VOLUME-CORRECTED ISOMER SHIFTS OF TRANSITION METAL ATOMS: CHARGE FLOW AND ELECTRONEGATIVITY SCALES IN ALLOYS

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The Mössbauer isomer shift provides a direct measure, sampled at the nucleus, of charge flow on or off an atomic site in a solid. Isomer shift data exist for a variety of nuclei as impurities in alloys, and while comparisons have been made with electronegativity scales, no universal correlation has emerged.¹ In this paper, we will show that, once volume effects are suitably accounted for, the isomer shifts of ⁵⁷Fe, ⁹⁹Tc, ¹⁸⁷Re, ¹⁹¹Ir, ¹⁹³Pt and ¹⁹⁷Au display common behavior. These are the only transition metals for which there are sufficient data of sufficient resolution to be considered.

In addition to volume effects, two factors contribute to the contact density at a transition metal nucleus and hence to the isomer shift, upon alloying. First, there may be an increase or decrease in d electron count, Δn_d , at the impurity site. The d electrons have no density at the nucleus but, by screening the s-p conduction electrons, an increase in d count produces a decrease in the contact charge density. Secondly, there may be a change in the non-d conduction electron count, Δn_c . As a result, the volume-corrected isomer shift for some given nucleus becomes

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

where C and R are constants and V is the atomic volume. Given the minus sign inside the bracket, R is positive and calculation suggests it is the order of 1/2 to 1. In other words, d and non-d terms oppose one another and are of the same order. We have already noted that the $\Delta S(\text{vol. corr.})$, for the six elements in question, will display common behavior. What is more, comparison with electronegativity scales, which are associated with the sum of Δn_d and Δn_c , will suggest that the ratio of $\Delta n_d / \Delta n_c$ is a constant. Non-d and d charge flow in opposite directions upon alloying, and, to a remarkable extent, the ratio of these two terms is a constant independent of impurity atom and independent of the host in which the impurity finds itself.

Making the volume correction involves obtaining the derivative and choosing the impurity volume. For Fe, Ta and Au there are experimental data on the effect of pressure, hence of volume, on ΔS . Now

$$\Delta S(\text{mm/sec}) = [0.00608Z \delta \langle r^2 \rangle \Delta \rho(0)] / E \quad (2)$$

where Z, $\delta \langle r^2 \rangle$, E 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 source and absorbed, respectively. Noting this, the Ru, Ir and Pt volume derivatives which are not known experimentally, can be obtained by scaling, i.e.

$$\left[\frac{dS}{dV} \right]_i = \left[\frac{dS}{dV} \right]_j \frac{[Z \delta \langle r^2 \rangle \rho_v(0) / E]_i}{[Z \delta \langle r^2 \rangle \rho_v(0) / E]_j} \quad (3)$$

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This has been evaluated using Kalvius and Shenoy's tabulated nuclear parameters² and recent estimates³ of the contact density of free-atom valence s electrons for $\rho_v(0)$. Scaling in this way assumes common valence electron-volume effects among the metals of interest here. Scaling off Fe and Ta produces results for which agree to 2% while using Au data produces values ~30% greater. More will be said of this shortly.

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Fig. 1. The volume-corrected isomer shifts for ⁵⁷Fe, ⁹⁹Ru, ¹⁸¹Ta, ¹⁹³Ir, ¹⁹⁵Pt and ¹⁹⁷Au in a variety of hosts. The solid lines are of common slope, after re-normalizing out nuclear parameters and valence s contact densities.

There is no unique choice of volume to attribute to an impurity site and, lacking space, we will not discuss the issue here. Following Ingalls we have chosen to attribute the host atomic volume to the impurity site, not so much because this is the physically intuitive choice (e.g. for alloys where Vegard's law holds) but because it works for the problem at hand.

The volume-corrected isomer shifts are plotted in Fig. 1 as a function of the column of the periodic table in which the host appears. These curves contrast with the uncorrected isomer shift data in several ways. For example, the raw ΔS displayed much greater spread, for any column, than is seen here. In some cases, the shape of the distribution has changed: for example, the raw data for ⁵⁷Fe have at the maximum at the Mn, Re column. The lines drawn on the plots are of common slope once one has divided the shifts by the normalizing factor $[2\delta\langle r^2 \rangle_p(0)]/E$. Note that the line appears a little too steep for Fe and a little too flat for Au. The discrepancy is in the same direction and of the same magnitude as the apparent discrepancy in the Fe, Ta, and Au volume derivatives. This comparison suggests that the mismatch is due to an error in one of the nuclear or atomic parameters entering Eqs. (2) and (3) for it seems unlikely that a discrepancy in both volume and alloying effects would match one another so exactly. In any case, the discrepancy lies within the uncertainty of the parameters used. There is at least one deviation which cannot be attributed to parameters: the noble metal points lie on a simple extension of the transition metal curve for ⁵⁷Fe and ¹⁹⁷Au while they lie below such a curve for ⁹⁹Ru and ¹⁹³Ir. Nevertheless, the striking feature of the results of Fig. 1 is the extent to which they display common behavior.

The average of the ΔS(vol.corr.) data is plotted as the curve in Fig. 2 and is compared with Pauling's atomic electronegativity scale. The vertical position and scale of the ΔS(vol.corr.) curve is set to match the Ti and Ni columns of the electronegativity plot and the dashed lines at either end of the curve are so drawn to remind the reader that they are determined by very little experimental

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Fig. 2. 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. 1. The solid line is the result of taking the average of the six sets of volume-corrected isomer shifts of Fig. 1 after scaling with Eq.(2). 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.

data.

There is a striking similarity between this (and other¹) electronegativity scale(s) 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. (1), biased (since $|R| < 1$) in favor of the non-d term. This offers the possibility of inferring d and non-d orbital 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.² The change in isomer shift from bottom to top of any of the cases in Fig. 1 corresponds to a difference in contact density which is of the order of that due to one free-atom valence electron: a large effect.

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. In turn, to the extent that the sets of volume-corrected shifts have a common scale, [i.e. normalized by $E/(Z\delta\langle r^2 \rangle c_v(0))$] 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 are considerable magnetic hyperfine data for impurities in ferromagnetic Fe, Co and Ni. Campbell and coworkers have applied Friedel screening theory⁵ to predict the hyperfine fields of polyvalent p-band metal (Ga to Se columns) impurity sites with considerable numerical success. Stearns has argued⁵ that the hyperfine fields correlate, instead, with volume. It is not our purpose to explore this argument here. It is, however, worth noting that Stearns used the same ΔV as were applied here and that other choices of ΔV worsen the hyperfine

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Fig. 3. Normalized magnetic hyperfine fields for impurities in ferromagnetic Fe compared with the Pauling electronegativity scale. Impurities known to have local moments (the crosses) have had the hyperfine field due to such moments subtracted out. The subtraction is crude because the moment values are ill-defined. Hyperfine fields are normalized by dividing by free-atom valence s contact densities.

field correlation much as they damage the commonality of IS (vol. corr.) A further connection can be made between the hyperfine field and isomer shift trends. Plots of the hyperfine fields versus electronegativity show elements to either side of the main body of the transition elements lying on a common curve while, in contrast to the isomer shift data, the main body of transition elements is bunched separately as is seen in Fig. 3. The first group of elements have orbital electronegativity terms which act in concert, whereas the d and non- d charge contribution of the transition metals act in opposition. In contrast to the charge response, this opposition apparently affects the magnetic response at an impurity site, as manifested by the hyperfine fields.

In the orbital electronegativity picture, developed⁶ by Simons, St. John and Bloch for nontransition metals, there are orbital valence, i , terms of the same principal quantum number, n , which act in concert. The relative role of s and p character is important to bonding and hence to the structure of an element, alloy or compound. Here we see the valence d shell of a transition metal acting in opposition to the non- d character (of higher quantum number n). Granted that the non- d charge overscreens the d (i.e. $|\Delta n_d / \Delta n_c| < 1$), the electronegativities of the transition metals can be understood in terms of d -band filling. The lighter elements of a transition metal row have less than half-filled d bands. The majority of d states are empty and occupied ligand electron orbitals can hybridize with these causing a net increase in d character at a transition metal site. With overscreening of Δn_d , by the non- d electrons, the light transition metals are electropositive. In the heavier transition metals, such as Ni and Cu with their filled or almost filled d bands, d band hybridization involves admixing ligand character into occupied d levels, lowering the d count. This, in turn, produces electronegativity. [Note that all but ^{181}Ta , of the elements considered here, fall within this latter class.]

The fact that d and non- d charge flow effects oppose one another has been evident⁴ for some time from a variety of experiments, some of which indicate flow on, and others flow off, a transition-metal site. The present analysis of the

isomer shift data contributes the suggestion that $\ln_2/\ln_1$ is constant, or at least nearly constant. The concept of the near proportionality of $\ln_1$ and $\ln_2$ is important to any coherent picture of electronegativities and bonding among transition and non-transition elements. Further experimental evidence is needed to test the extent of validity of this concept. Finally, while having the virtues of success and simplicity, the choice of volume made in the analysis is not obvious, and requires further investigation.

References

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