

Electronic theory of the alloy phase stability of Cu-Ag, Cu-Au, and Ag-Au systems

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It is demonstrated that electronic structure calculations using the local-density approximation with density-functional theory accounts for the distinctly different behaviors in the equilibrium phase diagrams among Cu-Ag, Cu-Au, and Ag-Au alloy systems. A detailed microscopic analysis is made based on the prescription proposed by Connolly and Williams.

I. INTRODUCTION

The alloy systems Cu-Ag, Cu-Au, and Ag-Au form an interesting group with regard to the equilibrium phase diagrams.¹ Among these, Cu-Au has occupied a special position, being regarded as a prototype system which undergoes an order-disorder phase transition, and many works have been done to analyze the phase diagram of this system.²⁻⁷ However, from the view point of the electronic theory, more interesting is the fact that the phase diagrams of the three systems are distinctly different among them, although the constituents are all noble metals: Cu-Ag has a tendency of segregation, Cu-Au has some ordered phases, and Ag-Au forms a homogeneous solid solution. Kittler and Falicov^{8,9} carried out an analysis by using a simple tight-binding model and partly succeeded in reproducing the difference between Cu-Au and Cu-Ag. However, their approach was not successful in detecting a meaningful difference between Cu-Au and Ag-Au. To our knowledge, no unified electronic theory is available which can cover all three cases. Therefore, development of such a theory based on *ab initio* electronic structure calculations is the main purpose of our work.

We first estimate heats of formation of some ordered compounds for these systems from the total-energy calculations with the local-density approximation to the density-functional theory. The calculated heat of formation is positive for Cu-Ag and negative for Cu-Au and Ag-Au, being consistent with experimental results. (A positive sign of heat of formation corresponds to a tendency of segregation in this work.) Besides, the heat of formation for Cu₃Au turns out to be almost twice that for CuAu₃, again being consistent with the well-known asymmetry with respect to the concentration in the phase diagram of the Cu-Au system.

We then follow the analysis proposed by Connolly and Williams.¹⁰ This enables us to estimate the many-body interaction potentials v_n which are defined as

$$\Delta E_i = \sum_n v_n \xi_{ni}, \quad (1)$$

where the subscript i stands for a specific atomic configuration of a system, ΔE_i is the total energy of the system with respect to the reference defined below, and ξ_{ni} are the multisite correlation functions associated with a cluster specified by n .

Once v_n is obtained, the ordering energy of a system E_0 , i.e., the energy of an ordered phase minus that of a disordered phase, can be estimated. It turns out that E_0 takes a fairly large negative value for the Cu-Au system, leading to strong stabilization of an ordered phase. This is in contrast to the case of the Ag-Au system where E_0 takes a very small negative value. This aspect is again very consistent with the experimental results. Our analysis clearly indicates that the qualitative difference between the Cu-Au and Ag-Au systems in the phase diagrams comes not only from the difference in the detailed electronic structures but also from the atomic-size difference of constituent atoms.

The electronic structure calculations seem to be fairly satisfactory in explaining the overall aspect of the phase diagrams of Cu-Ag, Cu-Au, and Ag-Au systems. Nevertheless, there are still some subtle problems concerning the accuracy in order to reproduce phase diagrams quantitatively. This will be argued in a subsequent paper,¹¹ where thermodynamic properties of the Cu-Au system will be discussed based on the statistical numerical calculations via the cluster-variation method.^{12,13}

Some comments will be made in Sec. II on the band-structure calculations. Calculated results of heat of formation and interatomic potentials will be presented in Sec. III. We present our conclusions in Sec. IV.

II. SOME REMARKS ON THE BAND-STRUCTURE CALCULATION

We use the augmented-spherical-wave (ASW) method¹⁴ to perform the band-structure calculations for pure metals A and B as well as for ordered compounds, A_3B and AB_3 with the $L1_2$ structure and AB with the $L1_0$ structure. The basic lattice is assumed to be fcc and A (or B) may be

one of Cu, Ag, and Au. The relativistic effect, except the spin-orbit interaction, is included.¹⁵ Neglect of the spin-orbit interaction may be allowed even for Au, because the d band is filled. For all the three elements, Cu, Ag, and Au, the ASW's of up to $l=3$ are taken into account as basis functions. As a local-density approximation to the density-functional method, we adopt the interpolation scheme proposed by Moruzzi *et al.*¹⁶

III. RESULTS AND DISCUSSIONS

A. Cu-Au system

The total energy per cubic unit cell in reference to the segregation limit is written as

$$\Delta E\{a; \text{Cu}_m \text{Au}_{4-m}\} = E\{a; \text{Cu}_m \text{Au}_{4-m}\} - mE\{a_{\text{Cu}}; \text{Cu}\} - (4-m)E\{a_{\text{Au}}; \text{Au}\}, \quad (2)$$

where m takes 0, 1, 2, 3, and 4, $E\{a; \text{Cu}_m \text{Au}_{4-m}\}$ is the total energy of ordered $\text{Cu}_m \text{Au}_{4-m}$ systems with the lattice constant a , and $E\{a_{\text{Cu}}; \text{Cu}\}$ and $E\{a_{\text{Au}}; \text{Au}\}$ are those for Cu and Au at their calculated equilibrium lattice constants, a_{Cu} and a_{Au} . The calculated total energies of Eq. (2) are fitted with a form

$$\Delta E\{a; i\} = (p_i/a)^{2n} - (q_i/a)^n + r_i, \quad (3)$$

where i stands for one of $\text{Cu}_m \text{Au}_{4-m}$. Very accurate overall fit can be achieved with $n=3.5$. The fitting parameters, p , q and r , the calculated equilibrium lattice constants, and heats of formation (the minimum values of $\Delta E\{a; \text{Cu}_m \text{Au}_{4-m}\}$ with respect to a) are listed in Table I.

The most important aspect in our total-energy calculations is that the heat of formation is negative for all of $m=1, 2$, and 3. This implies stabilization of ordered compounds, Cu_3Au , CuAu , and CuAu_3 , against segregation. The calculated heats of formation agree semiquantitatively with the corresponding observed low-temperature values -0.022 Ry (Cu_3Au), -0.027 Ry [$(\text{CuAu})_2$], and -0.012 Ry (CuAu_3).¹⁷ The relatively large discrepancy

for $(\text{CuAu})_2$ may be partly due to the neglect of the tetragonal lattice distortion in our calculation.

We then estimate the many-body interaction potentials $v_n(a)$ by using Eq. (1) combined with ξ_{ni} listed in Table I of Ref. 10. The fundamental assumption in the process of obtaining v_n is that the clusters consisting entirely of nearest neighbors contribute to the total energies; therefore, the largest cluster in the present case is a tetrahedron formed by nearest-neighbor sites. Although the assumption seems to be too simple, very small values of v_3 and v_4 for noble-metal alloys (see Ref. 10 and discussions below) may be regarded as fulfillment of, at least, the necessary condition for expanding the total energy in terms of such small clusters. Leaving the study of the convergence problem of such an expansion as a future work, we regard our v_n 's as renormalized ones in the sense that the farther-neighbor interactions are effectively included.

The results are shown in Fig. 1(a). In order to have deeper insights into v_n 's, their explicit expressions in the present approximation are given below [note that we adopt a convention such that A (B) in Table I of Ref. 10 corresponds to Au (Cu)]:

$$v_0(a) = \frac{1}{16} [\Delta E\{a; \text{Au}_4\} + 4\Delta E\{a; \text{CuAu}_3\} + 6\Delta E\{a; (\text{CuAu})_2\} + 4\Delta E\{a; \text{Cu}_3\text{Au}\} + \Delta E\{a; \text{Cu}_4\}], \quad (4)$$

$$v_1(a) = \frac{1}{4} (\Delta E\{a; \text{Au}_4\} + 2\Delta E\{a; \text{CuAu}_3\} - 2\Delta E\{a; \text{Cu}_3\text{Au}\} - \Delta E\{a; \text{Cu}_4\}), \quad (5)$$

$$v_2(a) = \frac{3}{8} [\Delta E\{a; \text{Au}_4\} - 2\Delta E\{a; (\text{CuAu})_2\} + \Delta E\{a; \text{Cu}_4\}], \quad (6)$$

$$v_3(a) = \frac{1}{4} (\Delta E\{a; \text{Au}_4\} - 2\Delta E\{a; \text{CuAu}_3\} + 2\Delta E\{a; \text{Cu}_3\text{Au}\} - \Delta E\{a; \text{Cu}_4\}), \quad (7)$$

$$v_4(a) = \frac{1}{16} [\Delta E\{a; \text{Au}_4\} - 4\Delta E\{a; \text{CuAu}_3\} + 6\Delta E\{a; (\text{CuAu})_2\} - 4\Delta E\{a; \text{Cu}_3\text{Au}\} + \Delta E\{a; \text{Cu}_4\}]. \quad (8)$$

TABLE I. Fitting parameters, p , q , and r , of the calculated total energies [Eq. (3)], and the corresponding equilibrium lattice constants and heats of formation for ordered CuAu, CuAg, and AgAu systems (in rydberg atomic units).

System	p	q	r	a_0	$\Delta E(a_0)$
Au ₄	8.584	11.677	2.155	7.692	0.0
CuAu ₃	8.217	11.013	1.932	7.474	-0.0100
(CuAu) ₂	7.877	10.450	1.788	7.237	-0.0205
Cu ₃ Au	7.474	9.749	1.586	6.986	-0.0191
Cu ₄	7.055	9.033	1.410	6.717	0.0
Ag ₄	8.075	10.444	1.513	7.611	0.0
CuAg ₃	7.819	10.076	1.502	7.396	0.0268
(CuAg) ₂	7.588	9.787	1.519	7.171	0.0348
Cu ₃ Ag	7.322	9.406	1.469	6.948	0.0253
AgAu ₃	8.447	11.347	1.960	7.665	-0.0134
(AgAu) ₂	8.331	11.073	1.815	7.640	-0.0178
Ag ₃ Au	8.207	10.769	1.662	7.624	-0.0130

In the present sign convention, the positive value of pair-potential parameter v_2 favors compound formation. As one can see from Fig. 1(a), v_3 and v_4 are an order of magnitude smaller than other v_n 's and do not play any significant role. A fairly strong lattice-constant dependence of v_1 in Fig. 1(a) can be understood from Eq. (5). More intuitively, v_1 in a simple pair-potential model¹⁸ is given by $\epsilon_{\text{AuAu}} - \epsilon_{\text{CuCu}}$, where ϵ_{AuAu} (ϵ_{CuCu}) is the effective pair potential between Au (Cu) atoms. If we take into account a lattice-constant dependence of ϵ_{AuAu} and ϵ_{CuCu} , it is natural

to expect that ϵ_{AuAu} (ϵ_{CuCu}) will take a minimum value at the equilibrium lattice constant of Au (Cu). Therefore the sign of v_1 changes from positive to negative as the lattice constant increases.

For a disordered alloy, ξ 's are given by $\xi_n = (1-2x)^n$ with x the concentration of copper¹⁰ and the total energy difference defined similarly to Eq. (2) is given by

$$\Delta E_D\{a; (\text{Cu}_x\text{Au}_{1-x})_4\} = \sum_{n=0}^4 (1-2x)^n v_n(a). \quad (9)$$

The heats of disordered-alloy formation for a given x , which are defined as the minimum values of Eq. (9) with respect to a , are shown in Fig. 2(a) together with the heats

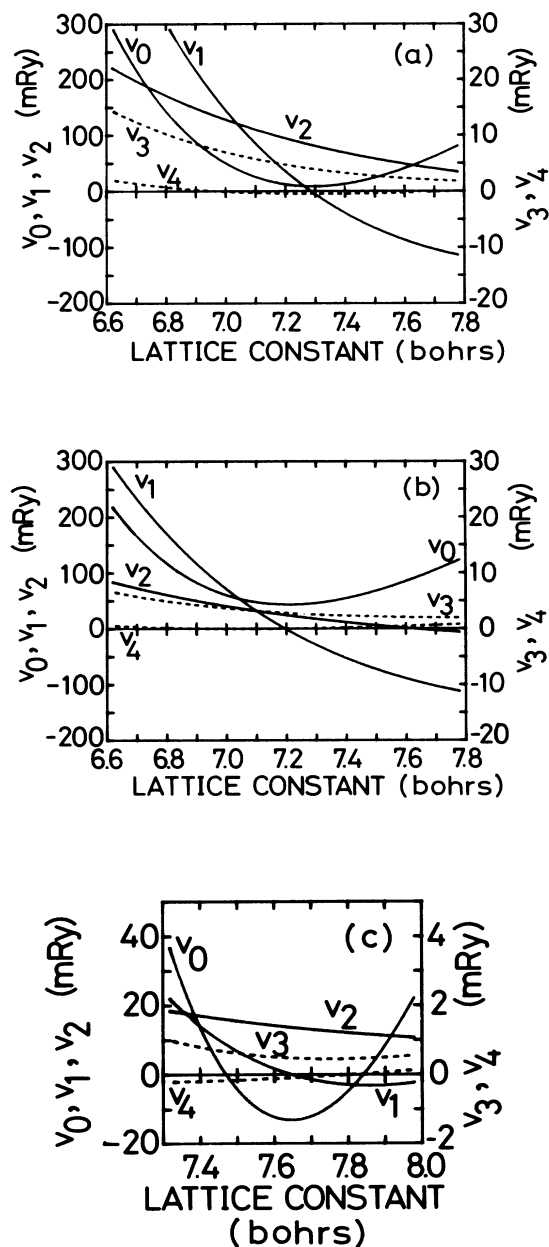


FIG. 1. The many-body interaction potentials given by Eqs. (4)–(8) for (a) Cu-Au, (b) Cu-Ag, and (c) Ag-Au systems. Note the enlarged scale for v_3 and v_4 .

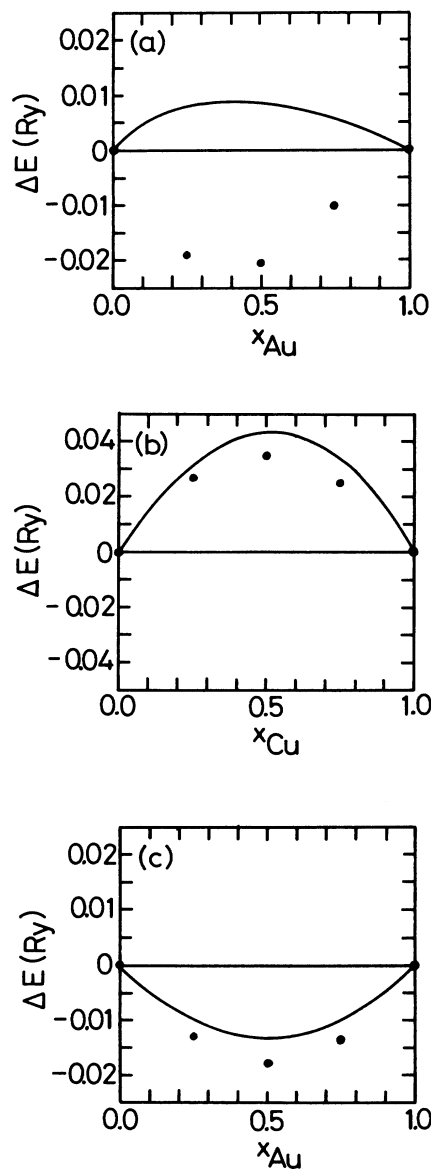


FIG. 2. Calculated heats of formation for (a) Cu-Au, (b) Cu-Ag, and (c) Ag-Au systems in the ordered (dots) and disordered (solid lines) phases.

of formations for ordered alloys. It is now clear from Eq. (9) that $v_0(a)$ is nothing but the energy of the disordered alloy with the 50-50 concentration.¹⁹ It is therefore reasonable that $v_0(a)$ takes a minimum at $a_D(\text{CuAu})$ which is approximately equal to the equilibrium lattice constant of the ordered CuAu, $a_0(\text{CuAu})$. Nevertheless a slightly larger value of $a_D(\text{CuAu})$ (by about 0.03 Å) compared with $a_0(\text{CuAu})$ is observed. This result is interpreted in the following way. The probability of having Cu-Cu and Au-Au pairs is larger in the disordered phase than in the ordered phase. Apparently the Au-Au pair favors a larger lattice constant compared to $a_0(\text{CuAu})$ while the Cu-Cu pair favors a smaller one. Therefore the two tendencies nearly cancel out but not perfectly, because an energy increase due to compression of the lattice constant is steeper than that due to expansion. This asymmetry of the total-energy curve produces a slight increase of lattice constant in the disordered phase. The ordering energy for the CuAu alloy with the 50-50 concentration, $E_0\{(\text{CuAu})_2\}$ is obtained by

$$E_0\{(\text{CuAu})_2\} = \Delta E\{a_0(\text{CuAu}); (\text{CuAu})_2\} - \Delta E_D\{a_D(\text{CuAu}); (\text{CuAu})_2\}, \quad (10)$$

which amounts to -0.029 Ry [see Fig. 2(a)]. Note again that the second term on the right-hand side of Eq. (10) is equal to $v_0(a)$ with $a = a_D(\text{CuAu})$. The origin of this large negative value, which implies the stabilization of the ordered phase with respect to the disordered phase, can be traced by using Eq. (4). The crucial ingredient is the large difference in the atomic radius between Cu and Au. $\Delta E\{a; i\}$'s other than for i equal to $(\text{CuAu})_2$ contribute also to $v_0(a)$ and take fairly large values at the equilibrium lattice constant of CuAu.

Similar analyses for Cu_3Au and CuAu_3 lead us to qualitatively the same conclusions with regard to the stability of the ordered phase and the change in the equilibrium lattice constant between the ordered and disordered phases.²⁰ The ordering energies E_0 for Cu_3Au and CuAu_3 are -0.027 and -0.016 Ry, respectively [see Fig. 2(a)]. The ordering energy is closely related to the critical temperature T_c of the order-disorder phase transition and actually the trend in T_c 's for Cu_3Au (663 K), CuAu (683 K), and CuAu_3 (~ 500 K) parallels that in E_0 's.¹

B. Cu-Ag system

The fitting parameters, p , q , and r in Eq. (3) for $\Delta E\{a; \text{Cu}_m\text{Ag}_{4-m}\}$ for $m=0, 1, 2$, and 3 are listed in Table I together with the calculated equilibrium lattice constants and heats of formation. In contrast to the Cu-Au system, the heats of formation for Cu_3Ag , $(\text{CuAg})_2$, and CuAg_3 take fairly large positive values. This is consistent with the experimental fact that the Cu-Ag system has a tendency of segregation.

v_n 's for the Cu-Ag system are shown in Fig. 1(b). Qualitatively, they behave similarly to those of the Cu-Au system. It is interesting to note that the present v_2 is also positive except at a region of relatively large a values. The positive v_2 favors ordering and it is consistent with the fact that v_0 , which corresponds to an energy of a com-

pletely random alloy with 50-50 concentration, is larger than that of the ordered $(\text{CuAg})_2$ compound. At the same time, however, the positive sign of v_2 is in conflict with the tendency of segregation in a usual pair-potential model. If we try to interpret the phase stability of the Cu-Ag system in terms of v_n 's, the crucial factor causing the tendency of segregation is the large positive value of v_0 even at its minimum point, and v_2 is not strong enough to make an ordered compound stable.

The heats of formation for the disordered Cu-Ag system, ΔE_D , are calculated along the same line as in the Cu-Au system [see Eq.(9)] and shown in Fig. 2(b). One may note in Fig. 2(b) that the slope of ΔE_D at the Cu-rich side is much steeper than that at the Ag-rich side. This aspect corresponds to the asymmetry of the solubility observed in the dilute-alloy regions of the Cu-Ag system.

C. Ag-Au system

The fitting parameters in Eq. (3) for $\Delta E\{a; \text{Ag}_m\text{Au}_{4-m}\}$ for $m=1, 2$, and 3 are listed in Table I together with the calculated equilibrium lattice constants and heats of formation. From our calculations, the equilibrium lattice constant of Ag is smaller than that of Au, while the reverse is true experimentally.²¹ However, the error is fairly small and will not affect the qualitatively important aspects of the present theory. As in the case of the Cu-Au system, ΔE 's for the ordered compounds of the Ag-Au system are negative at their equilibrium lattice constant. It is interesting to compare v_n 's for the Ag-Au system shown in Fig. 1(c) with those for the Cu-Au system. In the Ag-Au system, the ordering energy for the case of 50-50 concentration $E_0\{(\text{AgAu})_2\}$, which is defined similarly to Eq. (10) and shown in Fig. 2(c), is only -0.005 Ry. This value should be compared with the corresponding value -0.029 Ry for CuAu [see Fig. 2(a)]. As we stated in Sec. III A, one of the origins of large $E_0\{(\text{CuAu})_2\}$ is the large difference in the atomic size between Cu and Au. Therefore it is rather natural to expect a very much reduced value of $E_0\{(\text{AgAu})_2\}$, because there is only a minute difference in the lattice constant between Ag and Au. In relation to this, v_2 of the Ag-Au system is also fairly small compared with that of the Cu-Au system. The results are consistent with the fact that the Ag-Au system forms a homogeneous solid solution.

IV. CONCLUDING REMARKS

We performed the density-functional calculations of total energy for some binary ordered compounds with Cu, Ag, and Au as constituents. We then calculated the many-body interaction potentials v_n , following Connolly and Williams's prescription.¹⁰ Heats of formation and ordering energies obtained by these calculations account well for the different behaviors in the phase stability among Cu-Ag, Cu-Au, and Ag-Au systems. We pointed out the importance of the atomic-size difference between the constituent atoms with regard to the ordering energy. In all three systems studied here, the three-body and four-body potentials are an order of magnitude smaller than others. A physical context of the lattice-constant

dependence of v_1 was discussed. We believe this must play a significant role in the surface segregation problem,^{18,22} where v_1 is a crucial factor.

It may be instructive to make brief comments here on the role of detailed structure in the density of states (DOS) at the Fermi energy on the phase stability. It is widely accepted that the presence of a dip in DOS at the Fermi energy stabilizes the corresponding phase. In the present systems, we found an appreciable dip in CuAu and a relatively weak one in Cu₃Au, but no meaningful structures in CuAg and AgAu. Therefore, we conclude that there is no close correlation between the structure in DOS and the phase stability in noble-metal alloys.

Similar analyses to the present one will be made for other systems and the convergence problem in the cluster expansion of the total energy, Eq. (1), will be studied by enlarging a cluster size. Finally, a theoretical study of the

thermodynamic properties of the Cu-Au system based on the cluster-variation method will be presented in a forthcoming paper.¹¹

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¹⁹The positive value of $v_0(a)$ in Fig. 2 even at its minimum is due to accumulation of some errors in the present calculation. The dominant one in this context is the underestimation of heats of formation particularly for (CuAu)₂. Our underestimation of equilibrium lattice constants, the maximum discrepancy being about 1.5% for Cu, tends to make $v_0(a)$ more positive also, because a smaller lattice constant results in a larger bulk modulus, i.e., the curvature of $\Delta E(a; i)$. However, we would like to point out that $E_0\{(\text{CuAu})_2\}$ is affected only slightly by this inconvenience: The dominant error mentioned above cancels out to some extent between the two terms on the right-hand side of Eq. (10).

²⁰For Cu₃Au, a sudden increase of the lattice constant by about 0.005 Å was observed when temperature crosses the critical temperature from below (see Ref. 21). This is related to our result that the lattice constant is larger in the disordered phase than in the ordered one. More-detailed quantitative argument will be given in the forthcoming paper (Ref. 11).

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