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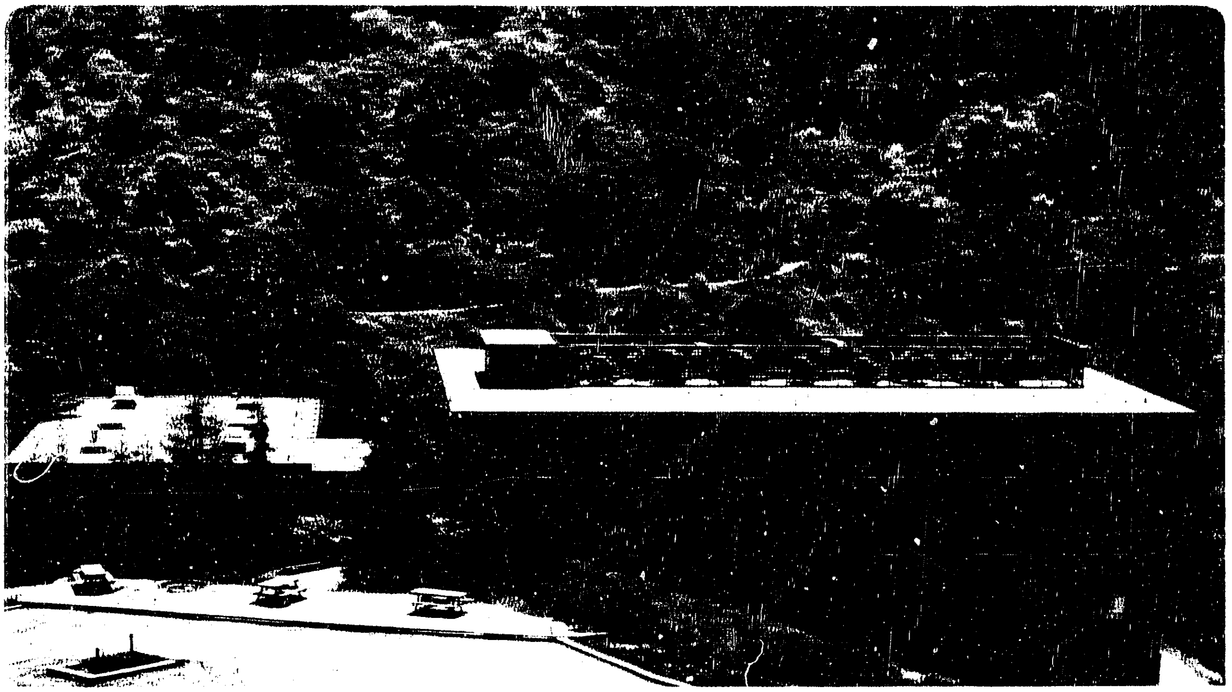

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GROUND STATE SEARCHES IN FCC INTERMETALLICS

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ABSTRACT

A cluster expansion is used to predict the fcc ground states, i.e., the stable phases at zero Kelvin as a function of composition, for alloy systems. The intermetallic structures are not assumed, but derived rigorously by minimizing the configurational energy subject to linear constraints. This ground state search includes pair and multiplet interactions which spatially extend to fourth nearest neighbor. A large number of these concentration-independent interactions are computed by the method of direct configurational averaging using a linearized-muffin-tin orbital Hamiltonian cast into tight binding form (TB-LMTO). The interactions, derived without the use of any adjustable or experimentally obtained parameters, are compared to those calculated via the generalized perturbation method extention of the coherent potential approximation within the context of a KKR Hamiltonian (KKR-CPA-GPM). Agreement with the KKR-CPA-GPM results is quite excellent, as is the comparison of the ground state results with the fcc-based portions of the experimentally-determined phase diagrams under consideration.

INTRODUCTION

The study of alloy phase stability is of utmost practical and technological importance. Recently, it has become possible, through several techniques, to perform first principles electronic structure calculations of ordered and disordered alloys. When a particular alloy system is studied theoretically, the first order of business is to solve the ground state problem. In other words, one first finds the minimum energy structures at all compositions and T=0K, and then performs non-zero temperature calculations using only these phases. A commonly used "method" for finding the ground states involves selecting several structures suspected of being the lowest energy states, calculating the energies of these structures, and then simply assuming that the true ground states are the ones in the set with the lowest calculated energies. This type of argument is, of course, not sound as it assumes what is to be proved. Thus, using this simple approach, it is quite likely that the true ground states of an alloy system will be missed.

Given an alloy system, finding the minimum energy structures with respect to all possible topological vatiations would, at best, be a Herculean task. Fortunately, however, the ground states of many alloys are superstructures of the fcc, bcc, or hcp lattices. The problem of determining the lowest energy superstructures of a given lattice (with respect to configurational variations) is one which, in favorable cases, may be solved exactly. It is precisely this type of ground state search which will be addressed in this paper.

The search is faciliatated by transposing the alloy problem onto an equivalent "Ising-like" problem. The energy may then be expanded exactly in cluster functions of Ising-spin-like variables [1-3]. The coefficients in the expansion are termed effective cluster interactions (ECI), and obviously play a critical role in the theoretical understanding of phase stability in alloys. Previously, phenomenological models were proposed to calculate the ECI's. However, there presently exist several methods of obtaining these composition-independent interactions from a first-principles approach [4-6]. In this paper, we use the method of direct configurational averaging (DCA) in conjunction with a linearized muffin-tin orbital Hamiltonian transformed into the tight-binding representation (TB-LMTO).

The idea of using cluster expansions to exactly solve the alloy ground state problem has been used in the past. These past searches have usually fallen into one of two classes: global searches, which solve for the ground states as a function of variations in the ECI's, and specific searches, where the ground states are determined for a given set of ECI's. Previous global searches on the fcc lattice have included either: 1) pair and multiplet interactions whose spatial extent is equal to or less than second nearest neighbor [7], or 2) pair interactions which extend through fourth nearest neighbor (or less), but with no multiplet interactions [8,9]. However, in many fcc-based alloys, it has been shown that both pair interactions up to fourth nearest neighbor (4NN) and multiplet interactions play a crucial role. The global searches are then, not applicable as they involve a much more limited set of interactions. Recently, a simple enumeration technique [10] has been proposed to perform a specific search including 4NN pairs and multiplets. This method is still incomplete, however, as many possible strucutres could have been missed. Thus, in this paper, we present for the first time, an exact ground state search on the fcc lattice including both pair and multiplet interactions which spatially extend through fourth nearest neighbor.

FORMALISM

Studying the configurational aspects of alloy energetics is greatly facilitated by modeling the alloy in a generalized "Ising-like" formalism. Each atom of the alloy is assumed to be located on a site of the given lattice. The atoms are each assigned a spin variable, σ_i, which is given the value +1 (-1) if an atom of type A (B) is located at site i. The entire configuration of the lattice of N sites may then be completely specified by the N-dimensional vector, $\sigma = (\sigma_1, \sigma_2, \ldots, \sigma_N)$. Sanchez, Ducastelle, and Gratias [1] then showed that any function of configuration could be expanded in terms of cluster functions. In particular, the energy is written

$$E = \sum_{\alpha} V_\alpha \sigma_\alpha \tag{1}$$

where the cluster functions, σ_α, are products of all the spin variables over a cluster α composed of n_α sites:

$$\sigma_\alpha = \langle \sigma_1 \sigma_2 \ldots \sigma_{n_\alpha} \rangle \tag{2}$$

and V_α represents the ECI for the cluster α. It is important to note that in this formalism, the ECI's are, by definition, concentration-independent, and hence, *the energy is linear in* σ_α.

The first principles approaches for calculating ECI's fall into three main classes: 1) Methods based on a perturbative treatment of the coherent potential approximation (CPA), most notably, the generalized perturbation method (GPM) [11], 2) Methods involving the calculation of energies of ordered superstructures, and, in conjunction with expansion (1), extraction of the ECI's from these computations [4,5], and 3) The method of direct configurational averaging (DCA) [6]. DCA is a method of perturbing not the averaged, CPA-medium, but rather a truly randomly generated configuration. Quantities are computed in real space for a given aperiodic configuration, and ensemble averaging is performed last, as required by the correct statistical treatment of the problem. In this paper, we use the method of DCA for several reasons: 1) Because it is formulated in real space in the framework of TB-LMTO, the parameters of the Hamiltonian and quantities involved all maintain a simple, intuitive, physical interpretation. 2) As explained above, the configurational averaging is done explicitly, and thus the technique is *not* inherently mean field in nature (as in the CPA-based theories). 3) The tight-binding formulation of the problem minimizes the amount of computer time required (with respect to some of the aforementioned methods) and thus, leads to an economical and practical advantage.

Once the ECI's are known, the energies of all possible configurations on the lattice may be obtained simply by considering variations of the cluster functions, σ_α, in Eq. (1). This most naturally lends itself to a study of the ground state problem. Thus, to find the ground state superstructures of an alloy system, one wants to obtain the minimum energy structures as a function of composition, at T=0K. Simply finding the minimum energy structures at each composition is insufficient, because each ground state structure must not only be lower in energy than any other structure at the same concentration, c, but it also must be stable with respect to any two-phase mixture of structures whose combined composition is c. Thus, when the energies of the ground states are plotted as a function of composition, they must all lie on a "convex hull". Any concave portion would indicate instability with respect to two other phases.

To find the ground states, then, one must search for the minimum of the energy. However, it is not permissible to minimize Eq. (1) unconditionally. The cluster functions are constrained by the fact that they must respresent a physical configuration on the lattice. The most direct way of expressing these constraints is to require that the probabilities of all configurations on some maximal cluster, α_{MAX}, be between 0 and 1. In addition, there is a normalization constraint. The same condition is then automatically satisfied for all of the subclusters of α_{MAX}. Because these probabilities are, by definition, functions of configuration, they can be expanded in cluster functions, analogous to Eq. (1).

The ground state problem may now be expressed in the following way: Minimize the objective function, E, subject to the constraints mentioned above. Since both the objective function and the constraints are linear in σ_α, this simply becomes a problem in linear programming. Linear programming not only guarantees that one finds a global energy minimum, but in addition, lends itself to an interesting geometrical picture: The problem is formulated in an n-dimensional space (n being the number of distinct subclusters of α_{MAX}) with m constraints imposed (m is the number of distinct configurations on α_{MAX}). Each of the constraints is an n-1 dimensional hyperplane, and their intersections form a convex polyhedron. The global energy minimum is then a vertex of this polyhedron, as proved within linear programming. In this way, one may exactly define the ground states for a given alloy system without resorting to phenomenological or adjustable parameters.

Previous studies on several alloy systems [3,4,12] have shown that, for the fcc lattice, incorporation of pair interactions up to the 4NN is sometimes essential to obtain the correct ground states. To include interactions with this spatial extent, we have formulated the fcc ground state problem with the 13 and 14 point cluster as maximal clusters. All atoms in the standard fcc cube define the 14 point cluster, and the 13 point cluster contains a central site and its 12 nearest neighbors. This approximation contains 742 distinct clusters, including all pair interactions up to the 6th nearest neighbor, excluding the fifth nearest neighbor pair. The large cluster is beneficial in two ways. First, more pair and multibody interactions can be included in the ground state analysis. Secondly, since the constraints are formulated on a larger cluster, one is less likely to obtain 'inconstructable ground states' (minima of the energy that do not correspond to a configuration on the lattice). The constraints were obtained with a computer code that uses group theory concepts to relate the cluster functions and the cluster probabilities. There are 554 constraints for the 14 point cluster and 288 for the 13 point cluster. Thus, for these clusters, the ground state problem is formulated in terms of a 742-dimensional space with 842 linear constraints imposed. The minimization of the energy was performed with a linear programming routine based on the simplex algorithm [13].

Including multibody interactions in the energy expansion is essential. With only concentration-independent pairs in the energy, the system becomes invariant under interchange of A and B atoms. In other words, all of the formation energies of the system are completely symmetric about c = 0.5, which is generally not observed in real alloy systems. One method for realizing the experimentally observed asymmetries present in real alloy systems is to allow the pair interactions to be concentration-dependent (but still configuration-independent). However, the addition of multiplet ECI's to the concentration-independent pairs will, in fact, produce the same effect [2,3]. These multiplet interactions have generally been considered to be small [14], however, recent work [2,3] has shown that any alloy system with strongly concentration-dependent pair interactions must by definition, have non-negligible multibody ECI's. General arguments based on the electron occupation of the d-band alone, which are applicable to the majority of transition metal alloys, suggest that the Pd-V system should have a strong asymmetry about c=0.5 [15], and thus, significant multiplet interactions. Thus, we choose to study the Pd-V system as a crucial test of the concentration-independent ECI's.

RESULTS

Linearized muffin-tin orbital (LMTO) calculations were performed for the pure elements Pd and V, both in the fcc structure. Both elements' total energies were minimized with respect to their lattice constants. Then, a linear dependence on concentration was assumed for the alloy lattice constant, and both LMTO Hamiltonians for pure Pd and V were cast into tight-binding form at this intermediate lattice constant [16]. Of course, the matrix elements of the Hamiltonian change upon alloying, and this is modeled as a shift between the on-site energies of the two metals. This shift is determined self-consistently along with the Fermi energy by imposing local charge neutrality, a reasonable approximation for a transition metal alloy, where charge transfers are known to be negligible. Off-diagonal disorder is treated within Shiba's approximation [17], $\beta_{AB}{}^2 = \beta_{AA}\beta_{BB}$, where β_{IJ} represents the hopping between atoms of types I and J.

DCA was used with the alloy Hamiltonian described above to calculate the ECI's for the system. Ten levels of recursion were used, along with a quadratic terminator, and the ECI's were averaged over 20-50 configurations. Pair interactions for the first through fourth and sixth nearest neighbors and all of the triplet interactions in the 13-14 point fcc cluster were computed. In addition, eight of the quadruplets in this cluster were calculated. The interactions show a good convergence with the number of points in the cluster, as the maximum absolute values of the pair, triplet, and quadruplet interactions are 4.7, 1.3, and 0.07 mRy, respectively. The set of 26 ECI's computed for this study represents the largest set of interactions yet calculated for any alloy system.

The results of the ground state search are presented in Fig. 1. For $c_{Pd} < 0.5$, we have obtained the $ZrGa_2$-type structure (at PdV_2 composition) and $L1_2$ (at PdV_3) as stable phases. The $ZrGa_2$-type structure may only be stabilized when interactions beyond the next-nearest neighbor are considered. At PdV, Pd_2V, and Pd_3V compositions, we find $L1_0$, $MoPt_2$-type, and DO_{22} to be the stable structures, respectively. For $c_{Pd} > 0.75$ the ordered structures, $D1_a$ and Pt_8Ti-type, are virtually on the tie line between DO_{22} and pure Pd, so that we can not make any definite conclusions, except that both structures will at least be competitive with other phases.

Although the interactions used in this paper are composition-independent, it has been shown [2,3] that in the limit N -> ∞ where N is the number of sites in the system, these interactions are equivalent to composition-dependent interactions which are averaged over all configurations of an alloy at concentration 0.5. Fig. 2 shows the first through fourth and sixth nearest neighbor pairs as calculated for Pd-V by the DCA using the LMTO Hamiltonian, and the concentration-dependent pair interactions (evaluated at $c = 1/2$) computed within the CPA-GPM within a fully self-consistent Korringa-Kohn-Rostoker (KKR) framework [12]. There is a striking similarity between the two sets of interactions, with the differences between the DCA and GPM results being less than 0.5 mRy for each interaction. Both theoretical studies also show a the close competition between the $L1_2$ and DO_{22} Pd_3V structures, as well as the necessity of including interactions extending beyond the second-neighbor pair: truncating the interaction set after the second-neighbor pair would stabilize the $L1_2$ structure, instead of the correct DO_{22}.

Ordered superstructures can be classified according to the dominant *special-point ordering wave* [18]. In fcc, there are three ordering wave families: <1 0 0>, <1 1/2 0>, and <1/2 1/2 1/2>. The $L1_2$ and $L1_0$ strctures belong to the <1 0 0> family, the $MoPt_2$, DO_{22}, and $D1_a$ belong to the <1 1/2 0> family. Fig. 1 clearly shows that the V-rich side is dominated by the <1 0 0> wave, the Pd-side by the <1 1/2 0>. Competition is close, however, particularly near composition Pd_3V: the $L1_2$ and DO_{22} structures have almost the same formation energies and there is experimental evidence [19] that the short-range order above the Pd_3V transition temperature is of <1 0 0> type, whereas the long-range order (DO_{22}) is of <1 1/2 0> type. For a given binary system to belong to more than one special-point family, either concentration-dependent interactions must be used, or , as in the present case, multiplet interactions must be taken into account. Only the latter approach allows for a rigorous ground state determination to be made through the linear programming algorithm, as explained above.

Comparison with experimental data for the Pd-V alloys indicates the accuracy of our calculations. The experimental results up to 1981 for the Pd-V system have been compiled by Smith [20]. High V content alloys order in the A15 structure with stoichiometry PdV_3 (prototype Cr_3Si). Thus, for $c_{Pd} < 0.5$, comparison with our theoretical predictions is not possible, as A15 is not a superstructure of fcc. However, at the Pd rich side of the phase diagram all ordered phases are superstructures of the fcc lattice. The presence of the $MoPt_2$-type structure at Pd_2V composition and the DO_{22} (Al_3Ti-type) at Pd_3V has been well established, and is predicted by our calculation. In addition, both Maldonado and Schubert [21] and Turek [22] observed the characteristic superstructure reflections of the B19 phase (AuCd-type) in alloys with composition PdV. The B19 is a monoclinic distortion of the $L1_0$ fcc superstructure, the ground state predicted at this stoichiometry, and its (meta)stability has not been determined unambiguously. Also, by using high energy proton irradiation to enhance the low-temperature diffusion, Cheng and Ardell [23] have also detected an ordered Pd_8V phase (Pt_8Ti-type), stable below 400°C. Thus, our results for the (meta)stability of an ordered Pt8Ti-type phase agree with these observations.

The subtle interplay between $L1_2$ and DO_{22} is well reproduced by the calculations on Pd_3V. In addition, analogous calculations were performed for several other transition metal alloy systems. In sum, interactions were computed and ground state analysis was performed for the six alloys formed by mixing A = (Rh, Pd, and Pt) with B = (Ti and V). In each case, the correct phase at A_3B stoichiometry is predicted: Rh_3V ($L1_2$), Rh_3Ti ($L1_2$), Pd_3V (DO_{22}), Pd_3Ti ($L1_2$), Pt_3V (DO_{22}), and Pt_3Ti ($L1_2$). These calculations indicate the flexiblility and reliablility of the method.

CONCLUSIONS

The accomplishments of this work are threefold: First, the energy expansion in terms of concentration-independent ECI's is seen to provide a valid description of the energetics of alloy systems. Even in the case of Pd-V, where the formation energies are strongly asymmetric about $c = 0.5$, these asymmetries are accurately represented by inclusion of multiplet terms in the expansion of the energy. In addition to the validity of this expansion, we have seen its practicality in facilitating the ground state search. Second, DCA has been used in the past [3,6,24,25] to predict general qualitative trends in alloy systems. However, we have shown here interactions computed from DCA with no adjustable parameters may be used as a quantitative tool in the study of alloy phase stability. The DCA requires substantially less computational effort than most other methods to compute effective cluster interactions, and hence, should be considered as a practical alternative when studying an alloy system. And finally, for the first time, an exact ground state search for a real alloy system has been performed for the fcc lattice including pairs up to fourth nearest neighbors and multiplets. The search is exact in the sense that with the interactions given, no other ground states may exist. Degeneracies or "inconstructable" structures are the only obstacles to this method, however, in the Pd-V system considered here, these difficulties are absent, thus leaving the results indisputable.

ACKNOWLEDGEMENTS

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Fig. 1. Formation Energies for the fcc Pd-V System. Filled squares represent stable phases predicted by the ground state analysis. Open squares show some competing metastable structures.

Fig. 2 Pd-V Effective Pair Interactions (50%) calculated from the DCA and KKR-CPA-GPM.

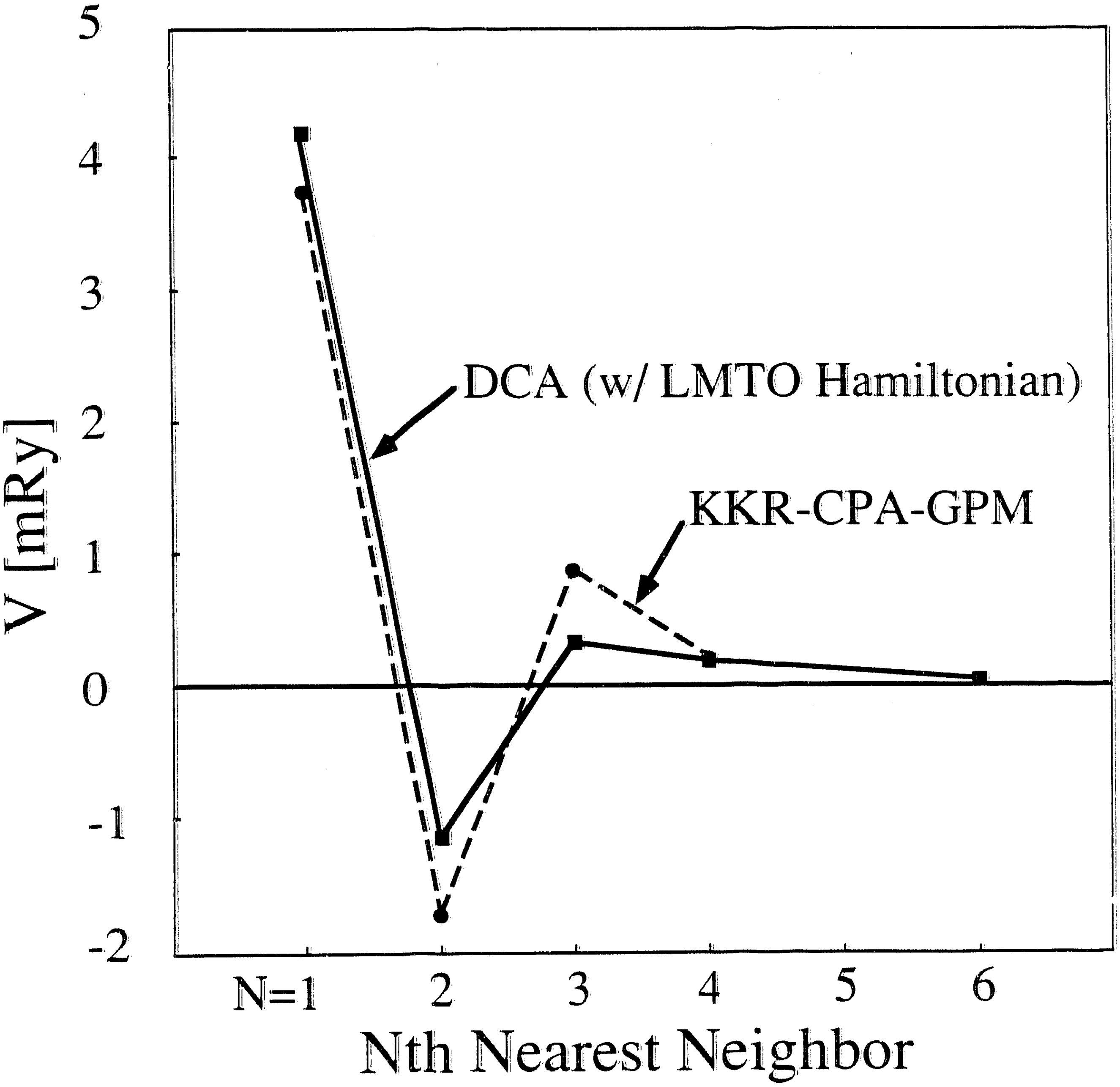
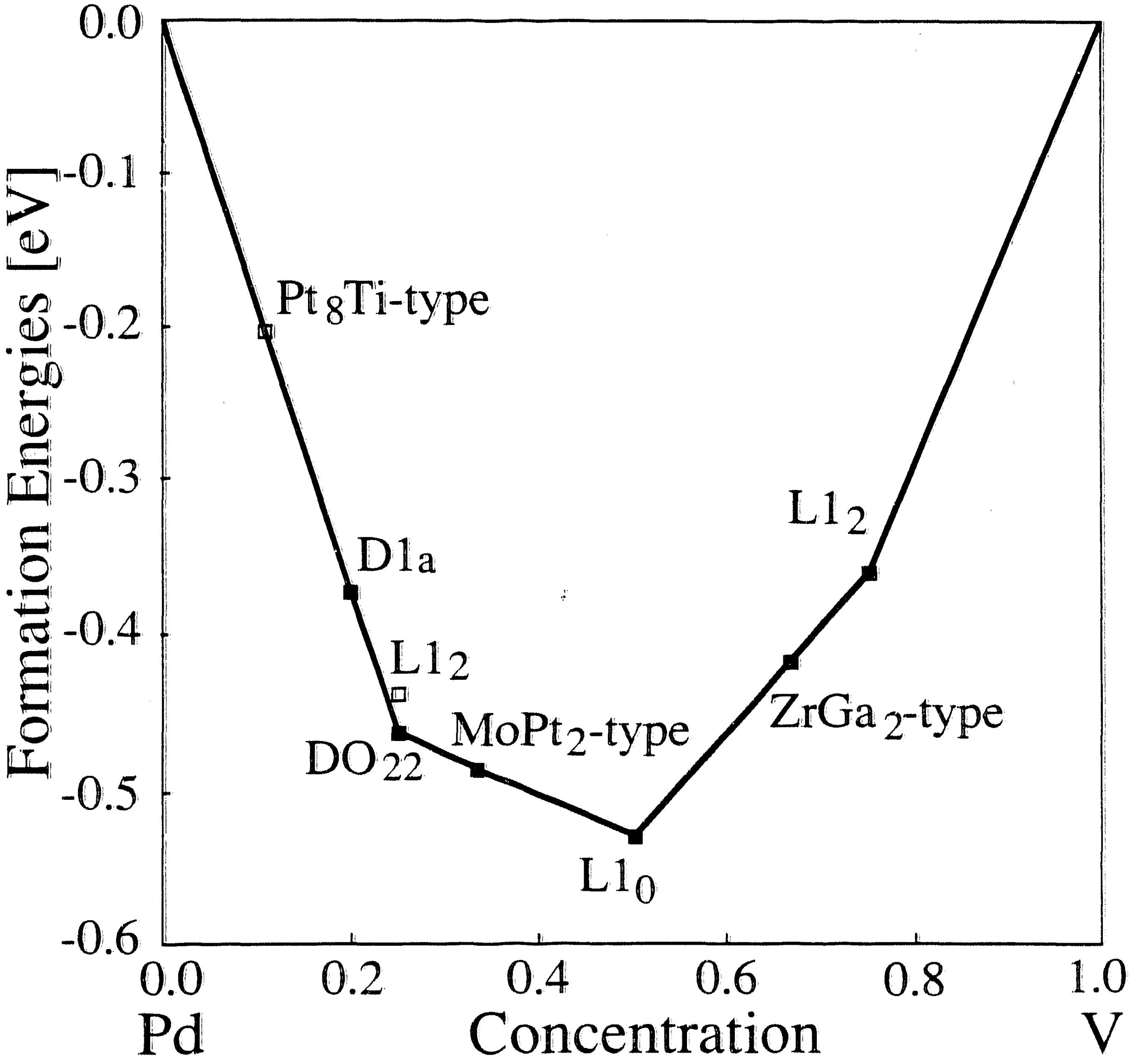

5
4
3
2
1
0
-1
-2
V [mRy]
DCA (w/ LMTO Hamiltonian)
KKR-CPA-GPM
N=1
2
3
4
5
6
Nth Nearest Neighbor

Figure 1



0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
Formation Energies [eV]
Pt$_8$Ti-type
D1a
L1$_2$
DO$_{22}$
MoPt$_2$-type
L1$_0$
ZrGa$_2$-type
L1$_2$
0.0
0.2
0.4
0.6
0.8
1.0
Pd
Concentration
V

Figure 2

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