Comment on volume-corrected isomer shifts of transition-metal impurities

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Using newly available Mössbauer isomer-shift data, it is found that a universal curve still can describe all the results for transition-metal impurities in all hosts for which data are available.

The Mössbauer isomer-shift data of transition-metal nuclei as impurities in metals were considered in a previous paper¹ where it was shown that, once volume effects were suitably accounted for, the data fell on a universal curve. The resulting volume-corrected isomer shifts receive contributions from any change in *d*-electron count Δn_d and any change in non-*d* conduction-electron count Δn_c , which occurs at the atomic site upon alloying. Comparison with various electronegativity scales suggested that, to remarkable extent, the ratio of Δn_d to Δn_c is a *constant* independent of impurity and independent of host. The question of the near proportionality of Δn_d and Δn_c is important to any coherent picture of transition-metal electronegativities and of bonding in transition-metal alloys. All the transition-metal Mössbauer data available to the authors was considered previously. There is now additional Mössbauer data² and the purpose of the present comment is to inspect its implications.

Rather extensive results for 57 Fe, 99 Pu, 181 Ta, 193 Ir, and 197 Au plus a limited data set for 195 Pt were considered previously. Of these, only 181 Ta, is a transition metal with an under half-filled *d* shell. There now exist more data for 195 Pt as well as results for 189 Os and 182 W: The latter providing a second example with a less-than-half-filled shell. With but one qualification, the new results reinforce the earlier conclusions. It would appear that a deviation from the universal behavior occurs when an element with less than a half-filled shell is alloyed with Rh and Pd which have almost filled 4*d* bands. More will be said of this later.

As discussed previously, the volume-corrected isomer shift is taken as

$$\Delta S_{\text{vol. corr.}} \equiv \Delta S - \left(\frac{dS}{dV}\right) \Delta V = C \left(\Delta n_c - R \Delta n_d\right) \quad , \tag{1}$$

where C and R are constants and V is the atomic

volume. An increase in d count screens the electrons contributing to the contact density at the nucleus and hence reduces the contact density, whereas an increase in the conduction-electron count contributes electrons with s-like components contributing to the contact density. Equation (1) assumes a constant ratio of the changes in s count and in total conduction-electron count (Δn_c). This suffices, providing that the ratio varies, at most, slowly across the Periodic Table. Given the minus sign inside the small parentheses, Ris positive and calculation suggests that it is of the order of $\frac{1}{2}$ to 1. In other words, the conduction and the *d* terms oppose one another and are of the same order. The volume correction requires estimates of the volume derivative and of ΔV . In the cases where there is pressure-dependent isomer-shift data for the pure metals, this was used to determine dS/dV. In cases where it is not known experimentally, we assume a common volume dependence scaled simply by the nuclear and atomic parameters appropriate to the particular element in question, i.e.,

$$\left(\frac{dS}{dV}\right)_{I} = \left(\frac{dS}{dV}\right)_{I} \frac{[Z\,\bar{\sigma}\,\langle r^{2}\rangle\,\rho_{r}(0)/E]_{I}}{[Z\,\sigma\,\langle r^{2}\rangle\,\rho_{r}(0)/E]_{I}} , \qquad (2)$$

where Z, $\delta \langle r^2 \rangle$, E, and $\rho_v(0)$ are the nuclear charge, the change in the square of the nuclear radius, the xray energy, and the contact density of a free-atom valence electron, respectively. Kalvius and Shenoy's tabulated nuclear parameters³ and recent estimates of the free-atom contact densities⁴ have been used. Scaling off Ta and Fe produces results which agree to 2%, while using Au produces values ~30% greater. Successful estimates of the volume correction involve ΔV based on the assumption that the impurity takes on the host volume in the alloy. This is not always the obvious choice as has been discussed previously.

The volume-corrected isomer shifts for all eight elements are plotted as a function of column of the

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FIG. 1. Volume-corrected isomer shifts for ⁵⁷Fe, ⁹⁹Ru, ¹⁸¹Ta, ¹⁸²W, ¹⁸⁹Os, ¹⁹³Ir, ¹⁹⁵Pt, and ¹⁹⁷Au in a variety of hosts. The solid lines are of common slope after scaling for nuclear parameters and valence s contact densities.

Periodic Table of the host element in Fig. 1. On the whole, the data are closely bunched, column by column. The raw experimental ΔS , on the other hand, show much more scatter. The straight lines drawn through the plots are of common slope once the shifts have been divided by the normalizing factor $[Z \delta \langle r^2 \rangle \rho_v(0)]/E$. Note that a common curvature occurs and that the straight-line slope shown is a little too flat for the Au data and a bit too steep for Fe. The slope discrepancy is of the same direction and magnitude as the above mentioned discrepancies in the Fe and Au volume derivatives. With two exceptions, any deviations of the $\Delta S_{\text{vol corr}}$ from a universal, rather narrowly defined, curve lie within the uncertainties of the nuclear and atomic parameters.

One exception was noted in the previous inspection¹ of $\Delta S_{\text{vol. corr.}}$, namely, that the shifts for noble metal hosts lie smoothly on the transitions-metal host curve for some impurities such as ¹⁹⁷Au and ⁵⁷Fe, while for other cases (most notably ⁹⁹Ru), they lie well below the curve.

The second exception was previously seen² in correlations of the raw experimental data where deviations are seen between impurities which have under or over half-filled d shells. The $\Delta S_{\rm vol, \ corr.}$ for ¹⁸¹Ta and ¹⁸²W show somewhat greater spread than their over halffilled shell counterparts. In particular, the points for the 4*d* hosts Rh and Pd, rise above their 3*d* and 5*d* counterparts. (Note, however, that the Ni host point lies lowest for ¹⁸¹Ta while Pt lies lowest for ¹⁸²W.) The facts that the Rh and Pd points lie higher here and that the noble-metal hosts lie sometimes on and sometimes below the general curve are not due to choice of nuclear parameters or of details of the volume correction. Pd and Pt have rather similar atomic volumes and it is reasonable to expect rather similar volume corrections. The spread seen in the Pd and Pt host points for ¹⁸¹Ta and ¹⁸²W is due to the raw experimental data.

The 4*d* metals display somewhat special behavior when acting as hosts. There is a general tendency for points associated with these metals to be highest in any column of the plots—details of the volume correction could be contributing to this trend. Also, the Rh and Pd host "rise" obtained for ¹⁸²W and ¹⁸¹Ta occurs in somewhat less pronounced form in the ⁵⁷Fe results. The only 4*d* impurity, for which there is data, is ⁹⁹Ru whose $\Delta S_{\text{vol. corr.}}$ are normal looking except for the very pronounced dip in the noble-metal points. The *d* bands of 4*d* metals tend to lie lower, with respect to the continuum, than the bands of their 3*d* and 5*d* counterparts. This is particularly pronounced in the vicinity of Rh, Pd, and Ag. The relative colors of Cu, Ag, and Au are associated with the fact that the top of the d band of Ag lies $\sim 2 \text{ eV}$ further below the Fermi level than in Cu or Au. The metallurgical properties of Rh and Pd are not dramatically different from those of Co, Ir, Ni, and Pt. The alloying properties of Rh (or Pd) sometimes differ from those of Co and Ir (or Ni and Pt) but as often it is Co (or Ni) which differs from its 4d and 5d counterparts. Packing considerations associated with atomic size are important to alloying and the 3d metals are significantly smaller than the others.

The suggestion that the 4*d* metals are somewhat different is at variance with generally accepted electronegativity scales. The electronegativities of the heavier 3*d* metals, rather than the 4*d*, differ from their counterparts in some column of the Periodic Table. There is a spread in the electronegativity values for any column which is substantial on the scale of the spread typical of any set of Mössbauer data. In this sense the $\Delta S_{\text{vol. corr.}}$ are at least as well defined as the electronegativities. More importantly, the two quantiies show the same general variation¹ across the Periodic Table.

Electronegativities involve the sum of electron count changes, i.e., $\Delta n_d + \Delta n_{cx}$ while as was discussed for Eq. (1), the isomer shifts involve the weighted difference of Δn_c and Δn_d . For the sum and difference to look as much alike, as they do in Ref. 1, implies that the *ratio* of Δn_d to Δn_c is a *constant*, independent of host and independent of impurity. The fact that the sum, i.e., the total charge transfer, is roughly an order of magnitude smaller than the difference only reinforces this conclusion. Such numerical differencing would tend to produce scatter in the one quantity versus the other. Nevertheless, the two quantities track one another quite well. The spread in the electronegativity values and the uncertainties in the volume correction do contribute to a substantial error bar to the constancy of the ratio. What is remarkable is the extent to which the constancy holds, making the several deviations, e.g., the behavior of less-than-half-filled *d*-shell impurities in Rh and Pd, of interest. In view of its implications for bonding in transition metal alloys and compounds, the issue requires further investigation by Mössbauer and other experimental means.

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