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^{57}Fe Mössbauer effect and magnetic properties in amorphous Fe-based alloys

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The magnetic properties of amorphous $Mg_{1-x}Fe_x$ alloys were studied by means of magnetization measurements and the ^{57}Fe Mössbauer effect. It was found that the apparent decrease with x of the Fe moment derived from magnetization measurements is due to deviations from a collinear ferromagnetic moment arrangement. The average effective hyperfine field $\langle H_{\text{eff}} \rangle$ observed in amorphous $A_{1-x}Fe_x$ alloys when A = Mg and Th was compared with literature data on amorphous alloys with A = Zr, Y, La, and Sn. A correlation was found to exist between $\langle H_{\text{eff}} \rangle$ and the corresponding values of the formation enthalpies. These results are in accordance with a model proposed earlier, in which the magnetic properties of amorphous alloys are largely determined by the presence of compositional short-range order. Sign and magnitude of the formation enthalpies are a measure of the nature and the degree of this compositional short-range order. In amorphous $A_{1-x}Fe_x$ alloys with A = Mg, Th, and Ge the room-temperature ^{57}Fe isomer shift was studied. Together with literature data on amorphous alloys with A = Y, Mg, Sn, Ge, and Sb the isomer shifts were analyzed in terms of a model proposed by Miedema and van der Woude.

I. INTRODUCTION

In a previous investigation of the magnetic properties of amorphous alloys composed of Fe and a nonmagnetic partner metal we obtained experimental indications that the presence of compositional short-range order (CSRO) has a large influence on the magnitude of the iron moment (μ_{Fe}).[1] We proposed that the nature (clustering between similar or dissimilar atoms) and the degree of CSRO can be expressed in terms of the sign and the magnitude of the heat of alloying (ΔH). In this way we were able to explain the decrease in Fe moment in amorphous alloys of the type $R_{0.33}Fe_{0.67}$ and $R_{0.70}Fe_{0.30}$ when the R component changes from R = La to Lu.[1,2] Subsequently, by using this correlation between μ_{Fe} and ΔH it also proved possible to analyze satisfactorily the magnetic properties of amorphous alloys in which Fe is combined with various semimetals or metalloids like Sn, Ge, C, Si, B, or P.[3] Attempts to analyze the magnetic properties of amorphous $A_{1-x}Fe_x$ alloys in this way failed, however, when A represents a nonmagnetic metal. We will show that this failure is associated with the unreliability of the magnitude of the Fe moments when these are derived from the results of magnetization measurements on several of the alloys. A successful analysis can be given, however, when the Fe moments are derived from Mössbauer spectroscopy.

When Fe is alloyed with a metal or semimetal the isomer shift (IS), obtained by means of ^{57}Fe Mössbauer spectroscopy, can increase as well as decrease. We have analyzed the IS in various amorphous Fe-base alloys using a model proposed earlier by Miedema and van der Woude.[4] Amorphous alloys appear to be well suited for such an analysis because they can be studied over a conveniently large concentration range, making it possible to estimate the IS value corresponding to the dilute limit. An advantage is that the difficulties associated with the presence of a volume-mismatch contribution to IS, which are present in dilute crystalline Fe alloys, are absent in amorphous alloys. This volume-mismatch contribution arises in dilute crystalline alloys owing to the fact that the Fe atoms occupy sites of the host-metal atoms where the latter usually are of a different size than the Fe atoms. In amorphous alloys the atoms of all of the composing elements can freely choose their own volume. Finally we will use the results of the IS analysis and investigate how far these can be used to find the origin of the Fe moment reduction in these alloys (3*d*-band filling due to charge transfer or 3*d*-band broadening due to hybridization).

II. EXPERIMENTAL

The amorphous alloys $Th_{1-x}Fe_x$ were prepared by means of the melt-spinning technique. The preparation of these alloys was already described elsewhere.[5] The amorphous alloys $Mg_{1-x}Fe_x$ and $Ge_{1-x}Fe_x$ were prepared by means of two-source co-evaporation of the elements onto aluminium metal as a substrate. The thickness of the amorphous films was typically 5000 Å. The evaporation rates of the two electron gun sources were controlled independently and quasicontinuously, and were feedback-stabilized by means of Airco Temescal film-deposition controllers (FDC-800-1). The base pressure of the high-vacuum system was about 5.10^{-8} Torr. The thickness calibration was made on pure crystalline metals by means of Talystep techniques. All films of the two types of binary alloys mentioned above were examined by x-ray diffraction after deposition (Cu $K\alpha$ radiation). Alloys having sharp diffraction peaks in their x-ray diagram were excluded from further physical examination.

The temperature dependence of the magnetization (σ) of the amorphous $Mg_{1-x}Fe_x$ alloys was studied in the range 4.2—300 K by means of an adaptation of the Faraday method, using magnetic fields up to 18 kOe. The magnetic isotherms at 4.2 K were studied with a magnetic field parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the film plane by means of a vibrating sample magnetometer.

The ^{57}Fe Mössbauer spectra were obtained with a spectrometer of the constant-acceleration type and a ^{57}Co-Rh source. The isomer shifts (IS) are given relative to the Natl. Bur. Stand. (U.S.) standard material $Na_2Fe(CN)_5 \cdot NO \cdot 2H_2O$ at $T = 295$ K. The hyperfine fields were calibrated by means of the field of α-Fe_2O_3 at $T = 295$ K (515 kOe).

III. EXPERIMENTAL RESULTS

Amorphous $Mg_{1-x}Fe_x$ alloys were obtained in the concentration range $0.3 \le x \le 0.8$. All of these alloys were found to become magnetically ordered at low temperature. A typical example of the temperature dependence of the magnetization is shown in Fig. 1. In all cases the paramagnetic-to-ferromagnetic transition was smeared out over a wide temperature range. The concentration dependence of T_c in $Mg_{1-x}Fe_x$ is shown in Fig. 2.

Studies of the magnetic isotherms at 4.2 K show that the magnetization parallel to the film plane is always larger than that perpendicular to the film plane. At the highest fields applied (18 kOe) both $\sigma_{\parallel}$ and $\sigma_{\perp}$ appear still to be unsaturated, even in alloys of relatively large Fe concentration (see, for instance Fig. 3). In all cases we observed a substantial hysteresis. The values of $\sigma_{\parallel}$ obtained at 4.2 K and 18 kOe have been used to obtain an indication of the magnitude of the average Fe moment (M) in these alloys. The concentration dependence of M is included in Fig. 2.

The ^{57}Fe Mössbauer spectra obtained on several of the amorphous $Mg_{1-x}Fe_x$ alloys at room temperature are shown in Fig. 4. Values of the corresponding isomer shifts (IS) and quadrupole splittings (QS) are listed in Table I, together with the values obtained from the Mössbauer spectra of several $Th_{1-x}Fe_x$ and $Ge_{1-x}Fe_x$ alloys. Low-temperature spectra of three $Mg_{1-x}Fe_x$ alloys are depicted in Fig. 5. Owing to the more or less random arrangement of the Fe and Mg atoms the spectra appear to be considerably broadened. The average effective hyperfine field, derived from the central position of the outermost peaks corresponds to $\langle H_{\text{eff}} \rangle = 275$, 275, and 254 kOe for $x = 0.7$, 0.6, and 0.4, respectively.

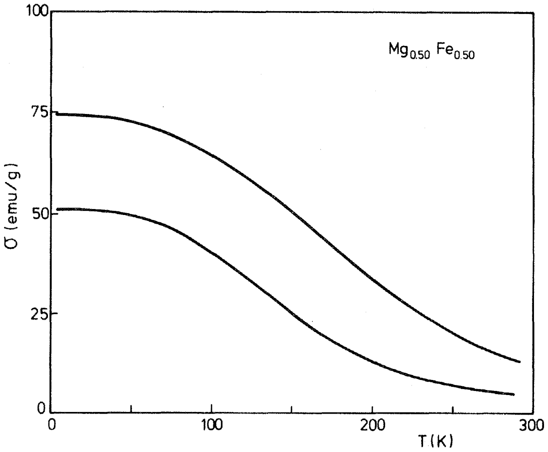

FIG. 1. Temperature dependence of the magnetization (σ) in amorphous $Mg_{0.50}Fe_{0.50}$. Upper curve $H = 9$ kOe, lower curve $H = 3$ kOe.

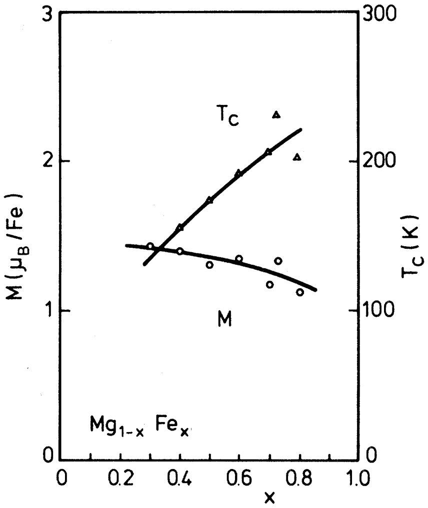

FIG. 2. Concentration dependence of the Curie temperature (T_c) and the average moment per Fe atom (M). The values of M were derived from the magnetization at 4.2 K and 18 kOe.

IV. DISCUSSION

From the measurements of the magnetic isotherms at 4.2 K, showing that $\sigma_{||} > \sigma_{\perp}$, it can be derived that the main component of the magnetization prefers a direction within the plane of the thin film. Neither the $\sigma_{||}$ nor the $\sigma_{\perp}$ isotherm appear to be saturated at 18 kOe. This could be taken to indicate the presence of a strong magnetocrystalline anisotropy. However, Fe alloys, in which the Fe atoms are the only atoms that carry a magnetic moment, are known not to be able to give rise to a substantial anisotropy. It is more likely, therefore, that the lack of saturation is the result of a not completely ferromagnetic moment arrangement.

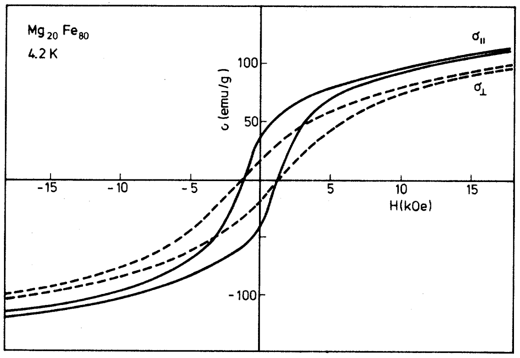

FIG. 3. Field dependence of the magnetization at 4.2 K measured parallel ($\sigma_{||}$) and perpendicular ($\sigma_{\perp}$) to the plane of the amorphous film.

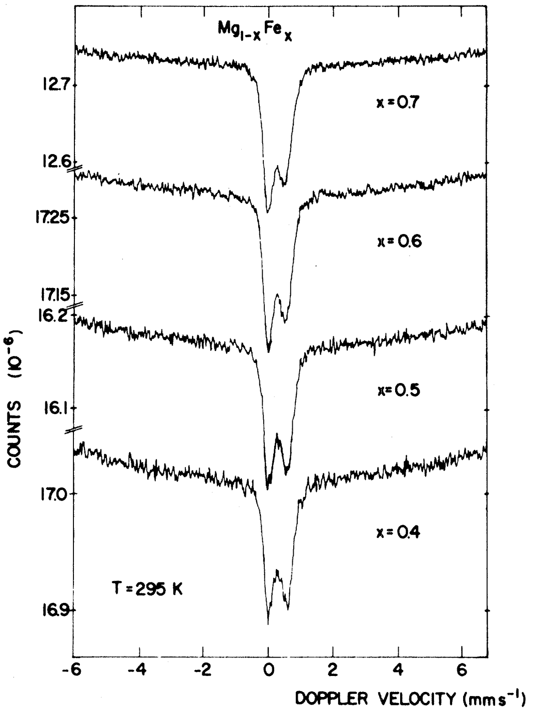

FIG. 4. ^{57}Fe Mössbauer spectra of various amorphous $Mg_{1-x}Fe_x$ films at 295 K.

The random atomic disorder in the amorphous alloy entails different Fe configurations with dissimilar nearest-neighbor distances. This leads to a distribution of exchange interactions meaning that magnetic couplings of both signs may be present simultaneously, although the centre of the distribution is situated well within the ferromagnetic-

TABLE I. Isomer shift (IS) and quadrupole splitting (QS) in various amorphous Fe-base alloys at room temperature.

Alloy	IS (mm/sec)	QS (mm/sec)
$Mg_{30}Fe_{70}$	+0.245	0.50
$Mg_{40}Fe_{60}$	+0.263	0.52
$Mg_{50}Fe_{50}$	+0.281	0.55
$Mg_{60}Fe_{40}$	+0.291	0.55
$Th_{33}Fe_{67}$	+0.172	0.44
$Th_{40}Fe_{60}$	+0.157	0.46
$Th_{55}Fe_{45}$	+0.113	0.48
$Th_{65}Fe_{35}$	+0.117	0.44
$Th_{80}Fe_{20}$	+0.090	0.44
$Ge_{45}Fe_{55}$	+0.615	0.48
$Ge_{60}Fe_{40}$	+0.625	0.49

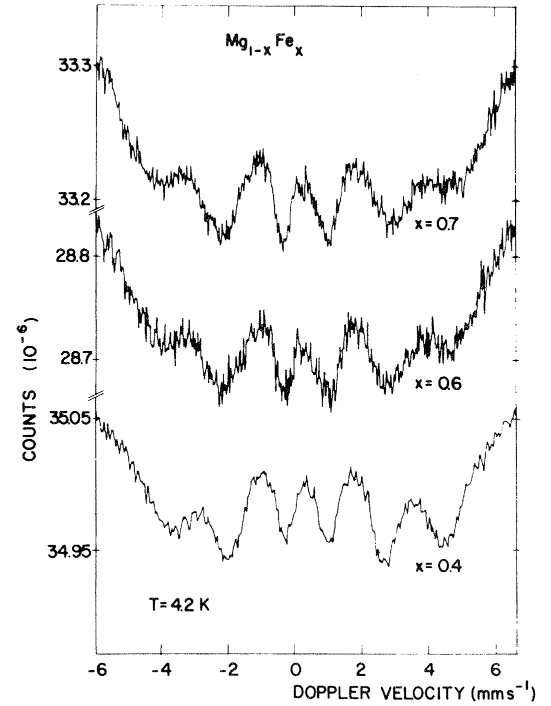

FIG. 5. ^{57}Fe Mössbauer spectra of various amorphous $Mg_{1-x}Fe_x$ films at 4.2 K.

coupling regime. A similar situation exists in amorphous $Y_{1-x}Fe_x$ alloys and to some extent also in amorphous $Th_{1-x}Fe_x$ alloys.[5,6] In previous investigations the magnetic moments in various amorphous alloys in which Fe is combined with different kinds of nonmagnetic elements were successfully analyzed in terms of a model in which account was taken of both the size difference between the $3d$ transition metal and its various nonmagnetic partners and the presence of a certain degree of compositional short-range order.[1,3] It will be clear from the foregoing that the results of the magnetic measurements in amorphous $Mg_{1-x}Fe_x$ alloys as well as several other series of amorphous Fe-base alloys are less suited to be interpreted in terms of this model since the presence of a noncollinear moment arrangement makes the value of the $3d$ moments derived from magnetic measurements rather uncertain. Since the magnitude of the ^{57}Fe-hyperfine field obtained by means of Mössbauer spectroscopy is less susceptible to uncertainties resulting from a noncollinear moment arrangement than the saturation moment it is still possible to analyze the magnetic properties of the various Fe-base alloys if one takes H_{eff} as a measure of the size of the Fe moments.

In the model it is assumed that the moment of a given $3d$ atom depends strongly on the number of the $3d$-atom nearest neighbors. This is a rather straightforward assumption, which, from the experimental point of view, has been well documented by means of numerous data obtained on crystalline $3d$ alloys and compounds.[7-9] All these data show that the $3d$ moment increases as the number of nearest $3d$ neighbors increases. In a more quantitative treatment one has to account for the difference in size between the nonmagnetic A atoms and the $3d$-transition metal T atoms in $A_{1-x}T_x$. We therefore use surface concentrations c^s in which we weight the concentration by the corresponding atomic cross sections, i.e., by the values of $V^{2/3}$ where V represents the atomic volume. This leads to the following relationship between x and c^s:

$$c_T^s = xV_T^{2/3}[xV_T^{2/3}+(1-x)V_A^{2/3}]^{-1} . \tag{1}$$

With the assumption that the magnetic moment of a $3d$ atom depends chiefly on the number of nearest $3d$-atom neighbors, one expects that in alloys having a statistical atomic arrangement, similar c_T^s values correspond to the same value of the saturation moment. In the presence of CSRO this will no longer be true.

It was generally accepted for a number of years that the atomic arrangement in amorphous alloys is purely statistical and similar to that in a dense random packing of hard spheres (DRPHS). At present there is an increasing tendency to question the validity of the DRPHS model. There is a growing list of experimental results of amorphous alloys obtained by means of magnetic measurements, nuclear magnetic resonance (NMR) and Mössbauer spectroscopy all of which can be explained in a satisfactory manner just by assuming the presence of a certain degree of CRSO between the constituent metal atoms. In order to have, at least qualitatively, a measure of the degree of CSRO in various amorphous alloys (prepared under similar circumstances) it is proposed that the nature and the degree of CSRO are determined by the sign and magnitude of the heat of alloying (ΔH). Positive values of ΔH in amorphous alloys $A_{1-x}T_x$ will lead to atomic arrangements in which the number of like atomic nearest-neighbors is larger than would follow from a statistical atomic distribution. The opposite is true if ΔH is negative. To show the existence of the relationship between ΔH and H_{eff} we have collected in Table II the average values $\langle H_{\text{eff}} \rangle$ of the effective hyperfine fields observed in amorphous $A_{1-x}Fe_x$ alloys having the same Fe surface concentration (c_{Fe}^s

TABLE II. Comparison of the average moment per Fe atom (M) derived from magnetization measurements and the average effective hyperfine field obtained by ^{57}Fe Mössbauer spectroscopy in amorphous Fe-base alloys of different composition (x) but having the same surface concentration ($c^s_{\mathrm{Fe}} = 0.5$, see text). The ratio of atomic volumes $(V_{\mathrm{Fe}}/V_A)^{2/3}$ is listed in column 2. The ΔH values pertain to formation enthalpies of (imaginary equilibrium) compounds of composition x calculated by means of the results listed by Miedema *et al.* in Ref. 10.

$A_{1-x}\mathrm{Fe}_x$	$(V_{\mathrm{Fe}}/V_A)^{2/3}$	x	M (μ_B)	$\langle H_{\mathrm{eff}} \rangle$ (kOe)	ΔH (kJ/g at.)
A = Zr	0.64	0.61	0.3[a]	165[a]	−35
Th	0.51	0.67	1.5	207	−15
Lu	0.54	0.65	1[a]	195[a]	−10
Y	0.51	0.66	1.5[b]	233[a]	−2
Sn	0.58	0.63	1.8[a]	226[b]	−2
La	0.46	0.68	1.4	298[a]	+7
Mg	0.64	0.61	1.1	275	+21

[a] The data are those given by Heiman and Kazama in Ref. 2.

[b] The data are given by Rodmacq *et al.* in Ref. 11.

= 0.5). Experimental data of the heat of alloying for these alloys are not available. Instead we will use values of the heat of formation of ordered equlibrium compounds calculated by means of Miedema's model.[10]

These values are included in the last column in Table II. We have plotted the $\langle H_{\mathrm{eff}} \rangle$ values versus the corresponding ΔH values in Fig. 6. These results show that there is indeed a close relationship between the Fe moments (as measured via H_{eff}) and ΔH. Some spread of the data points is present in Fig. 6. We note, however, that a (minor) part of the total hyperfine field at the Fe nuclei consists of the transferred hyperfine field, which measures the conduction-electron polarization due to the moments of the neighbor atoms. This transferred field may vary from one alloy to the other since the conduction-electron concentration and the moment arrangement are dissimilar. Keeping this in mind, the observed trend of an increasing $\langle H_{\mathrm{eff}} \rangle$ with increasing ΔH is rather convincing in establishing that the degree and the nature of the CSRO present in the various amorphous alloys play a rather important role in determinig their magnetic properties.

The reduction in $3d$ moment due to a decreasing number of $3d$-nearest-neighbor atoms (increasing number of atoms of the nonmagnetic partner) can be caused by an increase in charge transfer from the nonmagnetic partner atoms to the $3d$ atom which leads to a more complete $3d$-band filling. The reduction in $3d$ moment can, however, also be caused by a decrease in intra-atomic Coulomb repulsion between the $3d$ electrons (reduced exchange splitting between the $3d$ subbands of different spin direction) resulting from an enhanced $3d$-band broadening owning to hybridization of the $3d$ electrons with the s, p, or d valence electrons of the nonmagnetic partner element. It is difficult to tell which of these two effects (charge transfer or hybridization) prevails in the moment reduction. Since the ^{57}Fe Mössbauer isomer shift can be taken as a measure of the s-electron charge density at the Fe nucleus we will investigate in how far the results of the Mössbauer spectroscopy can be used to estimate the amount of charge transferred from the nonmagnetic component to iron upon alloying.

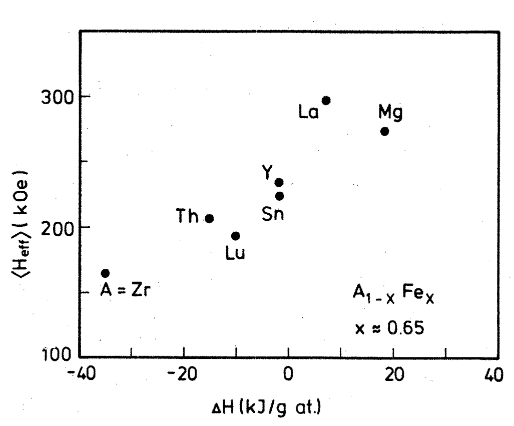

FIG. 6. Average effective hyperfine field in various amorphous alloys $A_{1-x}\mathrm{Fe}_x$ of the approximate composition $x = 0.65$, plotted versus the corresponding values of the formation enthalpies.

It was proposed by Miedema and van der Woude that the ^{197}Au isomer shift in Au alloys and compounds can be expressed in terms of electronegativities ϕ^* and electron densities at the atomic-cell boundaries n_{WS} (WS is the Wigner-Seitz cell).[4] Applying this model to the present class of materials one finds

$$\delta(IS)_{\max}=P'(\phi_A^*-\phi_{\mathrm{Fe}}^*)+Q'\,(n_{\mathrm{WS}}^A-n_{\mathrm{WS}}^{\mathrm{Fe}})/n_{\mathrm{WS}}^{\mathrm{Fe}}\ . \tag{2}$$

Here $\delta(\mathrm{IS})_{\max}$ represents the isomer shift (relative to α-Fe) in a dilute system where each Fe atom is surrounded by A atoms only. Within a given class of materials (Fe-base alloys) the quantities P' and Q' can be regarded as constants.

In the derivation of the first term of Eq. (2) it is assumed that there is a linear relationship between the change in the number of electrons (s and d together) per iron atom and the increase in the s-electron density at the Fe nucleus. Also it is assumed that the charge transfer relative to pure iron, for a given Fe atom completely surrounded by dissimilar neighbors, is proportional to the electronegativity difference $\phi_A^*-\phi_{\mathrm{Fe}}^*$, where the electronegativity ϕ_{Fe}^* is equal to 4.93 V.

The second term represents the analog of the repulsive term in the heat of formation, which in Miedema's model is due to the difference in electron density at the boundaries between dissimilar atomic cells. The sign of the coefficient Q' follows from the picture that the electron-density mismatch in transition-metal alloys is removed by means of $s\longrightarrow d$-electron conversion. Since s electrons reside predominantly in the outside regions of the atomic cell, conversion of s-type electrons into d-type ones results in a decrease of n_{WS}.[12] It follows that P' and Q' must be of the opposite sign.

We will now try to estimate the relative stength of the two contributions to the isomer shift [Eq. (2)] in the various amorphous Fe alloys investigated. To obtain the infinite solution limit $\delta(\mathrm{IS})_{\max}$ we have plotted the various IS values of the alloys $A_{1-x}\mathrm{Fe}_x$ (A = Th, Mg, and Ge) as a function of x in Fig. 7. Relative to α-Fe the value of $\delta(\mathrm{IS})_{\max}$ equals -0.21 mm/sec in the case of $\mathrm{Th}_{1-x}\mathrm{Fe}_x$. In the case of $\mathrm{Mg}_{1-x}\mathrm{Fe}_x$ and $\mathrm{Ge}_{1-x}\mathrm{Fe}_x$ the $\delta(\mathrm{IS})_{\max}$ are more difficult to estimate. In $\mathrm{Mg}_{1-x}\mathrm{Fe}_x$ the value $\delta(\mathrm{IS})_{\max}$ will be about $+0.1$ mm/sec while in $\mathrm{Ge}_{1-x}\mathrm{Fe}_x$ it will be around $+0.4$ mm/sec at least. The concentration dependence of the isomer shift was described in the literature for several other amorphous $A_{1-x}\mathrm{Fe}_x$ alloys where A is Zr, Sn, or Sb.[13–15] From the IS data reported, values of $\delta(\mathrm{IS})_{\max}$ were estimated by extrapolation ($x\rightarrow 0$) and included in the last column of Table III together with the $\delta(\mathrm{IS})_{\max}$ values of the alloys studied in the present investigation. From the values of the electronegativities ϕ^* and electron densities at the atomic-cell boundaries n_{WS} listed by Miedema *et al.*[10] we have calculated $\delta(\mathrm{IS})_{\max}$ values by means of Eq. (2). Since the experimental values of $\delta(\mathrm{IS})_{\max}$ seem most reliable in the case of A = Zr and Th, we have used them to fix P' and Q'. When the isomer shift is expressed in mm/sec one finds

$$\delta(\mathrm{IS})_{\max}=1.0\Delta\phi^*-2.2\Delta n_{\mathrm{WS}}/n_{\mathrm{WS}}^{\mathrm{Fe}}\ . \tag{3}$$

Inspection of the results listed in Table III shows that the sign of $\delta(\mathrm{IS})_{\max}$ is correctly predicted by means of Eq. (3). Also the absolute values are reproduced in a satisfactory way. The deviations from the experimental values are largest in the case of the Sn, Ge, and Sb. It is interesting to note that the heat of alloying of Fe, with these elements in particular, contains an additional term associated with the hybridization of the Fe $3d$ band with the s,p bands of the nonmagnetic component (the so-called R term, see Ref. 4). For these alloys Eqs. (2) and (3) are therefore incomplete since this hybridization should be accounted for by a similar term in the isomer-shift expression. The main ef-

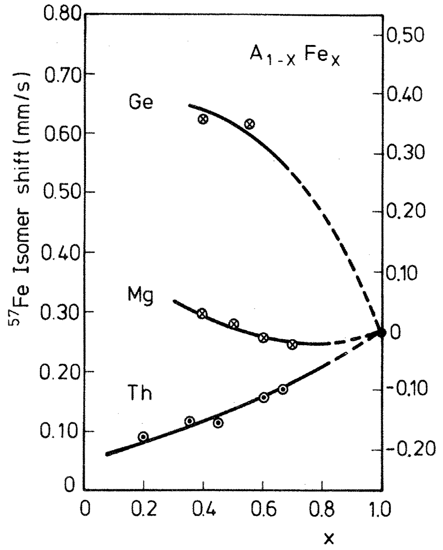

FIG. 7. Concentration dependence of the isomer shift in various amorphous alloys. The left-hand scale refers to the Natl. Bur. Stand. (U.S.) standard material $\mathrm{Na_2Fe(CN)_5{\cdot}NO{\cdot}2H_2O}$, the right-hand scale measures IS relative to α-Fe.

TABLE III. Electronegativities (ϕ^*) and electron densities at the atomic-cell boundaries (n_{WS}) of various nonmagnetic components A in amorphous $A_{1-x}\mathrm{Fe}_x$ alloys as listed by Miedema *et al.* in Ref. 10. The experimental and calculated values of the ^{57}Fe isomer shift $\delta(\mathrm{IS})_{\max}$ are given in mm/sec relative to α-Fe. The experimental values of several of the alloys were derived from literature data. These include data for A = Zr reported by Smit *et al.* in Ref. 13, data for reported A = Sn by Piecuch *et al.* in Ref. 14, and data for A = Sb given by Shigematsu *et al.* in Ref. 15. For the values listed in the two middle columns, see text.

A	ϕ^*	n_{WS}^{A}	$P'\Delta\phi^*$	$\dfrac{Q^*\Delta n_{\mathrm{WS}}}{n_{\mathrm{WS}}^{\mathrm{Fe}}}$	$\delta(\mathrm{IS})_{\max}^{\mathrm{calc}}$	$\delta(\mathrm{IS})_{\max}^{\mathrm{exp}}$
Th	3.30	2.10	−1.56	+1.35	−0.21	−0.21
Zr	3.40	2.69	−1.48	+1.11	−0.35	−0.35
Y	3.20	1.77	−1.66	+1.35	−0.31	−0.20
Mg	3.45	1.60	−1.42	+1.55	+0.13	+0.10
Sn	4.15	1.91	−0.36	1.42	+1.06	+0.4
Ge	4.55	2.57	−0.36	1.18	+0.82	+0.4
Sb	4.40	2.00	−0.51	1.37	+0.86	+0.42

fect of the hybridization is to broaden the $3d$ band and possibly also to increase the s,p density at the Fe sites. If this term were included in Eqs. (2) and (3) it would contribute negatively to the total IS and bring the calculated values more in agreement with the experimental values.

It follows from the discussion given above that the charge-transfer term that determines $\delta\,(\mathrm{IS})_{\max}$ is equal to $\delta(\mathrm{IS})_{\max}^{\mathrm{c.t.}} = P'\Delta\phi^* = -1.0\,|\,\Delta\phi^*\,|$. From the analysis of Miedema and van der Woude it can be derived that a difference in ϕ^* corresponding to $1\,V$ leads to a charge transfer equal to 0.5 electrons.[4] If we adopt the same value here this would mean that the isomer shift in alloys where Fe is completely surrounded by dissimilar atoms amounts to −2.0 mm/sec per added electron. This value is in satisfactory agreement with the results of an analysis of ^{57}Fe isomer shifts given by Walker *et al.* (about −1.5 mm/sec per added electron).[16]

The amount of charge transfer taking place in the limit $x \rightarrow 0$ in the various amorphous alloys $A_{1-x}\mathrm{Fe}_x$ can be compared in column 4 of Table III. In the alloys composed of two metals (A = Th, Zr, Y, or Mg) charge transfer is about equal in size and significantly larger than in the alloys composed of Fe and a semimetal (A = Sn, Ge, or Sb). More directly connected with the moment reduction, observed when Fe is alloying with A elements, is perhaps the second term (Q' term) in the expressions of $\delta(\mathrm{IS})$ since it is a measure of the $s \rightarrow d$ transfer and hence directly related to the $3d$-band filling upon alloying. The relative magnitudes of this term can be compared in column 5 of Table III. It is seen that this term shows little variation in the different alloys. If an increase in s charge density by one electron is again taken as leading to $\delta(\mathrm{IS}) = -2.0$ mm/sec and an increase in $3d$ charge density by one electron as leading to the same value but opposite in sign, the values of the Q' term in Table III suggest that (in the limit $x \rightarrow 0$) the $s \rightarrow d$ charge transfer equals about 0.3 electron per Fe atom in all the alloys considered. Finally we note that the necessity to include a hybridization term (R) in the description of $\delta(\mathrm{IS})$ in the last three alloy systems of Table III means that here an additional mechanism of $3d$-band broadening is present, able to reduce the $3d$ moments by means of a lower exchange splitting between the spin-up and spin-down $3d$ subbands.

In conclusion, we have shown by means of Mössbauer spectroscopy that the previously reported strong correlation between the $3d$ moment size and the heat of alloying exists also in amorphous alloys composed of Fe and a nonmagnetic metal. If standard magnetic measurements are used to estimate the value of the Fe moment in such alloys this correlation is difficult to establish due to deviations from a collinear-spin arrangement in the magnetically ordered state.

The sign of the ^{57}Fe isomer-shift change relative to α-Fe is negative in $\mathrm{Th}_{1-x}\mathrm{Fe}_x$, almost zero in $\mathrm{Mg}_{1-x}\mathrm{Fe}_x$, and positive in $\mathrm{Ge}_{1-x}\mathrm{Fe}_x$. This behavior, together with that reported in Mössbauer-effect investigations of other amorphous Fe-base alloys, could satisfactorily be explained by means of a model proposed earlier for Au alloys by Miedema and van der Woude. The isomer-shift data were interpreted in terms of charge-transfer and intra-atomic $s \rightarrow d$ conversion. They do not favor an interpretation of the Fe-moment reduction in these alloys as resulting mainly from an enhanced $3d$-band filling due to charge transfer. In $A_{1-x}\mathrm{Fe}_x$ alloys, where A is a high-valent non-transition metal (Sn, Ge, Sb) in particular, there is an additional contribution to the isomer shift due to a substantial hybridization of the $3d$ electrons with the valence electrons of the A component. In these cases the moment reduction will proceed mainly as a result of a diminished $3d$-band exchange splitting.

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