CHAPTER 3

FeSi : A 3d KONDO INSULATOR

The results of experimental studies carried out on pristine FeSi, a d-electron based Kondo insulator, are presented in this chapter. The transport properties of FeSi are known to be sample dependent [1–3]. According to the phase diagram [4] shown in Fig. 1.1 of Chapter 1, the homogeneity range of FeSi extends from 49 to 50.5 at.% of Si. Therefore, it is possible to prepare samples having identical phase with varying stoichiometries. A composition dependent study of Buschinger et. al [2] reveals that the variation of stoichiometry within the homogeneity range of FeSi has a profound influence on its transport and thermal properties. Even polycrystalline samples having an exact 1:1 stoichiometry of Fe and Si have physical properties which match well with that of a FeSi single crystals. It is, therefore, important that investigations be done on good quality samples to ensure measurements of the intrinsic physical property of the system. The quality of a sample is estimated from the value of its resistance ratio (RR), defined as the ratio of resistances at 4.2 K and 300 K, i.e., \( RR = \frac{R(4.2\text{K})}{R(300\text{K})} \) [5–8]. The RR of a sample gives an indication of the extent of the disorder present in the sample. Higher the RR, lower is the disorder and hence better is the sample. Keeping this in mind, in this work the transport properties of this system have been investigated by carrying out electrical resistivity measurements as a function of temperature \( \rho(T) \) and as a function of temperature and pressure \( \rho(T, P) \) on samples with \( RR = 2 \times 10^4 \). To investigate the effect of sample quality on the transport behaviour of FeSi system, \( \rho(T) \) and \( \rho(T, P) \) studies have been performed on samples with \( RR = 7 \) and compared with \( RR = 2 \times 10^4 \). Various models, including a new density of states (DOS) model referred to as the Gaussian DOS model proposed in the present studies, have been used to analyse the experimental data. These models are described and the results of the data analyses using them are discussed in detail in this chapter.
3.1 SAMPLES AND EXPERIMENTS

Several batches of polycrystalline FeSi samples were prepared by arc melting Fe(99.999%), Si(99.9999%), taken in close to 1:1 stoichiometric quantities, several times in a protective flowing inert Ar gas atmosphere. The arc melted buttons were vacuum sealed in a quartz tube and homogenised at 1000°C for 10 days. It is found that the samples with starting stoichiometry of Fe$_{1-x}$Si$_{1+x}$ with x < 0.002, prior to arc melting resulted in good quality with RR of the order of 10$^4$ or more, provided their weight losses were less than 0.2-0.3 wt.% after melting. A similar procedure was followed in the preparation of Ge substituted Fe$_{1-x}$Ge$_x$ (0 ≤ x ≤ 1) and Ru substituted Fe$_{1-x}$Ru$_x$Si (0 ≤ x ≤ 1) samples using Fe(99.999%), Si(99.9999%), Ge(99.9999%) and Ru (grade 1 from Johnson Matthey Chemicals, England) in stoichiometric quantities. Subsequent to the homogenization treatment, samples were cut to ~ 0.3 -0.5 mm thin circular discs using a diamond wheel for further experiments.

All the samples were characterised by X-ray diffraction (XRD) measurements using Siemens D500 powder diffractometer in the Bragg-Brentano geometry employing the Cu K$_{\alpha}$ radiation in the 2θ range of 20° to 120° at an interval of 0.05°. A Rietveld refinement of the XRD data was performed using Rietan-2000 programme [9] to obtain the lattice constant and the internal atomic position parameters for the elemental constituents of the sample. The room temperature resistivity measurements were carried out using Van der Pauw technique on the thin circular discs of uniform thickness by making four fine point pressure contacts at the periphery. The resistivity measurements in the 4 - 300 K temperature range were carried out in a dipstick cryostat, using a specially designed pressure contact assembly in the four probe geometry and the measurements below 4 K were carried out using liquid $^4$He evaporation refrigeration cryostat, described in Chapter 2. The high pressure electrical resistivity measurements have been performed using the opposed anvil type, miniaturized pressure locked cell, following the procedure described in Chapter 2.
3.2 RESULTS AND ANALYSIS

3.2.1 XRD Characterization and Rietveld Refinements

The XRD pattern for the some representative sets of polycrystalline FeSi samples of different RR values, designated as FeSi (RR=2 x 10^4), FeSi (RR=6 x 10^3) and FeSi (RR=7), are shown in Fig. 3.1. The sample having RR=2 x 10^4 is one of the largest RR values reported for polycrystalline FeSi samples, though single crystals of FeSi have been reported with RR of the order of ~ 10^5 [7, 12]. Large number of sample batches are found to have RR values between 1.8 x 10^3 and 6 x 10^3. These values of RR are similar to what is reported for polycrystalline samples in several studies [5, 13]. A few batches of FeSi samples were found to result in very low RR values ≤ 10^2 and among them the lowest RR value is seen to be 7 for the poorest quality sample, in which a large weight loss of ~ 1 wt.% after arc melting was observed. The diffraction peaks of the XRD patterns shown in Fig. 3.1 could be indexed to a cubic structure with space group P2_1_3 with Fe and Si atoms situated at the 4(a)-type positions in the simple cubic unit cell, with the positional co-ordinates (u, u, u), (1/2+u, 1/2-u, u), (u, 1/2+u, 1/2-u), (1/2-u, u, 1/2+u). It can be seen from Fig. 3.1 that except in FeSi (RR=7) sample, which has an unindexed small peak near 2θ=46.7 degree, none of the other samples have any impurity peak. Rietveld refinement of these XRD data have been carried out. A representative Rietveld fit to the XRD pattern of the FeSi (RR=2 x 10^4) sample is shown in Fig. 3.2. It can be seen from this figure that Rietveld refined curve fits the experimental data very well. The S parameter, indicating the goodness of the fit, is found to be within 1.34 to 1.63 for all the samples. The lattice parameters and the fractional atomic positions of Fe and Si extracted from the Rietveld refinement of the XRD data are shown in Table I. These refined parameters are compared with the reported values of Paschen et. al [7]. It can be seen that the fractional atomic position parameters u_Fe and u_Si obtained for the first two FeSi samples having large RR are in excellent agreement with reported single crystal X-ray values of Paschen et. al [7], whereas for the sample with RR = 7 the fractional atomic positions differ considerably. The lattice parameter of all the FeSi samples shown in Table I are well within the range of previously reported values of 4.483 Å to 4.493 Å [2, 5, 7, 14-16].

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Fig. 3.1. X-ray diffraction pattern of three representative FeSi samples. Indexing corresponds to FeSi structure of cubic B-20 type with space group P2₁3. Patterns are shifted vertically for clarity.
Fig. 3.2. Representative Rietveld fit to the XRD pattern of FeSi \((RR=2 \times 10^4)\). Experimental data (+), calculated data (solid line) and the difference plot (bottom).
TABLE I: Refined atomic coordinates for various sets of FeSi samples obtained from Rietveld analysis of the XRD data

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>Position</th>
<th>( u_{Fe} )</th>
<th>( u_{Si} )</th>
<th>( \rho_{300 K} ) (( \mu \Omega )-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSi (RR=2 x 10^4)</td>
<td>4.4890</td>
<td>4(a)</td>
<td>0.137</td>
<td>0.843</td>
<td>163</td>
</tr>
<tr>
<td>FeSi (RR=6 x 10^3)</td>
<td>4.4901</td>
<td>4(a)</td>
<td>0.140</td>
<td>0.844</td>
<td>243</td>
</tr>
<tr>
<td>FeSi (RR=7)</td>
<td>4.4920</td>
<td>4(a)</td>
<td>0.154</td>
<td>0.831</td>
<td>254</td>
</tr>
<tr>
<td>FeSi (Ref: Paschen et. al [7])</td>
<td>4.488</td>
<td>4(a)</td>
<td>0.137</td>
<td>0.842</td>
<td>165</td>
</tr>
</tbody>
</table>

3.2.2 Electrical Resistivity Studies in FeSi

The room temperature resistivity, \( \rho_{300 K} \), of above samples measured using Van der Pauw technique is shown in Table I. It can be seen that the value of \( \rho_{300 K} = 163 \pm 5 \mu \Omega \)-cm of FeSi (RR=2 x 10^4) sample is in excellent agreement with the reported value of 165 \( \mu \Omega \)-cm for a single crystal sample [7]. The \( \rho_{300 K} \) of the remaining FeSi samples are well within the range of 140 to 300 \( \mu \Omega \)-cm of the values reported in literature [2, 3, 5, 6, 13, 14]. The values of resistivity in the above range is consistent with a description of FeSi as a dirty metal at this temperature [3]. It can be inferred from Table I that there is a systematic variation of \( \rho_{300 K} \) with respect to RR values of the FeSi samples, i.e., \( \rho_{300 K} \) increases with decreasing RR values. This arises due to an increased impurity scattering caused by the increase in disorder with decreasing RR. Since the general feature of the FeSi (RR=2 x 10^4) sample is very close to that of the single crystalline sample of Paschen et. al [7], the transport studies carried out on this sample are described first.

The temperature dependence of the electrical resistivity, \( \rho(T) \), measured in 1.3 to 300 K temperature range, is shown in Fig. 3.3. A part of the same data for \( T \leq 50 \) K is shown in an expanded scale in the inset (a) of the figure. It can be seen that \( \rho(T) \) exhibits a clear two step increase with decreasing temperature with a broad shoulder around
Fig. 3.3. Variation of electrical resistivity as a function of temperature for the pristine FeSi(RR=2x10^4) sample. The fits for VRH and thermally activated behaviour models are also shown along with the experimental data. Inset (a) shows fit to VRH model in limited temperature range of 1.3 - 40 K. Note the deviation from the VRH behaviour below 5 K. Inset (b) shows a linear fit to the conductivity, σ(T), data in 1.3 – 5 K temperature range.
T = 75 ± 15 K separating the two regions. While the temperature coefficient of resistivity remains negative in the entire measured temperature range, a close scrutiny of the data reveals that the overall ρ(T) behaviour can be broadly classified into four temperature regimes. In regime I (300 to 200 K), ρ(T) shows a marginal increase with decreasing temperature. In regime II from 200-100 K, ρ(T) exhibits a rather strong T - dependence indicating a semiconductor like activated behaviour. In regime III from 50 to 5 K, there is very steep rise in resistivity with decreasing temperature. Regime IV: below 5 K, the steep rise in resistivity slows down and a tendency of resistivity saturation starts emerging with decreasing temperature. The variation of electrical conductivity, σ in a narrow temperature interval of 1.3 to 5 K is shown in inset (b) of Fig. 3.3.

3.2.3 Data Analysis

The models employed for data analysis are briefly described in this section.

3.2.3.1 The Thermally Activated Behaviour Model

As a first approximation, considering FeSi to be a small gap semiconductor, the simplest model that can be envisaged is the thermally activated behaviour model. In this model, the density of states (DOS) of FeSi is viewed to be similar to that of a semiconductor, in which the lower most edge of a broad conduction band and the upper most edge of valence band are separated by an energy gap Δe with the Fermi energy ε_F lying in the middle of the gap. A schematic of the DOS is shown in Fig. 3.4(a). The electrical conductivity, σ, in this model can be deduced as follows:

$$\sigma = 2e\eta\mu$$

(1)

where the factor 2 accounts for the contributions of holes in the valence band and electrons in conduction band. Here the mobility for the valence and conduction bands are assumed to be the same. The number density of carriers, n, in conduction band is given as

$$n = \int_{\Delta_e}^{\infty} f(E)D(E)dE$$

(2)

where D(E) is DOS and f(E) is the Fermi-Dirac distribution function. F(E) is given by

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1}$$

(3)
Fig. 3.4. A schematic representation of the density of states (DOS) for (a) the thermally activated behaviour model, (b) the step function DOS model and (c) the Gaussian DOS model as elaborated in the text.
At the temperature of interest taking \((E - E_F) \gg k_B T\), Fermi-Dirac distribution function reduces to \(f(E) \approx e^{(E_F - E)/k_B T}\). Using this \(f(E)\) and \(D(E) \sim E^{1/2}\) (assuming parabolic DOS of the free electron system) in Eq. 2 one gets

\[ n \sim e^{-\Delta_a/2k_B T} \]  

resulting in \(\sigma \sim e^{-\Delta_a/2k_B T}\). In other words, the electrical resistivity can be expressed as \(\rho = \rho_0 \exp(\Delta_a/2k_B T)\). Here \(\Delta_a\) is activation energy gap, \(k_B\) Boltzmann constant and \(\rho_0\) is the temperature independent pre-factor. This model has been widely used [2, 5, 6, 12, 18] to extract the energy gap by fitting the \(\rho(T)\) data in a small temperature range of 100-200 K.

### 3.2.3.2 The Step Function DOS Model

As described in Chapter 1, since FeSi is a Kondo insulator (Kl), the effect of electron correlation needs to be incorporated in the DOS. It is known that the correlation strongly renormalizes the noninteracting bands and narrows the bandwidths, which gives rise large peaks in the DOS at the gap edges [21]. The evidence for sharp features of the DOS in FeSi has been observed in high resolution angle resolved photoemission [24] and the tunneling spectroscopies [12]. Consistent with this is the step function DOS model, originally proposed by Jaccarino et al and subsequently extended by Mandrus et al. [20]. In this model, two rectangular bands defined in terms of step functions of very narrow width 'W' and height \(D(E)\), situated at valence band edge (VBE) and conduction band edge (CBE) and separated by an energy gap \(\Delta_e\), describe the DOS of FeSi. The Fermi energy \(E_F\) is symmetrically placed in the middle of the gap which is assumed to be temperature independent. A schematic illustration of step function DOS model is shown in Fig. 3.4(b). The expression for the electrical conductivity, \(\sigma\), given by Eq. (1). Here again the contributions of holes in the valence band and electrons in conduction band are taken into account. The number density of carriers, \(n\), in this model is obtained as

\[ n = \int_{\Delta_e}^{(\Delta_e + W)} f(E)D(E)dE \]  

The limits in Eq.(5) restrict the carriers only to those states lying in the narrow width \(W\) of the rectangular conduction band (cf. Fig. 3.4(b)). The magnitude of density of states \(D(E) = N g/W\), where \(N\) is the density of unit cells containing four FeSi units and \(g\) is the total number of states per unit cell. \(f(E)\) is the Fermi-Dirac distribution function. The
temperature dependence of mobility $\mu$ is taken as

$$\mu = \mu_0 T^{-\alpha}$$  \hspace{1cm} (6)$$

with exponent $\alpha = 1.5$ to account for the acoustic-phonon scattering [7, 14, 20]. Using above equations the conductivity can be deduced to have following closed form,

$$\sigma = 2e. \frac{Ng}{W^2}.\mu_0 T^{-1.5}.k_B T.\ln \left[ \frac{1 + \exp(-\Delta_s/2k_BT)}{1 + \exp[-(\Delta_s + 2W)/2k_BT]} \right]$$  \hspace{1cm} (7)$$

This model has been used for analysing experimental data in FeSi in previous studies [7, 14, 17, 19, 20]. Like the thermally activated behaviour model, this model is also found to describe conductivity data only in high temperature regime, although in a larger temperature range.

3.2.3.3 The Variable Range Hopping Model

In low temperature regime (T ≤ 50 K) the conductivity of FeSi is governed by variable range hopping (VRH) behaviour [2, 5, 12, 17, 18], known to arise due to localized states inside the gap [22] due to the presence of disorder. In this model the resistivity is described by an expression of the form $\rho = \rho_0 \exp[(T_0/T)^{1/d+1}]$ where $d$ is the dimension of the lattice [22]. The hopping parameter $T_0$ is given by, $T_0 = p\alpha^3/[N(E_F)k_B]$, where $p$ is a dimensionless constant, $N(E_F)$ is the density of states in the gap, $\alpha$ is the inverse of the localisation length and $k_B$ is the Boltzmann constant. There is a definite reason to believe that the VRH behaviour is intrinsic in FeSi as this behaviour has been reported in most of the FeSi samples including single crystals [2, 5, 12, 17, 18] except in ref. [7] and since purer samples have larger $T_0$ value. It is suggested [16] that there is an intrinsic disorder in FeSi structure, arising due to formation of phase/antiphase boundaries between two isomeric structures which may be a plausible reason for the VRH behaviour in FeSi (cf. section 1.5 of Chapter 1). Before closing this subsection, it should be pointed out that at temperatures ≤ 5 K, the conductivity data of FeSi can be described by a power law behaviour of type $\sigma = \sigma_0 + bT^m$, which indicate a metallic conductivity in this system [7, 17], typical of a disordered metal.

3.2.3.4 The Gaussian DOS Model

It should be pointed out that though the activated behaviour and the step function DOS models are well suited to understand the $\rho(T)$ behaviour in FeSi in the high temperature
regime, they are inadequate to even qualitatively account for the hopping conductivity behaviour seen in the 5-40 K range and the saturation of conductivity seen below 5 K. Therefore within the purview of any of these DOS models, the transport behaviour of FeSi can not be rationalized in a unified manner in all the temperature ranges. Since it is known that there is intrinsic disorder in FeSi structure [16], an appropriate DOS for FeSi would be one in which, in addition to correlation effects, the effect of disorder are taken into account. Introducing band tails to the the step function DOS model, could to a first approximation incorporate disorder effects in the correlation model. The resulting new disorder cum correlation model is referred to as Gaussian DOS model [11]. A schematic illustration of this model DOS is shown in Fig. 3.4(c). In this model the DOS, instead of step function with narrow width W situated at VBE and CBE, is assumed to have a Gaussian distribution with means at VBE and CBE, separated by an energy of $E_g$, and a full width at half maximum (FWHM) of the order of W. A mobility edge $E_{\mu}$ situated above and below Fermi energy $E_F$ separates the localized and delocalized states. The narrow FWHM of the gaussian, models the correlation effect and the tails in the band gap represent the disorder in the system. The existence of localized states between $E_{\mu}$ and $E_F$, naturally leads to the description of the transport behaviour in low temperature in terms of VRH mechanism. The presence of disorder apart from inducing the band tails also gives rise to a smearing [25] of the Fermi function, which leads to a finite $\sigma(T)$ at $T = 0$ K, consistent with the prediction of the several experimental studies [3, 7, 17]. In essence, the degree of disorder/correlation is dictated by the width ' W ' of the Gaussian. The larger W implies more disorder whereas the smaller W indicates larger correlation. The chemical substitution of either constituent in FeSi as well external pressure affects the band structure and the degree of disorder /and correlation. These effects are expected to reflect in the parameters defining the Gaussian DOS. On the average the effect of electronic band structure is captured by the parameter $E_g$, which in the absence of disorder/ correlation would be the energy gap in a conventional semiconductor (cf. Fig. 3.4(c)).

The electrical conductivity in the Gaussian DOS model can be obtained by replacing the shape of step function DOS by sum of Gaussians situated at the valence and the conduction band edges. In Eq. (1), $n$ for this model is obtained as

$$n = \int_{E_{\mu}}^{\infty} f(E)D(E)dE$$

(8)

Note that in this case the lower limit of integration is taken from mobility edge $E_{\mu}$. $E_{\mu}$ is
energy separation between Fermi level $E_F$ (taken as zero) and mobility edge. The gaussian DOS, $D(E)$, is taken as

$$D(E) = \frac{N_g}{\sqrt{2\pi}(W/2)} \left[ \exp\left(-2 \left( \frac{E - E_g/2}{W} \right)^2 \right) + \exp\left(-2 \left( \frac{E + E_g/2}{W} \right)^2 \right) \right]$$

(9)

The conductivity data is fitted to this model using $\mu_0$, $E_g$, $E_\mu$, and $W$ as fitting parameters with $\mu = \mu_0 T^{1.5}$ in high temperature regime ($T \geq 100$ K).

It should be noted that as such there is no sharply defined energy gap in this model. However for comparison with step function DOS model, a mobility gap ($\Delta_\mu$) defined as the energy separation between the two mobility edges situated at $-E_\mu$ & $E_\mu$ having a magnitude equal to 2 $E_\mu$ (cf. Fig. 3.4(c)) is equivalent to $\Delta_e$ of the former model. In order to make a comparison with energy gap $\Delta_e$ obtained from the thermally activated behaviour model, an equivalent effective energy gap, $\Delta_{eff}$, can be deduced from this model. This is done by first computing number density of carriers $n$ from Eq. (8) at several temperatures above 100 K using the parameters $\mu_0$, $E_g$, $E_\mu$, and $W$ extracted from the fits to the conductivity data. The set of $n(T)$ thus obtained is then fitted to the thermal activated formula of type $n \propto e^{-\Delta_{eff}/2k_B T}$ to extract $\Delta_{eff}$.

In the low temperature regime ($T \leq 50$K) where disorder plays an important role in governing the transport behaviour in FeSi, the temperature dependence of the mobility ($\mu = \mu_0 T^{1.5}$) used in high temperature regime does not remain valid. The exact variation of $\mu$ with temperature in presence of disorder is not very well known. Therefore, the experimental data in this temperature range has been analysed using the VRH model given in section 3.2.3.3. However, an estimate of the density of the localized states, $N(E_F)$, within the energy gap is obtained within the framework of the Gaussian DOS model by integrating $D(E)$ given in Eq. 9 from the limit $-E_\mu$ to $E_\mu$ and dividing by the energy separation between the two mobility edges (cf. Fig. 3.4(c)), i.e.,

$$N(E_F) = \frac{\int_{-E_\mu}^{E_\mu} D(E) dE}{2E_\mu}$$

(10)

The quantity $T_0$ and $N(E_F)$, are used to calculate the localization length $\alpha^{-1}$ using formula $\alpha^{-1} = [p / T_0 \cdot k_B N(E_F)]^{1/3}$.

At temperatures below 5 K, where the conductivity behaviour of FeSi deviates from the VRH behaviour, it becomes difficult to fit the data using the present DOS model because of
the lack of information about the temperature dependence of mobility in this temperature regime. However, the values of experimental conductivity at fixed temperatures below 5 K can be reproduced by calculating the conductivity using the Gaussian fit parameters $\mu_0$, $W$, $E_g$ and $E_\mu$ obtained from the fits in high temperature regime and by inserting a disorder parameter $\delta$ in Fermi-Dirac distribution function i.e., 
$$f(E) = \frac{1}{[1+e^{(E-E_F)/k_B(T+\delta)}]}$$
to simulate the temperature induced smearing [25]. Thus the conductivity of FeSi can be rationalized in the entire temperature range within the framework of the Gaussian DOS model.

3.2.3.5 Logarithmic Derivative Plot Analysis

The logarithmic derivative of conductivity, i.e., $w(T) = \frac{d\ln(\sigma(T))}{d\ln(T)}$ versus temperature plot analysis of Möbius et al. [23] provides a very useful method to discriminate metallic and insulating samples at low temperatures. Ideally a material is defined as a metal if it has finite conductivity at zero temperature, i.e., $\sigma \neq 0$ at $T=0$ K and it is regarded as insulator if $\sigma = 0$ at $T=0$ K. In reality the experimental measurements of $\sigma(T)$ terminate at finite temperatures, necessitating extrapolation of $\sigma$ upto $T = 0$ K to identify the nature of conduction. In the presence of disorder, as shown by Möbius et al. [23] [23], it is quite difficult to clearly identify the metal-insulator transition MIT from simply zero temperature extrapolation of $\sigma(T)$. However, MIT can be identified with least ambiguity from a $w(T)$ plot analysis [23]. Further, from this analysis one can also get information about the nature of the MIT. Since this analysis has been used in this thesis, it is worthwhile to give a brief account of this method here.

In presence of disorder conductivity exhibits exponential $T$ dependence like VRH behaviour in insulating regime and a power law behaviour in the metallic regime [23]. First considering the temperature dependence of $\sigma$ of a sample to be as a variable range hopping type,

$$\sigma(T) = \sigma_1 exp(-\left[\frac{T_0}{T}\right]^{1/4})$$  \hspace{1cm} (11)

gives $\sigma = 0$ at $T = 0$ K, indicating that the sample is insulating. On the other hand, considering that the temperature dependence of $\sigma$ follows a power law behaviour,

$$\sigma(T) = a + bT^p$$  \hspace{1cm} (12)

with $a > 0$, 'b' a positive or negative value and exponent 'p', a positive number results in
\[ \sigma \neq 0 \text{ at } T = 0 \text{ K, indicating a metallic behaviour of the sample. Taking the logarithmic derivative } w(T) = \ln(\sigma(T))/\text{dln}(T) \text{ of the Eq. 11 results in,} \]

\[ w(T) = 1/4 \left[ \frac{T_0}{T} \right]^{1/4} \quad (13) \]

for the insulating sample, implying that \( w(T) = \infty \) for \( T = 0 \text{ K} \). Whereas if the conduction is metallic, one gets from Eq. (12)

\[ w(T) = \frac{p_b T^p}{(a + b T^p)} \quad (14) \]

here \( w(T) = 0 \) for \( T = 0 \text{ K, i.e., } w(T \rightarrow 0) = 0 \) indicates metallic character of the conduction. In fact \( w(T) \) is an increasing function of temperature i.e., \( \frac{dw}{dT} > 0 \) for metallic conduction, whereas for insulating samples \( w(T) \) decreases with increasing temperature, i.e., \( \frac{dw}{dT} \leq 0 \). These properties of \( w(T) \) are very useful in identifying the MITs. To see how \( w(T) \) plot analysis is helpful in identifying the nature of the MIT, Möbius et al. [23] have taken two qualititative models, one suitable for continuous and the other for discontinuous MIT. The \( w(T) \) plot resulting from these model are reproduced in Fig. 3.5 and Fig. 3.6 for continuous and discontinuous MIT respectively. The characteristic features of these two figures are quite different. In the case of continuous MIT (cf. Fig. 3.5), there is a clear demarcation between the insulating and metallic regions. A straight line, called as separatrix, parallel to \( T \) axis separates the two regions. On the metallic side of MIT, \( w(T \rightarrow 0) = 0 \) and the slope of \( w(T) \) is positive. On the insulating side of MIT, \( w(T \rightarrow 0) = \infty \) or finite positive value and the slope \( \frac{dw(T)}{dT} \leq 0 \). Separatrix is at the verge of the insulating region. In contrast to Fig. 3.5, in the case of discontinuous MIT (cf. Fig. 3.6), the insulating region \( w(T) \) curve exhibits a minimum before it diverges as \( T \rightarrow 0 \), but at the MIT this minimum disappears and \( w(T) \rightarrow 0 \) as \( T \rightarrow 0 \text{ K on the metallic side.} \)

The nature of the MIT, thus can be inferred from the careful inspection of \( w(T) \) plot.

The numerical computation of \( w(T) \) from the measured conductivity data has been carried out by following the procedure described by Möbius et al.[23]. Considering \( \ln \sigma \) to be a linear function of \( \ln T \), i.e., \( \sigma = a + b \ln T \), in a window of \( k \) neighbouring points. Then \( w_{lf} \) is obtained by means of linear regression from the data within the window. This gives,
Fig. 3.5. Qualitative behaviour of $w(T)$ plot for the continuous MIT. Insulating regime (Dotted lines) and metallic regime (Dashed lines). Separatrix between insulating and metallic region (Full line).
Fig. 3.6. Qualitative behaviour of $w(T)$ for a discontinuous MIT. Insulating regime (Dotted lines) and metallic regime (Dashed lines). Separatrix between insulating and metallic region (Full line).
\[ w_{ij} = \frac{k \sum_i (\ln \sigma_i)(\ln T_i) - \sum_i \ln \sigma_i \sum_j (\ln T_j)}{k \sum_i (\ln T_i)^2 - (\sum_i \ln T_i)^2} \quad (15) \]

where the sum runs over all points within the window considered. This window is moved along the \( \ln \sigma \) versus \( \ln T \) curve to traverse all the data points to get the set of \( w(T) \). In order to minimize the numerical error arising from the nonlinearity of the dependence of \( \ln \sigma \) from \( \ln T \), \( w \) obtained in above expression is related to a mean temperature \( T_{ij} \) given as follows:

\[ \ln T_{ij} = \frac{k \sum_i (\ln T_i)^3 - \sum_i \ln T_i \sum_j (\ln T_j)^2}{2[k \sum_i (\ln T_i)^2 - (\sum_i \ln T_i)^2]} \quad (16) \]

With this, \( w_{ij} \) would be equal to \( w(T_{ij}) \) if \( \ln \sigma \) were a second order polynomial in \( \ln T \). In present studies numerical computation of \( w(T) \) has been carried out by using the above procedure.

### 3.2.4 Results of \( \rho(T) \) Analysis for FeSi (RR=2×10⁴)

In what follows the analysis of the temperature dependent resistivity data in FeSi (RR=2×10⁴) sample in terms of the three models (i) the thermally activated behaviour (ii) the step function DOS and (ii) the Gaussian DOS models are compared. A fit to the activated behaviour model to \( \rho(T) \) data of this sample is shown in Fig. 3.3. The fit is found to be very good with \( \chi^2 \sim 10^{-4} \) in a narrow temperature interval of 100-170 K. The energy gap \( \Delta_e \) extracted from the fit is found to be 700 K, which is in accordance with earlier studies [6, 18]. The step function DOS model fits conductivity \( \sigma(T) \) data in a wider temperature interval of 100 to 300 K range. A fit to this model is shown in Fig. 3.7. The values of \( W = 440 \) K and \( \Delta_e = 875 \) K obtained from this fit for FeSi (RR=2×10⁴) sample is within the range of the reported values of \( W = 300 \) to 450 K and \( \Delta_e = 600 \) to 950 K [7, 14, 20]. The conductivity data of FeSi fit equally well to the Gaussian DOS model using \( \mu_0, E_g, E_\mu \), and \( W \) as fitting parameters in the temperature range of 100-300 K. The fitted \( \sigma(T) \) is shown along with the experimental data in Fig 3.7. The \( \chi^2 \) of the fit in both cases is found to be \(< 10^{-3} \). The values of the fit parameters extracted for FeSi (RR=2×10⁴) are found to be \( 2E_\mu = 865 \) K, \( E_g = 875 \) K, \( W = 470 \) K with a prefactor \( \mu_0 = 1.2 \) m²K³/²V⁻¹s⁻¹. The value of \( W \) and the mobility gap \( \Delta_\mu = 2E_\mu \) deduced from this model compares well with the step size and \( \Delta_e \) obtained from the step function DOS model respectively. The effective energy gap, \( \Delta_{eff} \), deduced from this model is found to be 535 K. The magnitude of this gap is, however, lower than \( \Delta_e \) deduced from the
Fig. 3.7. Variation of electrical conductivity, \( \sigma(T) \), in FeSi(\( RR=2 \times 10^4 \)) showing the fits to the step function DOS model and the Gaussian DOS model in 100 – 300 K range.
activated behaviour model. The calculated values of $n$ at 200 and 300 K for FeSi are found to be $n_{200K}=0.31 \times 10^{28}$ m$^{-3}$ and $n_{300K}=0.8 \times 10^{28}$ m$^{-3}$, which are in good agreement with reported carrier concentrations from Hall measurements viz., $\sim 0.29 \times 10^{28}$ m$^{-3}$ and $2 \times 10^{28}$ m$^{-3}$ respectively [14], lending credibility to the present treatment.

At low temperature, i.e., between 5-40 K, $\rho(T)$ is observed to exhibit a VRH type behaviour. The fit to this model is also shown in Fig. 3.3. The hopping parameter $T_0$ deduced from this fit is found to be $1.56 \times 10^5$ which is in good agreement with the value reported for a single crystal of FeSi [12]. Further, the density of localised states $N(E_F)$ calculated using Eq. (10) is found to be $1.9 \times 10^{23}$ states-K$^{-1}$-m$^{-3}$. The value of the localization length $\alpha^{-1}$ calculated using $T_0$ and $N(E_F)$ is found to be 6.7 Å which is in good agreement of the reported value of 8.3 Å [18].

At temperatures below 5 K, $\rho(T)$ is found to deviate from the VRH behaviour as can be clearly seen from the inset (a) of Fig. 3.3. The conductivity data below 5 K fits to a power law behaviour of type $\sigma = \sigma_0 + bT^m$ with $m=1$ as shown in the inset (b) of Fig. 3.3. Here $\sigma_0 = 1.5 \Omega^{-1}$ m$^{-1}$, $b = 7.74 \Omega^{-1}$ m$^{-1}$- K$^{-1}$ are found from the linear fit. This indicates the presence of very small but finite conductivity at $T = 0$ K in FeSi. The metallic conductivity in FeSi close to $T = 0$ K has been also reported in earlier studies [7, 17, 23]. In this temperature regime, the electrical conductivity has been calculated at fixed temperatures as described in section 3.2.3.4. The value of disorder parameter $\delta = 25$ K is required in order to reproduce the experimental conductivity of 31.8 $\Omega^{-1}$m$^{-1}$ at 4.2 K. Similarly to match the conductivity of 4.4 $\Omega^{-1}$ m$^{-1}$ of FeSi measured at the lowest temperature of 50 mK [17], the required value of $\delta$ is found to be 18 K. This clearly demonstrates that in the presence of a disorder, a non-zero $\sigma$ for FeSi at $T = 0$ K can be realised within the framework of this model.

3.3 Sample Dependent Transport Behaviour of FeSi

3.3.1 Electrical Resistivity Studies

The electrical resistivity, $\rho(T)$, behaviour of the several samples of various RR values have been analyzed to investigate the effect of the quality of the samples on the transport properties of this system. In Fig. 3.8 the variation of normalised resistivity, $\rho(T)/\rho(300K)$,
Fig. 3.8. Variation of normalized resistivity, $\rho(T)/\rho(300K)$, with temperature for some representative FeSi samples with RR between 7 and $2 \times 10^4$. 
has been shown as a function of temperature for a few representative samples with RR varying from 2 x 10^4 to 7. It can be seen from this figure that ρ(T) curves of the samples with RR ≥ 10^3 look identical and almost merge in high temperature regime, while sample with RR = 7 exhibits a large deviation particularly in the low temperature regime. The experimental data of both the samples have been analyzed using the activated behaviour, the step function and the Gaussian DOS models in high temperature regime (T ≥ 100 K) and VRH model in low temperature regime (T ≤ 40 K). The results of these analysis are summarized in Table II.

It can be inferred from the table that the values of energy gap Δ, for a given model, for samples with RR ≥ 10^3 are nearly same within the spread of ~30 K. However Δ of the sample with lowest RR = 7 is found to be significantly lower than that of the samples with large RR. W is found to increase with decreasing RR, which within Gaussian DOS model is an indication of increase of disorder and/or reduction of correlation effect. The hopping parameter T_o is seen to decrease with RR for sample having RR of the order of ~10^5. The resistivity of the sample with RR = 7 is observed to deviate from VRH behaviour indicating the absence of the localized states inside the gap. In order to get the

TABLE II: Results of the fits of ρ(T) data of FeSi samples with different RR values using all the models described in the text. The energy gaps Δ_μ & Δ_eff obtained from the Gaussian DOS fits are shown along with corresponding gaps Δ_s & Δ_a deduced from step function DOS model and the activated behaviour model respectively for all the samples. The parameters W and E_g of the Gaussian DOS and the hopping parameter T_o are also shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Δ_s (K)</th>
<th>Δ_μ (K)</th>
<th>W (K)</th>
<th>E_g (K)</th>
<th>Δ_eff (K)</th>
<th>Δ_a (K)</th>
<th>T_o (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSi (RR= 2x10^4)</td>
<td>875</td>
<td>865</td>
<td>470</td>
<td>875</td>
<td>535</td>
<td>700</td>
<td>1.56x10^5</td>
</tr>
<tr>
<td>FeSi (RR= 6x10^3)</td>
<td>885</td>
<td>900</td>
<td>523</td>
<td>807</td>
<td>560</td>
<td>720</td>
<td>2.33x10^4</td>
</tr>
<tr>
<td>FeSi (RR= 7)</td>
<td>495</td>
<td>560</td>
<td>721</td>
<td>658</td>
<td>381</td>
<td>318</td>
<td>-</td>
</tr>
</tbody>
</table>
information about the type of conductivity prevalent in the temperature range between 5 to 30 K, the logarithmic derivative of conductivity \( w = \frac{\ln(\sigma)}{\ln(T)} \) versus T plot analysis (cf. section 3.2.3.5) [23] have been carried out for these samples. The results of these analysis is shown in Fig. 3.9 for two representative samples with \( RR = 2 \times 10^4 \) and 7. It can be seen from this figure that the slope of \( w(T) \) changes sign from negative to positive as RR is reduced from \( 2 \times 10^4 \) to 7 indicating the change in the nature of the conductivity. This gives an indication that sample with \( RR = 2 \times 10^4 \) is insulating, whereas another sample with \( RR = 7 \) has a tendency to metallise in this temperature range.

3.3.2 Pressure Dependent Electrical Resistivity Studies in FeSi

3.3.2.1 Pressure Effects on Energy Gap

The electrical resistivity of the FeSi (\( RR=2\times10^4 \)) sample has been measured as a function of temperature (4.2 to 300 K) and pressure upto 6.4 GPa to investigate the effect of external pressure on the energy gap and the ground state of this system using the apparatus described in Chapter 2. In Fig. 3.10(a), the electrical conductivity of FeSi (\( RR=2\times10^4 \)) is plotted for various pressures as a function of temperature. The experimental data has been analyzed using all the three models, mentioned earlier, in the higher temperature region (\( T \geq 100 \text{ K} \)). The fit to the Gaussian DOS model to the conductivity data at the various pressures investigated has been shown in Fig 3.10(a). In addition, the fit to activated behaviour model to the resistivity data is shown in the Fig. 3.11. The \( \chi^2 \) of the fits to all the three models are found to be within the range of \( 10^{-2} \) to \( 10^{-4} \), indicating good fits. The variation of energy gaps \( \Delta_a, \Delta_s \) and \( \Delta_{eff} \) deduced from the activated behaviour, the step function DOS and the Gaussian DOS models respectively, as function of pressure are shown in Fig. 3.12(a). From this figure, it is clear that energy gap \( \Delta \) deduced from all the models exhibit similar trends in the variation with pressure, i.e., \( \Delta \) decreases with increasing pressure. (\( \Delta \) denotes the energy gap in general). The variation of parameters \( E_g, W \) and \( E_\mu \) extracted from the fits of Guassian DOS model to the conductivity data of FeSi (\( RR=2\times10^4 \)) sample, as a function of pressure are shown in Fig. 3.13(a), (b) and (c) respectively. The parameter W is found to increase from a value of 470 K at 0 GPa to 622 K at 6.4 GPa pressure. \( E_g \) also increases with pressure from

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Fig. 3.9. Logarithmic derivative of conductivity \((w)\) versus \(T^{1/2}\) plot for two FeSi samples with \(RR = 7\) and \(2 \times 10^4\) in 5 to 30 K temperature range. The temperature scale \(T^{1/2}\) is chosen for better visibility of the plot.
Fig. 3.10. Variation of electrical conductivity, $\sigma(T)$, along with the fits to the Gaussian DOS model at various pressures (a) for FeSi (RR=2x10^4) and (b) FeSi(RR=7) samples.
Fig. 3.11 Variation of $\rho(T)$ in FeSi($RR=2\times10^4$) showing fits to the activated behaviour model for various pressures. Energy gap $\Delta_v$ have been extracted from fits in the 100-170 K region. The data at various pressures have been shifted along the ordinate axis for clarity
Fig. 3.12. Pressure dependence of energy gaps obtained from fits to the thermally activated behaviour model ($\Delta_a$), the step function DOS model ($\Delta_s$) and the Gaussian DOS model ($\Delta_{eff}$) for (a) FeSi (RR=2$x10^4$) and (b) FeSi (RR=7).
Fig. 3.13. Pressure dependence of the parameters (a) $E_g$, (b) $W$, (c) $E_\mu$, and (d) $n_{100K}$ deduced from the fits to the Gaussian DOS model in FeSi ($RR=2\times10^4$). The solid lines are guide to the eye.
875 to 1690 K. In contrast, the relative energy separation between the mobility edge and the Fermi energy is seen to decrease monotonically with increasing pressure as seen in the variation of $E_\mu$ (Fig. 3.13(c)). Using parameters $E_g$, $W$, and $E_\mu$ obtained from the fits of the conductivity data, the effective carrier concentrations at various temperatures $T \geq 100K$ have been calculated to deduce $\Delta_{\text{eff}}$ as described in section 3.2.3.4. The variation of $n_{100K}$, obtained at a fixed temperature of 100 K, with respect to pressure is shown in Fig. 3.13(d). It can be seen that $n_{100K}$ increases with increasing pressure, which leads to a decrease in $\Delta_{\text{eff}}$.

Such a pressure dependence of the conductivity data has also been investigated in FeSi of small RR. A representative fit to the Gaussian DOS model of the conductivity data in this sample at various pressures investigated are shown in Fig 3.10(b). The variation of energy gaps $\Delta_a$, $\Delta_s$ and $\Delta_{\text{eff}}$ deduced from the activated behaviour, the step function DOS and the Gaussian DOS models respectively, as function of pressure are shown in Fig. 3.12(b). Here again the trends in variation of $\Delta$ deduced from all the models are similar, i.e. $\Delta$ increases with increasing pressure. It should be noted that the variation of $\Delta$ in FeSi (RR = 7) with pressure is just opposite to the variation of $\Delta$ observed in FeSi (RR=2x10^4) sample (see Fig 12(a) and (b)). The parameters $W$, $E_g$, $E_\mu$ and $n_{100K}$ extracted from the fit to the Gaussian DOS model for this sample at various pressures are shown in Table III. It can be seen from this table that $W$ remains nearly independent of pressure and fluctuates around a value of 720 ± 30 K with increasing pressure, while

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$W$ (K)</th>
<th>$E_g$ (K)</th>
<th>$E_\mu$ (K)</th>
<th>$n_{100K}$ (carriers/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>720</td>
<td>660</td>
<td>280</td>
<td>9.25x10^{26}</td>
</tr>
<tr>
<td>0.5</td>
<td>738</td>
<td>790</td>
<td>290</td>
<td>9.15x10^{26}</td>
</tr>
<tr>
<td>1.1</td>
<td>690</td>
<td>805</td>
<td>330</td>
<td>6.40x10^{26}</td>
</tr>
<tr>
<td>2.0</td>
<td>750</td>
<td>890</td>
<td>350</td>
<td>5.65x10^{26}</td>
</tr>
<tr>
<td>3.5</td>
<td>730</td>
<td>1110</td>
<td>355</td>
<td>4.66x10^{26}</td>
</tr>
</tbody>
</table>

TABLE III: Results of the fits of $\sigma(T)$ data of FeSi (RR =7) with the Gaussian DOS model. The parameters $W$, $E_g$, $E_\mu$ and $n_{100K}$ extracted from the fits at various pressures investigated are shown.
$E_g$ increases substantially from 660 K at 0 GPa to 1110 K at 3.5 GPa. Here $E_\mu$ and $n_{eff}$ shows a trend just opposite to that seen in the large RR sample. $E_\mu$ increases from a value of 280 K at ambient pressure to 355 K at 3.5 GPa, while $n_{eff}$ decreases with increasing pressure (see Table III). The $\Delta_{eff}$ is found to increase for a value of 380 K at ambient pressure to 455 K at 3.5 GPa pressure (cf. Fig. 3.12(b)). These results are quite significant, since the two FeSi samples with different RR show an opposite trend in the variation of $\Delta$ when subjected to external pressures. This points out that disorder has an important role in the variation of $\Delta$ with pressure. In previous high pressure studies [27], $\Delta$ has been reported to increase with pressure, a trend similar to what is observed in the FeSi sample with RR=7. Since RR is related to defect states in the gap, it appears that the variation of $\Delta$ with pressure is intimately related to the presence of defect states in the KI gap. It is therefore important that focus should be first to understand the effect of pressure on these defect states before interpreting the pressure variation of $\Delta$, which will be attempted in the discussion section.

3.3.2.2 Pressure Effects on Localized States

The effect of the external pressure is seen to be more dominant in the low temperature region below 40 K on the good quality FeSi (RR= 2x10$^4$) sample. Here very large changes are seen in $\sigma$ values by increasing the pressure (cf. Fig. 3.10(b) ). While sample with RR = 2 x 10$^4$ exhibits a VRH behaviour in this temperature range, the sample with RR=7 deviates from this behaviour. The fits of the resistivity to the VRH model in the 5-40 K for all the pressures investigated in FeSi (RR=2x10$^4$) are shown in Fig. 3.14(a). The variation of $T_\sigma$ extracted from these fits is shown in Fig. 3.14(b) as function of pressure. It can be seen from this figure that the fit to the VRH formula at ambient pressure is very good but for higher pressures the resistivity starts deviating from the VRH behaviour for temperatures less than ~5 K and $T_\sigma$ decreases to ~15 K at a pressure of 6.4 GPa. The localization lengths $\alpha^{-1}$ have been calculated at all the pressures investigated using the values of $T_\sigma$ and $N(E_F)$ as described in section 3.2.3.4. The variation of $\alpha^{-1}$ with pressure is shown in Table IV. It can be seen that $\alpha^{-1}$ increases with increasing pressure indicating the delocalisation of the localised states under pressure.

The electrical conductivity ($\sigma_{cal}$) of FeSi at 4.2 K at various pressures has been
Fig. 3.14. (a) Variation of electrical resistivity, \( \rho(T) \), in the 4 – 40 K range for various pressures in FeSi (RR=2x10^4) showing fits to VRH model. (b) Variation of VRH parameter \( T_0 \) as a function of pressure.
TABLE IV: Variation of localization length $\alpha^{-1}$ with pressure in FeSi (RR=2x10^4) sample.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$\alpha^{-1}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.8</td>
</tr>
<tr>
<td>3.6</td>
<td>22.4</td>
</tr>
<tr>
<td>5.6</td>
<td>87.3</td>
</tr>
<tr>
<td>6.4</td>
<td>177</td>
</tr>
</tbody>
</table>

calculated by using the Gaussian fit parameters, deduced from the fits in the high temperature regime and by inserting a disorder parameter $\delta$ in Fermi-Dirac distribution function as described in section 3.2.3.4. It is found that with $\delta$ within the reasonable range of 23 K to 40 K, the experimental values of conductivity at 4.2 K for all the pressures can be reconciled. The temperature dependence of the measured conductivity, $\sigma(T)$ of FeSi (RR=2x10^4) sample is shown in Fig. 3.15(a) for the limited temperature range of 5-40 K for the various pressures investigated. A noteworthy feature of the results shown in this figure, is that $\sigma(T)$, which is of the variable range hopping type at ambient pressure, becomes more linear with increase in pressure in this temperature range. In fact, $\sigma(T)$ fits to $\sigma=\sigma_0+\sigma_1 T^{1/2}+\sigma_2 T$, with the coefficient of the linear term showing a systematic increase with increase in pressure. Observation of both exponents 1/2 and 1 for the temperature dependence of conductivity in the metallic regime have been earlier obtained in other amorphous systems [28] and have been argued to arise due to electron-electron interaction and disorder effects [29] and the possibility of the influence of phonons [28]. From the above fit the conductivity of FeSi (RR=2x10^4) has been extrapolated to $T=0$ K and the $\sigma(T=0)$ thus obtained is shown in Fig. 3.15(b) as a function of pressure. It is clear from this figure that as $T$ tends to zero, $\sigma(T)$ seems to approach zero at ambient pressure, as is expected for an insulator. In contrast at 3.6 GPa pressure, the extrapolated $\sigma(T=0)$ is unambiguously finite and is $\sim$5000 $\Omega^{-1}$m$^{-1}$. It is also seen that with increase in pressure the magnitude of $\sigma(T=0)$ increases to $\sim$5 x10^4 $\Omega^{-1}$m$^{-1}$, for a pressure of 6.4 GPa. It is important to mention that the values of the Mott’s minimum metallic conductivity, $\sigma_{\text{min}}$, reported for the FeSi system lies between 3700 and 7400 $\Omega^{-1}$m$^{-1}$ [3, 17]. Then from the present results it can be inferred that the system undergoes an insulator to metal transition at $T=0$, somewhere between ambient pressure and the 3.6 GPa.
Fig. 3.15. (a) Variation of electrical conductivity, \( \sigma(T) \), in the 5 – 40 K temperature range for all pressures investigated in FeSi \( (RR=2 \times 10^4) \). (b) Variation of zero temperature extrapolated conductivity, \( \sigma(T=0) \), of FeSi \( (RR=2 \times 10^4) \) as a function of pressure. Note that \( \sigma(T) \) becomes more linear in character and \( \sigma(T=0) \) becomes larger with pressure.
In order to verify more convincingly the occurrence of the metal to insulator transition (MIT) in this sample, the numerical derivative \( w = \frac{d\ln(\sigma(T))}{d\ln(T)} \) of the conductivity data at all the investigated pressures in the low temperature regime has been calculated numerically as described in section 3.2.3.5. The \( w \) versus \( T^2 \) plot for FeSi (RR=2x10^4) sample is shown in Fig. 3.16 for the different pressures. It is seen from this figure that \( w \) is a decreasing function of \( T \) as is expected for an insulator at ambient pressure. At external pressure of 3.6 GPa, the temperature dependence of \( w \) becomes an increasing function of temperature, re-iterating that the MIT in FeSi occurs in the 0 to 3.6 GPa range. This is in agreement with the inference drawn on the basis of the occurrence of \( \sigma_{\text{min}} \) from the \( \sigma(T) \) data shown in Fig. 3.15. It is worth pointing out that in the insulating side, \( w \) after showing an unambiguous increase with decrease in temperature, exhibits a downturn at the lowest of temperatures (cf. Fig. 3.16). This arises from the fact that the resistivity in FeSi becomes smaller than that predicted by the VRH formula and tends to saturate at very low temperatures, which has led to a suggestion that FeSi has a semimetallic ground state at \( T=0 \) [17]. Since from the inspection of the \( w(T) \) vs \( T \) plots (cf. Fig. 3.16) no minimum is seen as the pressure is varied, as was seen in ref. [23] for a typical discontinuous MIT (cf. Fig. 3.6), it can be concluded that the insulator metal transitions observed in the present investigation are possibly continuous. For FeSi sample with RR = 7, the \( w \) versus \( T \) plot shown in Fig. 3.9 suggests that in low temperature regime this sample would be metallic at the ambient pressure itself.

### 3.3.3 Band Structure Calculations

In order to investigate the effect of pressure on the band gap of FeSi, band structure calculations have been carried out [10] using the tight binding version of the LMTO method in the atomic sphere approximation for the actual lattice constants expected under the application of external pressure [32]. Keeping all other parameters same in the calculations excepting the lattice constant, a systematic but small increase was observed in the band gap as a function of a decrease in the lattice constant, as shown in Fig. 3.17. The lattice constants employed in the calculation were obtained from neutron diffraction measurements in the 0-8.4 GPa pressure range [32]. It can be seen from the figure that the magnitude of the gap is \( \sim 126 \text{ meV} \) (1460 K) at a lattice constant of 4.489 Å corresponding to that at ambient pressure, which is in good agreement with earlier calculations [31, 33].
Fig. 3.16. The logarithmic derivative of conductivity ($w$) versus $T^{1/2}$ in the 5-40 K temperature range for all pressures investigated in the FeSi (RR=2x10^4) sample. Note that $w$ increases with decrease in temperature at ambient pressure. For pressures greater than 3.6 GPa, $w$ decreases with temperature, possibly extrapolating to 0 as $T$ tends to 0.
Fig. 3.17. The variation of the indirect band-gap obtained from the TBL.MTO band structure calculations for lattice constants obtained from neutron diffraction as a function of pressure.
The band gap increases to 132 meV (1530 K) at 8.4 GPa, a mere 70 K increase. It should be noted that the increase of the similar magnitude is observed for the experimental gap in the poor quality FeSi sample with RR = 7 (cf. Fig. 3.12(b)). However, the variation of Δ with pressure (cf. Fig. 3.12(a)) in good quality FeSi sample with large RR = 2 x 10^4 is just opposite to the predictions of the band structure calculations. In the forthcoming section an explanation of the pressure dependence of Δ and its correlation with the RR of the sample is attempted within the framework of the proposed Gaussian DOS model.

3.4. DISCUSSION

It is interesting to see from Fig. 3.3 that within a limited temperature interval of 1.3 to 300 K, a variety of the transport mechanisms seems to be involved in dictating the ρ(T) behaviour of FeSi system. On the one hand FeSi behaves as a narrow gap semiconductor in high temperature regime (T ≥ 100 K), while on the other its conductivity exhibits a power law dependence at low temperatures (below 5 K) indicating a metallic character. The metallic character with moderate effective mass of ~10 has been observed in FeSi at very low temperature in several previous studies on polycrystalline as well as single crystal samples [3, 7, 17]. The saturation of resistivity has also been reported at low temperatures in several f electron based kondo insulators such as SmB6 and CeNiSn [30, 34, 35]. This raises a question as to whether the occurrence of the residual conductivity at low temperature is an intrinsic property of Kondo insulators (KI) or is an extrinsic effect due to the presence of impurities. Experimental findings in this regard are quite contradictory. The studies on single crystals of SmB6 [35] indicates that the resistivity saturation below 4 K is not an intrinsic property, but an impurity effect arising from the surface of the crystal. On the other hand, in CeNiSn the conductivity at low temperature is observed to increase for cleaner samples [34], indicating that the occurrence of the metallic conductivity at low temperature is an inherent property of the material. This then poses a natural question whether the ground state of FeSi and the related KI systems are insulating or metallic. This still remains as an unresolved question. However, in present Gaussian DOS model it is demonstrated that finite conductivity at zero temperature can be realised by considering the smearing of Fermi function due to the disorder.

The dependence of Δ observed in FeSi samples on the quality index RR (cf. Table II) can be understood within the framework of the Gaussian DOS
model as follows: The parameter $E_g$ decreases and $W$ increases with decreasing RR (see Table II). The decrease in $E_g$ can be attributed to band structure effect arising due to the local changes in structure. Band structure calculations [33] predict that even a small relative change of $\sim 0.005$ in the values of fractional atomic position of parameter $u_{Fx}$ and $u_{Si}$ can lead to a change in the relative separation of band edges by about 10 meV. It is seen from Table I that there is substantial change in values of $u_{Fx}$ and $u_{Si}$ for RR $= 2 \times 10^4$ and 7 samples. This could be the reason of the decrease of $E_g$. The net effect of decrease of $E_g$ could be a decrease of the energy gap. The increase in $W$ indicates enhancement in disorder, which is consistent with the fact that disorder increases with decreasing RR. The interplay of $W$ and $E_g$ lead to a decrease of $E_{\mu}$ with decrease in RR as can be seen from Table III. This implies that $E_{\mu}$ moves closer to $E_F$ with decreasing RR. The decrease in $E_{\mu}$ gives rise to an increase in effective carrier concentration, $n$, in the conduction band, which in turn results in the lowering of $\Delta_{eff}$. This explains the observed decrease of $\Delta$ in low RR sample.

Having discussed the effect of RR on the $\Delta$ of the samples at ambient pressure, attention is focused to understand the observed pressure dependence of $\Delta$ shown in Fig. 3.12(a) and (b) for FeSi samples with RR = $2 \times 10^4$ and 7 respectively. $\Delta$ is seen to decrease monotonically with pressure for the large RR sample and increases marginally for the small RR sample. This indicates that the evolution of the energy gap under application of external pressure is determined by the RR values of the samples. Band structure calculations in FeSi indicate that with increase in pressure the band gap increases. It is thus clear that though the band structure calculations reproduce the experimentally observed pressure dependence of $\Delta$ in low RR sample, they fail to explain the same for large RR sample. An explanation of the pressure dependence of $\Delta$ and its correlation with the RR of the sample based on the results of the quantitative analysis of the experimental data using the Gaussian DOS model can be given as follows: It is seen that pressure affects all the Gaussian parameters such as $W$, $E_g$, $E_{\mu}$ (see Fig. 3.13 and Table III). The interplay of these quantities governs values of the carrier concentration, $n$, which in turn dictate the final value of the effective energy gap $\Delta_{eff}$. The band structure calculations imply that the band edges move apart with increase in pressure. This in terms of Gaussian DOS model means an increase in $E_g$ with pressure (see Fig. 3.4(c)). For sample with RR $= 2 \times 10^4$, $E_g$ increases with pressure (cf. Fig. 3.13(a)) consistent with the prediction of band
structure calculations. On the other hand $W$ increases with (cf. Fig. 3.13(b)) pressure. The net effect of the competition between $W$ and $E_{\mu}$ is seen to result in decrease in $E_{\mu}$ (cf. Fig. 3.13(c)) with increasing the pressure. A decrease in $E_{\mu}$ implies the movement of $E_{\mu}$ towards $E_F$, which is equivalent to increase in the delocalization of the localized states. This is evident from the observed increase in the localisation length with increasing pressure (cf. Table IV). The delocalization gives rise to an additional contribution to the carrier concentration, $n$, with increasing pressure. This is consistent with the observed variation of $n_{100K}$ with pressure (cf. Fig. 3.13(d)). The increase in $n$ implies the lowering of $\Delta_{eff}$ with increasing pressure, which explains the decrease of $\Delta$ in the large RR sample under external pressure.

The increase of $\Delta$ for the sample with low RR = 7 with pressure can be explained as follows: $E_{\mu}$ lies close to $E_F$ at ambient pressure and increases merely by 65 K with increasing pressure (Table III). $W$ is seen to saturate at a value of $720 \pm 20$ K with pressure, this means most of the states inside gap are already delocalized at the ambient pressure itself. This is consistent with the fact that low temperature VRH behaviour is found to be absent in this sample. This means that there is no additional contribution to the effective carrier concentration $n$ from delocalization. On the other hand $E_g$ increases substantially by a value of $\sim 450$ K with increasing pressure upto 3.5 GPa. The net effect of this would be to increase the band gap (cf. Fig. 3.17) which means reduction in the number of activated charge carriers. Thus the net $n$ decreases with pressure for RR = 7 sample. The decrease in $n$ implies an increase of $\Delta_{eff}$ with increasing pressure. This explains the increase of $\Delta$ for low RR sample. It is noticeable that the pressure induced increase in $\Delta$ calculated from band structure is only $\sim 70$ K, which tallies with the measured increase of $\Delta_{eff}$ in FeSi (RR=7). From the above discussion it appears that the competition between magnitude of $E_g$, $W$ and the position of $E_{\mu}$ with respect to $E_F$ is responsible for the evolution of the energy gap under pressure in FeSi system. While $E_g$ can be attributed to the band structure effect, $W$ and $E_{\mu}$ depend on the degree of the disorder/correlation in the system and hence brings about the observed variation with change in RR of the sample.

3.5 SUMMARY

The transport of the pristine FeSi samples of various RR values have been investigated
as a function of temperature and pressure. A new DOS model, namely, Gaussian DOS model, has been proposed and used to analyze the experimental data. For comparison, the data has also been analyzed using various existing models. Sample quality is found to play a significant role in the measured transport behaviour. It is seen that samples with RR values above $\sim 10^3$ exhibit more or less identical behaviour particularly in high temperature regime with moderate change in low temperature regime, but the properties of samples with low RR deviate grossly. External pressure is seen to have a profound effect on both regimes of conduction in FeSi. In the low temperature regime, delocalization of electron states in the gap results in a shift in the mobility edge towards $E_F$, altering the zero temperature conductivity significantly. This gives rise to the observation of an insulator to metal transition as a function of pressure. The nature of the insulator to metal transition as inferred from the temperature dependence of the logarithmic derivative of conductivity, points to the fact that the transition is possibly continuous as in doped semiconductors. The predicted gap behaviour from band structure dictates that the band gap increases with increasing pressure. However the experimentally observed pressure dependence of $\Delta$ shows a decrease for large RR sample and a marginal increase for low RR sample. In a nutshell, the behaviour of $\Delta$ is a complicated outcome of the magnitude of the different contributions, viz., the number density of defect states, the shape of the band tails and the position of the mobility edge, which widely differ from sample to sample. The Gaussian DOS model incorporates these in its defining parameters. Within the purview of the model the temperature dependence of the conductivity is primarily dictated by the number density of carriers $n$ excited above $E_n$. Since the parameters entering the model $E_g$, $W_x$ and $E_\mu$ are small and of comparable magnitudes, any variation in these parameters can bring about observable changes in $n$ and therefore in $\sigma$. The band tailing arises out of disorder; this same disorder entails a smearing of the Fermi function. The latter is very important for giving rise to a non-zero conductivity at $T = 0 \text{ K}$. These results indicate that disorder plays a major role in determining the ground state transport properties in FeSi and related systems.
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