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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

AMORPHOUS METALLIC ALLOYS

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Amorphous metallic alloys.

Bibliography.

① General (including technical aspects)

Proceedings: Rapidly Quenched Metals
1. Brela (1972)
2. MIT (1975) - (MIT Press)
3. Brighton (1978) - (The Metals Society, London)
4. Sendai (1981) (in press).

Liquid & Amorphous Metals
LAM 4 - Grenoble (1980) - J. Phys. (Paris) - Coll.

Metallic glasses - Science & Technology (Budapest, 1976)

Books.
- Metallic glasses (American Society of Metals, 1976 (edit. ASM, Metals Park, Ohio, 1978)
- Glassy Metals I, edit. H.J. Güntherodt and H. Beck, (Topics in Applied Physics 46, Springer Verlag, Berlin 1981).

Reviews:
- R.W. Cahn, Cont. Phys. 21, 43 (1980)
- H.S. Chen, Rep. Prog. Phys. 43, 353 (1980)

② Magnetic properties.

Proceedings: Amorphous Magnetism (Plenum Press, vol. 1, 1973; vol. 2, 1977, N.Y.)
Intermag (IEEE Trans. Magn.)
MMM (J. Appl. Phys., march)

Books.
- H. Hauptrich & S. Kobe. Amorphe Ferro- und Ferrimagnetika (Akademie Verlag, Berlin 1980)
- Applications of Nuclear Techniques to the Studies of Amorphous Metals, edit. U. Gonser, (IAEA, Vienna 1981)
- Id. (Balatonfüred, Hungary, 1981) (Central Research Institute for Physics, Budapest, 1981).
- Liquid and Amorphous Metals, edit. E. Lüscher and H. Coufal (Sijthoff & Noordhoff, Holland) (1980).
- in Ferromagnetic Materials, vol. 1, edit. E.P. Wohlfarth (North-Holland, 1980). Chap. 6, by F.E. Luborsky
- in Handbook of P. & C. of R.E., edit. K. Gschneidner and L. Eyring (North-Holland), vol. 2, ch. 16, by J.J. Rhyne.

INTRODUCTION

① Different techniques of fabrication.

- Chemical (electroless) deposition:
  Ni P, Co P, Ni B, Co B...
- Electrodeposition:
  Ni P, Co P, Fe P, ...
- Evaporation, coevaporation,
  under high vacuum, into cold substrate
- Sputtering.
- Liquid quenching.
- Spark erosion (powders)
- Laser glazing (surfaces).
- Ion implantation. etc...

② Different domains of feasibility & stability.

"Pure" TM": Co, Ni, Fe

EVAPORATION $T_X \simeq 70$ °K.

Fe Si, Fe Ge, from 20.25 at% Si (Ge)
up to 100 — Si (Ge).

Fe B $15 \leq x_B \leq 100$

- SPUTTERING

Broad concentration ranges. Ex. RE Co
$(40 \leq x_{Co} \leq 80)$

- LIQUID QUENCHING.
  « TM. metalloid alloys : ~ eutectic. | Fe B, Pd Si
  « RE. NM (Cu, Ag, Au) } ~ eutectic.
  RE. Al
  - U Fe, U Co, U Cr ~ eutectic.
  « Cu Zr $(20 \leq x \leq 80)$
  « Co base alloys (very broad conc. ranges)
- Ion implantation ?.

③ Different families of materials

- Pure TM.
- Alloys of TM with sp elements: Fe B, Pd Si
- Alloys Mg Zn, Ca Mg (N-N)
- Alloys Ni Nb, Fe Zr (T_L-T_E)
- Alloys RE-N (RE Al), RE-MN (RE Au)
  RE-T_L (RE-Co)
- Alloys U Fe, U Co, ...
  etc...

(4) Are those alloys "amorphous" in the same sense?

- "glassy" ⇔ liquid quenched ⇔ T_g
- "amorphous" ⇔ no T_g (so far) ⇔ evaporated

(5) Are the properties (magnetic properties) related to the techniques of preparation or to the size of the samples rather than to the amorphous nature?

Ex. Influence of the size of the sample.

Small particles of a. $Fe_{75}Si_{15}B_{10}$ (Berkowitz et al., P.R.L. 1981)

Ex. Influence of the techniques of preparation.

a. YFe_2 - $T_c < 3.5$ °K (J.J. Rhyne et al. Phys. Rev. B 10, 4672 (1974))

sputtered $T_c \simeq 90$ °K [J. Chappert et al., J. M.M.M. 7, 175, (1978)]

liquid quenched $T_c = 270$ °K.

evaporated $T_c = 400$ °K [K. Lee and co., AIP Conf. Proc. 34, 100 (1975)]

c. YFe_2 $T_c = 548$ K

[J.J. Croat and J.F. Herbst, J. Appl. Phys. 53, 2294 (1982)]

In the previous examples:

- $\bar{\mu}_{Fe}$ decreases with size of amorphous particles and for equal sizes $\bar{\mu}_{Fe}$ (particles) < $\bar{\mu}_{Fe}$ (ribbons)
- Tremendous variation of T_c in various amorphous YFe_2 samples

What is responsible for such variations of the magnetic properties?

different types of disorder (chemical or topological)?

different degrees of disorder?

or variations in the short. range order (SRO)? (chemical or topological)?

More generally, there are:

- cases where T_c changes drastically between crystalline phases (Laves phases, Heusler alloys) and amorphous modifications [T_c (amorphous) decreases or increases]. Is it due to the lack of periodicity or to a change in SRO?
- cases where T_c is slightly affected by structural disorder. Does it simply that the SRO of crystalline counterparts is preserved in the amorphous state?

Outline of lectures.

I. Magnetic properties as local probes of SRO in amorphous alloys.

1) Local measurements (NMR, Möss-bauer ...) : EFG in paramagnetic alloys.
   - concentration fluctuations ("medium-range" scale) in ferromagnetic alloys.

2) Bulk measurements [$\chi(T)$, $M(o,H)$, $C_v(T)$, etc...]
   - "crystal field" effects in amorphous alloys with dilute RE.
   - various concentration effect (mainly, on T_c)

II. Effects of disorder on magnetic properties

1) From the emergence of a moment to the onset of ferromagnetic order.
   - Moment formation
   - Kondo effect
   - Spin glasses, cluster glasses, etc...
     (magnetic & transport properties)
   - Magnetic phase diagrams.

2) Transition-metal base ferromagnetic amorphous alloys.
   - Alloying effects on the moment at 0 K
   - Hyperfine fields at 0 K
     in amorphous matrices
     on impurities diluted in am. matrix

3) Rare-earth base magnetic alloys.

Conclusion.

- Alloying effects, chemical disorder versus topological disorder.
- Disorder versus SRO in amorphous metallic alloys.

Implications on structural models.

Part I

MAGNETIC PROPERTIES AS PROBES OF ATOMIC STRUCTURE IN AMORPHOUS METALLIC ALLOYS.

INTRODUCTION

SRO
- Coordination numbers : $Z_i(j)$ and $\Delta Z_i(j)$ } RADIAL
- Interatomic distances : $r_i(j)$ and $\delta r_i(j)$ } RADIAL
- Local symmetry — DIRECTIONAL

Magnetic properties

- Bulk : magnetic moment ($\vec{H}$) : $\vec{\mu}$ } ⇒ RADIAL (+ EFG)
  T_c
- Local : Mössbauer, neutrons, NMR
  - μ_{local}
  - $\vec{H}$
  - $P(H)$
  - I.S.
  - Pressure dependence.

  } ⇒ RADIAL (+ EFG) + ("medium range" information)

I. LOCAL MEASUREMENTS

[A] Studies of EFG.

Local measurements (Mössbauer, NMR)

Nuclei with $I > 1/2$:
non-spherical symmetry of the nuclear charge distribution
$\Rightarrow$ electric quadrupole moment Q interacting with EFG at the nuclear sites.

$$\mathcal{H}_Q = \frac{1}{6} \sum_{i,j=1}^{3} Q_{ij} V_{ij}$$

$$\mathcal{H}_Q = \frac{e^2 q Q}{4I(2I-1)} \left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2) \right]$$

Eigenvalues of EFG tensor:

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$

$\Rightarrow$ ν_Q (V_{zz}) $\Leftrightarrow$ departure from spherical symmetry

$V_{zz} \equiv eq$ { NMR $\rightarrow \nu_Q$; Mössbauer $\rightarrow \Delta E$

$\Rightarrow$ $\eta \Leftrightarrow$ departure from axial symmetry

$0 \leq \eta \leq 1$ $\quad \eta \equiv \dfrac{|V_{xx} - V_{yy}|}{|V_{zz}|}$ (asymmetry parameter)

Local symmetries in a crystal.

① Cubic (spheric). Ex. La_3Ga.

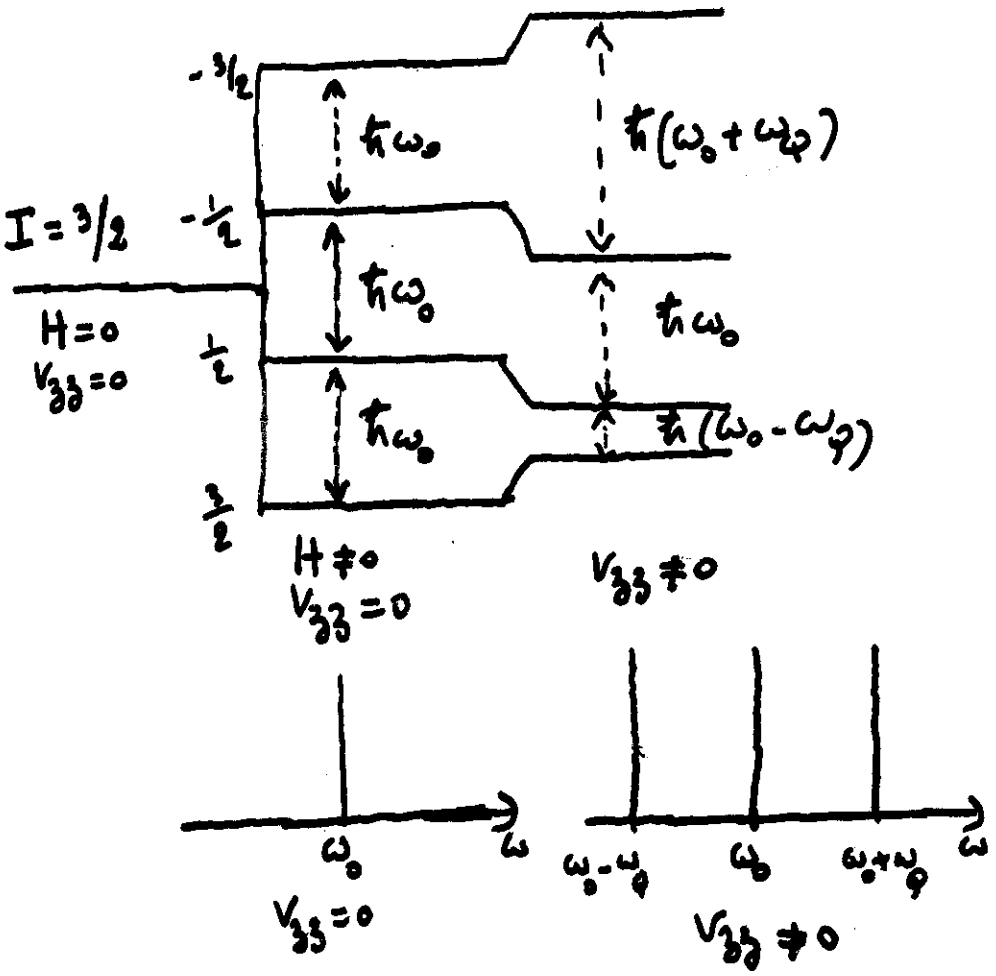
$$V_{xx} = V_{yy} = V_{zz} = 0.$$

② Axial. Ex. MoB_2

$$V_{xx} = V_{yy}$$
$$V_{zz} \neq 0$$
$$\eta = 0$$

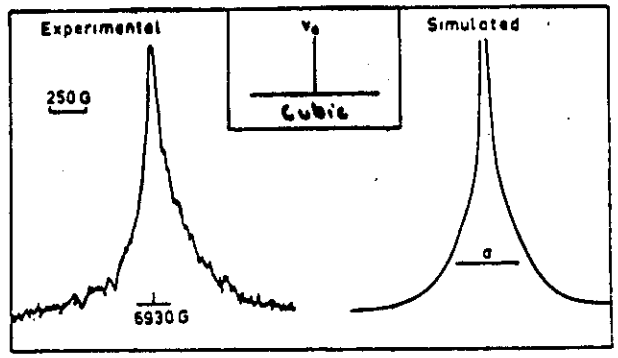
③ Non-axial. Ex. Ni_2B.

$$V_{zz} \neq 0$$
$$\eta \neq 0$$



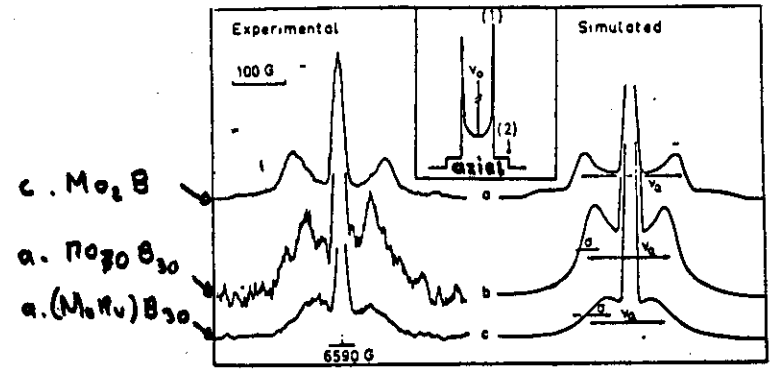
rf ω

$\omega_0 = \gamma H$ γ: nuclear gyromagnetic ratio



a. $La_{.93}Ga_{.25}$

Fig. 2

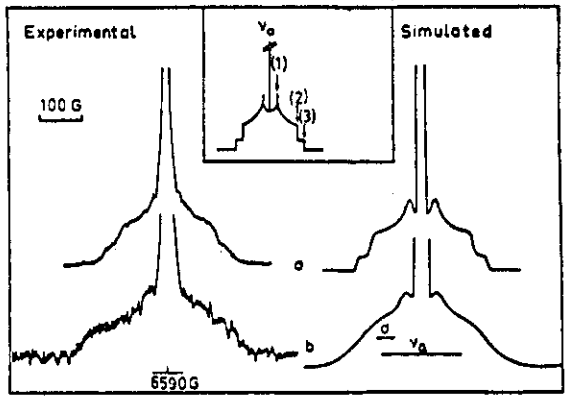


c. Mo_2B

a. $Mo_{.90}B_{.10}$

a. $(Mo_{.90}Ru)B_{.10}$

Fig. 3



c. Ni_3B

a $Ni_{.78}P_{.14}B_8$

Fig. 4

Conclusions : EFG about the GF sites.

i) Different types of local symmetries.

ii) $\overline{V_{\varphi}}$ close to the values obtained in crystalline counterparts.

iii) $\overline{\sigma}/\overline{V_{\varphi}} \equiv$ "degree of randomness" does not depend on the fabrication technique.

iv). Influence of chemical disorder. (a. $Mo_{Ru}B$ versus a. Mo_2B)

v) η is preserved in amorphous modifications.

[cf. P. Panissod et al. Phys. Rev. Lett. 1980].

Concentration effects in a. $Ni_{100-x}B_x$

Liquid-quenched ribbons

$x = 17.5$ at%
$x = 25$
$x = 31$
$x = 33$
$x = 35$
$x = 40$

(Allied)

P. Panissod (Strasbourg) | ICM Kyoto (Sept. 1982)
I. Bakonyi (Budapest) |

Phase diagram

($Ni_{23}B_6$ cubic)

Ni_3B orthorhombic (Pnma) (non-axial)

Ni_2B tetragonal (axial)

Ni_4B_3 orthorhombic (Pnma) (monoclinic) (non-axial)

^{11}B in crystl. compounds

$\eta = 0.6 \cdot 0.7$

c. Ni_3B

$\eta = 0$

c. Ni_2B

c. Ni_4B_3 (extrap.)

small η

^{11}B NMR Spectra in Michael Borides –

^{11}B in a-Ni:B

a-$Ni_{74}B_{26}$

a-$Ni_{69}B_{31}$

a-$Ni_{67}B_{33}$

a-$Ni_{65}B_{35}$

a-$Ni_{60}B_{40}$

^{11}B NMR Spectra in a-$Ni_{1-x}B_x$

Spectra are normalized to Unit area (bottom right) ; Top right: central part ; Left: Vert. x 5

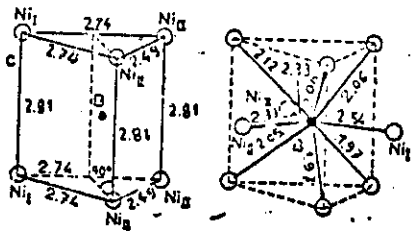
Conclusions. (from "B in a. Ni B)

i) Local symmetry around B is not necessarily the same as in crystalline counterparts.

Trends
but, maybe,
not a general rule.
⇒ one has to investigate each amorphous system in comparison with phase diagrams.

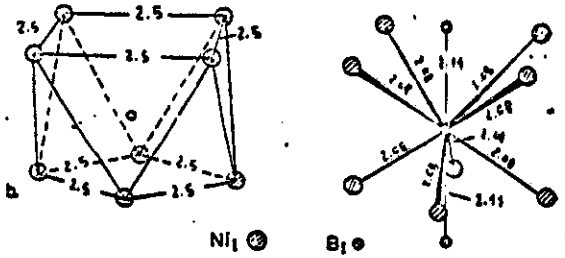
ii) In the a. Ni B system:
- continuous change of ν from strong to weaker anisotropy
- but the axial case of Ni_2B seems to be avoided in the amorphous state (≠ a. MoB_2).
- some elementary packing units seem to be favoured in the amorphous state (trigonal prisms !).
  pyramid apex ?
  [model simulations of Gaskell]

c. Ni_3B
Orthorhombic
(Pnma)



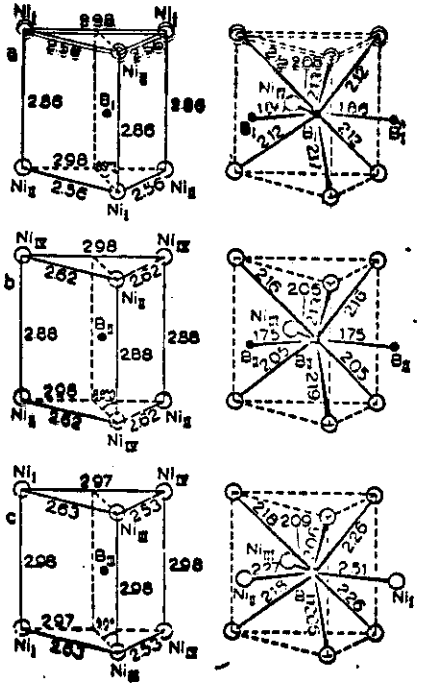
1 Boron Site
6 Ni_{an} (Trigonal prism)
+ 3 Ni_{an} (Pyramid Apex)
(non axial)

c. Ni_2B
Tetragonal



1 Boron Site
8 Ni_{an} (Anti cube)
(axial)

c. Ni_4B_3
Orthorhombic
(Pnma)



3 Boron Sites
Common:
6 Ni_{an} (Trigonal prism)
$\begin{cases} B_I \\ B_{II} \end{cases}$ + 1 Ni (Pyramid apex)
2 B
B_{III} + 3 Ni (Pyramid apex)
(Non axial)

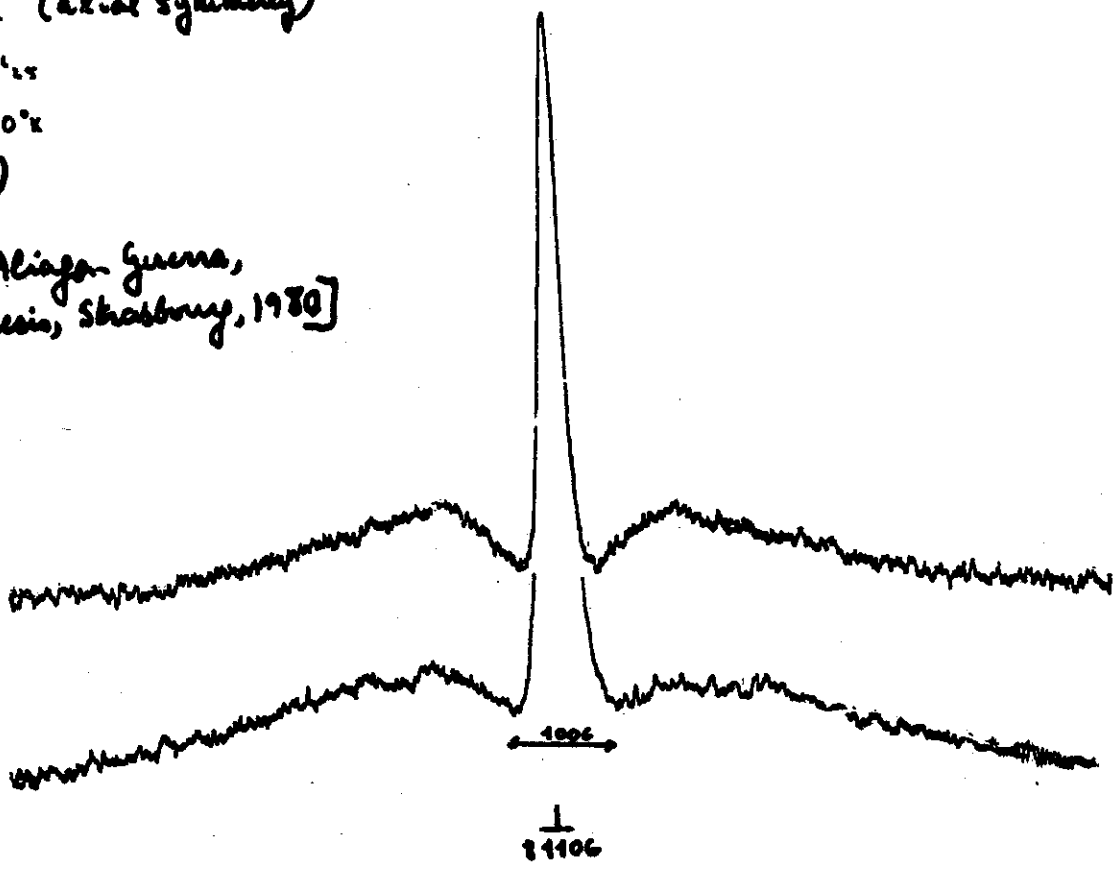
c. La_3Al (axial symmetry)

a. $La_{75}Al_{25}$

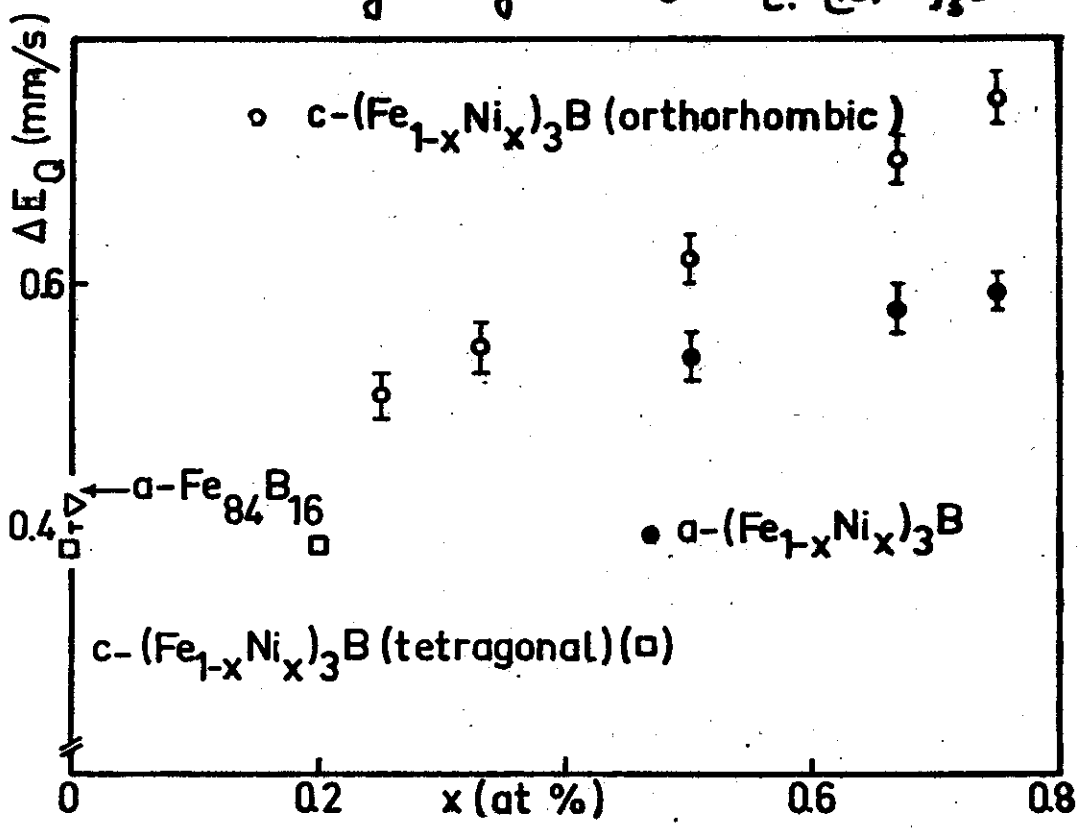
Al^{27}. 10°K

(I = 5/2)

[D. Aliaga-Guerra, Thesis, Strasbourg, 1980]



Symmetry about Fe in a: c: $(Fe,Ni)_3B$



[I. Vincze & F. van der Woude, J. Non Cryst. Sol. 42 (1980) 699]

(23)

B. NMR Spectra in ferromagnetic amorphous alloys

P(H) directly obtained by spin-echo NMR spectroscopy

In most cases, structures:

① Quadrupolar structures

V_Q large [J.D. et al., J. Appl. Phys. 50 (1979) 7668]

Ex. ^{59}Co diluted in a. $Fe_{79}P_{13}B_8$

V_Q is about the same as for ^{59}Co in c. Fe_3P [D. Aliga-Thesis, Strasbourg 1980]

Ex. a. $Eu_{80}Au_{20}$ [J.M. Friedt, 1980)

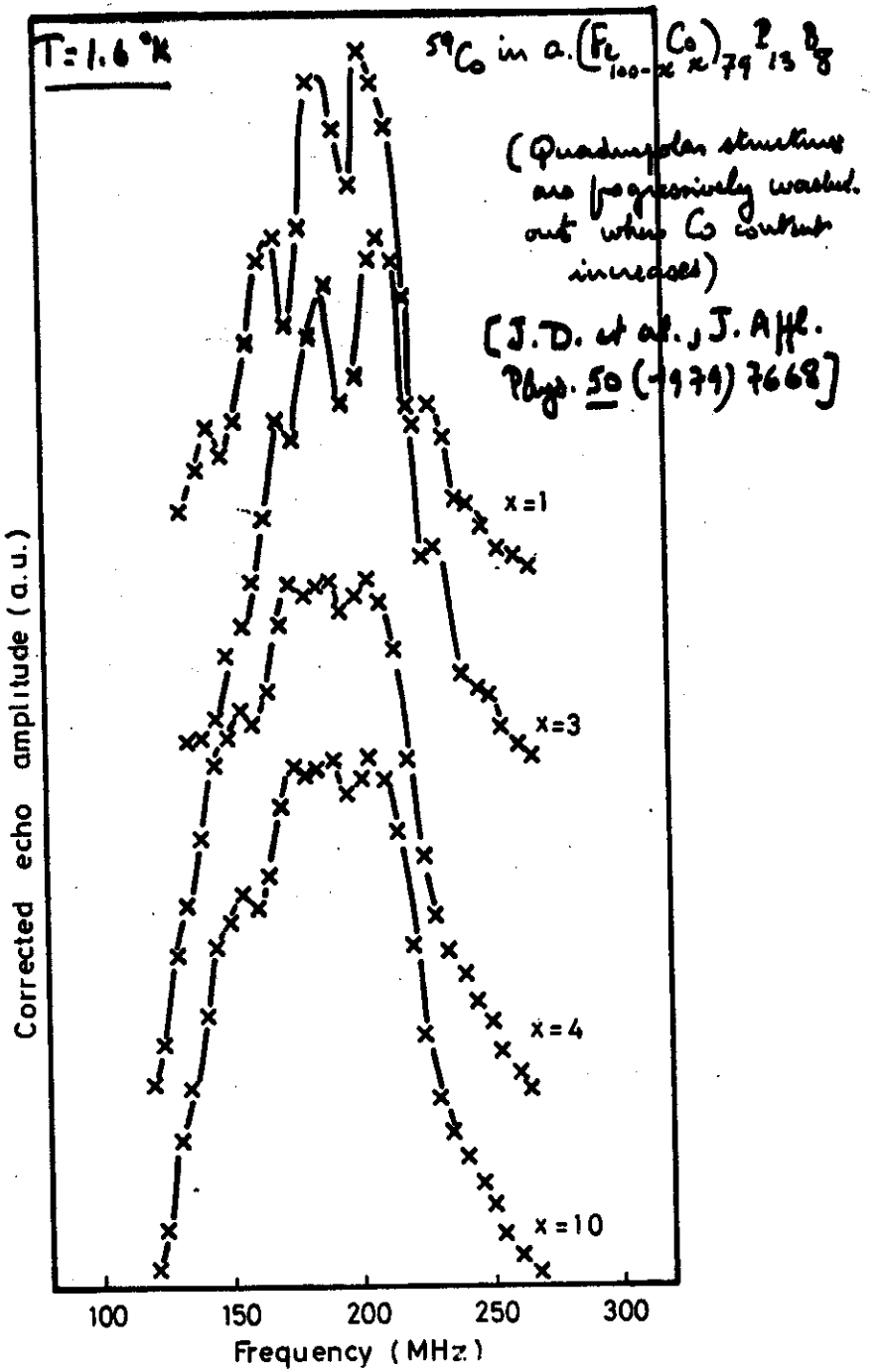
② Different magnetic states

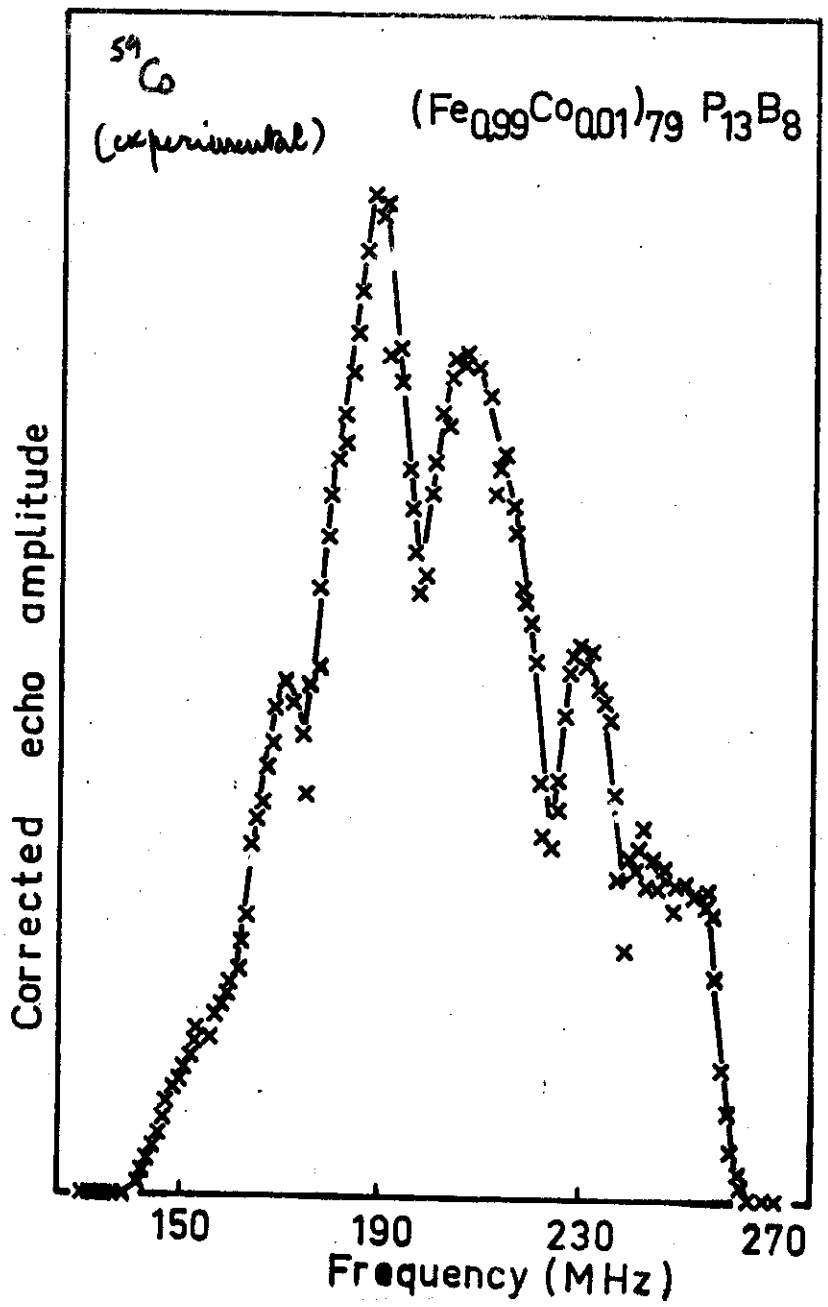
Ex. ^{55}Mn in a. $Fe_{79}P_{13}B_8$

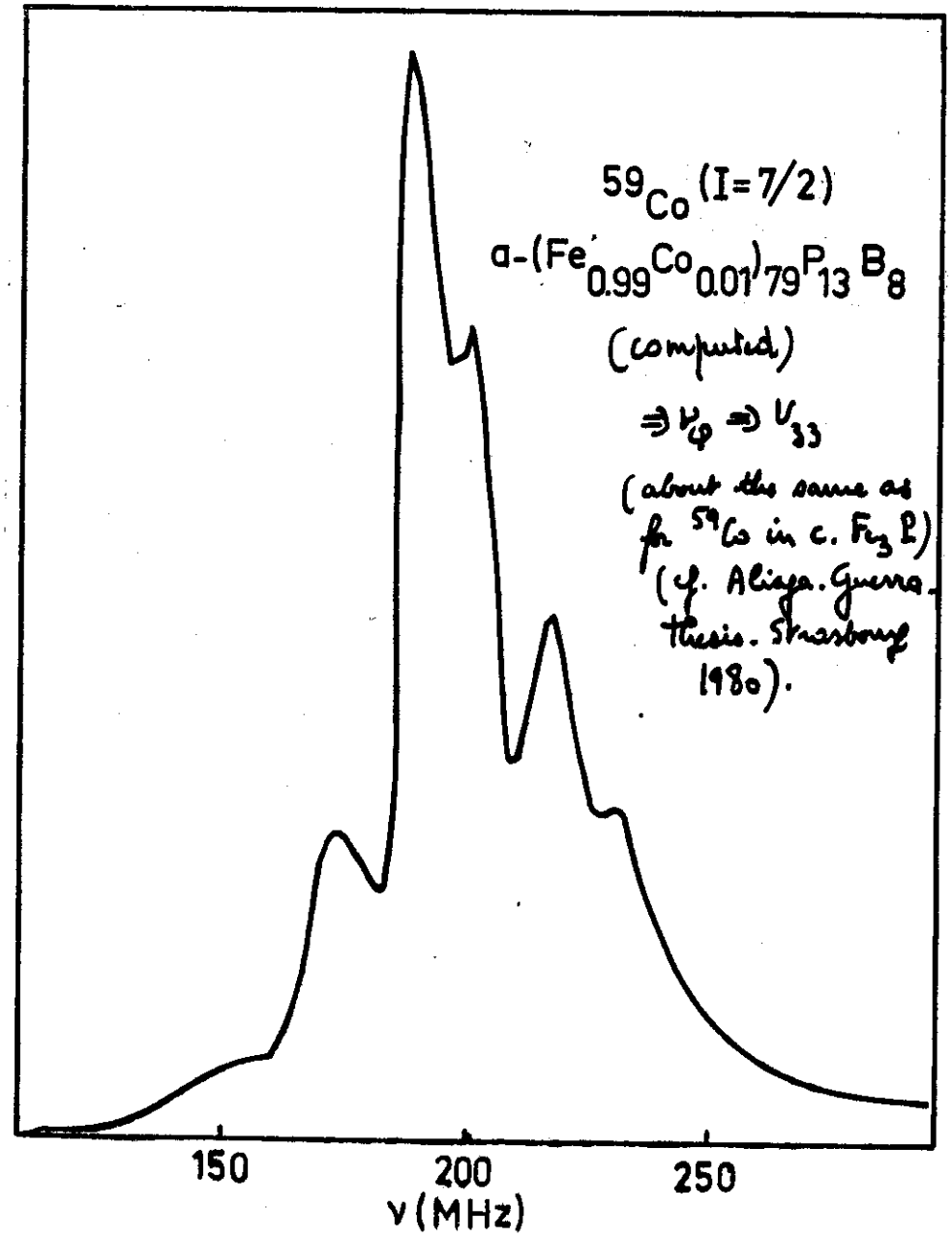
in a. $Fe_{75}I_{15}C_{10}$

cf. Cochoux, Parissoud ICM Kyoto (1982)

③ Other case: a. $Co_{100-x}B_x$ } ⇒ P(H)
a. FeB




^{59}Co
(experimental)
$(Fe_{0.99}Co_{0.01})_{79}P_{13}B_8$
Corrected echo amplitude
150
190
230
270
Frequency (MHz)


^{59}Co (I=7/2)
a-$(Fe_{0.99}Co_{0.01})_{79}P_{13}B_8$
(computed)
⇒ ν_Q ⇒ ν_{33}
(about the same as for ^{59}Co in c. Fe_3P)
(cf. Aliaga-Guerra, thesis, Strasbourg 1980).
150
200
250
ν (MHz)

For dilute Co ($x = 1$ to 4)

the width of the distribution $\Leftarrow$ EFG

3 quadrupolar structures $\Rightarrow \Delta\mu_{Co}$ small

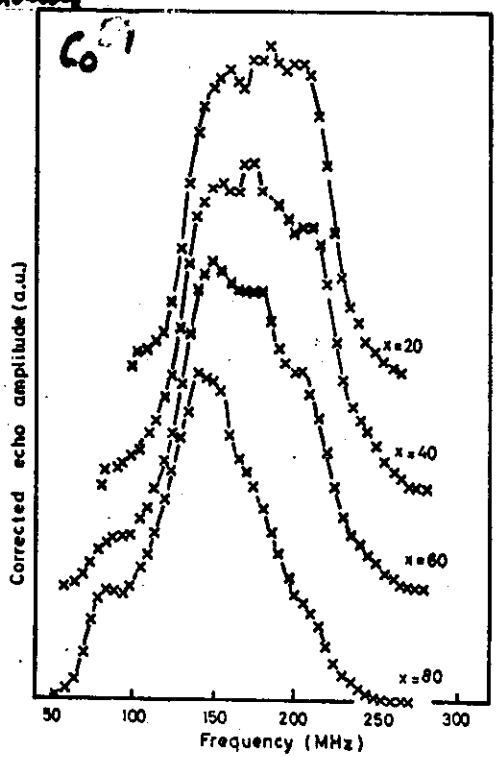
[selective site occupation for dilute Co in a. Fe P B, like in [c. Fe_3P / c. Fe_3Si (!)]

For concentrated Co,

no quadrupolar structure

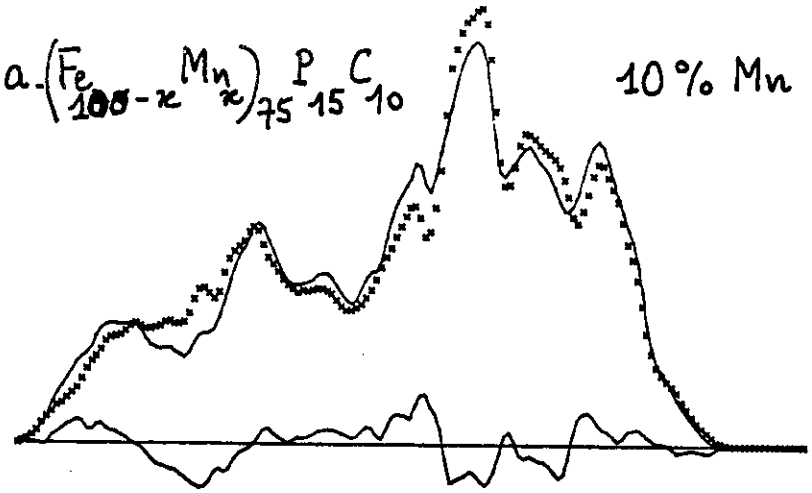
[V_Q small in cryst. Co_3B]

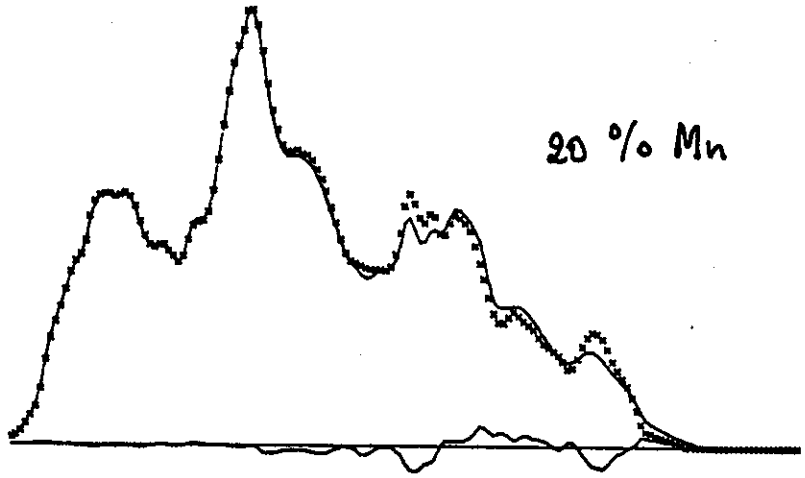
$\Delta[P(H)] \Leftarrow \Delta\mu_{Co}$

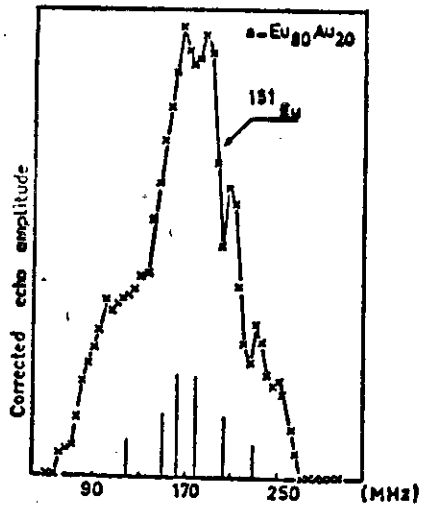


a. $Fe_{79}(Co_x)_{13}P_8B_8$

a. $(Fe_{100-x}Mn_x)_{75}P_{15}C_{10}$







J.M. Friedt et al.
LAM 4 Proc., J. Phys. Colloq.
C8, 41 (1980) 638.

Mössbauer ⇒ sign of V_{33}

Eu : $e^2 q_{33} Q = +15.5$ mm s^{-1} } q. J.M. Friedt et al.
$P(V_{33})$ = very narrow } J. Phys. F 12 (1982) 821
$\eta \simeq 0$

^{197}Au : $V_{33} < 0$ (also for ^{197}Au in a. $Gd_{80}Au_{20}$)

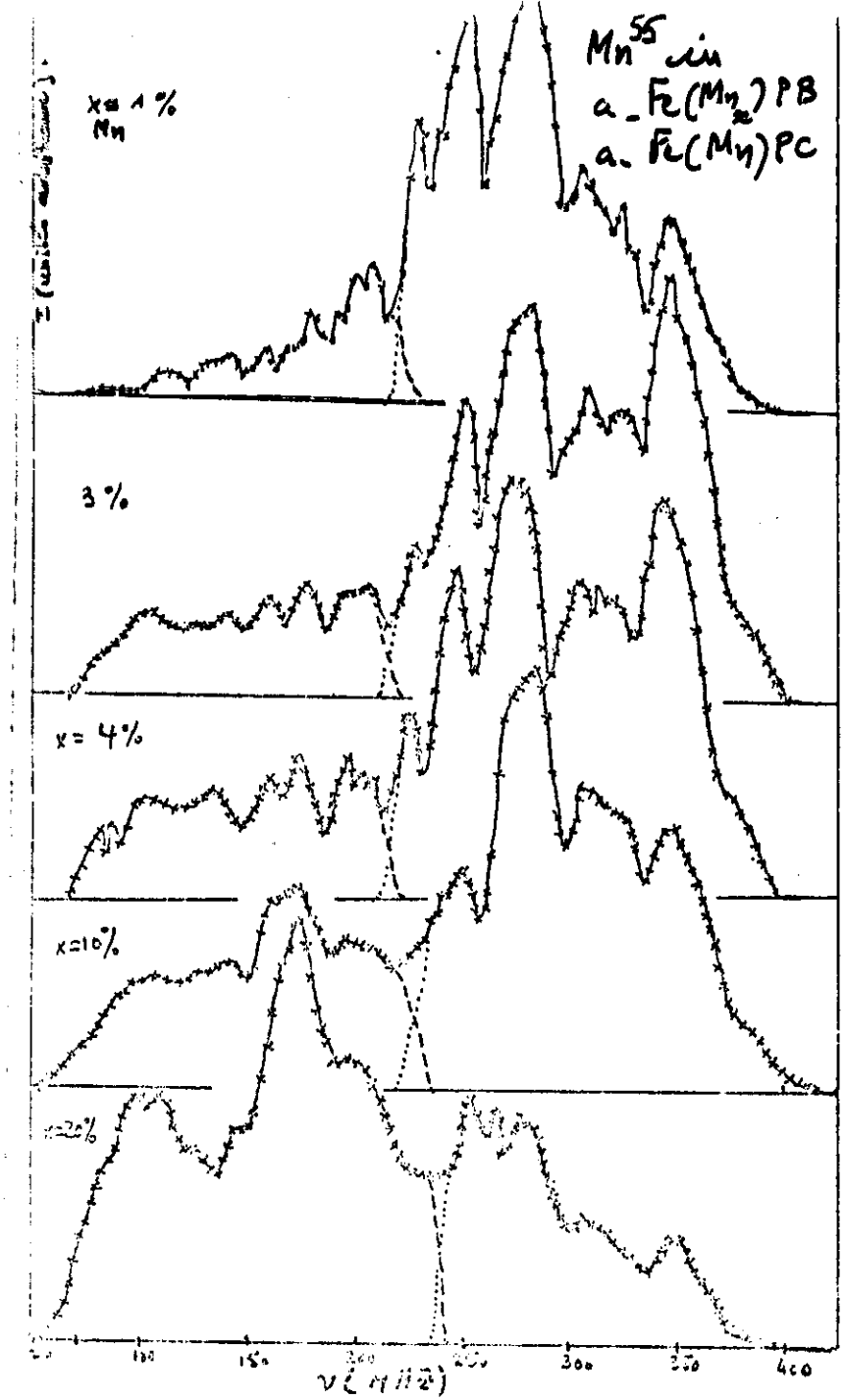
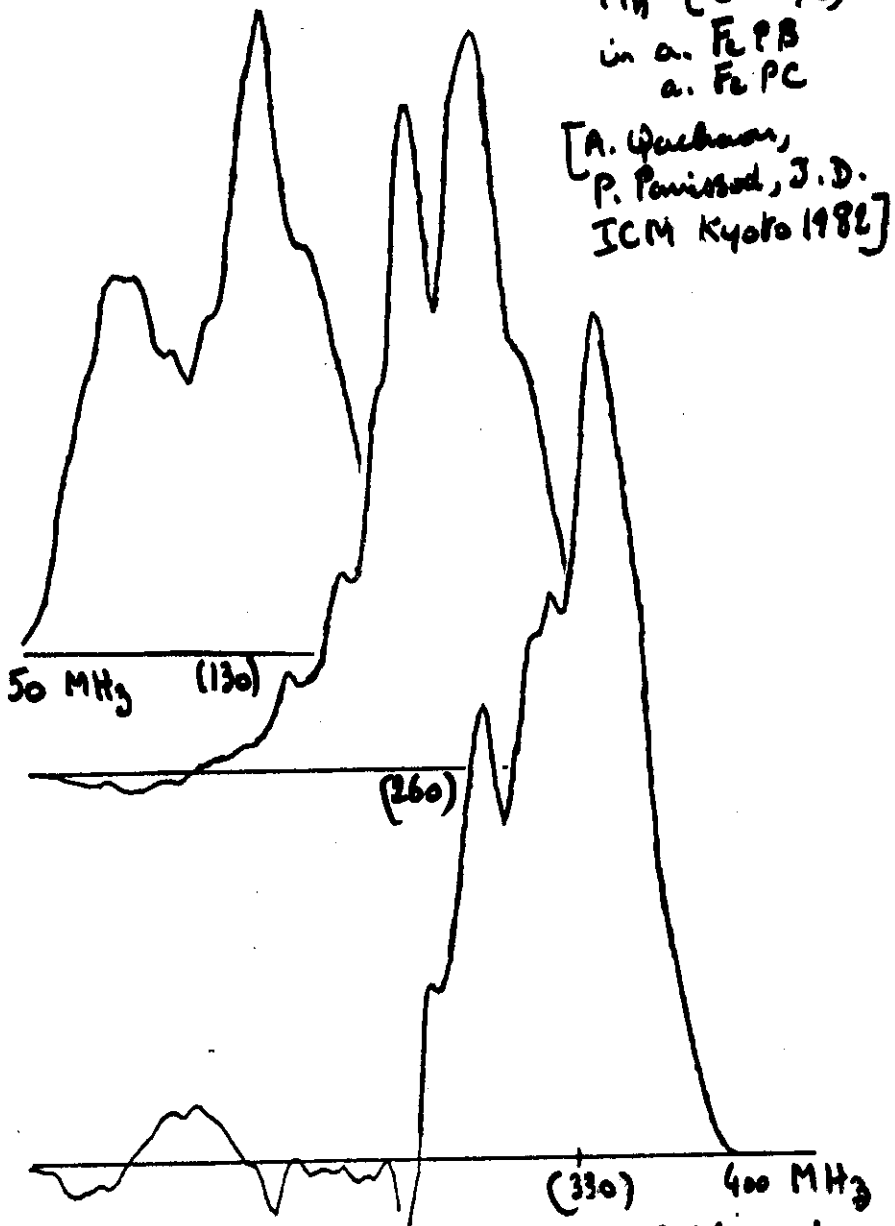


Fig 2a : Décomposition des spectres de résonance du système $(Fe_{100-x}Mn_x)_{75}P_{16}B_6Al_3$ et $(Fe_{100-x}Mn_x)_{75}Si_{10}B_{15}$

Mn^{55} ($I = 5/2$)
in a. Fe P B
a. Fe P C

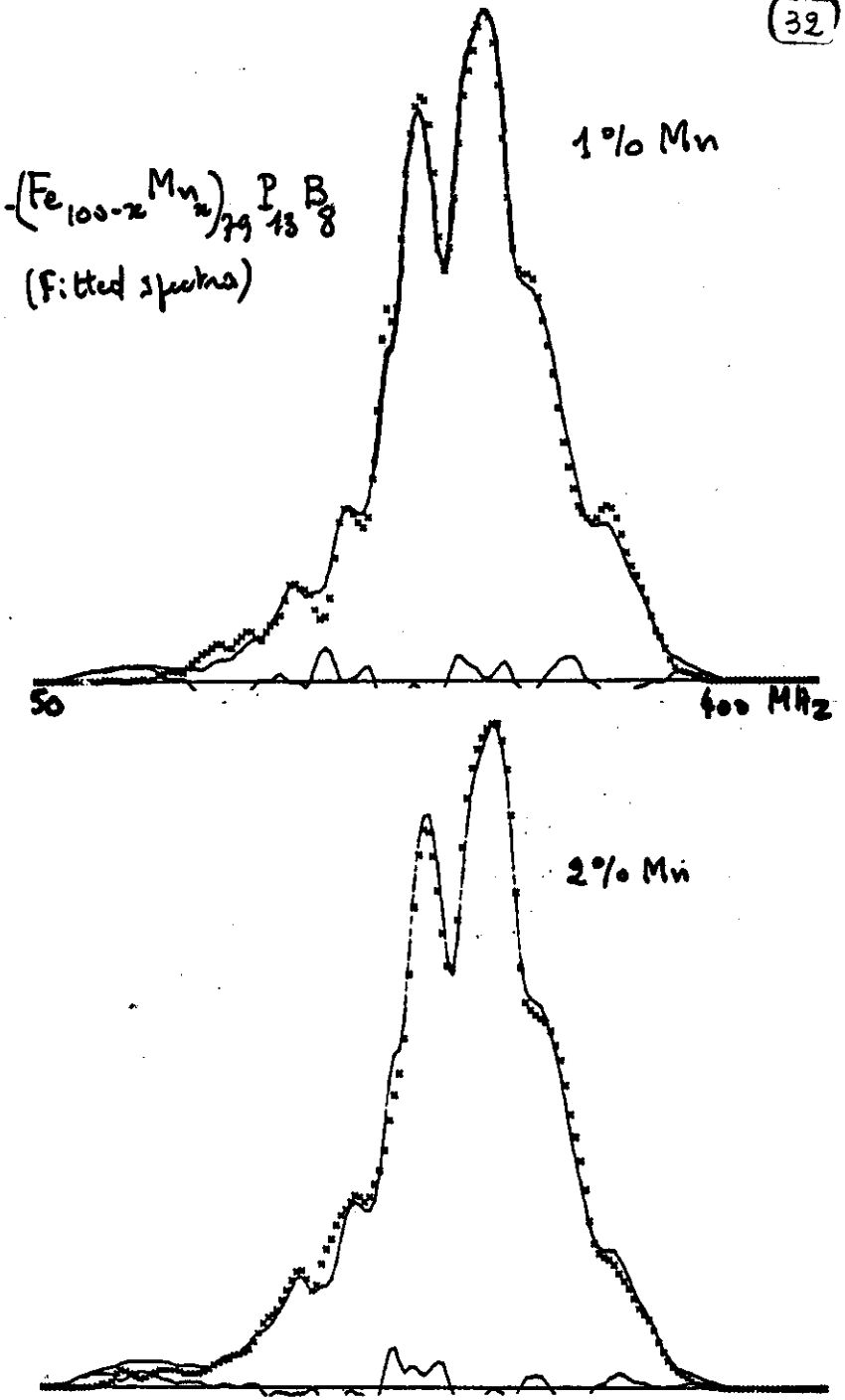
[A. Quachaou, P. Panissod, J.D. ICM Kyoto 1982]

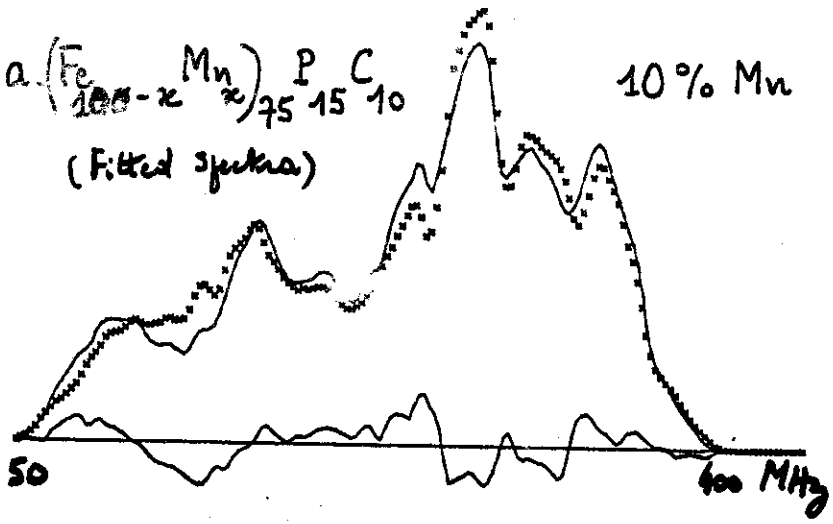


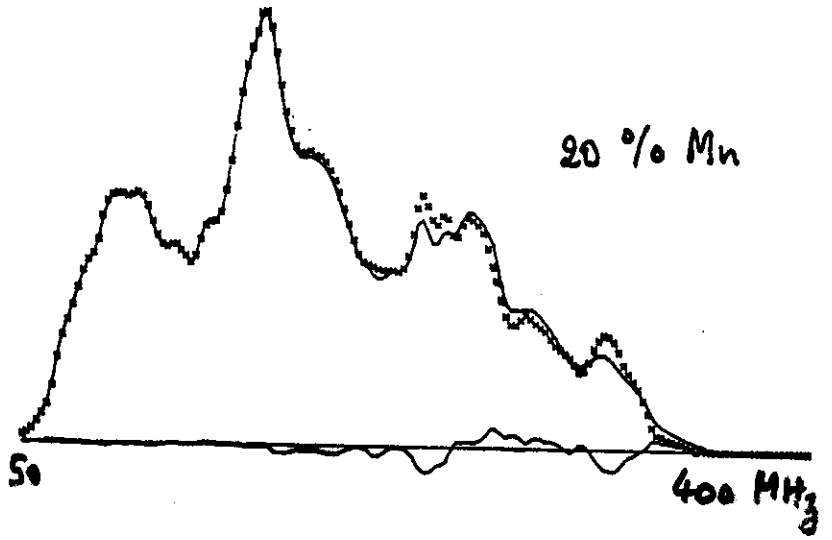
Example: Separation of three contributions in Mn NMR spectra.

$a\text{-}(Fe_{100-x}Mn_x)_{79}P_{13}B_8$

(Fitted spectra)







Conclusions on Mn

^{55}Mn in { a. $Fe_{79}P_{13}B_8$; a. $Fe_{75}P_{15}C_{10}$

→ 3 contributions to P(H)

① 50 – 200 kOe
becomes predominant at high x_{Mn}
Mn atoms with moments antiparallel to Fe moments.

② ~ 260 kOe → dilute limit.

③ ~ 330 kOe

cf. Mn^{55} in c. Ni
Y. Kitaoka et al., J. Phys. Soc. Japan 44 (1978) 142.

→ Each contribution has a quadrupole structure with same ν_Q for each and same ν_Q as for ^{59}Co in a. FePB (once corrected for different Q)

^{59}Co in a. electrodeposited Co P alloys.
Influence of excitation conditions

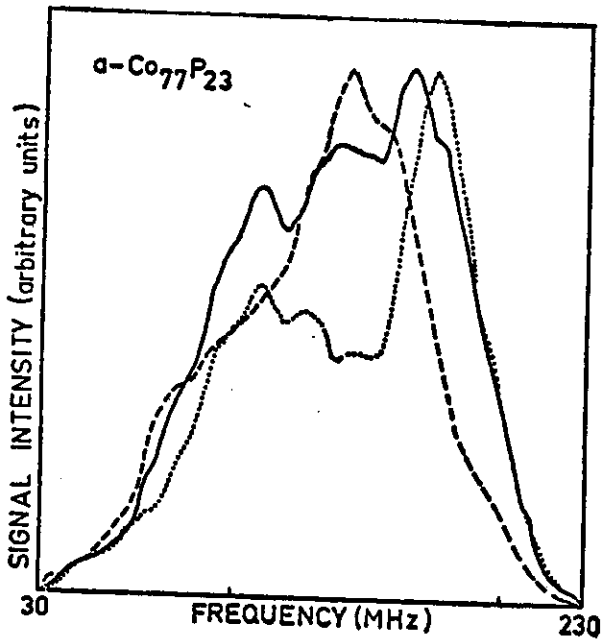


Figure 19 :

Spectre RMN du Co^{59} dans l'amorphe électrodéposé $Co_{77}P_{23}$ pour différentes conditions d'excitation :

(.....) H_1 = 0.05 oe
(——) H_1 = 0.10 oe
(-----) H_1 = 0.15 oe

J. D, & M. F. Lapierre
J. Phys. F 1976

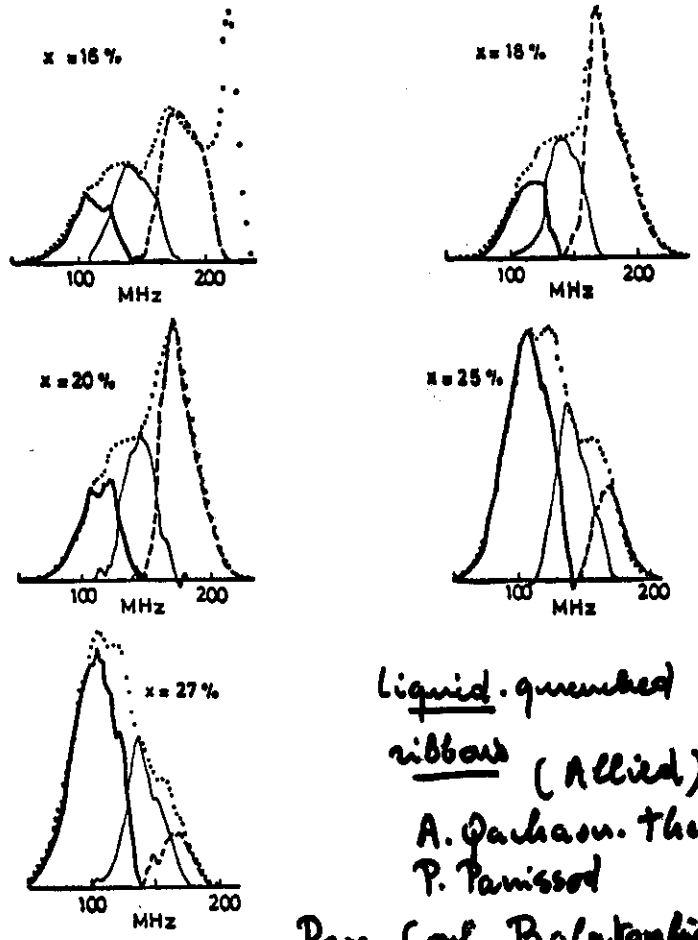
A. Yaouanc
thesis, 198).

[Compare with K. Raj et al.
AIP Conf. Proc. 31 (1976) 390]

Figure 12b :

Décomposition des spectres du système $Co_{100-x}B_x$; 14<x≤27 non recuits et soumis aux faibles excitations (H_1=0.05 oe) et dont la direction de $\vec{H}_1$ est aléatoire par rapport à la longueur des rubans amorphes.

^{59}Co

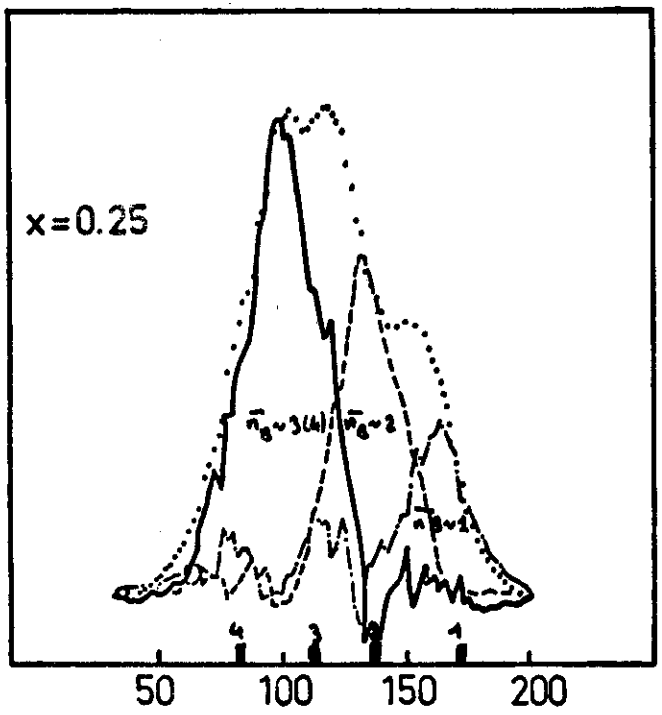


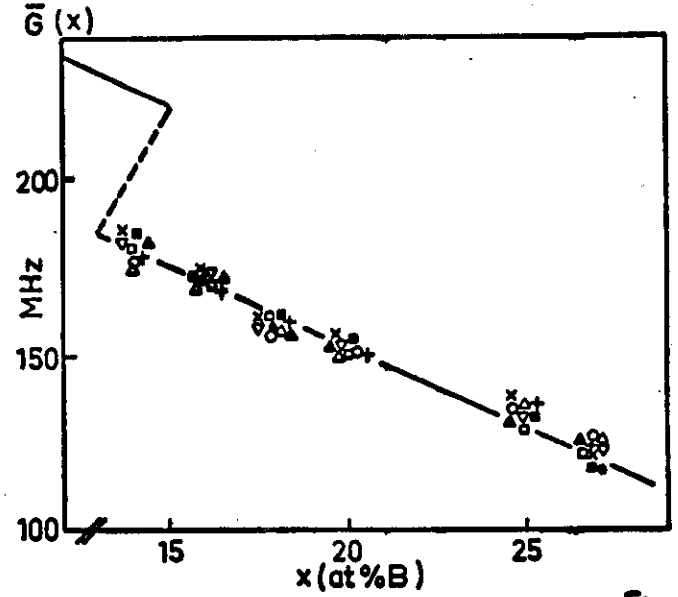
Liquid. quenched $Co_{100-x}B_x$ ribbons (Allied)
A. Yaouanc. Thesis, 1981
P. Panissod
Proc. Conf. Balatonfüred (Hungary) (1981).
vol. 1, p. 543

Assumptions for Self consistent separation :

1) 3 Lines contributing to spectra
2) Only the amplitude is experiment or concentration dependent

a $Co_{75}B_{25}$



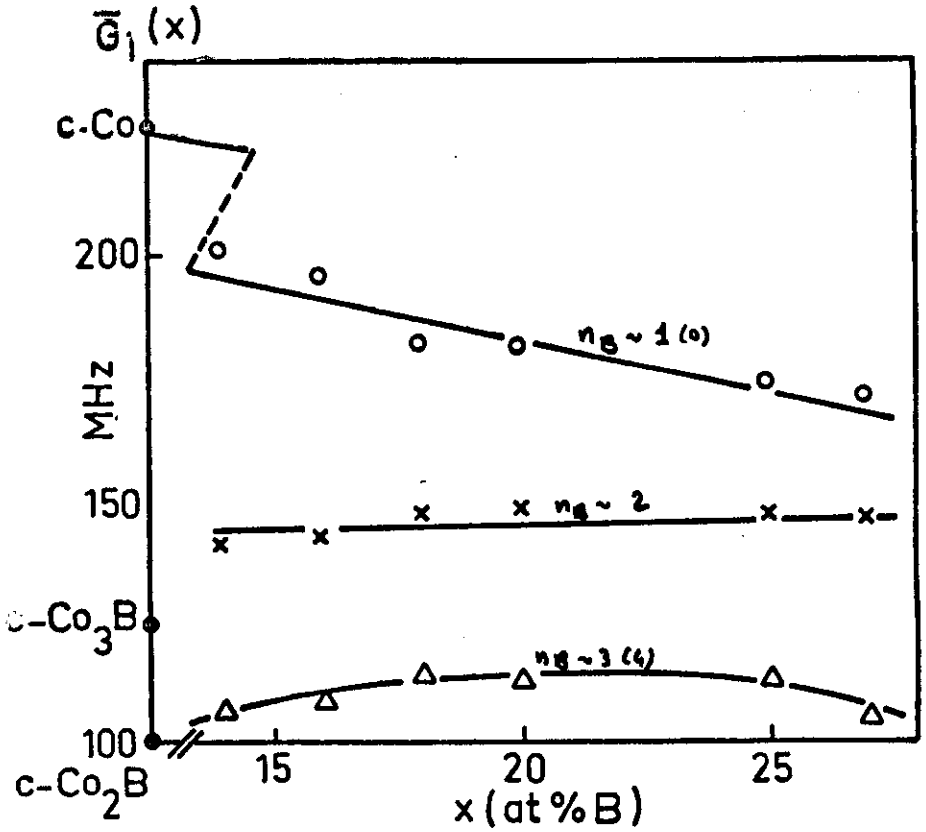


$\bar{G}(x)$, center of gravity of P(H) for ^{59}Co in a. $Co\,B_x$ versus B content.

Figure 4 : Evolution du centre de gravité $\bar{G}(x)$ en fonction de la concentration x de bore dans le système $Co_{100-x}B_x$, pour différentes conditions expérimentales :

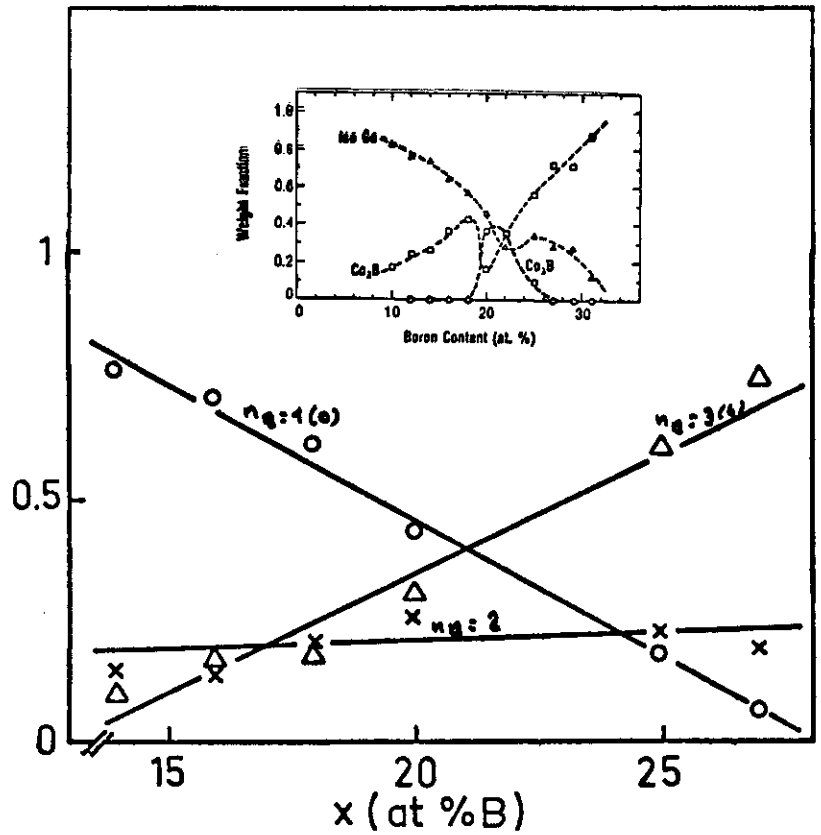
$\vec{H}_1$ appliqué parallèlement aux rubans amorphes	$\vec{H}_1$ aléatoire % à la géométrie des rubans
● : H_{1min} (=0.05oe) ; non recuit	X : H_1 = 0.05oe ; non recuit
○ : H_{1Max} (=0.15oe) ; non recuit	▼ : H_1 = 0.15oe ; non recuit
■ : H_1 = 0.05oe ; recuit	■ : H_1 = 0.05oe ; recuit
▲ : H_1 = 0.15oe ; recuit	▲ : H_1 = 0.15oe ; recuit
+ H_{1ins} (=0.1oe) ; recuit	

a $Co_{1-x}B_x$



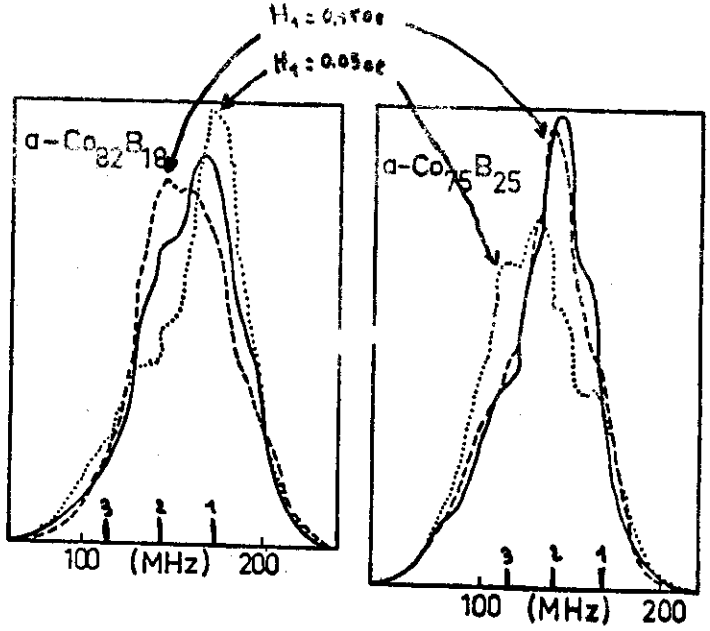
G_i, Center of gravity of each component of P(H) versus B content.

a $Co_{1-x}B_x$

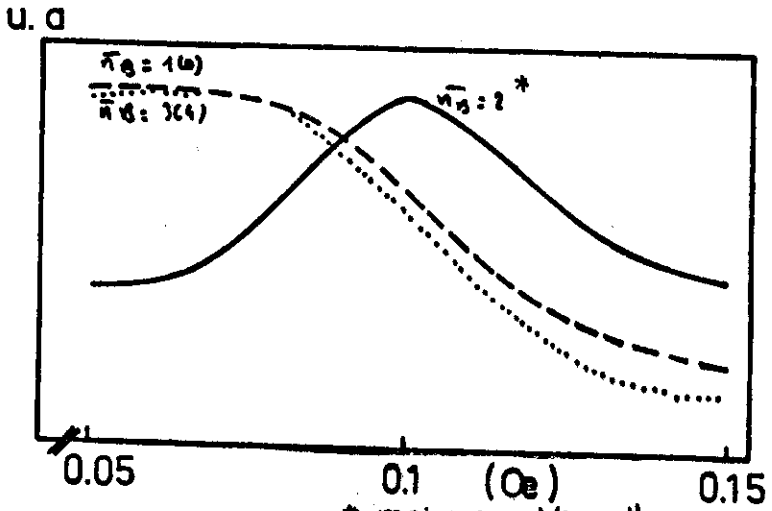


c Co n_B: 0 c. Co_2B n_B: 4

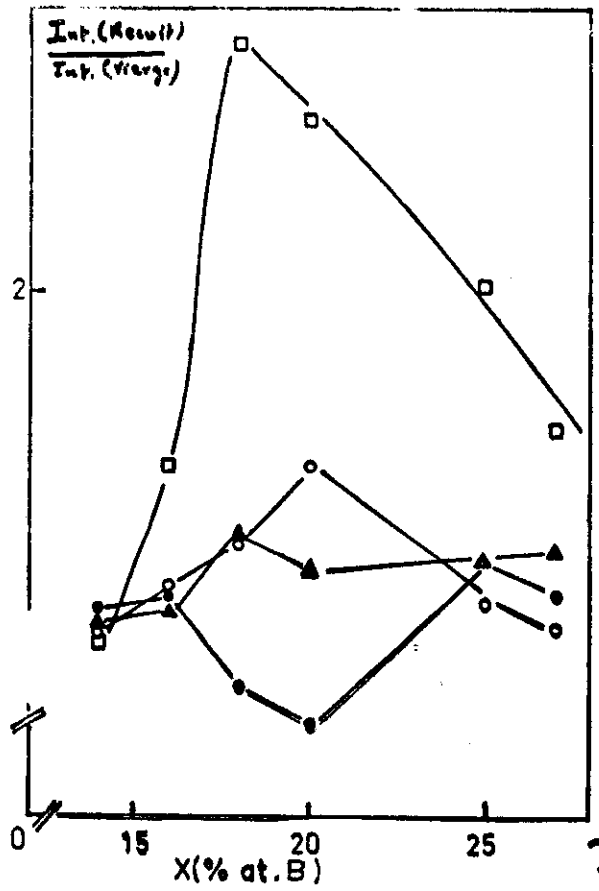
Respective concentration of each component of P(H) versus total B content.



Influence of excitation conditions.



* moins couplés au H_1
- pouvoir moins mobile
et/ou
+ fort anisotropie magnétique



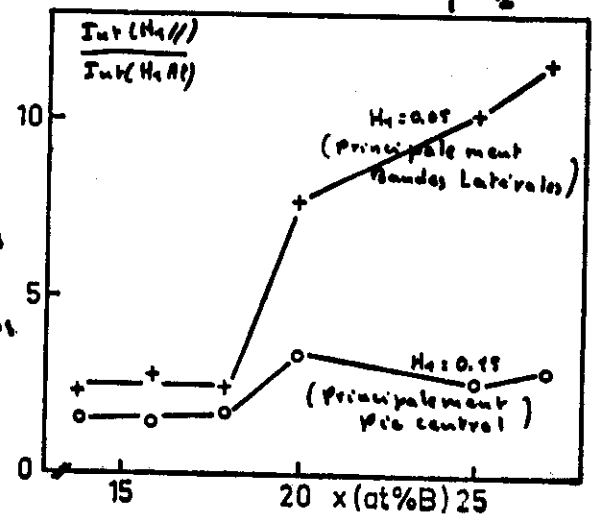
Influence du recuit

Influence of annealing on intensities of the lines.

Influence de l'orientation des rubans % au H_1

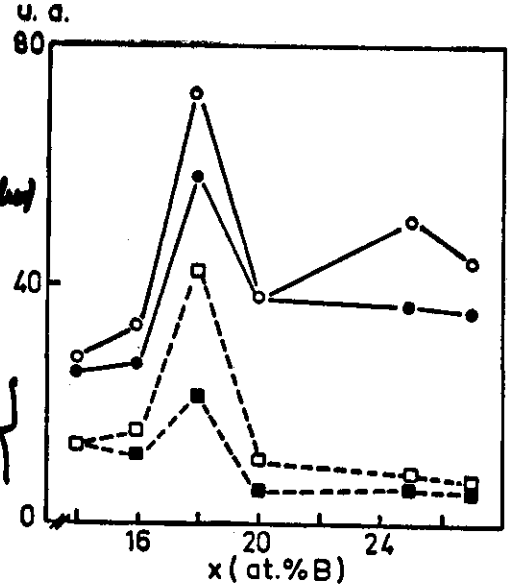
Pic central : Co dans des régions d'aimantation hors du plan des rubans

Influence of orientation of H_1.



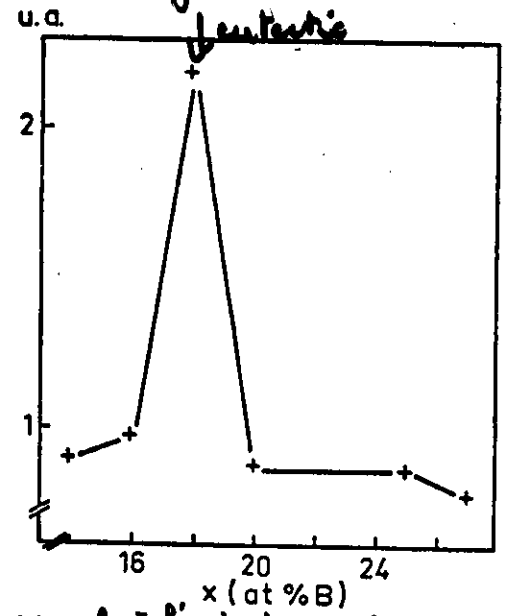
H_1 // ribbons
○ as-quenched
● annealed

H_1 random
□ as-quenched
■ annealed



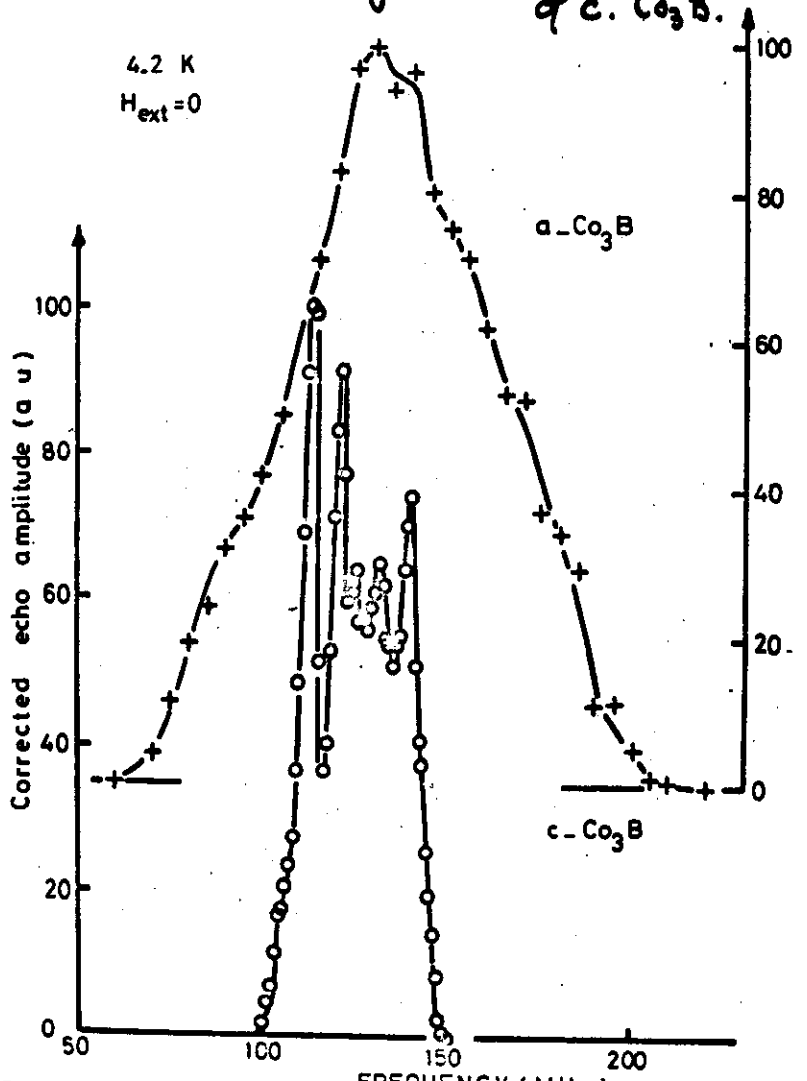
Signal Intensity versus concentration

Integrated intensity



Maximum de signal à l'eutectique ⇒ maximum de mobilité des parois

P(H) for ^{59}Co in a-Co_3B is not simply the broadened P(H) of c-Co_3B.



[J.D. et al., J. Mag. Mag. Mat. 15-18 (1980) 1373]

43)

a. $Co_{100-x}B_x$

^{59}Co signal arises mainly from Co nuclei located in domain walls.

3 types of "local" environment:

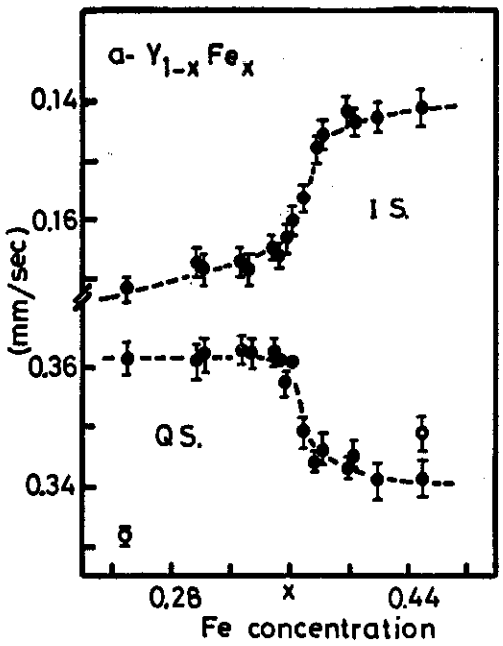
① $H_i \approx 180$ MHz (~3B or 4B) (around a Co site)
$\approx H(Co_2B)$
Relatively "homogeneous"

② $H_i \approx 180$ MHz (~1B)
^{59}Co with B rich environment.
Rather "homogeneous".

③ $H_i \approx 140$ MHz (~2B)
Associated with magnetization perpendicular to the plane of the ribbons.
(cf. columnar regions in Co P and Co)
sensitive to anneal treatment.

Eutectic composition:
Maximum integrated signal / mass unit.
⇒ Bloch walls free to move
⇒ larger spatial extension of the two "Homogeneous phases"?
⇒ minimum density of defects?

[M. Tennhover, J. Phys. Chem. Sol. (1981)]



Variation of the Isomer-shift and of the Quadrupole splitting around the eutectic composition [~35 at% Fe] in liquid-quenched a-Y Fe alloys.