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 $\hat{S}_i$

)

represents the configurational energy in which all atoms are relaxed to their nearest local equilibrium positions for the particular configuration σ

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, $\Delta E_{\mathrm{VD}}(x)$ can be easily obtained from LDA equations-of-state $\Delta E_{\mathrm{bulk}}(a$

Our task is to model this ‘‘effective $V_{\mathrm{rel}}(\mathbf{q}$

$\Delta E_{\mathrm{rel}}(\sigma)$ 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

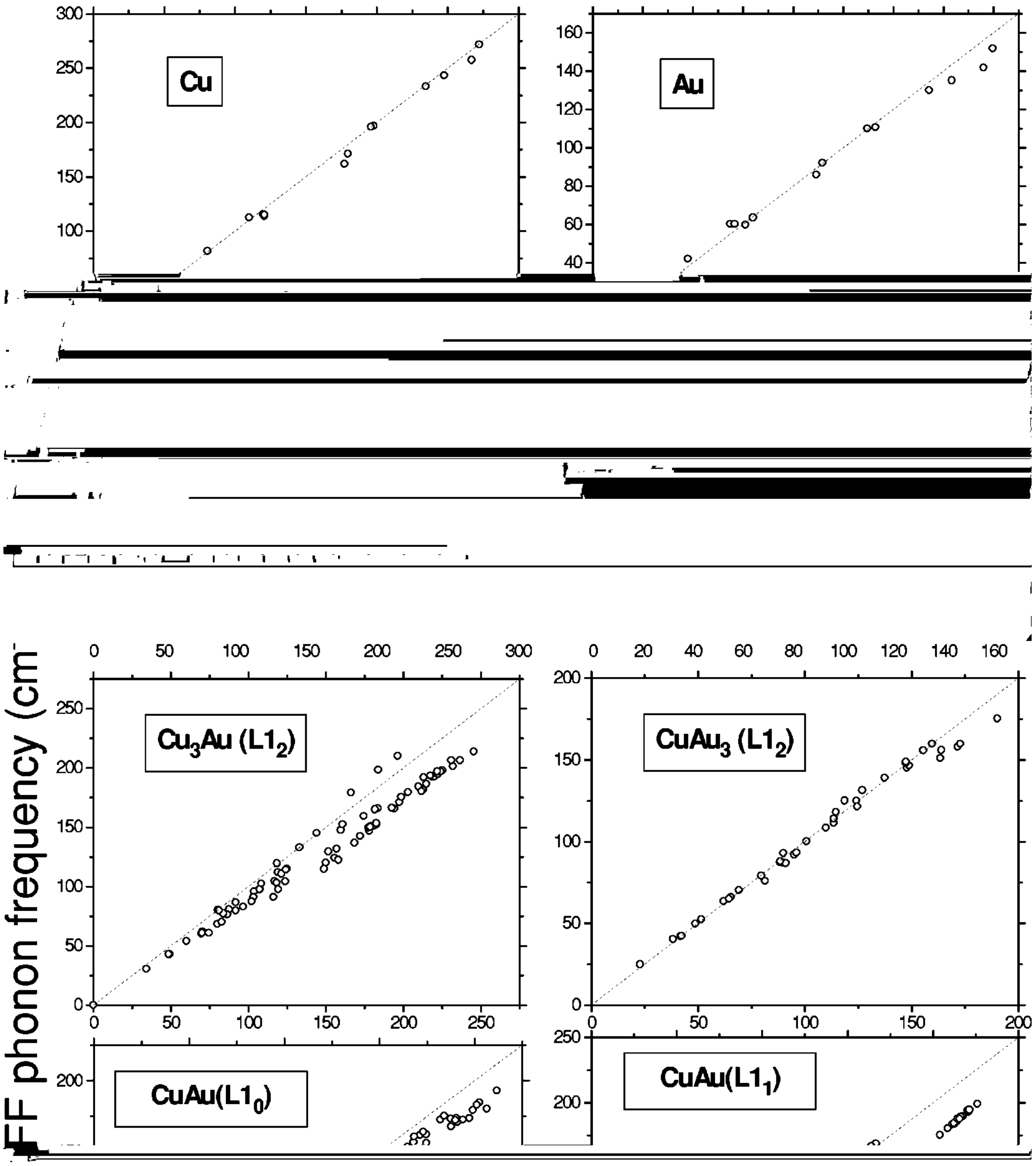
A. Input data used in constructing the force field

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 $\Delta E_{\mathrm{epi}}(A,a_s,\hat{G})$ 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 $\Delta H^{\mathrm{UR}}_{\mathrm{LDA}}(\sigma)$ for N_{E} structures $(20-30)$, so as to capture the chemical formation energies ΔE_{chem} of Eq. (7).

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 $\{E_{\mathrm{FF}}^{\mathrm{UR}}(\sigma)\}$ to $\{E_{\mathrm{LDA}}^{\mathrm{UR}}(\sigma)\}$ 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 $P_{ij}^{(I)}$ [Eq. (5)] to be adjusted.

C. Details

We use equal grids of radii $R_{ij}^{(I)}$ for the three interactions $(ij)=A\text{-}A$, $B\text{-}B$, and $A\text{-}B$. The maximum radius of the grid R_{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 $R_{\max}=9.3$ 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 $R_{\max}=11.3$ 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} ($\mathrm{Cu_3Au}$), ‘‘40,’’ DO_{22} ($\mathrm{CuAu_3}$), $V1$, $V2$, $V3$, $W1$, $W2$, $W3$, $Y1$, $Y2$, $Y3$, $Z1$, $Z2$, $Z3$, DO_{23} ($\mathrm{Cu_6Au_2}$), LPS3a ($\mathrm{Cu_9Au_3}$), $D1$, $D7$, Ni



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 $\mathrm{FF}_{\mathrm{UR+R}}$. In the $\mathrm{FF}_{\mathrm{UR+R}}$ fit we used the geometries that were obtained from the $\mathrm{FF}_{\mathrm{UR}}$ fit to the unrelaxed LDA energies. As seen in Table I, the Au-rich

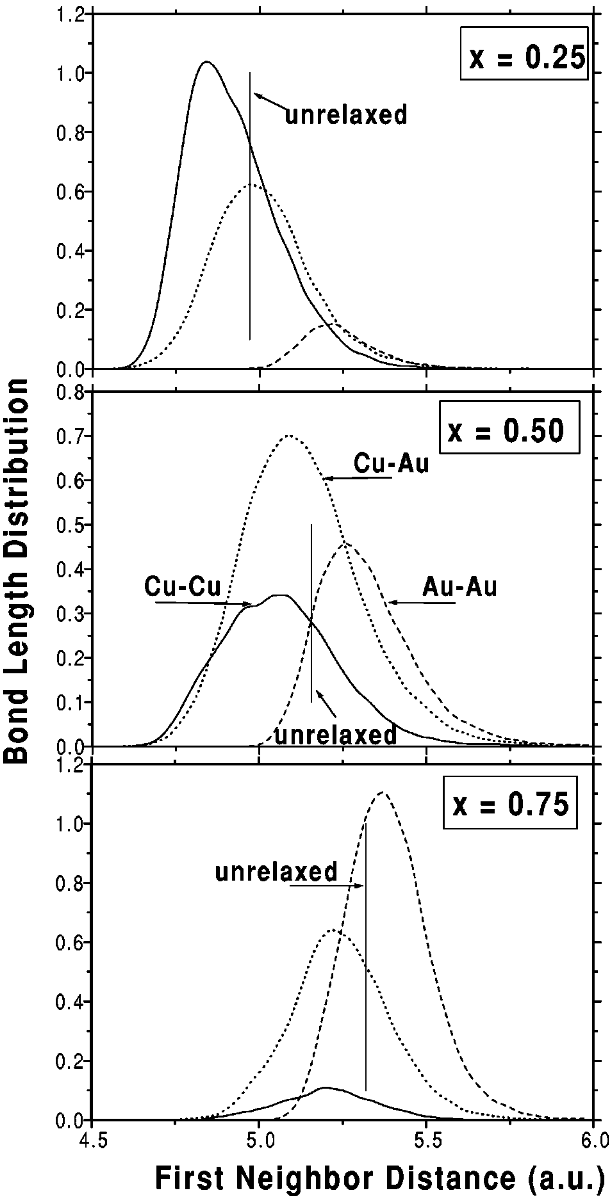


FIG. 7. Random alloy bond lengths calculated by fully relaxing 8000 supercells.

side exhibits very large relaxation, especially for structures with ⟨001⟩ ordering, e.g., $Z3$ ($\mathrm{CuAu_3}$), $\beta 2$ ($\mathrm{CuAu_2}$), 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 $L1_2$ ($\mathrm{CuAu_3}$) 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

$$\Delta H_{\mathrm{rand}}(0.25)=50.4-45.9=4.5,$$

$$\Delta H_{\mathrm{rand}}(0.50)=57.4-54.5=2.9,$$

$$\Delta H_{\mathrm{rand}}(0.75)=35.5-34.0=1.5. \tag{25}$$

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, $\mathrm{Cu_3Au}$ ($L1_2$), $\mathrm{CuAu_3}$ ($L1_2$), 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

[9] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984); S. M. Foiles and M. S. Daw, J. Mater. Res. **2**, 5 (1987); S. Rubini and P. Ballone, Phys. Rev. B **50**, 9648 (1994); Q. Xie and M. Huang, J. Phys.: Condens. Matter **6**, 11 015 (1994); Y. Ouyang and B. Zhang, Phys. Lett. A **192**, 79 (1994); M. Asta and S. M. Foiles, Phys. Rev. B **53**, 2389 (1996); J. D. Althoff, D. Morgan, D. de Fontaine, M. Asta, S. M. Foiles, and D. D. Johnson, *ibid.* **56**, R5705 (1997); S. Chantasiriwan and F. Milstein, *ibid.* **58**, 5996 (1998); V. Kuznetsov, K. Tsai, and T. Turkebaev, J. Phys.: Condens. Matter **10**, 8957 (1998).