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WHAT'S SPECIAL ABOUT TRANSITION METALS IN ALLOY PHASE FORMATION?

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WHAT'S SPECIAL ABOUT TRANSITION METALS IN ALLOY PHASE FORMATION?

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Of course, the d-electrons are special, though their bonding properties remain to be completely understood. It has been recognized, since the work of the Friedel school, that d band broadening is the dominant term contributing to transition metal cohesion. It is also generally recognized that in compound formation between transition-metals and polyvalent metals, hybridization between d-bands and polyvalent atom p bands provides a significant contribution to the energy (for example there is such a term in Miedema's scheme). What is less generally realized is that d-band hybridization leads to changes in d-electron counts at a transition metal site which are opposite in sign to the net charge transfer on or off the site. In this paper we review the "renormalized atom" picture of cohesion of the pure transition metals and consider the experimental evidence and the theoretical understanding of d charge transfer going the "wrong way". A picture of the electronegativity of transition metals based on this trend is developed. Charge transfer associated with equalizing the local chemical potentials in alloys is estimated. Friedel type model alloy calculations are reviewed. The implications of the experimental charge transfer information from Mössbauer isomer shifts to such model alloy calculations and to the strength of the Coulomb energy associated with charge transfer is considered.

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Introduction

It has been recognized since the early days of quantum mechanics that the metals of the transition elements involve relatively localized valence d electrons and relatively diffuse s-p conduction electrons. The respective roles of these two classes of electrons in alloy and compound formation has been the subject of vigorous debate over the years (1). The large anisotropy of the localized d orbital charge figured heavily in early thinking (2) concerning the ferromagnetism of Fe, Co and Ni, and of the exchange interactions involved. Undoubtedly anisotropy was considered important to alloy formation as well. In the intervening years, Hume-Rothery (3) developed his beautiful and simple rules for alloys of the main group metals; Pauling (4), Engel (5) and Brewer (6) extended the description to the transition elements. According to this early thinking, the d electrons played essentially no role in bonding because of their localization. In the early days Wigner (7) and later with the advent of energy band theory results, Friedel (8) and others (9,10) developed a picture where the most significant factor in transition metal alloy heats of formation is the broadening of the partially filled d-bands. This is made significant by the large number of d states. The two points of view have evolved since the debates at the 1966 Battelle meeting (1). Engel-Brewer theory is widely used today as a predictive scheme and d electrons have a role, but the most recent activity has emphasized the band theory approach and it is that which is reviewed here, as well as being represented in several other papers in this symposium.

In the next section we will review Friedel d-band bonding and other contributions to transition metal cohesive energies. Heine's description (11) of the d-band widths, so important to d-band bonding, will be considered. The remainder of the review will deal with alloys. Essential to alloy formation is any charge transfer between atomic sites and any interchange of d and non-d conduction electron count at a given site. Some experimental information concerning such trends is considered in Section III. In Section IV we propose a scheme for defining a transition metal electronegativity scale based on the tendency for the d-bands to gain or lose d character upon bonding. We consider the electronegativity of a transition metal to be not so much a tendency to gain or lose valence charge (which it is, presumably, for the nontransition elements) but to be a measure of the d electron bonding. One might expect that charge transfer will go from whichever component has the higher Fermi level to the component with the lower one. In Section V we will suggest why this may not be the dominant factor. Finally we will discuss the Friedel scheme as employed in model calculations of alloying and will consider the implications of the experimental charge transfer trends to such model calculations and to the energetics of charge transfer in alloy formation.

II. Cohesion in the Transition Elements

In the Friedel picture (8,9), the essential cause of the cohesion of a transition metal is the broadening of its incompletely filled band structure around the band center of gravity, C. This

is shown for the case of a rectangular density of states in Fig. 1. Placing one electron in the bands fills the shaded region of the

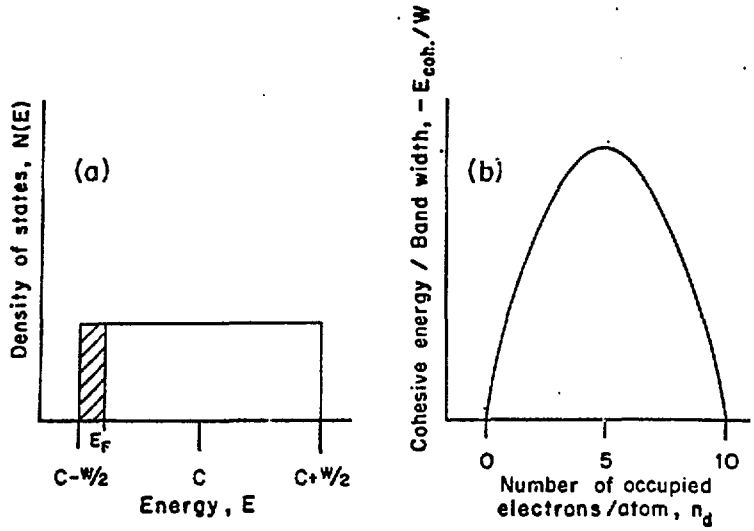


Fig. 1 - a) A model rectangular electronic density of states, of width W and center C, to represent the d-band of transition metals. The occupied levels for one electron (dashed) fill the band to the Fermi energy ε_F.
b) The ratio of the cohesive energy to the band width given by Eq. 2 as a function of the filling of the rectangular d-band density of states.

density of states. The energy gain is the difference in energy between C and the center of the shaded region. Putting a second electron in the bands involves filling states closer to C hence there is less energy gain. Once the band is half filled, the addition of more electrons involves filling "antibonding" states above C and a reduction in the cohesive energy gain as indicated in the second part of the figure. The resulting Friedel cohesive energy contribution is thus

$$E_{Fr} = \int_0^{\varepsilon_F} (\varepsilon - C)\, N(\varepsilon)\, d\varepsilon \qquad (1)$$

where ε_F and $N(\varepsilon)$ are the Fermi level and the density of states respectively. For the rectangular $N(\varepsilon)$ of Fig. 1,

$$E_{Fr} = -\frac{n_d\,(10-n_d)}{20}\, W\,, \qquad (2)$$

where W is the bandwidth and n_d is the number of electrons per atom occupying the d bands. Because W is not constant across a transition metal row, E_{Fr} does not peak symmetrically about N=5.

There are other contributions to cohesion as can be summarized by the evolution of the free atom electron levels into the density of states of the solid as is indicated (12) for Ti in Fig. 2. First, the atom must go from its d^2s^2 ground state configuration

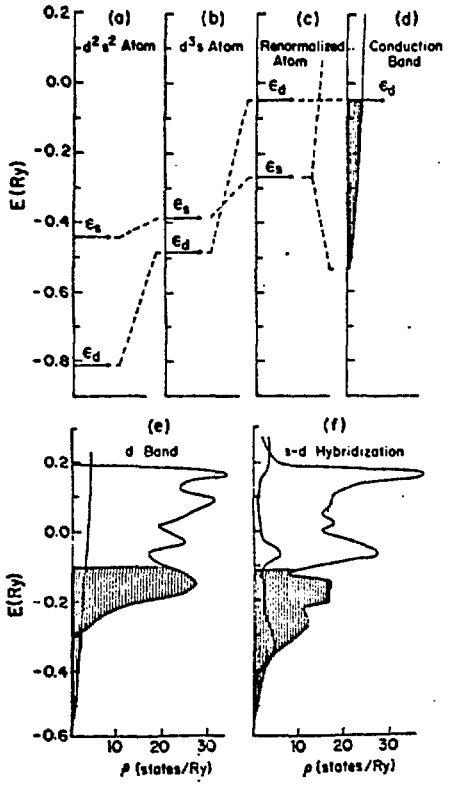


Fig. 2 - The various electron energy effects associated with going from a free transition element atom to the metal. (after Gelatt et al. (12)).

to d^3s which is roughly the configuration of the metal. The $d^{n-2}s^2$, $d^{n-1}s$ and d^n configurations of a transition metal atom lie rather close to one another and the $d^2s^2 \rightarrow d^3s$ promotion energy is much smaller that the 4.2 eV/atom associated with exciting the carbon atom out of its $2s^22p^2$ ground state into the $2s2p^3$ tetrahedral bonding state. Transition metal promotion energies of this sort were incorporated by Brewer in his scheme (6). Second, we take (b→c) the d^3s from atom into an equivalent atom whose charge is "renormalized" within the atomic Wigner-Seitz cell of the solid. This involves a substantial compression of charge since roughly one electron's worth of charge of the free atom resides outside the Wigner-Seitz cell appropriate to the solid. The charge renormalization causes the electron potential to be less attractive and the atomic s and d levels lie higher than they did in the free atom case. We then have the s electron levels broadening into a conduction band. In turn there is the Friedel broadening of the d bands and finally there may be hybridization between the d and non-d bands which makes a contribution to cohesion much like that of the d band broadening alone. The full energy of the metal, involving all these terms, may be written

$$E = \int_{\text{band minimum}}^{\epsilon_F} \epsilon N(\epsilon) d\epsilon - \text{double counted terms} \qquad (3)$$

As indicated, double counted interelectronic terms must be subtracted from such a sum. The energy of the free atom is

$$\sum n_i \varepsilon_i - \text{double counted terms} \tag{4}$$

where the sum is over valence shells, i, with occupancy n_i. The cohesive energy is the difference of (3) and (4). In general, the double counted terms of (3) and (4) are not the same and may not be omitted from the estimate of E_{Fr}.

The various contributions to the cohesive energy are summarized for the 3d and 4d metals in Fig. 3. These are based on nonrelativistic calculations employing renormalized atom potentials.

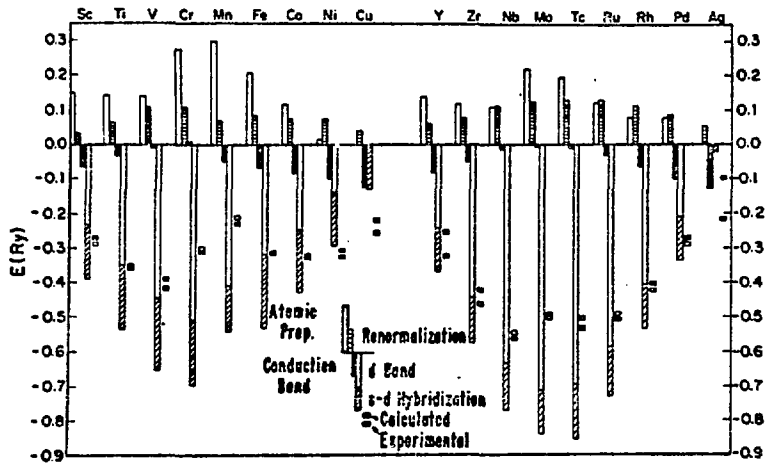


Fig. 3 - Contributions to the cohesive energies of the 3d and 4d transition metals due to the various effects summarized in Fig. 2. The calculated and experimental total energies are indicated by the filled and open bars respectively (after Gelatt et al. (12)).

The single most important factor, except for the noble metals, is the Friedel term. Since they have filled d-band, the noble metals have zero-valued Friedel terms. Conduction electron - d electron hybridization contributes significantly to the cohesive energies of both noble and non-noble transition elements. This hybridization plays an essential role in noble metal alloy formation. Note the modest role played by the promotion of the free atom ground state into an atomic configuration appropriate to the metal. The large positive level shifts seen on going from Fig. 2b to Fig. 2c are not catastrophic once the double counted valence-valence electron terms are properly subtracted, as shown in Eqs. (3) and (4).

The band widths, W, are important to the cohesive energies as is suggested by Eq. (2). Heine has derived a relation which provides insight into bandwidth behavior. He developed a Korringa-Kohn-Rostoker description (13) where d orbitals on different atomic sites interact via hybridization with states in the intermediate "muffin tin region" of the crystal. A single-site

hybridization or hopping integral

$$\gamma = A \int P_d(r)\ V_d(r)\ j_2(Kr)\ r^2 dv \tag{5}$$

was defined, where P_d is the radial d function, for a state whose energy is the d band center of gravity C; it is localized on a single site. V_d is the d-electron potential, A is an angular factor and j_2 is a spherical Bessel function associated with a muffin-tin plane wave whose K vector equals the square root of the difference in energy between C and the muffin-tin potential energy. By making arguments that the bonding orbital at the bottom of the bands is flat at some radius R, i.e.

$$\left[\frac{dP}{dr}\right]_R = 0,\ \varepsilon = \varepsilon_{min}\ , \tag{6}$$

and that the antibonding function at the top of the bands is noded, i.e.

$$P\ (R) = 0,\ \varepsilon = \varepsilon_{max} \tag{7}$$

Heine obtained

$$W = K\gamma^2 \left[\frac{n_2'(KR)}{j_2'(KR)} - \frac{n_2(KR)}{j_2(KR)}\right] \tag{8}$$

where n_2' and j_2' are the derivatives of these Bessel functions. Hodges et al. have shown (14) that this prediction reproduces the computed band widths, providing R is taken to be the atomic Wigner-Seitz radius, and Andersen et al. have refined (15) the description. Heine expanded the Bessel functions in their small argument limits, obtaining

$$W = \frac{112.5\ \gamma^2}{K^4 R^5} \tag{9}$$

Now KR is typically of the order of one. Despite this, Eq. (9) provides rather good insight to the volume dependence of d band widths. Calculations done as a function of volume indicate that W α R^{-N} where $3.2 \leq N \leq 5$ for any given transition metal with the smaller value characteristic of the lighter elements at the left hand end of a transition metal row. γ values vary significantly from element to element and this variation is as important as the variation in R for determining d bandwidth behavior.

Recently Andersen and MacIntosh have related (16) the band width to the electron density, ρ, at the Wigner-Seitz radius of a d orbital, whose energy is the band center of gravity, C. They obtained

$$W(ryd) = 12.5\ R\rho(R) \tag{10}$$

with R in atomic units. We have found this relationship to hold to better than ten percent for a set of relativistic band calculations. Note that this density is different than the sum of the electron density over the occupied d and non-d band states which enters Miedema's model (17) of alloy heats of formation.

As is indicated in Eq. 2, the position of C as well as the band broadening contributes to the total energy. For non-relativistic orbitals, C occurs at an energy where the logarithmic derivative of the wave function obeys (15,16) the relation

$$\left[\frac{r}{P}\left(\frac{dP}{dr}\right)\right]_{r=R} = -(\ell+1) \ , \qquad (11)$$

i.e., -3 for d functions*. Now, a C value is the measure of the atomic d level energy in the crystal. As is indicated in Fig. 2, it does not lie at the free atom value and this is due to having a crystal potential derived from a neutral atom's worth of charge which is constrained to lie within the atomic Wigner-Seitz cell. Typically one electron's worth of the charge of a free transition element atom lies outside its crystal Wigner-Seitz cell and it is the charge compression on going from the free atom to the metal which is responsible for the level shifts from Fig. 2b to 2c. The relative position of the C of one alloy component versus that of the other is important in applications of the Friedel model to alloy formation. Since the free atom levels do not accurately reproduce the relative positions of the C's in the crystals the free atom levels cannot be used to predict the energies of the metals and their differences cannot be used to predict energies of alloy formation. Moreover the centers of gravity in an alloy need not correspond to their pure metal values, due to volume and charge transfer effects. We shall next discuss the charge transfer.

III. Some Experimental Evidence Concerning Charge Transfer Associated with Transition Metal Alloy Formation

A variety of experiments measure the change in valence charge distribution upon alloy formation. Different experiments generally yield apparently inconsistent results concerning charge transfer on or off a site. This is because bonding and charge screening involve two rather different classes of valence electrons: the rather localized d electrons and the delocalized conduction electrons whose charge is concentrated in the outermost part of the Wigner-Seitz cell. Consider the Au-Ag alloy system.

Addition of small amounts of silver cause the color of Au to rapidly whiten. Since the color is determined by the position of the upper edge of the d bands below the Fermi level, ε_F, the whitening implies that the d bands are dropping in energy. Photoelectron spectra of Au core electron levels show (18) them to be dropping at a similar rate. Lower levels imply a deeper potential

*Relativistic calculations are referred to in several places in this review where spin-orbit split two component wave functions are used. Eq. 11 is then applied to the major component of the wave function for each of the pair of j quantum number values 3/2 and 5/2 obtaining two centers of gravity C_j. The two C_j values are weighted by their respective level degeneracies to obtain C.

at the Au site which can arise from a shift in valence charge out towards the surface of the atomic cell, or out of the cell entirely. Mössbauer isomer shifts, of which more will be said shortly, measure the s-like component of the conduction electron charge, and results for Au in the Au-Ag system indicate a substantial increase in conduction electron density at the Au site. Not only is this opposite in direction to that implied by the d band and core level shifts but it appears to involve more charge. These two disparate trends are understood (18,19) as arising from a decrease in d electron count accompanied by an increase in conduction electron charge. The filled Au d bands are involved in hybridization with the unoccupied conduction bands of the other constituent, in this case Ag. This admixture introduces Ag orbital character into the Au d bands and hence a reduction in occupied Au d electron count. Because d electrons are more localized than the conduction electrons the Au site potential (and hence the level shifts) are affected most by the transferred d electrons and the charge being measured is primarily d charge. Accurate estimates of the d and conduction electron count changes, Δn_d and Δn_c, are difficult to infer from experiment but it would appear (18,19) that the net charge flow

$$\delta = \Delta n_c + \Delta n_d \tag{12}$$

has the same sign as Δn_c. In other words net charge flow is onto the Au site. Results for other metallic transition and non-transition elements (18) suggest that charge flow is always onto the Au site. This is consistent with the Pauling electronegativity scale (4) but not with scales based on work functions.

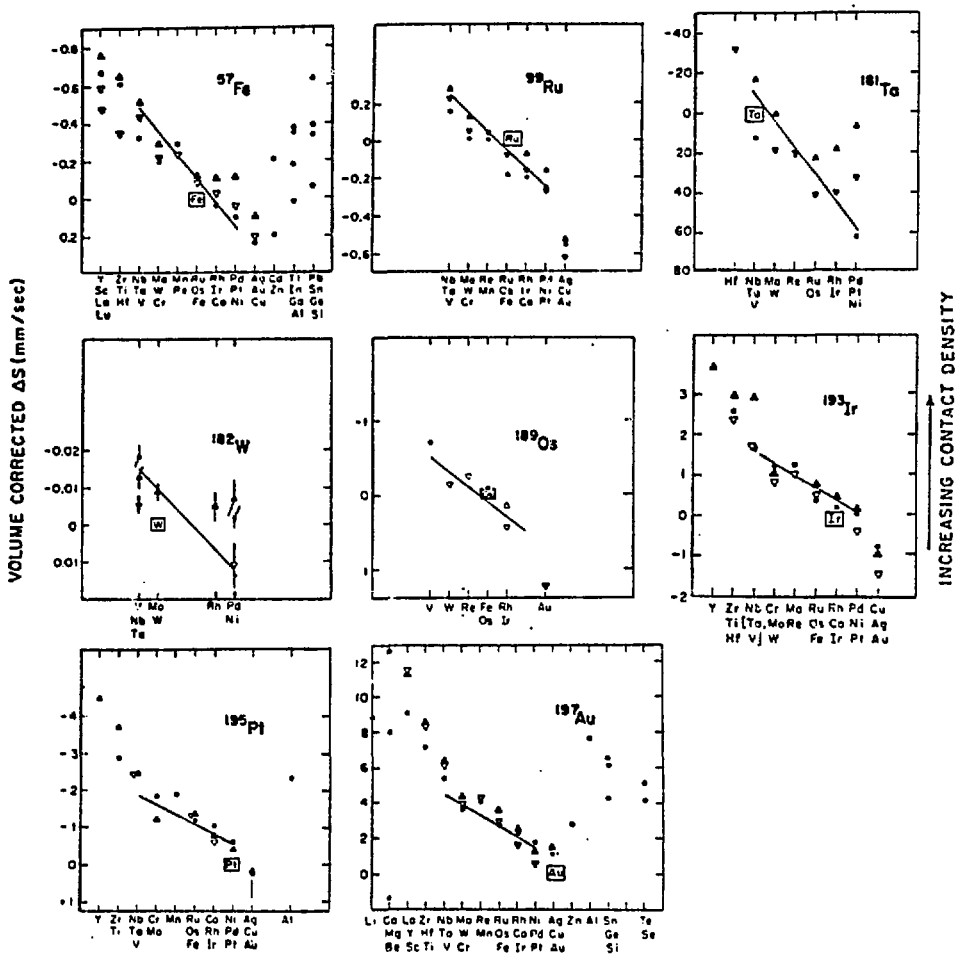
The Mössbauer effect isomer shift involves a nuclear transition where the nuclear size changes. A γ ray is emitted from a nucleus in a source and absorbed by a nucleus in a second sample. The shift is given by

$$S = \frac{[0.0608\ Z\ \delta\langle r^2\rangle]}{E_\gamma}\ \Delta\rho(0) \tag{13}$$

where S is the shift in (mm/sec) and Z, $\delta\langle r^2\rangle$, E_γ and $\Delta\rho(0)$ are the nuclear charge, the change in the square of the nuclear radius (10^{-3} Fm^2), the γ-ray energy (keV) and the change in electron contact density (a_0^{-3}) between the source and absorber. Therefore, if the other parameters are known, the experiment measures the difference in electron contact densities at the nucleus in question in the two samples. Unfortunately, the $\delta\langle r^2\rangle$ must be derived from some experiment and an estimate of $\Delta\rho(0)$. Not all elements have suitable Mossbauer nuclei. There are isomer shift data for the transition elements ^{57}Fe, ^{99}Ru, ^{181}Ta, ^{182}W, ^{189}Os, ^{193}Ir, ^{195}Pt and ^{197}Au as impurities in a variety of hosts. The shifts, after a correction is made for the volume mismatch between impurity and host, are summarized (20) in Fig. 4. The scales are different because of the different factors entering Eq. 13. The drawn lines are all of a "common" slope defined by

$$\text{Slope} = [KZ\delta\langle r^2\rangle\rho_v(0)]/E_\gamma \tag{14}$$

where K is a common constant and ρ_v is the free atom valence s contact density. It is seen that all the results conform to roughly the same scale and with some exceptions, display the same shape. In general, a transition element sustains an increase in contact density when alloyed to elements to its left and a decrease when mixed with transition elements to its right.



VOLUME-CORRECTED ISOMER SHIFTS

Fig. 4 - Volume corrected isomer shifts for ^{57}Fe, ^{99}Ru, ^{181}Ta, ^{182}W, ^{189}Os, ^{193}Ir, ^{195}Pt and ^{197}Au as dilute impurities in the various hosts (as indicated at the bottoms of the plots). The shifts have been plotted so that higher lying points are associated with increased electron contact density at the impurity nucleus. The straight lines are lines of common change in contact density, accounting for differences in atomic and nuclear parameters (see Eq. 13) on going from one impurity to another. Comparison of the lines with the data points provides a measure of the extent to which the data displays a common overall variation in scale (after ref. 20).

The changes in contact density may arise in two ways: changes in conduction count directly contribute while an increase in d-electron count, whose charge lies inside that of the conduction electrons, increases the screening of the conduction electrons reducing their density at the nucleus, i.e.

$$\Delta\rho(0) \propto \Delta n_c - R\Delta n_d \tag{15}$$

where R_d is a positive constant which atomic calculations indicate to be of the order of ½ to 1. The increased contact density associated with alloying one element with another to its left would appear to involve some combination of increased conduction and decreased d-electron count. Now, setting $\Delta n_d=0$, the full range of the isomer shifts plotted in Fig 4 correspond to a Δn_c of the order of 1 which is substantial. If alloying an element to another to its left had involved an increase, rather than a decrease, in d count, one would have had the second term of Eq. 15 of opposite sign to $\Delta\rho$, thus requiring an even larger Δn_c, implying, in turn, an atomic site charging in great excess of what seems reasonable for metallic systems. Thus, granted the magnitudes of the isomer shifts and the opposing effects if conduction and d-electron counts were both increased (or decreased), it would appear that the isomer shifts, taken alone, indicate that as a rule

$$\frac{\Delta n_c}{\Delta n_d} < 0$$

for alloying between a pair of transition elements. Photoemission data is less extensive for the elements other than Au. Based primarily on the gold results, one expects that

$$-1.1 > \frac{\Delta n_c}{\Delta n_d} > -1.5 \tag{16}$$

This has consequences for the energetics of alloy formation, as will be discussed in Section VI.

IV. An Electronegativity Scale for the Transition Elements

Consider the alloying of a pair of transition elements, for example, Au, with its filled d bands and Sc, with its almost empty d bands. An occupied Au d orbital, ψ_d^{Au}, admixes with a Sc d hole orbital, ψ_d^{Sc}, causing a change in wave function character of the occupied level. To lowest order in perturbation theory this change would be

$$\psi_d^{Au} \rightarrow \frac{\psi_d^{Au} + \lambda\psi_d^{Sc}}{[1+\lambda^2]^{1/2}} \tag{17}$$

where

$$\lambda \equiv \frac{\langle Au|V|Sc\rangle}{\varepsilon_{Au} - \varepsilon_{Sc}} \equiv \frac{\gamma}{\varepsilon_{Au} - \varepsilon_{Sc}} .$$

γ is the hybridization matrix element. The demoninator in Eq. 17 preserves the normalization, assuming the orthonormality of the ψ. The Sc d hole state has become occupied to the extent that it is admixed in and thus the Sc atom has gained in occupied d count. The change in d-count due to hybridization does not imply an equivalent change in overall d-band occupancy, for the Au d-bands have remained filled upon hybridization. The trend in the isomer shifts across the transition metal rows in Fig. 4 can be understood in terms of the relative availability of occupied and hole states for hybridization and the tendency, thus, to lose or gain d charge. It is possible to quantify this and thus to define and electronegativity scale.

Consider (21) a test atom inserted into a metal which has and occupied electron level ε_e, hybridized with the metal's d band hole states with energies ε_h, above ε_F. It follows from Eq. (17) that, the weight of d band character admixed into the test level is, in lowest order

$$\sum_h \frac{\gamma^2}{(\varepsilon_e-\varepsilon_h)^2}$$

A similar expression holds for the loss of orbital character associated with admixing a test atom hole with the set of occupied d band levels below ε_F. Thus, when the d bands of a transition metal are hybridized with a test atom which has electron levels δE below, and hole levels δE above ε_F, the resulting gain or loss of d-band character is

$$\Lambda \equiv \gamma^2 \int \left[\frac{\varepsilon_i-\varepsilon_F}{|\varepsilon_i-\varepsilon_F|}\right] \frac{N(\varepsilon_i)}{(|\varepsilon_i-\varepsilon_F|+\delta E)^2} d\varepsilon_i \qquad (18)$$

The square bracket contributes the minus sign associated with the admixture of d-band states below ε_f and a plus sign for hole states above. The hybridization matrix element has been assumed constant and taken out of the integral. Treating the hybridization as a two-step process in which a d-electron mixes with the continuum states and these, in turn, admix with the test atom, γ is, apart from a constant, given by Eq. 5 or 8. Given band theory estimates of $N(\varepsilon)$ and γ, Eq 18 may be evaluated (21). Assume Λ to be linearly related to the electronegativity, i.e.

$$\phi = -A\Lambda + B \qquad (19)$$

where the scale factors A and B are determined by linear recursion of Λ versus some established electronegativity scale (we have used Pauling's). The result of doing this appears in Fig. 5. The points are the result of an earlier calculation (21) in which γ was treated crudely. Since the positions of the muffin tin potentials necessary for estimating the wavevector K and in turn γ from Eqs. 5-9 were unknown, they were assumed equal to the energy of the bottom of the conduction bands. Subsequently we have constructed renormalized atom potentials and determined the muffin tin potentials,

the d-band centers of gravity. C, and the band widths, W, necessary for calculating γ from Eq. 8. The method used (14) yields separate conduction and d electron potentials and the two sets of lines in the Figure represent use of the two distinct muffin tins in estimating γ. Except for Pd and Ag, the present results are in substantial agreement with the earlier estimate.

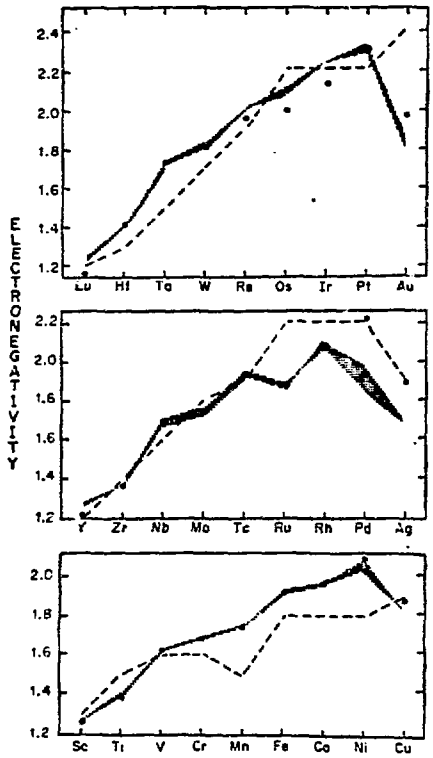


Fig. 5 - Comparison of transition metal electronegativities based on the tendency for d bands to gain or lose d charge by hybridization (the cross hatched region) with the Pauling electronegativity scale (dashed lines) and with an earlier estimate (ref. 21) which treated the hybridization matrix elements more crudely (see text).

The electronegativities are seen to rise more or less smoothly across a transition metal row and then drop on going to the noble metals. The deviations from smooth behavior are associated (21) with the Fermi level traversing peaks and hollows in the densities of states appropriate to the crystal structures of the metals involved. The dip on going to the noble metals is associated with the fact that the top of their d bands lie well below ε_F thus penalizing the mixing, i.e. the denominator of Eq. 18 increases markedly.

The Pauling scale shows plateaus at the upper ends of the transition metal rows as do ϕ based on work functions such as Miedema's scale described by him elsewhere in these proceedings. The band hybridization ϕ values, obtained here, rise most steeply at the start of a row but continue to rise across the remainder.

In doing this, these results mimic the isomer shifts of Fig. 4 which fall steeply at the start and then at a slower rate at the upper end of a row.

As for the noble metals, the present ϕ are inconsistent with the isomer shifts and with the Pauling scale which has Au and Cu more electronegative than their neighbors Pt and Ni respectively. The work functions, on the other hand, show a dip similar to that seen in Fig. 5.

There may well be no unique electronegativity scale which can be universally applied to all occasions where "electronegativity" is considered a useful parameter. The Pauling ϕ and the isomer shift data are consistent in suggesting that Au is the most electronegative of the metals. If a single parameter, electronegativity, is to describe charge transfer effects, then the Pauling choice is best. On the other hand, Au, Ag and Cu must have ϕ roughly equal to those of the middle of the transition element rows if the Miedema scheme (17) is to correctly describe the heats of formation upon alloying the noble metals with transition elements. For example, positive heats of formation occur between Au and W and between Ag and Mo, and this requires small electronegativity differences. One then requires at least two parameters to describe charge transfer. The interplay of d electron bonding and conduction electron transfer, as summarized in Eq. 16 may differ between transition and noble metals causing some of the inconsistency in the numerical definition of ϕ. There may, of course, also be differences in $\Delta n_c/\Delta n_d$ for a particular transition metal in its bonding with (a) another transition metal, (b) a metallic main group element and (c) a covalent main group element. Such differences, if they exist, are not detectable in the experimental data described in the previous section due to the numerical uncertainties of the analysis and of the data.

For alloying between a pair of transition elements, Miedema's scheme predicts a heat of formation consisting of

$$\Delta H_{ab} = F(c) \left\{ -P(\phi_a-\phi_b)^2 + Q(n_a^{1/3} - n_b^{1/3})^2 \right\} \qquad (20)$$

where F is a concentration dependent term factor, P and Q are positive constants and n_i is the electron density at the surface of the Wigner-Seitz cell of constituent i in its elemental form. With the band theory ϕ of Fig. 5, Eq. 20 yields+ a set of ΔH_{ab} values which are in as good agreement as those predicted with Miedema's values (17) using the existing experimental ΔH for transition metal alloys. In this sense, not only are the two scales much alike in overall features but they may be viewed as effectively <u>identical</u>.

+Using Miedema's value of P requires translating the present ϕ by linear recursion into the units used by Miedema. Miedema's values of $n^{1/3}$ are used, except for Ir and Pt, where a 10% increase improves the fit.

The d band ϕ's depend on the relative numbers of occupied and hole states and on their availability energetically. The latter dependence bears a resemblance to the Mulliken electronegativity scale (22) which is considered (23) elsewhere in these proceedings. The Mulliken scale is based on free atom ionization energies and electron affinities, in other words, on an atom's tendency to keep the valence electrons it already has plus its ability to attract additional valence electrons from other atomic species. The extent to which the valence levels are filled has not entered estimates of the Mulliken scale with the result (23), for example, of predicting that the noble metals are more electronegative than their transition metal counterparts. As discussed in earlier sections, the transition elements have a large number of levels close to the Fermi level and thus the bonding energy gained by band broadening is the most important single term in cohesion. The relative availability of these levels as holes versus occupied levels appears to be essential to d band bonding and, in turn, to electronegativity behavior.

V. Fermi Level Positions and Their Role in Charge Transfer

The idea that the relative positions of the Fermi levels of two elements is a measure of their relative electronegativities has been with us for some time. It underlies the use of work functions which, apart from including dipole contributions associated with the surface of a solid, indicate the positions of Fermi levels inside crystals. The purpose of this section is to estimate the contribution made by Fermi level mismatches to charge transfer in transition metal alloys. Noble metals will be neglected in what follows.

The Fermi level positions of the 3d, 4d and 5d metals are plotted in Fig. 6. These are based on band calculations employing relativistic renormalized atom potentials. The levels are plotted with respect to a common zero, the crystal zero, which would equal the vacuum zero if there were no dipole layer on the free metal surfaces. This is not necessarily the best possible set of ε_F but they have been derived in a common way and serve our purposes here.

Inspection shows that ε_F is shallowest for osmium. The simple argument that charge should flow until the local Fermi levels, or chemical potentials, are equal would suggest that Os loses charge to all other transition metals. Loss of charge, say at Os sites, has two effects. First, the Fermi levels falls lower in the Os density of states. Second, and more important, removal of charge deepens the potential causing the d bands, and the Fermi level in them, to drop. This effect involves the Coulomb shift due to the removal of d band electron population without any conduction electron screening. It can be estimated by comparing d bands levels calculated for renormalized positive ion $d^{n-1}s$ potentials to those calculated for the standard neutral $d^n s$ ground states. Removal of a whole d electron lowers the band center of gravity by 0.5 au (1 au=27eV) for Sc, 0.7 for Ni, and 0.5 for Pt. These shifts are large and as a consequence the d-band transfer necessary to bring Fermi levels to a common value tends to be small. The filling or emptying necessary to bring a pair of 3d elements other than Sc into line is of the order of 0.05e or less. The transfer

tends to be larger for Sc and the 4d and 5d elements and may be ∿ 0.1e for an alloy involving Y or Lu. [The Fermi levels of the noble metals fall in the conduction bands and we estimate that band occupancy changes, associated with Fermi level matching, of as much as 0.1e may occur for alloys of these elements as well.] d band occupancy changes of the order of 0.05 to 0.1e are smaller than the Δn_d suggested by experiment and by the hybridization estimates of the preceding section. Therefore, while not always insignificant, the relative positions of d band Fermi levels do not determine the direction of d band charge transfer.

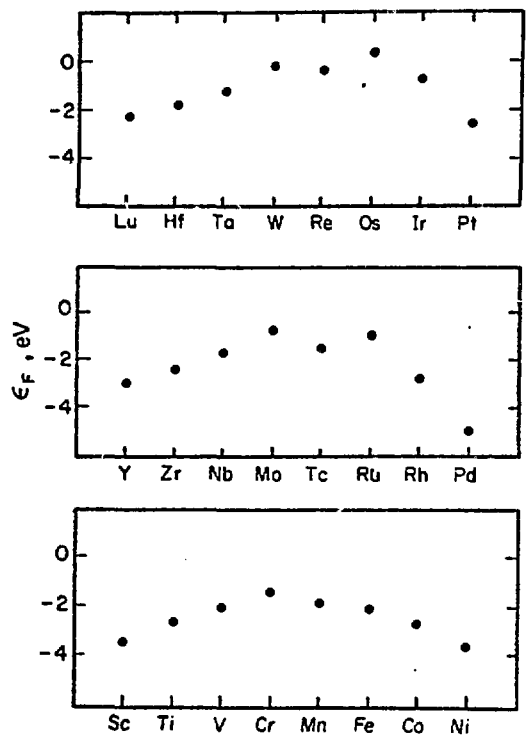


Fig. 6 - The Fermi levels of the transition elements, referenced to a common crystal zero. These are based on energy band results employed in ref. 21.

It should be recognized that, due to volume and other effects, the pure metal ε_F's may not be appropriate to the local chemical potential appropriate in an alloy. Further, one's estimate of this Δn_d contribution depends on whether one assumes there is or is not screening of this transfer. On the other hand, the energy contribution to alloy formation due to bringing the local chemical potentials into register is not strongly dependent on such assumptions of screening.

VI. The Friedel Model Applied to Alloying

As Ducastelle has displayed (24) elsewhere in these proceedings, band theorists have used the coherent potential approximation for the formation of alloys with significant success. What can be done with model descriptions which have the virtues of computational and intuitive simplicity? The Friedel band broadening scheme, employing the rectangular density of states of Fig. 1 with varying bandwidths from metal to metal, describes (8) the overall trend in transition metal cohesion quite well. Recently Pettifor (25) and Varma (26) have asked what are the consequences of using the same rectangular density of states in the description of alloy formation?

The single particle contribution to the total d electron energy (first term of Eq. 3) is

$$E = n_d C - \frac{n_d(10-n_d)W}{20} \tag{21}$$

and therefore the heat of formation for a 50-50 AB alloy is

$$\Delta E = n_{AB}C_{AB} - \frac{n_{AB}(10-n_{AB})W_{AB}}{20} - \tfrac{1}{2}\left\{n_A C_A - \frac{n_A(10-n_A)W_A}{20} + n_B C_B - \frac{n_B(10-n_B)W_B}{20}\right\} \tag{22}$$

where the number of electrons per atom in the alloy is

$$n_{AB} = \frac{n_A + n_B}{2} \quad . \tag{23}$$

Pettifor has shown that heats of formation obtained with Eq. 22 are in moderately good quantitative agreement with the tight binding coherent potential approximation results (27) of van der Rest et al. The width of some given rectangular density of states was chosen so that the second moment

$$\langle\varepsilon^2\rangle = \int (\varepsilon - C)^2 N(\varepsilon)\,d\varepsilon \tag{24}$$

is equal to that of the more accurate density of states. The alloy band center of gravity was taken to be the average

$$C_{AB} = \frac{C_A + C_B}{2} \tag{25}$$

of the separate metals. The alloy band width depends on the intrinsic widths of the two components <u>and</u> on the separation,

$$\Delta C \equiv C_B - C_A \tag{26}$$

of the two centers of gravity. Using tight binding theory, Pettifor estimated (28) the alloy band width to be

$$W_{AB} = \frac{W_A+W_B}{2}\left\{1+12\left(\frac{\Delta C}{W_A+W_B}\right)^2\right\}^{\frac{1}{2}} \qquad (27)$$

The A and B atom bandwidths and centers of gravity employed in Eqs. 25 and 26 may be taken to be the values for the pure metals. Such a case is plotted for the $Ta_{0.5}Pt_{0.5}$ in Fig. 7. Alternatively

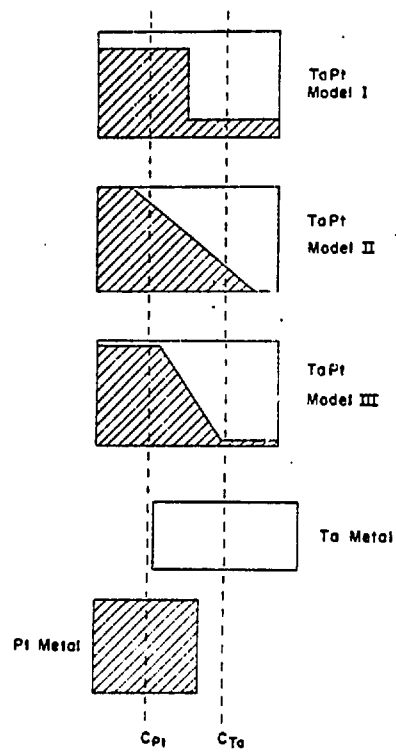


Fig. 7 - Several ways to factor a rectangular alloy density of states into the partial densities of states appropriate to the two constituent elements subject to the requirement that the centers of gravity of the partial densities of states are equal to those of the separate constuents. The case of $Pt_{0.5}Ta_{0.5}$ is illustrated. Model I is the scheme employed by Pettifor (25, 28) and Varma (26).

the C_A, C_B, W_A and W_B may be shifted to values appropriate to those atoms in the alloy in question due to charge transfer, volume modifications of the atomic sites or other factors. If

this is done and one wishes to estimate the heat of formation of the alloy, care must be taken to deal with the double counted terms of Eq. 3 which have been omitted in Eqs. 21 and 22. Let us consider this. In the class of band potential used in this paper, a d electron at the site interacts with the (n_d-1) other d electrons at the same site, hence the band center of gravity is

$$C = C' + (n_d - 1)\,U \tag{28}$$

where U is the intratomic effective d-d interaction term and C' that part of C not depending on the d-d interactions. The first term of Eq. 21 becomes,

$$n_d C = n_d C' + \frac{n_d(n_d-1)U}{2}\,, \tag{29}$$

not

$$n_d C = n_d C' + n_d(n_d-1)U$$

for otherwise each d-d interaction would be counted twice in the process; there are but $n(n-1)/2$ pairs of unlike d electrons at the site. Eq. 21 becomes

$$\begin{aligned} E &= n_d C' + \frac{n_d(n_d-1)U}{2} - \frac{n_d(10-n_d)W}{20} \\ &= n_d C - \frac{n_d(n_d-1)U}{2} - \frac{n_d(10-n_d)W}{20} \end{aligned} \tag{21a}$$

Now U will change if the site volume changes and the $n(n-1)$ factor multiplying U will change if there is charge transfer on or off the site. In such cases this term must be included in the energy estimate. If there are no such changes, the term has the same value in the pure metal and the alloy and may be neglected.

The interesting suggestion was made (25,26) that it is possible to factor the rectangular alloy density of states into A and B site partial densities of states such that it correctly describes charge transfer <u>and</u> correctly centers the A site's partial density of states at C_A and the B site's at C_B. They used the step factorization illustrated at the top of Fig. 7 where the height of the step is determined such that the centers of the partial densities of states match C_A and C_B. Except that C_A and C_B suffer a Coulomb shift with charge transfer, there is no free adjustable parameter built into the model which allows variationally for the various contributions to charge transfer such as d-band hybridization. The transfer given by the model may be estimated (25,26,28) by summing the A (or B) site partial density of states up to the Fermi level of the alloy (i e. so that there are n_{AB} occupied levels) and comparing the A (or B) site electron counts with the n_A (or n_B) characteristic of the original pure metal.

For the case at the top of Fig. 7 the d charge transfer is

$$\Delta n_A = \frac{n_B - n_A}{2} + 2\,\frac{\Delta C}{W_{AB}}\,\hat{n} \qquad (30)$$

where $\hat{n} = n_{AB}$ if $n_{AB} \leq 5$ and $\hat{n} = (10 - n_{AB})$ if $n_{AB} \geq 5$.

There are two terms contributing to this charge transfer, one depending on the initial d band occupancies, the other on the ratio of the level separation to the band width. In this model, the only dependence of charge transfer on alloy parameters is through this ratio. In general, the band center of gravity, C, is lower at the upper end of a transition metal row causing the two terms of Eq. 30 to be of opposite sign. Does this partitioning yield the d band charge transfer which we believe actually occurs? Pettifor's Δn_d for 50-50 alloys of Fe with other 3d elements are shown in Fig. 8. These were obtained with U set equal to zero, i.e. charge transfer shifts were neglected, and with C_A, C_B, W_A and W_B taking on the pure metal values. [The results are qualitatively the same for non-zero U.] Except for $Fe_{0.5}Cu_{0.5}$, the second term of Eq. 30 dominates and all the results are of opposite sign to the experimental trends inferred in Section III and to the band hybridization estimates of Section IV. One might assume a different factorization of $N(\varepsilon)$ still involving a single

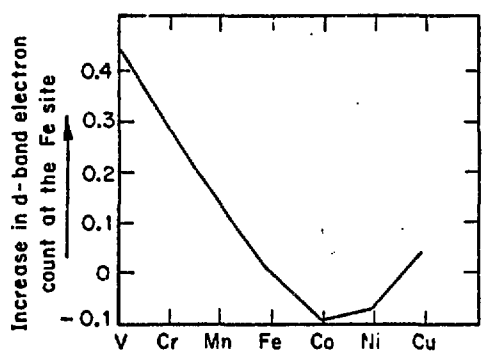


Fig. 8 - d electron transfer onto Fe sites in $Fe_{0.5}M_{0.5}$ alloys as predicted (25) by Pettifor using Model I of Fig. 7.

parameter, such as one of the two panels in the middle of Fig. 7. However, these choices affect details of the Δn_d values but do not modify the overall trend seen in Fig. 8. Not only does the charge transfer take the wrong sign but it seems too large in magnitude. Charging on the scale seen in the figure would seem to imply a substantial energy term favoring ordered over disordered alloys

for systems in which disorder is known to occur.

It is possible to reverse the sign of the Δn of Eq. (30). Consider a model (29) where, (1) the two alloy constituents are inserted into the alloy structure and each atom is allowed to interact with like but not unlike atoms, (2) local chemical potentials, i.e. the ϵ_p, are brought to a common value after the manner of the preceding section and (3) constituents A and B interact. The process of bringing the two local chemical potentials into register leads to smaller separations of the band centers of gravity and to a reversed sign of Eq. 29, while yielding quite similar ΔE. However, the magnitudes of the Δn remain troublesomely large. In our view, all aspects of d charge transfer cannot unambiguously be built into such simple schemes. Nonetheless, model calculations of this sort are valuable for the physical insight they provide and for the usefulness of the heats of formation they predict.

VII. The Energetics of Charge Transfer

Whether treated in terms of the simplified rectangular density of states model or with more rigorous detailed calculations, charge transfer affects the energy of alloy formation by modifying the centers of gravity and intrinsic band widths+ of individual alloy components and by the introduction of a Coulomb term explicitly into the heat of formation as in Eq. 21a. The effective U in Eqs. 28 and 21a may, in some order, differ but in first approximation they are the same. A value of 2 or 3eV is usually attributed to U. In this section we will note how such a value may come about and why it may be still smaller yet.

In Eq. 28 we are concerned with the shift in the d levels due to the introduction of an extra d electron at the site. Now the bare Coulomb interaction between a pair of atomic d electrons is of the order of 20 to 30eV but the process of bringing the extra electron onto the site causes the d electrons already there to change their charge distribution. In addition, the conduction electrons will flow in the opposite direction of the d transfer so as to screen the charge.

Herring asked (30) what is the energy for a d electron to hop in a crystal? Assuming that the non-d electrons screen to maintain site neutrality and that we normally describe the pure transition metals as being in $d^n s$ configurations, the process involved is

$$2\ (d^n s)\ \text{atoms} \rightarrow (d^{n+1}) + (d^{n-1}s^2)$$

and the energy, u, associated with the process is

$$u = E(d^{n+1}) + E(d^{n-1}s^2) - 2E(d^n s). \qquad (31)$$

+For example, hopping integrals between like (hence the intrinsic bandwidths) and unlike sites may be affected.

Substituting the second term on the right hand side of Eq. 21a into each of the terms on the right of Eq. 31 we have

$$u = \left\{(n+1)[(n+1)-1] + (n-1)[n-1)-1]-2n(n-1)\right\} \frac{U}{2} = U \qquad (32)$$

hence u and U are the same quantity. Using free atom spectral data to estimate the relative positions of the center of gravity of the three atomic configurations Herring found U to be ~3eV for Ni and it typically ranges between 1½ and 3eV for other 3d elements.

In Section III we noted that experiment suggests that not only is Δn_c, the conduction electron count change, opposite in sign to Δn_d but it is larger in magnitude as well. In other words the conduction electrons overshield; the site gaining d electrons becomes positively charged while the site losing a d electron gains and excess of electron charge. For this case Eq. 31 may be rewritten

$$u = E(d^{n+1}s^{-\delta}) + E(d^{n-1}s^{2+\delta}) - 2E(d^n s) = U-\delta V \qquad (33)$$

where U is the neutral atom Herring value and

$$-(1+\delta) \equiv \frac{\Delta n_c}{\Delta n_d} \quad . \qquad (34)$$

Spectral data for the positively charged $(d^{n-2}s^2)$ and (d^n) ion configurations can be used in combination with the neutral atom values to extrapolate to configurations appropriate to the first two terms on the right hand side of Eq. 33. V is of necessity positive, i.e. overscreening reduces u, and preliminary estimates indicate that u becomes zero valued for δ of the order of 0.2 to 0.3. These values lie in the middle of the experimental range indicated by Eq. 16! The experimental estimate of $\Delta n_c/\Delta n_d$ would thus suggest that, instead of bringing a site to a neutral charge the conduction electron response to d electron transfer is to reduce the Coulomb energy of such transfer to near zero. Unfortunately the uncertainties in the experimental values for $\Delta n_c/\Delta n_d$ are substaintial on the scale of concern to us here. It would appear that the Coulomb energy contribution to the alloy heat of formation is small but one can't say how small*. The U entering the level shift term, Eq. 28, is also small.

*We might note that Herring's estimate of U was not for alloying but for the magnetism of Fe, Co and Ni. The key parameter for magnetism is the ratio U/W. If the overscreening inferred for alloying is appropriate to this magnetic correlation problem, then U/W is quite small and a band theory description, neglecting local site correlations, should work quite well. This is the case.

VIII. Conclusion

In this review we have considered several of the electronic factors associated with the alloying of transition metals. These factors include, (1) d electron hybridization, which is determined by the relative availability of occupied d levels and holes, (2) band filling so as to equalize the local chemical potentials at different alloy sites, and (3) conduction electron screening of the d-electron effects. We argue that the energetically most important term is d band hybridization and in Section IV we derive an "electronegativity" scale based on the tendency for an element to gain or lose d count by hybridization. This scale agrees, in essential features, with Miedema's scale which was developed for use in estimating heats of formation [Eq. 20]. In fact, with suitable modification of other of the Miedema parameters the hybridization numbers can be used to replace the values of the Miedema d scale in estimates of transition metal-transition metal heats of formation. The greatest discrepancies between the Miedema and band hybridization scales on one hand and the Pauling electronegativity scale on the other, occur for the noble metals: cases where we believe (18) the Pauling scale properly indicates the tendency for net charge transfer. Now, while the noble metals are in many ways transition metal-like, they are indeed different. It may be that subtle differences in the relative roles of the various d and conduction electron bonding factors is at least partially responsible for the apparent discrepancy in electronegativity scales. In the last section we review some evidence suggesting that, due to screening, Coulomb effects arising from hybridization make only a small contribution, on the scale of d transfer, Δn_d, to the heat of formation of an alloy consisting of two transition elements. There is also such conduction - d compensation at the transition metal site in compound formation with a main group element. Miedema finds (17) it necessary to introduce a substantial "d-p bonding" term to his heat of formation, Eq. 20, when a transition metal and a polyvalent main group element are involved in compound formation. It may be possible to calculate this d-p energy in terms of imbalances in Coulomb screening and in factors such as band broadening.

While theory is beset with the problem that the heat of formation of a compound, or the difference in heats of two structures, involves numerical differencing of rather substantial terms it is on the experimental front where the effort is most needed. In fact, due to the paucity of experimental data, there is a growing tendency for theorists to measure the quality of their predictions by comparison with the calculations of others. Evaluated thermodynamic data such as that previously provided by Hultgren (31) badly needs updating. Experimental information such as that discussed in Section III also requires extension and refinement and the role of volume effects, only alluded to in this chapter, must be resolved.

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