Electronic theory for phase stability of nine AB binary alloys, with A = Ni, Pd, or Pt and B = Cu, Ag, or Au

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By performing the local-density-functional band calculations, we analyzed the phase stability of nine binary-alloy systems which are composed of Ni, Pd, or Pt as one element and Cu, Ag, or Au as the other. Most of the qualitative aspects of the phase diagrams of these systems are reproduced successfully. It is pointed out that the relativistic effect plays a crucial role in the phase stability of Pt-based alloys. A possibility is also suggested that AgPd with the $L1_1$ structure may be realized at low temperatures.

I. INTRODUCTION

Attempts at calculating the alloy phase diagrams from first principles are becoming very active recently.¹⁻⁸ Most of the approaches in these attempts consist of essentially two independent steps. One is the derivation of interatomic potentials v by means of the electronicstructure calculations and another is the free-energy calculation by using those potentials. As the theoretical tools in the first step, one may adopt the coherentpotential approximation which deals with random alloys, 1-3,9-11 or supercell band calculations for ordered allovs.^{4,7,8,12} This process of calculation not only produces v's but also reveals microscopic origins of phase stability of alloys. On the other hand, the cluster variation method¹³ (CVM) and the Monte Carlo simulation^{14,15} are frequently used in the second step. Both of these approaches become rather complicated in real systems because of the concentration dependence or the lattice-constant dependence of v's.

In the previous papers, $^{4-6}$ we studied the phase diagrams of noble-metal alloys, Cu-Ag, Cu-Au, and Ag-Au: we performed local-density-functional band calculations to derive the interatomic potentials following the Connolly-Williams prescription¹² and calculated the thermodynamic quantities with the CVM in the tetrahedron approximation.¹³ Similar analysis was also performed by Wei *et al.*⁷ Although there remain some problems in the quantitative aspects, particularly for those systems with a large lattice-constant mismatch between the constituent metals, most of the qualitatively important aspects in the noble-metal phase diagrams were successfully reproduced.

In the present work, we extend the analysis to the alloys which are composed of Cu, Ag, or Au as one element and one of Ni, Pd, or Pt as the other element. This paper deals mostly with the electronic structure analysis for the phase stability and the subsequent paper will discuss the thermodynamic properties. Although the electronic theories for the heat of formation of transitionmetal alloys were already developed with success, ^{16,17} they cannot be applied to the present systems which have filled or nearly filled d bands. All the nine systems have the same e/a ratio (the number of valence electrons per atom), but they show several variations in the phase diagrams:^{18,19} the three alloys with Ni as one constituent have a tendency of segregation: among those with Pd, Au-Pd and Cu-Pd form some ordered alloys and Ag-Pd is experimentally a homogeneous solid solution; Ag-Pt and Au-Pt have a tendency of segregation but Cu-Pt forms some ordered alloys. Among the ordered alloys of these systems, Cu-Pd and Cu-Pt are unique: the B2 structure, whose basic lattice is bcc, is stabilized near the 50%-50% concentration range of Cu-Pd, while CuPt is the only ever-known example of the $L1_1$ structure. We will show that all of these aspects can be well reproduced by the electronic-structure calculations. (Cu-Pd and Cu-Pt systems will be discussed only briefly in this paper and detailed discussion including the pressure effect will be presented in a separate paper.) Crucial roles of the relativistic effects in the Pt-based alloys will be pointed out. The present analysis also suggests a possibility of realizing the $L1_1$ structure for the Ag-Pd system at low temperatures.

We organize the present paper in the following way. The method of analysis is briefly described in Sec. II and results and discussions are presented in Sec. III. Concluding remarks are made in Sec. IV.

II. METHOD OF ANALYSIS

We will describe the calculational procedure only briefly, as it is essentially the same as that used by Terakura *et al.*⁴

First we calculate the heat of formation of some ordered alloys in reference to its segregation limit. (We deal with nonmagnetic states only, though magnetism may play important roles in the subtle aspects of phase stability for Ni-based alloys.) As for the ordered structures, we adopt A_3B and AB_3 with $L1_2$ (Cu₃Au-type)

<u>39</u> 5792

structure and AB with $L1_0$ [CuAu(I)-type] structure. We use the augmented spherical wave (ASW) method²⁰ including the relativistic effects except the spin-orbit interaction.²¹ The maximum angular momentum of the ASW's is limited to l=2 for Ni, Cu, Pd, and Ag and to l=3 for Pt and Au in order to reproduce a better agreement for the equilibrium lattice constants of pure metals. This choice seems to be arbitrary, but even if l=3 is used for all elements, the qualitative aspects of the results do not change. The heat of formation for $A_m B_{4-m}$ ordered alloy per atom is written as

$$\Delta E_{m}(a) = \frac{1}{4}E(a; A_{m}B_{4-m}) - \frac{m}{4}E(\alpha_{A}; A) - \left[1 - \frac{m}{4}\right]E(a_{B}; B) .$$
(1)

Here a_A and a_B are the equilibrium lattice constants of pure A and B metals, respectively. The dependence of cohesive energy on the lattice constant a is assumed to be

$$E(a; i = A_m B_{4-m}) = \frac{P_i}{a^7} - \frac{Q_i}{a^{3.5}} + R_i$$
(2)

and some calculated values for different *a*'s are fitted with these three parameters P_i , Q_i , and R_i for each system.⁴ The fitting is very accurate within the range of the atomic size calculated in this work.

The second step is to obtain effective many-body interactions v_n 's introduced by Connolly and Williams.¹² They are related to the heat of formation of the ordered alloys through

$$\Delta E_m(a) = \sum_n v_n(a) \xi_{nm} , \qquad (3)$$

where ξ 's are the multisite correlation functions as tabulated in Table I of Ref. 12 and Table I of this paper. In the tetrahedron approximation, five v_n 's (v_0, v_1, \ldots, v_4) are determined by the five ΔE 's of the ordered structures (A and B with fcc, A_3B and AB_3 with $L1_2$, and AB with $L1_0$). The heat of formation of completely disordered alloys is estimated by

$$\Delta E(a_D, x_A; \text{random}) = \sum_n (x_B - x_A)^n v_n(a_D) , \qquad (4)$$

where a_D is the lattice constant at which $\Delta E(a, x_A; \text{random})$ takes a minimum value. These effective many-body interactions can then be used in the

CVM to calculate the free energy at finite temperatures and one can calculate the mixing heat of formation, the order-disorder transition temperature, and other thermodynamic properties.

In the calculation, only the uniform part of the lattice relaxation was taken into consideration. So it was assumed that the two kinds of atoms occupy the lattice points of an undistorted fcc-type structure. (In the real alloy, some local relaxation will occur to lower the energy. The tetragonal lattice distortion of the $L1_0$ structure was also neglected in this calculation.) In order to analyze the contents of the heat of formation, we separate the elastic energy from the total heat of formation of the ordered alloy with a naive picture: the elastic part is defined as the sum of the energy required to compress or expand the constituent metals to the equilibrium volume of the ordered alloy in question. In this definition, the elastic energy is, of course, positive so far as some mismatch exists between the equilibrium lattice constants of the constituents. The remaining part of the heat of formation, which may be attractive or repulsive, may be called the band-structure energy or chemical energy. Although the treatment is very much simplified, the results agree with those obtained by a more sophisticated analysis²² within 15% except Au-Ni and Cu-Pd systems, where the two approaches produce about 25% difference because of the fairly large lattice constant mismatch. In any case, we have found that the qualitative aspects are not affected by the difference in the approach.

III. RESULTS AND DISCUSSIONS

The results of the calculated heat of formation are shown in Fig. 1. The solid circles are the heats of formation of the ordered alloys at zero temperature (the results of the electronic structure calculation) and the solid lines are those of the random alloys. The elastic and the chemical parts of the total heat of formation are also shown in the same figure by open circles and triangles, respectively.

All these results are qualitatively consistent with the experimentally obtained phase diagrams: the system which segregates into two phases at low temperatures has a positive heat of formation implying that the alloy formation is energetically unstable, while the system which forms a uniform solid solution or an ordered alloy has a negative heat of formation. This trend holds even if the

Formula	Structure	ξo	<u></u> لاً	ξ 2	٤з	 54
A	(fcc)	1	1	1	1	1
A_3B	$(L1_2)$	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1
AB	$(L1_0)$	1	Õ	$-\frac{1}{3}$	໐້	1
AB_3	$(L1_{2})$	1	$-\frac{1}{2}$	໐ັ	$\frac{1}{2}$	-1
B	(fcc)	1	-1^{2}	1	-1	1
AB	(<i>L</i> 1 ₁)	1	0	0	0	-1

TABLE I. Multisite correlation functions.

A. Segregation-type systems

The three systems with Ni as one of the constituents (Cu-Ni, Ag-Ni, and Au-Ni) all segregate, but the shapes of the miscibility gap differ entirely among them. The miscibility gap of the Cu-Ni system is narrow, and this system forms a homogeneous solid solution above 600 K. On the other hand, the Ag-Ni system segregates strongly, even above the melting point of Ni (1700 K). The Au-Ni system is intermediate between these two systems. The result of the electronic structure calculation correctly reflects this tendency of segregation: the Ag-Ni system has a very large positive heat of formation while in the Cu-Ni system, the heat of formation is positive, but the absolute value is small. It is therefore expected that Cu and Ni should mix with each other to form a homogeneous solid solution by the entropy effect at relatively low temperatures.



FIG. 1. Calculated heats of formation for (a) Cu-Ni, (b) Ag-Ni, (c) Au-Ni, (d) Cu-Pd, (e) Ag-Pd, (f) Au-Pd, (g) Cu-Pt, (h) Ag-Pt, and (i) Au-Pt systems. Solid circles and solid lines represent the heat of formation of ordered and disordered phases, respectively. The separate contributions from the elastic and chemical parts are shown by open circles and triangles, respectively. The heats of formation of *AB* ordered alloys with structure other than $L1_0$ are also shown in (d) (with *B2* structure), and in (e) and (g) (with $L1_1$ structure) by \times .

<u>39</u>

The ordering energy (the difference of the heat of formation between an ordered alloy and the corresponding random alloy) of the Au-Ni system is larger than that of the Ag-Ni system. The separation of the total heat of formation into the elastic and chemical part seems to be useful to understand the source of the variety among the segregation-type systems. One can find that the elastic energy has large values in systems containing Ni, while it plays a less important role in systems containing Pt. In case of Ni the large mismatch of the atomic size between Ni and the other elements (Ag,Au) prevents them from mixing and forming alloys. On the other hand, Pt does not form alloys even with the elements having about the same size. In this regard, Pt is in clear contrast to Pd which has a tendency of forming alloys with noble metals. It is thought that this nature of Pt is caused by its relatively large cohesive energy.²³ In the heavy elements like Pt, the relativistic effects play more important roles than in lighter elements like Ni and Pd. The point in this case is that the 6s orbital of Pt is pulled closer to nuclei by this effect and the s band is shifted downward in energy to result in an increase of d holes and thereby an enhancement of the *d*-band cohesion. This implies that the attractive interaction between Pt atoms may be strong enough for Pt to segregate in alloys. To confirm this relativistic effect, we calculated the heat of formation of the Ag-Pt system without relativistic correction and made the same analysis (Fig. 2). The result shows that the heat of formation of the Ag-Pt system would take a large negative value without relativistic effects and that the heat of formation of Ag alloys would increase in the order of the Periodic Table, i.e., Ag-Ni, Ag-Pd, and Ag-Pt. [As, Ni, Pd, and Ag are not so heavy, the correction due to relativistic effects is negligible. For example, the change of d-electron number in the atomic sphere by the relativistic effect is from 8.776 (nonrelativistic) to 8.722 (relativistic) for Pd, while from 8.869 to 8.248 for Pt.] The densities of states of the three systems Pd, Pt, and nonrelativistic Pt show in fact that the low-energy tail of the s band is significantly deeper in the case of Pt, compared with Pd and nonrelativistic Pt. The number of delectrons in the atomic sphere, as shown in Table II, is less in Pt than in the other two elements, supporting our



FIG. 2. Calculated heats of formation of the Ag-Pt system without relativistic correction.

TABLE II. Electron-number distribution in the atomic sphere for pure Ni, Pd, and Pt. Pt* corresponds to the calculation without relativistic corrections.

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	S	р	d	
Ni	0.655	0.751	8.593	
Pd	0.620	0.658	8.722	
Pt	0.753	0.820	8.248	
Pt*	0.516	0.494	8.869	

interpretation.

For all the five segregation-type systems studied here, an appreciable asymmetry with respect to the 50%-50% alloy case can be seen in their phase diagrams:¹⁹ in all cases, the solubility limit for Ni and Pt as solute in noble metals is larger than that for the reverse cases. The asymmetry in the calculated results [Figs. 1(a)-1(c), 1(h), and 1(i)] is qualitatively correct but seems to be weaker than the observed one. We will discuss this aspect more quantitatively in a forthcoming paper where theoretical phase diagrams will be presented.

B. Alloy-formation-type systems

The four systems, Au-Pd, Ag-Pd, Cu-Pd, and Cu-Pt, form stable alloys. Among them, only the Au-Pd system is known (with some uncertainty, however) to show the sequence of $L_{12}-L_{10}-L_{12}$ as stable ordered phases,¹⁹ which is compatible with the present theoretical framework. No ordered phases have been observed for the Ag-Pd system. Both of the Cu-Pd and Cu-Pt systems are unique in the sense that the stable structures of the 50%-50% concentration case are B2 (bcc base) for CuPd and L_{11} for CuPt: CuPt is the only ever-known example of the L_{11} structure. Despite these situations, the calculated heats of formation for the four systems are all negative [Figs. 1(d)-1(g)] being consistent with the tendency of alloy formation. However, detailed quantitative analyses reveal interesting features characteristic to each system.

The information of the heat of formation of the ordered alloys have been used in the CVM to calculate the formation enthalpy at finite temperatures and it is compared with experiments for Au-Pd (Ref. 24) and Ag-Pd (Ref. 25) in Figs. 3(a) and 3(b), respectively. In the case of the Au-Pd system, the agreement between the experiment and the calculation is excellent, taking the simplicity in the calculational method into account. Such a good agreement reflects the following aspects: (i) a fairly small size mismatch between Pd and Au causes no trouble of local lattice relaxation in the disordered phases; (ii) the observed ordered phases are correctly taken into account in the present calculation; (iii) the farther neighbor interactions beyond those included in the tetrahedron approximation may be fairly small. Although the first two aspects are obvious, the third one needs some additional proof, which will be discussed later in this section. As for the Ag-Pd system, the agreement between the calculated and the experimental formation enthalpy is poor. While item (i) in the above statements for Au-Pd is true also for



FIG. 3. Experimental and calculated mixing enthalpy of (a) Ag-Pd and (b) Au-Pd systems. Corresponding to the experimental condition, the temperatures were set as 1000 K for Ag-Pd and 298 K for Au-Pd.

Ag-Pd, the other two items may not be applicable to Ag-Pd. We first note that the heat of formation for the $L1_0$ structure is larger than the average of those for the two $L1_2$ structures. This fact implies that Ag-Pd of the $L1_0$ structure is unstable with regard to a decomposition into Ag_3Pd and $AgPd_3$ of the $L1_2$ structure. Because of this, we searched for more stable structures for AgPd. We chose B2 and $L1_1$ structures as possible candidates considering that they are observed for CuPd and CuPt, respectively. It turned out that the B2 structure is slightly less stable than the $L1_0$ structure while the $L1_1$ structure is definitely stabilized as is shown by \times in Fig. 1(e). This fairly large additional stabilization energy may suggest a possibility of realizing AgPt with the $L1_1$ structure at low temperatures. Experimental check of this prediction is highly desirable because the $L1_1$ structure has been thought to be unique for CuPt. Due to the same reason as before, the $L1_2$ structure of AgPd₃ is unstable now. We tried the $D0_{22}$ structure but it was less stable than the $L1_2$ structure. At present, we do not know whether there may be a stable ordered phase of AgPd₃ or not.

As we mentioned before, the negative heats of formation for the Cu-Pt and Cu-Pd systems are consistent with the experimental observation of the existence of ordered phase, despite our use of inappropriate structures. For both systems, we should note that the chemical energy is large and negative to overwhelm the large and positive elastic energy due to the large atomic size mismatch. However, Fig. 1(g) clearly indicates the inconsistency of our use of the $L1_0$ structure for CuPt in the sense that this phase should be unstable with regard to the decomposition into a mixture of Cu₃Pt and CuPt₃. It turned out that the observed $L1_1$ structure does in fact have a much lower energy than the $L1_0$ structure [X in Fig. 1(e)]. As for Cu-Pd, the assumed $L I_0$ structure is stable within the configurations studied here. However, as shown by \times in Fig. 1(d), the B2 structure is more stable for CuPd. In a subsequent paper, we will present detailed arguments on the microscopic origins of the structural stability of CuPd and CuPt.

Before closing this section, we discuss briefly some additional aspects of the tetrahedron approximation associated with the interaction-energy expansion of Eq. (3). Table I shows the multisite correlation functions ξ for $L1_0$, $L1_1$, and $L1_2$ structures in the tetrahedron approxi-

TABLE III. Heats of formation of AgPd, AuPd, and CuPt ordered alloys with the $L1_0$ and $L1_1$ structures (in mRy). Approximate values for the $L1_1$ structure in the tetrahedron approximation [Eq. (5)] are also shown in the third column.

	<i>L</i> 1 ₀	$L1_1$ (tetrahedron)	$L1_1$ (true)	
AgPd	-1.0	-0.9	-3.8	
AuPd	-7.6	-5.3	-7.0	
CuPt	-8.6	-6.6	-15.2	

mation. ξ of $L1_1$ is just the average of those of $L1_2$ for A_3B and AB_3 and is different from that of $L1_0$. This implies two facts. First, we can estimate the heat of formation for the $L1_1$ structure within the tetrahedron approximation $\Delta E (L1_1; \text{tetrahedron})$, using ξ for $L1_1$ in Table I and the interaction parameters v_0 to v_4 obtained earlier. $\Delta E (L1_1; \text{tetrahedron})$'s for Ag-Pd, Au-Pd, and Cu-Pt are presented in the third column of Table III. Table III also shows the heat of formation for the $L1_0$ structure $\Delta E (L1_0; \text{true})$ in the second column, which is rigorous within the present theoretical framework. The difference between the two energies can be expressed as

$$\Delta E(L 1_0; \text{true}) - \Delta E(L 1_1; \text{tetrahedron}) = -\frac{1}{3}v_2 + 2v_4 \quad .$$
(5)

For the alloy-formation-type systems, v_2 is generally positive, so that the right-hand side can be positive only when v_4 is sufficiently large and positive. However, this is not the case for all the three cases as is shown in Table III.²⁶ Therefore the tetrahedron approximation clearly breaks down for AgPd and CuPt. Second, the true heat of formation of the $L1_1$, $\Delta E(L1_1;true)$ can be obtained by performing the total-energy calculations directly for the $L1_1$ structure. The results were already shown in Figs. 1(e) and 1(g) by \times and listed again in the fourth column of Table III. Now the difference between $\Delta E(L1_1;true)$ and $\Delta E(L1_1; \text{tetrahedron})$ comes from the farther neighbor interactions beyond those included in the tetrahedron approximation. One can see that such interaction is significant in AgPd and CuPt to make the $L1_1$ structure more stable than the $L1_0$ structure and is insignificant in AuPd. The last fact was thought to be one of the reasons of the good agreement between the calculated and experimental formation enthalpy as shown in Fig. 3(b).

IV. CONCLUSION

We studied the phase stability of nine binary alloys which are composed of one of (Ni, Pd, Pt) and one of (Cu, Ag, Au) with the electronic-structure calculations. Most of the qualitatively important aspects of the phase diagrams of these alloys were correctly reproduced. It will be possible to obtain even a quantitative agreement by including longer-range interatomic interactions in the cluster-variation method, as was suggested in the case of AgPd, and by including the lattice relaxation effect as was discussed by Wei *et al.*⁷ By separating the heat of formation into the elastic and chemical parts, we interpreted the origins of the difference in phase diagrams of these alloys. In particular, the importance of the relativistic effect in Pt was clearly demonstrated. In the present work, we adopted the tetrahedron approximation of Connolly and Williams¹² in which only the $L1_0$ and $L1_2$ structures are taken into account as ordered phases. It was pointed out that in some cases, for example AgPd and CuPt, the inappropriateness of the choice of ordered structures was disclosed as the instability of a certain structure. With this process, we came to a conclusion that the $L1_1$ structure may be realized also for AgPd. This prediction should be checked experimentally, although the similarity of the x-ray scattering factor between Ag and Pd may make the experimental determination of the ordered phases of Ag-Pd rather difficult.

Despite several new findings, some important aspects remain unsolved. For example, we have not understood the microscopic origins of the difference among Cu, Ag, and Au. Au has the largest cohesive energy among them and at the same time has the greatest capability of forming alloys with other metals. This aspect is in contradiction with our story for Pt. The Cu-based alloys, Cu-Ni, Cu-Pd, and Cu-Pt, show rather strange behavior also. Among the three alloys, only Cu-Ni has a tendency of

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segregation despite the fact that the atomic size mismatch is the smallest for this system. The other way around, Pt forms alloy with Cu but not with Ag and Au. In this case, Cu-Pt has the largest atomic size mismatch. We are now analyzing these puzzling aspects. Full discussions on the thermodynamic properties of the alloys studied here will be presented in a forthcoming paper and more details about the structural problems for Cu-Pd and Cu-Pt will be discussed elsewhere.

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- ²⁶The chemical part of $\Delta E(L1_1;$ tetrahedron) for AB is equal to the average of the corresponding parts for the two separate $L1_2$ phases of A_3B and AB_3 . However, $\Delta E(L1_1;$ tetrahedron) for AB includes the elastic energy increase due to the size mismatch between A_3B and AB_3 , and thereby is larger than the average of the heats of formation of A_3B and AB_3 .