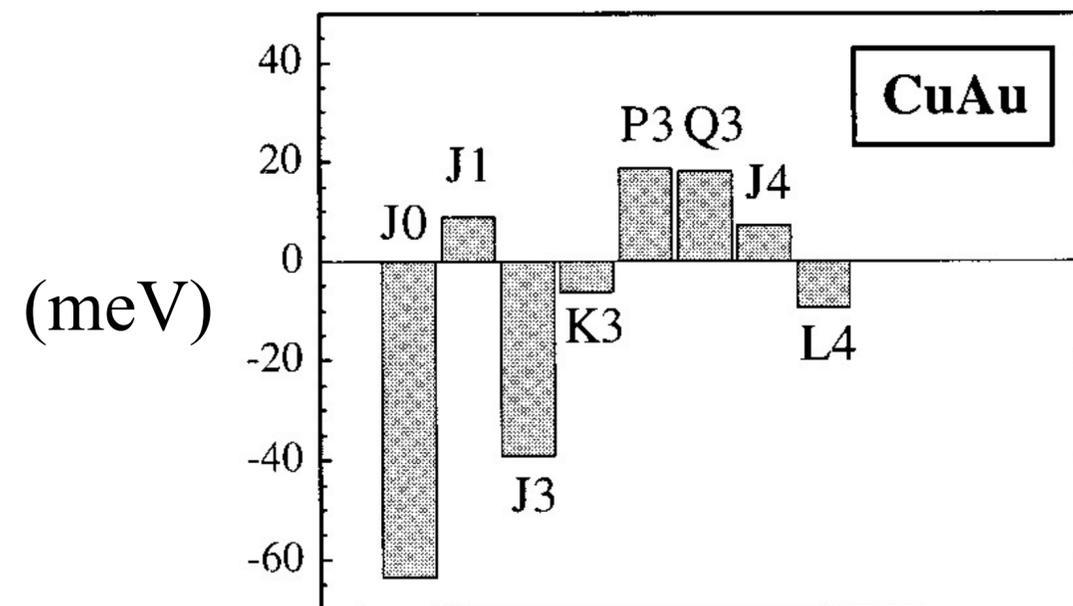
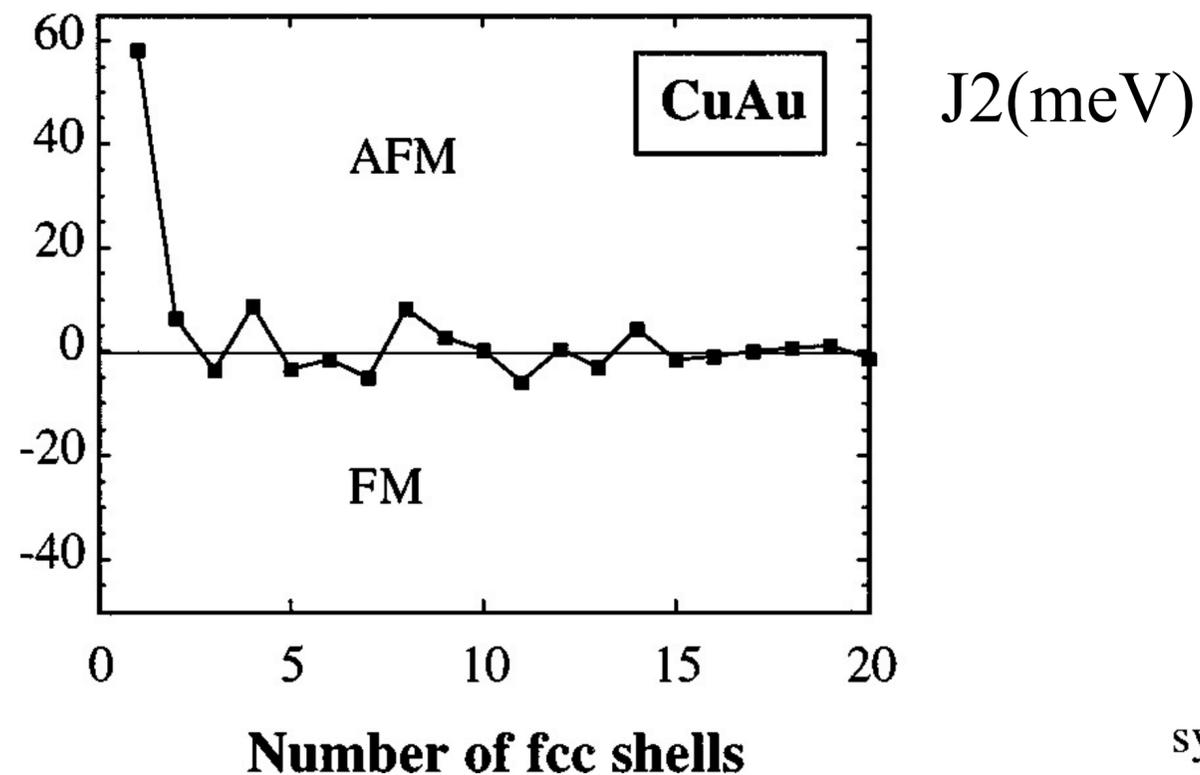
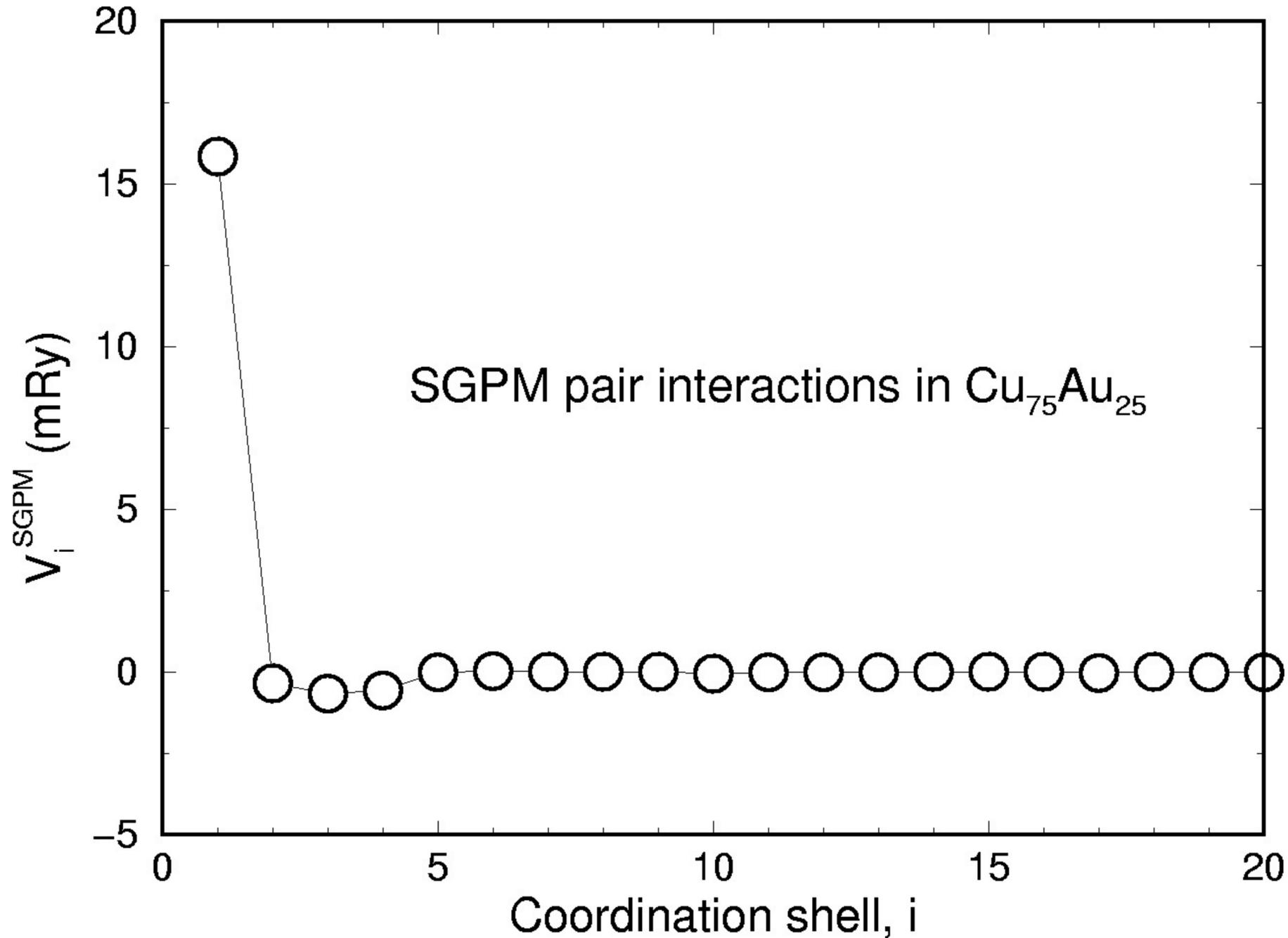


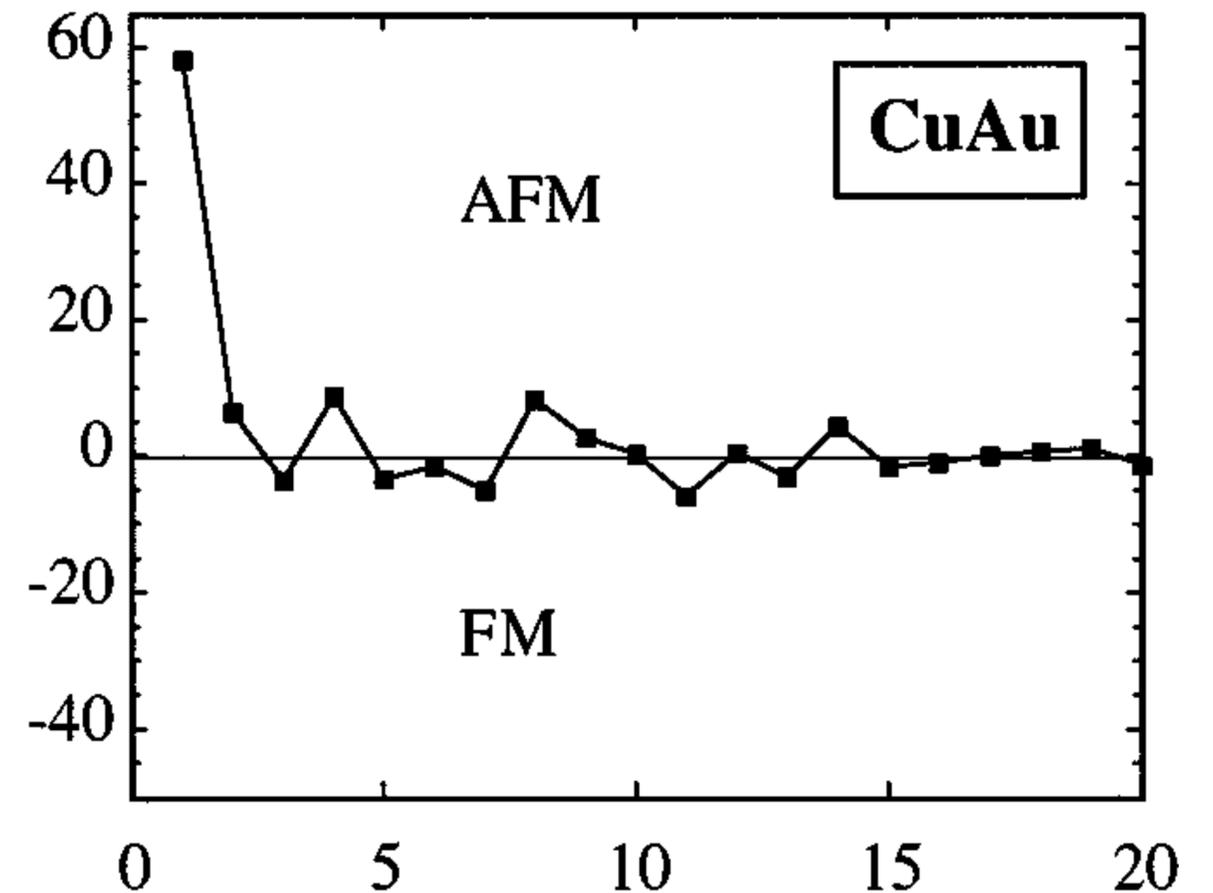
FIG. 6. Multibody interactions for the studied noble-metal alloy systems.

# SGPM vs CLE in CuAu

- SGPM:** 1) practically all the  $V^{(2)} = 0$  beyond the 4<sup>th</sup> c.s.  
2) all multisite interactions are very small



## Pair interactions from CLE



# Fermi surface and effective interactions in Cu-Pd alloys

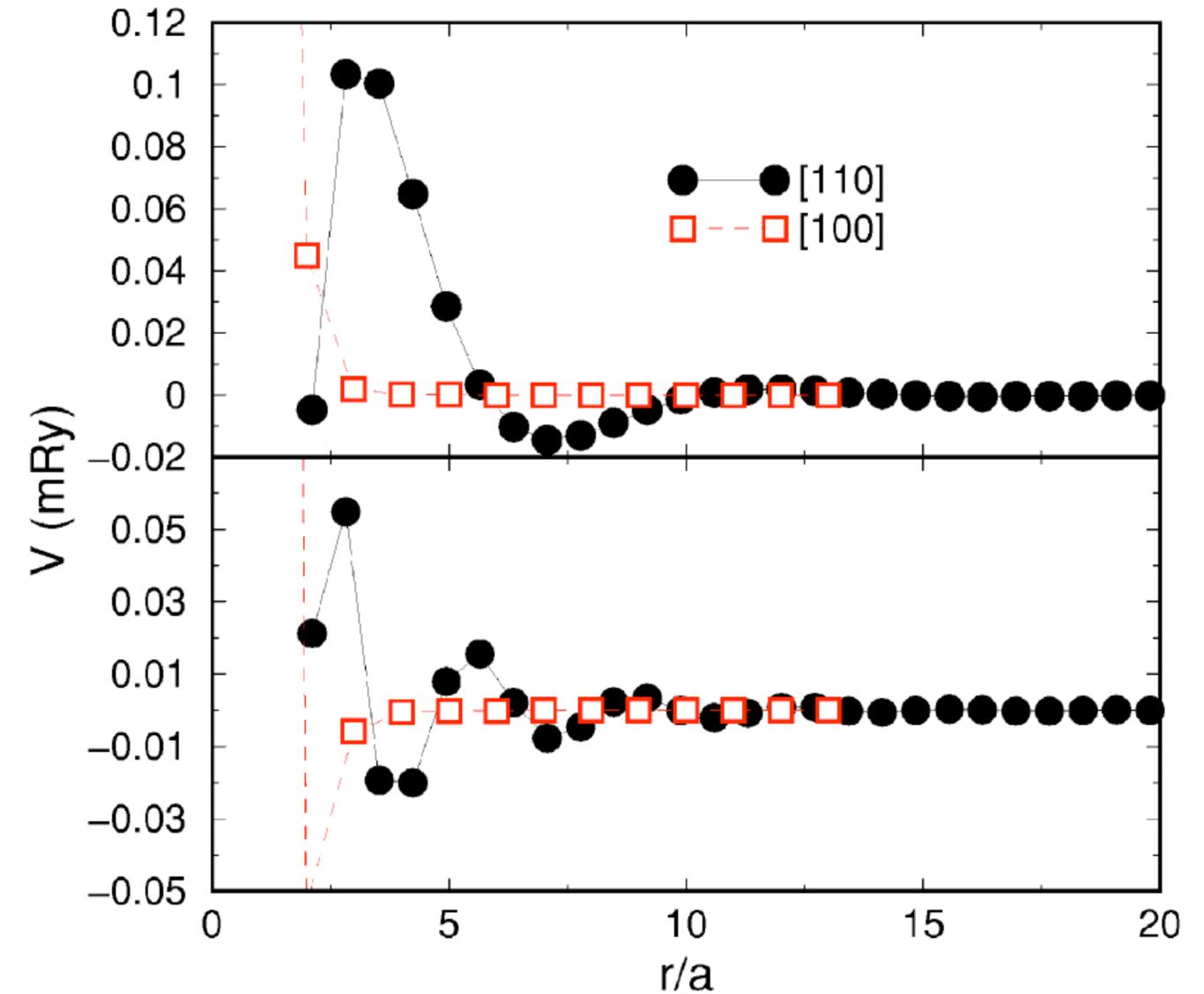
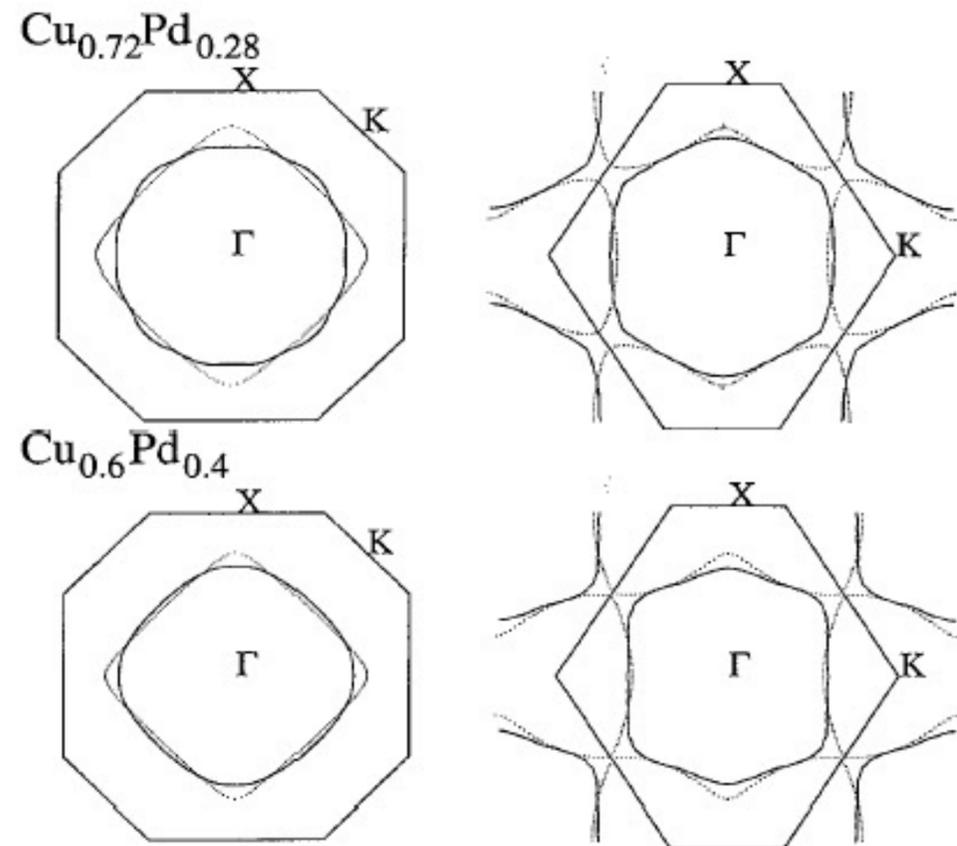
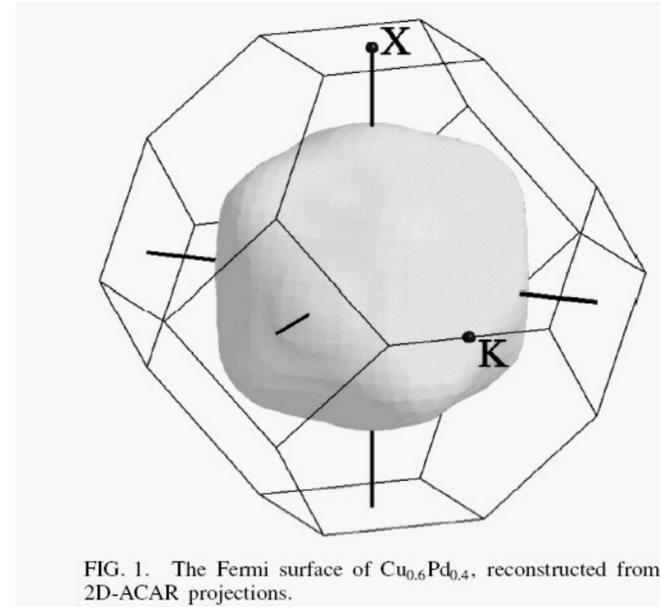


FIG. 13. (Color online) Pair interactions for  $\text{Cu}_{0.75}\text{Pd}$  (top panel) and  $\text{Cu}_{0.50}\text{Pd}$  (lower panel) shown in the [100] and [110] directions, the latter being the direction of the nesting vector.

# Fermi surface topological transition at $\sim 8-10$ at. %

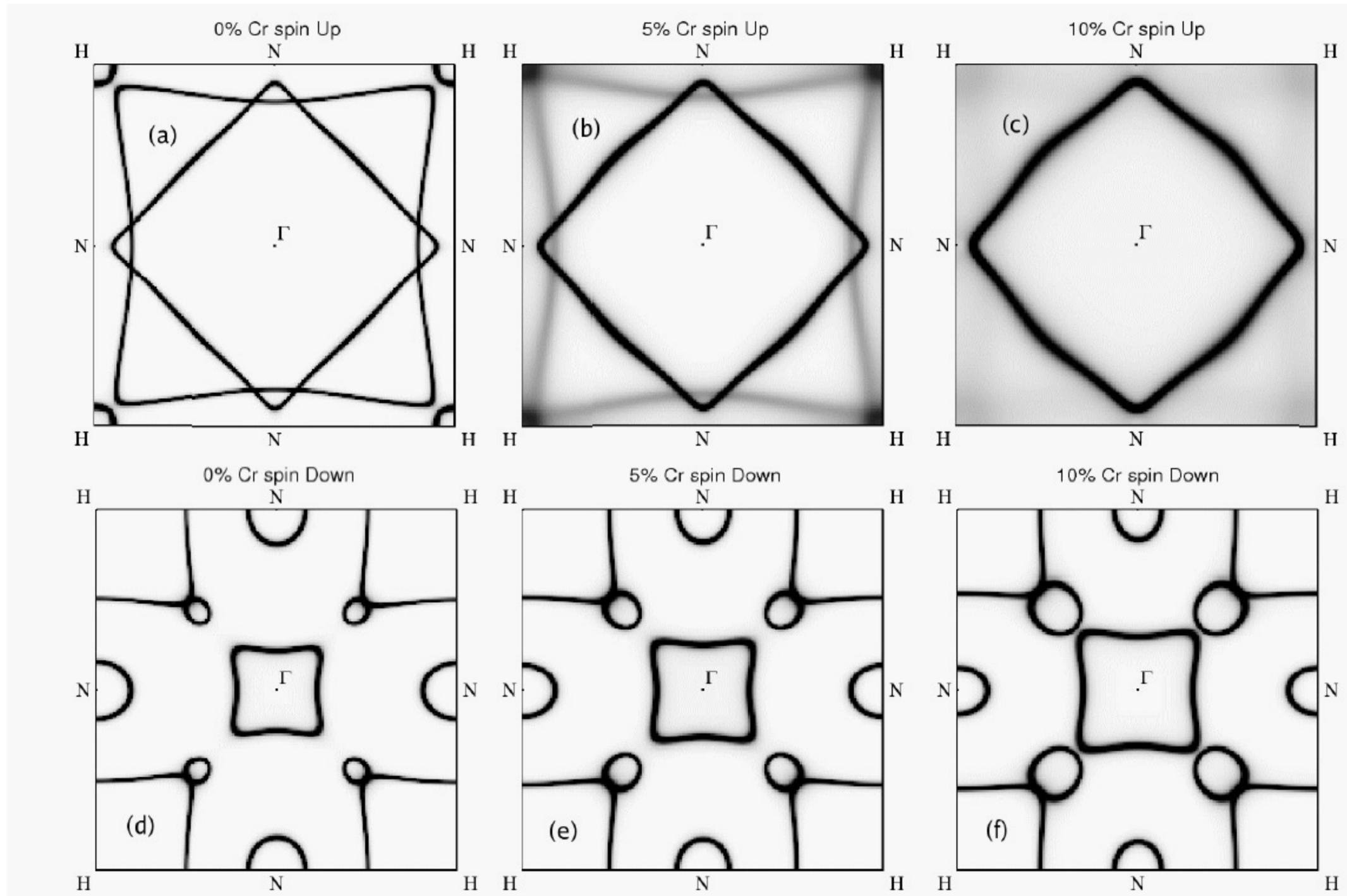
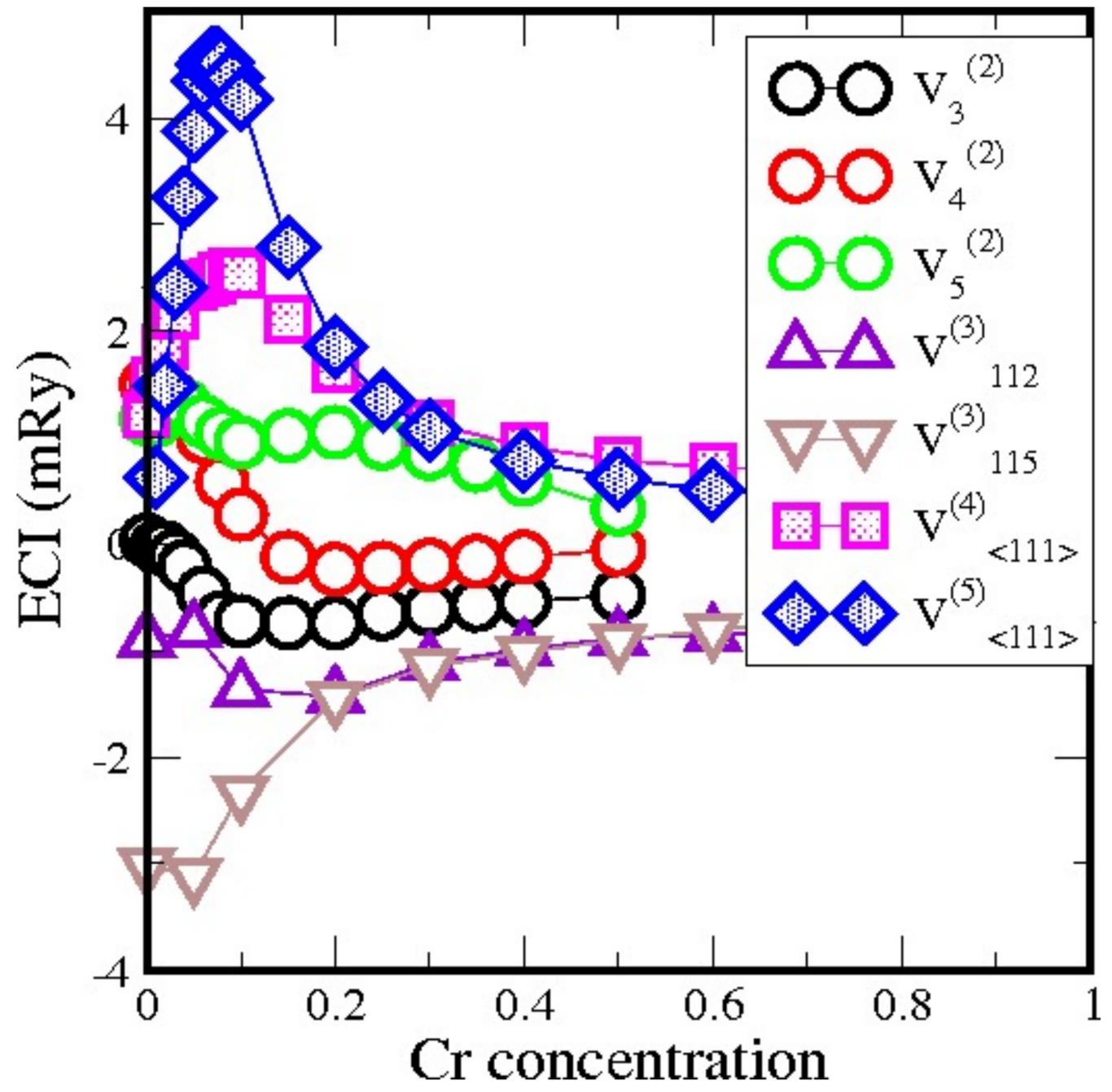
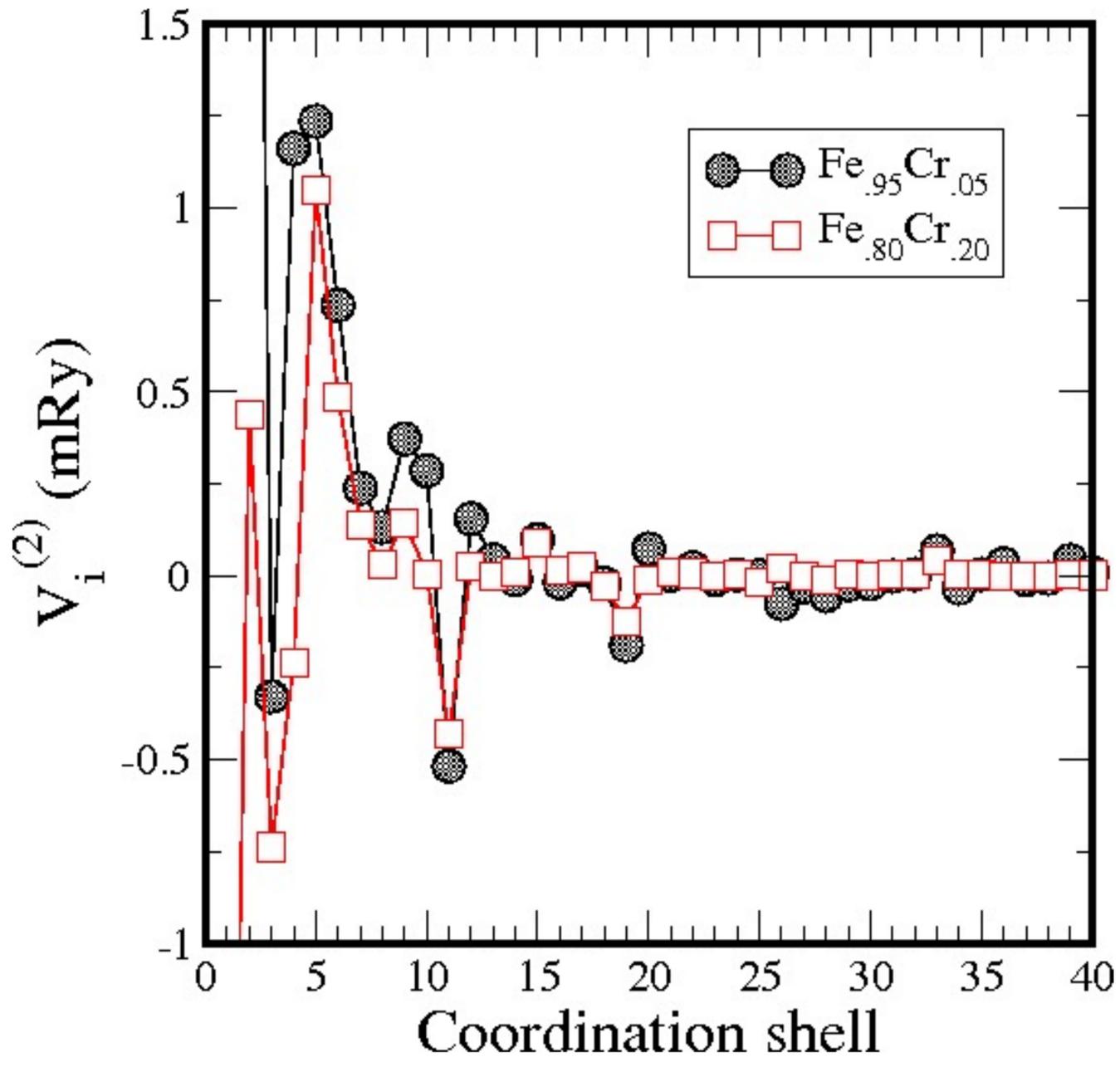


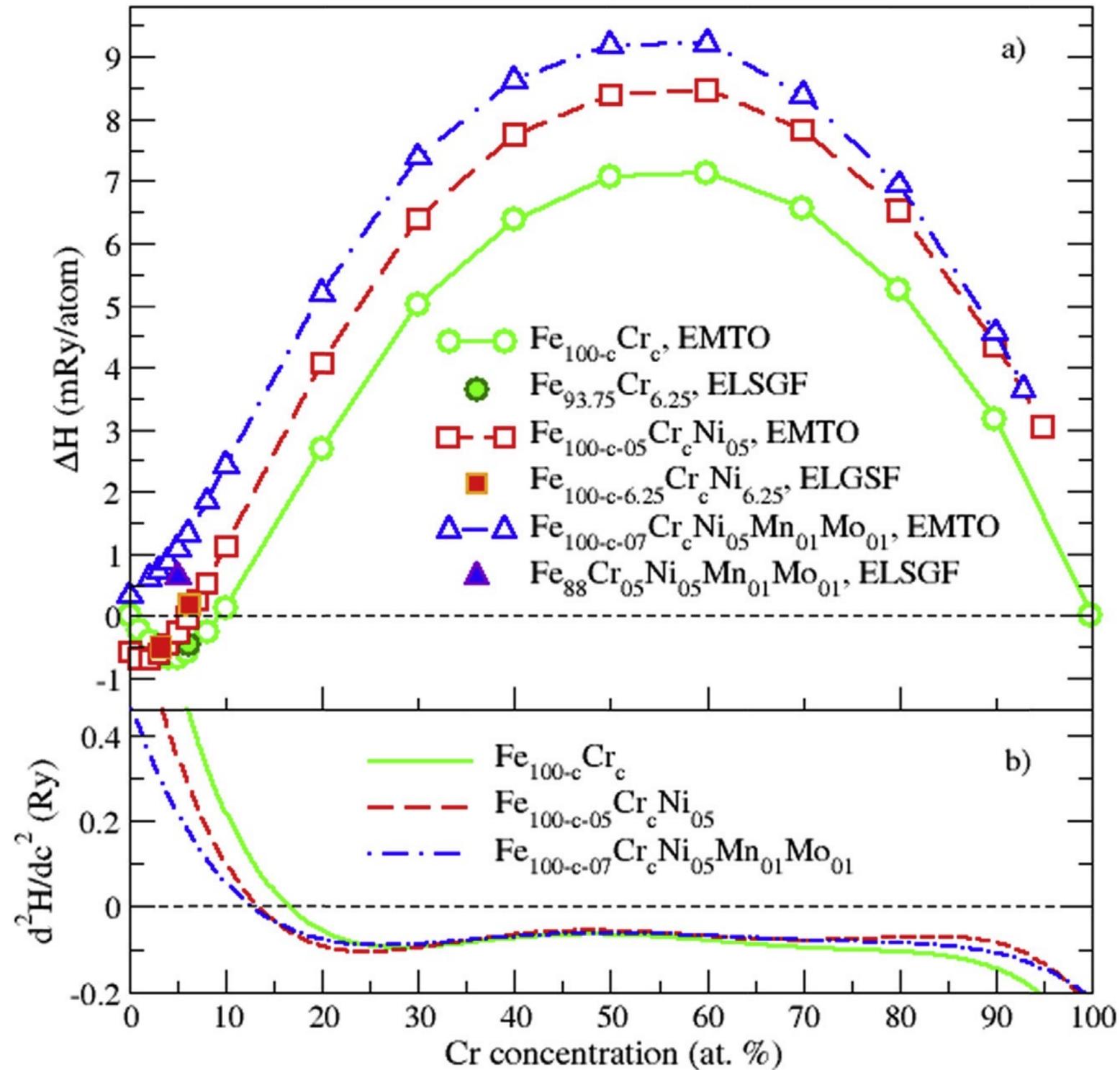
FIG. 6: Evolution of the Fermi surface of bcc Fe-Cr alloys with composition.

# Non-trivial concentration dependence of ECI

(in the ferromagnetic state)



# Continuous description of “energetics” of random alloys



Mixing enthalpy,  $\Delta H$ , and its second derivative with respect to concentration:  $\frac{d^2H}{dc^2}$  for Fe-Cr alloys.

Such calculations allow one to see the effect of alloying on the spinodal decomposition (the inflection point of  $\Delta H$ )

It is practically impossible to get reasonable smooth concentration dependences of  $\Delta H$  using supercell calculations.

# Effective chemical potentials by CPA I: formation energies of thermal vacancies in random alloys

$$E_f^0 = \min \frac{dE_0(A_{c(1-c_v)}B_{(1-c)(1-c_v)}Va_{c_v})}{dc_v} \Big|_{c_v=0}, \quad (1)$$

This is a formal definition, which provides the conservation of the alloy composition  $c_A/c_B = \text{const}$  (at  $T = 0\text{K}$ ).

Although CPA calculations seem to be perfect here, in fact they do not make sense here since usually vacancy-atom interactions are quite different for different alloy components.

Thus, either one should use a specific cluster expansion, or do direct calculations by using a relatively large supercell, which models the corresponding random alloy.

# Vacancy formation energies by combined supercell – CPA approach

In supercell calculations, the vacancy formation for a particular site  $i$  is

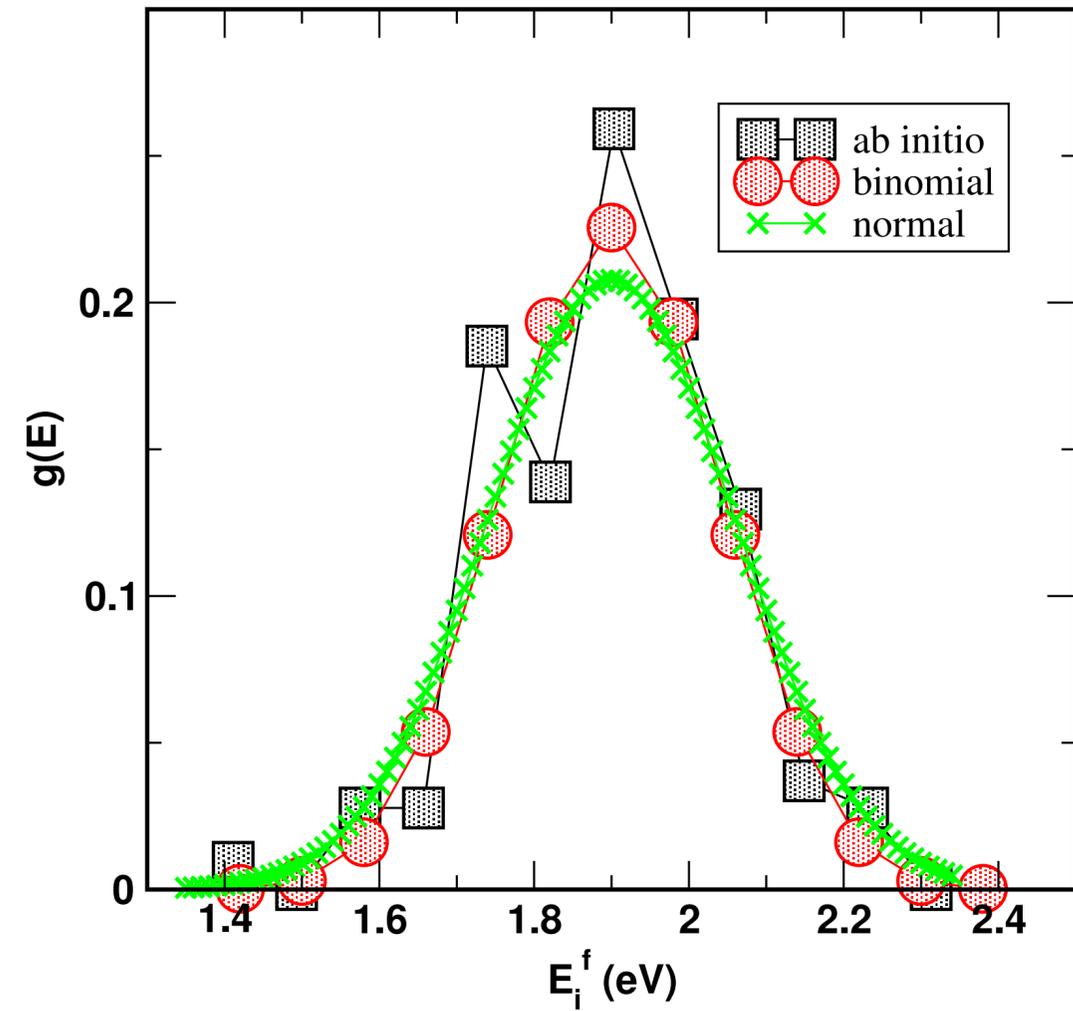
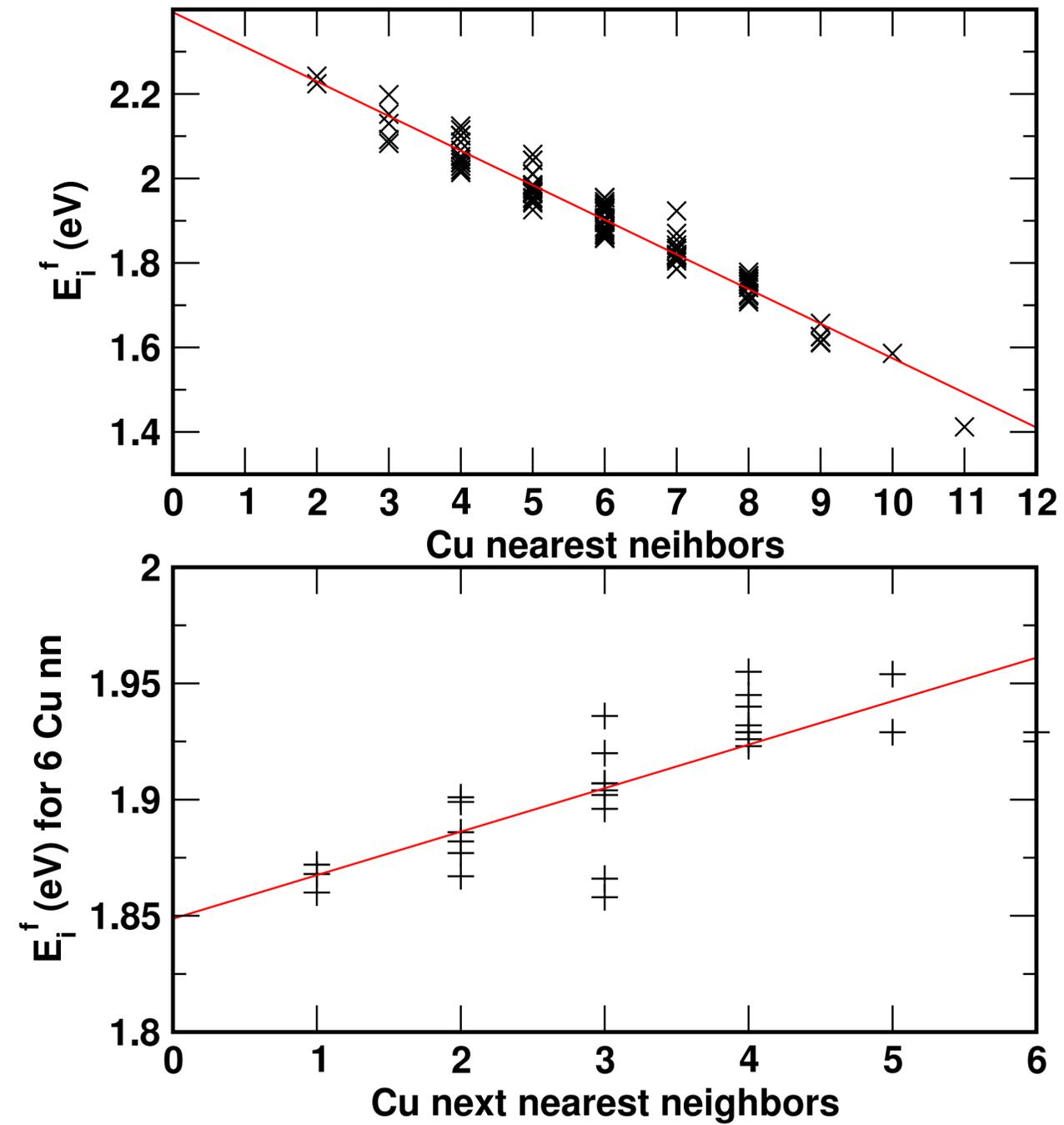
$$E_f^i = E_{vac}^i - \frac{N-1}{N} E_{all} - (N-1) \Delta c \mu_{eff},$$

where  $\mu_{eff} = \frac{\partial E_0(A_c B_{1-c})}{\partial c}$ . is the effective chemical potential

This term is needed to provide the composition conserving condition in the case of thermal vacancies.

In general, finding the effective chemical potential for a random alloy in supercell calculations requires a lot of computational effort, but it is a trivial (almost) task using CPA. The only condition is that both supercell and CPA electronic structure methods should be consistent. This is the case of, for instance, ELSGF and EMTO-CPA methods (Lyngby version of the code).

# ELSGF results for $\text{Cu}_{0.5}\text{Ni}_{0.5}$



$$g_b(E(n)) = \frac{12!}{2^{12} n! (12 - n)!},$$

$$g_n(E) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{(E - \langle E_f \rangle)^2}{2\sigma^2} \right],$$

# Surface segregation in random alloys by CPA methods

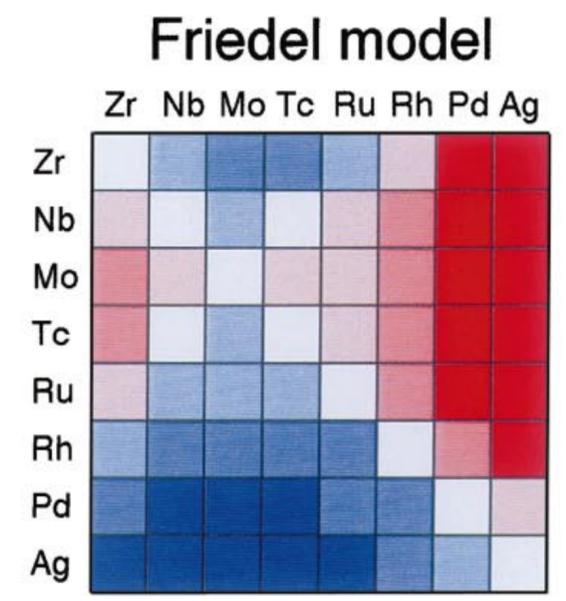
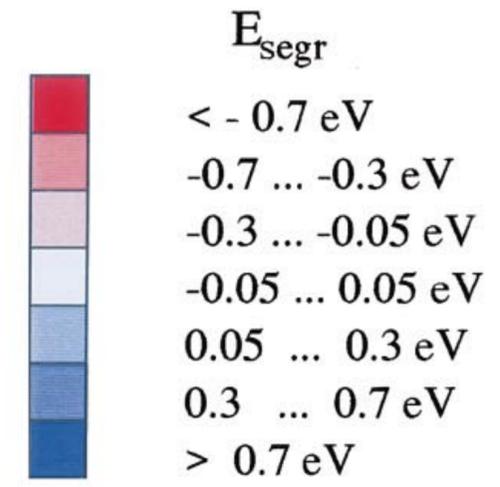
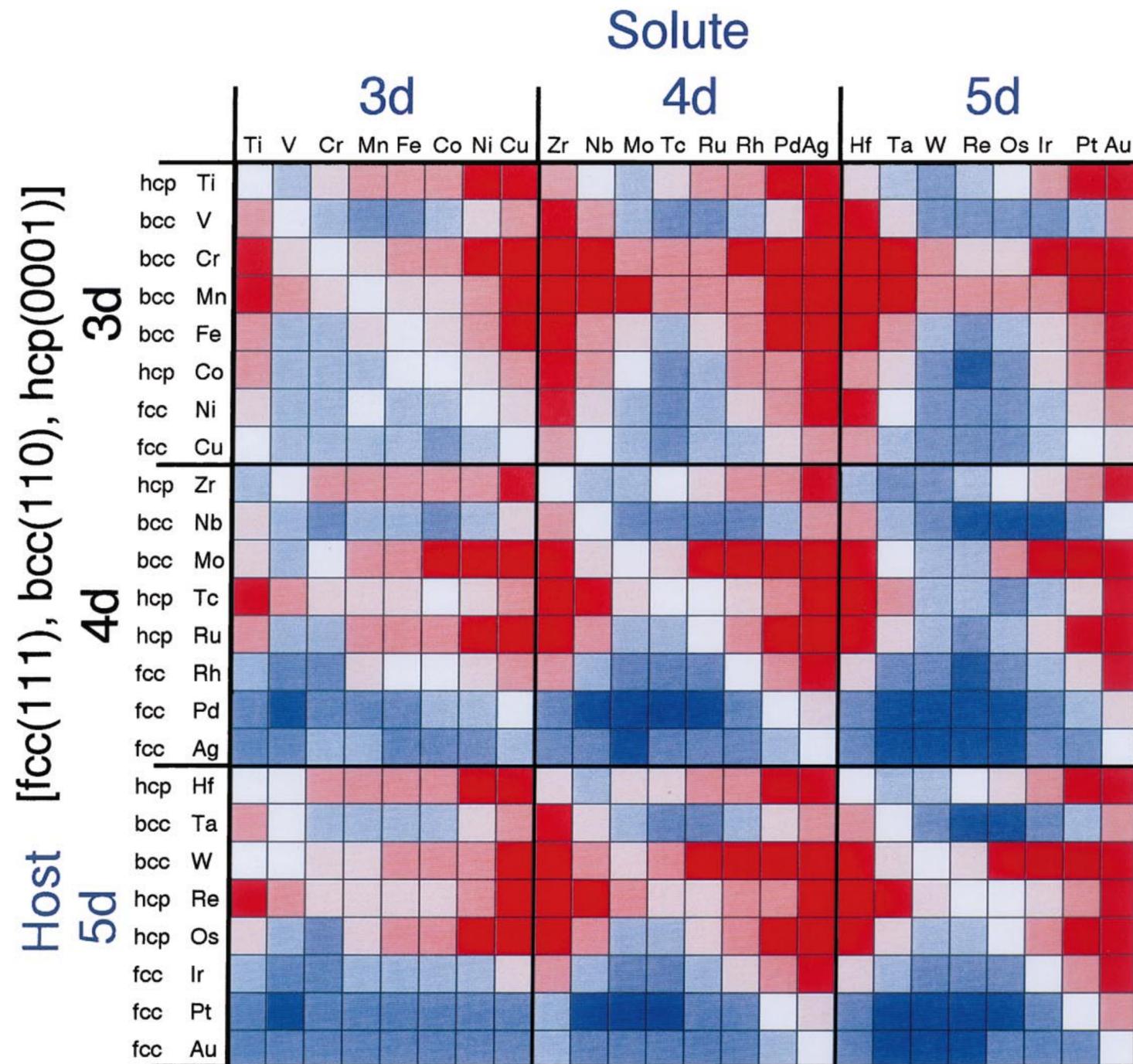
Surface segregation energy: 
$$E_{\text{segr},\lambda}^B = \frac{dE_{\text{surf}}(A_{1-c_\lambda}B_{c_\lambda})}{dc_\lambda}$$

Surface energy: 
$$E_{\text{surf}}(A_{1-c_\lambda}B_{c_\lambda}) = \sum_{\lambda'} (E_{\lambda'} - E_{\text{bulk}}) - \mu c_\lambda$$

Bulk effective chemical potential: 
$$\mu = \frac{dE_{\text{bulk}}(A_{1-c}B_c)}{dc}$$

Thus, in CPA method segregation energy is given by the difference of the effective chemical potentials in particular layer ( $\lambda$ ) and in the bulk.

# Surface segregation energies of impurities for the closed pack surfaces of transition metals by CPA



Ruban et al., 1998

# On segregation in multicomponent alloys: Surface segregation in austenite and FeCrCoNiMn alloys

A.V. Ruban\*

Comp. Mat. Sci. (2021)

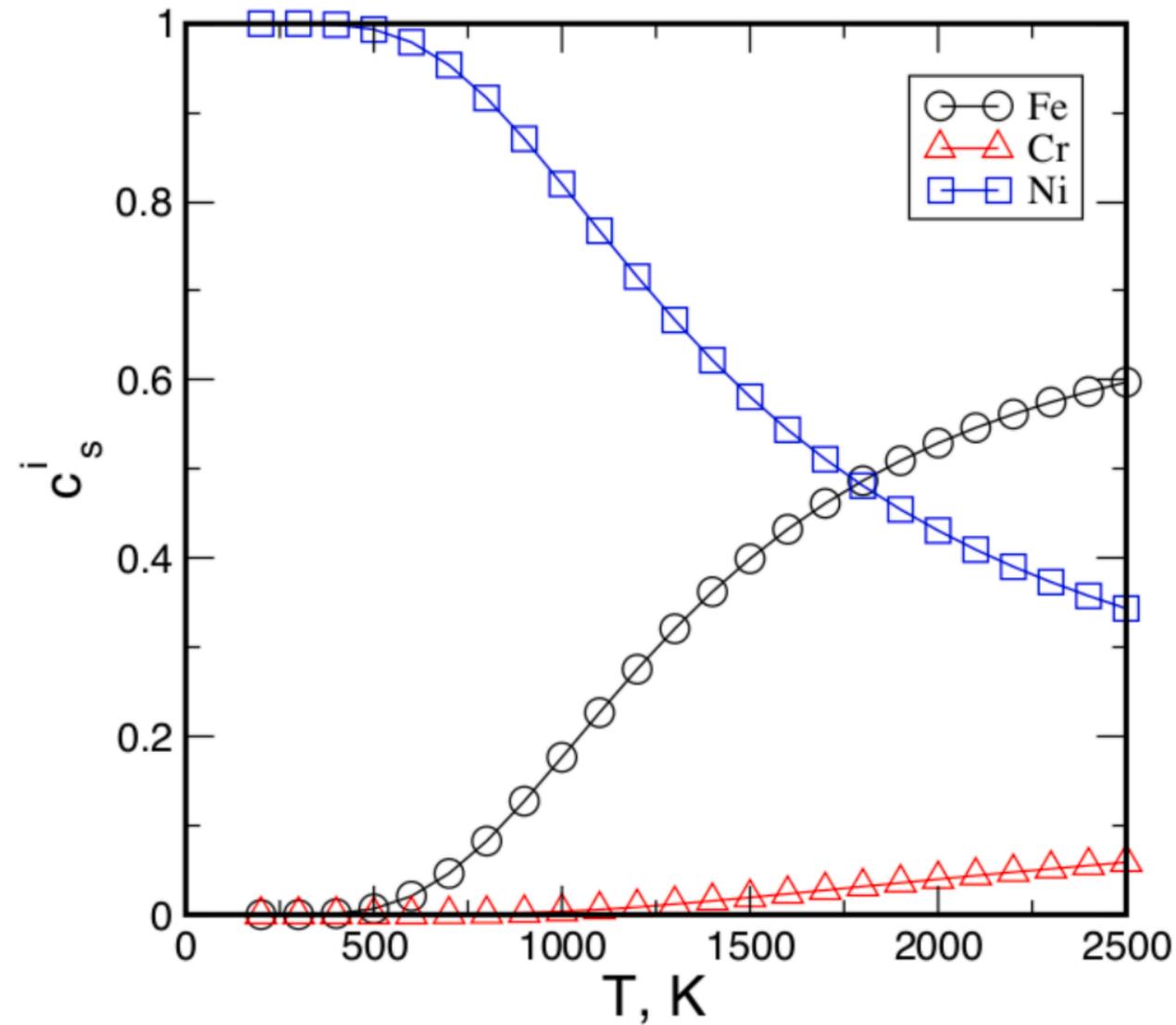


Fig. 1. Composition of the surface layer of Fe<sub>70</sub>Cr<sub>20</sub>Ni<sub>10</sub> random alloy as a function of temperature.

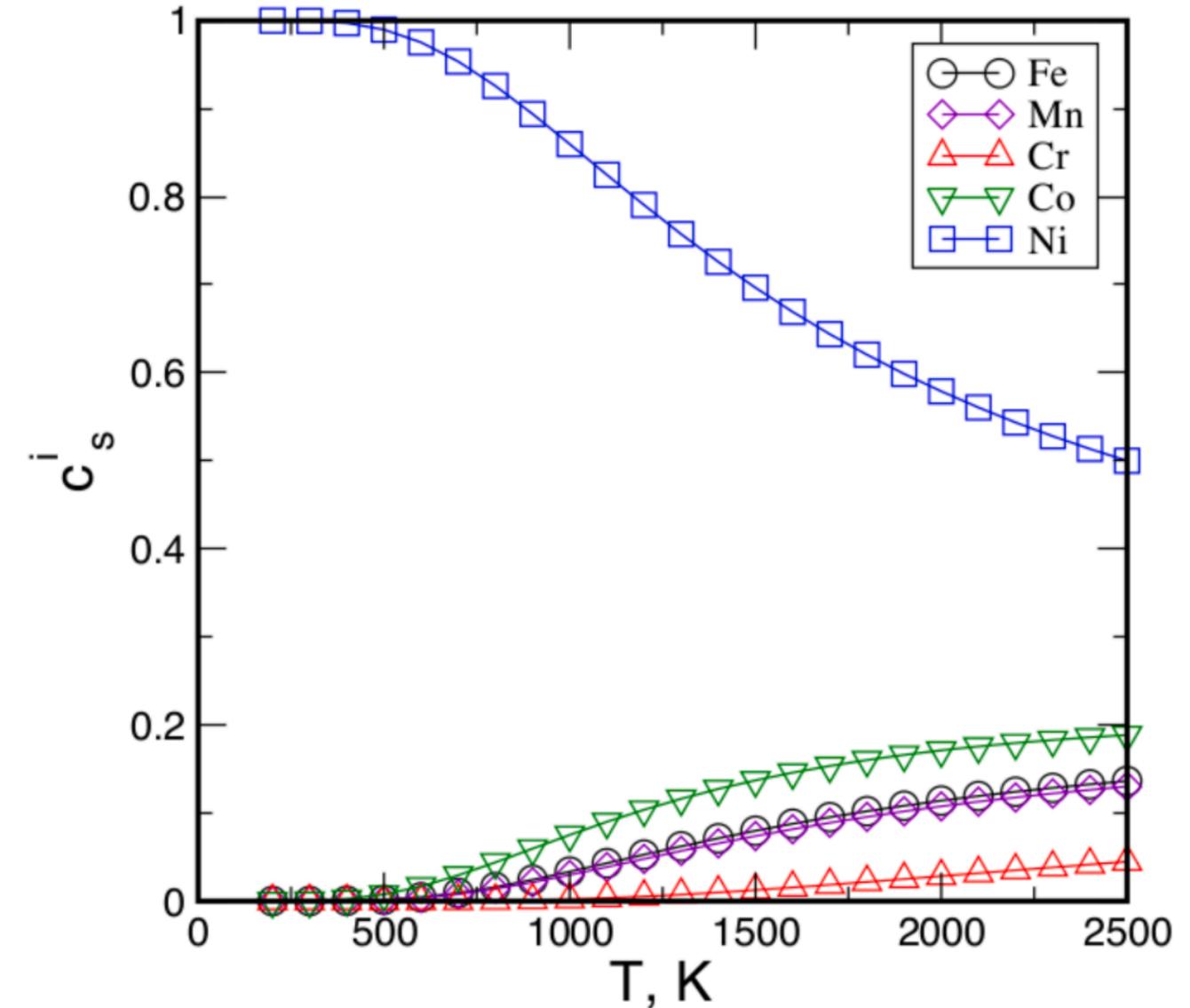
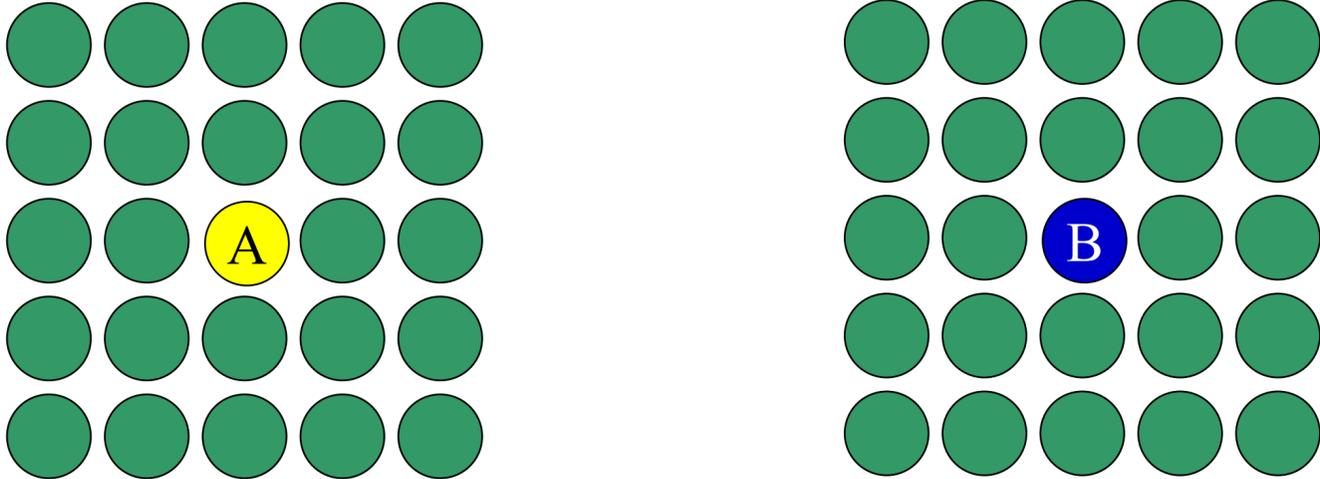


Fig. 2. Composition of the surface layer of FeMnCoCrNi random alloy as a function of temperature.

# Screened Coulomb interactions

Two parameters in the data file for alloy CPA calculations:

$$\tilde{g}(E) = cg^A(E) + (1-c)g^B(E)$$


However, there are actually no parameters in the CPA electronic structure calculations.

However, since it is a single-site approximation, which means that electron density of alloy components is determined only inside the corresponding atomic sphere. This creates problem in DFT self-consistent loop: one cannot solve accurately the Poisson equation. This problem is fixed by addition the screening contribution to the one-electron potential and electrostatic energy:

$$v_{\text{scr}}^i = -e^2 \alpha_{\text{scr}} \frac{q_i}{S}, \quad E_i^{\text{scr}} = \frac{e^2}{2} \beta q_i^2 \frac{\alpha_{\text{scr}}(R=0)}{S}$$