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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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AMORPHOUS METALLIC ALLOYS
(Parts 6 & 7)

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PART 6.

§ II. Ferromagnetic amorphous alloys based on TM.

- Itinerant versus localized magnetism.
- Alloying effects on $M(T=0)$, on T_C.
- Effects of structural disorder on Fe base alloys: amorphous Fe; Invar alloys.

A] Itinerant / localized magnetism.

Localized:

each "e" remains localized on a atom

- * intra atomic e.e interactions large
  ⇒ atomic moment on each lattice site (Hund's rules)
- * inter atomic exchange interact. small
- * compete with thermal disorder to define the magnetic order.

Itinerant:

each magnetic carrier is itinerant

- * in the average field of the other e and ions and electron levels from energy bands
- * weak e.e interactions which stabilize the ordered magnetic state
- * $\mu \propto n_\uparrow - n_\downarrow$

At first sight: localized ⟷ insulators
itinerant ⟷ metals.

In fact, 2 extreme cases:

* localized:

$U \gg W$ U ≡ average intra atomic Coulomb interaction.
W ≡ band width, atomic overlap, inter atomic interactions.

cf. RE

* itinerant: $U/W \ll 1$.

Transition metals (Ni, Co, Fe): loc. or itin.?
cf. Moriya.
Reviews by Shimizu (Rep. Prog. Phys. 1981)
Gautier (Les Houches).

Often, both models are invoked:
- localized: Curie-Weiss law
- band model: magn. properties at $T=0$

In TM base amorphous ferromagnets.

* localized approach very useful.

* Band ferromagnetism still appropriate.

cf. E. P. Wohlfarth, IEEE Trans. Magn. MAG 14, (1978) 935.
J. Schneider & K. Zaveta, Proc. RQ IV, Sendai (Jap.), 1981, in press.

B) ALLOYING EFFECTS

"Pure" amorphous Ni, Co, Fe.

Thin films, unstable against crystallization.

$$\frac{\mu_{Ni}(a)}{\mu_{Ni}(c)} \simeq 0.7 \text{ to } 0.8$$

$$\frac{\mu_{Co}(a)}{\mu_{Co}(c)} \simeq 1$$

$$\frac{\mu_{Fe}(a)}{\mu_{Fe}(bcc)} \simeq 0 \text{ to } 0.5$$

$T_c(a.Ni) \simeq 540\ K$ $[T_c(c.Ni) = 627\ K]$

$T_c(a.Fe) \simeq 0$ to $200\ K$

Amorphous alloys base on Ni, Co, Fe.

$\bar{\mu}$, mean moment per atom of alloy (in μ_B)

$\bar{\mu} = \mu_0 - a\,x$

Pure dilution : $a = \mu_0$

$\bar{\mu} = \mu_0 (1-x)$

Charge transfer : $a = \mu_0 + p$

$\bar{\mu} = \mu_0 - (\mu_0 + p)x$

$p \rightarrow$ number of electrons transfered to fill up the TM d bands.

Friedel's picture.

(see Gautier. Lectures notes)

Excess charge ΔZ introduced by the solute is completely screened $\Leftrightarrow$ local charge neutrality in a metal.

$$\Delta Z = \Delta Z_\uparrow + \Delta Z_\downarrow$$

$$\frac{d\bar{\mu}}{dx}(x \to 0) = \mu_B (\Delta Z_\uparrow - \Delta Z_\downarrow)$$

Strong ferromagnet : (pure c. Ni, c. Co)

- small $\Delta Z \Rightarrow \Delta Z_\uparrow = 0$
- ΔZ larger $\Rightarrow \Delta Z_\uparrow \neq 0$ (not a integer!)
  (virtual bound states)
  (departure from Slater-Pauling curves)

Weak ferromagnet (pure bcc Fe)

Screening picture more complicated.

($\Delta Z_\uparrow$ allways $\neq 0$!)

Experimental data.

- Ni P $\quad \frac{d\bar{\mu}}{dx}(a.NiP) < \frac{d\bar{\mu}}{dx}(c.NiP)$
- CoSi, CoP $\quad \frac{d\bar{\mu}}{dx}$ the same in a. and c. alloys.
- $Co_{80-x}T_xB_{20}$ (T = Fe, Mn, Cr, V)
  (D. Handley, SSC, 1981)
- $Fe_{79-x}T_xP_{13}B_8$ (T = Co, Ni, Mn, Cr, V)

$$\begin{cases} \Delta Z_\uparrow \simeq 0 & \text{for Co, Ni} \\ \Delta Z_\uparrow \neq 0 & \text{for Mn, Cr, V} \end{cases}$$

bcc Fe
(weak ferromagnet)

Co : $\Delta Z_\uparrow = +1$
Ni : $\Delta Z_\uparrow = +1.6$

a. $Fe_{79}P_{13}B_8$ is a strong ferromagnet
(as c. Fe_3B)

Why? * charge transfer?
from (sp) electrons of B
→ $d_\uparrow$ bands of Fe?

photoemission measurements: (Amamou a Krill)

① DOS (E_F) is practically the same in a. and c. Fe_3B.

② no evidence for a large charge transfer

* ③ hybridisation B 2p electrons with 3d bands.

cf. electronic structure calculations of T. Fujiwara, J. Phys. F 12 (1982) 661.

* Curie temperatures.

a) $\begin{cases} Fe_{80}P_{20-x}M_x \\ Fe_{80}B_{20-x}M_x \end{cases}$ (M = C, Ge, Si, Ga, Al ...)

cf. H. S. Chen and coll.
F. Luborsky and coll.
T. Masumoto and coll.

⇒ Size effects

b) $\begin{cases} \mu(x) \\ T_c(x) \end{cases}$ in a. FeSi, FeAu, FeO (Felsch)
a. FeP, FeB

⇒ amorphous Fe

C] Effect of structural disorder on amorphous Fe base alloys.

Fe is a special case.

α. Fe (bcc) - Ferro. $\mu = 2.2\,\mu_B$. High T_c
γ. Fe (fcc) - AF. $\mu = 0.5\,\mu_B$. T_N
small variations of lattice parameter
⇒ γ. Fe "weak" ferro, with $\mu = 0.5\,\mu_B$ and $T_c = 900$ K.
(W. Kümmerle and co., SSC 24 (1977) 33)

ε. Fe (hexagonal, P ~ 130 kbar): paramagnetic (and, possibly, superconductor)
(E. P. Wohlfarth, Phys. Lett. 75A (1979) 141)

Amorphous Fe : close-packed structure
Z ≈ 10 to 12 Fe n.n.

What happens when alloyed with P, B? or Zr

$T_c \nearrow$
$\mu \downarrow$ (at least for $x_B \geq 3$ at.%)

Invar properties ($15 \leq x_B \leq 25$)
α = coeff. of thermal expansion ≈ 0.
cf. "Invar region" in crystalline Fe-Ni alloys.

Features in magnetic properties of Invar all.

* T_c and μ may vary in an opposite way.

⑦

- T_c is depressed strongly and linearly when P is applied.

  $$\frac{dT_c}{dP} = -T_c^{-1}$$

  (cf. D. Wagner and E.P. Wohlfarth, J. Phys. F 11 (1981) 2417.)

- $\frac{M(T)}{M(0)}$ decreases with T more rapidly than predicted by a Brillouin function
- Large departure between the values of the spin-wave stiffness constant as determined from inelastic neutron scattering ~~and~~ from M(T).

Origin of the Invar effect.

- Wohlfarth: weak → strong ferromagnetism
- coexistence of two magnetic states of Fe $\left\{ \begin{array}{l} F \\ AF \end{array} \right.$ randomly distributed (Weiss, Kondorski) a segregated in small clusters.

Why is the Invar effect favoured in am. alloy?

- distribution of J (+ or −) following the distribution of interatomic distances and coordination numbers?
- inhomogeneities over a "medium range" scale?
- exact role of structural disorder?

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PART 7

HYPERFINE FIELDS IN METALLIC GLASSES

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We review recent experimental data obtained on hyperfine fields (hf) in amorphous metallic alloys. We restrict ourselves to magnetically ordered materials. Both the average value and the distribution of the hf are discussed for three different cases. First, we summarize the hf data on majority constituents such as transition metals (Fe, Co) and rare earth elements (Gd, Eu, Dy). In a second section, we first analyze the hf data on magnetic impurities (Ni, Co, Mn) diluted in Fe based amorphous ferromagnets (Fe–P–B, Fe–P–C). The case of ^{59}Co diluted or concentrated in amorphous Gd–Co alloys is analyzed with some detail. Finally, we review the data on transferred hf on simple metals (Au) and s–p elements (P, B) is various amorphous ferromagnets. For those three cases, the mean hf value is discussed in the light of hf data on both pure elements and compositionally related crystalline compounds. The hf distribution is analyzed in relation with the structure of these amorphous alloys (electronic structure, magnetic structures, atomic-scale or medium-range atomic order).

Introduction

Through their magnetic moments some nuclei can be used as probes of internal magnetic fields. In addition to these magnetic effects, the interactions between nuclei and electrons in metals can include and electrostatic contribution in the case of nuclei having an electric quadrupole moment. These quadrupolar effects will not be analyzed in this review of hyperfine fields in metallic glasses.

The magnetic interactions between nuclei with spin $\boldsymbol{I}$ and electrons of spin $\boldsymbol{s}_i$ are commonly expressed by the Hamiltonian [1]:

$$\mathcal{H}_i = 2\mu_B\gamma\hbar\boldsymbol{I} \times \left(\frac{8\pi}{3}\boldsymbol{s}_i\delta(\boldsymbol{r}_i) + \frac{\boldsymbol{l}_i}{r_i^3} + \frac{3(\boldsymbol{r}_i \cdot \boldsymbol{s}_i)\boldsymbol{r}_i}{r_i^5} - \frac{\boldsymbol{s}_i}{r_i^3} \right), \quad (1)$$

where μ_B is the BOHR magneton, γ the nuclear gyromagnetic ratio, $\boldsymbol{l}_i$ is the orbital moment of the electron i, $\boldsymbol{r}_i$ is the vector connecting the nucleus and the electron i. The orbital contribution $(\boldsymbol{I}.\boldsymbol{l}_i/r_i)$ is thought to be negligible for 3d transition metals, while it can be predominant for rare earths. The dipolar term $\{\boldsymbol{I}[3(\boldsymbol{r}_i.\boldsymbol{s}_i)\boldsymbol{r}_i/r_i^5] - (\boldsymbol{s}_i/r_i^3)\}$ is negligible in magnetically ordered metals or alloys. The contribution proportional to $\boldsymbol{I}.\boldsymbol{s}_i\delta(\boldsymbol{r}_i)$ is rather complex for metallic system with s, p, d electrons. This latter contribution includes:

(i) a merely "s" term ("contact" term) proportional to the s density of states at the nuclear site,

(ii) a core polarization (cp) term, arising from the polarization of the core electrons by the d magnetization. The cp contribution is generally negative for 3d electron systems. For an assembly of N electrons, the Hamiltonian of the magnetic interactions between nuclei and electrons is written as:

$$\mathcal{H} = \sum_i \mathcal{H}_i = -\gamma\hbar\boldsymbol{I}.\boldsymbol{H}, \quad (2)$$

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H being the effective field produced by the electrons at the nuclear site. We will restrict ourselves in this review to the case of ferromagnetic materials.

A quantitative analysis of the different contributions to hyperfine fields in crystalline ferromagnetic materials is a very difficult task, for it would require an exact evaluation of the electronic densities at the nuclear sites for both spin directions. This is made even more difficult in amorphous alloys, for which a detailed knowledge of the atomic structure is lacking. Hyperfine field data [illegible] when analyzed by experimentalists, for the most part, according to phenomenological approaches emphasizing the role of local atomic environments. The magnitude and the distribution of the hyperfine fields in amorphous ferromagnetic alloys are compared with those obtained in pure ferromagnetic elements and in compositionally related crystalline compounds. Reasonable relationships can then be established between hyperfine fields and atomic order [2].

Hyperfine field (hf) data as obtained by Mössbauer and NMR spectroscopy in various amorphous alloys will be reviewed in this paper as follows. In a first part, we summarize the hf data on majority constituents such as Fe, Co in transition metal based alloys, or Gd, Eu, Dy in rare earth based alloys. In a second section, we discuss first the case of magnetic impurities (Ni, Co, Mn) diluted in Fe based amorphous ferromagnets. The hf of ^{59}Co diluted in amorphous Gd–Ni or concentrated in amorphous Gd–Co alloys will be analyzed in the same section. Finally, we briefly review the data on transferred hf at nuclear sites of noble metals (Au) and s–p elements in various amorphous ferromagnets.

2. Host hyperfine fields in transition metal based and rare earth based amorphous alloys

2.1. Host hyperfine fields in Fe or Co amorphous alloys

Pure magnetic elements are not easily obtainable in the amorphous state. Thin films of Ni, Fe and Co were reported to be amorphous. But, due to the instability of the samples with respect to crystallization, and due to the small quantity of sample, very little is known about their bulk magnetic properties, and practically nothing about the hyperfine fields. Host Fe or Co hyperfine fields had therefore to be studied in alloys of Fe of Co with sp elements such as B, C, P, Si, Ge and Sn or with transition metals such as Zr, Y and Th. The minimum percentage of these additional elements, which are required to stabilize the amorphous structure, lies between 10 and 20 at.%, depending upon the elements and the fabrication technique. Within this context, it can be conjectured that the alloying effects will not be readily separated from the consequences of structural disorder in the hyperfine field studies of Fe or Co based amorphous alloys. Appropriate comparisons with pure crystalline materials, on the one hand, and with compositionally related crystalline compounds, on the other hand, must be made before invoking the role of the amorphous structure.

^{57}Fe Mössbauer spectroscopy has been widely used in the study of local magnetism in Fe based ferromagnetic amorphous alloys [3]. The NMR technique has been also employed – although less extensively so far – to determine the ^{57}Fe and ^{59}Co hf in metallic glasses [4]. We will focus on the low-temperature data concerning the magnitude and the distribution of the hyperfine fields. The temperature dependence of the hf was also measured in several amorphous systems, namely in Fe based alloys through Mössbauer spectroscopy [5]. This temperature dependence does not seem to depart significantly from that observed in crystalline counterparts when available [6,7]. It seems then that the specific character of the amorphous structure can be discussed more readily from the zerotemperature hyperfine field data. We will analyze first the ^{57}Fe and ^{59}Co host hyperfine fields in Fe and Co based amorphous alloys with sp elements. Then, we summarize the data on the change in host hyperfine field by substituting some amount of Cu, Ni, Co, Mn, Cr, C and Ti for Fe in Fe based amorphous alloys.

2.1.1. Fe and co alloys with s–p elements

Concerning the host hyperfine fields in amorphous materials, two pieces of information are of special interest, namely the average value of the hf and its distribution. The average value of the hf has to be compared with the magnetic moment as obtained from bulk measurements as a function of composition in various alloys. Several questions can then be raised: is there a definite,

quantitative relationship between the average hf and the magnetic moment? What does it imply about the relative importance of the different contributions to the hyperfine field? Once a quantitative relationship is established between the magnitude of the hf and that of the on-site moment, is it then possible to extract from the hf distribution any information about the atomic coordination about a magnetic site, and thus, to shed any light about the amorphous structure?

(a) Average hyperfine field and magnetic moment. From early neutron experiments on electrodeposited amorphous alloys [8], it was first noted that the ^{59}Co hyperfine coupling constant (ratio of the ^{59}Co hf to the Co moment) was about the same as that in pure crystalline Co irrespective of the P concentration. It was then suggested [9] that this constant value for $\bar{H}_{hf}/\bar{\mu}$ should arise from the same physical mechanisms as in crystalline Fe compounds with s–p elements for which this feature is well documented [10]. Subsequent ^{57}Fe NMR experiments in a series of amorphous Fe–P–B alloys [11] showed that ^{57}Fe $\bar{H}/\mu$ was indeed independent of composition (about 125 kOe/μ_B) and roughly the same as in related crystalline compounds, although sensitivity smaller than $\bar{H}/\mu$ in bcc Fe (156 kOe/μ_B). Such a feature was firmly established by ^{57}Fe Mössbauer spectroscopy in Fe based amorphous alloys with various s–p elements. Let us note that the average ^{57}Fe hf value does not drastically depend upon the fitting procedures adopted to evaluate the field distribution [12]. Before discussing further this proportionality between hf and magnetic moment, it might be useful to summarize the phenomenological model commonly used to analyze the hf data in host transition metals.

The transition metal hf can be described as the sum of two main contributions: one is proportional to the on-site moment, the other one is proportional to the surrounding moments:

$$H_{hf} = A\mu_L + B\bar{\mu}. \qquad (3)$$

The local term includes both a contact contribution (polarization of the conduction electrons due to the on-site moment through the coupling constant A_{4s}) and a core-polarization contribution (polarization of the inner s-shells through the coupling constant A_{3d}). The second term is the 4s contribution due to the overall polarization of the surrounding moments. Thus, the hf can be expressed as:

$$H_{hf} = H_{cp}^{loc} + H_s^{loc} + H_\Sigma \qquad (4)$$

or

$$H_{hf} = (A_{4s} + A_{3d})\mu_L + A_{4s}\bar{\mu}. \qquad (5)$$

Let us note that for Fe and Co, A_{4s} and A_{3d} have opposite signs. On the other hand, the coupling constant A_{3d} is though to be mostly atomic in nature, since it involves core s electrons and localized d electrons, while the constant A_{4s} may be sensitive to the metallic structure owing to the extended character of the s electrons. One might conjecture, *a priori*, that the very short electronic mean free path in amorphous alloys could result in a reduction of the overal polarization term.

Such an analysis applied to α- Fe gives: $H_{loc} = H_s + H_{cp} = -200$ kG and $H_\Sigma \simeq -145$ kG. The local hyperfine coupling constant is then $H_{loc}/\mu \simeq 90$ kG/μ_B [13], while the coupling constant for the total hyperfine field is 156 kG/μ_B. It is interesting to note that this phenomenological model gives a very poor description of the concentration dependence of the Fe hf in disordered bcc Fe–Ni and Fe–Co alloys [14].

In Co base crystalline compounds (Co_3B, Co_2B), and amorphous alloys (Co–B, Co–P, Co–P–B, Co–B–Si), the ^{59}Co hf as determined from NMR

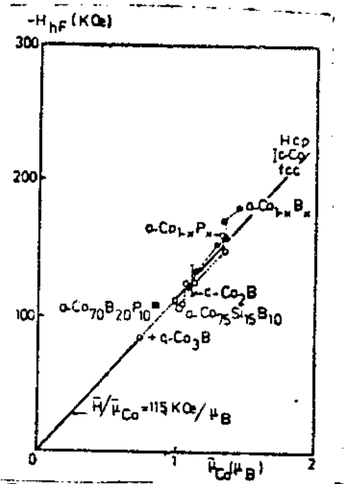

Fig. 1. H_{Co} versus Co moment in amorphous and crystalline Co based compounds.

at 4.2 K increases fairly linearly with the Co moment, yielding a hyperfine coupling constant value of 115 (± 10) kOe/μ_B (see fig. 1). This value was found to be 110 kOe/μ_B, independently of the P concentration, in amorphous Co–P alloys [15], and 125 kOe/μ_B in amorphous $Co_{100-x}B_x$ ($14 < x < 27$) alloys [16]. The $\bar{H}/\bar{\mu}$ ratio for amorphous $Co_{75}Y_{25}$ is the same as for a-Co–P alloys [17]. As shown in fig. 1, the Co hyperfine coupling value is not too drastically altered in Co based alloys with two sp elements such as P and B, or B and Si.

In fig. 2 are plotted the Fe hf versus the Fe moments for some Fe base crystalline compounds and amorphous alloys.

Let us analyze with more details the data for the various crystalline and amorphous compounds. The hyperfine coupling value is about 125 kOe/μ_B for Fe rich interstitial crystalline compounds. A linear $\bar{H}$ versus $\bar{\mu}$ relationship is obtained for the three Fe sites in Fe_3P as well as for the average Fe values in crystalline Fe_4N, Fe_3B, Fe_3C compounds (for references, see ref 11). Some departures from these regularities are observed when Fe content decreases in interstitial compounds, such as Fe_2P, FeB, $FeBe_2$. This might be due to some metallurgical difficulties in obtaining the correct stoichiometry (Fe_2P, FeB) or to a more efficient shielding of the Fe atoms by the interstitial elements ($FeBe_2$). The Fe $\bar{H}/\bar{\mu}$ ratio is significantly larger in crystalline Fe and for non-interstitial compounds such as Fe_3Si (sites I and II) and Fe_3Al (sites I and II), for which $\bar{H}/\bar{\mu}$ is about 155 kOe μ_B^{-1}.

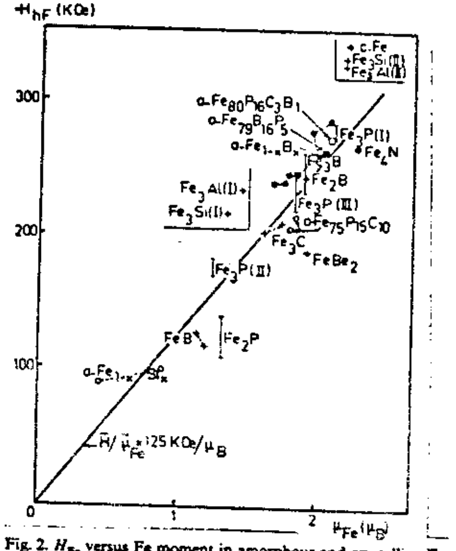

Fig. 2. H_{Fe} versus Fe moment in amorphous and crystalline Fe based compounds.

Similar trends are observed for Fe base amorphous alloys. In Fe based amorphous alloys with B, C, P, the Fe hf was found to scale with the Fe moment. In amourphous $Fe_{100-x}B_x$ alloys, this scaling is not perfect. Thus, the hyperfine coupling constant was found to be 125 kOe/μ_B for a-Fe_3B, and 140 kOe/μ_B for a-$Fe_{86}B_{14}$ [18]. The same trend was observed by Dubois [19]. An average value of 140 kOe/μ_B was obtained for a-$Fe_{100-x}B_x$ at 77 K by Franke et al. [20]. This proportionality seems to be preserved when C substitutes for B in a-$Fe_{84}B_{16-x}C_x$ ($2 \leq x \leq 10$) [21] or for P in a-$Fe_{80}P_{12.5}C_{7.5}$[22], where $\bar{H}/\bar{\mu}$ was found to be 135 kOe/μ_B. However, the Fe hf and the Fe moment were found to vary with concentration in an opposite way for the amorphous $Fe_{80}B_{20-x}C_x$ ($0 < x \leq 4$) [23] and also ~~far~~ for a series of $Fe_{84}B_{16-x}C_x$ ($0 < x \leq 4$) alloys [24]. These discrepancies might be attributable either to the approximate character of the $\bar{H}$ versus $\bar{\mu}$ relationship or to some short-range order effects in these ternary alloys. The Fe hyperfine coupling value was found to remain roughly constant when Be substitutes for B in a-$Fe_{82}B_{18-x}Be_x$ alloys [25] or when Si substitutes for B [19,24,26], in a-Fe–B–Si alloys.

For amorphous alloys of Fe with non-interstitial elements, the relationship between the Fe hf and the Fe moment is less evident than for Fe alloys with P, B, C. A rough proportionality between $\bar{H}$ (Fe) and $\bar{\mu}_{Fe}$ was reported for Fe rich Fe–Ge [27,28] and Fe–Y [29] amorphous alloys. However, there is some scattering among the $\bar{H}/\bar{\mu}$ values reported by different authors (125 and 147 kOe/μ_B, respectively, according to refs. 27 and 28. As indicated in fig. 2, the relationship between $\bar{H}$ (Fe) and μ_{Fe} is poorly defined in a-Fe–Si alloys [31]. Moreover, since the pioneering work of Sharon and Tsuet [32] on a-Fe–Pd–P alloys, it has been observed that the $\bar{H}/\bar{\mu}$ ratio is no longer constant over the concentration range close to the onset of ferromagnetism.

In conclusion, hyperfine fields and magnetic moments for ^{57}Fe and ^{59}Co in Fe based and Co based amorphous alloys with sp elements such as B, P, C are fairly proportional at least within the concentrated Fe or Co limits (72 to 84 at.%) yielding for ^{59}Co a hyperfine coupling constant of 115 to 125 kOe/μ_B (close to that for crystalline Co, i.e. 127 kOe/μ_B) and for ^{57}Fe a value for $\bar{H}/\bar{\mu}$ of 125 to 140 kOe/μ_B (slightly lower than the value for bcc Fe, i.e. 156 kOe/μ_B). These hyperfine coupling values are practically the same as those observed in compositionally related crystalline compounds, but they can significantly differ from those obtained for disordered Fe or Co based crystalline alloys. The proportionality between hf and magnetic moment for Fe and Co in amorphous alloys will be used in the following for various purposes, namely:

(i) to discuss the contributions to host hf in Fe and Co based amorphous alloys,

(ii) to analyze the effects of sp elements (B, P, C) on the host magnetic moments and hyperfine fields,

(iii) to explore the possibilities of obtaining some structural information from the hf distribution,

(iv) to determine the on-site moments in amorphous alloys containing two magnetic elements (Fe–Co, Fe–Ni, Fe–Mn base alloys).

(b) Contributions to the host hyperfine fields in Fe and Co based amorphous alloys with s–p elements. So far, we have neglected the sign of the ^{59}Co and ^{57}Fe hyperfine field. Nuclear orientation experiments on ^{59}Co in amorphous $Co_{80}P_{20}$ have ascertained that the sign of the field is negative [33]. Although it has not been verified to our knowledge, the ^{57}Fe hf sign is most likely negative as for ^{59}Co. On the basis of the quantitative relationship between hyperfine and magnetic moment, the different contributions to the hyperfine fields can be semi-quantitatively discussed.

It was first suggested that in amorphous alloys [9] and in related compounds [10] the conduction electron polarization contribution (local and non-local) to the ^{59}Co and ^{57}Fe hf might be very weak as compared with the core-polarization terms. This was recently argued in more details by Van Der Woude and Vincze [34] for Fe based amorphous alloys. We will discuss here the contributions to Fe hf in amorphous alloys. The Co hf contributions will be discussed in the following section along with the impurity hf in ferromagnetic amorphous hosts. By following Van Der Woude and Vincze [34], the hyperfine coupling constant ($\bar{H}/\bar{\mu}_{Fe} \simeq 130$ kOe/μ_B) is close to the experimental value for oxidic insulators where conduction electron polarization terms are absent. The case of amorphous Fe based alloys and related compounds would be therefore drastically different from that of pure crystalline Fe and of disordered Fe based alloys, such as Fe–Al, for example. For pure Fe and Fe alloys, half of the hf would originate from non-local contributions and, according to Van Der Woude and Vincze, a typical value for the core polarization contribution would be 65 kOe/μ_B. In amorphous Fe based alloys and related compounds, the cp polarization term would be twice that in pure Fe, while the neighbouring contribution (H_Σ) would be very small (~ 10%) and the local CEP contribution would be practically absent.

A different approach was recently proposed by Lines [35] for the hyperfine fields in iron–metalloid ferromagnetic metals. Instead of the aforementioned linear relationship between Fe hf and Fe moment, Lines claimed that the available data follow more closely the following relationship:

$$H(\mathrm{Fe}) = 90\ \mathrm{kOe}/\mu_B \times \bar{\mu} + 13\bar{\mu}^3, \tag{6}$$

where $\bar{\mu}$ is the average Fe moment.

The local hyperfine coupling constant would thus be about the same as that determined by Stearns for pure Fe [13] and therefore the local and non-local conduction-electron–polarization contributions would be non-negligible ($H_\Sigma/\bar{H}$ being 35 to 40% as in pure Fe).

The Lines's relationship (6) does not escape any criticism. It has been discussed in detail by Dubois [19]. In particular, it can be said that Lines's fit relies too much on compounds with low Fe moment, for which the relationship between hyperfine field and moment is less ascertained. On the other hand, the values for the on-site Fe moment are less firmly established than claimed by Lines. In addition, eq. (6) does not fit the data for Fe_3B and Fe_4N. From these reasons and others, it follows that relation (6) does not present the degree of universality and certainty given by its author. Nevertheless, the emphasis placed by Lines on the possibility of CEP contributions to host hf in Fe based amorphous alloys and related compounds deserves further discussion.

From available experimental data, there is little doubt that the neighbouring CEP contribution of Fe hf is not negligible. This can be deduced, for example, from the concentration dependence of the ^{57}Fe hf in $(Fe_xNi_{100-x})P_{14}B_6$ alloys. This composition effect was expressed by Chien et al. [36] as:

$$H_{Fe} = (232 + 33\bar{\mu})\text{kOe}. \tag{7}$$

The extrapolation to the dilute Fe limit was recently confirmed by Mössbauer experiments on an $Fe_4Ni_{34}Si_9B_{13}$ sample [37] which yielded an Fe hf value (at zero external field) of (230 ± 30)kOe. Within the dilute Fe limit, only the local contributions to Fe hf are of importance. It cannot be argued that the Fe moment would be smaller, the opposite is likely to be true [38]. Similar concentration effects were concluded by Sostarich et al. [39] for a-$(Fe_xNi_{1-x})_{80}B_{20}$ alloy, however with a somewhat smaller H_Σ contribution (10 to 20 kOe/μ_B). It seems then that the point of view of Van Der Woude and Vincze on the one hand and that of Lines on the other hand may represent two extreme descriptions of the Fe hf in amorphous alloys and related compounds. There might be some intermediate alternatives such as a CEP contribution which might be rather small (20 to 40 kOe/μ_B) as compared with the core-polarization one. The local and the non-local CEP contributions could more or less balance each other. A possible combination would be: $H_{loc} = H_{cp} + H_S^{loc} = -130$ kOe $+ 40 = -90$ kOe/μ_B, and $H_\Sigma = -40$ kOe/μ_B, so as to have about the same local hyperfine coupling constant as in pure Fe or in crystalline Fe_3Si [40] together with an overall coupling constant of about -130 kOe/μ_B.

(c) Mean hyperfine field and coordination number in the first atomic shell around the transition metal site. Since the work of Jaccarino and Walker [41], it has been widely admitted that the local environment about a transition metal site plays an important role in both the onset of a local magnetic moment and in its concentration dependence. This was verified in many substitutional and interstitial crystalline alloys and compounds. Owing to the relationship established between the mean hyperfine field and the local magnetic moments – at least for amorphous alloys of transition metals with interstitial-like elements (B, C, P) – is it then possible to use hyperfine field measurements in these alloys to probe local environments around the transition metal sites? Before the hyperfine field distribution can be analyzed in terms of coordination number distribution, some quantitative relationship between average hyperfine field and structure must be discussed. Amorphous alloys of interest for our discussion are constituted of Fe (or Co) with at least 15 at.% of s–p elements; the "non-magnetic" content is even larger for alloys with Si, Ge, or Y. In these circumstances, the probability for Fe (or Co) of having only Fe (or Co) atoms in the first atomic shell is negligibly small. The first question which has then to be answered is which one of the two coordination numbers (namely the number of parent atoms and the number of "non-magnetic" atoms) around the transition metal site is the most efficient parameter in determining the average hyperfine field. With respect to this problem, the situation is different in the crystalline cases depending on whether one deals with substitutional or interstitial compounds. It seems that a similar distinction must be made in compositionally related amorphous alloys.

In substitutional crystalline compounds such as Fe_3Si, Fe_3Al, the Fe moments and hyperfine fields are directly determined by the number of Fe first neighbours. This has been abundantly illustrated for Fe_3Si [40]. In amorphous Fe–Si alloys, the appearance of a Fe moment was related with the probability for a Fe atom of having at least six Fe first neighbours in the first atomic coordination shell [30]. Similar critical numbers were obtained in amorphous Fe–Ge [42], Fe–Sn [31,43], Fe–Sb [44] and Fe–Y [29]. For amorphous Fe–Y alloys [29], it was suggested that the Fe moment would increase with Fe neighbours from a few tenths of a Bohr magneton in sites with $Z_{Fe} = 6$ up to $2\mu_B$ in sites with $Z_{Fe} > 10$.

In interstitial crystalline compounds, the Fe moments and hyperfine fields are mainly determined by the metalloid (B, C, N) coordination numbers (Z_B, Z_C, Z_N). From a least squares fit of the available hf data on these various compounds, Dubois [19] obtained the following equations for H_{Fe} in kOe:

$$H_{Fe} = 375 - 36Z_B, \tag{8}$$

$$H_{Fe} = 376 - 57Z_C, \tag{9}$$

$$H_{Fe} = 374 - 73Z_N. \tag{10}$$

Experimental data on various Fe sites in Fe rich borides, carbides and phosphides crystalline compounds were analyzed by Lines [35] in a different way. Lines introduced an effective coordination number $Z_{eff} = \Sigma(C_M/R_{Fe-M})^n$, where R_{Fe-M} are the bond distances $R_{Fe-M} = R(M) - R(\text{Fe})$ (M being B, C, P), with the sum Σ running over all metalloid near neighbours, and the exponent n being empirically determined to be $n = 4.7$. By choosing the parameters C_M according to the ratio $C_c/C_B = 1.04$ and $C_p/C_B = 1.13$, Lines obtained for the on-site Fe moments a single function $\mu_{Fe} = f(Z_{eff})$. Values for C_M were taken as 2.18, 2.26 and 2.47 Å for B, C and P, respectively. The variation of H(Fe) for these various compounds as described by eq. (6) was then plotted versus Z_{eff} with μ_{Fe} as an implicit parameter. We discussed above the somewhat arbitrary character of Lines's phenomenological systematics. Applying such a "universal" relationship to hf values in amorphous alloys in order to obtain the "effective" metalloid coordination and then the real local environment seems to be a questionable approach.

A less ambitious approach is suggested by eqs. (8)–(10) for the Fe based interstitial crystalline compounds. By looking at the depression of H_{Fe} as a function of the metalloid coordination number, one can see that the effect of the metalloid environment is about the same for B, C and N when the coordination numbers are divided by the number of valence electrons (3, 4, 5, for B, C, N respectively). One then obtains for H_{Fe} in kOe:

$$H_{Fe} = 375 - 12\,Z_{ve}, \tag{8'}$$

$$H_{Fe} = 375 - 14\,Z_{ve}, \tag{9'}$$

$$H_{Fe} = 375 - 14.6\,Z_{ve}, \tag{10'}$$

where Z_{ve} is the number of valence electrons per formula for the metalloids.

In amorphous alloys, the average coordination number of metalloids (B) around a transition metal site can be estimated to vary as a function of x, the metalloid concentration, according to:

$$Z_B = Z_{TM}\frac{x}{(1-x)}, \tag{11}$$

where Z_{TM} is the number of TM atoms around the metalloid B.

The concentration dependence of the ^{59}Co hf in a-$Co_{100-x}B_x$ alloys can then be expressed as a function of Z_B. One B atom in the first atomic shell about a Co site depresses the ^{59}Co hf by 29.3 kOe, which makes about 10 kOe per valence electron. As shown in fig. 3, the concentration dependence of H_{Co} in a-Co–B, Co–B–Si and Co–P alloys can be plotted as a function of the number of s–p valence electrons per formula. One obtains an average slope of 135 kOe per valence electron.

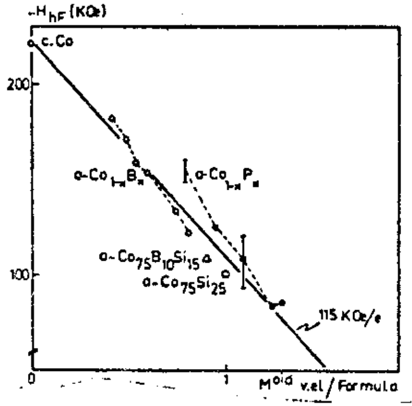

Fig. 3. H_{Co} versus number of valence electrons per formula in amorphous Co based alloys.

The data obtained by Franke et al. [20] on a-Fe–B alloys can be similarly plotted as a function of Z_B. One obtains a sloope of 26.7 kOe/B atom, which is significantly less than in crystalline Fe–B compounds (36 kOe/B atom, for $x > 25$ at.%). The concentration dependence of H_{Fe} can also be expressed as a function of Z_{ve} to give a gradient of 145 kOe/valence electron. The values of H_{Fe} for a-$Fe_{100-x}P_x$ alloys do not follow the same curve as for a-Fe–B alloys, as shown in fig. 4.

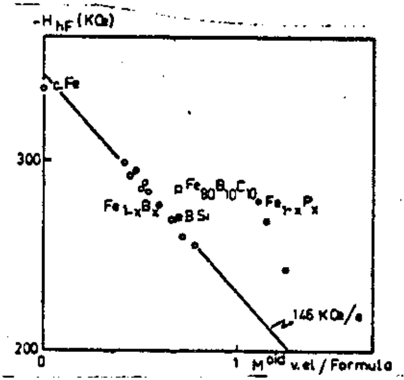

Fig. 4. H_{Fe} versus number of valence electrons per formula in amorphous Fe–B and Fe–P alloys.

In conclusion, it seems that the rough proportionality between Fe and Co hyperfine fields and the local moments is consistent with the predominant role played by the number of metalloid atoms around the transition metal sites in interstitial crystalline compounds and related amorphous alloys. This consistency must not be taken as a strict probe of the charge transfer model according to which the valence electrons from the s–p elements would fill up the empty states of the transition metal d bands. It has become clear from photoemission measurements that the concept of hybridization between sp and d bands is more realistic than the idea of charge transfer within a rigid band picture.

(d) Hyperfine field distribution and local atomic coordination. There is a common agreement among Mössbauer and NMR spectroscopists about the fact that the broad hyperfine field distributions observed in transition-metal-metalloid amorphous alloys reflect in some way the variety of possible environments about the *TM* sites. However, the hf distribution has been analyzed in various ways to give support to different structural models of metallic glasses. We will separately analyze the experimental hf distributions as obtained from Mössbauer spectroscopy and those determined by NMR measurements.

The hf distribution $P(H)$ is obtained from Mössbauer spectra as a result of complex fitting procedures. By forcing $P(H)$ to follow some analytical expressions determined *a priori*, one can be led to spurious conclusions, as happended in early Mössbauer experiments [45]. More recently, several fitting procedures [12,46,47] have been proposed to overcome the difficulties of extracting realistic hf distributions from broad Mössbauer spectra. Once a reasonable $P(H)$ is obtained, there are different ways to correlate $P(H)$ with the atomic structure. A first attitude is to analyze $P(H)$ without attempting any comparison with crystalline counterparts. Instead, the amorphous solid is regarded as a dense-random packing of hard spheres of the Bernal–Polk type. The hf distribution is then analyzed as the sum of contributions arising from Fe sites having the average Fe close-contact coordination of Bernal–Polk's liquid model. This analysis was succesfully carried out for the $P(H)$ of Fe in a-$Fe_{80}B_{20}$[48]. We saw above that the metalloid coordination about the Fe site is more effective than the Fe coordination in determining the Fe hf and moments in interstitial alloys and compounds.

A second attitude starts from the observation that the hf distribution encompasses the hf values for the different Fe sites in compositionally related compounds [49]. More recently, Vincze et al. [50] showed that $P(H)$ for a-$Fe_{75}B_{25}$ can be generated by assuming a gaussian broadening (with a half-width of 30 kOe) of the three lines corresponding to the three Fe sites (with $Z_B = 2, 3, 4$, respectively) in c-Fe_3B. The concentration dependence of the H_{Fe} in a-$Fe_{100-x}B_x$ $(15 \leqslant x \leqslant 25)$ is explained by a change in the relative intensities of these three contributions and by the onset of Fe clusters in Fe rich alloys. Irrespectively of the fabrication technique (sputtering versus liquid quenching) [51], the B coordination is thought to dominate the atomic-scale order together with the magnetic properties of the a-Fe–B alloys. The glass structure is then described as a "locally distorted nonstoichiometric Fe_3B quasicrystalline structure". More recently, ^{57}Fe Mössbauer spectra on liquid quenched a-$Fe_{100-x}B_x$ alloys $(12 \leqslant x \leqslant 25)$ were analyzed by Oshima and Fujita [52] within the same spirit as done by Vincze et al. However, by taking into account the effect of B atoms in the second atomic shell around an Fe atom, Oshima and Fujita were led to a different conclusion. According to these latter authors, a chemical order of the Fe_3B type develops only in near-stoichiometric alloys, but amorphous Fe–B alloys containing 16–19% B would have a high degree of short-range order of the bcc type. The most recent study by Dubois [19] of the hf distribution for ^{57}Fe in a-Fe–B alloys also concluded the existence of two different types of short-range order in these amorphous alloys. Alloys with B content larger than the eutectic composition $(x = 17.5$ at.%) are predominantly characterized by Fe sites with two or three borons in the first shell. The hf distribution for alloys containing less than 17 at.% would be the sum of two main contributions: one similar to that deduced for hypereutectic alloys, the other one arising from Fe atoms with no B atoms in the first atomic shell. Such a change in SRO around the eutectic composition might be related to the changes of slope reported for the density and for the bulk magnetization versus B content [53]. This could also explain the increase of the hyperfine coupling constant towards the pure Fe value when the B content decreases [54].

It seems that, even for amorphous alloys containing a glass former of the interstitial type, that the structural information that can be extracted from the hf distribution as provided from Mössbauer spectra have to be handled with care. An analysis of $P(H)$ in terms of the metalloid coordination about the *TM* site seems to be a reasonable approach. But any detailed interpretation needs to be ascertained by complementary experiments, such as small-angle X-ray or neutron scattering.

In the case of Fe based amorphous alloys with substitutional-like elements, the H_{Fe} distribution deduced from Mössbauer spectra for alloys in the concentration range for the appearance of ferromagnetism exhibits a low field contribution arising from "non-magnetic" Fe atoms [55]. This contribution can provide some information about the Fe coordination at the Fe sites through the critical number of Fe n–n required for Fe to carry a moment. By studying this low-field contribution as a function of composition, one can obtain a hint about the concentration dependence of the transition-metal coordination on the *TM* sites.

The spin–echo NMR technique presents some advantages as compared with Mössbauer spectroscopy in the sense that the hf distribution is directly obtained without fitting procedures. When measured in low excitation field conditions, all the ^{59}Co NMR spectra to date in Co based amorphous alloys have exhibited structures [2,9,56–59]. This point is analyzed with more detail by Panissod et al. [59]. These structures in the hf distribution for binary alloys can be easily related to a well-defined type of Co environment, through the average value of their hf contribution. However, the relative intensities of these contributions are not directly related to the number of Co nuclei experiencing these different types of local coordination. Nevertheless, some qualitative conclusions can be drawn from the ^{59}Co NMR spectra available so far for amorphous ferromagnetic alloys:

(i) the existence of these structures in the Co hf distribution and the concentration dependence of these structures imply some medium-range atomic correlations, which cannot be easily explained within a Bernal–Polk type of structure for metallic glasses. An approach of the Gaskell-type [60] would be more appropriate;

(ii) the ^{59}Co hf distribution in a-Co_3B cannot be generated by a simple broadening of the ^{59}Co spectrum in c-Co_3B [61];

(iii) the role of the metalloid coordination about the transition metal sites is of particular significance for both the structural and the magnetic properties of these amorphous alloys containing s–p elements. This can be illustrated by comparing the Co hf distribution in a-Co_3B and in a-$Co_{79}P_{13}B_8$, where Co carries the same average moment [62].

2.1.2. Changes in Fe hyperfine field due to Cu or transition metal impurities substituted for Fe in amorphous Fe based alloys

A great deal of experimental and theoretical work has been devoted to the study of the influence of dilute transition metal impurities on the magnetic properties of crystalline Ni, Co, Fe [63]. Results were best interpreted within the framework of the virtual bound state model of Friedel [64]. Hyperfine field measurements performed on the host yield information about the strength and the range of the magnetic perturbation created around the impurity sites.

The shift of the average Fe hf as a function of impurity concentration was studied by Mössbauer spectroscopy in a-$(Fe_{100-x}TM_x)_{79}P_{13}B_8$ alloys (with $1 \leqslant x \leqslant 4$ at.%, $TM =$ Ni, Co, Mn, Cr, V) [65]. These data together with the bulk magnetization results obtained on the same samples [38] resemble those obtained for the same impurities diluted in crystalline interstitial compounds such as Fe_3C, Fe_2B, Fe_3P, but they are in contrast with those obtained in αFe. Recently, Kemeny et al. performed the same study for Cu, Ni, Co, Cr, V and Ti diluted in a-$Fe_{78}B_{12}Si_{10}$ [66]. Their data are illustrated in fig. 5. As noted before [65], the varia-

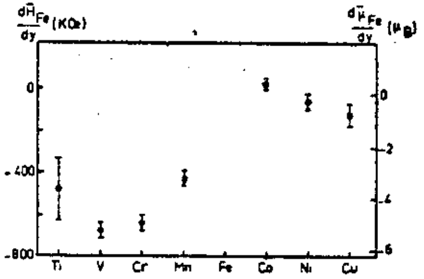

Fig. 5. Gradient of Fe hyperfine field and Fe moment for Cu and transition metal impurities in amorphous $Fe_{78}B_{12}Si_{10}$ (after ref. 66).

tion of the mean Fe hf and magnetic moment with *TM* dilute impurities is different from that observed in α-Fe where both d subbands are partially empty at the Fermi level. This variation is rather similar to that obtained in the crystalline Ni host, where only the d↓ subbands are partially empty at E_F. In both the Fe–P–B and Fe–B–Si hosts, the $P(H)$ for Fe remains unperturbed for Ni and Co substitutions, while $P(H)$ is strongly perturbed by the substitution of a few per cent of Cr and V. Intermediate perturbations are created by Mn impurities.

The effects on $\bar{H}_{\mathrm{Fe}}$ of transition metal substitutions over large concentration ranges have also been studied in several Fe based amorphous alloys. Ni substitution was investigated in a-$\mathrm{Fe}_{81}\mathrm{b}_{19}$ [67], a-$\mathrm{Fe}_{80}\mathrm{B}_{20}$ and a-$\mathrm{Fe}_{80}\mathrm{B}_{19}\mathrm{Si}_1$ [39], in a-$\mathrm{Fe}_{80}\mathrm{P}_{14}\mathrm{B}_6$ [36], in a-$\mathrm{Fe}_{75}\mathrm{B}_{25}$ [68] and in a-$\mathrm{Fe}_{77}\mathrm{Si}_{10}\mathrm{B}_{13}$ [69]. The concentration dependence of $\bar{H}_{\mathrm{Fe}}$ is practically the same in amorphous and crystalline $(\mathrm{Fe}_{1-x}\mathrm{Ni}_x)_{75}\mathrm{B}_{25}$ alloys [68], as shown in fig. 6, and it is mainly governed by the B content [67]. The change in $\bar{H}_{\mathrm{Fe}}$ is rather small for a one-Fe-to-one Ni substitution (very large in a-$\mathrm{Fe}_{40}\mathrm{Ni}_{40}\mathrm{B}_{20}$ [70]), but the conclusions that can be drawn from this fact are not straightforward, since Ni carries a moment in Ni concentrated alloys [39].

The effect on $\bar{H}_{\mathrm{Fe}}$ of Co substitution was studied in a-$\mathrm{Fe}_{81}\mathrm{B}_{19}$ [67] and in a-$\mathrm{Fe}_{80}\mathrm{B}_{20}$ [71]. The concentration dependence of $\bar{H}_{\mathrm{Fe}}$ follows the empirical relation:

$$\bar{H}_{\mathrm{Fe}} = (268 + 10.2\,\bar{\mu})\,\mathrm{kOe}, \tag{12}$$

with μ being the moment per transition metal atom.

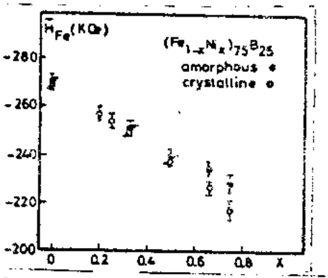

Fig. 6. Concentration dependence of $\bar{H}_{\mathrm{Fe}}$ in amorphous and crystalline $(\mathrm{Fe}_{1-x}\mathrm{Ni}_x)_{75}\mathrm{B}_{25}$ compounds (after ref. 68).

By assuming that μ_{Fe} remains constant, eq. (12) reads:

$$\bar{H}_{\mathrm{Fe}} = (134\mu_{\mathrm{Fe}} + 10.2\,\mu)\,\mathrm{kOe}. \tag{12'}$$

However these Mössbauer data should be analyzed again by taking into account the concentration dependence of the Co moment as can be determined by NMR [62].

The substitution of Mn for Fe was studied in a-$\mathrm{Fe}_{75}\mathrm{P}_{16}\mathrm{B}_6\mathrm{Al}_3$ [72–73] and in a-$\mathrm{Fe}_{75}\mathrm{P}_{15}\mathrm{C}_{10}$ [74]. The hf distribution for Fe is strongly perturbed when 10 and more at.% Mn substitute for Fe, and $P(H)$ exhibits a low-field component which rapidly increases with Mn content to give rise to a spin-glass-like behaviour when x_{Mn} reaches the range of about 30 at.%. The effects on $\bar{H}_{\mathrm{Fe}}$ of the Mn substitution is made especially complicated owing to the different magnetic states of Mn in these alloys as will be discussed below.

The Fe hf distribution is also strongly perturbed when Cr substitutes for Fe in a-$\mathrm{Fe}_{32}\mathrm{Ni}_{36}\mathrm{Cr}_{14}\mathrm{P}_{12}\mathrm{B}_6$ [75] and in a-$\mathrm{Fe}_{85-y}\mathrm{Cr}_y\mathrm{B}_{15}$ alloys [76]. The concentration dependence of $\bar{H}_{\mathrm{Fe}}$ is expressed as:

$$\bar{H}_{\mathrm{Fe}} = (294 - 7y)\,\mathrm{kOe} \tag{13}$$

or, by assuming that μ_{Fe} remains constant

$$\bar{H}_{\mathrm{Fe}} = (70\mu_{\mathrm{Fe}} + 69\bar{\mu})\,\mathrm{kOe}, \tag{13'}$$

Although it was deduced by Kemeny et al. [66] that μ_{Cr} is about zero within the dilute limit, the analysis of the H_{Fe} concentration dependence is difficult due to possible short-range effects. The dependence of H_{Fe} in crystalline $\mathrm{Fe}_{100-x}\mathrm{Cr}_x$ was found to be [77]

$$\bar{H}_{\mathrm{Fe}} = (118\mu_{\mathrm{Fe}} + 9\bar{\mu})\,\mathrm{kOe}. \tag{14}$$

This discrepancy might be more an alloying effect than a structural consequence.

The effect on H_{Fe} of the Mo substitution was also studied in some detail in a-$\mathrm{Fe}_{75}\mathrm{P}_{16}\mathrm{B}_6\mathrm{Al}_3$ [78] and in a-$\mathrm{Fe}_{80}\mathrm{B}_{20}$ [79,80]. Again, discrepancies with the behaviour of crystalline $\mathrm{Fe}_{100-x}\mathrm{Mo}_x$ alloys are noted. The Mo atoms are not likely to carry a substantial moment in a-$\mathrm{Fe}_{80}\mathrm{B}_{20}$, so that the mean Fe hf is found to vary as $\bar{H}_{\mathrm{Fe}} = 140\ \bar{\mu}_{\mathrm{Fe}}$(kOe) [80]. However, a low-field component is observed in $P(H)$ when x_{Mo} is larger than 5 at.%, which may suggest strong short-range order effects [78].

To summarize the results of the study of the host magnetic perturbations created by the substitution of *TM* for Fe in amorphous Fe based alloys, some qualitative conclusions can be proposed:

(i) the effects of *TM* impurities on H_{Fe} are significantly different in crystalline Fe and in amorphous alloys of Fe with s–p elements. This seems to be an alloying effect more than the signature of the amorphous state;

(ii) short-range order effects in the Fe hf distribution (visible even in dilute Fe based crystalline alloys) are likely to be amplified in amorphous hosts with about 20 at.% of s–p elements.

2.2. Host hyperfine fields in rare-earth based amorphous alloys

Experimental hf studies through Mössbauer and NMR spectroscopy on rare-earth based amorphous alloys are rather scarce as compared with those carried out on transition-metal based alloys. Early hf studies have already been reviewed in detail [81]. We will summarize only the most recent work on amorphous alloys based on S and non-S state rare-earth ions.

2.2.1. Amorphous alloys based on S-state rare-earths (Eu^{2+}, Gd^{3+})

Eu is divalent in a-$\mathrm{Eu}_{80}\mathrm{Au}_{20}$ [82]. Eu^{2+} and Gd^{3+} are S state ions. Their hyperfine field can be expressed as for transition metals by the sum of a local contribution (conduction electron polarization and core polarization) and of a non-local contribution according to eq. (4). Differences between H_{Eu} and H_{Gd} are usually attributed to the additional conduction electron in Gd^{3+}.

The hyperfine field on Eu^{2+} in a-$\mathrm{Eu}_{80}\mathrm{Au}_{20}$ was studied by Mössbauer and NMR spectroscopy [82]. The average hf $\bar{H}_{\mathrm{Eu}}$ was independently determined from both techniques to be 160 kOe. Substitution of Yb for Eu in a-$\mathrm{Eu}_{60}\mathrm{Yb}_{20}\mathrm{Au}_{20}$ results in an increase of $\bar{H}_{\mathrm{Eu}}$ ($\bar{H}_{\mathrm{Eu}} = 175$ kOe, according to Mössbauer measurements) [83], yielding an estimate of the non-local conduction-electron polarization contribution [$H_\Sigma = (+60 \pm 20)$kOe]. This transferred hyperfine field term, usually described by a "long-range" RKKY interaction, does not seem to be drastically damped by the very short electronic mean-free path in this amorphous alloy. Indeed, let us recall that $H_\Sigma = +200$ kOe in c-Eu–Pd_2, and $H_\Sigma = -115$ kOe in Eu metal). The core-polarization term H_{cp} is thought to be the same for Eu^{2+} and Gd^{3+} ions, $H_{\mathrm{cp}} = -340$ kOe. The local CEP contribution is then about +130 kOe. These latter values compare reasonably with systematics established in crystalline intermetallic Eu compounds. The amorphous nature of $\mathrm{Eu}_{80}\mathrm{Au}_{20}$ is reflected by the distribution of H_{Eu}. In this particular alloy with a large (but well defined) value of the electric quadrupole parameter and with a unique value (or very narrow distribution) of the Eu^{2+} isomer shift, the hf distribution is accounted for by directional fluctuations of the CE polarization as a function of radial distance from Eu sites. The modulus of $|H_S^{\mathrm{loc}}|$ and of $|H_\Sigma|$ are constant. But $|H_{\mathrm{hf}}| = |H_{\mathrm{loc}} + H_\Sigma|$ depends on the angle between the field and the average CE polarization. Narrow fluctuations of angle α can generate the experimental H_{Eu} distribution.

For Gd in a-$\mathrm{Gd}_{80}\mathrm{Au}_{20}$, an average value of hf has been determined by Mössbauer spectroscopy [83]: $H_{\mathrm{Gd}} = -(320 \pm 50)$kOe. Analysis of the data suggests that the local hf contribution is comparable with that in Gd metal: $H_{\mathrm{cp}} + H_S^{\mathrm{loc}} = -170$ kOe. The non-local contribution would be $H_\Sigma = -170$ kOe. Due to the amorphous character of the alloy, these two contributions add non-collinearly to give $\bar{H}_{\mathrm{Gd}} = -320$ kOe. The negative sign of H_Σ for Gd in $\mathrm{Gd}_{80}\mathrm{Au}_{20}$, opposite to the sign found for Eu^{2+} in $\mathrm{Eu}_{80}\mathrm{Au}_{20}$, might suggest that the exchange interactions in $\mathrm{Gd}_{80}\mathrm{Au}_{20}$ are mediated by d-like conduction electrons. The H_{Gd} distribution in a-$\mathrm{Gd}_{80}\mathrm{Au}_{20}$ can be accounted for the same way as for Eu in a-$\mathrm{Eu}_{80}\mathrm{Au}_{20}$.

2.2.2. Dy based amorphous alloys

Among non-S state rare-earth ions, only Dy has been the subject of hyperfine studies in rare-earth based amorphous alloys. Early Mössbauer experiments showed evidence for a competition between the orientation of the moment and that of the random anisotropy axis, resulting in non-collinear magnetic structures. On the other hand, it has been shown that the hf average values for Dy in amorphous alloys and crystalline counterparts are practically the same, owing to the fact that the 4f shell is well shielded from the influence of neighbouring atoms. A slight distribution of Dy hf (with a width of about 1%) is observed in amorphous alloys. More details can be found in the reviews of ref. 81.

More recent Mössbauer studies have made a comparison between relaxation effects on ^{161}Dy in amorphous and crystalline Dy–Ag [84]. The crystalline Dy–Ag is antiferromagnetic below $T_N = 60$ K, while the amorphous modification is ferromagnetic below $T_c = 18$ K. A quite different behaviour is observed in the two samples. In c-Dy–Ag, the magnetic pattern disappears around T_N, while in a-Dy–Ag it subsists well above T_c vanishing only around 140 K. This feature is interpreted as an effect of slow relaxation in the amorphous sample. It is suggested that at low temperature one tends towards a quasi-continuum of electronic states for a large number of coupled spins. Cross-relaxation could then occur within such groups of spins. This might be correlated with magnetic viscosity effects observed in a-Dy–Ag by bulk magnetic measurements at low temperature.

3. Impurity hyperfine fields

3.1. Magnetic impurities (Ni, Co, Mn) ferromagnetic amorphous alloys

3.1.1. H_{Ni} in amorphous $(Fe_xNi_{1-x})_{80}B_{20}$ alloys

The Ni hyperfine field was determined by ^{61}Ni Mössbauer spectroscopy on amorphous $Fe_{60}Ni_{20}B_{20}$, $Fe_{40}Ni_{40}B_{20}$ and $Fe_{20}Ni_{60}B_{20}$ alloys [39]. The relative width of the H_{Ni} distribution was found to be larger than in the case of Fe reaching 40% and 60% for the Ni_{20} and Ni_{40} samples, respectively. By making reasonable assumptions about the concentration dependence of μ_{Fe}, then μ_{Ni} can be estimated as was done in ref. 38. The concentration dependence of H_{Ni} can then be expressed as:

$$H_{Ni} = (20\mu_{Ni} + 100\bar{\mu})\ \text{kOe}. \tag{15}$$

A linear extrapolation to $x = 1$ gives a value of about 170 kOe for dilute Ni in a-Fe–P–B. This value is very close to that of H_{Ni} in c-Fe_3Si (160 kOe), but it differs markedly from that of H_{Ni} in α-Fe (234 kOe). The main contribution to H_{Ni} in a-$Fe_{80}B_{20}$ seems to arise from non-local CE polarization.

3.1.2. H_{Co} in amorphous ferromagnetic alloys

The Co hyperfine field in Co diluted ($x > 1$) amorphous $(Fe_{100-x}Co_x)_{79}P_{13}B_8$ alloys was studied by spin–echo NMR spectroscopy [62]. H_{Co} was also determined by NMR in a Co diluted Gd_2Ni amorphous alloy and in a series of $Gd_{100-x}Co_x$ amorphous alloys [85].

(a) H_{Co} in amorphous Fe–P–B alloys [62]. The average $\bar{H}_{Co}$ in amorphous Fe–P–B alloys within the dilute Co limit is about 200 kOe at 1.4 K. Again, this value is close to that of H_{Co} in c-Fe_3Si (193 kOe) [40], but far from that of H_{Co} in α-Fe (288 kOe).

The H_{Co} distribution is broad, but it is mainly quadrupolar in origin, with a quadrupole frequency close to that observed for Co diluted in crystalline Fe_3P [86]. This implies in turn that the magnetic distribution is exceptionally narrow. This latter feature might suggest for Co in a-Fe–P–B a preferential site substitution similar to that reported for transition metals in crystalline Fe_3P [87].

The concentration dependence of H_{Co} was measured in a-$(Fe_{100-x}Co_x)_{79}P_{13}B_8$ ($1 \leq x \leq 100$). As shown in fig. 7, the variation of H_{Co} content is very similar to that deduced from Mössbauer studies and bulk magnetic measurements on c-$(Fe_{1-x}Co_x)_2B$ [88].

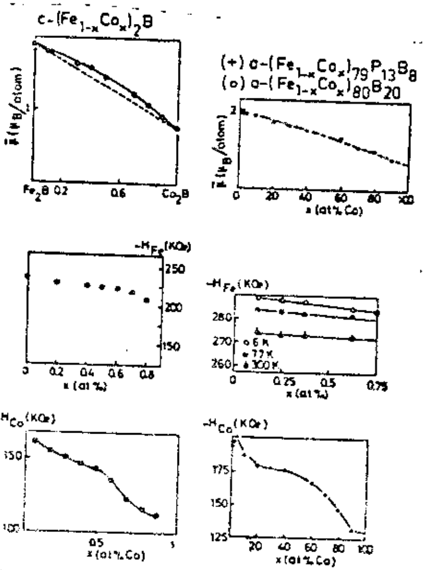

Fig. 7. Concentration dependence of average moment and average Fe and Co hyperfine fields in amorphous $(Fe_{100-x}Co_x)_{79}P_{13}B_8$ alloys (after refs. 62 and 71 and in crystalline $(Fe_{1-x}Co_x)_2B$ (after ref. 88).

(b) H_{Co} in amorphous $Gd_{67}Ni_{29}Co_4$ and in amorphous $Gd_{100-x}Co_x$ alloys [85]. The Co hf in amorphous $Gd_{67}Ni_{29}Co_4$ is 75 kOe at 1.4 K. In a-$Gd_{67}Co_{33}$, the H_{Co} distribution exhibits the same peak at 75 kOe, but an assymmetry develops on the low-field side. In a-$Gd_{63.5}Co_{36.5}$ and $Gd_{60}Co_{40}$ the H_{Co} distribution exhibits a second peak on the low-field side (between 5 and 30 kOe) while the position of the main peak at 75 kOe remains unchanged. From NMR experiments under external field, it is unambiguously concluded that these hyperfine fields are positive with respect to total magnetization. From comparison with the case of dilute Co in Gd and with the H_{Co} in crystalline Gd_4Co_3 and $GdCo_2$ compounds, it appears that the relationship between H_{Co} and the Co moment in the Gd–Co system is not simple. This might imply that local and non-local contributions to H_{Co} would be of the same order of magnitude. On the other hand, the great sensitivity of the H_{Co} with respect to composition over the 33–40 at.% Co concentration range suggests the appearance of different kinds of short-range order in the amorphous Gd–Co alloys, as has been observed by Mössbauer spectroscopy in amorphous Y–Fe alloys of similar compositions [89].

3.1.3. H_{Mn} in amorphous Fe–P–B and Fe–P–B alloys [16]

The Mn hyperfine field was determined by NMR in dilute $(Fe_{100-x}Mn_x)_{79}P_{13}B_8$ ($1 \leq x \leq 4$) and in more concentrated $(Fe_{100-x}Mn_x)_{75}P_{15}C_{10}$ ($x = 10$ and 20) amorphous alloys. Within the dilute limit a main contribution arises at around 260 kOe, which is the H_{Mn} value in c-Fe_3Si [40]. Strong quadrupolar effects are visible with a quadrupolar frequency very close to that observed for Co in a-Fe–P–B alloys, once an appropriate correction is made for the different quadrupole nuclear moments.

When the Mn content increases above 1 at.%, it becomes clear that the complex Mn NMR spectrum arises from three different contributions, namely that at 260 kOe which corresponds to the dilute limit, another one at about 330 kOe, and a low-field distribution ranging from 50 to 200 kOe. This latter contribution becomes dominant at higher Mn concentrations. These results are reminiscent of those obtained for H_{Mn} in crystalline Ni [90] where the low-field contribution was shown to arise from Mn atoms with moments antiparallel to the Ni moment.

3.2. Non-magnetic impurities in ferromagnetic amorphous alloys

3.2.1. Hyperfine fields on s–p elements in Fe based amorphous alloys

Hyperfine fields at ^{31}P nuclear sites were measured by NMR in a-$Fe_{75}P_{15}C_{10}$ [91] and in a-$Fe_{79}P_{13}B_8$ by using ^{56}Fe and ^{10}B enriched isotopes. In both alloys, H_P was found to be 27 kOe, in marked contrast with H_P in α-Fe (132.5 kOe) [92]. The hyperfine field for ^{11}B in a-$Fe_{80}B_{18}Ga_2$ is 26.4 kOe from NMR measurements [11]. Furthermore, H_B was found to increase with B content in the $Fe_{79}P_{21-x}B_x$ series to give in the dilute B limit, $H_B = 23.4$ kOe. Similar behaviour was reported for Al in crystalline $Fe_3Si_{1-x}Al_x$ compounds, where H_{Al} increases in magnitude when Al substitutes for Si [93].

From ^{11}B NMR measurements in amorphous $Fe_{80}B_{20}$, $Co_{80}B_{20}$ and $Fe_{80-x}Ni_xB_{20}$ alloys, $\bar{H}_B$ was found to be 24.6, 8.5 and about 5 kOe in Fe, Co, Ni based alloys, respectively [94], yielding CEP hf constants of 11.7, 6.5 and 10 kOe/μ_B, respectively. Moreover, $\bar{H}_B$ scales with the average magnetic moment $\bar{\mu}$ in amorphous $Fe_{80-x}Co_xB_{20}$ and $Fe_{80-x}Ni_xB_{20}$ alloys.

3.2.2. Hyperfine field on Au in amorphous $Eu_{80}Au_{20}$ and $Gd_{80}Au_{20}$

The transferred hyperfine field at Au sites in a-$Eu_{80}Au_{20}$ and $Gd_{80}Au_{20}$ alloys was determined by ^{197}Au Mössbauer spectroscopy [83]. H_{Au} was found to be the same in both alloys and very close to that of dilute Au in crystalline Gd [95]. This is consistent with the RKKY model predictions for transferred hf, since, according to the isomer shift values, the electron densities at Au are nearly the same in concentrated amorphous alloys and in diluted crystalline alloys. This suggests similar CE spin polarization parameters in these different systems. The 5d electron of Gd would influence the transferred field at the Gd site (H_Σ), but its effect at the Au site is weak.

4. Conclusion

To summarize the various information that can be obtained on metallic glasses through hyperfine field measurements, one might usefully distinguish the domains of electronic structure, magnetic structure and atomic structure.

4.1. Electronic structure

A detailed knowledge of the electronic structure of metallic glasses which would allow a calculation of the various contributions to the hyperfine field in these alloys is still missing. However, an estimate of these contributions is possible in favorable cases. One then realizes that the effect of amorphous disorder on the average hyperfine field values is minor, when the amorphous alloy is compared with appropriate crystalline counterparts. For example, H_{Fe} in Fe based amorphous alloys may differ from H_{Fe} in α-Fe, but its contributions are very much the same as in interstitial Fe based crystalline compounds. Similarly, the hf for transition-metal impurities in Fe based amorphous alloys are about the same as in crystalline $\mathrm{Fe_3Si}$, although significantly different from those in α-Fe. This implies a great similarity between the electronic structure of these amorphous alloys containing s–p elements and that of compositionally related compounds. Experimental hf data on amorphous alloys made of two transition metals are too scarce so far to anticipate whether these similarities with crystalline counterparts are as strong as in metal–metalloid alloys.

4.2. Magnetic structure

The hyperfine field coupling constant $\overline{H}/\overline{\mu}$ is sufficiently established to allow a determination of the on-site moments, at least for amorphous alloys containing interstitial-like elements. In some cases, the hf distribution can then be related to different magnetic sites. In rare-earth based amorphous alloys containing non-S state ions, the Mössbauer spectroscopy has proved a unique tool in studying the non-collinear magnetic structures generated by the random local anisotropy.

4.3. Atomic structure

The hf distribution, when correlated to hf studies of crystalline counterparts, can yield very useful information about the local coordination at the transition metal sites of amorphous alloys, especially when these alloys contain interstitial-like elements. NMR spectra in ferromagnetic amorphous alloys can yield information about the medium-range order over a scale corresponding to the width of the Bloch walls. In any case, these invaluable data need to be interpreted in relation with those obtained from various techniques, including small-angle scattering and high-resolution microscopy.

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