The electronic structure of disordered alloys with or without surface

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The active research field on the calculation of the electronic structure, as shown in this meeting, allows now to describe complex alloy problems as phase diagram in the bulk, segregation phenomena and order-disorder in semi-infinite alloy or multilayers... In this contribution we present a method based on a real-space configurational averaging procedure applied to a tight binding Hamiltonian to study such questions.

The determination of the electronic structure is needed to perform a phase diagram calculation from the “first principles”, i.e. avoiding the use of parameters /1/. For an infinite alloy, the Cluster Variation Method /1/, developed initially by Kikuchi and Monte Carlo method are expressed in terms of Effective Pair (and, if necessary, Cluster) Interactions. Various schemes have been developed to obtain the EPI /2-3/. The Effective Pair Interaction, \(E_{pq}\), involving sites p and q can be written as /2/:

\[
E_{pq} = \frac{1}{4} \left( V_{pq}^{AA} + V_{pq}^{BB} - V_{pq}^{AB} - V_{pq}^{BA} \right) \quad (1)
\]

where \(V_{pq}^{IJ}\) is the total energy of the alloy with an atom I at site p, an atom J at site q, embedded in the completely disordered medium. Such interactions are measured through diffuse intensities in neutron or X-ray scattering and have a simple physical meaning: for p and q nearest neighbors (n.n.), \(E_{pq} > 0\) (\(< 0\)) indicates an ordering (clustering) alloy.

In the Ising model for a semi-infinite alloy, in addition to the EPI, the Hamiltonian contains also terms as \(\Delta_{pq} = 1/2(V_{pq}^{AA} - V_{pq}^{BB})\). The segregation phenomena are, mainly, driven by the value of \((\Delta_{pq} - \Delta_{\infty,\infty})\) where p and q label two n.n. sites in the surface plane and \(\infty\) the bulk position. This term is usually interpreted as a bond breaking energy or a difference of surface tension.

For transition metals, it is well known /4/ that the total energy cannot written as a sum of pair energies. An exact expansion of the total energy, shows that, for a semi-infinite alloy, the first non-vanishing term is the “point” interaction \(\Delta_p = V_p^s - V_p^s\) \((V_p^s\) is the total energy of the system with an atom I at site p embedded in the completely disordered alloy). Now the leading term for the segregation is \((\Delta_p - \Delta_{\infty})\), where p label a site in the surface layer.
The electronic structure of disordered bulk binary alloy is mostly frequently determined within the Coherent-Potential Approximation (CPA). The CPA has been applied very successfully to a wide variety of alloys, either by tight binding or multiple scattering (KKR) frameworks. The extension of the CPA to semi-infinite systems leads to numerical difficulties, limiting his utilization. Another difficulty is the fact that the CPA is a mean-field theory and attempts to go beyond the single-site approximation revealed severe analyticity problems. Thus the inclusion of short or long range order is not straightforward. To avoid the difficulties in the use of the CPA, a method has been recently proposed to study the electronic structure of a binary alloy using a direct configurational averaging method. Developed for the bulk /2/, this approach has been extended to semi-infinite crystals /5/. This scheme interchanges the two steps used in the CPA framework: for a given configuration (the sites of the alloy are occupied randomly by an A or B atom, following some rule - having a given concentration profile, e.g.), all the quantities related to the electronic structure are computed. Then these quantities are averaged on independent configurations. A small number of configurations (10 to 15) have been found giving a satisfactory convergence for Effective Cluster Interactions, a slightly higher number (in order of 25) is necessary to describe the densities of states.

This approach has been applied to a tight binding Hamiltonian

\[ H(\sigma) = \sum_{n, \lambda} |n, \lambda > \epsilon_{\lambda}^{n} < n, \lambda | + \sum_{n \neq m, \lambda, \mu} \beta_{\lambda, \mu}^{nm} |m, \mu | \]  

(2)

where \( \sigma \) denotes a given configuration, \( \lambda \) and \( \mu \) label the orbitals (\( \lambda, \mu = 1,2, \ldots, 9 \) if s, p and d orbitals are considered), \( n \) and \( m \) are the lattice sites. The hopping integrals \( \beta_{AB} \) can be obtained from ab-initio calculations /6/, the off-diagonal disorder is taking into account through \( \beta_{AB} = (\beta_{AA} \beta_{BB})^{1/2} \). An important point is the determination of the on-sites energies \( \epsilon_{\lambda} \). All the calculation have been made supposing the local charge neutrality, which is well justified for the transition metals. In the bulk, for a given orbital, only two values \( \epsilon_{d} \) and \( \epsilon_{e} \) have to be considered. For an alloy with a surface, \( \epsilon_{d,s} \) have been found different from the bulk value \( \epsilon_{d} \) on the two or three first planes from the surface only.

Using the generalized phase shift approach, all the "point" and Effective Cluster Interactions are obtained as global quantities, where the differences between total energies are computed directly with finite size determinants /2/. The calculations are made in the real space with the recursion method /7/ and the use of optimal cluster size (few hundreds of atoms) /8/. Generally 6 levels of the continued fractions have ensured a good convergence /2/.

This approach has been used to determine Effective Cluster Interactions and phase diagrams /2-9/. Mainly we found similar results for the densities of states and the ECI as using TB-CPA, but at a much lower computational effort. This model has been used to investigate the surface segregation and order/disorder phenomena from an "ab-initio" point of view, i.e. all the quantities computed from the electronic structure. For example, we found, at any concentration of Ni, a very strong segregation of Cu on the surface plane of the CuNi alloy (fig 1). In such problems, all quantities are concentration dependent and thus the statistical and electronic structure have to be iterated to self-consistency simultaneously. Above \( T_{c} \), the critical temperature of the order-disorder transition, only the "point" energies are needed in the Bragg-Williams approximation. Below \( T_{c} \)
the variation of the Effective Pair Interactions must be studied. The EPI can change at or near the surface (for example fig. 2) but, generally, no change of sign for the EPI with two nearest neighbors atoms, has been found, indicating a similar behavior in the bulk or at the surface (clustering or ordering). This later point is important, because surface properties (catalysis, adsorption...) are sensitive to the local chemical arrangement.

Fig. 1: Equilibrium concentration of NiCu(001) alloy (T = 1.17K).
Full (dotted) line: bulk Ni concentration is 0.25 (0.75).

Fig. 2: Effective Pair Interactions (in eV)
for two n.n atoms in a NiCu(001) alloy,
1 denotes the surface plane. Full (dotted) line:
bulk Ni concentration is 0.25 (0.75).

The situation in the metallic multilayer is more complex: segregation, chemical order or disorder in the various layers, cristallographic structure... By the flexibility of the recursion method, this approach is a good tool to study such situations. Current work on this subject is under progress.

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