ing process shows that a deeper investigation of the high-energy TLS and any other anomalous amorphous modes and their distinction, if any, from normal phonon modes of comparable energy is necessary before a full understanding is reached.

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Heats of Formation of Transition-Metal Alloys

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This Letter proposes a scheme for obtaining the d-electron energy-band parameters to be used in a simple analytic model of the alloy heat of formation, ΔH. The scheme employs, as an intermediate step, the equalization of the local chemical potentials of the two sites. Calculations for $3d$, $4d$, and $5d$ metal alloys yield ΔH in accord with experimental trends, but, unlike earlier estimates, with d charge transfer in the direction indicated by experiment.

Predictions of heats of formation of alloys, ΔH, have been the object of considerable recent attention. Semiempirical schemes employing model parameters as well as electron energy band approaches have been used with semiquantitative success.

Miedema and associates employed[1] a cellular model for the heat of formation, which for transition metals has the form

$$\Delta H \propto [-P(\Delta\varphi)^2 + Q(\Delta n^{1/3})^2]. \tag{1}$$

The first term, involving difference in electronegativities, φ, of the constituent atoms, is negative and generally dominates, while the second, associated with mismatch in the electron densities, n, at the surfaces of the atomic Wigner-Seitz cells, is a competing positive term. Starting with work-function and bulk-modulus data, Miedema was able to adjust the φ and n so that the known signs of ΔH were reproduced. In a complmentary effort, Alonso and Girifalco performed[2] cellular calculations exploring the consequences of bringing the density, n, of the two alloy constitutents to a common value. In the band-theory description of transition-metal alloys, Stern early pointed out[3] the importance of the ratio $(C_A-C_B)/W_{AB}$, where W_{AB} is the alloy bandwidth and the C's are the centers of gravity of the d bands of the two alloy constituents. Friedel and others noted[4] that the trends in the heats of formation of the pure transition elements are well described by considering only the d bands and attributing to them rectangular densities of states. There have been extensive investigations[5,6] of alloys involving the coherent-potential approximation (CPA), employing various models of the density of states. Pettifor[7,8] and Varma[9] have applied Friedel's rectangular-$\rho(\epsilon)$ scheme to the alloy problem. With the same C_i and bandwidths, W_i, as were used by Van der Rest *et al.*[5] in their more detailed CPA calculations, almost identical ΔH were obtained.[7] Granted this numerical success, and the analytic simplicity of a rectangular $\rho(\epsilon)$, the scheme offers insight into the energetics of alloy formation and the choice of band parameters. The model also provides an estimate of d-electron transfer between A and B by factoring the alloy density of states into separate constituent partial densities of states, centered at C_A and C_B, as indicated in Fig. 1.

Using pure-metal C values, estimates of the direction of d transfer tend to be contrary to experimental evidence. The purpose of the present Letter is to propose a scheme for estimating band parameters appropriate to the alloy and to show that a rectangular band model utilizing such parameters predicts the correct sign of d transfer while yielding good estimates of ΔH.

We have previously considered[10] Mössbauer isomer-shift results for alloys. Sampling changes in electron density at the nucleus, the isomer shift measures changes in non-d conduction-electron count directly and changes in the d-electron count indirectly via their screening of the non-d. When these are taken with photoelectron energy shifts, which makes a different sampling of d with respect to non-d transfer, it appears that alloying of a pair of transition elements generally involves a gain in d-electron count by the element initially having fewer d electrons. Since non-d charge transfer occurs in the opposite direction and is larger in magnitude, the net charge transfer is to the element having more d electrons, consistent with electronegativity trends. The direction of d-electron transfer can be understood in terms of d-d hybridization: Alloying between a metal with almost filled d bands, such as Pd, and a partially filled metal, such as Sc, involves the mixing of Sc hole character into occupied Pd levels, causing depletion in Pd and increase in Sc d count in the occupied bands. This hybridization description was used to define charge transfer and, in turn, an electronegativity scale for the transition elements elsewhere.[11] The tendency for non-d transfer to be larger in magnitude and opposite to d implies an overscreening of d transfer, and hence a near-zero Coulomb energy cost. It should be emphasized that the analysis of the experimental data necessary to obtain individual d and non-d components of charge transfer can be complex and ambiguous. However, when volume effects are small, Mössbauer data alone yield the *sign* of the d-charge transfer unambiguously.

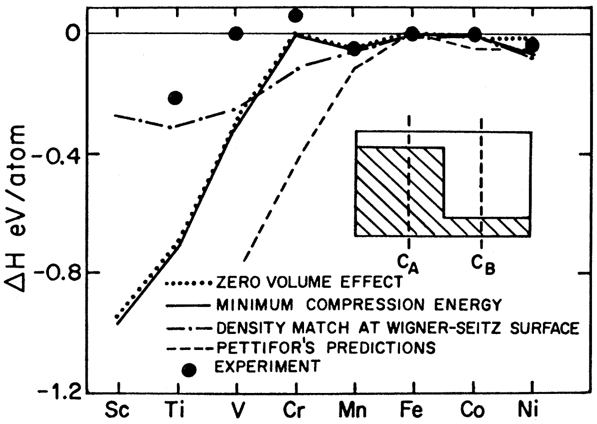

FIG. 1. Predicted heats of formation for 50-50 alloys of Fe with other $3d$ elements for three cases. Also included are Pettifor's results (Ref. 5). The inset shows a rectangular density of states for an alloy factored into A- and B-site partial densities of states.

The d-band heat of formation of an AB alloy with rectangular densities of states is[7,9]

$$\Delta H = N_{AB}C_{AB} - \frac{N_{AB}(10-N_{AB})W_{AB}}{20} - \frac{1}{2}\left\{N_A C_A + N_B C_B - \frac{N_A(10-N_A)}{20}W_A - \frac{N_B(10-N_B)}{20}W_B\right\}, \qquad (2)$$

where N_A, N_B, and $N_{AB}=(N_A+N_B)/2$ are the numbers of occupied d levels in metals A and B and the alloy, respectively, and[7,9]

$$C_{AB}=\tfrac{1}{2}(C_A+C_B)\,. \tag{3}$$

Taking the alloy bandwidth as the geometric mean of the widths of the pure metals with further broadening caused by mismatch in the constituent centers of gravity, we have

$$W_{AB}=[W_A W_B+3(C_A-C_B)^2]^{1/2}\,. \tag{4}$$

The factor of 3 in Eq. (4) was obtained[8] from site-hopping arguments. The change in d count at a site has been estimated,[7] assuming the stepped partial densities of states of Fig. 1, yielding

$$\begin{aligned}Q_A&=N_A(\text{alloy})-N_A\\&=\frac{(N_B-N_A)}{2}+2\hat{N}\,\frac{(\tilde{C}_B-\tilde{C}_A)}{W_{AB}}\,,\end{aligned} \tag{5}$$

where $\hat{N}=N_{AB}$ if $N_{AB}\leqslant 5$, and $\hat{N}=(10-N_{AB})$ if $N_{AB}\geqslant 5$. The $\tilde{C}$ are the centers of gravity after alloying. The $\tilde{C}$ tend to lie deeper in energy at the upper end of a transition-metal row so that the two terms oppose one another. Attributing[5,7,8] the pure metal centers of gravity to the alloy introduces $\tilde{C}_B-\tilde{C}_A$ which is a large fraction of W_{AB}. Then Eq. (5) indicates that d charge is transferred onto the heavier-atom site, contrary to experiment.

The following three-step process for determining the band parameters appropriate to an alloy leads to reasonable heats and d transfer of the correct sign.

(i) Bring constituents A and B to atomic site volumes appropriate to the alloy. Bandwidths and centers of gravity, to be used in Eqs. (2)–(4), are obtained for the pure metals at these volumes and the energy cost associated with the volume changes is estimated using bulk compressibility data.

(ii) The constituents are placed in the alloy but are allowed to interact *only* with like atoms, i.e., the C_A and C_B are appropriate to step (i) but the bandwidths are narrowed. The d charge, q, is transferred from one site to another so as to bring the local chemical potentials, ϵ_F, to a common value which results in $\tilde{C}_i$ values differing from C_i, requiring an energy

$$H'=\tfrac{1}{4}(\epsilon_F{}^B-\epsilon_F{}^A)[(N_B-N_A)-(\epsilon_F{}^B-\epsilon_F{}^A)/(U_B+U_A)-(U_A-U_B)/(U_A+U_B)]\,. \tag{6}$$

U_i is the Coulomb energy shift due to addition of a d electron at an i site, obtained by determining the position of C_i from band potentials constructed for different d-electron counts. Note that $q(U_A+U_B)=\epsilon_F{}^B-\epsilon_F{}^A$. The first term of Eq. (6) reflects a shift of energy of the N_A (or N_B) electrons at the A (or B) site by half the Fermi energy difference. Charge transfer involves an additional contribution $q^2(U_A+U_B)/4$, reflected in the second term of (6). The occurrence of U_i of different magnitudes at the two sites modifies the first two terms of (6) and causes C_{AB} to move off the value given by Eq. (3) and the effects of these on the heat of formation are incorporated into the third term of (6). The exact values of the U_i employed in (6) depend on the extent to which conduction electrons screen the d-charge transfer. In the present calculations U_i neglecting such screening have been employed. However, the detailed assumptions concerning the extent of the screening are not very important to the results, since the second and third terms of (6) are small.

(iii) The d bands of the two sites are allowed to interact, resulting in d hybridization and an alloy band width given by Eq. (4), inserting the $\tilde{C}_i$ of step (ii) and the W_i of step (i). This d hybridization is the most important factor determining the change in d-electron count at individual atomic sites.[11] Because of heavy screening, the intra-atomic and interatomic Coulomb energy associated with d charge transfer arising from hybridization is omitted.

The alloy ΔH then becomes the compression terms plus Eqs. (2) and (6). Results[12] are shown in Figs. 1 and 2 for several alloy sequences for which there are at least some experimental data.[1,13,14] The volumes for step (i) were chosen in three ways: First, sites were assumed to have the pure-metal values; second, given experimental molecular volumes V_M (which sometimes required interpolation from other compositions), site volumes were chosen so as to minimize the compressibility energy; third, given V_M, atomic volumes were chosen, in the spirit of Miedema[1] and Girifalco,[2] so that the electron densities of A and B were equal at the surfaces of the cells.

The results generally reproduce the experimental[14] trends, though there is some tendency to overshoot the mark: The positive heats in the middle of the Fe 4d row are too large in magnitude, as are some of the large negative heats. The experimental data for Fe 3d and Ni 3d indicate a break in smooth behavior between Cr and

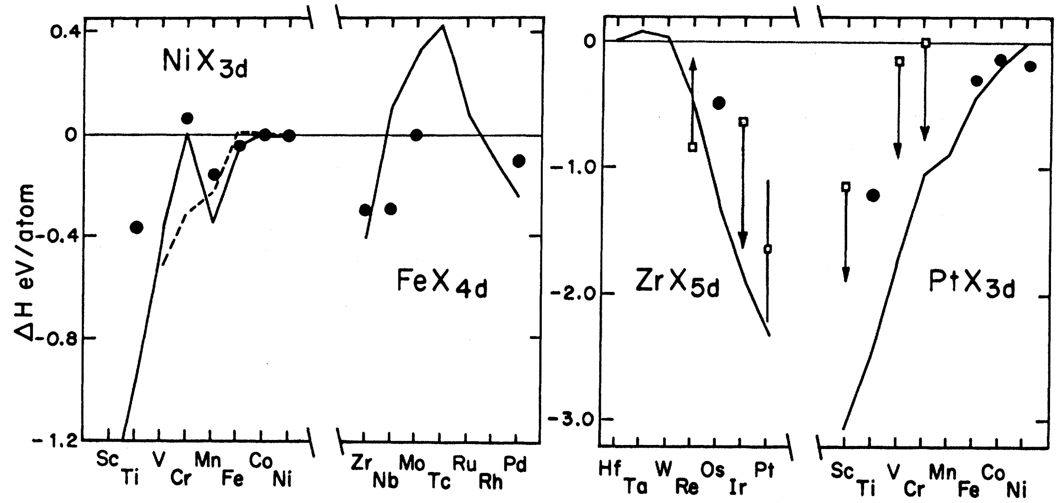

FIG. 2. Predicted heats of formation in the minimum-compression-energy approximation for 50-50 alloys: Ni with 3*d*, Fe with 4*d*, Zr with 5*d*, and Pt with 3*d* elements. The dashed curve is Pettifor's prediction (Ref. 5) for Ni 3*d* and the points are experiment (Ref. 14). Some of the experimental data (Ref. 13) provide bounds on Gibbs energies ΔG, as indicated by arrows.

Mn and the present calculations tend to yield such a break. Pettifor's results[7] for the same two alloy sequences are shown; the present results are in as good agreement with experiment. However, because of step (ii), $\tilde{C}_B - \tilde{C}_A$ is reduced in the present estimate, from that of Varma,[9] and much reduced from treatments employing pure metal values. This reverses the direction of *d* charge transfer. For example, instead of the transfer of 0.4 electron from V to Fe, there would be a transfer of 0.45 electron (no density matching) or 0.8 electron (with density matching) from Fe to V.

Energies are better estimated than charge transfer. In fact, divergent models produce quite similar energies. The point of step (ii) is to provide an approximate means for estimating the position of the $\tilde{C}_i$ for the alloy, without invoking the charge transfer of Eq. (5). Bringing the electron densities to a common value at the surfaces of the atomic cells makes a large contribution to ΔH when there is a large density mismatch. In such cases the effect is to reduce what would otherwise be a substantial negative ΔH (as for Fe-Sc and Fe-Ti in Fig. 1). This factor is not important in cases where positive ΔH occur such as Fe-Cr. It appears that the density term causes Eq. (1) to be positive in cases where density mismatch has little effect on ΔH and that the density term of (1) is mimicking other electronic factors which make positive contributions, as suggested[9] by Pettifor.

In this Letter we have seen a frequently encountered situation where similar energies are obtained for widely varying alloy wave functions, as manifested by the varying sign of *d* transfer. The self-consistency in the present approach associated with the introduction of alloy (rather than parent metal) parameters is the reason why the direction of *d* charge transfer agrees with experiment. We believe that, with care, such model calculations offer insight into both energetics and wave-function character associated with alloy formation and such insight will guide detailed *a priori* theory.

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[12]Relativistic renormalized d^ns^1 atom potentials were constructed as a function of atomic volume. d and non-d band centers of gravity and band extrema were determined. Electron densities were obtained with wave functions evaluated at centers of energy of the *occupied d* and non-d levels.

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New Type of d-Band–Metal Alloys: The Valence-Band Structure of the Metallic Glasses Pd-Zr and Cu-Zr

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The valence bands and core levels of the metallic glasses $Pd_{100-x}Zr_x$ ($65 \leq x \leq 75$) and $Cu_{100-x}Zr_x$ ($40 \leq x \leq 70$) and the polycrystalline pure components have been measured by ultraviolet photoelectron spectroscopy ($h\nu = 21.2$ and 40.8 eV) and x-ray photoemission spectroscopy ($h\nu = 1253.6$ eV). The valence-band spectra of the alloys are characterized by a large shift of the Cu and Pd d-band peaks to higher binding energies and a complete change of the shape of these bands to Gaussian-like peaks. This behavior is in contrast to crystalline d-band alloys studied to date.

Metallic glasses are presently the object of many investigations. The aim of our photoemission studies on metallic glasses is twofold. *Firstly*, we are interested in the electronic band structure of noncrystalline metals and alloys, in order to study the effect of the lack of crystal periodicity on the electronic states. We would like to correlate the electronic band structure with other physical properties such as superconductivity[1] and magnetism.[2] Moreover, we are interested in the relationship between the band structure and the glass forming ability.[3] *Secondly*, the glassy state offers the opportunity to study alloy concentrations which cannot easily be formed in the crystalline state. Therefore, we can study how the electrons of different transition metals behave on alloying.

In this work, we report the first detailed photoemission studies on a variety of Pd-Zr and Cu-Zr glasses. The glassy samples were prepared by rapid quenching from the liquid state using a novel piston and anvil apparatus[4] operating in high vacuum in the 10^{-8}-Torr range. Levitation melting was used in order to avoid any possible reaction between the liquid droplet and the crucible material. The glassy state of the splats was examined by x-ray diffraction.

For the pure components we used polycrystalline foils of Pd, Cu, and Zr which were cleaned by Ar-ion sputtering. The surface compositions of the glasses were checked by x-ray photoemission-spectroscopy (XPS), core-level spectroscopy, and Auger-electron spectroscopy (AES). Since cleaning by Ar-ion etching of the samples causes additional segregation especially in the case of Cu-Zr (reduction of Cu concentration in the surface region) the glasses were carefully scraped in the ultrahigh vacuum with a tungsten brush.