The development and construction of a versatile vibrating-sample magnetometer

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:


Metadata Record: https://dspace.lboro.ac.uk/2134/32173

Publisher: © N.A. Khalefa

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: https://creativecommons.org/licenses/by-nc-nd/4.0/

Please cite the published version.
THE DEVELOPMENT AND CONSTRUCTION OF A VERSATILE VIBRATING-SAMPLE MAGNETOMETER

by

NAJIM ABDULLAH KHALEFA, BSc, MPhil

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

September 1991

© by N.A. Khalefa, 1991
DEDICATION

To my wife and my children Kalid, Muthana, Nawfal and Solayman for all the sacrifices that they made in favour of my education.

* * * * *
# CONTENTS

Dedication

Acknowledgements ........................................ 1

Abstract ............................................. iii

CHAPTER 1: INTRODUCTION ............................ 1

CHAPTER 2: BASIC THEORY OF MAGNETISM ............. 6

2.1 Basic Magnetic Properties of Material .......... 6

2.2 The One-Body Approximation .................... 10

2.3 The Gutzwiller Approximation .................... 14

2.4 Some Consideration of the Relevance of these Models to Real Systems .................. 15

2.5 Electron Hole Attraction ......................... 15

2.5.1 Anderson Localisation ......................... 18

2.5.2 Factors that Affect $U$ and $W$ ................. 20

2.6 Transition Metal Magnetism ...................... 22

2.6.1 The Stoner Model for Itinerant Electrons .......... 24

2.6.2 Finite Temperature and Excitation Mechanisms .......... 27

2.7 Discussion of Susceptibility of Metals - Pauli Paramagnetism ................. 30

References ........................................... 41

CHAPTER 3: EXPERIMENTAL DETAILS AND EQUIPMENT .... 43

3.1 Introduction .................................... 43

3.2 The Apparatus .................................. 46

3.2.1 Temperature Regulation ....................... 47

3.2.2 Newport 7" Electromagnet Type E" ............... 49

3.2.3 Loudspeaker ................................ 54

3.2.4 Sample Rod and Transducer ................... 54
3.2.5 Conditioning Amplifiers ....... 54
3.2.6 Differential Amplifiers ....... 55
3.2.7 Lock-in Amplifier ............ 55
3.2.8 Computer ................. 55
3.2.9 Drive Unit ................. 56
3.3 The Principles of a Pick-up Coil .... 58
3.3.1 Coil Design ............... 59
3.4 Calibration of the Vibrating Sample Magnetometers ................. 72
3.5 Calibration Problems ........... 75
3.6 Automation of a Vibrating Sample Magnetometer ................. 77
3.6.1 The Multiplexer Units ....... 77
3.6.2 Magnet Power Supply Control Circuit ........... 79
3.7 Computer Programme Description .... 81
3.8 Measurement of Magnetisation ........... 82
3.9 Temperature Independent Paramagnetism .... 87
3.10 Conversion Factors Between SI and CGS Units ................. 88
References ................. 90

CHAPTER 4: SOME RELEVANT THEORY OF MAGNETISM .... 92
4.1 The Magnetic Properties of Atoms .... 92
4.2 Molecular (Mean) Field Theory .... 98
4.3 Molecular Field Theory for an Antiferromagnetic ................. 101
4.4 Temperatures Above the Neel Temperature (T>T_N) ................. 103
4.4.1 The Ordering Temperature (Neel Temperature) ................. 105
4.4.2 Susceptibility of an Antiferromagnetic at T<T_N .... 106
4.4.3 A More General Picture .... 108
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>The Exchange Interaction</td>
<td>112</td>
</tr>
<tr>
<td>4.6</td>
<td>Superexchange</td>
<td>115</td>
</tr>
<tr>
<td>4.6.1</td>
<td>Overlap of Half-Filled Orbitals</td>
<td>115</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Overlap of a Half-Filled Orbital with an Empty Orbital</td>
<td>116</td>
</tr>
<tr>
<td>4.6.3</td>
<td>Overlap of a Half-Filled Orbital with a Full Orbital</td>
<td>117</td>
</tr>
<tr>
<td>4.6.4</td>
<td>Interactions via Intermediary Anions</td>
<td>117</td>
</tr>
<tr>
<td>4.6.5</td>
<td>180° Cation-Anion-Cation Interactions</td>
<td>118</td>
</tr>
<tr>
<td>4.6.6</td>
<td>90° Cation-Anion-Cation Interactions</td>
<td>120</td>
</tr>
<tr>
<td>4.7</td>
<td>Diamagnetic Correction</td>
<td>121</td>
</tr>
<tr>
<td>4.8</td>
<td>References</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>High Resolution Powder Diffractometer (HRPD)</td>
<td>125</td>
</tr>
<tr>
<td>5.2</td>
<td>Target Station</td>
<td>128</td>
</tr>
<tr>
<td>5.3</td>
<td>Moderators</td>
<td>131</td>
</tr>
<tr>
<td>5.4</td>
<td>HRPD Diffraction Peak Shapes and Resolution</td>
<td>134</td>
</tr>
<tr>
<td>5.5</td>
<td>Crystal Structure Determination</td>
<td>136</td>
</tr>
<tr>
<td>5.6</td>
<td>Bragg's Law</td>
<td>138</td>
</tr>
<tr>
<td>5.6.1</td>
<td>Single Crystal Diffraction</td>
<td>138</td>
</tr>
<tr>
<td>5.6.2</td>
<td>Powder Diffraction</td>
<td>139</td>
</tr>
<tr>
<td>5.6.3</td>
<td>The Intensity of Bragg Reflections</td>
<td>139</td>
</tr>
<tr>
<td>5.7</td>
<td>Structure Within the Unit Cell</td>
<td>141</td>
</tr>
<tr>
<td>5.7.1</td>
<td>Structure Factors in Diffraction: the Effect of Thermal Motion</td>
<td>141</td>
</tr>
<tr>
<td>5.8</td>
<td>Diffraction with X-Rays</td>
<td>145</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page No</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>5.9</td>
<td>Experimental Neutron Scattering</td>
<td>147</td>
</tr>
<tr>
<td>5.9.1</td>
<td>Analysing Powder Diffraction Spectra</td>
<td>148</td>
</tr>
<tr>
<td>5.9.2</td>
<td>The Integrated Intensity in a Time of Flight Peak</td>
<td>148</td>
</tr>
<tr>
<td>5.10</td>
<td>The Excitations in Itinerant Magnets</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>155</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>157</td>
</tr>
<tr>
<td>6.2</td>
<td>Sample Preparation</td>
<td>160</td>
</tr>
<tr>
<td>6.3</td>
<td>Calibration of the VSM</td>
<td>160</td>
</tr>
<tr>
<td>6.4</td>
<td>Magnetisation of Dysprosium</td>
<td>163</td>
</tr>
<tr>
<td>6.5</td>
<td>Transition Metal Laves Phase Compounds</td>
<td>163</td>
</tr>
<tr>
<td>6.5.1</td>
<td>Mn$_2$Ti Structure</td>
<td>165</td>
</tr>
<tr>
<td>6.5.2</td>
<td>Mn$_2$Hf</td>
<td>172</td>
</tr>
<tr>
<td>6.5.3</td>
<td>Mn$_2$Zr</td>
<td>176</td>
</tr>
<tr>
<td>6.5.4</td>
<td>Mn$_2$Nb</td>
<td>177</td>
</tr>
<tr>
<td>6.6</td>
<td>Heusler Alloy Compounds</td>
<td>184</td>
</tr>
<tr>
<td>6.6.1</td>
<td>Pd$_2$MnIn</td>
<td>184</td>
</tr>
<tr>
<td>6.6.2</td>
<td>Ag$<em>{0.4}$Pd$</em>{1.6}$MnIn and Au$<em>{0.8}$Pd$</em>{1.2}$MnIn</td>
<td>186</td>
</tr>
<tr>
<td>6.6.3</td>
<td>Pd$_2$XnIn</td>
<td>186</td>
</tr>
<tr>
<td>6.7</td>
<td>Neutron Powder Diffraction</td>
<td>195</td>
</tr>
<tr>
<td>6.7.1</td>
<td>The (HRPD) Measurements on Heusler Alloys</td>
<td>195</td>
</tr>
<tr>
<td>6.8</td>
<td>Effects of Annealing Processes on the Hysteresis Loop of Fe-Ni Invar Alloys</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>208</td>
</tr>
<tr>
<td>7</td>
<td>DISCUSSION AND CONCLUSION</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>APPENDICES</td>
<td>218</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to express my warmest thanks to my supervisor, Professor Kurt Ziebeck, for his constant guidance and assistance and I am indebted to him for his most cooperative interest and help with this work.

I would also like to thank Dr David Williams for his constant guidance.

My thanks also to the other members of the research group, particularly Dr Klaus Neumann and Dr Dick Visser for many useful discussions. I would especially like to thank all the other past members of the research group as well as the present members.

Many of the technical staff of Loughborough University Physics Department deserve special mention for their cooperation and help.

I would like to thank my family for their constant inspiration and encouragement.

Janet Smith is also thanked for typing this thesis.

Finally, I would like to acknowledge the Ministry of Higher Education in Iraq for financial support, without which I could not have carried out my research.
ABSTRACT

A versatile and sensitive magnetometer has been developed and constructed. The design was based on the concept of a vibrating sample magnetometer originally suggested by S. Foner. A novel pick-up coil arrangement has been installed which minimises noise arising from mechanical vibrations of the magnet assembly or lateral movements of the sample. Consequently the magnetometer can be used not only for materials which have a spontaneous magnetisation, but also for weak paramagnetic specimen e.g. $10^{-6}$ emu/g. Currently the magnetometer is based on an electromagnet which enables a magnetic field up to (11 kG) to be applied to the specimen. However the design is such that it could be easily adaptable to fit into a cryomagnet so that higher field strengths can be used. The whole specimen assembly can be rotated about a vertical axis enabling any directional dependence of a specimen's magnetisation to be investigated. An Oxford Instruments flow cryostat enables temperatures between 2 and 300K to be achieved. The magnetometer is fully automated and controlled by a Commodore computer. This enables both magnetic field and temperature to be programmed so that once the sample has been installed the measurements can be carried out without manual intervention. The results are stored on a floppy disc and a hard copy listing is provided. All the results can be transferred to the mainframe computer which enables plots and manipulation of the data to be carried out. To demonstrate the versatility of the VSM a series of different experiments were undertaken. In these studies the magnetic hystereses, isotherms or the paramagnetic susceptibilities of materials containing transition metal atoms were investigated. Selection of the materials studied was based on current interest but included systems exhibiting invar behaviour spin fluctuations and spin glass behaviour. Preliminary measurements have also been undertaken on a new series of Heusler alloys containing rare earth elements and which are believed to be both magnetic and superconducting.
Recently the research into the properties of intermetallic compounds containing either transition or rare-earth elements has increased significantly due to the availability of high purity materials and the discovery of a wealth of new physical phenomena e.g. the co-existence of magnetism and superconductivity.

Transition metals have partially filled d shells which give rise to magnetic behaviour. Dependent upon the degree of overlap of the wave functions the magnetic properties will either have localised or itinerant behaviour. The degree of overlap can be varied by choosing alloys with different separation of the transition metal atoms. The rare earth systems are characterised by a partially filled 4f-electron shell. Apart from the special case of a half filled f-electron shell the unfilled f-electron level will give rise to a magnetic moment which in solids is well localised on the rare earth atom. The interaction between magnetic moments causes a variety of magnetic phenomena in the rare earth elements and their compounds. In addition to the purely magnetic effects an interaction between the magnetic degrees of freedom and the lattice degrees of freedom also leads to phenomena such as magnetostriction.

The work in this thesis is concerned primarily with ions in metals whose magnetic properties arise from electron spin and not from the orbital motion of the electrons. This situation occurs whenever the orbital motion of the electron responsible for the magnetic properties interacts strongly with the crystalline field of the lattice and the
orbital motion is therefore suppressed or 'quenched'. This tends to happen in transition metals whose d-electrons are not significantly screened by the outer electrons from the crystalline field. On the other hand, for rare earth ions whose magnetic properties arise from the more effectively screened f-shell quenching does not normally occur. In gadolinium, however, the ion itself is in a S-state and so has no orbital angular momentum and therefore its magnetic properties arise from spin contribution alone.

Transition metal compounds provide good systems for studying 3d magnetism. By suitable choice of compounds it is possible to investigate localised 3d magnetism (Heisenberg model) as well as itinerant electron magnetism (band model) in metals. Nearly all the properties of these materials depend, either directly or indirectly, on the electronic system.

Band theory accounts for the ground state properties of metallic systems, in particular their non-integral magnetic moments. In this model the exchange interaction between Bloch states gives rise to an imbalance of up and down spins thus producing a nett magnetic moment. However, band theory is less successful at finite temperature, particularly in accounting for the thermal variation of the bulk susceptibility. The strong thermal variations of many physical properties are easier to describe using a localised model. Consequently the inclusion of many body effects are required in order to account for these observations.

In localised models, the magnetism can usually be discussed by concentrating on the magnetic degrees of freedom of a free ion or by using an effective spin Hamiltonian. For itinerant (delocalised)
magnets, however, the possibility of the electrons to move around relatively freely through the crystal lattice means their wave functions are delocalised and thus translational degrees of freedom cannot be separated from their magnetic degrees of freedom, making a Heisenberg description inadequate. The delocalised wave function for the 3d type electrons are characterised by a band structure with a bandwidth $W$, which for the 3d electron (which carries the magnetism) is typically of the order $W = 5$ eV. The degree of overlap of d wave functions may be controlled by choosing a specimen in which the separation of the magnetic atoms are different or can be systematically varied; the radial extent of 3d functions is typically of the order 1-2Å. The magnetic and lattice degrees of freedom are closely related through several properties such as volume, structure and elasticity. These effects arise from the interatomic cohesive forces through the exchange interaction.

In this thesis it was our intention, with the aid of modern apparatus, to investigate and study the systematics of magnetic materials with a view to determining the relative proximities of the materials to the delocalisation boundary. An automated VSM was considered to be the most suitable apparatus for this study as it provided a wide range of versatility for measuring both magnetisation and susceptibility.

The existence of localised moments can be inferred from the magnitude of the susceptibility and from its temperature dependence. During this research a number of Laves phases compounds were investigated because the Laves phases structure represents a simple crystallographic arrangement in which to study the stability of the manganese moment. The magnetic properties of a new series of Heusler alloys based on the composition $\text{Pd}_2\text{XIn}$ ($\text{X} = \text{rare earth element}$) were also investigated.
Previous work has shown that alloys in the related series Pd$_2$XSn [1] are magnetic and superconducting at low temperatures i.e. <4K. The work concerned the preparation and characterisation of the structural and magnetic properties of these compounds. As an example of the variation due to a systematic heat treatment on the spontaneous magnetisation, we have selected the Fe-Ni alloys system. The most interesting of these compounds, Fe$_{65}$Ni$_{35}$, has an anomalously small thermal expansion below the Curie temperature. This phenomenon is known as the Invar effect and has been studied extensively. For alloys in the Fe-Ni system, local fluctuations in composition resulting in a heterogeneous magnetisation are believed essential for the Invar effect. The heat treatment led to a rearrangement of the atoms and caused an increase in the atomic short-range order, in agreement with other studies. Theoretical calculations for Fe-Ni alloys show important changes in magnetic properties can occur due to local environmental effects. In the present work a systematic study of the hysteresis loop as a function of magnetic field was made for Fe-Ni alloys with compositions 22 and 50 at % Ni without heat treatment and after annealing.

Finally, frustration of antiferromagnetism on a fcc lattice has been investigated by looking at field cooling effects on the susceptibility, of Pd$_2$MnIn alloys. Early measurements of the susceptibility and neutron diffraction studies suggest that the antiferromagnetic structure which occurs below 140°K is frustrated. This hypothesis is strengthened by the fact the magnetic structure is sensitive to the degree of chemical order. In general any antiferromagnetic structure on a fcc lattice must, in principle, be frustrated. Measurements were therefore undertaken on two compounds with the L2$_1$ structure namely Ag$_{0.4}$Pd$_{1.6}$MnIn and Au$_{0.8}$Pd$_{1.2}$MnIn. Both these materials order with the antiferromagnetic AF2 structure below 140°K.
The contents of the thesis are as follows. Chapter 2 includes a brief discussion of the basic theory of magnetism, and the magnetic properties of materials.

Chapter 3 is concerned with the experimental details and equipment used in this work. It includes a description of the principles of vibrating sample-magnetometers (VSM). This chapter also includes a description of the motion of a spin in a magnetic field, and a measurement of magnetisation is also reported in this chapter.

In Chapter 4 are some relevant theories of magnetism.

Chapter 5 describes the theoretical work that provides the background for pulsed neutron scattering.

The results obtained for Laves phase compounds, Heusler alloys and Fe-Ni alloys are reported in Chapter 6.

In Chapter 7, the discussion and conclusions of the results of Chapter 6 are given.

REFERENCES

2.1 BASIC MAGNETIC PROPERTIES OF MATERIALS

In its simple form, band theory states that materials with full bands are insulators, or semiconductors, while those with only partially filled bands are metals, or semi-metals. Band theory also predicts that this should remain the case even if the atoms of the material are greatly separated. The conduction electrons will become heavy and less mobile, but the material will remain metallic down to zero temperature.

Intuitively, this must be wrong and indeed, with this scheme, many compounds known to be insulators should be metallic, such as $3d^7$-CoO, which has a partially filled cobalt 3d band.

The insulating behaviour of these compounds derives from an electron-electron correlation energy. This provides a barrier to electron mobility, and disrupts the simple band picture in which electrons occupy itinerant Bloch states. An alternative picture is of electrons which are localised, in real space, on atomic sites, but with the provision that they can 'hop' from site to site, if the wave function overlap, and hence the bandwidth is sufficiently large. It is also assumed that the intrasite, interelectron correlations are sufficiently small within this framework. The most widely used model is the Hubbard model [Hubbard 1963-1964] [1,2] whose Hamiltonian is...
It is characterised by the two parameters $t_{ij}$ and $U$. The former is a kinetic energy term, and denotes the hopping of an electron from a site $i$ to a site $j$. It is normally taken to be zero, unless $i$ and $j$ are nearest neighbours. The latter denotes the extra energy required to place two electrons of opposite spin on the same site. $a_{j\sigma}^+(a_{i\sigma})$ is the creation (annihilation) operator for an electron, of spin $\sigma$, on site $j(i)$, and $n_{i\sigma}$ is the number operator for an electron of spin $\sigma$, on site $i$. The hopping integral is defined as:

$$H = \sum_{i,j,\sigma} t_{ij} a_{j\sigma}^+ a_{i\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$  \hspace{1cm} (2.1)$$

where $\phi_i$ is an atomic wave function, and is related directly to the parent (zero correlation) bandwidth. Since the band energy of a free electron is given by

$$\varepsilon(K) = \sum_{i} t_{ij} \exp(iK (R_i-R_j))$$  \hspace{1cm} (2.3)$$

It follows that the parent bandwidth, $W$, is just

$$W = 2Z t_{ij}$$  \hspace{1cm} (2.4)$$

where $Z$ is the coordination number. The correlation term, $U$, is essentially just an ionization potential, as an electron is removed from a donor atom, minus an electron affinity, as it is placed on a neighbouring acceptor atom, these being no longer equal when we are away from the electron limit. Conversely $U$ is much reduced from the free ion value.
In a system of zero correlations, the probability of a given site being occupied by zero electrons, one electron (twice), or two electrons are all 0.25, but as correlations are increased, double occupancy becomes unstable with respect to single occupancy, and one may regard the original band as being split into two sub-bands by the correlation energy. The separation increases with correlation, until an insulating state occurs, with the lower sub-band full and the upper empty. This occurs at $U-W$. The progression through increasing $W/U$ is shown in Figure 2.1, although the physical meaning of such a band structure of energy versus $K$ is unclear in the localised limit, indeed $K$ may not remain a good quantum number throughout the process [Wilson 1972] [3].

There are two obvious limiting cases to be considered. In the limit of $t_{ij} \gg U$, the ground state is metallic, while in the opposing limit, the ground state is that of an antiferromagnetic insulator. The antiferromagnetic coupling energy gives a Neel temperature, $T_N$, of

$$T_N = \frac{Z t_{ij}^2}{k_B U}$$

(2.5)

where $k_B$ is Boltzmann's constant. Above the Neel temperature, however, $k_B T$ is still well short of the electron excitation energy gap, of order $U$, and so the insulating state gives rise to a Curie-Weiss situation of interacting local moments, without long range order. Indeed, the existence of magnetic insulators can be viewed as evidence of localisation, since band insulators and semiconductors can have no net spin.

The most common approach used when investigating the properties of materials as one traverses between the above limits is the one-body approximation, see, for example, Cyrot, 1982 [4], Cyrot and Lacour
Figure (2.1): Hubbard-type model for description of carrier formation and movement, for a system based on a half-filled non-degenerate one electron band, in the presence of a uniform band splitting energy U. (a) Mott insulator with Hubbard gap $E_H$ and average separation U between sub bands. (b) Semi-metallic through overlap of Hubbard bands. (c) The free electron limit, $U=0$. 

2.2 THE ONE-BODY APPROXIMATION

Cyrot, 1972, took equation (2.1) and investigated the effect of altering the ratio $U/Zt_{ij}$ ($U/W$), on both the magnetic, and the insulating properties. Briefly, the route taken was to separate the last term in equation (2.1) into the contributions from charge and magnetisation, thus:

$$U_{ni^+} n_i^- = -\frac{U}{4} [n_{i^+} - n_{i^-}]^2 + \frac{U}{4} [n_{i^+} + n_{i^-}]^2$$

(2.6)

Assuming that charge fluctuations were unimportant, and replaceable by a constant, the magnetic fluctuations in the above were replaced by:

$$\sum_i \frac{U}{2} u_i(\tau) [n_{i+}(\tau) - n_{i^+}(\tau)]$$

(The reader is referred to Appendix A of Cyrot (1972)). Neglecting the time dependence, the Hamiltonian for one spin becomes:

$$H = \sum_{ij} t_{ij} a_i^+ a_j + \frac{\gamma}{2} - \frac{u}{2} m_i n_i$$

(2.7)

The moment being determined by

$$m_i = \langle n_{i^+} \rangle - \langle n_{i^-} \rangle$$
In the antiferromagnetic phase, it was assumed that [4]:

$$m_i = m \exp(i P \cdot R_i)$$

where $P$ is one half of a reciprocal lattice vector of a numerical solution for $m_i$. The results are shown in Figure (2.2). The zero temperature prediction is that there are three successive phases as $U/Zt_{ij}$ is increased. At a value of $U/Zt_{ij} = 0.36$ localised moments occur on the sites, but the material remains metallic. As correlation is further increased the system becomes insulating at $U/Zt_{ij} = 0.56$ (the value quoted are for f.c.c. systems). Also it is calculated, that the magnetic moment is non-integral, even in the insulating phase, $m_i$ tending to the atomic limit only as $U/Zt_{ij}$ tends to infinity.

Economou et al (1978) [6] in making studies of the Hubbard model at finite temperatures obtained (for weak correlation) the diagram in Figure (2.3). The system is a normal metal, being Pauli paramagnetic in the region marked p.p.m. As correlations are increased the system remains metallic, but acquires local moments, which may order at sufficiently low temperatures, for example. FeS is antiferromagnetic below its Neel temperature of 600K. This region is denoted C.W.M. As correlations are further increased, there is a transition to an antiferromagnetic insulator, A.F.I. within this region. If the temperature is increased, long range order will disappear at $T_N$, as one enters the other insulating region, I. As noted earlier in equation (2.5), this Neel temperature decreases, as $U$ increases.
Figure (2.2): Value of local magnetic moment as a function of the ratio \( u/w \) (Cyrot (1972)).
Figure (2.3): A schematic phase diagram for the Hubbard model in the temperature \((kT/t)\) and correlation \((U/Zt)\) plane, after de Marco et al. (1978). Phases shown are Pauli paramagnetic metallic (PPM), metallic with moments (CWM), antiferromagnetic insulator (AFI), and insulating (I).
2.3 THE GUTZWILLER APPROXIMATION

Another method that has been employed in predicting behaviour as correlation are progressively varied is that due to Gutzwiller (1965) [7], and Brinkman and Rice (1970) [8]. Here, the ground state wave function is approximated as

$$\psi_G = \pi_1 [1 - (1-g) n_{i\downarrow} n_{i\uparrow}] \psi_F$$  \hspace{1cm} (2.8)

where $\psi_F$ is the free electron wave function. The components that represent the double occupancy of sites is reduced by the introduction of $0 < g < 1$. Obviously, $g = 1$ corresponds to the zero correlation limit, where $g = 0$ corresponds to the high correlation limit, giving no double occupancy.

Brinkman and Rice (1970) [8] applied the problem to the metal-insulator transition for the case of one electron per atom, and found that the effective mass of the electrons, and the susceptibility diverge as $[1 - U/U_c]^{-1}$, where $U_c$ is the critical correlation energy needed to achieve delocalisation (and is approximately equal to the single electron bandwidth).

The magnetic phases present within the Hubbard model have been investigated, using the above approximations by Anderiotis (1981) and Ole's (1982) [10] for example. Anderiotis, using a one body approximation investigated the magnetic phase in the range of the non-integral number of electrons per site of $0 < n < 1$, in an attempt to verify the finding of Liu (1978) of a spin glass ground state. His findings are summarised as follows. A large value of U favours a ferromagnetism phase except when n is close to zero (where
paramagnetism is favoured), and when \( n \) is close to one (where antiferromagnetism is favoured). This was first noted by Nagoaka (1966) [9] for b.c.c. and f.c.c. lattices. Low values of \( U \) favour the paramagnetic phase, except again near \( n = 1 \), where antiferromagnetic order is again favoured. A spin glass state was indeed found over quite a wide range of the \((U/w,n)\) plane. Ole's (1982) on the other hand, using a correlated ground state (Gutzwiller) approximation found no such spin glass ground state.

2.4 SOME CONSIDERATION OF THE RELEVANCE OF THESE MODELS TO REAL SYSTEMS

As stated earlier, the studies of Economou et al., in 1978 produced the phase diagram in Figure (2.3) and in fact this compares quite favourably with experimental phase diagrams obtained by McWhan and Remeika (1970) [10] for \( V_2O_3 \) doped with chromium and titanium (Figure 2.4). The addition of chromium effectively dilates the system, increasing \( U/Zt \), whereas the addition of titanium effectively compresses the system decreasing \( U/Zt \). However, there is at least one important difference, in that the observed transitions are first order, whereas the calculations indicated the transitions to be continuous. Mott (1949) [11] actually predicted a first order transition due to coulombic considerations.

2.5 ELECTRON HOLE ATTRACTION

Electrons in the upper of the two Hubbard sub-bands, Figure (2.1), and the equal number of holes in the lower, will have a longer range coulomb attraction leading to binding and thus insulation unless the coulomb potential is sufficiently screened. Mott (1949) [11] proposed that because of this, a small number of free electrons and holes is not possible.
FIG (2.4): phase diagram for the metal-insulator transition in \(V_2O_3\) as a function of doping with Cr or Ti and as a function of pressure, after McWhan et al. (1971).
The screened potential has the form

\[ V(r) = \left( \frac{e^2}{4\pi \epsilon_0 r} \right) \exp \left( -\frac{\lambda r}{T_F} \right) \]  

(2.9)

where \( T_F \) is the screening constant, and \( \lambda \) is the background dielectric constant. When a coulomb potential binds an electron, the ground state has the Bohr radius

\[ a_0 = \frac{4\pi \epsilon_0 \hbar^2}{me^2} \]  

(2.10)

If \( \lambda \) is smaller than \( a_0 \), the electron will not be bound. Taking the Thomas-Fermi screening length

\[ \lambda^2 = \frac{e^2}{T_F} \frac{m}{\pi \hbar^2} N^{1/2} \]  

(2.11)

here \( N \) is the density of ionized electrons, then

\[ N^{-1/3} > 4 a_0 \]

has to be fulfilled for the metallic state to exist, leading to a discontinuous drop in the free electron-hole density at this value to zero. Hence, due to coulombic interactions, the transition has become discontinuous or first-order.
2.5.1 Anderson Localisation

A point, known to be of relevance in doped systems, for example, TiSe$_2$ doped with vanadium (Figure 2.5), is carrier localisation due to disorder.

Anderson (1958) [12] considered an electron moving through a medium in which the potential energy of the sites, $\varepsilon_i$, varies randomly between limits, so that

$$-\frac{W_A}{2} < \varepsilon_i < \frac{W_A}{2}$$

The electrons tend to become trapped in the regions of lowest potential energy, but admixing can occur between localised states. If, however, $\varepsilon_i$ fluctuates appreciably, then states that are spatially close are unlikely to be energetically close, and vice versa. It is found, that admixture with other tight binding states, does not delocalise an electron trapped in a potential well. Provided

$$(t_{ij}/W_A) \ll 1$$  \hspace{1cm} (2.12)$$

However, the criterion depends on the electron energy, and Mott (1967) [13] recognised that the state in the tail of a band would be more easily localised than states more towards the centre of a band. This opens up the idea of a 'mobility edge', the movement of which, across the Fermi energy, as disorder increases, will produce a transition from a delocalised to a localised material. Mott termed this disorder induced transition, the Anderson transition.
Figure (2.5): Temperature dependences of electrical resistivity and Hall coefficient of Ti$_{0.94}$V$_{0.01}$Se$_2$. The sign of the Hall coefficient is positive above $T = 60$K and is reversed at low temperatures. The Hall coefficients measured at fields of 2 and 18kOe are shown, after Uchida et al. (1980).
2.5.2 Factors that Affect U and W

In a crystal, interactions between anions and cations generally produce itinerant s and p bands. The wave function mixing stabilises the anion states, while destabilising the cation states. Transition-metal compounds contain outer d electrons, which often fall into the energy gap between the occupied anion p band, and empty cation s band, and if these d electrons are localised, then an increase by a fluctuation in d orbital occupancy from \( d^n \) to \( d^{n+1} \) will cost an energy \( U \) as before. However, this \( U \) may be reduced in magnitude quite considerably from values in the ionic limit. In compounds which contain elements from the first part of the transition metal series, mixing occurs between cation s, p and d states. This extends the, primarily, d wave functions, and so lowers the intra-site electron repulsion. Also, the 'd' wave function \( f_r \) may mix with anion wave functions \( \phi_r \) of the same symmetry representation \( r \), so that the crystal field wave function \( \psi_r \) is:

\[
\psi_r = N (f_r - \lambda \phi)
\]  

(2.13)

where \( N \) is a normalisation constant, and \( \lambda \) is the mixing parameter

\[
\lambda = \frac{\text{tr}^{Ca}}{(E_{n+1} - E_p)}
\]  

(2.14)

where \( \text{tr}^{Ca} \) is the anion-cation transfer integral, and the denominator is just the energy difference between the final and initial states of an electron so transferred.

\[
\text{tr}^{Ca} = \langle \psi_r | H | \phi_r \rangle = \epsilon \langle \psi_r | \phi_r \rangle
\]  

(2.15)
where the perturbation of the ionic potential of the anion array by presence of the $d^n$ cations is represented by $H$ (see, for example, Goodenough, 1972) [14].

The parameter, $\lambda$, tends to extend the crystal field wave function over the anions, and for a given cation, will increase as $n$ decreases. So, $U$ will be largest when $(E_{n+1} - E_p)$ is largest. It follows that the most probable configuration for localisation is that of a cation of low formal valence, from towards the centre of a longer period, e.g. Mn$^{+2}$. Lighter transition metal cations of low formal valence may have wave functions extended by cationic hybridization (Goodenough, 1972) e.g. Ti$^{+2}$, while wave function of heavier cations may have large values of $\lambda$, e.g. Zr$^{2+}$.

As stated previously, (equation 2.4), the bandwidth due to the interaction between tightly bound d-orbitals is:

$$W = 2Z t_{ij}$$ 

(2.16)

where

$$t_{ij} = \langle \psi_i | H | \psi_j \rangle = \varepsilon_{ij} \langle \psi_i | \psi_j \rangle$$ 

(2.17)

So any bandwidth due to transition-metal/anion/transition metal type interactions increases as

$$W \sim 2Z \varepsilon_{ij} N^2 \lambda^2$$ 

(2.18)
It is also worth noting that if the ligand p band falls between the two Hubbard bands, then the breakdown of insulation results from a closing of the p-d charge transfer gap, rather than the full Mott-Hubbard gap.

The effect of electronegativity can be seen, for example, in the classic Mott insulator/metal system, NiS_{x}Se_{2-x}; 0 < x < 2 (see Figure 2.6 and Wilson (1985). NiSe_{2} is a metal, while NiS_{2} is an insulator, despite the shorter interaction distance in the sulphide. This is because the selenium P-states are energetically closer to the nickel d-states, than are the sulphur P-states, so there is greater bandwidth from p-d mixing in the selenide. Note, also, that the insulating sulphide can be made metallic by the application of a pressure of 32 kbar at 22°C.

2.6 TRANSITION METAL MAGNETISM

The transition metals are those which have partly filled shells of d-electrons in some, at least, of their compounds. With increasing atomic number, the elements progress from those with a non-magnetic ground state (Sc, Ti, V) via the antiferromagnets Cr and Mn to the ferromagnets Fe, Co and Ni. The 3d electrons which give rise to the magnetic properties of these transition metals lie at the Fermi surface [15] and are therefore free to move through the metal. This electron itinerancy distinguishes the magnetism of the 3d metals and their magnetic alloys from the localised magnetism of the transition metal insulating compounds, where the magnetic moments are due to the electrons with highly localised wave functions lying well below the Fermi surface. A good description of the ground state properties of itinerant ferromagnets is given by the band model of magnetism based
Figure (2.6): Electronic phase diagram for the Ni(S/Se)$_2$ system. (Wilson (1972)).
on the local density function theory of Hohenberg et al [16] which correctly predicts ferromagnetism in Fe, Co and Ni and yields non-integral magnetic moments which are observed experimentally.

At finite temperature the Stoner model predicts a transition to the paramagnetic state via the thermal repopulation of one-electron states. At the Curie temperature $T_c$, a Stoner ferromagnet should resemble an exchange enhanced Pauli paramagnet.

2.6.1 The Stoner Model for Itinerant Electrons

Although the Weiss theory was successful in being able to account for ferromagnetism via exchange interactions, when applied to the transition metal ferromagnets, iron, nickel and cobalt, it was unable to account for a moment which is a non-integral number of Bohr magnetons.

Stoner [17,18] realised that an atomic orbital description of an electron in a metallic magnet was inadequate, and that a better description of the magnetic electrons could be obtained if they were distributed in electron energy bands. His model has one immediate advantage in that an electron in a band state had no orbital momentum. Stoner's basic premise was to assume that the electrons in a metal formed a free electron gas (Pauli [19]) in which the interaction was taken into account by a Weiss molecular field. The introduction of the molecular field causes the band to split into sub-bands by an amount $\Delta_{ex}$ (called the exchange splitting).

Thus at $T = 0$ all the electron states within the band are occupied up to the Fermi energy, while those above are empty. There is therefore a
net excess population of electrons in one sub-band (the majority band) compared with the other (the minority band), resulting in a net magnetisation as shown in Figure (2.7).

As in the theory of Weiss [22], Stoner assumed the molecular field to be proportional to the magnetisation of the sample (i.e. to the difference in the number of electrons in the two sub-bands \( n_+ - n_- \)):

\[
\gamma M = \gamma (n_+ - n_-) \, u_B
\]

where \( \gamma \) is the molecular field constant. Thus the exchange splitting \( \Delta_{\text{ex}} \) is given by:

\[
\Delta_{\text{ex}} = E_+ - E_- = -\frac{1}{2} \, \gamma (n_+ - n_-) = \text{Im}
\]

(2.19)

where \( I \) is the Stoner parameter. By considering a state with magnetic moment \( m \) and density of state per spin at the Fermi level \( N(E_F) \), \( m \) can be related to the exchange splitting by:

\[
m = \Delta N(E_F)
\]

(2.20)

The total energy of the system with magnetic moment \( m \) is given by:

\[
U_{\text{fm}} = U_{\text{pm}} + \frac{m}{2} \left[ \frac{m}{2NaN(E_F)} \right] - \frac{\text{Im}}{4Na}
\]

(2.21)

where \( U_{\text{fm}}, U_{\text{pm}} \) are the energy of the ferromagnet and paramagnetic states respectively. Thus the ferromagnetic state is stable if
Fig. (2.7): Schematic representation of the exchange split band in a simple Stoner model. Thermal excitation of the electrons from the majority band to the minority band occur.
which is the famous Stoner criterion for ferromagnetism.

2.6.2 Finite Temperature and Excitation Mechanisms

Although the Stoner theory of ferromagnetism is applicable to itinerant metallic magnets, severe difficulties occur at finite temperature.

In the Weiss model, with increasing temperature the moments maintain the same amplitude, but become increasingly disordered, until the Curie temperature is reached and \( \langle M_z \rangle = 0 \). Thus, above the Curie temperature the paramagnetic state can be described by the thermal disordering of well defined atomic spins, resulting in a static susceptibility which follows a Curie-Weiss law given by:

\[
X = \frac{C}{T-T_c}
\]  

(2.23)

The properties of a Stoner magnet at finite temperature are remarkably different, at any given temperature \( T \) the probability \( P_i \) of any given electron state \( i \) being occupied is governed by Fermi-Dirac statistics.

\[
P_i = \frac{1}{\exp \left( \frac{E_i-E_F}{k_B T} \right) + 1}
\]  

(2.24)

with increasing temperature in the Stoner model, electrons from the majority band are thermally excited into the minority band, and the ferromagnetism is thus destroyed by the reduction of the exchange splitting.
The Curie temperature $T_c$ is then given by

$$T_c \sim \Delta_{\text{ex}}$$

(2.25)

Above the Curie temperature the system becomes a simple Pauli paramagnet, in which the static susceptibility is

$$\chi \propto \frac{T}{T_F}$$

(2.26)

where $T_F$ is the Fermi temperature.

The excitation spectrum at low temperature consists of two types of excitation which are the single particle or Stoner modes in which just an excitation is shared by all the electrons. The single particle excitations which correspond to transitions from a spin-up to spin down band, form a continuum (the Stoner continuum).

Excitations with small or vanishing energy transfer $\omega$, are in general possible for finite momentum transfer $Q$ only; single particle excitations with zero momentum transfer ($Q=0$) cost a finite amount of energy, the exchange splitting $\Delta_{\text{ex}}$. The fact that no single particle excitations for small $Q$ and $\omega$ exist, leads to well defined collective excitations in that region, i.e. spin-waves in the ground state. For large $Q_o$, the spin waves enter the single particle continuum and become damped and therefore disappear as shown in Figure (2.8).

At finite temperature the atomic moments can themselves fluctuate and it is these fluctuations that are responsible for the phase transition from the ordered ferromagnetic state to disordered paramagnetic state.
Fig. (2.8) Spin wave spectra of an itinerant magnet. The spin-waves enter the Stoner continuum of single particle excitations and become overdamped.
The paramagnetic effects arise due to a coupling of the electron spin with the applied field (Pauli paramagnetic susceptibility). All substances have a basic diamagnetic term but it is always weak and it is very often masked by a much larger (positive) paramagnetic susceptibility. The basic diamagnetism is independent of temperature and is due to the effect of applied magnetic fields on the motion of inner electrons of the atoms [20]. The Pauli susceptibility is small and comparable to the diamagnetic contribution. In this section an expression for the Pauli susceptibility will be derived up to linear order in the magnetic field and up to quadratic order in temperature. The temperature independent part of the Pauli paramagnetic susceptibility is given by [21]:

\[ \chi = \mu_B^2 D(E_F) \text{ for } T = 0 \] (2.27)

where \( \mu_B \) = Bohr magneton

\[ D(E_F) = \text{density of states}. \]

Thus the susceptibility is proportional to the density of electron states at the Fermi level.

The magnetisation is determined by the difference in the number of magnetic moments pointing up and down. If there is a net number of moments pointing up, a macroscopic magnetic moment per volume element is observed [22]:

\[ M = - \mu_B (n_+ - n_-) \] (2.28)
where \( n_+ = \text{number of magnetic moment up electrons} \)

\( n_- = \text{number of magnetic moment down electrons}. \)

If for \( B = 0 \) the density of states is given by \( D(E) \), then with a magnetic field we have:

\[
D_+(E) = \frac{1}{2} D(E - \mu_B B)
\]

\[
D_-(E) = \frac{1}{2} D(E + \mu_B B)
\]

(2.29)

where \( \mu_B B \) is energy of electrons in the magnetic field \( B \).

The number of electrons is determined by [23]:

\[
n_{\pm} = \int \frac{dE}{\infty} D(E). f(E)
\]

\( f(E) \) being the Fermi-Dirac function is given by [24]:

\[
f(E) = \frac{1}{e^{(E-\mu)/\beta} + 1}
\]

(2.30)

where \( \beta = \frac{1}{k_B T} \)

\( k_B = \text{Boltzmann constant} \)

\( \mu = \text{the chemical potential}. \)

The chemical potential has to be adjusted such that the number of electrons is the same with and without a magnetic field. Because the shift due to \( \mu_B B \) is small, we can expand the density of states in terms of this small parameter:
This yields results in a number of electrons of:

\[ n = \frac{1}{2} \int_{-\infty}^{\infty} dE \, D(E) \, f(E) + \frac{1}{2} \mu_B B \int_{-\infty}^{\infty} dE \, D'(E) \, f(E) \]  

(2.32)

The first term \( \frac{1}{2} \int_{-\infty}^{\infty} dE \, D(E) \, f(E) \) is half the total number of electrons without a magnetic field. As \( \mu_B B \) is a small parameter the linear order is sufficient:

\[ n_+ + n_- = \int_{-\infty}^{\infty} dE \, D(E) \, f(E) \]  

(2.33)

The behaviour of the magnetisation is quite simple to understand from the temperature dependence of the Fermi function itself. The increase in energy of the electron when the temperature is raised from \( T = 0 \) comes about entirely because some electrons with energies within \( O(K_B T) \) below the Fermi energy \( (E_F) \) (the 'a' region of Figure 2.9) have been excited to an energy range of \( O(K_B T) \) above \( (E_F) \) (the 'b' region of Figure 2.9). The number of electrons per unit volume that have been so excited is the width \( K_B T \) of the energy interval times the density of states per unit volume \( D(E_F) \). Furthermore the excitation energy is of the order \( K_B T \), and hence the total thermal energy density is of the order \( D(E_F)(K_B T)^2 \). In Figure (2.9) the Fermi function \( f(E) \) is plotted at \( T = 0 \) and at room temperature for typical metallic densities \( (K_B T/\mu = 0.01) \). Evidently \( f \) differs from its zero temperature form only in a small region about \( \mu \) of width of a few \( K_B T \). Thus the way in which integrals of the form...
Figure (2.9): The Fermi Function at non-zero $T$. The distribution differs from its $T=0$ form because some electrons just below $\varepsilon_F$ (a region) have been excited to levels just above $\varepsilon_F$ (b region).
\[
\int_{-\infty}^{\infty} H(E) f(E) \, dE
\]
differ from their zero-temperature values

\[
\int_{-\infty}^{E_f} H(E) \, dE
\]
will be determined by the form of \( H(E) \) near \( E = \mu \).

The Sommerfeld expansion is applied to integrals of the form \( [2] \)

\[
\int_{-\infty}^{\infty} H(E) f(E) \, dE
\]
(2.34)

where \( f(E) \) is 'fermi function' equation (2.30).

Define

\[
K(E) = \int_{-\infty}^{E} H(E') \, dE'
\]
(2.35)

take the derivative of equation (2.35) with respect to \( E \)

\[
\frac{d}{dE} K(E) = \frac{d}{dE} \int_{-\infty}^{E} H(E') \, dE'
\]

\[
\frac{dK(E)}{dE} = H(E)
\]
(2.36)

By integrating equation (2.34) by parts:

\[
\int_{-\infty}^{\infty} \left( \frac{dK}{dE} \right) f(E) \, dE = K(E) f(E) \bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} K(E) f'(E) H(E)
\]
(2.37)

34
The first term vanishes at $+\infty$ because the Fermi function $= 0$ and at $-\infty$ because $K = 0$.

Take the Taylor expansion of $K(E)$ about $E = \mu$. $\frac{\partial f}{\partial E}$ is essentially different from zero only in the neighbourhood of $E = \mu$. It gives sharp peaks but $K$ does not change at that region.

$$K(E) = K(\mu) + \left. \frac{dK}{dE} \right|_{E=\mu} (E-\mu) + \frac{1}{2} \left. \frac{d^2K}{dE^2} \right|_{E=\mu} (E-\mu)^2$$  \hspace{1cm} (2.38)

If we re-express $K$ in terms of the original function $H(E)$ equation (2.35) we find that

$$\int_{-\infty}^{\infty} H(E)f(E) dE = \int_{-\infty}^{\infty} H(E) dE + \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{(E-\mu)^{2n}}{(2n)!} (-\frac{\partial f}{\partial E}) dE \frac{d^{2n-1}}{dE^{2n-1}} H(E) \bigg|_{E=\mu}$$  \hspace{1cm} (2.39)

Using equations (2.28) and (2.32) we obtain

$$M = \mu B^2 \int D'(E) f(E) dE$$

$$= \mu B^2 \int dE \left\{ \frac{d}{dE} (D(E) f(E) - D(E).f'(E)) \right\}$$

$$= \mu B^2 \int dE D(E) \left( -\frac{\partial f}{\partial E} \right)$$  \hspace{1cm} (2.40)

The Fermi distribution in a step function at $T = 0$ so

$$-\frac{\partial f}{\partial E} = \delta(E - E_F) \text{ with } M = \mu B^2 D(E_F)$$
Corrections at finite temperature are of the order:

\[
\frac{(k_B T)^2}{E_F}
\]  

(2.41)

The susceptibility takes the form:

\[
\chi = \mu_B^2 D(E_F) \text{ [Pauli paramagnetic susceptibility].}
\]

put \( \frac{E - \mu}{k_B T} = x \) in equation (2.39)

Then the result is

\[
\int_{-\infty}^{\infty} H(E) f(E) dE = \left[ \int_{-\infty}^{\infty} H(E) dE + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \frac{d}{dE^{2n-1}} H(E) \right]_{E=\mu}
\]

(2.42)

where \( a_n \) are dimensionless numbers given by

\[
a_n = \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!} \left(- \frac{d}{dx} \frac{1}{e^{x+1}}\right) dx
\]

(2.43)

It can be written in terms of the Riemann zeta function, \( \zeta(n) \), as

\[
a_n = (2 - \frac{1}{2^{2(n-1)}}) \zeta(2n)
\]

(2.44)

where \( \zeta(2n) = 2^{2n-1} \frac{\pi^{2n}}{(2n)!} B_n \)

(2.45)

\( B_n \) here are known as Bernoulli numbers [25].
In most practical calculations in metals physics, one rarely needs to know more than

\[ \zeta(2) = \frac{\pi^2}{6} \]  \hspace{1cm} (2.46)

According to this result equation (2.42) becomes

\[ \int_{-\infty}^{\infty} H(E)f(E)dE = \int_{-\infty}^{\mu} H(E)dE + \frac{\pi^2}{2} \frac{2}{6} (k_B T)^2 D'(\mu) \]  \hspace{1cm} (2.47)

Now if B = 0, the total number of electrons is

\[ n = \int_{-\infty}^{\infty} D(E) f(E) dE \]  \hspace{1cm} (2.48)

By using equation (2.48) we find

\[ n = \int_{-\infty}^{\mu} D(E) dE + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) \]  \hspace{1cm} (2.49)

\[ E_F \neq \mu \text{ for } T = 0 \text{ where } E_F = \text{Fermi energy.} \]

\[ n = \int_{-\infty}^{E_F} D(E) dE + \int_{E_F}^{\mu} D(E)dE + \frac{\pi^2}{6} (k_B T)^2 D'(E_F) \]  \hspace{1cm} (2.50)
The first term = n at T = 0, n is independent of temperature. The second term is \( D(E) \) \((\mu - E_F)\), but \( n = \text{const} \), this leads us to

\[
(\mu - E_F) \cdot D(E) + \frac{\pi^2}{6} (k_B T)^2 D'(E_F) = 0 \tag{2.51}
\]

After arrangement of equation (2.51) and divide by \( D(E_F) \) we find

\[
\mu = E_F - \frac{\pi^2}{6} (k_B T)^2 \frac{D'(E_F)}{D(E_F)} \tag{2.52}
\]

which determines the deviation of the chemical potential from \( E_F \).

The number of electrons at \( B \neq 0 \) is given by (2.32). From equation (2.50) we find that

\[
n_+ = \frac{1}{2} \left\{ \int_{-\infty}^{E_F} D(E) dE + D(E_F) (\mu - E_F) + \frac{\pi^2}{6} (k_B T)^2 \frac{D'(E_F)}{D(E_F)} \right\}
\]

\[
- \frac{1}{2} \mu_B B \left\{ \int_{-\infty}^{E_F} D'(E) \; dE + D'(E_F) (\mu - E_F) + \frac{\pi^2}{6} (k_B T)^2 D''(E_F) \right\} \tag{2.53}
\]

\[
n_- = \frac{1}{2} \left\{ \int_{-\infty}^{E_F} D(E) \; dE + D(E_F) (\mu - E_F) + \frac{\pi^2}{6} (k_B T)^2 \frac{D'(E_F)}{D(E_F)} \right\}
\]

\[
+ \frac{1}{2} \mu_B B \left\{ \int_{-\infty}^{E_F} D'(E) \; dE + D'(E_F) (\mu - E_F) + \frac{\pi^2}{6} (k_B T)^2 D''(E_F) \right\} \tag{2.54}
\]
The total magnetic moment is given in equation (2.28). Substituting from equations (2.53) and (2.54) in equation (2.28) we get

\[ M = + \mu_B^2 B \left\{ \int_{-\infty}^{E_F} D'(E) \, dE + D'(E_F) \, (\mu - E_F) + \frac{\pi^2}{6} (K_{BT})^2 \, D''(E_F) \right\} \]  

(2.55)

\[ = \mu_B^2 B \left\{ D(E_F) + D'(E_F) \, (\mu - E_F) + \frac{\pi^2}{6} (K_{BT})^2 \, D''(E_F) \right\} \]  

(2.56)

\[ = \mu_B^2 B D(E_F) \left\{ 1 + (\mu - E_F) \, \frac{D'(E_F)}{D(E_F)} + \frac{\pi^2}{6} (K_{BT})^2 \, \frac{D''(E_F)}{D(E_F)} \right\} \]  

(2.57)

But from equation (2.52)

\[ \mu - E_F = - \frac{\pi^2}{6} (K_{BT})^2 \frac{D'(E_F)}{D(E_F)} \]  

(2.58)

By substituting from equations (2.27) and (2.58) into equation (2.57) we get

\[ M = \mu_B^2 D(E_F) \cdot B \left\{ 1 - \frac{\pi^2}{6} (K_{BT})^2 \left[ \left( \frac{D'(E_F)^2}{D(E_F)} \right) - \frac{D''(E_F)}{D(E_F)} \right] \right\} \]  

(2.59)

\[ \chi_0 = \mu_B^2 D(E_F) \]

Divide equation (2.59) by B
\[ \chi(T) = \chi(0) \left[ 1 - \frac{e^2}{2} (k_B T)^2 \left[ \left( \frac{D'(E_F)}{D(E_F)} \right)^2 - \frac{D''(E_F)}{D(E_F)} \right] \right] \] (2.60)

where \( D(E_F), D'(E_F), D''(E_F) \) are the derivatives of the density of states at the Fermi level \( E_F \).

Equation (2.60) represents the formula with which to correct the Pauli susceptibility if \( E_F \gg k_B T \). The susceptibility of a free-electron is essentially independent of the temperature but correction for diamagnetism is necessary. The diamagnetic effect of the ion core increases considerably as the atomic number increases although it remains relatively small. Thus we obtain for the temperature dependent susceptibility in the lowest approximation.
REFERENCES


3.1 INTRODUCTION

During the course of this work a vibrating sample magnetometer was used to investigate the magnetic properties of the samples. A (VSM) is an apparatus in which a sample is vibrated perpendicular to a uniform magnetic field and the induced emf in a set of coils provides information about the magnetisation of the sample under investigation. For example, hysteresis loop experiments provide information concerning the magnetisation process in a magnetic field.

In general the apparatus can be used for a wide range of studies with only minor modifications. These differences will be discussed when the main parts of the apparatus are described later. The usual methods of measuring (magnetisation or susceptibility) can be divided into three major classes [1]:

1. Measurement of a force on a material in a non-uniform magnetic field.
3. Indirect measurement of phenomena which involve the magnetic properties e.g. magnetostriction, magnetic caloric effect, etc.

The force method is a sensitive technique which has been employed at Loughborough University to measure susceptibilities. With this method it is, of course, difficult to observe the magnetisation in a truly
uniform magnetic field since a field gradient is essential to produce a force on the sample. Objections to the use of the force method for magnetic measurement of highly anisotropic materials have recently been raised by Wolf [2].

The use of vibrating sample magnetometers (VSM) for the determination of magnetic properties of materials is now well established. Early VSM's have been described by Blackett (1956) [3], Van Oosterhout (1956) and Foner (1956) which were suitable for the detection of magnetic moments induced in samples exposed to an external magnetic field. The first detailed description of a VSM was given by Foner (1956-1959) and his original design has now become generic to many subsequent VSM's. All VSM's have at least two common features, a transducer mechanism to impart stable periodic vibration to the sample under investigation and a stationary assembly of detection coils. The time-dependent external field arising from the vibration of the magnetic moment induces an emf in the coils providing that the net instantaneous flux change from the vibration of the samples is non-zero. The induced emf is in principle proportional to the magnetic moment of the sample and thus also to its magnetisation. The design of a VSM hinges upon optimisation of the detection coil geometry, and vibration transducer. Auxiliary equipment such as cryostats are then constrained to have an acceptable sample volume and not to produce parasitic noise. The latter is predominantly determined by the mechanical isolation of the cryostat and balance of the transducers.

In the form of (VSM) shown in Figure (3.1), the specimen is vibrated at right angles to an applied magnetic field at a fixed frequency, usually about 33 Hz. An AC signal is then induced in the pick-up coils. The pick-up coils are placed with their axes parallel to the
1. Safety cover, 2. glass bell jar, 3. loudspeaker
4. transducer, 5. height adjustment, 6. evacuation port
7. Syphon entry arm, 8. vacuum jacket, 9. sample space,
10. electromagnet, 11. Sample holder, 12. electrical
vacuum lead through, 13. pick-up coil.

FIG(3.1) Low Temperature Vibrating-Sample Magnetometer
main magnetising field, so minimising spurious signals arising from field fluctuations. In any case, a sharply tuned signal-detecting system reduces unwanted background signals to a very low level. The transmission of spurious vibrations at the measured frequency must be carefully avoided. The usual method is to attach a small permanent magnet to the remote part of the vibrating system. This moves inside its own pick-up coils and provides a reference signal against which the signal produced by the sample can be measured accurately. This method of measuring magnetisation is a relatively sensitive one. A change in susceptibility, $5 \times 10^{-6}$ emu/g could be observed.

During the course of this work all the experiments involved straightforward measurement of the magnetisation using a VSM. Many different experimental arrangements have been employed to suit particular investigations, some are described in reference 4. In the next section the design and automation of the VSM used for the measurement in this thesis is described.

3.2 THE APPARATUS

The main features of the apparatus are: first, sample motion perpendicular to an applied field; and second, is the detection coil configuration. The saturation magnetisation of a magnetic material is determined from the voltage generated in a set of pick-up coils. The main parts of the apparatus are a loudspeaker, a transducer to provide a reference voltage, the conditioning amplifier type 2626, the power supply type SCT, a differential amplifier (Brookdeal 9454), an oscilloscope (OS 300), a temperature controller, a lock-in amplifier SR510 and a Commodore computer.
A block diagram of the main parts of the apparatus used for the experiments is shown in Figure (3.2).

3.2.1 Temperature Regulation

The cryostat used was an Oxford Instruments CF 1200 continuous flow cryostat [5], with a 3120 temperature controller, also manufactured by Oxford Instruments, which was used to measure the specimen temperature and to maintain temperature stability over the measured period. Temperature stability of better than ±0.1K was obtained. The sample space in the cryostat is surrounded by a copper radiation shield to reduce heat exchange between the internal and external walls of the cryostat.

Liquid nitrogen or helium is delivered to the cryostat by a vacuum insulated transfer tube inserted into a syphon entry arm via a feed capillary, which carries it to the copper heat exchanger. The helium exhausts via a second heat exchanger which cools the radiation shield before entering the helium return line. The temperature sensor is a chromel-Au/0.03% Fe-chromel thermocouple, one junction of which is connected with the heater and is fitted to the base of the heat exchanger. The thermocouple uses a liquid nitrogen reference junction and produces an emf ranging from -1.1 mV at 4K to +0.6 mV at 500K. It is calibrated at helium and nitrogen temperatures, and the system has a quoted stability of ±0.1K. 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 achieve a vacuum of less than 10^{-5} mbar. The specimen is top loaded into a 20 mm diameter
Fig (3.2); Schematic diagram of an automatic vibrating-sample magnetometer
cylindrical space where it can either be in vacuum or in an exchange gas. The loudspeaker assembly was placed at the top of an aluminium supporting plate and this plate was fixed on top of the electromagnet. The cryostat was sealed to the bottom of this plate by a plug using an 'O' ring. The loudspeaker assembly was enclosed in an airtight glass bell jar. The basic instrument is shown in Figure (3.1).

3.2.2 Newport 7" Electromagnet Type E"

The magnet used was a Newport Instruments Type E electromagnet which, when water-cooled, could take a current of ± 25 amps through its coils. It had 7" (17.8 cm) plane pole tips separated by a (4.3 ± 0.1) cm gap. The power supply for the electromagnet was a 250 VDC supply, which was capable of a maximum of ± 20 amps. In order to monitor accurately the current to the magnet a 0.1 ohm absolute resistor was placed in series with the magnet supply and the voltage measured across it using a digital voltmeter. To enable the resistor to cope with the large currents through it, it was necessary to immerse the resistor in an oil bath. The magnetic field produced by the electromagnet was measured in order to check that it was consistent with the maker's specifications. Before beginning a Hall probe was calibrated using a 4.4 kG permanent magnet, and the separation of the pole tips was measured. The tip separation was measured as (4.3 ± 0.1) cm. In measuring the field the electromagnet coil current was varied from 0 to 15 amp intervals. The results obtained are shown in Table (3.1), and are plotted as a graph in Figure (3.3). A comparison with the manufacturer's data is shown in Table (3.2) and plotted as a graph in Figure (3.4). From the graph and Figure (3.4), it can clearly be seen that the field produced by the electromagnet is in accordance with the manufacturer's specifications. The graph also enabled the susceptibility to be derived from the measured magnetisation of samples.
FIG(3.3)
Graph of Field Strength (KG) vs. Coil Current (Amp)
for pole gap of \((4.3 \pm 0.1)\) cm, using 10 cm diameter pole pieces
<table>
<thead>
<tr>
<th>Current (amp)</th>
<th>Field (KG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.13</td>
</tr>
<tr>
<td>1</td>
<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td>2.07</td>
</tr>
<tr>
<td>3</td>
<td>3.01</td>
</tr>
<tr>
<td>4</td>
<td>3.95</td>
</tr>
<tr>
<td>5</td>
<td>4.86</td>
</tr>
<tr>
<td>6</td>
<td>5.64</td>
</tr>
<tr>
<td>7</td>
<td>6.40</td>
</tr>
<tr>
<td>8</td>
<td>7.11</td>
</tr>
<tr>
<td>9</td>
<td>7.74</td>
</tr>
<tr>
<td>10</td>
<td>8.34</td>
</tr>
<tr>
<td>11</td>
<td>8.83</td>
</tr>
<tr>
<td>12</td>
<td>9.33</td>
</tr>
<tr>
<td>13</td>
<td>9.72</td>
</tr>
<tr>
<td>14</td>
<td>10.09</td>
</tr>
<tr>
<td>15</td>
<td>10.41</td>
</tr>
<tr>
<td>16</td>
<td>10.69</td>
</tr>
<tr>
<td>17</td>
<td>10.93</td>
</tr>
<tr>
<td>18</td>
<td>11.13</td>
</tr>
<tr>
<td>19</td>
<td>11.31</td>
</tr>
<tr>
<td>20</td>
<td>11.47</td>
</tr>
</tbody>
</table>
Figure (3.4) A Graph of Field vs Coil Current comparing the field produced by electromagnet with the manufacturer's data.

- Curve A ... plane tip magnet 7 face dia., 4.9 cm face gap
- Curve B ... plane tip magnet 7 face dia., 6 cm face gap
- Curve C ... plane tip magnet 7 face dia., 4.3 cm face gap
### TABLE 2

<table>
<thead>
<tr>
<th>Current (A) ± 0.01</th>
<th>Electro Magnet (kg ± 0.01)</th>
<th>Manufacturer's Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.3 cm pole gap</td>
<td>4.9 cm pole gap</td>
</tr>
<tr>
<td>0.00</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>1.00</td>
<td>0.95</td>
<td>1.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.92</td>
<td>2.20</td>
</tr>
<tr>
<td>3.00</td>
<td>2.76</td>
<td>2.90</td>
</tr>
<tr>
<td>4.00</td>
<td>3.48</td>
<td>3.60</td>
</tr>
<tr>
<td>5.00</td>
<td>4.26</td>
<td>4.30</td>
</tr>
<tr>
<td>6.00</td>
<td>4.90</td>
<td>5.10</td>
</tr>
<tr>
<td>7.00</td>
<td>5.43</td>
<td>5.60</td>
</tr>
<tr>
<td>8.00</td>
<td>5.95</td>
<td>6.20</td>
</tr>
<tr>
<td>9.00</td>
<td>6.44</td>
<td>6.80</td>
</tr>
<tr>
<td>10.00</td>
<td>6.86</td>
<td>7.40</td>
</tr>
</tbody>
</table>
3.2.3 Loudspeaker

This was a Radiospares model of 8Ω impedance maximum power capability of 15W and measuring approximately 11.5" in diameter. This particular model was chosen for its rugged construction, reasonably larger power rating and for its diameter which approximated to that of the space available. The large depth of cone suggested that large vibration amplitudes were possible. This was confirmed during tests when a peak-to-peak amplitude of 1 cm was produced. Although this amount of amplitude was not generally required, it may prove useful when measuring weakly magnetic materials. The large vibrational amplitude would improve detection by increasing the signal induced in the pickup coils. The diaphragm was reinforced using a hard plastic dome cut from a sphere. The loudspeaker was mounted on the housing flange using three spring loaded screws which provided balance for the loudspeaker, thus allowing the vertical adjustment of the sample rod.

3.2.4 Sample Rod and Transducer

(Bruel and Kjaer Type 4338 transducer)

The sample rod made out of glass was mounted on the transducer to provide a reference signal. The transducer is more convenient than the magnet and coil arrangement used in the original Foner design. A small slot was drilled into the bottom of the rod to hold the sample.

3.2.5 Conditioning Amplifiers

(Bruel and Kjaer Type 2626)

This is a simple amplifier with a selection of filters used to remove spurious signals.
3.2.6 Differential Amplifiers

(Brookdeal Differential AC Amplifier Type 9454)

This is also a simple amplifier with a selection of filters. It receives as input a mains filtered differential AC signal from the sample coil and delivers a single-ended output voltage.

3.2.7 Lock-in Amplifier

(Stanford Research System Type SR510) [PLLA]

The reference and sample signals are fed independently into the PLLA. A facility exists on the front panel for manually phase advancing or retarding one signal with respect to the other so as to obtain the required 180° phase shift.

3.2.8 Computer

(Commodore Model 3016 Console, and Model 4040 Drive)

The PLLA output is fed into the computer along with the field current value in accordance with an IEEE 486 interface. The computer programme, written in Basic, drives the power supply during automatic operation. A tabulated print-out is obtained of the value of the power supply (i.e. field) current (amps) against the corresponding sample magnetisation (emu/g).
3.2.9 Drive Unit

(Ling Dynamic Systems Type TP020 Oscillator)

This is a low frequency oscillator able to deliver a modest output voltage into a low impedance (4Ω) load. The frequency of vibration is not critical as far as the sample is concerned but it should be stable. A low frequency in the region 20-120 Hz is usually preferred so long as the mains frequency and its harmonics are avoided, for obvious reasons, while also avoiding the vibrator's resonant frequency, if any. Prior to constructing the new drive unit, three other laboratory oscillators were tested but found unsatisfactory. All had small, but significant, output voltage drifts, despite their good frequency stabilities. The performance specifications drawn up for the proposed drive unit were kept as simple as possible. The basic requirements were a stable single frequency and voltage signal. A circuit diagram is shown in Figure (3.5).

Several frequencies were tried but the frequency which gave the best reproducibility was 33.3 Hz. The fixed low voltage square wave output from the crystal oscillator was fed into two cascade second order active filters to remove the unwanted harmonics. The filtered output was then fed into a variable potential divider network, and from there into a fully encapsulated power amplifier able to deliver 30W of power into an 8Ω load. The power output capability was much in excess of requirements and so the potential divider network was arranged so that the amplifier output would not exceed 4V, with the output fused at 1.5A. The chosen frequency, maximum voltage and maximum current were suitable for use with both the loudspeaker and old vibrator.
All resistance values are in Ohms and capacitor values are in µFarads.

Fig (3.5) Drive Unit circuit diagram.
3.3 **THE PRINCIPLES OF A PICK-UP COIL**

Consider a dipole along the Z-axis with strength \( m \) located at the centre of a coil system. If the coil system were fed by a current \( i \) a field \( H_Z \) would be generated at the point where the dipole \( m \) was located. The flux due to the dipole and enclosed by the coil system is given by [6]

\[
\phi = m \frac{H_z}{i}
\]  

(3.1)

Now if the dipole is removed from the coil system and taken to a large distance so that after time \( t \) the flux \( \phi \) equals zero, during the removal of the dipole a voltage \( e_{\text{ind}} \) is induced in the pick-up coils.

\[
e_{\text{ind}} = -\frac{d\phi}{dt}
\]  

(3.2)

the time integral of which is:

\[
\int_0^t e_{\text{ind}} \, dt = -\int_{\phi}^\phi d\phi = \phi
\]  

(3.3)

If the factor \( H_z/i \) is a constant within a certain region the integral is independent of the position of the dipole within the region or of its volume. The pick-up coils are normally located in a magnetic field so that the magnetic moment of the sample can be measured as a function of external field. To see how this field can be prevented from contributing to the flux enclosed by the pick-up coils, consider a coil system fed by current \( i \) and enclosing a flux \( \phi \) of a non-homogeneous field \( H \). The flux can be written as:
\( \phi = u_0 \int H.dA \) 

(3.4)

where \( dA \) is an element of the area enclosed by one turn with the integration being performed for all turns.

Multiplication by \( i \) gives the potential energy \( E \) of the coil system in the field \( H \)

\[ E = u_0 i \int H.dA \] 

(3.5)

3.3.1 Coil Design

The most critical aspect of the (VSM) is the design of the pick-up coils. The size, number of turns, orientation, position and the number of coils will determine the sensitivity, repeatability and signal to noise ratio of the (VSM).

The main criteria for a good coil design are:

a) With the sample vibrating in the Z direction the coil design should reject signals due to vibrations in the X and Y directions.

b) The sensitivity should be independent of the sample position.

Fluctuations in the applied magnetic field should not produce any output signal. The first condition is fairly easily satisfied by placing the coils symmetrically about the sample with their axes parallel to the direction of the applied field and perpendicular to the direction of sample vibration. The voltage induced in a coil is then
\[ V = N \frac{d\phi}{dt} \]  

(3.6)

where \( N \) = number of turns in coil

\( \phi = \) flux through coil area (flux of electromagnetic field and sample field)

\[ \phi = \int_S B \cdot dA \]  

(3.7)

where \( dA \) = element of the area bounded by the coil.

For the arrangement of Figure (3.6a) any vibration along the X axis will induce in each coil a potential \( V_x \)

\[ V_x = N \frac{\partial \phi}{\partial x} \frac{dx}{dt} \]  

(3.8)

where \( x \) = sample position.

If the coils have equal numbers of turns and are placed at equal distances \( +X_0 \) and \( -X_0 \) either side of the sample, it follows from symmetry considerations that when the sample is at the origin

\[ \frac{\partial \phi}{\partial x} \bigg|_{+X_0} = - \frac{\partial \phi}{\partial x} \bigg|_{-X_0} \]  

(3.9)

So vibrations around the origin and along the axis of symmetry produce equal and opposite signals in each coil. Therefore in order to reduce the sensitivity with respect to vibrations in the Y direction, a coil arrangement symmetrical about the X-Z plane has to be used. It is possible to arrange the coils such that the desired signal \( V \) is entirely due to vibrations in the Z direction with
However problems may arise because a sample displacement $\phi / z$ is a function of the sample position:

Looking at this in the $X$ direction with the coils at $+X_0$ and $-X_0$ a displacement of the sample from the origin by a distance $\Delta X$ will produce a new $\phi / z$ in each coil. This can be estimated by using a Taylor series expansion to first order which gives

$$V = N \frac{\partial \phi}{\partial z} \frac{dz}{dt} \tag{3.10}$$

$$\left. \frac{\partial \phi}{\partial z} \right|_{X+\Delta X} = \left. \frac{\partial \phi}{\partial z} \right|_X + \Delta X \left. \frac{\partial^2 \phi}{\partial z^2} \right|_X \tag{3.11}$$

again from symmetry we can say that:

$$\left. \frac{\partial^2 \phi}{\partial z \partial x} \right|_{X_0} = \left. \frac{\partial^2 \phi}{\partial z \partial x} \right|_{-X_0} \tag{3.12}$$

So to first order the increased signal in one coil can be cancelled by an equal decrease of signal in the opposite coil. This indicates that a coil array should be used which is symmetric in any direction along which the effects of vibration and sample position are to be minimised. To maximise the effect of vibrations along the $Z$-axis, the coil array should be anti-symmetric about the $Z=0$ plane. Figure (3.6b) i.e. the bottom set of coils, must be wired in opposition to the top set. The coil arrangement of Figure (3.6b) will satisfy the three criteria originally stated for a sample at or close to the origin.
Fig. (3.6 a): A Simple Symmetric Coil Arrangement.

Fig. (3.6 a): A Symmetric Coil Configural in the (Z-Y) and (Z-X) Planes But Which is Anti-Symmetric in The (Y-X) Plane.
i.e. signal independence of sample position;
signal independence of vibrations in X and Y direction
signal independence of field fluctuations.

It is assumed that the sample dimensions are small compared to the coil/sample distance. For such cases the sensitivity can be maximised by adjusting the coil geometry. The full potential of sample vibration perpendicular to the applied field can only be realised if a suitable detection coil can be devised. In practice there are many configurations which can be used [7], see Figure (3.7). One of the most convenient detection-coil arrangements is the double coil shown in Figure (3.7a). An additional feature of this double-coil system is the fact that the two coils are connected in series but wound in opposition in order to obtain a net output signal. The arrangement to a large extent eliminates the effects of background noise due to magnetic field instability or mechanical vibrations of the magnet and coil systems. A single coil is often used when very high fields are required as shown in Figure (3.7b). This arrangement has proved both easy to assemble and most convenient in operation. Oval-shaped coils, shown in Figure (3.7c) have also been used to produce a wider saddle-point over which the sensitivity is a constant. The single-coil arrangement may be modified by addition of a pair of coils coaxial with the Z axis, Figure (3.7d). With such an arrangement, the magnitude and direction of the magnetic moment vector in space can be determined. The Z component is detected by the coaxial pair, and the component in the XY plane is determined by rotating the double coil. Figure (3.7e) shows a multiple-coil arrangement which attempts to maximise the induced voltage arising from the dipole field of the sample but at the expense of an additional thermal noise from the coils. Four coils of this multi-coil array have been used for a high
Figure (3.7): Example of useful detection coil arrangements described below
a. double coil, b. single-coil, c. oval-shaped coils,
d. the addition of a pair of coils coaxial with Z axis,
e. Multiple-coil, f. An efficient modification of multiple coil

g. the cross section of the coil geometry as shown in f.
field configuration. An efficient modification of Figure (3.7e) is shown in Figure (3.7f). This coil geometry, however, is not easily fabricated. Finally, the cross-section of coil geometry which reflects most of the dipole field symmetry properties is shown in Figure (3.7g). It is directly derived from Figure (3.7f), and leads to rather simple compilation of output voltage versus geometric parameters. The sample coil consists of four coils, connected in series, and mounted on to a frame which is clamped on to the pole pieces of the electromagnet. A diagram of one of its coils is shown in Figure (3.8a), together with the four coil arrangement actually used to detect the induced signal, Figure (3.8b).

The specimen was placed in a Teflon holder at the end of a rigid rod, which vibrated vertically in a uniform magnetic field. The sample was centred between the four coils which were connected in series. The resulting oscillating dipole field induced an AC voltage in the coils. The vertical component of the flux from the horizontal magnetic moment of the specimen intersected each coil in an opposite sense so that the net flux was not zero. The specimen was restricted to vibrate vertically and the net flux through each coil was finite and to a first approximation proportional to the displacement of the sample, see Figures (3.9) and (3.10). Therefore, an emf was induced in the coils. The magnitude of the signal depends on the magnetic properties of the specimen and also on its magnetisation. The voltage in the pick-up coils is

\[ V_o = KV(4\pi M_o) \]  

(3.13)

where \( V_o \) is the voltage induced in the pick-up coils by a sample of magnetisation \( M_o \) and volume \( V \), and \( K \) is a proportionality constant. A transducer was attached to the vibrating rod to which a DC voltage was
Fig. (3.8)  
Sample signal coil arrangement.
Fig. (3.9) X-axis sensitivity, as a function of absolute displacement
Fig. (3.10) Y-axis sensitivity, as a function of absolute displacement
applied producing a 'reference signal input' against which the 'sample signal input' was compared. Both signals had the same frequency of vibration. This signal was fed into a digital lock-in amplifier SR150 installation in the main console. A spectrographically pure Ni cylinder was used to calibrate the system and the sample was located at the saddle point as described below. The length of the sample rod was such that the specimens was initially located close to the saddle point. A vertical translation of the sample was made (i.e. along the Z-axis) and the observed signal monitored to find the position which corresponded to a maximum output signal. The sample was then translated in the X direction to find the position which corresponded to the minimum output signal, and along the Y direction (perpendicular to the paper for a maximum output signal). The sample was then located at a 'saddle point', the output signal being independent of small displacements of the sample in any direction. The interaction of three perpendicular symmetry planes of the coils determines the 'saddle point' for which all derivatives to the scalar sensitivity function vanish.

In a vibrating sample magnetometer, the position of the sample is varied sinusoidally over a small distance \( r(t) \). This induces a change of flux \( B(t) \) at a point \( r \) which is given by

\[
\dot{3}B(t) = u_o \dot{3}r(t). \text{grad} \{H(r)\} \tag{3.14}
\]

where \( u_o \) is the permeability of free space.

According to the principle of reciprocity [7] the magnetic flux \( \phi \) produced by a magnetic moment \( m \) in a coil of arbitrary geometry is equivalent to the field \( H(r) \) (at the position of the moment produced
by the same coil carrying a current \( I \). Thus the voltage induced in a
detection coil may be written as:

\[
V(t) = \sum_{n} \int \left( \frac{\partial B}{\partial t} \right) \cdot dA
\]

(3.15)

where \( A \) denotes the area vector of a single turn of the coil, the
summation is taken over \( n \) turns.

In order to calculate the magnetic field \( H(r) \), we shall assume that
the dimensions of the sample are small in comparison with the distance
between the sample and pick-up coils. Thus the dipole approximation
can be used and the magnetic field \( H(r) \), in the vicinity of the
detection coils can be written as [8]:

\[
H(r) = \frac{1}{4\pi} \left( \frac{m}{r^3} - \frac{3(m \cdot \hat{r})\hat{r}}{r^5} \right)
\]

(3.16)

where \( m \) is the magnetic dipole moment of the sample, \( r \) is a vector
from the dipole to the field point, \( \hat{r} \) is a unit vector. For example,
consider magnetic moment \( m \) aligned along the X-direction by an applied
field and vibrated in the Z direction at an angular frequency \( \omega \). In
this instance, \( \text{grad} \{ H(r) \} \) is given by a 3x3 matrix [9]. In this
section the application of the principle of reciprocity is used to
define the characteristic to design an optimum coil configuration.

The principle of reciprocity states that the mutual flux threading
through two coils is independent, of which one carries a current \( I \). If
coil one is replaced by magnetic material of moment \( M_1 \) then:

Since \( IdA_1 = M_1 dV_1 \), the mutual flux is
\[ \int_{S_1} H_2 \cdot d\alpha_1 = \int_{V_1} h_2 \cdot M_1 \, dV_1 \]  \hspace{1cm} (3.17)

Dropping subscripts we have

\[ \phi = \int_{V} M \cdot h \, dV = \mu \cdot h = \mu \cdot h_x \]  \hspace{1cm} (3.18)

where \( \phi \) = pick-up coil flux, \( M \) = magnetic moment vector, \( h \) = field vector arising from unit pick-up coil current, \( h_x \) = X component of field from unit pick-up coil current, \( V \) = sample volume, \( \mu \) = moment of the sample saturated in the X direction. All relevant dipole theory is included in

\[ \int m \, dV = \mu \]  \hspace{1cm} (3.19)

The advantages of sample vibration perpendicular to the applied field can be realised only if a suitable detection coil arrangement can be devised. In practice many satisfactory coil configurations can be found such as mentioned above. This is easily seen if we consider the time varying part of the vibrating dipole field. The scalar potential of a fixed dipole \( M \) at the origin and pointed along the X direction is

\[ \phi = \frac{M_x}{r^3} \]  \hspace{1cm} (3.20)

If \( M \) is vibrated in the Z direction with sufficiently small amplitude \( a \), the time varying potential in the surrounding space will be

\[ \phi_1 e^{i\omega t} \]  \hspace{1cm} (3.21)
where $\phi_1 = -a (\partial \phi / \partial z) = a M_x Z / r^5$. The flux pattern of the time varying part of the field is given by $-\nabla \phi_1$. Its configuration in the $xz$ plane is shown qualitatively in Figure (3.11).

### 3.4 CALIBRATION OF VIBRATING SAMPLE MAGNETOMETERS

An evaluation of two of the most widely accepted methods for calibrating vibrating-sample magnetometers is given. The comparison method uses a material of known magnetisation such as pure nickel to calibrate the system. In the slope method, the magnetometer is calibrated from the low field linear slope of the magnetisation curve of a sample of high permeability [10]. Although well designed magnetometers of this type presently exist, their ultimate accuracy is still dependent on the calibration technique used in the measurement process. We may thus write the calibration formula:

$$V_o = \frac{M_0 m_{st} ds}{m_s d_{st}}$$  \hspace{1cm} (3.22)

where $V_o$ is the voltage induced in the pick up coil by a sample of magnetisation $M_0$ and mass $m_s$, and $ds$ is the voltage and the subscripts st and s refer to the standard specimen and the specimen respectively. Demagnetising corrections were estimated for the appropriate axial ratios of the ellipsoidal specimen using the demagnetising factors given by Stoner (1945) [11]. The effective field $H_E$ is related to the applied field by the relation:

$$H_E = H - D_p V_o$$  \hspace{1cm} (3.23)
Fig. (3.11) Time varying part of dipole field in X-Z plane for vibration parallel to Z and dipole moment parallel to X.
where $D$ is the appropriate demagnetising factor and $\rho$ is the density. Magnetic isotherms were obtained by plotting $V_0$ versus $H_B$. At low temperatures the spontaneous magnetisation $\sigma_{OT}$ was obtained by extrapolation to $H_B=0$ of the high field parts of the isotherms. Near the Curie temperature, $\sigma_{OT}$ was determined from $\sigma^2$ versus $H/\sigma$ plots (Kouvel 1957) [12]. The saturation magnetisation $\sigma_{\infty}$ was derived from the spontaneous magnetisation $\sigma_{OT}$ versus $T$ curve by a $T^{3/2}$ extrapolation. The results were converted to Bohr magnetons per molecule, $u$, using the expression

$$u = M_{\infty}/N_B$$

(3.24)

where $M$ is the molecular weight, $N$ is Avogadro's number, and $B$ is the Bohr magneton. The susceptibility $X$ of the alloy under investigation in the paramagnetic balance is given by:

$$X = \frac{X_{pd} m_{pd} ds}{m_s d_{pd}}$$

(3.25)

which is equivalent to equation (3.22). Susceptibility and reciprocal susceptibility versus temperature curves were plotted for paramagnetic and antiferromagnetic alloys. Neel temperatures $\theta_N$ were measured and the paramagnetic Curie temperature $\theta_P$ was extrapolated using the following equation:

$$X = \frac{C}{T-\theta}$$

(3.26)
From the slope of the $X^{-1} \nu T$ curve, the effective Bohr magneton numbers could be obtained. It is apparent that the accuracy of any measurement depends directly upon how well one knows the susceptibility of the standard sample.

### 3.5 Calibration Problems

Vibrating-sample magnetometers are used in many laboratories, for both research and materials testing. In 1966 Case and Harrington [10] discussed some of the problems associated with the calibration of such magnetometers and noted that:

1. Each time a sample is placed in the instrument its position must be adjusted to within a few thousandths of an inch to obtain reproducibility. They found that a movement of only 0.02 in (0.51 mm) in the $Z$ direction produced a change of 0.8% in the output voltage from the pick-up coils.

2. In addition to signal strength considerations, one should also be concerned with the properties of the saddle point, for example, if the saddle point is narrow, it should be relocated every time a sample is changed. Such a procedure is time consuming and may even be impossible with weakly magnetic samples.

3. Care should be taken to ensure that the equilibrium position of the vibrating sample does not change during an experiment. This point may be important if measurements are made over a wide temperature range.
Mechanical coupling between the vibrating system and the fixed detection coils must be avoided. Although the coils are arranged for minimum sensitivity to external vibration, a noticeable background signal is obtained when the vacuum chamber of the cryostat touches the detection coils. Such mechanical effects are difficult to eliminate electronically because the spurious background signal has the same frequency as the sample signal and maintains a constant phase difference with respect to the sample signal. The unwanted background signal may also be field dependent if the coils subtend a region of non-uniform field. Usually the magnetometer and detection coils are both supported by the magnet, so that some mechanical coupling may be noticed at the highest sensitivity. This effect can be eliminated by shock mounting either the magnetometer or the detection coil system as required by the particular experiment. Rigid clamping of the detection coil to the magnet pole faces has also been successful.

Detection coils for VSM have been investigated by examining the output from a minute hypothetical pick-up coil. This approach circumvents the difficult problem of calculating signals induced in a detection coil and allows one to visualise the flux changes in the space surrounding a vibrating magnet and classify the various types of detection coils, the problem of designing detection coils with wide saddle points is discussed. This, of course, raises the difficult problem of calculating signals induced in a coil by a vibrating magnet. Unfortunately it is impossible to obtain closed expressions for such signals except in a few instances (Smith 1956) [13]. It is even more difficult to obtain expressions that will allow the width of the saddle point to be optimised for a given set of coils. A particular problem with the VSM was the tendency for particles of solids, air or water to collect in the lower region of the cryostat and prevent

76
smooth movement of the drive rod. A frozen drive rod forces one to shut down the system and warm it to room temperature. This mechanical problem was completely eliminated by the addition of helium exchange gas.

3.6 AUTOMATION OF A VIBRATING SAMPLE MAGNETOMETER

The experiment involves the measurement of the magnetisation of the specimen as a function of field and temperature. If carried out manually the measurements are time consuming because one run takes at least a day. For that reason, and the fact that the measurements are repetitive, a computer controlled measurement was designed. Computer controlled magnetisation measurements have been described in the literature [14, 15, 16]. A schematic diagram of the computer control programme for a VSM is shown in Appendix A. Fortunately the experiments are intrinsically slow and therefore a Commodore computer with IEEE data bus is adequate for the purpose. The computer control of various units is shown below.

3.6.1 The Multiplexer Units

Figure (3.12) 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 Figure (3.12), each user port was buffered by a transistor. In magnetisation experiments, there are two measurements which are required to be made by the DVM. These are:
Fig. (3.12) Circuit diagram of the automatic of vibrating-sample magnetometer.
1. Measurement of the current in the electromagnet: the DVM will measure a voltage drop across a 0.1Ω 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 the resistor 0.1Ω to determine the exact value of the current going to the electromagnet.

2. EMF of the specimen: the lock-in amplifier is required to measure the voltage from the pick-up coils which represent the magnetisation of the specimen.

3.6.2 Magnet Power Supply Control Circuit

An IEEE-486 compatible power supply to provide the current for electromagnetics was not available. Therefore a control circuit was designed to achieve computer control of the magnet power supply. Figure (3.12) shows the schematic diagram of the control circuit of the magnet power supply. The magnet circuit is controlled by an external multiturn potentiometer which rotates and can be set by using a stepper motor. A four-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 Figure (3.13). 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. This method was used to control the magnet current, firstly because the specimen takes some time to reach the set temperature and, secondly to prevent overshoot of the magnet current.
Fig. (3.13): Circuit diagram of 20 volt DC supply
An additional reason for this choice was the limited number of user port lines.

3.7 COMPUTER PROGRAMME DESCRIPTION

An example of the computer programme, used to acquire the data, is given in this section. Given the nature of experiments, the speed at which a programme written in BBC Basic operates is more than adequate for controlling the apparatus and obtaining readings from the PLLA. It was also necessary to store the data on a disc. The procedures which are essentially subroutines, are called when required. The flow diagram of the computer programme is shown in Appendix A. The programme consists of one main loop for the magnetic susceptibility measurements which use equation (3.22), and twelve subroutines for testing the specimen temperature, magnetic field current, and the voltage from the pick-up coils. The programme is divided into two parts: one for measuring hysteresis loops and the other to measure the susceptibility of the specimen. The programme starts with the initialisation followed by requesting the specimen title (AS), the minimum and maximum field currents (IK, Im) respectively, and there are four subroutines to change the directions of the current, see flow diagram. The programme also contains input statements for specimen mass (Sm), and standard specimen susceptibility. The command in line 145 is concerned with setting up the highest and lowest required temperature, and the command in line 250, requests the highest and lowest fields which are set by the statement in line 1600. The programme also contains pause commands for a certain time, to enable the set temperature to stabilise. Print #7 is concerned with setting the control parameter of the TC 1320 temperature controller. Print #5 (X₁), will obtain a reading from the lock-in amplifier to measure the
current. Print #5 (Q), reads the voltage from the pick-up coil via a lock-in amplifier.

The measurement subroutine sets the temperature and magnet field current and then the lock-in amplifier records the voltage from the pick-up coils. The computer then calculates the magnetic susceptibility from different values of field currents and gives the average value. Finally, the temperature, magnetic susceptibility and inverse susceptibility are printed out, and the measuring cycle is repeated until the final specimen temperature is reached.

3.8 MEASUREMENT OF MAGNETISATION

This section deals with the measurement of the magnetisation as a function of the magnetic field and temperature. From these investigations the Curie point can be obtained and a measurement of the permeability and susceptibility made. Methods for determining magnetisation can be divided into three groups as mentioned above.

Consider an isolated particle, spin quantum number \( S \) and magnetic moment \( u_S \), immersed in a static magnetic field \( H_0 \). The magnetic moment of the system is given by:

\[
u = \gamma_\hbar
\]

(3.27)

where \( \hbar \) is the Planck constant divided by 2\( \pi \). \( \gamma \) is the gyromagnetic ratio and is constant for a given nuclear species but is different for different elements, the gyromagnetic ratio is defined as

\[
\gamma = \frac{u}{\hbar S}
\]
The Hamiltonian of the system is given by

\[ H = -u H_0 \]  

(3.28)

which can be written as:

\[ H = -\gamma H_0 S \]

The eigenvalues of this Hamiltonian are:

\[ E = -\gamma H_0 m_s \]  

(3.29)

where \( m_s \) = magnetic quantum number, \( m_s \) is given by \( m_s = S, (S-1), (S-2), \ldots, -(S-2) \). The total number of the possible states of the spins is \((2S+1)\). The sample energy level diagram then consists of \((2S+1)\) equally spaced levels of separation \( \gamma H_0 \). If \( S \) is 1/2, the possible spin quantum numbers are \( \mp 1/2 \).

When a sample of spins is placed into magnetic field \( H \), the spins precess in the magnetic field according to allowed energy levels. For a system of identical \( S = 1/2 \) spins there will be two energy levels corresponding to the orientation of \( u \) either parallel or anti-parallel to \( H \). The tendency for the spins to populate the lower energy level is opposed by thermal motion which tends to equalise the populations. The equilibrium population of two energy levels at temperature \( T \) is given by the Boltzmann equation:

\[ \frac{N^+}{N^-} = \exp\left(-\Delta E/KT\right) \]  

(3.30)
where $N^+$ and $N^-$ are the number of spins in the upper and lower energy levels respectively, $K$ is the Boltzmann constant, $T$ is the absolute temperature, and $\Delta E$ is the energy separation between the energy levels which is given by $\gamma H_0$. Therefore equation (3.30) can be written as:

$$\frac{N^+}{N^-} = \exp\left(-\frac{\Delta E}{K T}\right) \quad (3.31)$$

A magnetic field $H$ acting on a spin of magnetic moment $u$ exerts a torque of $u \times H$. The equation of motion of the spin is found by equating this torque to the rate of change of angular momentum $J$:

$$\frac{dJ}{dt} = u \times H \quad (3.32)$$

where the angular moment $J$ is given by

$$J = u/\gamma$$

We can write equation (3.32) as

$$\frac{du}{dt} = u \times \gamma H$$

This equation tells us the direction of change of $u$ is perpendicular to both $u$ and $H$. The spin will precess at a constant angle about the magnetic field $H$, with precessional frequency given by the Larmor equation as follows:

$$\omega_0 = \gamma H \quad (3.33)$$
In order to describe the motion of macroscopic magnetisation we must consider a collection of identical spin $S = 1/2$ system. The resultant spin magnetisation is the sum over all the magnetic moments $u_i$ in the sample:

$$M = \sum_i u_i$$  \hspace{1cm} (3.34)

The equation of the motion $M$ is given by:

$$\frac{dM}{dt} = M \times \gamma H_0$$  \hspace{1cm} (3.35)

where $H_0$ is large field applied along the Z direction.

The Curie points in general vary by considerable amounts between samples and in some cases there is large thermal hysteresis. For a bibliography relating to experimental data on antiferromagnetic substances see T. Nagamiya, K. Yosida, and R. Kubo: Advances in Physics 4, 1-112 (1955); see especially Table 1. The value of $\theta$ is obtained by fitting an expression of the form of equation 3.26, to the susceptibility above the actual transition temperature $T_C$, where the Curie constant $C$ is equal to $Nu^2/3k$.

The magnetic induction may also be defined in terms of the intensity of magnetisation and the magnetic field in a specimen:

$$B = H + 4\pi M$$  \hspace{1cm} (3.36)
where \( M \) is the magnetisation per unit volume. The magnetic permeability is defined as

\[
u = \frac{B}{H}
\]  

(3.37)

The magnetic susceptibility per unit volume is defined as:

\[
x = \frac{M}{H}
\]

where \( M \) is the magnetisation, and \( H \) is the magnetic field intensity. Quite frequently the susceptibility may also be defined referring to unit mass or to a mass of the substance. The molar susceptibility is written \( x_m \) [17] (Appendix E).

\[
x_m = \frac{N\varepsilon^2}{m_c^2} \sum \overline{r^2} + 2N \sum_n \frac{|<n|\mu_z|0>|^2}{E_n - E_0}
\]  

(3.38)

where \( N \) is the Avogadro number, \( <n|\mu_z|0> \) is the matrix element of \( Z \) component of the orbital magnetic moment connecting the ground state with the excited state \( n \), and \( E_n - E_0 \) is the energy separation of the two states. The susceptibility in this case is independent of temperature, but the material is diamagnetic or paramagnetic according to whether the first or second term of (3.38) dominates. Then the diamagnetic susceptibility per unit volume is, if \( N \) is the number of atoms per unit volume:

\[
x = -\frac{Ze^2N}{m_c^2} \overline{r^2}
\]  

(3.39)

For more details see the next section.
There will be high frequency elements, which do not arise from within the ground term, that will contribute to a temperature independent paramagnetism labelled $X_{h}^{\text{mol}}$.

$$X_{h}^{\text{mol}} = \frac{2 N_A}{3} u_o u_B 2 \sum_n \frac{|\langle \psi_n | L+2S | \psi_o \rangle|^2}{E_n - E_o}$$ \hspace{1cm} (3.40)

The terms involving $S$ will be zero, as a result of the orthogonality of the spatial functions, and the denominator is generally replaced by some mean energy ($E$) for all relevant states, so that equation (3.40) can be written as:

$$X_{h}^{\text{mol}} = \frac{2 N_A}{3 E} u_o u_B 2 \sum_n |\langle \psi_n | L | \psi_o \rangle|^2$$ \hspace{1cm} (3.41)

For a $t_{2g}^n$ configuration, the ground state may be written as $|t_{2g,1}', t_{2g,2}', ..., t_{2g,n}'>$, and the excited states as $|t_{2g,1}, e, j', ..., t_{2g,n}>$. So that

$$\sum_n |\langle \psi_n | L | \psi_o \rangle|^2 = \sum_j |\langle e_j | L | t_1 \rangle|^2$$ \hspace{1cm} (3.42)

Now

$$\langle t_1 | L^2 | t_1 \rangle = \sum_{\text{all d states}} \langle t_1 | L | \alpha \rangle \langle \alpha | L | t_1 \rangle$$

$$= \sum_j |\langle t_1 | L | t_j \rangle|^2 + \sum_j |\langle e_j | L | t_1 \rangle|^2$$ \hspace{1cm} (3.43)
and recalling the isomorphism between $t_{2g}$ and $P$ orbitals we may write:

$$<P_i|L^2|P_i> = \sum_a <P_i|L|a><a|L|P_i>$$

$$= \sum_j |<P_j|L|P_i>|^2 = \sum_j |<t_j|L|t_i>|^2$$  \hspace{1cm} (3.44)

so that

$$\sum_i (\frac{1}{2}|<e_i|L|t_i>|^2) = n (|<t_1|L^2|t_1>| - |P_1|L^2|P_1|) = 4n$$  \hspace{1cm} (3.45)

and $x_h^{\text{mol}}$ becomes

$$x_h^{\text{mol}} = \frac{8n N_A \mu_B^2}{3E}$$  \hspace{1cm} (3.46)

### 3.10 Conversion Factors Between SI and CGS Units

Both CGS and SI units are now widely found in the literature, and so add to the general confusion, susceptibilities may be quoted per unit mass, per unit volume or per mole, as mentioned above. The volume susceptibility

$$(x^{\text{volume}} = \frac{3M}{3H})$$

where $M$ is magnetic moment per unit volume, is a dimensionless quantity $[m^3/m^3 = \text{siu/m}^3]([\text{cm}^3/\text{cm}^3 = \text{cgs/cm}^3])$. The mass and molar
susceptibility have dimensions of \([\text{m}^3/\text{kg} = \text{s}iu/\text{kg}]([\text{cm}^3/\text{g} = \text{cgs/g}])\) and \([\text{m}^3/\text{mol} = \text{s}iu/\text{mol}]([\text{cm}^3/\text{mol} = \text{cgs/mol}])\) respectively. For the reader's convenience, the following conversion factors are given:

\[
X^{\text{volume}} = 4\pi X^{\text{volume}}
\]

\[
\begin{align*}
\text{s}iu & \quad \text{cgs} \\
X^{\text{mass}} = 4\pi \times 10^{-3} X^{\text{mass}} \quad (3.47)
\end{align*}
\]

\[
\begin{align*}
\text{mol} & \quad \text{mol} \\
X = 4\pi \times 10^{-6} X \\
\text{s}iu & \quad \text{cgs}
\end{align*}
\]

For example, an \(S = 1/2\) Curie law at 300K yields a molar susceptibility of \(\sim 1.6 \times 10^{-8} \text{ s}iu/\text{mol} = \sim 1.2 \times 10^{-3} \text{ cgs/mol}\), where cgs is (centimetre-gram-second) and siu is system international unit.
REFERENCES


CHAPTER FOUR

SOME RELEVANT THEORIES OF MAGNETISM

4.1 THE MAGNETIC PROPERTIES OF ATOMS

It is found, in the presence of a local magnetic field, \( \mathbf{B}, \mathbf{A} = 1/2 \mathbf{B} \mathbf{r} \), where \( \mathbf{A} \) is the vector potential, when the interaction caused by an external magnetic field is small compared with the spin-orbit term, the unperturbed Hamiltonian can be taken for free atom Hamiltonian, \([1]\):

\[
H_O = \sum_{K=1}^{n} \left( \frac{1}{2m} p_K^2 - \frac{e^2}{4\pi\varepsilon_{0}r_K} + \xi(r_K) \mathbf{L}_K \cdot \mathbf{S}_K \right) + \sum_{KL} \frac{e^2}{4\pi\varepsilon_{0}r_{KL}} \tag{4.1}
\]

where the second term is electrostatic coloumb potential between the electron and the nucleus (taking the usual notation) is modified to become (Griffith 1961) \([1]\):

\[
H = H_O + H_1 \tag{4.2}
\]

This equation which is represented by the total Hamiltonian of the perturbation theory of the system which contains the "unperturbed" Hamiltonian, \( H_O \) is time-independent and \( H_1 \) is a small time-dependent perturbation \([2]\), where

\[
H_1 = \sum_{K=1}^{n} \left( \frac{\hbar}{m} \mathbf{A}_K \cdot \mathbf{p}_K + \frac{e^2}{2m} \mathbf{A}_K^2 + \frac{\hbar}{m} \mathbf{B} \cdot \mathbf{S}_K \right) \tag{4.3}
\]

The operator \( \mathbf{A} = 1/2 \mathbf{B} \cdot \mathbf{r} \).

92
Equation 4.3 can be written as:

$$H_1 = \sum_{K=1}^{n} \left( \frac{e}{2m} \mathbf{B} \cdot \mathbf{r}_K \cdot \mathbf{P}_K + \frac{e^2}{8m} |\mathbf{B} \cdot \mathbf{r}_K|^2 + \frac{\hbar}{m} \mathbf{B} \cdot \mathbf{S}_K \right)$$  \hspace{1cm} (4.4)$$

So

$$H_1 = \mu_B \mathbf{B} \cdot (\mathbf{L} + \mathbf{S}) + \frac{e^2}{8m} \sum_{K=1}^{n} |\mathbf{B} \cdot \mathbf{r}_K|^2$$  \hspace{1cm} (4.5)$$

where $\mu_B$ is the Bohr magneton [3], $\mu_B = \frac{e\hbar}{2m}$. It has the numerical value $= 9.27 \times 10^{-24} \text{ J} \text{T}^{-1}$. The first term is the paramagnetic component of $H_1$, and for atoms not in 1s state, this will dominate over the second diamagnetic term, which will be ignored for the present.

Wigner's theorem states that the matrix elements of any operator in the $(2J+1)$ dimensional space of eigenstates of $\mathbf{J}^2$ and $\mathbf{J}_z$ for given $J$, are proportional to the matrix element of $\mathbf{J}$ itself [4], so that

$$\langle \psi_i | \mathbf{L} + 2\mathbf{S} | \psi_i \rangle = g(\text{JLS}) \langle \psi_i | \mathbf{J} | \psi_i \rangle$$  \hspace{1cm} (4.6)$$

or

$$\langle \psi_i | \mathbf{L} + 2\mathbf{S} \cdot \mathbf{J} | \psi_i \rangle = g(\text{JLS}) \langle \psi_i | \mathbf{J}^2 | \psi_i \rangle$$  \hspace{1cm} (4.7)$$

where the proportionality constant is the spectroscopic (Landé g factor). The energy of an $M_J$ state is then [5]:

$$E_M = g(\text{JLS}) \mu_B M_J B$$  \hspace{1cm} (4.8)$$

Given that (2):
It follows simply that:

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

(4.12)

it is convenient for real atoms to replace the operator \( J \) by \( \gamma L \), where \( \gamma \) is a factor which may take account of the effect of the environment in which the atom is situated, so that [1]

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

(4.13)

except for \( J=0 \), in which case, by setting \( J = S - L \) cancelling out the factor of \( (S-L) \), and then putting \( J=0 \) we obtain

\[ g(J=0) = \gamma + (2-\gamma)(L+1) \]  

(4.14)
$H_1$ is regarded as a perturbation, small compared with the separation of $J$ levels of a given term, and it is assumed that the energy $E_i$ of a wave function, $\psi_i$, is expandable in a power series in $B$ (6), thus

$$E_i = W_i^0 + B W_i^I + B^2 W_i^{II} + ... \tag{4.15}$$

where, from perturbation theory:

$$W_i^I = \langle \psi_i | L_z + 2S_z | \psi_i \rangle \mu_B \tag{4.16}$$

$$W_i^{II} = \sum_{j \neq i} \frac{[\langle \psi_i | L_z + 2S_z | \psi_j \rangle \mu_B]^2}{(W_i^0 - W_j^0)} \tag{4.17}$$

and $B$ has been taken to be parallel to the Z-axis. The moment of an atom in a given state is then:

$$\mu = -\frac{\partial E_i}{\partial B} = (- W_i^I - 2W_i^{II}B - ...) \tag{4.18}$$

The moment per mole at temperature $T$ is obtained by thermal averaging over all states thus:

$$M = \frac{-W_i^0}{\sum_i \frac{(-W_i^I - 2W_i^{II}B - ...)}{e^{K_B T}} + \sum_i \frac{(-W_i^0)}{e^{K_B T}} - ...} \tag{4.19}$$

So that, the molar susceptibility is
This may be rewritten. If only one \(2S+1_L\) level is occupied, (that is only the lowest \((2J+1)\) states), then we have:

\[
x^\text{mol} = \frac{N_A \sum \frac{W^{I}_{J}}{K_BT} e^{-W^{I}/K_BT}}{\sum \frac{W^{II}_{J}}{K_BT} - 2 \sum W^{II}_{J}}
\]

so that in general

\[
x = \frac{\sum W^{J}_{J} (2J+1) X^\text{mol}_{SLJ} e^{-W^{J}/K_BT}}{\sum (2J+1) - \sum \frac{W^{J0}_{J}}{e^{K_BT}}}
\]

and the susceptibility due to all levels of the ground term is given by:

\[
x^\text{mol} = \frac{\sum_{J=L-S}^{L+S} \sum (2J+1) X^\text{mol}_{JLS} \exp\left[-\lambda J(J+1)/2K_BT\right]}{\sum_{J=L-S}^{L+S} \sum (2J+1) \exp\left[-\lambda J(J+1)/2K_BT\right]}
\]

where \(\lambda\) is the spin-orbit coupling term, so that

\[
W^{J0}_{J} = \frac{1}{J(J+1)}
\]
Returning to susceptibility for a system in which only the lowest \(2S+1L\) level is occupied, all others being thermally inaccessible, it is possible to evaluate equation (4.21) to be (Griffith 1961) (1):

\[
\chi^{\text{mol}} = \frac{\mu_0 N_A \mu_B^2 g^2 J(J+1)}{3k_B T} + \frac{\mu_0 2N_A \mu_B^2 (g-\gamma)(g-2)}{3\lambda \gamma}
\] (4.25)

The first term is just Curie's law, which may be rewritten as:

\[
\chi_{\text{Curie}}^{\text{mol}} = \frac{N_A}{3k_B T} \mu_0 \mu_B^2 \nu_{\text{eff}}^2
\] (4.26)

where, the effective moment is

\[
\nu_{\text{eff}} = g\sqrt{J(J+1)}
\] (4.27)

In fact, in many materials, the orbital angular momentum is quenched by an octahedral ligand field, in which case the spin only effective moment is

\[
\nu_{\text{eff}} = g\sqrt{S(S+1)}
\] (4.28)

where now \(g=2\).

The second term of the right hand side of equation (4.25) arises from the sum of expressions of the form

\[
-2[\langle \psi_i | L_z + 2S_z | \psi_i \rangle \mu_B]^2
\]

\[
(W_i - W_j^0)
\]

97
and is called the 'Van Vleck' or 'high frequency' or 'temperature independent' or 'second order Zeeman' paramagnetism. The evaluation of this second term is rather complicated, and the reader is referred to Griffiths (1961) (1). Plainly, the case in which there are states of the order of $K_B T$ above the ground state(s) will give rise to more complicated expression than

$$X_{SLJ}$$

for example, see Section 3.3.

4.2 MOLECULAR (MEAN) FIELD THEORY

It is often observed that in real materials, the ions behave collectively, so that below some critical temperature, interionic coupling permits spontaneous ordering of the ionic moments. Historically, the introduction of a phenomenological coupling term has proved useful. It is assumed that the interionic coupling can be replaced by an effective molecular field, or Weiss field ($H_W$), which is proportional to the magnetisation $M$, thus:

$$H_W = W M$$

(4.30)

where $W$ is the Weiss (or molecular) field constant.

At the ordering temperature, which for ferromagnets is the Curie temperature, $T_C$, it is clear that
\[ K_B T_C \sim \mu_o \mu H_W \] (4.31)

where \( \mu \) is the magnitude of the atomic moment. As an example, for iron, \( T_C = 1000K \), so that \( \mu_o H_W = B_W = 500T \). Now it is well known (see, for example, Kittel (1953) or Ashcroft and Mermin (7)) that the magnetisation of a magnetically dilute material is

\[ M = -N \frac{\partial F}{\partial B} = N \mu_B gJ B_J (\mu_B g J \Theta / K_B T) \] (4.32)

which, in the limit of \( K_B T \gg \mu_B B \), gives Curie's law again. \( B_J(x) \) is the Brillouin function and \( F \) the free energy. In the molecular field model, the 'X' in the Brillouin function becomes:

\[ X = \frac{\mu g}{K_B T} J(B + \mu_o W M) \] (4.33)

Now setting \( B \) to zero, we have

\[ \frac{M(T)}{M(0)} = \frac{K_B T}{N g^2 \mu_B^2 J^2 \mu_o} x \] (4.34)

as \( T \rightarrow 0 \), \( B_J(x) \rightarrow 1 \), then from (4.32)

\[ \frac{M(T)}{M(0)} = B_J(x) \] (4.35)

These two equations may be solved graphically i.e. \( M(T)/M(0) \) versus \( x \), the critical temperature being that at which (4.34) is tangential to
(4.35) at the origin (where $M > 0$). Now, as $x \to 0$, the slope of the Brillouin function is $(J+1)/3J$, which gives a Curie temperature of

$$ T_C = \frac{N g^2 \mu_B \mu_B J(J+1)W}{3k_B} = CW \quad (4.36) $$

At temperatures above $T_C$, the application of a field will produce a magnetisation, and so give a susceptibility. If $X$ is still small then

$$ B_j(x) \approx \frac{J+1}{3J} x - ... \quad (4.37) $$

and placing this in (4.32) and using (4.33) we have

$$ M = \frac{N \mu_B \mu_B g^2 J(J+1)(H+\omega M)}{3k_B T} \quad (4.38) $$

or

$$ M = \frac{C}{T} (H+\omega M) $$

leading to

$$ \frac{GM}{dH} = x = \frac{C}{(T-\theta_p)} \quad (4.39) $$

where

$$ \theta_p = \theta_w \quad (4.40) $$

which is the Curie-Weiss law. Comparison between (4.40) and (4.36) shows that $T_C$ and the paramagnetic Curie temperature $\theta_p$ are predicted to be the same. Experimentally, however, due to short range order effects above $T_C$ (see, for example, Gyorffy 1982 (8), Wilkinson and Small 1956 (9), $\theta_p$ is found to be somewhat larger than $T_C$. This is
to be remembered when interpreting a $1/X$ versus $T$ curve. Extracting the gradient at too low a temperature will yield an artificially large $\mu_{\text{eff}}$.

4.3 Molecular Field Theory for an Antiferromagnet

Just as interionic exchange leads to a $\theta_p$ in a ferromagnet, it leads to a $\theta_p$ in an antiferromagnet, as may easily be seen by considering a material divided into two sublattices, one 'spin up' and one 'spin down' when $T < T_N$.

For example, consider a b.c.c. lattice with corner sites occupied by atoms of sublattice one, and body sites occupied by atoms of sublattice two (Figure 4.1). The molecular field, $H_w$, acting on atoms of sublattice one may be written as:

$$H_w = W_{11} M_1 + W_{12} M_2$$  \hspace{1cm} (4.41)

where $M_1$ and $M_2$ are the sublattice magnetisations, and $W_{12}$ is the molecular field constant for nearest-neighbour interaction, and $W_{11}$ is for next-nearest-neighbour interactions. Similarly:

$$H_w = W_{21} M_1 + W_{22} M_2$$  \hspace{1cm} (4.42)

If the same types of atoms occupy the sites of both sublattices, then $W_{11} = W_{22}$ and $W_{12} = W_{21}$, and if we apply a field $H$, then

$$H_1 = H + W_{11} M_1 + W_{12} M_2$$  \hspace{1cm} (4.43)
Fig. (4.1)

Antiferromagnetic ordering of b.c.c lattice.

Fig. (4.2)

Induced rotation of sublattice magnetisation by an external field $H$. 

Easy direction
\[ H_2 = H + W_{12} M_1 + W_{11} M_2 \] (4.44)

The nearest-neighbour interactions we will put as antiferromagnetic, and so \( W_{12} \) is negative. \( W_{11} \) may be of any sign, depending on the material. Now at thermal equilibrium, the magnetisation is given by

\[ M_1 = \frac{1}{2} N g \mu_B S B_s(x_1) \] (4.45)

where

\[ x_1 = \frac{S g \mu_B \mu_0 H_1}{K_B} \] (4.46)

and \( B_s(x_1) \) is the Brillouin function as before. Similarly

\[ M_2 = \frac{1}{2} N g \mu_B S B_s(x_2) \] (4.47)

This is in comparison with equation (4.32), where \( N \) is the total number of atoms (with a dipole) per unit volume, and \( J \) has been set to \( S \).

4.4 TEMPERATURES ABOVE THE NEEL TEMPERATURE (\( T > T_N \))

Generally, in laboratory fields, saturation effects are negligible, and the Brillouin function may be replaced by (4.37) so that

\[ B_s(x) \sim \frac{[S(S+1)/3S]x}{6K_B T} \] (4.48)

and so

\[ M_1 = \frac{N g^2 \mu_B^2 S(S+1) \mu_0 H_1}{6K_B T} \] (4.49)
\[ M_2 = \frac{N g^2 \mu_B^2 S(S+1) \mu_0 H_2}{6k_B T} \] (4.50)

Assuming that \( H \), \( M_1 \) and \( M_2 \) are all parallel, then

\[ H_1 = | H + w_{11} M_1 + w_{12} M_2 | = H + w_{11} M_1 + w_{12} M_2 \] (4.51)

and similarly

\[ H_2 = H + w_{12} M_2 + w_{22} M_2 \]

So, the total magnetisation is

\[ M = M_1 + M_2 = \frac{N g^2 \mu_B^2 S(S+1) \mu_0 (2H + (w_{11} + w_{12})M)}{6k_B T} \] (4.52)

The sublattice Curie constants, \( C_1 \) and \( C_2 \), are taken so that \( C_1 = C_2 = C/2 \) for identical sublattices, leading to

\[ x = \frac{C}{(T - \theta_p)} \] (4.53)

where

\[ C = Ng^2 \mu_B^2 \mu_0 S(S+1)/3k_B \] (4.54)

and

\[ \theta_p = 1/2 C (w_{11} + w_{12}) \] (4.55)

So, depending on the relative sign and magnitude of \( w_{11} \) with respect to \( w_{12} \), \( \theta_p \) may be positive or negative. The form of equation (4.53) is
the same as (4.39). Many authors use the form \( X = C/(T + \theta_p) \) when considering antiferromagnetics resulting in confusion in the sign of any quoted paramagnetic Curie temperature. In the present work, and in the interests of clarity, the form \( X = C/(T - \theta_p) \) will be used throughout, and the sign of \( \theta_p \) will be quoted explicitly.

4.4.1 The Ordering Temperature (Neel Temperature)

The critical temperature at which spontaneous sublattice magnetisation occurs, may be found by solving equations (4.43) and (4.44), with \( H \) set to zero.

\[
M_1 = \frac{C}{2T} (W_{11}M_1 + W_{12}M_2) \quad (4.56)
\]

\[
M_2 = \frac{C}{2T} (W_{12}M_1 + W_{11}M_1) \quad (4.57)
\]

The solution yields the Neel temperature:

\[
T_N = \frac{1}{2} \frac{C}{(M_1 - M_2)} \quad (4.58)
\]

So, as one might expect, the stronger \( W_{12} \) becomes and the weaker \( W_{11} \) becomes, the larger \( T_N \) becomes. Now, using (4.55) we find

\[
\theta_p \frac{T_N}{W_{11} - W_{12}} = \frac{W_{11} + W_{12}}{W_{11} - W_{12}} \quad (4.59)
\]

hence if

\[
W_{11} = 0, \quad -\theta_p = T_N \quad (4.60)
\]
\[
W_{11} > 0, \quad -\theta_p < T_N \quad (4.60)
\]
\[
W_{11} < 0, \quad -\theta_p > T_N \]

105
In fact, there is an upper limit to the ratio of \( \frac{\theta_{FP}}{T_N} \), since if \( W_{11} \) becomes too large and negative, with respect to \( W_{12} \), the simple two sublattice configuration becomes unstable with respect to some other configuration (see Morrish 1965 for example) [10].

4.4.2 Susceptibility of an Antiferromagnet at \( T < T_N \)

At \( T < T_N \), and in the absence of any applied field, the spin on the two sublattices will be antiparallel, and colinear with the easy direction, defined by the crystalline anisotropy. If now a field \( H \) is applied parallel to \( M_1 \) and antiparallel to \( M_2 \), then \( X_1 \) and \( X_2 \) of equation (4.46) become:

\[
x_1 = \frac{g \mu_B \mu_0 S(H + W_{11}M_1 - W_{12}M_2)}{K_B T} \tag{4.61}
\]

\[
x_2 = \frac{g \mu_B \mu_0 S(-H - W_{12}M_1 + W_{11}M_2)}{K_B T} \tag{4.62}
\]

Now, at \( H = 0, M_1 = M_2 = M_0 \) and \( X_1 = X_2 = X_0 \), where

\[
x_0 = \frac{g \mu_B \mu_0 S(W_{11} - W_{12}) M_0}{K_B T} \tag{4.63}
\]

Provided saturation effects are again small, we may Taylor expand the Brillouin function about \( x_0 \), thus:

\[
B_S(x_1) = B(x_0) + \frac{g \mu_B \mu_0 S}{K_B T} \left( H + W_{11}(M_1 - M_0) + W_{12}(M_0 - M_2) \right) B_S'(x_0) \tag{4.64}
\]
\[ B_s(x_2) = B_s(x_0) - \frac{g \mu_B \mu_0 S}{K_B T} (H + W_{11}(M_0 - M_0) + W_{12}(M_1 - M_0)) B'(x_0) \] (4.65)

We know from (4.56) that the sublattice magnetisation is revealed by multiplying \( B_s(X_1) \) by \( 1/2 g \mu_B S \), and this then yields the susceptibility with \( H \) parallel to the easy direction.

\[ X_{11} = \frac{3}{8H} (M_1 - M_2) = \frac{N \mu_B^2 \mu_0 g^2 S^2 B_s(x)}{K_B T - \frac{1}{2}(W_{11} + W_{12}) u_B^2 g^2 S^2 N B_s'(x_0)} \] (4.66)

At \( T = 0K \), this predicts \( X_{||} (T = 0K) = 0 \). This is because, at absolute zero, the atoms on the two sublattices are aligned, to be either parallel or antiparallel to \( H \). The latter therefore can exert no torque on the moments, inducing no magnetisation change. As the temperature is increased, \( X_{||} (T) \) increases, until \( X_{||}(T_N) \) is equal to the Curie-Weiss value, and at \( T > T_N \) the above equation (4.66) reduces to \( X = C/(T - \theta_p) \), equation (4.53).

Now consider \( H \) applied perpendicular to the easy axis. The applied field will produce a torque, which will tend to rotate the moments to lie parallel to \( H \), as indicated in Figure (4.2). Any change in the magnitudes of \( M_1 \) and \( M_2 \) is neglected, as \( \phi \) is small. The rotation is opposed by the molecular fields, so that at equilibrium we have:

\[ |M_1^\prime (H + H_w)| = 0 \] (4.67)

and if

\[ H_w = H + W_{11} M_1 + W_{12} M_2 \] (4.68)
then, if $\phi$ equals the angle of induced moment rotation:

$$M_1 H \cos \phi - W_{12} M_1 M_2 \sin 2\phi = 0$$  \hspace{1cm} (4.69)

so that

$$M = (M_1 + M_2) \sin \phi = 2 M_2 \sin \phi$$  \hspace{1cm} (4.70)

Now, the total magnetisation is given by

$$M = (M_1 + M_2) \sin \phi = 2 M_2 \sin \phi$$  \hspace{1cm} (4.71)

Since $M_1 = M_2$, so that

$$X_\perp = -1/W_{12}$$  \hspace{1cm} (4.72)

which is a constant, and independent of $W_{11}$. Equation (4.53) reduces to (4.72) at $T = T_N$, and so the form of the expected curves are given in Figure (4.3) for $X ||$ and $X \perp$ with $W_{11} = 0$ and various values of $S$. (Compare with Figure 4.4, which is from Bizette and Tsai, 1954) [11].

4.4.3 A More General Picture

The above may be generalised by considering $n$ sublattices such that there are no important interactions between atoms of the same sublattice, so

$$H_i = H + \sum_{i' = 1}^{n} W_{i i'} M_{i'}$$  \hspace{1cm} (4.73)
Figure (4.3) Predicted susceptibility of an antiferromagnetic material as a function of temperature. (Morrish (1965)).
Figure 4.4) Susceptibility of a single crystal of MnF$_2$ (Vizette and Tsai (1954)).
where $W_{ii} = 0$.

By analogy with the preceding discussion

$$M_i = \frac{C}{nT} H_i = \frac{C}{nT} (H + \sum_{i'=1}^{n} W_{ii'}, M_{i'}) ; \quad i = 1, 2, \ldots n$$  \hspace{1cm} (4.74)

This gives a set of equations, and a total magnetisation

$$M = \sum_{i=1}^{n} M_i$$  \hspace{1cm} (4.75)

By adding the equation in (4.74), we have

$$\sum_{i=1}^{n} M_i (1 - \frac{C}{nT} \sum_{i'=1}^{n} W_{ii'}) = \frac{CM}{T}$$  \hspace{1cm} (4.76)

The expression in parenthesis may be factorised (as it is the same for all $i$), giving

$$M = \frac{CH}{T(1 - \frac{C}{nT} \sum_{i'=1}^{n} W_{ii'})}$$  \hspace{1cm} (4.77)

or

$$X = \frac{C}{T - \frac{C}{n} \sum_{i'=1}^{n} W_{ii'}}$$  \hspace{1cm} (4.78)

which is the Curie-Weiss law, with
\[ \theta_p = \frac{C}{n} \sum_{i'=1}^{n} W_{ii'} \]

As will be seen later, this may be rewritten in the form

\[ \theta_p = C \sum_{i'=1}^{n} \frac{2 Z_{ii'} J_{ii'}}{N g^2 u^2} = \frac{2S(S+1)}{3K_B} \sum_{i'=1}^{n} Z_{ii'} J_{ii'} \quad (4.79) \]

where \( J_{ii'} \) is the exchange interaction between atoms of the \( i^{th} \) and \( i'^{th} \) sublattices, and \( Z_{ii'} \) is the number of \( ii' \) interactions. One might also write

\[ \theta_p = \frac{2S(S+1)}{3K} \sum_{m=1}^{N'} Z_m J_m \quad (4.80) \]

where \( Z_m \) is the number of \( m^{th} \) nearest neighbours of a given atom, and \( J_m \) is the appropriate exchange interaction, and \( N' \) is the number of sets of neighbours with non-zero \( J_m \). Hence \( \theta_p \) is just the algebraic sum of all the exchange interactions acting on a particular atom, whereas the transition temperature \( (T_N) \) is a measure of the energy required to destroy the long range order.

4.5 THE EXCHANGE INTERACTION

The equation that is now raised is that of the origin of the Weiss field. By way of an example, if one considers the hydrogen molecule, then the singlet and triplet states have different energies (Goodenough (1963)) [12].
\begin{equation}
E_{\text{I}, \text{III}} = 2E_0 + \frac{(J_C + J_e)}{(1 + \alpha'2)}
\end{equation}

where $E_0$ is the unperturbed energy of a free hydrogen atom, $E_{\text{I}}$ and $E_{\text{III}}$ are the energies of the singlet and triplet states respectively, $\alpha'$ is the overlap integral, $J_C$ is the Coulomb integral and $J_e$ is the exchange integral. So, it follows that there is an effective spin coupling between the electrons of the parent hydrogen atoms, A and B, which can be written in the form

\begin{equation}
V_{AB} = -2 J_{AB} S_A \cdot S_B
\end{equation}

where

\begin{equation}
J_{AB} = \frac{1}{2} (E_{\text{I}} - E_{\text{III}}) = \frac{(J_e - \alpha'^2 J_C)}{(1 - \alpha'^4)}
\end{equation}

So, the stability of the singlet versus the triplet state depends on the sign of $J_{AB}$. If $J_{AB} > 0$ the triplet state is favoured, implying ferromagnetic coupling. Conversely if $J_{AB} < 0$ the singlet state is favoured, implying anti-ferromagnetic coupling. The generalisation of equation (4.82) leads to the Heisenberg exchange Hamiltonian.

\begin{equation}
H_{ex} = -\frac{1}{2} \sum_{ij} J_{ij} S_i \cdot S_j
\end{equation}

where $J_{ij}$ are the exchange parameters between atoms labelled $i$ and $j$, which have total spins $S_i$ and $S_j$ respectively. The factor 1/2 is
included in the sum. Now extracting the single atom Hamiltonian from (4.84), we have

\[
H_1 = -2J \sum_{j=1}^{Z} S_i S_j
\]  

(4.85)

where here the sum is over the Z nearest neighbours, the exchange integrals being sensitive to overlap. If we now wish to replace (4.85) by an effective field, so that \( H_1 \) has the form

\[
H_1 = -g \mu_B S_i H_w
\]  

(4.86)

we find

\[
H_w = \frac{2J}{g\mu_B} \sum_{j=1}^{Z} S_j
\]  

(4.87)

In the Weiss approximation, \( S_j \) is replaced by \( \langle S_j \rangle \) and

\[
M = N g \mu_B \langle S_j \rangle
\]  

(4.88)

so that

\[
H_w = \frac{2ZJ}{g\mu_B} \langle S_j \rangle = \frac{2ZJ}{Ng^2\mu_B^2} M
\]  

(4.89)

which is the Weiss molecular field model, with

\[
W = \frac{2ZJ}{Ng^2\mu_B^2}
\]  

(4.90)
4.6 **SUPEREXCHANGE**

The Heisenberg Hamiltonian (4.84) became the basis for many mathematical investigations. However, many antiferromagnetic materials have cations separated by anions, such as $\mathrm{O^{2-}}$, making direct Heisenberg exchange too small to account for the observed Neel temperatures. Kramers (1934) [13], introduced a superexchange mechanism to explain this indirect coupling. The problem was reformulated by Kaplan (see, for example, Silva and Kaplan (1973) [14], who used the Hubbard Hamiltonian (equation 2.1).

4.6.1 **Overlap of Half-Filled Orbitals**

Let us first assume that the ground state has exactly one electron at each site. If the spins are independent, then this state is $2^N$ fold degenerate. The first excited state is produced by the formation of one electron-hole pair, at the cost of energy $U$. In order to return the system to the ground state we must go to second order, and either the 'visiting' or the 'visited' electron returns. If two of the $2^N$ states in the ground state manifold are represented by $|m\rangle$ and $|n\rangle$ then the second-order matrix

$$\sum_k \sum_{\sigma} t_{kl} a_{i\sigma}^+ a_{k\sigma'} u_{ij} \sum_{\sigma'} t_{ij} a_{j\sigma}^+ a_{i\sigma} |m\rangle$$

(4.91)

It is obvious that $K=j$, and $L=i$, but may or may not equal $\sigma'$. So,

$$H^{\text{eff}} = -\sum_{ij\sigma} \frac{|t_{ij}|^2}{U} \left[ a_{i\sigma}^+ a_{j\sigma} a_{i\sigma}^+ a_{j\sigma} + a_{i\sigma} a_{j\sigma}^+ a_{j\sigma}^+ a_{i\sigma} \right]$$

(4.92)
Using commutation relationships (see, for example, White and Geballe, 1979 [15]) it is possible to show that

\[ H_{\text{eff}} = -2 \sum J_{ij} \left( \frac{1}{4} - S_i \cdot S_j \right) \]  

(4.93)

where

\[ J_{ij} = -2 \frac{|t_{ij}|^2}{U} \]  

(4.94)

which is antiferromagnetic in sign.

If there are unpaired electrons per atom, the exchange integral is

\[ J_{ij} = -2 \frac{t_{ij}^2}{4} S^2 U \]  

(4.95)

since

\[ S = n/2 \]  

(4.96)

The above represents the overlap of half-filled orbitals. The physical reason for the antiferromagnetic character of this superexchange lies in the fact that the transfer integrals \( t_{ij} \) carry an electron without change in spin and so, from the Pauli exclusion principle, the electrons must be antiparallel if transfer is to take place.

### 4.6.2 Overlap of a Half-Filled Orbital with an Empty Orbital

One might assume that the overlap of a half-filled orbital \( n \) at \( i \) with an empty orbital \( n' \) at \( j \), would be spin independent. This would indeed be the case, unless there also exists an orthogonal, half-filled orbital \( n'' \) at \( J \). Now within atoms orbitals are orthogonal and for orthogonal orbitals \( a' \) in (4.83) is zero, and so \( J_{ab} = J_e > 0 \). In this case, the intra atomic exchange coupling at the receiving site \( j \) favours the transfer of an electron of parallel spin to that in its orbital \( n'' \). The result is a third-order energy thus:
where $J_{\text{intra}}$ is the intra-atomic exchange parameter, $J_{n,n''}$.

4.6.3 Overlap of a Half-Filled Orbital with a Full Orbital

Again, one might assume that the overlap of a half-filled orbital $n$ at $i$ with a full orbital $n'$ at $j$, would result in no spin dependence. If again there exists an orthogonal orbital $n''$ at $j$, which is half full, the intra-atomic exchange at $J$ will favour the remaining electron in $n'$ to be parallel to that in $n''$, so that this type of overlap is again ferromagnetic, and the exchange parameter is third order:

$$J_{ij} = \frac{+2 t_{ij} J_{\text{intra}}}{4 \ S^2 U} \quad (4.98)$$

4.6.4 Interactions via Intermediary Anions

In the present work, due to the crystal structures of the materials that have been investigated, we are often concerned with the ways in which cations interact, while separated by one (or more) anions. There are three contributions to the superexchange:

a) the correlation effect, in which the cation spins are so coupled that they can simultaneously contribute to partial bond formation with the anion.

$$J_{ij} = \frac{+2 t_{ij} J_{\text{intra}}}{4 \ S^2 y^2} \quad (4.98)$$
b) the delocalisation effect, in which an electron is assumed to drift from one cation to the other. The transfer integral $J_{ij}$ is found to vary as the square of the cation-anion overlaps and so will be greatly affected by the covalency of the bonding.

c) The polarisation effect, which arises from terms not included in the simple Hubbard Hamiltonian. It is generally assumed that the contribution from polarisation is sufficiently small that they may be neglected from the discussion (Nesbet, 1960) [16].

The qualitative criteria for the sign and strengths of the various contributions to the exchange parameters is now discussed.

4.6.5 180° Cation-Anion-Cation Interactions

Consider transition metal cations in octahedral holes formed by anions, such that these coordination octahedra share a common corner as in the Perovskite structure. The metal $t_{2g}$ orbitals point between the anions, while the $e_g$ orbitals are directed towards the anions (Figure 4.5). It is easy to see that the overlap integral between a $t_{2g}$ and a $P_f$ orbital is zero, that is, the $t_{2g}$ and $P_f$ orbitals are orthogonal. Similarly the $e_g$ and $P_f$ orbitals are orthogonal, but $e_g$ and $P_{2g}$, and $t_{2g}$ and $P_f$ are not orthogonal. Electron transfer between $P_f$ and $t_{2g}$ is referred to as $\pi$ transfer, and between a $P_{2g}$ and an $e_g$ as $\sigma$ transfer [17]. The orbital overlap involved in $\sigma$ transfer is greater than that of $\pi$ transfer, and consequently $\sigma$ processes tend to be dominant. Following Goodenough (1963) [14], by way of example we will consider briefly the following cases:

i) the two cations having half-filled $t_{2g}$ and $e_g$ orbitals;

ii) the two cations having half-filled $t_{2g}$ but empty $e_g$ orbitals.
Fig. (4.5) Orbital overlap for 180 superexchange.

Fig. (4.6) Edge sharing octahedra.
a) Correlation effect
In case (i) $P_0$ spin antiparallel to the spins of the electrons in the $e_g$ orbitals can participate in partial bond formation, leading to antiferromagnetic coupling, and similarly the weaker $\pi$ transfer also leads to antiferromagnetic coupling. In case (ii) the $\pi$ transfer is similar to that of case (i) and the coupling is again antiferromagnetic. Although the $e_g$ orbitals are empty, the cationic spins are coupled via $\sigma$ transfer, as the $P_0$ spins within the covalent bond are stabilised through intra-cation exchange, again resulting in antiferromagnetic coupling. This will be weaker than in case (i) and it involves a third order effect.

b) Delocalisation effect
In case (i) the superexchange between half-filled $e_g$ orbitals must be antiferromagnetic and strong (equation 4.94). Also, the non-bonding $\pi_g$ orbitals will overlap via the $P_\pi$ orbitals, also contributing to the antiferromagnetic character of the exchange.

In case (ii), only $\pi$ transfer is present, and so weak antiferromagnetic exchange results.

4.6.6 90° Cation-Anion-Cation Interactions
For the hexagonal, or honeycomb structure that we are in the main concerned with in the present work, this is the most important form of exchange path within the layers.

It results, when octahedrally coordinated units share common edges, Figure (4.6). With regard to the delocalisation superexchange, the transfer integral for the $t_{2g}$ electrons varies as the $t_{2g}$-$t_{2g}$ overlap, rather than as the product of the $t_{2g}$-anion overlaps. The sign of this
superexchange may be obtained from equations (4.95), (4.97), (4.98). There also exists a correlation superexchange contribution for which there are three possible mechanisms:

1. Electrons in an anion S orbital couple the e\(_g\) orbitals of the two cations.

2. Electron in an anion P orbital couple a cation e\(_g\) orbital with a cation t\(_{2g}\) orbital. (The P orbital is a P\(_{\sigma}\) for one cation, and a P\(_{\pi}\) for the other).

3. Electrons in different P orbitals (P\(_{\sigma}\) orbitals for both cations), couple the cations e\(_g\) orbitals.

In cases (1) and (2), the sign is the same as for the 180° superexchange, although case (1) is weaker because of the small radial extent of the anion S orbitals. In case (3), J\(_{\text{intra}}\) is relied upon to couple the net spin on the anion, so that two electrons of like spin are excited to the cationic e\(_g\) orbitals and consequently the sign of this type of superexchange is the opposite of the 180° superexchange.

4.7 DIAMAGNETIC CORRECTION

So far the diamagnetic term of the Hamiltonian (equation 4.4) has been totally neglected. For strongly paramagnetic materials this may be of little consequence, but for low moment materials it will not be negligible, and in Chapter 6, the results are all displayed with the diamagnetism corrected for. Pascal [18] found that the diamagnetic contribution of a material is just an additive function of the components so that the molar diamagnetic component of M\(_{\text{m-n}}\) \(X^{\text{dia}}(M_{\text{m-n}})\)
is given by:

\[ x^{\text{dia}}(M')X_N = nX^{\text{dia}}(M) + nx^{\text{dia}}(x) \]  \hspace{1cm} (4.99)

Tables of such values may be found in many data books, for example, König (1966) [18].
REFERENCES


CHAPTER FIVE

NEUTRON SCATTERING

5.1 HIGH RESOLUTION POWDER DIFFRACTOMETER (HRPD)

INTRODUCTION

High resolution time-of-flight (TOF) powder diffraction on pulsed neutron sources has developed rapidly over the past five years to become a complementary technique of comparable power to conventional neutron and X-ray powder diffraction. The high resolution powder diffractometer, HRPD, has two principal contributions.

The effective width of moderator $\delta_m$ and the total length $L$ of the neutrons flight path is the principal quantity which defines the resolution. Thus the resolution increases with the total flight path length $R = \delta_m \cdot L$. The angular contribution to the resolution depends on the scattering angle $\phi_s$ and the pulse widths $\Delta \phi_s$ according to $R_{\text{ang}} = \cot (1/2 \phi_s) \cdot (1/2 \phi_s)$.  

The resolution in $d$ namely $R = \Delta d/d$ is given by [1]

$$ R = \frac{\delta_m}{L} + \cot \frac{\phi_s}{2} \Delta \phi_s $$  

(5.1)

HRPD at ISIS has an improvement in resolution of 5.7 times that of existing diffractometers and represents the first of a new generation of neutron diffractometers with a ($\Delta d/d$) resolution of less than 0.1% as shown in Figure (5.1) [2]. The true instrumental resolution,
Fig. 5.1 Comparison of the powder diffraction pattern of the standard $\text{Al}_2\text{O}_3$ measured on HRPD, with the previous best resolution data from IPNS (Inset).
however, has been observed in only a small number of experiments since sample broadening is often seen to play a dominant role in the determination of the peak shape, particularly at longer $d$-spacings. This leads to additional useful information about macroscopic properties, such as anisotropic crystallite size, strain distribution and sample homogeneity, but also results in a significant increase in complexity of peak-shape description and data-analysis strategy. In order to achieve $(\Delta d/d)$ resolution of around 0.05%, the primary flight path of a (TOF) diffractometer must be of the order of 100m. On a pulsed source operating at 50 Hz this introduces problems of multiple frame overlap, which can be eliminated by using choppers. HRPD has been designed with two disk choppers situated at approximately 6m and 9m from the moderator outside the bulk shielding. The three possible configurations of the choppers correspond to wavelength windows of 0.79 Å, 1.59 Å and 4.02 Å respectively, which may be moved to higher or lower wavelengths by phasing the choppers relative to the initial neutron pulse [3].

The primary flight path of HRPD is enclosed within a curved nickel-coated glass guide of cross-section 8 x 2.5 cm to attenuate the $\gamma$-rays and fast neutrons associated with the initial burst. The curved section of the guide, which extends from 6m to 60m from the moderator, has a radius of curvature of 18 km. These parameters represent the optimised configuration for a 50 Hz source in which no line of sight neutrons reach the sample yet the radius of curvature is sufficiently shallow to allow the transmission of sub-angstrom neutrons. The 60-90m straight section of the guide is necessary to smooth out beam inhomogeneities in the guide. The observed neutron flux is in good agreement with theoretical predictions. In particular, no neutrons are transmitted below a wavelength of 0.48 Å [4].
A schematic drawing of HRPD is given in Figure (5.2). Two sample positions are available, at 1m and 2m from the backscattering bank of detectors, with vertical access to both positions for sample environment instrumentation.

5.2 TARGET STATION [5]

The target, shown in Figure (5.3), consists of plates of depleted uranium, clad in zircaloy-2. Above the target are two Gd poisoned water moderators at room temperature, whilst below the target are two cryogenic moderators, one filled with supercritical hydrogen at 25K and 15 bar, and the other with liquid methane at 100K and 4 bar. The available refrigeration is 1.1 kW for the hydrogen and 0.7 kW for methane, both in excess of design requirements. Surrounding the target and moderator is a reflector containing a beryllium rod and heavy water.

The target-moderator-reflector assembly is cantilevered from the door which closes the back of the 3.2m diameter, 3.8m high target void vessel. This vessel contains helium gas as an inert atmosphere for cryogenic moderators, and gives rise to minimum neutron absorption. The bulk shielding of the target station is provided by a layer of steel and concrete 4.3m thick. Within the bulk shield there are 18 beam shutters, 2m thick and 4.4m high. To gain operational experience, light water was initially used for cooling both the target and reflector. The circuits behaved in an extremely predictable and stable manner and were later drained and filled with heavy water.
Fig. 5.2 Schematic layout of the HRPD machine.
Fig. 5.3 Uranium target.
The ISIS moderators are designed to optimise the production of a wide variety of beams with spectral and resolution characteristics which are matched to the suite of neutron scattering instruments. Four independent moderators are used in reflected wing geometry, two above and two below the target. A sectional drawing of the moderator layers of the ISIS target moderator-reflector system is given in Figure (5.4). The reflector is $D_2O$ cooled beryllium. To facilitate heat removal and to minimise radiation damage, the moderator materials are fluids. There are four moderators all of which use a thin layer of gadolinium neutron absorber (the poison layer) to improve the pulse shape. The four moderators comprise a 4.5 cm thick liquid methane moderator, at 100K poisoned with gadolinium at a depth of 2.25 cm, 4.5 cm thick ambient water moderator asymmetrically poisoned with gadolinium to give 1.5 cm and 3.0 cm effective thickness; a 8 cm thick supercritical hydrogen moderator at 25K; and 4.5 cm thick ambient water moderator poisoned with gadolinium at a depth of 2.25 cm. All beam lines can view a 100 cm$^2$ of moderator surface. ISIS has:

1. Seven beams viewing the high intensity, high resolution liquid methane ($CH_4$ moderator, which is optimised for pulse structure).

2. Three beams viewing a very high intensity face (A) and three beams viewing a high intensity, high resolution face (AP) of an ambient moderator.

3. The remaining two beams view an intermediate resolution ambient moderator, see Figure (5.5).
Fig. 5.4 Sections through the upper and lower moderator layers of the ISIS target-moderator-reflector system. N1-N9 are the beam directions on the North side of the experimental hall, while S1-S9 relate to the South side.
Fig. 5.5 The observed (...) and fitted (—) spectral distributions from three different moderators: A ambient poisoned moderator (TFXA); B 100 K liquid methane moderator (LAD); C 25 K liquid hydrogen moderator.
The intensities and time structure of the neutron pulses from the moderator were optimised using calculations based on Monte Carlo neutron transport codes. Experiments carried out in the low current target station at Los Alamos and experience gained at Argonne, enabled the spectral distributions displayed in Figure (5.6) [7] to be obtained.

5.4 HRPD DIFFRACTION PEAK SHAPES AND RESOLUTION

The peak shape in neutron (TOF) powder diffraction is more complex than that of the constant wavelength case, and must take account of the contributions of the moderator, diffractometer geometry and the effects of the sample. Early experiments on HRPD have shown a particularly rich variety of peak shapes, resulting from the uniquely high instrumental resolution [8]. The time structure of neutrons of a particular wavelength leaving the moderator is well modelled by the Ikeda-Carpenter function. The function for neutron scattering on a pulsed source is given by [9]:

\[ \phi(v,t) = \int dt' \, \phi(v,t') \left[ (1-R)\delta(t-t') + RB \theta(t-t') \exp(-B(t-t')) \right] \]

\[ = \frac{a}{\alpha} \left\{ (1-R)(\alpha t)^2 e^{-\alpha t} + 2R \frac{a^2 B}{(\alpha - B)^3} \times \left[ e^{-Bt} - e^{-\alpha t} (1+(\alpha - B)t \right. \right. \]

\[ \left. + \frac{1}{2} (\alpha - B)^2 \right] \right\} \]  

\[ \text{where } \phi(v,t) = \frac{\Sigma}{2} (\Sigma v t)^2 \exp(-\Sigma v t) \, t > 0 \]  

where \( \Sigma \) is the macroscopic neutron scattering cross-section of the moderator.

\[ a = \Sigma v \]
Fig. 5.6 Final observed (points), calculated (line) and difference profile plots for Al₂O₃ using the double exponential/Gaussian peak shape function.
and $R$ is the ratio of the area of the second term to the total area, 
$\delta(t-t')$ is the Dirac delta function; $B =$ time constants.

Work at the Rutherford Appleton Laboratory has shown that this function must be convoluted with Gaussian sample and instrumental contributions, and a Lorentzian shape contribution for a comprehensive peak shape description. Although mathematically complex the resulting function is a correct physical model for the peak shape, and has been highly successful in fitting individual peaks for a wide range of samples, with extraction of physically reasonable values for macroscopic sample parameters, as well as the expected moderator and geometrical terms. The measured resolution obtained from commissioning experiments on nickel oxide agrees closely with prediction, being around 0.05% at high and low wavelengths and rising to around 0.075% at wavelengths of 2.5 Å, see Figure (5.7).

5.5 CRYSTAL STRUCTURE DETERMINATION

When a basis is replicated around each lattice point the result is called a crystal structure [10]. Most solids are crystalline, that is, the atoms from which they are made, are arranged in regular array. The array can be maintained for many millions of atoms even in polycrystalline solids. Here grains are composed of many small crystallites having irregular orientation with each other. So long as the neutron wavelength is small compared with the crystallite size, it will appear crystalline to a neutron beam [11].

136
Fig. 5.7 (—) Predicted resolution $\Delta d/d$ (FWHM) for rings 1 and 20 ($R_1$ and $R_{20}$) as a function of wavelength. (—) Upper limit of the observed resolution of the backscattering detector on HRPD.
5.6 **BRAGG'S LAW**

If a neutron beam of wavelength $\lambda$ falls on a periodic array with a spacing $d$, the phase of the scattered waves will add up if the path difference is an integral multiple of $\lambda$. The condition for coherence in the reflected beam is Bragg's law.

$$\lambda = 2d \sin \theta$$  \hspace{1cm} (5.4)

since the $d$ spacing is proportional to wavelength, raw time of flight data can be plotted against a linear scale in $d$ spacing. The $d$ spacing is given as a function of the time of flight by [12]

$$d = \frac{ht}{2mL \sin \theta} \quad d \ (\text{nm}) = \frac{0.1978t \ (\mu\text{s})}{L \ (\text{mm}) \sin \theta}$$  \hspace{1cm} (5.5)

where $h =$ Planck's constant $= 6.6262 \times 10^{-34}$ Js

$t =$ time of flight

$m =$ neutron mass

$L =$ flight path

A crystal has a whole host of $d$ spacings.

5.6.1 **Single Crystal Diffraction**

When a crystal is illuminated by a white neutron beam containing all wavelengths, each set of planes selects the wavelength from the incident spectrum appropriate to its $d$ spacing, and a series of spots are produced at angles satisfying the laws of reflection. These are the Laue spots, which with a pulsed source are separated both in angle and in time of flight. Therefore a single crystal diffractometer must cover a range of scattering angles.
5.6.2 Powder Diffraction

There is no problem in satisfying the orientation condition with a powder. The incident beam picks out a crystallite with appropriate orientation. Every spacing scatters to every angle, but the reflections at a given angle have different wavelengths and so may be separated by time of flight.

5.6.3 The Intensity of Bragg Reflections

The elastic cross-section for neutron scattering on a pulsed source is given by:

$$\frac{d\sigma}{dn} = \sum_R b_R \exp \left[ i (K_0 - K_1) \cdot (R - R_0) \right]^2$$

(5.6)

where $b_R$ is the scattering length.

The double differential cross-section for neutron scattering on a pulsed source depends on scattering length which is given by [13]:

$$\frac{d^2\sigma}{dn dw} = \frac{K_1}{K_0} \left[ \bar{b}^2 \text{Scoh} (Q,w) + (\bar{b^2} - \bar{b}^2) \text{Sin}c (Q,w) \right]$$

(5.7)

where the bars represent averages of the scattering lengths over spins and isotopes and $S^{\text{coh}}$, $S^{\text{inc}}$ are the coherent and incoherent scattering functions, $d$ represents the solid angle.

For a single unit cell with volume $V_{\text{cell}}$, equation (5.6) may be transformed to:
\[
\frac{d\sigma}{d\Omega} = \frac{(2\pi)}{V_{\text{cell}}} \sum_\tau \delta(Q-\tau) F(\tau)^2
\]  \hspace{1cm} (5.8)

where \( Q = K_0 - K_1 \) is the scattering vector.

Here \( F(\tau) \) is the structure factor

\[
F(\tau) = \sum_\rho b_\rho \exp(i\tau \cdot \rho)
\]  \hspace{1cm} (5.9)

The \( \delta \) function simply confirms that intensity concentrates into sharp Bragg reflections at position \( \tau \). It has unit area, so the intensity of each peak is seen to be modulated by a structure factor depending on the scattering centre positions within the unit cell. In a powder spectrum each reflection at a given wavelength \( \lambda \) and scattering angle \( 2\theta \) is spread out into a cone - the Debye-Scherrer cone. The integrated cross-section for reflection of multiplicity \( Z_\tau \) into the cone is [12]:

\[
\sigma_\tau = \frac{\lambda^3 Z_\tau}{4 V_{\text{cell}} \sin \theta} |F(\tau)|^2
\]  \hspace{1cm} (5.10)

For a single crystal experiment, the integrated cross-section in a Laue spot is:

\[
\sigma_\tau = \frac{\lambda^4 |F(\tau)|^2}{2 V_{\text{cell}} \sin^2 \theta}
\]  \hspace{1cm} (5.11)

140
5.7 **STRUCTURE WITHIN THE UNIT CELL**

The intensity of Bragg reflections given in equation (5.8) depends on the square modulus of the structure factor $F(\tau)$. It looks in principle as if this equation can be inverted to give the nuclear density $\rho(x)$ as a function of the position $X$ within the unit cell:

$$
\rho(x) = \frac{1}{V_{\text{cell}}} \sum_{\tau} [F(\tau) \exp(-i\tau \cdot X)]
$$

(5.12)

The problem is that we cannot measure $F(\tau)$, only an intensity proportional to $|F(\tau)|^2$. We cannot measure both the real and imaginary parts. This is spoken of as the "phase problem" and has no easy solution.

5.7.1 **Structure Factors in Diffraction: the Effect of Thermal Motion**

So far it has been assumed that the nuclei are stationary on fixed sites. In fact all nuclei are in constant motion, especially at high temperatures. For structural studies it may be imagined that the motion blurs their position into the fuzzy clouds, as shown in Figure (5.8). The spread in position at a given thermal energy $KT$ depends on the steepness of the potential well arising from the neighbouring atoms. The figure shows a typical well, parabolic in the displacement $u$:

$$
V(u) = \frac{1}{2} \alpha u^2
$$

(5.13)
Figure 5.8 Thermal motion causes the positions of nuclei to be uncertain. The mean square spread in the displacement $u$ from the equilibrium position depends on the mean potential seen by the nucleus $V(u)$. The spread produces the Debye-Waller factor.
The higher the thermal energy, the higher up the well the atoms are able to climb and the greater the spread in position. This spread gives rise to a phase mismatch which causes all Bragg reflections to be reduced in intensity. Equation (5.8) is modified:

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)}{V_{\text{cell}}} \sum_{\tau} \delta(Q-\tau) |F(\tau)|^2 e^{-2W}$$

(5.14)

where $e^{-2W}$ is called the Deby-Waller factor. For the simple parabolic potential using a classical approximation:

$$W = \frac{1}{2} Q^2 \langle u^2 \rangle = \frac{1}{2} Q^2 \frac{KT}{a}$$

(5.15)

This factor provides the ultimate limitation of the accuracy obtainable in a neutron diffraction experiment. Resolution is limited by the size of the thermal cloud $\sim \langle u^2 \rangle^{1/2}$, whatever the maximum $Q$ value. The effect is reduced by cooling the sample, and this is therefore highly desirable for most pulsed neutron diffraction experiments. However, the quantum mechanical effect of zero-point motion means that cooling much below, e.g. 1/10 of the characteristic energy of the thermal vibration has little effect [15]. Figure (5.9) shows the Deby-Waller factor for iron at room temperature and at 77K. The $Q$ values at which the Deby-Waller factor drops to say, 10%, provide a criterion for the $Q$ range needed for a given material. Iron thus requires $Q_{\text{max}} \sim 200 \text{ nm}^{-1}$ at room temperature and $\sim 400 \text{ nm}^{-1}$ at 77K. A typical molecular crystal with $\langle u^2 \rangle^{1/2} \sim 0.1 \text{ nm}$ requires only $Q_{\text{max}} \sim 150 \text{ nm}^{-1}$.
Figure (5.9) The structure factor for scattering by iron atoms. The solid line shows the Debye-Waller factor from thermal motions attenuating the nuclear structure factor at 300 K and 77 K. The dashed line shows the X-ray form factor. The dots show the magnetic neutron scattering form factor.
5.8 DIFFRACTION WITH X-RAYS [16]

X-rays are scattered by electrons, not by the nuclei and scattered wavelets from different parts of the atom are not quite in phase. The scattering is attenuated with increasing \( Q \) by an electron form factor \( |f_e(Q)|^2 \). This is in addition to the Debye-Waller factor we have just considered. Figure (5.10) shows by the dashed line the electronic form factor. It falls rapidly compared with typical Debye-Waller factors. There is a natural limit on the spatial resolution possible with X-ray diffractions, given by the atomic radius.

On the other hand conventional X-ray sources differ from neutron scattering sources in being vastly cheaper. X-ray beams are also more intense than neutron beams in terms of quanta per unit area per second. The scattering lengths for X-rays are simply proportional to the number of atomic electrons \( Z \):

\[
b = r_o Z f_e(Q) \tag{5.16}
\]

where \( r_o \) is the classical electron radius of 2.818 fermis \((10^{-15} \text{m})\) [16]. This makes their scattering lengths, in general, rather large compared with neutron scattering length. Typically for metals X-ray penetration is only 25 \( \mu \text{m} \) and this is a serious disadvantage. Surfaces are frequently untypical of the bulk and need to be prepared with great care if they are not to be contaminated by oxidation.

The structure of all samples which were prepared during this research programme were initially investigated using X-ray diffraction techniques at room temperature. A Philips diffractometer with a broad focus tube PW2103/100 with a copper target (\( \lambda = 1.54 \, \text{\AA} \)) was used in
Fig. (5.10) The Guinier plot. The scattering intensity is plotted on a logarithmic scale against $Q^2$. The curve shows the plot for spherical particles. The dashed line shows the limiting slope at low $Q$ giving, in general, the radius of gyration.
conjunction with a PW1050/25 vertical goniometer. A compact amount of the finest fraction of the powder was enclosed in an aluminium holder, which was mounted at the centre of the goniometer. A proportional detector PW1965/20/30 was used with the diffractometer, and after electronic processing the output was displayed on a Servoscribe pen recorder. From the observed position of the Bragg peaks each line was indexed and the lattice parameter determined. To obtain an accurate value of lattice parameter, a Nelson-Riley extrapolation was used (18).

This method uses a plot of the lattice constant, $a_o$, against the functions $1/2 \left( \cos^2 \theta / \sin \theta + \cos^2 \theta / \theta \right)$. The line is extrapolated back to $\theta = 90^\circ$ to give the exact value of $a_o$.

5.9 EXPERIMENTAL NEUTRON SCATTERING

For total scattering experiments it is usual to measure the ratio of the scattering to the scattering from a vanadium sample of known incoherent scattering. Before taking the ratio of the two, the appropriate background measurements must be subtracted. The spectra must also be normalised by the appropriate monitor count $n$. We need in all four measurements:

1. A sample plus can spectrum $S_j$.
2. A can alone spectrum $C_j$.
3. The vanadium spectrum $V_j$.
4. The background spectrum $B_j$. 

147
The basic expression for the sample scattering cross-section is then:

\[
\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega} s \frac{S_j/n_s - C_j/n_c}{V_j/n_v - B_j/n_B}
\]  \hspace{1cm} (5.17)

Here we describe the four spectra which might be collected in scattered neutron experiments. It is best to choose a purely incoherent scatterer. Vanadium is the ideal material since its coherent scattering is a negligible 0.033 x 10^{-28} m^2, compared with its incoherent cross-section of 5.3 x 10^{-28} m^2. Vanadium samples can therefore contribute significantly to the background.

5.9.1 Analyzing Powder Diffraction Spectra

Powder spectra are usually analysed from the cross-section per unit cell \(d\sigma/d\Omega\) expressed as a function of the time of flight. Placzek and recoil corrections are not applied. They are vanishingly small, since the neutron momentum is absorbed by the whole crystal, giving a very large effective mass.

5.9.2 The Integrated Intensity in a Time of Flight Peak

The cross-section \(\sigma_\tau\) from the \(\tau\)th order reflection of a single unit cell has been defined in equation (5.10). Consider Figure (5.11), the integrated intensity \(I_\tau\) observed in a time of flight measurement depends on the wavelength interval \(\Delta\lambda = \lambda\cot\theta\Delta\theta\) picked out by a given spread \(\Delta2\theta\), and also on the fraction of the Deby-Scherrer cone which the counter intercepts:

\[
I_\tau = n_L(\lambda) N \lambda \sigma_\tau f
\]  \hspace{1cm} (5.18)
Figure 5.11 Analysing powder diffraction intensities. (i) Bragg peak intensities integrated over a peak depend on the fraction of the Debye Scherrer cone intercepted by the counter, and on the wavelength spread $\Delta \lambda = \lambda \cot \theta \Delta \theta$. (ii) Incoherent intensities as from our vanadium calibration, depend on the wavelength interval $\delta \lambda = h\delta t/m$, corresponding to our time channels $\delta t$, and on the counter solid angle $\Delta \Omega$. 
The intensity obtained from the differential cross-section, applicable for incoherent scattering, is quite different. It depends on the wavelength interval \( \delta \lambda = (h/m_e) \delta t \) corresponding to a time channel \( \delta t \). It also depends on the counter solid angle [12]

\[
\Delta \Omega = 2 \pi \sin 2 \theta \lambda \delta t
\]

(5.19)

\[
I(\delta t) = n_L(\lambda) \delta \lambda N_s \left( \frac{d\sigma}{d\Omega} \right) \delta \delta
\]

(5.120)

It can now be seen that the differential cross-section integrated over a reflection of total cross-section \( \sigma_t \) is

\[
\left( \frac{d\sigma}{d\Omega} \right) = \frac{\lambda \sigma_t m_L}{8 \pi \sin^2 \theta \hbar \delta t}
\]

(5.21)

Substituting the expression for \( \sigma_t \) from equation (5.10)

\[
\left( \frac{d\sigma}{d\Omega} \right) = \frac{1}{32 \pi} \frac{\lambda^4 \Sigma}{V_{\text{cell}} \sin^2 \theta \hbar \delta \delta} |F(\lambda)|^2
\]

(5.22)

Thus, the cross-section per reflection varies as \( \lambda^4 \).

5.10 THE EXCITATIONS IN ITINERANT MAGNETS (18)

For many magnetic metals, the model of spins localised on a given site is invalid and so a band model has to be used. The collective and single particle excitations associated with such a model can be investigated using neutron scattering.
For many magnetic metals, the model of spins on given sites is quite invalid. Itinerant magnetic metals have unpaired spins which are continually hopping from site to site. The electron energies form a band structure $E_K$, depending on the electron wave-vector $K$. The excitations in such a system are quite different from those in localised spin systems. The simplest model of an itinerant magnet is illustrated in Figure (5.12i). Spin 1/2 electron or holes move over the lattice with a mean site occupation probability $P_i < 1$. There are vacant sites 0, single occupied sites $\uparrow$ and $\downarrow$, and doubly occupied sites $\uparrow\downarrow$. The Pauli exclusion principle forbids double occupation with the same spin in a single band system. In the Hubbard-Hamiltonian the normal band structure energies $E_K$ (see Chapter Two) have an additional positive energy $I_{\text{eff}}$ when two electrons occupy the same site [19]:

$$H = \sum_K E_K n_K + \sum_\sigma I_{\text{eff}} n_\sigma n_{\sigma}$$

(5.23)

This positive intra atomic interaction hinders antiparallel spins and so favours ferromagnetism. Suppose the band energies are roughly parabolic with a band splitting $\Delta$ between up and down spin bands as shown in Figure (5.12ii).

At low temperatures spin flip excitations can only take place from the filled-up band below $E_F$ (heavy line) to the empty down band above $E_F$. The excitation energy $E_\psi$ depends on the wave-vector $Q = K_i - K_F$. At $Q = 0$, excitations from any value of $K_i$ have an energy equal to the band splitting $\Delta$. At a finite $Q'$ excitations from various values of $K_i$ cover a band of energies, as shown in Figure (5.12iii). These single
Fig. (5.12) The excitations in an itinerant magnet. (i) Unpaired electrons or holes about the lattice give vacant sites (0) singly occupied sites (†) or doubly occupied sites (‡) which must have opposite spin (ii). The band structure determines the excitations (iii) For \( Q = 0 \) the only possible transitions from full to empty levels have energy equal to the band splitting \( \Delta \). At finite \( Q \), the excitations cover a band of energies. These are the Stoner modes.
particle modes are called Stoner excitations. When the electron interaction effects are included, both single particle and collective modes are obtained. The latter is simply the spin wave mode.

The neutrons scattering function can be calculated in these systems through the imaginary part of the generalised susceptibility

$$\delta(Q,W) = \frac{1}{\pi} \left( \frac{1}{1-exp\left(-\frac{W}{KT}\right)} \right) \chi(Q,w)$$  \quad (5.24)$$

We may begin by neglecting electron interaction except insofar as the given rise to a band splitting. A 'non-interacting susceptibility' $\chi^{\text{non}}(Q,w)$ can then be calculated from the Lindhard summation. This involves the band energies $E_K$ and the corresponding Fermi function $f_K$ depending on the temperature. The summation is over all wave vectors in the Brillouin zone.

$$\chi^{\text{non}}(Q,w) = \sum_K \frac{(f_{K+Q} - f_K)M^2}{(E_{K+Q} - E_K - i\epsilon)}$$  \quad (5.25)$$

Here $\epsilon$ is a small imaginary number used to evaluate real and imaginary terms through the identity:

$$\lim_{\epsilon \to 0} \frac{1}{x+i\epsilon} = \frac{1}{x} - i\pi \delta(x)$$  \quad (5.26)$$

$M^2$ is a matrix element related to the form factor. Within the random phase approximation, an enhanced susceptibility depending on the interaction parameter $I_{\text{eff}}$ may be defined from

153
\[ x(Q,w) = \frac{x^{\text{non}}(Q,w)}{1 - I_{\text{eff}} x^{\text{non}}(Q,w)} \] (5.27)

This equation produces a collective spin-wave mode at low \( Q \). When this enters the single particle region it is damped out to give a broad intensity band. In the pure itinerant metals the spin waves have been intensively studied, but the Stoner mode intensity has proved more difficult to understand on account since energy transfers above 100 mev are generally required.

In principle, pulsed neutron sources can reach energies but conservation of energy and momentum criteria require large momentum transfers. Unfortunately for transition metals the magnetic form factors falls rapidly with momentum transfer so that the scattered intensity for large energy transfers is small.
REFERENCES


5. Boardman, B. Spallation Neutron Source: Description of Accelerator and Target RL-82-006.


6.1 **INTRODUCTION**

The main aim of the project was to develop an automated versatile VSM, in order to investigate a wide range of materials and to carry out a characterisation of their magnetic properties. The materials investigated included Laves phase compounds which are characterised by a weak susceptibility associated with metallic magnetism. In a series of Heusler alloys the paramagnetic susceptibility was determined as a function of temperature. The spontaneous magnetisation in the Invar system Fe-Ni was investigated for different degrees of atomic order.

The Laves phase materials studied have the hexagonal C14 structure. The compounds were based on the composition Mn$_2$T where T is a transition metal element. The sensitivity of the Mn moment to the interatomic distance is well established [1]. The four non-equivalent sites in α-Mn have significantly different moments associated with them. However, the Laves phase structure represents a simpler crystallographic arrangement in which to study the stability of the manganese moment. Results obtained on Mn$_2$T Laves compounds in which T is a non-magnetic element such as (Ti, Hf, Nb, Zr) suggests that the T-T interactions are positive for heavy (T) atoms and negative for light (T) elements. Consequently, the magnetism depends on the stability of the manganese moment and the nature of the magnetic structure will depend on the atomic separation and the competing interactions.

YMn$_2$ crystallises in the f.c.c. Laves phase (Fddm). Below 100K, the cubic Laves phase compounds YMn$_2$ orders magnetically with a complex
spin arrangement which has a very long period of modulation (400 Å) [2]. The moment per manganese at 4.2K is 2.7 \( \mu_B \) [3]. The transition at the Neel temperature is first order with a large hysteresis of 20K accompanied by a volume change of about 5% [4]. Above \( T_N \) the magnetic susceptibility increases with temperature and the thermal expansion coefficient is strongly enhanced.

The interpretation of thermal expansion results has led to the conclusion that thermally induced spin fluctuations are responsible for the enhanced thermal expansion coefficient in the paramagnetic phase. The confirmation for the existence of spin fluctuations in these compounds has been provided by paramagnetic neutron scattering [3,4]. In the local moment limit, e.g. to systems possessing Hund's rule moments, the paramagnetic magnetic phase transition is driven by transverse angular fluctuations between local moments of fixed amplitude. However in the case of YMn\(_2\) longitudinal spin fluctuations are believed to be of predominate importance.

It has recently been suggested that the increase in moment observed above the Neel temperature, could arise from a release of frustration. In the ordered state the magnetic interactions between nearest neighbours are negative and dominant. Frustration occurs since the manganese atoms are located on a regular tetrahedron and therefore the magnetic order cannot satisfy the interactions. A frustration of the magnetic interaction, cancelling the magnetic coupling in terms of the molecular field, is also observed in NdMn\(_2\) and ThMn\(_2\) compounds [5].

It was decided to carry out a series of susceptibility measurements on Pd\(_2\)MnIn to investigate the field dependence. Early susceptibility and neutron diffraction studies suggested that the antiferromagnetic structure which occurs below 140K in Pd\(_2\)MnIn is frustrated. This
hypothesis is strengthened by the fact that the magnetic structure is sensitive to the degree of chemical order, in particular between the Mn and In atoms. The general problem of frustration associated with antiferromagnetism on a f.c.c. lattice has been investigated by looking at the effect of field cooling on the susceptibility of Ag$_{0.4}$Pd$_{1.6}$MnIn and Au$_{0.8}$Pd$_{1.2}$MnIn.

A new series of Heusler alloys based upon Pd$_2$XIn (X is a trivalent rare-earth ion) were also investigated. These materials are of interest because an isostructural series Pd$_2$XSn exhibits both superconducting and magnetic properties at low temperature. Since in these materials the magnetic and superconducting degrees of freedom are believed to be decoupled, the change in the conduction electron concentration brought about by the replacement of Sn by In is critical for the establishment of the ground state properties. This investigation also included neutron powder diffraction experiments in order to establish the degree of atomic order and the possible existence of magnetic order.

Finally the VSM was used to investigate the effects of heat treatment on Fe-Ni Invar alloys of composition 22 and 50% Ni. In this region the magnetic properties change very rapidly with Ni concentration and are very sensitive to the atomic arrangement. The behaviour of the hysteresis loop in Fe-Ni alloys has been investigated for different states of annealing.

To provide a test of both reliability and sensitivity of the VSM, standard materials such as pure iron, nickel and dysprosium were chosen to calibrate it.
6.2 SAMPLE PREPARATION

All the alloys were prepared in an essentially similar manner by melting the appropriate proportions of spectrographically pure constituent elements. The starting elements were supplied by Johnson Matthey Chemicals Ltd as in Table (6.1), the details of which are given [6]. After the initial melt, the alloys were turned over and re-melted. To ensure good mixing care was taken to minimise weight loss by evaporation. Depending on the starting elements, ingots of 10 or 15g were produced with weight losses less than 0.5% in all cases. Specimens for magnetic measurements were cut from different parts of each ingot and the remainder were crushed to powder in a steel mortar. This powder was later used for X-ray and neutron diffraction studies. Each alloy was divided into two parts and placed in quartz tubes which were then evacuated. After flushing with pure argon gas the tubes were sealed leaving a 1/4 of atmosphere of Ar. The samples were annealed at 800°C for 24 hours before being either slow cooled (SC) or quenched into ice water. The alloys prepared are listed in Table 6.2.

6.3 CALIBRATION OF THE VSM

Pure nickel and iron were chosen as the calibration samples. Figure (6.1) displays the spontaneous magnetisation versus field for iron and nickel. Cylindrical specimens were machined from spectrographically pure rods of 5N purity. The ratio of cylinder length to diameter was 1.95 mm and 1.35 mm for iron and nickel respectively. These values were chosen on the basis of demagnetising factor and the compatibility with the sample space in the VSM. The saturation magnetisations for iron and nickel obtained in the present experiments were (216.8 and 55.1 emu/g) respectively, which are in agreement with those reported by Crangle [7]; the values were (217.6 and 55.1 emu/g) for iron and nickel respectively. It was concluded that the VSM worked in a satisfactory manner.
<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Atomic Number</th>
<th>Atomic Weight</th>
<th>Melting Point °C</th>
<th>Boiling Point °C</th>
<th>Minimum Purity</th>
<th>Density or Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>27</td>
<td>58.9332</td>
<td>1494</td>
<td>2900</td>
<td>99.5%</td>
<td>8.800</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Dy</td>
<td>66</td>
<td>162.50</td>
<td>1410</td>
<td>2600</td>
<td>99.9%</td>
<td>8.531</td>
</tr>
<tr>
<td>Erbium</td>
<td>Er</td>
<td>68</td>
<td>167.26</td>
<td>1520</td>
<td>2600</td>
<td>99.9%</td>
<td>9.044</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>Gd</td>
<td>64</td>
<td>157.25</td>
<td>1310</td>
<td>3000</td>
<td>99.9%</td>
<td>7.870</td>
</tr>
<tr>
<td>Hafnium</td>
<td>Hf</td>
<td>72</td>
<td>178.49</td>
<td>2230</td>
<td>5300</td>
<td>99.7%</td>
<td>13.276</td>
</tr>
<tr>
<td>Indium</td>
<td>In</td>
<td>49</td>
<td>114.82</td>
<td>156.634</td>
<td>2050</td>
<td>99.0%</td>
<td>7.260</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>26</td>
<td>55.847</td>
<td>1540</td>
<td>2760</td>
<td>99.98%</td>
<td>7.873</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>25</td>
<td>54.9380</td>
<td>1250</td>
<td>2120</td>
<td>99.9%</td>
<td>7.437</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>28</td>
<td>58.71</td>
<td>1455</td>
<td>2150</td>
<td>99.9%</td>
<td>8.578</td>
</tr>
<tr>
<td>Niobium</td>
<td>Nb</td>
<td>41</td>
<td>92.9064</td>
<td>2425</td>
<td>5000</td>
<td>99.0%</td>
<td>8.578</td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd</td>
<td>48</td>
<td>106.4</td>
<td>1554</td>
<td>3000</td>
<td>99.8%</td>
<td>11.995</td>
</tr>
<tr>
<td>Terbium</td>
<td>Tb</td>
<td>65</td>
<td>158.9254</td>
<td>1360</td>
<td>2500</td>
<td>99.9%</td>
<td>8.267</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn</td>
<td>50</td>
<td>118.69</td>
<td>231.9681</td>
<td>2720</td>
<td>99.99%</td>
<td>7.285</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>22</td>
<td>47.90</td>
<td>1670</td>
<td>3300</td>
<td>99.93%</td>
<td>4.508</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>23</td>
<td>50.9414</td>
<td>1920</td>
<td>3400</td>
<td>99.0%</td>
<td>6.09</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>Yb</td>
<td>70</td>
<td>173.04</td>
<td>824</td>
<td>1500</td>
<td>99.9%</td>
<td>6.966</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Zr</td>
<td>40</td>
<td>91.22</td>
<td>1850</td>
<td>4400</td>
<td>99.95%</td>
<td>6.507</td>
</tr>
</tbody>
</table>

**TABLE (6.1): PROPERTIES OF THE ELEMENTS**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₂ Er In</td>
<td>SC</td>
</tr>
<tr>
<td>Pd₂ Gd In</td>
<td>SC</td>
</tr>
<tr>
<td>Pd₂ Dy In</td>
<td>SC</td>
</tr>
<tr>
<td>Pd₂ Tb In</td>
<td>SC</td>
</tr>
<tr>
<td>Pd₂ Yb In</td>
<td>SC</td>
</tr>
<tr>
<td>Mn₂ Ti</td>
<td>SC</td>
</tr>
<tr>
<td>Mn₂ Zr</td>
<td>SC</td>
</tr>
<tr>
<td>Mn₂ Nb</td>
<td>SC</td>
</tr>
<tr>
<td>Mn₂ Hf</td>
<td>SC</td>
</tr>
<tr>
<td>Fe₅₀Ni₅₀</td>
<td>quenched into ice water</td>
</tr>
<tr>
<td>Fe₇₈Ni₂₂</td>
<td>quenched into ice water</td>
</tr>
</tbody>
</table>

**TABLE (6.2)**

161
Fig. (6.1) Spontaneous Magnetization of Iron and Nickel, (at room temperature).

Fig. (6.2) The Magnetization of Dysprosium as a function of temperature.
6.4 MAGNETISATION OF DYSPROSIUM

After the construction and calibration of the vibrating sample magnetometer, the magnetic properties of polycrystalline dysprosium, were investigated. The purpose of the experiment was to identify the phase transitions which occur at 85 and 179ºK in Dy and so provide a test of both reliability and sensitivity of the VSM. The magnetisation of the Dy sample was measured as a function of temperature in a field of 11 KG. The results are shown in Figure (6.2). The absolute accuracy of the VSM was checked several times by repeating the magnetisation measurement of pure dysprosium. The results agreed to better than 0.5%. Dysprosium is ferromagnetic at low temperatures but changes to a simple helix at 85ºK before becoming paramagnetic at 179ºK. These transitions are clearly visible in Figure (6.2). The results obtained in the present experiment are in rather good agreement with those reported by Crangle [7]. It was concluded that both the VSM and the thermometry functioned in a reliable manner.

6.5 TRANSITION METAL LAVES PHASE COMPOUNDS

In Figure (6.3) the unit cell of the C14 hexagonal Laves phase compound with the composition AB₂ is displayed. There are four A atoms, two B atoms at the 2a sites with symmetry 3m and six B atoms at the 6h sites with symmetry mm in the unit cell. Table (6.3) gives the values of the lattice constants a and c for the materials investigated in this thesis. The value of the ratio c/a is close to the ideal value for hcp (2√2/√3) = 1.63 [8]. The atoms are located in two hexagonal planes in the unit cell, given by x,y,z = 1/4 and x,y,z = 3/4. Both the origin of the unit cell and the point (1/2, 1/2, 1/2) are centres of inversion symmetry for this structure. However these points are
Fig. (6.3) The crystal structure of the C14 hexagonal Laves phase compound $AB_2$. 

C14 COMPOUND $AB_2$

○ A  ○ B(2a)  ○ B(6h)
not occupied by any atom in the Laves phase structure. The inversion
symmetry at (1/2, 1/2, 1/2) which allows the upper half of the unit
cell to be obtained by the operation of inversion symmetry gives rise
to structure factors which are all real.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure Type</th>
<th>a(A)</th>
<th>C(A)</th>
<th>c/a</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₂Ti</td>
<td>Mg Zn₂</td>
<td>4.831</td>
<td>7.939</td>
<td>1.643</td>
<td>hP₁₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P6₃/mmc</td>
</tr>
<tr>
<td>Mn₂Zr</td>
<td>Mg Zn₂</td>
<td>5.036</td>
<td>8.269</td>
<td>1.642</td>
<td>hP₁₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P6₃/mmc</td>
</tr>
<tr>
<td>Mn₂Nb</td>
<td>Mg Zn₂</td>
<td>4.868</td>
<td>7.973</td>
<td>1.638</td>
<td>hP₁₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P6₃/mmc</td>
</tr>
<tr>
<td>Mn₂Hf</td>
<td>Mg Zn₂</td>
<td>5.007</td>
<td>8.237</td>
<td>1.645</td>
<td>hP₁₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P6₃/mmc</td>
</tr>
</tbody>
</table>

TABLE 6.3: LATTICE PARAMETERS OF MATERIALS WITH MgZn₂ TYPE-STRUCTURE,
PREVIOUS WORK

6.5.1 Mn₂Ti Structure

The primitive unit cell of Mn₂Ti has atoms located at positions as
indicated in Table (6.4). Previous work on Mn₂Ti has been performed by
Shavishvili (1979) [13], who measured the magnetic susceptibility of
powdered Mn₂Ti over the range 77-800 K (Figure 6.4a), together with
results of the present work (Figure 6.4b) respectively. For this
compound a Curie-Weiss behaviour was reported in the temperature range
290-600 K. Shavishvili et al analysed their results in terms of a
Curie-Weiss law, finding the effective moment to be 2.7 μB/atom. The
results of Shavishvili et al are shown in Figure (6.4), and on the
basis of these results it was suggested that below 260 K Mn₂Ti becomes
antiferromagnetic. However anomalies such as reported by Shavishvili
et al, have been observed in the susceptibility of other binary Laves
phase compounds and attributed to structural phase transformations
[9,10].
<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Symbol</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₁</td>
<td>2a</td>
<td>0,0,0</td>
</tr>
<tr>
<td>Mn₂</td>
<td>6h</td>
<td>X,2X,1/4</td>
</tr>
<tr>
<td>Ti</td>
<td>4f</td>
<td>1/3,2/3,2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1/3,2/3,3</td>
</tr>
</tbody>
</table>

**TABLE 6.4: ATOMIC POSITIONS OF Mn₁, Mn₂ AND Ti ATOMS IN TiMn₂ FOR THE SPACE GROUP P6₃/mmc**

<table>
<thead>
<tr>
<th>Position</th>
<th>Atom</th>
<th>Atomic Parameters</th>
<th>Position</th>
<th>Atom</th>
<th>Neighbours</th>
<th>Distances (Å)</th>
<th>Next Neighbours</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(a) (0,0,0)</td>
<td>Mn₁</td>
<td>-</td>
<td>f</td>
<td>Ti-Ti</td>
<td>1f</td>
<td>2.950</td>
<td>1f,1f</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1701⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6(h) (X,2X,1/4)</td>
<td>Mn₂</td>
<td>X</td>
<td>3h</td>
<td>2.844</td>
<td>2a,1a</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0542⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0005</td>
<td></td>
<td>a</td>
<td>6h</td>
<td>2.414</td>
<td>6f</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td></td>
<td>h</td>
<td>6h</td>
<td>2.336</td>
<td>6f,2a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td></td>
<td>Mn₁Mn₂=</td>
<td>2f,2f,</td>
<td>2f</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R=0.051</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 6.5: ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS, TEMPERATURE FACTOR, NEIGHBOURS AND NEXT NEIGHBOURS FOR TiMn₂ [10]**

166
Fig. (6.4a) Reciprocal specific susceptibility as a function of temperature for alloys Mn2Ti, after Shavishvili, T. et al (1979) [13].

Fig. (6.4b) Reciprocal susceptibility of Mn2Ti as a function of temperature.
Fig. (6.5a) Susceptibility of Mn2Ti as a function of temperature.

Fig. (6.5b) Reciprocal susceptibility of Mn2Ti as a function of temperature.
The crystallographic structure of Mn$_2$Ti has been refined from single crystal X-ray diffraction data at 300°K. These phases generally form close to the stoichiometric composition AB$_2$ and the close packing of the constituent atoms occurs when the ratio of their atomic radii $R_A/R_B$ is 1.225. If it is assumed that two atoms make a 'contact' when their interatomic distance is smaller than the sum of the corresponding atomic radii, then, under the above conditions, only A-A and B-B contacts are possible [11]. The refined parameters of TiMn$_2$ are given in Table (6.5). Two distinct values were found for the interatomic distance (Ti-Ti) and (Mn-Mn) as can be seen in the same table. The results of the present magnetic measurements are shown in Figure (6.5a,b). In the present work the specific heat as a function of temperature was obtained using the continuous heating method, the results are shown in Figure (6.6). The results are in general agreement with those of Shavishvili et al, although the temperature range was more restricted in the present study. From Figure (6.5) it is clear that there is no evidence within the error bars of a transition at 260°K. The absence of a transition has also been confirmed by specific heat measurements which has a normal appearance as expected for a Debye solid. As yet there have been no neutron diffraction measurements to establish conclusively whether below 260°K Mn$_2$Ti orders antiferromagnetically. If a Curie-Weiss behaviour is assumed over the entire temperature range the present result yields an effective moment of 2.55μ$_B$/atom in good agreement with that reported by Shavishvili et al. However the use of a Curie-Weiss law for metallic magnets must be taken with caution. Furthermore the temperature variation of the susceptibility is small. It was therefore decided to carry out an analysis of susceptibility using the model derived in Section 2.7. In this model the susceptibility is derived assuming the magnetic electrons to be itinerant and represents
Fig. (6.6) Specific Heat measurements of Laves Phase Specimen as a function of Temperature using the pulsed Heating technique.
Fig (6.7)
X-ray intensities versus scattering angle (2θ) of Mn₂Ti
a temperature correction to the Pauli susceptibility. Figure (6.5a,b) shows the best least squares fit to be observed susceptibility using the following equation

\[ X(T) = X(0) + CT^2 \]  

(6.1)

The parameters of the best fit are given in Table 7.1. The results are quite reasonable since the model is based on itinerant magnetics. X-ray patterns were obtained at room temperature using a Philips diffractometer and Cu (Kα) radiation. The diffraction pattern is shown in Figure (6.7). It may be seen that the material is single phase with the Laves phase C14 structure as reported in Table (6.3).

The Bragg angles for crystals with hexagonal symmetry are given by [8]:

\[ \sin^2 \theta = \frac{1}{3a^2} (h^2 + \sqrt{3}hk + k^2) + \frac{1}{4c^2} L^2 \]  

(6.2)

### 6.5.2 Mn₂Hf

The susceptibility and reciprocal susceptibility versus \( T^2 \) of Mn₂Hf is shown in Figure (6.8a,b) together with the results of Shavishvili [13], Figure (6.9a) and the results of reciprocal susceptibility versus \( T \), Figure (6.9b) respectively. It may be seen that the agreement is not good. The susceptibility is low and the temperature dependence observed in the present work is extremely flat. According to Shavishvili, the Curie-Weiss law is satisfied, giving an effective moment \( \mu_{\text{eff}} = 2.2 \mu_B/\text{atom} \). The present results indicate only a modest change in the susceptibility with temperature. The absence of a phase transition is consistent with the specific results shown in Figure (6.6). As mentioned in Section 6.5.1, Figure (6.8a,b) shows the best
Fig. (6.8a) Susceptibility of Mn2Hf as a function of Temperature.

Fig. (6.8b) Reciprocal susceptibility of Mn2Hf as a function of temperature.
Fig. (6.9a) Reciprocal specific susceptibility as a function of temperature for alloys Mn$_2$Hf, after Shavishvili, T. et al (1979) [13].

Fig. (6.9b) Reciprocal susceptibility of Mn$_2$Hf as a function of temperature.
Fig (6.10) X-ray intensities versus scattering angle (2θ) of Mn2Hf.

Relative x-ray intensities

- 003, 102, 102
- 101, 101
- 002, 002
- 100, 100
- 020, 020
- 110, 110
- 111, 111
- 220, 220
- 222, 222
- 311, 311
- 333, 333
- 422, 422
- 444, 444
- 533, 533
- 644, 644
- 755, 755
- 866, 866
- 977, 977

θ

- 2θ
squares fit to observed susceptibility equation (6.1). X-ray data were obtained at room temperature. Figure (6.10) shows the powder diffraction pattern obtained. It may be seen that the diffraction pattern is consistent with a single phase material with the C14 structure.

6.5.3 Mn$_2$Zr

Calculations using a rigid band model (RBM) indicate that the B atoms B(2a) in Mn$_2$Zr can be ferromagnetic [9], and that there are many possible magnetic states, for the C14 compounds [9]. However further calculations have shown that although the Mn (2a) atoms can be ferromagnetic the overall magnetic state of Mn$_2$Zr will be paramagnetic [14]. For Mn (2a) in Mn$_2$Zr the density of states at the Fermi level $N(E_F)$ is 16.2 states/atom Ry spin), therefore the value of $N(E_F)$ that satisfies the Stoner condition must be less than 16.2, $T<16.2$ Ry. On this basis Laves Mn$_2$Ti should also be a paramagnet. It is predicted that there are other magnetic compounds where only the B(2a) atoms are magnetic and the Fermi level is situated at the peak of densities of states (DoS's) of B(2a) as in Mn$_2$Zr. In Figure (6.11a,b) the susceptibility and reciprocal susceptibility versus $T^2$ of Mn$_2$Zr is shown, together with the results of Shavishvili [13] and the results of $X^{-1}vT$ in Figure (6.12a,b) respectively. According to Shavishvili [13] assuming a Curie-Weiss behaviour an effective moment $\mu_{\text{eff}} = 2.4 \mu_B$/atom is obtained. As with Mn$_2$Ti the present results indicate that the susceptibility of Mn$_2$Zr varies only slightly with temperature. The specific heat versus temperature using pulse techniques is shown in Figure (6.6). Equation (6.1) has been used in this analysis, Figure 6.11(a,b) shows the best least squares fits to observed $X^{-1}vT^2$. X-ray diffraction data were obtained at room temperature and are shown in Figure (6.13). It may be seen that the material is single phase with the Laves phase C14 structure as reported in Table (6.6).
6.5.4 Mn₂Nb

The temperature dependence of the magnetic susceptibility of Mn₂Nb was measured using the (VSM) in the temperature range from 77 to 450⁰K and is shown in Figure (6.14a,b). The susceptibility and reciprocal susceptibility versus temperature of Mn₂Nb observed in the present work is extremely flat. There appears to be no previous reference in the literature to magnetic measurements having been made on this compound. The specific heat measurements versus temperature shown in Figure (6.6) indicate the absence of any transition within the temperature range covered in the experiment. Figure (6.14a,b) shows the best least squares fit to observed susceptibility using equation (6.1). X-ray diffraction patterns were obtained at room temperature, Figure (6.15). As with the other compounds it may be seen that Mn₂Nb was single phase with the C14 structure. The structural parameters obtained from these data are reported in Table (6.6).

<table>
<thead>
<tr>
<th>Compound</th>
<th>a(A)</th>
<th>c(A)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₂Ti</td>
<td>4.812</td>
<td>7.846</td>
<td>1.631</td>
</tr>
<tr>
<td>Mn₂Zr</td>
<td>5.016</td>
<td>8.086</td>
<td>1.612</td>
</tr>
<tr>
<td>Mn₂Nb</td>
<td>4.819</td>
<td>7.635</td>
<td>1.605</td>
</tr>
<tr>
<td>Mn₂Hf</td>
<td>5.113</td>
<td>8.245</td>
<td>1.613</td>
</tr>
</tbody>
</table>

TABLE 6.6: LATTICE PARAMETERS OF MATERIALS WITH C14 TYPE STRUCTURE - PRESENT WORK
Fig. (6.11a)
Susceptibility of Mn2Zr as a function of temperature.

Fig. (6.11b)
Reciprocal susceptibility of Mn2Zr as a function of temperature.
Fig. (6.12a) Reciprocal specific susceptibility as a function of temperature for alloys Mn2Zr, after Shavishvili, T. et al (1979) [13].

Fig. (6.12b) Reciprocal susceptibility of Mn2Zr as a function of temperature.
Fig (6.13)

X-ray intensities versus scattering angle (2θ) of Mn-Zr
Fig. (6.14a) Susceptibility of Mn2Nb as a function of temperature.

Fig. (6.14b) Reciprocal susceptibility of Mn2Nb as a function of temperature.
Fig (6.15)

X-ray intensities versus scattering angle (2θ) of Mg-Nb
Fig. (6.16) The L2₁ structure. In the ordered Pd₂X₁In₁, a and c sites are occupied by Pd atom, b and d sites by X and In atoms, respectively.

X = Dy, Er, Tb, Yb, Mn, ...
6.6 HEUSLER ALLOY COMPOUNDS

Heusler alloys are ternary intermetallic compounds with the L2₁ structure indicated in Figure (6.16). They are an interesting series for magnetic investigations because they offer an opportunity to study the effects of interatomic distance, atomic arrangement and electron concentration on the occurrence and type of magnetic order in 3d metallic systems [15]. Recently a new series of ternary intermetallic compounds have been reported which simultaneously exhibit both superconductivity and magnetisation. These materials were based on the composition PdₓXSn, where X represents a rare earth ion. In these materials it is believed that the magnetism is associated with the 4f rare earth electrons and the superconductivity with the sp conduction electrons. Since in these materials the magnetic and superconducting degrees of freedom are believed to be decoupled the change in conduction electron concentration brought about by the replacement of Sn by In should significantly influence the ground states properties [16]. It was therefore decided to investigate five new intermetallic compounds based on the composition PdₓXIn, viz Pd₂ErIn, Pd₂DyIn, Pd₂YbIn, Pd₂TbIn, Pd₂GdIn. All alloys were prepared by the same technique described in the section above. The magnetic susceptibility of each alloy is discussed in detail in the following sections.

6.6.1 Pd₂MnIn

In the L2₁ form of Pd₂MnIn, the Mn atoms are arranged on an fcc sublattice and at low temperature the magnetic moments on the Mn atoms order in the AF₂ structure as in MnO (i.e. the moments were aligned in ferromagnetic (111) planes, with neighbouring planes oriented antiparallel). In the B2 form of Pd₂MnIn the Mn and In atoms were arranged randomly at the body-centres of Pd sublattice, and at low
Fig. (6.17)

Susceptibility of Pd2MnIn as a function of Temperature (17)
temperatures adjacent Mn moments along the cube axes were oppositely aligned. The susceptibility versus temperature curve is shown in Figure (6.17) for the L2₁ structure. At 140°K the antiferromagnetic transition is observed.

6.6.2 Ag₀.₄Pd₁.₆MnIn and Au₀.₈Pd₁.₂MnIn
The susceptibility and reciprocal susceptibility versus temperature in fields of (3.95 and 8.34 KG) are shown in Figures (6.18 a,b and 6.19a,b) respectively. The results were obtained by cooling the sample from above the Neel temperature in a field of 3.95 KG and then measuring the susceptibility as a function of temperature. The process was then repeated after cooling in a field of 8.34 KG. Figure (6.18a,b) shows the phase transition at T_N, above Neel temperature the values of magnetic susceptibility at the difference field are essentially coincidental. Below T_N the values of the susceptibility are systematically different for the two fields. This result suggests that in Ag₀.₄Pd₁.₆MnIn the magnetism becomes increasingly frustrated below the phase transition. For the Au₀.₈Pd₁.₂MnIn sample the Neel temperature occurred below 77°K so that all the susceptibility measurements were carried out in the paramagnetic phase. The results in Figure (6.19a,b) confirm that since the system is in the paramagnetic state no frustration occurs.

6.6.3 Pd₂XIn
Magnetic properties of Pd₂XIn with X = Dy, Er, Yb, Tb, Gd have been investigated using susceptibility measurements for temperatures between 77 < T < 300°K. In addition neutron diffraction data have been obtained on Pd₂ErIn and Pd₂TbIn at 300°K. The susceptibility of Pd₂XIn (X = rare earth compounds) arises mainly from 4f electrons, but contributions are expected from the other electrons and in particular
Fig. (6.18a) Susceptibility of Ag0.4Pd1.6MnIn as a function of temperature.

Fig. (6.18b) Reciprocal susceptibility of Ag0.4Pd1.6MnIn as a function of temperature.
Fig. (6.19a) Susceptibility of Au0.8Pd1.2MnIn as a function of Temperature.

Fig. (6.19b) Reciprocal Susceptibility of Au0.8Pd1.2MnIn as a function of Temperature.
Figure (6.20a) Susceptibility of Pd2DyIn as a function of Temperature.

Fig. (6.20b) Reciprocal susceptibility of Pd2DyIn as a function of Temperature.
the lanthanide 5d electrons may make a significant contribution. The susceptibility and inverse susceptibility observed for all samples is plotted in Figures (6.20 to 6.24). The Curie-Weiss behaviour is apparent in these figures, the resulting $X^{-1}vT$ curve is a straight line which intercepts the temperature axis at the Curie-Weiss temperature ($\theta_p$), and has a slope ($1/c$). The observed effective moment ($\mu_{\text{eff}}$), and the Curie-Weiss temperature obtained from these curves are given in Table (6.7). The effective Bohr magnetons

$$\mu_{\text{eff}} = g_B \mu_B [J (J+1)]^{1/2}$$  \hspace{1cm} (6.3)

derived from the Curie constants have values (see Table (6.7)) which are close to theoretical values for trivalent rare-earth ions [18]. The effective Bohr magneton number $\mu_{\text{eff}}$ was obtained from the magnetic susceptibility in the following manner:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}} (\mu_B)$ exp.</th>
<th>$\mu_{\text{eff}} (\mu_B)$ Theory [17]</th>
<th>$(\theta_p)$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_2$DyIn</td>
<td>10.95 $\pm$ 0.237</td>
<td>10.60</td>
<td>0K $\pm$ 0.25</td>
</tr>
<tr>
<td>Pd$_2$ErIn</td>
<td>9.846 $\pm$ 0.319</td>
<td>9.60</td>
<td>3K $\pm$ 0.25</td>
</tr>
<tr>
<td>Pd$_2$YbIn</td>
<td>5.11 $\pm$ 0.248</td>
<td>4.50</td>
<td>3K $\pm$ 0.25</td>
</tr>
<tr>
<td>Pd$_2$TbIn</td>
<td>11.44 $\pm$ 0.327</td>
<td>9.70</td>
<td>2K $\pm$ 0.25</td>
</tr>
<tr>
<td>Pd$_2$GdIn</td>
<td>8.59 $\pm$ 0.263</td>
<td>7.94</td>
<td>1K $\pm$ 0.25</td>
</tr>
</tbody>
</table>

TABLE (6.7): RESULTS AND ANALYSIS OF THE SUSCEPTIBILITY OF HEUSLER ALLOYS, $\mu_{\text{eff}}$ AND $\theta_p$ ARE OBTAINED FROM HIGH-TEMPERATURE CURIE-WEISS FITS
Fig.(6.21a) Susceptibility of Pd2ErIn as a function of Temperature.

Fig.(6.21b) Reciprocal susceptibility of Pd2ErIn as a function of Temperature.
Figure (6.22a) Susceptibility of Pd2YbIn as a function of Temperature.

Figure (6.22b) Reciprocal susceptibility of Pd2YbIn as a function of Temperature.
Figure (6.23a) Susceptibility of Pd2TbIn as a function of Temperature.

Figure (6.23b) Reciprocal susceptibility of Pd2TbIn as a function of Temperature.
Fig.(6.24a)
Susceptibility of Pd2GdIn as a function of Temperature.

Fig.(6.24b)
Reciprocal susceptibility of Pd2GdIn as a function of Temperature.
Rearranging this equation gives

\[
\mu_{\text{eff}}^2 = \frac{3KX(T-\theta)}{N\mu_B^2} \tag{6.5}
\]

where \( N \) is Avogadro's number = \( 6.02217 \times 10^{23} \) /mole and the slope of \((1/X, T)\) is found from the graphs using

\[
K = 1.38 \times 10^{-16} \text{ erg/degree}
\]

\[
\mu_B = 9.274096 \times 10^{-21} \text{ erg/oersted}
\]

\[
\mu_B^2 = 8.6 \times 10^{-41} \text{ erg/oersted}
\]

6.7 NEUTRON POWDER DIFFRACTION

6.7.1 The (HRPD) Measurements on Heusler Alloys

The experimental procedure was described in Chapter 5. All the alloys were prepared similarly from spectrographically pure elements supplied by Johnson Matthey and Co Ltd. Details of the preparation have been presented earlier. The unit cell of Heusler alloys displayed in Figure (6.16) is comprised of four interpenetrating f.c.c. sublattices (a,b,c,d). For this structure the permitted Bragg reflections are those for which the Miller indices are unmixed. They have the following structure amplitudes [19]:

195
h.K.L. all odd \[ F(111) = |4 \left[ (f_a - f_c)^2 + (f_b - f_d)^2 \right]^{1/2} \] (6.6)

h.K.L. all even \[ F(200) = |4 \left[ f_a - f_b + f_c - f_d \right] | \]

\((h+K+L) = 4n+2\)

\((h+K+L) = 4n \left| F(220) = |4 \left[ f_a + f_c + f_b + f_d \right] | \right.\)

"hence, for a Heusler alloy, when \(fa = fb\)"

\[ F(111) = 4|f_b - f_d| \]

\[ F(200) = 4|2f_a - (f_b + f_d)| \] (6.7)

\[ F(220) = 4|2f_a + (f_b + f_d)| \]

where \(f_a, f_b, f_c\) and \(f_d\) are the average scattering structure factors for the A, B, C and D sublattices respectively. The structure factors \(F(111)\) and \(F(200)\) are order-dependent, but \(F(220)\) is independent of order. There are an infinite number of ways the system can disorder but there are seven preferential ways which lead to other structures of particular importance. In the present study the most important type of disorder was that which led to the B2 structure. In the B2 structure X and In atoms randomly occupy the b and d sites, and consequently the \((111)\) reflection disappears. There have been a considerable number of studies on the magnetic properties of ordered alloys with the Heusler structure especially magnetisation [19,20] and neutron scattering [21,22] measurements. Interests in the Heusler alloys containing Mn atoms are mainly concerned with investigating localised magnetic moment behaviour in a transition metal environment. The moments on the Mn atoms are localised [21,28,25]. Since the Mn-Mn magnetic atoms are in general separated by 4.6Å the exchange
interactions are long range via an s-d mechanism between d resonances [25, 26]. In this section the results of neutron diffraction measurements on Pd$_2$MnIn, Pd$_2$ErIn and Pd$_2$TbIn are presented. The HRPD powder diffractometer at the ISIS pulsed neutron source situated at the Rutherford Appleton Laboratory (RAL) was used to investigate the samples. The study was carried out at 5\degree K for Pd$_2$MnIn, Figure (6.25), and 300\degree K for Pd$_2$ErIn and Pd$_2$TbIn, Figures (6.26, 6.27) respectively and using flight times of 112 ms up to 210 ms. The high neutron flux available allows small samples to be studied. Background scattering coming from the sample consists of several components. Incoherent scattering from the sample appears as a constant cross-section on an absolute spectrum. Thermal diffuse scattering which also contributes to the background will be treated in detail in the following paragraph. The thermal diffuse scattering can vary significantly at high Q, but at low Q it is in general small. As the coherent Bragg intensities decrease as a function of the d spacing to the fourth power, the rest of the coherent scattering takes the characteristic form shown in Figures (6.25 to 6.27). To a first approximation the variation with Q can be described by the remainder from the Debye-Waller factor. The background scattering is given by [38].

\[ B(t) = \left( \frac{d\sigma}{dt} \right)_{inc} + \left( \frac{d\sigma}{dt} \right)_{coh} \left[ 1 - \exp\left(-2B \sin^2 \theta/\lambda^2\right) \right] \]  

(6.8)

In practice this gives a good description of the background, especially if the various constants are adjusted to give a best fit.
The crystallographic structure of the compounds under investigation are obtained from the coherent Bragg intensities since the materials i.e. Heusler alloys, have a cubic structure. The lattice spacing is given by:

\[
\frac{d}{2\sin(\theta)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

As discussed in Section (5.6) certain peaks, the superlattices reflections are sensitive to the degree of chemical order. It was therefore possible to establish the type and degree of chemical order by measuring their intensities.

The observed reflections for each data set were indexed and the lattice parameter determined. The results are summarised in Tables (6.8, 6.9, 6.10). It may be seen that in general the odd superlattice peaks are absent indicating complete B2 disorder.

<table>
<thead>
<tr>
<th>d-spacing</th>
<th>d hKL/a</th>
<th>h²+k²+l²</th>
<th>hKL</th>
<th>Lattice Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.241</td>
<td>8.0</td>
<td>8</td>
<td>220</td>
<td>6.369 (5)</td>
</tr>
<tr>
<td>1.835</td>
<td>11.93</td>
<td>12</td>
<td>222</td>
<td></td>
</tr>
<tr>
<td>1.425</td>
<td>19.79</td>
<td>20</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>1.297</td>
<td>23.87</td>
<td>24</td>
<td>422</td>
<td></td>
</tr>
<tr>
<td>1.231</td>
<td>26.52</td>
<td>27</td>
<td>333</td>
<td></td>
</tr>
<tr>
<td>1.124</td>
<td>31.805</td>
<td>32</td>
<td>440</td>
<td></td>
</tr>
<tr>
<td>1.060</td>
<td>35.763</td>
<td>36</td>
<td>442</td>
<td></td>
</tr>
<tr>
<td>1.007</td>
<td>39.62</td>
<td>40</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>0.961</td>
<td>43.51</td>
<td>44</td>
<td>622</td>
<td></td>
</tr>
<tr>
<td>0.918</td>
<td>47.68</td>
<td>48</td>
<td>444</td>
<td></td>
</tr>
<tr>
<td>0.883</td>
<td>51.53</td>
<td>51</td>
<td>552</td>
<td></td>
</tr>
<tr>
<td>0.849</td>
<td>55.747</td>
<td>56</td>
<td>642</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE (6.8):** Pd₂MnIn at 5°K
Fig. (6.25)

Diffraction pattern of Pd2MnIn obtained at the low resolution position of HRPD at ISIS
Fig. (6.26)

Diffraction pattern of Pd2ErIn obtained at the low resolution position of HRPD at ISIS.
Fig. (6.27)

Diffraction pattern of Pd2B1n obtained at the low resolution position of HRPD at ISIS.
<table>
<thead>
<tr>
<th>d-spacing</th>
<th>d hKL/a</th>
<th>$h^2+k^2+l^2$</th>
<th>hKL</th>
<th>Lattice Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6705</td>
<td>16.0</td>
<td>16</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>1.2536</td>
<td>27.9</td>
<td>28</td>
<td>331</td>
<td></td>
</tr>
<tr>
<td>1.1822</td>
<td>31.93</td>
<td>32</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>1.0568</td>
<td>39.96</td>
<td>40</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>0.9642</td>
<td>48.01</td>
<td>48</td>
<td>444</td>
<td></td>
</tr>
<tr>
<td>0.8935</td>
<td>55.91</td>
<td>56</td>
<td>642</td>
<td></td>
</tr>
<tr>
<td>0.7871</td>
<td>71.04</td>
<td>72</td>
<td>822</td>
<td></td>
</tr>
<tr>
<td>0.7464</td>
<td>80.12</td>
<td>80</td>
<td>840</td>
<td></td>
</tr>
<tr>
<td>0.6822</td>
<td>95.91</td>
<td>16</td>
<td>844</td>
<td></td>
</tr>
<tr>
<td>0.6545</td>
<td>104.19</td>
<td>104</td>
<td>862</td>
<td></td>
</tr>
<tr>
<td>0.6100</td>
<td>119.95</td>
<td>120</td>
<td>1042</td>
<td></td>
</tr>
<tr>
<td>0.5714</td>
<td>136.711</td>
<td>136</td>
<td>1060</td>
<td></td>
</tr>
</tbody>
</table>

TABLE (6.9): Pd$_2$ErIn at 300°K

<table>
<thead>
<tr>
<th>d-spacing</th>
<th>d hKL/a</th>
<th>$h^2+k^2+l^2$</th>
<th>hKL</th>
<th>Lattice Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.38</td>
<td>8.0</td>
<td>8</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>1.686</td>
<td>16.0</td>
<td>16</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>1.375</td>
<td>23.99</td>
<td>24</td>
<td>422</td>
<td></td>
</tr>
<tr>
<td>1.191</td>
<td>32.0</td>
<td>32</td>
<td>440</td>
<td></td>
</tr>
<tr>
<td>1.064</td>
<td>39.996</td>
<td>40</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>1.028</td>
<td>42.999</td>
<td>43</td>
<td>533</td>
<td></td>
</tr>
<tr>
<td>0.9723</td>
<td>47.995</td>
<td>48</td>
<td>444</td>
<td></td>
</tr>
<tr>
<td>0.9001</td>
<td>56.004</td>
<td>56</td>
<td>642</td>
<td></td>
</tr>
<tr>
<td>0.8425</td>
<td>64.0</td>
<td>64</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>0.7937</td>
<td>72.0</td>
<td>72</td>
<td>822</td>
<td></td>
</tr>
<tr>
<td>0.7179</td>
<td>88.248</td>
<td>88</td>
<td>664</td>
<td></td>
</tr>
<tr>
<td>0.6880</td>
<td>96.086</td>
<td>96</td>
<td>844</td>
<td></td>
</tr>
<tr>
<td>0.6603</td>
<td>104.007</td>
<td>104</td>
<td>862</td>
<td></td>
</tr>
<tr>
<td>0.6151</td>
<td>124.0</td>
<td>124</td>
<td>1042</td>
<td></td>
</tr>
<tr>
<td>0.5772</td>
<td>136.989</td>
<td>135</td>
<td>1060</td>
<td></td>
</tr>
<tr>
<td>0.5619</td>
<td>144.0</td>
<td>144</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>0.5459</td>
<td>151.286</td>
<td>152</td>
<td>1222</td>
<td></td>
</tr>
<tr>
<td>0.5196</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

TABLE (6.10): Pd$_2$TbIn at 300°K
6.8 EFFECTS OF ANNEALING PROCESSES ON THE HYSTERESIS LOOP OF Fe-Ni INVAR ALLOYS

6.8.1 Fe50Ni50, Fe78Ni22
Fe-Ni alloys are a very rich and interesting system. Particularly in the Invar range between 22 and 50 at % Ni, which has an f.c.c. structure. In this region anomalous behaviour is observed in some physical properties such as magnetostriction, thermal expansion etc (Nakamura 1976) [27]. Alloys which exhibit Invar behaviour have a small thermal expansion coefficient below the Curie temperature, a large forced volume magnetostriction and show a substantial pressure dependence of the magnetisation and Curie temperature etc [28]. For alloys in the Fe-Ni system, local fluctuations in compositions resulting in a heterogeneous magnetisation are believed essential for the Invar effect, which shows a maximum at the composition Fe65Ni35.

Iron rich alloys in the Fe-Ni series which have b.c.c. structure do not exhibit Invar behaviour. In spite of the considerable research effort the Invar problem is not yet completely understood. In a recent study (Gallas et al, 1989) [29], observed an increase in the line width of the Mossbauer spectra of Fe70Ni30 alloys which had been annealed at high pressure. The heat treatment led to a rearrangement of the atoms caused an increase in the short-range order, in agreement with other studies (Makarov and Puzey 1974) [30]. Present theoretical calculations for Fe-Ni alloys (Kakehashi 1988) [31] show that important changes in magnetic properties can occur due to local environmental effects. In the present work a systematic study of the hysteresis loop as a function of magnetic field was made for Fe-Ni alloys with compositions 22, 50 at % Ni. The saturation magnetisation was 86, 65 (emu/g) for Fe50Ni50, Fe78Ni22 respectively. The change in the area of the hysteresis loop with composition for Fe-Ni alloy is
Fig. (6.28a) Hysteresis Loop for Fe50Ni50 as a Function of Temperature, without heat treatment.

Figure (6.28b) Hysteresis Loop for Fe50Ni50 as a function of Temperature, after annealing.
Fig.(6.29a) Hysteresis Loop for Fe87Ni22 as a Function of Temperature, without heat treatment.

Fig.(6.29b) Hysteresis Loop for Fe87Ni22 as a Function of Temperature, after annealing
particularly large near 50 at % Ni (see Figure (6.28a,b), (6.29a,b)). This occurs presumably because of a strong competition between ferromagnetism (related to a positive exchange interaction between Fe-Ni and Ni-Ni pairs) and antiferromagnetism (favoured by negative exchange interaction between Fe-Fe pairs [Lawrence and Rossiter 1986] [32]. It is interesting to note that the theoretical work of Kakehashi (1988) [31] found that coupling between two neighbouring Fe atoms can be either ferromagnetic or antiferromagnetic, depending on the number of Fe nearest neighbours surrounding it.

Therefore, this composition (50 at % Ni) is expected to be very sensitive to structural changes like short range order or clustering. The results are summarised in Figures (6.28a,b) and (6.29a,b) where the change in hysteresis loop is shown for different heat treatments to the specimens. It can be observed in Figure (6.29a), that for 22 at % Ni there is no change in hysteresis following the behaviour of the hysteresis loop with annealing treatment as shown in Figure (6.28b), due to a change in short-range order. This change is probably related to atomic rearrangement like short-range ordering, clustering or a spinodal decomposition. The relevant properties of the two samples are listed in Table (6.11). In the case of amorphous alloys, the annealing process is considered to produce the main effects: a change in the chemical short-range order and a topological change in the structure, whereas in the case of an alloy in the crystalline state the only change possible is in the chemical order.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Fe$<em>{50}$Ni$</em>{50}$</th>
<th>Fe$<em>{50}$Ni$</em>{22}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average atomic mass (ama)</td>
<td>57.28</td>
<td>56.31</td>
<td>-</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>3.586</td>
<td>3.586</td>
<td>(33,34)</td>
</tr>
<tr>
<td>Melting temperature (K)</td>
<td>1710</td>
<td>1750</td>
<td>(35)</td>
</tr>
<tr>
<td>Saturation magnetic moment (μB/atom)</td>
<td>1.68</td>
<td>1.25</td>
<td>(37)</td>
</tr>
<tr>
<td>Curie temperature (K)</td>
<td>790</td>
<td>340</td>
<td>(34,37)</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td>407.8</td>
<td>315</td>
<td>(34,37)</td>
</tr>
<tr>
<td>Structure</td>
<td>fcc -phase</td>
<td>bcc -phase</td>
<td>(35,34)</td>
</tr>
</tbody>
</table>

**TABLE 6.11: PROPERTIES OF THE f.c.c. ALLOYS AT 290°K**
REFERENCES


CHAPTER 7
DISCUSSION AND CONCLUSION

The main aim of the project was to design and build an automated versatile magnetometer to be used for investigating the magnetic properties of relatively weak magnetic compounds. The design of the VSM used a novel pick-up coil arrangement to reduce to a negligible level signals coming from vibrations other than the vertical movement of the sample. Pure nickel and iron were chosen as the calibration samples. The results showed that the reliability and reproducibility of the VSM is satisfactory.

Calibration studies showed the lower limit of sensitivity was $5 \times 10^{-6}$ emu/g. Reproducibility was better than 0.5%.

In its present set up the VSM is mounted on an electromagnet and a 4.3 cm pole gap is used to allow access of a variable temperature cryostat. This reduces the maximum applied to 11 kG. There is no fundamental design reason why the VSM could not be used with a larger electromagnet or incorporated in a cryomagnet. In this way very much larger fields would be attainable. The availability of a larger magnet would enable more turns to be used on the pick-up coils with a corresponding increase in sensitivity. The increased space would also enable additional coils to be mounted. If these were placed orthogonally to the existing coils then two or three components of magnetisation could be measured simultaneously. This would give direct information regarding the intrinsic anisotropy of the magnetisation.
At present the VSM incorporates an Oxford Instruments flow cryostat which enables sample temperatures in the range 1.5 to 450 K to be attained. The upper temperature limit could be extended up to at least 1300 K using standard resistance methods for heating. Clearly it would be beneficial to have a high temperature facility. Currently the VSM is controlled by a Commodore computer. Whilst this is adequate, it does restrict data storage and manipulation. The laboratory is currently being re-equipped with IBM PCs and it will be beneficial to change the computer on the VSM. This will then allow direct visualisation of the data both on the VDU and in hard copy form. The basic routines would not significantly change.

The thermal and magnetic properties of some Laves phases alloy were studied using the VSM. There are in fact two types of Laves phase structure, the cubic C15 with space group Fd3m and C14 structure which is hexagonal with space group P63/mmc. The two structures are related by their stacking sequence in a way analogous to the inter-relationship of the f.c.c. and hcp structures. The Laves phase represents a simple crystallographic arrangement in which to study the stability of the manganese moment. The temperature dependence of the magnetic susceptibility was measured in the temperature range 77 to 450 K for the Laves phase compounds. Over the temperature range covered there is no evidence of a magnetic phase transition. In fact the specific heat has the normal appearance expected for a Debye solid. X-ray diffraction patterns obtained at room temperature confirmed that all the Laves phase compounds in this work were single phase with the C14 structure.
In general the results are in agreement with those of Shavishvili et al, although the temperature range was more restricted in the present study. The temperature variation of the susceptibility is small, therefore it was decided to carry out an analysis of the susceptibility using the following equation (2.60):

$$X(T) = X(0) + CT^2$$  \hspace{1cm} (7.1)

The factor $X(0)$ was varied, and the data in the high temperature range ($T > 150^\circ K$) was compared to the expression using a least squares analysis. The high temperature region was used in order to avoid problems due to short range order, but the agreement obtained is convincing down to low temperature, for example, see Figures (6.5, 6.8, 6.11, 6.14). The parameters obtained are given in Table (7.1). In order to calculate the diamagnetic contribution, the following equation has been used:

$$X_{\text{mol}} = -Z_1 \frac{Ne^2}{6mc^2} \langle r^2 \rangle$$  \hspace{1cm} (7.2)

where $Z_1$ is number of electrons in the atom

$\langle r^2 \rangle$ is the average square radius of the electron.

The diamagnetic contribution of a material is just an additive function of the components and is given by equation 4.99). The results of the diamagnetic calculation are shown in Table (7.1).
Heusler alloys were chosen for investigation because they offer an opportunity to study the effects of interatomic distance, atomic arrangement and electron concentration on the occurrence and type of magnetic order in 3d metallic systems. These materials were based on the composition Pd$_2$XIn where X represents a rare-earth atom. Isostructural components have been reported which are simultaneously superconducting and magnetic with the SP electrons responsible for the superconductivity and the 4f electrons associated with the rare earth atoms responsible for the magnetisation. The susceptibility of Pd$_2$XIn alloys arises mainly from 4f electrons but contributions are expected from the other electrons and in particular the lanthanide 5d electron makes a significant contribution. A Curie-Weiss behaviour was observed for all specimens. The effective Bohr magnetons $\mu_{\text{eff}}$ derived from the Curie constants have values (see Table 6.7) which are close to theoretical values for trivalent rare-earth ions.

Frustration arises with antiferromagnetic interactions whenever the geometry of the lattice is such that the neighbours of a given atom are themselves neighbours of each other. Consider a f.c.c. system:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diamagnetic emu/g contribution x 10$^{-6}$</th>
<th>$X(0)$ emu/g</th>
<th>C x 10$^{-5}$ emu/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$Ti</td>
<td>-0.0251</td>
<td>28.708</td>
<td>-1.8214</td>
</tr>
<tr>
<td>Mn$_2$Zr</td>
<td>-0.0276</td>
<td>34.848</td>
<td>-2.0393</td>
</tr>
<tr>
<td>Mn$_2$Nb</td>
<td>-0.0255</td>
<td>18.588</td>
<td>-1.5218</td>
</tr>
<tr>
<td>Mn$_2$Hf</td>
<td>-0.0271</td>
<td>13.908</td>
<td>-6.4220</td>
</tr>
</tbody>
</table>
all the spins on the corner sides will be parallel to each other and all the spins in the centre positions will be antiparallel. The distance between the corner and face centred positions is \( a/\sqrt{2} \) which is identical to the separation of the face centred positions themselves. However the exchange interaction will be negative and positive for the two identical distances respectively, therefore the system is frustrated.

Commercially e.g. transformers etc it is important to know the power dissipated in the magnetisation process. We have therefore measured the hysteresis loop of Fe-Ni alloys to demonstrate the versatility of the VSM. In the present work a systematic study of the hysteresis loop as a function of magnetic field was made for Fe-Ni alloys with compositions 22 and 50% Ni. The saturation magnetisation was 85 and 65 (emu/g) for Fe50 Ni50 and Fe78 Ni22 respectively. The change in hysteresis area with composition for Fe-Ni alloys is particularly large near 50 at % Ni, presumably because of a strong competition between ferromagnetism (related to a positive exchange interaction between Fe-Ni and Ni-Ni pairs) and antiferromagnetism (favoured by a negative exchange interaction between Fe-Fe pairs. The behaviour of the hysteresis loop with annealing treatment is shown in Figure (6.28b) due to the change in short-range order, this change is probably related to atomic rearrangements such as short-range order.

CONCLUSION

The thermal and magnetic properties of some Laves phase and Heusler compounds have been extensively studied to investigate and study the systematics of these materials. An automated (VSM) was considered to be the most suitable apparatus for this study as it provided a wide
range of versatility for measuring both magnetisation and susceptibility. The results of the Laves phase alloys are in general agreement with those of Shavishvili et al. The Heusler alloy containing rare earth elements compounds produced reasonable values for the effective Bohr magneton, slightly higher in magnitude than the Bohr magneton values for the individual tripositive ions Er, Gd, Yb, Tb and Dy. These studies provide an important first step before carrying out more detailed investigations at low temperature.

Work is currently in progress at Oxford and Sheffield to establish the transport and magnetic properties in the temperature range below 10K. Preliminary results indicate that the samples become superconducting at temperatures below 2K. The X-ray and neutron data indicated that the samples were chemically disordered into the B2 structure. It would be extremely interesting to repeat these studies on samples which have the L2₁ structure. In this way it would be possible to assess the effects of atomic order on the occurrence of magnetic and superconductivity and possibly understand the physical underlying mechanisms.
APPENDICES
APPENDIX (A)

FLOW DIAGRAM OF THE MAIN PROGRAM FOR
THE MAGNETIZATION MEASUREMENTS

START

POKE 59459,255; Set the User port as output port.

OPEN5,23; initialises the lock-in Amplifier file.
OPEN1,4,1; initialises the disc drive file
OPEN2,4,2; initialises the printer file.
OPEN7,7; initialises the Temperature controller file.

FOR Y = 0 TO 20

READ H(Y),MS(Y); i.e Read, Field and standard sample Magnetization

IF Y = 20 THEN YES

INPUT "TITLE"; A$
INPUT "specimen mass (gm)"; SM

INPUT "field current step"; N

INPUT "Max. field current"; IM

A

B
INPUT "Min. field current" IK

INPUT "RUN=1, RET=2, END=3"; J

IF J=2?

YES

NO

IF J=3?

YES

NO

INPUT "M-H Loop=1, MAGNETIZATION=2"; SS

YES

IF SS=1

NO

INPUT "start temperature"; T1

END
GOSUB 1100; subroutine to print the title

INPUT "Final temperature"; T2

INPUT "No. of temperature shot"; NS

INPUT "Temp. increase"; MM

INPUT "Gain option(0-5)"; G

INPUT "INT. option(0-7)"; S

INPUT "DERIVE option(0-7)"; D

PRINT \$7, "LR"; send remote command to the temperature controller

PRINT \$7, "LA"; send automatic command to the temperature controller

G$ = "GG" + STR$(G)
PRINT \$7, G$; send the gain command to the temperature controller

S$ = "GI" + STR$(S)
PRINT \$7, S$; send the integration command to the temperature controller

D$ = "GD" + STR$(D)
PRINT \$7, D$; send the derivative command to the temperature controller

FOR I = 0 TO NS
T(I) = T1 + (I*MM)

IF T0 > 450

YES

GOSUB 1450; subroutine to set the temperature of the sample

GOSUB 250; subroutine to set the magnetic current for the field

GOSUB 2000; subroutine to calculate the magnetic susceptibility of the sample

NEXT

IF I = NS

GOSUB 1600; subroutine to rest the field current
FOR 1=1 TO 6

- GOSUB 250; subroutine to increase the field current in positive direction
- GOSUB 400; subroutine to decrease the field current in positive direction
- GOSUB 570; subroutine to increase the field current in negative direction
- GOSUB 800; subroutine to decrease the field current in negative direction
- GOSUB 250; subroutine to set the field current in positive direction
- GOSUB 1000; subroutine to decrease the field current to zero
FLOW CHART TO SET THE TEMPERATURE OF THE SAMPLE

FROM THE MAIN PROGRAM

\[ V(I) = 65536 \times \frac{(T(I) - 3)}{496.7} \]

PRINT£7,"LA"; send the automatic command to the temperature controller

Wait for 1 sec

\[ T$ = "TS" + STR$(V(I)) \]

PRINT£7,T$ ; send the set temperature to the temperature controller

Wait for 1 sec

RETURN
POKE 59471,1; set the multiplexer to read the pick-up coil voltage, and rotate the stepper motor in clockwise direction.

Wait for 0.1 sec

IF X=10000

YES

Wait for 1 sec

PRINT$5,"Q"; set the lock-in amplifier to measure the voltage from the pick-up coil.

INPUT$5,M; input the measured voltage from the lock-in amplifier to the computer.
GOSUB 1500; subroutine to calculate the magnetic susceptibility.

X2 = X2 + X(I)

GOSUB 1250; subroutine to print the result

IF
SS=1

NO

IF
Z=IM/N

YES

RETURN
SUBROUTINE TO DECREASE THE FIELD CURRENT IN A POSITIVE DIRECTION

FROM THE MAIN PROGRAM

POKE 59471,0; set the multiplexer to read the field current, and rotate the stepper motor in anticlockwise direction

FOR Z=0 TO 10M/N

FOR X=0 TO 10000

POKE 59471,0; set the multiplexer to read the field current, and rotate the stepper motor in anticlockwise direction

Wait for .1 sec

PRINT$S,"X1"; set the lock-in amplifier to measure the field current.

INPUTS$,"Y1"; input the measured field current from the lock-in amplifier

IF Y>=Z*N+1M

YES

NO

A1

A2

B1 B2
YES

POKE 59471,1; set the multiplexer to read the pick-up coil voltage, and rotate the stepper motor in antclockwise direction

Wait for 0.1 sec

NO

IF Y=0

IF X=10000

NO

YES

Wait for 1 sec

PRINT$5,"Q"; set the lock-in amplifier to measure the voltage from the pick-up coil.

INPUT$5,M; input the measured voltage from the lock-in amplifier to the computer
GOSUB 1250; subroutine to print the result

IF Z=IM/N

RETURN
SUBROUTINE TO INCREASE THE FIELD CURRENT IN A POSITIVE DIRECTION

FROM THE MAIN PROGRAM

GOSUB 1000; subroutine to reset the field current.

FOR Z=0 TO IM/N

POKE 59471,2; set the multiplexer to read the field current, and rotate the stepper motor in a clockwise direction

FOR X=0 TO 10000

POKE 59471,2; set the multiplexer to read the field current, and rotate the stepper motor in a clockwise direction

Wait for .1 sec

PRINT$5,"XI"; set the lock-in amplifier to measure the field current.

INPUT$5,"Y1"; input the measured field current from the lock-in amplifier

IF Y>=Z*N+IK

YES

A1

NO

A2

B1

B2
YES

POKE 59471,7; set the multiplexer to read the pick-up coil voltage, reverse the field current and rotate the stepper motor in clockwise direction

Wait for 0.1 sec

NO

IF Y<=-1M

YES

Wait for 1 sec

IF X=10000

NO

PRINT£5,"Q"; set the lock-in amplifier to measure the voltage from the pick-up coil.

INPUT£5,M; input the measured voltage from the lockin amplifier to the computer
GOSUB 1250; subroutine to print the result

IF

Z=IM/N

NO

YES

RETURN
SUBROUTINE TO INCREASE THE FIELD CURRENT IN A NEGATIVE DIRECTION

FROM THE MAIN PROGRAM

POKE 59471,6; set the multiplexer to read the field current, reverse the field current and rotate the stepper motor in clockwise direction

FOR Z=0 TO IM/N

FOR X=0 TO 10000

POKE 59471,6; set the multiplexer to read the field current, reverse the field current and rotate the stepper motor in clockwise direction

Wait for .1 sec

PRINT£5,"X1"; set the lock-in amplifier to measure the field current.

INPUT£5,"Y1"; input the measured field field current from the lock-in amplifier

IF Y<=Z*N

YES

A1

NO

A2

B1

B2
POKE 59471.5; set the multiplexer to read the pick-up coil voltage, reverse the field current and rotate the stepper motor in antclockwise direction

Wait for 0.1 sec

IF X=10000

YES

Wait for 1 sec

PRINT$5,"Q"; set the lock-in amplifier to measure the voltage from the pick-up coil.

INPUT$5,M; input the measured voltage from the lock-in amplifier to the computer
GOSUB 1250; subroutine to print the result

IF Z=IM/N

RETURN
SUBROUTINE TO DECREASE THE FIELD CURRENT IN A NEGATIVE DIRECTION

FROM THE MAIN PROGRAM

POKE 59471,4; set the multiplexer to read the field current, reverse the field current and rotate the stepper motor in antclockwise direction

FOR Z=0 TO IM/N

FOR X=0 TO 10000

POKE 59471,4; set the multiplexer to read the field current, reverse the field current and rotate the stepper motor in antclockwise direction

Wait for .1 sec

PRINTE5,"X1"; set the lock-in amplifier to measure the field current.

INPUTE5,"Y1"; input the measured field field current from the lock-in amplifier

IF Y>=Z*N-IM

YES

A1

NO

A2

B1

B2
SUBROUTINE TO DECREASE THE FIELD CURRENT TO ZERO

1000 FROM THE MAIN PROGRAM

POKE 59471,0; set the multiplexer to read the field current, reverse the field current and rotate the stepper motor in an anticlockwise direction

FOR X=0 TO 10000

POKE 59471,0; set the multiplexer to read the field current, reverse the field current and rotate the stepper motor in anticlockwise direction

Wait for .1 sec

PRINT$5,"X1"; set the lockin amplifier to measure the field current.

INPUT$5,"Y1"; input the measured field field current from the lock-in amplifier

IF Y<=IK

YES

NO

A1

A2

B1
POKE 59471,1; set the multiplexer to read the pick-up coil voltage, reverse the field current and rotate the stepper motor in an anti-clockwise direction

Wait for 0.1 sec

IF X=10000 THEN YES

RETURN
SUBROUTINE TO STORE THE
TITLE ON A FLOPPY DISC

FROM THE MAIN PROGRAM

PRINT$2 A$: print the title on the disc

PRINT$2, "SEPC.MASS=", SM, "G"

PRINT$2 "H(KG)" , "M(EMU/G)"

PRINT$2 "H(KG)" , "X(EMU/G)"

RETURN
SUBROUTINE TO PRINT THE TITLE

FROM THE MAIN PROGRAM

PRINT A$; print the title on the screen

PRINT£1,A$; print the title on the printer

PRINT SEPC.MASS=.SM,G

PRINT£1,"SEPC.MASS=".SM,"G"

PRINT"H(KG)"."M(EMU/G)"

PRINT£1"H(KG)"."X(EMU/G)"

RETURN
SUBROUTINE TO CALCULATE AND TO PRINT THE MAGNETIC SUSCEPTIBILITY

FROM THE MAIN PROGRAM

\[ X(I) = (M \times 0.2331 \times 55.1/\text{VS} \times \text{SM} \times H(Y)) \]

PRINT \(Y\), \(T(I), H(Y), X(I)\); print the temperature, the magnetic field and the susceptibility of the sample on the screen

PRINT \(Y\), \(T(I), H(Y), X(I)\); print the temperature, the magnetic field and the susceptibility of the sample on the printer

RETURN
SUBROUTINE TO CALCULATE AND
PRINT THE MAGNETISATION FROM THE MAIN PROGRAM

PRINT E1, H(Y), (M*2331*55.1/V*S*M *H(Y)); print the magnetic field and the magnetisation of the sample on the printer

PRINT H(Y), (M*2331*55.1/V*S*M *H(Y)); print the magnetic field and the magnetisation of the sample on the screen

RETURN
SUBROUTINE TO CALCULATE

THE MAGNETIC SUSCEPTIBILITY

FROM THE MAIN PROGRAM

ZN = (IM-IK)/N + 1

X2 = X2/ZN

PRINT T(I),X2,1/X2; print the temperature susceptibility, and inverse susceptibility on the screen

PRINT £1,T(I),X2,1/X2; print the temperature susceptibility, and inverse susceptibility on the printer

RETURN
SUBROUTINE TO CALCULATE
AND TO SAVE THE RESULTS
ON FLOPPY DISC

3000

FROM THE MAIN PROGRAM

X(I)=(M*0.2331*55.1/VS*SM*H(Y))

PRINT$2 H(Y) T(I), H(Y), X(I); print the
temperature the magnetic field and the
susceptibility of the sample on the disc

RETURN