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Phenomenological Calculation of Thermodynamic Properties in Cu–Au Disorder Phase

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Abstract

The “phenomenological” calculation devised by Sanchez et al. is applied to calculate the concentration dependencies of lattice parameters and heat of mixing of Cu–Au disorder phase at 720 K. Predictions of the present theoretical study agree quite well with available experimental results. Moreover, unsymmetrical features obtained in the concentration dependencies of the Grand potential suggests that the symmetrical topology of phase boundaries in the “prototype” phase diagrams can be broken.

The Cluster Variation Method (CVM), which was originally devised by Kikuchi¹⁾ has been extensively applied to calculate the phase diagrams. In this model, the effect of the wide range atomic correlations essential at transition points can be reflected by explicitly incorporating multibody correlation functions into the free energy formula. The level of approximation is expressed by the largest cluster included in the free energy formula. The larger the cluster one employs, the better results are usually achieved. This can be clearly observed by comparing the topological features and transition temperatures obtained from different levels of approximations with those by the Monte Carlo simulation^{2,3)} which is model-free and is, therefore, expected to provide the most objective results. The overall topological features are well reproduced by Tetrahedron⁴⁾ or Tetrahedron–Octahedron approximation^{5–9)} for fcc based order–disorder phase transition on which the main emphasis has been placed. In particular, seven phase diagrams with first and second nearest neighbor pair interactions are created via T–O approximation, which concludes the first-ever successful investigation of coherent equilibria of fcc lattice.^{5–9)}

The “prototype” phase diagrams, however, are completely symmetrical around fifty atomic concentrations. This unrealistic feature is primarily due to the fact that the internal energy consists of concentration independent pairwise interactions. Moreover multibody interactions are not taken into considerations, either. In a real alloy system,

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atomic interactions depend not only on concentration but also on the environment (short range order). And the proper evaluation of the interaction forces are the subject of Band calculation since the origin of the interaction forces should be attributed to the electronic structure of the alloy.¹⁰⁾ The combination of Band calculation of atomic interactions and the CVM calculation of atomic correlations to obtain free energy with no adjustable parameters is termed “First principle calculation”, which claims both reliable physical models and strict performance of numerical manipulations. The effort along this approach is now under way.¹¹⁾

As the interface between “prototype” and “First principle approach”, Sanchez et al.¹²⁾ devised “phenomenological” calculation in which constant pair interactions of the “prototype” calculations are replaced by Lennard-Jones potential. The concentration dependency of the pair interaction is, therefore, taken into account through the lattice constants of a flexible lattice, while merely a replacive transition on a rigid lattice is investigated in the “prototype” calculation. Lennard-Jones parameters are determined from cohesive energies of constituents metals, heat of formation of an intermetallic compound and the lattice constants. They applied this method to Ni-Al system and were able to reproduce γ/γ' phase boundaries satisfactorily.

In this study, we extended their “phenomenological” approach to Cu-Au system which shows typical order-disorder transition, and calculated several thermodynamic quantities of the disorder phase. This is believed to be an essential step prior to the full evaluation of an entire phase diagram. In order to calculate the entropy term, the Tetrahedron Approximation in which pair, triangle and tetrahedron correlations are incorporated, is employed. Although these multibody correlations reflect merely the nearest neighbor environment, the adoption of the Tetrahedron approximation can be rationalized by the following considerations. According to the Ground state analysis for fcc based superlattice structures performed by Cahn et al.^{13,14)} and Kanamori et al.^{15,16)}, only 1st and 2nd nearest neighbor pair interactions are required to stabilize the number of the ordered compounds. Among them, P4/mmm ($L1_0$) and Pm3m ($L1_2$) appearing in the Cu-Au system are typical structures. When 2nd n. n. pair interaction vanishes these structures degenerate with I41/amd and I4/mmm (DO_{22}), respectively. However, these degeneracies could be lifted in favor for $L1_0$ and $L1_2$ which have a higher symmetry. Based on these arguments, in the study of Cu-Au disorder phase, one may reasonably neglect the multibody and the long distant pair interactions beyond the nearest neighbor, since the underlying ordered phases can be stabilized by the nearest neighbor pair interaction only. The Tetrahedron approximation is, therefore, quite suitable for this system for the study beyond Point (Bragg-Williams) and Pair (Bethe) approximations. Since the whole calculation procedure in the present study directly follows the one by Sanchez et al., the interested reader should refer to Ref. [12].

The Lennard-Jones potential is given by

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

where i and j stand for atomic species (Cu or Au). It should be noted that 6 and 12 are

usually assigned as the exponents for attractive and repulsive potential, respectively. However, in the present study, we adopted 4 and 8 which have been often used for metallic systems as appearing in Ref. [12]. In order to determine the coefficient terms of the above equation, cohesive energies of Cu and Au, heat of formation of Cu_3Au and lattice constants of these substances are adopted from Hultgren¹⁷⁾ and Pearson.¹⁸⁾ The calculated values of these coefficient terms are tabulated in the Table 1 and the resulting Lennard-Jones pair potentials are shown in Fig. 1. The bottom of the pair potential for Cu-Au is deeper than those for Cu-Cu and Au-Au, which indicates the ordering tendency of this system. Furthermore, the equilibrium atomic distance of Cu-Cu is shorter than that of Au-Au, which is the direct reflection of the lattice constants of each substances.

The internal energy is constructed from the Lennard-Jones pair potentials and, together with the entropy term evaluated by CVM, the Grand potential is calculated. The minimization of the Grand potential is carried out with respect to the volume as well as

Table 1

	e_{ij}° (Kcal/Mole)	r_{ij} (\AA)
Cu-Cu	13.48	2.5560
Cu-Au	14.94	2.7061
Au-Au	14.55	2.8839

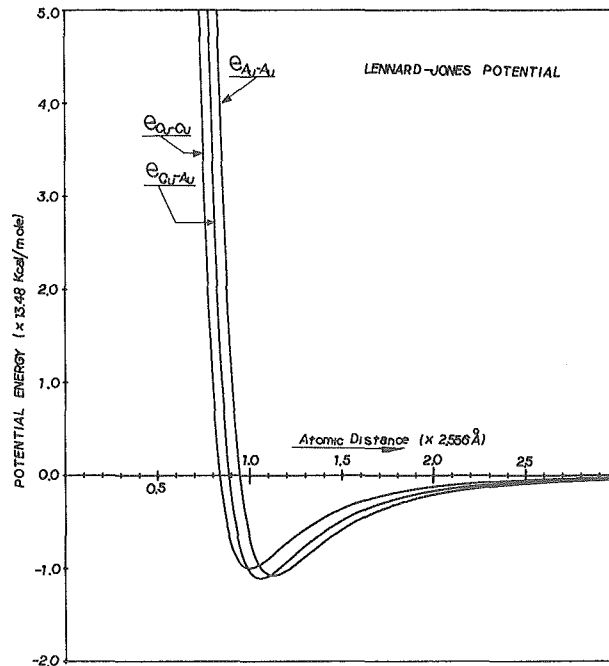


Fig. 1 Lennard-Jones Potential for Cu-Au system. The parameters employed are given in Table 1.

configurational variables (cluster concentrations). This two fold operation is necessary because of treating the replace transition on a flexible lattice. The minimization procedure automatically provides the optimum lattice constant and cluster concentrations in addition to the equilibrium Grand potential. Heat of mixing is also calculated by subtracting the internal energy from the linearly interpolated value of the cohesive energies

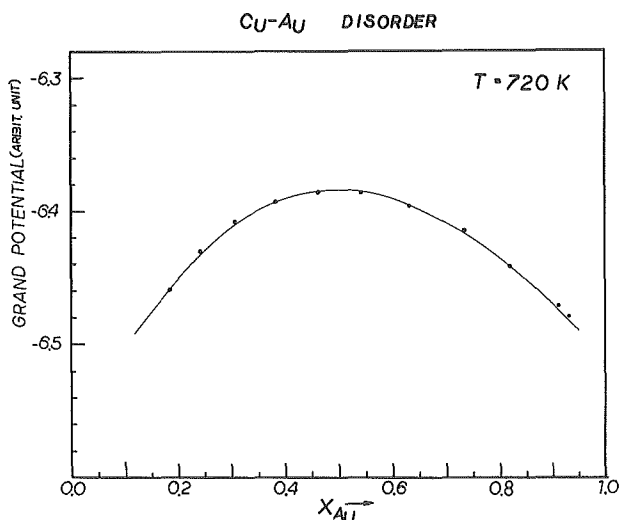


Fig. 2 Concentration dependency of Grand potential in arbitrary unit of disorder phase at 720 K. Horizontal axis indicates atomic concentration of Au.

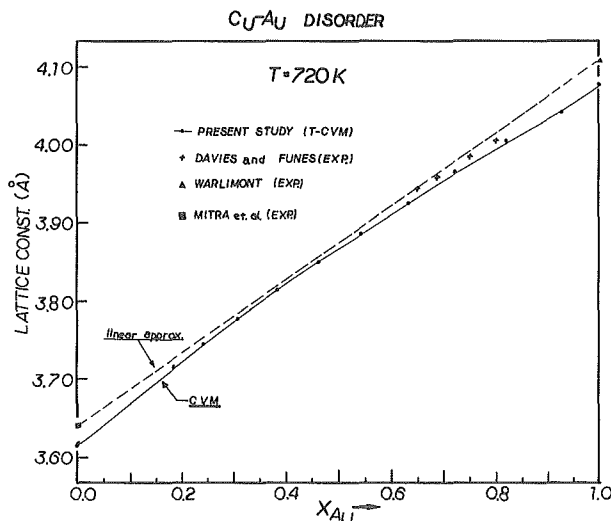


Fig. 3 Concentration dependency of lattice constant. Present CVM results are drawn by solid line and the four plus marks indicate experimental results by Davies and Funes.¹⁹⁾ Broken line is a linear interpolation of pure Cu and pure Au reported by Warlimont²³⁾ and Mitra et al.,²⁴⁾ respectively.

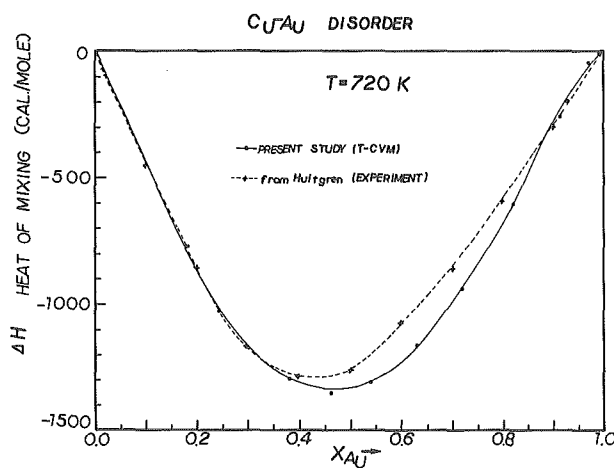


Fig. 4 Concentration dependency of Heat of Mixing of disorder phase. Present study is drawn by solid line and the experimental results quoted from Hultgren¹⁷⁾ are indicated by broken line.

of pure constituents. The concentration dependency of these quantities are examined at 720 K.

Fig. 2 shows the Grand potential. One can observe that the symmetry around fifty atomic concentrations typical for the "prototype" calculation is broken, which implies that the resulting phase diagram has an unsymmetrical topology of phase boundary which is the case for real phase diagrams. The concentration dependencies of lattice constant are shown in Fig. 3. The experimental values of Davies and Funes¹⁹⁾ are plotted by plus marks and the present calculation by CVM is drawn in solid lines. The broken line indicates linear interpolation of pure constituents. Finally, Fig. 4 shows the comparison of heat of mixing between experimental and theoretical results. The present CVM calculation is drawn by solid line while experimental ones quoted from Hultgren¹⁷⁾ are given in dotted line. In both Figs. 3 and 4, one can confirm that the overall agreement is excellent in both magnitude and tendencies.

As was described above, several thermodynamic properties of Cu-Au disorder phase are calculated by incorporating Lennard-Jones potential into Cluster Variation Method, and the agreement between available experimental results and the present study was found to be excellent. This is quite encouraging in performing the full calculation of an entire phase diagram. Also, the present study can be precursors to the ensuing more elaborate "First principle" calculations, since the whole algorithm is essentially the same although more severe restrictions would be imposed on the numerical calculations. In addition, the present calculation should be applied to obtain Short Range Order Diffuse Intensity,²⁰⁾ Spinodal Ordering loci²¹⁾ as well as Short Range Order Hardening²²⁾ which are all derived from the same free energy formula. All of these are the subjects of the forthcoming publications.

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