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An experimental investigation of the lattice-magnetism interactions in rare earth and transition metal compounds.

By
Jonathan William Taylor

A Doctoral Thesis.

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

December 1999.

For Emma, with love.
The nature of the physical world seems elegantly simple within a first approximation, however as one investigates further subtle complexities arise, which always tend to “complicate matters”.

“Nature has a simplicity and therefore a great beauty”

R. P. Feynman.

The purpose of fundamental research is to investigate these complexities and to somehow explain them. The subject of magnetism is a prime example of this ethos, it would appear that magnets still adhere themselves to pieces of iron, however the reasons why this should occur are not as simple as the effect itself, furthermore the effect will still be present whether or not anyone understands it!! One must therefore ask the question as to why anyone would spend time trying to understand the effect, the answer is as the mountain climber retorts, because it is there. This is driving force behind science, and has been since the time of the ancients. Modern science brings modern techniques, modern theories, but the underlying reason why research is done is the same as it ever was.

The subject of this thesis is the interaction between the magnetic system of a material and the nuclear lattice, and indeed it is an example of a “subtle complexity”.

J. W. Taylor December 1999
Abstract.

The interaction between magnetism and the nuclear lattice is investigated experimentally, using thermal expansion, magnetostriction, specific heat, magnetisation and neutron scattering measurements. Both localised moment systems, as represented by the rare earth compounds Tb$_2$AgIn, Pd$_2$GdIn and Cu$_2$GdIn, as well as transition metal compounds, Ni$_2$MnGa and V$_2$O$_3$ have been characterised at low temperatures. Measurements of the lattice properties are important due to the intrinsic coupling of magnetic degrees of freedom to them. The response of the lattice to magnetic order, and also to applied magnetic fields have been probed by the use of the aforementioned techniques. Such techniques allow the direct determination of the coefficient of linear thermal expansion, over a wide temperature range and the forced magnetostriction in applied fields of 0 to 7T. Indirect determination of the spontaneous magnetostriction and the total magnetic entropy contribution via measurements of isostructural compounds further enhance the range of experimental data available. The dynamic properties are characterised by spin polarised neutron scattering measurements.

The experimental results are presented and discussed. Various methods of coupling lattice and electronic degrees of freedom have been investigated. It is argued that in order to fully understand and appreciate the low temperature properties of the materials investigated such a coupling must be taken into account.
Acknowledgements.

Experimental scientific research is not a subject one can perform without a great deal of assistance. Furthermore it is important that one enjoys oneself from time to time when working, I would therefore like to express my sincerest thanks and gratitude to all those that have given their help, knowledge and time to me during my time at Loughborough.

I would especially like to thank the following people for their continual help and assistance over the three years of this project.

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Special thanks must go to Mr Bryan Dennis, without his technical assistance, enthusiasm and good nature working in the lab would not have been as enjoyable, nor would it have been as productive.

I would also like to thank all the other members of the technical division at the department of Physics in particular Mr John Oakley who constructed the dilatometer cell and Mr D. Insley who constructed the high temperature system, and have both subscribed to the “I need it as of yesterday” nature of experimental research. Thanks also to Mr “Chas” Chavda for help in the second year lab. Thanks also to my fellow research students, Tim, Frank, Harj, Mark and Irena in the condensed matter group for making my time at Loughborough enjoyable.

My sincerest thanks and love go to Emma for putting up with living with a Physicist, and not complaining about the mess!

Lastly, and by no means least thanks to my parents Jill and Allan for their continual support and encouragement.
List of Publications.

The work presented in this thesis is included in the following publications:

*Spin spin correlations in the insulting and metallic phases of the Mott system $V_2O_3$.*
J.W. Taylor et al., 1999, In press European Journal of Physics,

*Thermal Expansion and Magnetostriction in an Anomalous Gd Intermetallic Compound.*

*Renormalisation of the Neel temperature of a localised metallic antiferromagnet under the influence of an external field.*
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Chapter 1. Introduction.

Modern physics has a vast range of experimental techniques which one may apply to a system in order to try to understand the mechanisms that give rise to the observed properties. It is therefore important that one measures the basic properties of a system completely and with some accuracy. In so doing one may develop an understanding as to what the important physical processes are.

In the ever increasing topic of magnetism, basic research is generally always used to characterise a system before one uses more exotic experimentation to attempt to describe the pertinent mechanisms. However one should not forget that a great deal of important information may be revealed by performing detailed basic research.

The nature of the interaction between the magnetic system and the lattice of a material is of interest since there must exist a coupling between the two in order that one may observe phenomenon such as magnetostriction. The mechanisms of the magnetic interaction with the lattice are non-trivial, it is therefore necessary to develop methods that allow one to probe the interplay and quantify it.

Although the effect of the magnetic system can be observed in many measurements, such as specific heat, resistivity etc. the measurement of the lattice response directly is the measurement that is of the most use. To this end one must either perform a diffraction experiment, or use a dilatometer, the latter can provide much higher resolution and allow greater range in temperature and applied field.
The work presented in this thesis demonstrate that the coupling of the magnetic and lattice degrees of freedom are directly measurable and of interest scientifically. The lattice response of materials have been investigated as a function of temperature and applied field using the technique of high resolution capacitance dilatometry and high resolution neutron powder diffraction.

The technique of capacitance dilatometry affords the greatest resolution in the measurement of dilation, furthermore the technique is easily applied to the measurement of thermal expansion and magnetostriction and to both high and low temperature regimes. It is these reasons that promoted the development, construction and optimisation of the two separate dilatometer systems that are described later in this work.

In elemental form there exist only a small number of metals which exhibit magnetic order. The magnetism is a result of partially filled electron shells. The two groups of elements that exhibit magnetic order as different as the underlying physics that describes the order. The 3d transition metals Fe, Ni, Co and Mn are all itinerant systems, the partially filled electron shells are delocalised and participate in the Fermi surface of the material. Materials containing these elements generally exhibit similar magnetic properties, that is to say that Ni is a ferromagnetic at room temperature as is the alloy Ni$_2$MnGa, although the Curie temperature is dramatically reduced. Materials containing rare earth atoms exhibit interesting magnetic properties. The 4f electron shells that carry the magnetic moment are well shielded by the outer orbitals, therefore the rare earth group represent elemental local moment systems. The rare earth elements are easily alloyed a property which is of some use as the magnetic properties of the end material are generally very different from the initial elements, i.e. Gd is a localised ferromagnet but the alloy Pd$_2$GdIn is a low temperature localised antiferromagnet.
Chapter 1. Introduction.

The magnetic properties of the 4f group is summarised in Fig. 1.1.

![Graph](image)

*Fig. 1.1. The magnetism of the rare earth group for the RE$^{3+}$ ions.*

The results presented later in this work focus on metals containing rare earth and transition metal magnetic atoms. The low temperature magnetic and lattice properties of the rare earth Heusler alloys; Pd$_2$GdIn; Cu$_2$GdIn; Tb$_2$AgIn have been investigated using the technique of capacitance dilatometry. The magnetic structure of Tb$_2$AgIn has been investigated using powder neutron diffraction. These materials all exhibit interesting low temperature magnetic phases, which show an appreciable lattice response to an external applied magnetic field, implying that the magnetic system is strongly coupled to the lattice.
Another interesting aspect of the coupling of the magnetic and lattice degrees of freedom is the effect that a large instantaneous lattice deformation has on the magnetic order. The result of such a deformation usually has a large impact on the magnetism of the material. The effect of large spontaneous lattice deformations have been investigated on two materials, the shape memory alloy Ni$_2$MnGa and the oxide V$_2$O$_3$ which exhibits the metal insulator transition, the magnetic correlations in the high temperature phase of V$_2$O$_3$ have been investigated using spin polarised neutron scattering. The results of these investigations again show the importance of the lattice magnetism interaction.

The structure of the thesis will now be presented.

The theory required to describe both the lattice and the magnetic system as a function of temperature is discussed in Chapter 2. The volume expansion of a material is described using a thermodynamic approach, it is shown that the volume expansion that a material exhibits is a function of the free energy. It is shown that the volume expansion arises due to the anharmonicity of the crystal lattice. The quasiharmonic approach is used to describe a quantitative method of determining the Grüneisen parameter the measure of lattice anharmonicity. This approach is expanded to allow one to define a magnetic and electron Grüneisen parameter.

The physical reasons behind magnetism are discussed. The magnetic moment as a function of temperature is described using mean field approach for both ferro and antiferromagnetic systems. The physical reasons underpinning the coupling of the magnetic and lattice degrees of freedom is discussed, for both localised and itinerant electron systems. A quantitative explanation of the volume and forced magnetostriction for both cases is presented.
Chapter I. Introduction.

The development, construction and operation of the two high resolution capacitance dilatometers is discussed in Chapter 3. A review of techniques used for the determination of the thermal expansion of a material is presented. The technique of high resolution capacitance dilatometry is discussed in detail. The construction, operation and data analysis techniques are described for the two automated dilatometers, these being a low temperature device 1.5K<T<300K with a 7T superconducting solenoid, and a high temperature device 300K<T<850K.

A short discussion of neutron diffraction and spin polarised neutron scattering is presented in Chapter 4. Together with a discussion of the two neutron instruments used for this work. These being the high resolution neutron diffractometer D2B (ILL Grenoble France) and the TOF spin polarised neutron spectrometer D7 (ILL Grenoble France).

The remainder of the thesis is devoted to the presentation of results gained using the low and high temperature dilatometer systems, detailed magnetisation measurements, and neutron investigations. In the interest of brevity the discussion of results/conclusions is presented at the end of each of the results chapters.

The results presented in this work are summarised as follows:-

Chapter 5:- investigations of the ferromagnetic shape memory alloy Ni$_2$MnGa.

Chapter 6:- Investigations of the rare earth localised antiferromagnet Tb$_2$AgIn and the rare earth paramagnet Lu$_2$AgIn .

Chapter 7:- Investigations of the rare earth localised antiferromagnets Pd$_2$GdIn and Cu$_2$GdIn and the paramagnet Pd$_2$LuIn.

Chapter 8:- Investigation of the metal-insulator transition system V$_2$O$_3$. 

5
Chapter 2. Theoretical review.

2.1. Introduction.

The nature of this thesis is the investigation of the influence of magnetism on the lattice dynamics of materials. If a magnetic subsystem is sufficiently coupled to the lattice of a material, one may expect that a change in the magnetic system will influence the lattice. Such an effect will more than likely result in the lattice system becoming strained. If this is the case then the influence may be measured experimentally. One must not neglect the nature of thermally induced lattice strains i.e. thermal expansion, since the variation of the system temperature is known to cause a profound effect on not only the lattice, but also the magnetism of materials.

One may investigate a number of variables relating to the strain of a material, these being:

1. Thermal expansion.
2. Forced magnetostriction.
3. Spontaneous magnetostriction.

In order that one may understand and interpret the experimental results produced by the investigation of the above mentioned variables, one must consider the theoretical aspects of the system in question.

It is obvious that a clear understanding of the origin of magnetism of materials is required. Further one must understand the nature of thermal expansion in materials. In order for such an understanding to develop one must investigate the thermal properties of the lattice system, and thus the physical origin of thermal expansion.
One should note that although the thermodynamical, and quantum theories pertaining to the phenomenon of thermal expansion have been known since the early part of the 1900's, precise calculations i.e. first principle calculations, of thermal expansion for real materials have only recently been completed [1,2]. These calculations have only been undertaken for relatively simple systems. This illustrates the poignant fact that the nature of thermal expansion in real systems is non-trivial.

Efforts to describe the magnetostriction (and other magnetically driven phenomena e.g. GMR and CMR) in materials is currently a very active research topic, especially since the discovery of materials exhibiting the phenomenon of giant magnetostriction.

This chapter is structured as follows:

1. The theory required to describe the phenomenon of thermal expansion. The phenomenological explanation for thermal expansion will be presented, i.e. the necessity of the anharmonic crystal potential. The thermodynamical relationships for the bulk will be presented. A definition of strain will be given, in order to appreciate the possibility of isotropic or anisotropic thermal expansion effects.

2. The theories required to describe magnetism. The behaviour of both local moment and itinerant electron systems will be discussed. Further the phenomena of magnetic ordering and transitions will be investigated, in order that one may understand the effects of both temperature and applied field on the magnetic structure and properties of materials.

In particular the magnetism of the 4f group and the transition metals will be discussed, since the alloys of these two groups are the subject of the experiments performed for this work.
3. The response of the crystal lattice to magnetism will be discussed, in order that one may understand the origins of both spontaneous and forced magnetostriction.

4. Several theories, that attempt to explain the aforementioned physical effects will be discussed. Predictions of Stoner theory, and the theory of spin fluctuations will be evaluated, with respect to spontaneous magnetostriction.
2.2. A phenomenological explanation of thermal expansion.

The subject of thermal expansion is one which is difficult to discuss in isolation, as it is closely related to other thermodynamic / physical properties Fig. 2.1.

For a full thermodynamic explanation of thermal expansion one must consider other effects / properties of the material. These properties include the following:-

The specific heat of the material, either taken to be at constant volume $C_v$ or constant pressure $C_p$.

The compressibility of the material, either isothermal $\chi_T$, or adiabatic $\chi_s$.

---

*Fig. 2.1. The interrelationship between, Temperature (T), Stress ($\sigma$), Strain ($\varepsilon$), Entropy (S), Magnetisation (M) and Magnetic Field (H) [3]*
2.3. Thermodynamic Interpretation of volume expansion. Chapter 2. Theoretical review.

One may, however, explain the origins of thermal expansion within a phenomenological framework. Such an explanation is sufficient to determine the nature of thermal expansion, and further, to illustrate that thermal expansion is a direct consequence of the anharmonic nature of the potential in which the atoms reside. Such a discussion considers only the vibrations of atoms in the solid.

One may consider a simple ionic cubic crystal, as shown in Fig. 2.2. The constituent atoms of the system are shown at their equilibrium positions. It is clear that the atoms are free to vibrate. Such vibration will occur about the mean atomic position within the lattice. Further one may assume that as the temperature of the system is raised from $T_1$ to $T_2$ the internal energy of the system is increased. The net effect of such an increase in the internal energy of the system will be to increase the amplitude of the atomic vibrations.

![Fig. 2.2. The arrangement of atoms in a primitive cubic unit cell.](image-url)
The effect of the increase in the amplitude of the atomic vibrations is an increase of the mean separation of the atoms. From Fig. 2.3, one can see that the amplitude \( a \) is given by:

\[ a = \frac{(C-x)}{2} \]

where \( C \) is the nuclear separation of atoms taken at their mean positions, i.e. \( C \) represents the static lattice constant and \( x \) is a constant.

\[ \begin{array}{c}
\text{\( C \)}} \\
\text{\( X \)}}
\end{array} \]

\[ \begin{array}{cccc}
\text{\( T_1 \)}} \\
\text{\( T_2 \)}}
\end{array} \]

**Fig. 2.3.** Schematic representation of a chain of atoms at \( T_1 \) and \( T_2 \) illustrating the increase in atomic separation, and the increase of atomic vibration amplitudes due to an increase in temperature.

One may express the potential energy of the assembly of atoms as a function of the displacement from the equilibrium position of the atom.

\[ v = f(a) \]  \hspace{1cm} (2.1)

One may therefore express the potential energy as a series expansion thus:

\[ v = n_1a + n_2a^2 + n_3a^3 + \ldots \ldots \ldots \]  \hspace{1cm} (2.2)

Where \( n_1, n_2, n_3 \ldots \) are constants. If the restoring force at zero displacement is zero then \( n_1 \) must be zero. Further a term that is linear in \( a \) would cause the system to be unstable, thus one obtains:

\[ v = n_2a^2 + n_3a^3 + \ldots \ldots \ldots \]  \hspace{1cm} (2.3)

If all coefficients above \( n_2 \) were zero, the equation would reduce to:

\[ v = n_2a^2 \]  \hspace{1cm} (2.4)
This situation corresponds to the simple harmonic oscillation of the atom about the equilibrium position. For this case the potential energy of the atom is equal to the square of the displacement from the equilibrium position. This condition is called the *harmonic approximation* with the term $n_2$ being positive in order to produce a stable crystal lattice. A crystal lattice described by the harmonic approximation would exhibit no thermal expansion as a function of temperature. The term $n_3$ (the first anharmonic term) accounts for the repulsion of atoms as they approach one another, and is therefore negative.

![Graph](image)

**Fig. 2.4.** Schematic representation of the potential energy $V$ as a function of ion separation $r$. The components due to Coulomb interaction and effective atom repulsion are also shown.

Thus in order to allow thermal expansion as a function of temperature one must include the anharmonic terms in the potential energy of the atoms. Therefore one may state that the thermal expansion is a direct consequence of the anharmonic nature of the atomic potential.

One may determine the approximate nature of the thermal expansion as a function of temperature.
At low temperatures the energy of the system is a minimum. Thus one may neglect the anharmonic terms in the energy expansion, and the lattice will exhibit zero thermal expansion as $T \to 0\text{K}$, since the separation remains equal to $a$. At higher temperatures, the anharmonic terms cannot be neglected. The motion of the atoms, and the associated oscillation, will no longer be symmetrical about the original equilibrium positions. The mean separation of atoms will thus increase, and a thermal expansion will be observed.

Such a simple model is sufficient to illustrate why the phenomenon of thermal expansion occurs. However it is clear that the anharmonic terms do not simply switch on at a distinct temperature, but are present at all temperatures. One may therefore state that the anharmonic terms become more significant as the temperature is increased. Further one may state that at high temperatures the anharmonic terms are the predominant terms.

This simple model assumes that the electrons of the material have no effect on the thermal expansion of the material\(^1\) which is obviously incorrect if one wishes to consider the thermal expansion of metallic materials. Further the model assumes an isotropic distribution of frequencies in the assembly of atoms, this too is incorrect. To correct for these deficiencies one must consider the ideas put forward by Debye.

With reference to Fig.2.4. it can be seen that the curve of the total potential energy is not symmetric about the minimum at the equilibrium separation. If one takes the system from a low temperature $T_1$ to a high temperature $T_2$. The change of potential energy from an increase in the separation of the atoms is smaller as opposed to the change in potential from a reduction of separation, when the system temperature is increased. Thus the system expands as the temperature is increased.

\(^1\)The core electrons are assumed to move with the ion cores in an adiabatic manner
If one considers a change in energy of the longitudinal vibrations in a crystal, caused by a change in temperature, an increase of ion separation \( r \), by \( \Delta r \) will result. This change in ion separation is a direct consequence of the anharmonic nature of the ion potential.

For \( T \gg \theta_0 \) the relationship between \( V \), and \( \Delta r \) is generally linear with temperature, thus the value of the expansion coefficient is approximately constant. For \( T<\theta_0 \) the relationship between \( V \) and \( \Delta r \) is not even approximately proportional to \( T \). Hence the expansion coefficient goes to 0 as \( T \to 0 \)K, further the change in length of the sample is observed to be almost constant at low temperatures. Fig. 2.5 & 2.6.

---

![Graph](image-url)

Fig. 2.5. \( dl/l_0 \) as a function of temperature for Cu from [4].
2.2.1. The physical interpretation of the change in length $dl$.

It is convenient at this point to discuss what is measured experimentally in order to determine the thermal expansion of a material. Any experiment that measures thermal expansion must measure symbiotically the thermal strain of the material. This must be measured with reference to an initial position. It is convenient for this discussion to take this reference position as the atomic separation at $T \rightarrow 0K$. However experimentally one may define any reference position.

The thermal strain is defined as

$$\frac{dl(T)}{l_0}$$  \hspace{1cm} (2.5)

$dl(T)$ is the measured strain of the material as a function of temperature $l_0$ is the reference position.

The measured dilation of the sample is $dl(T) = l(T) - l_0$

The function $dl(T)/l_0$ for Cu is shown in Fig. 2.5.

One can therefore define the linear thermal expansion coefficient as :-

$$\alpha = \frac{1}{l_0} \left( \frac{dl}{dT} \right)_p$$  \hspace{1cm} (2.6)

Where $l_0$ is a reference position.

$dl$ is the change in length of the material.

$dT$ is the change in temperature of the system.

If the system in question is isotropic i.e. $da = db = dc$ then one may define the volume expansion coefficient as:-

$$\beta = 3\alpha = \frac{1}{V_0} \left( \frac{dV}{dT} \right)_p$$  \hspace{1cm} (2.7)
2.3. Thermodynamic interpretation pertaining to isotropic volumetric expansion.

It is clear that the simple explanation for the thermal expansion of materials given previously is not sufficient to fully describe the phenomenon. If one wishes to study the effects of temperature on an assembly of atoms one requires a thermodynamic approach. The dimensional changes of the lattice are such as to minimise the free energy $F$. The free energy can have various contributions coming from the static lattice, lattice vibrations, itinerant electrons, magnetic ions etc. The thermal expansion may therefore also be considered as a sum of various contributions.

The Helmholtz free energy is defined as:

$$F = U - TS$$  \hspace{1cm} (2.8)

Where $U$ is the internal energy of the crystal.

$T$ is the thermodynamic temperature.

$S$ is the entropy.
If one takes a crystal at \( T = 0 \)K, and increases the temperature of the crystal to \( T' \) whilst keeping the volume constant then the free energy of the crystal is a function only of temperature \( F = F(T) \). In order to complete such a process the crystal volume must be constrained by the application of external pressure. The pressure is defined as

\[
p = -\left( \frac{dF}{dV} \right)_T \tag{2.9}
\]

If the pressure is removed the crystal volume will change by an amount \( \Delta V \). This change in volume will be such as to minimise the free energy of the crystal at \( T' \).

One may write \( F(T,V) \) as an expansion in powers of the volume change \( \Delta V \) thus:-

\[
F(T,V) = F_0(T,V_0) + \Delta V F'_0(T,V_0) + \frac{1}{2} (\Delta V)^2 F''_0(T,V_0) + \ldots \ldots \tag{2.10}
\]

\( F' \) and \( F'' \) are defined as the first \( \left( \frac{\partial F}{\partial V} \right)_T \) and second order derivatives \( \left( \frac{\partial^2 F}{\partial V^2} \right)_T \) of the free energy with respect to volume (at constant temperature). The isothermal bulk modulus of the crystal is defined as :-

\[
B_T = -V \frac{dp}{dV} \tag{2.11}
\]

Therefore \( B_T = VF''_0 \) \tag{2.12}

The equilibrium volume of the crystal at \( T' \) will be such that \( \left( \frac{dF}{dV} \right)_{T'=0} = 0 \)

Therefore:-

\[
\left( \frac{dF}{dV} \right)_T = 0 = F'_0(T) + \Delta V F''_0(T) \tag{2.13}
\]

The increase in volume at \( T' \) is given by:-

\[
\frac{\Delta V}{V} = -\frac{1}{V} \frac{F'_0(T)}{F''_0(T)} \tag{2.14}
\]

It is evident that the volume expansion is related to the ratio of the derivatives of the free energy with respect to volume at each temperature, \( T \). It is appropriate to introduce the interrelationship of the specific heat
and thermal expansion. Essentially one must examine the volume dependence of the vibrational modes of the lattice. Debye (1913) extended his theory for specific heat to account for the volume dependence of vibration modes, by utilising an equation of state. The essence of the Debye theory is the approximation of the dispersion of the modes of lattice vibrations by a linear function. Assuming a simple lattice structure one may have two modes of vibration, longitudinal and transverse, one may assume that all frequencies are allowed up to a maximum frequency $\nu_D$. Debye obtained the density of states as shown in Fig. 2.7.

Fig. 2.7. The frequency distribution function $f(v)$ as described by the Debye model.
2.3 Thermodynamic Interpretation of volume expansion. Chapter 2. Theoretical review.

The contribution to the internal energy arising from the temperature dependent lattice vibrations is given by:

\[ U_o = \frac{9N}{\nu D} \int_0^{\nu_D} \left[ \frac{h\nu^3}{e^{h\nu/kT} - 1} \right] d\nu \]  

(2.15)

Where \( N \) is the number of oscillators in the system \( \nu_D \) is the Debye frequency as defined in Fig. 2.7.

Thus one may define the internal energy contribution arising from the temperature dependence of the lattice vibrations as a product of \( T \) and a function of \( \theta/T \) where

\[ \theta = \frac{h\nu_D}{k} \]  

(2.16)

Similarly one may express the temperature dependent part of the free energy in a similar manner.

\[ F_o = T \cdot f(\theta/T) \]  

(2.17)

The Debye equation of state is written in the form:-

\[ P = -(\partial U_o/\partial V) + \gamma (U_D/V) \]  

(2.18)

Where:-

\[ \gamma = -(V/\theta)(\partial\theta/\partial V)_T = \frac{d\ln\theta}{d\ln V} \]

\( \gamma \) is the Grüneisen constant. Since the Debye theory states that \( \theta \) is independent of temperature one should expect that \( \gamma \) should also be temperature independent.

Differentiating (2.18) with respect to \( T \) at constant volume yields:-

\[ (\partial P/\partial T)_V = \gamma (C_v/V) \]  

(2.19)

But:-

\[ (\partial P/\partial T)_V = -(\partial V/\partial T)_p (\partial P/\partial V)_T \]  

(2.20)

Remembering the relationships for the isothermal bulk modulus \( B_T \) (2.11) and the volume coefficient of expansion \( \beta \) (2.7), substitution into (2.19) yields:-

\[ \gamma = \beta VB_T/C_v \]  

(2.21)

This may also be written as:-

\[ \gamma = \beta VB_p/C_p \]  

(2.22)
Therefore:

\[ \beta V B_T / C_V = \beta V B_\gamma / C_P \]  \hspace{1cm} (2.23)

It was originally thought [5, 6] that \( B_T \) was independent of temperature, this assumption therefore led to Grüneisen's rule:

\[ \beta \propto C_V \] \hspace{1cm} (2.24)

Experimentally it has been shown that Grüneisen's rule only holds at higher temperatures i.e. \( T > 0 \).

The reasons why the rule does not hold at low temperature, and can only be regarded as an approximation is due to the bulk modulus \( B_T \) not being a constant, as a function of temperature. Furthermore the Debye characteristic temperature is also a function of temperature since the phonon dispersion is more complicated than that assumed by Debye. Therefore \( \gamma \) becomes a function of temperature.

It is clear that for an isotropic solid the thermal expansion can be regarded as proportional to the specific heat \( C_V \) since:

\[ \frac{\beta \text{ isotropic}}{3} = \alpha \quad \therefore \quad \alpha = \frac{C_V \gamma}{3V B_T} \] \hspace{1cm} (2.25)

One may therefore expect that the thermal expansion at low temperatures will be a function of \( T^3 \).

That \( \beta \) has to vanish at \( T = 0 \)K can be seen immediately due to:

\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = - \frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_T \] \hspace{1cm} (2.26)

If the 3rd law applies to the solids in question, then as \( T \to 0 \) one would expect that \( \beta \to 0 \).
2.3.1. The Grüneisen Parameter.

One may also interpret the Grüneisen parameter in terms of the vibrational frequency spectra. If one assumes that all particles are vibrating at the same frequency \( v \), then the frequency dependence as a function of volume is related to \( \gamma \) by:

\[
\gamma = -\frac{d(\ln v)}{d(\ln V)} \tag{2.27}
\]

This is the original formulation of \( \gamma \), as given by Grüneisen.

However it is clear that a range of frequencies exist. Characterised by a frequency distribution function \( f(v) \). This function defines the number of vibrational modes per unit range. Thus we may think that each frequency mode \( v_i \) is associated with a particular value of \( \gamma \), i.e. \( \gamma_i \).

Much theoretical work has been done in order to sum the values of \( \gamma_i \) over the frequency range in question, such work allows the definition of the Grüneisen parameter to become:

\[
\gamma = \sum \gamma_i \tag{2.28}
\]

Within the quasiharmonic approach (the quasiharmonic approach will be described later) one may assume that \( \gamma \) is the weighted average of all \( \gamma_i \) values. The weight for each mode being its contribution to the specific heat at constant volume. Thus one may expect that the Grüneisen parameter will show a temperature variation. As with all Debye based theories one must define the limiting temperature ranges for which the approximation is valid.

The low \((\gamma_0)\), and high temperature \((\gamma_\infty)\) limiting values for the Grüneisen parameter become:

\[
\gamma_0 = -\frac{d(\ln \theta_0)}{d(\ln V)} \quad \text{and} \quad \gamma_\infty = \left(\sum_{j=1}^{3N} \gamma_j\right) / 3N \tag{2.29 & 2.30}
\]

Where:- \( \theta_0 \) is the low temperature value of the Debye temperature.

\( N \) is the number of vibrating particles in the assembly.

Since one may measure the values of \( \gamma \) as a function of temperature, by evaluating the specific heat, volume expansion and bulk modulus as a function of temperature one may compare the numerical values of \( \gamma_0 \) and \( \gamma_\infty \) with the measured variation of \( \gamma \). However one should note that such an
analysis of the Grüneisen parameter is not simple since the measurement of bulk moduli as a function of temperature is difficult.

If the potential is harmonic then it can be shown that \( \gamma \) is zero, this is evident since a harmonic crystal exhibits zero thermal expansion. Thus the analysis of \( \gamma \) is essentially a measure of the anharmonicity of the vibrational modes in the crystal potential.
2.4. Contributions to the thermal expansion of metals.

The preceding explanation for the volume expansion is purely a thermodynamic treatment, with respect to the lattice of the material, and thus applies to both metals and non-metals. However the effect and origin of certain contributions to the thermal expansion of metals must be accounted for. The two most significant contributions coming from conduction electrons and magnetic moments. Such contributions are obviously important, if one wishes to understand the nature of the thermal expansion of metals and the thermal expansion of magnetic materials.

The details will be discussed more fully below, however it is prudent to first clarify the physics of the quasiharmonic approximation. Although a brief mention of the quasiharmonic approach has been made, no details have been given. The quasiharmonic approach to lattice vibrations is of some importance since in a purely vibrational model (as has been implied in previous sections) the lattice vibrations do not interact with any other degrees of freedom. This therefore negates any electron interaction, and thus any contribution from the electrons, to the thermal expansion of metals. Such contributions arise from the redistribution of electron density by the dynamic deformation of the lattice caused by a phonon. Further to this the harmonic approach as stated previously negates the thermal expansion of materials completely. It is important therefore to briefly describe the quasiharmonic approach, as a method of allowing the coupling to other degrees of freedom. In addition to this one must describe some corrections which must be made to such a model.
2.4 Contributions to the thermal expansion of metals.

Chapter 2. Theoretical review.

2.4.1. The quasiharmonic approximation.

As stated previously in a purely vibrational model of the lattice, interactions between the vibrations, and other degrees of freedom are neglected. The vibrations are governed by the potential energy, which is only a function of the atomic positions. In a harmonic approach the thermal expansion is absent since $\langle \Delta x \rangle = 0$.

It is clear therefore that the thermal expansion is an anharmonic effect and arises due to the higher order contributions.

The quasiharmonic model treats the atomic vibrations as harmonic, but assumes that the frequencies have a volume dependence $\omega_j(V)$. This explanation has been put forward by Barron et al. 1980 [7]. Others take the quasi-harmonic approach to imply both a volume and a temperature dependence of the frequencies i.e. $\omega_j(V,T)$.

In such an approximation the lattice vibrational entropy $S_V$ becomes the sum of separate contributions arising from the volume dependent frequencies present in the system:

$$ S_V = \sum_j S_j \tag{2.31} $$

From this it follows that the specific heat is also expressible as a sum of separate contributions, as is the Grüneisen parameter. (eq. 2.27)

Generally one may expect that the Grüneisen parameter becomes the average of all $\gamma_i$. As such one may expect $\gamma$ to be constant as a function of temperature since the change of $\gamma_i$ of some modes of vibration may compensate for others. It is, however, known that most solids do not exhibit a constant $\gamma$ as a function of temperature. One may interpret this as a variation in frequency of the components of $\gamma$ as a function of temperature.

At low temperatures $T<<\theta_D$ the lattice entropy is of the form:

$$ S_V = \sqrt[3]{3} BT^3 + \sqrt[5]{5} CT^5 + \ldots \tag{2.32} $$

If there are no other contribution to the entropy, then the volume expansion has a similar form:

$$ \beta = bT^3 + cT^5 + \ldots \tag{2.33} $$
For this case no provision is made to account for the electrons of the material. These are assumed to be tightly bound to the ion core. The temperature dependence stated above is therefore the general expression for the low temperature behaviour for an insulating material.

In order to obtain a similar expression for a metal one must account for the "free" conduction electrons, the entropy of which have a volume and temperature dependence. Before discussing the thermal expansion of metals and the contribution of the conduction electrons to the thermal expansion it is important to note some corrections to the quasiharmonic approach. The quasiharmonic approximation is only valid for small atomic vibrations, although in a crystal the thermal vibration of a single mode is small, the interaction between modes are such as to produce an appreciable atomic displacement. For this reason one must account for strongly anharmonic effects, which are present in all but the hardest crystal lattices.

2.4.1. The electronic contribution.
The conduction electrons of a metal contribute to the thermal expansion due to the volume dependence of their entropy, for low temperatures, i.e. below the Fermi temperature $T << \varepsilon_F/kT$, the entropy is given as:-

$$S_e = \frac{2}{3} \pi^2 k^2 T N(\varepsilon_F)$$  \hspace{1cm} (2.34)

Where $N(\varepsilon_F)$ is the total density of states per spin, per unit energy range at the Fermi surface of the metal.

It is clear that the term is linear in $T$, although there are terms of higher orders in $T$, i.e. $T^3$, $T^5$, these contributions ($T$, $T^5$) to the total entropy are negligible, when compared to the contribution coming from the lattice of the material. One may define the electronic Grüneisen parameter as:-

$$\gamma_e = \frac{\beta_e B T V}{C_e}$$  \hspace{1cm} (2.35)

Where $\beta_e$ is the electron contribution of the thermal expansion.

For free electrons it has been shown [8] that $N(\varepsilon_F) \propto V^{2/3}$. 

\[ \text{25} \]
However in a metal which does not obey a free electron model complications arise due to details of the band structure and contributions arising from overlapping bands and from electron phonon interaction. For a simple metal the total thermal expansion coefficient may be written as a sum of lattice and electronic contributions. Thus:

\[ \beta = \beta_l + \beta_e = \frac{\chi_e}{V} (C_1 \gamma_1 + C_e \gamma_e) \]  

(2.36)

In the low temperature approximation i.e. \( T \ll \theta \) one may write:

\[ \beta = aT + bT^3 + cT^5 + \cdots \]  

(2.37)

Here the electronic contribution is linear in \( T \), and in analogy to the low temperature specific heat, should be observable as a linear contribution as \( T \to 0K \), the observation of which is only possible at low temperatures, as the lattice term becomes negligible and the lattice modes are “frozen” out. One should note that the conduction electrons contribute to the bulk modulus, and thus the complete separation of lattice and electronic terms is not possible. This approximation therefore only holds for materials whose bulk modulus is virtually temperature independent. This is true for most metals. For metals which exhibit strong electron phonon interaction the electronic bulk modulus is more difficult to determine. For the case regarding the latter, the separation of electronic and lattice contributions is non-trivial.

2.4.2. The magnetic “contribution” to the thermal expansion.

The magnetism of a material will give rise to an associated lattice deformation when the system orders magnetically. Furthermore below the ordering temperature there will be a magnetic “component” to the thermal expansion of the material. The magnitude of such an effect is related to magneto-elastic coupling.

The magnetic contribution to the thermal expansion is therefore the spontaneous magnetostriction of the material in question.

If one considers the magnetic system alone (and in isolation from the electronic and lattice systems) one may consider the entropy $S_m$ associated with the magnetism, and define the magnetic contribution to the volume expansion as:

$$\beta_m = \chi_T \left( \frac{\partial S_m}{\partial V} \right)_T$$  \hspace{1cm} (2.38)

Thus one may similarly define a magnetic contribution to the specific heat as:

$$C_m = \left( \frac{\partial S_m}{\partial T} \right)_V$$  \hspace{1cm} (2.39)

Thereby it is possible to introduce the magnetic Grüneisen parameter:

$$\gamma_m = \left( \frac{\partial S_m}{\partial \ln V} \right)_T / C_m$$  \hspace{1cm} (2.40)

$$= \beta_m V / \chi_T C_m$$  \hspace{1cm} (2.41)

This derivation is general, and it does not fully describe the temperature dependence of the spontaneous magnetostriction.

The temperature dependence of the magnetic contribution is not obvious and is strongly dependent on the material, and the nature of the magnetic system therein.

Previous work [7] has demonstrated that determining the temperature dependence of $\beta_m$ is problematic. Generally however one may state that in the low temperature limit, and from (2.37). The low temperature volume expansion of a metallic magnetic material will take the form :-

$$\beta = (a T^2) + a T + b T^3 + c T^4 + \cdots$$  \hspace{1cm} (2.42)
Where the bracketed term arises due to the magnetic contribution. The value for \( n \) however depends upon the type of magnetic order in the material, and the associated magnetic excitations as indicated in Table 2.1.

<table>
<thead>
<tr>
<th></th>
<th>Ferromagnetic ( n )</th>
<th>Antiferromagnetic ( n )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local moment model</td>
<td>3/2</td>
<td>3</td>
<td>9/10</td>
</tr>
<tr>
<td>(Spin wave theory)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Itinerant electron model</td>
<td>1</td>
<td></td>
<td>11</td>
</tr>
</tbody>
</table>

**Table 2.1.** Factors defining the temperature dependence of the magnetic contribution to the thermal expansion, where \( n \) refers to (2.42)

A more detailed discussion of the nature of the spontaneous magnetostriction will be given later. Although one may easily speak of contributions of either electronic, lattice or magnetic origin to the thermal expansion or the specific heat the details depend upon the sample. For example in systems which exhibit strong electron phonon coupling the separation of the lattice and electronic components is non-trivial for reasons stated above [12,13]. Furthermore the separation of a magnetic contribution to the thermal expansion on the grounds of a theoretical temperature dependence becomes difficult when the component in question has the same observed dependence as for other subsystems. Such cases are illustrated in Table 2.1.
2.5. Magnetism of materials, and associated magnetic effects.

Magnetism is one of the oldest branches of science. The physical effects of ferromagnetism were first discovered by the Greeks, and reported in literature around the 8th century B.C. Although at that time the mechanisms behind the observed phenomenon of the lodestone or magnetite (Fe₃O₄) ore were not known the subject was of great philosophical interest, and has remained so until today.

In order to understand the properties and intrinsic physical characteristics of magnetic materials one must discuss several points:

1. The bulk magnetic properties and characteristics of the four main classes of magnetic materials, and in particular the magnetic susceptibility.

2. The microscopic mechanisms behind magnetism.

3. The effect of temperature and applied magnetic fields on the magnetic system, such that one may understand the processes behind the magnetic ordering of materials.

One may then discuss the observed response of the lattice of a material as a response influenced by magnetic order, and as a response to the application of a magnetic field. As this work is the result of experiments to investigate the lattice response to the aforementioned effects it is of some importance that one understands the mechanisms behind the observed phenomena, and why they should exist.

One should however note that the topic of magnetism and magnetic effects is vast, and that in general experimental results on a single material cannot easily be attributed to any single cause, but rather to the interaction of many. Thus it is somewhat difficult to discuss all the poignant aspects of the subject.
2.5.1. The bulk properties of magnetic materials.

The magnetic properties of matter arise as a consequence that under certain circumstances some atoms or ions behave as elementary magnetic dipoles. The physical reasons behind the atomic dipoles are the motion of charge around the nucleus of the atom and the intrinsic magnetic moment of an electron (spin). If one considers these dipoles to have no influence on each other then one arrives at the case of para- or diamagnetism, that is to say one may induce a bulk magnetic moment that is proportional to the applied field. In such a case one may talk of the magnetic susceptibility (either molar, mass or volume susceptibility), which is a measure of the rate of change of the bulk magnetic moment with applied field, thus:

\[ \chi = \frac{m}{H} \]  

Where:
- \( \chi \) is the magnetic susceptibility
- \( m \) is the moment produced by,
- \( H \) the intensity of the magnetising field.

The origin of the magnetic moment will be discussed later, however one may state that the atomic moment may arise from either "localised" core electrons, as in magnetic insulators, and metals of the lanthanide group or by the delocalised electrons at the Fermi surface of a metal such as in the 3d "itinerant" magnetism of certain atoms of the transition metal series (Fe, Ni, Co and antiferromagnetic Cr and Mn).

Thus there are clearly two distinct types of atomic magnetism, the local moment case, and the itinerant case.

Further if one allows atomic moments to interact then one has an associated exchange energy between adjacent dipoles (in the most simple case). This interaction may produce at low temperatures a state with some degree of magnetic order. The effect of crystalline anisotropy will create an energy barrier for the simultaneous and unrestricted rotation of all moments with respect to the crystallographic axes.

The nature of magnetic ordering must be discussed, as must the anisotropy energy of the crystal, and the nature of the exchange energy. Furthermore, one must discuss the response of the system to both a change in temperature and an applied field.

Before commencing a discussion of the bulk magnetic properties of materials one must first define what is implied by the term bulk moment, or magnetisation of a sample.

If one considers a magnetic field \( H \) applied to a sample in vacuum, a magnetic induction \( B \) is induced. The polarisation of the space due to this induction can be revealed by the observation of the effect of placing a magnetic material in the field.

\[
B = \mu_0 (H + M)
\]  

(2.44)

Where:- \( M \) is the magnetisation of the substance. 

The volume integral of \( M \), \( \int M \, dv \) taken over the whole volume of the sample is called the magnetic moment, or bulk magnetic moment.

2.5.1.1. Diamagnetism.

Diamagnetic materials have a negative magnetic susceptibility. The magnetisation of the material tends to oppose the action of the magnetic field. Furthermore the magnetisation is proportional to the applied magnetic field. The relationship between the diamagnetic susceptibility \( \chi_d \), and magnetisation and the applied field is thus:

\[
M = \chi_d H
\]  

(2.45)

The action of an applied magnetic field on a diamagnetic substance alters the motion of core electrons. Hence the magnetic moment due to the motion of electrons is altered and an induced magnetic moment appears. The diamagnetism of a material is found to be temperature independent.

If one considers Lenz's law of electromagnetic induction which states that the application of a field on an electric current is such that the induced magnetic field is oriented such as to oppose the inducing field. Therefore the induced magnetisation is negative, and so is the magnetic susceptibility. One should note that the diamagnetic susceptibility is small in magnitude \( (\chi_d \approx -10^{-5}) \) when compared to that resulting from paramagnetic moments. (One or two orders of magnitude less than the paramagnetic susceptibility)
2.5. Magnetism of materials.

One exception is the case of superconductors which exhibit strong diamagnetism. This results from the induced supercurrents within the material which are created whenever an external magnetic field is applied. The diamagnetic susceptibility of a superconductor $\chi_d \approx -1$.

2.5.1.2. Paramagnetism.

The magnetic behaviour of paramagnetic substances is again characterised by a linear response of the magnetisation to the applied magnetic field. However the paramagnetic susceptibility is positive. The relationship between the paramagnetic susceptibility $\chi_p$, magnetisation and the applied field is thus:

$$M = \chi_p H$$  \hspace{1cm} (2.46)

Above the Curie temperature ferromagnetic materials exhibit paramagnetic behaviour, with a linear temperature dependence of the inverse susceptibility ($1/\chi_p$). The intercept on the temperature axis is the paramagnetic Curie temperature $\theta_p$. Although $\theta_p$ and $T_C$ are usually close they are rarely exactly the same.

The temperature dependence of the paramagnetic magnetic susceptibility is characterised by the Curie-Weiss law, which takes the form:

$$\chi_p = \frac{C}{T - \theta_p}$$  \hspace{1cm} (2.47)

Here $C$ is the Curie constant.

One must remember that paramagnetism can be an effect of either localised moments, or itinerant electrons.

In addition to the magnetic contribution of localised moments, systems with conduction electrons exhibit Pauli paramagnetism. Pauli paramagnetism is a weak effect which has no dependence on temperature and arises due to the nature of the free electrons. A schematic representation of the temperature dependence of the inverse susceptibility of a paramagnetic material is shown in Fig. 2.8.
2.5. Magnetism of materials.

Chapter 2. Theoretical review.

2.5.1.3. Ferromagnetism.

Ferromagnetism is the behaviour of certain materials, that at some high temperature $T > T_C$ exhibit paramagnetic behaviour. However at $T_C$ (the Curie temperature) energy arguments favour ferromagnetic order. That is to say the magnetic moments of the atom arrange in some preferred orientation such that the orientation of adjacent moments are parallel with respect to each other. The spontaneous magnetisation of the material dramatically increases at the ferromagnetic transition.

In terms of the magnetic susceptibility the material exhibits Curie-Weiss like behaviour above $T_C$. At $T_C$ the susceptibility diverges.

Weiss used the idea of a molecular field present in the material which acts on the elementary atomic moments in such a manner as to cause them to orient in some preferred direction. The direction is a function of the crystalline anisotropy.

In the magnetically ordered state the magnetisation of the material as a function of applied field is essentially non-linear, and exhibits hysteresis.

Further properties of the ferromagnetic state includes the formation of ferromagnetic domains. The formation of domains occurs in such a manner as to minimise the overall free energy of the material.

*Fig. 2.8. Temperature dependence of the inverse susceptibility of a paramagnetic material exhibiting the Curie Weiss law.*
If the material is inserted into an external magnetic field the abundance of domains is altered, the magnetic field will flip the domain orientation if the energy exceeds the crystalline anisotropy energy, and is sufficient to exceed the energy needed to shift the barrier between two adjacent domains, with the barrier being a Bloch Wall. If the magnitude of the magnetic field is sufficiently high a single domain will be formed.

An increase of the field will rotate the domain orientation into the direction of the magnetic field, assuming that one may overcome the crystalline anisotropy energy barrier.

Once the material is magnetised to some extent by an external field, and the field is removed, the net magnetisation of the material is far greater than that of the unmagnetised or "Virgin" state. Thus the effect of hysteresis is demonstrated. The hysteresis of ferromagnetic materials is the essential reason for their technical importance in the modern world.

The nature of the magnetic order, and the physical reasons why it should occur are discussed later.

If the ferromagnetic material is heated beyond $T_c$ the magnetism is destroyed, and the material returns to the unmagnetised state. The magnetisation as a function of temperature is shown in Fig. 2.9.

![Magnetisation graph](image)

**Fig. 2.9.** Magnetisation as a function of temperature for a ferromagnetic material in a small applied magnetic field $B \neq 0$. (The dotted line indicates the $B=0$ case.)
2.5.1.4. Antiferromagnetism.

Antiferromagnets constitute a class of materials for which below a certain temperature (the Néel temperature $T_N$) the minimisation of energy favours the antiparallel orientation of elementary atomic moments subsystems. The orientation is a preferred antiparallel arrangement of two magnetic moment subsystems, the moments constituting each subsystem are coupled ferromagnetically. The two subsystems are coupled antiferromagnetically. The net effect of antiferromagnetic order is to reduce the overall macroscopic magnetisation of the sample to zero while having an ordered state on the atomic level. Antiferromagnetic order may be taken to be an antiparallel orientation of moments in a lattice plane, or between two adjacent planes.

Such a configuration lends itself to other more complex permutations of moment orientations depending again on the strength of the crystalline anisotropy, and thus to the crystalline symmetry.

Above the ordering temperature, the material exhibits a Curie-Weiss like susceptibility, with a negative intercept $\theta_P$ on the temperature axis of the inverse susceptibility as a function of temperature.

The behaviour of the magnetisation as a function of temperature usually shows a maximum at the Néel temperature. This may not occur in all samples, also such a maximum does not implicitly indicate antiferromagnetic order, (Pd is one such example, where a maximum in the susceptibility is observed without the presence of AF order). The only conclusive proof of antiferromagnetic order is by neutron diffraction.
2.5. Magnetism of materials.  

2.5. The origin of the atomic moment.
Magnetism arises from the motion of electrons. Firstly we investigate the magnetism of a single electron.

2.5.2. The moment of a single electron.
If one considers an electron with mass $m_e$ travelling in an orbit of radius $r$. The angular velocity is thus:

$$\dot{\theta} = \frac{\partial \theta}{\partial t} \quad (2.48)$$

The electron will cover $\theta/2\pi$ turns per second, and therefore generates a current of $-e\theta/2\pi$. The moment due to a current $i$ in a closed loop (here of cross section $S = \pi r^2$) is $M = i S$. For this case the orbital magnetic moment of a single electron is therefore:

$$M = -\frac{1}{2} e \theta r^2 \quad (2.49)$$

The orbital angular momentum is thus:

$$L = m_e \theta r^2 \quad (2.50)$$

Thus the orbital magnetic moment is proportional to the angular momentum $L$.

$$M = -\frac{e}{2 m_e} L \quad (2.51)$$

This is a result using a purely classical approach, however it is well known that a classical approach is not appropriate. From quantum mechanics the motion of an electron in a central Coulombic potential is characterised by four integer quantum numbers $n, l, m_l$ and $s$.

The projection of the orbital angular momentum $L_z$ onto the quantisation axis $O_z$ is equal to $\hbar m$. Therefore the projection of the orbital moment when projected onto this axis is also quantised:

$$M_z = -m \mu_B \quad (2.52)$$

Where the constant $\mu_B = \frac{e\hbar}{2m_e}$ is called the Bohr magneton, and represents the atomic unit of the orbital magnetic moment.
The electron itself possesses an intrinsic angular momentum that is independent of the orbit in which it resides, since the electron has intrinsic spin. The spin of the electron is quantised in units of $s = \pm 1/2$, the projection onto the $Oz$ axis gives $s_z = \pm 1/2$. The magnetic moment associated with the intrinsic spin of the electron is given by:

$$M_s = \frac{e}{m_e} s$$  \hspace{1cm} (2.53)

This is twice the value for the orbital case. Since $s_z$ takes half integer values the Bohr magneton is also the unit of the spin magnetic moment.

This explanation takes care of the moment caused by a single electron. Now we must consider the more usual case of the magnetism of an atom. For this case one must examine the interaction of spin and orbit angular momentum.

2.5.2.2. The moment of a single atom.

The nuclear magnetic moment is $\approx 1000$ times smaller than the electronic moment, thus one may assume that the magnetism of atoms, and thus materials in general is a consequence of electrons. Thus in order to examine the magnetism of an atom one must consider the electron shells only. In order to determine the moment of the atom we must consider the manner in which electrons "fill" shells of the atom. In this way one must also consider the interaction between electrons in the same shell. This essentially determines the moment of a single atom.

The Russel-Saunders coupling is one that is common in atoms that exhibit magnetic effects.

If one has an electron shell consisting of $n$ electrons one may sum the individual spins ($s$) of the electrons in order to acquire the total spin ($S$) of the shell thus:

$$S = \sum_{i=1}^{n} s_i$$  \hspace{1cm} (2.54)
Similarly one may sum the orbital momentum \( l \) in order to acquire the total orbital momentum \( L \) of the shell i.e.:-

\[
L = \sum_{i=1}^{n} l_i
\]  

(2.55)

The effect of the spin orbit interaction is to couple \( S \) and \( L \), giving a total angular momentum for the shell \( J \):-

\[
J = L \pm S
\]  

(2.56)

The manner in which the electrons fill the shell is governed by the Pauli exclusion principle, that is to say that no two electrons with the same set of quantum numbers may be present in the same atom.

In order to minimise energy the electrons fill the shells according to "Hund's" rules:-

1. \( S \) will take the maximum value consistent with the Pauli exclusion principle.
2. \( L \) takes the maximum value consistent with the Pauli exclusion principle after the first rule has been satisfied.
3. \( J \) will take the value \( L-S \) for a shell that is less than half full, and \( L+S \) for a shell that is more than half full.

When the shell is completely full \( L, S, \) and \( J \) are all zero, in this case the shell has no intrinsic magnetism, except that coming from the weak diamagnetic contribution.

For the case of partially filled shells, i.e. those which have non-zero \( L, S, \) and \( J \), one may convert the quantum numbers \( L, S, \) and \( J \) to the corresponding angular momentum vectors:

\[
L^2 = L(L+1)(\hbar)^2
\]  

(2.57)

\[
S^2 = S(S+1)(\hbar)^2
\]  

(2.58)

\[
J^2 = J(J+1)(\hbar)^2
\]  

(2.59)

The corresponding magnetic moment vectors, resulting from the spin momentum, and the orbital momentum respectively are:-

\[
M_S = 2\mu_B (S(S+1))^{1/2}
\]  

(2.60)

\[
M_L = \mu_B (L(L+1))^{1/2}
\]  

(2.61)
The resultant magnetic moment precesses around \( \mathbf{J} \). It is given by the sum of the spin and orbital moment.

\[
M_{\text{tot}} = M_S + M_L
\]  

One may resolve the total magnetic moment into a time independent component that is in the direction of \( \mathbf{J} \), \( M_J \), and a high frequency component perpendicular to \( \mathbf{J} \) that has a time averaged value of zero.

If one considers the time independent component only it may be shown that the resultant moment \( M_J \) in the \( \mathbf{J} \) direction is:

\[
|M_J| = g \mu_B (J(J+1))^{1/2}
\]  

Where \( g \) is the Landé splitting factor, and is expressed in terms of \( L, S \) and \( J \):

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

One may now consider the magnetism of an array of atoms.

2.5.3. The magnetism of local moment systems.

Local moment magnetism arises when the electron shells carrying the atomic magnetic moment are well shielded by the outer electron shells. Such a case becomes clear when one examines the radial distribution of electrons in atomic Tb, a rare earth ferromagnet. Fig.2.10. It is clear that the electrons carrying the moment, those of the 4f orbital, are well shielded from neighbouring atoms by the outer electron shells.

Fig. 2.10. The radial distribution of electrons in atomic Tb from [14]
However one must also consider the possibility that local moment systems may also possess some itinerant character, as the localised moment of the atom, (which in some rare earth cases can produce an extremely large magnetic field) can polarise the outer electrons i.e. those which are involved in conduction, and give rise to a small extra contribution to the magnetism. One must also consider the effect of the crystalline electric field on the properties of the local moment system. Orbital angular momentum is not a good quantum number for the rare earth series, only J is well defined. The action of the CEF is to split the degeneracy of J.

Next we shall investigate the paramagnetism of a local moment paramagnetic substance. The nature of magnetic ordering and the temperature / field dependence of such a system will be discussed later.

2.5.3.1. The paramagnetic susceptibility of an array of local moment atoms.

In the paramagnetic temperature region and at relatively small fields the total magnetic moment per mole is given by:-

\[ N\langle M_{J^+} \rangle = NG^2 \mu_B^2 J(J+1) B_0 / 3kT \]  

(2.65)

The molar susceptibility \( \chi_m \) of the sample in an applied field \( B_0 \)

\[ \chi_m = M_J / B_0 \]  

(2.66)

Thus:-

\[ \chi_m = \frac{M_J}{B_0} = g^2 J(J+1) \frac{N\mu_B^2}{3kT} = p^2 \frac{N\mu_B^2}{3kT} \]  

(2.67)

Where \( p_{\text{eff}} = g(J(J+1))^{1/2} \) is the paramagnetic effective Bohr magneton number. This is easily accessible experimentally, and is useful in determining the sample quality.

If the system obeys the Curie law:-

\[ \chi_m = C_MT^{-1} \]  

(2.68)

Where \( C_M \) is the molar Curie constant.

Then

\[ p^2_{\text{eff}} = \frac{3k}{N\mu_B^2} C_M \]  

(2.69)
If the system obeys the Curie-Weiss law then
\[ \chi_M = C_M (T-\theta)^{-1} \]  \hspace{1cm} (2.70)
Relationship (2.69) is unaffected.

2.5.4. The magnetism of itinerant electron systems.
Previously we have discussed only the magnetism associated with localised moment systems. The magnetism of metals (negating the 4f rare earth metals), and alloys do not in general possess local moment character but are instead itinerant. The reasons behind this is that the partially filled electron shells that carry the moment i.e. the 3d shell in the transition metal series, are also involved in the conduction band of the material, that is to say these electrons are "free" to move throughout the crystal. Thus the electron wavefunction is delocalised from the ion core unlike in the local moment case. In such a system one must therefore treat the electrons collectively using a band approach, thus the magnetism of such systems is a collective phenomenon. Firstly we shall consider the reason why such systems have an induced moment in an applied field, thus one may explain why itinerant systems occur with a spontaneous magnetic moment.

2.5.4.1. A simple model of itinerant electron paramagnetism.
One must consider the contribution of conduction electrons to the total moment of a metal. It is more simple to consider only the spin magnetic moment of the metal (since the orbital moment due to the orbital momentum is quenched in 3d transition metals and usually is a complex function of the applied field).
In a paramagnetic material the magnetic moment in zero field may have any orientation. However in an applied field the spin moment may only have two orientations, parallel or antiparallel with respect to the direction of the applied field. The effect of the application of an applied field on the occupation of electron states of a paramagnetic metal is shown in Fig. 2.11.
The effect of the field is to change the energy of the parallel and antiparallel spin states as follows:
\[
\Delta E_{\text{mag}} \uparrow\uparrow = -m_B B \\
\Delta E_{\text{mag}} \uparrow\downarrow = +m_B B
\] (2.71) (2.72)

Hence the density of states is shifted relative to each other by \(2m_B B\). It is clear therefore that the antiparallel spin state may reduce its energy by the reversal of the spin orientation of some electrons thereby increasing the population of the parallel spin oriented band. Only the electrons within an energy interval \(\Delta E = m_B B\) of the Fermi energy are affected by this process. The difference in population between the two states is \(g(\varepsilon_F)m_B\), thus the net magnetic moment is obtained as \(g(\varepsilon_F)m_B^2\).

The paramagnetic susceptibility becomes:
\[
\chi = g(\varepsilon_F)m_B^2\mu_0
\] (2.73)

The above explanation is taken at 0K. Above this temperature one must account for the change in density of states due to thermal effects, i.e. one must consider the Fermi-Dirac function. The temperature dependence of the Fermi function is small at \(T \ll T_{\text{Fermi}}\) one may expect that the temperature dependence of \(\chi\) is small also.

\[\text{Fig. 2.11. The field induced moment due to band electrons at } T = 0\text{K.}\]
The paramagnetic contribution from itinerant electrons is therefore a small effect. The Pauli exclusion principle will suppress the tendency of all electrons to align with the external field via the process described previously.

2.5.4. The effect of temperature on the magnetic system: Magnetic ordering and magnetic transitions.

One must consider the effect of a temperature change on the magnetic system, simply because if the temperature of a system is changed the response of the magnetic system can be dramatic. That is to say that the magnetic system will order in a co-operative manner, and that the subsequent order will be long range if the temperature is reduced below the critical temperature for the transition.

In terms of energy arguments one can say that the total magnetic energy is minimised at all temperatures, with the minimisation favouring magnetic order below the transition temperature.

One may think of the total magnetic energy ($F_{\text{Tot}}$) being a sum of four contributions:

\[ F_{\text{Tot}} = F_{\text{Dip}} + F_{\text{Exch}} + F_{\text{Aniso}} + F_{\text{MagneTo}} \]  

(2.74)

Where

- $F_{\text{Dip}}$ is the dipolar exchange energy.
- $F_{\text{Exch}}$ is the exchange interaction energy.
- $F_{\text{Aniso}}$ is the magnetocrystalline anisotropy energy.
- $F_{\text{MagneTo}}$ is the magnetoelastic energy.

One must consider the origins of these contributions, in order to understand their importance for magnetic order. It is appropriate to state at this juncture that interaction is essential for magnetic order to occur, without it the atomic dipoles will have no preferred orientation.

The magnetoelastic energy is responsible for many of the magnetoelastic effects, such as spontaneous magnetostriction. It will be discussed more fully in the next section.

One must define an appropriate order parameter. For a ferromagnetic material this is the spontaneous magnetisation of the system, for an
antiferromagnetic system the spontaneous sublattice magnetisation is the order parameter.
It will be shown later that using the magnetisation as the order parameter the magnetic transition is second order.
Firstly we shall discuss the origin and the nature of the interaction energies indicated above.

2.5.4.1. Magnetic interactions: Dipolar exchange.
One may expect, on a purely intuitive basis that the interactions between localised atomic moments result from their associated magnetic fields, i.e. the dipolar interaction. However the magnitude of the dipole interaction energy is far too small to explain the high values of the critical temperatures for the 3d ferromagnets.
The direct dipolar interaction energy is given by:-

\[ U = \frac{1}{r^3} \left( m_1 \cdot m_2 - 3(m_1 \cdot r)(m_2 \cdot r) \right) \] (2.75)

Where:-

\[ r = \text{interatomic separation.} \]

The magnitude of the atomic moments is of the order:-

\[ m_1 \approx m_2 \approx g \mu_B \] (2.75)

Thus:

\[ U \approx \frac{(g \mu_B)^2}{r^3} \] (2.76)

Therefore \( U \approx 10^9 \) J per atom, whereas the thermal energy at \( T_c^{FE} = 1000K \approx 10^7 \) J per atom. Thus the dipolar interaction cannot be the predominant contribution to magnetic order, since the magnetic order would thermally obliterated.
By far the most important contribution comes from the electrostatic interaction from the electrons. This will now be discussed.
2.5.4.2. Magnetic interactions: Direct exchange.

Quantum mechanics does not allow the relative directions of two interacting spins to change without the spatial distribution of charge changing also. Consider the spatial distribution of charge associated with the electronic shell of an ion with nonzero $J$, i.e. one which carries a magnetic moment (i.e. the 3d shell, or 4f shell), when placed in the vicinity of another such ion. There is a tendency for orbital overlap between the wavefunctions of the respective electron shells of the two ions. In such a case one must apply the Pauli exclusion principle to such regions, such that no single quantum state may be occupied twice. If one of the orbital wavefunctions is symmetric, then the spin part must be antisymmetric (and visa versa). Therefore if the spin state of the shell is altered by reversing the direction of the spin, the orbital symmetry will change. The spatial charge distribution will alter also in order to accommodate this. This implies a correlation between the spin states of two adjacent electron orbitals. One may think of this correlation as a direct interaction between the two spin vectors ($S_i$ and $S_j$) of the adjacent electron orbitals that is proportional to their scalar product, $S_i \cdot S_j$.

If one were to write the Schrödinger equation for the entire system there would be a contribution to the total Hamiltonian, as a result of the aforementioned effect.

$$H_{\text{Heis}}^{\text{Spin}} = -2J_{ij} S_i \cdot S_j$$  \hspace{1cm} (2.77)

Where: $J_{ij}$ is the effective exchange constant.

This is known as the Heisenberg Hamiltonian.

When applied to a three dimensional lattice, where a given atom is surrounded by $n$ neighbours, it becomes necessary to sum the contributions to the exchange from the interaction between neighbours.

$$H_{\text{Heis}}^{\text{Spin}} = -2 \sum_{<i,j>} J_{ij} S_i \cdot S_j$$ \hspace{1cm} (2.78)

The physical meaning of the effective exchange constant is that a positive value of $J$ leads to a ferromagnetic coupling between spins (corresponding to a triplet state of two coupled spins) and that a negative value of $J$ leads to antiferromagnetic coupling of spins (a singlet state of two coupled spins).
This mechanism is classed as direct exchange and arises from direct Coulomb interaction. While correct in itself it is only viable when the adjacent magnetic atoms are within a "critical" distance, the critical distance being governed by the amount of wavefunction overlap that occurs to give rise to the effect. Such an explanation of magnetic exchange interaction will not be suitable if the atoms carrying the moments are not crystallographic nearest neighbours. Also one should note that the Heisenberg Hamiltonian only applies to systems which have a high degree of local moment character, although if the electron orbitals which carry the local moment are well screened as in the 4f group the direct exchange is prohibited, as there can be no orbital overlap. It is clear therefore that other mechanisms must be present in magnetic materials where the previously mentioned exceptions to solely direct exchange are present (and in itinerant electron systems). Such exchange mechanisms are classed as indirect exchange, of which there are essentially two mechanisms: superexchange, where exchange is mediated by non-magnetic nearest neighbours, (which will not be discussed here) and the RKKY (Ruderman Kittel Kasuya Yosida) interaction, relying on the polarisation of conduction electrons. The RKKY exchange interaction is the significant interaction for local moment metallic magnets, i.e. the elements and intermetallic alloys of the lanthanide group. The details of the RKKY interaction will now be discussed.
2.5.4.3. Magnetic Interactions: RKKY interaction.

One may explain the nature of the RKKY interaction as follows. Consider a metallic lattice consisting of atoms which possess a local moment. It is clear that the ion cores will be surrounded by the conduction electron gas. It is the effect of the local moment (located on the lattice site) on the conduction electron that must be considered.

The local moment on the lattice site will make it favourable for conduction electron bands to be occupied by an electron/s with a parallel magnetic moment to the local moment, conversely it will be unfavourable for an antiparallel arrangement. Thus the conduction electrons become polarised. The electron with parallel magnetic moment will distort its wave function in order to take advantage of the local magnetic field. This occurs by the mixing of other electron states with the same spin orientation, thus the spin density at the position of the local moment is increased.

If one considers the parallel oriented moments then, the wave functions of the added states are such as to be in phase with each other at the lattice site, thus constructive interference occurs.

The conduction band electrons possess a range of different wave vectors. As the radial distance from the ion core is increased destructive interference occurs, resulting from the phase difference between electron wave vectors. Thus the arrangement of electrons with parallel moments is changed to have an oscillatory appearance. Considering the antiparallel orientated electrons then, these electrons behave such as to minimise the overall size of the wave function in the vicinity of the local moment (the previous argument regarding destructive interference due to wave vector dispersion holds also). Thus there is an associated oscillatory behaviour of antiparallel spin arrangement also.

The result is an overall long range spin density oscillation. The overall charge distribution remains constant, since the attraction of parallel spins is negated by those with antiparallel spins. The Hamiltonian for the local moment spin (S) and that of the conduction electron (s) is given by:

\[ H = -J \sum_i S_i s_i \] (2.79)
One may now consider the neighbouring local moment on the adjacent lattice site. Depending on whether the atom feels the +ve or -ve part of the conduction electron spin density polarisation wave, the interaction will be ferro or antiferromagnetic, respectively. That is to say that the neighbouring ion sees the electron polarisation; and it will orient itself accordingly, either parallel or antiparallel.

The nature of the net spin density wave (ρ) can be seen in Fig. 2.12, and within a free electron model is described by [14]:

\[
\rho = -\left(\frac{9\pi Z^2 J \sigma}{4E_F}\right) F(x)
\]  

(2.80)

Where:
- \( Z \) is the Number of conduction electrons per atom
- \( E_F \) is the free electron Fermi energy.
- \( F(x) = x^4 (x \cos x - \sin x) \) (\( x = 2kFr \))

![Fig. 2.12. Spin density as a function of radial distance from the ion core.](image)

Of course this explanation accounts for the interaction between two ions. In reality the system is three dimensional. The interaction that a central ion feels is the sum of interactions from the surrounding ion cores.
De Gennes [15] treated such an assembly of local moments in order to obtain the overall measure of the RKKY interaction. The Weiss constant (from a molecular field approach) is shown to be:

\[
\theta = \left[ \frac{3\pi J^2 (g - 1)^2 J(J+1)}{4kE_F} \right] \sum F(x)
\]  

(2.81)

Where \( \sum F(x) \) is the result of summing the RKKY interaction over all surrounding cores.

If one considers an isostructural series of rare earth compounds, one may assumes that \( Z, E_F \) and \( F(x) \) are constant, the transition temperature is shown to be a linear function of the De Gennes factor \( \Lambda \):

\[
\Lambda = \left( (g - 1)^2 J(J+1) \right)
\]  

(2.82)

2.5.4.4. Magnetic interactions: Magnetocrystalline anisotropy energy.

The magnetocrystalline anisotropy energy essentially reflects the symmetry of the crystal system. If one assumes that the dominant force aligning the moments of the system is isotropic, then under an applied field the moments rotate to obtain the lowest energy configuration with respect to the applied field. One may assume this would be parallel to the applied field (for ferromagnetism). However if one considers the susceptibility of an antiferromagnetic structure as a function of crystal orientation one immediately sees a crystal orientation dependence of the susceptibility. Also one may consider the directional dependence of the magnetisation of Fe. This orientational dependence is the effect of the magnetocrystalline anisotropy energy \( MAE \).

In essence \( MAE \) operates to determine an easy direction in which the spontaneous magnetisation may lie with reference to the symmetry of the crystal. The orientation of the magnetic moments for which the lowest energy configuration is obtained is called the easy direction. If one applies a field that is out of plane with the easy direction work must be done by the field to rotate the direction of magnetisation out of the easy axis. The \( MAE \) is
therefore related to the degree of rotation of the moment (i.e. out of the easy axis).

For cubic symmetry the MAE is expressed as a function of the direction cosines \((\alpha_1, \alpha_2, \alpha_3, \ldots)\) as follows:

\[
E_{\text{Aniso}} = K_0 + K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2 + K_3(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2)^2 + \ldots \tag{2.83}
\]

The origin of the MAE is related to the mechanisms by which moments can sense the symmetry of the crystal. The MAE exists in the anisotropy of the magnetic exchange interactions. The charge distribution on magnetic atoms depends on the spin direction via the spin orbit interaction (see sec. 2.5.4.2.). Consider the model proposed for direct exchange. If the moment of the atom is rotated by an applied field the wavefunction overlap changes. Therefore the magnitude of the interaction energy changes also.

2.5.4.5. Mean field theory: Spontaneous magnetisation of a ferromagnet.

Weiss (1907) postulated that a large field exists in a ferromagnet, the field would therefore act upon the local moments that existed in the ferromagnet. This approach assumes an average value for the atomic moment \(\langle m_j \rangle\). The magnitude of the molecular field is \(\approx 10^5 \text{T}\). Such a field cannot originate from dipolar interactions. One may think of the field as resulting from the interatomic interactions present in the sample, as discussed in the previous sections.

It is important to remember that the mean field approach is inadequate, failing to predict the presence of spin waves at low temperatures.

One must account for the internal field present in a ferromagnetic material. The field becomes the sum of the applied and the internal field:

\[
B_0 = B_{\text{internal}} + B_{\text{applied}} \tag{2.84}
\]

The intrinsic spontaneous magnetisation is

\[
\sigma_{B,T} = N_s \langle m_j \rangle \tag{2.85}
\]

Where \(N_s\) is defined as the number of atoms per unit mass.

---

This content is a part of the theoretical review for magnetism of materials, specifically discussing the magnetic anisotropy energy (MAE) and its relation to the symmetry of the crystal. The MAE is expressed as a function of the direction cosines of the moment, and its origin is related to the mechanisms by which moments sense the symmetry of the crystal. The mean field theory is also discussed, highlighting the limitations of this approach and the need to account for internal fields in ferromagnetic materials.
The internal field may now be defined as

\[ B_{\text{internal}} = N_s \gamma_m \langle m_{jz} \rangle \]  

\[ \text{(2.86)} \]

Where \( \gamma_m \) is the molecular (mean) field coefficient.

The ratio of the intrinsic magnetisation at a field \( B \) and temperature \( T \), and zero field and zero temperature is as follows:

\[ \frac{\langle m_{jz} \rangle}{Jg\mu_B} = \frac{\sigma_{B,T}}{\sigma_{0,0}} = B_s(x) \]  

\[ \text{(2.87)} \]

Where \( B_s(x) \) is a modified Brillouin function to account for the internal field. The magnetic energy is given by \( kT = Jg\mu_B B_o \), and must be altered to include the mean field constant, and internal field. Thus \( x \) becomes:

\[ x = Jg\mu_B B_{\text{ext}} N_s \gamma_m \langle m_{jz} \rangle / kT \]  

\[ \text{(2.88)} \]

If one now considers the case when the applied field is zero, that is the spontaneous magnetisation. \( X = Jg\mu_B N_s \gamma_m \langle m_{jz} \rangle / kT \)

\[ \frac{\langle m_{jz} \rangle}{Jg\mu_B} = \frac{\sigma_{B,T}}{\sigma_{0,0}} = \left[ \frac{kT}{N\gamma_m (Jg\mu_B)^2} \right] Jg\mu_B N_s \gamma_m \langle m_{jz} \rangle / kT \]  

\[ \text{(2.89)} \]

A graphical solution may be obtained in order to determine the intrinsic magnetisation of a ferromagnet as a function of temperature.

The reduced spontaneous magnetisation \( (m(T)/m(0)) \) as a function of reduced temperature \( (T/T_C) \) is shown in Fig. 2.13.

The Curie temperature is the point at which the magnetisation is reduced to zero. In this way one may think of the magnetisation as the order parameter.
2.5.4.6. Mean field theory: Spontaneous magnetisation of an antiferromagnet.

As the spontaneous macroscopic magnetisation of a "perfect" antiferromagnet is zero, one may consider the spontaneous microscopic magnetisation of the ferromagnetic sublattice systems. The nature of simple antiferromagnetism is such that the lattice of the material consists of two sublattice systems, the sublattice systems being ferromagnetically coupled in themselves, but with opposite magnetisation relative to each other.

The spontaneous magnetisation of the two sublattices are thus:

\[
\sigma_A = \frac{1}{2} N_s \langle m_j \rangle_A \quad \text{For sublattice A} \tag{2.90}
\]

\[
\sigma_B = \frac{1}{2} N_s \langle m_j \rangle_B \quad \text{For sublattice B} \tag{2.91}
\]

One must then define the mean fields which act on each sublattice.

\[
B^A_{\text{int,\ emal}} = q_{AA} \sigma_A + q_{AB} \sigma_B \tag{2.92}
\]

\[
B^B_{\text{int,\ emal}} = q_{BA} \sigma_A + q_{BB} \sigma_B \tag{2.93}
\]

One must account for the interactions from nearest neighbours and second nearest neighbours as follows. In this case the two sublattices are identical. Therefore:

\[
q_{AB} = q_{BA} = -q_1 \quad \text{for 1st nearest neighbours}
\]
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\[ q_{AA} = q_{BB} = -q_2 \] for 2\textsuperscript{nd} nearest neighbours

Where \( q_1 \) and \( q_2 \) are positive.

One may thus write the spontaneous magnetisation in zero applied field of both sublattices as in sec 2.5.4.5.

\[
\begin{align*}
(\sigma_A)_t &= \frac{1}{2} N_s J g \mu_B B_j (X_A) \\
(\sigma_B)_t &= \frac{1}{2} N_s J g \mu_B B_j (X_B)
\end{align*}
\]

Where:

\[
X_A = J g \mu_B B_j^A / kT \\
X_B = J g \mu_B B_j^B / kT
\]

Since \( \sigma_A = -\sigma_B \), and |\( \sigma_A \)|=\( \sigma_S \) then:-

\[
\sigma_A = \frac{1}{2} N_s J g \mu_B B_j (X_s)
\]

Clearly this is similar to the theory outlined for the ferromagnetic case. Thus if one substitutes \( q_1 - q_2 = q \) (equivalent to \( \gamma_m \)), and \( \sigma_0 = NJ g \mu_B \), one obtains the equations for the ferromagnetic solution. Each sublattice is magnetised in a similar manner to the ferromagnetic case, however since the sublattice magnetisations are equal and opposite the net spontaneous magnetisation of the material is zero. The Néel temperature is the point at which the reduced magnetisation of either sublattice is reduced to zero. In this way one may think of the sublattice magnetisation as the order parameter Fig 2.14.

![Fig. 2.14. The spontaneous magnetisation (m(T)/m(0)) of both sublattices of an antiferromagnetic material as a function of reduced temperature (T/T_C)](image)
2.6. Magnetostriction: The response of the lattice to magnetism.

Due to the dependence of the magnetic interactions, \( (2.74) \), on the distance between magnetic ions, an elastic and magnetic body exhibits magnetoelastic or magnetostrictive effects. The dimensions and the elastic properties of the material depend directly on its magnetic state. Conversely the magnetic state of the body is indirectly dependent on the stresses, both internal, as well as applied.

These effects have been observed in all types of material, e.g. para-, dia-, ferro- and antiferro-magnetic materials, as well as superconductors. The study of such phenomena has been of interest for more than 150 years. In this work we are primarily interested in the direct magnetoelastic effects of magnetic order on the bulk dimension of a sample, and the magnetoelastic effect due to an external field being applied to the sample.

In the previous section we discussed the nature and the origin of the magnetic interaction energy. The physical reason why materials exhibit magnetoelastic effects arises from the strain dependence of the magnetic interaction energies. Thus one may define this as a magnetoelastic energy contribution to the total magnetic energy of the material.

In this section we must discuss the physical nature of two distinct aspects of magnetoelasticity:

i. The spontaneous magnetostriction. This is the response of the lattice to magnetic ordering in the material.

ii. The forced magnetostriction. This is the response of the lattice to the application of an external field and can be either measured when the material is magnetically ordered, or in the paramagnetic state.
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2.6.1. Spontaneous magnetostriction.

Firstly we shall consider the observed effect of spontaneous magnetostriction, which is thought to be the most fundamental of the many magnetovolume effects. [16]

Consider a sphere of Nickel cooled from above $T_c$ (631K) to low temperature. Measurement of the linear coefficient of thermal expansion yields a volume anomaly at $T_c$ Fig. 2.15. i. That is to say that the response of the lattice system to the magnetic ordering is directly observed. If one were then to subtract the contributions to the thermal expansion arising from the lattice and electron subsystems, one may obtain the magnetic contribution to the thermal expansion. One may then obtain the spontaneous magnetostriction by integrating the curve of the magnetic contribution thus:

$$\frac{\partial l_{mag}(T)}{\partial T} = \int_0^T \alpha_{mag}(dT)$$  \hspace{1cm} (2.97)

Further if one assumes that the system is isotropic then one may obtain the volume magnetostriction $(\omega)$ which is simply:

$$\omega = 3 \left( \frac{\partial l_{mag}(T)}{\partial T} \right)$$  \hspace{1cm} (2.98)

The result of this operation will therefore yield the spontaneous volume magnetostriction, Fig. 2.15. ii.

The spontaneous volume magnetostriction is seen to vary approximately as the square of the magnetisation $\langle M^2 \rangle$ of the material.

$$\omega = a \langle M^2(T) \rangle$$  \hspace{1cm} (2.99)

Where $a$ is a constant that signifies the magnitude of magnetoelastic coupling, i.e. the dependence of the magnetic system to the lattice system. The magnetic effect does not disappear directly at $T_c$ due to the effect of short range order that is present in the system, this is confirmed by experiment [17].

This effect is generally observed in magnetic materials the magnitude of the effect being governed by the degree of coupling of the lattice system to the magnetic system.
It is clear that the origins of the spontaneous magnetostriction are dependent upon the physical nature of the magnetism present in the material. Thus we may now consider the case for a local moment and itinerant electron system.

![Graph showing temperature dependence of linear thermal expansion and spontaneous volume magnetostriction of Ni and FeNi](image)

**Fig. 2.15.** The temperature dependence of, i. linear thermal expansion, and ii. spontaneous volume magnetostriction of Ni and FeNi from [18].

### 2.6.1.1. Spontaneous magnetostriction: Local moment picture.

Here we must consider the effect of local moment interactions on the volume of the system, and the effect of non spherical charge distribution that is present in some local moment systems.

Consider a ferromagnetically ordered ground state, with the magnetic Hamiltonian:

\[ H = \sum J_{ij} \langle r \rangle S_i S_j \]  

(2.100)

If the nearest neighbour interactions dominate then the system can gain magnetic energy by contracting the lattice if \( \partial J_{nn} / \partial \tau \) is negative. Above \( T_c \) the average of parallel and antiparallel nearest neighbour interactions will average to zero, therefore the magnetovolume interaction will average to zero. For this case there will be a magnetic term tending to expand the lattice as the system is warmed above \( T_c \). The equilibrium separation of
nearest neighbours will be determined by the minimisation of the magnetic term $\partial V$ and the elastic term $(\partial V)^2$ [19].

For systems with this configuration the magnetic contribution to the thermal expansion is [20]:

$$\alpha_{mag}(T) = \kappa \sqrt{- \frac{\partial \ln J_{\mu}}{\partial \ln V}} \frac{\partial}{\partial T} \left( - \sum J_{\mu}(S_i.S_j) \right)$$  \hspace{1cm} (2.101)

Where $\kappa$ is the compressibility.

$\left( \frac{\partial \ln J_{\mu}}{\partial \ln V} \right)$ is the magnetic Grüneisen parameter.

If the mean field theory is used then one may express the energy of a ferromagnet as:

$$E = - \frac{1}{2} W M^2 + \frac{1}{2} \kappa \omega^2$$  \hspace{1cm} (2.102)

Where $W$ is the molecular field constant

$\kappa$ is the compressibility

Thus one may define the total energy as a sum of exchange, as defined by $WM^2$, and elastic energy $\propto \omega^2$. Differentiating (2.102) with respect to $\omega$ yields the spontaneous magnetostriction as:

$$\omega_s = \frac{1}{2} \kappa \left( \frac{d W}{d \omega} \right) M^2$$  \hspace{1cm} (2.103)

As $W$ is proportional to $J$, (the effective exchange in mean field theory), the spontaneous magnetostriction can be expressed as:

$$\omega_s \propto \kappa \left( \frac{d J}{d \omega} \right) M^2$$  \hspace{1cm} (2.104)

Thus the magnetoelastic coupling constant $a$ is proportional to $\left( \frac{d J}{d \omega} \right)$ in the mean field approach. The physical picture of the above is thus:- The volume of the material will change such as to minimise the magnetic free energy coming from the increase of exchange $J$.

If we have a well defined local moment system with a non-spherical charge distribution, i.e. a non $s$ state rare earth, then one may consider Fig. 2.16. as a representation of the crystal field induced magnetovolume effect.
Fig. 2.16. Schematic representation of the crystal field magnetovolume effect. Full lines indicate the low temperature charge distribution, dotted lines represent the high temperature equivalent.

With reference to Fig. 2.16, at low temperatures the negatively charged lobes of the rare earth site will point toward neighbouring ion sites. Therefore by Coulombic interaction the system will contract. At higher temperatures the rare earth site will occupy all crystal field states, including those which are not in direct alignment with the nearest neighbour sites, thus the attraction between the rare earth and the neighbour sites will be reduced. The effect being that the neighbours will occupy positions as to increase the volume of the system. This effect therefore leads to a positive thermal expansion contribution from the magnetic system [19].
2.6.1.2. Spontaneous magnetostriction: Itinerant electron picture.

We shall now discuss the spontaneous magnetostriction arising from band electrons.

Considers a simple band picture of a ferromagnet above $T_c$, Fig. 2.17. In this configuration the number of + spins is equal to the number of - spins, as the systems orders the bands become polarised, as to increase the population of the + spin subband. This in turn reduces the population of the - spin subband. The transition between electron states continues until the kinetic energy of the system becomes balanced with the increase of magnetic energy. The increase of kinetic energy can be accommodated by an increase in bandwidth, in so doing the interatomic separation will decrease, and a net spontaneous magnetostriction will be observed.

This explanation of the magnetostriction of band electrons, is in the framework as put forward by Stoner [21]. The Stoner theory assumes that $m = \langle m \rangle$

If one considers the increase in kinetic energy of the electrons $\Delta E_k$ and takes only terms dependent on $\Delta E_s$ and $\omega$, and further neglecting any volume dependence of the exchange integral, the magnetic energy of the system is [16] :-

$$E = \Delta E_k + \frac{\kappa \omega^2}{2} \quad (2.105)$$

Where $K$ is the compressibility and,

$\Delta E_k$ represents the magnetic energy gain and $\frac{\kappa \omega^2}{2}$ represents the elastic energy. Assuming the approximations to be correct then the spontaneous magnetostriction is proportional to $\Delta E_k$ which in turn is proportional to $M^2$ as in the local moment case, therefore we have:-

$$\omega = a \kappa \langle M^2 \rangle (T) \quad (2.106)$$
Fig. 2.17. Schematic representation of the band mechanism of spontaneous magnetostriction. i. The paramagnetic state. ii. The ferromagnetic state, large kinetic energy, small volume. iii. Ferromagnetic, large volume, small kinetic energy.

At this point we should note the inadequacies of the Stoner model of spontaneous magnetostriction, the essence of which being the assumption that the moment disappears at $T_C$. Hence the spontaneous magnetisation of the system disappears also, therefore the spontaneous magnetostriction is zero above $T_C$ Fig. 2.18. This however is not always the case.

Fig. 2.18. Schematic representation of the moment ($m$) and magnetisation ($M = Nm$, where $N$ is the number of atoms per unit volume) of the band model (a), and the local moment model, (b)

The assumption that the atomic moment collapses above $T_C$ is not necessarily correct, neutron scattering measurements have shown there to be a moment above $T_C$ for FeNi Invar alloy [22]. This would suggest that some itinerant systems have non zero moment at high temperature $T > T_C$. 

60
A model has been proposed by Moriya [23], that assumes that spin fluctuations in the system are such as to cause a finite moment to remain above $T_C$. One should stress that this model only applies to weakly magnetic itinerant magnets. A full description of the model may be found in [24]. The results of the theory that are pertinent to this discussion are now presented, and compared to results from the theory of Stoner.

At $T_C$ one may define:

$$\omega_m(T_C) = -\frac{2}{5} \alpha \xi [M(0)]^2 \tag{2.107}$$

Where $M(0)$ is the magnetisation at 0K, and can be deduced from the Arrot plot (The plot of $M^2$ as a function of $H/M$)

One may calculate [24] the correct value for the square of the magnitude of the spin fluctuation $S^2_L$, further one may assume a correlation between $S^2_L$ and the magnetisation of the system below $T_C$ and thus relate the spontaneous magnetostriction to the magnetic moment in the material.

At $T<T_C$:

$$\omega_m(T) = -\frac{2}{5} \alpha \xi \left\{ [M(0)]^2 - [M(T)]^2 \right\} \tag{2.108}$$

For $T>T_C$:

$$\omega_m(T) - \omega_m(T_C) = \frac{3}{5} \frac{\alpha \xi}{\chi(T)} \tag{2.109}$$

$\chi(T)$ is the uniform magnetic susceptibility.

Since $1/\chi(T)$ increases with temperature above $T_C$ one obtains a positive contribution to the thermal expansion from the magnetic system, which as a function of temperature has the form:

$$\omega_m(T) = \frac{3}{5} \frac{\alpha \xi}{g \frac{1}{\chi(T)}} \left\{ \frac{1}{\chi(T)} - \frac{1}{\chi(0)} \right\} \tag{2.110}$$

Where $g = F_{v}[\rho_{eff}]^3$ is the coefficient of $M^4$ in the Landau expansion of the free energy.
The positive contribution to the thermal expansion given by this formalism is in contrast to earlier work based on the Stoner theory which neglect spin fluctuations, in this framework for $T < T_C$:

$$\omega^\text{Stoner}_m(T) = -\alpha \kappa \left\{ (M(0))^2 - (M(T))^2 \right\}$$  \hspace{1cm} (2.111)

and for $T > T_C$

$$\omega^\text{SW}_m(T) - \omega^\text{SW}_m(T_C) = 0$$  \hspace{1cm} (2.112)

\textbf{Fig. 2.19.} \textit{i.} The schematic representation of the moment and magnetisation in the framework of the spin fluctuation theory \textit{ii.} The predicted temperature dependence of the spontaneous magnetostriction of the Stoner and spin fluctuation theory[19].
2.6.2. Forced magnetostriction.
The forced magnetostriction is the dilatory response of a material when placed in an external magnetic field. The forced magnetostriction considered here may be considered as Joule magnetostriction, that is to say the volume of the sample remains constant.

For a single crystal sample the forced magnetostriction is found to be strongly anisotropic, one may expect such a result, since the magnetisation of the material depends upon the magnetocrystalline anisotropy energy.

Since the spontaneous magnetostriction is a function of the magnetisation of the material, one may note that the observed forced magnetostriction will also be a function of magnetisation of the sample.

Fig. 2.20. The dilatory effect of forced and spontaneous magnetostriction on a spherical sample.
The physical reasons why the lattice should respond to an external magnetic field are identical to those described in the previous sections, that is to say the lattice subsystem will suffer a volume change in order to balance the energy gained by the magnetic subsystem from the magnetic field.

The spontaneous magnetostriction is:

\[ \omega = a \kappa \langle M^2 \rangle \]  

(2.113)

By differentiating with respect to \( H \) one obtains the relationship for forced magnetostriction \( \frac{\partial \omega}{\partial H} \).

\[ \frac{\partial \omega}{\partial H} = 2aM \frac{\partial M}{\partial H} \]  

(2.114)

Since the susceptibility is defined as \( \chi = \frac{\partial M}{\partial H} \) the forced magnetostriction becomes:

\[ \frac{\partial \omega}{\partial H} = 2aM \chi \]  

(2.115)

Thus one may determine the magnitude and sign of the magnetovolume coupling constant from the measurement of the forced magnetostriction and the susceptibility.
2.7. Summary.

A phenomenological explanation of the volume expansion of an ionic material has been presented. Within a thermodynamic framework the volume expansion has been shown to be a function of the ratio of the free energy $F$ at two distinct temperatures.

The physical interpretation of the Grüneisen parameter has been discussed. The relationship between specific heat, volume expansion and bulk modulus has been presented. The quasiharmonic approach has been discussed as a theoretical approach that allows the coupling of lattice and electronic degrees of freedom. Following on from this one may then state that the low temperature volume expansion has contributions from the lattice and the conduction electrons in the material.

The contribution to the volume expansion from magnetic effects have been discussed, in the low temperature limit.

The nature of magnetism has been discussed. The origin of the atomic moment has been presented, together with a discussion of the bulk properties of materials exhibiting dia-, para-, ferro-, antiferro-magnetism.

The contributions to the magnetic free energy have been presented and discussed.

The temperature dependence of the magnetisation has been discussed in the mean field framework proposed by Weiss. To this end results from both ferromagnetic materials and antiferromagnetic materials have been presented.

The phenomenon of magnetostriction has been discussed, for both local moment and itinerant electron systems. The forced magnetostriction has been similarly treated.
2.8. References.

Chapter 3. Instrumentation.

3.1. Introduction.

The experimental physicist relies upon devices with which to perform experiments. If one wishes to perform an experiment, and to make some conclusions from that experiment, two basic items are required, in order that one may argue that the conclusions drawn are scientifically correct:-

1. A sample of high quality on which to perform the experiment.
2. A device that will measure the required parameter to a high degree of accuracy.

The first is often not as simple as one may expect, since the production of quality samples relies on both the quality of the starting materials i.e. materials with a low concentration of impurities, and the quality of the equipment used to make the samples. One must estimate the concentration of impurities introduced into the sample during the production process.

The second is also not simple, since the quality of data from an experiment relies on the design and operation of the instrument (as well as the sample), which by definition is also a function of quality.

Hence in order to perform a valid experiment, which produces data that one may argue as being correct is essentially a function of quality, both of the sample and of the instrument used.

The purpose of this chapter is to explain and describe the design, optimisation and operation of instruments used to evaluate the thermal expansion and forced magnetostriction of intermetallic alloys.
The chapter may be summarised as follows:-

1. To introduce various techniques available to the experimental physicist for the evaluation of the sample dilation $\delta l$, in order that one may determine the thermal expansion of a material as a function of temperature.

2. To describe in detail the technique of high resolution capacitance dilatometry, and how one may employ such a method to measure the thermal expansion, and the forced magnetostriction of a material, with a very high resolution.

3. To describe the design and operation of both, a low temperature cryomagnet dilatometer system (LTDS), and a high temperature dilatometer system (HTDS).
3.2. Introduction to dilatometry.

Dilatometry is essentially, the investigation of the response of the sample dimension, nominally length change, as a result of a perturbation of the sample environment. The perturbation may be either sample temperature, or applied magnetic field. The measurement of the sample response leads to the evaluation of the thermal expansion and the forced magnetostriction respectively.

An experiment that determines the change in length of the sample due to a change in temperature is a direct probe of the lattice response. The response of the lattice is a result of a change in free energy caused by a change in temperature. Magnetostriction is a direct probe of the lattice response to a change of the free energy due to a change in applied magnetic field. Further one may also evaluate the order of magnitude to which the magnetic lattice system (spins) is coupled to the structural lattice.

Dilatometry has been of scientific interest since the late 1800’s. The first dilatometer used an optical method to measure magnetostriction. The discovery of magnetostriction in iron, by Joule (1842) [1], was the catalyst for experimental investigations of length change using dilatometers.

The first reported dilatometer used for the specific purpose of evaluating the thermal expansion of a material was the “Henning tube” (Henning 1907), the instrument measured the sample expansion relative to a fused silica tube.

If one wishes to determine the thermal expansion of a sample, it is of some use to evaluate the order of magnitude of length change involved in a typical experiment.

A general rule is that a material will undergo a change in length of approximately 1% from 0K to the melting point, i.e. the order of magnitude for $\delta l/l_0$ is therefore 0.01 (where $l_0$ is the original sample length). Thus if one measures a sample with a nominal length of 20mm, the overall change in length one may expect from 0K to the melting point is $\approx$200µm. If one considers a typical melting point of $\approx$1000K, this change in length
amounts to a length change of $\Delta l/\Delta T = 2 \times 10^{-7}$ mK$^{-1}$ or $\alpha = 2 \times 10^{-5}$ K$^{-1}$

Where $\alpha$ is the coefficient of linear thermal expansion.

However as one reduces the change in temperature the resulting thermal expansion $\delta l/l_0(T)$ is much smaller than the estimate given above. The nominal length of the sample is also a parameter that must be considered when evaluating the required resolution of an instrument, since a larger sample will produce a larger dilation for the same $\Delta T$. Further to these constraints one must also consider the theoretical nature of the thermal expansion at low temperatures. At low temperatures the thermal expansion of a non metallic material varies as a power of absolute temperature as a result from excitations of the phonon modes in the lattice. Thus as one reduces the temperature the observed expansion is reduced for the same $\Delta T$, since phonon modes are frozen out below $\theta_D$. For a metallic sample the electronic contribution has to be considered. The absolute expansion is scaled up by a term linear in absolute temperature, this contribution is due to the movement of "free" electrons at the Fermi surface. Hence one obtains the expression for the thermal expansion of a metal (chapter 2): $aT + bT^3 = \alpha$, for $T << \theta_D$.

In an experiment the measured parameter is usually the average $\alpha(T)$ ($\bar{\alpha}$) evaluated from a set of discrete values of $\delta l(T)$ hence.

$$\bar{\alpha} = \frac{1}{l_0} \frac{\delta l}{\delta T} \quad (3.1)$$

One may define a value of $\alpha$ for a typical metal at room temperature to be $\approx 10^{-5}$ K$^{-1}$, such that if the temperature change $\Delta T = 1$K, and one has an instrumental resolution of $\delta l/l_0 \approx 10^{-7}$, the evaluation of the thermal expansion is accurate to $\approx 1\%$. One may say therefore that the same accuracy can be achieved by reducing the instrument resolution, and increasing the overall length of the sample ($l_0$), or by increasing $\Delta T$. However if $\Delta T > 5\%$ of $T$, then one must correct for the temperature interval in order to evaluate $\alpha(T)$ [2].

As stated previously the low temperature thermal expansion is reduced, such that for $(\theta_D / 20) \approx T$, the thermal expansion $\alpha \approx 10^{-7}$. In order to
maintain the required accuracy for $\alpha(T)$ one must increase the experimental resolution, $\delta l/l_0 \approx 10^{-9} \rightarrow 10^{-10}$, this corresponds to a length change resolution of $\delta l \approx 20 \text{pm} \rightarrow 2 \text{pm}$, respectively for a 10mm sample. Hence in order to evaluate the low temperature thermal expansion one requires an instrument capable of resolving an absolute change in length of the order of pm ($10^{-12}$m).

It is clear that, as in thermal expansion, the measured experimental parameter for magnetostriction $\delta l(H)$ is an averaged value, evaluated from a discrete set of values of $\delta l(H)$. The same explanation of sensitivity, resolution and accuracy hold for magnetostriction, as discussed previously.

However it is somewhat more difficult to apply the same rational for an estimation of the order of magnitude of length change involved in a typical magnetostriction experiment. The change in length as a function of applied field $\delta l(H)$, depends upon not only, the applied magnetic field but also the sample temperature, and more importantly the magnitude of the magneto-coupling constant, that is the degree to which the spin is coupled to the lattice. This parameter governs the amount of lattice distortion observed for an applied field.

One may however estimate that the maximum observable magnetostriction possible before sample fracture is $\delta l/l_0 \approx 10^2$ (the largest observed magnetostriction being $\delta l/l_0 \approx 10^{-2}$ for the rare earth Laves phase compound TbFe$_2$,) whilst the smallest observed magnetostriction is $\delta l/l_0 \approx 10^{-9}$ [3].

It is poignant to note that if one measures the thermal expansion of a material, that is either in a magnetically ordered state, or which undergoes a magnetic phase transition one intrinsically measures the spontaneous magnetostriction, that is the response of the lattice to the magnetic phase transition. Further one may isolate the "spontaneous magnetostrictive component" of the thermal expansion, by either measuring an isostructural compound that is nonmagnetic and then performing a subtraction of the two data sets, or by a theoretical calculation of the "lattice" component of the magnetic sample followed by a similar subtraction. The process of
such data analysis relies on the possibility that the physical processes
governing the lattice expansion, and the spontaneous magnetostriction are
independent of each other, which may not be the case for all systems.

3.2.1. Methods for evaluation of $\delta l$.

It is clear that since the scientific community has been interested in the
evaluation of both, the thermal expansion and the magnetostriction of
materials, there have been various experimental methods developed to
obtain such data. As is usual, some techniques have become more
popular than others, be it for reasons of sensitivity, or ease of use.
Before an evaluation of the various methods used to measure sample
dilation one may state that all methods may be used to measure both
thermal expansion and magnetostriction of a material. Further one may
adapt most of the methods described in the subsequent sections to
measure any type of sample, i.e. polycrystalline, single crystal, or
amorphous systems. However one must again state the importance of
sample quality, and quality of sample preparation.

There are two types of dilatometer available:-

1. An absolute device, where the dilation of the material is
evaluated directly.

2. A relative device, where the sample dilation is measured
relative to a standard material. The actual sample dilation
is calculated by data analysis.

Further to the basic two types of dilatometer there are three basic methods
available which one may utilise to measure the sample dilation.
The three basic methods are summarised as:-

1. Optical methods, such as interferometry.
2. Electrical methods, such as strain gauge extensometers,
electrical capacitance.
3. Diffractive techniques, i.e. X-ray and neutron diffraction.

A brief description of these methods is now given.
3.2.2 Optical methods.

The basic principle underlying optical methods for the evaluation of thermal expansion, and magnetostriction, is that of interferometry.

In essence an interferometer system is constructed by either; the use of the sample (Highly polished) as a mirror; or by a system of interconnecting levers that translates the dilation of the sample to an interferometer mirror, or to an etalon.

The dilation of the sample is therefore observed as movement of interference fringes, this response can thus be measured either visually or by the use of a photocell system.

The earliest example of the use of an optical interferometer for measurement of sample dilation, is that of by Fizeau (1864) [4]. The Fizeau interferometer utilises a highly polished sample placed upon an optically flat glass plate. One may adjust the angle between the specimen face and the glass plate such that when the system is illuminated with monochromatic light a set of interference fringes is produced. Hence if one monitors the movement of the fringe pattern as the system temperature is changed one may calculate the sample dilation, and thus the thermal expansion of the material.

The resolution of this type of interferometer design lies with the resolution with which one may measure the movement of the fringe pattern.

The basic optical detection limit is \( \approx 100^{th} \rightarrow 1000^{th} \) of a fringe, hence a basic system resolution of \( \delta l \approx 1 \rightarrow 10 \text{nm} \) is achievable.

Therefore resolution of the order of \( \delta l/l_0 \approx 10^{-7} \rightarrow 10^{-9} \) is achievable using the optical method. The system relies on the quality of the optical surfaces, i.e. the resultant surface roughness of the sample after polishing, and the stability and wavelength \( (\lambda) \) of the light source.

Advances in laser technology have therefore improved the stability of interferometer systems.

Resolutions of \( \delta l/l_0 \approx 10^{-9} \) have been achieved using optical systems, such systems are based upon either, a Fabry-Perot multiple pass etalon, or an optical amplifier system [5,6].
3.2.3 Electrical methods.

Methods of determining the sample dilation electrically can be categorised as follows:

1. Strain gauge extensometers.
2. Capacitance systems.
3. Inductance systems.

3.2.3.1 Strain Gauge Extensometers.

The strain gauge technique relies upon the nature of the resistance of a material when it is subjected to strain. When a thin cross section of a metallic material is strained, the length is increased, and the cross section is reduced, this has the net effect of an increase in electrical resistance. It is this basic principle that allows one to measure the sample dilation with a strain gauge. The sensitivity of the technique can be increased by the design of the strain gauge itself. If the gauge is fabricated with several small cross section wires in series, the overall change in resistance will be increased per unit sample dilation.

The overall advantage of the system is the ease of implementation, the only detection electronics required is a sensitive resistance bridge. The sensitivity of the overall system is limited by the resolution of the resistance bridge, and the gauge factor \( GF \) i.e. the relative change of gauge length as a function of relative change in resistance.

\[
\frac{\delta l_{\text{Gauge}}}{l_{\text{Gauge}}} = GF \frac{\delta R}{R}
\]  

(3.2)

Where \( GF \) is the gauge factor, \( R \) is the resistance (\( \Omega \)) and \( l \) is the Length (m).

It is clear that the measured \( \delta l/l_0 \) is that of the gauge, and not the sample, hence the system relies on an adhesive that translates the strain of the sample to the gauge. Hence the system has the disadvantage of being reliant on the adhesive used. The technique is further limited by the operating temperature range of the adhesive.

Advantages of the strain gauge technique is the versatility, and wide range of strain gauge design. Gauges that measure both the transverse and longitudinal strain are readily available from gauge manufacturers.

The optimised resolution of the strain gauge technique is \( \delta l/l_0 \approx 10^{-6} \) [4].
3.2.3.2 Capacitance systems.

One may measure the dilation of a sample by using a system that allows the sample dilation to alter either, the spacing, or the effective area of a parallel plate capacitor.

Essentially the method is described by the simple relationship between, electrical capacitance (C), effective area (A) and electrode separation (d).

\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d} \] (3.3)

Where \( \varepsilon_0 \) is the Permittivity of free space and \( \varepsilon_r \) is the relative permittivity of dielectric material.

If one uses the effective area as a measure of the sample extension, the electrode separation is maintained at a constant value, the transducer system is linear with sample dilation. However if one utilises the dilation of the sample to alter the separation of the electrodes the transducer system becomes extremely sensitive as the electrode separation is reduced.

The sensitivity and resolution of the capacitance method is essentially a function of the sensitivity and resolution of the capacitance measurement system, and as such improvements in the techniques used to measure changes in capacitance have dramatically improved the resolution and sensitivity of the capacitance method.

Generally the more popular technique for the measurement of sample dilation using the capacitative method is the variable gap technique, since it affords far greater sensitivity and resolution.
3.2.3.2.1 Two terminal resonant methods.
The first variable gap dilatometers (c.1955) used the two terminal capacitance technique. The capacitance transducer is incorporated into a resonating LC circuit. The technique relies upon the tracking of the resonant frequency, in order to determine the sample dilation [7]. This technique has the inherent problem of the simultaneous measurement of the circuit lead capacitance. It is therefore clear that problems will occur if the lead capacity changes, e.g. due to thermal drifting of the circuit. However this basic method of capacitance dilatometry already gives a resolution of $\frac{\delta l}{l_0} \approx 10^{-7}$.

Before a discussion of the more usual technique of the 3 terminal capacitance dilatometry, it is poignant to note that the resonant frequency tracking technique has also been applied to a microwave cavity oscillator [8]. The microwave cavity oscillator operates in the TEM mode at 9.5GHz. The sample is mounted in the lower part of the resonator. Changes in the length of the sample alter the spacing between the central conductor and the lower plate of the resonant cavity, thus the resonant frequency of the system is altered. The change in frequency is tracked using the heterodyne frequency modulation technique. The system has a useful resolution of $\frac{\delta l}{l_0} \approx 10^{-7}$.

3.2.3.2.2 Three terminal methods.
The three terminal technique is by far the most popular method used for high resolution dilatometry measurements.

The technique relies on work by Thompson (1958) [9] on the development of ratio transformer capacitance bridges. The design and operation of such devices will be discussed later.

The ratio bridge allows a three terminal connection to the capacitor, thus the lead capacitance is negated and does not effect the measured capacitance.

The earliest bridges gave a usable capacitance resolution of $10^{-6}$ pF. More modern devices, coupled with lock-in detection techniques give a capacitance resolution of $10^{-7}$ pF [10,11].
3.2. Introduction To Dilatometry.

The stated resolution in capacitance measurement gives a usable instrument resolution of \( \delta l/l_0 \approx 10^{-10} \).

Such a high resolution system lends itself to the measurement of both thermal expansion, and magnetostriction at very low temperatures, \( T \ll T_D \) (The technique can be used from mK to well above room temperature) with high accuracy and high resolution.

Experimental problems using such a system relate to:-

1. Sample mounting and cell design: The design of the cell and the method of mounting the sample is critical, as one must avoid "stray" thermal expansion that may arise from the use of adhesives, and dissimilar materials.

2. Detection system stability: One should note that the ratio bridge system relies on a standard capacitance/s for operation and calibration. Any drift in calibration will translate directly to the quality of the data obtained. Hence the system must be designed in such a manner as to minimise such drifts.

A full description of the three terminal capacitance dilatometry technique will be given in the next section.

3.2.3.3. Inductive systems.

The inductive method of dilatometry operates by the dilation of the sample being transmitted to the inner coil of a mutual inductance. The inductance of the detector varies linearly as a function of displacement. The resolution of this method depends upon the resolution of the differential transformer. Linear Variable Differential Transformers (LVDT) with resolutions below the micron level have been available since the early 1960's. The inductive method allows a resolution of \( \delta l/l_0 \approx 10^{-5} \) to be achieved if an optimised system is used.
However a system utilising a LVDT is very susceptible to applied magnetic fields, and thus can not be used to measure magnetostriction. Care must be taken to avoid contamination of the LVDT with ferromagnetic particles, and to ensure that the detector is situated away from the stray field of any ferromagnetic samples.

Although systems utilising the LVDT are widely available commercially the technique does not lend itself to a research environment.

3.2.4 Diffractive methods.
If one can measure the lattice parameter of a material at two different temperatures it is clear that the thermal expansion co-efficient may be calculated. One clear advantage of this method is the absolute nature of the data obtained. Further the diffractive technique is the only method that allows one to examine the sample on a microscopic level.

There are two separate methods one may use to evaluate the lattice parameter of a sample:—

1. X-ray diffraction.

Of the two methods X-rays provide the most convenient method available, since large scale experimental facilities are not required for the production of X-rays.

3.2.4.1 X-ray diffraction.
The use of X-ray diffraction for the characterisation of samples is common, since it provides a convenient "in house" method of structure determination.
A standard X-ray diffractometer is capable of resolving $\delta a/a \approx 10^{-5}$. Hence one may utilise such a system to evaluate the thermal expansion of materials at low temperatures. One is limited by sensitivity to temperatures above $\approx 0/10$ i.e. $T \geq 15$~20K. Improved sensitivity can be obtained by using an oscillating back reflection technique, although the resolution is
only increased by a factor of 10 and one requires high quality single crystal samples [12].

3.2.4.2 Neutron diffraction.
Although the technique of neutron diffraction is powerful, resolution in terms of resolving lattice expansion is low.
The two high resolution instruments in Europe are:-

1. The diffractometer D2B ILL Grenoble France. $\delta a/a \approx 10^{-4}$ [13].

2. HRPD (High resolution powder diffractometer)Isis Oxon. UK. $\delta a/a \approx 10^{-4}$ [14].

Thus one must use such instruments for experiments which are better suited to the neutron technique e.g. magnetic structure determinations, than for the measurement of thermal expansion and magnetostriction.
3.2.5. Types of dilatometer.
It is convenient to describe a dilatometer in terms of the method with which the sample dilation is measured. As stated previously two basic types of dilatometer exist.

3.2.5.1 The absolute dilatometer.
It is clear that the only method that allows one to evaluate the sample dilation directly, is that of diffraction. Such methods are intrinsically absolute.

All other methods described can be made to operate in an absolute manner. If one wishes to measure the absolute sample dilation one must essentially satisfy two conditions:-

1. Thermally isolate the sample from the dilatometer system, or sample cell. Such isolation can be achieved by the use of low thermal conductivity spacers.
2. Heat the sample directly, i.e. one must not rely on the thermal conductivity of the sample cell to heat the sample. Thus one must physically attach a heater to the sample itself in order to satisfy this constraint.

The nature of operation of an absolute system is therefore achieved, if the sample is heated directly, and isolated in such a manner as to negate heating of the dilatometer system, therefore any dilation measured can be attributed to the sample.

It is obvious that such a system is difficult to realise, since it is both difficult to remove thermal conduction to the dilatometer system, and therefore to physically heat only the sample. (This second constraint is essentially reliant on the sample size. It is obviously quite difficult to attach a heater to a small sample).
3.2.5.2 The relative dilatometer.

The relative dilatometer operates by measuring the sample dilation relative to the dilation of the dilatometer system itself, hence the experimentally measured sample dilation includes a component which is determined by the characteristic expansion of the dilatometer. Thus one may calculate the actual sample dilation by removing the dilatometer component using a data analysis routine.

The relative dilatometer allows a much greater flexibility for both sample size, and dilatometer design.

In order that a relative dilatometer will allow an accurate measurement of sample dilation the dilatometer must be constructed from a material which has a simple characteristic thermal expansion, and which is highly reproducible. Further the material used must have accurate thermal expansion data available over the temperature range of interest, in order that one is able to calculate the actual thermal expansion of the sample.

The relative type of dilatometer negates the problems associated with the absolute method of measurement, since one neither has to thermally isolate the sample, or heat the sample directly. However there are certain problems associated with the relative method of measurement.

One requires the system to be fabricated from a material that is well characterised by previous measurements. Further one must fabricate the entire cell from the same material so as to minimise cell contribution from different materials (The cell effect).

If a relative dilatometer is used the method of sample attachment becomes an important factor, since sample fixation may introduce extra expansion into the system that may not be reproducible, e.g. the thermal expansion of an adhesive.

*In short:*

\[ d_{\text{meas.}} = d_{\text{sample}} \]

*For an absolute dilatometer.*

\[ d_{\text{meas.}} = d_{\text{sample}} + d_{\text{system}} \]

*For a relative dilatometer.*

(3.4, 3.5)
3.2.6. Summary.

If one considers the various methods available, with which to measure small length changes, it is clear that the method of capacitance dilatometry has one of the highest resolutions available (Table 3.1.).

If one wishes to accurately measure the thermal expansion at very low temperatures, one must use a technique that offers the highest resolution.

<table>
<thead>
<tr>
<th>Method of measurement.</th>
<th>Resolution of measurement. ($\delta l/l_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron diffraction.</td>
<td>$\approx 10^{-4}$</td>
</tr>
<tr>
<td>X-Ray diffraction.</td>
<td>$\approx 10^{-5} \rightarrow 10^{-6}$</td>
</tr>
<tr>
<td>Optical Interferometry.</td>
<td>$\approx 10^{-7} \rightarrow 10^{-8}$</td>
</tr>
<tr>
<td>Optical Amplifiers.</td>
<td>$\approx 10^{-9}$</td>
</tr>
<tr>
<td>Strain gauge extensometers.</td>
<td>$\approx 10^{-6}$</td>
</tr>
<tr>
<td>Inductive (LVDT) based dilatometers.</td>
<td>$\approx 10^{-8}$</td>
</tr>
<tr>
<td>Two terminal capacitance.</td>
<td>$\approx 10^{-7}$</td>
</tr>
<tr>
<td>Three terminal capacitance.</td>
<td>$\approx 10^{-9} \rightarrow 10^{-10}$</td>
</tr>
</tbody>
</table>

Table 3.1. The various methods for measurement of small length changes, and the associated resolutions.
Further to the question of resolution one must also consider the ease of application of the technique. Although capacitance dilatometry does not offer a true absolute measurement, as with diffractive methods, such a method may be improvised by design. Further the capacitance technique offers simple design criteria. The method may be easily applied to both low and high temperature instruments. The design of complex optical systems is negated when using an electrical technique, as is the problem of irreproducibility due to adhesives used to attach strain gauges to the sample.

The ease of use, and the high resolution of the capacitance method thus allows one to measure both the thermal expansion and magnetostriction over a wide temperature range, and over a large range of applied magnetic fields.

It is for these reasons that the three terminal capacitance method was chosen for the dilatometers that have been used in this investigation.
3.3. Three terminal capacitance dilatometry.

3.3.1. Introduction.
As stated previously the method of three terminal capacitance dilatometry offers one of the highest resolutions possible, for the measurement of small length changes.
The reason why the technique offers such a high resolution is due to the work of Thompson in the early 1960’s. His work resulted in the optimisation of the method for measuring small changes in electrical capacitance using a transformer ratio arm capacitance bridge [9].
Such a bridge allows one to use a three terminal connection to the measured capacitance, as opposed to a two terminal connection. This technique allows the parasitic capacitance of the connections to the transducer to be eliminated from the measurement circuit.
One may also consider further advantages of using a capacitance based transducer:-

1. A perfect capacitor dissipates no power. Thus one may apply high voltages to the device without generating unwanted heat in the application. One should note that at high voltages the signal to noise ratio (S/N) is reduced.

2. A perfect capacitor generates no noise, unlike resistive elements which are limited by thermal noise.

3. A perfect capacitor is linear with applied voltage, unlike inductive systems which require some degree of linearisation.
3.3.1. Relationship between $C$ and $d$.

It is clear that capacitance measurement offers a high resolution method for the evaluation of the capacitor gap. Hence one may exploit such a method to measure small changes in length. If one uses a system where the change in length to be measured is coupled to a freely moving capacitor electrode, such that:-

$$\delta l_{\text{sample}} = \delta l_{\text{capacitor}} \quad (3.6)$$

The relationship between the capacity $C$, and the electrode separation $d$, for a pair of electrodes (ignoring edge effects) is:-

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \quad (3.7)$$

If one then differentiates with respect to $d$, one obtains a relationship for the sensitivity for measuring $\delta C$, for a given change in electrode separation $\delta d$.

$$\frac{\delta C}{\delta d} = -\frac{\varepsilon_0 \varepsilon_r A}{d^2} \quad (3.8)$$

The capacitance varies as $1/d$, and the sensitivity varies as $1/d^2$. Hence a lower value of electrode separation produces a dramatic increase in sensitivity.

In order to exploit the technique one requires:-

1. A sufficiently small initial electrode separation in order to obtain:-
   i. A measurable initial capacitance.
   ii. A substantial change in capacitance $\delta C$ for an associated $\delta d$

2. A device that is able to detect as small a $\delta C$ as possible.

3. A plane plate capacitor using a guard ring, in order to obtain better $E$ field homogeneity.
if one experimentally satisfies the above criteria, one maximises the resolution of the capacitance detection system, and hence that of the dilatometer system.

The work by Thompson on optimisation of the ratio arm transformer bridge, allows a detection of capacitance of approximately one part in $10^7$ (i.e. aF resolution)

3.3.2. Principles of the transformer ratio arm bridge.

The principle of the ratio arm capacitance bridge is analogous to that of a simple Whetstone bridge. The ratio between the capacitance of a standard (contained within the bridge) balance capacitor, and the experimental capacitance are compared. Hence when the two capacitances are equal the bridge is at the null position. This describes the simple resistive ratio arm bridge, (Fig. 3.1). One may balance the bridge by the use of a variable capacitor. Although one may use such a bridge over a wide range of frequencies and capacitances the resolution seldom exceeds 0.1%.

Fig. 3.1. A simple schematic of a ratio arm bridge.

The use of transformer ratio arms in the bridge system increases the accuracy and resolution of the system (over a resistive ratio arm bridge) to $\approx 10^{-7}$ (optimised)
The ratio arms do not suffer from ageing effects, temperature drift or voltage effects. Hence the transformer ratio arms are found to be extremely stable.

The transformer ratio arm bridge consists of a toroidal core made from a high permeability material with two sets of secondary turns, one set excites the "standard" side of the bridge, the second set excites the experimental side of the bridge. If one considers all the magnetic flux to be confined to the core, then the ratio of the open circuit voltages on the secondary turns is equal to the ratio of the number of turns. One may alter the ratio by the use of taps on the secondary turnings. With the ratio fixed the voltage induced on the secondary turnings is highly invariant.

Fig. 3.2.a. A simple schematic of a typical ratio transformer bridge.

Fig. 3.2.b. The ratio bridge circuit schematic showing the parasitic capacitance components.
If one considers Fig. 3.2.a then it can be seen that the secondary turns act as the ratio arms of the capacitance bridge, with the standard capacitor $C_s$ and the experimental capacitor $C_x$ forming the other two arms.

Hence at the balance condition:

$$V_s \cdot C_s = V_x \cdot C_x \Rightarrow \frac{C_x}{C_s} = \frac{V_s}{V_x} = \frac{N_s}{N_x}$$

(3.9)

The balance condition is not affected by the parasitic capacitances connected between the $+Ve (H)$ and $-Ve(L)$ side of $C_x$ and $C_s$ to the ground terminal $G$ (At the junction of the ratio arms)

The parasitic capacitances L-G shunt the detector, whilst the parasitic capacitances H-G are across the secondary turns of the transformer. If one considers the transformer as an ideal system then the current drawn by H-G parasitic capacitances will not affect the voltages $V_s$ and $V_x$.

The point $G$ is a guard point (earth). Therefore $C_{L-G}$ and $C_{H-G}$ will not affect the measured capacitance.

The major advantage of the three terminal bridge is therefore, that the lead capacitances to $C_x$ are negated, and only act to shunt the detector.

Further one may use a guard electrode around one, or both capacitance electrode/s, also connected to the bridge guard $G$, in order to improve the $E$ field homogeneity between the electrodes. The capacitance of the guard ring does not contribute to the measured capacitance.

The accuracy, and stability of the bridge system are a consequence of the stability of the ratio arms of the transformer.

There are three methods of achieving the balance condition, depending upon the design of the capacitance bridge system.

The three methods affect only the standard side of the bridge:

1. **The fixed ratio method.** The system is balanced using two equal ratio arms, one each for the unknown side and the standard side of the bridge. A variable standard capacitor is used to balance the system.

2. **The multiple divider, single fixed standard method.** The standards of the bridge consists of 2 sets of inductive voltage dividers and a single fixed standard capacitor.

3. **The single divider, multiple fixed standards method.** The standards of the bridge consist of a single inductive voltage divider (direct taps on
the secondary turns of the transformer) and multiple fixed standard capacitors.

3.3.2.1 The relationship between detector current and off balance voltage.

If one considers the impedances, of the generator G, the bridge transformer T, and the detector D, to be low, and that the parasitic capacitance's $C_{p1,2,3}$ are high, then the current passing through the detector is given by:

$$I_D = 2 \pi f_i V(C_1 - C_2) \cos(2 \pi f_i t)$$  \hspace{1cm} (3.10)

The voltage on each of the equal transformer arms is $V(t) = V_0 \sin(2\pi f_i t)$

In order to detect the null position one must employ phase sensitive detection.

If one considers the detector current $I_D$ and a reference signal $V_{ref}$, which is in phase with the excitation voltage, the following relationships exist:

$$I_D + \pi/2 \propto (C_1-C_2)$$  \hspace{1cm} (3.11)

$$I_D \propto (g_{12}) \quad g_{1,2} \text{ is the conductance associated with } C_{1,2} \quad (3.12)$$

Hence one may therefore use such a system to evaluate the conductance of the experimental capacitance by using a zero phase shift, and by introducing a conductance standard in the bridge circuit.

One must now consider the nature of the three terminal connection.

The electrodes surrounding the $V+$, and $V-$ (The outer conductor of a coaxial cable) electrodes are connected to the ground point G of the bridge. Hence the capacitance of these leads is not measured. Thus the capacitive contribution of the leads is negated.

![Fig. 3.3. Schematic diagram of a three terminal capacitor and guard ring.](image)
3.3.3 Considerations for the three terminal capacitance dilatometry technique.

There are several factors that limit the performance of the three terminal capacitance measurement technique.

3.3.3.1 Stability of the bridge, and the detection system.

The stability of the bridge is intrinsically limited by two factors:

1. The stability of the standard "balance" capacitance/s contained within the bridge system. Modern capacitance bridge systems contain several standard capacitances, which balance against the experimental capacitance in order to measure several ranges of $C_{\text{exp}}$. The stability of the standards is a function of system temperature, since the thermal expansion of the material used to construct the standard will affect the value of $C$. Modern bridges contain some type of temperature controlled environment for the housing of the standard capacitances, and are subject to strict temperature limitations for the operating environment.

2. In order to detect the null position a Phase Sensitive Detection system is required, thus the system relies upon a reference voltage signal that is in phase with the excitation signal of the bridge. The design and use of a P.S.D. is a limiting factor for the detection of a true null position. The use of a lock-in amplifier greatly improves the resolution of a bridge since the method benefits from a high noise rejection factor.

Fig. 3.4. Typical three terminal connection to the ratio arm bridge.
3.3.3.2 Determination of the effective area for the experimental capacitance.

The uncertainty in the determination of the effective area A, of the capacitor system contributes an intrinsic error that limits the absolute accuracy of the detection of the electrode separation. The area A can only be determined to within 1% of the actual value.

3.3.3.3 Fabrication of the experimental capacitor.

The fabrication of the experimental capacitor and the nature of capacitance are limiting factors for the performance of the experimental system.

One must consider several factors:-

1. Fringing effects that occur at the edge of the capacitor affect the measured capacitance and must be accounted for. The use of an annular guard ring around the –Ve electrode reduces the effect of fringing of the electric field between the plates. In order to maximise the effect of the guard ring the annular separation of the two plates must be minimised. This constraint is a major factor when considering adhesives for the fabrication of the guarded –Ve electrode, since one must consider the effect of the thermal expansion of the adhesive.

One may correct for the distortion of the E field, by reference to the original work on guarded electrodes by Thompson [15].

The capacitance of the guarded capacitor is given by:

\[
C = \varepsilon_0 \frac{\pi r^2}{d} \left[ 1 + \frac{\varepsilon_s d}{\varepsilon_s d + 0.22 w} \cdot \left( 1 + \frac{w}{2r} \right) \right]
\]

(3.13)

Where \(w\) is the annular separation of the electrode and the guard ring.

\(\varepsilon_s\) is the relative permittivity of the insulation between the guard ring and the electrode.
Retaining terms only linear in \( \frac{w}{r} \) then one finds:-

\[
C = \varepsilon_0 \frac{\pi r^2}{d} \left[ 1 + \frac{\varepsilon_d d}{\varepsilon_d d + 0.22 w r} \right]
\]  \hspace{1cm} (3.14)

Since the effect is only a weak function of \( d \) the correction factor is approximately constant [16].

2. Tilt of the experimental capacitor will affect the measurement of the capacitance, and must therefore be taken into account. Further one must also account for the effect of damage/ surface roughness to / of the capacitor plate faces.

![Fig. 3.5. Tilt of the capacitor electrodes.](image)

A simple method to experimentally determine the contribution arising from both the tilt and the surface roughness of the capacitor is to measure the maximum capacitance the cell can produce before the electrodes short, and the conductance goes to a maximum. A high value for the maximum capacitance demonstrates a small tilt of the electrodes, and / or a low surface roughness.

From Fig. 3.5 the maximum capacitance corresponds to the situation where \( a = d \) therefore:-

\[
C_{\text{max}} = \varepsilon_0 \frac{\pi r^2}{a}
\]  \hspace{1cm} (3.15)
If the electrode separation is corrected for tilt and surface damage then the relationship between $d$ and $C_{\text{exp}}$ becomes:

$$d = \varepsilon_0 \frac{\pi r^2}{C_{\text{exp}}} \left[ 1 + \left( \frac{C_{\text{exp}}}{C_{\text{max}}} \right)^2 \right]$$  \hfill (3.16)

In an experimental situation where the temperature of the system is changing, one must consider the effect of the thermal expansion of the capacitor plates, since radial expansion will change the effective area, and hence the measured capacitance. Thus one must correct for the radial expansion $\delta r$.

(Experimental corrections, i.e. corrections to the measured capacitance for radial expansion of the electrodes, and the treatment of the cell effect will be considered in a later section)
3.4. The Low Temperature Dilatometer System (LTDS).

The low temperature dilatometer system is a high resolution capacitance dilatometer. The system was designed and built for the specific purpose of high resolution measurements of thermal expansion with a temperature range of 1.5K → 300K, and high resolution studies of magnetostriction in applied fields up to 7T.

The system consists of:-

1. A $^4$He cryostat containing a variable temperature insert, sample stick and a 7T cryomagnet.
2. A computer controlled high resolution capacitance measurement system, consisting of an automated General Radio GR1616 high res. capacitance bridge and a model SR510 Lock-in amplifier.
3. A "state of the art" Lakeshore Model 340 cryogenic temperature controller.
4. Fully remote system control via a PC controlled IEEE 488.2 interface bus and a 96 channel ISA digital (TTL) IO card.

3.4.1. Introduction to Cryogenic systems.

The measurement of thermal expansion, and the investigation of structural and magnetic phase transitions of materials necessitates the use of devices that are able to alter the sample environment temperature. Further if one wishes to measure the magnetostriction (spontaneous and forced) of intermetallic alloy systems one requires sample temperatures both above and below the transition temperature of the sample in question. Transition temperatures range from well above room temperature for ferromagnetic transition metals to below 1K for some rare earth alloys.

Essentially the design of all cryostats is similar, the difference being in the method of cooling used.

A cryostat consists of a vacuum insulated dewar, containing liquid refrigerant used to cool the sample. The sample is usually located in an evacuated sample rod or chamber.
There are several general methods of sample cooling:-

1. Direct immersion cryostat systems: This type of system has the sample vacuum chamber directly immersed in the liquid cryogen. The base temperature of such systems is limited by the boiling point of the cryogen used. The system can be cooled to temperatures less than the boiling point of the cryogen, by evacuating the space holding the cryogen, and cooling the sample environment using the enthalpy of vaporisation of the cryogen.

2. Variable Temperature Insert (VTI) systems: This method uses the flow of liquid cryogen into a small chamber to cool the sample vacuum chamber. (The flow is achieved either by a siphon effect, or by slight evacuation of the VTI chamber (dynamic space)). The obtainable base temperature also depends upon the cryogen used (as in 1). However the VTI system allows a more efficient use of the refrigerant during cooling by evaporation, since one does not need to cool a large mass of liquid as well as the sample chamber. Further such a design allows the use of a cryomagnet whilst the system is at base temperature.

3. Continuous flow systems: Here a continuous flow of cryogen is delivered to a heat exchanger, which then cools the system. Such systems can be extremely compact in size, and are therefore useful for optical/X-ray applications.

4. Refrigerator systems: This method requires the continuous pumping of liquid/gas refrigerant in a continuous cycle. Such systems include
   
i. closed cycle refrigerators (Displex) with base temperatures of 4.2K $\rightarrow$ 14K.
   
   ii. Dilution refrigerators, with base temperatures in the mK range.
Fig. 3.6. Various types of cryostat cooling system that may be located in a common cryostat (Courtesy of Oxford instruments, Research Instruments UK).

<table>
<thead>
<tr>
<th>Cryogen.</th>
<th>Boiling point /K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$He</td>
<td>3.2</td>
</tr>
<tr>
<td>$^4$He</td>
<td>4.21</td>
</tr>
<tr>
<td>N$_2$</td>
<td>77.3</td>
</tr>
</tbody>
</table>

*Table 3.2. Data for commonly used liquid cryogens.*
3.4.2. Design of Oxford instruments 7T SMD cryostat.

The cryostat used for the low temperature dilatometer system was an Oxford Instruments Superconducting Magnet Dewar, containing a 7 Tesla compensated superconducting solenoid in a 30l liq. $^4$He bath. A vacuum insulated 60l N$_2$ dewar is used for thermal shielding of the $^4$He dewar. Sample cooling is achieved using a dynamic flow of $^4$He supplied by a variable temperature insert system also located in the $^4$He bath. The base temperature achievable at the VTI when pumping on a the VTI dynamic space with a 600lmin$^{-1}$ two stage rotary pump is $\approx 1.5$K. The maximum temperature of the system is 300K. The temperature of the VTI is monitored and controlled by a Oxford Instruments 3120 temperature controller, connected to a 27Ω RhFe sensor and a 30Ω resistive heater. The pumpable sample rod is located in the VTI with a square cut brass thread, used to maximise heat conduction to the sample space. The dynamic sample space is sealed with a sliding O ring seal (Fig. 3.6). The magnet is operated by a Oxford instruments 60A superconducting magnet power supply, which controls both output current and a superconducting switch system thus allowing the magnet to run in “persistent mode”. An Oxford instruments sweep unit is used to control the current output of the power supply.

Ancillary vacuum equipment comprises of, two rotary pump backed oil diffusion pumps (Fig 3.7). These are used to evacuate the sample vacuum chamber, the main dewar vacuum space and the VTI vacuum space (Fig 3.6). A high throughput (600 lmin$^{-1}$) sealed rotary pump used to pump the VTI dynamic space, $^4$He gas flow is regulated by a Oxford Instruments VC30 gas flow controller. The exhaust from the main $^4$He dewar is monitored using a gas flow meter, an overpressure valve is included for safety. $^4$He boil off from the main dewar is approximately 300cchr$^{-1}$. Cryogen levels in the cryostat are monitored using a Oxford Instruments N$_2$ “capacitance type” level meter, and a $^4$He “superconducting type” level meter.
Fig. 3. Schematic diagram of (a.) The VTI unit and (b.) The SMD cryostat system.

- Sample Stick assembly, electrical and Vacuum connections.
- VTi Dynamic space vacuum connection.
- VTi vacuum connection, Main dewar vacuum connection.
- VTi & Magnet Support system top plates.
- N2 Fill port.
- *He Fill port and transfer tube guide.
- *He Dewar.
- Baffle set.
- VTi Sub assembly.
- VTi *He capillary tube.
- VTi *He pick up tube.
- Magnet support rods.
- 7T compensated solenoid.
- VTi 4He Flow Needle valve.
- VTi sample rod sliding seal.
- VTi 4He Pick up tube.
- Sample rod thermal connection.
- VTi capillary tube.
- Heat exchanger. (*He supply to VTi dynamic space.)
- VTi Temperature control sensor and resistive heater.
- VTi Electrical and vacuum connections.
- Optical window set.
- Optical window set.
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Fig. 3.7. Schematic diagram of the ancillary pumping system.
3.4.3. Temperature control.
Any measurement at temperatures other than ambient requires a method of controlling the temperature of the measurement system, and of the sample environment itself.
To achieve temperature control one requires an automated system, with the ability to measure the temperature of the system and control the heat input to the system, such that the system temperature becomes stable at a temperature required by the user.
It is clear, that in order to achieve a stable temperature environment the heat supplied to the system must equal the cooling power of the system.
In order to achieve such an equilibrium situation one requires a device that has the ability to alter the heat input to the system.
The core elements of such a system are as follows:

1. A heating source.
2. A cooling source.
3. A means to measure the temperature.
4. A means to evaluate the difference (error) between a required temperature (setpoint) and the current system temperature.
5. A system that can alter the heat input to the system to minimise the temperature error, using a feedback control equation.

![Temperature control system diagram](image)

*Fig. 3.8. Schematic diagram of a temperature control system.*
The key factor that limits the achievable stability of the system, is the control equation used. The equation must modulate the heating source output in such a manner as to keep the temperature both, stable, and at the setpoint. One must remember that:

1. A cryogenic system seldom has a linear response, since poor thermal conductivity causes thermal lags in the system response.
2. The specific heat as a function of temperature is not constant, thus the energy required to change, and stabilise the temperature is a non linear function of $T$.
3. Cryogenic design seldom produces a system that has an overall balanced heat loss, conversely a system heater can rarely have a balanced heat input into the system. Such problems introduce further sources of non linearity into the system.

### 3.4.3.1. Three term temperature control.

The most common method of feedback temperature control uses a 3 term equation to modulate the system heater output. The three terms being

1. Proportional (P) component.
2. Integral (I) component.
3. Derivative (D) component.

The overall control equation is given as:

$$\text{Heater output} = P \cdot e + I \int e \, dt + D \frac{de}{dt}$$

Where $e = \text{Setpoint temperature} - \text{Actual temperature}$.

#### 3.4.3.1.1. Proportional (P) component.

The proportional term, or gain, scales the heater output in proportion with the error on the setpoint.

$$\text{Heater output} = P \cdot e. \tag{3.18}$$

Hence the error must always be nonzero in order to actuate the heater. The proportional term acts as a on/off control term. The use of proportional control alone will not result in a stable temperature at the required setpoint, however it must be used to scale the heater output to the approximate cooling power. The measured parameter for the proportional component is a unit of the heater output amplification.
3.4.3.1.2. Integral (I) component.
The integral term integrates the system temperature error over a pre-set time period. The integral component is added to the proportional component to achieve stable control.

\[ \text{Heater output (I)} = PI \int_{t_1}^{t_2} (e) \, dt \]  

(3.19)

The integral term obviates the need for an error between the setpoint and the required temperature. If the error is zero the heater will have a constant output, and therefore control to the required setpoint. The integral component is proportional to the period of oscillation or time constant of the cryogenic system, when measured operating under an open control loop.

3.4.3.1.3. Derivative (D) component.
The derivative setting acts on the rate of change of the setpoint error and scales the heater output as a function of that change.

\[ \text{Heater output (D)} = PD \frac{de}{dt} \]  

(3.20)

The derivative output will act to stabilise a rapidly changing error signal. The derivative setting is related to the time constant of the system.

The action of various PID control algorithms is shown in Fig. 3.9.
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**Fig. 3.9.** The effect of various control terms to a change in setpoint as a function of time.
3.4.3.2. Temperature control for the low temperature system.
The choice of temperature sensor is critical to any cryogenic system. The
sensor used must give accurate temperature measurement over the entire
temperature range used.
Further if the system is to be used in a magnetic field, the response of the
sensor output to applied magnetic fields must be negligible.
Sensor calibration must also be considered. Most sensors come either,
uncalibrated, with a minimal set of calibration data, or with generic curve
data (Standard curves must be scaled by the user, usually by calibrating
against Liq. N2). "In house" calibration may be achieved providing one has
access to a fully calibrated sensor.
Essentially sensor types are broadly split into:-
1. Those which act as a resistive load. (Ge resisters /Pt RTD's)
2. Those which act as a voltage source. (Diode based sensors)

<table>
<thead>
<tr>
<th>Sensor type</th>
<th>Sensor unit</th>
<th>Min. Temperature $T_{\text{min}}$ / K</th>
<th>Max. Temperature $T_{\text{max}}$ / K</th>
<th>Accuracy $T_{\text{min}} \rightarrow T_{\text{max}}$ / mK</th>
<th>Magnetic field limits, T/K &amp; B/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Diode</td>
<td>V</td>
<td>1.4</td>
<td>325</td>
<td>$\pm 20 \rightarrow \pm 50$</td>
<td>$T &lt; 60 \text{K B &lt; 5T}$</td>
</tr>
<tr>
<td>GaAlAs Diode</td>
<td>V</td>
<td>1.4</td>
<td>325</td>
<td>$\pm 15 \rightarrow \pm 90$</td>
<td>$T &gt; 4 \text{K B &lt; 5T}$</td>
</tr>
<tr>
<td>Cernox.</td>
<td>Ω</td>
<td>0.3</td>
<td>325</td>
<td>$\pm 5 \rightarrow \pm 150$</td>
<td>$T &gt; 1 \text{K}$</td>
</tr>
<tr>
<td>Carbon Glass</td>
<td>Ω</td>
<td>1.0</td>
<td>325</td>
<td>$\pm 5 \rightarrow \pm 55$</td>
<td>$T &lt; 300$</td>
</tr>
<tr>
<td>Germanium Resistor</td>
<td>Ω</td>
<td>0.05</td>
<td>5</td>
<td>$\pm 5 \rightarrow \pm 35$</td>
<td>Not recommended</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt RTD</td>
<td>Ω</td>
<td>14</td>
<td>870</td>
<td>$\pm 20 \rightarrow \pm 200$</td>
<td>$T &gt; 30 \text{K}$</td>
</tr>
<tr>
<td>RhFe</td>
<td>Ω</td>
<td>1.4</td>
<td>325</td>
<td>$\pm 10 \rightarrow \pm 35$</td>
<td>Not recommended</td>
</tr>
<tr>
<td>Thermocouple, (General)</td>
<td>V</td>
<td>3</td>
<td>1600</td>
<td>$\pm 2 \text{K}$</td>
<td>$T &gt; 10 \text{K}$</td>
</tr>
</tbody>
</table>

Table 3.3. Typical cryogenic temperature sensor characteristics.
Three sensors are used for temperature control in the low temperature dilatometer system. A dual control loop (2 sensors 2 heaters) is located in the sample space. The two loops are used to monitor / maintain sample environment temperature control. A single sensor control loop is used to monitor and control the VTI in the cryostat. In effect this system limits the cooling power supplied to the sample space.

### 3.4.3.2.1. VTI temperature control loop.

The VTI temperature sensor is a 27Ω RhFe device supplied by Oxford instruments (Table 3.4.). The temperature is controlled by an Oxford instruments Model 3120 temperature controller, using a 3 term PID algorithm. Heating is achieved using a 30Ω canister type resistive heater, in turn the controller is operated via a IEEE 488.2 interfaced with a PC. The standard 4 point method is used to connect sensor to controller. The temperature controller is capable of achieving temperature stability to ±0.1K of the setpoint value. The VTI control loop is used to control the cooling load applied to the sample space at sample temperatures larger than 20K. The calibration data for the sensor is shown in table 3.4.

<table>
<thead>
<tr>
<th>Resistance at 273.16K</th>
<th>Resistance at 77.352K</th>
<th>Resistance at 4.222K</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.029Ω</td>
<td>7.2350Ω</td>
<td>2.3704Ω</td>
</tr>
</tbody>
</table>

*Table 3.4. Calibration data (ITS 90) for 27ΩRhFe VTI control sensor.*

### 3.4.3.2.1. Sample environment control loops.

Sample environment temperature measurement and control is achieved using two separate control loops:
Loop one consists of a Cernox™ CX-1050-AA sensor and a 50Ω canister type heater.
The sensor and heater are located at the base of the sample cell,
(Fig. 3.12)
Loop two consists of a Cernox™ CX-1050-AA sensor and a 100Ω non-inductively wound resistive wire heater located between the cold end of the sample stick and the sample cell (Fig. 3.12).

Temperature control is achieved using a Lakeshore™ Model 340 temperature controller (Dual input). Control loop one is input to channel A, loop 2 is input to channel B. The 340 utilises a 3 term PID control algorithm. Channels A & B can be controlled independently of each other with different setpoints. The Model 340 is interfaced via an IEEE 488.2 board to a PC. The control loops operate to minimise the difference between channel A and B, and therefore to minimise the sample temperature gradient.

The controller is capable of control to ±1mK of the setpoint for T≤10K and ±10mK for T>10K. Both sensors were calibrated against a calibrated carbon glass sensor from 2K to 300K. The Cernox sensor type exhibits a logarithmic dependence of R upon T, with a negative temperature coefficient of resistance (Fig. 3.10). A 100 point calibration interpolation table of Log R vs. T was produced for each sensor from the raw calibration data. These tables were then input into the Model 340 controller EPROM, in order to allow the system to convert from sensor units to actual temperature.

![Fig. 3.10 Generic curve of resistance as a function of temperature for a Cernox temperature sensor. (Inset shows LogR as a function of T).](image)
3.4.4. LTDS sample cell.
Design of the experimental dilatometer is of obvious importance, one must not only consider proper sample mounting, but also the design of an appropriate plane plate capacitor. One must observe the size constraints due to the limited sample space volume in the cryostat, and also consider the application of correct cryogenic wiring (and techniques) to the sample cell. This is of some importance since one must use coaxial cable to connect the sample cell to the capacitance bridge. The diameter and construction of such cable will increase the heat leak into the system.
The sample stick used in the LTDS cryostat has an inner diameter of \( \approx 49\text{mm} \), with a useable internal length of \( \approx 110\text{mm} \) for experimental equipment. (Fig 3.12). The sample stick is screwed into the square cut brass thread of the VTI system, which provides a large thermal contact to the cooling load of the cryostat. When used the threads are lightly greased using Apeizion N type, to ensure optimal thermal contact.
Internally the sample stick provides several points for thermal anchoring of electrical wiring. The approximate temperatures of the thermal anchor points being: 80K, 77K, 30K and 4.2K. The wiring loom of the cryostat stick is thermally anchored at these points, using a cryogenic varnish to ensure proper thermal contact.

3.4.4.1 Types of dilatometer cell.
As stated previously (sec 3.2) there are two basic types of cell design, the relative and the absolute type. Both types have been used with the method of capacitance dilatometry [17]. Early cell designs used the sample to form one part of the capacitor. However the use of the sample as an electrode is seldom used in modern dilatometers, and should be avoided. Such a method limits the quality and reproducibility of results and also limits the sample size and type.

Fig. 3.11 demonstrates the basic dilatometer cell design for the relative and the absolute type of dilatometer. Further to these methods one may also employ a cell that utilises non-parallel capacitor plates [18].
Brandl and Griessen describe such a dilatometer cell, and also describe how one may correct the experimental data for the non-uniformity of the electrodes.

Rotter et al. [19] describe a novel cell used for the measurement of forced magnetostriction, whereby the sample is mounted between the capacitor electrodes. The method utilises a non-parallel electrode configuration. One must be aware that such a design will inherently measure the forced electrostriction of the sample. Such problems are also inherent to the dilatometer described by Snyder et al., [20] where the electrodes are separated by the sample to be measured. There are obvious problems associated with sample preparation and sample mounting.

![Diagram of dilatometer cells](image)

**Fig. 3.11.** The two basic types of dilatometer cell.

### 3.4.4.2 Design of the LTDS dilatometer cell.

The dilatometer cell used for the LTDS is of the relative type, with a parallel plate three terminal capacitance transducer. The dilation of the sample $\delta l(T) / \delta l(H)$, is transmitted directly to the $+Ve$ electrode of the transducer, which is held independently by two Copper Beryllium (Cu 98%, Be 2%) diaphragm springs. The springs act as to hold the free electrode parallel to the guarded $-Ve$ electrode of the transducer, and allow the $+Ve$ electrode to move freely with the dilation of the sample.
The design of the diaphragm springs was such as to minimise the force required to traverse the low plate electrode. (Fig. 3.12) The guarded low plate electrode was produced using Stycast 1285GT glass loaded epoxy resin as the guard electrode spacer material. Stycast 1285GT exhibits low thermal expansion, and has a high performance at low temperature. The cell is designed in such a manner as to alleviate the need for adhesives or clamps when mounting the sample. The cell was constructed from High Conductivity Oxygen Free Copper (HCOF Cu). This material was chosen for two reasons:-

1. Since copper has a high thermal conductivity the time taken for the cell to reach thermal equilibrium would be short. Although material with higher thermal conductivity (Ag) could be used, HCOF Cu was chosen since high quality thermal expansion data is available (see #2).
2. HCOF copper is a standard material, thus there exists very accurate thermal expansion data, which one may use to correct for the cell expansion. The data used is the accepted standard of Kroeger and Swenson [11].

The cell was designed to accept samples with dimensions of:-

| Sample diameters between: | ≈2mm → ≈10mm. |
| Sample lengths between | ≈9mm → ≈30mm. |

The system is therefore ideal for the measurement of both polycrystalline materials and single crystal samples. The sample cell design and connection to the sample stick and heater system is shown in Fig. 3.12. Electrical connections to the sample cell and thermometry is via ultra miniature Pt connectors. Ultra miniature coaxial (50pF m⁻¹) cable is used in the sample stick to excite the transducer system.
Details of capacitance transducer.
- Radius of High plate = 10.5 mm.
- Radius of low plate = 9.5 mm.
- Thickness of guard ring insulation = 0.24 mm.
- Effective area \(= 2.83 \times 10^{-4} \pm 6.5 \times 10^{-6} \text{ m}^2\)
- \(\varepsilon_s\) Stycast epoxy @ 1000 Hz = 6.3
- \(C_{\text{max}} = 120 \text{ pF}\)

---

**Fig 3.12.** The LTDS dilatometer cell and sample stick schematic diagram.
3.4.4.3. Sample cell commissioning.
As the dilatometer cell is of the relative type, one must commission the cell in order to evaluate the “Cell effect” to the measured data. This is an essential step as it allows one to evaluate the absolute sample dilation, and thus the absolute linear thermal expansion coefficient for subsequent experiments.
One must also evaluate the maximum capacitance the sample cell produces, in order that one may correct for the tilt and surface damage of the capacitor electrodes (Sec. 3.3).

3.4.4.3.1. Evaluation of the “cell effect” to thermal expansion.
In order to evaluate the “Cell effect” a sample of HCOF Cu, from the same batch as that used to manufacture the sample cell, was measured over the entire range in zero field. It is clear that the measured sample dilation of a Cu sample, in a relative dilatometer manufactured from Cu should be zero, therefore one may attribute any measured dilation (or deviation from zero) to the effect of the sample cell. The absolute magnitude of the sample cell effect was found to be <3.5μm @ 1.5K. The deviation from zero during the commissioning run was attributed to the effect of differential thermal expansion of the cell as a result of the Stycast epoxy resin used to manufacture the capacitor electrodes. The cell effect data was similar to data for Stycast epoxy resin measured by [21].
In order to facilitate simple data analysis the data taken during the commissioning experiment were fitted with a 7th order polynomial ($r^2 = 0.999$). The polynomial coefficients could therefore be used to correct subsequent experimental data. (As discussed later).

3.4.4.3.2. Evaluation of the magnetostrictive “cell effect”.
Since the system also allows the measurement of the forced magnetostriction the cell effect due to the application of a magnetic field must also be evaluated. This was achieved by measuring the sample cell response to the application of a magnetic field, with a sample of HCOF Cu. Thus any deviation from zero can be attributed to the magnetostrictive cell
effect. The maximum field of 7T was applied over a period of 100mins (0.0011 Ts\(^{-1}\)) in order to minimise sample heating due to the production of eddy currents in the sample cell. The magnetostrictive cell effect was determined to be \(\leq 1\text{nm} \ T^{-1}\).

3.4.4.3.3. Evaluation of the maximum capacitance.
The capacitor electrodes were machined to be absolutely flat, in order to achieve this each electrode assembly was lapped using 1\(\mu\)m diamond paste until a mirror finish was achieved. In order to evaluate both, the surface roughness, and the degree of parallelism of the assembled capacitance cell, the maximum capacitance was measured. The capacitance of the cell before the system conductance goes to maximum was measured. This value was taken to be the point at which the electrodes were at minimum separation. Thus one may correct the experimental data as discussed in Sec. 3.6.

The maximum capacitance was found to be 120pF, this corresponds to either, a surface roughness of 11\(\mu\)m, the surface roughness factor is 0.11, or a electrode tilt of 1.01mrad. Experimentally one cannot distinguish between the contributions of tilt and surface roughness.

3.4.4.3.4. Experimental data analysis.
The analysis of experimental data for the evaluation of the thermal expansion coefficient and magnetostriction is a three part process:-

1. The correction of experimental values of capacitance taken during the experiment, allowing the evaluation of a corrected electrode separation.
2. Evaluation of the absolute \(\delta l/l_0 (T)\) or \(\delta l/l_0 (H)\).
3. Evaluation of the coefficient of linear thermal expansion (\(\alpha\)) or coefficient of forced magnetostriction (\(\lambda\)).
3.4.5. Capacitance measurement system.

The capacitance measurement system is an essential component of the low temperature dilatometer. The system schematic for the capacitance measurement system is shown in Fig. 3.13. The system consists of 3 major components.

3.4.5.1. The General radio 1616 high resolution Bridge.

The GR1616 bridge unit is a high resolution AC transformer ratio arm capacitance measurement system, capable of resolving changes in capacitance at the atto farad (aF) level. The bridge operates in the manner described in Sec. 3.3.

The GR1616 consists of a toroidal core transformer, the ratio arms of the bridge are transformer windings tapped on the standard side of the bridge in decimal steps of \(-1, 1, 2, 3, \ldots, 9, 10\), and on the unknown side of the bridge in decade steps of \(x100, x10, x1\). 12 separate capacitance standards are used in decade steps from 1aF to 100nF. The combination of ratio arms and standard capacitances give a range of capacitance measurement from 0.1aF to 1μF when using a three terminal connection to the unknown.

Temperature stability of the bridge is achieved by housing 6 of the capacitance standards in a temperature insulated enclosure, with a thermal time constant of 6hrs.

The bridge is calibrated to provide maximum resolution in the temperature range of 296K ± 1K at a frequency of 1kHz.

The magnitude of the excitation voltage applied to the primary winding should not exceed 0.16 of the applied frequency \(f\).

The bridge is supplied with an excitation signal of 1kHz (±1Hz) with RMS voltage between 10±1V to 160±1V.
3.4.5.2. Stanford research systems Model SR510 Lock-In amplifier.
The model SR510 lock-in amplifier is used to detect the bridge balance condition. The amplifier has a single ended voltage input with a 1nV resolution (with x10 expand function). The unit offers a high degree of signal noise rejection, from several in line filter systems, and a low noise high gain AC amplifier. The phase sensitive detection system is supplied with an external reference voltage source, that is in phase with the capacitance bridge excitation signal (see below). The SR510 has a GPIB computer interface and allows full remote control of the system.

3.4.5.3. Excitation voltage and reference signal supply.
The excitation signal for the bridge is produced by a General radio Model GR1301-B oscillator. The sinusoid signal is amplified by a precision AC voltage amplifier (Gain = 10). The excitation signal frequency used is 1kHz, rms. Voltage output from the GR1301-B is between 1V and 16V. An unamplified signal is tapped from the AC voltage amplifier and fed to a EG&G Brookdeal model 9422 reference unit, the reference unit produces a signal of 1mV rms. This signal is used as the reference input of the lock-in amplifier. An oscilloscope is used to ensure that there is zero phase difference between the reference signal and the bridge excitation signal. Phase adjustment comes from either the reference unit or the Lock-in amplifier.

3.4.5.4. General considerations.
The capacitance measurement system is housed in a temperature controlled electronics 19” rack unit. The capacitance bridge is housed within a faraday cage unit, to reduce noise injection from the surrounding area. The entire system is earthed at a common ground point to avoid the introduction of ground loops to the system. The system is wired using high quality coaxial cable throughout. Connections to the experimental cell is by GR900 coax connectors and triaxial cable, the outer shield is connected to earth. The common earth from the cryostat is connected to the GR1616 ground point.
3.4.5.5. Operation of the capacitance measurement system.

The capacitance bridge was automated, such that the computer control system was able to remotely balance the capacitance bridge. Automation of the bridge is facilitated by the use of a position sensitive detection system mounted on four of the decade arms of the bridge, those being: 10pF, 1pF, 0.1pF and 0.01pF.

The position sensitive detection system consists of 4 RS servo ten turn potentiometers, coupled to the decade motion system via a 6:1 reduction gearbox. The potentiometers (pots) are supplied with a stabilised 5V DC signal, the voltage dropped across the pots is proportional to the decade position. This voltage is input to a Keithly model 181 nanovoltmeter. The voltmeter contains a GPIB interface, enabling remote access to the voltage across the pot, by a computer. Therefore, by the use of a interpolation table, the computer can deduce the decade position. A digital (TTL IO card) interface on the pot supply allows the computer to switch the voltage supply to any of the 4 pots. The decades of the bridge can be moved using a TTL interfaced stepper motor control unit, and associated decade stepper motors. Hence the computer is able to move any of the four decades to any of the 10 positions, (0 to 9) enabling remote balance of the bridge unit.

The capacitance of the dilatometer cell is measured exactly using the relationship of the off balance voltage and the balance capacitance. Since the off balance voltage is linear with off balance capacitance, one may produce a linear regression equation, based on a 20 point calibration against a 1pF standard capacitor.

Thus one may calculate the true experimental capacitance using the off balance voltage to evaluate the difference between the true capacitance and the capacitance selected on the front panel of the capacitance bridge ΔC. Since the capacitor is not perfect, the relationship between off balance voltage and off balance capacitance is not linear over a wide rage of ΔC. Therefore to reduce the error on the measured capacitance, the bridge is automatically balanced if the voltage offset is greater than a preset value.
In doing this the performance of the bridge, both accuracy, and available measurement frequency is optimised.

3.4.5.5.1. Performance of the capacitance measurement system.

The performance of the capacitance measurement system is limited by the stability of the capacitance bridge, and the S/N ratio of the off balance voltage. The stability of the bridge can only be maximised if one removes any thermal fluctuation of the bridge, which is obviously very difficult. However one may improve the S/N ratio by increasing the magnitude of the excitation signal. This has the effect of increasing the observed sensitivity of the bridge unit. A resolution of $1\rightarrow 5$ aF is achievable when the bridge is excited with 120V rms. Thermal drift of the bridge is quoted at 50ppm K$^{-1}$. at the calibration temperature of 296K ± 1K. At temperatures outside this range the performance of the bridge is greatly reduced. Readings of capacitance can be taken at a frequency of 50Hz, when polling the lock-in amplifier. The bridge balance time is $\leq 100$secs.
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Connections to the experimental capacitance.

Decade position sensor control unit. TTL Interface.

Stepper Motor Control system. TTL Interface.

4.5000V

GR1616

4.2k 4.5k

Lakeshore model 340 temperature controller

Detector output connection from bridge

Connection to ref. Input.

Reference unit feed.

175µV

SR510 Lock-in amp. 0 Phase adjust

EG&G Brookdeal Reference unit

Low noise voltage amplifier. (Gain = 10)

Stabilised 30V supply for amplifier

GR1616 Decade stepper motor drive unit.

GR1616 Low.

GR1616 High.

GR1616 Earth.

GR1301-B Oscillator.

486 DX33 PC with GPIB & TTL IO control capability

96 channel TTL IO connection

Fig. 3.13. Schematic diagram of the capacitance measurement and control system.
3.5. The High Temperature Dilatometer System (HTDS).

The high temperature dilatometer system is a high resolution capacitance dilatometer, with a temperature range of 300 → 900K.

The capacitance measurement system for the HTDS is identical to that used by the LTDS. The experimental capacitance is measured using the GR1616 capacitance bridge with the SR510 Lock in amplifier as the null point detector (See sec.3.4.5). The dilatometer itself is manufactured from three fused quartz tubes, the guarded three terminal capacitor is manufactured from brass. The low plate electrode and the associated guard ring is formed using Stycast 1285GT epoxy resin. The capacitors are attached to the fused quartz tube system using epoxy resin (Fig. 3.14).

The sample is held between the two inner quartz tubes at the centre of the device. The dilatometer can accept samples up to 10mm in diameter, and up to 50mm in length. The sample is heated by a non-inductively wound Thermo-coax heating element (5.5 Ohm) that is driven by an AC thyristor drive, rectified by a transformer system built in house. The system has a maximum temperature of ≈900K.

Temperature control is achieved using a Eurotherm 818 temperature controller, with a maximum resolution of 0.1K. The temperature sensor used is a type K thermocouple placed below the sample position in the device.

System cooling is achieved by connection to the mains water supply to the brass heat sinks located at the top and bottom of the dilatometer, a small flow meter is used to monitor coolant flow around the system.

The system can be evacuated to a pressure <1.5x10^-5 mbar using a 2" oil diffusion pump. The sample enclosure can be filled with a low pressure atmosphere of 4He exchange gas, to ensure that the entire sample reaches an isotherm for the measurement cycle.

The correction term for tilting of the capacitor plates \( C_{\text{max}} \) was evaluated as \( C_{\text{max}} = 30 \mu\text{F} \), this corresponds to a maximum surface roughness of ≈7μm, or a tilt of ≈ 2 mRad.
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Fig. 3.14. Schematic diagram of the HTDS.

Details of capacitance transducer.

- Radius of High plate = 4.8 mm.
- Radius of low plate = 2.9 mm.
- Thickness of guard ring insulation = 0.25 mm.
- Effective area = $2.6 \times 10^{-2}$ m$^2$
- $\varepsilon_s$ Stycast epoxy@1000Hz = 6.3
- $C_{MK} = 30$ pF

Upper vacuum flange. Connections for Three terminal sensor
Thermo coax heater & Coolant flow out.

Three terminal capacitance transducer, connect to existing measurement system.

Water cooled thermal sinks (Brass)

Inner quartz tube, holds high capacitor plate.

Support rods.

Outer vacuum casing (Stainless steel)

Heater.

Sample position. Outer quartz tube. Holds guarded low plate.

Inner quartz tube, holds temperature sensor (Thermocouple.)

Lower water cooled thermal sink.

Threaded adjuster.

Bottom Vacuum flange. Connections for Coolant flow in & K type thermocouple for the 818 temperature controller.
3.6. Data acquisition and data analysis.

In order to simplify the operation of a scientific instrument one may implement a computer controlled data acquisition system. This not only allows the system to be operated efficiently, but also allows fast, and accurate collection of data. The use of modern computer control techniques allow the collection of data at a higher rate than manual collection of data would permit. Further computer control of an experiment enables one to implement strict constraints on the collection of data.

A data acquisition system contains the following components:

1. A suitable system that allows remote control of devices/instruments, and therefore enables the remote collection of data. The 2 most common remote control protocols used for remote control of instruments are:-
   i. GPIB IEEE 488.2.
   ii. PC onboard Serial link.

   Further for control of remote switching devices a TTL I/O device may be used.

2. An instrument/s capable of communication using the aforementioned protocols, to collect and transmit data when required.

3. A computer to control the I/O operations of the system, using a predetermined algorithm.

3.6.1 HTDS & LTDS data acquisition system.

Both dilatometer systems use a common control program, the program allows remote operation of all system devices, as well as control of the custom built automatic bridge system. Further the program controls data acquisition, and data analysis.
Overall control of devices is achieved by the use of a standard PC computer (486 SX25) containing the following ISA cards:

1. IO Tech GPIB IEEE 488.2 bus controller card.
   The GPIB card is used to control the following instruments:
   i. LakeShore Model 340 Cryogenic temperature controller (LTDS).
   ii. SRS Sr510 Lock-In amplifier (Common capacitance measurement system).
   iii. Keithly 181 Nanovoltmeter (Common capacitance measurement system).
   iv. Oxford Instruments Model 3120 Temperature controller (LTDS)

2. PIO-96 96 channel programmable digital IO card.
   The IO card is used to control the GR1616 bridge stepper motor control system, and the GR1616 decade position sensors.

The onboard PC serial port (COM1) is used to control the Eurotherm 818 (HTDS) furnace temperature controller.

IO control is implemented using a standard computer programming package (MS Visual Basic for DOS.). Data is saved in the form of ASCII data files on the hard disk of the control computer.

3.6.2. Data acquisition algorithm.

The LTDS is used to measure both the thermal expansion and the magnetostriction of materials. The control program uses two separate control algorithms to control data acquisition for each case. (The HTDS measures only thermal expansion.)

For the purposes of data analysis one must evaluate a reference point for the sample electrode separation, in order to evaluate $\delta l(T)$, and $\delta l(H)$.
3.6.2.1. Thermal expansion data acquisition.

The data acquisition algorithm for the collection of thermal expansion data essentially uses a set point control method. Thus the controller changes the setpoint of the system, waits for the system to become thermally stable, and then measures the electrode separation of the dilatometer cell. This algorithm is repeated for a preset number of iterations, with a preset temperature step, in order to complete the experiment.

It is clear that the quality of the data rests with the degree of sample cell temperature stability. The measurement of the electrode separation whilst the cell temperature is continually changing will result in the collection of spurious data. The data acquisition program consists of two phases:

1. Stabilisation of sample cell,
2. Measurement of data.

In order to ensure that data acquisition occurs only when the sample cell is thermally stable a three loop control algorithm was developed.

The control program monitors the following aspects of the system, in order to determine if the sample cell is stable.

1. **Sample cell temperature.** The sample cell temperature is monitored at two points (See 3.4.4.2). Thus the cell temperature differential can be evaluated. The model 340 is used to control the temperature of both the sample cell and the sample stick cold end, thus the system is able to control the magnitude of the sample cell temperature differential. In order for the measurement process to progress the cell temperature/s must be:
   
   \( i \). Within a certain value of their respective setpoints.
   \( ii \). Stable over time, to within a certain temperature fluctuation.
   \( iii \). Within a certain range in cell temperature differential.

2. **Cryostat VTI Temperature.** The VTI temperature is monitored using the 3120 controller. The VTI temperature is controlled to within 0.1K of the setpoint, the VTI controller is used to reduce the cooling effect on the sample cell when the system is at high temperatures (T > 20K). The VTI control loop allows the model 340 controller to minimise the thermal gradient across the sample cell as the cooling power to the sample environment is reduced.
3. **Sample cell stability.** The change in sample cell electrode separation over time is evaluated, by taking 30 values of electrode separation over a period of 30 seconds, the change in sample length over time can calculated. Thus the control program can evaluate when the sample, and the sample cell are stable. One should note that this method is by far the most sensitive method of determining the stability of the sample cell, as the sample cell is by far the most sensitive sensor of the sample cell thermal stability. The cell stability is monitored until the system settles to within a predetermined range of stability. The constraint used to control the sample cell stability is that of rate of change in time of the sample length the system usually stabilises to $\frac{\partial l}{\partial t} \approx 5 \mu m/s$.

When the sample cell is determined to be stable the program enters the measurement routine. The system measures 10 values of capacitance, and electrode separation. To ensure that the capacitance measurement system will give the greatest accuracy the bridge is balanced before each measurement of electrode separation. The measured values of electrode separation are subsequently analysed at a later stage to produce the sample thermal expansion data.

The system is then reset with different temperature control setpoints. The data acquisition algorithm is looped until a final temperature is reached. One should note that this method of data acquisition is used for both the low and high temperature system. The HTDS algorithm differs in the number of temperature control loops used. The HTDS utilises only one temperature setpoint control loop.

Calculate new values for all setpoints.

Initialise system with new setpoints.

Input Initial Parameters. $T_{\text{Start}} \rightarrow T_{\text{final}}$, $\Delta T$

System temperatures, and error on setpoints. VTI temperature and error on setpoint.

Monitor Dilatometer cell stability

Monitor system stability.

Is system within stability constraints

Constraint parameters

For $I = 1$ to $10$

Collect data for cell temperature setpoint errors and electrode separation.

Balance GR1616?

Balance GR1616 algorithm.

Save data files on hard disk.

Is $\Delta T + T_{\text{present}} > T_{\text{final}}$?

Yes

END PROGRAM

Fig 3.15. Flow chart diagram for the collection of thermal expansion data for the LTDS & the HTDS
3.6.2.2. Magnetostriction data acquisition.

In order to measure the magnetostriction a simple continuous data acquisition algorithm is used. Such a method is employed as it allows simple operation of the magnetostriction measurement system.

Since the cryomagnet charging system is not computer controlled the data logging system must be synchronised by hand.

The essential parameter of a magnetostriction experiment is the temperature stability of the cell. Thus the algorithm proceeds in two steps; first the 340 temperature controller is used to alter the system setpoint, and is monitored until the system is stable; secondly the magnet sweep system is enabled to start the charging process. The applied field is "swept" from the initial field to the final field at a constant rate. (This is achieved using a constant current charging method.) The field is swept at a slow rate in order to avoid sample cell heating due to the formation of eddy currents within the sample and sample cell. Further charging the magnet at a low sweep rate ensures that the field in the magnet is proportional to the supply current, with as low an offset as possible.

Values of system temperature and electrode separation are logged at a preset rate, whilst the magnet is energised. The system is capable of logging data at a rate of 1Hz. At the end of the energisation run the data logging system is stopped.

The data analysis system (See sec 3.6) can then be used to calculate both the sample magnetostriction and the absolute values of the applied field at each point.
3.6.3. Data analysis methods.

Raw data acquired using the computer control system must be analysed in order to evaluate either the thermal expansion, or the magnetostriction of the sample. Although the data analysis can be undertaken manually using a spreadsheet program such as MS Excel™, it is far simpler to use an automatic program.

The data analysis program was written in order to allow simple evaluation of the required sample parameters. As stated previously one requires a reference electrode position for the evaluation of $\delta l$.

For analysis of thermal expansion data (Both LTDS and HTDS) this reference position is taken to be the electrode separation at 293K. The reference position can be evaluated using the raw data set by interpolation between two sets of electrode separations above and below the reference temperature.

For analysis of magnetostriction data the initial electrode separation is taken as the reference position. Further to the need for an electrode reference position one also requires the original length of the sample. For calculation of $\delta l(T)/l_0$ the sample length at room temperature is used. This value is found using a Micrometer, or a similar device. For calculation of $\delta l(H)/l_0$ one can determine the sample length at the temperature of the experiment by using thermal expansion data.

Corrections to the data are undertaken in two steps.

1. Corrections to the measured electrode separation for E field fringing and the radial expansion of the capacitor electrodes are evaluated as the system acquires the raw sample data.

2. Corrections for the sample cell effect on $\delta l$, and corrections due to the use of a relative sample cell, in order to evaluate the absolute sample data are evaluated as part of the data analysis routine.
3.6.3.1. Data analysis for low temperature thermal expansion.
As stated before an ideal capacitor with radius \( r \) and separated by a distance \( d \) will have an overall capacitance amounting to:

\[
C = \frac{\varepsilon_0 \varepsilon_r \pi r^2}{d} \quad (3.21)
\]

Since the experiment is performed in either vacuum, or with a low pressure \(^4\text{He} \) exchange gas \( \varepsilon_r \) is reduced to 1.

However the \(-\text{Ve} \) capacitor plate is surrounded by a grounded guard ring to reduce large fluctuations, or fringing of the electric field at the edges. One may correct the measured capacitance using:

\[
C = \frac{\varepsilon_0 \pi r^2}{d} \left[ 1 + \frac{\varepsilon_s d}{\varepsilon_r d + 0.22 w} \frac{w}{r} \right] \quad (3.22)
\]

The term in square brackets can be taken to be constant since it is only a weak function of \( d \). Hence one can calculate the constant term and apply a correction to the calculation of \( d \). Thus:

\[
\zeta = \left[ 1 + \frac{\varepsilon_s d}{\varepsilon_r d + 0.22 w} \frac{w}{r} \right] \quad (3.23)
\]

So:

\[
C = \varepsilon_0 \frac{\pi r^2}{d} [\zeta] \quad (3.24)
\]

Therefore:

\[
d = \varepsilon_0 \frac{\pi r^2}{C} [\zeta] \quad (3.25)
\]

For the geometry of the experiment \( r = 10\text{mm}, \varepsilon_s = 6.3@1000\text{Hz}, w = 0.24\text{mm} \) and \( d = 200\mu\text{m} \)

The correction term is therefore calculated to be 2.1% of the ideal capacitance.

It should be noted that this factor amounts to the largest correction (\( \approx 2\% \)) performed in the experiment. Other corrections (corrections for tilt and thermal expansion of the plates) amount to <0.1% of the measured value.
3.6.3.1.1. Corrections for radial thermal expansion of the capacitor plates

The correction for thermal expansion is easily performed since one has the standard data for the thermal expansion of HCOF Cu, and the room temperature dimensions of the dilatometer cell system. The standard data for $\Delta l/l_0$ (HCOF Cu) from Kroeger and Swenson is modelled by application of a 7th order polynomial equation ($r^2 = 0.99$), thus at any temperature one can evaluate the factor ($x$) of relative radial expansion:

$$x = \Delta r/r_0$$  \hspace{1cm} (3.26)

Hence the change in radius at temperature $T$ ($\Delta r$) becomes:

$$\Delta r = x r_0$$  \hspace{1cm} (3.27)

Therefore one can calculate the radius of the capacitor plates at any given temperature:

$$r = r_0 - \Delta r$$  \hspace{1cm} (3.28)

Thus one can calculate the electrode separation at any temperature, corrected for thermal expansion of the capacitor plates:

$$d_{\text{meas.}} = \varepsilon_0 \frac{\pi (r_0 - \Delta r)^2}{C_{\text{meas.}}}$$  \hspace{1cm} (3.29)

This corrective term is a maximum when $\Delta r$ is evaluated at 1.5K hence $\Delta r(T)$ is a maximum. Using the geometry of the LTDS capacitance transducer the correction at 1.5K amounts to 0.7% of the actual electrode separation.

3.6.3.1.2. Corrections for the tilt of the capacitor plates.

Corrections due to the non parallel nature of the dilatometer cell electrodes (Sec. 3.3.3.3) is applied in the following manner:

$$d_{\text{meas.}} = \varepsilon_0 \frac{\pi (r_0 - \Delta r)^2}{C_{\text{meas.}}} \left[1 + \left(\frac{C_{\text{meas.}}}{C_{\text{max.}}}\right)^2\right]$$  \hspace{1cm} (3.30)

It is immediately obvious that the error i.e. the magnitude of the correction factor increases to the maximum of 2 as one increases the measured experimental capacitance $C_{\text{meas.}}$ towards $C_{\text{max.}}$.

However if one is prudent and uses an experimental capacitance in the range 10-30pF, the net effect of the correction term is reduced.
3.6.3.1.3. Correction of cell effect and calculation of $\Delta l/l_0$

One must correct for the cell effect, as this is by far the biggest error in the experimental measurement. The measured change in sample length ($\Delta l$) is calculated using the reference electrode separation, thus:-

$$\Delta l_{\text{meas}} = d_{293K} - d(T)$$ \hspace{1cm} (3.31)

One corrects for the cell effect thus:

$$\Delta l(T)_{\text{Corrected}} = \Delta l(T)_{\text{meas}} - \Delta l(T)_{\text{Cell Effect}}$$ \hspace{1cm} (3.32)

From this point one can evaluate the absolute value of the factor $\Delta l/l_0$:

$$\frac{\Delta l(T)}{l_0} = \left[ \left( \frac{\Delta l(T)_{\text{Corrected}}}{l_0} \right) + \left( \frac{\Delta l(T)}{l} \right) \text{ Standard copper Data} \right]$$ \hspace{1cm} (3.33)

Where $l_0$ is the length of the sample measured at 293k.

From this point one can then evaluate the linear coefficient of thermal expansion $\alpha$ by taking the derivative of $\Delta l(T)/l_0$ as a function of temperature since:

$$\alpha = \frac{1}{l_0} \left( \frac{\Delta l}{\Delta T} \right)$$ \hspace{1cm} (3.34)

This factor is evaluated using Microcal™ since no correction for fitness of temperature interval is needed since such corrections are handled by the program, or by the standard method, (if $\alpha$ is evaluated manually one must correct for fitness of temperature step when $\Delta T$ is greater than 5% of the temperature T.)
3.6.3.2. Data analysis for high temperature thermal expansion.

The analysis of data for high temperature thermal expansion is essentially identical in nature to that outlined for the low temperature system. The raw electrode separation / temperature data, as collected by the operating system is corrected for fringing of the $E$ field at the edge of the electrodes, and for the tilt / surface damage of the electrodes. One should note that corrections for the radial expansion of the capacitor plates is not required, as the transducer system is housed within a temperature controlled thermal mass, (Fig. 3.14).

Since little high quality thermal expansion data is available for fused quartz (The material the HTDS is constructed from), in order to calculate the absolute sample thermal expansion a fit was made to the difference between the accepted values for thermal expansion of $\text{HCOF Cu}$ [22], and the experimentally measured values. Such a correction routine not only normalises the experimental data to an absolute scale but also corrects the experimental data for the "Cell effect".

The experimental values were obtained for a cylindrical sample of HCOF Cu, measured during the commissioning run of the high temperature system.

The reference electrode separation at $T = 293\text{K}$ was evaluated by linear regression in the region $T = 300 \rightarrow T = 360\text{K}$. In this region the thermal expansion of most samples is linear in temperature (if one ignores the possibility of phase transitions occurring in the sample in this range of $T$).

Thus one may calculate the change in sample length as a function of temperature, using:-

$$\Delta l_{\text{Meas}} = d_{293\text{K}} - d(T)$$

(3.35)

The correction for $\Delta l_{\text{meas}}$ accounting for the relative nature of the dilatometer and the experimental cell effect

$$\frac{\Delta l(T)}{l_0} = \left[ \frac{\Delta l(T)_{\text{meas}} + \Delta l_{\text{cell effect}}}{l_0} \right](T)$$

(3.36)

Values for $\alpha(T)$ were calculated from this data as described previously.
3.6. Data Acquisition and Data Analysis.

Chapter 3. Instrumentation.

3.6.3.3. Data analysis for low temperature magnetostriction.

The method of raw data collection for the measurement of magnetostriction, was essentially a continuous data acquisition loop. The system acquires data whilst the superconducting solenoid is ramped between an initial and a final field. Since there is no method at present with which to measure the applied field within the cryostat, a linear regression is used to calculate the field applied to the sample at time $t$. The initial and final fields are accurately determined from the current flowing in the solenoid, and the data is acquired with a constant time delay between measurements. It is reasonable to assume the applied field varies linearly in time between the initial and final fields, since the field is ramped over a long period of time $\approx 110$ mins, and the current is increased at a constant rate $\frac{dl}{dt} = \text{constant}$.

It is therefore simple to calculate the field applied to the sample for each measurement point using a regression between the initial and final fields.

The reference electrode separation required to evaluate $\delta l(H)$ is taken to be the initial separation at the start of the field sweep, thus one can calculate $\delta l(H)$ using:

$$\Delta l(H)_{\text{Max}} = d_{\text{Start ramp}} - d(H)$$

It is thus simple to evaluate $\delta l(H)/l_0$ knowing the original sample length.
3.7. Summary.

The major research methods available for the measurement of sample dilation have been discussed, from this discussion one can conclude that the technique of three terminal capacitance dilatometry is the method that gives the highest resolution in $dl$.

The technique of capacitance dilatometry is discussed, including a description of the transformer ratio arm bridge and phase sensitive detection system required to achieve a resolution of $dl/l_0 \approx 10^{-10}$.

A brief introduction to cryogenic systems is presented, including a brief description of cryogenic temperature sensors, and PID three term temperature control.

The design and operation of a low temperature three terminal capacitance dilatometer system (LTDS) has been presented. The characteristics of the LTDS are, $1.5K < T_{\text{sample}} < 300K$, $T < H_{\text{sample}} < 7T$.

The design and operation of a high temperature three terminal capacitance dilatometer system (HTDS) has been presented. The system characteristics of the HTDS are, $300K < T_{\text{sample}} < 850K$.

The characteristics of the dilatometer control program have been discussed. The methods of data analysis for the LTDS and the HTDS are described, including the corrections required for normalisation of the data to a true scale for the linear coefficient of thermal expansion.
3.8. References.

6. Andres, K., 1961, Cryogenics, 2, 93.
Chapter 4. Aspects of neutron scattering.

4.1. Introduction.

The advent of nuclear reactors in 1945 [1] has led to neutron diffraction becoming a topic of some importance in condensed matter physics. However it was shown nine years earlier (1936) [2] that the neutron could be diffracted by a crystalline substance, and the neutron-crystal interaction could be described by wave mechanics.

The necessity to unambiguously determine both, nuclear and magnetic structure of materials and lattice and magnetic excitations has led to a large research effort in the area of neutron scattering. One may section this ever increasing research topic into two broad areas those being elastic and inelastic neutron scattering. For the interests of brevity and relevance to this work only elastic scattering will be discussed.

This chapter may be summarised as follows:-

1. The physical nature of neutron scattering will be discussed. Such that one may understand the reasons for performing both unpolarised as well as spin polarised neutron scattering experiments to determine nuclear and magnetic structures and excitations.

2. To describe the design of the neutron diffractometer D2B, and the polarised neutron spectrometer D7. The methods of data analysis will also be discussed for both instruments.
4.2. Properties of the neutron.

The essential properties of the neutron which make it a powerful probe of condensed matter are as follows:-

\( \text{i. Electrically neutral.} \)
\( \text{ii. } m_{\text{Neutron}} \approx m_{\text{Proton}} \)
\( \text{iii. Nuclear spin } = \frac{1}{2} \)
\( \text{iv. Nuclear magnetic moment } = -1.93 \cdot \mu_N (\mu_N = \frac{e\hbar}{2m_p}) \)

The energy of a neutron with a wave vector \( k \) is:­

\[ E = \frac{\hbar^2 k^2}{2m} \quad (4.1) \]

Where \( m \) is the neutron mass. One may quote the energy of the neutron in units of meV, taking \( m \) to be 9.383\( \times \)10\(^8\) eV so:-

\[ \frac{\hbar^2}{2m} = 2.08 \text{meV} \ \AA^2 \quad (4.2) \]

In terms of neutron wavelength:-

\[ \lambda = \left( \frac{\hbar^2}{2mE} \right)^{1/2} \]
\[ \lambda = \sqrt{9.04E} \ \AA \quad (4.3) \]

Thus a neutron with an energy of \( E=25 \)meV has a wavelength of \( \lambda=1.81 \)\( \AA \).

This wavelength is of the same order of magnitude as the lattice spacing in solids, therefore the diffraction of neutrons from condensed matter can show prominent interference effects. Neutron beams with low energies are referred to as being cold, the opposite being true for high energy beams. The approximate energies of various types of beam are given in *table 1*.

<table>
<thead>
<tr>
<th>Type</th>
<th>E [meV]</th>
<th>T [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold</td>
<td>0.1 → 10</td>
<td>1.5 → 114</td>
</tr>
<tr>
<td>Thermal</td>
<td>10 → 100</td>
<td>114 → 1140</td>
</tr>
<tr>
<td>Hot</td>
<td>100 → 500</td>
<td>1140 → 5700</td>
</tr>
<tr>
<td>Epithermal</td>
<td>&gt;500</td>
<td>&gt; 5700</td>
</tr>
</tbody>
</table>

*Table 4.1. Approximate energies of neutron beams.*

One characteristic of crystalline solids is the three dimensional periodic manner in which the constituent atoms arrange themselves. Such solids may be examined by investigation of the way in which they scatter radiation. The total intensity of a diffracted beam is the sum of the components of radiation scattered by individual atoms, and is a function of the structure factor \( F \), thus for a crystalline material the total scattered intensity (coherent) \( (I_{coh}) \) is a function of crystallographic orientation \([1]\).

\[
I_{coh} = \frac{\pi N_c}{2\kappa^2} \sum_{hkl} 4\pi F_{hkl}^2 d_{hkl}^2 
\]

(4.4)

Where \( d_{hkl} \) is the lattice spacing of the relevant planes, \( N_c \) is the number of unit cells per unit volume and \( \kappa \) is the scattering vector. The summation is taken over all planes that are capable of giving reflections with the neutron wavelength used i.e. \( d \geq \lambda/2 \). Where \( F_{hkl}^2 \) is the square of the structure factor of the unit cell for the \( hkl \) reflection and is given by where the sum is taken over all atoms in the unit cell:

\[
F_{hkl}^2 = \left| \sum b \exp \left( 2\pi \left( \frac{h}{a_0} + \frac{k}{b_0} + \frac{l}{c_0} \right) \right) \right|^2
\]

(4.5)

Where \( b \) is the scattering length for the atom at each position.

Although, as shown previously the order of magnitude of \( \lambda \) for the neutron is similar to that for x-rays, however the physical processes that govern the two separate techniques are quite different. For x-ray diffraction the principal interaction is between the x-ray photon and the electron via the electron charge. For neutron diffraction one of the two principle interactions is between the neutron and the nucleus of the atom. The neutron scattering technique therefore allows a clear picture of the nuclear structure of the material to be gained. The second principle interaction of neutron diffraction is between the neutron and the magnetic moment of the atom (if the atom is magnetic), therefore one may also determine the magnetic structure of the material in question. The very fact that one may probe both the nuclear and magnetic structure of materials using neutron diffraction makes neutron diffraction an essential tool for many branches of modern physics.

4.3.1. The nuclear cross section for a neutron.  
The geometry of the scattering problem is shown in Fig. 4.1 [3].

Fig. 4.1. The scattering geometry for neutrons.  
A neutron with a wave vector \( \mathbf{k} \) is scattered into a state with a wave vector \( \mathbf{k}' \). The momentum transfer is \( \hbar \kappa \), where \( \kappa \) is the scattering vector described by:  
\[
\hbar \kappa = \hbar \mathbf{k} - \hbar \mathbf{k}' \tag{4.6}
\]
One should note that if one considers an elastic scattering event then the magnitude of the initial and final wave vectors must be equal such that \( \kappa = \mathbf{k} - \mathbf{k}' = \tau \). Where \( \tau \) is a reciprocal lattice vector.

The basic quantity that is measured is the effective cross section.  
\[
\sigma_{\text{eff}} = \frac{\text{No.of scattering events/time}}{\text{Incident flux density}} \tag{4.7}
\]
The unit of cross section is area (1 barn = 10^{-24} \text{m}^2)

One may define a total cross section and a differential cross section. The double differential cross section is the fraction of incident neutrons with incident energy \( E \) scattered into an element solid angle \( d\Omega \), with an energy between \( E' \) and \( E' + dE' \). The double differential cross section is denoted by:  
\[
\frac{d^2\sigma}{d\Omega dE'} \tag{4.8}
\]
It is clear that the double differential cross section contains both elastic and inelastic events.
To consider only energy integrated scattering (i.e. counting neutrons without employing energy analysis) results in the differential cross section, this can be written as:

$$\frac{d\sigma}{d\Omega} = \int_{-\infty}^{\infty} dE \frac{d^2\sigma}{d\Omega dE}$$  \hspace{1cm} (4.9)

This scattering is usually dominated by elastic events.

From [3] one may describe differential cross section as:

$$\frac{d\sigma}{d\Omega} = \left| \langle k' | \hat{V} | k \rangle \right|^2$$  \hspace{1cm} (4.10)

Where $\hat{V}$ is defined as the interaction potential between the neutron and the target sample.

$\hat{V}$ is not constant throughout the sample but varies according to the arrangement of atoms. If one considers elastic neutron scattering events from bound nuclei then the interaction potential (within the Born approximation) is given by:

$$\hat{V}(r) = 2\pi \hbar^2 / m b \delta(r - R)$$  \hspace{1cm} (4.11)

Where $b$ is the scattering length and $R$ is the position of the nucleus.

One may define the total cross section as the sum of two separate components, namely the coherent cross section, and the incoherent cross section, thus:

$$\frac{d\sigma}{d\Omega}_{\text{total}} = \left( \frac{d\sigma}{d\Omega}_{\text{coherent}} \right) + \left( \frac{d\sigma}{d\Omega}_{\text{incoherent}} \right)$$  \hspace{1cm} (4.12)

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{coherent}} = |b|^2 \left| \sum_i \exp(ik \cdot R_i) \right|^2$$  \hspace{1cm} (4.13)

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{incoherent}} = N|b - \bar{b}|^2$$  \hspace{1cm} (4.14)

There is a profound difference between the coherent cross section and the incoherent cross section. Notably coherent scattering may only occur if stringent geometrical conditions are met by the system. However coherent scattering is produced by strong interference between waves scattered by different nuclei.

In contrast to this incoherent scattering exhibits no such feature, that is to say due to the randomness of the phase of the scattered neutron no
interference occurs, and the cross section is completely isotropic. One may think of the differences as follows: since the scattering length varies from one isotope to another, the incoming neutron does not see a crystal of uniform scattering potential, but one where the scattering varies from one point to the next. It is only the average scattering potential that can give rise to interference effects and therefore coherent scattering, thus the coherent scattering cross section is proportional to $|b|^2$. The deviations from the average potential cannot give interference effects but give rise to incoherent scattering. The deviations do not affect the coherent cross section. The incoherent cross section is proportional to the mean-square deviation from the average scattering potential i.e. $(b - b)^2 = b^2 - b^2$.

4.3.2. Magnetic neutron scattering.

If a neutron travels through a material that has a magnetic moment then the neutron will be scattered. The magnetic scattering occurs as a result of the interaction between the magnetic field caused by the magnetic moment arising due to the electronic structure, and the magnetic moment of the neutron.

The scattering amplitude of a point dipole of S Bohr magnetons is given by [4]:

$$b = S \frac{e^2 \gamma}{mc^2} = 0.27 \cdot 10^{-12} \text{ cm}$$  

(4.15)

Where $m$ is the electron mass, $e$ the charge, $c$ the speed of light and $\gamma$ the magnetic moment in nuclear magnetons.

The magnitude of the observed magnetic scattering depends on several factors:

1. The form factor of the material, i.e. the Fourier transform of the spatial distribution of the magnetic moments.
2. The magnitude of the magnetic moment.
3. The relative orientation between the neutron moment and the sample moment.

Although 1. and 2. are experimentally uncontrollable it is possible to alter the relative orientation of the neutron moment with respect to the moment.
of the sample. This technique of neutron scattering is termed as “spin polarised” as the incident neutron beam is polarised with respect to the direction of the neutron spin.

For magnetic scattering the magnetisation density of the electrons \( M_e(r) \) interacts with the dipole field of the neutron. The magnetisation density of the electrons is the sum of spin and angular momentum contributions \( M_s(r) \) and \( M_L(r) \) respectively [5].

\[
M_e(r) = M_L(r) + M_s(r) = M_L(r) - g \mu_B S(r)
\]  (4.16)

The interaction potential for magnetic scattering is then:

\[
V_e = \frac{1}{4\pi\mu_B} M_e(r) B_n(r)
\]  (4.17)

Where \( B_n(r) \) is the dipole field of the neutron.

For unpolarised neutrons the coherent scattering from an ordered magnetic material is a function of the sum of magnetic and nuclear structure factors \( F_{mag}^2 \) and \( F_{nuc}^2 \) where [1]:

\[
F_{nuc}^2 \approx \sum b \exp(2\pi i \left( \frac{h}{a_0} + \frac{k}{b_0} + \frac{l}{c_0} \right))
\]  (4.18)

\[
F_{mag}^2 \approx \sum p \exp(2\pi i \left( \frac{h}{a_0} + \frac{k}{b_0} + \frac{l}{c_0} \right))
\]  (4.19)

Where \( p \) is evaluated from the form factor for the particular scattering angle and atom.

The total structure factor is then [1]:

\[
F^2 = F_{nuc}^2 + q^2 F_{mag}^2
\]  (4.20)

Where \( q^2 = \sin^2 \alpha \). \( \alpha \) is taken as the angle between the scattering and magnetisation vectors.

Although one may obtain information on the magnetic state of a sample with an unpolarised beam, it is far more useful to use a polarised beam of neutrons. Yet more information may be obtained if one knows the polarisation of the neutron before and after the scattering event.

One may think of only two distinct orientations of the neutron moment or spin with respect to an applied magnetic field, these are parallel and anti-parallel. The production of a polarised beam is non-trivial, and the degree
of polarisation is strongly energy and method dependent [6]. There are two commonly used methods of achieving a polarised beam. These will be described below.

4.3.2.1. Selective magnetic Bragg reflection by a single crystal.
The nuclear scattering length is angle independent, and the magnetic scattering of a ferromagnet is dependent on the magnetic form factor. The ratio between the two components will therefore vary in a magnetic material as one looks at individual Bragg peaks. Further the magnetic component alters sign for the spin up neutrons when compared to spin down neutrons. Therefore one may theoretically arrange a system whereby the nuclear and the up spin components will exactly (more or less) cancel out, thus what is left is a uniquely polarised beam. This method of polarisation may be realised using the (111) reflection from the Heusler alloy Cu$_2$MnAl.

4.3.2.2. Polarising supermirrors.
Neutrons may be reflected by total reflection at the surface of a magnetised mirror. The reflection depends upon the spin state of the neutron Fig.4.2. By proper selection of materials one may “engineer” a neutron mirror that reflects only one spin state. The effectiveness of the end device may be improved by using a multilayer coating with alternating layers of magnetic and non magnetic material. The maximum efficiency obtainable is high when the system has been optimised $\approx 99\%$. The supermirror technique was developed and optimised at the ILL by Schärpf [7].

![Fig. 4.2. Schematic of the reflectivity $R$ as a function of $\theta/\lambda$ for the two eigenstates of the neutron.](image)
4.3.3. The polarisation dependent cross section.

The calculation of the polarisation dependent cross section and the final scattered polarisation have been thoroughly treated in [8,9]. We may assume that there exists a purely nuclear, purely magnetic, and a nuclear-magnetic interference term to the cross section. For the examples given below the spin orbit interaction is either zero or quenched.

The nuclear part has the form:

\[ \nu_n = \frac{2\pi\hbar^2}{m} \left( T_0 + T_1 \cdot \hat{s} \right) \]  (4.20)

Where \( T_0 \) is of the type \((b^+(I+1)+b^-I)/(2I+1)\) which appears in the coherent cross section. \( T_1 \) is of the type \((b^+ - b^-)/(2I+1)\), which appear in the incoherent cross section. \( I \) is the nucleus spin operator, \( b^+ \) and \( b^- \) are scattering lengths and \( \hat{s} \) is the neutron spin operator.

There will be a superposition of incoherent and coherent scattering, these effects will depend upon the beam polarisation and the magnetic nuclear interference. The incoherent scattering appears as a polarisation dependent background, thus care must be exercised when correcting the data.

The magnetic term has the form:

\[ \nu_m = \left( \frac{2\pi\hbar^2}{m} \right) \left( \frac{2\gamma_0^2}{m_c^2} \right) \sum_j \exp(i\xi_j) S_\perp \cdot \hat{s} \]  (4.21)

Where \( S_\perp = \hat{s} - (\hat{k} \cdot \hat{s}) \hat{k} \) is the projection of \( \hat{s} \) onto the plane perpendicular to the scattering vector, as shown in Fig. 4.3. Therefore for magnetic scattering only spin components perpendicular to the scattering vector are effective. This allows the use of polarisation analysis on magnetic systems, by setting the direction of the incident polarisation with respect to the scattering vector. In this way one may distinguish the different components of the scattering. It is this technique that is employed on the spectrometer D7, described later in this chapter.

---

4.3.4. Spin flippers and the flipping ratio.
Spin flippers are devices that may be used to rotate the direction of spin of a polarised neutron beam, thus one may induce a $\pi$ rotation of the neutron spin. The use of such devices allows one to measure the flipping ratio $R$, of the sample. That is the ratio of the flux of neutrons that are flipped by magnetic interaction in the sample and then scattered into a detector to the flux of neutrons that remain with their original spin orientation.

4.3.4.1. The flipping ratio $R$.
The intensity of a Bragg reflection from purely nuclear scattering is proportional to the square of the nuclear structure factor $F_N$ \[1\]:
\[
I \approx |F_N(q)|^2
\] (4.22)

For magnetic Bragg scattering the intensity is proportional to the square of the magnetic structure factor $F_M$:
\[
I \approx |F_M(q)|^2
\] (4.23)

For spin polarised neutrons the intensity is proportional to the square of the structure factors:
\[
I \approx |F_N(q) \pm F_M(q)|^2
\] (4.24)

There are contributions proportional to $|F_N(q)|^2$ and $|F_M(q)|^2$ and also an interference term proportional to $F_N(q) \cdot F_M(q)$.

---

Fig. 4.3. The vector relationships for magnetic neutron scattering.

One may exploit the interference term using spin polarised neutrons. The sign of the magnetic structure factor will change if the neutron spin is reversed with respect to an external field.

This results in:

\[ I_{\parallel \parallel} \approx |F_N(q) + F_M(q)|^2 \] for the spin parallel case \hspace{1cm} (4.25)

\[ I_{\perp \perp} \approx |F_N(q) - F_M(q)|^2 \] for the antiparallel case \hspace{1cm} (4.26)

The flipping ratio is defined as the ratio of these two intensities:

\[ R = \frac{I_{\parallel \parallel}}{I_{\perp \perp}} = \frac{|F_N + F_M|^2}{|F_N - F_M|^2} \approx 1 + 4 \frac{F_M}{F_N} \hspace{1cm} (4.27) \]

4.3.4.2. The operation of a Larmor \( \pi \) Spin flipper.

In order that one may flip the spin of the neutron one must first have a well polarised neutron beam, secondly a guide field is required.

The flipper is essentially a magnetic field, that is engineered to rotate the spin by \( \pi \) over the length of the device. Thus the neutron spin will precess as it travels through the device. The characteristics of the device being such that the neutron spin undergoes a \( \pi \) Larmor precession. This type of device utilises a DC field, a schematic is shown in Fig. 4.4.

From [11] the field required to produce a spin turn of \( \pi \) is given as:

\[ H_x = \frac{67.825}{\lambda L} \hspace{1cm} (4.28) \]

Where \( \lambda \) is the neutron wavelength [\( \text{Å} \)] and \( L \) is the path length of the device [cm].

The action of the guide field is to maintain the neutron beam polarisation by preventing a random precession due to stray magnetic fields.

The use of this type of device allows the measurement of both flipping ratio and polarisation \( P \):

\[ P = \frac{(R - 1)}{(R - 1)} \hspace{1cm} (4.29) \]

Most neutron diffraction experiments i.e. those using elastic neutron scattering are carried out using two axis diffractometers. The general operation of such a device is as follows. The neutron beam is almost completely monochromated by reflection from a crystal. The wavelength of the incident neutrons can be altered by adjusting the scattering angle of the monochromator crystal. The neutrons scattered from the sample are counted by some type of detector which can be rotated about the sample position i.e. about 20. Detectors are based upon nuclear reactions caused by the incident scattered neutron, the detection can be either conventional gas ionisation or solid state scintillation. The resolution of the instrument is determined by the collimation of the neutron beam, before the monochromator, before the sample and before the detector.

This section will describe the basic characteristics and uses of two neutron instruments used for experiments presented later in this thesis.
4.4. The high resolution neutron diffractometer D2B.

The diffractometer D2B Fig. 4.5 & 4.6 is a high resolution two axis diffractometer with a 64 element multidetector. The instrument is versatile in terms of sample environment and range of measurement. D2B was used to investigate the magnetic phase diagram of the Heusler alloy Tb₂AgIn, as a function of temperature and applied field (Chapter 6). To this end a 5T cryomagnet in a VTI type helium cryostat was used to provide the sample environment.

The characteristics of the instrument are as follows [12]:

The diffractometer D2B is placed on the thermal beam H11 in the reactor hall at ILL Grenoble France. D2B is characterised by the very high take-off angle (135°) for the monochromator, which has a relatively large mosaic spread of 20' to compensate for the corresponding intensity loss. The monochromator is 300 mm high, focusing vertically onto about 50 mm; this large incident vertical divergence is matched by 200 mm high detectors and collimators. A complete diffraction pattern is obtained after about 100 steps of 0.025° in 2θ since the 64 detectors are spaced at 2.5° intervals. Such scans take typically 30 minutes; scans may be repeated to improve the statistics. There is about 4 % λ/2 and λ/3 contamination despite the Ge[hkl] monochromator. The resolution of D2B is \( \Delta d/d \approx 10^{-4} \).

Wavelengths and respective Ge reflections are shown in table 4.2.

<table>
<thead>
<tr>
<th>Ge (hkl)</th>
<th>( \lambda [\text{Å}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>557</td>
<td>1.051</td>
</tr>
<tr>
<td>337</td>
<td>1.277</td>
</tr>
<tr>
<td>551</td>
<td>1.464</td>
</tr>
<tr>
<td>335</td>
<td>1.594 (optimum)</td>
</tr>
<tr>
<td>331</td>
<td>2.398</td>
</tr>
<tr>
<td>113</td>
<td>3.152</td>
</tr>
</tbody>
</table>

Table 4.2. Wavelength and respective Ge monochromator reflections for D2B.
Fig 4.5. Schematic diagram of the two axis diffractometer D2B (Courtesy of ILL).

Fig 4.6. The diffractometer D2B with 6T cryomagnet in place (Courtesy of ILL).
4.4.2. D2B data analysis.
D2B provides the user with a traditional type of output file, the utility program \textit{sumd2b} is used to reduce the multidetector data into a format that is useable and normalised to the incident monitor count. As D2B is primarily used to undertake structural investigations one may then use any of the readily (via internet) available structural refinement packages. Commonly, however, the program FULLPROF is used to treat the experimental data. The program FULLPROF is downloadable from the internet.

Fullprof is a Rietveld [12,13] refinement package that operates a multi phase refinement algorithm for both nuclear and magnetic structures, using either a control file interface, or a GUI (latest version).

4.4.3. The high resolution TOF spin polarised spectrometer D7.
The instrument D7 Fig. 4.7 & 4.8 is a multidetector diffuse scattering spectrometer and has the following characteristics [14]: D7 was designed to study diffuse scattering arising from disorder phenomena in solids, such as point defects and short range order. The diffuse scattering intensity appears in between the structural Bragg reflections. It is usually weak and may contain both elastic and inelastic contributions. D7 features a unique combination of full 3-dimensional polarisation analysis using a multidetector set-up with time-of-flight energy analysis. A doubly focusing graphite monochromator is situated in the cold source beam guide immediately downstream from IN6. The monochromatic beam passes through a supermirror polariser, a Mezei spin flipper and a disk chopper (all removable). A removable set of three orthogonal Helmholtz coils, wide enough for a furnace or orange cryostat to enter, is placed around the sample position in order to define the incident beam polarisation direction. Four banks of 16 $^{3}$He detectors are placed around the sample position at a distance of 1.5 m. The detector banks are mounted on air cushions and can be moved separately. Each bank contains an assembly of permanent magnets to provide the guide field, followed by 8 separate supermirror polarisers. In this configuration, only 8 detectors in each bank can be used. The guide field and analyser supermirrors can be replaced by a
4.4 Neutron Instruments.

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radial collimator for measurements without polarisation analysis, which allows all 16 detectors of each bank to be used. In total, there are 6000 supermirrors on D7. The detectors can cover scattering angles from 7 to 160 degrees. Full 3-dimensional polarisation analysis enables the experimental separation of incoherent, coherent and magnetic components. The following modes of measurement are possible:

i. No Polarisation Analysis. Unpolarised neutrons - no analysis after scattering

ii. Z-polarisation analysis. Two measurements: with and without spin-flip. Allows the separation of nuclear and magnetic scattering

iii. XYZ-Polarisation Analysis. Six measurements. Allows separation into coherent, nuclear spin incoherent and magnetic contributions

Each of these measurements can be performed as a diffraction measurement with the chopper removed or as a time-of-flight measurement.

D7 operates at the following wavelengths: 3.1, 4.8, 5.7 Å

With reference to Fig.4.7 the main components of the instrument D7 are described as follows:

Beam polariser The device used is a supermirror which provides a high polarisation efficiency over a wide wavelength band.

Guide field The neutron beam polarisation is maintained using a vertical guide field. The guide field is created by permanent magnets and must be present over the entire neutron flight path from the beam polariser to the detectors.

Mezei Spin flipper A coil producing a well defined horizontal magnetic field with a sharp transition at the coil surface: π-coil with Brookhaven correction

XYZ coils A set of three Helmholtz coils around the sample position producing magnetic fields in mutually orthogonal directions. This allows the incident neutron spin direction to be defined for magnetic scattering experiments.

Polarisation analysers 32 supermirror benders are installed in front of the detectors, incorporating a total of 6000 individual polarising supermirrors.
Fig 4.7. Schematic representation of the instrument D7 * denotes position of XYZ spin turn coils (Courtesy of ILL).

Fig 4.8. The high resolution TOF spin polarised spectrometer D7.
4.4.4. D7 data analysis.

Data are analysed using the XYZ technique, this allows unambiguous separation of the magnetic, coherent, nuclear spin incoherent cross sections for the sample. A full description of the technique can be found in [5,11]. For brevity only the results will be presented.

Further to the XYZ technique the raw data must be normalised to the incident monitor, and then corrected for:-

1. The finite flipping ratio, and polariser/detector pair efficiency.
2. Multiple scattering. (Not discussed)
3. Normalised to an absolute scale. This is achieved by the measurement of a vanadium standard.

4.4.4.1 The XYZ-difference method.

As stated previously the XYZ-difference method allows the unambiguous separation of the coherent, spin incoherent and the magnetic scattering cross sections for a polarised neutron powder diffuse scattering instrument such as D7. Only the salient points will be presented here, a full description of the technique is presented by Schärpf and Capellmann [5]. Furthermore a full description of the instrument D7 is presented by Schärpf [11].

The XYZ-difference methods relies upon the vector nature of the magnetism-neutron interaction. The co-ordinate system is such that Z is taken as the vertical direction.

Experimentally in order to facilitate the use of the XYZ method six cross sections must be measured, these are:-

1. Z spin flip cross section (SF).
2. Z non spin flip cross section (NSF).
3. X spin flip cross section (SF).
4. X non spin flip cross section (NSF).
5. Y spin flip cross section (SF).
6. Y non spin flip cross section (NSF).

In order to measure these cross sections the direction of the incident neutron polarisation is rotated into the Z, X and Y direction by an external magnetic field produced by the orthogonal Helmholtz coils that are placed
around the sample position Fig 4.7 & 4.8. The rotation of the neutron polarisation is adiabatic, and the applied field is such as not to alter the magnetisation of the sample. Capellmann and Schärpf state that the experimentally measured double differential cross sections are related to the coherent, spin incoherent and magnetic scattering cross sections in the following manner:

\[
\frac{\partial^2 \sigma^x_{++}}{\partial \Omega \partial \omega} = \frac{1}{2} \frac{\partial^2 \sigma_{\text{paramag}}}{\partial \Omega \partial \omega} \cos^2 \alpha + \frac{1}{3} \frac{\partial^2 \sigma_{\text{spin incoh}}}{\partial \Omega \partial \omega} + \frac{2}{3} \frac{\partial^2 \sigma_{\text{coh}}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{\text{iso incoh}}}{\partial \Omega \partial \omega} \tag{4.30}
\]

\[
\frac{\partial^2 \sigma^x_{++}}{\partial \Omega \partial \omega} = \frac{1}{2} \frac{\partial^2 \sigma_{\text{paramag}}}{\partial \Omega \partial \omega} \sin^2 \alpha + \frac{1}{3} \frac{\partial^2 \sigma_{\text{spin incoh}}}{\partial \Omega \partial \omega} + \frac{2}{3} \frac{\partial^2 \sigma_{\text{coh}}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{\text{iso incoh}}}{\partial \Omega \partial \omega} \tag{4.31}
\]

\[
\frac{\partial^2 \sigma^y_{++}}{\partial \Omega \partial \omega} = \frac{1}{2} \frac{\partial^2 \sigma_{\text{paramag}}}{\partial \Omega \partial \omega} \cos^2 \alpha + \frac{1}{3} \frac{\partial^2 \sigma_{\text{spin incoh}}}{\partial \Omega \partial \omega} + \frac{2}{3} \frac{\partial^2 \sigma_{\text{coh}}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{\text{iso incoh}}}{\partial \Omega \partial \omega} \tag{4.32}
\]

\[
\frac{\partial^2 \sigma^z_{++}}{\partial \Omega \partial \omega} = \frac{1}{2} \frac{\partial^2 \sigma_{\text{paramag}}}{\partial \Omega \partial \omega} \cos^2 \alpha + \frac{2}{3} \frac{\partial^2 \sigma_{\text{spin incoh}}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{\text{coh}}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{\text{iso incoh}}}{\partial \Omega \partial \omega} \tag{4.33}
\]

Where \( \alpha \) is the angle between the scattering vector and the field direction of the spin turn coil (x direction that is in the scattering plane).

By combining the experimentally measured cross sections one may separate the different contributions. For a powder sample one may assume that the correlation functions \(<<M_iM_j>>\) for \(I = XYZ\) are all equal, and the mixed correlation functions are zero.

The paramagnetic double differential cross section is then:

\[
\left( \frac{\partial^2 \sigma_{\text{paramag}}}{\partial \Omega \partial \omega} \right)_{++} = 2 \left( \frac{\partial^2 \sigma^x_{++}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma^y_{++}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma^z_{++}}{\partial \Omega \partial \omega} \right) \tag{4.36}
\]

\[
\left( \frac{\partial^2 \sigma_{\text{paramag}}}{\partial \Omega \partial \omega} \right)_{++} = 2 \left( 2 \frac{\partial^2 \sigma^x_{++}}{\partial \Omega \partial \omega} - \frac{\partial^2 \sigma^x_{++}}{\partial \Omega \partial \omega} - \frac{\partial^2 \sigma^x_{++}}{\partial \Omega \partial \omega} \right) \tag{4.37}
\]

The nuclear spin incoherent double differential cross section is:

\[
\left( \frac{\partial^2 \sigma_{\text{spin incoh}}}{\partial \Omega \partial \omega} \right)_{++} = \frac{2}{3} \left( \frac{\partial^2 \sigma^x_{++}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma^y_{++}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma^z_{++}}{\partial \Omega \partial \omega} \right) \tag{4.38}
\]
The sum of the coherent and isotope incoherent differential cross sections is:

\[
\frac{\partial^2 \sigma_{\text{coh}}}{\partial \Omega \partial \omega} + \frac{\partial^2 \sigma_{\text{iso}}}{\partial \Omega \partial \omega} = \frac{1}{2} \frac{\partial^2 \sigma_{\text{paramag}}}{\partial \Omega \partial \omega} - \frac{1}{3} \frac{\partial^2 \sigma_{\text{spin}}}{\partial \Omega \partial \omega} \quad (4.39)
\]

Coherent scattering cannot be distinguished from isotope incoherent scattering. Irrespective of the polarisation of the incident beam the scattered intensity of the beam due to scattering by unpolarised nuclear spins is always 1/3 without flip and 2/3 with flip of the incident neutrons.

**4.4.4.2. Finite flipping ratio correction.**

To correct for the inefficiencies in the Flipper / polariser / analyser chain, (of which there are 32 combinations, since there are 32 analysers) a finite flipping ratio correction is performed. The XYZ scattering of a fused quartz sample is measured. Fused quartz is characterised by a broad diffuse scattering with no magnetic cross section and no nuclear spin incoherent cross section. The flipping ratio for each detector \( R_n \) is measured:

\[
R_n = \frac{I_{\uparrow \uparrow}}{I_{\downarrow \downarrow}} \quad (4.40)
\]

An average flipping ratio (percentage) for D7 is \( \bar{R} = 30\% \pm 1.5 \)

From \( R_n \) one can determine the polarisation product for each detector:

\[
(p_{\text{polariser}} p_{\text{analyser}} p_{\text{Flipper}})_n = \frac{R_n - 1}{R_n + 1} \quad (4.41)
\]

This may then be used to correct for the finite flipping ratio of the measured data, as it includes all polarisation losses by depolarisation of the beam in the polariser analyser and guide fields, and efficiencies in the polariser, flipper and analyser.

The correction to the measured intensity for each detector \( n \) can be performed using:

\[
I_{\text{NSF}}^{\text{Corr}} = I_{\text{NSF}} + \frac{1}{R_n - 1} (I_{\text{NSF}} - I_{\text{SF}}) \quad (4.42)
\]

\[
I_{\text{SF}}^{\text{Corr}} = I_{\text{SF}} + \frac{1}{R_n - 1} (I_{\text{NSF}} - I_{\text{SF}}) \quad (4.43)
\]
4.4.4.3. Vanadium normalisation.

For absolute normalisation of data one may use the scattering of a sample of known and well defined cross section. Vanadium is just such a sample, since it is nearly an ideal incoherent scatterer. The incoherent cross section of Vanadium is given as 5.187b, and the coherent cross section is 0.0184b [15]. Since the scattering is nearly all incoherent the angular scattering is isotropic. Therefore all detectors should ideally "see" the same number of neutrons. However due to absorption and detector inefficiency this is never quite so. Thus one must correct for such deviations using the data taken from a Z polarisation measurement of a vanadium sample.

4.5. Summary.

A brief discussion of nuclear and magnetic neutron scattering has been presented, to support the experimental neutron scattering results in this work.

The design of the high resolution neutron diffractometer D2B is discussed, together with a brief description of data analysis procedures in order to aid the reader in subsequent chapters.

The design of the high resolution TOF spectrometer D7 has been discussed. A brief discussion of the XYZ-difference method for the separation of the coherent, nuclear spin incoherent and the magnetic scattering cross sections is given. A brief discussion of the necessary corrections to data for such an instrument is also presented.
4.6 References.

15. Neutron cross sections online@ILL.fr.
Chapter 5. An investigation of the lattice and magnetic properties of the Ferromagnetic shape memory alloy Ni$_2$MnGa

5.1. Introduction.

The shape memory effect for the Heusler alloy Ni$_2$MnGa is a rare example of a ferromagnetically ordered compound, for which a Martensitic phase transition occurs within the magnetically ordered state. It is this observation, and the possibility of studying the mutual influence of a magnetic field, on the magnetic properties and the crystallographic lattice, that has motivated substantial research activity on this alloy.

Since the discovery that Ni$_2$MnGa crystallises in the Heusler L2$_1$ structure (Webster (1968) [1]) there has been a continued interest in the physical properties of this intermetallic compound. The structural and magnetic properties of Ni$_2$MnGa were characterised more fully by Webster and Ziebeck (1984) [2,3] who found that Ni$_2$MnGa transforms from a ferromagnetically ordered L2$_1$ Heusler structure, with $a_{293K} = b_{293K} = c_{293K} =$ 5.822Å, to a disordered tetragonal phase, with $a_{4.2K} = b_{4.2K} = 5.90Å$ & $c_{4.2K} = 5.566Å$, with $c/a = 0.94$. The system is ferromagnetically ordered in both the crystallographically ordered phase, and the crystallographically distorted phase, with a Curie temperature $T_C \approx 375K$. The magnetic order as determined using neutron scattering is that the alloy has an ordered magnetic moment of 3.86µ$_B$ associated with the Mn$^{3+}$ site. In the paramagnetic state the effective magnetic moment is determined as $P_{eff} = 4.75µ_B$.

The transition from the ordered L2$_1$ phase to the disordered tetragonal phase has been shown to be a Martensitic Phase transition (MT) [4-6], defined as a displacive, diffusionless, first order phase transition, from a highly symmetric high temperature phase, to a distorted phase at low temperature. Since the early work on the alloy most properties of the
system have been investigated to some degree, using a number of experimental methods. [7-9] All experimental results show that the system undergoes a Martensitic phase transition at \( \approx 200\text{K} \), and that the system is ferromagnetically ordered below \( T_C \approx 380\text{K} \).

Work by Bozhko et al. [10] has shown that both the Martensitic transition temperature and the Curie temperature of the alloy are highly sensitive to sample stoichiometry.

Many measurements, such as specific heat [11] and ultrasound studies [12] have demonstrated the existence of a transition at a temperature of \( \approx 20\text{K} \) higher than the MT, to a premartensitic state.

Conclusive proof of a premartensitic phase in the alloy comes from inelastic neutron scattering experiments [13-16]. Several anomalies in the parent state are observed, with a nearly complete softening of the [110] \( TA_2 \) mode as the sample temperature is reduced. The mode softening is caused by the formation of a premartensitic state in the parent phase. The parent structure undergoes a commensurate periodic lattice distortion, which in turn leads to the transition to the incommensurate Martensitic state at \( T_M \).

The precursor state is such that the periodic lattice distortion has a strong coupling to the homogeneous strains in the parent state. Therefore one may expect a lattice anomaly to appear at the onset of the pre-Martensitic state, characterised by a volume increase of the unit cell [12] and at \( T_M \) when the system undergoes a commensurate-incommensurate transition. A large lattice anomaly has been observed by Ullakko (1996) [8] at the Martensitic transition in the system, furthermore measurements of the elastic constants in \( \text{Ni}_2\text{MnGa} \) have confirmed the effect of the MT on the lattice. Anomalies associated with the precursor state have also been observed in such measurements, at a higher temperature than \( T_M \).

It has been demonstrated that the processes involved in the MT are sensitive to sample stoichiometry, variation of the Ni and Mn concentration [17] result in a variation of \( T_M \) and in the lattice modulation observed at \( T_M \).
Off stoichiometric Ni-Mn-Ga alloys also show a step like transition at $T_M$ in measurements of sample strain, during both, heating and cooling. Theoretical efforts based on Landau expansions of the free energy [18-20] have successfully modelled the magnetisation of Ni$_2$MnGa, reproducing the step like discontinuity at $T_M$ observed in magnetisation measurements as a function of temperature, furthermore such a theoretical treatment predicts the suppression of this transition as the applied field is increased to 18KOe.

Band structure calculations by Fujii et al. (1989) [21] have indicated that the MT is driven by a Band Jahn-Teller effect from the Mn$^{3+}$ ion seen as a hump in the density of states at $\varepsilon_F$. The possibility of a band Jahn-Teller effect explains the large lattice strains observed at $T_M$ and therefore the anomalies observed in the specific heat and elastic constants.

The application of an external magnetic field on Ni$_2$MnGa has been shown to cause a large magnetoelastic effect, furthermore the magneto-elastic effect is seen to increase in magnitude at temperatures below $T_M$ indicating a strong coupling of the field to the inhomogeneous strains in the sample.

It is important to clarify, using a sensitive technique, the lattice properties of Ni$_2$MnGa in both the ordered and the Martensitic state. The lattice response to an external applied magnetic field should also be investigated. In order to experimentally clarify the properties of the lattice, and in particular the change of lattice characteristics with the application of magnetic fields, a detailed study has been carried out of the thermal expansion of polycrystalline and single crystal Ni$_2$MnGa over a wide temperature range, using high resolution capacitance dilatometry. The effects of the Martensitic phase transition and the low temperature lattice properties have been studied.

It is pertinent at this point to expand upon the character of the Martensitic phase transition.
5.2. The Martensitic phase transition.

The term Martensitic transition applies in general to any diffusionless phase transformation in which the two phases are related by shear deformations [22]. In general there are two types of structural transitions:

1. Lattice distortive displacement.
2. Shuffle displacement.

The character of the two types of Martensitic transition can be seen in Fig. 5.1. The lattice distortive displacement contributes to a homogeneous strain in the material by converting one Bravais lattice to another, whilst the shuffle displacement within the unit cell produce no net strain. A general displacement transition can involve both types of displacement, however a Martensitic transition must involve shear dominant, lattice distortive transitions [23].

![Fig. 5.1. i. Simple shuffle displacement, ii. Simple lattice distortive displacement, from [23].](image-url)
5.2. The Martensitic transition.

For a material that undergoes a Martensitic phase transition one may assume that the strain is the order parameter [22]. Thus from the investigation of the material strain as a function of temperature one will obtain clear information regarding the structural transition.

5.3. Experimental.

The thermal expansion of 2 separate samples of the Heusler alloy Ni₂MnGa over a temperature range of 1.5K to 750K has been evaluated using 2 separate high resolution three terminal capacitance dilatometers. This technique was employed since it is widely accepted as the most sensitive method for measuring change in length \(dl\), easily giving achievable resolutions of \(dl/l_0 = 10^{-10}\). [24-25]

The low temperature data was acquired using a \(^4\)He cryostat containing a compensated 7T superconducting solenoid. The sample environment temperature measurement was achieved using two Cernox temperature sensors. This type of sensor exhibits a very low field dependence over the entire temperature range of operation. The temperature control system enabled sample environment control to within 1mK below 10K and \(\approx 10\)mK above.

Full details of the dilatometer systems can be found in Chapter 3.

Experimental data were taken using two methods. On heating, the sample environment temperature was controlled to a given setpoint using a pre-configured PID control algorithm. The sample cell capacitance and hence the sample change in length \(dl\) was sampled when the system reached stability at the setpoint.

On cooling the sample environment was cooled at a pre-determined rate of \(\approx 1\)K \(\text{min}^{-1}\) with the temperature ramp being controlled by the temperature controller. Data were taken at a predetermined sampling rate, (Max 1Hz) as the system cooled.

Magnetisation measurements were performed on a separate single crystal sample using a Quantum design SQUID magnetometer.
5.3.2. Sample preparation.

Three separate samples of the Heusler alloy Ni$_2$MnGa were prepared:

A polycrystalline and two separate single crystal samples.

The polycrystalline sample was prepared by melting the constituent elements of 4N purity in an argon arc furnace. The ingot was flipped and re-melted 4 times to ensure homogeneity. The sample weight loss after melting was determined to be <1%.

The thermal expansion sample was then prepared using the flop-cast method resulting in a cylindrical sample of diameter 6.5mm. The ends were cut parallel by spark erosion, resulting in a sample of length 20.05mm. The sample was then annealed at 600K for 24 hours. A sample of the original melt was powdered for X-ray analysis to confirm the composition and structure of the sample.

The single crystal sample (#1) was grown using the Bridgeman technique from constituents of 5N purity, the resulting crystal was oriented with the [110] crystallographic axis along the direction of growth. The orientation of the crystal was confirmed using Laue back-reflection X-ray photography.

Using spark erosion the crystal was cut for thermal expansion measurements such that the end faces of the sample were parallel, resulting in a sample length of 9.1mm. The sample was then annealed in the same manner as the polycrystalline sample, namely at 600K for 24 hours. This sample was used for the measurement of thermal expansion presented later in this chapter. The sample was determined to be off stoichiometry (see subsequent text) by accurate measurement of the Martensitic transition temperature.

The single crystal sample (#2) was pulled from the melt using the Czochralski technique and a tri arc furnace designed and built in the department of Physics at Loughborough University, the resulting sample was ≈ 2mm in diameter with the (110) crystallographic axis aligned in the growth direction. It was determined by measurement of the Martensitic transition temperature that the sample was of the correct stoichiometry.
5.4. The thermal expansion of polycrystalline Ni$_2$MnGa.

The thermal expansion of polycrystalline Ni$_2$MnGa will now be presented.

5.4.1. Thermal expansion from 4.2K to 800K with zero field for polycrystalline Ni$_2$MnGa.

The thermal expansion of the polycrystalline Ni$_2$MnGa sample (Length ($l_0$) at $T = 293K = 20.05mm$) was determined over a temperature range of 4.2K to 755K using both the high and low temperature capacitance dilatometers.

The dimensionless linear strain ($dl(T)/l_0$) for the polycrystalline sample is shown in Fig. 5.2. The data was taken using a heating cycle.

![Graph showing thermal expansion data]

*Fig. 5.2. Dimensionless linear strain ($dl(T)/l_0$) as a function of temperature for polycrystalline Ni$_2$MnGa (data taken on heating the sample).*

The data show a low temperature anomaly at 194K, corresponding to the Martensitic phase transition temperature ($T_M$), and a high temperature anomaly at 377K which is attributed to the ferromagnetic-paramagnetic phase transition temperature ($T_C$).

The two data sets shown in *Fig. 5.2.* exhibit a smooth transition from the low temperature (cryostat), to the high temperature (furnace) data. Within
the temperature interval for which the data series overlap excellent agreement is obtained.

5.4.2. Thermal expansion from 4.2K to 300K with applied magnetic fields of 0T to 2.5T for polycrystalline Ni$_2$MnGa.
Further investigations have concentrated on the Martensitic phase transition at $T_M = 194$K, and the low temperature properties of the alloy. The dependence of sample length on applied magnetic field and thermal cycling have been determined experimentally and are shown in Fig. 5.3.

![Graph showing thermal expansion](image)

*Fig. 5.3.* Dimensionless linear strain ($d(l(T))/l_0$) as a function of temperature and applied magnetic field for polycrystalline Ni$_2$MnGa.

On heating a zero field cooled sample, in either zero field or in a field of 0.5T *Fig. 5.3*, the sample strain ($d(l(T))/l_0$) at the Martensitic phase transition is negative. The sample therefore contracts when heated past $T_M$.

On cooling the sample in a field of 0.5T *Fig. 5.3*, the sample strain ($d(l)/l_0$) at the Martensitic phase transition is negative indicating contraction.

On cooling the sample in a field the sample strain is in the opposite direction to that for the zero field cooled sample.

Furthermore the data for the 0.5T field cooled sample indicate a reduction of the Martensitic phase transition temperature, $T_M$, to a value of 175K.
On heating the sample in a field of 1T Fig. 5.3 the sample strain \( \frac{dl}{l_0} \) is positive indicating sample expansion at \( T_M \). The Martensitic phase transition temperature, occurs at \( T_M = 195K \) on heating the sample in a field of 1T.

The heating and cooling cycles shown in Fig. 5.3 clearly show the hysteretic nature of the phase transition. Such behavior is expected since the Martensitic transition is a first order anomaly, and thus one may expect to observe some temperature hysteresis.

For this sample the hysteresis is defined as: \( T_{M, \text{Heating}} - T_{M, \text{Cooling}} = 20K \).

Further investigations using thermal cycling and larger applied fields Fig. 5.3 demonstrate that the system becomes locked in a different state. This state occurs when the sample is cooled past \( T_M \) with an applied field for the first time.

The data indicate that this state is irreversible with temperature and fields employed in this investigation i.e. if \( T<T_c \).

The new state, attained by cooling the sample in an applied magnetic field is characterized by a decrease in sample length at the Martensitic phase transition on cooling (strain \( \frac{dl}{l_0} \) is negative, indicating contraction), as opposed to an increase in sample length at the Martensitic phase transition on cooling observed for the previously unmagnetised zero field cooled sample (strain \( \frac{dl}{l_0} \) is positive, indicating expansion).
The coefficient of linear thermal expansion ($\alpha$) was calculated for the polycrystalline sample and can be seen in Fig. 5.4.

![Graph](image)

*Fig. 5.4. Coefficient of linear thermal expansion ($\alpha$) as a function of temperature and applied magnetic field for polycrystalline Ni$_2$MnGa.*

Comparing the coefficient of linear thermal expansion ($\alpha$) Fig. 5.4 for the previously unmagnetised zero field cooled sample, and the field cooled sample, indicate that the thermal expansion coefficient associated with the Martensitic phase transition alters sign.

Data taken for the cooling cycle in an applied field of 0.5T Fig. 5.4 also show an anomaly at $T = 225K$. This feature is well outside the experimental uncertainty.

Based on this observation one can tentatively suggest, that the observed anomaly is a response of the lattice, to the formation of a premartensitic state, which only occurs on cooling from high temperatures. This premartensitic state has been further investigated using magnetisation measurements, the results of which will be presented later in this chapter.
5.5. The thermal expansion of single crystal Ni$_2$MnGa [110].
The low temperature thermal expansion of a single crystal sample of Ni$_2$MnGa (#1) (Length at T= 293K = 9.1mm) was determined over the temperature range 1.5K to 300K using a high resolution capacitance dilatometer discussed previously. The thermal expansion of the sample in applied fields of up to 3T was also evaluated.
The low temperature thermal expansion of the single crystal sample of Ni$_2$MnGa is now presented.

5.5.1. Thermal expansion of single crystal Ni$_2$MnGa [110] from 4K to 300K in zero field.
The single crystal was oriented to have the [110] crystallographic direction along the axis of the cryostat, such that the change in length along the [110] direction was directly measured in the experiment. This orientation was chosen since inelastic neutron scattering measurements indicate a phonon softening of the TA$_2$ mode along this direction.
The dimensionless linear strain for thermal cycling in zero field is shown in Fig. 5.5.

![Graph showing dimensionless linear strain as a function of temperature for a single crystal of Ni$_2$MnGa[110].]

Fig. 5.5. Dimensionless linear strain ($dL(T)/L_0$) as a function of temperature for a single crystal of Ni$_2$MnGa[110].
The observed strain \((dl/l_0)\) as a function of temperature Fig. 5.5 shows a large anomaly associated with the Martensitic phase transition at:
\[ T_M = 258.1 \text{K}, \text{ on heating, and } T_M = 242 \text{K on cooling}. \]
The magnitude of the structural transition is large when compared to the data acquired from the polycrystalline sample with strain \((dl/l_0)\) at \(T_M = 11.72 \times 10^{-3}\) on heating, and \(9.14 \times 10^{-3}\) on cooling.
In a similar manner to the polycrystalline sample, the observed strain for the single crystal sample at the Martensitic transition show a distinct temperature hysteresis with:
\[ T_{M \text{Heating}} - T_{M \text{Cooling}} = 12.1 \text{K}. \]
Hysteresis is also observed in strain with: \(dl/l_0 \text{ Heat} - dl/l_0 \text{ Cool} = 2.58 \times 10^{-3}\).

5.5.2. Thermal expansion of single crystal \(\text{Ni}_2\text{MnGa} [110]\) from 4K to 300K in applied magnetic fields of 0T to 2T.
The sample \(dl/l_0\) taken when thermally cycling in applied magnetic fields is shown in Fig. 5.6. The sample orientation for this experiment was identical to that in Sec. 5.5.1.

![Fig. 5.6. Dimensionless linear strain \((dl(T)/l_0)\) as a function of temperature and applied field for a single crystal of \(\text{Ni}_2\text{MnGa} [110]\).](image)
The data acquired when measuring the sample strain \((dl/l_0)\) as a function of temperature in an applied magnetic field \(\text{Fig. 5.6}\) demonstrates that heating the unmagnetised sample in a field suppresses the phase transition temperature such that 0.5T reduces the transition temperature to, \(T_M = 256.7\)K.

The data further indicate that when the unmagnetised sample is cooled in a magnetic field \((B=0.5T)\), the direction of the sample strain at the Martensitic transition is reversed, such that the sample contracts when passing through the phase transition, in contrast to the data shown in \(\text{Fig.5.5}\) for the zero field cooled sample.

The observed magnitude of the sample strain at the Martensitic phase transition is reduced by cooling in a field by \(\approx 40\%\), while the temperature hysteresis is increased to 16K.

If one now compares the gradient of the sample strain in the region \(T<T_M\) for the unmagnetised zero field cooled sample (\(\text{Fig.5.5. Run 2}\)) and the field cooled sample (\(\text{Fig.5.5. Run 4}\)), a distinct change in slope is observed, indicating a greater thermal expansion of the field cooled sample when it is in the Martensitic state.

The data acquired for thermal cycling with an applied field of 2T show a marked decrease in the observed temperature hysteresis to \(\Delta T_H = 12.9\)K.

One can conclude that reversal in the direction of the sample strain is caused by cooling a previously unmagnetised sample, through the Martensitic phase transition in an applied field.

This change in sample characteristics is irreversible in the low temperature limit i.e. \(T<T_C\).

The sample strain in the region of the Martensitic transition can be seen more clearly in \(\text{Fig. 5.7}\).
Fig. 5.7. Dimensionless linear strain \((dL(T)/L_0)\) as a function of temperature and applied field for a single crystal of \(\text{Ni}_2\text{MnGa}\) [110].

If one compares the observed sample strain for both, the single crystal and the polycrystalline sample of \(\text{Ni}_2\text{MnGa}\), it is clear that the qualitative behavior of both samples is the same. Such that cooling either sample in an applied magnetic field causes a reversal in direction of the observed sample strain associated with the Martensitic phase transition. The two sets of data are distinguished by an order of magnitude difference \((\times 30)\) in the observed strain that is observed at \(T_M\) between the single- and the polycrystalline samples.

The low temperature anomaly associated with the structural phase transition in the single crystal sample is very sharp in temperature \((\Delta T=5\text{K})\) Fig 5.5-5.7. This is consistent with a first order phase transition. For the polycrystalline sample the sample strain at \(T_M\) is smeared over a wider temperature range \((\Delta T = 30\text{K})\) Fig 5.2-5.3.
The polycrystalline sample shows no change in the magnitude of the sample strain associated with the Martensitic transition, between the non-field cooled, and the field cooled samples. This is to be expected since the measured strain for the polycrystalline sample is an average over all crystallographic directions.

5.5.3. Thermal expansion of pressure treated single crystal Ni$_2$MnGa [110] from 4K to 300K.

The difference in length change between the polycrystalline material and the single crystal can, in view of the relatively large strain involved in the Martensitic phase transition, be attributed to contributory forces which are being exerted onto a single grain in the polycrystalline material by its neighboring grains.

In order to test this hypothesis experiments were conducted on a single crystal that had been subjected to uniaxial pressure along the [110] direction.

A single crystal (#1) [110] of Ni$_2$MnGa was annealed at 650K for 24 hours and then compressed along the [110] direction. Compression was achieved using an Instron™. The sample was placed between the anvils of the Instron™ with the [110] direction parallel to the direction of applied pressure. The pressure was slowly increased to ~90Mpa, the sample was then cooled to a temperature of 77K using liquid N$_2$. The applied pressure was kept constant during the cooling operation. During the entire process the sample remained in the elastic region, this was confirmed by the simultaneous production of a Force Vs compression graph during the process.

The effect of sample compression and cooling to T<T$_M$ is a change in the population of magnetic domains in the sample, one may therefore postulate, that this will affect the observed thermal expansion of the sample.

The sample strain acquired for thermal cycling in zero field, for the compression treated single crystal is shown in Fig. 5.8.
The observed sample strain \( \frac{dl(T)/L_0}{T} \) as a function of temperature a pressure treated single crystal of Ni\(_2\)MnGa [110].

\[ d(\ell(T)/L_0) \times 10^{-6} \]

\[ T [K] \]

The observed sample strain Fig. 5.8 shows an anomaly associated with the Martensitic phase transition at 258K on heating and 248K on cooling. The direction of the sample strain at \( T_M \) is positive on heating, indicating expansion, and negative on cooling indicating contraction. The observed trend in the pressure treated single crystal, is the same as that observed in both the untreated single crystal and the polycrystalline sample after cooling the sample in an applied magnetic field. The magnitude of the strain associated with the Martensitic transition in the compression treated sample Fig. 5.8 is reduced by \( \approx 60\% \), when compared with the non pressure treated single crystal Fig 5.5-5.7. The overall magnitude of the sample strain of the pressure treated single crystal Fig. 5.8 is similar to that observed for the polycrystalline sample Fig5.2-5.3.
Magnetisation measurements were made using a Quantum Design SQUID (Superconducting Quantum Interference Device) magnetometer, with a temperature range of $1.8\text{K} \rightarrow 400\text{K}$ ($\pm 0.1\text{K}$) a range in $B$ of $-5.5\text{T} \rightarrow +5.5\text{T}$ ($\pm 1\times 10^{-4}\text{T}$) and a resolution of $1\times 10^{-6}$ e.m.u. g$^{-1}$ ($1\times 10^{-5}$ JT$^{-1}$kg$^{-1}$).

5.6.1. Magnetisation measurements of polycrystalline Ni$_2$MnGa.
The low field magnetisation Fig. 5.9 of a 100mg sample of polycrystalline Ni$_2$MnGa was measured at 0.05T, as a function of temperature for heating and cooling in the temperature range 100K to 300K.

![Figure 5.9](image_url)

**Fig. 5.9.** The magnetisation as a function of temperature for polycrystalline Ni$_2$MnGa.

The magnetisation data indicates the first order nature of the Martensitic transition at $T_M = 199\text{K}$ on heating and $T_M = 180\text{K}$ on cooling. The observed temperature hysteresis is 19K. The magnetisation data is therefore in agreement with the dilatometry data with regards to the Martensitic transition temperature.
5.6.2. Magnetisation measurements of single crystal Ni₂MnGa.
The susceptibility of a single crystal sample (#2) Ni₂MnGa was measured as a function of temperature, for both heating and cooling. The measurement was repeated at a number of applied fields in a range of 0.25T to 0.75T. The single crystal structure was confirmed using Laue back reflection x-ray photography. The orientation of the sample was confirmed as having the [110] parallel to the direction of growth. A small piece of the sample was cut using spark erosion and mounted in the magnetometer with the [110] direction along the cryostat axis.

![Graph](image)

**Fig. 5.10.** The susceptibility of single crystal Ni₂MnGa (#2) as a function of temperature, and applied field. H denotes data taken during heating, C denotes data taken during cooling.

The low field results indicate the Martensitic transition occurs at T_m = 210K, a value which is consistent with that for a stoichiometric sample of Ni₂MnGa. The position of the Martensitic transition is indicated in **Fig. 5.10**. The low field data also show an anomaly in the sample susceptibility at higher temperatures, this is commensurate with the formation of a pre-Martensitic transition in the sample, where the pre-Martensitic transition is formed at T_1, where T_1 > T_M. The position of T_1 is indicated in **Fig. 5.10**. If
the formation of a pre-Martensitic state is resolved in the susceptibility then it is in contradiction with [13] who believe that the magnetisation of the alloy is not sensitive to the strain evolved by the formation of a pre-Martensitic state, but only the strain evolved at the Martensitic transition. It is clear from the results presented in Fig. 5.10 that the magnitude of the applied field has a twofold effect on the susceptibility.

1. The magnitude of the anomaly at $T_1$ in the susceptibility is reduced to zero at $B \approx 0.55T$.
2. The magnitude of the anomaly at $T_M$ in the susceptibility is reduced to zero at $B \approx 0.75T$.

It is clear therefore that the applied magnetic field has a large effect on both the Martensitic transition and the formation of the pre-Martensitic phase.

5.6. Discussion.

It is clear from the dilatometry results that cooling a single crystal Ni$_2$MnGa in a modest magnetic field causes a transition in the sample, such that the strain evolved at $T_M$ is reoriented from the [110] axis. Therefore the action of the field is to alter the direction in which the unit cell displacement occurs. This behaviour is reflected in both single crystal and polycrystalline samples.

In the unaltered state (when the sample has not been cooled past $T_M$ cycled in a field) the unit cell displacement occurs along the [110] axis of the crystal. This is confirmed by inelastic neutron scattering where the $T_A^2_{110}$ phonon branch exhibits a nearly complete softening at the Martensitic transition.
It is clear from the experimental observations that cooling the sample in an applied field produces a field induced modification of the dynamics of the Martensitic transition. If one assumes that the unit cell dilation is along the [110] direction of the crystal then one may calculate the theoretical linear strain evolved at $T_M$ due to such a unit cell dilation.

Using the unit cell parameters from neutron scattering data.

\[ a_{293K} = b_{293K} = c_{293K} = 5.822\text{Å}, \text{ at } T = 300\text{K} \]
\[ a_{4.2K} = b_{4.2K} = 5.90\text{Å} \quad \text{and} \quad c_{4.2K} = 5.566\text{Å}, \text{ at } T < T_M. \]

One finds a strain of $\frac{d[l][110]}{l_0[110]} = 13397 \times 10^{-6}$ should be evolved at $T_M$ this value is in good agreement with the dilatometry data for the [110] single crystal Fig. 5.5. One must now consider the altered state dilation.

From the experimental results Fig. 5.6. it is clear too that the strain evolved at $T_M$ when cooling the crystal in an external field is of a different magnitude and sign.

One may introduce a simple shuffling of the unit cell dimensions in order to test what must occur in order to obtain such a drastically different lattice effect at $T_M$.

If one modulates the unit cell dimensions of the low temperature phase, such that “a” changes to “c”, and “b” remains as “b”, such that:

\[ a_{293K} = b_{293K} = c_{293K} = 5.822\text{Å}, \text{ at } T = 300\text{K} \]
\[ a_{4.2K} = 5.566\text{Å}, \quad b_{4.2K} = c_{4.2K} = 5.90\text{Å} \text{ at } T < T_M. \]

...and then recalculates the strain along the [110] direction.

Under this scenario the theoretical linear strain at $T_M$ is:

\[ \frac{d[l][110]}{l_0[110]} = -14869 \times 10^{-6} \]

This is of the correct sign and order of magnitude. The difference between the calculated and observed strains being a function of the actual sample volume that exhibits the proposed remodulation. One may therefore assume that approximately 80% of the sample volume undergoes the proposed remodulation.

The effect of the external magnetic field on the character of the Martensitic transition has been described by Ullakko et al. [26] who report a reorientation of the twin structure of Ni$_2$MnGa as a result of application of an external field with a resultant strain of the order of $\frac{d[l]}{l_0} \approx 1.5 \times 10^{-3}$. 
Discussion.

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This is a factor of 10 smaller than the strain reported here.

The volume anomaly at $T_m$ is large enough to have a profound impact on the magnetisation of the material. The bulk magnetisation is reduced by $\approx 73\%$ at $T_m$ due to the dilation of the unit cell. However, the effect of cooling the sample in a field does not have such a profound effect on the magnetisation of the material as on the structural properties. The observed jump in magnetisation that has been attributed to the formation of a premartensitic state ($T_1$) is not seen in the expansion measurements, this being the case one may assume that the change in magnetisation at $T_1$ is a result of a shuffle displacement in the unit cell possibly driven by a Jahn Teller type distortion of the Mn$^{3+}$ ions.

The effect of uniaxial pressure on the Martensitic transition is clear, the magnitude of the strain of the zero field cooled sample at $T_m$ is drastically reduced (to almost zero), with an accompanying reversal of sign. One may imply from this one of two possible explanations: the effect of pressure is to reduce the degree of magnetism in the material by changing the domain population in the sample, or pressure introduces a large amount of dislocations into the crystal which act to limit the magnitude of the structural transition at $T_m$ by in effect reducing the number of grains that are allowed to distort at $T_m$.

The difference between the observed Martensitic transition temperatures for the different sample used for this investigation must be explained. It is not as one may first assume a function of sample quality, in a structural sense, but is a factor of Ni concentration, and in essence the sensitivity of the structure to changes in Ni doping.

The difference in the observed value of $T_m$ between the polycrystalline sample and the single crystal sample is $\approx 60K$. For an “on stoichiometry” sample $T_m$ should be $\approx 200K$.

The difference can be attributed to overdoping with Ni, such that the sample becomes Ni$_{2+x}$Mn$_{1-x}$Ga. The overdoping of Ni results in Ni atoms encroaching onto the Mn lattice sites as reported by Bozhko et al. [10] who calculate the variation of $T_m$ as a function Ni doping. From [10] and using the value of $T_m$ from our experimental data, one may calculate a
5.7. Discussion. Chapter 5. An investigation of the SMA Ni$_2$MnGa

tentative value for x.
For the single crystal sample used for the dilatometric investigation i.e. single crystal sample #1 this calculation yields $x = 0.06$. The single crystal sample #2 was determined to be stoichiometric by the same rational. The reason why this has such a drastic effect on the properties of the material can be attributed to the induced crystallographic distortion that chemical disorder creates. The Heusler L2$_1$ structure has a high symmetry, if Mn ions are replaced with Ni ions the effective difference between the respective ion radii introduces a distortion to the unit cell.
The effect on the character of the Martensitic transition by the application of an external magnetic field is supported by magnetisation measurements.

5.8. Conclusion and summary.

The structural and magnetic properties of the shape memory effect material Ni$_2$MnGa have been investigated. Measurements made as a function of both temperature and field indicate that the single crystal used in the investigation has a large lattice distortion at $T_M$, larger by a factor of 10 than any other reported strain. The effect of cooling the sample in a magnetic field is dramatic, changing both the sign and the magnitude of the strain evolved at $T_M$. This effect is explained by a simple remodulation of the unit cell dimensions. The magnetisation of the material has been extensively studied, there is a large effect on the magnetism of the material due to the structural transition. Clear evidence of a premartensitic state is observed in the magnetisation. A clear dependence on applied field is also observed in the magnetisation measurements.
5.7. References.

Chapter 6. 
An investigation of the structural and magnetic properties of the Heusler alloy RE\textsubscript{2}AgIn. (RE=Tb, Lu).

6.1. Introduction.
Investigation of the (H-T) plane of the phase diagram of a magnetic material enables not only the critical temperature to be established but also the order of the phase boundaries. For an antiferromagnetic material the application of a field serves to renormalise the magnetic transition to lower temperatures.

For a given critical applied field $H_c$ the difference between the magnetic energies associated with the applied field being parallel or perpendicular to the sublattice magnetisation becomes equal to the anisotropy energy. For $H>H_c$ the sublattice magnetisation will always be perpendicular to the applied field, producing a spin flop phase. If the applied magnetic field exceeds $H_{c2}$ where the magnetic energy is equal to the exchange energy then the antiferromagnetic order is destroyed.

The phase diagram therefore comprises of three phase boundaries which meet at a tri-critical point.

For some systems $H_c = H_{c2}$ here the systems goes from antiferromagnetic order to ferromagnetic order, giving rise to meta-magnetic behaviour.

Interest in the ternary $Z_2XY$ compounds stems from their simple crystallographic structure [1- 4], in the chemically ordered state this is the Heusler L$_{21}$ structure. The L$_{21}$ structure can be obtained by chemically ordering to the B2 structure. In the B2 structure the XY atoms interchange sites to form a CsCl structure. The Heusler alloy Tb$_2$AgIn is found to crystallise in the chemically disordered B2 structure.

The crystallographic structure of the Heusler L$_{21}$ structure and the effect of site occupation due to preferential chemical disorder in the Heusler B2 structures is shown in Fig 6.1.
Fig. 6.1. i. The crystallographic structure of the Heusler $L_2_1$ described by 4 interpenetrating FCC sublattices. ii. Preferential chemical disorder arising from the Heusler $L_2_1$ structure, from [5].
6.2. Experimental.

The thermal expansion of the Heusler alloy Tb$_2$AgIn was evaluated over a temperature range of 1.5K to 300K using high resolution three terminal capacitance dilatometry. This technique was employed since it is widely accepted as the most sensitive method for measuring a change in length ($dl$), easily giving achievable resolutions of $dl/l_0 = 10^{-10}$.

The low temperature data was acquired using a $^4$He cryostat containing a compensated 7T superconducting solenoid. The sample environment temperature measurement was achieved using two Cernox temperature sensors. This type of sensor exhibits a very low field dependence over the entire temperature range of operation. The temperature control system enabled sample environment control to within 1mK below 10K and ≈10mK above.

Full details of the dilatometer systems can be found in Chapter 3.

Powder neutron diffraction data were obtained using the diffractometer D2B at the ILL Grenoble France. The diffractometer was operated at a wavelength of 1.594Å in high resolution mode. The sample environment was a VTI type $^4$He cryostat with a 6T vertical superconducting solenoid. Further details of the instrument may be found in Chapter 4.

The magnetisation measurements were performed using a SQUID magnetometer manufactured by Quantum design.

Specific heat measurements were performed using a modified quasi adiabatic heat pulse calorimeter designed and built in the Department of Physics Loughborough University, further details of the calorimeter may be found in [6]
6.2. Experimental. Chapter 6. Structural and magnetic properties of RE$_2$AgIn.

20g polycrystalline samples of Tb$_2$AgIn and Lu$_2$AgIn were prepared by melting the constituent elements of 4N purity in an argon arc furnace. The ingot was flipped and re-melted 4 times to ensure homogeneity. The sample weight loss after melting was determined to be <1%.

The thermal expansion samples was then prepared using the flop-cast method resulting in a cylindrical sample of diameter 6.5mm. The ends were cut parallel by spark erosion. The final sample dimensions are shown in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>Thermal expansion / magnetostriction sample length. [mm]</th>
<th>Weight loss after initial melting. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$_2$AgIn</td>
<td>22.20 ± 0.02</td>
<td>&lt; 0.8%</td>
</tr>
<tr>
<td>Lu$_2$AgIn</td>
<td>20.34 ± 0.02</td>
<td>&lt; 0.8%</td>
</tr>
</tbody>
</table>

*Table 6.1. Thermal expansion and magnetostriction sample details.*

Samples for the measurement of specific heat were prepared by spark erosion. A small piece of alloy ≈ 1.5g was prepared. One side of the sample was polished to improve thermal conductivity. The sample was attached to the heater stage of the calorimeter using a known mass of Apizion N type grease.

A 5g powder sample of Tb$_2$AgIn was produced for neutron diffraction work by crushing a sample of the alloy to a particle size of < 100µm.
6.3. Low temperature thermal expansion of RE₂AgIn.

The linear strain of a sample of Tb₂AgIn was evaluated directly by the measurement of the change in sample length as a function of temperature using a three terminal capacitance dilatometer discussed previously. One may determine the linear coefficient of thermal expansion by the relationship:

\[ \alpha(T) = \frac{1}{l_0} \left( \frac{dl}{dT} \right) \]

(6.1)

The coefficient of linear thermal expansion for Tb₂AgIn is shown in Fig. 6.2.

Fig. 6.2. Coefficient of linear thermal expansion as a function of temperature for the Heusler alloy Tb₂AgIn T_N = 58.54±0.01K.

The low temperature thermal expansion is dominated by a sharp peak in \( \alpha \) at \( \approx 58 \)K. This anomaly is assumed to be a result of the onset of long range antiferromagnetic order. As a result of this the material exhibits a large spontaneous magnetostriction at \( T_N \). The high temperature (\( T>T_N \)) thermal expansion remains almost constant.
6.3. Thermal expansion.

Chapter 6. Structural and magnetic properties of RE$_2$AgIn.

It is possible to separate the magnetic contribution to the linear coefficient of thermal expansion $\alpha_{\text{mag}}$ by means of an isostructural phonon blank removal. The phonon blank used for this investigation was Lu$_2$AgIn, as the structure is identical to that of the magnetic compound. The mass difference between the two materials is small, therefore the phonon dominated lattice properties are similar, thus one may expect that the high temperature thermal expansion of the two alloys will be nearly identical.

The subtraction of the thermal expansion of Lu$_2$AgIn from that of Tb$_2$AgIn yields an estimate of the magnetic contribution to the thermal expansion:

$$\alpha_{\text{mag},\text{phon,elec}}^{\text{Tb}_2\text{AgIn}} = \alpha_{\text{mag,phon,elec}}^{\text{Tb}_2\text{AgIn}} - \alpha_{\text{phon,elec}}^{\text{Lu}_2\text{AgIn}}$$ (6.2)

$\alpha_{\text{mag},\text{phon,elec}}^{\text{Tb}_2\text{AgIn}}$ is the linear thermal expansion of the magnetic compound and $\alpha_{\text{phon,elec}}^{\text{Lu}_2\text{AgIn}}$ is the linear thermal expansion of the phonon blank.

Since the compound containing Lu does not order magnetically the thermal expansion may be considered to arise only from the electronic and lattice contributions. If they are not coupled $\alpha(T)$ will comprise of two terms proportional to $T$ and $T^3$ namely

$$\alpha(T) = aT + bT^3 \quad \text{(For } T << \theta_D)$$ (6.3)

where "a" and "b" are constants and $\theta_D$ is the Debye temperature.

Therefore at low temperatures $T \leq \theta_D/\sqrt{12}$ a plot of $\alpha(T)/T$ versus $T^2$ should produce a linear variation. A linear relation between $\alpha(T)/T$ and $T^2$ holds for Lu$_2$AgIn below $\sim$30 K. The results from such a fit can be found in Table 6.2.

<table>
<thead>
<tr>
<th></th>
<th>$a \times 10^{-8} [\text{K}^{-1}]$</th>
<th>$b \times 10^{-10} [\text{K}^{-2}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$_2$AgIn</td>
<td>$6.0 \pm 1.0$</td>
<td>$2.5 \pm 0.3$</td>
</tr>
<tr>
<td>Lu$_2$AgIn</td>
<td>$3.0 \pm 1.0$</td>
<td>$1.1 \pm 0.1$</td>
</tr>
</tbody>
</table>

*Table 6.2. Linear (a) and cubic (b) coefficients from a straight line fit to the low temperature thermal expansion of RE$_2$AgIn (RE = Tb, Lu)*

The coefficient of linear thermal expansion for Lu$_2$AgIn is shown in *Fig. 6.3.* (The thermal expansion of Tb$_2$AgIn is also displayed in order to demonstrate the high temperature convergence of the two data sets).
6.3. Thermal expansion. 

Chapter 6. Structural and magnetic properties of RE$_2$AgIn.

Fig. 6.3. Coefficient of linear thermal expansion as a function of temperature for the Heusler alloy Lu$_2$AgIn (the thermal expansion of Tb$_2$AgIn is plotted to demonstrate the high temperature convergence of the two data sets).

By means of subtraction of the two data sets one may then evaluate the magnetic contribution $\alpha_{\text{mag}}$ to the thermal expansion for the sample. The results of this process are presented in Fig. 6.4.

Fig. 6.4. The magnetic contribution $\alpha_{\text{mag}}$ to the thermal expansion for Tb$_2$AgIn (errors bars are taken as the maximum deviation between the Lu and Tb data sets).
Integrating the magnetic contribution to the thermal expansion yields the spontaneous volume magnetostriction of the sample Fig. 6.5, as:

$$\omega_{\text{mag}} = \int_{0}^{T} \alpha_{\text{mag}} \, dT$$  \hspace{1cm} (6.4)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.5.png}
\caption{The spontaneous magnetostriction as a function of temperature for the Heusler alloy Tb$_2$AgIn.}
\end{figure}

It is clear from Fig. 6.4 & 6.5 that a substantial magnetic contribution exists above $T_N$ this is ascribed to the presence of short range magnetic order in the material up to a point of $2T_N$ (120K) giving rise to an appreciable magnetostrain. At $T_N$ the spontaneous volume magnetostriction is $\approx 8 \times 10^{-5}$ Above this point the magnetic contribution to the thermal expansion and the spontaneous magnetostriction are both zero.

In a similar manner to that described previously one may evaluate the magnetic contribution to the specific heat, this enables one to evaluate the magnetic Grüneisen parameter, $\gamma_m \equiv \partial \ln U_m / \partial \ln V$ which simplifies to

$$\alpha_m = - \left( \frac{B_T m}{3V} \right) C_m$$

where $B$ is the isothermal bulk modulus.

The magnetic contribution to the specific heat is shown in Fig. 6.6 together with the approximation to the magnetic Grüneisen parameter.
Fig. 6.6. The magnetic contribution to the specific heat \( (C_m) \) and the magnetic contribution to the volume expansion \( (\beta_m) \), and the ratio \( \beta_m / C_m \), as a function of reduced temperature for Tb$_2$AgIn.

The internal magnetic energy at 0 K can be determined from the area of the specific heat anomaly as a function of temperature. In Fig. 6.7, the relative internal magnetic energy is plotted as a function of reduced temperature.

\[
\frac{U_m(T)}{U_m(0)} = \frac{\int_0^\infty C_m(\tilde{T})d\tilde{T}}{\int_0^\infty C_m(\tilde{T})d\tilde{T}} \quad (6.5)
\]

In the absence of any coupling to the lattice this gives directly the thermal evolution of the spin-spin correlation function.
6.3. Thermal expansion. Chapter 6. Structural and magnetic properties of RE$_2$AgIn.

![Graph showing relative internal magnetic energy of Tb$_2$AgIn as a function of reduced temperature.](image)

**Fig. 6.7.** The relative internal magnetic energy of Tb$_2$AgIn as a function of reduced temperature.

The total volume change that the lattice undergoes from 0K<T<300K is approximately 1.01% for both the magnetic and nonmagnetic compounds, a value one may expect. The volume deformation at T=0K as a result of magnetic order is approximately 0.016%.

It is clear that the relative internal magnetic energy is a complex function of temperature, the presence of substantial short range magnetic order above $T_N$ is confirmed by such an analysis.
6.4. Forced magnetostriction results.

The isothermal longitudinal forced magnetostriction \( \frac{\partial l(H)}{l_0} \) of \( \text{Tb}_2\text{AgIn} \) was measured at 4.2K, well below \( T_N \) in applied magnetic fields of up to 7T and is shown in Fig. 6.8.

![Graph showing forced magnetostriction isotherms of \( \text{Tb}_2\text{AgIn} \) at 4.2K](image)

**Fig. 6.8.** Longitudinal forced magnetostriction isotherms of \( \text{Tb}_2\text{AgIn} \) at 4.2K

On the initial field sweep (on a zero field cooled sample) from \( 0T \rightarrow 7T \) (○) there is little change in the magnetostriction up to 2T beyond this the magnetostriction is clearly a complex function of the applied field. Interestingly on removal of the field the forced magnetostriction follows a different path (ρ) with a clear minimum at 3T. Increasing the field for a second time from \( 0T \rightarrow 7T \) the magnetostriction follows a similar path with a minimum at \( \approx 4T \). Subsequent measurements confirm that the magnetostriction of the sample is locked into this cycle.

On initial examination the forced magnetostriction of this samples appears strange, essentially because the magnetostrictive effect is large \( \approx 0.13\% \) which is several orders of magnitude greater than in the magnetic transition metals such as iron. However it is well known that Tb and alloys
containing \( \text{Tb}^{+3} \) exhibit large magnetostrains, with the technical alloy Terfenol D (comp) being an example.

The behaviour of the material with respect to the applied field may be explained if one assumes that the applied field rotates the sublattice magnetisation, producing a large "canted" ferromagnetic component. On removal of the field the ferromagnetic component remains locked in at low temperatures due to the disorder in the sample pinning the relaxation of domain walls. One is then left in a different magnetic state with a substantially reduced volume \( \approx 0.1\% \), which exhibits a large \( \approx 1\text{T} \) hysteresis on application and removal of the applied field.

### 6.5. Neutron scattering results.

The crystallographic structure of \( \text{Tb}_2\text{AgIn} \) was determined above the Neel temperature at 100K using the neutron diffractometer D2B. The diffractometer was fitted with a 6T vertical cryomagnet to enable the measurement of diffraction data as a function of both temperature and applied magnetic field.

The coherent scattering lengths for Tb, Ag and In are sufficiently different, as to allow the degree of atomic order to be determined. A refinement was carried out using a model with a space group of \( \text{Pm}\overline{3} \text{ m} \), and the rare earth atoms located at (000) and the In and Ag atoms randomly distributed at \( \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle \). The model gave excellent agreement with the observed data with a \( \chi^2 \) factor of <2%. The refined lattice parameter was found to be 3.683Å. The result of the refinement is shown in Fig. 6.9.

Refinement was also carried out using a chemically ordered Heusler L2\(_1\) structure, the result of the refinement process yields a higher \( \chi^2 \) value than for the disordered B\(_2\) structure thus one may conclude that the sample crystallised in the chemically disordered B\(_2\) structure.
Fig. 6.9. Neutron diffraction pattern of Tb$_2$AgIn at T=100K. Rietveld fit of the nuclear structure (see text for details) gives $\chi^2 < 2$.

A diffraction pattern taken at T = 4.2K revealed extra peaks attributed to the presence of antiferromagnetic order in the sample occurring at a position commensurate with the doubling of a cube edge. The magnetic structure can be characterised by a propagation vector $\mathbf{K} = [00\frac{1}{2}]$.

Fig. 6.9. Neutron diffraction pattern of Tb$_2$AgIn at T=4.2K. Rietveld fit of the nuclear structure and magnetic structure (see text for details) gives $\chi^2 < 4$. 
With a doubling of the unit cell along the 'c' direction.

Diffraction patterns were obtained at the following applied fields and temperatures for Tb$_2$AgIn (Table 6.3).

<table>
<thead>
<tr>
<th>Applied Field [T]</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. [K]</td>
<td>4, 45, 55, 75, 75, 85, 55, 70, 40, 50, 45, 60, 4, 45, 80, 85, 80, 65, 75, 70, 55, 65</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 6.3. Summary of diffraction data taken as a function of field and temperature for Tb$_2$AgIn.*

This allows the direct measurement of both the thermal variation of the magnetic order and also the effect of an applied field. The data were analysed by evaluating the background subtracted integrated intensity of the [00½] magnetic peak. The approximation to the HT plane of the phase diagram was produced by matrix interpolation of these data and is shown in *Fig. 6.10.*

*Fig. 6.10. The (H-T) phase diagram of Tb$_2$AgIn (0T data is included as a guide to the approximated form of the antiferromagnetic response as a function of temperature using $T_N \approx 65$K).*

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From the rate of decrease of the intensity of the [00½] peak one may infer a Neel temperature of \( \approx 65K \). From these results one cannot comment on the presence of short range order in zero field, however substantial non zero intensity remains above \( T_N \) in the 1T data from this one may imply the presence of significant antiferromagnetic order in the sample. The effect of the an applied field is to suppress the antiferromagnetic phase transition and also the maximum temperature at which short range order ceases to exist in the sample. At a field of 6T the temperature at which a magnetic signal is destroyed is \( \approx 60 \) K a reduction of 40% on the zero field figure.

### 6.6. Discussion.

The thermal expansion of both the magnetic and non magnetic compound appears "normal" i.e. the order of magnitude is the same as for other metallic compounds. However the magnetic contribution to the thermal expansion is large, and exhibits a large degree of short range order in the sample up to 2\( T_N \). Many compounds containing \( \text{Tb}^{3+} \) exhibit a large magnetostrictive effect since the magnetism is strongly coupled to the lattice via a large crystal field contribution chapter 2. However this does not explain the large magnetic contributions to the thermal expansion above \( T_N \). Tentatively one may attribute this short range order to the effect of chemical, and structural disorder in the sample. (Which in the case of \( \text{Tb}_2\text{AgIn} \) is large).

The results gained from the measurement of the forced magnetostriction again demonstrate the large magnetocoupling effect in this compound. More interestingly however is the net effect of the application of a high magnetic field. The difference between the initial and final magnetostriction data sets is obvious. One may attribute the observed results to the emergence of a large canted ferromagnetic component to the magnetisation as a function of applied field. The fact that the large magnetovolume anomaly remains with zero field may be attributed to the structural disorder present in the material with the net effect of pinning the
domain structure in place. If one heats the system past a certain point the volume anomaly disappears as thermal effects destroy the domain structure.

The magnetisation of Tb$_2$AgIn was measured at 4.2K, well below $T_N$ in order to further understand the magnetic behaviour of the compound and is shown in Fig. 6.11.

![Graph](attachment:fig6_11.png)

**Fig 6.11.** Magnetisation as a function of field for Tb$_2$AgIn at 4.2K. Inset shows magnetisation in the form of an Arrott plot ($M^2$ Vs. $H/M$)

The low temperature magnetisation is not a simple function of applied field, as one may expect from a antiferromagnet, but instead shows a continuous evolution of a ferromagnetic component (rather than a spin flop). The magnetisation data displayed in the form of an Arrott plot can be seen as the inset to **Fig 6.11**.

The exact dependence of the volume to the applied field is complex, one may however argue a $M^2$ dependence (chapter 2 & 7) however from **Fig 6.12**, it is clear that such a dependence does not implicitly exist, however both the low and the high field region exhibit linear components.
6.6 Discussion.

Chapter 6. Structural and magnetic properties of RE\textsubscript{2}AgIn.

Fig. 6.12. Magnetostriction of Tb\textsubscript{2}AgIn as a function of the square of the specific magnetisation ($M^2$) at 4.2K.

The evolution of a ferromagnetic component to the magnetisation of Tb\textsubscript{2}AgIn is also seen in the neutron diffraction data as a function of field. The diffraction data obtained as a function of field show extra diffraction peaks that can not be attributed to the nuclear structure or the antiferromagnetic structure Fig. 6.14-6.16. Furthermore the intensity of these peaks is a positive function of applied field. The thermal /applied field evolution of the diffraction peaks attributed to a ferromagnetic component is shown in Fig. 6.13. The canted ferromagnetic component to the magnetisation of Tb\textsubscript{2}AgIn has been evaluated by fitting a canted ferromagnetic model to the diffraction data taken as a function of field using the program FULLPROF. The fitted model uses the same antiferromagnetic structure as that used for the zero field low temperature diffraction data. In order to refine the fit to the extra diffraction peaks resulting from the canted ferromagnetic component "switching on" as a function of field the magnetic moment directional vector components ($x,y,z$) on the Tb\textsuperscript{3+} sites have been refined. This has the effect of allowing the magnetic moment to be rotated out of the plane of magnetisation as a function of field. The results of this refinement are shown in Fig 6.14-6.16.
6.6. Discussion.

Chapter 6. Structural and magnetic properties of RE₂AgIn.

Fig. 6.13. Evolution of the canted ferromagnetic component of Tb₂AgIn

Fig. 6.14. Refinement of the antiferromagnetic / canted ferromagnetic phase of Tb₂AgIn. The diffraction data were obtained at 55K with an applied field of 1T. The primary diffraction peak resulting from the presence of a canted ferromagnetic component is at 25° 2θ.

The refinement of the model has a χ² = 10.
Fig. 6.15. Refinement of the antiferromagnetic / canted ferromagnetic phase of Tb₂AgIn. The diffraction data were obtained at 50K with an applied field of 4T. The refinement of the model has a $\chi^2 = 11$.

Fig. 6.16. Refinement of the antiferromagnetic / canted ferromagnetic phase of Tb₂AgIn. The diffraction data were obtained at 45K with an applied field of 5T. The refinement of the model has a $\chi^2 = 13$. 
From the refinement of canted ferromagnet model the degree to which the magnetic moments are pulled out of the plane can be reproduced i.e. their relative orientation to the field direction. One may therefore visualise the rotation of the magnetic moments, and understand the physical nature of the canted ferromagnetic component to the magnetisation. The spatial orientation of the canted moments as a function of applied magnetic field is shown in Fig. 6.17. It is clear that the relative orientation of the moments rotate to align with the field, however the system does not become 100% ferromagnetic. Such a result agrees with the diffraction data which show a small amount of antiferromagnetic intensity remaining at high fields.

Fig. 6.17. The effect of applied field on the spatial orientation of magnetic moments in Tb$_2$AgIn (AFI). The applied field direction is along the x axis.
From the antiferromagnetic phase diagram of Tb$_2$AgIn Fig. 6.10, it can be seen that the temperature at which the antiferromagnetism in the sample is destroyed is strongly dependent on the applied field, as is the evolution of the canted ferromagnetic component to the magnetism Fig. 6.13. These results imply that the magnetocrystalline anisotropy energy in this sample is low. A possible reason for such a condition is that the chemical disorder in the sample places the Tb ions in a modulated crystal field that favours a low anisotropy energy, other compounds in the RE$_2$AgIn series containing heavy rare earth ions, Ho and Dy are ferromagnetic systems with a Curie temperature that is similar to the ordering temperature in Tb$_2$AgIn thus one may imply that Tb$_2$AgIn is close to a magnetic instability in the compound series.

One should note that at 6T, the maximum field available during the neutron experiment, there is still some antiferromagnetism in the system. This is unlikely to be quenched by a field of 7T (the maximum field available for the magnetostriction experiment). One may therefore state that the magnetostriction results do not constitute a meta-magnetic transition to a ferromagnetic state, but rather a "meta-stable" magnetic state that has a greater ferromagnetic character than antiferromagnetic at high field, and that once this state is obtained (by the application of ≈7T) it is easily destroyed by the activation of lattice vibrations in the sample.
6.7. Summary and conclusions.

A systematic study of the magnetic and lattice properties of Tb$_2$AgIn has been undertaken.
Measurements of the thermal expansion show a large spontaneous magnetostriction at $T_N$, and demonstrate the presence of short range order in the sample up to a temperature of $\approx 2T_N$, this effect is also confirmed by neutron scattering results.
Neutron scattering results confirm that the compound has the chemically disordered B2 Heusler structure and orders antiferromagnetically below $\approx 65$K with a propagation vector of [00½]. The presence of short range antiferromagnetic order above the thermodynamic transition temperature of $\approx 60$K is confirmed by the neutron diffraction measurements as a function of field. i.e. One observes a non-zero intensity of the [00½] antiferromagnetic diffraction peak at 1T up to 80K.
The lattice response to an external applied field has been characterised by measurement of the forced magnetostriction. The magnetostriction results show an anomalously large magnetostrain, and the presence of a field stabilised "nearly meta-magnetic" phase transition.
The effect of an applied field on the magnetic structure is the production of a large field induced canted ferromagnetic component to the antiferromagnetism which is clearly visible in the neutron diffraction results.
Measurement of the (H-T) phase diagram using neutron diffraction show a large suppression of the antiferromagnetic transition caused by the application of an external applied field and the evolution of the aforementioned ferromagnetic component in the sample.
The extinction of magnetic order in the sample is found follow an approximately $B^2$ dependence.
6.8. References.

Chapter 7. Thermal expansion and magnetostriction of the rare earth intermetallic compounds $\text{TM}_2\text{RE}_n$ 

($\text{RE} = \text{Gd, Lu. TM} = \text{Cu, Pd}$)

7.1. Introduction.

Inter-metallic compounds containing rare earth elements exhibit a wide variety of properties including GMR, CMR, giant magnetostriction and heavy fermion behaviour to name but a few. For systems in which coherent lattice and magnetic degrees of freedom are involved polarised neutron scattering can sometimes be employed to determine not only the temporal and spatial dependence of the modes but also the absolute magnitude. In many cases it is not possible to experimentally separate the different contributions and unambiguously identify the mechanism or mechanisms involved. Analysis of experimental data therefore usually proceeds with resort to models. In order to quantify the influence of certain mechanisms, studies have been made on systems in which the number of degrees of freedom, have been restricted. This has led to considerable interest in compounds in which the sole magnetic element is gadolinium. Gadolinium has a particularly stable 4f shell, it is an S state ion, and is therefore unaffected by the crystal field. Furthermore the coupling of the lattice and electronic degrees of freedom arising from spin-orbit interaction is expected to be negligible. Despite this potential simplification, some Gd compounds are found to have unusual low temperature properties. In particular for $\text{Gd}_{1-x}\text{Y}_x\text{Ni}_2\text{Si}_2$ [1,2,3] alloys, $\text{GdCu}_2\text{Si}_2$, $\text{GdGa}_2$, $\text{GdCu}_5$ [3] and $\text{Pd}_2\text{GdIn}$ [4] an enhanced specific heat has been reported above the Néel temperature giving rise to an anomalously enhanced linear contribution. For the former alloys this behaviour was thought to arise from extensive short range ferromagnetic correlations extending well above the Néel temperature.
However for Pd$_2$GdIn extensive analysis suggests that lattice degrees of freedom are involved. The thermal expansion, forced magnetostriction and low temperature magnetisation of Pd$_2$GdIn, Cu$_2$GdIn and the non magnetic isostructural compound Pd$_2$LuIn have been investigated.

Preliminary specific heat and magnetisation measurements [4] indicate that Pd$_2$GdIn orders magnetically at $\approx$ 10K. However the order appears to be complex, being antiferromagnetic in zero field but transforming to ferromagnetism under the influence of a moderate applied magnetic field. The saturation moment extrapolated to 0 K is approximately $8\mu_B$, which is $1\mu_B$ more than the 7 $\mu_B$ expected for a Gd$^{3+}$ (gJ) ion. However in the paramagnetic phase there is good agreement between the observed, effective moment and the free ion value of Gd$^{3+}$. The additional moment observed in the ground state was tentatively attributed to the polarisation of the Pd (4d) band by the Gd (4f) local moments. However the specific heat is enhanced and remains so beyond 20K. Measurements made on isostructural compounds in which the Gd was replaced by Lu or the Pd by Cu did not reveal anomalous behaviour which suggested a possible 4f-4d involvement in Pd$_2$GdIn.
7.2. Experimental.

20g polycrystalline samples of Pd$_2$GdIn, Cu$_2$GdIn and Pd$_2$LuIn were prepared by melting the appropriate quantities of spectrographically pure (4N) elements, in an argon arc furnace. X-ray powder diffraction confirmed the materials to be single phase and to have the Heusler structure and cell parameters as reported in the literature. Details of the samples measured can be found in *table 7.1*.

Measurement of the thermal expansion and forced magnetostriction were made using a sensitive three terminal capacitance method which enabled length changes of $dl/l_0 \approx 10^{-10}$ to be detected. Details of the dilatometer system used for the measurement of thermal expansion and magnetostriction can be found in *chapter 3*.

The sample details are summarised in *Table 7.1*.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal expansion / magnetostriction sample length. [mm]</th>
<th>Weight loss after initial melting. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_2$GdIn</td>
<td>20.38 ± 0.02</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Pd$_2$LuIn</td>
<td>21.93 ± 0.02</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Cu$_2$GdIn</td>
<td>17.75 ± 0.02</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

*Table 7.1. Thermal expansion and magnetostriction sample details.*

Although magnetisation measurements on these materials have previously reported, further measurements were undertaken as result of anomalies observed in the forced magnetostriction investigation. The magnetisation measurements were carried out as before using a SQUID magnetometer manufactured by Quantum Design.
7.3. Low temperature thermal Expansion of TM$_2$REIn.

The thermal expansion coefficients observed for the three compounds Pd$_2$GdIn, Cu$_2$GdIn, and Pd$_2$LuIn, between 2 and 300K are shown in Fig. 7.1.

*Fig. 7.1.* The coefficient of linear thermal expansion for Pd$_2$GdIn for 2K<T<300K. The inset shows the low temperature thermal expansion 5K<T<14K of Cu$_2$GdIn, Pd$_2$GdIn and Pd$_2$LuIn.

Above approximately 20K the variation of $\alpha$ with temperature is similar for all three compounds. Since the compound containing Lu does not order magnetically the thermal expansion may be considered to arise only from the electronic and lattice contributions. If they are not coupled $\alpha(T)$ will comprise of two terms proportional to $T$ and $T^3$ namely

$$\alpha(T) = aT + bT^3 \quad \text{(For } T<<\theta_D)$$

(7.1)

where $a$ and $b$ are constants and $\theta_D$ is the Debye temperature. Therefore at low temperatures $T\leq \theta_D/12$ a plot of $\alpha(T)/T$ versus $T^2$ should produce a linear variation. A linear relation between $\alpha(T)/T$ and $T^2$ holds for Pd$_2$LuIn below ~30 K. A least square fit was then used to determine the coefficients of the linear and cubic terms. The results of this analysis are given in table 7.2 together with those obtained for Pd$_2$GdIn and Cu$_2$GdIn, and the measured values for the Néel temperature.
7.3. Thermal expansion.

Table 7.2. Linear (a) and cubic (b) coefficients from a straight line fit to the low temperature thermal expansion of Pd$_2$REIn (RE = Gd, Lu) and Cu$_2$GdIn. Where the coefficients apply to the thermal expansion in the low temperature limit $T \ll \theta_B$ such that $\alpha(T) = aT + bT^3$, and measured values for the Néel temperature.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_2$GdIn</td>
<td>0.101 ± 0.002</td>
<td>4.4 ± 0.3</td>
<td>9.599 ± 0.001</td>
</tr>
<tr>
<td>Pd$_2$LuIn</td>
<td>0.107 ± 0.001</td>
<td>4.0 ± 0.2</td>
<td>—</td>
</tr>
<tr>
<td>Cu$_2$GdIn</td>
<td>0.062 ± 0.002</td>
<td>5.0 ± 0.03</td>
<td>10.4 ± 0.01</td>
</tr>
</tbody>
</table>

Since the latter two compounds order magnetically only data above 12K was used in the analysis. It may be seen from table 7.2 that the values for the coefficients are very similar for the three compounds. The thermal expansion data for the non magnetic sample were then used to extract the approximate magnetic thermal expansion $\alpha_{\text{mag}}(T)$ in the two compounds containing Gd as:

$$
\alpha_{\text{mag}} = \alpha_{\text{mag, sample}} - \alpha_{\text{phon, blank}}
$$

(7.2)

$\alpha_{\text{mag, phon, elec}}$ is the linear thermal expansion of the magnetic compound and $\alpha_{\text{phon, blank}}$ is the linear thermal expansion of the phonon blank.

The magnetic thermal expansion so obtained is plotted as a function of temperature in Fig. 7.2. for Pd$_2$GdIn and in Fig. 7.3. for Cu$_2$GdIn. A similar method may be applied to specific heat data, thus one may isolate, by means of an isostructural phonon blank removal, the magnetic contribution to the specific heat $C_{\text{mag}}$, this technique has been employed on data taken using a modified adiabatic heat pulse calorimeter [5]. The magnetic component to the specific heat is shown in Fig. 7.2. i & ii. for both compounds.
Fig. 7.2. The magnetic contribution to the specific heat ($C_m$) and the magnetic contribution to the volume expansion ($\beta_m$), and the ratio $\beta_m / C_m$, as a function of reduced temperature for i. Pd$_2$GdIn and ii. Cu$_2$GdIn.

From Fig. 7.2. i & ii. spontaneous magnetostriction is clearly visible with a maximum in the vicinity of the Néel temperatures. For both compounds the maximum in the specific heat and magnetic thermal expansion are in good agreement. At $T_N$ the spontaneous volume magnetostriction ($\omega_0 = \frac{\Delta V}{V} = 3 \frac{\Delta L}{L}$) is estimated to be $\approx 5 \times 10^{-6}$ and $\approx 20 \times 10^{-6}$ for Pd$_2$GdIn and Cu$_2$GdIn respectively. Integrating the magnetic contribution to the thermal expansion $\alpha_{mag}(T)$ leads to a direct determination of the spontaneous volume magnetostriction $\omega_{mag}$. The result of such an analysis is shown in Fig. 7.3.

Fig. 7.3. The volume magnetostriction as a function of reduced temperature for Pd$_2$GdIn and Cu$_2$GdIn
The change in magnetostriction Fig. 7.2. i & ii. is clearly larger in the copper compound whereas the relative jump in specific heat at $T_N$ is essentially the same for both compounds [3], the ratio $C/\beta$ being $11/5$ for Pd$_2$GdIn and $10/20$ for Cu$_2$GdIn. Below $T_N$ the specific heat of the palladium compound has an unusual linear dependence on temperature and above the Neél temperature exhibits some degree of short range order. On the other hand, the thermal expansion does not possess the same degree of short range order. As a consequence $C_m$ is not proportional to $\beta_m$ over the entire temperature range where magnetic order occurs. The specific heat of Cu$_2$GdIn has a thermal variation more generally observed in magnetic phase transitions. The short range order is less pronounced than in Pd$_2$GdIn but follows that observed in the thermal expansion. However $C_m$ is still only proportional to $\beta_m$ over a limited range of temperature so the magnetic Grüneisen relation does not hold. The ratio of the magnetic to other contributions (electronic and lattice) at $T_N$ is approximately 12:1 for specific heat measurements and for thermal expansion 7:1 (Cu$_2$GdIn) and 2:1 (Pd$_2$GdIn).

A simple relationship exists between the magnetoelastic contribution to the thermal expansion and the magnetic specific heat. The ratio $\beta(T)/C_m$ plotted in Fig. 7.2. i & ii. leads to the determination of a magnetic Grüneisen parameter $\gamma_m \equiv \partial \ln U_m / \partial \ln V$ which simplifies to $\alpha_m = - (B \gamma_m / 3V) C_m$ where $B$ is the isothermal bulk modulus. The magnetic Grüneisen relation provides information on the dependence of the isotropic magnetic interaction energy $U_m$ on the interatomic separation. The total volume change between 0 and 300 K as given by

$$\frac{\partial V}{V_0} = \int_0^{300} 3\alpha(T) dT$$

is 1.12, 1.15% and 1.01% for Pd$_2$GdIn, Cu$_2$GdIn and Pd$_2$Luln respectively. The volume deformation at 0K which the lattice undergoes as a result of magnetic long range order is obtained using

$$\omega_0 = \int_{T > T_N} 3\alpha_m(T) dT$$

(7.4)

to give $2 \times 10^{-3}$% and $10 \times 10^{-3}$% for Pd$_2$GdIn and Cu$_2$GdIn respectively. The data was extrapolated to zero Kelvin assuming a linear variation.

The internal magnetic energy at 0 K can be determined from the area of the specific heat anomaly as a function of temperature. In Fig. 7.5, the relative internal magnetic energy is plotted as a function of reduced temperature.

$$\frac{U_m(T)}{U_m(0)} = \frac{\int C_m(T) dT}{\int_0^\infty C_m(T) dT} \tag{7.5}$$

In the absence of any coupling to the lattice this gives directly the thermal evolution of the spin-spin correlation function.

This ratio is plotted for Pd$_2$GdIn and Cu$_2$GdIn as a function of reduced temperature in Fig. 7.4, from which it may be seen that the variation is very similar in both compounds.

![Graph showing the relative internal magnetic energy of Pd$_2$GdIn and Cu$_2$GdIn as a function of reduced temperature.](image)

**Fig. 7.4.** The relative internal magnetic energy of Pd$_2$GdIn and Cu$_2$GdIn as a function of reduced temperature.
If $\alpha_m$ is proportional to $C_m$ the internal magnetic energy can also be obtained using the magnetic thermal expansion. However the magnetic Grüneisen relation does not hold for these compounds.

The magnetic order is associated with the Gd atoms which in the case of Pd$_2$GdIn induces a small moment on the palladium atoms. The field dependence of magnetic isotherms (as seen in the magnetostriction results and low temperature magnetisation data) below $T_N$ suggest that the magnetic order is complex with a continuous evolution towards ferromagnetism rather than a spin flop transition. Since Gd is a $S$ state ion the moment is relatively stable and unaffected by crystalline electric fields. Furthermore the cubic environment would suggest anisotropy effects are small. For fields of $\sim 2T$ the magnetic energy $\mu H$ associated with the Gd moments is comparable to $kT_N$ and therefore only moderate fields are required to establish ferromagnetism. The Curie-Weiss behaviour of the susceptibility above $T_N$ is consistent with local moment behaviour in which the magnetic phase transition is driven by transverse fluctuations of the Gd moment. Although below $T_N$ in Pd$_2$GdIn the Gd moments partially polarise the 4d Pd band producing an extra $\sim 1\mu_B$ to the observed magnetisation this does not constitute a local moment. Magnetisation measurements show that magnetic short range order above $T_N$ has disappeared by $\sim 15$ K. Within a local moment model e.g. Heisenberg system the magnetic contribution to the thermal expansion arises from the thermal variation of the spin-spin correlation function and the dependence of the exchange integral with distance. For an itinerant system amplitude fluctuations are important which leads to an additional degree of freedom which can influence the thermal expansion.
7.4. Magnetostriction and magnetisation results.

The isothermal longitudinal forced magnetostriction \( \frac{\Delta L}{L} = \frac{\ell(H) - \ell(0)}{\ell(0)} \) was measured at several temperatures in fields up to 7T for each sample. The results for Pd\(_2\)GdIn are shown in Fig. 7.5.

![Graph showing longitudinal forced magnetostriction isotherms for Pd\(_2\)GdIn.](image)

Fig. 7.5. Longitudinal forced magnetostriction isotherms for Pd\(_2\)GdIn.

With the exception of the isotherm corresponding to approximately the Néel temperature i.e. \( T = 9.59 \) K all the isotherms are initially negative before having a positive slope with the minimum in the forced magnetostriction occurring for fields \( \leq 0.5T \). Previous magnetic isotherms [3] were measured in field steps of 0.5T and so it was not possible to ascertain whether there is an associated change in magnetisation.
Therefore the magnetisation was re-measured in the ordered phase using field steps of 0.1T and is shown in Fig. 7.6.

Fig. 7.6. The magnetisation of Pd$_2$GdIn as a function of applied magnetic field at T= 2K. The inset shows the magnetisation data in the Arrott plot form (M$^2$ as a function of H/M)

Although the isotherm obtained at 2K and shown in Fig. 7.6. does not appear to have any anomaly, if the data is plotted in the form of an Arrott plot (M$^2$ versus H/M), inset to Fig. 7.6. a change in slope is observed around 0.5T.

Clearly the magnetic transition is not a spin flop but a continuous transformation.

The precise dependence of sample volume on applied magnetic field depends upon the magnetisation process of the material. On the application of a field the sublattice magnetisation rotates and at a large enough field $H_{sf}$ the moment will become canted and produce a ferromagnetic component. $H_{sf}$ will depend upon the magnetocrystalline anisotropy energy of the system. One may argue that the forced magnetostriction of a material should behave with a $B^2$ dependence. The forced magnetostriction of Pd$_2$GdIn as a function of $B^2$ is shown in Fig. 7.7.
It is clear from this figure that the $B^2$ dependence of the magnetostriction holds only for a limited range in field and temperature.

**Fig. 7.7.** The forced magnetostriction isotherms for Pd$_2$GdIn as a function of $B^2$.

The forced magnetostriction observed in Cu$_2$GdIn and shown in Fig. 7.8. has a different field dependence compared to that of Pd$_2$GdIn.

**Fig. 7.8.** Longitudinal forced magnetostriction isotherms for Cu$_2$GdIn. The inset shows the forced magnetostriction isotherms for the nonmagnetic Pd$_2$LuIn.
7.4 Magnetostriction. Chapter 7. Thermal expansion and magnetostriction of TM$_2$REIn.

Below $T_N$ the forced magnetostriction shows a distinct anomaly at approximately 0.5 T. However the anomaly is not the same as that observed in Pd$_2$GdIn since it involves a zero change in the magnetostriction as a function of field. The anomaly is more pronounced for increasing field and at 4.2K a significant hysteresis is observed. Above approximately 3 T there is very little field dependence observed in the magnetostriction.

The forced magnetostriction of the non-magnetic compound Pd$_2$Luln is shown as the inset to Fig. 7.8. The observed magnetostriction is small, when compared to that for the magnetically ordered sample. The magnetostriction for the non-magnetic compound is similar to that for the magnetic sample for $T > T_N$.

Fig. 7.9. The magnetisation of Cu$_2$GdIn as a function of applied magnetic field at $T = 2K$. The inset shows the magnetisation data in the Arrott plot form ($M^2$ as a function of $H/M$)

Detailed magnetisation measurements for Cu$_2$GdIn undertaken in the magnetically ordered phase are shown in Fig. 7.9. Again the magnetic transition which is continuous can be seen in the Arrott plot as an inset to Fig. 7.9.

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7.5. Discussion.

The magnitude of the thermal expansion coefficient observed for all three compounds is similar and appears quite 'normal'. It may be compared with $10^{-3}$ observed for materials exhibiting giant magnetostriction or with a value close to zero for Invar materials. The total volume change between 0 and 300 K again is very close for the three compounds indicating a small magnetic component. This was confirmed by subtracting an electron and phonon contribution from the two Gd compounds, assuming all three components are uncoupled. If the magnetic contributions to the specific heat and thermal expansion are compared for the two magnetic compounds differences are revealed. At $T_N$ the jump $\Delta C_m$ in the magnetic specific heat is similar for both compounds, whereas the spontaneous magnetostriction is significantly smaller in Pd$_2$GdIn. A comparison of the thermal evolution of the magnetic specific heat and thermal expansion reveals that a magnetic Grüneisen relation does not hold. The magnitude of $V$ and $B$ may be considered similar for both compounds and not to vary significantly over the temperature range considered. Thus the coupling to the lattice is different in both compounds. This difference is highlighted in the results obtained in the force magnetostriction measurements.

Magnetisation measurements reveal that the magnetisation process is different in both magnetic compounds with Pd$_2$GdIn having a complex structure. Spin wave measurements on several ferromagnetic Heusler compounds including one close to an antiferromagnetic instability indicate that the exchange interactions are of long range and oscillatory as expected for an RKKY mechanism. Unfortunately the high absorption cross section for thermal neutrons hinders the establishment of the magnetic structure. In the absence of this information it is not possible to comment in detail on the magnetisation process.

If this is the case in Pd$_2$GdIn, the forced magnetostriction would arise from the polarisation of the Pd 4d band. This would then decrease as a function of temperature as is observed. Since the applied field $\mu H \approx kT_N$
the forced magnetostriction may be expected to remain finite for large fields above $T_N$.

Gd is expected to have a stable moment of fixed amplitude the possible itinerant behaviour could arise from the polarisation of the Pd 4d band. The possibility of amplitude fluctuations provides an additional mechanism for thermal expansion.

In a mean field itinerant model the spontaneous magnetostriction is given by:

$$\omega_m(0,0) = B^{-1}K M^2(0,0) \quad (7.6)$$

where $B^{-1}$ is the isothermal compressibility and $K$ is the magnetoelastic coupling constant.

By integrating the spontaneous magnetostriction $\beta_m(0,T)$, $\omega_m(0,0)$ was found to be very small in both compounds, thus indicating that $B^{-1}K$ is also small which is as one may expect as $B^{-1}$ is of the order of $10^{-10}$. Within the same model $B^{-1}K$ can also be obtained from the forced volume magnetostriction $\delta \omega(0,0)/\delta H$ which is related at 0K to the high field susceptibility by:

$$\frac{\delta \omega}{\delta H} = 2B^{-1}K \chi_{HF}(0,0) M(0,0) \quad (7.7)$$

It has been suggested that the presence of spin fluctuations in these compounds may be an important factor governing the lattice magnetism interaction. In the spin fluctuation framework as proposed by Moriya [6] the volume magnetostriction as a function of field and temperature is related to the magnetisation state of the material by:

$$\omega_m(H,T) - \omega_m(0,0) = B^{-1}K [M^2(H,T) - M^2(0,0)] \quad (7.8)$$

Such a relationship enables the product $B^{-1}K$ to be determined.
Furthermore one may expect that the forced magnetostriction will be a linear function of $M^2$. Fig. 7.10 shows the forced magnetostriction as a function of $M^2$. It is clear from Fig. 7.10 that the forced magnetostriction is indeed a linear function of $M^2$ at $T=15K$ i.e. in the paramagnetic phase, however when the sample is magnetically ordered, the data show only a near approximation to linearity.

The gradient of the forced magnetostriction as a function of $M^2$ (which approximates to the product $B^{-1}\kappa$) in the antiferromagnetically ordered phase and that for the unordered phase are different with:

$$(B^{-1}\kappa)^{AF} = 7.02 \times 10^{-9} \pm 5.3 \times 10^{-11} (\text{JT}^{-1}\text{Kg}^{-1})^{-2}$$

$$(B^{-1}\kappa)^{PM} = 6.64 \times 10^{-9} \pm 4.3 \times 10^{-12} (\text{JT}^{-1}\text{Kg}^{-1})^{-2}$$

The difference, which is outside the experimental errors must be a result of the temperature dependence of the bulk modulus, as one may expect the magnetoelastic coupling to be temperature independent.
7.6. Conclusion and summary.

Low temperature thermal expansion and magnetostriction measurements have been carried out on two magnetic rare earth intermetallic Heusler (L2₁) alloys, namely Pd₂GdIn and Cu₂GdIn. In order to facilitate data analysis, and separate the magnetic contribution to the thermal expansion and hence the spontaneous volume magnetostriction, an isostructural paramagnetic compound has also been measured.

This analysis showed that the spontaneous volume magnetostriction was significantly less in the Pd compound than in the Cu compound. The magnetic specific heat however was found to be similar in both compounds.

Extraction from the specific heat data of the approximation to the spin-spin correlation function indicates that both magnetic compounds exhibit second order phase transitions from the magnetically ordered to the paramagnetic phase.

Both low temperature magnetisation and forced magnetostriction measurements on Pd₂GdIn demonstrate the presence of a continuous field induced transition from the antiferromagnetically ordered state to a mixed state with a ferromagnetic component. This is in contradiction to the magnetisation and forced magnetostriction of Cu₂GdIn where no continuous transition is observed. However a field induced transition is observed in both the magnetisation and magnetostriction data at 0.5T for Cu₂GdIn.

Since Gd is an S state compounds containing Gd should exhibit no unusual magnetoelastic phenomena, as the magnetic / lattice coupling should be small, one must therefore attribute the observed magnetostriction to polarisation of the Pd 4d band electrons by the Gd 4f shell. Such interaction introduces further degrees of freedom to the system, which may account for the unusual properties of these rare earth compounds.
7.7. References.

Chapter 8. Observation of spin-spin correlations in 
\( V_2O_3 \) using the spin polarised multidetector 
instrument D7.

8.1. Introduction.

Materials exhibiting metal-insulator (Mott) transitions have received considerable attention ever since Mott suggested the possibility of this many body phenomenon \[1\]. The materials most extensively studied are various vanadium oxides, in particular vanadium sesquioxide \( V_2O_3 \) and its alloys with chromium \[2\]. Below 155K \( V_2O_3 \) is an insulating antiferromagnet. Near 155K a sharp phase transition to a metallic state \[3\] without long range magnetic order \[4\] takes place and around 550K the material gradually transforms back to an insulating phase \[2\]. The high temperature transition can be transformed to an abrupt phase transition by doping with Cr \[5\]. The insulator to metal transition, which occurs at low temperature in stoichiometric \( V_2O_3 \), is accompanied by a monoclinic distortion of the trigonal (corundum) structure \[4,5\]. In spite of considerable experimental and theoretical effort the precise mechanisms giving rise to these phase transitions remains unclear.

Preliminary polarised neutron scattering experiments \[6\] indicated that the metallic phase differs dramatically from the low temperature antiferromagnetic phase not only in its electrical properties but also magnetically. The loss of long range antiferromagnetic order does not seem to be caused by the disordering of well defined local moments but instead is due to a substantial change in electronic structure. The paramagnetic scattering observed at large wave vectors (Q), appeared too small to be compatible with disordered local moments. Furthermore the observed paramagnetic intensity at large Q was very much lower than the \( Q = 0 \) value given by the uniform susceptibility. The polarised neutron spectrometer employed did not permit an investigation of the small wave vector response. These observations indicate a strong similarity of the metallic phase in \( V_2O_3 \) to itinerant ferromagnets above the Curie
8.1. Introduction. Chapter 8. Spin-spin correlations in \( \text{V}_2\text{O}_3 \)

In these systems magnetic fluctuations of strong intensity are observed only for small wave vectors and decrease rapidly with increasing \( Q \) indicating strong short-range ferromagnetic correlations. Presented here are the results of a detailed polarised neutron investigation of the magnetic fluctuations in \( \text{V}_2\text{O}_3 \) using the spin polarised spectrometer D7. Polarised neutron scattering enables an unambiguous measurement of the paramagnetic response, including the wave vector and frequency dependence.

The measurements have been carried out in all three phases namely in the insulating region at 120K, in the metallic phase at 300K and finally at 600K in the high temperature insulating phase.

8.2. Properties of \( \text{V}_2\text{O}_3 \).

At room temperature \( \text{V}_2\text{O}_3 \) is a reasonably good metal with resistivity of the order \( 10^{-3} \) \( \Omega \text{cm} \). When the temperature is decreased below \( \approx 155K \) the compound undergoes a first order phase transition from a metallic to an insulating state, accompanied by an increase in resistivity of approximately seven orders of magnitude [3]. Associated with the transition which exhibits an hysteresis of 10-12K as one may expect from a first order phase transition, is a change in crystal structure [5] from the corundum structure with space group \( \text{R}3\text{c} \) to a monoclinic phase with space group \( \text{I}2/\text{a} \), (a non conventional space group setting of \( \text{C}2/\text{c} \)). A volume expansion of 3.5% occurs on cooling through the transition [10]. In the low temperature phase the system orders antiferromagnetically with the \( \text{V} \) moments coupled ferromagnetically in the monoclinic (010) layers, originating from the (110) hexagonal planes, with adjacent planes coupled antiferromagnetically [4]. Thus the monoclinic distortion in the low temperature phase is believed to be magnetostrictive in origin. There are four and six vanadium atoms in the monoclinic and the rhombohedral cell respectively, with each vanadium atom contributing two 3d electrons. The antiferromagnetically ordered moment per vanadium atom was determined to be 1.2 \( \mu_\text{B} \), much less than the 2\( \mu_\text{B} \) expected for two 3d electrons on \( \text{V}^{3+} \),
and has been attributed [11] to a contribution of 1\(\mu_B\) from localised electrons and 0.2\(\mu_B\) from itinerant electrons. Interpretation of heat capacity measurements have lead to the conclusion that the metallic phase is characterised by a large electronic contribution 54.6 mJ \(K^{-2} mol^{-1}\) per V atom [12].

In the metallic phase the magnetic susceptibility is anomalously high but drops abruptly by a factor of nearly 2 at the transition [13]. NMR [14] and susceptibility measurements have been combined to separate the contributions to the measured susceptibility in the metallic phase into temperature independent diamagnetic (dia) and van Vleck (vv) parts and a temperature dependent 3d part obeying a Curie-Weiss law

\[
\chi(T) = \chi_d + \chi_{vv} + \chi_{dia}
\]  

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

with 

\[
C = 0.657 \text{ emu mole}^{-1} K \text{ and } \theta = -600 \text{ K giving } \mu_{\text{eff}} = 2.37 \mu_B \text{ per vanadium atom. Over the temperature range for which the Curie-Weiss behaviour is reported, namely 155 to 300 K, the observed susceptibility only falls by 20\%. Between 300 and -550 K the susceptibility is only weakly dependent on temperature. Above ~ 550 K the observed susceptibility has been analysed to yield a Curie-Weiss behaviour with } \theta = -600 \text{ K and } \mu_{\text{eff}} = 2.69 \mu_B \text{ per vanadium atom. However this analysis is valid only if } \chi_{vv} \text{ takes the value 0.21 emu/mol, which corresponds to the value of } \chi_{vv} \text{ calculated for vanadium [15]. The calculated spin only values of } \mu_{\text{eff}} \text{ for } V^{3+} \text{ and } V^{4+} \text{ are 2.83 } \mu_B \text{ and 3.87 } \mu_B \text{ per vanadium atom respectively.}
8.3. Experimental.

A $V_2O_3$ powder sample (Johnson Matthey) was checked by X-ray diffraction at room temperature and found to be single phase. It has the corundum structure (space group $R\bar{3}c$) with cell parameters:

\[ a=4.9475(7) \text{ Å} \text{ and } c=14.004(7) \text{ Å}, \]

in good agreement with earlier reported data [5] for the stoichiometric compound. Susceptibility measurements carried out using a SQUID magnetometer over the temperature range 4 to 300 K, revealed an anomaly at \( \approx 155 \) K in agreement with earlier measurements [13]. An anomaly at this temperature was also observed in the electrical resistivity from measurements made on a compacted pellet.

Measurement of the paramagnetic response as a function of wave vector was carried out using the polarised neutron spectrometer D7 at the ILL Grenoble. An incident neutron wavelength of 4.84Å was used. The 32 detectors enabled simultaneous measurement of the response over the wave vector range \( 0.1 < Q < 2.5 \) Å\(^{-1}\). Polarisation of the incident beam and analysis of the scattered beam was made using polarising supermirrors. Further details of the instrument can be found in chapter 4.

The average flipping ratio of the 32 detector systems was found to be \( 30 \pm 1.5 \).

For measurements at 120 K and 300 K the 20 g powder sample was contained in a thin walled aluminium tube located in a helium flow cryostat. A non inductively wound furnace was used for the high temperature measurements at 600K. The scattering from the sample was placed on an absolute scale using the vanadium normalisation. This procedure was verified using the nuclear spin incoherent scattering from the sample, which is expected to arise entirely from the presence of vanadium. The observed differential cross section was \( 0.84 \pm 0.02 \) barns/str/atm which compares favourably with the reported value for vanadium of 0.826 barns/str/atm [17].
An unambiguous separation of the paramagnetic scattering from all other contributions was made using the \( XYZ \) method as described in chapter 4. Vanadium has a large nuclear spin incoherent scattering which is wave vector independent but necessitates data of good statistical significance in order to obtain the paramagnetic component from the spin flip channel.

The polarised neutron technique not only enables the isothermal determination of the magnetic cross section but also its spatial and temporal dependence. If the scattering is placed on an absolute scale the measurements provide a powerful test of theory. The experiment on \( \text{V}_2\text{O}_3 \) was concerned only with the wave vector dependence of the magnetic response, with the scattering integrated over an energy range up to \( \approx 30 \text{ meV} \). If relativistic effects are unimportant and spin is conserved the observed scattering will extrapolate to the cross section at \( Q=0 \) given by the uniform susceptibility \( \chi \).

The spin-spin correlation function \( \langle S_q S_q \rangle \) at \( Q=0 \) is given by:

\[
\sum_i \langle S_i S_i \rangle = 3 k_B \chi (8.3)
\]

which is related to the partial differential cross section by:

\[
\frac{d\sigma}{d\Omega} = \sum_j \frac{2}{3} \langle S_i \cdot S_j \rangle (r_{0j})^2 f^2 (8.4)
\]

where \( (r_{0j}) = 0.54 \times 10^{-13} \text{ cm} \) and \( f \) is the form factor which is unity at \( Q = 0 \).

The magnetic correlation function

\[
S(q, \omega) = \int dt e^{-i \omega t} \sum_{i,j} e^{i q (R_i - R_j)} \langle S_i(t) \cdot S_j(0) \rangle (8.5)
\]

is related to the imaginary part of the dynamic susceptibility:

\[
S(q, \omega) = \frac{1}{1 - e^{-\hbar \omega / kT}} \chi''(q, \omega) (8.6)
\]

A sum rule for the scattering can then be defined:

\[
\sum_q \int d\omega \ S(q, \omega) = \int d\omega \sum_q \int dt e^{-i \omega t} \sum_{i,j} e^{i q (R_i - R_j)} \langle S_i(t) \cdot S_j(0) \rangle (8.7)
\]

which yields

\[
N(S^2) = NS(S+1) (8.8)
\]
In the ordered ground state the Bragg peaks contribute \((bS)^2\) and the spin waves \((1-b^2)S^2 + S\) (where \(b\) is the reduction factor due to longitudinal fluctuations). In order to obtain the sum rule it is necessary to integrate up to the maximum spin wave energy. For some systems this may not be experimentally feasible, but the technique described above which places the scattering onto an absolute scale enables a precise comparison with model calculations of the wave vector and energy dependence of the response. For local moment systems well above the ordering temperature \(T_N\) the correlation \(<S_iS_j> = S(S+1)\) and the sum rule is recovered. Again the integration has to be over the same energy range which is typically equal to \(k_B T_N\). However in the paramagnetic phase the response is quasi-elastic with the magnetic weight peaked at zero energy. However local magnetic moments are meaningful variables only if the magnetic excitation spectrum \(\omega_{\text{mag}}\) and charge excitation spectrum \(\omega_{\text{ch}}\) are separated.
8.4. Results.

The spin flip scattering as measured in the low temperature insulating phase at 120 K Fig. 8.1. was consistent with that reported by Moon [4]. Within the wavevector range studied the (001), (010) and (-201) antiferromagnetic Bragg peaks were clearly resolved. The intensity of these peaks are consistent with the proposed antiferromagnetic structure in which the vanadium moments of $1.2 \mu_B$ are ferromagnetically coupled in (110) planes of the hexagonal lattice with adjacent planes coupled antiferromagnetically. The uniform background observed below ~1 Å$^{-1}$ corresponds to a cross section of 0.0075 b./str/fu.

![Graph](image)

*Fig. 8.1. Spin flip scattering of V$_2$O$_3$ in the low temperature insulating phase at T = 120K.*

On raising the temperature above 155K the form of the magnetic scattering significantly altered with the sharp antiferromagnetic peaks disappearing as expected.
The wave vector dependence of the paramagnetic scattering observed at 300K Fig 8.2. and 600K Fig 8.3. was similar, with the main feature being the enhancement of the scattering at small wave vectors and around strong nuclear Bragg peaks.

**Fig. 8.2.** Paramagnetic scattering of V$_2$O$_3$ in metallic phase at T = 300K.

**Fig. 8.3.** Paramagnetic scattering of V$_2$O$_3$ in the high temperature insulating phase at T = 600K.
Such behaviour is expected if there exist spatial correlations of the magnetisation density which are ferromagnetic in nature. Unpolarised neutron scattering carried out at 200K on a single crystal specimen also reported the presence of ferromagnetic correlations \[9\]. Measurements carried out around the position of the antiferromagnetic wavevectors did not reveal any significant enhanced scattering. The two temperatures at which measurements were made in the paramagnetic phase, namely 300 and 600K correspond approximately to twice and four times the transition temperature at which the paramagnetic state occurs. Experimental constraints did not permit measurements to be made below \(0.2\) Å\(^{-1}\) and therefore obtain a precise determination of the correlation length. An "estimate" was obtained using the value of the cross section at \(Q=0\) as given by the uniform susceptibility. This analysis indicated that the range of correlation 6-9 Å did not effectively change between 300 and 600K. The value of the correlation length obtained in this way is similar to that observed in \(\text{V}_5\text{O}_9\) \[8\]. The total amount of scattering per vanadium atom was obtained by integrating the observed scattering up to a wave vector determined by the atomic volume \((\Omega)\) namely \(Q_0 = \left(\frac{6\pi^2}{\Omega}\right)^{\frac{1}{3}}\).

\[
\langle M_1 M_4 \rangle = \left[ \frac{\Omega}{2\pi^2} \right] \int_0^{Q_0} Q^2 \langle M_{-Q} M_Q \rangle \, dQ
\] (8.9)

This yielded an amplitude per vanadium atom of 0.35(1)\(\mu_B\), 0.35(1)\(\mu_B\) and 0.5(1)\(\mu_B\) at 120, 300 and 600K respectively. The value obtained at 120K did not include the magnetic Bragg scattering, only the magnetic diffuse scattering. These values should not be interpreted as atomic moments. The energy integration has not been carried out over the appropriate bandwidth but over the corresponding thermal energy range.

The loss of long range magnetic order does not give rise to an increase in the magnetic diffuse scattering as would be expected for thermally disordered local moments of 1.2\(\mu_B\). The amplitude observed at 290 K is smaller than the 0.61 \(\mu_B\) reported for \(\text{V}_5\text{O}_9\) obtained using similar experimental conditions \[8\]. A value of 0.5(1) \(\mu_B\) per vanadium atom was
obtained for V$_2$O$_3$ in earlier polarised neutron experiments [6] using high energy neutrons which enabled an energy integration over twice the thermal energy range.

8.5. Discussion.

The thermal variation of the uniform susceptibility is complex but has been analysed to reveal Curie-Weiss behaviour over discrete regions namely 155 to 300 K and above 600 K [17]. The values of the effective moment in each regime are different and inconsistent with the theoretical values expected for V$^{3+}$ or V$^{4+}$ and with the value estimated from the observed ground state moment. Furthermore the paramagnetic Curie temperature derived for each regime, namely -600 K is high. In the metallic phase similar behaviour is observed for systems in which the Fermi level falls close to a peak in the density of states. Castellani et al. [18] have proposed that the susceptibility in the metallic phase is characteristic of a narrow band Stoner enhanced Pauli paramagnet. In the non interacting limit the susceptibility and Sommerfeld coefficient of the specific heat are related to the bare density of states by

$$\frac{\chi}{13.71} = \frac{\gamma}{0.212} = N(e_F) \quad (8.10)$$

where $\chi$ is in $\mu$emu mol$^{-1}$, $\gamma$ is in mJ (mol K$^2$)$^{-1}$ and $N(e_F)$ is given by states/eV atom. The magnitude of both the susceptibility $\chi = 10^3 \mu$emu/mol and the Sommerfeld coefficient $\gamma = 54.6$ mJ (mol K$^2$)$^{-1}$ in the metallic phase are anomalously large producing a value for the density of states $N(e_F)$ substantially greater than that calculated. The value for $\gamma$ was obtained by suppressing the transition temperature and extending the metallic phase to lower temperatures by either changing the stoichiometry or by the application of pressure. Thus care must be taken in attributing the $\gamma$ values derived in this way to the metallic state of pure V$_2$O$_3$ at ambient pressure. Recent specific heat measurements [16] indicate that the metallic state of V$_2$O$_3$ looks quite different as a function of band filling (change in stoichiometry) or of pressure. Furthermore the analysis and the band
8.5. Discussion.

Chapter 8. Spin-spin correlations in V$_2$O$_3$.

Structure calculations do not include many body effects such as electron-electron and electron phonon interactions which influence $\chi$ and $\gamma$. McWhan [12] has pointed out for such systems that $\chi/\gamma << 1$ implies strong electron-phonon interaction, $\chi/\gamma \approx 1$ implies spin fluctuations and $\chi/\gamma >> 1$ implies paramagnons, and on the basis of the analysis it was concluded that spin fluctuations dominate in V$_2$O$_3$.

Significant thermal variation of the uniform susceptibility at temperatures well below that corresponding to the Fermi temperature is observed in many strongly correlated magnets such as MnSi, ZrZn$_2$, Ni, Fe etc [19]. In these materials neutron measurements have shown that the paramagnetic state is characterised by spin fluctuations which can persist up to many times the ordering temperature [7]. It is the presence of the spatial correlations in V$_2$O$_3$ and the underlying mechanism that is the key to understanding the metal insulator transition.

The magnetic moment per vanadium atom obtained at 77K in the antiferromagnetic phase is significantly smaller than the $2\mu_B$ expected for a V$^{3+}$ ion. Several possibilities for this behaviour have been proposed including, itinerancy of the 3d electrons (covalency) [18], a crystal field model in which an isolated V$^{3+}$ ion in an octahedral field has opposing spin and orbital moments [14] and a band model in which one of the two 3d electrons is completely polarised and the other only partially [11]. Recent polarised neutron measurements [20] show that the moment on the vanadium atoms is almost entirely due to electrons in the doubly degenerate orbitals which are supposed to give rise to orbital ordering. Significant negative moment amounting to some 6% of the total was found on the oxygen sites which could only occur due to covalency.
The thermal variation of the moment in the antiferromagnetic phase would suggest a transition to a paramagnet well above the first order phase transition at 155K where long range magnetic order in fact disappears. However the disappearance of long range magnetic order at 155K is not the result of thermal disorder of local moments of fixed amplitude.

At the metal-insulator transition there is a significant change in crystal structure involving \( \approx 3.5\% \) reduction in the volume of the lattice in the metallic phase, with the vanadium-vanadium distances becoming shorter and less differentiated and the vanadium-oxygen distances remaining essentially unchanged.

The occurrence of magnetic moments in metallic magnets depends on correlation effects and the band width which is essentially determined by the nearest neighbour metal-metal distance. In the case of vanadium this has been extensively studied in compounds such as Au\(_4\)V [21]. The absence of nearest neighbour V-V interactions is believed to be important for the formation of local vanadium moments. Theoretically the volume dependence of the magnetic moment in bcc vanadium has been studied by Hattox et al [22] who found that a local moment is formed for V-V distances given by \( 2.85\text{Å} < d_{\text{VV}} < 3.8\text{Å} \). The loss of magnetic order observed in \( \text{V}_2\text{O}_3 \) is not dissimilar to the behaviour found in \( \text{YMn}_2 \) where a paramagnetic state is established at a first order phase transition involving a \( \approx 5\% \) reduction in cell [23] volume. This behaviour is associated with a collapse of the local Mn moment. However it may be noted that the level of scattering in \( \text{V}_2\text{O}_3 \) towards the zone boundary e.g. between \( \approx 0.6 \) and \( 1 \text{Å}^{-1} \) does not effectively increase on warming to 290K as would be expected on the loss of long range magnetic order corresponding to a moment of \( (g\mu_s) \sim 1.2 \mu_B \). Although the paramagnetic state of \( \text{YMn}_2 \) is characterised by well defined spin fluctuations, [24] these occur around the staggered wave vector. In \( \text{V}_2\text{O}_3 \) the spin fluctuations are of a ferromagnetic nature and are clearly responsible for the jump in susceptibility at the first order phase transition. Since \( \text{V}_2\text{O}_3 \) orders antiferromagnetically fluctuations may be expected around the staggered
wave vector particularly close to the Néel temperature. However, as the transition at 155K is not a true magnetic phase transition, being of first order, thermodynamic fluctuations should not be important. Clearly the ferromagnetic correlations persist beyond 600K and are not simply residual short range order but arise from a fundamental change in the wave function. At the phase transition there is a change by seven orders of magnitude in the electrical conductivity reflecting the increased overlap of the d functions. Thus whilst antiferromagnetic coupling dominates the ferromagnetic exchange below 155K this could alter when the mechanism changes with the introduction of a conduction band.

8.6. Conclusion and summary.

The paramagnetic phase of V$_2$O$_3$ comprises of a metallic phase $T_N<T<550$K and a high temperature insulating phase 550K<$T$, and is characterised by a ferromagnetically correlated spin density similar to that observed in the paramagnetic phase of transition metal ferromagnets [7]. The onset of ferromagnetic correlations at the metal-insulator transition accounts for the abrupt jump in the uniform susceptibility. Associated with this transition is the loss of long range magnetic order. However the transition which is of first order is not a true Néel temperature but arises from a substantial change in the crystallographic and electronic structure. The reduction in atomic volume which also occurs on the establishment of the metallic state arises from an instability in the local vanadium moment. The present result clearly indicates a substantial reduction in the paramagnetic moment within the thermal energy range. A similar observation is obtained for NiS [25] which also undergoes a metal insulator transition with a change in atomic volume and a collapse of long range magnetic order.

Whilst similarities exist between the volume collapse and moment instability detailed differences in the paramagnetic response are to be expected owing to differences in crystallographic structure and electronic configuration of the metal atoms. Vanadium which is at the beginning of
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the 3d series will have a more extended wave function, and indeed direct V-V interactions along the c direction are reported to influence the physical properties of $V_2O_3$. It is probable that the ferromagnetic correlations in the paramagnetic phase are a manifestation of these V-V interactions.

The absence of substantial thermal variation of the correlations clearly indicates that their origin is not one of residual short range order arising from thermal fluctuations close to the transition temperature but arise from details of the electronic structure. Further measurements extending to lower wave vectors are required to quantify the range of correlations. However there are no polarised neutron spectrometers presently available on which to carry out such investigations.
8.7. References.
