Transition-metal interactions in aluminum-rich intermetallics

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Abstract

The extension of the Generalized Pseudopotential Theory (GPT) to transition-metal (TM) aluminides produces pair and many-body interactions that allow efficient calculations of total energies. In aluminum-rich systems treated at the pair potential level, one practical limitation is a transition-metal over-binding that creates an unrealistic TM-TM attraction at short separations. Even with this limitation, the GPT pair potentials have been used effectively in total energy calculations for systems with TM atoms at separations greater than 4 Å. An additional term may be added for systems with shorter TM atom separations, formally folding repulsive contributions of the 3- and 4-body interactions into the pair potentials, resulting in structure-specific interatomic potentials. We have performed numerical ab-initio total-

energy calculations using VASP for an AlCoNi compound in a particular quasicrystalline approximant structure. The results allow us to fit a correction of the form a/r^b to the GPT pair potentials .

I. INTRODUCTION

Total energy calculations are an important tool in theoretical condensed matter physics, giving insight into structures and mechanical properties of solids [1,2]. Accurate calculations of total energy are notoriously difficult. Theoretically, one must solve the Schroedinger equation simultaneously for all electrons in the presence of fixed atomic nuclei. Density functional theory simplifies this problem by reducing it to the self-consistent solution of Schroedinger's equation for a single electron in a potential that depends upon the electron density. Even with this simplification, such full ab-initio methods are computationally demanding [3], usually limited to systems of less than a hundred atoms, and may not yield immediate physical insight once an answer is obtained.

Instead, one may expand the energy in terms of pair and many-body interatomic potentials [1,2,4,5] so that the total energy appears as an explicit function of atomic separations. Depending on the physical system under study and the type of information sought, the expansion may often be truncated after a small number of terms. Such a truncated expansion trades off a degree of accuracy in favor of computational simplicity and potentially greater physical insight as compared with a full ab-initio approach.

Many physical systems have been studied using interatomic potentials [6–11]. These potentials are especially simple in the case of non-transition metals. There, the d-electron shells are either empty or else are deeply buried under the Fermi energy level, allowing rapidly convergent expansions of the total energy. The presence of partially filled d-bands in transition metals complicates the analysis. The d-band electronic states are highly localized in the vicinity of the atoms and have strong angle-dependence. In contrast to non-transition metals, transition metal d-bands are at or near the Fermi level. Total energy expansions will not converge as quickly as for non-transitions metals, and 3- and 4-body interactions may contribute significantly [12].

Moriarty [11] developed a rigorous treatment for transition metals in the context of the Generalized Pseudopotential Theory (GPT). The treatment was later extended to binary and ternary alloys of aluminum with first row transition metals [13]. These studies found that 3- and 4-body interactions could be important in determining energetic and mechanical stability of structures with large TM concentrations. The treatment of d-electron interactions created strong attractive interactions at unphysically short distances in the pair potentials, balanced by repulsive forces contained in 3- and 4-body interactions. We wish to modify the pair potentials to remove this unphysical attraction so that a truncation of the total energy expansion at the level of pair potentials will be more accurate when transition metal atoms are near neighbors.

One motivation for this study is the need for fast total energy calculations in systems with short TM separations to enable structural relaxation, molecular dynamics and Monte Carlo simulations. We focus our attention on Al-Co-Ni compounds in decagonal quasicrystalline structures [14]. The precise modification required depends on the particular structure studied, but should be at least approximately valid for many similar structures. Furthermore, the modifications obtained may allow us to treat Al-Co-Cu and Al-Cu-Ni decagonal phases [15] because the Cu-Cu interactions do not appear to require modification [13]. Limited numbers of full ab-initio calculations are sufficient to determine the required modifications.

We intend to apply these potentials to predict the structures of decagonal quasicrystals [16]. A great deal of experimental data is available that identifies the positions of most atoms and identifies the chemical identity of many of those. However, in order to determine the quasicrystal structures from X-ray diffraction one faces degenerate structures because elements near each other in a row of the periodic table (such as Co, Ni and Cu) have similar X-ray form factors. A common approach to this problem is to supplement the experimental data with total energy calculations. This approach is well established in crystallography [17].

The newly modified pair potentials can be applied to total energy calculations in quasicrystals and related structures with a great reduction in computational times compared with the full ab-initio calculations. The time savings results from two features of the potentials. First, the potentials themselves depend on composition and atomic volume but not the structure to which they will be applied, so they may be precalculated and then applied repeatedly with a simple lookup and interpolation. Second, to calculate the change in energy when a single atom is moved, only interactions affecting that atom are needed. If the interactions are cut off at a certain spatial separation, the time required to calculate the change in total energy becomes independent of the number of atoms in the complete structure. In contrast, full ab-initio methods must recalculate the entire system when a single atom is moved.

In section II, GPT potentials are briefly described and the difficulty of truncating the total energy expansion at pair potentials is discussed. Section III gives details about the methods we employ to determine the needed modifications. In section IV, we present the results of our full ab-initio calculations and the modified pair potentials are introduced.

II. INTERATOMIC POTENTIALS

JOHN: PLEASE REVISE OR ENHANCE THE FOLLOWING DISCUSSION OF GPT.

The Generalized Pseudopotential Theory starts with a full ab-initio representation of the total energy. Only valence electrons are treated, and the interactions of valence electrons with ionic cores are treated via pseudopotentials. A mixed basis is employed allowing *sp* electrons to be represented as superpositions of plane waves, while *d* electrons are represented as localized states. The energy and the electron density are expanded in terms of weak *sp* pseudopotential matrix elements $W_{kk'}$, $sp - d$ hybridization Δ_{kd}, and $d - d$ tight-binding matrix elements $\Delta_{dd'}$. The interatomic potentials can be calculated as functions of these matrix elements. For an alloy, the GPT expands the total energy in the form:

$$E(\vec{R}_i^{\alpha}) = E_{vol} + \frac{1}{2}\sum_{\alpha\beta}\sum_{ij}{}' \, v_2^{\alpha\beta}(R_{ij}) + \frac{1}{6}\sum_{\alpha\beta\gamma}\sum_{ijk}{}' \, v_3^{\alpha\beta\gamma}(R_{ij}R_{jk}R_{ki}) + ... \tag{1}$$

where $\vec{R}_i$ is the set of all positions of N ions in the metal, E_{vol} is a volume term which includes all single-ion contributions, and v_2, v_3,... are the two-, three-, and many-ion interatomic potentials. The primes on sums over ion positions exclude all self-interaction terms. Indices $\alpha, \beta, \gamma, \cdots$ run over all chemical species, and indices $i, j, k, \cdots = 1, \cdots, N$ run over the individual ions. All the interatomic potentials are atomic volume and composition-dependent, but structure-independent. They are functions of the relative positions of small subsets of atoms, independent of the positions of all other atoms in a structure. The entire dependence on the structure comes analytically through the summations over all N ions. This makes these potentials transferable among different structures at fixed atomic volume and composition. Detailed treatments of GPT are given in references [11,18,13].

The separation of total energy between the 2- and higher-body terms is not unique in principle, since we can add contributions to v_2 provided we make suitable subtractions from v_3 or higher-body interactions. In the GPT potentials, the total energy is calculated to second order in the weak pseudopotential $W_{kk'}$, so their contribution to the total energy enters only in the volume term and the pair potentials v_2. The $d-d$ tight-binding contributions are carried to all orders in the matrix element $\Delta_{dd'}$. Terms are allocated to pair- and many-body potentials according to how many distinct ionic position explicitly enter. Thus the pair potentials v_2 contain contributions that are even powers of $\Delta_{dd'}$ associated with repeated hopping of d electrons back and forth between a pair of ions. The three-body interactions contain a term of third order order proportional to $\Delta_{dd'}\Delta_{d'd''}\Delta_{d''d}$ and terms of fourth order proportional to $\Delta^2_{dd'}\Delta^2_{d'd''}$, as well as higher-order terms. The four-body interaction starts at fourth order.

The overbinding in v_2 at short distances results from the contribution of second-order in $\Delta_{dd'}$. This term is attractive because it relates to d-band broadening resulting from d electron hopping. The attraction is strong at short distances because the matrix element for atoms separated by distance r varies roughly as r^{-5}. Contributions of higher order in $\Delta_{dd'}$ should balance this attractive contribution of the second order term. However, as discussed above, only certain higher order terms are explicitly included in v_2. The others belong to the many-body potentials.

JOHN: DOES THE ABOVE DISCUSSION IMPLY THAT THE TM ATTRACTION MIGHT BE CORRECT FOR AN ISOLATED PAIR OF TM ATOMS SURROUNDED BY ALUMINUM? DO WE ALSO NEED TO DISCUSS MANY-BODY TERMS CONNECT-

ING A TM PAIR WITH SURROUNDING ALUMINUM ATOMS?

Fig 1 shows the Al-Al and Al-TM pair potentials for Al-Co-Ni [13]. These are calculated in the aluminum-rich limit, but in practice they do not depend strongly on composition. The first minima of the Al-TM pair potentials occur near 2.3 Å with depths of about 0.2 eV (Al-Ni) and 0.3 eV (Al-Co). Rather than a potential minimum, the Al-Al potential exhibits a shoulder near 3 Å. The TM-TM pair potentials are shown in Fig. 2. The TM overbinding is most evident for Co. The Co-Co potential has a depth of 2.1 eV at 1.7 Å. The NiNi potential depth of 0.1 eV at 2.2 Å is not obviously unreasonable, but in the following we will find it requires some modification. The Co-Ni pair potential v_2^{CoNi} is defined as an average of the Co-Co and Ni-Ni potentials,

$$v_2^{CoNi} \equiv (v_2^{CoCo} + v_2^{NiNi})/2. \tag{2}$$

This amounts to a perturbative expansion of $v_2^{\alpha\beta}$ in the difference in atomic number $Z^\alpha - Z^\beta$. Clearly v_2^{CoNi} so-defined suffers overbinding due to the overbinding of v_2^{CoCo}.

We wish to devise potentials for Al-Co-Cu and Al-Cu-Ni as well as Al-Co-Ni. Previously the Al-Cu potentials were found to be well behaved up to large Cu composition [13] so perhaps no modification of v_2^{CuCu} is needed. Our modification to v_2^{CoCo} obtained for Al-Co-Ni compounds may be approximately valid for these other compounds. We previously defined [13] v_2^{CoCu} as equal to v_2^{NiNi} because Ni lies between Co and Cu in the periodic table. Thus our modified Ni-Ni potential should serve as an approximate modified Co-Cu potential. For the modified Cu-Ni potential we may take $(v_2^{CuCu} + v_2^{NiNi})/2$, using the modified Ni-Ni potential. The so-obtained Al-Co-Cu and Al-Co-Ni potentials should still be validated using full ab-initio calculations.

III. MODIFICATION OF PAIR POTENTIALS

As discussed above, the unphysical short-ranged attraction in the TM-TM pair potentials is balanced by repulsive terms contained in the three- and higher-body potentials. If one chooses to truncate the GPT expansion at the pair potential level, these repulsive many-body contributions must be "folded in" to effective pair potentials. Formally, we may define an effective pair potential by averaging over atomic positions, holding a single pair of ions fixed [18]

$$v_2^{eff} \equiv v_2 + < v_3 > + < v_4 > + \cdots . \tag{3}$$

The redefined three- and four-body interactions then must act on deviations of a particular structure from isotropy and homogeneity. Within the simplified model GPT [11], the four-body interaction oscillates with respect to angles between atoms, with a nearly zero mean, so it does not contribute to v^{eff}. The third-order contribution to v_3 also averages away, but the fourth order contributions to v_2 survive, yielding a short-ranged repulsive term proportional to $\Delta_{dd'}^2$ balancing against the attractive second order term in v_2.

Inspired by the short-ranged repulsion found in equation. (3) and the power law variation of $\Delta_{dd'}$ within the model GPT [18], we propose to modify the full GPT pair potentials $v_2^{\alpha\beta}$ by adding terms of the form

$$U^{\alpha\beta}(r) = a(r_0/r)^b \tag{4}$$

where a and b are positive and depend upon the elements α and β of pair potential modified. The value r_0 is a common atomic separation in quasicrystals of 2.55 Å. Then the effective pair potential is written as

$$V^{\alpha\beta}(r) = v_2^{\alpha\beta}(r) + U^{\alpha\beta}(r). \tag{5}$$

We determine the unknowns a and b by matching binding energies and forces obtained from full ab-initio calculations on a quasicrystal approximant. Cockayne and Widom [19,20] suggested a structure for decagonal AlCoCu. An approximant of that structure is shown in fig 3 with Ni atoms replacing Cu. The orthorhombic unit cell (a=23.3 Å, b=7.57 Å, c=4.09 Å) contains 50 atoms ($Al_{34}Co_{10}Ni_6$). Most atoms occupy either z=0.25 or z=0.75 layers. Al atoms at the centers of hexagons occupy the z=0.5 layer. Two Co atoms occupy symmetric positions around these central Al atoms. In AlCoCu, alternation of Co and Cu on tile edges is thought to be energetically advantageous [19]. We find that alternation of Co and Ni shown in Fig. 3 is slightly *dis*advantageous in AlCoNi.

To investigate TM bonding energetics, we alter the basic structure shown in Fig. 3 by swapping a Co atom on a horizontal tile edge (atom b in fig 3) with the Ni atom on the other horizontal tile edge (atom c). Focusing on near-neighbor interactions, we find this swap of atoms replaces 4 CoNi bonds with 2 CoCo and 2 NiNi bonds, all of length = 2.55 Å. These numbers are twice as large as is apparent by inspection of Fig. 3, the extra factor of 2 coming from periodic boundary conditions in the direction perpendicular to the plane.

Now consider the energy change evaluated using pair potentials. Atoms b and c occupy nearly equivalent sites. An exact symmetry in the Al atom positions guarantees that no bond involving an Al atom is affected by the swap. We already noted the change in TM near-neighbor interactions. At further neighbors, with separations of 4.6 Å or greater, we also find interchanges between CoCo and NiNi bonds for pairs of CoNi bonds. If the approximate form (2) of v_2^{CoNi} as the average of v_2^{CoCo} and v_2^{NiNi} were valid, all changes in bonding would exactly cancel each other, resulting in a vanishing energy change. We presume that approximation (2) is more accurate at large separations than small separations. Thus we attribute the entire energy change of the bc swap to near neighbor binding energy differences

$$\Delta E_1 = 2V^{CoCo} + 2V^{NiNi} - 4V^{CoNi} \tag{6}$$

where $V^{\alpha\beta}$ denotes the strength of the pair potential evaluated at the near-neighbor distance 2.55 Å.

Next we swap one of the Co atoms inside the tiles (atom e) with one of the Ni on a horizontal tile edge (atom a). Two CoNi bonds are broken and two CoCo bonds are produced after this swap. All other interactions that are affected are Al-TM interactions, which we presume to be described accurately by the GPT pair potentials. This swap energy can be written as:

$$\Delta E_2 = 2V^{CoCo} - 2V^{CoNi} + V^{AlTM} \tag{7}$$

where V^{AlTM} represents a calculable collection of interactions between Al atoms and TM atoms at many separations. V^{AlTM} should be described accurately by the unmodified GPT pair potentials.

Lastly, we replace the Co-Ni pair on one horizontal tile edge (atoms c and d) with Al atoms. Then we swap one of the newly introduced Al (at position c) with a Ni atom on the other horizontal tile edge (atom a). This breaks two CoNi bonds. All other interactions are either Al-TM or Al-Al interactions, and again those are described well within the GPT. The energy change of this swap is

$$\Delta E_3 = -2V^{CoNi} + V^{AlTM} + V^{AlAl} \tag{8}$$

where V^{AlAl} and V^{AlTM} represent collections of interactions involving Al atoms that, as before, we presume to be accurately calculable within the unmodified GPT.

Full ab-initio values for the energy changes ΔE_1, ΔE_2 and ΔE_3 were calculated using VASP [21]. VASP calculates total energies within the local density approximation using pseudopotentials to treat valence-core electron interactions. We performed calculations using a 4x4x4 k-space grid and also using a 4x4x8 k-space grid to observe the convergence as k-points are added. All calculations were done using medium precision which expected to be sufficient for out needs. We iterate the self-consistent calculation until an accuracy of 10^{-6} eV is achieved.

By comparing the energy differences ΔE_1, ΔE_2 and ΔE_3 calculated by VASP with the same quantities calculated with the unmodified GPT potentials, we can obtain the values of $U^{\alpha\beta}$ evaluated at the near neighbor separation 2.55 Å. Specifically, when energy changes calculated by unmodified GPT are subtracted from energy changes calculated by VASP, assuming that the contributions V^{AlAl} and V^{AlTM} are accurately calculated with the unmodified GPT, we find

$$\begin{aligned} \Delta E_1^{VASP} - \Delta E_1^{GPT} &= 2U^{CoCo} + 2U^{NiNi} - 4U^{CoNi} \\ \Delta E_2^{VASP} - \Delta E_2^{GPT} &= 2U^{CoCo} - 2U^{NiNi} \end{aligned} \tag{9}$$

$$\Delta E_3^{VASP} - \Delta E_3^{GPT} = -2U^{CoNi}.$$

Since each correction $U^{\alpha\beta}(r)$ involves two unknowns, a and b, equation (9) consists of three equations in six unknowns. Additional information is obtained from the forces on atoms calculated by VASP. By examining the forces on the Co-Ni pair (atoms c and d) in Fig. 3, and on the Co-Co and Ni-Ni pairs created by the bc swap, we obtain three additional equations governing the derivatives of $U^{\alpha\beta}$ at the near-neighbor separation. This additional information allows closure of the equations and determination of the unknowns.

IV. RESULTS

Table I shows the energy differences ΔE_i in equations 6-8 calculated using GPT pair potentials and VASP. Comparing the VASP data for the two grid sizes, we note that the signs and approximate magnitudes of ΔE_i are consistent with each other. One immediate result from table I is that mixed Co-Ni bonds are disfavored over pure Co-Co and Ni-Ni bonds. The energy difference ΔE_1 results from breaking 4 CoNi bonds and producing 2 CoCo and 2 NiNi bonds. ΔE_1 calculated by VASP is negative, showing that the swap lowers the system energy. This means that for AlCoNi, similar TM atoms prefer to reside near each other on the tile edges. Cockayne and Widom found the opposite for the case of AlCuCo using mock ternary potentials [19], and this was confirmed later using a full ab-initio technique [20].

Also concerning the calculated values of ΔE_1, we see that the averaged potential approximation (2) is fairly accurate. GPT yields $\Delta E_1 = 0$ because it employs this approximation. The small value of ΔE_1 obtained by VASP confirms that this approximation is not far off the mark.

Fig. 4 shows the x-component of the total force on certain TM atoms. Our (4x4x4) and (4x4x8) VASP calculations yield forces that agree to 0.06 eV/Å or better. We examine the horizontal bonds ab and cd in Fig. 3 in both the original and swapped configurations.

As expected, at 2.55 Å, GPT pair potentials predict attractive forces between TM pairs while the actual forces obtained from VASP are repulsive. The small force asymmetry on atoms in the CoNi pair is due to the different ways Co and Ni atoms interact with their surrounding environments. The difference between the forces calculated by our two methods is greatest for Co-Co bonds and smallest for Ni-Ni bonds, consistent with our expectation that overbinding is more severe for Co than for Ni.

Calculated corrections to the GPT pair potentials are given in table II. Examining the magnitude of $U^{\alpha\beta}$ at r=2.55 Å (i.e. the value of a), we note that U^{NiNi} is smaller than U^{CoCo}, as is expected since Ni is closer to a noble transition metal structure, with its d-band almost full. It should be noted that r=2.55 Å is not the potential minimum. It is the nearest neighbor distance that the calculations were performed at. $V^{\alpha\beta}$ and $F^{\alpha\beta}$ are, respectively, the binding energy and force of the modified GPT (eq.(5)) at the near neighbor distance. The large powers of inverse length we obtain show that our modifications of the GPT pair potentials fall off rapidly beyond the near-neighbor separation. The modified potentials are illustrated in fig. 5. The (4x4x4) and (4x4x8) VASP calculations agree in positions of the potential minima to about 0.05 Å and agree in the values at the minima to about 0.02 eV.

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TABLES

TABLE I. Total energy differences defined by equations (6)-(8) as calculated by VASP and GPT. Units are eV/cell.

Energy	GPT	VASP (4x4x4)	VASP (4x4x8)
ΔE_1	0.000	-0.020	-0.031
ΔE_2	0.116	0.298	0.279
ΔE_3	-0.945	-1.384	-1.419

TABLE II. Modifications for GPT potentials, $U^{\alpha\beta}(r) = a(\frac{r_0}{r})^b$ where r_0=2.55 Å. Units of a and $V^{\alpha\beta}$ are eV while b is dimensionless and $F^{\alpha\beta}$ has units of ev/Å.

$\alpha\beta$	a	b	$V^{\alpha\beta}$	$F^{\alpha\beta}$
CoCo	0.319	16.6	0.0946	0.978
CoNi	0.237	19.3	0.0941	0.994
NiNi	0.140	21.3	0.0779	0.674

FIGURES

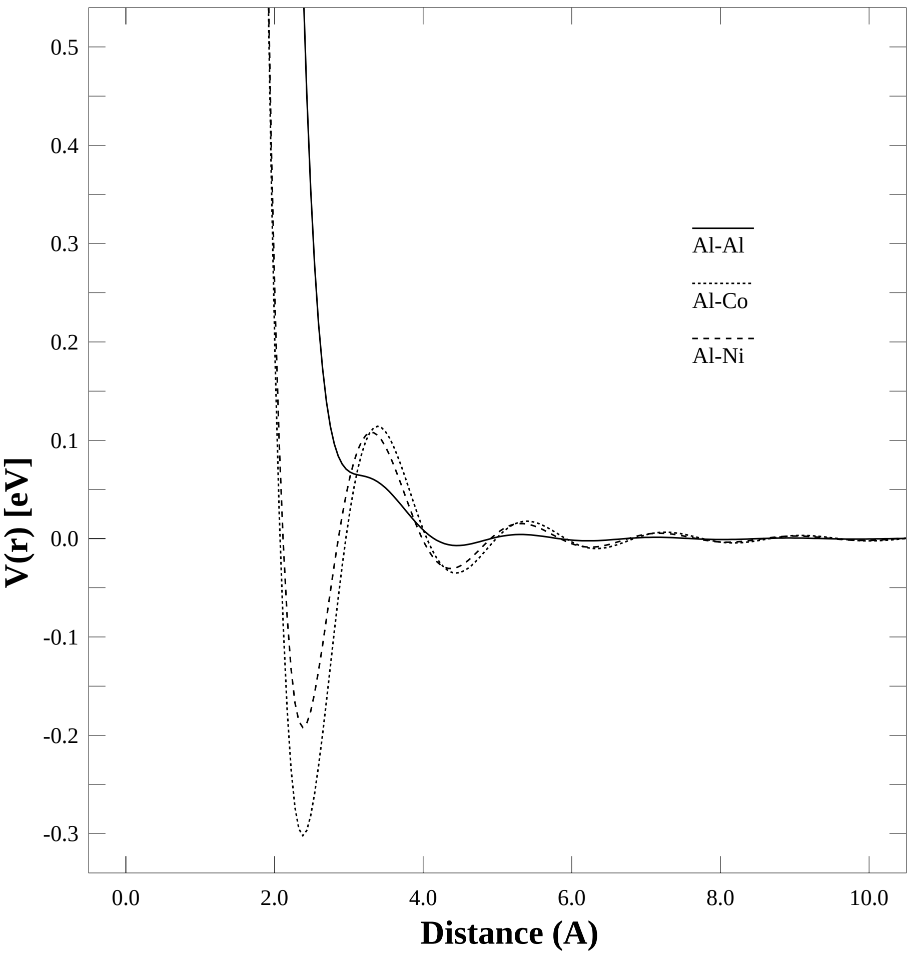

FIG. 1. GPT interatomic pair potentials for Al-Al, Al-Co and Al-Ni.

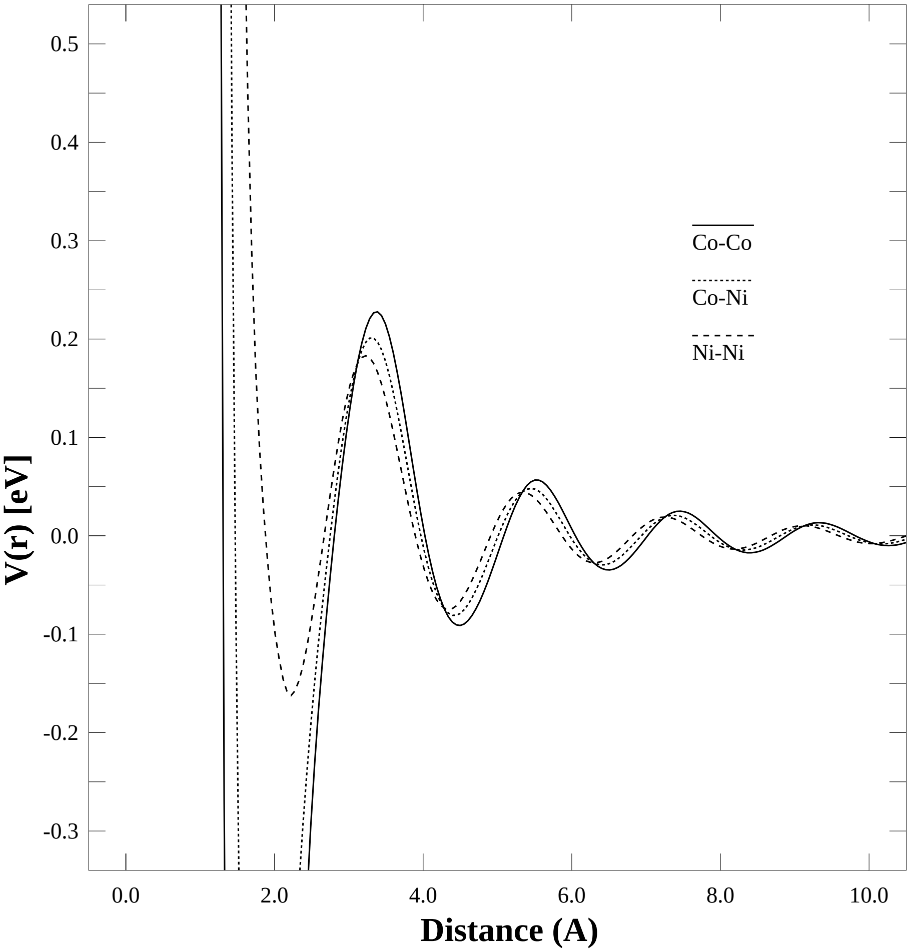

FIG. 2. GPT interatomic pair potentials for Co-Co, Co-Ni and Ni-Ni.

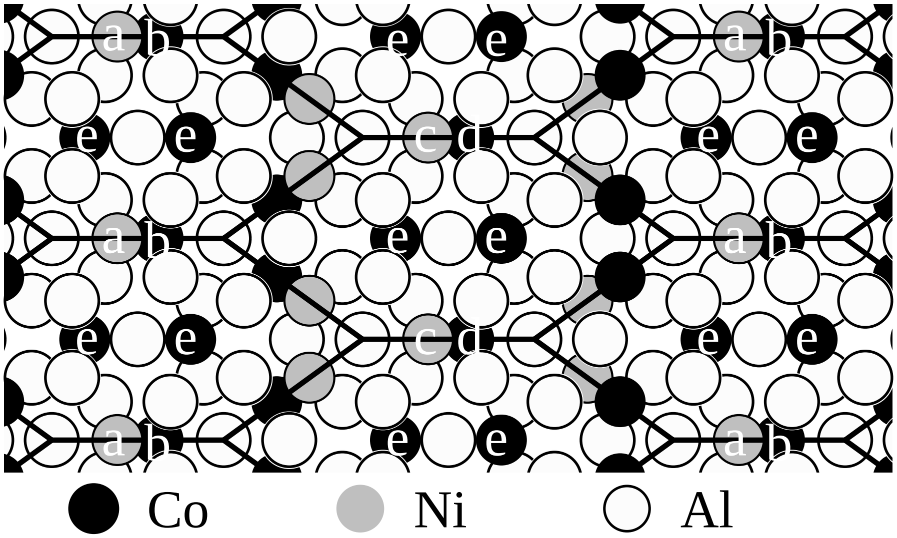

FIG. 3. The initial structure used in our calculations. Labeled atoms participate in swaps.

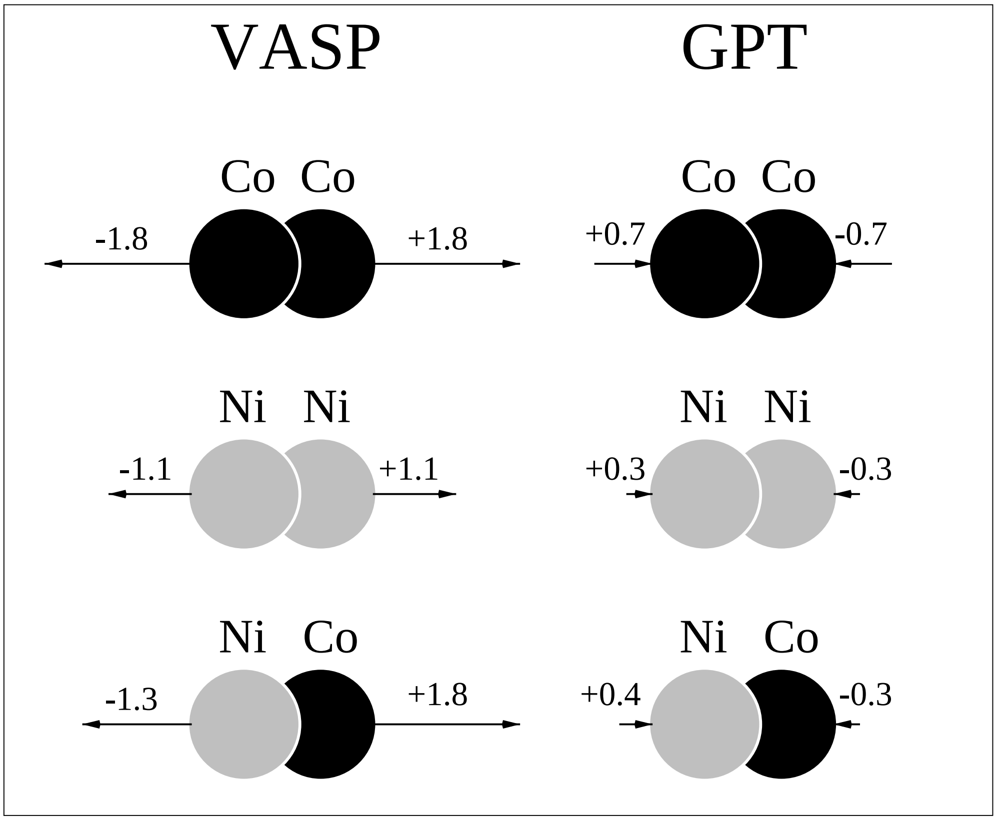

FIG. 4. Horizontal components of forces on transition metal atom pairs calculated from the GPT and VASP.

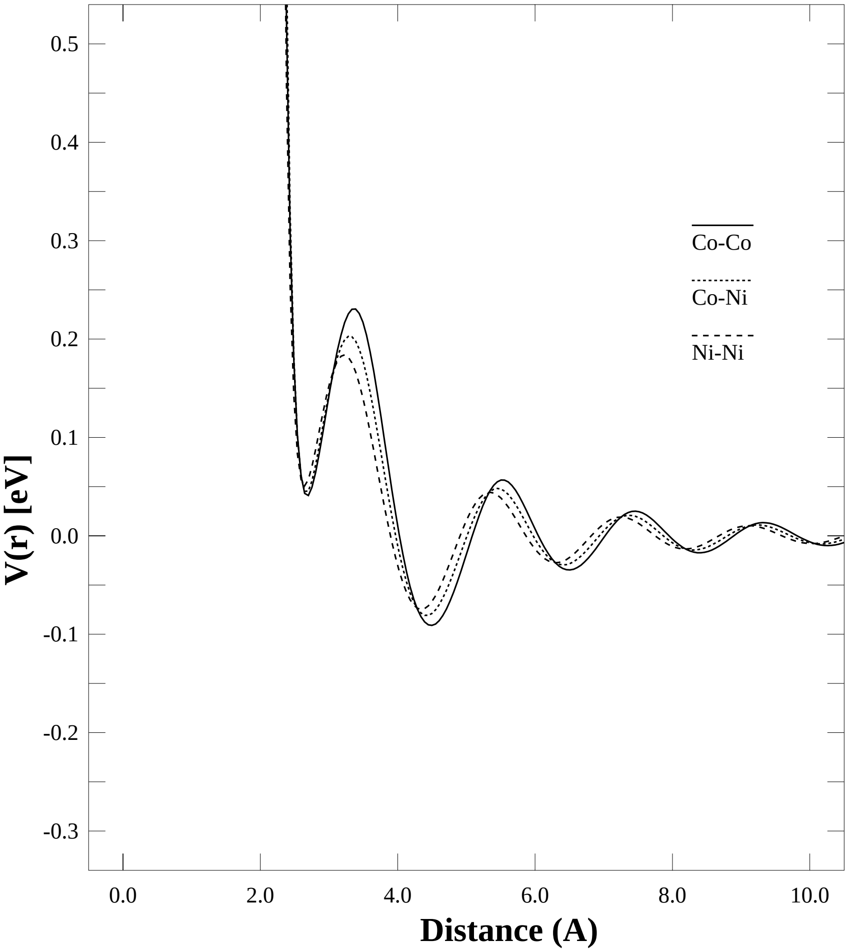

FIG. 5. Modified transition metal pair potentials using the parameters in table II.