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CALCULATIONS OF ALLOY PHASES WITH A DIRECT MONTE-CARLO METHOD

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ABSTRACT

A method for calculating the boundaries that describe solid-solid phase transformations in the phase diagrams of alloys is described. The method is first-principles in the sense that the only input is the atomic numbers of the constituents. It proceeds from the observation that the crux of the Monte-Carlo method for obtaining the equilibrium distribution of atoms in an alloy is a calculation of the energy required to replace an A atom on site i with a B atom when the configuration of the atoms on the neighboring sites, κ , is specified, $\delta H_{\kappa}(A \rightarrow B) = E_B(\kappa) - E_A(\kappa)$. Normally, this energy difference is obtained by introducing interatomic potentials, v_{ij} , into an Ising Hamiltonian, but we calculate it using the embedded cluster method (ECM). In the ECM an A or B atom is placed at the center of a cluster of atoms with the specified configuration κ , and the atoms on all the other sites in the alloy are simulated by the effective scattering matrix obtained from the coherent potential approximation. The interchange energy is calculated directly from the electronic structure of the cluster. The table of $\delta H_{\kappa}(A \rightarrow B)$'s for all configurations κ and several alloy concentrations is used in a Monte Carlo calculation that predicts the phase of the alloy at any temperature and concentration. The detailed shape of the miscibility gaps in the palladium-rhodium and copper-nickel alloy systems are shown.

INTRODUCTION

Phase diagrams of alloys are extremely useful to materials scientists who wish to design processes to improve the physical properties of materials through control of their micro structure. It has long been a goal of alloy theory to use electronic structure calculations to predict phase stabilities from first principles. Since most of the binary phase diagrams are known, theoretical predictions will be more useful when they can make reliable predictions about ternaries and quaternaries, but the early results that we will discuss here indicate that they can provide a useful feedback for experimental studies of binaries.

A number of theories for predicting the structure of an alloy as a function of concentration and temperature are based on the assumption that its energy can be obtained from an Ising model Hamiltonian

$$H = \frac{1}{2} \sum_{ij} [v_{ij}^{AA} p_i^A p_j^A + v_{ij}^{BB} p_i^B p_j^B + v_{ij}^{AB} (p_i^A p_j^B + p_i^B p_j^A)] \quad (1)$$

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where p_i^A is one if the atom at site i is an A atom, and zero if it is not. Theorists have made efforts over the years to write the exact expression for the total energy of an alloy in the form of this Hamiltonian,¹⁻⁴ and to calculate the interatomic potentials, $V_{ij}^{\alpha\beta}$, from the electronic structure. The major reason for the popularity of this approach is that Ising Hamiltonians have been extensively studied by experts on statistical mechanics, and the statistical part of the problem can proceed along standard lines once the parameters in the Hamiltonian are available. The present work is based on the observation that it is not necessary to introduce interatomic potentials if the Monte Carlo (MC) method⁵ is used for the statistical mechanics.

The crux of the MC method for obtaining the equilibrium distributions of atoms in an alloy is a calculation of the energy required to replace an A atom on site i with a B atom when the configuration of the atoms on the neighboring sites, κ , is specified, $\delta H_\kappa(A \rightarrow B) = E_B(\kappa) - E_A(\kappa)$. A random number Z between zero and one is generated and the atoms at site i are interchanged only if a condition is satisfied, such as $Z < \exp(-\delta H_\kappa/2k_B T)$. In the MC calculations done to date, δH is obtained from the Ising model in Eq. (1), but we calculate it directly from the electronic structure of the alloy using the embedded cluster method (ECM) of alloy theory. The ECM has reached its highest stage of development in a paper by Gonis, Butler, and Stocks,⁶ and is in turn based on the coherent potential approximation (CPA) for the electronic states of random substitutional alloys.⁷

In order to describe this approach in more detail, let us recall that, in one of the ways that the CPA can be stated,⁸ attention is focused on the one-electron Green's functions $G_A(E)$, $G_B(E)$, and $G_C(E)$. The function $G_C(E)$ describes the propagation of an electron through a periodic lattice that has an effective scatterer described by the scattering matrix $t_C(E)$ on every lattice site. The propagators $G_A(E)$ and $G_B(E)$ are calculated for a system that has $t_C(E)$ on every lattice site except for the central site, which has the scattering matrix $t_A(E)$ or $t_B(E)$ on it. The $t_A(E)$ and $t_B(E)$ describe the scattering from an A or B atom. The CPA condition that defines $t_C(E)$ may be written

$$C_A G_A(E) + C_B G_B(E) = G_C(E). \quad (2)$$

An example of quantities that can be calculated with the CPA are the densities-of-states (DOS) functions

$$\begin{aligned} \rho(E) &= -\frac{1}{\pi\Omega_0} \text{Im} \int G_C(E, \mathbf{r}, \mathbf{r}) d\mathbf{r} \\ \rho_A(E) &= -\frac{1}{\pi\Omega_0} \text{Im} \int G_A(E, \mathbf{r}, \mathbf{r}) d\mathbf{r} \\ \rho_B(E) &= -\frac{1}{\pi\Omega_0} \text{Im} \int G_B(E, \mathbf{r}, \mathbf{r}) d\mathbf{r} \end{aligned} \quad (3)$$

where the integrals are over the volume Ω_0 of the central unit cell. To the accuracy attainable with the CPA, which is very good, $\rho(E)$ is the DOS of the alloy. The DOS of the A or B atoms in the alloy is, on the average, $\rho_A(E)$ or $\rho_B(E)$.

The CPA is a single-site approximation, which means, e. g., that the fluctuations of the densities of states of the A atoms about $\rho_A(E)$ due to their local environments cannot be calculated. The ECM⁶ is a way to go beyond the single-site approximation, although it is not as well founded theoretically as the CPA. Operationally, the ECM is applied by constructing Green's functions $G_A^\kappa(E)$ and $G_B^\kappa(E)$ for systems that have A or B atoms on the central site and some chosen configuration, κ , of A and B atoms on the sites of the first few nearest-neighbor shells. The effective scattering matrix $t_C(E)$, which is calculated with the ordinary CPA, is placed on all the other lattice sites. We have developed a technique for calculating the energies $E_A(\kappa)$ and $E_B(\kappa)$ in an alloy from $G_A^\kappa(E)$ and $G_B^\kappa(E)$. These $E_A(\kappa)$ and $E_B(\kappa)$ will certainly have a dependence on the configuration κ .

A first approximation to the energy of an atom in a solid can be calculated from its density of states function $\rho_i(E)$ with the frozen potential approximation

$$E_i = \int_{-\infty}^{E_F} (E - E_F) \rho_i(E) dE \quad (4)$$

We use this level of approximation in the work reported here. It is consistent with the approximation made in the generalized perturbation method (GPM) for calculating the $V_{ij}^{\alpha\beta}$'s put forward by Ducastelle and Gautier⁹ and applied extensively by Sluiter and Turchi¹⁰. It is also consistent with the approximation made by Gonis et al.,² who used the two and three atom ECM to calculate $V_{ij}^{\alpha\beta}$'s. The density functional method of Gyorffy and Stocks¹¹ has been used to find phase boundaries, and it also relies on the frozen potential approximation.

The Green's functions $G_A^\kappa(E)$ and $G_B^\kappa(E)$ obtained from the ECM can be used to calculate density of states functions $\rho_{A,i}^\kappa(E)$ and $\rho_{B,i}^\kappa(E)$ for every atom in the cluster according to (3). Thus the interchange energy between a cluster with an A or B atom at the center may be calculated from

$$\delta H_\kappa = E_B(\kappa) - E_A(\kappa) = \sum_i \left[\int (E - E_F) \rho_{B,i}^\kappa(E) dE - \int (E - E_F) \rho_{A,i}^\kappa(E) dE \right], \quad (5)$$

where the sum goes over all atoms in the cluster. These ECM calculations are carried out with codes developed at the Oak Ridge National Lab as extensions of state-of-the-art KKR-CPA¹² programs.

We have also developed a version of the theory described above within the context of the tight-binding model. Very few first-principles band-theory calculations are carried out with the tight-binding method, but it is common to represent the results of calculations done with other methods by a tight-binding interpolation scheme.¹³ The resulting model is relatively easy to deal with in both CPA and ECM calculations. It has the further advantage that other studies of ordering in alloys have been carried out using this model.^{2,10} It suffers in comparison with the KKR-CPA

because there is no way to make this model self-consistent, but it should require less computer time. It can be used to carry out surveys of large numbers of systems.

CALCULATIONS

The interchange energies for the palladium-rhodium alloy at 50% concentration are shown in Fig. 1. The cluster is taken to be the central atom plus the first nearest-neighbor shell. This alloy has a face centered cubic lattice so there are 12 atoms in the nn shell and hence there are $2^{12} = 4,096$ different configurations κ , but they are all related by symmetry to 144 configurations. The 144 interchange energies in Fig. 1 are plotted against the number of rhodium atoms n_{Rh} in the nn shell. In a nearest neighbor Ising model, the interchange energies are simply $\delta H = C n_{Rh}$, where C is a constant. The spread in our energies is rather small for Pd-Rh, and they fall fairly close to the straight line that the Ising model would predict. The slight asymmetry in these interchange energies is quite important, as will be seen.

Figure 1. The interchange energies δH_{κ} for a 50% palladium-rhodium alloy expressed in degrees Kelvin plotted against the number of rhodium atoms in the nearest-neighbor shell.

It is necessary to carry out a KKR-CPA calculation and then 288 ECM calculations for each alloy concentration in order to obtain the 144 interchange energies. At the present time, this can consume up to fifteen hours of Cray YMP cpu time. By moving to a massively parallel computer, the Intel iPSC/860, this was reduced to two hours of cpu time. By modern standards, this is a small computation that can be used to survey a large number of systems.

We calculated the interchange energies for Pd-Rh at five different concentrations, 5%, 25%, 50%, 75%, and 95%. The energies are different for each concentration, but the differences are sufficiently small that they do not show up well in a drawing like the one in Fig. 1. The differences do have a noticeable effect on the phase boundary, however, as will be shown.

The interchange energies were put into a fairly standard Monte Carlo code of the kind that has been described in the literature.¹² Of course, the code had to be modified to recognize each of the 4,096 different configurations of nn atoms and to find the proper δH_K from the calculated table to put into the test $Z < \exp(-\delta H_K/2k_B T)$. We use the grand canonical version of the Monte Carlo method in which the concentrations are not held fixed throughout. With our sign convention, the interaction energies in Fig. 1 correspond to a ferromagnetic type of order, which means, in the alloy context, that they predict a miscibility gap. The time involved in calculating the phase boundary shown in Fig. 2 using the Monte Carlo technique was of the order of one hour of cpu time on a Cray YMP, quite negligible compared to the time required to generate the interchange energies.

Figure 2. Points on the boundary of the miscibility gap in the palladium-rhodium alloy system. The solid diamond shapes are the experimental results of Shield and Williams.¹⁵ The solid circles are the result of Monte Carlo calculations using the interchange energies for all concentrations. The open circles are the result of Monte Carlo calculations using only the interchange energies for the 50% alloy.

It can be seen from Fig. 2 that the difference between the boundary of the miscibility gap obtained using all the δH_K and the one obtained using just the δH_K corresponding to a 50% alloy is not great, but it is certainly worth the extra effort. Putting in the concentration dependence of the δH_K narrows the gap. The miscibility gap calculated with the 50% δH_K has its highest point at about $C_{Rh} = 0.38$, and this asymmetry arises from the fact that, although the average of the δH_K is zero, the shape of the curve shown in Fig. 1 is not symmetrical about zero. The miscibility gap calculated with all the δH_K has its highest point at $C_{Rh} = 0.42$, so the asymmetry is reduced. The highest temperature of the gap is slightly above 1,260 °Kelvin, while the highest experimental number measured¹⁵ is 1,188 °Kelvin. This must be considered very good agreement. The

experiment seems to show an asymmetry that puts the highest point of the curve in the rhodium-rich part of the phase diagram, in contradiction to the calculation. This will be discussed later.

The interchange energies for a 50% copper-nickel alloy are shown in Fig. 3. This alloy system also has the fcc lattice, so there are 144 energies on this drawing. Several points can be seen immediately from this figure. The magnitudes of the δH_K are smaller than the Pd-Rh values by almost a factor of four, which should translate into a much smaller transition temperature. The spread in the δH_K for a given number of nickel atom in the nn shell is much greater than for Pd-Rh, and the curve of δH_K versus n_{Ni} does not resemble a straight line. Thus, the interactions are not Ising-like at all.

Figure 3. The interchange energies δH_K for a 50% copper-nickel alloy expressed in degrees Kelvin plotted against the number of nickel atoms in the nearest-neighbor shell.

The boundary of the miscibility gap in the copper-nickel alloy system calculated with these δH_K is shown in Fig. 4. As expected, the highest transition temperature is a little over 320 °Kelvin, and the miscibility gap is quite asymmetrical. The highest point on the curve is at $C_{Ni} = 0.8$. The asymmetry is in good agreement with the phase diagram reported in the literature,¹⁶ but they report a transition temperature at the highest point of 595 °Kelvin. Later measurements¹⁷ and predictions based on inverse Monte Carlo calculations¹⁸ suggest a much lower value of 495 °Kelvin. Even later measurements with an atom-probe field-ion microscope indicate¹⁹ a still lower transition temperature of 400 °Kelvin. Our results on Cu-Ni must be considered preliminary because we have not yet calculated the interchange energies for different concentrations of the alloy, but they seem to be giving reasonably good results.

Figure 4. Points on the boundary of the miscibility gap in the copper-nickel alloy system.

DISCUSSION

It has been shown that a conceptually simple and computationally straight-forward procedure based on the KKR-CPA, the ECM, and the Monte Carlo method leads to remarkably detailed predictions for solid-solid phase boundaries in real alloy phase diagrams. It happens that the systems that were convenient for us to study at this stage show ferromagnetic-type ordering that leads to a miscibility gap, but the method will work equally well for antiferromagnetic ordering that will lead to the appearance of intermetallic compounds like CuAu and Cu_3Au . We have already seen this in our tight-binding work, where we have gotten results similar to that of Sluiter and Turchi¹⁰ on their 9-3 alloy model.

Other first principles calculations have been done on the palladium-rhodium system. Nicholson, Gyorffy, and Stocks²⁰ used the density functional approach¹¹ to find a phase boundary. Calculations with the GPM and the cluster variational method (CVM) for statistical mechanics were performed on Pd-Rh, along with a mean-field calculation.²¹ All of these calculations lead to a transition temperature at the highest point of the miscibility gap that is considerably higher than ours, approximately 1,600 °Kelvin. This can be explained to some extent by the observation that all of them use cruder approximations for the entropy than the Monte Carlo method. Monte Carlo and CVM calculations on simple Ising models have been compared,²² and the CVM gives higher transition temperatures. An interesting aspect of these calculations is that they all predict that the highest point on the miscibility gap should be on the palladium rich side, to an even greater degree than our direct Monte Carlo calculations. If we continue to predict that the asymmetry of the miscibility gap is different from experiment as we improve the direct Monte Carlo method, it might be that experimentalists should look again at the phase boundary.

We are not aware of other first-principles calculations on copper-nickel. The inverse Monte Carlo is a calculation,¹⁸ but it uses interatomic potentials from experiment. The predictions that we make for this case should also serve as an encouragement to experimentalists to nail down this phase boundary more definitely.

One of the exciting things about the direct Monte Carlo method described here is that there are so many ways that it can be improved. The first thing that should be done is to make all the calculations semi-relativistic. This might have some effect on Pd-Rh. The next thing is to go beyond the frozen potential approximation for the interchange energies. It would not require very much more time to calculate the energies in the Harris approximation.²³ On a somewhat longer time scale, the method can be generalized to include changes in the atomic charges and also the movement of the atoms off their lattice sites.

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