Magnetic properties of amorphous alloys have received considerable attention during the recent years because of their technological applications and due to a wide variety of rich physical phenomena they offer from the fundamental point of view. Amorphous alloys are characterized by structurally disordered networks in which each atom constitutes a structural unit. Structural disorder in amorphous alloys, in turn, leads to changes in their electronic and magnetic properties as compared to those of their crystalline counterparts in which lattice periodicity and crystal structure play a decisive role in determining the basic properties. The bond and chemical disorder results in a distribution of magnetic moments and exchange interaction thereby affecting the magnetic properties of metallic glasses. The random electrostatic fields due to random atomic arrangements create local anisotropies via spin-orbit coupling giving rise to a variation in the orientation of magnetic moments. In addition, structural disorder is found to introduce new magnetic structures like speromagnetism, asperomagnetism and sperimagnetism which possess a non-collinear spin structure. The existence of positive and negative exchange interactions leads to spin-glass behaviour in many amorphous alloys. Transport properties of metallic glasses also differ considerably from those of the corresponding crystalline alloys.

Historically, it was Gubanov [1], who in 1960 first predicted theoretically the existence of amorphous ferromagnetism, based on the argument that the band structure of crystalline solids does not change in any fundamental way upon transition from crystalline to liquid or amorphous state. This implies that the band structure is essentially controlled by short range order. Ferromagnetism, which comes into existence because of the direct positive exchange interactions between the neighbouring spins, therefore, should not be destroyed. The predictions of Gubanov were experimentally verified only after first amorphous ferromagnetic $Fe - P - C$ alloy was prepared by Duwez and Lin [2,3] by rapid quenching of the melt. Since then a large number of amorphous alloys have been prepared and studied in detail. The new effects and phenomena associated with amorphous alloys have led to new theoretical concepts and huge amount of experimental work resulted in the deeper understanding of disordered systems. Properties and the associated phenomena exhibited by these alloys have formed the subject of several books and review articles [4-17].

1.1. Preparation and Characterization

Amorphous alloys can be prepared by a number of techniques [4,6,11]. These techniques are broadly classified into two categories: (i) melt-quenching and (ii) deposition.
Splat quenching is the simplest form of melt-quenching. In this method, a liquid alloy droplet is squeezed between a rapidly moving piston and a fixed anvil. Alloys obtained by this method are in the form of thin discs of 1-3 cm in diameter and 20-60 μm in thickness. Another simple and the most popular technique is melt-spinning. This method employs a jet from which alloy melt is dropped onto a rapidly moving wheel made of a material with high thermal conductivity such as copper. Continuous ribbons of amorphous alloys are obtained by this method and higher cooling rates (10^6 K/sec) are achieved compared to splat-quenching. Laser quenching [18] is another form of melt-quenching technique. In this method, a short and highly intense laser beam is used to melt a portion of a thin metallic surface, which is then cooled rapidly by the surrounding crystal. The cooling rates achieved in this way are in the range of 10^{10} to 10^{12} K/sec.

The above-mentioned melt-quenching techniques are useful to prepare amorphous alloys in a narrow concentration range around the eutectic point. Preparation of amorphous alloys in the concentration range away from the eutectic point requires different techniques such as (a) thermal evaporation [19], in which metals constituting the alloy are evaporated in vacuum and condensed onto a cooled substrate, (b) sputter deposition [20], where atoms are deposited on a substrate by removing them from the source under bombardment with energetic inert gas atoms. When very high cooling rates of the order of 10^{14} K/sec are required, ion-implantation technique [21] is used. In addition, electro-deposition [22] and solid state reaction [23] are some of the occasionally used techniques.

Techniques such as x-ray, electron and neutron diffraction are mostly used to characterize amorphous alloys. A typical diffraction pattern of an amorphous alloy consists of diffuse rings or broad peak at low scattering angles. However, it is extremely difficult to distinguish purely amorphous materials from micro-crystalline materials with crystallites of size less than 20 Å using diffraction methods. A more refined x-ray technique, known as extended x-ray absorption fine structure (EXAFS), is particularly useful in probing the local atomic structure of amorphous alloys [24]. Neutron scattering is a powerful technique in probing short-range atomic order. Since neutron scattering amplitude of an individual nucleus varies with different isotopes and their spin states, coherent and incoherent scattering takes place depending upon whether or not the neutron waves scattered by different nuclei interfere with one another. While the coherent neutron scattering provides useful information about the collective structure and atomic pair correlation function, the incoherent neutron scattering gives important clues about localized vibration and atomic diffusion. Techniques such as nuclear magnetic resonance (NMR) and Mossbauer spectroscopy are useful in probing nearest-neighbour environments and magnetic hyperfine fields.

Various techniques are available for analyzing the chemical composition of disordered alloys.
Some of these techniques are atomic absorption spectroscopy, x-ray fluorescence, electron micro-probe analysis, Auger spectroscopy and secondary-ion mass spectroscopy.

1.2. Short-range order

In amorphous solids, atomic positions are strongly correlated in the nearest-neighbour shell but uncorrelated beyond a few interatomic spacings. In other words, glassy alloys possess short-range atomic order but no long-range atomic order and the structure of these solids resembles that of the liquids from which they have been obtained by quenching. Short-range atomic order or simply short-range order (SRO) varies from one amorphous material to the other and is of two types: compositional or chemical short-range order (CSRO) and geometrical short-range order (GSRO). In many glassy alloys, the chemical composition on a local scale is different from the macroscopic average and this deviation is called CSRO. The CSRO is confined to the first nearest-neighbours and hence can be described in terms of the deviation of the nearest-neighbour composition from the average. The topological short-range order (TSRO) describes the short-range order in the atomic positions regardless of the chemical identity of individual atoms. This type of SRO is present in all the glassy alloys including the single-component glasses made up of one kind of atoms only. In addition, geometrical distortions, which are independent of topology, can also occur in such elementary glasses and the corresponding short-range order is known as distortional short range order (DSRO). Therefore, the geometrical short-range order (GSRO), which characterizes local atomic structure includes both TSRO and DSRO.

1.3. Types of disorder

All glassy or amorphous materials are characterized by a complete lack of translational symmetry but the degree and type of short-range atomic order or local order varies from glass to glass. Different types of short-range order give rise to various kinds of disorder that have a direct bearing on the magnetic properties of these alloys [11,25].

(a) Topological disorder:

Topological disorder results when translational symmetry in the positions of atoms is completely absent and the nearest, next-nearest neighbour coordination number varies from site to site. A topologically disordered structure cannot be distorted back into a crystal. Topological disorder is intrinsic to the amorphous structure.
(b) **Chemical disorder**:

When different types of atoms or molecules irregularly occupy the lattice sites without disturbing the periodicity of an ordered structure, the chemical disorder results. In such cases, the translational symmetry of the atoms or molecules is broken by the chemical identity of the objects that occupy the lattice sites. Further complication can arise if in a binary or quasi-binary alloy, the concentration of one species of atoms is increased at the expense of the other. The disorder that results by changing the composition is known as compositional disorder. Compositional disorder includes substitutional disorder. A similar situation can also occur in a structurally disordered lattice. Thus, chemical and compositional disorder can occur in both crystalline and amorphous solids.

(c) **Site-disorder**:

The fluctuation in the coordination number arising from the random occupation of sites on a regular crystalline lattice or an aperiodic amorphous network constitutes site disorder.

(d) **Bond disorder**:

Bond disorder results when wild variation in the bond lengths and bond angles destroy the periodicity of the lattice or long-range atomic order. The bond-disordered network remains topologically equivalent to the crystal.

From the above description, it is clear that the site- and bond-disorder are included in topological and chemical/compositional disorder, and the terms "amorphous" and "disordered" cannot be used interchangeably. All amorphous solids are disordered but all disordered systems need not be amorphous. While the topological disorder alone is specific to amorphous solids, the other types, i.e., site-, bond-, chemical- and compositional disorder are found in both crystalline and amorphous materials.

1.4. **Effect of disorder on magnetic properties**

The basic requirements for magnetic order in a solid are (i) the existence of magnetic moments associated with unpaired electrons on atoms or ions in a solid and (ii) an interaction which couples these microscopic moments. These requirements are sufficient for a vast majority of
metallic and insulating magnetic materials whose magnetic moments are localized on the atomic sites. However, these concepts do not hold for certain class of materials known as itinerant magnetic systems in which magnetic electrons are itinerant and magnetic moments arise from the exchange splitting of spin-polarized d-band. In the latter case, the density of states (DOS) at the Fermi level, $E_F$, plays a crucial role in deciding the type of magnetic order. The effect of various types of disorder on these magnetic properties are discussed below.

(a) **Density of states (DOS):**

Fig. 1.1 shows a schematic representation of the density of states, $N(E)$, for transition metals with fcc or bcc structure [13]. The DOS curve (ignoring the fine structure present in many crystalline solids) consists of two peaks resulting from the covalent splitting of the quasi atomic-like electronic energy levels into bonding and anti-bonding states. The shape and width of electronic bands from which DOS curves are computed, are basically controlled by the overlap of electronic wave functions on the neighbouring sites (which, in turn, depends on the nearest-neighbour distance or interatomic spacing) and by the crystalline symmetry. Since the nearest-neighbour (NN) atomic configurations in amorphous solids resembles that in their crystalline counterparts and the average NN distance is close to that of the corresponding crystalline solid, the effect of disorder is to smear out the sharp features of DOS curve and leave the value of DOS at $E_F$ more or less unaltered.

(b) **Magnetic moments:**

A magnetic moment exists on an atom whenever there are unpaired electrons. Whether such a moment can persist or not when an atom becomes an ion in a solid, even a metal, depends on the extent of overlap of the wave functions of electrons in different shells on neighbouring ions. For example, considerable overlap of outer or valence electron wave functions on neighbouring ions, particularly in a metal, leads to a spread of atomic levels into energy bands of delocalized states. By comparison, the overlap of the d-shell electron wave functions for neighbouring ions in a metal is weak and hence d-band is much narrower than s-band in transition metal-based alloys. However, in rare earth based alloys, the f-electron wave functions for the neighbouring ions do not overlap because 4f shell is surrounded by 5s and 6p shells. As a consequence, the electrons in 4f-shell are localized. This picture is particularly appropriate to a magnetic ion in an insulator because electron-electron interactions in them are so strong as to open up a correlation gap in the effective density of states and make rf-band narrower enough to localize the magnetic electrons. In metals, (particularly in transition metals) the delocalized s electrons complicate the situation since they are not only an extra source of itinerant magnetic moments
Fig. 1.1 Schematic representation of the electronic density of states (DOS) curve for amorphous (dashed curve) and crystalline (solid curve) 3d transition metals.

Fig. 1.2 Variation of exchange coupling with the distance between spins of 3d transition metals.
tends to align the moments \( \vec{m} \) and \( \vec{p}_j \) parallel to the line joining the sites i and j. Dipolar interactions are weak, long-ranged and anisotropic since they depend on the orientation of the moments relative to \( \vec{r}_{ij} \). The net dipolar field is identically zero at sites in a lattice of cubic symmetry. In amorphous systems, however, it is distributed both in magnitude and direction. A much stronger interaction is the quantum mechanical exchange interaction. Exchange interaction is an effective electrostatic interaction between two electrons which depends on the relative orientation of their spins. This isotropic Heisenberg interaction is given by \[ H_{ij} = -2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \] (1.2)

(c) Interaction between moments:

The appearance of a magnetically ordered structure like ferromagnetism requires an interaction to couple the magnetic moments. The classical dipolar interaction of the form \[ \mathcal{H}^d_{ij} = \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - \frac{3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \] (1.1) tends to align the moments \( \vec{m} \) and \( \vec{p}_j \) parallel to the line joining the sites i and j. Dipolar interactions are weak, long-ranged and anisotropic since they depend on the orientation of the moments relative to \( \vec{r}_{ij} \). The net dipolar field is identically zero at sites in a lattice of cubic symmetry. In amorphous systems, however, it is distributed both in magnitude and direction. A much stronger interaction is the quantum mechanical exchange interaction. Exchange interaction is an effective electrostatic interaction between two electrons which depends on the relative orientation of their spins. This isotropic Heisenberg interaction is given by \[ H_{ij} = -2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \] (1.2)

where \( J_{ij} \) is the exchange coupling constant between spins at sites i and j. \( J_{ij} \) is positive for ferromagnetic coupling and negative for antiferromagnetic coupling. The Bethe-Slater curve [11] shown in Fig. 1.2 indicates roughly how the exchange constant varies with distance between magnetic shells in 3d transition metals. It is seen from Fig. 1.2 that the distribution of interatomic separations in amorphous solids leads to a distribution of exchange interaction which may sometimes include interactions of either sign. Apart from direct exchange, there are other exchange mechanisms like superexchange via ligands and indirect exchange via conduction electrons also known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. A distribution in the interatomic separations gives rise to a distribution of indirect exchange also. For
instance, superexchange is negative for $180^\circ$ metal-ligand-metal bonds and weakly positive for $90^\circ$ bond angles [11, 25]. The RKKY interaction arises when the magnetic electrons of one atom induce a spin polarization in the conduction electrons which overlaps another atom and affects its magnetic electrons. RKKY interaction oscillates as a function of distance $r$ and couples $4f$ shell spins/moments in rare earths. The long-range and oscillatory nature of RKKY interaction is not only responsible for spin glass behaviour in many dilute magnetic alloys but also leads to helical spin structure in many crystalline rare earth metals and compounds. In amorphous systems, RKKY interaction gives rise to positive or negative exchange coupling between moments depending on their separation but its range is severely restricted compared to that in their crystalline counterparts due to rapid decay of spin polarization amplitude with distance.

(d) Magnetic anisotropy:

Amorphous materials are generally assumed to be isotropic since there is no long-range atomic order. However, magnetic anisotropy in such systems has been observed and it reflects the existence of short-range-order in amorphous alloys. The local magnetic anisotropy that results from spin-orbit interaction or the anisotropy of local crystal field has strong influence on the nature of magnetic order in the ground state and coercivity of amorphous magnetic materials [26]. From a simple model calculation, Chi and Alben [27] have shown that when the local random anisotropy is small, the coercivity is small and high coercivities are obtained as the local anisotropy is increased. In addition, the magnetic field cooling, cold rolling and stress annealing of amorphous materials induce different forms of magnetic anisotropies. Various mechanisms [28] have been proposed to explain these anisotropies.

1.5. Magnetic order in amorphous solids

A wide variety of magnetic order [11, 15, 25, 29] exists in amorphous solids even in the presence of various kinds of disorder. Chemical and structural disorder in amorphous materials produces an inequivalency of sites that leads to a distribution (i) in the magnitude of moments, (ii) in exchange interactions and (iii) induces large randomly varying electrostatic fields giving rise to locally varying single-site anisotropy [11, 15, 25]. Although magnetic order depends sensitively on distance and local environments, the structural disorder does not affect the collective magnetic order such as ferromagnetism in any fundamental way. The basic features of ferromagnetism observed in crystalline solids are retained in amorphous systems. However, in practice, it is rare to find antiferromagnetism in amorphous materials since antiferromagnetism demands that identical moments occupy neighbouring sites with antiparallel coupling throughout the amorphous structure. Moreover, it is difficult to conceive a random structure which can
be subdivided into two (or more) interpenetrating ferromagnetic sub-lattices with neighbouring \textit{inter-sublattice} moments aligned \textit{antiparallel} to one another, as is usually done in crystalline systems [11,15,25]. Another collinear magnetic order commonly found in many amorphous alloys is \textbf{ferrimagnetism}. Ferrimagnetism arises when two different types of magnetic ions occupy sites of two amorphous subnetworks such that \textit{intra-subnetwork} moments are aligned parallel while inter-subnetwork moments are aligned antiparallel and the average magnitude of moments on each subnetwork is distinctly different from the other. Since the magnitude of moments on two subnetworks is not the same, a finite spontaneous magnetization exists. In addition to these familiar types of collinear magnetic order, \textbf{non-collinear} magnetic structures like speromagnetism, \textbf{asperomagnetism} and \textbf{sperimagnetism} occur in amorphous alloys. These non-collinear magnetic structures involve a competing random anisotropy and exchange interaction; the local anisotropy tries to align the magnetic moments along the locally varying crystal field axis while the exchange interaction tries to align the moments parallel or antiparallel to one another depending on whether the exchange is positive or negative [11,15,25]. Speromagnetic state is the one in which localized moments are cooperatively frozen in random directions below a certain ordering temperature $T_o$ such that there is no net magnetization. Speromagnetism is exhibited by systems in which random anisotropy is comparable to exchange coupling and exchange coupling between the spins fluctuates in sign. Asperomagnetism arises when randomly placed localized moments of a given species are frozen in different orientations below an ordering temperature $T_o$ but with some orientations more likely than others. Therefore, an \textbf{asperomagnet} has a net spontaneous magnetization. Asperomagnetism appears in those systems in which exchange is positive and the exchange coupling and random anisotropy are of comparable strengths. \textbf{Sperimagnetism} comprises two or more magnetic species with moments of at least one species frozen in random orientations within a hemisphere on one subnetwork and antiferromagnetically coupled to the moments (that have ferromagnetic coupling between them) occupying sites of the other amorphous subnetwork. Sperimagnetism is to ferrimagnetism what speromagnetism is to \textbf{ferromagnetism} except that sperimagnet has a net spontaneous magnetization.

\section*{1.6. Low-lying Magnetic Excitations}

Having briefly described the types of ground state (i.e., at $T = 0$ K) magnetic order prevalent in spin systems with quenched disorder in the previous section, this section is devoted to the changes in the magnetic order (i.e., magnetic excitations) brought about by increasing temperature in crystalline and amorphous \textbf{ferromagnets}.

In a crystalline \textbf{ferromagnet}, the local deviation from the perfect alignment does not remain confined to a microscopic region of space but propagates like a wave due to exchange coupling between the spins. These low-lying magnetic excitations are called spin-waves. A spin wave can
be thought of as one spin reversal coherently spread over the entire crystal. All the conventional spin-wave theories are based on localized-electron picture, in which the magnetic electrons are localized on atomic orbitals. However, in metallic systems, the magnetic electrons have itinerant character. Thus, localized-electron and itinerant-electron models form two exactly opposite descriptions of the low-lying magnetic excitations.

1.6.1. Localized-electron Model

Within the framework of the localized-electron model, Felix Bloch [30] was first to introduce the concept of spin waves in a ferromagnet. The spin waves are thermally excited and their energy is quantized. In analogy with a phonon, which represents the particle associated with a quantized lattice wave, the corresponding particle for a quantized spin wave is called a magnon. The Hamiltonian that describes the Heisenberg interaction between spins localized at the neighbouring sites i and j is given by [31,32]

$$\mathcal{H} = -\frac{1}{2} \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$  \hspace{1cm} (1.3)

where $J_{ij}$ is the exchange integral. At low temperatures, the spin deviations as well as the fraction of spin reversals are small and spin waves are independent of one another. Thus, in the linear approximation, the magnon dispersion relation for crystalline ferromagnets, in which the direct Heisenberg exchange interaction is confined to the nearest neighbours only, is expressed as [31,32]

$$E(k) = \hbar \omega_k = 2JSz(1 - \gamma_k)$$  \hspace{1cm} (1.4)

with

$$\gamma_k = \frac{1}{z} \sum_{\delta} \exp(i\vec{k} \cdot \vec{\delta})$$

where the summation is carried out over z nearest neighbours. In the long wavelength limit, i.e., $|\vec{k} \cdot \vec{b}| \ll 1$, the dispersion relation for simple cubic, fcc, and bcc lattices with lattice constant 'a' takes the form

$$\hbar \omega_k = Dk^2 + Ek^4 + \cdots$$  \hspace{1cm} (1.5)

where the spin wave stiffness coefficient $D = 2JSa^2$ is a measure of the exchange interaction and the coefficient $E$ is related to average mean square range of exchange interaction $<r^2>$ through the relation $E = -<r^2> D/20$. The spontaneous magnetization, $M(T,0)$, at any temperature is given by
where $M(0,0) = g \mu_B N S$ and $n_k$ is the number of spin waves in thermal equilibrium at temperature $T$ given by the Bose-Einstein distribution function. The final expression for $M(T,0)$ has the form [31]

$$\Delta m(T,0) = \frac{[M(0,0) - M(T,0)]}{M(0,0)} = \frac{g \mu_B}{M(0,0)} \left[ \xi(3/2) \left(\frac{k_B T}{4 \pi D}\right)^{3/2} + 15 \pi \beta \xi(5/2) \left(\frac{k_B T}{4 \pi D}\right)^{5/2} \right]$$

where $\xi(3/2) = 2.612$ and $\xi(5/2) = 1.341$ are the Reimann $\xi$ functions and $\beta = \frac{r^2}{r}$. The $T^{3/2}$ and $T^{5/2}$ terms in Eq.(1.6) arise from the $k^2$ and $f c^4$ terms in the dispersion relation. Eq.(1.5), respectively. The higher order terms of the form $k^6$, $k^8$, etc. in Eq.(1.5), if retained, give rise to additional correction terms [33] to $\Delta m(T,0)$ that are proportional to $T^{7/2}$, $T^{9/2}$ etc.

Application of an external magnetic field (or in the presence of any other fields such as dipolar fields, anisotropy fields, etc.) gives rise to an energy gap in the spin-wave spectrum and the dispersion relation gets modified to

$$\hbar \omega_k = g \mu_B H_{eff} + D k^2 + E k^4 + \cdots$$

with $H_{eff} = H - 4 \pi N M(0) + H_A$, where $N$ is the demagnetizing factor, $H_A$ is the anisotropy field and $g \mu_B H_{eff}(= k_B T_g)$ is the energy gap. Consequently, in the presence of magnetic field, the expression for magnetization also gets modified and takes the form [31]

$$\Delta m(T,H) = \frac{[M(0,H) - M(T,H)]}{M(0,H)} = \frac{g \mu_B}{M(0,H)} \left[ Z(3/2,t_H) \left(\frac{k_B T}{4 \pi D}\right)^{3/2} + 15 \pi \beta Z(5/2,t_H) \left(\frac{k_B T}{4 \pi D}\right)^{5/2} \right]$$

where the Bose-Einstein integral functions

$$Z(s,t_H) = \xi(s) F(s,t_H) = \sum_{n=1}^{\infty} n^{-s} \exp(-nt_H)$$

with

$$t_H = T_g / T = g \mu_B H_{eff} / k_B T$$

allow for the energy gap in the spin-wave spectrum.

The spin wave theory discussed so far assumes that the spin waves, when thermally excited, propagate independent of one another so that the superposition of spin waves is a valid approximation. However, as the temperature is increased from low temperatures, the interaction
between spin waves becomes important and these interactions have to be taken into account. Spin-wave interactions are mainly of two types: kinematic interaction and dynamic interaction [31,33]. The kinematic interaction arises due to the fact that the maximum number of spin deviations that can occur at any site carrying a spin $S$ is $2S$. For instance, if $S = 1/2$, two spin deviations cannot reside at the same site and the kinematic interaction, which prevents this situation, is a repulsive one. The dynamic interaction arises because it costs less energy for a spin to suffer a deviation if the neighbouring spins have also undergone deviations. This dynamic interaction is of the attractive type. An analysis of the magnon-magnon interactions in the Heisenberg ferromagnets, due to Dyson [33], has demonstrated that at low temperatures, the kinematic interactions are negligibly small and the dynamic magnon-magnon interactions lead to a thermal renormalization of spin-wave energies [31,33], i.e.,

$$\hbar \omega_k = g \mu_B H_{eff} \ D(T) k^2 + \cdots$$

with

$$D(T) = D(0) \left(1 - D_{5/2} T^{5/2}\right)$$

and

$$D_{5/2} = \frac{\pi \sigma^2}{(g \mu_B/M(0,0)) \left(k_B/4\pi D(0)\right)^{5/2}} \xi(5/2)$$

Moreover, the dynamic interaction gives rise to a $T^4$ correction [33] to $M(T,0)$. In addition to the direct Heisenberg exchange interactions between the spins on the neighbouring $d$ shells, the $d$ spins in the localized model interact indirectly with one another via the conduction electron $s$ spins. This magnon-electron interaction also renormalizes the spin wave stiffness coefficient $D(T)$ according to the expression [34]

$$D(T) = D(0) \left(1 - D_2 T^2\right)$$

However, the contribution to $D(T)$ arising from the $T^2$ term in Eq.(1.12c) is several orders of magnitude smaller than that due to the $T^{5/2}$ term in Eq.(1.12a) since the $s - d$ interaction is very weak compared to the direct $d - d$ interaction. Hence, for all practical purposes the spin wave stiffness renormalizes according to Eq.(1.12a) in the localized-electron model.

**Spin waves in amorphous ferromagnets**:

Ample experimental evidence [35,36] exists in the literature to indicate that amorphous ferromagnets, like their crystalline counterparts, exhibit well-defined long-wavelength spin-wave excitations which follow the normal ferromagnetic dispersion relation given by Eq.(1.5) or Eq.(1.7) and the magnetization varies with temperature according to the expression Eq.(1.6) or Eq.(1.8).
However, the magnetization curve for amorphous ferromagnets falls below that of the corresponding crystalline ferromagnet and is much steeper. This implies that the value of spin wave stiffness for amorphous ferromagnets is lower with the result that the spin waves can be easily excited in them. Starting from the Heisenberg Hamiltonian and using the quasi-crystalline approximation, Kaneyoshi [13,37] arrived at the following expression for the spin wave energy of an amorphous ferromagnet:

\[ E(k) = 2S\rho_0 \int J(r_{ij})g(r_{ij})[1 - \exp(-i\mathbf{k} \cdot \mathbf{r}_{ij})]d^3r_{ij} \]  

where \( \rho_0 = N/V \) is the average density, \( r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j| \) and \( g(r_{ij}) \) is the normalized pair correlation function which denotes the probability of finding atoms at the site \( j \) when an atom occupies the site \( i \). In the long-wavelength limit, Eq.(1.13) reduces to [13,36,37]

\[ E(k) = D k^2 \]  

(1.14a)

with

\[ D = \frac{1}{3}S\int r^2 J(r)F(r)dr \]  

(1.14b)

where \( F(r) = 4\pi r^2 \rho_0 g(r) \) is the radial distribution function. In amorphous systems, the exchange integral is not constant but fluctuates around a certain average value. \( J(r_0) \) such that \( J(r) = J(r_0) + \Delta J(r) \Delta J(r) \) is the root mean square fluctuation in the exchange integral due to structural disorder. Exchange fluctuations reduce the spin wave stiffness as [36]

\[ D = D_o (1 - \delta) \]  

(1.15a)

with

\[ D_o = (1/3)z S J(r_o) r_o^2 \text{ and } S = 2z \Delta r/r_o \Delta J/\langle J(r_o) \rangle \]  

(1.15b)

Similarly, the structural disorder in amorphous ferromagnets gives rise to fluctuations in the magnetic moment around a certain average value. Hence, the spin at the site \( i \) can be taken as \( S_i = S_o + \Delta x_i \). Such fluctuations \( \Delta x_i \) also lead to the diminished value of \( D \) and Eq.(1.15a) retains its form with \( S \) given by [13,37]

\[ \delta = \langle \Delta x_i^2 \rangle / S_o^2 \]  

(1.15c)

Thus, the effect of the fluctuations in the exchange interaction and magnetic moment on the spin wave stiffness constant is to reduce the mean value by a factor \( 1 - \delta \). The factor \( \delta \) in Eq.(1.15a) has a weak dependence on external field as well as temperature due to a slight variation [13,37] of the second moment \( \langle \Delta x_i^2 \rangle \) with field and temperature whereas \( \delta \) arising from \( \Delta J(r) \) is independent of field but depends weakly on temperature through the temperature dependence of \( Ar \) [36].
1.6.2. Itinerant-electron Model

The itinerant-electron model for magnetism, first proposed by Bloch [38] in connection with the ferromagnetism of an electron gas, was later developed by Slater [39] and Stoner [40] to explain the magnetic properties such as non-integral values of saturation magnetization per atom at 0 K, large coefficients of \( T \) term in low temperature specific heat etc., which could not be explained in terms of the localized-electron model. The itinerant-electron model is based on the band theory of electrons in solids and regards magnetic carriers as itinerant or Bloch electrons. The interaction between Bloch electrons splits \( d_{-}\) band into spin-up (\( \uparrow \)) and spin-down (\( \downarrow \)) sub-bands and hence gives rise to ferromagnetism. Wohlfarth, Edwards and coworkers [41-43], while applying the Stoner theory to many ferromagnetic metals, made suitable refinements so as to make it more realistic. However, the basic ideas of Stoner theory remained the same. In the Stoner theory [13,40-43], the exchange interaction between the magnetic electrons is represented by a molecular field, \( H_m \), proportional to the magnetization, i.e.,

\[
H_m = \frac{1}{2} n I \zeta
\]

(1.16)

where \( n \) is the number of electrons per atom and \( \zeta = M/n\mu_B \) is the relative magnetization so that \( n^+ - n^- = n \zeta \) and \( n^+ + n^- = n \). Here \( n^+ \) and \( n^- \) are the number of \( \uparrow \) and \( \downarrow \) spins per atom, respectively, and \( I \) is the Stoner parameter representing the effective interaction between the magnetic electrons. According to this theory, for ferromagnetism to occur, i.e., for \( \zeta > 0 \), the Stoner criterion

\[
I = N(E_F) > 1
\]

(1.17)

must be satisfied, where \( N(E_F) \) is the density of states at the Fermi level \( E_F \). When Eq.(1.17) is satisfied, a range of values of \( I \) exists such that the relative magnetization at 0A", \( \zeta_0 \), can take values of either \( \zeta_0 = 1 \) or \( 0 < \zeta_0 < 1 \). The cases \( \zeta_0 = 1 \) and \( 0 < \zeta_0 < 1 \) are realized in strong itinerant and weak itinerant ferromagnets, respectively. The former case arises when spin-up (\( \uparrow \)) sub-band is completely filled and Fermi-level lies in the spin-down (\( \downarrow \)) sub-band so that further band splitting does not increase the magnetization (Fig. 1.3(a)). The latter one arises when the band splitting is small with the result that none of the spin sub-bands is completely filled and the Fermi level lies in both the sub-bands (Fig. 1.3(b)). The temperature and field dependence of magnetization, \( \zeta(T,H) \) obtained from the Stoner equations, is given by the expression [40-43]

\[
n^+ = \frac{1}{2}[n \pm \zeta(T,H)] = \int_0^\infty \frac{N(E)dE}{\exp\left\{\frac{(E-\mu_c+1/2)nI\zeta+\mu_BH}{k_BT}\right\}}
\]

(1.18)

where \( \mu_c \) is the chemical potential and \( \mu_B H \) is the additional term due to the external magnetic field. Eq.(1.18) can be solved for \( \zeta(T,H) \) numerically or analytically by eliminating \( \mu_c \).
Fig. 1.3 Exchange splitting of energy bands in a (a) strong itinerant ferromagnet and (b) weak itinerant ferromagnet according to the band model.
(a) Strong itinerant ferromagnetism ($Co = 1$)

In this case, the spontaneous magnetization, $M(T\|0)$, decreases slowly due to excitations of particles from filled spin-up sub-band to partially filled spin-down sub-band (generally known as Stoner single particle excitations). For such excitations, there exists an energy gap $\Delta$, which is the energy difference between the Fermi level (located in the spin-down sub-band) and the top of the filled spin-up sub-band (Fig. 1.3(a)). At low temperatures, the spontaneous magnetization for strong-itinerant ferromagnets varies with temperature as $[41-43]$

$$M(T,0)/M(0,0) = 1 - A T^{3/2} \exp(-\Delta/k_B T)$$  (1.19)

where $M(T, 0) = n\mu_B\zeta(T, 0)$. The effect of external magnetic field is to increase the energy gap further and Eq.(1.19) remains the same except that $A$ has to be replaced by $A + 2\mu_B H$.

(b) Weak itinerant ferromagnetism ($\zeta_o < 1$):

The band splitting in weak itinerant ferromagnets is small and the Fermi level lies in both the sub-bands. This implies that both spin $\uparrow$ and spin $\downarrow$ sub-bands are partially filled (Fig. 1.3(b)) and there is no energy gap for single particle excitations from spin $\uparrow$ to spin $\downarrow$ sub-band concomitant with spin reversals. The contribution to thermal demagnetization of spontaneous magnetization due to single particle excitations in weak itinerant ferromagnets has the form $[41-43]$

$$M(T,0)/M(0,0) = [1 - (T/T_C)^2]^{1/2}$$  (1.20)

The existence of a significant contribution of Stoner single particle excitations of either strong itinerant type, Eq.(1.19), or weak itinerant type, Eq.(1.20), to the temperature dependence of magnetization in certain temperature ranges has been established experimentally in a large number of ferromagnetic transition metals and alloys. However, at very low temperatures, the magnetization follows the usual $T^{3/2}$ law which cannot be accounted for in the Stoner theory. In addition, Stoner theory fails to predict the proper value of $T_C$ and the Curie-Weiss behaviour of magnetic susceptibility above $T_C$. Such a failure of the Stoner theory is primarily due to the underlying assumption that the thermally excited electrons and holes move independently in a common mean field. Number of attempts have been made to improve upon the Stoner theory by taking into account the collective nature of the electron-hole excitations with the result that the existence of spin waves as collective excitations and exchange enhanced spin fluctuations [44-48] can now be explained satisfactorily. Essential details of these aspects are given below.
1.6.2A. Spin waves in itinerant-electron model

Spin waves, whose existence could not be envisaged in the band model originally, have subsequently found a natural place in the itinerant electron model, as was first shown by Herring and Kittel [44] in their phenomenological theory of spin waves. In the band model, the collective excitations of particles with a spin reversal, but without a change in wavevector $k$, are spin waves of wavevector $k$ whereas the individual spin-flip excitations with or without change in wavevector are the single-particle excitations. The spin wave dispersion relation in the long wavelength limit, calculated within the framework of the itinerant-electron model [34,44,45], has the same form as that in the localized-electron model, i.e., Eq.(1.7). However, at finite temperatures, the magnon-magnon interactions and magnon-single particle interactions become important. The effect of these interactions within the itinerant-electron model is to renormalize the spin wave energy through the renormalization of spin wave stiffness coefficient according to the relation [34,44,45]

$$D(T) = D(0) \left(1 - \frac{T^2}{D^2} \right)$$

(1.21)

where the parameter $D(0)$ is the value of $D(T)$ at 0 K, and depends on the exchange splitting of spin $\uparrow$ and spin $\downarrow$ sub-bands and on the dispersion relation of the single-particle energies. The dominant $T^2$ term in Eq.(1.21) arises from magnon-single particle interactions whereas the $X^{5/2}$ term originates from the magnon-magnon interactions and is much smaller compared to the $T^2$ term. Hence the $T^{5/2}$ term in Eq.(1.21) is generally neglected and the $D(T)$ varies as $T^2$ in the itinerant-electron model in contrast with the $T^{5/2}$ variation of $D(T)$ (Eq.(1.21a)) in the localized-electron model.

1.6.2B. Spin fluctuations in itinerant-electron model

Considerable improvement of the Stoner model has been achieved by the inclusion of the spin fluctuation effects [46-48]. Significant advancement in this direction has been made by Moriya and his coworkers [46,47], who treated spin fluctuations within the framework of self-consistent renormalization theory. The major success of Moriya's theory is the prediction of Curie-Weiss behaviour of susceptibility above $T_C$ and a reasonably accurate value for $T_C$. According to this theory, the spin-wave contribution in weak itinerant ferromagnets, though present at low temperatures, is not as significant as the exchange-enhanced $T^2$ contribution to magnetization and for temperatures close to $T_C$, the spin fluctuation contribution dominates and is given by [46,47]

$$\left[\frac{M(T,0)}{M(0,0)}\right]^2 = \left[1 - \left(\frac{T}{T_C}\right)^{4/3}\right]$$

(1.22)
A refined version of Moriya's theory, due to Lonzarich and Taillefer [48], provides a better quantitative description of the experimental results because it (i) includes the transverse as well as longitudinal local spin-density fluctuations, (ii) incorporates a natural temperature dependent cut-off wavevector for the thermally excited modes and (iii) uses band structure and other parameters appropriate to known weak itinerant ferromagnets like $\text{Ni}_{13}\text{Al}$ and MnSi rather than to the special electron gas model, employed earlier by Moriya and Kawabata [47]. This theory predicts that the contributions to magnetization arising from spin wave (SW) excitations and single-particle (SP) excitations plus local spin-density fluctuations (LSF) depend on temperature in accordance with the expressions [48]

$$\left[\frac{M(T,0)}{M(0,0)}\right]_{\text{SW}} = 1 - B T^{3/2}$$  \hspace{1cm} (1.23a)

at low temperatures and

$$\left[\frac{M(T,0)}{M(0,0)}\right]_{\text{SP+LSF}}^2 = \left[1 - \left(\frac{T}{T_c}\right)^4\right]$$  \hspace{1cm} (1.23b)

for a wide range of intermediate temperatures. Furthermore, according to this theory [48], for temperatures close to $T_C$, the local spin-density fluctuations alone should contribute to $M(T)$ and that this contribution varies with temperature as

$$\left[\frac{M(T,0)}{M(0,0)}\right]_{\text{LSF}}^2 = \left[1 - \left(\frac{T}{T_C}\right)^{4/3}\right]$$  \hspace{1cm} (1.23c)

The temperature dependence of magnetization in different temperature ranges predicted by Eqs.(1.23a)-(1.23c) has indeed been observed in a number of weak itinerant ferromagnets [49,50]. Despite the success that the above-mentioned theory [46-50] has enjoyed in accounting quantitatively for essentially all the measured properties of weak itinerant ferromagnets, including magnetization, the spin-fluctuation theory as developed by Moriya and co-workers [46,47] has recently been criticized [51] on the grounds that this theory has too many adjustable parameters and wrongly predicts that the averaged square local moment is an increasing function of temperature above $T_C$. However, even the theory, due to Hirsch [51], which dispenses with the spin fluctuations and gets rid of the above flaw in Moriya's theory, fails to predict the $T^{4/3}$ dependence of $M^2(T,0)$ observed in many weak itinerant ferromagnets (primarily because the local spin-density fluctuations are completely ignored in this theory).

The theoretical models described so far breakdown completely in the critical region (i.e., for temperatures in the immediate vicinity of the Curie temperature) where critical fluctuations of the order parameter (spontaneous magnetization in the present case) play a crucial role. In the following section, a brief account of the theoretical predictions concerning the behaviour of magnetization, susceptibility and other thermodynamic quantities in this temperature region and for temperatures well above $T_C$ is given.
1.7. Thermal Critical Phenomena

In zero external magnetic field, the ferromagnetic (FM)-to-paramagnetic (PM) phase transition at the critical point, $T_c$, is a second-order phase transition. The spontaneous magnetization, which is the order parameter in this case, goes continuously to zero at $T_c$ with a critical exponent $\beta$. The zero-field susceptibility, magnetic part of specific heat and the spin-spin correlation length diverge at $T_c$ with the critical exponents $\gamma, \alpha$ and $\nu$, respectively. These critical exponents are universal in the sense that they depend only on the lattice dimensionality, $d$, and order parameter dimensionality, $n$, and possess exactly the same values for widely different systems if all of them are described by the same values of $d$ and $n$[52,53]. From the scaling arguments and using renormalization group (RG) ideas, the total free energy density, $g(T,H)$, consisting of the singular, $g_{\text{sing}}(T,H)$ and non-singular, $g_0$, parts, can be written as [54-56]

$$g(T,H) = g_0(T) - g_{\text{sing}}(\varepsilon, h) = g_0(T) - |\varepsilon|^{2-\alpha} Y_\pm(\varepsilon) = (1 - \alpha)(2 - \alpha) T_c^{-1} Y_\pm(0) |\varepsilon|^{2-2\Delta} (1.24)$$

where the prefactor $|\varepsilon|^{2-\alpha}$ in Eq.(1.24) accounts for the shrinkage in volume under the scale transformation which leaves the total free energy invariant, $\alpha$ is the specific heat critical exponent, $\varepsilon = (T - T_c)/T_c - H$ (the ordering field), $\Delta$ is the gap exponent and the plus and minus signs refer to temperatures above and below $T_c$. If the macroscopic volume is set equal to unity, i.e., $V = 1$, the physical quantities such as magnetization, susceptibility and specific heat are straightaway obtained from the field and temperature derivatives of $g(T,H)$. Thus, the zero-field specific heat, $C(T,0)$, magnetization, $M(T,H)$, and the 'in-field' susceptibility, $\chi(T,H)$ are given by the expression [52-56]

$$C(T,0) = -T (\partial^2 g/\partial T^2)_{H=0} \equiv (1 - \alpha)(2 - \alpha) T_c^{-1} Y_\pm(0) |\varepsilon|^{2-\alpha} (1.25)$$

$$M(T,H) = - (\partial g / \partial H) T \quad M(\varepsilon, h) = |\varepsilon|^{\beta} f_\pm(\varepsilon) = |\varepsilon|^{\beta} f_\pm(\varepsilon) / |\varepsilon|^\Delta (1.26)$$

and

$$\chi(T,H) = \partial M(T,H) / \partial H = |\varepsilon|^{-\gamma} \partial [f_\pm(\varepsilon) / |\varepsilon|^\Delta] / \partial h (1.27)$$

where $\beta = 2 - \alpha - \Delta$, $\gamma = 2 - \alpha - 2\Delta$, and $f_\pm = (\partial Y_\pm / \partial h)_T$. The 'zero-field' quantities such as spontaneous magnetization, $M(T,0)$ and 'zero-field' susceptibility, $\chi(T,0)$, are then obtained by taking the limit $h = H \to 0$ and expanding $f_\pm(\varepsilon) / |\varepsilon|^\Delta$ in Taylor series around $h = 0$ as

$$f_\pm(\varepsilon) / |\varepsilon|^\Delta \simeq f_\pm(0) + (h / |\varepsilon|^\Delta)f'_\pm(0) + \cdots (1.28)$$
Hence one obtains

\[ M(T,0) = m_o |\epsilon|^{1-\delta}, \quad \epsilon < 0 \]  
\[ \chi(T,0) = \left( \frac{m_o}{h_o} \right) |\epsilon|^{-\gamma}, \quad \epsilon > 0 \]  

where \( m_o = f_-(0) \) and \( m_o/h_o = f_+(0) \) are the asymptotic amplitudes for spontaneous magnetization and initial susceptibility, respectively. As \( \epsilon \rightarrow 0, |\epsilon|/h \rightarrow 0 \) the scaling-equation-of-state (SES) represented by Eq.(1.26) can be rewritten in a more convenient form [56], i.e.,

\[ M(\epsilon, h) = h^{5/7} \left( f_o(0) + \left( |\epsilon| / h^{1/7} \right) f'_o(0) + \cdots \right) \]

where \( f_o \) is analytic at \( |\epsilon| = 0 \) and can be directly related to \( f_- \) and \( f_+ \). In the limit \( |\epsilon|/h^{1/7} \rightarrow 0 \), the function \( f_o(z) \) can be expanded in a Taylor series around \( z = 0 \) with the result

\[ M(\epsilon, h) = h^{5/7} \left[ f_o(0) + \left( |\epsilon| / h^{1/7} \right) f'_o(0) + \cdots \right] \]

Thus, the critical \( M \) versus \( H \) isotherm at \( |\epsilon| = 0 \) is described by the expression

\[ M(0, H) = f_o(0) H^{1/\delta} \]  
\[ H = D M^{\delta} \]

with \( \Delta = \beta \delta \) and \( D = f_o^{-\delta} \). Furthermore, at \( |\epsilon| = 0 \) and in the absence of the external magnetic field (\( H = 0 \)), the spin-spin correlation function, defined as \( G(r) = \langle (S(r) - \langle S \rangle)(S(0) - \langle S \rangle) \rangle \), varies with distance \( r \) as \[52,53,55,57]\]

\[ G(r) = N |T|^{-(d-2+\eta)} \text{ large } |r|, \quad \epsilon = H = 0 \]  
\[ \xi(T) = \xi_0^{\frac{\beta}{7}} |\epsilon|^{1-\eta}, \quad H = 0. \]  

(1.316)

Note that in all the foregoing equations \( H \) denotes the field that is obtained by correcting the external magnetic field for the demagnetizing field.

It is customary to determine the critical exponents \( \beta \) and \( \gamma \) from bulk magnetization data taken in external magnetic fields by using a specialized form of the general scaling-equation-of-state (SES), Eq.(1.26), proposed by Arrott and Noakes [58], i.e.,

\[ \left( \frac{H}{M} \right)^{1/\theta} = a' \epsilon + b' M^{1/\beta} \]  

(1.32)
where the coefficients $a'$ and $b'$ are \textit{temperature-independent}. According to the Arrott-Noakes SES (Eq.(1.32)), the $M(T, H)$ data taken in the critical region, when plotted in the form of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ (known as the modified Arrott plot) isotherms with the proper choice [57] of $\beta$ and $\gamma$, fall on a set of parallel straight line isotherms (especially in the high-field region) with the critical isotherm at $T_c$ passing through the origin. The high-field linear portions of these isotherms when extrapolated to $H \to 0$ yield intercepts on the ordinate and abscissa from which $M(T,0)$ and $\chi(T,0)$ are computed. The $M(T,0)$ and $\chi(T,0)$ data so obtained are analyzed in terms of the Eqs.(1.29a) and (1.29b). The `zero-field' quantities such as $C(T,0), M(T,0)$ and $\chi(T,0)$, when analyzed in terms of single power law expressions (1.25), (1.29a) and (1.29b), yield only the \textit{average} values for the exponents since these expressions are strictly valid for temperatures in the close proximity to $T_C$ whereas the experimental data for such quantities are generally taken over a wide temperature range in the critical region. The exponents obtained in this way not only depend on the temperature range used but also could significantly differ from the true asymptotic values [56,57,59]. The expressions for the quantities $C(T,0), M(T,0)$ and $\chi(T,0)$ must, therefore, include both \textit{analytic} and \textit{non-analytic} 'correction-to-scaling' (CTS) terms [53-56,59,60] arising from the nonlinear relevant and irrelevant scaling fields, respectively.

From the generalized magnetic equation of state that takes into account the effect of nonlinear relevant and irrelevant scaling fields, the 'zero-field' quantities $C(T,0), M(T,0)$ and $\chi(T,0)$ are calculated with the result [56,60]

\begin{equation}
C(T,0) \equiv (1-\alpha)(2-\alpha)T_C^{-1}Y_\pm(0) |\varepsilon|^{-\alpha (1+\varepsilon)} [1 + a_{C1} |\varepsilon|^\Delta_1 + a_{C2} |\varepsilon|^\Delta_2 + a_{C} \varepsilon + b_{C} \varepsilon^2 + \cdots] 
\end{equation}

\begin{equation}
M(T,0) = H |\varepsilon|^\beta [1 + a_{M1} |\varepsilon|^\Delta_1 + a_{M2} |\varepsilon|^\Delta_2 + a_{M} \varepsilon + b_{M} \varepsilon^2 + \cdots] 
\end{equation}

and

\begin{equation}
\chi(T,0) = A_{x} |\varepsilon|^{-\gamma} [1 + a_{x1} |\varepsilon|^\Delta_1 + a_{x2} |\varepsilon|^\Delta_2 + a_{x} 6 + b_{x} \varepsilon^2 + \cdots] 
\end{equation}

where the leading non-analytic (analytic) terms $|\varepsilon|^\Delta_1$ and $|\varepsilon|^\Delta_2$ ($\varepsilon$ and $\varepsilon^2$) originate from the nonlinear irrelevant (relevant) scaling fields. The \textit{renormalization} group (RG) theories [53-55,60-66] predict that the confluent corrections to the dominant singular behaviour involve only a \textit{single leading} exponent $A = 0.550 \pm 0.016$ (i.e., $A = \Delta_2$ and $\Delta_1 = 0$) for an ordered (crystalline) isotropic 3D Heisenberg ferromagnet whereas such corrections include [63-66] the leading exponent $\Delta_1 = 0.115 \pm 0.009$ in addition to $\Delta_2 = 0.550 \pm 0.016$ for quench-disordered 3D Heisenberg systems. In keeping with the general practice, we discussed the critical behaviour in terms of the linear variables $\varepsilon$ and $h$ so far. However, as we shall see later, the behaviour of a magnetic system (that undergoes a second-order phase transition) over a wide range of temperatures, which embraces the critical region, is better described in terms of nonlinear variables $\varepsilon = (T - T_C)/T_C \ll \varepsilon /t$ and $h = H/t$ where $t \sim T/T_C$. In analogy with the linear \textit{case}, free energy density in nonlinear variables is given by [56]
While the scaling equation of state (SES) assumes a form \[56\]

\[ M(T, H) = M(\tilde{\epsilon}, \tilde{h}) = | \tilde{\epsilon} |^\beta \tilde{f}_\pm(\tilde{h}) / | \tilde{\epsilon} |^\Delta \]  

similar to its linear counterpart, Eq.(1.25), the Arrott-Noakes (AN) SES gets modified to \[56\]

\[ M^{1/\beta} = a(-\tilde{\epsilon}) + b t^{-1/\gamma} (H/M)^{1/\gamma} \]  

Unlike the original AN SES (Eq.(1.32)), the modified AN SES, Eq.(1.36), has an additional factor of \( t^{-1/\gamma} \) and the coefficients \( a \) and \( b \) are temperature-dependent. The 'zero-field' quantities \( C(T, 0), M(T, 0) \) and \( \chi(T, 0) \) are obtained from \( g(T, H) \) Eq.(1.34), in the same way as in the case of linear variables and the final expressions \[56\] for these quantities are given below.

**Single Power Laws**:

\[ C(T, 0) = (1 - \alpha)(2 - \alpha) T_c^{-1} \tilde{Y}_{\pm}(0) \ | \tilde{\epsilon} |^{-\alpha} (1 - \tilde{\epsilon})^2 \]  

\[ M(T, 0) = m_o \ | \tilde{\epsilon} |^\beta \quad \tilde{\epsilon} < 0 \]  

and

\[ \chi(T, 0) = \left( m_o / h_o \right) \ | \tilde{\epsilon} |^{-\gamma} \quad \tilde{\epsilon} > 0 \]  

**With the inclusion of CTS terms**:

\[ C(T, 0) = A_c \ | \tilde{\epsilon} |^{-\alpha} \left[ 1 + a_{C1} | \tilde{\epsilon} |^{\Delta_1} + a_{C2} | \tilde{\epsilon} |^{\Delta_2} + a_C \epsilon \cdots \right] \]  

\[ M(T, 0) = B_M \ | \tilde{\epsilon} |^\beta \left[ 1 + a_{M1} \epsilon + a_{M2} | \tilde{\epsilon} |^{\Delta_1} + a_M \epsilon + \cdots \right] \]  

and

\[ \chi(T, 0) = A_x \ | \tilde{\epsilon} |^{-\gamma-1} \left[ 1 + a_{x1} | \tilde{\epsilon} |^{\Delta_1} + a_{x2} | \tilde{\epsilon} |^{\Delta_2} + a_x \tilde{\epsilon} \cdots \right] \]

The above expressions (Eq.(1.38)), include (only the leading terms) the analytic ( \( \tilde{\epsilon} \) ) and non-analytic ( \( | \epsilon |^{\Delta \epsilon} \) ) corrections in nonbilinear variables arising from nonlinear relevant and irrelevant scaling fields, respectively. As already mentioned above, in the presence of nonlinear relevant and irrelevant scaling fields, the Arrott-Noakes SES in nonlinear variables has the form \[56\]

\[ M^{1/\beta} = B(-\tilde{\epsilon}) + (B/A) t^{-1/\gamma} (H/M)^{1/\gamma} \]  

\( g(T, H) = g_o(T) \tilde{g}_\text{sing}(\tilde{\epsilon}, \tilde{h}) = g_o(T) - | t \in \Delta - \alpha Y_\pm(h/| \tilde{\epsilon} |^\Delta) \)  

(1.34)
with

$$B^m = [B_M(1 + \tilde{a}_M \tilde{\varepsilon})]^{1/\beta} \simeq A_M(1 + \tilde{a}_M \tilde{\varepsilon})$$

(1.40a)

and

$$B/A = [B_M(1 + \tilde{a}_M \tilde{\varepsilon})]^{1/\beta}[\tilde{A}_x(1 + \tilde{a}_x \tilde{\varepsilon})]^{1/\gamma} \simeq A'(1 + \tilde{a}_x \tilde{\varepsilon})$$

(1.40b)

$$B \cdot [B_M(1 + \tilde{a}_M_1 | \tilde{\varepsilon} | A_1 + \tilde{a}_M_2 | \tilde{\varepsilon} | A_2)]^{1/\beta} \simeq \tilde{A}_M(1 + \tilde{a}_M_1 | \tilde{\varepsilon} | A_1 + \tilde{a}_M_2 | \tilde{\varepsilon} | A_2)$$

(1.41a)

and

$$B/A = [\tilde{B}_M(1 + \tilde{a}_M_1 | \tilde{\varepsilon} | A_1 + \tilde{a}_M_2 | \tilde{\varepsilon} | A_2)]^{1/\beta}[\tilde{A}_x(1 + \tilde{a}_x \tilde{\varepsilon} + \tilde{a}_x_2 | \tilde{\varepsilon} | A_2)]^{1/\gamma}$$

(1.41b)

where the expressions for $B$ (= $a$ in Eq.(1.36)) and $B/A$ (= $b$ in Eq.(1.36)) given by Eq.(1.40) or Eq.(1.41) correspond to the cases when only the relevant scaling fields or the irrelevant scaling fields are present. The important features of the modified Arrott-Noakes SES in nonlinear variables (Eq.(1.39)) are that apart from yielding the true asymptotic critical exponents, it accounts for the temperature variation of the slope of the Arrott plot isotherms commonly observed for a large number of crystalline and amorphous ferromagnets [56,57]; a feature that does not find any explanation in terms of the original AN SES because the coefficients $a'$ and $6'$ in Eq.(1.32) do not depend on temperature.

Sections 1.6 and 1.7 have mainly dealt with the effect of temperature on magnetization in amorphous ferromagnets. The following section addresses itself to the theoretical developments that have taken place until now in understanding the magnetic and thermodynamic behaviour of dilute magnets.

### 1.8. Percolation Critical Behaviour

Percolation concepts were introduced by Broadbent and Hammersley [67] as early as in 1957 and considerable progress has been made since then towards the understanding of percolation phenomena [68-73]. In order to bring out clearly the underlying concept, consider a crystal lattice in which some sites are occupied by particles and the remaining sites are vacant. The nearest neighbour particles, connected by bonds, form finite clusters. As the concentration of particles, $p$, is gradually increased, the cluster size increases and a concentration, known as the percolation threshold, $p_c$, is reached at which an infinite cluster (for an infinite lattice)
appears; the infinite cluster extends from one end of the lattice to the other. If the bonds are of conducting type, at $p_c$ the solid is said to be conducting or percolating, that the current can now percolate from one side to the other of the lattice. Thus, the percolation threshold $p_c$ marks the transition from finite clusters to an infinite cluster. The transition occurring at the percolation critical point is a second-order phase transition and in analogy with the thermal critical behaviour, is characterized by percolation critical exponents. The order parameter in this case is the percolation probability, $P(p)$, defined as the fraction of occupied sites belonging to the infinite cluster. $P(p)$ is zero for $p < p_c$ and finite for $p > p_c$. The percolation exponents associated with various quantities are defined as follows [68-73].

The mean number of clusters

$$N(p) \sim (p - p_c)^{2 - \alpha_p}, \quad (1.42a)$$

percolation probability (order parameter)

$$P(p) \sim (p - p_c)^{\beta_p} \quad p > p_c, \quad (1.42b)$$

mean size of finite clusters

$$S(p) \sim (p - p_c)^{-\gamma_p}, \quad (1.42c)$$

and order parameter at $p = p_c$

$$P(p_c) \sim h^{1/\delta_p} \quad (1.42d)$$

where $\alpha_p, \beta_p, \gamma_p$ and $\delta_p$ are the percolation critical exponents and the parameter $h$, generally known as the ghost field, performs a function similar to that of the magnetic field [70,71]. If $C(r, p)$ is the probability that a site at $r$ is occupied and connected to the site at origin, the connectedness length is given by

$$\xi(p) \sim (p - p_c)^{-\nu_p} \quad (1.420)$$

A number of physical systems, including the dilute magnetic systems, which are of interest to this thesis, exhibit a percolation behaviour of this type. Magnetic dilution can be achieved in different ways. One way of achieving dilution in magnetic systems is by randomly replacing magnetic atoms on a lattice by non-magnetic ones. This type of magnetic dilution is called the random site-dilution. The Hamiltonian for the random site-diluted magnetic systems can be written as [74]

$$\mathcal{H}_s = -\sum \mathbf{S}_i \cdot \mathbf{S}_j \eta_i \eta_j \quad (1.43a)$$

where $\mathbf{S}_i$ is the spin vector at site $i$, $J$ is the exchange constant and $\eta_i$ is the uncorrelated site disorder variable which takes values 0 or 1 such that $\langle \eta_i \rangle = p$, where $\langle \rangle$ denotes the configurational average and $p$ is the concentration of magnetic atoms. At this stage, it is necessary to distinguish between two types of disorder; quenched disorder and annealed disorder [74]. In
systems with quenched disorder, the **configurational** averages over spin variables are independent of thermal averages whereas in the case of annealed disorder, the disorder variables are in thermal equilibrium with the system and hence the configurational and thermal averages are not independent. The site probability distribution for quenched site-disorder is given by [71]

\[ P(\eta_i) = (1 - p) \delta(\eta_i) + p \delta(\eta_i - 1) \]  

(1.436)

The other way in which a magnetic system can be magnetically diluted is by randomly removing exchange bonds and this type of dilution is known as the random bond-dilution. The Hamiltonian for bond-diluted system is of the form [71]

\[ \mathcal{H}_b = -\sum S_i \cdot \vec{J} \cdot \vec{S}_j \eta_{ij} \]  

(1.44a)

where the uncorrelated disorder variables \( \eta_{ij} \) are associated with the exchange bonds. The probability distribution for quenched bond-dilution is given by

\[ P(\eta_{ij}) = (1 - p) \delta(\eta_{ij}) + p \delta(\eta_{ij} - 1) \]  

(1.44b)

where \( p \) is the bond concentration. Quenched dilute magnetic systems exhibit percolation critical phenomena in the vicinity of percolation threshold, \( p_c \), which is the critical magnetic concentration below which only the finite spin clusters are present and no long-range magnetic order exists even for temperatures as low as \( T = 0 \) K. However, for \( p > p_c \) an infinite spin cluster (and hence long-range magnetic order) appears. The point \( Q(p - p_c, T = 0) \) denoting the percolation critical point for dilute magnets is characterized by percolation critical exponents as defined for pure geometrical percolation earlier. A correspondence or analogy between the quantities associated with critical exponents in pure geometrical percolation and magnetic percolation can be drawn and the same is given below [71].

<table>
<thead>
<tr>
<th>Geometrical percolation</th>
<th>Magnetic percolation</th>
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<tr>
<td>mean number of clusters</td>
<td>zero field free energy</td>
</tr>
<tr>
<td>percolation probability (order parameter)</td>
<td>spontaneous magnetization (order parameter)</td>
</tr>
<tr>
<td>mean size of cluster</td>
<td>initial susceptibility</td>
</tr>
<tr>
<td>pair connectedness function</td>
<td>correlation function</td>
</tr>
<tr>
<td>connectedness length</td>
<td>spin-spin correlation length</td>
</tr>
</tbody>
</table>

The above correspondence also brings out the similarity between percolation and thermal critical phenomena. Using scaling arguments, the singular part of free energy \( f_{\text{sing}}(p, h) \) for the dilute magnetic systems described above with \( p \) close to the percolation critical point can be written as [70-75]
where $\epsilon_p = q_1 (p - p_c) / p_c; \ h = H$. The + and - signs refer to $p > p_c$ and $p < p_c$, respectively, and the parameters $q_o$ and $q_1$ are model-dependent parameters introduced to make $f(p, h)$ a universal function. Eq.(1.45) yields the following expressions for the order parameter (i.e., the spontaneous magnetization at 0 K, in the present case) and initial susceptibility:

\[ M(p, 0) = \frac{\partial f}{\partial h} = m_p (p - p_c)^\beta_p \quad p > p_c \]  

and

\[ \chi(p, 0) = \frac{\partial^2 f}{\partial h^2} = \chi_p (p - p_c)^\gamma_p \quad p > p_c \]

where $\beta_p = 2 - \alpha_p - \Delta_p$, $m_p = q_0 (q_1/p_c)^\delta \partial F_\pm / \partial h$, $\gamma_p = 2 \Delta_p - 2 + \alpha_p$ and $\chi_p = q_0 (q_1/p_c)^\eta \partial^2 F_\pm / \partial h^2$. The percolation correlation function varies with distance $r$ as

\[ C(r, p) \sim r^{-(2 - 4 + \eta_p)} \]

while the associated percolation correlation length, $\xi_p$, diverges at $p_c$ with an exponent $\nu_p$ according to the power law

\[ \xi_p(p, 0) \sim (p - p_c)^{-\nu_p} \quad p > p_c \]

Moreover, for $p > p_c$, long-range ferromagnetic order is present in a dilute magnetic system with $J > 0$. For such a system, the spin wave stiffness coefficient, $D(p)$, and the Curie temperature, $Tc(p)$, go to zero as $p \rightarrow p_c$ with the exponents $\theta_p$ and $\phi_p$, defined as [70-74]

\[ D(p) = d_p (p - p_c)^\theta_p \quad p > p_c \]  

and

\[ Tc(p) = t_p (p - p_c)^\phi_p \quad p > p_c \]

where the thermal-to-percolation crossover exponent $\phi_p$ is related to $\nu_p$ as $\phi_p = \nu_p / \nu_T$, $\nu_T$ is the critical exponent for the thermal correlation length. Another quantity of interest in the percolation phenomena is the macroscopic conductivity, $E$, in randomly diluted resistor network. In such a network $\Sigma = 0$ for $p < p_c$ and for $p > p_c$, the functional behaviour of $E$ is characterized [70-74] by the exponent $\sigma_p$, such that

\[ \Sigma(p) = \Sigma_p (p - p_c)^\sigma_p \]

The conductivity, $E(p)$, of the resistor network is related to the spin-wave stiffness coefficient, $D(p)$, in dilute isotropic ferromagnets through the expression [74]

\[ \Sigma(p) = D(p) P(p) \]
where $P(p)$ is the percolation probability and using the definitions of $D(p)$, $P(p)$ and $E(p)$ in Eq.(1.49), one obtains the scaling relation

$$\theta_p = \sigma_p - \beta_p.$$  

(1.50)

The percolation exponents defined above are similar to thermal critical exponents and are universal in that they do not depend on the details and type of lattice but depend only on the lattice and order parameter dimensionalities.

A complete knowledge of the structure of percolating cluster at threshold is necessary to understand the properties of random systems such as dilute magnets, random resistor networks etc. In order to study the percolation behaviour, three distinctly different models have been proposed for the structure of the percolating cluster at $p_c$.

(a) **Node-link model** :

This model was proposed by Skal and Shklovskii [76] and independently by De Gennes [76]. In the node-link picture (Fig. 1.4(a)), the backbone of infinite cluster is considered as a superlattice of small clusters set on nodes which are connected by one-dimensional random paths or links. The average distance between the nodes is the correlation or connectedness length, $\xi$, while the length, $L$, along the random one-dimensional path between nodes diverges at $p_c$ with an exponent $\zeta$ [72,74,77], i.e.,

$$L \sim (p - p_c)^{-\zeta}.$$  

(1.51)

This model predicts that the thermal behaviour of the percolating lattice for $T > 0$ should be that of a collection of one-dimensional chains if $L > \xi(T)$ or that of a true $d$-dimensional system if $L < \xi(T)$, where $\xi(T)$ is the linear chain thermal correlation length. The node-link model also makes specific predictions about the scaling relations between different exponents [72,74,77], i.e.,

$$\phi_p = \zeta = \nu_p / \nu_T, \quad \theta_p = 2(\zeta - \nu_p) \quad \text{and} \quad \sigma_p = (d - 2)\nu_p + \zeta.$$  

(1.52)

The Skal-Shklovskii-de Gennes model describes the system properly only in dimensions $d > 3$ whereas for $d < 3$, it yields results that are inconsistent with experimental findings.

(b) **Node-link-blob picture** :

The node-link-blob picture for the percolating cluster due to Stanley and Coniglio [78] is an
Fig. 1.4 Models for the structure of percolating cluster at threshold: (a) node-link model, (b) node-link-blob model and (c) self-similar fractal model.
improvised version of the node-link picture. In this model, two types of bonds in the backbone of the incipient infinite cluster are distinguished: the links or single bonds, also known as the cutting bonds such that if the link is cut, the cluster breaks into parts, and the multiply connected bonds, which lump together in 'blobs'. The infinite cluster at and above $p_c$ is made up of nodes connected by links and blobs. The blobs are assumed to have self-similar structure. Based on the hierarchical node-link-blob picture (Fig. 1.4(b)) for the infinite cluster, Golden [79] predicts that the conductivity exponent $\sigma_p$ should obey the inequality, known as the Golden inequality, $\sigma_p < 2$ for $d - 3$. This prediction is consistent with the simulation results.

(c) **Self-similar fractal structure:**

The word fractal was introduced by Mandelbrot [80] to describe objects with fractal dimension $d$ smaller than the euclidean dimensionality of the underlying lattice [80]. Roughly speaking, if the mass or size $s$ of a system varies as $(\text{length})^d$, then $d$ is called the fractal dimensionality. The infinite cluster is assumed to have a self-similar fractal structure (Fig. 1.4(c)) and using the scaling arguments, the fractal dimensionality $d$ and the spectral or fracton dimensionality $\tilde{d}$ are expressed in terms of the percolation exponents [81] as

$$
\tilde{d} = d - (\beta_p/\nu_p)
$$

and

$$
\tilde{d} = 2(d\nu_p - \beta_p)/(\sigma_p - \beta_{\tilde{d}} - 2\nu_p)
$$

(1.536)

Within the framework of the self-similar fractal picture, Alexander and Orbach [81] conjectured that for the infinite percolating cluster at threshold

$$
3 = 4/3
$$

(1.53c) independent of the euclidean dimensionality $d$.

In this and the preceding sections, a brief resume of the theories existing in the literature about the magnetic behaviour of amorphous ferromagnets was provided. In the next section, a similar survey of the theoretical models proposed so far to understand the transport properties of amorphous metallic alloys is presented.

1.9. Electrical Resistivity in Amorphous Alloys

The behaviour of electrical resistivity of amorphous alloys in general is quite different from that of the corresponding crystalline systems. The salient features of the electrical resistivity
data taken on a large number of metallic glasses are [82-85]:

(a) The residual resistivities $\rho_o$ of amorphous alloys are considerably larger than those of their crystalline counterparts but similar in magnitude to that of the corresponding liquids.

(b) The temperature coefficient of resistivity (TCR) is small and usually positive for alloys with $\rho_o < 150 \mu\Omega \text{ cm}$ and negative for alloys with $\rho_o > 150 \mu\Omega \text{ cm}$. Such a relation between the magnitude of $\rho_o$ and TCR has come to be known as the Mooij correlation [86].

(c) In a number of alloys, resistivity as function of temperature goes through a minimum at a temperature $T_{\text{min}}$ and resistivity saturates at high temperatures at a value $\sim 150 \mu\Omega \text{ cm}$.

The resistivity minimum in most of the 3$d$ transition metal-metalloid alloys occurs at temperatures as low as 20 K [82-85, 87,88], but in some transition metal based alloys containing Cr, Mn, Mo, V, W etc., the resistivity minimum is found to occur at temperatures $T \sim 250 \text{ K}$ [82-85,89]. The origin of resistivity minimum is not yet clearly understood. A number of theoretical models have been proposed to explain the resistivity minimum and other characteristic features of resistivity behaviour in amorphous materials. None of these models on its own can describe the variation of resistivity in the entire temperature range. Therefore, assuming the validity of Mathiessen's rule, the contributions to total resistivity arising from different scattering mechanisms are considered to be additive. A brief description of some relevant theoretical models is given below.

1.9.1. Mott s-d scattering model

This model, originally proposed by Mott [90] for transition metals and alloys, assumes that the current is carried by nearly free $s$ electrons which are scattered from fluctuations in the local environment (arising from structural disorder) into the vacant states above the Fermi level in the $d$-band. The electrical resistivity is, thus, proportional to $N(E_F)$ the density of $d$ states (DOS) at the Fermi level. The temperature dependence of resistivity arises because of the shift in $E_F$ with increasing temperature. The expression for resistivity given by this model is [84,85,90]

$$\rho_{\text{Mott}}(T) = \rho(0) \left\{ 1 - \frac{\pi^2}{6} (k_B T)^2 \left[ 3 \left( \frac{N'(E_F)}{N(E_F)} \right)^2 - \frac{N''(E_F)}{N(E_F)} \right] \right\}$$

where $N'(E_F)$ and $N''(E_F)$ are the first and second energy derivatives of DOS at $E = E_F$, respectively. For the nearly filled $d$-band, the TCR is negative. The energy derivates of $N(E)$ at $E_F$ for amorphous metals are expected to be extremely small, hence the Mott model when applied to amorphous materials gives a weak temperature dependence of resistivity [85].
1.9.2. Diffraction Model

This model, originally proposed by Ziman [91] for simple liquid metals, is based on the following assumptions [84,85,91]. (a) The electronic transport properties can be described by the Boltzmann transport equation, (b) the interaction between the conduction electrons and ions can be described by a pseudo potential and (c) the conduction electrons are assumed to be nearly free and the scattering potential is weak enough to be treated by first-order perturbation theory. Evans et al. [92] extended the Ziman theory to include liquid transition metals by using the muffin-tin potential and arrived at the following expression for resistivity [82,84,85,92,93]

\[ \rho \simeq \frac{30 \pi^3 \hbar^3}{m e^2 k_F^2 E_F \Omega} \sin^2[\eta_2(E_F)] S_T(2k_F) \]  

(1.55a)

where \( k_F \) and \( E_F \) are the Fermi wavevector and Fermi energy, respectively, \( \Omega \) is the volume, \( \eta_2(E_F) \) is the \( d \) partial-wave phase shift describing the scattering of the conduction electrons by the ion-cores which carry a muffin-tin potential centered around each ion position and \( S_T(2k_F) \) is the structure factor. The temperature dependence of \( \rho \) comes from the temperature dependence of \( S_T(2k_F) \). Within the framework of the diffraction model, there are several ways [93] of calculating the \( S_T(k) \), however, the one using a Debye spectrum due to Nagel [93] yields the expression

\[ S_T(k) \sim 1 + [S_0(k) - 1] e^{-2W_k(T)} \] 

(1.55b)

where \( S_0(k) \) is the static structure factor and \( e^{-2W_k(T)} \) is the Debye-Waller factor, with \( W_k(T) \) in the Debye approximation given by [87,94]

\[ W_k(T) = W_k(0) + 4 W(0) \left( \frac{T}{\Theta_D} \right)^2 \int_{0}^{\Theta_D/T} \frac{z dz}{\varepsilon^2 - 1} \] 

(1.56a)

with

\[ W_k(0) = 3 \hbar^2 k^2 / 8 M k_B \Theta_D \] 

(1.56b)

where \( M \) is the atomic mass and \( \Theta_D \) is the Debye temperature. Substituting Eq.(1.56) in Eq.(1.55), one obtains [87]

\[ \rho(T) \simeq \frac{30 \pi^3 \hbar^3}{m e^2 k_F^2 E_F \Omega} \sin^2[\eta_2(E_F)] S_T(2k_F) \left[ 1 + [S_0(2k_F) - 1] e^{-2[W(T)-W(0)]} \right] \] 

(1.57)

where \( W(T) = W_{2k_F}(T) \) and \( W(0) = W_{2k_F}(0) \) are the values of \( W_k(T) \) and \( W_k(0) \) at \( k = 2k_F \) respectively, i.e.,

\[ W(0) = 3 \hbar^2 k_F^2 / 2 M k_B \Theta_D \] 

(1.58)
The temperature coefficient of resistivity (TCR), \( \alpha \), can be calculated from Eq.(1.57) as [87]

\[
\alpha = \frac{1}{\rho} \frac{\partial \rho}{\partial T} = \frac{2}{S_T(2k_F)} \frac{\partial W(T)}{\partial T} = \frac{8}{S_T(2k_F)} \frac{W(0)}{T} \times \left\{ 2 \left( \frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{z dz}{e^z - 1} - \frac{1}{e^{\Theta_D/T} - 1} \right\}
\]  

(1.59)

Eq.(1.59) clearly shows that \( \partial W(T)/\partial T > 0 \) for all temperatures and hence \( \alpha \) is negative if \( S_T(2k_F) > 1 \) and positive if \( S_T(2k_F) < 1 \). In other words, negative TCR is expected only when \( 2k_F \) lies close to \( k_p \), the position of first peak in \( S(k) \), whereas a positive TCR is expected when \( 2k_F \) is far away from \( k_p \). In the low- and high-temperature asymptotic limits, Eq.(1.57) simplifies to

\[
p(T) \sim C + BT^2 \quad \text{for} \quad T \ll \Theta_D \]  

(1.60a)

\[
p(T) \sim C' + BT \quad \text{for} \quad T \gg \Theta_D \]  

(1.60b)

where the constants \( C, B, C' \) and \( B' \) are related to various parameters of Eq.(1.57). Thus, according to the diffraction model, resistivity varies as \( T^2 \) at low temperatures and linearly at high temperatures. In order to facilitate a direct comparison with experiments, Eq.(1.57) is written in a different form [87] as

\[
\tau(T) = \frac{\rho(T)}{\rho(0)} = a_1 + a_2 e^{-2[W(T)-W(0)]} = a_1 + a_2 \exp \left\{ -8W(0) \left( \frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{z dz}{e^z - 1} \right\}
\]  

(1.61a)

with

\[
a_1 = \frac{1}{l} \left[ S_o(2k_F) - 1 \right] e^{-2[W(T)-W(0)]}
\]  

(1.616)

and

\[
a_2 = a_1 [S_o(2k_F) - 1]
\]  

(1.61c)

where \( T_o = 273.15 \) K is the ice temperature.

The diffraction model has been successfully used to describe the electrical resistivity behaviour of a large number of low resistivity (\( \rho_o < 150 \mu \Omega \) cm) amorphous alloys. However, the model does not provide an adequate description in the case of high resistivity materials.
1.9.3. Kondo spin-flip model

The model was originally conceived by Kondo [95] to explain the resistivity minimum in dilute crystalline alloys consisting of a non-magnetic host containing a few ppm of magnetic impurities. The scattering of conduction electrons of the host from the localized spin of local magnetic impurities gives rise to spin-dependent increase in the resistivity at low temperatures, which in combination with the contribution to resistivity arising from the usual electron-phonon scattering at high temperatures produces a minimum in the total resistivity of these alloys [84,95]. Using the perturbation theory in the second Born-approximation, Kondo calculated the spin-dependent part of resistivity with the result [84,95]

\[ \rho_K(T) = \rho_M [1 + J c \ln(T/T_K)] \]  

(1.62)

where \( c \) is the magnetic impurity concentration, \( J \) is the local exchange and \( T_K \) is the Kondo temperature defined as \( k_B T_K = D \), the conduction band width. When \( J \) is negative, the resistivity increases at low temperatures giving rise to negative TCR. The unphysical logarithmic divergence in the original expression for \( \rho_K(T) \), Eq.(1.62), was later removed by introducing the concept of spin compensation which asserts that effective local moment decreases with decreasing temperature and finally vanishes at \( T = 0 \) K. Taking this aspect into account, Hamann [96] obtained a modified expression for the Kondo contribution to resistivity as

\[ \frac{\Delta \rho}{\rho} = 1 - \frac{\ln(T/T_K)}{[\ln^2(T/T_K) + S(S+1)\pi^2]^{1/2}} \]

(1.71)

The above expression ensures that the resistivity saturates at a finite value at low temperatures. Although the Kondo model is strictly applicable to dilute crystalline materials only, it has been employed to explain the resistivity minimum in a number of amorphous alloys including concentrated magnetic systems with reasonable success. However, certain inconsistencies have surfaced while applying the Kondo model to concentrated amorphous systems [83-85].

1.9.4. Two-level-tunneling model

The observation of resistivity minimum in a large number of amorphous alloys regardless of whether they are magnetic or nonmagnetic has prompted some workers to propose scattering mechanisms which are inherent to the amorphous structure itself. One such model is the two-level tunneling model [97] which is the structural analogue of the Kondo model. The amorphous state is a high energy metastable state and there exist a number of local atomic configurations which are energetically equivalent. Even though many of these are not favorable for tunneling,
there exist a significant number of atoms or group of atoms which can tunnel between the states of equivalent energy. In the simplest form, they constitute the two-level systems (TLS) [83-85,97]. The model due to Cochrane et al. [97] considers a potential well with two minima of equal energy and asserts that the electron scattering by such two-level states is analogous to the Kondo scattering. This approach leads to the following expression for the contribution to total resistivity arising from electron-TLS scattering [83-85,97]

\[ \rho_{TLS}(T) = -c \ln(k_BT^2 + A^2) \] (1.64)

where A is the energy difference between the two atomic tunneling states and c is a constant whose magnitude depends only on the number of sites and the strength of the coulomb interaction. The tunneling model, thus predicts that the resistivity increases as the temperature is lowered and finally saturates at low temperatures.

### 1.9.5. Coherent exchange scattering model

Another model, which, like the Kondo model, is applicable to magnetic systems, is the so-called coherent exchange scattering model. This model was proposed by Asomoza et al. [98] to describe the unusual resistivity behaviour of rare earth based amorphous alloys. This model deals with a system in which magnetic ions of angular momenta \( J_R \) are coupled to the conduction electron spin \( S \) by an exchange interaction of the form

\[ \mathcal{H}_{ex} = -\Gamma \sum_{R} \vec{S}_r \cdot \vec{J}_R \delta(\tau - R) \] (1.65a)

Using this Hamiltonian, the magnetic contribution to resistivity is calculated within the framework of nearly free-electron model of Ziman, i.e., the diffraction model for the transport properties of liquid metals and amorphous alloys. The exchange scattering contribution to resistivity, obtained by taking into account the interference between the scattered waves from neighbouring magnetic ions, is given by [84,98]

\[ \rho_{CES}(T) = \rho_m [1 + c m(2k_F)] \] (1.656)

with

\[ \rho_m = \frac{m^2 k_F^2 \cdot J(J + 1)}{4 \pi n e^2 \hbar^3} \] (1.65c)

where \( n \) is the number of conduction electrons per atom, \( c \) is the magnetic concentration and \( m(2k_F) \) is magnetic structure factor calculated at \( k = 2k_F \) and defined as

\[ m(2k_F) = \sum_{j} \delta c < S_j \cdot S_k > \exp[-i(2k_F)(\vec{R}_j - \vec{R}_k)] \] (1.65d)

The first term in Eq.(1.656), arising from independent scattering by magnetic ions, does not
depend on the magnetic ordering of the system. The second term due to coherent exchange scattering by the neighbouring ions is non-zero at low temperatures where the spins are correlated and vanishes at high temperatures. The change in resistivity due to magnetic ordering is either positive or negative depending on whether the interference between the scattered waves is constructive, i.e., when $m(2k_F) > 1$ or destructive, i.e., when $m(2k_F) < 1$.

1.9.6. Spin-disorder model

The spin-disorder model, applicable to ferromagnetic materials, deals with the scattering of conduction electrons by spin-waves. The spin-disorder model for amorphous ferromagnets developed by Richter et al. [99], considers a Heisenberg spin system in which spins are localized at the sites of an amorphous network and conduction electrons get scattered from these localized spins (moments) through the $s-d$ exchange interaction. Using the nearly free-electron concept, the magnetic part of resistivity in the spin-wave approximation is given by [87,99]

$$\rho_{SD}(T) = \rho_{SD}(0) \left[ 1 + \frac{\Omega_C}{(2\pi)^2 S} \Gamma(\frac{3}{2}) \xi(\frac{3}{2}) \left( \frac{k_BT}{D_{SW}} \right)^{3/2} + \frac{1}{J_S(2k_F)} \left[ \frac{\pi^2}{3S} \left( \frac{k_BT}{D_{SW}} \right)^2 - F(T) \right] \right]$$

(1.66a)

with

$$\rho_{SD}(0) = (2\Omega_C/3h^3) [(\Omega/N\epsilon) m S J_s]^2 J_S(2k_F)$$

(1.66b)

where $N_C$ is the number of electrons, $\Omega_C$ and $\Omega$ are the atomic and sample volumes, respectively, $S$ is the spin of local atomic magnetic moment, $D_{SW}$ is the spin wave stiffness coefficient, $T$ and $\xi$ are the gamma and Riemann zeta functions, respectively, $J_{sd}$ is the exchange coupling constant and $J_S(2k_F) = \int_0^{2k_F} k^3 S_m(k) dk$. $S_m(k)$ is the static magnetic structure factor. The $T^{3/2}$ term in Eq.(1.66a) is the net result of a partial cancellation of two competing $T^3/2$ terms; one arising from incoherent (momentum non-conserving) electron-magnon scattering and increasing with increasing temperature, and the other originating from the elastic scattering of conduction electrons from randomly oriented temperature-dependent local moments and decreasing with increasing temperature, whereas the $T^2$ term in Eq.(1.66a) is the coherent electron-magnon scattering term. The function $F(T)$, arising because of structural disorder, constitutes only a minute correction to the $T^2$ term indicating thereby that the coherent electron-magnon scattering is not significantly altered by the presence of quenched disorder. $\rho_{SD}(0)$ and the $T^{3/2}$ term both go to zero for crystalline ferromagnets but possess finite values in the case of amorphous ferromagnets. In addition, the coefficient of the $T^{3/2}$ term in amorphous magnets is expected to be roughly two orders of magnitude [99] larger than that of $T^2$ term. Thus, the spin-disorder model predicts that at low temperatures, $\rho_{SD}(T)$ should vary as $T^{3/2}$ in amorphous ferromagnets in contrast with the $T^2$ variation in crystalline systems [87,99].
1.9.7. Quantum corrections to the resistivity

In highly disordered systems, the motion of electrons at low temperatures is diffusiv rather than ballistic [85] and this realization has prompted many workers [100-103] to propose quantum corrections to the normal Boltzmann conductivity arising from enhanced electron-electron interaction (EEI) effects and Quantum interference (QI) or weak localization (WL) effects. The conduction electrons in disordered systems with high values of resistivity undergo more frequent collisions than in crystalline systems. Such an increased scattering reduces the effective electronic screening and hence enhances the electron-electron interactions. The enhanced electron-electron interaction gives rise to an additional contribution to conductivity, which can be expressed as [101]

\[ \Delta \sigma_{\text{EEI}}(T) = \left[ \sigma(T) - \sigma(0) \right]_{\text{EEI}} = \left( \frac{e^2}{4 \pi^2 \hbar} \right) \sqrt{2} \left( \frac{4}{3} - \frac{3}{2} \left( \frac{\hbar}{k_B T} \right) \right) \left( \frac{k_B T}{\hbar D} \right)^{1/2} \]  

(1.67a)

with

\[ \tilde{F}_o = \left( \frac{32}{3F} \right) \left[ \left( \frac{1 + \frac{1}{2} F}{} \right)^{3/2} - \frac{3}{4} F - 1 \right] \]  

(1.676)

where \( F \) is the average static screened coulomb interaction potential over the Fermi surface and \( D \) is the diffusion constant. Eq.(1.67a) rewritten in the following form represents the EEI contribution to resistivity

\[ \frac{\rho_{\text{EEI}}(T)}{\rho_{\text{EEI}}(0)} = 1 - \rho_{\text{EEI}}(0) \left( \frac{1.294}{\sqrt{2}} \right) \left( \frac{4}{3} - \frac{3}{2} \tilde{F}_o \right) \left( \frac{k_B T}{\hbar D} \right)^{1/2} \]  

(1.68)

The contribution to total resistivity due to the electron-electron interaction is thus proportional to \( \sqrt{T} \).

In addition, the electrons in disordered systems undergo multiple scattering and the electron mean free path is of the order of the interatomic spacing. At low temperatures, these collisions are elastic, and hence the electron wave functions retain their phase over large distances. Therefore, there exists a finite probability for two partial waves of the electron, originating from a point (origin) and propagating in opposite directions on a given path, to return to the origin in phase and interfere constructively. In other words, the multiple elastic scattering leads to a phase coherence between partial waves scattered from nearby ions and hence enhances the probability for an electron to return to its origin. The electron localization gives rise to high resistivity in disordered materials. If the disorder is strong enough, the electrons get completely localized leading to a transition from metallic to the insulating state. However, if the disorder is not sufficiently strong, the above-mentioned weak localization or quantum interference effects become important. As the temperature is increased from absolute zero, the inelastic electron-phonon scattering tends to destroy the phase coherence and thereby leads to an increase in conductivity.
In addition, a number of other scattering processes such as inelastic electron-magnon scatter
in $\omega$, external magnetic field and Zeeman splitting of spin sub-bands can also destroy the phase
coherence and delocalize electrons. The final expression for the contribution to total resistivity
arising from weak localization in the presence of spin-orbit and inelastic scattering and including
the splitting of spin sub-bands, is given by [102-104]

$$\rho_{WL}(T) = \rho_{WL}(0) \left[ 1 - \rho_{WL}(0) \left( \frac{e^2}{2\pi^2\hbar} \right) \left( \frac{\epsilon}{c\hbar} \right)^{1/2} \left( 3\sqrt{B_2} - \sqrt{B_\phi} \right) \right]$$ (1.69a)

with

$$B_2 = B_{ie} + \frac{2}{3}B_{so} + \frac{4}{3}B_s$$

$$B_{ie} = B_{ie} + 2B_s$$ (1.69c)

where $B_j = (c h / 4\pi D)\tau_j$; $j = ie, so, s, \phi$ and $\tau_{ie}, \tau_{so}, \tau_{s0}$ and $\tau_s$ are the phase coherence, inelastic
scattering, spin-orbit scattering and spin scattering times, respectively. If $B_{so} < B \ll B_{ie}$, Eq.(1.69) reduces to

$$\rho_{WL}(T) = \rho_{WL}(0) \left[ 1 - \rho_{WL}(0) \left( \frac{e^2}{2\pi^2\hbar} \right) (D\tau_{ie})^{-1/2} \right]$$ (1.70)

In the case of inelastic electron-phonon interaction, the relaxation time $\tau_{ep}$ varies as $\tau_{ie}^{-1}$ a $T^p$
(where p ranges between 2 and 4) for $T < \Theta_D$ and $\tau_{ie}^{-1} \propto T$ for $T > \Theta_D$. Thus, the variation of resistivity due to weak localization effects is of the form

$$\rho_{WL}(T) \propto T^{-p/2} \quad \text{for} \quad T < \Theta_D \quad \text{(1.71a)}$$

$$\rho_{WL}(T) \propto \sqrt{T} \quad \text{for} \quad T > \Theta_D \quad \text{(1.71b)}$$

The temperature dependences of $\rho_{WL}(T)$ and $PEEI(T)$ due to weak localization and electron-electron interaction effects predicted by Eqs.(1.71) and (1.68), respectively, have been found in
a number of metallic glasses [85,105].

1.10. Aim and Scope of the Thesis

Amorphous (a-) $Fe_{90+y}Zr_{10-y}$ and $Fe_{90-x}Co_xZr_{10}$ alloys have attracted considerable attention during recent years because they exhibit widely different but interesting physical phenomena [106]. The novel physical phenomena that these alloys exhibit are: weak itinerant-electron ferromagnetism [106], invar effect [107], broad distribution of magnetic hyperfine fields with finite probability even at zero fields [108-112] and electrical resistivity minima at temperatures close to $T_C$[113]. Moreover, the alloys with $y = 0$, 1 and $0 < x < 4$ present an additional feature
in that a transition to a spin-glass (SG)-like state, known as reentrant (RE) state, occurs at a temperature $T_{RE}$, which lies well below the paramagnetic (PM) to ferromagnetic (FM) phase transition (Curie) temperature, $T_C$. The PM-FM, PM-SG and FM-RE phase transition lines for $a - Fe_{90+y}Zr_{10+y}$ alloys meet at 93 at.\% Fe. The nature of the reentrant state and the transition to such a state remained controversial (due to the conflicting results reported in the literature) until recently when the direct observation of magnetic domains even in the RE state by Lorentz electron microscopy [119] and Kerr-effect method [120] as well as the neutron depolarization measurements [121] coupled with magnetic and Mossbauer results [118] unambiguously demonstrated that the reentrant state is a mixed state in which cluster spin-glass order coexists with long-range ferromagnetic order and that the transition to such a state is not a true thermodynamic phase transition.

Failure to detect any propagating features in the inelastic neutron scattering experiments [122] on $a - Fe_{91}Zr_{g}$ at any temperature $T < T_c$ within the momentum transfer range $0.05 \, \AA^{-1} < q < 0.12 \, \AA^{-1}$ has been interpreted as a total absence of spin waves in $a - Fe_{90+y}Zr_{10+y}$ alloys. However, detailed analysis of spontaneous magnetization data [123] on $a - Fe_{90+y}Zr_{10+y}$ alloys revealed that spin wave excitations are mainly responsible for thermal demagnetization at low temperatures, while single-particle excitations plus local spin-density fluctuations (LSF) and LSF dominantly contribute to the decrease of magnetization in the intermediate temperature range and for temperatures close to $T_C$, respectively. A similar type of conflicting reports have also been made for $a - Fe_{90+y}Zr_{10+y}$ alloys. While early BM study [106] on the $a - Co_{90}Zr_{10}$ alloy (which does not exhibit reentrant behaviour at low temperatures and behaves like a conventional ferromagnet down to the lowest temperature [106]) provides strong evidence for weak-itinerant ferromagnetism in this alloy, the recent low-temperature specific heat measurements [124] on $a - Fe_{90+y}Co_x Zr_{10}$ alloys indicate that the Co-rich alloys, including $a - Co_{90}Zr_{10}$, behave like strong-itinerant ferromagnets. These contradictions have been the main motivating factors for a detailed study of the low-lying magnetic excitations in $a - Fe_{90+y}Zr_{10-y} Zr_{10}$ and $a - Fe_{90-x}Co_x Zr_{10}$ alloys.

In addition, the FM-PM phase transition in the above mentioned amorphous alloy series has given rise to much controversy [116,125] in the recent years because the early BM data [126,127] taken in the critical region yielded values for the spontaneous magnetization and 'zero-field' susceptibility critical exponents $\beta$ and $\gamma$ that are 1.4 times larger than those theoretically predicted for an isotropic 3D Heisenberg ferromagnet. These unphysically large exponent values have been taken to reflect large fluctuations in the exchange interactions and a transition to the spin glass state directly at $T_C$. Subsequent analysis of new high-precision BM data [125,128] on $a - Fe_{90}Zr_{10}$ and reanalysis of earlier BM data [125] on $a - Fe_{91}Zr_{g}$ and $a - Fe_{92}Zr_{8}$ alloys as well as the ac susceptibility results [125,129] revealed that the values of the critical exponents $\beta$, $7$ and $6$ (exponent for the critical isotherm) are close to the theoretically predicted estimates for 3D Heisenberg ferromagnets. This raises serious doubts about the genuineness of
the unphysically large exponent values reported [127] for \( a - Fe_{90-y}Co_yZr_{10} \) alloys. Moreover, the exponent values reported earlier in the literature are only the effective exponents and the true asymptotic values that the theory predicts. This necessitated a detailed study of thermal critical behaviour in \( a - Fe_{90+y}Zr_{10-y} \) and \( a - Fe_{90-y}Co_yZr_{10} \) alloys.

The thermal critical behaviour associated with the FM-PM phase transition at \( T_c \) had been extensively studied experimentally in a number of amorphous as well as crystalline systems. By comparison, a similar study of percolation behaviour near the critical concentration or percolation threshold, \( p_c \) (at which PM-FM, PM-SG and FM-RE phase transition lines meet) has received little or even no attention for various reasons. While dilute magnets with quenched disorder have long been regarded as model systems [73] to study percolation critical behaviour, the sole attempt [130] to experimentally determine the percolation exponents for such systems reported in the literature is plagued with thermal-to-percolation crossover effects. All the theoretical models, proposed so far to describe percolation phenomena, treat site- or bond-percolation on a regular crystalline lattice and assume [70-75] the validity of the famous Harris criterion even in the strong disorder limit to describe the percolation critical behaviour of quenched random site- or bond-diluted ferromagnets. Furthermore, the nature of magnetism in \( a - (Fe_pNi_{1-p})_{80}(B,Si)_{10} \) and \( a - (Fe_pNi_{1-p})_{80}P_{14}B \) alloys is not clearly understood as conflicting results with regard to strong or weak itinerant ferromagnetism in these alloys exist in the literature (as was the case for the \( a - Fe_{90-y}Co_yZr_{10} \) alloys too). In order to test the validity of the predictions of existing percolation theories and to resolve the controversy surrounding the nature of magnetism in these alloys, a detailed study of low-lying magnetic excitations and percolation critical behaviour in them was undertaken. The main reasons for the choice of these alloy systems for the intended type of study are: (i) unlike amorphous \( Fe - ZT \) alloys, these alloys exhibit the critical concentration \( p_c \) on the \( Fe-\)poor side, (ii) \( Ni \) atoms in them carry negligibly small moment [131] and hence act as magnetic dilutents (i.e., essentially quenched random site-dilution occurs when \( Fe \) is progressively replaced by \( Ni \)), (iii) the thermal correlation length in \( (Ni - Fe)-metalloid \) alloys diverges at \( T_c \) even for compositions close to \( p_c [132] \), (iv) the thermal critical behaviour for concentrations close to \( p_c \) in these alloy systems has already been exhaustively studied [57,59,133], and (v) inelastic neutron scattering experiments have revealed that well-defined spin wave excitations [134] exist for \( p > p_c \) in such systems.

The electrical resistivity [113,135-137] in \( a - Fe_{90+y}Zr_{10-y} \) and \( a - Fe_{90-y}Co_yZr_{10} \) alloy systems as a function of temperature goes through a minimum at temperatures \( T_{\text{min}} = T_c \approx 250 \) K compared to that \( (T_{\text{min}} - 12 \) K) in amorphous 3d transition metal-metalloid alloys. A large temperature range below \( T_{\text{min}} \) in these alloys, therefore, facilitates a detailed study of the effect of enhanced electron-electron interaction, weak localization or quantum interference and magnetic excitations such as magnons, single particle excitations and local spin-density fluctuations (LSF) on the temperature dependence of electrical resistivity. Moreover, such an investigation enables us to ascertain whether a 'one-to-one' correspondence exists between the
results of BM and electrical resistivity measurements so far as the magnetic excitations in these alloys is concerned.

Keeping the above remarks in mind, the main objectives of this thesis are:

(i) To make an in-depth study of low-lying magnetic excitations in $a - Fe_{90+y}Zr_{10-y}$, $Fe_{90-x}Co_xZr_{10}$, ($Fe_pNi_{1-p}B_{80}(B, Si)$ and $a - (Fe_pNi_{1-p})_{80}P_{14}$ alloys.

(ii) To investigate the thermal critical behaviour of $a - Fe_{90+y}Zr_{10-y}$ and $a - Fe_{90-x}Co_xZr_{10}$ alloys in detail.

(iii) To test the validity of the predictions based on the percolation theories and to determine percolation exponents for three-dimensional quenched random site-diluted ferromagnets.

(iv) To identify the various scattering mechanisms responsible for resistivity minima in $a - Fe_{90+y}Zr_{10-y}$ and $a - Fe_{90-x}Co_xZr_{10}$ alloys and to determine their relative magnitudes.

In order to achieve the above mentioned objectives, experimental probes such as bulk magnetization, ferromagnetic resonance and electrical resistivity were chosen. Apart from the introduction chapter, the thesis contains four chapters. The second chapter deals with the experimental details whereas the remaining three chapters describe the present results and discuss them under the headings Low-lying magnetic excitations, Thermal and Percolation critical behaviour, and electrical resistivity. Each of these three chapters is self-contained in the sense that following a thorough discussion of the relevant experimental results, the conclusions are summarized and the references cited are listed at end of each chapter.
References


