A detailed Mossbauer study on amorphous Fe$_{80-X}$Pr$_X$B$_{20}$ (0≤X≤8) alloys

N. Rajya Lakshmi and B. Bhanu Prasad

M.V.S.R. Engineering College, Nadergul, Hyderabad-501 510, India.

Abstract

^{57}Fe Mossbauer Spectroscopy has been used to study the temperature dependence of magnetic hyperfine field, spin-wave excitations and critical exponent (β) in the ternary alloy Fe$_{80-X}$Pr$_X$B$_{20}$ (0≤X≤8) over a temperature interval 4.2 K - 300 K. In amorphous Fe$_{80-x}$Pr$_x$B$_{20}$ alloys, the effective magnetic hyperfine field H$_{eff}$(T) decreases with increase in temperature for all concentrations of Pr in the binary Fe$_{80}$B$_{20}$. The Curie temperature(T$_c$) of these samples Fe$_{78}$Pr$_2$B$_{20}$ (S1), Fe$_{76}$Pr$_4$B$_{20}$ (S2), Fe$_{74}$Pr$_6$B$_{20}$ (S3) and Fe$_{72}$Pr$_8$B$_{20}$ (S4) are found to be 580 ± 10 K , 525 ± 10 K, 470 ± 10 K and 410 ± 10 K, respectively. Similarly, the effective magnetic hyperfine field at 0 K, H$_{eff}$(0) of these S1, S2, S3 and S4 samples is found to be 280 kOe, 265 kOe 251 kOe and 248 kOe , respectively. It is observed that H$_{eff}$ (T) / H$_{eff}$ (0) decrease much faster with increase in T/T$_c$. Similarly, the Curie temperature (T$_c$) of these samples decreases with increase in the concentration of Pr in the binary Fe$_{80}$B$_{20}$. The reduced magnetic hyperfine field versus reduced temperature follows the Handrich's model. It is observed that H$_{eff}$ (T) / H$_{eff}$ (0) decrease much faster with increase in T/T$_c$. Spin-wave excitations and the critical exponent in the amorphous Fe$_{80-x}$Pr$_x$B$_{20}$ alloys are also explained and discussed.

INTRODUCTION

There have been extensive efforts to experiment with different alloy compositions based on iron-boron systems to understand the role of transition metal and metalloid atoms in glass formation. From this, it is possible to understand their influence on the

thermal stability and the magnetic properties of the alloys. Considerable studies have been reported on binary alloys such as Fe-B [1].   Currently there is interest in the study of ternary systems such as Fe-RE-B (RE = Rare- Earth) alloys [2]. Short- range order in amorphous alloys is a fascinating aspect for their applications. Until recently, despite the close similarities in between Praseodymium and Neodymium [3] and in the $RE_2Fe_{14}B$ compounds [4], relatively few studies have been performed on the Fe-Pr-B system. Much of the work carried out so far has been concentrated on NdFeB alloys, but PrFeB magnets have received much attention lately [5]. Because of the size differences between Pr and Fe ions, the local symmetry around Fe decreases markedly. This may be most probably due to the increase in the free volume in the structure. Praseodymium atoms   are randomly   distributed   in the   amorphous structure, but   due   to   atomic   size differences   the   new   local structure   is less symmetrical than $Fe_{80}B_{20}$. Thus, a large number of highly disordered sites are created. The substitutions of iron atoms by much larger Pr atoms caused dramatic changes in the short-range order in the amorphous $Fe_{80}B_{20}$ structure. Low concentrations of Pr atoms in $Fe_{80}B_{20}$ caused a large distortion of nearest neighbours.

Thus, rare earth atoms with orbital moment are known to give rise to large random magnetic anisotropy in amorphous alloys through spin-orbit coupling. As this interaction couples an atomic moment to its local environment, it is of great concern to investigate structural short-range order in such alloys to understand   local properties of anisotropy. Thus, in this paper, a detailed Mossbauer study on amorphous $Fe_{80-x}Pr_xB_{20}$ ($2 \leq X \leq 8$) alloys has been presented.   The variation of effective   magnetic hyperfine   field $H_{eff}(T)$ with   temperature   for   different concentrations,   spin-wave excitations and the critical exponent in the amorphous $Fe_{80-x}Pr_xB_{20}$ alloys are also explained and discussed for the various concentrations of Pr in amorphous $Fe_{80-x}Pr_xB_{20}$ ($2 \leq X \leq 8$) alloys.

EXPERIMENTAL

Amorphous ribbons of **$Fe_{80-x}Pr_xB_{20}$** ($2 \leq X \leq 8$), prepared by melt spinning under inert atmosphere were   procured from our other researchers.   These ribbons were about 1 mm wide and about 30 μm thick. The amorphous state of the alloys was checked by X − ray diffraction. Mossbauer measurements were performed using a conventional constant acceleration spectrometer in the temperature range 4.2 K-300 K in the standard transmission geometry.

RESULTS AND DISCUSSION

Figure 1   shows the Mossbauer Spectra of amorphous $Fe_{80-x}Pr_xB_{20}$ (X=2,4,6,8) alloys   at different temperatures. The Six-line pattern, which is indicative of the

ferromagnetic state of the samples is observed as in Fig.1. Large line widths in the Six- line Mossbauer Spectra of amorphous $Fe_{80-x}Pr_XB_{20}$ (X=2,4,6,8) alloys is usually explained by involving the existence of a distribution of values of hyperfine magnetic fields which arise from the amorphous nature of solids. However, it is observed here that the broadening in not same for all lines and that the line width increases from the central to the outermost lines of the spectrum.i.e. $\Gamma_{1,\,6}>\Gamma_{2,\,5}>\Gamma_{3,4}$. This shows that the major broadening is caused by the hyperfine magnetic field distribution. Furthermore, an asymmetry in line widths as well as some asymmetry in line intensities is also observed.

The Temperature dependence of hyperfine magnetic fields of amorphous $Fe_{80-x}Pr_xB_{20}$ (x=2, 4, 6, 8) alloys is shown in Fig.2. From the figures, it is clear that the effective magnetic hyperfine field, $H_{eff}(T)$ decreases with increase in temperature for all concentrations of Pr in $Fe_{80}B_{20}$ as shown in Fig. 2. The Curie temperature (T_c) of amorphous $Fe_{80-x}Pr_xB_{20}$ (x = 2, 4, 6, 8) alloys is determined by extrapolation method as shown in Fig.2 and the values of T_c of amorphous $Fe_{78}Pr_2B_{20}$ (S1), $Fe_{76}Pr_4B_{20}$ (S2), $Fe_{74}Pr_6B_{20}$ (S3) and $Fe_{72}Pr_8B_{20}$ (S4) alloys are found to be 580 ± 10 K , 525 ± 10 K, 470 ± 10 K and 410 ± 10 K, respectively which are less than the Curie temperature (T_c) of binary alloy such as $Fe_{80}B_{20}$ $(T_c = 685\pm 3K)$ [1] as shown in Table 1. Similarly, the effective magnatic hyperfine field, $H_{eff}(0)$, at 0 K for amorphous $Fe_{78}Pr_2B_{20}$ (S1), $Fe_{76}Pr_4B_{20}$ (S2), $Fe_{74}Pr_6B_{20}$ (S3) and $Fe_{72}Pr_8B_{20}$ (S4) alloys is found to be 280 kOe, 265 kOe, 251 kOe and 248 kOe , respectively (Table 1). From Table 1, it is clear that the addition of large sized rare earth to iron- boron decreases Curie temperature. The decrease in T_c with increase in the concentration of Pr atoms in $Fe_{80}B_{20}$ is caused by two factors: 1. The decrease in the number of the transition metal atoms in the alloy and 2. The change in the exchange interactions.

Also, it was found that the hyperfine magnetic field, $H_{eff}(T)$ and the Curie temperature(T_c) decrease with the increase in Pr content for Low concentrations because Pr atoms in $Fe_{80}B_{20}$ causes a large distortion of nearest neighbours. Because of the size differences between Pr and Fe ions, the local symmetry around Fe decreases markedly. This may be most probably due to the increase in the free volume in the structure. Praseodymium atoms are randomly distributed in the amorphous structure, but due to atomic size differences the new local structure is less symmetrical than $Fe_{80}B_{20}$. Thus, a large number of highly disordered sites are created. In $Fe_{80-x}Pr_xB_{20}$ the Pr atoms affect the structure only in their immediate environment, creating sites with very low symmetry. Hence, the hyperfine magnetic field, $H_{eff}(T)$ decreases with increase in temperature. The reduced magnetic hyperfine field versus reduced temperature follows the Handrich's model [6].

TABLE - 1

The Curie Temperature (T_c) and $H_{eff}(0)$ of amorphous $Fe_{80-x}Pr_xB_{20}$ (x=2,4,6,8) alloys

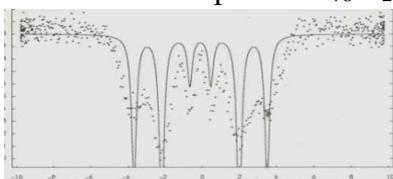| Composition	Curie Temperature,T_c (K)	$H_{eff}(0)$ in kOe
$Fe_{74}Pr_2B_{20}$	580	280
$Fe_{74}Pr_4B_{20}$	525	265
$Fe_{74}Pr_6B_{20}$	470	251
$Fe_{74}Pr_8B_{20}$	410	248

According to average molecular - field model the Curie temperature

$$T_c =   2<Z> J_{Fe-Fe} S_{Fe}(S_{Fe}+1)/3K_B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

where S_{Fe} is the spin of iron, J_{Fe-Fe} is the exchange integral and $<Z>$ is the average number of Fe nearest neighbors of Fe atoms. The Above relation indicates that T_c is directly proportional to $<Z>$ and to $J_{Fe-Fe.}$ [7]. Hence, the addition of large size rare earth to iron- boron decreases Curie temperature.

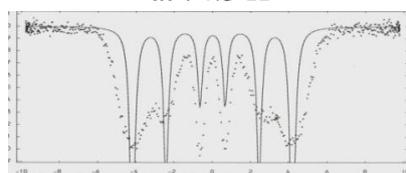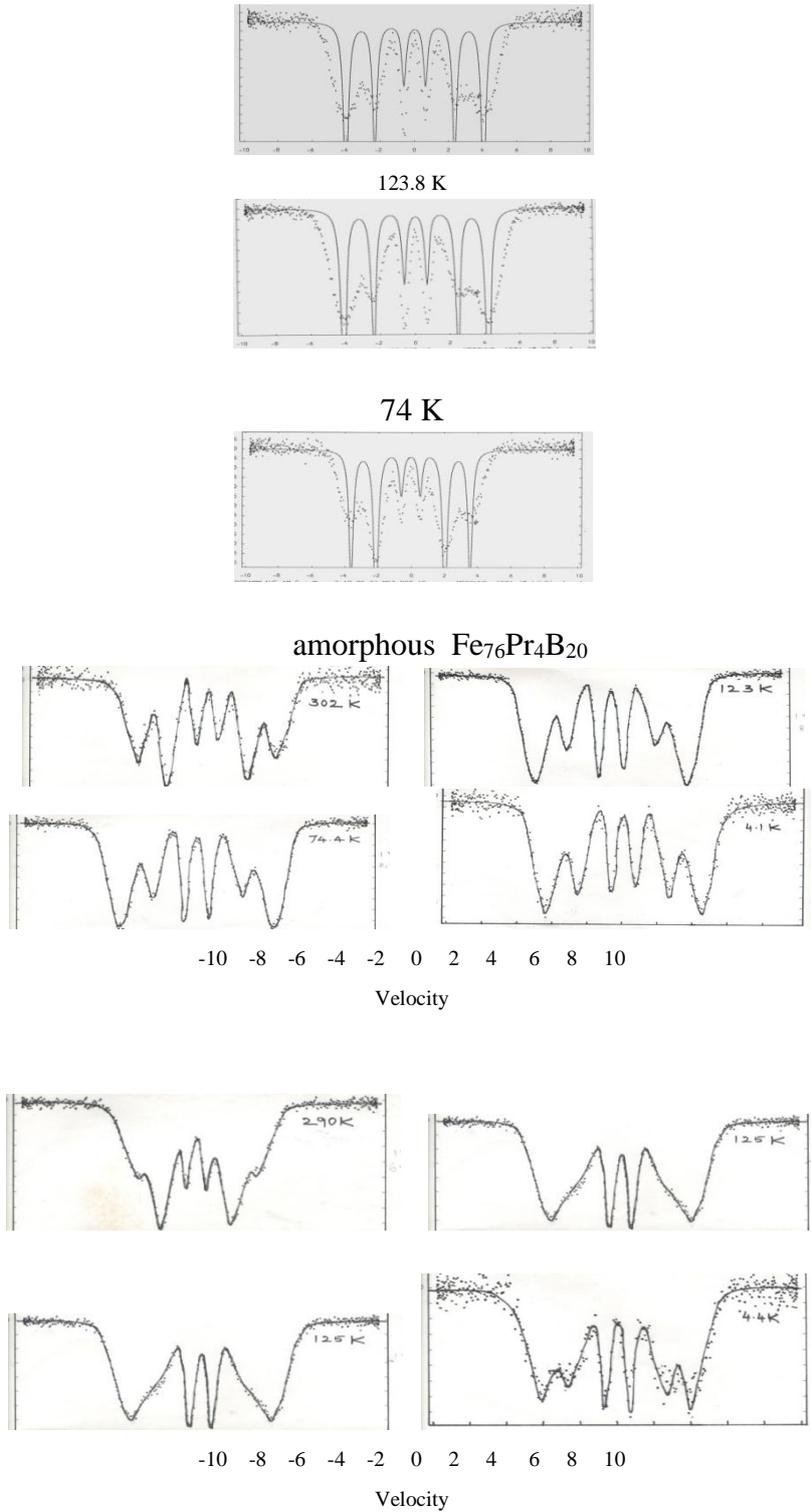At 303.19 K amorphous $Fe_{78}Pr_2B_{20}$

at 123.1 K
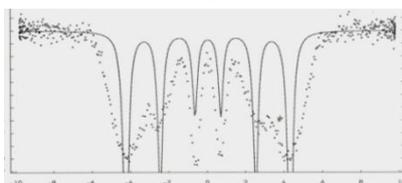
at 74.3 K

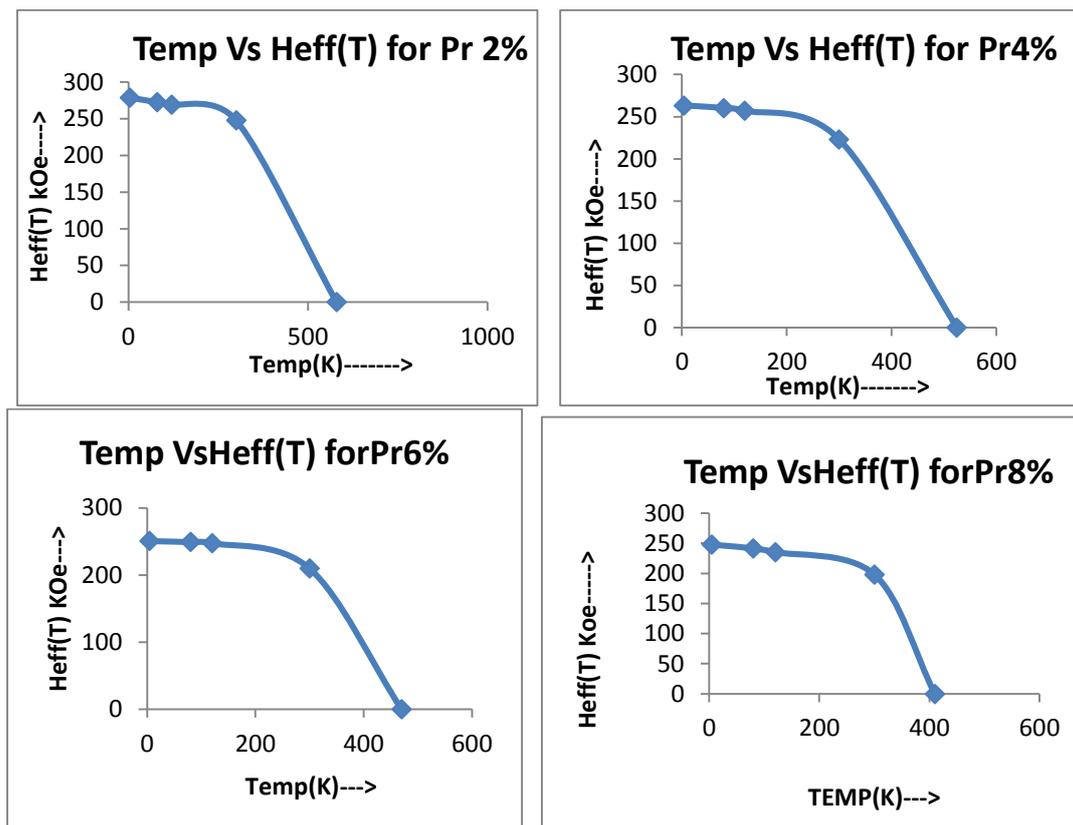
amorphous $Fe_{74}Pr_6B_{20}$ 289.33 K

123.8 K

74 K

amorphous Fe₇₆Pr₄B₂₀

-10 -8 -6 -4 -2 0 2 4 6 8 10

Velocity

-10 -8 -6 -4 -2 0 2 4 6 8 10

Velocity

Figure 1: Mossbauer Spectra of amorphous $Fe_{80-X}Pr_XB_{20}$ (X=2,4,6,8) alloys at different temperatures.

Figure 2: Temperature dependence of effective magnetic hyperfine field $H_{eff}(T)$ of amorphous $Fe_{80-x}Pr_xB_{20}$ (x=2,4,6,8) alloys

Reduced magnetic hyperfine field (RMHF), $H_{eff}(T) / H_{eff}(0)$ vs. reduced temperature, (T/ T_c) of amorphous $Fe_{80-x}Pr_xB_{20}$ (x=2,4,6,8) alloys is plotted in Fig.3 with experimental points shown as Δ. Our observation is that the plots $H_{eff}(T) / H_{eff}(0)$ vs. T/T_c are not much different from those results of amorphous $Fe_{80}B_{20}$ reported by others [1]. The observed rapid decrease in reduced hyperfine field, $H_{eff}(T)$ is explained by Handrich's model for amorphous ferromagnets if one assumes a temperature dependent δ, a measure of fluctuations in the exchange interactions in such solids.

Figure 3 also shows the plots of the Brillouin curves of Handrich's model for $\delta = 0$ and $\delta = 0.5$ for S = 1. Thus, in Fig. 3, the experimental data lie below the Brillouin curve as observed for other amorphous alloys. This observation is usually attributed to the distribution of exchange interactions in the amorphous ferromagnets arising from the random environment around magnetic atoms.
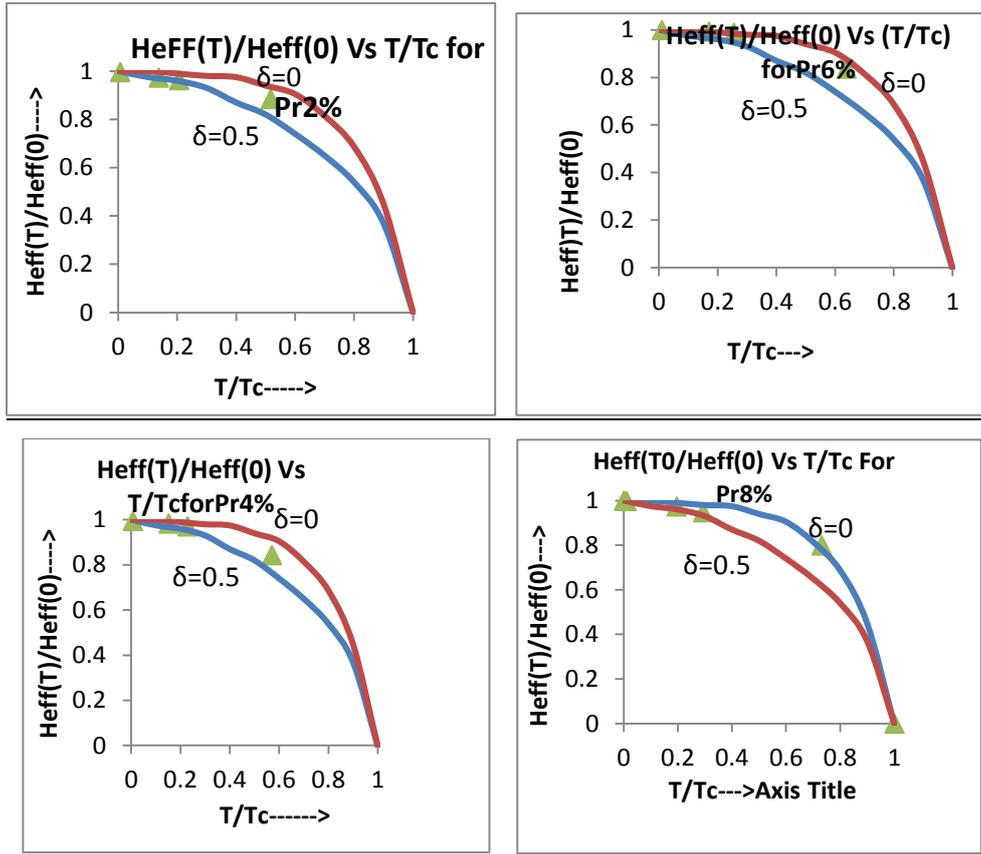
Figure 3 Reduced hyperfine magnetic field (RHMF) H_{eff} (T) / H_{eff} (0) vs. reduced temperature, (T/ T_c) of amorphous $Fe_{80-x}Pr_xB_{20}$ (x=2, 4, 6, 8) alloy with experimental points shown as Δ. The plots show theoretical curves of Handrich's model for δ = 0 and δ = 0.5.

Handrich[6] obtained an analytical expression for the reduced magnetization of an amorphous ferromagnet given by

$$m(T) = M(T)/M(0) = H_{eff}(T)/H_{eff}(0) = \tfrac{1}{2} B_s[(1+δ)x] + \tfrac{1}{2} B_s[(1-δ)x] \ldots\ldots(1)$$

where B_s is the Brillouin function for spin S. x = [3S/(S+1)](m/t), and t = T/T_c . The parameter 'δ' is a measure of random fluctuations in the exchange interaction and its value lies between 0 and 1. Equation (1) reduces, when δ = 0, to the formula for the reduced magnetization applicable to crystalline ferromagnets. Thus, $H_{eff}(T)/H_{eff}(0)$ decreases much faster with increase in T/T_c. Hence, the observed rapid decrease in reduced hyperfine magnetic fields in this alloy is explained well by Handrich's model [6] used for amorphous ferromagnets.
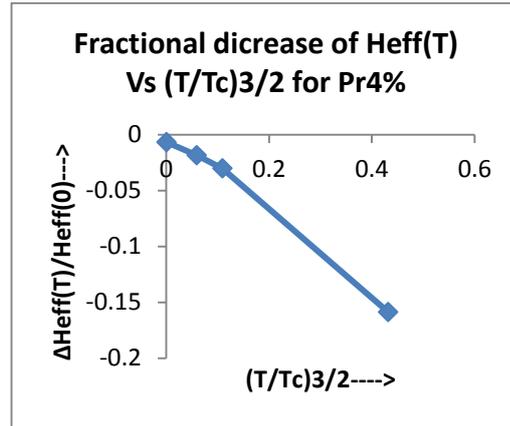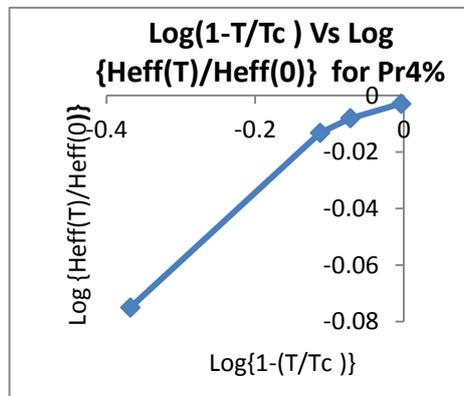
Figure 4: $[\Delta H_{eff}(T) / H_{eff}(0)]$ vs. $(T/ T_c)^{3/2}$ for amorphous $Fe_{76}Pr_4B_{20}$ alloy with experimental points.

Figure 4 shows the variation of $[\Delta H_{eff}(T) / H_{eff}(0)]$ with $(T/ T_c)^{3/2}$ for amorphous $Fe_{76}Pr_4B_{20}$ alloy. It is possible to obtain the value of the critical exponent (β) from the temperature dependence of H_{eff}. Since $M_s(T)$ is proportional to $H_{eff}(T)$, near T_c the following relation will hold:

$$H_{eff}(T)/H_{eff}(0) = D[1 - (T/T_c)]^{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where β is one of the critical exponents and D is a constant close to 1.0. Similarly, the variation of log of reduced hyperfine fields of amorphous $Fe_{76}Pr_4B_{20}$ alloy with log of $[1-T/T_c]$ is shown in Fig.5. The plot shows that this power law is followed by the amorphous $Fe_{76}Pr_4B_{20}$ alloy not only close to T_c, but over an extended temperature interval. From the slope and intercept, β and D values are calculated for amorphous $Fe_{76}Pr_4B_{20}$ alloy and are found to be 0.209 ± 0.02 and 1.009 ± 0.03. These values are in good agreement with the other amorphous materials .

Figure 5 : log $[H_{eff}(T) / H_{eff}(0)]$ vs Log $[1-T/ T_c]$ for amorphous $Fe_{76}Pr_4B_{20}$ alloy with experimental points.

TABLE - 2

Composition	Curie Temperature T_c (K)	D ± 0.03	β ± 0.02	D
$Fe_{74}Pr_4B_{20}$	525	1.009	0.209	

In general,   temperature dependence of magnetization M (T), of a ferromagnet can be written as

$$M (T) = M (0) (1-BT^{3/2} -CT^{5/2} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

where B and C are constants.

Equation $H_{eff}(T)/H_{eff}(0) = B_S(x)$ can be arranged to give

$$[M (T)-M (0)]/M (0) = - BT^{3/2}- CT^{5/2} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

or

$$[M (T)-M (0)]/M (0) = - B_{3/2}(T/T_c)^{3/2}- C_{5/2}(T/T_c)^{5/2} \quad \dots\dots\dots\dots\dots\dots (5)$$

It should be noted that the $T^{3/2}$ law is always obtained for a quadratic dispersion relation and is independent of the specific model for the magnetic interactions. In particular, it has been shown that a $T^{3/2}$ law is also expected in a macroscopic continuum model showing that lattice periodicity is not required [8]. On the other hand, it is necessary to assume lattice periodicity in order to derive the higher order term in the expression of (M), since $H_{eff}(T)$ for magnetic metallic glasses [1] is approximately proportional to $M_s(T)$, the Bloch Law can also be applied to $H_{eff}(T)$. Thus, the temperature dependence of $H_{eff}(T)$ can be expressed as

$$[H_{eff} (T) - H_{eff} (0)] / H_{eff}(0) = \Delta H_{eff} / H_{eff} (0) = B \, T^{3/2} + C \, T^{5/2} + ------ \quad \dots\dots..(6)$$

$$= B_{3/2} (T/T_c)^{3/2}+C_{5/2} (T/T_c)^{5/2} \quad \dots\dots\dots\dots\dots\dots (7)$$

where B, C, $B_{3/2}$ and $C_{5/2}$ are the same constants as mentioned in the above equations [7].

The dominant $T^{3/2}$ dependence can be clearly seen in Fig. 4. For alloys containing light rare- earths like La, Ce,Pr etc., the linear $T^{3/2}$ dependence was found [9]. The coefficients B and C in the present case can be conveniently determined by plotting $\Delta H_{eff}(T)/H_{eff}(0)1/ T^{3/2}$ vs. T (Fig. 6) for amorphous $Fe_{76}Pr_4B_{20}$ alloy.
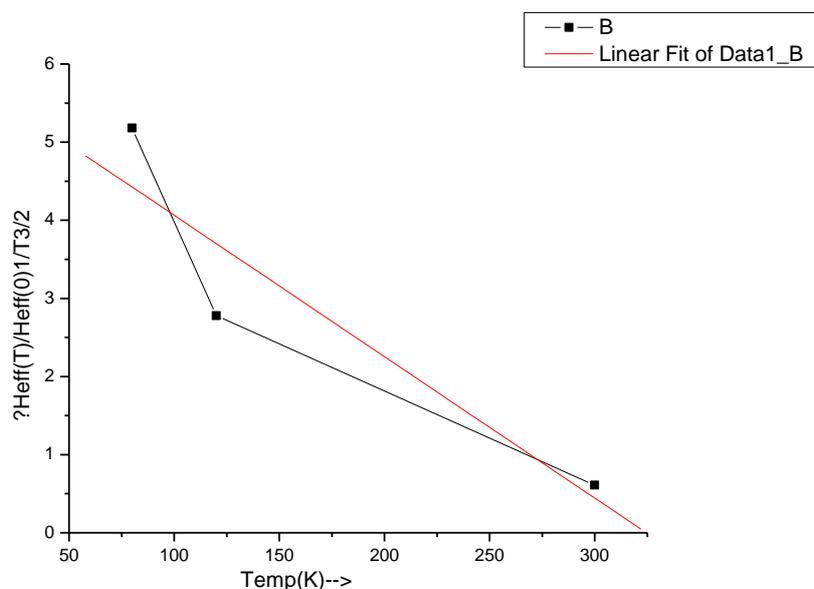
**Figure 6:** $\Delta H_{eff}(T)/H_{eff}(0)1/ T^{3/2}$ vs. T of amorphous $Fe_{76}Pr_4B_{20}$ alloy

From the intercept and the slope of the straight line, the values of B $= 5.873 \pm 1$ x $10^{-6}deg^{-3/2}$ and C $= 1.81 \pm 0.5$ x 10^{-8} $deg^{-5/2}$ have been determined. From the measured value of $T_c = 525K$, $B_{3/2} = 0.0705$ and $C_{5/2} = 0.1142$ have been determined. These values are compared with those [9] of crystalline Fe, Ni, $Fe_{80}B_{20}$ which are shown in Table 2.

Table 2

	Tc(K)	B $(10^{-6}deg^{-3/2})$	C $(10^{-8}deg^{-5/2})$	$B_{3/2}$	$C_{5/2}$	References
Crystalline Fe	1042	3.4±0.2	0.1 ± 0.1	0.114±0.007	0.04±0.04	[1,10]
Crystalline Ni	637	7.5±0.2	1.5 ± 0.2	0.117±0.003	0.15±.0.02	[1,10]
$Fe_{80}B_{20}$	685 ± 3	22±1	1.4 ± 0.5	0.4 ± 0.05	0.17±0.08	[1,10]
$Fe_{74}Pr_6B_{20}$	540 ± 10	12.32±1	3.28 ± 0.5	0.1546±0.05	0.222	
$Fe_{74}Pr_4B_{20}$	525 ± 10	5.873±1	1.81 ± 0.5	0.0705	0.1142	

From Table 2, one can conclude that

1. In general, the Values of B and $B_{3/2}$ are slightly large in comparison with crystalline ferromagnets. The coefficient B is related to the exchange constant and in general larger due to chemical disorder for amorphous alloys than for crystalline materials[11].

2. The Values of B and $B_{3/2}$ are smaller than $Fe_{80} B_{20}$. This shows that due to alloying by light rare earth elements the exchange constant decreases. Because of the quite different atomic radii of rare earth and iron, one can postulate a large size effect as an essential contribution to the decrease of ferro magnetic exchange between iron atoms.

3. Coefficient B is about two to three orders of magnitude larger than the coefficient C in this temperature region. This result agree with the result on crystalline solids.

| -10 | -8 | -6 | -4 | -2 | 0 | 2 | 4 | 6 | 8 | 10 |

Velocity
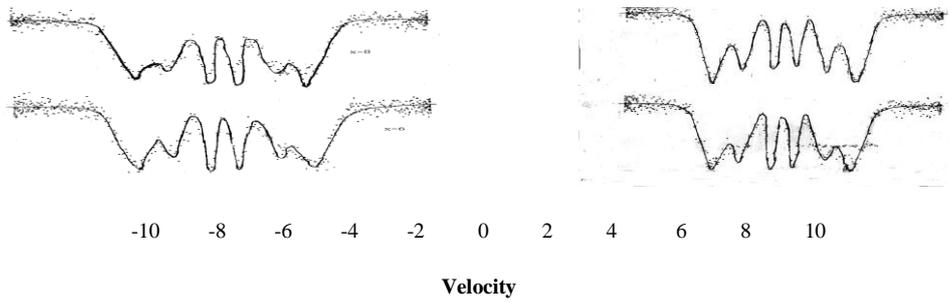
Figure 7 Mossbauer Spectra of Amorphous $Fe_{80-x}Pr_xB_{20}$ (0≤ X ≤ 8) alloys at 4.2 K for X = 2 %, 4 %, 6 % and 8 % (from bottom)
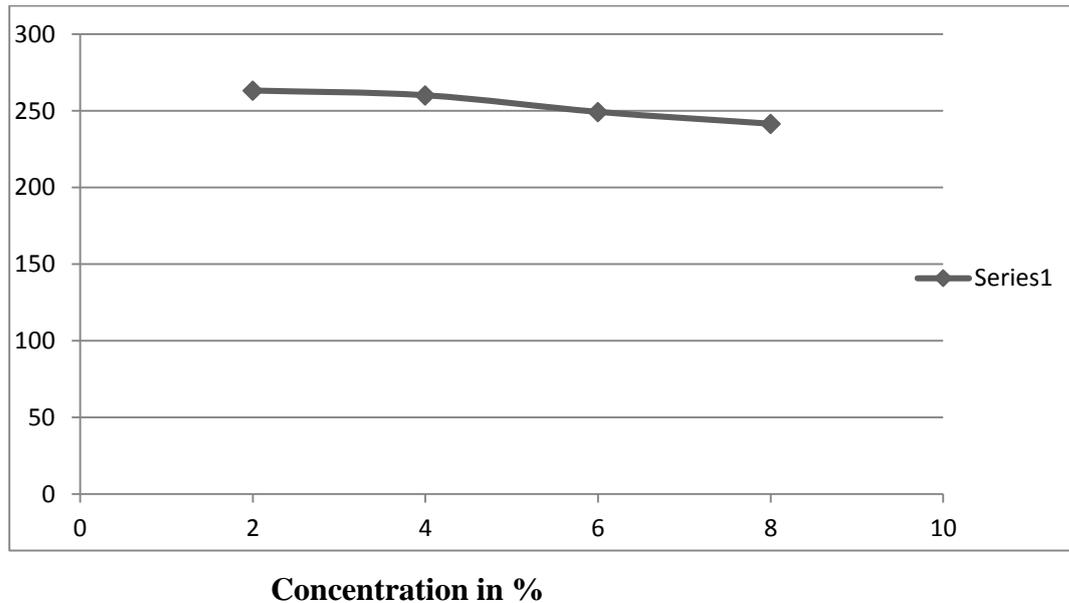
Concentration in %

Figure 8: Concentration dependence of the effective magnetic field (H_{eff}) of amorphous

$Fe_{80-x}Pr_xB_{20}$ (0≤ X ≤ 8) alloy for X = 2 %, 4 %, 6 % & 8 %

Figure 7 shows the Mossbauer spectra of amorphous $Fe_{80-x}Pr_xB_{20}$ ($0 \leq X \leq 8$) alloys for at 4.2 K for X = 2 %, 4 %, 6 % and 8 % (from bottom). When large atoms replace iron there will be a change in the line positions, line widths and hence in hyperfine fields. The substitutions of iron atoms by much larger Pr atoms causes dramatic changes in the short-range order in the amorphous $Fe_{80}B_{20}$ structure. Low concentrations of substitution of Pr atoms causes a large distortion of nearest neighbours.

Figure 8 shows the concentration dependence of the effective magnetic field (H_{eff}) of amorphous $Fe_{80-x}Pr_xB_{20}$ ($0 \leq X \leq 8$) alloy for x = 2 %, 4 %, 6 % and 8 %. Figure 8 shows that the effective magnetic hyperfine field (H_{eff}) decreases with increase in the concentration of Pr in $Fe_{80}B_{20}$.

CONCLUSIONS

In amorphous $Fe_{80-x}Pr_xB_{20}$ ($2 \leq X \leq 8$) alloy the Pr atoms affect the structure only in their immediate environment, creating sites with very low symmetry.   The substitutions of iron atoms by much larger Pr atoms causes dramatic changes in the short-range order in the amorphous $Fe_{80}B_{20}$ structure. In amorphous $Fe_{80-x}Pr_xB_{20}$ alloy,   the effective magnetic hyperfine field $H_{eff}(T)$ decreases with increase in temperature for all concentrations of Pr in the binary $Fe_{80}B_{20}$. Similarly, the Curie temperature (T_c) of the sample decreases with increase in   the concentration of Pr in the binary $Fe_{80}B_{20}$. The reduced magnetic hyperfine field versus reduced temperature follows the Handrich's model. It is observed that $H_{eff}(T) / H_{eff}(0)$ decrease much faster with increase in T/T_c. The magnetic hyperfine field decreases with increase in the concentration of Pr in $Fe_{80}B_{20}$.

REFERENCES

[1]   Chien C.L., Phys. Rev. **B18** (1978) 1003 and references therein.

[2]   Kopcewicz M., Idzikowski B. and Wnzeciono A.,   J. Magn. Magn. Mat. **125** (1993) 29

[3]   Chem   S.Y., Chem H.Y., Chang S.F., Boltish E.B., Sankar S.G., Langhlin D.E. and Wallace W.E., J.Appl. Phys. **64** (1988) 5510.]

[4]   Noh T.H., Jeung W.Y., Kang I.K., Shin S.H., and J.J.lee, J. Appl . Phys.

70 (1991) 6591

[5]   Davies H.A., Harland C., Batencourt J.I. and Mendoza R.G.,proc. of MRS Symp on advanced hard and soft magnetic materials, Eds Michael Coey et al.(Warrendale U.S.A. 1999) p.27

[6]   Handrich K, Phys. Status Solidi **32** (1969) K55

[7]   Hassanain N, Lassri H, Krishnan R and Berrada A. *J. Magn. Magn. Mate* **315-318***, (1995)* 146.

[8]   Rhyne J.J., Lynn J.W., Lubersky F.E. and Walter J.L., J.Appl. Phys. **50** (1979) 1583

[9]   Bhatnagar Anil K., Bhanu Prasasd B and Jagannathan R, Physical Review **B29** (1984) 4896

[10] Cochrane R.W. and Cargill G.S., Phy. Rev. Lett. **32** (1974) 476

[11] Handley R.C.C.,   Amorphous Metallic Alloys, ed. Lubersky F.E., Butterworths 1983, P.257