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Energetics of transition-metal alloy formation: Ti, Zr, and Hf alloyed with the heavier 4*d* and 5*d* elements

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Total-energy calculations yielding heats of formation for ordered compounds of Ti, Zr, and Hf alloyed with Tc, Re, Ru, Os, Rh, Ir, Pd, and Pt are presented. There exist both experimentally based phase diagrams and a substantial number of experimental heats of formation for these systems, and the present results are in accord with these; e.g., the co-occurrence of compounds at differing compositions is correctly predicted. The heats, as a function of the fractional alloy composition x, generally differ markedly from the $x(1-x)$ dependence so often envoked. An explanation of the heat behavior for the Ti-, Zr-, and Hf-depleted alloys is found in their densities of states and is associated with the d bands of the other alloy constituent being decoupled from the Fermi level.

I. INTRODUCTION

In recent years, increasing numbers of *a priori* band theory estimates have been made of cohesive energies of the elemental solids and of heats of formation of compounds. The reasons for this have included efforts to understand bonding trends and the desire to augment experimental thermodynamic data which are employed in phase diagram constructs. One problem has been the lack of experimental data with which to test the calculations. To help remedy this, Topor and Kleppa have made[1] calorimetric measurements of the enthalpies of formation for a number of 50%-50% compounds of Ti, Zr, and Hf alloyed with elements at the right-hand ends of the 4*d* and 5*d* rows. Gachon and collaborators have also obtained[2] calorimetric results for a number of these systems and for some of these systems off 50%-50% concentration. In the present paper we will compare calculated heats of formation for ordered stoichiometric compounds, based on total energy, self-consistent, scalar-relativistic, linear-augmented Slater-type orbital[3] (LASTO) band calculations with these experimental results. Of concern will be the variations in bonding trends with varying alloy constituent and with varying alloy concentration. The bonding, as manifested by the calculated heats and suggested by the experimental phase diagrams, displays marked deviations from what simple arguments would suggest for such binary alloys. The systems to be considered are Ti, Zr, and Hf alloyed with the

Tc	Ru	Rh	Pd
Re	Os	Ir	Pt

block of the Periodic Table.

The plan of this paper is as follows. The first set of results will be for the 50%-50% alloys where the agreement between theory and experiment is of the order of the scatter in experiment. (These particular results have been reported elsewhere[4] along with a comparison with other theoretical predictions. This comparison will not be repeated here.) This is followed by results for Ti, Zr, and Hf poor 3:1 compounds. In the case of the Pd and Pt alloy systems, these 3:1 compounds display a greater heat, *per atom*, than do the 50%-50% systems. However, these 3:1 heats drop on moving to the left in the Periodic Table, e.g., from Pd to Rh and then to Ru. This drop is so sharp that by Ru (or Os) the 3:1 phase loses out in competition to having a two-phase mix of the 50%-50% compound plus pure Ru (or Os). Attention is then turned to the Ru-Zr, Rh-Zr, Ph-Zr, and Pt-Ti, systems at varying alloy composition. Now the simplest argument is that the strength of the bonding as a function of alloy composition should go as the number of unlike nearest-neighbor atom pairs. Neglecting structural considerations, this function is simply $x(1-x)$, where x is the concentration of one alloy constituent and $(1-x)$ is the concentration of the other. The calculated and experimental heats ΔH do not conform to this. Instead of having a maximum at 50%-50% composition as $x(1-x)$ does, the Pd and Pt systems have ΔH's for Pd and Pt rich systems which are as great, or greater than those at 50%-50%. The skewing of ΔH decreases on moving to the elements to the left of Pd or Pt. By the time Ru and Os are reached, the heats to either side of 50%-50% have dropped substantially below a $x(1-x)$ curve with a resulting reduction in the occurrence of ordered compounds off 50%-50% composition. Inspection of calculated electron densities of states will indicate the reason for the skewing of the Pd and Pt systems' ΔH and the disappearance of this skewing upon going to Ru and Os.

Calculations are done for different crystal structures at a given composition as well as for differing composition. As a rule, the correct crystal structure is calculated to have the stablest ΔH and the occurrence or nonoccurrence of phases at differing composition is correctly predicted.

II. CALCULATIONS

The present estimates will employ self-consistent, scalar-relativistic, linear-augmented Slater-type orbital[3] band calculations. The calculations are scalar relativistic in the sense spin-orbit coupling is neglected in the conduction bands. The calculations employ a basis set of analytic wave functions, in this case Slater-type orbitals. Rather than using this basis set everywhere in space, the basis functions are "augmented" inside nonoverlapping spheres drawn around atomic sites by wave functions which are solutions for the actual effective potentials within the spheres. A muffin-tin potential is employed where only spherical terms are kept within the spheres and a constant potential is employed in the interstitial. Going to a "full potential" which varies in the interstitial region and has nonspherical terms inside the spheres represents a significant increase in computational effort and has been neglected here. Much of the success of the present results depends on the fact that most of the compounds of concern here are geometrically well packed in the sense that a substantial fraction of the crystal volume can be included in the nonoverlapping spheres *and* the atomic sites are of such symmetries that there are no low-l components in the full crystal potential at the sites. In calculating ΔH, one takes the difference in the calculated total energy for the compound and the appropriate sum of total energies calculated for the elemental metals which are also well packed. Non-muffin-tin corrections are important when the compound is ill packed as is the case for PtHf in the CrB structure[5] or Au_3Ta in the $A15$ phase.[6]

The calculations have been done for sets of special k points in reciprocal space where the number of k points is more than enough to establish the total energy and sufficient to define the general features of the density of states—the numbers of k points are not, in general, sufficient for an accurate determination of the density of states at the Fermi level. (For example, 100 k points in the irreducible wedge of the Brillouin zone were used for the CsCl structure and 42 for the $MoSi_2$ structure). Other aspects of the LASTO method, as applied to ordered transition-metal compounds, are reviewed elsewhere.[5–7]

One issue requires mention, namely the crystal volume at which a calculation is done, because the variation of total energy with assumed crystal volume is significant on the scale of the comparisons to be made here. General experience with calculations employing muffin-tin potentials is that the process of varying the crystal volume so as to obtain the energy minimum yields a crystal volume which is smaller than experiment. In order to avoid the extra number of calculations involved in such a search, calculations were done for both the compounds and the reference elemental metals at the observed lattice volumes. This is not entirely straightforward since some of the crystallographic data[8] are suspect for this purpose. For example, the ratio of V, the molecular volume in the compound, to the sum of the elemental volumes, V_0 generally lies between 0.92 and 0.95 for all the 50%-50% compounds of concern here except those of Pd and Pt. However, a few V/V_0 lie measureably outside this range and are thus suspect. The most likely sources of the problem are deviations from exact 50%-50% stoichiometry and the presence of impurities in the samples. In several cases the calculations were done for V/V_0 between 0.93 and 0.94, consistent with the overall trend, rather than assuming the value to be inferred from the crystallographic data. Substantial spreads were found in V/V_0 belonging to some of the Pd and Pt compounds, e.g., PtHf had V/V_0 of 0.90 and 0.98 for the two reported crystal structures with the high-temperature phase having the smaller lattice volume. (There is some variation of V/V_0 with how well packed a crystal structure is but this is not of importance here.) Granted the scatter, there is some suggestion that the Pd and Pt compounds suffer a weaker contraction, e.g., V/V_0 is larger, than do the other compounds of concern and PtHf, for example, will be reported with the calculations done at $V/V_0=0.96$. Similar considerations apply when going off 50%-50% composition where, again, the best protection against spurious experimental volumes is a scan over all the experimental data. One cannot simply apply the 50%-50% V/V_0 values to other compositions because $V/V_0 \rightarrow 1.0$ in the limit of a dilute amount of A alloyed with B. In addition there is a skewing of V/V_0 depending on which element is the majority constituent. As a rule[9] for the systems of concern here, alloys with Ti, Zr, or Hf the major component have V/V_0 which are larger than those where these elements are the minority constituents. For the most part, the experimental crystallographic data provide the basis for defining reasonable trends in V/V_0 upon which to base the calculations. The same V/V_0 was employed in calculations for different structures at the same composition.

Some of the structures have different lattice constants in different directions and where possible, experimental c/a ratios were employed. Some structures involve atoms having coordinates in the unit cell which are not determined by symmetry. For example, the $MoSi_2$ structure, which occurs frequently as 2:1 transition-metal compounds, has a $AABAAB$ stacking of bcc 100 layers and the A-A and A-B planar spacings are, in general, not equal. These spacings are often not determined in a crystallographic study and, when they are, they are not determined to sufficient accuracy for total-energy band theory purposes. An error in these spacings corresponds to an optical phonon and this can contribute to a substantial error in a computed ΔH as has been shown previously.[6] These spacings (within some given unit cell) have been determined variationally in the present calculations.

III. RESULTS: 50%-50% COMPOUNDS

The calculated enthalpies of formation obtained for the 50%-50% compounds are plotted in Fig. 1 along with experiment. The experimental results, connected by the solid lines, are the results of Topor and Kleppa,[1] the vertical height of the crosses being their stated experimental uncertainties. The other crosses, not in parentheses, are the results of Gachon *et al.*[2] while those in parentheses are noncalorimetric results. Calculations have been done for more than one ordered crystal structure, at common V/V_0, for a number of systems and generally the calculations indicate the greatest binding for those structures which are observed to occur experimentally. It might be noted that the CsCl structure is reported as occurring for

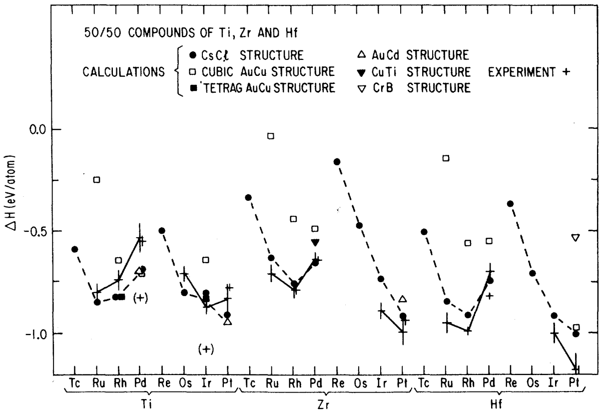

FIG. 1. Calculated and experimental heats of formation of some 50%-50% compounds of Ti, Zr, and Hf. The solid lines connect the calorimetric results of Topor and Kleppa and the experimental crosses in parentheses were obtained by other than calorimetric means. The dashed lines connect the most binding of the calculated ΔH.

all but five systems—ReZr and ReHf where no 50%-50% phases are reported though there are phases at other compositions, and PdZr, PdHf, and IrHf for which full crystallographic solutions have not been obtained. These three phases are apparently not any of the standard structures. Not knowing what they are, calculations were done for these compounds taken to be in the CsCl structure. The resulting ΔH should thus be somewhat smaller in magnitude than the values appropriate to the actual structures.

The one notable failure of the calculations is in the sorting out of structures for PtHf where both the CrB and CsCl structures are observed experimentally. The calculations indicate[6] the CrB structure to be much worse bound than the CsCl. Now CrB is one of the most ill-packed crystal structures considered in Fig. 1. The structure has large interstitial holes and the atomic sites have low symmetry. As has been discussed elsewhere,[6] the muffin-tin potentials used here are ill-equipped to treat such a structure with the same degree of accuracy as they do the close-packed systems. The other systems represented in Fig. 1 are well packed, as are the elemental metals whose total energies are used as references.

The agreement between the dashed line, representing the most binding of the calculated ΔH, and the measured ΔH in Fig. 1 is very good, but by no means excellent. The "bend up," where a Pd compound's ΔH is smaller than that for Rh, is reproduced. The bend up is lacking for Pt versus Ir alloyed with Zr and Hf (though experiment does suggest a bend up for PtTi versus IrTi, it is within the experimental uncertainties and may well not be occurring). Simple electronegativity arguments, where Pd and Pt are more electronegative than Rh and Ir, would suggest that there should be no bend up since the greater the electronegativity difference with respect to those of Ti, Zr, and Hf presumably implies the greater ΔH. Miedema's parametrization[10] of compound heats of formation relies heavily on such an electronegativity difference and thus he fails to reproduce the bend up for the Pd compounds. Simple *d*-band bonding-antibonding arguments suggest that a bend up should occur: Assuming the lower half of the alloy's *d*-band levels to be bonding and the upper half antibonding, it follows that the binding will be greater in that alloy whose *d* bands are closer to being half-filled. RhTi, for example, comes closer to this than does PdTi. Band occupancy factors may thus operate in opposition to electronegativity effects. This difference in bonding between the Pd and Pt compounds may be rationalized in terms of band occupancies as well: namely Pd, Ag, and, to a lesser extent, Rh, have *d*-band levels which lie low in energy with respect to the non-*d* bands, as compared with their positions in other transition metals. This causes Ag's *d* bands to lie lower with respect to the Fermi level than do Au's or Cu's and it causes Pd's Fermi level to be higher in the *d* bands than those in Pt or Ni. This causes Pd to have fewer empty states in the *d* bands. Now, both band theory and experiment show that an essential feature of alloying either Pd or Pt is a filling of their *d* bands and this process must saturate sooner for Pd, because of its having fewer empty *d* states to fill and this could inhibit the bonding in Pd compounds relative to that in the Pt alloys. The results obtained, going off 50%-50% composition, suggest that this argument is, in some senses, incomplete.

IV. RESULTS: 3:1 COMPOUNDS

For a compound $A_xB_{(1-x)}$ to be stable relative to a two-phase mix of a pair of compounds, $A_yB_{(1-y)}$ and $A_zB_{(1-z)}$, with compositions to either side of it, ΔH must satisfy

$$\Delta H(A_xB_{(1-x)}) < \left|\frac{x-y}{y-z}\right| \Delta H(A_zB_{(1-z)}) + \left|\frac{x-z}{y-z}\right| \Delta H(A_yB_{(1-y)}) \,, \qquad (1)$$

where it should be remembered that stable compounds have negative ΔH (if they were taken to have positive ΔH the $<$ sign would be replaced by $>$). For an A_3B compound to then be stable relative to a two-phase mix of AB plus a terminal A phase (whose ΔH, by definition, equals zero) we have

$$\Delta H(A_3B) < \tfrac{1}{2}\Delta H(AB) \,. \qquad (2)$$

The solid lines of Fig. 2, are just this bound, i.e., the calculated $\Delta H(A_3B)$ must be below these lines for the compounds to be predicted to be stable. The Ru and Os compounds have ΔH above the lines, consistent with the fact that no such 3:1 compounds are observed. The other systems do have 3:1 compounds and the calculated ΔH do lie below the lines. The Rh and Ir compounds all form in the Cu_3Au structure while those for Pd and Pt usually form in the Ni_3Ti structure and occasionally in the Cu_3Au. Ni_3Ti has 16 atoms in its unit cell which is too

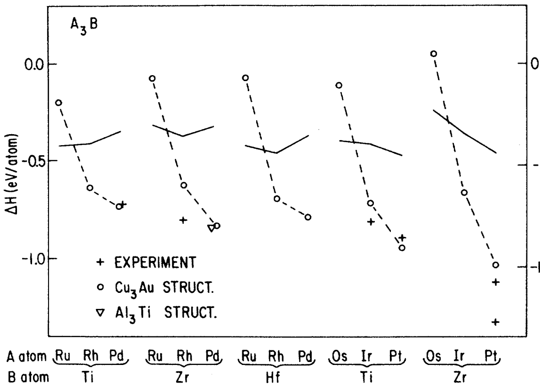

FIG. 2. Calculated and experimental (the crosses) heats of formation for some A_3B compounds (A = Ru, Rh, Pd, Os, Ir, Pt, and B = Ti, Zr, Hf). The solid lines define the energy below which a calculated ΔH must lie if the associated A_3B compound is to be stable relative to a two-phase mix of the AB compound and pure metal A.

large for us to deal with, hence computations have been done for the Cu_3Au structure for all the compounds. The resulting ΔH agree with the available experiment to within the scatter seen in the one case, Pt_3Zr, where there has been more than one determination.

V. RESULTS: $Ru_{1-x}Zr_x$, $Rh_{1-x}Zr_x$, $Pd_{1-x}Zr_x$, $Pt_{1-x}Ti_x$

The top panel of Fig. 3 displays tracings of the phase diagrams[11] for these systems while below the lower panel are listed the crystal structures of the observed ordered compounds (except for Pt_5Ti_3, an orthorhombic structure with 32 atoms in the crystallographic unit cell). The ΔH of the lower panel have been flipped over, relative to the earlier figures, so that increased binding is upwards, reflecting the way the phase diagrams are plotted. Crudely, the ΔH track the phase diagrams with the largest binding generally associated with the highest observed melting temperatures. Note that the heats are quite large, 0.5–1.0 eV/atom.

Consider $Rh_{1-x}Zr_x$ first. The fact that the ΔH for Rh_3Zr lies above the line drawn between ΔH(RhZr) and the zero for pure Rh implies that it meets the conditions of Eqs. (1) and (2) and is predicted to be a stable compound. Similarly ΔH for $RhZr_2$ lies above the RhZr–pure Zr line so it too is predicted to be stable. The problem here is that the wrong $RhZr_2$ structure has the large ΔH. The calculated ΔH for the observed $CuAl_2$ structure is badly underestimated and this is due to its being an ill-packed structure. The calculated ΔH for Rh_2Zr, taken to be in the $MoSi_2$ structure, lies well below the line

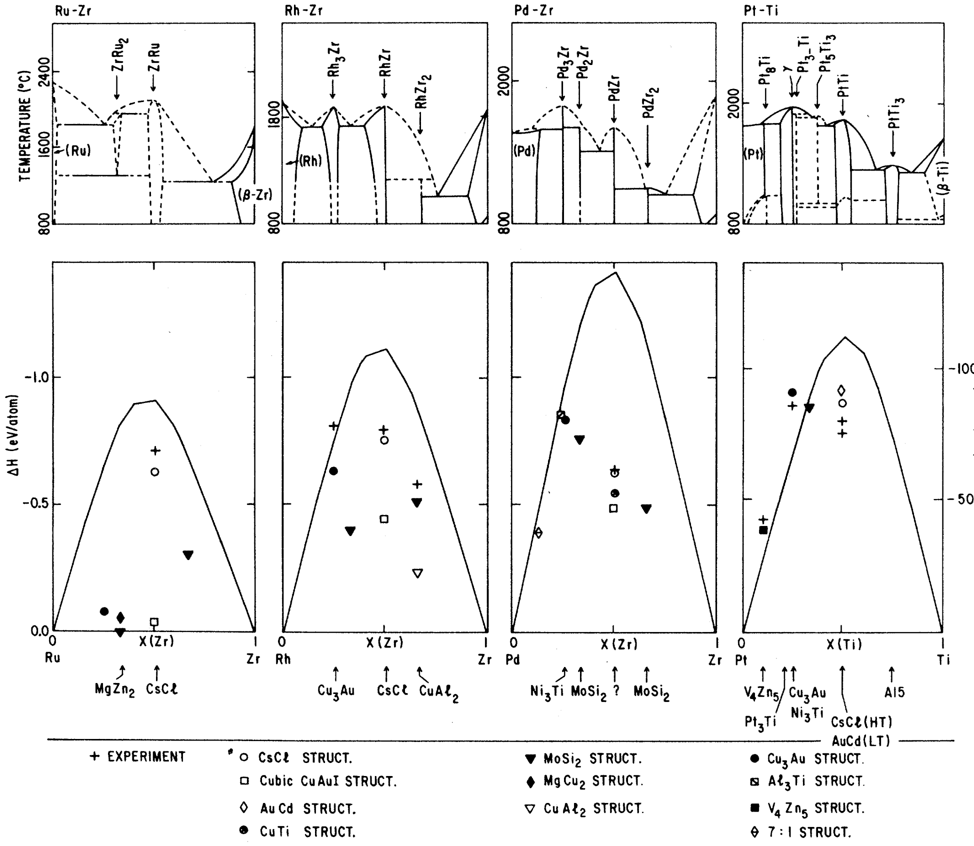

FIG. 3. Heats of formation and phase diagrams for the Ru-Zr, Rh-Zr, Pd-Zr, and Pt-Ti systems. The top panel shows tracings of the experimentally determined phase diagrams while the lower shows calculated and experimental heats for a number of compositions and structures. The solid lines are Miedema's predictions as a function of composition. Below the lower panel are indicated the structures in which the observed phases occur.

between the ΔH for Rh_3Zr and RhZr, thus it is predicted to not occur and it does not.

Consider, now, $Ru_{1-x}Zr_x$. All the non 50%-50% ΔH lie below the lines which can be drawn between ΔH(RuZr) and the zeros of the terminal phases. This is consistent with experiment since none of these calculated structures have been observed. Ru_2Zr is reported to occur as a high-temperature phase in the hexagonal Laves $MgZn_2$ structure. This system has too large a unit cell for us to deal with so, instead, calculations were done of ΔH for the cubic Laves $MgCu_2$ phase. The resulting ΔH is near zero valued and, granted the similarities in the local atomic environments in the two Laves structures, we expect it should lie higher, that is closer to a line between ΔH(RuZr) and the Ru zero. The use of muffin-tin potentials is expected to introduce some error into the ΔH of a Laves phase since these phases are not geometrically well-packed structures.

Go now to the results for $Pd_{1-x}Zr_x$. The largest calculated ΔH, for each of the Pd_3Zr, Pd_2Zr, PdZr, and $PdZr_2$ compositions, lie essentially on a straight line and this line intersects the Pd and Zr ordinates above zero. Hence each phase is calculated to be stable relative to a two-phase mix of the systems to either side of it. As a result, ordered Pd_3Zr, Pd_2Zr, PdZr, and $PdZr_2$ phases are predicted to occur and they do occur experimentally.

Perhaps the most striking feature of the Pd-Zr results is that the ΔH for Pd_3Zr is substantially larger than that for PdZr (remember that the ΔH are defined per atom, *not* per molecular unit.) At some point this trend must break because the ΔH must go to zero in the limit of a dilute amount of Zr in Pd. A calculation was done for 7:1 compound on an ordered fcc lattice. This structure does not occur but we have found it a useful artificial "dilute" structure[12] for calculating final-state hole effects associated with photoemission. Here we see that the calculated ΔH for the structure has satisfactorily bent back towards zero. At this composition, a disordered fcc Pd solution phase is observed to occur and the closeness of the 7:1 ΔH to a line between Pd_3Zr and the zero of pure Pd suggests that the disordered phase is only slightly favored over an ordered one.

Finally, consider $Pt_{1-x}Ti_x$. No attempt was made to calculate $PtTi_3$ in the ill-packed *A*15 structure with its compressed lines of Ti atoms. Mattheiss and Hamann have pointed[13] out that full potentials must be employed to get such a band structure right and our total-energy calculations[6] for the ΔH of $AuTa_3$ in this structure bear this out. We have also neglected calculations for Pt_5Ti_3 because of its uneconomically large unit cell. Similar to Pd-Zr, the Pt-Ti results show the ΔH for Pt_3Ti to be at least as large as that for PtTi. The calculations also indicate that Pt_2Ti in a likely $MoSi_2$ structure phase loses out to a two-phase mix of PtTi and Pt_3Ti and this is consistent with the fact that such a 2:1 compound is not observed.

An interesting feature of the Pt-Ti system is that an ordered, dilute Ti compound is observed to exist. This is Pt_8Ti which is a body-centered tetragonal structure with two layers, one of which is plotted in Fig. 4. A layer consists of an *almost* square lattice with Pt's in (100) and (110) positions with respect to the Ti. The coordinates x_1 and x_2 are not equal. If they were both equal to $\frac{1}{3}$ and if the ratio of the lattice constants were

$$a/c=\frac{3}{\sqrt{2}}=2.1213\ ,$$

this would then be an undistorted fcc lattice. However for Pt_8Ti, $x_1=0.327$, $x_2=0.333$, and $a/c=2.133$ so it is a slightly distorted fcc phase, with the Pt's closest in the plane to the Ti shifted in towards it as befits the fact that Ti is smaller than Pt. [The other phase reported in this structure is V_4Zn_5 with $x_1=0.348$, $x_2=0.328$, and an a/c more nearly corresponding to a bcc lattice.] Calculations were done for Pt_8Ti with the observed lattice constants and with both sets of x_i. The ΔH obtained with the reported values for Pt_8Ti is plotted in Fig. 3. It is seen to be in good accord with experiment, that is to be stable relative to a two-phase mix of Pt_3Ti and pure Pt. The calculation with V_4Zn_5's internal coordinates yielded a ΔH which was small in magnitude and nonbinding (i.e., positive). As is the case with the layered $MoSi_2$ structure discussed earlier, small deviations in atomic lattice positions from those of a uniform lattice can have substantial effects on ΔH.

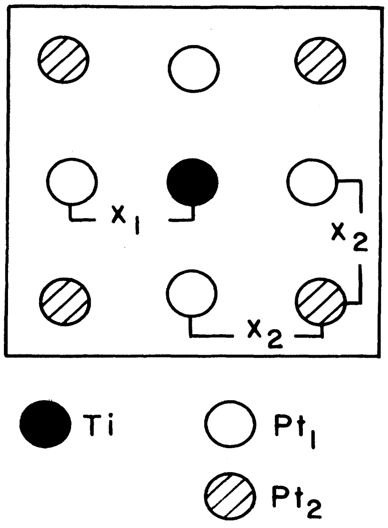

FIG. 4. One of the two planes of the unit cell of the body-centered V_4Zn_5 structure in which Pt_8Ti orders. x_1 and x_2 are internal coordinates which are approximately, but not exactly equal to $\frac{1}{3}$ due to the different sizes of the constituent atoms.

The solid line ΔH of Fig. 3 are Miedema's model predictions which show a weak skewing towards Ru, Rh and Pd in the first three panels and a weak skewing, in the wrong direction, towards Ti in the last. The variation in Miedema's ΔH with concentration is at variance with both the experimental and the presently calculated ΔH and with the phase-diagram behavior. (While it is perhaps unfair to demand it of the model, the variation in Miedema's ΔH implies simultaneously stable phases at

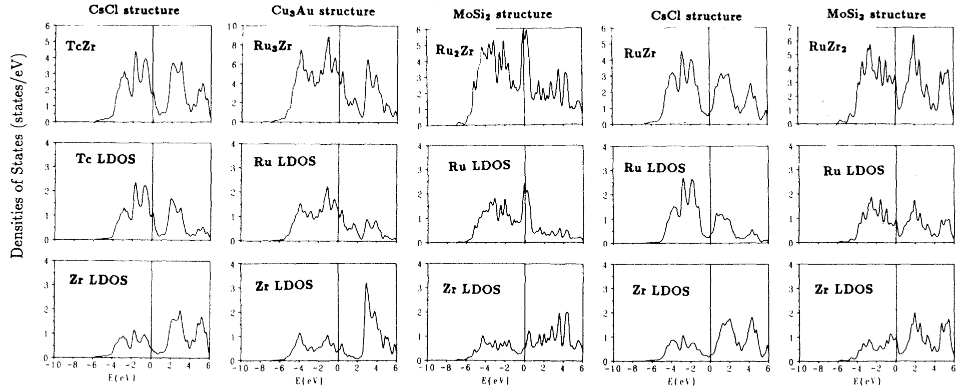

FIG. 5. Calculated densities of states for some Ru_xZr_{1-x} systems and for TcZr in the CsCl structure. The top panels are the full densities of states while the lower panels are the individual site densities of states defined by the charge within the atomic sphere in question. Note that while the vertical scale of the plots varies from case to case, the scale for any set of local density of states, appropriate to some given compound, is kept the same.

5:1, 3:1, 2:1, 1:1, 1:2, 1:3, etc.) The skewing of Miedema's ΔH is too weak for the Rh-Zr, Pd-Zr, and Pt-Ti systems, while the overall width of his ΔH peak is too great for Ru-Zr. The overall scale of his results is particularly bad for Pd-Zr.

VI. RESULTS: DENSITIES OF STATES AND SUBBAND FILLING

In Fig. 3 it was seen that the ΔH of the Pt- and Pd-rich alloys rose, or stayed level out to the 3:1 compounds while a modest drop was encountered on going from RhZr to Rh_3Zr and a severe decline was associated with the Ru-rich systems. An explanation for this is to be found in the calculated densities of states for these systems. Consider the densities of states for TcZr and for some of the Ru-Zr alloys shown in Fig. 5. The top panel displays the total density of states of a system while the lower panels are the local, individual site, densities of states defined by the charge residing in the atomic sphere around a site. In the case of RuZr, a compound with a substantial ΔH, the Fermi level falls *above* the bands having primarily Ru character. In contrast, Ru_2Zr, Ru_3Zr, and TcZr, compounds all having modest ΔH, have Fermi levels falling *within* the A atom, Tc or Ru site, bands.

It would appear that substantial ΔH occur when the hybridization of B-atom in this case Zr, wave-function character into the A-atom d-like bands is sufficient so that these bands become filled and then may *float free* of the Fermi level ε_F. (Inspection of the charge inside the atomic spheres indicates this band filling to be principally due to hybridization and not to any significant charge transfer from the B to the A atom sites.) Once no longer pinned to ε_F, these "bonding" levels adjust their position so as to maximize the binding. There has been a widely held view that large binding in transition-metal alloys occurs when there is substantial separation between the bands of primarily A and primarily B-like character and when the bonding A-like bands are filled while the B-like "antibonding" levels are empty. Requiring that large bonding is only associated with such a half-filling would imply that such bonding can only occur over a *narrow range* of alloy composition contrary to what is seen in Fig. 3. While ε_F is seen to fall in a hollow above the Ru-like and below the Zr-like bands in RuZr, cases are to be seen in Figs. 6–8 where large ΔH attend the interception

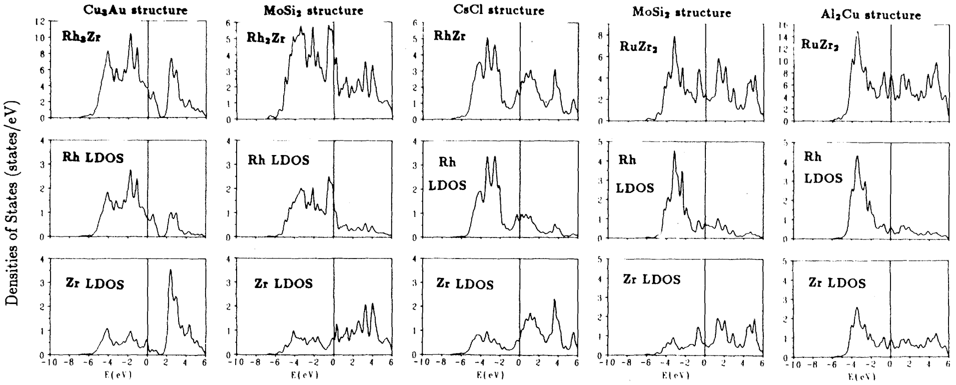

FIG. 6. Calculated densities of states for some Rh_xZr_{1-x} compounds. See Fig. 5 for more details.

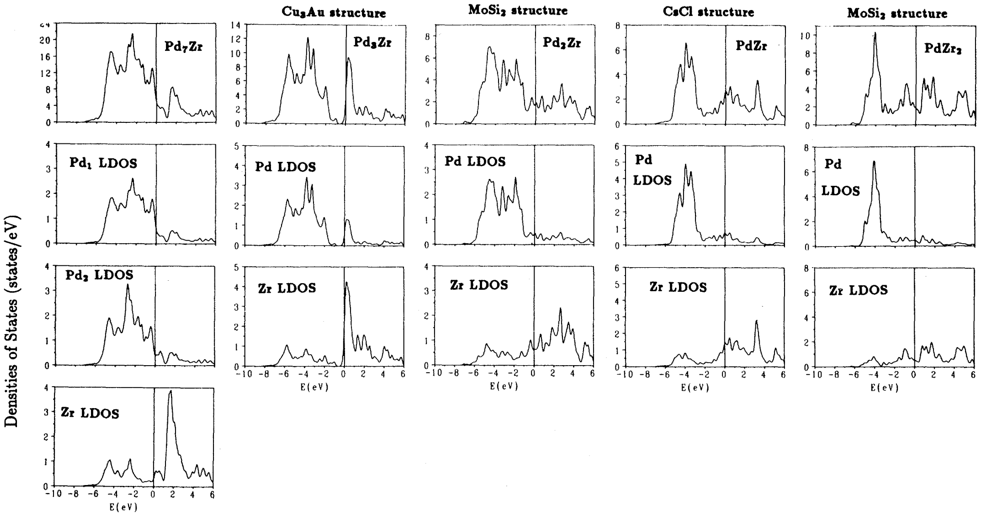

FIG. 7. Calculated densities of states for some Pd_xZr_{1-x} compounds. The Pd_1 site of Pd_7Zr is appropriate to six of the Pd's which are nearest neighbors to the Zr site while Pd_2 is a single Pd a little further away. See Fig. 5 for more details.

of ε_F with the Zr (or Ti) bands. As can be seen for RhZr in Fig. 6, ε_F intercepts the lower edge of the Zr-like bands yet the alloy has a large ΔH.

Rh_2Zr, in the $MoSi_2$ structure, has its Fermi level intercepting the upper peak of the Rh site bands and the structure has so small a ΔH that is not in serious competition as a phase. This upper peak in the A site density of states appears in Ru_2Zr, Pd_2Zr, and Pt_2Ti as well; however, in the last two cases ε_F falls above these bands and ΔH is large. The Fermi level also falls in the upper edge of the Rh bands in Rh_3Zr and here ΔH is measureably smaller than that for the 50%-50% compound though larger than ΔH for Rh_2Zr (see Fig. 3). Depending on how large one views the reduction in ΔH on going from RhZr to Rh_3Zr, one may or may not have the one case where one could argue that a ΔH of significant size has attended ε_F intercepting the A-like features of the band structure.

For the Pd-Zr and Pt-Ti systems, ε_F falls above the Pd- or Pt-like d bands for the 3:1 as well as the 2:1 compounds and large ΔH occur while Pd_7Zr and Pt_8Ti have ΔH of half the magnitude and ε_F which intercept the Pd

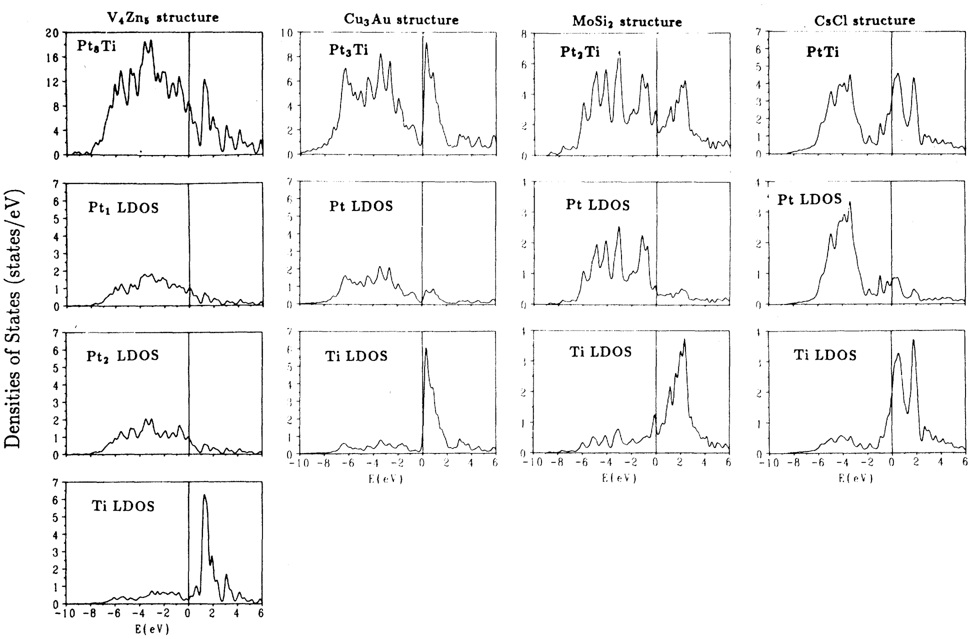

FIG. 8. Calculated densities of states for some Pt_xTi_{1-x} compounds. Pt_1 of Pt_8Ti has the x_1 coordinate, (100), position of Fig. 4 while Pt_2 has the (x_2x_20) position. See Fig. 5 for more details.

and Pt site bands.

Ti, Zr, and Hf have four valence electrons, thus the *most* that they can supply to the *A* site band filling, whether by hybridization or charge transfer, is four electrons per *B* atom. Now elemental Pt and Pd have roughly a half-electron's worth of holes in the top of their *d* bands thus if Ti, Zr, and Hf were completely "efficient," that is supplied all four of their valence electrons for such band filling, one such atom could requite up to about eight Pd or Pt atoms. Pure Rh and Ir have $\sim 1\frac{1}{2}$ *d* holes, hence a single *B* atom could fill up to something between two and three Rh or Ir atoms worth of bands. Ru and Os, having $\sim 2\frac{1}{2}$ *d* holes would have the filling saturate before going to the Ru_2Zr or Os_2Ti concentration while Tc and Re having $\sim 3\frac{1}{2}$ can barely be requited at 1:1 composition. Now Ti, Zr, and Hf are not expected to be completely efficient in this process, that is not all their valence charge will simply have the effect of filling the *A* site subbands. As a result, Tc bands in TcZr (Fig. 5) are not filled, nor are Rh in Rh_2Zr (Fig. 6). It would appear that the process is efficient enough to produce subband filling for the 1:1 Ru and Rh compounds and for 3:1 compounds involving Pd and Pt. The same subband filling, with the same trend in ΔH, has been encountered elsewhere[14] for the Nb-Pd alloy system.

VII. CONCLUSION

Twenty four systems of Ti, Zr, and Hf alloyed with the right-hand ends of the 4*d* and 5*d* transition element rows have been investigated. This has involved calculating the heats of formation of 69 compounds of varying composition and structure. These ΔH have been based on first-principles electronic structure calculations where the most significant approximation has been the use of the local-density approximation for the potential. The muffin-tin construct has also been used in the potential and its use is found to not adversely affect the ΔH calculated for well-packed crystal structures. The calculated ΔH are satisfactory in accord with experimental heats data and with observed phase-diagram behavior. In the latter case this implies that the stable compounds are correctly predicted from a number of possible compounds of differing structure and composition. This includes the correct prediction of the co-occurrence of compounds of differing composition.

While not new to the present results, one feature of the densities of states deserves noting, namely they consist of separate *d* subbands. While there is some hybridization between them, each subband has a bandwidth which reflects the number and distance to *like* nearest-neighbor atoms. For example, the subbandwidths for the 50%-50% compounds are essentially half those of the elemental metals. Over the years there has been a tendency to model the *d* bands of a transition-metal alloy in terms of a single rectangular *d*-band density of states. This is inappropriate, particularly when going off 50%-50% concentration.

The ΔH are substantial for the bulk of the 50%-50% compounds. This is not surprising for two reasons. First, electronegativity considerations suggest strong bonding since Ti, Zr, and Hf are rather electropositive metals while the elements they are being alloyed with are not. Second, the *d* bands of the compounds are roughly half-filled, thus the lower bonding half of the bands is filled while the antibonding are not. What is more surprising, is the variation in ΔH with composition. At first glance one expects ΔH to vary as $x(1-x)$, where x is the fractional composition of one of the alloy components, since this is a measure, on average, of the number of unlike nearest neighbors and hence of the bonding between such neighbors. In systems such as RuZr and OsTi, the ΔH are peaked up much more sharply at 50%-50% concentration than $x(1-x)$ would indicate. In contrast, systems such as PdZr and PtTi have ΔH, *per atom,* which are larger for Pt-and Pd-rich systems than they are at 50%-50% and this is not associated with having half-filled bands in the alloy. This skewing of the ΔH has been observed in previous calculations[15] though, to our knowledge, no explanation has been offered. Both the large ΔH for the Pd-and Pt-rich alloys, the "small" values for Ru-and Os-rich alloys and the small values for Tc and Re compounds at 50%-50% composition have an explanation suggested by the reported densities of states (Figs. 5–8). This is that large ΔH occur when the Pd, Ru, or like *d* bands in the compound are filled and thus decoupled from, falling below, the Fermi level. Charge transfer and hybridization are then allowed to better act on these occupied levels so as to maximize the bonding

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