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# Potential energies of characteristic atoms on basis of experimental heats of formation of AuCu and $AuCu_3$ compounds (Ⅰ)

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**Abstract:** The systematic science of alloys(SSA) is a framework of the total energy and total volume able to be separated. The potential energy sequences of characteristic atoms at the central sites of the basic clusters in the fcc-based lattice Au-Cu system are separated out from smaller experimental heats of formation of $L1_0$-AuCu and $L1_2$-$AuCu_3$ compounds only, by nine potential energy $E$-functions and through the use of structural unit inversion method. From these potential energy sequences, the potential energies and heats of formation of the disordered $Au_{1-x}Cu_x$ alloys at 0 K are calculated. The potential energies, heats of formation and $T_c$-temperatures of order-disorder transitions of the $L1_0$-AuCu, $L1_2$-$Au_3Cu$ and $L1_2$-$AuCu_3$ compounds, as well as the $Au_3Cu$-, AuCu- and $AuCu_3$- type ordered alloys with maximal ordering degrees are calculated too. The results show that the 5th $E$-function may be chosen for developing it into the free energy-, enthalpy-, vibrational energy- and vibrational entropy-functions for describing thermodynamic properties of the compounds, ordered and disordered phases and for establishing the phase diagram of the Au-Cu system in the future.

**Key words:** systematic science of alloys; Au-Cu system; potential energy; heat of formation; order-disorder transition temperature

## 1 Introduction

An alloy system contains three structure levels: the phase level of organizations, atomic level of phases and electronic level of atoms. In order to get a entirely understanding of the alloy systems, to establish phase diagrams and to search a method for designing of alloys, the SSA framework[1−4] has been established based on two scientific philosophy propositions. A diversity of structures, properties and features of whether matter or nonmatter systems should be attributed to combination and arrangement of structural units in the structural unit sequence. For examples, the diversity of atoms in the atomic system is attributed to arrangement of electrons in the electronic orbital (state) sequence described by four quantum numbers, which are the main quantum number, angular quantum number, magnetic quantum number and spin quantum, under the influence of nuclei; the diversity of substances in the matter system is attributed to compositions of elements in the periodic sequence of elements; the diversity of quantities in metrology is described by combination and arrangement of basic numbers in the basic number sequence, which are Arabic numerals; the diversity of species in the biological system is attributed to splices of the genes in the gene sequence; and the diversity of individual characters in character system is described by combination and arrangement of stroke elements in the stroke element sequence, which are the dot, horizontal, vertical, left-falling, right-falling, turning and hook strokes. And a systematic theory of any complex system described quantitatively should be constructed by structural unit sequence-, equation- and information-chains. Besides the quantum-mechanics of free atom system, there is few or no one described quantitatively. The SSA framework is constructed indeed by the structural unit sequence-, equation- and information-chains.

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### 1.1 Models and structure unit sequence chain

The atomic level of alloy phases in the SSA framework involves three models for constructing diversity of structures and properties of alloy phases [5−8].

1) The basic cluster overlapping(BCO) model, of which the structural units are a pair of basic cluster sequences in a based lattice (such as fcc, hcp and bcc) of binary alloy systems, with each cluster consisting of a central atom, the first neighbor configuration, the second neighbor configuration and the third neighbor configuration. The actions of the BCO model are to give information about an atomic arrangement of alloy phases described by overlapping pattern of basic clusters and to determine the splitting order on the potential energy, volume and electronic structure of the central atoms, which may have one, two and three splitting orders respectively corresponding to the basic clusters with one, two and three neighbor configurations. Using one order split the basic $B_i^\alpha$-cluster consists of a central $A_i^\alpha$ atom and the first neighboring configuration [(*I*−*i*)Au, *i*Cu], which contains *i* Cu-atoms and (*I*−*i*) Au-atoms. Here the symbol $\alpha$ denotes Au or Cu; *I* is the coordinative number and equals 12 for the fcc based lattice; and *i* can change from 0 to 12.

2) The characteristic atom arranging(CAA) model, of which the structural units are a pair of characteristic atom sequences, with each characteristic atom being the central atom of a specific basic cluster. The characteristic $A_i^\alpha$ atom has own characters at the ground state: potential energy $\varepsilon_i^\alpha(0)$, volume $V_i^\alpha(0)$ and electronic structure $\psi_i^\alpha(0)$. The actions of the CAA model are to give information about an atomic arrangement of alloy phases described by potential energy pattern, volume pattern and electronic structure pattern of the characteristic atoms occupied at the various lattice sites in intermetallics[5−8], to derive equations for calculating concentrations of various characteristic atoms and configurational entropy of ordered and disordered alloys as functions of composition($x$) and ordering degree($\sigma$) and to establish composition-ordering degree dependent $E(x, 0, \sigma)$, $V(x, 0, \sigma)$ and $\psi(x, 0, \sigma)$ functions of potential energy, volume and electronic structure of alloy phases at 0 K or without considering temperature effect.

Therefore, in a based lattice the variations in potential energy, volume and electronic structure of intermetallics, various type ordered alloys and disordered alloys with composition and ordering degree can be calculated by the same information about a pair of potential energy sequences, a pair of volume sequences and a pair of electronic structure sequences, which belong to a pair of characteristic atom sequences.

3) The characteristic crystal mixing(CCM) model, of which the structure units are a pair of invented characteristic crystal sequences, with each characteristic crystal consisting of the same characteristic atoms of the identical potential energy, identical volume and identical electronic structure. The actions of the CCM model are to establish a set of temperature($T$) dependent functions of the energetic and volumetric properties consisting of the general thermal expansion coefficient $\beta^{\mathrm{v}}(T)$ function, general thermal expansion volume $V^{\mathrm{v}}(T)$ function, general vibrational capacity $C_p^{\mathrm{v}}(T)$ function, general vibrational energy $U^{\mathrm{v}}(T)$ function, general vibrational entropy $S^{\mathrm{v}}(T)$ function, enthalpy $H(T)$ function and free energy $G(T)$ function of the characteristic crystals and to derive a set of composition-temperature-ordering degree dependent functions of the the general thermal expansion coefficient $\beta^{\mathrm{v}}(x, T, \sigma)$, general thermal expansion volume $V^{\mathrm{v}}(x, T, \sigma)$, general vibration heat capacity $C_p^{\mathrm{v}}(x,T,\sigma)$, general vibrational energy $U^{\mathrm{v}}(x, T, \sigma)$, general vibration entropy $S^{\mathrm{v}}(x, T, \sigma)$, enthalpy $H(x, T, \sigma)$ and characteristic free energy $G^*(x, T, \sigma)$ without containing configuration entropy $S^{\mathrm{c}}(x, \sigma)$ of alloy phases. And finally, by combining the $G^*(x, T, \sigma)$ function with partition function, the free energy $G(x, T, \sigma)$ function can be derived, where the $G(x, T, \sigma)$ function contains configuration entropy $S^{\mathrm{c}}(x, \sigma)$.

These three models are proposed in order to overcome disappointments of the atomic pair interaction model and central atom model[9] as well as effective cluster interaction model[10−12].

### 1.2 Equation and information chains

#### 1.2.1 Additive law of *q*-properties of characteristic crystals

According to CCM model, the extensive properties $q(x, T, \sigma)$, $q_A(x, T, \sigma)$, $q_B(x, T, \sigma)$ of a given alloy phase and its components can be obtained by an additive law of the $q$-properties of characteristic crystals (in terms of CCA law)[5−8]:

$$\begin{cases} q(x,T,\sigma)=\sum\limits_{i=0}^{I} x_i^{\mathrm{A}}(x,\sigma)q_i^{\mathrm{A}}(T)+\sum\limits_{i=0}^{I} x_i^{\mathrm{B}}(x,\sigma)q_i^{\mathrm{B}}(T) \\ q_A(x,T,\sigma)=\sum\limits_{i=0}^{I} x_i^{\mathrm{A}}(x,\sigma)q_i^{\mathrm{A}}(T)/x_{\mathrm{A}} \\ q_B(x,T,\sigma)=\sum\limits_{i=0}^{I} x_i^{\mathrm{B}}(x,\sigma)q_i^{\mathrm{B}}(T)/x_{\mathrm{B}} \end{cases} \tag{1}$$

where $x_i^{\mathrm{A}}(x,\sigma)$ and $x_i^{\mathrm{B}}(x,\sigma)$ are the concentrations of the characteristic atoms.

#### 1.2.2 Nine $E(x, 0, \sigma)$- and nine $V(x, 0, \sigma)$-functions of alloy phases at 0 K

In order to make Eq.(1) become a simple, applicable and separable $q(x, 0, \sigma)$ function (here $q$ denotes $E$ or $V$), three type relations of $q_i^{\mathrm{A}}$ and $q_i^{\mathrm{B}}$ with $i$ have been designed[1, 8]:

Type Ⅰ of straight line relation:

$$\begin{cases} E_i^{\mathrm{A}} = E_0^{\mathrm{A}} + (i/I)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) \\ E_i^{\mathrm{B}} = E_I^{\mathrm{B}} + [(I-i)/I](E_0^{\mathrm{B}} - E_I^{\mathrm{B}}) \end{cases} \tag{2}$$

Type Ⅱ of concave parabola relation:

$$\begin{cases} E_i^{\mathrm{A}} = E_0^{\mathrm{A}} + (i/I)^2(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) \\ E_i^{\mathrm{B}} = E_I^{\mathrm{B}} + [(I-i)/I]^2(E_0^{\mathrm{B}} - E_I^{\mathrm{B}}) \end{cases} \tag{3}$$

Type Ⅲ of convex parabola relation:

$$\begin{cases} E_i^{\mathrm{A}} = E_0^{\mathrm{A}} + (2i/I)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) - (i/I)^2(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) \\ E_i^{\mathrm{B}} = E_I^{\mathrm{B}} + [2(I-i)/I](E_0^{\mathrm{B}} - E_I^{\mathrm{B}}) - \\ \qquad [(I-i)/I]^2(E_0^{\mathrm{B}} - E_I^{\mathrm{B}}) \end{cases} \tag{4}$$

where $E_0^{\mathrm{A}}$ and $E_I^{\mathrm{B}}$ denote, respectively, potential energies of the primary $C_0^{\mathrm{A}}$ and $C_I^{\mathrm{B}}$ characteristic crystals; $E_I^{\mathrm{A}}$ and $E_0^{\mathrm{B}}$ denote, respectively, potential energies of the terminal $C_I^{\mathrm{A}}$ and $C_0^{\mathrm{B}}$ characteristic crystals.

By combining Eqs.(2), (3), (4) and substituting them into Eq.(1), nine $E(x, 0, \sigma)$ functions can be obtained. In Table 1 the nine general $E(x, 0, \sigma)$-functions of alloy phases can be used to compounds, ordered and disordered alloy phases. In Table 2, the nine $E(x, 0, 0)$-functions can be used to the disordered alloy phase only.

### 1.3 Methodology

From the first proposition, an inference can be drawn: "The whole can be reproduced from parts". For example, the whole of a tree can be reproduced from a seed, a leaf or a branch of the tree in biologic systems; The whole information of an alloy system can be reproduced from disordered alloys, ordered alloys or intermetallics. This means that "The total potential energies and total volumes of a few alloys can be separated into the potential energy sequence and volume sequence of the characteristic crystals (atoms), from which the whole information about energetic and volumetric properties, electronic and crystalline structures of all alloy phases can be reproduced". Therefore, the systematic study for an alloy system in the SSA framework is divided into three step investigations.

**Table 1** Nine general potential energy $E(x, 0, \sigma)$-functions of alloy phases at 0 K

| No. | Type |  | Function |
|---|---|---|---|
|  | A | B |  |
| 1 | I | I | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left(\frac{i}{I}x_i^{\mathrm{A}}\right)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left(\frac{I-i}{I}x_i^{\mathrm{B}}\right)(E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 2 | I | II | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left(\frac{i}{I}x_i^{\mathrm{A}}\right)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left[\left(\frac{I-i}{I}\right)^2 x_i^{\mathrm{B}}\right](E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 3 | I | III | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left(\frac{i}{I}x_i^{\mathrm{A}}\right)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left[\frac{2I(I-i)-(I-i)^2}{I^2}x_i^{\mathrm{B}}\right](E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 4 | II | I | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left[\left(\frac{i}{I}\right)^2 x_i^{\mathrm{A}}\right](E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left(\frac{I-i}{I}x_i^{\mathrm{B}}\right)(E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 5 | II | II | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left[\left(\frac{i}{I}\right)^2 x_i^{\mathrm{A}}\right](E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left[\left(\frac{I-i}{I}\right)^2 x_i^{\mathrm{B}}\right](E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 6 | II | III | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left[\left(\frac{i}{I}\right)^2 x_i^{\mathrm{A}}\right](E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left[\frac{2I(I-i)-(I-i)^2}{I^2}x_i^{\mathrm{B}}\right](E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 7 | III | I | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left(\frac{2Ii-i^2}{I^2}x_i^{\mathrm{A}}\right)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left(\frac{I-i}{I}x_i^{\mathrm{B}}\right)(E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 8 | III | II | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum_{i=0}^{I}\left(\frac{2Ii-i^2}{I^2}x_i^{\mathrm{A}}\right)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left[\left(\frac{I-i}{I}\right)^2 x_i^{\mathrm{B}}\right](E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |
| 9 | III | III | $E(x,0,\sigma) = x_{\mathrm{A}}E_0^{\mathrm{A}} + x_{\mathrm{B}}E_I^{\mathrm{B}} + \sum\left(\frac{2Ii-i^2}{I^2}x_i^{\mathrm{A}}\right)(E_I^{\mathrm{A}} - E_0^{\mathrm{A}}) + \sum_{i=0}^{I}\left[\frac{2I(I-i)-(I-i)^2}{I^2}x_i^{\mathrm{B}}\right](E_0^{\mathrm{B}} - E_I^{\mathrm{B}})$ |

**Table 2** Nine potential energy $E(x, 0, 0)$-functions of disordered alloy phases at 0 K

| No. | Type |  | Function |
|---|---|---|---|
|  | A | B |  |
| 1 | I | I | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+x_{\mathrm{A}}x_{\mathrm{B}}[(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})]$ |
| 2 | I | II | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+x_{\mathrm{A}}x_{\mathrm{B}}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+\frac{(I-1)x_{\mathrm{A}}^2x_{\mathrm{B}}+x_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |
| 3 | I | III | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+x_{\mathrm{A}}x_{\mathrm{B}}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+\frac{(I-1)x_{\mathrm{A}}x_{\mathrm{B}}^2+Ix_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |
| 4 | II | I | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+\frac{(I-1)x_{\mathrm{A}}x_{\mathrm{B}}^2+x_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+x_{\mathrm{A}}x_{\mathrm{B}}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |
| 5 | II | II | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+\frac{(I-1)x_{\mathrm{A}}x_{\mathrm{B}}^2+x_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+\frac{(I-1)x_{\mathrm{A}}^2x_{\mathrm{B}}+x_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |
| 6 | II | III | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+\frac{(I-1)x_{\mathrm{A}}x_{\mathrm{B}}^2+x_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+\frac{(I-1)x_{\mathrm{A}}^2x_{\mathrm{B}}+Ix_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |
| 7 | III | I | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+\frac{(I-1)x_{\mathrm{A}}^2x_{\mathrm{B}}+Ix_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+x_{\mathrm{A}}x_{\mathrm{B}}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |
| 8 | III | II | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+\frac{(I-1)x_{\mathrm{A}}^2x_{\mathrm{B}}+Ix_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+\frac{(I-1)x_{\mathrm{A}}^2x_{\mathrm{B}}+x_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |
| 9 | III | III | $E(x,0,0)=x_{\mathrm{A}}E_0^{\mathrm{A}}+x_{\mathrm{B}}E_I^{\mathrm{B}}+\frac{(I-1)x_{\mathrm{A}}^2x_{\mathrm{B}}+Ix_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_I^{\mathrm{A}}-E_0^{\mathrm{A}})+\frac{(I-1)x_{\mathrm{A}}x_{\mathrm{B}}^2+Ix_{\mathrm{A}}x_{\mathrm{B}}}{I}(E_0^{\mathrm{B}}-E_I^{\mathrm{B}})$ |

1) The aims of the first step investigation are to choose $E(x, 0, \sigma)$ and $V(x, 0, \sigma)$ functions and to determine a pair of potential energy sequences and a pair of volume sequences of characteristic crystals (atoms), through resolving nine $E(x, 0, \sigma)$- and $V(x, 0, \sigma)$-functions on the basis of FP-calculated heats and volumes of formation of several intermetallics only, or of experimental heats and volumes of formation of several intermetallics only and several disordered alloys only by the structural unit inversion method; to determine a pair of electronic structure sequences of characteristic crystals (atoms), according to potential energies and volumes of characteristic crystals (atoms), then to study energetic properties, volumetric properties and electronic structures of alloy phases at ground state (0 K).

2) The aims of the second step investigation are to obtain energetic and volumetric properties of characteristic crystals as function of temperature, to obtain the energetic and volumetric property equations of alloy phases as functions of composition, temperature and ordering degree and then to study energetic and volumetric properties, crystalline parameters and electronic structures of alloy phases in the whole ranges of composition, temperature and ordering degree.

3) The aims of the third step investigation are to study stability, transformation and equilibrium of alloy phases, to establish phase diagram and to provide a systematic knowledge about energetic and volumetric and structural properties, crystalline and electronic structures of characteristic crystal (atom) sequences for designing applied alloys. That is called as design engineering of characteristic crystal (atom) sequences of alloy systems.

The Au-Cu system has a diversity of alloy phases, which include intermetallics with various space groups, ordered alloys with $Au_3Cu$-, AuCu-, and $AuCu_3$-types and disordered alloys, a relative simplicity for systematical study, which indicates all solid phases exist in the fcc-based lattice only, and is rich in order-disorder phenomena with phase transitions at $Au_3Cu$, AuCu and $AuCu_3$, that leads to the fact that it has become a studying platform for nearly all theories and experimental techniques of alloys. Now, it is also used as the platform systematically to represent the SSA framework through a series of works. The outline of remainder of this work is as follows. In the next section, the results are presented. The potential energy sequences of the $A_i^{\mathrm{Au}}$ and $A_i^{\mathrm{Cu}}$ characteristic atoms are calculated by nine $E$-functions at 0 K; The potential energies and heats of formation of disordered $Au_{1-x}Cu_x$ alloys are calculated by nine $E$-functions at 0 K; The potential energies and heats of formation and critical $T_c$-temperatures of the order-disorder transformation of $Au_3Cu$, AuCu and $AuCu_3$ compounds are calculated by nine *E*-functions; The potential energies and heats of formation and critical $T_c$-temperatures of the order-disorder transformation of $Au_3Cu$-, AuCu- and $AuCu_3$-type ordered $Au_{1-x}Cu_x$ alloys, and some general conclusions are then presented.

## 2 Results

### 2.1 Potential energy sequences of characteristic atoms

The experimental data show that from 0 K to 560 K for AuCu compound and from 0 K to 400 K for $AuCu_3$ compound, their heats of formation have no variations with temperature[13]. Therefore, it can be considered that the $\Delta H_{\rm exp}$(AuCu, 298, 1)=$\Delta E$(AuCu, 0, 1)=−8 745 J/mol, and $\Delta H_{\rm exp}$($AuCu_3$, 298, 1)=$\Delta E$($AuCu_3$, 0, 1)= −7 164 J/mol[13], which are smaller respectively than $\Delta H_{\rm exp}$(AuCu, 298, 1)=−9 337 J/mol and $\Delta H_{\rm exp}$($AuCu_3$, 298, 1)=−7 268J /mol[14−15]. From the smaller experimental heats of formation, the potential energy $E_i^{\rm Au}(0)$ and $E_i^{\rm Cu}(0)$ sequences of the $A_i^{\rm Au}$ and $A_i^{\rm Cu}$ characteristic atoms in the Au-Cu system separated out by nine *E*-functions in Table1 are listed in Table 3 and shown in Fig.1. From these results, it can be known that the potential energy sequences obtained from nine *E*-functions are different and that the $E_i^{\rm Au}(0)$ and $E_i^{\rm Cu}(0)$ sequences obtained by the 4th, 5th and 7th *E*-functions are different too, even the average potential energies of the compounds, ordered and disordered alloys calculated by them are, respectively, equivalent. The 2nd and 3rd *E*-functions have the same characters (see results of 2.2, 2.3 and 2.4 in the present section).

### 2.2 Energetic properties of disordered $Au_{1-x}Cu_x$ alloys and their components

Fig.2 shows the distribution of the $x_i^{\rm Au}(x)$ and $x_i^{\rm Cu}(x)$ of characteristic atoms in the disordered $Au_{1-x}Cu_x$ alloys.

According to the potential energy sequences of the characteristic atoms in Table 3, the $E(x, 0, 0)$, $E_{\rm Au}(x, 0, 0)$ and $E_{\rm Cu}(x, 0, 0)$ potential energies of disordered $Au_{1-x}Cu_x$ alloys and their components as well as their $\Delta H(x, 0, 0)$ heats of formation calculated by nine *E*-functions in Table 2 are listed in Table 4 and shown in Fig.3. From these results, the following knowledge can be obtained.

1) The average $E(x, 0, 0)$ potential energies of the disordered $Au_{1-x}Cu_x$ alloys obtained from nine *E*-functions are different each other. The average $E_{\rm Au}(x, 0, 0)$ and $E_{\rm Cu}(x, 0, 0)$ potential energies of the Au and Cu components obtained by nine *E*-functions are different each other too. But there is no *E*-function, which can well describe the experimental heats of formation in the whole compositional range. It has been discovered that the transformation of the disordered $Au_{0.5}Cu_{0.5}$ alloy to ordered AuCu alloy is fast at temperatures below 573 K so that it is rather difficult to fully suppress ordering on quenching[17−20]. Therefore, the experimental heats of formation of so-called disordered alloys in the compositional range (atomic fraction) 25%⩽$x$(Cu)⩽75% are referred to partly-ordered alloys with short-range ordering degrees. The details will be reported in the second part of this investigation.

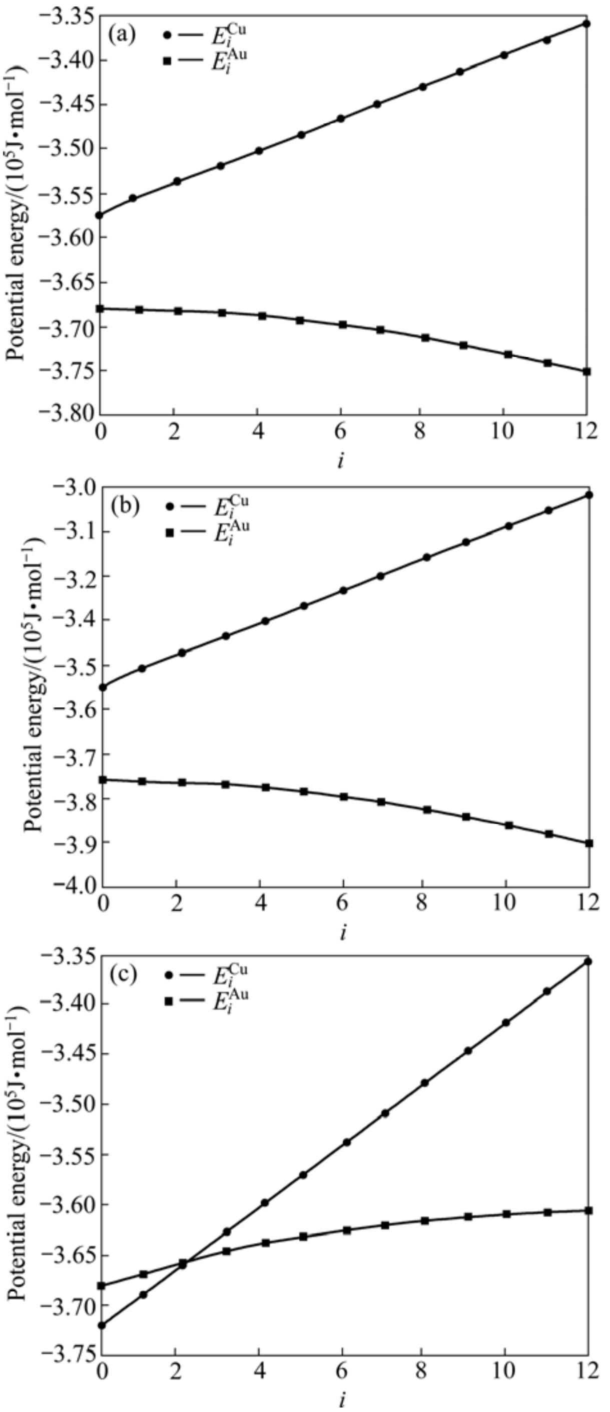


**Fig.1** Potential energy $E_i^{\rm Au}(0)$ and $E_i^{\rm Cu}(0)$ sequences of $A_i^{\rm Au}$ and $A_i^{\rm Cu}$ characteristic atoms in Au-Cu system obtained by the 4th (a), 5th (b) and 7th (c) *E*-functions

2) The average potential energies and heats of

**Table 3** Potential energy sequences of $A_i^{\mathrm{Au}}$ and $A_i^{\mathrm{Cu}}$ characteristic atoms in Au-Cu system calculated by nine *E*-functions at 0 K (J/mol)

| No. | *i* | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1** | $E_i^{\mathrm{Au}}$ | −368 000* | −369 130 | −370 259 | −371 389 | −372 518 | −373 648 | −374 777 | −375 907 | −377 036 | −378 166 | −379 295 | −380 425 | −381 554 |
| | $E_i^{\mathrm{Cu}}$ | −349 554 | −348 425 | −347 295 | −346 166 | −345 036 | −343 907 | −342 777 | −341 648 | −340 518 | −339 389 | −338 259 | −337 130 | −336 000* |
| 2 | $E_i^{\mathrm{Au}}$ | −368 000 | −370 589 | −373 178 | −375 768 | −378 357 | −380 946 | −383 535 | −386 124 | −388 713 | −391 303 | −393 892 | −396 481 | −399 070 |
| | $E_i^{\mathrm{Cu}}$ | −328 753 | −329 910 | −330 967 | −331 923 | −332 779 | −333 534 | −334 188 | −334 742 | −335 195 | −335 547 | −335 799 | −335 950 | −336 000 |
| 3 | $E_i^{\mathrm{Au}}$ | −368 000 | −369 381 | −370 763 | −372 144 | −373 525 | −374 906 | −376 288 | −377 669 | −379 050 | −380 432 | −381 813 | −383 194 | −384 576 |
| | $E_i^{\mathrm{Cu}}$ | −343 247 | −343 197 | −343 046 | −342 794 | −342 442 | −341 989 | −341 436 | −340 781 | −340 026 | −339 171 | −338 214 | −337 158 | −336 000 |
| 4 | $E_i^{\mathrm{Au}}$ | −368 000 | −368 050 | −368 201 | −368 453 | −368 805 | −369 258 | −369 812 | −370 466 | −371 221 | −372 077 | −373 033 | −374 090 | −375 247 |
| | $E_i^{\mathrm{Cu}}$ | −357 407 | −355 623 | −353 839 | −352 055 | −350 271 | −348 487 | −346 704 | −344 920 | −343 136 | −341 352 | −339 568 | −337 784 | −336 000 |
| 5 | $E_i^{\mathrm{Au}}$ | −368 000 | −368 162 | −368 647 | −369 456 | −370 589 | −372 046 | −373 826 | −375 929 | −378 357 | −381 108 | −384 182 | −387 581 | −391 303 |
| | $E_i^{\mathrm{Cu}}$ | −352 055 | −349 491 | −347 150 | −345 031 | −343 136 | −341 463 | −340 014 | −338 787 | −337 784 | −337 003 | −336 446 | −336 111 | −336 000 |
| 6 | $E_i^{\mathrm{Au}}$ | −368 000 | −367 827 | −367 309 | −366 446 | −365 237 | −363 683 | −361 784 | −359 540 | −356 950 | −354 014 | −350 734 | −347 108 | −343 137 |
| | $E_i^{\mathrm{Cu}}$ | −368 111 | −367 888 | −367 219 | −366 104 | −364 543 | −362 536 | −360 083 | −357 184 | −353 839 | −350 048 | −345 812 | −341 129 | −336 000 |
| 7 | $E_i^{\mathrm{Au}}$ | −368 000 | −366 842 | −365 786 | −364 829 | −363 974 | −363 219 | −362 564 | −362 011 | −361 558 | −361 206 | −360 954 | −360 803 | −360 753 |
| | $E_i^{\mathrm{Cu}}$ | −371 902 | −368 910 | −365 918 | −362 926 | −359 935 | −356 943 | −353 951 | −350 959 | −347 967 | −344 975 | −341 984 | −338 992 | −336 000 |
| 8 | $E_i^{\mathrm{Au}}$ | −368 000 | −375 444 | −382 241 | −388 390 | −393 892 | −398 747 | −402 954 | −406 514 | −409 427 | −411 693 | −413 311 | −414 282 | −414 605 |
| | $E_i^{\mathrm{Cu}}$ | −282 147 | −290 749 | −298 602 | −305 708 | −312 065 | −317 675 | −322 537 | −326 651 | −330 016 | −332 634 | −334 504 | −335 626 | −336 000 |
| 9 | $E_i^{\mathrm{Au}}$ | −368 000 | −368 993 | −369 899 | −370 719 | −371 453 | −372 101 | −372 662 | −373 137 | −373 525 | −373 827 | −374 043 | −374 173 | −374 216 |
| | $E_i^{\mathrm{Cu}}$ | −349 463 | −349 370 | −349 089 | −348 622 | −347 967 | −347 126 | −346 097 | −344 882 | −343 480 | −341 890 | −340 114 | −338 150 | −336 000 |

* The values are taken from Ref.[16]; ** Up till now, we cannot give a reasonable method to separate the potential energies of characteristic atoms by the first function. Therefore, it cannot be used at present.

formation of the disordered $Au_{1-x}Cu_x$ alloys obtained by the 5th *E*-functions are higher than corresponding experimental values. It may be chosen to describe the Au-Cu system, considering that the experimental heats of formation of the so-called disordered alloys are referred to those of partly-ordered alloys with short-range ordering degrees.

### 2.3 Energetic properties of $L1_2$-$Au_3Cu$, $L1_0$-AuCu and $L1_2$-$AuCu_3$ compounds

In the SSA framework, the crystalline structures of compounds are described by the characteristic atom occupation pattern, in which one can distinguish characteristic atoms occupied at the lattice sites (see Fig.4).

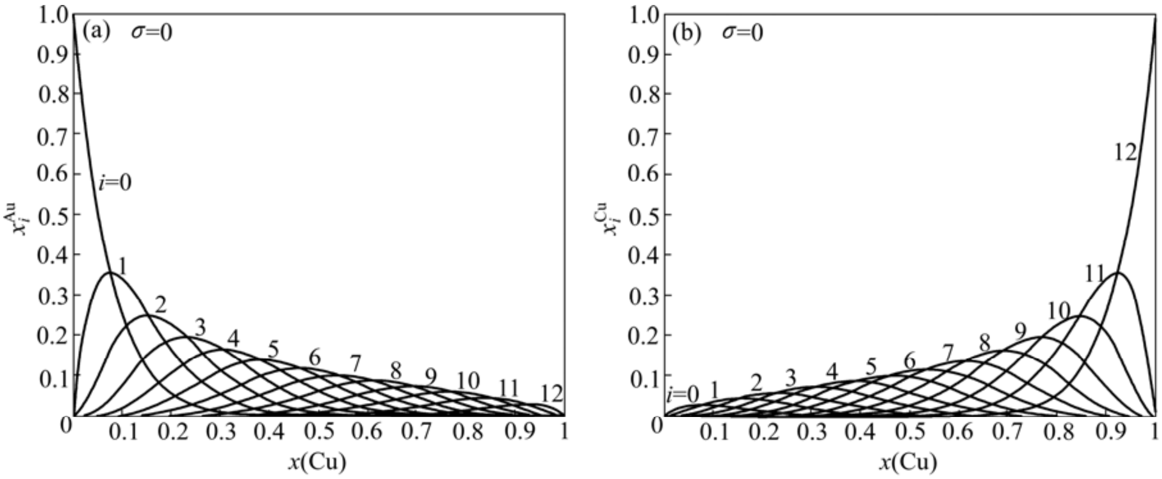


**Fig.2** Concentrations $x_i^{Au}(x)$ and $x_i^{Cu}(x)$ in disordered $Au_{1-x}Cu_x$ alloys as functions of composition *x*(Cu)

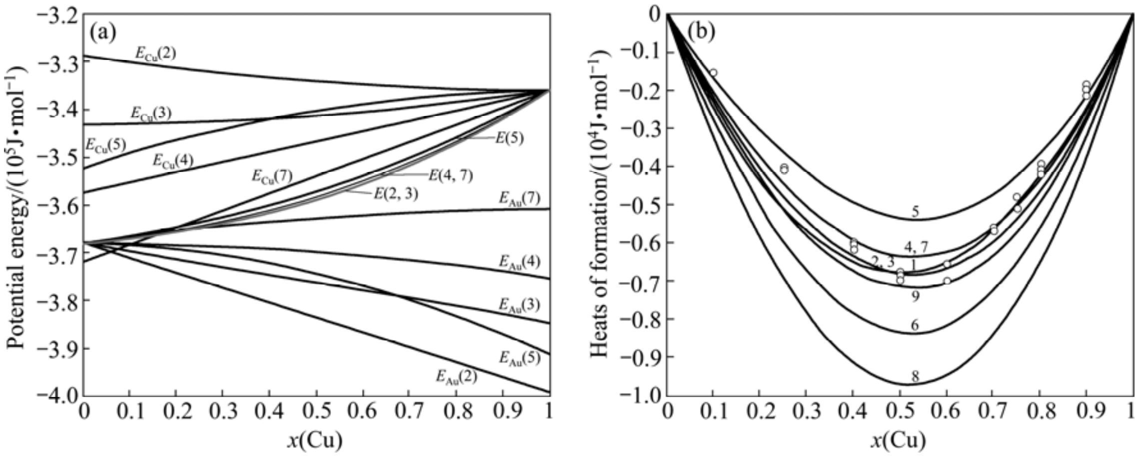
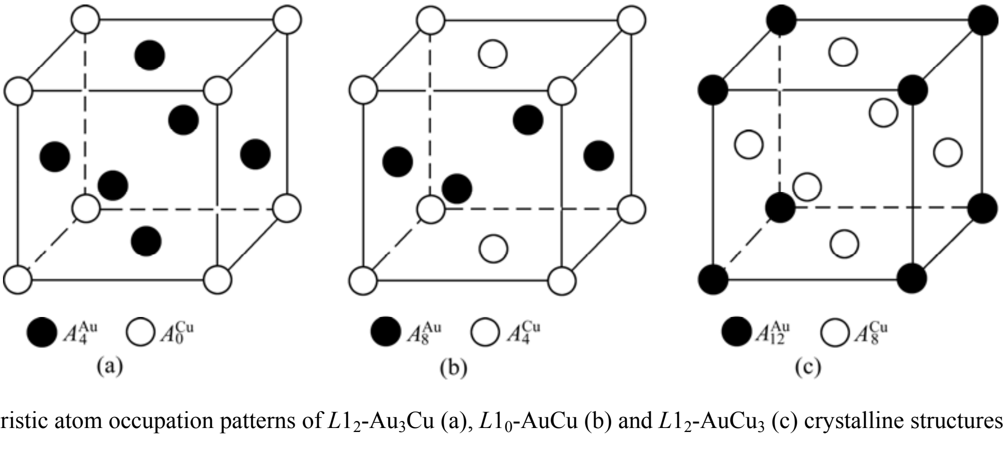


**Fig.3** Average potential energies *E*(*x*, 0, 0), $E_{Au}$(*x*, 0, 0) and $E_{Cu}$(*x*, 0, 0) of disordered $Au_{1-x}Cu_x$ alloys and their components calculated from the 2nd, 3rd, 4th, 5th and 7th *E*-functions (a) and Δ*H*(*x*, 0, 0) for the disordered $Au_{1-x}Cu_x$ alloys calculated from nine *E*-functions, together with experimental heats of formation at 320 K[15] (denoted by circles) (b)



(a) (b) (c)

**Fig.4** Characteristic atom occupation patterns of $L1_2$-$Au_3Cu$ (a), $L1_0$-AuCu (b) and $L1_2$-$AuCu_3$ (c) crystalline structures

**Table 4** Potential energies $E(x, 0, 0)$, $E_{\mathrm{Au}}(x, 0, 0)$, $E_{\mathrm{Cu}}(x, 0, 0)$ and heats of formation $\Delta H(x, 0, 0)$ of disordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys calculated by nine $E$-functions at 0 K (J/mol)

| No. | | $x$(Cu) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 0.1 | 0.25 | 0.3 | 0.4 | 0.5 |
| 1 | $E_{\mathrm{Au}}(x)$ | −368 000 | −369 355 | −371 389 | −372 066 | −373 422 | −374 777 |
| | $E_{\mathrm{Cu}}(x)$ | −349 554 | −348 199 | −346 166 | −345 488 | −344 133 | −342 777 |
| | $E(x)$ | −368 000 | −367 240 | −365 083 | −364 093 | −361 706 | −358 777 |
| | $\Delta H(x)$ | 0 | −2 440 | −5 083 | −5 693 | −6 506 | −6 777 |
| 2 | $E_{\mathrm{Au}}(x)$ | −368 000 | −37 1107 | −375 768 | −377 321 | −380 428 | −383 535 |
| | $E_{\mathrm{Cu}}(x)$ | −328 753 | −33 0075 | −331 810 | −332 322 | −333 246 | −334 037 |
| | $E(x)$ | −368 000 | −36 7004 | −364 778 | −363 821 | −361 555 | −358 786 |
| | $\Delta H(x)$ | 0 | −2 204 | −4 778 | −5 421 | −6 355 | −6 786 |
| 3 | $E_{\mathrm{Au}}(x)$ | −368 000 | −369 658 | −372 144 | −372 973 | −374 630 | −376 288 |
| | $E_{\mathrm{Cu}}(x)$ | −343 247 | −343 121 | −342 681 | −342 468 | −341 943 | −341 285 |
| | $E(x)$ | −368 000 | −367 004 | −364 778 | −363 821 | −361 555 | −358 786 |
| | $\Delta H(x)$ | 0 | −2 204 | −4 778 | −5 421 | −6 355 | −6 786 |
| 4 | $E_{\mathrm{Au}}(x)$ | −368 000 | −368 127 | −368 566 | −368 779 | −369 305 | −369 963 |
| | $E_{\mathrm{Cu}}(x)$ | −357 407 | −355 266 | −352 055 | −350 985 | −348 844 | −346 704 |
| | $E(x)$ | −368 000 | −366 841 | −364 438 | −363 441 | −361 120 | −358 333 |
| | $\Delta H(x)$ | 0 | −2 041 | −4 438 | −5 041 | −5 920 | −6 333 |
| 5 | $E_{\mathrm{Au}}(x)$ | −368 000 | −368 408 | −369 821 | −370 505 | −372 194 | −374 311 |
| | $E_{\mathrm{Cu}}(x)$ | −352 055 | −349 125 | −345 282 | −344 148 | −342 101 | −340 348 |
| | $E(x)$ | −368 000 | −366 480 | −363 686 | −362 598 | −360 157 | −357 330 |
| | $\Delta H(x)$ | 0 | −16 80 | −3 686 | −4 198 | −4 957 | −5 330 |
| 6 | $E_{\mathrm{Au}}(x)$ | −368 000 | −367 565 | −366 058 | −365 327 | −363 525 | −361 266 |
| | $E_{\mathrm{Cu}}(x)$ | −368 111 | −367 549 | −365 602 | −364 659 | −362 331 | −359 414 |
| | $E(x)$ | −368 000 | −367 563 | −365 944 | −365 127 | −363 047 | −360 340 |
| | $\Delta H(x)$ | 0 | −2 763 | −5 944 | −6 727 | −7 847 | −8 340 |
| 7 | $E_{\mathrm{Au}}(x)$ | −368 000 | −366 677 | −364 943 | −364 431 | −363 507 | −362 715 |
| | $E_{\mathrm{Cu}}(x)$ | −371 902 | −368 312 | −362 926 | −361 131 | −357 541 | −353 951 |
| | $E(x)$ | −368 000 | −366 841 | −364 438 | −363 441 | −361 120 | −358 333 |
| | $\Delta H(x)$ | 0 | −2 041 | −4 438 | −5 041 | −5 920 | −6 333 |
| 8 | $E_{\mathrm{Au}}(x)$ | −368 000 | −376 505 | −387 662 | −390 953 | −396 895 | −401 983 |
| | $E_{\mathrm{Cu}}(x)$ | −282 147 | −291 975 | −304 866 | −308 670 | −315 536 | −321 415 |
| | $E(x)$ | −368 000 | −368 052 | −366 963 | −366 268 | −364 352 | −361 699 |
| | $\Delta H(x)$ | 0 | −3 252 | −6 963 | −7 868 | −9 152 | −9 699 |
| 9 | $E_{\mathrm{Au}}(x)$ | −368 000 | −369 134 | −370 622 | −371 061 | −371 854 | −372 532 |
| | $E_{\mathrm{Cu}}(x)$ | −349 463 | −349 228 | −348 411 | −348 016 | −347 040 | −345 817 |
| | $E(x)$ | −368 000 | −367 144 | −365 070 | −364 148 | −361 928 | −359 175 |
| | $\Delta H(x)$ | 0 | −2 344 | −5 070 | −5 748 | −6 728 | −7 175 |

| No. | | $x$(Cu) | | | | |
|---|---|---|---|---|---|---|
| | | 0.6 | 0.7 | 0.75 | 0.9 | 1 |
| 1 | $E_{\mathrm{Au}}(x)$ | −376 133 | −377 488 | −378 166 | −380 199 | −381 554 |
| | $E_{\mathrm{Cu}}(x)$ | −341 422 | −340 066 | −339 389 | −337 355 | −336 000 |
| | $E(x)$ | −355 306 | −351 293 | −349 083 | −341 640 | −336 000 |
| | $\Delta H(x)$ | −6 506 | −5 693 | −5 083 | −2 440 | 0 |

Continue

| No. | | $x$(Cu) | | | | |
|---|---|---|---|---|---|---|
| | | 0.6 | 0.7 | 0.75 | 0.9 | 1 |
| 2 | $E_{\mathrm{Au}}(x)$ | −386 642 | −389 749 | −391 303 | −395 963 | −399 070 |
| | $E_{\mathrm{Cu}}(x)$ | −334 695 | −335 221 | −335 434 | −335 873 | −336 000 |
| | $E(x)$ | −355 474 | −351 579 | −349 401 | −341 882 | −336 000 |
| | $\Delta H(x)$ | −6 674 | −5 979 | −5 401 | −2 682 | 0 |
| 3 | $E_{\mathrm{Au}}(x)$ | −377 945 | −379 603 | −380 432 | −382 918 | −384 576 |
| | $E_{\mathrm{Cu}}(x)$ | −340 493 | −339 569 | −339 057 | −337 323 | −336 000 |
| | $E(x)$ | −355 474 | −351 579 | −349 401 | −341 882 | −336 000 |
| | $\Delta H(x)$ | −6 674 | −5 979 | −5 401 | −2 682 | 0 |
| 4 | $E_{\mathrm{Au}}(x)$ | −370 754 | −371 678 | −372 190 | −373 925 | −375 247 |
| | $E_{\mathrm{Cu}}(x)$ | −344 563 | −342 422 | −341 352 | −338 141 | −336 000 |
| | $E(x)$ | −355 039 | −351 199 | −349 061 | −341 719 | −336 000 |
| | $\Delta H(x)$ | −6 239 | −5 599 | −5 061 | −2 519 | 0 |
| 5 | $E_{\mathrm{Au}}(x)$ | −376 855 | −379 826 | −381 472 | −387 050 | −391 303 |
| | $E_{\mathrm{Cu}}(x)$ | −338 890 | −337 726 | −337 254 | −336 281 | −336 000 |
| | $E(x)$ | −354 076 | −350 356 | −348 309 | −341 358 | −336 000 |
| | $\Delta H(x)$ | −5 276 | −4 756 | −4 309 | −2 158 | 0 |
| 6 | $E_{\mathrm{Au}}(x)$ | −358 552 | −355 382 | −353 626 | −347 674 | −343 137 |
| | $E_{\mathrm{Cu}}(x)$ | −355 909 | −351 815 | −349 547 | −341 860 | −336 000 |
| | $E(x)$ | −356 966 | −352 885 | −350 566 | −342 442 | −336 000 |
| | $\Delta H(x)$ | −8 166 | −7 285 | −6 566 | −3 242 | 0 |
| 7 | $E_{\mathrm{Au}}(x)$ | −362 057 | −361 532 | −361 319 | −360 879 | −360 753 |
| | $E_{\mathrm{Cu}}(x)$ | −350 361 | −346 771 | −344 975 | −339 590 | −336 000 |
| | $E(x)$ | −355 039 | −351 199 | −349 061 | −341 719 | −336 000 |
| | $\Delta H(x)$ | −6 239 | −5 599 | −5 061 | −2 519 | 0 |
| 8 | $E_{\mathrm{Au}}(x)$ | −406 216 | −409 595 | −410 964 | −413 790 | −414 605 |
| | $E_{\mathrm{Cu}}(x)$ | −326 307 | −330 211 | −331 793 | −335 058 | −336 000 |
| | $E(x)$ | −358 270 | −354 026 | −351 586 | −342 931 | −336 000 |
| | $\Delta H(x)$ | −9 470 | −8 426 | −7 586 | −3 731 | 0 |
| 9 | $E_{\mathrm{Au}}(x)$ | −373 097 | −373 548 | −373 730 | −374 107 | −374 216 |
| | $E_{\mathrm{Cu}}(x)$ | −344 347 | −342 631 | −341 680 | −338 457 | −336 000 |
| | $E(x)$ | −355 847 | −351 906 | −349 692 | −342 022 | −336 000 |
| | $\Delta H(x)$ | −7 047 | −6 306 | −5 692 | −2 822 | 0 |

According to the potential energy sequences of the characteristic atoms in the fcc-based Au-Cu system, the potential energies $\varepsilon_i^{\mathrm{Au}}$ and $\varepsilon_i^{\mathrm{Cu}}$ of characteristic atoms occupied at the *i*th sites in the cell, the average potential energies $E(x, 0, 0)$ and heats of formation $\Delta H(x, 0, 0)$ of the compounds can be calculated by CCA law. If the vibrational contribution to and the effect of variation in ordering degree on the entropy and enthalpy are neglected, the critical $T_{\mathrm{c}}(0)$-temperature of the order-disorder phase transformation is calculated by the potential energy difference divided by the congfigurational entropy difference:

$$T_{\mathrm{c}}(x,0,\sigma_{\max})=\frac{E(x,0,\sigma_{\max})-E(x,0,0)}{S^{\mathrm{c}}(x,\sigma_{\max})-S^{\mathrm{c}}(x,0)} \tag{10}$$

The results are listed in Table 5 and shown in Fig.5, from which the following knowledges can be obtained:

1) The average potential energies of these compounds obtained from the 2nd to 9th *E*-functions are equal each to each, but their potential energies of characteristic atoms are different each to each.

2) The average potential energies and heats of

**Table 5** Potential energies of characteristic atoms ($\varepsilon$, in $10^{-19}$ J/atom), total potential energies ($E$, in J/mol), heats of formation ($\Delta H$, in J/mol) and order-disorder transformation temperatures ($T_c$, in K) of $L1_2$-Au$_3$Cu, $L1_0$-AuCu and $L1_2$-AuCu$_3$ compounds at 0 K

| No. | $L1_2$-Au$_3$Cu | | | | |
|---|---|---|---|---|---|
| | $\varepsilon_4^{Au}$ | $\varepsilon_0^{Cu}$ | $E$ | $\Delta H$ | $T_c$ |
| 1 | −3.860 83 | −3.622 83 | −366 777 | −6 777 | 362.37 |
| 2 | −3.921 34 | −3.407 24 | −365 956 | −5 956 | 251.85 |
| 3 | −3.871 26 | −3.557 46 | −365 956 | −5 956 | 251.85 |
| 4 | −3.822 35 | −3.704 21 | −365 956 | −5 956 | 324.51 |
| 5 | −3.840 84 | −3.648 75 | −365 956 | −5 956 | 485.48 |
| 6 | −3.785 37 | −3.815 15 | −365 956 | −5 956 | 2.58 |
| 7 | −3.772 27 | −3.854 44 | −365 956 | −5 956 | 324.51 |
| 8 | −4.082 35 | −2.924 21 | −365 956 | −5 956 | −215.40 |
| 9 | −3.849 79 | −3.621 88 | −365 956 | −5 956 | 189.53 |
| Exp. | | | −365 736$^a$ | −5 736$^b$ | 473$^c$ |

| No. | $L1_0$-AuCu | | | | |
|---|---|---|---|---|---|
| | $\varepsilon_8^{Au}$ | $\varepsilon_4^{Cu}$ | $E$ | $\Delta H$ | $T_c$ |
| 1 | −3.907 65 | −3.576 00 | −361 036 | −9 036 | 391.98 |
| 2 | −4.028 68 | −3.448 97 | −360 746 | −8 746 | 340.11 |
| 3 | −3.928 53 | −3.549 12 | −360 746 | −8 746 | 340.11 |
| 4 | −3.847 38 | −3.630 26 | −360 746 | −8 746 | 418.70 |
| 5 | −3.921 34 | −3.556 30 | −360 746 | −8 746 | 592.82 |
| 6 | −3.699 47 | −3.778 17 | −360 746 | −8 746 | 70.47 |
| 7 | −3.747 23 | −3.730 41 | −360 746 | −8 746 | 418.70 |
| 8 | −4.243 36 | −3.234 29 | −360 746 | −8 746 | -165.32 |
| 9 | −3.871 26 | −3.606 38 | −360 746 | −8 746 | 272.70 |
| Exp. | | | −360 746$^a$ | −8 746$^b$ | 683$^c$ |

| No. | $L1_2$-AuCu$_3$ | | | | |
|---|---|---|---|---|---|
| | $\varepsilon_{12}^{Au}$ | $\varepsilon_8^{Cu}$ | $E$ | $\Delta H$ | $T_c$ |
| 1 | −3.954 48 | −3.529 17 | −378 166 | −6 777 | 362.37 |
| 2 | −4.136 02 | −3.474 00 | −391 303 | −7 164 | 376.99 |
| 3 | −3.985 79 | −3.524 08 | −391 303 | −7 164 | 376.99 |
| 4 | −3.889 11 | −3.556 30 | −391 303 | −7 164 | 449.65 |
| 5 | −4.055 51 | −3.500 84 | −391 303 | −7 164 | 610.61 |
| 6 | −3.556 31 | −3.667 24 | −391 303 | −7 164 | 127.71 |
| 7 | −3.738 89 | −3.606 38 | −391 303 | −7 164 | 449.65 |
| 8 | −4.297 03 | −3.420 33 | −391 303 | −7 164 | −90.27 |
| 9 | −3.878 42 | −3.559 87 | −391 303 | −7 164 | 314.67 |
| Exp. | | – | −351 164$^a$ | −7 164$^b$ | 663$^c$ |

a: Calculated from the experimental cohesive energy of the elemental solids[16] and $\Delta H$[13]; b: Taken from Ref.[13]; c: Taken from Ref.[21].

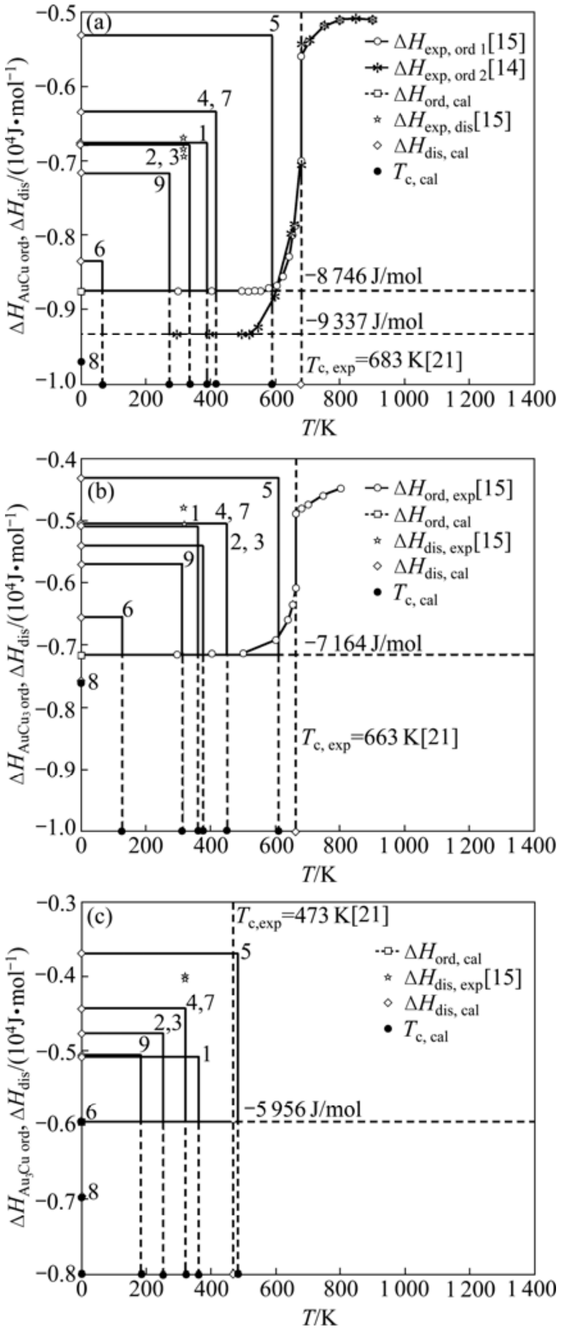


**Fig.5** $\Delta H_{\text{ord}}(0)$–$\Delta H_{\text{dis}}(0)$—$T_c$ interrelated patterns of AuCu (a), AuCu$_3$ (b) and Au$_3$Cu (c) compounds relative to corresponding disordered Au$_{1-x}$Cu$_x$ alloys calculated from nine $E$-functions together with experimental data

formation of the $L1_0$-AuCu and $L1_2$-AuCu$_3$ compound obtained by the 2nd to 9th $E$-functions are equal respectively to corresponding experimental values, but only the $T_c$-temperatures obtained by 5th $E$-function are closer by experiment values than ones obtained by other $E$-functions.

3) The average potential energies and heats of formation of the $L1_2$-Au$_3$Cu compound calculated from the 2nd to 9th $E$-functions are equal each to each and closer by the experiment values, but only the $T_c$-temperature obtained by the 5th $E$-function is closer by experiment value than ones obtained by other $E$-functions.

4) The $\Delta H_{\text{ord}}(0)$–$\Delta H_{\text{dis}}(0)$ — $T_c(0)$ interrelated

patterns of the AuCu, $AuCu_3$ and $Au_3Cu$ compounds relative to corresponding disordered alloys obtained respectively from nine *E*-functions show that the heats of formation and $T_c$-temperatures calculated by 5th *E*-function can be satisfactory for describing experimental values at the same time.

### 2.4 Energetic properties of $Au_3Cu$-, AuCu- and $AuCu_3$-type ordered $Au_{1-x}Cu_x$ alloys

In the SSA framework, the ordering of disordered alloys is attributed to degeneracy in the energy, volume and electronic structure states of characteristic atoms, and the disordering of ordered alloys is attributed to split in the energy, volume and electronic structure states of characteristic atoms. According to the potential energy sequences and concentrations $x_i^{Au}(x,\sigma)$ and $x_i^{Cu}(x,\sigma)$ in the ordered $Au_{1-x}Cu_x$ alloys with ordering degree $\sigma$, their energetic properties can be calculated by nine *E*-functions in Table 1. The concentrations $x_i^{Au}(x,\sigma_{max})$ and $x_i^{Cu}(x,\sigma_{max})$ of characteristic atoms and some energetic properties of $Au_3Cu$-, AuCu- and $AuCu_3$-type ordered $Au_{1-x}Cu_x$ alloys with maximal ordering degrees are shown in Figs.6 and 7, but only the calculated energetic properties of the Au-Cu-type ordered alloys are listed in Table 6.

According to Eq.(10), the critical temperatures $T_c(x, 0, \sigma_{max})$ of $Au_3Cu$-, AuCu- and $AuCu_3$-type $Au_{1-x}Cu_x$ alloys translated into the disordered alloys described by

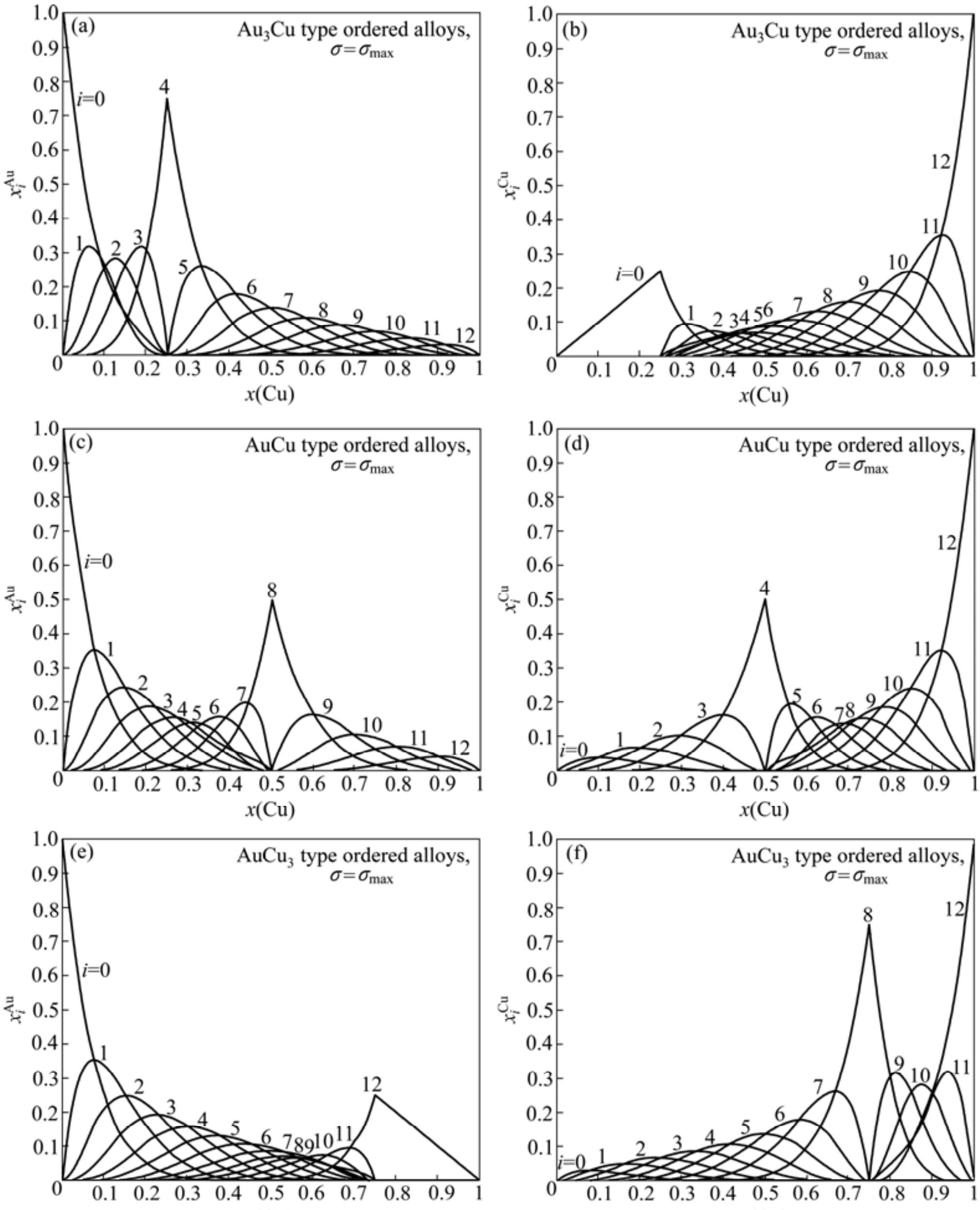


**Fig.6** Concentrations $x_i^{Au}(x,\sigma_{max})$ and $x_i^{Cu}(x,\sigma_{max})$ of characteristic atoms in $Au_3Cu$-, AuCu- and $AuCu_3$-type ordered $Au_{1-x}Cu_x$ alloys with maximal ordering degrees

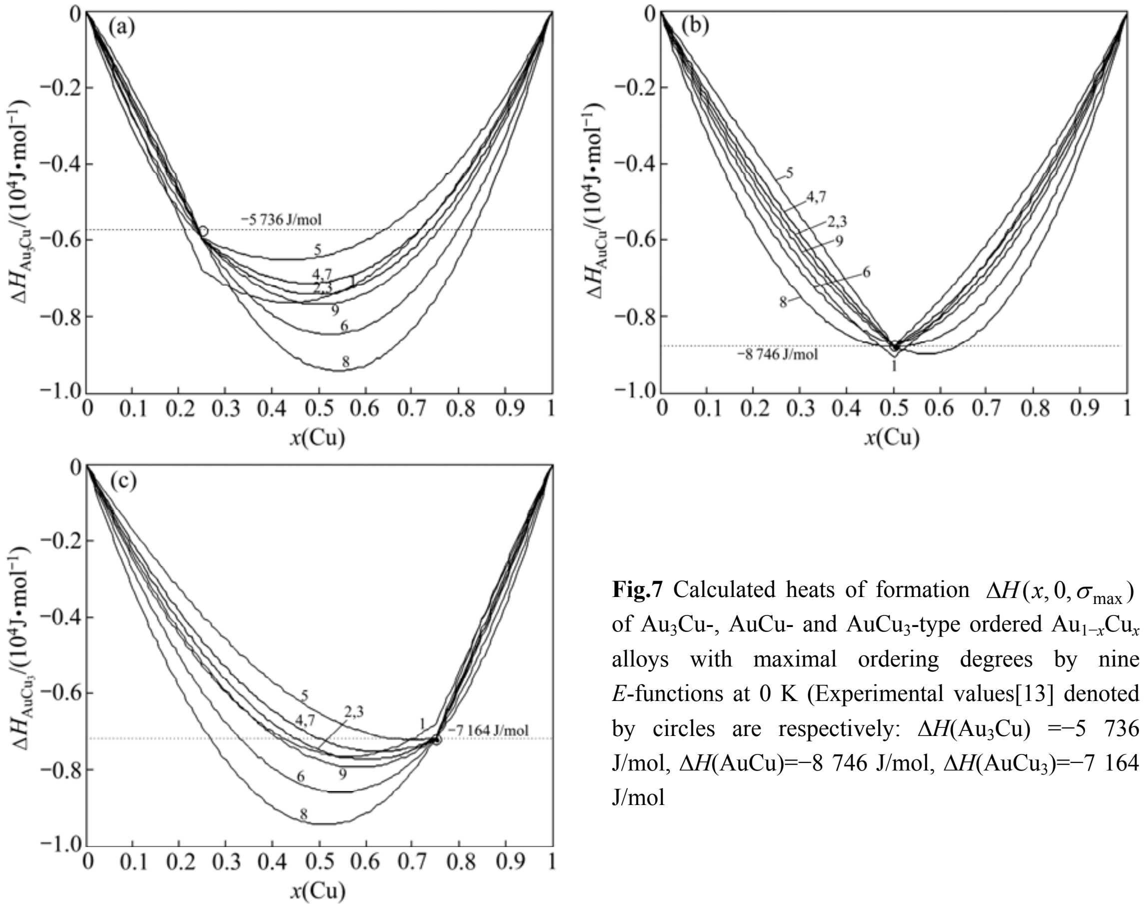


**Fig.7** Calculated heats of formation $\Delta H(x,0,\sigma_{\max})$ of $Au_3Cu$-, AuCu- and $AuCu_3$-type ordered $Au_{1-x}Cu_x$ alloys with maximal ordering degrees by nine *E*-functions at 0 K (Experimental values[13] denoted by circles are respectively: $\Delta H(Au_3Cu)$ =−5 736 J/mol, $\Delta H$(AuCu)=−8 746 J/mol, $\Delta H(AuCu_3)$=−7 164 J/mol

**Table 6** Potential energies $E(x,0,\sigma_{\max})$ and heats of formation $\Delta H(x,0,\sigma_{\max})$ of AuCu-type ordered $Au_{1-x}Cu_x$ alloys with maximal ordering degree calculated by nine *E*-functions at 0 K (J/mol)

| No. | | x(Cu) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 0.1 | 0.25 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.75 | 0.9 | 1 |
| 1 | *E*(*x*) | −368 000 | −367 330 | −365 648 | −364 906 | −363 152 | −361 036 | −356 752 | −352 106 | −349 648 | −341 730 | −336 000 |
| | Δ*H*(*x*) | 0 | −2 530 | −5 648 | −6 506 | −7 952 | −9 036 | −7 952 | −6 506 | −5 648 | −2 530 | 0 |
| 2 | *E*(*x*) | −368 000 | −367 065 | −365 202 | −364 451 | −362 742 | −360 746 | −356 796 | −352 361 | −349 957 | −341 977 | −336 000 |
| | Δ*H*(*x*) | 0 | −2 265 | −5 202 | −6 051 | −7 542 | −8 746 | −7 996 | −6 761 | −5 957 | −2 777 | 0 |
| 3 | *E*(*x*) | −368 000 | −367 065 | −365 202 | −364 451 | −362 742 | −360 746 | −356 796 | −352 361 | −349 957 | −341 977 | −336 000 |
| | Δ*H*(*x*) | 0 | −2 265 | −5 202 | −6 051 | −7 542 | −8 746 | −7 996 | −6 761 | −5 957 | −2 777 | 0 |
| 4 | *E*(*x*) | −368 000 | −366 920 | −364 976 | −364 233 | −362 597 | −360 746 | −356 651 | −352 144 | −349 731 | −341 833 | −336 000 |
| | Δ*H*(*x*) | 0 | −2 120 | −4 976 | −5 833 | −7 397 | −8 746 | −7 851 | −6 544 | −5 731 | −2 633 | 0 |
| 5 | *E*(*x*) | −368 000 | −366 599 | −364 474 | −363 752 | −362 276 | −360 746 | −356 330 | −351 662 | −349 229 | −341 511 | −336 000 |
| | Δ*H*(*x*) | 0 | −1 799 | −4 474 | −5 352 | −7 076 | −8 746 | −7 530 | −6 062 | −5 229 | −2 311 | 0 |
| 6 | *E*(*x*) | −368 000 | −367 563 | −365 979 | −365 197 | −363 239 | −360 746 | −357 294 | −353 107 | −350 734 | −342 475 | −336 000 |
| | Δ*H*(*x*) | 0 | −2 763 | −5 979 | −6 797 | −8 039 | −8 746 | −8 494 | −7 507 | −6 734 | −3 275 | 0 |
| 7 | *E*(*x*) | −368 000 | −366 920 | −364 976 | −364 233 | −362 597 | −360 746 | −356 651 | −352 144 | −349 731 | −341 833 | −336 000 |
| | Δ*H*(*x*) | 0 | −2 120 | −4 976 | −5 833 | −7 397 | −8 746 | −7 851 | −6 544 | −5 731 | −2 633 | 0 |
| 8 | *E*(*x*) | −368 000 | −367 997 | −366 659 | −365 849 | −363 674 | −360 746 | −357 728 | −353 759 | −351 414 | −342 910 | −336 000 |
| | Δ*H*(*x*) | 0 | −3 197 | −6 659 | −7 449 | −8 474 | −8 746 | −8 928 | −8 159 | −7 414 | −3 710 | 0 |
| 9 | *E*(*x*) | −368 000 | −367 190 | −365 396 | −364 637 | −362 866 | −360 746 | −356 921 | −352 548 | −350 151 | −342 102 | −336 000 |
| | Δ*H*(*x*) | 0 | −2 390 | −5 396 | −6 237 | −7 666 | −8 746 | −8 121 | −6 948 | −6 151 | −2 902 | 0 |

nine *E*-functions have been calculated. The $T_c(0)$-temperatures obtained from 5th *E*-function are closer respectively by the experimental values than from other *E*-functions (see Fig.8).

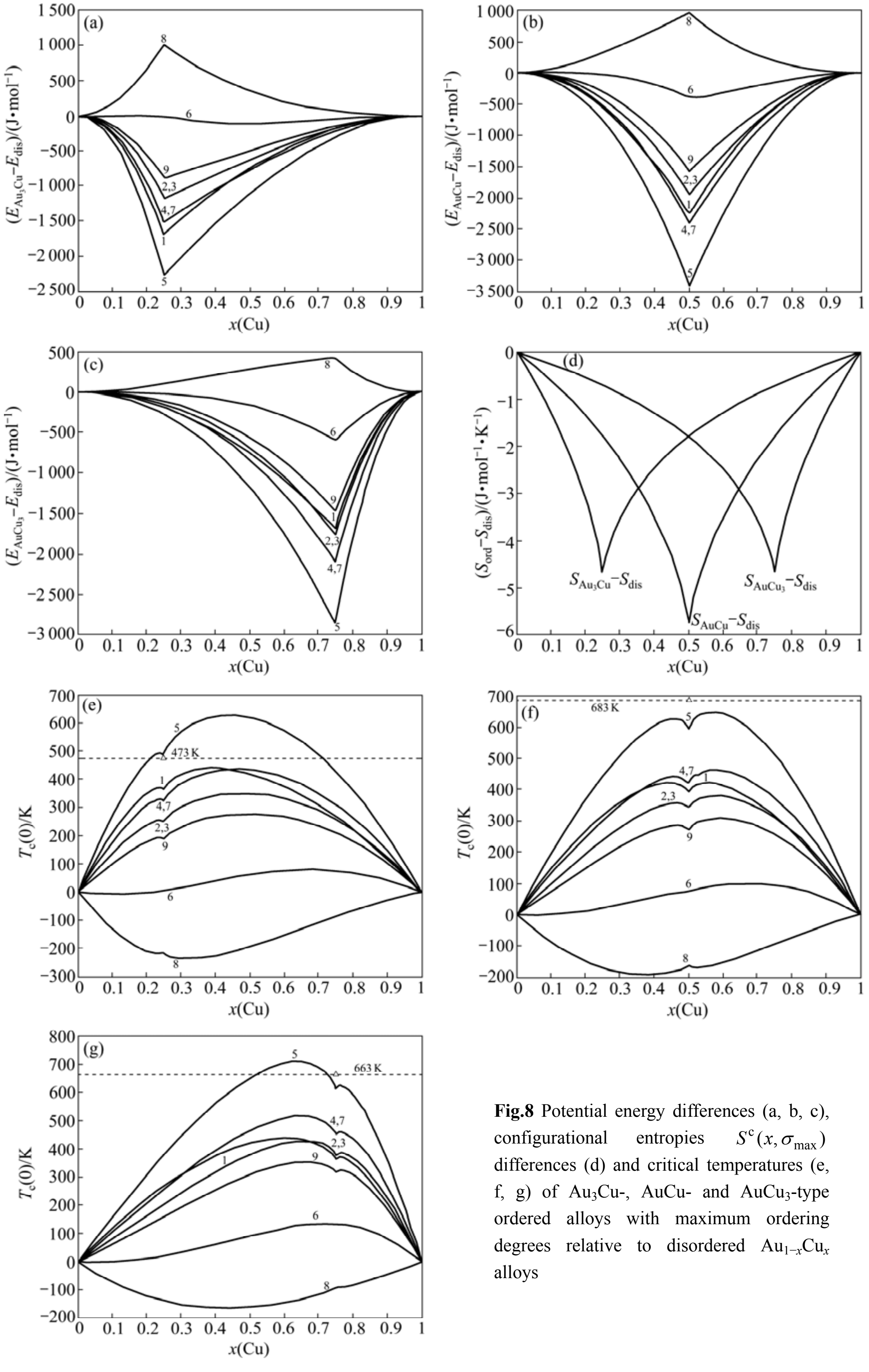


**Fig.8** Potential energy differences (a, b, c), configurational entropies $S^c(x,\sigma_{max})$ differences (d) and critical temperatures (e, f, g) of $Au_3Cu$-, AuCu- and $AuCu_3$-type ordered alloys with maximum ordering degrees relative to disordered $Au_{1-x}Cu_x$ alloys

# 3 Conclusions

1) From the smaller experimental heats of formation of the $L1_0$-AuCu and $L1_2$-$AuCu_3$ compounds, only the potential energy sequences have been separated out by nine *E*-functions. Although the potential energies of the $L1_2$-$Au_3Cu$, $L1_0$-AuCu and $L1_2$-$AuCu_3$ compounds calculated from the 2nd to 9th *E*-functions are equal each to each, the potential energies of their characteristic atoms are not equal each to each.

2) According to the potential energy sequences of the nine *E*-functions, the heats of formation of the disordered $Au_{1-x}Cu_x$ alloys have been calculated. But there is no *E*-function, which can well describe the experimental heats of formation in the whole compositional range. It has been discovered that the so-called experimental disordered $Au_{1-x}Cu_x$ alloys are the partly ordered alloys with short range ordering degree, which will be reported in the second part of this investigation.

3) The $T_c(0)$ -temperatures of the $Au_3Cu$, AuCu and $AuCu_3$ compounds obtained from the 5th *E*-function are closer by the experimental values than from other *E*-functions. The $T_c(0)$-temperatures of these three compounds obtained from the other *E*-functions are greatly lower than experimental ones.

4) The 5th *E*-function may be chosen for developing it into the free energy, enthalpy, vibrational energy and vibrational entropy functions for describing the composition- temperature-ordering degree dependence of thermodynamic properties of the compounds, ordered and disordered phases, and for establishing the phase diagram of the Au-Cu system in the future.

5) Although the potential energy sequences of characteristic atoms are separated out from the experimental heats of formation of both $L1_0$-AuCu and $L1_2$-$AuCu_3$ compounds only, which can be used for calculating energetic properties of compounds, ordered and disordered alloys. This demonstrates that the first scientific philosophy proposition about the diversity of structures and properties of the system is correct, and that the whole energetic information can be reproduced from a part energetic information.

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