MODELLING AND THEORIES OF ALLOY PHASE BEHAVIOR

DISCLAIMER

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ABSTRACT. It has been recognized since the early work of Hume-Rothery and others that many trends in alloy phase formation are readily understood in terms of physically plausible atomic parameters. For example, a substitutional alloy can only occur if there is not too great a difference in the sizes of the alloy constituents, so as not to require too great a cost in the elastic energy associated with deforming the lattice. This has led, in turn, to the introduction of so-called structural maps where two (or more) such atomic parameters are employed as the coordinates and well defined regions are observed to be associated with particular crystalline phases. These coordinates sometimes involve the difference in atomic parameters, such as the difference in the sizes of the constituent atoms, and sometimes involve an average, such as the average d-band occupancy of constituent transition element metals. An alternative approach to the emphasis on atomic parameters has been the consideration, as pioneered by Pearson, of how atoms are packed in some crystal structure and how this controls what the constituent atoms may be. Recently this has led to the utilization of Wigner-Seitz (sometimes called Voronoi or Dirichlet) constructs of the atomic cells in a crystal structure and, in turn, to the observation that sometimes two crystals which are nominally considered to have the same crystal structure according to normal crystallographic designation should, in fact, be considered to be different. The Wigner-Seitz cell constructs have also offered a framework for understanding trends in the magnetic and chemical properties of particular phases as well as making coordination between crystalline and glassy structures. Neither of the above approaches--correlations with atomic parameters or with packing considerations--provide numerical estimates of quantities of thermodynamic interest such as heats of formation. Such heats are being calculated with varying rigor and varying computational complexity ranging from model Hamiltonians employing atomic parameters to intricate electron band theory calculations. This chapter will attempt to provide the reader

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with a sense of some of successes and some of the problems when employing the above approaches to trace out trends in alloy phase behavior. Because of space limitations, this review will be highly selective.

I. ATOMIC PARAMETERS AND STRUCTURAL MAPS

For the most part, the elemental solids form in crystal structures which correlate with the number of their valence electrons. For example, neglecting the magnetic solids, the sequence

occurs upon traversing the transition metal rows. With one modification:

describes transition metal alloying, provided that strong compound formation does not occur upon alloying, and the average d-band occupancy determines the crystal structure which occurs. Here tcp refers to the topologically close-packed structures, such as the $\text{Al}_5(\text{Cr}_3\text{Si})$, σ and αMn phases, the first two being Frank-Kasper phases of which more will be said in the next section. These tcp phases have atomic sites in polyhedral environments which do not lend themselves to the planar stacking of atoms and hence the systems are not ductile. This is important in high strength steels and superalloys since these tcp phases compete for the refractory transition metal alloy components, such as V, Mo and W. The atomic sites have different numbers of nearest neighbors and hence are of different size, i.e. differences

Fig. 1 The phase diagram of the Mo-Ir system.

Fig. 2 A Darken-Gurry mapping of the elements with a solubility in either of the allotropic phases of iron greater or less than an arbitrarily chosen value of 5 atomic percent (ref. 3).

in atomic size of the constituent atoms are important to the formation of these phases. The α Mn structure is closely related to, while not being¹ a Frank-Kasper phase. It too has sites of different size which accommodate Mn atoms of differing magnetic moment (Mn atoms with substantial magnetic moments have much larger volumes than do those with near zero moments). The Mn atoms in the α (and β) Mn structure(s) may truly be said to be forming alloys where it is alloy components of differing magnetic moment, rather than differing nuclear charge, which are involved. Sequence (2) is to be seen in the Mo-Ir phase diagram² illustrated in Fig. 1. Here one goes from bccMo $\rightarrow$ tcp $\rightarrow$ hcp $\rightarrow$ fccIr. Note that DO₁₉ structure is simply a (111) ordered atomic restacking of an fcc lattice where the Mo enters the Ir substitutionally in the terminal fcc phase.

While the average valence electron count may be important to what phase occurs, the ability to form a substitutional alloy requires that there neither be too great a difference in atomic size nor too great a strength of chemical bonding between the solute and the solvent, for otherwise ordered compounds are favored. This has led to the implementation of Darken-Gurry plots where one coordinate is the atomic radius and another the electronegativity--the idea of the latter being that a large electronegativity difference implies strong bonding. Such a plot, as obtained³ by Waber et al. for Fe as the solvent, appears in Fig. 2. Here almost perfect separation is obtained between

Fig. 3 A Darken-Gurry-type solubility map for impurities in Cu employing elemental Wigner-Seitz radii and calculated heats of solution as the coordinates (ref. 4). Note that three ranges of solubility have been differentiated here as contrasted with the two of Fig. 2.

Fig. 4 A map differentiating ready glass formation in metallic alloys where one coordinate is the heat of mixing and the other, the ratio of small atom's to the larger's atomic radius (ref. 5). Glass formation is generally favored providing $\Delta H_m < -5$ Kcal/mole and the radius ratio is less than ~ 0.86 .

those alloys having more and those less than 5% solubility as defined by an ellipse with its principle axes parallel to the map coordinates. Lopez and Alonso have considered such solubility maps where the electronegativity coordinate has been replaced by the heat of solution and their result⁴ for Cu alloys is shown in Fig. 3. Here they consider three ranges of solubility, against the two in Fig. 2, and obtain reasonable separation with roughly elliptical boundaries whose axes, however, are no longer parallel to the map coordinates.

Fig. 6 A structural map for ANB_8-N octet compounds, having eight valence electrons per molecular unit, employing combinations of effective orbital radii, the abscissa effectively being a measure of relative s versus p bonding and the ordinate an electronegativity difference (ref. 8).

and in turn defined the maximum of an effective radial orbital

$$r_{\ell} \equiv \hat{\ell}(\hat{\ell} + 1)/Z. \quad (4)$$

Employing s and p r_{ℓ} they obtained the structural map shown in Fig. 6 for the so-called octet compounds formed of main group elements where the sum of the constituent's valence electrons equals eight. There is good separation between the various structures. Note that the abscissa involves the average of the elemental $(r_p - r_s)$ while the ordinate involves the difference in $(r_p + r_s)$.

One problem with the atomic parameters employed in such mappings is that they are not unrelated to one another. For example, in defining the chemical potential in terms of a single parameter for a metallic system that parameter would be the electron density in the interstitial region. The failure of the points in Fig. 5 to lie on a single smooth curve is a measure of the failure of such an oversimplified description of chemical potentials and the deviations from such a curve are presumably primarily due to crystal potential effects.

When dealing with maps for transition metal alloys it proves useful to employ one coordinate which is a measure of the d-band occupancy. Since the top of the d bands are more easily defined than the bottoms, which are heavily mixed with s-p character, we've found it

Fig. 7 The occurrence and nonoccurrence of transition metal AB_2 Laves phases as a function of the volume ratio $[V(A) + \Delta V]/V(B)$ and the average alloy d-band electron hole count (calculated at 1:2 composition). Open circles denote $MgCu_2$ phases, solid circles the $MgZn_2$ and half-circles when both occur. The x's indicate cases for which Laves phases have not been reported (ref. 9).

useful to define the occupancy in terms of the d hole count, $\bar{N}_h$, which is the number of unoccupied states per atom between the top of the d bands and Fermi level. Using the weighted average of the constituent atom's d hole counts, $\bar{N}_h$, as one coordinate, for the 1:2 AB_2 transition element-transition element alloys, a structural map⁹, sampling whether these compounds do or do not form in Laves structures appears in Fig. 7. The second coordinate is a measure of the volume difference between atoms A and B. A volume difference is to be expected because the Laves phases are Frank-Kasper structures with markedly different site volumes at the two species of atomic sites. Now it so happens that these structures form with a molecular volume which is smaller than the sum of the elemental volumes, i.e. ΔV is negative where

$$\Delta V \equiv V(AB_2) - V(A) - 2V(B) \quad (5)$$

In the map this volume contraction has been attributed to the A atom which is larger, sloshier and more electropositive than the B. The x's in the plot denote cases where either an AB_2 compound of different

Fig. 8 Ranges of effective d-band hole count associated with binary non-Laves tcp phases of the transition metal alloys, except those of Mn (ref. 10). To the right are shown the ratios of the elemental metal volumes (the A atom is to the right and the B atom to the left in the alloy labels and in the periodic table). The dashed lines indicate a range $1.2 < V(A)/V(B) < 1.4$ in which tcp phase formation appears to be especially favorable.

symmetry occurs or no compound of such composition has been reported. There is an extraordinary division between the Laves and non-Laves regions with rectangular bounds which contrast with the elliptical bounds seen in some of the earlier figures. The x's within the bounds

are for systems where no compounds of AB_2 composition have been reported (and where Laves structures might well occur).

Equation 2 suggests that there may be a range of N_h in which the $t\bar{c}p$ phases, other than the Laves structures occur. This is the case¹⁰ and a plot of the range of N_h for which this happens appears in Fig. 8. The elemental hole counts inferred from energy band calculations (and employed in Fig. 7) have been adjusted so as to provide a better defined range of N_h . The main feature of this adjustment is to make the Ti, V and Cr columns of the transition elements more alike than they truly are (see Fig. 4 of Ref. 10 for a plot of the adjusted values versus their band theory counterparts). The $t\bar{c}p$ alloys occur with a varying range of N_h implying a varying range of stoichiometry since

$$\bar{N}_h(A_{1-x}B_x) \equiv (1-x)N_h(s) + xN_h(B) . \quad (6)$$

The ratios of the elemental volumes are plotted to the right. When a compound's ratio falls in the favored region, indicated by the dashed lines, it tends to have a wide range of N_h and also FeTc and FeRe with their apparently unfavorable N_h do have volume ratios in the "favorable" regime. A wide range in N_h arises in two ways: there may be more than one $t\bar{c}p$ phase involved but also there may be a range in stoichiometry in a given phase. A range in stoichiometry implies substitutional disorder, i.e. A atoms on B sites, or vice versa, or alternatively the introduction of vacancies. From Fig. 8 it would appear that such a range of stoichiometry is more likely when the relative sizes of the constituents is "right." Note that this favored region is not centered on a volume ratio of one.

There have been many mappings of compounds of the main group elements, of the transition elements and between main group and transition elements. With well chosen coordinates, maps with two coordinate provide reasonable separation between structures. Of recent interest is the work¹¹ of Pettifor where he has defined an effective Mendeleev number for the elements where they are ordered according to chemical properties rather than nuclear charge. Using this quantity as both coordinates he has generated a two-dimensional map for the 1:1 compounds. The region involving the octet compounds of Fig. 6 shows similar good separation. One of the less successful regions includes the transition element-transition element systems and this is replotted in Fig. 9 using more recent crystallographic data¹² than was available to Pettifor (leading to changes in assignments of crystal structures for a few systems). Also, when more than one crystal structure was reported for some system, both are indicated in Fig. 9 without any attribution as to which is the most stable. Certain of the structures are associated with well defined regions of the map while others, such as FeB (the open diamonds) are scattered across it. There is one problem associated with structure attributions which deserves mention here. Consider the CsCl and CuAuI crystal structures which consist of alternate (100) layers of A and B atoms on the bcc

Fig. 9 A segment of the Pettifor map of 1:1 structures

and fcc lattices respectively. One structure can be taken into the other respectively by a tetragonal distortion: tetragonally distorting the CsCl structure until its c/a ratio equals $\sqrt{2}$ yields the cubic form of CuAuI. Now TiRh, TiIr and TaRu, which lie on the edge of a CsCl region in Fig. 9, have c/a , in the sense defined above, between 1.12 and 1.14, much closer to the c/a of 1.0 characteristic of CsCl than that of cubic CuAuI. Therefore, while they have the tetragonal symmetry characteristic of CuAuI (the 100 layering gives it tetragonal symmetry even if its three lattice vectors are equal), rather than the cubic of CsCl, the three compounds might be better considered to be bcc-like rather than fcc-like as implied by the CuAuI label. More will be said concerning this in the next section.

There has been considerable two-dimensional mapping of structures at 1:1 and other compositions which space does not allow to be reviewed here. These usually involve distinctly different parameters for the two coordinates and usually do better¹³ than what is seen in Fig. 9. However, Pettifor's mapping with but a single intrinsic parameter, the effective Mendelev number, is remarkable in how well it does.

One recent mapping effort deserves mention before leaving this section. There has been considerable interest in icosahedral phases which are neither crystalline nor glassy, having long range orientational but no long range periodic order. A number of these icosahedral phases involve ternary systems which also form in topologically close-packed crystal structures, such as $Al_6Mg_{11}Zn_{11}$. While there is some question as to whether the local atomic environments are the same in the crystalline and icosahedral phases, the occurrence of both led Villars and coworkers to construct¹⁴ a structural map for these crystalline phases, the intent being to identify other systems which might order icosahedrally. Villars et al. found it necessary to employ a six-dimensional map in order to isolate the structure of interest and this, in our view, is unsatisfying. On the other hand, it would appear the mapping has provided a promising set of candidates to be scanned for icosahedral ordering.

II. CRYSTAL STRUCTURES AND WIGNER-SEITZ CELLS

Instead of considering atomic parameters and what crystal structures correlate with particular ranges of these parameters one can, instead, consider the crystal structures themselves. One can, for example, consider the packing of hard spheres in some structure, observe what spheres touch and how this touching changes as the lattice is distorted. Using such observations, over the years, Pearson has provided¹⁵ considerable insight into the circumstances under which particular phases occur.

In a tour de force, Frank and Kasper observed¹⁶ several systems where atoms were packed in particular twelve, fourteen, fifteen and sixteen-fold nearest neighbor environments and they then asked what crystal structures could be formed by the packing of such environments. This led to the definition of a number of hypothetical crystal

Fig. 10 Some Wigner-Seitz (i.e. Voronoi or Dirichlet) polyhedra appropriate to atomic sites in various crystal structures. The (0,0,12,0) and (0,0,12,4) are two of the four Frank-Kasper polyhedra while the (0,3,6,0) is one of the Bernal environments. See text for a definition of the labels.

structures, some of which have been subsequently seen and some of which may well exist though they have yet to be reported. These Frank-Kasper structures include the Laves, σ and $\text{Al}_5(\text{Nb}_3\text{Sn})$ phases and constitute a major class of crystal structures which are important to transition metal alloy formation.

Implicit in the above discussions is the question of what sort of local environment does a crystal structure provide a particular atomic site--how many nearest neighbors does the site have, what is the site symmetry and how many nearest neighbors are shared by a nearest neighbor pair? This question can be addressed by constructing Wigner-Seitz (or Voronoi or Dirichlet) atomic cells. In doing this, one wishes cell boundaries where the planes separating adjacent cells are positioned in proportion to the atomic radii of the atoms concerned. A clever, computationally efficient, algorithm has been devised^{17,18} for this which involves identifying the corners of the polyhedron. Some sample Wigner-Seitz polyhedra, encountered in crystal structures appear in Fig. 10. Here the notation (a,b,c,d,...) indicates that there are a faces with 3 edges, b with 4, c with 5, d with 6, etc. where the number of edges, of course, indicates how many nearest neighboring sites are shared by the nearest neighbor pair responsible for the face. The Frank-Kasper phases involve two or more of the (0,0,12,0) and (0,0,12,4) which are shown and the (0,0,12,2) and (0,0,12,3) which are not. The (0,3,6,0) [along with the (0,2,8,0) and (0,4,4,0) which aren't shown] are environments originally defined by Bernal as the interstitial sites in glasses but which are common to small atom sites, such as boron, in many crystal structures.

For some years there has been the question of whether αMn is a Frank-Kasper phase. The structure has 58 atoms in a unit cell in four different types of sites. Recently Wigner-Seitz cell constructs have shown¹ these to be (0,0,12,4), (0,0,12,4), (0,0,12,0), which are of the Frank-Kasper type and (0,1,10,3) which, with its four-fold facet, is not. Inspection of its Wigner-Seitz cells thus indicates that αMn is not a Frank-Kasper phase though it closely resembles them. Now Frank and Kasper originally designated their structure as "topologically close-packed." We think it appropriate to extend the tcp designation to structures, such as αMn , which share so many common features.

Pearson has employed¹⁹ Wigner-Seitz cell constructs in order to resolve a more general crystallographic complication. There are many situations where systems, nominally having the same crystal structure, have such different c/a ratios or such different internal coordinates (which define exactly where atoms lie in the unit cell) that the local atomic environments are quite different, so that while the systems have common symmetry they have different bonding neighbors, hence different chemistry. Such a case arose concerning TiRh, TiIr and TaRu and Fig. 9. These systems are nominally in the CuAuI structure, which being a layered stacking of the fcc lattice would seem to imply 12 nearest atomic neighbors to each site. However, the c/a ratios of these compounds suggests that they are weakly distorted CsCl structures and that Wigner-Seitz cell constructs would indicate fourteen nearest neighbors which is characteristic of bcc lattices (such as CsCl's). Pearson has argued that in cases such as these, the symmetry designation incompletely defines the structure and that it is meaningful to make a more complete designation. We agree.

One traditional approach to the question of where the atoms are in a glassy solid has been the "quasicrystalline" model where the atoms in a glass are presumed to have the local environments encountered in the glass's crystalline counterpart. [The term "quasicrystal" has also been applied to the recently discovered icosahedral phases, but its usage here, for glassy environments, long predates this.] While it is unclear experimentally as to the extent that it's true, this view led to the inspection²⁰ of the crystalline transition metal rich-metalloid phases for those phases having "disorderly" structures. By disorderly we mean that the metal finds itself in a number of quite different local environments, implying a complicated radial distribution function (when averaged over the different sites). The inspection indicated that disorderly crystal structures tended to correlate with the ready occurrence of glass formation and the scan suggested some systems, which had hitherto not received much consideration, as ready glass formers. Further, it has been observed that the Ni rich-P glass system is polymorphic, that is, there are two distinct glasses at the same concentration, with distinct local structural configurations, whose occurrence depends upon how the glass is made. It has been also observed²¹ that Ni rich-P systems form in crystalline phases where the P has distinctly different environments, one being of the Bernal type and others, which occur in $Ni_{12}P_5$, are not. This can be seen in Table 1. In addition, NMR and atomic density information make it possible to associate a particular crystalline environment with a particular glass. These observations suggested scanning other transition metal-metalloid systems for other cases where polymorphism might be favored. This has been done²¹ for the phosphides, silicides and borides of the magnetic 3d elements as listed in Table 1. For the most part, the metalloid sites in the phosphides and borides take the form of the (0,4,4), (0,3,6) and (0,2,8) Bernal environments and of these only Cr-B looks like a contender for polymorphism. Quite different metalloid sites (implying quite different bonding?) occur for the silicides. Here all but Co-Si look like candidates for polymorphism with Ni-Si the most likely. It

Table 1

Voronoi polyhedra for the metalloid site in transition-metal rich phosphides, silicides and borides

Ni ₃ P	(0.3.6)	Ni ₃ Si	(0.12.0)	Ni ₃ B	(0.3.6)
Ni ₁₂ P ₅	(0.3.8),(0.4.8)	δNi ₂ Si	(0.4.4.5)	Ni ₂ B	(0.2.8)
Ni ₂ P	(0.3.6)	θNi ₂ Si	(0.6.0.5)	mNi ₄ B ₃	(0.3.6)
		Ni ₂ Si ₂	(1.4.4.5.1) etc	oNi ₄ B ₃	(0.3.6)
Co ₂ P	(1.2.5.3)	Co ₂ Si	(0.5.2.8)	Co ₂ B	(0.3.6)
				Co ₂ B	(0.2.8)
Fe ₃ P	(0.3.6)	Fe ₃ Si	(0.6.0.8)	Fe ₂ B	(0.3.6)
εFe ₂ P	(0.3.6)	Fe ₂ Si ₃	(0.2.8.1)	Fe ₂ (B,P)	(0.3.6)
Fe ₂ P	(0.3.6)			[Fe ₂ B ₂ P]	(0.3.6)
				Fe ₂ B	(0.2.8)
Mn ₃ P	(0.3.6)	Mn ₃ Si	(0.6.0.8)	Mn ₄ B	(0.4.4)
Mn ₂ P	(0.3.6)	Mn ₂ Si ₃	(0.2.8.1)	Mn ₂ B	(0.2.8)
		Mn _{0.815} Si _{0.185}	(0.0.12),(0.0.12.2)		
Cr ₃ P	(0.3.6)	Cr ₃ Si	(0.0.12.0)	Cr ₂ B	(0.2.8)
		Cr ₂ Si ₃	(0.2.8),(0.2.8.2)	Cr ₂ B ₃	(0.2.8)
					(0.8.0.2.2)

might be noted that the "different" sites tend to crop up when 5:3, 12:5 or 3:2 crystalline phases occur, i.e. the very occurrence of such phases suggests the likelihood of polymorphism.

As already noted, an atomic environment as measured by the Wigner-Seitz construct not only counts the number of atoms in the nearest neighbor shell but also the number of nearest neighbors common to a nearest neighbor pair. Having 6 as compared with, say, 5 such neighbors will generally imply that the neighbors are spread out further radially from the bond line and thus, other things being equal, the two atoms on the bond line will lie closer together. Both the closer proximity and the sharing of more common neighbors should affect the chemical and magnetic coupling between sites. Frank and Kasper termed the 6-fold lines "major ligands" but granted the usage of the word ligand in chemistry they might be better termed "major ligates" or "major ligand lines" (and the 4-fold "minor" ligand lines). Nelson observed²² that these may usefully be viewed as disclinations, that is as -72° disclinations introduced into icosahedra in a higher order space which is then projected down into three dimensions. Now the packing of equal sized atoms around a bond line is equivalent to packing regular tetrahedra with a common edge. It so happens that one can pack a noninteger number, five and a fraction, of such tetrahedra hence geometric considerations frustrate such packing. Nelson observed that the average number of common nearest neighbors in a Frank-Kasper structure comes very close to this noninteger number. Thus, the packing in this class of structures acts to relieve the frustration. It has also been shown²³ that the examination of such nets of disclinations offers insight into the supersymmetry associated with the three-dimensional space-group representations of centered crystals which have nonunique asymmetric units in their descriptions.

The new classes of 3d-rare earth hard magnets, with their "square" hysteresis loops of large area, tend to be tcp phases (though not strictly Frank-Kasper phases). There are important nets of major ligand lines in these systems which can be related to their magnetic

Fig. 11 The major ligand line (disclination) network in the Frank-Kasper A15 crystal (such as Nb_3Sn). Displayed is the cubic unit cell with only the majority, larger, atoms (2 per face) shown. The minority, smaller atoms are not shown and lie at the corners and the body center of the cube. The disclinations form separate chains parallel to the x, y and z axes. Here four atoms are shown for each of the chains on the near faces of the cube, the center two of each four being associated with the unit cell: the outside two lie in adjacent cells. The chains involve (0,0,12,2) Wigner-Seitz cells where the two disclinations connect a site to the neighbors on the chain. These cells are severely distorted, being compressed along the chain and quite large radially, normal to the chain. The small atom sites (not shown) have (0,0,12,0) cells and hence no disclinations.

magnetic properties²⁴⁻²⁶. In these magnets the 3d elements carry most of the magnetic energy while the rare earths are responsible for the anisotropy which is so necessary if these are to be useful magnets. It has been observed²⁴ that those 3d sites having the largest local magnetic moments lie on these major ligand lines and this has led to a search²⁵ for other structures, having transition metal atoms on such lines, which might be suitable hosts for hard magnetism. The disclination lines also serve²⁶ to define the crystal field axes at the rare earth sites and hence the rare earth anisotropies. One suspects that superconducting properties can sometimes be usefully related to disclination nets as well. Consider the A15 structure to which Nb_3Sn belongs. It is a Frank-Kasper structure with the disclination lines sketched in Fig. 11. These lines consist of separate chains of closely spaced atoms parallel to the x, y and z axes separately and, for years, these chains have been considered an essential feature of the superconductivity of these materials. However, second only to the A15's among traditional superconducting compounds are systems such as $\text{NbC}_x\text{B}_{(1-x)}$ which form in the NaCl structure which has no such ligand lines. The situation for the new high T_c superconductors is unclear.

The existence of an intimate relationship between magnetism, superconductivity and chemical activity was emphasized by B. T. Matthias over the years, i.e. one compound might be active in one

way and it or a near neighboring compound active in another. There are even some correlations²⁷ between catalytic activity and bulk magnetism. What has been suggested here is that in systems having Frank-Kasper or tcp structures, the major ligand lines seem to have a relevance to magnetic, superconducting and chemical properties; 5-fold bond lines predominate and there are relatively sparse, chemically important major ligand lines. This view breaks down when going to lower coordinated systems where 4-fold minor ligand lines tend to predominate as in covalently bonded compounds. Therefore, while Wigner-Seitz constructs may be a useful tool in our overall understanding of crystal structures and how they form, tracing the major ligand lines may be of much less universality in its usefulness. This issue remains to be charted.

III. PREDICTIONS OF ALLOY HEATS OF FORMATION

Structural maps employing atomic parameters and observations concerning the atomic packing associated with some crystal structure may provide insights into the occurrence of particular phases in particular alloy systems but they do not provide numerical estimates of the thermodynamic quantities underlying the relative stabilities of the competing phases. It so happens that the difference in energy between such phases may be as small as 10^{-8} the energy of an individual phase. Individual energies are not calculated to such an accuracy but it is often possible to calculate separate total energies to a sufficient common accuracy that the resulting calculated energy difference between phases is of the requisite accuracy. There is a wide range in the intrinsic accuracy of the calculated heats of formation published in the literature and an even wider range, of the order of 10^7 , in the scale of the computational effort--ranging from hand calculator efforts to hours on a supercomputer.

Obviously one employs the easiest means when it works but often at the cost of also employing such means to cases where they are unreliable or even yield wrong results. One of the "best buys" because of its computational simplicity is the model Hamiltonian of Miedema's which employs⁷ as parameters the variables in Fig. 5. Slightly more complicated is the d-band bonding model of Pettifor²⁸ and Varma²⁹ for transition metal alloys where both the elemental metals and compounds are given rectangular electron densities of state. Here the essential parameters are the elemental band centers of gravity, the band widths and the extent of band occupancy. This scheme has been used³⁰ as an interpolation scheme for the 1:2 alloys with the band parameters adjusted to fit experimental thermodynamic data (just as Miedema's parameters were adjusted to yield agreement with alloying trends). The results are superior to Miedema's as they should be since they were developed and applied to a much smaller set of alloys. Neither approach deals properly with the structure of the phases--the numerical successes, such as they are, of the methods relying on smooth trends in structural behavior across sequences of systems. There is a whole array of more rigorous approaches to alloy

heats, one being the approach of Colinet and coworkers discussed elsewhere in these proceedings. In the remainder of this section we will consider several of the assumptions and approximations common to some of the more rigorous quantum mechanical estimates of the total energies in solids followed by three sample sets of results, of the authors, to provide some sense to the current level of success.

Electron band theory employs a one-electron crystal potential and solves for one-electron eigenvalues and eigenfunctions in this potential. These states are then occupied in increasing energy until the proper number of states, per atom, is accommodated in the crystal. This defines the Fermi energy, ϵ_F . From these occupied eigenfunctions a charge density and, in turn, a potential may be generated and the process iterated. In doing this, a common potential is used for occupied and unoccupied levels below and above ϵ_F . This works for electron states which are sufficiently delocalized, having only a small fraction of their probability at an individual atomic site. Such a band theory is not appropriate when there are partially occupied sets of localized levels such as the open 4f shells of the rare-earth elements. This does not appear to be an issue for the metals of concern here.

Of the approximations normally employed in band theory calculations, there is one intimately coupled to the above assumption. It is the utilization of local density potentials. In such a potential, interelectron terms other than the direct Coulomb interaction are taken to depend on the density of all electrons at that point in space where the electron sampling the potential is located. Now exchange and correlation effects are inherently nonlocal in nature but Hohenberg, Kohn and Sham have shown³¹ that this local density approximation is the correct leading term in an effective potential in which one-electron equations are to be solved when describing the ground state properties (which include the total energy) of a system. There is yet to be a consensus as to the correct leading correction term, to be used in computations to this local density potential.

Now solids were considered shortly after the advent of quantum mechanics and it was recognized that there are two regions in a solid, one in the vicinity of an ion core where the potential is essentially spherical (and which is most important to the total energy) and the other in the interstitial region between ion cores. It was only natural to mentally draw spheres around the cores. For ordered crystalline solids, of concern here, these spheres are ordered in periodic arrays, the electronic wavefunction is periodic and in reciprocal space the pseudomomentum, k , associated with individual one-electron states is a good quantum number. It is then natural to divide the solution of the problem into two parts, one involving the spheres and the other the region between. There are three obvious choices for sphere size:

- One, shrink the spheres down to the sizes characteristic of the atomic cores and orthogonalize the interstitial wavefunctions, such as plane waves, to the atomic cores. The orthogonalization introduces terms into an effective one-electron potential

- which will, in general, cause it to depend on the angular momentum, ℓ , of the wavefunction even if the bare potential is universal. The orthogonalized plane wave, OPW, and pseudopotential methods fall under this choice and the coordinates of Fig. 6 are closely related to such methods.
- Two, expand the spheres so that, on average, they fill space. Thus some space will be twice occupied and an equal volume will be unoccupied. Then solve the quantum mechanics equations carefully inside the spheres. The interstitial region has been put out of existence. The augmented spherical wave, ASW, method is an example of such a scheme.
- Three, expand the spheres so that they touch, or almost touch. Solve the equations carefully inside the spheres and match these solutions to wavefunctions constructed from combinations of plane waves, or gaussians, or exponential functions etc. in the interstitial region. The APW, KKR, LAPW, LASTO, etc. methods do this.

The above methods involve solving one-electron equations which have been derived variationally for the many-electron system and the starting point is usually a common one-electron type of potential which will be described below though it may look different if turned into a pseudopotential.

Traditionally only the spherical term in the potential is included when integrating for one-electron wave functions in the atomic spheres and only a constant term--a "muffin-tin" potential is employed in the interstitial region. "Full potential" calculations are increasingly being done where aspherical terms are included within the atomic spheres and the interstitial potential, with its "ruffles", is treated realistically. This is particularly important when the atomic sites have low symmetry, such as at a surface or interface, or when a structure is ill-packed with an unusually large fraction of the crystal volume in the interstitial region. The cost in computing time may be as much as an order of magnitude on going from muffin-tin to full crystal potentials. Of course, the above mentioned ASW method avoids the computational effort associated with the interstitial region by having none. As will be seen shortly, the ASW method sometimes yields heats of formation which are in accord with calculations dealing explicitly with the interstitial region but this is not always the case.

Other physical approximations are made in the course of band theory calculations: the core electrons are or are not included in the self-consistent process and relativistic one-electron equations are or are not solved. Numerical approximations are also made since there are expansions in reciprocal space and in spherical harmonics which must be truncated somewhere: e.g., while there may not be g-like ($\ell=4$) bands in a solid, there are g-like components in the charge density at a site which may be viewed as being associated with the tails of orbitals centered on adjacent sites. These high ℓ charge components can be significant³².

One motive for calculating heats of formation is to augment our thermodynamic data base, particularly for metastable phases which are

inaccessible experimentally. There are, for example, phases which appear in ternary systems but not in the binaries forming their bounds yet it would be desirable when constructing the ternaries to have thermodynamic data for the binaries. This, of course, raises the question of whether the thermodynamic parameters entering a particular phase diagram construct are, in fact, strict thermodynamic quantities or, instead, effective parameters whose values depend, in part, on the model employed in the construct. Consider Fig. 1 with its terminal solution phases. In most constructs, the energy for the fcc terminal phase is taken to be

$$\begin{aligned} E(\text{Mo}_x\text{Ir}_{1-x}) &= (1-x)E(\text{fccIr}) + xE(\text{fccMo}) \\ &= (1-x)E(\text{fccIr}) + x[E(\text{bccMo}) + \Delta E(\text{bcc} \rightarrow \text{fccMo})] \end{aligned} \quad (7)$$

where ΔE is the structural energy difference involved in promoting bccMo into the fcc structure. Equation 7 neglects the loss or gain in energy associated with the fact that solute and solvent atoms are neighbors and bonded to one another. The intermediate hcp solution phase of Fig. 1 would be similarly treated, i.e. at 1:1 we require

$$\begin{aligned} \frac{1}{2} \Delta E(\text{bcc} \rightarrow \text{fccMo}) &> \frac{1}{2} \Delta E(\text{bcc} \rightarrow \text{hcpMo}) \\ &+ \frac{1}{2} \Delta E(\text{fcc} \rightarrow \text{hcpIr}) < \frac{1}{2} \Delta E(\text{fcc} \rightarrow \text{bccIr}) \end{aligned} \quad (8)$$

for the hcp phase to be stable relative to a bcc or fcc phase at this composition. The implication from the left hand inequality is

$$\begin{aligned} [\Delta E(\text{bcc} \rightarrow \text{hcpMo}) - \Delta E(\text{bcc} \rightarrow \text{fccMo})] + \Delta E(\text{fcc} \rightarrow \text{hcpIr}) \\ = \Delta E(\text{fcc} \rightarrow \text{hcpMo}) + \Delta E(\text{fcc} \rightarrow \text{hcpIr}) < 0 \end{aligned} \quad (9)$$

and granted that the second term is positive, since fccIr is stable, this would imply that hcpMo is to be more stable than its fcc counterpart. For twenty years it has been recognized³³ that the structural ΔE found applicable to equations such as (7) in phase diagram constructs are much smaller than the ΔE resulting from band theory. This issue has become impossible to overlook with the recent generation of band calculations. The problem is illustrated in Fig. 12 for the hcp-fcc structural energy differences. The solid line depicts the values³⁴ of Kaufman and Bernstein standardly used in phase diagram constructs and the dashed line indicates ASW band theory results³⁵ of Skriver plus muffin-tin potential results of the present authors (here the two band theory treatments yield identical results). There is an order of magnitude discrepancy in the two sets of ΔE and a disagreement in sign for Ta and W implying no intermediate hcp phase, (which occurs for W-Ir as well as Mo-Ir, though not for Ta-Ir) within the

Fig. 12 fcc-hcp structural energy differences for the 5d transition element metals Lu through Au. The open circles are Skriver's ASW predictions (ref. 35) and the filled circles muffin-tin potential results of the authors. The solid line is Kaufman and Bernstein's estimate (ref. 24).

assumptions underlying Eq. 7. There have been several reconsiderations^{36,37} of the experimental thermodynamic data with emphasis on the bcc-fcc energy difference for W. These suggest that larger structural ΔE , than those traditionally used, are consistent with experiment though the "best" values are perhaps as much as a factor of two smaller than the band theory estimates. This issue remains to be resolved.

The heat of formation of a compound involves the difference between the enthalpy of the compound and the weighted average of those for the elemental solids. Now for the transition and noble metals, the elemental solids are close-packed systems and one might expect that an accurate heat of formation can be calculated if the compound is similarly close-packed. That this is the case is suggested for the Au-Hf systems in Fig. 13. The top panel shows the phase diagram while the bottom displays heats of formation obtained with local density muffin-tin potential calculations. Calculations were done for AuHf in both the CsCl and CuTi structures³². While CsCl involves alternate (100) layers of Cs and Cl atoms in the bcc lattice, CuTi involves a double stacking, first two (100) layers of Cu and then two of Ti in the same bcc lattice. The calculations correctly predict the CuTi structure to be the more stable of the two phases. Consider Au₃Hf in the Cu₃Ti structure. Its energy lies below the line drawn between pure Au and Au₂Hf. Therefore, Au₃Hf is calculated to be stable relative to a two phase system involving these two. Similarly Au₂Hf's heat lies below the line between Au₃Hf and AuHf, so it's stable and the same situation holds across the sequence of alloys. The four compounds, taken in their correct structures, are calculated to be stable

Fig. 13 The Au-Hf system. At the top is the phase diagram and at the bottom are calculated heats of formation for Au₃Hf, Au₂Hf, AuHf and AuHf₂ in the CuTi, CsCl, MoSi₂ and Cu₃Ti structures (with the exception of CsCl, these are the structures appropriate to the Au-Hf system).

with respect to one another and to the terminal phases. Au₂Hf is calculated to be the most weakly stable with respect to competition from its neighboring Au₃Hf and AuHf phases and this is consistent with this compound displaying the weakest feature in the phase diagram. Thus, the essential features of the phase diagram are reproduced by the calculations. It should be emphasized that all the compounds considered here are close-packed. It might also be expected that total energy difference, between a compound and reference elemental solids or between compounds, would be most accurate when there are no severe differences in d and non-d charge counts at individual atomic sites (i.e., no significant charge flow). This condition is reasonably well met in Au-Hf.

Fig. 14 Calculated heats of formation of ordered 1:1 Pt-5d element phases (ref. 38). The asterisks are experimentally obtained heats (enthalpies) and the panel at the bottom indicates the observed phase diagram behavior (the horizontal bars for PtTa and PtIr separate the differing high and low temperature phase behavior). Except for the Miedema values, the results were obtained with scalar relativistic, local density, muffin-tin potential total energy calculations.

Calculations³⁸ for Pt alloyed with its 5d neighbors, Lu through Ir, appear in Fig. 14. At the bottom is indicated the phase diagram behavior for the 1:1 alloys. The BFe structure involves a unit cell which was beyond the means of the computational machinery to deal with and has been neglected. The asterisks represent experimental

heats data. Amongst the ordered phases, those for PtTa and PtW are calculated³⁸ to be suppressed by competition from ordered phases at other compositions, that is their calculated heats lie above the lines drawn between heats of adjacent phases in the sense of Fig. 12. No calculations were done for disordered phases which prevail here for PtW (PtTa and PtIr are two phase at low temperatures). The CsCl structure is correctly calculated to be stabler than CuAuI for PtHf but there are serious problems with PtHf in the CrB structure. This structure is ill-packed, comprised of close Cr-B pairs with large interstices along lines between pairs. The atomic sites are of low symmetry with nonspherical terms as low as $l=1$ in the site potential. The upper of the two plotted calculated heats was obtained with muffin-tin potentials with nonoverlapping atomic spheres. These spheres are smaller than usual due to the ill-packed nature of the structure. The more bound value for the CrB heat was obtained with a muffin-tin potential calculation where an empty atomic sphere was dropped into the interstice. This halves the error in this heat relative to those of the competing compounds. We expect that CrB's heat can be brought into line by employing full potential calculations. This issue will be investigated in the future. This set of alloys was shown because the calculation for PtHf in the CrB structure is, by far, the worst case we've encountered. Other than this, the heats represented here are consistent with phase diagram behavior and in semiquantitative agreement with the experimentally reported values (the disagreement for PtLu and PtHf is of the order of the experimental uncertainties).

Also shown in Fig. 14 are heats of formation calculated with Miedema's model Hamiltonian. They are consistently more bound than those from the band calculations and this is typically the case for transition metal alloys. The Miedema values are in as good agreement with experiment here although this is not the case for some transition metal alloy sequences and we would argue that the sign for PtRe and the magnitude for PtW is inconsistent with known phase diagram behavior.

Another sampling of heats of formation, calculated with muffin-tin potentials, is shown in Fig. 15. These are for ordered 1:1 compounds of Pd and Pt alloyed with the bottom ends of the 4d and 5d rows. Miedema values for the heats, which are not shown, lie below the band theory values much as in Fig. 14. Here, again, the band theory heats are in accord with the available experimental data, the asterisks. Note that the spread in the experimental data is of the order of the disagreements between theory and experiment. One also sees, for those cases where an ordered phase is reported to be the ground state, that the calculations have correctly predicted the stabler among the competing ordered phases--the one exception being PtHf in the ill-packed CrB structure. (As with Fig. 14, calculations were not done for the FeB structure.) There is an indication of a stronger tendency for compound formation for Pt alloyed with the 5d elements than for alloying between 5d and 4d and these, in turn, show stronger compound formation than Pd alloyed with the 4d. Two factors contribute to this. First, the d bandwidths of the 5d elemental

Fig. 15 Calculated heats (enthalpies) of formation of ordered 1:1 compounds of Pd and Pt alloyed with the bottom ends of the 4d and 5d metal rows (Y through Mo and Lu through W). The asterisks are experimentally obtained heats and the panel at the bottom indicates the observed phase diagram behavior. For the three systems with question marks (PdY, PdZr and PdHf) the most recent phase diagrams indicate the existence of 1:1 compounds but X-ray structure tables (ref. 12) do not list their structures. (From Fig. 9 one expects PdY most likely to be FeB or CsCl and PdZr and PdHf to be CrB, CsCl and/or CuTi.)

metals are greater than those in the 4d and all other things equal this could imply^{27, 28, 29} greater bandwidths, hence stronger bonding, in the compounds as well. Second, the relative positions of the centers of gravity of the d bands of the separate alloy components affects^{28, 29} the alloy's bandwidth, for the greater the separation, the greater that bandwidth and the resulting bonding energy. Pd (and Ag and La) is unusual in having d bands which lie unusually low with respect to the non-d bands. This affects both the d band occupancy and the above mentioned band separation. It is the interplay of these two factors which affects the bonding trends seen in Fig. 15.

In this section we have concentrated on trends in the structural heats of the elemental transition metals and heats of formation of ordered transition metal compounds which have been obtained by the present authors. There is, of course, other important work in the field such as that³⁹ of the Berkeley group on covalently bonded elemental solids and compounds. Considerable advances⁴⁰ have also been made for substitutionally disordered systems where both the enthalpy

and the configurational entropy must be dealt with. The message to be taken away from this section is that total energy calculations can yield accurate heats of formation though these may sometimes require large computer investments. For example, PtHf in the CrB structure is not satisfactorily dealt with in the muffin-tin approximation and one must go to full potentials which are expected to remedy this case. The total energy calculations described here use local density theory based potentials which are held in bad repute by many chemists who deal with small molecular systems (but who offer no useful alternative for solid state calculations). Calculated cohesive energies, that is the difference in energy between free atoms and a solid, can be ⁴¹ as much as 1 eV per atom in error. This is unsatisfactory and arises from the very different nature of a solid with its constrained charge density and an atom with multiplet effects, not encountered in a metal, and a charge density tailing off into the vacuum. Calculated heats of adsorption of ad molecules on solid surfaces are also unsatisfactory. The situation appears to be different for a heat of formation of a compound where the similarities between the compound and the reference solids leads to similar, cancelling errors in the total energies. Assuming this to be so, we are still not in a position where band theory can compete with experiment in the exploration of phase diagrams (though, of course, it is, when searching for low-lying metastable phases which may not be readily accessible to the experimenter). One problem is that the full exploration of competing phases requires consideration of structures with large unit cells and the scale of a calculation, employing current computational means, goes as the cube of the number of atoms in the unit cell. The σ and α Mn structures which are important competing phases in transition metal alloys involve 30 and 58 atoms in the unit cell respectively, though the symmetry of the latter is body-centered implying that a calculation need deal with but 29 distinct atoms. Large unit cells of 50 to 100 atoms also offer a way to study the heats of systems which are structurally as well as substitutionally disordered. To compound the problem, many of these large unit cell systems are ill-packed with low site symmetries. For example, the Frank-Kasper σ and Al₅ (8 atoms/unit cell) phases involve the Frank-Kasper polyhedra which can be quite distorted. The major ligand lines of the Al₅ structure were illustrated in Fig. 11. These involve large atomic cells which are compressed severely along the ligand lines implying substantial $k=2$ components in the crystal potentials. Matheiss and Hamann have observed ⁴² that a proper accounting of the band structure of the Al₅'s requires the use of full potentials and this will likely prove to be the case for the tcp phases in general. Efforts are under way to devise alternative band theory techniques where the scale of a calculation depends on a smaller power of the number of atoms. Even without this, the total energy calculations of today allow considerable exploration of the stabilities and metastabilities of alloy phases.

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