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Volume sequences of characteristic atoms separated from experimental volumes of AuCu and $AuCu_3$ compounds

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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 volume sequences of characteristic atoms at the central sites of the basic clusters in the fcc-based Au-Cu system are separated out from the experimental volumes of $L1_0$-AuCu and $L1_2$-$AuCu_3$ compounds at room temperature only, by nine volume V-functions. From these volume sequences, the volumes, volumes of formation, ordering (excess) volumes and volume mismatch degrees of the $L1_0$-AuCu, $L1_2$-$AuCu_3$ and $L1_2$-Au_3Cu compounds, Au_3Cu-, AuCu- and $AuCu_3$-type ordered alloys with maximal ordering degree, and disordered $Au_{1-x}Cu_x$ alloys are calculated. Among these functions, only ordering volumes of the compounds and ordered alloys obtained by the 6th V-function are negative, i.e., the destruction of the superlattice is accompanied by an increase in volume, which is identical with the experimental results. Accompanying conclusions, the different descriptions of volumetric properties between traditional alloy theories and SSA framework are discussed.

Key words: systematic science of alloys; Au-Cu system; atomic volume; volume of formation; ordering volume; volume mismatch

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1 Introduction

In order to get an entire understanding of the alloy systems, to establish phase diagrams and to search a method for designing of alloys, the SSA framework[1] has been established on the basis of 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; and a systematic theory of any complex system described quantitatively should be constructed by structural unit sequence-, equation- and information-chains. The SSA framework is constructed indeed by the structural unit sequence-, equation- and information-chains.

1.1 Models and structure unit sequence-chain

An alloy system contains three structure levels: the phase level of organizations, atomic level of phases and electronic level of atoms. The atomic level of alloy phases in the SSA framework involves three models for constructing diversity of structures and properties of alloy phases[1−4].

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, and each cluster consists of a central atom, the first neighbor configuration, the second neighbor configuration and the third neighbor configuration. The actions of the BCO model are as follows: 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.

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In the present work, the long-period superlattice structure AuCu Ⅱ is not concerned. Therefore, to use one order split is enough, where the basic B_i^α-cluster consists of a central A_i^α atom and the first neighboring configuration [(*I*−*i*)Au, *i*Cu], which contains *i* Cu-atoms and (*I*−*i*) Au-atoms. Here, the symbol α denotes Au or Cu; *I* is the coordinative number and equals 12 for the fcc-based lattice; *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, and each characteristic atom is the central atom of a specific basic cluster. The characteristic A_i^α 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 as follows: 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; 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 (σ); 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.

Therefore, in a based lattice alloy system 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, and each characteristic crystal consists of the same characteristic atoms with the identical potential energy, identical volume and identical electronic structure. The actions of the CCM model are as follows: to establish a set of temperature (T) dependent functions of the energetic and volumetric properties consisting of general volume $V^{\mathrm{v}}(T)$ function, the general thermal expansion coefficient $\beta(T)$ 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 general volume $V^{\mathrm{v}}(x,T,\sigma)$, general thermal expansion coefficient $\beta^{\mathrm{v}}(x,T,\sigma)$, 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, combining the $G^*(x,T,\sigma)$ function with partition function the general free energy $G(x,T,\sigma)$ function can be derived, where the $G(x,T,\sigma)$ function contains configuration entropy $S^{\mathrm{c}}(x,\sigma)$. This action will be presented in the future.

These three models are proposed in order to overcome disappointments of the atomic pair interaction model and central atom model[5] as well as effective cluster interaction model[6−9].

1.2 Equation- and information-chains

1.2.1 Additive law of *q*-properties of characteristic crystals (atoms)

According to CCM model (or CAA model), the extensive properties $q(x,T,\sigma)$, $q_{\mathrm{A}}(x,T,\sigma)$, $q_{\mathrm{B}}(x,T,\sigma)$ of a given alloy phase and its components can be obtained by an additive law of the *q*-properties of characteristic crystals (atoms) (in terms of CCA law or CAA model))[1]:

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

where $x_i^{\mathrm{A}}(x,\sigma)$ and $x_i^{\mathrm{B}}(x,\sigma)$ are the concentrations of the characteristic crystal (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 types of relations of q_i^{A} and q_i^{B} with i have been designed[1, 10−12]:

Type I of straight line relation:

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

Type II of concave parabola relation:

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

Type III of convex parabola relation:

$$\begin{cases} q_i^{\mathrm{A}} = q_0^{\mathrm{A}} + (2i/I)(q_I^{\mathrm{A}} - q_0^{\mathrm{A}}) - (i/I)^2(q_I^{\mathrm{A}} - q_0^{\mathrm{A}}) \\ q_i^{\mathrm{B}} = q_I^{\mathrm{B}} + [2(I-i)/I](q_0^{\mathrm{B}} - q_{\mathrm{I}}^{\mathrm{B}}) - \\ \qquad [(I-i)/I]^2(q_0^{\mathrm{B}} - q_{\mathrm{I}}^{\mathrm{B}}) \end{cases} \tag{4}$$

where q_0^{A} and q_I^{B} denote, respectively, corresponding properties of the primary C_0^{A} and C_I^{B} characteristic crystals (atoms); q_I^{A} and q_0^{B} denote, respectively, corresponding properties of the terminal C_I^{A} and C_0^{B} characteristic crystals (atoms).

By combining Eqs.(2), (3), (4) and substituting them into Eq.(1), nine $q(x,0,\sigma)$ functions can be obtained, which can be used to compounds, ordered and disordered alloy phases; and nine $q(x,0,0)$ -functions, which are derived from corresponding $q(x,0,\sigma)$ functions and can be used to the disordered alloy phase only[1, 10−13].

1.3 Methodology

1.3.1 Inference from the first proposition

The whole can be reproduced from a few parts. For example, the whole of a tree can be reproduced respectively from a seed, a leaf or a branch of the tree, and the whole of a sheep can be reproduced respectively from a egg cell or a body cell of the sheep in biologic systems; the whole information of an alloy system can be reproduced respectively from a few disordered alloys, a few ordered alloys or a few 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 in an alloy system can be reproduced. Therefore, the systematic study for an alloy system in the SSA framework is divided into three step investigations.

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 a few intermetallics only, or of experimental heats and volumes of formation of a few intermetallics only or a few 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); and finally to study energetic properties, volumetric properties and electronic structures of alloy phases as function of composition (x) 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, as well as some physical properties 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 properties, crystalline and electronic structures of characteristic crystal (atom) sequences for designing applied alloys. That is called as design engineering of characteristic atom sequences of alloy systems.

The potential energy sequences of A_i^{Au} and A_i^{Cu} characteristic atoms separated out from experimental heats of formation of some disordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys only[12, 14] and of $L1_0$-AuCu and $L1_2$-$\mathrm{AuCu_3}$ compounds only[13, 15] have been performed, respectively. In this work, the volume sequences of the A_i^{Au} and A_i^{Cu} characteristic atoms are separated out from experimental volumes of the $L1_0$-AuCu and $L1_2$-$\mathrm{AuCu_3}$ compounds.

1.3.2 Survey for descriptions of volumetric properties of alloys in traditional alloy theories

These descriptions are as follows[16−17]: the molar volume, average atomic volume and cell volume of alloys; the volume of formation and change on disordering of intermetallics; the partial atomic volume of components in an alloy, effective atomic volume instead of partial atomic volume and realistic volume instead of partial atomic volume; the volume mismatch of the constituent atoms represented by the ratio of the partial atomic volume of the minor component to that of the elemental volume of the major component.

1.3.3 Volumetric properties of alloys in SSA framework by taking Au-Cu system as an example

1) The volume sequences of characteristic atoms of components Au and Cu represent the realistic volumes of atoms surrounded by various neighbor configurations, and the results are listed in Table 1 and shown in Fig.1.

2) The volumetric properties of disordered and ordered alloys are presented in Section 2.2 and 2.3: the volumes (V_i^{Au}, V_i^{Cu}) and concentrations (x_i^{Au}, x_i^{Cu}) of characteristic atoms in a given alloy; the average atomic volume $V_{\mathrm{a}}(x)$, average atomic volume of formation $\Delta V_{\mathrm{a}}^{\mathrm{m}}(x)$, average volume $V(x)$ and average volume of formation $\Delta V_{\mathrm{c}}^{\mathrm{m}}(x)$ of a cell for a given alloy; average atomic volume ($V_{\mathrm{Au}}(x)$, $V_{\mathrm{Cu}}(x)$) and average atomic volume (lattice parameter) of formation ($\Delta V_{\mathrm{Au}}^{\mathrm{m}}(x)$, $\Delta V_{\mathrm{Cu}}^{\mathrm{m}}(x)$) of components Au and Cu; the ordering (excess) atomic volume $\Delta V^{\mathrm{ex}}(x)$ which is

Table 1 Volume sequences of characteristic atoms calculated by nine *V*-functions on the basis of experimental volumes of $L1_0$-AuCu and $L1_2$-AuCu$_3$ compounds (in nm^3)

No.	Volume sequence	i												
		0	1	2	3	4	5	6	7	8	9	10	11	12
1	V_i^{Au}	16.958 11	16.964 49	16.970 86	16.977 23	16.983 60	16.989 98	16.996 35	17.002 72	17.009 09	17.015 47	17.021 84	17.028 21	17.034 58
	V_i^{Cu}	11.888 84	11.882 47	11.876 09	11.869 72	11.863 35	11.856 98	11.850 60	11.844 23	11.837 86	11.831 49	11.825 11	11.818 74	11.812 37
2	V_i^{Au}	16.958 11	16.958 45	16.958 79	16.959 13	16.959 47	16.959 81	16.960 15	16.960 49	16.960 83	16.961 17	16.961 51	16.961 85	16.962 19
	V_i^{Cu}	12.084 69	12.041 19	12.001 48	11.965 55	11.933 40	11.905 03	11.880 45	11.859 65	11.842 63	11.829 39	11.819 93	11.814 26	11.812 37
3	V_i^{Au}	16.958 11	17.003 84	17.049 56	17.095 29	17.141 02	17.186 74	17.232 47	17.278 19	17.323 92	17.369 64	17.415 37	17.461 10	17.506 82
	V_i^{Cu}	11.540 05	11.541 94	11.547 62	11.557 07	11.570 31	11.587 33	11.608 13	11.632 71	11.661 08	11.693 23	11.729 16	11.768 87	11.812 37
4	V_i^{Au}	16.958 11	16.956 22	16.950 55	16.941 09	16.927 86	16.910 84	16.890 03	16.865 45	16.837 08	16.804 93	16.769 00	16.729 29	16.685 80
	V_i^{Cu}	12.179 53	12.148 94	12.118 34	12.087 74	12.057 15	12.026 55	11.995 95	11.965 35	11.934 76	11.904 16	11.873 56	11.842 97	11.812 37
5	V_i^{Au}	16.958 11	16.958 13	16.958 20	16.958 30	16.958 45	16.958 64	16.958 88	16.959 15	16.959 47	16.959 83	16.960 23	16.960 68	16.961 17
	V_i^{Cu}	12.087 74	12.043 76	12.003 60	11.967 27	11.934 76	11.906 07	11.881 21	11.860 18	11.842 97	11.829 58	11.820 02	11.814 28	11.812 37
6	V_i^{Au}	16.958 11	16.952 40	16.935 25	16.906 67	16.866 66	16.815 22	16.752 35	16.678 04	16.592 31	16.495 14	16.386 54	16.266 51	16.135 05
	V_i^{Cu}	12.363 12	12.359 29	12.347 82	12.328 69	12.301 92	12.267 50	12.225 43	12.175 71	12.118 34	12.053 32	11.980 65	11.900 34	11.812 37
7	V_i^{Au}	16.958 11	17.001 61	17.041 32	17.077 25	17.109 40	17.137 77	17.162 35	17.183 15	17.200 17	17.213 41	17.222 87	17.228 54	17.230 43
	V_i^{Cu}	11.634 90	11.649 69	11.664 48	11.679 27	11.694 06	11.708 84	11.723 63	11.738 42	11.753 21	11.768 00	11.782 79	11.797 58	11.812 37
8	V_i^{Au}	16.958 11	16.959 09	16.959 98	16.960 79	16.961 51	16.962 14	16.962 70	16.963 16	16.963 55	16.963 84	16.964 05	16.964 18	16.964 22
	V_i^{Cu}	12.078 57	12.036 06	11.997 23	11.962 11	11.930 68	11.902 95	11.878 92	11.858 58	11.841 95	11.829 01	11.819 76	11.814 22	11.812 37
9	V_i^{Au}	16.958 11	16.990 98	17.020 99	17.048 14	17.072 43	17.093 86	17.112 44	17.128 16	17.141 02	17.151 02	17.158 16	17.162 45	17.16388
	V_i^{Cu}	11.745 82	11.746 28	11.747 67	11.749 98	11.753 21	11.757 37	11.762 46	11.768 46	11.775 40	11.783 25	11.792 03	11.801 74	11.812 37

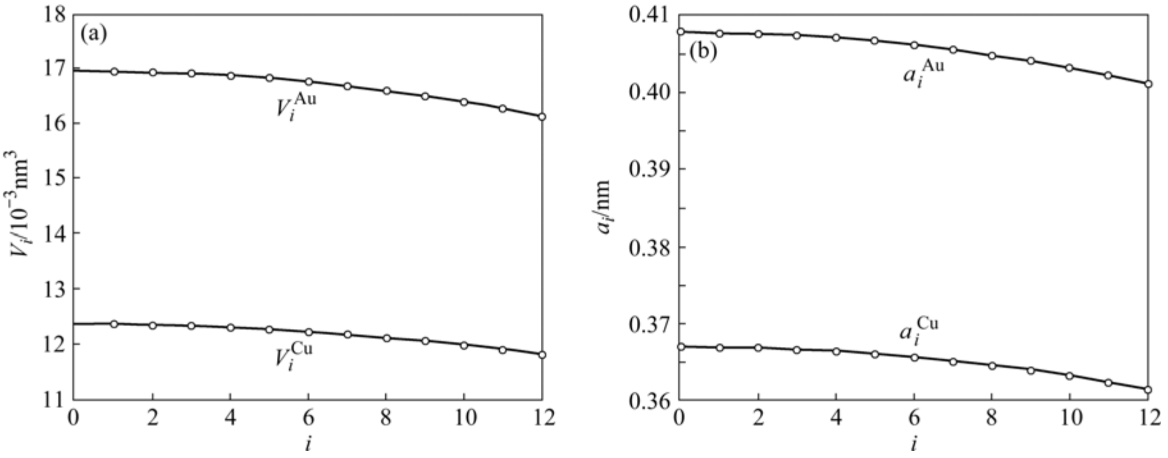

Fig.1 Volume $V_i^{\text{Au}}, V_i^{\text{Cu}}$ (a) and lattice parameter $a_i^{\text{Au}}, a_i^{\text{Cu}}$ (b) sequences obtained by the 6th V-function

defined as the difference in average atomic volumes between ordered and disordered alloys.

3) The volumetric properties of $L1_0$-AuCu, $L1_2$-AuCu$_3$ and $L1_2$-Au$_3$Cu compounds are presented in Section 2.4: the volumes ($V_i^{\text{Au}}, V_i^{\text{Cu}}$) and numbers ($n_i^{\text{Au}}$, n_i^{Cu}) of characteristic atoms in a cell; the total volume V_c and total volume of formation $\Delta V_\text{c}^\text{m}$, lattice parameter a and lattice parameter of formation Δa^m of a cell; ordering (excess) atomic volume ΔV^ex of compounds and ordering lattice parameter Δa^ex; average atomic volumes (V_{Au}, V_{Cu}), average atomic volumes of formation ($\Delta V_{\text{Au}}^\text{m}, \Delta V_{\text{Cu}}^\text{m}$) and average ordering (excess) atomic volume ($V_{\text{Au}}^\text{ex}, V_{\text{Cu}}^\text{ex}$) of formation of components Au and Cu; and volume mismatch degree.

Average atomic volume mismatch degree of characteristic atoms inside α component (α=Au or Cu) is

$$\begin{cases}\Delta m_V^\alpha = \sum_i n_i^\alpha \left|(V_i^\alpha - V_\text{a}^\alpha)\right| \div \sum_i n_i^\alpha V_\text{a}^\alpha \\ V_\text{a}^\alpha = \sum_i n_i^\alpha V_i^\alpha \div \sum_i n_i^\alpha \end{cases} \tag{5}$$

Average atomic volume mismatch degree of characteristic atoms between components Au and Cu is

$$\begin{cases}\Delta m_V = \sum_\alpha \sum_i n_i^\alpha \left|V_i^\alpha - V_\text{a}\right| \div \sum_\alpha \sum_i n_i^\alpha V_\text{a} \\ V_\text{a} = \sum_\alpha \sum_i n_i^\alpha V_i^\alpha \div \sum_\alpha \sum_i n_i^\alpha \end{cases} \tag{6}$$

If there is no splitting atomic volume state, Eq.(6) becomes

$$\begin{cases}\Delta m_V^0 = \sum_\alpha n_\alpha \left|(V_\alpha^0 - V_\text{a}^0)\right| \div \sum_\alpha n_\alpha V_\text{a}^0 \\ V_\text{a}^0 = \sum_\alpha n_\alpha V_\alpha^0 \div \sum_\alpha n_\alpha \end{cases} \tag{7}$$

The total average atomic volume mismatch degree of a compound is

$$\Delta m_V^T = \Delta m_V + \sum_\alpha (n_\alpha / n_T) \Delta m_V{}^\alpha \tag{8}$$

In Eqs.(5)−(7), V_i^α and n_i^α are, respectively, atomic volume and number of the A_i^α characteristic atoms in a cell; V_a^α, average atomic volume of the α-component; V_a, average atomic volume of the compound; V_α^0, atomic volume of the α-element; n_α, number of atoms of the α-component; n_T, total number of atoms in a cell; V_a^0, average atomic volume of the element; V_a, average atomic volume of the compound.

2 Results

2.1 Volume sequences of A_i^{Au} and A_i^{Cu} characteristic atoms

The volume sequences of A_i^{Au} and A_i^{Cu} characteristic atoms are separated out from the experimental average atomic volumes (V_{AuCu}=14.447 1 × 10^{-3}(nm^3), V_{AuCu}= 13.122 5×10^{-3}(nm^3) [17]) of $L1_0$-AuCu and $L1_2$-AuCu$_3$ compounds at room temperature by nine volume V-functions. The results are listed in Table 1, from which the following knowledge can be obtained.

1) The volume sequences of the characteristic atoms obtained by nine V-functions are different each other.

2) In the remainder of this section it has been demonstrated that the volumetric properties of alloy phases in the Au-Cu system should be described by the 6th $V(x)$-function. This means that the relation of V_i^{Au} and V_i^{Cu} with i is described by the following equation:

$$\begin{cases}V_i^{\text{Au}} = V_0^{\text{Au}} + (i/I)^2 (V_I^{\text{Au}} - V_0^{\text{Au}}) \\ V_i^{\text{Cu}} = V_I^{\text{Cu}} + [2(I-i)/I](V_0^{\text{Cu}} - V_I^{\text{Cu}}) - \\ \qquad [(I-i)/I]^2 (V_0^{\text{Cu}} - V_I^{\text{Cu}}) \end{cases} \tag{9}$$

2.2 Volumetric properties of disordered $Au_{(1-x)}Cu_x$ alloys

According to the volume sequences of characteristic atoms in Table 1, the volumes $V(x)$, $V_{Au}(x)$ and $V_{Cu}(x)$ of disordered $Au_{1-x}Cu_x$ alloys and their components as well as their volumes of formation $\Delta V^{m}(x)$ are calculated by the 2nd−9th V-functions, as listed in Table 2 and shown in Fig.2, from which the following knowledge can be obtained.

1) The average atomic volumes $V_{g.Z}(x)$ and lattice parameters $a_{g.Z}(x)$ calculated by the 6th $V(x)$-function are in the best agreement with experimental values, and have positive deviation respectively from Zen's law and Vegard's law (details in Section 3.2).

2) The volumes of formation $\Delta V^{m}(x)$ of disordered $Au_{1-x}Cu_x$ alloys calculated by the 2nd−9th

Table 2 Average volumetric properties $V(x)$, $V_{Au}(x)$, $V_{Cu}(x)$ and $\Delta V^{m}(x)$ of disordered $Au_{1-x}Cu_x$ alloys calculated by the 2nd−9th V-functions at room temperature (in $10^{-3}nm^3$)

No.*	Pro-perty	x(Cu)												
		0	0.1	0.2	0.25	0.3	0.4	0.5	0.6	0.7	0.75	0.8	0.9	1
2	$V_{Au}(x)$	16.958 1	16.958 5	16.958 9	16.959 1	16.959 3	16.959 7	16.960 2	16.960 6	16.961 0	16.961 2	16.961 4	16.961 8	16.962 2
	$V_{Cu}(x)$	12.084 7	12.035 0	11.990 3	11.969 8	11.950 6	11.915 9	11.886 1	11.861 4	11.841 6	11.833 6	11.826 9	11.817 1	11.812 4
	$V(x)$	16.958 1	16.466 2	15.965 2	15.711 8	15.456 7	14.942 2	14.423 1	13.901 1	13.377 4	13.115 5	12.853 8	12.331 6	11.812 4
	$\Delta V^{m}(x)$	0	0.022 6	0.036 2	0.040 1	0.042 3	0.042 4	0.037 9	0.030 4	0.021 4	0.016 7	0.012 3	0.004 7	0
3	$V_{Au}(x)$	16.958 1	17.013 0	17.067 9	17.095 3	17.122 7	17.177 6	17.232 5	17.287 3	17.342 2	17.369 6	17.397 1	17.452 0	17.506 8
	$V_{Cu}(x)$	11.540 1	11.544 8	11.554 6	11.561 3	11.569 3	11.589 1	11.613 8	11.643 5	11.678 3	11.697 5	11.718 0	11.762 7	11.812 4
	$V(x)$	16.958 1	16.466 2	15.965 2	15.711 8	15.456 7	14.942 2	14.423 1	13.901 1	13.377 4	13.115 5	12.853 8	12.331 6	11.812 4
	$\Delta V^{m}(x)$	0	0.022 6	0.036 2	0.040 1	0.042 3	0.042 4	0.037 9	0.030 4	0.021 4	0.016 7	0.012 3	0.004 7	0
4	$V_{Au}(x)$	16.958 1	16.953 4	16.943 6	16.936 8	16.928 8	16.909 1	16.884 4	16.854 6	16.819 9	16.800 7	16.780 2	16.735 5	16.685 8
	$V_{Cu}(x)$	12.179 5	12.142 8	12.106 1	12.087 7	12.069 4	12.032 7	11.996 0	11.959 2	11.922 5	11.904 2	11.885 8	11.849 1	11.812 4
	$V(x)$	16.958 1	16.472 3	15.976 1	15.724 6	15.471 0	14.958 5	14.440 2	13.917 4	13.391 7	13.128 3	12.864 7	12.337 7	11.812 4
	$\Delta V^{m}(x)$	0	0.028 8	0.047 1	0.052 9	0.056 6	0.058 7	0.054 9	0.046 7	0.035 6	0.029 5	0.023 2	0.010 8	0
5	$V_{Au}(x)$	16.958 1	16.958 2	16.958 3	16.958 4	16.958 4	16.958 7	16.958 9	16.959 3	16.959 7	16.959 9	16.960 1	16.960 6	16.961 2
	$V_{Cu}(x)$	12.087 7	12.037 5	11.992 3	11.971 6	11.952 1	11.917 0	11.887 0	11.861 9	11.842 0	11.833 9	11.827 1	11.817 2	11.812 4
	$V(x)$	16.958 1	16.466 1	15.965 1	15.711 7	15.456 6	14.942 0	14.422 9	13.900 9	13.377 3	13.115 4	12.853 7	12.331 5	11.812 4
	$\Delta V^{m}(x)$	0	0.022 6	0.036 1	0.040 0	0.042 2	0.042 2	0.037 7	0.030 2	0.021 2	0.016 6	0.012 2	0.004 6	0
6	$V_{Au}(x)$	16.958 1	16.943 7	16.914 2	16.893 8	16.869 6	16.810 0	16.735 2	16.645 4	16.540 4	16.482 3	16.420 4	16.285 3	16.135 1
	$V_{Cu}(x)$	12.363 1	12.353 5	12.333 7	12.320 1	12.303 9	12.264 0	12.214 0	12.153 8	12.083 6	12.044 7	12.003 3	11.912 9	11.812 4
	$V(x)$	16.958 1	16.484 7	15.998 1	15.750 4	15.499 9	14.991 6	14.474 6	13.950 4	13.420 7	13.154 1	12.886 7	12.350 1	11.812 4
	$\Delta V^{m}(x)$	0	0.041 2	0.069 2	0.078 7	0.085 5	0.091 8	0.089 3	0.079 8	0.064 6	0.055 3	0.045 2	0.023 2	0
7	$V_{Au}(x)$	16.958 1	17.007 8	17.052 5	17.073 0	17.092 2	17.127 0	17.156 7	17.181 4	17.201 2	17.209 2	17.215 9	17.225 7	17.230 4
	$V_{Cu}(x)$	11.634 9	11.652 7	11.670 4	11.679 3	11.688 1	11.705 9	11.723 6	11.741 4	11.759 1	11.768 0	11.776 9	11.794 6	11.812 4
	$V(x)$	16.958 1	16.472 3	15.976 1	15.724 6	15.471 0	14.958 5	14.440 2	13.917 4	13.391 7	13.128 3	12.864 7	12.337 7	11.812 4
	$\Delta V^{m}(x)$	0	0.028 8	0.047 1	0.052 9	0.056 6	0.058 7	0.054 9	0.046 7	0.035 6	0.029 5	0.023 2	0.010 8	0
8	$V_{Au}(x)$	16.958 1	16.959 2	16.960 2	16.960 7	16.961 1	16.961 9	16.962 6	16.963 1	16.963 6	16.963 8	16.963 9	16.964 1	16.964 2
	$V_{Cu}(x)$	12.078 6	12.030 0	11.986 3	11.966 3	11.947 5	11.913 5	11.884 5	11.860 3	11.841 0	11.833 2	11.826 6	11.817 0	11.812 4
	$V(x)$	16.958 1	16.466 3	15.965 4	15.712 1	15.457 0	14.942 6	14.423 5	13.901 4	13.377 8	13.115 8	12.854 0	12.331 7	11.812 4
	$\Delta V^{m}(x)$	0	0.022 8	0.036 5	0.040 4	0.042 6	0.042 7	0.038 3	0.030 8	0.021 7	0.017 0	0.012 5	0.004 8	0
9	$V_{Au}(x)$	16.958 1	16.995 7	17.029 4	17.044 9	17.059 5	17.085 7	17.108 2	17.126 8	17.141 8	17.147 8	17.152 9	17.160 3	17.163 9
	$V_{Cu}(x)$	11.745 8	11.747 0	11.749 4	11.751 0	11.753 0	11.757 8	11.763 8	11.771 1	11.779 6	11.784 3	11.789 3	11.800 2	11.812 4
	$V(x)$	16.958 1	16.470 8	15.973 4	15.721 4	15.467 5	14.954 5	14.436 0	13.913 4	13.388 2	13.125 2	12.862 0	12.336 2	11.812 4
	$\Delta V^{m}(x)$	0	0.027 3	0.044 5	0.049 8	0.053 1	0.054 7	0.050 8	0.042 7	0.032 2	0.026 4	0.020 5	0.009 3	0

*: Up till now, we cannot give a reasonable method to separate volume of characteristic atoms by the first function. Therefore, it cannot be used at present.

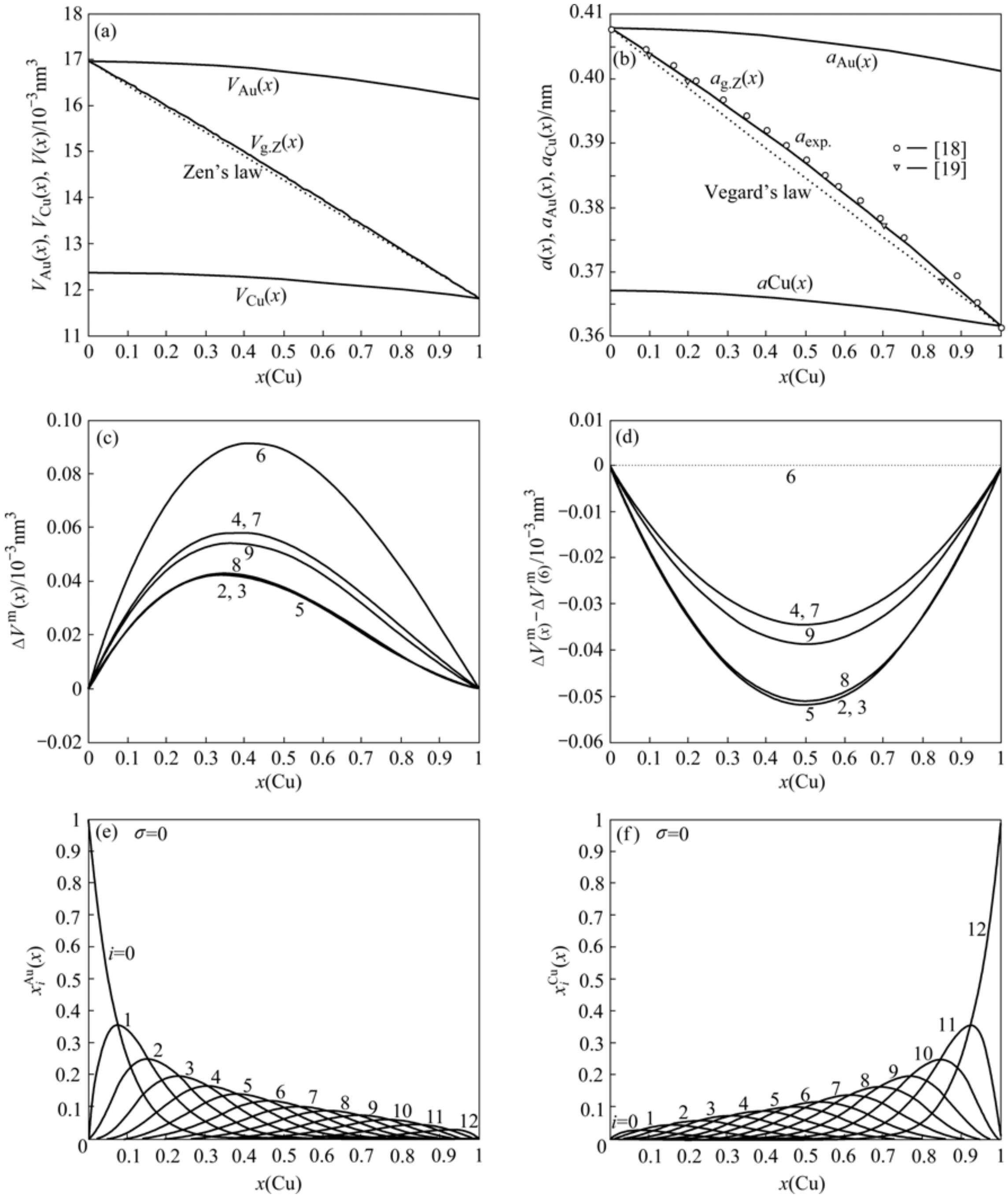

Fig.2 Volumetric properties: (a), (b) Average atomic volumes (lattice parameters) $V(x)$, $V_{Au}(x)$ and $V_{Cu}(x)$ ($a(x)$, $a_{Au}(x)$ and $a_{Cu}(x)$) of disordered $Au_{1-x}Cu_x$ alloys and their components calculated by the 6th $V(x)$-functions at room temperature, together with experimental lattice parameters[18−19]; (c) volumes of formation $\Delta V^m(x)$ of disordered $Au_{1-x}Cu_x$ alloys calculated by the 2nd−9th $V(x)$-functions; (d) Deviations of average volumes of disordered $Au_{1-x}Cu_x$ alloys calculated by the 2nd−9th V-functions from ones calculated by the 6th $V(x)$-function; (e), (f) Concentrations $x_i^{Au}(x)$ and $x_i^{Cu}(x)$ of characteristic atoms in disordered $Au_{1-x}Cu_x$ alloys

$V(x)$-functions have positive values, in which the values obtained by the 6th $V(x)$-function is the largest.

2.3 Volumetric properties of ordered $Au_{1-x}Cu_x$ alloys

According to the volume sequences of characteristic atoms in Table 1, the volumes $V(x)$, $V_{Au}(x)$ and $V_{Cu}(x)$ of $L1_2$-Au_3Cu, $L1_0$-AuCu and $L1_2$-$AuCu_3$ type ordered $Au_{1-x}Cu_x$ alloys and their components as well as their volumes of formation $\Delta V^m(x)$ and ordering volumes $\Delta V^{ex}(x)$ are calculated by the 2nd−9th $V(x)$-functions. The volumetric properties of $L1_2$-Au_3Cu-type, $L1_0$-AuCu-type and $L1_2$-$AuCu_3$-type ordered $Au_{1-x}Cu_x$ alloys at room temperature are shown in Figs.3−5 and listed in Tables 3−6.

From these results the following knowledge can be obtained.

Table 3 Average volumetric properties $V(x)$, $V_{\mathrm{Au}}(x)$, $V_{\mathrm{Cu}}(x)$, $\Delta V^{\mathrm{m}}(x)$ and $\Delta V^{\mathrm{ex}}(x)$ of $L1_2$-$\mathrm{Au_3Cu}$-type ordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys with maximal ordering degree calculated by 2nd−9th V-functions at room temperature (in 10^{-3}nm^3)

No.	Property	x(Cu)												
		0	0.1	0.2	0.25	0.3	0.4	0.5	0.6	0.7	0.75	0.8	0.9	1
2	$V_{\mathrm{Au}}(x)$	16.958 1	16.958 6	16.959 1	16.959 5	16.959 7	16.960 0	16.960 4	16.960 7	16.961 1	16.961 3	16.961 5	16.961 8	16.962 2
	$V_{\mathrm{Cu}}(x)$	12.084 7	12.084 7	12.084 7	12.084 7	12.029 0	11.953 5	11.904 0	11.869 3	11.844 7	11.835 3	11.827 8	11.817 3	11.812 4
	$V(x)$	16.958 1	16.471 2	15.984 2	15.740 8	15.480 4	14.957 4	14.432 2	13.905 9	13.379 6	13.116 8	12.854 5	12.331 7	11.812 4
	$\Delta V^{\mathrm{m}}(x)$	0	0.027 6	0.055 3	0.069 1	0.066 1	0.057 6	0.046 9	0.035 2	0.023 5	0.018 0	0.013 0	0.004 8	0
	$\Delta V^{\mathrm{ex}}(x)$	0	0.005 0	0.019 0	0.029 0	0.023 7	0.015 2	0.009 0	0.004 8	0.002 2	0.001 3	0.000 7	0.000 1	0
3	$V_{\mathrm{Au}}(x)$	16.958 1	17.019 1	17.095 3	17.141 0	17.165 4	17.214 2	17.263 0	17.311 7	17.360 5	17.384 9	17.409 3	17.458 1	17.506 8
	$V_{\mathrm{Cu}}(x)$	11.540 1	11.540 1	11.540 1	11.540 1	11.548 9	11.572 3	11.601 4	11.635 3	11.673 5	11.694 1	11.715 8	11.762 1	11.812 4
	$V(x)$	16.958 1	16.471 2	15.984 2	15.740 8	15.480 4	14.957 4	14.432 2	13.905 9	13.379 6	13.116 8	12.854 5	12.331 7	11.812 4
	$\Delta V^{\mathrm{m}}(x)$		0.027 6	0.055 3	0.069 1	0.066 1	0.057 6	0.046 9	0.035 2	0.023 5	0.018 0	0.013 0	0.004 8	0
	$\Delta V^{\mathrm{ex}}(x)$	0	0.005 0	0.019 0	0.029 0	0.023 7	0.015 2	0.009 0	0.004 8	0.002 2	0.001 3	0.000 7	0.000 1	0
4	$V_{\mathrm{Au}}(x)$	16.958 1	16.952 6	16.938 8	16.927 9	16.918 3	16.896 4	16.870 7	16.841 3	16.808 0	16.790 0	16.771 1	16.730 3	16.685 8
	$V_{\mathrm{Cu}}(x)$	12.179 5	12.179 5	12.179 5	12.179 5	12.136 0	12.069 4	12.016 4	11.970 1	11.927 8	11.907 6	11.887 8	11.849 5	11.812 4
	$V(x)$	16.958 1	16.475 3	15.987 0	15.740 8	15.483 6	14.965 6	14.443 5	13.918 6	13.391 8	13.128 2	12.864 5	12.337 6	11.812 4
	$\Delta V^{\mathrm{m}}(x)$	0	0.031 7	0.058 0	0.069 1	0.069 2	0.065 8	0.058 3	0.047 9	0.035 8	0.029 4	0.023 0	0.010 7	0
	$\Delta V^{\mathrm{ex}}(x)$	0	0.003 0	0.010 9	0.016 2	0.012 6	0.007 1	0.003 4	0.001 2	0.000 1	−0.000 1	−0.000 2	−0.000 1	0
5	$V_{\mathrm{Au}}(x)$	16.958 1	16.958 2	16.958 3	16.958 5	16.958 6	16.958 8	16.959 1	16.959 4	16.959 8	16.960 0	16.960 2	16.960 7	16.961 2
	$V_{\mathrm{Cu}}(x)$	12.087 7	12.087 7	12.087 7	12.087 7	12.031 4	11.955 1	11.905 0	11.869 9	11.845 0	11.835 6	11.827 9	11.817 3	11.812 4
	$V(x)$	16.958 1	16.471 1	15.984 2	15.740 8	15.480 4	14.957 3	14.432 1	13.905 7	13.379 5	13.116 7	12.854 4	12.331 7	11.812 4
	$\Delta V^{\mathrm{m}}(x)$	0	0.027 6	0.055 3	0.069 1	0.066 0	0.057 5	0.046 8	0.035 1	0.023 4	0.017 9	0.012 9	0.004 7	0
	$\Delta V^{\mathrm{ex}}(x)$	0	0.005 0	0.019 1	0.029 1	0.023 9	0.015 3	0.009 1	0.004 9	0.002 2	0.001 3	0.000 7	0.000 1	0
6	$V_{\mathrm{Au}}(x)$	16.958 1	16.941 4	16.899 8	16.866 7	16.837 8	16.771 6	16.693 9	16.604 9	16.504 5	16.450 1	16.392 7	16.269 6	16.135 1
	$V_{\mathrm{Cu}}(x)$	12.363 1	12.363 1	12.363 1	12.363 1	12.345 3	12.297 9	12.239 0	12.170 5	12.093 3	12.051 5	12.007 7	11.914 0	11.812 4
	$V(x)$	16.958 1	16.483 5	15.992 5	15.740 8	15.490 1	14.982 1	14.466 5	13.944 3	13.416 6	13.151 1	12.884 7	12.349 6	11.812 4
	$\Delta V^{\mathrm{m}}(x)$	0	0.040 0	0.063 5	0.069 1	0.075 7	0.082 3	0.081 2	0.073 6	0.060 5	0.052 3	0.043 2	0.022 6	0
	$\Delta V^{\mathrm{ex}}(x)$	0	−0.001 2	−0.005 7	−0.009 6	−0.009 9	−0.009 5	−0.008 1	−0.006 2	−0.004 0	−0.003 0	−0.002 0	−0.000 6	0
7	$V_{\mathrm{Au}}(x)$	16.958 1	17.013 1	17.075 0	17.109 4	17.124 1	17.150 6	17.173 3	17.192 2	17.207 4	17.213 6	17.218 9	17.226 5	17.230 4
	$V_{\mathrm{Cu}}(x)$	11.634 9	11.634 9	11.634 9	11.634 9	11.655 9	11.688 1	11.713 8	11.736 1	11.756 6	11.766 4	11.775 9	11.794 4	11.812 4
	$V(x)$	16.958 1	16.475 3	15.987 0	15.740 8	15.483 6	14.965 6	14.443 5	13.918 6	13.391 8	13.128 2	12.864 5	12.337 6	11.812 4
	$\Delta V^{\mathrm{m}}(x)$	0	0.031 7	0.058 0	0.069 1	0.069 2	0.065 8	0.058 3	0.047 9	0.035 8	0.029 4	0.023 0	0.010 7	0
	$\Delta V^{\mathrm{ex}}(x)$	0	0.003 0	0.010 9	0.016 2	0.012 6	0.007 1	0.003 4	0.001 2	0.000 1	−0.000 1	−0.000 2	−0.000 1	0
8	$V_{\mathrm{Au}}(x)$	16.958 1	16.959 4	16.960 7	16.961 5	16.961 8	16.962 4	16.962 9	16.963 4	16.963 7	16.963 9	16.964 0	16.964 1	16.964 2
	$V_{\mathrm{Cu}}(x)$	12.078 6	12.078 6	12.078 6	12.078 6	12.024 1	11.950 4	11.901 9	11.868 0	11.843 9	11.834 8	11.827 4	11.817 2	11.812 4
	$V(x)$	16.958 1	16.471 3	15.984 3	15.740 8	15.480 5	14.957 6	14.432 4	13.906 2	13.379 9	13.117 1	12.854 7	12.331 9	11.812 4
	$\Delta V^{\mathrm{m}}(x)$	0	0.027 7	0.055 3	0.069 1	0.066 1	0.057 8	0.047 2	0.035 5	0.023 8	0.018 3	0.013 2	0.004 9	0
	$\Delta V^{\mathrm{ex}}(x)$	0	0.005 0	0.018 9	0.028 7	0.023 5	0.015 1	0.008 9	0.004 7	0.002 1	0.001 3	0.000 7	0.000 1	0
9	$V_{\mathrm{Au}}(x)$	16.958 1	16.999 7	17.046 4	17.072 4	17.083 5	17.103 5	17.120 7	17.135 0	17.146 5	17.151 2	17.155 1	17.160 9	17.163 9
	$V_{\mathrm{Cu}}(x)$	11.745 8	11.745 8	11.745 8	11.745 8	11.748 0	11.753 7	11.760 8	11.769 1	11.778 4	11.783 5	11.788 8	11.800 1	11.812 4
	$V(x)$	16.958 1	16.474 3	15.986 3	15.740 8	15.482 8	14.963 6	14.440 8	13.915 5	13.388 9	13.125 4	12.862 0	12.336 2	11.812 4
	$\Delta V^{\mathrm{m}}(x)$	0	0.030 7	0.057 3	0.069 1	0.068 5	0.063 8	0.055 5	0.044 8	0.032 8	0.026 6	0.020 5	0.009 2	0
	$\Delta V^{\mathrm{ex}}(x)$	0	0.003 5	0.012 9	0.019 3	0.015 3	0.009 1	0.004 8	0.002 1	0.000 6	0.000 2	0	−0.000 1	0

Table 4 Average volumetric properties $V(x)$, $V_{Au}(x)$, $V_{Cu}(x)$, $\Delta V^{m}(x)$ and $\Delta V^{ex}(x)$ of $L1_0$-AuCu-type ordered $Au_{1-x}Cu_x$ alloys with maximal ordering degree calculated by the 2nd−9th V-functions at room temperature (in $10^{-3}nm^3$)

No.	Pro-perty	x(Cu)												
		0	0.1	0.2	0.25	0.3	0.4	0.5	0.6	0.7	0.75	0.8	0.9	1
2	$V_{Au}(x)$	16.958 1	16.958 5	16.959 0	16.959 2	16.959 5	16.960 1	16.960 8	16.961 1	16.961 4	16.961 5	16.961 6	16.961 9	16.962 2
	$V_{Cu}(x)$	12.084 7	12.050 8	12.018 7	12.003 4	11.988 5	11.960 0	11.933 4	11.882 4	11.849 7	11.838 2	11.829 2	11.817 5	11.812 4
	$V(x)$	16.958 1	16.467 8	15.970 9	15.720 3	15.468 2	14.960 1	14.447 1	13.913 9	13.383 2	13.119 0	12.855 7	12.331 9	11.812 4
	$\Delta V^{m}(x)$	0	0.024 2	0.042 0	0.048 6	0.053 8	0.060 3	0.061 9	0.043 2	0.027 1	0.020 2	0.014 2	0.005 0	0
	$\Delta V^{ex}(x)$	0	0.001 6	0.005 7	0.008 5	0.011 5	0.017 9	0.024 0	0.012 8	0.005 8	0.003 5	0.001 9	0.000 3	0
3	$V_{Au}(x)$	16.958 1	17.015 0	17.077 0	17.110 5	17.146 2	17.226 4	17.323 9	17.360 5	17.397 1	17.415 4	17.433 7	17.470 2	17.506 8
	$V_{Cu}(x)$	11.540 1	11.542 5	11.5467	11.549 5	11.552 8	11.560 6	11.570 3	11.616 1	11.663 0	11.686 9	11.711 2	11.761 0	11.812 4
	$V(x)$	16.958 1	16.467 8	15.970 9	15.720 3	15.468 2	14.960 1	14.447 1	13.913 9	13.383 2	13.119 0	12.855 7	12.331 9	11.812 4
	$\Delta V^{m}(x)$	0	0.024 2	0.042 0	0.048 6	0.053 8	0.060 3	0.061 9	0.043 2	0.027 1	0.020 2	0.014 2	0.005 0	0
	$\Delta V^{ex}(x)$	0	0.001 6	0.005 7	0.008 5	0.011 5	0.017 9	0.024 0	0.012 8	0.005 8	0.003 5	0.001 9	0.000 3	0
4	$V_{Au}(x)$	16.958 1	16.953 0	16.941 2	16.932 3	16.920 8	16.888 1	16.837 1	16.810 5	16.782 0	16.767 1	16.751 8	16.719 7	16.685 8
	$V_{Cu}(x)$	12.179 5	12.155 1	12.130 6	12.118 3	12.106 1	12.081 6	12.057 2	11.991 9	11.938 3	11.914 4	11.891 9	11.850 5	11.812 4
	$V(x)$	16.958 1	16.473 2	15.979 1	15.728 8	15.476 4	14.965 5	14.447 1	13.919 3	13.391 4	13.127 6	12.863 9	12.337 4	11.812 4
	$\Delta V^{m}(x)$	0	0.029 7	0.050 2	0.057 1	0.062 0	0.065 7	0.061 9	0.048 6	0.035 3	0.028 7	0.022 4	0.010 4	0
	$\Delta V^{ex}(x)$	0	0.000 9	0.003 0	0.004 2	0.005 4	0.007 0	0.007 0	0.001 9	−0.000 4	−0.000 7	−0.000 8	−0.000 4	0
5	$V_{Au}(x)$	16.958 1	16.958 2	16.958 3	16.958 4	16.958 5	16.958 9	16.959 5	16.959 8	16.960 1	16.960 3	16.960 4	16.960 8	16.961 2
	$V_{Cu}(x)$	12.087 7	12.053 5	12.021 0	12.005 5	11.990 4	11.961 7	11.934 8	11.883 2	11.850 1	11.838 5	11.829 4	11.817 5	11.812 4
	$V(x)$	16.958 1	16.467 7	15.970 9	15.720 2	15.468 1	14.960 0	14.447 1	13.913 8	13.383 1	13.118 9	12.855 6	12.331 9	11.812 4
	$\Delta V^{m}(x)$	0	0.024 2	0.041 9	0.048 5	0.053 7	0.060 2	0.061 9	0.043 1	0.027 0	0.020 1	0.014 1	0.004 9	0
	$\Delta V^{ex}(x)$	0	0.001 6	0.005 8	0.008 5	0.011 6	0.018 0	0.024 2	0.012 9	0.005 8	0.003 6	0.002 0	0.000 3	0
6	$V_{Au}(x)$	16.958 1	16.942 7	16.907 1	16.880 0	16.845 2	16.746 6	16.592 3	16.511 8	16.425 9	16.380 8	16.334 4	16.237 5	16.135 1
	$V_{Cu}(x)$	12.363 1	12.358 2	12.349 7	12.344 0	12.337 4	12.321 5	12.301 9	12.209 3	12.114 5	12.066 1	12.016 9	11.916 3	11.812 4
	$V(x)$	16.958 1	16.484 2	15.995 6	15.746 0	15.492 9	14.976 5	14.447 1	13.930 3	13.407 9	13.144 8	12.880 4	12.348 4	11.812 4
	$\Delta V^{m}(x)$	0	0.040 7	0.066 7	0.074 3	0.078 5	0.076 7	0.061 9	0.059 7	0.051 8	0.046 0	0.038 9	0.021 4	0
	$\Delta V^{ex}(x)$	0	−0.000 5	−0.002 5	−0.004 4	−0.007 0	−0.015 0	−0.027 5	−0.020 1	−0.012 8	−0.009 4	−0.006 3	−0.001 7	0
7	$V_{Au}(x)$	16.958 1	17.009 5	17.059 3	17.083 6	17.107 5	17.154 4	17.200 2	17.209 9	17.217 7	17.221 0	17.223 8	17.228 0	17.230 4
	$V_{Cu}(x)$	11.634 9	11.646 7	11.658 6	11.664 5	11.670 4	11.682 2	11.694 1	11.725 6	11.751 5	11.763 1	11.773 9	11.794 0	11.812 4
	$V(x)$	16.958 1	16.473 2	15.979 1	15.728 8	15.476 4	14.965 5	14.447 1	13.919 3	13.391 4	13.127 6	12.863 9	12.337 4	11.812 4
	$\Delta V^{m}(x)$	0	0.029 7	0.050 2	0.057 1	0.062 0	0.065 7	0.061 9	0.048 6	0.035 3	0.028 7	0.022 4	0.010 4	0
	$\Delta V^{ex}(x)$	0	0.000 9	0.003 0	0.004 2	0.005 4	0.007 0	0.007 0	0.001 9	−0.000 4	−0.000 7	−0.000 8	−0.000 4	0
8	$V_{Au}(x)$	16.958 1	16.959 3	16.960 4	16.960 9	16.961 5	16.962 5	16.963 6	16.963 8	16.963 9	16.964 0	16.964 1	16.964 2	16.964 2
	$V_{Cu}(x)$	12.078 6	12.045 5	12.014 1	11.999 1	11.984 5	11.956 7	11.930 7	11.880 8	11.848 9	11.837 6	11.828 9	11.817 4	11.812 4
	$V(x)$	16.958 1	16.467 9	15.971 1	15.720 5	15.468 4	14.960 2	14.447 1	13.914 0	13.383 4	13.119 2	12.855 9	12.332 0	11.812 4
	$\Delta V^{m}(x)$	0	0.024 4	0.042 2	0.048 8	0.054 0	0.060 4	0.061 9	0.043 3	0.027 3	0.020 4	0.014 4	0.005 1	0
	$\Delta V^{ex}(x)$	0	0.001 6	0.005 7	0.008 4	0.011 4	0.017 6	0.023 6	0.012 6	0.005 6	0.003 4	0.001 9	0.000 3	0
9	$V_{Au}(x)$	16.958 1	16.996 9	17.034 5	17.052 9	17.071 0	17.106 4	17.141 0	17.148 3	17.154 3	17.156 7	17.158 9	17.162 1	17.163 9
	$V_{Cu}(x)$	11.745 8	11.746 4	11.747 4	11.748 1	11.748 9	11.750 9	11.753 2	11.764 4	11.775 9	11.781 7	11.787 7	11.799 8	11.812 4
	$V(x)$	16.958 1	16.471 9	15.977 1	15.726 7	15.474 4	14.964 2	14.447 1	13.918 0	13.389 4	13.125 5	12.861 9	12.336 0	11.812 4
	$\Delta V^{m}(x)$	0	0.028 3	0.048 2	0.055 0	0.060 0	0.064 4	0.061 9	0.047 3	0.033 3	0.026 7	0.020 4	0.009 1	0
	$\Delta V^{ex}(x)$	0	0.001 1	0.003 7	0.005 3	0.006 9	0.009 7	0.011 1	0.004 6	0.001 1	0.000 3	−0.000 1	−0.000 2	0

Table 5 Average volumetric properties $V(x)$, $V_{\text{Au}}(x)$, $V_{\text{Cu}}(x)$, $\Delta V^{\text{m}}(x)$ and $\Delta V^{\text{ex}}(x)$ of $L1_2$-AuCu$_3$-type ordered Au$_{1-x}$Cu$_x$ alloys with maximal ordering degree calculated by 2nd−9th V-functions at room temperature (in 10^{-3}nm^3)

No.	Pro-perty	x(Cu)												
		0	0.1	0.2	0.25	0.3	0.4	0.5	0.6	0.7	0.75	0.8	0.9	1
2	$V_{\text{Au}}(x)$	16.958 1	16.958 5	16.959 0	16.959 2	16.959 4	16.959 9	16.960 4	16.961 0	16.961 7	16.962 2	16.962 2	16.962 2	16.962 2
	$V_{\text{Cu}}(x)$	12.084 7	12.040 2	11.999 4	11.980 5	11.962 5	11.929 2	11.899 8	11.874 1	11.852 2	11.842 6	11.831 7	11.817 9	11.812 4
	$V(x)$	16.958 1	16.466 7	15.967 1	15.714 5	15.460 3	14.947 6	14.430 1	13.908 8	13.385 0	13.122 5	12.857 8	12.332 3	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.023 2	0.038 1	0.042 8	0.045 9	0.047 8	0.044 8	0.038 2	0.028 9	0.023 7	0.016 3	0.005 4	0
	$\Delta V^{\text{ex}}(x)$	0	0.000 5	0.001 9	0.002 7	0.003 6	0.005 4	0.006 9	0.007 8	0.007 6	0.007 0	0.004 0	0.000 7	0
3	$V_{\text{Au}}(x)$	16.958 1	17.013 7	17.070 9	17.100 4	17.130 6	17.193 9	17.263 0	17.342 2	17.441 8	17.506 8	17.506 8	17.506 8	17.506 8
	$V_{\text{Cu}}(x)$	11.540 1	11.544 0	11.551 6	11.556 9	11.563 1	11.578 2	11.597 2	11.619 9	11.646 4	11.661 1	11.695 5	11.757 4	11.812 4
	$V(x)$	16.958 1	16.466 7	15.967 1	15.714 5	15.460 3	14.947 6	14.430 1	13.908 8	13.385 0	13.122 5	12.857 8	12.332 3	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.023 2	0.038 1	0.042 8	0.045 9	0.047 8	0.044 8	0.038 2	0.028 9	0.023 7	0.016 3	0.005 4	0
	$\Delta V^{\text{ex}}(x)$	0	0.000 5	0.001 9	0.002 7	0.003 6	0.005 4	0.006 9	0.007 8	0.007 6	0.007 0	0.004 0	0.000 7	0
4	$V_{\text{Au}}(x)$	16.958 1	16.953 2	16.942 7	16.935 1	16.925 8	16.901 2	16.866 5	16.817 0	16.741 5	16.685 8	16.685 8	16.685 8	16.685 8
	$V_{\text{Cu}}(x)$	12.179 5	12.146 9	12.114 3	12.097 9	12.081 6	12.049 0	12.016 4	11.983 7	11.951 1	11.934 8	11.904 2	11.853 2	11.812 4
	$V(x)$	16.958 1	16.472 6	15.977 0	15.725 8	15.472 6	14.960 3	14.441 4	13.917 0	13.388 2	13.122 5	12.860 5	12.336 4	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.029 1	0.048 1	0.054 2	0.058 2	0.060 5	0.056 2	0.046 4	0.032 1	0.023 7	0.019 0	0.009 5	0
	$\Delta V^{\text{ex}}(x)$	0	0.000 3	0.000 9	0.001 3	0.001 6	0.001 8	0.001 3	−0.000 4	−0.003 5	−0.005 8	−0.004 2	−0.001 3	0
5	$V_{\text{Au}}(x)$	16.958 1	16.958 2	16.958 3	16.958 4	16.958 5	16.958 8	16.959 1	16.959 7	16.960 5	16.961 2	16.961 2	16.961 2	16.961 2
	$V_{\text{Cu}}(x)$	12.087 7	12.042 7	12.001 5	11.982 4	11.964 1	11.930 5	11.900 8	11.874 8	11.852 6	11.843 0	11.831 9	11.818 0	11.812 4
	$V(x)$	16.958 1	16.466 6	15.966 9	15.714 4	15.460 2	14.947 5	14.430 0	13.908 8	13.385 0	13.122 5	12.857 7	12.332 3	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.023 1	0.038 0	0.042 7	0.045 8	0.047 7	0.044 7	0.038 1	0.028 9	0.023 7	0.016 2	0.005 4	0
	$\Delta V^{\text{ex}}(x)$	0	0.000 5	0.001 9	0.002 7	0.003 6	0.005 5	0.007 0	0.007 9	0.007 7	0.007 1	0.004 1	0.000 8	0
6	$V_{\text{Au}}(x)$	16.958 1	16.943 3	16.911 6	16.888 7	16.860 5	16.786 1	16.681 2	16.531 5	16.303 5	16.135 1	16.135 1	16.135 1	16.135 1
	$V_{\text{Cu}}(x)$	12.363 1	12.355 2	12.339 7	12.329 1	12.316 6	12.285 9	12.247 5	12.201 6	12.148 0	12.118 3	12.048 7	11.923 5	11.812 4
	$V(x)$	16.958 1	16.484 5	15.997 2	15.748 8	15.497 4	14.986 0	14.464 4	13.933 5	13.394 6	13.122 5	12.866 0	12.344 7	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.041 0	0.068 3	0.077 1	0.083 0	0.086 2	0.079 1	0.062 9	0.038 5	0.023 7	0.024 5	0.017 8	0
	$\Delta V^{\text{ex}}(x)$	0	−0.000 2	−0.000 9	−0.001 6	−0.002 6	−0.005 6	−0.010 2	−0.016 9	−0.026 0	−0.031 6	−0.020 7	−0.005 4	0
7	$V_{\text{Au}}(x)$	16.958 1	17.008 4	17.054 7	17.076 3	17.097 0	17.135 2	17.169 1	17.198 2	17.221 6	17.230 4	17.230 4	17.230 4	17.230 4
	$V_{\text{Cu}}(x)$	11.634 9	11.650 7	11.666 5	11.674 3	11.682 2	11.698 0	11.713 8	11.729 6	11.745 3	11.753 2	11.768 0	11.792 7	11.812 4
	$V(x)$	16.958 1	16.472 6	15.977 0	15.725 8	15.472 6	14.960 3	14.441 4	13.917 0	13.388 2	13.122 5	12.860 5	12.336 4	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.029 1	0.048 1	0.054 2	0.058 2	0.060 5	0.056 2	0.046 4	0.032 1	0.023 7	0.019 0	0.009 5	0
	$\Delta V^{\text{ex}}(x)$	0	0.000 3	0.000 9	0.001 3	0.001 6	0.001 8	0.001 3	−0.000 4	−0.003 5	−0.005 8	−0.004 2	−0.001 3	0
8	$V_{\text{Au}}(x)$	16.958 1	16.959 2	16.960 3	16.960 8	16.961 2	16.962 1	16.962 9	16.963 5	16.964 0	16.964 2	16.964 2	16.964 2	16.964 2
	$V_{\text{Cu}}(x)$	12.078 6	12.035 1	11.995 2	11.976 7	11.959 1	11.926 6	11.897 8	11.872 7	11.851 3	11.842 0	11.831 2	11.817 8	11.812 4
	$V(x)$	16.958 1	16.466 8	15.967 3	15.714 8	15.460 6	14.947 9	14.430 3	13.909 0	13.385 1	13.122 5	12.857 8	12.332 4	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.023 3	0.038 3	0.043 1	0.046 2	0.048 1	0.045 1	0.038 4	0.029 0	0.023 7	0.016 3	0.005 5	0
	$\Delta V^{\text{ex}}(x)$	0	0.000 5	0.001 8	0.002 7	0.003 6	0.005 3	0.006 8	0.007 6	0.007 3	0.006 7	0.003 8	0.000 7	0
9	$V_{\text{Au}}(x)$	16.958 1	16.996 1	17.031 1	17.047 5	17.063 1	17.091 9	17.117 5	17.139 5	17.157 2	17.163 9	17.163 9	17.163 9	17.163 9
	$V_{\text{Cu}}(x)$	11.745 8	11.746 8	11.748 6	11.749 9	11.751 4	11.755 2	11.759 8	11.765 3	11.771 8	11.775 4	11.783 8	11.798 9	11.812 4
	$V(x)$	16.958 1	16.471 2	15.974 6	15.723 1	15.469 6	14.957 2	14.438 7	13.915 0	13.387 4	13.122 5	12.859 8	12.335 4	11.812 4
	$\Delta V^{\text{m}}(x)$	0	0.027 6	0.045 6	0.051 4	0.055 2	0.057 4	0.053 4	0.044 4	0.031 3	0.023 7	0.018 3	0.008 5	0
	$\Delta V^{\text{ex}}(x)$	0	0.000 4	0.001 2	0.001 6	0.002 1	0.002 7	0.002 7	0.001 6	−0.000 8	−0.002 7	−0.002 2	−0.000 8	0

Table 6 Lattice parameters $a(x)$, $a_{\mathrm{Au}}(x)$, $a_{\mathrm{Cu}}(x)$, $\Delta a^{\mathrm{m}}(x)$, $\Delta a^{\mathrm{ex}}(x)$ of disordered with full disorder and ordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys with maximal ordering degree calculated by the 6th V-function (in 10^{-1}nm)

Alloy	Parameter	x(Cu)												
		0	0.1	0.2	0.25	0.3	0.4	0.5	0.6	0.7	0.75	0.8	0.9	1
Dis-ordered alloys	$a_{\mathrm{Au}}(x)$	4.078 3	4.077 1	4.074 8	4.073 1	4.071 2	4.0664	4.0604	4.0531	4.0445	4.0398	4.0347	4.023 6	4.011 2
	$a_{\mathrm{Cu}}(x)$	3.670 5	3.669 6	3.667 6	3.666 3	3.664 7	3.6607	3.6557	3.6497	3.6427	3.6387	3.6346	3.625 4	3.615 2
	$a(x)$	4.078 3	4.040 0	3.999 8	3.979 1	3.957 9	3.9141	3.8686	3.8213	3.7723	3.7472	3.7216	3.669 2	3.615 2
	$\Delta a^{\mathrm{m}}(x)$	0	0.008 0	0.014 2	0.016 6	0.018 5	0.0211	0.0219	0.0209	0.0182	0.0162	0.0138	0.007 7	0
	$\Delta a^{\mathrm{ex}}(x)$	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathrm{Au_3Cu}$-type ordered alloys	$a_{\mathrm{Au}}(x)$	4.078 3	4.077 0	4.073 6	4.071 0	4.068 6	4.063 3	4.057 0	4.049 8	4.041 6	4.037 2	4.032 5	4.022 3	4.011 2
	$a_{\mathrm{Cu}}(x)$	3.670 5	3.670 5	3.670 5	3.670 5	3.668 8	3.664 1	3.658 2	3.651 4	3.643 6	3.639 4	3.635 0	3.625 5	3.615 2
	$a(x)$	4.078 3	4.039 9	3.999 4	3.978 3	3.957 0	3.913 3	3.867 9	3.820 8	3.772 0	3.746 9	3.721 4	3.669 2	3.615 2
	$\Delta a^{\mathrm{m}}(x)$	0	0.007 9	0.013 7	0.015 8	0.017 7	0.020 3	0.021 1	0.020 3	0.017 8	0.015 9	0.013 6	0.007 7	0
	$\Delta a^{\mathrm{ex}}(x)$	0	−0.000 1	−0.000 5	−0.000 8	−0.000 8	−0.000 8	−0.000 7	−0.000 6	−0.000 4	−0.000 3	−0.000 2	−0.000 1	0
AuCu-type ordered alloys	$a_{\mathrm{Au}}(x)$	4.078 3	4.077 1	4.074 2	4.072 0	4.069 2	4.061 3	4.048 8	4.042 2	4.035 2	4.031 5	4.027 7	4.019 7	4.011 2
	$a_{\mathrm{Cu}}(x)$	3.670 5	3.670 0	3.669 2	3.668 6	3.668 0	3.666 4	3.664 5	3.655 3	3.645 8	3.640 9	3.635 9	3.625 8	3.615 2
	$a(x)$	4.078 3	4.040 0	3.999 6	3.978 7	3.957 3	3.912 8	3.866 2	3.819 5	3.771 1	3.746 3	3.721 0	3.669 1	3.615 2
	$\Delta a^{\mathrm{m}}(x)$	0	0.008 0	0.014 0	0.016 2	0.017 9	0.019 8	0.019 4	0.019 1	0.017 0	0.015 3	0.013 2	0.007 6	0
	$\Delta a^{\mathrm{ex}}(x)$	0	0	−0.000 2	−0.000 4	−0.000 6	−0.001 3	−0.002 4	−0.001 8	−0.001 2	−0.000 9	−0.000 6	−0.000 2	0
$\mathrm{AuCu_3}$-type ordered alloys	$a_{\mathrm{Au}}(x)$	4.078 3	4.077 1	4.074 6	4.072 7	4.070 5	4.064 5	4.056 0	4.043 8	4.025 1	4.011 2	4.011 2	4.011 2	4.011 2
	$a_{\mathrm{Cu}}(x)$	3.670 5	3.669 8	3.668 2	3.667 2	3.665 9	3.662 9	3.659 1	3.654 5	3.649 1	3.646 1	3.639 2	3.626 5	3.615 2
	$a(x)$	4.078 3	4.040 0	3.999 8	3.979 0	3.957 7	3.913 7	3.867 7	3.819 8	3.769 9	3.744 2	3.719 6	3.668 7	3.615 2
	$\Delta a^{\mathrm{m}}(x)$	0	0.008 0	0.014 1	0.016 4	0.018 3	0.020 6	0.021 0	0.019 4	0.015 8	0.013 2	0.011 8	0.007 2	0
	$\Delta a^{\mathrm{ex}}(x)$	0	0	−0.000 1	−0.000 1	−0.000 2	−0.000 5	−0.000 9	−0.001 5	−0.002 4	−0.003 0	−0.002 0	−0.000 5	0

1) Even through the volume sequences of characteristic atoms in Table 1 are separated out from the experimental volumes of $L1_0$-AuCu and $L1_2$-$\mathrm{AuCu_3}$ compounds only, the volumes of the $L1_2$-$\mathrm{Au_3Cu}$ compound calculated by the 2nd−9th $V(x)$-functions are equal each to each (15.740 8×10^{-3}nm^{-3}), and in good agreement with the experimental volume (15.773 1×10^{-3}nm^{-3})[16], but their average atomic volumes $V_{\mathrm{Au}}(x)$ and $V_{\mathrm{Cu}}(x)$ of Au and Cu components are different each other.

2) The volumes of the $L1_0$-AuCu compound calculated by the 2nd−9th $V(x)$-functions are equal to experimental volume (14.447 1×10^{-3}nm^{-3}), but their average atomic volumes $V_{\mathrm{Au}}(x)$ and $V_{\mathrm{Cu}}(x)$ of Au and Cu components are different each other.

3) The volumes of the $L1_2$-$\mathrm{AuCu_3}$ compound calculated by the 2nd−9th $V(x)$-functions are equal to experimental volume (13.122 5×10^{-3}nm^{-3}), but their average atomic volumes $V_{\mathrm{Au}}(x)$ and $V_{\mathrm{Cu}}(x)$ of Au and Cu components are different each other.

4) Tables 3−5 show that the volumes of formation $\Delta V^{\mathrm{m}}(x)$ calculated by the 2nd−9th $V(x)$-functions are of positive values. But only the ordering volume $\Delta V^{\mathrm{ex}}(x)$ calculated by the 6th $V(x)$-function are negative, which is coincident with the experimental result. Therefore, only the 6th $V(x)$-function can be used to describe volumetric properties of Au-Cu system.

2.4 Volumetric properties of $L1_2$-$\mathrm{Au_3Cu}$, $L1_0$-AuCu and $L1_2$-$\mathrm{AuCu_3}$ compounds

From Table 7 following knowledge can be obtained: The volumetric properties of these three compounds are of the same results as listed in Tables 3−6. The volumes of formation of these three compounds are

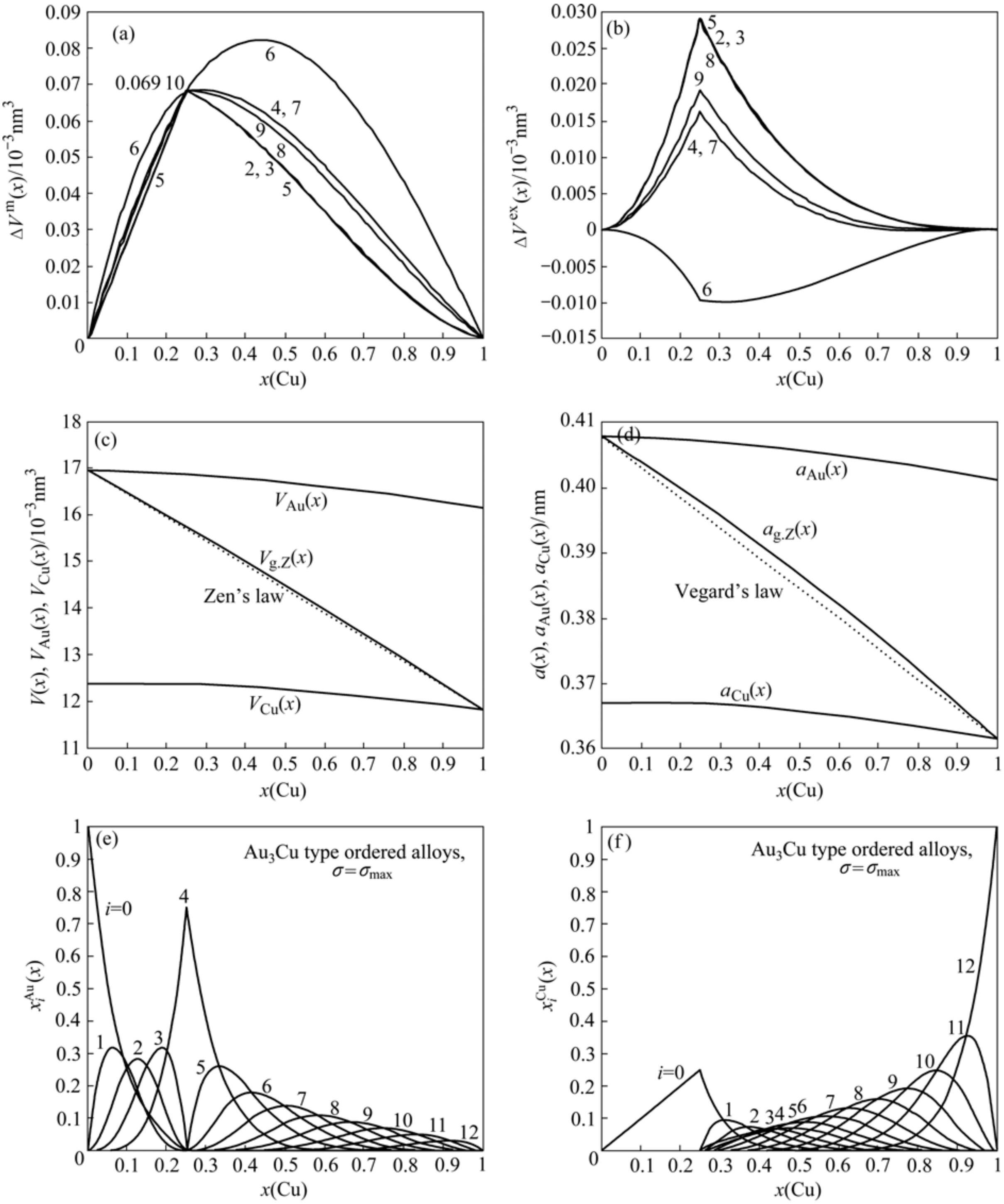

Fig.3 Formation of volume $\Delta V^{\text{m}}(x)$ (a) and ordering volume $\Delta V^{\text{ex}}(x)$ (b) of $L1_2$-Au$_3$Cu-type ordered Au$_{1-x}$Cu$_x$ alloys with maximal ordering degree calculated by the 2nd−9th V-functions at room temperature (in 10^{-3}nm^3); average atomic volumes $V(x)$, $V_{\text{Au}}(x)$ and $V_{\text{Cu}}(x)$ (c) and average lattice parameters $a(x)$, $a_{\text{Au}}(x)$ and $a_{\text{Cu}}(x)$ (d) of $L1_2$-Au$_3$Cu-type ordered Au$_{1-x}$Cu$_x$ alloys with maximal ordering degree calculated by the 6th V-functions at room temperature; concentrations $x_i^{\text{Au}}(x)$ (e) and $x_i^{\text{Cu}}(x)$ (f) of $A_i^{\text{Au}}(x)$ and $A_i^{\text{Cu}}(x)$ characteristic atoms in $L1_2$-Au$_3$Cu-type ordered Au$_{1-x}$Cu$_x$ alloys

of positive values, to which the contribution of the Au-component is negative, the contribution of the Cu-component is positive, and $x(\text{Cu})\times\Delta V^{\text{m}}_{\text{Cu}} > \left|x(\text{Au})\times\Delta V^{\text{m}}_{\text{Au}}\right|$. The ordering volumes of these three compounds are of negative values, i.e., $V_{\text{ord}} < V_{\text{dis}}$, to which the contribution of the Au-component is positive ($\Delta V^{\text{ex}}_{\text{Au}}$, negative), the contribution of the Cu-component is negative ($\Delta V^{\text{ex}}_{\text{Cu}}$, positive), and $\left|x(\text{Au})\times\Delta V^{\text{ex}}_{\text{Au}}\right| > x(\text{Cu})\times\Delta V^{\text{ex}}_{\text{Cu}}$ as disordering compounds. The volume mismatch degrees of characteristic atoms between

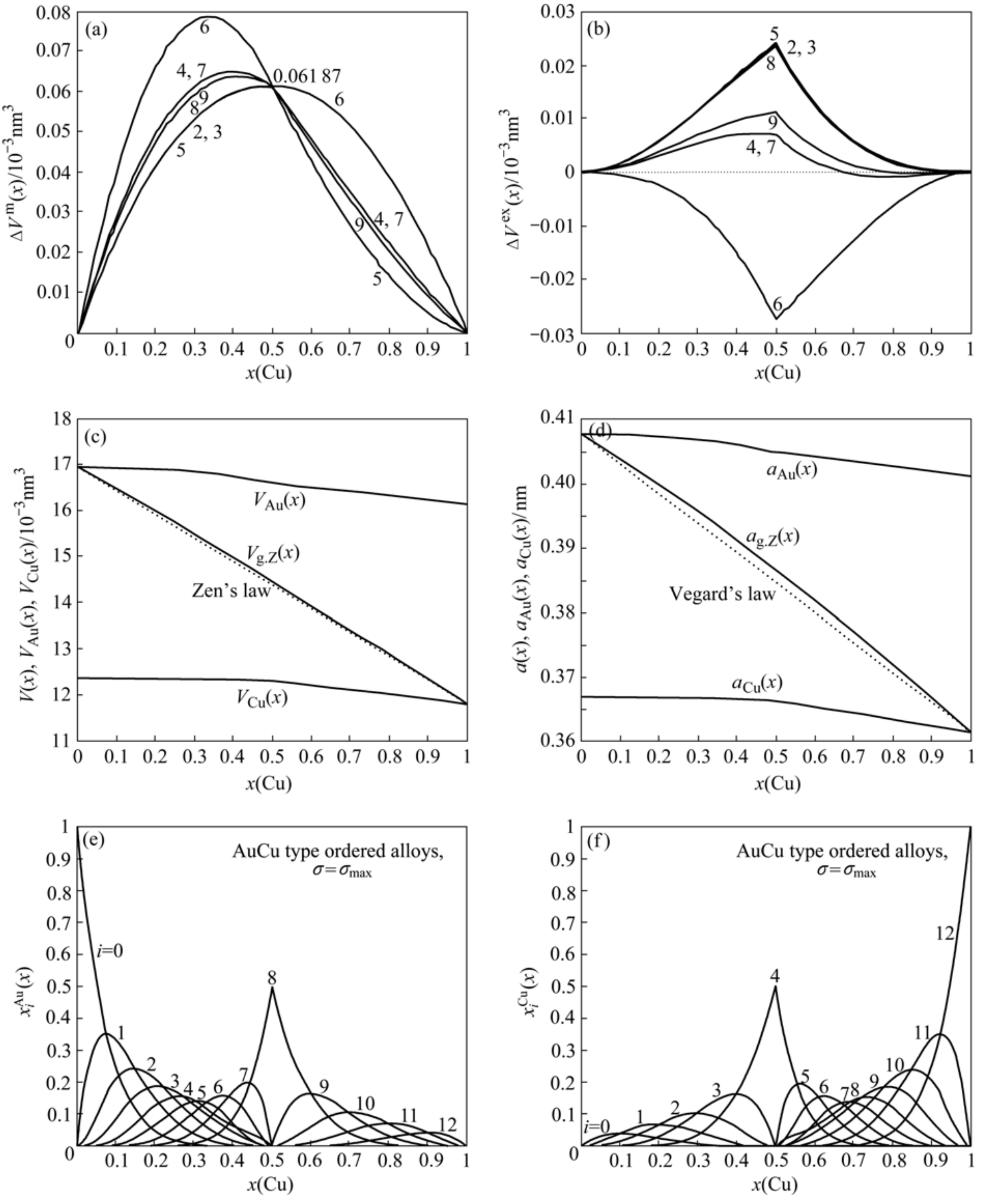

Fig.4 Formation of volume $\Delta V^{\mathrm{m}}(x)$ (a) and ordering volume $\Delta V^{\mathrm{ex}}(x)$ (b) of $L1_0$-AuCu-type ordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys with maximal ordering degree calculated by the 2nd−9th V-functions at room temperature; average atomic volumes $V(x)$, $V_{\mathrm{Au}}(x)$ and $V_{\mathrm{Cu}}(x)$ (c) and average lattice parameters $a(x)$, $a_{\mathrm{Au}}(x)$ and $a_{\mathrm{Cu}}(x)$ (d) of $L1_0$-AuCu-type ordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys with maximal ordering degree calculated by the 6th V-functions at room temperature; concentrations $x_i^{\mathrm{Au}}(x)$ (e) and $x_i^{\mathrm{Cu}}(x)$ (f) of $A_i^{\mathrm{Au}}(x)$ and $A_i^{\mathrm{Cu}}(x)$ characteristic atoms in $L1_0$-AuCu-type ordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys

constituents Au and Cu for these three compounds are smaller than those of atoms between pure elements Au and Cu, respectively. There is no volume mismatch degree Δm_V^{α} inside the component in these three compounds. But the AuCuⅡ with a long-period superlattice structure has one, which will be presented in the future.

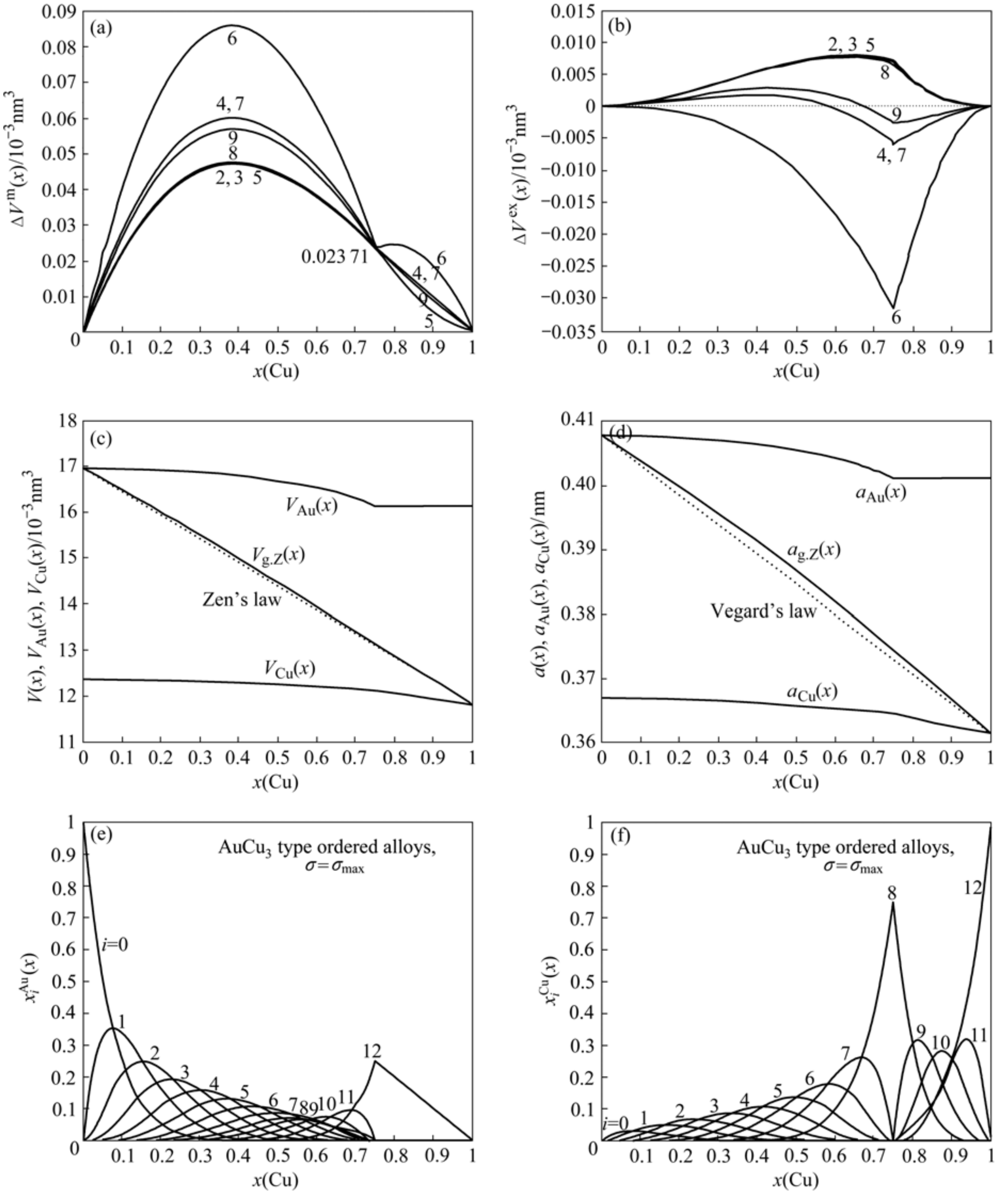

Fig.5 Formation of volume $\Delta V^{m}(x)$ (a) and ordering volume $\Delta V^{ex}(x)$ (b) of $L1_2$-AuCu$_3$-type ordered Au$_{1-x}$Cu$_x$ alloys with maximal ordering degree calculated by the 2nd−9th V-functions at room temperature; average atomic volumes $V(x)$, $V_{Au}(x)$ and $V_{Cu}(x)$ (c) and average lattice parameters $a(x)$, $a_{Au}(x)$ and $a_{Cu}(x)$ (d) of $L1_2$-AuCu$_3$-type ordered Au$_{1-x}$Cu$_x$ alloys with maximal ordering degree calculated by 6th V-functions at room temperature; concentrations $x_i^{Au}(x)$ (e) and $x_i^{Cu}(x)$ (f) of $A_i^{Au}(x)$ and $A_i^{Cu}(x)$ characteristic atoms in $L1_2$-AuCu$_3$-type -type ordered Au$_{1-x}$Cu$_x$ alloys

3 Discussion and conclusions

3.1 Relation of volumes and potential energies of characteristic atoms

In the Au-Cu system, the volume change and potential energy change of A_i^{Au} and A_i^{Cu} characteristic atoms consequence on changing nearest neighbor configuration indicated by i number of Cu-atoms have different correlations.

The relation of ε_i^{Au} and ε_i^{Cu} with i is described by the following equation[13]:

Table 7 Volumetric properties of $L1_0$-AuCu, $L1_2$-AuCu$_3$ and $L1_2$-Au$_3$Cu compounds calculated by the 6th V-functions (V in 10^{-3}nm^3, a in 10^{-1}nm)

Compound	Group	A_i^α /cell	n_i^α /cell	V_i^α	V_c/cell	$\sum n_i^{Au}V_i^{Au}$ /cell	$\sum n_i^{Cu}V_i^{Cu}$ /cell	ΔV_c^m /cell	ΔV_c^{ex} /cell
Au$_3$Cu	$Pm3m$ ($L1_2$)	A_4^{Au} A_0^{Cu}	3 1	16.866 7 12.363 1	62.963 1	50.600 0	12.363 1	0.276 4	−0.038 4
AuCu	$P4$/mmm ($L1_0$)	A_8^{Au} A_4^{Cu}	2 2	16.592 3 12.301 9	57.788 5	33.184 6	24.603 8	0.247 5	−0.109 9
AuCu$_3$	$Pm3m$ ($L1_2$)	A_{12}^{Au} A_8^{Cu}	1 3	16.135 0 12.118 3	52.490 1	16.135 0	36.355 0	0.094 8	−0.126 4

Compound	V/atom	V_{Au}/atom	V_{Cu}/atom	ΔV^m/atom	ΔV_{Au}^m / atom	ΔV_{Cu}^m / atom
Au$_3$Cu	15.740 8 (15.750 4)	16.866 7 (16.893 8)	12.363 1 (12.320 1)	0.069 1 (0.078 7)	−0.091 5 (−0.064 3)	0.550 7 (0.507 7)
AuCu	14.447 1 (14.474 6)	16.592 3 (16.735 2)	12.301 9 (12.214 0)	0.061 9 (0.089 3)	−0.365 8 (−0.222 9)	0.489 6 (0.410 6)
AuCu$_3$	13.122 5 (13.154 1)	16.135 0 (16.482 3)	12.118 3 (12.044 7)	0.023 7 (0.055 3)	−0.823 1 (−0.475 8)	0.306 0 (0.232 3)

Compound	ΔV^{ex} / atom	ΔV_{Au}^{ex} / atom	ΔV_{Cu}^{ex} / atom	Δm_V	Δm_V^0
Au$_3$Cu	−0.009 6	−0.027 1	0.043 0	0.107 3	0.123 1
AuCu	−0.027 5	−0.142 9	0.088 0	0.148 5	0.178 9
AuCu$_3$	−0.031 6	−0.347 3	0.073 6	0.114 8	0.149 6

* The values of disordered alloys listed in parentheses are taken from Table 2

$$\begin{cases} \varepsilon_i^{Au} = \varepsilon_0^{Au} + (i/I)^2(\varepsilon_I^{Au} - \varepsilon_0^{Au}) \\ \varepsilon_i^{Cu} = \varepsilon_I^{Cu} + \left[(I-i)/I\right]^2(\varepsilon_0^{Cu} - \varepsilon_I^{Cu}) \end{cases} \tag{10}$$

where ε_0^{Au} =−368 kJ/mol, ε_I^{Au} =−391.303 kJ/mol, ε_I^{Cu} =−336 kJ/mol, ε_0^{Cu} =−352.055 kJ/mol.

By comparing Eqs.(9) and (10), the following knowledges can be obtained: for the Au-characteristic atoms, the potential energy lowers with increasing the i number of Cu-atoms, and the volume reduces. For the Cu-characteristic atoms, the potential energy lowers with increasing the (I−i) number of Au-atoms, but the volume rises.

This different correlation will be explained by electronic structure sequences of A_i^{Au} and A_i^{Cu} characteristic atoms in the future.

3.2 Relation between Zen's law and general Zen's law

In Pearson's book of 1972, "The crystal chemistry and physical of metals and alloys"[20], we are informed that there is a Zen's law. The average atomic volume of a solid solution is the concentration-weighted average of the atomic volumes of the elements. For Au-Cu alloys, it is

$$V(x) = x(\mathrm{Au})V_{Au}^0 + x(\mathrm{Cu})V_{Cu}^0 \tag{11}$$

According the SSA framework, the average atomic volume of an alloy is the concentration (x_i^A, x_i^B)-weighted average of the splitting atomic volumes (V_i^A, V_i^B) of the characteristic atoms, represented by Eq.(6), which may be named as additive law of characteristic atomic volume. It has been demonstrated that the equation of average atomic volume of intermetallic compounds, ordered and disordered alloys for Au-Cu system is

$$V(x,T,\sigma) = x_{Au}V_0^{Au}(T) + x_{Cu}V_I^{Cu}(T) + \sum_{i=0}^{I}\left[\left(\frac{i}{I}\right)^2 x_i^{Au}(x,\sigma)\right]\left(V_I^{Au}(T) - V_0^{Au}(T)\right) + \sum_{i=0}^{I}\left[\frac{2I(I-i)-(I-i)^2}{I^2}x_i^{Cu}(x,\sigma)\right]\cdot \left(V_0^{Cu}(T) - V_I^{Cu}(T)\right) \tag{12}$$

For the disordered alloys only, Eq.(12) becomes

$$V(x,T,0) = x_{Au}V_0^{Au}(T) + x_{Cu}V_I^{Cu}(T) + \frac{(I-1)x_{Au}x_{Cu}^2 + x_A x_{Cu}}{I}\left(V_I^{Au}(T) - V_0^{Au}(T)\right) + \frac{(I-1)x_{Au}^2 x_{Cu} + Ix_{Au}x_{Cu}}{I}\cdot \left(V_0^{Cu}(T) - V_I^{Cu}(T)\right) \tag{13}$$

where V_0^{Au} =16.958 11×10^{-3}nm^3, V_I^{Au} =16.135 05×10^{-3}nm^3, V_I^{Cu} =11.812 37×10^{-3}nm^3, V_0^{Cu} =12.363 12×

10^{-3}nm^3.

If after forming solid solution there is no splitting of atomic volume state, Eqs.(12) and (13) become into Eq.(11). Therefore, the additive law of volumes of characteristic atoms may be also named as the general Zen's law.

3.3 Relation between Vegard's law and general Vegard's law

The Vegard's law indicates that the average lattice parameter of a solid solution is the concentration-weighted average of the lattice parameters ($a_{\mathrm{A}}^0, a_{\mathrm{B}}^0$) of the constituent elements. For $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys, it is:

$$a_V(x)=x_{\mathrm{Au}}a_{\mathrm{Au}}^0+x_{\mathrm{Cu}}a_{\mathrm{Cu}}^0 \tag{14}$$

In the SSA framework, the average lattice parameter of an alloy may be similarly obtained by the concentration ($x_i^{\mathrm{A}}, x_i^{\mathrm{B}}$)-weighted average of the lattice parameter ($a_i^{\mathrm{A}}, a_i^{\mathrm{B}}$) of the characteristic crystals, which may be thought to be obtained by splitting lattice parameter states of the constituent elements. If we use the lattice parameters of characteristic crystal instead of volumes of corresponding characteristic atoms, Eqs.(12) and (13) become, respectively

$$\begin{aligned} a(x,T,\sigma)={}&x_{\mathrm{Au}}a_0^{\mathrm{Au}}(T)+x_{\mathrm{Cu}}a_I^{\mathrm{Cu}}(T)+\\ &\sum_{i=0}^{I}\left[\left(\frac{i}{I}\right)^2 x_i^{\mathrm{Au}}(x,\sigma)\right]\left(a_I^{\mathrm{Au}}(T)-a_0^{\mathrm{Au}}(T)\right)+\\ &\sum_{i=0}^{I}\left[\frac{2I(I-i)-(I-i)^2}{I^2}x_i^{\mathrm{Cu}}(x,\sigma)\right]\cdot\\ &\left(a_0^{\mathrm{Cu}}(T)-a_I^{\mathrm{Cu}}(T)\right) \end{aligned} \tag{15}$$

$$\begin{aligned} a(x,T,0)={}&x_{\mathrm{Au}}a_0^{\mathrm{Au}}(T)+x_{\mathrm{Cu}}a_I^{\mathrm{Cu}}(T)+\\ &\frac{(I-1)x_{\mathrm{Au}}x_{\mathrm{Cu}}{}^2+x_{\mathrm{A}}x_{\mathrm{Cu}}}{I}\left(a_I^{\mathrm{Au}}(T)-a_0^{\mathrm{Au}}(T)\right)+\\ &\frac{(I-1)x_{\mathrm{Au}}{}^2x_{\mathrm{Cu}}+Ix_{\mathrm{Au}}x_{\mathrm{Cu}}}{I}\left(a_0^{\mathrm{Cu}}(T)-a_I^{\mathrm{Cu}}(T)\right) \end{aligned} \tag{16}$$

where, a_0^{Au}=0.407 83 nm, a_I^{Au}=0.401 12 nm, a_I^{Cu}= 0.361 52 nm, a_0^{Cu}=0.367 05 nm.

If there is no split of lattice parameter state, Eqs.(15) and (16) become Eq.(14). Therefore, the additive law of lattice parameter of characteristic crystals may be also named as the general Vegard's law.

3.4 Difference between Vegard's law and Zen's law

The lattice parameter $a(x)$ of disordered $\mathrm{Au}_{1-x}\mathrm{Cu}_x$ alloys can be obtained approximately by Vegard's law and by Zen's law. The latter may be rewritten as

$$a_Z(x)=\left(x_{\mathrm{Au}}(a_{\mathrm{Au}}^0)^3+x_{\mathrm{Cu}}(a_{\mathrm{Cu}}^0)^3\right)^{(1/3)} \tag{17}$$

Eqs.(14) and (17) are not equal in value. In order to understand the difference between Vegard's law and Zen's law, the first and the second derivative of $a_V(x)$ and $a_Z(x)$ with respect to x have been obtained, respectively:

$$\begin{cases} \dfrac{\mathrm{d}a_V(x)}{\mathrm{d}x_{\mathrm{Au}}}=a_{\mathrm{Au}}^0-a_{\mathrm{Cu}}^0\\ \dfrac{\mathrm{d}^2a_V(x)}{\mathrm{d}x_{\mathrm{Au}}{}^2}=0 \end{cases} \tag{18}$$

$$\begin{cases} \dfrac{\mathrm{d}a_Z(x)}{\mathrm{d}x_{\mathrm{Au}}}=(1/3)\left((a_{\mathrm{Au}}^0)^3-(a_{\mathrm{Cu}}^0)^3\right)\cdot\\ \qquad\left(x_{\mathrm{Au}}(a_{\mathrm{Au}}^0)^3+x_{\mathrm{Cu}}(a_{\mathrm{Cu}}^0)^3\right)^{(-2/3)}\\ \dfrac{\mathrm{d}^2a_Z(x)}{\mathrm{d}x_{\mathrm{Au}}{}^2}=(-2/9)\left((a_{\mathrm{Au}}^0)^3-(a_{\mathrm{Cu}}^0)^3\right)^2\cdot\\ \qquad\left(x_{\mathrm{Au}}(a_{\mathrm{Au}}^0)^3+x_{\mathrm{Cu}}(a_{\mathrm{Cu}}^0)^3\right)^{(-5/3)}<0 \end{cases} \tag{19}$$

From Eqs.(18) and (19), it can be known that the $a_V(x)$ is a linear function of concentration x, and the $a_Z(x)$ is a convex function of concentration x. This means that $a_Z(x)>a_V(x)$ in the range $0<x<1$. Using the same method, it can be demonstrated that $a_{\mathrm{g.Z}}(x,T,\sigma)>a_{\mathrm{g.V}}(x,T,\sigma)$.

We suggest that the general Zen's law should be adopted in theory, because the volume is an extensive property, which obeys the additive law (Eq.(1)), but the lattice parameter is not extensive property.

3.5 Relationship between partial and average molar (atomic) properties of components

In the SSA framework, the integral extensive property q of a given alloy is described directly by combination of the average molar (atomic) properties q_{A} and q_{B} of A- and B-components (see Eq.(1)).

The traditional thermodynamics of alloys is a framework of the total energy and total volume unable to be separated. Therefore, the integral extensive property of a given alloy is described indirectly by the partial molar properties q'_{A} and q'_{B} of A- and B-components [21]:

$$q(x)=x_{\mathrm{A}}q'_{\mathrm{A}}(x)+x_{\mathrm{B}}q'_{\mathrm{B}}(x) \tag{20}$$

According to definition of the partial molar property[21], it can be derived that

$$\begin{cases} q'_{\mathrm{A}}(x)=q(x)-x_{\mathrm{A}}\mathrm{d}q(x)/\mathrm{d}x_{\mathrm{A}}\\ q'_{\mathrm{B}}(x)=q(x)-x_{\mathrm{B}}\mathrm{d}q(x)/\mathrm{d}x_{\mathrm{B}} \end{cases} \tag{21}$$

The general relation expression between the partial and average molar properties of alloy components have been established:

$$\begin{cases} q'_{\mathrm{A}}(x)=q_{\mathrm{A}}(x)+x_{\mathrm{B}}\mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{A}}-\\ \qquad x_{\mathrm{B}}{}^2\left(\mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{A}}-\mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{A}}\right)\\ q'_{\mathrm{B}}(x)=q_{\mathrm{B}}(x)+x_{\mathrm{A}}\mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{B}}-\\ \qquad x_{\mathrm{A}}{}^2\left(\mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{B}}-\mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{B}}\right) \end{cases} \tag{22}$$

The partial molar (atomic) property functions derived from nine $q(x)$-functions of binary disordered alloys are shown in Table 8.

From these equations, the following inferences can be drawn.

1) From Eq.(21), it can be known that the partial molar properties q'_{A} and q'_{B} are dependent on the integral property function, but independent on it is combinational means of average molar properties of alloy components. This means that their partial properties do not represent the average properties of components.

2) From Eq.(22), the identical equation between the integral property of the partial molar properties and the combinational property of the average molar properties of components can be derived:

$$x_{\mathrm{A}} q'_{\mathrm{A}}(x) + x_{\mathrm{B}} q'_{\mathrm{B}}(x) \equiv x_{\mathrm{A}} q_{\mathrm{A}}(x) + x_{\mathrm{B}} q_{\mathrm{B}}(x) \tag{23}$$

3) From Eq.(22), the differential equation and its constraining equation between partial and average molar properties can be derived, respectively,

$$\begin{cases} \Delta q_{\mathrm{A}}(x) = q'_{\mathrm{A}}(x) - q_{\mathrm{A}}(x) = x_{\mathrm{B}} \mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{A}} - \\ \qquad x_{\mathrm{B}}{}^2 \left(\mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{A}} - \mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{A}}\right) \\ \Delta q_{\mathrm{B}}(x) = q'_{\mathrm{B}}(x) - q_{\mathrm{B}}(x) = x_{\mathrm{A}} \mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{B}} - \\ \qquad x_{\mathrm{A}}{}^2 \left(\mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{B}} - \mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{B}}\right) \end{cases} \tag{24}$$

and

$$x_{\mathrm{A}} \Delta q_{\mathrm{A}}(x) + x_{\mathrm{B}} \Delta q_{\mathrm{B}}(x) = 0 \tag{25}$$

4) From Eq.(22), the Gibbs-Duhem equation can be derived:

$$\begin{cases} \mathrm{d}q'_{\mathrm{A}}(x) = x_{\mathrm{B}}\left[2(\mathrm{d}q_{\mathrm{A}}(x) - \mathrm{d}q_{\mathrm{B}}(x)) + x_{\mathrm{A}}\mathrm{d}\left(\mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{A}}\right) + \right. \\ \qquad \left. x_{\mathrm{B}}\mathrm{d}\left(\mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{A}}\right)\right] \\ \mathrm{d}q'_{\mathrm{B}}(x) = -x_{\mathrm{A}}\left[2(\mathrm{d}q_{\mathrm{A}}(x) - \mathrm{d}q_{\mathrm{B}}(x)) - \right. \\ \qquad \left. x_{\mathrm{A}}\mathrm{d}\left(\mathrm{d}q_{\mathrm{A}}(x)/\mathrm{d}x_{\mathrm{B}}\right) - x_{\mathrm{B}}\mathrm{d}\left(\mathrm{d}q_{\mathrm{B}}(x)/\mathrm{d}x_{\mathrm{B}}\right)\right] \end{cases}$$

$$x_{\mathrm{A}} \mathrm{d}q'_{\mathrm{A}}(x) + x_{\mathrm{B}} \mathrm{d}q'_{\mathrm{B}}(x) = 0 \tag{26}$$

3.6 Relationship between lattice parameter and ordering degree of $\mathrm{Au_3Cu}$-, AuCu- and $\mathrm{AuCu_3}$-type ordered alloys

The relationship between the lattice parameter and ordering degree σ of compounds like $\mathrm{AuCu_3}$ cannot be reliably measured, since the accessible equilibrium range of long range ordering σ is too limited. This difficulty was side-stepped by GIALANELLA et al[22−23], who used a ball-mill to progressively destroy ordering degree in $\mathrm{Ni_3Al}$, which has the same superlattice as $\mathrm{AuCu_3}$. In the SSA framework, this relation can be satisfactorily described. The results are shown in Figs.6 and 7.

Table 8 Nine partial molar (atomic) property $q'_{\alpha}(x)$ -functions of binary disordered alloys in SSA framework

No.	Function
1	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 + \left[(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right]x_{\mathrm{B}}^2$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right]x_{\mathrm{A}}^2$
2	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 + \left[\left(I(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (2I-1)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 - \left[(2I-1)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)/I\right]x_{\mathrm{B}}^2$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left(I(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (I-2)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 + \left[(2I-1)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)/I\right]x_{\mathrm{A}}^3$
3	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 + \left[\left(I(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 + \left[(2I-1)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)/I\right]x_{\mathrm{B}}^2$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left(I(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (3I-2)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 - \left[(2I-1)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)/I\right]x_{\mathrm{A}}^3$
4	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 - \left[\left((I-2)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - I(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 + \left[(2I-1)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0)/I\right]x_{\mathrm{B}}^3$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left((2I-1)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + I(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 - \left[(2I-1)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0)/I\right]x_{\mathrm{A}}^3$
5	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 - \left[\left((I-2)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (2I-1)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 + \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^3$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left((2I-1)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (I-2)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 - \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^3$
6	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 - \left[\left((I-2)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 + \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^3$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left((2I-1)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (3I-2)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 - \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^3$
7	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 + \left[\left((3I-2)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - I(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 - \left[(2I-1)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0)/I\right]x_{\mathrm{B}}^3$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + I(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 + \left[(2I-1)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0)/I\right]x_{\mathrm{A}}^3$
8	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 + \left[\left((3I-2)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (2I-1)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 - \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^3$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (I-2)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 + \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^3$
9	$q'_{\mathrm{A}} = q_{\mathrm{A}}^0 + \left[\left((3I-2)(q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^2 - \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{B}}^3$ $q'_{\mathrm{B}} = q_{\mathrm{B}}^0 + \left[\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) + (3I-2)(q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^2 + \left[(2I-1)\left((q_I^{\mathrm{A}} - q_{\mathrm{A}}^0) - (q_0^{\mathrm{B}} - q_{\mathrm{B}}^0)\right)/I\right]x_{\mathrm{A}}^3$

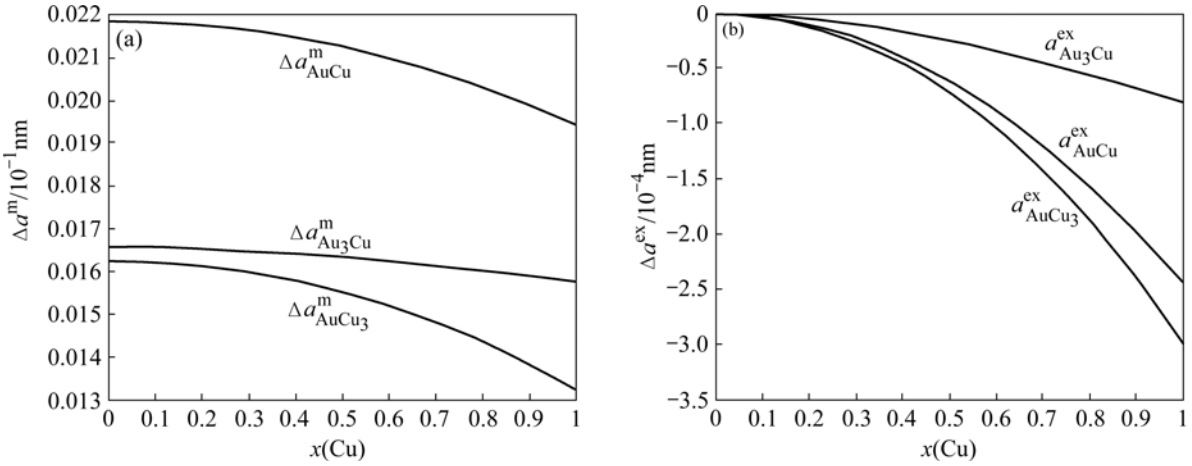

Fig.6 Relationship between lattice parameter and ordering degree for $L1_2$-Au_3Cu, $L1_0$-AuCu and $L1_2$-$AuCu_3$ compounds

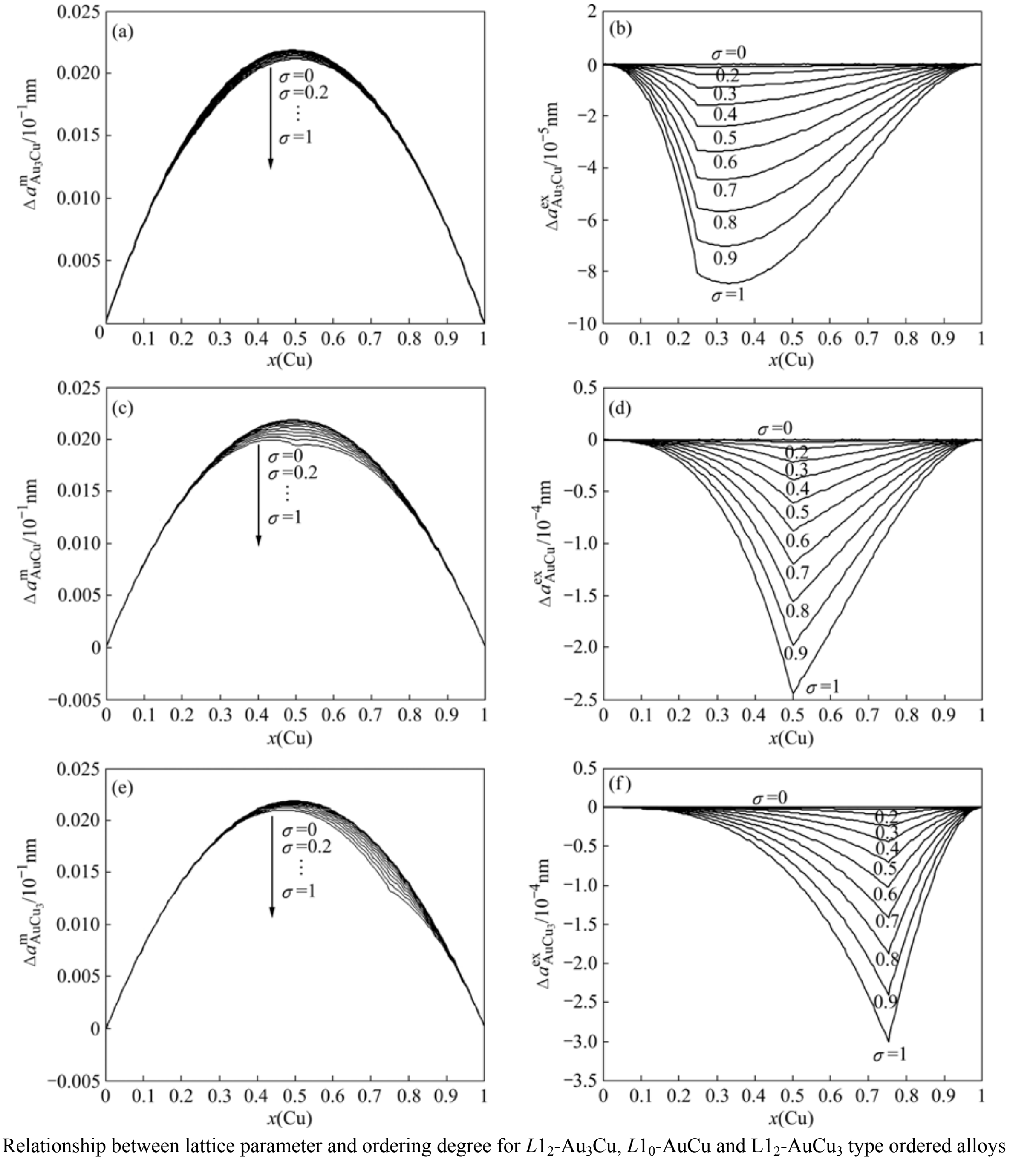

Fig.7 Relationship between lattice parameter and ordering degree for $L1_2$-Au_3Cu, $L1_0$-AuCu and $L1_2$-$AuCu_3$ type ordered alloys

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