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Mössbauer-effect study of spin- and charge-density changes in Fe-Al alloys

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The influence of Al concentration on the ^{57}Fe- and ^{119}Sn-site hyperfine (hf) fields and isomer shifts has been studied for a series of Fe-Al alloys containing up to 15 at. % Al and 0.8 at. % ^{119}Sn, with use of Mössbauer-effect spectroscopy. The observed changes of the hf fields and the isomer shifts have been interpreted in terms of spin- and charge-density changes, respectively. Linear correlations have been revealed between the following quantities: the hf field $H(0,0)$ and the isomer shift $I(0,0)$ of undisturbed neighbor configurations; the average hf field $\bar{H}$ and the average isomer shift $\bar{I}$; the average hf field $\bar{H}$ and the average number of Al atoms in the first two neighboring shells, $\bar{N}_A$. From the first two correlations the following hf coupling constants have been determined: (a) the hf coupling constant for s-like itinerant electrons yielding 528 kOe/s electron and 3108 kOe/s electron for Fe and Sn atoms, respectively, and (b) the average hf coupling constant yielding 987 kOe/s electron for ^{57}Fe and 1290 kOe/s electron for ^{119}Sn. From the correlations between $\bar{H}$ and $\bar{N}_A$ the changes in spin or charge densities caused by one Al atom per unit cell η have been deduced. From the Fe-site results $\eta=0.10$ was found for the changes in both the itinerant and localized spin densities. From the Sn-site results $\eta=0.09$ for itinerant and $\eta=0.04$ for localized spin-density changes have been deduced.

I. INTRODUCTION

Binary iron-rich Fe-Al alloys, in addition to iron-rich Fe-Si alloys, are examples of systems where saturation magnetization decreases linearly with the increase of Al concentration x, for $x \leq 0.15$.[1,2] The rate of the decrease $d\bar{\mu}/dx = -2.2\mu_B$, which is being interpreted in terms of a simple dilution of the Fe-site magnetic moments. This experimental observation is also often expressed by saying that Al atoms act like magnetic holes in the iron matrix, i.e., they enter into it by neither disturbing the original band structure of iron nor contributing of its own to the magnetic structure.[3]

However, such an interpretation seems to be oversimplified and it is in disagreement with the dependence of the average hyperfine field on Al concentration. In particular, it has been shown, that the hf field decreases much slower than the average magnetic moment.[4] This proves that substitution of Fe atoms by Al atoms causes some additional change in the spin density as seen by Fe nuclei.

The aim of this investigation is to study the nature of these additional changes in more detail than reported in literature by using the Mössbauer effect of ^{57}Fe and ^{119}Sn nuclei as a tool. Let us recall first the widely accepted point of view that the resultant Fe-site hf field in metallic iron, H^{Fe}, has two dominant contributions:

$$H^{\mathrm{Fe}}=H_0^{\mathrm{Fe}}+H_{\mathrm{thf}}^{\mathrm{Fe}} . \tag{1}$$

The first term is the intrinsic contribution, H_0^{Fe}, which is due to the polarization of the core electrons (1s, 2s, and 3s), while the second term is the total hf-field contribution transferred from the host-lattice atoms and itinerant electrons. It consists of two parts as follows:

$$H_{\mathrm{thf}}^{\mathrm{Fe}}=\sum n_i \Delta H_i + H_{\mathrm{CEP}}^{\mathrm{Fe}} , \tag{2}$$

where ΔH_i is the distinct transferred field contributed by one of the n_i neighbors in the ith-neighbor shell and $H_{\mathrm{CEP}}^{\mathrm{Fe}}$ originates from the conduction-electron polarization. In other words, H_0^{Fe} and ΔH_i have local character and origin, while $H_{\mathrm{CEP}}^{\mathrm{Fe}}$ has an itinerant one. The results of many previous experiments (see Ref. 4 and references therein) indicate that in iron-rich binary alloys Fe-X, particularly in Fe-Al, the core-electron polarization remains constant or may be disturbed only slightly on substituting Fe atoms by X atoms. This is most likely the reason for the measured behavior of the magnetic moment of Fe-Al. Thus, the smaller decrease of the average hyperfine field, $\bar{H}$, should be related mainly to the behavior of the

$H_{\mathrm{CEP}}^{\mathrm{Fe}}$ contribution, i.e., to a behavior of the spin density of the itinerant electrons.

Changes in spin and charge densities taking place in the iron matrix upon substituting Fe atoms by X atoms can be seen in more detail by carrying out the Mössbauer effect measurements not only at ^{57}Fe nuclei, but also at ^{119}Sn nuclei. The latter must be introduced into the iron matrix at an appropriate low concentration, i.e., as undisturbing probe atoms, which will leave the original electronic structure of the alloys effectively unchanged.[5] Since Sn nuclei have no magnetic moment of their own they will "probe" only the $H_{\mathrm{thf}}^{\mathrm{Fe}}$ contribution of the hyperfine field of Eq. (1). Therefore, measuring changes of the Sn-site hyperfine field versus Al concentration in particular, provides valuable information on the changes in the polarization of the conduction-band electrons. In this paper the results obtained for a series of seven samples of Fe-Al containing up to about 15 at. % Al and about 0.8 at. % ^{119}Sn are presented and interpreted in terms of spin- and charge-density changes.

II. EXPERIMENTAL

A. Sample preparation

A series of seven samples containing up to about 15 at. % Al has been prepared by melting appropriate amounts of 99.99%-pure iron and aluminium in an induction furnace in a clean argon atmosphere. The melting process was repeated four times. Probe atoms of tin enriched to 91% in a ^{119}Sn isotope were introduced into the matrix of Fe-Al alloys by melting them with an appropriate amount of tin in an arc furnace, again in a clean argon atmosphere. The melting was repeated three times. All samples were chemically analyzed. The results are summarized in Table I. The samples for the Mössbauer-effect measurements were obtained by filing the melted samples with a diamond file to an average grain size of about 60 μm.

TABLE I. Results on the chemical composition of the studied $\mathrm{Fe}_{1-x-y}\mathrm{Al}_x\mathrm{Sn}_y$ alloys.

Probe no.	x (at. %)	y (at. %)
0	0	0.43
1	0.99	0.81
2	1.34	0.80
3	3.84	0.66
4	7.41	0.83
5	9.27	0.79
6	11.20	0.81
7	14.80	0.37

B. Spectra measurements

The room-temperature Mössbauer spectra were measured with a constant-acceleration spectrometer having a 1024-channel analyzer. The Fe-site spectra were taken with the use of the ^{57}Fe 14.4-keV γ rays emitted by a source of ^{57}Co in rhodium and with a proportional counter. The Sn-site spectra were measured with 23.9-keV γ rays emitted by ^{119}Sn nuclei from a $\mathrm{CaSnO_3}$ source and detected by a NaI scintillation counter. As a calibration standard, a 25-μm-thick foil of iron was used.

III. SPECTRA ANALYSIS

Both ^{57}Fe-site and ^{119}Sn-site spectra were computer analyzed with either of the two following methods.

A. Method I

Method I is based on a least-squares iteration procedure. Each spectrum is assumed to be formed by superposition of a number of contributing subspectra having different splittings, isomer shifts, and relative intensities. The number and relative contributions of these subspectra then follow from the binomial distribution of Fe, Al, and Sn atoms within the first two neighboring shells. Only the most probable configurations were taken into account, which sum up to an overall probability of greater than 98%. Their relative contributions were, however, taken as free parameters in the computer-fit procedure to allow for possible inhomogenities of the atomic distribution. It was further assumed that linear superposition of field and isomer shift changes holds also.

B. Method II

Method II has been proposed and used by Window[6] first. It deduces the field distribution directly from the measured Mössbauer spectrum by means of Fourier analysis. Agreement between the results obtained with both methods can be regarded as a final check for the analysis of the spectra to be consistent and to yield meaningful parameters.

TABLE II. Fit values of hyperfine-field parameters deduced from the ^{57}Fe-site spectra. All fields are given in kOe. The meaning of the parameters is described in the text.

x (at. %)	$H(0,0)$	ΔH_1^A	ΔH_2^A	$\bar{H}_{\mathrm{I}}$	$\bar{H}_{\mathrm{II}}$
0	−330.4			−330.4	−330.7
0.99	−331.1	−25.0	−7.5	−326.15	−326.6
1.34	−331.2	−24.7	−7.0	−325.3	−326.0
3.84	−331.65	−25.2	−11.2	−320.4	−321.9
7.41	−334.8	−22.8	−9.4	−313.1	−314.3
9.27	−335.95	−27.2	−8.9	−307.5	−310.4
11.20	−338.35	−26.0	−8.85	−305.3	−304.9
14.80	−337.9	−26.7	−9.5	−298.4	−300.0

IV. EXPERIMENTAL RESULTS AND THEIR EVALUATION

A. ^{57}Fe-site measurements

1. Hyperfine fields

^{57}Fe-site Mössbauer spectra of the investigated samples are displayed in Fig. 1(a). A calibration spectrum of metallic iron has been added for comparison. The influence of Al substitution of Fe nearest and next-nearest neighbors (NN and NNN, respectively) on the hyperfine fields is revealed most clearly by the two outermost lines, which develop characteristic structures with increasing Al concentration.

The corresponding field distribution obtained with method II is placed alongside each related spectrum [Fig. 1(b)]. Here, the influence of Al substitution manifests itself (i) in a decrease of the intensity of the single-peak distribution, characteristic for pure iron, and (ii) in the development of

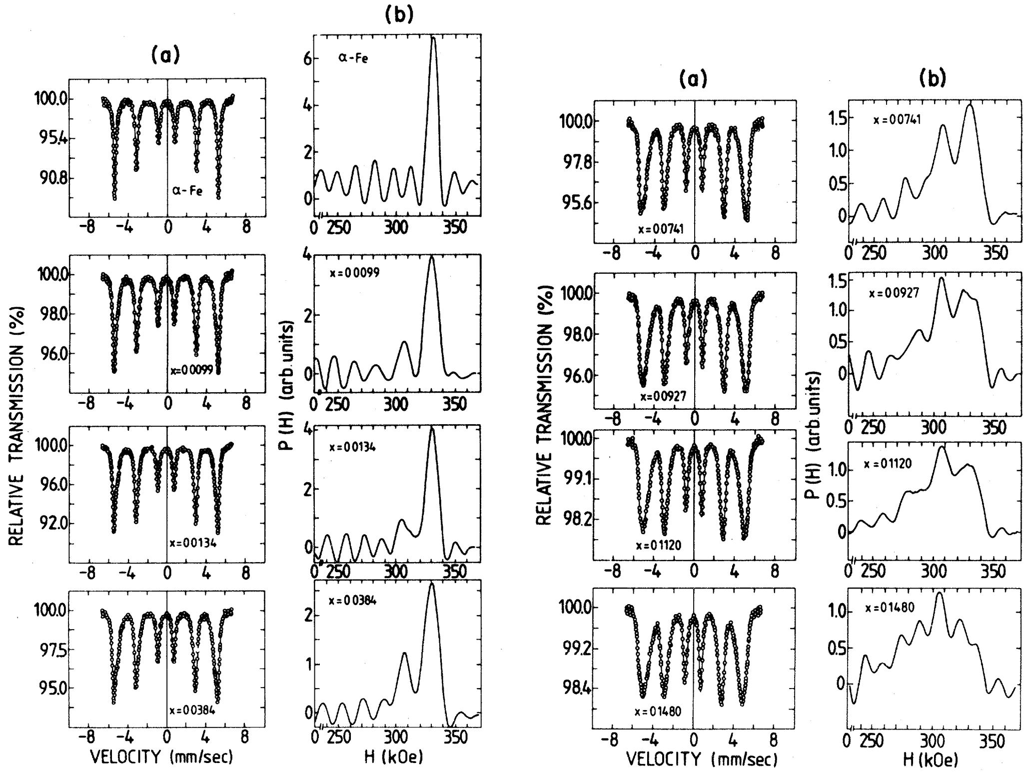

FIG. 1. (a) Room-temperature Mössbauer spectra for the ^{57}Fe site of the $Fe_{1-x}Al_x$ system as a function of the Al concentration, x. (b) hf field distributions obtained from the Mössbauer spectra shown in (a) by means of method II (see text for details).

new peaks, whose number and intensities are characteristic features for the atomic distribution of a given sample. From the field distributions the average hyperfine fields have been deduced. Those obtained from method II in this investigation are denoted by $\overline{H}_{\mathrm{II}}$ and are collected in Table II together with the following parameters obtained from method I: $H(0,0)$, i.e., the hf field at Fe atoms having no NN and NNN Al atoms, ΔH_1^A and ΔH_2^A, i.e., the changes in the ^{57}Fe hf field by one Al atom placed in the first- or second-neighbor shell, respectively, and $\overline{H}_I$, the average field calculated from method I, i.e., according to equation

$$\overline{H}_I=\sum H(m,n)P(m,n)\Big/\sum P(m,n)\ , \qquad (3)$$

where $H(m,n)$ is the field at an Fe atom having the NN and NNN configuration (m,n), and $P(m,n)$ stands for the probability of that configuration. As a check of consistency for analyzing the spectra with both methods, one can compare the average hf fields, $\overline{H}_{\mathrm{I}}$ and $\overline{H}_{\mathrm{II}}$ obtained from method I and II, respectively. The hyperfine-field parameters ΔH_1^A, ΔH_2^A, $H(0,0)$, and $\overline{H}$ also agree well with values reported in the literature.[3]

a. The local hyperfine field H(0,0). Let us start the explanation of these results with the field $H(0,0)$. As one can easily see from Fig. 2 the $H(0,0)$ values increase with increasing Al concentration. The normalized value of $H(0,0)$, $h_0=H(0,0)/330.4$, marked by open circles, increases linearly. The best fit to the experimental data can be described by the equation $h_0=1.000+0.0018x$, with correlation coefficient $r=0.97$. Since the field $H(0,0)$ is negative, this means that the effective density of spin-down electrons at Fe nuclei having no Al atoms within their vicinity of the first two neighboring shells increases with increasing Al concentration. This increase of the spin-down density according to Eq. (2) can be taken as an indication of an increase of $H_{\mathrm{CEP}}^{\mathrm{Fe}}$, i.e., of the spin-down density in the conduction band.

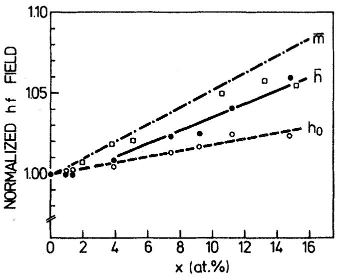

FIG. 2. ^{57}Fe-site hyperfine fields of the $\mathrm{Fe}_{1-x}\mathrm{Al}_x$ system, normalized to the hf field of α-iron (Al concentration $x=0$) as a function of x. Open circles represent the hf fields for the configuration (0,0), h_0; full circles mark the average hyperfine field normalized to constant Fe concentration, $\overline{h}$; squares indicate the values taken from Ref. 4; the broken line ($\overline{m}$) represents the linear equation, which fits to the magnetic moment per Fe atom using the results of Ref. 1.

b. $\Delta H_1^A,\Delta H_2^A$ field shifts. When one Al atom substitutes an Fe atom in the vicinity of the probing Fe atom, then the hyperfine field "seen" by the latter will be reduced, since $\Delta H_{1,2}^A$ are of negative sign too. Our present results indicate a slight increase of ΔH_1^A and ΔH_2^A with increasing Al concentration too. The possible sources for these changes will be discussed later (see Sec. V).

c. The average field $\overline{H}$. The average field $\overline{H}$ decreases with increasing Al concentration. The decrease is linear, in the whole range studied. In contrast, Stearns[3] observed linear behavior of $\overline{H}$ only up to around 10 at. % Al. The discrepancy is thought to be due to some differences in the degree of homogeneity between our samples and those of Stearns. The important feature, however, is that the hf field $\overline{H}$ decreases slower than the magnetic moment, as already mentioned by Stearns.[3] Why does this happen? Let us first rewrite Eq. (1) as follows:

$$H(x,n_1,n_2)=H_0(x)+(n_1\Delta H_1+n_2\Delta H_2)+H_{\mathrm{CEP}}(x)\ . \qquad (1'a)$$

In Eq. (1′a) $n_1=(8-m)$ and $n_2=(6-n)$ now are the numbers of Fe atoms in the first- and second-neighbor shells. Generally the Al atoms do not just remove Fe atoms but also introduce their own electronic configurations. Hence they will also cause changes of $H_0(x)$ and $H_{\mathrm{CEP}}(x)$. In order to see the actual changes in the average spin densities, which will take place in the iron matrix when some Fe atoms are replaced by Al atoms, one should normalize the hf field to constant Fe concentration, i.e., one should consider the quantity $H_N=H/(1-x)$. In addition, H_N has been normalized to the hf field of pure Fe ($x=0$), i.e., to $H_{\mathrm{Fe}}=-330.4$ kOe.

The average hf field following from Eq. (1′a) is given by

$$\overline{H}(x)=\overline{H}_0(x)+\overline{H}_{\mathrm{CEP}}(x)+\overline{n}_1\Delta H_1(x)+\overline{n}_2\Delta H_2(x)\ , \qquad (1'b)$$

where

$$\overline{n}_1=(1-x)8,\quad \overline{n}_2=(1-x)6\ ,$$

and the first two terms can be approximated by the following equations:

$$\bar{H}_0(x)=H_0(0)+\Delta H_0(x),\quad \Delta H_0(x)=\gamma x\ , \qquad (1'c)$$

$$\bar{H}_{\mathrm{CEP}}(x)=H_{\mathrm{CEP}}(0)+\Delta H_{\mathrm{CEP}}(x),\quad \Delta H_{\mathrm{CEP}}(x)=\alpha x\ .$$

A normalized average hf field, $\bar{h}(x)$, useful for comparison with the average magnetic moment of iron in the alloy of an overall magnetic moment $\bar{\mu}$, $\bar{m}=\bar{\mu}/(1-x)/\mu_{\mathrm{Fe}}$, then turns out to be given as follows:

$$\bar{h}(x)=\frac{\bar{H}_N}{1-x}=\left[\frac{H_0(0)+H_{\mathrm{CEP}}(0)}{1-x}+[(\alpha+\gamma)x+8\Delta H_1(x)+6\Delta H_2(x)]\right]\Big/ H_{\mathrm{Fe}}\ . \qquad (1'd)$$

For small concentrations x and with the assumptions $\Delta H_{1,2}(x)\approx\Delta H_{1,2}(0)$ and $\gamma=0$ being reasonable from our experimental results, we arrive at

$$\bar{h}(x)\approx 1+x\left[\frac{H_0(0)+H_{\mathrm{CEP}}(0)+\alpha}{H_{\mathrm{Fe}}}\right]. \qquad (1'e)$$

Let us next write down, with the use of the same notation, the normalized field $h_0(x)$ for the undisturbed NN and NNN configurations, i.e., for $n_1=8$ and $n_2=6$, as follows:

$$h_0(x)=[H_0(x)+H_{\mathrm{CEP}}(0)+(1-x)(\alpha+\gamma)x$$
$$+8\Delta H_1(x)+6\Delta H_2(x)]/H_{\mathrm{Fe}}\ . \qquad (1'f)$$

With the use of the same assumption for $\Delta H_{1,2}(x)$ and γ as before, Eq. (1'f) transforms to

$$h_0(x)\approx 1+(\alpha/H_{\mathrm{Fe}})x\ . \qquad (1'g)$$

In Fig. 2 the results for $\bar{h}(x)$ and $h_0(x)$ are shown by full and open circles, respectively. Obviously, this normalized average field, $\bar{h}(x)$, increases with Al concentration x in contrast to $\bar{H}(x)$. Thus, in fact, Al atoms, regarded as magnetic holes, in addition, increase the effective density of spin-down electrons of the remaining Fe atoms. The rate of this increase is not the same in the whole range of the Al concentration, but it can be divided into two steps:

(i) Up to about 4 at. % Al $d\bar{h}/dx\approx dh_0/dx$, i.e., the field $\bar{h}$ follows h_0.

(ii) Above about 4 at. % Al the field $\bar{h}$ increases much faster than h_0 as $d\bar{h}/dx\approx 2.5dh_0/dx$. What does $d\bar{h}/dx\approx dh_0/dx$ mean? From Eqs. (1'e) and (1'g) one deduces for $x\ll 1$ the following relation:

$$\frac{d\bar{h}}{dx}:\frac{dh_0}{dx}=[H_0(0)+H_{\mathrm{CEP}}(0)+\alpha]:\alpha\ . \qquad (1'h)$$

Combining this relation with the experimental result for small x, $d\bar{h}/dx:dh_0/dx\approx 1$, we arrive at the following condition for the involved hf-field contributions of bcc iron: $H_0(0)+H_{\mathrm{CEP}}(0)=0$. The value $H_0(0)=-185$ kOe reported in Ref. 7, we now get as an estimate for the conduction-electron contribution $H_{\mathrm{CEP}}(0)=+185$ kOe. This value agrees well with the theoretically estimated value of + 200 kOe.[8]

This condition and result for small x means further that the total measured transferred hf field in pure bcc iron originates from the distinct NN and NNN contributions, $8\Delta H_1(0)+6\Delta H_2(0)$, only. The result $\bar{h}(x)\approx h_0(x)$ invokes further that the average spin density at Fe sites in the $\mathrm{Fe}_{1-x}\mathrm{Al}_x$ system at $x\ll 1$ is equal to that of its undisturbed Fe sites, i.e., to that of the (0,0) configurations. In other words, small substitutions of Fe atoms within an iron matrix neither disturb the localized spin densities and, hence, $\Delta H_{1,2}$, nor the core-electron contribution $H_0(0)$, to the total hf field. Instead it increases the effective density of the spin-down itinerant electrons, and, hence, causes an initial change of the hf field by $H_{\mathrm{CEP}}(x)-H_{\mathrm{CEP}}(0)=\alpha x$, where $\alpha=59.5$ kOe/x at. %.

In Fig. 2 also the normalized average magnetic moment, $\bar{m}(x)$, is plotted for comparison with $\bar{h}(x)$ and $h_0(x)$. As with $\bar{h}(x)$ and $h_0(x)$, $\bar{m}(x)$ also turns out to be not a constant as it should be for a simple dilution of the number of Fe moments by the Al atoms. Instead, $\bar{m}$ also increases linearly and even faster than $\bar{h}$. In fact, the $\bar{m}$ values taken from Ref. 1 are well described by the equation $\bar{m}=0.998+0.0053x$, $r=0.997$, i.e., the increase of $\bar{m}$ is $d\bar{m}/dx=0.0053$. It is found to be related with the gradients of h_0 and $\bar{h}$ by the relation $d\bar{m}/dx\approx dh_0/dx+d\bar{h}/dx$. The deviation between $\bar{m}(x)$ and $\bar{h}(x)$ again indicates that the simple hole-dilution model does not hold strictly for substitution of Fe by Al atoms.

It is interesting here to compare the influence of Al atoms on the magnetic and electronic structure of iron matrix with that of Cr atoms. Figure 3 shows the dependence of h_0 (open squares) and of $\bar{h}$ (solid circles) on Cr concentration x after Ref. 10. Contrary to Fe-Al in Fe-Cr, $h_0(x)$ follows $\bar{h}(x)$ in the whole range of x studied. From relation (1′h) it then again follows that for the Fe-Cr system the condition

$$H_0(0)=-H_{\mathrm{CEP}}(0)$$

must hold for small x values. Hence, the x dependencies of the normalized hf field $\bar{h}(x)$ and $h_0(x)$ of Fig. 3 again are due to the variation of the conduction-electron contribution, αx, only.

However, at somewhat larger substitutions, x the conditions and, hence, the figures for $H_0(x)$ and $H_{\mathrm{CEP}}(x)$ turn out to be different in the Fe-Al and Fe-Cr systems. We think this is due mainly to the fact that neither Al nor Cr atoms are undisturbing substitutes in the bcc Fe lattice, i.e., they do not just act as magnetic holes. Thus, the local transferred fields $\Delta H_i(0)$ in Eq. (1′a) are different for both cases and differ from the values expected for simple "hole" substitution as well. This will be discussed in more detail in Sec. V A 4. There we will show, however, that Cr is closer to this ideal "hole" substitution than Al. On the other hand, since Cr atoms, while not disturbing their Fe surroundings, bear their own magnetic moment, the localized contributions $\Delta H_{1,2}$ given in Ref. 10 must be considered as the sum of the removed Fe contribution $\Delta H_{1,2}^{0}$ and that of the introduced Cr contribution $\Delta H_{1,2}^{\mathrm{Cr}}$. Putting together all these conditions and results, i.e., $H_0(0)=-H_{\mathrm{CEP}}(0)$, $H_0(0)=-185$ kOe, $\Delta H_1^{*}=(\Delta H_1^{0}+\Delta H_1^{\mathrm{Cr}})=-31.5$ kOe, and $\Delta H_2^{*}=(\Delta H_2^{0}+\Delta H_2^{\mathrm{Cr}})=-23.0$ kOe, and, in addition, assuming the ratio of $\Delta H_1^{*}/\Delta H_2^{*}$ holds also for $\Delta H_1^{0}/\Delta H_2^{0}$, we arrive at the following results for the distinct hf contributions in pure bcc iron (all in units of kOe): $\Delta H_1^{0}=-26.7$, $\Delta H_2^{0}=-19.5$, $H_{\mathrm{CEP}}(0)=+185$, $H_{\mathrm{thf}}(0)=8\Delta H_1+6\Delta H_2^{0}=-330$ kOe. The local transferred fields introduced by Cr NN and NNN atoms then would be $\Delta H_1^{\mathrm{Cr}}=-4.8$ kOe and $\Delta H_2^{\mathrm{Cr}}=-3.5$ kOe. These figures look quite confident since the ratio $\Delta H_1/\Delta H_2=1.37$ is the same for the Fe and Cr contributions, $\Delta H_{1,2}^{0}$ and $\Delta H_{1,2}^{\mathrm{Cr}}$, respectively. With the reasonable assumption that the transfer mechanism is the same for Fe and Cr neighbors from the relation $\Delta H_1^{0}/\Delta H_1^{\mathrm{Cr}}=\mu_{\mathrm{Fe}}/\mu_{\mathrm{Cr}}$, we estimate the localized moment at the Cr site in bcc Fe to be $0.4\mu_B$, which again looks reasonable.

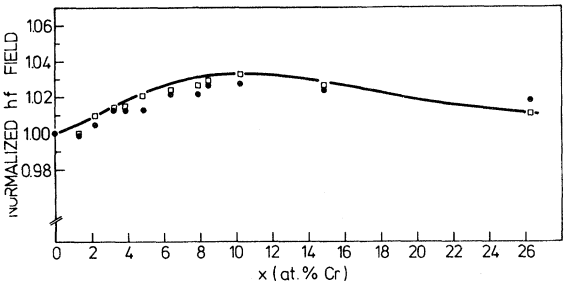

FIG. 3. ^{57}Fe-site hf fields of the $\mathrm{Fe}_{1-x}\mathrm{Cr}_x$ system, normalized to the hf field of α-Fe at $x=0$, after Ref. 10. Full circles represent the average hf fields normalized to constant Fe concentration, while the squares stand for the hf fields for the configuration (0,0). Full curve shows the hf-field behavior predicted by Eq. (8) of Ref. 5.

2. *Isomer shifts*

The fit values of the isomer shift parameters are collected in Table III. The nomenclature and meaning of $I(0,0)$, $\Delta I_{1,2}^{A}$, and $\bar{I}(x)$ is the same as introduced for the hf field in Sec. IV A 1 before. Apparently, $I(0,0)$ is positive and increases linearly with the Al concentration with a gradient of $dI(0,0)/dx=0.0022$ mm sec^{-1} (at. %)$^{-1}$. Such a behavior of $I(0,0)$ means that the charge density of electrons in the conduction band decreases, i.e., Al "dissolves" the charge of the itinerant electrons. The parameters ΔI_1^{A} and ΔI_2^{A} measure the changes of local charge densities and are independent of the Al concentration within the error limits. Both are positive, indicating that the effective charge density at the Fe nuclei is reduced when an Al atom is placed in their vicinity.

The average isomer shift $\bar{I}$ (relative to that of α-iron) is positive and increases linearly with a gradient of $d\bar{I}/dx=0.0043$ mm sec^{-1} (at. %)$^{-1}$. This means that on average the charge density at the Fe nucleus has been decreased. This is of course a consequence of the decrease observed for both the itinerant and localized electron densities.

B. ^{119}Sn-site measurements

1. *Hyperfine fields*

^{119}Sn-site Mössbauer spectra are shown in Fig. 4(a) together with corresponding field distributions, which are placed alongside [Fig. 4(b)]. Similarly, as in case of Fe-Cr alloys,[5] the shape of the ^{119}Sn-site spectra depends on the Al concentration. This means that the field is dependent on the configuration of the atomic vicinity and results for an alloy in a hf-field distribution. Since the origin of this field is the same as in the case of ^{57}Fe, with exception of the intrinsic part, i.e., the first term in Eq. (1), it should change due to second term in Eq. (1)

TABLE III. Fit parameters for the isomer shifts as obtained from the ^{57}Fe-site spectra. Isomer shifts are in mm/sec. The meaning of the parameters is described in the text.

x (at. %)	$\Delta I(0,0)^{a}$	ΔI_1^A	ΔI_2^A	$\bar{I}^{a}$
0.99	0.0102	0.032	0.001	0.018
1.34	0.0120	0.035	−0.002	0.021
3.84	0.0139	0.029	−0.004	0.025
7.41	0.0224	0.022	−0.001	0.037
9.27	0.0285	0.022	0.006	0.051
11.20	0.0316	0.022	0.004	0.059
14.80	0.0347	0.026	0.005	0.070

[a] Relative to α-Fe isomer shift.

with the local atomic configuration too. The spectra were again fitted with methods I and II. The results are summarized in Table IV. Obviously, the values of the average fields, $\bar{H}_{\rm I}$ and $\bar{H}_{\rm II}$ are practically the same, proving the consistency of the analysis and results.

a. $H(0,0)$ field results. The values of $H(0,0)$ are normalized again to the hf field at $x=0$, $h_0=H(0,0)/(-82.3)$, and presented in Fig. 5. Apparently, they increase linearly with Al concentration and fit to the equation $h_0=0.968+0.0475x$, with $r=0.98$.

As the Sn-site field in an iron matrix is negative,[9] the increase of h_0 again means an effective increase of the density of itinerant spin-down electrons. This is in agreement with h_0 behavior discussed above for the Fe site (see Fig. 2).

b. ΔH_1 and ΔH_2 results. Application of method I in the analysis of the spectra permits one to determine the changes of the hf field by one Al atom located in the first- and second-neighboring shells, ΔH_1^A and ΔH_2^A, respectively. Their values are negative and increase only slightly with Al concentration. The former means that the effective negative spin density at Sn nuclei having one Al neighbor is diminished, while the latter means that

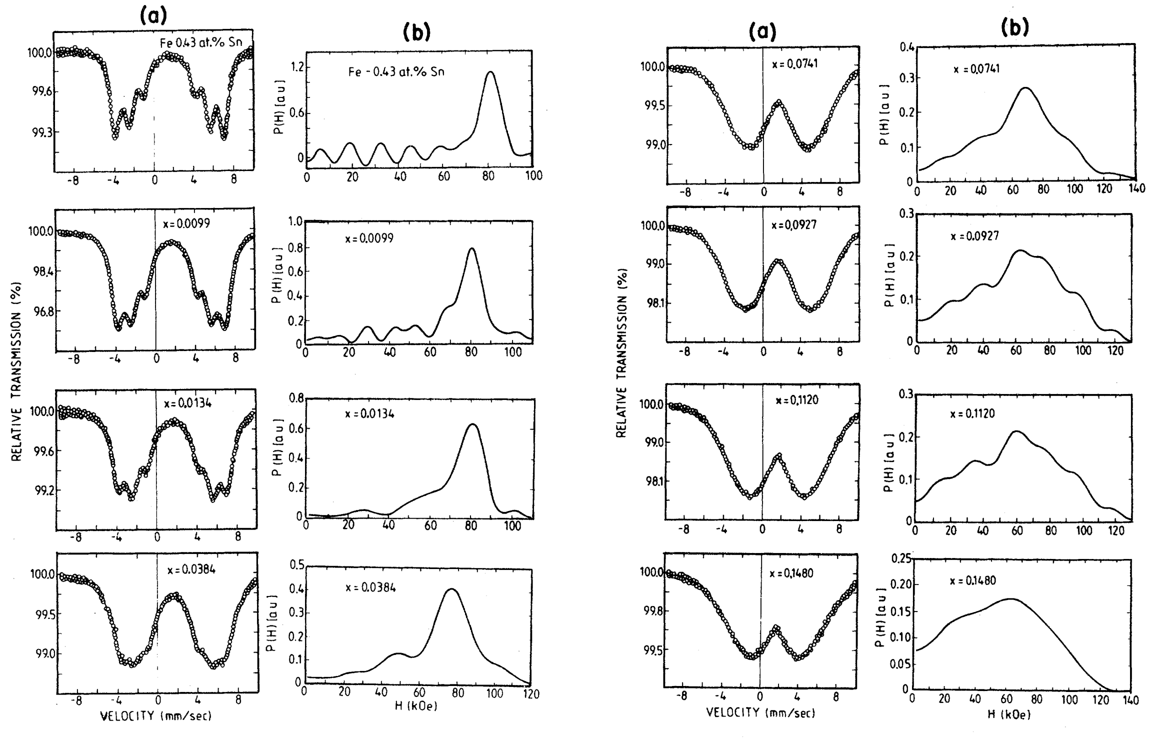

FIG. 4. (a) Room-temperature Mössbauer spectra for the ^{119}Sn site of the $Fe_{1-x}Al_x$ systems as a function of Al concentration, x. (b) hf-field distributions obtained from the Mössbauer spectra shown in (a) by means of method II.

TABLE IV. Fit values of hyperfine-field parameters deduced from the ^{119}Sn spectra. All hyperfine fields are in kOe. The meaning of the parameters is given in the text.

x (at.%)	$H(0,0)$	ΔH_1^S	ΔH_2^S	ΔH_1^A	ΔH_2^A	$\bar{H}_{\mathrm{I}}$	$\bar{H}_{\mathrm{II}}$
0	−82.3	−22.4	−7.65			−78.6	−79.25
0.99	−80.3	−22.0	−10.3	−27.3	−15.0	−76.1	−76.1
1.34	−82.7	−25.0	−5.7	−28.4	−15.3	−74.8	−75.2
3.84	−100.25			−29.6	−19.2	−72.4	−70.25
7.41	−101.95			−27.65	−16.6	−62.4	−63.65
9.27	−117.2			−30.0	−18.7	−60.2	−60.8
11.20	−128.3			−31.4	−20.35	−58.7	−58.6
14.80	−135.4			−31.75	−20.95	−57.8	−55.75

the effect is well localized.

In the case of the samples containing 0.99 and 1.34 at. % of Al due to the comparable concentration of Sn, the substitution of Fe neighbors by Sn atoms has been taken into account too when fitting the spectra. This permitted us to determine the shift ΔH_1^S and ΔH_2^S of the hf field due to one Sn atom being first- or second-nearest neighbor, respectively. Their values obtained are shown in Table IV. One can see that they are practically equal to the corresponding values found for the Fe–0.43-at. % Sn sample with zero Al concentration ($x=0$). This can be regarded as a proof that Sn and Al atoms act independently of each other, i.e., their influence on the spin density is additive. A similar effect was found previously for Sn and Cr atoms.[5]

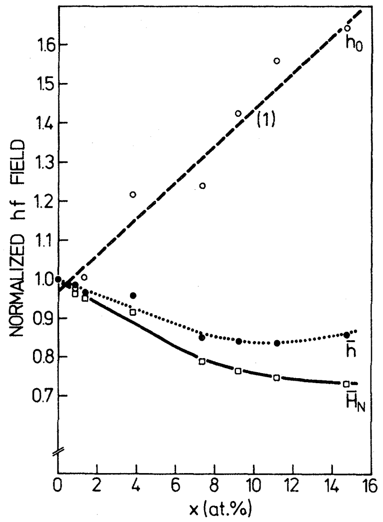

FIG. 5. hf fields at the ^{119}Sn site of the $\mathrm{Fe}_{1-x}\mathrm{Al}_x$ system, normalized to the hf field of α-Fe as a function of Al concentration, x. Open circles represent the hf fields for the configuration (0,0), h_0 and Eq. (1) $h_0=0.968+0.0475x$ fit to the data. The coefficient of correlation is $r=0.98$. Squares represent the measured average hf field $\bar{H}_N$ and the solid circles represent $\bar{H}_N$ normalized to constant Fe concentration, $\bar{h}$.

c. Average field $\bar{H}$. Figure 5 shows the normalized average field,

$$\bar{H}_N=\frac{\bar{H}_{\mathrm{I}}+\bar{H}_{\mathrm{II}}}{-(78.6+79.2)} .$$

One can see that it decreases with Al concentration. However, it is different from the average field at the Fe site in two ways: (i) the decrease here is not linear, but seems to saturate below $x=0.2$, and (ii) the average Sn-site field normalized to constant Fe concentration, i.e., $\bar{h}=\bar{H}_N/(1-x)$, also decreases whereas in the case of ^{57}Fe, $\bar{h}$ was found to increase (Fig. 2).

2. *Isomer-shift results*

The fit values for $I(0,0)$, $\Delta I_{1,2}$, and $\bar{I}$ are collected in Table V. One can see that $I(0,0)$ is positive with respect to $I(0,0)$ of the Fe–0.43-at. % Sn sample and increases linearly with Al concentration according to the equation $I(0,0)=0.0012+0.0021x$, $r=0.79$. This means that the effective charge density of s-like electrons increases upon substitution of Fe by Al, as it is "seen" by the Sn nuclei being in the configuration (0,0). This again is in contrast to the Fe-site point of view, where Fe atoms situated in the corresponding configuration experienced a decrease of effective s-like electron density. When, however, in their vicinity one Al atom appears, then one observes also an effective increase of charge density ($\Delta I_1^A, \Delta I_2^A>0$). This is contrary to the Fe-site observation, where the appearance of Al neighbors was accompanied by a decrease of effective charge density.

The average isomer shift, $\bar{I}=\bar{I}^{\text{Fe-Al}}-I^{\text{Fe}}$, is posi-

TABLE V. Fit values of the isomer-shift parameters, deduced from the ^{119}Sn spectra. All isomer shifts are in mm/sec. The meaning of the parameters is given in the text.

x (at. %)	$I(0,0)$	ΔI_1^S	ΔI_2^S	ΔI_1^A	ΔI_2^A	$\bar{I}$
0	1.525	0.162	0.035			1.548
0.99	0.005[a]	0.200	0.080	0.018	0.008	−0.005[a]
1.34	0.009[a]	0.388	0.001	0.019	0.001	0.000[a]
3.84	0.010[a]			0.020	0.013	0.006[a]
7.41	0.005[a]			0.015	0.014	0.010[a]
9.27	0.011[a]			0.029	0.020	0.0105[a]
11.20	0.042[a]			0.004	0.002	0.020[a]
14.80	0.031[a]			0.010	0.005	0.032[a]

[a]Relative to the isomer shift of Fe—0.43 at. % Sn.

tive and increases linearly according to the equation $\bar{I}=-0.0039+0.0021x$, $r=0.96$. This indicates that, on average, the effective *s*-electron density at Sn sites increases upon substituting Fe by Al. This is again just opposite to the Fe-site observation.

V. INTERPRETATION AND DISCUSSION OF THE RESULTS

The magnetic hyperfine field of 3*d* systems is known to be a measure of the electron-spin density. Therefore its changes measure change of the spin density. Similarly, the isomer shift is proportional to the density of *s*-like electrons, hence, its changes measure the related changes in the charge density of these electrons at the probing nucleus.

The results presented in the preceding section give evidence that substitution of Fe atoms by Al atoms leads to changes in both hf fields and the isomer shifts. In other words, changes of the spin and charge densities will take place in an iron matrix into which Al atoms have been substituted for Fe ones.

As we have shown recently for the Fe-Cr system[10] such changes are correlated with each other. Let us discuss next whether the changes of spin and charge densities observed in the Fe-Al alloy system are correlated in a similar way.

A. Discussion of ^{57}Fe-site results

1. *Correlation H(0,0)-I(0,0)*

Figure 6 illustrates for the ^{57}Fe site how the hf-field difference $\Delta H(0,0)=H(0,0)-H_{\text{Fe}}$ depends on the corresponding isomer-shift difference $\Delta I(0,0)=I(0,0)-I_{\text{Fe}}$, where H_{Fe} and I_{Fe} are the hf-field and the isomer shift of pure α-iron, respectively. The data can be fitted with a linear equation of the following form:

$$-\Delta H(0,0)=-1.42+257.7\Delta I(0,0)\ , \qquad (4)$$

where the coefficient of correlation is $r=0.96$.

The observed correlation proves that the change in spin density is directly related to that of the charge density. Combination of the slope of Eq. (4) $dH(0,0)/dI(0,0)=257.7$ kOe$(\text{mm}\,\text{sec}^{-1})^{-1}$ with the relation between the change of the isomer shift, dI, and the corresponding change of the number of *s*-like electrons, dN_s, given by Walker and co-workers as $dI/dN_s=2.05$ mm per *s* electron,[11] finally yields that the unique change of the spin polarization "seen" as change in the hf field, $dH(0,0)/dN_s$, is equivalent to an hf-field change of 528 kOe per *s* electron. Since both $dH(0,0)$ and $dI(0,0)$ reflect spin- and charge-density changes,

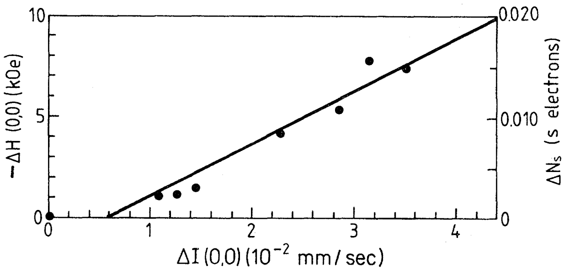

FIG. 6. hf-field differences $\Delta H(0,0)=H(0,0)-H_{\text{Fe}}$ plotted as a function of the isomer shift, $\Delta I(0,0)$ of the $\text{Fe}_{1-x}\text{Al}_x$ system as deduced from the ^{57}Fe-site spectra. Data fit to equation $-\Delta H(0,0)=-1.42+257.7\Delta I(0,0)$. The coefficient of correlation is $r=0.96$. The right-hand ordinate is calibrated in numbers of transferred *s*-like electrons, ΔN_s, which correspond to the measured hf-field change, $\Delta H(0,0)$.

respectively, at ^{57}Fe nuclei having in their NN and NNN vicinity no Al atoms, the estimated hf-field coupling constant of 528 kOe per s electron is related to α in Eq. (1′c). It determines the valuable relation between the change of the itinerant s-like electrons and the corresponding change of H_{CEP} of the ^{57}Fe hf field. Remarkably, it is 4 times smaller than that found previously for Fe-Cr alloys.[10]

From the correlation established above, one can further conclude which changes in the conduction band will take place upon substituting Al for Fe. The increase $I(0,0)$ clearly indicates a decrease of the effective charge density of s-like itinerant electrons. This is accompanied by an increase of $H(0,0)$, having negative sign. In other words, the spin-down density of the s-like itinerant electrons increases, whereas their charge density decreases with increasing Al concentration. That means Al "attracts" s-like itinerant electrons. To describe this process quantitatively, the right-hand ordinate of Fig. 6 has been scaled in numbers of those s-like electrons ΔN_s, being transferred effectively from the conduction band, according to the scaling factor given in Ref. 11. Since the effective density of spin-down electrons increases, spin-up electrons are transferred effectively. This is similar to the behavior observed in the Fe-Cr system.[10]

2. *Correlations between* $(\Delta H_1^A, \Delta H_2^A)$ *and* $(\Delta I_1^A, \Delta I_2^A)$

The parameters $\Delta H_1^A, \Delta H_2^A, \Delta I_2^A, \Delta I_2^A$ given in Tables II and III measure the change of the spin or charge density at the ^{57}Fe site, if an Al atom has been introduced in the first- or second-neighbor shell, respectively. All these parameters are nearly independent of Al concentration, i.e., they reflect local changes of the electron and spin configurations only. The average values are: $\Delta \bar{H}_1^A = -25.4$ kOe, $\Delta \bar{H}_2^A = -8.9$ kOe, and $\Delta \bar{I}_1^A = 0.026 \pm 0.005$ mm/sec, $\Delta \bar{I}_2^A = 0.0009 \pm 0.0040$ mm/sec. Since the value of $\Delta \bar{I}_2^A$ still has a rather large experimental error, we will use only quantities of the first-neighbor shell, i.e., $\Delta \bar{H}_1^A$ and $\Delta \bar{I}_1^A$, to find the relations between the hf-field contributions and the number of polarized electrons here. Their ratio is $\Delta \bar{H}_1^A / \Delta \bar{I}_1^A = 955$ kOe(mm sec^{-1})$^{-1}$ from which, by use of $dI/dN_s = 2.05$ mm sec^{-1} per s electron as above, one gets for the local ^{57}Fe hf coupling constant $dH_1/dN_s = 1957$ kOe per s electron. Now we are in position to answer also the question on what kind of local spin and charge changes are seen by Fe nuclei having Al atoms in their neighborhood. Towards this end let us notice that substitution of an Fe atom by an Al atom decreases the effective density of spin-down electrons as well as the effective charge density. Using the above local hf coupling constant, $dH_1/dN_s = 1957$ kOe per s electron, one may estimate that the effective decrease of spin and charge density at the Fe nuclei caused by one Al atom amounts to 0.013 spin-down s-like electrons, if Al atom is situated in the first-neighbor shell or to 0.005, if the Al atom is located in the second-neighbor shell. The corresponding figures for Cr are 0.012 and 0.007.[10]

3. *Correlation* $\bar{H}$-$\bar{I}$

The correlations between the hf field and the isomer shift, which have been shown to hold for the itinerant electrons (Sec. V A 1) as well as for the localized ones (Sec. V A 2), imply that the average field $\bar{H}$ should also be correlated with the average isomer shift, $\bar{I}$. Evidence for this correlation provides Fig. 7, which shows the dependence of $\bar{H}$ on $\bar{I}$. The $\bar{H}$-$\bar{I}$ data can be best described by the following linear equation: $\Delta \bar{H} = -2.60 + 481\bar{I}$, where the correlation coefficient is $r = 0.99$. Combination of the gradient $d\bar{H}/d\bar{I} = -481$ kOe(mm sec^{-1})$^{-1}$ with the above-used scaling factor[11] for the isomer shift per number of s-like electrons, $dI/dN_s = 2.05$ mm per s electron, now yields the average hf coupling constant $d\bar{H}/dN_s = 987$ kOe per s electron. It finally allows us to calibrate

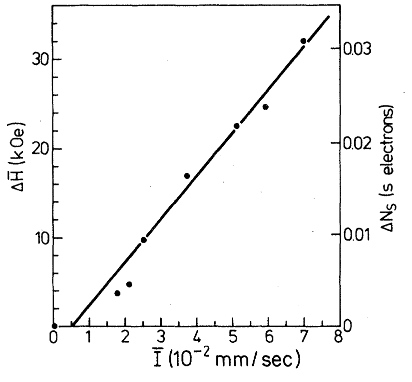

FIG. 7. Difference $\Delta \bar{H} = \bar{H} - H_{\mathrm{Fe}}$ plotted as a function of the average isomer shift, $\bar{I}$, as obtained for the $\mathrm{Fe}_{1-x}\mathrm{Al}_x$ system from the ^{57}Fe-site Mössbauer spectra. The fit to the data is given by the equation $\Delta \bar{H} = -2.60 + 481.3\bar{I}$. The coefficient of correlation is $r = 0.99$. The right-hand ordinate is calibrated in numbers of the transferred s-like electrons, ΔN_s, corresponding to the measured change of the hf field, $\Delta \bar{H}$.

the observed average changes of the hf field or the isomer shift in corresponding numbers of transferred s-like electrons, ΔN_s (see right-hand ordinate of Fig. 7). Thus, on average, the Fe nuclei see a reduced effective density of spin-down electrons and of charge. As a consequence, after substituting Fe atoms by Al atoms the Fe atoms effectively have lost on average spin-down electrons.

4. *Correlation* $\bar{H}$-$\bar{N}_A$

Like in Fe-Cr alloys,[10] the spin- and charge-density changes caused by substitution of Fe atoms by Al atoms manifest themselves in a twofold way:

(a) through changes in the spin and charge densities of itinerant electrons, and

(b) through local changes in the electron spin and the charge densities at Fe nuclei due to the Al atoms in their atomic vicinity.

Since both effects have their source in substituting Fe atoms by Al atoms, there should be also a correlation between the spin- and charge-density changes and the number of Al atoms. Let us consider the average hf field $\bar{H}$ being a measure of the average spin density, and the average number of Al atoms in the two first-neighbor shells, $\bar{N}_A$. Figure 8 shows the dependence of these two quantities. One can see that it is again best described by a linear equation: $-\bar{H}=330.8-14.25\bar{N}_A$, $r=0.99$.

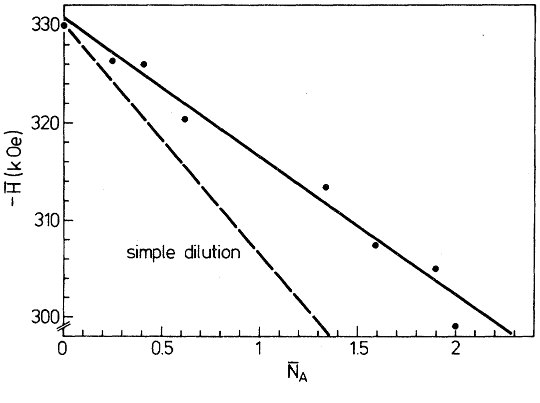

FIG. 8. Average ^{57}Fe-site hf-field data, $\bar{H}$, plotted vs the average number of Al atoms in the first two neighboring shells, $\bar{N}_A$. Solid line represents the fit to the data given by equation $-\bar{H}=330.8-14.25\bar{N}_A$. The coefficient of correlation is $r=0.99$. The broken line shows the predicted linear dependence in the case of a simple dilution.

It means that one Al atom being first or second neighbor decreases the average hf field by 14 kOe. This is equivalent to a diminuition of the spin density by 0.014 s-like spin-down electrons.

Dividing $\bar{N}_A$ by 7, one obtains the average number of Al atoms per unit cell, $\bar{M}$. Hence, $d\bar{H}/d\bar{M}=-100$ kOe per unit cell [against -123 kOe per unit cell for Cr (Ref. 10)]. This means that the effectivity of Al atoms is smaller than that of Cr atoms concerning their disturbance of the Fe-site spin density. Now one easily calculates also the effectivity of an hypothetical atom, which would simply remove the Fe-spin density; i.e., of something to be called a "spin hole." For such a spin hole, $(d\bar{H}/d\bar{M})_0=-165$ kOe per "hole" unit cell to reduce the hf field of α-Fe from -330 kOe to zero by substitution of the two Fe atoms per unit cell with "hole" atoms. Now, one can quantitatively express the effectivities of Al and Cr atoms in terms of such a "spin hole." Let us define the effectivity of any substituent atom X by

$$\epsilon_X=\left[\frac{d\bar{H}}{d\bar{M}}\right]_X \Big/ \left[\frac{d\bar{H}}{d\bar{M}}\right]_0 100\% \; .$$

Then, $\epsilon_{\text{Al}}=60\%$ and $\epsilon_{\text{Cr}}=75\%$ follow for $X=\text{Al}$ and Cr, respectively.

Finally, knowing $d\bar{H}/d\bar{M}$ and $d\bar{M}/dN_s$, one can also deduce the change in spin-down s-electron polarization caused by one Al atom per unit cell, $dN_S/d\bar{M}$. For the itinerant electrons we got $dH(0,0)/dN_s=528$ kOe per s electron. Hence, using

$$\frac{(d\bar{H}/d\bar{M})}{(dH(0,0)/dN_s)}=\frac{d\bar{H}}{dH(0,0)}\frac{dN_s}{d\bar{M}} \; ,$$

and taking into account $d\bar{H}/dH(0,0)=\frac{988}{528}=1.87$, one obtains $\frac{100}{528}=1.87dN_s/d\bar{M}$, i.e., $dN_s/d\bar{M}=0.10$ s electron per Al atom per unit cell instead of 0.037 for Cr.[10] For the localized electrons because $dH_1/dN_s=1957$ kOe per s electron, with the use of

$$\frac{(d\bar{H}/d\bar{M})}{(dH_1/dN_s)}=\frac{d\bar{H}}{dH_1}\frac{dN_s}{d\bar{M}}$$

and taking into account $d\bar{H}/dH_1=\frac{987}{1957}=0.50$, one deduces in the same way as before the relation $0.051=0.50dN_s/d\bar{M}$, and finally achieves $dN_s/d\bar{M}=0.10$ s electron per Al atom per unit cell instead of 0.038 for Cr.[10] Thus, the $dN_s/d\bar{M}$ contributions to itinerant and localized s electrons per Al atom per unit cell are of the same magnitude.

5. Dependence of the average hf field on the Al concentration

In Ref. 10 a new formula describing the dependence of the Fe-site average hyperfine field on the concentration of the solute atoms has been proposed for binary alloys of iron. The formula derived there has the following form:

$$\bar{H}(x)=330-\bar{M}\eta\frac{d\bar{H}}{dN_s},\quad \eta=\frac{dN_s}{d\bar{M}}\ . \tag{5}$$

This formula can now be used to calculate η independently for comparison with the calculations of η carried out in the previous section. Assuming the distribution of Al atoms to be random, Eq. (5) can be rewritten in the form

$$\bar{H}(x)=330-1976\eta x\ . \tag{5a}$$

On the other hand, from our above experimental results (see Sec. IV A 1) one gets

$$\bar{H}(x)=329-204x\ . \tag{5b}$$

Equation (5a) transforms into (5b) for $\eta\approx0.10$. This obviously is exactly the result deduced independently in Sec. V A 4.

This η value for Al substituents $\eta=0.10$, is about 4 times larger than that for Cr. Hence, the effective redistribution of the spin (charge) density caused by one solute atom X per unit cell within an α-iron matrix is much more pronounced for Al than for Cr.

B. Discussion of ^{119}Sn-site results

1. Correlations between $H(0,0)$ and $I(0,0)$

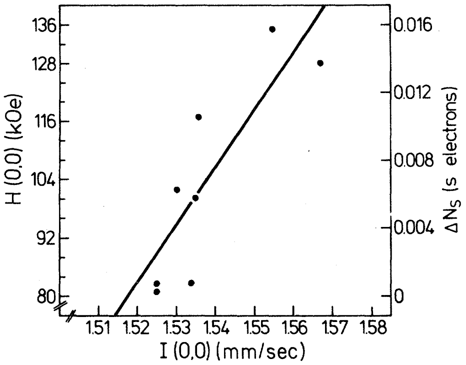

FIG. 9. ^{110}Sn-site hf-field data, $H(0,0)$, of the $Fe_{1-x}Al_x$ system plotted as a function of the related isomer-shift data, $I(0,0)$. The straight line represents the fit to the data given by the equation $H(0,0)=-1771+1219I(0,0)$. The coefficient of correlation is $r=0.85$. The right-hand side ordinate is calibrated in numbers of transferred s-like electrons, ΔN_s, corresponding to the measured changes in $H(0,0)$.

In Fig. 9 the hf field $H(0,0)$ is plotted as a function of the corresponding isomer shift, $I(0,0)$, for the ^{119}Sn-site results of Tables IV and V. Here the correlation is not as clear as in the case of the Fe-site results. This is due mainly to the larger errors in determining the values of the parameters describing the Sn-site spectra because of the worse resolution in the case. The coefficient of correlation now is $r=0.85$ and the data fit with the linear equation $H(0,0)=-1771+1219I(0,0)$. From the gradient $dH(0,0)/dI(0,0)=1219$ kOe$(\text{mm}\,\text{sec}^{-1})^{-1}$ and by taking into account the scaling factor between the tin-site isomer shift and the number of s-like electrons, N_s given in Ref. 12, $dI/dN_s=2.55$ mm sec^{-1} per s electron, one obtains the following hf coupling constant for itinerant s electrons: $dH(0,0)/dN_s=3108$ kOe per s electron. Using this result, one can calibrate the observed hf-field increase in numbers of transferred s-like itinerant electrons, ΔN_s (see right-hand ordinate of Fig. 9). One notices that the maximal observed charge transfer here amounts to 0.016 electrons, which agrees well with the value of 0.015 deduced above in Sec. V A from the Fe-site results (see Fig. 6).

Let us discuss next what kind of the spin- and the charge-density changes take place in the conduction band as seen by the Sn nuclei. Towards this end we notice that an increase of Al concentration is accompanied by two results:

(i) an increase of the effective spin-down s-electron density, and

(ii) an increase of the effective s-electron charge density.

Result (i) agrees with that observed at the Fe site not only qualitatively, but even quantitatively. Result (ii), however, disagrees with the Fe-site behavior, since Fe nuclei, having no Al atoms in their vicinity, experience a decrease of the effective charge density with increasing Al concentration.

2. Correlation between $(\Delta H_1^A,\Delta H_2^A)$ and $(\Delta I_1^A,\Delta I_2^A)$

The values of these parameters as given in Tables IV and V are nearly independent of Al concentration, which is similar to the results observed for Fe sites. The average values are $\Delta\bar{H}_1^A = -29.4\pm1.8$ kOe, $\Delta\bar{H}_2^A = -18.0\pm2.4$ kOe, yielding the ratio $R_H = 1.63$, and $\Delta\bar{I}_1^A = 0.016\pm0.008$ mm/sec, $\Delta\bar{I}_2^A = 0.009\pm0.007$ mm/sec, yielding the ratio $R_I = 1.78$. We notice that $R_H \approx R_I$, i.e., the local changes of the spin density are again correlated with those of the charge density. Thus, one can calculate the local hyperfine coupling constant for the first-neighbor shell $\Delta\bar{H}_1/\Delta\bar{I}_1 = 1838$ kOe(mm sec^{-1})$^{-1}$ achieving $dH_1/dN_s = 4686$ kOe per s electron, and for the second neighbor from $\Delta\bar{H}_2/\Delta\bar{I}_2 = 2000$ kOe (mm sec^{-1})$^{-1}$ achieving $dH_2/dN_s = 5100$ kOe per s electron.

Hence, the hyperfine coupling constant for localized s-like electrons is nearly equal for the two first-neighbor shells yielding an average value of $dH_{1,2}/dN_s = 4893$ kOe per s electron. In other words, the change of the hyperfine field at the Sn nuclei caused by one Al atom being first neighbor is equivalent to 0.006 electrons or to 0.004 electrons if Al atom is the second neighbor. Thus, the differences between the Sn-site point of view and that of the Fe site do not only exist in the absolute values of the disturbances expressed in terms of transferred s-like electrons, but also in the direction of these changes. In particular, Al atoms placed in the vicinity of Fe atoms decrease the Fe charge density as well as the effective Fe spin-down electron density, whereas in the vicinity of Sn atoms they cause the Sn-site charge density to increase and the effective density of spin-down electrons to decrease, but about 50% less in magnitude than at Fe nuclei. The following explanation can be suggested: If Al atoms are neighbors of Fe atoms, the spin-down electrons are transferred from Fe to Al (0.10 per Al atom per unit cell) and cause a decrease of both the hyperfine field and the charge density at the ^{57}Fe nuclei. On the other hand, if Al atoms are placed in the vicinity of Sn atoms, then the Sn atoms attract some spin-up electrons from the Al substitutent. This will lead to a decrease of the ^{119}Sn isomer shift in full agreement with our presented observations.

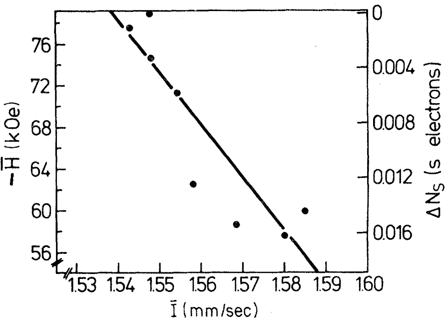

FIG. 10. ^{119}Sn-site average hf-field data, $\bar{H}$ for the $Fe_{1-x}Al_x$ system plotted as a function of the average isomer-shift data, $\bar{I}$. The straight line represents the fit to the data given by the equation $-\bar{H} = 857 - 506\bar{I}$. The coefficient of correlation $r = 0.82$. Right-hand side ordinate is calibrated in numbers of the transferred s-like electrons, ΔN_s, corresponding to the measured changes in $\bar{H}$.

3. Correlation between $\bar{H}$ and $\bar{I}$

The dependence of the average hyperfine field $\bar{H}$ on the average isomer shift $\bar{I}$ is illustrated in Fig. 10. Although in this case the data scatter more than in the case of the Fe site, they fit reasonably to the following linear equation: $-\bar{H} = 817 - 506\bar{I}$, where the correlation coefficient is $r = 0.89$. Using the gradient $d\bar{H}/dI = 506$ kOe (mm sec^{-1})$^{-1}$ and taking into account the result of Ref. 12 on $dI/dN_s = 2.55$ mm sec^{-1} per s electron, one can again calculate the average hyperfine coupling constant yielding $d\bar{H}/dN_s = 1290$ kOe per s electron. Using this value one can calibrate the observed changes of the average hf field (or the average isomer shift) as above in numbers of the transferred s-like electrons, ΔN_s (see right-hand ordinate of Fig. 10). Obviously, the maximal transfer amounts here to 0.016 electrons, which is in contrast to the 0.032 electrons seen by the Fe nuclei and deduced above. However, in the former case, only the transfer of s-like itinerant electrons has been considered, whereas the Fe nuclei can see also the changes of core s electrons or even the indirect changes in the density of itinerant 4s-like electrons, e.g., caused by changes in the screening power of the 3d electrons when substituting Fe atoms by Al atoms. In particular, the increase of the magnetic moment per Fe atom with Al concentration (see Fig. 2) is most likely accompanied by such a change of the screening power being indicated by the distinct numbers, i.e., 0.032 and 0.016 of maximally transferred s electrons.

From Fig. 10 we further conclude that with increasing Al concentration the average charge density at Sn nuclei increases too, whereas their effective spin-down electron density decreases. Hence, spin-up electrons must have been transferred from Al neighbors to the central Sn probing atom.

4. *Correlation between $\bar{H}$ and $\bar{N}_A$*

Figure 11 gives evidence that the average hyperfine field $\bar{H}$, as in the case of the ^{57}Fe site discussed above, is strongly correlated with the average number of Al atoms in the first two neighboring shells, $\bar{N}_A$, fitting to a linear relation of the form of $-\bar{H}=78-7.1\bar{N}_A$, where the coefficient of correlation is $r=0.89$. From this equation it follows that one Al atom being first or the second neighbor of the Sn atoms will diminish its hf field on average by 7.1 kOe. This is equivalent to -50 kOe per Al atom per unit cell. If, however, Al would act like a "spin hole," then $d\bar{H}/d\bar{M}=-39.0$ kOe per Al atom per unit cell. Hence the Sn-site field being regarded as a measure of the spin polarization of the itinerant conduction electrons reveals only an enhancement of the Al dilution by 28% as compared to that predicated for the simple "hole-dilution" case.

Now, knowing $d\bar{H}/d\bar{M}$ and $d\bar{H}/dN_s$ one can also calculate the change in polarization caused by one Al atom per unit cell, $dN_s/d\bar{M}$, as seen by the hf field of the Sn nuclei. For the itinerant electrons we obtained above $dH(0,0)/dN_s=3108$ kOe per s electron. Hence, with the use of

$$\frac{(d\bar{H}/d\bar{M})}{(dH(0,0)/dN_s}=\frac{d\bar{H}}{dH(0,0)}\frac{dN_s}{d\bar{M}},$$

and taking into account $d\bar{H}/dH(0,0)=\frac{1290}{3108}=0.42$, one obtains $49.9/1290=0.42dN_s/d\bar{M}$, yielding $dN_s/d\bar{M}=0.09$ electrons per Al atom per unit cell.

For the "localized" electrons we obtained the result $dH_{12}/dN_s=4893$ kOe per s electron. With the use of

$$\frac{(d\bar{H}/d\bar{M})}{(dH_{12}/dN_s)}=\frac{d\bar{H}}{dH_{12}}\frac{dN_s}{d\bar{M}},$$

and taking into account $d\bar{H}/dH_{12}=\frac{1290}{4893}=0.26$, one obtains $\frac{49.9}{4893}=0.26dN_s/d\bar{M}$, yielding $dN_s/d\bar{M}=0.04$ electrons per Al atom per unit cell.

Comparing these figures with those obtained for the Fe site before, one realizes that for the transfer of itinerant electrons the relation

$$\left[\frac{dN_s}{d\bar{M}}\right]_{\text{Fe}}\approx\left[\frac{dN_s}{d\bar{M}}\right]_{\text{Sn}}$$

holds. This is in agreement with the above-discussed expectation and can be taken as a final proof for a correct analysis of the experimental results and their interpretation. On the other hand, for the localized electrons the comparison yields

$$\left[\frac{dN_s}{d\bar{M}}\right]_{\text{Fe}}\approx 2\left[\frac{dN_s}{d\bar{M}}\right]_{\text{Sn}}.$$

This means that the localized spin-density change caused by an Al atom effects the spin and charge configuration at the Fe site much stronger than at the Sn site. This has been related to changes in the core polarization of the Fe atom which is due most likely to changes in the $3d$-like polarization as it is supported by the increase of the magnetic moment per Fe atom shown in Fig. 2.

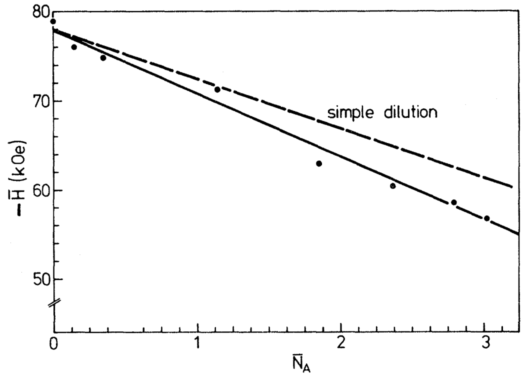

FIG. 11. Average ^{119}Sn-site hf field, $\bar{H}$, for the $\text{Fe}_{1-x}\text{Al}_x$ system plotted vs the average number of Al atoms in the first two neighbor shells, $\bar{N}_A$. The straight line represent the fit to the data described by the equation: $-\bar{H}=78-7.1\bar{N}_A$. The coefficient of correlation is $r=0.99$. The broken line shows the hf-field dependence in the case of a simple dilution by "spin-hole-like" substitute atoms.

6. *Average hyperfine field $\bar{H}$*

The measured Sn-site average hf field $\bar{H}$ decreases with Al concentration. This decrease, however, is not linear as it can be seen from the experimental data marked by squares in Fig. 5. Also, the average hf field normalized to constant Fe concentration, i.e., $\bar{h}$, decreases (solid circles in Fig. 5). This is contrary to the behavior of the average hf field normalized to constant Fe concentration at the Fe site, which increases linearly according to $\bar{h}=0.993+0.0043x$, with $r=0.98$, indicating an increase of the effective density of spin-down electrons per Fe nucleus. Let us discuss here, why the Sn nuclei do not "see" this increase in electron-spin density. Notice first that the average field depends on the population of different atom configurations (m,n). Their population in turn depends on how atoms are distributed in the matrix.

As can be seen from Table VI the distribution of Sn atoms is not random. This will not influence the Fe-site hf fields because of the low concentration of Sn atoms ($\leq 0.8\%$), but turns out to be crucial in determining the Sn-site average hf-field values. Table VI shows the measured abundance of the (0,0) configurations, $P(0,0)$, i.e., those where Sn nuclei have neither Al nor Sn neighbors in the first two neighbor shells, as well as that expected for random distribution, $P_0(0,0)$. Obviously, the measured abundances of the (0,0) configurations are much smaller than $P_0(0,0)$.

The average number of Al atoms "seen" by the Sn nuclei in their first-neighbor shells, $\bar{N}_A$, have also been calculated and are listed in Table VI. For all samples one obtains $\bar{N}_A > \bar{N}_0$, where $\bar{N}_0$ is the average number of Al atoms for random Sn distribution. The deviation from randomness,

$$\delta = \left[\frac{\bar{N}_A - \bar{N}_0}{\bar{N}_0} \right] 100\% \,,$$

varies between 10% for Fe—0.99 at. % Al and 130% for Fe—3.84 at. % Al. Hence, the measured average hf field has to be corrected for this inhomogeneity. Towards this end we have calculated the values of the average field, $\bar{H}_0$, assuming that

(a) the distribution of the Sn atoms is random, and

(b) the $H(0,0)$ field changes according to the equation which fits to the measured $H(0,0)$ values, i.e., $h_0 = 0.968 + 0.475x$, and the average values for ΔH_1^A and ΔH_2^A are used.

The average hf field calculated in this way is presented in Fig. 12 by the solid triangles. Apparently, this field turns out to be almost constant, i.e., the average effective density of spin-down electrons per Sn atom does not change by substituting Al for Fe. If we normalize this average hf field to constant Fe concentration, we obtain the results marked by open triangles in Fig. 12. Obviously, these average hf-field data increase linearly with the Al concentration and fit to the equation: $\bar{h}^* = 0.952 + 0.017x$. Hence, at the Sn site the effective density of the spin-down electrons in fact behaves similarly to that at the Fe site shown in Fig. 2 by solid circles.

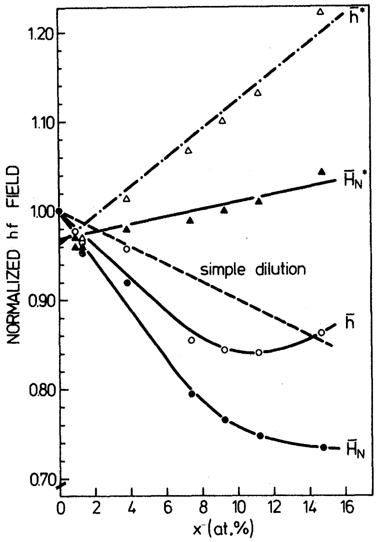

FIG. 12. Average Sn-site hf fields normalized at $x=0$ for the $\mathrm{Fe}_{1-x}\mathrm{Al}_x$ system plotted as a function of the Al concentration, x. Solid circles give the measured ^{119}Sn-site hf field, $\bar{H}_N$ while open circles represent the ^{119}Sn site hf fields normalized to constant Fe concentration, $\bar{h}$. Solid triangles denote $\bar{H}_N$ corrected for inhomogenities in the Sn distribution, $\bar{H}_N^*$, and open triangles represent $\bar{h}$ corrected for the inhomogenities, $\bar{h}^*$. The broken line indicates the behavior predicted for the simple dilution with "spin-hole—like" substituents.

Using the same relations between H_{Sn}, $H_{\mathrm{CEP}}(0)$, and $H_{\mathrm{thf}}(0)$ as in Sec. IV A 1 c and the result for $H_{\mathrm{thf}}(0) = -306$ kOe and $H_{\mathrm{Sn}} = -82.5$ kOe, we arrive at $H_{\mathrm{CEP}}(0) = +223.5$ kOe, which compares fairly well to $H_{\mathrm{CEP}}(0) = +185$ kOe deduced from the ^{57}Fe-site results before.

VI. CONCLUSIONS

The present investigation of a series of Fe-Al alloys based on ^{57}Fe and ^{119}Sn Mössbauer effect spectroscopy and on the interpretation of the re-

TABLE VI. The meaning of the parameters is given in the text.

x (at. %)	0.99	1.34	3.84	7.41	9.27	11.20	14.80
$P_0(0,0)$	0.782	0.740	0.527	0.303	0.229	0.152	0.081
$P(0,0)$	0.733	0.588	0.088	0.087	0.033	0.025	0.022
$\bar{N}_A$	0.136	0.350	1.136	1.853	2.370	2.788	3.013
$\bar{N}_0$	0.124	0.179	0.493	0.981	1.103	1.337	1.923
δ (%)	9.5	95.5	130.5	88.9	114.9	108.5	56.7

sults obtained in terms of spin- and charge-density changes leads to the following conclusions:

(1) Substitution of Fe atoms by Al atoms causes a redistribution of electrons in the iron matrix, which reflects itself in changes both of the hyperfine field (spin density) and of the isomer shift (charge density).

(2) Spin- and charge-density changes take place both for the conduction electrons, for which the spin-up electron density is reduced, as well as for the localized electrons.

(3) Spin- and charge-density changes are linearly correlated. The simplest explanation of this is to assume that only the density of spin-up electrons is changed.

(4) The correlations mentioned in (3) permitted evaluation of hyperfine coupling constants both for ^{57}Fe and for ^{119}Sn nuclei.

(5) The average hyperfine field is linearly correlated with the average number of Al atoms in the vicinity of, both the ^{57}Fe and the ^{119}Sn nuclei.

(6) The correlation mentioned in (5) in combination with the knowledge of the hyperfine coupling constants enabled us to calculate the change of the spin density caused in the unit cell by one Al atom.

(7) The effect of an Al atom can be regarded to 60% only as a "spin hole" as far as the related change of hyperfine field is concerned.

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