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# Theoretical Study on the Phase Stability of Au−Pd System

Satoshi TAKIZAWA

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**Abstract**

Combining the electronic structure calculation and Cluster Variation Method, we study the phase stability of the Au−Pd system from the first-principles. Because of the small size mismatch between the constituents, the calculated mixing heats of formation agree well with the experimental results.

## 1. Introduction

There are several attempts for drawing the alloy phase diagrams [1, 2] from first-principles, *i.e.*, without any parameter fitted to the experimental results. Most of such approaches consist of two independent steps. The first one is the electronic structure calculation based on the local density approximation in the density functional formalizm [3] which gives us the total energy of the system with a given atomic configuration and the second one is the method in the statistical mechanics with which one can obtain thermodynamical quantities such as the entropy at finite temperatures, the order−disorder transition temperature and so on. In both parts we may have several different approaches: for the total energy calculation, one may adopt the coherent potential approximation (CPA) [4] and generalized perturbation method (GPM) [5] which deal with random alloys, or supercell band calculations for ordered alloys. On the other hand, the cluster variation method (CVM) [6] and the Monte Carlo simulation [7] are frequently used as a method of statistical mechanics. Although there remains problems in the quantitative aspects, most of the qualitatively important features in the phase diagrams were reproduced for noble-metal alloys [1].

In this article, we will try to draw a phase diagram for the Au−Pd system from the first-principles. Au and Pd make an isostructural alloy system, namely, their random alloys have the f.c.c. structure over the whole range of concentrations as well as both of the constituent metals. Furthermore, they undergo order−disorder transitions at the stoichiometries of 3 : 1, 1 : 1 and 1 : 3, and form ordered compounds with the $L1_0$ and $L1_2$ structures (Fig. 1). These ordered structures are also based on the f.c.c. lattice. This system has a favorable feature for our preliminary calculation because the experimental phase diagram is rather simple and it shows a typical order−disorder transition. We use the augmented-spherical

Department of Metallurgical Engineering, Faculty of Engineering, Hokkaido University

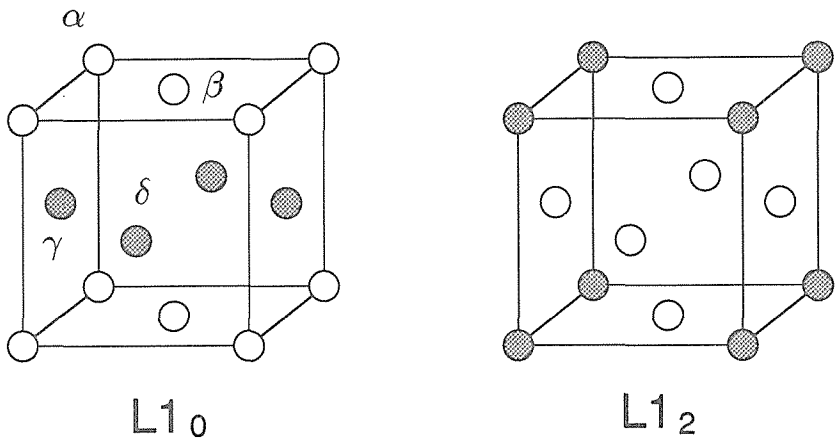


**Fig. 1** The two ordered structures and the four sublattices based on the f.c.c. lattice. The shaded and open circles represent A and B atom, respectively.

wave (ASW) [8] method as the electronic structure calculation and the CVM as the technique in statistical mechanics. For the estimation of internal energy and entropy, the tetrahedron approximation was employed both in the cluster expansion of the internal energy [9] and in the CVM, which is regarded as a minimum meaningful approximation in a discussion of f.c.c.-based systems.

Before beginning the discussions, we would like to make a comment on the use of the ASW method. The structural energy difference of noble metals is very small and electronic structure calculations erroneously predict the b.c.c. structure as the ground state crystal structure [10]. So one may think that we should use more precise method than the ASW. The reasons why we adopt this method are, firstly, its calculational efficiency and, secondly, the expectation that the systematic error cancels as we deal only f.c.c.-based structures in this research. The result seems to be fine even with the ASW method used.

## 2. Methods of Calculation

Since the procedure for the electronic structure calculation has been amply demonstrated in the previous publications, the main emphasis of the present section is placed on the CVM. In this section we will describe the CVM applied to a discussion of the phase stability in f.c.c.-based binary alloys which consist of two kinds of atoms, A and B, and derive the expression for the free energy at finite temperatures.

In the discussion of the relative stability among different phases one needs to know the free energy of the system at finite temperatures. Without any interatomic interactions between the atoms, the free energy of a random system per atom can be written as

$$\frac{F}{N}=\epsilon_A\cdot x_A+\epsilon_B\cdot x_B+kT\,(x_A\ln x_A+x_B\ln x_B)\,. \tag{1}$$

Here $N$, $\epsilon_i$ and $x_i$ represent the number of atoms in the system, the energy and the concentration of the atom $i$ (=A or B), respectively. But in this model the information of the interatomic correlation is not taken into account. In order to take the interatomic interac-

tions into account properly, it is necessary to introduce pair probabilities $\{x_{ij}\}$ and pairwise interactions $\{\epsilon_{ij}\}$ and to write the free energy as a function of $\{x_{ij}\}$ and $\{\epsilon_{ij}\}$. This problem is theoretically equivalent with the Ising-spin model and the exact solutions for 3-dimensional systems are not known even for the simplest case, *i.e.*, a simple cubic lattice with only nearest neighbor interactions. The CVM is a method to obtain an approximate solution for this problem.

### 2. 1 Sublattices and Cluster Probability Variables

In order to deal with ordered phases which are observed in experiment we introduce four sublattices, $\alpha$, $\beta$, $\gamma$ and $\delta$ (Fig. 1). In the completely random phase all sublattices are equivalent and are occupied by A or B atoms with the probabilities propotional to their concentration. But below the transition temperature these sublattices are not equivalent any more and the system changes to a low symmetry state. For example in the $L1_0$ structure two of the four sublattices, say, the $\alpha$ and $\beta$ sites are equivalent and differentiated from the $\gamma$ and $\delta$ sites which are equivalent between them, while in the $L1_2$ structure three of the four become equivalent.

Now we consider tetrahedra which are obtained by connecting the nearest neighbor atoms in the f.c.c. fundamental lattice. Every tetrahedron contains all kinds of sublattice sites. We define the probability variables $x_{ijkl}$ as the probability of finding a tetrahedron with an $i$ atom on its $\alpha$ site, $j$ on $\beta$, k on $\gamma$ and $l$ on $\delta$, respectively. $x_{ijkl}$ has to satisfy the normalization condition

$$\sum_{i,j,k,l=\mathrm{A\ or\ B}} x_{ijkl}=1 . \tag{2}$$

The pair and point probability variables can be obtained from $\{x_{ijkl}\}$ by a contraction;

$$x_{\alpha\beta,ij}=\sum_{k,l=\mathrm{A\ or\ B}} x_{ijkl} , \tag{3}$$

$$x_{\alpha,i}=\sum_{j,k,l=\mathrm{A\ or\ B}} x_{ijkl} . \tag{4}$$

Here $x_{\alpha\beta,ij}$ represents the probability of finding a pair which has an $i$ atom on the $\alpha$ site and a $j$ on $\beta$ and $x_{\alpha,i}$ the ratio of the $\alpha$ site which is occupied by an $i$ atom. When the system consists of $N$ atoms, it contains $2N$ tetrahedron clusters, $6N$ pair clusters and $N$ point clusters. Therefore, the number of the $i-j$ pairs on the $\alpha-\beta$ sublattices will become $Nx_{\alpha\beta,ij}$ and so on.

### 2. 2 Internal Energy

What we have to do next is to express the internal energy of a system with an arbitrary atomic configuration as a function of the cluster variables $\{x_{ijkl}\}$ defined above. We assume that the internal energy of the system can be written as a sum of the energy of tetrahedra;

$$E=\sum_{i,j,k,l=\mathrm{A\ or\ B}} \epsilon_{ijkl}\cdot x_{ijkl} , \tag{5}$$

where $\epsilon_{ijkl}$ represents the energy of tetrahedra with an $i$ atom on the $\alpha$ site, $j$ on $\beta$ and so on. It is natural to think that the energy of a tetrahedron does not depend on the configuration of atoms in the tetrahedron since all the four vertices are geometrically equivalent in the tetrahedron cluster:

$$\epsilon_{AAAB}=\epsilon_{AABA}=\epsilon_{ABAA}\cdots. \tag{6}$$

We will further assume that the energy of the clusters is simply estimated by the formation energy of the five ordered crystals, *i.e.*, A and B with the f.c.c. structure, $A_3B$ and $AB_3$ with the $L1_2$ structure and AB with the $L1_0$ structure, because each of these five ordered structures consists of only one kind of clusters.

The formation energies $\Delta E(a)$ are obtained with the ASW method and are expressed as a function of the lattice constant of the fundamental f.c.c. lattice, $a$, in order to count the elastic contributions due to the volume mismatch.† The energies were measured from the segregation limit which is the energy of the system in case that the constituent atoms exist apart in elemental solids. In the total energy calculation the relativistic effects except the spin-orbit interaction was included following the prescription proposed by Koelling and Harmon [11] and the exchange-correlation potential of Moruzzi *et al.* [12] was used. The maximum angular momentum of the augmented-spherical waves were taken to be $l=2$ for Pd and $l=3$ for Au in order to attain better agreement for the equilibrium lattice constants of pure metals with experiment.

### 2.3 Entropy

The configurational entropy can be obtained from the number of states. So we should count the number of different arrangements specified by a set of $\{x_{ijkl}\}$. First we consider the number of different arrangements of tetrahedra which is given as

$$W_4=\frac{(2N)!}{\prod_{i,j,k,l=\mathrm{A\ or\ B}}(2Nx_{ijkl})!}\ . \tag{7}$$

In $W_4$, however, we have "inconsistent" arrangements in which, for example, A−A and B−B pairs meet at the same place. Therefore we have to make a correction to $W_4$. Since two tetrahedra share one edge in an f.c.c. lattice, the probability of finding "consistent" pairs at one edge shared by two tetrahedra is $(x_{\sigma\tau,ij})^2$. The probability that all the pair clusters in the whole system are consistent is

$$C_{4-2}=\prod_{\sigma>\tau,ij}\{(x_{\sigma\tau,ij})^{2\cdot Nx_{\sigma\tau,ij}}\}\ . \tag{8}$$

As the number of arrangements of pair clusters is

$$W_2=\prod_{\sigma>\tau}\frac{N!}{\prod_{i,j}(Nx_{\sigma\tau,ij})!}\ , \tag{9}$$

†It is important to include the effect of volume mismatch in a study of the phase stability of alloys. See for example Ref. [13]

we obtain the correction term due to the consistency of pairs

$$C_2=\prod_{\sigma>\tau}\left\{N!\times\prod_{i,j}\frac{(x_{\sigma\tau,ij})^{2Nx_{\sigma\tau,ij}}}{(Nx_{\sigma\tau,ij})!}\right\}. \tag{10}$$

Similarly, the probabilities of finding a consistent points at a vertex of tetrahedra and pairs are given by $(x_{\sigma,i})^8$ and $(x_{\sigma,i})^{12}$, respectively. Thus in the whole system the corrections are

$$C_{4-1}=\prod_{\sigma,i}(x_{\sigma,i})^{8\cdot(N/4)x_{\sigma,i}} \tag{11}$$

$$C_{2-1}=\prod_{\sigma,i}(x_{\sigma,i})^{12\cdot(N/4)x_{\sigma,i}}. \tag{12}$$

Because we have

$$W_1=\prod_{\sigma}\frac{(N/4)!}{\prod_i\{(N/4)x_{\sigma,i}\}!} \tag{13}$$

as the number of the arrangements of points, the correction due to the consistency of points is

$$C_1=\prod_{\sigma}\left\{(N/4)!\times\prod_i\frac{(x_{\sigma,i})^{5Nx_{\sigma,i}}}{[(N/4)x_{\sigma,i}]!}\right\}. \tag{14}$$

So far, we treated the corrections due to the consistency of pairs and points independently. But as there is no inconsistency within a tetrahedron cluster, it is over-corrected. This correction to the over-correction is

$$C'=\{\prod_{\sigma,i}(x_{\sigma,i})^3\}^{2N}. \tag{15}$$

Collecting the terms discussed above, we have as the statistical weight,

$$W\{x_{ijkl}\}=\frac{W_4C_2C_1}{C'} \tag{16}$$

and as the configurational entropy

$$\begin{aligned}S\{x_{ijkl}\}&=k\ln W\\&=Nk\left[-2\sum_{ijkl}x_{ijkl}\ln x_{ijkl}+\sum_{\sigma\tau,ij}x_{\sigma\tau,ij}\ln x_{\sigma\tau,ij}-\frac{5}{4}\sum_{\sigma,i}x_{\alpha,i}\ln x_{\alpha,i}\right].\end{aligned} \tag{17}$$

### 2.4 Free Energy

Now the expression of the free energy can be obtained by combining the results derived above;

$$\begin{aligned}\frac{F}{N}&=\frac{E-TS}{N}\\&=\sum_{i,j,k,l}\epsilon_{ijkl}x_{ijkl}\\&\quad+kT\left[-2\sum_{ijkl}x_{ijkl}\ln x_{ijkl}+\sum_{\sigma\tau,ij}\ln x_{\sigma\tau,ij}-\frac{5}{4}\sum_{\sigma,i}x_{\sigma,i}\ln x_{\sigma,i}\right].\end{aligned} \tag{18}$$

An equilibrium state under a set of given temperature and symmetry can be obtained by minimizing the free energy, with respect to $\{x_{ijkl}\}$ as well as a lattice constant. (Note that our expansion for the internal energy is volume dependent). The phase boundary can be determined by introducing chemical potential and by finding a crossover point between the ground potential curves of two different phases specified by equivalent sublattices.

## 3 Results and Discussions

The mixing heat of formation of the Au−Pd system at 298K was calculated for the random alloy [14] and compared with the result of an experiment [15] and it is shown in Fig. 2. In this figure, the solid and broken line represent the calculated and experimental mixing heats of formation, respectively. The formation enthalpies for the ordered compounds are also shown in this figure by open circles. The two curves agree excellently in spite of the simple approximation assumed in the calculation.

We think that this agreement is not an accidental one but reflecting the fortunate condition for the approximation. Firstly, the Au−Pd system shows the sequence of ordered structures $L1_2-L1_0-L1_2$ (with some uncertainty, however) in the experiment which is compatible with the present theoretical framework. Secondly, the volume mismatch between constituent atoms is small for this system: the atomic sphere radii at the equilibrium volumes for Au and Pd are 3.01Bohr and 2.89Bohr, respectively, and the resulting elastic energy at the equiatomic stoichiometry is 2.5mRy per atom, which is estimated as a sum of the elastic energy of two constituent metals with a lattice constant at the equiatomic composition, while, for example, the corresponding quantity for the Cu−Au system is 21.3mRy per atom. The volume mismatch causes local distortions of the crystal in order to relax energy for the random alloy and this effect is not included in the theoretical framework. For this system, however, this effect will be small and therefore our approach will be expected to work fairy well. Finally, the estimation of the internal energy as a sum of the energy of tetrahedra seems to be a relatively good approximation for this system: The estimated formation energy for the $L1_1$ structure is −5.3mRy per atom, while the value

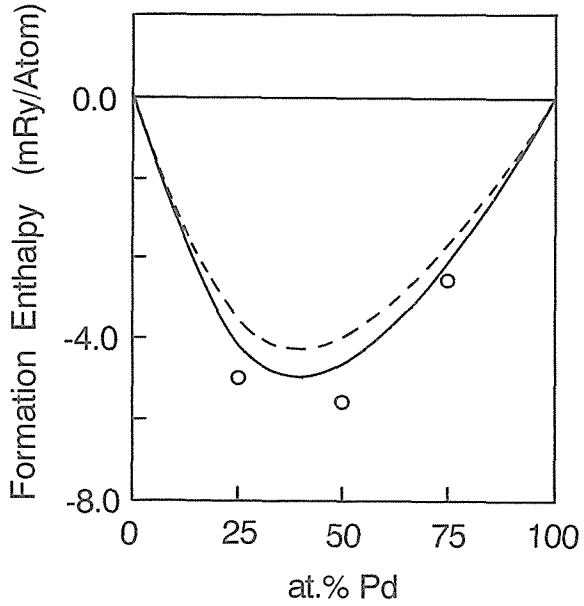


**Fig. 2** The mixing enthalpies for the Au−Pd random alloys.

obtained directly from the band structure calculation is −7.0mRy per atom. In the case of Cu−Au system the corresponding values are 0.90mRy per atom and 3.36mRy per atom. Note that this discrepancy between the energies of the hypothetical and real $L1_1$ should not be related with the elastic effect because there is little volume difference between the hypothetical and real $L1_1$ structures for both of the Cu−Au and Au−Pd system.

Encouraged by the good agreement of the mixing enthalpy, we proceed to an attempt for drawing a theoretical phase diagram. The resultant phase diagram as well as the experimental one is shown in Fig. 3. Although the mixing enthalpy was reproduced fairly well, the

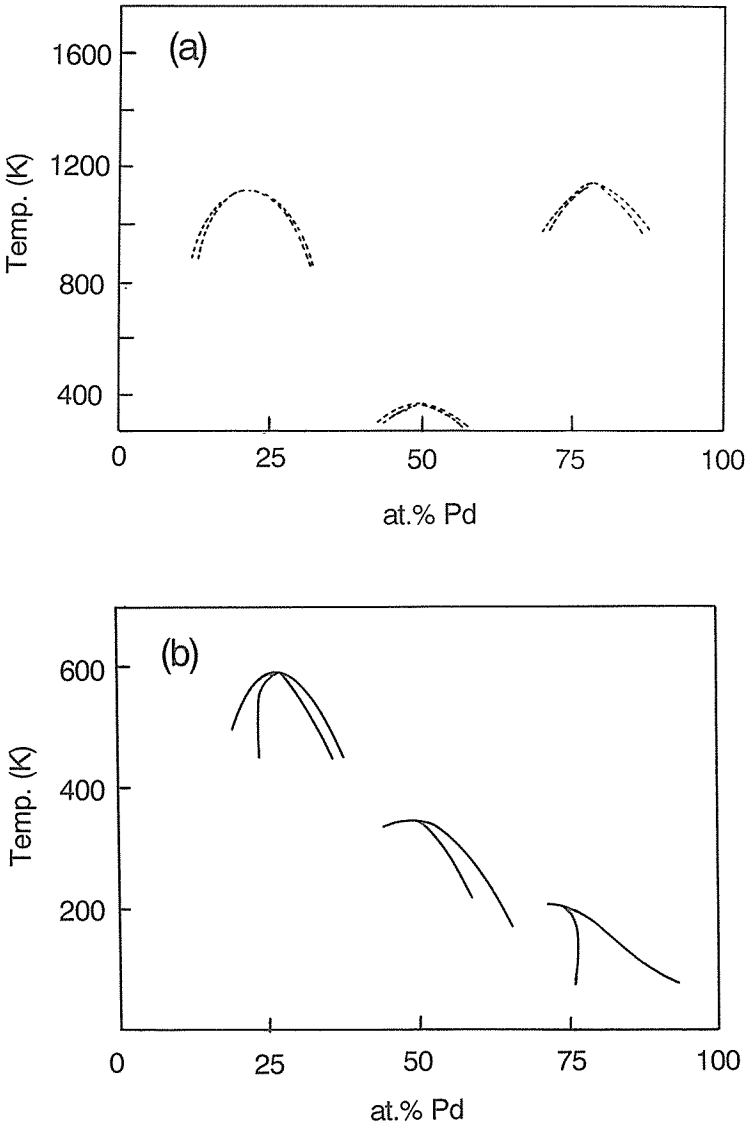


**Fig. 3** The experimental (a) and theoretical (b) phase diagram of the Au−Pd system.

theoretical phase diagram has a completely different appearance from the experimental one [16]. In the experiment the order−disorder transition temperature in the vicinity of equiatomic composition is reported to be much lower than that of the $L1_2$ compounds, $Au_3Pd$ and $AuPd_3$, while in our result the transition temperatures at three stoichiometries, 1 : 3, 1 : 1 and 3 : 1, are nearly the same order. In a naïve speculation the transition temperature is likely to be higher at the 1 : 1 stoichiometry than the other, because the number of unlike atoms pair is the largest in the $L1_0$ structure. (If the interatomic interaction is a compound formation type, each atom in the system will sit on a site with neighboring unlike atoms.) Therefore it is expected that the transition temperature will not be so small at the equiatomic stoichiometry compared with other stoichiometries. Considering that there are some controversial results in different experiments† and that the calculation can reproduce the qualitative aspect of the phase stability, we think that the existing phase diagrams should be re-examined carefully, although our calculational method is not fully reliable to discuss the order−disorder transition temperature so accurately.

## 4 Acknowledgements

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†Nagasawa (17) reported that the critical temperature for the $L1_0$−disorder transition is about 650-700K, while Okamoto and Massalski (18) indicates about 380K.

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