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Phenomenological Calculation of $L1_0$-disorder Transition Temperature in an Au-Pd System

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Abstract

A phenomenological calculation based on the tetrahedron approximation of the Cluster Variation Method with a Lennard-Jones type energy expression is performed to calculate the transition temperature of $L1_0$-disorder phases in an Au-Pd system. The transition temperatures are placed between 300K-350K depending upon the two kinds of Lennard-Jones parameters employed. The origin of the discrepancy between the present calculation and experimental phase diagrams in discussed.

1. Introduction

A phenomenological calculation of a phase diagram by utilizing the Cluster Variation Method [1] (hereafter abbreviated as CVM) with a phenomenological energy expression which is obtained by fitting the thermodynamic experimental data to an assigned potential has been recognized as a powerful means to investigate thermodynamic properties of a material. Among the various phenomenological schemes, the one that utilizes the Lennard-Jones type potential has been applied to various calculations of thermodynamic properties as well as phase diagrams. In fact, the thermodynamic properties of Cu-Au disorder phase [2] and the phase boundaries of γ/γ' of Ni_3Al [3] were reproduced with a high accuracy. On the other hand, the limit of the applicability has been recently realized by the calculation of an entire phase diagram of the Cu-Au system. [4, 5] The transition temperatures estimated for the characteristic three ordered phases are quite high as compared with the experimental phase diagram. The shortcoming, however, is originates neither in the Lennard-Jones potential nor from the current level of entropy expression based on the tetrahedron cluster, but is mainly caused by the neglect of the local lattice relaxation process for a system having a large difference in atomic size, by which the internal energy of the disorder phase becomes unrealistically high leading to the overstabilization of the order phases. This is the common fault of the thermodynamic model in which the atomic interaction energies are assigned to a uniformly deformable lattice as a function of the lattice parameter. In fact, more elaborate first-principles calculation also shares this inconvenience. [7] In order to avoid this shortcoming, therefore, it is deemed indispensable either to evaluate the elastic energy rigorously so that spatial inhomogenuity of atomic distance can be taken into accouunt, which is by far more tractable in general cases, or to avoid the systems in which constituents have large

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differences in atomic size.

Most of the CVM works for fcc based lattice, so far, have been centred around the tetrahedron approximation of which applicability is, in a rigorous sense, limited to the $L1_0$ or $L1_2$ ordered phases. [6] This is because only the nearest neighbor pair interaction can be incorporated into the tetrahedron cluster and, moreover among the various ordered phases stabilized by positive effective pair interaction, the degeneracy is lifted toward $L1_0$ and $L1_2$ phases due to higher symmetry. Cu-Au system is a typical system which undergoes $L1_0$ and $L1_2$ phase transition, and numerous CVM work based on the tetrahedron approximation has been advanced for this system. [4, 5, 7, 8] In contrast, quite few theoretical work has been performed on Au-Pd system [9] which is also characterized by $L1_0$ and $L1_2$ ordered phases. As is shown in Fig. 1, the two experimental phase diagrams for Au-Pd obtained by separate groups [10, 11] do not show a good agreement, especially for $L1_0$-disorder transition the two phase boundaries are far away. The main purpose motivated in this study is to examine the $L1_0$-disorder transition temperature of Au-Pd system from the theoretical point of view based on the tetrahedron approximation of the CVM with Lennard-Jones potential. Since Au and Pd have a similar atomic size, the anticipated error described above may be safely avoided.

The organization of this paper is as follows: In the next section, the outline of the phenomelogical calculation is briefly reviewed and the calculated Lennard-Jones type potentials are presented. In the third section, the obtained phase boundaries and other thermodynamic properties are demonstrated, and a discussion follows.

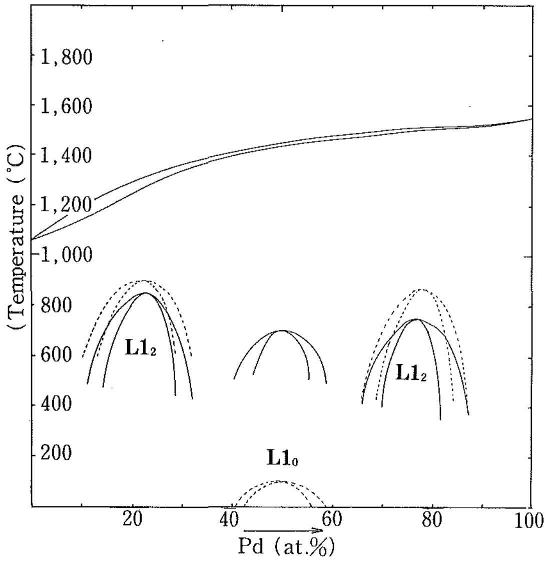

Fig. 1 Experimental Phase diagram of Au-Pd system. The horizontal axis is the atomic concentration of Pd. The solid lines are determined by Nagasawa et al. [10] and broken lines are cited from Okamoto et at. [11]

2. Calculation Procedure and the Lennard-Jones type potential

Within a framework of the tetrahedron approximation of the CVM with the nearest neighbor pair interaction energy, the free energy functional of a system is formally written as [3]

$$F=\frac{1}{2}qN\sum_{ij}e_{ij}(r)y_{ij}+k_BT\cdot S(x_i^{(\alpha)},\ y_{ij}^{(\alpha\beta)},\ z_{ijk}^{(\alpha\beta\gamma)},\ w_{ijkl}^{(\alpha\beta\gamma\delta)}) \qquad (1)$$

where q is the coordination number, N the total lattice points, e_{ij} is the pair iteraction energy between i and j atoms at distance r, $x_i^{(\alpha)}$, $y_{ij}^{(\alpha\beta)}$, $z_{ijk}^{(\alpha\beta\gamma)}$ and $w_{ijkl}^{(\alpha\beta\gamma\delta)}$ are, respectively, the probability of finding atomic configurations specified by subscripts on a sublattice specified by superscripts. These probabilities are termed state variables. The equilibrium state of the system can be obtained by minimizing the free energy functional F with respect to both state variables and atomic distance at a given temperature T. This two-fold minimization procedure is necessary to introduce the concentration dependency into the pair interaction energy through the dependency of a lattice parameter on a concentration. The pair interaction energy $e_{ij}(r)$ is, as is described in the previous section, assigned by Lennard-Jones type potential in the following manner.

The Lennard-Jones type potential for a condensed system can be given as the sum of repulsive and attractive interaction potentials. The former becomes dominant as the two atoms come close together, while the latter becomes significant as the two atoms are separated away, and the equilibrium atomic distance is determined by the competition of the two forces. Then, the potential energy depends on an atomic distance r and is generally written as

$$e_{ij}(r)=e_{ij}^0\left\{\left(\frac{r_{ij}}{r}\right)^m-\left(\frac{m}{n}\right)\left(\frac{r_{ij}}{r}\right)^n\right\} \qquad (2)$$

where i and j represent the atomic species, r_{ij} and e_{ij}^0 are termed the Lennard-Jones parameter, and 8 and 4 are generally assigned to m and n as the optimum exponent for metallic systems. [3] Given a binary system, prior to the minimization process of the functional F, six unknown parameters e_{ii}^0, e_{jj}^0, e_{ij}^0, r_{ii}, r_{jj} and r_{ij} should be determined in order to express the internal energy E(r) in the manner given in the eq. (1) ;

$$E(r)=\frac{1}{2}qN\sum_{ij}e_{ij}(r)y_{ij} \qquad (3)$$

Although, as described above, the pair probability y_{ij} is a variational parameter by which the free energy functional is minimized, for a pure metal and stoichiometric ordered compound at an equilibrium state the atomic arrangements are uniquely fixed and, therefore, the Y_{ij} 's can be given *a pri•o'ri*. Also, at the equilibrium atomic distance E(r) should be minimum, which leads to the following condition

$$\left(\frac{dE(r)}{dr}\right)_{r=a}=0 \qquad (4)$$

where a is the equilibrium lattice parameter. Then, the Lennard-Jones type potential can be determined by utilizing the experimental data of cohesive energies, heats of formation and lattice parameters of pure elements and a stoichiometric ordered compound in the mold of eqs. (3) and (4) with particular y_{ij} values for each substance. This procedure, however, does not fix the parameter uniquely for a system which contains more than two

Table 1 The calculated Lennard-Jones parameter and employed experimental data of cohesive energies (pure Au and Pd), heat of formation (AuPd) and lattice constants.

Lennard-Jones Parameter (normalized by equil. e_{AuAu} and r_{AuAu})		Cohesive Energy, heat of formation (cal/mol)		Lattice Constant (Å)
e^0_{AuAu}	1.000	Au	−87,300	4.0785
r_{AuAu}	1.000			
e^0_{AuPd}	1.019	AuPd	−87,675	3.9805
r_{AuPd}	0.974			
e^0_{PdPd}	0.966	Pd	−84,330	3.8907
r_{PdPd}	0.954			

intermetallic ordered compounds. Since a self-consistent procedure to assure the uniqueness has not been found as yet, it is considerd to be reasonable to utilize the experimental data of the intermetallic compound which is situated most closely to the concentration of interest. In this study, $L1_0$ ordered compound, of which y_{ij} 's are given as

$$\left.\begin{aligned} y_{ii}=y_{jj}=\frac{1}{6} \\ y_{ij}=\frac{2}{3} \end{aligned}\right\} \tag{5}$$

are adopted, and the Lennard-Jones potentials are expressed as [3, 15]

$$e^0_{ii}=-\frac{2}{q}E_i \tag{6}$$

$$r_{ii}=\frac{a_i}{\sqrt{2}} \tag{7}$$

$$e^0_{ij}=-\frac{1}{2q}\frac{[6E_M-E_i\Delta_3^4-E_j\Delta_4^4]^2}{[6E_M-E_i\Delta_3^8-E_j\Delta_4^8]} \tag{8}$$

and

$$r_{ij}=\frac{a_M}{\sqrt{2}}\left[\frac{6E_M-E_i\Delta_3^8-E_j\Delta_4^8}{6E_M-E_i\Delta_3^4-E_j\Delta_4^4}\right]^{1/4} \tag{9}$$

where E_i (E_j) the cohesive energy of, a pure element i (j), E_M the heat of formtion of $L1_0$ stoichiometric ordered compound, a_i (a_j) and a_M the lattice paramenter of the pure metal i (j) and the ordered compound, respectively, and Δ_3 and Δ_4 are defined as

$$\Delta_3=\frac{a_i}{a_M} \tag{10}$$

and

$$\Delta_4=\frac{a_j}{a_M} \tag{11}$$

For the Au-Pd system, available thermodynamic data are limited to the measurement of heat of formation by Darby [12] and the lattice parameter by Maeland et al. [13], which are both carried out at 298K. Shown in Fig. 2 by a solid line is the employed heats of formation data of Darby from which one can estimate −87,675 (cal/mol) for the heat of formation at 50 at. %. The obtained parameters together with employed ther-

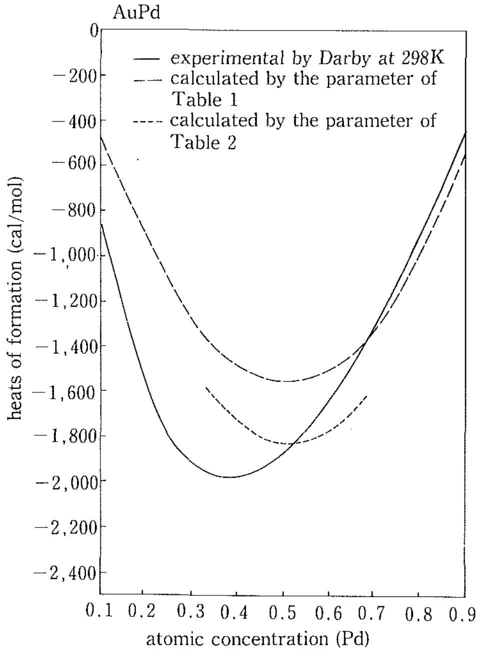

Fig. 2 The heat of mixing of Au-Pd at 298K. The solid line is experimental measurement by Darby[12], broken line and dotted line are calculated results by using the Lennard-Jones potential tabulated in Table 1 and 2, respectively.

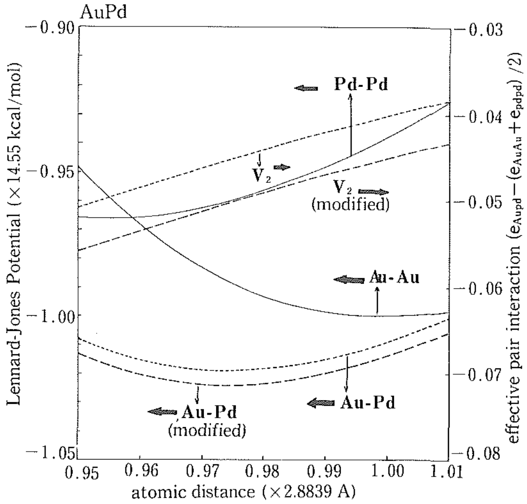

Fig. 3 The calculated Lennard-Jones potential as a function of atomic distance. Both vertical and horizontal axes are normalized by cohesive energy (14.55kcal/mol) and equilibrium nearest neighbor atomic distance (2.8839 Å) of pure Au. Solid lines indicate Pd-Pd and Au-Au pair potentials. Dotted and broken curves shown lower part in the figure are Au-Pd pair potentials. The former is obtained by utilizing the thermodynamic data at 298K, while the latter is obtained by the procedure described in the manuscript. The dotted and broken lines shown in the upper part of the figure are nearest neighbor effective pair potentials. The indication of dotted and broken lines are the same with pair potentials mentioned above.

modynamic data are tabulated in Table 1 and a magnified view of the calculated Lennard-Jones potential is shown in Fig. 3. The vertical axis and horizontal axis are, respectively, normalized by the equilibrium values of e_{AuAu} and r_{AuAu}. As indicated in the figure, the Au-Au and Pd-Pd potentials are drawn by solid lines and the Au-Pd potential is given by a dotted line. Furthermore, in order to manifest the ordering tendency, the effective pair interaction energy which is defined by

$$v_2 = e_{ij} - \frac{e_{ii} + e_{jj}}{2} \tag{12}$$

is shown in the figure. The effective pair interaction is negative for entire range of atomic distance, which is a certain indication of the ordering tendency of this system.

The validity of the eq. (5) is limited merely to OK. At higher temperatures, the pair

Table 2 The adjusted Lennard-Jones parameters. The heat of formation and lattice parameter of AuPd(50 at. %) are reversely calculated by using the obtained parameters e^0_{AuPd}, r_{AuPd} and eqs. (8) and (9).

Lennard-Jones Parameter (normalized by equil. e_{AuAu} and r_{AuAu})		heat of formation of AuPd ($L1_0$) (cal/mol)	Lattice Constant of AuPd ($L1_0$) (Å)
e^0_{AuPd}	1.024	−87,939	3.9810
r_{AuPd}	0.974		

probabilities deviate from these values due to the entropy effect. Then, the employment of thermodynamic data at 298K together with the relation (5) is anticipated to induce errors, because this sheme fictitiously regards 298K as OK and shifts the temperature scale. In fact, the recalculated heat of mixing at 298K by including the entropy term which is shown in Fig. 2 by broken line deviates from the original experimental value quite markedly for the entire concentration range. What was attempted in this study to avoid this inconvenience is to optimize the Lennard-Jones parameter in such a way that the resultant heat of formation provides a good fit with experimental one near 50 at. %. It should be noted that the modification is necessary only for e^0_{ij} and r_{ij} because the validity is broken only for eqs. (5), (8) and (9) unless the lattice vibration effect is considered for pure metals. The Parameters which were optimized are tabulated in Table 2 and the calculated heat of mixing is depicted by a dotted line near 50 at. % in Fig. 2. The modified Lennard-Jones potential for Au-Pd pair as well as the effective pair interaction energies are drawn by broken lines in Fig. 3. It can be seen that the effective pair interaction becomes deeper as compared with the previous potential, implying the stabilization of the ordered phase. This modification, on the other hand, reversely fixes the heat of formation and lattice parameter of $L1_0$ ordered compound at OK. The calculation yields −87,939 (cal/mol.) and 3.9810 (Å), respectively, for the heat of formation and lattice constant, which shows reasonable agreement with the first-principles calculation. [14]

3. Results and Discussion

The present scheme, as described in the previous section, demands a two-fold minimization procedure, one with respect to state variables and the other with respect to the atomic distance. Therefore, the optimized lattice parameter can be obtained as a by-product by the latter procedure. Shown in Fig. 4 is the concentration dependency of the calculated lattice parameter at 298K. It can be observed that the agreement with the experimental data of Maeland et al. [13] is excellent for the entire concentration range. It stould be, however, reemphasized that the lattice vibration is not taken into account in the present calculation. Fig. 5 shows the $L1_0$-disorder phase boundary for the two kinds of Lennard-Jones type potentials. The broken line is for the potential (Table 1) which was obtained by using the thermodynamic data of heat of formation at 298K. The solid line is the one for a modified Lennard-Jones potential (Table 2) determined by adjusting the parameters in such a way that the experimental data of heats of mixing at 298K can be well reproduced. As described previously, the former procedure fictitiously regards the

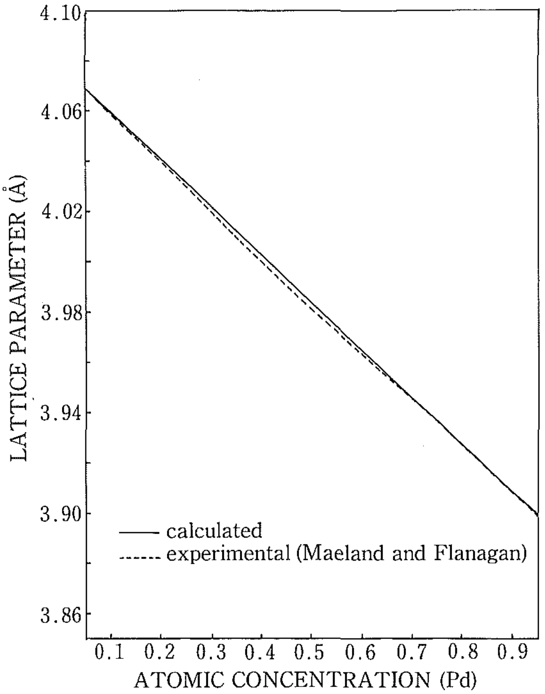

Fig. 4 Concentration dependency of lattice parameter at 298K. The solid and broken lines are, respectively, the present calculation and experimental data by Maeland et al. [13]

298K as OK, which incorrectly underestimates the heat of formation of the $L1_0$ compound by the amount of entropy effect at 298K. The results indicate that the modified potential gives a higher transition temperature, which is reasonable because of the strengthening of unlike pair bonding due to the stabilized heat of formation of the ordered compound. This is also in accordance with the deeper effective pair interaction as shown in Fig. 3. The long range order parameter is defined as the difference of the fractional occupancy of α-sublattice and β-sublattice, and its temperature dependency is demonstrated in the Fig. 6. The result indicates the nature of the transition is strongly first order.

The two potentials were, in a rigorous sense, not quite satisfactory. The former one apparently underestimates the heat of mixing, which understabilizes the order phase. The modified one reproduces experimental data only near equiatomic composition. The cause of the discrepancy should be posed in terms of the type of potential employed. Despite the vast applications of the Lennard-Jones type potential, the validity is not assured for metallic systems. In particular, the descriptions of the cohesive nature of the noble metal, the transition metal and their intermetallic compound by a single potential may not be fully rationalized. Also, the neglect of the tetragonality of AuPd ordered compound may cause the error. However, as far as the $L1_0$-disorder transition temperature is concerned, in view of the excellent agreement of lattice parameter (Fig. 4) and the fairly reasonable reproducibility of the heat of mixing (Fig. 2), the true transition

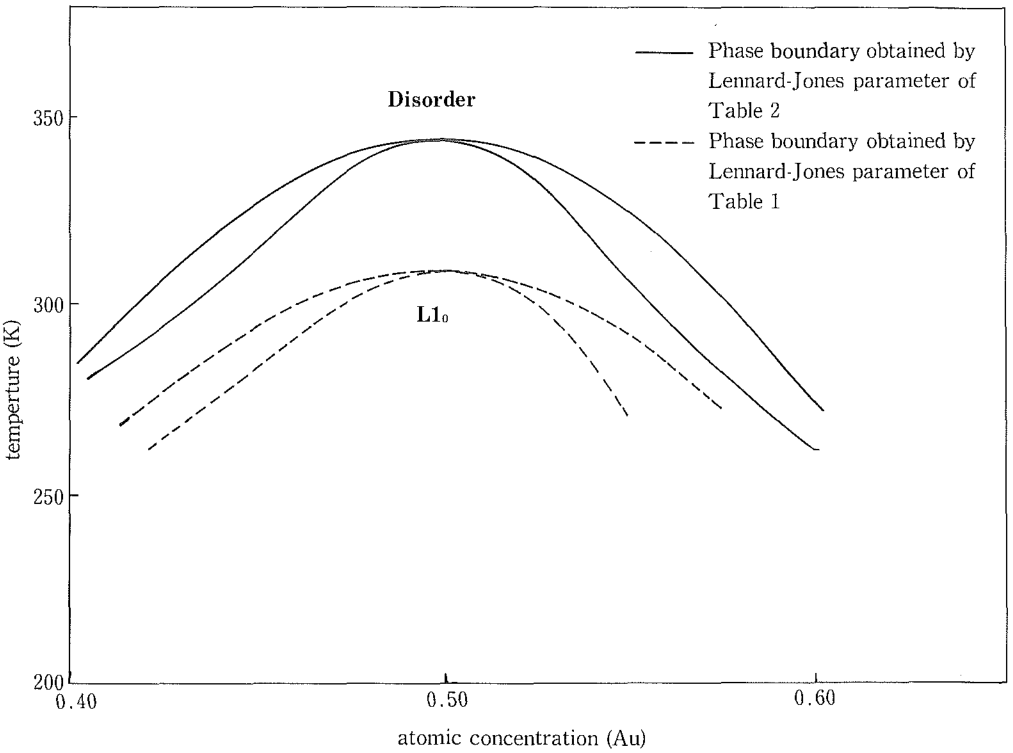

Fig. 5 The phase boundaries between $L1_0$ and disorder phase. The broken line is obtained by the Lennard-Jones potentials tabulated in Table 1, while the solid line corresponds to the Lennard-Jones parameter in Table 2.

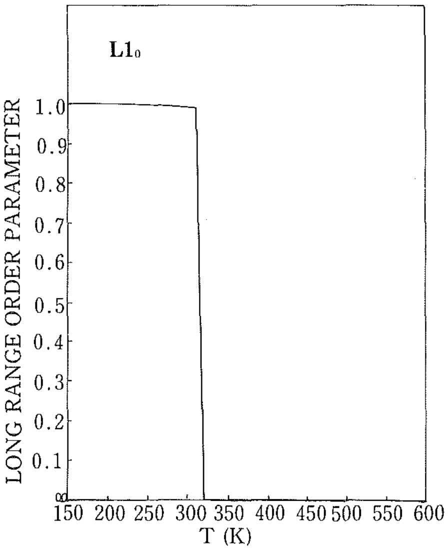

Fig. 6 The temperature dependency of Long Range Order parameter which is defined as the difference of fractional occupancy between α-sublattice and β-sublattice. The figure indicates strongly first order character.

temperature would not be far away from the present result. The abnormal discrepancy can be sought rather as an experimental error. The experiment was performed by a quenching technique rather than by an in-situ method. Then, if the quenching rate is not fast enough, the disorder phase undergoes an order transition giving rise to fictitious superlattice spots. Precise experiments based on in-situ techniques is awaiting.

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