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Title
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Permalink
https://escholarship.org/uc/item/9mh7f2zb

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Publication Date
1992-04-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

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New Developments in the "ab Initio" Determination of Transition Metal Alloy Phase Diagrams

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April 1992

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Résultats récents sur la détermination des diagrammes de phases auto-cohérents d'alliages à base de métaux de transition

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Certain classes of temperature-composition binary alloy phase diagrams can now be computed in an "ab-initio" approach. No adjustable or experimentally fitted parameter is used. The expectation value of the energy is expressed in terms of an expansion of cluster probabilities , where the prefactors, the Effective Cluster Interaction, are related to the alloy electronic structure. This framework is used to study the MoRe alloy for two situations: bulk and semi-infinite crystal bounded by a (001) surface. In both cases, good agreement with experimental data is found.

Ab-initio determinations of transition metal alloys phase diagram have known important improvements in recent years /1/. At zero Kelvin, heats of formation, lattice parameters and elastic moduli of simple intermetallics compouds at theire stoichiometric composition have been predicted with success. Similar calculations for off-stoichiometric compositions are more delicate. One very efficient way to obtain the full (c-T) phase diagram is to expand the free-energy (or any necessary quantity) in cluster functions /2-3/. This approach allows, at first, to determine exactely the ground states /4/. Than the phase diagram can be obtained by well established method as the Cluster Variation Method. In this short communication, we shall present the main features of the general framework. The MoRe alloy will be studied for bulk and semi-infinite alloy.

In a binary alloy (AB) , a pseudo-spin variable is introduced : $\sigma_p = +1$ (-1) if the site p is occupied by a A (B) atom. Considering a set of lattice points, denoted as the cluster α, it has been shown that cluster functions $\phi_\alpha(\sigma)$ can be constructed so as to form an orthonormal set in the configurational space /5/. A convenient choice is to take

$$\phi_\alpha(\sigma) = \sigma_p \sigma_{p'} \sigma_{p''}....$$

(1)

if p, p', p''.... are the atoms of the cluster α. Thus any function of configurations, $f(\sigma)$, can be expanded into this basis:

$$f(\sigma) = \sum_{\alpha} f_{\alpha}\phi_{\alpha}(\sigma) \tag{2}$$

From a thermodynamical point of view, the expectation value of $f(\sigma)$ is, at a given temperature and chemical potential, given by

$$<f> = \sum_{\alpha} f_{\alpha}\xi_{\alpha} \tag{3}$$

where the multisite correlation functions ξ_{α} are ensemble averages of the corresponding cluster functions:

$$\xi_{\alpha} = <\sigma_p\sigma_{p'}\sigma_{p''}....> \tag{4}$$

In this way it is possible to compute the expectation value of the internal energy. The expansion coefficients E_{α} are called the Effective Cluster Interactions (ECI) and it has been shown the ECI can be computed directely from the electronic structure. For instance, the Effective Pair Interactions for $\alpha = (p,q)$ are given by

$$E_{pq} = \frac{1}{4} (W_{AA} + W_{BB} - W_{AB} - W_{BA}) \tag{5}$$

where W_{IJ} is the average total energy of the whole system with an I atom at site p and a J atom at site q. The W's are large numbers but cancellation of terms leads to much smaller number. Similar expressions have been derived for triplets, quadruplets, ... /6/. It has also been shown that only a few ECI have to be considered to obtain good convergence of the internal energy.
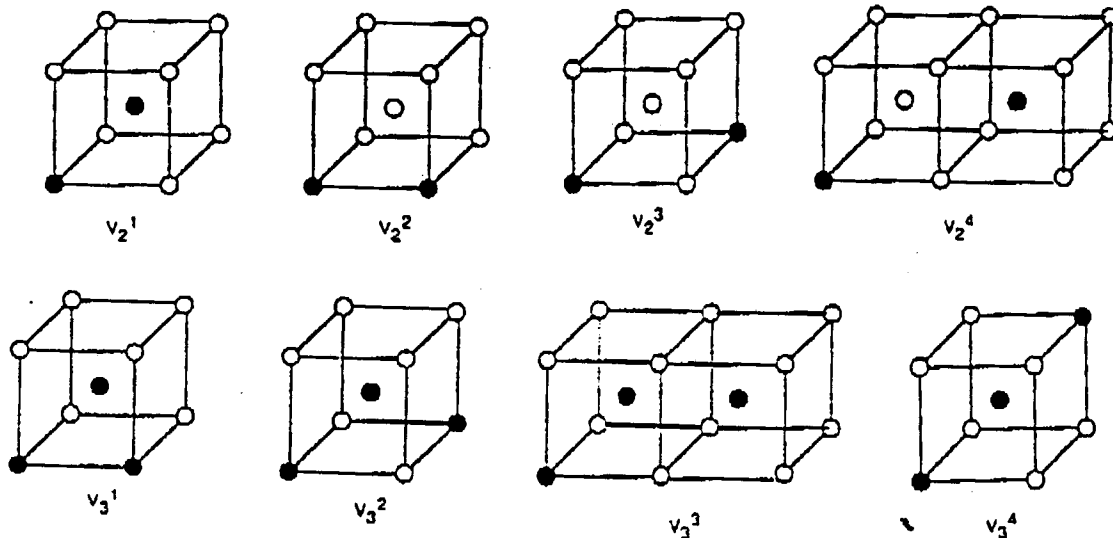
Since all possible configurations of the system and the embedded cluster are considered, the ECI are concentration-independent. Another way to compute the ECI, is to take only configurations having a fixed average concentration. In that case, the ECI are concentration-dependent. Both approaches are strictly equivalent /2/ but the convergence rate of the series is different. In a certain sense, concentration-dependent ECI seem to have more "physical" significance, but both approaches bear the same information. Moreover, exact relations between the two types of ECI have been derived. The complete description can be found in reference 2. It has also been established that the concentration-independent ECI are equivalent to concentration-dependent ECI at $c = 1/2$. This is due to the exponentially greater number of configurations existing at $c = 1/2$ than at any other concentration.

The ECI can be computed from the electronic structure by a Direct Configurational Averaging /6/. This is performed by keeping the cluster α constant and averaging on a small number of configurations for the other atoms. It has been found that 20-50 configurations are largely sufficient. This calculation can be realised by using a tight-binding Hamiltonian. The recursion method allows a direct space calculation where s and p orbitals can be considered. Also no symmetry is required and this scheme is well adapted to low-symmetry situations , as surfaces for instance.

This approach has been used for various systems. For instance the fcc ground states of the PdV alloy have determined rigourously by minimizing the configurational

energy. Twenty-six concentration-independent ECI have been computed and the asymmetry in the formation energy has been well described. The agreement with experimental results is quite excellent /4/. Let us insist on the fact that this calculation has been made without the use of any adjustable or experimentally derived parameters. By using volume correction , the miscibility gap of the RhPd alloy has been obtained with good agreement with the experimental data /7/.

In this paper, we have applied this scheme to study the MoRe alloy. Two cases will be considered: bulk and semi-infinite alloy. For the bulk no ordered structures on a bcc lattice have been reported for temperature above 750°K /8/. The (001) MoRe alloy has been studied in detail by quantitative LEED and the concentration profile was deduced from the experimental data /9/. In this calculation, we consider a tight-binding Hamiltonian with only d band. Numerous calculations and theoretical arguments have shown that the influence of the sp electrons on the electronic properties of transition metals far from the edges of the series is small. Pure bulk Mo and Re have very similar first neighbor distances. The hopping integrals for the pure elements have been choosen by following the Harrison prescription /10/. The hopping integrals between different types of atom are taken as the geometrical mean of the value for the pure elements. The diagonal elements of the Hamiltonian are ajusted such that average local neutrality is ensured. This procedure takes into account the Coulombian contribution and the crystal field variation and the transition metals are well described by a local charge neutrality /6/. Ten levels of the continued fractions are computed. The used cluster for the recursion method is the exact cluster /11/. Thirty configurations are used.


Figure 1: The studied Effective Cluster Interactions on a bcc lattice.

1. MoRe bulk

Two averaging modes have been considered. At first, the average is performed over all the possible configurations of the system. Concentration-independent ECI are obtained. In figure 1, we report the studied ECI on the bcc lattice. The corresponding values of the ECI are given in fig. 2.

At first it must be noticed that these ECI lead to an ordering temperature of 100°K which is in agreement with experimental observations. The relative values of the different ECI are very interesting. As it is well known the nearest neighbor Effective Pair Interaction (EPI) V_2^1 is the leading term in the cluster stability. According to the experimental results, a small value of V_2^1 was expected. With a value of 0.002 eV, this is the case. The question is now the values of the higher order EPI. According to the nodes theorem /12/, the EPI must present at least two nodes as a function of the band filling. It could be possible that the position of the Fermi level is very near of one of these nodes, leading to a very small value of V_2^1 which is here of the same order or even smaller than the second to fourth neighbors EPI usually found for other systems. In fact, as it can be inferred from fig. 2, the EPI for this system are found to follow the general behavior : $V_2^1 >> V_2^3$, V_2^4 (in absolute values). Similar remarks can be made for the triplet interactions. In other systems they have been found to be typically of the order of a few meV (up to 0.01 eV). In such a case the Effective Triplet Interactions would be larger than V_2^1. In fact it is not the case and, as usually observed, we found that the triplet interactions are at least one order of magnitude smaller than V_2^1.
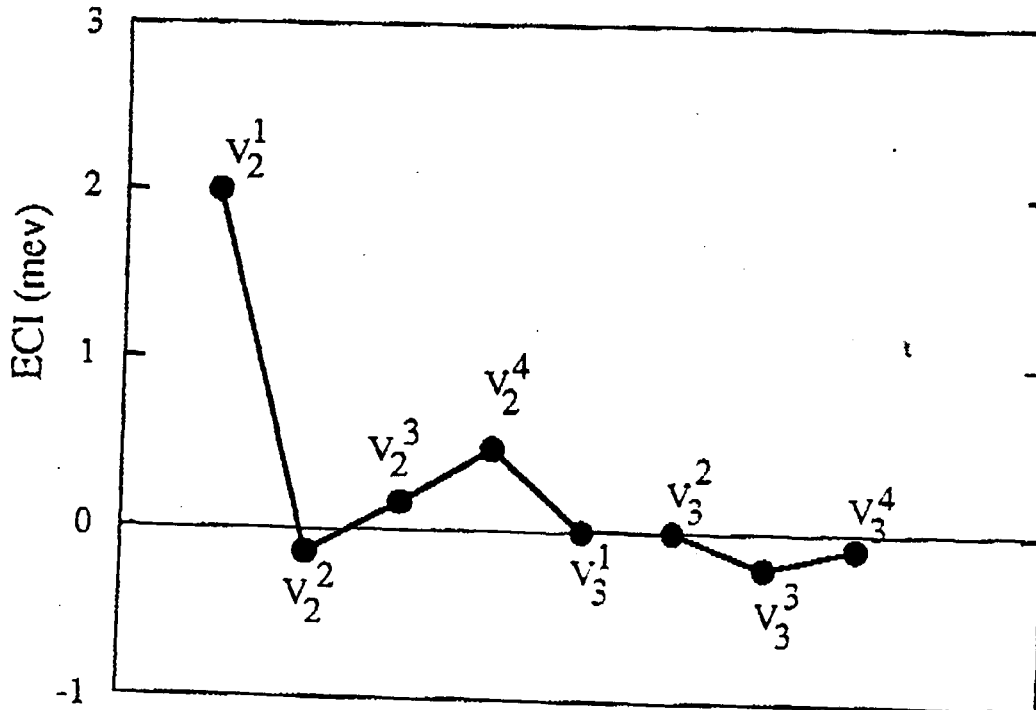
Figure 2: Values of the concentration-independent ECI of the MoRe bulk alloy (in meV). The labels are given in figure 1.

We have also computed the ECI obtained within a fixed concentration averaging. The EPI, V_2^1 and V_2^2, are not very sensitive to the concentration. This is not surprising, since the concentration independent ECI, V_α are related to the concentration-dependent ECI , $\tilde{V}_\alpha(c)$ by

$$V_\alpha = \tilde{V}_\alpha(c) + \sum_{\alpha \, in \, \beta} (-\sigma)^{(n_\beta - n_\alpha)} \tilde{V}_\beta(c) \qquad (6)$$

where $n_\beta(n_\alpha)$ are the number of the sites in the cluster $\beta(\alpha)$ /2/. Here $\sigma = 2c - 1$. Since the Effective Triplets Interactions are small, the variation of the EPI versus the concentration is small.

2. MoRe(001) alloy

In the bulk all sites are equivalent. It is no more the case when, for instance, the 3D lattice symmetry is broken, as for a semi-infinite alloy. In such a case, the point energy has to be considered /13/. In this calculation, the band structure contribution and the ion-ion repulsion described by a Born-Mayer pair potential have been determined. On figure 3, is reported the equilibrium concentration profile for the (001) surface orientation. Theorical predictions and experimental results are in excellent agreement : a very strong Mo segregation occurs in the surface plane , followed by a Mo depletion (as compared to the bulk value) on the second plane. For the third plane, we predict a slight Mo segregation, whereas Dötsch et al found no Mo concentration variation.
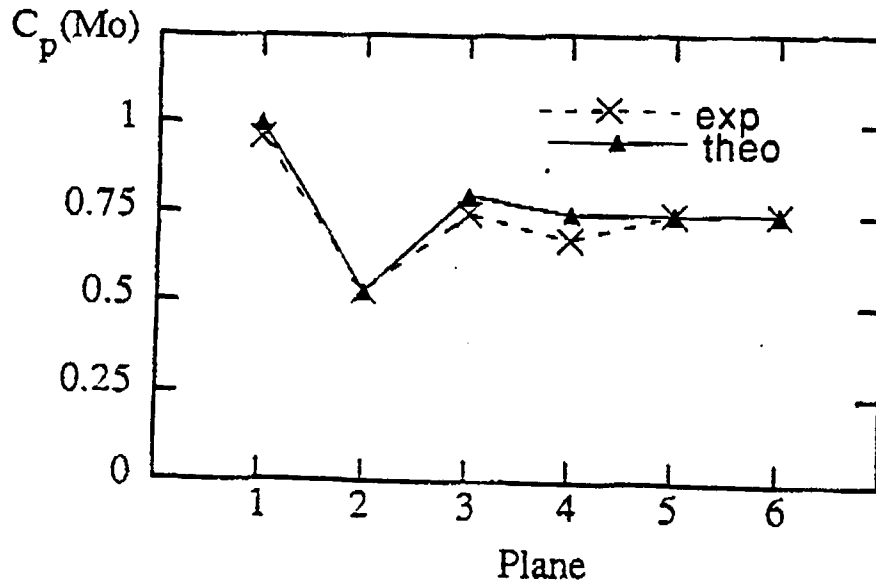
Figure 3: Segregation profile of the MoRe (001) alloy with a Bulk Mo concentration of 75%: theoretical predictions ($T = 200°K$) and the experimental result of Dötsch et al /9/ . The index 1 denotes the surface plane.

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Since here we considered a temperature higher than the bulk order-disorder transition value, we have assumed the alloy to be completely disordered: In that case the segregation is driven only by the point energy term. Otherwise the EPI and , eventually higher order ECI, would contribute /14/.

In summary, we have presented a general framework which allows to study the stablity of a binary alloy for any geometrical arrangement, without the use of any adjustable or experimentally fitted parameter. This is achieved by using an expansion in terms of cluster functions and computing the coefficients in this expansion (the Effective Cluster Interactions) from the electronic structure. The MoRe alloy has been studied into details. For the bulk and for the (001) semi-infinite alloy, good agreement with experimental results is found. Other applications are now under investigation.

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