Lattice Inversion Method and *ab initio* Pair Potentials in Cu-Ag, Cu-Au and Ag-Au Intermetallic Compounds *

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The lattice inversion method is used to construct ab initio pair potentials in the noble-metal alloy systems Cu-Ag, Cu-Au and Ag-Au from the elemental crystals and a L1$_2$ binary superstructure as references. Also, we present an alternative method for the determination of the three-dimensional Möbius functions by using the Kronecker expansion.

The idea of inverting an individual function from its lattice summation has drawn a lot of researching interest in the past few years.[1-5] Probably, the idea (i.e. the so-called lattice inversion method) may develop into a powerful scheme for the simulation of a variety of solid-state problems from first-principles and thereby overcome the well-known difficulty encountered in any empirical method, i. e., the applicability of the potential functions which are constructed merely by fitting to the experimental properties of crystals near equilibrium.

To study intermetallic compounds, the determination of pair potential between a pair of different atoms is of particular importance. Therefore, the main purpose of this letter is to use the lattice inversion method to construct this kind of pair potential. Consider the fcc structure. The basic equations of the lattice inversion method can be written as

$$F(r) = \sum_{n=1}^{\infty} w(n)f(\sqrt{n}r) \tag{1}$$

and

$$f(r) = \sum_{n=1}^{\infty} m(n)F(\sqrt{n}r) , \tag{2}$$

where $w(n)$ is the number of atoms in the shell with radius $\sqrt{n}r$ for the fcc structure. The determination of $w(n)$ is as follows. If $2n$ can not be decomposed into a sum of three square non-negative integers then $w(n) = 0$. When such a decomposition is feasible, i. e. $2n = l_1^2 + l_2^2 + l_3^2$, we set the decomposition number as $(1)z_1(n)$, when $l_1 \neq l_2 \neq l_3 \neq 0$; $(2)z_2(n)$, when $l_1 \neq l_2 \neq l_3 \neq 0$ or $l_1 \neq l_2 \neq l_3 \neq 0$; $(3)z_3(n)(=0,1)$, when $(l_1,l_2,l_3)=(0,l,l)$; $z_4(n)(=0,1)$, when $(l_1,l_2,l_3)=(0,0,l)$; $z_5(n)(=0,1)$, when $(l_1,l_2,l_3=(l,l,l)$, then $w(n)=z_1(n) \times 48 + z_2(n) \times 24 + z_3(n) \times 12 + z_4(n) \times 6 + z_5(n) \times 8$.

In Eq. (2), $m(n)$ is the three-dimensional Möbius function on fcc lattice, which can be calculated according to the following relation: [5]

$$m(n) = \mu(2n) \quad \text{and} \quad \sum_{n|\beta k} w(n)\mu\left(\frac{\beta k}{n}\right) = \delta_{\beta k} , \tag{3}$$

where $\beta = 2$ for fcc lattice. Here, we propose an alternative but equivalent formula for calculating $m(n)$:

$$m(n) = \frac{1}{w(1)}\delta(n,1) + \sum_{q=1}^{\infty}(-1)^q \sum_{p_1,p_2,\cdots,p_q=2}^{\infty} \frac{w(p_1)w(p_2)\cdots w(p_q)}{w(1)^{q+1}}\delta(n,p_1p_2\cdots p_q) , \tag{4}$$

where $\delta(x,y)$ is the Kronecker function. The above formula is a generalization of the Kronecker expansion of Möbius function on a unitary semigroup to the fcc lattice.[4]

Now we present the construction of pair potentials in a binary alloy system. The present method is based on the following points. (1) The cohesive energy of a crystal lattice can be sufficiently represented by a lattice summation over two-center terms. The two-center terms, i.e. the pair potentials, effectively contain the many-center correlations. That is to say, the pair potentials in fact include the many-atom potentials which can be reduced to pairwise ones, as discussed by Dorfman and Fuks[6] and Recio *et al.*,[7]

$$E_{\text{coh}} = \frac{1}{2}\sum_{i\neq j}\phi_{\alpha\beta}(|\boldsymbol{R}_i - \boldsymbol{R}_j|) . \tag{5}$$

(2) The cohesive energies as functions of nearest-neighbour distances for elements and alloys are described by the universal equation proposed by Rose *et al.*, which is summarized from first-principles calculations for a variety of representative systems and constructed by the sublimation energy E_s, the equilibrium lattice constant a_e and the bulk modulus B,[8]

$$E_{\text{coh}}(r) = -E_s\left[1 + \alpha\left(\frac{r}{r_{1e}} - 1\right)\right]\exp\left[-\alpha\left(\frac{r}{r_{1e}} - 1\right)\right], \tag{6}$$

where r_{1e} is the equilibrium nearest-neighbour distance ($= a_e/\sqrt{2}$), $\alpha = \sqrt{9\Omega_e B/E_s}$, Ω_e is the equilibrium volume of a unit cell. For ordered alloys, the cohesive energies refer to the energies per unit cell, including a few atoms with distinct species. (3) For A-B alloy system, two elemental crystals A, B (fcc) and an alloy superstructure A_3B ($L1_2$) are selected to be the reference systems to determine the pair potentials $\phi_{aa}(r)$, $\phi_{bb}(r)$ and $\phi_{ab}(r)$. The cohesion equations are obtained from the *ab initio* results of Wei *et al.*[9]

For elemental systems A, B with fcc structure, the cohesive energy per atom can be written as

$$E_{\text{coh}}(\alpha, r) = \frac{1}{2}\sum_{n=1}^{\infty} w(n)\phi_{\alpha\alpha}(\sqrt{n}r)(\alpha = A, B) , \tag{7}$$

therefore the pair potential between a couple of like atoms is

$$\phi_{\alpha\alpha}(r) = 2\sum_{n=1}^{\infty} m(n)E_{\text{coh}}(\alpha, \sqrt{n}r) . \tag{8}$$

The superstructure A_3B ($L1_2$) defines four sublattices: three contain A atoms and one contains B atom. Each sublattice is a simple cubic structure. Viewed from the site of a B atom, the corner vertices (cv) are occupied by B atoms and the face centers (fc) are occupied by A atoms. The cohesive energies per B atom is

$$\frac{1}{2}\sum_{i}^{\text{cv}}\phi_{bb}(R_i) + \frac{1}{2}\sum_{i}^{\text{fc}}\phi_{ab}(R_i) . \tag{9}$$

Viewed from the site of an A atom, the corner vertices are occupied by A atoms while one third of the face centers are occupied by B atoms and the other two thirds are occupied by A atoms. The cohesive energies of an A atom is

$$\frac{1}{2}\sum_i^{cv} \phi_{aa}(R_i) + \frac{1}{3}\sum_i^{fc} \phi_{aa}(R_i) + \frac{1}{6}\sum_i^{fc} \phi_{ab}(R_i) \ . \tag{10}$$

Therefore the cohesive energy per unit cell is

$$E_{coh}(A_3B, r) = \frac{1}{2}\sum_{n=1}^{\infty} w(2n)[\phi_{aa}(\sqrt{2n}r) + \phi_{bb}(\sqrt{2n}r)]$$

$$+ \sum_{n=1}^{\infty} w(n)\phi_{aa}(\sqrt{n}r) + \sum_{n=1}^{\infty} w(2n-1)\phi_{ab}(\sqrt{2n-1}r) \ . \tag{11}$$

Rewritting the above equation as

$$\sum_{n=1}^{\infty} w(2n-1)\phi_{ab}(\sqrt{2n-1}r) = E_{ab}(r) \ , \tag{12}$$

and

$$E_{ab}(r) = E_{coh}(A_3B, r) - 2E_{coh}(A, r) - \frac{1}{2}\sum_{n=1}^{\infty} w(2n)[\phi_{aa}(\sqrt{2n}r) + \phi_{bb}(\sqrt{2n}r)] \ , \tag{13}$$

then the inversion of Eq. (12) becomes

$$\phi_{ab}(r) = \sum_{n=1}^{\infty} m'(2n-1)E_{ab}(\sqrt{2n-1}r) \ , \tag{14}$$

where

$$m'(2n-1) = \frac{1}{w(1)}\delta(2n-1,1) + \sum_{q=1}^{\infty}(-1)^q \sum_{p_1,p_2,\cdots,p_q=2}^{\infty} \frac{w(2p_1-1)w(2p_2-1)\cdots w(2p_q-1)}{w(1)^{q+1}}$$

$$\cdot \delta(2n-1,(2p_1-1)(2p_2-1)\cdots(2p_q-1))$$

$$= \frac{1}{w(1)}\delta(2n-1,1) + \sum_{q=1}^{\infty}(-1)^q \sum_{p_1,p_2,\cdots,p_q=2}^{\infty} \frac{w(p_1)w(p_2)\cdots w(p_q)}{w(1)^{q+1}}\delta(2n-1,p_1 p_2 \cdots p_q) \tag{15}$$

$$= m(2n-1) \ .$$

Table 1. First-principles results of lattice constant a_e, sublimation energy E_s and bulk modulus B of Cu, Ag, Au and their ordered alloy structures Cu_3Ag, Cu_3Au, Ag_3Au, calculated by Wei *et al.* using LAPW (Ref. 9). The lattice constants are in angstroms, the sublimation energies are in eV/unit cell, the bulk moduli are in Mbar.

System	a_e	E_s	B	System	a_e	E_s	B
Cu	3.577	4.33	1.44	Cu_3Ag	3.731	16.20	1.37
Ag	4.057	3.53	1.06	Cu_3Au	3.738	17.48	1.40
Au	4.106	4.35	1.80	Ag_3Au	4.068	15.12	1.25

Table 2. Predicted equilibrium lattice constants a_e and heats of formation ΔH of CuAg, CuAu, AgAu with $L1_0$ structure and $CuAg_3$, $CuAu_3$, $AgAu_3$ with $L1_2$ structure (the first row). The second row is the results of Wei *et al.* The lattice constants are in angstroms, the heats of formation are in eV/atom.

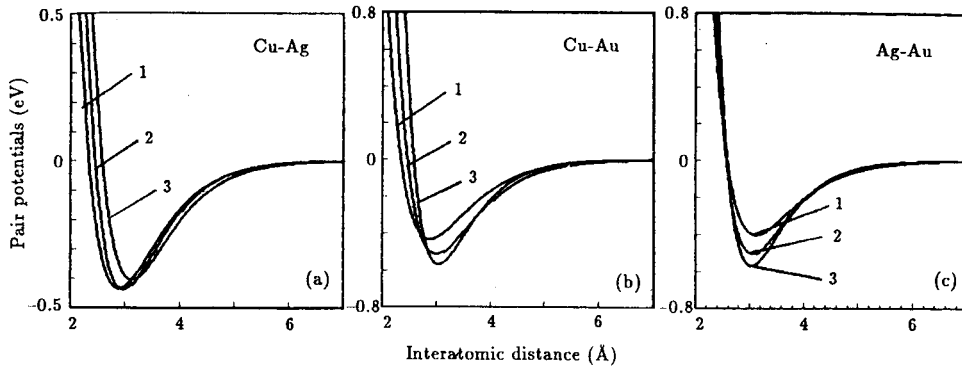| System	CuAg	$CuAg_3$	CuAu	$CuAu_3$	AgAu	$AgAu_3$
a_e	3.847	3.954	3.898	4.016	4.079	4.079
	3.848	3.963	3.887	3.991	4.096	4.093
ΔH	0.124	0.057	−0.066	−0.029	−0.119	−0.044
	0.100	0.070	−0.060	−0.025	−0.070	−0.055

Fig. 1. The pair potential functions $\phi_{aa}(r)$, $\phi_{ab}(r)$ and $\phi_{bb}(r)$ of the systems Cu-Au,
Cu-Au and Ag-Au.
(a) Cu-Ag: 1—$\phi_{Cu-Cu}(r)$; 2—$\phi_{Cu-Ag}(r)$; 3—$\phi_{Ag-Ag}(r)$,
(b) Cu-Au: 1—$\phi_{Cu-Cu}(r)$; 2—$\phi_{Cu-Au}(r)$; 3—$\phi_{Au-Au}(r)$,
(c) Ag-Au: 1—$\phi_{Ag-Ag}(r)$; 2—$\phi_{Ag-Au}(r)$; 3—$\phi_{Au-Au}(r)$.

Figure 1 shows the pair potentials in three noble-metal intermetallic compounds. The general characteristic feature of the curves $\phi_{ab}(r)$ is that they locate between the curves $\phi_{aa}(r)$ and $\phi_{bb}(r)$. In order to test the transferability of the inverted pair potentials, the equilibrium lattice constants and the heats of formation for some $L1_0$ and $L1_2$ superstructures of the studied intermetallic compounds are calculated and listed in Table 2. The octahedral distortion of $L1_0$ structure is neglected, but this effect is found to be insignificant in predicting structural energy.[9] In general, the predicted results are in agreement with the *ab initio* results of Wei *et al.*

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