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INVESTIGATION OF THE THERMAL AND MAGNETIC PROPERTIES OF SOME Ce BASED HEAVY ELECTRON SYSTEMS.

by

WALID YASS HUSSEN
BSc, MSc

A Doctoral Thesis
submitted in partial fulfilment of the requirements
for the award of Doctor of Philosophy of the
Loughborough University Technology
1990

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ABSTRACT

The aim of this project was an investigation of the thermal and magnetic properties of highly correlated electron systems. To carry out the experiments it was necessary to design, construct, and automate a calorimeter and a Faraday susceptibility balance. The calorimeter was used to determine the specific heat of powder samples from 1.5 K to 300 K using a pulse technique. Initially the performance of the calorimeter was verified using spectrographically pure copper samples. The specific heat of CePt$_2$ and LaPt$_2$ has been measured in the temperature range from 3 K to 100 K. The f-electron contribution to the specific heat of CePt$_2$ was determined by subtracting the measured specific heat of isostructural LaPt$_2$ from CePt$_2$. This difference revealed a Schottky anomaly at temperatures between 15 K and 100 K, which enabled the crystal-field splitting of the $J$=5/2 ground state manifold of Ce$^{3+}$ to be deduced.

For magnetic susceptibility measurements, a comparison method was used in which the microbalance was calibrated using a specimen of spectrographically pure palladium. The magnetic susceptibilities of five samples (CeSi$_{1.8}$Cu$_2$, CeSi$_{2.2}$Cu$_2$, CePt$_2$, CePt$_3$, and LaPt$_2$) were measured at several applied magnetic fields over the temperature range 3.7 K to 300 K. The paramagnetic Curie temperature $\theta_c$ and effective moment $\mu_{\text{eff}}$ of these samples were determined from the experimental results.

The results are discussed with reference to current theories of heavy electron systems.
DECLARATION

This is to certify that I am responsible for the work submitted in this thesis and that the original work is my own except where due reference to previous work has been noted. I also certify that neither the thesis nor the original work contained herein has been submitted to this or any other institution for a higher degree.

W.Y.Hussen
Dedicated to:
my wife and children
Ausama and Marwa
ACKNOWLEDGEMENTS

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I would also like to thank the technical staff of the main workshop and the electronic workshop for their help in constructing and maintaining the cryostat and associated equipment.

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CHAPTER 1

INTRODUCTION

1.1 General Introduction;

Ce compounds have attracted considerable experimental and theoretical interest because of the unique role played by their 4f electrons in determining their unusual physical properties. The 4f electrons are subject to two main types of forces from their local environment. First, the periodic array of charges in the crystal produces an electric field which acts on an ion producing a Crystalline Electric Field. This causes a Stark splitting of the free-ion energy levels, and by modifying the electronic orbits, it has an important influence on the magnetic properties. There are also forces which couple the 4f electrons of the different ions. These may take various forms, but the most important are of the exchange type, giving rise to cooperative magnetic properties. In the cubic symmetry the 6-fold degenerate J=5/2 multiplet of the Ce$^{3+}$ ion splits into a doublet and a quartet. The experiments suggest that in these materials the electronic occupation of the 4f shell of the rare earth ions changes either continuously or discontinuously as the temperature, external pressure or composition of these materials is varied. In certain ranges of temperature, pressure or composition these materials exist in the so called mixed or intermediate valence state in which the energy required to excite an f-electron from the ionic shell to the conduction band is small or zero. The average occupation of the f-shell in the mixed valence state is non-integral due to the fluctuation of the electrons between the localised f-shell and the band states and this results in the very unusual electronic and magnetic properties of these materials. In Ce compounds with mixed-valent character the coexistence of one magnetic configuration (Ce$^{3+}$:4f$^1$ with J=5/2), and of one nonmagnetic configuration (Ce$^{4+}$:4f$^0$ with J=0) is assumed. Cerium compounds which valence fluctuation
include not only non-integrals valent material with nonmagnetic ground states (CeSn$_3$) but also trivalent materials where the fast spin fluctuations suppress magnetic order (CeAl$_3$) and trivalent materials with antiferromagnetic ground states where the thermodynamic properties reflect the presence of spin fluctuations (CeAl$_2$, CeIn$_3$). Their properties have been interpreted using the concept of a "Kondo lattice" [1] in which the magnetic moments are reduced in the ordered phase due to the Kondo fluctuations. It is quite clear experimentally that the ground-state properties of the non-magnetic valence fluctuation (CeCu$_2$Si$_2$, CeCu$_6$, CeAl$_3$) are those of a Fermi liquid[2]. In addition to the finite susceptibilities, large linear coefficients of electronic specific heat are also observed, suggesting a high density of states due to a narrow hybrid 4f level at the Fermi energy.

1.2 Structure of the Thesis;

The thesis is divided into seven chapters covering the development of the research, from the design, construction, and automation, of a specific heat calorimeter and a Faraday magnetic susceptibility balance to the final results and conclusion. The outline of each chapter of the thesis are as follows;

CHAPTER 1

This chapter gives a general introduction to the properties of Ce compounds. The structure of the whole volume of the thesis is also present in this chapter.

CHAPTER 2

In this chapter, method of measuring specific heat at low temperatures are reviewed. The design and construction of a calorimeter for specific heat measurements, using the pulse method, in the temperature range from 1.5 K to
CHAPTER 3

In this chapter, the automation of the specific heat calorimeter is described in detail. The design and the principle of operation of electronic circuits are given, as well as the automation hardware and software requirements.

CHAPTER 4

This chapter deals with the design, construction, and automation of a Faraday susceptibility balance. The mechanical, electronic, and detailed operating characteristics are presented. A general description with flow chart of the automation is given, as the detail tends to be system specific.

CHAPTER 5

In this chapter, a general theories of specific heat, and magnetic susceptibility of metals are review. The emphasis in the chapter is mainly on theoretical concepts which have found application to Ce compounds.

CHAPTER 6

The experimental properties of a large number of Ce compounds are reviewed. Following this, the experimental results and analysis of magnetic susceptibility, neutron, and specific heat of some Ce compounds measured during the present work are presented. The results contain the neutron diffraction on a powder sample of CePt₂ in temperature range between 10 K to 300 K, the magnetic susceptibilities of five samples (CeCu₁.₈Si₂, CeCu₂.₂Si₁.₈, CePt₂, CePt₃, and
LaPt$_2$), and the specific heat of:

a. Pure copper samples for calibration purposes.
b. CePt$_2$ and LaPt$_2$ sample, in temperature range of 3 K to 100 K.

**CHAPTER 7**

Contains conclusions for the results achieved during the present work. Many suggestions are recommended for future work which will be useful to lead the present research a step forward.
CHAPTER 2

EXPERIMENTAL TECHNIQUES AND EQUIPMENT FOR SPECIFIC HEAT MEASUREMENTS

2.1 Methods of Measurement;

In general there are four methods used for measuring the specific heat of solids at low temperature. These are, the AC, the relaxation, the pulse and continuous methods. The AC method and the relaxation methods are used to measure the heat capacity of small specimen (1-100 mg) in non-adiabatic calorimetry. For larger specimen (>200 mg) the heat capacity is measured using the pulse and continuous methods in isothermal and adiabatic calorimetry.

2.1.1 The AC Method;

In this method, the specimen is attached by a weak thermal link of conductance, \( K \), to a cold copper block. Heat is supplied to the specimen at a frequency \( \omega \) and the \( \omega \) component of the temperature rise is given by [3];

\[
\Delta T_\omega = \frac{P_\omega}{\omega C} \quad (2-1)
\]

where \( P_\omega \) is the applied heat of the frequency component \( \omega \), and \( C \) is the heat capacity of the specimen plus the heat capacity of the addenda. It should be noted that long relaxation times \( \tau_1 \) between the specimen and surroundings, are not necessary in this method.
If the thermal conductance ($K_{in}$) of the specimen is low, then the measured signal will not accurately reflect the heat capacity. An internal relaxation time ($\tau_2$) to describe this effect has been proposed by Sullivan and Seidel [3];

$$\tau_2 = \frac{C}{K_{in}}$$  \hspace{1cm} (2.2)

They showed that;

$$\frac{\omega \tau_1}{10} > 1 > 10 \omega \tau_2$$ \hspace{1cm} (2-3)

is the condition for 1% accuracy.

This method is used to measure the specific heat near transitions and measurements on specimens weighing only a few micrograms. Such measurements provide, however, only a relative measurement of the specific heat and must be calibrated by another method to obtain an absolute value. In addition, the experiment must be run at several frequencies to insure the absence of spurious effects due to poor thermal conductivity of the specimen.

### 2.1.2 The Relaxation Method;

In this method, the copper block is stabilised at some temperature ($T_0$). Current is then passed through the heater, dissipating power ($P$) and raising the temperature of the thermometer-specimen assembly to ($T_0 + \Delta T$) where $\Delta T = P / K$, and ($K$) is the thermal conductance of the thermal link (wires) between the specimen and the copper block. The current in the heater is then turned off, and the specimen
temperature relaxes exponentially[4, 5];

\[ T = T_0 + \Delta T e^{-t/\tau} \]  
(2-4)

to \( T_0 \) with a time constant

\[ \tau = C / K \]

where \( C \) is the heat capacity of the specimen plus the heat capacity of the addenda.

### 2.1.3 The Continuous Method

In this method, a constant power \( Q \) is supplied to the specimen and the temperature \( T \) is frequently measured as a function of time \( t \).[6] If no heat leak exist between the specimen and its surroundings, the heat capacity is given by;

\[ C(T) = \frac{dQ}{dT} = \frac{(dQ)}{dt} \frac{(dT)}{dt} \]  
(2-5)

where \( (dQ / dt) \) is the rate of heat input and \( (dT / dt) \) is the rate of temperature rise. The usual procedure is to assume;

\[ C(T) = \frac{Q}{\Delta T / \Delta t} \]  
(2-6)

and to calculate \( C(T) \) from the measured power \( Q \) and the finite quantities \( \Delta T \).
2.1.4 The Pulse Method ( Nernst-Method) ;

In this method, the specimen is heated; the heat capacity is obtained from division of the applied energy $\Delta Q$ by the increase in temperature $\Delta T$,[7, 8]; i.e

$$C(T) = \frac{\Delta Q}{\Delta T} \quad (2-7)$$

In the pulse method the specimen is in thermal equilibrium before and after the heating period. Consequently $C(T)$ measures an equilibrium property of the specimen. In contrast, the continuous method necessarily involves non-equilibrium properties of the specimen since heat current must be flowing in it. A disadvantage of the heat pulse method is that each specific heat value is obtained relatively slowly, and in consequence, the density or data points is low compared with the continuous method.

2.2 The Cryostat;

The cryostat consisted of two concentric silver glass dewars, designed to work in the temperature range from 1.5 K to 300 K. The schematic diagram of the cryostat is shown in fig (2.1). The inner dewar containing the calorimeter, could be filled with either liquid helium-4, or nitrogen depending on the temperature range, if liquid helium was used, the outer dewar was filled with liquid nitrogen. The calorimeter was suspended by thin walled stainless steel tubes from a brass plate as shown in fig (2.2). A copper can enclosed the calorimeter and was sealed by
indium wire to the brass plate by tightening twelve screws. In this manner the calorimeter could be evacuated. The whole calorimeter assembly was suspended from a flange at the top of the helium dewar by 3 stainless steel tubes. Two of these tubes of diameter 7 mm were used to evacuate the calorimeter can and for carrying the experiment wires from the top of the cryostat to the calorimeter. The third tube of diameter 3 mm was used to operate the thermal switch by evacuating or pressurising the bellows. The length of these stainless steel tubes was 1.5 m. In addition to three stainless steel tubes, another stainless steel tube of diameter 7 mm and 1 m long from the top plate, is used to fill the inner glass dewar with liquid helium-4 by using a transfer tube. Three copper radiation shields are soldered to the stainless steel tubes at appropriate distance to minimise heat leaks.

2.3 The Vacuum System;

A pumping system capable of creating a vacuum of up to 10^{-5} mbar was used to evacuate the calorimeter. The same system could also be used to pump the glass dewar or to operate the thermal switch. It consisted of a rotary pump (100 l/min) and a diffusion pump (500 l/s) along with its associated pipe work and valve board. Pirani gauges were used to measure pressures down to 10^{-3} mbar and Penning gauges were used for measuring pressures down to 10^{-6} mbar. Fig(2.3) shows the schematic diagram of the high vacuum system. An inlet valve enabled an exchange gas to aid cooling of the calorimeter or gas to operate the thermal switch to be admitted into the system.

2.4 The Liquid Helium-4 Pumping System;

The liquid helium-4 pumping system is a one stage rotary pump and is shown in fig (2.4). Helium-4 is transferred to the cryostat via a vacuum insulated
transfer tube inserted through the top of the cryostat. The boil-off from the liquid helium-4 bath is recuperated through a copper pipe to the recovery line and monitored by a flowmeter. During pumping, valve (2) is closed, and valve (1) is opened. the Bourdon gauge (G) is used to measure the pressure over the pumped helium-4.

2.5 The Calorimeter;

Fig (2.2) shows a schematic diagram of the calorimeter assembly. The calorimeter was contained in a small thin walled cylindrical copper can (specimen holder) and was fixed tightly by means of 4 10 BA bolts. The body of the calorimeter was covered with tissue paper glued on by GE7031 low temperature varnish [9]. This reduced the possibility of the heater windings shorting onto the calorimeter. Heat was supplied by a (500 Ω) resistance heater which was made by winding about 20 m of 0.05 mm diameter constantan wire. The heater wire was noninductively wound on to the calorimeter to eliminate any magnetic field which may effect the thermometer. A silicon-diode or germanium thermometer was screwed onto the top of the specimen holder. The specimen holder was suspended from the radiation shield by means of nylon threads of about 0.1 mm diameter, the thread was attached to eyelets in the calorimeter and to the stainless steel tubes. The adiabatic copper shield was made as thin as possible to obtain a minimum thermal response time. The shield itself was supported by three tubes of thin-walled stainless steel. The electrical wire were thermal anchored to the top plate of the cryostat and the radiation shield. The electric wiring from the radiation shield to the specimen thermometer and heater was made by five 0.05 mm constantan wires and two of 0.05 mm copper wires as voltage and current leads. The whole apparatus was suspended from the top plate by three 3 mm stainless steel tubes.
2.5.1 The Specimen Heater;

To improve the accuracy in determining the electric power introduced into the resistance heater, the voltage and current, and therefore the heater resistance, must remain constant between readings. Constantan and manganin are used fairly extensively as heater wires in low temperature calorimetry because both constantan and manganin have a very small temperature coefficient of resistance, manganin more so than constantan. The total changes in resistance over the temperature range 10-250 K are 6% and 10% for constantan and manganin respectively [10].

The second potential error arises from the fact that the leads carrying the heater current dissipate energy themselves. Part of the heat generated in the leads flows to the specimen and part to the shield, for this reason the specimen heater resistance should be much greater than the resistance of the the leads, so that the amount of heat is very small compared to the amount generated into specimen. The asymmetrical method [11] of connecting the leads to the heater winding was used to eliminate errors due to heat generated in these leads. In this method, half the heat generated in each current lead should flow to the specimen and the other half should flow to the shield. The specimen heater of 500 $\Omega$ of 0.05 mm diameter insulated constantan wire was wound evenly on to a tissue paper which was stuck round the body of the calorimeter with a low temperature varnish GE7031. This varnish was also used to keep the windings fixed firmly on the calorimeter. About 40 mm of 0.1 mm copper wires was joined to each end of the heater winding and firmly anchored to the top of the calorimeter by GE7031 varnish. The end of each copper wire was joined to constantan wire 0.5 m long and of 0.05 mm diameter. The amount of heat generated in the leads was approximately;
\[ \frac{R_L}{R_H} \times 100 = \frac{1}{20} \times 100 = 5\% \]

of the total heat generated.

2.5.2 The Specimen Heater Circuit;

The circuit diagram for the specimen heater is shown in fig (2.5). The RS-3347 programmable current source was used to regulate the current to the specimen heater. It is a three terminal adjustable current source featuring a 10000:1 range in the operating current, excellent regulation and a wide range of dynamic voltage of between 1-30 V. Requiring only an external resistor to set the current, this device can operate as a true floating current source. This external resistor \( R_{set} \) is used to determine the heater current \( I_H \) according to the equation;

\[ I_H = \frac{67.7 \, \text{mv}}{R_{set}} \]  \hspace{1cm} (2-8)

where \( I_H \) is the heater current in mA and \( R_{set} \) is the external standard resistor in \( \Omega \).

The heater current can be set manually by using a multi turn potentiometer or automatically by the programmable resistor circuit which is controlled by the computer. A 30 V stabilised d.c. power supply was used to supply the required voltage to the heater current source. To reduce the effects of any high frequency heating, a 0.04 \( \mu \)F capacitor was connected in parallel with the heater within the calorimeter, and all leads to the specimen heater and the thermometer were screened. The heater power input to the specimen was determined by measuring the voltage drop across a 100 \( \Omega \) resistance which was connected in series with the heater, and the voltage drop across it. When the heater current was switched off, the current from the current source was passed through a dummy resistance whose value was equal
to the heater and lead resistances. This maintained the stability of the heater current by keeping the load on the current source constant;

2.6 Shield Control;

Fig(2.6) shows the circuit diagram of the shield temperature control. The shield temperature was controlled by using a commercial 318-Temperature Controller. In isothermal calorimetry, a 4-wire rhodium-iron sensor was fixed to the shield, to monitor the temperature. In adiabatic calorimetry a differential thermocouple of 0.05 mm constantan-copper was used with the temperature controller to sense the temperature difference between the shield and specimen. The shield heater was 68 Ω of 0.1 mm constantan wire which was noninductively wound on to the shield. In an equilibrium adiabatic condition the power to the heater shield exactly balances the thermal losses to the surrounding. Thus

$$i_0^2 x R = K x \Delta T_{sh}$$  \hspace{1cm} (2-9)

where $i_0$ is the current in the heater shield winding of resistance $R$, $\Delta T_{sh}$ is the shield-specimen temperature differential, and $K$ is a thermal transfer coefficient (containing both radiative and conductive components). During a measurement, $\Delta T_{sh}$ remains approximately constant, but the power input has to be increased by an amount necessary to heat the shield at the same rate as the specimen; i.e

$$i^2 x R = K x \Delta T_{sh} + C x \left(\frac{dT}{dt}\right)$$  \hspace{1cm} (2-10)

where $i$ is the heater current of the shield, $C$ is the heat capacity of the specimen and $dT / dt$ the rate of temperature increase.
2.7 The Heat Transfer between Specimen and Shield;

The heat transfer between the specimen and shield plays an important role in specific heat measurements. There are three sources of heat transfer; heat may be transferred by conduction, convection or radiation. The heat transfer by convection can be eliminated by partial evacuation of gas from the cryostat. In addition, such factors as joule heating in electrical leads, mechanical vibration, adsorption of gases may contribute to the heat transfer. The following methods were used to calculate the heat transferred by these processes.

2.7.1 Conduction of Heat by a Gas;

For approximately parallel surfaces at temperatures $T_1$ and $T_2$ the heat transferred, $Q$, by conduction through a residual helium gas at low pressure is given by [12];

$$Q = 0.028 a_o P_m x (T_2 - T_1) A$$

(2-11)

where $a_o$ is the accommodation coefficient for helium, assumed to be 0.5, $P_m$ is the pressure in torr ($10^{-5}$ torr), and $A$ is the surface area of the specimen, approximately 12 cm$^2$. Hence the heat loss due to conduction for $T_2 - T_1 = 0.5$ would be;

$$Q = 0.028 x 0.5 x 10^{-5} x 0.5 x 12$$
$$= 0.84 \mu W$$
2.7.2 Heat Transfer through a Solid;

The heat flow $Q_s$ through a solid of uniform cross-section $A$ and length $l$, if the ends of it are at temperature $T_1$ and $T_2$ is given by [12];

$$Q_s = \frac{A}{l} \int_{T_1}^{T_2} \lambda(T) dT$$  \hspace{2cm} (2-12)

where $\lambda(T)$ is the temperature-dependent thermal conductivity of the solid.

The mean thermal conductivity is given by

$$\bar{\lambda} = \frac{1}{(T_2 - T_1)} \int_{T_1}^{T_2} \lambda(T) dT$$  \hspace{2cm} (2-13)

For a specimen at 4 K and with the shield at 3.5 K, then the rate of loss of heat due to conduction down two leads of 0.005 mm diameter copper wire ( $\lambda = 2$ W/cm.K) and five leads of 0.05 mm diameter constantan wire ( $\lambda = 0.006$ W/cm.K), each 50 cm long is;

$$Q_s = [0.006 \times 5 \times \pi \times (0.025)^2 + 2 \times 2 \times \pi \times (0.025)^2] \times 0.5 / 50 \times 10^{-2}$$

$$= 0.78 \mu W$$

For a specimen at temperatures higher than 77 K, and the shield being 0.5 K colder, the mean thermal conductivity of the copper is not changed, but that of the constantan wire is increased to become $\lambda = 0.22$ W/cm. K.
2.7.3 Heat Transfer by Radiation;

For two plane parallel surfaces each of area A, and emissivities $\sigma_1$ and $\sigma_2$, and at respective temperatures $T_1$ and $T_2$, the heat transfer by radiation per unit time for $\sigma_1$ and $\sigma_2 \ll 1$, is:

$$Q = \sigma A \left( T_1^4 - T_2^4 \right) \frac{E}{2}$$  \hspace{1cm} (2-14)

where $\sigma = 5.67 \times 10^{-12} \text{ Wcm}^{-2} \text{deg}^{-4}$ is Stefan's constant.

For a specimen at 4 K and with the shield at 3.5 K, then for copper $\sigma = 0.6$, so the heat lost to the shield by radiation is:

$$Q = 5.67 \times 10^{-12} \times 12 \times (4^4 - 3.5^4) \times 0.3$$
$$= 0.0021 \mu \text{W}$$

For the specimen at 100 K and the shield at 99 K, then

$$Q = 5.67 \times 10^{-12} \times 12 \times (100^4 - 99^4) \times 0.3$$
$$= 80.4 \mu \text{W}$$

From this we can see, that the rate of loss of heat due to radiation increases rapidly above 100 K compared to the heat lost due to conduction. To reduce the heat lost by radiation the temperature of the specimen and shield must be equal (i.e. $T_1 = T_2$); this condition can be achieved by using an adiabatic calorimeter.
2.7.4 Other cause of Heat Transfer;

2.7.4.1 Joule Heating;

The joule heating in the heater leads was 5% of the total heat generated in the specimen heater. By using the asymmetrical method[11], one of the potential leads was connected to the current lead at the specimen, and the other potential lead was connected to the other current lead at the shield. In this method, half the heat generated in each current lead should flow to the specimen and the other half should flow to the shield. This is therefore corrected for, by including the heat generated in one lead. At low temperature, when heat losses from the sides of the leads are small, half the heat from the leads eventually reaches the specimen. At higher temperatures the heat losses from the sides of the leads increases[13] and the assumption becomes invalid.

2.7.4.2 Gas Adsorption;

The thermal energy required to desorb a layer of adsorbed gas from a surface is of the same order of magnitude as the latent heat of vaporisation. As the temperature of the specimen surface is raised, gas desorption begins and part of any electrical feed to the calorimeter is employed in this desorption process. The gas adsorption problem can be avoided by using a mechanical thermal switch.

2.8 The Thermal Switch;

The use of helium as an exchange gas to accelerate the attainment of
temperature equilibrium between the specimen and the surroundings can be accompanied by many disadvantages in low temperature calorimetry. These are, firstly, the gas adsorption onto the surface of the specimen giving rise to errors in the measured values of specific heat. Secondly, to pump out the exchange gas from the vacuum space, to give satisfactory thermal isolation of the specimen takes a long time. To overcome these disadvantages it is now usual to employ some form of mechanical heat switch to establish and break thermal connection between the specimen and its surrounding. There are two important considerations for the use of a thermal switch, these are;

i- it should exert sufficient pressure to ensure good thermal contact with specimen.

ii- it must be possible to release the contact between the switch and the specimen without large energy inputs to the specimen.

The general layout of the mechanical thermal switch is shown in fig(2.2). The thermal switch design is similar to one described in detail in reference[14]. The principle of operation is as follows; A tombac bellows closed on one side by a copper plate, and was solidly attached at the other, to the cryostat top plate and linked by a stainless steel tube, to a pressurised helium gas cylinder. When the bellows was filled with helium gas under pressure of about 1.5 bar the extended bellows pressed the thermal link against the copper plate. The thermal link was 0.5 mm diameter copper wire fixed on to the top of the specimen calorimeter. To switch off this contact the helium gas inside the bellows was pumped out by means of the vacuum system.

2.9 The Specimen Thermometer;

Two types of thermometers were used to measure the temperature of the specimen from 1.5 K to 300 K; via a germanium resistance thermometer and a
silicon diode thermometer. A germanium resistance thermometer was used from 1.5 K to 100 K with good reproducibility compared to a carbon-resistor. A silicon diode thermometer was used from temperatures of 30 K to 300 K, with high sensitivity compared to a platinum thermometer[15].

2.9.1 The Germanium Resistance Thermometer;

The thermometer was calibrated by LAKESHORE CRYOGENICS, against a pair of Rhodium-Iron thermometers to an accuracy of ±3 mK below 27 K, and calibrated to the EPTS-76 standard against a pair of platinum thermometers to an accuracy of ±5 mK above 27 K, calibrated to the IPTS-68 standard. To ensure that the specimen and the thermometer leads were at the same temperature, the four leads from the thermometer, two potential and two current were connected to 80 mm long copper wires of 0.05 mm diameter which were wound on the top of the specimen holder. Four leads 0.5 m long of 0.05 mm diameter copper and constantan wires were used to connect the current and the potential leads of the thermometer to the radiation shield. The thermometer was calibrated between 1.5 K and 100 K by the manufacturers. Fig(2.7) shows the calibration curve of the germanium thermometer.

2.9.2 The Germanium Thermometer Circuit;

According to the instruction of the manufacturer of the germanium thermometer, different currents are needed at different temperatures for precise measurement of temperature and also to avoid any excessive Joule heating effect. The thermometer resistance is achieved by passing the current from a precision current source through the resistances and sensing the voltage developed across the resistance. With a 4-wire connection the lead resistance have negligible effect and
only the value of the thermometer resistance is measured. The Datron DVM is capable of measuring the resistance in the 4-wire configuration and we have used this facility to measure the resistance of the germanium thermometer without using an external current source.

The 4-wire connection shown in fig(2.8), using two screened twisted pair cables is also suitable for measuring high resistance with long cables since the effects of leakage and capacitance between the leads is eliminated[16]. To reduce the effects of any high frequency heating, a (0.04 μf) capacitor was connected in parallel with the thermometer within the calorimeter can.

2.9.3 Silicon Diode Thermometer;

Forward biased silicon diodes are being widely used as cheap and convenient sensors. Temperature sensing has been carried out with these diodes by passing a constant current in the forward direction and measuring the voltage drop across the diode. The current is usually 10 μA. A diode is more sensitive and is more nearly linear over more of their usable range, than the carbon, germanium, or platinum thermometers. The sensitivity of the diode is quite high at the lower temperature. This makes it possible to observe changes of less than 1 mK with this diode. They can also be used over a wider temperature range, but with less reproducibility. The equipment needed to determine temperature using a diode thermometer consists of a constant current source (normally 10 μA), a very high input impedance DVM, and a calibration curve or table. Fig(2.9) shows the voltage-temperature characteristics of a silicon diode. A precision current source circuit shown in fig(2.10) was designed to supply the current to the silicon diode.
Fig (2.1) : Schematic description of the cryostat

1- feedthrough for electrical wires.
2- high vacuum outlet for the vacuum can.
3- inlet pipe for the thermal switch.
4- inlet pipe for the liquid He transfer siphone.
5- inlet copper pipe for the liquid N2 transfer.
6- top place of the cryostat.
7- radiation shield for the liquid He.
8- vacuum can.
9- liquid N2 glass dewar.
10- liquid He glass dewar.
11- high vacuum outlet for the vacuum glass dewar.
12- outlet for pumping the He gas.
Fig(2.2): Schematic description of the adiabatic calorimeter

1- pumping pipe for bellows of mechanical heat switch
2- pumping pipe for high vacuum can
3- feedthrough for electrical wires
4- vacuum can
5- indium seal
6- support thermal switch
7- support of radiation shield
8- bellows of thermal heat switch
9- copper wire as thermal heat switch
10- radiation shield
11- support for sample holder
12- sample thermometer
13- radiation shield heater
14- sample heater
15- sample holder
16- nylon wire
17- thermal anchoring of wires
18- radiation shield thermometer
Fig (2.3): High vacuum system
Fig(2.4) Schematic view of the liquid helium-4 pumping system
To multiplexer circuit

From DC voltage source

To the programmable resistor circuit

From the User port

To multiplexer

Fig (2.5): circuit diagram of the heater current source
Fig(2.6); A circuit diagram of shield temperature control

3120-Temperature controller

A +
B -
C +I
D -V
E +V
F -I

DIFFERENTIAL THERMOCOUPLER

68 OHM
SHIELD HEATER

RHODIUM-IRON THERMOMETER

SPECIMEN JUNCTION

CONSTANTAN WIRE

COPPER WIRE

SHIELD JUNCTION

Cryostat
GERMANIUM RESISTOR

Fig(2.7)
Fig (2.8): Circuit diagram of measuring the resistance of germanium thermometer
Si DIODE

Figure (2.9)
Fig(2.10): circuit diagram of the precision current source for the Si-diode thermometer
CHAPTER 3

AUTOMATION OF THE CALORIMETER FOR SPECIFIC HEAT MEASUREMENTS

3.1 Introduction;

The automation of the specific heat measurement was designed to optimise the time needed to acquire and analyse data, so minimising manual intervention. In general the measurements are time-consuming with a single run from 1.5 K to 300 K taking up to several days. Several systems for automated data acquisition or data recording and analysis have been described in the literature\cite{17, 18, 19}. The rapid development of high performance digital voltmeters (DVM), automatic AC-bridges and reproducible semiconductor thermometers made feasible the full automation of the experiment\cite{20}. Automatic systems capable of recording data and computing results during the course of experiment have been described by several authors\cite{21, 22, 23}. In these systems, however, it is still necessary to make external adjustments of system parameters to account for the rapid variation of specific heat at low temperatures or in the neighbourhood of anomalies. From this point of view only on-line computer techniques may achieve complete automatic operation of the calorimeter, the computer taking decisions concerning the control-parameters on the basis of the results obtained\cite{24, 25, 26, 27, 28}.

The system was designed to work on-line with the computer controlling both the experiment and the processing of the measured data, finally storing the results on
disc and producing a hard copy print out. In this chapter the general features of the electronic system are outlined and the computer program controlling the experiment are presented in the form of flow diagrams. A schematic diagram of the data acquisition and control system is shown in fig(3.1).

3.2 Computer Control of the Specific Heat Measurements;

Like most microcomputers the BBC can be programmed either in BASIC or in machine code if higher operating speeds are necessary. Since specific heat experiments are slow we have found that BASIC is adequate for this application. The BBC microcomputer incorporates a 1 MHz port which it can be interfaced with an IEEE data bus. An additional eight-bit port, the "User port" allows switching of the external circuits under program control using a minimum amount of extra circuitry. Data from the BBC was printed using an EPSON printer; the data was also stored in disc files. Thus an interface can be considered as hardware support for the software to enable the computer to control the peripheral device. It is worthwhile to explain very briefly the IEEE-488 Interface and the User port.

3.2.1 IEEE-488 Interface;

The IEEE-488 Interface provides a standard input/output interface between a computer and up to 14 other instruments and peripherals. It allows digital data to be transferred between the instruments and the computer in any combination. In addition, it is possible for computers with IEEE-488 interfaces to be connected to each other and with the interface then enabling rapid transfer of data between the computer[29]. Data transfer rates of 1 Million Bytes per second are feasible. The range of instruments available is very large, and includes such
diverse items as Digital Voltmeters, Disc Drives, Printers and Plotters. Any computer with an IEEE-488 interface can connect to these pieces of equipment without any problems of incompatibility. With respect to operating with the IEEE bus, there are only three operating states, controller, talker, and listener. The controller (computer) coordinates communications on the bus by commanding the other devices connected to it. In the talking state information can be put on the bus, where, as the listing state accepts messages that have been placed on the bus. The controller, generally both talks and listens. Individual instruments or peripherals connected to the bus may have one or either capability, for example, the Datron 1071 DVM, and the Oxford 3120- Temperature Controller can act as both as talker and listener, as commanded by the controller.

3.2.2 User Port;

There are two 6522 VIA's (Versatile Interface Adapters) inside the BBC Micro[30]. One of these is dedicated to the MOS and controls the keyboard, sound, etc. The other drives the parallel printer and the user port. Each VIA chip is housed inside a large 40 pin package. It contains two fully programmable bidirectional 8 bit Input/Output ports. All of port B lines, PB0-PB7, and CB1, CB2 are available directly on the user port connector. The port B connector is shown in fig(3.2). The port B lines can be programmed independently to act as input, output, bidirectional or handshake signals. We have used the user port PB0-PB7 as output to control the multiplexer relays and the programmable current source.

3.3 Heater Current Control;

Since the heat capacity of solids at low temperature varies rapidly with temperature, it is very desirable to have a device for controlling the heating power
supplied to the specimen. In an automated system it is necessary for the heater supply to be controlled by the computer. The circuit diagram of the heater current source control system is shown in fig(3.3). The heater can be set manually by using the multiturn potentiometer or automatically by a computer controlled relay circuit. The controller consists of sixteen resistors providing current ranges from 1 \( \mu \text{A} \) to 10 mA, and are switched in by sixteen relays. A pulse from the computer is used to drive a 16-bit up/down counter (SN74193), decoder(SN74154), and buffer drivers(SN7407) for the relays. The up/down counter is driven by two lines from the computer user port. A further user port line is used to switch the heater on and off so that only three lines are required to operate the power supply remotely. A 5 volt dc supply is used to drive the counter, buffer driver, and relays.

3.4 The Multiplexer Unit;

A multiplexer is a logic circuit that accepts several data inputs but allows only one at a time to get through to the DVM. The routing of the desired data input to the output is controlled by data selected input. Referring to the circuit diagram fig(3.4), it can be seen that the multiplexer consists of four relays, a decoder(SN74138), and buffer driver(SN7407). Two lines from the computer user port are used to control the multiplexer circuit. For specific heat experiments the DVM is required to perform three measurements. These are;

i. Heater voltage.

ii. Heater current; DVM will measure the voltage drop across a resistance(100 \( \Omega \)) whilst the current from a current source is flowing through it. The computer will divide this voltage by the value of the resistor to determine the exact value of current going to the heater.
iii. Thermometer voltage for the silicon diode thermometer or thermometer resistance for the germanium thermometer

3.5 Data Transmission Technique;

3.5.1 Data Transmission from the DVM;

The IEEE interface allows the DVM to form part of a system, outputting measurement data to other parts of that system. In addition, the DVM can be instructed, via the interface, to remotely select the instrument's facilities. Thus the DVM is able to receive programming information (listener) and to output data (talker) [31]. The DVM can be operated under remote control, when ASCII coded programming instructions are received from a computer, or in local control when the DVM is operated from its front/rear controls. In both cases output of the results or parameters are available at both the DVM display and via the interface. When operating in remote, it requires an address command followed by a series of device dependent messages or commands to change the various ranges, function and operating modes. A series of these commands can be sent together as a program string; i.e

PRINT5,"R0F3T1="

where R0 is the range, in this case autorange, F3 is the dc voltage function, T1 is the external Trigger command, and "=" is the string terminator command. The DVM address is set manually using a six way miniature switch near the interface connector on the rear panel. Five of the switches are used to set the address, and using a binary code, this enables any address in the range 0 to 30 to be used, i.e a binary code of 00101 is address 5. The output from the DVM to the computer consists of an ASCII character string in scientific notation, with range and
function data.

3.5.2 Data Transmission from the Temperature Controller;

The 3120-GPIB interface enables the temperature controller to be linked to instruments via the IEEE-488 interface bus [32]. The 3120-GPIB interface may be given a valid address on the bus by use of the block of five switches on the interface board. The same address is used for both talker and listener functions. As supplied, the temperature will be set to address 7 and this address is used in the program. A command from the computer to the temperature controller consists of a series of alphanumeric characters, terminated by a line-feed character (0A in hexadecimal). All commands consist of 1, 2, or 3 letters, optionally followed by a number sent in ASCII code as an unsigned decimal integer. For example "MS" instructs the temperature controller to send a measured temperature. The output from the temperature controller to the computer consists of a series of alphanumeric characters, terminated by a line-feed character. Example of a typical output is "MT,0273.1,K". The first field starts with an M to indicate a measurement. This is followed by a T to indicate temperature has been measured. The numerical field always consists of seven characters. The unit field consists of either one or two characters, or a single space if no unit is appropriate.

3.6 Computer Program Description;

Programming for the system, is performed in BASIC language. The flow diagram of the computer program is shown in fig(3.5). It is considered worthwhile to describe some of the program commands that are used with the IEEE interface, disc drive, and user port.
3.6.1 IEEE-Interface and Disc Drive Programming;

a. Initialising the interface and disc drive;

The CST Procyon IEEE-Interface must be selected as the current filing system before it can be used. The operating system command *IEEE is used for this purpose. This command will clear the interface hardware and set the interface into a known state. This command should be put at the top of the program using the IEEE interface. The *DISC command is used for the disc files.

b. Sending strings and numbers to devices;

The PRINT£ statement is used to send characters from the computer to a device. This statement is used in the disc and tape filing systems to send values to the files which are opened using OPENIN or OPENOUT and can be used to save strings or numbers. To send a string to a device the statement below is used;

\[ \text{PRINT£device,string$} \]

where device is the address of the device, and string$ is either a string variable, a string constant, or a string expression. The IEEE filing system can only send numerical values to a device in a string using PRINT£. Firstly the number to be sent must be converted into a string, and then the string is sent using PRINT£.
c. Reading strings and numbers from devices;

TO read strings from a device, the statement INPUT£ is used as indicated below;

\[
\text{INPUT£device,stringvar$}
\]
device, is the address of the device and stringvar$ is a string variable. IEEE measuring devices will often send out their readings in the form of character strings representing numbers. Using INPUT£ it is not possible to read these directly into numeric variables, they must be read into string variables and then be converted into their numeric values. The BASIC function VAL is used for this purpose. VAL reads a single number from a string and converts it to a numerical value.

3.6.2 User Port Programming;

Using the user port (port B) 8 bidirectional lines can be individually programmed as either inputs or outputs under control of the Data Direction Register (DDRB). Placing a "0" in a bit of a DDR will cause the corresponding line of the port to be defined as an input line. Where as "1" will cause it to be defined for output. The lines are controlled by a bit in an Output Register (ORB) and an Input Register (IRB). When programmed as an output, a port line will be controlled by a corresponding bit in the output register. Fig(3.6) shows the schematic diagram of these registers. For example if we want to set all the port lines as output, the following command is used;

\[
?&FE60=&FF
\]
where (?) is the output command, &FE60 is the hexadecimal address of a data
register, and &FF is the hexadecimal number which is equivalent to the binary number (11111111). The same command could be used with slight modification for sending logic "0" or "1" to individual port lines, for example the command;

?&FE62=&FF

will cause the computer to send logic "1" to a port line. Likewise

?&FE62=&01

will send logic "1" to (PB0) line only while all the other lines remain "0".

3.6.3 Initialisation Phase;

In the input section of the program, values are established for the title of the specimen (A$), specimen molar mass (SM), number of points in the drift curve(N2) (see fig(3.7)), number of points in the line fitted to the drift curve(N9), and flag variables (J), (I), and (K). After these quantities have been entered, the flag variables are checked to determine which subroutine is to be performed. If the flag variable (J) is found to be 1, then an additional "IF" statement which checks variable (I) would switch the program to a subroutine which checks the parameters loaded. If (J) is set at (2), the program goes to the measuring cycle subroutine and if (J) is (6), it would go to the end of the program. There are four subroutines which are used which test the specimen heater current, specimen temperature, specimen drift temperature, and shield temperature, before the measuring cycle subroutines begins.
3.6.4 Measuring Cycle;

The complete measuring cycle using the pulse method is shown in terms of a temperature-time graph in fig (3.7). During the initial drift period (tN1), the temperature of the specimen is measured repeatedly (N1) times, (every 1 sec). In the heating period (Z3) it is not necessary to measure the temperature, but the heater voltage and current must be measured. It should be noted that the heating period must be known to a precision much greater than is necessary in timing the observation of the temperature in the drift period. Following the heat pulse, the specimen temperature is measured repeatedly (N2) times, (every 1 sec) to give a post heating drift curve. Following the measuring cycle the computer has to make a number of calculations before it can print out the temperature and the specific heat. Firstly the value of the energy supplied to the specimen is calculated;

$$\Delta Q = I_H \times V_H / Z3 \quad (3.1)$$

The temperature is determined from the measured resistance of the germanium thermometer or measured voltage if a silicon diode thermometer is used, by interpolation of the respective thermometer calibration data. The temperature rise ($\Delta T$), and the average temperature are calculated at the midpoint of the heating period from a linear extrapolation of the lines fitted to the temperature points in the pre and post drift period. Then the heat capacity is calculated as follows;

$$H_C = \Delta Q / \Delta T \quad (3.2)$$

The heat capacity of the specimen is obtained following the subtraction of the empty calorimeter heat capacity from the total heat capacity of the specimen plus the empty calorimeter. The heat capacity of the empty calorimeter was measured several times (2 K to 100 K), and fitted to the equation;
HE = A + BT + CT^3 + DT^5 \quad (3.3)

In the temperature range of 77 K to 300 K, the heat capacity of the empty calorimeter was calculated by using a linear interpolation method. Finally the results are printed out, and stored in a disk file, and the measuring sequence is repeated until the temperature range requested has been covered.

3.6.5 Linear Least-Squares Fit;

One of the most widespread uses of computers in physics is the fitting of theoretical curves to experimental data. If a number of measurements are made of the same physical quantity and if these measurements are subject to random error, then the theory of least squares, states that the most probable value of the measured quantity is that which makes the sum of the squares of the errors a minimum. This theorem is applied as follows to the problem of finding the straight line which agrees best with a set of experimentally determined points. If there are only two points, there is a problem because the two constants which define a straight line can not be unequivocally determined from these two points. But, in general, there will be more points available than constants to be determined. Suppose that the various points have coordinates, X1Y1, X2Y2, X3Y3, ..., and that it is known that X and Y are related by an equation of the form;

\[ Y = ZV + SL \times X \quad (3.4) \]

where ZV is the intercept and SL is the slope.

The problem is to find the values for the constants ZV and SL, since these define
the straight line. In general, the line will not pass exactly through any of the points since each is subject to a random error. Therefore each point has an error which is given by its deviation from the straight line. For example equation (3.4) states that the value of Y corresponding to X=X_1 is \((ZV + SL \cdot X_1)\). If the first experiment points has a value of \(Y=Y_1\), then \(U_1\), the error in the first point, is given by;

\[
U_1 = (ZV + SL \cdot X_1) - Y_1 \tag{3.5}
\]

The errors in the other points can be calculated in a similar fashion, and then the expression for the sum of the squares of these errors becomes;

\[
UT = \sum (U^2) = (ZV + SL \cdot X_1 - Y_1)^2 + (ZV + SL \cdot X_2 - Y_2)^2 \tag{3.6}
\]

According to the theory of least squares, the "best" straight line is that which makes the sum of the squared errors a minimum. Therefore, the best value of \(ZV\) is found by differentiating equation (3.6) with respect to \(ZV\) and equating the result to zero;

\[
\frac{\partial \sum (U^2)}{\partial ZV} = 2(ZV + SL \cdot X_1 - Y_1) + 2(ZV + SL \cdot X_2 - Y_2) + \ldots = 0
\]

or

\[
\Sigma ZV + SL \Sigma X - \Sigma Y = 0 \tag{3.7}
\]

The best value of \(SL\) is found in a similar way;

\[
\frac{\partial \sum (U^2)}{\partial SL} = 2X_1(ZV + SL \cdot X_1 - Y_1) + 2X_2(ZV + SL \cdot X_2 - Y_2) + \ldots = 0
\]

or

\[
ZV \Sigma X + SL \Sigma X^2 - \Sigma XY = 0 \tag{3.8}
\]

Equations (3.7) and (3.8) are the normal equations. Simultaneous solution of these two equations yields the best values of \(ZV\) and \(SL\), which can be substituted into equation (3.4) to give the equation of the line.
Let;

\[ \Sigma ZV = N7 \cdot ZV \]

where \( N7 \) weighting factor.

Then equation (3.7) become;

\[ N7 \cdot ZV + SL \Sigma X - \Sigma Y = 0 \] (3.9)

Then from equations (3.8) and (3.9) we can get;

\[ ZV = \frac{\Sigma X^2 \Sigma Y - \Sigma X \Sigma XY}{N7 \Sigma X^2 - (\Sigma X)^2} \] (3.10)

and

\[ SL = \frac{N7 \Sigma XY - \Sigma X \Sigma Y}{N7 \Sigma X^2 - (\Sigma X)^2} \] (3.11)

The standard deviation, \( UD \), of the original data points from the fitted line is obtained by calculating, \( UT \), from equation (3.6), and using that value in the following expression;

\[ UD = \left( \frac{UT}{C0} \right)^{1/2} \] (3.12)

where \( C0 = N-2 \), \( N \) is the number of data points.

The measuring cycle program introduces a linear least-squares subroutine that calculates the least-squares slope (\( SL \)), intercept (\( ZV \)), and their uncertainties (\( UD \)) from a set of points \( X(I), Y(I) \). In this subroutine we used the following symbols;

\[ X1 = (\Sigma X)^2 \]

\[ X2 = \Sigma X^2 \]

\[ XY = \Sigma XY \]
When the subroutine is entered it initialises, a set of variables; $X_1=0, X_2=0, Y_1=0, XY=0$, and uses them in the FOR-NEXT loop to compute the various sums needed for equations (3.10)------(3.12). Once these have been calculated, $Z_V$, and $S_L$ are evaluated according to equations (3.10) and (3.11). $(UT)$ is then initialised and calculated to evaluate the $(UD)$ value by using equation (3.12). The subroutine is written so that it performs no input or output functions, but only operates on data in the specified manner. It can therefore be used easily with other programs when a linear least-squares fit is needed.

3.6.6 Interpolation of the Thermometer Calibration Data;

a. Germanium thermometer;

Leung and Kos[33] proposed an interpolation method suitable for very high-precision data, with the considerable advantage of simplicity and flexibility. In this method the calibration data are divided into $N$ segments with a two-point overlap of adjacent segments. Each segment is fitted to a polynomial of degree $M$ and should contain about $2M$ data points. In applying this method to the calibration data of germanium thermometers, the interpolation fits are carried out using the logarithmic values of the resistance $R$ and the temperature $T$. If the temperature of a data point in the $n$th segment is represented by $T_n(R)$ where $n=1,2..., N$ and $R$ is the corresponding resistance, then all the data points in the segment $n$ are fitted to the polynomial;
\[
\ln T_n(R) = \sum_{m=0}^{M} A_{nm} (\ln R)^m 
\]  
(3.13)

to determine the coefficients \(A_{nm}\). Subsequently these coefficients and equation (3.11) are used to determine the temperature \(T_n^M(R)\) corresponding to any value \(R\) within the segment \(n\).

b. Silicon-diode thermometer;

At temperatures above about about 30 K the forward voltage of the silicon-diode at constant current (10 \(\mu\)A) increases very linearly with temperature. A linear interpolation is used to calculate the temperature corresponding to measured forward voltages of the thermometer. To find the temperature value \((TE)\) from a measured diode voltage \((VT)\), located between \(V(I)\) and \(V(I-1)\) in the calibration data of the thermometer; the interpolated value is given by;

\[
TE = T(I) + \frac{T(I)-T(I-1)}{V(I)-V(I-1)} (VT-V(I)) 
\]  
(3.14)

This equation together with calibration data of the diode thermometer is used in the program to calculate the temperature from measuring the diode forward voltage.

3.6.7 Checks and Adjustments Carried Out by the Computer in Each Measurement Cycle;

The computer sets heating interval, heater current, and the thermometer resistance range, needed for the next measurement cycle. After each measurement cycle the computer checks the thermometer resistor, before the heating period
begins and restores this resistance range to the after heating period. It also checks the temperature increment and the temperature of the specimen, to set the new value of the heating period and heating current, for the next measurement cycle. In controlling the isothermal shield, the computer sends the value of the set temperature to the temperature controller of the shield prior to the next measured cycle.
Fig(3.1); Schematic diagram of the automatic specific heat measurement
Fig(3.2); USER PORT CONNECTOR
Fig(3.3): Programmable resistor circuit for the heater current source or thermometer current source

C1 Up/Down Binary counter (74193)
C2 1-of-16 decoder/demultiplexer (74154)
C3 Hex Buffer/driver (7407)
C4 Single pole reed relay
Fig(3.A): Multiplexer circuit diagram
FLOW DIAGRAM OF MAIN PROGRAM OF SPECIFIC HEAT MEASUREMENT

START

Set up various dimensional arrays

Initialise heater current, cu = 0
heater voltage, v = 0
reference resistance, R = 100 OHM

? &FE62 = &FF; i.e. Set the user port as Output port

*IEEE; i.e initialise IEEE interface

FOR I = 0 TO 61

READ V(I), T(I); i.e. read thermometer calibration data

IF I = 60?

NO

YES

A

Fig(3.5)
FOR \( I = 0 \) TO 59

READ \( A(I), B(I) \); i.e. read holder correction heat capacity

IF \( I = 59 \)

YES

INPUT YS; complete

INPUT AS; title

Initialise the number of points in after drift; \( N_2 \) and line fitted after points; \( N_9 \)

INPUT "start shield temperature"; TB

GOSUB 4355; subroutine to set starting shield temperature

A
INPUT "Sample mass (mol)"; SM
PRINT "Number of points after drift"; N2
PRINT "Number of fitted points after drift"; N9
INPUT "Do you wish to change it"; Q$
IF
Q$ = 'Y$
YES
INPUT "New number of points after drift"; N2
INPUT "New number of fitted points after drift"; N9
INPUT "test=1, measure=2, end=3"; J
NO
Q$ <> 'Y$
A
INPUT "shield temperature=10 sample temperature=11 heater current=12 test temperature drift=13 measure sample temperature several times=14"N

INPUT "RUN=4,RETURN=5";K

IF K=?

INPUT "How many shots";NP

A

IF J=?

END

B1

B2

A2

A3

A1

C
INPUT "is a short printout"; P$

VDU2; i.e. switched on the printer

PRINT "title"; AS

VDU1,11; i.e. line feed command for the printer

PRINT "sample mass"; SM

VDU1,11; i.e. line feed command for the printer

VDU3; i.e. to switch off the printer

FOR N=0 TO NP

GOSUB 1570: subroutine for measured sequence

VDU2: command to switch on the printer

PRINTN,K(N),HC(N),UD(N),KR(N)
HP(N),SJ(N),SZ(N),SH(N),D(N); i.e. print the result on screen and printer

VDU1,11; i.e. line feed command for the printer

VDU3; i.e. command to switch off the printer

Wait time for 3 sec

GOSUB 4635: subroutine to set the shield temperature

IF N=NP

GOSUB 2450: subroutine to store the data on floppy disc

NO

YES
GOSUB 1290; subroutine to measure the drift temperature

GOSUB 710; subroutine to measure the temperature several times

GOSUB 4460; subroutine to measure the shield temperature

GOSUB 5160; subroutine to measure the temperature by the Ge thermometer.

GOSUB 2715; subroutine to measure the temperature by using Silicon diode.
FLOW CHART FOR THE SUBROUTINE TO MEASURE THE SHIELD TEMPERATURE

FROM THE MAIN PROGRAM

*IEEE; i.e initialise the IEEE-Interface

PRINT$7,"LM"; i.e send manual command to the temperature controller

PRINT$7,"TS0"; i.e send the lower temperature to the temperature controller

PRINT$7,"MS"; i.e send the measured temperature command to the temperature controller

INPUT$7,R$; i.e input the measured temperature string from controller to the computer

UU$=MID(R$,4.7), UU=VAL(UU$); i.e convert the temperature string to the number value

T1=UU

PRINT$7,"TS65535"; i.e send the maximum temperature string to the temperature controller
PRINT£7,"MS"; i.e. send the measured temperature command to the temperature controller

INPUT£7,R$; i.e. input the measured temperature string from controller to the computer

UU$=MID(R$, 4, 7), UU=VAL(UU$); i.e. convert the temperature string to the number value

T2=UU

PRINT T1;"K"; T2;"K"; print the result on screen

RETURN
FLOW CHART FOR THE SUBROUTINE
TO MEASURE THE HEATER CURRENT

785 FROM THE MAIN PROGRAM

?&FE60=&31; i.e set the multiplexer on heater current

*IEEE;i.e initialise the IEEE interface

PRINT$5,"R0F3=";send the autorange and DC voltage command to the DVM

FOR J1=1 TO 5

PRINT$5,"@=";send the Trigger signal to the DVM

Wait for 10 sec

INPUT$5,ADS;input the measured voltage string from the DVM to the computer

AD=VAL(ADS),AE=AD/RE;i.e calculate the heater current

PRINT"Heater current";AE,"AMP"

IF J1=5

RETURN
FLOW CHART FOR THE SUBROUTINE TO MEASURE THE TEMPERATURE DRIFT

1290 FROM THE MAIN PROGRAM

GOSUB 5160; subroutine for autorange resistance measurement for the Ge-Thermometer.
GOSUB 2715; subroutine for measure the DC voltage for the Si-Thermometer

N1=8, T=TIME; Initialization

FOR I2=1 to N1

IF TIME<(T-(I-1)*Z)

YES

PRINE5,"@="; send the Trigger command to the DVM

Wait Time for 1 sec

INPUT5,RS; input the measured resistance of the Ge-Thermometer from the DVM to the computer.
INPUT5,VTS; input the measured voltage of the Si-Thermometer to the computer.

NO

A

B
\( R(12) = \text{VAL}(R5) \): calculate the resistance value from string for Ge-Thermometer.
\( V(12) = \text{VAL}(VT2) \): calculate the voltage value from string for Si-Thermometer.

\[
\text{FOR } I2 = 1 \text{ TO } N1
\]

\( TD(12) = 0; Ts = 0; R = R(12); VT = V(12); \)
\( \text{i.e initialization} \)

GOSUB 2715; subroutine to calculate the temperature from the measured resistance of the Ge-Thermometer.
GOSUB 2870; subroutine to calculate the temperature from the measured voltage of the Si-Thermometer.

\( TI(12) = TE \)
IF I2<2
  YES
  TD(I2)=(TI(I2)-TI(I2-1))*100/Z
  NO

IF I2<3
  YES
  PRINT"TEMPERATURE=";TE;"K"
  PRINT"TEMP. GRAD.=";TD(I2);"K/S"
  PRINT"TEMP.CURVE=";TS
  NO

IF I2=N1
  YES
  RETURN
  NO
FLOW CHART FOR THE SUBROUTINE TO MEASURE THE SAMPLE TEMPERATURE NUMBER OF TIME

FROM THE MAIN PROGRAM

INPUT "HOW MANY TEMP. MEASURE" : GZ

FOR I2 = 1 TO GZ

GOSUB 5160; subroutine to measure the resistance of the Ge-thermometer. GOSUB 2870; subroutine to measure the voltage of the Si-thermometer.

GOSUB 2715; subroutine to calculate the temperature from measured resistance for the Ge-thermometer. GOSUB 2870; subroutine to calculate the temperature from measured voltage for the Si-thermometer.

Send VDU2 to switch on the printer

PRINT12: "TEMP. = " ; TE; " K"; on screen and printer.

A

B
T1 = TIME/100

PRINT;"AT";T1

VDU1,11; line feed command for the printer

VDU3; switch off command for the printer.

Wait for 20 sec

IF 12 = GZ?

RETURN

NO

YES
FLOW CHART FOR THE SUBROUTINE OF THE SPECIFIC HEAT MEASURING SEQUENCE

1570 FROM THE MAIN PROGRAM

GOSUB5160; subroutine to measure the resistance of the Ge-thermometer.
GOSUB2715; subroutine to measure the voltage of the Si-thermometer.

D(N)=Z3; Heater interval

IF P$=Y$ YES

PRINT"Heater interval=":D(N);" sec"

N1=15; No. of points before heating
UT=0, CO=0; Initialise to calculate the standard deviation.

T=TIME

FOR I3=0 TO (N1-1)

IF TIME<(T+T*Z) NO

A

YES

B
*IEEE: initialize the IEEE interface

PRINT$5,"@="; send Trigger command to the DVM

Wait for 1.5 sec

INPUT$5.R$; input the measured resistance of the Ge-thermometer from the DVM to the computer.

INPUT$5.VTS; input the measured voltage of the Si-thermometer from the DVM to the computer

R(I3)=VAL(R$); calculate the resistance value from the string.

VT(I3)=VAL(VTS); calculate the voltage value from the string.

IF I3=N1-1

T1=TIME

?&FE60=&B9; set the multiplexer for measuring the heater voltage

A
PRINT£5,"R0F3=";send autorange and DC voltage command to the DVM

Wait for 1 sec

PRINT£5,"@=";send the Trigger command to the DVM

Wait for 20 sec

INPUT£5,VS; input the measured heater voltage from the DVM to the computer

V=VAL(VS); calculate the heater voltage value from the string

IF DS=Y$ THEN
  YES
ELSE
  NO

PRINT"V=",V; heater voltage on screen

?&FE60=&B1; set the multiplexer for measuring the heater current

Wait for 1 sec
PRINT$5,"@\:";send the Trigger command to the DVM

Wait for 20 sec

INPUT$5,CUS;input the measured heater current from the DVM to the computer

CU=VAL(CUS),CU=CU/R; calculate the heater current value

PRINT"I\:";CU,on screen

IF TIME<(T1+(D(N)*100))

?&FE60=&65;set the multiplexer for measuring the temperature

T9=TIME

GOSUB5160; subroutine to measure the resistance of the Ge-thermometer
GOSUB2715; subroutine to measure the voltage of the Si-thermometer

A
FOR I3=N1 TO (N1+N2-1)

IF TIME<(T9+Z*(I3-N1))

NO

YES

PRINT$:@=";send the Trigger signal to the DVM

Wait for 1.5 sec

INPUT$;input the measured resistance from the DVM to the computer.

INPUT$;input the measured voltage from the DVM to the computer

R(I3)=VAL(R$);calculate the resistance value from the string for Ge-thermometer.

VT(I3)=VAL(VTS);calculate the voltage value from the string for the Si-thermometer.

IF I3=N1+N2-1

NO

YES
FOR I3=0 TO (N1+N2-1)

R=R(I3) or VT=VT(I3)

GOSUB2715; subroutine to calculate the temperature from measured resistance for the Ge-thermometer.
GOSUB2870; subroutine to calculate the temperature from measured voltage for the Si-thermometer.

IF I3=N1+N2-1

NO

YES

GOSUB920; subroutine to calculate the temperature drift of the sample

FOR I3=0 TO (N1+N2-1)

YES

IF I3>N1-1

NO

X=I3*(Z/100), UV=X*S1+Z1

X=I3*(Z/100)+D(N)

UV=UV*10000; UV=INT(UV)

UV=UV/10000

A

B
U(I3) = TI(I3) \cdot UV

UT = UT + U(I3) \cdot U(I3)

C0 = C0 + 1

PRINT TI(I3), U(I3), (I3+1); on screen

IF I3 < N1 + 1

IF I3 < N5

IF I3 > 14

A

B
\[ HP(N) = V \times CU; \text{calculate the heater power} \]

IF \[ P_S = Y_S \]

YES

NO

\[ \text{PRINT } V, CU; \text{print the heater current and voltage} \]

\[ \text{PRINT } K1; \text{print the initial sample temperature on screen.} \]

\[ \text{PRINT } Y_M; \text{print the final sample temperature on screen} \]

\[ \text{PRINT } S1, S2; \text{print the slope of line before and after heating on screen} \]

\[ \text{US} = UT \div CU; UD(N) = \text{SQR}(US); \text{calculate the standard deviation} \]

IF \[ P_S = Y_S \]

YES

NO

\[ \text{PRINT } K_R(N), UD(N), K_L(N); \text{print the sample temperature rise, standard deviation and error} \]
A

IF KR(N) < 0.0001

YES

NO

HC(N) = HP(N) * D(N) / KR(N); calculate the heat capacity

HZ = HP(N) * D(N) / KT; calculate the heat capacity from average final temp.

IF P5 = YES

YES

NO

PRINT HC(N): print the sample heat capacity on screen

GOSUB 4780; subroutine to calculate the holder heat capacity

SH(N) = (HC(N) - AD) / SM; calculate the sample specific heat

SZ(N) = (HZ - AD) / SM; calculate the specific heat from average final temp.

SJ = (HP(N) * D(N) * UD(N) / (KR(N) * KR(N) * SM; calculate the error in specific heat

PRINT N, KA(N), SH(N); print N, sample temperature and the specific heat on screen

A1

A2
PRINT:"TIME":D(N):TIME:print the heater interval and the time on screen

IF
KR(N)>KA/30
   YES
   Z3=Z3
   NO

IF
KR(N)<KA(N)/100
   YES
   Z3=Z3+30
   NO

RETURN

PRINT:"TEMP.TOO SMALL";
at KA(N)
FLOW CHART FOR THE SUBROUTINE
TO MEASURE THE RESISTANCE OF
THE Ge-THERMOMETER

FROM THE MAIN PROGRAM

PRINT$5,"R7F101=":send resistance measure, 10M range, scientific, and full status commands to the DVM

RTI=7

?&FE60=(&65;set the multiplexer on the temperature measured.

PRINT$5,"@="; send the Trigger command to the DVM

Wait: for 2 sec

INPUT$5.R$; input the measured resistance from the DVM to the computer

R=VAL(R$); calculate the value of the resistance from the string

IF R>3000

YES

NO

PRINT$5,"R6"; send 1M range command to the DVM

A1

A2
RT1=6

PRINT£5, "@="; send the Trigger command to the DVM

Wait... for 2 sec

INPUT£5, RS; input the measured resistance from the DVM to the computer

R=VAL(RS); calculate the value of the resistance from the string

IF R>2000

YES

NO

PRINT£5, "R5=": send 100k range command to the DVM

RT1=5

PRINT£5, "@="; send the Trigger command to the DVM

Wait... for 2 sec
INPUT$5,R$; input the measured resistance from the DVM to the computer

R=VAL(R$); calculate the value of the resistance from the string

IF 
R>100

YES

NO

PRINT$5,“R3=“; send 1k range command to the DVM

RT1=3

PRINT$5,“@=“; send the Trigger command to the DVM

Wait := for 2 sec

INPUT$5,R$; input the measured resistance from the DVM to the computer

R=VAL(R$); calculate the value of the resistance from the string

A1

A2
IF \( R > 10.0 \)

YES

PRINT£5,"R1=":send 0.001 k range command to the DVM

RT1=1

PRINT£5,"@=":send the Trigger command to the DVM

Wait for 2 sec

INPUT£5,RS;input the measured resistance from the DVM to the computer

R=VAL(R$);calculate the value of the resistance from the string

IF \( R > 5.9 \)

YES

RETURN

NO

PRINT"TEMP.Exceeds 100K:on screen

END
FLOW CHART FOR THE SUBROUTINE X
TO STORE THE RANGE OF THE DVM FOR MEASURING THE RESISTANCE OF THE Ge-TERMOMETER

FROM THE MAIN PROGRAM

PRINT5,"F1=";Send the resistance measure command to the DVM

IF RT1=1

PRINT5,"R1=";Send 10 OHM range to the DVM

IF RT1=3

PRINT5,"R3=";Send 1 K range to the DVM

IF RT1=5

PRINT5,"R5=";Send 100 K range to the DVM

IF RT1=6

PRINT5,"R6=";Send 1 M range to the DVM

PRINT5,"R7=";Send 10 M range to the DVM

RETURN
FLOW CHART FOR THE SBROUTINE TO CALCULATE THE TEMPERATURE FROM MEASURED RESISTANCE OF THE Ge-THERMOMETER

FROM MAIN PROGRAM

IF \( R \geq 304.7 \)

YES

\( A = 8.5527; B = -0.98376; C = -0.030535; D = 0.005981 \)

NO

IF \( R \geq 517 \)

YES

\( A = 7.3075; B = 7.7136; C = 1.4359; D = 0.082192 \)

NO

IF \( R \geq 287.89 \)

YES

\( A = -10.754; B = 7.7136; C = 1.4359; D = 0.082192 \)

NO

IF \( R \geq 129.78 \)

YES

\( A = 9.8885; B = -3.2578; C = 0.5075; D = -0.032336 \)

NO

IF \( R \geq 64.456 \)

YES

\( A = 10.008; B = -3.2565; C = 0.49182; D = -0.030409 \)

NO

IF \( R \geq 35.9684 \)

YES

\( A = 2.0011; B = 2.3647; C = -0.82103; D = 0.071593 \)

NO

IF \( R \geq 18.7735 \)

YES

\( A = 7.1776; B = -2.1754; C = 0.5036; D = -0.056985 \)

NO

A1

A2
A1

IF \( R \geq 8.6822 \)

YES

A1

NO

A2

A=7.6124; B=-2.6751; B=0.6917; D=-0.080277

A=10.797; B=-7.0411; B=2.6899; D=-0.38336

GT=A+B*LN(R)+C*LN(R)+D*LN(R)^3

TE=EXP(GT)

RETURN
FLOW CHART OF THE SUBROUTINE TO CALCULATE THE TEMPERATURE DRIFT OF THE SAMPLE

FROM THE MAIN PROGRAM

N5=0,N6=N1; initialise the number of temperature points before heating the sample.

GOSUB 3410: subroutine of the least square line fitting in the for drift period

S1=SL; The slope of the line fitted to the number of temperature points in the fore drift period

ZI=ZV; The intercept of fitting line of the fore drift points.

N5=N1+N9; N6=N1+N2; initialise the after drift condition.

GOSUB 3410; subroutine of the least square fitting in the after drift

S2=SL; The slope of the line fitted to the number of temperature points in the after drift period

ZF=ZV; The intercept of fitting line of the after drift points.

XB=X1/X7; calculate the average time value
CB = Y1/N7; calculate the average temperature value.

XM = N1*Z/100 + D(N)/2; calculate the time from the fore drift to the middle of the heating period.

YM = (YB - S1*(XB - XM)); calculate the average final temperature at the middle of the heating period.

K1 = Z1 + S1*XM; calculate the initial sample temperature.

K2 = ZF + S2*XM; calculate the final sample temperature.

KR(N) = K2 - K1; calculate the temperature rise.

ZF = Z1 + KR(N); calculate the final intercept.

KT = YM - K1; calculate the temperature rise from the average final temperature and initial temperature.

KL = ABS(KT - KR(N)); calculate the absolute difference between both temperature rise.

KA(N) = 0.5*(K1 + k2); calculate the temperature of the sample.

RETURN.
FLOW CHART FOR THE SUBROUTINE TO CALCULATE THE TEMPERATURE FROM THE MEASURED VOLTAGE OF THE Si-TERMOMETER

2870 FROM THE MAIN PROGRAM

FOR I=0 TO 61

IF VT>V(I)

NO

YES

VV=VT-V(I)

V7=T(I)-T(I-1)

V8=V(I)-V(I-1)

V9=V7/V8

TE=(T(I)+VV*V9)*10000

TE=TE/10000

RETURN
FLOW CHART FOR THE SUBROUTINE
TO MEASURE THE VOLTAGE OF THE
Si-THERMOMETER

2715 FROM THE MAIN PROGRAM

?&FE60=65;Set the multiplexer on the
thermometer voltage measured

PRINT$;"ROF3=";Send the autorange and
DV voltage command to the DVM

PRINT$;"@=";Send the Trigger
command to the DVM

Wait for 2 sec

INPUT$;VTS;input the measured voltage
from the DVM to the computer

VT=VAL(VTS);calculate the voltage value
from string

IF VT>0.3279

NO

PRINT"TEMP.EXCEEDS 300K";
on screen

YES

RETURN

END

A9
FLOW CHART OF THE SUBROUTINE OF THE LEAST-SQUARE FITTING

3410 FROM THE MAIN PROGRAM

X1=0,X2=0,X3=0,Y1=0,XY=0; initialises a set of variables

FOR J=N5 TO (N6-1)

Y1=Y1+T(I(J))

X8=0

IF N5=0

X8=Z3

X9=J*(Z/100)+X8

X1=X1+(X9*X9)

XY=XY+X9*T(I(J))

IF N5=N1-1

DE=N7*X2-X1*X1

SL=(N7*XY-X1*Y1)/DE

ZV=(Y1*X2-X1XY)/DE

RETURN
FLOW CHART OF THE SUBROUTINE TO STORE DATA ON FLOPPY DISC

FROM THE MAIN PROGRAM

*DISC: initialise the disc drive

 ncols%=10; nrows%=11; i.e number of columns and rows

 file%=OPENOUT("d.EXAMPLE"); open the file

 PRINTEfile%,"DATA"; verification string

 PRINTEfile%.ncols%; output number of columns

 PRINTEfile%.nrows%; output number of rows

 PRINTEfile%."AS"; output data title

 PRINTEfile%,"ca", "ka", "hc", "ud", "kr", "hp", "sj", "sz", "sh", "z3"; i.e. output columns titles

 FOR I=0 TO nrows%

 PRINTEfile%., N, KA(N), HC(N), UD(N), KR(N), HP(N), SJ(N), SH(N), D(N); output each row in turn

 A

 B

 A11
IF N=nrows%  

NO

YES

CLOSEfile%; close the file

RETURN
Logic "0" Associated (PB) line is an input
Logic "1" Associated (PB) line is an output
Fig (3.6) : Data Direction Register and Output Input Register.
Fig (3.7); Schematic diagram of a measuring cycle: T1 to TN2; measured sample temperature; K1, K2; initial and final temperature of heating step; Z3; heating time; tN9; thermal equilibrium time; Z5; time interval between sample temperature measurement.
N1; the number of the temperature points in the drift period; N9; number of points of thermal equilibrium time.
CHAPTER 4

LOW TEMPERATURE MAGNETIC SUSCEPTIBILITY MEASUREMENTS

4.1 Introduction;

The great majority of magnetic susceptibility measurements of paramagnetic and antiferromagnetic solids have been made using the force method. In this method a specimen is placed in a non-uniform magnetic field where the force acting on it is given by [34];

$$F = \frac{1}{2} \chi_v \nabla H^2 dV$$  \hspace{1cm} (4.1)

Where $\chi_v$ is the volume susceptibility of the specimen, $\nabla H$ is the gradient of the magnetic field, and the integral is taken over the volume of the specimen.

If it is assumed that $\chi_v$ is constant over the specimen, then;

$$F = \frac{1}{2} \chi_v \int \nabla H^2 dV$$  \hspace{1cm} (4.2)

For small specimen whose $V$, $H$ and $\nabla H$ are constant, then:

$$F = \frac{1}{2} \chi_v V \nabla H^2$$  \hspace{1cm} (4.3)

If the specimen is displaced by the force in one direction only, and the field and field gradient in that direction are $H$ and $\partial H/\partial X$ respectively, then:
Now, if we consider the mass susceptibility $\chi$ instead of $\chi_v$, then $\chi = \chi_v / \rho$, where $\rho$ is the density of the specimen. Then equation (4.4) become:

$$F = \chi_v V H \frac{\partial H}{\partial X}$$  \hspace{1cm} (4.4)

where $m$ is the mass of specimen. This form of the force relation is more commonly used than equation (4.4), because the measurement of mass is much more straightforward than measurement of volume. The measurement of magnetic susceptibility by using equation (4.5), is called the Faraday method. The Faraday method was used in the present work. Because of the difficulty of measuring $\partial H/\partial X$ accurately the absolute value of the susceptibility was measured by comparison of the force acting on a standard specimen of known susceptibility and of similar dimensions to that of the specimen to be investigated, in a magnetic fields corresponding to currents of 4, 6, 8, and 10 A at room temperature. A cylinder 4x30 mm of spectrographically pure palladium having a susceptibility of $5.4 \times 10^{-6}$ e.m.u/g, as taken as the standard sample.

From equation (4.5), the force acting on the palladium sample is given by:

$$F_{pd} = \chi_{pd} m_{pd} H \frac{\partial H}{\partial X}$$  \hspace{1cm} (4.6)

and the force acting on specimen under investigation is given by:

$$F = \chi m H \frac{\partial H}{\partial X}$$  \hspace{1cm} (4.7)

By dividing equation (4.6) by equation (4.7), we get:
this equation is used in the present work to calculate the specimen susceptibility. Since an electrobalance was used to measure the force a null displacement technique was employed. In this technique the restoring force of the balance exactly compensates the force exerted by the field on the specimen. Consequently the specimen never moves out of its zero position and therefore remains always in the same field configuration.

4.2 Measurement of the Force;

The mass change of the specimen is measured by using a MARK3 MICRO-FORCE BALANCE MODEL 3A40. The head unit of the microbalance, made with precision galvanometers, electromagnetically balances the torque produced by the weight of the specimen. A current flows through it in exact proportion to the applied weight and this current operates a meter for visual reference and also provides a voltage output. In addition to generating a current proportional to the weight, this servo-action ensures a rapid response and makes the balance insensitive to external vibration [35]. The voltage from the Micro-force balance is measured by a digital voltmeter for different applied magnetic fields as indicated by the current flowing in the electromagnet. This voltage is equal to the mass change in the specimen, and the mass change is equivalent to the force exerted on the specimen through;

\[ E = F = mg \] (4.9)

The voltage equivalent to the force \( F_{pd} \) acting on the Pd specimen was measured for different magnetic field currents. The magnetic susceptibility of the specimen was calculated for different magnetic field currents by using equation (4.8) and a \( F_{pd} \) lookup table in the computer program. The magnetic susceptibility of a pure paramagnet is independent of the field and thus the average value of the specimen
magnetic susceptibility was determined by using the following equation;

\[ \chi_{av} = \frac{\chi(10) + \chi(8) + \chi(6) + \chi(4)}{4} \]  \hspace{1cm} (4.10)

When a small fraction \( x \) of a ferromagnetic impurity is present, the magnetisation of which is \( \sigma \) per unit mass, the apparent susceptibility of the whole specimen is given by [37];

\[ \chi_{mp} = (1-x) \chi + \frac{x \sigma}{H} \] \hspace{1cm} (4.11)

where \( \chi \) is the true susceptibility of paramagnetic component.

The susceptibility \( \chi \) can be determined by plotting the \( \chi_{mp} \) as a function of \( H^{-1} \) which gives a straight line which intercepts the susceptibility axis at the true susceptibility point \( \chi(H=0) \).

### 4.3 Magnet Power Supply;

The magnet used was a Newport Instruments Type A electromagnet which, when water-cooled can take a current of 20 Amps through its coils. It had 10 cm diameter plane pole tips separated by a 3.5 cm gap. The power supply for the electromagnet was a 240 V DC (ST-240) supply, which was capable of providing upto 20 Amps[38]. This supply was operated in constant current mode. The magnetic field current was controlled manually by a multi turn potentiometer. In order to measure accurately the current to the magnet a 0.1 \( \Omega \) absolute resistance was connected in series with the magnet power supply and the voltage drop across it was measured by using a DVM. Magnetic fields at the specimen position were measured for a number of field currents using a fluxmeter and a search coil. The magnet calibration curve is shown in fig(4.1).
4.4 Cryostat;

The CF1200 is a continuous flow cryostat designed by Oxford Instruments for use between the pole pieces of an electromagnet [36]. Liquid Nitrogen or Helium is delivered to the cryostat by a vacuum insulated transfer tube inserted into a syphon entry arm. The 3120-Temperature Controller also manufactured by Oxford Instruments is used to measure the specimen temperature and to maintain temperature stability over the necessary period. Temperature stability of better than ±0.1 K was obtained. A AuFe-Chromal thermocouple is normally used with temperature controller, for temperature sensing because of its weak magnetic effects. A base temperatures of 3.6 K could be obtained with temperatures continuously variable up to 500 K. The vacuum jacket of the cryostat was maintained at least 10⁻⁵ mbar. The vacuum equipment consisted of an oil diffusion pump (150 l/sec) and a rotary pump (100 l/min). The rotary pump is used to evacuate the cryostat to a pressure of less than 10⁻¹ mbar, and the diffusion pump is used to achieved vacuums of less than 10⁻⁵ mbar. The specimen is top loaded into a 20 mm diameter cylindrical space were it can either be in vacuum or in an exchange gas. In the vacuum space, the specimen tube is surrounded by a radiation shield to reduce heat exchange between the internal and external walls of the cryostat. The temperature controlled region extends over the bottom 100 mm of the specimen space. A copper specimen holder was suspended from the Micro-balance by a light weight rod of material with high resistance, e.g thin-walled stainless tube of length 52 cm and 4 mm diameter. The Micro-balance assembly was placed at the top of an aluminium supporting plate and this plate was fixed onto a wall. The cryostat was sealed to the bottom of this plate by a plug using an 'O' ring. The Micro-balance assembly was enclosed in an airtight glass Bell jar, as shown in fig(4.2).
4.5 Automation of Magnetic Susceptibility Measurements;

The experiment involves the measurement of the magnetic susceptibility of the specimen as a function of both field and temperature. If carried out manually the measurement are time consuming because one run takes at least one day. For this reason, and the fact that the measurements are repetitive, a computer control measurement was designed. Computer controlled magnetic susceptibility measurements have been described in the literature\[39, 40, 41\]. A schematic diagram of the computer control of the magnetic susceptibility is shown in fig(4.3). Fortunately the magnetic susceptibility experiment is intrinsically slow and we have found that BBC computer with IEEE data bus is adequate for our purposes. The control system is similar to that used in specific heat measurement, but with the following differences.

4.5.1 The Multiplexer Unit;

Fig(4.4) shows the circuit diagram of the multiplexer unit. The multiplexer switching is a two pole three position relay controlled by one line from the computer user port. A 12 volt DC supply from the stepper motor driver board was used to drive the multiplexer relay. As shown in fig(4.4), each user port was buffered by a transistor. In magnetic susceptibility experiments there are two measurements which are required to be made by the DVM. These are;

a. The current in the electromagnet; the DVM will measure a voltage drop across a 0.1 $\Omega$ resistor in series with the coil of the electromagnet whilst the current from a power supply is flowing through the electromagnet. The computer will then divide the measured voltage by the value of resistor 0.1 $\Omega$ to determine the exact value of current going to the electromagnet.

b. Force acting on the specimen; the DVM is required to measure the voltage from the Micro-balance which represent the force acting on the specimen.
4.5.2 Magnet Power Supply Control Circuit;

An IEEE-488 compatible power supply to provide the current for the electromagnet was not available. Therefore a control circuit was designed to achieve computer control of the magnet power supply. Fig(4.5) shows the schematic diagram of the control circuit of the magnet power supply. The magnet current is controlled by an external multiturn potentiometer which rotates and can be set by using a stepper motor. A 4-phase unipolar stepper motor driver board RS332-098 was used to drive a stepper motor. A 20 volt DC power supply for the stepper motor driver board was designed, as shown in fig(4.6). The direction and the angle of rotation of the stepper motor can be set by using two lines from the computer user port. In order to have manual control of the magnet current a three pole two position switch was connected between the internal and the external multiturn potentiometer. We have used this method to control the magnet current, firstly, because the specimen takes some time to reach the set temperature and, secondly to prevent possible overshoot of the magnet current. An additional reason for this choice was the limited number of user port lines.

4.6 Computer Program Description;

4.6.1 Initialisation Phase;

The program was written which complemented the hardware safety features permitted flexibility of operation, whilst keeping interaction between the user and peripheral equipment to a minimum. The user selects the experiment required (e.g. test of field current, force, or susceptibility measurement) and specifies the maximum field, data point density and sample mass etc. The flow diagram of the computer program is shown in fig(4.7). The program consists of one main loop to the magnetic susceptibility measurement, and three subroutines for testing the specimen temperature, magnetic field current, and the force acting on the specimen. The program starts with the initialisation followed by requesting the specimen title (A$), specimen mass (P), standard specimen mass (Q), standard
specimen susceptibility (Z), and the flag variables (I) and (O). After these quantities have been entered, the flag variables are tested to determine which subroutine is to be performed. If the flag variable (J) is found to be 1, then an additional IF statement checks the test variable (O). Similarly, if J was 2, then the program switches to the measurement subroutine, and if J was 3, it goes to the end of the program. The program contains three subroutines for testing the specimen temperature, magnetic field current, and the specimen force, before starting the measuring cycle. Another subroutine is called to store the results.

4.6.2 Measuring Cycle;

The measurement subroutine sets the specimen temperature and magnetic field current and then the DVM records the voltage from the Micro-balance. The computer then calculates the magnetic susceptibility value for different values of field currents by using the equation (4.9). It calculates the average magnetic susceptibility by using equation (4.10) and the standard deviation. Finally, the temperature, magnetic susceptibility, inverse magnetic susceptibility and standard deviation is printed out, and the measuring cycle is repeated until a final specimen temperature is reached.
The magnet calibration curve

Fig (4.1)
1. Safety cover, 2. glass bell jar, 3. Microbalance
4. sample rod, 5. high adjustment, 6. evacuation port
7. Syphon enter arm, 8. vacuum jacket, 9. sample space,
10. sample holder, 11. electroamagnet, 12. heater,
13. electrical vacuum lead through.

Fig(4.2); Low Temperature Magnetic Susceptibility System.
Fig 4.3: Schematic diagram of the automatic magnetic susceptibility measurement.
Fig( 4.4 ) : Circuit diagram of the automatic magnetic susceptibility measurement
DC power supply

4-phase unipolar stepper motor driver board
RS 332-098

Stepper Motor

Manual multturn potentiometer

Manual/automatic SWITCH

Fig(4.5); Schematic diagram of the control circuit of the current of electromagnet
Fig. 4.6: Circuit diagram of 2D yehl. DC supply
FOLW DIAGRAM OF MAIN PROGRAM OF MAGNETIC SUSCEPTIBILITY MEASUREMENT

START

Set up various dimensional arrays

*IEEE; i.e initialize IEEE interface

PRINTES, "R0F3="; i.e Set the DVM as autorange and DC voltage

?&FE62=&FF; i.e
Set the user port as output port:

FOR Y = 0 TO 3

READ I(Y), B(Y), R(Y); i.e
Read, current, empty sample and standard sample force

IF Y = 3?

YES

NO

INPUT "TITLE"; A$

INPUT " specimen mass (gm)" ; p

INPUT " standard sample mass (gm)" ; Q

INPUT " standard sample susceptibility" ; Z

Fig(4.7)
INPUT "1 = Test, 2 = Measure, 3 = End": J

IF J = 2 THEN
  INPUT "4 = Temperature, 5 = Field, 6 = Force": O
  
  IF O = 2 THEN
    Set the multiplexing relay to measure the field voltage by the DVM:
  END IF

  FOR J4 = 1 TO 5
    PRINT $5, "@ = ";
    i.e. send the trigger signal to DVM
  NEXT

  INPUT $5, VS; i.e. input the measured voltage from DVM to the computer

  V = VAL(VS) I = V/R; i.e. calculate the field current from string value

  PRINT "Field current about"; V "Amp" on screen

END IF

GOSUB 1205; i.e subroutine to measure the force on sample

A
PRINT£7,"LR"; i.e
Send Remote control to the temperature controller

PRINT£7,"MS"; i.e send measured temperature to the temperature controller

INPUT£7,RS; i.e input the measured temperature

VS=MID(RS,4,7).V=VAL(VS); i.e Calculate the temperature value from input string

PRINT V; i.e Print the temperature value on screen

INPUT "Temperature increase";N

INPUT "Start Temperature";T3

INPUT "Final Temperature";T4

INPUT "No of Temp. shot"; NS

INPUT "Field increase"; M

INPUT "Final Field current"; IR

INPUT "Start field current"; I5

VDU2: command to switch on the printer

A1
PRINT "TITLE"; AS on screen and printer

Send VDU1, 11 command to printer; i.e Line Feed command

PRINT "Spec. MASS (gm)="; P

Send VDU1, 11 command to printer; i.e Line feed command

PRINT "Standard Spec. MASS (gm)="; Q

VDU1, 11 i.e line feed command to the printer

VDU3; switch off command for the printer

FOR I = 0 TO NS

T(I) = T3 + (I * N)

i.e increase the Temp. one step

IF T(I) > T4

YES GOSUB 1860: Subroutine to store the results

NO

GOSUB 1330: subroutine to set the Temp.

GOSUB 1205: subroutine to measure the force voltage at zero field current

GOSUB 1435: subroutine to set the field current and measure the force voltage
Calculate the average susceptibility

\[ X(I) = \frac{W}{(IR - IS)/N + 1} \]

\[ X(I) = 0 \]

FOR \( Y = 0 \) TO 3

\[ X(I) = X(I) + (A(Y) - X(I))^2 \]

IF \( Y = 3 \)

\[ SS(I) = \text{SQR}(X(I)/3) \]

i.e. to calculate the standard deviation

VDU2; send the switch on command to the printer

PRINT, I(I), X(I), 1/X(I), SS(I); i.e. print the result data on screen and printer

Send VDU1, 1I command to printer; i.e. line feed command

Send VDU3 command to switch on the printer

GOSUB 1700: subroutine to reset the field current to zero

IF \( I = NS \)

NO

YES

GOSUB 1860: subroutine to store the results
FLOW CHART FOR THE SUBROUTINE TO SET THE FIELD CURRENT AND MEASURE THE FORCE VOLTAGE

1. FROM THE MAIN PROGRAM

   FOR Y=0 TO (IR-IS)/M

   FOR X=0 TO 60

       ?&FE60=&BF; i.e send the direction and zero signal to the stepper motor

       Wait for 0.2 sec

       ?&FE60=&3F; i.e send the positive signal to the stepper motor

       IF XL=60

           NO

           YES

           FOR L=0 TO 100

               ?&FE60=&BF; i.e send the direction and zero signal to the stepper motor and set the multiplexer to read the field

               PRINT$."@="; i.e

               Send the Trigger signal to DVM

       G

       A

       L
INPUT5, US; i.e.
input the measured voltage from DVM to the computer

U = VAL(US), II = U/R; i.e.
Calculate the field current from field voltage

IF II = IS + (Y*M) NO
IF II > IR NO

?&FE60=&DF; i.e.
Set the multiplexer to measure the sample force voltage by DVM

Wait Time 3 sec

PRINT5, "@="; i.e.
Send the Trigger signal to DVM

INPUT5, F$; i.e. input the force voltage from DVM to computer

FR = VAL(F$); i.e.
calculate the force voltage from string

F(Y) = FR - FZ; i.e.
calculate the real sample force from measured force and empty sample force
RR = F(Y) - R(Y), TL = B(Y) - R(Y),
QQ = Q'Z*RR; calculate the
susceptibility at one value of field
current

NO

IF

Y = (IR - IS)/M

YES

RETURN
FLOW CHART FOR THE SUBROUTINE TO SET THE TEMPERATURE

1330 FROM THE MAIN PROGRAM

V(I)=65536*(T(I)-3)/497.8; i.e. convert the temperature to number

PRINT$7,'LA'; i.e send automatic command to the temperature controller

TS="TS"+STR$(V(I)); i.e. Convert the number to the string value

PRINT$7,TS; i.e. send the set temperature to the temperature controller

RETURN
FLOW CHART OF SUBROUTINE TO
RESET THE FIELD CURRENT TO ZERO

1700 FROM THE MAIN PROGRAM

FOR X=1 TO 360

??FE60=7F; i.e send the direction and zero signal to the stepper motor

Wait 0.2sec

??FE60=FF; i.e send the positive signal to the stepper motor

IF X=360

YES

FOR TT=0 TO 1000

??FE60=7F; i.e send the zero to the stepper motor

PRINT "$", i.e Send the Trigger signal to DVM to read the field current

B

A
FOR I=0 TO nrows%

PRINT file%, T(I), X(I), 1/X(I), SS(I)
  i.e output the data

IF I=nrows%
  No
  YES

CLOSE file%

RETURN
FLOW CHART OF SUBROUTINE TO STORE
THE DATA IN FLOPPY DISC

FROM THE MAIN PROGRAM

*DISC; i.e initialise the disc drive

ncols%=4; nrows%=NS; i.e input number of columns and rows

file%=OPENOUT("susce1"); i.e open the file

PRINT$FILE%,"DATA" i.e verification string

PRINT$FILE%,ncols%; i.e output number of columns

PRINT$FILE%,nrows%; i.e output number of rows

PRINT$FILE%,"AS"; output data title

PRINT$FILE,"T(K)","X(emu/g)"
"1/X(g/emu)","ST"; i.e output column title

A
INPUT $V_S$, i.e. input the field voltage from DVM to the computer.

$V_V = \text{VAL}(V_S)$, i.e. convert the string value to number.

IF $V_V < 0.002$

RETURN
CHAPTER 5

THEORETICAL REVIEW

5.1 Thermodynamics;

From the first and second laws of thermodynamics, we can get [42, 43];

\[ dQ = T \, dS = dU + dW \] (5.1)

where \( dQ \) is the amount of heat absorbed by the system.
\( dU \) is the increase in energy of the system.
\( dW \) is the amount of work done by the system.
and \( dS \) is the change in entropy.
The heat capacity of the solid is measured at constant pressure, but theoretically it is calculated at constant volume, and it is represented respectively by the following equations;

\[ C_p = \left( \frac{dQ}{dT} \right)_p \] (5.2)

\[ C_v = \left( \frac{dQ}{dT} \right)_v \] (5.3)

Substituting equation (5.1) in to equation (5.2), we obtain;

\[ C_p = T \left( \frac{dS}{dT} \right)_p \] (5.4)

\[ C_v = T \left( \frac{dS}{dT} \right)_v \] (5.5)

From Maxwell’s relations, we may write;
\[ dS = \left( \frac{\partial S}{\partial T} \right)_v \, dT + \left( \frac{\partial S}{\partial V} \right)_T \, dV \]  

and

\[ \frac{\partial S}{\partial T}_p = \left( \frac{\partial S}{\partial T} \right)_v + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \]  

Then we may write the difference between \( C_p \) and \( C_v \) as follows:

\[ C_p - C_v = T \left( \frac{\partial S}{\partial T} \right)_p - T \left( \frac{\partial S}{\partial T} \right)_v \]  

Substituting equation (5.7) into equation (5.8), we get;

\[ C_p - C_v = T \left( \frac{\partial S}{\partial T} \right)_T + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p - T \left( \frac{\partial S}{\partial T} \right)_v \]

But

\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_T \]

then;

\[ C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p \]  

Because

\[ \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial V}{\partial P} \right)_T = 1 \]

Then

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Substituting equation (5.10) in to equation (5.9), we obtain;

\[ (\frac{\partial P}{\partial T})_v = -\frac{\frac{\partial V}{\partial V}}{\left(\frac{\partial V}{\partial P}\right)_T} \]  

(5.10)

The difference between \( C_p \) and \( C_v \) for most solids decreases rapidly as the temperature decreases, but it is always greater or equal to zero at room temperature. Thus if \( C_p \) is known for all temperatures then \( C_v \) may be calculated provided the temperature dependence of the molar volume \( V \), the isothermal compressibility \( K_T \) and the volume expansion \( \beta \) are known. The best approximate solution to equation (5.12) is due to Nernst and Lindemann[44], in which equation (5.12)
becomes;

\[ C_p - C_v = A C_p^2 T \]  (5.13)

Where the parameter A is nearly temperature independent. A good approximation to the value of A is given by [45];

\[ A = \frac{0.0051}{T_s} \]  (5.14)

where \( T_s \) is the melting point in K.

5.2 Elementary Statistical Mechanics;

Let us consider a system which has a fixed number \( N \) of particles. Then the partition function \( Z \) is defined by [46];

\[ Z = \sum_n e^{\frac{E_n}{kT}} \]  (5.15)

where \( E_n \) is the energy levels of system and \( k \) is Boltzman's constant. The Helmholtz free energy \( F \) is related to the partition function by;

\[ F = -kTN \ln Z \]  (5.16)

and

\[ F = U - TS \]  (5.17)

All of the thermodynamic equilibrium properties of the system can be derived from equations (5.16) and (5.17). The following quantities are determined;
\[ S = -(\frac{\partial F}{\partial T})_v \] (5.18)

\[ C_v = (\frac{\partial U}{\partial T})_v \] (5.19)

\[ \mu = -(\frac{\partial F}{\partial H_z})_v \] (5.20)

where \( S \) is the entropy, \( C_v \) the specific heat at constant volume, and \( \mu \) is the average component of magnetic moment along the applied field \( H_z \).

5.3 Theories of the Lattice Specific Heat;

5.3.1 Classical Theory;

Consider a system containing a linear chain of \( N \) atoms, then the vibrational energy of these atoms can be expressed as the energy of \( N \) harmonic oscillators. The energy of a simple harmonic oscillator of mass \( m \) and frequency \( \nu \) is given by [47];

\[ \varepsilon = \frac{p^2}{2m} + 2\pi^2 m \nu^2 q^2 \] (5.21)

where \( p^2/2m \) is the kinetic energy and \( 2\pi^2 m \nu^2 q^2 \) is the potential energy. Thus the average energy of a harmonic oscillator according to classical statistical
mechanics is given by;

$$\langle \epsilon \rangle = \frac{\int_{0}^{\alpha} \frac{\epsilon d\epsilon}{e^{\frac{\epsilon}{kT}}}}{\int_{0}^{\alpha} \frac{d\epsilon}{e^{\frac{\epsilon}{kT}}}} = kT \quad (5.22)$$

For a simple harmonic oscillator in one dimension. Then the vibrational energy of N harmonic oscillators in three dimensional is given by;

$$E = 3NkT \quad (5.23)$$

Thus the specific heat per mole is;

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3Nk = 3R = 25.08 \quad (5.24)$$

where R is the gas constant, and k is the Boltzmann constant. This value which is known as the Dulong and Petit value, is in quite good agreement with the observed total heat capacity of many solids, including metals, at somewhat elevated temperatures, and often down to room temperature, but the agreement fails at low temperatures.

5.3.2 Einstein's Theory;

Einstein assumed the atoms of a solid vibrate independently of each other, but with the same frequency. The possible energy levels of an oscillator are given by [47,48];
\[ \varepsilon_n = (n + \frac{1}{2}) \hbar \nu, \quad n = 0, 1, \ldots \]  \hspace{1cm} (5.25)

where \( \hbar \) is Planck's constant, and \( \nu \) is the frequency of the mode.

From Boltzmann's law,

\[
P_l(\varepsilon_n) = \frac{\frac{\varepsilon_n}{kT}}{Z} = \frac{e^{\frac{\varepsilon_n}{kT}}}{\sum_{n=0}^{\infty} e^{\frac{\varepsilon_n}{kT}}} = \frac{e^{\frac{\hbar \nu}{kT}}}{\sum_{n=0}^{\infty} e^{\frac{\hbar \nu}{kT}}} \hspace{1cm} (5.26)
\]

The average energy per atom is given by;

\[
\langle \varepsilon \rangle = \sum_{n=0}^{a} n \hbar \nu P_l(\varepsilon_n) = \frac{\sum_{n=0}^{\infty} n \hbar \nu e^{\frac{\hbar \nu}{kT}}}{\sum_{n=0}^{\infty} e^{\frac{\hbar \nu}{kT}}} \hspace{1cm} (5.27)
\]

consider the following;

\[
Z = \sum_{n=0}^{\infty} e^{\frac{n \hbar \nu}{kT}} = \frac{1}{\hbar \nu} \left( \frac{kT}{1 - e^{\frac{\hbar \nu}{kT}}} \right) \hspace{1cm} (5.28)
\]

Differentiating this equation with respect to \( 1/kT \), we get;

\[
\frac{\partial Z}{\partial (\frac{1}{kT})} = - \sum_{n=0}^{\infty} n \hbar \nu e^{\frac{n \hbar \nu}{kT}} \frac{\hbar \nu e^{\frac{\hbar \nu}{kT}}}{\left( 1 - e^{\frac{\hbar \nu}{kT}} \right)^2} \hspace{1cm} (5.29)
\]
Substituting equation (5.28) and (5.29) into equation (5.27) we get:

\[ \langle \varepsilon \rangle = \frac{\hbar \nu}{kT} \frac{e^{\frac{\hbar \nu}{kT}} - 1}{e^{\frac{\hbar \nu}{kT}} + 1} \]  

(5.30)

Then the vibrational energy of a system containing \( N \) atoms is:

\[ E = 3N \langle \varepsilon \rangle = \frac{3N\hbar \nu}{kT} \frac{e^{\frac{\hbar \nu}{kT}} - 1}{e^{\frac{\hbar \nu}{kT}} + 1} \]  

(5.31)

The specific heat per mole:

\[ C_v = \frac{\partial E}{\partial T} = 3R \left( \frac{\hbar \nu}{kT} \right)^2 \frac{e^{\frac{\hbar \nu}{kT}}}{e^{\frac{\hbar \nu}{kT}} - 1} \]  

(5.32)

The Einstein temperature is defined by:

\[ T_E = \frac{\hbar \nu}{k} \]

Then equation (5.32) becomes:

\[ C_v = 3R \left( \frac{T_E}{T} \right)^2 \frac{\frac{T_E}{T}}{\frac{T_E}{T} - 1} \]  

(5.33)

At high temperature \( T >> T_E \), this equation reduces to equation (5.24). At low temperature \( T << T_E \), the equation (5.33) reduces to the following expression:
Thus, the calculated specific heat in this model is not in good agreement with the observed specific heat at low temperatures, because it is found experimentally that for most solids, the lattice specific heat is proportional to $T^3$ and its not to $(e^{TE/T})$ as shown by the Einstein model.

5.3.3 Debye Theory;

The essential difference between the Debye model and the Einstein model is that Debye considers the vibrational modes of a system as a whole, whereas Einstein's starting point was to consider the vibration of a single atom assuming the atomic vibrations to be independent of each other. Then, the number of possible modes of vibration $g(u)\, du$ of a continuous medium, in the frequency interval between $u$ and $u+du$ is given by [48, 49];

$$g(u)\, du = \nu_D^3 \, du$$

(5.35)

where $\nu_D$ is Debye frequency and is equal to;

$$\frac{9N}{4\pi V} \left( \frac{2}{C_t} + \frac{1}{C_l} \right)^{-1}$$

where $V$ is the volume, $C_t$ and $C_l$ are the transverse and longitudinal wave velocity.

Thus the vibrational energy of the system can be found by using equations (5.30) and (5.35);
\[ E = \int_{0}^{\nu_{D}} g(\nu) \frac{h\nu}{\hbar v^2} \, d\nu \]

\[ = 9N \left( \frac{kT}{h\nu_{D}} \right)^3 kT \int_{\frac{x_{m}}{x}}^{\frac{3}{x-1}} dx \]

\[ \text{(5.36)} \]

where \( x = \frac{h\nu}{kT} \), \( x_{m} = \frac{h\nu_{D}}{k} = \frac{\theta_{D}}{T} \), and \( \theta_{D} \) is the Debye temperature. Then the specific heat per mole is;

\[ C_{v} = \frac{\theta_{D}}{T} \int_{0}^{\theta_{D}/T} \frac{x^4 e^x}{(e^x-1)^2} \, dx \]

\[ \text{(5.37)} \]

At high temperatures \( T >> \theta_{D} \), \( e^x = x \), and the specific heat equation becomes;

\[ C_{v} = 3Nk \]

\[ \text{(5.38)} \]

a result identical with the classical theory. At very low temperature, such that \( T << \theta_{D} \), the upper limit of integration equation(5.37) may be replaced by;

\[ \int_{0}^{\theta_{D}/T} \frac{x^3}{e^x-1} \, dx = 6 \sum_{n=0}^{6} \frac{1}{n} = \frac{\pi^4}{15} \]

so that
and the specific heat is given by;

\[ E = \frac{3}{5} \pi^4 N k T \left( \frac{T}{\theta_D} \right)^3 \]

and the specific heat is given by;

\[ C_v = \frac{\partial E}{\partial T} = \frac{12}{5} \pi^4 N k \left( \frac{T}{\theta_D} \right)^3 \] (5.39)

Yielding the Debye $T^3$ approximation. It is customary to test the applicability of the Debye approximation by calculating $\theta_D$ as a function of temperature by fitting a Debye curve to the experimental heat capacity curve at various temperatures. If the Debye approximation was strictly valid, then $\theta_D$ determined in this way would be independent of temperature. However, as $C_v$ measurements became more accurate, it was found that $\theta_D$ is not really a constant but varies with temperature. The Debye theory does not provide exact agreement with the measured heat capacities of solids in the temperature region between $T > \theta_D/50$ and the high temperature limit. The variation of $\theta_D$ is however usually less than $\pm 20\%$ of the value at absolute zero so a typical value provides reasonable agreement with experiment.

5.4 The Theory of the Electronic-Specific Heat;

5.4.1 Classical Electron Theory;

According to classical electron theory, the electronic specific heat per mole is given by [47];

\[ C_v = \frac{3}{2} N k \] (5.40)

where $N$ is the number of conduction electrons per mole.

Using this model the calculated specific heat of metals is higher than for insulators at high temperatures. But experiments show that the difference of the specific heat between metals and insulators is very small. This difficulty is removed when
Fermi-Dirac statistics is used to determine the electronic specific heat of the system.

5.4.2 Fermi-Dirac Theory;

Consider \( n(\epsilon)d\epsilon \) the number of electrons actually occupying states of energy between \( \epsilon \) and \( \epsilon + d\epsilon \), and \( f(\epsilon) \) is the probability that an electron will occupy the states of energy \( \epsilon \). It then follows that \([50, 51]\):

\[
n(\epsilon)d\epsilon = N(\epsilon)f(\epsilon)d\epsilon \quad (5.41)
\]

Electrons are fermions, and it is a well known result of modern statistical mechanics that, for particles obeying Fermi-Dirac statistics,

\[
f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_f)/kT} + 1} \quad (5.42)
\]

where \( N(\epsilon) \) is the density of states and \( \epsilon_f \) is the Fermi energy. Then the total energy is given by;

\[
E = 2\int_0^\alpha \epsilon f(\epsilon)N(\epsilon)d\epsilon
\]

\[
= 2\int_0^\alpha \frac{\epsilon N(\epsilon)}{e^{(\epsilon - \epsilon_f)/kT} + 1} d\epsilon \quad (5.43)
\]

The evaluation of these integrals is found in [49], and it gives the following approximation;

\[
E = E_0 + \frac{1}{3} (\pi kT)^2 N(\epsilon_f) \quad (5.44)
\]
where

\[ E_0 = 2 \int_0^{\varepsilon_g} \varepsilon \, N(\varepsilon) \, d\varepsilon \]

is temperature independent.

Thus the electronic heat capacity per mole is;

\[
C_v = \frac{dE}{dT} = \frac{2}{3} \pi^2 k^2 T N(\varepsilon_f) = \gamma T
\]

This important formula allows us to determine the density of states of electrons from the measured specific heat. It is of interest to note that the electronic specific heat rises linearly with T.

Now, at low temperatures, the specific heat associated with the lattice vibrations is proportional to \( T^3 \), so that the total specific heat of a metal may be represented by;

\[
C_v = \gamma T + \beta T^3
\]

This expression is, at least qualitatively, in agreement with experiment. At low temperature (Helium temperatures) the linear term predominates and this allows one to determine the electronic specific heat from experiment.
5.5 Specific Heat Associated with Internal Degrees of Freedom;

One sometimes observes contribution to the specific heat from other degrees of freedom of the system than those considered above. In particular, some solids may exhibit a specific heat at low temperatures which is anomalous in comparison with the lattice contribution. Consider a two-state system, with a ground state at $E_1=0$, and upper state $E_2=E$, with degeneracy $n_1$, and $n_2$ respectively. The partition function for the two-state system is given by [52];

$$Z(T) = n_1 \times 1 + n_2 e^{-\beta E}$$

where $\beta = 1/kT$

Then the free energy is given by;

$$F(T) = -kTN*\ln(Z)$$

$$= -kTN*\ln[n_1 + n_2 e^{-\beta E}] \tag{5.47}$$

From (5.18) and (5.47);

$$S = \frac{\partial F}{\partial T}$$

$$= -kN*\ln(n_1 + n_2 e^{-\beta E}) + kTN \frac{n_2 e^{-\beta E} (\frac{E}{kT^2})}{n_1 + n_2 e^{-\beta E}}$$

$$= kN* \{ \ln(n_1 + n_2 e^{-\beta E}) + \frac{E}{T} \frac{n_2 e^{-\beta E}}{n_1 + n_2 e^{-\beta E}} \} \tag{5.48}$$

From equations (5.18), (5.47), and (5.48), we get;

58
U = F + TS
\[ U = -kTN\ln[n_1 + n_2 e^{-\beta E} + kTn\ln[n_1 + n_2 e^{-\beta E}]] + NE\frac{n_2 e^{-\beta E}}{n_2 + n_1 e^{-\beta E}} \]
\[ = NE\frac{n_2 e^{-\beta E}}{n_2 + n_1 e^{-\beta E}} \]  
(5.49)

From equations (5.19) and (5.49);

\[ C_v = \frac{\partial U}{\partial T} = \frac{E e^{-\beta E} (n_1 + n_2 e^{-\beta E}) - n_2 e^{-\beta E} e^{\beta E}}{kT^2} = NE n_2 \left( \frac{E e^{-\beta E}}{kT^2} \right) \]
\[ = Nk n_1 n_2 \left( \frac{E e^{-\beta E}}{kT^2} \right) \]  
(5.50)

A plot of specific heat versus temperature shows a peak. Peaks of this type in the specific heat are called Schottky anomalies, and are observed at low temperatures in some solids. Schottky anomalies are observed in a variety of solids; for example paramagnetic ions where there is a crystal field splitting of the ground state.

The total entropy of the system is obtained from the definition;

\[ S = \int_0^\alpha \frac{C_v(T)}{T} dT \]
\[ = N \ln n_1 n_2 k \int_0^\alpha \left( \frac{E e^{-\beta E}}{kT^2} \right) \frac{e^{-\beta E}}{(n_1 + n_2 e^{-\beta E})^2} \]

Let
\[ X = \frac{E}{kT} \text{ and } dX = \frac{E}{kT^2} dT \]

Then
Let

\[
A = \frac{n_2}{n_1} \quad \text{and} \quad \frac{1}{1 + Ae^{-X}} = \frac{A e^{-X}}{(1 + Ae^{-X})}
\]

Substituting in equation (5.51) we get;

\[
S = Nk \int_0^\alpha X \left( \frac{1}{1 + Ae^{-X}} \right) dX
\]

By partial integration we get;

\[
S = Nk \int_0^\alpha \frac{X}{1 + Ae^{-X}} dX - \int_0^\alpha \frac{1}{1 + Ae^{-X}} dX
\]

\[
= -Nk \int_0^\alpha \frac{1}{1 + Ae^{-X}} dX
\]

By using;

\[
\int \frac{dX}{b + c e^{aX}} = \frac{X}{b} \cdot \frac{1}{ab} \ln(b + c e^{aX})
\]
Then

\[ S = Nk \left( \frac{X}{1} + \frac{1}{1} \ln(1 + A e^{-X}) \right) \]

\[ = Nk \left( \lim (X-X) - \ln(1 + \frac{n^2}{n}) \right) \]

\[ = Nk \ln(1 + \frac{n^2}{n}) \quad (5.52) \]

5.6 The Static Paramagnetic Susceptibility;

Paramagnetism requires the existence of partly filled electronic shells. Thus paramagnetic compounds are essentially those containing transition or Lanthanide group elements. Of these, the rare earth group (incomplete 4f shell) and iron group (incomplete 3d shell) are most extensively studied. In the following section the classical and quantum-mechanical description of paramagnets is presented.

5.6.1 Classical Theory;

Consider a system containing \( N \) magnetic dipole moments \( \mu \) per unit volume. Assume the interaction between the dipoles is weak, so that the field in which a given dipole finds itself is equal to the applied field \( H \), and that the magnetic field is constant or varies very slowly with time. Suppose the dipoles to be freely rotating, then according to the Langevin-Debye theory, the magnetic moment per unit volume is given by [47];

\[ M = N\mu L\left(\frac{\mu H}{kT}\right) \quad (5.53) \]

where \( L(X) \) is the Langevin function. For \( \mu H \ll kT \) this reduces to the simple expression;
M = \frac{\text{Nu}^2 H}{3kT} \\
or \\
\chi = \frac{\text{Nu}^2 H}{3kT} \tag{5.54}

where that \(\mu\) is of the order of one Bohr magneton=9.27 \times 10^{-21} \text{ G}^{-1}.

At room temperature the condition \(\mu H << kT\) is satisfied and the relation \(\chi = C/T\) is known as the Curie law.

5.5.2 Quantum Theory;

Consider a system containing \(N\) atoms per unit volume. According to quantum theory, the magnetic moment of a given atom or ion is not free to rotate but is restricted to a finite set of orientations relative to the applied field. In the absence of a magnetic field, the ground state of this system is defined by the total angular momentum quantum number \(J\), and each state is characterised by \(|J, M_J\rangle\), with \(M_J = J, (J-1), \ldots, -(J-1), -J\). When the magnetic field is applied, the ground state is split into \(2J+1\) levels. These energy levels are the eigenstates of the perturbing Hamiltonian \([53, 54]\);

\[ H = -M_J g \mu_B H \tag{5.55} \]

where \(\mu_B\) is the Bohr magneton.

\(g\) is the Lande \(g\)-factor or spectroscopic splitting factor and it is given by;

\[ g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \]

The possible components of the magnetic moment are; \(m = M_J g \mu_B\).
Then the partition function is;

$$Z = \sum_{E_i} e^{\frac{M \mu_B H}{kT}}$$  \hspace{1cm} (5.56)

The probability $P_i$ of occupation of each state of energy $E_i$ is given by the Boltzmann law;

$$P_i = \frac{e^{\frac{E_i}{kT}}}{\sum_{i} e^{\frac{E_i}{kT}}}$$  \hspace{1cm} (5.57)

The magnetisation is given by;

$$M = \sum_i m_i P_i = \frac{\sum_{i} M_i g \mu_B e^{\frac{M \mu_B H}{kT}}}{\sum_{i} e^{\frac{M \mu_B H}{kT}}}$$  \hspace{1cm} (5.58)

with $X = g \mu_B H / kT$, this expression becomes;
The partition function is;

\[ M = N g \mu_B J \sum J \frac{X^M_J}{\sum J} \cdot e^J \]

\[ Z = \sum J e^{X^M_J} \]

\[ = e^X (1 + e^X + (e^X)^2 + \ldots + (e^X)^J) \]

then, it is convenient to express \( Z \) in the form;

\[ Z = \frac{\text{Sinh}(\frac{2J+1}{2J} X)}{\text{Sinh}(\frac{X}{2J})} \]  

(5.60)

From equations (5.59) and (5.60), we get;

\[ M = N g \mu_B J \left\{ \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} X\right) - \frac{1}{2J} \coth\left(\frac{X}{2J}\right) \right\} \]

\[ = N g \mu_B J B_J(X) \]  

(5.61)

where \( B_J(X) \) is the Brillouin function.

This equation implies saturation of the magnetisation at low temperatures, e.g all dipoles ultimately will be directed along \( H \). The equation (5.61) is similar to the Langevin equation (5.53), the difference being that the latter holds for freely rotating
dipoles only. In fact, if $J \rightarrow \infty$ the Brillouin function becomes identical with (5.53).

For

$$M = \frac{N g^2 J(J+1)\mu_B^2}{3kT}H$$

For $X<<1$, (e.g. when magnetic field energy is small compared to the thermal energy), expansion of the hyperbolic function gives;

$$\text{Coth} (X) = \frac{1}{X} + \frac{X}{3} + O(X^3) \ldots .$$

Then

$$B_J = \frac{J+1}{3J} X$$

and

$$M = \frac{N g^2 J(J+1)\mu_B^2}{3kT}H$$

and the paramagnetic susceptibility is given by;

$$\chi = \frac{N g^2 J(J+1)\mu_B^2}{3kT} \quad (5.62)$$

This equation is identical with the classical equation (5.54) because the total magnetic moment $\mu_J$ associated with $J$ is given by;

$$\mu_J^2 = g^2 J(J+1) \mu_B^2$$

We note that from susceptibility measurements in the range where the Curie law holds, it is possible to determine the effective number of Bohr magnetons;
5.7 The Antiferromagnetic State;

Consider a system of identical magnetic atoms, which are distributed in two antiparallel sublattices A and B with magnetisation $M_A$ and $M_B$. In the absence of a magnetic field, $|M_A| = |M_B|$. Let $W_{AB} = W_{BA} = -W(W > 0)$ be the molecular field coefficient between the two sublattices and $W_{AA} = W_{BB} = W'(W > 0)$ the molecular field coefficient inside each sublattice. In the molecular field approximation the exchange interactions are equivalent to a magnetic field. In an applied magnetic field, the total field acting on each sublattice is [46,53,55];

$$H_A = H - W M_B + W'M_A$$

$$H_B = H - W M_A + W'M_B$$

The the magnetisation is given by;

$$M_A = \frac{C}{T} (H - W M_B + W'M_A)$$

$$M_B = \frac{C}{T} (H - W M_A + W'M_B)$$

with

$$C = \frac{N g^2 J(J+1)\mu_B^2}{3k}$$

where $N$ is the number of atoms of each sublattice per unit volume (cm$^3$). Then the total magnetisation;
where \( M = M_A + M_B \)

\[
\chi = \frac{M}{H} = \frac{2C}{T - \theta}
\]

and the susceptibility is given by;

\[
\chi = \frac{M}{H} = \frac{2C}{T - \theta}
\]  \hspace{1cm} (5.65)

with \( \theta = C(W - W') \)

where \( \theta \) is the Curie temperature, and the Neel temperature is given by;

\( T_N = C(W' + W) \)

### 5.8 Crystal Field Effects on Localised Magnetic Moments:

Calculation of the magnetic susceptibility for a rare earth ion including crystalline electric fields will be discussed below.

Let the Hamiltonian operator be given by \( H_0 \). If a magnetic field \( H \) is applied, the change in energy is small. Apply perturbation theory and develop the change in the Hamiltonian up to second order in \( H \):

\[
H(H) = H_0 + HH_1 + H^2H_2
\]

The energy takes the form;

\[
E = E_0 + HE_1 + H^2E_2
\]

Denoting the various crystal field levels by \( \nu \). Then;
\[ E_{\nu} = \epsilon_{\nu} = \langle \nu | \mathcal{H}_0 | \nu \rangle \]

\[ E_{1,\nu} = \langle \nu | \mathcal{H}_1 | \nu \rangle \]

\[ E_{2,\nu} = \sum_{\nu} \frac{1}{E_{\nu} - E_{\nu'}} \langle \nu' | \mathcal{H}_1 | \nu \rangle^2 + \langle \nu | \mathcal{H}_2 | \nu \rangle \quad (5.66) \]

where

\[ \sum_{\nu} \]

indicates a sum over all levels \( \nu' \) with \( \nu' \neq \nu \).

The Hamiltonian operator for quantum system with magnetic field is given by:

\[ \mathcal{H} = \sum_i \frac{1}{2m_i} \left( \frac{e_i}{c} \mathbf{A}_i \right) + V \quad (5.67) \]

where \( i \) is the number of electrons, and \( \mathbf{A}_i \) vector potential with \( \text{curl} \mathbf{A} = \mathbf{H} \).

Then \( \mathbf{A} = (A_x, A_y, A_z) \) and \( \mathbf{H} = (0, 0, H) \)

\( A_x = -1/2 \ YH \)

\( A_y = 1/2 \ XH \)

\( A_z = 0 \)

Inserting \( \mathbf{A} \) into the Hamiltonian, equation (5.67) it becomes;

\[ \mathcal{H} = \sum_i \left( \frac{P_i^2}{2m_i} + \frac{e_i}{2mc} (X_i P_{yi} - Y_i P_{xi}) + H^2 \frac{e_i^2}{8mc^2} (X_i^2 + Y_i^2) \right) + V \quad (5.68) \]

Now identifying the various contributions;
\[ \mathcal{H}_0 = \sum_i \frac{p_i^2}{2m_i} + V \]

The contribution without magnetic field determines the crystal field level scheme.

\[ \mathcal{H}_1 = -\sum_i \frac{e_i}{2m_i c} (X_i p_y - Y_i p_x) \]

\[ = -\frac{L_z}{\hbar} \]

\[ = -\mu_B m_z \]

where \( L_z \) is an angular momentum operator of electron \( i \), \( \mu_B = e\hbar/2m_i c \) Bohr magneton, and \( m_z \) is the projection of the magnetic moment along the \( Z \)-axis.

\[ \mathcal{H}_2 = \sum_i \frac{e_i^2}{p m_i c^2} (X_i^2 - Y_i^2) \]

This contribution is the diamagnetic contribution, \( \mathcal{H}_2 \) is only a small contribution and it can be neglected.

The partition function \( Z \) is defined by:

\[ Z = \sum_v e^{-\beta \varepsilon_v} \]

with

\[ \varepsilon_v = \varepsilon_v^0 + H. \varepsilon_v^1 + H^2. \varepsilon_v^2 \]

containing the effects of the magnetic field \( H \), and \( \beta = 1/K_B T \), where \( K_B = \)
Boltzmann factor.

The expectation value of the magnetic moment is \( [53,54] \):

\[
< M_\alpha > = \frac{1}{Z} \sum_\nu \mu_\alpha e^{-\beta \varepsilon_\nu}
\]

\[
= \frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial H} |_\alpha \quad \text{as} \quad \varepsilon_\nu . H = -\mu_\nu . H
\]

The paramagnetic susceptibility is defined as:

\[
\chi_\alpha = \lim_{H \to 0} \frac{\partial < \mu_\alpha >}{\partial H}
\]

\[
= -\frac{1}{\beta} \frac{1}{Z^2} \frac{\partial Z}{\partial H} |_\alpha + \frac{1}{\beta} \frac{1}{Z} \frac{\partial^2 Z}{\partial H^2} |_\alpha \quad \text{(5.69)}
\]

The first contribution is;

\[
\frac{1}{Z^2} \frac{(\partial Z)^2}{\partial H} |_\alpha = \frac{1}{Z} \frac{(\partial Z)^2}{\partial H} |_\alpha
\]

\[
= \left( \frac{1}{Z} \sum_\nu \mu_\alpha e^{-\beta \varepsilon_\nu} \right)^2 \to 0 \quad \text{as} \quad H \to 0
\]

i- because there is no net magnetic moment if the field \( H = 0 \).

ii- because of time inversion invariance.

\[
\frac{1}{Z} \sum_\nu \mu_\alpha e^{-\beta \varepsilon_\nu}
\]
change sign under time inversion, as the energy must be invariant \( \Rightarrow 0 \).

The second contribution is;

\[
\frac{\partial Z}{\partial H} = -\beta \sum_v (\varepsilon_v' + 2H \varepsilon_v^2) e^{-\beta \varepsilon_v} \]

\[
\frac{\partial^2 Z}{\partial H^2} = -\beta \sum_v \{2\varepsilon_v^2 - \beta (\varepsilon_v' + 2H \varepsilon_v^2)^2\} e^{-\beta \varepsilon_v} \]

\[
\lim_{H \to 0} \frac{1}{Z} \frac{\partial^2 Z}{\partial H^2} = \frac{\beta}{Z_0} \sum_v \{\beta (\varepsilon_v')^2 - 2\varepsilon_v^2\} e^{-\beta \varepsilon_v} \]

Then

\[
\chi_\alpha = \frac{1}{Z_0} \sum_v \left\{ \frac{|<v|\mu|v>|^2}{K_B T} - 2 \sum_{v'} \frac{|<v|\mu|v>|^2}{\varepsilon_v - \varepsilon_{v'}} \right\} e^{-\beta \varepsilon_v} \quad (5.70) \]

The first term in this equation gives the temperature dependence of the magnetic susceptibility and the second gives a relatively temperature independent paramagnetism [53,54].

The second term becomes;

\[
2 \sum_{v,v'} \frac{|<v|\mu|v>|^2}{\varepsilon_v^0 - \varepsilon_{v'}^0} e^{-\beta \varepsilon_v^0} \quad \text{rename } v \leftrightarrow v' \]

\[
= \sum_{v,v'} \frac{|<v'|\mu|v>|^2}{\varepsilon_v^0 - \varepsilon_v^0} e^{-\beta \varepsilon_v^0} + \sum_{v,v'} \frac{|<v|\mu|v>|^2}{\varepsilon_v^0 - \varepsilon_{v'}^0} e^{-\beta \varepsilon_{v'}^0} \]

71
\[ \sum_{\nu, \nu'} e^{-\beta \varepsilon_{\nu'}} - e^{-\beta \varepsilon_{\nu}} = |\varphi_{\nu}^\dagger \mu_{\alpha}^{\dagger} \varphi_{\nu'}|^{2} \]

For \( \nu' = \nu \)
\[ e^{-\beta \varepsilon_{\nu'}} - e^{-\beta \varepsilon_{\nu}} = (1 - \beta \varepsilon_{\nu}^{0} + \ldots) - (1 - \beta \varepsilon_{\nu}^{0} + \ldots) = -\beta (\varepsilon_{\nu}^{0} - \varepsilon_{\nu}^{0}) \]

\[ \chi_{\alpha} = \frac{1}{Z_{0}} \sum_{\nu, \nu'} e^{-\beta \varepsilon_{\nu'}} - e^{-\beta \varepsilon_{\nu}} |\varphi_{\nu}^\dagger \mu_{\alpha}^{\dagger} \varphi_{\nu'}|^{2} \quad (5.71) \]

where \( Z_{0} = \sum_{\nu} e^{-\beta \varepsilon_{\nu}} \)

5.9 Intermediate Valence in 4f Systems;

5.9.1 The Valence Transition;

Elemental Ce has two FCC phases; the higher volume \( (a_{0} = 5.15 \text{ Å}) \), local-magnetic moment \( \gamma \) - phase and the lower volume \( (a_{0} = 4.85 \text{ Å}) \) Pauli Paramagnetic \( \alpha \) - phase [55,56]. High pressure experiments have been used to study the passage from \( \gamma \) state to \( \alpha \) state in elemental Ce, in dilute Ce alloys and in several Ce compounds. From a temperature versus pressure \((T,P)\) phase diagram (Fig(5.1)), the cerium ions primarily have the trivalent \( 4f^{1}(5d6s)^{3} \) structure in the \( \gamma \) state. Application of pressure increasingly favours the tetravalent \( 4f^{0}(5d6s)^{4} \) structure. There is a large decrease in radius for the tetravalent atoms because removal of the \( 4f \) electron decreases the screening of the nuclear charge so that the outer \( 5d6s \) valence electrons are drawn in closer to the nucleus. The valence \( (z) \) in the \( \alpha \) state is not four. One form of evidence, based on the empirical correlations
between valence and metallic radius which are found in the periodic table, suggests a non-integral valence, midway between \( z = 3 \) and \( z = 4 \), \[57\]. In a plot of metallic radius against atomic number (Fig.5.2) \[58\] \( \alpha\text{-Ce} \) does not lie on the smooth extrapolated curve for tetravalent elements, but at an intermediate position. Thus by linear interpolation one would assign an intermediate valence \((IV)\), \( z = 3.67 \). Valence transitions can also be driven at ambient pressure by alloying e.g in \( \text{Ce}_{1-x}\text{RE}_x \) (where \( \text{RE} \) represent a rare earth or related solute). In addition many compounds of cerium exhibit non-integral valence at ambient conditions, e.g \( \text{CeN} \).

5.9.2 The Mixed-Valent State;

A necessary condition for non-integral valence is that two bonding states \( 4f^n(5d6s)^m \) and \( 4f^{n-1}(5d6s)^{m+1} \) of the rare earth ion are nearly degenerate. In the gas phase most rare earths are divalent, but in the solid state most are trivalent, due to the large cohesive energy gained by promoting a 4f electron into a bonding state. In the case of cerium the ambivalent tendency arises from the fact that the 4f orbital is more spatially extended than for the other rare earths. If there are inequivalent lattice sites an homogeneous mixed-valent compounds such as \( \text{Sm}_2\text{S}_4 \) may be formed. If on the other hand all rare earth sites are equivalent a homogeneous mixed-valent (HMV) compound is formed. The nature of the electronic level is shown in Fig.5.3 \[61\]. In this diagram, the density of states of a very narrow f-band which is degenerate with a broad band labelled d, since it is often associated with 5d and 6s states of the rare earth ion. If the Fermi level is in the f-band, the f states have mixed occupation of \( 4f^n \) and \( 4f^{n-1} \). The large interatomic Coulomb \( U \) characteristic of 4f states means that other valence states are very unfavourable, as illustrated by the \( 4f^{n-2} \) level in Fig.5.3, which is shifted by \( U \) to a larger binding energy. Depending on the type of experiment \[60\] a homogeneous mixed-valent compound may show either a single response (Mossbauer isomer shift, lattice constant), or a double response (X-ray Photoemission experiments (XPS)). This indicates that either an averaging process has taken place or that a superposition of different states is observed reminiscent of the two electronic configurations.
5.9.3 Valence Fluctuations;

The mixed-valence state can be thought of as a mixture of $4f^n$ and $4f^{n+1}$ ions, the energies of which are nearly degenerate. At any given site, 4f charge fluctuations between the two configurations occur on a time scale $\tau_{vf}$, the so-called valence fluctuation time or interconfiguration fluctuation time (ICF). Experiments such as XPS which probe on a time scale much shorter than $\tau_{vf}$ will see both configurations, but isomer shift measurements which probe on a time scale longer than $\tau_{vf}$ will see only one intermediate configuration[59]. Quantum mechanically this situation must be understood in terms of the hybridisation of the two configurations; schematically the hybridised wavefunction is;

$$|\psi\rangle = a_n |f^n\rangle + a_{n-1} |f^{n-1}\rangle$$  \hspace{1cm} (5.72)

Valence fluctuation cerium compounds include not only non-integral valent materials with nonmagnetic ground states (CeSn$_3$) but also trivalent materials where the fast spin fluctuations (which arise from the proximity of the 4f level to the Fermi level) suppress magnetic order (CeAl$_3$) and trivalent materials with antiferromagnetic ground states where the thermodynamic properties reflect the presence of such spin fluctuations (CeAl$_2$, CeIn$_3$).

5.9.4 Non-magnetic Ground State;

In ordinary rare-earth compounds the 4f electrons are highly localised and possess well-defined moments obeying atomic spectral rules taken into account through Hund's rules. These moments exhibit characteristic crystal field splittings and also interact weakly with the conduction electrons through the sf exchange interaction. This interaction which is well known, has been introduced by
Ruderman and Kittel, and developed by Kasuya and Yosida; it is therefore called the RKKY interaction[72]. In the γ state the susceptibility of the cerium is of a Curie-Weiss form (Fig(5.4)), apropos trivalence, but in the α state the susceptibility is that of an enhanced Pauli-paramagnet: much too large to represent simple tetravalence, but also non-diverging as \( T \to 0 \), indicating that the moments of the Ce\(^{3+}\) ions are quenched by the valence fluctuations.

5.9.5 Fermi Liquid Behaviour ;

The situation of a localised level, degenerate and hybridising with the conduction band and in close proximity to the Fermi level bears a strong resemblance to the problem of magnetic moment formation in dilute alloys. Although there are important differences between the dilute and concentrated limits. In particular, in the dilute limit there is a crossover from free moment behaviour at high temperatures to a strong-coupling Fermi liquid in the ground state[62]. In the concentrated materials a crossover connects the high-temperature Curie-Weiss behaviour to the low temperature, enhanced Pauli paramagnetic behaviour.

5.9.6 Field Dependence of Magnetisation;

The presence of Ce\(^{3+}\) impurities in mixed-valence cerium intermetallics is widely suspected. These are believed to contribute an extrinsic low-temperature Curie'tail' to the susceptibility which does not reproduce from sample to sample. The true temperature-independent susceptibility \( \chi(T) \) is related to the measured susceptibility by;

\[
\chi_{\text{meas}}(T) = \chi(T) + \chi_{\text{imp}}(T)
\]

(5.73)

where \( \chi_{\text{imp}}(T) \) includes the effects both of foreign impurities and extrinsic Ce\(^{3+}\) impurities. When \( \chi(T) \) is constant at low temperatures, as in many mixed-valence
materials, $\chi_{\text{imp}}$ can be easily subtracted out under the assumption that it is of the form $C_{\text{imp}}/T$. This impurity contribution can be saturated in high fields; the saturated part of the magnetisation corresponds to the same number of impurities as $C_{\text{imp}}$ and the slope of the high-field magnetisation corresponds to $\chi(T)$, for example, CeSn$_3$ [63]. There is a low-temperature contribution to $\chi(T)$ in CeCu$_2$Si$_2$ that is field dependent below 15 T. Lieke et al [64] have taken this as a sign of impurities. Magnetisation measurement on CeAl$_3$ up to 11 T[66] show signs of an impurity contribution which saturates around 7 T.

5.9.7 Splitting of the Free-ion Multiplet by the Crystalline Electric Field;

Each multiplet of the free ion is characterised by the quantum number $J$. This state, which is $2J+1$ degenerate, is associated with the $D_J$ representation of the rotation group. This means that the wave functions $|J,M_J\rangle$ of the multiplet transforms with the $D_J(R)$ matrix as one executes a rotation $R$. Let $G$ be the point group of symmetry of the site where the ion under study lies. The perturbing electric potential is invariant in the symmetry operations of $G$. $D_J$ is then reducible into the irreducible representations $\Gamma_i$ of the group $G$;

$$D_J = \sum_i n_i \Gamma_i$$  \hspace{1cm} (5.74)

where $n_i$ is the number of times $\Gamma_i$ appears in this decomposition. Group theory allows one to predict the splitting of each multiplet by the crystalline electric field; however it does not allow the determination of the energy level $E_i$ of this splitting.
5.9.8 Theories of the Ground State;

a. The Anderson Lattice;

The starting point for many theories of the valence instability is the Anderson lattice [67]. The Anderson lattice contains two types of states, the localised, highly correlated 4f states, and the itinerant uncorrelated conduction band states. The degeneracy of the 4f sites is ignored, leading to the Hamiltonian:

\[
H_f = \sum_{i,s} E_i f_{is}^+ f_{is} + \sum_{i,s} U f_{is}^+ f_{-i,-s} f_{-i,-s} f_{i,s} \]  \hspace{1cm} (5.75)

in which \(f_{is}^+\) and \(f_{is}\), respectively, create and destroy an electron of spin \(\delta\) in the \(f\) orbital of site \(i\). The first term represents the binding energy of a single \(f\) electron to the screened nucleus. The second term represents the Coulomb interaction between two \(f\) electrons, of opposite spin, located on the same ion. The conduction band is assumed to be composed of uncorrelated itinerant states, mainly of \(d\) character. These are described by the Hamiltonian:

\[
H_d = \sum_{k,\delta} \epsilon_d(k) \, d_{k\delta}^+ \, d_{k\delta} \]  \hspace{1cm} (5.76)

in which \(d_{k\delta}^+\) and \(d_{k\delta}\), respectively, create and destroy an electron of spin \(\delta\) in the Bloch state labelled by wavenumber \(k\). These two types of states are assumed to be coupled via a one-electron transfer term;
The first term takes an electron out of the conduction band and places it in the 4f shell at site i, and the second term represents the reverse process. This hybridisation term is spin conserving.

b. Charge Fluctuations and Spin Fluctuations;

The Anderson lattice model contains the hybridisation mechanism which allows both the local 4f electron spin and the local 4f charge to change[65]. The intra-ionic Coulomb interaction $U$ effects the dynamics of the 4f spin and the 4f charge in different ways. It tends to stabilise the local 4f moment, and tends to produce slowly time-varying spatial regions which exhibit short-range magnetic order. Thus as $U$ is increased, thermal spin fluctuations are expected to become more numerous and the system is expected to produce a bigger response to an applied magnetic field. A measure of the fluctuations of the spin about its average value is given by the following equation;

$$
\chi^{\alpha\beta}(q,\omega) = \int_{-\alpha}^{+\alpha} \frac{dt}{2\pi} \exp(i\omega t) \left\{ \langle[S^\alpha(q,t) S^\beta(q,0)]> - \delta_{\alpha\beta} <S^\alpha(q,0)>^2 \right\} \tag{5.78}
$$

where $S(q)$ is the spatial Fourier transform of the $f$ spin density.
Fig(5.1): Cerium phase diagram

Fig(5.2): Metallic radius against atomic number for the rare-earth metals (data from Gschneidner 1961).
Fig(5.3): Schematic density of states of a mixed valence system. The atomic 4f levels are purely occupied: the energy to remove an electron from a $4f^n$ ion is at the Fermi energy, and that to remove an electron from a $4f^{n-1}$ ion shifted by $U$ to larger binding. The d band represent a broad featureless band.

Fig(5.4): Susceptibility of Cerium (Lawrence and Parks 1976)
CHAPTER 6

EXPERIMENTAL RESULTS

6.1 Review of the Experimental Properties;

6.1.1 Magnetic Susceptibility;

The reported susceptibility values for cerium compounds are shown in table(6.1).

Table(6.1): Susceptibility data for Cerium intermetallics. $\mu^\text{eff}$ and $\theta$ are obtained from high-temperature Curie-Weiss fits.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu^\text{eff}(\mu_B)$</th>
<th>$\theta$ (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeSn3</td>
<td>2.54</td>
<td>-220</td>
<td>[63]</td>
</tr>
<tr>
<td>CeBe13</td>
<td>2.65</td>
<td>-200</td>
<td>[66]</td>
</tr>
<tr>
<td>CeAl3</td>
<td>2.63</td>
<td>-46</td>
<td>[67]</td>
</tr>
<tr>
<td>CeCu2Si2</td>
<td>2.62</td>
<td>-164</td>
<td>[71]</td>
</tr>
<tr>
<td>CeCu6</td>
<td>2.69</td>
<td>-45</td>
<td>[68]</td>
</tr>
<tr>
<td>$\beta$-Ce</td>
<td>2.61</td>
<td>-41</td>
<td>[69]</td>
</tr>
<tr>
<td>CeAl2</td>
<td>2.52</td>
<td>-32</td>
<td>[72]</td>
</tr>
<tr>
<td>CeIn3</td>
<td>2.54</td>
<td>-50</td>
<td>[63]</td>
</tr>
<tr>
<td>CeSn3</td>
<td>2.54</td>
<td>-220</td>
<td>[63]</td>
</tr>
<tr>
<td>CeSn2.7In0.3</td>
<td>2.54</td>
<td>-128</td>
<td>[63]</td>
</tr>
</tbody>
</table>
The nearly trivalent materials CeSn$_3$ and CeBe$_{13}$ show a broad maximum near 150 K, with Curie-Weiss-like behaviour at high temperatures and effective moments close to the trivalent free-ion value. Strongly mixed-valent CeN shows a broad maximum near 900 K; α-Ce might show similar behaviour were the results not terminated by the α–γ phase transition. Trivalent CeAl$_3$, CeCu$_6$, CeCu$_2$Si$_2$ show Curie-Weiss-like monotonic susceptibilities down to very low temperatures; CeAl$_3$ shows a maximum at 0.7 K while CeCu$_2$Si$_2$ becomes superconducting at 0.5 K. The other trivalent materials (β-Ce, CeAl$_2$, CeIn$_3$) order antiferromagnetically at low temperatures; the susceptibilities show Curie-Weiss behaviour above $T_N$. The susceptibility of CeSn$_3$ is very similar, in all features to that observed for transition metal Palladium, i.e it shows a finite $\chi(0)$ comparable in magnitude to that of α-cerium, a broad maximum near 100 K, and Curie-Weiss behaviour at higher temperatures.

6.1.2 Specific Heat;

In the cerium intermetallics, large linear coefficients of electronic specific heat ($\gamma$) are consistently observed. Amazingly large ($\gamma$) coefficients are observed in CeCu$_6$, CeCu$_2$Si$_2$, and CeAl$_3$ (table 6.2). In CeCu$_2$Si$_2$ a linear variation of the specific heat occurs below 1 K, and a maximum in the specific heat occurs at 3.5 K, with an integrated entropy close to $(R \ln 2)$. In CeAl$_3$ a broad maximum occurs near 25 K with an entropy of the order of $(R \ln 6 - \ln 2)$ and below 0.3 K the specific heat is linear. In both cases the $J=5/2$ level is probably split into three doublets; the very-low-temperature behaviour involving the ground-state doublet, and a maximum occurring at higher temperatures due to the remaining four levels. In the more strongly trivalent compounds antiferromagnetic transitions and / or crystal field effects influence the specific heat. For β-Ce, CeAl$_2$ and CeIn$_3$ large specific heat anomalies occur at $T_N$ with integrated entropies not very different from $(R \ln 2)$. At higher temperatures the entropy of the higher lying multiplets must be generated. In CeAl$_2$ and CeIn$_3$ a broad maximum centred near 40 K and 160 K, respectively, contain most of the remaining entropy $(R \ln 6 - R \ln 2)$. CeAl$_2$ order magnetically
below 3.8 K as shown by the peak in the specific heat curve[72]. The specific heat of CePd$_3$, CeBe$_{13}$, etc, shows a maximum at a temperature which is comparable to the Debye temperature $\theta_D$ so that the lattice contribution is not small at $T_{\text{max}}$. The specific heat and magnetic-susceptibility measurements show that CePt$_3$ undergoes a magnetic transition at $T_N=1$ K into an antiferromagnetic state[75]. The f-electron contributions to the specific heat of CeCu$_2$Ge$_2$, and CeRu$_2$Ge$_2$, exhibit Schottky anomalies at temperatures between 50 K to 250 K[74].

Table(6.2) : Specific heat data for Cerium intermetallics, where $\gamma$ is the linear electronic coefficient of specific heat, and $\Delta S(T_{\text{max}})$ is an estimate of the entropy under the peak.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma$ (mJ/Mol.K$^2$)</th>
<th>$\Delta S(T_{\text{max}})$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeCu2Si2</td>
<td>1000</td>
<td>0.9Ln2</td>
<td>[71]</td>
</tr>
<tr>
<td>CeCu6</td>
<td>1600</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td>CeAl3</td>
<td></td>
<td>RLn6/2</td>
<td>[67]</td>
</tr>
<tr>
<td>CeAl2</td>
<td></td>
<td>1/2ln6/2</td>
<td>[72]</td>
</tr>
<tr>
<td>CePd3</td>
<td>37</td>
<td></td>
<td>[72]</td>
</tr>
<tr>
<td>CeBe13</td>
<td>115</td>
<td></td>
<td>[73]</td>
</tr>
<tr>
<td>CeSn3</td>
<td>53</td>
<td></td>
<td>[73]</td>
</tr>
</tbody>
</table>

6.2 Sample Preparation;

Samples (15 g) were prepared by the repeated melting of the appropriate
quantities of spectrographically pure starting elements in an argon arc furnace. The purity of the starting elements was 99.999%, 99.99%, 99.99%, 99.999%, and 99.8% for the Cu, Ce, La, Pt, and Si respectively, and the weight loss after melting was less than 0.6% for all alloys. Following the melting, the resulting ingot was crushed in a hardened steel pestle and mortar. Several pieces suitable for susceptibility measurements were selected and the remainder of each ingot was crushed to a powder with a particle size less than 200 μm. The resulting powder and the samples for susceptibility measurements were sealed under vacuum in a quartz ampule and annealed at 850 °C for 24 hours before being quenched into iced water. A subsequent X-ray diffraction pattern revealed the materials to be single phase and to have the appropriate structures, as shown in table 6.3[76].

Table(6.3): Configuration symmetry of the Ce compounds structure

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Structure</th>
<th>Space group</th>
<th>Lattice parameter(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CePt 2</td>
<td>Cu2Mg</td>
<td>Fd3m</td>
<td>7.71</td>
</tr>
<tr>
<td>CePt 3</td>
<td>AuCu3</td>
<td>Pm3m</td>
<td>4.16</td>
</tr>
<tr>
<td>LaPt 2</td>
<td>Cu2Mg</td>
<td>Fd3m</td>
<td>7.7</td>
</tr>
<tr>
<td>CeCu1.8Si2</td>
<td>ThCr2Si2</td>
<td>I4/mmm</td>
<td>a=4.0891</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=9.9116</td>
</tr>
<tr>
<td>CeCu2.2Si2</td>
<td>ThCr2Si2</td>
<td>I4/mmm</td>
<td>a=4.0856</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=9.9101</td>
</tr>
</tbody>
</table>
6.3 Neutron Diffraction;

6.3.1 Introduction;

The compound CeCu$_2$Si$_2$ has extremely sample dependent properties, and depending on stoichiometry, a superconducting or non superconducting ground state is reported to occur[82]. After extensive crystallographic investigations [83, 84, 85] it is now realised that CeCu$_2$Si$_2$ exists in two different versions with two different ground states. The effect is most pronounced when the Cu content is varied. The addition of up to 30% of Cu yields a superconducting sample with a transition temperature of 0.6 K. Samples with less than the nominal Cu content are non superconducting. Recently [86], the crystallographic differences between two samples CeCu$_{1.8}$Si$_2$ and CeCu$_{2.2}$Si$_2$ was determined using neutron powder diffraction experiments. These measurements enabled a relationship between the structural parameter z (defining the distance of Ce to Si) and the occurrence of superconductivity to be established. Thus it is clearly important that the samples are well characterised and their crystallographic structures established. With the exception of the CePt$_2$ system all the materials investigated in the present thesis had been extensively investigated by other researchers. Consequently their crystallographic structures were known. In the case of CePt$_2$ and LaPt$_2$ these materials were prepared in the department as described in section (6.2).

Confirmation that the CeCu$_{2.2}$Si$_2$ and CeCu$_{1.8}$Si$_2$ compounds were single phase and had the (I4/mmm) structure was obtained using X-ray powder diffraction. More detailed structural information was provided by neutron diffraction data.

6.3.2 Neutron Diffraction of CePt$_2$;

Powder neutron diffraction patterns were recorded between 10 K and 300 K for CePt$_2$, using the powder diffractometer Polaris on the pulsed neutron source located at the Rutherford Appleton Laboratory. The specimen of volume 2 cc was contained in a thin-walled Vanadium can of 10 mm diameter. Data were collected for all reflections with lattice spacings larger than 0.325 Å which corresponds to the (20, 10, 8) reflection. Fig(6.1) shows the diffraction patterns and resulting fits, at
a temperature of 150 K. The refinements were carried out using a least square fitting program. For the MgCu₂ structure there are no free parameters, thus only the lattice parameter and isotropic temperature factors were refined using the 380 reflections observed. Since the experiments were carried out at low temperatures the temperature factors were found to be essentially zero. A $\chi^2$ test of 4.88 indicated that the agreement between the observed and calculated structure was good. Details of the refined structure are given in table (6.4).

Table (6.4)

<table>
<thead>
<tr>
<th>Space group</th>
<th>Cu2 Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameter (Å)</td>
<td>7.71</td>
</tr>
<tr>
<td>Atomic Position</td>
<td>Ce</td>
</tr>
<tr>
<td></td>
<td>8a</td>
</tr>
<tr>
<td></td>
<td>x=0</td>
</tr>
<tr>
<td></td>
<td>y=0</td>
</tr>
<tr>
<td></td>
<td>z=0</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td></td>
<td>16d</td>
</tr>
<tr>
<td></td>
<td>x=5/8</td>
</tr>
<tr>
<td></td>
<td>y=5/8</td>
</tr>
<tr>
<td></td>
<td>z=5/8</td>
</tr>
</tbody>
</table>

No magnetic structure was detected at low temperatures i.e. $T=10$ K. Thus, in the temperature range studied CePt₂ does not order magnetically, in good agreement with specific heat and magnetic susceptibility measurement at low temperature.

6.4 Magnetic Susceptibility Results;

To successfully calibrate the balance, requires either that the sample be as small as the volume over which H dH/dX is constant, or that it be of identical geometry to the specimen used and located precisely at the same position in the field. We have adopted the latter method and calibration was effected using a pure Palladium sample (for which a susceptibility of $5.23 \times 10^{-6}$ emu.g⁻¹ was assumed) of approximately the same dimension as the sample under investigation.
Measurements were made in several applied fields up to 8 kOe so that the effects of possible ferromagnetic impurities would be immediately apparent. The homogeneity of each sample was confirmed by comparing the susceptibility of three specimens taken from each ingot. The susceptibilities for CePt$_2$, CePt$_3$, LaPt$_2$, CeCu$_{1.8}$Si$_2$, and CeCu$_{2.2}$Si$_2$ are plotted in figs (6.2), (6.3), (6.4), (6.5), and (6.6), respectively. The data are taken over the temperature range 3.7 K - 300 K for all samples except CeCu$_{1.8}$Si$_2$ which is measured in temperature range from 3.7 K to 25 K and from 77.3 K to 300 K. From Fig (6.4), it is clear that the susceptibility of LaPt$_2$ is temperature independent and thus it is not meaningful to derive an effective magnetic moment. The susceptibility for all other samples exhibits Curie-Weiss-like behaviour at high temperatures and monotonically increases with decreasing T at lower temperatures. The susceptibility of Ce compounds arises mainly from 4f electrons, but contributions are expected from the other electrons; and in particular the lanthanide 5d electrons make a significant contribution. The inverse susceptibility for the samples CePt$_2$, CePt$_3$, CeCu$_{1.8}$Si$_2$, and CeCu$_{2.2}$Si$_2$ is plotted in Fig (6.7), (6.8), (6.9), and (6.10), respectively. The Curie-Weiss behaviour is apparent in these figures; the resulting curve is a straight line which intercepts the temperature axis at the Curie temperature (Θ), and has a slope (1/C).

The observed effective moment ($μ_{\text{eff}}$), and the Curie temperature are given in table (6.5), using the theory developed in chapter (5) the results can be compared to the experimental values of the effective magnetic moment, assuming $J=5/2$ and $g=6/7$ for Ce$^{3+}$, e.g.

$$μ_{\text{eff}} = μ_λ g_λ \sqrt{J(J+1)}$$

$$= 2.54μ_λ$$
Table (6.5): Results and analysis of the susceptibility of Ce compounds

$\mu_{\text{eff}}$ and $\theta$ are obtained from high-temperature Curie-Weiss fits

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma_{\text{eff}} (\mu\beta)$</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CePt$_2$</td>
<td>2.62</td>
<td>-62.5</td>
</tr>
<tr>
<td>CePt$_3$</td>
<td>2.37</td>
<td>-60</td>
</tr>
<tr>
<td>LaPt$_2$</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>CeCu1.8Si$_2$</td>
<td>2.60</td>
<td>-50.0</td>
</tr>
<tr>
<td>CeCu2.2Si$_2$</td>
<td>2.39</td>
<td>-56.6</td>
</tr>
</tbody>
</table>

To calculate the magnetic susceptibility of CePt$_2$ the following method was used. In the ionic state Ce$^{3+}$ has one electron and the ground state multiplet is characterised by $J=S/2$. From group theory [76, 77] the $2J+1=6$ levels of the free ion are split by the cubic crystal field into $\Gamma_7(2)+\Gamma_8(4)$. The wave functions for Ce$^{3+}$ of cubic crystal field, acting on $J=5/2$ are given by [78]:

\[
|11\rangle = \sqrt{\frac{1}{6}} |\frac{5}{2}\rangle - \sqrt{\frac{5}{6}} |\frac{3}{2}\rangle \quad \Gamma_7
\]

\[
|12\rangle = \sqrt{\frac{5}{6}} |\frac{3}{2}\rangle - \sqrt{\frac{1}{6}} |\frac{5}{2}\rangle
\]
The susceptibility $\chi_z$ is determined by matrix elements of the form;

$$<\nu|J_z|\upsilon>$$

$\nu, \upsilon=1, \ldots, 6$

The diagonal and off-diagonal matrix elements are easily calculated. A straightforward calculation yields for the diagonal elements with;

$$<\upsilon|J_z|\upsilon> = \frac{5}{2} \frac{1}{6} + \frac{5}{2} \frac{3}{6} = \frac{5}{6} \quad \text{for} \; \upsilon, \upsilon = 1, 2$$

$$<\upsilon|J_z|\upsilon> = - \frac{3}{2} \frac{1}{6} + \frac{5}{2} \frac{5}{6} = \frac{11}{6} \quad \text{for} \; \upsilon, \upsilon = 3, 4$$

$$<\upsilon|J_z|\upsilon> = \frac{1}{2} \quad \text{for} \; \upsilon, \upsilon = 5, 6$$

In the same manner the calculation of the off-diagonal matrix elements yields;

$$<\upsilon|J_z|\upsilon> = 0 \quad \text{for} \; \upsilon, \upsilon = 2, 3, 4, 5, 6$$
\[ \langle \nu | J_z | \nu' \rangle = \frac{\sqrt{5}}{5} \left( -\frac{5}{2} \right) \cdot \frac{\sqrt{5}}{6} \cdot \frac{3}{2} = \frac{4\sqrt{5}}{3} \quad \text{for } \nu, \nu' = 1, 3, 4 \]

Using the above wave functions and equation (5.71), a least square fit to the observed susceptibility was carried out. The resulting fit gave an energy level splitting between the ground state and an excited quartet level of 430 K. The comparison between the measured and calculated susceptibilities is shown in fig(6.11). However, the calculated energy level splitting is much larger than that indicated by the specific heat measurement. The results of a second calculation carried out, fixing the splitting at 84 K, as indicated by the specific heat measurement, is compared with the observed results in fig(6.12).

6.5 Specific Heat Results;

6.5.1 Specific Heat of Copper;

The first measurements made after construction of the calorimeter were of the heat capacity of the empty sample holder. The heat capacity of the sample holder was plotted as a function of temperature is shown in fig (6.13), (6.14), and (6.15). The absolute accuracy of the calorimeter was checked several times by determining the specific heat of pure copper samples. Results of specific heat measurements for spectrographically pure copper (99.999% Johnson and Mathey) are plotted in Fig(6.16), and (6.17) as a function of temperature. Below 10 K, the results for the pure copper are presented in Fig(6.18) in the form of plots \( \frac{C_p}{T} \) against \( T^2 \). The data points \( (\frac{C_p}{T}, T^2) \) were fitted using a least squares routine and the formula;

\[ C_p = \gamma T + \beta T^2 \]

The Debye temperature, \( \theta_D \) is related to the lattice contribution(\( \beta \)) by;
the values of $\gamma$ and $\theta_{D}$ are presented in table (6.6). For comparison, the coefficients $\gamma$ and $\beta$ for a copper reference specimen [79] and [80] are also given in table (6.6).

Table (6.6): The $\gamma$ and $\theta_{D}$ of pure copper sample

<table>
<thead>
<tr>
<th>$\gamma$ (mJ/Mol.K2)</th>
<th>$\theta_{D}$(K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.69589</td>
<td>345±3</td>
<td>present work</td>
</tr>
<tr>
<td>0.69434</td>
<td>344.5</td>
<td>[79]</td>
</tr>
<tr>
<td>0.69597</td>
<td>343.89</td>
<td>[80]</td>
</tr>
</tbody>
</table>

Above 10 K, the relative deviation of the pure copper sample, from the values reported in the literature [80, 81] is shown in Fig(6.19). The deviation (% $\Delta C$) is defined by:

$$
\%\Delta C = \left( \frac{C_{P} - C_{\text{standard}}}{C_{\text{standard}}} \right) \times 100
$$

where $C_{P}$ is the measured specific heat from the present work, and $C_{\text{standard}}$ is the specific heat of copper as given by references [80] and [81]. As shown in Fig(6.19), the maximum percentage deviations of the present experiments from the copper reference data of [80] and [81] are $\pm$ 5%. It may be concluded that agreement is rather good.
6.5.2 Specific Heat of the CePt$_2$ and LaPt$_2$;

Fig(6.20) and (6.21) show the specific heat of CePt$_2$ and LaPt$_2$, respectively, as measured in a low temperature calorimeter as a function of the temperature. From the specific heat measurements below 10 K one can determine both $\gamma$ and the Debye temperature $\theta_D$. Fig(6.22) shows the variation of $C_p/T$ with $T^2$ for CePt$_2$, and the values of $\gamma = 137.641$ mJ.K$^{-2}$.Mol$^{-1}$ and $\theta_D = 269.358$ K were determined from a least squares fit of a straight line to the data points. In Fig(6.23) the $C_p/T$ vs $T^2$ is plotted for LaPt$_2$ sample, for which the calculated values of $\gamma$ and $\theta_D$ are $\gamma = 3.564$ mJ.K$^{-2}$.Mol$^{-1}$ and $\theta = 153$ K. To determine the 4f-electron contribution, $\Delta C$, to the total specific heat of CePt$_2$, the specific heat of LaPt$_2$ was subtracted from the specific heat of CePt$_2$. Since LaPt$_2$ has no 4f-electrons, and its specific heat is assumed to be characterised by a small $\gamma$ term arising from the s,p,d electrons. In Fig(6.24), the specific heat $\Delta C(T)$ of the 4f-electrons is presented, which enables the evaluation of the entropy. No correction was made for the small difference in mass between Ce and La. This will result in a small systematic error which, however is expected to be below 1% and therefore within the uncertainty of the measurements. The solid line represents Schottky specific heat calculated for a CF-level scheme with a ground state doublet separated from an a excited quartet level by 85 K. $\Delta C(T)$ shows a pronounced peak around 40 K which we interpret as a Schottky anomaly due to crystal-field splitting between a low-lying doublet and an excited quartet within the $(2J+1)$ fold degenerate 4f-level. For $4f^1$ a $J=5/2$ manifold splitting into $\Gamma_7(2)+\Gamma_8(4)$ occurs. The entropy associated with the crystal-field splitting between the lowest measured temperature and 100 K was computed by a Simpson's rule integration from the data presented in Fig(6.24). The following result was obtained;

$$S = \int_{\theta}^{a} \frac{\Delta C_p}{T} dT$$

$$= 7.21 \text{ J/Mol.K}$$

From chapter 5, equation (5.52) predicts that the value of entropy should be
S=9.133 J/Mole K for n_2=4, n_1=2, and S=3.371 J/Mole K for n_2=2, n_4=4. Thus from the measured and calculated entropy we infer that a doublet must be the ground state (\( \Gamma_7(2) \)) with a quartet as an excited level (\( \Gamma_8(4) \)).
CeP\text{t}2

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig6.2}
\caption{Graph showing the relationship between $X \times 10^6$ e.m.u./g and TEMP. K for CePt2.}
\end{figure}
CePt3

![Graph showing CePt3](Fig(6.3))
LaPt2

![Graph](image)

Fig(6.4)
CeCu1.8Si2

Fig(6.5)
CeCu$_2.2$Si$_2$

Fig(5.6)
$CeP_{\frac{1}{2}}$
CePt₃

![Graph showing the relationship between 1/x * 10⁴ gm/e.m.u. and TEMP, k.](image)
CeCu$_{1.8}$Si$_2$
CeCu2.2Si2

\[ \frac{1}{x} \times 10^{-4} \text{(g/cm}^3) \]

\[ \text{Temperature} \times 10^3 \text{(K)} \]

Fig(6.10)
Fig (6.11)
Fig(6.12)
HOLDER HEAT CAPACITY

Fig(6.13)
HOLDER HEAT CAPACITY

Fig(6.14)
Empty sample heat capacity
Specific heat of pure Cu

Fig(6.17)
Fig(6.19)
CePt$_2$

Fig. (6.20)

SPECIFIC HEAT (J/MOL.K)

TEMPERATURE (K)
LaPt$_2$

Fig. (6.21)
CePt₂

Fig(6.22)
Fig(6.23)
ΔC(T) J/Mol.K

Fig(6.2.4)

T [K]

ΔC(T) J/Mol.K
CHAPTER 7

CONCLUSION AND RECOMMENDATIONS
FOR FUTURE WORK

7.1 Introduction;

Many researchers have extensively investigated the experimental and theoretical properties of Intermediate Valence (IV) compounds. Among the large number of systems which exhibit Intermediate Valence phenomenon cerium and its compounds are probably most extensively studied. For experimentalists, this apparent attraction essentially is due to the large number of properties which show quite distinct and sometimes really drastic deviations from the behaviour expected for localised 4f-systems. Among these properties are isostructural phase transitions involving large volume changes, driven by temperature, pressure or alloying. The specific heat is dominated by a large electronic contribution ($\gamma$), and the magnetic susceptibility does not in general exhibit a Curie-like behaviour at low temperature. When reviewing the subject it was found that the thermal and magnetic properties of Ce compounds were extensively studied. In the present thesis, it was decided to pay particular attention to measurement and analysis these properties. The conclusions of this research and recommendations for future studies which might be useful for other researchers are presented.

7.2 Conclusions;

The thermal and magnetic properties of some Ce compounds have been extensively studied. To carry out these studies a low temperature specific heat calorimeter and a Faraday susceptibility balance have been designed, built and automated. Some of the samples were provided by other workers but the CePt$_2$ was prepared in the department and its structure investigated using X-ray and neutron diffraction. The following points can be concluded from the present work;
1. Within the experimental error of ± 5% in C_p, the values for the Debye temperature \( \theta_D \) (\( T < 10 \)) and the electronic specific heat coefficient \( \gamma \) agree well with the data determined by other authors [80, 81].

2. The deviation of the measured specific heat of pure copper in the present work from the copper reference equation could arise from a number of causes; A first possibility is that the accuracy of the specific heat measurement is limited by the error associated with measurement of the temperature and the temperature calibration. The passage of a direct current through a germanium resistance thermometer leads to a temperature gradient being established from one end to the other, due to the Peltier heat liberated and absorbed at the junctions with the leads [87, 88]. The magnitude of the difference between a d.c measurement and a true resistance measurement can be as high as 1.5% at room temperature, 0.2% at 80 K, 0.02% at 50 K and less than 1 part in 10^6 below 10 K. The corresponding temperature errors are less than 0.1 mK below 20 K, but rise to 200 mK at 100 K. By making comparative measurements on standard resistors it was shown that increasingly large errors occurred as the resistance were lowered at temperature <30 K. The calibration data for the germanium thermometer was fitted to an equation of the form \( \ln R = a \ln T \). The temperatures obtained from this approximate fit deviated slightly from the calibrated value. An alternative origin for the discrepancy is the possibility of calorimeter error. The adiabatic shield should be at a uniform temperature over its whole area and should be kept accurately at the temperature of the calorimeter. Adiabatic calorimetry becomes increasingly difficult because of the temperature offset of adiabatic shield during the heating period may result in an uncompensated heat flow to or from the calorimeter. A third possibility is a systematic error due to slight differences in the vacuum between the first and second run.

3. The results of the specific heat measurements of CePt_2 and LaPt_2 indicate that the magnitude of the entropy of the Schottky anomaly may be satisfactorily explained by comparing the experimental values with those computed from equation (5.52). In conclusion we have put forward calorimetric evidence for the existence of a Schottky anomaly in CePt_2 at 40 K. We interpret this anomaly as arising from the crystal-field excitations within a 4f^1(J=5/2) configuration of Ce-ions with two
fold splitting of the levels $\Gamma_7(2)+\Gamma_8(4)$. These results point to the existence of highly localised 4f-electrons in CePt$_2$.

4. From the present study of the temperature variation of the susceptibility, we have seen that the susceptibility of some cerium compounds shows Curie Weiss behaviour at temperatures above 25 K. At low temperatures the susceptibility is observed to be surprisingly high, namely $10 \times 10^{-6}$ e.m.u/g. These observations point to the presence of an impurity contribution to the susceptibility as is sometimes seen in Ce intermetallic compounds.

5. An estimated error in the results of the magnetic susceptibility measurements of about 2% is due to the external vibration. Such mechanical effects are difficult to eliminate electronically because the spurious background signal has the same effect as the sample signal.

6. Neutron diffraction experiments on CePt$_2$ suggest a non magnetic ground state down to 4 K, in good agreement with those derived from specific heat and magnetic susceptibility measurements.

7. Although the best least square fit to the susceptibility suggests a crystal field splitting of 430 K this result is not consistence with that obtained from specific heat measurements, which indicate a value of 85 K. Both the measured susceptibility and specific heat data are in good agreement with earlier measurements obtained[89] over a more restricted temperature range. This suggests that the discrepancy between the model and the observation arises primarily from the inadequacies of the theory. This is quite reasonable since the model used is based on localised moments in an insulating environment. It is well known that platinum has high a susceptibility and is therefore easily polarisable by the presence of magnetic moments[90]. Thus any model to describe the magnetic properties of CePt$_2$ must be based on the band structure. The analysis presented above represents an initial step to wards a detailed understanding of the magnetism in this material.
7.3 Recommended Suggestions For Future Studies;

With respect to cerium compounds, in particular, we may list the following as an experimental programme which should be performed in the future;

1. To measure precisely the susceptibility of CePt$_2$ below 3.7 K to confirm the maximum value of the susceptibility.

2. To confirm the specific heat curve for CePt$_2$ and LaPt$_2$ for which the existing data show some scatter.

3. To measure the specific heat of the CePt$_3$. 
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