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Further comparison of model predictions with measured Fe-site spin- and charge-density changes in various bcc Fe-based alloys

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Previously measured spin- and charge-density changes in bcc iron caused by replacing its atoms by Al, Si, Ge, Sn, V, and Cr are being compared with the two-parameter Miedema model. The fairly good agreement found between the experimental and the model values permits us to separate the direct *s*-electron charge transfer from the *s*-*d*–electron conversion part from the total observed charge-density change. It turns out that for *s*-*p* solutes the dominant process in the *s*-electron redistribution is due to *s*-*d*–electron conversion, while for 3*d* solutes the direct *s*-electron transfer is more important.

Calculation of magnetic hyperfine (hf) fields (related to spin densities) and of isomer shifts (related to charge densities) from first principles is still an unsolved theoretical problem for Fe-based alloys. On the other hand, a large body of experimental results has been accumulated mainly with Mössbauer effect (ME) spectroscopy within the last two decades. Consequently, various model descriptions of the measured quantities emerged. In a previous publication[1] we tested the one-parameter models, by Friedel,[2] by Stearns,[3] and a one-parameter formula by Miedema.[4] We have shown there that the best description of our experimental results on *FeX* alloys ($X=$Al,Si,Sn,Ge,V,Cr) has been achieved in terms of Stearns's model. We also concluded there that the disagreement between our experimental results and the one-parameter formula derived by Miedema to account for the charge transfer might be due to the fact that with ME one measures primarily the effective change of the *s*-electron charge density within the ^{57}Fe nuclear volume. This change may be due to a direct transfer of *s*-like electrons from one atom to another as well as to *s*-*d*–electron conversion due to a change of the screening power. Since this formula takes into account the first effect only, it is the aim of this consideration to compare our experimental results with the model of Miedema in more detail.

This model was already used to explain the systematics of isomer shifts of ^{99}Ru, ^{193}Ir, ^{195}Pt, and ^{197}Au in transition-metal alloys,[5,6] as well as of ^{57}Fe isomer shifts in various amorphous Fe-based alloys.[7] According to this model the isomer shift $\delta I_{\max}$ (relative to α-Fe) in a dilute system where each Fe atom has only impurity atoms X as neighbors can be represented by the following formula:

$$\delta I_{\max}^{\text{calc}} = P'(\phi_X^* - \phi_{\text{Fe}}^*) + Q'(n_{ws}^{x} - n_{ws}^{\text{Fe}})/n_{ws}^{\text{Fe}} + C \ , \qquad (1)$$

where P' and Q' represent characteristic quantities of a given Mössbauer isotope and of a given class of materials, and C is a constant related to the presence of a volume-mismatch contribution to the isomer shift. C is zero if the studied system is formed by two transition metals. There is also evidence[8–10] that for the transition-metal–metaloid systems (including Fe with Al, Si, Sn, and Ge) the average volume per impurity atom is close to the volume of the transition-metal atom. In other words, for these cases the corresponding corrections to the isomer shift in terms of C must be very small. Therefore, in the following application of Miedema's model, we have neglected C. ϕ_X^* and ϕ_{Fe}^* are electronegativities and n_{ws}^X, n_{wx}^{Fe} stand for the electron density at the Wigner-Seitz atomic cell interface of X-atom and Fe-atom lattices, respectively. Hence, to calculate $\delta I_{\max}^{\text{calc}}$ from formula (1), one needs to know the values of P' and Q'.

Experimental values $\delta I_{\max}^{\text{expt}}$ can be obtained in two ways: (I) from the knowledge of the individual contribution to δI by each X atom, situated in the first-neighbor shell ΔI_1, and (II) by extrapolation after plotting the δI values measured in

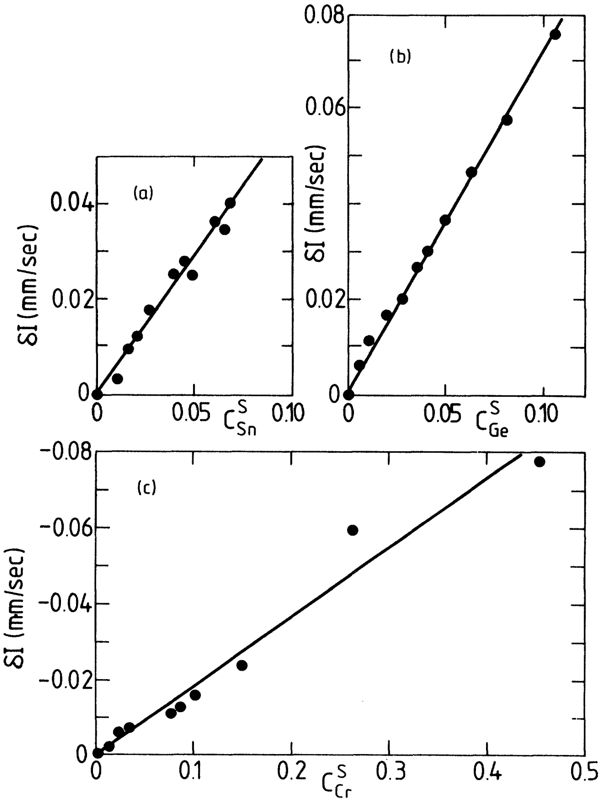

FIG. 1. Average isomer shift δI as a function of the contact surface concentration C_X^s for (a) Fe-Sn, (b) Fe-Ge, and (c) Fe-Cr alloys. The straight lines are the best fits to the data.

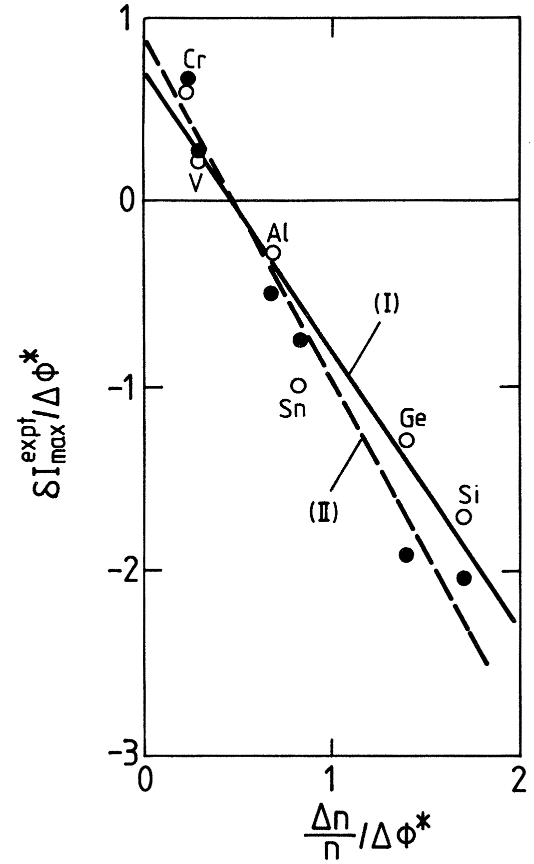

FIG. 2. $\delta I_{max}^{expt}/\Delta\phi^*$ vs $(\Delta n/n)/\Delta\phi^*$ for the measured systems. Open circles indicate δI_{max}^{expt} values calculated from method I; full circles stand for values deduced from method II. The straight lines are the best fits to the data.

a given alloy series $X_{1-c}Fe_c$ versus the contact surface concentration C_X^s, defined as follows:

$$C_X^s = (1-c)V_X^{2/3}[cV_{Fe}^{2/3} + (1-c)V_X^{2/3}]^{-1} , \qquad (2)$$

where V_X and V_{Fe} stand for the molar volumes of X atoms and Fe atoms, respectively. Using the ΔI_1 values obtained in our previous experiments[1,11-15] we calculate $\delta I_{max}^{expt}(I) = 8\Delta I_1$ for the studied systems. On the other hand, we plot δI vs C_X^s and arrive by extrapolation to $C_X^s = 1$ at the value for $\delta I_{max}^{expt}(II)$. Some examples of such plots are given in Fig. 1. The values of $\delta I_{max}^{expt}(I)$ and $\delta I_{max}^{expt}(II)$ obtained are collected in Table I.

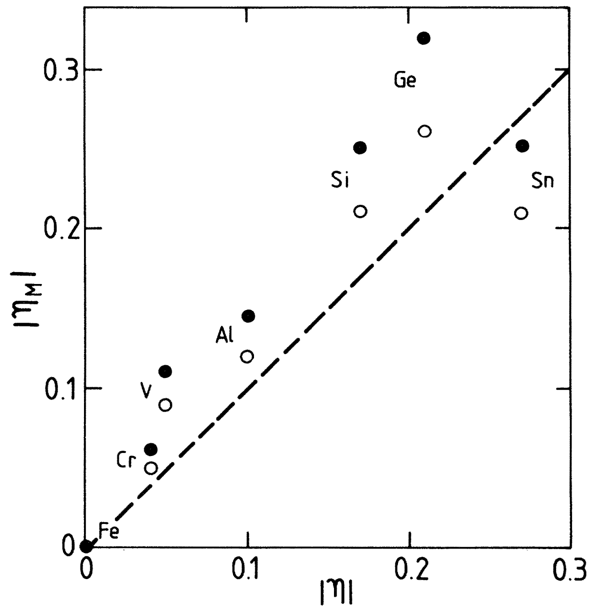

FIG. 3. Absolute values of η_M plotted as a function of the absolute experimental values of η. Open circles indicate the values obtained by method I, and full circles those derived with method II.

Next we calculate the values of P' and Q'. Towards this end we have plotted $\delta I_{max}^{expt}/\Delta\phi^*$ as a function of $(\Delta n_{sw}/n_{sw}^{Fe})/\Delta\phi^*$ (see Fig. 2). Open circles stand for the values calculated in method I and closed circles for the ones obtained in method II. The data could be fitted with the following linear relations:

$$\delta I/\Delta\phi^* = 0.71 - 1.50\frac{\Delta n}{n}/\Delta\phi^* , \qquad (3.1)$$

$$\delta I/\Delta\phi^* = 0.90 - 1.85\frac{\Delta n}{n}/\Delta\phi^* . \qquad (3.2)$$

Therefore the formula (1) can now be written as follows:

$$\delta I_{max}^{calc} = 0.71\Delta\phi^* - 1.50\Delta n/n , \qquad (4.1)$$

$$\delta I_{max}^{cal} = 0.90\Delta\phi^* - 1.85\Delta n/n . \qquad (4.2)$$

It is interesting to note that the values of Q' and P' are very close to those found for amorphous alloys,[7] 0.75 and −1.65, respectively. This, we think, confirms that the volume-mismatch correction C for the crystalline Fe-based alloys is

TABLE I. Maximal experimental δI_{max}^{expt} and calculated δI_{max}^{calc}, changes of the isomer shifts in mm/sec (relative to α-Fe) for Fe-X alloys as obtained by methods I and II. For details see text.

X	$\delta I_{max}^{expt}(I)$	$\delta I_{max}^{expt}(II)$	$\delta I_{max}^{calc}(I)$	$\delta I_{max}^{calc}(II)$
Al	0.208	0.363	0.255	0.296
Si	0.408	0.472	0.426	0.520
Ge	0.488	0.733	0.536	0.651
Sn	0.815	0.584	0.430	0.511
V	−0.152	−0.178	−0.175	−0.232
Cr	−0.170	−0.183	−0.099	−0.129

TABLE II. Comparison between measured changes η of spin and charge densities per solute atom X per unit cell and theoretical values η_M derived from the Miedema model. The indications I and II refer to different ways in the calculations described in the text, whereas the indices s and s-d label the contributions to η_M, which are due to direct s-electron charge transfer and to s-d-electron conversion, respectively.

X	η^{a}	η_M(I)	η_M(II)	η_M^{s}(I)	$\eta_M^{s\text{-}d}$(I)	η_M^{s}(II)	$\eta_M^{s\text{-}d}$(II)
Al	−0.10	−0.125	−0.145	0.25	−0.375	0.32	−0.465
Si	−0.17	−0.21	−0.25	0.08	−0.29	0.10	−0.35
Ge	−0.27	−0.26	−0.32	0.13	−0.39	0.17	−0.49
Sn	−0.21	−0.21	−0.25	0.27	−0.48	0.34	−0.59
V	0.05	0.09	0.115	0.24	−0.15	0.30	−0.185
Cr	0.04	0.05	0.06	0.10	−0.05	0.12	−0.06

[a] References 1, 11–15.

indeed of minor importance. We also would like to mention here that in Miedema's model used for the description of the heat of formation of iron with s-p elements an additional term R had to be introduced to account for the hybridization of the Fe 3d band with s-p bands. Since its role in the isomer shift description has not been worked out we have not taken it into account in our analysis.

The remaining differences between the calculated and the experimental $\delta I_{\max}$ values to be seen from Table I and Fig. 3 cannot simply be related to the R term, since they also exist for V and Cr where R should vanish. Based on formulas (4) and using for ϕ^* and n_{sw} values as given in Ref. 5, we calculated $\delta I_{\max}^{\text{calc}}$. These are summarized in Table I.

In order to see how the Miedema model does compare with our experimental η values (η being a change of spin or charge density caused by one impurity atom per unit cell) we have to express $\delta I_{\max}^{\text{calc}}$ in a corresponding number of electrons. Towards this end we use the relation between the isomer shift and number of s-like electrons after Ref. 16, $dI/dN_s = 2$ mm/sec s-electron, which has been used for the calculation of the η values too. Namely, dividing $\delta I_{\max}^{\text{calc}}$ by this factor, we get the Miedema model value for η, which we call η_M. The η_M values obtained in this way for cases (I) and (II) described before are given in Table II together with our experimental η values. For a better comparison they are also plotted against each other in Fig. 3. From Table II and Fig. 3 it is obvious that a general relation between η_M and η exists. In particular, the change of sign for Cr and V is reproduced properly by the model. Concerning the absolute values, we can see that in all cases, except Sn, the η_M values are slightly larger than the η values.

Let us briefly turn to the question of how this Miedema model does compare with the one-parameter model by Stearns. Inspection of Figs. 3 and 4 leads us to the conclusion that formally the correlation between η and ΔV looks better than that between η and η_M, i.e., the description of the measured spin and charge-density changes observed in α-iron is generally better in terms of the Stearns model. However, the model of Miedema offers a deeper and perhaps more realistic insight into the problem, as it

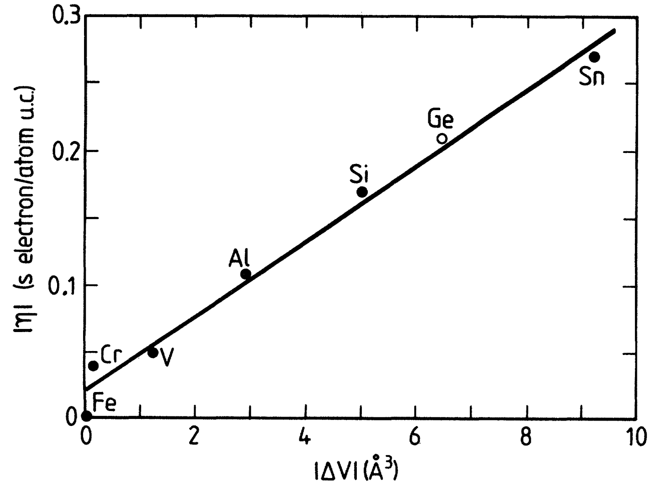

FIG. 4. Absolute value of η as a function of the absolute value of the atomic volume misfit, $\Delta V = V(X) - V(\text{Fe})$ (from Ref. 1).

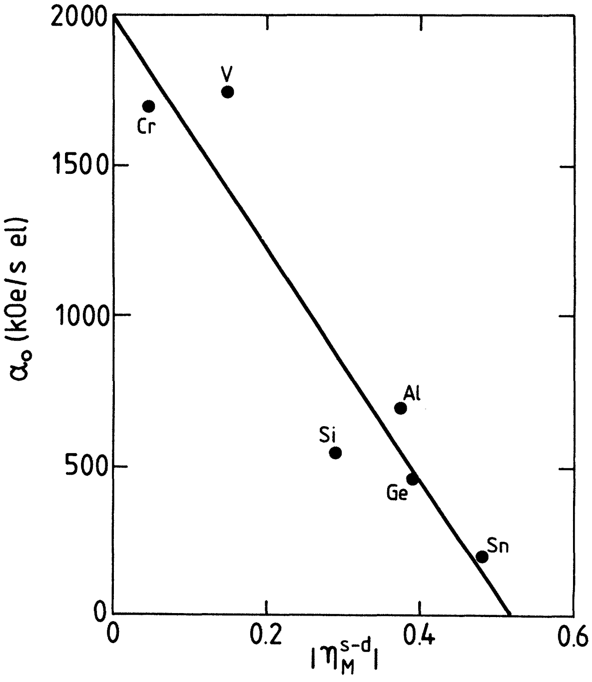

FIG. 5. Measured hf coupling constant for itinerant electrons, α_0, vs the absolute value $\eta_M^{s\text{-}d}$ of the s-d-electron conversion contribution to η_M. The straight line is the best fit to the data.

distinguishes, *a priori,* between pure *s*-electron density changes (direct influence on the isomer shift) and an s-d-electron conversion (indirect influence on the isomer shift), giving thereby a possibility of tracing these two contributions for different solutes.

The last two columns of Table II present the partial contributions, η_M^s and $\eta_M^{s\text{-}d}$, to the resultant η_M. We see that in case of the s-p solutes the s-d-electron conversion dominates and results consequently in a diminution of the effective charge density at the Fe neighbor site, while for V and Cr, it is the direct *s*-electron transfer which constitutes the main contribution to the electron redistribution. Similar behavior has been observed for amorphous alloys of iron.[7] This may also be the reason for the hyperfine coupling constants of itinerant electrons, α_0, as deduced from our measurements[1,11-15] to be dependent on the solute. As shown in Fig. 5, α_0 depends linearly on $\eta_M^{s\text{-}d}$ and yields as best fit to the data the following:

$$\alpha_0 = 2000 - 3840\eta_M^{s\text{-}d} \ . \tag{5}$$

This correlation suggests considering α_0 as consisting of two terms: a pure Fermi contact term α_0^s and a term related to the screening effect, $\alpha_0^{s\text{-}d}$, which depends on the s-d-electron conversion. From the above correlation of Eq. (5) we estimate $\alpha_0^s = 2000$ kOe/s electron, which is very close to the theoretical estimates by Watson and Freeman[17] and by Goodings and Heine.[18] For Cr and V apparently the direct *s*-electron transfer dominates and, consequently, the corresponding experimental α_0 values are close to α_0^s. From relation (5) it also follows that the hf coupling constant for the s-d-electron conversion effect is about twice α_0^s and, hence, will change the hf field more efficiently than the direct *s*-electron charge transfer.

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