Study of Electronic Phase Transitions at High Pressures

Thesis submitted to
Mangalore University
for the award of 'the degree of
Doctor of *Philosophy*
in Physics

by

P.K. Thiruvikraman

Raman Research Institute
and
National Aerospace laboratories

Bangalore

September, 1999

DECLARATION

I hereby declare that the work forming the subject matter of this thesis, has been carried out by me under the supervision of Dr.T.G.Ramesh, Deputy Director, Material Science Division, National Aerospace Laboratories, Bangalore and Visiting Scientist, Raman Research Institute, Bangalore. This work has not been submitted in part or full to any Institute or University for the award of any degree or diploma.

Place: Bangalore

P. K. Thiruvikraman

Date: 20-09-99 (P.K.Thiruvikraman)

CERTIFICATE

I hereby certify that the entire work embodied in this thesis has been carried out by the candidate, Mr.P.K.Thiruvikraman under my guidance in the Material Science Division, National Aerospace Laboratories, Bangalore, and Raman Research Institute, Bangalore and that no part of it has been submitted for the award of any other degree or diploma.

T.G. Ramesh

(Dr.T.G.Ramesh)
Material Science Division
National Aerospace Laboratories
Bangalore- 560 017
and
Visiting Scientist, Raman Research
Institute, Bangalore – 560 080

Acknowledgement

This thesis is the result of nearly six years of work. It is my pleasant duty to acknowledge the people who helped me in different ways.

I would like to thank my thesis supervisor Dr. T. G. Ramesh for his patient guidance. He helped me out whenever my work seemed to have reached a dead end. He taught me a simple but powerful method of dealing with Physics problems.

Dr. Shubha made an invaluable contribution in the design and fabrication of the experimental set-ups used in this project. She was always willing to lend her expertise in helping me out in the lab.

I thank Mr. K. Jagannatha Rao for his help in the fabrication and mounting of the high pressure cells used in the present work. His constant company and ready wit kept in good spirits.

The experimental work described in this thesis was carried out at the National Aerospace laboratories. I thank the Director, NAL and the head of the Material Science Division for allowing me to work at NAL.

I thank Raman Research Institute for providing me with a fellowship and extending all possible help towards the completion of the work. I will always cherish the friendly academic atmosphere which I encountered here.

I would like to thank Prof. N. V. Madhusudhana, Head, Liquid Crystal lab, RRI for his kind interest in my work. I thank Prof. Rajaram Nithyananda for his interest and the useful suggestions which he offered from time to time.

I thank Dr. Sudha Mahadevan for providing the Chacogenide samples and Dr. P. S. Gopalakrishnan for help in thinning the Chromium alloys.

The administrative staff of RRI, especially Mr. G. V. Srinivasa, Mr. Krishnammaraju, Ms. Marissa and Mr. Radhakrishna were very helpful in administrative matters.

RRI has one of the most well-maintained libraries, which simplified locating books and journals. The library staff were very prompt in helping me to locate any books or references and in xeroxing papers.

I would like to thank the computer section in RRI especially Ramadurai and Jacob Rajan for their prompt help whenever I approached them.

I also thank the staff of the RRI canteen who cheerfully supplied tea and coffee at any hour of the day.

During my stay at RRI, I have developed a large number of friends. Some of them helped me academically while others contributed to keep me in 'high spirits'. I name only a few of them. I hope those whom I have not named here will excuse me.

Aravinda Narayanan has been my freind, philosopher and guide for many years now. His readiness to discuss Physics was indeed a great asset to me. He also coaxed me back whenever i tended to lose focus. I am indebted to him for going through the thesis very carefully and correcting each and every small mistake which had crept in. His suggestions were especially useful in improving the quality of this thesis.

Sobha Warrier was of great help in many matters both academic as well as non-academic.

I learnt a lot through my discussions with Jana, Sreejith, Andal, Saravanan and many of the other students at RRI. Sushil and Dipanjan prevented things from getting too monotonous. Many of the other students and staff at RRI have helped on numerous occasions.

Finally I thank all my teachers to whom I owe my knowledge and my parents for their support and encouragement which allowed me to continue my education.

Preface

Introduction

This thesis titled, "Study of Electronic phase transitions at high pressures" , mainly deals with the experimental study of magnetic phase transitions in metallic systems.

Phase transitions and critical phenomena are one of the most active areas of research in recent decades [1, 2]. The ideas of scaling and universality which were first formulated in the area of critical phenomena, have found wide application in other areas of Physics also.

The field of critical phenomena has seen a close interplay of theory and experiment , which has proved quite fruitful in understanding and unifying the diverse phase transitions which are encountered in nature .

Starting with the Weiss theory of Ferromagnetism [3], new theories have been continuously formulated and subjected to experimental verification. Landau [4] generalized all the mean field theories using the very powerful concept of an order parameter, which is zero in the less ordered phase and non-zero in the more ordered phase.

Starting from the opposite viewpoint of a microscopic Hamiltonian, the Ising and Heisenberg [2] models were formulated to obtain exact solutions which could be tested against experiment. However till date analytical solutions have not been possible for any of these models in three dimensions [2].

To evaluate the relative merits of these theories, required the measure-

ment of various thermodynamic quantities like specific heat, Susceptibility and magnetization as a function of temperature. It was found that the temperature variation of these quantities could be accurately described by expressions of the form [2]:

$$C \sim ((T - T_c)/T_c)^x \qquad (1)$$

Where C is the thermodynamic quantity, T_c the transition temperature and x is the exponent characterizing this transition.

The values of the exponents seemed to depend only on the dimension of the space and number of components of the order parameter [2]. This gave rise to the concept of 'Universality' in phase transitions.

One of the most widely studied phase transitions in the solid state are the magnetic phase transitions. Although this was one of the first transitions to be studied, the confirmation of universality in these systems is complicated by the effects of anisotropy, impurities and defects [5].

However after a preliminary understanding of the various phenomena, workers in this field have gone on to pose more interesting questions, like the effect of disorder on the critical behaviour near a phase transition [6, 7]. The question was whether the presence of strong disorder like in a glass with no translational order would completely smear out a transition and even if the transition is not smeared out whether the critical exponents would be the same. Earlier experiments and theoretical studies have not answered this question [7, 8] in a complete manner.

The work described in this thesis was mainly motivated by the above-mentioned questions. Another important question is the nature of magnetism in ferromagnetic glasses. The nature of magnetism is not completely understood in ferromagnetic metals like Iron, Cobalt and Nickel even in the crystalline state . Hence it would be optimistic to expect a complete understanding in the amorphous state. However, since there is only short range

order in the glassy state one can study the differences introduced in the magnetic state due to the absence of the long-range order which is present in the crystalline state.

The variety of phase transitions is greatly enriched by the study of these transitions under the application of High Pressures. The appearance of new phases under Pressure is one of the unexpected developments in this field.

The application of pressure also helps us to access new regions of the phase diagram and study the nature of the phase transitions near critical points, which are far above atmospheric pressure.

The phase transitions studied herein were charaterized using tools like specific heat,resistivity and thermopower.

Chapter 1

Chapter 1 of the thesis gives a general introduction to phase transitions and critical phenomena. The concepts which will be used later on in the thesis like the Landau theory of phase transitions, order parameter, critical exponents etc will be introduced and the notation used will be clarified.

Chapter 2

Chapter 2 gives a detailed description of the High Pressure arrangement, i.e, the piston-cylinder apparatus as well as the methods used for measuring the high pressures. The ac resistivity and thermopower measuring system are also described in this chapter.

Chapter 3

Specific heat has been used in our work as a tool to study and characterize the various transitions [9] as it is one of the most sensitive tools which can be used for this purpose. It is more sensitive than transport properties like resistivity which have also been used to track transition temperatures

as a function of pressure. Properties like resistivity need not be directly related to the order parameter whereas specific heat is, because it is the second derivative of the free energy.

Chapter 3 gives a general introduction to the various methods which have been used till date in the measurement of specific heat. Various methods like adiabatic calorimetry, Pulse methods, differential scanning calorimetry and ac calorimetry are described and their relative merits discussed in detail. From such a comparative study of all the methods used till date and described in the literature it turns out that ac calorimetry is ideally suited for the study of continuous phase transitions. A brief survey of the literature on ac calorimetry is given in this chapter. This survey is used to introduce the basic concepts involved in ac calorimetry. The modifications introduced by different workers from time to time and the rationale behind them are elucidated . This survey is used to compare the ac calorimetry technique developed by us with the techniques described in the literature.

Chapter 3 also includes a description of the ac calorimetric set-up developed by us. This includes a description of the electronic circuitry and associated instrumentation required for the ac calorimeter. Experiments used to calibrate and test the ac calorimeter are described in this chapter. The study of the specific heat of Nickel was undertaken to test the working of the ac calorimeter. The specific heat of Nickel was measured near the transition from the ferromagnetic to the paramagnetic state. The critical exponent characterizing the behaviour near the Curie temperature was determined from an analysis of the data. The specific heat exponent $\alpha \sim -0.13$ is in agreement with literature values [10].

The basic principle [11] of ac calorimetry is that an oscillatory heat input is supplied to the sample and the resulting temperature oscillations are measured. The specific heat of the sample is related to the amplitude of

the temperature oscillations by the expression :

$$C = \frac{I_o^2 R}{\omega m \Delta T_{ac}} \tag{2}$$

This equation is derived under the assumption that the heat loss to the surroundings is negligible compared to the heat supplied to the sample. The validity of this assumption is tested by a measurement of ΔT_{ac} as a function of frequency and power. These measurements are described in chapter **3.**

Since the above expression involves the resistivity of the sample, we have made a provision for the simultaneous measurement of the resistivity of the sample. Earlier workers in this field [12] have corrected for the variation of the resistivity variation of the sample by carrying out a separate experiment. However a simultaneous measurement of the sample resistance of the sample is important in the case of metallic glasses in which the sample resistance can be history-dependent [13, 14].

We have also developed a feedback mechanism by which the power supplied to the sample can be kept constant. This is useful to keep the value of ΔT_{ac} within reasonable limits. Ideally ΔT_{ac} should be kept as small as possible as the value of specific heat obtained by this method is an average over the temperature range ΔT_{ac}. The temperature range ΔT_{ac} should be have a minimum value especially in the study of critical phenomena wherein the specific heat is a rapidly varying function of temperature near the critical point.

We have used a "plus-minus" square wave for heating the sample. The voltage passes successively through +V,0,-V and 0 for each quarter-cycle of the waveform. **A** detailed description of the Electronic circuits fabricated for this purpose are given in this chapter. This type of waveform had been used by Xin et al [15]. The advantage is that the square wave does not have a second harmonic component which can interfere with the measurement of ΔT_{ac}.

The resistance across the sample is calculated from the measured value

of the voltage across the sample. Since a square wave was used, the peak value of the square wave is used in the calculation of the resistance. The peak value of the voltage was obtained by recording the voltage across the sample for more than one time period of the oscillation. The values of the voltage which are nearly zero are rejected and the remaining values are averaged to calculate the resistance of the sample.

A detailed description of the entire process of the resistance measurement as well as the automatic power control is given in this chapter.

To judge the suitability of the ac calorimetric technique for measurement of specific heat at high pressures, the specific heat of Nickel was measured as a function of temperature at different pressures. The Curie temperature of Nickel was identified up to a pressure of 20 kbar. An important result of this study was that the fractional change in the specific heat at T_c decreases as the pressure is increased. It is shown that this result cannot be understood on the basis of mean field theory. Due to experimental constraints on the number of leads which can be taken out of the high pressure cell, the high pressure specific heat measurements were done without a simultaneous measurement of resistance. The sample resistance was determined in a separate experiment. dT_c/dP for Nickel was found to be approximately 0.6 ^{o} C, which is slightly higher than the literature value of 0.4 ^{o} C.

Chapter 4

Chapter 4 gives an account of the transport properties of some metallic glasses. These metallic glasses are mainly composed of the transition metals Iron and Cobalt. The resistivity and thermopower of metallic glasses were studied as a function of both temperature and pressure. The transport properties of simple metallic glasses have traditionally been interpreted in terms of Ziman's theory of liquid metals [16], which has been modified and extended to the case of metallic glasses. This theory has also been used in the case of metallic glasses containing transition metals with mixed success

. We try to interpret our data on the basis of Ziman's theory and point out the discrepancies between the theory and our results. We also point out how transport property measurements can be used to study structural rearrangements due to thermal cycling or due to increase in pressure.

The interesting results described in this chapter are:

1) While the temperature coefficient of resistance (a) of Iron- based metallic glasses are positive, α is negative in case of Cobalt-rich glasses.

2) The Curie point transition is not seen in the resistivity data while there is a clear change of slope in the thermopower .

These results are discussed and possible explanations suggested.

Chapter 5

The study of Curie temperature as a function of temperature in the metallic glasses $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ and $Co_{65}Fe_5Mo_2B_{12}Si_{16}$ is described in chapter 5. The variation of T_c as a function of pressure is useful in deciding whether the magnetism is itinerant or localized. It is shown that the experimental values of dT_c/dP is consistent with the itinerant model.

Chapter 6

Chapter 6 describes results on the antiferromagnetic Chromium alloys $Cr_{0.995}Re_{0.005}$ and $Cr_{0.99}Re_{0.01}$. Resistivity and Thermoelectric power were used to track the Neel temperature as a function of pressure in these two alloys.

The resistivity in Chromium is described by a two-band model due to Fedders and Martin [17]. According to this model, there is a condensation of electron-hole pairs in the antiferromagnetic state (AFM). The electrons which go into these pairs are unavailable for conduction and hence the resistivity in the AFM phase (R) is higher than the value R_p, extrapolated from the

paramagnetic phase. This resistivity anomaly is expressed as [17]:

$$\frac{\Delta R}{R}(T) = \frac{R - R_p}{R} \tag{3}$$

According to the two-band model the conductivity is divided into two components [18], a, and σ_n, where σ_r comes from the noncondensing reservoir and σ_n from the nesting parts of the Fermi surface that condense to form electron-hole pairs.

Thus σ_r is unaffected by the condensation, with a, $= \sigma_{rp}$ at all temperatures T , whereas the conductivity σ_n in the AFM phase is decreased relative to the conductivity σ_{np} at the same temperature extrapolated from the paramagnetic phase in the 'ratio

$$\frac{\sigma_n}{\sigma_{np}} = \int_{-\infty}^{+\infty} \frac{\Delta^2}{(E^2 + \Delta^2)^{3/2}} \frac{dE}{exp[(E^2 + \Delta^2)^{1/2}/k_B T] + 1} \tag{4}$$

where $2\Delta(T)$ is the temperature-dependent energy gap.

The resistivity anomaly defined previously then follows:

$$\frac{\Delta R}{R} = g\frac{\sigma_{np}}{\sigma_p} \tag{5}$$

Where

$$g = \frac{\sigma_{np} - \sigma_n}{\sigma_{np}} = 1 - \frac{\sigma_n}{\sigma_{np}} \tag{6}$$

is the fraction of the nesting octahedra that condenses, and

$$\frac{\sigma_{np}}{\sigma_p} = \frac{\sigma_{np}}{\sigma_r + \sigma_{np}} \tag{7}$$

is the fraction of the total Fermi surface in the octahedra.

We proceed by assuming a reasonable number [17]for the fraction of the Fermi surface which is in the Octahedra and calculate the energy gap due to the creation of an electron-hole pair. While the fraction of the Fermi surface

which is in the octahedra will change slightly with pressure and composition [18], we ignore it as a first approximation, in our calculation of the energy gap. The energy gap is a function of temperature and has its maximum value at **0k.** At any finite temperature it has a value less than this and decreases to zero at the Neel temperature. We have the ratio of the gap at temperature T to its value at **0k,** i.e, $\Delta(T)/\Delta(0)$ as the order parameter describing the anti-ferromagnetic to paramagnetic transition.

The energy gap is calculated by the following steps:

1) Assume some value for the energy gap.

2)Evaluate the value of g corresponding to this value of **A.**

3)Calculate the corresponding value of the resistivity anomaly.

4) Calculate the difference between the experimental and theoretical values of the resistivity anomaly.

5) Iteratively calculate the value of **A** which minimizes this difference. This gives the value of A for that temperature.

6) This procedure is repeated for all the temperatures for which the experimental data is available.

7) From this a curve of A as a function of temperature is generated.

We are able to fit an equation of the form

$$\Delta(T) = \Delta(0)\left(\frac{T_n - T}{T_n}\right)^{\beta} \tag{8}$$

The value of β in most cases is around **0.5,** which is characteristic of a mean field type of transition [4].

The thermopower of Chromium alloys was also used to track the transition from the AFM phase to the paramagnetic phase. The thermopower anomaly, unlike the resistivity anomaly,does not reduce with increasing pressure, in fact it increases with increase in pressure. This is useful in tracking the transition to higher pressures. The transition from the AFM to the

paramagnetic phase is seen as a large decrease in the thermopower

Chapter 7

Chapter 7 deals with the glass transition in a Chalcogenide glass $As_{40}Se_{30}Te_{30}$. The glass transition temperature was determined as a function of pressure in this system using the technique of differential thermal analysis (DTA). The differential Thermal Analyzer was first calibrated by studying the melting transition in Indium and a structural transition in Potassium Nitrate.

Electrical Conductivity was also used to determine the glass transition temperature as a function of pressure. The glass transition temperatures obtained by the two given techniques were found to agree reasonably well. The glass transition was also studied for different heating rates to throw light on the kinetic nature of this transition.

Other than studying the glass transition, the conductivity data was of interest in studying the nature of transport processes in these disordered semi-conductors.

Since the Chalcogenide glasses are semiconductors. the electrical conductivity is given by [3]:

$$\sigma(T) = \sigma_o \exp(-\Delta/k_B T) \tag{9}$$

Where A is the mobility gap. The magnitude of this gap is found to decrease with pressure. Another experimental result obtained is that the magnitude of the gap is larger in the supercooled liquid state when compared to the glassy state.

The experimental values of dT_g/dP are used to see which of the models for the glass transition is more appropriate.

The work described in this thesis is partially contained in the following papers:

i) Measurement of specific heat near T_c in some magnetic systems , P.K.Thiruvikraman and T.G.Ramesh , pg 174, Advances in High Pressure Science and Technology, Universities Press(India) Ltd, Hyderabad, 1997

ii) Pressure Effecton T_g in $As_{40}Te_{30}Se_{30}$ Chalcogenide glass , T.G.Ramesh, P.K.Thiruvikraman, V.Shubha, Sudha Mahadevan, A.Giridhar and K.Jagannatha Rao, pg 153, Advances in High Pressure Science and Technology, Universities Press (India) Ltd, Hyderabad, 1997

iii) An AC technique for the simultaneous measurement of Specific heat and Resistivity P.K.Thiruvikraman, T.G.Ramesh and V.Shubha (Communicated to Review of Scientific Instruments)

iv) Resistivity and thermopower in the study of the Antiferromagnetic to paramagnetic transition in Chromium Rhenium alloys.

P.K.Thiruvikraman and T.G.Ramesh (Communicated to Phys.Rev.B)

References

[1] L.P. Kadanoff, W.Gotze, D. Hamblay, R.Hecht, E.A.S. Lewis, V.V. Palciaskas, Martin Rayl, J. Swift, D. Aspens and J. Kane, Rev.Mod.Phys. **39** (2), 1967

[2] The Theory of Critical phenomena, J.J. Binney, N.J. Dowrick, A.J. Fisher and M.E.J. Newman, Clarendon Press, Oxford, 1992

[3] C. Kittel, Introduction to Solid State Physics, 3rd Edition, Wiley Eastern (Pvt Ltd), New Delhi, 1971

[4] Principles of Condensed Matter Physics, P.M. Chaikin and T.C. Lubensky, Cambridge University Press, 1995

[5] L.J. De Jongh and A.R. Miedema, Advances in Physics, **23** (1), 1974

[6] A.B. Harris, J.Phys.C **7,** 1671 (1974)

[7] G. Grinstein and A. Luther, Phys.Rev B 13, 1329 (1976)

[8] T.C.Lubensky in Ill-Condensed Matter, Proceedings of Les Houches school, Edited by Roger Balian, Roger Maynard and Gerard Toulouse, 1978

[9] E.S.R.Gopal, Specific heats at low temperatures, Plenum Press, London, 1966

[10] D.L. Connelly, J.S. Loomis and D.E. Mapother, Phys.Rev.B ,**3(3)** ,924 (1971)

[11] P.F. Sullivan and G. Seidel, Phys.Rev., , 679 (1968)

[12] A.Bonilla and C.W. Garland , J.Phys.Chem.Solids 35, 871 (1974)

[13] K.V.Rao, page 401, Amorphous Metallic alloys, ed F.E.Luborsky, Butterworth and co ltd, 1983

[14] V.Shubha,T.G.Ramesh and A.K.Bhatnagar, 183,Advances in High pressure Science and technology, Ed. A.K. Singh, Tata McGraw-Hill, New Delhi 1995

[15] X.C.Jin, P.H.Hor, M.K.Wu and C.W.Chu, Rev.Sci.instrum, **55(6)**, 993 (1984)

[16] J.M. Ziman, Phil.Mag, 6, 1014 (1961)

[17] E. Fawcett et al, Rev.Mod.Phys, **66(1)**, 25 (1994)

[18] Mcwhan,D.B and T.M. Rice, Phys.Rev.Lett, 19, (1967)

Contents