

## Comparison of model predictions with the measured Fe-site spin and charge-density changes in $\alpha$ -iron: Mössbauer-effect study of $\text{Fe}_{1-x}\text{Ge}_x$ alloys

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Using the Mössbauer effect we studied the influence of substituting Fe atoms by Ge atoms on the hf fields and isomer shifts for a series of  $\text{Fe}_{1-x}\text{Ge}_x$  alloys containing up to about 9 at. % Ge. From the linear correlations between the hf fields and corresponding isomer shifts we calculated the hf coupling constants:  $\alpha_0=460$  kOe per  $s$  electron for the non-localized electrons,  $\alpha_{1,2}=780$  kOe per  $s$  electron for the electrons localized within the first two neighbor shells,  $\bar{\alpha}=275$  kOe per  $s$  electron the average value. Using these hf coupling constants and assuming the linear correlation between the average hf field and the average number of Ge atoms within the first two neighbor shells, we calculated the change of spin (charge) density at the Fe site caused by one Ge atom per unit cell,  $\eta$ , to be equal to  $-0.21$ . This agrees well with the model of Stearns, but disagrees with those of Friedel and Miedema.

### I. INTRODUCTION

Substitution of Fe atoms by other elements into bcc iron causes changes both in the hyperfine (hf) field and in the isomer shift. In other words, the electronic structure of the iron matrix is changed upon the substitution. Extensive experimental and theoretical studies have been carried out on this subject. Their common aim was to understand the observed phenomena.

Two different experimental approaches to the problem using hyperfine interaction studies can be chosen:

- (a) studies of the influence of the substituents mainly on the Fe-site hf field,
- (b) studies of the hf fields at the substituted atom in the iron matrix.

Those mentioned under (a) are with the use of the Mössbauer effect and NMR techniques mainly, while those of (b) are applying different techniques.

Theoreticians have been rather involved in their attempt to explain the results obtained by the experiments of type (b) since these seemed to be more attractive than those reported by the experiments of type (a). In fact, the hf fields at the different impurities in iron revealed a wide variation in sign and magnitude, while changes of the Fe-site field caused by the impurities do not depend so strongly on the type of the impurities.

The following more or less phenomenological models have been postulated:

(i) Friedel's model,<sup>1</sup> which assumes that the difference in valence between the host and impurity atoms is the dominant source of electron redistribution leading, therefore, to a net spin polarization at the impurity site.

(ii) Stearns's<sup>2</sup> model, which ascribes the origin of the hf field at an impurity to the difference in the atomic volume between the host and impurity atoms,  $\Delta V$ .

(iii) Miedema's<sup>3</sup> model, which explains changes in the electronic structure in terms of the difference in the chemical potential between the host and impurity atoms,  $\Delta\phi$ .

These three models reflect the classic ideas of Hume-Rothery<sup>4</sup> that three atomic parameters, valence, size, and electronegativity, are basic in determining alloy phase stability.

The first two models were already the subject of controversy between those who see arguments in favor of Friedel's model<sup>5</sup> and Stearns herself who gave arguments supporting her point of view.<sup>6</sup> On the other hand, Watson and Bennett,<sup>7</sup> who normalized the measured impurity-site hf field to the free atom's valence  $s$  electrons, have shown that the correlation of normalized fields with both the valence and the atomic volume is good. They concluded that way, because the two quantities are somehow related with one another, as postulated by Hume-Rothery.<sup>4</sup>

As already emphasized by Knight<sup>8</sup> and realized by Watson and Bennett,<sup>7</sup> it is important to normalize the measured hf field when making systematics

of the hf fields. We think that the normalization is crucial, hence the problem is to have a proper normalizing constant. The ideal case would be to have the absolute change of spin or charge density caused by the impurity.

In a recent paper,<sup>9</sup> we showed a way of calculating the change of spin (charge) density at Fe site per one Cr atom per unit cell,  $\eta$ , which is based on correlations between the hf fields and corresponding isomer shifts as well as between the average hf field and the average number of Cr atoms in the two-shell vicinity of the Fe nuclei. These correlations turned out to also hold for FeSn,<sup>10</sup> FeAl,<sup>11</sup> FeSi,<sup>12</sup> and FeV.<sup>13</sup> In particular, they enabled us to calculate  $\eta$  for all these impurities and therefore to test properly the models of Friedel and Stearns. As shown previously,<sup>13</sup>  $|\eta|$  depends linearly both on  $|\Delta V|$  and  $|\Delta Z|$ . In fact, based on the results obtained for Cr, Sn, Al, Si, and V, it was not possible to give preference to one of the two models.

However, as already emphasized by Campbell and Vincze,<sup>5</sup> one should compare hf fields of elements having similar atomic volumes but different positions in the Periodic Table (i.e., atomic numbers  $Z$ ) or vice versa in order to properly test the models. The best candidate for such a comparison would be Ca. From our correlations between (a)  $|\eta|$  vs  $|\Delta V|$  and (b)  $|\eta|$  vs  $|\Delta Z|$ , one would expect  $|\eta|=0.66$  for the (a)-type correlation and  $|\eta|=0.08$  for the (b)-type correlation. Unfortunately, Ca does not make a solid solution with Fe, therefore this case cannot be realized. As the next best choice we have selected Ge as the impurity. It forms a random solution with Fe up to about 10 at. % of Ge. It also offers a good chance to test the two models, since according to Friedel's model one expects  $|\eta|=0.08$ , while the model of Stearns predicts  $|\eta|=0.20$ . This difference in the expected values of  $\eta$  is big enough to allow a proper distinction between the two models. In the following we present results obtained by Mössbauer spectroscopy on a series of Fe<sub>1-x</sub>Ge<sub>x</sub> alloys containing up to about 9 at. % Ge.

## II. EXPERIMENTAL

### A. Sample preparation

Samples of Fe<sub>1-x</sub>Ge<sub>x</sub> alloy containing up to about 9 at. % Ge have been obtained by melting to-

gether 99.999% purity iron with a proper amount of 99.999% purity germanium. The melting process was carried out several times in an arc furnace in a clean argon atmosphere. The mass of each sample was about 300 mg. All three samples were chemically analyzed. The results obtained are shown in Table I.

### B. Spectral measurements

A standard spectrometer with a 1024-channel analyzer was used to collect the Fe-site room-temperature Mössbauer spectra in a transmission geometry. The samples for the Mössbauer-effect measurements were obtained by filing the bulk samples to particles of an average size of about 60  $\mu\text{m}$ .

<sup>57</sup>Co in rhodium matrix was used as a source of the gamma rays of 14.4 keV energy. A 25- $\mu\text{m}$ -thick metallic iron foil was taken as a standard for calibration.

## III. SPECTRAL ANALYSIS

The spectra were computer analyzed with two independent methods.

### A. Method I

Based on the superposition of Lorentzian lines, method I yielded the following quantities:  $H_1(0,0)$ , i.e., the hf field at Fe nuclei of undisturbed atomic configuration within the first two neighbor shells;  $\Delta H_1$  and  $\Delta H_2$ , i.e., the hf field shifts caused by one Ge atom situated in the first (NN) or second neighbor (NNN) shell, respectively;  $I(0,0)$ , i.e., the isomer shift of undisturbed atomic configuration;  $\Delta I_1$  and  $\Delta I_2$ , i.e., the isomer shift due to one NN or NNN Ge atom, respectively. The probabilities  $P(m,n)$  of atomic configurations of Fe atoms having  $m$  NN and  $n$  NNN Ge atoms have been calculated assuming random distribution of Ge atoms in the iron matrix. Alternative fits with  $P(m,n)$  as free parameters did not improve their quality. The hf field and the isomer shift of a configuration  $(m,n)$  then are given by

$$H(m,n) = H(0,0) - m\Delta H_1 - n\Delta H_2$$

and

TABLE I. Chemical composition of the Fe<sub>1-x</sub>Ge<sub>x</sub> samples.

Probe No.	1	2	3	4	5	6	7	8	9	10
$x$ (at. %)	0.46	0.91	1.53	2.20	2.79	3.22	3.93	5.08	6.57	8.60

$$I(m,n) = I(0,0) + m\Delta I_1 + \Delta I_2.$$

The average hf field  $\bar{H}_1$  and the average isomer shift  $\bar{I}$  have been calculated as  $H(\bar{m}, \bar{n})$  and  $I(\bar{m}, \bar{n})$  by weighting the configurations according to  $P(m,n)$ .

### B. Method II

This method gives the hf field distribution from the measured Mössbauer spectrum by means of a Fourier analysis.<sup>14</sup> From the hf field distribution

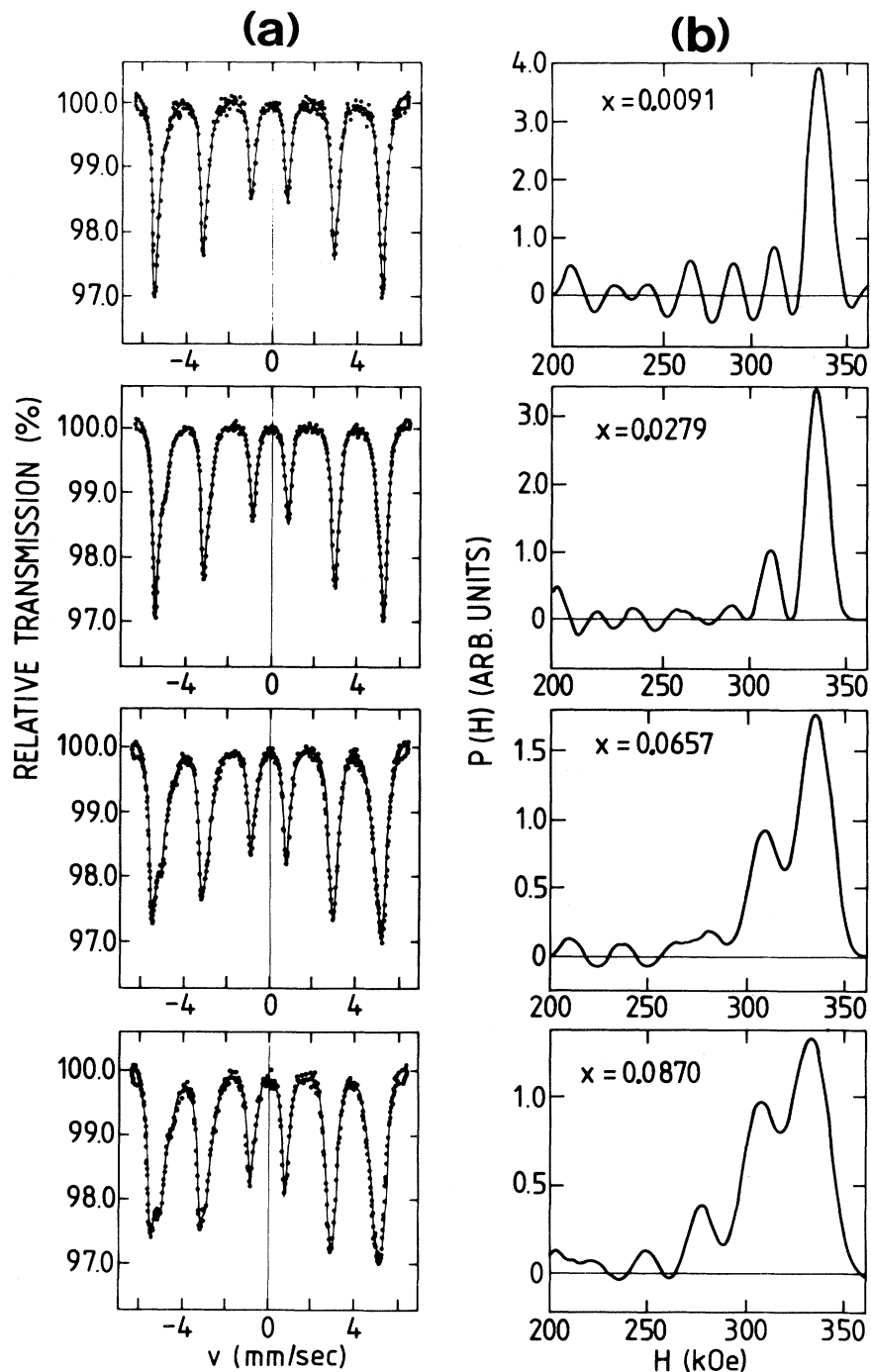


FIG. 1. (a) Room-temperature Mössbauer spectra of selected  $\text{Fe}_{1-x}\text{Ge}_x$  samples. The solid lines represent the fitted spectra obtained by method I. (b) Hyperfine field distributions as obtained by method II and attributed to the spectra of (a).

one can determine the average hf field  $\bar{H}_{II}$  and the field corresponding to the undisturbed atomic configuration,  $H_{II}(0,0)$ .

#### IV. EXPERIMENTAL RESULTS

Figure 1(a) shows typical Mössbauer spectra of the studied samples. As in the case of other solutes studied previously, the influence of Ge atoms on the hf field is revealed most pronounced by the outermost hf lines, which develop some structure as the Ge concentration increases.

##### A. The hf fields

The corresponding hf field distributions are plotted in Fig. 1(b). The effect of Ge atoms shows up here in a decrease of the intensity of the single-peak hf field distribution characteristic for pure iron, as well as in development of extra peaks at smaller hf fields.

The hf field parameters deduced from the measured spectra by means of the two methods are presented in Table II. Obviously,  $\bar{H}_I$  and  $\bar{H}_{II}$  as well as  $H_I(0,0)$  and  $H_{II}(0,0)$  agree well. This proves that both methods yield consistent and meaningful results.

##### 1. The hf field $H(0,0)$

Figure 2 shows the hf field  $H(0,0)$  as a function of Ge concentration  $x$ . It can be readily seen that this field increases linearly with  $x$ . Since the hf field is negative, it follows then that Fe nuclei having no Ge atoms within their two-shell neighborhood experience an effective increase of the spin-down  $s$ -electron density. The same effect was previously observed with other impurities<sup>9-13</sup> and has been attributed to a change in the conduction-band polarization as well as to the influence of the more distant solute atoms. From our recent NMR studies,<sup>15</sup>

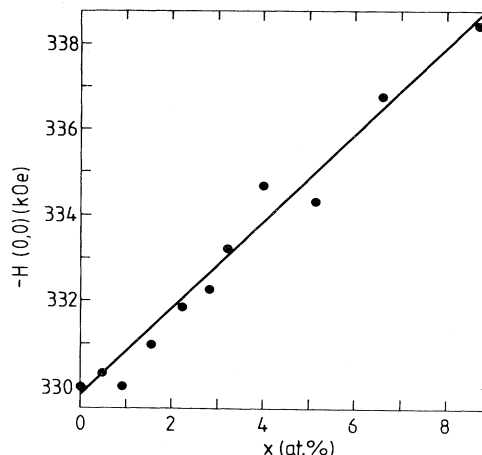


FIG. 2. hf field  $H(0,0)$  of the undisturbed atomic neighbor configuration vs the concentration of Ge,  $x$ . The solid line represents the best fit to the data.

however, there is clear evidence that the main contribution to the  $H(0,0)$  change with  $x$  is due to the contributions of the more distant neighbor shells.

##### 2. The hf field shifts, $\Delta H_1$ and $\Delta H_2$

Ge atoms in the two-shell vicinity of the Fe nuclei, are found to change the hf field by  $\Delta H_1 = -23.2 \pm 1.6$  kOe and  $\Delta H_2 = -8.1 \pm 1.2$  kOe, per Ge atom in the first- and second-neighboring shell, respectively. These two quantities agree well with those reported in literature.<sup>16-18</sup>

##### 3. The average hf field $\bar{H}$

The average hf field  $\bar{H}_I$  as obtained by method I is plotted in Fig. 3 as a function of  $x$ . It decreases linearly with  $x$  and is fitted best by the following equation:  $-\bar{H}_I = 329.3 - 1.161x$ , with  $r=0.99$  being the coefficient of correlation. The dotted line illus-

TABLE II. Fitted average values and contributions of the hf fields (in kOe) in Fe-Ge alloys.

$x$ (at. %)	$H_I(0,0)$	$\Delta H_1$	$\Delta H_2$	$\bar{H}_I$	$H_{II}(0,0)$	$\bar{H}_{II}$
0.46	-330.5	-19.2	-6.6	-328.0	-329.5	-328.2
0.91	-330.0	-22.1	-6.7	-328.2	-329.7	-328.5
1.53	-331.0	-22.9	-10.0	-327.7	-330.4	-327.8
2.20	-331.9	-23.5	-9.2	-326.7	-330.5	-327.9
2.79	-332.3	-23.75	-8.55	-325.8	-330.5	-326.9
3.22	-333.25	-24.1	-9.0	-325.7	-331.4	-326.1
3.93	-334.7	-23.8	-8.7	-325.5	-333.3	-325.0
5.08	-334.3	-24.3	-8.1	-322.5	-333.2	-322.8
6.57	-336.8	-24.0	-7.5	-321.9	-334.15	-320.8
8.70	-338.5	-24.15	-6.9	-319.3	-334.2	-318.8

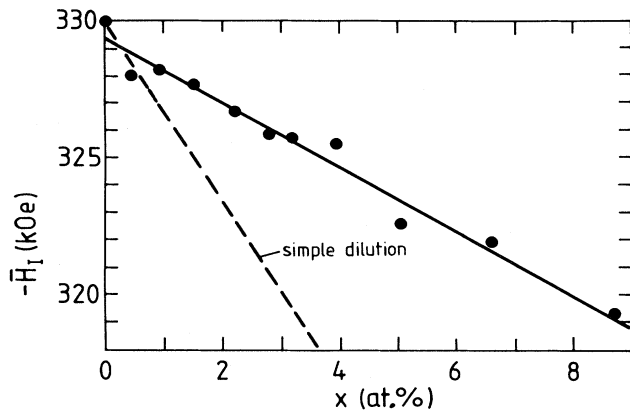


FIG. 3. Average hf field  $\bar{H}_1$  vs the Ge concentration  $x$ . The solid line represents the best fit to the data.

trates the  $\bar{H}(x)$  dependence for simple dilution behavior, which assumes that a Ge atom only removes the original hf field contribution of the substituted Fe atom. The actual deviation between the observed  $\bar{H}(x)$  and that expected for simple dilution reaches here 65%, in contrast to only 13% observed in the case of V.<sup>13</sup>

### B. The isomer shifts

The corresponding fit parameters for the isomer shifts are compiled in Table III. The meanings of  $I(0,0)$ ,  $\Delta I_1$ ,  $\Delta I_2$ , and  $\bar{I}$  correspond with those introduced for the hf fields before.  $\Delta I(0,0) = I(0,0) - I_{Fe}$ , with  $I_{Fe}$  being the center of gravity of the pure iron spectrum.

#### 1. The isomer shift change $\Delta I(0,0)$

In Fig. 4  $\Delta I(0,0)$  is plotted versus the Ge concentration  $x$ . A linear increase of  $\Delta I(0,0)$  with  $x$  is observed, showing that the  $s$ -electron density at Fe atoms with no Ge atoms within their two-shell vi-

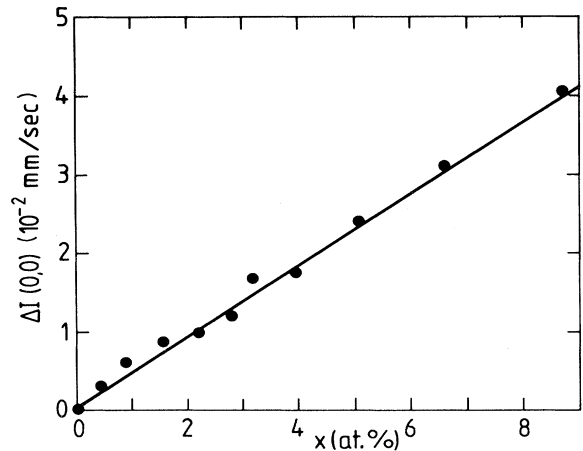


FIG. 4. Difference between the isomer shift of the undisturbed atomic configuration and that of pure  $\alpha$ -Fe,  $\Delta I(0,0) = I(0,0) - I_{Fe}$  as a function of the Ge concentration  $x$ . The best data fit is shown by the solid line.

cinity decreases with increasing impurity concentration  $x$ . This behavior was also observed previously with other impurities.<sup>9-13</sup>

#### 2. The changes of the isomer shifts $\Delta I_1$ and $\Delta I_2$

These two parameters which measure the local change of the  $s$ -electron density are independent of the Ge concentration within our error limits. Their average values are as follows:  $\Delta I_1 = 0.061 \pm 0.007$  mm/sec,  $\Delta I_2 = -0.003 \pm 0.009$  mm/sec. As in the case of Al (Ref. 11)  $\Delta I_1$  is positive, indicating a decrease of the  $s$ -charge density for Fe nuclei having one Ge nearest neighbor.  $\Delta I_2$  is zero within the error limits.

#### 3. The average isomer shift $\bar{I}$

As shown in Fig. 5, the average isomer shift  $\bar{I}$  is positive and increases linearly with  $x$ . This indicates that the average Fe-site  $s$ -charge density is reduced by the presence of Ge atoms and, hence, decreases with increasing  $x$ . This decrease is due to  $\Delta I(0,0)$  and  $\Delta I_1$ .

## V. DISCUSSION

The results presented in Sec. IV provide experimental evidence that substitution of Fe atoms by Ge atoms will change both the hf field ( $s$ -electron spin density) and the isomer shift ( $s$ -electron charge density). The observed linear dependences of the hf fields and of the isomer shifts on the Ge concentration  $x$  indicate linear correlations also hold between

TABLE III. Fitted average values and contributions of the isomer shifts (in mm/sec) of Fe-Ge alloys.

$x$ (at. %)	$\Delta I(0,0)$	$\Delta I_1$	$\Delta I_2$	$\bar{I}$
0.46	0.0034	0.058	-0.013	0.0051
0.91	0.0064	0.064	-0.022	0.0096
1.53	0.0088	0.074	0.001	0.0172
2.20	0.0101	0.063	-0.003	0.0206
2.79	0.0123	0.064	0.005	0.0268
3.22	0.0169	0.062	-0.007	0.0308
3.93	0.0179	0.0625	0.000	0.0366
5.08	0.0239	0.054	0.007	0.0469
6.57	0.0310	0.051	0.004	0.0583
8.70	0.0407	0.053	0.002	0.0762

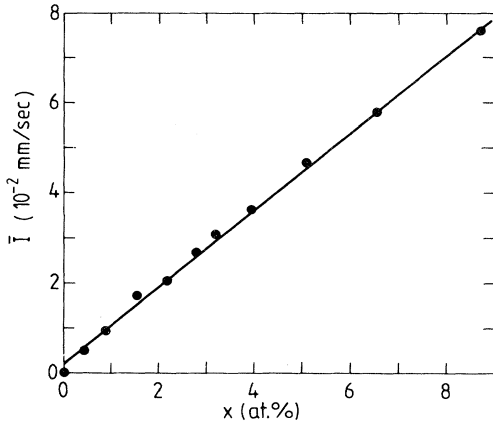


FIG. 5. Average isomer shift  $\bar{I}$  as a function of the Ge concentration,  $x$ . The solid line stands for the best fit to the data.

the hf fields and the isomer shifts themselves. Let us next discuss these correlations in more detail.

#### A. Correlation $H(0,0)-I(0,0)$

Figure 6 shows how the changes in the hf field of the undisturbed atomic configuration  $\Delta H(0,0) = H(0,0) - H_{\text{Fe}}$  depend on the corresponding changes in the isomer shift,  $\Delta I(0,0) = I(0,0) - I_{\text{Fe}}$ . The data fit to the following equation:

$$-\Delta H(0,0) = -0.50 + 225.6\Delta I(0,0), \quad r = 0.98.$$

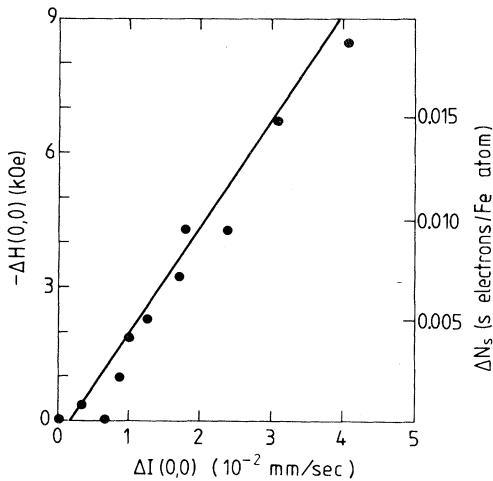


FIG. 6. Difference between the hf field of the undisturbed atomic configuration and that of pure  $\alpha$ -Fe,  $\Delta H(0,0) = H(0,0) - H_{\text{Fe}}$ , as a function of the corresponding difference in the isomer shift,  $\Delta I(0,0)$ . The solid line illustrates the best fit to the data.  $\Delta N_s$  is the effective change in the number of  $s$ -like electrons, which corresponds to the measured changes  $\Delta H(0,0)$  or  $\Delta I(0,0)$ .

Combining the slope of the above equation and the relation between the change of the isomer shift and attributed change of the number of  $s$ -like electrons,  $dN_s$ , which from Ref. 19 is  $dI/dN_s = 2.05$  mm/sec per  $s$  electron, one gets for the related hf coupling constant  $\alpha_0 = dH(0,0)/dN_s$ , the value of 462.5 kOe per  $s$  electron.

From the results in Fig. 6 one concludes the effective increase of the spin-down density, as mentioned in Sec. IV A 1, to be due to a decrease in spin-up electron density at the Fe nuclei having the (0,0) atomic configuration. The knowledge of  $\alpha_0$  allows one to scale the measured changes of  $\Delta H(0,0)$  and  $\Delta I(0,0)$  in corresponding numbers of  $s$ -like electrons,  $\Delta N_s$  (see right-hand ordinate of Fig. 6).

#### B. Correlation between $\Delta H_{1,2}$ and $\Delta I_{1,2}$

For dilute alloys these parameters are shown to be independent of the Ge concentration  $x$ . As a consequence (a) the spin charge density changes as represented by  $\Delta H_{1,2}$  and  $\Delta I_{1,2}$ , respectively, must be well localized and (b) the changes in the spin density must be correlated with the corresponding changes in the charge density of the  $s$  electrons. In other words, the above results provide a basis for evaluating also the hf coupling constants  $\alpha_{1,2} = d\Delta H_{1,2}/dN_s$ . For the first-neighbor shell one gets  $\alpha_1 = 780$  kOe per  $s$  electron. Unfortunately, the small value and rather large experimental error of  $\Delta I_2 = -0.003 \pm 0.009$  mm/sec makes a proper evaluation of  $\alpha_2$  impossible. However, from our previous studies of FeCr (Ref. 9) and FeV (Ref. 13) alloys, where the  $\Delta I_2$  parameter could be determined much more accurately, one arrives at  $\alpha_1 \approx \alpha_2$ . Knowing  $\alpha_{1,2}$ , one is further able to express the measured changes in the hf field,  $\Delta H_{1,2}$ , or in the isomer shift,  $\Delta I_{1,2}$ , in terms of changes in the number of  $s$ -like electrons,  $\Delta N_{1,2}^s$ . Assuming for the present case that  $\alpha_1 = \alpha_2$ , one obtains  $\Delta N_1^s = -0.030$ ,  $\Delta N_2^s = (+)0.010$   $s$  electrons.

#### C. Correlation $\bar{H} - \bar{I}$

As expected from the discussion above these two quantities also depend linearly on each other. This is illustrated in Fig. 7, where the solid line represents the best data fit, which is given by the equation

$$-\bar{H}_1 = 329.6 - 133.9\bar{I}, \quad r = 0.99.$$

Using this relation together with the scaling factor<sup>19</sup> for the isomer shift per number of  $s$ -like electrons,  $dI/dN_s = 2.05$  mm/sec per  $s$  electron as introduced above, one obtains an average hf coupling constant  $\alpha = d\bar{H}/dN_s = 275$  kOe per  $s$  electron, which in turn

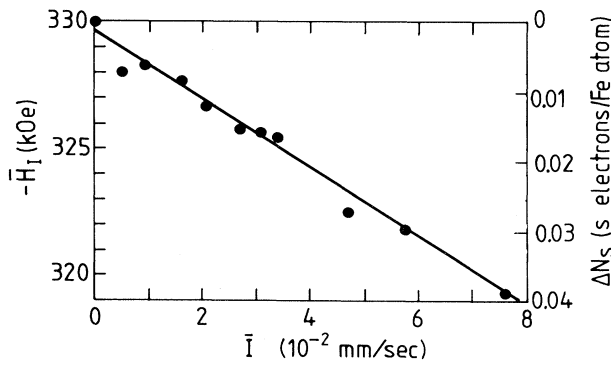


FIG. 7. Average hf field  $\bar{H}_1$  vs the average isomer shift  $\bar{I}$ . The solid line represents the best fit to the data.  $\Delta N_s$  gives the effective change in the number of  $s$ -like electrons, which corresponds to the measured change in  $\bar{H}_1$  or  $\bar{I}$ .

allows one to calibrate the measured changes of  $\bar{H}$  or  $\bar{I}$  in terms of the corresponding numbers of  $s$ -like electrons,  $\Delta N_s$  (see right-hand ordinate of Fig. 7).

#### D. Correlation $\bar{H} - \bar{N}$

In our previous investigations of Fe- $X$  systems<sup>9-13</sup> ( $X = \text{Al, Si, Sn, V, or Cr}$ ) we have shown that in all cases the average hf field  $\bar{H}$  was correlated linearly with the average number of  $X$  atoms in the first two neighbor shells,  $\bar{N}$ . This correlation enabled us to evaluate the change of the hf field per one impurity atom per unit cell,  $d\bar{H}/d\bar{M}$ , and, hence, together with the knowledge of the hf coupling constants, to calculate finally the corresponding changes in spin or charge density per solute atom per unit cell,  $\eta = dN_s/d\bar{M}$ .

Figure 8 provides evidence that this is also the case for the Fe-Ge system. Here the correlation

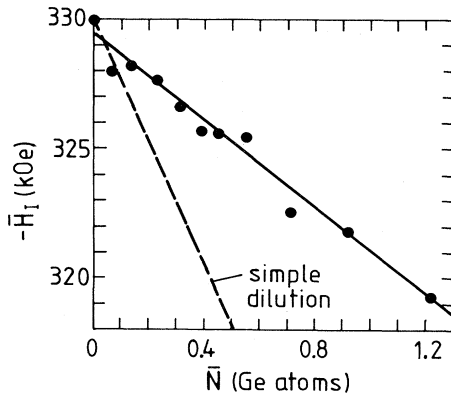


FIG. 8. Average hf field  $\bar{H}_1$  vs the average number of Ge atoms  $\bar{N}$  within the first two neighbor shells. The solid line illustrates the best fit to the data.

$\bar{H} - \bar{N}$  can be described by  $-\bar{H} = 329.3 - 8.3\bar{N}$ ,  $r = 0.99$ , from which one arrives at  $d\bar{H}/d\bar{M} = 58$  kOe/atom per unit cell, ( $7\bar{M} = \bar{N}$ ). The impurity character of Ge atoms in  $\alpha$ -Fe can be expressed also in terms of the above-mentioned "spin-hole" effect  $(d\bar{H}/d\bar{M})_0 = H_{\text{Fe}}/2$ , yielding

$$\epsilon_{\text{Ge}} = \frac{d\bar{H}/d\bar{M}}{(d\bar{H}/d\bar{M})_0} \times 100 = 35\%.$$

This is the lowest value of  $\epsilon$  we have observed so far.<sup>13</sup>

#### E. Evaluation of the $\eta$ value

The  $\eta$  value introduced above can be determined in two independent ways<sup>9</sup>:

(i) Based on the knowledge of  $d\bar{H}/d\bar{M}$ ,  $\alpha_0$ ,  $\alpha_{1,2}$ , and  $\bar{\alpha}$ , one can use the following identities:

$$\frac{d\bar{H}/d\bar{M}}{\alpha_0} \equiv \frac{\bar{\alpha}}{\alpha_0} \eta,$$

$$\frac{d\bar{H}/d\bar{M}}{\alpha_{1,2}} \equiv \frac{\bar{\alpha}}{\alpha_{1,2}} \eta.$$

(ii) Based on the knowledge of  $\bar{\alpha}$  one can fit the measured  $\bar{H}(x)$  with the theoretical expected dependence  $\bar{H}(x) = H_{\text{Fe}} + 2\bar{\alpha}\eta x$ .

By both ways one obtains consistently the value  $|\eta| = 0.21$ .

#### F. Comparison between experiment and theoretical models

The experimental result of  $|\eta| = 0.21$  agrees well with the value of 0.20 expected from Stearns's model. In Fig. 9 the related systematics of all stud-

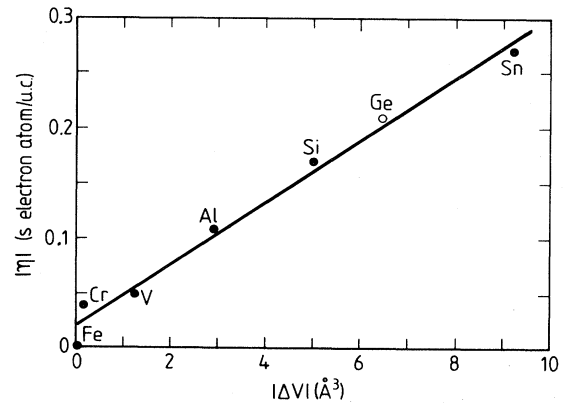


FIG. 9. Absolute values of  $\eta$  as a function of the absolute values of the atomic volume difference  $\Delta V$  between the host and the solute atom. The solid line is the best fit to the data, which are plotted as full circles.

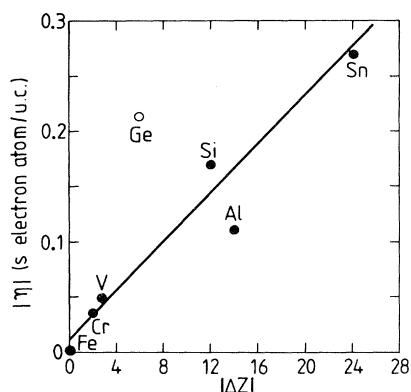


FIG. 10. Absolute values of  $\eta$  plotted vs the absolute values of the difference in the atomic number,  $\Delta Z$ , between the host and the solute atom. The solid line is the best fit to the data, which are shown by the closed circles.

ied impurities is illustrated. The solid line shows the best fit to the data as obtained without taking the case of Ge into account.

In Fig. 10 the systematics of our Fe-*X* results is shown as related to Friedel's model.<sup>13</sup> Obviously the value  $|\eta| = 0.08$  expected for the Fe-Ge case according to Friedel's model has not been confirmed experimentally.

A third model to be compared with our results is that proposed by Miedema.<sup>3</sup> According to this model the relation between the charge transferred per atom,  $\Delta Z_a$ , and the difference in the electronegativity,  $\Delta\phi$ , for solid solutions of two metals of which at least one is a transition metal, is given by  $\Delta Z_a = 2\Delta\phi(1 - c_a)P$ , where  $c_a$  is the concentration of metal *A*. *P* is a parameter equal to  $0.6V^{-1}$  when both metals are transition metals or  $0.85V^{-1}$  when only one component of the solid solution is a transition metal.

For comparison of the Miedema model with our quantity  $\eta$ , i.e., with the charge transfer per one impurity atom of the two atoms within the unit cell of  $\alpha$ -iron, one must calculate the Miedema value  $\Delta Z_a$  for  $c_a = 0.5$ . In Fig. 11 these Miedema values  $\eta_M = \Delta Z_a$  ( $c_a = 0.5$ ) are plotted on the abscissa.

From comparison with the experimental values on the ordinate it is clear that no meaningful correlation between the two quantities exists. We want to emphasize, however, that this does not mean that the Miedema model does not properly describe the process of charge transfer in the studied alloys. One should take into account that in Miedema's model the total charge transfer per atom is considered,

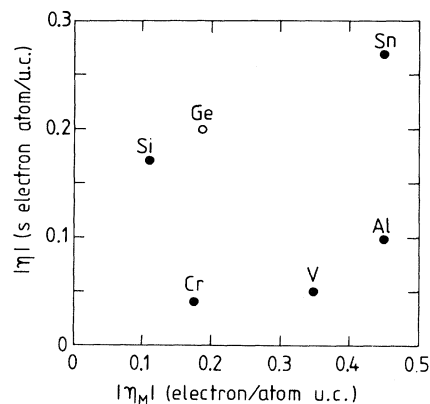


FIG. 11. Absolute experimental values of  $\eta$  plotted vs the absolute values of  $\eta_M$  as deduced from Miedema's model. For details see text.

while with the Mössbauer effect one measures primarily the effective change of the *s*-electron charge density within the <sup>57</sup>Fe nuclear volume mainly. In fact, the measured change of the isomer shift,  $\Delta I$ , for the Fe-based alloys is related to the density of 3*d*- and *s*-like electrons by the relation<sup>20</sup>

$$\Delta I = a\delta n_{4s} - b\delta n_{3d}.$$

Since an increase of the 3*d*-electron density  $\delta n_{3d}$  at the probing Fe atom will increase its shielding effect on the outer *s*-like electrons, the second term has the opposite sign. Hence, the changes of 4*s*-like and 3*d*-like electron densities around impurity atoms will influence the isomer shift in an opposite way.

This means that it may even happen that both the 3*d*- and 4*s*-like charge densities increase or decrease in such a way that the resultant  $\Delta I$  becomes zero. From this Mössbauer-effect result, one would then conclude that there is no charge transfer at all, which of course is incorrect. For these reasons the fact that  $|\eta_M| > |\eta|$  for all Fe-*X* systems studied here does not mean that Miedema's model is not correct. What is really surprising to us, however, is the fact that  $\eta_M$  for neighboring elements, e.g., V and Cr, is so much different, namely, 0.35 and 0.17, respectively, while this apparently is not the case for our experimental  $\eta$  values.

In conclusion, we would like to stress that for the studied impurities of iron-based alloys the best theoretical description of the Fe-site charge density changes "seen" by the Mössbauer effect is that by Stearns,<sup>2</sup> which is based on the misfit  $\Delta V$  of the atomic volumes.



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