An investigation of magnetic properties of some rare earth Heusler alloys

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<td>040094123</td>
</tr>
<tr>
<td>VOL. NO.</td>
<td>28 JUN 1996</td>
</tr>
<tr>
<td></td>
<td>27 JUN 1997</td>
</tr>
<tr>
<td></td>
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An Investigation of Magnetic Properties of Some Rare Earth Heusler Alloys

by

Muhammed Omar Babateen

A Doctoral Thesis Submitted in Partial Fulfilment of the Requirements for the Award of Doctor of Philosophy of the Loughborough University of Technology

July 1994

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IN THE NAME OF ALLAH THE MOST BENEFICIENT
THE MOST MERCIFUL

DEDICATION

To my wife and children Omar, Ammar, Abrar and Amjad
for all the sacrifices that they made in favour of
my education.

**********
This is to certify that I am responsible for the work submitted in this thesis, that the original work is my own except as specified in acknowledgements or in footnotes, and that neither the thesis nor the original work contained therein has been submitted to this or any other institution for a higher degree.

M. O. Babateen

12 July 1994
ABSTRACT

The magnetic properties of some rare earth based Heusler alloys have been investigated. Rare earth Heusler alloys of the form Pd$_2$Reln exhibit magnetic behaviour characterised by magnetic moments localised on the rare earth atoms. X-ray and neutron diffraction investigation show that all alloys crystallise in the cubic L2$_1$ Heusler structure with space group $Fm\bar{3}m$.

The crystal field splitting is investigated using inelastic neutron scattering technique. The observed crystal field transitions have been identified as magnetic in origin by their temperature and wave-vector dependence. Analysis of the data shows that the energies and intensities may be interpreted on the basis of a crystalline electric field model for rare earth atoms with cubic point symmetry. The crystal field parameters for the compounds of Pd$_2$HoIn, Pd$_2$ErIn, Pd$_2$YbIn, and Pd$_2$YbSn are determined on the basis of the LLW formalism.

The neutron scattering results are used to determine the crystal field level scheme and the results are compared with the crystal field splitting in the isostructural Sn series. This comparison shows that the crystal field parameters between the same rare earth compounds in the alloy series Pd$_2$ReIn and Pd$_2$ReSn exhibit scaling properties. The neutron scattering data are also fitted to the bulk magnetisation both as a function of temperature and applied magnetic field. A satisfying agreement is achieved between calculated and measured magnetisation.
The magnetic properties of these compounds are also investigated through the measurement of magnetic susceptibility as a function of temperature and the magnetisation as a function of applied field and temperature. The paramagnetic susceptibilities show Curie-Weiss behaviour for all of the investigated alloys. The experimental effective magnetic moments are found to be slightly higher than expected on the basis of free rare earth ion calculation. This small difference is attributed to the spin polarisation of conduction electrons. Deviations from a Curie-Weiss behaviour are observed at low temperature, these can be understood and modelled using crystal field model.
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Acknowledgement

I am deeply indebted to Dr. K. U. Neumann for his patient supervision and invaluable guidance which enabled me to complete this project successfully. My sincere thanks are extended to Professor K. R. A. Ziebeck who supplied me with so much useful advice and practical assistance. I would like to express my gratitude to Professor J. Crangle for undertaking the magnetisation measurements on the Sheffield SQUID magnetometer, and for his helpful suggestions and discussions. I take particular pleasure in acknowledging my friend and colleague Dr. N. K. Zayer for his assistance and constant encouragement. My thanks also to Dr. H. Murphy for many useful discussions. Special acknowledgements to the help of Dr. Dick Visser and Dr. John Samson.

I wish to thank the Paul Scherrer Institute in Würenlingen (Switzerland) and the Rutherford Laboratory for giving me the opportunity to perform neutron scattering experiments. I am most grateful to Professor A. Furrer and Mr. F. Fauth for their continuous help whilst working at the Paul Scherrer Institute.

My sincere thanks are extended to the members of the mechanical and electronic workshops at the physics department, Loughborough University for their cheerful co-operation. Dr. Tahseen Rafik, Dr. Ismail H. Farhan and Miss Muna Hamdi are gratefully acknowledged for their friendship and moral support. Thanks are also due to Catherine Johnson for suggesting improvement to the text.

My special thanks go to my wife and children for their generous patience and understanding whilst undertaking this work. Finally I am grateful to the government of Saudi Arabia for giving me this opportunity to continue my higher studies.
CHAPTER ONE

INTRODUCTION

1.1 General Introduction

Inter-metallic compounds containing rare-earth elements exhibit a number of magnetic characteristics which make them of interest. Recently the research into the properties of such compounds has increased significantly due to the presence of new physical phenomena such as the coexistence of magnetism and superconductivity as observed in Pd$_2$YbSn [1] and Pd$_2$ErSn [2].

Rare earth systems are characterised by a partially filled 4f-electron shell. Therefore, the magnetic characteristics of metallic rare-earth systems are determined almost exclusively by these 4f electrons in the ion core. On the other hand, a partially delocalization of 4f electrons gives rise to collective phenomena such as heavy fermion behaviour [3,4].

Earlier work [5-7] has shown that various physical properties of rare-earth compounds are significantly influenced by the electrostatic interaction of the rare earth ion with the surrounding charges. Extensive studies of this behaviour have led to the development of the crystal field theory and its application to metals and their alloys. In addition to the electrostatic force, the 4-f electrons are under the influence of other forces which couple the 4f electrons of the different ions.
In this work a systematic study of the rare earth based Heusler alloys of the form Pd$_2$ReIn has been carried out. Determination of the crystal field splitting is of paramount importance in understanding the low temperature magnetic properties. The crystal field levels have been investigated in some selected members of the series and have been fitted to the magnetisation data.

1.2 The Main Objectives of the Research

Rare earth magnetism is an example of localised magnetism because the 4f shell in these elements is deeply buried within the atom and the magnetic moment which is associated with it is highly localised. The rare earth Heusler alloys are a good candidate for investigating localised magnetism. It is the objective of this work to study the magnetic interactions in a systematic series of the form Pd$_2$ReIn. In order to do this we have investigated the crystal field splitting since it plays an important role in determining the thermodynamic and magnetic properties. Crystal field splitting in heavy rare earth based Heusler alloys containing indium was measured by inelastic neutron scattering experiments. The results were compared with those obtained on similar related alloys in the Pd$_2$ReSn series. The results of the crystal field investigation were used to calculate magnetic isotherms which were then compared with experimental measurements of magnetisation. The magnetic isotherms in M-H plots show good agreement between the theoretical and the experimental curves which confirm the importance of the combined effect of the crystal field and the Zeeman interaction.
1.3 Structure of the Thesis

The thesis is divided into seven chapters covering the development of the research from a background introduction to the subject to the final conclusion. An outline of each chapter is presented below.

**Chapter 1**
This chapter is a general introduction to the research carried out and points out the aims and objectives of the research. It also presents a summary outline of the thesis.

**Chapter 2**
Chapter 2 covers the background of the theory of rare earth elements and their compounds. The RKKY interaction is described in this chapter as indirect interaction between rare earth ions, including polarization of the conduction electrons.

**Chapter 3**
This chapter presents a detailed review of crystal field theory and its relation to the splitting of the energy levels in the rare earth compounds.

**Chapter 4**
Chapter 4 discusses the theory of neutron scattering and presents the relation between inelastic neutron scattering and crystal field splitting.
Chapter 5
This chapter contains the experimental results concerning the structure determination and measurement of the magnetic susceptibilities of the rare earth Heusler alloys. It also describes the experimental system used in carrying out these experiments.

Chapter 6
This chapter describes the experimental work on inelastic neutron scattering carried out at the Rutherford Laboratory and the Paul Scherrer Institute (Switzerland). All the results of the crystal field splitting are shown and discussed in this chapter.

Chapter 7
A summary of the experimental results and the conclusion of the whole thesis are presented. Some suggestions are made for further work in this area.

References
CHAPTER TWO

Magnetism of Rare Earth Metals and Their Alloys

2.1 Introduction

The rare earth elements are a sub-group in the periodic table in which the 4f shell is progressive filled from Lanthanum (La) to Lutetium (Lu) with the 5s, 5p and 6s shells already filled. The electronic structure of rare earths is normally given by \((5s)^2(5p)^6(4f)^n(5d)^1(6s)^2\), where \(n\) increases from 0 (Lanthanum) to 14 (Lutetium) as the atomic number increases from 57 to 71 [1]. The outer shell electron structure which determines the chemical properties of elements is the same for all rare earth metals. The electrons in the incomplete 4f shell are responsible for the magnetic properties of this series of elements. The 4f shell is located inside the 5s and 5p shells. In a solid there is essentially no overlap between two 4f wave functions centred on neighbouring atoms, which means that the 4f electron configuration can be considered to be close to the electronic wave function of the atom [2].

Electron-electron interactions among the 4f electrons at each atomic site are in fact strong enough to produce a localised magnetic moment. In metallic alloys, the 5d and 6s levels are partially filled and they form part of the conduction electron band. The observed magnetic order in the rare earth
alloys is caused by an indirect exchange mechanism between involving electrons [3].

A general description of the properties of rare earth metals and alloys may be found in [2-5]. There have been many investigations of the basic properties of compounds with normal rare earths, the main results of which have been presented by Gignoux [6]. Various physical properties are listed in table (2.1). Table (2.2) summarises the magnetic and related properties of rare earth metals. For the following it is useful to give a brief discussion of some general magnetic properties of rare earths and rare earth alloys.

2.2 Crystallographic and Band Structure

The composition and crystal structure of intermetallic compounds are governed by geometric, electronic, and electrochemical factors [2]. Pure rare earth metals have a hexagonal closed pack structure except for four elements; Eu crystallises in a body-centre cubic structure, Sm has a rhombohedral structure, while Yb has a face centred cubic structure at room temperature and Ce has many allotropic phases.

The atomic volume of rare earth atoms decreases linearly from La (1.88Å) to 1.73Å for Lu, with the exception of Eu and Yb (see table (2.1)).

2.3 Magnetic Moment of Rare Earths

The rare earths are paramagnetic at sufficiently high temperatures and show different magnetic ordering at low temperatures. Measurements of the
Table (2.1) Ref. [3]

Room temperature physical properties of the rare earth metals and their melting and boiling points*: dhcp = double-hexagonal close-packed, fcc = face-centered cubic, bcc = body-centered cubic, hcp = hexagonal close-packed

<table>
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<th>Crystal structure</th>
<th>Lattice constants (Å)</th>
<th>Metallic radius (Å)</th>
<th>Atomic volume* (cm³/mol)</th>
<th>Density (g/cm³)</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
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* After Beaudry and Gschneidner (1978).
** Data for coordination number 12.
† Rhombohedral is the primitive cell. The close-packed layer stacking is ABABCBCAC with symmetries chhchhchhc in nine layers.
‡ Low temperature form is hcp.
Table (2.2) Ref. [3]

Magnetic properties of rare earth metals

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<th>Rare earth metal</th>
<th>Z</th>
<th>S</th>
<th>L</th>
<th>J = L ± S</th>
<th>Spect. state</th>
<th>Magnetic moment in</th>
<th>Easy axis</th>
<th>Hex. sites</th>
<th>Tm</th>
<th>Cubic Tc</th>
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<td></td>
<td>g g\sqrt{J(J+1)} obs.</td>
<td>(g - 1)^2 \times J(J + 1) at 0 K</td>
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* Spectroscopic state = \((2S + 1)J_x\) with X = S, P, D, F, G, H, I as L = 0, 1, 2, 3, 4, 5, 6 respectively.

** Antiferromagnetic ordering in the light rare earths prevents the measurement of the saturation magnetic moment.

† See Ref. [3].

†† Tm for fcc Ce is 16.8 K.
magnetic susceptibility at high temperatures are characterised by the Curie-Weiss law:

\[ \chi = C/(T - \theta_p) \]  \hspace{1cm} (2.1)

Where \( \theta_p \) is the paramagnetic Curie temperature [1,2] and \( C \) is the Curie constant which is defined by:

\[ C = 2N\mu / 3k_B \]  \hspace{1cm} (2.2)

\( \mu \) is the magnetic moment.

\( k_B \) is the Boltzmann constant.

The magnetic moment of rare earths is directly related to the presence of the 4f shell. In the ionic state the total spin \( S \) and the total orbital angular momentum \( L \) are coupled together to give the total angular momentum \( J \), yielding

\[ \mu_{\text{eff}} = \mu B_{J} \sqrt{J(J+1)} \]  \hspace{1cm} (2.3)

Where \( B_{J} \) is the Landé' factor which is defined as:

\[ B_{J} = 1 + [J(J+1)+S(S+1)-L(L+1)]/2J(J+1) \]  \hspace{1cm} (2.4)

The values of \( S, L \) and \( J \) can be obtained by applying Hund's rules which describe the energetically stable state subject to Pauli's exclusion principle.

Hund's rules are as follows:
(1) The spins $S_i$ of all 4f-electrons combine to give the maximum value of $S$ while being consistent with the Pauli exclusion principle.

(2) Whilst satisfying the first rule and the Pauli exclusion principle form the largest value of $L$, so $|L| = \sum m_i$

(3) The value of the total angular momentum $J$ is $|J| = |L - S|$ when the shell is less than half full (for example light rare earth metals), and $|J| = |L + S|$ if the shell is more than half full (such as rare earth metals containing more than seven 4f electrons). For a half filled shell $L = 0$, so that $J = S$.

Some of the heavy rare earth elements show ferromagnetic behaviour at low temperature such as Holmium (Ho) and Erbium (Er), where the Curie temperature for both of them is $T_c = 20K$ [7,8]. Some other elements show antiferromagnetic order such as the elements in between Terbium (Tb) and Thulium (Tm). They pass through an antiferromagnetic or a more complicated state before reaching the ferromagnetic ground state. For example magnetic measurements on single or polycrystalline Terbium [9,10], indicate that it is ferromagnetic below 221 K and paramagnetic above 230 K; the transition from the paramagnetic state to the magnetically ordered state appears at the Néel temperature $T_N = 229 K$, and the transition from the intermediate state to the ferromagnetic state at $T_c = 221 K$ (Curie temperature). Holmium has two magnetic transitions, where the Curie temperature is located at 20 K while the Néel temperature is 133 K. Gadolinium(Gd) is shown to be ferromagnetic near room temperature. Table(2.2) shows the different transition points for the various rare earth elements.
2.4 Specific Heat of Rare Earth Metals and their Alloys

Specific heat is a physical property which yields information on the electronic density of states at the Fermi level and the existence of phase transitions of rare earth metals or alloys. At low temperatures it can be analysed [2] by:

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

where the first term represents the electronic specific heat, and \( \gamma \) is proportional to the electronic density of states at the Fermi level and given by:

\[ \gamma = \frac{2\pi^2}{3} k_B^2 n(E_F) \]

\( n(E_F) \) is the density of states at the Fermi level for one spin direction, \( N \) is the number of atoms. The second term in (2.5) is the phonon contribution. The last term arises from magnetic contributions.

Fig (2.1) represents a schematic curve for the specific heat as a function of temperature for a typical rare earth metal. The magnetic phase transition (close to the Neél point) appears as a sharp peak in the specific heat.

2.5 The Electrical resistivity of Rare Earth Metals

Electrical resistivity is a physical property which is affected by the magnetism of the inner 4f shell, so it is used to observe the occurrence of either
Fig (2.1) : Specific heat of Ho as measured by Gerstein et al.[11]. The dashed curve is the magnetic contribution to the specific heat.
magnetic or structural phase transitions. The total resistivity ($\rho$) of a solid is formed from three contributions[2],

$$\rho = \rho_{res} + \rho_{ph} + \rho_m$$

where $\rho_{res}$ is the residual resistivity which arises from the scattering of conduction electrons by impurities, $\rho_{ph}$ is the lattice resistivity due to phonons, $\rho_m$ is the magnetic resistivity due to the disordered component of 4f electron magnetic moment.

Fig.(2.2) illustrates the electrical resistivity as a function of temperature for a single crystal of Ho as measured by Strandburg et al. [12]. The Néel state appears below 140 K. The dashed curves are the spin only contribution to the resistivity, and the dot-dashed curve is the resistivity calculated for the c-axis by Elliot et al. [13]. Fig (2.3) shows the electrical resistivity for the rare-earth Heusler alloy ($GdInAg$) as measured by Galera et al. [14]. The resistivity shows a small sharp peak at very low temperature due to a magnetic phase transition.

2.6 The Important Magnetic Interactions

There are two main interactions which play a significant role in describing the magnetic moment of the 4f electrons [15]:

1- Two ion interactions which describe the coupling between 4f electrons and neighbouring ions.
Fig. (2.2) : Electrical resistivity versus temperature for Ho single crystal, ref. [12]

Fig. (2.3) : Electrical resistivity as a function of temperature for Ag₂GdIn, ref. [14]
2- Single ion interactions that act independently at each ionic site such that the state of the 4f electron at a particular site is unaffected by the magnetic state of their neighbours [34].

The direct exchange interaction which arises from the overlap of 4f wavefunctions is much too small to account for the transition temperatures in rare earth metals. Therefore the direct overlap of neighbouring 4f orbitals may be ignored. The dominant exchange interaction between the 4f electrons of neighbouring rare-earth ions is an indirect exchange via a polarisation of the conduction electrons. This is called the RKKY interaction and will be described in more detail below.

The most important of the single-ion interactions in rare earth metals is the electrostatic interaction between the rare earth ions and their nearest neighbours. In an ionic crystal a magnetic ion will be subject to a non uniform electric field arising from its neighbouring ions. This is called crystal field interaction, and is of importance in determining the low temperature magnetic behaviour of compounds containing rare earth elements. Hybridisation with conduction electrons is of particular importance in metals where its influence may be described in a manner similar to that for ionic compounds. The crystal field effect will be discussed in detail in chapter (3).

The RKKY Interaction

The RKKY interaction is a mechanism for magnetic coupling between localised magnetic moments in metals. It depends on the ability of conduction electrons to interact magnetically with the local moments and to
propagate the polarisation between different magnetic atoms. This interaction was described first by Ruderman and Kittel and developed further by Kasuya and Yosida [16,17].

If a rare earth atom is embedded in a crystalline environment, then its magnetic moment $S$ will interact with other moments and in particular with the spin of conduction electrons. This interaction between a localised moment $S$ of the 4f electrons and the spin of the conduction electrons $s$ is described well by a phenomenological Hamiltonian of the form [3]:

$$\mathcal{H} = -\Gamma S \cdot s$$

where $\Gamma$ is an interaction constant that depends on the degree of overlap of the wavefunctions of $s$ and $f$ electrons.

In rare earth metals the spin orbit coupling energy is greater than the thermal energy $(k_BT)$ and the crystal field energy splitting, so the spin $S$ can be replaced by its projection $(g_J-1)\mathbf{J}$ on $\mathbf{J}$ of the ground state. Then the $s$-$f$ exchange interaction Hamiltonian is written [2] as:

$$\mathcal{H} = -\Gamma (g_J-1)s \cdot \mathbf{J}$$

If $S(R_n)$ is the total spin of the rare earth ion at the position $R_n$, then the Hamiltonian which describes the interaction of the conduction electrons of spin $s(r)$ with the localized electrons is given by:
\[ \mathcal{H} = -\sum_n \Gamma(r - R_n) \mathcal{S}(s) \mathcal{S}(R_n) \]  

(2.10)

where \( \Gamma(r - R_n) \) is the interaction constant.

The conduction electrons wavefunction is described by Bloch functions:

\[ |k\sigma\rangle = \Psi_{k\sigma}(r) = e^{ik \cdot r} \psi_k(r) |\sigma\rangle = \Psi_k(r) |\sigma\rangle \]  

(2.11)

Where \( \Psi_k(r) \) is the spatial part of the wavefunction and \( |\sigma\rangle \) is the spin part.

Using the completeness relationship for the set of Bloch wavefunctions

\[ \sum_{k,\sigma} |k\sigma\rangle \langle k\sigma| = 1 \]  

(2.12)

the Hamiltonian can be written as

\[ \mathcal{H} = \sum_{kk'\sigma\sigma'} |k\sigma\rangle \langle k\sigma| \mathcal{H}_{k\sigma} \langle k'\sigma'| \]  

(2.13)

with the average value of the Bloch function:

\[ \langle k\sigma|\mathcal{H}|k'\sigma'\rangle = -\sum_n \int d^3r \psi_{k'}(r) \Gamma(r - R_n) \psi_k(r) (\sigma | S(r), S_n | \sigma') \]  

(2.14)

The Bloch functions have the property:

\[ \Psi_k(r) = e^{-i\mathbf{k} \cdot \mathbf{R}_n} \psi_k(r + \mathbf{R}_n) \]  

(2.15)

because
\[ |k\sigma\rangle = \psi_{k\sigma}(r) = \exp(i\mathbf{k}\cdot r)u_{\sigma}(r)|\sigma\rangle = \psi_{k}(r)|\sigma\rangle \]  \hspace{1cm} (2.16)

The conduction electron spin operator in eq.(2.14) acts on \(|\sigma\rangle\) or \(<\sigma|\) of the Bloch function; therefore the following formula can be written:

\[ \langle \sigma|\mathbf{S}(r)\mathbf{S}_n|\sigma\rangle = s_{kk'} \cdot \mathbf{S}_n \]  \hspace{1cm} (2.17)

where \(s_{kk'}\) is the conduction electron spin expectation value between states \(|k'\sigma')\rangle\) and \(|k\sigma\rangle\).

by substitution equations (2.15) and (2.17) in eq.(2.14), the following is obtained:

\[ \int d\tau \psi_{k}^{*}(\tau)\Gamma(\mathbf{r}-\mathbf{R}_n)\psi_{k'}(\mathbf{r})\mathbf{S}_n \cdot \mathbf{S}_{kk'} = e^{-i(k-k')\mathbf{R}_n}\int d\tau \psi_{k}^{*}(\mathbf{r}-\mathbf{R}_n)\Gamma(\mathbf{r}-\mathbf{R}_n)\psi_{k}(\mathbf{r}-\mathbf{R}_n)\mathbf{S}_n \cdot \mathbf{S}_{kk'} \]  \hspace{1cm} (2.18)

The Hamiltonian takes the form:

\[ \mathcal{H} = -(g\mu\text{B}) \sum_{kk'n} \Gamma(k,k')e^{i(k-k')\mathbf{R}_n}\mathbf{S}_n \cdot \mathbf{S}_{kk'} \]  \hspace{1cm} (2.19)

where

\[ \Gamma(k,k') = \int d\tau \psi_{k}^{*}(\tau)\Gamma(\mathbf{r})\psi_{k'}(\mathbf{r}) \]  \hspace{1cm} (2.20)

However \(\Gamma(k,k')\) and its dependence on \(k\) and \(k'\) is not well known. The RKKY theory uses the approximation that the interaction is considered to be a point interaction for \(\Gamma(\mathbf{r})\), i.e.
\[ \Gamma(r) = \Gamma \delta(r) \quad \text{(2.21)} \]

Therefore its Fourier transform has the form:

\[ \Gamma(k, k') = \Gamma \quad \text{(2.22)} \]

From a physical point of view the RKKY interaction can be understood as a localised spin \( S \) polarising conduction electrons around the lattice site. Different numbers of spin up (+) or spin down (-) conduction electrons are located around the lattice site, resulting in a modulation of the spin density in the conduction electron band. The spin up and spin down densities of conduction electrons due to the s-f interaction are then given by[3]:

\[
\rho_{\pm}(r) = \frac{1}{2} N \pm \frac{(3N)^2 \pi (g_J - 1)}{E_F} \Gamma \sum_x F(2k_F |x - R_n|) J_{\pm} \quad \text{(2.23)}
\]

where

\[
F(x) = \frac{x \cos x - \sin x}{x^4} \quad \text{(2.24)}
\]

\( N \) is the total number of conduction electrons,
\( n \) is the average conduction electron to atom ratio
\( E_F \) is the Fermi energy level

The spin polarisation produced by the spin \( S_n \) located on the atom \( n \) interacts via conduction electrons with the spin \( S_m \). Within second order perturbation theory the interaction energy between the two spins is given by:
\[
E = \sum_{k,k',\sigma,\sigma'} \langle k^0\sigma|\Delta|k'^0\sigma'\rangle \langle k'^0\sigma'|\Delta|k^0\sigma\rangle f_k(1-f_{k'}) \quad \text{(2.25)}
\]

where \(f_k\) is the Fermi-Dirac function which is defined by:

\[
f_k = \frac{1}{e^{(E_k-E_F)/k_B T} + 1}
\]

The summation in eq.(2.25) is made over the occupied \(k\) states and the empty \(k'\) states.

2.7 Susceptibility of Metals (Pauli Paramagnetism)

The contribution of conduction electrons to the magnetic moment of metal is discussed here. The problem can be treated within the independent electron approximation [18]. By considering the spin magnetic moment only, without charge, for a system with volume \(V\) the contribution to the magnetisation density from each electron is \(-\mu_s/V\) or \(+\mu_s/V\) when the spin is parallel or antiparallel to the external field \(H\) respectively as shown in Fig.(2.4). The magnetisation is determined by the difference in the number of magnetic moments pointing up or down, and the magnetisation is given by:

\[
M = -\mu_s (n_+ - n_-) \quad \text{(2.26)}
\]

where \(n_\pm\) is the number of electrons per unit volume with spin up (+) or spin down (-) which can be expressed as:
\[ n_{\pm} = \int \! dE D_{\pm}(E) f(E) \]  \hspace{1cm} \text{(2.27)}

where \( f(E) \) is the Fermi Dirac function and \( D_{\pm}(E) \) is the density of states in the absence of an external magnetic field which is defined by:

\[ D_{\pm}(E) = \frac{1}{2} D(E) \]  \hspace{1cm} \text{(2.28)}

The energy of each electronic level with spin parallel to the field is shifted up from its zero field value by \( \mu_b H \). Therefore the number of levels with energy \( E \) in the presence of \( H \) is the same as that with energy \( E \mp \mu_b H \). Then the density of state in the presence of the magnetic field can be written as:

\[ D_{\pm}(E) = \frac{1}{2} D(E \mp \mu_b H) \]  \hspace{1cm} \text{(2.29)}

Since \( \mu_b H \) is a small parameter, then the density of states can be expanded in a Taylor series as:

\[ D_{\pm}(E) = \frac{1}{2} D(E \pm \mu_b H) = \frac{1}{2} D(E) \pm \frac{1}{2 \mu_b H} D'(E) \]  \hspace{1cm} \text{(2.30)}

yielding

\[ n_{\pm} = \frac{1}{2} \int \! dE D(E) f(E) \pm \frac{1}{2 \mu_b H} \int \! dE D'(E) f(E) \]  \hspace{1cm} \text{(2.31)}

Now using integration by parts, the magnetisation density can be given as:

\[ M = \mu_b^2 H D(E_f) \]  \hspace{1cm} \text{(2.32)}
Therefore the susceptibility can be written as:

\[ \chi = \frac{M}{H} = \mu_B^2 D(E_f) \]  

which is known as Pauli paramagnetism and is essentially independent of temperature.

The electrons in a partially filled band of a metal occupy the available levels in accordance with the Fermi-Dirac distribution law. At 0 K this distribution is such that all levels up to the Fermi level are full, and all higher levels are completely empty; see figure (2.5a). For an illustration using a free electron model, the heavy lines indicate the density of occupied levels and the light lines indicate the density of available levels.

At higher temperatures the thermal energy excites some electrons into higher levels above the Fermi level, and therefore the number of electrons increases from zero to some finite value (fig. (2.5b)). Thus the electron density of occupied levels just below the Fermi level decreases.

For \( E_f \gg k_B T \), the temperature dependent correction to the Pauli susceptibility is given by:

\[ \chi(T) = \chi(0) \left[ 1 - \frac{\pi^2}{6} (k_B T)^2 \left( \frac{D'(E_f)}{D(E_f)} \right)^2 - \frac{D''(E_f)}{D(E_f)} + \ldots \right] \]  

\[ \text{(2.34)} \]
Total energy, kinetic + magnetic, of electrons

Fig.(2.4): Pauli paramagnetism [33]
(a) The orbital in the shaded regions are occupied
(b) The excess of spin up electrons in the magnetic field

Fig.(2.5): Electron distribution (a) at 0 K, (b) at a high temperature.
The susceptibility of a free electron gas is essentially independent of the temperature but corrections for diamagnetism are necessary. The diamagnetic effect of the ion core increases considerably as the atomic number increases but remains relatively small.

2.8 General Properties of Rare Earth Heusler Alloys

Intermetallic compounds which have the general formula \( X_2YZ \) are called Heusler Alloys. They were first synthesised by Heusler in 1898 [19]. He showed that the alloys of Cu-Mn-Sn and Cu-Mn-Al have spontaneous ferromagnetism which is very similar to that of nickel [19]. It was shown that other alloys with similar composition (such as Cu\(_2\)MnIn, Cu\(_2\)MnGa and alloys based on silver) have the same structure and magnetic properties.

Recently alloys with Heusler form have been synthesised containing rare earth elements as one of the constituent. These include Pd\(_2\)ReSn [22-26], Ag\(_2\)Reln [14,27], Au\(_2\)Reln [28] and Cu\(_2\)Reln [29]. The structure and magnetic properties of Pd\(_2\)ReSn have been investigated by Donaberger et al. [24]. They determined that these compounds form the L2\(_1\) structure. Compounds containing Tm and Yb have been reported to be superconducting [23]. However the magnetic susceptibility of these two compounds was reported to deviate from the Curie behaviour at low temperatures, which was attributed to crystalline electric field effects. Further studies on the alloy series Pd\(_2\)ReSn were carried out by Li et.al. [30] using neutron inelastic scattering. They showed that alloys containing Ho and Er have magnetically ordered ground states at low temperature. In the present investigation Heusler alloys based on Pd\(_2\)Reln have been prepared and investigated.
Fig. (2.6) : The Heusler Alloy $L2_1$ structure
The Crystallographic Structure

All Heusler alloys are formed essentially from the ordered combination of two binary compounds $XY$ and $XZ$, each of which have the CsCl structure [20]; for example PdIn and PdHo yields the Heusler alloys Pd$_2$HoIn. These alloys crystallise in the cubic L2$_1$ structure with a unit cell of space group $Fm\bar{3}m$ as illustrated in fig. (2.6). This type of structure may be visualised as a system of four inter-penetrating fcc sublattices A,B,C and D. X atoms occupy the $A(-, -, -)$ and $C(-, -, -)$ sites, the Y atoms occupy the sites $B(-, -, -)$ and $Z$ atoms occupy the D(0,0,0) sites.

X-ray Diffraction

The efficiency of X-ray scattering of a given atom is described by the quantity $f$ (the atomic scattering factor) which is defined as:

$$f = \frac{\text{the amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$$

The scattering factor depends on the wavelength of the incident beam and the scattering angle. For any atom scattered in the forward direction the scattering factor is equal to the atomic number. As the scattering angle increases $f$ decreases and the scattered waves become more and more out of phase. Values for each atom as a function of $\sin \theta / \lambda$ are tabulated in ref.[31]. The scattered waves from each of the atoms in the unit cell are
added. The amplitude of each wave is given by the appropriate value of \( f \) for the scattering atom considered and the value of \((\sin \theta / \lambda)\) involved in the reflection. The phase of each wave is given by:

\[
\varphi = 2\pi(hu+kv+lw) \tag{2.35}
\]

where \((hkl)\) are the Miller indices, \(u\), \(v\) and \(w\) are the coordinates of atoms. The scattered wave in a complex exponential form is given by:

\[
f e^{i\varphi} = e^{2\pi i(hu+kv+lw)} \tag{2.36}
\]

The structure factor is formed from the resultant wave scattered by all atoms of the unit cell. It describes how the scattered beam is affected by the atomic arrangement, and is expressed in the following form:

\[
F(hkl) = \sum_n f_n e^{2\pi i(hu_n+kv_n+lw_n)} \tag{2.37}
\]

where the summation is carried over all atoms of the unit cell. The absolute value \( |F| \) gives the amplitude of the resultant wave in terms of the amplitude of the wave scattered by a single electron. The Bragg intensity of the beam diffracted by all the atoms in the unit cell is proportional to \( |F|^2 \).
Structure Factors of Heusler Alloys

As discussed above the unit cell of Heusler alloys is comprised of four interpenetrating fcc sublattices, and substituting the coordinates in eq.(2.37) yields:

\[ F(hkl) = 4\left[ f_A e^{\pi i(h/2 + k/2 + l/2)} + f_C e^{\pi i(h+k+l)} + f_D e^{\pi i(3h/2 + 3k/2 + 3l/2)} \right] \quad \text{(2.38)} \]

Diffraction patterns for this structure have permitted Bragg reflections (with non zero structure amplitudes) when the Miller indices (hkl) are unmixed as illustrated in the following manner:

1. The Miller indices are all odd
   In this case substituting values of hkl in equation (2.39) yields
   \[ F(hkl) = 4\left[ f_A - f_B \right]^2 + \left[ f_B - f_D \right]^2 \frac{1}{2} \]
   e.g. \( (h \ k \ l) = (1 \ 1 \ 1) \) or \( (3 \ 1 \ 1) \), etc.

2. The Miller indices are all even, and \( h+k+l = 4n+2 \), where \( n \) is any integer
   \[ F(hkl) = 4\left[ f_A - f_C + f_B - f_D \right] \]
   e.g. \( (h \ k \ l) = (2 \ 0 \ 0) \), \( (222) \), etc.

3. The Miller indices are all even, and \( h+k+l = 4n \)
   \[ F(hkl) = 4\left[ f_A + f_B + f_C + f_D \right] \]
   e.g. \( (h \ k \ l) = (2 \ 2 \ 0) \), \( (400) \), etc.
The principal reflections are the reflections for which \( h+k+l = 4n \), and are independent of chemical order. This means they occur at the same positions and with the same intensities in the patterns of both ordered and disordered alloys. The other reflections are order dependent [20]. The change in the positions of atoms causes a change in Bragg intensities. Determination of the nature of these changes is obtained by calculating the structure factors \( F \) for each atomic arrangement and by calculating the degree of chemical order.

For Heusler alloys, which have the site occupation shown in fig.(2.6), the structure factor can be written as:

\[
\begin{align*}
F(111) &= 4 \left| f_z - f_y \right| \\
F(200) &= 4 \left| f_z + f_y - 2f_x \right| \\
F(220) &= 4 \left| f_z + f_y + 2f_x \right|
\end{align*}
\]
References


3.1 Historical Background

Crystal field theory plays an important role in understanding the energetic level structure of ions in solids. It strongly affects the magnetic properties of rare earth metals and alloys.

The application of symmetry principles in crystal field theory was first reported by Bethe in 1929 [1]. He showed how the degeneracy of the levels of a free ion is partly removed when it is placed in a crystal at a site of given symmetry. Kramers in 1930 [2] suggested that the electronic levels in molecules containing an odd number of electrons must give rise to an even number for the degeneracy of the level under electrostatic interactions. Spectroscopic transitions as measured in optical experiments on samples containing trivalent rare earth elements was identified by Freed in 1931 [3] as transitions between the levels within the 4f configuration. Van Vleck (1932) was the first to apply the idea of crystal fields to calculations of the magnetic properties of transition element compounds for samples with crystal fields of cubic symmetry [4]. Condon and Shortley (1935) introduced a theoretical interpretation dealing with crystal field splitting as a small perturbation of the levels of a free ion. Their method of explicit calculations were suitable only for moderately complex systems and its use is normally restricted to two or less electrons or holes in the f-shell [5]. Subsequently the
theory was developed further by Racah (1943, 1949) who improved the theoretical techniques to encompass atoms having more than two f-electrons [6,7].

A first principle calculation of crystal field parameters is complicated. However, by using symmetry arguments Stevens (1952) [8] has written the Hamiltonian in terms of operator equivalents and simplified the procedure. Some details of this method will be discussed in section (3.5). A brief discussion of the physical basis of crystal field theory was given by Herzfield and Meijer (1961) [9]. They worked out the symmetry properties of various terms in the typical Hamiltonian, and also covered several topics related to crystal field theory. Hutchings in 1964 [10] clarified the connection between the various forms of crystal field Hamiltonians by calculating the energy levels on the basis of a simple charge ionic model of the crystal lattice. Watson et al (1965) discussed the contribution of conduction electrons to crystal field Hamiltonian [11]. A comprehensive review of the crystal field theory has been given by Newman (1971) [12]. The foundation of crystal field theory in metals has been investigated by Chan and Lam (1978) [13] and interpreted in terms of electronic band structure.

In the present investigation an experimental determination of the crystal field transition energies has been carried out for some selected rare earth compounds within an energy range of either 0 meV to 20 meV or 2 meV to 500 meV. In the next sections the theory pertinent to the description of crystal fields is presented. For further details ref [8,17] should be consulted.
3.2 The Isolated Ion

3.2.1 The Ground State of the Free Ion

The unpaired electrons in any particular ion exist in a single sub-shell and have energies appropriate to it. Within a given shell n of an atom there are an \( l \) sub-shells, where \( l \) is the orbital angular momentum. Each electron has \((2l +1)\) possible orbital states available to it, each of which corresponds to a magnetic quantum number \( m_l \) where \( m_l \) can have the values \((l, l - 1, l - 2, ..., -l)\). For each of these states there are \((2S+1)\) spin states. Therefore for a given \( l \), the total number of possible states is \((2S+1)(2l +1)\). This implies that according to Pauli's exclusion principle the maximum number of electrons contained in the sub-shell is \(2(2l +1)\). For an f-shell, \( l =3 \), the maximum number of electrons is thus 14. The electrons combine in an atom to produce a stable state of least energy (the ground state).

In the Russel Sanders coupling scheme Coulomb and exchange interactions are taken into account. This coupling is shown by the vector diagram, figure (3.1), where the \( i^{th} \) electron has spin \( s_i \) and orbital vector \( l_i \). The spin \( s_i \) of individual electrons \((i =1,2,...,n)\) are coupled through the spin-spin interaction to give:

\[
\mathbf{s} = \sum_{i=1}^{n} s_i
\]

and the orbital \( l_i \) of the electrons \((i =1,2,...,n)\) combine to give

\[
\mathbf{l} = \sum_{i=1}^{n} l_i
\]
Fig. (3.1) : Russel Saunders Coupling
The resultant $s_j$ and $l_j$ are coupled through the spin-orbit interaction \(14\) to give the resultant total angular momentum $j$.

In order to determine the most stable spin and orbital configuration one may use Hund's rules as described in chapter 2. The state having the lowest energy is the one with minimum $J$ in the lower half of unfilled shell or with maximum $J$ in the upper half. To illustrate this an example is given for two cases [15]:

1. Holmium (Ho$^{+3}$), has 10 electrons in the f-shell thus

   \[ J = 3 \]

   \[ |s| = \sum_{i=1}^{10} s_i = 2 \]

   \[ |l| = \sum_{i=1}^{10} l_i = 6 \]

   \[ |J| = |l + s| = 8 \]

   and with a ground state degeneracy of $2J+1 = 17$

2. Cerium (Ce), has 1 electron in the f-shell (< half full)

   where

   \[ |s| = s = 1/2 \]

   \[ |l| = l = 3 \]

   \[ |J| = |l - s| = 5/2 \]

   and with a degeneracy of $2J+1 = 6$
3.2.2 The Hamiltonian of the Free Ion

There are different interactions within the free ion which contribute to form the Hamiltonian of a many electron atom. The most important of these interactions are [16]:

1. The Coulomb interaction of the electrons with a nucleus of charge Ze.
2. The interaction of a given electron with all other electrons. The Hamiltonian is given in the form:

\[ H_c = -\frac{n}{2m} \sum_i \nabla_i - \sum_i \sum_{j \neq i} \frac{Ze^2}{r_{ij}} + \sum \frac{e^2}{r_{ij}} \]

where \( r_{ij} = |r_i - r_j| \) is the distance between the electrons i and j.

The first term on the right hand side is the sum of the kinetic energy of all electrons. The second term is the interaction between the electrons and the nucleus (Coulomb attraction). The third term arises due to the electron - electron interaction (Coulomb repulsion).

3. A magnetic field is produced by the orbital motion of a single charged particle around the nucleus. An interaction arises between the orbital momentum and the spin. This is called the 'Spin Orbit Coupling' and its contribution to the Hamiltonian takes the form:

\[ H_{so} = \sum_j \lambda_j \hat{l}_j \cdot \hat{s}_j \]

The magnitude of this interaction is determined by the coupling coefficients \( \lambda_j \) where \( i \) and \( j \) range over all electrons. The Hamiltonian becomes...
\[ H = H_c + H_{so} \]  \hspace{1cm} (3.3)

3.3 Interaction of the Ion with the Crystalline Environment

3.3.1 The Contribution of the Crystal Field

By placing the ion in a crystal the influence of its neighbours yields additional contributions. A term which describes the effect of the crystal field \( H_{cf} \) has to be added to the Hamiltonian in equation (3.3), thus:

\[ H_{tot} = H_c + H_{so} + H_{cf} \]  \hspace{1cm} (3.4)

The treatment of the crystal field effect will depend on how the strength of the effective potential compares with \[17\] :

- the multiplet splitting between atomic energy levels.
- the spin-orbit coupling of the electrons in the atom.

We have to distinguish between three cases:

1. Weak Crystal Field

In this case the crystal field energy is smaller than the spin orbit coupling energy. Hence the total angular momentum \( J \) stays nearly a good quantum number and the crystal field acts on the degenerate \( J \) eigenstates.

The crystal field can be considered as a small perturbation because the energy differences between the multiplets are larger than the energy of the crystalline field. The situation can be treated by perturbation theory. It removes partially the \((2J+1)\)-fold degeneracy of the ground state multiplet.
This is applicable for the rare earth alloys where the spin-orbit coupling is larger than the crystal field.

2. Intermediate Crystal Field

In this case the spin-orbit energies are very much less than the crystal fields and also much less than the atomic multiplets, which are raised by the electron-electron interaction, so the crystal field splitting is intermediate between the spin orbit energy and the separation of L-S terms in the free atom. In this case the crystal field influences only the orbital motion of the electrons. It will split the \((2l +1)\) -fold degenerate orbital. This situation is found in transition metals and their alloys.

3. Strong Crystal Field

The crystal field energy is stronger than the electronic repulsion energy which is responsible for LS coupling. This situation is encountered mainly in the 4d and 5d group (palladium and platinum groups) and also for certain complexes in the iron group.

Here we are only concerned with the first case where the crystalline electric interaction is smaller than the spin-orbit coupling.

3.3.2 Crystal Field Energy Levels

It was shown above that a free rare earth ion possesses a total angular momentum \(J\), where \(J\) depends on the number of electrons in the 4f shell. Each level is \((2J+1)\) fold degenerate. On placing this ion in a crystal, it will be subjected to the presence of its neighbours, the effect of which is to
reduce the symmetry of the full three-dimensional rotation group plus the inversion symmetry (spherical symmetry) to some finite rotation group as determined by the crystallographic point symmetry [18,19]. As a consequence of the symmetry reduction the free ion energy levels are split into sub levels. The number of splitting and the degeneracy of the various energy levels may be determined by using the symmetry arguments, but the level separation and their order are determined by the size of the matrix elements.

Figure (3.2) describes two examples of the splitting of an f-level state of the free ion when it is located in a crystal field of cubic point symmetry. Figure (3.2a) explains the case of holmium (Ho\(^{3+}\)), with \(J=8\). The 17-fold degenerate ground state multiplet is split into one singlet \(\Gamma_1\), two doublets \(\Gamma_3^{(1)}\) and \(\Gamma_3^{(2)}\) and four triplets \(\Gamma_4^{(3)}\), \(\Gamma_4^{(2)}\), \(\Gamma_5^{(1)}\) and \(\Gamma_5^{(2)}\). Another example is shown in figure (3.2b) for the case of Yb with \(J=7/2\) for which the free atom ground state is \(2J+1=8\)-fold degenerate. This splits into three sub levels; two doublets \(\Gamma_6^{(1)}\), \(\Gamma_7\), and one quartet \(\Gamma_8\).

3.4 Outline of Crystal Field Theory

Crystal field theory represents an attempt to describe the electrostatic forces acting on magnetic atoms in a solid. The simplest model of crystal field theory is the 'Point Charge Model' [10]. For an ionic state it treats the neighbours surrounding a reference ion as a collection of classical point charges or extended charge distributions (see figure (3.3)). The electrostatic potential resulting from these charges can then be calculated. The effect of this potential on the reference ion is evaluated. The strength of the interaction is described in terms of a number of adjustable parameters.
Fig. (3.2 a) : The splitting of the ground states of Ho ion under the effect of the crystal field (cubic point symmetry)

Fig. (3.2 b) : The splitting of the ground states of Yb ion under the effect of the crystal field (cubic point symmetry)
These parameters may be fitted to experimental data such as inelastic neutron spectra. The crystal field in a metal is appreciably modified by conduction electrons due to the hybridization of the f electron wave function with the conduction electron bands [13]. For rare earth compounds crystal field parameters determined experimentally usually reproduce the observed spectra with considerable accuracy.

The theory outlined below is based on a point charge model applying an operator equivalent method developed by Stevens[8]. The theory is more general since the point charge model is not applicable to metals due to the presence of conduction electrons. However the symmetry part of the formulation carries over to the description of metals. CF-parameters may be used, selecting those which fit best with experimental observations. The formulation was developed by Stevens [8] and LLW [24].

The electrostatic crystal field potential at the site of a particular rare earth ion due to the surrounding point charges is given by [20]:

\[ V(r, \theta, \phi) = \sum_j \frac{q_j}{|\mathbf{R}_j - \mathbf{r}|} \]

\[ \text{(3.5)} \]

where \( q_j \) is the charge at the \( j^{th} \) neighbouring ion, and \( \mathbf{R}_j \) is the distance between the point charge and a point \((r, \theta, \phi)\) near the origin, see figure (3.4).

Here \( r, \theta \) and \( \phi \) are the usual spherical co-ordinates.

When there is no overlap between the charge distribution or a neighbouring atom with the 4f wave function, the crystalline potential satisfies Laplace's equation \( \nabla^2 V = 0 \), so it can be expressed in terms of spherical harmonics:
Fig. (3.3): Eightfold cubic coordination

- Pd
- Rare earth ion

Fig (3.4): The interaction between a charge near the origin and a point charge $q_i$
\[ V(r, \theta, \phi) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} K_n^m r^n Y_n^m(\theta, \phi) = \sum_{n,m} V_n^m \] 

where \( K_n^m \) is the multipole moments [20], and the spherical harmonics are defined as:

\[ Y_n^m(\theta, \phi) = (-1)^s \left\{ \frac{(2n+1)(n-|m|)!}{2(n+|m|)!} \right\}^2 \frac{1}{\sqrt{2\pi}} P_n^{|m|}(\cos \theta)e^{im\phi} \]

where

\[ P_n^{|m|}(x) = \frac{(1-x^2)^{n+|m|}}{2^nn!} \frac{d^{n+|m|}}{dx^{n+|m}}(x^2-1)^n \]

The spherical harmonics \( Y_n^m(\theta, \phi) \) are chosen to be normalised to 1. Common spherical harmonics are given in table (3.1).

For the determination of the crystal field energy levels only a small number of terms in the infinite sum are needed, because the cubic point symmetry of the crystalline electric field limits the number of terms occurring in the expansion [8,10]. All terms of \( n > 2l \), where \( l \) is the orbital quantum number of the single magnetic electron, vanish. Therefore for the 3d-group ion the expansion is taken only up to fourth degree (\( n = 4 \)) while it is taken up to the sixth degree (\( n = 6 \)) for the 4f-group ions. Also all terms in this sum for which \( n \) is odd have zero matrix element [11]. This is because matrix elements of potential terms \( V_n^m \), which are in the form \( \int \mathbf{u} \cdot \mathbf{V}_n^m \mathbf{\varphi} \mathbf{d}\tau \) (\( \mathbf{u}, \mathbf{\varphi} \) being f electron wave functions), should be invariant under a change of sign of all three coordinates \( x, y \) and \( z \). Because the product \( \mathbf{u} \cdot \mathbf{\varphi} \) has even parity, the potential \( V_n^m \) should have even parity in order to have non zero matrix elements. The term for \( n=0 \) is negligible because it affects only the zero of the energy scale which merely results in a constant shift of all energy levels.
The potential energy of interaction between a magnetic ion with charge \( q \), with origin at 0 and a point charge \( q_j \) at \( 0' \) is given by:

\[
H_J = \sum_i q_i V(r) = \sum_i \sum_j \frac{q_i q_j}{|r_j - r_i|}
\]

where \( \sum_i \) is carried out over all electrons in the unfilled 4f-shell. \((r, \theta, \phi)\) denote the coordinates of the charge \( q_i \).

Having determined the crystal field Hamiltonian, the next step is the evaluation of the matrix elements of the perturbing Hamiltonian between free ion states. Then the matrix elements can be diagonalised in order to find the energy levels and the wave functions of the rare earth ion in the crystal field. Detailed information on such calculations can be found in Wybourne [21]. In the following we are going to discuss briefly the Stevens operator equivalent method.

The crystal field potential functions has been considered as a sum:

\[
\sum_{n,m} V_n^m = V_2^0 + V_4^0 + V_6^0 + V_6^6
\]

where

\[
\begin{align*}
V_2^0 &= (3z^2 - r^2) \\
V_4^0 &= \Sigma (35z^4 - 30r^2z^2 + 3r^4) \\
V_6^0 &= \Sigma (231z^6 - 315r^2z^4 - 5r^6) \\
V_6^6 &= \Sigma (x^6 - 15x^4y^2 + 15x^2y^4 - y^6)
\end{align*}
\]
where the summations are taken over the co-ordinates of all electrons. So the Hamiltonian can be expressed as a sum of polynomials in $x_i$, $y_i$, and $z_i$, but using these one is required to go back to single electron wave functions for the calculations [22]. Alternatively it is more convenient to use the Stevens operator equivalent method [8] where one replaces $x$, $y$, and $z$ by the components of angular momentum operators $J_x$, $J_y$, and $J_z$. A difficulty arises in making this replacement in that $x$, $y$ and $z$ commute but $J_x$, $J_y$ and $J_z$ do not. This difficulty can be solved by replacing the product $x_y$ by a symmetrical product for $xy$, e.g. by $\frac{1}{2}(J_xJ_y+J_yJ_x)$; more complicated expressions can be dealt with similarly.

To rewrite the Hamiltonian in its most common form [19]:

$$H_{of} = \sum_{n,m} A_{n}^{m} \langle r^n \rangle \theta_n O_{n}^{m}$$  \hspace{1cm} (3.11)$$

where $\theta_n$ are numerical constants called multiplicative factors. Theoretically they are denoted by $\theta_2 = \alpha$, $\theta_4 = \beta$, $\theta_6 = \gamma$ [22].

$O_{n}^{m}$ are known as Stevens operators and defined below.

$\langle r^n \rangle$ is the average of the 4f ion radius and it is defined by:

$$\langle r^n \rangle = \frac{\int [R(r)]^2 r^n r^2 dr}{\int [R(r)]^2 r^2 dr}$$

and $R(r)$ represents the radial part of the one electron wave function.

A list of the factors $\alpha$, $\beta$, $\gamma$, and $\langle r^n \rangle$ for different rare earth ion is given in table (3.2).

The quantity $A_{n}^{m} \langle r^n \rangle$ may be given in another form:
The most general operator equivalent potential with cubic point symmetry, within a manifold of angular momentum $J$ vectors can be written as:

$$H_J = B_4(O_4^2 + 5O_4^4) + B_6(O_6^2 - 21O_6^4).$$ ------(3.13)

Where the $z$-axis (axis of quantisation) has been chosen along a four-fold axis, and

$$O_4^2 = 35J^4 - [30J(J+1) - 25]J^2 - 6J(J+1) + 3J^2(J+1)^2$$

$$O_4^4 = \frac{1}{2}(J_+^4 + J_-^4)$$

$$O_6^2 = 231J^6 - 105[3J(J+1) - 7]J^4 + [105J^2(J+1)^2 - 525J(J+1) + 294]J^2 - 5J^3(J+1)^3 + 40J^2(J+1)^2$$

$$O_6^4 = \frac{1}{4}[11J^2 - J(J+1) - 38](J_+^4 + J_-^4) + \frac{1}{4}(J_+^4 + J_-^4)[11J^2 - J(J+1) - 38]$$

Lea, Leask and Wolf [22] investigated the effect of the cubic crystal field Hamiltonian (3.13) on the angular momentum $J$ as a function of the ratio between the fourth and sixth degree terms. They calculated the eigenvectors and eigenvalues as a function of two parameters ($W$ and $x$). All these are listed in tables for all integral and half integral values of $J$ between $J=2$ and $J=8$. They introduced the two parameters $W$ and $x$ by rewriting equation (3.13) in the form:
\[ H_d = \frac{x}{F(4)} (O^4 + 5O^6) + \frac{1-|x|}{F(6)} (O^6 - 21O^8) \] \hspace{1cm} \text{(3.15)}

The following substitutions have been used:

\[ B_4 = \frac{Wx}{F(4)} \hspace{1cm} \text{(3.16)} \]
\[ B_6 = \frac{W(1-|x|)}{F(6)} \hspace{1cm} \text{(3.17)} \]

Here \(-1 < x < +1\) and the parameter \(W\) determines the overall energy scale. \(x\) measures the relative strength of the fourth to the sixth order terms.

A computer program has been written to diagonalize the Hamiltonian (equation 3.15). The program calculates the crystalline field eigenvalues and eigenstates for a cubic site symmetry within the LLW formalism.
Table (3.1): Some of the more commonly occurring spherical harmonics

\[ Y_2^0 = \frac{1}{4} \left( \frac{5}{\pi} \right)^{1/2} (3 \cos^2 \theta - 1) \]

\[ Y_2^{\pm 2} = \frac{1}{4} \left( \frac{15}{2\pi} \right)^{1/2} \sin^2 \theta e^{\pm 2i\phi} \]

\[ Y_4^0 = \frac{3}{16} \left( \frac{1}{2\pi} \right)^{1/2} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \]

\[ Y_4^{\pm 2} = \frac{3}{8} \left( \frac{5}{2\pi} \right)^{1/2} \sin^2 \theta (7 \cos^2 \theta - 1) e^{\pm 2i\phi} \]

\[ Y_4^{\pm 3} = \mp 3 \left( \frac{35}{\pi} \right)^{1/2} \sin^3 \theta \cos \theta e^{\pm 3i\phi} \]

\[ Y_4^{\pm 4} = \frac{3}{16} \left( \frac{35}{\pi} \right)^{1/2} \sin^4 \theta e^{\pm 4i\phi} \]

\[ Y_6^0 = \frac{1}{32} \left( \frac{13}{\pi} \right)^{1/2} (231 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5) \]

\[ Y_6^{\pm 2} = \frac{1}{64} \left( \frac{1365}{\pi} \right)^{1/2} \sin^2 \theta (33 \cos^4 \theta - 18 \cos^2 \theta + 1) e^{\pm 2i\phi} \]

\[ Y_6^{\pm 3} = \mp \frac{1}{32} \left( \frac{1365}{\pi} \right)^{1/2} \sin^3 \theta (11 \cos^3 \theta - 3 \cos \theta) e^{\pm 3i\phi} \]

\[ Y_6^{\pm 4} = \frac{3}{32} \left( \frac{91}{2\pi} \right)^{1/2} \sin^4 \theta (11 \cos^2 \theta - 1) e^{\pm 4i\phi} \]

\[ Y_6^{\pm 6} = \frac{1}{64} \left( \frac{3003}{\pi} \right)^{1/2} \sin^6 \theta e^{\pm 6i\phi} \]
Table (3.2): List of $<r^n>$ for $n = 2, 4, 6$, multiplicative factors $\alpha, \beta, \gamma$

ref. [21]

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<tr>
<th></th>
<th>$&lt;r^2&gt;$ (Å)</th>
<th>$&lt;r^4&gt;$ (Å)</th>
<th>$&lt;r^6&gt;$ (Å)</th>
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<th>$\beta \times 10^4$</th>
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<td>13860</td>
</tr>
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References


CHAPTER FOUR  

Neutron Scattering

4.1 Introduction

The neutron is a highly effective probe for the investigation of condensed matter. It has properties which combine to make neutron scattering a suitable technique for investigation of the magnetic properties of solids: It has no charge, which means its interactions with matter are confined to short-range nuclear interaction. The neutron can penetrate into the bulk of a solid sample without having to overcome a Coulomb barrier due to electrostatic forces. It is characterised by an intrinsic magnetic moment which enables it to interact with the magnetic moment of unpaired electrons in magnetic atoms. The wavelength of a thermal neutron is of the order of 1Å. This value is comparable to the separation of atoms in a solid. This means that the arrangements of atoms in a solid is able to act as a diffraction grating for neutrons. Neutrons are therefore suited for the investigation of the atomic structure of solids. Furthermore, the kinetic energy of thermal neutrons are of the order of 25 meV, which is a typical thermal energy and therefore of the order of the energies for collective excitations in solids. Thus it is appropriate to study the atomic dynamics of condensed matter by inelastic scattering experiments, where the simultaneous transfer of momentum and energy is observed.
In order to have a clear picture of what is happening when a neutron interacts with a solid, the principles of neutron scattering are reviewed in this chapter. This will shed some light on the background in which we are interested, such as inelastic neutron scattering from paramagnetic ions. Details of neutron scattering theory can be found in several refs. [1,2,3 & 4].

4.2 The Interactions Between Neutrons and Solids

In scattering experiments atoms in a target are bombarded with neutrons. These neutrons are scattered by the target and subsequently detected. This provides us with the intensity as a function of the scattered angle, or alternatively as a function of the energy transfer of the scattered neutrons in the case of inelastic scattering. Experimentally nuclear scattering arises from an interaction between the neutron and the nucleus of the atom. For magnetic materials there is an additional scattering mechanism. This arises due to the interaction between the magnetic moment of the neutron and the magnetic moment produced by the spin and orbital momentum of unpaired electrons. This is called “magnetic scattering”. Magnetic scattering arises due to an electromagnetic (magnetic dipole-dipole) interaction and is therefore entirely different from nuclear scattering [7].

The scattering configuration is illustrated in fig.(4.1). The sample is located in the beam of the incident neutron. The detector is set at angle $2\theta$ with respect to the direction of the incident beam. The scattering vector can be defined by:

$$Q = k_i - k_f.$$

-------- (4.1)
where $k_f$ and $k_i$ are the final and initial wave vector for the neutron respectively (see fig.(4.2).

If the incident neutron is travelling with velocity $v_i$ and the scattered neutron is travelling with velocity $v_s$, then the momentum transfer is given by:

$$hQ = mv_s - mv_i$$  \hspace{1cm} (4.2)

where $m$ is the mass of the neutron. From the above equation the energy transfer can be defined as:
\[ \hbar \omega = \frac{1}{2} m y^2 - \frac{1}{2} m y^2 \]  \hspace{1cm} \text{(4.3)}

or

\[ \Delta E = E_f - E_i = \frac{\hbar^2}{2m} [k_f^2 - k_i^2] \]  \hspace{1cm} \text{(4.4)}

where \( \hbar \omega \) or \( \Delta E \) is the energy transferred to the sample, \( E_i \) and \( E_f \) represents the incident and scattered neutron energies.

If \( \Delta E = 0 \) and \( |k_f| = |k_i| \) then the scattering is elastic. On the other hand, for \( \Delta E \neq 0 \) the scattering is inelastic. For inelastic scattering; the neutron is losing or gaining energy through its interaction with the sample.

### 4.3 Scattering Cross-Section

The interaction of a neutron incident upon a sample can be defined in terms of a cross section \( \sigma \). If the incident beam is characterised by a uniform flux \( \Phi \) then the total cross section is defined as:

\[ \sigma = \frac{N}{\Phi} \]  \hspace{1cm} \text{(4.5)}

where \( N \) is the total number of scattered neutrons per unit time (the number scattered in all directions). If the incident neutrons are scattered into a solid angle \( d\Omega \) per unit time, then the differential neutron scattering cross section \( \frac{d\sigma}{d\Omega} \) is angle dependent and integrated over the energies.

\[ \frac{d\sigma}{d\Omega} = \text{(number of scattered neutrons/unit time/unit solid angle)} \]
4.3.1 The Differential Cross-Section for Elastic Scattering

For elastic scattering the energies of both the incident and scattered neutrons are identical. This can be described by the differential cross section [8] as:

\[
\frac{d\sigma}{d\Omega} = \frac{1}{\Phi} \sum W_{k_i \rightarrow k_f}
\]  \hspace{1cm} (4.6)

where \(\Phi\) is the flux of the incident neutrons, \(W_{k_i \rightarrow k_f}\) is the number of transferred neutrons per unit time from the state \(k_i\) to the state \(k_f\) which can be evaluated using Fermi's Golden rule [7] as:

\[
\sum W_{k_i \rightarrow k_f} = \frac{2\pi}{\hbar L^3} \rho_{k_f} |\langle k_f | V | k_i \rangle|^2
\]  \hspace{1cm} (4.7)

where the neutron and the scattering system are considered to be in a large box of volume \(L^3\), \(\rho_{k_f}\) is the density of the final unperturbed states and \(V\) is the interaction potential between the neutron and the scattering system, which will be defined in the next section.

The flux of the incident neutrons is given by:

\[
\Phi = \frac{h \rho_{k_i}}{L^3 m}
\]  \hspace{1cm} (4.8)

by substituting eq.(4.7) and eq.(4.8) into eq.(4.6), the neutron scattering cross section can be written as:
4.3.2 Inelastic Scattering

For this type of scattering there is a difference between the energy of the incident and the scattered neutrons. If $E_i$ and $E_f$ are the initial and final energies of the neutron, $E_{\text{t},i}$ and $E_{\text{t},f}$ are the initial and final energies of the target sample (the scattering system) respectively, then the conservation law of energy is:

$$E_i + E_{\text{t},f} = E_i + E_{\text{t},i}$$

or

$$\hbar \omega = E_f - E_i = E_{\text{t},f} - E_{\text{t},i}$$

The energy transferred to (or from) the sample may be taken up (or given off) within a single elementary excitation. In mathematical terms the conservation of the energy is represented by a $\delta$-function. The expression for the double differential neutron scattering cross section becomes:

$$\frac{d^2\sigma}{d\Omega d\omega} = \left| \frac{k_f}{k_i} \left( \frac{m}{2\pi \hbar^2} \right) \right|^2 \left| \langle k_f | V | k_i \rangle \right|^2 \delta \left( \hbar \omega + E_{\text{t},f} - E_{\text{t},i} \right)$$

where

$$\int \delta \left( \hbar \omega + E_{\text{t},f} - E_{\text{t},i} \right) dE_{\text{t},i} = 1$$

The partial differential cross section including all possible scattering processes can be given by taking the sum over all initial states $\lambda_i$ which
occur with probability $R_i$ and over all the final states of the target $\lambda_f$. For polarized neutron scattering experiment a summation has to be carried out over all initial and final polarisation states $\sigma_i$ and $\sigma_f$ of the neutron. In this way the master formula for the double differential cross section can be obtained [1]:-

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \left( \frac{m}{2\pi\hbar^2} \right)^2 \sum_{\lambda_i, \sigma_i} P_{\lambda_i} P_{\sigma_i} \sum_{\lambda_f, \sigma_f} \left| \langle \lambda_f, \sigma_f | V | \lambda_i, \sigma_i \rangle \right|^2 \delta\left( \hbar\omega + E_{\lambda_f} - E_{\lambda_i} \right) (4.13)$$

4.4 The Interaction Potential

The interaction potential ($V$) consists of two parts, the nuclear interaction potential ($V_N$) which yields the nuclear scattering contribution, and the magnetic interaction potential ($V_M$) which produces the magnetic scattering contribution:

Nuclear Scattering

The range of the nuclear potential is known to be very short compared to the wavelength of the thermal neutrons which are used in scattering experiments. This means that the neutron-nucleus scattering is isotropic, and within the first Born approximation may be characterised by a single parameter $b$ known as the scattering length. The nuclear interaction potential between the neutron and the sample can be described in the form:

$$V_n = \frac{2\pi\hbar^2}{m} \sum b \delta(x - R_i)$$

---------(4.14)
Where $r_i$ and $R_i$ are the instantaneous positions of neutron and nucleus, respectively. The sum is carried out over all atoms in the sample.

The double differential nuclear scattering cross section for an unpolarized beam is obtained by substitution of eq.(4.14) into equation (4.13).

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{1}{N}\right) \sum_{i} P_i \left| \sum_{l} b_l (\lambda_f | e^{i R_i} | \lambda_i) \right|^2 \delta(h\omega + E_{\lambda_f} - E_{\lambda_i}) \tag{4.15}$$

where

$$\langle k_f | V_n | k_i \rangle = \sum_{i} b_l e^{i R_i}$$

The dependence on $\sigma_i$ and $\sigma_f$ disappeared because for unpolarised beams both spin states are equally probable.

**The Magnetic Scattering**

The coupling between the neutron dipole moment and the magnetic moment of unpaired electrons as determined by their spin and orbital moments produces a magnetic interaction potential. This can be expressed as:

$$v_{\sigma}(r) = -\gamma \mu_\sigma \frac{2\mu_\sigma}{r^2} \left( \text{Cur} \frac{e \times \hat{r}}{r^2} + \frac{1}{\hbar} \frac{P \times \hat{r}}{r^2} \right) \tag{4.16}$$

where the first term arises from the orbital motion of the electron, $\sigma$ is the spin state of the neutron, and $P$ is the momentum of the electron with spin $\sigma$.

The scattering cross section from a sample containing many unpaired electrons is obtained by substituting eq.(4.16) in the master formula.
eq. (4.13). The matrix elements \( \langle \xi_f \sigma_f \lambda_f | \hat{V}_m | \xi_i \sigma_i \lambda_i \rangle \) have to be evaluated by first calculating the matrix elements between the plane wave states \( |\xi_i\rangle \) and \( |\xi_f\rangle \). It can be shown that [5]:

\[
\langle \xi_f | V_m | \xi_i \rangle = 4\pi\mu_B^2 \mu_B \mathcal{D}_L (\xi_i - \xi_f) 
\]

where \( \mathcal{D}_L \) is the magnetic interaction operator which is given by:

\[
\mathcal{D}_L = \sum_i \left[ \hat{\mathbf{L}} \cdot \left( \hat{\mathbf{S}}_i \times \hat{\mathbf{L}} \right) + \frac{i}{\hbar} \left( P_i \times \hat{\mathbf{L}} \right) \right] e^{iQ_L} 
\]

\( \hat{\mathbf{S}}_i \) is the angular spin momentum operator of the electron.

For the evaluation of the matrix elements over the neutron spin states \( |\sigma_i\rangle \) and \( |\sigma_f\rangle \) for unpolarized neutron, the matrix elements of products of the neutron spin operator \( \hat{\sigma} \) satisfy the condition:

\[
\sum_{\alpha} P_{\alpha} \sum_{\beta} |\sigma_i \sigma_k \sigma_f \rangle = \delta_{\alpha \beta}
\]

where \( \alpha \) and \( \beta \) label the co-ordinate axis. Thus the double differential cross section takes the form:

\[
\frac{d^3\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \left( \frac{r_o}{N_m} \right)^2 \sum_k \sum_{\xi} \sum_{\lambda} \langle \lambda_i | Q_m | \lambda_f \rangle \langle \lambda_i | Q_m | \lambda_i \rangle \delta (\hbar \omega + E_{\xi_i} - E_{\xi_f})
\]

\( N_m \) is the number of the magnetic ions.
\( r_o \) is the classical radius of the electron.
4.5 The Correlation Function

The correlation function is used to relate the neutron scattering cross section to the thermal averages of operators belonging to the target sample. It is useful for calculating various properties of the scattering system. The physical significance of the terms that occur in the scattering cross section is best seen by expressing it in terms of correlation functions [8]. To rewrite the double differential cross section in terms of the correlation function considering the general interaction potential between the neutrons and the target: (as given by equation (4.14)). Following the derivation as given in ref. [7] and using the Fourier transform of:

\[ V_j(q) = \int d^2r e^{iQ \cdot r} \hat{V}_j(r) \]  

(4.21)

and with the help of the \( \delta \)-function:

\[ \delta(\hbar \omega + E_n - E_f) = \frac{1}{2\pi\hbar} \int dt \exp \{-it(\hbar \omega + E_n - E_f)\} \]  

(4.22)

and by using the following identity

\[ \langle \sigma_f | \hat{V} | \sigma_i \rangle^* = \langle \sigma_i | \hat{V}^* | \sigma_f \rangle \]

the double differential cross section can be obtained as:
\[
\frac{d^2\sigma}{d\Omega d\omega} = k_t \frac{1}{k_i} \frac{1}{2\pi\hbar} \int dt \exp(-i\omega t) \sum_{j'} \hat{V}^+(Q) \hat{V}(Q) Y_{j'}
\]  

(4.23)

where \( \hat{V}^+ \) is the Hermitian conjugate of \( \hat{V} \). The horizontal bar represents an average over nuclear spin orientations and isotope distribution, and \( Y_{j'} \) is the correlation function which is given by:

\[
Y_{j'}(Q,t) = \left\{ \exp(-iQ \cdot \hat{R}_j) \exp(iQ \cdot \hat{R}_j(t)) \right\}
\]  

(4.24)

When the average of the product of the potentials is independent of the nuclei then eq.(4.24) can be written as:

\[
\frac{d^2\sigma}{d\Omega d\omega} = N k_t \frac{1}{k_i} \left| V_j(Q) \right|^2 S(Q,\omega)
\]  

(4.25)

where

\[
S(Q,\omega) = \frac{1}{2\pi\hbar N} \int dt \exp(-i\omega t) \sum_{j'} Y_{j'}(Q,t)
\]  

(4.26)

This equation is called the "scattering function".

In equation (4.26) the double differential neutron scattering cross section can be seen to be represented by the product of two factors: the first factor depends on the properties of the individual scatterers in the target, and the second factor is related to the structure and dynamical behaviour of the target sample.
4.6 Coherent and Incoherent Scattering

In practice two types of scattering are distinguished. Firstly the coherent scattering which occurs when the scattered waves from atoms in different spatial positions interfere, and hence the neutron wavefunctions have to be added taking into account their phase differences. Secondly the incoherent scattering which occurs whenever there is an element of randomness involved in the scattering process from various scattering centres. Incoherent scattering occurs because the nuclei of a given atom in the solid are not necessarily the same or in the same state. The atoms may be different isotopes of the same element. Each isotope will have its own characteristic value of the scattering length \( b \) and the isotopes will be distributed randomly among the atomic positions for a given element. Therefore the double differential cross section comprises two parts, a coherent part which is proportional to the mean square of the scattering length \( b \), and an incoherent part which is proportional to the deviation of the mean scattering length. For nuclear scattering the total double differential cross-section can be written as:

\[
\frac{d^2\sigma}{d\Omega d\omega} = \left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{coh} + \left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{incoh}
\]

\[
------------------(4.27)
\]

with

\[
\left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{coh} \propto \langle b^2 \rangle \quad \text{and} \quad \left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{incoh} \propto \langle b^2 \rangle - \langle b \rangle^2
\]
where averages are taken including different isotopes and nuclear spin states.

The coherent scattering yields Bragg peaks which are highly $Q$ dependent. It also yields inelastic scattering in the form of phonon scattering.

4.7 Discussion of Neutron Scattering and Crystal Field Splitting

The inelastic neutron scattering technique has proved to be the most versatile experimental tool for studying the crystal field splitting in metallic systems, since the energy differences of crystal field states can be determined directly. Detailed information on the crystal field levels can be obtained through the positions of inelastic peaks and the peak intensities. The peak positions of inelastic scattering in the observed experimental spectra measure the energy level separation, while the square of matrix elements of the transition probabilities determine the peak intensities. In order to illustrate the relationship between the crystal field splitting and inelastic neutron scattering a brief discussion is given below of the paramagnetic scattering law for an unpolarized neutron scattering experiment.
The Scattering Function

The scattering function $S(Q, \hbar\omega)$ is proportional to the double differential cross-section as given by [8-10]:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_i}{k_f} S(Q, \hbar\omega)$$

(4.28)

On the other hand the imaginary part of the dynamic susceptibility $\chi''(Q, \hbar\omega, T)$ is related to the scattering function:

$$S(Q, \hbar\omega) = \frac{1}{2\pi} \left[ \frac{g_N r_{\Theta}}{\mu_B} \right] \chi''(Q, \hbar\omega, T) / \left[ 1 - \exp(-\hbar\omega / k_B T) \right]$$

(4.29)

where $g_N = -1.91$ (magnetic moment of the neutron)

$r_{\Theta} = 2.8 \times 10^{-13}$ cm (the classical electron radius)

$\mu_B = \frac{e\hbar}{mc}$ is the Bohr magneton

and $k_B$ is the Boltzmann constant.

By applying the Kramers-Kronig relation, the imaginary susceptibility can be given in terms of bulk susceptibility as:

$$\chi''(Q, \h, T) = \chi'(0, 0, T) F^2(Q) P(Q, \h\omega, T) \hbar\omega \pi$$

(4.30)

where $F(Q)$ is the magnetic form factor and $P(Q, \h\omega, T)$ is known as the spectral function and is normalized to 1.
\[ \int_{-\infty}^{\infty} P(Q, h\omega, T) d(h\omega) = 1 \] \hspace{1cm} (4.31)

From eq.(4.30) and (4.31) the scattering can be rewritten as:

\[ S(Q, h\omega) = \frac{1}{2} \left[ \frac{\delta N}{\mu_B} \right]^2 F^2(Q) \chi_m(T) P(Q, h\omega, T) \omega / \left[ 1 - \exp(h\omega / k_B T) \right] \] \hspace{1cm} (4.32)

The total magnetic cross-section is defined by [8]:

\[ \sigma_{mag} = 4\pi \int S(Q, h\omega) d(h\omega) \text{ at } Q = 0 \] \hspace{1cm} (4.33)

**Calculation of the Magnetic Cross Section in the Absence of Crystal Field**

1. No Magnetic Interactions Between Ions (Curie's Case)

For a stable rare earth ion in a metal, ignoring the interaction between magnetic atoms, the susceptibility is given by:

\[ \chi_m(T) = g_J^2 J(J+1) \mu_B^2 / 3k_B T \]
\[ = P_{loc}^2 \mu_B^2 / 3k_B T \] \hspace{1cm} (4.34)

\( P_{loc} = g_J \sqrt{J(J+1)} \) is the local magnetic moment. In this case the thermal energy is small compared to the intraconfigurational multiplet splitting and the interactions between neighbouring ions are negligible. The spectrum is a
Lorentzian centred at $\hbar \omega = 0$, with a width as given by the Korringa relation [8],

$$\frac{1}{2} \Gamma(T) = \alpha k_B T \tag{4.35}$$

where

$$\alpha = 4\pi N(E_F) J_{ex} (g_J - 1)^2 \tag{4.36}$$

$N(E_F)$ is the density of conduction electrons at the Fermi level, and $J_{ex}$ is the exchange interaction constant.

If $k_B T$ is very small compared to the interaconfigurational multiplet splitting, then

$$\frac{1}{1 - e^{-\hbar \omega/k_B T}} = 1 - 1 + \frac{k_B T}{\hbar \omega} + \frac{k_B T}{\hbar \omega} + \frac{(k_B T)^2}{\hbar \omega} + \cdots \sim \frac{k_B T}{\hbar \omega}$$

The higher terms are ignored because they are very small.

The spectral function behaves like a $\delta$-function, so eq.(4.32) takes the form:

$$\sigma_{mag} = \frac{4\pi}{2} \left[ \frac{g_N \mu_B}{\mu_B} \right]^2 \chi_{st} (T) k_B T \tag{4.37}$$

and using eq.(4.33) the magnetic cross section can be given in terms of local magnetic moment :

$$\sigma_{mag} = \frac{4\pi}{6} (g_N \mu_B)^2 P_{loc}^2 \tag{4.38}$$
It is clear from this equation that the total magnetic cross-section is independent of temperature.

2. Magnetic Interactions Between Ions

In this case the susceptibility follows the Curie-Weiss behaviour in the paramagnetic region and is given by:

\[ \chi_{\text{m}}(T) = \frac{P^2}{3k_B} \mu_B^2 \left( T - \theta \right) \]

where \( \theta \) is the Curie-Weiss temperature. The total magnetic cross-section becomes:

\[ \sigma_{\text{mag}}(T) = \frac{2\pi}{3} \left( g_N r_e \right)^2 \frac{P^2}{P^2} \left( T - \theta \right) \]

Comparing eq.(4.38) and eq.(4.40), it is clear that there is a difference in the value of \( \sigma_{\text{mag}} \) in the case of Curie Weiss behaviour. This difference is a factor of \( \frac{T}{T - \theta} \) and it must be taken into account in the calculation of scattering intensity.
Determination of Magnetic Susceptibility in the Presence of Crystal Field Splitting

In the presence of crystal field splitting the static susceptibility is separated into two terms:

\[ \chi_m P(Q,\hbar\omega,T) = \sum_{m} \chi^{m}_c P_{nm} (Q,\hbar\omega,T) + \frac{1}{2} \sum_{m\neq n} \chi^{mn}_v \left(1 - e^{-\frac{\Delta nm}{k_B T}}\right) P_{mn} (Q,\hbar\omega - \Delta nm T) \]

\[ \text{(4.41)} \]

The first term on the right hand side belongs to the Curie susceptibility of the \( m \)th level

\[ \chi^{m}_c = \frac{\mu_B^2}{k_B T} g_J^2 P_m \left| \langle m \mid J_z \mid m \rangle \right|^2 \]

\[ \text{----------------- (4.42)} \]

The second term is related to the Van Vleck susceptibility

\[ \chi^{mn}_v = 2\mu_B^2 g_J^2 P_m \frac{\left| \langle n \mid J_z \mid m \rangle \right|^2}{\Delta_{nm}} \]

\[ \text{----------------- (4.43)} \]

The Van Vleck susceptibility arises due to the transition between the two eigen energy states \( E_n \) and \( E_m \).

\[ \Delta_{nm} = E_n - E_m \]

\( P_m \) is the occupational probability and it is defined by

\[ P_m = \frac{e^{-E_m / k_B T}}{Z} \int \]

\[ \text{(4.44)} \]
where $Z$ is the partition function. In a compound of cubic symmetry, it can be shown that:

$$|\langle n | J_z | m \rangle|^2 = |\langle n | J_x | m \rangle|^2 = |\langle n | J_y | m \rangle|^2$$

So that the total transition probability between two levels is given by [12]:

$$2|\langle n | J_z | m \rangle|^2 = |\langle n | J_\perp | m \rangle|^2$$ \hspace{1cm} \begin{equation} \text{(4.44)} \end{equation}

where $J_\perp$ is the component of the total angular moment operator perpendicular to the scattering vector $Q$. Now the scattering function becomes:

$$S(Q, \hbar \omega) = \frac{1}{4} (g_s r_s) F^2(Q) g_s^2 \sum_{n,m} P_m |\langle n | J_\perp | m \rangle|^2 (\hbar \omega - \Delta_{nm})$$ \hspace{1cm} \begin{equation} \text{(4.45)} \end{equation}

This equation is used to extract information from inelastic neutron scattering concerning the crystal field splitting. For the analysis of inelastic neutron scattering spectra, it is necessary to find the best values of parameters ($W$, $x$) (defined in sect. 3.4) which produce the best fit to the observed spectra. In order to do this both the peak positions and their intensities in inelastic neutron scattering spectra have to be taken into account.
References:


5.1 Introduction

This chapter discusses in detail the measurement of the magnetic susceptibility of some rare-earth compounds. Two methods were used, namely

- the Faraday balance.
- the SQUID System (Sheffield University).

A series of Heusler alloys were investigated namely samples containing rare earth elements and having the composition (Pd$_2$ReIn, Pd$_2$YbSn), where Re = Gd, Tb, Dy, Ho, Er, and Yb. All samples were prepared in the Physics Department at Loughborough University using the method described below.

A detailed description of the two methods used to determine the magnetic properties is also presented, followed by an exposition of the experimental results.

5.2 Sample Preparation

An argon arc furnace was used to melt the appropriate proportions of pure constituent elements. The argon is allowed into the system at a pressure of
2×10^{-1} bar. The system was flushed through several times before the melting took place. An electric dc generator was used to produce an arc between the electrode and the copper plate which was water-cooled to prevent overheating.

The cleaning process involved melting titanium using the arc. The Ti was kept molten for ~ 1 min. This process removes oxygen and other contaminants from the atmosphere. If the titanium is still shiny after melting then the atmosphere is considered clean and free from oxygen. The sample was then melted, starting with the highest melting point material first. Due to the underside of the sample being in contact with the cool copper plate a small layer of material remained solid. This prevented contaminants from the plate mixing with the alloy. After switching off the arc and allowing the sample to cool down, the electrode was used to turn the sample over and to re-melt the sample again in order to produce a homogenous alloy. All samples were re-melted at least 5 times.

All the materials were of at least 99% purity. The weight losses during melting were about 0.05% for all the Heusler alloys (except for the alloy with Yb for which the weight loss was about 1.5%). This was caused by evaporation of Yb during the melting process. The weight loss for all other components was within 0.7%.

All samples were crushed into a fine powder, using a steel pestle and mortar. Powder samples were investigated using X-ray diffraction, and then their magnetic properties were determined by susceptibility measurements. A selection of samples were investigated in inelastic neutron scattering experiments.
5.3 STRUCTURE DETERMINATION

5.3.1 The Apparatus

All powder samples were examined by X-ray diffraction using a Phillips diffractometer with Cu $K_{\alpha}$ radiation. A broad focus PW2103/100 copper radiation tube was used in conjunction with a PW1050/25 vertical goniometer. A proportional detector PW1965/20/30 was connected to the counting equipment. The detector was fixed on the diffractometer axis, and it was driven at a constant angular velocity. A suitable amount of the finest powder was placed on an aluminium sample holder, which was mounted at the centre of the goniometer [3]. The diffraction pattern was displayed using a pen recorder.

5.3.2 X-Ray Diffraction Results Of Heusler Alloys

All measurements were taken at room temperature. The x-ray tube was supplied with 40kV and 30mA. The rate meter at full scale amounted to 200-2000 counts/sec and the pen recorder speed was 600 mm/h.

X-ray diffraction patterns of Pd$_2$ReIn compounds are shown in figures fig(5.1) to (5.6), with Re= Gd, Tb, Dy, Ho, Er, Yb. The pattern for Pd$_2$YbSn is shown in figure (5.7). The patterns are consistent with the compounds crystallising in the face centred cubic L$_{21}$ structure. The unit cell has space group symmetry Fm$\bar{3}$m, and it gives rise to Bragg reflections with non zero structure amplitudes when the Miller indices (hkl) of the scattering factor are all even or all odd numbers as discussed earlier in chap.2. For ordered Heusler alloys there are three groups of reflections which are defined with the following structure factors:
1. $h,k,l$ are all odd
   \[ F(111) = F(311) = 4(f_{\text{Re}} - f_{\text{In}}) \]

2. $h,k,l$ all even and $\frac{1}{2}(h+k+l)$ is odd
   \[ F(200) = 4(2f_{\text{Pd}}f_{\text{Re}} - f_{\text{In}}) \]

3. $h,k,l$ all even and $\frac{1}{2}(h+k+l)$ is even
   \[ F(220) = 4(2f_{\text{Pd}} + f_{\text{Re}} + f_{\text{In}}) \]

where the $f$'s are the average scattering factors for the atoms in the respective sublattices.

The structure factor $F(220)$ belongs to the principal reflections which are unaffected by the state of chemical order. The structure factors $F(111)$ or $F(311)$ and $F(200)$ depend on the degree of chemical order. There are various ways the system can disorder. In the present study the calculated structure factors for the superlattice reflections are very small approximately 1% of the structure factor for the principle reflections. Therefore the disordered B2 structure could have occurred. In this structure the Re and In atoms randomly occupy the B and D sites and consequently for complete disorder the (111) reflection disappears. For an ordered Heusler alloy $\text{Pd}_2\text{ReIn}$, Pd atoms are localised at A and C sites, while the rare earth and In atoms occupy the B and D sites, respectively.

The Bragg reflections of each sample were indexed on the basis of a cubic cell and the lattice parameters were calculated using the following relationship [2]:
\[ \sin^2 \theta = \frac{\lambda^2(h^2 + k^2 + l^2)}{4a^2} \]
Fig. (5.1): X-ray diffraction pattern of Pd$_2$GdIn at room temperature
Fig. (5.2): X-ray diffraction pattern of Pd$_2$Tbn at room temperature
Fig. (5.3): X-ray diffraction pattern of Pd$_2$DyIn at room temperature
Fig. (5.4): X-ray diffraction pattern of Pd$_2$H Ol at room temperature
Fig.(5.5): X-ray diffraction pattern of Pd$_2$ErIn at room temperature
Fig. (5.6): X-ray diffraction pattern of Pd$_2$Ybln at room temperature
Fig. (5.7): X-ray diffraction pattern of Pd$_2$YbSn at room temperature
The results of the calculations are given in table (5.1). The absence of the reflections (111) and (311) in the compounds containing Gd, Dy and Er indicates that the complete disorder between Re and In atoms cancels the intensity of the (h k l) lines. These two lines appeared in the other compounds. Small additional peaks also occur due to the sample holder and due to the presence of some small amount of impurity phase. The extra peaks were observed clearly in Pd₂Holn and Pd₂YbSn.

Table (5.1) The lattice constants of Pd₂Reln for (h,k,l) = (4, 2, 2):

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₂GdIn</td>
<td>68.4</td>
<td>6.716±.0132</td>
</tr>
<tr>
<td>Pd₂TbIn</td>
<td>68.0</td>
<td>6.746±.045</td>
</tr>
<tr>
<td>Pd₂DyIn</td>
<td>68.7</td>
<td>6.685±.013</td>
</tr>
<tr>
<td>Pd₂Holn</td>
<td>68.7</td>
<td>6.685±.012</td>
</tr>
<tr>
<td>Pd₂ErIn</td>
<td>68.9</td>
<td>6.668±.005</td>
</tr>
<tr>
<td>Pd₂YbIn</td>
<td>69.5</td>
<td>6.618±.011</td>
</tr>
<tr>
<td>Pd₂YbSn</td>
<td>69.0</td>
<td>6.659±.054</td>
</tr>
</tbody>
</table>

5.4 Magnetic Susceptibility Measurements

5.4.1 The Faraday Method

This method is the one most often used for measuring paramagnetic susceptibility. It is suitable for weak magnetic materials such as
Fig.(5.8) : Low temperature magnetic susceptibility system
(Faraday balance)
Fig. (5.9): The force exerted on a standard sample as a function of the sample position.
paramagnetic or antiferromagnetic materials. The principle of this method depends on the measurement of the force exerted upon the sample which is suspended between two magnetic pole pieces in a gradient field (see figure 5.8).

The force which is exerted upon a specimen placed in a non-uniform magnetic field may be calculated from the variation of its free energy with position [1] as:

$$F = m \chi H \frac{\partial H}{\partial z}$$

where $m$ is the mass of the specimen and $\frac{\partial H}{\partial z}$ represents the vertical gradient of the field $H$ and $\chi$ is the magnetic susceptibility. The position of the specimen is chosen such that the greatest force is obtained (see figure 5.9).

Since it is difficult to measure $H \frac{\partial H}{\partial z}$ accurately, a standard sample of known susceptibility (e.g. pure Titanium or Palladium) is usually used for calibration purposes. If the force on the standard sample is:

$$F_n = \chi_n m_n H \frac{\partial H}{\partial z}$$

then the susceptibility of the investigated sample can be calculated as

$$\chi_{\text{sample}} = \left( \frac{\chi_n m_n}{F_n m_{\text{sample}}} \right) F_{\text{sample}}$$
Fig. (5.10): Schematic Diagram of Faraday System.
Measurements of the force were made at different currents giving rise to different magnetic field strengths. A fit to a straight line was used to calculate the slope of force versus current; the susceptibility could then be obtained from equation (5.3) using the slope of the straight line for the sample and the standard sample respectively.

5.4.1.1 Experimental Set-up

The experimental set-up for the Faraday Balance is shown in fig. (5.10). It can be divided into three main parts:

- the mechanical part which includes the sample holder, the cryostat and the vacuum system,

- the electromagnetic part which includes the electromagnet and its DC power supply.

- the electronic control part which includes all the electronic measuring equipment (e.g. the electric balance, the temperature controller and the DVM) and the computer controllers.

A. The Mechanical Part

This part is responsible for holding the sample at the right position between the two magnetic poles of the electromagnet. Its main components are:

**The Cryostat:** A continuous flow cryostat model CF1200 (designed by Oxford Instruments) was used to encase the sample and its holder. The vacuum jacket of the cryostat was maintained at $10^{-5}$ mbar. Liquid nitrogen
or helium was delivered to the cryostat by a vacuum insulated transfer tube inserted into a siphon entry arm [4].

**The Vacuum System:** The vacuum system consists of an oil diffusion pump and a rotary pump. The rotary pump was used to evacuate the cryostat to a pressure of less than $10^{-1}$ mbar, and the diffusion pump to evacuate the cryostat to a pressure of $10^{-1}$ to $10^{-5}$ mbar.

**The Sample Holder:** A non-magnetic rod of length 60 cm was used to hold the sample at one of its ends. The other end was top-loaded through an access on the top of the cryostat. The sample and its holder were passed through a cylindrical space of 20 mm diameter inside the cryostat where they were situated either in vacuum or in an exchange gas atmosphere of reduced pressure.

**B. The Electromagnet Part**

The magnetic field is generated by a 3.5cm adjustable gap electromagnet which can take up to 20Amp of DC current. This current is supplied by a separate DC power supply unit. The amount of current that passes into the magnet windings can be controlled either manually (from the unit front panel) or automatically. When set to automatic mode, a precision multturn potentiometer (which controls the current output) is driven by a precision stepper motor. The stepper motor driver receives two signals from the computer; one is to set the direction of rotation (increase or decrease the current) and the other is the clock pulses which causes the motor to move one step per pulse.
To measure the current that passes into the electromagnet, a 0.1Ω resistance is connected in series with the winding and a digital voltmeter (DVM) is connected across this resistance to measure the voltage across it which is then converted into a current using Ohm's law \((I = \frac{V}{R})\).

C. The Electronic Control Part

This part is responsible for controlling the current that passes through the electromagnets (by controlling the DC supply to the electromagnet), controlling the sample temperature through the temperature controller and measuring the voltage output of the electric balance. The main system in this part is an IBM compatible personal computer which, besides controlling the overall system functions, is also used to perform all the calculations of susceptibility and present the final results in a graphic form and/or to produce an ASCII output file.

The Temperature Controller: The function of the temperature controller is to maintain the sample at a set temperature. It can be operated manually (from the front panel) or automatically under computer control using the IEEE interface. The heat exchanger, which is located at the bottom of the sample space, is fitted with an AuFe temperature sensor and a heater. These are connected to the temperature controller [5]. The thermocouple uses a liquid nitrogen reference junction and produces an emf from -1.1 mV at 4K to +8.6mV at 500K. It was calibrated at helium and nitrogen temperatures, and the system has a quoted stability of ±0.1K. The other junction of the thermocouple was connected with the heater and was fitted to the base of the heat exchanger.
For the purpose of low temperature measurements, liquid nitrogen or liquid helium was driven by a gas flow pump from a separate storage vessel through an evacuated transfer tube to the cryostat. The coolant flows through the heat exchanger of the cryostat where the temperature is measured and the heater is used to control the temperature.

**The Micro-Force Electric Balance:** The force exerted on the specimen is measured by the Micro-Force Electric Balance model 3A40. The head unit of the micro balance, made with a precision galvanometer, electromagnetically balances the torque produced by the weight of the specimen. A current flows through it in exact proportion to the applied force and this current operates a meter for visual reference and also provides a voltage output. In addition to generating a current proportional to the force, this servo action ensures a rapid response and makes the balance insensitive to external vibration. The voltage from the micro-force balance is measured by a digital voltmeter for different applied magnetic fields as indicated by the current flowing in the electromagnet.

**The Overall System Control:** As stated earlier, the overall system control was undertaken by an IBM compatible personal computer. The control was achieved by two means:

- through an IEEE bus where the computer controls the temperature controller and the digital voltmeter function.
- the Peripheral Interface Board (PIB) which was plugged inside the computer and which was used to generate the signals required to drive the
Fig. (5.11 A): The flow chart of the main program of magnetic susceptibility measurements
SWITCH THE MULTIPLEXER TO READ VOLTAGE ACROSS THE RESISTOR

READ THE VOLTAGE AND CALCULATE THE CURRENT \( i = \frac{v}{r} \)

TURN THE MOTOR (POT) ONE STEP CLOCKWISE TO REDUCE THE CURRENT

IS \( i \) < 0.01amp?

NO

YES

RETURN TO THE MAIN PROGRAM

Fig. (5.11 B) : Re-setting the field current
stepper motor. The board was also used to drive a multiplexer unit which was used to multiplex two inputs into the digital voltmeter.

The main steps of the control program for one measurement are

1. Variable declaration: different variables used in the program are declared with the appropriate dimensions.
2. Set the IEEE interface and the PIB ports.
3. Set the experimental parameters which include
   - Name of the sample
   - Date and time of experiment.
   - Sample weight.
   - Starting field current (ISTART).
   - Final field current (IFINAL).
   - Step field current (IFIELD).
   - Starting sample temperature (TSTART).
   - Final sample temperature (TFINAL).
   - Step temperature (TSTEP).
   - Number of snapshots taken to measure the micro force electric balance at each current (NSHOTS).
   - The name of the output data file.
4. Read the data of the empty and standard samples from a pre-stored data file.
5. Reset the field current to 0.
6. Set the sample temperature to TSTART.
7. Set the field current to ISTART.
8. Take a number of measurements as defined by NSNAPS.
9. Step up the field current by ISTEP and repeat the above step until the current reaches IFINAL.

10. Reset the field current to 0.

11. Step up the temperature by TSTEP and repeat steps 7 to 10 until the temperature reaches TFINAL.

Figure (5.11) shows the flowchart of the system software.

5.4.2 The SQUID System

The SQUID (Super-conducting Quantum Interference Device) is a highly sensitive instrument used to measure magnetic moments down to $10^{-8}$ emu. It mainly consists of a superconducting ring with a small insulating layer known as the 'weak link' (see figure 5.12). Its resolution reaches down to $10^{-14}$ T ($10^{-10}$ Gauss). The flux passing through the ring is quantised once the ring has gone superconducting but the weak link enables the flux trapped in the ring to change only by discrete amounts. Quantised changes in flux occur as a result of tunnelling by electrons through a Josephson weak link in the SQUID ring. These quantised changes are used by the instrument to calculate the magnetic moment of the sample [8].

5.5 The Experimental Results

The measurements carried out by using the Faraday system were based on the measurement of the force exerted on the sample.

Some of the results were obtained by using the SQUID system. This second experimental investigation allowed a more precise determination of the magnetic properties.
specimen mount traverses slowly

Fig. (5.12): SQUID magnetometer
The magnetic susceptibilities were measured in the temperature range 5K to 120K for the two compounds Pd$_2$Ybln and Pd$_2$YbSn. For all other samples the measurements were in the temperature range 77 K < T < 300 K. The thermal variation of susceptibility and inverse susceptibility are plotted in figs. [5.13 - 5.24]. It is to be noted that the magnetic susceptibility of Pd$_2$Ybln follows Curie-Weiss behaviour with some deviations at temperature below 20 K. This deviation is attributed to crystal field effects. All other samples follow a Curie-Weiss behaviour within the temperature range investigated here.

\[ \chi(T) = \frac{C}{T - \theta}, \]  

\[ \text{Where } C = \frac{N \mu_{\text{eff}}^2}{3k_B}, \]  

\( N \) : is the effective number of atoms per unit volume (Avogadro's number).  

\( k_B \) : is the Boltzmann's constant.

The resulting \( \chi^{-1} \) versus T curve is a straight line which intercepts the temperature axis at the Curie-Weiss temperature (\( \Theta_p \)), and has a slope (1/C), where C is the Curie-Weiss constant. Within the above mentioned range of temperature no magnetic ordering was observed in any of the samples investigated and the deviation from Curie-Weiss behaviour which was observed in Pd$_2$Ybln was not seen in the compound Pd$_2$YbSn.

The effective paramagnetic moments were obtained from plots of the inverse susceptibility as a function of temperature in the following way:

The magnetic susceptibility \( \chi \) is given by equation (5.4).
Rearranging the above equation yields

$$\mu_{s}^{2} = \frac{3k_{B} (\text{Molecular Weight})}{N\mu_{s}^{2}} \text{slope of } (1/\chi, T)$$

The results of experimental effective magnetic moments and the theoretical values for free rare-earth ions, with the experimental value for the paramagnetic Curie temperature are given in table (5.2). The theoretical value of the effective magnetic moments for free rare-earth ions is obtained by using Hund's rule as:-

$$\mu_{s} = g_{s}[J(J+1)]^{1/2} \quad \text{------(5.5)}$$

Examining the effective magnetic moment, one can observe that the experimental value is slightly larger than the theoretical one (for a free rare earth ion). This can be explained by the polarisation of the conduction electrons which effectively modify the size of the magnetic moment of the rare earth ion.

Due to the complete isolation of the rare-earth atoms, it can be expected that magnetic susceptibility will follow the Curie law, i.e. C/T. However experimentally a Curie-Weiss law $c/(T - \theta_{p})$ is observed which will show that this law is characteristic of the indirect interaction between the spins. Due to this interaction an internal field (molecular field) of amount $\alpha_{w}M_{w}$ is created and superimposed upon the applied field. In this case the total magnetic field is

$$H_{tot} = H + \alpha_{w}M_{w} \quad \text{-----------------(5.6)}$$
Where $H$ is the applied field (external field), $M_w$ is the bulk magnetisation, and $\alpha$ is the mean field constant.

The intensity of magnetisation at temperature $T$ is

$$M = (n\mu_{\text{eff}}^2\mu_b^2 / 3k_B T)H_{\text{tot}}$$  \hspace{1cm} \text{(5.7)}$$

$n$ here is the number of atoms per unit volume. By solving equation (5.7) and dividing by $H$ one obtains the Curie-Weiss law as

$$\chi_s = n\mu_{\text{eff}}^2\mu_b^2 / 3k_B T(T - n\mu_{\text{eff}}^2\mu_b^2\alpha_w / 3k_b) = C / (T - \theta_p)$$  \hspace{1cm} \text{(5.8)}$$

where $C$ is the Curie constant, $\theta_p = n\mu_{\text{eff}}^2\mu_b^2\alpha_w / 3k_b$ (i.e. Paramagnetic Curie temperature)

The high magnetic field susceptibility offers a very sensitive test for the crystal field effects and the exchange interactions. Therefore the measurements of susceptibility against temperature are repeated for all samples using the SQUID magnetometer with magnetic field up to 5 Tesla. The results of inverse susceptibility versus temperature for Pd$_2$HoIn and Pd$_2$YbIn are shown in figures (5.25) and (5.26). A deviation from the Curie-Weiss behaviour is observed by a curvature at low temperature. This deviation may be observed more clearly by plotting the effective magnetic moment $\mu_{\text{eff}}$ against temperature, see figures (5.27, 5.28). In the absence of crystal field effects $\mu_{\text{eff}}$ should be independent of temperature. However a reduction in $\mu_{\text{eff}}$ values is observed. This deviation is ascribed to crystal field effects. The paramagnetic Curie-Weiss temperature for these samples are calculated from the inverse susceptibility as determined by the extrapolation of the Arrott plots for high magnetic fields and the results are presented in table (5.2). Due to the application of high fields the Curie-Weiss
temperatures show smaller values compared to the values obtained at low field (0.45 Tesla) as measured by Faraday system.

**Table (5.2) Measured and calculated effective magnetic moments and their $\theta_p$ values of Pd$_2$ReIn and Pd$_2$YbSn**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_{\text{eff (measured)}}$</th>
<th>$\mu_{\text{eff (calculated)}}$</th>
<th>$\theta_p$(Faraday)</th>
<th>$\theta_p$(SQUID)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_2$TbIn</td>
<td>9.705</td>
<td>9.7</td>
<td>+12.88</td>
<td>------</td>
</tr>
<tr>
<td>Pd$_2$DyIn</td>
<td>10.81</td>
<td>10.6</td>
<td>+7.084</td>
<td>------</td>
</tr>
<tr>
<td>Pd$_2$HoIn</td>
<td>11.176</td>
<td>10.6</td>
<td>-17.83</td>
<td>-2.65</td>
</tr>
<tr>
<td>Pd$_2$ErIn</td>
<td>12.172</td>
<td>9.6</td>
<td>------</td>
<td>-2.341</td>
</tr>
<tr>
<td>Pd$_2$YbIn</td>
<td>4.93</td>
<td>4.5</td>
<td>-7.85</td>
<td>-6.749</td>
</tr>
<tr>
<td>Pd$_2$YbSn</td>
<td>5.52</td>
<td>4.5</td>
<td>-6.465</td>
<td>------</td>
</tr>
</tbody>
</table>
Fig. (5.13): Susceptibility of Pd₂TbIn as a function of temperature

Fig. (5.14): Reciprocal susceptibility of Pd₂TbIn as function of temperature
Fig. (5.15): Susceptibility of Pd$_2$DyIn as a function of temperature

Fig. (5.16): Reciprocal susceptibility of Pd$_2$DyIn as function of temperature
Fig. (5.17): Susceptibility of Pd$_2$HoIn as a function of temperature

Fig. (5.18): Reciprocal susceptibility of Pd$_2$HoIn as function of temperature
Fig. (5.19): Susceptibility of Pd₂ErIn as a function of temperature

Fig. (5.20): Reciprocal susceptibility of Pd₂ErIn as function of temperature
Fig. (5.21): Susceptibility of Pd$_2$YbIn as a function of temperature

Fig. (5.22): Reciprocal susceptibility of Pd$_2$YbIn as function of temperature
Fig. (5.23): Susceptibility of Pd$_2$YbSn as a function of temperature

Fig. (5.24): Reciprocal susceptibility of Pd$_2$YbSn as function of temperature
Fig. (5.25): Reciprocal susceptibility versus temperature for Pd₂HoIn
(as measured by the SQUID magnetometer)

Fig. (5.26): Reciprocal susceptibility versus temperature for Pd₂YbIn
(as measured by the SQUID magnetometer)
Fig.(5.27): Effective magnetic moment vs temperature for Pd$_2$HoIn

Fig.(5.28): Effective paramagnetic moment versus temperature for Pd$_2$YbIn
References

CHAPTER SIX

EXPERIMENTAL INVESTIGATION OF THE CRYSTAL FIELD SPLITTING

6.1 Introduction

Inelastic Neutron Scattering experiments were carried out using two different spectrometers.

1. The Triple Axis Spectrometer (TAS) at the reactor Saphir at the Paul Scherrer Institute Switzerland.

2. The Time Focused Crystal Analyser Spectrometer (TFXA) at the Rutherford Laboratory Reactor (ISIS).

Three samples of composition Pd₂YbSn, Pd₂YbIn and Pd₂HoIn were investigated at the reactor Saphir on the triple axis spectrometer IN2. The spectrometer was operated in the neutron energy loss configuration with the energy of the scattered neutrons (EA) kept fixed at 14.96 meV. This gave rise to an energy resolution of 1 meV.

To gain intensity, the measurements were carried out using a double bent graphite monochromator as well as a horizontally bent graphite analyser, both with a (002) scattering planes. As a consequence no collimation was used between the neutron source and the detector. Beryllium or pyrolitic
graphite filters were inserted into the scattered neutron beam to reduce higher order contamination [1]. The samples were sealed under a Helium atmosphere in cylindrical Al containers. The samples were mounted in a dispelix which had a low temperature capability of about 10K. Constant Q scans were carried out at different temperatures ranging between 10K and 80K for scattering vectors Q, in the range $1.45 \text{ Å}^{-1} \leq |Q| \leq 3.5 \text{ Å}^{-1}$.

6.2 The Triple Axis Spectrometer (TAS)

A schematic diagram of the triple axis spectrometer is given in fig. (6.1). $\theta_m$ is the angle between the single crystal monochromator and the incident beam. A beam of neutrons with a wide range of wavelengths is incident onto the monochromator. Only the wavelengths which satisfy the Bragg conditions for the monochromator angle are scattered onto the sample. $\theta_A$ is the angle between the beam scattered by the sample and the analyser. The scattered beam of wavelength $\lambda_t$ is diffracted by the analyser through an angle of $2\theta_A$ into the detector.

The principle of operation of the TAS is a simple use of Bragg diffraction to define the scattered neutron energies. It is composed of three axis [2]. The first axis is a rotation of the monochromator crystal to select a particular wavelength ($\lambda_m$) of the neutrons incident on the specimen. The sample is located on the second axis and the neutrons are scattered by the sample through an angle of $\varphi$ with wavelength $\lambda_t$. An analysing crystal is fixed on this axis which leads to the analysis of the neutrons scattered in a given direction determined by the orientation $k_f$. After the analyser a detector is located on the final axis. The flexibility of the triple axis for its main purpose of inelastic
Fig (6.1): The basic configuration of Triple-Axis Spectrometer

Fig (6.2): A schematic diagram of the Triple-Axis Spectrometer
scattering lies in its ability to probe a chosen point in \((Q, \omega)\) space. An energy scan is performed by scanning either \(k_i\), keeping \(k_f\) fixed or \(k_f\), keeping \(k_i\) fixed (equation 4.1). \(Q\) is kept constant by adjusting the scattering angle at the sample position \(\phi\) and the crystal orientation with respect to \(k_i\) such that \(k_i - k_f\) is unchanged (equation 4.4)

### 6.3 The Time Focused Crystal Analyser Spectrometer

The time focused crystal analyser spectrometer (TFXA) is an indirect geometry time of flight inelastic scattering spectrometer, using a time-focused pyrolytic graphite analyser to achieve good counting rates combined with good energy resolution over a wide range of energy transfers. It is based on a time focused arrangement in which the sample and detector arrays are in the same plane, and the analysing crystal is set parallel to this plane. Fig. (6.3) illustrates the principle of the time focused analyser [3-5]. The crystal analyser spectrometer is situated on the ambient beam, N8, at a distance of 12 m from the ambient moderator of the pulsed source. Standard collimator design illuminates a sample area of 50(v)x25(h) mm². The layout of the spectrometer is shown in fig.(6.4).

Three samples were investigated namely Pd₂DyIn, Pd₂ErIn and Pd₂TbIn. The sample is positioned on the end of a rod (sample stick) in a cryostat. Two samples can be fixed on the sample holder at the same time and the whole tube is inserted inside the cryostat (known as an I.L.L orange cryostat) which is shown in fig. (6.5). The cryostat is designed for use in the temperature range~1.5 K to 313 K.
Fig (6.3): The principle of the Time Focussed Analyser

Fig (6.4): Time Focussed Crystal Analyser
Fig. (6.5) : Sectional view of the orange cryostat
6.4 The Inelastic Scattering Results

A. Pd$_2$Holn

Elastic Scans

For inelastic measurements of the crystal field levels care must be taken that these levels are not affected by Bragg reflections. For this purpose an elastic scan was carried out for each sample in the Q-range between 1.5 Å$^{-1}$ and 3.5 Å$^{-1}$. The scan for Pd$_2$Holn is shown in fig. (6.6).

Inelastic Scans

The measurements were performed on a powder sample of 30 gm using a TAS and within a temperature range of 10 - 80 K and for various scattering vectors in the range of 1.45 Å$^{-1}$ - 3.5 Å$^{-1}$. The spectra obtained indicate that two distinct crystal field excitations are observed at 3.0 meV and 6.3 meV fig. (6.7). Peaks at the right hand side of the elastic line, i.e. positive neutron energy transfers result from neutron energy loss process producing excitations. It was noted that the intensities for both transition energies decreased with increasing temperature as expected due to the depopulation of the crystal field ground state Fig. (6.8). For magnetic excitations it is expected that the intensity will decrease with increasing scattering vector in accordance with the square of the magnetic form factor F(Q) as given by equation (4.45). Fig (6.9) displays the variation of inelastic spectra lines at constant temperature, for different Q values. It may be seen that the intensity decreases as Q increases indicating that the scattering is magnetic in origin.
Fig. (6.6) : The Q-scan of Pd₂Ho₁n

The shaded peaks represent the reflections from sample holder (Aluminium)
Fig. (6.7): Crystal field splitting for Pd2HoIn

The measured values are indicated by crosses. The full line is the fit to the data. The lower line (dotted line) shows the contribution from the crystal field transitions.
Fig. (6.8) : Spectra of crystal field excitations for Pd₂HoIn at different temperature and constant Q-value (Q=1.45 Å⁻¹)
Fig. (6.9) : Spectra of crystal field excitations for Pd$_2$HoIn at constant temperature (T = 10 K) and different Q-values
Additional scattering is observed as a small shoulder being located close to the elastic line on the right hand side, see fig.(6.7). This contribution is attributed to chemical disorder in which some Ho atoms are located on Pd lattice sites. This assumption is supported by the investigation of compounds for which Ho is substituted by a transition metal such as \( \text{Pd}_2\text{MnIn} \) [6] where the degree of chemical order may be changed systematically by heat treatment [7]. In such a case the additional scattering may be interpreted as a consequence of crystal field transitions of Ho, but with a different level scheme to that shown in fig.(6.11). This explanation is consistent both with neutron and X-ray diffraction data figures (5.4) and (6.7).

**Determination of Crystal Field Parameters \( W, x \):**

Crystal field parameters may be determined from fitting a model to the experimental data. The energy dependence on \( x \) as calculated by Lea et al [8] allows to fit the energy values near \( x = 0.35 \), see fig. (6.10). A comparison of the observed intensities with the calculated transition probabilities shows that the best fit yields crystal field parameters of \( W = 0.0267 \) and \( x = 0.354 \). In this case the ground state is \( \Gamma_5^{(1)} \).

**The Crystal Field Level Scheme**

The crystal field level scheme for Ho\(^{3+}\) in \( \text{Pd}_2\text{HoIn} \) is shown in fig. (6.11). The observed inelastic peaks correspond to the \( \Gamma_3^{(1)} \rightarrow \Gamma_3^{(1)} \) transition at 3 meV and to the transition \( \Gamma_5^{(2)} \) at 6.3 meV. The total splitting of the system is determined to be 16 meV.
Fig. (6.10): Energy levels and their eigenvalues for Ho$^{3+}$ [8]. The value of x derived from the experimental data is also included.
Fig. (6.11): CEF level scheme for Ho$^{3+}$ in cubic Pd$_2$HoIn
B. Pd$_2$YbIn:

The Q-scan for Pd$_2$YbIn at the elastic setting of the TAS is shown in fig. (6.12) and the inelastic neutron spectra shown in fig.(6.13). According to LLW the ground state J-multiplet $^2F_{7/2}$ of Yb$^3$ is split by the cubic crystal field into two doublets $\Gamma_6$, $\Gamma_7$ and a quartet $\Gamma_8$. A single crystal field transition is observed experimentally only at 6.5 meV. The magnetic origin of this inelastic line is confirmed by the Q and T variation of the intensities. By a similar procedure as for the Ho compound the crystal field parameters were determined to be; $W = -0.7058$ and $x = -0.7758$. No other excitations were observed up to an energy transfer of 20 meV.

C. Pd$_2$YbSn

The elastic scan is shown in fig. (6.14) and the inelastic neutron measurements are presented in fig. (6.15). Only one excitation was observed at 3.5 meV. The observed intensity decreases with increasing temperature and scattering vector which indicates that the scattering is of magnetic origin.

The selection rules governing transitions between the levels in both compounds of Yb give rise to observable transitions between the quartet and each of the doublets. The transition matrix elements are independent of the crystal field parameters [9] and they are found to be comparable in magnitude amounting to 7.778 for the $\Gamma_8 \rightarrow \Gamma_6$ transition and 6.0 for the transition matrix element between $\Gamma_8$ and $\Gamma_7$. The matrix element for a transition between the doublets is equal to zero. Therefore two inelastic
Fig. (6.12): The Q-scan of Pd$_2$YIn
Fig. (6.13): The spectra of crystal field splittings for Pd₂YbIn

The measured values are indicated by crosses. The full line is the fit to the data. The lower line (dotted line) shows the contribution from the crystal field transitions.
Fig. (6.14) : The Q-scan of Pd$_2$YbSn

Intensity vs. $q$ (A$^{-1}$) plot.
Fig. (6.15): The spectra of crystal field splittings for Pd$_2$YbSn

The measured values are indicated by crosses. The full line is the fit to the data. The lower line (dotted line) shows the contribution from the crystal field transitions.
transitions may be expected, but only one transition was resolved. To understand this situation a closer inspection of the spectra reveals that the inelastic transitions are accidentally superimposed on top of one another. This means a range of \( W \) and \( x \) parameters are required for which either the ground state multiplet is a quartet with two doublets having an almost equal energy separation to the ground state or, alternatively, a configuration for which the order of the multiplets is reversed.

It is noticed that a substitution of In by Sn in the Heusler structure namely \( \text{Pd}_2\text{YbSn} \) results in a reduction in the overall splitting. This reduction in the overall energy of the splitting is related to the concentration of the conduction electrons as determined by either In or Sn. This will be discussed in detail later in this chapter.

**D. \( \text{Pd}_2\text{DyIn} \), \( \text{Pd}_2\text{ErIn} \) and \( \text{Pd}_2\text{TbIn} \)**

The neutron inelastic scattering experiments were performed on the systems \( \text{Pd}_2\text{DyIn} \) and \( \text{Pd}_2\text{ErIn} \) at ISIS. The experiment carried out on \( \text{Pd}_2\text{DyIn} \) proved inconclusive, due to the high absorption cross section of Dy. The data obtained from the measurements of \( \text{Pd}_2\text{DyIn} \) were then used as a background correction to be subtracted from the measurements on other compounds.

Inelastic neutron spectra for \( \text{Pd}_2\text{ErIn} \) are shown in fig. (6.16). The spectra exhibit two inelastic peaks at energy transfers of 6.6 meV and 11.8 meV at 4 K, which can be identified as crystal field transitions. Following the work of LLW [8], the crystal field splits the ground state multiplet \( 4f^{11}(^4I_{15/2}) \) into three
quartets $\Gamma_8^{(1)}, \Gamma_6^{(2)}, \Gamma_6^{(3)}$ and two doublets $\Gamma_6, \Gamma_7$. The overall energy splitting of the system is found to be 19.9 mev. The crystal field level scheme is shown in fig. (6.17). The variation of intensities with different temperature is shown in fig. (6.18) and (6.19). At 50 K a third transition is observed at 4 meV. The intensity of this peak increases as the temperature increases.

Neutron scattering investigation of Pd$_2$TbIn revealed no observable crystal field transitions. However, with the experimental set-up used crystal field transitions should have been observable as both absorption cross section of Tb and the overall crystal field splitting are comparable to that of Er compound. The absence of crystal field transition in Pd$_2$TbIn is therefore puzzling and further investigations are needed in order to illustrate that point.

6.5 Extrapolation of Crystal Field Parameters

The parameters of Pd$_2$ErIn are determined experimentally and are used to explore the behaviour of CF parameters for other members of the series using the following extrapolation scheme [8].

$$W'(x') = \left[ \frac{\alpha'_s F'(4)}{\alpha_s F(4)} \right] W_x$$  \hspace{1cm} \text{(6.1)}

$$W'(1-|x'|) = \left[ \frac{\alpha'_s F'(6)}{\alpha_s F(6)} \right] W(1-|x|)$$  \hspace{1cm} \text{(6.2)}
Fig. (6.16): The spectra of crystal field splittings for Pd$_2$ErIn

Fig. (6.17): CEF level scheme for Er$^{3+}$ in cubic Pd$_2$ErIn
Fig. (6.18): The variation of the inelastic scattering intensities with temperature for Pd$_2$ErIn
Fig. (6.19) : The variation of the inelastic scattering intensities with temperature for Pd$_2$ErIn
where \( W', \alpha' \) represent the scaled parameters for a different rare earth of the series with

\[
\alpha_4 = \theta_4 \left< r^4 \right>, \\
\alpha_6 = \theta_6 \left< r^6 \right>
\]

\( \theta_4, \theta_6 \) are the Stevens multiplicative factors, and \( \left< r^4 \right>, \left< r^6 \right> \) are the relativistic radial integrals of the 4f electrons as given in table (3.1) as well as with the multiplicative factors and values of \( F(4) \) and \( F(6) \) for different rare-earth elements. The calculation for the scaled crystal field parameters of \( \text{Pd}_2\text{ErIn} \) are given in table (6.1).

6.6 Comparison of Crystal Field Parameters of \( \text{Pd}_2\text{ReIn} \) and \( \text{Pd}_2\text{ReSn} \)

The crystal field parameters of the two isostructural series \( \text{Pd}_2\text{ReIn} \) and \( \text{Pd}_2\text{ReSn} \) are compared. It is observed experimentally that the crystal field parameters in both groups exhibit scaling properties. The crystal field splitting of \( \text{Pd}_2\text{HoSn} \) and \( \text{Pd}_2\text{ErSn} \) has been determined by Li et. al.[7]. The comparison of the crystal field splitting in both groups of In and Sn compounds indicated no significant alteration in the order of the crystal field splitting or their relative separation by an exchange of the third element of In for Sn. An overall change in energy scale of the crystal field level scheme is observed in the Yb compounds. This behaviour may be understood on the basis that the scaling of crystal field parameters is correlated with the concentration of conduction electrons as determined by In or Sn. Within the compound the rare earth atom is located at the centre of a cube surrounded
by 8 Pd atoms as nearest neighbours located at the corners of the cube. The Pd atoms are the source of the crystal field potential which causes the splitting. The In or Sn atoms are the next nearest neighbours to the rare earth atom and they have negligible direct influence on the magnitude of the matrix elements which determine the crystal field splitting. A substitution of In by Sn will increase the number of conduction electrons. These additional conduction electrons are more delocalised and influence the charge located on the Pd atoms. This screening leads to a reduction of the effective charge on the Pd atoms, the result of which is a reduction of the overall crystal field splitting on going from the In to the Sn compound. The comparison between the crystal field parameters and overall energy splitting is presented in table (6.2).

Table (6.1): Scaled crystal field parameters using experimental parameters of Pd$_2$ErIn

<table>
<thead>
<tr>
<th>Rare earths</th>
<th>$\alpha'^{\prime}_4 F^{(4)} / \alpha_4 F^{(4)}$</th>
<th>$\alpha'^{\prime}_6 F^{(6)} / \alpha_6 F^{(6)}$</th>
<th>W</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>3.5857078</td>
<td>-0.420284</td>
<td>0.0713</td>
<td>-0.824</td>
</tr>
<tr>
<td>Dy</td>
<td>-1.579828</td>
<td>0.627639</td>
<td>0.0446</td>
<td>-0.580</td>
</tr>
<tr>
<td>Ho</td>
<td>-.0814043</td>
<td>-0.69768</td>
<td>0.0341</td>
<td>0.3904</td>
</tr>
<tr>
<td>Er</td>
<td>1</td>
<td>1</td>
<td>0.0267*</td>
<td>0.3543*</td>
</tr>
<tr>
<td>Tm</td>
<td>3.3986409</td>
<td>-1.33069</td>
<td>-0.0462*</td>
<td>0.3544*</td>
</tr>
<tr>
<td>Yb</td>
<td>-33.43736</td>
<td>5.304529</td>
<td>-0.7058</td>
<td>-0.776</td>
</tr>
</tbody>
</table>

* Experimental parameters

136
Table (6.2) Comparison of crystal field parameters between the isostructural series \( \text{Pd}_2\text{ReIn} \) and \( \text{Pd}_2\text{ReSn} \)

<table>
<thead>
<tr>
<th>Re</th>
<th>( \text{Pd}_2\text{ReIn} )</th>
<th>OES</th>
<th>( \text{Pd}_2\text{ReSn} )</th>
<th>ref.</th>
<th>( \text{Pd}_2\text{ReSn} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>0.0713</td>
<td>-0.824</td>
<td>14.8</td>
<td>0.053</td>
<td>-0.785</td>
</tr>
<tr>
<td>Dy</td>
<td>-0.0446</td>
<td>-0.5801</td>
<td>16.0</td>
<td>-0.036</td>
<td>-0.509</td>
</tr>
<tr>
<td>Ho</td>
<td>0.0341</td>
<td>0.3904</td>
<td>19.9</td>
<td>0.0287</td>
<td>0.3248</td>
</tr>
<tr>
<td>Er</td>
<td>-0.0461</td>
<td>0.3544</td>
<td>19.9</td>
<td>-0.040</td>
<td>0.292</td>
</tr>
<tr>
<td>Tm</td>
<td>-0.0953</td>
<td>-0.5837</td>
<td>15.9</td>
<td>0.076</td>
<td>-0.513</td>
</tr>
<tr>
<td>Yb</td>
<td>-0.7058</td>
<td>-0.7758</td>
<td>18.8</td>
<td>-0.530</td>
<td>-0.722</td>
</tr>
</tbody>
</table>

OES = overall energy splitting in meV.

**6.7 Calculation of the Magnetic Susceptibility and Magnetisation in Rare Earth Alloys**

The information on crystal field level schemes in these compounds can be used to understand the magnetic properties as obtained from magnetisation or magnetic susceptibility as a function of temperature.

For the calculation of either \( \chi \) or \( M(H) \) the important interactions are the Zeeman term due to the external magnetic field effect \( H \) and the crystal field contributions. The combined effect of the crystal field and the Zeeman interaction will be taken into account in the calculation of the magnetisation.

The interaction between magnetic moments will not be included in these calculations for the following reason: no magnetic ordering has been observed experimentally for temperatures above 2K. This implies that magnetic interactions between rare earth atoms are weak. Furthermore the paramagnetic Curie temperature as given in table (5.2) are low thus
supporting the notion of a weak magnetic coupling between magnetic moments [11,12].

The crystal field Hamiltonian has matrix elements of the form:

$$H_{cf} = \sum_{m_p m_r} a_{m_p}^* a_{m_r} \langle J, m'_j | V_q | J, m_j \rangle$$

The energy levels (eigenvalues) $E_v$ and eigenfunctions can be calculated by a diagonalization of the matrix given by equation (6.3). The eigenfunction can be given in the form:

$$|v> = \sum_{m=J}^J a_m^{(v)} |J, m>$$

The contribution of the magnetic field is included by choosing $H$ along the $Z$-axis. Within the basis $|J, m_j>$, this can be given as:

$$\langle J, m_j | H_B | J, m'_j \rangle = \langle J, m_j | g \mu_B J_z | J, m'_j \rangle = \langle J, m_j | g \mu_B m'_j | J, m'_j \rangle = g \mu_B m_j \delta_{m_j, m'}$$

The full matrix for the Hamiltonian including the crystal field and the external magnetic contribution is used for calculating the eigenvectors and eigenvalues of the crystal field matrix. Thus for a given eigenstate of the CF Hamiltonian the magnetic moment has the following form:
The energy levels $E_v'$ can be expanded in terms of the small parameter $H$, as:

$$E_v' = E_v^0 + H E_v^{(1)} + H^2 E_v^{(2)} + \ldots \quad \text{(6.7)}$$

$v$ is associated with the energy states in zero field ($H=0$), and $i$ is used to distinguish the levels which have the same energy when $H=0$. This leads to first and second order corrections to the energies given by:

$$E_v^{(1)} = -g\mu_B \langle v | J_z | v \rangle$$

$$E_v^{(2)} = -g^2\mu_B^2 \sum_{E_v' \neq E_v} \frac{\langle v | J_z | v' \rangle^2}{E_v' - E_v} \quad \text{(6.8)}$$

These values are used to calculate the magnetic susceptibility of $N$ atoms at a finite temperature $T$, and it is given by:

$$\chi = -\frac{N}{k_B T} \sum_v \frac{\partial E_v}{\partial H} e^{-\beta E_v / H} \quad \text{(6.9)}$$

By using equations (6.7) and eq.(6.8), the susceptibility takes the form:

$$\chi = -\frac{N}{k_B T} \sum_v \frac{[(E_v^{(1)})^2 - E_v^{(2)}]}{P_v} \quad \text{(6.10)}$$
where $P_v$ is the population probability and is defined by:

$$P_v = \frac{e^{-E_v/kT}}{\sum_v e^{-E_v/kT}} \tag{6.11}$$

In order to obtain the magnetisation, the matrix elements of $\langle J, m_I|H_{cf} + H_z|J, m'_I \rangle$ are diagonalized for each value of the magnetic field $H$. Having obtain the eigenvalues and the eigenfunctions the magnetic moment may be calculated according to:

$$m_v = \langle \nu|g\mu_B J_z|\nu \rangle \tag{6.12}$$

and the total magnetic moment will be:

$$m = \sum_v m_v P_v \tag{6.13}$$

The calculations were performed using a computer program. The program calculates the magnetisation for different magnetic fields and the susceptibility at different temperatures. The crystal field parameters in terms of $W$ and $x$ have been obtained experimentally from inelastic neutron scattering measurements of Pd$_2$ErIn and are used in the calculation of the magnetisation at different magnetic fields.
Magnetisation Calculation on Powder Samples

The magnetisation measurements reported here have been carried out on powder samples. In general for a single crystal the magnetisation will depend on the orientation of the externally applied magnetic field with respect to the crystallographic axis. For a powder the crystallites are oriented randomly, and consequently in order to obtain the magnetisation for a powder sample the magnetic moment has to be calculated for all directions of the external field with respect to the crystallographic axis and the average has to be carried out. This average is a spherical average which requires a large number of magnetisation with different orientations to be calculated for each value of the applied magnetic field. Thus the whole process is very time consuming and it requires a large number of magnetisation calculations.

However, the demands on the required number of different magnetisation to be calculated for the average can be cut down to a manageable number by realising that the magnetisation in a single crystal is restricted by symmetry. In the Heusler compounds of interest here there is only one magnetic atom. Its magnetisation is determined by its site symmetry. As a consequence the macroscopic magnetisation also reflects this symmetry. With the crystal field Hamiltonian as given in equation (6.3) the macroscopic magnetic moment for a magnetic field applied in the direction \( \mathbf{r} \) written as:

\[
M(\mathbf{r}) = M_0 + M_A \left[ A_4 Y_4^0(\theta,\phi) + A_4 Y_4^4(\theta,\phi) \right] + M_6 \left[ A_6 Y_6^0(\theta,\phi) + A_6 Y_6^4(\theta,\phi) \right] \quad (6.13)
\]

where \( Y(\theta,\phi) \) are the spherical harmonics. The value \( M_0 \) is the average magnetic moment with spherical symmetry, while \( M_A \) and \( M_6 \) are those
contributions which vary with the angles $\theta$ and $\varphi$. The equation has three parameters, and thus it suffices to calculate the magnetisation for three different directions within a single crystal and to use matrix inversion in order to obtain the $M$ coefficients as shown in fig. (6.20). This is achieved by choosing for example the (001), (110), and (111) directions resulting in:

$$
\begin{align*}
M_{00} &= M_0 + M_1 C_{12} + M_2 C_{13} \\
M_{11} &= M_0 + M_1 C_{12} + M_2 C_{23} \\
M_{111} &= M_0 + M_1 C_{12} + M_2 C_{33}
\end{align*}
\quad \text{-------(6.14)}
$$

The coefficients $c_{ij},...,c_{33}$ are determined by the geometrical parameters as given by the orientations (001), (110) and (111). This equation may be inverted yielding:

$$
\begin{pmatrix}
M_0 \\
M_1 \\
M_2
\end{pmatrix} = \begin{pmatrix}
1 & C_{12} & C_{13} \\
1 & C_{22} & C_{23} \\
1 & C_{32} & C_{33}
\end{pmatrix}^{-1} \begin{pmatrix}
M_{00} \\
M_{11} \\
M_{111}
\end{pmatrix}
\quad \text{----------(6.15)}
$$

The value $M_0$ is the average value as determined in powder measurements.

6.8 Discussion of the Magnetisation Results

The experimental parameters $W$, and $x$ of the crystal field measurements for Pd$_2$ErIn were used to calculate the magnetisation as a function of applied magnetic field. The experimental measurements were carried out using a SQUID magnetometer. The theoretical and experimental magnetic isotherms are plotted in fig.(6.21), where the calculated magnetisation is represented by the solid line. It can be seen that theoretical calculations are close to the experimental results at temperatures of 50 K, 100 K and 200 K. The
deviation from the experimental results increases with decreasing temperatures. This deviation between the theoretical and experimental results is attributed to the effect of the interactions between magnetic moments. The effect is clearly visible at low temperatures.

The experimental crystal field parameters of Pd$_2$ErIn have been used to obtain the W, x parameters for other member of the series. The scaled parameters are used in the calculation of the magnetisation as a function of magnetic field. The calculations indicate good overall agreement of the theoretical M-H plots with the experimental results as shown in fig. (6.22) for Pd$_2$HoIn and in fig.(6.23) for Pd$_2$YbIn. This agreement as seen in the different compounds of Pd$_2$ReIn breaks down at temperatures less than 10 K.
Fig. (6.20): Calculated magnetisation of single crystal Pd$_2$HoIn in (001), (110) and (001) crystallographic orientations
Fig. (6.21): The magnetic isotherms of Pd$_2$ErIn. The crosses are the experimental values.
Fig. (6.22) : The magnetic isotherms of Pd\textsubscript{2}HoIn. The crosses are the experimental values.
Fig. (6.23) : The magnetic isotherms of Pd$_2$YbIn. The crosses are the experimental values.
References


CHAPTER SEVEN

Summary and Conclusion

This thesis is concerned with the experimental investigation of the magnetic properties of rare earth Heusler alloys of the form Pd$_2$ReIn, where Re = Ho, Dy, Er, Tb, and Yb. The systems may be envisaged in terms of magnetic moments localised on the 4f shell of the rare earth atoms, with various forces acting between these moments. The alloys based on the composition Pd$_2$ReIn and Pd$_2$ReSn are metallic systems in which the magnetic properties are determined by the rare earth atoms.

The structural characterisation of all compounds was carried out using X-ray diffraction which indicated that all samples formed in the cubic Heusler structure with space group $\overline{Fm\overline{3}m}$. The X-ray spectra for all samples were shown in chapter 5 and revealed phase impurities in some of these samples as were observed in Pd$_2$HoIn and Pd$_2$ErIn and Pd$_2$YbIn. This impurity contribution has no significant effect on the magnetic properties except the extra inelastic scattering which was observed in Pd$_2$HoIn near the elastic line.

The possibility of magnetic ordering at low temperature was initially investigated by the measurement of the magnetic susceptibility in the temperature range between room temperature and 2K as discussed in chapter 5. No magnetic phase transitions were observed for any of the compounds investigated. The inverse susceptibility versus temperature
indicated Curie-Weiss behaviour with a small Curie-Weiss temperature (\( \theta_p = -2.65 \) K for \( \text{Pd}_2\text{Holn} \), \( -2.34 \) K for \( \text{Pd}_2\text{Erln} \) compound and \( -6.749 \) K for \( \text{Pd}_2\text{Ybln} \)). The paramagnetic Curie temperature is a measure of the strength of magnetic interactions between rare earth atoms and magnetic moments. For all compounds investigated here the interactions are found to be weak.

Inelastic neutron scattering experiments were carried out and the results have been presented in chapter 6. Crystal field transitions were observed in the compounds \( \text{Pd}_2\text{Holn} \), \( \text{Pd}_2\text{Erln} \), \( \text{Pd}_2\text{Ybln} \) and \( \text{Pd}_2\text{YbSn} \). The fit of crystal field parameters to the inelastic neutron spectra allowed a systematic study of selected members of the series. A simple 'point charge model' may be invoked for understanding the systematics in the crystal field level scheme. The crystal field level scheme was interpolated to obtain the crystal field parameters for other compounds in the series.

The crystal field parameters of the series \( \text{Pd}_2\text{ReIn} \) were compared with those of the isostructural series \( \text{Pd}_2\text{ReSn} \). The comparison revealed that the crystal field level scheme is not significantly altered by a substitution of the third element In (or Sn). However a reduction in the overall crystal field splitting was observed for the Yb compounds. This reduction is ascribed to the change in the number of the conduction electrons without a change of the nearest neighbour environment of the rare earth atom. The substitution of In by Sn will increase the number of conduction electrons by one. For free atoms Sn has two 5p electrons compared to one for In. Taking into account that the 5f wavefunctions are more extended than the 4f wave functions and locating the Sn atom within a metallic alloy it is to be expected that the additional electron is delocalised. While having to screen the additional nuclear charge on the Sn lattice site the large spread of the 5p-electronic wavefunction will alter the effective charge on the Pd atoms leading to a reduction in its value for the Sn.
compound compared to In. This interpretation is valid within a simple point charge model for the crystal field splitting. As indicated in chapter 3 the crystal field splitting in a metallic compound is also due to hybridisation of the 4f wavefunction with conduction electrons. However it may serve to simplify the picture of understanding the systematics of the crystal field schemes in the alloys of interest.

The crystal field parameters determined in the present thesis are used to model magnetisation measurements. The model parameters include the external magnetic field as well as the crystal field parameters as obtained from the neutron scattering experiments. The magnetic moment was self consistently iterated for each value of the external magnetic field with respect to the crystallographic axis as explained in chapter 6. Thereafter a powder average was carried out for each value of the external magnetic field, assuming that the induced magnetic field is always parallel to the external magnetic field direction a good description was obtained for the magnetisation both as a function of applied magnetic field and temperature. Deviations in the calculations from the experimental magnetic isotherms were apparent at low temperatures, where the magnetic correlations become increasingly important. As indicated above the magnetic interactions are found to be weak due to the low values of paramagnetic Curie-Weiss temperature and due to the absence of magnetic order down to a temperatures of 2K.

Suggestions for Future Work

Further experiments are recommended to observe the possibility of magnetic order below 2 K. For this purpose neutron diffraction experiments have to be performed to confirm the nature and structure of the magnetic order at low temperatures.
As discussed before, previous investigations of \( \text{Pd}_2\text{ReSn} \) samples indicated that some alloys become superconducting at temperatures below 2 K. It would therefore be extremely interesting to investigate these samples by measuring electrical resistivity in a temperature range extending down to 2 K. In addition to resistivity measurements specific heat measurements would add further information and insight and provide a valuable test of the crystal field parameters as determined here.

The measurements presented here enabled the crystal field splitting to be established. It is suggested that the inelastic scattering experiment on \( \text{Pd}_2\text{DyIn} \) be repeated. In doing so it will be necessary to choose neutrons of a wavelength which is not so highly absorbed by Dy or by choosing an isotopically enriched sample.