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Volume-corrected isomer shifts of transition-metal impurities: An orbital electronegativity scale

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It is shown that, once volume effects are accounted for, a universal curve describes the Mössbauer isomer shifts of ^{57}Fe, ^{99}Ru, ^{181}Ta, ^{193}Ir, ^{195}Pt, and ^{197}Au impurity nuclei in a variety of hosts. The curve defines an "orbital" electronegativity associated with non-*d* electron charge flow on or off these transition-metal atoms in alloys. The shape of the curve is remarkable in the extent to which it agrees with the "total" electronegativity scales of Pauling, Gordy-Thomas, and others. This agreement suggests that *d* and non-*d* charge flow are simply proportional to one another to an extent we find surprising.

The purpose of this paper is to indicate that, once volume effects[1] are accounted for, an extraordinary correlation occurs between the isomer shifts of a variety of transition-metal nuclei (^{197}Au, ^{195}Pt, ^{193}Ir, ^{181}Ta, ^{99}Ru, and ^{57}Fe) in a wide range of hosts indicating strikingly common chemical behavior. Electronegativity, a measure of the tendency for charge to flow on or off an atomic site, underlies many model descriptions of compounds and alloys. The Mössbauer isomer shift provides a direct measure of charge flow, as sampled by the nucleus, and while the isomer shifts of impurity nuclei and electronegativity data have been compared[2] no consistent picture has emerged. There appears to be an electronegativity factor associated with the non-*d* conduction electrons of transition metals which is well defined, column by column of the Periodic Table.

The isomer shift involves[3] the difference in contact interaction, ΔS (mm/sec), between source and absorber, where

$$S=[0.00608Z\delta\langle r^2\rangle\rho(0)]/E_\gamma \tag{1}$$

and Z, $\delta\langle r^2\rangle$, E_γ, and $\rho(0)$ are the nuclear charge, the change in the square of the nuclear radius (10^{-3} fm^2), the γ-ray energy (keV), and the electron contact density (a_0^{-3}) of the source or absorber, respectively. $\rho(0)$ has contributions from the non-*d* valence electrons, $\rho_v(0)$, and from the ion core. The core contribution is almost the same in source and absorber and hence ΔS depends primarily on $\Delta\rho_v(0)$. S is a measure of non-*d* conduction-electron density at the nucleus and is affected by two chemical effects, i.e., any charge flow on or off the atomic site and by any interchange of *d* and non-*d* character at the site. It is also affected by any difference in the atomic volume at the impurity site relative to the impurity atom in its elemental form. It is necessary to subtract the volume contributions from the experimental ΔS in order to ascertain the chemical effects. An increase in non-*d* character, Δn_c, at the atomic site increases $\rho_v(0)$ whereas an increase in *d* count, Δn_d, screens the outer valence electrons, reducing $\rho_v(0)$. Atomic calculations indicate that the ratio, R, of the *d* screening term to the non-*d* term is about -0.5 to -1. Thus

$$\Delta\rho_v(0)\propto\Delta n_c+R\Delta n_d\,;\quad R<0\,. \tag{2}$$

We expect that both terms contribute because approximate charge neutrality should be maintained, i.e.,

$$\Delta n_c+\Delta n_d\sim 0\,. \tag{3}$$

In what follows, we will assume that $\Delta\rho_v(0)\propto C\Delta n_c$, where C is a constant common to all the transition metals of concern. This assumption simplifies the analysis and is supported by the results.

The experimental ΔS are plotted, for several of the elements of concern[4,5] here, in Fig. 1. From impurity to impurity and from row to row of the Periodic Table for the hosts, a common pattern is, at best, only crudely to be seen in the plots. The volume correction requires an estimate of the effect of volume on ΔS as well as the volume attributable to the impurity site in the alloy. The former is easier. For Ta,[6] Fe,[7] and Au,[8] there are experimental data of the effect of pressure, hence of volume,[9] on the isomer shift. Lacking similar data for Ru, Ir, and Pt, the volume dependence can be obtained by scaling off the known values by taking ratios of Eq. (1), namely,

$$\left(\frac{\Delta S}{\Delta V}\right)_i=\left(\frac{\Delta S}{\Delta V}\right)_j\frac{[Z\delta\langle r^2\rangle\rho_v(0)/E_\gamma]_i}{[Z\delta\langle r^2\rangle\rho_v(0)/E_\gamma]_j}\,, \tag{4}$$

where Kalvius and Shenoy's nuclear data[3] and free-

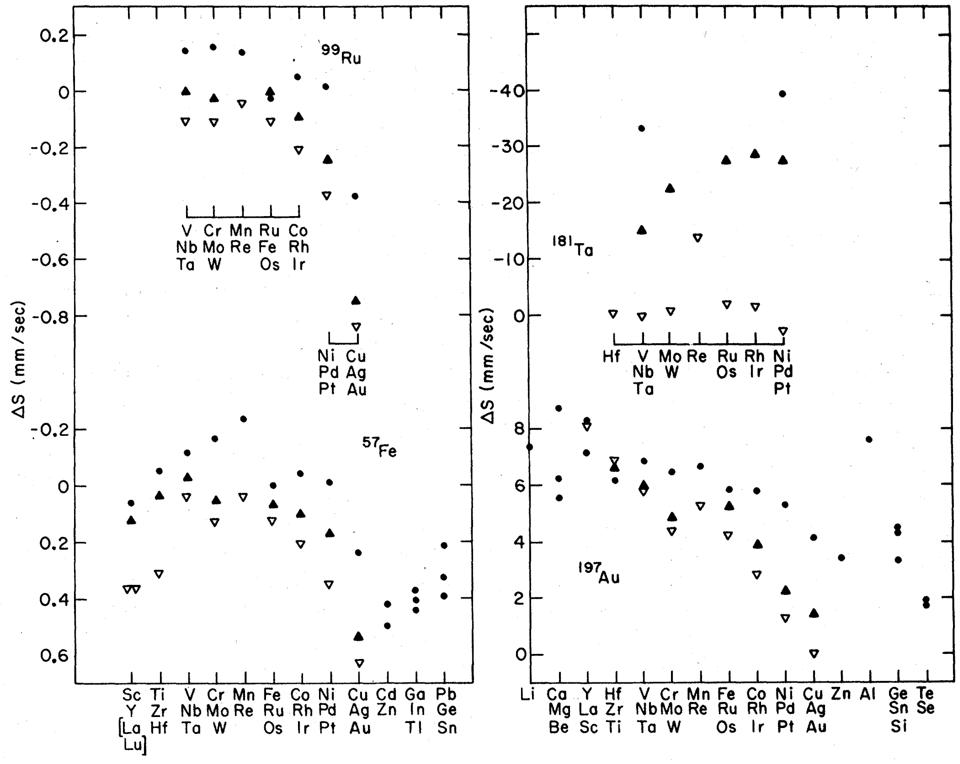

FIG. 1. Experimental isomer shifts of ^{99}Ru, ^{57}Fe, ^{181}Ta, and ^{197}Au impurities in various hosts as a function of the column in the Periodic Table in which the host lies. The vertical order of hosts for any given column of the figure is indicated by the listings below.

atom valence *s* electron contact densities[10] are used. Scaling in this way assumes common valence electron volume effects among the metals of concern here. There are also uncertainties associated with the $\delta\langle r^2\rangle$ values. Scaling off Fe and Ta yields results which agree to within 2% while using the Au data produces results ~30% greater. We have taken the average of the three predictions obtaining $\Delta S/\Delta \ln(1/V)$ of 1.12, 3.2, and −2.64 mm/sec for Ru, Ir, and Pt, respectively. Since, from simple normalization arguments, one expects S to vary roughly as $1/V$, the derivatives of S are expressed in terms of inverse volume.

The choice of impurity-site volume presents greater difficulties because there is no unique choice.[11] In a few of the alloys, such as Au_xPt_{1-x}, the sites preserve their volumes since the alloy volume is nearly a weighted average of the constituents, namely,

$$V(A_xB_{1-x}) \simeq xV(A) + (1-x)V(B)\,, \tag{5}$$

but for the majority this is not a good approximation. There is only limited crystallographic data of the volume associated with an impurity; the volume on the site plus the distortion in the surrounding medium. Use of these data does not give any uniformity to the isomer-shift results. Ingalls attributed[1] the host volume to the impurity site in obtaining the volume corrected results for ^{57}Fe displayed in Fig. 2. The results for different elements in the same column of the Periodic Table

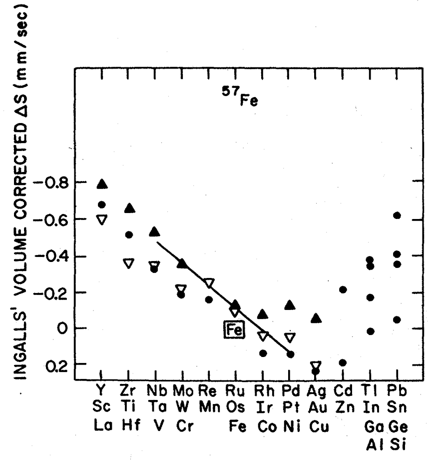

FIG. 2. Volume-corrected isomer shifts for ^{57}Fe in a variety of hosts as obtained by Ingalls (Ref. 1). The vertical order of hosts for any given column of points is indicated by the listing beneath.

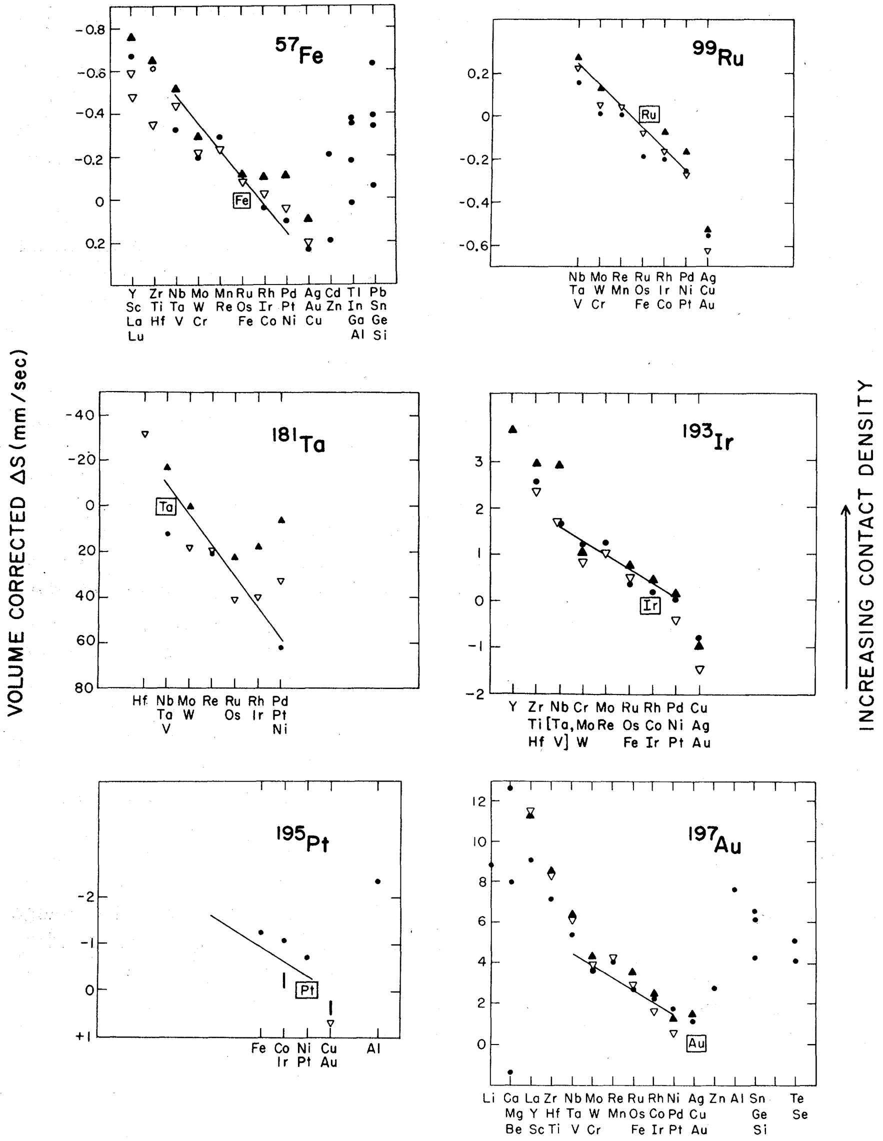

FIG. 3. Volume-corrected isomer shifts for ^{57}Fe, ^{99}Ru, ^{181}Ta, ^{193}Ir, ^{195}Pt, and ^{197}Au in a variety of hosts. The solid lines are of common slope, K after scaling for nuclear parameters and valence s contact densities in the manner of Eq. (6). A few differences occur between the ^{57}Fe results and those plotted in Fig. 2 and these are due to using more recent experimental data.

have moved together (compared with the raw data of Fig. 1) and the overall shape of the distribution is somewhat different. We will adopt Ingalls' choice of volume for all the isomer-shift data even when Eq. (5) holds.

The isomer shifts, with the volume terms subtracted out, are plotted for the Mössbauer impurities in Fig. 3. These encompass all the transition-metal impurity nuclei for which there is sufficient experimental data of sufficient resolution. Subtraction of the volume term moves the bulk of the data together, column by column. *Both* the experimental data *and* the volume corrections are important to character of the results: in some cases the experimental data dominates, in others the volume corrections are numerically larger.

Not only is the data for a given Mössbauer nucleus and a given column of the Periodic Table bunched together but the curves appropriate to the different Mössbauer nuclei have quite similar shape. Consider the host elements ranging from the V to the Ni column, for which there is the most data. It appears that the isomer shift varies nearly linearly in this region. The slope of any set of data for a given Mössbauer nucleus should be proportional to the nuclear parameters and to the contact interaction characteristic of the valence shell, i.e.,

$$\text{Slope} = [KZ\,\delta\langle r^2\rangle \rho_v(0)]/E_\gamma \,. \qquad (6)$$

Using the data employed in Eq. (4) and choosing a *common* value of the constant K, the straight lines

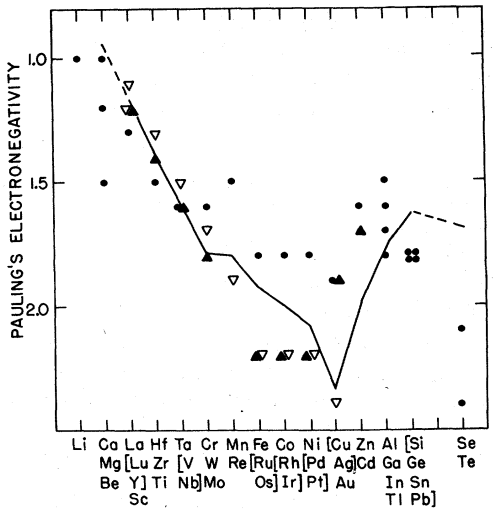

FIG. 4. Comparison of the volume-corrected isomer shifts with the Pauling electronegativity scale. Electronegativity values are plotted for those hosts for which ΔS appear in Fig. 3. The solid line is the result of taking the average of the six sets of volume-corrected isomer shifts of Fig. 3 after scaling with Eq. (6). The vertical position and scale of the line is set to match at the Ti and Ni columns of the electronegativity plot. The dashed segments at either end of the line are to remind the reader that these extrema are determined by very little experimental data.

drawn through the V-Ni region of Figs. 2 and 3 are obtained. There is a suggestion that the slope for the 3*d* element Fe is slightly less and that for the 5*d* elements, Ir and Au, slightly greater than this choice. There are other small discrepancies to be seen between one set of shifts and another. For example, the noble-metal shifts for Ir and Ru lie below the V-Ni line, while for Fe and Au they are on the line. Some of the variation may be due to an inconsistent set of nuclear and $\rho_v(0)$ parameters: The deviation in slope between Fe and Au is of a direction and magnitude consistent with the above mentioned discrepancy in the prediction of the $\Delta S/\Delta \ln(1/V)$ volume derivative from Fe and Au data. The tendency for the noble-metal shifts to be low for Ir and Ru cannot be blamed on the parameters employed in Eq. (6). What is remarkable is the extent to which all the data falls on a *universal curve*.

Compare Figs. 2 and 3 with Pauling's electronegativity scale[12] (Fig. 4) and with that of Gordy and Thomas[13] (Fig. 5), for the moment ignoring the solid lines. The shape is much the same with minima occurring at the noble metals. There are other electronegativity scales, some of which[14] have all the noble metals lying higher, with Au more electropositive than a number of the transition elements. Except for this feature, the Mössbauer data agree with these scales as well as they do with those of Figs. 4 and 5.

A discrepancy does occur for the Se column where the conventional electronegativities dips much more rapidly than the Mössbauer data. However, the Mössbauer data for this column is very sparse. The spread in any column is much the same for both Mössbauer and electronegativity data. In addition, there are no clear systematics in either sets of data rationalizing this spread, for example, one cannot draw parallel curves for 3*d*, 4*d*, and 5*d* rows. Therefore we have averaged the Mössbauer data for any given column for all six impurities obtaining the solid lines in Figs. 4 and 5. The curves have been scaled to match the Ti and Ni columns of the figures.

There is a striking similarity between the electronegativity trends and the isomer-shift curve. The former is presumably associated with total charge flow, i.e., the sum of Δn_d and Δn_c, while the latter makes a sampling of the difference in the manner of Eq. (2), biased (since $|R| < 1$) in favor of the non-*d* term. This offers the possibility of inferring *d* and non-*d* orbital[15] electronegativities associated with Δn_d and Δn_c, respectively. Granted the bias in the isomer-shift term, it provides, in first approximation, a measure of the non-*d* orbital electronegativity. The extent of the bias, of course, depends on the total charge flow associated with alloying. Charge flow, larger than we find plausible in metals would occur if Δn_d and Δn_c did not approximately balance one another.[16] The change in isomer shift from bottom to top of any of Figs. 2 and 3 corresponds to a difference in contact den-

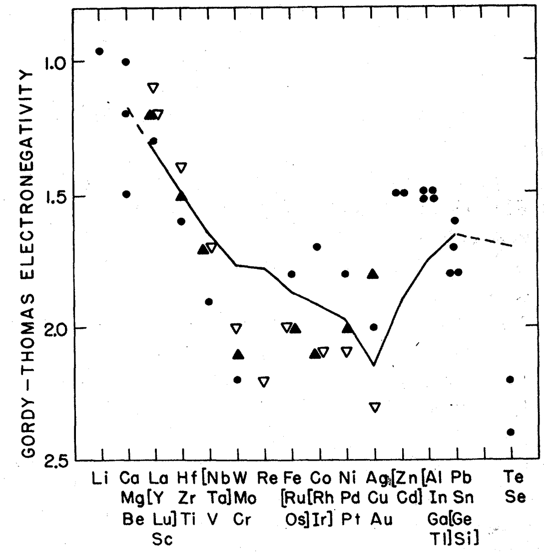

FIG. 5. Comparison of the volume-corrected isomer shifts with the Gordy-Thomas electronegativity scale after the manner of Fig. 4.

sity which is of the order of that due to one free-atom valence electron: a large effect.

Given Eqs. (2) and (3), any agreement between the conventional total electronegativities and the volume corrected isomer shifts of any given impurity nuclei implies that the ratio of Δn_d to Δn_c is a constant, as hypothesized. In turn, to the extent that the sets of volume-corrected shifts have a common scale, [in the manner of Eq. (6)] implies a *common* ratio of the d to non-d orbital electronegativities for all six elements. This is surprising in view of the possibility of the formation of bound states. There may be manifestations of such bound-state behavior in the apparently systematic deviations of Mn, Fe, Co, and Ni from their 4d and 5d counterparts in the total electronegativities but not in the isomer-shift data, as well as in the deviations seen for the polyvalent p band elements, such as Cd and Se, seen in Figs. 4 and 5.

By examining a large array of Mössbauer data and subtracting volume effects, we have, for the first time, a coherent picture of all the isomer-shift data for transition-metal impurities in alloys. The resultant picture is of opposing d and non-d charge flow or orbital electronegativity terms whose ratio is remarkably constant. This ratio must be tested with other evidence.

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[1] R. Ingalls, Solid State Commun. 14, 11 (1974); see also F. van der Woude and G. A. Sawatzky, Phys. Rep. 12C, 335 (1974). The implications of volume-corrected shifts are also discussed by R. L. Ingalls, Bull. Am. Phys. Soc. 18, 1591 (1973); and by R. Ingalls, F. van der Woude, and G. A. Sawatzky, in Mössbauer Isomer Shifts, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, to be published).

[2] See, for example, P. H. Barrett, R. W. Grant, M. Kaplan, D. A. Keller, and D. A. Shirley, J. Chem. Phys. 39, 1035 (1963).

[3] G. M. Kalvius and G. K. Shenoy, At. Data Nucl. Data Tables 14, 639 (1974).

[4] Another element for which extensive isomer-shift data are available is the nontransition-metal, Sn. As might be expected, it does not follow the same pattern of behavior and is not considered further here.

[5] G. Kaindl, D. Salomon, and G. Wortman, Phys. Rev. B 8, 1912 (1973); F. E. Wagner, G. Wortman, and G. M. Kalvius, Phys. Lett. A 42, 483 (1973); D. Agresti, E. Kankeleit, and B. Persson, Phys. Rev. 155, 1339 (1967); A. B. Buyrn and L. Grodzins, Phys. Lett. 21, 389 (1966); S. M. Qaim, Proc. Phys. Soc. 90, 1065 (1967); and where there are discrepancies in the data, we have consistently chosen the Kaindl *et al.* and Wagner *et al.* data.

[6] G. W. Wortmann, W. B. Holzapfel, G. Kaindl, G. M. Kalvius, and D. Salomon, Bull. Am. Phys. Soc. 18, 546 (1973).

[7] See, R. Ingalls, Phys. Rev. 155, 157 (1967), and Ref. 1.

[8] L. D. Roberts, D. O. Patterson, J. O. Thomson, and R. P. Levey, Phys. Rev. 179, 656 (1969).

[9] We have used K. A. Gschneidner's [Solid State Phys. 16, 309 (1964)] compressibilities to convert the pressure data to volume-dependent isomer shifts. Use of these data has introduced a slightly different value for the volume dependence of Au from that deduced in Ref. 8.

[10] R. E. Watson and L. H. Bennett, Phys. Rev. B 15, 502 (1977).

[11] R. E. Watson and L. H. Bennett, *Charge Density and Electronic Structure of Alloys*, edited by L. H. Bennett and R. H. Willens (Metallurgical Soc. of AIME, New York, 1974).

[12] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell U.P., Ithaca, N.Y., 1960), p. 93.

[13] W. Gordy and W. J. O. Thomas, J. Chem. Phys. 24, 439 (1956).

[14] E. T. Teatum, K. A. Gschneidner, Jr., and J. T. Waber, Los Alamos report No. 4003 (1968) (unpublished).

[15] This concept of orbital electronegativities has been used elsewhere, e.g., J. St. John and A. N. Bloch [Phys. Rev. Lett. 33, 1095 (1974); and references to G. Simons therein] have considered s and p electron terms.

[16] See, for example, R. M. Friedman, J. Hudis, M. L. Perlman, and R. E. Watson, Phys. Rev. B 8, 2433 (1973); and C. D. Gelatt, Jr. and H. Ehrenreich, Phys. Rev. B 10, 398 (1974).