Evidence for significant structural differences between the ferromagnetic metallic glasses $Fe_{1-x}P_x$ and $Fe_{1-x}B_x$, $x \approx 0.18$

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The qualitatively different line amplitude patterns in the Mössbauer Zeeman spectra for iron-boron and iron-phosphorus ferromagnetic glasses are quantitatively analyzed for the examples $Fe_{82}B_{18}$ and $Fe_{83}P_{17}$ in terms of correlations between isomer shift, hyperfine field, and quadrupole energy. The commonly accepted notion that these materials are all, on a local scale, basically distorted and stoichiometrically perturbed forms of the closely related tetragonal crystalline Fe_3B and Fe_3P structures is refuted.

Increasing acceptance is found in the literature[1–7] of the inference that the binary transition-metal—metalloid glasses $(T)_{1-x}M_x$ $(0.15<x<0.25)$ are, on a local scale, structurally based on distorted forms of the relevant crystalline composition $(T)_3M$. Certainly, they tend to revert to these forms upon crystallization, together with a little elemental transition metal (the proportion of which scales with the deviation of x from 0.25).[8,9] It is the purpose of this paper to point out an apparent exception to this rule—namely, that of $Fe_{1-x}B_x$. By examining the detailed Zeeman ^{57}Fe Mössbauer spectra of amorphous $Fe_{82}B_{18}$ and amorphous $Fe_{83}P_{17}$ we establish from linewidth asymmetry patterns that, whereas the phosphide results conform with an interpretation based on a distorted tetragonal Fe_3P structure, the boride analog cannot be understood in a similar manner in terms of tetragonal crystalline Fe_3B. This result runs directly counter to the tenets of almost all the extensive literature on the iron-boron glasses to date and as such requires careful scrutiny.

In this paper we report first the detailed results of room-temperature Mössbauer measurements on amorphous $Fe_{82}B_{18}$ and amorphous $Fe_{83}P_{17}$. Both glasses are ferromagnetic at room temperature and therefore exhibit typical six-line ^{57}Fe Zeeman spectra L_i $(i=1-6)$ as shown in Fig. 1. Despite their basic similarities the two spectra have one glaring difference involving the relative intensities I_i of the 1,6, 2,5, and 3,4 spectra lines, namely, $I_i > I_{7-i}$ in the boride and $I_i < I_{7-i}$ in the phosphide. Generally speaking, all ferromagnetic iron-boron glasses (with varying composition x) exhibit the qualitative intensity pattern of Fig. 1(a) and all iron-phosphorus glasses that of Fig. 1(b), so that this feature points to a significant general difference between the local iron environments in each type. Although this qualitative observation has been pointed out before,[10] we shall here give the first quantitative analysis of its proper interpretation and of its importance in assessing local structure.

The ^{57}Fe Mössbauer absorption spectra were obtained in standard transmission geometry with a conventional constant acceleration spectrometer using a ^{57}Co in Pd source. The six-line Zeeman spectra, containing 512 channels, have excellent statistical quality. The amorphous samples were prepared by injecting the melt on the outside surface of a rotating drum.[11,12] They are in the form of long ribbons 1 mm wide and 35 μm thick. X-ray measurements exhibited diffraction patterns typical for a glassy material. Absorbers of a total area 2 cm^2 were formed by placing sections of the ribbon parallel to each other and holding them in place with an adhesive tape.

The relevant equations required for a complete interpretation of Mössbauer Zeeman spectra have been given earlier[13–15] and will be set out here without detailed derivations. The six-line positions L_i for an arbitrary iron nuclear site are given by

$$\begin{aligned} L_1 &= \delta - g_1\mu_N H + u - \alpha_+ \ , \\ L_2 &= \delta - g_2\mu_N H - u + \alpha_- \ , \\ L_3 &= \delta - g_3\mu_N H - u - \alpha_- \ , \\ L_4 &= \delta + g_3\mu_N H - u + \alpha_- \ , \\ L_5 &= \delta + g_2\mu_N H - u - \alpha_- \ , \\ L_6 &= \delta + g_1\mu_N H + u + \alpha_+ \ , \end{aligned} \tag{1}$$

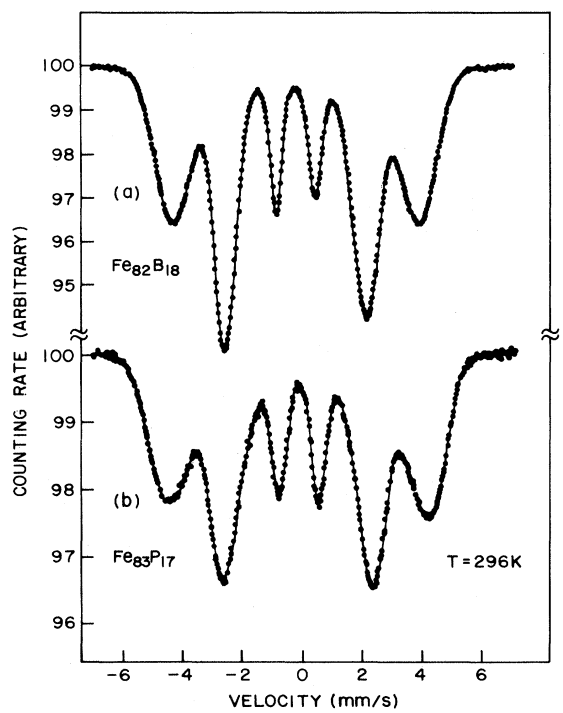

FIG. 1. Room-temperature Mössbauer Zeeman spectra for amorphous $Fe_{82}B_{18}$ and amorphous $Fe_{83}P_{17}$. The solid curves are the best least-squares computer fit to the data using six independent asymmetric Gaussian distributions of natural-width Lorentzian lines.

in which δ is the isomer shift, H the hyperfine field, $g_1=0.2448$, $g_2=0.1418$, $g_3=0.0388$, μ_N is the nuclear magneton, and u and $\alpha_\pm$ are, respectively, the first- and second-order perturbational shifts due to electric quadrupole energies. For an amorphous ferromagnet for which all spins are approximately parallel, angular averages require $\langle u\rangle=0$ and $\langle\alpha_+\rangle=3\langle\alpha_-\rangle$ when the spectrum is sampled over all iron sites.[15] In Figs. 1(a) and 1(b) the (centroid) line positions therefore involve only three site-averaged independent quantities $\langle\delta\rangle$, $\langle H\rangle$, and $\langle\alpha_-\rangle$. The degree of overdetermination of these equations, together with the necessary line-area A_i conditions $A_1=A_6$, $A_2=A_5$, $A_3=A_4$, will be used to assess the accuracy of the line-fitting procedure.

The data have been computer least squares fitted to six independent asymmetric Gaussian distributions of natural-width Lorentzian lines, using one Lorentzian per channel. Line asymmetries are, in general, much larger for outer lines (1,6 and 2,5) than for inner lines (3,4) and larger for the phosphide than the boride. The maximum asymmetry (ratio of Gaussian half-widths at half-heights) for the outer lines is ≈ 1.9 in $Fe_{83}P_{17}$ and ≈ 1.2 in $Fe_{82}B_{18}$. The final fits are indicated by the continuous curves in Fig. 1 and provide details of the (asymmetric) Gaussian distributions involving (centroid) positions $\langle L_i\rangle$, areas A_i, and mean-square widths $W_i^2=\langle(L_i-\langle L_i\rangle)^2\rangle$ as shown in Table I. Our first check, of area ratios A_1/A_6, A_2/A_5, A_3/A_6, reveals an overall rms deviation from unity of less than 1% and a maximum deviation (A_2/A_5 for $Fe_{82}B_{18}$) of 1.9%. Analyzing the six Eqs. (1) for the five parameters $\langle\delta\rangle$, $\langle H\rangle$, $\langle u\rangle$, $\langle\alpha_\pm\rangle$ for each material (treating u as the formally overdetermined parameter) we find, for $Fe_{82}B_{18}$,

$$\langle\delta\rangle=+0.064,\quad \mu_N\langle H\rangle=16.34,\quad \langle\alpha_+\rangle=0.028\ ,$$
$$\langle\alpha_-\rangle=0.012,\quad \langle u\rangle=-0.004\pm0.005\ , \tag{2}$$

and, for $Fe_{83}P_{17}$,

$$\langle\delta\rangle=+0.143,\quad \mu_N\langle H\rangle=16.46\ ,\ \langle\alpha_+\rangle=0.080\ ,$$
$$\langle\alpha_-\rangle=0.013,\quad \langle u\rangle=-0.012\pm0.002\ , \tag{3}$$

all in mm/sec and $\langle\delta\rangle$ with respect to iron metal at room temperature. The one standard deviation (70% confidence) limits on $\langle L_i\rangle$ estimated by the least-squares computer program for the respective fits to the data are 0.004 for the boride and 0.007 for the phosphide. Combining this information with our known restrictions $\langle u\rangle=0$ and $\langle\alpha_+\rangle=3\langle\alpha_-\rangle$ indicates an accuracy of about 0.005 and 0.020 for the linear parameters of Eq. (1) for the boride and phosphide, respectively. Writing $\langle\alpha_+\rangle+\langle\alpha_-\rangle=4\epsilon$, it follows that $\epsilon(Fe_{82}B_{18})=0.010\pm0.002$ and $\epsilon(Fe_{83}P_{17})=0.023\pm0.005$ mm/sec. These ϵ values are important since they are directly related to the mean square of the quadrupole distribution $\langle E_Q^2\rangle$ [where $E_Q(e^2Qq/4)\times(1+\eta^2/3)^{1/2}$ in conventional Mössbauer notation][16] via the equation[14]

$$\langle E_Q^2\rangle=5\langle u^2\rangle=5|g_E|\mu_N\langle H\rangle\epsilon\ , \tag{4}$$

where $g_E=-0.1031$, and therefore provide directly the rms quadrupole distributions

$$\sigma(E_Q)=0.29(1)\ \text{mm/sec},\quad \langle u^2\rangle=0.017(1)\ (\text{mm/sec})^2,\ \text{for } Fe_{82}B_{18}\ ;$$
$$\sigma(E_Q)=0.44(5)\ \text{mm/sec},\quad \langle u^2\rangle=0.039(8)\ (\text{mm/sec})^2,\ \text{for } Fe_{83}P_{17}\ ; \tag{5}$$

where $\sigma(x)$ for any variable x signifies the average $\langle(\Delta x)^2\rangle^{1/2}$, where $\Delta x=x-\langle x\rangle$.

The very obvious linewidth pattern difference between the two glass spectra of Fig. 1 can be quantified via the linewidth difference equations[14,15]

$$W_6^2-W_1^2=4g_1\mu_N(\langle\Delta H\,\Delta\delta\rangle+\langle\Delta H\,\Delta u\rangle),\quad W_5^2-W_2^2=4g_2\mu_N(\langle\Delta H\,\Delta\delta\rangle-\langle\Delta H\,\Delta u\rangle)\ ,$$
$$W_4^2-W_3^2=4g_3\mu_N(\langle\Delta H\,\Delta\delta\rangle-\langle\Delta H\,\Delta u\rangle)\ . \tag{6}$$

Using W_i values from Table I we find this overdetermined set to be consistent to the extent that they enable the determination of the fluctuation correlations

$$\langle\Delta H\,\Delta\delta\rangle=+0.043(3),\quad \langle\Delta H\,\Delta u\rangle=-0.039(3),\ \text{for } Fe_{82}B_{18}\ ;$$
$$\langle\Delta H\,\Delta\delta\rangle=-0.079(1),\quad \langle\Delta H\,\Delta u\rangle=-0.019(1),\ \text{for } Fe_{83}P_{17}\ ; \tag{7}$$

TABLE I. Centroid line positions $\langle L_i\rangle$ in mm/sec, areas A_i in arbitrary units, and mean-square linewidths $W_i^2=\langle(L_i\langle L_i\rangle)^2\rangle$ in (mm/sec)^2 for the six independent asymmetric Gaussian distributions of natural-width Lorentzian lines which give the best least-squares computer fit to the Zeeman Mössbauer spectra of Fig. 1. Line positions are given with respect to the isomer shift $\langle(L_1+L_2+L_5+L_6)\rangle/4$ as origin.

		$i=1$	2	3	4	5	6
	$\langle L_i\rangle$	−4.0267	−2.3057	−0.6364	0.6555	2.3037	4.0287
$Fe_{82}B_{18}$	A_i	1.789	2.054	0.608	0.608	2.094	1.792
	W_i^2	0.3070	0.1028	0.0231	0.0349	0.1529	0.3109
	$\langle L_i\rangle$	−4.1085	−2.3119	−0.6375	0.6655	2.3320	4.0884
$Fe_{83}P_{17}$	A_i	1.360	1.335	0.499	0.499	1.322	1.360
	W_i^2	0.5020	0.2208	0.0540	0.0443	0.1877	0.4069

in $(\mathrm{mm/sec})^2$ to the accuracy indicated. Since both isomer shift and hyperfine field are determined by local environment, the correlation $\langle \Delta\delta\,\Delta H \rangle$ should be a sensitive measure of local structure. In particular, if local glass environment is merely a somewhat distorted form of some crystalline equivalent, then there should be an approximate correspondence of $\langle \Delta\delta\,\Delta H \rangle$ values between the crystal structure in question and the glass.

Our expectations for the correlaton $\langle \Delta H\,\Delta u \rangle$ in this same quasicrystalline glass model[3] are quite different. The parameter u involves the polar angles (θ, ϕ), which measure the direction of hyperfine field with respect to the principal crystal-field axes at each iron site, in a fashion for which $\langle u \rangle = 0$ if θ and ϕ are random.[14,15] We therefore expect $\langle \Delta H\,\Delta u \rangle \rightarrow 0$ for a ferromagnetic glass in a true quasicrystalline *limit* no matter what the crystal is, since θ and ϕ vary randomly throughout the glass independently for each "crystalline" iron site with its well-defined values of hyperfine field, isomer shift, and quadrupole magnitude, etc.

In their crystalline phases Fe_3P and Fe_3B are tetragonal, with local environments which are very similar.[17,18] In x-ray refinement each seems to have three crystallographically inequivalent iron sites, although Mössbauer spectra reveal that these are split to a measurable degree in the phosphide. Mössbauer data are available at room temperature for both[8,19-21] and establish that

$$\langle \Delta H\,\Delta\delta \rangle = -0.02,\quad \langle \Delta H\,\Delta u \rangle = +0.04 \text{ for crystalline } Fe_3B,$$
$$\langle \Delta H\,\Delta\delta \rangle = -0.07,\quad \langle \Delta H\,\Delta u \rangle = +0.08 \text{ for crystalline } Fe_3P, \qquad (8)$$

in $(\mathrm{mm/sec})^2$.[22] Comparing Eqs. (7) and (8) we see that there is complete consistency with the idea that amorphous $Fe_{83}P_{17}$ contains a local structure which resembles a distorted form of crystalline Fe_3P. For amorphous $Fe_{82}B_{18}$, on the other hand, we see absolutely no indication of any resemblance to distorted Fe_3B.

If there is any tendency to retain a quasicrystalline environment in the boride glass then we suggest that a more likely candidate for this structure might be the orthorhombic cementite structure which is stable in Ni_3B and Co_3B. It requires about 50% admixture of Ni to tetragonal Fe_3B in order to stablize the cementite structure,[23] and the Mössbauer data on mixed orthorhombic $(Fe,Ni)_3B$ cementite crystals and equivalent $(Fe,Ni)_3B$ glasses[24,25] show qualitatively the same Zeeman linewidth asymmetry pattern not only as each other but as the whole series of glasses $Fe_{1-x}B_x$, $(0.15 < x < 0.25)$. It is this linewidth (or equivalently line-amplitude) pattern which we now see [through Eqs. (6)] as a kind of "fingerprint" of local structure in ferromagnetic glasses and which appears to rule out the tetragonal Fe_3B crystal structure as a prototype on which to base models of the iron-boron glasses.

We note with interest that crystalline Fe_3P, Ni_3P, and Co_3P all appear to be structurally equivalent (i.e., tetragonal) so that the cementite structure does not seem to be as energetically competitive for phosphide metalloids. We therefore anticipate that mixed $(Fe,Ni)_3P$ systems, for example, will show that same Zeeman linewidth asymmetry pattern as $Fe_{83}P_{17}$ in Fig. 1(b).

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