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Bonding effects in dilute transition-metal alloys

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The Mössbauer isomer-shift data of transition-metal nuclei as impurities in metals were considered in previous papers where it was shown that, once volume effects were suitably accounted for, the data fell on a "universal" curve. In this paper, the deviations from universality are examined in more detail in an attempt to better understand the alloying behavior. It is found that atom A as an impurity in metal B does not sustain a shift of the same magnitude as atom B does when it is an impurity in metal A . The results are discussed in terms of d -band hybridization and of the asymmetry in the solubility behavior in transition-metal-alloy phase diagrams.

I. INTRODUCTION

The Mössbauer isomer shift provides a direct measure of charge flow on or off an atomic site during alloy or compound formation. As we have discussed¹ previously, an extraordinary correlation occurs between the isomer shifts of a variety of transition-metal nuclei (^{57}Fe , ^{99}Ru , ^{181}Ta , ^{182}W , ^{189}Os , ^{193}Ir , ^{195}Pt , and ^{197}Au) when these atoms are dilute impurities in a wide variety of metal hosts. Once volume effects are accounted for, the variation in isomer shift as a function of host metal resembles in a striking way the electronegativity difference between host and impurity. In other words, the isomer shift, ΔS , can be expressed approximately by

$$\Delta S \cong K(\phi_h - \phi_i) \quad (1)$$

where ϕ_h and ϕ_i are the electronegativities of the host and impurity, respectively, and K is a constant. While chemical intuition is satisfied by having charge transfer, as manifested by ΔS , correlate with electronegativity trends, the full implications of the isomer-shift data to transition-metal alloying have not been recognized.

The purpose of the present paper is to make a quantitative comparison of the isomer-shift trends obtained for the different impurities and for different hosts. It will become clear that there is no reciprocity,

that is, A as an impurity in B does not sustain a shift of the same magnitude as B in A . This implies that, after having removed the dependence of any shift upon nuclear and atomic parameters, Eq. (1), with or without extra terms, is not a universal equation if K is taken as a constant. An equation of this form does crudely indicate overall trends, but does not encompass the details of transition-metal bonding with its interplay of d and non- d electron effects. Some suggestions of the bonding trends across the transition series will be inferred from the ΔS behavior.

Detailed comparison of the isomer-shift data is complicated in three ways: (i) by the fact that ΔS depends on nuclear and atomic parameters which are specific to the element in question, (ii) because volume corrections cannot be applied uniquely, and (iii) because of the uncertainties in the raw data. To reduce these problems, we will concentrate on obtaining the average slope of the variation in ΔS for some given impurity with varying hosts, and similarly for some given host with varying impurities. We concentrate on the $5d$ row of impurities as the only row for which there are data for a number of Mössbauer nuclei. The matter of volume corrections is dealt with in Sec. II, with discussion concerning nuclear and atomic parameters later. We believe that the trends in the average slopes provide insights into transition-metal alloying which were not previously available from previous analyses of the isomer-shift data.

II. ISOMER SHIFTS AND VOLUME CORRECTIONS

The isomer shift, ΔS (mm/s), involves the difference in contact interaction between two samples (a source and an absorber), where

$$S = [0.00608Z\delta\langle r^2\rangle\rho(0)]/E_\gamma, \quad (2)$$

and Z , $\delta\langle r^2\rangle$, E_γ , and $\rho(0)$ are, respectively, the nuclear charge, the change in the square of the nuclear radius (10^{-3} fm²), the γ -ray energy (keV), and the electron-contact density (a_0^{-3}) at the nucleus of the source or absorber.

The electron-contact density $\rho(0)$ has contributions from the s -like components of the valence electrons, $\rho_v(0)$, and from the ion core. The core contribution has little variation from sample to sample so that the change in contact density measures $\Delta\rho_v(0)$. This contact-density change is affected by any change in the s -electron count at the site, by any screening of the s charge due to changes in other orbital components of the valence-electron charge, and by any difference in the atomic-site volume between source and absorber. The d electrons are active in d -electron bonding, and an increase in d charge will, in general, screen the more diffuse s - p components resulting in a reduction in the contact density. This screening can be expressed by

$$\Delta\rho_v(0) = C\rho_s(0)(\Delta n_c + R\Delta n_d), \quad (3)$$

where Δn_d and Δn_c are the changes in d -like and non- d conduction electron-charge count. R is negative due to the s - d screening. C is a scaling coefficient which we have chosen to normalize with respect to the contact density of a free-atom s electron, $\rho_s(0)$. C then depends on the normalization of the conduction-electron charge within the Wigner-Seitz cell in the crystal as well as on the s -like fraction of the chemically active conduction-electron charge. The screening constant R also depends on details of the screening of conduction electrons by the d electrons and on the s -like fraction of the total conduction-electron charge. Relativistic Hartree-Fock calculations for atoms, constrained to be normalized within a Wigner-Seitz cell in the course of the calculation, indicate that $-0.15 < R < -0.25$ for the $5d$ elements (and equals -0.22 and -0.35 for Ru and Fe, respectively) if the conduction-electron charge is assumed to be entirely s like.

The screening constant R in the metal differs from the free-atom value. Most important to this difference is that the wave function character of the conduction electrons being screened is different from that of the electrons involved in charge transfer. The magnitude of R is larger in the metal than in the free atom because the fraction of s character associated with all conduction electrons being screened is greater than the fraction associated with those states

near the Fermi level which are involved directly in charge transfer. R in the metal is typically two to three times the free-atom value. Inasmuch as approximate charge neutrality is expected to be maintained, Δn_c and Δn_d must be opposite in sign and of the same magnitude. The two terms in the bracket of Eq. (3) are thus of the same sign and the second term is expected to be the smaller in magnitude.

It is necessary to subtract any volume contribution from the experimental ΔS in order to ascertain chemical effects. In general, the atomic volume of an alloy is different from the concentration-weighted average of the volumes of the separate constituents, i.e.,

$$V_{AB} \neq c_A V_A + c_B V_B, \quad (4)$$

where the c 's are the molar concentrations and V_A and V_B the elemental volumes of A and B , respectively. In the case of dilute impurities, A , in host B , the volume deviation of the alloy from V_B arises from both the site volume of A and from the distortions induced in the surrounding medium. It has been traditional to use elastic continuum theory^{2,3} to apportion these volume effects. There are a number of roughly equivalent versions of this theory providing estimates of V_A^B , the volume of the impurity A in the host B . One version is

$$V_A^B = V_A + (V_B - V_A) \frac{4\mu_B}{4\mu_B + 3K_A}, \quad (5)$$

where μ_B is the shear modulus of the host and K_A the bulk modulus of the impurity. The model involves the adjustment of the surrounding medium to the presence of an elastic impurity sphere of the wrong size and some given compressibility. The adjustment brings the impurity to an appropriate size, considering the relative sizes and compressibilities of the impurity and host.

In addition to the impurity volume, an estimate is required of the contribution to ΔS associated with the volume readjustment. Volume derivatives are available from experimental pressure-dependent studies for Fe,⁴ Ta,⁵ and Au.⁶ Normalizing these derivatives by dividing by the nuclear parameters of Eq. (2) and by the contact density $\rho_s(0)$ of Eq. (3), the values obtained for the $5d$ elements, Ta and Au, are equal to within 2%, with a larger value obtained for the $3d$ element, Fe. Presuming a smooth variation along the $5d$ row, accurate derivatives can be found for the intermediate $5d$ elements. A considerably greater uncertainty is associated with interpolating between Fe and the $5d$ elements to obtain the Ru derivative.

In the limit that the fraction on the right-hand side of Eq. (5) approaches unity, the impurity takes on the host volume. Ingalls showed,⁴ that, under the assumption $V_A^B = V_B$, the volume-corrected isomer shifts for ⁵⁷Fe as an impurity in various transition-metal hosts coalesced to a curve which was largely in-

dependent of the row in the periodic table of the host. We showed¹ that the same correction works as well, or better, for the other sets of impurity-isomer-shift data, bringing them to a common shape. The raw and volume-corrected ΔS data for ^{197}Au are shown in Figs. 1 and 2 as an example. Volume corrections employing Eq. (5) would yield results intermediate between the two figures. The data show no marked dependence on the crystal structure of either the host or the impurity, other than to the extent that particular crystal structures tend to be associated with particular columns of the periodic table.

The experimental volume derivatives, $d\Delta S/dV$, for Fe, Ta, and Au all indicate an increase in contact density with decreasing volume as would be expected if the valence electrons are simply being squeezed. The change in $\rho(0)$ would come from the renormalization of the non- d conduction electrons plus the changes in screening of these electrons due to the compression of the d electrons. In addition, some change inevitably occurs in the relative d and non- d electron counts in the Wigner-Seitz cell upon compression. It is expected that these changes are small; to the extent that they do occur, they are, of course, not included in the electron counts of Eq. (3).

The data of Fig. 2 correlate well with known electronegativity trends, greater charge flow onto gold being associated with hosts further to the left of Au in the plot. There are certain deviations in the details from trends characteristic of most electronegativity scales and there are some deviations between the results for one impurity element and another. In most electronegativity scales, the noble metals are considered to be less electronegative than the transition metals immediately to their left. Thus the ΔS associated with the noble-metal hosts (column 11) would be expected to lie above the points immediately to their left in Fig. 2. Instead, they are seen to lie

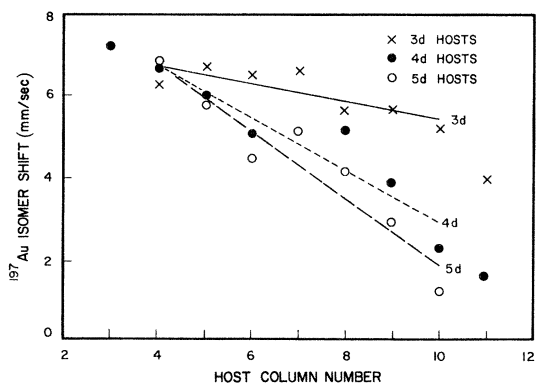


FIG. 1. Measured isomer shifts of ^{197}Au as a dilute impurity in various hosts. The lines are least-squares fits.

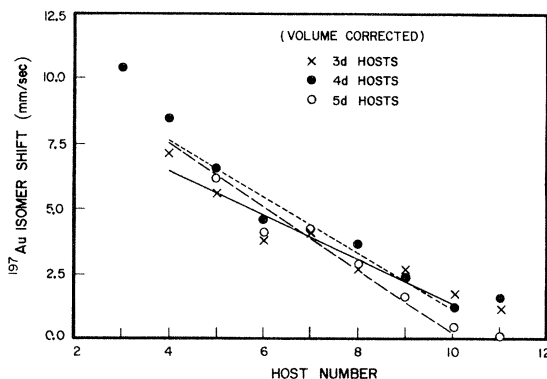


FIG. 2. Volume-corrected isomer shifts of ^{197}Au as a dilute impurity in various hosts. The lines are least-squares fits.

a bit below on a line connected with the data to the left; for other impurities such as Ru and Os (there is no noble-metal host data for W and Ta) the noble-metal host points lie well below a line connecting the transition-metal host points. Fits determining the slope, for some given impurity, of ΔS data across a sequence of transition-metal hosts will be obtained below. Granted the apparent irregularity as to where the noble-metal host points lie, they will be omitted from such fits.

Another deviation from common behavior amongst the volume corrected ΔS occurs¹ in a case not displayed here when Rh and Pd act as hosts for Ta and W. Instead of lying along the downward-sloped curve, as is the case for Au in Fig. 2, they rise with the Rh point above that for Ru and the Pd point above the Rh. In contrast, Co and Ni, and Ir and Pt display the "standard" downward trend for these impurities. This break in behavior is not an artifact of the volume corrections; Wagner and coworkers discerned⁷ its presence in their raw ΔS data. It would appear that Rh and Pd simply behave differently as hosts for under half-filled d -shell impurities such as Ta and W. (There is no data for W and Ta in Ag but if there were, it might well show the same deviation.) The Rh and Pd host points will nevertheless be included in the ΔS slope fits which follow. Their inclusion affects the quantitative details but not the qualitative conclusions.

In order to compare ΔS for different impurities, the nuclear parameters and contact densities of Eq. (2) must be divided out, obtaining normalized shifts

$$\Delta S^n = \Delta S / [Z \delta \langle r^2 \rangle \rho_v(0) / E \gamma] \quad (6)$$

The nuclear parameters have been taken from Kalvius and Shenoy⁸ and their products are listed in the first column of Table I. Following the traditional treatments⁹ of Knight shifts, where it is usual to normalize solid-state hyperfine fields with free-atom terms, we will employ the free-atom valence s -

TABLE I. Nuclear parameters and free-atom valence s -radial contact density.^a

	$\frac{Z\delta\langle r^2\rangle}{E_\gamma}$	Free-atom $\rho_s(0)$ (a_0^{-3})	Renormalized $\rho_n(0)$ (a_0^{-3})
Fe	-25.8	38.7	108
Ru	9.78	112	308
Ta	-498	582	1181
W	-0.148	668	1383
Os	-4.18	892	
Ir	5.80	1009	1810
Pt	-5.18	1144	1869
Au	8.79	1297	1906

^aAlso listed are the valence s -contact densities of an atom normalized to the metallic Wigner-Seitz cell during the course of the calculation. The atomic results involve a relativistic Hartree-Fock calculation with a finite-sized nucleus, with $\rho_s(0)$ obtained by sampling over the nucleus. The nuclear parameters are from Kalvius and Shenoy (Ref. 8).

electron-charge contact densities, $\rho_s(0)$, in the normalization. These contact densities are listed in the second column of the table. The consequences of making alternate choices for $\rho_v(0)$, which more faithfully reflect conduction-electron character in the metal, will be considered shortly.

III. ISOMER SHIFTS FOR $5d$ IMPURITIES

A. Variation of the shifts for a given impurity

We wish to compare the normalized isomer shifts for the different $5d$ impurities in transition-metal hosts ranging from the Ti through the Ni columns. Except for the noble-metal hosts, there is too little data for other nontransition-metal hosts for meaningful comparison. The noble-metal hosts will be considered later. Granted certain scatter in the ΔS^n and the deviations from common behavior mentioned above, the simplest measure of chemical or alloying trends is the average slope, $d\Delta S^n/dN_h$ of a line such as those plotted in Fig. 2. The derivative is taken with respect to the column in the periodic table in which the host elements lie. Least-squares fits were made separately to the data for hosts Ti through Ni, Zr through Pd, and Hf through Pt.

Slopes for the volume-corrected ΔS^n , where the impurity is assumed to have the host volume, appear in Fig. 3. Roughly a factor-of-3 change in $d\Delta S^n/dN_h$ is seen on going from Ta to Pt, over and above any

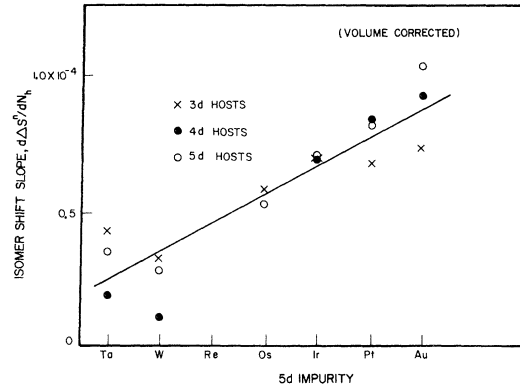


FIG. 3. Volume-corrected normalized isomer-shift slopes, $d\Delta S^n/dN_h$, for $5d$ impurity atoms vs their column in the periodic table. These slopes, i.e., the variations of the isomer shift for some given impurity as a function of the column in the periodic table in which the host resides, were obtained from plots similar to Fig. 2 for each impurity atom. The line is drawn to guide the eye.

scatter in the results. This variation cannot be described in terms of models such as Eq. (1) which assume "reciprocal" behavior, which would give

$$\Delta S^n(\text{Ta in Pt}) = -\Delta S^n(\text{Pt in Ta}) .$$

Instead, we have

$$\Delta S^n(\text{Ta in Pt}) \approx -0.3\Delta S^n(\text{Pt in Ta}) .$$

Errors in the choice of normalizing factors appearing in Eq. (6) can, of course, affect the inferred trend. There are uncertainties in the change in nuclear size $\delta\langle r^2\rangle$, which could be responsible for the tungsten points lying slightly below their counterparts for Ta, but errors in the nuclear parameters cannot be responsible for the overall variation. There is also the question of the choice of valence-electron contact density, $\rho_v(0)$, employed in Eq. (6). Free-atom wave functions provide, at best, an approximate value of $\rho_v(0)$ appropriate to the metal. The conduction electrons contributing to ΔS are normalized within the Wigner-Seitz (WS) sphere and they are not purely s -like in character. The effect of normalization can be roughly accounted for by evaluating $\rho(0)$ with atomic s functions which are normalized to the WS sphere in the course of a self-consistent atomic calculation. A set of $\rho_n(0)$, which were obtained in this way, appear in the third column of Table I. The variation in contact density on going from Ta to Pt is smaller, fractionally, than that obtained with the free-atom densities, i.e., the ratio

$$1 > \frac{\rho_n(0):\text{Ta}}{\rho_n(0):\text{Pt}} > \frac{\rho_s(0):\text{Ta}}{\rho_s(0):\text{Pt}} . \quad (7)$$

This inequality implies that, upon normalization

with the $\rho_n(0)$, the ΔS^n for Ta would be reduced relative to those for Pt. Then in turn, the Ta slope would be smaller and there would be a greater, not smaller, fractional variation in the plotted derivatives than seen in Fig. 3. Also, the non- d conduction electrons in a metal are not entirely s -like in nature; the bottom state of a free-electron band is s -like, but as one goes higher in the band the fraction of s character decreases. Granted this, less s weight, on average, is expected in the fuller bands of Pt than in the emptier ones of Ta. Accounting for the fractional weighting, the resulting conduction-electron contact densities $\rho_c(0)$ are smaller than the $\rho_n(0)$ and since the reduction is greatest for Pt,

$$\frac{\rho_c(0):\text{Ta}}{\rho_c(0):\text{Pt}} > \frac{\rho_n(0):\text{Ta}}{\rho_n(0):\text{Pt}} > \frac{\rho_s(0):\text{Ta}}{\rho_s(0):\text{Pt}} \quad (7a)$$

This implies that the variation in $d\Delta S^n/dN_h$ is even greater than indicated in Fig. 3, and that this variation is not an artifact of the normalization procedure.

The volume correction applied to the ΔS^n above is more severe than that predicted by the elastic continuum model of Eq. (5) and it is worth having some measure of how the volume correction affects any conclusions drawn from Fig. 3. Let us consider the derivatives associated with the volume *uncorrected* ΔS^n data and presume that these provide a bound on what would be obtained with other correction schemes. The resulting least-squares fit appears in Fig. 4. There is a greater spread in the $d\Delta S^n/dN_h$ in Fig. 4, but the overall variation is much the same as in Fig. 3. Certain details of one plot are mirrored in

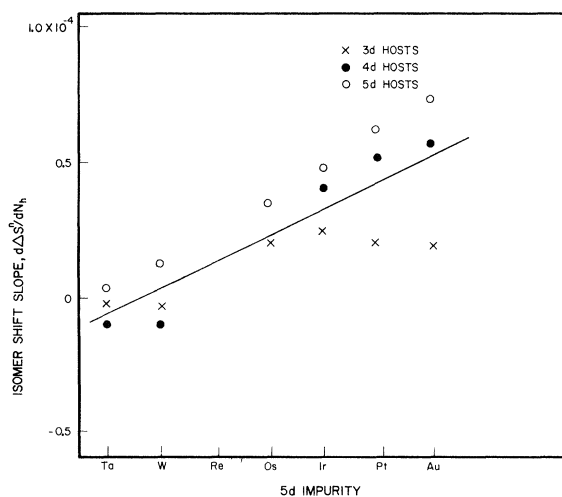


FIG. 4. Normalized isomer-shift slopes, $d\Delta S^n/dN_h$, for $5d$ impurity atoms vs their column in the periodic table, uncorrected for volume. These slopes were obtained from plots similar to Fig. 1 for each impurity atom. The line is drawn to guide the eye.

the other; the points for ^{182}W in $4d$ hosts and for ^{195}Pt and ^{197}Au in $3d$ hosts lie low in both figures. While perhaps indicating "real" alloying tendencies, such details are within the combined uncertainties of experimental data and fits made to it.

It would appear that there is a real variation in $d\Delta S^n/dN_h$ across the $5d$ series which is neither due to normalization considerations nor due to details of volume corrections. The important result is that reciprocal behavior is not observed; bonding effects at atom A as an impurity in metal B are not simply the inverse of what atom B samples as an impurity in A .

B. Variation of the shifts for a given host

An alternate measure of isomer-shift trends is to compare the ΔS^n of the different impurities for some given host. A least-squares fit for the average slope of such a set, $d\Delta S^n/dN_i$, is more susceptible to the vagaries of the normalization scheme and is based on fewer data points than were the fits reported in Figs. 3 and 4. Also for some hosts there is ^{182}W and/or ^{181}Ta impurity data while for others there is none and this affects the fits. Fits were done with these impur-

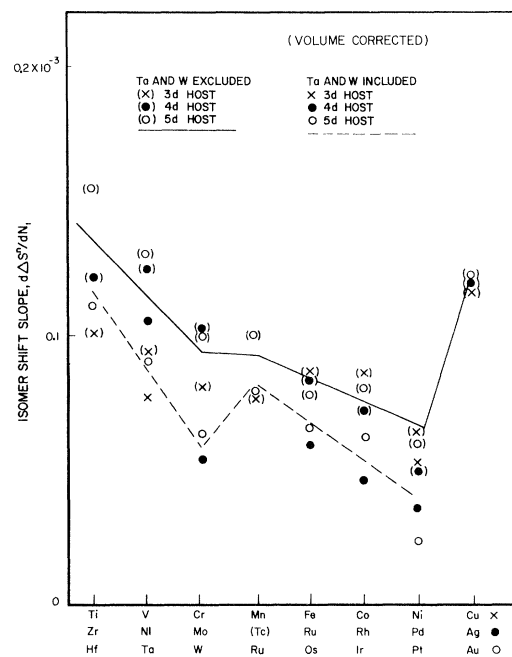


FIG. 5. Volume-corrected normalized isomer-shift slopes, $d\Delta S^n/dN_i$, for a given host vs host column of the periodic table. These slopes, which are the variation of the isomer shift for some given host as a function of the column of the periodic table appropriate to the $5d$ impurity, were obtained from plots of the volume-corrected isomer shift of $5d$ impurity atoms in a given host.

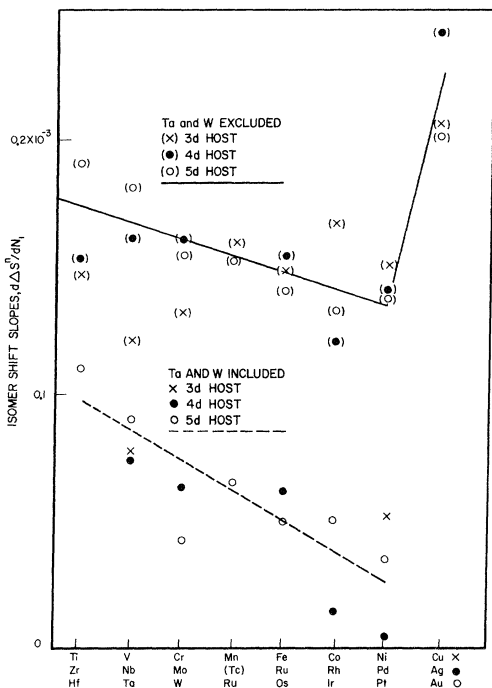


FIG. 6. Same as Fig. 5, except without volume correction.

ities omitted and with these impurities included, for the cases for which there is such data. The slopes for the volume-corrected ΔS^n are summarized in Fig. 5: points for slopes with Ta and W excluded are shown in parentheses. As in Figs. 3 and 4, lines have been drawn to guide the eye. The $d\Delta S^n/dN_i$, where Ta and W are excluded, lie higher, but both sets of slopes show the same downward trend on going from Ti column hosts to the Ni column. This is the inevitable consequence of the trend already seen in Fig. 3 except here more structure is suggested. The $d\Delta S^n/dN_i$ are quite different for noble-metal hosts than for the transition metals immediately to their left. Also, there appears to be a break in the downward trend in the vicinity of Cr, Mo, and W hosts which have half-filled d bands. No equivalent break is indicated in the impurity slopes of Fig. 3, but this may be due to lack of Re data points in that figure; Re does not have a suitable nucleus for isomer-shift measurements.

Similar fits for the volume-uncorrected $d\Delta S^n/dN_i$ appear in Fig. 6. There is a greater scatter in the points, typical of using the uncorrected data, but the basic trend is the same; slopes decrease on going from the Ti host column to the Ni column and rise to their largest values for noble-metal hosts. The fits including ^{181}Ta and ^{182}W are further below the fits without them than was the case in Fig. 5. It is unclear as to whether or not there is a break in the

downward trend in the vicinity of Cr, Mo, and W.

As already indicated, the downwards trends of Figs. 5 and 6 are simply a different measure of the same effect seen in upwards trends of the $d\Delta S^n/dN_h$ in Figs. 3 and 4. Figures 5 and 6 offer more detail (and greater uncertainty). There is a suggestion that the $d\Delta S^n/dN_i$ break from smooth variation across the transition elements in the vicinity of half-filled host d shells and there is a marked difference between noble-metal and transition-metal hosts.

IV. ISOMER SHIFTS FOR Fe, Ru, AND Os IMPURITIES

The isotopes ^{57}Fe and ^{99}Ru are the only two which are appropriate for isomer-shift studies in the $3d$ and $4d$ rows of the periodic table. They and ^{189}Os happen to be in the same column of the table allowing inspection of trends in ΔS^n down as well as across the periodic table. Greater difficulties are encountered in making any volume correction to the Ru data.

Volume derivatives $d\Delta S^n/dV$ may be inferred from experimental pressure-dependent studies for Ta, Au, and Fe. For Ta and Au, the derivatives are almost exactly the same and similar values are assumed for the derivatives of the other $5d$ elements. The derivative for Fe is quite different, raising the question of what should be employed for Ru; the average of the Fe and the $5d$ values was used.

The slope, $d\Delta S^n/dN_h$, for each of Fe, Ru, and Os as impurities, measured across the sequence of $3d$, $4d$, or $5d$ hosts, appears in Fig. 7. Slopes are shown for both the uncorrected and the volume-corrected

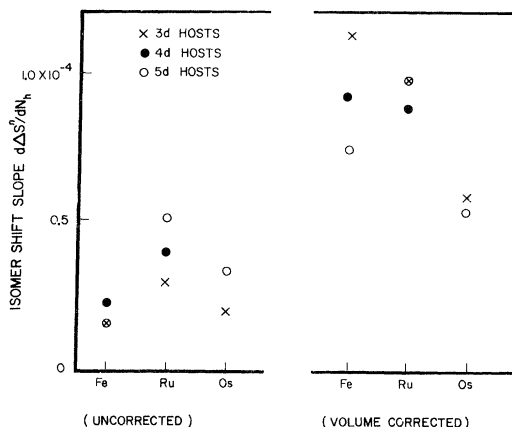


FIG. 7. Volume-corrected and -uncorrected normalized isomer-shift slopes, $d\Delta S^n/dN_h$, for ^{57}Fe , ^{99}Ru , and ^{189}Os as dilute impurities vs their row in the periodic table. These slopes, i.e., the variations of the isomer shift for each of the three impurity atoms as a function of the column in the periodic table in which the host resides, were obtained from plots similar to Fig. 2 for the three impurity atoms.

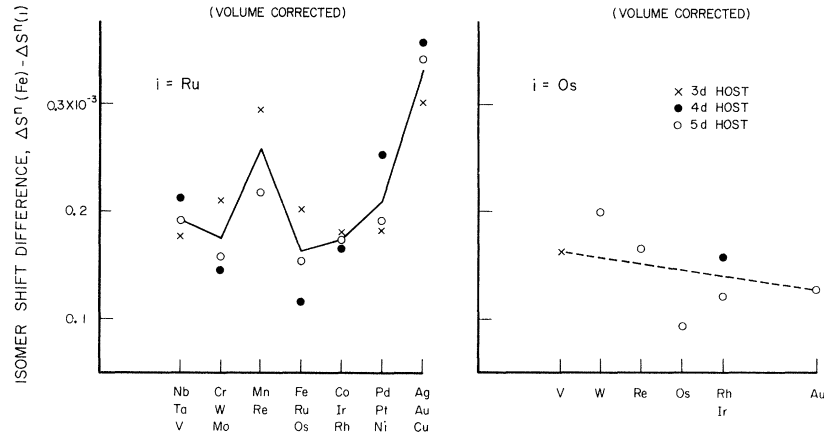


FIG. 8. Difference in volume-corrected normalized isomer shift, ΔS^n , for ^{99}Ru with respect to ^{57}Fe , and for ^{189}Os with respect to ^{57}Fe as a function of host column in the periodic table.

ΔS^n . No clear trend emerges. More information is available in Fig. 8, where the difference in ΔS^n for a pair of impurities in some given host is considered. Figure 8 is limited to the volume-corrected case; the uncorrected are almost identical in shape, but are shifted so that Fe-Ru lies just above and Fe-Os slightly below zero. There is a strong indication that Fe and Ru impurities respond quite differently to being imbedded in the noble metals. There is also the suggestion of a break in alloying behavior for hosts with half-filled bands. Since there are only one-third as many points in the $\Delta S(\text{Fe}) - \Delta S(\text{Os})$ plot, little can be said other than it would appear that the normalized ΔS^n are largest for Fe among these three elements.

V. DISCUSSION

The magnitudes of the isomer shifts indicated in the figures are quite substantial. If measured in terms of the contact density of a free-atom valence s electron, the change in volume-corrected shift associated with going from a host from the Ti column to a noble-metal host is equivalent to a change in s -electron count of the order of one electron at the impurity site. Due to the interplay of conduction and d -electron bonding effects, the net charge transfer on or off a site is, of course, much less. Larger effects are evident for impurities to the right than to the left in the periodic table or, equivalently, larger effects are associated with the hosts to the left. The noble metals do not follow this reciprocal behavior. As an impurity, Au behaves much like its neighbors immediately to its left, Pt and Ir, while, as can be seen in Figs. 5, 6, and 8, the shifts associated with noble-metal hosts are quite different from those of the transition metals immediately to their left.

When viewing the ΔS data, it should be remembered that not all of the results were obtained for stable substitutional alloys; the solubilities of some impurities in some of the hosts are vanishingly small. In such cases, the samples were prepared by ion implantation. Neither any variation in solubility nor any variation in the preference for bcc versus fcc versus hcp structures among the transition elements has any discernable effect on the results. Granted the experimental scatter, "smooth" trends are seen.

As already discussed, transition-metal alloying involves an interplay of d -band bonding, of conduction-band screening of the electron transfer associated with d bonding, and of direct conduction-band bonding. An increase in contact density is associated with an increase in s - p conduction electron count at an atomic site, whereas an increase in d -electron count increases the screening of the conduction electrons already present, thus reducing the contact density. This leads to Eq. (3)

$$\Delta\rho_v(0) = C\rho_s(0)(\Delta n_c + R\Delta n_d) \quad , \quad (3)$$

where R is a negative factor appropriate to the d screening of some given impurity element. Upon alloying, Δn_c and Δn_d are generally expected to be opposite in sign, thereby making a contribution of common sign to $\Delta\rho(0)$. This tendency for compensating s - and d -charge flow is consistent with band-theory calculations¹⁰ and with the analysis¹¹ of isomer shifts taken with other experimental results for Au alloys. More important, charge compensation provides the best way to rationalize the occurrence of large $\Delta\rho(0)$ in metallic systems. An isomer shift which is numerically equivalent to a change in valence s -electron count of the order of one is best understood in terms of s - d screening with the net charge at an atomic site typically one-tenth rather than one electron. The

large magnitudes of the volume-corrected ΔS pretty well force this conclusion.

In addition, the signs of the ΔS and of their slopes indicate that a transition element gains contact density when alloyed with an element to its left and loses when the latter is to the right. In other words, the element to the right, such as Au or Pt, gains conduction electrons and loses d count when alloyed with elements to the left such as Ta and W. Such a loss is readily understood. Pt, for example, has an almost-filled d band. Hybridization with Ta, for example, causes the Ta unoccupied wave function character to be admixed into this nearly filled band. This admixture causes a reduction in the Pt d count associated with these bands. Alloying tends to cause the Pt d bands to fill, but hybridization of Ta wave function character into the Pt bands nevertheless causes the net Pt d count to be reduced — site d -electron count is not synonymous with d -band filling. This argument can be extended¹² to partially filled d bands, where there is competition between loss of d character in the initially occupied levels, and gain by the filling of unoccupied d levels through hybridization. Whatever the detailed origin, it appears that the signs and the magnitudes of the volume-corrected ΔS slopes clearly indicate the occurrence of s - d screening and the direction of s - (and d -) charge transfer. Some question can arise if one prefers an alternate volume correction; the slopes for the uncorrected Ta and W impurity shifts (Fig. 4) are near-zero valued. In such a case, the above arguments are not firm. However, we believe they do hold, even for Ta and W, given any plausible volume correction.

The above conclusions are the same as were reached earlier.¹ The new conclusion is that the variation of the slopes of ΔS is neither random nor small. The observed variation implies a systematic lack of reciprocity, that is, the chemical bonding in the alloys, as monitored by the isomer shift, is different for atom A imbedded as an impurity or dilute alloying element in host B than for impurity B in host A . Therefore, while the ΔS results indicate charge transfer in the direction consistent with electronegativity trends, the magnitude of the charge transfer cannot be described by a simple dependence on the difference in some atomic parameters, such as the electronegativities. The charge transfer depends on which element is the host and which the impurity.

Recently, van der Woude and Miedema have suggested¹³ adding a second term, involving the difference in atomic electron densities, to Eq. (1). This additional term improves the fit to the experimental trend, but does not account for the lack of reciprocity. It is possible to multiply Eq. (1) or the two-parameter version¹³ by an asymmetry factor that differentiates between A and B as to which is the host. Miedema¹⁴ has introduced such a factor in dealing with heats of alloy formation which tends to skew the

calculated heats in the right direction. This factor is not asymmetric enough to be adopted *per se* for charge transfer as manifested in the Mössbauer data. More important, we believe such a factor should explicitly reflect d -bonding effects for transition-metal-transition-metal alloys.

It is pertinent to ask if the observed charge-transfer trend is due to a variation in conduction-electron screening rather than to a real trend in chemical bonding associated with alloy phase formation. In other words, can the d transfer be much the same for A in B as for B in A , but the screening of the d charge be different? This seems unlikely. Granted that Δn_c and Δn_d are of opposite sign, the two factors make contributions of common sign to ΔS and thus the greater the conduction-electron screening, the greater the slope of ΔS . In general it is believed that increased host conduction-electron density enhances the screening. This enhancement would produce a trend which is opposite to the observed trend in Fig. 5, where the slopes are less for Ni and Pt hosts than for Ti and Hf. Even if it is argued that screening somehow becomes less effective for increased conduction-electron density, it is hard to rationalize the magnitude of the observed trend. Since Δn_d and Δn_c make contributions of the same sign to ΔS , a change in slope of a factor of about 3 would imply a change in the Δn_c screening term which is greater than 3. The variation in the conduction-electron densities across the transition metals is relatively small. With the exception of the column-IV elements (Ti, Zr, Hf), the variation in atomic volume across a transition-metal row is about 25%. Also, the conduction-electron occupation number (i.e., the non- d character) does not change by much more than this percentage across a row, except for the noble metals. As a result, the variation in conduction-electron density is modest. The resulting variation in screening is much less than the observed variation in Figs. 5 and 6. It may be that changes in such screening are partially responsible for the sharp break, seen in the figures, between the noble metals and the transition elements immediately to their left.

A. Alloy phase stability

The bonding implicit in the asymmetry seen in the isomer-shift behavior may be related to the alloy solubility limits for transition-metal alloys. Hume-Rothery has postulated¹⁴ a "relative valency effect," namely that the maximum mutual-terminal solubility of two elements is related to their respective valences, the amount of the solid solution in the element of lower valence being greater. Hume-Rothery applied this rule to, and it appears to have validity for, the noble metals, considered as having valence 1, alloyed with the polyvalent B -subgroup metals. As an example, Cu can dissolve over 13 at. % Ge in its

primary solid solution, whereas Ge dissolves far less than 1 % of Cu. The relative valency rule appears to be less general¹⁴ when two polyvalent *B*-subgroup metals are alloyed with each other.

There also appears to be a relative valency effect of this nature for transition-metal–transition-metal alloys. In attempting to check this, the database is less certain than for the nontransition metals, and the effect of intervening phases is an important complicating factor. Nevertheless, it does appear to have some applicability. Consider an alloy of, say, Ta and Pt. Ta dissolves only 12 % Pt, whereas Pt dissolves at least 17 % Ta, and if ordered fcc compounds are considered as extensions of the primary solid solubility, then up to 50 % Ta is “soluble” in Pt.

It is instructive to obtain the mutual solubilities of Ta and Pt using the Engel-Brewer correlation model.¹⁵ In this model certain electron configurations are assigned to the principal crystal structures and the solubilities are determined by these crystal-structure considerations. It is not our purpose here to discuss the model or certain aspects of its terminology with which we might take issue. Its consequences are worth consideration. Ta is considered to have the electron configuration $5d^56s$. All five of the $5d$ electrons are unpaired, as expected from Hund's Rule. The bcc crystal structure, considered to be stable for $s + p$ electron-to-atom ($e/at.$) ratios of 1.0 to 1.5, is obtained from the one $6s$ electron per Ta atom. When Pt, with an $s + p$ $e/at.$ of 3 from its electron configuration of $5d^76s6p^2$, is added, the limiting solubility would be reached when 25 % Pt is dissolved in the bcc Ta to give the $s + p$ $e/at.$ of 1.5. However, to maximize bonding, Pt will unpair its 4 internally paired d electrons and use the empty $s + p$ orbitals of Ta for bonding. This hybridization reduces the solubility to 12.5 % Pt in bcc Ta. At the other end of the diagram, 25 % Ta will dissolve in fcc Pt according to this model which favors the fcc structure for $s + p$ $e/at.$ of 2.5 to 3.0. Since the Ta configuration ($5d^56s$) already has only unpaired d electrons, no admixture is allowed. The atomic configurations employed here are inconsistent with assignments derivable from energy-band theory, however.

The Engel-Brewer model has a mechanism for explaining asymmetry in alloy solubilities which can be translated into band-theory notation. The nearly empty d -band metals maintain their configurations on alloying, the nearly full d -band metals permit hybridization of the antibonding d electrons. The isomer-shift results, although not depending on the crystal structures, also require an asymmetry of the hybridi-

zation behavior in a manner not unlike the Engel-Brewer theory.

B. Conclusion

It is evident that the variation in isomer-shift slopes is not an artifact of details of the volume corrections or of the normalization process. Furthermore, the variation does not seem to be explainable solely in terms of conduction-electron impurity screening. It seems inescapable that the Mössbauer results provide a measure of real changes in d (and perhaps $s-p$) bonding associated with alloying. Not only is Δn_d different in magnitude for atom A in host B than for atom B in host A , but this difference involves more than factors such as changes in crystal structure with the attendant changes in the number of nearest neighbors.

A few years ago, Wagner and co-workers⁷ greatly augmented the experimental database on Mössbauer isomer shifts associated with transition-metal impurities, thus allowing sufficient data to scan for trends. They⁷ discerned certain trends in the raw data. Previously, after having been volume corrected, it appeared¹ that the shifts provided strong evidence concerning the direction of both conduction and d -electron transfer associated with alloying. Now, from consideration of the slopes of the isomer-shift data, there seems to be strong indications of systematic variation in d -bonding effects which lie outside the noise associated with experimental uncertainties and quirks in the analysis. It is possible to say crudely that “larger” bonding, in the sense of larger hybridization and charge transfer, is associated with hosts, such as Hf, with nearly empty d bands and “smaller” with hosts, such as Pt, with nearly filled d bands. Bonding effects are again increased for the noble-metal hosts, as seen in Fig. 5. Beyond this, it is impossible to disentangle these bonding effects quantitatively given the isomer-shift data alone. Such understanding may come from consideration of other types of experiment and with further theoretical investigation.

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