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Heats of formation of transition-metal alloys: Full-potential approach and the Pt-Ti system

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The heats of formation, ΔH, of the ordered phases of Pt-Ti are calculated using various approximations. This alloy system was chosen because of the availability of experimental data for ΔH for both high- and low-symmetry phases. The difference in the calculated heats of formation between a muffin-tin and a full-potential treatment can be substantial, as much as 0.25 eV/atom. While the total energies of the compounds and the reference elemental metals are all lowered (i.e., increased in binding), the change in ΔH depends on which energy is lowered more. For PtTi in the high-symmetry CsCl structure, ΔH is reduced, implying that the decrease of the total energy due to the full potential is larger for the elemental reference solids than for the compound. The calculated heats of formation are in accord with the experimental values and the known phase-diagram behavior, i.e., all the low-temperature phases predicted to occur as a function of composition are in fact observed.

I. INTRODUCTION

The heats of formation of compounds and the associated entropies provide the basis for understanding and constructing phase diagrams. Knowledge of these quantities offers the prospect of disentangling which of the observed phases are intrinsically stable and which phases might be expected to arise upon varying the means of fabrication. Such modeling of alloy phase behavior is, obviously, of considerable technological relevance. The experimental measurement of a heat of formation ΔH can be tedious; in addition, there are many cases where the ΔH of stable as well as metastable phases are simply not accessible. In recent years, total-energy electronic structure calculations have offered another means of estimating ΔH:

$$\Delta H = E_c - \sum_i x_i E_i \ , \tag{1}$$

where E_c is the calculated total energy of the compound, E_i is the calculated total energy of the element i, and x_i is the concentration of element i in the compound. The present authors have previously estimated[1-3] ΔH for ordered transition-metal–transition-metal compounds with band-structure calculations employing local-density muffin-tin potentials. These calculated ΔH were in reasonable accord with experiment[4] for compounds whose atomic packing is similar to that of the reference elemental solids of Eq. (1). Although there has been a lack of experimental data for *ill-packed* low-site-symmetry structures, there have been suggestions[5] that the calculated ΔH using muffin-tin potentials for such cases are not in line with those of well-packed systems. In recent calorimetric investigations, Selhaoui has reported[6] results for a number of Pt-Ti systems including $PtTi_3$, which forms in the Cr_3Si ($A15$) structure. This is a Frank-Kasper phase[7] that involves linear chains of majority atoms that are compressed to abnormally small nearest-neighbor approaches along the chain lines. Mattheiss and Hamann have observed[8] that band-structure calculations employing muffin-tin potentials, which are spherical at atomic sites, do not yield correct band structures for such phases and that full-potential treatments must be employed instead. Selhaoui's ΔH experimental data for an $A15$ phase allows a comparison between theory and experiment for the ΔH of an $A15$ versus other better-packed phases. The purpose of the present paper is to explore the consequences of going from muffin-tin to full-potential estimates of ΔH for the various phases of the Pt-Ti system.

Experimental ΔH are available for most of the observed ordered phases in the Pt-Ti system. There are calorimetric results for Pt_3Ti, PtTi, and $PtTi_3$ as well as emf measurements for Pt_8Ti and Pt_3Ti. All of these will be dealt with in the calculations. PtTi forms in the AuCd phase at low temperatures and undergoes a martenistic transformation to the high-temperature CsCl at

~1100 °C (a high temperature compared with those normally encountered in such transitions). The CsCl phase would appear to be involved in the ΔH measurement, but both phases will be represented in the calculations. Three different structures have been reported for Pt_3Ti at or near 3:1 composition. The most commonly encountered one is the Cu_3Au structure and is the one reached[6] in the ΔH measurement. The other two structures involve 16 and 28 atoms in their unit cells, making them costly for total-energy estimates, and so the Pt_3Ti calculations will be limited to the Cu_3Au structure. There is also a Pt_5Ti_3 phase with 16 atoms per unit cell for which there is no experimental ΔH. This, too, will be neglected. Pt_8Ti is an ordered structure on a slightly distorted fcc lattice, the distortions in Pt positions arising from the accommodation to the presence of larger Ti atoms. With one exception, the calculations will be done for the compounds and for the elemental metals at their observed lattice volumes. In the case of PtTi in the high-temperature CsCl phase, calculations will be done at the smaller volume characteristic of the AuCd structure as well as at the observed high-temperature volume.

These self-consistent calculations have been done using local-density potentials (with no shape approximations) and the linearized-augmented Slater-type orbital (LASTO) method.[9] This method employs Slater-type orbitals (STO's) to construct the wave functions in the interstitial region, augmented by explicit solutions of the radial wave equations within the spheres round each atomic site. The resulting matrices to be diagonalized are thus like those of a tight-binding scheme and could be fit to yield parameters for a tight-binding scheme. The choice of the Slater-type orbitals is important to the results and here they have been determined variationally for the elemental metals. In many of the previously reported calculations, the STO set was limited to a single *s*, *p*, and *d* orbital, implying a 9×9 matrix if there is only one atom in the unit cell. Given such a set, it can be augmented by employing more STO's. In this paper we will consider an augmented basis set consisting of two *s*, *p*, and *d* orbitals and a single *f*-like orbital, the latter resembling the "polarization" basis function of quantum-chemistry calculations. Comparison for several elemental metals indicates that the LASTO method with such an augmented basis set yields total energies that are in essential agreement with those of linearized-augmented-plane-wave (LAPW) calculations.

In what follows, we will be concerned with the consequences on estimates of ΔH of going from single STO basis sets to augmented ones, and from muffin-tin to full potentials. In each case, the calculations for the compound and those for the elemental metals are obtained with the same approximations, i.e., the same sets of STO, the same atomic spheres, and the same treatment of the potential. The calculations have been taken to self-consistency, treating the atomic cores fully relativistically, but neglecting spin-orbit effects for the valence electrons (the scalar-relativistic approximation). The effect on ΔH of including the missing spin-orbit terms for the valence electrons will also be inspected.

The largest effect on ΔH is associated with going from the muffin-tin to the full-potential treatment, causing both the compound and the elemental metals to become increasingly bound. In the case of $PtTi_3$ in the *A*15 structure, with its low-symmetry Ti sites, the effect is most important for the compound, and the calculated ΔH increases measurably upon going to the full-potential treatment. What is surprising is that the *reverse* occurs; i.e., ΔH decreases, for Pt_3Ti and for PtTi in its two phases. This reverse is larger the better packed the compound is and happens because going to full potentials is more important for the E_i of the elemental metals than it is for the energy of the compound.

II. RESULTS

The major results are plotted in Fig. 1. In the top panel is a tracing of the phase diagram[10] of the Pt-Ti system. The hatched areas indicate the compounds of concern here, all of which occur over a finite composition

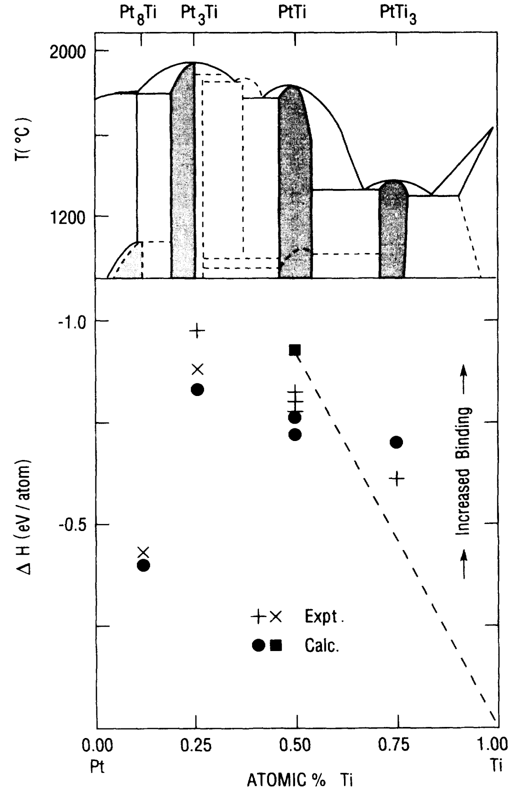

FIG. 1. The upper section shows a rough tracing of the phase diagram (from Ref. 10) for the Pt-Ti system. The hatching indicates those ordered phases of concern in the paper. The lower section displays experimental and calculated (full-potential, augmented basis set with spin-orbit coupling) heats of formation as a function of Pt-Ti composition. Increased binding has been plotted upwards. The crosses indicate calorimetric measurements and the ×'s indicate emf measurements. At 50:50 concentration, the square indicates the calculated heat for the low-temperature AuCd structure, which correctly shows greater binding than the results for the high-temperature CsCl structure (circles). The higher of two CsCl structure results is for the observed AuCd volume and the lower is for the higher-temperature CsCl volume.

range. The dashed line at ~1100 °C for PtTi indicates the transition from the low-temperature AuCd structure to the high-temperature phase having the CsCl structure. The bottom panel of the figure compares experimental ΔH with the best calculated values, i.e., those involving full potentials, augmented basis sets, and spin-orbit coupling. For PtTi the square represents the result for the AuCd structure, the circle closest to it is the CsCl structure but with the observed AuCd structure's volume, and the lower circle is the CsCl structure at the observed CsCl structure's volume. It is the ΔH of the high-temperature CsCl phase that is to be compared with experiment at 50:50 composition. The agreement of the calculated ΔH with experiment is of the order of the scatter in experimental values seen for those cases where more than one experiment has been done. This agreement is one-tenth of an eV per atom or better. (We might note that we expect that some of the most recent experimental ΔH have been determined with an accuracy that is better than this.)

The calculated ΔH indicate the coexistence of the observed phases of differing composition at low temperatures. Consider the dashed line drawn between the ΔH for the AuCd structure and the zero for pure Ti. The fact that the calculated ΔH for $PtTi_3$ lies above this line indicates that $PtTi_3$ is calculated to be stable relative to a two-phase mix of PtTi (AuCd structure) and pure Ti. The fact that the PtTi (AuCd structure) point lies above a line that could be drawn between the Pt_3Ti and $PtTi_3$ ΔH indicates it to be stable relative to a mix of these two phases, and similar arguments may be extended to show that Pt_3Ti and Pt_8Ti are also stable relative to the other competing stable phases of different composition.

Figure 2 shows the variation in ΔH for various approximations in the band calculations where the *same* approximation is used for each of the total energies of Eq. (1). The results for the CsCl structure are taken at the observed low-temperature AuCd structure's volume. The most pronounced effect is associated with going from the single STO muffin-tin to the single STO full-potential calculation. $PtTi_3$ gains substantially in total energy, and hence in its ΔH, due to the more rigorous treatment of the charge density at the low-symmetry Ti sites. In contrast, for a number of the other phases—the CsCl structure in particular—ΔH decreases on going to the full potential. This implies that the full-potential treatment is relatively more important to the elemental E_i's than it is to the total energy of the compound. The introduction of valence-electron spin-orbit terms has a small effect on ΔH, while going from the single to augmented STO basis sets has the least effect of all, namely that the pairs of plotted points touch for all the phases in this case.

The above estimates were done employing the observed lattice constants, and it is generally found that the local-density approximation yields total-energy minima for volumes that are somewhat smaller than the observed. The consequences of this for the CsCl structure phase are explored in Fig. 3, where ΔH are plotted as a function of

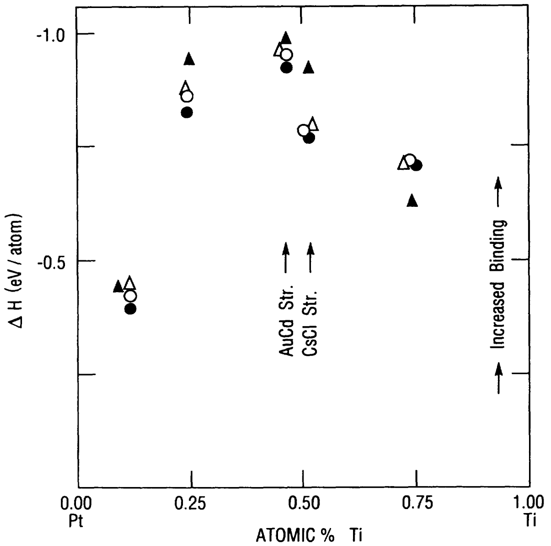

FIG. 2. Calculated heats of formation as a function of Pt-Ti composition in several approximations. The closed triangles indicate muffin-tin-potential results (single STO's and no valence-electron spin-orbit coupling). The open triangles replace the muffin-tin by the full potentials and the open circles indicate the full-potential results with the augmented STO sets. The closed circles have already been displayed in Fig. 1 and represent full-potential calculations involving augmented STO basis sets and spin-orbit coupling. The calculations have been done for the systems at their observed crystal volumes, except for the CsCl structure, which has been calculated at the observed (lower-temperature) volume of the AuCd structure.

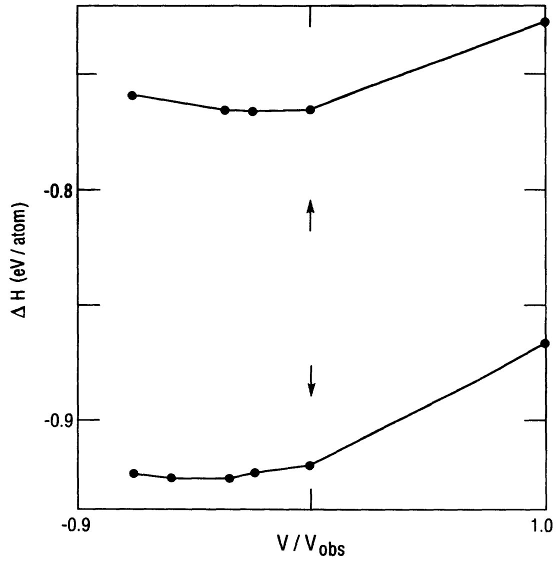

FIG. 3. ΔH as a function of the compound's atomic volume for PtTi in the CsCl structure relative to the observed volume V_{obs}. The volumes of elemental Pt and Ti, employed in E_i of Eq. (1), have been kept at their observed values. The muffin-tin results (lower curve) are for the single STO without spin-orbit coupling (i.e., the closed triangles of Fig. 2), while the full-potential results (upper curve) involve the augmented STO basis sets and spin-orbit coupling (the closed circles of Fig. 2). The arrows indicate the observed AuCd structure's volume.

the lattice volume of the compound. (The elemental reference energies E_i, have been evaluated at their observed lattice volumes.) The one case is for the muffin-tin potential, a single STO, and no spin orbit, while the other involves full potentials, augmented STO, and spin orbit, i.e., the closed triangles and circles of Fig. 2, respectively. The observed AuCd volume is about 5% smaller than for the CsCl structure. Since the latter volume was obtained at ~1300 K, presumably the former is more characteristic of PtTi at low temperatures. In any case, the full-potential calculation has its energy minimum at a larger volume, closer to the experimental values than that obtained using muffin-tin potentials. What is more important, however, is that reasonable changes in volume have but a modest effect on the resulting ΔH. This observation is of some practical importance because a search for energy minima is quite costly in computer time for full-potential calculations of larger unit-cell systems, such as Pt_8Ti and $PtTi_3$.

III. DISCUSSION

Both the calculated and the experimental heats of formation of Figs. 1 and 2 are skewed in favor of Pt-rich concentrations. As has been discussed previously,[2,3] this is due to band-filling effects, as can be seen here for the densities of states plotted in Fig. 4. The calculations are based on rather limited sets[11] of special k points that are sufficient for determining the total energies, but details of the density-of-states plots should not be taken too seriously. The Pt-like subbands lie below those of Ti and, with the exception of Pt_8Ti, these Pt-like bands are completely occupied. This is in contrast to Pt metal, with its partially occupied d bands. The subband filling is associated with hybridization of Ti wave-function character into these bands. Earlier muffin-tin calculations[2] for a set of Pt compounds indicate a near zero change in Pt-site d-electron count upon alloy formation. This implies that the band filling is not just associated with "charge

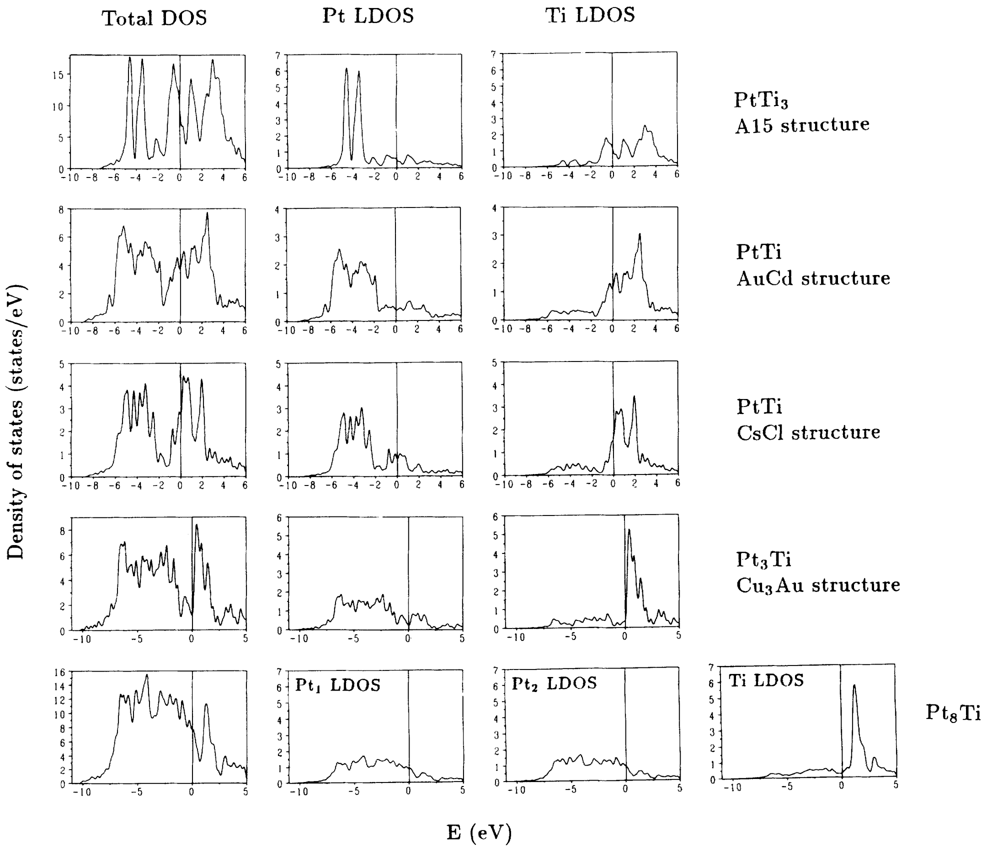

FIG. 4. Densities of states and local densities of states (LDOS) for various Pt-Ti compounds. The zeros of the energy plots are the calculated Fermi levels. The total densities of states in the left-hand column indicate the density for the set of atoms in the unit cell, hence the AuCd structure, which has twice the number of atoms in the unit cell of the CsCl structure, has twice the overall density of states that CsCl has. The local densities of states are obtained for the charge in the atomic spheres at respective Pt and Ti sites; i.e., the interstitial region is not accounted for in the LDOS. In the case of Pt_8Ti, there are two inequivalent Pt sites in the crystal structure: the Pt_1 lie in (100) directions, while the Pt_2 lie in (110) directions relative to the Ti sites.

transfer" due to Ti electrons transferring into the empty Pt levels, but there is a compensating reduction in the overall Pt *d* count due to hybridization of Ti wave-function character into the Pt subband. In the case of $PtTi_3$, the Pt atoms are rather far apart and the Pt subband has a very atomic appearance with its spin-orbit split doublet. The Pt subbands take on more complex character as the Pt concentration increases and Pt atoms come closer together. The Pt subbands are filled in Pt_3Ti, as well as in PtTi. Pt_3Ti has a ΔH (and a melting temperature) comparable to those of the 50:50 compounds. In the case of Pt_8Ti, the single Ti does not have the charge necessary to hybridize with the eight Pt atoms so that the Pt subbands may be filled. The Fermi level thus intersects these subbands and ΔH is seen to fall off. This is consistent with earlier muffin-tin-potential investigations[2,3] involving a number of alloy sequences with substantial ΔH, comparable to those obtained here. Large ΔH were associated with having the lower-lying subbands (such as Pt's) filled, while the Fermi level could intersect the higher-lying "antibonding" subbands (Ti's here) with less adverse effect on the bonding energy. In first approximation one expects the largest heats of formation at 50:50 concentration because of the possibility of having bonding from the maximum number of unlike nearest-neighbor pairs. Second, skewing occurs, favoring the filling of the low-lying subbands. As in Fig. 1, this skewing is the rule in the phase diagrams of alloy systems involving one member from the beginning and the other from the end of the transition-metal rows.

In Fig. 1 we see that the AuCd structure is more stable than the high-temperature CsCl structure for PtTi, as it should be, and that the calculated CsCl structure ΔH is in reasonable accord with experiment. The difference in the calculated ΔH of the two phases, 0.16 eV/atom, seems rather large. However, at the phase transition, the temperature times the entropy change must equal ΔH, and the transition temperature in this case is very high. Presumably, vibrational entropy is the primary contributor to ΔS, and we are not prepared to estimate that. There are electronic entropy contributions[12] as well, and given the densities of states for the two phases, these may be estimated. This can only be estimated approximately, given the crude determination of the densities of states. A ΔS of the right sign to account for $\sim$ 20 % of the calculated ΔH may be obtained from Fig. 4. It remains to be seen if the vibrational entropy can account for the remainder. There is some experimental basis for taking a ΔH of this magnitude seriously for such systems. One of the heats for PtTi was measured above and another below the transition temperature. The two heats are the same but their error bars encompass the calculated energy difference. HfNi is also reported[10] to undergo an allotropic transformation at 1170 °C and heats have been measured[4,6] above and below this temperature. (Note that Hf and Ni lie in the same columns of the Periodic Table as Ti and Pt, respectively.) The low-temperature heat is $\sim$0.11 eV/atom larger in magnitude. This is consistent in sign and magnitude with the present calculations for PtTi, though it should be noted that HfNi would appear to involve a transformation between a different pair of structural phases. The calculated energy difference seems large, but is within the realm of what is observed experimentally.

If agreement to $\sim$0.1 eV/atom or better may be deemed reasonable, then the calculated heats of Fig. 1 are in reasonable accord with experiment. Going from muffin-tin to full potentials has shifted the ΔH calculated for PtTi (CsCl) versus $PtTi_3$ (*A* 15) by 0.25 eV/atom. Similarly, on previous muffin-tin calculations[1] for $AuTa_3$ in the *A* 15 structure (but for which no experimental ΔH exists), comparison[13] with the calculated ΔH for adjacent 50:50 compounds suggested that the *A* 15 phase was calculated to be $\sim$0.25 eV/atom less bound than it ought to be relative to the 50:50 phases if the *A* 15 phase is to occur. Since the *A* 15 is ill packed, it is not surprising that a full-potential treatment is important. Comparisons among the remaining phases indicate that the full-potential treatment is also significant when sorting out the relative heats. The largest effect on ΔH upon going from muffin-tin to full potentials occurs not for the *A* 15, but instead for the CsCl structure. The *loss* of binding of $\sim$0.15 eV/atom implies that the full potential is more important to the energies of the elemental metals than it is for the compound. This shift introduces a change of as much as a tenth of eV/atom in the ΔH of PtTi (CsCl) relative to phases *other* than the *A* 15, and this is significant. It should be noted that a common set of atomic spheres was employed for the various compounds and that it was required that these spheres do not overlap. The Ti sphere radius, then, was set by the Ti-Ti distance along the Ti chains of the $PtTi_3$ (Cr_3Si) structure. This is measurably smaller than what could be allowed for the other compounds or for elemental Ti. Given the Ti sphere radius, it was possible to set the Pt radius to the value equal to touching spheres in fcc Pt. Thus the Ti spheres were squeezed whereas the Pt's were not, relative to their intrinsic elemental sizes. Going to a different choice of sphere radii for PtTi (CsCl) (and for the elemental reference energies) has little effect on ΔH calculated in the full-potential approximation, but can be substantial for the muffin-tin result. ΔH calculated with the muffin-tin approximation can be said to be hostage to the choice of radii. Going from atomic sphere or muffin-tin approximations to full-potential treatments is at least an order of magnitude more expensive in computer time. These less-costly schemes may be gainfully used to estimate the binding of alloys, if employed judiciously. However, exact measures of what local-density theory predicts for alloy formation requires employing a full-potential treatment.

ACKNOWLEDGMENTS

We wish to acknowledge comments from J.-C. Gachon concerning the structural energy differences associated with allatropic transitions in compounds formed from the Ti and Ni columns of the Periodic Table. This work was supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH-00016, and by a grant of computer time at the National Energy Research Supercomputer Center (NERSC), Livermore, CA.

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[2] R. E. Watson, J. W. Davenport, and M. Weinert, Phys. Rev. B **36**, 6396 (1987).

[3] R. E. Watson, M. Weinert, J. W. Davenport, and G. W. Fernando, Phys. Rev. B **39**, 10 761 (1989).

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[5] See Ref. 1 for the case of $AuTa_3$ and Ref. 2 for PtHf in the CrB structure.

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[8] L. F. Mattheiss and D. R. Hamann, Solid State Commun. **38**, 689 (1981).

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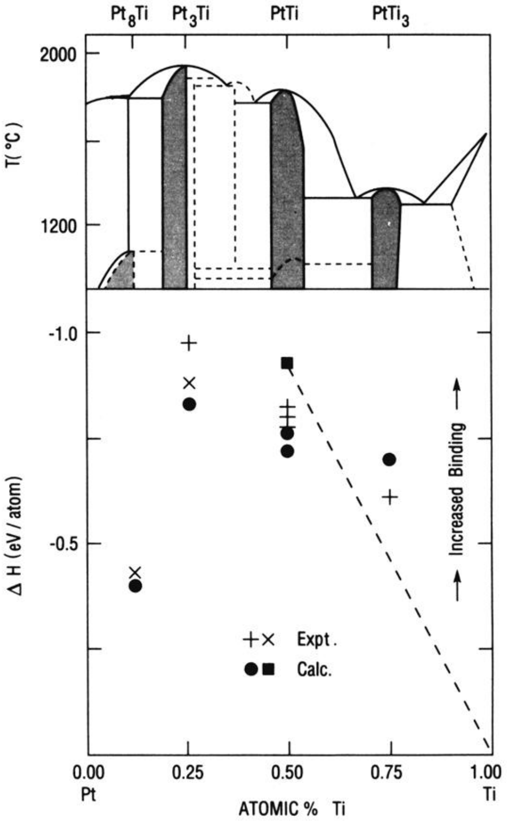
[10] W. G. Moffatt, *The Handbook of Binary Phase Diagrams* (Genium, Schenectady, NY, 1991).

[11] A set of 84 special k points was used for the CsCl structure, sets of 64 k points were used for the $A15$, Cu_3Au, and AuCd structures, and 138 k points were used for Pt_8Ti.

[12] See, e.g., G. Grimvall, Phys. Scr. **12**, 173 (1975); R. E. Watson and M. Weinert, Phys. Rev. B **30**, 1641 (1984).

[13] In the case of the Au-Ta system, the stable phase near 50:50 concentration is *not* AuTa but is instead Au_2Ta_3. Au_2Ta_3 is a layered structure consisting of two (100) planes of Au followed by three of Ta. The early muffin-tin calculations correctly predicted that the stability of Au_2Ta_3 suppresses the occurrence of a 50:50 compound. Relative to the calculated ΔH for Au_2Ta_3, the muffin-tin ΔH for the $A15$ phase is out of line by even more than the 0.25 eV/atom implied by comparison with ΔH calculated for the 50:50 compounds.



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