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NEUTRON DIFFRACTION AND ULTRASONIC STUDIES OF MAGNETIC ORDERING IN RARE EARTHS

by

GEORGE HENDRIK FREDERIK BRITS

THESIS
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ABSTRACT

The character of magnetic phase transitions has enjoyed considerable attention lately. In theoretical calculations based on renormalization group methods, Mukamel, Krinsky and Bak showed that the n=4 component Landau - Ginzburg - Wilson Hamiltonian appropriate for describing the spiral magnets Tb, Dy and Ho, exhibits one stable fixed point, consequently expect the helical ↔ paramagnetic phase transition in these metals to be of second order and predict a value of \( \beta = 0.39 \) for the power law that describes the spontaneous magnetization in the critical region. Barak and Walker, on the other hand, showed that according to their calculations the Hamiltonian does not lie in the domain of the stable fixed point and consequently expect the transition to be of first order. Experimental support for both the predicted second order nature and the first order nature is reported in the literature. Furthermore, the existence of a new "vortex" magnetic phase immediately below the Néel temperature has been proposed by Amitin et al.

In the light of the contradictory theoretical and experimental status of the nature of the transition, a high resolution neutron diffraction investigation was undertaken for Ho and Dy. This was supplemented by measurements of ultrasonic attenuation and velocity on Dy. Our neutron diffraction measurements showed that the order parameter varies continuously through the transition point of Dy and Ho, thus indicating a second order nature for the transition. A value of \( \beta = 0.39 \) was obtained for Dy. This was supported by the lack of thermal hysteresis in both diffraction and ultrasound measurements. No evidence was found in support of the proposed vortex magnetic structure. An intriguing, still unexplained observation was however made: the value of the Néel temperature as indicated by the two techniques during simultaneous measurements differed.

The c axis sinusoidally modulated ↔ paramagnetic phase transition in Er was also investigated. This transition, of which very little is known both theoretically and experimentally, was observed as of second order. The value of the \( \beta \)-exponent was found to exhibit cross-over behaviour from a value of around 0.31 close to the Néel temperature to a mean field value at lower temperatures. The anomaly in the value of the transition temperature as indicated by simultaneous measurement of neutron diffraction and ultrasonics was also observed for Er, but found to disappear upon annealing of the crystal.
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1.4 THE CRYSTALS
1.1 INTRODUCTION

The magnetic properties of the rare earths have attracted considerable attention [1] since material of reasonable purity became available through the pioneering work at the Ames Laboratories [2]. Their "normal" electronic structure, as exhibited by the heavy rare earths (eg. Gd, Tb, Dy, Ho and Er), is \([\text{Xe}]4f^{n}5d^{1}6s^{2}\) with the 4f shell giving rise to the magnetic behaviour. The 4f level is well below the Fermi level and the integral number of 4f electrons per atom, integral valence and intrinsic magnetic moment are not a function of temperature and pressure\(^+\).

The 4f electrons are deeply seated at distances of 0.2 - 0.3 Å from the nucleus and are well shielded from the effect of the electric crystal field associated with the positive ions. Thus, unlike the well-known case of 3d ions where the orbital angular momentum is quenched in the solid state, both spin and angular momenta make their full contribution in the solid state. The total angular momentum \(J = S+L\) is a good quantum number and can be accurately obtained using Hund's rules.

The 4f wave functions do not overlap appreciably and are coupled by the indirect Ruderman-Kittel interaction as mediated by the conduction electrons. As discussed in Section 1.2 this long range oscillatory interaction, together with crystal field effects, leads to the fascinating spin structures observed for these materials [6].

Considerable interest currently surrounds the nature of the phase transitions in helically ordered Tb, Dy and Ho. An investigation as to the character of the helical↔ paramagnetic phase transition in Dy and Ho crystals, employing neutron scattering and ultrasonic velocity and attenuation measurements, constitutes a major part of this thesis. An

\(^+\)Exceptions to the normal rare earth behaviour are the so-called anomalous rare earths (Ce, Eu, Yb and compounds of Ce, Eu, Yb and Sm), which have attracted considerable attention during the last decade. These materials exhibit properties such as intermediate valence, concentrated Kondo and heavy fermion behaviour as well as possible triplet superconductivity for certain materials [3,4,5].
anomaly associated with a proposed vortex magnetic structure for Dy was searched for and the incommensurate ↔ commensurate phase transition for Dy at $T_C$ was investigated in the vicinity of the Curie temperature. In conclusion the c axis sinusoidally modulated ↔ paramagnetic phase transition of Er was studied.

1.2 MAGNETIC ORDERING IN THE HEAVY RARE EARTHS

1.2.1 The Ruderman-Kittel-Kasuya-Yosida interaction

Calculations of band structures [7] of the heavy rare-earths show that the 5d and 6s levels have substantially higher energies than the 4f level. Furthermore, the 5d and 6s wave functions of neighbouring atoms overlap appreciably in contrast to the 4f wave functions which are well localized [7]. The metal consequently behaves like a collection of tripositive ions localized on a lattice with the 5d and 6s electrons contributing to the sea of conduction electrons.

The intricate magnetic ordering exhibited by these metals results from an indirect interaction between the 4f wave functions and can be described in terms of the following Hamiltonian[8]:

$$H = H_{iso \, ex} + H_{an \, ex} + H_{cf} + H_{ms}.$$  

(1.1)

In Eq. (1.1) $H_{iso \, ex}$ denotes the well-known Ruderman-Kittel-Kasuya-Yosida interaction and will be discussed below. $H_{an \, ex}$ results from the nonsphericity of the 4f wave function and does not normally lead to large effects. $H_{cf}$ originates from the interaction of the magnetic moments with the crystalline electric field while $H_{ms}$ refers to the magnetostriction effects which arise from modulations of the anisotropic exchange and crystal field interactions as a result of strains.

The isotropic exchange contribution $H_{iso \, ex}$ corresponds to an indirect long-range oscillatory interaction between the localized 4f magnetic moments which is accomplished via the polarization of the conduction electrons. Such indirect exchange was first considered by
Fröhlich and Nabarro [9] in a first order calculation pertaining to the nuclear spin interaction in metals and this was extended to second order by Ruderman and Kittel [10]. These ideas were applied to the case of 4f magnetism by Kasuya [11,12] and Yosida [13]. Consider an interaction between the conduction electrons with spin $\vec{s}$ at $\vec{r}$ and the localized 4f electrons with spin $\vec{s}_n$ at $\vec{r}_n$:

$$H_{s,f} = - \sum_n \Gamma_{s,f}(\vec{r} - \vec{r}_n) \vec{s}(\vec{r}) \cdot \vec{s}_n. \quad (1.2)$$

Let the conduction electrons with spin $\sigma$ at $\vec{r}$ be described by Bloch wave functions

$$\psi_{k,\sigma}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} U_k(\vec{r}) |\sigma>, \quad (1.3)$$

where $U_k(\vec{r})$ is periodic with the lattice. Using second quantization techniques the Hamiltonian (1.2) can be written as [1]

$$H_{s,f} = - \sum_{k,k'} \Gamma_{s,f}(\vec{k},\vec{k'}) e^{i(\vec{k} - \vec{k'}) \cdot \vec{R}_n} \vec{s}_n \cdot \vec{s}_{k',k}, \quad (1.4)$$

with $s_{k',k}^z = \frac{i}{2} (C_{k',\uparrow}^+ C_{k,\uparrow} - C_{k',\downarrow}^+ C_{k,\downarrow})$,

$$s_{k',k}^+ = C_{k',\uparrow}^+ C_{k,\uparrow},$$

and $s_{k',k}^- = C_{k',\downarrow}^+ C_{k,\downarrow}, \quad (1.5)$

where $C_{k,\sigma}^+$ and $C_{k,\sigma}$ are the creation and annihilation operators of conduction electrons with spin $\sigma$.

The exchange interaction constant $\Gamma_{s,f}(\vec{r} - \vec{r}_n)$, which is given by

$$\Gamma_{s,f}(\vec{k},\vec{k'}) = \int d^3r \psi_{k,\sigma}(\vec{r}) \Gamma_{s,f}(\vec{r}) \psi_{k}(\vec{r}), \quad (1.6)$$

is related to its Fourier transform $\Gamma_{s,f}(\vec{q})$ by

$$\Gamma_{s,f}(\vec{r} - \vec{r}_n) = \frac{1}{N} \sum q \Gamma_{s,f}(\vec{q}) e^{i(\vec{r} - \vec{r}_n) \cdot \vec{q}}, \quad (1.7)$$
\[ \tilde{q} = \tilde{k} - \tilde{k}'. \]

The conduction electrons are polarized by their interaction with the 4f electrons. The polarization, which has an oscillatory component, in turn interacts with other localized 4f electrons resulting in an indirect exchange interaction between localized 4f magnetic moments. Yosida [13] calculated the spin polarization by considering the conduction electrons in the free electron approximation with wave functions given by

\[ |k^0,\sigma> = \phi^0_{k,\sigma} = e^{i\tilde{k} \cdot \tilde{r}} |\sigma> . \]  

A first-order perturbation calculation leads to a polarization proportional to \( \Gamma_{s,f}(0)/E_F \), which does not vary with distance. The second order perturbation for the energy is obtained by considering the perturbed wave functions given to first order by [1]

\[ \phi_{k,\sigma} = \phi^0_{k,\sigma} - \frac{m}{\hbar^2} \sum_{k'} \frac{\Gamma_{s,f}(k' - k)/(k^2 - k'^2)}{\Sigma_n} e^{i(k'-k) \cdot \tilde{R}_n} \times \]
\[ \left[ \pm S^0_n \phi^0_{k',\sigma} \pm \pm S^0_n \phi^0_{k',\sigma} \right] . \]  

where the summation \( \Sigma \) is over all states \( |k'^0\sigma> \), excluding those when \( E_{k'} = E_{k'} \). After retaining only terms of first order in \( \Gamma_{s,f} \) and making some approximations, the spin density

\[ \rho^{\sigma}(\tilde{r}) = \frac{\Sigma}{k_F} \sum_{k=0}^\infty <\sigma|\phi_{k,\sigma}|^2|\sigma> \]  

becomes, after manipulation

\[ \rho^{\sigma}(\tilde{r}) = N_F \frac{3N}{16E_F} \sum_q \Gamma_{s,f}(q)f(q)\sum_n \left[ e^{i\tilde{q} \cdot (\tilde{r} - \tilde{R}_n)} + e^{-i\tilde{q} \cdot (\tilde{r} - \tilde{R}_n)} \right] , \]  

with \( f(q) = 1 + \frac{4k_F^2 - q^2}{4k_F^2 q} \ln \left[ \frac{4k_F + q}{2k_F - q} \right] \)  

Both the first order (Fröhlich-Nabarro) and second order (Ruderman-Kittel) effects are contained in Eq. (1.11). The Ruderman-Kittel expression for the spin density follows from this equation by assuming a point interaction \( \Gamma_{s,f}(\tilde{r}) = \Gamma_{s,f}(\delta(\tilde{r})) \).
\[ \rho_{\pm}(r) = N_{\pm} \frac{(3N)^2}{E_F} \pi \Gamma_{s,f} \sum_{n} F \left[ 2k_F |\vec{r} - \vec{R}_n| \right]^Z_{S_n}, \]  
(1.13)

where \( F(x) = \frac{x \cos x - \sin x}{x^6} \).  
(1.14)

Since \( J \) is a good quantum number for the rare earth metals, \( S_n^Z \) can be replaced in Eq. (1.13) by \((g_J - 1)J_n^Z\).

Finally, consider the interaction energy between the two spins \( \vec{S}_m \) and \( \vec{S}_n \) located on different atoms

\[ E = \sum_{k,k',\sigma,\sigma'} \frac{<k^0|H|\sigma_f >k^0|\sigma_f><k^0|H|\sigma_f >k^0|\sigma_f| f_{k_k}(1-f_{k_k'})}{E_k - E_{k'}}. \]  
(1.15)

where \( f_k \) is the Fermi-Dirac function. Performing the summation over occupied \( k \) and unoccupied \( k' \) states and writing the result for total angular momenta \( \vec{J}_n \) and \( \vec{J}_m \) lead to

\[ E = \frac{(3N)^2}{2E_F} \pi \Gamma_{s,f}^2 (g_J - 1)^2 \sum_{n,m} \vec{J}_n \cdot \vec{J}_m F(2k_F |\vec{R}_n - \vec{R}_m|). \]  
(1.16)

It follows that the Hamiltonian describing the effective interactions between the localized 4f ions is given by

\[ H_{iso \ ex} = H_{f,f'} = - \sum_{n,m} J_{f,f'} (\vec{R}_n)_{n,m} \vec{J}_n \cdot \vec{J}_m, \]  
(1.17)

where \( (\vec{R}_{n,m})_{n,m} = \vec{R}_n - \vec{R}_m \)

and the exchange interaction constant is given by

\[ J_{f,f'} (\vec{R}_{n,m}) = \frac{(3N)^2}{2E_F} \pi |\Gamma_{s,f}(0)|^2 (g_J - 1)^2 F(2k_F |\vec{R}_n - \vec{R}_m|). \]  
(1.18)

This is a long-range interaction which decreases proportionally to \( R^{-3} \) and oscillates with frequency \((2k_F)^{-1}\).
1.2.2 Spin structures for Dy, Ho, Er and the RKKY interaction

The magnetic ordering exhibited by the three heavy rare earth metals Dy, Ho and Er as was observed from various experimental measurements is discussed below. A summary is given in Table 1.1, which also includes information on the magnetic ordering observed for Tb and Tm.

For Dy a neutron diffraction study at Oak Ridge [14] distinguished two magnetic phase transitions. Below $T_N \approx 179$ K the spins align ferromagnetically in the hexagonal plane. Looking down the c axis the spins in successive planes form a planar helical structure. The interlayer turn angle is a function of temperature and varies from $43.2^\circ$ at $T_N$ to $26.5^\circ$ at $T_C$ (85–90 K). It is incommensurate with the underlying crystallographic structure except at a few singular temperatures. At $T_C$ a first order transition to a basal plane ferromagnetic structure, in which the moments align along the easy a axis, was observed.

Holmium orders in a simple spiral below $T_N \approx 133$ K, with a tendency of the moments to "bunch" around easy directions below 45 K [15]. This is deduced from the appearance of fifth and seventh order harmonics of the (0 0 $\ell$) reflections and is ascribed to the planar hexagonal anisotropy. The interlayer turn angle decreases from $50^\circ$ at $T_N$ and reaches final values at $T_C$ (20 K) of between $36.7^\circ$ and $30^\circ$, the latter being commensurate with the underlying crystallographic lattice. Below $T_C$ the magnetic moments order in a conical ferromagnet, with a semi-cone angle of $80.5^\circ$ and a modulation wave-vector $Q = \frac{1}{6}$ in units of $b_3 = \frac{2\pi}{C}$ corresponding to an interlayer turn angle of $30^\circ$ [15].

Three regions of magnetic order were observed for Er in the first neutron scattering investigation at Oak Ridge [17]. Below $T_N \approx 85$ K, the spins are directed along the c axis. Although the spins in any given basal plane layer are identical, the amplitude of the spins in successive layers is modulated sinusoidally. This modulation has a period of seven magnetic layers (3.5 c) and $Q = \frac{2}{7} b_3$. Below 54 K a helical basal plane component of the magnetic moment develops. The wave vector associated with the helimagnetic component is identical
### Table 1.2

<table>
<thead>
<tr>
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<tr>
<td><strong>FERROMAGNETIC</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>T(_c)(K)</strong></td>
<td>221</td>
<td>85–90</td>
<td>20</td>
<td>19</td>
<td>38</td>
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<tr>
<td><strong>ANTIFERROMAGNETIC</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>bunching of moments</strong></td>
<td>45</td>
<td>54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>squaring up of sinusoidal modulation</strong></td>
<td>75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>T(_N)(K)</strong></td>
<td>223</td>
<td>179</td>
<td>133</td>
<td>85</td>
<td>56</td>
</tr>
</tbody>
</table>

[^f]: References [16, 20, 21, 22]
[^f]: References [16, 23, 24, 25]
[^f]: References contained in the text
to that associated with the c axis sinusoidally modulated component. The development of a third order harmonic along the c axis was also observed. Finally a transition to a conical ferromagnetic structure was observed below $T_C \approx 18$ K. More detailed studies by Habenschuss et al [18] and Atoji [19] confirm the general features of these results. In addition, the third harmonic was found to exist at temperatures of up to 75 K while harmonics of up to 17th order were observed at low temperatures. This gives rise to a "squaring up" of the sinusoidal modulation.

The occurrence of a helical spin structure was first theoretically treated by Yoshinori [26] for rutile type crystals. Kaplan [27] accounted for the occurrence of magnetic satellite reflections in Cr as originating from an expected helical structure, while Villain [28] presented a more general molecular field treatment.

For the case of zero anisotropy, the total energy calculated from the Hamiltonian of Eq. (1.17) and expressed in terms of the Fourier transforms $J_{f,f',(\vec{q})}$ and $\vec{S}_q$ of respectively the exchange interaction constant and the spin, is

$$E = - \sum_{\vec{q}} J_{f,f',(\vec{q})} \vec{S}_q \cdot \vec{S}_{-\vec{q}}.$$  \hspace{1cm} (1.19)

Traditional convention is followed by writing formulae in terms of spin. For most of the rare earths $\vec{J}$ is a good quantum number and $\vec{S}$ must be replaced by $(g_J - 1)\vec{J}$.

Under the restraint that $\vec{S}_n^2 = \text{constant}$ for all n, a minimum in energy, which occurs for that $\vec{q} = \vec{Q}$ for which $J_{f,f',(\vec{Q})}$ is a maximum, is obtained when

$$\vec{S}_n = N^{-\frac{1}{2}} \left| \vec{S}_Q e^{i\vec{Q} \cdot \vec{R}_n} + \vec{S}_{-\vec{Q}} e^{-i\vec{Q} \cdot \vec{R}_n} \right|,$$ \hspace{1cm} (1.20)

which has components

$$S_n^x = S \cos(\vec{Q} \cdot \vec{R}_n + \alpha)$$

$$S_n^y = S \cos(\vec{Q} \cdot \vec{R}_n + \alpha)$$ \hspace{1cm} (1.21)

$$S_n^z = 0.$$
For Dy, Enz [29] showed that a basal plane ferromagnetic spin structure is expected when the positive exchange interaction constant between neighbouring hexagonal planes $J_1$ is larger than the negative next nearest interaction $J_2$. However, a helical arrangement is expected when $|4J_2| > |J_1|$. A transition between the ferromagnetic and helical states is ascribed to a temperature dependence of the exchange interactions.

Introducing the thermal average $\langle \vec{s}_{m} \rangle = \vec{s} \, B_S \, |2J_{f,f'}(\vec{q})S^2/k_B T|$ of the spin [30], it can be shown that the Néel temperature — the highest temperature to which the antiferromagnetic ordering persists — is

$$T_N = 2J_{f,f'}(\vec{q}) \frac{S(S+1)}{3k_B}.$$  \hspace{1cm} (1.22)

Above $T_N$ the susceptibility $\chi = \frac{C}{T-\theta_p}$ is characterized by the paramagnetic Curie temperature

$$\theta_p = 2J_{f,f'}(0) \frac{S(S+1)}{3k_B}.$$  \hspace{1cm} (1.23)

1.2.3 **Crystal field anisotropy**

In order to account for the variety of spin structures, the magnetic anisotropy has to be taken into account. This arises from a single ion contribution originating in the interaction between the large multipole moments of the $4f$ wave function and the hexagonal crystalline field [31]. The anisotropy energy can be expanded in spherical harmonics $\gamma_{l}^{m}(\theta,\phi)$, with $\theta$ and $\phi$ the angles between the direction of the magnetization and the c and a axes respectively:

$$E_K = K_2 \gamma_{2}^{0}(\theta,\phi) + K_4 \gamma_{4}^{0}(\theta,\phi) + K_6 \gamma_{6}^{0}(\theta,\phi) + K_8 \sin^{6}\theta \cos^{6}\phi.$$ \hspace{1cm} (1.24)

For positive uniaxial anisotropy coefficients $K_2$ the magnetic moments prefer to lie in the basal plane while for negative $K_2$ the c axis is preferred. The sixfold basal plane anisotropy is usually much smaller than the uniaxial anisotropy. Experimental values of the anisotropy constants are given in Table 1.2 for the heavy rare earths.
Table 1.2[31]

<table>
<thead>
<tr>
<th></th>
<th>$K_2$ 10$^6$ ergs/cm$^3$</th>
<th>$K_4$ 10$^6$ ergs/cm$^3$</th>
<th>$K_6^6$ 10$^6$ ergs/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>560</td>
<td>46</td>
<td>2.4</td>
</tr>
<tr>
<td>Dy</td>
<td>550</td>
<td>54</td>
<td>-7.6</td>
</tr>
<tr>
<td>Ho</td>
<td>200</td>
<td>14</td>
<td>27.0</td>
</tr>
<tr>
<td>Er$^\ast$</td>
<td>140</td>
<td>-20</td>
<td>-13.8</td>
</tr>
<tr>
<td>Tm$^\ast$</td>
<td>-340</td>
<td>-26</td>
<td>7.2</td>
</tr>
</tbody>
</table>

* Theoretical values

The anisotropy Hamiltonian can be written as [32]

$$
H_{cf} = A_2^0 < r^2 > Y_2^0(S) + A_4^0 < r^4 > Y_4^0(S) + A_6^0 < r^6 > Y_6^0(S) + A_2^6 < r^2 > [Y_2^6(S) + Y_6^2(S)] ,
$$

(1.25)

where $A_p^m$ are the crystal field potentials and $< r^n >$ are averages over the 4f wave functions.

The magnetic ordering of Er and Tm which are characterized by uniaxial anisotropy will now be discussed, followed by a discussion of the magnetic ordering in Tb, Dy and Ho.

1.2.4 Molecular field theory and the c axis modulated structure of Er

Er (and Tm) are characterized by a uniaxial anisotropy energy [30]

$$
W(S^2) = D [(S^2)^2 - \frac{1}{3} S(S+1)] ,
$$

(1.26)

with D negative. Equation (1.26) is obtained from Eq. (1.25) with $A_2^0 < r^2 > = \frac{1}{2} D$ and $A_4^0 = A_6^0 = A_2^6 = 0$.

The exchange field on the $n$th spin, resulting from the contributions of the remaining spins, is

$$
H_n^i = 2 \sum_m J_{i,m} \langle \vec{R}_{n,m} \rangle S^i_m ; i = x, y, z ,
$$

(1.27)
with \( <\vec{S}_n^i> = S_n^i = \frac{\text{Tr} \sum_i e^{\beta [H_n^{X,Y,Z} + H_n^{X,Y,Z} - W(S_n^Z)]}}{\text{Tr} e^{\beta [H_n^{X,Y,Z} + H_n^{X,Y,Z} - W(S_n^Z)]}} \)
\[ (1.28) \]

Just below \( T_N \), the exchange field is small and Eq. (1.28) can be expanded in powers of the exchange field. Assuming that the basal plane components of the exchange field \( H_n^X = H_n^Y = 0 \) and retaining only terms linear in \( H_n^Z \), it can be shown that

\[
S_n^Z = \frac{\beta H_n^Z \text{Tr}(S_n^Z)^2 e^{-\beta W(S_n^Z)}}{\text{Tr} e^{-\beta W(S_n^Z)}} \quad (1.29)
\]

which has a solution \( \sigma_n^Z = \sigma^Z \cos(\vec{q} \cdot \vec{R}_n + \alpha) \).

This sinusoidal modulation exists up to the Néel temperature of

\[
k_B T_N = 2J_{f,f'}(\vec{q}) \frac{S(S+1)}{3} \left[ 1 - \frac{D}{k_B T_N} \frac{4S(S+1)-3}{15} \right], \quad (1.30)
\]

which is higher than the Néel temperature obtained for zero anisotropy (Eq. (1.22)).

The solution containing higher terms in \( H_n^Z \) has the form

\[
\sigma_n^Z = \sum_p \sigma_{2p+1}^Z \cos[(2p+1)\vec{q} \cdot \vec{R}_n]. \quad (1.31)
\]

This solution results in the appearance of higher order harmonics. The fundamental has a \((T_N - T)^{1/2}\) temperature dependence, while the higher harmonics vary with \((T_N - T)^{(2p+1)/2}\). The solution immediately below \( T_N \) is thus given only by the fundamental, with the higher order harmonics becoming non-negligible at lower temperatures.

If the basal plane component of the exchange field is taken into account, it can be shown that

\[
\sigma_n^X = \frac{2}{3} \beta S(S+1) \sum_{f,f'} \sum_{m,n} \left( \frac{\beta H_n^Z}{30} \frac{(4S^2+4S-3)}{(2S^2+2S+1)} \right) \quad (1.32)
\]
The general solution of Eq. (1.32) is
\[ \sigma_n^x = \sum_{\nu=0}^{\infty} \sigma_\nu \ e^{i\nu \cdot \mathbf{Q} \cdot \mathbf{R}_n}, \]  
which yields when only considering the fundamental,
\[ \sigma_n^x = \sin(\mathbf{Q} \cdot \mathbf{R}_n + \alpha), \]
and \[ \sigma_n^y = \cos(\mathbf{Q} \cdot \mathbf{R}_n + \alpha). \]

The Néel temperature is given by
\[ k_B T_N = \frac{2}{3} \frac{J_{f_s, f_s}}{f_s} \langle \mathbf{Q} \rangle S(S+1) + \frac{2D}{15} (S-\frac{3}{2})(S+\frac{3}{2}). \]

A comparison of Eqs. (1.30) and (1.35) shows that \( T_{N_L} < T_{N_N} \). It is furthermore noticed that the wave vector describing both the c axis modulated structure below \( T_{N_N} \) and the basal plane helical component below \( T_{N_L} \) is given by that \( \mathbf{q} = \hat{\mathbf{Q}} \) at which \( J_{f_s, f_s}(q) \) has its maximum and is consequently identical for both modulations and also independent of the anisotropy energy.

A favourable comparison exists between the theory and the experimental situation for Er (Section 1.2.2). Below \( T_{N_N} = 85 \text{ K} \) the spins are modulated sinusoidally along the c axis, with higher order harmonics observed as high as 75 K. Below \( T_{N_L} \) a basal plane helical component develops having the same period of modulation as the c axis modulated structure.

1.2.5 Spin wave theory and magnetic ordering for Dy and Ho [1]

To describe the basal plane ordering observed for Tb, Dy and Ho the anisotropy Hamiltonian eq. (1.25) is rewritten by grouping together terms proportional to \((S^z)^2\), \((S^z)^4\) and \((S^z)^6\) while retaining the \([Y^6_6(S) + Y^6_6(S)]\) term:
\[ H_{cf} = \sum_n \{ P_2(S^z_n)^2 + P_4(S^z_n)^4 + P_6 (S^z_n)^6 + P_6^+ [(S^z_n)^6 + (S^z_n)^6] \} \]  

The ordering can now be accounted for by taking \( P^0_2 > 0 \), \( P^0_4 = P^0_6 = 0 \) (these two contributions do not affect the ordering in the basal plane) and \( P^0_6 \neq 0 \) in the anisotropy Hamiltonian Eq. (1.25). For the helical ordering, firstly considering only the \( P^0_6 \) contribution, the total Hamiltonian that describes the system is
\[ H = - \sum_{n,m} \sum_{n',m'} J_{f,f'}(\tilde{R}_{n,m}) \bar{S}_n \cdot \bar{S}_m + P_z \sum_n (S^n_z)^2. \]  

(1.36)

The anisotropy term introduces an additional field \(-2P_z S^n_z\) in the exchange field of Eq. (1.27)

\[ H_n^i = 2 \sum_m J(\tilde{R}_{n,m}) \langle S^i_m \rangle - 2P_z S^n_z \delta_{iz}. \]  

(1.37)

The equation of motion for a spin \(\bar{S}_n\) induced by this field is

\[ i\hbar \frac{d\bar{S}_n}{dt} = [H, \bar{S}_n]. \]  

(1.38)

For small deviations in spin, the motion has an oscillatory nature with frequency

\[ \hbar \omega_{q} = S \sqrt{C_{q} D_{q}} \]  

(1.39)

with \(C_q \approx 2J_{f,f'}(\bar{Q}) - 2J_{f,f'}(0) + 2P_z\)

(1.40)

and \(D_q \approx \sum_{i,j} \left[ \frac{\sigma^2 J_{f,f'}(\bar{Q})}{\sigma_i \sigma_j} \right] q_i q_j \) for small \(\bar{Q}\).

Including a non-zero \(P^6\) contribution in the anisotropy energy and minimizing the energy, the angle \(\phi_n\) that describes the helimagnetic structure

\[ S^n_x = S \cos\phi_n \quad \text{and} \quad S^n_y = S \sin\phi_n \]

is obtained:

\[ -\sum_m J_{f,f'}(\tilde{R}_{n,m}) \sin(\phi_m - \phi_n) - 6P^6 S^n \sin 6\phi_n = 0. \]  

(1.41)

A series expansion in \(P^6\) yields

\[ \phi_n = \phi_n^0 + \varepsilon \sin 6\phi_n^0 + \ldots, \]  

(1.42)
with \( \phi_n^0 = Q R_n + \alpha \), the value without basal plane anisotropy, \( (1.43) \)

\[
\varepsilon = \frac{12 P_6^6 S^4}{2J_{f',f}(\bar{Q}) - J_{f',f}(5\bar{Q}) - J_{f',f}(7\bar{Q})}.
\] \( (1.44) \)

The associated change in energy is given by:

\[
\Delta E = -\frac{1}{4} N S^2 \varepsilon^2 \left[ 2J_{f',f}(\bar{Q}) - J_{f',f}(5\bar{Q}) - J_{f',f}(7\bar{Q}) \right],
\] \( (1.45) \)

and the frequency by

\[
(\hbar \omega)^2 = S^2(A^2 - B^2) + S^2(41A_q + 31B_q - 72A_b)\varepsilon^2[J_{f',f}(\bar{Q}) - J_{f',f}(5\bar{Q}) - J_{f',f}(7\bar{Q})],
\] \( (1.46) \)

where

\[
A_q = 2J_{f',f}(\bar{Q}) - J_{f',f}(\bar{Q} - \bar{Q}) - J_{f',f}(\bar{Q} + \bar{Q}) - J_{f',f}(\bar{Q} - \bar{Q}) + P_2,
\]

and

\[
B_q = J_{f',f}(\bar{Q} + \bar{Q}) + J_{f',f}(\bar{Q} - \bar{Q}) - J_{f',f}(\bar{Q} + \bar{Q}) + P_2.
\] \( (1.47) \)

Both frequencies, Equations (1.39) and (1.46), are zero for \( q = 0 \). As a result of the \( \varepsilon^2 \) factor in the second term of Equation (1.46), the \( P_6^6 \) contribution can be neglected for the normal spiral and need only be taken into account to describe the distorted spiral at low temperatures where the occurrence of fifth and seventh harmonics in the neutron diffraction spectra are observed as in holmium.

Consider the basal plane ferromagnetic structure with \( P_6^6 = 0 \). The preceding description does not hold for the ferromagnetic structure since this would require

\[
J_{f',f}(\bar{Q}) - J_{f',f}(5\bar{Q}) - J_{f',f}(7\bar{Q}) = 0.
\] \( (1.48) \)

Consequently the calculations are repeated, taking into account both the \( P_2^2 \) and \( P_6^6 \) contributions. The Hamiltonian describing the system is:

\[
H = -\sum_{m,n} J_{f,f'}(\bar{R}_{n,m}) \bar{S}_n \cdot \bar{S}_m + \sum_n \left\{ P_2(S_n^z)^2 + P_6^6(S_n^+)^6 + (S_n^-)^6 \right\},
\] \( (1.49) \)
The solution of the equation of motion yields an oscillation with frequency

\[ \hbar \omega_q = 2S[J_{q,f}(0) - J_{q,f}(q) - 36S^4p_6^4][J_{q,f'}(0) - J_{q,f'}(q) + p_2^2 - 6S^4p_6^4]^{1/2}. \] (1.50)

1.2.6 Magneto-elastic effects in Dysprosium

Dispersion curves for spin waves measured along the a and c axes [33,34] at temperatures in both the ferromagnetic and helimagnetic regions are in reasonable qualitative agreement with the expected behaviour. Figure 1.1 depicts the Fourier transform of the exchange integral at 4.7 K and 78 K in the ferromagnetic region and 98 K in the helimagnetic region. The curves at 4.7 K and 78 K exhibit maxima corresponding to minima in the spin wave dispersion curves at \( q = 0.1 \) and \( q = 0.15 \) respectively. The last value is close to the value of the wave vector in the helically ordered region directly above \( T_C \). This indicates that the exchange energy favours a helical arrangement of moments even in the ferromagnetic region! It will be shown below that the ferromagnetic ordering at low temperatures has a magneto-elastic origin.

At low temperatures the dominant contribution to the free energy is given by the lowest order magnetostriction of cylindrical symmetry, and by the hexagonal anisotropy of the undistorted crystal lattice. The ferromagnetic alignment allows the crystal lattice to distort in order to minimize the total energy through an elastic coupling to the magnetic system. However, this contribution to the free energy falls off sharply with increasing temperature and above \( T_C \) the exchange energy of the undistorted lattice, which favours helical ordering, dominates. In this helical ordering of spins the successive planes containing the ferromagnetically aligned spins are prevented from undergoing the deformation (that would minimize the total free energy) as a result of the internal cancellation of spins on a macroscopic scale. This is known as "lattice clamping" [35].
Expressions for the elastic and magneto-elastic energies of the hexagonal rare earth crystals follow from the general treatment of magnetostriction by Callen and Callen [36]. Irreducible strains $\varepsilon_i^{\nu,j}$ with the symmetry of the hexagonal closed-packed structure and elastic constants $C_{j,h}^{\mu}$ are used and these are related to the Cartesian strains and stiffness constants by relations given in [36]. The magneto-elastic coupling constants $b_i^{\mu,j}$ generally contain both one- and two-ion contributions, $\mu = \alpha, \gamma$ or $\epsilon$ indicates the type of representation, and the subscript $i = 1$ or 2 for the $\gamma$ and $\epsilon$ strains indicates the two numbers of the two-dimensional basis. In describing the spiral to ferromagnetic transition in Dy and Tb, one needs only to consider strains developed for magnetization in the basal plane and the elastic and magneto-elastic energies can then be written as [37]
\[ E^\chi_e = \frac{1}{4} C^\gamma (\epsilon^\gamma_1)^2 + (\epsilon^\gamma_2)^2 \]  
(1.51)

and \[ E^\gamma_{me} = -\frac{1}{4} B^\gamma_{rs} \{ \epsilon^\gamma_x (\alpha^2_x - \alpha^2_y) + 2 \epsilon^\gamma_y \alpha_x \alpha_y \}, \]  
(1.52)

where \( \alpha_x \) and \( \alpha_y \) are the direction cosines of the magnetization relative to the two mutually perpendicular basal plane crystallographic axes.

Using the equilibrium strains, obtained by minimizing the equilibrium energy \( E^\gamma_{ms} = E^\gamma_e + E^\gamma_{me} \) with respect to \( \epsilon^\gamma_1 \) and \( \epsilon^\gamma_2 \), the equilibrium energy can be written as:

\[ E^\gamma_{ms} = E^\gamma_{ms} = -\frac{1}{8} C^\gamma (\lambda^\gamma)^2. \]  
(1.53)

The temperature dependence of the \( \lambda^\gamma \) magnetostriction constant is of one-ion origin:

\[ \lambda^\gamma(T) = \lambda^\gamma(0) \hat{I}_{\frac{3}{2}} \left[ L^{-1}(\sigma) \right]. \]  
(1.54)

In Equation (1.54), \( \hat{I}_{\frac{3}{2}} \) is the normalized hyperbolic Bessel function

\[ I_{\frac{3}{2}} / I_{1/2} \text{ where } I_{\ell + \frac{1}{2}} (X) = \int_{-1}^{1} Y^\ell_{\ell} (m') e^{Xm'} dm' \text{ is the hyperbolic (1.55) Bessel function, and } L^{-1}(\sigma) \text{ is the inverse Langevin function of the reduced magnetization } \sigma. \text{ The energy } E^\gamma_{me} \text{ of Equation (1.51) as well as the hexagonal planar anisotropy } E_A \text{ may serve as the driving energy for the spiral to ferromagnetic transition. The latter contribution is given by}

\[ E_A = -2|P^6_{6}(0)| S \hat{I}_{13/2} \left| L^{-1}(\sigma) \right|. \]  
(1.56)

For Dy at 0 K the two contributions are of comparable size, but since at low temperatures \( \langle I_{\frac{3}{2}} \rangle^2 \approx \sigma^6 \) and \( \hat{I}_{13/2} \approx \sigma^{21} \) the dominant driving mechanism at \( T_c \approx 85 \text{ K for Dy is of magneto-elastic origin. This has been verified by Cooper [37] by comparing the energy } E_{me} \text{ with the energy required to collapse the helical structure using an applied magnetic field.
1.3 PHASE TRANSITIONS

In the previous section, the magnetic ordering and diversity of possible spin structures for the heavy rare-earths were discussed. This, however, fails to describe the detailed behaviour of the magnetic system in the vicinity of the transition point between two states of different magnetic order. Such a transition can be described in terms of an order parameter which assumes a non-zero value below the transition or critical point, but is zero above [38]. The change in order parameter can be either continuous (second order) or discontinuous (first order) [39], as determined by the lowest order discontinuous derivative of the free energy [40].

1.3.1 Second order phase transitions

The order parameter that characterizes a continuous phase transition does not depend on the detailed nature of the system, but on the components of the order parameter - the dimensionality of the spin Hamiltonian for magnetic systems - and the space dimensionality of the lattice [38]. This universal behaviour results from the fact that a phase transition is a cooperative phenomenon where the balance in the forces that dominate on either side of the critical point results in the development of long-range correlations which exhibit large fluctuations in both time and position [41]. The correlation length of a system, which is the minimum size to which a system can be reduced without qualitatively changing its properties, diverges at the critical point.

The order parameter $f(\varepsilon)$ that describes the behaviour of a system near the critical point is related to the variable $\varepsilon$ that drives the system through the transition [41]

$$f(\varepsilon) \propto \varepsilon^\lambda,$$  \hspace{1cm} (1.57)

with the critical exponent $\lambda$ given by

$$\lambda = \lim_{\varepsilon \to 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon}.$$  \hspace{1cm} (1.58)
A number of power laws [38,41-45] appropriate to describing a magnetic phase transition are given in Table 1.3 in terms of the reduced temperature

\[ t = \varepsilon = \frac{T - T_{\text{crit}}}{T_{\text{crit}}} \]

(1.59)

where \( T_{\text{crit}} \) is the value of the temperature \( T \) at the critical point.

The dimensionality of the system is \( d \), and \( h \) is the reduced magnetic field.

**TABLE 1.3**

<table>
<thead>
<tr>
<th></th>
<th>( T &lt; T_{\text{crit}} )</th>
<th>( T &gt; T_{\text{crit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous magnetization</td>
<td>( M_0(T) )</td>
<td>( B(-t)\beta )</td>
</tr>
<tr>
<td>Initial magnetic susceptibility</td>
<td>( X_0(T) )</td>
<td>( \Gamma'(\tau)\alpha' )</td>
</tr>
<tr>
<td>Magnetization at ( T_{\text{crit}} )</td>
<td>( M(H) )</td>
<td>( \Delta h^{1/\delta} )</td>
</tr>
<tr>
<td>Critical specific heat</td>
<td>( C_M(T) )</td>
<td>( A'(\tau)^{-\alpha} )</td>
</tr>
<tr>
<td>Correlation length</td>
<td>( \xi )</td>
<td>( E'(\tau)^{-\nu} )</td>
</tr>
<tr>
<td>Correlation function for spins separated by ( r )</td>
<td>( \Gamma(r) )</td>
<td>( \frac{e^{-r/\xi}}{r^{d-2+\eta}} )</td>
</tr>
</tbody>
</table>
An active field of theoretical activity has been the derivation of scaling relationships using thermodynamic methods and often employing "plausible assumptions" that have not been generally established. Two of the most well-known inequalities are predicted by Rushbrooke (Eq. 1.60) and by Griffiths (Eq. 1.61)

\[ \alpha' + 2\beta + \gamma' \geq 2, \quad (1.60) \]

\[ \alpha' + \beta(1+\delta) \geq 2. \quad (1.61) \]

Experimental measurements (after taking into account error bars) usually satisfy these equations as equalities. A large number of other inequalities have been derived by Griffiths, by Fisher and by other workers, and some of these are given below [41]

\[ \gamma' \geq \beta(\delta-1), \quad (1.62) \]

\[ d(\delta-1) \geq (2-\eta)(\delta+1), \quad (1.63) \]

\[ (2-\eta)\nu \geq \gamma, \quad (1.64) \]

\[ d\nu \geq 2-\alpha \quad (1.65) \]

The fact that exponent inequalities are often satisfied as equalities finds some justification in the static scaling law hypothesis which assumes that the Gibbs potential \( G(\epsilon, H) \) is a generalized homogeneous function. Thus there exist two parameters \( a_\epsilon \) and \( a_H \) such that

\[ G(\lambda^{a_\epsilon} \epsilon, \lambda^{a_H} H) = \lambda G(\epsilon, H) \quad (1.66) \]

for any value of the number \( \lambda \). Using this assumption it can be shown that Eqs. 1.60 - 1.65 hold as equalities. A further consequence of the scaling law hypothesis is the equality of the primed and unprimed critical point exponents. Finally, the scaling hypothesis predicts
the specific form of the magnetic equation of state and this has been
corroborated by a number of detailed experimental studies [41, 44, 47].

Kadanoff [44] presented intuitive arguments in support of the
scaling hypothesis. Consider a magnetic system and let the lattice be
divided into cells of length $L a_0$ $(1 \leq L \leq \xi / a_0)$. This has the
effect of reducing all the spins contained in a cell to one effective
spin:

$$< \sigma > = L^{x-d/F}(L^y, L^h). \quad (1.67)$$

The lattice parameter is denoted by $a_0$, $d$ is the lattice
dimensionality, $h$ is the magnetic field, $F$ is an unknown function and
$x$ and $y$ are unknown exponents. The length of the cell is a
non-essential detail and can be omitted from Eq. (1.67) if this
equation has the form

$$< \sigma > = \frac{h}{|h|} t^{d-x \frac{1}{y}} f \left( -\frac{t}{|h|^{y/x}} \right). \quad (1.68)$$

All critical indices can be expressed as combinations of the two
exponents $x$ and $y$. It follows that

$$\beta = \frac{d-x}{y}. \quad (1.69)$$

Differentiation or integration of $< \sigma >$ with respect to $\varepsilon$ or $h$ yields
$\alpha (= \alpha')$, $\gamma (= \gamma')$ and $\delta$ also in terms of $x$ and $y$, thus giving as
equalities the Rushbrooke and Griffiths Eqs. (1.60) and (1.61).

The mean-field theory [41] of magnetism was the first attempt at
describing a phase transition and is based on the assumption that each
magnetic moment interacts equally with all other moments through a
molecular field $H_M$ which is proportional to the average
magnetization $M$ ($H_M = \lambda M$):

$$M = M_0 B_S \left[ \frac{\mu_B}{k_B T} S (H + M) \right] \quad (1.70)$$

$$= M_0 B_S \left[ \frac{\mu_B}{k_B T} S\lambda M \right] \quad \text{for } H = 0, \quad (1.71)$$
with the Brillouin function:

$$B_S(x) = \frac{2S+1}{2S} \coth \left( \frac{2S+1}{2S} x \right) - \frac{1}{2S} \coth \left( \frac{1}{2S} x \right).$$  (1.72)

A refinement of the mean-field approach incorporates the nature of the molecular field parameter $\lambda$ through the exchange interaction between spins [41]:

$$E = - 2J_{n,m} \bar{S}_n \cdot \bar{S}_m.$$  (1.73)

Considering only nearest-neighbour interactions, the Hamiltonian of the system can be written as:

$$H^{(D)} = - J \sum_{<n,m>} \bar{S}_n \cdot \bar{S}_m,$$  (1.74)

where $D$ indicates the dimensionality of the spin and $-J$ the exchange interaction constant between nearest neighbours $<nm>$.

For $D = 1$ the classical, one-dimensional magnetic moments can acquire values of $\pm 1$. The Hamiltonian for this, the Ising model, is

$$H = - J \sum_{<n,m>} S^x_n S^x_m.$$  (1.75)

This model was introduced by Lenz in 1920 and solved for one and two dimensional lattices by Ising in 1925 and Onsager [48] in 1944 respectively.

For $D = 3$ the Heisenberg Hamiltonian is obtained:

$$H = - J \sum_{<n,m>} (S^x_n S^x_m + S^y_n S^y_m + S^z_n S^z_m).$$  (1.76)

The model assumes an isotropic interaction between well-localized nearest neighbour spins. Due to the large anisotropy observed for the rare earth metals, Eq. (1.76) does not describe these materials very well. A numerical study by Jasnow and Wortis [49] showed that the inclusion of anisotropy in the $D = 3$ Heisenberg Hamiltonian yields the critical exponents found for the $D = 1$ Ising model.
Table 1.4 lists values of some of the critical exponents predicted by the mean field model and the Ising and Heisenberg models for three dimensional lattices. For the latter two cases exact solutions do not exist.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\nu$</th>
<th>$\delta$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean field</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Ising $D=1$, $d=3$</td>
<td>0.125</td>
<td>0.312</td>
<td>1.25</td>
<td>0.635</td>
<td>5.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Heisenberg $D=3$, $d=3$</td>
<td>-0.16</td>
<td>0.380</td>
<td>1.38</td>
<td>0.705</td>
<td>4.8</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Of the recent theoretical descriptions of phase transitions, that achieved by renormalization group calculations has enjoyed a fair measure of success. An outline of its philosophy and applicability to the planar helical ↔ paramagnetic phase transitions in Dy and Ho is discussed below.

1.3.2 Renormalization group calculations [51]

Away from the critical region the correlation length of the system is small and the behaviour is determined by the detail and magnitude of the exchange interactions. In the critical region where $\xi$ diverges due to the cooperative behaviour, the dimensionality $2m$ of the Hamiltonian that describes the system, the number of components of the order parameter $n$ as well as the dimensionality $d$ of the lattice primarily determine the behaviour of the system. Such a diverging correlation length contains a large number of degrees of freedom which renders the problem unsolvable. The aim of the renormalization group approach is to drastically reduce these by replacing it with smaller sets of effective degrees of freedom through repeatedly dilating the system by a factor $\delta$. The interactions are similarly transformed for successive dilations by a transformation $T$ which is identical for all dilations:
\( \tau(H_0) = H_1, \quad \tau(H_1) = H_2, \quad \tau(H_2) = H_3, \ldots \) \hspace{1cm} (1.77)

The renormalization group simplification that these effective interactions are of short range assumes that the original interaction is also of short range, which is a good approximation for a large variety of systems. The first dilation can then be determined by studying a small region of approximate size \( \delta a_0 \) of the system, where \( a_0 \) is the original spacing.

Although the range of interaction increases for successive dilations, the degrees of freedom that must be considered to find the interaction constants between effective interactions remain limited because each new set of effective interactions is constructed from a preceding dilated set. After \( n \) dilations the separation between effective interactions is of the same order of magnitude as the correlation length \( \xi \):

\[ \delta^n a_0 \approx \xi. \] \hspace{1cm} (1.78)

The description of the system in the critical region is now reduced to a limited number of degrees of freedom and can be solved. The cooperative behaviour which characterizes the phase transition is associated with a fixed point Hamiltonian \( H^* \) of \( \tau \) since at the transition point the correlation length is infinite and the system transforms into itself:

\[ \tau(H^*) = H^*. \] \hspace{1cm} (1.79)

Different domains of cooperative behaviour are exhibited if more than one fixed point Hamiltonian exists.

Mukamel and Krinsky [52] constructed the Landau-Ginzburg-Wilson Hamiltonian for a number of physical systems having a \( n \geq 4 \) component order-parameter \( \phi_i = \phi_1, \phi_2, \ldots, \phi_n \) and characterized by a reduction in symmetry group from \( G_0 \) to \( G \) with \( G \in G_0 \).
\[ H = \int \frac{d^3 \mathbf{x}}{3} H(\phi, \frac{\partial \phi}{\partial \mathbf{x}}^i, \ldots). \]  

(1.80)

The density of the Hamiltonian, \( H \), is invariant under the symmetry group \( G_0 \) and can, assuming that \( H \) is an analytical function of \( \phi \) and its derivatives and that the \( m \)-components of \( \phi \) transform into one another according to one irreducible representation \( R \) of \( G_0 \), be written as a bi-term polynomial, with terms:

\[ H^2(\phi) = -\frac{1}{2} \sum_{i=1}^{n} \phi_i^2 + \sum_{p}^{n} \alpha_{i,j,k}^{p} \phi_i \phi_j \phi_k - \ldots \]  

(1.81)

\[ H^2(\phi, \frac{\partial \phi}{\partial x^k}, \ldots) = \sum_{i,j=1}^{n} \frac{d}{d} \sum_{k=1}^{n} A_{i,j,k}^{\phi} \phi_i \phi_j \phi_k + \ldots \]  

(1.82)

The second term of \( H^2(\phi) \) is a summation over the third order invariants of the group \( G_0 \) but it vanishes at the transition point. Since the phase transitions under consideration are driven by only one thermodynamic variable (temperature), Mukamel and Krinsky propose that this term should not be included in the Hamiltonian. The critical point is then characterized by \( r = 0 \) for second order phase transitions \( [40] \).

The first term of \( H^2 \) also vanishes at \( T_{\text{crit}} \). This is achieved by either dismissing the term or when \( A_{i,j,k}^{\phi} \rightarrow 0 \) at \( T_{\text{crit}} \), as is the case for the planar helical \( \leftrightarrow \) paramagnetic phase transition in Tb, Dy and H. 

The irreducible representation \( R \) of \( G_0 \) is obtained in the following way: The group \( G_0^r \) of \( k \), a vector in the first Brillouin Zone, consists of those symmetry elements of \( G_0 \) that leave \( k \) invariant. Applying these to \( k \) produces a set of vectors called the star of \( k \). The irreducible representations of \( G_0 \) are classified according to \((k, p)\), where the representation \( p \) has a dimensionality \( \ell_p \). The functions which transform into one another as a basis of \((k, p)\) have the form:

\[ \psi_{k,m,j}^{\ell_p}(\mathbf{r}) = U_{k,m,j}^{\ell_p}(\mathbf{r}) e^{ik \cdot \mathbf{r}} \quad m = 1, \ldots, s \]  

(1.83)

\[ j = 1, \ldots, \ell_p. \]
where the dimensionality of \((\vec{k}, p)\) is \(n = s \ell_p\). For Tb, Dy and Ho the star of \(\vec{k}\) consists of

\[
\pm \vec{k} = \pm (0 \ 0 \ k) \frac{2\pi}{c}, \tag{1.84}
\]

each of these having two equivalent perpendicular directions of spin in the basal plane. The order parameter consequently has four components:

\[
\psi_{\pm k, p} = \phi_p \pm i \tilde{\phi}_p \tag{1.85}
\]

\[
= \sum_\vec{r} S_{\vec{r}, p} e^{\pm i \vec{k} \cdot \vec{r}}; \ p = x, y,
\]

where \(S_{\vec{r}, p}\) is the \(p\) component of the spin localized at \(\vec{r}\).

The calculations by Mukamel, Krinsky and Bak [52-54] to derive the critical behaviour of a number of magnetic systems consider Hamiltonians of the form

\[
H = -\frac{1}{2} \sum_{i=1}^{n} [r \phi_i^2 + (\nabla \phi_i)^2] - \sum_p \sum_{i,j,k,l} \beta_{i,j,k,l}^p \phi_i \phi_j \phi_k \phi_l, \tag{1.86}
\]

which does not include anisotropic terms since these are not considered to affect the critical behaviour of the system to first order in \(\epsilon[53]\).

Considering translational invariance with respect to the hexagonal point group \(D_{6h}\), Bak and Mukamel [54] obtained the following Landau-Ginzburg-Wilson Hamiltonian for Tb, Dy and Ho:

\[
H_0 = -\frac{1}{2} \left[ r (\phi_x^2 + \phi_y^2 + \phi_y^2 + \phi_y^2) + (\nabla \phi_x)^2 + (\nabla \phi_x)^2 + (\nabla \phi_y)^2 + (\nabla \phi_y)^2 \right] \]

\[
- U_1 (\phi_x^2 + \phi_y^2 + \phi_y^2 + \phi_y^2)^2 - U_2 (\phi_x \phi_y - \phi_y \phi_x)^2. \tag{1.87}
\]

This equation is rewritten in terms of variables
\[ \eta_1 = \sqrt{2} \left( \phi_x + \phi_y \right), \quad \eta_2 = \sqrt{2} \left( \phi_x - \phi_y \right), \]
\[ \tilde{\eta}_2 = \sqrt{2} \left( \phi_x + \phi_y \right), \quad \tilde{\eta}_1 = \sqrt{2} \left( \phi_x - \phi_y \right), \]

which describe the spiral components of the magnetization:

\[ H_8 = -\frac{1}{2} \sum_{i=1}^{2} \left[ r(\eta_i^2 + \tilde{\eta}_i^2) + (\nabla \eta_i)^2 + (\nabla \tilde{\eta}_i)^2 \right] \]
\[ - u \left( \frac{1}{2} \sum_{i=1}^{2} (\eta_i^2 + \tilde{\eta}_i^2) \right)^2 - v \sum_{i=1}^{2} (\eta_i^2 + \tilde{\eta}_i^2)^2, \]  

where \( u = u_1 - \frac{1}{4} u_2 \) and \( v = \frac{3}{2} u_2 \)

Mukamel and Krinsky [53,55] showed, using Wilson's renormalization technique [51] in \( d = 4 - \varepsilon \) dimensions, that for infinitesimal \( \varepsilon \) a stable fixed point is found for this Hamiltonian, and obtained the following results for the exponents:

\[ \nu = \frac{1}{2} + \frac{3(m-1) \varepsilon}{4(5m-4)} + \frac{(m-1)(20m^2 + 253m - 334)\varepsilon^2}{16(5m-4)^2} \]  

\[ \eta = \frac{(m-1)(2m-1)\varepsilon^2}{4(5m-4)^2}. \]  

Values of \( \alpha, \beta \) and \( \gamma \) are found from the scaling relationships. Mukamel and Krinsky emphasize that the predicted values of the exponents may not be precise and also that the determination of the stability of the fixed point may be ambiguous for three dimensional systems, since \( \varepsilon = 1 \) is large. Bearing this in mind, the exponents predicted for Tb, Dy and Ho are:

\[ \beta = 0.39, \quad \nu = 0.70, \quad \gamma = 1.39, \]  

\[ \eta = 0.02, \quad \alpha = -0.17. \]

These values are very close to that predicted by the three-dimensional Heisenberg model.

Barak and Walker [56] however, argued that although the Renormalization Group transformation exhibits a stable fixed point, the transition will only be of second order if the initial Hamiltonian lies in the domain of the stable fixed point. They found the following Hamiltonian density for Tb, Dy and Ho:

\[ -H = r \mathbf{S} \cdot \mathbf{S}^* + \frac{2}{3} \frac{\partial \mathbf{S}^*}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{S}^*}{\partial \mathbf{x}} + U_1 (\mathbf{S} \cdot \mathbf{S}^*)^2 + U_2 |\mathbf{S} \cdot \mathbf{S}^*|^2, \]  

(1.93)
where the spin density is a complex vector in the $x,y$-plane:

$$
\bar{S}(\bar{r}) = \bar{S} e^{i\bar{Q} \cdot \bar{r}} + \bar{S}^* e^{-i\bar{Q} \cdot \bar{r}}
$$

(1.94)

with the summation over $\alpha = x,y,z$ and $\bar{Q}$ in the $z$-direction.

$U_2 > 0$ yields the observed helical magnetic moment arrangement, while a linearly polarized structure is predicted for $U_2 < 0$. A schematic flow diagram for $H$ is shown in Figure 1.2 [56]. An initial Hamiltonian density given by Eq. (1.93) with $U_2 > 0$ and $U_2 \ll U_1$ will pass close to the unstable isotropic fixed point of Fig. 1.2 and consequently the authors predicted a first order transition. It is feasible that over some temperature interval away from $T_N$, the system could show critical behaviour with exponents associated with the (unstable) isotropic fixed point, but a cross over to a first order transition is still expected.

![Schematic flow diagram for the Hamiltonian of eq. 1.93 as given by [56]. $U_1$ and $U_2$ are given in units of $\varepsilon/4K_4 = 2\pi \varepsilon$ and the correct location of the fixed points for $\varepsilon=1$ is shown.](image-url)
1.3.3 Experimental observations of the planar helical ↔ paramagnetic phase transition in Tb, Dy and Ho

The nature of the planar helical ↔ paramagnetic phase transition in Tb, Dy and Ho as observed from a selection of experiments is listed in Table 1.5. The results of these measurements will be discussed in some detail in later sections.

In view of the experimental and theoretical uncertainty of the nature of the helical ↔ paramagnetic phase transition in these materials, a considerable part of this thesis has been devoted to experiments aimed at elucidating the nature of the transition at $T_N$ for Dy and Ho single crystals.

**TABLE 1.5**

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Metal</th>
<th>Order</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron diffraction</td>
<td>Ho</td>
<td>II</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Dy, Tb</td>
<td>II</td>
<td>58</td>
</tr>
<tr>
<td>Specific heat</td>
<td>Tb</td>
<td>II</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>Ho</td>
<td>II</td>
<td>60</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>Ho</td>
<td>I</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>Tb, Dy</td>
<td>II</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Dy</td>
<td>II</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Dy</td>
<td>I</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>Ho</td>
<td>I(weak?)</td>
<td>65</td>
</tr>
</tbody>
</table>
THE CRYSTALS

Some of the crystallographic properties of Dy, Ho and Er are given in Table 1.6 [4]. Relevant information for the single crystals that were employed in this investigation is listed in Table 1.7. The relative resistance ratios for the two dysprosium crystals were measured with a 4-wire technique using a nanovolt Tinsley 5545A potentiometer. A current of 100 mA was supplied by a Keithley 227 constant current source. Fine gold wire was used as electrical conductors and attached to the crystals by means of spot welding. An earlier unsuccessful attempt at measuring the resistance indicated that the geometry of the sample was important. For this measurement a sample measuring 0.75 x 0.75 x 5.5 mm$^3$ was cut from each original crystal using spark erosion, with the crystallographic c axis along the length of the sample. Both crystals were simultaneously submerged into the liquid helium over a period of ca. 40 min while their temperature was monitored using a Au,0.07%-Fe vs. chromel thermocouple.

<table>
<thead>
<tr>
<th></th>
<th>Density g/cm$^3$</th>
<th>Atomic radius (Å)</th>
<th>Structure</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>8.540</td>
<td>1.775</td>
<td>h.c.p.</td>
<td>3.593</td>
<td>5.655</td>
<td>1.574</td>
</tr>
<tr>
<td>Ho</td>
<td>8.781</td>
<td>1.767</td>
<td>h.c.p.</td>
<td>3.578</td>
<td>5.626</td>
<td>1.572</td>
</tr>
<tr>
<td>Er</td>
<td>9.045</td>
<td>1.758</td>
<td>h.c.p.</td>
<td>3.560</td>
<td>5.595</td>
<td>1.572</td>
</tr>
<tr>
<td>Crystal</td>
<td>Supplier</td>
<td>Year</td>
<td>Purity (%)</td>
<td>$\frac{r_{30K}}{r_{4K}}$</td>
<td>Geometry</td>
<td>Orientation</td>
</tr>
<tr>
<td>--------</td>
<td>------------------</td>
<td>------</td>
<td>------------</td>
<td>--------------------------</td>
<td>----------</td>
<td>-------------</td>
</tr>
<tr>
<td>Dy(I)</td>
<td>Metals Research</td>
<td>1979</td>
<td>99.99</td>
<td>12.5</td>
<td>cylinder</td>
<td>random</td>
</tr>
<tr>
<td>Dy(II)</td>
<td>Ames Iowa</td>
<td>1984</td>
<td>99.99</td>
<td>67.6</td>
<td>cube</td>
<td>oriented</td>
</tr>
<tr>
<td>Ho</td>
<td></td>
<td></td>
<td>99.99</td>
<td>-</td>
<td>cylinder</td>
<td>random</td>
</tr>
<tr>
<td>Er(I)</td>
<td>Goodfellow Metals</td>
<td>1984</td>
<td>99.99</td>
<td>-</td>
<td>cylinder</td>
<td>oriented</td>
</tr>
<tr>
<td>Er(II)</td>
<td>Same batch</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>cylinder</td>
<td>oriented</td>
</tr>
<tr>
<td>Er(III)</td>
<td>Same batch</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>disk</td>
<td>oriented</td>
</tr>
</tbody>
</table>
2.1 CRYOGENIC SYSTEMS

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2.1 CRYOGENIC SYSTEMS

2.1.1 The flow cryostat

Since the Air Products cold finger (Paragraph 2.1.2) was not available at the time when the study of phase transitions reported in this thesis commenced, a nitrogen gas flow cryostat was designed by the author and manufactured at Pelindaba. As shown in Figure 2.1, the copper block situated at the heart of the cryostat is cooled down with a regulated stream of cold nitrogen gas obtained by passing the gas through copper coils immersed in a bath of liquid nitrogen. The vacuum-insulated stainless steel connection line between the copper coils and the cryostat was of flexible double-walled construction and the diffractometer could be rotated by ±10° without this connection line exerting an undue stress on the cryostat. For the same reason a flexible Tygon pipe was employed to evacuate the cryostat.

![Diagram of the flow cryostat]

Fig. 2.1 The flow cryostat
By passing a regulated current through an element wound around the copper block, temperatures in the range between 78 K and room temperature could be obtained. Three elements of resistances 20 Ω, 20 Ω and 60 Ω respectively were available, suitable combinations of which could accommodate any of the three high-resolution temperature controllers at our disposal (Paragraph 2.1.3).

The crystals were mounted on an aluminium platform on top of an 8 mm long thin-walled stainless steel pipe and enclosed in a helium filled aluminium hood. Heat transfer to the crystal was effected primarily through this transfer gas and the thermal gradient across the crystal, measured using two thermocouples (Au,0.07%–Fe vs chromel), was less than 0.02 K. Samples were tied to the abovementioned aluminium platform using thin aluminium wire and when necessary GE 7031 varnish was used sparingly.

The copper block housed a Lake Shore DT-500 K silicon diode temperature sensor and a Au,0.07%–Fe vs chromel thermocouple which were respectively used as control sensors for a Lake Shore DTC-500 and THOR S-3010 temperature controller. Sample temperatures were typically controlled to ±0.02 K when the Lake Shore controller was used and ±0.05 K with the THOR instrument. Temperature increments as small as 0.04 K were attained with the Lake Shore controller.

2.1.2 The Air Products cold finger

An Air Products and Chemicals model DE-202-OSP two-stage closed-cycle helium refrigerator was employed to study the c axis sinusoidally modulated ↔ paramagnetic phase transition at 85 K in erbium. This system, consisting of an air-cooled helium compressor, an expander module and interconnecting high-pressure gas lines, was capable of reaching temperatures down to 11.5 K. Higher temperatures were attained by resistive heating of the copper block on which the sample was mounted. Samples were mounted inside a "home-made" aluminium hood which was filled with helium gas (Figure 2.2). To allow free thermal expansion of the sample it was again tied to the sample stalk using thin aluminium wire. The use of glue (GE 7031 varnish) was avoided when possible.
Sample temperatures were controlled to ±0.02 K and incremented in steps as small as 0.04 K using an Air Products APD-F temperature controller. Temperature gradients over the specimen were less than 0.02 K.

![Diagram](image)

Fig. 2.2 The aluminium hood

2.1.3 Temperature control and measurement

The three temperature controllers employed in this study are listed in Table 2.1 together with relevant characteristics:
### TABLE 2.1

<table>
<thead>
<tr>
<th>Cryogenic system</th>
<th>Lake Shore DTC-500</th>
<th>Thor S-3010</th>
<th>Air Products APD-F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow Cryostat</td>
<td>Flow Cryostat</td>
<td>Cold Finger</td>
</tr>
<tr>
<td>Sensor</td>
<td>Diode</td>
<td>Thermocouple</td>
<td>Diode</td>
</tr>
<tr>
<td>Sensor current</td>
<td>(µA) 10</td>
<td>n.a.</td>
<td>100</td>
</tr>
<tr>
<td>Mode of control</td>
<td>Proportional Integral</td>
<td>Proportional Integral</td>
<td>Proportional Integral</td>
</tr>
<tr>
<td></td>
<td>Differential</td>
<td>Differential</td>
<td>Differential</td>
</tr>
<tr>
<td>Maximum power output</td>
<td>(W) 60*</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Setpoint graduations</td>
<td>(µV) 100</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Temp. graduations</td>
<td>(K) 0.04</td>
<td>0.10</td>
<td>0.004</td>
</tr>
<tr>
<td>Smallest practical temperature steps</td>
<td>(K) 0.04</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>Control specified</td>
<td>(K) ±0.01</td>
<td>±0.01</td>
<td>±0.01</td>
</tr>
<tr>
<td>Control observed over 30 min interval</td>
<td>(K) ±0.02</td>
<td>±0.05</td>
<td>±0.02</td>
</tr>
<tr>
<td>Control observed over 2 min interval</td>
<td>(K) ±0.01</td>
<td>±0.01</td>
<td>±0.02</td>
</tr>
</tbody>
</table>

*With Lake Shore model 8016 power booster*

The Lake Shore and Air Products controllers, being capable of both smaller temperature graduations and better temperature control than the Thor controller, were used for those studies requiring the highest temperature resolution. However as the setpoint of the Thor controller could be set by computer, it was sometimes convenient to use it in preference to the other two controllers for less demanding investigations. The Thor controller was also employed for all the ultrasonic measurements as the output from a thermocouple (used as control sensor) was found to be independent of the application of a r.f. signal to the sample, in contrast to the output from a diode.
temperature sensor which was detrimentally affected.

Sample temperatures were measured using two Au,0.07%-Fe vs chromel thermocouples, one being employed to measure the sample temperature and the second to monitor the temperature gradient across the sample. The two thermocouple leads were soldered together using a 80% Au - 20% Sn alloy and Indalloy Flux no 1. The output from the thermocouples were measured using two HP 3478A, 5½ digit multimeters, one of these being sampled by computer every 3 seconds. This voltage measurement was converted to a temperature reading and displayed on the computer terminal. The number of voltage measurements subsequently collected for one datum point (e.g. one neutron diffraction scan or one peak intensity measurement) was averaged and displayed together with the statistical deviation s. The actual deviation in temperature was taken as +2s. The absolute accuracy of the HP multimeters was equivalent to a temperature accuracy of +0.05 K.

2.2 ULTRASONIC ATTENUATION AND VELOCITY MEASUREMENT [66]

A signal from an oscillator, operating at the fundamental frequency or an overtone of the fundamental frequency of a quartz transducer which is bound to a flat, smooth area of a sample, is employed to generate either a longitudinal (compressional) or a transverse (shear) ultrasonic stress wave in the sample by virtue of the piezoelectric effect. If a second face exists parallel to the first, this sound wave is reflected from the sample-air interface with negligible loss and subsequently travels through the sample a number of times if the sample attenuation is not too large. Each time the wave is incident upon the face containing the transducer, a small amount of its energy is converted to electrical energy by the transducer and is displayed on an oscilloscope screen after appropriate amplification. Due to energy losses of the wave to the sample, the successive echoes diminish in amplitude: the rate of decrease gives a quantitative indication of the attenuation of the wave if the energy losses at the transducer-sample bond as well as the diffraction losses are small. The velocity may be found from the time interval between echoes if the length of the sample is known.
2.2.1 The ultrasonic apparatus

The MATEC system employed for the measurement of ultrasonic attenuation and velocity consisted of the following units:

7700 pulse modulator and receiver
760 V r.f. plug-in (10 - 90 MHz frequency range)
110 high resolution frequency source
112 B decade dividers and dual delay generator
1204 B master synchronizer and exponential generator
2470 B automatic attenuation recorder
60,70 r.f. impedance matching units
2465 300 MHz Tektronix oscilloscope
5383 A Hewlett Packard frequency counter

A schematic diagram of the system is shown in Fig. 2.3.

The model 7700 pulse modulator and receiver can generate single and double r.f. pulses of up to 800 V in amplitude at a repetition rate between 5 and 500 pulses per second. In the single pulse modes the pulse widths can be varied between 0.2 and 5.2 μs or between 1.0 and 101 μs. The double pulses can individually be varied between 0.2 and 5.2 μs in width and separated by 1 to 101 μs or by 10 to 100 μs.

2.2.2 Attenuation measurement [66]

The attenuation of a plane stress wave travelling through a homogeneous solid is described by

$$\sigma(x,t) = \sigma_0 e^{-\alpha x} e^{i(kx-\omega t)}, \quad (2.1)$$

where the attenuation factor is given by

$$\alpha = 20 \log_{10} \frac{\sigma(x_1)}{\sigma(x_2)} \left(\frac{x_2-x_1}{\log_{10} x_2-x_1}\right) [\text{dB/cm}]. \quad (2.2)$$
Fig. 2.3  Schematic diagram of the MATEC ultrasonic apparatus

The intensity of the wave is described by

\[ I(x) = I(0) e^{-\gamma x}, \]

where \( \gamma \) determines the decay of the energy flux and

\[ \gamma = 2\alpha. \]

The MATEC system employed in this investigation can measure the attenuation of a wave in three ways:

(1) A calibrated exponential waveform generated by the model 1204 B master synchronizer and exponential generator can be matched to the chain of echoes and the attenuation can be found from the decay constants in dB/s, independent of the sample length and velocity. The
exponential waveform is calibrated by sending a pulse, having the same frequency as that applied to the transducer, through the same amplifying and detecting circuitry as the echo.

(ii) The model 2470 B automatic attenuation recorder can be employed to compare a single echo to an internal D.C. voltage reference to give the attenuation in dB. This method is particularly valuable when the attenuation in the sample is so large as to preclude a double echo technique.

(iii) In the basic mode of operation of the 2470 B, the peak heights of two selected echoes are differentially compared in a logarithmic voltmeter. High sensitivity to attenuation changes is achieved while common changes in system sensitivity is rejected. This is assisted by an automatic gain control facility which keeps the operating level for the first selected echo constant. The accuracy of the 2470 B is 0.05 dB per dB with a maximum accumulated error of 0.5 dB.

All attenuation measurements in this investigation were executed in the double-echo mode.

2.2.3 Velocity measurement [66]

The MATEC model 122 B employs a pulse echo overlap technique for velocity measurement and provides the interfacing between the model 110 high resolution frequency source, operating at a frequency with corresponding period equal to the round trip time of a wave in the sample, and the model 7700 pulse modulator and receiver. This frequency can be found to one part in $10^5$ through a perfect overlap of two strobed echoes. The velocity is then given by

$$v = 2d \cdot f, \quad (2.5)$$

where $d$ is the thickness of the sample and $f$ the frequency corresponding to the round trip time.

The absolute accuracy of velocity measurement depends, amongst other things, on the accuracy with which the sample length is known as well as instrumental specifications, and was 0.1% for this investigation.
2.2.4 Sample preparation

The ultrasonic measurements executed in this investigation were usually performed along the c axes of the hexagonal rare earth crystals. The appropriate orientation, found by back reflection Laue X-ray photography, was transferred directly onto a spark erosion machine and the subsequently planed surface was perpendicular to the desired direction to within 0.5°. A perfectly parallel second surface (within one part in $10^5$) was planed after gluing the first surface to a base that was planed to achieve perfect parallelism with respect to the planing disk. Surface oxides were removed from the planed surfaces by etching the crystal in a 50% lactic acid – 50% nitric acid mixture for between 30 and 60 seconds. A transducer was then stuck to one of these surfaces using Araldite standard epoxy and allowed to cure for 24 hours at a temperature of approximately 60 °C and a pressure of $10^4$ N cm$^{-2}$. A bond thickness of less than 0.02 mm was obtained by using a small amount of epoxy (less than 1 mm$^3$) and carefully "screwing" the transducer onto the surface. The 4 mm diameter transducers of fundamental frequency 10 MHz with one gold plated face were obtained from Valpey Fisher.

2.3 NEUTRON DIFFRACTION

2.3.1 Diffraction conditions [67]

The scattering of neutrons by an atom occurs as a result of the interaction between the neutron and the nucleus and is independent of the Bragg angle $\theta$ for typical neutron wavelengths of the order of 1 Å. The amplitude of the nuclear scattering is of the same order of magnitude for most atoms. Since the neutron possesses a magnetic moment, additional scattering from the electrons that contribute to the magnetic moment of the atom occurs. This scattering decreases with an increase in $\theta$ since the spatial distribution of the electrons that contribute to the magnetic moment is comparable to the typical wavelength of the neutrons.
The main distinction between neutron and X-ray scattering is that X-rays scatter from the total electronic distribution around the atom and do not interact with magnetic moments.

The amplitude per unit cell of an unpolarized neutron beam diffracted from the \((h \ k \ l)\) plane is given by the structure factor \(F_{hk\ell}\), which has two contributions arising from the nuclear and the magnetic scattering respectively:

\[
|F_{hk\ell}|^2 = |F_{\text{nuc}\ell}|^2 + |F_{\text{magn}}|^2,
\]

\[
F_{\text{nuc}\ell} = \sum_n b_n e^{2\pi i (\frac{h x_n}{a} + \frac{k y_n}{b} + \frac{l z_n}{c})},
\]

\[
F_{\text{magn}} = \sum_n \bar{\xi}_n p_n e^{2\pi i (\frac{h x_n}{a} + \frac{k y_n}{b} + \frac{l z_n}{c})},
\]

where the summation is over all the atoms in the unit cell, \(b_n\) is the nuclear scattering length for the \(n\)th atom, \(p_n = (\frac{e^2 \gamma}{2mc^2})g_J f_J\) is the magnetic scattering length, \(\gamma\) is the moment of the neutron in nuclear magnetons, and \(\bar{\xi} = \xi(\xi, \bar{K}) - \bar{K}\) is the magnetic interaction vector, with \(\xi\) a unit vector normal to the \((h \ k \ l)\) plane and \(\bar{K}\) a unit vector along the direction of the atomic magnetic spin.

The magnetic form factor \(f_J\) is a combination of the form factors \(f_S\) and \(f_L\) for respectively the spin and orbital contributions to the total magnetic moment, and accounts for the variation of the intensity of magnetic scattering as a function of Bragg angle.

For \(\bar{J}_n = J_n\),

\[
\bar{\xi}_n p_n = - (\frac{e^2 \gamma}{2mc^2})g_J f_J |\bar{J}_n - \bar{\xi} \cdot \bar{J}_n|,
\]

\[
(\frac{e^2 \gamma}{2mc^2})g_J f_J \bar{J}_n \quad \text{for the component of } \bar{J} \text{ perpendicular to } \bar{\xi},
\]

\[
0 \quad \text{for the component of } \bar{J} \text{ along the scattering vector } \bar{\xi}.
\]
The structure factor for magnetic scattering now reduces to:

$$F_{\text{magn}} = -(\frac{e^2 \gamma}{2mc^2}) e^{\Sigma f_i \phi} J_1 e^{2\pi i \left( \frac{hx_n}{a} + \frac{ky_n}{b} + \frac{\ell z_n}{c} \right)}.$$  \hspace{1cm} (2.11)

In the case of helical magnetic ordering it can be shown \cite{[67]} that Eq. (2.11) becomes

$$|F_{\text{magn}}|^2 = \left(\frac{e^2 \gamma}{2mc^2}\right)^2 g_j^{2J_1} \{\Sigma f_i e^{i[\omega+\alpha] + 2\pi \left( \frac{hx_n}{a} + \frac{ky_n}{b} + \frac{\ell z_n}{c} \right]}\}^2$$

$$+ e^{i[(\omega+\alpha) + 2\pi \left( \frac{hx_n}{a} + \frac{ky_n}{b} + \frac{\ell z_n}{c} \right]} \{\Sigma f_i e^{i[\omega+\alpha] + 2\pi \left( \frac{hx_n}{a} + \frac{ky_n}{b} + \frac{\ell z_n}{c} \right]}\}^2, \hspace{1cm} (2.12)$$

where $\phi$ is the angle between the spiral axis and $\omega$, $\omega$ is the interlayer turn angle and $\alpha$ is an arbitrary constant.

The resulting conditions for constructive interference of the magnetic intensities, found by inspection of the two sets of exponents

$$(\omega+\alpha) \pm 2\pi \left( \frac{hx_n}{a} + \frac{ky_n}{b} + \frac{\ell z_n}{c} \right)$$  \hspace{1cm} (2.13)

in equation (2.12), are

(i) the value of either exponent must increase by an integer from one magnetic layer to the next and

(ii) this value must be constant for all atoms in one layer.

The magnetic intensity will consequently be observed as satellite reflections which are found at reciprocal lattice points that have been displaced from the nuclear reciprocal lattice points by a component parallel to the spin spiral axis. The magnitude of this displacement is such that the increment
\[ 2\pi \left( \frac{hx_n}{a} + \frac{ky_n}{b} + \frac{\ell z_n}{c} \right) = \pm \omega \] (2.14)
from layer to layer.

For the planar helical magnetic structures of dysprosium and holmium, the spiral axis lies along the c axis, successive planes are separated by c/2 and consequently the magnetic satellites will be displaced from the nuclear positions (h k \ell) by a reciprocal lattice vector (0 0 \delta \ell) with \delta \ell = \frac{\omega}{\pi}. For erbium, since the various spin structures (sinusoidal, antiphase domain and conical ferromagnet are all modulated with respect to the c axis, the reflected magnetic intensity will be found at reciprocal lattice points displaced from the nuclear points (h k \ell) by (0 0 \delta \ell). No magnetic intensity, however, is associated with the (0 0 \ell) nuclear reciprocal lattice points for the sinusoidal regime (85 K - 52 K) since the spins lie parallel or antiparallel to the c axis for this structure.

2.3.2 The reactor spectrum

The neutrons produced by $^{235}$U fission in the core of a reactor typically have an energy distribution around a few MeV and have to be slowed down through energy loss to a suitable moderator to effect its efficient capture by other uranium nuclei [68]. The flux density of thermal neutrons (0-1 MeV) in the core of the SAFARI-I light water moderated experimental reactor at Pelindaba is approximately $2 \times 10^{13}$ neutrons s$^{-1}$ cm$^{-2}$ for the operational power level of 5 MW. On a few occasions which will be specifically indicated in the text, the reactor was operated at 10 MW. The equilibrium energy spectrum of the neutrons that emerge from the reactor has a Maxwellian distribution characterized by the moderator temperature T. A beam of neutrons is obtained from the core of the reactor using a suitable collimator. The neutron flux emerging from this collimator with wavelengths between $\lambda$ and $\lambda + d\lambda$ is given by [69,70]:

\[ \phi(\lambda) = \frac{4N}{\sqrt{\pi}} \frac{h \lambda^5}{m} e^{-\frac{\lambda^2}{\lambda^2}} \] (2.15)
where \( N \) is the total number of neutrons per unit volume and 
\[
\lambda_0 = \frac{h}{\sqrt{2mkT}}
\]
is the wavelength corresponding to the most probable velocity in the Maxwellian distribution. (2.16)

The maximum value of \( \phi(\lambda) \) occurs at a wavelength of
\[
\lambda_m = \frac{h}{\sqrt{5mkT}},
\]
which yields wavelengths of 1.13 \( \text{Å} \) and 1.04 \( \text{Å} \) for moderator temperatures of 300 K and 350 K respectively. A typical reactor spectrum is shown in Figure 2.4 [67].

Fig. 2.4 A typical intensity vs wavelength distribution for a neutron beam emerging from a reactor [67]
2.3.3 Monochromatization

Monochromatization of a neutron beam from a reactor can be achieved by Bragg reflection from a suitable single crystal, as illustrated in Figure 2.5 [67].

Fig. 2.5 Production of a monochromatic beam

Materials commonly used for monochromator crystals include copper, germanium, graphite, beryllium, lead, LiF, NaCl and CaF$_2$ [70]. The wavelength of the monochromatic beam can be varied by either selecting different crystallographic reflections or varying the angle of reflection. The design of the neutron diffraction facility of the SAFARI-I reactor allows a choice of fixed diffraction angles of $25^\circ$, $50^\circ$, $75^\circ$ or $100^\circ$ [71]. For this investigation the monochromatic beam was obtained from the (1 1 1) reflection of a Ge monochromator at a diffraction angle of $25^\circ$. The monochromator was used in the transmission mode and was fully bathed in radiation.

The diffracted wavelength was found by measuring the peak positions of a number of reflections from a Ni powder and fitting these to the crystal structure and lattice constants of Ni, and was:

$$\lambda = 1.402 \, \text{Å} \pm 0.002 \, \text{Å}$$  \hspace{1cm} (2.18)

The width $\delta \lambda$ of the monochromatic beam is [67]
\[ \delta \lambda = 2\beta \cos \theta \quad (2.19) \]

where \( \beta \) is the angle of divergence of the collimator.

The mosaic spread of the monochromator crystal should preferably be large to give maximum intensity. For a mosaic spread of the same magnitude as \( \beta \), a maximum intensity is obtained while the spread in \( \lambda \) is still determined by the collimator divergence.

2.3.4 Harmonic contamination of the monochromatic beam

When a beam of neutrons of wavelength \( \lambda \) is diffracted from the \((h \ k \ell)\) plane of a monochromator, the \(n(h \ k \ell)\) planes diffract neutrons of wavelength \(\lambda/n\) into the beam. Due to the Maxwellian distribution of the reactor spectrum, usually only the second order contamination is significant and for primary wavelengths below the maximum of the distribution curve, even this can be kept to a minimum. For longer wavelengths (roughly above 1.1 Å) the contamination may be filtered out with a suitable material which has an absorption resonance for the \(\lambda/2\) component of the beam. A good filter typically reduces the intensity of the contamination by two orders of magnitude at the expense of the primary beam which is attenuated by less than 50% [67,68]. Further, with some monochromators the primary beam may be selected in such a way that the reflection that gives rise to the second order contamination is forbidden due to the internal cancellation of contributions from the different atoms in the unit cell [67]. The Ge \((1 \ 1 \ 1)\) reflection employed for this investigation is an example of this class of monochromators, since the structure factor for the \((2 \ 2 \ 2)\) reflection of Ge is zero.

2.3.5 Transmission

A beam of neutrons is attenuated upon passing through a material due to the absorption of neutrons by the nuclei of the constituent atoms. The intensity of the emergent beam is given by [72]

\[ I = A_{hk\ell} I_0 \quad (2.20) \]
where $I_0$ is the intensity of the incident beam, and $A_{hkl}$ is the transmission factor

with

$$A_{hkl} = \frac{1}{V} \int_V e^{-\mu(p+q)} dV,$$

(2.21)

where $\mu$ is the mean linear absorption coefficient, $V$ is the volume of the sample, $p$ is the path length of the beam incident on volume element $dV$, and $q$ is the path length of the beam reflected from volume element $dV$.

This integral can be solved rigorously for only a number of shapes. If a precise knowledge of the transmission is required, it is preferable to use a sample of one of these shapes, the most commonly used being parallel-sided plates, cylinders and spheres. Numerical methods have been described for cases where this integral can not be solved rigorously.

In the special case where a narrow monochromatic beam of neutrons passes through a parallel-sided homogeneous isotropic sample which is large enough to cover the total beam cross-section and is orientated with its surfaces perpendicular to the incoming beam direction, the emerging intensity is given by [73]

$$I = I_0 e^{-\mu t} = I_0 e^{-\frac{N}{A} \rho \sigma_a t},$$

(2.22)

where $t$ is the thickness of the sample, $N$ is Avogadro's number, $\rho$ is the density, $\sigma_a$ is the absorption cross section and $A$ is the atomic weight.

Values of the nuclear absorption cross section and the linear and mass absorption coefficients for the rare earth elements Dy, Ho and Er are given in Table 2.2 and compared with the X-ray values [67], while Fig. 2.5 shows a plot of $e^{-\mu t}$ vs $t$ for Dy, Ho and Er.
### TABLE 2.2

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic no</th>
<th>Cross sections for true absorption ($10^{-24}$ cm$^2$)</th>
<th>Mass absorption coefficient (cm$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Neutrons $\lambda=1.08$ Å</td>
<td>X-rays $\lambda=1.54$ Å</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>66</td>
<td>580</td>
<td>77 000</td>
</tr>
<tr>
<td>Holmium</td>
<td>67</td>
<td>50</td>
<td>35 100</td>
</tr>
<tr>
<td>Erbium</td>
<td>68</td>
<td>120</td>
<td>37 200</td>
</tr>
</tbody>
</table>

**Figure 2.6** $e^{-\mu t}$ vs $t$ for Dy, Ho and Er
Consider reflection from a crystal face as illustrated in Fig. 2.7. The distance that a neutron travels through the crystal in the Bragg position is equal to \( 2x/\sin \theta \), where \( x \) is the penetration depth of the neutron into the crystal. The values of the Bragg angles for the reflections of Dy, Ho and Er that were studied in this investigation were between 10° and 15°. Thus the total distance that a neutron travels through the crystal upon being Bragg reflected is equal to between 8 and 11 times the penetration depth into the crystal. It can be seen from Fig. 2.6 that due to the high absorption in particularly Dy only a thin "skin" of the crystal is seen during a neutron scattering investigation.

Fig. 2.7 Reflection from a crystal face
2.3.6 Extinction [67]

When a beam of neutrons is diffracted by a perfect crystal, the beam will become increasingly attenuated as a result of the process of reflection by successive planes. The penetration distance is of the order of $10^{-6}$ cm at the Bragg angle. This attenuation of the incident neutron beam, called primary extinction, is appreciably larger than the attenuation due to the nuclear absorption of the neutrons and occurs only when the crystal is in the Bragg position.

In a perfect crystal the total reflection as described above occurs over a very small angular range $2\alpha$ near the Bragg angle with $2\alpha$ less than a second of arc for neutrons:

$$S = \frac{\lambda^2 N_c}{\pi \sin \theta} F_{hkl}$$  \hspace{1cm} (2.23)

where $N_c$ is the number of unit cells per unit volume, $F_{hkl}$ is the structure factor of the unit cell for the $(h \, k \, l)$ reflection and $\theta$ is the Bragg angle.

Usually a crystal is not perfect, but may be thought of as being divided into small domains of perfect crystallinity, called mosaic blocks, by dislocations. These mosaic blocks are typically misoriented from one another by a few degrees of arc to perhaps 0.5°. Each of these individual mosaic blocks reflects at a slightly different angle when the crystal is rotated through the mean reflecting position, with the result that the neutron beam penetrates much deeper into the crystal. For one particular Bragg angle the neutron beam will still travel through a number of mosaic blocks of identical orientation. The consequent attenuation of the beam is called secondary extinction.
The total extinction is the sum of the primary extinction inside the mosaic blocks and the secondary extinction due to the screening effect of mosaic blocks of similar orientation. When the dimensions of the mosaic blocks are such that primary extinction is negligible, the crystal is said to be ideally imperfect.

The effect of extinction is most pronounced for the strongest reflections because these scatter the maximum amount of energy from the incident beam [74]. The integrated intensity obtained by rotating a crystal is [75]

\[ R^\theta = \int_{-\infty}^{\infty} \frac{QT}{Y} \frac{W(\Delta)}{1 + \frac{QT}{Y} W(\Delta)} d\Delta, \quad (2.24) \]

where \( \Delta \) is the angular deviation of a block from the mean Bragg angle \( \theta \); \( Y \) is the direction cosine of the incident beam with respect to the normal to the crystal face, \( T \) is the mean free path length through the crystal,

\[ Q = \frac{\lambda^3 N_e^2}{\sin 2\theta} \frac{F_{hk\ell}^2}{F_{hk\ell}}, \quad (2.25) \]

and \( W(\Delta) = \sqrt{2} g e^{-2\pi g^2 \Delta^2} \) gives the Gaussian distribution of mosaic blocks [67,74],

where \[ g = \frac{1}{2\sqrt{\pi} \eta}, \quad (2.26) \]

with \( \eta \) the "mosaic spread" parameter.

When the peak reflection is small, the denominator is nearly unity, and for a crystal of volume \( V \),

\[ R^\theta \sim QV \quad (2.28) \]

Furthermore, the extinction increases with increasing wavelength, the correction factor being [70]
\[(P^2 + \frac{S}{\mu}) P\lambda^2 \quad (2.29)\]

with \(p\) the polarization factor, \(\mu\) the linear absorption coefficient, and \(P, S\) constants representing the amount of primary and secondary extinction.

In Zachariasen's treatment [76] the extinction factor \(y\) of a plane wave of neutrons incident upon a crystal is given by

\[P = P_k \cdot y, \quad (2.30)\]

where \(P\) is the intensity of the diffracted beam, and

\[P_k = I_0 V A_{hkl} (\mu) Q \quad (2.31)\]

in the kinematic approximation, with \(I_0\) the intensity of the incident beam, \(V\) the irradiated volume of the crystal, and \(A_{hkl} (\mu)\) the transmission factor (Paragraph 2.3.5).

Assuming the Darwin [77] model of approximately spherical domains of equal size having the Gaussian distribution of equation (2.26), Zachariasen based his model on the exchange of energy between the incident and diffracted beam through intensity rather than amplitude coupling. Zachariasen obtained a factor \(y\) by which \(QV\) for the crystal must be multiplied to yield the observed integrated intensity:

\[y = \frac{1}{\sqrt{1+2x}} \quad (2.32)\]

where \(x = \beta Q \{ t + \frac{T - t}{\sqrt{1 + (\beta/g)^2}} \}, \quad (2.33)\]

\[\beta = \frac{2}{3} \frac{t}{\lambda}, \quad (2.34)\]

and \(t\) is the mean free path length through a mosaic block.
The $Q_0 (T - T_p)$ term corresponds to the primary extinction while the $\frac{R_0 (T - T_p)}{\sqrt{1 + (\beta/\theta)^2}}$ term represents the secondary extinction.

When $\beta Q_0 T < 0.02$, which is usually the case, the primary extinction can be neglected so that the equation for secondary extinction becomes

$$x = \frac{r}{\lambda} \frac{QT}{\sqrt{1 + (\beta/\theta)^2}} \quad (2.35)$$

where $r = \frac{2}{3} t$ is the radius of a mosaic sphere. \quad (2.36)

For the rare earths studied in this investigation, this condition relates to primary extinction being negligible if the radius $r$ of a mosaic block is smaller than approximately 5000 Å.

### 3.4 THE NEUTRON DIFFRACTION FACILITY

#### 2.4.1 The facility

A plan view of the neutron diffraction facility at Pelindaba, which was developed by Raubenheimer and de Vries [71], is shown in Figure 2.8 and an elevated view in Figure 2.9.

The main beam from the reactor core is collimated through an open pipe constructed from mild steel, poly-ethylene and $B_4C$ laminations to attenuate respectively stray $\gamma$-radiation, fast and thermal neutrons [78]. A three position shutter constructed from the same lamination has one uncollimated open position and another containing a soller slit collimator. Because the intensity of the collimated beam was reduced to 20% of the intensity of the uncollimated beam, the soller slit collimator was never used.

Optimization of the monochromator crystal was attained with the counter in the zero position by means of a translation of the monochromator along the lathe bed (Fig. 2.8) and two independent "cradle rotations". A soller slit collimator designed to fit into any of the radial ports at $25^0$, $50^0$, $75^0$ or $100^0$ was also not used due to excessive intensity loss. A double slit collimator, consisting
Fig. 2.8 Plan view of the neutron diffraction facility

Fig. 2.9 Elevated view of the neutron diffraction facility
of two disks of 25% $B_4C$-impregnated resin with holes in their centres, was employed. One disk was placed approximately 40 cm inside the port, while the second disk was placed just outside the port in front of the monitor counter. A double walled $B_4C$ filled pipe collimator with an inside diameter of 2.2 cm and a length of 50.0 cm was placed in front of the BF$_3$ counter. The counter was housed inside a 30.0 cm diameter double walled pipe of wall thickness 9.5 cm which was filled with boron impregnated paraffin wax. The pipe walls were manufactured from an Al-B lamination. This shielding attenuated both fast (paraffin) and thermal ($B_4C$) neutrons.

A 20th Century Electronics PFC-300-U235 disk-shaped parallel-plate fission chamber monitor counter was placed in the neutron beam just outside the port. Diffraction intensity measurements were performed against monitor counts and not against time, to negate the effect of variations in reactor power. The monitor absorbed approximately 0.04% of the neutron flux incident on it. The main counter was a Reuter Stokes RSN-108S-MG BF$_3$-counter enriched to 96% of $^{10}B$. The sensitivity of the counter for thermal neutrons is 36 cps/nv and the efficiency parallel to the axis of the detector larger than 80%. The detecting ability of a neutron counter depends on the ionization caused by the products of the neutron absorption reaction as the uncharged neutrons do not produce ionization [67]. The absorption reaction for $^{10}B$ which has a neutron absorption cross section of approximately 2300 barns is

$$^{1}H_0 + ^{10}B \rightarrow \begin{cases} \ \ \ \ \ 7Li + ^4He + 2.78 \text{ MeV} \ (7\%) \\ \ \ \ \ \ \ 3Li + ^4He + 2.31 \text{ MeV} \ (93\%) \end{cases}$$

$$7Li^* \rightarrow 7Li + \gamma + 0.48 \text{ MeV}$$

The lithium and helium nuclei have path lengths of approximately 5 mm in BF$_3$ gas and together produce about 7x10$^4$ ion pairs. The pulses produced by $\gamma$-radiation have approximately 1% of the height of the pulses produced by neutron radiation, i.e. $\gamma$-radiation is well discriminated against.
An ORTEC MOD 142 preamp was used with the monitor counter and an ORTEC MOD 121 with the main counter. Each counter employed an ORTEC 490 B amplifier and single channel analyzer.

2.4.2 The kappa-phi diffractometer

Figure 2.10 shows a diagram of the two-axis κϕ-goniometer which was adapted to the neutron diffraction facility at Pelindaba by De Vries and Adrian [79] and manufactured along the lines of a goniometer introduced for X-ray crystallography by ENRAF-NONIUS.

Both the κ and ω and the κ and ϕ axes intersect and these points of intersection coincide. The angles between both sets of axis are $50^\circ \pm 0.02^\circ$. Alignment of the diffractometer was achieved with the aid of a helium-neon laser beam which, when aligned to the axis of the collimating pipe between the monochromator and the sample, defines the path of the neutron beam. The unit of rotation of the diffractometer is the deci-milli-circumference (dmc) with $1 \text{dmc} = 10^{-4} \times 360^\circ$. The ω and 2θ axes can be stepped in 0.25 dmc while the κ and ϕ axes can be stepped in 1 dmc. The mathematical crystal setting formalism is based mainly on the method described by Bussing and Levy [80] with a re-definition of the relevant co-ordinate systems and the instrument matrix R, which consists of five rotations (discussed in [79]) instead of the usual three used for an Eulerian goniometer. The angle settings for the ω, κ and ϕ rotations are derived from this instrumentation matrix. Furthermore, two pseudo-axes were introduced, viz. (1) an azi-

![Diagram of the κϕ-goniometer](image)

**Fig. 2.10** The κϕ-goniometer
muth axis which rotates the crystal around the scattering vector and (2) a \( \chi \) axis which rotates the crystal in a vertical plane through the scattering vector. These rotations are effected through simultaneous rotations around the \( \omega \), \( \kappa \) and \( \phi \) axes. The computer employed for control of the diffractometer was a HP 1000.

2.4.3 The intensity scans

The diffraction configuration employed was such that the beam reflected from the crystal was "parallel" to the main collimated beam from the reactor. In this arrangement the longer wavelengths in the collimated beam have larger Bragg angles than the shorter wavelengths resulting in a sharper reflection as illustrated in Figure 2.11 [70].

\[ \text{Figure 2.11: Two arrangements for measuring Bragg reflections of a single crystal. In the "parallel" arrangement (i) the longer wavelengths have larger glancing angles whereas the reverse is true for the "non-parallel" arrangement (ii). This results in sharper reflections for the "parallel" arrangement [70].} \]

In the "parallel" configuration the width of the rocking curves is proportional to the mosaic spread of the monochromator and sample crystals [67]. This width is larger in the "non-parallel" configuration, being roughly proportional to the sum of the mosaic spread and the angle of collimation.
The integrated intensity of a reflection is measured by counting the number of neutrons reflected into a counter when the crystal is rotated through a small angular range about the Bragg angle [70]. For the purpose of this investigation these intensities were determined by executing scans in the normal beam equatorial geometry where the crystal is rotated about an axis lying in the reflecting plane as illustrated in Figure 2.12 [70]. In this geometry the velocity with which a reciprocal lattice point passes through the Ewald sphere is a function of the Bragg angle only, and the view of the source is identical for all reflections. In the general inclination method where the crystal rotates around the goniometer head axis, the variation in the velocity with which a reciprocal lattice point passes through the Ewald sphere is more complex. Furthermore, those reciprocal lattice points lying close to the goniometer head axis cannot cut across the Ewald sphere.

\[ \text{Fig. 2.12. The Ewald sphere and the sphere through the reciprocal lattice point P (with centre at the origin of the reciprocal lattice). The } \phi \text{-rotation moves P to Q, the } \chi \text{-rotation moves Q to R and the } \omega \text{-rotation moves R to the reflecting position S [70].} \]
Two types of scans can be executed to determine the integrated intensity of a reflection: (i) the $\omega$-scan in which the crystal is rotated and the counter kept stationary at the diffraction angle, or (ii) the $\omega,2\theta$-scan in which both the crystal and the counter are rotated, the counter being rotated at twice the angular velocity of the crystal. These two scans are illustrated in Figure 2.13 [70].

The preferred scan is that one which yields the true integrated intensity by illuminating the smallest volume in reciprocal space. The $\omega,2\theta$-scan which was used to measure all the integrated intensities for this investigation is usually preferred in neutron scattering because of the large bandwidth of the incident neutron beam. A $\omega$-scan is usually preferred at low Bragg angles when the mosaic spread of the crystal is large, as illustrated in Figure 2.14 [70]:

---

Fig. 2.13 Idealized measurement of a $(hkl)$ reflection by $\omega$-scan or by $\omega,2\theta$-scan [70]
A third method for measuring the integrated intensity of a reflection is to keep both the crystal and the counter stationary at the Bragg position. A prerequisite for this method is a strongly convergent incident beam. In neutron diffraction work the convergence of the incident beam is usually appreciably less than that required to give the true integrated intensity. This method may nevertheless be fruitfully employed if only a qualitative indication of the scattered intensity is required.

Fig. 2.14 Diagrams illustrating: (i) $\omega$, $2\theta$-scan for a perfect crystal illuminated by radiation of spectral range $\delta\theta = \tan \delta \delta \lambda / \lambda$, (ii) $\omega$-scan for a crystal with a large mosaic spread [70]
CHAPTER III

3.1 INTRODUCTION

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3.1 INTRODUCTION

Experimental investigations into the magnetic ordering in dysprosium and holmium are discussed in this chapter. A number of these, employing neutron diffraction and ultrasonic techniques, were concerned with the nature of the planar helical $\leftrightarrow$ paramagnetic phase transition at $T_N$. Following the observation of this transition as of second order, the characterization of the phase transition was extended to measurements of the power law exponents that describe the spontaneous sublattice magnetization and the ultrasonic attenuation and velocity in the critical region.

An interesting anomaly in the value of $T_N$, as indicated by simultaneous neutron diffraction and ultrasonic measurements, was observed for Dy(II) during the abovementioned investigation.

The existence of a proposed vortex magnetic structure in dysprosium was furthermore investigated and hysteresis behaviour in holmium at temperatures well below the transition was studied.

Finally, measurements of the incommensurate (planar helical) $\leftrightarrow$ commensurate (planar ferromagnetic) phase transition in dysprosium were also conducted to determine the nature of this transition.

3.2 ORDER OF THE PLANAR HELICAL $\leftrightarrow$ PARAMAGNETIC PHASE TRANSITION IN DYSPROSIUM AND HOLMIUM

Renormalization group calculations by Mukamel, Krinsky and Bak [52-55] indicated the existence of a fixed point, thus predicting a continuous phase transition at $T_N$ for the rare earths Dy, Ho and Tb as was indicated in Section 1.3.2. Experimental support regarding the second-order nature of the transition is found by a number of investigations:

(1) A neutron diffraction investigation on Ho indicated that the sublattice magnetization varies smoothly through $T_N$ and is described by a $\beta$-exponent power law below $T_N$, with $\beta=0.39 \pm 0.04, -0.03$ [57]. Neutron diffraction measurements performed on Dy also indicated
a continuous transition with $\beta=0.39 \pm 0.04, -0.02$ [58]. Likewise the transition at $T_N$ was observed as continuous for Tb from neutron scattering measurements [58]. The determination of the critical exponents for Tb is problematic since ferromagnetic ordering persists to well into the small helically ordered region [58].

(ii) A specific heat investigation on a Ho single crystal (absolute accuracy of $\pm 0.5\%$ in specific heat measurements and a resolution of $\pm 0.08$ K in temperature) failed to observe any latent heat at the transition point as expected at a second order transition [60]. Jayasuriya et al. [59] previously also studied Tb but failed to observe any latent heat at $T_N$. Thermal expansion measurements on Dy showed no discontinuous change in length to within $10 \times 10^{-7}$ [62] and $2 \times 10^{-7}$ [63]. Tindall and Steinitz [62] also observed no such discontinuity for Tb.

Calculations by Barak and Walker [56] indicated that the initial Hamiltonian for these systems lies outside the domain of the stable fixed point and hence expected the transition to be of first order. A number of experiments, which observe this transition as of first order, have been reported:

(i) A strain discontinuity of $30 \times 10^{-6}$ along the a axis of Ho was observed at $T_N$ by Tindall et al. [61]. No strain discontinuity was observed along the c axis (within $1.5 \times 10^{-6}$). However, later thermal expansion measurements along the a axis of a new Ho single crystal by the same group [65] failed to confirm the existence of the a axis anomaly. Furthermore, a splitting of the Néel temperature when a magnetic field is applied along the a axis is observed, indicating the possible existence of a new magnetically ordered region [65].

(ii) Zochowski et al. [64] studied the critical thermal expansion of a high purity Dy crystal at $T_N$ and suggested that the transition is weakly first order: Firstly, a thermal hysteresis of 0.2 K was deduced by comparing the results of slow heating and cooling runs and employing a linear extrapolation to zero heating or cooling rate. It is questionable whether the reported small hysteresis effect can be established from these non-equilibrium measurements. Secondly, Zochowski et al. observed for the critical part of the thermal expansion above $T_N$ a marked deviation from the expected exponent description below a temperature of $(T_N + 0.13)$ K. Reference to both these aspects will be made when discussing our own experimental results on dysprosium.
The previous neutron diffraction measurements on the Dy(I) crystal at Pelindaba [58] were executed primarily to determine the value of the $\beta$-critical exponent, as was the investigation by Eckert and Shirane on Ho [57]. Neither of these publications reported a detailed investigation in the vicinity of the critical temperature. In view of the contradicting theoretical predictions and experimental observations of the nature of this transition, a number of high resolution neutron diffraction measurements were performed on the Dy(I), Dy(II) and Ho crystals. The resolution in temperature was improved by a factor 2.5 to ±0.02 K and the neutron intensities by a factor 10 compared to the previous investigation on Dy(I). These neutron diffraction measurements were complemented by ultrasonic attenuation and velocity measurements on Dy(I) and Dy(II).

The general procedure for the neutron diffraction measurements is outlined below. Specific detail relating to individual investigations is given in tabulated format.

3.2.1 Data collection

The crystal was first orientated at room temperature on the $\kappa\phi$-diffractometer after which the scattering vector of the desired nuclear reflection was placed in the scattering position, usually in such a way that one of the basal plane axes is in the plane defined by the $\omega$-rotation of the diffractometer (floor of the reactor). The orientation was then carefully transferred to the sample stalk of the cryostat. This procedure resulted in an almost vertical orientation for the cryostat which prevented peripherals such as the vacuum pipe, the nitrogen supply and return lines (flow cryostat), the high pressure lines (Air Products cold finger) and electrical and thermocouple leads from entering the neutron beam. It also minimized the strain on the $\kappa$-and $\phi$-axes. The crystal was tied to the sample stalk using a few (4-6) strands of 0.25 mm dia. aluminium wire. On occasion, a small amount of GE-7031 varnish (less than 2 mm$^3$) was also used to secure the crystal to the platform but the use of glue
was avoided whenever possible. This procedure was followed to facilitate the free thermal expansion of the crystal. Two Au, 0.07% Fe vs chromel thermocouples were stuck onto diagonally opposite ends of the crystal with GE-7031 varnish to which a fine aluminium powder had been added. The thermocouples were furthermore held in position by lightly tying them down with the thin aluminium wire.

After placing the crystal on the diffractometer, the crystal was orientated and the desired reflection placed in the scattering position. Hereafter the crystal was slowly cooled down to a predetermined temperature. After temperature stability had been reached a number of scans were executed. These were either peak intensity counts with both crystal and counter held stationary or $\omega, 2\theta$-scans as discussed in Paragraph 2.4.3. During a scan, the temperature was sampled by computer at 3 sec. intervals. Such a group of scans executed at one temperature is called a "datum point" (dp). A number of datum points were executed for either increasing or decreasing temperatures, allowing sufficient time for temperature stabilization between increments. The average temperature and neutron count associated with each datum point were calculated after discarding all scans having a statistical deviation 2s in temperature larger than a predetermined value, typically 0.02 K.

At least one datum point was usually collected well into the paramagnetic region for a reliable "background intensity" point.

3.2.2 Neutron diffraction measurements

Peak intensity neutron counts, performed on the Dy(I), Dy(II) and Ho crystals, resulted in a high count rate and also avoided a "spread out" of the observed magnetization near $T_N$ due to critical scattering (Section 2.4.3). The particulars of each run are given in Table 3.1. The values of $T_N$ indicated in the table are "eyeball" estimates from the magnetization curves. Initial investigations on all three crystals indicated that the change in position of the magnetic satellite reflections due to the variation of the interlayer turn angle as a function of temperature was less than 0.4 dnm for the temperature ranges under consideration. Consequently no adjustment to the diffractometer axes was made during a run.
### TABLE 3.1

<table>
<thead>
<tr>
<th>Satellite reflection</th>
<th>Dy (I)</th>
<th>Dy (II)</th>
<th>Ho</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RUN A</td>
<td>RUN B</td>
<td>RUN C1</td>
</tr>
<tr>
<td>Stabilization time</td>
<td>45</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>Start of run</td>
<td>175.46</td>
<td>175.34</td>
<td>180.07</td>
</tr>
<tr>
<td>End of run</td>
<td>177.44</td>
<td>177.58</td>
<td>177.37</td>
</tr>
<tr>
<td>Background meas.</td>
<td>180.37</td>
<td>178.36</td>
<td></td>
</tr>
<tr>
<td>Néel Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature control</td>
<td>±0.02</td>
<td>±0.02</td>
<td>±0.02</td>
</tr>
<tr>
<td>Increments near $T_N$</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Av. increment (range)</td>
<td>0.11</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Type of scan</td>
<td>peak intensity counts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scans per datum point</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Scans discarded / dp.</td>
<td>1.3</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>Duration of scan</td>
<td>(min)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Total duration of run</td>
<td>(h)</td>
<td>80</td>
<td>100</td>
</tr>
</tbody>
</table>

The intensity of the magnetic satellite reflection was approximately 4 times smaller for Dy(II) than for Dy(I) as a result of its smaller size and crystallographic superiority (narrower diffraction peaks). This was compensated for by working at a reactor power of 10 MW instead of 5 MW as well as increasing the counting time per datum point by a factor 2. Since the thermal neutron absorption cross-section of holmium is approximately 11 times smaller than that
of dysprosium, a substantially shorter counting time is needed to obtain neutron counts of comparable statistics (crystal sizes were of the same order).

The four runs on Dy(II) were executed successively to investigate the possible existence of thermal hysteresis in the value of $T_N$. This is the same crystal on which Zochowski et al. [64] observed a thermal hysteresis of 0.2 K in thermal expansion measurements. The results of these investigations are depicted in Figures 3.1, 3.2 and 3.3.

![Graph showing temperature dependence of peak intensity](image)

**Fig. 3.1** Temperature dependence of the (0 0 2-6) peak intensity for two independent runs (triangles and circles respectively) showing that the observed magnetic scattering is continuous through $T_N$. 
Fig. 3.2 Temperature dependence of the (0 0 2-δ) peak intensity for four successive runs (1:■, 2:□, 3:●, 4:○) on Dy(II)

Fig. 3.3 Peak neutron intensities of the (0 0 2-δ) reflection of Ho in the vicinity of $T_N$ indicating a continuous transition. Only one measured point in two is depicted in order to enhance clarity.
The order parameter is continuous within the resolution of the experiment. The absence of thermal hysteresis in the value of $T_N$ obtained in two successive sets of measurements consisting of a cooling run followed by a heating run (Figure 3.2) also indicates a second order phase transition in contradiction to the observation of a thermal hysteresis in thermal expansion measurements on the same crystal [64]. As a result of this result, it was decided to complement these measurements by investigating the possible existence of thermal hysteresis in ultrasonic attenuation and velocity measurements.

3.2.3 Ultrasonic measurements

Ultrasonic attenuation and velocity measurements were performed on Dy(I) and Dy(II). Due to the unfavourable geometry of the Ho crystal, it was excluded from the ultrasonic study.

The particulars for the two runs on Dy(I) and Dy(II) respectively are given in Table 3.2, followed by a few general remarks.

<p>| TABLE 3.2 |
|-----------------|-----------------|
|                | Dy(I)           | Dy(II)          |</p>
<table>
<thead>
<tr>
<th></th>
<th>Run E</th>
<th>Run F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of ultrasonic wave</td>
<td>(MHz)</td>
<td>Longitudinal c axis</td>
</tr>
<tr>
<td>Direction of propagation</td>
<td></td>
<td>179.20</td>
</tr>
<tr>
<td>Frequency of ultrasonic wave</td>
<td></td>
<td>175.30</td>
</tr>
<tr>
<td>Start temperature</td>
<td>(K)</td>
<td>60</td>
</tr>
<tr>
<td>Turning point</td>
<td>(K)</td>
<td>178.50</td>
</tr>
<tr>
<td>Time expended at turning point</td>
<td>(min)</td>
<td>177.03</td>
</tr>
<tr>
<td>End temperature</td>
<td>(K)</td>
<td></td>
</tr>
<tr>
<td>Néel temperature</td>
<td>(K)</td>
<td></td>
</tr>
<tr>
<td>Temperature control</td>
<td>(K)</td>
<td>±0.02</td>
</tr>
<tr>
<td>Temperature increments near $T_N$</td>
<td>(K)</td>
<td>0.02 - 0.03</td>
</tr>
<tr>
<td>Average increment(range)</td>
<td>(K)</td>
<td>0.05</td>
</tr>
<tr>
<td>Time interval between measurements</td>
<td>(min)</td>
<td>5</td>
</tr>
</tbody>
</table>
Care was exercised during the cooling period not to overshoot the temperature at which each run was to commence before control was established. The temperature of the crystal was read and displayed on a computer terminal to two decimals at intervals of 3 sec. for the duration of each run. Ultrasonic measurements were only taken when at least ten consecutive identical temperatures were obtained and then only if the ultrasonic variables remained unchanged during this period. A typical time interval between measurements was 5 min.

The ultrasonic velocity and attenuation measurements for heating and cooling runs are depicted in Figure 3.4 for Dy(I) and Figure 3.5 for Dy(II).

**Fig. 3.4** Ultrasonic velocity (squares) and attenuation (circles) vs temperature for Dy(I). Closed symbols refer to measurements made during cooling and open symbols to heating data.
Fig. 3.5 Ultrasonic velocity (squares) and attenuation (circles) vs temperature for Dy(II). Closed symbols refer to measurements made during cooling and open symbols to heating data.

It is clear that for both crystals no hysteresis is observed in the value of $T_N$ from either heating or cooling runs. This observation corroborates the observations of the previous section and confirms the second order nature of the planar helical $\leftrightarrow$ paramagnetic phase transition in Dy.

The value of $T_N$ is found from the maximum in the attenuation anomaly and from the point of inflection in the velocity anomaly [81]. A value of $T_{N} = 177.03 \text{ K}$ is indicated for Dy(I), which is in excellent agreement with the value of $T_{N} = 177.05 \text{ K}$ found from neutron diffraction measurements (Paragraph 3.2.2). A value of $T_{N} = 179.33 \text{ K}$ is indicated for Dy(II), which is in disagreement with the value of $T_{N} = 178.85 \text{ K}$ observed from neutron diffraction measurements. This difference will be discussed in the ensuing sections.
3.2.4 **Hysteresis effects in Ho in the ordered region**

As indicated in the previous section, the sublattice magnetization exhibits no thermal hysteresis in the ordered region immediately below \( T_N \), indicating a second order phase transition. A natural extension of the investigation would be to determine the value of the critical exponents \( \beta \) and \( \gamma \) that characterize a second order phase transition. (The results of such an investigation on the two dysprosium crystals are discussed in Section 3.4.)

During the investigation on Ho however, thermal hysteresis was observed in the sublattice magnetization in the ordered region well below \( T_N \). As the existence of such an effect would yield different values of \( \beta \) for measurements taken upon either cooling or heating, the extent of the hysteresis was subsequently investigated.

Table 3.3 lists the particulars of three independent runs executed from above \( T_N \) to respectively 79 K (run G), 85.1 K (run H) and 113.1 K (run I) and back to above \( T_N \). The integrated intensity of both the \((0 0 2)\) nuclear reflection and the \((0 0 2 - 6)\) magnetic reflection was measured. The results are depicted in Fig. 3.6

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Ho</th>
<th>Run G</th>
<th>Run H</th>
<th>Run I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature stabilization time (min)</td>
<td></td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Start of run (K)</td>
<td>130.8</td>
<td>79</td>
<td>130.1</td>
<td>85.1</td>
</tr>
<tr>
<td>End of run (K)</td>
<td>79</td>
<td>79</td>
<td>51.5</td>
<td>85.1</td>
</tr>
<tr>
<td>Néel temperature (K)</td>
<td></td>
<td></td>
<td></td>
<td>128.5</td>
</tr>
<tr>
<td>Temperature control (K)</td>
<td></td>
<td>±0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of scan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. of scans per dp.</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>No. of scans discarded per datum point</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Duration of scan (min)</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Total duration of run (h)</td>
<td>74</td>
<td>59</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3.6 Integrated intensity measurements vs temperature for the (0 0 2-δ) reflection of Ho for three runs extending from $T_N$ to 79 K(G), 85.1 K(H) and 113.1 K(I) respectively. For the (0 0 2) nuclear reflection only the measurements of run G (79 K) are depicted. Closed symbols refer to measurements taken during cooling and open symbols to measurements during heating.

These measurements indicate the existence of a thermal hysteresis loop in the sublattice magnetization extending from ca. 105 K to at least 79 K. (Due to the limitation of the liquid nitrogen flow cryostat, the investigation had to be limited to a lowest temperature of 79 K.) No hysteresis was observed in the nuclear intensity.
In the case of dysprosium it can be seen from Figure 3.18 (Section 3.5) that the sublattice magnetization is hysteresis-free within experimental resolution down to temperatures of \( \approx 160 \text{ K} \) \((T_N - 20 \text{ K})\). The search for hysteresis effects in dysprosium was not pursued further, firstly because the magnetization curves are certainly hysteresis-free for the temperature ranges over which the \( \delta \)-experiments were conducted. Secondly, the reflected intensity for the Ho crystal is substantially higher than for either Dy(I) (10x) or Dy(II) (40x) due to absorption, crystallographic perfection and crystal geometry. To maintain reasonable counting statistics, the lower reflected intensities can be compensated for by increasing the counting time, but this would require an extremely long time to cover such a wide temperature range. (The investigations depicted in Fig. 3.18 and discussed in Section 3.5 took respectively 78 h and 242 h to complete!)

3.3 SIMULTANEOUS MEASUREMENT OF NEUTRON DIFFRACTION AND ULTRASONICS

3.3.1 Observation of a "\( \Delta T_N \) anomaly" for Dy(II)

The planar helical plus-paramagnetic phase transition in Dy and Ho belongs to the universality class characterized by a \( n=4 \)-component order-parameter [54]. The prediction that this transition is of first order, based on the assertion that the initial Hamiltonian lies outside the domain of the stable fixed point [56] is refuted by the experimental results of the previous two paragraphs which observe this transition as of second order. The behaviour of the spontaneous sublattice magnetization for a second order phase transition near \( T_N \) is described by a \( \delta \)-exponent power law

\[
M = B t^\delta, \quad (3.1)
\]

where \( t = \left( \frac{T_N - T}{T_N} \right) \) is the reduced temperature. Using renormalization group methods, a value of \( \delta = 0.39 \) is predicted for this class of systems [53] (Section 1.3.2).
To obtain the value of $\beta$ from neutron diffraction measurements in the critical region, a weighted least squares fit is performed on the scattered intensity vs. reduced temperature data — after a number of corrections to the intensity measurements (Paragraph 3.4.1). The values of $\beta$, $T_N$ and the magnetic prefactor $B$ are treated as variables in the fitting routine. Since the value of $t$ depends critically on $T_N$ it could be advantageous to determine $T_N$ by an independent technique and use this value as an additional constraint in the fitting procedure. One possibility would be to locate the position of $T_N$ by observing the cusp in the critical scattering at $T_N$. It was found, however, that the critical scattering was small and resided almost completely under the Bragg peak. As an alternative it was decided to determine $T_N$ from c-axis ultrasonic attenuation and velocity measurements performed simultaneously with the neutron diffraction experiment.

Initial measurements on Dy(II) however, indicated that the value of $T_N$, as indicated by ultrasonic measurements, was appreciably higher than the value of the transition point indicated by the neutron diffraction measurements. An experiment which simultaneously measured the peak diffracted intensities and ultrasonics was performed to investigate this effect. The particulars for this run are given in Table 3.4, together with particulars for a second similar run, which followed the first after the crystal had been thermally cycled between 170 K ($T_N - 10$ K) and 210 K ($T_N + 30$ K) for a total of five times over a period of 15 hours. This second run was executed to investigate the effect of variations in the internal strain of the crystal, as a result of its thermal treatment, on the value of $T_N$. Changes of up to 13 K in the value of $T_N$ were reported from thermal expansion measurements on Dy [82], while changes of up to 3 K were reported for a 50% Tb - 50% Ho alloy which has the same spin structure as Dy [83]. (The existence of such an effect would render the results of high resolution measurements in the vicinity of $T_N$ meaningless!)
| Magnetic satellite reflection | \((0\ 0\ 2-\delta)\) | \((0\ 0\ 2-\delta)\) |
| Temperature stabilization time (min) | 10 | 10 |
| Start of run (K) | 180.25 | 180.30 |
| End of run (K) | 177.20 | 176.80 |
| Néel temperature (K) | 178.85 | 179.33 |
| Temperature control* | ±0.04 | ±0.005 |
| Temp. increments near \(T_N\) (K) | 0.09 | 0.03/0.04 |
| Av. temp. increment(range) (K) | 0.09 | 0.09 |
| Type of scan | Peak int. counts | Peak int. counts |
| No. of scans per datum point | 4 | 4 |
| No. of scans discarded per datum point | 1.5 | 1.5 |
| Duration of scan (min) | 10 | 10 |
| Type of ultrasonic wave | Longitudinal | Longitudinal |
| Direction of propagation | c axis | c axis |
| Frequency of ultrasonic wave (MHz) | 10 | 10 |

*Since the r.f. signal had a large detrimental effect on the output from a Si-diode temperature sensor, but virtually none on the output from a Au,0.07% Fe vs. chromel thermocouple, the THOR-temperature controller had to be used, with the resulting slightly poorer temperature control. The control statistics given for the ultrasonic measurement is better than that for the neutron measurements due to the substantially shorter time involved to perform a measurement.
The results for the two runs, shown in Figure 3.7, clearly indicate a difference of 0.45 K in the values of $T_N$ as observed from the two techniques. The fact that these measurements were executed simultaneously excludes the possible conjecture that this effect may be ascribed to errors in temperature measurement. This effect will be called a "$\Delta T_N$ anomaly". Furthermore, no variation in the value of $T_N$ is observed after repeated thermal cycling. This latter result is in agreement with a similar measurement on the Dy(I) crystal by van Doorn et al. [84].

To ascertain that this $\Delta T_N$ anomaly could not be trivially explained, a number of experiments were conducted as described in Sections 3.3.2, 3.3.3 and 3.3.4.

![Ultrasonic attenuation and velocity vs. temperature](image)

Fig. 3.7 Simultaneously measured ultrasonic attenuation and velocity and peak scattered neutron intensity vs. temperature before (●) and after (■) repeated thermal cycling.
3.3.2 $T_N$ as a function of frequency

To test whether ultrasonic measurements are a reliable method of finding the value of $T_N$, a further two runs were conducted at frequencies of 30 MHz and 50 MHz respectively. Velocity measurements were however not performed at 50 MHz, since the high attenuation of the sound wave at this frequency resulted in the second echo in the echo pattern being too small to effect a reasonable overlap. The particulars of these two runs are listed in Table 3.5 and the results depicted in Fig. 3.8. For comparison the attenuation at 10 MHz, measured simultaneously with the neutron diffraction run J1, is also depicted.

**TABLE 3.5**

<table>
<thead>
<tr>
<th>Type of ultrasonic wave</th>
<th>Longitudinal c axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction of propagation</td>
<td>RUN K</td>
</tr>
<tr>
<td>Frequency of ultrasonic wave (MHz)</td>
<td>30</td>
</tr>
<tr>
<td>Start temperature (K)</td>
<td>177.80</td>
</tr>
<tr>
<td>End temperature (K)</td>
<td>180.95</td>
</tr>
<tr>
<td>Néel temperature (K)</td>
<td>179.33</td>
</tr>
<tr>
<td>Temperature control (K)</td>
<td>± 0.005</td>
</tr>
<tr>
<td>Temperature increments near $T_N$ (K)</td>
<td>0.03/0.04</td>
</tr>
<tr>
<td>Average temperature increment (range) (K)</td>
<td>0.06</td>
</tr>
<tr>
<td>Time interval between measurements (min)</td>
<td>5</td>
</tr>
</tbody>
</table>

From Fig. 3.8 it is clear that the value of $T_N$ is not influenced by the frequency of the sound wave for the frequency range 10 MHz to 50 MHz. The value of $T_N$ indicated by the velocity measurements at 30 MHz (not shown) is also $T_N = 179.33 \, \text{K}$, in agreement with the results of the attenuation measurements.
3.3.3 Neutron absorption and the $\Delta T_N$ anomaly

The penetration depth of a neutron beam incident on the (0 0 2) face of the cubically shaped Dy(II) crystal at a glancing angle of 14.4° is no more than a fraction of a millimetre due to nuclear absorption (Figure 2.6). A trivial explanation of the $\Delta T_N$ anomaly would be possible if the value of $T_N$ as observed from scattering off the (0 0 2) and (0 0 2) crystal faces differed. This is possible if, for example, an impurity concentration gradient existed along the c axis of the crystal: it has been shown that the value of $T_N$ decreases with impurity concentration for Gd [85] and it is reasonable to assume that the same would be true for Dy. The simultaneous measurement of neutron diffraction and ultrasonics was consequently repeated after a 180° rotation of the crystal to scatter off the (0 0 2) face. The particulars of the scan are given in Table 3.6 and the results are depicted in Figure 3.9. It is evident that these measurements agree with the previous results and confirm the $\Delta T_N$ anomaly.
TABLE 3.6

<table>
<thead>
<tr>
<th></th>
<th>Dy(II) RUN M</th>
<th>Dy(II) RUN N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NEUTRONS ULTRASONICS</td>
<td>NEUTRONS ULTRASONICS</td>
</tr>
<tr>
<td>Magnetic satellite reflection</td>
<td>(0 0 2-δ) 10</td>
<td>(0 0 2-δ) 10</td>
</tr>
<tr>
<td>Temperature stabilization time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start temperature</td>
<td>(K) 180.21</td>
<td>179.10</td>
</tr>
<tr>
<td>End temperature</td>
<td>(K) 177.32</td>
<td>174.75</td>
</tr>
<tr>
<td>Néel temperature</td>
<td>(K) 178.85 179.33</td>
<td>177.05 177.03</td>
</tr>
<tr>
<td>Temperature control</td>
<td>(K) ±0.04 ±0.005</td>
<td>±0.04 ±0.005</td>
</tr>
<tr>
<td>Temp. increments near $T_N$</td>
<td>(K) 0.09 0.03/4</td>
<td>0.07 0.03/4</td>
</tr>
<tr>
<td>Av. temp. increment(range)</td>
<td>(K) 0.10 0.07</td>
<td>0.09 0.06</td>
</tr>
<tr>
<td>Type of scan</td>
<td>Peak int. counts</td>
<td>Peak int. counts</td>
</tr>
<tr>
<td>No. of scans per datum point</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>No. of scans discarded per datum point</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Duration of scan</td>
<td>(min) 10</td>
<td>10</td>
</tr>
<tr>
<td>Type of ultrasonic wave</td>
<td>longitudinal</td>
<td>longitudinal</td>
</tr>
<tr>
<td>Direction of propagation</td>
<td>c axis</td>
<td>c axis</td>
</tr>
<tr>
<td>Frequency of ultrasonic wave</td>
<td>(MHz) 10</td>
<td>10</td>
</tr>
</tbody>
</table>

![Graph](image)

**Fig. 3.9** Simultaneously measured ultrasonic attenuation and velocity and peak neutron intensity scattered off the (002) face of Dy(II) vs temperature
3.3.4 The \( C_{44} \) elastic constant

A final test of the \( \Delta T_N \) anomaly for the Dy(II) crystal was to measure the ultrasonic velocity of a shear wave propagating along the a axis and polarized along the c axis simultaneously with the neutron diffraction measurements. From simultaneous neutron diffraction and ultrasonic velocity measurements performed in this configuration on Dy (I), Van Doorn et al. [84] observed that \( \Delta C_{44} \), the magnetically renormalized value of \( C_{44} \), was proportional to the square of the sublattice magnetization over a large temperature range. The value of \( C_{44} \) was found by subtracting a linear extrapolation of the measurements in the paramagnetic region from \( C_{44} \) in the planar helically ordered region. The particulars for this experiment on Dy(II) are given in Table 3.7. The measurements are depicted in Figure 3.10. Values of \( T_N = 179.33 \) K and \( T_N = 178.85 \) K are again indicated by these two techniques respectively, in confirmation of the results of the preceding paragraphs.

### Table 3.7

<table>
<thead>
<tr>
<th>Magnetic satellite reflection</th>
<th>Dy (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature stabilization time</td>
<td>(min)</td>
</tr>
<tr>
<td>Start temperature</td>
<td>(K)</td>
</tr>
<tr>
<td>End temperature</td>
<td>(K)</td>
</tr>
<tr>
<td>Néel temperature</td>
<td>(K)</td>
</tr>
<tr>
<td>Temperature control</td>
<td>(K)</td>
</tr>
<tr>
<td>Temperature increments near ( T_N )</td>
<td>(K)</td>
</tr>
<tr>
<td>Temperature increments away from ( T_N )</td>
<td>(K)</td>
</tr>
<tr>
<td>Type of scan</td>
<td>(deg)</td>
</tr>
<tr>
<td>Angular range of scan</td>
<td>(deg)</td>
</tr>
<tr>
<td>Step size in ( \omega )</td>
<td>(deg)</td>
</tr>
<tr>
<td>No of neutron scans per datum point</td>
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<tr>
<td>No of scans discarded per datum point</td>
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</tr>
<tr>
<td>Duration per scan</td>
<td>(min)</td>
</tr>
<tr>
<td>Type of ultrasonic wave</td>
<td>(MHz)</td>
</tr>
<tr>
<td>Frequency of ultrasonic wave</td>
<td>transverse</td>
</tr>
<tr>
<td>RUN 0</td>
<td></td>
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<tr>
<td>NEUTRONS</td>
<td></td>
</tr>
<tr>
<td>ULTRASONICS</td>
<td></td>
</tr>
<tr>
<td>(0 0 2-5) 10</td>
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</tr>
<tr>
<td>184.4</td>
<td></td>
</tr>
<tr>
<td>167.5</td>
<td></td>
</tr>
<tr>
<td>178.85 ±0.04</td>
<td>179.33 ±0.005</td>
</tr>
<tr>
<td>0.11</td>
<td>0.80</td>
</tr>
<tr>
<td>ω,28</td>
<td>1.728</td>
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<td>0.036</td>
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<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td></td>
</tr>
<tr>
<td>transverse</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>
3.3.5 **Search for a $\Delta T_N$ anomaly in Dy(I)**

To determine whether the $\Delta T_N$ anomaly also occurs for the Dy(I) crystal, a similar investigation to that described in Section 3.3.1 was carried out on this crystal. The particulars of this run are also given in Table 3.6. The velocity and attenuation measurements are depicted in Figure 3.11 as well as the peak intensity counts. Unlike the case for Dy(II), the values of $T_N$ as indicated by ultrasonics and neutrons respectively are identical within experimental resolution. An investigation of the dependence of the value of $T_N$ on the frequency of the ultrasonic wave again yielded no effect for the frequency range 10 MHz to 50 MHz.
Fig. 3.11 Simultaneously measured ultrasonic attenuation and velocity and peak scattered neutron intensity vs temperature for Dy(I)

3.4 CRITICAL EXPOONENTS $\beta$ AND $\gamma$

As discussed in previous sections, earlier renormalization group calculations [52-54] predicted that the planar helical $\leftrightarrow$ paramagnetic phase transition as exhibited by Dy, Ho and Tb is of second order and the behaviour of the sublattice magnetization in the Néel temperature is described by a $\beta=0.39$ critical exponent. This prediction was supported by subsequent neutron diffraction measurements. Eckert and Shirane reported a value of $\beta=0.39$ (+0.04, −0.03) for Ho [57] and Du
Plessis et al. a value of $\beta=0.39 \pm 0.04$, $-0.02$ for Dy [58]. The high resolution neutron diffraction measurements complemented with ultrasonic attenuation and velocity measurements and reported in Section 3.2, failed to observe the discontinuous behaviour at the critical point predicted by more recent renormalization group calculations [56]. To comprehensively evaluate the nature of this phase transition, the investigation was extended to determine the value of $\beta$ for both Dy(I) and Dy(II). This re-investigation of an exponent that has already been shown to agree with the earlier renormalization group prediction (for Dy(I)) was prompted by the anomalous behaviour of the Dy(II) crystal reported in Section 3.3 as well as the fact that an improvement of a factor 2.5 in temperature control and a factor 10 in neutron intensities could be obtained compared to the previous investigation on Dy(I) [58].

3.4.1 Corrections to data

The sublattice magnetization is related to the intensity of the magnetic satellite reflection through [73]:

$$I_{\text{magn}} \propto M^2 = A t^{2\beta}$$  \hspace{1cm} (3.2)

However, a number of other factors contribute to the scattered intensity and have to be corrected for to obtain the purely magnetic intensity.

1) The general background intensity was obtained from a linear extrapolation of the scattered intensity in the regions adjacent to the magnetic peak, as illustrated in Figure 3.12.

2) The distance in reciprocal space between the magnetic satellite reflection and the origin changes due to the variation of the interlayer turn angle with temperature. This results in a change in the magnetic form factor (which decreases with $\sin \theta/\lambda$ [67]). For the temperature ranges over which the runs on the two dysprosium crystals extended, the variation in the square of the magnetic form factor is
Fig. 3.12 A typical $\omega,2\theta$-scan for Dy, showing the subtraction of background estimated at less than 0.05% from the data of Koehler et al. [6]. This variation is an order of magnitude less than the statistical error $\sqrt{N/N}$ on the largest measured intensities and was consequently ignored.

3) The neutron beam is subject to secondary extinction as discussed in Section 2.3.6. The magnitude of the extinction is difficult to calculate since it is, amongst others, a function of the mosaic spread $\Delta(\eta)$ of the crystal and the mean free path length $t$ of a neutron through a mosaic block - with both quantities usually unknown. A more empirical approach is consequently often employed to correct for the effect of secondary extinction. A number of these are:
(a) The levelling off of the Bragg scattered intensity $I(\Sigma)$ as a function of $\Sigma^{\text{OT}}$ using a Monte Carlo technique is attributed to extinction [86]. In general, $\Sigma$ can not be estimated accurately, but a comparison of the calculated and measured ratios for the magnetic and nuclear scattered intensities at a fixed temperature does yield the extinction at this temperature. The value of $\Sigma$ can then be found from the $I(\Sigma)$ vs $\Sigma$ curve and consequently the extinction for any intensity.

(b) Du Plessis et al. [58] evaluated the ratio of the intensities of a strong and a weak satellite reflection and observed a marked decrease at low temperatures. Assuming that the extinction in the case of the weak reflection is negligible, the parameter $x$ in Zachariasen's equation

$$ y = \frac{1}{\sqrt{1 + 2x}} $$

(3.3)

for the extinction factor $y$ can be found.

(c) Eckert and Shirane [57] compared the intensities of four different satellite reflections and simply rejected the data for the strongest reflection as being influenced by extinction.

(d) In the present investigation the measurements were restricted to a few Kelvin below the transition temperature, where the intensity of the magnetic reflection is weak and Equation (2.24) for the integrated intensity from a rotating crystal reduces to

$$ R^\theta \approx Q \nu $$

(3.4)

The reflection is consequently subject to very little extinction. During the analysis of the data the temperature range below $T_N$ over which the least squares fit was performed was incrementally decreased by repeatedly discarding the intensity measurement at the lower extremity of the temperature range. If
these intensities were still subjected to extinction, it would be reflected in the value of \( \beta \) which should approach a limiting value - the extinction free value - as the temperature range is repeatedly reduced.

(4) At the phase transition the exchange interaction forces and the thermal agitation compete with equal vigour, with the result that the magnetic moments order in dynamically fluctuating localized domains. These domains which have a maximum size at the transition temperature undergo large fluctuations in both position and time and are characterized by a relaxation time \( \tau_q \) which is larger than the time of transit \( t_d \) of a neutron through a domain. These fluctuating domains consequently give rise to coherent scattering. At temperatures below and above \( T_N \), order or disorder respectively dominates and the relaxation time of the fluctuations decreases sharply to values below \( t_d \).

The abovementioned scattering near the transition point is called critical scattering [67] and is asymmetrical with respect to \( T_N \):

\[
I_C = C_\pm |t|^{-\gamma}
\]

\[
t = \frac{T_N - T}{T_N}
\]

where the subscripts \( + \) and \( - \) refer to values above and below \( T_N \). The value of \( \gamma \) is considered the same above and below the transition on account of the scaling hypothesis.

To find the magnitude of the critical scattering below \( T_N \) the values of \( \gamma \) and \( C_+ \) are first obtained from a \( \log I_C \) vs \( \log t \) plot. The value of \( C_- \) can then be calculated using Schofield's parametric representation of the equation of state [87]:

\[
C_- = C_+ \left[ \frac{2\Delta(\gamma - 1)}{(1-2\beta)\gamma} \right]^{(\gamma-1)}
\]

3.4.2 Critical exponents of Dy(I)

The particulars of the measurements performed on Dy(I) are listed in Table 3.8.
TABLE 3.8

<table>
<thead>
<tr>
<th></th>
<th>Dy(I) Run P</th>
<th>Dy(II)* Run Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic satellite reflection</td>
<td>(0 0 2-δ)</td>
<td>(0 0 2-δ)</td>
</tr>
<tr>
<td>Temperature stabilization time</td>
<td>(min) 15</td>
<td>45</td>
</tr>
<tr>
<td>Start temperature</td>
<td>(K) 174.17</td>
<td>175.06</td>
</tr>
<tr>
<td>End temperature</td>
<td>(K) 183.14</td>
<td>186.49</td>
</tr>
<tr>
<td>Background measurement</td>
<td>(K) 198.50</td>
<td>196.46</td>
</tr>
<tr>
<td>Néel temperature from least squares fit</td>
<td>(K) 177.18</td>
<td>179.09</td>
</tr>
<tr>
<td>Temperature control</td>
<td>(K) ±0.03</td>
<td>±0.02</td>
</tr>
<tr>
<td>Temperature increments near $T_N$</td>
<td>(K) 0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Average temp. increment (range)</td>
<td>(K) 0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Type of scan</td>
<td>ω,2θ</td>
<td>ω,2θ</td>
</tr>
<tr>
<td>Angular range of scan</td>
<td>(deg) 1.980</td>
<td>2.592</td>
</tr>
<tr>
<td>Step size</td>
<td>(deg) 0.036</td>
<td>0.036</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Duration of scan</td>
<td>(min) 29</td>
<td>45</td>
</tr>
</tbody>
</table>

* Reactor power = 10 MW

Values of $\gamma = 1.2 \pm 0.2$ and $C_+ = 0.20 \pm 0.02$ were attained from a log I vs log t plot for the paramagnetic data, as illustrated in Fig. 3.13, using a value of $T_N = 177.15$ K.

A fit of data below $T_N$ gives the least squares values of $\beta$ and $T_N$ as shown in Table 3.9 for decreasing temperature ranges. The highest temperature point included in each range was 176.995 K.
Fig. 3.13  log I vs log t plot for Dy(I)

TABLE 3.9

<table>
<thead>
<tr>
<th>Fit depicted in Fig. 3.14</th>
<th>Lowest temperature included</th>
<th>$\beta$</th>
<th>$T_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>176.497</td>
<td>0.382</td>
<td>177.19</td>
</tr>
<tr>
<td></td>
<td>176.369</td>
<td>0.385</td>
<td>177.19</td>
</tr>
<tr>
<td></td>
<td>176.310</td>
<td>0.387</td>
<td>177.19</td>
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<tr>
<td></td>
<td>176.197</td>
<td>0.393</td>
<td>177.19</td>
</tr>
<tr>
<td></td>
<td>176.061</td>
<td>0.392</td>
<td>177.19</td>
</tr>
<tr>
<td></td>
<td>175.968</td>
<td>0.385</td>
<td>177.19</td>
</tr>
<tr>
<td></td>
<td>175.820</td>
<td>0.386</td>
<td>177.18</td>
</tr>
<tr>
<td></td>
<td>175.759</td>
<td>0.384</td>
<td>177.18</td>
</tr>
<tr>
<td></td>
<td>175.659</td>
<td>0.379</td>
<td>177.18</td>
</tr>
<tr>
<td></td>
<td>175.580</td>
<td>0.374</td>
<td>177.18</td>
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<tr>
<td></td>
<td>175.501</td>
<td>0.373</td>
<td>177.18</td>
</tr>
<tr>
<td></td>
<td>175.411</td>
<td>0.372</td>
<td>177.17</td>
</tr>
<tr>
<td></td>
<td>175.182</td>
<td>0.367</td>
<td>177.17</td>
</tr>
<tr>
<td></td>
<td>174.936</td>
<td>0.358</td>
<td>177.16</td>
</tr>
<tr>
<td></td>
<td>174.695</td>
<td>0.363</td>
<td>177.16</td>
</tr>
<tr>
<td></td>
<td>174.464</td>
<td>0.355</td>
<td>177.15</td>
</tr>
<tr>
<td></td>
<td>174.171</td>
<td>0.348</td>
<td>177.15</td>
</tr>
</tbody>
</table>
From Table 3.9 it can be seen that the critical exponent assumes smallest values when lower temperature measurements are included in the fit. This is attributed to extinction. When successive smaller ranges below $T_N$ are considered, the value of the exponent tends to $\beta = 0.39 \pm 0.01$. This value is considered to be extinction free. The corresponding Néel temperature is $T_N = 177.19 \pm 0.03$ K.

The effect of extinction is illustrated in Figure 3.14 which depicts the

(i) experimentally measured intensities,

(ii) theoretical curve corresponding to the critical scattering and

(iii) theoretical curve for $M^2$ for the three least squares fits (1), (2) and (3) indicated in Table 3.9.

[Graph showing integrated intensity vs. temperature for Dy(I) with points and curves indicating different fits with $T_N$ and $\beta$ values.]
The value of $\beta = 0.39 \pm 0.01$ is in good agreement with the predicted value of $\beta = 0.39$. The value of $\gamma = 1.2 \pm 0.2$ on the other hand does not compare favourably with the predicted value of $\gamma = 1.39$. It must however be pointed out that the neutron scattered intensities in the paramagnetic region resulting from critical scattering are very weak and a reliable analysis of these measurements is not feasible - hence the large error bar on the value of $\gamma$.

### 3.4.3 Critical exponents of Dy(II)

The particulars of the measurements performed on Dy(II) are also listed in Table 3.8. For the neutron diffraction measurements, the bulk of the crystal was screened from neutrons using cadmium foil in such a way that only two small pillars were exposed to the neutron beam as illustrated in Fig. 3.15.

![Diagram of Dy(II) crystal with neutron beam and Cd-shielding](image)

**Fig. 3.15** The Dy(II) crystal indicating the Cd shielding

From Figure 3.16, which is a log $I$ vs log $t$ plot of the measurements in the paramagnetic region, it can be seen that the relationship $I_{C+} = C_+ |t|^{-\gamma}$ is not obeyed with a unique value of $\gamma$. Rather it seems that the best description is given by two distinct slopes that intersect at a temperature of $(T_N + 2.8)$ K. One recalls that a deviation from the exponent description of the critical part of the thermal expansion of the Dy(II) crystal in its paramagnetic region was reported by Zochowski et al. for temperatures below $(T_N + 0.13)$ K.
Thus in both experiments the Dy(II) crystal behaved anomalously in the paramagnetic region near $T_N$. Whether these effects as well as the $\Delta T_N$ effect of paragraph 3.3.1 are related, await further detailed studies.

In view of the uncertainty regarding the critical scattering for the Dy(II) crystal in its paramagnetic region, the measurements in the ordered region were rather analyzed using the value of $\gamma = 1.2$ obtained for the Dy(I) crystal. The amplitude of the critical scattering was found empirically by executing least squares fits over a fixed temperature range using different values of $C_\pm$. The appropriate value of $C_\pm = 0.35$ was indicated by the best fit, as observed from the $\chi^2$ fitting parameter. The critical scattering correction is small and the preceding pragmatic approach will not seriously effect the $\beta$ fit.

![Graph showing log I vs log t for Dy(II)](image)

**Fig. 3.16** Log I vs log t plot for Dy(II)

Table 3.10 shows values of $\beta$ and $T_N$ obtained from least squares fits executed over decreasing temperature ranges below $T_N$. The highest temperature measurement included in each range was 178.986 K. The theoretical curves corresponding to the three ranges indicated in Table 3.10 are compared to the experimental measurements in Figure 3.17.
<table>
<thead>
<tr>
<th>Fit depicted in Fig. 3.17</th>
<th>Lowest temperature included</th>
<th>$\beta$</th>
<th>$T_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>178.496</td>
<td>0.381</td>
<td>179.18</td>
</tr>
<tr>
<td></td>
<td>178.323</td>
<td>0.374</td>
<td>179.17</td>
</tr>
<tr>
<td></td>
<td>178.163</td>
<td>0.367</td>
<td>179.16</td>
</tr>
<tr>
<td></td>
<td>178.027</td>
<td>0.353</td>
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<td></td>
<td>177.843</td>
<td>0.337</td>
<td>179.13</td>
</tr>
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<td>2</td>
<td>177.674</td>
<td>0.335</td>
<td>179.13</td>
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<tr>
<td></td>
<td>177.550</td>
<td>0.328</td>
<td>179.12</td>
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<td>177.380</td>
<td>0.321</td>
<td>179.11</td>
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<td></td>
<td>177.124</td>
<td>0.312</td>
<td>179.10</td>
</tr>
<tr>
<td></td>
<td>177.828</td>
<td>0.309</td>
<td>179.09</td>
</tr>
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<td>176.547</td>
<td>0.309</td>
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<td>176.245</td>
<td>0.306</td>
<td>179.09</td>
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<tr>
<td>3</td>
<td>175.911</td>
<td>0.302</td>
<td>179.08</td>
</tr>
<tr>
<td></td>
<td>175.577</td>
<td>0.306</td>
<td>179.09</td>
</tr>
</tbody>
</table>

From Table 3.10 and Fig. 3.17 it is clear that the transition is described by different values of the critical exponent for different temperature regions below $T_N$. A value of $\beta = 0.39$ adequately describes the magnetization for only a limited region of 0.8° below $T_N$. The deviation of the experimentally measured points from the theoretical curve corresponding to $\beta = 0.39$ at lower temperatures is again ascribed to extinction. It is noticed that the extinction for the Dy(II) crystal is substantially larger than was the case for Dy(I). This is attributed to the fact that the Dy(II) crystal is of
higher quality than the Dy(I) crystal, as is evident from their relative resistance ratios (62.6 for Dy(II) and 12.5 for Dy(I)) and the relative widths of the attenuation peaks (0.1 K for Dy(II) and 0.5 K for Dy(I)).

![Graph showing integrated intensity vs. temperature for Dy(II)](image)

Fig. 3.17 Integrated intensity vs. temperature for Dy(II) (●). Also indicated are the three curves for $H^2$ corresponding to the fits discussed in the text.

3.5 DISCONTINUOUS BEHAVIOUR OF THE ORDER PARAMETER BELOW $T_N$

The nature of the basal plane helical ↔ paramagnetic phase transition in Dy and Ho was investigated to high resolution in the preceding part of this chapter and was observed as continuous, with an exponent that describes the sublattice magnetization which is equal to the renormalization group value of $\beta = 0.39$ in the case of Dy(I) (this investigation) as well as for Ho [57]. Amitin et al.
[88, 89] however, analyzed electrical resistance and magnetic specific heat measurements in the vicinity of $T_N$ and found unreconcilable behaviour above and below $T_N$. Furthermore, no reasonable fit of the specific heat measurements to the scaling relationship

$$\frac{C_M}{T} \propto t^{-\alpha} \quad (3.8)$$

for which the renormalization group method predicts a value of $\alpha = -0.17$ was obtained. Their measurements could also not be explained in terms of a first order transition [56, 89]. To explain the observed behaviour, Amitin et al. [89] proposed that in the vicinity of $T_N$ dysprosium might be approximated by a quasi-degenerate two-dimensional model. This assumption is valid if the interplanar interactions $J_z$ are small compared to the intraplanar interactions $J$. Energy considerations [89] favour the formation of a vortex magnetic structure in which the spins are inclined with respect to an arbitrary axis by an angle $\phi_i$, with adjacent angles nearly equal.

Considering only nearest neighbour interactions, the Hamiltonian in two dimensions can be written as [90]

$$H = -JS^2 \sum_{\vec{r}} \cos |\Delta \phi(\vec{r})|, \quad (3.9)$$

where $$\Delta \phi(\vec{r}) = \phi_i - \phi_j. \quad (3.10)$$

Further $$\sum \Delta \phi(\vec{r}) = 2\pi q; \quad q = 0, \pm 1, \pm 2, \ldots \quad (3.11)$$

where the summation is over a closed path containing the centre of a vortex.

By writing

$$\phi(\vec{r}) = \bar{\phi}(\vec{r}) + \psi(\vec{r}), \quad (3.12)$$
where $\psi(\vec{r})$ denotes the deviation from the angular distribution of spins $\phi(\vec{r})$ for a particular configuration, an expansion of the energy of the system around a local minimum of $H$ yields

$$H - E_0 = J S^2 \iint d^2 \vec{r} (\nabla \psi)^2 - 4\pi^2 J S^2 \iint d^2 \vec{r} d^2 \vec{r}' \rho(\vec{r}) g(\vec{r} - \vec{r}') \rho(\vec{r}')$$

$$+ 2\pi J S^2 \iint d^2 \vec{r} d^2 \vec{r}' \rho(\vec{r}) \rho(\vec{r}') \ln \frac{R}{r_0}$$

(3.13)

where $R$ is the radius of the system, $r_0$ a cut-off value for $\vec{r}$, $g(\vec{r})$ the Green function of the square lattice with $g(0) = 0$, and $\rho(\vec{r}) = \frac{1}{2\pi} \nabla^2 \phi(\vec{r})$ the vortex distribution function.

The first term represents low-energy spin wave excitations and the second the interaction energy of the vortices. The last term ensures that the system remains electrically neutral, i.e. that the total vorticity of the system tends to zero, which is achieved through the coupling of the vortices in pairs of opposite rotation.

The behaviour of the magnetic specific heat predicted by this model is [91]

$$\frac{C_M}{T} \propto \tau^{-2} e^{-b/\sqrt{\tau}}$$

(3.14)

$$\tau = \frac{T - T_1}{T_1}$$

(3.15)

with $T_1$ the Kosterlitz-Thouless transition temperature (which is presumably slightly below $T_N$).

This prediction proved to be an adequate description of the behaviour of the specific heat observed by Amitin et al. [89] for the range $0.00005 < \tau < 0.012$. At $T_1$ the spin wave excitations are responsible for destroying the vortex structure, while the lower boundary at a temperature $T_2$ is determined by the increase in the crystal-field anisotropy [92], which restores the three-dimensional nature of the system. According to Amitin et al. [63] this transition was observed for dysprosium as a strain discontinuity of
in thermal expansion measurements along the c axis. This discontinuity, which occurred at a temperature of $T_2 = 171.1 \text{ K}$, 7.8 K below the Néel temperature, was only observed upon cooling. Its absence upon heating was ascribed to the fact that the long range order of the helical state is retained because "internal fields in the magnetically ordered region suppress the transition into the vortex state".

Neutron scattering measurements were executed to investigate the existence of this vortex magnetic structure: coherent neutron scattering is not expected from this structure as the net vorticity is zero. Furthermore, even if a helical ordering co-existed with the vortex structure, at least a discontinuity in the order parameter should occur at the temperature $T_2$.

Two sets of integrated neutron scattered intensity measurements, each consisting of a cooling run followed by a heating run, were performed over temperature ranges extending to 12.5 K and 19.5 K below $T_N$ respectively. The particulars of the two sets of runs are given in Table 3.11 and the measurements depicted in Figure 3.18.

| TABLE 3.11 |

<table>
<thead>
<tr>
<th>Magnetic satellite reflection</th>
<th>RUN R1</th>
<th>RUN R2</th>
<th>RUN S1</th>
<th>RUN S2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature stabilization time (min)</td>
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<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start temperature (K)</td>
<td>178.4</td>
<td>164.4</td>
<td>178.7</td>
<td>157.6</td>
</tr>
<tr>
<td>End temperature (K)</td>
<td>164.4</td>
<td>178.9</td>
<td>157.6</td>
<td>178.5</td>
</tr>
<tr>
<td>Pause at turning point (h)</td>
<td>2</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background measurement (K)</td>
<td>186.5</td>
<td></td>
<td>193.0</td>
<td></td>
</tr>
<tr>
<td>Néel temperature (K)</td>
<td></td>
<td></td>
<td></td>
<td>17.1</td>
</tr>
<tr>
<td>Temperature control (K)</td>
<td></td>
<td></td>
<td></td>
<td>± 0.02</td>
</tr>
<tr>
<td>Average temperature increments (K)</td>
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<td></td>
<td>0.7</td>
</tr>
<tr>
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<td>$\omega_{2\theta}$</td>
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</tr>
<tr>
<td>Angular range of scan (deg)</td>
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<td>1.728</td>
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Fig. 3.18 Temperature dependence of the integrated \((0\,0\,2-\delta)\) satellite intensity for the two runs respectively indicated by circles and squares. Closed symbols refer to the cooling part of each run and open symbols to the heating part.

The absence of any discontinuous behaviour of the order parameter below \(T_N\) contradicts the proposed vortex magnetic ordering. It is consequently concluded that the magnetic ordering in the antiferromagnetic phase is the basal plane helical structure. This ordering occurs either upon cooling from the paramagnetic region or upon heating from the ferromagnetic region.

3.6 THE INCOMMENSURATE ↔ COMMENSURATE PHASE TRANSITION IN DYSPROSIUM

In contrast to the antiferromagnetic↔paramagnetic phase transition in dysprosium and holmium, the ferromagnetic↔antiferromagnetic phase transition is well documented and known to be of first order (Section 1.2.8). In the helical phase the wave vector that describes the modulation of the magnetic moments is incommensurate with the underlying hexagonal lattice, except at a number of discrete temperatures. On the other hand, the wave vector that describes the
ferromagnetic phases of these elements is commensurate with the crystal lattice, having a value of \( q = 0 \) for the basal plane ferromagnetic structure of Dy [6] and a value of \( q = \frac{1}{6}b_3 \) for the conical ferromagnetic structure of Ho [14].

The field of incommensurate <-> commensurate phase transitions has been actively studied for a number of physical systems following the pioneering work of Frank and Van der Merwe [93 - 95]. The transition in a uniaxial periodic system passing from the commensurate to the incommensurate phase is associated with the creation of domain walls, separating domains of commensurate commensurate order in the incommensurate phase [96,97].

In two dimensions the difference between the wave vectors \( q \) and \( q_0 \) that describe respectively the incommensurate and commensurate phases vanishes on approaching the transition while the mean spacing between the domain walls diverges. The behaviour of the wave vector in the transition region can be described by a \( \beta \)-exponent power law

\[
q(\delta) - q_0 \propto (\delta - \delta_c)^\beta
\]

(3.16)

where \( \delta \) is the driving force (e.g. temperature) and \( \delta_c \) is the value of \( \delta \) at the transition point.

A \( \beta \)-exponent of 0.5 was predicted for a two-dimensional system [98,99] and initially also thought to apply to a three-dimensional system [100,101]. However, Fisher and Fisher [96] and Nattermann [97] showed that a minimization of the free energy of a three-dimensional system leads to a value of \( \beta = 0 \). The free energy of the system, with \( \ell \) the mean spacing between domain walls and \( L \) the length of the system of cross-sectional area \( A \) is [96]

\[
F_V(\ell) = \frac{L}{\ell} \mu_0(T,\delta) - \frac{L}{\ell} T S_A(T,\delta,\ell) + \frac{L}{\ell} A W(T,\delta,\ell).
\]

(3.17)

\( U_0(T,\delta) \) is the energy of a localized domain in a commensurate matrix per unit area and varies smoothly through the transition,
\( S_A(T, \delta, \ell) \) originates in the confinement of a domain wall due to its encompassment by other domain walls and consists of the entropy associated with (i) the mean position coordinate of the domain wall, \( k_B \ln (\ell/a) \), which is not significant in the general case where \( A \) diverges at the transition point, and (ii) the loss of entropy as a consequence of the restriction that the domain walls may not touch or overlap,

\( W(T, \delta, \ell) \) originates in the free energy of interaction between domain walls, which decays exponentially through the transition if the underlying interactions have a short range nature

\[
W(\ell) \sim W_0 \bar{q} e^{-K/\bar{q}}, \tag{3.18}
\]

where \( |\bar{q}| = \frac{2\pi}{p\ell} \) measures the degree of incommensurability in the commensurate phase of order \( p \) and \( K = \frac{2\pi p}{\xi} \), with \( \xi \), the uniaxial correlation length.

For three-dimensional systems the last term dominates the behaviour in the critical region, which is then described by:

\[
\bar{q}(\delta) \propto \frac{1}{\ln(\delta - \delta_c)^{-1}} \tag{3.19}
\]

Theodorou [102] analysed the data of Koehler et al. on their Ho(B) crystal [14] and found that the mean-field behaviour was not obeyed, but that the transition was described by

\[
\bar{q} - \bar{q}_c \propto \left( \frac{T-T_c}{T_c} \right)^\beta \tag{3.20}
\]

with \( \beta = 0.34 \pm 0.08 \).

Since this fit was valid up to 40 K above \( T_c \), and the mean-field model is only valid in a narrow temperature range around
$T_c$ [102, 103], Theodorou contends that the power law behaviour cannot be explained with a model based on commensurate domains separated by incommensurate domain walls.

The behaviour of the incommensurate↔commensurate transition in Dy at $T_c$ was studied as part of this investigation employing $\omega$,$2\theta$ neutron diffraction scans over the $(0 0 2+\delta)$ satellite reflections, including the $(0 0 2)$ nuclear reflection. The particulars of two runs, a cooling run immediately followed by a heating run, are listed in Table 3.12.

**TABLE 3.12**

<table>
<thead>
<tr>
<th></th>
<th>Dy (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RUN T1</td>
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<tr>
<td>Magnetic satellite reflection</td>
<td>(0 0 2−\delta) ↔ (0 0 2+\delta)</td>
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<tr>
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<td>Start temperature (K)</td>
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<td>End temperature (K)</td>
<td>80</td>
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<td>Curie temperature (K)</td>
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</tr>
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<td>Néel temperature (K)</td>
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</tr>
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<td>Average temperature increments near $T_c$ (K)</td>
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</tr>
<tr>
<td>Type of scan</td>
<td>$\omega$, $2\theta$</td>
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<td>Angular range of scan (deg)</td>
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<td>Number of scans per datum point</td>
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<tr>
<td>Duration of scan (min)</td>
<td>32</td>
</tr>
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</table>

The angular positions of the reflections - obtained by fitting both a parabola and a centroid to the experimental data points - agreed to ±0.02° for the two fits.

The interlayer turn angles for the $(0 0 2+\delta)$ satellite reflections
\[ \omega_\pm = \frac{q c}{2} \]  

(3.21)

were obtained from the angular positions of the reflections using

\[ \sin (\Theta_{\text{nucl}} \pm \epsilon_\pm) = \frac{\lambda}{2c} (\ell \pm \frac{\omega_\pm}{2\pi}) \]  

(3.22)

where \( \epsilon_\pm \) denotes the angular displacement of the (0 0 2±\delta) satellite reflections from the nuclear reflection and \( \Theta_{\text{nucl}} = \text{arc} \sin(\lambda/c) \) is the Bragg angle for the nuclear reflection.

The data was corrected for the c axis thermal expansion [104]. This correction however, had an effect of not more than 0.1° in turn angle over the temperature range investigated – compared to assuming a fixed value for c.

---

**Fig. 3.19.** Temperature dependence of the helical turn angle for dysprosium. For clarity only every second point is shown for the region below 101 K.
The values of the turn angles for the (0 0 2−δ) and (0 0 2+δ) satellite reflections are depicted in Figure 3.19. As a consequence of the thermal hysteresis in T_C, the values of the turn angle near T_C obtained upon heating are approximately 0.3° lower than the values obtained upon cooling.

The first order nature of the ferromagnetic ↔ antiferromagnetic phase transition is illustrated in Figure 3.20, where squares and triangles respectively indicate the values of the sum of the integrated intensity of the two satellites and the ferromagnetic intensity obtained from the (0 0 2) reflection (after subtraction of the nuclear scattering). The helically magnetic scattered intensity is obtained from the sum of the (0 0 2−δ) and (0 0 2+δ) intensities. Each of these is substantially less intense than the (0 0 2) nuclear reflection on which the ferromagnetic scattered intensity is superimposed. The latter intensity is consequently expected to be subject to appreciably more extinction as seen in Fig. 3.20.

Fig. 3.20 The temperature dependence of the sum of the integrated intensities for the (0 0 2−δ) and (0 0 2+δ) satellite reflections is depicted by squares. Also indicated by triangles is the ferromagnetic scattering observed from the (0 0 2) reflection. Results observed upon cooling are indicated by closed symbols and results observed upon heating by open symbols.
Finally, the validity of Eqs (3.19) or (3.20) as a description for the temperature dependence of the incommensurate wave vector is considered. The results for the interlayer turn angle as observed upon cooling were fitted to Eqs (3.19) and (3.20) using a value of $T_C = 86.0$ K. Excellent agreement with the mean-field theory of Eq (3.19) is observed as shown in Fig. 3.21 for a large temperature range of 32 K above $T_C$. In contrast, no agreement was found between the experimental data and the $\beta$-exponent behaviour of Eq (3.20) as is indicated in Fig. 3.22. It is evident from Fig. 3.20 that ferromagnetic scattering extends to not more than 8 K above $T_C$. Consequently the agreement up to a temperature $T_C + 32$ K with a model based on the existence of ferromagnetic domains is surprising. It is clear that these incommensurate→commensurate transitions are at present not well understood and it would be of interest to study other incommensurate→commensurate systems.

Fig. 3.21  The wave vector $(q - q_C)/b_3^*$ versus $(\ln t)^{-1}$ where $t = (T - T_C)/T_C$, indicating mean-field behaviour for dysprosium
Fig. 3.22 A logarithmic plot of $\ln \left( \frac{q - q_c}{b_3^*} \right)$ vs $\ln t$ where $t = (T - T_C)/T_C$, showing that a $\beta$-exponent power law is not obeyed.
CHAPTER IV

4.1 INTRODUCTION

4.2 ORDER OF THE c AXIS SINUSOIDALLY MODULATED ↔ PARAMAGNETIC PHASE TRANSITION IN ERBIUM

4.2.1 Neutron diffraction measurements
4.2.2 Ultrasonic measurements

4.3 SIMULTANEOUS MEASUREMENT OF NEUTRON DIFFRACTION AND ULTRASONICS

4.4 THE CRITICAL EXONENTS β AND γ

4.5 INFLUENCE OF ANNEALING ON THE $\Delta T^*_N$ EFFECT OF ERBIUM

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4.1 INTRODUCTION

The nature of the magnetic ordering in erbium has been the subject of a number of earlier neutron diffraction investigations: in a first investigation [17] first order satellites associated with all \((h k \ell)\) reflections, except the \((0 0 \ell)\) reflections, were observed below \(T_N\), indicating a transition to an antiferromagnetic phase in which the magnetic moments exhibit a sinusoidal modulation along the \(c\) axis. Later investigations [18,19] revealed the existence of higher order satellite reflections - the third and fifth harmonics exist at temperatures up to 75 K and 55 K respectively - indicating a gradual squaring up of the sinusoidal modulation. None of these investigations, however, attempted to address the nature of the phase transition. A few other investigations were conducted in the vicinity of the Néel temperature:

(i) Measurement of longitudinal attenuation at the phase transition [105] indicated that the critical attenuation above \(T_N\) in erbium is well described by the predictions of Laramore and Kadanoff for an isotropic rare earth metal [106,107]. This analysis assumed that the phase transition was of second order.

(ii) Muon spin relaxation measurements in the vicinity of \(T_N\) indicate that the relaxation rate \(\Lambda(T)\) does not exhibit the mean field temperature dependence \((T-T_N)^{\frac{1}{2}}\) [108]. This has been interpreted as indicating a possible first order transition.

Apart from the general mean field estimates, theoretical predictions of the nature of this transition, which belongs to a universality class characterized by a \(n=2\) component order parameter [109], are equally lacking.

An experimental investigation into the nature of the \(c\) axis sinusoidally modulated \(\leftrightarrow\) paramagnetic phase transition was consequently
undertaken, utilizing neutron diffraction and ultrasonic techniques, to determine

(i) the order of the transition,
(ii) the critical exponent $\beta$ that describes the spontaneous magnetization (for a second order phase transition), and
(iii) the behaviour of the ultrasonic velocity and attenuation in the critical region.

The erbium crystals employed for these investigations and designated as Er(I), Er(II) and Er(III), come from the same batch and were obtained from Goodfellow Metals (Section 1.4). The different crystals are distinguished as follows:

(i) Er(I) has the narrowest and most symmetrical diffraction peak of all three crystals. This crystal however is not suitable for ultrasonic measurements.
(ii) Er(II) is of a slightly inferior crystallographic quality compared to Er(I). It has a geometry suitable for ultrasonic measurements.
(iii) Er(III) is a thin disk shaped crystal, cut from a third erbium crystal for measurement of the critical exponent $\beta$. A thin sample was required to minimize the effect of extinction in the neutron diffraction measurements.

4.2 ORDER OF THE c AXIS SINUSOIDALLY MODULATED $\leftrightarrow$ PARAMAGNETIC PHASE TRANSITION IN ERBIUM

4.2.1 Neutron diffraction measurements

Peak intensity measurements of the (1 0 5) magnetic satellite reflection were conducted on the Er(I) crystal. Particulars of the run are listed in Table 4.1 and the measurements depicted in Figure 4.1.
It is evident that the order parameter varies continuously through $T_N$. A second neutron diffraction investigation, details of which are also listed in Table 4.1, was subsequently carried out. In this investigation the variation of the spontaneous magnetization was firstly measured for temperatures increasing through the transition point. This was immediately followed by a second run during which the temperatures were decreased through $T_N$. This was done in order to investigate the possible existence of thermal hysteresis in the value of $T_N$, which would be indicative of a first order phase transition. These measurements are depicted in Figure 4.1. It can be seen that no hysteresis exists in the value of $T_N$ as observed for the heating or the cooling run. This, together with the continuous behaviour of the order parameter through the transition point, provide convincing evidence that the c-axis sinusoidally modulated $\leftrightarrow$ paramagnetic phase transition in erbium is of second order. The value of the transition point for both erbium crystals, as indicated in Fig.4.1, is $84.95\,\text{K}$. 
### TABLE 4.1

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<td>Frequency of ultrasonic wave</td>
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#### 4.2.2 Ultrasonic measurements

As a final investigation into the order of the sinusoidally modulated ↔ paramagnetic phase transition in Er, the attenuation and velocity anomalies of a 10 MHz longitudinal sound wave propagating along the c axis of the Er(II) crystal were measured for a cooling run, immediately followed by a heating run. The particulars of these two runs are listed in Table 4.1 and the measurements depicted in
Fig. 4.2 Ultrasonic verlocity (squares) and attenuation (circles) vs. temperature for Er(II). Closed symbols refer to measurements made during cooling and open symbols to heating data.

Figure 4.2. No hysteresis is observed between the values of $T_N$ as indicated by the two runs respectively. The value of $T_N$ indicated by both these runs is 85.21 K. This behaviour is characteristic of a second order phase transition and confirms the results of Section 4.2.1.

Similarly as to the case of Dy(II), an apparent discrepancy exists between the values of $T_N$ as indicated by neutron diffraction and ultrasonic measurements respectively. However, as these measurements were not conducted simultaneously, the existence of such a small difference between the two observed values of $T_N$ may be considered dubious. It was consequently decided to measure the ultrasonic variables simultaneously with the neutron diffraction measurements. The investigation of this difference, called a "$\Delta T_N$ anomaly" in analogy to the observation of a similar effect on Dy(II), is discussed in the following section.
4.3 SIMULTANEOUS MEASUREMENT OF NEUTRON DIFFRACTION AND ULTRASONICS

The velocity and attenuation of a 10 MHz longitudinal ultrasonic wave propagating along the c axis of the Er(II) crystal were measured simultaneously with the neutron diffraction investigation of peak scattered intensity discussed in Section 4.2.1 (RUN VI of Table 4.1). A replot of the neutron diffraction measurements (circles) is shown in Figure 4.3. Also shown are the simultaneously measured velocity and attenuation. The simultaneous measurements indicate a difference of 0.26 K between the values of the transition points indicated by the two techniques: \( T_N = 84.95 \) was found from the neutron diffraction measurements and \( T_N = 85.21 \) K from the ultrasonic measurements.

![Graph](image-url)

**Fig. 4.3** Simultaneously measured ultrasonic attenuation and velocity and peak neutron intensity vs temperature for Er(II)
As mentioned in Section 3.3.2, this anomaly may be trivially explained if the value of $T_N$ as indicated by ultrasonic measurements were a function of the frequency of the ultrasonic wave. An investigation of the value of $T_N$ at frequencies of 30 MHz and 50 MHz was conducted. The particulars of these two runs are indicated in Table 4.2.

**Table 4.2**

<table>
<thead>
<tr>
<th>Type of ultrasonic wave</th>
<th>RUN X (MHz)</th>
<th>RUN Y (MHz)</th>
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</thead>
<tbody>
<tr>
<td>Direction of propagation</td>
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<td></td>
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<tr>
<td>Frequency of ultrasonic wave</td>
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<td>50</td>
</tr>
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<td>Start temperature (K)</td>
<td>91.15</td>
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<tr>
<td>End temperature (K)</td>
<td>78.80</td>
<td>78.85</td>
</tr>
<tr>
<td>Néel Temperature (K)</td>
<td>85.21</td>
<td>85.21</td>
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<td>Temperature control (K)</td>
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<td>0.21</td>
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<tr>
<td>Time interval between measurements</td>
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</tbody>
</table>

The attenuation of the longitudinal sound wave along the c axis is depicted in Figure 4.4 for the frequencies 10, 30 and 50 MHz. The velocity is similarly depicted in Figure 4.5. From these two figures it is clear that $T_N$ is not a function of the frequency of the sound wave, at least for the frequency range 10-50 MHz. The conjecture that a frequency dependence of the value of $T_N$ might explain the $\Delta T_N$ anomaly, in Er(II) is consequently refuted, and it is concluded that a $\Delta T_N$ anomaly similar to that observed in Dy(II), exists for Er(II).
Fig. 4.4  Ultrasonic attenuation measured at 10 MHz (●), 30 MHz (■) and 50 MHz (▲) as a function of temperature.

Fig. 4.5  Ultrasonic velocity measured at 10 MHz (●), 30 MHz (■) and 50 MHz (▲) as a function of temperature.
4.4 The critical exponents $\beta$ and $\gamma$

The $c$ axis sinusoidally modulated $\leftrightarrow$ paramagnetic phase transition in erbium was shown to be of second order within experimental resolution (Section 4.2). An investigation to determine the value of the $\beta$-exponent that describes the critical behaviour of the spontaneous magnetization near $T_N$ was undertaken on the thin disk shaped crystal Er(III). Preceding any integrated measurements of the spontaneous magnetization, the upper temperature limit for the existence of higher order magnetic satellite reflections, corresponding to a squaring up of the sinusoidal modulation, was determined. Integrated intensity measurements as a function of temperature were carried out on the $(101-3\delta)$ magnetic satellite reflection. The particulars of this run are indicated in column 2 of Table 4.3, and the results are depicted in Figure 4.6. It

![Graph](image)

**Fig. 4.6** Integrated intensity vs. temperature for the $(101-3\delta)$ magnetic satellite reflection of Er
is clear that the intensity of the third harmonic vanishes above 75 K, i.e. above this temperature the modulation of the wave vector has a purely sinusoidal nature and only the intensity of the first order harmonic needs to be considered to determine the intensity of the spontaneous sublattice magnetization. The subsequent study of the phase transition was limited to this region.

To determine the values of the critical exponents $\beta$ and $\gamma$, integrated intensity scans of the $(1 \ 0 \ \delta)$ magnetic satellite were performed as a function of temperature. The particulars for this run are listed in column 1 of Table 4.3 and the results are depicted in Fig. 4.7.

**TABLE 4.3**

<table>
<thead>
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<td>(min)</td>
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<td>Temp stabilization time</td>
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</tr>
<tr>
<td>Néel temperature</td>
<td>85.05</td>
</tr>
<tr>
<td>Background measurement</td>
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<td>Temperature control</td>
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<tr>
<td>Temp increments near $T_N$</td>
<td>(K)</td>
</tr>
<tr>
<td>Av. temp increments (range)</td>
<td>(K)</td>
</tr>
<tr>
<td>Type of scan</td>
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<tr>
<td>Angular range of scan</td>
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<tr>
<td>Step size</td>
<td>(deg)</td>
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<td></td>
</tr>
<tr>
<td>Duration of scan</td>
<td>(min)</td>
</tr>
<tr>
<td>No. of scans discarded per datum point</td>
<td></td>
</tr>
</tbody>
</table>
The corrections that have to be made to the data, preceding a fit to the $\beta$-exponent power law, were discussed in detail in Section 3.4.1, and are only mentioned briefly:

(i) A background subtraction was performed.

(ii) No change in the angular position of the reflection, due to a change in the value of the wave vector that describes the modulation along the $c$ axis as a function of temperature, was observed. This is to be expected since the wavelength of the modulation remains constant at 7 magnetic layers for the whole temperature range between 54 K and $T_N$ [17].

(iii) Since the study was limited to a small region below $T_N$, the intensity of the $(1\ 0\ 6)$ satellite reflection was low. Furthermore, the path length of the neutron beam through the crystal was approximately 1.25 mm. From Figure 3.6 and the arguments in Section 3.4.1, the extinction was not expected to be significant. Measurements at low temperatures were nevertheless repeatedly discarded for successive least squares fits in order to reveal the influence of extinction, if any, on the intensity measurements. This approach, however, revealed a very interesting behaviour of the $\beta$-exponent as discussed below.

(iv) From an analysis of the paramagnetic data, the value of the critical exponent that describes the critical scattering in the vicinity of $T_N$, as well as the amplitude of the critical scattering above $T_N$ in Fig. 4.7 are found as $\gamma = 1.45 \pm 0.10$ and $C_+ = 0.35 \pm 0.05$. A correction for the critical scattering below $T_N$ was made using Schofield's [87] parametric representation of the equation of state (eq. (3.7)).

A least-squares fit of the results in the ordered region yields $\beta = 0.45$ and $T_N = 85.05$ K. The satisfactory fit to the experimental points is indicated by a solid line in Figure 4.7.
Fig. 4.7 Integrated scattered neutron intensity vs temperature. Theoretical fit to experimental data (circles): solid line: spontaneous magnetization, broken line: critical scattering.

The effect of systematically deleting the lower temperature points from the analysis was investigated. It was found that the calculated value of $\beta$ is decreased in a continuous manner and two such fits, for which the lowest temperature was restricted to respectively 84.08 K and 84.44 K, are shown in Fig. 4.8. Thus values of $\beta$ between 0.38 and 0.41 are observed in small temperature regions of up to 1 K below $T_N$, but it changes to a value of $\beta = 0.45$ for $T_N - T \geq 4$ K. Habenschuss et al. [18] observed a linear curve for the intensity vs.
temperature plot of the $(10 \delta)$ reflections over a larger temperature range below $T_N$. This result agrees with mean field calculations which predict $\beta=0.5$. It is concluded that cross-over occurs for sinusoidally ordered erbium from a value for $\beta$ of around 0.39 to a mean field value.

![Graph](image)

**Fig. 4.8** Integrated scattered neutron intensity vs. temperature illustrating the effect of reducing the range included in the analysis of experimental data

### 4.5 INFLUENCE OF ANNEALING ON THE $\Delta T_N$ EFFECT OF ERBIUM

Since $\Delta T_N$ effects were observed for Dy(II) and Er(II), but not for Dy(I), possible common characteristics between the former two crystals should be considered. One possibility, considered during the final stages of this investigation, is the influence of annealing on
the phenomena. The Dy(II) and Er(II) crystals were investigated as received: In the case of Er(II) it was obtained directly from Goodfellow metals and subsequently used for our experiment, while the Dy(II) crystal was first experimented upon in Canada [64] before we received it. On the other hand, the Dy(I) crystal was annealed as part of a previous investigation [84].

The Er(II) crystal was placed in a tantalum crucible and sealed in a quartz tube under a vacuum of $5 \times 10^{-5}$ torr. It was annealed for 48 h at 950 °C and care was taken to both warm it up and cool it slowly over ca. 8 h periods.

A simultaneous experiment to determine $T_N$ from neutron scattering and ultrasonics was again carried out. Relevant detail is given in Table 4.4 and the results are depicted in Fig. 4.9.

### Table 4.4

<table>
<thead>
<tr>
<th>Magnetic satellite reflection</th>
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<th>ULTRASONICS</th>
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</thead>
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<td>(K)</td>
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<td>End of run</td>
<td>(K)</td>
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<tr>
<td>Néel temperature</td>
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</tr>
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<td>Temperature control</td>
<td>(K)</td>
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</tr>
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<td>Av. Temp. increment (range)</td>
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</tr>
<tr>
<td>Duration of scan</td>
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<tr>
<td>No. of scans discarded per dat.pt</td>
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</tr>
<tr>
<td>Type of ultrasonic wave</td>
<td></td>
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</tr>
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<td>Direction of propagation</td>
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<td>10</td>
</tr>
<tr>
<td>Frequency of ultrasonic wave</td>
<td>(MHz)</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4.9 Simultaneously measured ultrasonic attenuation and velocity and peak neutron intensity vs. temperature for Er(II) after annealing in vacuum for 48 h at 950 °C.

It is evident that the $\Delta T_N$ effect as previously observed for Er has disappeared after annealing of the crystal and that the Néel temperatures observed from the results of neutron scattering and ultrasonics agree for the annealed crystal.

The importance to also investigate the influence of annealing on the $\Delta T_N$ effect of Dy(II) is obvious. Unfortunately, no more neutron beam time is available for this purpose at present, but such an experiment is scheduled for the middle of 1988.
5.1 CONCLUSIONS
5.1 CONCLUSIONS

The results presented in Chapters 4 and 5, of which some have already been published [110-114], are discussed in this section. Results that seem to be well established, as well as aspects that warrant further investigation will be indicated. The interpretation will in some instances inevitably be of a speculative nature.

The first question addressed by this investigation concerns the nature of the theoretically well studied [52-56] helically ordered ↔ paramagnetic phase transition in Dy and Ho, as well as the nature of the sinusoidally ordered ↔ paramagnetic phase transition in Er. The result of high resolution neutron scattering experiments clearly indicates the absence of hysteresis in the position of $T_N$ as observed from heating and cooling runs. Furthermore, continuous spontaneous magnetization curves were observed in detailed measurements in the vicinity of $T_N$ for all three elements. It is concluded that within the accuracy of the experiments described in Chapters 3 and 4 these phase transitions are of a continuous nature (i.e. of second order). This conclusion is corroborated by the results of ultrasonic attenuation and velocity measurements on Dy and Er which also do not show any hysteresis in $T_N$ between heating and cooling runs.

In the case of Ho a small hysteresis effect manifested by small anomalies in the magnetization has been observed well below $T_N$ in the ordered region. The hysteresis behaviour was observed in the temperature region $T_N-50$ K to $T_N-30$ K and no hysteresis was evident down to 20 K below $T_N$. This effect, which was not investigated in great detail, may be related to anomalies in elastic constants, c axis strain [114] and electrical resistance [115] reported in the literature for the helically ordered region of the rare earths. The latter anomalies are ascribed to small energy perturbations arising at temperatures where the spiral structure becomes commensurate with an integer multiple of the c axis spacing [116]. It is gratifying that the preceding effect will not have an influence on critical properties measured near $T_N$. 
The observation of a $\Delta T_N$ anomaly for Dy(II) has been an intriguing part of this investigation and an appreciable amount of time was spent on it. It may well be that this effect will disappear upon annealing of the crystal as has been the case with the smaller $\Delta T_N$ effect in erbium. This will be investigated towards the middle of 1988 when neutron beam time becomes available.

It is further relevant to compare the results of detailed studies of the phase transition and critical exponents as measured on the rather pure Dy(II) crystal (resistance ratio 62.5) and the less pure Dy(I) crystal (resistance ratio 12.5). For Dy(I) a unique value of $\gamma = 1.2 \pm 0.2$ was observed from the paramagnetic critical scattering. A limiting value of $\beta = 0.39 \pm 0.1$ is observed as $t \rightarrow 0$. The influence of extinction as one moves to lower temperatures seems to be fairly small. For Dy(II) it was not possible to find a unique value of $\gamma$ in the paramagnetic region. Furthermore, it is observed that a value of $\beta = 0.39$ describes the magnetization for only a limited region of 0.8 K below $T_N$ and the calculated $\beta$ then changes continuously to reach a value of 0.31 at $T_N - 4$ K. It will be of interest to investigate whether these results are changed after an annealing of the crystal. One possibility concerning the continuous change in the $\beta$ values of Dy(II) is that the high quality Dy(II) crystal (as evidenced by its large resistance ratio and narrow attenuation peak at $T_N$) is subject to considerably more extinction than the Dy(I) crystal. Thus, the decrease in $\beta$ values as intensities measured at lower temperature are included would be ascribed to extinction.

Considerable experimental attention has recently been given to a study of the helically magnetic$\leftrightarrow$paramagnetic phase transition of Dy, Ho and Tb using specific heat [59,60], thermal expansion [61-65] and electrical resistance [88] measurements. Amitin et al. [63,88,89] in a series of provocative papers claim the existence of experimental evidence that a vortex spin structure exists in Dy between $T_N$ and $T_N - 7.8$ K. Our investigation, in a detailed neutron scattering study, failed to find evidence for a vortex spin structure [109,110].
Some attention was also given to the commensurate ↔ incommensurate first order phase transition of Dy at its Curie point. The behaviour of the spiral wave vector was investigated employing neutron diffraction measurements and observed to obey a molecular field temperature dependence up to 32 °K above $T_C$ [111]. This model [96-101] assumes the existence of ferromagnetic domains in the helical (incommensurate) region. However, our measurements only observed ferromagnetic order up to $T_C + 6$ K. First order phase transitions are presently not sufficiently understood and an extension of these measurements to other commensurate ↔ incommensurate systems (like Ho) is called for.

The behaviour of the order parameter of Er is of interest. Theoretically this system has not been discussed in detail. The exponent $\beta$ takes a value of 0.38 near $T_N$ and then crosses over smoothly to a near mean-field value of 0.45 at $T_N - 4$ K. An extension of this measurement to lower temperatures in order to confirm that the mean-field value of $\beta = 0.5$ is observed is currently under way.

In conclusion some future experiments are indicated. Apart from a simultaneous neutron and ultrasonic measurement on Dy(II) after it has been annealed, one also envisages neutron scattering and ultrasonic studies of high purity Ho or other helically ordered materials (for instance Ho-Tb alloy crystals [113]). In the more recent studies of critical exponents on higher purity rare earth materials most of these were concerned with specific heat and electrical resistivity measurements. A thorough study of the critical attenuation and velocity above $T_N$ will be a useful complement to the abovementioned techniques. In the case of the velocity measurements it will have to extend high up in the paramagnetic region (even to above room temperature) in order to reliably obtain the unrenormalized phonon velocities and thus the critical contribution. It will also be of interest to observe whether the anomalous critical neutron scattering and thermal expansion observed in the paramagnetic region of Dy(II) persist after the crystal has been annealed.
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