CHAPTER 4

TRANSPORT STUDIES IN FeSi\(_{1-x}\)Ge\(_x\)

The results of the isoelectronic Ge substitution studies in the FeSi\(_{1-x}\)Ge\(_x\) system are discussed in this chapter. These studies have been carried out by electrical resistivity measurement: (i) as function of temperature for 0 ≤ x ≤ 0.25 and (ii) as function of temperature and pressure for x=0.05 and 0.2. It is believed that the Kondo insulating (KI) gap in FeSi arises due to the hybridization of a broad conduction band, mainly consisting of the s,p bands of Si, and a localized 3d band of Fe [1, 2]. The change in lattice volume has a direct bearing on the strength of this hybridization. For example lattice expansion is expected to weaken the hybridization and hence should lead to a decrease of the KI gap. On the other hand the contraction of the lattice by the application of external pressure should result in increase of the KI gap. Having presented the effect of lattice contraction by external pressure on pristine FeSi in previous chapter, in this chapter we concentrate on the effect of the lattice expansion on the KI gap, which can be effected by chemical substitution of FeSi. There have been several studies on the variation of KI gap in FeSi with chemical substitution: Replacing Fe with Ir [2] or Co [3] results in extrinsic electron doping of FeSi and a decrease in Δ. Experiments on Al substitution for Si [4, 5] results in extrinsic hole doping leading to metallicity with heavy mass features.

In these chemical substitution studies, in addition to an increase in lattice parameter there is also an introduction of charge carriers, both of which have an effect on Δ. With isoelectronic substitution and high pressure studies, on these samples one can study the effect of change in lattice volume alone on the transport properties. With this in mind, the studies of isoelectronic substitution on Si sites by Ge in FeSi\(_{1-x}\)Ge\(_x\) series have been undertaken.

4.1 RESULTS: Ge SUBSTITUTION STUDIES

4.1.1 XRD Characterization and Rietveld Refinements

For the range of composition investigated by XRD (0 ≤ x ≤ 1) in the series FeSi\(_{1-x}\)Ge\(_x\), 97
it was found that the single-phase regime was restricted to \(0 \leq x \leq 0.25\). For \(x = 1\), the samples were single phase with a HCP structure, with \(a = 4.9926 \text{ Å} \) and \(c = 4.0598 \text{ Å}\) in accordance with literature [6]. The samples with \(x = 0.5\) and \(x = 0.75\) had at least a mixture of two phases. For this reason, in what follows the present studies are restricted to the samples having a Ge concentration, \(x \leq 0.25\). The powder XRD pattern of FeSi\(_{1-x}\)Ge\(_{x}\) samples are depicted in Fig. 4.1(a). From this, it is clear that diffraction lines other than that due to FeSi structure are absent for all values of \(x\) studied. This indicates the phase purity of these samples. It can be seen from the Fig. 4.1(a) that with increase in Ge concentration, the XRD peaks shift systematically towards lower angles indicating the expansion of lattice. The Rietveld refinement to the XRD data of all the Ge substituted samples to FeSi-type structure is found to be very good for all the spectra shown in Fig. 4.1(a). A representative Rietveld fit to the XRD pattern of a sample is shown in Fig. 4.2. The S parameter, a measure of the goodness of the fit, is found to be less than \(\sim 1.7\) for all the samples indicating that fits are very good. The lattice parameters and the fractional atomic position parameters for Fe, Si and Ge, i.e., \(u_{Fe}, u_{Si}\) and \(u_{Ge}\) respectively, extracted from the Rietveld refinement of the XRD data of FeSi\(_{1-x}\)Ge\(_{x}\) samples with \(0 \leq x \leq 0.25\) are shown in Table I. The matching of fractional atomic position parameters for Si and Ge atoms, (i.e., \(u_{Si}\) and \(u_{Ge}\)) shown in this table clearly indicates that Ge has successfully replaced Si for all the samples with \(0.05 \leq x \leq 0.25\). The variation of the lattice parameter as a function of Ge concentration, \(x\) is shown in Fig. 4.1(b). It is seen that the lattice parameter increases monotonically with Ge substitution. This expansion of the lattice can be expected, on account of the larger atomic radius of Ge as compared to Si.

**TABLE I:** Refined atomic coordinates and lattice parameters for FeSi\(_{1-x}\)Ge\(_{x}\) samples obtained from the the Rietveld analysis of the XRD data. S parameter shows the goodness of the fit.

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>Position</th>
<th>(u_{Fe})</th>
<th>(u_{Si})</th>
<th>(u_{Ge})</th>
<th>S parameter</th>
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<tr>
<td>0</td>
<td>4.4890</td>
<td>4(a)</td>
<td>0.137</td>
<td>0.843</td>
<td>-</td>
<td>1.35</td>
</tr>
<tr>
<td>0.05</td>
<td>4.5049</td>
<td>4(a)</td>
<td>0.139</td>
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<td>0.838</td>
<td>1.6</td>
</tr>
<tr>
<td>0.15</td>
<td>4.5230</td>
<td>4(a)</td>
<td>0.137</td>
<td>0.840</td>
<td>0.840</td>
<td>1.67</td>
</tr>
<tr>
<td>0.20</td>
<td>4.5287</td>
<td>4(a)</td>
<td>0.140</td>
<td>0.844</td>
<td>0.844</td>
<td>1.42</td>
</tr>
<tr>
<td>0.25</td>
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<td>4(a)</td>
<td>0.137</td>
<td>0.836</td>
<td>0.836</td>
<td>1.65</td>
</tr>
</tbody>
</table>
Fig. 4.1. (a) Powder X-ray diffractograms of FeSi$_{1-x}$Ge$_x$ system (0 ≤ x ≤ 0.25). Indexing corresponds to FeSi structure. (b) Variation of lattice parameter with Ge concentration, x, as obtained from Rietveld refinements. Solid line is guide to the eye.
Fig. 4.2: Rietveld fit to the XRD pattern of a representative sample, viz., FeSi$_{0.85}$Ge$_{0.15}$. Experimental data (+), calculated data (solid line) and the difference plot (bottom).
4.1.2 Electrical Resistivity Studies

The room temperature resistivity, \( \rho(300\text{K}) \), of FeSi\(_{1-x}\)Ge\(_x\) samples measured using the Van der Pauw method is found to decrease by increasing Ge concentration from 163 \( \mu\Omega\)-cm for \( x=0.0 \) to 90.3 \( \mu\Omega\)-cm for \( x=0.25 \). The resistivity ratio RR is observed to decrease with increasing Ge concentration from a value of \( 2 \times 10^4 \) for \( x=0 \) to 12 for \( x=0.25 \). The variation of resistivity, \( \rho \), of FeSi\(_{1-x}\)Ge\(_x\) as a function of temperature is shown in Fig. 4.3. It can be seen from this figure that \( \rho(T) \) of all the samples exhibits an increase with decreasing temperature. Further, \( \rho(T) \) of \( x=0.0 \) and 0.05 samples show a clear two-step increase separated by a broad shoulder around 75 \( \pm \) 15 K with decreasing temperature. This shoulder diminishes progressively with increasing Ge concentration and \( \rho(T) \) curve becomes smoother for samples with \( x>0.15 \) with decreasing temperature. In the case of Ge substitution of \( x = 0.25 \), there is an increase in resistivity with increasing temperature beyond 200 K indicating setting in of a metallic behaviour, but below this temperature a monotonic increase in \( \rho(T) \) with decrease in temperature is observed. In rest of the samples \( \rho(T) \) remains nearly independent of the temperature between 200 and 300 K range. The \( \rho(T) \) data of all the FeSi\(_{1-x}\)Ge\(_x\) (\( x = 0.0 \) to 0.25) have been analyzed by using the thermally activated behaviour, the step function DOS and the Gaussian DOS models in high temperature regime (\( T \geq 100 \)) and VRH model in low temperature regime (\( T \leq 40\text{K} \)), following the procedures described in section 3.2.3 of Chapter 3. The fits of the experimental data to the thermally activated behaviour model is shown in Fig. 4.4 in \( \log(\rho) \) versus 1/T plot. It can be seen from this figure that \( \rho(T) \) data fit very well to this model in 100 to 170 K temperature range. The values of \( \chi^2 \) of the fit are found to be between \( \sim 10^{-2} \) and \( 10^{-3} \) for all the samples. The energy gap \( \Delta_e \) deduced for this fit is seen to decrease by increasing Ge concentration, from a value of 700 K for \( x=0.0 \) to a value of 110 K for \( x = 0.25 \). The conductivity data of FeSi\(_{1-x}\)Ge\(_x\) (\( x = 0.0 \) to 0.25) fitted to the Gaussian DOS model using \( \mu_0, E_g, E_\mu, \) and \( W \) as fitting parameters is shown in Fig. 4.5. A representative fit to the step function DOS model is also shown in the inset of this figure. The fits are seen to be very good in 100 to 300 K range with \( \chi^2 \) values between \( \sim 10^{-2} \) and \( 10^{-4} \), except for the sample \( x=0.25 \) which fits only between 100 and 200 K because of the appearance of the metallic conductivity beyond this temperature. The energy gap \( \Delta_s \) extracted from the step function DOS model is also found to decrease a value of 870 K for \( x=0.0 \) to a value of 310 K for \( x = 0.25 \).
Fig. 4.3. Variation of electrical resistivity, $\rho$, as a function of temperature in 4.2 to 300 K range for FeSi$_{1-x}$Ge$_x$ with $0 \leq x \leq 0.25$ for the different Ge concentration.
Fig. 4.4. Variation of logarithm of resistivity, $\ln(\rho)$, as function of $T^{-1}$ fitted to the thermally activated behaviour model.
Fig. 4.5. Variation of conductivity as a function of temperature fitted to the Gaussian DOS model in FeSi$_{1-x}$Ge$_x$. Inset shows a representative fit of conductivity data to the step function DOS model for FeSi sample.
The effective energy gap, $\Delta_{\text{eff}}$, obtained from the fits of the Gaussian DOS model again is found to decrease from a value of 535 K for $x=0.0$ to a value of 250 K for $x = 0.25$. The variation of $\Delta_a$ and $\Delta_s$ are shown in Fig. 4.6 and $\Delta_{\text{eff}}$ in Fig. 4.7(d) as a function of Ge concentration $x$. It is noticeable that the energy gap $\Delta$ deduced from all the models shows a similar trend of variation with $x$. The variation of parameters such as FWHM of Gaussian $W$, relative separation between Fermi energy and mobility edge $E_{\mu}$, and effective carrier concentration $n_{100K}$ calculated at 100 K, extracted from the fits to Gaussian DOS model to the conductivity data of FeSi$_{1-x}$Ge$_x$ are shown in Fig. 4.7(a), (b) and (c) respectively as a function of $x$. It is seen that $E_{\mu}$ decreases and $n_{100K}$ increases with increasing Ge concentration $x$.

The electrical conductivity calculated at 4.2 K, $\sigma_{4.2K}$, by using the Gaussian fit parameters, obtained from the fits in high temperature regime and by inserting a disorder parameter $\delta$ in Fermi-Dirac distribution function is shown in Fig. 4.7(c) along with experimentally measured conductivity as a function of $x$. It is found that with $\delta$ within a reasonable range of $\sim 12$ to 25 K, the experimental values of $\sigma_{4.2K}$ for all the samples can be reconciled. It is pertinent to mention that $\sigma_{4.2K}$ increases by more than three orders of magnitude (cf. Fig. 4.7(e)) with increasing Ge concentration from a value of $31.7 \, \Omega^{-1}\text{m}^{-1}$ for $x = 0$ to $9.523 \times 10^4 \, \Omega^{-1}\text{m}^{-1}$ for $x = 0.25$. This increase in $\sigma_{4.2K}$ is moderate up to $x \leq 0.15$ followed by a drastic increase beyond this concentration. In order to investigate whether the system undergoes an insulator to metal transition near $x = 0.2$ from where the sizeable increase in $\sigma_{4.2K}$ is observed, the variation $\sigma(T)$ in 1.2 to 40 K temperature range for $x = 0$ and $x = 0.2$ samples is presented in a loglog plot in Fig. 4.8(a). It is seen that $\sigma(T)$ of both the sample show saturation below 5 K. In fact below 5 K, the $\sigma(T)$ of these samples can be described by a power law behaviour of type $\sigma = \sigma_0 + bT^m$, which is more apparent in $\sigma(T)$ depicted in the inset of Fig. 4.8(b) in the temperature range of 1.3 to 5 K. The extrapolated $\sigma(T=0 \text{K})$ deduced from the fit to above expression was found to be $5500 \, \Omega^{-1}\text{m}^{-1}$ for $x = 0.2$ sample, which is well within the range of minimum metallic conductivity, $\sigma_{\text{min}}$, of 3700 - 7400 $\Omega^{-1}\text{m}^{-1}$ reported for this system [3]. On the other hand $\sigma(T=0\text{K})$ obtained for $x=0$ sample is 1.5 $\Omega^{-1}\text{m}^{-1}$, that is below the $\sigma_{\text{min}}$, implying that this sample is an insulator. This then, based on Mott's the minimum metallic criterion [7], implies a possible insulator to metal transition around $x=0.2$ in FeSi$_{1-x}$Ge$_x$ system.
Fig. 4.6. Variation of energy gaps $\Delta_s$ deduced from the thermally activated behaviour model and $\Delta_s$ from the step function DOS model with Ge concentration, $x$, in FeSi$_{1-x}$Ge$_x$. 
Fig. 4.7. Variation of parameters (a) $W$, (b) $E\mu$, (c) $n_{\text{100K}}$, (d) $\Delta_{\text{eff}}$ and (e) $\sigma_{\text{cal}}$ at 4.2 K along with $\sigma_{\text{exp}}$ deduced from the fits to Gaussian DOS model as a function of $x$ in FeSi$_{1-x}$Ge$_x$. The solid lines are a guide to the eye.
Fig. 4.8. (a) Variation of $\sigma(T)$ of $x=0.0$ and 0.2 samples in the 1.3 to 40 K temperature range. Inset shows linear fit to $\sigma(T)$ data in 1.3 to 5 K range for both the samples. (b) Logarithmic derivative $w$ versus $T^{1/2}$ plot for $x=0.0$ and 0.2 samples.
Further, in the low temperature regime of 5 - 40 K, the $\rho(T)$ data of FeSi$_{1-x}$Ge$_x$ has also been analyzed using the VRH model. It is found that $\rho(T)$ of the samples with $x \leq 0.15$ fits well with this model, but the temperature range of the fit shrinks from 5 - 40 K for $x=0$ to 25 - 40 K for $x=0.15$. However, for the sample with $x \geq 0.2$, the $\rho(T)$ data does not fit to the VRH model in any temperature range. The values of $T_0$ extracted from the fits for the samples with $x \leq 0.15$ are found to decrease from $1.56 \times 10^5$ for $x=0$ to $4.73 \times 10^5$ for $x=0.15$. Since $T_0$ decreases with $x$ and ceases to exist beyond $x \geq 0.2$, it can be speculated that all the localised states within gap get delocalized for $x \geq 0.2$. In order to investigate whether FeSi$_{1-x}$Ge$_x$ system undergoes an insulator to metal transition in 5 to 40 K temperature range near $x \sim 0.2$, the logarithmic derivative $w(T)$ has been computed using the procedure described in section 3.2.3.5 of Chapter 3. The $w(T)$ plot is shown in Fig. 4.8(b) for two samples $x= 0$ and 0.2. It can be seen that slope of $w(T)$ is negative for the sample with $x = 0$ indicating the insulating behaviour of sample in this temperature range. On the other hand the slope of $w(T)$ becomes positive for the sample with $x = 0.2$ implying that sample may be metallic in this temperature range.

4.2 BAND STRUCTURE CALCULATIONS

It is known that band structure does predict the occurrence of a band gap of the right magnitude in FeSi [10], but the bandwidths are grossly overestimated. It is therefore interesting to enquire whether band structure calculations can predict the systematic change in $\Delta$ due to Ge substitution in FeSi. With this objective band structure calculations have been performed [9] using the tight binding version of the linearized muffin tin orbital method in atomic sphere approximation (TB-LMTO-ASA) [11]. The calculated DOS for FeSi is shown in Fig. 4.9(a). The value of the calculated band gap is obtained to be 118 meV ($\sim$1400 K), which is in good agreement with earlier calculations [10]. In order to obtain the change in band gap due to lattice expansion corresponding to Ge substitution, the band structure in FeGe is calculated for the same structure as FeSi, with a lattice parameter of 4.535 Å, the value corresponding to the 25% Ge substituted sample. The corresponding DOS curve is shown in Fig. 4.9(b). The gap value obtained from this calculation is 51 meV ($\sim$ 600 K). It should be remarked that the decrease in $\Delta$ obtained from the band structure calculations is consistent with the trend in the variation of $\Delta$ observed experimentally.
Fig. 4.9. The density of states in FeSi and FeGe shown as a function of energy obtained from TBLMTO calculations; the Fermi levels are at 0.100 Ryd and at 0.118 Ryd for FeSi and FeGe respectively.
4.3 EFFECT OF EXTERNAL PRESSURE

4.3.1 Pressure Effects on Energy Gap

The electrical resistivity measurements of the FeSi$_{1-x}$Ge$_x$ samples with $x = 0.05$ and 0.2 have been performed as a function pressure upto $\sim 7$ GPa and 5.5 GPa respectively, using the opposed anvil type miniaturized pressure locked cell described in Chapter 2, in the temperature range of 4.2 to 300 K. In Fig. 4.10(a) and (b), the electrical conductivity ($\sigma(T)$) of $x=0.05$ and 0.2 samples are plotted respectively for a few representative pressures as a function of temperature. It is observed that conductivity, $\sigma(T)$, of both the samples increases with increasing pressure. In the higher temperature region, ($T \geq 100$ K) the experimental data of both the samples have been analyzed using the thermally activated behaviour, the step function DOS and the Gaussian DOS models for all the pressures to extract the relevant parameters. A representative fit to the thermally activated behaviour model is shown in Fig. 4.11 for the sample with $x=0.05$ for a few representative pressures. It is seen that this model fits very well in 100-170 K temperature range for both the sample at all the applied pressures with $x^2$ values $< 10^{-2}$. Fits to the Gaussian DOS model to the $\sigma(T)$ data are shown in Fig. 4.10(a) and (b) for $x=0.05$ and 0.2 samples respectively. The variation of the energy gap $\Delta_{\sigma}$ and $\Delta_{\sigma}$, extracted from the thermally activated behaviour and the step function DOS model are shown in Fig. 4.12(a) and (b) for $x=0.05$ and 0.2 samples respectively as a function of pressure. The variation of effective energy gap $\Delta_{\text{eff}}$ deduced from the Gaussian DOS models as function of pressure are shown in Fig. 4.13(e) and Fig. 4.14(e) respectively for both the samples. Here again the energy gaps $\Delta$, deduced using all models, exhibit similar trends of variation with pressure for a given sample, i.e. for $x=0.05$, $\Delta$ shows an initial decrease upto a pressure of $\sim 1$ GPa but increases with further increase in pressure upto $\sim 7$ GPa. In $x=0.2$ sample, $\Delta$ shows a monotonic increase with increase in pressure upto 5.5 GPa. Further, the variation of parameters $E_g$, $W$, $E_\mu$, $n_{100K}$ extracted from the fits of Guassian DOS model, as a function of pressure are shown in Fig. 4.13(a), (b), (c) and (d) respectively for $x=0.05$ and Fig. 4.14(a) - (d) for $x=0.2$ respectively. It is found that that $W$ and $E_g$ increase with increasing pressure in both the samples. It is important to mention that for pristine FeSi also these parameters have shown the similar variation with pressure (cf. section 3.3 of Chapter 3). For $x=0.05$ sample the parameters $E_\mu$ and $n_{100K}$ exhibit a non-monotonic
Fig. 4.10. Variation of electrical conductivity $\sigma(T)$ along with the fits to the Gaussian DOS model at a few representative pressures (a) for FeSi$_{0.95}$Ge$_{0.05}$ and (b) FeSi$_{0.8}$Ge$_{0.2}$ samples.
Fig. 4.11. Variation of $\rho(T)$ of FeSi$_{0.95}$Ge$_{0.05}$ fitted to the thermally activated behaviour model at a few representative pressures between 0 and 7 GPa. Data have been arbitrarily shifted along the ordinate for the clarity. The energy gap $\Delta$ have been deduced from the fit in the 100-170 K temperature region.
Fig. 4.12. Pressure dependence of energy gaps $\Delta_s$ and $\Delta_a$, extracted from the thermally activated behaviour and the step function DOS models respectively (a) for FeSi$_{0.95}$Ge$_{0.05}$ and (b) for FeSi$_{0.8}$Ge$_{0.2}$. 
Fig. 4.13. Pressure dependence of parameters (a) $E_g$, (b) $W$, (c) $E_{\mu}$, and (d) $n_{100K}$ and (e) $\Delta_{\text{eff}}$ deduced from the fits to the Gaussian DOS model in FeSi$_{0.95}$Ge$_{0.05}$. The solid lines are a guide to the eye.
Fig. 4.14. Pressure dependence of parameters (a) $E_g$, (b) $W$, (c) $E_{\mu}$, and (d) $n_{100K}$ and (e) $\Delta_{\text{eff}}$ deduced from the fits to the Gaussian DOS model in FeSi$_{0.8}$Ge$_{0.2}$. The solid lines are a guide to the eye.
variation with pressure, i.e., $E_{\mu}$ decreases and $n_{100K}$ increases upto $\sim 1$ GPa pressure and beyond this pressure $E_{\mu}$ increases and $n_{100K}$ decreases (cf Fig. 4.13(c) and (d)). On the other hand for $x=0.2$ sample, parameters $E_{\mu}$ increases and $n_{100K}$ decreases monotonically with increasing external pressure (cf. Fig. 4.14 (c) and (d)).

4.3.2 Pressure Effects on Localized States

The high pressure conductivity data in low temperature regime of 5 - 40 K range is analysed in this section. The temperature dependence of the $\sigma(T)$ in this regime is shown in Fig. 4.15(a) for $x=0.05$ sample for various pressures investigated. It is clear from the figure that as $T$ tends to zero, $\sigma(T)$ seems to approach zero at ambient pressure, as is expected for an insulator. An important feature of the results shown in Fig. 4.15(a), is that temperature dependence of $\sigma$ in the 5 - 40 K temperature range, which is of the variable range hopping type at ambient pressure, becomes more linear with increase in pressure. In fact VRH range is seen to shift at higher temperature between 15-30 K with increasing pressure and the $T_0$ extracted from these fits are seen to decrease by about two orders of magnitude from a value of $1.656 \times 10^4$ K at 0 GPa to $1.07 \times 10^2$ K at 7 GPa. The value of the localization length $\alpha^{-1}$ has been calculated for all the pressures using value of $T_0$ and the $N(E_F)$, deduced using the procedure described in section 3.2.3.4 of Chapter 3. The variation of $\alpha^{-1}$ with pressure is shown in Table II. It is found that $\alpha^{-1}$ increases monotonically with increasing pressure from a value of 12 Å at ambient pressure to 93 Å at 7 GPa pressure. This indicates that the net effect of external pressure in the low temperature regime is to induce delocalization of the localized states inside the gap which could lead to a MIT beyond a critical pressure. In order to investigate whether sample $x=0.05$ undergoes insulator to metal transition under pressure, the $\sigma(T)$ have been extrapolated to zero temperature. This is done by using an expression of $\sigma=\sigma_0+\sigma_1 T^{1/2}+\sigma_2 T$, which fits $\sigma(T)$ data of this sample very well with the coefficient of the linear term showing a systematic increase with increase in pressure. The zero temperature extrapolated conductivity $\sigma(T=0)$ deduced from the fits to above expression at various pressures between 0 to 7 GPa is shown in Fig. 4.15(b). It is seen from the figure that $\sigma(T=0)$ tends to zero for pressures upto $\sim 3$ GPa, beyond which it extrapolates to finite values of $\sim 2.1 \times 10^4 \, \Omega^{-1}\text{m}^{-1}$ at $\sim 5$ GPa, indicating that insulator to metal transition (MIT) might occur at pressures greater than 3 GPa. In order to obtain the precise value

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Fig. 4.15. (a) Variation of $\sigma(T)$ in the 5 – 40 K temperature range for all pressures investigated in FeSi$_{0.95}$Ge$_{0.05}$. (b) Variation of zero temperature extrapolated conductivity $\sigma(T=0)$ of FeSi$_{0.95}$Ge$_{0.05}$ as a function of pressure. Note that $\sigma(T)$ becomes more linear in character and $\sigma(T=0)$ becomes larger with pressure.
TABLE II: Variation of localization length $\alpha^{-1}$ with pressure in FeSi$_{0.95}$Ge$_{0.05}$ sample.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$\alpha^{-1}$ (Å)</th>
</tr>
</thead>
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<td>7</td>
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</tr>
</tbody>
</table>

of the critical pressure at which the MIT occurs[12], the logarithmic derivative $w(T)$ of the conductivity data of $x = 0.05$ sample at all the pressures investigated have been computed. The plot of $w$ versus $T^{1/2}$ is shown in Fig. 4.16 for FeSi$_{0.95}$Ge$_{0.05}$. A careful look at Fig. 4.16 indicates that the temperature dependence of $w$ changes gradually from having a negative temperature co-efficient to a positive temperature co-efficient with increase in pressure. The change of sign of $dw/dT$ occurs beyond $\sim 1.7$ GPa, implying that the insulator to metal transition occurs between $\sim 1.7$ GPa and $\sim 3$ GPa, close to that inferred from Fig. 4.15. The inspection of the $w(T)$ plot (cf. Fig. 4.16) reveals that nature of observed MIT in $x=0.05$ is probably continuous as no minimum is seen in $w(T)$ curve. Similar conclusion was drawn for the pressure induced MIT in FeSi(RR=2x10$^4$) sample described in Chapter 3. It can, therefore, be concluded that the insulator to metal transitions observed in the FeSi$_{1-x}$Ge$_x$ system under external pressure are possibly continuous.

The conductivity in the FeSi$_{0.8}$Ge$_{0.2}$ sample, as mentioned in section 4.1.2 and shown in Fig. 4.8, is seen to be in metallic regime at the ambient pressure itself in the low temperature regime. The $\sigma(T=0)$ of this sample is found to increase with pressure and attains a value of $9.8 \times 10^4 \ \Omega^{-1}m^{-1}$ at 5.5 GPa. The electrical conductivity at 4.2 K has been calculated using the Gaussian fit parameters as described in section 3.2.3.4 at
Fig. 4.16. The logarithmic derivative of conductivity (w) versus $T^{1/2}$ in the 5 - 40 K temperature range, for all pressures investigated in the FeSi$_{0.95}$Ge$_{0.05}$ sample. Note that w increases with decrease in temperature for pressure upto ~2 GPa, beyond which it shows a tendency to extrapolate to 0 as T tends to 0.
various pressures for both samples $x=0.05$ and 0.2. It is found that values of conductivity measured experimentally can be reproduced from the calculations for the disorder parameter $\delta$ varying within the reasonable range of 22 to 33 K for $x=0.05$ and 14 - 23 K for $x=0.2$.

4.4 DISCUSSION

At first the results of Ge substitution studies in FeSi$_{1-x}$Ge$_x$ are discussed. The energy gap $\Delta$, deduced from all the models, is seen to decrease monotonically with increasing Ge substitution at Si site (cf. Fig. 4.6 and Fig. 4.7(d)). Since the substitution of Ge at Si site leads to expansion of the lattice (cf. Fig. 4.1(b)), it will be useful to present the variation of $\Delta$ as a function of lattice parameter to examine its effect. Therefore, the variation of $\Delta_q$ as a function of lattice parameter is plotted in Fig. 4.17(a) for Ge substituted FeSi$_{1-x}$Ge$_x$ sample. In the same figure, the effect of lattice expansion on $\Delta$ have also been compared for Al substituted FeSi$_{1-x}$Al$_x$ samples of Friemelt et al. [4]. It can be seen that the depression in $\Delta$ is faster in Al substitution than for Ge substitution at Si site. This is because Al substitution at Si site not only expands the lattice, but also contributes additional charge carriers (holes) leading to faster decrease of energy gap. It thus appears that the isoelectronic substitution at Si site permits the retention of the Kondo insulating states for much larger values of the lattice parameter. Further, in FeSi$_{1-x}$Al$_x$ system it is reported that a crossover from insulating to metallic low temperature conductivity takes place at $0.005 < x < 0.01$, indicating a metal to insulator transition (MIT) for carrier concentration between 2.2 and $4.4 \times 10^{26}$ m$^{-3}$ [14]. In the case of FeSi$_{1-x}$Ge$_x$, MIT has been inferred from the minimum metallic conductivity $\sigma_{\min}$ as well as $\omega$-plot analysis (cf. Fig. 4.8(a) and (b)) to occur near $x=0.2$. Clearly the concentration of substituents at which MIT occurs is much larger for Ge than Al as substituent. It is worthwhile to invoke the hybridization gap model to examine whether the variation of $\Delta$ observed in the present studies as a function of lattice parameter can be explained within realms of this model. According to this model $\Delta$ varies as $V^2$, where $V$ is the hybridization strength as described in Chapter 1. The net effect of the lattice expansion is to decrease hybridization strength $V$ which, in turn, gives rise to a decrease in $\Delta$. Since lattice expands with Ge substitution, the experimentally observed decrease in $\Delta$ with increasing $x$ appears to be consistent with the hybridization gap model. On similar lines one expects that the contraction of lattice
Fig. 4.17. Variation of $\Delta_a$ in terms of lattice parameter in (a) FeSi$_{1-x}$Ge$_x$ (present studies) and FeSi$_{1-x}$Al$_x$ (Friemelt et al. [4]), (b) FeSi (RR=2x10$^4$), (c) FeSi (RR=7), (d) FeSi$_{0.95}$Ge$_{0.05}$ and (e) FeSi$_{0.8}$Ge$_{0.2}$. 
due to external pressure should give rise to an increase $\Delta$ for FeSi sample. To examine this $\Delta_a$ of pristine FeSi samples with $RR = 2 \times 10^4$ and 7, obtained from the fits of activated behaviour model at various pressures, have been plotted as a function of lattice parameter in Fig. 4.17(b) and (c) respectively. Here the variation of lattice parameter in FeSi with external pressure has been taken from the works of Wood et al. [17], from which the rate of change of lattice parameter $'a'$ for unit GPa applied pressure ($\text{da/dP} \sim 0.00836 \text{Å/GPa}$) has been obtained from the slope of the linear portion of the $a$ vs. $P$ curve. Assuming a similar $\text{da/dP}$ for $x=0.05$ and $x=0.2$ samples, the pressure dependence of $\Delta_a$ of these samples in terms of the lattice parameters are shown in Fig. 4.17(d) and (e) respectively. It is inferred from these figures that the pressure dependence of $\Delta$ for the samples with low RR (e.g. FeSi ($RR=7$) cf. Fig. 4.17(c)) and FeSi$_{0.8}$Ge$_{0.2}$ ($RR=247$) (cf. Fig. 4.17(e)) are found to increase with the contraction of lattice and hence comply with the predictions of the hybridization gap model. However, the samples with large RR values do not follow the pressure dependence of their $\Delta$ as per the predictions of this model. For example, $\Delta_a$ in FeSi ($RR = 2 \times 10^4$) is seen to decrease monotonically and in FeSi$_{0.95}$Ge$_{0.05}$ ($RR=1400$) it is found to exhibit a nonmonotonic variation with decreasing the lattice parameter. These results indicate that the variation of $\Delta$ in FeSi$_{1-x}$Ge$_x$ cannot be rationalized solely within the purview of the hybridization gap model even qualitatively.

Now attention is focused to understand the results of Ge substitution studies from the results of quantitative analysis of experimental data within the framework of Gaussian DOS model. As mentioned earlier, in this model the interplay of the parameters $W$, $E_g$ and $E_\mu$ and their evolution under chemical substitution or external pressure governs the final value of the effective energy gap in FeSi and related systems. The observed variation of $\Delta$ with Ge substitution in this model can be explained based on these parameters as follows: Here $W$ increases with $x$ (Fig. 4.7 (a)) which can happen either due to increase in disorder or decrease in correlation. $E_g$ (not shown) decreases with $x$ which is consistent with the prediction of the band structure calculation. The net effect of variation of $W$ and $E_g$ turn out to be a decrease in $E_\mu$ (cf. Fig. 4.7(b)). This means mobility edge comes closer to $E_F$ with increasing $x$. This implies the delocalization of the localized states inside the gap and an increase in localization length. This is consistent with the fact that $T_0$ decreases with increasing $x$ for $x \leq 0.15$ and vanishes beyond $x \geq 0.2$. Due to decrease in $E_\mu$, the effective carrier concentration $n$ excited into the conduction band increases. This
can be inferred from the variation of $n_{100K}$ with $x$ (cf. Fig. 4.7(c)). The increase in $n$ is equivalent to a decrease in the $\Delta_{eff}$ as seen in Fig. 4.7(d). This explains the decrease of $\Delta$ with increasing $x$ in FeSi$_{1-x}$Ge$_x$.

Having discussed the results of Ge substitution studies in FeSi$_{1-x}$Ge$_x$, attention is focused on the pressure dependence of $\Delta$ for $x=0.05$ and 0.2 samples. For sample with $x = 0.05$, $\Delta$ shows a non-monotonic variation with pressure (cf. Fig. 4.12 (a) and 4.13(e)), i.e., $\Delta$ decreases with pressure upto $\sim 1$ GPa and increases beyond this pressure. This can be understood as follows: the parameter $W$ increases rapidly upto $\sim 1$ GPa, while $E_g$ remains unchanged upto $\sim 3$ GPa pressure. This means the effect of disorder/correlation dominates over the effect of electronic structure for low pressures. This is seen to result in a decrease of $E_\mu$ upto $\sim 1$ GPa (cf. Fig. 4.13(c)). The decrease in $E_\mu$, as mentioned in above paragraph, ultimately gives rise to a decrease in $\Delta_{eff}$ for low pressures. For higher pressures beyond $\sim 1$ GPa, the rate of increase of $W$ with pressure slows down, but $E_g$ starts increasing which becomes more rapid beyond $\sim 3$ GPa. This means that the electronic structure effect dominates over disorder/correlation at higher pressures. Here $E_\mu$ increases with pressure whose net effect is a decrease in $n$. It can be seen from Fig. 4.13(d) that $n_{100K}$ decreases beyond $\sim 1$ GPa pressure. A decrease in $n$ is equivalent of an increase of $\Delta_{eff}$. Thus the competition between the disorder/correlation effect and the band structure effect lead to a non-monotonic variation of $\Delta$ with pressure observed in $x=0.05$ sample.

In the $x = 0.2$ sample, the observed monotonic increase of $\Delta$ with pressure (12(b) and 14(e)) can be understood as follows: Here $E_g$ and $W$ both increase with pressure (cf. Fig. 4.14(a) and (b)). $W$ increases at an average rate of $\sim 15$ K/GPa, whereas the rate of increase for $E_g$ is found to be $\sim 40$ K/GPa. This means that the effect of band structure dominates over the effect of disorder/correlation. This is seen to result in a monotonic increase in $E_\mu$ (cf. Fig. 4.14(c)), the net effect of which would be a decrease in $n$ and hence an increase in $\Delta_{eff}$ with increasing pressure, observed experimentally (cf. Fig. 4.14(e)).

It should be remarked that the pressure dependence $\Delta$ in FeSi$_{1-x}$Ge$_x$ appears to exhibit a striking correlation with the ambient pressure RR values of the samples. It can be recalled from Chapter 3 that for FeSi sample with large RR $= 2 \times 10^4$, $\Delta$ was found
to decrease with pressure, while for low RR sample $\Delta$ was observed to increase. Here for $x=0.05$ sample with intermediate RR $= 1.4 \times 10^4$, $\Delta$ shows a decrease followed by an increase and for $x=0.2$ sample with low RR $= 247$, $\Delta$ increases monotonically with increasing pressure. This can be explained as follows: in the sample with large RR, the effect of disorder/correlation dominates over band structure effect resulting in a decrease in $\Delta$ with pressure. While in the sample with intermediate RR, both these effects compete with each other resulting in non-monotonic variation of $\Delta$. In the low RR sample, the band structure effect dominates over the disorder/correlation effect giving rise to an increase in $\Delta$ with pressure.

4.5 SUMMARY

Isoelectronic Ge substitution studies in FeSi$_{1-x}$Ge$_x$ have been carried out via electrical resistivity measurements as a function of temperature for $x=0$ to 0.25 and as a function of temperature and pressure for $x=0.05$ and 0.2. The experimental data has been analysed using the thermally activated behaviour, the step function DOS and the Gaussian DOS models in high temperature regime ($T \geq 100$ K) and a VRH model in low temperature regime ($T \leq 40$ K). $\Delta$ deduced using all models is seen to decrease with increasing Ge concentration $x$. In the low temperature regime ($T < 40$ K), samples with $x \leq 0.15$ exhibit VRH behaviour which is absent for samples with $x \geq 0.2$. The variation of $T_0$ has an influence on the variation of $\Delta$. From these analyses, it is inferred that system exhibits an MIT for $x \sim 0.2$ in low temperature regime. For $x=0.05$ sample, $\Delta$ exhibits a non-monotonic variation with pressure. In the low temperature regime this sample undergoes an MIT near 3 GPa pressure. The nature of MIT is inferred to be continuous. While for sample with $x=0.2$, $\Delta$ increases monotonically with pressure. The variation of $\Delta$ under pressure and with Ge substitution have been rationalised within the framework of the Gaussian DOS model. It is seen that the position of mobility with respect to Fermi energy dictates the final value of the effective energy gap in both the cases.
REFERENCES