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A phase-stability study of PdRh alloys

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Abstract. The aim of this communication is to apply the augmented-space recursion technique coupled with the orbital-peeling method, which was introduced by us earlier (Dasgupta I, Saha T and Mookerjee A 1995 *Phys. Rev. B* **51** 3413) as a computationally powerful methodology, to study the phase stability of PdRh alloys.

1. Introduction

Alloys are multiphase systems and it is of great interest to the condensed-matter physicist to find out when and under what conditions a particular phase becomes favourable for a given alloy system. This study of phase formation requires accurate approximations to the configuration energy as well as the use of statistical models to obtain the configurational entropy. Over the past few years it has become possible to combine *ab initio* quantum mechanical electronic structure calculations for alloy energetics with statistical mechanical models for the configurational entropy so as to perform a phase-formation study without the use of adjustable and experimentally determined parameters.

One approach essentially involves the expansion of the alloy configuration energy in terms of the concentration deviations at each site from the uniform background of a perfectly disordered solid solution and truncation of the expansion series depending upon the accuracies required. One may interpret the process of phase ordering and segregation as the loss of stability of the uniform perfectly disordered background against static concentration waves (the Fourier transform of the concentration deviations at each site). The stability limit of the concentration waves, i.e., the temperature at which this instability first sets in, is determined by the vanishing of the second derivative of the free energy. The concept of the stability limit, analogous to the critical point in higher-order transitions, is generally extended into metastable regions (below first-order transition lines) defining the so-called ordering spinodal.

We have recently developed a scheme [1] for the calculation of the alloy configurational energy based on the method of augmented-space recursion (ASR) [2] coupled with the orbital-peeling technique [3]. Our scheme is similar to other methods based on embedding clusters in an effective medium (ECM). The calculation involves the description of the electronic structure of the components as well as averaging over different configurations of the system. It is precisely in this averaging scheme that different methods based on the ECM differ from one another. In the CPA-ECM [4] the averaging is done within the framework of the single-site coherent potential approximation. In the direct configuration averaging

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(DCA) [5] the averaging is done directly by summing up over a finite number of different random configurations. The CPA, although generally successful, has all the drawbacks of a single-site mean-field theory, neglecting clustering and short-ranged ordering effects, which may be significant near a phase boundary. In the DCA, on the other hand, since averaging is done by brute force, in principle one can never be sure whether sufficiently many configurations have been sampled or not—in particular, the ones with high probability weightings. However, the ASR technique provides a convenient means of configuration averaging which is not restricted by the above limitations and which systematically includes the most probable configurations with the correct weightings, so we may ensure that the moments of the density of states up to a predetermined order are *exactly* reproduced [1].

In the present communication, our aim will be apply the ASR orbital-peeling method for the study of phase segregation in PdRh alloy systems. We shall also apply mean-field approximation for the entropy contribution to obtain the instability temperatures.

2. Methodology

It has been shown [4] that the configuration energy for a binary alloy A_xB_{1-x} may be expanded as

$$E(\{n_i\}) = V^{(0)} + \sum_{i=1}^N V_i^{(1)} \delta x_i + (1/2) \sum_{i,j=1}^N V_{ij}^{(2)} \delta x_i \delta x_j + \dots \quad (1)$$

Here n_i takes the value 1 or 0 according to whether the site i is occupied by an A atom or not. The concentration of A atoms is then $x = \langle n_i \rangle$ and $\delta x_i = n_i - x$. The coefficients $V^{(0)}$, $V_i^{(1)}$, $V_{ij}^{(2)}$ are the effective renormalized cluster interactions (renormalized in the sense that all possible scatterings off clusters of a definite size embedded in an average medium are included).

The renormalized effective pair interactions (EPI) express the correlation between two sites and are the most dominant quantities in the analysis of phase stability. The single-site interaction, though volume and concentration dependent, is structure insensitive and is usually not considered in stability analysis. We will retain terms up to pair interactions in the configuration energy expansion. Higher-order interactions may be included for a more accurate and complete description.

The effective pair interaction can be expressed as follows:

$$V_{ij}^{(2)} = E_{ij}^{AA} + E_{ij}^{BB} - E_{ij}^{AB} - E_{ij}^{BA} \quad (2)$$

where E_{ij}^{IJ} is the average energy of the disordered alloy in which the species I and J are embedded at the sites i and j respectively. It gives the interchange energy associated with two sites embedded in an otherwise disordered medium. In the linearized density functional approximation the total energy of the solid consists of two terms: the band-structure energy E_{BS} and the electrostatic contribution E_{ES} which includes Coulomb repulsion of ions and the correction for double counting in the band-structure term. It is usually assumed that for energy differences of the type involved in the definition of the EPI, the electrostatic contributions approximately cancel one another and one is left principally with the band-structure contribution. This assumption has been shown to be justified for a number of alloy systems. Thus what is needed is to calculate the band-structure energies with fixed occupancies of the sites i and j in an otherwise completely disordered lattice.

Considering only the band energy contribution, the EPI can be written in a convenient form in terms of the generalized phase shift $h(E)$ as

$$V_{ij}^{(2)} = - \int_{-\infty}^{E_F} h(E) dE$$

with

$$h(E) = (1/\pi) \text{Im} m \log \left\{ \frac{\det\langle G^{AA} \rangle \det\langle G^{BB} \rangle}{\det\langle G^{AB} \rangle \det\langle G^{BA} \rangle} \right\} \quad (3)$$

where $\langle \dots \rangle$ indicates configuration averaging over all sites except the sites i and j where the embedding takes place.

The orbital-peeling method gives an efficient method for directly obtaining the EPI without going through the large cancellations implied in the defining equation. The orbital-peeling method has been described at some length in earlier studies [1, 9]. We shall not repeat that description once again, but refer readers to the earlier studies for details. We employ the augmented-space recursion coupled with the linearized muffin-tin orbitals method [6] (the TB-LMTO-ASR method) for a first-principles determination of the configuration-averaged *peeled* Green functions $\langle G_k^{IJ} \rangle_{ii}$, where $G_k^{IJ} = (zI - H_k^{IJ})^{-1}$, where H_k^{IJ} is the random Hamiltonian with the sites i and j occupied by atoms of the type I and J , and $k - 1$ rows and columns related to the angular momenta associated with the site i deleted (or peeled off) ($k = 1, \dots, 9$). The EPI are then given in terms of the zeros and poles of these Green functions. These zeros and poles are obtained directly from the continued-fraction coefficients which are the output of the TB-LMTO-ASR method.

Finally, a few comments on the TB-LMTO-ASR method are in order.

(i) The augmented-space theorem gives the *exact* configuration-averaged Green function and the only approximation involved is that of terminating the continued-fraction expansion of the Green function in the recursion method. Detailed estimates of the various termination errors exist (see [12]). We may therefore keep the errors due to the termination within prescribed error limits. This necessitates good computational resources being at our disposal. However, we have further used the point group symmetries of the full augmented space of the homogeneously disordered binary solid to drastically reduce the rank of the irreducible subspace on which the effective recursion takes place. It is this that allows us to obtain accurate results with moderate computational facilities. Moreover, since recursions in different irreducible subspaces do not mix, the different recursions can be done in parallel on different CPU.

(ii) The LDA self-consistency is obtained within the ASR. This takes into account crucial effects like charge transfer on alloying. To systematize the calculation, we first carry out the TB-LMTO-CPA method fully self-consistently, then use the converged potential parameters to begin the ASR self-consistency loop. In practice this cuts down the long LDA iteration times considerably, as, at the very start, most of the charge transfer is taken care of in a single-site mean-field sense.

3. Calculation of the instability temperatures

As mentioned in the introduction, the study of phase formation requires accurate approximations to the configurational energy as well as the use of statistical models to obtain the configurational entropy. The configurational energy within the pair interaction can be represented in Fourier space as the product of the Fourier transforms of the effective

pair interaction $V(\mathbf{k})$ and that of the pair correlation function $Q(\mathbf{k})$:

$$E \simeq (N/2) \sum_{\mathbf{k}} V(\mathbf{k}) Q(\mathbf{k})$$

where N is the number of atoms.

Minimization of E will naturally occur for states of order characterized by maxima in the $Q(\mathbf{k})$ pair correlation spectrum located in the regions of the absolute minima of $V(\mathbf{k})$. Consequently, much can be predicted about the types of ordering reaction to be expected from a study of the shape of $V(\mathbf{k})$ —particular, from a search of its absolute minima (the so-called special or Lifshitz points). At these special points,

$$\nabla_{\mathbf{k}} V(\mathbf{k}) = 0. \quad (4)$$

This was pointed out by Lifshitz [7] and Khatchaturyan [8]. Different types of ordered structure can be related directly to the minima of $V(\mathbf{k})$.

In other words, given the knowledge of concentration wave vectors, one can readily predict the most stable ordered structure of the system at low temperatures. This is comparable to the knowledge derived from studies like those based on x-ray, electron and neutron diffraction. A peak at the Γ point, $\mathbf{k} = (000)$, indicates phase separation, while a peak at the X point, $\mathbf{k} = (100)$, in a fcc lattice suggests ordering in the Cu_3Au - or CuAu -ordered structures. Peaks away from special points may correspond to the formation of long-period superstructures. A well-known example is provided by the CuPd alloys.

Within a simple mean-field approximation, the stability temperature T_0 can be obtained in the following way.

If we add the expression for the dominant quadratic term in the average energy to that of the configurational entropy under the simple mean-field approximation we obtain an expression for the free energy:

$$F = \sum_{i,j} V_{ij}^{(2)} (x_i - x)(x_j - x) + \kappa_B T \sum_i [x_i \ln x_i + (1 - x_i) \ln (1 - x_i)]$$

where x_i is the concentration of the species A at the i th site and x is the average concentration of that species. If we define a configuration variable γ_i^0 as $\langle \delta x_i \rangle_0$ (the symbol $\langle \dots \rangle_0$ denotes microcanonical averaging), which is the variable relevant to the stability analysis, then the harmonic term in the Taylor expansion of the above free energy is

$$F^{(2)} = (N/2) \sum_{\mathbf{k}} \Gamma(\mathbf{k}) F(\mathbf{k}) \Gamma(\mathbf{k})$$

where $\Gamma(\mathbf{k})$ is the Fourier transform of γ_i^0 and $F(\mathbf{k}) = \kappa_B T + x(1 - x)V(\mathbf{k})$.

The stability of a solid solution with respect to a small-amplitude concentration wave of a given wave vector \mathbf{k} is guaranteed as long as $F(\mathbf{k})$ is positive definite. Instability sets in when $F(\mathbf{k})$ vanishes:

$$F(\mathbf{k}) = \kappa_B T_0 + x(1 - x)V(\mathbf{k}) = 0. \quad (5)$$

It appears from the above expression that under a simple mean-field approximation the spinodal is always a parabola in the (T, x) phase diagram, symmetric about $x = 0.5$. It is the concentration dependence of the effective pair interactions which brings about the asymmetry.

4. Results and discussion

The PdRh alloy system provides a convenient test case for the application of the methodology because of its particularly simple phase diagram, which consists of only liquid and fcc solid-solution phases. It is one of the few alloy systems that does not show polymorphism and there is relatively little transfer of charge or size disparity between the atoms. Application of d-band-like arguments for PdRh alloys with almost filled d bands gives a clustering tendency at low temperatures.

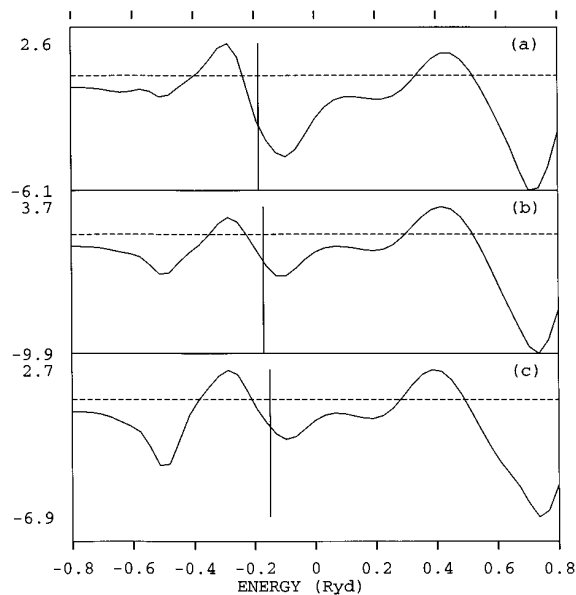


Figure 1. The nearest-neighbour pair interaction V_1 versus energy for $\text{Pd}_x\text{Rh}_{1-x}$ alloys: (a) $x = 0.25$; (b) $x = 0.5$; and (c) $x = 0.75$. Vertical lines mark the Fermi energies.

Figure 1 shows the plot of nearest-neighbour effective pair interactions for the alloys $\text{Pd}_{75}\text{Rh}_{25}$, $\text{Pd}_{50}\text{Rh}_{50}$ and $\text{Pd}_{25}\text{Rh}_{75}$ as functions of the band-filling energy \dagger . We note that the plot is dominated by the negative value of the nearest-neighbour pair interaction. In figure 2 we plot the effective pair interactions at the Fermi energy up to the sixth-nearest neighbour for the 50–50 PdRh alloy. This shows that the pair interactions in PdRh decay rapidly as functions of the neighbour distance and the dominant interaction $V_{1\dagger}$ is negative. In a magnetic analogy, this would correspond to a ferromagnetic interaction. In an alloy, this means that constituent atoms prefer to be surrounded with atoms of their own kind. In other words, the alloy will tend to phase separate and will exist as a mixture of two phases.

In table 1 we quote the numerical values of the pair interactions up to fourth-nearest neighbours as obtained from the KKR-CPA-GPM (Turchi *et al* [9]), using the grand canonical DCA (Wolverton *et al* [10]) and from the present methodology. We note that the agreement of the numerical values from the different methodologies is reasonable and better

\dagger Care must be taken here since different papers define pair energies with slightly different factors and some include 'per spin' while others do not. For comparison, all numbers have been reduced to the same definition and units.

\ddagger $V_n = V_{ij}^{(2)}$ where r_i and r_j are n th-nearest neighbours of each other.

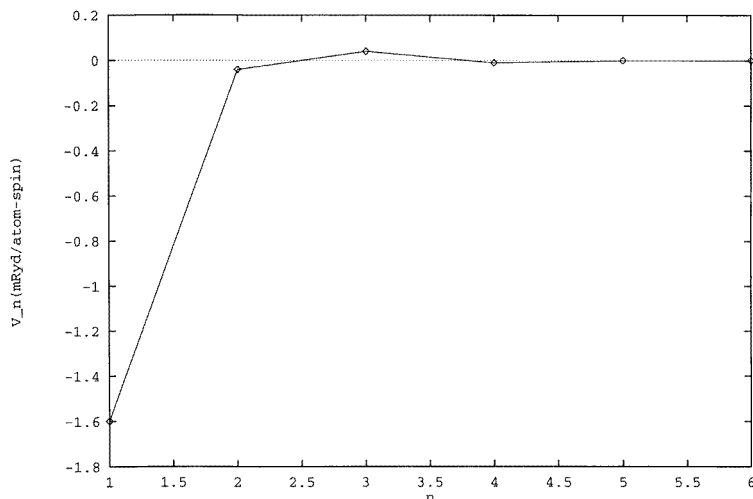


Figure 2. V_n as a function of n for the Pd₅₀Rh₅₀ alloy system.

Table 1. Effective pair interactions in mRyd/atom for various distances between the pairs for a 50–50 PdRh alloy. The TB-LMTO-DCA values are taken from Wolverton *et al* [10] and the KKR-GPM values from Turchi *et al* [9].

Pair interaction	TB-LMTO-DCA	KKR-GPM	TB-LMTO-ASR
V_1	−0.764	−0.85	−0.80
V_2	$\simeq 0$	−0.05	−0.02
V_3	$\simeq 0$	−0.12	0.1
V_4	$\simeq 0$	$\simeq 0$	$\simeq 0$

than that for other alloy systems [1]. This may be attributed to the fact that since PdRh is a simple system, in the context of the smaller charge transfers and degree of disorder present between the constituents, the difference between different methodologies may not be significant. A systematic study of the effect of using various alloy Hamiltonians on the numerical values of the effective pair interactions for PdRh alloys has been made by Wolverton *et al* [10]. The starting alloy potential parameters were made consistent with the alloy Wigner–Seitz radius by applying the volume derivative correction. Thus the potential parameters, to start with, will contain the information on the concentration, which will be found to be important for the desired asymmetry of the spinodal curve (to be discussed later). The nearest-neighbour pair interaction calculation for the alloy Hamiltonian parametrized with TB-LMTO calculations in which Pd and Rh are each at their own equilibrium lattice constants has also been carried out. In such a scheme the potential parameters do not bear the concentration dependence. This calculation has been found to give larger negative values for the nearest-neighbour pair interactions for each concentration, as compared with the earlier scheme. For the 50–50 alloy V_1 is found to be -2.71 mRyd/(atom spin) in the latter scheme as compared with the value of -2.6 mRyd/(atom spin) obtained in the systematic study of Wolverton *et al* [10].

We have calculated $V(\mathbf{k})$ by Fourier transformation spanning six nearest-neighbour shells. This method contrasts favourably with the direct calculation of $V(\mathbf{k})$ in \mathbf{k} -space and

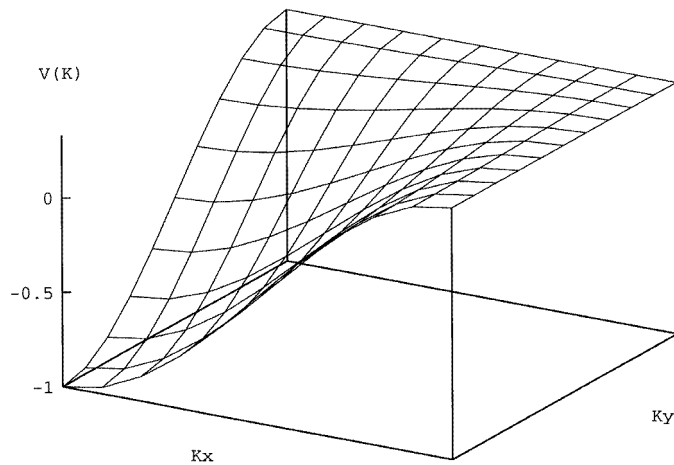


Figure 3. The $V(\mathbf{k})$ surface for Pd₅₀Rh₅₀ on the $k_z = 0$ plane.

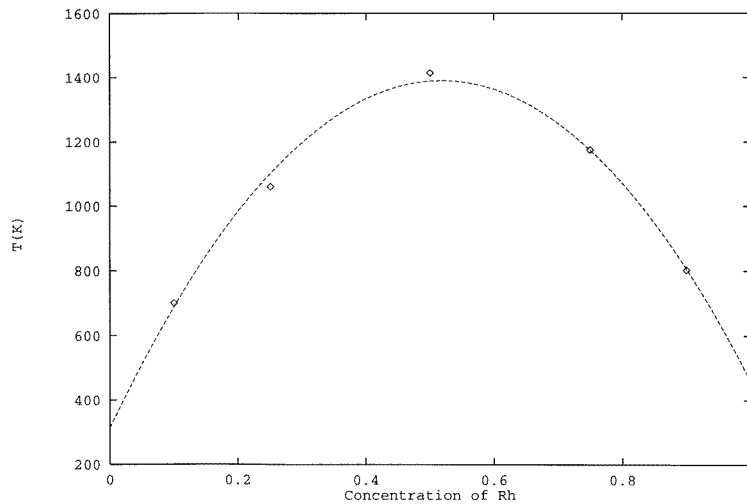


Figure 4. The spinodal curve for PdRh. The points indicate calculated values while the solid line is the cubic-spline fit through these points.

is justified by the fast convergence of V_n with shell number as shown in figure 2. In figure 3 we plot the $V(\mathbf{k})$ surface for the Pd₅₀Rh₅₀ alloy on the plane $k_z = 0$. The minimum at the Γ point indicates a clustering instability. In figure 4 we plot the stability limit temperatures for $x = 0.1, 0.25, 0.5, 0.75$ and 0.9 (x is the concentration of Pd in the alloy).

The points outline a roughly parabolic curve: the spinodal. We note that the instability temperature at $x = 0.25$ is larger than that at $x = 0.75$. This is in agreement with experimental observation of the nature of the miscibility gap giving the phase boundary between the solid-solution phase and the phase-separated phase. In terms of the ECI, the

physical reason for the observed asymmetry can be understood in the following way: pure Rh has a smaller equilibrium volume than Pd. The potential parameters of the TB-LMTO Hamiltonian which contain information on the concentration are consistent with the alloy Wigner–Seitz radius. This decreases linearly from the Pd-rich side to the Rh-rich side, making the nearest-neighbour interaction (the dominant one in the determination of the stability limit) more attractive on the Rh-rich side.

The maximum point in the spinodal curve which corresponds to the maximum temperature of the miscibility gap turns out to be 1380 K, which is 190 K higher than the experimentally predicted value [11]. The overestimation is contributed to the entropy estimate which is a simple mean-field one and always gives elevated estimates of transition temperatures. Furthermore, neglect of the phononic contribution to the entropy also leads to a rise in the calculated temperature.

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