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# MÖSSBAUER STUDY OF AMORPHOUS Fe-P ALLOYS

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## АННОТАЦИЯ

Даются предварительные результаты мессбауэровских измерений электролитических аморфных сплавов Fe-P. Найдено очень широкое распределение сверхтонкого поля и относительно большие изомерные сдвиги. Подробно обсуждаются проблемы, представляющие интерес для дальнейших исследований.

## KIVONAT

Előzetes Mössbauer eredményeket közlünk elektrolitikus Fe-P amorf ötvözetekre. Nagyon széles hiperfinom tér eloszlásokat és viszonylag nagy izomér eltolódásokat találtunk. Részletesen tárgyaljuk a további vizsgálatokra érdemes problémákat.

## ABSTRACT

Preliminary Mössbauer results are represented on electrodeposited Fe-P amorphous alloys. Very broad hyperfine field distributions and relatively large isomer shifts have been found. Problems worthy of further investigation are discussed in details.

## INTRODUCTION

Since the development of Fe-B metallic glasses, the first iron based binary system prepared by rapid quenching from the melt, much Mössbauer work has been done on that model system. Little attention has been paid, however, to electrodeposited Fe-P alloys since the paper by J.Logan and E.Sun [1]. The possible reason is that electrodeposition does not allow the direct control of the composition and the presence of impurities and inhomogeneities is more probable.

On the other hand, the results on crystalline iron phosphides and metallic glasses containing phosphorous raise questions worthy of further investigation. The role of the preparation process in determining the structure of amorphous materials is also to be studied.

a) The magnetization and the hyperfine field of iron-light metalloid (Be,B,C,Al,Si,P) crystalline intermetallic compounds and metallic glasses can be well described by the donor model assuming a charge transfer from the metalloids into the 3d band of the metal [2]. In the materials not containing phosphorous the isomer shift can also be explained by this model because the increase of the isomer shift also suggests the increase of the number of 3d electrons.

As a consequence of the donor model, a negative correlation can be expected between the hyperfine field and the isomer shift: the hyperfine field decreases, the isomer shift increases with the increase of the number of 3d electrons. This correlation is valid for a number of crystalline iron-metalloid compounds [3] and for the Fe-B metallic glasses [4] (dashed line on Fig. 1). The isomer shifts in Fe-P and Fe-P-B crystalline compounds, however, is larger and fails to fulfil this correlation (Fig. 1). (The advantage of this plot is that it can be studied even if the site-assignment is not unambigouos.)

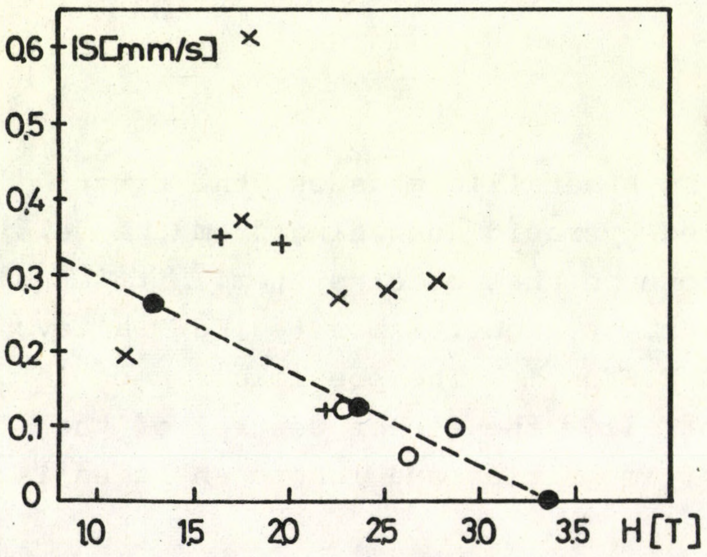

*Fig. 1. Correlation between the hyperfine field and isomer shift in Fe-P-B crystalline intermetallic compounds. The dashed line corresponds to the Fe-B case. /● FeB, $Fe_2B$ and α-Fe [4], o $Fe_{2.88}P_{0.05}B_{0.95}$ [5], + $Fe_5PB_2$ [6], x $Fe_2P$ and $Fe_3P$ [5]/*

According to the donor model the isomer shift should be a linear function of $A = \sum_i d_i x_i (1 - \sum_i x_i)^{-1}$ where $x_i$ and $d_i$ are the concentration and the number of donated electrons for the i-th metalloid component respectively. The points for the phosphorous containing metallic glasses are well above the line for the iron-boron alloys also in this case (Fig. 2).

The donor model turned out to be an appropriate first approximation of the electronic structure. To arrive at a more physical description, however, the study of Fe-P amorphous alloys is promising because of the deviations of the isomer shift and the high valency of phosphorous. The comparison with crystalline intermetallic compounds and even solid solutions [8] is also possible.

b) According to Logan and Sun [1], the eutectic composition plays an important role in the determination of the properties of Fe-P electrodeposited alloys. This is reflected by the maximum of the isomer shift, the minimum of the quadrupolar interaction and by the sharpest Curie temperature at the eutectic composition.

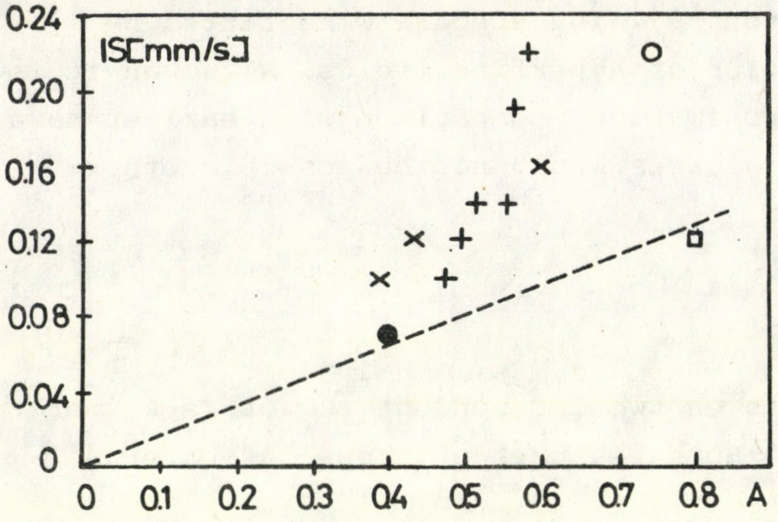

*Fig. 2.*

*The isomer shift as a function of A, the number of electrons accepted by an iron atom /see text/ for some metallic glasses.* + $Fe_{79}P_xB_{21-x}$; x $Fe_{94-x}P_6B_x$; o $Fe_{75}P_{15}C_{10}$ */data from Ref. 7/;* ● $Fe_{80}B_{20}$; ☐ $Fe_2B$ [4]. $d_B = 1.6$, $d_C = 2.0$ *and* $d_P = 2.4$ *have been assumed for the number of donated electrons* [2].

These data indicate unclear structural changes on the atomic as well as on a larger scale.

The hyperfine field distribution is broader than that in the melt-quenched metallic glasses, so it offers a better possibility to study short range order and inhomogeneities than in the other metallic glasses.

## EXPERIMENTAL

The samples have been prepared by electrodeposition in a way similar to that of Logan and Sun [1]. The composition and temperature of the electrolyte have been kept constant and the sample composition has been changed by using different current densities. The phosphorus concentration has been estimated by measuring the Mössbauer spectra of crystallized samples and determining the intensity ratio of the sextets corresponding to α-Fe and $Fe_3P$. (Thanks to Mrs M.Hossó for annealing the samples in a magnetic balance. The magnetization curves are in a qualitative agreement with the Mössbauer results.) Because of the possible presence of other phases, the absolute values may suffer from systematic errors. Two independent set of samples have been measured to check the reproducibility of the method.

Mössbauer spectra have been measured at room and at liquid nitrogen temperature. At room temperature two spectra with different intensity ratios have been measured by polarizing the samples with a permanent magnet and changing the angle between the sample plane and the γ-ray direction [9]. The spectra were fitted by assuming binomial distribution of hyperfine fields. Although it is certainly not the best approximation, comparison with earlier data on Fe-B and other metallic glasses would not be possible otherwise.

## RESULTS AND DISCUSSION

In Table I. the results on two independent sets of Fe-P amorphous alloys are presented. Some features of these data are as follows:

a) The results for the two series of samples are very close to each other, especially at the higher current densities. This supports the possibility of preparing well defined samples by electrodeposition.

b) The data for the spectra taken with different intensity ratios are also in appropriate agreement, the differences are characteristic of the systematic errors.

c) In three cases clear disagreement can be found between the isomer shifts deduced from the spectra taken at room temperature with different intensity ratios. The inhomogeneities in the samples produced at lower current densities are a possible explanation but this point needs further investigation.

d) Not only the shape but even the width of the hyperfine field distribution is very ill-defined. Although the mean square deviation of the hyperfine fields is much larger than that for Fe-B metallic glasses (~3.3 T at 80 K), even broader distributions could have been expected on the basis of the valence difference between P and B or comparison of the hyperfine fields of $Fe_3P$ and $Fe_3B$ crystalline compounds.

These preliminary results are only the first step in renewing the study of electrodeposited Fe-P amorphous alloys. Further studies on the dependence on the electrolyte composition, the temperature and the current density are necessary to learn more about the structural and magnetic properties and electronic structure of these materials.

*Table I. Mössbauer results on* $Fe_{100-x}P_x$ *amorphous alloys*

| j mA/cm$^2$<br>x at.% | T K | $I_2$ | | $\bar{H}$ T | | $\overline{IS}$ mm/sec | | $\sigma$ T | | $\Gamma$ mm/sec | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 200 | 295 | 4.10 | 4.21 | 23.7 | 23.7 | 0.25 | 0.25 | 3.91 | 4.53 | 0.53 | 0.56 |
| 22.2 | 295 | 1.44 | 1.28 | 24.5 | 24.2 | 0.24 | 0.25 | 3.99 | 3.96 | 0.55 | 0.54 |
| | 80 | 0.64 | 0.74 | 27.8 | 28.0 | 0.36 | 0.37 | 4.31 | 4.34 | 0.58 | 0.58 |
| 150 | 295 | 3.93 | 4.18 | 22.9 | 22.2 | 0.30 | 0.26 | 4.14 | 4.83 | 0.53 | 0.52 |
| 23.0 | 295 | 1.69 | 0.89 | 23.7 | 23.3 | 0.35 | 0.26 | 4.20 | 4.00 | 0.56 | 0.54 |
| | 80 | 0.61 | 0.86 | 27.2 | 26.7 | 0.37 | 0.40 | 4.35 | 4.31 | 0.60 | 0.59 |
| 100 | 295 | 4.08 | 4.14 | 20.2 | 19.0 | 0.30 | 0.32 | 4.65 | 4.84 | 0.48 | 0.49 |
| 25 | 295 | 1.05 | 0.83 | 21.0 | 19.7 | 0.34 | 0.38 | 4.41 | 4.77 | 0.54 | 0.56 |
| | 80 | 0.63 | 1.18 | 25.3 | 23.4 | 0.42 | 0.44 | 4.41 | 5.39 | 0.63 | 0.57 |

j is the current density used for the sample preparation. The intensity ratio of the lines was around 3 : $I_2$ : 1.25, $\bar{H}$ and $\sigma$ are the average and the mean square deviation of the hyperfine fields, $\overline{IS}$ is the average isomer shift and $\Gamma$ is the width of the component Lorentzian lines. The two columns correspond to two independent series of samples.

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Note added in proof:

We learnt after the Conference that Mössbauer investigations on melt-quenched Fe-P alloys had been carried out by M.Takahashi and M.Koshimura, Jpn.J.Appl.Phys. 18, 685 (1979). The comparison of the results on samples prepared by different methods seems to be very promising.

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