

Changes in the electronic structure of iron induced by substitutional impurity W atoms

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By means of Mössbauer-effect spectroscopy, we study changes in the electronic structure of iron induced by substitutional impurity W atoms in a series of $\text{Fe}_{1-x}\text{W}_x$ alloys containing up to about 9 at. % W. From the measured changes of the hyperfine (hf) fields and isomer shifts, and based on the correlations between the hf fields and isomer shifts as well as between the average hf field and the average number of W atoms in the two-shell environment of the Fe nuclei, we deduce that W atoms increase the Fe-site spin (charge) density when situated within the first two shells and decrease it when situated outside the first two shells. The average effect of this oscillatory behavior is that the average spin density follows the simple dilution behavior while the average charge density remains constant. We can account for this behavior by postulating that the majority spins flip into the minority-spin state at a constant rate of $\frac{1}{2}\sigma_{\text{Fe}}$, σ_{Fe} being the net *s*-electron spin polarization in the nuclear volume of pure Fe. Finally, we evaluate the average change of the spin density caused by one W atom per unit cell, η , and find that it is consistent with the model predictions by Stearns [Phys. Rev. 147, 439 (1966)] and by Miedema [J. Less-Common Met. 32, 1117 (1973)].

I. INTRODUCTION

It is well known that introducing foreign atoms into metallic iron causes changes in its electronic structure. In general, these changes may be very complex, since densities of all electrons, i.e., those with spin-up and spin-down from all shells residing on iron atom, can be affected by the substitution and, in addition, in a way characteristic for a given solute atom. Fortunately, the real situation, although not very simple, seems to be not so complex either. Already Hume-Rothery¹ pointed out the importance of the three atomic parameters: valence, size, and electronegativity in determining alloy phase stability. In other words, these very three parameters are expected to be responsible for the changes in the electronic structure on alloying. The role they play has not yet been worked out in detail and the theoretical approach to the problem still remains on the level of a single-impurity approximation.² There have been, however, the generally phenomenological models postulated by Friedel,³ Stearns,⁴ and Miedema⁵ in order to account for the experimentally revealed changes.

By testing the models we hope to recognize the proper sources of the changes in the electronic structure of iron, i.e., changes in spin and charge densities. To carry out a meaningful test, however, one has to compare properly-calculated model predictions with proper experimental data. This means that (a) if one wants to test, e.g., the model by Friedel with that by Stearns one has to compare experimental results, i.e., changes in spin or charge densities caused by elements having *similar atomic volumes but different atomic numbers or vice versa*; (b) for the comparison one has to use not raw data [e.g., hyperfine (hf) fields, isomer shifts], but spin or charge densities expressed in absolute units.

We have recently shown (see Ref. 6 and our papers cited therein), for the case of using the Mössbauer-effect spectroscopy as a tool of investigation, how one can ex-

press the directly measurable quantities, i.e., hf fields and isomer shifts in terms of the spin and charge densities, respectively. We have also tested all three models,⁶ for Fe-Ge among others, i.e., the case where the impurity differs greatly in atomic volume in comparison with that of iron. The original aim of the present investigation was to further test the three models for the Fe-W system, i.e., the case where there is a big difference in the atomic charge and a small one between the atomic volume.

Within the course of elaborating on our data we found that the behavior of W is very unusual in that the average isomer shift (i.e., average charge density) at the Fe nuclei remains constant and simultaneously the average hf field (i.e., average spin density) decreases according to a simple-dilution law. Consequently, in this paper we mainly concentrate on explaining this unusual behavior rather than on testing the models, leaving the latter as a subject of a separate publication.

II. EXPERIMENTAL

A. Sample preparation

The samples of $\text{Fe}_{1-x}\text{W}_x$ alloys have been arc-melted in an atmosphere of pure argon from iron and tungsten of 99.999% and 99.99% purity, respectively. The melting process was repeated several times, the total mass of samples was 300–400 mg and the crucible was water cooled. Therefore, no further treatment was applied in order to randomize W-atom distribution. The samples were chemically analyzed and the results obtained are shown in Table I.

TABLE I. Chemical composition of the $\text{Fe}_{1-x}\text{W}_x$ samples.

Probe no.	1	2	3	4	5
<i>x</i> (at. %)	1.20	2.95	5.26	6.87	8.89

B. Spectral measurements

The Fe-site room-temperature Mössbauer spectra were collected in a transmission geometry on samples which were obtained by filing the bulk samples to particles of an average size of about $60\ \mu\text{m}$. ^{57}Co in rhodium matrix was used as a source of the γ rays of 14.4-keV energy. For calibration a $25\text{-}\mu\text{m}$ -thick iron foil was used.

III. SPECTRAL ANALYSIS

The Mössbauer spectra were computer analyzed with a superposition method (SM) and with a field-distribution method (FDM). For the more detailed description of the methods we refer the reader to Ref. 6. Here we only note that using the SM and assuming the additivity in hf field and isomer-shift changes, we evaluate hf fields $H(m,n)$ and isomer shifts $I(m,n)$ at Fe nuclei having m W atoms in their first-neighbor (NN) shell and n W atoms in their second-neighbor (NNN) shell. We also evaluate probabilities of the atomic configurations $P(m,n)$.

From the data we calculate the hf field changes: Due to one W atom situated in NN, $\Delta H_1 = H(1,0) - H_1(0,0)$, and due to one W atom situated in NNN, $\Delta H_2 = H(0,1) - H_1(0,0)$. We evaluate in a similar way corresponding changes in the isomer shifts, ΔI_1 and ΔI_2 .

Finally, we calculate the average hf field \bar{H}_I and the average isomer shift \bar{I} as $H(\bar{m}, \bar{n})$ and $I(\bar{m}, \bar{n})$ by weighting the configurations according to $P(m,n)$.

The FDM yields the hf distributions from the measured spectra from which one can determine the average hf field \bar{H}_{II} and the field corresponding to the undisturbed atomic configuration, $H_{II}(0,0)$. As the FDM is model independent, consistency of its results with those obtained from the SM can be taken as evidence that the more detailed latter way of analysis yielded meaningful results.

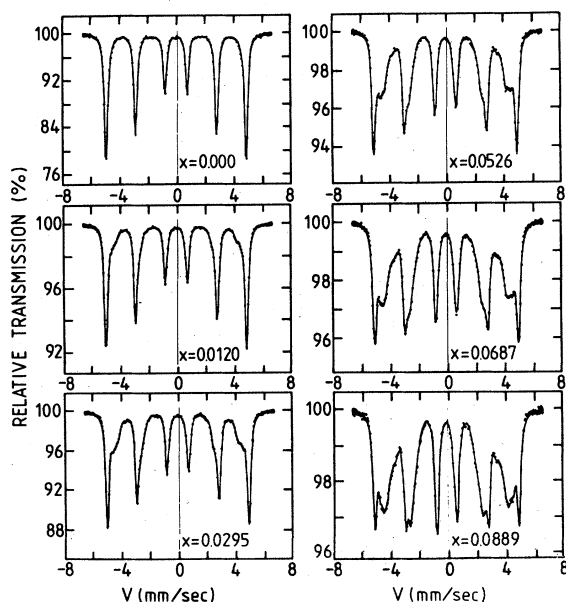


FIG. 1. (a) Room-temperature Mössbauer spectra of $\text{Fe}_{1-x}\text{W}_x$ samples. The solid lines are the fitted spectra by means of the SM.

IV. EXPERIMENTAL RESULTS

Figure 1 shows the Mössbauer spectra of the studied samples. The influence of W atoms on the hf fields manifests itself most drastically by the outermost hf lines, which develop clear structure as the concentration of W atoms increases.

A. The hf fields

The corresponding hf-field distributions are plotted in Fig. 2. Here, the influence of impurity atoms shows up in development of new peaks at smaller hf fields and in a decrease of the intensity of the single-peak hf-field distribution characteristic of pure iron.

The hf-field parameters evaluated from the measured spectra by means of the two methods are collected in Table II. As can be readily seen, \bar{H}_I and \bar{H}_{II} as well as $H_I(0,0)$ and $H_{II}(0,0)$ are in good accord. Therefore, the results obtained in the present analysis can be regarded as meaningful.

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

The hf field $H(0,0)$ is presented in Fig. 3 as a function of the tungsten concentration, x . The increase of this field, being here nonlinear, is a common feature with previously studied impurities, and it implies that Fe atoms of undisturbed atomic configurations experience an effective increase of the spin-down s -electron density. This effect can be attributed to a change in the conduction-band polarization and the influence of more distant W atoms (out-

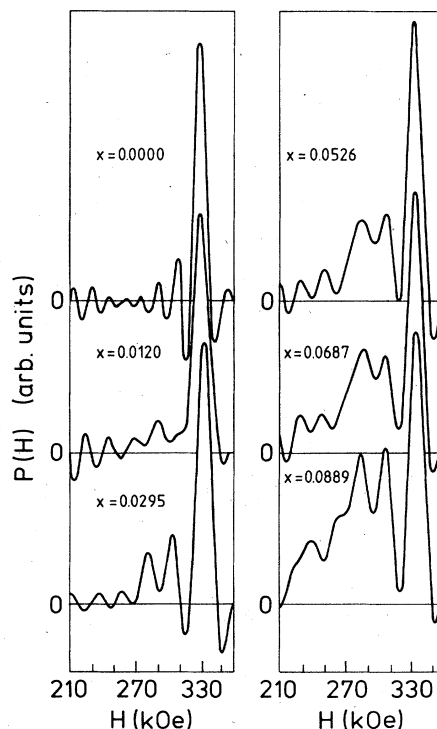


FIG. 2. Hyperfine-field distributions obtained by FDM and attributed to the spectra of Fig. 1.

TABLE II. Fitted average values, contributions of the hf fields (in kOe), and the average number of W atoms within the NN-NNN environment in $\text{Fe}_{1-x}\text{W}_x$ alloys.

x	$H_I(0,0)$	ΔH_I	ΔH_{II}	\bar{H}_I	$H_{II}(0,0)$	\bar{H}_{II}	\bar{N}	\bar{N}_0
0	329.9			329.9	330.7	330.7		
1.20	331.4	-47.5	-27.3	324.6	332.7	326.1	0.180	0.161
2.95	333.1	-42.7	-27.4	318.7	333.3	322.2	0.446	0.390
5.26	334.8	-38.9	-25.75	309.2	335.1	311.6	0.870	0.720
6.87	335.7	-39.1	-25.8	301.3	335.4	305.1	1.101	0.912
8.89	336.7	-36.7	-23.9	294.5	336.4	297.2	1.417	1.245

side the first two coordination-shells). Our recent NMR studies, however, seem to give evidence that the latter effect is dominant.⁷

2. The hf field shifts ΔH_I and ΔH_{II}

We have found that one W atom lowers the hf field at ^{57}Fe nucleus on average by $\Delta\bar{H}_I=41.0\pm 4.2$ kOe when situated in NN, and by $\Delta\bar{H}_{II}=26.0\pm 1.4$ kOe, when in NNN. From Table II one can note, however, that contrary to previously studied systems, $\Delta H_{I,2}$ for the present case decrease rather meaningfully with x . This is in our opinion due to the shortcomings of the two-shell approximation used in the analysis of the spectra, which show up so clearly here because of the large values of $\Delta H_{I,2}$ (in fact, the largest we have found among the impurities we studied to date). The influence of the more-distant solute atoms is expected to increase with their concentration x , i.e., the two-shell approximation gets worse for large x . In order to estimate the value of ΔH_3 we have fitted our spectra for $x_1=0.0120$ and $x_2=0.0295$ and obtained the following figures. For x_1 : $\Delta H_1=-47.2$, $\Delta H_2=-26.6$, and $\Delta H_3=+6.2$; for x_2 : $\Delta H_1=-44.4$, $\Delta H_2=-27.3$, and $\Delta H_3=+6.7$, all in kOe. ΔH_3 turned out to be not large enough to be detected as a satellite line with NMR measurements.⁸ Application of the three-shell model in the evaluation of other spectra has not been carried out due to the drastic increasing with x number of parameters.

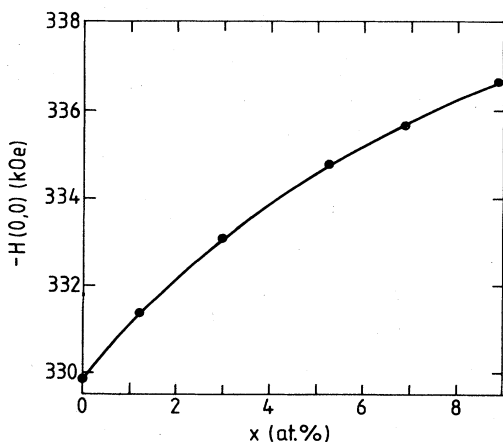


FIG. 3. Hyperfine field $H(0,0)$ of the unperturbed atomic configuration vs x , the concentration of W. The solid line is to guide the eye.

3. The average hf field \bar{H}

As illustrated in Fig. 4, the average hf field, \bar{H} (average over \bar{H}_I and \bar{H}_{II}) falls linearly with x according to the equation $-\bar{H}=330.6-3.91x$, with $r=0.998$ being the coefficient of correlation. The dashed line shows the $\bar{H}(x)$ behavior for simple-dilution dependence. We note that the actual behavior only slightly differs from it and constitutes, together with Fe-V (Ref. 7), the best approximation to the simple-dilution behavior we know. A possible explanation of this and of the constant value of \bar{I} will be outlined in Sec. VI.

B. The isomer shifts

The best-fit parameters for the isomer shifts are given in Table III. The meanings of $I(0,0)$, ΔI_1 , ΔI_2 , and \bar{I} correspond with those introduced for the hf fields in Sec. III.

1. The isomer shift $I(0,0)$

As shown in Fig. 5 the isomer shift of undisturbed atomic configuration decreases linearly its absolute value with the increasing W concentration x according to the equation $I(0,0)=-0.1062+0.0029x$, $r=0.997$. This means that the s -electron density at Fe atoms without W atoms in their two-shell environment decreases with increasing x . Such behavior was also observed for all other impurities we studied (Ref. 6 and our papers cited therein).

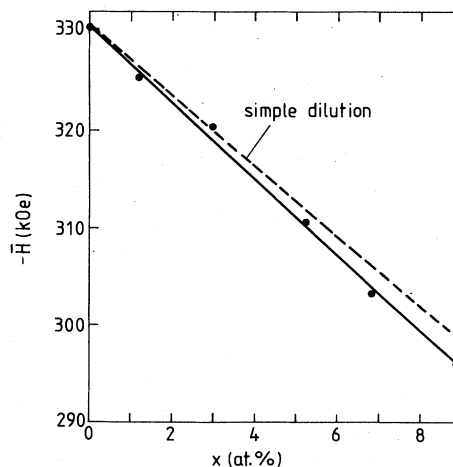


FIG. 4. The average hf field \bar{H} vs x , W concentration. The solid line stands for the best fit to the data.

TABLE III. Fitted average values and contributions of the isomer shifts (in mm/sec) in $\text{Fe}_{1-x}\text{W}_x$ alloys.

x (at. %)	$I(0,0)$	ΔI_1	ΔI_2	\bar{I}
0	-0.1059			-0.1059
1.20	-0.1025	-0.030	-0.014	-0.1057
2.95	-0.0982	-0.033	-0.011	-0.1063
5.26	-0.0917	-0.027	-0.014	-0.1070
6.87	-0.0848	-0.023	-0.015	-0.1049
8.89	-0.0807	-0.017	-0.014	-0.1025

2. The changes of the isomer shifts ΔI_1 and ΔI_2

These two parameters, being a measure of a local disturbance of the s -electron density, are (as expected) concentration independent within the error limits. They have the following average values: $\Delta \bar{I}_1 = -0.026 \pm 0.006$ mm/sec, $\Delta \bar{I}_2 = -0.014 \pm 0.002$ mm/sec. Their negative values imply that appearance of the W atom within the two-shell vicinity of the Fe atom increases its s -charge density.

3. The average isomer shift \bar{I}

The last column of Table III displays the values of the average isomer shift \bar{I} (relative to the source). We note that \bar{I} , within the error limits, does not depend on x . This is an exceptional case among those we studied to date and we shall discuss it in more detail in the following section.

V. DISCUSSION

The experimental material we present in Sec. IV reveals that substitution of Fe atoms by W atoms brings about

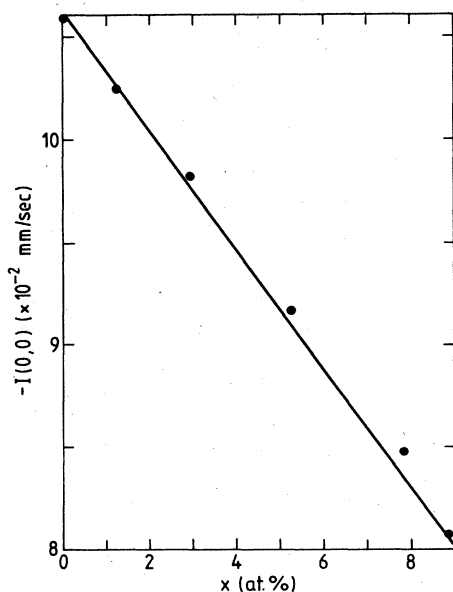


FIG. 5. Isomer shift $I(0,0)$ of the unperturbed atomic configuration vs x , the concentration of W. The solid line stands for the best fit to the data.

changes in the electronic structure of the matrix which manifests itself in alternation of the hf parameters. However, contrary to our previous observations on Fe- X ($X = \text{Al, Si, Sn, Ge, Cr, V}$) the average s -charge density at Fe nuclei remains obviously constant. In the following we shall express the measured changes of the hf parameters in terms of the corresponding spin and charge densities as well as discussing what the implication of the constancy of \bar{I} is.

A. Correlation between $H(0,0)$ and $I(0,0)$

Figure 6 provides evidence that the changes in the hf field of the undisturbed atomic configuration $\Delta H(0,0) = H(0,0) - H_{\text{Fe}}$ depend linearly on the corresponding changes in the isomer shift, $\Delta I(0,0) = I(0,0) - I_{\text{Fe}}$, up to $x \leq 3$ at.%. The data fit to the following equation: $-\Delta H(0,0) = 0.03 + 414.7 \Delta I(0,0)$, $r = 0.9995$.

This correlation together with the relation between the change of the isomer shift, dI , and attributed change of the number of s -like electrons, dN_s , which according to Ref. 9 is $dI/dN_s = 2.05$ mm/sec per s electron, permits the evaluation of the related hf coupling constant, $\alpha_0 = dH(0,0)/dN_s = 850$ kOe per s electron.

Figure 6 enables us also to conclude that the effective increase of the density of spin-down electrons, which was mentioned in relation with Fig. 3, is due to the decrease in spin-up electron density at the Fe nuclei of the undisturbed atomic configuration. The knowledge of α_0 permits further the scaling of these decreases in corresponding number of s -like electrons (see right-hand ordinate of Fig. 6).

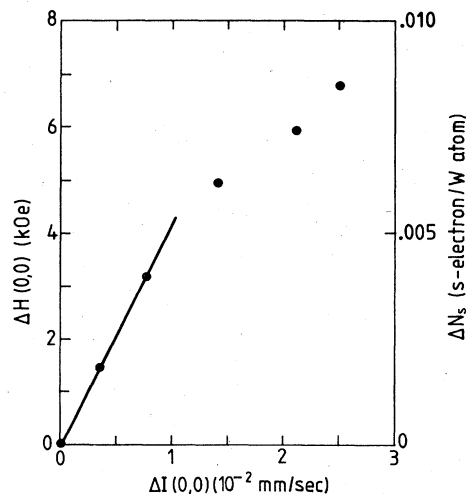


FIG. 6. Difference between the hf field of the unperturbed atomic configuration and that of pure iron, $\Delta H(0,0) = H(0,0) - H_{\text{Fe}}$ vs the corresponding difference in the isomer shift, $\Delta I(0,0)$. The solid line is the best fit to the data (up to $x \leq 3$ at. %), ΔN_s is the effective change in the number of s -like electrons which corresponds to the measured changes of $\Delta H(0,0)$ or $\Delta I(0,0)$.

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

The parameters ΔH_1 , ΔH_2 , ΔI_1 , and ΔI_2 measure local perturbances in spin and charge densities induced by one impurity atom being in the NN or in NNN vicinity. As such they are expected to be concentration independent. Their values compiled in Table II and III remain constant, within about 20% error limits. Because the accuracy of the present experiment is not better, we shall take constancy of these parameters for granted.

Using the average values, we note that the ratios

$$R_H = \frac{\Delta H_1}{\Delta H_2} = 1.58 \pm 0.25$$

and

$$R_I = \frac{\Delta I_1}{\Delta I_2} = 1.86 \pm 0.69$$

are equal within the error limits. This proves, in our opinion, that again the local density perturbances are correlated. These correlations enable us to calculate the local hf coupling constants $\alpha_1 = d\Delta H_1/dN_s = 3200$ kOe per s electron and $\alpha_2 = d\Delta H_2/dN_s = 3770$ kOe per s electron (here we again used for dI/dN_s the value after Ref. 9). We see that $\alpha_1 \approx \alpha_2$, i.e., the same mechanism must be responsible for the local perturbances of electron densities. By use of $\alpha_{1,2}$ values, we can express the measured changes of hf fields $\Delta H_{1,2}$ in terms of the related numbers of s -like electrons. We obtain $\Delta N_1^s = 0.013$ and $\Delta N_2^s = 0.007$, i.e., the W atom acts similar to Cr and V atoms as it increases the local electron density at Fe nuclei which is opposite to the influence of Al, Sn, Si, and Ge.^{6,10}

C. Correlation between \bar{H} and \bar{I}

We have here a very unusual and unique case. With increasing W concentration we observe a linear, almost simple-diluted, decrease of the average hf field \bar{H} , which corresponds to a decrease of the Fe-site density of spin-down electrons, with simultaneously constant value of the average isomer shift \bar{I} , i.e., the average charge density at the Fe sites remains unchanged. How can it be accounted for? We shall discuss a possible explanation later. Here we only want to mention that, in fact, there must be a flow of charge to and from Fe atoms because

(a) W atoms placed outside the NN-NNN environment decrease the charge density at the Fe atoms.

(b) W atoms placed within the NN-NNN environment of the Fe atoms do increase their charge density, as discussed in Sec. V B.

Obviously there must be a compensation of the two effects as on average there is no change in the charge density.

This "degenerated" correlation $\bar{H}-\bar{I}$ makes it impossible to evaluate the corresponding hf coupling constant $\bar{\alpha}$, and consequently to determine the change of spin or charge density induced by one W atom per unit cell η from the way used before.⁶ We shall, however, determine η in Sec. V E. In Sec. VI we shall discuss in more detail a possible

mechanism to account for the presently observed $\bar{H}(x)$ and $\bar{I}(x)$ behavior.

D. Correlation between \bar{H} and \bar{N}

Figure 7 supplies evidence that the average hf field \bar{H} is correlated with the average number of W atoms within the NN-NNN environment \bar{N} . The correlation is not only linear: $\bar{H} = -329.3 + 24.9\bar{N}$, $r=0.999$, but it follows the simple-dilution behavior. [As shown in Table II the actual number of W atoms within the NN-NNN vicinity \bar{N} exceeds by about 20% the number expected from the random distribution, \bar{N}_0 . This also explains why in $\bar{H}-x$ ordinates $\bar{H}(x)$ deviates by 18% from the simple-dilution behavior.] Therefore W atoms as solutes of the Fe matrix turn out to behave in an extremely unique way; they do simply dissolve the average Fe-site spin density, and simultaneously they do not alter the average charge density.

E. Evaluation of the η value and comparison with the model predictions

In order to evaluate η we used two alternative relationships:⁶

$$d\bar{H}/d\bar{M} \equiv \bar{\alpha}\eta \quad (1a)$$

(\bar{M} being the number of impurities per unit cell), or

$$\bar{H}(x) \equiv H_{Fe} + 2\bar{\alpha}\eta x \quad (1b)$$

However, in the present case $\bar{\alpha}$ cannot be determined as usually, therefore we shall try to estimate η on a slightly different way. We note, namely, that the following identity also holds:

$$\frac{d\bar{H}/d\bar{M}}{dH(0,0)/dN_s} \equiv \frac{d\bar{H}/dx}{dH(0,0)/dx} \quad (2)$$

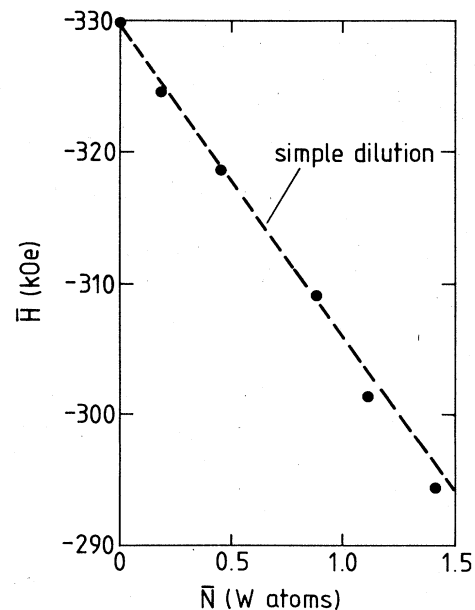


FIG. 7. Average hf field \bar{H} vs the average number of W atoms within the first two neighbor shells, \bar{N} .

Using for $dH(0,0)/dx$ the value of 1.076 which holds for $x \leq 3$ at. %, and based on Eq. (2) we arrive at $\eta=0.09$. This remains in a good accord with predictions obtained both from the Stearns and the Miedema models,^{10,11} but disagrees definitely with the value of 0.54 expected from the model involving the difference of the atomic charges.¹⁰

VI. FINAL CONSIDERATIONS

A. A possible explanation of the measured behavior of $\bar{H}(x)$ and $\bar{I}(x)$

Let $\rho^\uparrow, \rho^\downarrow$ denote the effective density of s -like electrons with spin up and spin down, respectively, at Fe nuclei in Fe-W alloy and $\rho_{\text{Fe}}^\uparrow, \rho_{\text{Fe}}^\downarrow$ represent the same in pure iron. Then our present results can be expressed in the following way:

$$\langle \rho^\uparrow - \rho^\downarrow \rangle = (1-x)(\rho_{\text{Fe}}^\uparrow - \rho_{\text{Fe}}^\downarrow) = (1-x)\sigma_{\text{Fe}}, \quad (3)$$

$$\langle \rho^\uparrow + \rho^\downarrow \rangle = (\rho_{\text{Fe}}^\uparrow + \rho_{\text{Fe}}^\downarrow). \quad (4)$$

$\langle \rangle$ stands for the average value.

Let us further assume that

$$\langle \rho^\pm \pm \rho^\pm \rangle = \langle \rho^\pm \rangle \pm \langle \rho^\pm \rangle. \quad (5)$$

Then Eqs. (3) and (4) can be written as follows:

$$\langle \rho^\uparrow \rangle - \langle \rho^\downarrow \rangle = \rho_{\text{Fe}}^\uparrow - \rho_{\text{Fe}}^\downarrow - x(\rho_{\text{Fe}}^\uparrow - \rho_{\text{Fe}}^\downarrow), \quad (3')$$

$$\langle \rho^\uparrow \rangle + \langle \rho^\downarrow \rangle = \rho_{\text{Fe}}^\uparrow + \rho_{\text{Fe}}^\downarrow. \quad (4')$$

From (3') and (4') we obtain

$$\langle \rho^\uparrow \rangle = \rho_{\text{Fe}}^\uparrow - \frac{x}{2}(\rho_{\text{Fe}}^\uparrow - \rho_{\text{Fe}}^\downarrow) = \rho_{\text{Fe}}^\uparrow - \frac{x}{2}\sigma_{\text{Fe}}, \quad (6)$$

$$\langle \rho^\downarrow \rangle = \rho_{\text{Fe}}^\downarrow + \frac{x}{2}(\rho_{\text{Fe}}^\uparrow - \rho_{\text{Fe}}^\downarrow) = \rho_{\text{Fe}}^\downarrow + \frac{x}{2}\sigma_{\text{Fe}}. \quad (7)$$

Equations (6) and (7) describe changes in average densities of spin-up and spin-down electrons in iron, respectively, induced by substituting its atoms by W. We see that to account for the observed behavior of $\bar{H}(x)$ and $\bar{I}(x)$ the density of spin-up electrons of pure iron, $\rho_{\text{Fe}}^\uparrow$, decreases with x at constant rate, namely $\frac{1}{2}\sigma_{\text{Fe}}$. Simultaneously, the density of spin-down electrons increases at the same rate. In other words, changes in the electronic structure of iron which occur on substituting its atoms by W atoms as seen within the nuclear volume of the probe ^{57}Fe nuclei can be, in general described in terms of a spin-flip phenomenon: The density of spin-down s -like electrons increases at the cost of the density of spin-down s -like electrons with the rate equal to 50% of the total spin density of s -like electrons in pure iron, σ_{Fe} .

We can further use Eqs. (6) and (7) in order to estimate the value of σ_{Fe} . Towards this end we note that

$$\langle \sigma \rangle = \langle \rho^\uparrow(x=0.5) \rangle - \langle \rho^\downarrow(x=0.5) \rangle = \eta. \quad (8)$$

Using (6)–(8) we get

$$-\frac{1}{2}\sigma_{\text{Fe}} = \eta = 0.09. \quad (9)$$

It follows then from (9) that $\sigma_{\text{Fe}} = -0.18$. According to

the scale given in Ref. 9 this is equivalent to $\sigma_{\text{Fe}} \approx -0.4$ in atomic units, which in turn seems to be a rather good estimate as compared to -0.6 as calculated by Callaway and Wang.¹² Knowledge of σ_{Fe} enables further evaluating of the corresponding hf coupling constant A based on the relationship

$$H_{\text{Fe}} = A\sigma_{\text{Fe}}. \quad (10)$$

Taking $H_{\text{Fe}} = 330$ kOe, we obtain from (10)

$$A = 1833 \text{ kOe/s electron}.$$

This figure is very close to the value of 1708 or 1800 kOe/s electron deduced from the calculations by Goodings and Heine¹³ or by Watson and Freeman,¹⁴ respectively, for the hf coupling constant concerning the hf field which originates from the polarized $4s$ -like electrons as well as from the $4s$ -like electrons being hybridized with the $3d$ band.

B. Other interesting cases of $\bar{H}(x)$ and $\bar{I}(x)$ behavior

We think that it is worth considering two more interesting cases of $\bar{H}(x)$ and $\bar{I}(x)$, namely,

$$(i) \bar{H}(x) = \text{const and } \bar{I}(x) = (1-x)I_{\text{Fe}},$$

$$(ii) \bar{H}(x) = (1-x)H_{\text{Fe}} \text{ and } \bar{I}(x) = (1-x)I_{\text{Fe}}.$$

Concerning case (i), it is easy to show that the following conditions are necessary to realize it:

$$\langle \rho^\uparrow \rangle = \rho_{\text{Fe}}^\uparrow - \frac{1}{2}x(\rho_{\text{Fe}}^\uparrow + \rho_{\text{Fe}}^\downarrow), \quad (11)$$

$$\langle \rho^\downarrow \rangle = \rho_{\text{Fe}}^\downarrow - \frac{1}{2}x(\rho_{\text{Fe}}^\uparrow + \rho_{\text{Fe}}^\downarrow). \quad (12)$$

From Eqs. (11) and (12) it follows then that in order to keep the average spin-density constant and simultaneously to simply dissolve the average charge-density, one has to decrease both the density of spin-up and spin-down electrons of pure iron at the same rate, equal to 50% of the total charge density of pure iron.

Concerning case (ii), we arrive at the following conditions:

$$\langle \rho^\uparrow \rangle = \rho_{\text{Fe}}^\uparrow - x\rho_{\text{Fe}}^\uparrow = (1-x)\rho_{\text{Fe}}^\uparrow, \quad (13)$$

$$\langle \rho^\downarrow \rangle = \rho_{\text{Fe}}^\downarrow - x\rho_{\text{Fe}}^\downarrow = (1-x)\rho_{\text{Fe}}^\downarrow, \quad (14)$$

i.e., when both \bar{H} and \bar{I} are simply diluted it means that both spin-up and spin-down s -like bands of pure Fe are simply diluted.

VII. CONCLUSIONS

The present study of a series of $\text{Fe}_{1-x}\text{W}_x$ alloys by means of Mössbauer-effect spectroscopy permits the development of the following conclusions:

(1) Substitution of iron atoms by W atoms induces changes in the electronics structure of iron which is evidenced by changes of s -electron spin and charge densities in the nuclear volume.

(2) Appearance of W atoms within the environment of the first two shells increases the Fe-site spin or charge density by 0.013 s electrons for one W atom placed in NN, and by 0.007 s electrons per one W atom placed in NNN.

(3) W atoms situated outside the NN-NNN environment decrease the Fe-site charge density in such a way that the effect mentioned under (2) is compensated, i.e., the average charge density remains constant.

(4) The average spin density is, within the error limits, simply diluted. This and the constant value of the average charge density can be accounted for by postulating

that spin-up spins flip into the spin-down state with a rate equal to 50% of the net spin density in pure iron which we estimate as $-0.18 s$ electrons.

(5) The average change of spin density caused by one W atom per unit cell $\eta=0.09$ is in agreement with predictions based on the models by Stearns as well as by Miedema.

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