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Fitting of accurate interatomic pair potentials for bulk metallic alloys using unrelaxed LDA energies

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We present a general and simple method for obtaining accurate, local density approximation (LDA-) quality interatomic potentials for a large class of bulk metallic alloys. The method is based on our analysis of atomic relaxation, which reveals that the energy released in the relaxation process can be approximated by calculating the epitaxially constrained energies of the constituents A and B. Therefore, the pair potential is fitted to the LDA-calculated epitaxial energies of the constituents (to capture the relaxation energies), and to the unrelaxed energies of ordered A_nB_m compounds (to capture the fixed-lattice ''chemical'' energy). The usefulness of our approach is demonstrated by carrying out this procedure for the $\mathrm{Cu}_{1-x}\mathrm{Au}_x$ alloy system. The resulting pair potential reproduces the relaxed LDA formation energies of ordered compounds rather accurately, even though we used only unrelaxed energies as input. We also predict phonon spectra of the elements and ordered compounds in very good agreement with the LDA results. From the calculations for $\approx 10\,000$ atom supercells representing the random alloy, we obtain the bond lengths and relaxation energies of the random phase that are not accessible to direct LDA calculations. We predict that, while in Cu-rich alloys the Cu-Cu bond is shorter than the Cu-Au bond, at higher Au compositions this order is switched. Furthermore, we find that Au-rich $\mathrm{Cu}_{1-x}\mathrm{Au}_x$ alloys have ground states that correspond to (001) superlattices of n monolayers of fcc Au stacked on m monolayers of the $L1_0$ CuAu-I structure. The potential developed in this work is available at the site http://www.sst.nrel.gov/data/download.html for interested users. [S0163-1829(99)03525-0]

I. INTRODUCTION

This paper deals with the energies of atomic configurations needed in constructing a thermodynamic description of substitutional alloys. Such a thermodynamic description concerns the energies of various ordered, random, partially ordered, and partially disordered configurations of a *bulk* alloy (not a surface) with full site occupancies (no vacancies). There are currently two general approaches to describing the energies of such general substitutional lattice configurations: (i) *The cluster expansion (CE) method.*[1,2] Here one expands the total energy of an atomically relaxed lattice configuration σ in a set of ''effective cluster interactions'' $\{J\}$

$$E_{\mathrm{CE}}(\sigma)=J_0+J_1x+\sum_{i,j} J_{ij}\hat{S}_i\hat{S}_j+\sum_{i,j,k} J_{ijk}\hat{S}_i\hat{S}_j\hat{S}_k+\cdots. \tag{1}$$

The lattice sites $i=1\cdots N$ are occupied by an A atom (in which case the spin variable $\hat{S}_i$ takes the value -1) or by a B atom ($\hat{S}_i=+1$), and J_{ij} are pair energies, J_{ijk} are three-body energies, etc. A set of spin values $\{\hat{S}_i(i=1,\ldots,N)\}$ defines a lattice configuration σ. In this approach, $E_{\mathrm{CE}}(\sigma)$ represents the configurational energy in which all atoms are relaxed to their nearest local equilibrium positions for the particular configuration σ. Since explicit atomic position coordinates are thereby integrated away, no geometric (i.e., atomic positions) or dynamic (i.e., phonons) information is obtainable from the knowledge of $E_{\mathrm{CE}}(\sigma)$. Instead, σ represents the symmetry and the crystal type alone. In recent years it has been shown[3] (a) how can the effective cluster interactions $\{J\}$ be obtained from first-principles local density approximation (LDA) calculations, (b) how can the convergence of the series Eq. (1) be accelerated by combining real and reciprocal space representations,[4] and, once the cluster interactions $\{J\}$ are given, (c) how can Eq. (1) be subjected to Monte Carlo simulations, yielding both zero temperature ground state structures and finite-temperature thermodynamic quantities of the nonvibrating lattice.[5–7]

(ii) The interatomic potential approach.[8] Here one constructs a ''force field'' (FF), expressing the total energy $E_{\mathrm{FF}}(\sigma,\{\mathbf{R}_i\})$ of a ''spin'' configuration σ explicitly in terms of the positions $\{\mathbf{R}_i\}$ of all atoms, i.e., its Born-Oppenheimer surface. Usually the force field is cast in terms of simple interatomic potentials, such as

$$E_{\mathrm{FF}}(\sigma,\{\mathbf{R}_i\})=U(\Omega)+\sum_{i,j} V_{ij}(\mathbf{R}_i,\mathbf{R}_j)+\sum_{i,j,k} V_{ijk}(\mathbf{R}_i,\mathbf{R}_j,\mathbf{R}_k)+\cdots, \tag{2}$$

where $U(\Omega)$ is a volume (Ω) term, V_{ij} are pair potentials, V_{ijk} are three-body potentials, etc. Since the atomic positions $\{\mathbf{R}_i\}$ are included explicitly, Eq. (2) contains both geometric and phonon information. There is no general theory of what analytic forms should the functions $\{V_{ij},V_{ijk},\ldots\}$ assume, and so one uses guessed forms inspired by specific theoretical frameworks, e.g., density functional,[9,10] tight-binding,[11,12] or pseudopotential theory.[8] Examples of force-fields for metallic systems include the embedded atom method[9] (EAM), the effective medium theory[10] (EMT), the tight-binding inspired[11,12] classic potentials, while examples in semiconductor systems include the valence force field,[13] the shell model,[14] the Tersoff potential,[15] and others.[16] In recent years, it has been shown how the interatomic potentials can be fit from experiment and theory, and how Eq. (2) can be used in continuous space Monte Carlo simulations (involving simultaneous spin-flips and atomic displacements) to obtain thermodynamic information.[17]

A major problem in deriving force fields or cluster expansions from the local denisty approximation (LDA) is the need to obtain and fit *relaxed* energies for numerous structures, since it has been shown[18] that the atomic relaxation can sensitively control alloy phase stability. In the present work we aim to derive a force field from the LDA data that are easily obtainable in direct calculations: energies of the elemental solid constituents A and B in different strain configurations and *unrelaxed* energies of a set of simple ordered compounds $\{A_nB_m\}$. Our strategy can be easily applied to any metallic alloy, providing accurate, LDA-quality potentials from a few inexpensive (i.e., unrelaxed) first-principles calculations. The resulting force field has the following simple form:

$$E_{\mathrm{FF}}(\sigma,\{\mathbf{R}_i\})=U(x,\Omega)+\frac{1}{N}\sum_{i,j}\sum_{\mathbf{l}}V_{ij}(|\mathbf{R}_i-\mathbf{R}_j+\mathbf{l}|). \tag{3}$$

In this expression, E_{FF} is the total energy per atom, i and j label atoms in the unit cell, N is the number of atoms in the cell, $\mathbf{l}$ is the superlattice vector, and the sum over $\mathbf{l}$ extends over all cells of the crystal. The first term in Eq. (3) is the homogeneous electron gas term[19] and depends on the average atomic volume Ω and the composition x.[20] It is written as

$$U(x,\Omega)=a(x)\frac{\Omega(x)}{\Omega}+b(x)\frac{\Omega(x)^2}{\Omega^2}+c(x)\frac{\Omega(x)^3}{\Omega^3}, \tag{4}$$

while the pair interactions[21] are written as cubic splines:

$$V_{ij}(R)=\sum_{I=1}^{3}P_{ij}^{(I)}\left(1-\frac{R}{R_{ij}^{(I)}}\right)^3\theta(R_{ij}^{(I)}-R). \tag{5}$$

For a binary $A_{1-x}B_x$ alloy there are only three pair interaction functions V_{ij}, corresponding to $I=A\text{-}A$, $A\text{-}B$, and $B\text{-}B$ pairs. The range of the interaction is given by the cutoff radii $R_{ij}^{(I)}$. Within the region limited by the cutoff, the expansion represents a complete set of basis functions. These functions have continuous first and second derivatives, which are essential for calculating the elastic constants and phonon frequencies.

Our FF can be compared with the embedded atom method[9] and the effective medium theory:[10] In all three cases the main problem is to find good pair interactions.[22] The other terms [the embedding energy in EAM or EMT, or the term $U(x,\Omega)$ in the present case] are obtained as the difference between the total energy and the energy of the pairs, by making very simple assumptions. Our $U(x,\Omega)$ is much simpler than what is commonly used in EAM work, yet it is sufficient for the treatment of dense metallic alloys. As is the case in all methods of force field generation, a crucial point is to assess to what extent the pair potentials can be used in very different atomic configurations. In our case, the adopted format for $U(x,\Omega)$ would exclude its use in low density systems, such as surfaces. On the other hand, our three pair interaction functions $V_{AA}(R)$, $V_{BB}(R)$, and $V_{AB}(R)$, are determined with precision for a very broad range of interatomic distances R. Thus, as long as only pairs are needed to describe the dense atomic configurations, our FF can be used in all sorts of dense atomic arrangements, either face-centered cubic, bcc, or noncubic configurations. The claim is partially verified in this work, where we deal with fcc and some bcc based configurations, and in our previous work on the system Ni-Al, where fcc and bcc had to be dealt with simultaneously.[19]

Previous constructions of force fields differ widely in the type of physical quantities used to fit the potential. In fact, there seems to be no general consensus on which collection of physical properties should be fitted to construct a good bulk alloy force field: cohesive energies, lattice constants, bulk moduli, defect formation energies, etc. Therefore, we start our theoretical development by establishing which type of physical input should be used to obtain a bulk force field that accurately describes bulk relaxation energies.[18]

II. DESCRIBING THE ATOMIC RELAXATION IN COMPOUNDS

Having selected a rather general form of a pair potential in Eqs. (3)–(5), its free parameters could be fitted to numerous choices of physical quantities. Since we are interested in accurate energetics $E_{\mathrm{FF}}(\sigma,\{\mathbf{R}_i\})$ for arbitrary bulk configurations, let us first examine the physical content of such energies. The formation enthalpy of configuration σ with composition x,

$$\Delta H(\sigma)=E(\sigma)-xE(A)-(1-x)E(B), \tag{6}$$

can be expressed[23] as a sum of three terms

$$\Delta H(\sigma)=\Delta E_{\mathrm{VD}}(x)+\Delta H_{\mathrm{chem}}(\sigma)+\Delta E_{\mathrm{rel}}(\sigma). \tag{7}$$

Here, the volume-deformation (VD) energy $\Delta E_{\mathrm{VD}}(x)$ is the energy required to bring the pure elements A and B (with the equilibrium lattice constants a_A and a_B, respectively) to a common lattice constant a. The change in the energy is given by

$$\Delta E_{\mathrm{VD}}(x)=\min_a[(1-x)\Delta E_{\mathrm{bulk}}(A,a)+x\Delta E_{\mathrm{bulk}}(B,a)]. \tag{8}$$

To capture ΔE_{VD} one needs to emulate the bulk moduli of pure A and B. Second, $\Delta H_{\mathrm{chem}}(\sigma)$ is the energy change due to intermixing of the pure A and B solids already prepared at the lattice constant a and forming the structure σ with all atoms at the ideal unrelaxed (UR) lattice sites. To capture $\Delta H_{\mathrm{chem}}(\sigma)$ we need to emulate the unrelaxed LDA formation energy of a compound σ:

$$\Delta H_{\mathrm{chem}}(\sigma)=\Delta H_{\mathrm{LDA}}^{\mathrm{UR}}(\sigma)-\Delta E_{\mathrm{VD}}(x). \tag{9}$$

Finally, $\Delta E_{\mathrm{rel}}(\sigma)$ is the relaxation energy gained by allowing the atoms in structure $AB(\sigma,\mathrm{UR},a)$ to relax from the ideal sites to minimize the total energy. The energy change is given by

$$\Delta E_{\mathrm{rel}}(\sigma)=\Delta H_{\mathrm{LDA}}^{(\mathrm{R})}(\sigma)-\Delta H_{\mathrm{LDA}}^{(\mathrm{UR})}(\sigma). \tag{10}$$

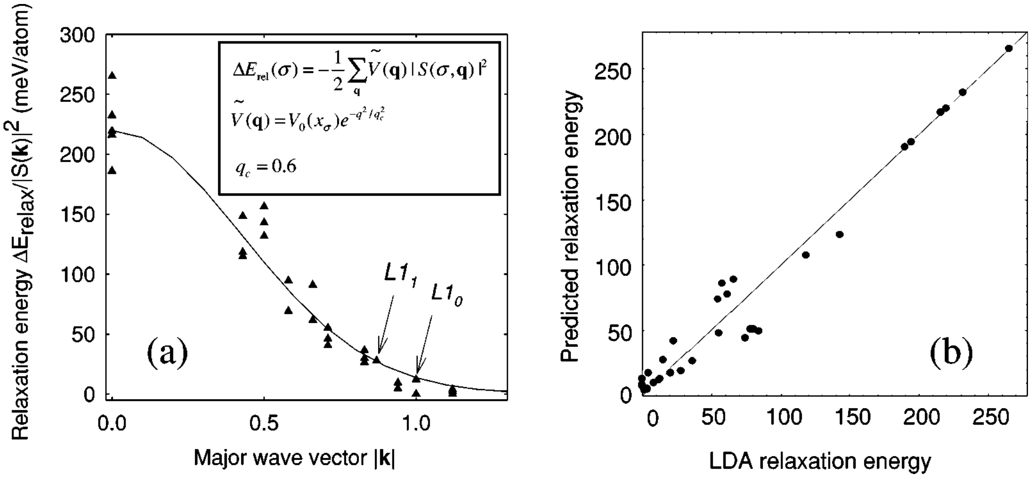

FIG. 1. (a) The LDA relaxation energy $\Delta E_{\rm rel}(\sigma)$ as a function of the major wave number for ordered Cu-Au structures (symbols). Solid line is from Eq. (18). (b) Comparison between the directly calculated LDA relaxation energies $\Delta E_{\rm rel}(\sigma)$ and those obtained using the simple formula of Eq. (18).

We aim to develop a general method for constructing force fields that treats all the contributions in Eq. (7) *simultaneously*. We note that the volume deformation energy, $\Delta E_{\rm VD}(x)$ can be easily obtained from LDA equations-of-state $\Delta E_{\rm bulk}(a)$ calculations for the pure constituents A and B. The chemical contribution $\Delta H_{\rm chem}(\sigma)$ requires only knowledge of the energies of compounds *without relaxation*, which are easily obtainable from LDA calculations. Thus, our fit will use as input both the elastic properties of the constituents and the unrelaxed chemical energies of compounds. The behavior of the $\Delta E_{\rm rel}(\sigma)$ term in Eq. (7) is less well understood, and it has proven to be difficult to reproduce using fitted force fields. To understand which type of input quantities should be fitted so as to reproduce $\Delta E_{\rm rel}(\sigma)$, consider the classical elastic (els) energy Hamiltonian[24,25]

$$\delta E_{\rm els}(\{\hat S_i,u_{i\alpha}\})=\sum_{i\alpha,j\beta}\Phi_{i\alpha,j\beta}u_{i\alpha}u_{j\beta}+\sum_{i,j\beta}K_{i,j\beta}\hat S_i u_{j\beta}, \tag{11}$$

where i,j label the lattice sites, Greek indices denote the Cartesian components of vectors, and $u_{i\alpha}$ are the atomic displacements. $\Phi_{i\alpha,j\beta}$ is the harmonic force constant between atoms i and j, and $K_{i,j\beta}$ is the Kanzaki force[24] along the Cartesian direction β on site j due to an atom at site i. The first term represents the harmonic elastic energy due to displacements of atoms, while the second term gives a coupling between the spin configurational ($\hat S_i$) and elastic ($u_{i\alpha}$) degrees of freedom. For a given configuration σ the atomic displacements are found from the equilibrium (zero force) condition

$$\frac{\delta E_{\rm els}}{\partial u_{j\beta}}=\sum_i K_{i,j\beta}\hat S_i+2\sum_{i\alpha}\Phi_{i\alpha,j\beta}u_{i\alpha}=0, \tag{12}$$

which can be solved in reciprocal space[25,26] to give the relaxation energy in terms of the spin variables only

$$\Delta E_{\rm rel}(\sigma)=-\frac{1}{2}\sum_{\mathbf q}V_{\rm rel}(\mathbf q)|\mathbf S(\boldsymbol\sigma,\mathbf q)|^2, \tag{13}$$

where $S(\sigma,\mathbf q)$ is the structure factor of configuration σ

$$S(\sigma,\mathbf q)=\sum_j \hat S_j e^{-i\mathbf{qR}_j}. \tag{14}$$

The pair interaction $V_{\rm rel}(\mathbf q)$ is given by

$$V_{\rm rel}(\mathbf q)=\sum_{\alpha,\beta}K^*_\alpha(\mathbf q)[D^{-1}(\mathbf q)]_{\alpha,\beta}K_\beta(\mathbf q), \tag{15}$$

where $D(\mathbf q)$ is the lattice Fourier transform of the force constant matrix Φ, i.e., it is proportional to the dynamical matrix, and

$$K_\beta(\mathbf q)=\sum_j K_{i,j\beta}e^{-i\mathbf{qR}_j}. \tag{16}$$

The inverse of the dynamical matrix appearing in Eq. (15) is nonanalytic at the zone-center Γ point since the acoustic frequencies tend to zero and the sound velocity depends on the direction of $\mathbf q\to 0$. This leads to a nonanaliticity of $V_{\rm rel}(\mathbf q)$ at the Γ point, i.e., $V_{\rm rel}(\hat q)$ depends on the direction $\hat q$ of the wave vector at the origin.[25,26] Equation (13) suggests that the relaxation energy is a simple function of the structure factor in reciprocal space. One could obtain the parameters $K_{i,j\beta}$ and $\Phi_{i\alpha,j\beta}$ directly from the LDA, as done in the computational alchemy linear response method.[27] However, such a treatment alone is not always satisfactory since the LDA relaxation energies exhibit several features that are beyond the simple second order expansion of Eq. (11): (i) Direct LDA calculations of relaxation energies predict nonzero relaxations of the c/a ratio in tetragonal (e.g., $L1_0$) and trigonal ($L1_1$) structures, while $\Delta E_{\rm rel}$ obtained from Eq. (13) is zero for both $L1_0$ and $L1_1$.[28] (ii) The Hamiltonian (11) does not include higher-order (e.g., anharmonic) effects, i.e., terms involving higher powers of S_i and $u_{i\alpha}$. For instance, it has been shown[7] that anharmonic elastic relaxations are important in the size mismatched noble metal alloy systems. To see the form of the "effective $V_{\rm rel}(\mathbf q)$" produced by explicit LDA energy minimizations [i.e., not limited by (i) and (ii) above], we plotted in Fig. 1(a) as solid symbols the ratio $\Delta E^{\rm LDA}_{\rm rel}(\sigma)/|S(\sigma,\mathbf q)|^2$ as a function of the major structure wave number, i.e., that $\mathbf q$ for which $|S(\sigma,\mathbf q)|^2$ is maximal.

Our task is to model this ‘‘effective $V_{\rm rel}(\mathbf{q})$’’ in a simple way that goes beyond the harmonic response Eq. (11), and reveals which type of physical quantities we should include in a FF fit to accurately capture atomic relaxation. Singularity of the function $V_{\rm rel}(\mathbf{q})$ at the origin $\mathbf{q}\rightarrow 0$ leads to a directional dependence of the relaxation energies for long-period superlattice $(A)_n/(B)_n$. This is illustrated in Fig. 1(a) by many data points at $q=0$ corresponding to different superlattice orientations $\hat{G}$. This long-period limit is given by the ‘‘constituent strain’’[4] energy, which can be calculated from the following expression:

$$\Delta E_{\rm CS}(x,\hat{G})=\min_{a_s}[(1-x)\Delta E_{\rm epi}(A,a_s,\hat{G}) + x\Delta E_{\rm epi}(B,a_s,\hat{G})]. \tag{17}$$

Here x is the composition of structure σ and $\Delta E_{\rm epi}(A,a_s,\hat{G})$ is the epitaxial deformation energy[29] describing the solid constituent strained epitaxially on a substrate plane $\hat{G}$ with lattice constant a_s and allowed to relax in the direction orthogonal to the substrate plane. Equation (17) states that the strain energy of a long-period superlattice along $\hat{G}$ is given by the sum of the strain energies of the pure constituents deformed to a common in-plane lattice constant perpendicular to $\hat{G}$. The important anharmonic effects on the elastic energies are included via the epitaxial functions $\Delta E_{\rm epi}(A,a_s,\hat{G})$. The long-period superlattice limit fixes the functional form of $V_{\rm rel}(\mathbf{q})$ near $\mathbf{q}=0$ to be used in Eqs. (13). To determine its behavior at finite $\mathbf{q}$, we note in Fig. 1(a) that the relaxation energy is generally a decreasing function of the major wave number length q, and reaches the smallest values in the structures with all their weight at the Brillouin zone boundary (e.g., $L1_0$, $L1_2$, $L1_1$ in Table I). Thus, it is possible to approximately reproduce the LDA values of $\Delta E_{\rm rel}(\sigma)$ using Eq. (13) but changing $V_{\rm rel}(\mathbf{q})$ to a simple function:

$$\tilde{V}_{\rm rel}(\mathbf{q})=\frac{\Delta E_{\rm VD}(x_\sigma)-\Delta E_{\rm CS}(x_\sigma,\hat{q})}{4x_\sigma(1-x_\sigma)}\exp[-(q/q_c)^2]. \tag{18}$$

The wave vector cutoff q_c is the only adjustable parameter, which we find to be approximately $0.6(2\pi/a_0)$ for both Cu-Au and Ni-Au. The functional form of Eq. (18) is shown as solid line in Fig. 1(a). Figure 1(b) compares the LDA relaxation energies $\Delta E_{\rm rel}(\sigma)$ with the results obtained via Eq. (13) with $\tilde{V}_{\rm rel}(\mathbf{q})$ from Eq. (18). This simple expression is applied to $\approx$40 structures yielding an rms error of 10 meV/atom. Figure 1(b) shows that even though Eq. (18) is constructed using only the epitaxial deformation energies of the constituents pure A and pure B (i.e., like-atom interactions A-A and B-B) and, therefore, does not have information about unlike-atom (A-B) interactions, it provides a reasonable description of the relaxation energies of A_nB_m compounds. This suggests that the ingredients of Eq. (18) [or equivalent physical quantities] are important inputs to any FF that needs to reproduce atomic relaxation. *Therefore, the force fields should be fitted to reproduce the elastic response functions* $\Delta E_{\rm bulk}(A,a)$ *and* $\Delta E_{\rm epi}(A,a_s,\hat{G})$. This conclusion serves as a basis for the present approach to constructing force fields for bulk metallic alloys using as input chemical energies from unrelaxed compounds and relaxation energies from epitaxial constituents.

087TABLE I. Formation enthalpies (in meV/atom) of ordered Cu-Au compounds calculated directly from the LDA (see Ref. 7) and from the fitted force field using unrelaxed and a few relaxed structures ($\mathrm{FF_{UR+R}}$), as describd in Sec. IV B 1. Structures are described in Table III of Ref. 7.

Structure	Unrelaxed		Relaxed	
	LDA	$\mathrm{FF_{UR+R}}$	LDA	$\mathrm{FF_{UR+R}}$
$L1_0$ (CuAu)	-36.1	-32.1	-48.2	-54.4
$B2$ (CuAu)	-29.9	-31.5	-29.9	-33.0
$L1_1$ (CuAu)	$+60.3$	$+62.8$	$+32.5$	$+33.3$
‘‘40’’ (CuAu)	-19.0	-18.3	-23.0	-26.3
$V2$ (CuAu)	$+170.6$	$+180.0$	$+52.2$	$+47.3$
$W2$ (CuAu)	$+15.7$	$+17.6$	-20.9	-24.9
$Y2$ (CuAu)	$+59.5$	$+59.3$	-4.2	-4.5
$Z2$ (CuAu)	$+136.4$	$+131.7$	-6.7	-7.8
$L1_2$ ($\mathrm{Cu_3Au}$)	-37.3	-37.3	-37.3	-37.3
$D0_{22}$ ($\mathrm{Cu_3Au}$)	-32.7	-32.9	-32.8	-33.4
$D0_{23}$ ($\mathrm{Cu_3Au}$)	-33.3	-35.1	-33.6	-35.8
LPS3a ($\mathrm{Cu_3Au}$)	-34.1	-35.8		
$SQS14_a$ ($\mathrm{Cu_3Au}$)	$+56.5$	$+48.0$	$+5.5$	$+4.5$
$V1$ ($\mathrm{Cu_3Au}$)	136.1	132.2	78.6	65.8
$W1$ ($\mathrm{Cu_3Au}$)	22.0	22.8	7.0	8.1
$Y1$ ($\mathrm{Cu_3Au}$)	21.8	20.2	-1.3	-3.9
$Z1$ ($\mathrm{Cu_3Au}$)	76.5	71.4	10.6	7.7
$L1_2$ ($\mathrm{CuAu_3}$) 2)	-17.3	-17.3		
$D0_{22}$ ($\mathrm{CuAu_3}$)	-10.6	-10.9	-11.8	-10.9
$SQS14_a$ ($\mathrm{CuAu_3}$)	37.8	37.3	-5.2	-10.3
$V3$ ($\mathrm{CuAu_3}$)	79.5	86.9	5.1	6.7
$W3$ ($\mathrm{CuAu_3}$)	21.1	22.3	7.8	6.8
$Y3$ ($\mathrm{CuAu_3}$)	19.4	19.8	-1.0	-8.3
$Z3$ ($\mathrm{CuAu_3}$)	50.0	48.3	-28.2	-31.0
$\alpha1$ ($\mathrm{Cu_2Au}$)	123.0	122.2	61.4	63.0
$\beta1$ ($\mathrm{Cu_2Au}$)	51.0	47.5	-3.8	-2.2
$\gamma1$ ($\mathrm{Cu_2Au}$)	-14.2	-5.5	-18.4	-18.2
$\alpha2$ ($\mathrm{CuAu_2}$)	86.4	92.7	2.1	13.4
$\beta2$ ($\mathrm{CuAu_2}$)	40.1	37.6	-40.8	-36.0
$\gamma2$ ($\mathrm{CuAu_2}$)	1.7	4.5	-6.7	-13.8
Ni_8Nb-type ($\mathrm{Cu_8Au}$)	9.3	3.0	-9.1	-4.7
$\mathrm{Ni_8}$Nb-type ($\mathrm{CuAu_8}$)	30.9	8.4	18.2	-3.1
$D1$ ($\mathrm{Cu_7Au}$)	6.8	3.2	6.8	3.2
$D7$ ($\mathrm{CuAu_7}$)	12.9	8.4	12.9	8.3

For the present study we have chosen Cu-Au as the prototypical binary alloy system with a large (12% in lattice constant) size mismatch. Cu-Au is a challenging test case for any force field that strives to reproduce all the terms in Eq. (7), since the formation enthalpies $\Delta H(\sigma)$ are very small in this system, and we expect that the relaxation energy

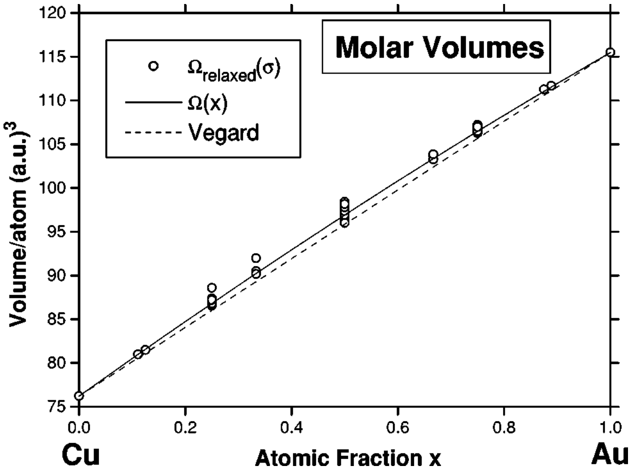

FIG. 2. Volume $\Omega(x)$ as a function of the composition x (full line), Vegard's rule (dashed line), and the atomic volumes obtained by fully relaxing all structures with the FF (circles).

$\Delta E_{\text{rel}}(\sigma)$ plays a significant role. Furthermore, accurate LDA data[7,29,30] are available for many ordered configurations, both relaxed and unrelaxed, and there are accurate experimental data on interatomic distances and thermodynamic functions.

III. GENERATING THE FORCE FIELD

A. Input data used in constructing the force field

As discussed in the previous section, the LDA input used in our procedure are as follows. (a) The unit cell volumes for N_Ω compounds [in practice we used $N_\Omega=4$, namely the two elements plus A_3B $(L1_2)$ and AB_3 $(L1_2)$]. (b) The bulk moduli of the solid elements so as to capture the volume deformation energy ΔE_{VD} of Eq. (7). (c) The N_D energies $\Delta E_{\text{epi}}(A,a_s,\hat{G})$ for the epitaxially deformed solid elements along a few directions $\hat{G}$ and substrate lattice parameters a_s, so as to capture the relaxation energy Eq. (10). These correspond to pure solid element A with a fixed lattice constant a_s perpendicular to $\hat{G}$ and relaxed lattice constants parallel to $\hat{G}$. (d) The *unrelaxed* formation enthalpies $\Delta H^{\text{UR}}_{\text{LDA}}(\sigma)$ for N_{E} structures $(20-30)$, so as to capture the chemical formation energies ΔE_{chem} of Eq. (7).

B. The force field generation steps

Our method of generating the force field consists of 4 steps.

(i) Obtain an interpolation form for the volume $\Omega(x)$. For this purpose we make a polynomial interpolation of the volumes of the $N_\Omega=4$ structures: A (fcc), A_3B $(L1_2)$, AB_3 $(L1_2)$, and B (fcc). This is shown in Fig. 2.

(ii) Expand the homogeneous gas term linearly in the parameters $P^{(I)}_{ij}$. For the aforementioned $N_\Omega=4$ structures σ, the equilibrium volume Ω_σ equals the interpolated volume $\Omega(x_\sigma)$ at the composition x_σ of σ. Then from Eqs. (4) and (3), now written for the enthalpy of formation [Eq. (6)], we obtain

$$a(x_\sigma)+b(x_\sigma)+c(x_\sigma) = \Delta H^{\text{UR}}_{\text{LDA}}(\sigma)-\frac{1}{N}\sum_{i,j}\sum_{\mathbf{l}} V_{ij}(|\mathbf{R}_i-\mathbf{R}_j+\mathbf{l}|). \tag{19}$$

To obtain the equilibrium volume $\Omega_\sigma=\Omega(x_\sigma)$, we equate the derivative of the enthalpy with respect to Ω to zero:

$$\frac{a(x_\sigma)}{\Omega_\sigma}+2\frac{b(x_\sigma)}{\Omega_\sigma}+3\frac{c(x_\sigma)}{\Omega_\sigma} = \frac{1}{N}\frac{d}{d\Omega_\sigma}\sum_{i,j}\sum_{\mathbf{l}} V_{ij}(|\mathbf{R}_i-\mathbf{R}_j+\mathbf{l}|). \tag{20}$$

To obtain the bulk modulus B_σ, we note that there are two ways to determine the elastic constant: from the acoustic phonons near the zone center and from the second derivatives of the total energy with respect to the strain components. Though not well known (but shown in Ref. 19), any force field model that has pair interactions and a volume-dependent term requires a vanishing second derivative of the volume term $U(x,\Omega)$, if the two approaches to define elastic constants are to coincide. This gives

$$\frac{d^2U}{d\Omega^2_\sigma}=2\frac{a(x_\sigma)}{\Omega^2_\sigma}+6\frac{b(x_\sigma)}{\Omega^2_\sigma}+12\frac{c(x_\sigma)}{\Omega^2_\sigma}=0. \tag{21}$$

Equations (19)–(21) allow us to solve for $a(x_\sigma)$, $b(x_\sigma)$, and $c(x_\sigma)$ in linear terms of the parameters $P^{(I)}_{ij}$ contained in the expansion for $V_{ij}(|\mathbf{R}_i-\mathbf{R}_j+\mathbf{l}|)$. Then interpolating in x we obtain the functions $a(x)$, $b(x)$, and $c(x)$ also linear in $P^{(I)}_{ij}$.

(iii) Fit the bulk moduli of the solid elements. The expression for the bulk modulus is also linear with $P^{(I)}_{ij}$. It is equated to the LDA value

$$\frac{1}{9\Omega}\sum_{\mathbf{l}}\left(R^2\frac{d^2V}{dR^2}-2R\frac{dV}{dR}\right)\Big|_{\mathbf{R}=\mathbf{l}}=B_{\text{LDA}}. \tag{22}$$

These equations for the two elements will be added constraints for the parameters $P^{(I)}_{ij}$.

(iv) Fit unrelaxed enthalpies of ordered compounds while retaining a maximum smoothness of the FF. In this step we require that our FF values for the enthalpies of various compounds match the LDA values in the RMS sense. We would like to this while having at the same time the smoothest possible potential of the shortest range consistent with the data. Longer range interactions should be introduced only if this improves the fit. Thus, with the constraints given by Eq. (22) we minimize

$$\lambda\sum_I\int_0^\infty\left(\frac{d^3V_I}{dR^3}\right)^2R^n\,dR + \sum_{\sigma}^{N_D+N_E}[E^{\text{UR}}_{\text{FF}}(\sigma)-E^{\text{UR}}_{\text{LDA}}(\sigma)]^2=\text{min}. \tag{23}$$

This is a very simple process because $V_{\alpha\beta}$ and $E^{\text{UR}}_{\text{FF}}$ are both linear in the parameters $P^{(I)}_{ij}$. In Eq. (23) the sum in I is over the pair interactions A-A, B-B, and A-B. The power n of R in the integrand acts to force a short range potential while the minimization of the derivative of $V_{\alpha\beta}$ acts to enforce a

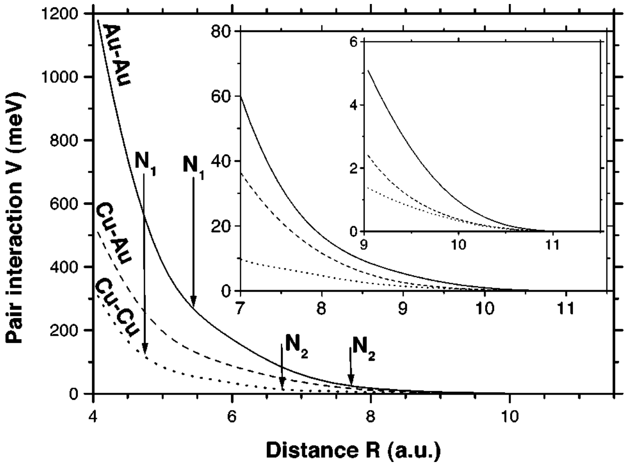

FIG. 3. The force field pair potentials $V_{ij}(r)$ (in meV). Arrows denote the first and second nearest neighbor bond lengths in fcc Cu and fcc Au. The inset shows the large R behavior.

smooth potential. The weighting parameter λ controls how much of the fit value is determined by the maximum smoothness and the shortest range condition [the first integral in Eq. (23)], or the enthalpy fit [the second sum in Eq. (23)]. The interaction cutoff radii $R^{(I)}$ must be chosen optimally: if they are too small, we cannot fit all N_E energies $\{E^{\rm UR}_{\rm FF}(\sigma)\}$ to $\{E^{\rm UR}_{\rm LDA}(\sigma)\}$ because many structures could become linearly dependent leading to the divergence of the determinative equations used in the fit. On the other hand, if the cutoffs are too large, there may be too many parameters $P^{(I)}_{ij}$ [Eq. (5)] to be adjusted.

C. Details

We use equal grids of radii $R^{(I)}_{ij}$ for the three interactions $(ij)=A\text{-}A$, $B\text{-}B$, and $A\text{-}B$. The maximum radius of the grid $R_{\rm MAX}$, that is the cutoff, was varied between 11.3, 13.3, 15.3, 17.3, and 19.3 Bohr. We could obtain equivalent fitting quality for all cutoffs, and for the same values of the parameters n and λ. Only for the very small cutoff $R_{\rm max}=9.3$ Bohr the fitting was impossible. To compare the cutoff with the interatomic distances, we mention that the first-neighbor distance is 4.75 Bohr in bulk fcc Cu and 5.47 Bohr in fcc Au (LDA results). Therefore, the cutoff $R_{\rm max}=11.3$ Bohr corresponds to the fifth shell of neighbors in fcc Cu and the fourth in fcc Au. When relaxing the configurations, we found useful to set a hard core radius (3.6 Bohr) at which the potentials $V_{ij}(R)$ became infinite. That way we could avoid spuriously relaxing into configurations with very small interatomic distances. After relaxation we find the many interatomic distances and verify that they are all much larger than the hard core radius. Thus the hard core radius had no effect other than avoid falling into unphysical energy minima. The structure definition of the configurations used here is given in Table III of Ref. 7. We use $N_E=32$ unrelaxed structures: $B2$ (CsCl), $L1_0$, $L1_1$, $\alpha1$, $\alpha2$, $\beta1$, $\beta2$, $\gamma1$, $\gamma2$, DO_{22} (Cu_3Au), "40," DO_{22} ($CuAu_3$), $V1$, $V2$, $V3$, $W1$, $W2$, $W3$, $Y1$, $Y2$, $Y3$, $Z1$, $Z2$, $Z3$, DO_{23} (Cu_6Au_2), LPS3a (Cu_9Au_3), $D1$, $D7$, Ni_8Nb-type (Cu_8Au), Ni_8Nb-type ($CuAu_8$), $SQS14_a$, and $SQS14_b$. The $N_D=11$ epitaxial deformation energies of elements were Cu = two (100) epitaxials, two (110), two (201), and one (111); Au = one (100), one (110), one (201), and one (111). During the epitaxial fitting process we approximate the out-of-plane lattice constant $a_\parallel$ from the volume-conserving condition $a_\parallel \cdot a_s^2=\Omega_A$, given Ω_A and a_s, instead of obtaining $a_\parallel$ by minimizing the total energy for each set of parameters.

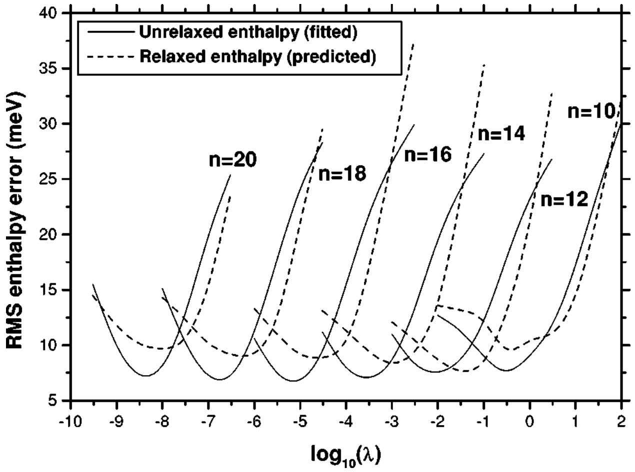

FIG. 4. Root mean square errors of unrelaxed and relaxed energies as function of the fitting parameters (n,λ) in Eq. (23). We used interaction cutoff distance $R_{\rm max}=11.3$ Bohr.

IV. RESULTS

A. The resulting force field

The resulting FF is available via the World Wide Web at URL http://www.sst.nrel.gov/data/download.html The functions $V_{ij}(R)$ are plotted in Fig. 3. The zero of the potential corresponds to infinite interatomic separation. One observes that the interactions V_{ij} are purely repulsive. The attractive part being taken care of by the homogeneous gas term $U(x,\Omega)$ in Eq. (3). Observe that $V_{AB}(R)$ is very different from the geometric mean between $V_{AA}(R)$ and $V_{BB}(R)$, as implied by the simple model often used in alloy studies.[31]

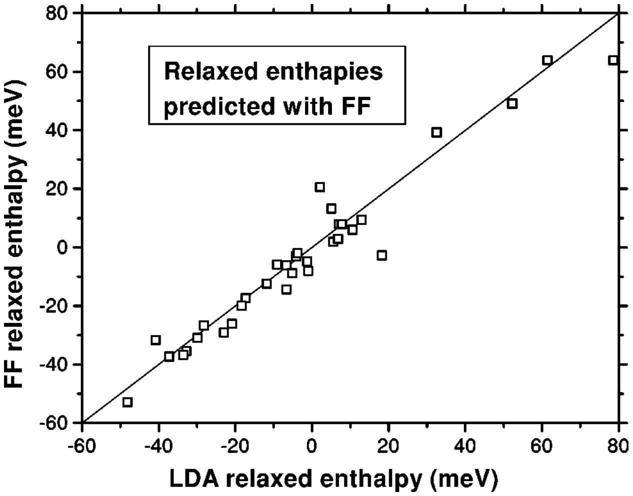

FIG. 5. The relaxed enthalpies predicted from the $\mathrm{FF}_{\mathrm{UR+R}}$ *vs* the LDA results from Ref. 7.

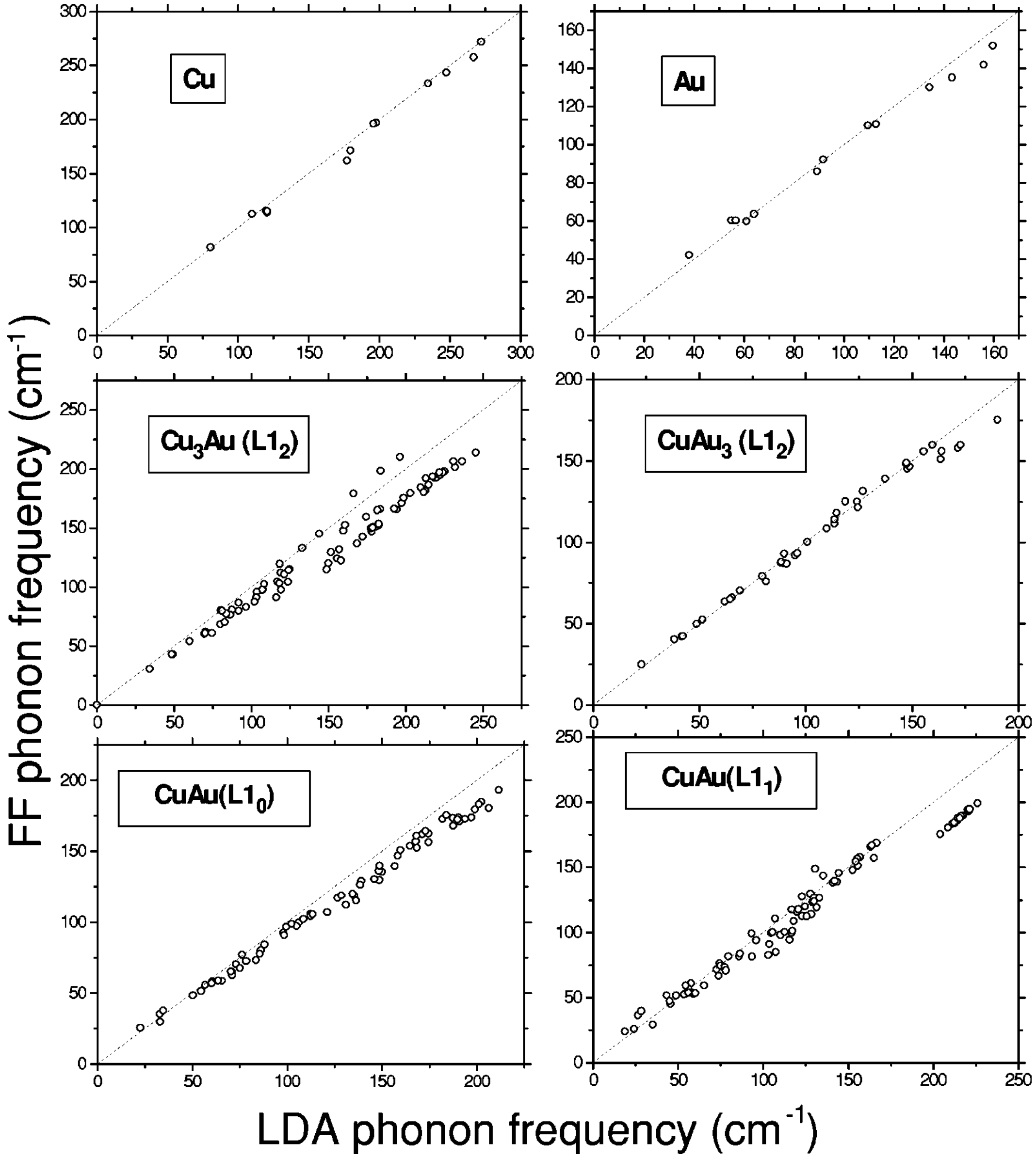

FIG. 6. FF phonon frequencies compared with those obtained from the LDA (Ref. 34) for fcc Cu, fcc Au, $L1_2$ (Cu_3Au), $L1_2$ ($CuAu_3$), $L1_0$ (CuAu), and $L1_1$ (CuAu).

B. Predictions

We next discuss the predictions of the FF for quantities that were not fitted in the generation process.

1. Relaxed enthalpies of ordered compounds and random alloys

One of the objectives of a good FF is to predict relaxation energies for a wide range of ordered and disordered configurations. We have previously calculated the relaxed LDA energies of $N_E = 34$ ordered configurations.[7] We now test how well does our FF predict the *relaxed* LDA energies of the compounds,[32] given that the only input used in its construction is unrelaxed energies. Note that in Cu-Au the relaxation energies are very large and strongly configuration dependent (Table I). Figure 4 shows the *fitted* rms error of the unrelaxed energies and the *predicted* rms error for the relaxed enthalpies, both plotted as functions of the smoothing parameter λ and power n in Eq. (23). Observe that, as long as the cutoff $R_{\max}$ (defined in Sec. III C) is not too large, the rms error of the predicted *relaxed* energy is minimum near the values of n and λ where the rms error of the fitted *unrelaxed* energy is also minimum. Thus, fitting unrelaxed energies and epitaxial deformation energies of the pure elements guides the fit correctly into predicting relaxed energies of ordered compounds. Using as input 32 unrelaxed energies plus 11 epitaxial deformation energies gives for $n = 12$ a prediction error of 8.0 meV/atom for the relaxed configurations. The predicted FF relaxed enthalpies are compared to the LDA relaxation in Fig. 5. We see that our force field fitted to unrelaxed energies predicts very well the relaxed LDA energies of all configurations. If we fit *both* the relaxed and unrelaxed LDA energies (a total of 63 structures) the rms error for the relaxed configurations drops to 6.1 meV/atom, while the quality of the fit for the unrelaxed energies is the same. In what follows we refer to this force field as FF_{UR+R}. In the FF_{UR+R} fit we used the geometries that were obtained from the FF_{UR} fit to the unrelaxed LDA energies. As seen in Table I, the Au-rich

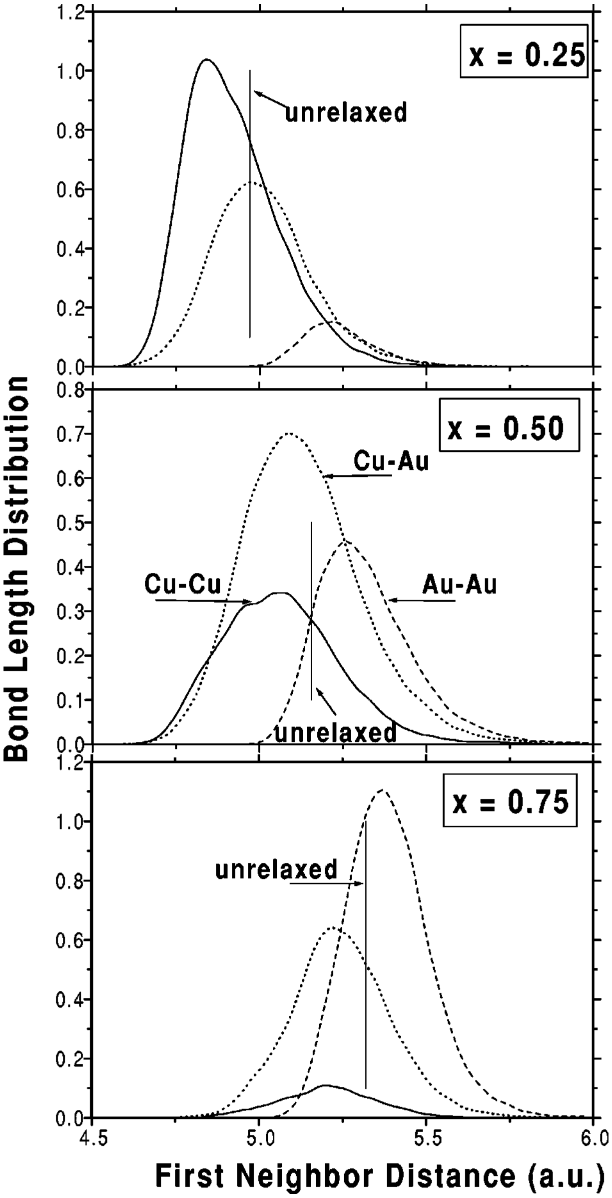

FIG. 7. Random alloy bond lengths calculated by fully relaxing 8000 supercells.

side exhibits very large relaxation, especially for structures with ⟨001⟩ ordering, e.g., $Z3$ ($CuAu_3$), $\beta 2$ ($CuAu_2$), and $L1_0$ (CuAu) (see Table I). This can be understood on the basis of our earlier work (Fig. 5 in Ref. 29) where it was showed that the strain energy required to bring the constituents to a common lattice constant along [001] is anomalously low due to strong anharmonic lattice softening of Cu. For instance, starting from a high unrelaxed energy, $Z3$ relaxes to lower its energy slightly below the cubic $L1_2$ ($CuAu_3$) structure. The relaxation energies of random configurations are difficult to calculate by direct methods since they require large supercells. We have calculated the relaxation energy of Eq. (10) for random alloys with composition $x=0.5$ by relaxing the energy of large supercells and averaging the resulting total energies over different random arrangements of atoms. The largest supercell had 8000 atoms (20 times larger than the primitive cell in each direction). At this size, the results are almost equal for the different configurations. The mixing enthalpy $\Delta H_{\mathrm{rand}}(x)$ at composition x can be written as the sum of the unrelaxed (UR) energy of the random configuration plus the energy lowering ΔE_{rel} due to atomic relaxation

$$\Delta H_{\mathrm{rand}}(x)=\Delta E_{\mathrm{UR}}(x)+\Delta E_{\mathrm{rel}}(x). \tag{24}$$

For the principal compositions, the results (in meV/atom) are

$$\begin{aligned}\Delta H_{\mathrm{rand}}(0.25)&=50.4-45.9=4.5,\\ \Delta H_{\mathrm{rand}}(0.50)&=57.4-54.5=2.9,\\ \Delta H_{\mathrm{rand}}(0.75)&=35.5-34.0=1.5.\end{aligned} \tag{25}$$

Note that in Cu-Au the relaxation energy is as large as the chemical (=unrelaxed) fixed-lattice energy. We find that the relaxation energy oscillates as a function of the supercell size, converging rather slowly. For the cell size used to obtain our results the oscillations are already negligible, but it does take a few thousands of atoms to achieve this.

2. Phonons of ordered compounds

One of the advantages of the FF with respect to the cluster expansions is its ability to deal with atomic motion. The phonon frequencies ω are the eigenvalues of the following eigenvalue problem:[33]

$$\omega^2(\mathbf{q})e_{i\alpha}(\mathbf{q})=\sum_{j,\beta} D_{i\alpha,j\beta}(\mathbf{q})e_{j\beta}(\mathbf{q}), \tag{26}$$

where $D_{i\alpha,j\beta}(\mathbf{q})$ is the dynamical matrix given by

$$D_{i\alpha,j\beta}(\mathbf{q})=(M_iM_j)^{-1/2}\sum_{\mathbf{l}}\frac{\partial^2 V}{\partial R_{i\alpha}\partial R_{j\beta}}\exp[i\mathbf{q}(\mathbf{R}_i-\mathbf{R}_j+\mathbf{l})], \tag{27}$$

$$\frac{\partial^2 V}{\partial R_{i\alpha}\partial R_{j\beta}}=-2\left[\frac{\delta_{\alpha\beta}}{R}V'_{ij}(R)-\frac{x_\alpha x_\beta}{R^3}V'_{ij}(R)+\frac{x_\alpha x_\beta}{R^2}V''_{ij}(R)\right]_{\mathbf{R}=\mathbf{R}_i-\mathbf{R}_j+\mathbf{l}}, \tag{28}$$

and $e_{i\alpha}(\mathbf{q})$ are phonon displacement eigenvectors. Using our FF the force constants are given explicitly by Eq. (27), where i,j denote the atoms within the unit cell, M_i are the atomic masses, Greek indices α,β label the Cartesian components of the position vectors $\mathbf{R}_i$. The other symbols have their usual meaning. We have calculated the phonon spectra of Cu, Au, Cu_3Au ($L1_2$), $CuAu_3$ ($L1_2$), CuAu ($L1_0$), and CuAu ($L1_1$) using our FF and Eqs. (26)–(27), and compared the results with the LDA phonon frequencies obtained previously in Ref. 34 using the density functional perturbation theory. The excellent agreement of our FF phonon frequencies with the LDA results (Fig. 6) is very reassuring because no explicit phonon data were used in the fit. No imaginary phonon frequency was found in FF, indicating that all the studied compounds are dynamically stable.

3. Bond lengths of the random alloys

We used the 8000 atom supercell to determine the nearest neighbor bond lengths in random alloys. The results are shown in Fig. 7 for the compositions $x=0.25$, 0.50, and 0.75. It is interesting that at $x=0.75$ the Cu-Cu bond length becomes longer than the Cu-Au bond length. This finding agrees well with the LDA predictions,[7] and the results obtained from EMT-type force field,[35] but disagrees with the study of Mousseau and Thorpe,[36] who used a simple alloy EAM model[37] fitted for the pure elements only. This bond length inversion phenomenon has been established experimentally[38] in the Ni-Au system, and there are indications that it may be true also for[39] $\mathrm{Cu}_{1-x}\mathrm{Au}_x$.

4. Ground state search

The ground state search was made differently on the Cu-rich and on the Au-rich sides of the phase diagram: On the Au-rich side, we considered up to 16 planes of Cu and planes of Au, in any order. On the Cu-rich side, it was clear that only the small supercell configurations $L1_2$, ''40,'' DO_{22}, and the like had a chance of being the ground state. Thus, we considered up to 8 planes such as (Cu,Cu), (Cu,Au), (Au,Cu). We used both the LDA-based cluster expansion[7] and the LDA-fitted FF to determine the ground states vs composition. We find that both approaches agree on the essential features of the phase diagram. (i) At $x=0.5$, the $L1_0$ structure has the lowest formation energy among all the configurations in both methods. (ii) On the Cu-rich side, the configuration $L1_2$ ($\mathrm{Cu_3Au}$) has the lowest formation enthalpy. Therefore, the ground state line is simple on the Cu-rich side: it consists of a line from Cu to $L1_2$ ($\mathrm{Cu_3Au}$) at $x=0.25$ and then to $\mathrm{L1_0}$ (CuAu) at $x=0.5$. These features are common to CE and FF. (iii) For the Au-rich side we find that within the $\mathrm{Cu}_{1-x}\mathrm{Au}_x$ composition range $0.63<x<0.87$ the ground states are formed by a quasicontinuum of configurations that may be thought of as $L1_0$ (CuAu) stacked on Au. For instance, the ground state at $x=0.75$ with 16 planes is a $(\mathrm{Au})_8/(\mathrm{CuAu})_4$ superlattice along $\langle 001\rangle$. Our LDA cluster expansion also predicts[7] (001) superlattices as ground states in the Au-rich region: $(\mathrm{Cu})/(\mathrm{Au})_2$ at $x=\frac{2}{3}$ and $(\mathrm{Cu})/(\mathrm{Au})_4/(\mathrm{Cu})/(\mathrm{Au})_4/(\mathrm{Cu})/(\mathrm{Au})_2/(\mathrm{Cu})/(\mathrm{Au})_2$ at $x=\frac{3}{4}$. The energy differences with respect to other (001) superlattices are very small (only a few meV/atom). The surprising prediction of Au-on-CuAu superlattices along $\langle 001\rangle$ as ground states has a simple explanation: the relaxed $L1_0$ (CuAu) structure has a tetragonal distortion $c/a\approx 0.9$, i.e., a contraction along the c axis and an expansion in the basal plane. This results in a in-plane lattice parameter of 7.55 Bohr, which is only 2.3% smaller than the lattice parameter of unstrained fcc Au. Therefore, $L1_0$ (CuAu) can be deposited on Au with small epitaxial strain energy, and the total energy is approximately the weighted average between $L1_0$ and fcc Au. This also suggests that it should be possible to grow such multilayers experimentally.

V. SUMMARY

We have showed that pair interaction potentials are able to describe the Cu-Au alloy system, which has a large constituent size mismatch. Significantly, the knowledge of the unrelaxed formation enthalpies, together with the epitaxial deformation energies of the elements, is sufficient to predict relaxation and even the phonon spectra of the intermetallic compounds. No knowledge of compound relaxation has to be assumed. To attain a good predictive power one must (i) fit the pair potentials to a large number of unrelaxed enthalpies, (ii) fit the pair potentials to a large number of epitaxially deformed elements, and (iii) add a volume-dependent term to lift the Cauchy restrictive relations. We found that the unlike atoms pair interaction V_{A-B} could not be guessed from the pair interactions of like atoms V_{A-A} and V_{B-B} but is an independent function that must be extracted from the data set. For this reason we used an unusually large number of unrelaxed compound energies in the data set. In a certain way, pair potentials compete with cluster expansions in the description of an alloy. The pair potentials have the advantage of describing chemical and elastic properties simultaneously, but at the cost of a more complicate fitting. Unlike the cluster expansion, the present potentials show that the interaction is short ranged indeed, physically consistent with the heavy screening of atoms by the free electrons of the metal. The potential developed in this work is available at the site http://www.sst.nrel.gov/data/download.html

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