

Alloy Gene Gibbs Energy Partition Function and Equilibrium Holographic Network Phase Diagrams of AuCu-Type Sublattice System

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ABSTRACT

Taking AuCu-sublattice system as an example, we present two discoveries and a method. First, the alloy gene sequences are the central characteristic atom sequences in the basic coordination cluster sequences. Second, the transmission mode of the information about structures and properties of the alloy genes is described by the alloy gene Gibbs energy partition function. The most valuable method in the system sciences is "the whole obtained from a few parts". We have established the alloy gene database and holographic alloy positioning system of the Au-Cu system, as well as alloy gene Gibbs energy partition function and equilibrium holographic network phase diagrams of the AuCu-type sublattice system. It means that a standard way for researchers to share predictive algorithms and computational methods may be produced during designing advanced alloys.

Keywords: Alloy Gene Gibbs Energy Partition Function; Holographic Alloy Positioning System; Equilibrium Holographic Network Phase Diagrams; Systematic Metal Materials Science; Au-Cu System

1. Introduction

There are 81 kinds of metal elements accounting for 79% in the Element Periodic Table, of which several alloy system groups can be composed: $C_{81}^2 = 3240$ kinds of binary alloy systems, $C_{81}^3 = 85320$ kinds of ternary alloy systems, $C_{81}^4 = 1663740$ kinds of quaternary alloy systems, and so on. In order to quickly and efficiently discover advanced alloys, we have to establish the Systematic Metal Materials Science (SMMS) by new thinking modes and methods of system sciences [1] (Supplementary Section 1).

"A diversity of structures of a system is attributed to combination and arrangement of structural units in the basic structure unit sequences". It is the first philosophic proposition of system sciences. Now, we deliver an extensive definition of the gene sequence: the gene sequence is a basic structure unit sequence carrying a set of transmission information about structures and properties for determining diversity of structures and properties of a system, which may be a biologic or non-biologic system. Therefore, it is our first task to seek alloy gene (AG) sequences for establishing the SMMS framework.

We have discovered that the AG-sequences are the central characteristic atom sequences in the basic coordination cluster sequences (**Supplementary Figure S1(c)**). In the fcc-based lattice Au-Cu system, the basic coordination clusters $B_i^{Au} = A_i^{Au} \cdot [(I-i)Au + iCu]$ and $B_i^{Cu} = A_i^{Cu} \cdot [(I-i)Au + iCu]$ consist of the central characteristic atoms A_i^{Au} and A_i^{Cu} respectively, and the nearest coordinative configuration [(I-i)Au + iCu]. Here, *I* is the coordinative number and equal to 12; *i* is the number of Cu-atoms and can change from 0 to 12; (*I-i*) is the number of Au-atoms. Therefore, the AG-sequences of the Au-Cu system are the central characteristic atom A_i^{Au} - and A_i^{Cu} -sequences respectively in the B_i^{Au} - and B_i^{Cu} -sequences. They may be used to replace

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atomic pair-sequence [2] and atomic cluster-sequences [3,4], as well as other structural unit sequences [5-7] in the current alloy theories, because they have more analogous characters to biologic gene sequences: (1) The AG A_{i}^{Au} - and A_{i}^{Cu} -sequences carry a set of transmission information: coordinative configurations, electronic structures, physical and thermodynamic properties, which have been obtained by the AG-theory (Supplementary Section 1). (2) Based on the AG-information, a Holographic Alloy Positioning (HAP) system of the Au-Cu system has been established by "the Whole Obtained from a few Parts" (WOP) method (Section 2). (3) AGinformation may be transmitted to alloy phases by AG-Gibbs energy partition function (Section 3). The Equilibrium Holographic Network Phase (EHNP) diagrams of the AuCu-type sublattice system have been obtained by the HAP system (Section 4). (4) Alloy genes may be interconvertible, the essence of the order disorder transition can be explained by the AG-concentrations distributions (Figure 4). (5) Alloy genes will be used to design alloys, which may be called as the AG-arranging design.

2. Holographic Alloy Positioning System

The main objective of the HAP system of an alloy system is to provide a set of EHNP diagrams for designing advanced alloys. The HAP system of the Au-Cu system consists of AG-theory, AG-Gibbs energy partition functions of Au₃Cu-, AuCu- and AuCu₃-type sublattice systems and balance theory between sublattice systems (**Figure 1**). Its performing procedures are as follows: (1) The first step is to establish AG-database obtained by the AG-theory, only using experimental mixed enthalpies



Figure 1. Holographic alloy positioning system of Au-Cu system.

 $(\Delta H_{exp}^{m}(T))$ and mixed volumes $(\Delta V_{exp}^{m}(T))$ of the AuCu and AuCu₃ compounds [8,9] (**Supplementary** Figures S2 and S5). (2) The second step is respectively to establish EHNP diagrams of the Au₃Cu-, AuCu- and AuCu₃-type sublattice systems, according to the AG-Gibbs energy partition functions of Au₃Cu-, AuCu- and AuCu₃-type sublattice systems and the Bragg-Williams sublattice models [10,11]. (3) The third step is to establish EHNP diagrams of the Au-Cu system based on the balance theory between sublattice systems. So much information is obtained by computing technique and a few experimental data, *i.e.*, WOP method (Supplementary Section 1.5).

3. AG-Gibbs Energy Partition Function

"A diversity of properties of a system is attributed to contents and transmission mode of the information of basic structure unit sequences". It is the second philosophic proposition of system sciences. The transmission mode of AG-information is described by AG-Gibbs energy $\Omega(x,T)$ -partition function, which consists of the AG-Gibbs energy transmission $G^*(x,T)$ -function and AG-arranging structure $g(x_i^{Au}(x,T), x_i^{Cu}(x,T))$ -function (Supplementary Section 2).

An equilibrium order \rightleftharpoons disorder transition of the AG-arranging structure of an alloy is defined as that "the AG-Gibbs energy levels $(G_i^{Au}(T), G_i^{Cu}(T))$ and AG-concentrations $(x_i^{Au}(x,T), x_i^{Cu}(x,T))$ occupied at the $G_i^{Au}(T)$ - and $G_i^{Cu}(T)$ -energy levels can respond immediately and change synchronously with each small variation in temperature". It has following general behaviors: (1) The order \rightarrow disorder transition upon heating and disorder \rightarrow order transition upon cooling proceed along the same minimal mixed Gibbs energy $\Delta G_{\min}^m - T$ path, *i.e.*, there exists no a so-called hysteresis phenomenon between both transitions. (2) The $\Delta G_{\min}^m - T$ path is continuous and has no jumping phenomenon.

4. EHNP-Diagrams of AuCu-Type Sublattice System

"Properties are determined by structures; properties should be suitable for environments; environments change structures". It is the fourth philosophic proposition of system sciences (the third one is presented in Supplementary Section 1.2). The man's knowledge of relationships of structures, properties and temperature for alloys has been changed from single causality to systematic correlativity, due to discoveries of alloy gene sequences and their information transmission mode, and establishments of the AG-Gibbs energy partition function and HAP system. This systematic correlativity may be described by a set of HNP diagrams.

An EHNP diagram consists of curves linked by the

network (q, x, T)-points as functions of the state q, composition x and temperature T. Each position inside the phase region and on the phase boundary (PB) curve may be marked by the (q, x, T)-point, where the alloy state q denotes the AG-concentrations $(x_i^{Au} \text{ and } x_i^{Cu})$, mixed Gibbs energy ΔG^m , order degree σ , configurational entropy S^c , mixed characteristic Gibbs energy ΔG^{*m} , mixed enthalpy ΔH^m , mixed potential energy ΔE^m , mixed volume ΔV^m , generalized vibration free energy X^{ν} , generalized vibration energy U^{ν} , generalized vibration entropy S^{ν} , mixed heat capacity ΔC_n^m , mixed thermal expansion coefficient $\Delta \alpha^m$ and activities (a_{Au} and a_{Cu}). Each kind of the q-EHNP diagram includes four diagrams: three-dimension q - x - T phase diagram, two-dimension $q_x - T$, $T_q - x$ and $q_T - x$ path phase diagrams. In the text the $\Delta G^m(x,T)$, $\sigma(x,T)$, $S^c(x,T)$, $x_i^{\text{Au}}(x,T)$ and $x_i^{\text{Cu}}(x,T)$ EHNP diagrams are presented. The other EHNP diagrams are shown in Supplementary Figure 6. The calculations of all diagrams are performed by compositional step $\Delta x =$ 0.5at.% and temperature step $\Delta T = 1$ K. These diagrams are interconnected. Therefore, a set of information about structures, properties and their variations with temperature of a designed alloy in the equilibrium state can be predicated by interlinking method and without calculation.

4.1. Mixed Gibbs Energy and Order Degree EHNP Diagrams

Using the minimal mixed Gibbs energy path method, we have obtained the three-dimension $\Delta G^m - x - T$ and $\sigma - x - T$ EHNP diagrams, and two-dimension $\Delta G_x^m - T$, $\sigma_x - T$, $T_{\Delta G^m} - x$, $T_{\sigma} - x$, $\Delta G_T^m - x$ and $\sigma_T - x$ path phase diagrams. From these diagrams, we have obtained following main understandings: (1) From **Figures 2(a)** and **(a')**, it can be known that there are ordered phase region (denoted by the symbol "O"), disordered phase region (denoted by the symbol "D"), AuCu compound consisted of A_8^{Au} and A_4^{Cu} genes (denoted by the symbol "C"), and the $\Delta G_{PB}^m(x,T)$ - and

 $\sigma_{PB}(x,T)$ -phase boundary curves in the each diagram. (2) From **Figures 2(b)** and **(b')**, it can be known that the Au_{47.5%}Cu_{52.5%} alloy has the highest critical temperature $T_c = 836$ K, which is higher than the critical temperature (833K) of the Au_{50%}Cu_{50%} alloy, that agrees with the experimental phenomenon (see **Figure 2(c')**). (3) From **Figures 2(c)** and **(c')**, it can be known that the phase diagrams can be respectively divided into the several regions by some $T_{\Delta G^m} - x$ and $T_{\sigma} - x$ curves. It is very useful to enrich the EHNP diagrams. (4) From **Figure 2(c')**, we have discovered that all experimental jumping temperatures (T_j) , which are denoted by symbols " * "[12] and "0" [13], approach to the iso-order $T_{\sigma=0.65} - x$ curve. The experimental $T_j - x$ curve is very analogous to the equilibrium $T_{PB} - x$ curve, *i.e.*, $T_c - x$ curve. However, the experimental jumping longrange order degree (σ_j^{LR}) of the AuCu compound is about 0.8, and the corresponding short-range order degrees (σ^{SR}) is about 0.40. These phenomena show that the experimental order \rightarrow disorder transition belongs in metastable and non-equilibrium. (5) The isocompositional $\Delta G_x^m - T$ and $\sigma_x - T$ path diagrams (**Figures 2(d)** and (**d'**)) will be used to establish EHNP diagrams of the Au-Cu system.

4.2. Configuration Entropy and AG-Concentration EHNP Diagrams

The configuration entropy $(S^{c}(x,T))$ and AG-concentration $(x_i^{Au}(x,T), x_i^{Cu}(x,T))$ EHNP diagrams have been established, based on the AG-arranging structure $g(x_i^{Au}(x,T),x_i^{Cu}(x,T))$ -function in the $\Omega(x,T)$ -function. From Figures 3 and 4, it can be known that each kind of q-EHNP diagram includes not only the 4-type diagrams indicated above, but also other-type diagrams. From Figure 3, we have obtained following main understandings: (1) The configuration entropy of each ordered alloy can change continually from the configuration entropy of the maximum order degree σ_{\max} state to one of the ideal disordered state, that need not to induct any parameter. It means that we should take the ideal disordered state as the standard. (2) The structural units used for calculating configuration entropy should be in agreement with the structural units used for calculating corresponding energy levels. These are two rules to establish partition function. However, these rules are often neglected in the currently used thermodynamic models of alloy phases [14].

From Figure 4, we have obtained following main understandings: (1) The AG-concentration EHNP diagram may be described by two modes: the $x_i^{Au} - x - T$ and $x_i^{Cu} - x - T$ EHNP diagrams (Figures 4(a) and (a')) in the AG-arranging crystallography [15], where the x_i^{Au} and x_i^{Cu} are the probabilities occupied at the lattice points; the $x_i^{Au} - x - i$ and $x_i^{Cu} - x - i$ EHNP diagrams (Figures 4(a), (a'), (c) and (c')) in the AG-arranging band theory, where the x_i^{Au} and x_i^{Cu} are the probabilities occupied at the $G_i^{Au}(T)$ and $G_i^{Cu}(T)$ energy levels. (2) There exists a probability of AG-arranging structures in the alloy phases, which is described by the AGconcentration $(x_i^{Au}(x,T), x_i^{Cu}(x,T))$ functions. This probability leads to atom-scale heterogeneity of properties of alloys. (3) There exists an emergent phenomenon of AG-arranging structures in the ordered alloy phases, which is defined as that some AG-concentrations of the alloy in ordered state are larger than one in the disordered state, such as x_9^{Au} , x_8^{Au} , x_7^{Au} , x_3^{Cu} , x_4^{Cu} and x_5^{Cu} (Figures 4(b)-(c')). (4) Alloy genes may be inter-



Figure 2. Mixed Gibbs energy and order degree EHNP diagrams. (a), (a'), Three-dimension $\Delta G^m - x - T$ and $\sigma - x - T$ diagrams with phase boundary curves $\Delta G_{PB}^m(x,T)$ and $\sigma_{PB}(x,T)$; (b), (b'), Two-dimension isocompositional $\Delta G_x^m - T$ and $\sigma_x - T$ path diagrams with phase boundary curves $\Delta G_{PB}^m(T)$ and $\sigma_{PB}(T)$; (c), (c'), Two-dimension iso-mixed Gibbs energy $T_{\Delta G^m} - x$ and iso-order degree $T_{\sigma} - x$ diagrams with phase boundary curves $\Delta G_{PB}^m(x)$ and $\sigma_{PB}(x)$; (d), (d'), Two-dimension isothermal $\Delta G_T^m - x$ and $\sigma_T - x$ diagrams with phase boundary curves $\Delta G_{PB}^m(x)$ and $\sigma_{PB}(x)$.



Figure 3. Configuration entropy EHNP diagrams of the AuCu-type sublattice system. a) Three-dimension $S^c - x - T$ phase diagram with phase boundary curve $S_{PB}^{c}(x,T)$; b) Three-dimension $S^{c,Au} - x - T$ phase diagram with phase boundary curve $S_{PB}^{c,Au}(x,T)$ of the Au-component; c) Three-dimension $S^{c,Cu} - x - T$ diagram with phase boundary curve $S_{PB}^{c,Cu}(x,T)$ of the Au-component; c) Three-dimension $S^{c,Cu} - x - T$ diagram with phase boundary curve $S_{PB}^{c,Cu}(x,T)$ of the Cu-component; d) Three-dimension $(S^{c,Au}, S^{c,Cu}) - x - T$ combinational phase diagrams with phase boundary curves $S_{PB}^{c,Au}(x,T)$ and $S_{PB}^{c,Cu}(x,T)$ of the Au- and Cu-components.

convertible. The essence of the order \rightarrow disorder transition of the stoichiometric AuCu compound consisting of A_8^{Au} - and A_4^{Cu} -alloy genes is that the A_8^{Au} - and A_4^{Cu} -alloy genes are split into the A_i^{Au} - and A_i^{Cu} -sequences, respectively; otherwise the essence of the disorder \rightarrow order transition of the stoichiometric disordered AuCu alloy is that the A_i^{Au} - and A_i^{Cu} -sequences are degenerated into the A_8^{Au} - and A_4^{Cu} -alloy genes (**Figures 4(d)** and (**d**')).

5. Conclusions

In this paper, these creative achievements are of broad significances: (1) Four philosophic propositions of system sciences will prove stimulating to researchers working on general system sciences, matter systems and social systems, and who may well find value in using them as a philosophic thinking logic for establishing various system science frameworks. (2) the AG-sequence instead of compositional atoms, compositional atom pairs and compositional atom clusters successively proposed during last one hundred years will prove stimulating to researchers working on physics, chemistry and material science, and who may well find value in using it as basic structure unit sequence for establish SMMS framework. (3) The AG-Gibbs energy partition function composed of AG-Gibbs energy level model of chemical potential and AG-statistic model of entropy replaces two current functions: one is composed of atom pair energy level model



Figure 4. AG-concentration EHNP diagrams. (a), (a'), Three-dimension $x_i^{Au} - x - T$ and $x_i^{Cu} - x - T$ diagrams; (b), (b'), Three-dimension $x_i^{Au} - x - i$ and $x_i^{Cu} - x - i$ diagrams of the ordered Au_(1-x)Cu_x alloys with maximum order degree σ_{max} at 0K; (c), (c'), Three-dimension $x_i^{Au} - x - i$ and $x_i^{Cu} - x - i$ diagrams of the perfectly disordered Au_(1-x)Cu_x alloys; (d), (d'), Three-dimension $x_i^{Au} - T - i$ and $x_i^{Cu} - T - i$ path diagrams of disordering for the stoichiometric AuCu compound.

of chemical potential and compositional atom statistic model of entropy; another one is composed of electron energy level model of chemical potential and compositional atom cluster model of entropy. That will prove stimulating to researchers working on physics, chemistry and materials science, and who may well find value in using it as a theoretic foundation for establishing alloy system sciences of binary and ternary alloy systems. (4) The HAP system based on the AG-Gibbs energy partition function and the WOP method will prove stimulating to researchers working on physics, chemistry and materials science, and who may well find value in using it as a platform for establishing EHNP diagrams of alloy systems. (5) The great holographic alloy database consisting of AG-database and EHNP diagrams of alloy systems will prove stimulating to others working on materials engineering, and who may well find value in using it as a tool for materials discovery, design, manufacture and application, which may be called as "AG-Arranging (AGA) Engineering". The investigation in AuCu-type sublattice system may be analogous to Mendel's investigation in genetic characters of peas.

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Supplementary Information

1. Alloy Gene (AG) Theory of Au-Cu System

1.1. New Thinking Modes of System Sciences

'A diversity of structures of a system is attributed to combination and arrangement of structure units in the basic structure unit sequence'. It is the first philosophic proposition of system sciences proposed by us. For examples, the diversity of species in the biological system is attributed to splices of some biological genes in the biological gene sequences; the diversity of free atom states in the free atom system is attributed to arrangement of electrons in the electronic orbital (state) sequence described by four quantum numbers; the diversity of crystalline species in the geometric crystallography is attributed to combination of symmetric elements in the symmetric element sequence; the diversity of music scores in the music system is attributed to combination and arrangement of notes in the music note sequence, and so on. This philosophic proposition guides us to seek the most important structure units for designing advanced alloys. They are the central characteristic atoms in the basic coordination clusters, and called as alloy genes (AG).

"A diversity of properties of a system is attributed to the contents and transmission mode of the information of the basic structure unit sequences". It is the second philosophic proposition of system sciences proposed by us. It is also essential condition to establish a systematic science theory of a certain system. It is a protracted and tortuous history to research structures, properties, evolutions and functions of the biologic gene sequences for establishing biosystematics. It is another good example to research structures, properties, evolutions and functions of electronic state sequences for establishing systematic science of free atom system. Through a longterm exploring we have proposed a fictitious structure unit (Supplementary Section 1.3), which is the characteristic crystal consisted of the same alloy genes with known potential energy and volume, and with the same based lattice to the alloy system. Then, we have established the valence bond theory and thermodynamics of characteristic crystals. By both these theories, we can calculate the valence electron structures of characteristic crystals, which may represent ones of alloy genes, and the physical and thermodynamic properties of characteristic crystals, which may represent contributions of alloy genes to properties of alloys. Now, we have discovered that the transmission mode of the AG-in-formation about structures and properties can be described by the AG-Gibbs energy partition function.

1.2. Structural Levels of Alloy Systems

"The complexity and entirety of a complex system are

attributed to the multilevel of the structures and properties and to the various correlatives between different structural levels, between different properties and between the structures and properties." It is the third philosophic proposition of system sciences proposed by us.

The SMMS framework contains three levels: the electron-structures of atoms, atom- and electron (valence bond)-structures of phases and phase-structures of organizations (Supplementary Figure S1(a)), which are simplified as atom-, phase- and organization-levels, respectively. The traditional crystallography and thermodynamics of alloys contain phase-level and organizationlevel. The first-principles electron theory of alloys belongs in the electron-structures of phases (Supplementary Figure S1(b)). Therefore, traditional alloy theories have no atom-level theory, *i.e.*, AG-theory.

1.3. Structural Unit Sequences of the Au-Cu Alloy System

In order to explain diversities of structures and properties of alloy phases, we proposed three structural unit sequences.

Basic coordination cluster B-sequences:

basic coordination cruster *D*-sequences. $B_0^{Au} \cdots B_i^{Au} \cdots A_{12}^{Au}$; $B_0^{Cu} \cdots B_i^{Cu} \cdots B_{12}^{Cu}$. They are formed by the central characteristic atoms (A_i^{Au}, A_i^{Cu}) and the nearest coordinative configuration [(12-i)Au + iCu]. The alloy phase is formed by the Basic Coordination Cluster Overlapping (Simplified as BCO model) (Supplementary Figure S1(c)).

Alloy genes A-sequences: $A_0^{Au} \cdots A_i^{Au} \cdots A_{12}^{Au}$; $A_0^{Cu} \cdots A_i^{Cu} \cdots A_{12}^{Cu}$. They are the central characteristic atoms of basic coordination clusters. The alloy phase is formed by the Alloy Gene Arranging (Simplified as

AGA model) (Supplementary Figure S1(c)). Characteristic crystal C-sequences: $C_0^{Au} \cdots C_i^{Au} \cdots C_{12}^{Au}$; $C_0^{Cu} \cdots C_i^{Cu} \cdots C_{12}^{Cu}$. Each fictitious characteristic crystal consists of the same characteristic atoms. The alloy phase is formed by the Characteristic Crystal Mixing (Simplified as CCM model) (see Supplementary Figure S1(d), Supplementary Section 1.6).

Recently, we have discovered that the alloy gene sequences are very useful to design advanced alloys.

1.4. The Separated Theory of Potential Energies and Volumes of Alloy Genes

The AG-theory consists of three parts (Supplementary Figure S2(a)): separated theory of potential energies and volumes of alloy genes [16,17], valence bond theory [18,19] and thermodynamics of characteristic crystals (see Equations (9) to (24)).

The extensive properties q(x,T), $q_A(x,T)$,

 $q_{R}(x,T)$ functions of a given alloy phase and its components can be obtained by a transmission law of the



Figure S1. Theoretic levels and three structural unit sequences. a) Theoretic levels in SMMS framework; b) Theoretic levels in the traditional alloy theory; c) Basic coordination cluster sequences and AG-sequences: $B_0^{Au} \cdots B_8^{Au} \cdots B_{12}^{Au}$, $B_{12}^{Cu} \cdots B_4^{Cu} \cdots B_0^{Cu} \cdots B_0^{Cu}$ and $A_0^{Au} \cdots A_8^{Au} \cdots A_{12}^{Au}$, $A_{12}^{Cu} \cdots A_4^{Cu} \cdots A_0^{Cu}$; d) The characteristic crystal-sequences: $C_0^{Au} \cdots C_8^{Au} \cdots C_{12}^{Au}$, $C_{12}^{Cu} \cdots C_4^{Cu} \cdots C_0^{Cu}$.



Figure S2. AG-theory and AG-properties. a) AG-theory based on the experimental techniques or the first-principles electron theory of alloys; b), c) AG-potential energies ε_i^{Au} - and ε_i^{Cu} -sequences, v_i^{Au} - and v_i^{Cu} -sequences; d), e) Potential energy curves of alloy genes: $W_0^{Au}(r)\cdots W_8^{Au}(r)\cdots W_{12}^{Au}(r)$, $W_{12}^{Cu}(r)\cdots W_4^{Cu}(r)\cdots W_0^{Cu}(r)$; f), g) Gibbs energy curves: $G_0^{Au}(T)\cdots G_8^{Au}(T)\cdots G_{12}^{Au}(T)$, $G_{12}^{Cu}(T)\cdots G_0^{Cu}(T)$.

extensive q-properties of alloy genes, which may be simplified as AGT law:

$$\begin{cases} q(x,T) = \sum_{i=0}^{I} x_{i}^{A}(x,T) q_{i}^{A}(T) + \sum_{i=0}^{I} x_{i}^{B}(x,T) q_{i}^{B}(T) \\ q_{A}(x,T) = \sum_{i=0}^{I} x_{i}^{A}(x,T) q_{i}^{A}(T) / x_{A} \\ q_{B}(x,T) = \sum_{i=0}^{I} x_{i}^{B}(x,T) q_{i}^{B}(T) / x_{B} \end{cases}$$
(1)

where, the *q* denotes potential energy (*E*) and volume (*v*), which are the functions as temperature (*T*); the $x_i^A(x,T)$ and $x_i^B(x,T)$ are the concentrations of the alloy genes; which are the functions of the composition (*x*) and temperature (*T*); x_A and x_B denote compositions of the *A* and *B* components, respectively.

In order to make the Equation (1) become the simple, applicable and separable $q(x,T,\sigma)$ function, three type relations of q_i^A and q_i^B with *i* have been designed:

(i)Type I of linear relation,

$$\begin{cases} q_i^A = q_0^A + (i/I) (q_I^A - q_0^A) \\ q_i^B = q_I^B + [(I-i)/I] (q_0^B - q_I^B) \end{cases}$$
(2)

(ii)Type II of concave parabola relation,

$$\begin{cases} q_i^A = q_0^A + (q/I)^2 (q_I^A - q_0^A) \\ q_i^B = q_I^B + [(I-i)/I]^2 (q_0^B - q_I^B) \end{cases}$$
(3)

(iii)Type III of convex parabola relation,

$$\begin{cases} q_{i}^{A} = q_{0}^{A} + (2i/I)(q_{I}^{A} - q_{0}^{A}) - (i/I)^{2}(q_{I}^{A} - q_{0}^{A}) \\ q_{i}^{B} = q_{I}^{B} + [2(I-i)/I](q_{0}^{B} - q_{I}^{B}) \\ -[(I-i)/I]^{2}(q_{0}^{B} - q_{I}^{B}) \end{cases}$$
(4)

where, the q_0^A and q_I^B denote, respectively, *q*-properties of the primary state alloy genes; the q_I^A and q_0^B denote, respectively, *q*-properties of the terminal state alloy genes.

By combining Equations (2)-(4) and substituting them into Equation (1), nine q(x,T) functions can be obtained. In **Supplementary Table S1** the nine general q(x,T)-functions of alloy phases can be used to compounds, ordered and disordered alloy phases. In **Supplementary Table S2**, the nine q(x,T)-functions can be used for the disordered alloy phases only.

1.5. Methodology

The most valuable method in the systematic science is "the whole obtained from a few parts", which may be simplified as the WOP method. It means that a system can be reproduced from it's a few parts. Such as the whole of a tree can be reproduced from a seed, a branch or even a leaf of this tree. It means also that the whole information of a system can be obtained from the infor-

Table S1. Nine general q(x,T)-functions of alloy phases at T K^{*}.

No.	Туре А В	Functions
1	ΙI	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left(\frac{i}{I}x_{i}^{A}\right) \left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \sum_{i=0}^{I} \left(\frac{I-i}{I}x_{i}^{B}\right) \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)$
2	I II	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left(\frac{i}{I}x_{i}^{A}\right) \left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \sum_{i=0}^{I} \left[\left(\frac{I-i}{I}\right)^{2}x_{i}^{B}\right] \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)$
3	I III	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left(\frac{i}{I}x_{i}^{A}\right) \left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \sum_{i=0}^{I} \left[\frac{2I(I-i) - (I-i)^{2}}{I^{2}}x_{i}^{B}\right] \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)$
4	II I	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left[\left(\frac{i}{I}\right)^{2} x_{i}^{A} \right] \left(q_{I}^{A}(T) - q_{0}^{A}(T) \right) + \sum_{i=0}^{I} \left(\frac{I-i}{I} x_{i}^{B} \right) \left(q_{0}^{B}(T) - q_{I}^{B}(T) \right)$
5	II II	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left[\left(\frac{i}{I}\right)^{2} x_{i}^{A} \right] \left(q_{I}^{A}(T) - q_{0}^{A}(T) \right) + \sum_{i=0}^{I} \left[\left(\frac{I-i}{I}\right)^{2} x_{i}^{B} \right] \left(q_{0}^{B}(T) - q_{I}^{B}(T) \right)$
6	II III	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left[\left(\frac{i}{I}\right)^{2} x_{i}^{A} \right] \left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \sum_{i=0}^{I} \left[\frac{2I(I-i) - (I-i)^{2}}{I^{2}} x_{i}^{B} \right] \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)$
7	III I	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left(\frac{2Ii - i^{2}}{I^{2}}x_{i}^{A}\right) \left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \sum_{i=0}^{I} \left(\frac{I - i}{I}x_{i}^{B}\right) \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)$
8	III II	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum_{i=0}^{I} \left(\frac{2Ii - i^{2}}{I^{2}}x_{i}^{A}\right) \left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \sum_{i=0}^{I} \left[\left(\frac{I - i}{I}\right)^{2}x_{i}^{B}\right] \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)$
9	III III	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \sum \left(\frac{2Ii - i^{2}}{I^{2}}x_{I}^{A}\right) \left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \sum_{i=0}^{I} \left[\frac{2I(I - i) - (I - i)^{2}}{I^{2}}x_{I}^{B}\right] \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)$

*: Here, the $x_{i}^{A} = x_{i}^{A}(x,T)$ and $x_{i}^{B} = x_{i}^{B}(x,T)$.

427

No.	Type A B	Functions
1	ΙI	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + x_{A}x_{B}\left(\left(q_{I}^{A}(T) - q_{0}^{A}(T)\right) + \left(q_{0}^{B}(T) - q_{I}^{B}(T)\right)\right)$
2	I II	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + x_{A}x_{B}(q_{I}^{A}(T) - q_{0}^{A}(T)) + \frac{(I-1)x_{A}^{2}x_{B} + x_{A}x_{B}}{I}(q_{0}^{B}(T) - q_{I}^{B}(T))$
3	I III	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + x_{A}x_{B}(q_{I}^{A}(T) - q_{0}^{A}(T)) + \frac{(I-1)x_{A}x_{B}^{2} + Ix_{A}x_{B}}{I}(q_{0}^{B}(T) - q_{I}^{B}(T))$
4	II I	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \frac{(I-1)x_{A}x_{B}^{2} + x_{A}x_{B}}{I}(q_{I}^{A}(T) - q_{0}^{A}(T)) + x_{A}x_{B}(q_{0}^{B}(T) - q_{I}^{B}(T))$
5	II II	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \frac{(I-1)x_{A}x_{B}^{2} + x_{A}x_{B}}{I}(q_{I}^{A}(T) - q_{0}^{A}(T)) + \frac{(I-1)x_{A}^{2}x_{B} + x_{A}x_{B}}{I}(q_{0}^{B}(T) - q_{I}^{B}(T))$
6	II III	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \frac{(I-1)x_{A}x_{B}^{2} + x_{A}x_{B}}{I}(q_{I}^{A}(T) - q_{0}^{A}(T)) + \frac{(I-1)x_{A}^{2}x_{B} + Ix_{A}x_{B}}{I}(q_{0}^{B}(T) - q_{I}^{B}(T))$
7	III I	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \frac{(I-1)x_{A}^{2}x_{B} + Ix_{A}x_{B}}{I}(q_{I}^{A}(T) - q_{0}^{A}(T)) + x_{A}x_{B}(q_{0}^{B}(T) - q_{I}^{B}(T))$
8	III II	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \frac{(I-1)x_{A}^{2}x_{B} + Ix_{A}x_{B}}{I}(q_{I}^{A}(T) - q_{0}^{A}(T)) + \frac{(I-1)x_{A}^{2}x_{B} + x_{A}x_{B}}{I}(q_{0}^{B}(T) - q_{I}^{B}(T))$
9	III III	$q(x,T) = x_{A}q_{0}^{A}(T) + x_{B}q_{I}^{B}(T) + \frac{(I-1)x_{A}^{2}x_{B} + Ix_{A}x_{B}}{I}(q_{I}^{A}(T) - q_{0}^{A}(T)) + \frac{(I-1)x_{A}x_{B}^{2} + Ix_{A}x_{B}}{I}(q_{0}^{B}(T) - q_{I}^{B}(T))$

Table S2. q(x,T)-functions of disordered alloy phases at T K.

mation of it's a few parts.

Due to the discovery of alloy genes and the establishments of holographic alloy positioning (HAP) system and a big database consisting of the AG-database and the holographic network phase diagrams of alloy systems, a standard method for researchers to share predictive algorithms and computational methods may be produced. The whole information of an alloy system and a designed alloy may be obtained. This study will create a new way of intelligent design advanced alloys and lead to fundamental variations in the metallic materials science.

1.6. The Choices of Potential Energy E-function and Volume V-function in the Au-Cu System

The 5th E-function in **Supplementary Table S1** has been chosen for describing Au-Cu system, according to the calculated values of the mixed enthalpies

 $\Delta H^m(x,0,\sigma_{\max})$, excess potential energies

 $\Delta E^{ex}(x, 0, \sigma_{max})$ and the lowest critical temperatures $T_c(x)$ of AuCu- and AuCu₃-type sublattice ordered Au_(1-x)Cu_x alloys with maximum order degrees, based on potential energies of the A_i^{Au} - and A_i^{Cu} -sequences separated from mixed enthalpies of the AuCu and AuCu₃ compounds respectively by nine E-functions at room temperature (**Supplementary Figure S3**).

The 6th V-function in **Supplementary Table S1** has been chosen for describing Au-Cu system, according to the calculated values of the mixed volumes $\Delta v^m(x, T_r, \sigma_{max})$

and excess volumes $\Delta v^{ex}(x, T_r, \sigma_{max})$ of the AuCu- and AuCu₃-type sublattice ordered Au_(1-x)Cu_x alloys with maximum order degrees based on volumes of the A_i^{Au} - and A_i^{Cu} -sequences separated from experimental volumes of AuCu and AuCu₃ compounds respectively by the 2nd-9th v-functions at room temperature (**Supplementary Figure S4**).

In the Au-Cu system, the correlative function between potential energies of alloy genes is,

$$\begin{cases} \varepsilon_i^{\mathrm{Au}} = \varepsilon_0^{\mathrm{Au}} + (i/I)^2 \left(\varepsilon_I^{\mathrm{Au}} - \varepsilon_0^{\mathrm{Au}}\right) \\ \varepsilon_i^{\mathrm{Cu}} = \varepsilon_I^{\mathrm{Cu}} + \left[(I-i)/I\right]^2 \left(\varepsilon_0^{\mathrm{Cu}} - \varepsilon_I^{\mathrm{Cu}}\right). \end{cases}$$
(5)

The potential energy function of alloys is,

$$\varepsilon(x,T) = x_{Au}\varepsilon_{0}^{Au}(T) + x_{Cu}\varepsilon_{I}^{Cu}(T) + \sum_{i=0}^{I} \left[\left(\frac{i}{I}\right)^{2} x_{i}^{Au} \right] \left(\varepsilon_{I}^{Au}(T) - \varepsilon_{0}^{Au}(T)\right) + \sum_{i=0}^{I} \left[\left(\frac{I-i}{I}\right)^{2} x_{i}^{Cu} \right] \left(\varepsilon_{0}^{Cu}(T) - \varepsilon_{I}^{Cu}(T)\right) \right]$$
(6)

The correlative function between volumes of alloy genes is:

$$\begin{cases} v_i^{Au} = v_0^{Au} + (i/I)^2 (v_I^{Au} - v_0^{Au}) \\ v_i^{Cu} = v_I^{Cu} + [2(I-i)/I] (v_0^{Cu} - v_I^{Cu}) \\ - [(I-i)/I]^2 (v_0^{Cu} - v_I^{Cu}) \end{cases}$$
(7)



Figure S3. Energetic properties and critical temperatures of AuCu- and AuCu₃-type sublattice ordered Au_(1-x)Cu_x alloys with maximal order degrees calculated by nine E-functions. a), b) Mixed enthalpy $\Delta H^m_{AuCu}(x)$ and $\Delta H^m_{AuCu_3}(x)$, here the experimental values are denoted by symbol " \circ "; c), d) Excess potential energy differences $\Delta E^{ex}_{AuCu}(x)$ and $\Delta E^{ex}_{AuCu_3}(x)$ relative to disordered Au_(1-x)Cu_x alloys; e), f) Critical temperature $T^m_{c,AuCu}(x)$ and $T^m_{c,AuCu_3}(x)$, here the experimental values are denoted by symbol " Δ ".

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Figure S4. Volumetric properties of AuCu- and AuCu₃-type sublattice ordered Au_(1-x)Cu_x alloys with maximal order degrees calculated by nine V-functions. a), b) Mixed volumes of formation $\Delta V_{AuCu}^{m}(x)$ and $\Delta V_{AuCu_{3}}^{m}(x)$; c), d) Excess volume differences $\Delta V_{AuCu}^{ex}(x)$ and $\Delta V_{AuCu_1}^{ex}(x)$ relative to disordered $Au_{(1-x)}Cu_x$ alloys.

The volume function of alloys is,

$$v(x,T) = x_{Au}v_{0}^{Au}(T) + x_{Cu}v_{I}^{Cu}(T) + \sum_{i=0}^{I} \left[\left(\frac{i}{I}\right)^{2} x_{i}^{Au} \right] \left(v_{I}^{Au}(T) - v_{0}^{Au}(T)\right)$$

$$+ \sum_{i=0}^{I} \left[\frac{2I(I-i) - (I-i)^{2}}{I^{2}} x_{i}^{B} \right] \cdot \left(v_{0}^{Cu}(T) - v_{I}^{Cu}(T)\right)$$
(8)

where, $\varepsilon_0^{Au} = -3.8140 \text{ eV}$, $\varepsilon_I^{Au} = -4.0555 \text{ eV}$, $\varepsilon_0^{Cu} = -3.6488 \text{ eV}$, $\varepsilon_I^{Cu} = -3.4824 \text{ eV}$; $v_0^{Au} = 16.9581(10^{-3} \text{ nm}^3)$, $v_I^{Au} = 15.5213(10^{-3} \text{ nm}^3)$, $v_0^{Cu} = 12.6828(10^{-3} \text{ nm}^3)$, $v_I^{Cu} = 11.8124(10^{-3} \text{ nm}^3)$, $I = 12.6828(10^{-3} \text{ nm}^3)$, $V_I^{Cu} = 11.8124(10^{-3} \text{ nm}^3)$, $V_I^{Cu} = 12.6828(10^{-3} \text{ nm}^3)$, $V_I^{Cu} = 11.8124(10^{-3} \text{ nm}^3)$, $V_I^{$ 12.

Their features are as follows (Supplementary Figures 2(b) and (c), Supplementary Table S2):

The ε_i^{Au} decreases with increasing number *i* of Cuatoms in the coordinative configuration: $\left(\varepsilon_{i}^{\mathrm{Au}}-\varepsilon_{0}^{\mathrm{Au}}\right)=\left(i/I\right)^{2}\left(\varepsilon_{I}^{\mathrm{Au}}-\varepsilon_{0}^{\mathrm{Au}}\right).$

The ε_i^{Cu} decreases with increasing number (*I-i*) of Au-atoms in the coordinative configuration: $\left(\varepsilon_{i}^{\text{Cu}} - \varepsilon_{I}^{\text{Cu}}\right) = \left[\left(I - i\right)/I\right]^{2} \left(\varepsilon_{0}^{\text{Cu}} - \varepsilon_{I}^{\text{Cu}}\right).$ The v_{i}^{Au} decreases with increasing number *i* of Cu-

atoms in the coordinative configuration:

$$\left(v_{i}^{\text{Au}} - v_{0}^{\text{Au}}\right) = \left(i/I\right)^{2} \left(v_{I}^{\text{Au}} - v_{0}^{\text{Au}}\right)$$

The v_i^{Cu} increase with increasing number (I-i) of Auatoms in the coordinative configuration:

$$\binom{(v_i^{Cu} - v_I^{Cu})}{-[(I-i)/I]^2(v_0^{Cu} - v_I^{Cu})} - \frac{[(I-i)/I]^2(v_0^{Cu} - v_I^{Cu})}{-[(V_0^{Cu} - V_1^{Cu})^2(v_0^{Cu} - v_I^{Cu})]^2}$$

1.7. Valence Electron Structures of **AG-Sequences**

It is a very-very difficult problem to obtain electronic structures, physical and thermodynamic properties of alloy genes. After knowing the potential energies and volumes of alloy genes, a fictitious 'characteristic crystal' has been proposed in order to resolve this difficult problem. It is an fcc-based consisting of the same alloy genes with known potential energy and volume in the fcc-based lattice Au-Cu system. Therefore, there are C_i^{Au} - and C_i^{Cu} -sequences of characteristic crystals corresponding to A_i^{Au} - and A_i^{Cu} -sequences. The C_0^{Au} and C_{12}^{Cu} are called as primary state characteristic crystals, *i.e.*, Au- and Cu- pure metals. The C_{12}^{Au} and C_0^{Cu} are called as terminal state characteristic crystals.

After knowing the potential energies and volumes of alloy genes, the valence electron structures, single bond radii and potential energy curves of alloy genes can be calculated based on the valence bond theory of characteristic crystals and using inverse calculation method; and then, the Debye temperatures and bulk moduli of characteristic crystals can be obtained. These results are shown in **Supplementary Figures S2(d)** and (e), and listed in **Supplementary Table S3**. The valence electron

Table S3. The valence electron structures (the number of free electrons (s_f) , covalent electrons (s_c, d_c) and non-valent electrons (d_n)), volumes(v), potential energies (ε) and single bond radii (R) of alloy genes, cohesive energy (E_c) , Debye temperatures (θ) and bulk moduli (B) of characteristic crystals.

C^{α}	val	ence electrons	s in outer sl	hell	v	3	R	E_c	θ	В
\mathcal{O}_i	d_n	d_c	S _c	S_f	10^{-3} nm ³	(eV/at.)	10^{-1} nm	(J/mol)	(K)	(GPa)
<u>Au characteristic crystals</u>										
$C_{\scriptscriptstyle 0}^{\scriptscriptstyle m Au}$	3.4013	5.8506	0	1.7481	16.9581	-3.8130	1.3428	368000	165.00	170.99
$C_{\scriptscriptstyle 1}^{\scriptscriptstyle { m Au}}$	3.4016	5.8523	0	1.7461	16.9524	-3.8146	1.3426	368162	165.06	171.17
$C_2^{ m Au}$	3.4007	5.8578	0	1.7415	16.9353	-3.8197	1.3423	368647	165.22	171.69
$C_3^{ m Au}$	3.3995	5.8669	0	1.7336	16.9067	-3.8281	1.3417	369456	165.49	172.58
$C_4^{ m Au}$	3.399	5.8793	0	1.7216	16.8667	-3.8398	1.3409	370589	165.87	173.83
$C_{\scriptscriptstyle 5}^{\scriptscriptstyle { m Au}}$	3.3994	5.8951	0	1.7055	16.8152	-3.8549	1.3397	372046	166.37	175.45
$C_6^{ m Au}$	3.3998	5.9143	0	1.6859	16.7524	-3.8733	1.3383	373826	166.98	177.46
$C_7^{ m Au}$	3.4005	5.9368	0	1.6627	16.6780	-3.8951	1.3367	375929	167.70	179.86
$C_8^{ m Au}$	3.4014	5.9626	0	1.636	16.5923	-3.9203	1.3348	378357	168.52	182.68
$C_{\scriptscriptstyle 9}^{\scriptscriptstyle m Au}$	3.404	5.9912	0	1.6048	16.4951	-3.9488	1.3326	381108	169.47	185.94
$C_{\scriptscriptstyle 10}^{\scriptscriptstyle m Au}$	3.4074	6.0229	0	1.5698	16.3865	-3.9806	1.3302	384182	170.52	189.67
$C_{\scriptscriptstyle 11}^{\scriptscriptstyle m Au}$	3.4138	6.0569	0	1.5293	16.2665	-4.0159	1.3274	387581	171.70	193.89
$C_{\scriptscriptstyle 12}^{\scriptscriptstyle m Au}$	3.4218	6.0936	0	1.4847	16.1351	-4.0544	1.3244	391303	172.99	198.65
					Cu characteristi	c crystals				
$C_{\scriptscriptstyle 0}^{\scriptscriptstyle \mathrm{Cu}}$	4.2877	5.0495	0	1.6628	12.3631	-3.6478	1.1793	352055	345.81	134.68
C_1^{Cu}	4.3485	5.0119	0	1.6396	12.3593	-3.6212	1.1782	349491	344.58	133.76
C_2^{Cu}	4.411	4.9762	0	1.6129	12.3478	-3.5969	1.1768	347150	343.53	133.05
C_3^{Cu}	4.4737	4.9426	0	1.5837	12.3287	-3.5750	1.1753	345031	342.66	132.56
$C_4^{ m Cu}$	4.5366	4.9111	0	1.5523	12.3019	-3.5553	1.1735	343136	341.96	132.27
C_5^{Cu}	4.6006	4.8815	0	1.5179	12.2675	-3.5380	1.1715	341463	341.45	132.20
C_6^{Cu}	4.6648	4.854	0	1.4812	12.2254	-3.5230	1.1693	340014	341.10	132.34
C_7^{Cu}	4.7309	4.8282	0	1.4409	12.1757	-3.5103	1.1669	338787	340.96	132.70
$C_8^{ m Cu}$	4.7982	4.8042	0	1.3976	12.1183	-3.4999	1.1642	337784	340.99	133.28
$C_9^{ m Cu}$	4.866	4.7821	0	1.3519	12.0533	-3.4918	1.1612	337003	341.21	134.09
$C_{\scriptscriptstyle 10}^{\scriptscriptstyle m Cu}$	4.9345	4.7618	0	1.3037	11.9807	-3.4860	1.1581	336446	341.61	135.15
$C_{\scriptscriptstyle 11}^{\scriptscriptstyle \mathrm{Cu}}$	5.0053	4.7429	0	1.2519	11.9003	-3.4826	1.1547	336111	342.20	136.44
$C_{\scriptscriptstyle 12}^{\scriptscriptstyle m Cu}$	5.0778	4.7254	0	1.1968	11.8124	-3.4814	1.1511	336000	343.00	138.00

In the free atom system, the electron structures of atoms are described by four quantum numbers. The outshell electron structures of the Au- and Cu- free atoms at the basic states are respectively $5d^{10}6s^1$ and $3d^{10}4s^1$.

The electronic structure units of the alloy genes are valence electrons described by four quantum numbers: free electron (s_f) , covalent electron (s_c, p_c, d_c, f_c) , magnetic electron (d_m, f_m) and non-valence electron (p_n, d_n, f_n) . In the Au-Cu system, the valence electron structures of AG-sequences are listed in **Supplementary Table S3**. The valence electron structures of the primary states $(\psi_0^{Au}, \psi_{12}^{Cu})$ and terminal states $(\psi_{12}^{Au}, \psi_0^{Cu})$ of alloy genes are as follows:

$$\begin{split} \psi_0^{\text{Au}} &= 5d_n^{3.4013} 5d_c^{5.8506} 6s_f^{1.7481}; \\ \psi_{12}^{\text{Au}} &= 5d_n^{3.4218} 5d_c^{6.0936} 6s_f^{1.4847}. \\ \psi_{12}^{\text{Cu}} &= 3d_n^{5.0778} 3d_c^{4.7254} 4s_f^{1.1968}; \\ \psi_0^{\text{Cu}} &= 3d_n^{4.2877} 3d_c^{5.04954} 4s_f^{1.6628}. \end{split}$$

The essence of properties of alloy genes can be explained by their valence electron structures.

The essence for forming fcc-based lattice: As changing from ψ_0^{Au} to ψ_{12}^{Au} , the d_n -electrons slightly increase (3.4012/atom \rightarrow 3.4218/atom) and occupy at the *d*-energy band e_g state; and the *d_c*-electrons obviously increase (5.8506/atom \rightarrow 6.0936/atom) and occupy at the *d*-energy band t_{2g} state. Therefore, each A_i^{Au} -atom possesses 12 covalent bonds to form fcc-based lattice.

As changing from ψ_{12}^{Cu} to ψ_0^{Cu} , the d_n -electrons obviously decrease (5.0778/atom $\rightarrow 4.2877/atom$), few of them occupy at the d-energy band t_{2g} state, besides filling the e_g state fully; the d_c -electrons obviously increase (4.7254/atom $\rightarrow 5.0495/atom$) and occupy at the d-energy band t_{2g} state. Each A_i^{Cu} -atom possesses 12 covalent bonds to form fcc-based lattice.

For these reasons, the intermetallics, ordered and disordered alloys formed by A_i^{Au} - and A_i^{Cu} -sequences possess fcc-based lattice.

The essence for variations in potential energies and volumes of alloy genes:

As changing from ψ_0^{Au} to ψ_{12}^{Au} , the s_f -electrons decrease: 1.7481/atom \rightarrow 1.4847/atom, and the decreased s_f -electrons are translated into d_c -electrons. It results in falling ε_{12}^{Au} potential energy: -3.813 eV/atom $\rightarrow -4.0544 \text{ eV/atom}$, shorting single bond radus: 1.3428 $\times 10^{-1} \text{ nm} \rightarrow 1.3244 \times 10^{-1} \text{ nm}$, and reducing v_{12}^{Au} volume: 16.9581 $\times 10^{-3} \text{ nm}^3 \rightarrow 16.1351 \times 10^{-3} \text{ nm}^3$. Therefore, The ε_i^{Au} -potential energies decrease and the v_i^{Au} -volumes reduce with increasing number *i* of CuAs changing from ψ_{12}^{Cu} to ψ_0^{Cu} , the s_f -electrons increase: 1.1968/atom \rightarrow 1.6628/atom, and the d_c - electrons increase: 4.7254/atom \rightarrow 5.0495/atom. It results in falling ε_0^{Cu} potential energy: $-3.4814 \text{ eV}/atom \rightarrow$ -3.6478 eV/atom, lengthening single bond radius: 1.1511 $\times 10^{-1} \text{ nm} \rightarrow 1.1793 \times 10^{-1} \text{ nm}$, and expanding v_0^{Cu} volume: 11.8124 $\times 10^{-3} \text{ nm}^3 \rightarrow 12.3631 \times 10^{-3} \text{ nm}^3$. Therefore, the ε_i^{Cu} -potential energies decrease and v_i^{Cu} -volumes increases with increasing number (*I-i*) of Au-atoms in the coordinative configurations, that is contrary to the expected behavior.

1.8. The Thermodynamics Properties of AG-Sequences

In the SMMS framework, the Gibbs energy $(G_i(T))$ of each characteristic crystal (or ally gene) may be split into two parts: a temperature-independent contribution of potential energy (E(0)), of which the variation with temperatures has been accounted in the attaching vibration energy, and a temperature-dependent contribution of generalized vibration free energy $(X^{\nu}(T))$, but both are configuration(i)-dependent (Equation (9)). The enthalpy $(H_i(T))$ of each characteristic crystal may be also split into two parts: a temperature-independent contribution of potential energy (E(0)) and a temperature-dependent contribution of generalized vibration energy $(U^{\nu}(T))$ (Equation (10)). The generalized vibration free energy includes the generalized vibration energies $(U^{v}(T))$, which include Debye vibration energies $(U^{D}(T))$ and attaching vibration energies $(U^{E}(T))$, and the contribution of the generalized vibration entropies $(S^{\nu}(T))$, which include Debye vibration entropies $(S^{D}(T))$ and attaching vibration entropies $(S^{E}(T))$, the generalized vibration heat capacity $(C_p^v(T))$, which include Debye vibration heat capacity $(C_p^D(T))$, attaching vibration heat capacity $(C_p^E(T))$. The attaching vibration energy includes contributions of electron excitation, energy of formation of holes, variation of potential energy with temperature, and so on. Therefore, the multi-level energetic functions of characteristic crystals at T K as follows:

$$\begin{cases} G_{i}^{Au}(T) = E_{i}^{Au}(0) + X_{i}^{Au,v}(T) = H_{i}^{Au}(T) - TS_{i}^{Au,v}(T) \\ G_{i}^{Cu}(T) = E_{i}^{Cu}(0) + X_{i}^{Cu,v}(T) = H_{i}^{Cu}(T) - TS_{i}^{Cu,v}(T) \end{cases}$$
(9)
$$\begin{cases} H_{i}^{Au}(T) = E_{i}^{Au}(0) + U_{i}^{Au,v}(T) \end{cases}$$

$$\begin{cases} X_i^{\operatorname{Au},v}(T) = U_i^{\operatorname{Au},v}(T) - TS_i^{\operatorname{Au},v}(T) \\ X_i^{\operatorname{Cu},v}(T) = U_i^{\operatorname{Cu},v}(T) - TS_i^{\operatorname{Cu},v}(T) \end{cases}$$
(11)

$$\begin{cases} X_i^{\text{Au},D}(T) = U_i^{\text{Au},D}(T) - TS_i^{\text{Au},D}(T) \\ X_i^{\text{Cu},D}(T) = U_i^{\text{Cu},D}(T) - TS_i^{\text{Cu},D}(T) \end{cases}$$
(12)

$$\begin{cases} X_i^{\operatorname{Au}.E}(T) = U_i^{\operatorname{Au}.E}(T) - TS_i^{\operatorname{Au}.E}(T) \\ X_i^{\operatorname{Cu}.E}(T) = U_i^{\operatorname{Cu}.E}(T) - TS_i^{\operatorname{Cu}.E}(T) \end{cases}$$
(13)

$$\begin{cases} U_i^{\operatorname{Au},v}(T) = U_i^{\operatorname{Au},D}(T) + U_i^{\operatorname{Au},E}(T) \\ U_i^{\operatorname{Cu},v}(T) = U_i^{\operatorname{Cu},D}(T) + U_i^{\operatorname{Cu},E}(T) \end{cases}$$
(14)

$$\begin{cases} U_i^{\operatorname{Au},D}\left(T\right) = \int\limits_{0}^{T} C_{p,i}^{\operatorname{Au},D}\left(T\right) \mathrm{d}T \\ T \end{cases}$$
(15)

$$\left[U_i^{\operatorname{Cu}.D}\left(T\right) = \int_0^T C_{p,i}^{\operatorname{Cu}.D}\left(T\right) \mathrm{d}T \right]$$

$$\begin{cases} S_{i}^{\text{Au.}\nu}(T) = S_{i}^{\text{Au.}D}(T) + S_{i}^{\text{Au.}E}(T) \\ S_{i}^{\text{Cu.}\nu}(T) = S_{i}^{\text{Cu.}D}(T) + S_{i}^{\text{Cu.}E}(T) \end{cases}$$
(17)

(16)

$$\begin{cases} S_i^{\operatorname{Au},D}(T) = \int_0^T \frac{C_{p,i}^{\operatorname{Au},D}(T)}{T} dT \\ S_i^{\operatorname{Cu},D}(T) = \int_0^T \frac{C_{p,i}^{\operatorname{Cu},D}(T)}{T} dT \end{cases}$$
(18)

$$\begin{cases} S_i^{\operatorname{Au}.E}\left(T\right) = \int_0^T \frac{C_{p,i}^{\operatorname{Au}.E}\left(T\right)}{T} dT \\ S_i^{\operatorname{Cu}.E}\left(T\right) = \int_0^T \frac{C_{p,i}^{\operatorname{Cu}.E}\left(T\right)}{T} dT \end{cases}$$
(19)

 $\begin{cases} U_i^{\operatorname{Au}.E}(T) = \int_0^T C_{p,i}^{\operatorname{Au}.E}(T) dT \\ U_i^{\operatorname{Cu}.E}(T) = \int_0^T C_{p,i}^{\operatorname{Cu}.E}(T) dT \end{cases}$

$$\begin{cases} \theta_{i}^{Au} = \theta_{0}^{Au} \times \sqrt{E_{i}^{Au}(0) / (V_{i}^{Au}(0))^{(2/3)}} / \sqrt{E_{0}^{Au}(0) / (V_{0}^{Au}(0))^{(2/3)}} \\ \theta_{i}^{Cu} = \theta_{l}^{Cu} \times \sqrt{E_{i}^{Cu}(0) / (V_{i}^{Cu}(0))^{(2/3)}} / \sqrt{E_{12}^{Cu}(0) / (V_{12}^{Cu}(0))^{(2/3)}} \\ \int_{p,i}^{Q_{i}^{Au,D}} (T) = 9R \left(\frac{T}{\theta_{i}^{Au}}\right)^{3} \int_{0}^{\theta_{i}^{Au}/T} \frac{e^{x}x^{4}}{(e^{x}-1)^{2}} dx \end{cases}$$
(20)

$$\begin{cases} P^{Cu.D}(T) = 9R\left(\frac{T}{\theta_i^{Cu}}\right)^3 \int_0^{\theta_i^{Cu}/T} \frac{e^x x^4}{\left(e^x - 1\right)^2} dx \end{cases}$$
(21)

$$\begin{cases} C_{p,0}^{\text{Au}.E}(T) = 1.858993 \times 10^{-10} T + 4.222584 \times 10^{-6} T^2 \\ C_{p,12}^{\text{Au}.E}(T) = 2.763134 \times 10^{-4} T + 5.481502 \times 10^{-6} T^2 \end{cases}$$
(22)

$$\begin{cases} C_{p,12}^{\text{Cu},E}(T) = 0.00168035T + 2.826912 \times 10^{-6}T^2 \\ C_{p,0}^{\text{Cu},E}(T) = 0.00564614T + 3.632353 \times 10^{-6}T^2 \end{cases}$$
(23)

where, $\theta_0^{Au} = 165 \text{ K}$, $\theta_{12}^{Au} = 175.21 \text{ K}$, $\theta_{12}^{Cu} = 343 \text{ K}$, $\theta_0^{Cu} = 343.07 \text{ K}$.

It can be demonstrated that the general correlative functions between other energetic properties (q) of characteristic crystals (ally genes) at *T* K are as follows

$$\begin{cases} q_{i}^{Au}(T) = q_{0}^{Au}(T) + (i/I)^{2} \left[q_{I}^{Au}(T) - q_{0}^{Au}(T) \right] \\ q_{i}^{Cu}(T) = q_{I}^{Cu}(T) + \left[(I-i)/I \right]^{2} \left[q_{0}^{Cu}(T) - q_{1}^{Cu}(T) \right] \end{cases}$$
(24)

The AG-thermodynamic properties of characteristic crystals (ally genes) of Au-Cu system are shown in **Supplementary Figure S5**.

2. Alloy Gene Gibbs Energy Partition Function

In this section we present the AG-Gibbs energy partition function of AuCu-type sublattice alloy system, which includes AG-Gibbs energy transmission law, and AGarranging function, as well as other functions of thermodynamic properties.

Characteristic Gibbs energy function:

The characteristic Gibbs energy $G^*(x,T)$ function can be obtained by the AGT law (S1):

$$G^{*}(x,T) = \sum_{i=0}^{12} \left(x_{i}^{Au}(x,T) \times G_{i}^{Au}(T) + x_{i}^{Cu}(x,T) \times G_{i}^{Cu}(T) \right)$$
(25)

Partition function of the alloy:

$$\Omega(x,T) = g\left(x_i^{\operatorname{Au}}(x,T), x_i^{\operatorname{Cu}}(x,T)\right) \\ \times \exp\left[-G^*(x,T)/(kT)\right]$$
(26)





Figure S5. Curves of AG-thermodynamic properties in Au-Cu system. a), b) Generalized vibration heat capacity curves: $C_{p,0}^{Au,v} \cdots C_{pi}^{v,Au} \cdots C_{p12}^{v,Au}$, $C_{p,i}^{Cu,v} \cdots C_{p,i}^{Cu,v} \cdots C_{p,12}^{Cu,v}$; c), d) Generalized vibration energy curves: $U_0^{Au,v} \cdots U_i^{Au,v} \cdots U_{12}^{Au,v}$, $U_0^{Cu,v} \cdots U_{12}^{Cu,v} \cdots U_{12}^{Cu,v}$; e), f) Generalized vibration entropies curves: $S_0^{Au,v} \cdots S_i^{Au,v} \cdots S_{12}^{Au,v}$, $S_0^{Cu,v} \cdots S_{12}^{Cu,v}$; g), h) Generalized vibration entropies curves: $I_0^{Au,v} \cdots I_{12}^{Au,v}$, $S_0^{Cu,v} \cdots S_{12}^{Cu,v} \cdots S_{12}^{Cu,v} \cdots S_{12}^{Cu,v} \cdots S_{12}^{Cu,v}$; g), h) Generalized vibration entropies curves: $I_0^{Au,v} \cdots I_{12}^{Au,v}$, $S_0^{Cu,v} \cdots S_{12}^{Cu,v} \cdots S_{12}^{Cu,v} \cdots S_{12}^{Cu,v}$; g), h) Generalized vibration free energy curves: $X_0^{Au,v} \cdots X_1^{Au,v} \cdots X_1^{Au,v} \cdots X_1^{Cu,v} \cdots X_1^{Cu,v} \cdots X_1^{Cu,v}$; i), j) Enthalpy of formation curves: $H_0^{Au} \cdots H_i^{Au} \cdots H_{12}^{Au}$, $H_0^{Cu} \cdots H_1^{Cu} \cdots H_{12}^{Cu}$; k), l) Gibbs energy curves: $G_0^{Au} \cdots G_1^{Au} \cdots G_{12}^{Au}$, $G_{12}^{Cu} \cdots G_0^{Cu} \cdots G_0^{Cu}$.

AG-arranging function extending to all G_i^{Au} - and G_i^{Cu} -energy levels:

$$g\left(x_{i}^{\mathrm{Au}}\left(x,T\right),x_{i}^{\mathrm{Cu}}\left(x,T\right)\right)$$

$$=\frac{\left[N\sum_{i=0}^{I}\left(x_{i}^{\mathrm{Au}(1)}+x_{i}^{\mathrm{Cu}(1)}\right)\right]!}{\left(\sum_{i=0}^{I}Nx_{i}^{\mathrm{Au}(1)}\right)!\left(\sum_{i=0}^{I}Nx_{i}^{\mathrm{Cu}(1)}\right)!}\times\frac{\left[N\sum_{i=0}^{I}\left(x_{i}^{\mathrm{Au}(2)}+x_{i}^{\mathrm{Cu}(2)}\right)\right]!}{\left(\sum_{i=0}^{I}Nx_{i}^{\mathrm{Au}(2)}\right)!\left(\sum_{i=0}^{I}Nx_{i}^{\mathrm{Cu}(2)}\right)!}$$
(27)

Concentrations of the A_i^{Au} and A_i^{Cu} alloy genes at the $G_i^{Au}(T)$ - and $G_i^{Cu}(T)$ -energy levels::

$$\begin{cases} x_i^{\text{Au}}(x,T) = x_i^{\text{Au}(1)}(x,T) + x_i^{\text{Au}(2)}(x,T) \\ x_i^{\text{Au}}(x,T) = x_i^{\text{Au}(1)}(x,T) + x_i^{\text{Au}(2)}(x,T) \end{cases}$$
(28)

Concentrations of the A_i^{Au} and A_i^{Cu} alloy genes occupied at the (1) and (2) sublattice points:

$$\begin{cases} x_i^{\mathrm{Au}(1)}(x,T) = v^{(1)} P_{\mathrm{Au}}^{(1)} \omega_i^{(1)} \\ x_i^{\mathrm{Cu}(1)}(x,T) = v^{(1)} P_{\mathrm{Cu}}^{(1)} \omega_i^{(1)} \\ x_i^{\mathrm{Au}(2)}(x,T) = v^{(2)} P_{\mathrm{Au}}^{(2)} \omega_i^{(2)} \\ x_i^{\mathrm{Cu}(2)}(x,T) = v^{(2)} P_{\mathrm{Cu}}^{(2)} \omega_i^{(2)} \end{cases}$$
(29)

Probabilities of Au and Cu atoms occupied at (1) and (2) sublattice points:

$$\begin{cases} P_{Au}^{(1)} = x_{Au} + (1 - v^{(1)})\sigma, \\ P_{Cu}^{(1)} = 1 - P_{Au}^{(1)} = 1 - \left[x_{Au} + (1 - v^{(1)})\sigma\right] \\ P_{Au}^{(2)} = x_{Au} - v^{(1)}\sigma, \\ P_{Cu}^{(2)} = 1 - P_{Au}^{(2)} = 1 - (x_{Au} - v^{(1)}\sigma). \end{cases}$$
(30)

Fractions of the (1) and (2) sublattice points:

$$\begin{cases} v^{(1)} = N^{(1)}/N = 1/2 & \text{Definition of order degree:} \\ v^{(2)} = N^{(2)}/N = 1/2 & (31) \end{cases}$$

$$\sigma = \frac{P_{Au}^{(1)} - x_{Au}}{1 - v^{(1)}} = \frac{P_{Cu}^{(2)} - x_{Cu}}{1 - v^{(2)}} = \frac{x_i^{Au(1)}}{v^{(1)}v^{(2)}w_i^{(1)}} - \frac{x_{Au}}{v^{(2)}} = \frac{x_i^{Cu(2)}}{v^{(1)}v^{(2)}w_i^{(2)}} - \frac{x_{Cu}}{v^{(1)}}$$

The probability $\omega_i^{(1)}$ of the coordinative cluster

[(I-i)Au, iCu] surrounding the (1)-sublattice point:

(32)

$$\omega_{i}^{(1)} = \omega_{i'}^{(2)} \times \omega_{(i-i')}^{(1)} = \sum_{i=k'}^{K} \left[C_{8}^{i'} \left(P_{Au}^{(2)} \right)^{(8-i')} \left(P_{Cu}^{(2)} \right)^{(i')} \times C_{4}^{(i-i')} \left(P_{Au}^{(1)} \right)^{\left[4 - (i-i')\right]} \left(P_{Cu}^{(1)} \right)^{(i-i')} \right]$$
(33)

In the $\omega_i^{(1)}$ equation, the probability $\omega_{i'}^{(2)}$ of coordinative cluster $[(8-i')\operatorname{Au},i'\operatorname{Cu}]$ occupied at the (2)-sublattice points, and the probability $\omega_{(i-i')}^{(2)}$ of coordinative cluster [4-(i-i')Au,(i-i')Cu] occupied at the (1)-sublattice points:

$$\begin{cases} \omega_{i'}^{(2)} = \sum_{i'=k}^{K} \left[C_8^{(i')} \left(P_{Au}^{(2)} \right)^{(8-i')} \left(P_{Cu}^{(2)} \right)^{(i')} \right] \\ \omega_{(i-i')}^{(1)} = \sum_{i'=k}^{K} \left[C_4^{(i-i')} \left(P_{Au}^{(1)} \right)^{\left[4-(i-i')\right]} \left(P_{Cu}^{(1)} \right)^{(i-i')} \right] \end{cases}$$
(34)

where, the i' is the number of the Cu atoms occupied at the (2)-sublattice points.

The probability $\omega_i^{(2)}$ of coordinative cluster $\lceil (I-i) \operatorname{Au}, i\operatorname{Cu} \rceil$ surrounding the (2)-sublattice point:

$$\omega_{i}^{(2)} = \omega_{i'}^{(1)} \times \omega_{(i-i')}^{(2)} = \sum_{i'=k}^{K} \left[C_{8}^{i'} \left(P_{Au}^{(1)} \right)^{(8-i')} \left(P_{Cu}^{(1)} \right)^{(i')} \times C_{4}^{(i-i')} \left(P_{Au}^{(2)} \right)^{\left[4 - (i-i')\right]} \left(P_{Cu}^{(2)} \right)^{(i-i')} \right]$$
(35)

where, the i' is the number of the Cu atoms occupied at the (1)-sublattice points.

In the $\omega_i^{(2)}$ equation, the probability $\omega_{i'}^{(1)}$ of coordinative cluster $\left[(8-i') \operatorname{Au}_i i' \operatorname{Cu} \right]$ occupied at the (1)sublattice points, and the probability $\omega_{(i-i')}^{(2)}$ of coordinative cluster $\left[4 - (i-i') \operatorname{Au}_i (i-i') \operatorname{Cu} \right]$ occupied at the (2)-sublattice points:

$$\begin{cases} \omega_{i'}^{(1)} = \sum_{i'=k}^{K} \left[C_8^{i'} \left(P_{Au}^{(1)} \right)^{(8-i')} \left(P_{Cu}^{(1)} \right)^{(i')} \right] \\ \omega_{(i-i')}^{(2)} = \sum_{i'=k}^{K} \left[C_4^{(i-i')} \left(P_{Au}^{(2)} \right)^{\left[4-(i-i')\right]} \left(P_{Cu}^{(2)} \right)^{(i-i')} \right] \end{cases}$$
(36)

In the Equations (32) to (35), *k* and *K* take their values, according to

$$\begin{cases} k = 0, K = i, & \text{if } i \le 4; \\ k = i - 4, K = i, & \text{if } 4 < i \le 8; \\ k = i - 4, K = 8, & \text{if } 8 < i \le 12. \end{cases}$$
(37)

The maximum order degree σ_{max} as function of composition x_{Au} :

For the stoichiometric alloy, due to
$$P_{Au}^{(1)} = 1$$
,
 $\sigma_{max} = 1$;
For the alloys with $x_{Au} < v^{(1)}$, due to $P_{Au}^{(2)} = 0$,
 $\sigma_{max}(x) = x_{Au}/v^{(1)}$;
For the alloys with $x_{Au} > v^{(1)}$, due to $P_{Au}^{(1)} = 1$,
 $\sigma_{max}(x) = (1 - x_{Au})/(1 - v^{(1)})$.
The methods for calculating $\omega^{(1)}$ and $\omega^{(2)}$ are

The methods for calculating $\omega_i^{(1)}$ and $\omega_i^{(2)}$ are listed in **Supplementary Tables S4** and **S5**.

The configurational entropies of alloy and components:

$$\begin{cases} S^{c}(x,T) = k_{B} \ln\left(g\left(x_{i}^{Au},x_{i}^{Cu}\right)\right) = x_{Au}S^{Au.c}(x,T) + x_{Cu}S^{Cu.c}(x,T) \\ S^{Au.c} = -\frac{R}{x_{Au}} \left\{ \left(\sum_{i=0}^{I} x_{i}^{Au(1)}(x,T)\right) \ln\left(\sum_{i=0}^{I} \left(P_{Au}^{(1)}\omega_{i}^{(1)}\right)\right) + \left(\sum_{i=0}^{I} x_{i}^{Au(2)}(x,T)\right) \ln\left(\sum_{i=0}^{I} \left(P_{Au}^{(2)}\omega_{i}^{(2)}\right)\right) \right\} \\ S^{Cu.c} = -\frac{R}{x_{Cu}} \left\{ \left(\sum_{i=0}^{I} x_{i}^{Cu(1)}(x,T)\right) \ln\left(\sum_{i=0}^{I} \left(P_{Cu}^{(1)}\omega_{i}^{(1)}\right)\right) + \left(\sum_{i=0}^{I} x_{i}^{Cu(2)}(x,T)\right) \ln\left(\sum_{i=0}^{I} \left(P_{Cu}^{(2)}\omega_{i}^{(2)}\right)\right) \right\} \end{cases}$$
(38)

		$\omega_{r}^{(2)}$			$\mathcal{O}_{(i^{-f})}^{(i)}$			
	— i	i'	$C_8^{i'}$	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^{\!(\!8-i')}\left(P^{(2)}_{\scriptscriptstyle B} ight)^{\!(i')}$	(i-i')	$C_4^{(i-i^{'})}$	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^{\left[4-(i-i') ight]}\left(P^{(1)}_{\scriptscriptstyle B} ight)^{(i-i')}$	
	0	0	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^{\!\!8}\left(P^{(2)}_{\scriptscriptstyle B} ight)^{\!0}$	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	
	1	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^{\!8}\left(P_{\scriptscriptstyle B}^{(2)} ight)^{\!0}$	1	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^3\left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	
	1	1	8	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^7 \left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	
	2	0	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^{\!\!8}\left(P^{(2)}_{\scriptscriptstyle B} ight)^{\!0}$	2	6	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^2$	
	2	1	8	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^7 \left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	1	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^3\left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	
	2	2	28	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^6 \left(P^{(2)}_{_{\mathcal{B}}} ight)^2$	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	
	3	0	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^{\!\!8}\left(P^{(2)}_{\scriptscriptstyle B} ight)^{\!0}$	3	4	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1 \left(P^{(1)}_{\scriptscriptstyle B} ight)^3$	
$0 \le i \le 4$	3	1	8	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^7 \left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	2	6	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^2\left(P_{\scriptscriptstyle B}^{(1)} ight)^2$	
	3	2	28	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^6 \left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	1	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^3\left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	
	3	3	56	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^5 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$	0	1	$\left(P^{(1)}_{_{\mathcal{A}}} ight)^4\left(P^{(1)}_{_{\mathcal{B}}} ight)^0$	
	4	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^{\!\!8}\left(P_{\scriptscriptstyle B}^{(2)} ight)^{\!0}$	4	1	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^0\left(P_{\scriptscriptstyle B}^{(1)} ight)^4$	
	4	1	8	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^7 \left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	3	4	$\left(P_{\scriptscriptstyle {\cal A}}^{\scriptscriptstyle (1)} ight)^1 \left(P_{\scriptscriptstyle {\cal B}}^{\scriptscriptstyle (1)} ight)^3$	
	4	2	28	$\left(P_{_{A}}^{(2)} ight)^{6}\left(P_{_{B}}^{(2)} ight)^{2}$	2	6	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^2\left(P_{\scriptscriptstyle B}^{(1)} ight)^2$	
	4	3	56	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^5 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$	1	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^3\left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	
	4	4	70	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^4$	0	1	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^4\left(P_{\scriptscriptstyle B}^{(1)} ight)^0$	
	5	1	8	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^7\left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	4	1	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^0\left(P_{\scriptscriptstyle B}^{(1)} ight)^4$	
	5	2	28	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^6 \left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	3	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^1\left(P_{\scriptscriptstyle B}^{(1)} ight)^3$	
	5	3	56	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^5 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$	2	6	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^2\left(P_{\scriptscriptstyle B}^{(1)} ight)^2$	
	5	4	70	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^4$	1	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^3\left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	
	5	5	56	$\left(P_{_{\!\!A}}^{(2)} ight)^3\!\left(P_{_{\!\!B}}^{(2)} ight)^5$	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	
4 0	6	2	28	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^6 \left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	4	1	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^0\left(P_{\scriptscriptstyle B}^{(1)} ight)^4$	
$4 < i \leq 8$	6	3	56	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^5 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$	3	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^1\left(P_{\scriptscriptstyle B}^{(1)} ight)^3$	
	6	4	70	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^4$	2	6	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^2\left(P_{\scriptscriptstyle B}^{(1)} ight)^2$	
	6	5	56	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^5$	1	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^3\left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	
	6	6	28	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^6$	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	
	7	3	56	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^{\!$	4	1	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^0\left(P_{\scriptscriptstyle B}^{(1)} ight)^4$	
	7	4	70	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^4 \left(P^{(2)}_{\scriptscriptstyle B} ight)^4$	3	4	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^1\left(P_{\scriptscriptstyle B}^{(1)} ight)^3$	

Table S4. The methods for calculating the probability $\omega_i^{(1)}$ of coordinative cluster [(I-i)Au, iCu] surrounding the (1)-sublattice point in AuCu-type order alloys.

Y. Q. XIE ET AL.

Continued							
	7	5	56	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^{3}\left(P^{(2)}_{_{\mathcal{B}}} ight)^{5}$	2	6	$\left(P^{(1)}_{_{\mathcal{A}}} ight)^2\left(P^{(1)}_{_{\mathcal{B}}} ight)^2$
	7	6	28	$\left(P^{(2)}_{_A} ight)^2\left(P^{(2)}_{_B} ight)^6$	1	4	$\left(P^{(1)}_{_{\mathcal{A}}} ight)^3\left(P^{(1)}_{_{\mathcal{B}}} ight)^1$
	7	7	8	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^1 \left(P^{(2)}_{\scriptscriptstyle B} ight)^7$	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^0$
	8	4	70	$\left(P^{(2)}_{_A} ight)^4 \left(P^{(2)}_{_B} ight)^4$	4	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^0 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$
	8	5	56	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^5$	3	4	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1 \left(P^{(1)}_{\scriptscriptstyle B} ight)^3$
	8	6	28	$\left(P^{(2)}_{_A} ight)^2\left(P^{(2)}_{_B} ight)^6$	2	6	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^2$
	8	7	8	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^{\!\!1}\left(P^{(2)}_{_{\mathcal{B}}} ight)^{\!\!7}$	1	4	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^3\left(P^{(1)}_{\scriptscriptstyle B} ight)^1$
	8	8	1	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^0\left(P^{(2)}_{_{\mathcal{B}}} ight)^8$	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^0$
	9	5	56	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^3\left(P^{(2)}_{\scriptscriptstyle B} ight)^5$	4	1	$\left(P^{(1)}_{\scriptscriptstyle \! A} ight)^0\left(P^{(1)}_{\scriptscriptstyle \! B} ight)^4$
	9	6	28	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^2\left(P^{(2)}_{\scriptscriptstyle B} ight)^6$	3	4	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1\left(P^{(1)}_{\scriptscriptstyle B} ight)^3$
	9	7	8	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^1 \left(P^{(2)}_{\scriptscriptstyle B} ight)^7$	2	6	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^2$
	9	8	1	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^0\left(P^{(2)}_{_{\mathcal{B}}} ight)^8$	1	4	$\left(P^{(1)}_{_{\mathcal{A}}} ight)^3\left(P^{(1)}_{_{\mathcal{B}}} ight)^1$
9 . ; < 12	10	6	28	$\left(P^{(2)}_{_A} ight)^2\left(P^{(2)}_{_B} ight)^6$	4	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^0 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$
o < <i>t</i> ≤ 12	10	7	8	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^1 \left(P^{(2)}_{\scriptscriptstyle B} ight)^7$	3	4	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1\left(P^{(1)}_{\scriptscriptstyle B} ight)^3$
	10	8	1	$(P_{A}^{(2)})^{0}(P_{B}^{(2)})^{8}$	2	6	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^2$
	11	7	8	$\left(P^{(2)}_{_A} ight)^1 \left(P^{(2)}_{_B} ight)^7$	4	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^0\left(P^{(1)}_{\scriptscriptstyle B} ight)^4$
	11	8	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^0 \left(P^{(2)}_{\scriptscriptstyle B} ight)^8$	3	4	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1 \left(P^{(1)}_{\scriptscriptstyle B} ight)^3$
	12	8	1	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^0\left(P^{(2)}_{_{\mathcal{B}}} ight)^8$	4	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^0 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$

The mole potential energies of the alloy and components:

$$\begin{cases} E(x,T) = x_{Au}E^{Au}(x,T) + x_{Cu}E^{Cu}(x,T) \\ E^{Au}(x,T) = (1/x_{Au})\sum_{i=0}^{I=12} x_i^{Au}(x,T)E_i^{Au}(0) \\ E^{Cu}(x,T) = (1/x_{Cu})\sum_{i=0}^{I=12} x_i^{Cu}(x,T)E_i^{Cu}(0) \end{cases}$$
(39)

The Debye vibration energies of alloy and components:

$$\begin{cases} U^{D}(x,T) = x_{Au}U^{Au,D}(x,T) + x_{Cu}X^{Cu,D}(x,T) \\ U^{Au,D}(x,T) = (1/x_{Au})\sum_{i=0}^{I=12} x_{i}^{Au}(x,T)\int_{0}^{T} C_{p,i}^{Au,D}(T) dT (40) \\ U^{Cu,D}(x,T) = (1/x_{Cu})\sum_{i=0}^{I=12} x_{i}^{Cu}(x,T)\int_{0}^{T} C_{p,i}^{Cu,D}(T) dT \end{cases}$$

The attaching vibration energies of alloy and components:

$$\begin{cases} U^{E}(x,T) = x_{Au}U^{Au.E}(x,T) + x_{Cu}X^{Cu.E}(x,T) \\ U^{Au.E}(x,T) = (1/x_{Au})\sum_{i=0}^{I=12} x_{i}^{Au}(x,T)\int_{0}^{T} C_{p,i}^{Au.E}(T) dT \quad (41) \\ U^{Cu.E}(x,T) = (1/x_{Cu})\sum_{i=0}^{I=12} x_{i}^{Cu}(x,T)\int_{0}^{T} C_{p,i}^{Cu.E}(T) dT \end{cases}$$

The generalized vibration energies of the alloy and components:

$$\begin{cases} U^{\nu}(x,T) = x_{Au}U^{Au,\nu}(x,T) + x_{Cu}U^{Cu,\nu}(x,T) \\ U^{Au,\nu}(x,T) = (1/x_{Au})\sum_{i=0}^{l=12} x_i^{Au}(x,T)U_i^{Au,\nu}(T) \\ U^{Cu,\nu}(x,T) = (1/x_{Cu})\sum_{i=0}^{l=12} x_i^{Cu}(x,T)U_i^{Cu,\nu}(T) \end{cases}$$
(42)

			$\omega_{i}^{(2)}$		$\mathcal{O}^{(1)}_{(i-r)}$			
	<i>i</i>	i'	$C_8^{i'}$	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^{(8-i')}\left(P_{\scriptscriptstyle B}^{(1)} ight)^{(i')}$	(i-i')	$C_4^{\scriptscriptstyle (i-i')}$	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^{\!\!\left[4-(i-i') ight]}\left(P^{(2)}_{\scriptscriptstyle B} ight)^{\!\!\left(i-i' ight)}$	
	0	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^8\left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	0	1	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^4 \left(P^{(2)}_{_{\mathcal{B}}} ight)^0$	
	1	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^8\left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	1	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	
	1	1	8	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^7 \left(P^{(1)}_{\scriptscriptstyle B} ight)^1$	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^0$	
	2	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^8\left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	2	6	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	
	2	1	8	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^7 \left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	1	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	
	2	2	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^6 \left(P^{(1)}_{\scriptscriptstyle B} ight)^2$	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^0$	
	3	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^8\left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	3	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^{\!\!1} \left(P_{\scriptscriptstyle B}^{(2)} ight)^{\!\!3}$	
$0 \le i \le 4$	3	1	8	$\left(P_{\scriptscriptstyle \! A}^{(1)} ight)^7 \left(P_{\scriptscriptstyle \! B}^{(1)} ight)^1$	2	6	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	
	3	2	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^6 \left(P^{(1)}_{\scriptscriptstyle B} ight)^2$	1	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	
	3	3	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^5\left(P^{(1)}_{\scriptscriptstyle B} ight)^3$	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^0$	
	4	0	1	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^8\left(P^{(1)}_{\scriptscriptstyle B} ight)^0$	4	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^0\left(P_{\scriptscriptstyle B}^{(2)} ight)^4$	
	4	1	8	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^7 \left(P^{(1)}_{\scriptscriptstyle B} ight)^1$	3	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^1 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$	
	4	2	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^6 \left(P^{(1)}_{\scriptscriptstyle B} ight)^2$	2	6	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	
	4	3	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^5\left(P^{(1)}_{\scriptscriptstyle B} ight)^3$	1	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	
	4	4	70	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^0$	
	5	1	8	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^7 \left(P_{\scriptscriptstyle B}^{(1)} ight)^1$	4	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^0\left(P_{\scriptscriptstyle B}^{(2)} ight)^4$	
	5	2	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^6 \left(P^{(1)}_{\scriptscriptstyle B} ight)^2$	3	4	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^1 \left(P^{(2)}_{\scriptscriptstyle B} ight)^3$	
	5	3	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^5\left(P^{(1)}_{\scriptscriptstyle B} ight)^3$	2	6	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	
	5	4	70	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$	1	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	
	5	5	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^3\left(P^{(1)}_{\scriptscriptstyle B} ight)^5$	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^0$	
	6	2	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^6 \left(P^{(1)}_{\scriptscriptstyle B} ight)^2$	4	1	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^0\left(P^{(2)}_{_{\mathcal{B}}} ight)^4$	
4	6	3	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^5\left(P^{(1)}_{\scriptscriptstyle B} ight)^3$	3	4	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^1 \left(P^{(2)}_{\scriptscriptstyle B} ight)^3$	
$4 < i \le 8$	6	4	70	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$	2	6	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	
	6	5	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^3\left(P^{(1)}_{\scriptscriptstyle B} ight)^5$	1	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^3\left(P_{\scriptscriptstyle B}^{(2)} ight)^1$	
	6	6	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^6$	0	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^4 \left(P_{\scriptscriptstyle B}^{(2)} ight)^0$	
	7	3	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^5\left(P^{(1)}_{\scriptscriptstyle B} ight)^3$	4	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^0\left(P_{\scriptscriptstyle B}^{(2)} ight)^4$	
	7	4	70	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$	3	4	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^1 \left(P^{(2)}_{_{\mathcal{B}}} ight)^3$	
	7	5	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^3\left(P^{(1)}_{\scriptscriptstyle B} ight)^5$	2	6	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^2$	
	7	6	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^6$	1	4	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^3\left(P^{(2)}_{\scriptscriptstyle B} ight)^1$	

Table S5. The methods for calculating the probability $\omega_i^{(2)}$ of coordinative cluster [(I-i)Au, iCu] surrounding the (2)-sublattice point in AuCu-type order alloys.

Continued							
	7	7	8	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^{\!\!1} \left(P^{(1)}_{\scriptscriptstyle B} ight)^{\!\!7}$	0	1	$\left(P^{(2)}_{_A} ight)^4\left(P^{(2)}_{_B} ight)^0$
	8	4	70	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^4 \left(P^{(1)}_{\scriptscriptstyle B} ight)^4$	4	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^0\left(P_{\scriptscriptstyle B}^{(2)} ight)^4$
	8	5	56	$\left(P_{\scriptscriptstyle A}^{(1)} ight)^3\left(P_{\scriptscriptstyle B}^{(1)} ight)^5$	3	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^1 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$
	8	6	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^6$	2	6	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^2\left(P_{\scriptscriptstyle B}^{(2)} ight)^2$
	8	7	8	$\left(P^{(1)}_{_A} ight)^1\left(P^{(1)}_{_B} ight)^7$	1	4	$\left(P^{(2)}_{_{\mathcal{A}}} ight)^3\left(P^{(2)}_{_{B}} ight)^1$
	8	8	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^0 \left(P^{(2)}_{\scriptscriptstyle B} ight)^{\!\!8}$	0	1	$\left(P^{(2)}_{_A} ight)^4\left(P^{(2)}_{_B} ight)^0$
	9	5	56	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^3\left(P^{(1)}_{\scriptscriptstyle B} ight)^5$	4	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^0\left(P^{(2)}_{\scriptscriptstyle B} ight)^4$
	9	6	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^6$	3	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^1 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$
	9	7	8	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1 \left(P^{(1)}_{\scriptscriptstyle B} ight)^7$	2	6	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^2\left(P^{(2)}_{\scriptscriptstyle B} ight)^2$
	9	8	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^0 \left(P^{(2)}_{\scriptscriptstyle B} ight)^8$	1	4	$\left(P^{(2)}_{_A} ight)^3\left(P^{(2)}_{_B} ight)^1$
0 . : . 12	10	6	28	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^2\left(P^{(1)}_{\scriptscriptstyle B} ight)^6$	4	1	$\left(P^{(2)}_{_A} ight)^0\left(P^{(2)}_{_B} ight)^4$
8<1512	10	7	8	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1 \left(P^{(1)}_{\scriptscriptstyle B} ight)^7$	3	4	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^1 \left(P_{\scriptscriptstyle B}^{(2)} ight)^3$
	10	8	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^0 \left(P^{(2)}_{\scriptscriptstyle B} ight)^{\!\!8}$	2	6	$\left(P^{(2)}_{_A} ight)^2\left(P^{(2)}_{_B} ight)^2$
	11	7	8	$\left(P^{(1)}_{\scriptscriptstyle A} ight)^1 \left(P^{(1)}_{\scriptscriptstyle B} ight)^7$	4	1	$\left(P^{(2)}_{_A} ight)^0\left(P^{(2)}_{_B} ight)^4$
	11	8	1	$\left(P^{(2)}_{\scriptscriptstyle A} ight)^0 \left(P^{(2)}_{\scriptscriptstyle B} ight)^8$	3	4	$\left(P^{(2)}_{_A} ight)^1 \left(P^{(2)}_{_B} ight)^3$
	12	8	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^0\left(P_{\scriptscriptstyle B}^{(2)} ight)^8$	4	1	$\left(P_{\scriptscriptstyle A}^{(2)} ight)^0 \left(P_{\scriptscriptstyle B}^{(2)} ight)^4$

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The Debye vibration entropies of the alloy and components:

$$\begin{cases} S^{D}(x,T) = x_{Au}S^{Au,D}(x,T) \\ + x_{Cu}S^{Cu,D}(x,T) \\ S^{Au,D}(x,T) = (1/x_{Au})\sum_{i=0}^{I=12} x_{i}^{Au}(x,T) \int_{0}^{T} \frac{C_{p,i}^{Au,D}(T)}{T} dT \\ S^{Cu,D}(x,T) = (1/x_{Cu})\sum_{i=0}^{I=12} x_{i}^{Cu}(x,T) \int_{0}^{T} \frac{C_{p,i}^{Cu,D}(T)}{T} dT \end{cases}$$

$$(43)$$

The attaching vibration entropies of the alloy and components:

$$\begin{cases} S^{E}(x,T) = x_{Au}S^{Au,E}(x,T) \\ + x_{Cu}S^{Cu,E}(x,T) \\ S^{Au,E}(x,T) = (1/x_{Au})\sum_{i=0}^{I=12} x_{i}^{Au}(x,T) \int_{0}^{T} \frac{C_{p,i}^{Au,E}(T)}{T} dT \\ S^{Cu,E}(x,T) = (1/x_{Cu})\sum_{i=0}^{I=12} x_{i}^{Cu}(x,T) \int_{0}^{T} \frac{C_{p,i}^{Cu,E}(T)}{T} dT \end{cases}$$

$$(44)$$

The generalized vibration entropies of the alloy and components:

$$\begin{cases} S^{\nu}(x,T) = x_{Au}S^{Au,\nu}(x,T) + x_{Cu}S^{Cu,\nu}(x,T) \\ S^{Au,\nu}(x,T) = (1/x_{Au})\sum_{i=0}^{I=12} x_i^{Au}(x,T)S_i^{Au,\nu}(T) \\ S^{Cu,\nu}(x,T) = (1/x_{Cu})\sum_{i=0}^{I=12} x_i^{Cu}(x,T)S_i^{Cu,\nu}(T) \end{cases}$$
(45)

The generalized vibration free energies of the alloy and components:

$$\begin{cases} X^{\nu}(x,T) = x_{Au} X^{Au,\nu}(x,T) + x_{Cu} X^{Cu,\nu}(x,T) \\ X^{Au,\nu}(x,T) = (1/x_{Au}) \sum_{i=0}^{I=12} x_i^{Au}(x,T) X_i^{Au,\nu}(T) \quad (46) \\ X^{Cu,\nu}(x,T) = (1/x_{Cu}) \sum_{i=0}^{I=12} x_i^{Cu}(x,T) X_i^{Cu,\nu}(T) \end{cases}$$

The enthalpies of the alloy and components:

$$\begin{cases} H(x,T) = x_{Au} H^{Au}(x,T) + x_{Cu} H^{Cu}(x,T) \\ H^{Au}(x,T) = (1/x_{Au}) \sum_{i=0}^{I=12} x_i^{Au}(x,T) (E_i^{Au}(0) + U_i^{Au,\nu}(T)) \\ H^{Cu}(x,T) = (1/x_{Cu}) \sum_{i=0}^{I=12} x_i^{Cu}(x,T) (E_i^{Cu}(0) + U_i^{Cu,\nu}(T)) \end{cases}$$

$$(47)$$

The characteristic Gibbs energies of the alloy and components:

$$\begin{cases} G^{*}(x,T) = x_{Au}G^{*Au}(x,T) + x_{Cu}G^{*Cu}(x,T) \\ G^{*Au}(x,T) = (1/x_{Au})\sum_{i=0}^{l=12} x_{i}^{Au}(x,T)G_{i}^{Au}(T) \\ G^{*Cu}(x,T) = (1/x_{Cu})\sum_{i=0}^{l=12} x_{i}^{Cu}(x,T)G_{i}^{Cu}(T) \end{cases}$$
(48)

The Gibbs energies of the alloy and components:

$$\begin{cases} G(x,T) = x_{Au}G^{Au}(x,T) + x_{Cu}G^{Cu}(x,T) \\ G^{Au}(x,T) = (1/x_{Au})(G^{*Au}(x,T) - TS^{Au.c}(x,T)) \\ G^{Cu}(x,T) = (1/x_{Cu})(G^{*Cu}(x,T) - TS^{Cu.c}(x,T)) \end{cases}$$
(49)

The mixed heat capacity of the alloy:

$$\Delta C_{p}^{m}(x,T) = \Delta C_{p}^{m,v}(x,T) + \Delta C_{p}^{m,s}(x,T)$$

$$\Delta C_{p}^{m,v}(x,T) = \sum_{i=0}^{I} x_{i}^{Au}(x,T) \left(C_{p,i}^{Au,v}(T) - C_{p,0}^{Au,v}(T) \right)$$

$$+ \sum_{i=0}^{I} x_{i}^{Cu}(x,T) \left(C_{p,i}^{Cu,v}(T) - C_{p,12}^{Cu,v}(T) \right)$$

$$\Delta C_{p}^{m,s}(x,T) = \sum_{i=0}^{I} \frac{\partial x_{i}^{Au}(x,T)}{\partial \sigma} \cdot \frac{d\sigma}{dT} \left(H_{i}^{Au}(T) - H_{0}^{Au}(T) \right)$$

$$+ \sum_{i=0}^{I} \frac{\partial x_{i}^{Cu}(x,T)}{\partial \sigma} \cdot \frac{d\sigma}{dT} \left(H_{i}^{Cu}(T) - H_{12}^{Cu}(T) \right)$$
(50)

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The activities of the components:

$$\begin{bmatrix}
a_{Au}(x,T) = x_{Au} \cdot \exp(\Delta G_{Au}^{*m}(x,T)/RT) \\
a_{Cu}(x,T) = x_{Cu} \cdot \exp(\Delta G_{Cu}^{*m}(x,T)/RT) \\
\Delta G^{*Au}(x,T) = (1/x_{Au}) \sum_{i=0}^{I-12} x_i^{Au}(x,T) (G_i^{Au}(T) - G_0^{Au}(T)) \\
\Delta G^{*Cu}(x,T) = (1/x_{Cu}) \sum_{i=0}^{I-12} x_i^{Cu}(x,T) (G_i^{Cu}(T) - G_I^{Cu}(T))
\end{cases}$$
(51)

The volumes of the alloy and components:

$$\begin{cases} v(x,T) = x_{Au}v^{Au}(x,T) + x_{Cu}v^{Cu}(x,T) \\ v^{Au}(x,T) = (1/x_{Au})\sum_{i=0}^{I=12} x_i^{Au}(x,T)v_i^{Au}(T) \\ E^{Cu}(x,T) = (1/x_{Cu})\sum_{i=0}^{I=12} x_i^{Cu}(x,T)v_i^{Cu}(T) \end{cases}$$
(52)

The mixed volume thermal expansion coefficient of the alloy:

$$\begin{cases} \Delta\beta^{m}(x,T) = \Delta\beta^{m,v}(x,T) + \Delta\beta^{m,s}(x,T) \\ \Delta\beta^{m,v}(x,T) = \sum_{i=0}^{I} x_{i}^{Au}(x,T) \left(\beta_{i}^{Au,v}(T) - \beta_{0}^{Au,v}(T)\right) + \sum_{i=0}^{I} x_{i}^{Cu}(x,T) \left(\beta_{i}^{Cu,v}(T) - \beta_{12}^{Cu,v}(T)\right) \\ \Delta\beta^{m,s}(x,T) = \sum_{i=0}^{I} \left(\frac{1}{v_{i}^{Au}(T)}\right) \frac{\partial x_{i}^{Au}(x,T)}{\partial\sigma} \cdot \frac{d\sigma}{dT} \left(v_{i}^{Au}(T) - v_{0}^{Au}(T)\right) + \sum_{i=0}^{I} \left(\frac{1}{v_{i}^{Cu}(T)}\right) \frac{\partial x_{i}^{Cu}(x,T)}{\partial\sigma} \cdot \frac{d\sigma}{dT} \left(v_{i}^{Cu}(T) - v_{0}^{Au}(T)\right) \\ \end{cases}$$
(53)

It should be emphasized that the new $\Omega(x,T)$ -function can be used to describe both long-distance order and short-distance order states of alloy phases, because our model includes the sublattice model and coordinative model (Equation (32)), and that, the thermodynamic properties of alloy components need no representatives by the partial molar properties. We have proved that the partial molar properties cannot represent the average properties of the corresponding components [20].

3. EHNP Diagrams of Thermodynamic Properties of AuCu-type Sublattice Alloy System

According to three-dimension $\Delta G^m - x - T$ and $\sigma - x - T$ EHNP diagrams, we have obtained other q - x - T EHNP diagrams of the AuCu-type sublattice system in **Supplementary Figure S6**.

It should be emphasized that from each three-dimension q-x-T EHNP diagram we can obtain isocompo-

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Figure S6. The q-x-T EHNP diagrams of the AuCu-type sublattice system. a) Mixed Gibbs energy $\Delta G^m - x - T$ three-dimension EHNP diagram; b) Mixed characteristic Gibbs energy $\Delta G^{*m} - x - T$ three-dimension EHNP diagram, without including configuration entropy; c) Mixed enthalpy $\Delta H^m - x - T$ three-dimension EHNP diagram; d) Mixed potential energy $\Delta E^m - x - T$ three-dimension EHNP diagram, without including variations in AG-potential energies with temperatures; e) Mixed volume $\Delta V^m - x - T$ three-dimension EHNP diagram; f) Generalized mixed vibration free energy $\Delta X^v - x - T$ three-dimension EHNP diagram; g) Generalized mixed vibration energy $\Delta U^v - x - T$ three-dimension EHNP diagram, including variations in AG-potential energies with temperatures; h) Generalized mixed vibration entropy $\Delta S^v - x - T$ three-dimension EHNP diagram; i) Heat capacity $C_p^m - x - T$ three-dimension EHNP diagram; j) Thermal expansion coefficient $\alpha - x - T$ three-dimension EHNP diagram; k) $a_{Au} - x - T$ three-dimension diagram; l) $a_{Cu} - x - T$ three-dimension diagram.

sitional $q_x - T$, isoproperty $T_q - x$, and isothermal $q_T - x$ path phase diagrams. These diagrams are interconnected to form a big database about structures, properties and their variations with temperature of alloy systems. Therefore, the man's knowledge of relationships of structures, properties and environments for alloy systems has been changed from single causality to systematic correlativity.