Transition-metal interactions in aluminum-rich intermetallics

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Abstract

The extension of the first-principles 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 in the absence of balancing many-body contributions. Even with this limitation, the GPT pair potentials have been used effectively in total-energy calculations for Al-TM systems with TM atoms at separations greater than 4 Å. An additional potential term may be added for systems with shorter TM atom separations, formally folding repulsive contributions of the three- and higher-body interactions into the pair potentials, result-

ing in structure-dependent TM-TM potentials. Towards this end, we have performed numerical *ab-initio* total-energy calculations using VASP (Vienna *Ab Initio* Simulation Package) for an Al-Co-Ni compound in a particular quasicrystalline approximant structure. The results allow us to fit a short-ranged, many-body correction of the form $a(r_0/r)^b$ to the GPT pair potentials for Co-Co, Co-Ni, and Ni-Ni interactions.

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, however. Theoretically, one must solve the Schrödinger equation simultaneously for all electrons in the presence of fixed atomic nuclei. Density-functional theory (DFT) [3,4] simplifies this problem by reducing it to the self-consistent solution of Schrödinger's equation for a single electron in a potential that depends upon the electron density. Even with this simplification, full *ab-initio* DFT electronic-structure methods are computationally demanding [5], 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 total energy in terms of pair and many-body interatomic potentials [1,2,6–8], 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* electronic-structure approach.

Many metallic systems been studied using such quantum-based interatomic potentials, including aluminum and its alloys with both transition and non-transition metals [9–14]. These potentials are especially simple in the case of non-transition metals. There, the d-electron energy bands are either empty or else are completely filled and deeply buried below the Fermi energy level, allowing rapidly convergent expansions of the total energy and an accurate description in terms of only radial-force interactions [15]. The presence of partially filled d-bands at or near the Fermi level in transition metals complicates the analysis. The occupied d-band electronic states are highly localized in the vicinity of the atoms, leading to directional or covalent bonding with a strong angular dependence. Consequently, total-energy expansions will not converge as quickly as for non-transitions metals, and three- and higher-body angular-force interactions may contribute significantly [2,6,16,17].

Moriarty [17] has developed a rigorous DFT treatment of interatomic potentials for transition metals (TMs) 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 [14]. These studies found that three- and four-body interactions could be important in determining thermodynamic and mechanical stability of structures with large TM concentrations. The explicit treatment of d-electron interactions in the GPT produces a strong attractive interaction at unphysically short distances in the pair potentials, which is balanced by repulsive forces contained in the many-body interactions. For specific structural environments, however, it is possible to directly modify the short-ranged part of the TM-TM 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. Here we wish to consider the construction of such effective pair potentials for important transition-metal aluminide systems.

One motivation for this study is the need for fast total-energy calculations in Al-TM systems with short TM-TM separations to enable structural relaxation, and more generally, molecular-dynamics and Monte-Carlo simulations. We focus our attention on Al-Co-Ni compounds in decagonal quasicrystalline structures [18]. The precise modifications required in the Co-Co, Co-Ni, and Ni-Ni pair potentials depend on the particular structure studied, but they 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 [19] because the Cu-Cu interactions do not appear to require modification [14]. Limited numbers of *ab-initio* electronic-structure calculations, which effectively sum the pair and many-body total-energy contributions, are sufficient to determine the required modifications, and this is the strategy that we follow here.

We intend to apply these potentials to predict the structures of decagonal quasicrystals [20]. 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 [21].

The effective pair potentials developed here can be applied to total energy calculations in quasicrystals and related structures with a great reduction in computational times compared with the *ab initio* electronic-structure calculations themselves. The time savings results from two general features of the potentials. First, for a given atomic volume and composition the potentials 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 finite spatial separation, the time required to calculate the change in total energy becomes independent of the number of atoms in the complete structure. This is so-called order-N scaling. In contrast, *ab-initio* electronic-structure methods must recalculate the entire system when a single atom is moved, typically resulting in order-N^3 scaling.

In Sec. II, GPT interatomic potentials are briefly reviewed and the issues surrounding the truncation of the total energy expansion at the pair-potential level in Al-TM systems are discussed. Section III gives details about the scheme we employ to determine the needed modifications to the TM-TM pair potentials. In Sec. IV, we discuss the results of our full *ab-initio* electronic-structure calculations and the modified TM-TM pair potentials developed using them.

II. GPT INTERATOMIC POTENTIALS

The generalized pseudopotential theory starts with a full *ab-initio* DFT representation of the total energy in the standard local-density approximation (LDA). The usual small-core approximation is used to separate the treatment of valence and core electrons and the electron-ion interaction for the valence electrons is handled by means of optimized nonlocal pseudopotentials. A mixed valence-wavefunction basis is employed allowing *sp* states to be

represented as superpositions of plane waves, while d states are represented in terms of localized, atomic-like d states. The electron density and total energy are systematically expanded in terms of the resulting weak matrix elements in this basis: sp pseudopotential matrix elements $W_{kk'}$, sp-d hybridization matrix elements Δ_{kd} and S_{kd}, and d-d tight-binding-like matrix elements $\Delta_{dd'}$ and $S_{dd'}$. In real space, the total energy may be cast in terms of well-defined interatomic potentials, which can be calculated as functionals of these matrix elements. For a general multicomponent alloy, the GPT total-energy expansion takes the form

$$E_{\rm tot}(\vec{R}_i) = NE_{\rm vol}(\Omega, \mathbf{c}) + \frac{1}{2}\sum_{\alpha\beta}{\sum_{ij}}' v_2^{\alpha\beta}(R_{ij};\Omega,\mathbf{c}) + \frac{1}{6}\sum_{\alpha\beta\gamma}{\sum_{ijk}}' v_3^{\alpha\beta\gamma}(R_{ij},R_{jk},R_{ki};\Omega,\mathbf{c}) + \cdots \ , \tag{1}$$

where $\vec{R}$ is the set of all positions of N ions in the metal, $E_{\rm vol}$ is a volume term that includes all collective and one-ion contributions that are independent of structure, and $v_2^{\alpha\beta}$, $v_3^{\alpha\beta\gamma}, \ldots$ are the two-, three-, and higher many-ion interatomic potentials. The primes on sums over ion positions exclude all self-interaction terms. Indices $\alpha, \beta, \gamma, \ldots$ run over all chemical species, and indices $i, j, k, \ldots$ run over the individual ion positions. The volume term and all of the interatomic potentials depend on the atomic volume Ω and a composition vector $\mathbf{c}$, but are independent of structure. The potentials are functions of the relative positions of small subsets of atoms, independent of the positions of all other atoms in the system. The entire dependence on the structure comes analytically through the summations over ion positions. This makes these potentials transferable among different structures at fixed atomic volume and composition. The full details of the first-principles GPT for transition-metal systems are given in Refs. [17] and [14]. A simplified model version of the theory has also been developed [22], using canonical d-bands to obtain analytic representations of the multi-ion potentials.

In general, the separation of the total energy into two- and higher-body terms is not entirely unique, since one can always add contributions to the pair potential $v_2^{\alpha\beta}$ provided one makes suitable subtractions from $v_3^{\alpha\beta\gamma}$ and/or higher-body potentials. Within the GPT,

the uniqueness of the potentials is established by ensuring that their desired properties of structure independence and full transferability are consistent with the matrix elements that define them. In this regard, the total energy is normally calculated to second order in the pseudopotential $W_{kk'}$, so that *sp* contributions enter only in the volume term and the pair potentials. The TM *d*-*d* and *sp*-*d* contributions to each potential, on the other hand, are carried to all orders in the matrix elements $\Delta_{dd'}$, etc. Terms are allocated to pair- and many-body potentials according to how many distinct ionic positions explicitly enter. Thus, for example, the TM pair potentials v_2^{TM-TM} contain contributions that are even powers of $\Delta_{dd'}$ associated with repeated hopping of d electrons back and forth between a pair of ions, with the leading term proportional to $\Delta_{dd'}\Delta_{d'd}$. The three-ion TM potentials contain corresponding terms of third order proportional to $\Delta_{dd'}\Delta_{d'd''}\Delta_{d''d}$ and terms of fourth order proportional to $\Delta_{dd'}^2\Delta_{d'd''}^2$, as well as higher-order terms. The four-ion TM potentials start at fourth order in $\Delta_{dd'}$.

The tight-binding-like *d*-*d* contributions to the TM potentials are modulated by *sp*-*d* hybridization, *d*-state nonorthogonality, and other factors such as *d*-band filling, but nonetheless, they give valuable insight into the expected short-range behavior of the potentials. In particular, one expects a strong attractive contribution to v_2^{TM-TM} at short distances resulting from the second-order term in $\Delta_{dd'}$. This term is attractive because it directly relates to the second moment of the *d*-band density of states and hence to the *d*-band width and the additional cohesion provided by partial *d*-band filling. The attraction is strong at short distances because the matrix element for atoms separated by distance r varies roughly as r^{-5}, the behavior obtained for pure canonical d bands. In addition, one expects this attractive contribution to be maximum near half-filling of the d bands and to vanish for completely filled or empty d bands. Thus the expected overbinding in v_2^{TM-TM} will show a clear chemical dependence, with decreasing magnitudes for Co-Co, Co-Ni, and Ni-Ni interactions.

For short-range TM interactions, repulsive contributions from higher-order terms in $\Delta_{dd'}$ will balance the attractive contribution of the second-order term in v_2^{TM-TM}, provided that the local concentration of TM atoms is sufficiently high. In general, the detailed balance

obtained involves the three-, four-, and possibly higher-ion potentials. Near half-filling of the d bands, however, the repulsive contributions will be dominated by the fourth-order terms in $v_3^{TM-TM-TM}$. This in turn suggests a simple scheme to modify the TM pair potentials at short range to incorporate the balance directly, a scheme that we will develop in Sec. III. First, however, we examine the actual calculated GPT pair potentials for the Al-Co-Ni system of interest here.

Figure 1 shows the Al-Al and Al-TM pair potentials for Al-Co-Ni [14]. 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. As expected, the TM overbinding is most evident for Co. The first minimum in the Co-Co potential has a depth of 2.1 eV at 1.7 Å. The corresponding Ni-Ni potential depth of 0.1 eV at 2.2 Å is not obviously problematic, but in the following we will find it requires some modification. In the present applications, 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 effective pair 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 [14], so no modification of v_2^{CuCu} is suggested. Our modification to v_2^{CoCo} obtained for Al-Co-Ni compounds may be approximately valid for these other compounds. We previously defined [14] 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 Al-Co-Cu and Al-Co-Ni potentials so-obtained will, of

course, still need to be validated using full *ab-initio* calculations.

III. MODIFICATION OF PAIR POTENTIALS

As discussed above, the 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" into effective pair potentials. Formally, one may define an effective pair potential by averaging over atomic positions, holding a single pair of ions fixed:

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

Such potentials have been previously considered in the context of the simplified model GPT [22] and canonical d bands for central transition metals. There it was found that the four-body interaction oscillates with respect to angles between atoms, with a nearly zero mean, so it does not contribute significantly to v_2^{eff}. The third-order contribution to $v_3^{\alpha\beta\gamma}$ also approximately averages away, but the fourth-order contribution to $v_3^{\alpha\beta\gamma}$ contributes strongly, yielding a short-ranged repulsive term proportional to $\Delta_{dd'}^2 \Delta_{d'd}^2 \sim r^{-20}$ balancing against the attractive second-order term in $v_2^{\alpha\beta}$.

Inspired by the short-ranged repulsion found in Eq. (3) and the power law variation of $\Delta_{dd'}$ within the model GPT [22], 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 the pair potential modified. Our expectation, which is confirmed below, is that b is large in all cases, so that $U^{\alpha\beta}$ is indeed short-ranged. In our applications, the quantity r_0 is taken as a common atomic separation in quasicrystals of 2.55 Å. Then at a fixed atomic volume and composition the effective pair potential can be 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 energies and forces obtained from full *ab initio* electronic-structure calculations on a quasicrystal approximant. Cockayne and Widom [23,24] previously suggested a structure for decagonal Al-Co-Cu. 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 Al-Co-Cu, alternation of Co and Cu on tile edges is thought to be energetically advantageous [23]. We find that alternation of Co and Ni shown in Fig. 3 is slightly *dis*advantageous in Al-Co-Ni.

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 four Co-Ni bonds with two Co-Co and two Ni-Ni 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 two 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 Co-Co and Ni-Ni bonds for pairs of Co-Ni 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 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 Co-Ni bonds are broken and two Co-Co 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 Co-Ni 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 (Vienna *Ab Initio* Simulation Package) [25]. 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 is expected to be sufficient for our 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 the 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

$$\begin{aligned} \Delta E_1^{VASP} - \Delta E_1^{GPT} &= 2U^{CoCo} + 2U^{NiNi} - 4U^{CoNi} \\ \Delta E_2^{VASP} - \Delta E_2^{GPT} &= 2U^{CoCo} - 2U^{NiNi} \\ \Delta E_3^{VASP} - \Delta E_3^{GPT} &= -2U^{CoNi} \ . \end{aligned} \tag{9}$$

Since each correction $U^{\alpha\beta}(r)$ involves two unknowns, a and b, Eq. (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 Eqs. (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 four Co-Ni bonds and producing two Co-Co and two Ni-Ni bonds. ΔE_1 calculated by VASP is negative, showing that the swap lowers the system energy. This means that for Al-Co-Ni, similar TM atoms prefer to reside near each other on the tile edges. Cockayne and Widom found the opposite for the case of Al-Cu-Co using mock ternary potentials [23], and this was confirmed later using a

full *ab-initio* technique [24].

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 here. The small value of ΔE_1 obtained by VASP confirms that this approximation is not far off the mark.

Figure 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 Co-Ni 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 modifications to the GPT pair potentials are given in Table II. Examining the magnitude of $U^{\alpha\beta}$ at r=r_0=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 the end of the $3d$ transition series, with its d-bands almost full. It should be noted that r=2.55 Å is not the potential minimum. It is rather the nearest-neighbor distance at which the calculations were performed. The quantities $V^{\alpha\beta}$ and $F^{\alpha\beta}$ are, respectively, the energy and force calculated from the modified GPT potentials [Eq.(5)] at the near-neighbor distance r_0. The large values of b we obtain show that our modifications of the GPT pair potentials fall off rapidly beyond the near-neighbor separation and confirm our expectations based on Eq. (3). 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.

V. DISCUSSION

The original GPT interatomic potentials were derived from first principles without reference to specific structures. Their applicability to, and transferability among, a broad range of structures was verified [14]. The pair potentials alone apply to Al-rich structures in which TM atoms are well separated, but fail due to an unphysical short-ranged TM attraction. Our modification of the GPT potentials is restricted to TM pair potentials. Since the correction $U^{\alpha\beta}(r)$ is negligible beyond 3 Å, our corrections only affect energies and forces among neighboring TM atoms.

In idealized decagonal AlNiCo and AlCuCo quasicrystal models, neighboring TM atoms always occur in specific atomic environments consisting of zig-zag chains of TM atoms at 2.5 Å spacing surrounded by Al atoms at special positions [20,23,24]. A variety of quasicrystal and approximant structures differ in the arrangement of these chains in space, but share the same local structure around the TM atoms. Our modified GPT potentials are therefore strictly transferable within this class of quasicrystal structures.

While the modified GPT potentials are not strictly transferable outside this special class of structures, we do believe they are qualitatively transferable. Comparing figures 2 and 5, we have replaced obviously unphysical pair potentials with a set that appears qualitatively realistic. Both original and modified pair potentials are transferable among structures without TM neighbors. The modified pair potentials provide a reasonable, though non-rigorous, extension to structures with TM neighbors.

As a test of our modified pair potentials, we relaxed the basic structure using both original and modified GPT pair potentials, and using VASP. In all three runs we relaxed the structure until all atomic forces were less than 0.001 eV/Å. Under VASP relaxation (4× 4×4 k-space grid), Al atoms moved 0.19 Å on average, followed by Ni with an average displacement of 0.16 Å and Co with an average displacement of 0.15 Å. Relaxation under the modified GPT potentials produced a structure close to the VASP relaxed structure. The differences between modified GPT and VASP relaxed positions are less than 0.07 Å for

every TM atom, with an average difference of 0.05 Å/TM atom. In contrast, relaxation under the original GPT pair potentials yielded a maximum TM relaxed position difference of 0.20 Å and an average TM difference of 0.13 Å.

As a result of our modifications, the TM atoms relax in the correct directions and move approximately the correct distances. This is not the case using the original GPT potentials. Since TM separations move away from r_0 under relaxation, our proper behavior under relaxation demonstrates a type of transferability of the potentials.

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REFERENCES

[1] J. Hafner, *From Hamiltonians to Phase Diagrams* (Springer-Verlag, Berlin Heidelberg, 1987).

[2] D. G. Pettifor, *Bonding and Structure of Molecules and Solids* (Clarendon Press, Oxford, 1995).

[3] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[4] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[5] *Ab-initio* studies of Al-rich intermetallics include: M. Windisch, M. Krajci and J. Hafner, J. Phys: Condens. Matter **6**, 6977 (1994); G. Trambly de Laissardiere and T. Fujiwara, Phys. Rev. B **50**, 9843 (1994); G. Trambly de Laissardiere, D. Nguyen Manh, L. Magaud, J. P. Julien, F. Cyrot-Lackmann and D. Mayou, Phys. Rev. B **52**, 7920 (1995); R. F. Sabiryanov, S. K. Bose and S. E. Burkov, J. Phys: Condens. Matter **7** 5437 (1995); M. Krajci, J. Hafner and M. Mihalkovic, Phys. Rev. B **56** 3072 (1997);

[6] A. E. Carlsson, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich and D. Trunbull (Academic, New York, 1990), Vol 43, p.1.

[7] I. McC. Torrens, *Interatomic Potentials* (Academic, New York, 1972).

[8] A large collection of interatomic-force applications in condensed matter physics can be found in Phil. Mag. A **58** No. 1 (1988).

[9] J. A. Moriarty and A. K. McMahan, Phys. Rev. Lett. **48**, 809 (1982); A. K. McMahan and J. A. Moriarty, Phys. Rev. B **27**, 3235 (1983).

[10] M. Krajci and J. Hafner, Phys. Rev. B **46**, 10669 (1992)

[11] R. Phillips, J. Zou, A. E. Carlsson, and M. Widom, Phys. Rev. B **49**, 9322 (1994).

[12] M. Windisch, J. Hafner, M. Krajci and M. Mihalkovic, Phys. Rev. B **49**, 8701 (1994)

[13] M. Mihalkovic, W.-J. Zhu, C. L. Henley, and R. Phillips, Phys. Rev. B **53**, 9021 (1996).

[14] J. A. Moriarty and M. Widom, Phys. Rev. B **56**, 7905 (1997); M. Widom and J. A. Moriarty, Phys. Rev. B **58**, 8967 (1998); M. Widom, I. Al-Lehyani and J. A. Moriarty, Phys. Rev. B **62**, 3648 (2000).

[15] J. A. Moriarty, Phys. Rev. B **26**, 1754 (1982).

[16] M. W. Finnis, A. T. Paxton, D. G. Pettifor, A. P. Sutton and Y. Ohta, Philos. Mag. A **58**, 143 (1988).

[17] J. A. Moriarty, Phys. Rev. B **38**, 3199 (1988).

[18] A.-P. Tsai, A. Inoue and T. Masumoto, Mat. Trans. JIM **30**, 463 (1989).

[19] L. X. He, Y. K. Wu and K. H. Kuo, J. Mat. Sci. Lett. **7**, 1284 (1988); A.-P. Tsai, A. Inoue and T. Masumoto, Mat. Trans. JIM **30**, 300 (1989).

[20] M. Mihalkovic, I. Al-Lehyani, Y. Wang, M. Widom, N. Moghadam, J. A. Moriarty, C. L. Henley, and E. Cockayne, in preparation.

[21] *X-ray structure determination; a practical guide* , G. H. Stout, L. H. Jensen. p 370 (Wiley, New York, 1989).

[22] J. A. Moriarty, Phys. Rev. B **42**, 1609 (1990) and **49**, 12431 (1994).

[23] E. Cockayne and M. Widom, Phys. Rev. Lett. **81**, 598 (1998).

[24] M. Widom, I. Al-Lehyani, Y. Wang and E. Cockayne, Mat. Sci. Eng. A, to appear (2000).

[25] G. Kresse and J. Hafner, Phys. Rev. B **47**, RC558 (1993); G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

TABLES

TABLE I. Total-energy differences defined by Eqs. (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 transition-metal pair potentials, $U^{\alpha\beta}(r) = a(r_0/r)^b$ where r_0=2.55 Å. The quantities $V^{\alpha\beta}$ and $F^{\alpha\beta}$ are the energy and force calculated at r=r_0 from the modified GPT potential, Eq. (5). 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

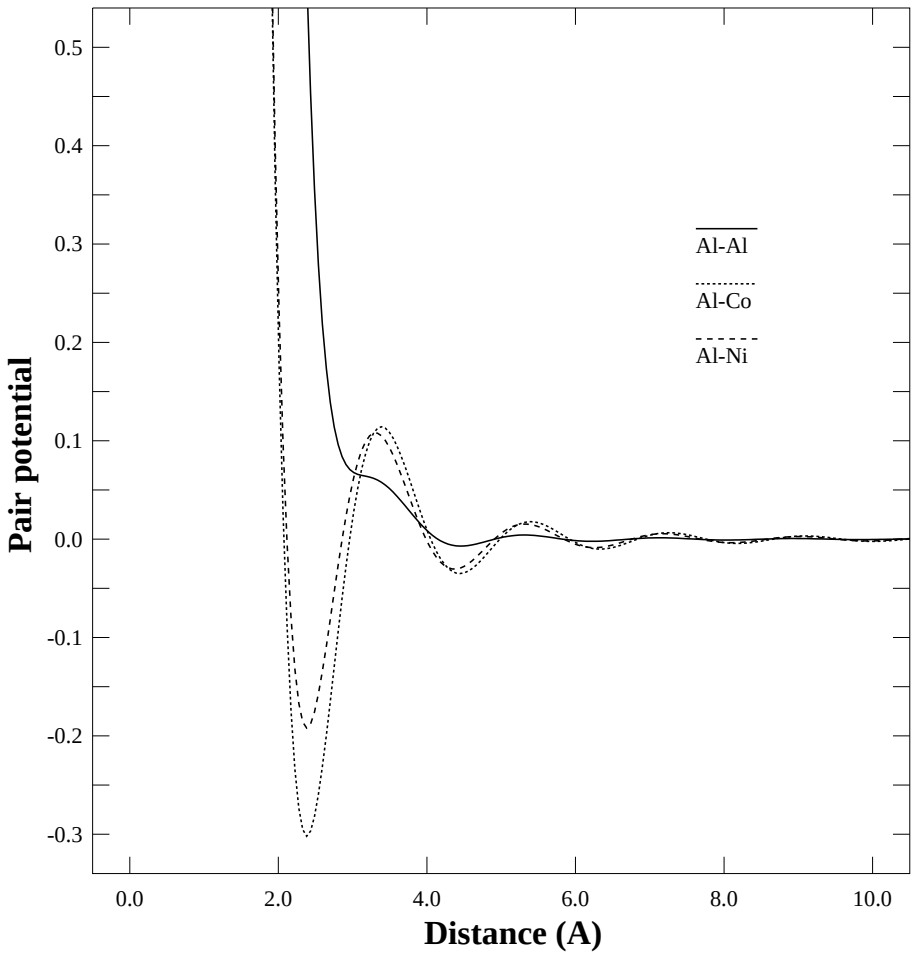

FIG. 1. GPT interatomic pair potentials for Al-Al, Al-Co and Al-Ni.

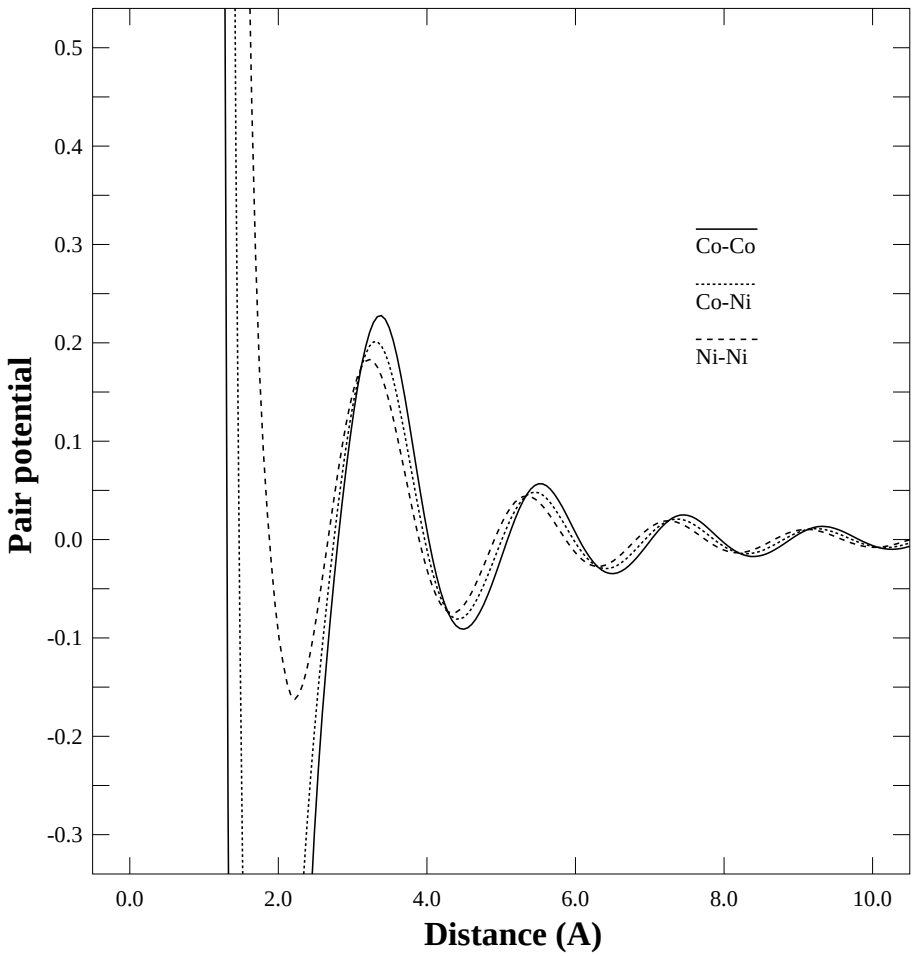

FIG. 2. GPT interatomic pair potentials for Co-Co, Co-Ni and Ni-Ni.

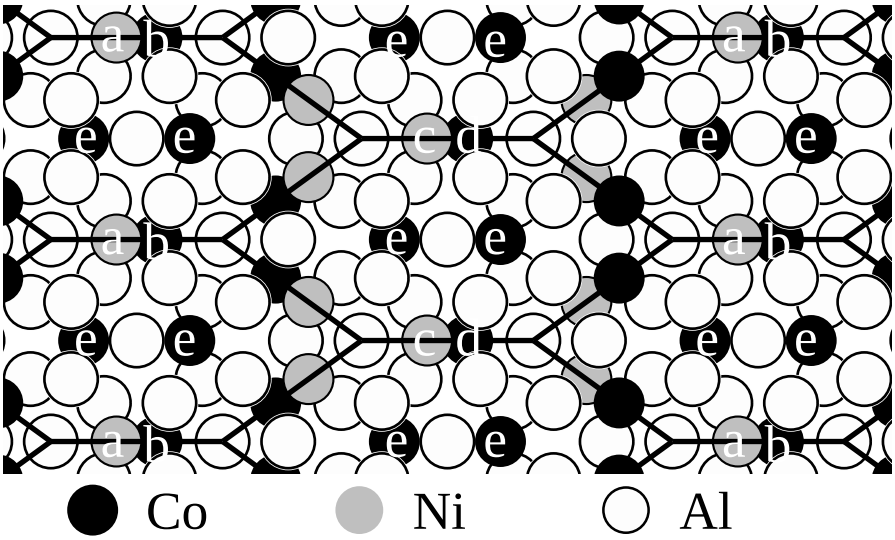

FIG. 3. The initial structure used in our calculations. Labeled atoms participate in swaps.

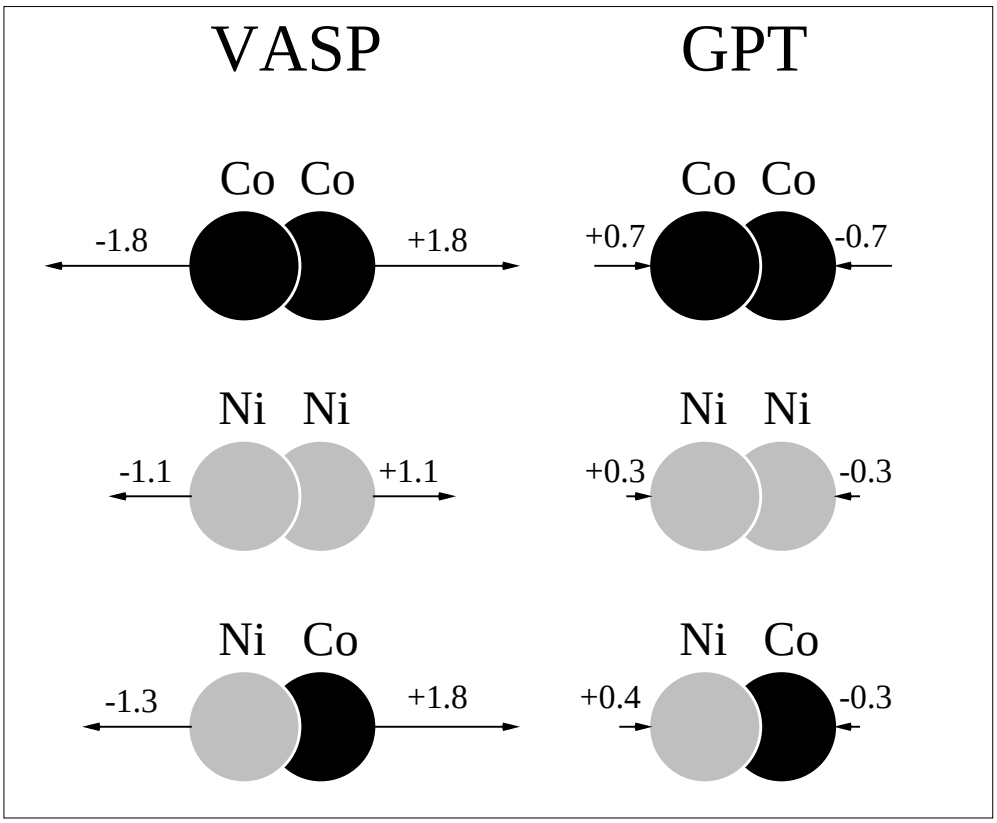

FIG. 4. Horizontal components of forces (in eV/Å) on transition metal atom pairs calculated from the GPT and VASP.

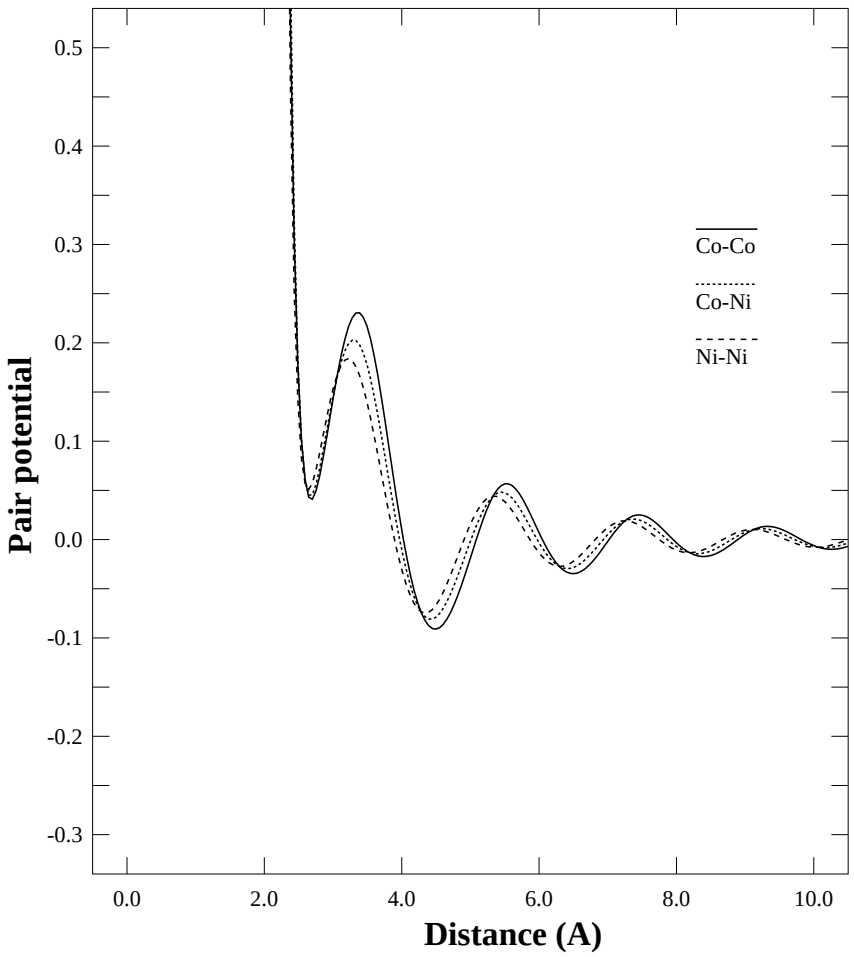

FIG. 5. Modified transition-metal GPT pair potentials using the parameters in Table II.