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First-principles calculation of heats of formation for Au–Cu, Au–Pd and Au–Ag alloys with thermal vibration effects

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Abstract. By employing the Debye–Grüneisen model, the lattice vibration effects are incorporated into the first-principles scheme to calculate the heats of formation of disordered phases for Au-based alloys. Significant improvement over the previous results without lattice vibration effects is achieved for the Au–Cu system; this can be attributed to the fairly strong temperature dependence of the bulk modulus of constituent elements.

1. Introduction

Recently, study of the alloy phase stability based on the first-principles approach has been advanced by various methods [1–5]. In most of these studies, the following two-step approach has been adopted: the first step is to extract the effective cluster interaction energies by using the cluster expansion method (CEM) [6] to evaluate the total energies in the ground state by electronic structure calculation based on the local-density-functional approximation for the selected ordered phases including pure metals; the second step is to estimate the configurational entropy by either the cluster variation method (CVM) [7] or Monte Carlo calculation [8]. Although such methods have been successful in yielding the main topological features of a phase diagram, serious discrepancies with the experimental phase diagram have been reported [1] for the order–disorder transition temperature and width of the single-phase field of the ordered phase. These are particularly emphasized for a system which has a large difference between the atomic sizes of its constituent elements.

The discrepancies can be partly attributed to neglect of the lattice vibration effect including anharmonicity. Since the anharmonicity in the lattice vibration is closely related to the elastic properties of a system such as thermal expansion and bulk modulus, neglecting this effect causes an error in determining the transition temperature, solubility limit, etc, which are affected by softening of the lattice at elevated temperatures.

Although the lattice dynamics are a central concern of solid state physics and various sophisticated approaches to determine the phonon-related properties have been attempted, most of them are not fully compatible with the present first-principles formalism of alloy phase stability. An efficient procedure for incorporating the lattice vibration effects in a quasi-harmonic approximation, however, has been proposed by Morruzi *et al* [9] for a pure element and extended by Becker *et al* [10] for an alloy

system based on the Debye–Grüneisen model. By employing this method, the present study is undertaken to examine the lattice vibration effects on the calculated heats of formation of a disordered solid state solution for three Au-based alloy systems: Au–Cu, Au–Pd and Au–Ag.

In fact, the thermodynamic properties including the phase diagram for these systems have been calculated from first-principles [1, 2, 11, 12, 17], and the concentration dependences of the heats of formation obtained are in fairly reasonable agreement with experiment for the Au–Ag and Au–Pd systems. Serious discrepancies with experimental results, however, have been found for the Au–Cu system. The calculated heats of formation are systematically underestimated over the entire concentration range. Since the atomic sizes of Cu and Au differ by 12%, a large elastic energy is anticipated to be involved in the estimated heats of formation, which is believed to be the main source of the discrepancy. The excess elastic energy, however, could be partly relaxed when softening of the lattice at elevated temperatures is properly taken into consideration. Therefore, instead of employing a unique set of the energies evaluated in the ground state for the entire temperature range of interest, introduction of the temperature dependence into the effective interaction energies is essential.

The organization of the present paper is as follows. The main emphasis of the present study is placed on the Au–Cu system. In the next section, the calculation procedure and the theoretical background are briefly reviewed. The final section is devoted to results and discussion.

2. Calculation procedure

The calculation procedure of the conventional first-principles method without thermal vibration effects, has been amply demonstrated in previous reports [1–5, 11, 12]. Hence, only the essential recipe [9, 10] for introducing the thermal vibration effects is briefly reproduced for completeness.

The principal ingredient is to derive a free energy $F^{(m)}(r, T)$ for a phase m , where m represents A_4 ($m = 1$) and B_4 ($m = 5$) with a FCC structure, A_3B ($m = 2$) and AB_3 ($m = 4$) with an $L1_2$ structure, and A_2B_2 ($m = 3$) with an $L1_0$ structure, from the electronic binding energy curve $E_{el}^{(m)}(r)$ evaluated by electronic structure calculation for a phase m in the ground state for a given lattice parameter r . In the present work, we adopt the augmented-spherical-wave (ASW) method [23], setting the angular momentum cut-off l_{max} for the basis function to be $l_{max} = 2$ for Cu, Ag and Pd and $l_{max} = 3$ for Au. Relativistic effects except for the spin-orbit interaction are included following the prescription proposed by Koelling and Harmon [24]. Even though this correction has relatively minor effects for the fourth- and fifth-row elements Cu, Pd and Ag, it sometimes changes qualitative aspects of the phase stability for alloys including heavier elements such as Au [25]. In order to ensure consistency, we included the relativistic effects for the lighter elements.

In general, $F^{(m)}(r, T)$ is given as the sum of three terms as follows:

$$F^{(m)}(r, T) = E_{el}^{(m)}(r) + E_{vib}^{(m)}(r, T) - TS_{vib}^{(m)}(r, T) \quad (1)$$

where r is the lattice constant, and $E_{el}^{(m)}(r)$, $E_{vib}^{(m)}(r, T)$ and $S_{vib}^{(m)}(r, T)$ are the electronic binding energy, the thermal vibration energy and the vibration entropy,

respectively. In the Debye-Grüneisen model [9], the vibration energy is given by

$$E_{\text{vib}}^{(m)}(r, T) = E_0 + 3k_B T D(\Theta_D/T) \quad (2)$$

where k_B is the Boltzmann constant, Θ_D is the Debye temperature, E_0 is the zero-point energy given as $E_0 = \frac{9}{8}k_B\Theta_D$, and $D(\Theta_D/T)$ is the Debye function [13]. The vibrational entropy is given by

$$S_{\text{vib}}^{(m)}(r, T) = 3k_B \left\{ \frac{4}{3} D(\Theta_D/T) - \ln[1 - \exp(-\Theta_D/T)] \right\}. \quad (3)$$

It should be noted that, by following the original prescription of Morruzi *et al* [9], the Debye temperature Θ_D is given as $41.63(rB/M)^{1/2}$, where M is the average mass, the numerical constant is a scaling factor which gives approximate agreement with empirical data, and the bulk modulus B is derived from the calculated binding curve. Also, the Grüneisen constant γ is evaluated from $\gamma = -1 - (V/2)[(\partial^2 P/\partial V^2)/(\partial P/\partial V)]$ where P is the pressure obtained from the binding curve and V is the volume. This particular expression for γ is identical with that originally proposed by Dugdale and MacDonald [28].

The ordinary procedure to derive a set $\{v_i\}$ of effective interaction energies is based on the CEM applied to the electronic energy $E_{\text{el}}^{(m)}(r)$, which merely introduces the r -dependence to the internal energy. On the other hand, the present method uses the CEM on the free energy $F^{(m)}(r, T)$ of each phase derived from equations (1)–(3):

$$v_i(r, T) = \sum_m \{\xi_i^{(m)}\}^{-1} F^{(m)}(r, T) \quad (4)$$

where $\{\xi_i^{(m)}\}$ is the correlation function for a cluster i of phase m . Note that, since the CEM in the present study is performed on the total energies of the five distinct structures ($m = 1, \dots, 5$), the effective interaction energies are derived for four kinds of nearest-neighbour cluster up to regular tetrahedron as well as v_0 , the energy of the complete random solid solution at 50 at.%.

Once the effective interaction energies have been derived, the free-energy functional of a phase specified by $\{\xi_i\}$ is given by

$$F(r, T) = \sum_{i=0}^4 v_i(r, T) \xi_i - TS(\{\xi_j\}) \quad (5)$$

where $S(\{\xi_j\})$ is the mixing entropy of a fixed FCC lattice. The rest of the procedure is to minimize the free-energy functional F with respect to both the lattice constant r and the set $\{\xi_i\}$ of correlation functions at a given temperature T . It is noted that the tetrahedron-octahedron approximation [21, 22] of the CVM is employed to evaluate the configurational entropy term in equation (5).

Finally, the set $\{v_i(r, T)\}$ of effective interaction energies and the set $\{\xi_i^*\}$ of optimized correlation functions yield the heats of formation $\Delta H(c, T)$ of a disordered solid solution through

$$\Delta H(c, T) = \sum_{i=1}^5 v_i(r, T) \xi_i^* - (1-c)H_A(T) - cH_B(T) \quad (6)$$

where H_A and H_B are the cohesive energies for metals A and B, respectively, and c is the concentration of element B linearly related to the point correlation function ξ_1 through $c = 1 - 2\xi_1$.

3. Results and discussion

Figures 1, 2 and 3 show the heats of formation of a disordered solid solution for the Au–Cu, Au–Pd and Au–Ag systems, respectively. In each figure, the experimental results are shown as thin full curves with open circles [14–16], while the theoretical results with and without [11, 17] thermal vibration effects are indicated as bold curves and broken curves, respectively. One can see that a great improvement is achieved by the present calculation with the thermal vibration effects for the Au–Cu system. The downward shift of the entire curve implies that the disordered phase is stabilized by the contribution of the thermal vibration effects. For both Au–Pd and Au–Ag systems for which fairly reasonable agreement between experiment and theory have already been achieved without thermal vibration effects, no significant differences are observed. It is believed that the discrepancies between the calculated curves and the experimental curve for the Au–Pd system are due to systematic overestimation of the heats of formation of ordered compounds in their ground states. We would like to emphasize, however, that the correct topological features, characterized by asymmetry of experimental curve, are correctly reproduced by the calculations.

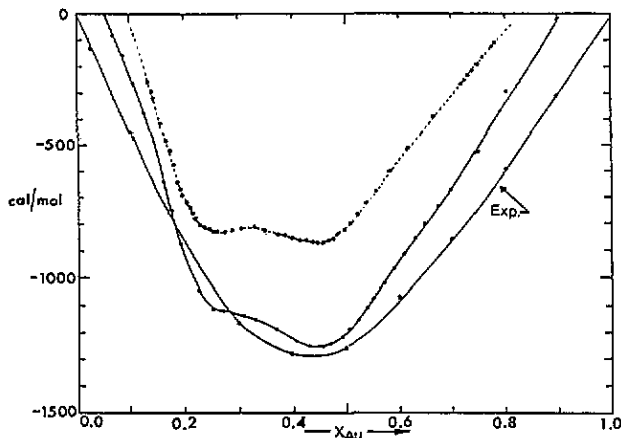


Figure 1. Heats of formation of a disordered solid solution for the Cu–Au system at 720 K, where the horizontal axis is the atomic concentration of Au: $\cdots\circ\cdots$, first-principles calculation [11] without thermal vibration effects; $\text{---}\bullet\text{---}$, present results with thermal vibration effects; $\text{---}\circ\text{---}$, experimental data [14].

Also, it should be pointed out that the ‘double minima’ appearing in the theoretical curves for Au–Cu are artefacts introduced mainly by the CEM when performed on a limited set of ordered compounds. Close observation of the theoretical curve suggests that the curve is pulled downwards in the vicinity of the Cu_3Au and AuCu stoichiometries, which implies that the heats of formation of these two ordered compounds in the ground state (as indicated by $E_{\text{el}}^{(\text{Cu}_3\text{Au})}$ and $E_{\text{el}}^{(\text{CuAu})}$) are overly reflected via equations (1) and (4)–(6). A detailed analysis is under way with an increasing number of ordered compounds including fictitious compounds using the cluster expansion formula, equation (4), which is expected to smooth the entire curve.

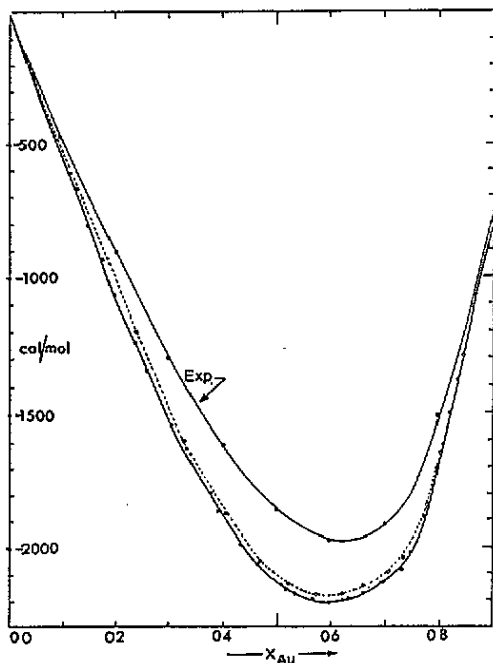


Figure 2. Heats of formation of a disordered solid solution for the Au-Pd system at 298 K as a function of the atomic concentration of Au. The curves have the same meanings as in figure 1, except that the experimental data were taken from [15].

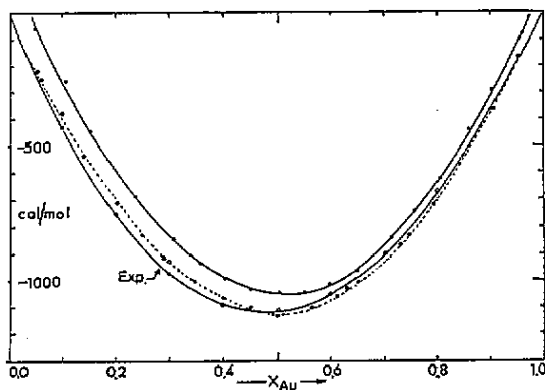


Figure 3. Heats of formation of a disordered solid solution for the Au-Ag system at 800 K as a function of the atomic concentration of Au. The curves have the same meanings as in figure 1, except that the experimental data were taken from [16].

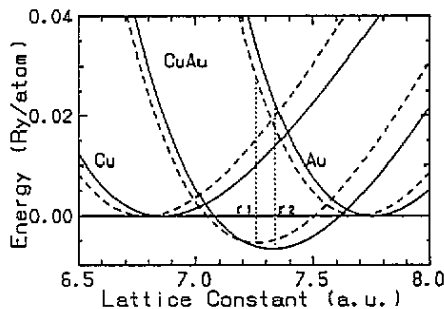


Figure 4. Heats of formation of Cu, CuAu ($L1_0$) and Au as functions of the lattice constant: ---, electronic energy contribution $E^{(m)}(r)$ at $T = 720$ K for each phase; —, $F^{(m)}(r, T)$ at $T = 720$ K for each phase. r_1 and r_2 indicate the equilibrium lattice constants for the $E^{(m)}(r)$ and $F^{(m)}(r, T)$ curves, respectively.

In order to clarify the stabilization mechanism of the disordered phase by the thermal vibration effects, the heats of formation curves for Cu, Au and CuAu ($L1_0$) are magnified in figure 4. For each phase, the broken curves and full curves represent $E^{(m)}(r)$ and $F^{(m)}(r, T = 720$ K), respectively. Hence, the former indicate the heats of formation without thermal vibration effects, while the latter represent the heats of

formation with thermal vibration effects. It should be noted that the reference state of the heats of formation is the segregation limit at each temperature. The equilibrium lattice constants, which correspond to the minima of the energy curves, elongate when vibrational effects are included in the calculation, which suggests thermal expansion.

Another important feature of the energy curves is that the curvature at the equilibrium lattice constant, which is related to the bulk modulus of the solids, changes when vibrational effects are taken into account. This 'softening' may be caused by elongation of the lattice constant.

The heats of formation of an alloy can be formally decomposed into two factors: the elastic energy and the chemical driving force. The elastic energy expended to form a phase with the equilibrium lattice constant r^* may be estimated as

$$E_{\text{elastic}}(r^*, T) = c^* F^{(\text{Au})}(r^*, T) + (1 - c^*) F^{(\text{Cu})}(r^*, T) \quad (7)$$

where c^* is the concentration of Au in the phase of interest. It can be easily seen in figure 4 that the elastic energy to form an $L1_0$ ordered phase with the lattice constant r_1 at $T = 0$ K is greatly reduced at $T = 720$ K by the thermal expansion of the lattice constant from r_1 to r_2 and the lattice softening manifested by the reduction in the curvature of the heats of formation curves. Essentially the same arguments can be applied to account for the relaxation effect.

The temperature dependences of the bulk modulus for Au and Cu are calculated and compared with the experimental dependences [18,19] in figures 5(a) and 5(b), respectively. The full curves and broken curves indicate the present calculations and the experimental measurements, respectively. Although the experimental data are available in a limited temperature range, the calculation produces the correct tendency. The deviation of the calculated results from the experimental data can be ascribed to the inevitable error originally involved in the overestimated cohesive energy, which is thought to be a genuine error in electronic structure calculations based on the local-density approximation in the density-functional theory [26]. It is noticeable that the bulk modulus has quite a large temperature dependence which leads to the relaxation mechanism described above. Furthermore, it should be recognized that such a mechanism is manifested for a system which has a large difference between the atomic sizes of the constituent elements such as the Au-Cu system.

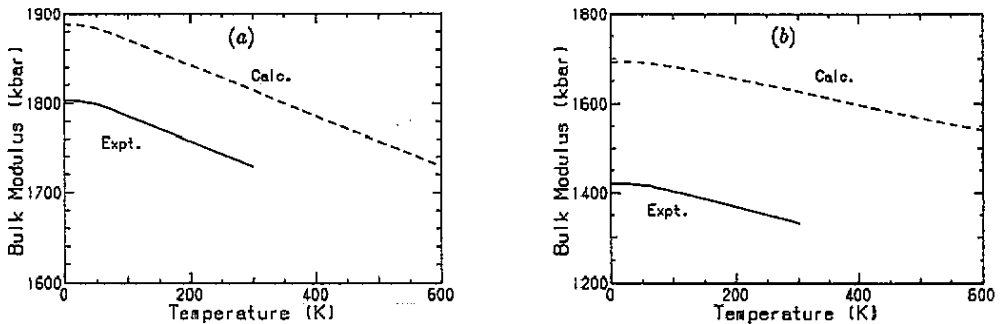


Figure 5. Temperature dependence of the bulk modulus for (a) Au and (b) Cu: —, experimental data [18,19]; - - -, calculated results.

The effective interaction energies extracted for the Au-Cu system with thermal vibration effects at $T = 720$ K are compared with those at 0 K in figure 6. In addition to the shift of the entire curve towards the right-hand side due to thermal expansion, a significant downward shift is also observed for v_0 , which is another indication of the stabilization of the disordered phase.

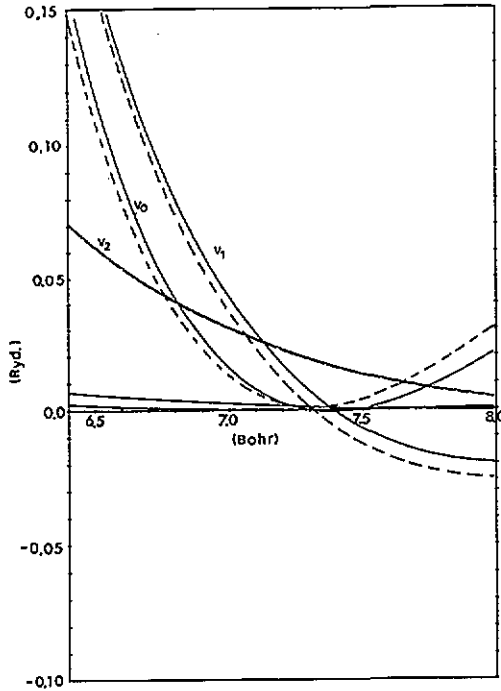


Figure 6. Extracted effective interaction energies for the Au-Cu system, where v_i indicates an i -point cluster, and v_3 and v_4 are both quite small and situated near the zero-energy level: ---, electronic contribution only for each cluster energy; —, values with thermal vibration effects at 720 K.

Although the calculation of the phase diagram and thermodynamic quantities of the Au-Cu system have been attempted by various methods, a fully successful result has not yet been achieved by the first-principles calculations. The disagreements have been heavily ascribed to the neglect of the local distortion effect [27] which is inseparable from the lattice thermal vibration.

The theory of local distortion is proposed by Khachatryan [20] based on the harmonic approximation. The essential quantity required to estimate the relaxation energy is the dynamical matrix which can, in principle, be obtained by the phonon dispersion relation. The major stumbling block, however, is the fact that the local distortion alters the crystal lattice symmetry and the validity of the CVM for a cubic system is anticipated to break down. Moreover, the harmonic approximation does not lead to thermal expansion.

The method adopted in the present study, on the other hand, incorporates the lattice softening due to the thermal expansion of a uniformly deformable lattice. Although the Debye model is a primitive model and the correctness of the description

is, in general, limited to the low-temperature portion for which the long-wave phonon is dominant, the essential features of thermal expansion and the phonon-related properties are well reproduced. A most satisfactory result may be obtained by incorporating the thermal vibration effects into a lattice which is allowed to distort locally, which is the next task in this series of first-principles calculations. We believe that the present study takes an important step towards the fully satisfactory achievement of first-principles calculations.

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References

- [1] Mohri T, Terakura K, Oguchi T and Watanabe K 1988 *Phase Transformation '87* ed G W Lorimer (London: Institute of Metals) p 433
- [2] Mohri T and Watanabe K 1988 *Trans. Iron Steel Inst. Japan* **28** 783
- [3] Wei S H, Mbaye A A, Ferreira L G and Zunger A 1987 *Phys. Rev. B* **36** 4163
- [4] Sigli C, Kosugi M and Sanchez J M 1986 *Phys. Rev. Lett.* **57** 253
- [5] Turchi P E A, Sluiter M, Pinski F J, Johnson D D, Nickolson D M, Stocks G M and Staunton J B 1991 *Phys. Rev. Lett.* **67** 1779
- [6] Connolly J W and Williams A R 1983 *Phys. Rev. B* **27** 5169
- [7] Kikuchi R 1951 *Phys. Rev.* **81** 998
- [8] Binder K 1986 *Monte Carlo Methods in Statistical Physics (Springer Current Topics in Physics 7)* ed K Binder (Berlin: Springer) p 1
- [9] Morruzzi V L, Janak J F and Schwarz K 1988 *Phys. Rev. B* **37** 790
- [10] Becker J D, Sanchez J M and Tien J K 1991 *Mater. Res. Soc. Symp. Proc.* **213** 113
- [11] Mohri T, Terakura K, Oguchi T and Watanabe K 1988 *Acta Metall.* **36** 547
- [12] Mohri T, Terakura K, Takizawa S and Sanchez J M 1991 *Acta Metall.* **39** 493
- [13] Mayer J E and Mayer M G 1977 *Statistical Mechanics* (New York: Wiley)
- [14] Orr R L 1960 *Acta Metall.* **8** 489
- [15] Darby J B Jr 1966 *Acta Metall.* **14** 265
- [16] White J L, Orr R L and Hultgren R 1957 *Acta Metall.* **5** 747
- [17] Mohri T, Takizawa S and Terakura K 1990 *Mater. Trans. Japan Inst. Met.* **31** 315
- [18] Overton W C Jr and Gaffney J 1955 *Phys. Rev.* **98** 969
- [19] Neighbours J R and Alers G A 1958 *Phys. Rev.* **111** 707
Collard S M and Mclellan R B 1991 *Acta Metall.* **39** 3143
- [20] Khachaturyan A G 1983 *Theory of Structural Transformations in Solids* (New York: Wiley)
- [21] Mohri T, Sanchez J M and de Fontaine D 1985 *Acta Metall.* **33** 1171
- [22] Sanchez J M and de Fontaine D 1978 *Phys. Rev. B* **17** 2926
- [23] Williams A R, Kubler J and Gelatt C D Jr 1979 *Phys. Rev. B* **19** 6094
- [24] Koelling D D and Harmon B N 1977 *J. Phys. C: Solid State Phys.* **10** 3107
- [25] Takizawa S, Terakura K and Mohri T 1989 *Phys. Rev. B* **39** 5792
- [26] Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133
Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864
- [27] Terakura K, Mohri T and Oguchi T 1989 *Mater. Sci. Forum* **37** 39
- [28] Dugdale J S and MacDonald D K C 1953 *Phys. Rev.* **89** 832