NMR AND MÖSSBAUER STUDIES OF THE AMORPHOUS SYSTEM $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$

A. Amamou and J. Durand

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California Institute of Technology
W. M. Keck Laboratory of Engineering Materials

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by

A. Amamou and J. Durand

In collaboration with R. Raj, Yale University, J. I. Budnick, University of Connecticut and R. Hasegawa, Allied Chemical Corporation.

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Professor Pol Duwez, principal investigator.

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ABSTRACT

Combined NMR, spin-echo and Mössbauer experiments have been performed to obtain hyperfine field distributions of the transition metal and metalloid elements in splat-cooled amorphous $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ alloys. These distributions are related to the local environments of the elements. The NMR signals are observed in the low frequency range 20 - 60 MHz and all the nuclei, i.e. Fe, P and B, may contribute to the spectral distribution. The resolution of the spectra into that due to Fe and (P + B) nuclei was made possible by using samples prepared with an Fe^{56} isotope. The Fe distribution thus obtained shows general agreement with the Mössbauer field distribution. From a careful analysis of the NMR data, the hyperfine field at the B nuclei in these amorphous alloys is found to range from 24 to 26 KG increasing with B content. An upper limit of 8 KG for the half-width is attributed to this distribution.

The Mössbauer spectra of the Fe^{57} nuclei resemble those for the crystalline $\text{Fe}_{75}\text{P}_{25-x}\text{B}_x$ alloys. A fit of our spectra shows a field distribution which suggests the presence of structure. Such a structure may correspond to various Fe sites, also seen in the crystalline alloys. The distributions generally lie between about 160 and 330 KG, with a maximum at about 260 KG. These spectra do not show the presence of Fe nuclei with essentially zero hyperfine field as was obtained for amorphous Fe-Pd-P by Sharon et al. and for amorphous Fe-P by Logan et al. With increasing B content the center of gravity of the Fe distribution shifts to higher values. From a systematic study of the NMR lines and other considerations it is concluded that the P field distribution is broad and its hyperfine field is between 20 and 35 KG for the higher P concentration alloys.

INTRODUCTION

The determination and understanding of local atomic arrangements is of major interest in studies of amorphous materials. Microscopic probes such as x-ray, electron and neutron scattering have been used extensively to obtain this information. Mössbauer and NMR experiments, also probe the local environments around a given atom by measuring the hyperfine field distribution at the nucleus of the atom. For example, Sharon et al.¹ have used the Mössbauer technique to study local configurations around Fe sites in amorphous Fe-Pd-P. However, the applicability of the Mössbauer technique is limited to specific radioactive nuclei.² In the case of amorphous transition metal-metalloid systems, only alloys containing Fe⁵⁷ have been extensively studied. On the other hand, NMR can be applied to a wide variety of nuclei including Fe⁵⁷. The only atoms to which NMR cannot be applied are the ones for which the nuclear spin is zero.

The ability to observe an NMR signal from a particular nucleus in a magnetically ordered state is a complicated function of several factors: one among them is isotopic abundance. Due to the low isotopic abundance of Fe⁵⁷ (2.87%), it is not an especially favorable nucleus for NMR work, compared to, for example, Mn (100%). Thus in an amorphous alloy where Fe is present along with other elements with larger isotopic abundance, a combined approach of NMR and Mössbauer could be a useful one to provide accurate hyperfine field distributions for both the metal and metalloid atoms.

Fe₇₉P_{21-x}B_x is an excellent system for the study of hyperfine field distributions. The Fe field distribution can be acquired by a Mössbauer

study and can be compared with that obtained by NMR to check the fitting procedure. In addition, the large isotopic abundance of metalloid atoms, i.e. P (100%) and B¹¹ (81.8%), makes them especially attractive for NMR measurements. It should be noted that metalloid hyperfine fields have not yet been reported in any amorphous alloy. This information is helpful for a wide variety of reasons - to understand conduction electron polarization and spin transfer effects, to shed light on the local environments of metalloid atoms and to compare these fields with their crystalline counterparts. The knowledge of these hyperfine field values is also necessary to extend our present theoretical calculations on crystalline systems into the area of amorphous materials.

THE Fe-P-B SYSTEM

The electronic and magnetic properties of splat-cooled amorphous Fe-P-B alloys have been reviewed by Durand in this conference proceedings as well as elsewhere.³ We will summarize only some relevant features.

In Fe₇₉P_{21-x}B_x alloys, B can be substituted for P to a large extent (3 < x < 17 at.%) in the amorphous phase. X-ray spectra on the Fe₇₉B₂₁ foils exhibited traces of microcrystalline phases. Both the value of $\bar{\mu}$ (the average magnetic moment per Fe atom) and T_c (the Curie temperature) increases as B replaces P. The value of $\bar{\mu}$ varies between about 1.96 and 2.01 μ_B and T_c between 670 to 770°K over the entire series. Furthermore, these variations in comparison with similar variations in the closest crystalline Fe₇₅P_{25-x}B_x compounds suggest the presence of short range ordering. The NMR as well as

Mössbauer experiments were performed on foils of these alloys. The central portions of the splat-cooled foils were removed due to their larger compositional inhomogenities.

EXPERIMENTAL

Spin-Echo: The NMR measurements on amorphous $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ alloys were made at 1.3 K and in zero external magnetic field. Nearly identical excitation conditions (pulses: $3\mu\text{s}$ each, power: low) were employed to observe signals in these alloys.

The normalized spin-echo spectra corrected for a single power of frequency in some representative alloys are shown in Fig. 1. The important features of these spectra are: (i) a broad maximum in the spectral distribution, (ii) a shift of the maximum to higher frequencies with increasing B composition, (iii) an increase in asymmetry on the high frequency side with increasing P composition, and (iv) similar excitation conditions for the spin-echo, which suggests that enhancement factors are nearly the same for all the samples.

In principle the observed spectral intensity could arise from all of the elements since with the detection sensitivity available no signals were found in the low frequency range as well as at higher frequencies. In order to resolve this question two samples were prepared with an Fe^{56} isotope; namely $\text{Fe}^{56}_{79}\text{P}_6\text{B}_{15}$ and $\text{Fe}^{56}_{79}\text{P}_{16}\text{B}_5$. The nuclear spin for Fe^{56} is zero, thus the resonance due to Fe is not observed in samples containing only this isotope. The magnetic properties of the Fe^{56} samples, i.e. the magnetic moment and Curie temperature, on the other hand, are essentially the same as that for samples with the same composition containing natural iron.

Fig. 1. Spin-echo spectra at 1.3 K of several amorphous $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ alloys.

The NMR signal strength depends on both the number and upon the properties of the nuclei present in the sample even if the enhancement factors for the nuclei are assumed to be the same. Thus in the sample $\text{Fe}_{79}\text{P}_5\text{B}_{16}$, for example, the contribution to the spectral distribution from each of the nuclei at a given frequency would be approximately: Fe^{57} (173), P^{31} (500), B^{11} (1300) and B^{10} (300). This means that the P^{31} and B^{11} signals are expected to be stronger than the Fe^{57} and B^{10} . The enhancement mechanism in magnetically ordered materials is important and cannot be ignored. These mechanisms are not well understood and, among other factors, are proportional to the hyperfine fields at the respective nuclei. The above numbers would be accordingly modified.

Figure 2 shows the actual intensity of both the natural Fe and the Fe^{56} samples. The echo amplitudes have been normalized with respect to the mass of the samples to obtain the relative magnitudes of the spectra. As expected, the Fe^{56} samples showed distributions with lower intensities than the natural Fe samples. The dotted lines represent the difference between the two spectra and correspond to the field distribution for the Fe. The relative height of the distribution should be treated with caution due to the assumptions involved but these difference spectra strongly suggest structure in the Fe hyperfine field distributions.

The variation of maximum echo amplitude, normalized to the mass of the samples, with the B concentration is shown in Fig. 3. The amplitude increases with the B composition. This result indicates that the maximum in the NMR spectra arises predominately from the B nuclei since the Fe composition in the alloys remains constant and if the maximum had been produced by P the curve would show the opposite

Fig. 2. Relative hyperfine field distributions of two amorphous $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ ($x = 5, 15$) samples. Each sample is compared with the sample of same composition but containing ^{56}Fe isotopes. The dotted spectra represent approximately the difference between the two distributions and are due to the ^{57}Fe nuclei.

Fig. 3. Variation of peak echo amplitude per unit mass as a function of composition (x) in $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ alloys. The behavior of the single point for the 5% Boron sample could reflect the growing dominance of phosphorus in the spectrum at lower x.

behavior. Since B^{11} is in greater abundance (82%) than B^{10} (18%), the maximum is associated with the B^{11} nuclei. The average B field in these amorphous alloys is about 25 KG with the maximum line-width of about 8 KG assuming a low intensity broad P distribution. The B hyperfine field increases slowly with x consistent with the trend observed in the crystalline alloys. The B field in Fe and in Fe_2B are $< 4^4$ and 30 KG^5 respectively. This means that the B field increases with the B content in Fe as is found in the present amorphous alloys. The B enters with two less s-p electrons than P and thus reduces the electron concentration in the alloys, a situation similar to the crystalline alloys $Fe_{75}Si_{25-x}Al_x$ in which Al enters with one less electron than Si. It is interesting to note that the Al hyperfine field has also been shown to increase linearly with x.⁶

No clear sharp resonance corresponding to P is seen in these alloys. The appearance of a high frequency tail in the NMR spectra, however, suggests its presence.

Mössbauer Absorption Measurements: The Mössbauer measurements were performed, at room temperature, with a standard spectrometer operating in a constant acceleration mode;⁷ the source was Co^{57} in Cu and the specimens were about 40 microns in thickness. For all the $Fe_{79}P_{21-x}B_x$ amorphous alloys, the absorption spectrum as a function of the source velocity shows six overlapping but well defined peaks. The spectrum is roughly symmetrical with the symmetry axis close to that of the zero velocity. If we denote V_i as the velocity of the i th peak, the ratios V_6/V_1 , V_5/V_2 and V_4/V_3 are approximately the same as in pure iron, corresponding to a hyperfine field of about 250 KG. Finally we note that no significant absorption is detected at the velocity of pure iron ($\pm 5.325\text{ mm/s}$).

The experimental spectra as shown in Fig. 4, can likely be fitted by a continuous hyperfine field distribution assuming a given shape as a function of H . However we have chosen to determine the hyperfine field distribution $P(H)$ by a method proposed by Hesse and Rubartsh;⁸ this method does not presuppose a $P(H)$ shape. In such a fit we assume that all the sextuplets have the same average shift, no quadrupolar splitting and the same linewidth as in pure iron (0.38 mm/s); the relative intensities of the lines being 3: R: 1 where R can be adjusted. A detailed study of the Mössbauer spectra and the fitting method will be presented in a further publication; in this paper we discuss the main features of our preliminary results. For all the investigated alloys a first fit was performed assuming the hyperfine field to lie between 0 and 400 KG. $P(H)$ was determined for 40 values. The results showed that no significant probability occurred below 160 KG and above 330 KG. Therefore the investigated field range was reduced to 150 - 350 KG and the experimental spectrum could be fitted as well [Figs. 5(a) and 5(b)]. The obtained $P(H)$ versus H curves are asymmetrical for both samples with a rather broad tail below a maximum of about 250 KG [see Fig. 5 which refers to both Figs. 5(a) and 5(b)]; the contribution at low fields decreases slightly when the Boron content is increased. Moreover $P(H)$ exhibits some bumps which suggest the existence of a structure in the hyperfine field distribution. It may be suggested that such bumps could arise from a microcrystalline structure in whole or in part of the alloy; however the samples studied can be considered as amorphous according to the current criteria: the x-ray pattern shows a broad first peak without any bump, the Curie transition is very sharp (1 to 3°K) and the behavior of the resistivity at high temperature exhibits an

Fig. 4. Relative Mössbauer absorption versus the source velocity at $T = 300$ K for amorphous $\text{Fe}_{79}\text{P}_5\text{B}_{16}$. The full line represents the fit results.

Fig. 5(a). Hyperfine field distribution $P(H)$ vs. H , for amorphous $\text{Fe}_{79}\text{P}_{16}\text{B}_5$ at $T = 300$ K in the ϵ short range order, compared with values determined in crystalline Fe_3P (full lines) after ref.: E. J. Lisher *et al*: J. Phys. C7, 1344 (1974) and in crystalline $\text{Fe}_{3.03}\text{P}_{0.81}\text{B}_{0.19}$ (dashed lines) after ref. 10.

Fig. 5(b). Hyperfine field distribution $P(H)$ vs. H , for amorphous $\text{Fe}_{79}\text{P}_5\text{B}_{16}$ at $T = 300$ K in the ϵ_1 short range order, compared with values determined in crystalline $\text{Fe}_{3.01}\text{P}_{0.35}\text{B}_{0.65}$ (full lines) and $\text{Fe}_{2.85}\text{P}_{0.05}\text{B}_{0.95}$ (dashed lines) after ref. 10.

irreversible crystallization process similar to that observed in "good" amorphous alloys. Therefore the bumps in the hyperfine field distribution, more likely, have to be related to the amorphous state. Previous structural studies⁹ on some amorphous transition metal alloys showed that the coordination number of each atom is the same as in the crystalline counterpart. Thus, the $P(H)$ shape may arise from the presence of iron atoms with various local environments which can be compared to those of the Fe-P-B crystalline alloys. Some previous studies on such alloys showed that hyperfine field values can be associated with each iron site; for $\text{Fe}_{75}\text{P}_{25-x}\text{B}_x$, the Mössbauer data is separated into four contributions for the ϵ phase and three contributions for ϵ_1 phase.¹⁰ The hyperfine field values vary significantly with P and B content and the difference between the extreme values decreases when B is increased. The comparison between the results of the amorphous and the crystalline alloys have to be considered with caution since the compositions are not the same and the effect of iron concentration has not been determined. However, in our hyperfine field distribution the bumps occur at values which are close to those of the crystalline state (Fig. 5); these results suggest the presence of iron sites with first near neighbor configurations in the amorphous structure comparable to those found in the crystalline structure. So far, our results do not allow a clear separation between the two types of short range orders (SRO) ϵ and ϵ_1 , as shown in magnetic studies.³ Only some trends can be observed: (i) the line-width at half intensity is slightly larger for the ϵ SRO region (51 ± 3 KG) than in ϵ_1 SRO region (45 ± 2 KG), (ii) the average hyperfine field H , defined as the center of gravity of $P(H)$ ($H = \frac{\sum_i P(H_i) H_i}{\sum_i P(H_i)}$),

is 248 ± 2 KG in the ϵ -SRO and 256 ± 2 in the ϵ_1 -SRO. Finally let us note that in $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ the ratio between the average magnetic field and the magnetic moment $\bar{H}/\mu$ is constant and equal to $126 \text{ KG}/\mu_B$; this value is close to that found in the crystalline counterpart and in a large number of crystalline compounds of transition metals with s-p elements.^{12, 13}

It should be noted that the Fe Mössbauer field distributions (Fig. 5) are similar to the ones obtained by the NMR measurements (Fig. 2). The center of gravity of the two distributions is in agreement when corrected for the temperature difference. The analysis of our Mössbauer field distributions do not indicate the presence of nuclei with essentially zero hyperfine field as was found to be the case in amorphous Fe-P (Logan et al.¹¹) and in Fe-Pd-P (Sharon et al.¹).

SUMMARY AND CONCLUSIONS

The NMR measurements on the magnetically ordered splat-cooled amorphous $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ alloys show that the spectral distribution is a combined result of signals arising from the Fe, P, and B nuclei. A partial resolution of the NMR spectra into that due to Fe and (P + B) nuclei is made by using samples enriched in Fe^{56} . The Fe distributions thus obtained are not inconsistent with the Mössbauer results on the same samples indicating an overall consistency in the fitting of the Mössbauer data and the assumption of constancy of enhancement factor based on nearly identical excitation conditions employed in the excitation of the NMR spectra.

The center of gravity of the Fe hyperfine field distribution varies

linearly with the B composition. This also implies a linear variation of the Fe field with the average Fe moment. The slope of the line is $126 \text{ KG}/\mu_B$, a value reported for several of interstitial crystalline compounds. It is interesting to note that for amorphous Co-P alloys, the ratio of Co hyperfine field and its moment was also found to be constant.¹⁴ The half width of Fe distribution remains practically constant around 80 KG. By comparing the variation of Fe hyperfine field distribution in the amorphous $\text{Fe}_{79}\text{P}_{21-x}\text{B}_x$ system with that of crystalline $\text{Fe}_{75}\text{P}_{25-x}\text{B}_x$, we believe that the short range atomic ordering, at least in the first neighbor shell in these amorphous alloys, is similar to that observed in their crystalline counterparts.

The broad maximum in the NMR spectra is associated with the B^{11} nuclei which are the more abundant of the two B-isotopes. This identification is supported by the variation of the echo amplitude with Boron composition (x) under constant excitation conditions. The B hyperfine field varies linearly with x just as does the Fe field. This observation implies scaling of the B hyperfine field with the average Fe moment and indicates that short range spin polarization effects are important. The average B hyperfine field in the amorphous alloys is 25 KG with a maximum line-width of $\sim 8 \text{ KG}$, compared to an Fe hyperfine field of 260 KG and a line-width of $\sim 80 \text{ KG}$. The small line-width observed for the B suggests a homogeneity in the nearest neighbor magnetic environments surrounding the metalloid atom.

The P resonance is not well resolved in the NMR spectra; however, its presence is clearly seen at higher frequencies when the P content is increased. We believe that the P resonance is spread out thus making it difficult to observe. The present investigation, along with a rough comparison of the NMR spectrum with a Mössbauer spectrum on a

$\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$ sample suggests that the P field lies in the range of 20 - 35 KG.¹⁵ It is possible to make a rough prediction for the P line-width. The ratios of Fe and B hyperfine fields to their line-widths (in units of magnetic field) are approximately the same, i.e. ~ 3 . If the same ratio is assumed for the P, then its line-width lies in the range 7 - 12 KG, or 12 - 22 MHz consistent with the observed broad distribution at higher frequencies in our spectra for high P composition.

If this reasoning is also applied to similarly coordinated amorphous Co-P alloys, in which one finds for the Co nuclei the ratio of field to line-width to be 1 - 1.5, the P line in Co-P could be as wide as its hyperfine field. This might be the reason that the P NMR has not been reported in amorphous Co-P alloys.¹⁴

In order to gain a more complete characterization of the P and B resonances, we have begun to prepare the binary amorphous $\text{Fe}_{79}^{56}\text{P}_{21}$ and $\text{Fe}_{79}^{56}\text{B}_{21}$ along with the samples $\text{Fe}_{16}^{56}\text{P}_{16}\text{B}_{5}^{10}$ and $\text{Fe}_{5}^{56}\text{P}_{5}\text{B}_{16}^{10}$. In addition, amorphous samples of Fe-P-B alloys enriched in Fe^{57} are being prepared in order to make further a detailed comparison of the Mössbauer fitting procedure with the NMR spectrum.

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