SUMMARY AND CONCLUSIONS

This thesis has examined the ground state and the evolution of the energy gap in a d-electron based Kondo insulator (KI) FeSi using temperature dependent conductivity for which transport measurements were carried out. Isoelectronic chemical substitutions by Ge at Si site and Ru at Fe site followed by high - pressure studies on pristine and substituted samples have been carried out. While the high temperature (T ≥ 100K) properties of FeSi was seen to be consistent with the narrow gap KI, the low temperature behaviour was found to be primarily governed by disorder. The experimental data has been systematically analysed by first assuming FeSi as a conventional semiconductor and then incorporating the additional features in the density of states (DOS), consistent with a correlated insulator. Towards this, the data was first analyzed using the simple thermally activated behaviour model. This model was found to fit the resistivity data in a narrow temperature range of 100-170 K. Subsequently, the step function DOS model which incorporates the effect of electron correlation has been employed. This model was found to explain the data very well in the high temperature range of 100 - 300 K. Nevertheless, neither model could rationalize the transport behaviour seen at low temperatures (T ≤ 50 K); for that a variable range hopping (VRH) model was used to fit the data. In order to rationalize the transport behaviour of FeSi in a unified manner in the entire temperature regime, it was felt essential to incorporate the effect of disorder in the DOS. Keeping this in mind a new density of states model, namely, the Gaussian DOS model that accounts for disorder in addition to electron-electron correlation was proposed and used for the first time for quantitative analysis of the experimental data (section 3.2.3.4) of this system. This model was found to explain consistently the resistivity behaviour of the present system as a function of temperature, composition and pressure. In the high temperature regime, fit parameters defining the Gaussian DOS yield an effective energy gap Δ_{eff}, and in the low temperature regime the existence of localized states between E_{μ} and E_{F}, leads to the description of the transport behaviour in terms of variable range hopping mechanism. Within the purview of this model finite conductivity at zero temperature could be
realised by considering the smearing of Fermi function due to disorder.

For carrying out the experiments, two experimental setups, (i) a continuously operating liquid \(^{4}\)He evaporation cryostat and (ii) a miniature high pressure cell were indigenously developed and automated. The former set-up was used in the low temperature measurements down to \(\sim 1\) K, while with the latter transport measurements up to a pressure of \(\sim 8\) GPa in 4.2 to 300 K temperature range were carried out. The size of both the apparatus permits their insertion into a 50 mm neck diameter liquid helium storage dewar in order to carry out experiments quickly with minimal consumption of liquid helium.

The effect of disorder on the transport properties of FeSi was brought about by carrying out temperature and pressure dependent electrical conductivity studies on various FeSi samples having different RR values varying by three orders of magnitude. The samples with RR values above \(\sim 10^3\) were seen to exhibit almost identical behaviour particularly in high temperature regime with moderate change in low temperature regime, but the properties of samples with low RR were found to deviate grossly. External pressure was 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 gave 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. The predicted gap behaviour from band structure dictates that the band gap increases with increasing pressure. However the experimentally observed pressure dependence of \(\Delta\) showed a decrease for large RR sample and a marginal increase for low RR sample. The pressure dependence of \(\Delta\) in various samples were found to be dictated by 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. 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 \(E_\mu\). Since the parameters entering the model \(E_g, W, \) and \(E_\mu\) are small and are of comparable magnitudes, any variation in these parameters can bring about observable changes in \(n\) and therefore in \(\sigma\).
Isoelectronic Ge substitution studies in FeSi$_{1-x}$Ge$_x$ (x = 0.0 to 0.25) showed an increase in lattice parameter with increasing Ge concentration, indicating the expansion of lattice. The KI gap $\Delta$ was found to decrease with increasing Ge concentration, consistent with hybridization model. However, lattice contraction brought about by the application of external pressure was found to have dramatic effect on $\Delta$ of Ge substituted samples. For the sample with x=0.05, $\Delta$ showed a non-monotonic variation, i.e., an initial decrease followed by an increase with increasing pressure. Whereas for x=0.2, $\Delta$ was found to increase with pressure. These results showed that the pressure dependent behaviour of $\Delta$ in this system could not be consistently explained within the purview of the hybridization model. From the analysis of conductivity data of FeSi$_{0.95}$Ge$_{0.05}$ at various pressures, occurrence of the insulator to metal transition was inferred near $\sim$3 GPa pressure in low temperature regime (5 - 40K). The nature of MIT was predicted to be continuous. The variation of $\Delta$ under pressure and with Ge substitution have been rationalised within the framework of the Gaussian DOS model.

Isoelectronic Ru substitution studies in Fe$_{1-x}$Ru$_x$Si (x = 0.0 to 0.30) also showed an overall increase in lattice parameter with increasing Ru concentration. The energy gap $\Delta$ and hopping parameter $T_0$, deduced from the analysis, showed a non-monotonic variation with Ru concentration, an initial decrease followed by an increase with minima at $x \sim$0.06. The electrical conductivity measured at 4.2K also exhibited a maximum near $x = 0.06$ and its value was found to exceed the minimum metallic conductivity expected for this system. It was surmised from these results that with substitution of Ru in FeSi, the system undergoes a transformation from a FeSi-type correlated insulator to a RuSi-type band semiconductor via an intermediate metallic phase. Band-structure calculations were carried out for several concentrations of Ru. Values of $\Delta$ extracted from these, show an initial flat behaviour followed by an increase with Ru concentration, implying that band picture is inadequate in understanding this system particularly in the low Ru concentration regime. While the evolution of $\Delta$ in Ru substitution in Fe$_{1-x}$Ru$_x$Si could be qualitatively understood based on the Fu and Doniach model, the Gaussian DOS model was found to explain quantitatively the resistivity behaviour of Ru substituted samples at ambient pressure as well as at high pressures. The unusual variation of $\Delta$ in these studies, could be understood within the framework of the Gaussian DOS model in terms of delocalisation of the defect states in gap (as indicated by the variation of $T_0$) leading
to the movement of $E_{\mu}$ towards $E_F$. The position of the mobility edge was thus seen to play an important part in determining the transport behaviour in this system.

Efforts are underway to extend the Gaussian model in understanding of the magnetic and thermal properties, such as susceptibility and specific heat, of this system. It will be worthwhile to investigate the magnetic and thermal properties properties of Ge and Ru substituted FeSi samples for clearer understanding of the evolution of the ground state with these substitutions.
LIST OF PUBLICATIONS

JOURNAL PAPERS

1. Evolution of the Kondo Insulating Gap in Fe$_{1-x}$Ru$_x$Si
   Awadhesh Mani, A. Bharathi, S. Mathi Jaya, G. L. N. Reddy, C.S. Sundar and
   Y. Hariharan

2. Study of Normal and Superconducting States of MgCNi$_3$ upon Fe and Co Substitution and
   External Pressure
   T. Geetha Kumary, J. Janaki, Awadhesh Mani, Mathi Jaya, V. S. Sastry, Y. Harihamn,
   T. S. Radhakrishnan and M. C. Valsakumar,

3. Pressure Induced Insulator- Metal Transition of Localized States in FeSi$_{1-x}$Ge$_x$
   Awadhesh Mani, A. Bharathi and Y. Hariharan

4. Superconducting Behaviour of Nb/Fe Multilayers
   L. S. Vaidhyanathan, Awadhesh Mani, Rita Saha, R. Nagendran, K. Gireesan,
   R. Baskaran, M. P. Janawadkar, Y. Hariharan and T. S. Radhakrishnan
   J. Alloys and Compounds 326 (2001) 280

5. Metal – Insulator Transition in Fe$_2$Va$_{1-x}$Si$_x$
   S. Jamima Balaselvi, Awadhesh Mani, A. Bharathi, Nithya Ravindran and Y. Hariharan
   J. Alloys and Compounds 326 (2001) 183

6. Positron lifetime studies in the Kondo Insulator FeSi
   A. Bharath, Y. Hariharan, Awadhesh Mani and C.S. Sundar

7. Resistivity studies in the Kondo Insulator, FeSi$_{1-x}$Ge$_x$
   A. Bharathi, Awadhesh Mani, G. V. Narashimha Rao, C.S. Sundar and Y. Hariharan
   Physica B 240 (1997) 1

8. Structural and Superconducting properties of Nb-Ti alloy thin films
   Awadhesh Mani, L. S. Vaidhyanathan, Y. Hariharan, M. P. Janawadkar and
   T. S. Radhakrishnan

9. Positron lifetime studies in the Kondo Insulator FeSi
   A. Bharathi, Y. Hariharan, Awadhesh Mani and C. S. Sundar
   Materials Science Forum 255-256 (1997) 512
10. Structural and Superconducting properties of Nb-Ti alloy thin films, Awadhesh Mani, L. S. Vaidhyanathan, Y. Hariharan, M. P. Janawadkar and T. S. Radhakrishan
* Cryogenics 36* (1996) 937

**CONFERENCES / SYMPOSIA PAPERS**

11. Miniature High Pressure Cell for Electrical Resistacne Measurements
Awadhesh Mani, A. Bharathi, V. S. Sastry and Y. Hariharan
* Eighteenth International Cryogenic Engineering Conference, ICEC-18,(eds.)
  K. G. Narayankheddkar, Narosa Publishing House, New Delhi, India, P615 (2000) *

12. Electrical Resistivity and Positron life time studies in the Kondo Insulating System FeSi_{1-x}Ge_x
A. Bharathi, Y. Hariharan, Awadhesh Mani and C. S. Sundar

13. Sub-gap Structures in Nb/AlO_x/Nb Josephson Tunnel Junctions
Awadhesh Mani, M. P. Janawadkar, Y. Hariharan, R. Baskaran and T. S. Radhakrishan

14. High Pressure Studies on Superconducting Pervoskite MgCnI_3
Awadhesh Mani, T. Geetha Kumary, M. C. Valsakumar, J. Janaki, , Mathi Jaya, V. S. Sastry, Y. Hariharn, and T. S. Radhakrishnan

15. Insertable Miniature High Pressure Cell for Electrical Transport Measurements
Awadhesh Mani, A. Bharathi, V. S. Sastry and Y. Hariharan

16. Effect of Disorder and Pressure on the Kondo Insulating System FeSi_{1-x}Ge_x
Awadhesh Mani, A. Bharathi, Nithya Ravindran and Y. Hariharan

17. Electrical Resistivity Measurements as Function of Temperature Pressure and Magnetic Field
18. Studies on Kondo Insulating FeSi
A. Bharathi, Awadhesh Mani, Nithya Ravindran, S. Mathi Jaya, C.S. Sundar and Y. Hariharan

19. Superconductivity in Multilayered Nb/Fe Films
L. S. Vaidhyanathan, Awadhesh Mani, K. Giresan, M. P. Janawadkar, Y. Hariharan and T. S. Radhakrishnan

20. Positron Life Time Measurements Across the Metal – Insulator Transition in V2O3

21. Studies on effect of Ru doping in Kondo Insulating System Fe1−xRuxSi
Awadhesh Mani, A. Bharathi, Nithya Ravindran, Y. Hariharan and C.S. Sundar

22. High Pressure Studies in FeSi
Awadhesh Mani, Nithya Ravindran, A. Bharathi and Y. Hariharan

23. Superconducting Behaviour of Mo/Nb/Mo Sandwich Structures
L. S. Vaidhyanathan, Awadhesh Mani, M. P. Janawadkar, Y. Hariharan and T. S. Radhakrishnan

24. N+ Ion Induced Electrical Conductivity in Poly(P-Phenylene Sulfide)
A. Das, S. Dhara, Awadhesh Mani and A. Patnaik

25. Resistivity and X-Ray Diffraction studies in FeSi1−xGex
Bharathi, Y. Hariharan, Awadhesh Mani, C. S. Sundar, G. V. Narashimaha Rao, G. Ghosh and V. S. Sastry
26. Structural Instability in Nb-Ti alloy Thin Films  
Awadhesh Mani, L. S. Vaidhyanathan, Y. Hariharan, M. P. Janawadkar and T. S. Radhakrishan  

27. Superconducting Tunneling studies on Nb/Al₂O₃-Al/Nb Junction  
Awadhesh Mani, Y. Hariharan, M. P. Janawadkar, R. Baskaran and T. S. Radhakrishan  