Systematics of the Isomer Shifts of ^{57}Fe in Various Hosts

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A new systematics of the ^{57}Fe isomer shifts (δ) in various elemental hosts is presented. δ values measured for ^{57}Fe impurities, amorphous alloys, and crystalline intermetallics were used. The volume-corrected δ values are found to have the same or very close values to that of the corresponding intermetallics and amorphous phases. Contrary to earlier systematics, it is shown that no drastic downturn of the δ values in the region of metalloid hosts can be justified. The new systematics facilitate the interpretation of the great number of experimentally determined values.

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The 14.413-keV γ transition of ^{57}Fe is the most frequently used in Mössbauer spectroscopy. The experiments provide the isomer-shift (δ) values which are used to conclude the chemical bond between the iron and surrounding atoms.[1] This isomer shift depends on the difference in contact interactions between source and absorber:

$$\delta = \frac{2\pi c}{3E_\gamma} Ze^2 \Delta\langle r^2\rangle \Delta\rho(0)\,, \qquad (1)$$

where c is the velocity of light, E_γ is the γ energy, Z and $\Delta\langle r^2\rangle$ are the nuclear charge, the change of the mean-square nuclear radius between ground and first isomeric states, respectively. $\Delta\rho(0)$ is the difference of the contact electron density at the nucleus caused by different electronic states of the source and the absorber. Since $\Delta\langle r^2\rangle$ is negative, a negative (positive) isomer shift means that the contact electron density has increased (decreased) at the nucleus. $\Delta\rho(0)$ has contributions from non-d valence (mostly s) electrons and from the ionic core. The latter can be considered to be almost the same in both source and absorber. Therefore, δ depends primarily on the s-electron and indirectly on d-electron density, the latter because of screening. The electron density is also affected by volume changes of the iron atoms, an effect which should be corrected for in order to ascertain chemical effects.

Numerous attempts were made[2-5] to develop correlations between δ values of ^{57}Fe and electronic configurations in various elemental host lattices. This was done because the systematics might facilitate the understanding of the electronic structure of iron in various complex systems, alloys, and compounds in the crystalline as well as in the amorphous state. Ingalls, van der Woude, and Sawatzky[4] suggested a correlation between the δ values and the number of outer electrons of the host atoms. A gradual increase of the δ values was found up to $11(d^9s^2)$ outer electrons and, above this number, an abrupt decrease.

In their work, the volume correction was made in such a way that the volume of the impurity iron atoms equaled the volume of the host atom. Because of the large volume differences, in some cases the corrections were very large and possibly exaggerated, as can be concluded from the great difference between the corrected impurity δ values and the δ values of intermetallics. Another possible source of error was that the iron (and Co when a ^{57}Co source was used in various hosts) has vanishingly small solubility in some hosts (mostly in metalloids) and the iron (cobalt) precipitates out of the host lattice in the form of intermetallics. For such precipitates δ may not be corrected as would be done if the iron atoms were situated in the solid solution. In the case of very low solubility, ion implantation offers the possibility of introducing iron. The formation of damaged sites, however, requires caution in reaching conclusions on atomic positions from the analysis of the Mössbauer spectra.

In the past years new ^{57}Fe δ values have been obtained for numerous amorphous alloys and crystalline intermetallics where large volume corrections can be avoided. We have collected these new δ values and included them in the new systematics.

The δ values shown in Fig. 1 have three main sources: (1) ^{57}Co diffused in various hosts from Refs. 6 and 7, and our results when the experimental δ values found in the literature were controversial.[8] (2) Ion-implanted ^{57}Co sources mostly in host elements in which the solubility of Co and Fe is extremely low. New δ values were determined by As, Bi, Mg, Sb, and Te hosts. (3) Fe containing amorphous alloys and intermetallics.[9-20]

The following points should be noted concerning the reliability of these δ values. In order to avoid any gas intake in the sample during the preparation of new ^{57}Co sources the diffusion was carried out *in vacuo* instead of the H_2 atmosphere that was used in Ref. 6. For ion-implanted samples the dose dependence and the thermal evolution of the Mössbauer spectra were studied in order to select the proper spectral component characteristic of monomeric ^{57}Co of ^{57}Fe atoms. This attribution does

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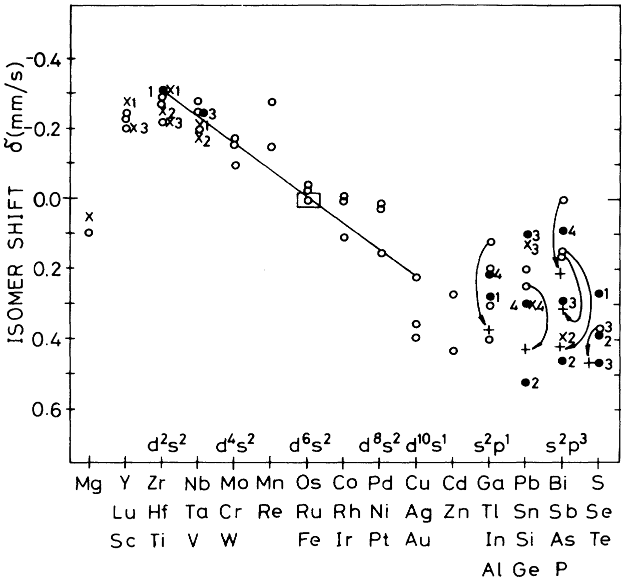

FIG. 1. The volume-corrected isomer-shift (δ) values of ^{57}Fe in various hosts (○, +) and the experimental (δ) values in intermetallics (●) and in amorphous alloys (×) vs the outer electron number of the neighboring atoms. (+) Corrected δ values obtained by using host atomic volumes calculated from interatomic distances between neighboring atoms. The symbols of the elements at the bottom of the figure are arranged, from top to bottom, in the same order as their corrected δ values (○). For s^2p^3 and s^2p^4 configurations only Bi, Sb, As, and Te (denoted by 3) δ values are shown, respectively. The numbers indicate to which element the intermetallics or the amorphous phase belong. The values for intermetallics and amorphous samples were taken from the following references: $FeZr_3$ (Ref. 9); $Fe_{0.4}V_{0.6}$, $FeAl_3$, $FeGa_3$, $FeGe_2$, $FeSn_2$, and $FeAs_2$ (Ref. 10); $FeSi_2$ (Ref. 11); $FeSb_2$ (Ref. 12); FeS_2, $FeSe_2$, and $FeTe_2$ (Ref. 13); and FeP_2 (Ref. 14). Amorphous samples: Fe-Mg (Ref. 15); Fe-Y (Ref. 16); Fe-Sc (Ref. 17); Fe-Zr, Fe-Ti, Fe-Hf, Fe-Nb, Fe-Ta, Fe-Mo (Ref. 18); Fe-Si (Ref. 19); Fe-Ge (Ref. 20); and Fe-Sb (Ref. 12).

not ensure that the ^{57}Co or ^{57}Fe are substitutional atoms, but it is certain that the implanted atoms were surrounded by unlike atoms (at low iron concentrations the average δ values show no or slight concentration dependence[21]). Amorphous alloys with the minimum iron content possible were chosen to minimize the probability of iron-iron contact. Intermetallics with the lowest iron content were chosen where nearest-neighbor atoms were exclusively not iron atoms. The inspection of the δ values of amorphous systems and intermetallics of one type of iron-host atom combination showed that the maximum spread of δ values was 0.05 mm/s. It was also seen that the volume correction for the impurity ion in some hosts, made on the assumption that the volume is equal to the host volume, is exaggerated. Therefore, similar to Ref. 22 we corrected the experimental δ values by calculating equilibrium impurity volumes (V_0) using the elastic continuum theory[23,24] for strained structures:

$$\Delta\delta = \frac{0.615B_M}{0.615B_M + B_{\mathrm{Fe}}}\,\frac{V_M - V_{\mathrm{Fe}}}{V_{\mathrm{Fe}}}\,\frac{\partial\delta}{\partial\ln V}, \tag{2}$$

where V_M and B_M are, respectively, the molar volume and the bulk modulus of the host matrix taken from Ref. 25. The value of the isomer shift derivative $\partial\delta/\partial\ln V = 1.37$ mm/s was obtained from high-pressure measurements.[26] The corrected δ values for metallic hosts obtained this way were very close to the δ values of the amorphous and crystalline intermetallics, as was also found for the ^{197}Au impurity in various matrices.[22] The contribution of the second-order Doppler shift due to the impurity- and matrix-atom mass differences[27] was not taken into account because the magnitude of this correction for room-temperature measurements was estimated to be less than 0.02 mm/s. The experimental δ values of amorphous and crystalline intermetallics lie within 0.05 mm/s, indicating that the volume contractions of a few percent of the crystalline intermetallics relative to the amorphous phases do not greatly affect the electronic density of the iron in these cases either.[28] It is interesting to include the Mg host because it is strongly electropositive and its outer electron configuration is $3s^2$.

In type-IV, -V, and -VI hosts, the available volume for an iron atom to regularly substitute the host atom is smaller than what can be calculated from the molar volume of the host. Therefore the V_0 values, using the host atomic volume obtained from the interatomic distance between the nearest-neighbor host atoms, were also calculated. The resulting δ values are shown at the end of the arrows (by plusses) in Fig. 1.

Two regions can be distinguished in the plot of δ versus the outer electron number shown in Fig. 1. The central part of the curve includes the transition-metal hosts and indicates a proportionality. Because of the different volume corrections the curve is somewhat less steep than that found in earlier systematics.[4,5] There is a clear indication of the decreasing contact s-electron density towards noble metals with high electronegative values. The second part of the curve from $d^{10}s^2p^n$ (in the region of p metals, semimetals, and metalloids) shows low contact density and no special correlation with the outer electron number of the hosts. The distribution of the δ values in one column is probably caused by structural and bonding effects which is not our aim to analyze further here. In spite of the scatter, however, the data clearly show that an abrupt down turn of δ to -0.6 mm/s (4,5) in this region cannot be justified. In this region the bonds between iron and host involve a high degree of electron hybridization mostly of the host p and iron d bands. The relative fraction of the polar and covalent bond is not known, but for metalloids of relatively low electronegativity the latter is dominant. Unfortunately, there are no independent results for atomic electron densities, but, e.g., for $CoSi_2$ theoretical calculations showed negligible ionicity and very similar electron densities in the component atoms in comparison to the atoms in the elemental lattice.[29,30]

In a very recent paper[31] the dominance of the $3d^6$ configuration electronic structure of the impurity iron in *sp* metals was established. This result would imply a larger impurity volume and consequently a smaller volume correction in Eq. (2). Thus more positive δ values than those denoted by open circles in Fig. 1 are expected for impurity iron in *sp* metals and semimetals, a consequence which is also suggested by the δ values of their amorphous and intermetallic phases. Furthermore, the more positive δ values in these elemental hosts help to overcome the difficulties concerning a common interpretation of the trends of the δ values for Fe *sp* nearest-neighbor host atoms in iron-based alloys presented in Ref. 32.

It should also be noted that for electron configurations lower than d^2 the contact density shows a slight decrease although the electropositivity of the hosts increases. This is a real effect because the δ values of the amorphous Fe-Sc and Fe-Y phases have less negative δ values than phases such as Fe-Zr. Furthermore, the δ values of Fe in Mg and in amorphous Fe-Mg are even more positive. This observation suggests that at very low-*d* density of the hosts, the charge flow towards iron slightly decreases.

The charge transfer Δq to iron in transition-metal alloys can be explained adequately by the model and the calculation of Watson and Bennett.[33] By this model *s* electrons (Δn_c) are transferred from the more electropositive atoms and simultaneously an opposite *d*-electron flow (Δn_d) diminishes the charge on the more electronegative atom:

$$\Delta q = \Delta n_c - R\Delta n_d\,. \tag{3}$$

R is a positive constant with a value between 0 and 1. Also, this model does not exclude an intra-atomic *s-d* conversion. Recent calculations of Watson, Davenport, and Weinert[34] have shown that the charge transfer to Au and Pt alloyed with Hf and Lu decreases relative to Nb and Ta. According to the authors, the reason can be that the *d* bands in Hf and Lu are largely empty, there are fewer occupied levels into which Au *d* character can be hybridized, and there are more empty levels which can be hybridized into the Au and Pt *d* bands. Thus, the largely empty *d* band reduces charge transfer. The calculated orbital population numbers clearly document this tendency. Present results for Fe also support the existence of this electronic process.

In summary, the volume-corrected isomer-shift values of ^{57}Fe are found to have the same or very similar values as the δ values of the corresponding intermetallics and amorphous phases. This effect shows that the volume corrections based on the continuum elastic model give more realistic δ values. In transitional-metal hosts, a proportionality between the corrected δ values and the outer electron numbers is suggested. No special correlation between these numbers in *sp* metals and in semimetals was found. The isomer-shift systematics in various matrices show no single correspondence between the contact density of ^{57}Fe and the electronegativity of its neighboring atoms. The complex equilibrium of the electron densities in the various levels and screenings prevent the simple interpretation of δ values in terms of electronegativity of the host atoms. The new systematics of the δ values, on the other hand, facilitate the interpretation of the great number of experimentally determined values and the proper recognition of the various bonding tendencies.

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Nevertheless, negative δ values could not be obtained after any reasonable volume correction.

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