CHAPTER II

Electrical Transport Measurements

2.1 Introduction

Detailed investigations on transport properties of solids provide valuable information about the electronic structure and various scattering processes that are responsible for the electronic transport. Glasses, produced by rapid quenching, also show a fill[ spectrum of electronic behaviour similar to that of crystalline solids. That is, glasses show properties, which range from those of a superconductor, normal metallic conductor, semiconductor to that of an insulator. Theoretical interpretation of the electronic transport in glasses has been a difficult problem due to the lack of translational invariance in their atomic arrangement. Another difficulty arises from the fact that the electron mean free path is very small in highly disordered glassy alloys. Studies on the transport properties of metallic glasses have shown some peculiar and
interesting features which seem to be characteristic of the glassy state [1-4]. Among various transport coefficients, electrical resistivity is the one which is simpler in measurement and provides bulk of valuable information on the electronic transport. It is a sensitive probe to study structural disorders and various scattering processes that occur in a given material and to study phase transformations as well as phase transitions. However, it is by no means trivial to interpret the observed magnitude of resistivity and its temperature dependence in amorphous/highly disordered metals. This is because, in addition to the dependence on the intrinsic mechanisms involved, the electrical resistance is also sensitive to factors like possible differences in the free volume in an amorphous solid, as a consequence of different rates at which a melt has been rapidly quenched [5], structural relaxation [6], changes in local atomic arrangement [7], remnant crystallinity [8] and electron mean free path of the order of interatomic spacing in the solid [9], to name a few.

Resistivity studies on metallic glasses as a function of composition, temperature, magnetic field and other parameters have been reported extensively to understand their electronic transport behaviour. In particular, resistivities of iron-rich metallic glasses which are based on a composition $\text{Fe}_{80}\text{M}_{20}$ or close to it, where $\text{M}$ is a single metalloid or a combination of metalloids like B, Si, P and C have been extensively reported in literature, in which element like Ni, Cr and Co have been partially substituted for Fe [10-17].

The behaviour of electrical resistivity of amorphous metallic alloys, is in general, quite different from that of the corresponding crystalline systems. First it is possible to produce metallic glasses for a given system like Fe-B, Fe-Si-B, Ni-Zr, Ni-P etc with a continuous range of room temperature resistivity values by changing composition within the range in which the amorphous nature is preserved.

A few of the salient features of the electrical resistivity data taken on a large number of metallic glasses with regard to the variation of electrical resistivity ($\rho$) with temperature can be summarized as below [2,18-21]

(a) The room temperature resistivities, $\rho(\text{RT})$, and residual resistivities, $\rho_o$, of amorphous alloys are considerably larger than those of their crystalline counterparts, but are of similar magnitude as that of the corresponding liquids.
This is because the dominant scattering mechanism responsible for resistivity is scattering from the structural disorder \[2,18-21\]

(b) The overall change in the resistivity of a metallic glass from low temperature (-4 K) to that nearest at its crystallisation temperature is usually less than \(10^6\) [1]

(c) The temperature coefficient of resistivity (TCR) in some metallic glasses can be changed continuously from positive to negative by changing its composition continuously like in Ni-P system [21-a] The temperature coefficient of resistivity, (TCR), defined as \(a = \rho^{-1}(d\rho/dT)\), is small and usually positive for alloys with \(\rho_o < 150 \mu\Omega\cdot\text{cm}\) and negative for alloys with \(\rho_o \cdot 150 \mu\Omega\cdot\text{cm}\), over a wide range of temperature [3,4,17,22] Such a relation between the magnitude of \(\rho_o\) and TCR has come to be known as the Mooij correlation [23]

(c) In a number of alloys containing large amounts of ferromagnetic and antiferromagnetic elements, resistivity as a function of temperature goes through a minimum (\(\rho_{\text{min}}\)) at a temperature \(T_{\text{min}}\) in the temperature range 4-300 K, below which \(\rho\) shows either \(\ln T\) or \(T^{-1}\) dependence with temperature [24-27] and at higher temperatures resistivity saturates to a value \(\sim 150 \mu\Omega\cdot\text{cm}\)

The resistivity minimum in most of the 3d transition metal-metalloid alloys occur at temperatures as low as 20 K [2,19-21,28,29], but in some transition metal based alloys containing Cr, Mn, Mo, V, W, etc the resistivity minimum can occur at temperature \(T > 250\) K [2,19-21,30] A number of theoretical models have been proposed to explain the resistivity minimum, and the corresponding low temperature resistivity anomaly and other characteristic features of resistivity behaviour in amorphous materials, but none of these models, on its own, can describe the variation of resistivity in the entire temperature range Matheissen’s rule which states that the contributions to total resistivity of a solid arising from different scattering mechanisms are additive, is also considered to be valid in amorphous solids Therefore, one needs to take into account of all possible known scattering mechanisms to explain the observed resistivity behaviour as a function of temperature, magnetic field etc

In this chapter we present the results of resistivity measurements on a-
\( \text{Fe}_{68}\text{Ni}_{1+\lambda}\text{Mo}_x\text{Si}_{2}\text{B}_{16} \) (\( x=0,1,2 \) and 3) as a function of Mo concentration and temperature and try to interpret these within the framework of current theoretical models available

### 2.2 Theoretical Models

Over the years a number of theories have been proposed to interpret the experimentally observed anomalous resistivity behaviour in amorphous metallic alloys, magnetic as well as non-magnetic, as a function of composition and to predict the exact form of its temperature dependence. These include

1. Ziman-Faber diffraction model
2. Mott s-d scattering model
3. Two level tunneling model
4. Localisation and electron interaction/Quantum interference effects.

#### 2.2.1 Ziman-Faber Diffraction Model

This model considers the effect of scattering of conduction electrons from the potential of the disordered lattice. Originally proposed by Ziman \footnote{31} for simple liquid metals, this theory is based on the following assumptions \footnote{2,21,31}

- The electronic transport properties can be described by the Boltzmann transport equation.
- The interaction between the conduction electrons and ions can be described by a pseudo potential.
- The conduction electrons are assumed to be nearly free \( (i.e., k_f \gg l, k_f \) is the Fermi wave vector, \( l \) is the electron mean free path) and the scattering potential is weak enough to be treated by first-order perturbation theory \( \text{(Born approximation is valid)} \).

Evans et al \footnote{32} extended the Ziman theory to include liquid transition metals in the transport properties of metallic glasses by using the muffin-tin potential and arrived at the following expression for resistivity \footnote{2,19,21,32,33}.
\[ \rho = \frac{30\pi \hbar^3}{me^2 k_F^2 E_F \Omega} \sin^2 \left[ \eta_2(E_F) \right] S_T(2k_F) \] (21)

where \( k_F \) and \( E_F \) are the Fermi wave vector and Fermi energy respectively. \( \Omega \) is the atomic 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, at \( k = 2k_F \). 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 [33] of calculating the \( S_T(k) \). However, the one using a Debye Spectrum due to Nagel [33] yields the expression

\[ S_T(k) = 1 + \left[ S_0(k) - 1 \right] e^{-2w_T(k)} \] (22)

where \( S_0(k) \) is the static (equilibrium) structure factor and \( e^{-2w_T(k)} \) is the Debye-Waller factor, with \( W_k(T) \) in the Debye approximation given by \[28,34\]

\[ W_k(T) = W_k(0) + 4W_k(0) \left( \frac{T}{\theta_D} \right)^2 \int_0^T \frac{zdT}{e^T - 1} \] (23)\text{a}

where

\[ W_k(0) = \frac{3\hbar^2 k^2}{2Mk_F \theta_D} \] (2.3)\text{b}

where \( M \) is the atomic mass, \( \theta_D \) is the Debye temperature, \( k \) is the wave vector and \( k_F \) is the Boltzmann constant. Substituting Eq (2.3) in Eq. (2.2), one obtains [28]

\[ \rho_{str}(T) = \frac{30\pi \hbar^3}{me^2 k_F^2 E_F \Omega} \sin^2 \left[ \eta_2(E_F) \right] \left[ 1 + S_0(2k_F) - 1 \right] e^{-2[w(T) - w(0)]} \] (2.4)

where \( \rho_{str} \) is the structural contribution to \( \rho \) and \( W(T) = W_{2k_F}(T) \) 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.,

\[ W(0) = W_{2k_F}(0) = \frac{3\hbar^2 k_F^2}{2Mk_F \theta_D} \] (2.5)

dropping the subscripts \( 2k_F \) and \( \text{str} \) for simplicity, the temperature coefficient of resistivity (TCR), \( \alpha \), can be calculated from Eq (2.4) as [28]

\[ \alpha = \frac{1}{\rho} \left( \frac{d\rho}{dT} \right) = 2 \left[ \frac{1 - S_T(2k_F)}{S_T(2k_F)} \right] \frac{\partial W(T)}{\partial T} \]
Since \( \frac{\Delta W(T)}{\Delta T} > 0 \) for all temperatures, Eq (2.6) demonstrates that \( a \) is negative if \( S_\tau(2k_\text{F}) > 1 \) and positive if \( S_\tau(2k_\text{F}) < 1 \). The relative positions of \( 2k_\text{F} \) and \( k_p \), the wave vector at which the first peak in \( S(k) \) appears, determines the sign of \( a \). In other words, negative TCR is expected only when \( 2k_\text{F} \) lies close to \( k_p \) whereas a positive TCR is expected when \( 2k_\text{F} \) is far away from \( k_p \).

In low and high temperature asymptotic limits, Eq (2.4) simplifies to:

\[
\rho(T) \sim C + BT^2 \quad \text{for } T \ll \theta_D \quad (2.7a)
\]
\[
\rho(T) \sim C' + BT \quad \text{for } T \gg \theta_D \quad (2.7b)
\]
where the constants \( C, B, C', \) and \( B' \) are related to various parameters in Eq (2.4). 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. (2.4) is written in a different form [28] as

\[
\tau(T) = \frac{\rho(T)}{\rho(0)} = a_1 + a_2 e^{-2[\omega(T) - \omega(0)]}
\]

\[
= a_1 + a_2 \exp \left[ -8W(0) \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D} \frac{zd\zeta}{e^\zeta - 1} \right] \quad (2.8a)
\]

with

\[
a_1 = \left\{ 1 + \left[ S_\tau(2k_\text{F}) - 1 \right] e^{-2[\omega(T) - \omega(0)]} \right\}^{-1} \quad (2.8b)
\]

and

\[
a_2 = a_1 S_\tau(2k_\text{F}) - 1 \quad (2.8c)
\]

where \( T_0 = 273.15 \) K is the ice temperature.

or

\[
S_\tau(2k_\text{F}) = 1 + \frac{a_2}{a_1} \quad (2.9)
\]

One can also estimate \( \theta_D \) for a given glass from the Eqs. (2.7a) and (2.7b), since

\[
\alpha = \frac{1}{\rho_{RT}} \left[ \frac{d\rho}{dT} \right] \frac{C}{\theta_D} \quad \text{for } T \gg \theta_D \quad (2.10)
\]

\[
\beta = \frac{1}{\rho_{RT}} \left[ \frac{d\rho}{dT^2} \right] = \frac{\pi^2}{6} \left( \frac{C}{\theta_D^2} \right) \quad \text{for } T \ll \theta_D \quad (2.11)
\]

where \( C \) is a constant. From Eqs. (2.10) and (2.11), we get
The diffraction model has been successful in describing the electrical resistivity behaviour of a large number of low resistivity (\(\rho < 150 \ \mu\Omega\cdot\text{cm}\)) amorphous alloys. However, the model does not give an adequate description in the case of high resistivity glassy materials.

### 2.2.2 Mott s-d Scattering Model

This model, originally proposed by Mott [9] 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, resulting in high resistivities. In the case of transition metal alloys, the electrical resistivity, \(\rho\) is composed of two parts, \(\rho = (\rho_s + \rho_d)\), where \(\rho_s\) is the contribution from the sp-band and \(\rho_d\) is that from the d-band. The basic assumption is that the effective mass of the d-electrons is too large for them to contribute significantly to the conduction process [22].

Since the number of vacant states in a d band is proportional to the d-density of states (DOS), \(N_d(E_f)\), the electrical resistivity is proportional to \(N_d(E_f)\). The temperature dependence of resistivity arises because of the shift in Fermi energy level, \(E_f\), with increasing temperature. The expression for resistivity, given by this model is [2,9,21]

\[
\rho_{\text{mott}}(T) = \rho(0) \left[ 1 - \frac{\pi^2}{6} (k_B T)^2 \left( \frac{N'(E_f)}{N_d(E_f)} - \frac{N''(E_f)}{N_d^2(E_f)} \right) \right]
\]

or

\[
\left[ \frac{1}{N_d} \frac{dN_d}{dE} - \frac{1}{N_d} \frac{d^2N_d}{dE^2} \right]_{E_f}^{E_f}
\]

where \(N'(E_f)\) and \(N''(E_f)\) are the first and second energy derivatives of DOS at \(E = E_f\), respectively.

If one assumes that the d band is nearly full, and that \(N_d(E) = C(E_0 - E)^{1/2}\), where \(E_0 < E\), then Eq (2.13) reduces to
\[ \rho(T) = \rho(0) \left[ 1 - \frac{\pi^2}{6} (k_B T)^2 (E_0 - E_F)^{-2} \right] \]  \hspace{1cm} (2.14)

where \( E_0 \) is the energy of the filled d-band level.

Thus, \( \rho(T) \) should decrease as \( T^2 \) with increasing \( T \). If one includes the effect of temperature dependence and smearing of the d-band density of states [35] one finds that it leads to a contribution of \( \rho(T) \) which can either increase or decrease with \( T \) in a manner consistent with Mooij correlation.

This model gives rise to a large negative value of TCR if the Fermi level lies in a region where the d band is rapidly varying. However, such a model would be applicable only to those systems where there is a significant difference in the mobilities of the s and d electrons. For very high resistivity materials, where all mobilities are very low, this model breaks down. The energy derivatives of \( N_d(E) \) at \( E_F \) for amorphous metals are expected to be extremely small, and hence, the Mott model when applied to amorphous materials gives a weak temperature dependence of resistivity [21].

### 2.2.3 Two Level Tunneling Model

The observation of resistivity minimum in a large number of amorphous alloys, regardless of whether they are magnetic or non-magnetic, 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 [25], which is the structural analogue of the Kondo model [36]. The amorphous state is a highly metastable state and there exists a number of local atomic configurations which are energetically equivalent leading to 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) [2,20,21,24]. The TLS model due to Cochrane et al [25] considers a potential well with two minima of equal energy and asserts that the electron scattering by such two level states is analogous to Kondo scattering, giving rise to a contribution to the resistivity, which increases with decreasing temperature. This approach leads to the following expression for the contribution to the total resistivity arising from electron-TLS scattering [2,20,21,25]

\[ \rho_{TLS}(T) = -C \ln(k_B T^2 + A^2) \]  \hspace{1cm} (2.15)
where C is a constant, whose magnitude depends only on the number of sites and the strength of Coulomb interaction, $2k_B\Delta$ is the energy splitting between the tunneling states. If $\Delta$ is small, then $p(T)$ will vary as $-C'\ln T$, where $C'$ is a new constant. Tsuei [27] has suggested that this mechanism is most probably responsible for producing a TCR<0, i.e., negative over a wide temperature range in high resistivity metals. He found that a better fit to the resistivity data of amorphous $(Ni_{50}Pd_{25})_{73.5}P_{26.5}$ is given by the resistivity contribution of the form,

$$p(T) = \rho_0 \, C \ln(k_B T^2 + \Delta^2)$$  \hspace{1cm} (2.16)

rather than $p(T)$ proportional to $T$ at higher temperatures as predicted by the Ziman theory.

Thus, this model predicts that resistivity increases as the temperature is lowered and finally saturates at low temperatures.

### 2.2.4 Weak Localisation and Quantum Interference Effects

In highly disordered systems in which the electron mean free path is of the order of atomic spacing, motion of electrons at low temperatures is diffusive rather than ballistic [21] and this realization has prompted many workers [37-40] to propose quantum corrections to the normal Boltzmann conductivity, arising from enhanced electron-electron interaction (EEI) effects and quantum interference (00 or weak localisation (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 thus enhances the electron-electron interactions. The enhanced electron-electron interaction gives rise to an additional contribution to conductivity, which can be expressed as [38]

$$\Delta\sigma_{\text{EEI}}(T) = \left[\sigma(T) - \sigma(0)\right]_{\text{EEI}} = \frac{e^2}{4\pi\hbar^2} \left[\frac{1.294}{\sqrt{2}} \left(\frac{4}{3} - \frac{3}{2} F_\sigma\right)\right]^{1/2}$$  \hspace{1cm} (2.17a)

$$F_\sigma = \frac{32}{3F} \left[\frac{1}{2} F^2 - \frac{3}{4} F - 1\right]$$  \hspace{1cm} (2.17b)

where $F$ is the average static screened Coulomb interaction potential, over the Fermi surface and $D$ is the diffusion constant. Eq. (2.17) represents the EEI contribution to resistivity.
The contribution of electron-electron interaction to total resistivity is thus proportional to $\sqrt{T}$. It turns out that the effect of this Coulomb anomaly is an additional contribution to the resistivity, which varies as $-T^{-1.2}$ at low temperatures (below 20 K). This effect was first noticed by Rapp et al. [41] in magnetic metallic glasses. Since then it has been found in a number of metallic glasses, magnetic and non-magnetic type.

In addition, electrons in disordered systems undergo multiple scattering when the electron mean free path is of the order of the interatomic spacing. At low temperatures, these collisions are elastic, and hence the electron wavefunctions retain their phase over large distances. Therefore, there exists a finite probability for the 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, multiple elastic scattering leads to phase coherence between the partial waves scattered from nearby ions and hence enhances the probability for an electron to return to its origin, hence of `localisation' [21]. The result of this electron localisation process is that the electrical resistivity in the presence of such scattering in disordered materials is higher than would be calculated from the quasi-classical Boltzmann approach. If the disorder is strong enough, the electrons can get completely localised leading to a transition from metallic to the insulating state. However, if the disorder is not sufficiently strong, the weak localisation or quantum interference effects leads to relatively higher resistivity. Since phase coherence is responsible for the weak localisation, this also means that any process, which destroys the phase coherence of the two electron partial waves will reduce the additional resistivity (due to localisation). A process, which is known to destroy the phase-coherence, is inelastic scattering. As the temperature is increased from absolute zero, the inelastic electron-phonon scattering sets in at finite temperatures which tends to destroy the phase coherence and thereby leads to an increase in conductivity or a decrease in the resistivity, a result opposite to the normally observed behaviour in metals in which the resistivity should increase with rise in temperature due to electron-phonon scattering.
Mott and Kavesh [42] and later Howson [43] made suggestions that the resistivity minimum in metallic glasses may be due to a competition between a negative TCR due to QIE, mentioned above, and a positive TCR due to the normal Boltzmann conductivity. Whether the conductivity due to the QIE will dominate or the Boltzmann conductivity will dominate is determined by the ratio of inelastic scattering time to elastic scattering time \((\tau_i/\tau_e)\). At low temperatures, \(\tau_i\) is always greater than \(\tau_e\) so QIEs may determine the behaviour of \(\sigma(T)\). Mott and Kavesh [42] have predicted that \(T_m \propto \rho^{-2}\), where \(T_m\) is the temperature at which minimum resistivity is observed. Mickey et al. [44] have shown that QIEs are not likely to be responsible for a low temperature resistivity minimum except in alloys with a very weak spin-orbit coupling.

A number of other scattering processes, such as inelastic electron-magnon scattering, external magnetic field and Zeeman splitting of spin sub-bands, can also destroy the phase coherence and delocalise the electrons. The final expression for the contribution to total resistivity arising from weak localisation in the presence of spin-orbit and inelastic scattering and including the splitting of spin sub-bands, is given by [39,40,45],

\[
\rho_{w1}(T) = \rho_{w1}(0) \left[1 - \rho_{w1}(0) \left(\frac{e^2}{2\pi^2 \hbar^2} \left(\frac{e}{\hbar}\right)^{1/2} \left(3\sqrt{B_2} - \sqrt{B_\phi}\right)\right)^2\right] \tag{2.19a}
\]

with

\[
B_2 = B_{ic} + \frac{4}{3} B_{so} + \frac{2}{3} B_s \tag{2.19b}
\]

\[
B_\phi = B_{ic} + 2B_s \tag{2.19c}
\]

where \(B_j = \left(\frac{\gamma}{4e\hbar \Gamma_j}\right)\), \(j = \text{ie}, \text{so}, \phi\) and \(\Gamma_\text{ie}, \Gamma_\text{so}, \Gamma_\phi\) are the phase coherence, inelastic scattering, spin-orbit scattering and spin scattering times, respectively. If \(B_{so} \ll B \ll B_{ic}\), Eq. (2.19a) reduces to

\[
\rho_{w1}(T) = \rho_{w1}(0) \left[1 - \rho_{w1}(0) \left(\frac{e^2}{2\pi^2 \hbar^2} \left(\frac{e}{\hbar}\right)^{1/2} (\Gamma_{ic})^{-1/2}\right)^2\right] \tag{2.20}
\]

In the case of inelastic electron-phonon interaction, the relaxation time \(\tau_{cp}\) varies as

\[
\tau_{cp}^{-1} \propto T^p \text{ (where } p \text{ ranges from } 2 \text{ to } 4 \text{) for } T < \theta_H \text{ and}
\]
Thus, the resistivity due to weak localisation effects is of the form,

\[ \rho_{\text{w1}}(T) \propto -T^p \quad \text{for } T<\theta_0 \]
\[ \rho_{\text{w1}}(T) \propto T^{1.2} \quad \text{for } T>\theta_0 \]

(2.21a, 2.21b)

The temperature dependence of \( \rho_{\text{w1}}(T) \) and \( \rho_{\text{ee}}(T) \) due to weak localisation and electron-electron interaction effects predicted by Eqs (2.21) and (2.18), respectively, have been found in a number of metallic glasses [21,46]

### 2.2.5 Magnetic Contribution to Resistivity

The existence of significant magnetic contribution to the electrical resistivity in magnetically concentrated amorphous alloys like Fe80B20, though expected, has been ignored earlier [47]. Earlier workers [8,17] tried to explain the intermediate and high temperature dependence of resistivity in terms of the diffraction model [33], which takes into account not only the scattering of conduction electrons by the ion-cores that carry a muffin-tin potential but also the change in the shape of the structure factor, \( S(k) \), with temperature. The reasons for this appear to be twofold: firstly in both magnetic and non-magnetic glasses, the resistivity shows same temperature dependence in the intermediate and high temperature regions. Secondly, the diffraction model yields quadratic and linear temperature dependence of \( \rho \) at low (\( T<9 \Delta \)) and high (\( T>6\Delta \)) temperature, respectively. There are several works, which contradicted the simple \( T^2 \) dependence of resistivity for ferromagnetic alloys at intermediate temperature [32,48]. A sharp anomaly in the temperature derivative of resistivity at the Curie temperature, reminiscent of the critical resistivity behaviour, normally found in crystalline ferromagnets, has been observed in such glasses [49]. These observations assert that in addition to a contribution due to scattering of conduction electrons from the structural disorder, electron magnon scattering (which at low temperatures gives rise to a quadratic temperature dependence for crystalline ferromagnetic 3d transition metals) should also give a contribution to \( \rho \) in magnetic glasses and hence the approach of completely neglecting the magnetic contribution to resistivity, \( \rho_{\text{mag}}(T) \), while analyzing the resistivity data on FM glasses is not exactly correct. Theoretical investigations [50,51] that pursue this line of thinking and use
spin-wave approximation to calculate $\rho_{\text{mag}}(T)$ for amorphous ferromagnets is given below.

The spin-disorder model, applicable to FM materials, deals with the scattering of conduction electrons by spin waves. The spin-disorder model for amorphous ferromagnets developed by Richter et al [51], considers a Heisenberg spin system in which spins are localised at the sites of an amorphous network and conduction electrons get scattered from these localised 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 [28,51]

$$
\rho_{\text{SD}}(T) = \rho_{\text{SD}}(0) \left\{ 1 + \frac{\Omega_c^2}{(2\pi)^2 S} \left[ \frac{3}{2} \xi \left( \frac{3}{2} \right) \left( \frac{k_BT}{D_{\text{sw}}} \right)^3 \right] + \frac{1}{J_s(2k_F)} \left[ \frac{\pi^2}{3 \xi} \left( \frac{k_BT}{D_{\text{sw}}} \right)^2 - F(T) \right] \right\} \tag{2.22a}
$$

with

$$
\rho_{\text{SD}}(0) = \left( \frac{2\Omega_c}{3h^3} \right) \left[ \frac{\Omega}{\Omega_c} \right] mS_{\text{sd}} \left( \frac{2k_F}{\Omega} \right) \tag{222b}
$$

where $N_c$ is the number of electrons, $\Omega_c$ and $\Omega$ are the atomic and sample volumes, respectively. $S$ is the spin of the local atomic magnetic moment, $D_{\text{sw}}$ is the spin wave stiffness coefficient, $\Gamma$ and $\xi$ are the gamma and Riemann Zeta functions, respectively, $J_{\text{sd}}$ 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 $T^3$ term in the Eq (222a) is the net result of a partial cancellation of two competing $T^{12}$ 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 dependant local moments decreasing with increasing temperature, whereas the $T^2$ term in Eq (222a) 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. Both $\rho_{\text{SD}}(0)$ and the $T^{3/2}$ term are zero for crystalline ferromagnets.
but possess finite values in the case of amorphous ferromagnets. In addition, the coefficient of $T^{3\frac{1}{2}}$ term in amorphous magnets is expected to be roughly two orders of magnitude [51] larger than that of $T^{2}$ term. Thus, the spin-disorder model predicts that at low temperatures, $\rho_{\text{si}}(T)$ should vary as $T^{4\frac{1}{2}}$ in amorphous ferromagnets in contrast with the $T^{2}$ variation in crystalline systems [28,51]. However, measurements on some magnetic metallic glasses reveal that the competing contributions to $\rho_{\text{mag}}(T)$ due to the incoherent and elastic components of electron-magnon scattering almost balance each other so that at low temperatures the $T^{3\frac{1}{2}}$ term is negligibly small compared to the $T^{2}$ term [28].

In addition to the above models, other theoretical works, viz. the Kondo-Spin Flip model [36], the coherent exchange scattering model [52] have also been proposed which calculate the magnetic contribution to $\rho$ in dilute magnetic alloys and rare earth based alloys respectively.

2.3 Experimental Details

Electrical resistivity measurements for $a$-$Fe_{68}Ni_{14-x}Mo_xSi_2B_{16}$ ($x=0,1,2$ and 3) have been carried out in the temperature range 10-300 K using a API) closed cycle refrigerator [53], the schematic diagram of which is shown in Fig 2 I. Samples were in thin ribbon form of ~25-30 μm thickness and ~5 mm width obtained from Allied Signals, (USA), prepared by melt spinning technique.

The closed cycle refrigerator works on the principle of Joule-Thomson effect. The cryogenic system is formed from basic modules which, include compressor modules, expander modules, inter-connecting hoses and interfaces. The high pressure helium gas from the compressor enters the refrigerator (expander) and the low pressure helium gas returns to the compressor. The inter-connecting hoses carry the refrigerant between the compressor module and the expander module. Together they form a closed-loop system.

The expansion of helium gas in the refrigerator has two stages one which cools the lower section of the sample well to 10 K and the other which cools the upper section of the sample well to 40 K.

The temperature of the sample area is controlled by using a resistance heater on
Fig. 2.1 Schematic diagram of closed cycle refrigerator.
the expander cold tip. Silicon diode is used as a temperature sensor. One sensor is located at the expander cold tip and the other is on the sample holder in the sample area.

A four probe dc-method was employed for the measurements. Amorphous ribbons of length 2-3 cm and 1-2 mm width were cut and to avoid local crystallisation and for better stability, current and voltage contacts were made on the sample with 42 gauge copper wire, using a silver epoxy. The sample is fixed to a sample holder using a scotch masking which can withstand low temperatures. The sample mounting permits changes in the sample dimensions during thermal cycling and thereby avoids stress-induced effects, which could otherwise affect the results in stress sensitive materials like metallic glasses. The sample space is filled with 99.99% pure helium as an exchange gas.

A schematic of the four terminal setup for electrical resistance measurements is shown in Fig 2.2. The linearity of I vs V was checked for the contacts to be ohmic. The resistance was measured using a constant current programmable source (Keithley Model No 224) and a nanovoltmeter (Keithley Model No 181). The current during the measurement is kept constant (3 mA) up to one part in $10^4$ and the voltage is measured to an accuracy of 0.01 μV and relative accuracy of 1 to 5 parts in $10^4$. Parasitic thermoelectric voltages are eliminated by reversing the polarity of current at a given temperature. The relative accuracy of resistance measurement is about a few parts per million. The temperature is monitored using a microprocessor-based temperature controller (Model 5500-1-25) to an accuracy of ±0.5 K.

In all the cases, the width of the sample and the length between the voltage leads for each measurement were measured using a travelling microscope with an accuracy of 0.01 mm. A number of readings were taken over the whole dimensions of the sample to get a good accuracy in these measurements. The measurement of thickness posed a problem because of thin samples. A sensitive screw gauge was used to measure thickness at various positions over the whole length in order to get a reasonably accurate average value of thickness. A better method would have been to measure the density and then to find out the thickness. However, since we are more interested in the temperature dependence of p, we did not follow the density method to find out the thickness due to small amount of the sample at our disposal. The error in
Keithley 181 Nanovoltmeter

Fig 2.2 Four terminal setup to measure electrical resistance
the measurement of the absolute value of $p(RT)$ mainly determined by the error in the thickness measurement. The estimated error in the absolute value of $p$ is $\pm 10\%$. However, the relative resistivity ratios are much more accurate and the error in these measurements is better than $1^\circ$ neglecting any effects due to thermal expansion or contraction.

### 2.4 Results and Discussion

The resistance measurements of Fe$_{68}$Ni$_{14-x}$Mo$_x$Si$_2$B$_{16}$ alloys have been carried out in the temperature 10-300 K. A sample with $x$ at% of Mo will be referred as $S_x$ sample hereafter. $p(RT)$ vs $x$ is shown in Fig. 2.3(a) and are listed in Table (2.1). It is observed that an increase in Mo concentration increases $p(RT)$ as found earlier in similar Mo substituted systems. Since the values of $p(RT)$ are less than 150, one expects from Mooij correlation, the temperature coefficient of resistivity $\frac{p}{dT}$, to be positive near RT. Table (2.1) lists $\frac{p}{dT}$ for all the samples. It is seen that for all the samples $TCR > 0$ as expected from Mooij’s correlation. As can be seen from Fig. 2.3(a) one also notes that as Mo concentration $x$ increases, which leads to an increase in $p(RT)$, the corresponding TCR decreases which is also consistent with Mooij’s correlation. The $p(RT)$ vs TCR is also shown in Fig. 2.3(b). Fig. 2.4 shows the resistivity ratio $RR = \frac{p(T)}{p(300)}$ vs T in the temperature range 10-300 K for $x = 0, 1, 2$ and $3$. $x = 4$ did not give repeatable results, hence data on this sample is not discussed. This was most probably the result of some crack developing along the length of the sample since the sample was a wide one and was prepared by a two nozzle method.

Fig. 2.4 clearly shows that in most of the higher temperature region (200-300 K) RR is almost linear with small scatter. Lower the value of $x$, larger is the 'almost' linear region in temperature. RR shows a minimum in RR vs T data, and the temperature at which this minimum is observed, depends upon the Mo concentration $x$. This temperature shall be referred as $T_{min}$ hereafter. Since the lowest temperature was limited to $\sim 10$ K, a larger amount of data could not be collected below $T_{min}$ for $x = 0, 1$.
Fig 2.3(a) TCR at RT, (a) and Room temperature resistivity, p(RT) as a function of Mo concentration, x

Fig 2.3(b) The plot of p(RT) vs TCR
Table 2.1 Different parameters calculated from resistivity data

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>$t_{\text{min}}$ (K)</th>
<th>$\text{TCR}(\alpha)$ at RT (K$^{-1}$)</th>
<th>$\rho$(RT) $\mu$Ω-cm</th>
<th>$\Omega$ (K)</th>
<th>D (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15</td>
<td>2538e-4</td>
<td>973</td>
<td>332</td>
<td>7.3e-4</td>
</tr>
<tr>
<td>1</td>
<td>21</td>
<td>1724e-4</td>
<td>1110</td>
<td>390</td>
<td>1.858e-4</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>0.9715e-4</td>
<td>1140</td>
<td>350</td>
<td>3.8e-4</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>0.4107e-4</td>
<td>1233</td>
<td></td>
<td>*5 15e-4</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>0.6962e-4</td>
<td>1315</td>
<td></td>
<td>83c-4</td>
</tr>
</tbody>
</table>

* represents for the first minimum of x=3 sample
and 2 samples. For $x=3$ sample, one seems to observe two minima, one at 110 K and another a very weak one at about 12 K as shown in Figs 2 5(a) & (b) in which the curves drawn show for the smoothened data $\frac{p}{dT}$ at higher temperatures becomes smaller as Mo concentration value $x$ increases. The temperature dependence of RR of the sample $S_0$ ($Fe_{68}Ni_{14}Si_2B_{16}$, $x=0$) is similar to that of other iron rich metallic glasses like $Fe_{80}B_{20}$ or $Fe-B-Si$. As $x$ increases the resistivity minimum becomes flatter/shallower, and for the sample $S_1$ ($Fe_{68}Ni_{14}Mo_{1}Si_2B_{16}$, $x=3$), it is comparatively much flatter. To show this clearly RR vs T data for $S_1$ is shown separately in Fig. 2.6 where the flat portion of the low temperature region where minimum is observed is indicated by dashed curve and the observed weak minimum at $\sim$10 K with the minimum at 110 K are indicated by the arrows. Similar observation has been reported in literature for Mo containing Fe-B glasses [11,54,55]. We analyse the temperature dependence of RR of these samples using the theoretical ideas discussed earlier. For this we separate the temperature region in three (1) $T>150$ K, (2) $T_{min}$-$T<150$ K and (3) $T<T_{min}$

2.4.1 Behaviour of RR for $T\geq150$ K

Figs 2 7 and 2 8 show RR vs T for 100 K $T<300$ K and 200 K $T<300$ K regions for the four samples respectively. One can easily see that while $S_0$ sample has RR vs T linear region between 100 and 300 K, as $x$ increases data starts to show departure from this linear behaviour more and more as one goes down in temperature from 300 K. This is clearly visible for $S_1$ sample. In the temperature region 200-300 K almost linear behaviour is observed for all the samples, although one observes a very small hump at $\sim$250 K for $S_1$ sample. Since 0n, the debye temperatures for these samples are expected to be between 300-400 K as reported in literature [56,57], one may consider applying the Ziman theory in the temperature region 200 K$<T<300$ K where $p_xT$ may be expected although it should be strictly valid only in the region $T<\theta_D$. Since these glasses are highly magnetic there may be some contribution of the magnetic scattering to the total $p$. Hence, both contributions must be considered in analysing resistivity data as a function of temperature.
Fig 2.5(a) The resistivity ratio $\frac{\rho(T)}{\rho(\text{RT})}$ vs $T$ in the temperature range 10-50 K showing the first $T_{\text{min}}$ for Fe$_{68}$Ni$_{14-x}$Mo$_x$Si$_2$B$_{16}$ ($x=3$) alloy.

Fig 2.5(b) The resistivity ratio $\frac{\rho(T)}{\rho(\text{RT})}$ vs $T$ in the temperature range 35-120 K showing the second $T_{\text{min}}$ for Fe$_{68}$Ni$_{14-x}$Mo$_x$Si$_2$B$_{16}$ ($x=3$) alloy.
Fig 2.6 The resistivity ratio $RR = \rho(T)/\rho(RT)$ vs $T$ in the temperature range 10-300 K for $\text{Fe}_{0.6}\text{Ni}_{1.4-x}\text{Mo}_x\text{Si}_2\text{B}_{16}$ $(x=3)$ alloy with the minima indicated by the arrows in the respective regions.
Fig 27 The resistivity ratio $RR = \rho(T)/\rho(RT)$ vs T in the temperature range 100-300 K for $\text{Fe}_{68}\text{Ni}_{14-x}\text{Mo}_x\text{Si}_2\text{B}_{16}$ ($x=0-3$) alloys.
The resistivity ratio \( \rho(T)/\rho(\text{RT}) \) vs T in the temperature range 200-300 K for Fe\(_{68}\)Ni\(_{14-x}\)Mo\(_x\)Si\(_2\)B\(_{16}\) (x=0-3) alloys.
Experiments which claim to have observed a magnetic contribution to \( p \) fall under two categories

(a) A magnetic contribution proportional to \( T^2 \). Thummes et al [46] found qualitative evidence of a \( T^2 \) magnetic term in \( \text{Ni}_{80-x}\text{Fe}_x\text{Si}_{16} \) (2.4≤\( x \)≤16) metallic glasses. Kaul et al [28] quantitatively found the same on FeBC alloys. Bhatnagar et al [54] found \( T^2 \) term in FeNiMoSiB alloys.

(b) A magnetic contribution proportional to \( T^{1.2} \). In Fe-Ni-P-B glasses Babic et al [48] obtained a \( T^{1.2} \) term for \( T<\frac{T_c}{3} \) Kettler and Rosenberg [58] found a \( T^{1.2} \) term in Ni-based \( \text{Ni}_{80-x}\text{Fe}_{16}\text{Si}_{14} \) (\( x=0-19 \)) and in \( \text{Ni}_{77-x}\text{Fe}_{x}\text{B}_{16}\text{Si}_{10} \) (\( x=0-15 \)) systems. Also Das et al [46] and Rita Singhal et al [59] have discussed in detail about the \( T^2 \) and \( T^{1.2} \) contribution to magnetic resistivity of Co-rich alloys and FeMoB_{20-x}Si_{x} alloys respectively. The contribution of \( T^{1.2} \) term to resistivity \( \rho_{\text{mag}}(T) \) is at least two orders of magnitude greater than the one arising from \( T \) term. These theories predict \( T^{1.2} \) power law for \( p(T) \) at low temperatures in amorphous transition metal alloys which contrasts the \( T^2 \) dependence found in these materials.

Thus, it is quite clear that a controversy still exists in deciding the relative weights of the magnetic contributions of the \( T^{1.2} \) and \( T^2 \) terms to the total resistivity in ferromagnetic metallic glasses. Although in our data, number of points are not very large we have still tried to fit our data to the combined contributions arising from the diffraction model and from the magnetic scattering.

According to Matheissen’s rule

\[
P(T) = \rho_{\text{str}}(T) + \rho_{\text{mag}}(T)
\]

where \( \rho_{\text{str}}(T) \) is the structural contribution and \( \rho_{\text{mag}}(T) \) is the magnetic contribution to the electrical resistivity. Since

\[
\rho_{\text{str}}(T) \propto T \quad \text{Near RT} \quad (2.24a)
\]

\[
P_{\text{str}}(T) \propto T^2 \quad T<\theta_0, \quad (2.24b)
\]

while

\[
\rho_{\text{mag}}(T) = aT^{1.2} + bT^2 \quad T<T_c \quad (\text{Curie temperature})
\]

Thus, total resistivity ratio, \( RR_1 \) can be written as
Resistivity data for 200 \( K < T < 300 \) K has been fitted to \( \frac{\rho_{\text{Total}}(T)}{\rho_{\text{Total}}(300)} = A + BT + CT^2 + DT^{1/2} \) to see which expression gives lower \( \chi^2 \) value. The fitted parameters are given in Table (2 2). The coefficient \( B \) of \( T \) in Eq (2 26) is of the order of \( 10^{-4} K^{-1} \) which also agrees well with earlier reported results [54]. It is seen that inclusion of either \( CT^2 \) or \( DT^{3/2} \) term to \( A + BT \) does improve \( \chi^2 \) but very little, not by an order of magnitude. There does not seem to be much difference in fitting whether one chooses \( T^{1/2} \) and \( T^2 \) term for \( \rho_{\text{mag}} \). Thus our data is not able to distinguish between these two dependences of \( \rho_{\text{mag}}(T) \). When we used \( \frac{\rho_{\text{Total}}(T)}{\rho_{\text{Total}}(300)} = A + BT + CT^2 + DT^{1/2} \) to fit the data unphysical results (negative coefficients) were obtained. Hence, both \( T^2 \) and \( T^{1/2} \) contributions cannot be present in \( \rho_{\text{mag}}(T) \) together. It is also seen from Table (2 2) that \( D \), the coefficient of \( T^{1/2} \) is about 3 orders of magnitude smaller than \( C \), the coefficient of \( T^2 \) in the fitting for \( T \geq \theta_D \). Hence, \( T^2 \) term is dominant in \( \rho_{\text{mag}}(T) \). It should be pointed out that any quantitative data analysis involving more terms (here four) demands more resolution of the data.

2.4.2 Behaviour of RR for \( I_{\text{min}} < I < 150 \) K

Fig 2 9 shows the RR vs \( T \) in this region, i.e., 10-120 K for all the samples. Total resistivity ratio, \( \frac{\rho_{\text{Total}}(T)}{\rho_{\text{Total}}(300)} \) can be written as

\[
RR_T = \frac{\rho_{\text{Total}}(T)}{\rho_{\text{Total}}(300)} = A + CT^2 + DT^{1/2} \quad T \geq \theta_D
\]  

(2.27)

where \( FT^2 \) term comes from \( \rho_{\text{structure}} \). Again, it was found that fitting to the above expression for \( T_{\text{min}} < T < 150 \) K, the fit was not good and \( D \) came out to be negative which is not acceptable since \( T \) increases spin disorder and hence \( \rho_{\text{mag}} \) must increase with increase in \( T \). Thus, the assumption that \( FT^2 \) term is the really dominant term in \( \rho_{\text{mag}}(T) \) as reported by Kaul et al [28] is quite good. Fig 2 10 display RR vs \( T \) which shows that RR does vary as \( T^2 \) well for all the samples from 50 K < \( T < 150 \) K except for So sample for which \( T^2 \) variation seems to be good only for 70 K < \( T < 150 \) K. The
Table 2.2 Fitting parameters for different expressions in 200-300 K range for resistivity variation.

(i) $A + BT$

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>A</th>
<th>$B$ ($K^{-1}$)</th>
<th>$\chi''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9232</td>
<td>2.539e-4</td>
<td>3.227e-8</td>
</tr>
<tr>
<td>1</td>
<td>0.9600</td>
<td>1.719e-4</td>
<td>6.606e-8</td>
</tr>
<tr>
<td>2</td>
<td>0.9706</td>
<td>9.715e-5</td>
<td>2.059e-8</td>
</tr>
<tr>
<td>3</td>
<td>0.9876</td>
<td>4.107e-5</td>
<td>4.678e-9</td>
</tr>
</tbody>
</table>

(ii) $A + BT + CT^2$

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>A</th>
<th>$B$ ($10^{-4}$) ($K^{-1}$)</th>
<th>$C$ ($10^{-7}$) ($K^{-2}$)</th>
<th>$\chi''$ ($10^{-8}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9300</td>
<td>1.984</td>
<td>1.108</td>
<td>2.468</td>
</tr>
<tr>
<td>1</td>
<td>0.9629</td>
<td>1.485</td>
<td>0.4702</td>
<td>5.613</td>
</tr>
<tr>
<td>2</td>
<td>0.9800</td>
<td>0.2102</td>
<td>1.521</td>
<td>0.5067</td>
</tr>
<tr>
<td>3</td>
<td>0.9902</td>
<td>0.1980</td>
<td>0.4247</td>
<td>0.3595</td>
</tr>
</tbody>
</table>

(iii) $A + BT + DT^3$

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>A</th>
<th>$B$ ($10^{-4}$) ($K^{-1}$)</th>
<th>$D$ ($10^{-10}$)</th>
<th>$\chi''$ ($10^{-9}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9276</td>
<td>2.272</td>
<td>2.820</td>
<td>2.485</td>
</tr>
<tr>
<td>1</td>
<td>0.9619</td>
<td>1.599</td>
<td>1.327</td>
<td>5.630</td>
</tr>
<tr>
<td>2</td>
<td>0.9768</td>
<td>0.5924</td>
<td>4.004</td>
<td>0.543</td>
</tr>
<tr>
<td>3</td>
<td>0.9893</td>
<td>0.3081</td>
<td>1.082</td>
<td>0.369</td>
</tr>
</tbody>
</table>
Fig 2.9 The resistivity ratio $RR = \rho(T)/\rho(RT)$ vs $T$ in the temperature range $10-120$ K for $\text{Fe}_{68}\text{Ni}_{14-x}\text{Mo}_x\text{Si}_2\text{B}_{16}$ ($x=0-3$) alloys.
Fig 2.10 The resistivity ratio $\frac{\rho(T)}{\rho(RT)}$ vs $T^2$ in the temperature range 10-150 K for $\text{Fe}_{x}\text{Ni}_{14-x}\text{Mo}_x\text{Si}_2\text{B}_{16}$ (x 0-3) alloys.

Table 2.3 Fitting parameters to $A + GT^2$ above $T_{\text{min}}$ to 150 K.

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>A</th>
<th>G</th>
<th>$\chi^*$</th>
<th>Fit Range AT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9420</td>
<td>9.416e-7</td>
<td>1.556e-7</td>
<td>20-150</td>
</tr>
<tr>
<td>1</td>
<td>0.9769</td>
<td>5.001e-7</td>
<td>1.783e-9</td>
<td>25-150</td>
</tr>
<tr>
<td>2</td>
<td>0.9804</td>
<td>2.760e-7</td>
<td>3.596e-9</td>
<td>30-150</td>
</tr>
<tr>
<td>3</td>
<td>0.9942</td>
<td>3.142e-8</td>
<td>7.971e-10</td>
<td>125-150</td>
</tr>
</tbody>
</table>
corresponding fit coefficients are listed in Table (2.3)

The coefficient of $T^2$ term $\sim 10^{-7}$ $K^{-2}$ (coefficient $G$) agrees well with that reported by Kaul et al (28) except for $x=1$ & 3, where the coefficient is lower than the reported, by an order magnitude i.e., $(3.0-5.5 \times 10^{-8} K^{-2})$ Thummes et al [46] obtain a $T^2$ term coefficient of this order $(\approx 3 \times 10^{-8} K^{-2})$ in a series of Ni-rich samples

Thus our analysis of RR vs $T$ seems to disagree with the results of Kettler et al (58) and Singhal et al [59] who found that their results are better described by a positive $T^{1.2}$ magnetic term over and above the structural $T^2$ term However, this result is in agreement with that of Kaul et al [28] and Bhatnagar et al [54], who observed that the low temperature resistivity in amorphous magnetic materials could be described by a $T^2$ term alone, which includes both the magnetic and structural contributions

As we do not see much improvement in the $\chi^2$ values, from the fits of data of high temperature to $A+BT$ and $A+BT+CT^2$, due to additional $T^*$ term, we conclude that $\rho_{str}(T)$ dominates $\rho_{mug}(T)$ in the entire temperature range above $I_{\text{mag}}$, but one should not ignore magnetic contribution completely

From these results we can calculate $\theta_D$, using the diffraction model which is given by Eq (2.12) as

$$\theta_D = \frac{\pi^2}{6} \left( \frac{\alpha}{\beta} \right)$$

where

$$\alpha = \frac{1}{\rho_{(300)}} \left( \frac{d\rho}{dT} \right)$$

and

$$\beta = \frac{1}{\rho_{(300)}} \left( \frac{d\rho}{dT^2} \right)$$

From above fitting Eq (2.26) & (2.27)

$$\theta_D = \frac{\pi^2}{6} \left( \frac{B}{F} \right)$$

But fitting RR vs $T^2$ for $T<\theta_D$, includes both contributions structural and magnetic From Fig 2.10 one determines $G$ (Eq. (2.27)). Fitting data RR vs $T$ to $A+BT+CT^2$ for $T>\theta_D$ gives $C$

hence $F = G-C$ or
Using this expression \( \theta_1 \) has been calculated for \( S_0, S_1 \) and \( S_2 \), only. Since \( S_1 \) shows a resistance minimum at higher temperatures (~110 K) hence it is not possible to fit low \( T (T<\theta_1) \) data to \( T^2 \). Values of \( \theta_1 \) vs \( X \) are listed in Table (2.1). It is seen that these do lie between 300 to 400 K as reported for other iron-rich metallic glasses in which similar analysis has been performed [56, 57].

**2.4.3 Behaviour of RR for \( T < T_{\text{min}} \)**

In the study of \( \text{Fe}_{68}\text{Ni}_{14-x}\text{Mo}_x\text{Si}_2\text{B}_{16} \) alloys all the samples show a minimum in resistivity at a characteristic temperature \( T_{\text{min}} \), which are listed in Table (2.1). \( T_{\text{min}} \) is found by noting the value of \( T \) at which \( d\rho/dT \) becomes zero. The values of \( T_{\text{min}} \) for these samples increase from 15-25 K as \( x \) varies from 0-2. Smoothened RR data vs \( T \) in the range 10-50 K are shown in Fig 2 11(a)-(c) for \( S_0, S_1 \) and \( S_2 \), samples respectively. This behaviour is similar to that of the Cr containing alloys and other Mo containing alloys [11, 14, 55]. For \( x=3 \), \( T_{\text{min}} \) drastically increased to 110 K. The resistivity data for this sample also seems to show an additional minimum, although a very weak one occurring around 10-15 K, as shown in Fig 2 15(a) & (b). (All the samples show a negative TCR below \( T_{\text{min}} \)). Fig 2 12 shows \( T_{\text{min}} \) vs \( \rho(RT) \). For the first three samples \( T_{\text{min}} \propto \rho \). Errors in the values of \( T_{\text{min}} \) are determined by the flatness of the resistivity variation near these temperatures. Similar results have been reported for glassy alloys \( \text{Fe}_{68-x}\text{Cr}_x\text{B}_{20} \) [14], and \( \text{Fe}_{68-x}\text{Mo}_x\text{B}_{20} \) [55] although it has been reported that \( T_{\text{min}} \) in glassy \( \text{Fe}_{68-x}\text{Mo}_x\text{B}_{20} \) [11] alloy increases up to \( x=4 \) then reduces for \( x=6 \). Before resistivity results are analyzed for \( T > T_{\text{min}} \), a brief description of resistivity behaviour around \( T_{\text{min}} \) in other iron-rich metallic glasses as reported in the literature is given below.

Almost all iron-rich metallic glasses show a resistance minimum in \( R \) vs \( T \) data if one reaches low enough temperatures. The behaviour of \( T_{\text{min}} \) varies with the type of the elements that constitute the alloy, their composition and thermal treatment. For instance, in \( \text{Fe}_{80}\text{B}_{20-x}\text{C}_x \) alloy [28], \( T_{\text{min}} \) increases with increasing carbon content.
The resistivity ratio $RR = \rho(T)/\rho(RT)$ vs $T$ in the temperature range 10-50 K for $\text{Fe}_{68}\text{Ni}_{14-x}\text{Mo}_x\text{Si}_2\text{B}_{16}(x=0-2)$ alloys.
Fig 2.12 The plot of $\rho(\text{RT})$ vs $T_{\text{min}}$. 
Fig 2.13 shows the $T_{\text{min}}$ vs Fe at% and Ni at% of various metallic glasses. The values of $T_{\text{min}}$ of $\text{Fe}_x\text{T}_{80-x}\text{B}_{20}$ (T=Co, Ni) alloys fall between 10-25 K where as for Fe-(Cr/W)-B alloys the $T_{\text{min}}$ is increasing drastically with increase in Cr or W concentration. Similar observation can be seen in $\text{Fe}_{40-x}\text{Ni}_{40}\text{Cr}_x\text{B}_{20}$ [60]. In $\text{Fe}_{x}\text{Ni}_{20}$ alloy [29] it increases with iron composition till 55 at% and decreases thereafter in $\text{Au}_{1-x}\text{Ni}_x$ alloy [61]. $T_{\text{min}}$ increases with Ni concentration. Addition of Ni or Co for Fe in metallic glasses with Fe-rich composition based on $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{80}\text{B}_{20-x}\text{Si}_x$ does not shift $T_{\text{min}}$ very much, but addition of Cr [14,62] or Mn [63] shifts $T_{\text{min}}$ substantially. It has been observed that in the absence of Ni, the addition of Cr and V leads to double minimum in resistivity, one at low temperature ~20 K and the other at higher temperature, above 100 K [14,62]. Sas et al [30] have shown that in case of $\text{Fe}_{x}\text{T}_{17}\text{B}_{17}$ alloys (where T= Pd, Pt, Fe, Ni, Rh, Co and Cu) the $T_{\text{min}}$ does not shift significantly, where as for T=Ir, Mn, Ta, W, Ru, V, Cr, Os and Nb, $T_{\text{min}}$ is shifted towards higher temperatures. By observing the overall results in these alloys, it may be noted that the addition of elements of the groups VB, V1B and VIIB, i.e., for the elements, which are located to the left of iron in the periodic table, shifts the $T_{\text{min}}$ towards higher temperatures. Whereas addition of the elements in the groups VIII and IB, that is to the right of Fe, does not change $T_{\text{min}}$ significantly.

Since a resistivity minimum in p vs T data at low temperatures in pure metals with a few parts per million magnetic impurities (like Mn in Cu), has been associated with the Kondo type s-d exchange scattering [64], one is tempted to claim that the observed resistivity minima in iron-rich metallic glasses may be due to Kondo type scattering. High purity Pd-Si and Pd-Si-Cu glasses show no $\rho_{\text{min}}$ [1], however, an addition of controlled quantities of Co, Fe, Cr and Mn to amorphous Pd$_{80}$Si$_{20}$ resulted in a $\rho_{\text{min}}$ and the $T_{\text{min}}$ increased with the magnetic impurity [65,66]. Thus, $\rho_{\text{min}}$ in this system has been explained on the basis of Kondo type s-d exchange scattering [65]. Thus, below $T<T_{\text{min}}$, p(T) is expected too be proportional to ln T with a negative slope. p(T) should eventually saturate at very low temperatures. If Kondo type scattering is considered responsible for $\rho_{\text{min}}$, then the application of magnetic field.
Fig. 2.13 $T_{\text{min}}$ vs Fe and Ni at% for different amorphous alloys.
should change $\rho(T)$ behaviour. However, Cochrane et al [25] observed that $\ln T$ dependence of resistivity is unaltered by an applied magnetic field of 45 kOe. It was therefore, suggested by them that the resistivity minimum may not have its origin in the Kondo effect. It may not be due to magnetic impurities alone, it must also be related to the amorphous structure of these materials. They explained $\rho_{\text{min}}$ using two-level tunneling model described in Sec. 2.2.3

In order to look for possible explanation of the temperature dependence of resistivity behaviour of these alloys, near and below $T_{\text{min}}$, we consider the predictions of various theories, which were outlined briefly earlier in this chapter. The resistivity minimum and negative TCR at low temperature have been observed in a number of metallic glasses whether ferromagnetic or not. The resistivity minimum cannot be explained using the Ziman diffraction model, and hence one has to look for an alternate explanation.

Harlier analysis of $\rho$ vs $T$ data for such glasses in the temperature region $T \cdot T_{\text{min}}$ has been usually carried out using $\ln T$ dependence of $\rho$ [66,67]. This $\ln T$ behaviour also comes from the scattering from two level states as suggested by Cochrane et al [25]. On the other hand, Tsuei [26] has shown that this anomalous electron transport is due to an attractive interaction between conduction electrons and localised excitations arising from a structural disorder in the atomic arrangement in a glass. He found that the resistivity can be expressed as

$$\rho(T) = A + B\rho(N) + C \ln\left[ T^2 + \Lambda^2 \right]$$

where $A$, $B$ and $C$ are constants and $\rho(N)$ is the resistivity due to other scattering mechanisms. The coefficient $C$ is a measure of the abundance of the effective tunneling configurations. If $A$ is zero or $\Delta \sim T$, then one would see a simple $\ln T$ behaviour. Inclusion of $\Lambda^2$ in the logarithmic term leads to flattening of the resistivity, the strength of which depends upon the ratio of $T$ and $A$.

More recently, theories based on quantum interference effects arising due to extremely small electron mean free path are being used to explain $\rho$ vs $T$ behaviour of high $\rho(\text{RT})$ metallic glasses as described in Sec. 2.2.4. In particular, the electron interaction effects consider the modification of the effective Coulomb interaction in the presence of high degree of structural disorder which leads to $T^{1/2}$ dependence of $\rho$.
below $T_{mn}$ with a negative slope. Rapp et al. [41] reanalyzed earlier $p$ vs $T$ data on a number of iron-rich metallic glasses and have shown that the resistivity for temperature below $T_{mn}$ can be fitted to $a_2\sqrt{T}$, where $a_2$ is a constant. Numerous reports indicate that the temperature dependence of resistivity of many magnetic and non-magnetic metallic glasses can be fitted to $T^{1.5}$ reasonably well below $T_{mn}$, at which minimum in resistivity is observed, with negative slope as predicted by Coulomb interaction theories [68].

While nowadays, there is a preference to fit $p$ vs $T$ data on metallic glasses using the interaction effects, here, we present both the fits, i.e., $(p-p_{mn})/\rho_{mn}$ vs $\ln T$ as well as $T^{1.2}$ in Figs. 2.14(a) & (b) and 2.15(a) & (b) for all the samples where the respective figures “(b)” are separately shown for the second minimum of $S_\uparrow$. It is noted that it is hard to say whether one is a better fit over other given the constraint that data here is only limited to 10 K and above.

The slopes of $\ln T$ fits for different samples are given in Table (2.4). These have similar magnitude as found for other iron-rich metallic glasses with low $T_{mn}(<30$ K). For example, Kaul et al. [28] have reported values of $B$ ranging from $(1.81$ to $-4.32) \times 10^4$ K$^{-1}$ for Fe$_{80}$B$_{20-x}$C$_x$.

Since $x=3$ sample has two minima, Fig. 2.15(b) shows $(p-p_{mn})/\rho_{mn}$ vs $T^{1.2}$ in the region 36 K to 100 K. It is seen that, $(p-p_{mn})/\rho_{mn}$ vs $T^{1.2}$ data exhibit a linear behaviour for all the samples, but the slopes which are also shown in Table (2.4) are smaller ($-1.0 \times 10^4$ to $-2.5 \times 10^4$) K$^{-1.2}$ than those obtained by Rapp et al. [41] and Bhatnagar et al. [54] on iron-rich glasses by a factor of 2 to 3. This may be since our data points below $T_{mn}$ are less in number and are not closely spaced and hence deviation (scatter in the data) is more.

According to the Coulomb or electron-electron interaction theory [68] the major contribution to the resistivity arises from the diffusion channel, which predicts an additional term to the conductivity, which, in absence of spin-orbit interaction theory is
given by [14]

$$
\sigma_D(H,T) = \frac{13}{\sqrt{2 \pi}} \frac{e^2}{4\pi^2 h} \left( \frac{k_B T}{hD} \right)^{1/2} \left\{ \frac{4}{3} + \lambda i \left( \frac{3}{2} + \frac{g_3(b)^2}{13} \right) \right\}
$$

(2.32)
Fig 2. 14(a) The plots of \( \frac{(\rho - \rho_{\text{min}})}{\rho_{\text{min}}} \) vs ln T for amorphous Fe\(_{x0}\)Ni\(_{14-x}\)Mo\(_x\)Si\(_2\)B\(_{16}\) (x=0-3) alloys where for x=3 data represents for its first minimum.

Fig 2. 14(b) The plot of \( \frac{(\rho - \rho_{\text{min}})}{\rho_{\text{min}}} \) vs ln T for amorphous Fe\(_{x0}\)Ni\(_{14-x}\)Mo\(_x\)Si\(_2\)B\(_{16}\) (x=3) alloy representing data for its second minimum.
Fig 2 15(a) The plots of \( (\rho - \rho_{\text{min}})/\rho_{\text{min}} \) vs \( V^2 \) for amorphous \( \text{Fe}_{50}\text{Ni}_{14-}\text{x}\text{Mo}_x\text{Si}_2\text{B}_{16} \) (\( x=0-3 \)) alloys where for \( x=3 \) data represents for its first minimum.

Fig 2 15(b) The plots of \( (\rho - \rho_{\text{min}})/\rho_{\text{min}} \) vs \( T^{1.2} \) for amorphous \( \text{Fe}_{50}\text{Ni}_{14-}\text{x}\text{Mo}_x\text{Si}_2\text{B}_{16} \) (\( x=3 \)) alloy representing data for its second minimum.
<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>A</th>
<th>B (10^{-4}) (ln K)</th>
<th>$\Delta T$ (K)</th>
<th>$\chi^2$</th>
<th>$a_1$</th>
<th>$a_2$ (K^{-1/2})</th>
<th>$\Delta T$ (K)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.553e-4</td>
<td>-1.815</td>
<td>10-14</td>
<td>1.569e-11</td>
<td>3.727e-4</td>
<td>-1.054e-4</td>
<td>10-14</td>
<td>3.168e-11</td>
</tr>
<tr>
<td>1</td>
<td>0.0032</td>
<td>-4.598</td>
<td>10-20</td>
<td>3.700e-10</td>
<td>0.0029</td>
<td>-2.305e-4</td>
<td>10-20</td>
<td>1.039e-9</td>
</tr>
<tr>
<td>2</td>
<td>0.0013</td>
<td>-3.913</td>
<td>10-24</td>
<td>2.229e-10</td>
<td>7.869e-4</td>
<td>-1.634e-4</td>
<td>10-24</td>
<td>1.230e-10</td>
</tr>
<tr>
<td>3</td>
<td>0.0022</td>
<td>-3.486</td>
<td>10-35</td>
<td>3.130e-10</td>
<td>0.0018</td>
<td>-1.559e-4</td>
<td>10-35</td>
<td>4.983e-10</td>
</tr>
<tr>
<td>3</td>
<td>0.0044</td>
<td>-9.618</td>
<td>35-110</td>
<td>6.986e-10</td>
<td>0.0023</td>
<td>-2.410e-4</td>
<td>35-110</td>
<td>1.864e-9</td>
</tr>
</tbody>
</table>
is a measure of the electron-phonon interaction. The function $g_\hbar(h)$ has the asymptotic form $0.056h^3$ for $h \ll 1$ and $(h^4 \ll 3)$ for $h \cdot l$ where $h = \hbar \omega/k_B T$ and the other constants have their usual meaning.

From Eq. (2.32), an upper limit for $\lambda$, the diffusion constant has been calculated by assuming $\lambda = 0$. These values are higher than the reported values of $3.5 \times 10^{-4}$ cm$^2$/s for similar glasses using the similar analysis [54] by an order of magnitude. Further confirmation of the results reported here below $T_{\text{min}}$ can only be done if additional measurements like magnetic field dependence of resistivity are performed at low temperatures.

2.5 Summary

1. In these alloys, a resistivity minimum is observed at around 15 K for $x = 0$ and it increases drastically to 110 K for $x = 3$. The alloy with $x = 3$ Mo-at% shows a double minimum with the first minimum occurring around 10-15 K, and second minimum at about 110 K.

2. As $\rho(\text{RT})$ increases, TCR, $\alpha(\text{RT})$ decreases. The values of $T_{\text{min}}$, $\rho(\text{RT})$ increase with increase of Mo content. The values of Debye temperature, $\theta_D$, for these alloys lie in between 300-400 K. Table (2.1) lists the values of $\rho_{\text{RT}}$, $T_{\text{min}}$, $\alpha(\text{RT})$, $\theta_D$ for each sample.

3. At higher temperatures, i.e., (200-RT) the temperature dependence of resistivity is found to be nearly linear and follows an equation of the type $A + BT$, the values of the coefficient $B$ are presented in Table (2.2). This region has also been fitted to an equation of the form $A + BT + CT^2$ in which the $T^2$ term gives magnetic contribution to resistivity and the linear term $T$ comes from the structural contribution to resistivity and the fit parameters are tabulated in Table (2.2). Data in this region is also fitted to an expression $A + BT + CT^2$, in which the $T^2$ term gives magnetic contribution. The coefficients are listed in Table (2.2). There is not much difference in the fits with either of these terms and hence our data is not able to distinguish between these two $T^2$ and $T^{1/2}$
dependences of $\rho_{\text{mag}}(T)$ Also since the coefficient of $T^{-1.2}$ is about 3 orders of magnitude smaller than that of $T^2$ term, $T^2$ term is dominant in $\rho_{\text{mag}}(T)$

(4) Above $T_{\text{min}}$ up to 150 K, a quadratic temperature dependence of resistivity is observed and the data in this region has been fitted to an equation of the form $A+GT^2$ and the values are tabulated in Table (2.3). The Fig. 2 10 shows the plot of $p(T)/p(RT)$ vs $T^2$. The samples show $T^2$ dependence in the range 50-150 K except for the sample $S_0$, for which $T^2$ variation seems to be good only in the range 70-150 K. The coefficient of $T^2$ is $10^{-7}K^{-2}$

(5) Below $T_{\text{min}}$ a logarithmic behaviour of resistivity with temperature as shown in Fig. 2 14(a & b) is observed. The data in this region has been fitted to an empirical relation of the form $A+B\ln T$. This $\ln T$ behaviour comes from two level states. The values are tabulated in Table (2 4). The data is also fitted to an expression of the form $a_1+a_2\sqrt{T}$, represented in Fig. 2 15(a & b), and the values are tabulated in Table (2 4) where $T^{1.2}$ dependence is due to electron interaction effects. Both the fits are reasonably good and it is hard to say which one is better over the other given the constraint that data here is limited only 10 K and above.
2.6 References


U Mizutani, Prog. Mat. Sci., 28 (1983) 97


9. N F Mott, Phil. Mag., 26 (1972) 1249


31 J M Ziman, Phil. Mag., 6 (1961) 1013


53 APD Cryogenics, Inc, Superconductor Characterisation Cryostat Technical Manual - P/N 257171A


64 S C H Lin, J. Appl. Phys., 40 (1969) 2173


