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CHEMICAL COMPOSITION AND MAGNETIC INTERACTIONS IN AMORPHOUS TRANSITION METAL-METALLOID ALLOYS*

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A study of magnetic interactions in the amorphous transition metal-metalloids is of considerable interest. Magnetic moments of the metal atoms in these systems lie close to the values found in analogous crystalline systems and like the latter follow the trend according to the Slater-Pauling curve. But the extent of charge-transfer from the metalloid to the metal atoms needs further investigations. In certain cases, the magnetic properties of these systems strikingly differ from the crystalline systems of similar compositions due to the presence of chemical environment of multiple types. The Curie temperatures (T_c) of these metalloids, unlike the crystalline systems, are significantly influenced by thermal history. However, like the crystalline systems they follow the Bethe-Slater relationship as a function of the radius of the *d*-shell of the transition metal ion. Structural disorder, in general, results in the lowering of T_c compared to the crystalline systems.

Mössbauer studies of iron-rich systems are characterised by the relative intensities of the hyperfine spectra and exhibit large line-widths due to the random distribution of the atoms. The plots of reduced hyperfine field *vs.* reduced temperature show significant deviations from crystalline behaviour. Attempts to obtain detailed magnetic phase-diagrams using different techniques show the existence of spin-glass in addition to para- and ferro-magnetic phases. Not much study has been carried out on the reversibility of the different transitions. Variations is the critical compositions may be explained on the basis of competing interactions. Distribution in the interatomic distances also influence the critical concentration due to their effect on the exchange interactions. The critical exponents except β are found to be close to values predicted for the three-dimensional Heisenberg model.

Although these systems are amorphous they show the existence of spin-waves. Compared to crystalline systems these systems show $T^{3/2}$ dependence over a wider range of temperature. The values of stiffness constants indicate that spin-waves in amorphous ferro-magnets have lower energies of excitation and a description of localised spins with short range interactions is more appropriate. Attempts to apply the itinerant electron model do show the Arrot-Belov-Kouvel (ABK) plots to be linear. They however exhibit curvatures at low fields which is attributed to concentration fluctuations in these amorphous ferromagnets. The different aspects of magnetic interaction mentioned are discussed in some detail in the light of recent literature.

Key Words : Magnetic Interactions; Amorphous; Transition Metal-Metalliods; Mössbouer Effect; Curie Temperatures; Bethe-Slater Relationship; Spin-Glass; Paramagnetic-Ferromagnetic Phases; Heisenberg Model; Arrot-Belov-Kouvel (ABK) Plots

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INTRODUCTION

THE growth of interest on the subject of amorphous alloys in the last decade is indeed phenomenal. The explosive literature on the subject is partly governed by the search for new materials with potential technological applications and partly by the scientific curiosity to look for and understand unusual structural situations such as those obtained in amorphous materials. The reader may refer to any of the books that have appeared very recently for a comprehensive treatment of different aspects of the subject of amorphous materials.[1-5] Gubanov[6] theoretically foresaw the existence of ferromagnetism in amorphous solids in 1960. Around the same time, the advent of amorphous ferromagnets began as a laboratory curiosity with the investigations of Duwez[7] and co-workers and now has become a subject of industrial curiosity, attracting more and more workers from different fields into its fold. The present title is chosen for the review keeping in mind that magnetism in itself is quite an interesting field and this property in amorphous materials is likely to continue to be of considerable concern for quite sometime to come both from theoretical as well as experimental points of view. The subject matter has been sub-divided into different sections purely for the convenience of presentation and in a way reflect the patterns of literature on the subject of magnetism in general.

MAGNETIC MOMENTS OF TRANSITION METAL ATOMS IN TRANSITION METAL-METALLOIDS

Amorphous magnetic alloys, prepared by various techniques[4] possess a chemical composition T_xG_{1-x} with $x \simeq 0.8$. Here T = Fe, Co or Ni or a combination of these $3d$ elements, or a combination of them with other $3d$ elements such as V, Cr or Mn; G represents metalloids from group III A like B, IVA, such as C, Ge, Si, Sn or Va like P or more often a combination of these elements. The average magnetic moment, μ, per transition metal atom for various alloy compositions is listed in Table I.[2] These values have been obtained from bulk saturation magnetisation measurements utilising a force balance method or vibration magnetometer. The data clearly show that the presence of metalloid atoms decreases the value of μ relative to the values for pure transition metals, $2.2\mu_B$ for Fe, $1.7\mu_B$ for Co and $0.6\mu_B$ for Ni. This is a feature common for amorphous and crystalline alloys. For instance $\mu = 1.91\mu_B$ for Fe_2B and the reduction is attributed to charge-transfer from B to Fe. The differences in the reduction in alloys containing varying amounts of different metalloid atoms are attributed to the amount of charge-transfer from the metalloid atom which in turn is governed by the number of s-p electrons on the metalloid. Several attempts have been made to formulate simple rules that govern the observed trends. The use of generalised Slater-Pauling model by Mizoguchi *et al.*[8] in the amorphous magnets with composition $(Fe_{1-x}TM_x)_{80}P_{10}B_{10}$ (TM = Ni, Co, Mn, Cr, V), showed several features with trends similar to those in crystalline alloys. The Slater-Pauling curve obtained by plotting magnetic moment per TM atom *vs.* the number N of TM outer electrons showed a maximum toward the lower value of N as in transition metal borides (Fig. 1). A distinguishing feature

TABLE I

Average magnetic moment, μ per transition metal atom in various transition metal-metalloids (Ref. 2, p. 92 and references therein)

Alloy Composition	$\mu(\mu_B)$
$Fe_{80}P_{20}$	2.1
$Fe_{80}B_{20}$	1.94
$Fe_{80}P_{14}B_6$	1.85
$Fe_{70}Ni_{10}B_{20}$	1.86
$Fe_{70}Ni_{10}P_{14}B_6$	1.64
$Fe_{60}Ni_{20}B_{20}$	1.69
$Fe_{40}Ni_{40}B_{20}$	1.31
$Fe_{40}Ni_{40}P_{14}B_6$	1.23
$Fe_{40}Co_{40}B_{20}$	1.79
$Co_{80}B_{20}$	1.28
$Co_{78}P_{22}$	1.18
$Ni_{80}P_{20}$	0.05

is a shift of the maximum to lower values of N in amorphous compared to crystalline systems with $\Delta N = 0.3$. Otherwise, the same linear decrease of the moment between iron and nickel is observed. Luborsky,[9] from these trends concluded that roughly boron atoms transfer a charge of about one electron and phosphorous two electrons to the transition metal atoms. Such a prediction would mean that even variation of metalloid concentrations in systems such as $Fe_{40}Ni_{40}(P, B)_{20}$ should

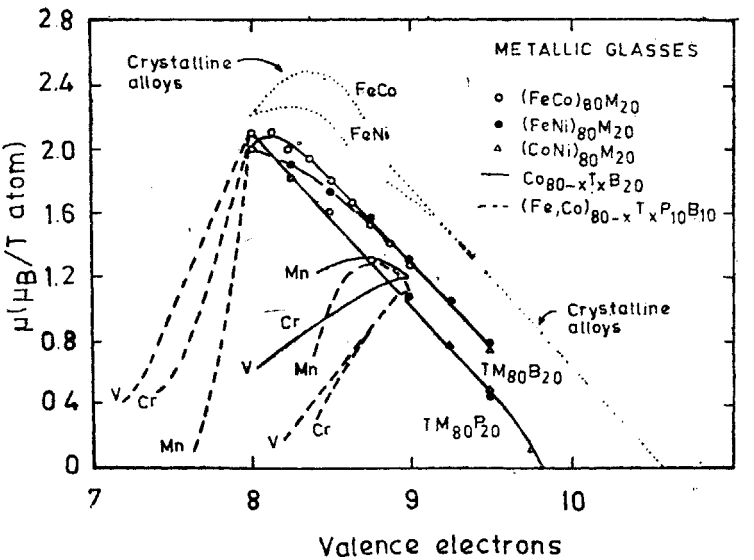

FIG 1 Dependence of mean saturation moment per transition metal atom on average transition metal valence electron concentration.[8]

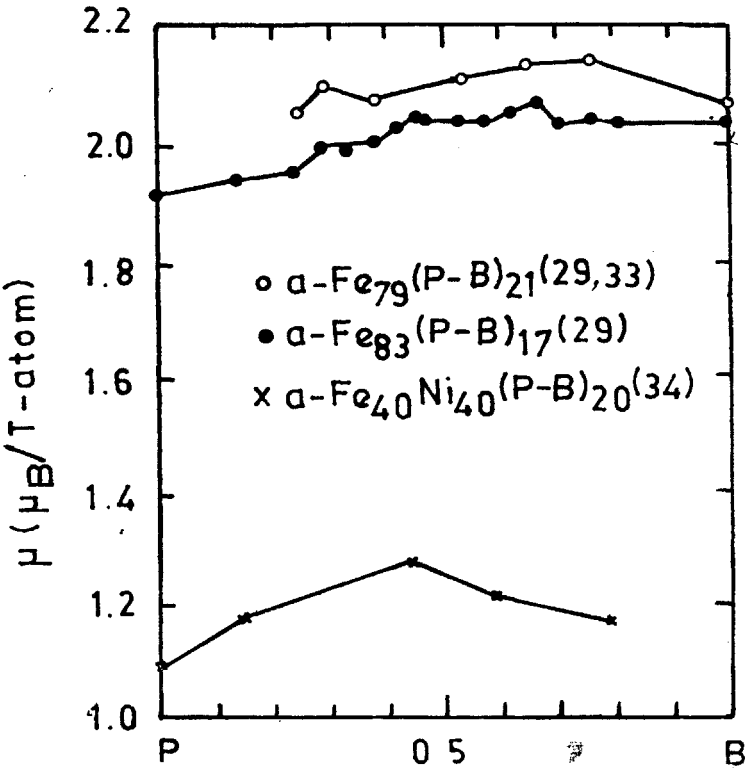

FIG 2 Changes in the average magnetic moment in *a*-transition metal-metalloid alloys with relative concentrations of P and *B* atoms.[10]

show a monotonic decreasing trend as P is replaced by B. This is not, however, found to be the case as shown in Fig. 2.[10] Thus it is difficult to account for details of moment variation in a simple manner. The above example suggests the importance of other aspects which can significantly influence the variation of magnetic moment with composition such as chemical bonding. It should at the same time be stressed that chemical bonding in amorphous alloys can be more difficult to handle than in crystalline systems. This may be highlighted, for example, by the observation that *a*-$Fe_{0.5}Si_{0.5}$ and *a*-$Co_{0.5}Sn_{0.5}$ are magnetic whereas the corresponding crystalline systems are non-magnetic.[11,12] Thus, amorphous systems can give rise to chemical environments of multiple type favouring existence of a magnetic moment.

Considerable work has also been reported on ternary alloys with no agreement regarding the moment to be associated with different transition metal atoms.[13] Mizoguchi *et al.*[8] concluded from the results on the alloys *a*-$(Fe, M)_{80}P_{10}B_{10}$ mentioned earlier that Fe, Co and Ni possess approximate magnetic moments 2, 1 and $0\mu_B$ per atom respectively. A similar result is obtained by Sherwood[14] on *a*-$(Fe, Co, Ni)_{75}P_{16}B_6Al_3$. Yamauchi and Mizoguchi[15] on a study of ternary alloys with a

single *TM* element found μ_{Fe} and μ_{Co} when taken equal to 2.6 and 1.6 μ_B respectively, the magnetic data agree reasonably well with values obtained using the rigid band model. Durand[16] on the other hand concludes in the investigation of a-$(Fe_xNi_{100-x})_{79}P_{13}B_8$ series that the moment per Ni atom increases steeply from zero at $x = 0$ to roughly a constant value of 0.4 μ_B for x 30 at per cent O'Handley *et al.*[17] have shown from a rigid band model analysis that Ni should have a non-zero moment in amorphous $Ni_{80}B_{20}$ alloy and B and P metalloid atoms donate 1.6 and 2.4 electrons per atom respectively to the *d*-bands of the *TM* atom. In a comprehensive study of the Fe–P–B alloys, Durand and Yung[18] are able to account for the rate of reduction of iron moment when one metalloid is retained at constant percentage and the other substituted for iron, using a charge transfer model assuming B and P donate 1.4 and 1.6 electrons respectively to the Fe-*d* bands. The later value for P is significantly different from the one derived by O'Handley[17] mentioned earlier. Kaul[13] has rationalised the differing observations stated above by putting forth the idea that not only the moments of Ni and Fe atoms vary with Fe concentration as revealed by neutron diffraction in crystalline alloys, but also the number of electrons donated by the metalloid atoms to the transition metal *d*-bands. Such a hypothesis has been justified on the basis of the coherent potential approximations.[19,20]

Curie Temperatures

The curie temperatures of amorphous alloys are of much greater interest than of crystalline metairals for (1) they are influnced by composition due to the moment of the constituting elements, (2) by structural disorder (3) chemical bonding of the metalloids with the *TM* which cannot be understood in a simple way as in crystalline systems for reasons mentioned earlier. We discuss below the dependence of T_c on these different factors and briefly mention the different arguments and models proposed to explain the observations. T_c for amorphous nickel has been determined to be 540 K which is about 15 per cent lower than the crystalline Ni.[21] Extraploated estimate of T_c for amorphous iron from a study of a-FeZr alloy leads practically to 0 K.[22] Cobalt-based amorphous alloys have the characteristic property of having $T_c > T_x$ where T_x is the crystallisation temperature as shown for instance by a comparison of the Mössbauer spectra recorded with increasing temperature.[23] That Co based alloys indeed differ in their behaviour from Fe based alloys can also be illustrated with the cases of a-Co_xP_{1-x} and a-Fe_xP_{1-x} systems.[18,24] With increasing x, T_c increases for the cobalt alloy leading to an extrapolated value of 1400 K for $x = 1$ unlike in a-(Fe–P–B) alloy which shows a decrease with increasing x leading to T_c of 340 K for $x = 1$. This may be understood as due to the presence of Fe–Fe pairs that interact antiferromagnetically depressing the curie temperature.

Since the first approach by Gubanov,[6] reduction in T_c by structural disorder has been envisaged by theoretical analysis by various workers.[25–27] In the light of these theories, when the lowering of T_c from crystalline systems is of the order of

10 to 15 per cent, the influence of structural disorder can easily be understood as due to the smaller density ($\sim$ 3 per cent) in the amorphous state affecting the exchange integral in a molecular field model. A small but significant lowering of T_c in amorphous to crystalline systems has been observed in cases such as a-$Fe_{75}P_6B_{19}$, a-Fe_3B and a-Fe_3P.[18,28,29] But when a drastic effect occurs as in a-YFe_2, the differences cannot be accounted for without going through a detailed band structure calculation. Comparatively, only a few calculations have been made to account for T_c variations with composition using the itinerent magnetism model.[30,31] The direct exchange interaction in amorphous magnets may be given by the semiempirical Bethe-Slater curves as a function of the radius of d-shell, R_d and of the atomic separation, R. Chen *et al.*[32] have thus shown that when T_c values of different glasses are plotted against R/Rd, the influence of metalloid addition and alloying among the transition metals on T_c can be qualitatively accounted for. The T_c dependence on composition in the alloys $(Fe_xNi_{1-x})_{80}B_{20}$, $(Fe_xNi_{1-x})_{80}B_{19}Si_1$ and $(Fe_xNi_{1-x})_{80}P_{14}B_6$ has been well accounted for in terms of the relationships between near neighbour exchange interaction and x put forward by Foo and Wu using the coherent potential approximation for disordered ferromagnetic binary alloys.[13,33]

The T_c values measured by magnetic measurements are found to be significantly lower than values obtained by Mössbauer measurements which monitors the hyperfine field at a microlevel. This is a trend that has been observed in crystalline systems as well and is attributed to relaxation effects which the Mössbauer probe experiences close to T_c and is governed by the relaxation times. Yet another property which distinguishes amorphous magnets is the influence of thermal history on the curie temperatures which can be pronounced in some of these alloys. For example, in the case of $Fe_{78}B_9Si_3$ the T_c shifts to lower values with higher rate of heating as sensed by differential scanning calorimetry.[34] Similar thermal effects on T_c observed for a-Ni-rich Fe—Ni—B glass by Davies and Gregan[35] has been attributed to structural relaxation effects associated with the diffusion of boron atoms.[35]

Mössbauer Spectroscopic Measurements

Mössbauer spectroscopic measurements have provided insight into magnetic properties in those systems which contain suitable isotopes such as ^{57}Fe, ^{161}Dy etc., which act as Mössbauer probes.[36] With this technique it is possible to have access to informations which are not otherwise possible as it has the advantage of probing at the microlevel and of monitoring the magnetic phenomena with associated hyperfine interactions. The Mössbauer profiles of a number of iron rich ferromagnetic glassy alloys reported are similar. They all exhibit a well-resolved six-finger pattern with relative intensities close to 3 : 4 : 1 : 1 : 4 : 3 compared to 3 : 2 : 1 : 1 : 2 : 3 observed for iron foil and many crystalline alloys.[37–42] The spectral line-widths also are significantly broader. We reproduce in Fig. 3 the Mössbauer spectra of $Fe_{72}Ni_8Mo_2B_{16}Si_2$ over the temperature 80 to 750 K range as a representative example.[43] The transformation from ferro- to para-magnetic state above T_c is

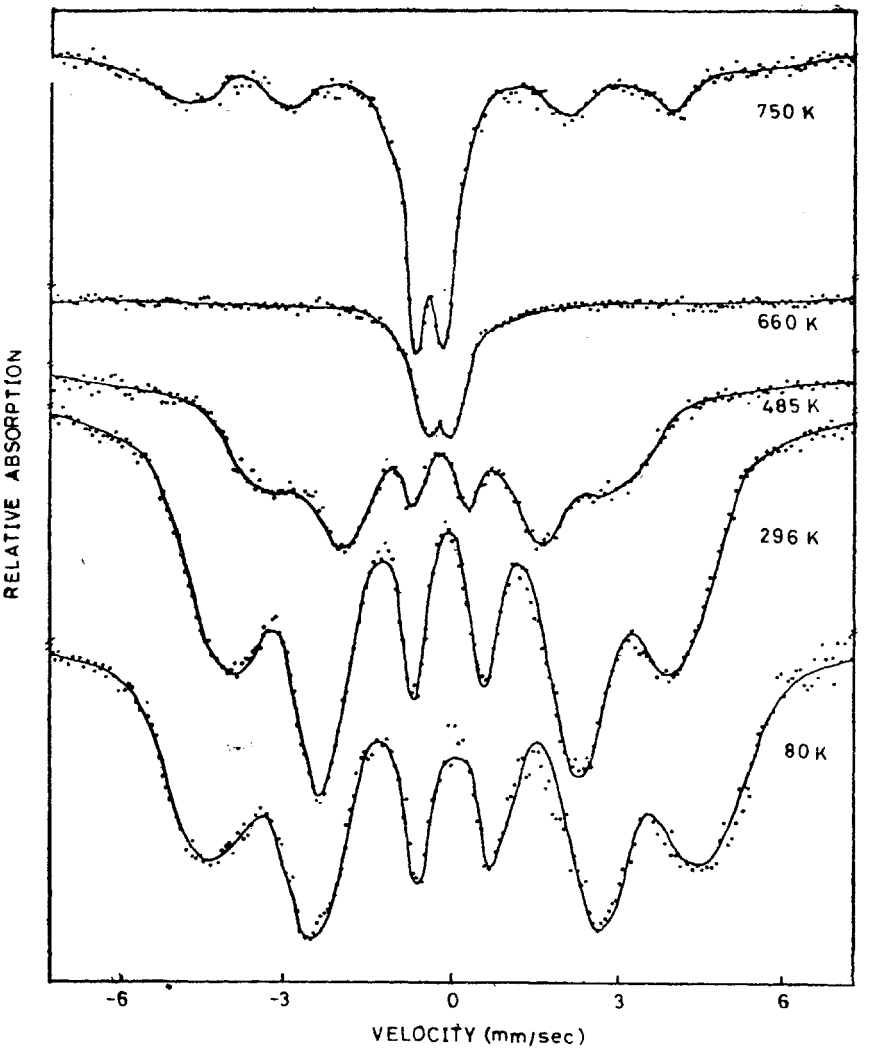

FIG 3 Mössbauer spectra of a-$Fe_{72}Ni_8Mo_2B_{16}Si_2$ between 80 and 750 K.[43]

shown by a change from a six-finger pattern to a quadrupole split doublet. As a typical example, we give the least square fit experimental parameters, viz., line positions, line-widths and relative peak-areas obtained for the room temperature Mössbauer spectrum in Table II.[43] The large line-widths quoted should be compared with a value of 0.28mm/sec obtained for the experimental line-width for natural iron. The characteristically broad lines with a symmetric profile uniformly observed in all the magnetic amorphous alloys arise due to iron atoms finding themselves in a variety of coordinations with random distribution of electric field gradient, which is significant as shown by the quadrupole-split paramagnetic spectra above T_c and which below T_c adds to the spectral line-widths without shifting the

TABLE II

Line-position, line-width and peak-areas of the Mössbauer spectrum[43] *of* a-$Fe_{72}Ni_8Mo_2B_{16}Si_2$

	Mössbauer lines					
	I	II	III	IV	V	VI
Line position (mm/sec)	−4.144	−2.347	−0.684	+0.496	+2.139	+3.898
(FWHM) (mm/sec)	1.758	1.283	0.537	0.671	1.534	1.714
Peak area (arbitray units $\times 10^6$	1.368	1.426	0.386	0.430	1.599	1.263

line positions. A survey of literature shows that extensive analysis of Mössbauer spectra of amorphous alloys throw light on the following aspects.[36] (1) Temperature-dependence of magnetisation (2) Distribution of hyperfine field and its temperature dependence and (3) Phase-transformations and associated phenomena. An attempt is made in this section to highlight these features as observed in the so-called metallic glasses.

The major handle that has been found to be of considerable value is the measurement of the hyperfine-field as given by the splitting of the spectra due to the internal magnetic field. The relative intensities of the six-finger pattern depends on the orientation of the magnetic field relative to the electric field gradient in the principal axes system.[44] Thus, the significantly different relative intensities in amorphous alloys compared to that in natural iron arises due to the fact that although the hyperfine field has a distribution, the components are predominantly oriented alike and in these cases along an axis perpendicular to the ribbon plane or close to such a description.[45] The magnitude of the hyperfine field depends on the contributions due to the Fermi-contact interaction, the dipolar and orbital contibution. At room temperature the amorphous alloys exhibit hyperfine-fields close to $\sim$ 270kOe which is significantly less than the valus for natural iron *viz.* 330kOe. This clearly shows that bonding between the metalloid atoms and the metal atoms in these alloys is quite important. It has been experimentally shown for these ferromagnets that the average hyperfine field is proportional to the bulk magnetisation with the proportionality constant being $\sim$135kOe/μ_B where μ_B is the Bohr magneton. Fig. 4 shows a plot of the reduced magnetic field against reduced temperature for a few metallic glasses in addition to the Brillouin function for $S = \frac{1}{2}$ for comparison as it describes the temperature-dependence for many crystalline ferromagnets such as iron. It is seen that the temperature-dependence for amorphous alloys differ significantly from the crystalline alloys and gives rise to a 'flatter' curve compared to the Brillouin function for $S = \frac{1}{2}$. This is found to be quite characteristic of many of the amorphous alloys studied although the disordered alloys also show a similar trend but to a much lesser extent.[46] This behaviour can be explained on the Handrich's[47] model based on the effective molecular field approach according to which the Brillouin function can be written in the modified form :

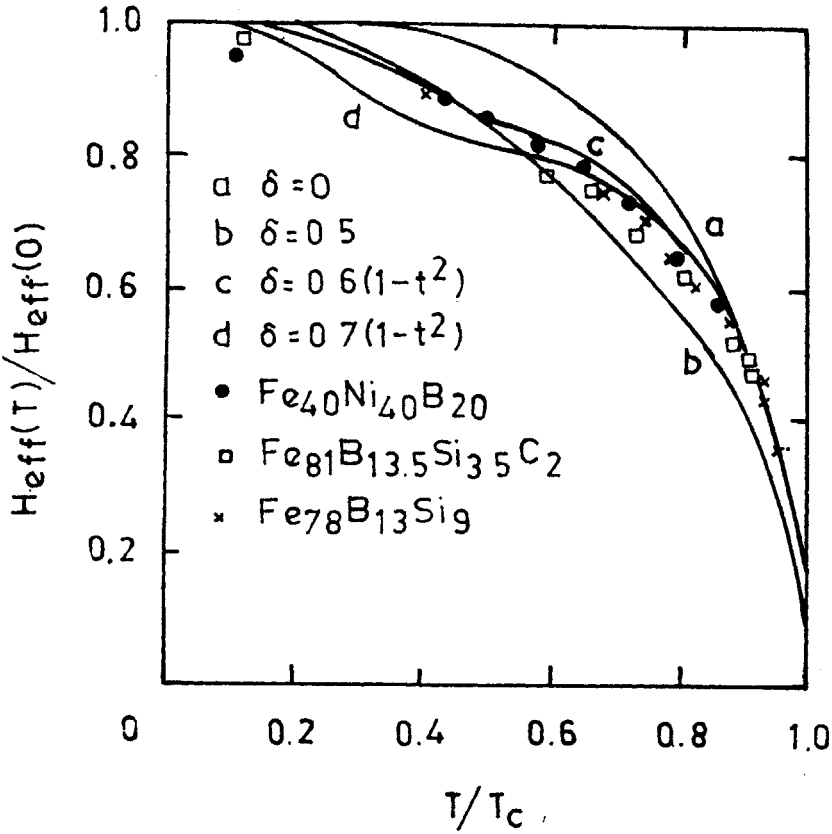

FIG 4 Reduced hyperfine magnetic fields *vs* reduced temperature-solid lines are drawn using eq. (1) with different values of ∂.[36]

$$h = \frac{H_{eff}(T)}{H_{eff}(O)} = \frac{B_s[(1+\partial)x]}{2} + \frac{B_s[(1-\partial)x]}{2}, \qquad \ldots(1)$$

where B_s is the Brillouin function for spin S, $x = [3S/S+1]\,(h/t)$, $t = T/T_c$, and ∂ is a measure of the fluctuations occuring in the exchange interactions due to the random distribution of atoms in these solids and its value lies between zero and unity. For $\partial = 0$ expression (1) reduces to the form applicable to crystalline ferromagnets. It is found that in order to obtain a qualitative agreement with experimental points the values ∂ as high as 0.5 have to be used but even then quantative agreement remains far from satisfactory. Prasad *et al.*[36–39] showed that this agreement can be considerably improved if ∂ is assumed to have a temperature dependence, given by $\partial(t) = \partial_0(1 - t^2)$. Fig. 4 shows that most of the experimental points lie on the theoretical lines assuming temperature dependence of ∂ of the above form with $\partial_0 = 0.6$ and 0.7. Subsequently, various authors have theoretically looked into the possible reasons for the temperature-dependence of magnetisation which cannot be explained fully on the Handrich's model. Fahnle[48] has

attempted the Monte Carlo simulations in disordered ferromagnets for a simple cubic lattice. Fig. 5 shows his results obtained for a finite lattice. The high temperature tails are found to depend on the lattice size but the low temperature data are found not to be influenced by lattice size considerations and reproduce the flattening behaviour observed experimentally. In these calculations consideration has been given both for the fluctuations of the exchange interactions (bond-disorder) as well as of the magnetic moments (site-disorder). Correlations between the exchange fluctuations (correlated bond-disorder) have been found to lead to enhanced flattening effect in the temperature dependence of reduced magnetisation. By way of rationalising the temperature-dependence observed by Prasad *et al.*[36–39] Kaneyoshi and Tamura[49] have considered the possibility of temperature-dependent distribution of magnetic moments. These authors have justified their approach on the ground that the line-widths of the Mössbauer spectra are found to decrease monotonically with temperature. However, it is found that the empirical expression suggested by Prasad *et al.*[36–39] gives a much better fit with experimental data than the expression of Kaneyoshi and Tamura particularly in the region $0.4 < T/T_c < 0.7$, where the deviation is maximum from the Brillouin function. This is attributed to the possible error in assuming a monotonic function for temperature, dependence of distribution

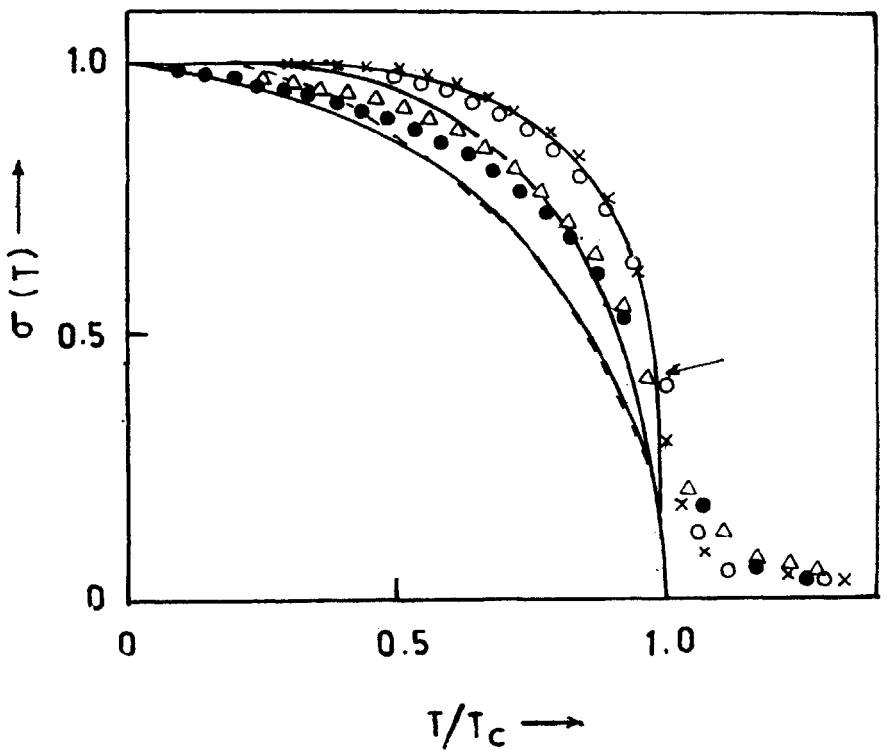

FIG 5 Monte-Carlo simulations of temperature dependence of reduced saturation magnetisation (T) for crystalline, bond- and site-disordered cubic Ising systems and experimental data.

as evidended for instance by a quadratic dependence of the line-width obtained by Narendra babu *et al.*[43] using a model-independent analysis of hyperfine-field as discussed below.

The broad and overlapping spectral lines in the Mössbauer spectra of metallic glasses are attributed to a hyperfine field distribution, $P(H)$, arising from a large number of non-equivalent sites. A number of methods have been developed to analyse the spectrum to obtain $P(H)$. The model independent approach due to Window is being widely used for this purpose and modifications for this procedure have been suggested.[50-52] A representative result of $P(H)$ analysis obtained using Window's method for the amorphous alloy is reproduced in Fig. 6. The results of such analyses lead to the following observations. The $P(H)$ curves obtained for most of the amorphous alloys are smooth, well-defined, structureless and usually exhibit a single maximum in the distribution. The oscillatory behaviour is an artefact due to the truncation of the Fourier series. The $P(H)$ curves are characterised by the parameters $H(P)$, the most probable field, ΔH half-width and $\bar{H}$, the average field. The significantly wide distribution in the hyperfine field in amorphous alloys may be appreciated from the fact that ΔH values have been found to be between 60 and 90kOe compared to $\sim$ 43kOe for disordered alloys.[46] The spread in the hyperfine field at room temperature is found to have a range for the value of the magnetic moment from 1.0 μ_B to 2.65 μ_B, thus indicating that the range extends even beyond that of α-iron (2.2 μ_B). The temperature-dependence of the average field and the maximum field show trends similar to those discussed in the earlier section. Mössbauer spectra clearly distinguish amorphous alloys which have magnetic inhomogenity from those which do not. This may be well illustrated by the a typical Mössbauer spectra reported by Chien[53] for a-($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$) reproduced in Fig. 7 which may be compared for example with Fig. 2. In this case, the $P(H)$ distribution shows a pronounced asymmetric distribution with two significant peeks which has been attributed to two different types of near neighbour environment.[53,54] The Mössbauer results pertaining to phase transformations are discussed in the ensuing sections.

Magnetic Phase-Diagrams

(*a*) *Nature of the Phases and Comparison with Crystalline Systems*

The nature of interaction between two 3*d*-impurity atoms such as Mn, Cr, Fe etc., in a non-magnetic host such as the noble metals like Cu, Ag or, Au has been shown to depend on the nature of the impurity atoms as well as those of the hosts. Concentration of the impurity atoms is the key factor in deciding the nature of the interactions. At very low concentration, e.g., $<$ 50ppm the interaction is very weak. This single impurity regime is referred to as the Kondo[55] regime. At very large concentrations, $>$ 20 at per cent, the direct exchange interactions lead to an ordered magnetic state. In the intermediate concentration range, in the first phase between 0.1 and 10 at per cent, the impurites interact strongly enough through the RKKY[56] interaction but direct exchange forces are relatively unimportant. In this

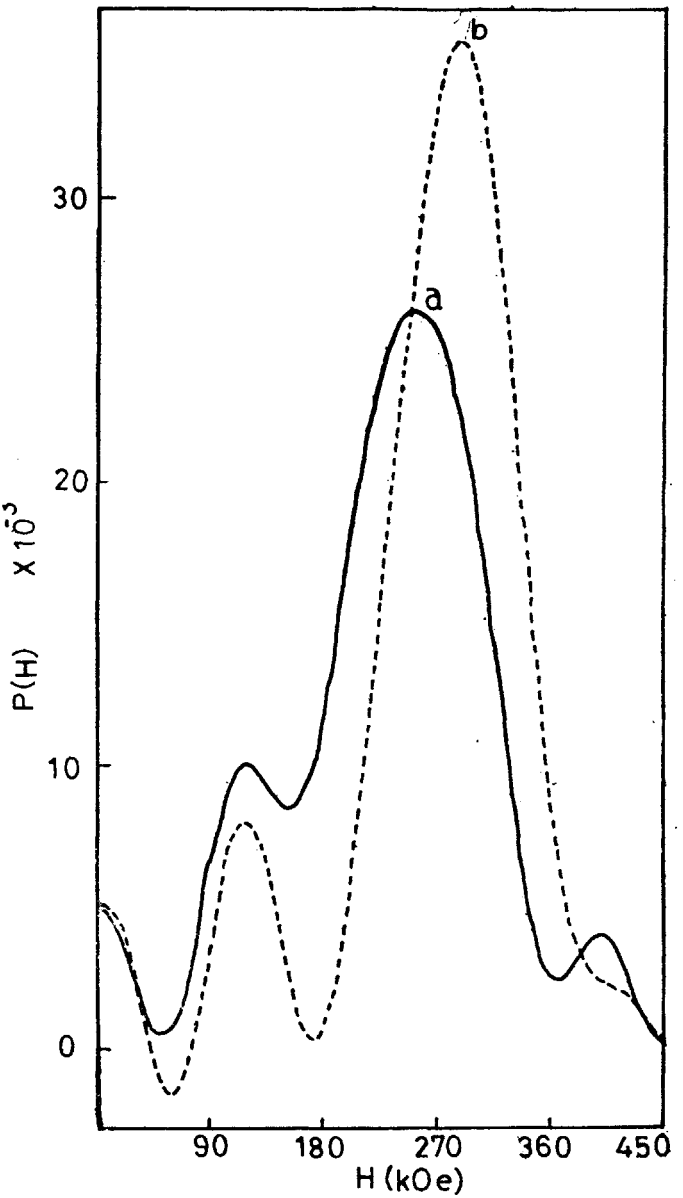

FIG 6 Distribution of hyperfine-field at 80 K for a-$Fe_{72}Ni_{10-x}Mo_xB_{16}Si_2$ alloys (a for $x = 6$; b for $x = 2$).[43]

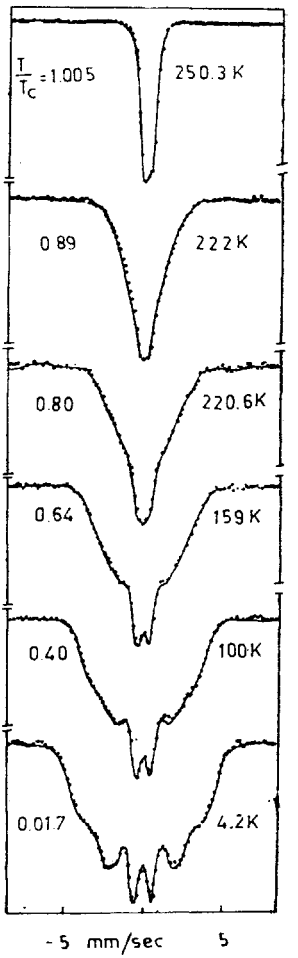

FIG 7 Mössbauer spectra of a-$Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ in the temperature range 4 to 260 K.[53]

region, the RKKY-coupling can be both positive as well as negative due to the randomness in the distribution of the exchange interactions and is referred to as the spin-glass region. In the subsequent region with the impurity concentration ranging between 10 and 20 at per cent, the spin-glass situation coexists with the onset of

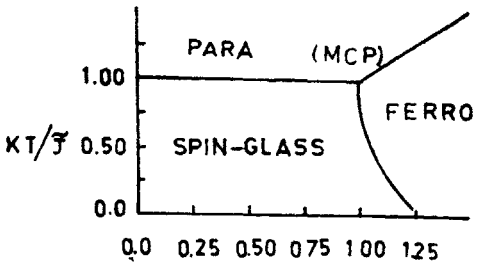

FIG 8 A schematic magnetic phase-diagram based on the model of Sherrington and Kirkpatrick.[58]

direct exchange and is variously referred to as 'cluster glass', mictomagnetism etc. Edwards and Anderson[57] were the first to suggest a lower magnetic state without long range order with randomly oriented spins leading to spin-glass behaviour. They proposed a ground state for the system whose order parameter is taken to be the spatial average of the square of the thermal average of the spins over a given configuration. Following this suggestion, Sherrington and Kirkpatric[58] put forward a model in which the distribution of exchange energies are characterised by a mean value $\tilde{J}_0$, a measure of the ferromagnetic exchange coupling and $\tilde{J}$ the width of the pair exchange distribution $\tilde{J}_{ij}$. Solution of this infinite range model leads to the phase diagram shown in Fig. 8. Based on the type of interactions discussed above, there appear three phases, paramagnetic, ferromagnetic and spin-glass which meet at a multi-critical point (MCP).

The experimental realisation of magnetic phase diagrams with the above features should be considered to be less than quantitative particularly due to the absence of a clear-cut change over from one phase to another as a function of impurity concentrations. One of the most well-studied systems in these studies pertains to the magnetic phase diagram of Au–Fe alloys constructed from anomalies observed in various experimental results.[59] In view of the range of interactions that come into question a number of experimental techniques such as ac and dc susceptibilities, specific heat measurements, muon spin resonance, ferromagnetic resonance, Mössbauer spectroscopy neutron scattering studies, Hall Effect etc., which have been earlier employed to obtain the magnetic phase diagrams for the study of impurity interactions between magnetic atoms at various concentrations in crystalline systems, have been brought into bearing in the investigation of amorphous magnets as well.[60–66] Before discussing the results of these studies it may be stated that among the three phases in the phase diagram, spin-glass has attracted maximum attention. This term in literature is rather broadly used to refer to a region with competing interactions resulting in frustration. The frustration may occur in any type of materials that include magnetically dilute or concentrated, crystalline or amorphous, metallic or insulating. Recent works show the inherent difficulties in handling the spin glass problems theoretically as well and re-examine many concepts such as linear response theory, the concept of low-temperature phase having a lower free-energy compared to the phase at higher temperature etc.[2]

Fig. 9 illustrates the typical phase diagrams obtained for amorphous alloys.[67] The phase-diagram shows a multicritical point with a critical concentration, a 'reentrant' transition as a function of temperature at relatively low temperature regions and a para to ferromagnetic and reverse transformation at higher temperatures. Based on these magnetic phase diagram investigations, the following observations may be made. The amorphous alloys permit study of spin-glass state over a wider region of concentration due to more favourable phase diagrams. The phase diagrams also show that in very dilute concentrations, the spin-freezing temperature, T_f, is proportional to the concentration of impurity atoms such as Fe, Co, or Mn. A nonlinear dependence appears beyond a particular concentration which is characteristic of the system in question. For instance the linear behaviour is observed in $Fe_xPd_{80-x}Si_{20}$ even upto 7 at per cent compared to most other alloys such as $Fe_xNi_{80-x}P_{12}B_8$ etc., where linearity is limited to much lower concentration of about only 2 at per cent.[16,64] The slope of the curve indicating the para to ferromagnetic transformation by the change in T_c with composition is also characteristically different from system to system. Lack of knowledge about the transition from spin-glass to cluster glass-type interaction, magnetic inhomogenity, etc, makes it difficult to discuss such trends in a definite manner.

(*b*) *Critical Concentration*

In an alloy of the type A_xB_{1-x} where B is non-magnetic, chemical disorder leads to percolation. At a critical concentration, x_p, many of the A atoms form bulk clusters. The remaining ones form isolated clusters. Thus above x_p magnetic ordering sets in and long-range interactions are important. And below x_p short-range interactions are important x_p critically depends on the range of interaction and for the nearest neighbour coupling it is $2/N$ where N is the number of the nearest

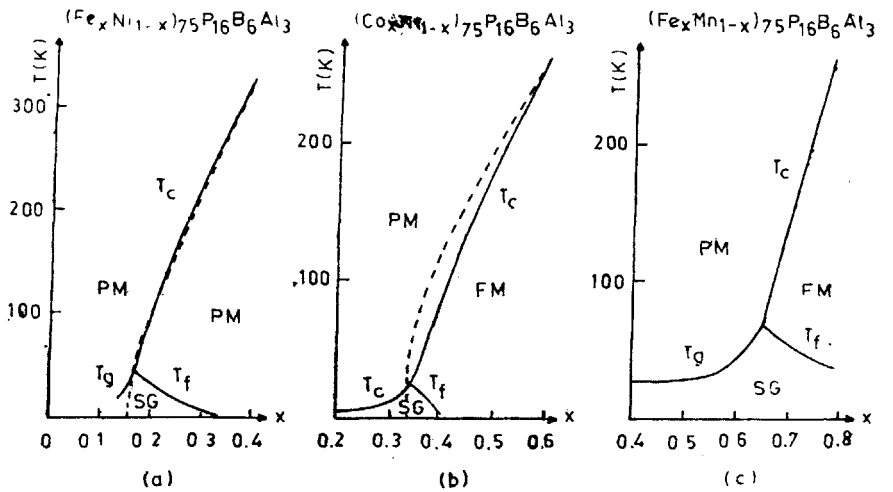

FIG 9 Phase diagrams for three series of a-$(A_xB_{1-x})P_{16}B_6Al_3$ Dashed lines are from theoretical models [(Ref. 68) and references therein].

neighbours. In amorphous alloys assuming dense random packing N has a value between 10 and 12 giving $x_p = 0.2$.[68] Experimentally observed x_p values significantly deviate from the above value for the following reasons. Most of the systems studied are ternary or quaternary systems. x_p as mentioned earlier depends on chemical and topological disorder and thus metalloid atoms can be expected to play an importont role. The nature of the interactions between different transition metal atoms in these systems will also influence x_p. This is well brought out as shown by the phase diagrams of $(A_xB_{1-x})_{75}P_{16}B_6Al_3$, where ($A$, B) and (Fe, Ni), (Co, Ni) and (Fe, Mn) where the critical concentrations differ significantly (Fig. 9). The critical concentrations reflect the differences between alloys with good moments such as Fe–Ni, alloys with discontinuous appearance of moments such as Ni–Co and Fe–Sn base alloys and alloys with competing interactions such as Fe–Mn, Fe–Cr and Co–Mn base alloys. The much higher critical concentration observed for Fe–Mn base alloys for instance, is attributed to the antiferromagnetic contribution by manganese.[69] In iron rich amorphous alloys, however, with a distribution of interatomic distance, due to the Fe-Fe interaction which significantly differs with interatomic distance, no simple explanation can be considered unequivocal.

(c) *Spin Glass Behaviour*

By way of illustrating how different experimental techniques may be employed in the study of magnetic interactions both from the point of interest of magnetism in amorphous materials as well as in spin-glass phase in general, discussion of some of the works reported in literature may be appropriate at this point. A temperature-dependent study of low-field magnetic susceptibility on magnetic glasses such as a-$(Fe_xNi_{1-x})_{97}P_{13}B_8$ and a-$(Fe_{0.2}Ni_{0.8})_{75}P_{16}B_6Al_3$ show sharp cusps similar to those found in well-established dilute spin-glasses, the maximum shifting to higher temperatures with increasing values of x.[16] Temperature-dependence of magnetisation in the B alloys show broad maxima typical of reentrant phase transition.[70] Different theoretical models which either employ a phase transition approach or invoke a spin-freezing mechanism have been proposed to describe spin-glass behaviour.[57,71] But no single theory fully explains all the experimental features. Recently. the frequency-dependence of ac susceptibility has been shown to be of value in ascertaining which of the theoretical descriptions, equilibrium or non-equilibrium phase transition metastable state or thermally activated phase change, is more appropriate.[72] Such detailed investigations are relatively scarce in literature. Ferromagnetic resonance has been employed to study the reentrant behaviour in a-$(Fe_xNi_{1-x})_{75}$ $P_{16}B_6Al_3$ and a-Fe_xB_{100-x} alloys.[61,66] In the iron-boron alloys, the onset of spin-glass behaviour is discerned by the observation that the FMR line-widths are independent of temperature above 130 K but show an increasing value as temperature is lowered, the increase being more significant, lower the iron content. The temperature dependence of resonance field has been found to be dependent on the heating or cooling rates lending credence to the suggestion that the spin-glass state is inherently non-ergodic.[2] The spin-glass transition in a-Fe_xSn_{100-x} has been studied by temperature variations in magnetization.[73] A reversible trend close to

T_c and an irreversible behaviour below T_f have been observed and the magnetic phase diagram obtained. It would be quite interesting to study this system by Mössbauer spectroscopy as both iron and tin sites can be examined by this technique.

Critical Behaviour

The critical behaviour of amorphous transition metal-metalloids mainly pertains to ferromagnets. The detailed behaviour of systems undergoing a second order phase transition close to the Curie temperature where the ordered state appears has attracted great deal of attention in crystalline materials and attempts have been concentrated in the study and comparison of similar situations between crystalline and amorphous systems and within amorphous systems as well. Current approaches to critical phenomena pertain to the adherence to the static scaling hypothesis suggested by Domb, Hunter and Widom.[74] It is based on the assumption that close to critical point the Gibb's potential or other equivalent thermodynamic potentials can be expressed as a homogeneous function of two variables, the reduced temperature $\epsilon = (T - T_c)/T_c$ and field conjugate to the order parameter. For a ferromagnet the order parameter is the magnetisation M and the conjugate field is the magnetic field H and near T_c as $H = 0$, the equation of state may be written as

$$\frac{H}{|\epsilon|^{\beta+\gamma}} = f_{\pm}\frac{M}{|\epsilon|^{\beta}}, \qquad \ldots(2)$$

where the $\pm$ refer to the sign of $|\epsilon|^{\beta}$ is the critical exponent describing the temperature-dependence of spontaneous magnetisation just below T_c with

$$M \sim (T_c - T)^{\beta}, (H = 0) \qquad \ldots(3)$$

and γ is the critical exponent describing the temperature-dependence of susceptibility above T_c with

$$\lim_{H\to 0}\left(\frac{H}{M}\right) = \chi^{-1} \sim (T_c - T)^{\gamma}. \qquad \ldots(4)$$

Though the functional relation depends on the sign of the static scaling hypothesis expressed by eq. (2) implies that the normalised quantities, $H|\epsilon|^{-(\beta+\gamma)}$ and $M|\epsilon|^{-\beta}$ are uniquely related though relate to situations both below and above T_c. Further, the hypothesis leads to a relationship of the critical exponents of the form

$$\beta + \gamma - \beta\delta = 0, \qquad \ldots(5)$$

where δ is the exponent for the critical isotherm

$$M \sim H^{1/\delta}\ (T = T_c,\ H \to 0) \qquad \ldots(6)$$

The scaling hypothesis was put on a firm theoretical ground by Wilson[75] using the renormalization group transformation. The methods and results of this approach have been reviewed. The theoretical values of the critical exponents have been

derived to be $\beta = 0.3647 \pm 0.0012$, $\gamma = 1.3866 \pm 0.0012$ and $\nu = 0.7054 \pm 0.0011$ for the three dimensional Heisenberg model.[76] The soundness of the theoretical approach has been demonstrated by careful neutron scattering experiments and magnetic measurements on EuO and EuS which gave $\beta = 0.37 \pm 0.015$, $\gamma = 1.40 \pm 0.03$ and $\nu = 0.70 \pm 0.02$.[77] The transition metals Fe, Co, and Ni also exhibit critical exponents close to the theoretical values within experimental errors.[78] The major cause of deviation from theoretical values is the existence of long-range interactions such as due to dipolar forces in real systems. Kadanoff *et al.*[79] have analysed the influence of these interactions and their analysis is helpful in estimating the critical region. Testing the applicability of the scaling hypothesis for amorphous ferromagnets is of great interest as a positive answer would imply that these amorphous alloys are magnetically isotropic on a microscopic scale and systems having a distribution of exchange interactions can indeed exhibit a second order phase transformation. The experimental determinations of critical exponents in these systems have been carried out using magnetisation data, Mössbauer spectroscopy and specific heat measurements. The studies have to be naturally limited to systems which have curie temperature below crystallisation temperature. One of the early investigations in these lines is due to Mizoguchi *et al.*[80] who showed the validity of the scaled magnetic equation of state for a-$Co_{70}B_{20}P_{10}$. Representative results for critical constants gathered from published literature as given in Table III. It is seen that the critical exponents except β, which shows noticeable deviation, exhibit values close to the ones predicted from the three-dimensional Heisenberg model and satisfy eq. (5). An idea about the extent of critical region may be obtained using the relationship due to Kadanoff *et al.*[79] who have suggested that long-range interactions are negligible provided

$$|\epsilon| \geqslant \frac{g\mu_B SM(O)^{1/\beta(\partial-1)}}{kT_c} \equiv t_c, \qquad \ldots(7)$$

where β and ∂ have the same significance as discussed earlier and the other terms have their usual significance. In amorphous alloys the extent of critical region has been found to be significantly larger than in crystalline materials. For instance, in a-$Fe_{10}Ni_{70}B_{19}Si_1$ in the critical region $|\epsilon| = 0.1$ for $T < T_c$ and $|\epsilon| = 0.08$ for $T > T_c$ the value of t_ϵ is determined to be 2×10^{-3} compared to $|\epsilon| = 10^{-2}$ for crystalline materials.[81] Yet another noteworthy feature that characterises the amorphous alloys is the higher value of β which is found to be close to 0.41 compared to 0.365 for a Heisenberg ferromagnet (Table III). Several reasons have been suggested for the higher values. In the light of a Monte-Carlo analysis of a 20^3 spin model with a 2^3 bond cluster, Poon and Durand[82] have suggested that the missing exchange bonds are responsible for the higher β values. The role of defects resulting in higher β is supported by the observation that for free surfaces β values as high as 0.75 are possible.[83] Within the amorphous ferromagnets, those containing more than one transition metal ions such as a-$Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ have been found to have higher values for the critical exponents. In such cases, decomposition of the data on the basis of two environments has been found to lead to values in conformity with other amorphous alloys.[84]

TABLE III

Comparison of critical constant of amorphous ferromagnets and crystalline systems

	β	γ	δ
a-$Co_{70}B_{20}P_{10}$	0.402 ± 0.007	1.342 ± 0.025	4.39 ± 0.05[80]
a-$Fe_{80}P_{13}C_7$	0.38 ± 0.02	1.30 ± 0.05	4.47 ± 0.05[a]
a-$Fe_{20}Ni_{60}P_{14}B_6$	0.39 ± 0.02	1.33 ± 0.05	4.45 ± 0.07[b]
a-$Fe_{10}Ni_{70}B_{19}Si_1$	0.42 ± 0.02	1.35 ± 0.04	4.49 ± 0.04[81]
a-$Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$	0.43 ± 0.02	1.33 ± 0.05	4.43 ± 0.17[84]
Iron	0.389	1.33	4.35[78]
Nickel	0.378	1.34	4.58 ± 0.02[78]

[a]K Yamada Y Ishikawa Y Endo and T Masumoto *Solid State Commun* **16** (1975) 1335
[b]S N Kaul *Phys Rev* **B23** (1981) 1205

SPIN-WAVE THEORY AND AMORPHOUS MAGNETS

Whether spin-waves exist under the structural condition of short-range order is of interest from the theoretical point of view since in amorphous materials with random distribution of atoms the so called "wave-vector" k is not a good quantum number and no simple description of Brillouin zone exists.[85] Even before the advent of ferromagnetic metallic glasses, Herring and Kittel[86] from field theoretical arguments and Kaneyoshi[87] on a dense random packing of atomic spheres in these solids showed that spin-wave theory has a wider applicability than originally envisaged by the Heitler London-Heisenberg model. In the last decade large amount of data based on neutron scattering, low temperature magnetisation, Mössbauer and ferromagnetic resonance measurements have been gathered to demonstrate the existence of well defined long wave-length spin-wave excitations.[24,36–39,88–90] They have been found to follow a normal ferromagnetic dispersion relation,

$$E_k = \Delta + Dk^2 + Ek^4 + \ldots, \qquad \ldots(8)$$

where $\Delta \ll Dk^2$ denotes on effective energy gap resulting from dipole-dipole interaction. At low temperatures, magnetisation, as in crystalline ferromagnets, follows the Heisenberg model relations,

$$\left[M(O) - \frac{M(T)}{M(O)}\right] = \frac{M(T)}{M(O)} = BT^{3/2} + CT^{5/2} + \ldots, \qquad \ldots(9)$$

where the symbols have their usual significance. Among the many experimental evidences available for spin-waves in these materials, those due to neutron scattering bring to light certain features which cannot be observed otherwise. Mook *et al.*[91] have observed in a neutron-scattering study of a-CoP a "roton-like" structure with a minimum near the wave-vector Q corresponding to the first peak in the structure factor $a(k)$. Alben[92] performed Monte Carlo calculations and attributed the results to static structural correlations. In neutron inelastic scattering experiments, certain peaks appear in addition to those which can be accounted for on the basis of spin-

wave excitations. These additional peaks have been attributed to a new type of elementary excitation as a result of the randomness of the structure and the term 'amorphions' has been introduced by Handrich.[93] It has been shown that the dispersion of spin waves may have entirely different structures depending on the spatial dependence of exchange interaction.[5] Evidence for the same is obtained on the basis of neutron diffraction experiments. On the other hand, magnetisation and hyperfine field data from Mössbauer spectra lend themselves to straight-forward explanation on the basis of eq. (9). The plot of $1 - H_{\text{eff}}(T)/H_{\text{eff}}(O)$ *vs.* $T^{3/2}$ gives rise to linear relationship for $(Fe_xNi_{1-x})_{75}P_{16}B_6Al_3$ for $x = 0.3$, 0.5, 0.65 and 1.0. Over a wide temperature range as shown in Fig. 10.[94] This has been shown to be the case for a number of amorphous alloys such as $Fe_{40}Ni_{40}B_{20}$,[41] $Fe_{81}B_{13.5}Si_{3.5}C_2$ etc., studied by Mössbauer spectroscopy.[42] Low temperature magnetisation studies also give identical results.[89,90] On the same system there is fair agreement in the temperature range over which $T^{3/2}$ dependence is observed.[88,94,95] A closer inspection of these data reveals several differentiating features between crystalline and amorphous alloys. For a ferromagnet, in the crystalline state, crystal momenta are quantised and the conventional spin wave theory leads to the following relationship between B and C in eqn. (2) and the spin-wave stiffness constant D :

$$B = \zeta\left(\frac{3}{2}\right)\left[\frac{g\mu_B}{M(O)}\right]\left(\frac{k_B}{4\pi D}\right)^{3/2} \qquad \ldots(10)$$

and

$$C = \zeta\left(\frac{5}{2}\right)\left[\frac{g_{\mu B}}{M(O)}\right]\left(\frac{k_B}{4\pi D}\right)^{5/2}\left(\frac{3\pi\langle r^2\rangle}{4}\right), \qquad \ldots(11)$$

where $\zeta(3/2) = 2.612$ and $\zeta(5/2) = 1.341$ are the Reiman zeta functions and $\langle r^2\rangle$ is the average mean square range of the exchange interaction and the other symbols have their usual significance. In crystalline systems it is found that $T^{3/2}$ dependence based on eqn. (2) is restricted to $\sim 0.15T_c$. In striking contrast, in amorphous alloys $T^{3/2}$ dependence is found to be valid from $0.2T_c$ even upto $0.4T_c$. In $Fe_{40}Ni_{40}P_{14}B_6$, for instance low temperature magnetisation measurements show $T^{3/2}$ dependence upto $\sim 0.35T_c$.[8] Secondly, the values of $B_{3/2}$ are four to five times larger in amorphous alloys than values observed for crystalline systems and is definitely characteristic of the glassy state. They all exhibit comparable values for

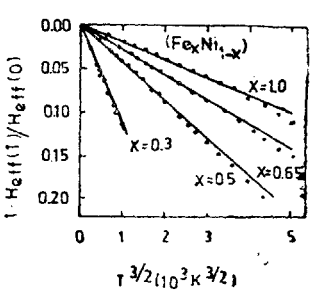

FIG 10 Plot of $1\text{-}H_{\text{eff}}(T)/H_{\text{eff}}(O)$ *vs* $T^{3/2}$ in $a\text{-}(Fe_xNi_{1-x})_{75}P_{16}B_6Al_3$.[94]

the coefficient of $T^{5/2}$ term. The values obtained for various systems are compared with crystalline systems in Table IV. Chien and Hasagawa[96] have explained the $T^{3/2}$ dependence over a wider temperature range on the basis of the relative values of B and C in eqn. (9). For crystalline ferromagnets $C_{5/2}/B_{3/2} \simeq 1$ and for amorphous ferromagnets it is significantly less and is ~ 0.3. It has been shown that such a result can be computer simulated for an amorphous ferromagnet with damped short-range interactions.[97] This implies that a description by localised spins with short-range interactions is closer to the real situation in amorphous ferromagnets. The large B also implies smaller D, the spin-wave stiffness constant. In general, that the stiffness constant D of amorphous ferromagnets is less than that of corresponding crystalline ferromagnets implies that spin waves in amorphous ferromagnets have lower energies of excitation. This is in agreement with the theoretical result of Tahier-Kheli's[85] random bond model where the density of states $\rho_{am}(W)$ is shown to have a form reproduced in Fig. 11. The result also will mean that as temperature increases magnetisation falls more rapidly in amorphous systems than for the crystalline systems which are composition-wise comparable and the curie temperature is lower for the amorphous ferromagnet. These results are in broad agreement with experimental observations.[2]

TABLE IV

Comparison of critical constants for amorphous ferromagnets and crystalline systems[84,99]

	$B(10^{-6}K^{-4/2})$	$C(10^{-8}K^{-3/5})$	$B_{3/2}$	$C_{5/2}$	T_c(K)
$Fe_{75}P_{16}B_6Al_3$	18.6	—	—	—	630
$(Fe_{0.30}Ni_{0.70})_{75}P_{16}B_6Al_3$	124	—	—	—	258
$Fe_{10}Ni_{70}B_{19}Si_1$	212	23.2	0.54	0.110	186.5
$Fe_{13}Ni_{67}B_{19}Si_1$	127	9.7	0.56	0.115	268.5
$Fe_{20}Ni_{60}P_{14}B_6$	154	13.9	0.53	0.100	228
$Fe_{29}Ni_{19}P_{14}B_6Si_2$	70	3.7	0.51	0.100	375
Crystalline Fe	3.4	0.1	0.115	0.040	1043
Crystalline Ni	7.5	1.5	0.119	0.150	631

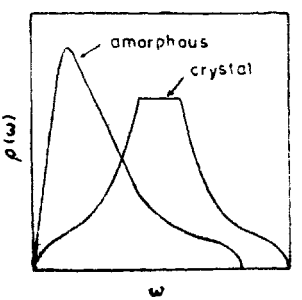

FIG 11 A schematic representation for the spin-wave density of states in an amourphous ferromagnet.

A scrutiny of the published low temperature neutron diffraction and magnetisation data in crystalline ferromagnetic metals shows a linear correlation between $T_c^{3/2}$ and $1/B$.[98] Similar is found to be the case for amorphous ferromagnets as well with however the essential difference that the data lie well below those for crystalline ferromagnets. Such a linear correlation between $B_{3/2}$ and $T_c^{3/2}$ means that D is directly proportional to T_c. This is subtantiated by the observations on a-Fe–B–X (X = P, C, Si, Ge) and $Fe_{40}Ni_{40}B_{20-x}P_x$ alloys.[99,100] It has been however pointed out that extrapolation of these data lead to zero D values for finite value of T_c, a result inconsistent with the prediction of a theory proposed by Katsuki and Wohlfarth[101] based on the itinerant electron model. Such a discrepency may be attributed to errors in extrapolation from large T_c values. Kaul,[89] on a similar investigation has shown that amorphous nickel-rich transition metal-metalloid alloys having a wide range of T_c values show a linear relationship between D and T_c. Such a plot is found to have a finite D value for $T_c = 0$ whereas for the nearest neighbour Heisenberg model for $S = 1$, the theoretical variation predicts $D = 0$ for $T_c = 0$ (Fig. 12). This has been explained by assuming a relationship of the form $D = D_0 + mT_c$ Similar result has been obtained for the amorphous alloys $(Fe_{1-x}Ni_x)_{77}Si_{10}B_{13}$ and $(Co_{1-x}Ni)_{75}P_{16}B_6Al_3$.[102,103] This result *viz.*, the plot between D and T_c has a positive intercept for $T = 0$, has been explained in terms of direct exchange interaction involving not only the nearest neighbours but also the next nearest neighbours.[89]

In principle, measurements leading to spin-wave stiffness constant D should be considered by considering both spin-wave and single particle excitations. It turns out that the latter contributions are not significant in a-alloys such as $Fe_{40}Ni_{40}P_{14}B_6$, Fe–Ni–P–B alloy.[88] This, however, is not always the case. The itinerant electron model, although is conceptually more difficult to apply, it is considered to be more appropriate as it encompasses many of the 'localised' features as well. Wohlfarth[101] has attempted a judicious blend of theory and empiricism to enable experimentalists to apply the itinerant electron model to complicated alloys, such as the amorphous magnets. Within the Stoner-Wohlfarth model for homogeneous weak itinerant ferromagnets the following relations are obtained :—[104]

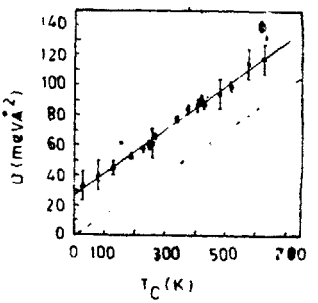

FIG 12 Spin-wave stiffness constant D *vs* Curie temperatures of various transition metal-metalloids.[89]

(*i*) The functional dependence of magnetisation on the field H and temperature T is given by

$$[\sigma(H, T)]^2 = [\sigma(0, 0)]^2\left[1 - \left(\frac{T}{T_c}\right)^2\right] + 2x(0, 0)\left[\frac{H}{\sigma}\left(\frac{H}{T}\right)\right] \quad ...(12)$$

where $x(0, 0)$ is the zero-field differential susceptibility at 0 K. This relationship implies that $[\sigma(H, T)]^2$ *vs.* $H/\sigma(H, T)$ isotherms in the temperature range $T \ll T_f$ where T_f is related to the density of single particle states at the Fermi level, should be a set of parallel lines. These plots are referred to as the Arrot Belov Kouvel (ABK) plots.

(*ii*) The above mentioned isothermal plot should pass through the origion for $T = T_c$. The slope and intercept of such a plot gives $2x(0, 0)$ $[\sigma(0, 0)]^2$ and $[\sigma(0, T)]^2$ which according to eq. (12) is equal to $[\sigma(0, 0)]^2$ $[1 - (T/T_c)]^2$, respectively. This result means that $\sigma^2(0, T)$ *vs.* T^2 plots should be linear. $\sigma(0, 0)^2 \sim T_c^2 \sim x(0, 0)^{-1}\,|C - C_{crit}|$ and $q_c/q_s \sim T_c^{-1}$, where q_c and q_s are the magnetic moments per atom deduced from the Curie Weiss constant and saturation magnetisation respectively. In the exceptional case of a-Y_xNi_{1-x} the linear relationship between $\sigma(H, T)^2$ *vs.* T^2 has been observed both over a very wide range of temperature as well as concentration.[104,105] The ABK plots which have been obtained for several amorphous alloys such as a-$Ni_{84}P_{16}$, a-$Ni_{48\cdot2}Cu_{51\cdot8}$, $M_{90}Zr_{10}$ (M = Fe, Co, Ni) do show linearity over a wide range of $H/\sigma(H, T)$ value.[104,106] These plots show curvatures which change from converse to concave as T passes from values above T_c to below T_c and are almost symmetical about T_c. The deviations from linearity at low fields has been attributed to concentration fluctuation of the magnetic atoms within the ferromagnetic phase.[104]

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