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Magnetic properties of amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$ and crystalline Fe_3B

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Amorphous samples of Fe_xB_{100-x} $(72 \leq x \leq 86)$ have been studied by ^{57}Fe Mössbauer spectroscopy and in some cases by magnetization measurements. The magnetic ordering temperature (T_C) decreases sharply with increasing Fe concentration; from 760 K ($Fe_{72}B_{28}$) to 552 K ($Fe_{86}B_{14}$). The value of T_C of amorphous pure Fe has been extrapolated to about 220 K. Well-defined hyperfine field distributions $\{P(H)\}$ have been found. The mean hyperfine field is found to be proportional to the average Fe moment with a ratio of about 130 kOe/μ_B. The shape of $P(H)$ for each alloy is practically independent of temperature. At low temperatures, the effective hyperfine field (H_{eff}) shows a temperature dependence of $H_{\text{eff}}(T) = H_{\text{eff}}(0)(1 - BT^{3/2} \cdots)$ due to spin-wave excitations. The value of $B_{3/2} = B(T_C)^{3/2}$ increases with Fe concentration. As the Fe concentration is increased in these alloys, the reduced hyperfine field decreases faster with reduced temperature due to a systematic change in the distribution of exchange interactions. A correlation of $H_{\text{eff}}(0)$ and the isomer shift exists for crystalline and amorphous Fe-B systems. Crystalline Fe_3B ($T_C \sim 800$ K) has been found after crystallizing amorphous samples with $x > 75$ under high heating rates. At $T < T_C$, Fe_3B shows at least three magnetically inequivalent sites, whereas at $T > T_C$, electric quadrupole interactions are observed. The crystal structure of Fe_3B is likely to be tetragonal rather than orthorhombic.

I. INTRODUCTION

Recently there has been considerable interest in amorphous magnetic solids.[1] Because of the special ways (liquid-quench, vapor-quench, etc.) in which they are made, the atomic arrangements in these solids are not periodic. Consequently, many solid-state properties found in amorphous solids are significantly different from their crystalline counterparts. Since many amorphous solids contain transition metal and rare-earth elements, magnetic phenomena in the absence of a crystalline lattice are of particular interest. Already a great variety of magnetic phenomena have been observed in amorphous magnetic solids. It is well recognized that due to the topological disorder in these solids, there are distributions of exchange interactions and magnetic moments instead of sharply defined ones as in crystalline solids. The details of these distributions together with the random single-ion anisotropy primarily determine the specific magnetic behavior of these materials.[2] It is, however, experimentally difficult to measure these distributions directly.

While many of the amorphous magnetic solids are multielement systems (e.g., $Fe_{40}Ni_{40}P_{14}B_6$),[3] the amorphous state of pure elemental metals is intrinsically of great importance. However, they are apparently difficult to make and they are metastable only in a very small temperature range.[4] Consequently there are only a few and often conflicting reports on their magnetic behavior. There is even concern as to whether some of the transition metals can be made amorphous at all. On the other hand, binary alloys (e.g., Fe-B,[5] Fe-P,[6] Tb-Fe,[7] etc.) can be made in the amorphous form and are stable over a relatively large temperature range. The concentration of amorphous binary alloys can be continuously varied over a wide range. From the trends exhibited by these samples one hopes to extrapolate into other concentration regions, in particular, the amorphous state of pure metals.

The magnetic properties of amorphous metal-metalloid systems are governed mainly by the species and concentrations of the metallic elements.[8] The presence of the metalloid atoms is thought mainly to stabilize the amorphous state. However, there is increasing experimental evidence which indicates that the metalloid atoms notably affect the magnetic properties as well. Furthermore, the influence due to various kinds of metalloid elements appears to be quite different.[9–11] The binary systems, such as Fe-B, represent the simplest amorphous metal-metalloid systems.

Binary Fe_xB_{100-x} can be made amorphous using the liquid-quench technique over a reasonably large concentration range ($72 \lesssim x \lesssim 86$).[5,12] Most reports agree that samples with Fe concentration more than 2 at.% outside this range cannot be made amorphous using the liquid-quench technique, although there are reports which claim that the upper Fe concentration limit could be as high as 91 at.%.[13] Of the amorphous Fe-B samples, the eutectic composition of $Fe_{80}B_{20}$ has been extensively studied.[14–16] There are also some recent studies of magnetization, Curie temperature, magnetostriction, and crystallization behavior of amorphous Fe-B.[5,12,13]

In this work, amorphous Fe_xB_{100-x}($72 \leq x \leq 86$) have been studied by ^{57}Fe Mössbauer spectroscopy and in some cases magnetization measurements. The Curie temperatures of the samples have been determined. The hyperfine interactions, and in particular the distributions of hyperfine fields, have been measured from 4.2 K to the Curie temperature. The distributions of magnetic moments, the distributions of exchange interactions and the behavior of amorphous pure Fe have been inferred. The hyperfine interactions of crystalline Fe_3B in both the ferromagnetic and the paramagnetic states have been determined.

II. EXPERIMENTAL

Amorphous samples of Fe_xB_{100-x} ($72 \leq x \leq 86$) have been made by liquid-quench technique.[17,18] They are in the form of long ribbons, typically 25 μm thick and 1 to 3 mm wide. All samples are found to be amorphous by x-ray diffraction. The $Fe_{72}B_{28}$ sample may contain a few percent of crystalline phase, which is difficult to detect using x-ray analysis.[12] The detailed experimental procedure of Mössbauer spectroscopy and magnetization measurements have been described elsewhere.[12,15,19]

III. RESULTS AND DISCUSSION

A. Magnetic ordering temperatures (T_C)

The magnetic ordering temperatures (T_C) of amorphous Fe_xB_{100-x} ($72 \leq x \leq 86$) have been determined by the onset of the magnetic hyperfine interaction under no external magnetic field. This can be conveniently measured by the thermal-scan method in which the transducer is set at a velocity near the centroid of the spectrum.[15] Two such scans are shown in Fig. 1 for $Fe_{82}B_{18}$ and $Fe_{72}B_{28}$. For samples with $x > 78$, T_C is sufficiently below the crystallization temperature (T_{CR}) that T_C can be accurately measured without crystallizing the samples (e.g., $Fe_{82}B_{18}$ as shown in Fig. 1). For samples with $x < 78$, even for a relatively high heating rate (~15 K/min), the sample crystallizes in the vicinity of T_C (e.g., $Fe_{72}B_{28}$ as shown in Fig. 1). The measured values of T_C of amorphous Fe_xB_{100-x} are shown in Fig. 2 as a function of Fe concentration. The value of T_C decreases sharply from 760 ± 10 K for $Fe_{72}B_{28}$ to 552 ± 3 K for $Fe_{86}B_{14}$. These values are in good agreement with some of those reported in the literature[5,12] but differ from others. In particular the values of T_C obtained for Fe_xB_{100-x} ($79 \leq x \leq 91$) by Fukamichi *et al.* level off at high Fe concentration.[13] This feature is not observed in the present work.

The change of T_C from amorphous $Fe_{72}B_{28}$ to $Fe_{86}B_{14}$ amounts to a decrease of about 15 K for each additional at.% of Fe. This *decrease* of T_C with increasing Fe content in Fe_xB_{100-x} for $72 \leq x \leq 86$ is opposite to what one might intuitively expect. The Curie temperatures of amorphous Fe_xB_{100-x} with low

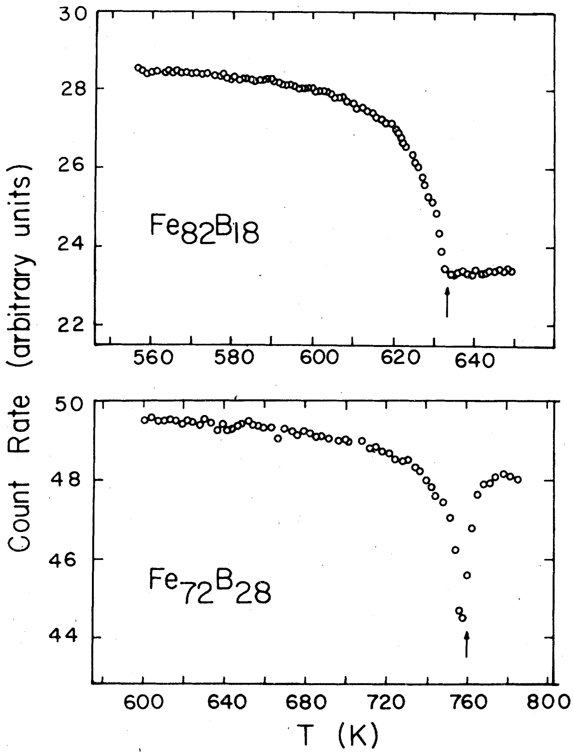

FIG. 1. Determination of T_C of amorphous $Fe_{82}B_{18}$ and $Fe_{72}B_{28}$ using the thermal-scan method at a heating rate of about 15 K/min. The arrows indicate the values of T_C.

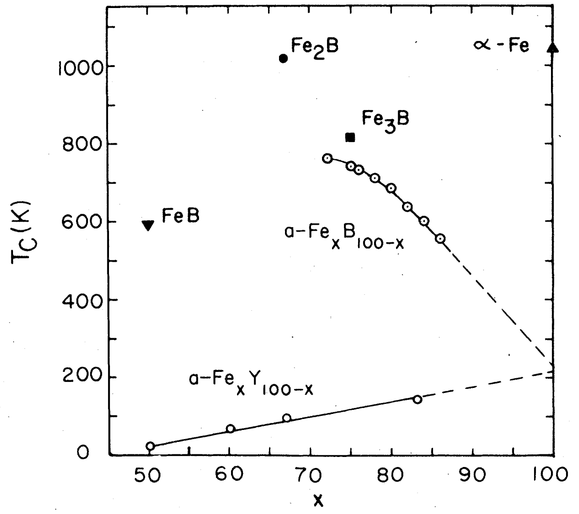

FIG. 2. Magnetic ordering temperatures of crystalline α-Fe, FeB, Fe_2B, Fe_3B, and of amorphous Fe_xB_{100-x} and amorphous Fe_xY_{100-x} as a function of Fe concentration. The value for FeB is taken from Ref. 23; the values for Fe_xY_{100-x} are taken from Ref. 20.

Fe concentration have not been measured. However, since amorphous boron should have a very small magnetic ordering temperature (if it is magnetic at all), T_C for amorphous Fe-B samples with low Fe concentrations is expected to *increase* with increasing Fe content. Thus if amorphous Fe-B could be made for the entire composition range, the value of T_C should have a maximum at some mid-Fe concentration.

The amorphous state of pure Fe is of particular interest. However, to our knowledge, no value of T_C for amorphous pure Fe has been directly measured. From the present results for amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$, a value of $T_C \simeq 220$ K can be extrapolated for amorphous pure Fe as shown in Fig. 2. Obviously a large error must be attached to this value of T_C from such an extrapolation. However, from the values of T_C for amorphous $Y_{100-x}Fe_x$ $(33 \leq x \leq 83)$ reported recently,[20] a value close to 220 K can also be extrapolated (Fig. 2). Thus from both of these extrapolations, a value of about 220 K appears to be reasonable. In addition, studies of amorphous $Tb_{100-x}Fe_x$ $(72 \leq x \leq 82)$[7] and Fe_xP_{100-x}[6] have extrapolated to similar values. The studies of amorphous $Y_{100-x}Fe_x$ further indicate that spin-glass ordering occurs only for samples with low Fe concentration and ferromagnetism exists for samples with high Fe concentration.[20] One therefore can conclude that amorphous pure Fe should be ferromagnetic with a T_C of about 220 K. Given the low crystallization temperature for amorphous pure Fe[4] it will be difficult to directly measure this value of T_C.

By using the molecular-field result for the Curie temperature

$$T_C = \frac{2z_{\mathrm{av}}J_{\mathrm{FeFe}}S(S+1)}{3k_B} , \tag{1}$$

where S is the spin and k_B is the Boltzmann constant, it has been argued that subtle changes in the atomic structure of amorphous Fe_xB_{100-x} $(72 \leq x \leq 88)$ cause the value of T_C to decrease significantly with increasing Fe content.[5] Specifically, as the Fe concentration increases, the structure is supposed to change from a dense random packing structure to a body-centered-cubic (bcc)-like structure so that z_{av} in Eq. (1) changes from about 12 to about 8. It should be noted that the above scheme is based on one crucial assumption, that is, the average exchange interaction (J_{FeFe}) remains *constant*, so that the decrease of T_C is a direct consequence of the reduction of z_{av}. However x-ray diffraction measurements on amorphous Fe-metalloid alloys and amorphous Fe suggest that the dense random packing structure remains an approximately valid picture for these cases.[21] One therefore does not expect a drastic change in the average coordination number in Fe_xB_{100-x} $(72 \leq x \leq 86)$. Furthermore, since α-Fe has a bcc structure, it is difficult to account for the very different values of T_C for crystalline and amorphous Fe if the structure in Fe_xB_{100-x} is approaching a bcc state with increasing Fe concentration. In fact, as indicated by Ichikawa, as far as coordination number and nearest-neighbor distance are concerned, amorphous Fe would be closer to face-centered-cubic (fcc) structure than a bcc structure.[22] We therefore argue instead that the large reduction of T_C in amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$ is primarily the result of the decrease in the average exchange interaction. This is perhaps not too surprising since it is well known that J_{FeFe} depends sensitively on the Fe-Fe distance so that in crystalline Fe the exchange interactions in the fcc state (γ-Fe) are substantially smaller than those in the bcc (α-Fe) state.

Also shown in Fig. 2 are the values of T_C of crystalline Fe-B compounds. Crystalline α-Fe $(T_C = 1043$ K), FeB $(T_C = 598$ K),[23] and Fe_2B $(T_C = 1015$ K)[24] are well known and have been extensively studied. In addition, the compound Fe_3B is known to be highly unstable and difficult to synthesize in pure form.[25] However it has been found that by crystallizing amorphous $Fe_{80}B_{20}$ the crystalline state of Fe_3B can be obtained.[16,26] The value of T_C for Fe_3B is about 800 K.[15,16,26] As shown in Fig. 2, the value of T_C for the four crystalline compounds containing Fe and B show no clear correlation among themselves nor with those of amorphous Fe-B. This is perhaps not too surprising since the crystal structure, the Fe-Fe distances, the number of neighbors, etc., are all very different for these Fe-B crystalline compounds. On the other hand, in amorphous Fe_xB_{100-x} the variables which determine the value of T_C vary smoothly as one changes the composition.

B. Hyperfine interaction of Fe_xB_{100-x} at 4.2 K

1. Magnetic hyperfine spectra of amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$

Mössbauer spectra of amorphous Fe_xB_{100-x} at 4.2 K are shown in Fig. 3. In each case, the spectrum is composed of well defined but broadened lines. Such spectra are commonly observed in amorphous magnetic solids in which the large number of inequivalent Fe sites causes a distribution of hyperfine fields $\{P(H)\}$.[27,28] The fact that each of the six spectral lines shows no fine structure suggests that the $P(H)$ is quasicontinuous. But samples which have been made under less desirable quenching conditions or compositions often show spectra which reveal ill-resolved or even well-resolved extra lines in two or more of the six spectral lines. Careful x-ray diffraction measurements indicate that such samples are partially crystalline.[29]

Although the existence of a $P(H)$ is quite apparent, it is not unreasonable to also expect a distribution of isomer shifts $\{P(I.S.)\}$ in amorphous magnetic solids. However, the well-defined doublet spectra of many amorphous solids observed at $T > T_C$ indicate that the $P(I.S.)$ is very narrow and can be well approximated by a single average isomer shift.[30] It is only when the $P(H)$ is also very narrow that the effects due to $P(I.S.)$ are particularly notable.[31]

In amorphous solids where the atomic site symmetry is generally less than cubic one expects nonzero electric field gradients (EFG). Indeed, in every amorphous solid (except those where crystallization prevents such measurements) one observes a quadrupole splitting at $T > T_C$.[30] At $T < T_C$, because the angular factor is spatially averaged to be nearly zero, the *effective* EFG is expected to be negligible.[32] This is manifested by the fact that the line positions of the six spectral lines are very symmetric about the centroid of the spectrum. Recently, by noting the slight difference of the intensities of the No. 2 and No. 5 peaks of the spectrum of $Fe_{80}B_{20}$, it has been concluded that a distribution of sizable effective EFG's exists in the alloy.[33] However, as described elsewhere,[31] the slight difference in intensities may not necessarily be caused by the nonzero effective EFG. Experimentally there is much evidence which argues against a sizable effective EFG. For example, one observes a slight asymmetry in line intensities but not in line positions which would be highly sensitive to the effective EFG. Also a systematic dependence of the intensity asymmetry on the metalloid composition has recently been observed in amorphous $Fe_{40}Ni_{40}P_yB_{20-y}$ $(0 \leq y \leq 20)$.[34] It is highly unlikely that such a systematic variation could be caused by a corresponding systematic variation in the effective EFG. Instead, the difference in the line intensities can be accounted for by a slight correlation between $P(H)$ and $P(I.S.)$. Of course such a correlation would be difficult to extract if the asymmetry is very small (e.g., those shown in Fig. 3). But in amorphous $(Fe_{0.2}Co_{0.8})_{80}P_{17}Al_3$ where a pronounced asymmetry is observed, such a correlation has indeed been found.[31]

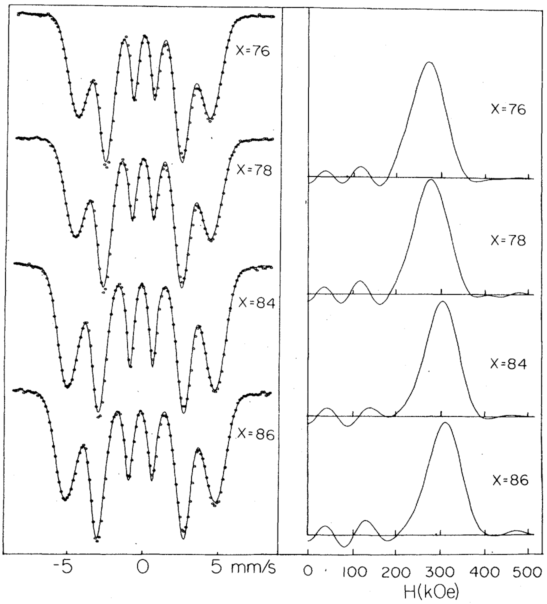

FIG. 3. Mössbauer spectra of amorphous Fe_xB_{100-x} at 4.2 K. The deduced hyperfine field distributions $\{P(H)\}$ are shown on the right.

2. Hyperfine field distribution $\{P(H)\}$

There are a number of ways in which one can obtain qualitative and quantitative information about the $P(H)$ contained in the spectrum.[27,35,36] Detailed tests indicate that the Fourier series method by Window and the method by Hesse and Rübartsch are quantitatively more reliable than others.[28,36] Both of these methods have comparable accuracy and the former has been used in the present work. In each method there are parameters whose values must be properly chosen. These parameters include the number of terms in the series (in Window's method), the grid size with which to divide the hyperfine fields and the "smoothness parameter" (in Hesse and Rübartsch method). The statistical accuracy of the spectrum and the structure of $P(H)$ primarily dictate the choice for the values of the parameters. Choosing the values incorrectly often gives erroneous information in the form of spurious "bumps" in the resultant $P(H)$.[28,36]

The details of Window's method as applied to the spectra of amorphous magnetic solids have been described elsewhere.[28] In the analyses of the spectra of Fe_xB_{100-x}, we have assumed a single isomer shift in each spectrum and no effective quadrupole interaction as mentioned above. Detailed tests indicate that for the spectra shown in Fig. 3, a cosine series with 12 to 20 terms is appropriate. The deduced $P(H)$ are shown in Fig. 3 next to each spectrum. The solid curve for each spectrum is the best-fit result with the incorporation of the $P(H)$. In each case, a smooth and essentially structureless $P(H)$ has been found. However, it should be mentioned that this type of simple $P(H)$ is not found in all amorphous magnetic solids; notable exceptions are $(Fe\text{-}Mo)_{75}P_{16}B_6Al_3$[37] and $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$,[38] in which more complicated $P(H)$ have been found.

For each $P(H)$, one can define several characteristic values: the peak of the field distribution $\{H_{peak}\}$, the half-width of the distribution at half maximum $\{\Delta H\}$, and the average hyperfine field

$$H_{mean} = \int HP(H)\,dH \ . \qquad (2)$$

These values for the $P(H)$ of Fe_xB_{100-x} at 4.2 K are shown in Fig. 4. These are practically the values at $T = 0$ K. The values of H_{peak}, H_{mean} and ΔH vary smoothly with Fe concentration. For $Fe_{72}B_{28}$, the values of H_{peak} and H_{mean} are slightly greater than those expected from the trend established by the other samples. For Fe_xB_{100-x}, the value of H_{mean} is slightly smaller than that of H_{peak} due to the slight asymmetry in the $P(H)$. As shown in Fig. 4, the values of both H_{peak} and H_{mean} increase with Fe concentration whereas ΔH remains approximately constant. This indicates that in this Fe concentration range the shape of $P(H)$ is essentially independent of the Fe concentration. For samples with higher Fe content the entire $P(H)$ simply shifts to higher H values.

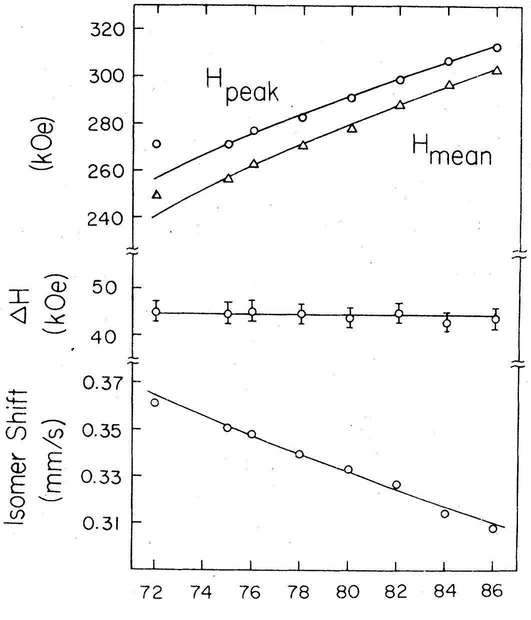

FIG. 4. Peak values (H_{peak}), the mean values (H_{mean}), the widths (ΔH) of $P(H)$, and the isomer shifts of amorphous Fe_xB_{100-x} at 4.2 K as a function of Fe concentration.

We again attempt to extrapolate to the case of amorphous pure Fe. According to the trend set by amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$, amorphous pure Fe should have an H_{peak} or H_{mean} of about 350 kOe. This value is rather close to the value of 340 kOe for crystalline α-Fe. However, in contrast to crystalline α-Fe, the extrapolated width of $P(H)$ for amorphous Fe appears to be quite large. Since amorphous Fe should also contain many inequivalent Fe sites, a $P(H)$ with a sizable width is not unexpected.

It is well extablished in amorphous Fe-metalloid solids that due to a very large number of inequivalent Fe sites one invariably finds a distribution of hyperfine fields.[27] The detailed causes for the particular shape of $P(H)$, such as those shown in Fig. 3, remain speculative. This is partly because the precise atomic arrangements in an amorphous solid are still difficult to ascertain.[20] However, even given a structure associated with a particular model (e.g., the dense random packing of hard spheres) it is by no means simple to calculate the hyperfine fields of the Fe atoms. As previously noted there is a similarity between the measured $P(H)$ and the binomial distribution function,[27]

$$\text{Probability}(n) = \frac{12!}{n!(12-n)!}\left(\frac{x}{100}\right)^n \times \left(1-\frac{x}{100}\right)^{12-n} , \qquad (3)$$

$$n = 0, 1, 2, \ldots, 12 ,$$

which is the probability of finding n Fe neighbors in amorphous Fe_xB_{100-x} assuming a coordination number of 12. It is tempting therefore to assume that the hyperfine field of an Fe atom can be determined by the number of its Fe neighbors, or alternatively by the number of its metalloid neighbors. By requiring that either that each Fe neighbor contributes a fixed amount to the hyperfine field (e.g., about 25 kOe)[39] or that each metalloid neighbor decreases H by a fixed amount,[27] the binomial distribution function can be transformed into a calculated $P(H)$ which compares rather well with the measured $P(H)$. This model of simple addition of individual hyperfine fields not only has been applied to amorphous solids but to crystalline alloys, particularly dilute alloys.[40] While this simple model is useful to qualitatively describe the $P(H)$ it is difficult to justify theoretically whether one can use this model to determine quantitatively the contribution to the hyperfine field due to various species of neighbors. It should be noted that a single binomial distribution function with only one particular coordination number (e.g., 12) is overly simplistic. X-ray experiments indicate there is a distribution of coordination numbers centered about 12 in amorphous Fe-metalloid alloys.[21] In addition, Eq. (3) completely ignores the differences in the atomic radii of various species in the solid.

It is well known that in crystalline Fe interstitial compounds (e.g., Fe_3C, FeB, Fe_2B, Fe_3P, etc.) the magnetic moment of Fe (μ_{Fe}) is, to a good approximation, proportional to the Fe hyperfine field (H_{eff}). Despite the wide range in the values of the moment, nearly constant ratios of H_{eff}/μ_{Fe} from 130 to 140 kOe/μ_B have been found.[41,42] This is presumably the result of a much smaller conduction-electron contribution to the hyperfine field than in the case of a metal.[41] One suspects then that such a proportionality perhaps also holds in amorphous Fe-metalloid alloys. However, since in amorphous ferromagnets the distribution of moments is usually not directly measured, one compares the average moment per Fe ($\bar{\mu}_{Fe}$) with the average hyperfine field (H_{mean}) as defined in Eq. (2). As shown in Fig. 4, H_{mean} for Fe_xB_{100-x} increases monotonically with Fe concentration. The values of $\bar{\mu}_{Fe}$ for Fe_xB_{100-x} have been reported by Hasegawa *et al.*,[5] Luborsky *et al.*[12] and also measured in this work. In all these cases, $\bar{\mu}_{Fe}$ is found to increase monotonically with Fe concentration consistent with the increase in H_{mean}. Numerically, the values of $\bar{\mu}_{Fe}$ obtained from these measurements differ by a few per cent. Using the average values of $\bar{\mu}_{Fe}$, the ratio of $H_{mean}/\bar{\mu}_{Fe}$ is found to increase slightly from about 125 kOe/μ_B for $Fe_{75}B_{25}$ to about 140 kOe/μ_B for $Fe_{86}B_{14}$. Similar values of the ratio have been found in other amorphous Fe-metalloid systems.[28,43] The consistency of the ratio suggests that the Fe hyperfine field is to a good approximation proportional to its moment. It follows then that the distribution of hyperfine fields provides a reasonably accurate description of the distribution of magnetic moments which is otherwise difficult to measure. The measured $P(H)$ in amorphous Fe_xB_{100-x} in Fig. 3 indicates that there is a sizable distribution of Fe moments with a halfwidth of about 0.3 μ_B. The slight increase of the ratio $H_{mean}/\bar{\mu}_{Fe}$ with Fe content might be due to the increasing importance of the conduction electron contribution to the hyperfine field.

3. Isomer shift

The average isomer shift (relative to ^{57}Co in Cr) of amorphous Fe_xB_{100-x} is shown in Fig. 4. The isomer shift decreases smoothly with increasing Fe concentration. At temperatures other than $T \simeq 0$ K, one measures an average center shift which is the sum of the isomer shift and the second-order Doppler shift. The average center shift of amorphous Fe_xB_{100-x} as a function of temperature is shown in Fig. 5. For clarity only four compositions with Fe concentration of 72, 78, 82, and 86 at.% are shown. At high temperatures ($T \geq 250$ K) the center shift decreases linearly with temperature, due to the second-order Doppler effect.[32] The rate of decrease agrees very well with the value of -7.29×10^{-4} mm/sec/K expected for the 14.4 keV γray of ^{57}Fe as shown by the straight lines. From the similarity of the curvatures at low temperatures, the average Debye temperatures for samples with different Fe content do not appear to vary significantly.

Because of the temperature dependence of the center shift and the hyperfine field, meaningful comparison between samples with different Fe concentrations must be done at the same temperature and at T close to 0 K. The hyperfine fields and the isomer shifts of amorphous Fe_xB_{100-x} ($72 \leq x \leq 86$) at 4.2 K are shown in Fig. 6 as a function of Fe concentration. Also shown are the values for the crytalline compounds of FeB, Fe_2B, and α-Fe. Our measured values for Fe_2B are in excellent agreement with those of previous experiments.[24] The values for FeB are taken from those in the literature.[23,44] From Fig. 6 one notes that in the Fe-B system the average hyperfine field (H_{eff}) increases smoothly with increasing Fe concentration, and the isomer shift decreases smoothly with increasing Fe concentration. This somewhat surprising result indicates that, unlike the magnetic exchange interactions, the *average* hyperfine interactions in Fe-B are *not* very sensitive to whether the structure is crystalline or amorphous, but depend mainly on the Fe concentration. One further notes from Fig. 6 that the two curves are strongly correlated; viz. the sample which exhibits a larger hyperfine

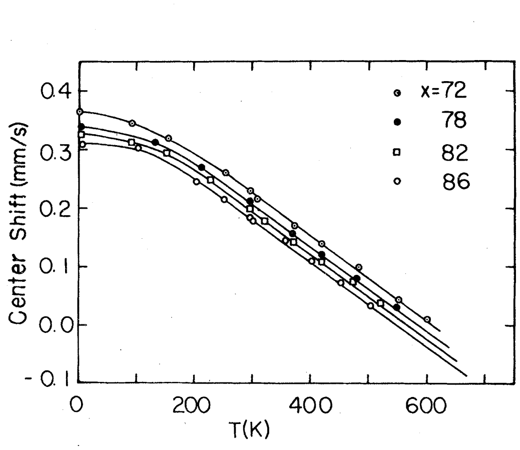

FIG. 5. Temperature dependences of the center shifts of amorphous Fe_xB_{100-x} with $x = 72$, 78, 82, and 86, relative to ^{57}Co in Cr at room temperature.

field shows a smaller isomer shift. In fact, as shown in Fig. 7, the hyperfine fields and the isomer shifts of Fe-B are related by a *linear empirical* equation

$$I.S.(x) = (I.S.)_0 - 0.0011 H_{\mathrm{eff}}(x)\ \mathrm{mm/sec} \qquad (4)$$

where $H_{\mathrm{eff}}(x)$ is in kOe and $(I.S.)_0 = 0.66$ mm/sec when a ^{57}Co in Cr source is used.

C. Temperature dependence of the hyperfine field

Mössbauer spectra of amorphous Fe_xB_{100-x} at various temperatures have been measured. For a typical example, the spectra of $Fe_{76}B_{24}$ are shown in Fig. 8. Also shown in Fig. 8 are deduced $P(H)$ obtained from these spectra. For increasing temperatures, the $P(H)$ shifts to lower H values as expected. The shape of $P(H)$ is virtually unchanged and the width (ΔH) of $P(H)$ steadily decreases with increasing T. This indicates that the various hyperfine fields have essentially the same temperature dependence. This common temperature dependence can be represented by that of the characteristic values of $P(H)$ (H_{peak}, H_{mean}, etc.). Since a single Curie temperature is shared by all hyperfine fields in the $P(H)$, the value of ΔH must consequently decrease. A similar con-

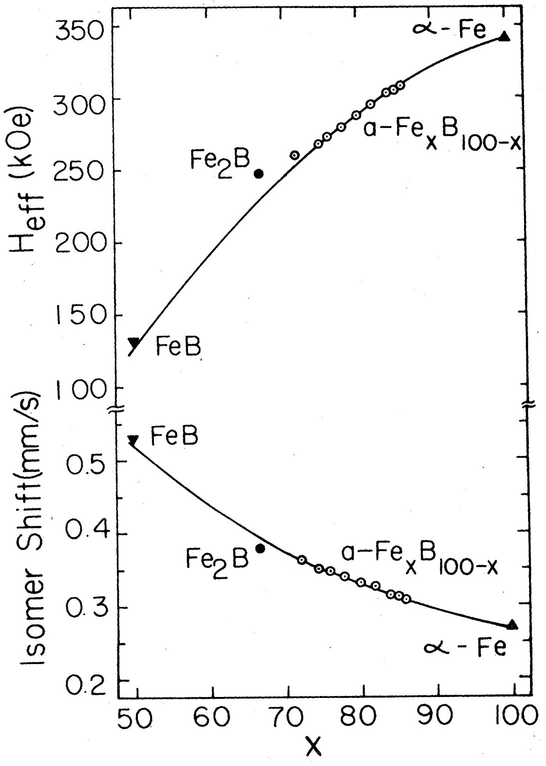

FIG. 6. Effective hyperfine fields and the isomer shifts of crystalline FeB, Fe_2B, α-Fe, and amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$ at 4.2 K as a function of Fe concentration. The isomer shifts are relative to ^{57}Co in Cr at room temperature.

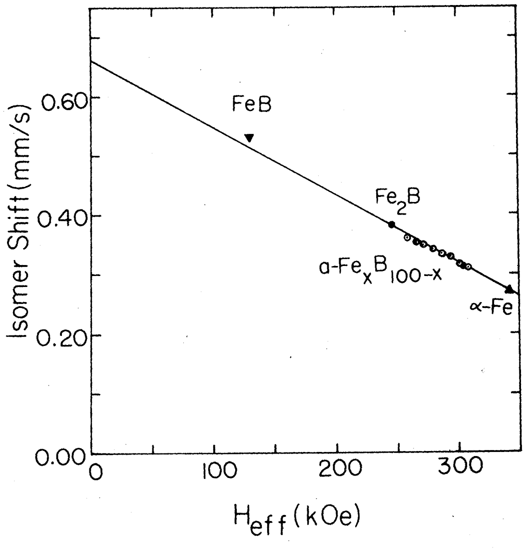

FIG. 7. Isomer shifts vs effective hyperfine field of crystalline FeB, Fe_2B, α-Fe, and amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$ at 4.2 K. The isomer shifts are relative to ^{57}Co in Cr at room temperature.

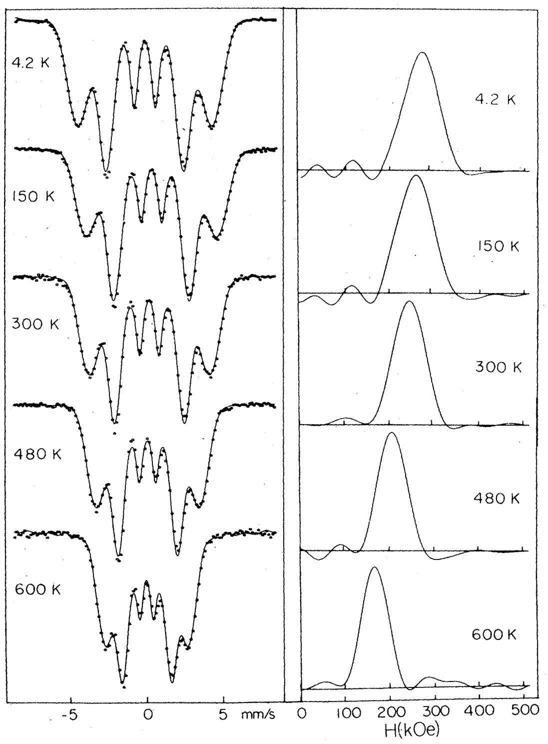

FIG. 8. Mössbauer spectra and $P(H)$ of amorphous $Fe_{76}B_{24}$ at various temperatures.

clusion has also been made for other amorphous Fe-metalloid systems.[43]

The temperature dependence of the hyperfine field for amorphous Fe_xB_{100-x} is shown in Fig. 9. For clarity, not all the samples are shown and for some samples only a fraction of the data points are displayed. One notices from Fig. 9 that various curves of amorphous Fe_xB_{100-x} cross in the vicinity of 300 K. This is due to the fact that the saturation hyperfine field *increases* with Fe concentration whereas the value of T_C *decreases* with Fe concentration. This unusual behavior dictates that the concentration dependence of the hyperfine field be determined at T close to 0 K. At higher temperatures, e.g., 300 K, the concentration dependence of the hyperfine field is completely different from that measured at 4.2 K.

TABLE I. Coefficients B and $B_{3/2}$ for amorphous Fe_xB_{100-x} $(75 \leq x \leq 86)$.

	$B(10^{-6}\ K^{-3/2})$	$B_{3/2}=B(T_C)^{3/2}$	
$Fe_{75}B_{25}$	17 ± 2	0.35	Mössbauer
	15 ± 2		Magnetization
$Fe_{80}B_{20}$	22 ± 2	0.395	Mössbauer
	26 ± 2[a]		Magnetization
$Fe_{82}B_{18}$	25 ± 2	0.40	Mössbauer
	31 ± 2[a]		Magnetization
$Fe_{86}B_{14}$	33 ± 2	0.43	Mössbauer
	34 ± 2[a]		Magnetization

[a] Taken from Ref. 49.

For amorphous ferromagnets the decrease of the magnetization and the hyperfine field at low temperatures has a temperature dependence of

$$\frac{H_{\mathrm{eff}}(T)}{H_{\mathrm{eff}}(0)}=1-BT^{3/2}\cdots \tag{5}$$

$$=1-B_{3/2}\left(\frac{T}{T_C}\right)^{3/2}\cdots \tag{6}$$

due to the excitation of ferromagnetic spin waves. The $T^{3/2}$ dependence has been observed in a number of amorphous ferromagnets by magnetization, Mössbauer and ferromagnetic resonance measurements.[45–47] For several alloys in Fe_xB_{100-x} a $T^{3/2}$ dependence of the hyperfine field has been observed using the Mössbauer effect. The values of the B coefficients have been determined and are shown in Table I. We have also determined the B value for $Fe_{75}B_{25}$ by magnetization measurements. The two B values for $Fe_{75}B_{25}$ are in good agreement. This agreement between Mössbauer and magnetization measurements has also been observed in several other Fe-metalloid alloys [e.g., $Fe_{75}P_{15}C_{10}$,[46] $(Fe\text{-}Ni)_{75}P_{16}B_6Al_3$[48]]. This indicates that the hyperfine field exhibits the *same* temperature dependence as that of the spontaneous magnetization. Recently Hasegawa *et al.* have also measured the B coefficients for Fe_xB_{100-x} by magnetization.[49] As seen in Table I their results are also in reasonable agreement with those found using the Mössbauer effect.

Our results indicate that from $Fe_{75}B_{25}$ to $Fe_{86}B_{14}$ the value of the B coefficient increases by about a factor of 2. From Fig. 10 where the values of B and

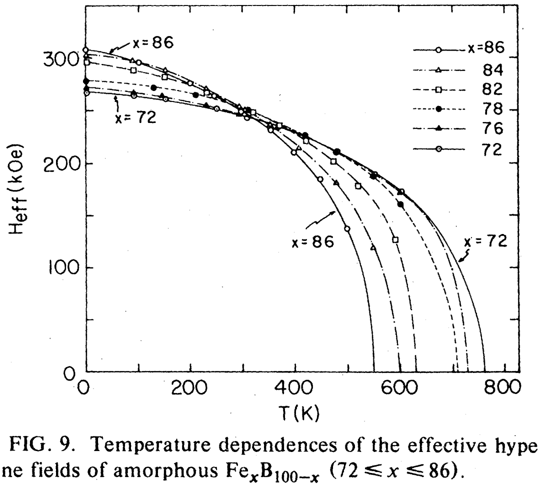

FIG. 9. Temperature dependences of the effective hyperfine fields of amorphous Fe_xB_{100-x} $(72 \leq x \leq 86)$.

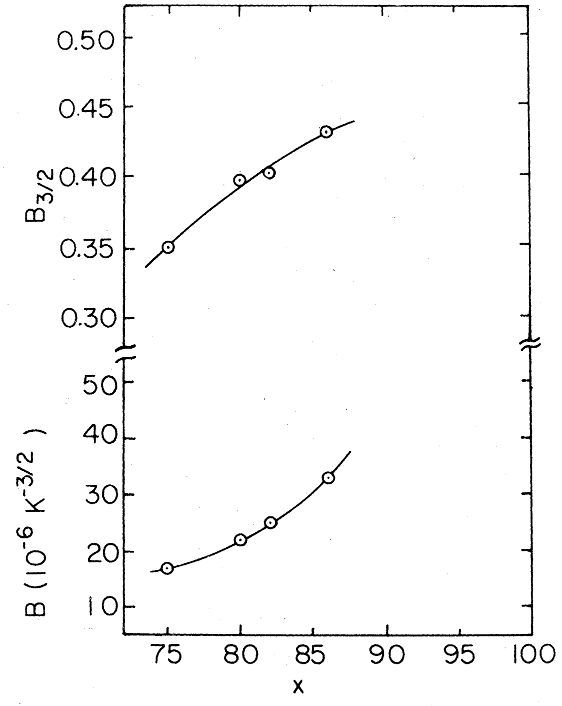

FIG. 10. Coefficients B and $B_{3/2}=B(T_C)^{3/2}$ for amorphous Fe_xB_{100-x} $(75 \leq x \leq 86)$.

$\bar{B}_{3/2}$ are shown, much larger values of B can be expected for samples with even higher Fe concentration. However, since T_C decreases with Fe content as shown in Fig. 2, the value of $B_{3/2}$ increases less sharply with Fe concentration. The extrapolated value of $B_{3/2}$ for amorphous pure Fe should be about 0.5 which is considerably larger than the value of 0.11 for crystalline αFe.[50]

The reduced hyperfine fields versus reduced temperature of amorphous Fe_xB_{100-x} are shown in Fig. 11. Again for clarity only the temperature dependence of those of $Fe_{76}B_{24}$ and $Fe_{86}B_{14}$ are shown. It is clear that the behavior of the amorphous solids is quite different from crystalline α-Fe (shown by the dashed curve) in that these curves lie considerably lower than that of α-Fe, a feature generally observed in many amorphous ferromagnets.[15,27,46] Among the amorphous Fe_xB_{100-x} samples, the higher the Fe concentration the lower the curve. This is also reflected by the monotonic increase of the coefficient $B_{3/2}$ as mentioned above. Thus barring any unexpected reversal of this trend amorphous pure Fe should have the *lowest* curve, which is dramatically different from that of crystalline α-Fe.

Theoretical studies indicate that the lower reduced magnetization curve for amorphous ferromagnets is due to the existence of a distribution of magnetic exchange interactions $\{P(J)\}$,[51] a situation not necessarily exclusive to amorphous solids but which also occurs in crystalline disordered alloys. In principle, by comparing the experimental data with theoretical calculations one can obtain information about $P(J)$, which is difficult to measure directly. Unfortunately, because of the approximations used in most of the theoretical calculations, only qualitative agreement for the temperature dependence exists between theory and experiment. Quantitatively, the experimental data do not agree with the theoretical results over the entire temperature range.[3,15]

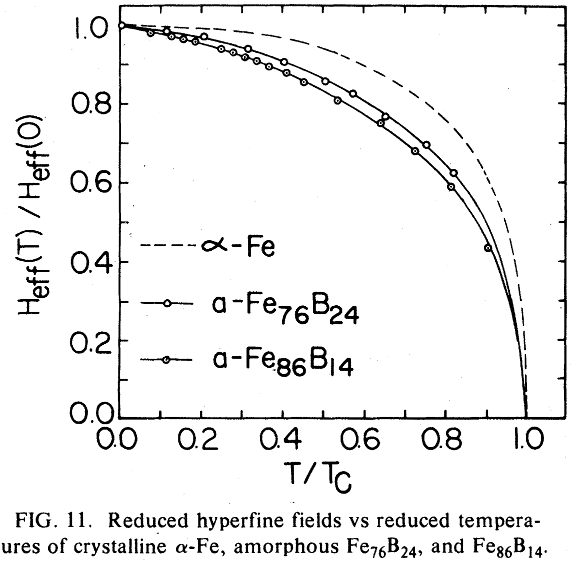

FIG. 11. Reduced hyperfine fields vs reduced temperatures of crystalline α-Fe, amorphous $Fe_{76}B_{24}$, and $Fe_{86}B_{14}$.

In the simplest case $P(J)$ is a single-maximum function with a peak at J_0 and a halfwidth of ΔJ. Roughly speaking, the value of T_C is proportional to J_0 and the parameter $\delta = \Delta J / J_0$ dictates the amount of deviation of the temperature dependence of the reduced magnetization from that of the crystalline case ($\delta = 0$). In the amorphous Fe_xB_{100-x} solids, the progressively lower curves for samples with higher Fe concentrations indicate that δ increases monotonically with increasing Fe content. The monotonic decrease in J_0 with Fe content, manifested by the decrease in T_C, will lead to an increase in δ. It is therefore difficult to ascertain the dependence of ΔJ alone on Fe content. However, it was earlier concluded that amorphous Fe is likely to be ferromagnetic rather than a spin glass. Theoretical studies indicate that for the existence of an amorphous ferromagnet, the value of $\Delta J / J_0$ cannot be too large; for example, according to an Ising calculation, $\Delta J / J_0$ should be less than about 0.8.[52] On this basis the value of ΔJ for amorphous Fe-B is likely to decrease with increasing Fe concentration.

D. Crystallization and crystalline Fe_3B

The amorphous state is a metastable state which undergoes irreversible crystallization processes at high temperatures and transforms into crystalline phases. As has been previously shown, the kinetic process of crystallization not only depends on temperature but also on the time period during which heating takes place.[15,53] In general, an amorphous sample will crystallize in a much shorter time when it is heated at a higher temperature.

After crystallization the only possible magnetic phases are FeB, Fe_2B, Fe_3B, and α-Fe. As previously shown, the crystalline phase of FeB never occurs after crystallizing amorphous $Fe_{80}B_{20}$.[15] This same conclusion has been found in amorphous Fe_xB_{100-x} ($72 \leq x \leq 86$) as well. This is hardly surprising since the Fe concentration of 72 to 86 at.% is very different from that of FeB (50 at.%) but much closer to Fe_2B (66.6 at.%), Fe_3B (75 at.%), and α-Fe (100 at.%).

Although crystalline Fe_3B in pure form is very difficult to synthesize because of its high instability, it has been shown by Hasegawa *et al.*[16] and Chien[15,26] than when amorphous $Fe_{80}B_{20}$ is crystallized under a high heating rate the major crystalline phase is indeed Fe_3B. The instability of Fe_3B is confirmed by the fact that Fe_3B transforms rapidly into Fe_2B and α-Fe at elevated temperatures and that under a low heating rate Fe_3B does not appear at all.[15] In the present work, crystallization studies of amorphous Fe_xB_{100-x}

($72 \leq x \leq 86$) under high heating rates (~15 K/min) have been performed using the thermal-scan method. The details of this method have been described elsewhere.[15] The presence of Fe_3B can be easily identified by its Curie temperature of about 800 K which is distinctively different from those of amorphous Fe_xB_{100-x} ($72 \leq x \leq 86$) ($T_C = 552$ to 760 K), crystalline Fe_2B ($T_C = 1015$ K), and α-Fe ($T_C = 1043$ K). For the amorphous Fe-B samples studied, the crystalline phase of Fe_2B appears in greatly different amounts depending upon whether the Fe concentration is less than or greater than 75 at.%. For samples with $x > 75$, Fe_3B is the main crystalline phase. The amount of Fe_3B increases steadily as x is decreased toward 75. For samples with $x < 75$ however, the amount of Fe_3B decreases dramatically and one finds predominantly Fe_2B and α-Fe.

The very different crystalline constituents for samples with $x > 75$ and $x < 75$ can be explained as follows. The Fe concentrations of $72 \leq x \leq 86$ are in the proximity of 75 at.% as in crystalline Fe_3B. One therefore expects Fe_3B to be the main crystalline phase after crystallization for *all* of these amorphous samples. To balance the original composition in the amorphous state, a small amount of α-Fe and Fe_2B will of course be found depending on the Fe concentration. This situation would indeed occur if Fe_3B were a stable phase. In reality because of the instability of Fe_3B, this situation is realized only for samples with $x > 75$ and only under high heating rates. For samples with $x < 75$, it is much more favorable to form Fe_2B because of its higher stability.

From the above discussion it is clear that in order to obtain the maximum amount of crystalline Fe_3B one should crystallize amorphous $Fe_{75}B_{25}$. However, since the concentration of 75 at.% is right at the boundary of two concentration regions with different crystallization behavior, the maximum amount of Fe_3B is achieved in a sample with x slightly larger than 75. The amorphous sample of $Fe_{76}B_{24}$ has been chosen for this purpose. This allows the possibility of a small amount (up to 4 at.%) of α-Fe. Amorphous $Fe_{76}B_{24}$ has been crystallized under a heating rate of about 20 K/min. The status of the sample is monitored by Mössbauer spectroscopy using the thermal-scan method.[15] The temperature of the sample is quickly reduced from 825 K, after the observation of the onset of crystallization and a sharply defined magnetic ordering temperature of about 800 K. This is to prevent the possibility of the decomposition of Fe_3B into Fe_2B and α-Fe. Upon cooling the sample only one magnetic ordering temperature (at about 800 K) has been observed. Mössbauer measurements indicate that the crystallized sample is essentially single phase Fe_3B.

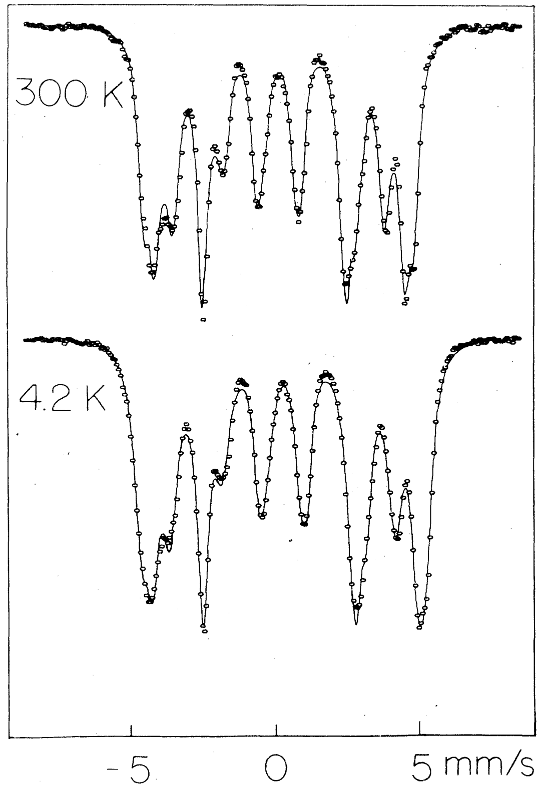

FIG. 12. Mössbauer spectra of crystalline Fe_3B at 4.2 and 300 K.

Mössbauer spectra of crystalline Fe_3B at 300 and 4.2 K are shown in Fig. 12. It should be noted that there are no measurable absorption lines corresponding to α-Fe or FeB. It is clear that each spectrum is a superposition of at least three magnetic hyperfine patterns. Both spectra have been fitted to three six-line patterns. The best-fit parameters obtained for the spectrum at 4.2 K are shown in Table II. Pattern

TABLE II. Parameters of the three magnetic hyperfine patterns of crystalline Fe_3B at 4.2 K.

Pattern No.	H_{eff} (kOe)	Isomer shift (mm/sec)[a]	$\frac{1}{2}(e^2qQ)_{\mathrm{eff}}$ (mm/sec)[b]
1	242 ± 2	0.40 ± 0.01	−0.18 ± 0.04
2	284 ± 2	0.295 ± 0.01	0.2 ± 0.04
3	305 ± 2	0.37 ± 0.01	−0.06 ± 0.04

[a] With respect to ^{57}Co in Cr.

[b] Assuming an asymmetry parameter $\eta = 0$.

No. 1 shows a narrow line width which is expected for a single site, whereas the line widths of Patterns No. 2 and 3 are about twice as broad. This indicates that both Patterns No. 2 and No. 3 are probably not single site but consist of two or more sites with closely spaced hyperfine field values. It is therefore not too surprising that assuming three six-line patterns does not give an excellent fit to the spectra as shown in Fig. 12. The area ratio of the three six-line patterns are difficult to determine with accuracy. However, an area ratio of 1 : 1 : 1 gives a poor fit to the data.

We have earlier shown in Sec. III B 3 that in the Fe-B system, amorphous or crystalline, the average magnetic hyperfine field and the average isomer shift appear to be strongly correlated. It is interesting to note that the *average* values of crystalline Fe_3B also lie close to the two curves shown in Fig. 6.

Each of the three six-line patterns of Fe_3B shows a small effective quadrupole interaction. This indicates that none of the sites have cubic symmetry. The values of the effective quadrupole interaction are of the order of 0.2 mm/sec. Clear evidence of the electric quadrupole interaction can be seen from the spectrum of Fe_3B in the paramagnetic state. The Mössbauer spectrum of crystalline Fe_3B at 825 K, which is above its Curie temperature, is shown in Fig. 13. This spectrum has been acquired in only a short time (~10 min), because crystalline Fe_3B will decompose into Fe_2B and α-Fe after prolonged heating at this temperature. Since both Fe_2B and α-Fe have much higher values of T_C, any Fe_2B and α-Fe in the sample will result in six-line spectra whose positions are very different from those of Fe_3B . Thus it is evident from Fig. 13 that the crystallized sample is essentially all Fe_3B with no significant trace of Fe_2B and α-Fe.

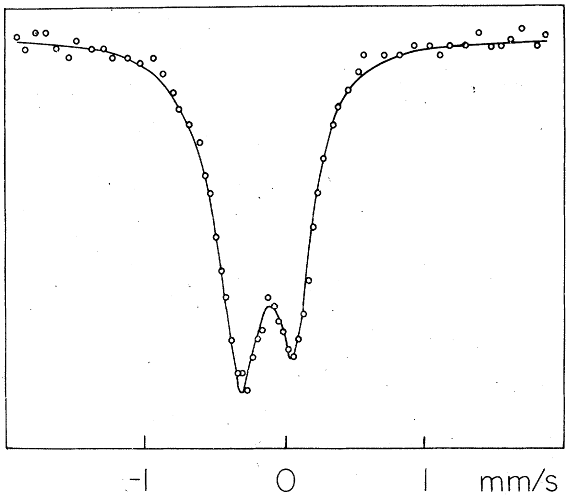

FIG. 13. Mössbauer spectrum of crystalline Fe_3B at 825 K.

The Mössbauer spectrum of crystalline Fe_3B shown in Fig. 13 exhibits essentially two unequal absorption peaks with a separation of 0.38 ±0.01 mm/sec. Since this separation is much larger than the difference in isomer shifts for various sites as shown in Table II, the two peaks must be due to electric quadrupole interaction. The reason for the asymmetric doublet rather than the symmetric doublet as usually observed in polycrystalline samples is that there are at least three inequivalent Fe sites. Due to the difference in their isomer shifts and the quadrupole splittings, a superposition of several symmetric doublets would lead to an asymmetric doublet spectrum. It may be noted that the separation of 0.38 ±0.01 mm/sec for paramagnetic Fe_3B measured at 825 K is in good agreement with the value of 0.40 ±0.02 mm/sec measured at 850 K when amorphous $Fe_{80}B_{20}$ has been crystallized.[15] The asymmetry of the doublet is less obvious in the latter case because of the absorption lines due to α-Fe which is also present in the sample.

Because of the availability of both amorphous $Fe_{75}B_{25}$ and crystalline Fe_3B it is particularly interesting to compare the hyperfine interactions in these two cases. First of all, it should be noted that the spectra of amorphous and crystalline Fe_3B, as shown in Figs. 3 and 12, are obviously different. In Fig. 14, the $P(H)$ of amorphous $Fe_{75}B_{25}$ at 4.2 and 300 K,

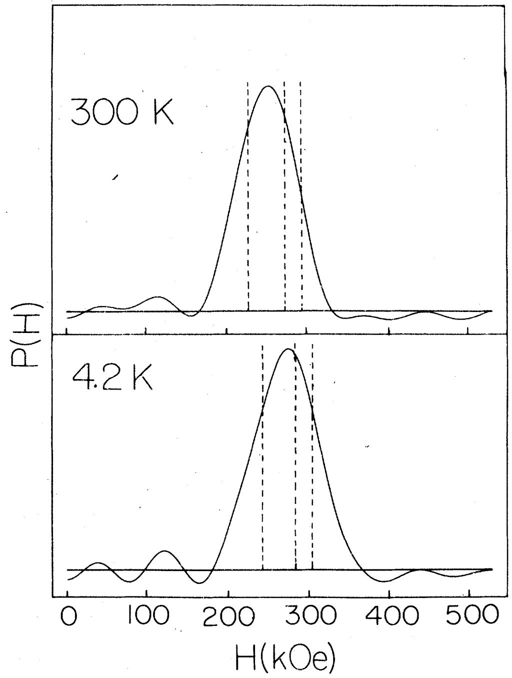

FIG. 14. Comparison of the hyperfine fields in amorphous and crystalline Fe_3B at 4.2 and 300 K. The curves are obtained from amorphous Fe_3B and the dashed lines are obtained from crystalline Fe_3B.

and the magnetic hyperfine field values (illustrated by the vertical lines) of crystalline Fe_3B at the same temperature are compared. It is noted that the $P(H)$ of amorphous $Fe_{75}B_{25}$ at 4.2 K envelops the field values of crystalline Fe_3B, although the peak value of $P(H)$ does not coincide with any of the three crystalline values. In fact, the wide $P(H)$ of amorphous $Fe_{75}B_{25}$ envelops *all* H values of crystalline α-Fe, Fe_2B, and Fe_3B but not that of FeB. The mean hyperfine field, as defined by Eq. (2) for amorphous $Fe_{75}B_{25}$ and the average hyperfine field for crystalline Fe_3B are similar. This may therefore suggest a correlation between amorphous and crystalline Fe_3B. However, it should be noted, as described in Sec III B 3 that, the *mean or average* hyperfine field in the Fe-B system apparently depends on the Fe concentration and is *not* very sensitive to whether the structure is crystalline or amorphous.

As shown in Fig. 14, between 4.2 and 300 K, the positions of the crystalline hyperfine field values (dashed lines) with respect to the $P(H)$ in the amorphous case are notably different. This is partly the result of slightly different values of T_C of about 740 and 800 K for amorphous and crystalline Fe_3B respectively. This effect is mainly due to the fact that the hyperfine fields of a crystalline solid decrease *less* with increasing temperature than those in an amorphous solid, a feature which has been generally observed and illustrated in Fig. 11. Thus a comparison between amorphous and crystalline Fe_3B must be done at T close to 0 K.

There is considerably controversy concerning the crystal structure of crystalline Fe_3B. The crystal structure of Fe_3B was first postulated to be orthorhombic since both Co_3B and Ni_3B are orthorhombic.[25] Assuming an orthorhombic structure, the lattice parameters of $a = 4.454$ Å, $b = 5.433$ Å, and $c = 6.656$ Å have been extrapolated for Fe_3B. However, as noted by Fruchart and Michel,[25] while the values of a and c are comparable to those of Co_3B and Ni_3B, the value of b is much larger. Since this orthorhombic structure is known to be stable only when the ration of b/a lies within certain limits, it is therefore unclear whether Fe_3B is indeed orthorhombic. The first x-ray measurements of Fe_3B obtained from crystallizing amorphous $Fe_{80}B_{20}$ indicated that Fe_3B had an orthorhombic structure.[16] However Walter *et al.*[54] have recently shown from detailed x-ray diffraction analyses that the crystal structure of Fe_3B is *tetragonal* with cell parameters of $a = 8.63$ Å and $c = 4.29$ Å. This tetragonal structure is the same as that of Fe_3P.

Since the Fe sites in the tetragonal and the orthorhombic structures are quite different, the parameters obtained from the Mössbauer spectra of crystalline Fe_3B can perhaps shed additional light on the crystal structure of Fe_3B. In the orthorhombic structure there are two crystallographically inequivalent Fe sites with an Fe-site ratio of 2 to 1, whereas in the tetragonal structure there are three crystallographically inequivalent Fe sites with a site ratio of 1 : 1 : 1. In the magnetically ordered state the number of magnetically inequivalent sites could potentially be greater than, although often equal to, the number of crystallographically inequivalent sites. We have shown that there are at least three magnetically inequivalent sites in crystalline Fe_3B so it is unlikely that its structure would be orthorhombic. It therefore appears that the crystal structure of Fe_3B is much more likely to be tetragonal, in accordance with the conclusion of Walter *et al.*[54]

Our data further suggest that the number of magnetically inequivalent sites in Fe_3B is likely to be greater than three. Their hyperfine field values are such that they can be approximated by three six-line patterns but their area ratio is not 1 : 1 : 1 and not all of the three patterns show narrow line widths. It should be noted that or Fe_3P, which is isostructural to tetragonal Fe_3B, Lisher *et al.*[55] have in fact found at least six inequivalent Fe sites.

ACKNOWLEDGMENTS

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