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The phenomenological calculation of a Cu-Au phase diagram with a Lennard-Jones type potential on a uniformly deformable lattice

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Abstract

By using the Lennard-Jones type potential, the phenomenological calculation of the Cu-Au phase diagram was attempted. The phase boundaries of order-disorder transition showed a considerable shift toward higher temperatures over the entire concentration range. The discrepancy is explained in terms of local lattice relaxation.

The phenomenological calculation of thermodynamic properties of alloy phases by using experimental data is one of the powerful approaches to alloy thermodynamics. Sanchez et al. [1] obtained the γ/γ' phase boundaries of Ni-Al system by combining the Cluster Variation Method (hereinafter abbreviated as CVM) with the phenomenological Lennard-Jones type potentials which are extracted from experimental data of heats of formation and lattice parameters of both pure constituents and an ordered compound. We also performed the calculations of the concentration dependency of heat of formation and lattice parameter of disorder phase for the Cu-Au system at 720K [2] based on the same method devised by Sanchez et al. Both calculations were quite satisfactory to achieve an overall agreement with experimental data. The calculations were, however, confined to a limited portion of the entire phase diagram and thermodynamic quantities of a single phase. In order to examine the method more critically, a calculation for an entire phase diagram of the Cu-Au system is attempted.

The Cu-Au system has been attracting wide attention by theorists because of the peculiar topological features of the phase diagram characterized by three ordered compounds. The initial stage of the phase diagram calculations was devoted within a framework of the Ising model with an antiferromagnetic interaction. The Bragg-Williams model [3] and the quasichemical approximation [4] were cleary unsatisfactory for reproducing both topological features of phase boundaries and transition temperatures. The first successful calculation may be attributed to van Baal [5] who applied the tetrahedron approximation of Kikuchi's Cluster Variation Method [6]. According to the ground state analysis of Cahn et al. [7, 8] and Kanamori et al. [9, 10], both the $L1_0$ and $L1_2$ ordered structures are stabilized by the positive first nearest neighbor and the negative second nearest neighbor pair interac-

tions. The tetrahedron approximation, however, incorporates merely the first nearest neighbor pair interaction. In order to lift the degeneracy between $L1_0$ (P4/mmm) and A_2B_2 (I41/amd) at the stoichiometry of 1/2, and that between $L1_2$ (Pm3m) and DO_{22} (I4/mmm) at the stoichiometry of 1/4, the implementation of the second nearest neighbor pair interaction is indispensable. This was achieved by Sanchez et al. [11] based on the higher level of approximation, namely the tetrahedron-octahedron approximation. The introduction of the larger cluster certainly improved the accuracy of the transition temperatures. One can appreciate this by comparing the results with those of Monte Carlo simulation [12, 13] which are deemed to provide the most objective results. These CVM calculations achieved in the mold of Ising model have been termed as "prototype calculations". The serious drawback involved in the prototype calculations, however, is the fact that the resultant phase diagram is completely symmetrical around fifty atomic percent. This inconvenience could be lifted either by introducing the concentration dependency into the pair interaction energies or by adding the many-body interactions. The latter approach was adopted by de Fontaine et al. [14] with the tetrahedron interaction energies, and they achieved an excellent agreement with the experimental phase diagram.

The first approach is more promising to perform further realistic calculations. Since it has been confirmed both theoretically and experimentally that the atomic interactions are largely affected by atomic configurations, it is indispensable to introduce the configurational dependency into the theoretical framework. The phenomenological calculation mentioned above is a tractable method which can incorporate the concentration dependency of the pair interactions through a lattice parameter, and links the prototype calculations with the more elaborate first principles calculation. Among the configration variables, the concentration is the most primitive parameter which provides merely the point probability. And neglecting the contribution of Short Range Order parameters to the interaction energies makes it possible to introduce the Lennard-Jones type potential on a uniformly deformable lattice. Since the details of the calculation procedure have been amply demonstrated in the previous publications[1], we simply provide the potential parameters employed for the present study calculation in the Table 1. These were extracted from the experimental data of the lattice parameters and cohesive energies or heat of formation of pure elements and a Cu_3Au stoichiometric ordered compound[15].

The entire phase diagram calculated is presented in Fig. 1. The temperature dependencies of Long Range Order parameters at a selected stoichiometric composition is shown in Fig. 2 which indicates that the order of the transition is of the first order. At other stoichiometries, the first order transitions are also comfirmed. These are certainly consistent with experimental facts. However, as compared with the experimental phase diagram[16], the phase boundaries are remarkably shifted upward. This serious discrepancy can be explained in the following manner.

Due to the transition from order phase to disorder phase, the number of like atom pairs increases. In the present model, these pairs are arranged on a lattice which deforms uniformly without allowing local lattice relaxation. This implies that the pair interaction

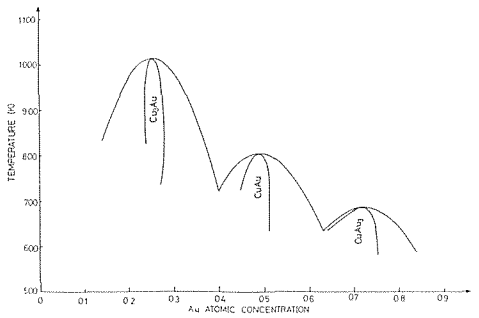

Fig. 1 The Cu-Au phase diagram obtained by phenomenological calculation which constitutes of the tetrahedron approximation of the Cluster Variation Method with the Lennard-Jones type pair potential.

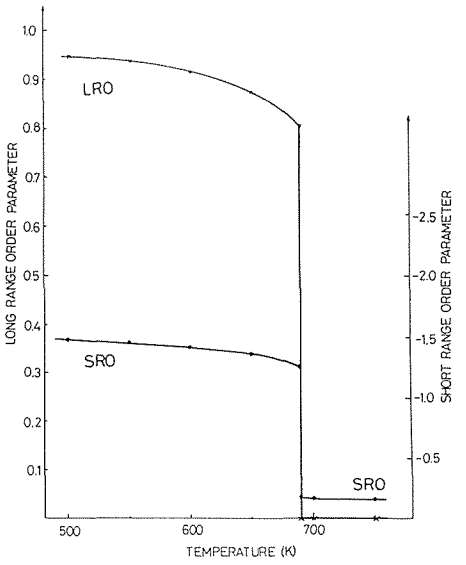

Fig. 2 The calculated temperature dependencies of the Long Range Order parameter and the Short Range Order parameter at $CuAu_3$ stoichiometric composition.
The transition temperature is estimated to be 689K.

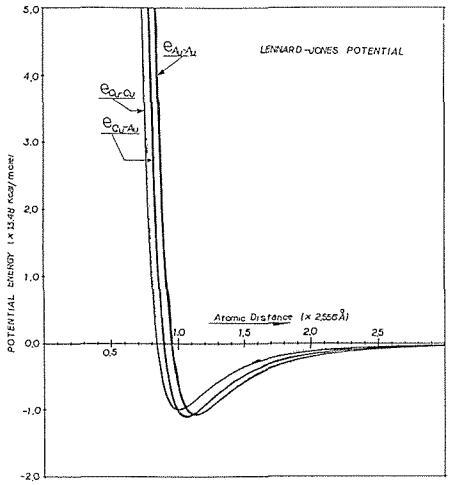

Fig. 3 Lennard-Jones Potential for Cu-Au system. The parameters employed are given in Table 1.

Table 1 The employed Lannard-Jones parameters. e^0_{ij} anb r_{ij} define the Lennard-Jones type potential.

$$e_{ij}(r)=e^0_{ij}\left[\left(\frac{r_{ij}}{r}\right)^8-2\left(\frac{r_{ij}}{r}\right)^4\right],$$

between species i and j at a distance r.

	e^0_{ij} (Kcal/Mole)	r_{ij} (Å)
Cu-Cu	13.48	2.5560
Cu-Au	14.94	2.7061
Au-Au	14.55	2.8839

energies for both Cu-Cu and Au-Au pairs are evaluated at the same atomic distance. Furthermore, the unsymmetrical feature of the Lennard-Jones type potential shown in Fig. 3 indicates that the repulsive interaction has a much sharper dependency on atomic distance. Then, at smaller lattice parameters, the pair interaction energy of larger species is anticipated to increase drastically. For instance, at the Cu_3Au stoichiometry, the Au-Au pair is compelled to have an atomic distance which is far smaller than that of pure Au and slightly larger than that of pure Cu. Accordingly, the increase in the interaction energy of Au-Au pair is drastic, while slight for the Cu-Cu pair. At the CuAu stoichiometry, on the other hand, the interaction energy of Cu-Cu pair is further increased but drastically reduced for the Au-Au pair as compared with the Cu_3Au stoichiometry. These seem to be the major reasons

for the remarkable raise of transition temperatures of the entire phase diagram of which tendency is most emphasized at Cu_3Au stoichiometry.

Several similar inconveniences are experienced in the first principles calculations of the phase diagrams and the thermodynamic properties of Cu-Ag system and Cu-Au system[17, 18]. In the Cu-Ag system, quite narrow solubility limits resulted, while in the Cu-Au system, in addition to the raise of phase boundary, a considerable amount of the short range order was retained even in the disorder phase up to higher temperatures. Although the calculation procedure of the interaction energies are quite different between the phenomenological and the first principles methods, both approaches take the concentration dependency of interaction energies into account through the lattice parameter of a uniformly strained lattice. For these phases of which constituent species have a larger difference in atomic size, it is indispensable to take the effect of local lattice relaxation into the calculation, which is the subject of future work.

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