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MAGNETIC FORM FACTOR OF THULIUM
AND TERBIUM METALS

Ph. D. Thesis Submitted to Iowa State University, August 1970

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MAGNETIC FORM FACTOR OF THULIUM AND TERBIUM METALS

Torben Otto Brun

ABSTRACT

The magnetic form factors of thulium and terbium have been measured with polarized neutrons. For the two metals the samples that were used in the experiment were single crystals. Both thulium and terbium crystallize in the hexagonal close-packed structure.

The form factor of thulium was measured at 4.2°K and in a magnetic field of 10 kOe applied parallel to the c-axis. The magnetic structure of thulium at 4.2°K and in low fields (less than 28 kOe) applied parallel to the c-axis is an antiphase domain structure with a net ferromagnetic moment parallel to the c-axis. The magnitude of the moment is $1 \mu_B$ per atom. In this experiment the magnetic form factor of this ferromagnetic moment has been determined.

The form factor of terbium was measured at 298°K and in a magnetic field of 22 kOe applied parallel to both the a- and the b- axis. Terbium is paramagnetic at 298°K , and the magnitude of the induced moment in a field of 22 kOe is $0.8 \mu_B$ per atom for the two directions of the field. The magnetic form factor of the induced moment has been measured in this experiment. Within the experimental uncertainty the form factors for the directions of the magnetic field were identical.

Theoretical form factors has been calculated for both thulium and terbium using the 4f wave functions of Freeman and Watson. A comparison between the theoretical and experimental form factors indicates that the free ion wave functions of Freeman and Watson are too contracted for both metals.

V
v

TABLE OF CONTENTS

ABSTRACT	Page iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
APPENDIX	viii
I. INTRODUCTION	1
II. CROSS SECTIONS FOR POLARIZED NEUTRONS	6
III. MATRIX ELEMENTS OF THE MAGNETIC INTERACTION OPERATOR	24
IV. EXPERIMENTAL PROCEDURES	39
A. Instrument	39
B. Method of Operation	51
C. Corrections	58
V. RESULTS	59
A. Thulium	59
B. Terbium	62
VI. CONCLUSIONS	68
VII. LITERATURE CITED	80
VIII. ACKNOWLEDGMENTS	83
IX. APPENDIX A	84
X. APPENDIX B	87

LIST OF TABLES

	Page
Table 1. Some magnetic properties for the heavy rare earth metals	4
Table 2. Coefficients for ground state $M_J = J$ for the tripositive rare-earth ions ($C_8 = 0$)	33
Table 3. Polarization and flipping efficiency	48
Table 4. Thulium	61
Table 5. Terbium	67

LIST OF FIGURES

	Page
Fig. 1. A schematic diagram of a polarized neutron spectrometer	7
Fig. 2. The ANL neutron diffractometer	45
Fig. 3. The ANL neutron diffractometer	46
Fig. 4. The magnetic form factor for thulium	69
Fig. 5. The magnetic form factor for terbium	70
Fig. 6. The ratio of the observed and the theoretical form factor for thulium	74
Fig. 7. The ratio of the observed and the theoretical form factor for terbium	75

1. INTRODUCTION

The arrangement of the moments in a magnetic material can be studied by neutron diffraction. If a beam of thermal neutrons is incident upon a magnetic sample, the neutron spin will interact with the unpaired electrons surrounding the magnetic ions. From the pattern of scattered neutrons it is then possible to determine the way in which the magnetic moments are oriented in the sample.

The strength of interaction between the spin of a neutron and the unpaired electrons belonging to one ion is proportional to the product of the magnitude of the magnetic moment of the ion and the neutron magnetic form factor, $f(\bar{\kappa})$. The vector $\bar{\kappa}$ is the neutron scattering vector defined by $\bar{\kappa} = \bar{k} - \bar{k}'$ where $\bar{k}$ and $\bar{k}'$ are the wave vectors of the incident and scattered neutrons. The form factor is normalized to 1 for $\bar{\kappa} = 0$ (forward scattering).

A determination of the neutron magnetic form factor for a magnetic ion provides detailed information about the distribution of unpaired or magnetic electrons surrounding the ion. The magnetic form factor can be defined as a normalized Fourier transform of the magnetization density of an atom or ion. For an atom where the total orbital angular momentum L of the unpaired electrons is not quenched by the crystal field, the magnetization density $M(\bar{r})$ is a sum of the spin magnetization density, $M_S(\bar{r})$, and the orbital magnetic moment density $M_L(\bar{r})$. Trammell (1), Steinsvoll et al. (2) and Lovesey and Rimmer (3) have given definitions for $M_S(\bar{r})$ and $M_L(\bar{r})$. The magnetic form factor for neutron scattering is analogous to the X-ray atomic scattering factor which is a Fourier

transform of the total electronic charge density.

The neutron diffraction group at Massachusetts Institute of Technology has measured the magnetic form factors for the 3-d transition metals Fe (4), Co (5) and Ni (6) using polarized neutrons. Steinsvoll et al. (2) have measured the magnetic form factor of terbium metal. However, they were able to determine the form factor accurately only for large values of κ . Wedgwood (7) has very recently reported polarized neutron data for the form factor of uranium in uranium sulfide.

The neutron diffraction group at Oak Ridge National Laboratory has determined the magnetic structure of a number of rare earth metals and compounds using unpolarized neutrons. They have reported form factors for Ho (8) and Er (9) which were determined from single crystal diffraction patterns. The same group has also measured the form factors of rare earth ions in Nd_2O_3 (10) and ErO_3 (10) by studying the paramagnetic scattering of neutrons from powders of the two compounds.

In the present experiment the magnetic form factors for thulium and terbium metal have been measured using the polarized neutron technique reported by Nathans and coworkers (4). If the interaction between the magnetic atom and the neutron spin is smaller than the interaction between the nuclei of the atom and neutron, the form factor can be determined very accurately by using this technique. For both thulium and terbium this implies that the ferromagnetic moment per atom has to be less than 2 Bohr magnetons (μ_B).

The crystal structure of Tm is hcp with $a=3.537\text{\AA}$ and $c=5.504\text{\AA}$. At 4.2°K the magnetic structure of Tm has been determined by neutron

diffraction (11, 12) to be an antiphase domain structure in which the moments are aligned parallel (+ layers) or anti-parallel (- layers) to the c-axis. These moments are stacked such that four positive layers are followed by three negative layers. The net ferromagnetic moment per atom has been measured as $1.001 \pm 0.005 \mu_B$ by Richards and Legvold (13). It is the magnetization density of this ferromagnetic component that is studied in the present experiment.

Terbium, like thulium, crystallizes in hcp structure with $a=3.601\text{\AA}$ and $c=5.694\text{\AA}$. From magnetic (14) and neutron (15) measurements it has been established that terbium is ferromagnetic at low temperatures with a saturation moment of $9.34 \mu_B$ per atom. At room temperature terbium is paramagnetic; by applying a magnetic field of 25 kOe one can induce a moment of approximately $0.9 \mu_B$ per atom. In the present experiment the form factor of this induced moment has been measured.

Steinsvoll et al. (2) measured the form factor of Tb in the ferromagnetic state but the large moment per atom made it impossible to do the measurements using polarized neutrons except for large values of κ .

The magnetic form factor of an ion can be calculated if the wave function describing the state of the unpaired electrons is known. The magnetic properties of the rare earth metals indicate that the magnetic moments of the atom are produced by unpaired electrons in the 4f shell. In Table 1 the 4f-electron configuration and the quantum numbers S, L and J are shown for the ground state of the tripositive ions using Russells-Saunders coupling scheme and Hund's rule. The values for gJ and $\sqrt{J(J+1)}$ correspond to the theoretically expected values for the

Table 1. Some magnetic properties for the heavy rare earth metals.

Metal	$4f^n$	S	L	J	g	g^J	μ_o	$g\sqrt{J(J+1)}$	μ_{eff}
Gd	7	7/2	0	7/2	2	7	7.55	7.94	7.98
Tb	8	3	3	6	3/2	9	9.34	9.72	9.77
Dy	9	5/2	5	15/2	4/3	10	10.19	10.64	10.64
Ho	10	2	6	8	5/4	10	10.34	10.60	11.2
Er	11	3/2	6	15/2	6/5	9	9	9.58	9.9
Tm	12	1	5	6	7/6	7	7.14	7.56	7.62

ordered and the effective moments of the ions. The moments μ_0 and μ_{eff} are the experimental values (13, 14, 16) in μ_B per atom for the saturation and paramagnetic moments of the metals. The agreements between gJ and μ_0 and between $g\sqrt{J(J+1)}$ and μ_{eff} show that it is a good approximation to calculate the magnetic properties of the heavy rare earth metals from the ground state of the tripositive ions. Therefore, the quantum numbers in Table I will be used to evaluate the form factors for thulium and terbium.

Trammell (1) and Lovesey and Rimmer (3) have derived the mathematical expressions that are necessary to calculate the form factors. In the formulas the form factors are expressed in terms of linear combinations of radial integrals that contain the radial part of the one-electron wave functions. The numerical values for these integrals have been tabulated by Blume, Freeman and Watson (17) for the rare earth tripositive ions.

The theoretical form factors for thulium and terbium are calculated by the method described by Lovesey and Rimmer (3); the experimental and theoretical form factors are compared using the numerical values of Blume et al. (17) for the radial integrals.

In the following two chapters the theory that is used for the interpretation of the present measurements is discussed. Chapter II contains a discussion of the scattering cross section for polarized neutrons and Chapter III is concerned with the derivation of the theoretical expression for the form factors. In Chapter IV the experimental method is described. The data are presented in Chapter V and in the last Chapter, VI, the experimental data are compared with the theory.

II. CROSS SECTIONS FOR POLARIZED NEUTRONS

In a conventional polarized neutron experiment a beam of monochromatic polarized neutrons is scattered from a single crystal sample. The number of neutrons scattered in a particular direction is counted by a detector. In Fig. 1 is shown a schematic of a typical polarized neutron experiment. The monochromator produces a beam of monochromatic neutrons having their spin $\vec{s}$ parallel to the polarizing field $\vec{H}_p$. The radio-frequency coil is tuned such that the monochromatic neutrons reverse the direction of their spins going through the coil. By switching the radio-frequency off and on, the neutrons incident on the sample will have their polarization vector $\vec{P}$ parallel or antiparallel to $\vec{H}_p$.

In the experiments described here only elastic coherent scattering (Bragg scattering) of neutrons has been studied. The quantity that has been measured is the ratio of the intensities of a Bragg reflection for $\vec{P}$ being parallel or antiparallel to $\vec{H}_p$. This ratio is called the flipping ratio R . It will be shown at the end of this chapter that one can determine the magnetic form factor $f(\vec{\kappa})$ from R .

In this chapter the polarized neutron cross section for a Bragg reflection will be derived starting from the differential cross section given by Blume (18). Blume (18,19) and Schermer (20) have discussed the cross section and polarization effects in slow neutron scattering. These three papers are the main references for this chapter.

The cross section will be calculated specifically for the thulium and terbium experiments and the expression for the cross section will be used for the interpretation of the experimental data.

Fig. 1. A schematic diagram of a polarized neutron spectrometer

The differential cross section (18) for scattering of a polarized beam of neutrons with wave vector $\bar{k}$ is given in the Born approximation by:

$$\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_{\alpha, \alpha'} p_{\alpha} \text{Tr}[\langle \alpha | V^+(\bar{k}) | \alpha' \rangle \langle \alpha' | V(\bar{k}) | \alpha \rangle \rho] \times \delta\left(\frac{\hbar^2}{2m} (k'^2 - k^2) + E_{\alpha'} - E_{\alpha}\right) \quad (2.1)$$

where: p_{α} = probability of the scattering system being in the initial state $|\alpha\rangle$;

$V(\bar{\kappa})$ = Fourier transform of the interaction between the neutron and the scatterer;

$\bar{\kappa} = \bar{k} - \bar{k}'$, where $\bar{k}$ and $\bar{k}'$ are, respectively, initial and final wave vectors of the neutron;

ρ = density matrix operator for the neutron spin $\bar{s} = \frac{1}{2} \tilde{1} + \bar{P} \cdot \bar{s}$,

where $\tilde{1}$ is the two by two unit matrix, $\bar{s}$ is one-half times the Pauli spin matrices, and $\bar{P}$ is the neutron polarization vector

($|\bar{P}| = 0$ for unpolarized neutrons, $|\bar{P}| = 1$ for polarized neutrons).

The trace in equation 2.1 is understood to be taken only with respect to the neutron spin coordinates.

The derivation of the cross section of Bragg reflection will be done in three steps. First, the potential $V(\bar{\kappa})$ will be discussed; second, the matrix elements of $V(\bar{\kappa})$ will be calculated; third, the trace will be taken.

The Fourier transform $V(\bar{\kappa})$ is defined by:

$$V(\bar{\kappa}) = \int d^3r \exp(i\bar{\kappa} \cdot \bar{r}) V(\bar{r}, \bar{s}) \quad (2.2)$$

where $\bar{r}$ and $\bar{s}$ are the neutron space and spin coordinates measured with

respect to the scatterer.

If the scattering system is a magnetic crystal, the neutron interacts principally with the nuclei of the atoms and with the magnetic electrons surrounding the nuclei. The latter interaction is between the magnetic field created by the unpaired electrons and the spin of the neutron. It is this interaction that has been studied in this experiment. In addition, slow neutrons interact in a number of other ways with matter. However, the resulting scattering amplitudes are smaller than the amplitudes for neutron-nuclei and neutron spin-magnetic electron interaction by a factor that is of the order of the ratio between the electron mass and the neutron mass. Examples of these weak scattering mechanisms are neutron dipole-nuclear dipole, direct neutron-electron, and neutron spin-neutron orbit scattering. The latter interaction is called the Schwinger effect and has been observed experimentally by Shull (21) in vanadium. None of these weaker effects will be considered in the derivations below.

The potential $V(\vec{r}, \vec{s})$ for a crystal is the sum over all the potentials $V_i(\vec{r}, \vec{s})$ of the individual nuclei or electrons in the crystal, and the different interactions in $V_i(\vec{r}, \vec{s})$ are determined by symmetry as discussed by Messiah (22). These different types of potentials all lead to the same general form of $V(\vec{\kappa})$ in equation 2.2.

$$V(\vec{\kappa}) = b(\vec{\kappa}) + \vec{c}(\vec{\kappa}) \cdot \vec{s} \quad (2.3)$$

where $b(\vec{\kappa})$ and $c(\vec{\kappa})$ refer to the scattering system.

For neutron-nuclei scattering $V_j(\vec{r}, \vec{s})$ is usually represented by a Fermi-pseudopotential:

$$V_j(\bar{r}, \bar{s}) = \frac{2\pi\hbar^2}{m} (b_j + b'_j \bar{I}_j \cdot \bar{s}) \delta(\bar{r} - \bar{R}_j) \quad (2.4)$$

where $\bar{R}_j$ and $\bar{I}_j$ are the position and nuclear spin of the j th atom, and b_j and b'_j are scattering lengths. Conventionally the scattering lengths b_j^+ and b_j^- for the two possible total spin states $I_j + \frac{1}{2}$ and $I_j - \frac{1}{2}$ are used instead of b_j and b'_j . Expressing b_j and b'_j in terms of b_j^+ and b_j^- , $V(\bar{r})$ for neutron-nuclei scattering becomes:

$$\begin{aligned} V_N(\bar{k}) &= b_N(\bar{k}) + \bar{c}_N(\bar{k}) \cdot \bar{s} \\ &= \frac{2\pi\hbar^2}{m} \left(\sum_j \exp(i\bar{k} \cdot \bar{R}_j) \times \frac{(I_j+1)b_j^+ + I_j b_j^-}{2I_j+1} \right) \\ &\quad + \frac{2\pi\hbar^2}{m} \times 2 \left(\sum_j \exp(i\bar{k} \cdot \bar{R}_j) \times \frac{b_j^+ - b_j^-}{2I_j+1} \bar{I}_j \right) \cdot \bar{s} \end{aligned} \quad (2.5)$$

The subscript N is used to indicate nuclear scattering.

In order to evaluate the cross section for magnetic interaction one has to consider the potential energy $V_e(\bar{r}, \bar{s})$ of an electron in the magnetic field created by the neutron spin. In the non-relativistic limit of the Dirac equation $V_e(\bar{r}, \bar{s})$ becomes:

$$V_e(\bar{r}, \bar{s}) = -2 \frac{e\hbar}{2m_e c} \times \bar{s}_e \cdot \bar{H}(\bar{r}, \bar{s}) \quad (2.6)$$

$$= \frac{e\hbar}{2m_e c} \times \frac{1}{\hbar} (\bar{p}_e \cdot \bar{A}(\bar{r}, \bar{s}) + \bar{A}(\bar{r}, \bar{s}) \cdot \bar{p}_e)$$

where the vector-potential $\bar{A}(\bar{r}, \bar{s}) = \gamma\mu_n \times \frac{\bar{s} \times (\bar{r} - \bar{r}_e)}{|\bar{r} - \bar{r}_e|^3}$ and the

field $\bar{H} = \nabla \times \bar{A}$. The symbols m_e , $\bar{p}_e$, $\bar{r}_e$, and $\bar{s}_e$ refer to the mass, momentum and coordinates of the electron. The operator $\gamma\mu_n \bar{s}$ = magnetic

moment of the neutron = $\frac{\gamma e \hbar}{mc} \bar{s}$; the constant $\gamma = -1.91$ for neutrons.

A higher order term proportional to $\bar{A} \cdot \bar{A}$ has been neglected in equation 2.6.

The Fourier transform, $V_{Me}(\bar{\kappa})$, of equation 2.6 can be calculated by partial integration. Using the identity:

$$\int \frac{\bar{r}}{r^3} \exp(i\bar{q} \cdot \bar{r}) d^3 r = 4\pi i \frac{\bar{q}}{q^2}$$

$V_{Me}(\bar{\kappa})$ for the e th electron becomes:

$$\begin{aligned} V_{Me}(\bar{\kappa}) = & \frac{2\pi\hbar^2}{m} \times \frac{\gamma e^2}{m_e c^2} \times \frac{1}{\kappa^2} [(\bar{\kappa} \times (2\exp(i\bar{\kappa} \cdot \bar{r}_e) \bar{s}_e \times \bar{\kappa})) \\ & - \frac{i}{\hbar} \bar{\kappa} \times \{\bar{p}_e \cdot \exp(i\bar{\kappa} \cdot \bar{r}_e) + \exp(i\bar{\kappa} \cdot \bar{r}_e) \bar{p}_e\}] \cdot \bar{s} \end{aligned} \quad (2.7)$$

The subscript M stands for magnetic scattering.

For a crystal containing magnetic ions the magnetic part of $V(\bar{\kappa})$ is the sum over $V_{Me}(\bar{\kappa})$ of all the unpaired electrons. If one replaces $\bar{r}_e$ with $\bar{R}_j + \bar{r}_{nj}$, where $\bar{R}_j$ = position of the j th nucleus and $\bar{r}_{nj}$ = position of the n th magnetic electron belonging to the j th nucleus, the magnetic part of the operator $V(\bar{\kappa})$ can be written as

$$\begin{aligned} V_M(\bar{\kappa}) = & \frac{2\pi\hbar^2}{m} \sum_j \exp(i\bar{\kappa} \cdot \bar{R}_j) \\ & \times \left[\frac{\gamma e^2}{m_e c^2} \times \frac{1}{\kappa^2} (\bar{\kappa} \times \{(\sum_n \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) 2 \bar{s}_{nj}) \times \bar{\kappa}\}) \right. \\ & \times \frac{\gamma e^2}{m_e c^2} \times \frac{1}{\kappa^2} \times \left(\frac{i}{\hbar} \right) (\bar{\kappa} \times \sum_n \{\bar{p}_{nj} \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) + \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) \bar{p}_{nj}\})] \cdot \bar{s} \end{aligned} \quad (2.8)$$

The constant $\frac{\gamma e^2}{m_e c^2}$ in equation 2.8 has the dimension of a length and its magnitude is 0.54×10^{-12} cm. The coherent nuclear scattering lengths are between 0.3×10^{-12} cm. and 1.0×10^{-12} cm for nearly all the different nuclei (23) in the periodic table. Thus, the magnetic scattering operator $V_M(\bar{\kappa})$ and the nuclear operator $V_N(\bar{\kappa})$ are of the same order of magnitude. From the expression from $V_M(\bar{\kappa})$ in equation 2.8 it can be seen that $V_M(\bar{\kappa})$ is of the form $V_M(\bar{\kappa}) = \bar{c}_M(\bar{\kappa}) \cdot \bar{s}$. Trammell (1) has shown that for elastic scattering of thermal neutrons the operator in the { } bracket in the last line of equation 2.8 can be expressed in terms of the orbital angular momentum $\bar{L}_{nj}$ of the nth electron:

$$\begin{aligned} \bar{p}_{nj} \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) + \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) \bar{p}_{nj} = \\ - i\hbar \bar{\kappa} \times \frac{1}{2} \{ \bar{L}_{nj} f(\bar{\kappa} \cdot \bar{r}_{nj}) + f(\bar{\kappa} \cdot \bar{r}_{nj}) \bar{L}_{nj} \} \end{aligned} \quad (2.9)$$

Equation 2.9 and the function $f(\bar{\kappa} \cdot \bar{r}_{nj})$ are both given by Trammell (1). The limits of both $f(\bar{\kappa} \cdot \bar{r}_{nj})$ and $\exp(i\bar{\kappa} \cdot \bar{r}_{nj})$ for $\bar{\kappa} \rightarrow 0$ are 1. Therefore, the magnetic interaction operator $\bar{m}_j$, the expression enclosed by the square bracket in equation 2.8, can for small $\bar{\kappa}$ be written as:

$$\begin{aligned} \bar{m}_j &= \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} (\bar{\kappa} \times ((2 \bar{S}_j + \bar{L}_j) \times \bar{\kappa})) \\ &= \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} (\bar{\kappa} \times (g \bar{J}_j \times \bar{\kappa})) \end{aligned} \quad (2.10)$$

where $\bar{S}_j = \sum \bar{s}_{nj}$ = total spin angular momentum, $\bar{L}_j = \sum \bar{L}_{nj}$ = total orbital angular momentum and $\bar{J}_j$ = total angular momentum. If one assumes Russell-

Saunders coupling for the unpaired electron, $\bar{J} = \bar{L} + \bar{S}$ and $g = \text{Landé factor} = 1 + (J(J+1) + S(S+1) - L(L+1))/(2J(J+1))$.

From equation 2.10 it can be seen that the operator $\bar{m}_j$ is proportional to the operator for the magnetic moment, $g\bar{J}_j$. It can be shown (1, 2, 3) that for finite $\bar{\kappa}$, $g\bar{J}_j$ in equation 2.10 has to be substituted by the Fourier transform $\bar{M}_j(\bar{\kappa})$ of the magnetization density of the j th atom:

$$\bar{M}_j(\bar{\kappa}) = \int \exp(i\bar{\kappa} \cdot \bar{r}) \bar{M}_j(\bar{r}) d^3r \quad (2.11)$$

where the total magnetization density $\bar{M}_j(\bar{r})$ is the sum of the spin and orbital magnetization densities.

In order to calculate the cross section given by equation 2.1 one has to evaluate the matrix elements of the operator $V(\bar{\kappa})$ between the initial and final states of the scatterer. In this experiment one is interested in the elastic scattering. Therefore, only matrix elements between states having the same energy will be considered. The operator $V(\bar{\kappa})$ is the sum of $V_N(\bar{\kappa})$ and $V_M(\bar{\kappa})$. From equations 2.5 and 2.8 it can be seen that $V(\bar{\kappa})$ contains operator products like $\exp(i\bar{\kappa} \cdot \bar{R}_j)\bar{I}_j$ and $\exp(i\bar{\kappa} \cdot \bar{R}_j)\bar{m}_j$. In the Hamiltonian for the scatterer it is a good approximation (20) to assume that neither the nuclear spin nor the magnetic electrons of an ion are coupled to the position of the ion. Under this assumption the matrix elements of the three operators $\bar{R}_j$, $\bar{I}_j$, and $\bar{m}_j$ can be treated independently. The states describing the positions and spins of the nuclei will be denoted by $|n\rangle$ and $|l\rangle$ respectively. The magnetic electrons of an ion will be described in the Russell-Saunders coupling by kets of the form $|SLJM\rangle$.

For the system of the nuclear positions the inelastic or phonon scattering will be ignored. Only matrix elements between $|n\rangle$ and $|n'\rangle$ where $|n'\rangle = |n\rangle$, will be considered. Since the nuclei position operator $\exp(i\vec{\kappa} \cdot \vec{R}_j)$ is common to all operators in $V(\vec{\kappa})$, all terms in the elastic scattering cross section will be multiplied by the same Debye-Waller factor. If secondary extinction effects (24) are small, the Debye-Waller factor will not affect the flipping ratio. Therefore, it will be ignored in the derivation of the cross section. Consequently the position operator will be substituted by its eigenvalue, $\exp(i\vec{\kappa} \cdot \vec{R}_j)$, where $\vec{R}_j$ is the equilibrium position of the j th atom.

Both terbium and thulium have only one stable isotope, Tb^{159} for terbium and Tm^{169} for thulium. Therefore, the scattering lengths b_j^+ and b_j^- and the nuclear spin I_j are the same for all the atoms in the pure metals. Consequently, in calculating the cross section one does not have to perform averages over the isotope distribution. The isotopic incoherent cross section is zero for both elements.

The matrix elements of the nuclear spin operator $\vec{I}_j$ will be calculated assuming a quasi-elastic approximation, $E_{\alpha'} = E_{\alpha}$, for all α' in the summation over α' in equation 2.1. Under this assumption the summation over α' can be performed. In evaluating the trace in equation 2.1 one will get terms like $\langle \vec{I}_j \cdot \vec{I}_{j'} \rangle$ and $\langle \vec{I}_j \times \vec{I}_{j'} \rangle$, where the brackets $\langle \rangle$ denote thermal averages. $\langle \vec{I}_j \cdot \vec{I}_{j'} \rangle$ (20) and $\langle \vec{I}_j \times \vec{I}_{j'} \rangle$ (20) are given by:

$$\langle \vec{I}_j \cdot \vec{I}_{j'} \rangle = \langle \vec{I}_j \rangle \cdot \langle \vec{I}_{j'} \rangle (1 - \delta_{jj'}) + \langle \vec{I}_j \cdot \vec{I}_j \rangle$$

and

$$\langle \vec{I}_j \times \vec{I}_{j'} \rangle = \langle \vec{I}_j \rangle \times \langle \vec{I}_{j'} \rangle + i \langle \vec{I}_j \rangle \delta_{jj'} \quad (2.12)$$

The experiment of terbium metal was done at room temperature with an applied field of about 25 kOe. Under these conditions it is a good approximation to assume that the nuclear polarization is negligible. The only term in equation 2.12 different from zero will be $\langle \bar{I}_j \cdot \bar{I}_j \rangle$. It contributes only to the incoherent scattering and not to the coherent Bragg reflections.

For thulium the situation is different. The experiment was done at 4.2°K in a magnetically ordered state. The effect of nuclear polarization was studied by measuring the flipping ratio of one of the Bragg reflections at 4.2°K and 1.8°K. The result of this experiment is discussed in Chapter V. It is estimated that the nuclear polarization at 1.8°K is 1% for thulium, but the conclusion from the experiment is that the effect of 1% nuclear polarization cannot be detected.

For both thulium and terbium the nuclear spin dependent term in $V_N(\bar{\kappa})$, equation 2.5, can therefore be neglected in the calculation of the coherent elastic scattering cross section. The incoherent part of the cross section will only contribute to a neutron spin independent background and is of no interest in this experiment.

If all the assumptions above are taken into account, the matrix element $B_N(\bar{\kappa})$ of the operator $V_N(\bar{\kappa})$ is given by:

$$B_N(\bar{\kappa}) = \sum_j \exp(i\bar{\kappa} \cdot \bar{R}_{nj}) b \quad (2.13)$$

where $b = \text{coherent nuclear scattering length} = \frac{(1 + I)b^+ + Ib^-}{2I + 1}$. The scattering length b for terbium is 0.76×10^{-12} cm (2, 23) and for thulium 0.69×10^{-12} cm (11, 23).

In the derivation of the matrix elements of the magnetic part of $V(\bar{\kappa})$ one has to evaluate matrix elements of the magnetic interaction operator $\bar{m}_j$ and of the nuclear position operator $\exp(i\bar{\kappa} \cdot \bar{R}_j)$. From equation 2.8 $V_M(\bar{\kappa})$ can be written as:

$$V_M(\bar{\kappa}) = \frac{2\pi\hbar^2}{m} \sum_j \exp(i\bar{\kappa} \cdot \bar{R}_j) \bar{m}_j \cdot \bar{s}$$

where:

$$\begin{aligned} \bar{m}_j = & \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} \bar{\kappa} \times \left[\left\{ \sum_n \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) 2 \bar{s}_{nj} \right\} \times \bar{\kappa} \right. \\ & \left. - \frac{i}{\hbar} \sum_n \{ \bar{p}_{nj} \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) + \exp(i\bar{\kappa} \cdot \bar{r}_{nj}) \bar{p}_{nj} \} \right] \end{aligned} \quad (2.14)$$

The matrix elements of the position operator can be calculated assuming the same approximations used in the derivation of $V_N(\bar{\kappa})$. Therefore, as in the nuclear case, the operator is substituted by its eigenvalue $\exp(i\bar{\kappa} \cdot \bar{R}_j)$.

In order to evaluate the matrix elements of $\bar{m}_j$, the quantum numbers describing the initial and final states of the unpaired electrons have to be known. For the heavy rare earth metals, Table 1 shows that the magnetic properties of an atom in the metal can be explained if the 4f-electron configuration for the metal atom is that of a free tripositive (3+) ion. The ground state of the free 3+ ion, assuming Russell-Saunders coupling and Hund's rule, will therefore be used in calculating the matrix elements of $\bar{m}_j$.

The Tm^{+3} ion has 12 f-electrons. The ground state of the ion in spectroscopic notation is the 3H_6 state corresponding to $S = 1$, $L = 5$

and $J = 6$. Similarly the ground state of Tb^{+3} having 8 f-electrons is the 7F_6 state ($S = L = 3$ and $J = 6$).

The excited states of the free ion with different eigenvalues S , L , and J have much higher energies than the ground state. They will be neglected in the calculation of the neutron cross section. Only matrix elements between $2J + 1$ eigenstates of J_z will be considered. They will be written as:

$$\langle M' | \bar{m}_j | M \rangle = \langle SLJM' | \bar{m}_j | SLJM \rangle \quad (2.15)$$

where M and M' are eigenvalues of J_z .

The measurement of the form factor of thulium was done at $4.2^\circ K$. The neutron diffraction measurements (11, 12), together with magnetization data (13), have shown that the magnetic moments of the atoms form a ferrimagnetic structure with each atom having its maximum ordered moment $\mu_B g J$. The initial state of a thulium atom is therefore the same for all atoms and can be written as $|SLJJ\rangle$, where the axis of quantization has been taken as the direction of the moment. Final states having M' different from M will give rise to inelastic magnon scattering and will be ignored. Therefore, $\langle J | \bar{m}_j | J \rangle$ is the only element that will contribute to the elastic scattering.

For thulium the matrix-element $\bar{C}_M(\bar{\kappa})$ of $V_M(\bar{\kappa})$ to be used in calculating the elastic cross section can now be written as:

$$\bar{C}_M(\bar{\kappa}) \cdot \bar{s} = \frac{2\pi\hbar^2}{m} \left\{ \sum_j \exp(i\bar{\kappa} \cdot \bar{R}_j) \langle J | \bar{m}_j | J \rangle \right\} \cdot \bar{s} \quad (2.16)$$

Equation 2.16 is valid for any of the heavy rare earth metals in their fully ordered state. It must be remembered, however, that the

vector $\langle J | \bar{m}_j | J \rangle$ is evaluated in a coordinate system having its z axis along the direction of the moment of the jth atom. Since this direction may vary from atom to atom, the dot or cross product of $\bar{C}_M(\kappa)$ with any vector will be quite complicated.

The form factor experiment on terbium was performed by studying the neutron scattering from an induced moment in the paramagnetic phase of terbium. Magnetization measurements (14) show terbium to be paramagnetic above 230°K; at room temperature the susceptibility follows a Curie-Weiss law with the paramagnetic Curie-temperature, θ_p of 239 K. for the susceptibility measured perpendicular to the hexagonal axis. The effective moment μ_{eff} is equal to $7.62 \mu_B$.

The applied magnetic field H used to induce the moment in terbium was about 25 kOe; so, the magnetic energy $gM\mu_B H$ for all M between -J and J was much less than the energy of the incident neutrons (~ 300 kT). In evaluating the cross section, equation 2.1, it is therefore valid to use the quasi-electric approximation, $E_{\alpha'} = E_{\alpha}$, for all α' . In the expression for the cross section, terms similar to those in equation 2.12 will appear. The thermal average over initial states for the operator $\bar{m}_j$ will give:

$$\langle \bar{m}_j \cdot \bar{m}_{j'} \rangle = \langle \bar{m}_j \rangle \cdot \langle \bar{m}_{j'} \rangle + \langle \bar{m}_j \cdot \bar{m}_j \rangle - \langle \bar{m}_j \rangle \cdot \langle \bar{m}_{j'} \rangle \delta_{jj'}$$

and

$$\langle \bar{m}_j \times \bar{m}_{j'} \rangle = \langle \bar{m}_j \rangle \times \langle \bar{m}_{j'} \rangle + i \langle \bar{m}_j \rangle \delta_{jj'} \quad (2.17)$$

In equation 2.17 only the first term on the right hand side of both equations will give rise to coherent elastic scattering. The other

terms contribute to the incoherent background. Therefore, they will not be considered in this derivation.

The thermal average of $\bar{m}_j$ has been derived in Appendix A. The approximations used in Appendix A are valid for terbium. The quantity $\langle \bar{m}_j \rangle$ is given by equation A8 to be:

$$\langle \bar{m}_j \rangle = \frac{\mu_B g H}{(2J+1)k(T-\Theta_p)} \sum_M M \langle M | \bar{m}_j | M \rangle \quad (2.18)$$

where the axis of quantization is parallel to $\bar{H}$ and T has been substituted by $T - \Theta_p$.

The matrix element $\bar{C}_M(\bar{\kappa})$ of $V_M(\bar{\kappa})$ to be used in calculating the cross section for terbium can therefore be written as:

$$\bar{C}_M(\bar{\kappa}) \cdot \bar{s} = \frac{2\pi\hbar^2}{m} \left\{ \sum_j \exp(i\bar{\kappa} \cdot \bar{R}_j) \langle \bar{m}_j \rangle \right\} \cdot \bar{s} \quad (2.19)$$

The summation over the initial and final states and the matrix elements $\langle \alpha' | V(\bar{\kappa}) | \alpha \rangle$ have now been calculated for the elastic coherent part of the scattering cross section given in equation 2.1. This contribution, which gives rise to Bragg reflections, has a cross section given by:

$$\left(\frac{d\sigma}{d\Omega} \right)_{\text{elastic constant}} = \left(\frac{m}{2\pi\hbar^2} \right)^2 \text{Tr} \{ (B_N^+(\bar{\kappa}) + \bar{C}_M^+(\bar{\kappa}) \cdot \bar{s}) (B_N(\bar{\kappa}) + \bar{C}_M(\bar{\kappa}) \cdot \bar{s}) \} \quad (2.20)$$

where $B_N(\bar{\kappa})$ and $\bar{C}_M(\bar{\kappa})$ is given by equation 2.13 and equation 2.16 (or equation 2.19) respectively.

The trace taken with respect to the neutron spin coordinates can be evaluated using the equations given by Messiah (25). The result is:

$$\begin{aligned} \left(\frac{2\pi\hbar^2}{m} \right)^2 \times \left(\frac{d\sigma}{d\Omega} \right)_{\text{elast. coherent}} &= B_N^+(\bar{\kappa}) B_N(\bar{\kappa}) + \frac{1}{4} \bar{C}_M^+ \cdot \bar{C}_M(\bar{\kappa}) \\ &+ \frac{1}{2} \bar{P} \cdot (B_N^+(\bar{\kappa}) \bar{C}_M(\bar{\kappa}) + \bar{C}_M^+(\bar{\kappa}) B_N(\bar{\kappa})) \\ &+ \frac{1}{4} i \bar{P} \cdot (\bar{C}_M^+(\bar{\kappa}) \times \bar{C}_M(\bar{\kappa})) \end{aligned} \quad (2.21)$$

From equation 2.21 it can be seen that the equations 2.12 and 2.17 used in the quasi-elastic approximation come from the second and fourth term in equation 2.21.

The calculation of $\langle M | \bar{m}_j | M \rangle$ for thulium and terbium will be given in the following chapter. It will be shown that the result for $\bar{C}_M(\bar{\kappa})$ in both cases can be written as:

$$\bar{C}_M(\bar{\kappa}) = \frac{2\pi\hbar^2}{m} \sum_j \exp(i\bar{\kappa} \cdot \bar{R}_j)^2 p_j \bar{q}_j \quad (2.22)$$

where:

$$p_j = \frac{\gamma e^2}{2m_e c^2} \mu_j f_j(\bar{\kappa})$$

$$\frac{\gamma e^2}{2m_e c^2} = .27 \times 10^{-12} \text{ cm}$$

μ_j = magnitude of magnetic moment of j th atom in Bohr magnetons,

$f_j(\bar{\kappa})$ = magnetic form factor of j th atom, and

$\bar{q}_j$ = magnetic interaction vector = $(\hat{\kappa} \cdot \hat{\mu}_j)\hat{\kappa} - \hat{\mu}_j$

where $\hat{\kappa}$ and $\hat{\mu}_j$ are unit vectors in the direction of the scattering vector and magnetic moment respectively.

In polarized neutron experiments one studies the polarization dependence of the cross section. Therefore the only Bragg reflections of interest are the ones for which the last two terms in equation 2.21 are different from zero.

In the case of thulium, the fourth term is zero since the moments of all the atoms are either parallel or antiparallel to the hexagonal c -axis in the $(4+, 3-)$ magnetic structure. Furthermore, μ_j in equation 2.22 is the same for all j , since $\mu_j = gJ(=7\mu_B)$ for all j . Due to inversion symmetry, $f_j(\bar{\kappa})$ is also independent of j ; p_j is therefore not a

function of j for Tm . The unit vector $\hat{\mu}_j$ can be written as $\hat{\mu}_j = a_j \hat{c}$ where $\hat{c}$ is a unit vector in the $+c$ direction and $a_j = +1$ or -1 .

Since the magnetic structure has a seven-layer repeat distance along the c -axis, a_j can be Fourier expanded:

$$a_j = \sum_{n=0}^6 \alpha_n \exp(i n \bar{\tau}_m \cdot \bar{R}_j) \quad (2.23)$$

where $\bar{\tau}_m = \frac{4\pi}{7c} \times \hat{c}$ and $\alpha_0 = 1/7$ for the $(4+, 3-)$ structure. The vector $p_j \bar{q}_j$ for thulium can therefore be written as:

$$p_j \bar{q}_j = \frac{\gamma e^2}{2m_e c^2} (\mu_{\text{ferro}} f(\bar{\kappa}) \bar{q} + \sum_{n=1}^6 \alpha_n \mu f(\bar{\kappa}) \bar{q} \exp(i n \bar{\tau}_j \cdot \bar{R}_j)) \quad (2.24)$$

where $\mu_{\text{ferro}} = \alpha_0 \mu = 1 \mu_B$ and $\bar{q} = (\hat{\kappa} \cdot \hat{c}) \hat{\kappa} - \hat{c}$.

After inserting equation 2.22 and equation 2.24 into equation 2.21, one will have to evaluate expressions of the form $\sum_j \exp(i(\bar{\kappa} + n \bar{\tau}_m \cdot \bar{R}_j))$. This sum is zero unless $\bar{\kappa} + n \bar{\tau}_m$ is equal to a reciprocal lattice vector. Therefore, the third term in equation 2.21 containing products like $B^+ C_M$ will only be different from zero for the nuclear Bragg reflections. The second term $C^+ C$ will contribute to both the nuclear Bragg reflections and to the purely magnetic satellite reflections. The latter will not be considered here since they do not depend on $\bar{P}$.

The elastic coherent and neutron spin dependent part of the cross section (equation 2.1) can now be written down for thulium. The expressions for the intensity of the scattered neutrons to be used in interpreting the data will be proportional to:

$$\left(\frac{d\sigma}{d\Omega}\right) \propto |F(\bar{\tau})|^2 \{b^2 + 2bp\bar{q} \cdot \bar{P} + p^2 q^2\} \quad (2.25)$$

where $\bar{\tau}$ = reciprocal lattice vector, $F(\bar{\tau})$ = structure factor, and $p(\bar{\tau})$ = magnetic scattering length = $\frac{\gamma e^2}{2m_e c^2} \mu_{\text{ferro}} f(\bar{\tau})$.

For terbium the evaluation of equation 2.21 is simpler than in the case of thulium since neither p_j nor $\bar{q}_j$ in equation 2.22 depend on j . One finds that equation 2.25 is valid for interpretation of the experimental results for terbium if one substitutes μ_{ferro} with the induced moment and $\hat{c}$ in $\bar{q}$ by a unit vector in the direction of the applied field.

In a polarized neutron experiment the incident neutrons going through the sample will be partially depolarized if the direction of $\bar{P}$ is not parallel or antiparallel to the direction of the magnetization of the sample. In order to avoid a significant change in the magnitude of $\bar{P}$ in the sample, one orients the crystal in the beam such that $\bar{P}$ and $\bar{\mu}_j$ are parallel or antiparallel. Under these conditions the second term in the { } bracket in equation 2.25 becomes $2bpq^2P$. Furthermore, for a ferro- or ferri-magnetic structure, a magnetic field strong enough to create one single domain is applied parallel to $\bar{P}$ and $\bar{\mu}$. This is done to minimize depolarization from domain boundaries and to avoid corrections due to a domain population that usually is unknown.

Using the formula for the scattered intensity, equation 2.25, the flipping ratio R for a particular Bragg reflection will be given by:

$$R = \frac{b^2 + 2bpq^2 + p^2q^2}{b^2 - 2bpq^2 + p^2q^2} \quad (2.26)$$

where the neutron polarization P has been assumed to be plus or minus one and $\bar{q} \cdot \bar{P} = q^2$.

Since it is possible in a polarized neutron experiment to measure

R very accurately (26), one can in most cases determine p or the ratio p/b from equation 2.26 with very small uncertainties. In practice one has to modify equation 2.26 to take into account the fact that P differs from the ideal value.

III. MATRIX ELEMENTS OF THE MAGNETIC INTERACTION OPERATOR

The magnetic interaction operator $\bar{m}$ for an ion with n unpaired electrons is given by equation 2.14. In Chapter II it was shown that the matrix elements of $\bar{m}$ needed for interpretation of the thulium and terbium experiments were of the form $\langle SLJM | \bar{m} | SLJM \rangle$.

The elements will be calculated using the method developed by Johnston (27), Johnston and Rimmer (28), and Lovesey and Rimmer (3). It will first be shown that equation 2.22 is correct. This implies that the vector $\langle SLJM | \bar{m} | SLJM \rangle$ is proportional to the magnetic interaction vector $\bar{q}$:

$$\langle SLJM | \bar{m} | SLJM \rangle = 2\bar{q}p \quad (3.1)$$

where $\bar{q} = \hat{\mu} \times (\hat{z} \times \hat{\mu})$. The z -axis is the axis of quantization.

The constant p is the magnetic scattering length. It is defined by equation 2.22 to be:

$$p = \frac{\gamma e^2}{2m_e c^2} \mu F(\bar{\kappa})$$

The magnetic moment μ corresponding to the matrix element in equation 3.1 is equal to gM , where g is the Landé factor. The magnetic form factor $f(\bar{\kappa})$ is defined for $\bar{\kappa} \rightarrow 0$ by: $f(\bar{\kappa}) \rightarrow 1$ for $\bar{\kappa} \rightarrow 0$.

From equation 3.1 the form factor will be calculated using the expression for the matrix elements given by Johnston (27). Johnston and Rimmer (28) and Lovesey and Rimmer (3). In order to compare this method with the method of Trammell (1) the form factor for thulium will also be calculated using the approach of Trammell.

Lovesey and Rimmer (3) define a magnetic scattering operator $\bar{D}^\perp$. The operators $\bar{m}$ and $\bar{D}^\perp$ are related in the following way:

$$\bar{m} = - \frac{\gamma e^2}{m_e c^2} \cdot 2\bar{D}^\perp$$

Equation 3.1 can therefore be written:

$$-\langle SLJM | \bar{D}^\perp | SLJM \rangle = \frac{1}{2} \bar{q} g M_f(\bar{\kappa}) \quad (3.2)$$

The article by Lovesey and Rimmer (3) will be used as the main reference for this chapter. Direct references to this work will be denoted by LR. For example, the equation in the article by Lovesey and Rimmer that defines $\bar{D}^\perp$ will be referred to as LR equation 2.40a.

The matrix elements of the q th spherical component of $\bar{D}^\perp$ is given by LR equation 5.45 to be:

$$\langle \ell^n \otimes JM | D_q^\perp | \ell^n \otimes J' M' \rangle = \sqrt{4\pi} \sum_{K', K''} \{ A(K'', K') + B(K', K'') \} \quad (3.3)$$

$$\times \sum_{Q'' Q'} Y_{K''}^{Q''}(\hat{\kappa}) \langle K' Q' J' M' | JM \rangle \langle K'' Q'' K' Q' | 1q \rangle$$

The electron wave functions on the left hand side are labelled by the electron configuration ℓ^n and by quantum numbers J and M for the total angular momentum and its z -component. The number $\otimes$ is introduced to distinguish between possible multiple occurrences of J . For thulium and terbium one finds from equation 3.1 that:

$$\ell^n: 4f^n; \otimes = \otimes': S, L; J = J' \text{ and } M = M'$$

where S and L are the total spin and total orbital angular momenta,

respectively. The number n is the number of unpaired electrons.

The matrix element in equation 3.3 has been evaluated under the assumption that all unpaired electrons belong to a single atomic shell of orbital momentum ℓ (e.g. the 4f shell). Furthermore, all the electrons are assumed to have the same radial wave function $R_{n\ell}(r)$ where the function $R_{n\ell}(r)$ is defined by the following equation for the one-electron wave function:

$$|\ell m\rangle = \frac{1}{r} R_{n\ell}(r) Y_{\ell}^m(r)$$

On the right hand side of equation 3.3 the constants K and Q are quantum numbers for the angular momentum operator $(\bar{K})^2$ and for the z -component of $\bar{K}$. The allowed values of K'' , K' and Q'' , Q' are determined by the coefficients A and B and by the two Clebsch-Gordon coefficients.

In equation 2.14 the magnetic interaction operator consists of two sums over the unpaired electrons. The first sum depends on the spin $\bar{s}_n$ of the single electrons. The second sum contains the momentum $\bar{p}_n$ or, using equation 2.9, the orbital angular momentum $\bar{\ell}_n$ for the n th electron. In the calculation of the matrix element of $\bar{D}^{\perp}$, the coefficients $A(K'', K')$ and $B(K'', K')$ represent respectively the orbital and spin components of the magnetic interaction. They are defined by LR equation 5.24 and LR equation 5.32 through 5.34.

In the particular case of interest $A(K'', K')$ and $B(K'', K')$ are functions of n , ℓ , S , L and J . For thulium one has $n = 12$, $\ell = 3$, $S = 1$, $L = 5$, and $J = 6$. For terbium $n = 8$, $\ell = 3$, $S = 3$, $L = 3$ and

$J = 6$. The coefficients A and B depend also on linear combinations of the radial integrals $\langle j_K \rangle$, where $\langle j_K \rangle$ is defined by LR equation 5.10 to be:

$$\langle j_K \rangle = \int_0^{\infty} |R_{n\ell}(r)|^2 j_K(\kappa r) dr \quad (3.4)$$

The function $j_K(\kappa r)$ is the spherical Bessel function of order K , and κ is the length of the scattering vector.

After inserting the values of n , ℓ , S , L and J in LR equation 5.24 and LR equations 5.32 through 5.34, both $A(K'', K')$ and $B(K'', K')$ become linear combinations of the integrals $\langle j_K \rangle$. The coefficients of $\langle j_K \rangle$ depend only on K , K' and K'' . The sum, $A(K'', K') + B(K'', K')$, on the right hand side of equation 3.3 determines, therefore, how the matrix elements of $\bar{D}^{\perp}$ depend on the length of the scattering vector. The angular dependence of the matrix element is determined by the product of the spherical harmonic and the Clebsch-Gordon coefficients.

For matrix elements both the two electron wave functions in the element have the same quantum numbers S , L and J , $A(K'', K')$ and $B(K'', K')$ are only different from zero for $K'' = K' \pm 1$ and $K' = 1, 3 \dots 2l + 1$. Furthermore, the following relations (LR equations 5.25 and 5.33) exist between the coefficients for $K'' = K' + 1$ and $K'' = K' - 1$:

$$\frac{B(K'-1, K')}{B(K'+1, K')} = \frac{A(K'-1, K')}{A(K'+1, K')} = \left(\frac{K'+1}{K'} \right)^{1/2} \quad (3.5)$$

Using these equations and $M' = M$, the q th spherical component of the matrix element on the left hand side of equation 3.2 becomes:

$$-\langle \text{SLJM} | D_q^\perp | \text{SLJM} \rangle = \sqrt{4\pi} \sum_{K'} \frac{1}{\sqrt{K'+1}} \langle K' 0 \text{JM} | \text{JM} \rangle$$

$$\times \{A(K'-1, K') + B(K'-1, K')\}$$

(3.6)

$$\times [\sqrt{K'+1} \langle K'-1 \ 0 \ K' 0 | 1q \rangle Y_{K'-1}^q(\hat{x}) + \sqrt{K'} \langle K'+1 \ 0 \ K' 0 | 1q \rangle Y_{K'+1}^q(\hat{x})]$$

where $K' = 1, 3, 5, \dots, 2\ell + 1$.

The x-, y- and z-components of the vector, $-\langle \text{SLJM} | \bar{D} | \text{SLJM} \rangle$, will be calculated in order to verify equation 3.2. This vector will be denoted by $\bar{D}$:

$$\bar{D} = -\langle \text{SLJM} | \bar{D}^\perp | \text{SLJM} \rangle$$

D_x , D_y , and D_z are related to D_q by: $D_0 = D_z$ and $D_{\pm 1} = \mp \frac{1}{\sqrt{2}}(D_x \pm i D_y)$.

$$D_z = \sum_{K'} \sqrt{\frac{3K'}{2K'+1}} \langle K' 0 \text{JM} | \text{JM} \rangle \{A(K'-1, K') + B(K'-1, K')\}$$

$$\times [P_{K'-1}(\cos \Theta) - P_{K'+1}(\cos \Theta)] \quad (3.7)$$

where $P_{K'}(\cos \Theta)$ are Legendre polynomials. The angle Θ is the angle between $\hat{x}$ and $\hat{z}$. The spherical harmonics, $Y_K^0(\hat{x})$, has been substituted by the polynomials, $P_K(\cos \Theta)$.

In deriving equation 3.7 the following relation between Clebsch-Gordon coefficients has been used:

$$\sqrt{(K'+1)(2K'-1)} \langle K'-1 \ 0 \ K' 0 | 10 \rangle = -\sqrt{K'(2K'+3)} \langle K'+1 \ 0 \ K' 0 | 10 \rangle \quad (3.8)$$

The x-component of $\bar{D}$ is found from equation 3.6 to be:

$$\begin{aligned}
D_x = & \sqrt{4\pi} \sum_{K'} \frac{1}{\sqrt{K'+1}} \langle K' 0 J M | J M \rangle \{ A(K'-1, K') + B(K'-1, K') \} \\
& \times \left[\sqrt{\frac{(K'+1)(K'-1)}{K'}} \langle K'-1 0 K' 0 | 1 0 \rangle \operatorname{Re} Y_{K'-1}^1(\hat{\kappa}) \right. \\
& \left. - \sqrt{\frac{K'(K'+2)}{K'+1}} \langle K'+1 0 K' 0 | 1 0 \rangle \operatorname{Re} Y_{K'+1}^1(\hat{\kappa}) \right]
\end{aligned} \tag{3.9}$$

where $\operatorname{Re} Y_K^1(\hat{\kappa}) = \frac{1}{2}(Y_K^1(\hat{\kappa}) + Y_K^{1*}(\hat{\kappa}))$.

The expression on the right hand side of equation 3.9 becomes equal to the y-component of $\bar{D}$ if $\operatorname{Re} Y_K^1(\hat{\kappa})$ is substituted by $\operatorname{Im} Y_K^1(\hat{\kappa}) = \frac{1}{2i}(Y_K^1(\hat{\kappa}) - Y_K^{1*}(\hat{\kappa}))$.

In the derivation of equation 3.9 the following two equations, valid for $q = +1$ and -1 , have been used:

$$\begin{aligned}
\langle K'-1 q K' 0 | 1 q \rangle &= -\sqrt{\frac{K'-1}{2K'}} \langle K'-1 0 K' 0 | 1 0 \rangle \quad \text{and} \\
\langle K'+1 q K' 0 | 1 q \rangle &= \sqrt{\frac{K'+2}{2(K'+1)}} \langle K'+1 0 K' 0 | 1 0 \rangle
\end{aligned} \tag{3.10}$$

The z-axis, defined as the axis of quantization, is the only axis whose direction has been fixed. In order to simplify the equations for the components of $\bar{D}$ the x-axis will be taken in the direction of the projection of $\bar{\kappa}$ onto the plane perpendicular to $\bar{z}$. In this Cartesian coordinate system D_y becomes zero and the angular dependence of D_x contains only the angle Θ .

With this simplification, the spherical harmonics in equation 3.9 can be expressed in terms of associated Legendre polynomials. By using the recursion relations for Legendre polynomials, D_x can be written as:

$$D_x = -\cot \Theta \sum_{K'} \sqrt{\frac{3K'}{2K'+1}} \langle K' 0 J M | J M \rangle \{A(K'-1, K') + B(K'-1, K')\} \quad (3.11)$$

$$\times [P_{K'-1}(\cos \Theta) - P_{K'+1}(\cos \Theta)]$$

where equation 3.8 has been used to simplify the equation.

By comparing equation 3.7 and equation 3.11 it can be seen that with this choice of coordinate system the vector $\bar{D}$ has the form:

$$\bar{D} = (D_x, D_y, D_z) = D_z (-\cot \Theta, 0, 1) \quad (3.12)$$

In the same coordinate system the magnetic interaction vector $\bar{q}$ is given by:

$$\begin{aligned} \bar{q} &= (q_x, q_y, q_z) = (-\sin \Theta \cos \Theta, 0, \sin^2 \Theta) = \\ &\sin^2 \Theta (-\cot \Theta, 0, 1) \end{aligned} \quad (3.13)$$

Equations 3.12 and 3.13 show that $\bar{D}$ is indeed proportional to $\bar{q}$:

$$\bar{D} = \bar{q} \times \frac{D_z}{\sin^2 \Theta} \quad (3.14)$$

By comparing equations 3.2 and 3.14, it can be seen that, in order to verify equation 3.2, D_z has to have the following form:

$$D_z = \frac{1}{2} \sin^2 \Theta g M f(\bar{\kappa}) \quad (3.15)$$

Since the form factor $f(\bar{\kappa})$ is defined to be equal to unity when $\bar{\kappa}$ is equal to zero, it remains to be shown that:

$$\lim_{\bar{\kappa} \rightarrow 0} D_z(\bar{\kappa}) = \frac{1}{2} \sin^2 \Theta g M \quad (3.16)$$

In the expression for D_z , equation 3.7, the sum $A(K'-1, K') + B(K' - 1, K')$ is the only term that depends on the length of $\bar{\kappa}$. Using LR equations 5.24, 5.32, and 5.43, this sum can be written as:

$$A(K'-1, K') + B(K'-1, K') = F(K') \cdot \langle j_{K'-1} \rangle + G(K') \langle j_{K'+1} \rangle \quad (3.17)$$

where $F(K')$ and $G(K')$ are constants that depend on K' , n , l , S , L and J . From the definition of $\langle j_K \rangle$, equation 3.4, one finds that:

$$\lim_{\kappa \rightarrow 0} \langle j_K \rangle = \begin{cases} 1 & \text{for } K=0 \\ 0 & \text{for } K>0 \end{cases} \quad (3.18)$$

Thus, for $\kappa = 0$, the right hand side of equation 3.17 is zero unless $K' = 1$.

The sum over K' in equation 3.7 will contain only the first term, $K'=1$, in the limit $\bar{\kappa} \rightarrow 0$. Therefore, the left hand side of equation 3.16 becomes:

$$\lim_{\bar{\kappa} \rightarrow 0} D_z(\bar{\kappa}) = \langle 10JM | JM \rangle F(1) \{P_0(\cos \Theta) - P_2(\cos \Theta)\} \quad (3.19)$$

The constant $F(1)$ can be calculated from LR equations 6.7 and 6.10. The result is:

$$F(1) = -\frac{1}{3} \sqrt{J(J+1)} g \quad (3.20)$$

where g = Landé factor. The Clebsch-Gordon coefficient (29) in equation 3.19 can be written as:

$$\langle 10JM | JM \rangle = -\frac{1}{3} \sqrt{J(J+1)} \frac{-M}{J} \quad (3.21)$$

Using equations 3.20 and 3.21, one obtains for equation 3.19 the

following:

$$\lim_{\bar{\kappa} \rightarrow 0} D_z(\bar{\kappa}) = \frac{1}{3} gM \{P_0(\cos \Theta) - P_2(\cos \Theta)\} = \frac{1}{2} gM \sin^2 \Theta \quad (3.22)$$

The z-component of $\bar{D}$ has therefore the limiting value specified by equation 3.16.

It has now been proven that the matrix element of $\bar{m}$, $\langle SLJM | \bar{m} | SLJM \rangle$, has the form given by equation 3.1. The magnetic form factor can be calculated from the expression for the matrix element. Using equations 3.7 and 3.15, one finds for the form factor:

$$f_M(\bar{\kappa}) = \frac{2}{\sin^2 \Theta gM} \times \sum_{K'} \sqrt{\frac{3K'}{2K'+1}} \langle K' 0 JM | JM \rangle \times \{A(K'-1, K') + B(K'-1, K')\} \times [P_{K'-1}(\cos \Theta) - P_{K'+1}(\cos \Theta)] \quad (3.23)$$

where $K' = 1, 3, 5$, and 7 for a f-shell. The subscript M has been used to indicate that $f(\bar{\kappa})$ depends on the quantum number M only through the product $\frac{1}{M} \langle K' 0 JM | JM \rangle$. Therefore, the form factors, $f_{M'}(\bar{\kappa})$ and $f_M(\bar{\kappa})$, are related to each other by comparatively simple equations.

In the special case that the magnetic quantum number M is equal to J , $f_J(\bar{\kappa})$ (30) can be written in the following way:

$$\sin^2 \Theta gJ f_J(\bar{\kappa}) = \sum_K \{X_{K-1} (c_K \langle j_{K-1} \rangle + c_{K+1} \langle j_{K+1} \rangle)\} \quad (3.24)$$

where $K = 1, 3, 5$, and 7 if the unpaired electrons belong to an f-shell.

The constant X_K is defined by:

$$X_K = 2 \left\{ \frac{(K+1)(K+2)}{6(2K+3)} \right\}^{1/2} \times [P_K(\cos \Theta) - P_{K+2}(\cos \Theta)] \quad (3.25)$$

Table 2. Coefficients for ground state $M_J = J$ for the tripositive rare-earth ions ($C_8=0$)

Ground State	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_2/c_1
Ce $^2F_{5/2}$	2.1429	3.4285	0.2290	0.7635	0.0088	0.1050	0	1.6000
Pr 3H_4	3.2000	5.2622	-0.2359	-0.3216	-0.0446	-0.2834	0.0056	1.6444
Nd $^4I_{9/2}$	3.2725	5.9001	-0.4995	-0.6055	0.0928	0.3461	-0.0149	1.8030
Pm 5I_4	2.4000	5.4303	-0.2596	-0.1678	0.0122	-0.1565	0.0056	2.2626
Sm $^6H_{5/2}$	0.7143	3.8731	0.1102	0.1504	-0.0103	0.0091	0	5.4219
Tb 7F_6	9.0000	3.3333	0	0.6792	-0.1226	0.0849	-0.0276	0.3704
Dy $^6H_{15/2}$	10.0000	5.3333	-0.5345	-0.1945	0.0612	-0.3018	0.1379	0.5333
Ho 5I_8	10.0000	6.1333	-0.7483	-0.6803	0.3065	0.3583	-0.2758	0.6133
Er $^4I_{15/2}$	9.0000	5.8667	-0.3207	-0.3887	-0.0612	-0.1132	0.2758	0.6519
Tm 3H_6	7.0000	4.6667	0.5345	0.1944	-0.4292	-0.0659	-0.1379	0.6667
Yb $^2F_{7/2}$	4.0000	2.6667	1.0690	0.3887	0.2452	0.0377	0.0276	0.6667

The coefficients, C_K , (30) have been calculated for the tripositive rare earth ions in their ground state. The results are given in Table 2.

For the thulium experiment it has been assumed that the form factor can be calculated assuming a 4f-electron configuration corresponding to the 3H_6 state with $M = J$. Using equation 3.24 and Table 2, the form factor for thulium when $\Theta = 90^\circ$ becomes:

$$f(\bar{\kappa}) = f(\kappa, \Theta) = \langle j_0 \rangle + 0.5952 \langle j_2 \rangle - 0.0828 \langle j_4 \rangle + 0.0095 \langle j_6 \rangle \quad (3.26)$$

The coefficients to $\langle j_K \rangle$ in equation 3.24 are functions of Θ . For example, the form factor for $\Theta = 30.92^\circ$ is given by:

$$f(\kappa, \Theta) = \langle j_0 \rangle + 0.8581 \langle j_2 \rangle - 0.0481 \langle j_4 \rangle - 0.0081 \langle j_6 \rangle \quad (3.27)$$

where the value $\Theta = 30.92^\circ$ corresponds to the angle between the scattering vector for the $(10\bar{1}3)$ reflection in thulium and the hexagonal c-axis (direction of the magnetic moment).

For the interpretation of the experimental form factor for thulium, equation 3.26 will be used for Bragg reflections whose scattering vectors are perpendicular to the c-axis. The Miller indices for these reflections are of the form, $(h, k, \bar{m}, 0)$, where $\bar{m} = -(h + k)$. For Bragg reflections with the fourth index, l , different from zero, the form factors will be calculated from equation 3.24 using the appropriate values of Θ . For example, equation 3.27 will be used for the $(10\bar{1}3)$ reflection.

The thermal average, $\langle \bar{m} \rangle$, in equation 2.18 has to be calculated for the interpretation of the terbium experiment. Using equation 3.1 and

equation 3.15 $\langle \bar{m} \rangle$ becomes:

$$\langle \bar{m} \rangle = 2q \frac{\gamma e^2}{2m_e c^2} \frac{g\mu_B H}{(2J+1)k(t-\theta_p)} \frac{2}{\sin^2 \theta} \sum_M MD_z \quad (3.28)$$

The sum over M in equation 3.28 can be written as:

$$\sum_M MD_z = \sum_{K'} \left[\sum_M \langle K' 0 JM | JM \rangle \right] \times \sqrt{\frac{3K'}{2K'+1}} \quad (3.29)$$

$$\times \{A(K'-1, K') + B(K'-1, K')\} \times (P_{K'-1}(\cos \theta) - P_{K'+1}(\cos \theta))$$

where the expression for D_z in equation 3.7 has been used. Using equation 3.21 and the orthogonality relations for Clebsch-Gordon coefficients, one finds that:

$$\sum_M \langle K' 0 JM | JM \rangle = -\frac{1}{3}(2J+1)\sqrt{J(J+1)} \delta_{K',1} \quad (3.30)$$

Therefore, equation 3.29 becomes:

$$\sum_M MD_z = -\frac{1}{2}(2J+1)\sqrt{J(J+1)} \{A(0,1) + B(0,1)\} \sin^2 \theta \quad (3.31)$$

By combining the results of equations 3.17, 3.20, 3.23 and 3.24, one finds that $A(0,1)+B(0,1) = \frac{1}{3} g\sqrt{J(J+1)} \times (\langle j_c \rangle + \frac{c_2}{c_1} \langle j_2 \rangle)$. For equation 3.31 one then obtains:

$$\sum_M MD_z = \frac{1}{6} \sin^2 \theta g(2J+1)J(J+1) \times \{\langle j_o \rangle + \frac{c_2}{c_1} \langle j_2 \rangle\} \quad (3.32)$$

The thermal average, $\langle \bar{m} \rangle$, in equation 3.28 can therefore be written as:

$$\begin{aligned} \langle \bar{m} \rangle &= 2\bar{q} \frac{\gamma e^2}{2m_e c^2} \frac{g^2 J(J+1) \mu_B H}{3k(T - \Theta_p)} \left\{ \langle j_0 \rangle + \frac{c_2}{c_1} \langle j_2 \rangle \right\} \\ &= 2\bar{q} \frac{\gamma e^2}{2m_e c^2} \mu f(\kappa) \end{aligned} \quad (3.33)$$

where μ = the induced magnetic moment in Bohr magnetons and $f(\kappa)$ = magnetic form factor = $\langle j_0 \rangle + \frac{c_2}{c_1} \langle j_2 \rangle$. From equation 3.33 it can be seen that $\langle \bar{m} \rangle$ has the form that was assumed in deriving equation 2.22.

For the interpretation of the terbium experiment the following form factor will be used:

$$f(\kappa) = \langle j_0 \rangle + 0.3704 \langle j_2 \rangle \quad (3.34)$$

where c_2/c_1 has been taken from Table 2.

The experimental form factor for thulium and terbium has been measured for a number of Bragg reflections using a modified form of equation 2.26. In principle, one can determine a radial wave functions, $R_{n\ell}(r)$, from an experimental form factor using equation 3.26 or equation 3.34 and the inverse transform of equation 3.4. Unfortunately, the number of Bragg reflections that were measured for both thulium and terbium was too small to make an experimental $R_{n\ell}(r)$ meaningful. Instead, theoretical form factors were calculated from equations 3.26, and 3.34 using the wave functions calculated by Blume, Freeman and Watson (17). These theoretical

form factors have then been compared to the experimental form factors.

The coefficients, C_K , in Table 2 and the numerical coefficients to $\langle j_K \rangle$ in the expressions for the form factors were calculated on an electronic computer. The expressions for C_K and C_{K+1} in equation 3.24 can be found from equation 3.23 using the formulas for $A(K', K')$ and $B(K', K')$ given by LR equations 5.24 and 5.32 through 5.34. The numerical values of the coefficients, C_K and C_{K+1} , were calculated using the quantum numbers l , n , S , L , and J together with the appropriate fractional parentage coefficients given by Nielson and Koster (31).

To check the computer programs, the form factor for thulium in the 3H_6 state with $M = J$ was derived using the method described by Trammell (1). The derivation is given in Appendix B. The form factor, $f(\bar{\kappa})$, is given by equation B16.

The spin contribution to $f(\bar{\kappa})$ is expressed as linear combinations of the integrals $\langle j_K \rangle$ defined by equation 3.4. The spin part of $f(\bar{\kappa})$ in the method by Johnston, Rimmer and Lovesey can be found by setting all the orbital constants, $A(K'-1, K')$, in equation 3.23 equal to zero. A comparison shows that the two different methods give the same result.

In the approach of Trammell, the electron momentum $\bar{p}_n$ is written in terms of the orbital angular momentum $\bar{l}_n$ using equation 2.9. The orbital contribution to $f(\bar{\kappa})$ is a linear combination of the radial integrals, $\langle g_K \rangle$ (1, 17). These integrals are different from $\langle j_K \rangle$. Blume, Freeman and Watson (17) have tabulated the $\langle g_K \rangle$ integrals as well as the $\langle j_K \rangle$ integrals. Using the numerical values of $\langle g_K \rangle$ and $\langle j_K \rangle$, the orbital contribution from equation B16 agrees with the contribution

from $A(K'-1, K')$ alone in equation 3.23 for several values of θ .

Similar agreement for terbium was found between the form factor calculated from Table 2 and the one given by Steinsvoll et al. (2).

The numerical agreement between the two methods has been taken as proof that the computer program generating the coefficients C_K is correct.

IV. EXPERIMENTAL PROCEDURES

The experimental technique that was used in the present investigation is discussed in this chapter. A description of the equipment is given in the first section of the chapter. The second section contains a discussion of the method that was used for the collection of the data. An explanation of the corrections that have been applied to the data is given in the last section of the chapter.

A. Instrument

The instrument that was used to collect the data for the thulium and terbium experiments is called a polarized neutron diffractometer. The present experiments were performed using a neutron diffractometer that was designed and built by Argonne National Laboratory. This diffractometer is temporarily installed at the Ames Laboratory Research Reactor.

In this section a discussion of the properties of a typical polarized neutron diffractometer will be given. This discussion will be followed by a description of the instrument used in the present investigation.

In Fig. 1 a schematic diagram of a typical diffractometer is shown. A collimated beam of thermal neutrons from a nuclear reactor is incident on the monochromating crystal that produces a monochromatic beam of neutrons by Bragg scattering. The crystal in a polarized neutron diffractometer is a ferromagnetic crystal magnetized by the polarizing field, $\bar{H}_p$. The scattering vector for the Bragg reflection is perpendicular to $\bar{H}_p$, so the cross section for the incident neutrons is proportional to $(b + p)^2$ or $(b - p)^2$ for the two possible spin states of the neutrons. In certain

ferromagnetic materials some of the Bragg reflections have the property that $p = b$. Since the cross section is proportional to $(b - p)^2$ for one of the spin states of the incident neutrons, monochromating crystals of these materials are used to produce a monochromatic beam that is almost completely polarized.

A collimating field that is parallel to $\bar{H}_p$ is shown in Fig. 1. This field of about 130 Oe is constant and is maintained along the neutron path between the monochromating crystal and the sample crystal. The function of this field is to prevent stray magnetic fields from depolarizing the neutrons along the path. A third field shown in Fig. 1 is the analyzing field which is used to magnetize the sample. The analyzing field is also parallel to $\bar{H}_p$.

In the path between the monochromating crystal and the sample the neutrons go through the center of a solenoid, the r.f. coil. The field produced by the solenoid is parallel to the wave vector of the neutrons. If the radio-frequency of the current in the solenoid is equal to the Larmor frequency of the neutron spin in the collimating field, some of the neutrons will change the direction of their spins. The probability that a neutron will reverse its spin going through the coil can be made very close to unity by adjusting the amplitude of the r.f. current. By switching the r.f. current on and off, the monochromatic neutrons incident on the sample will have the direction of their spin either antiparallel or parallel to the analyzing field.

In a conventional form factor experiment the sample is a single crystal oriented in the beam so that the monochromatic neutrons are scattered

by a Bragg reflection. The scattered neutrons are then counted by a neutron detector that is positioned in the Bragg scattered beam.

The sample is usually mounted in the analyzing field in such a way that a given crystallographic axis is parallel to the field. In practice this axis is one of the directions of easy magnetization. Since the direction of one of the crystal axes is given, the orientation of the sample in the monochromatic beam can be specified completely by the angle between the direction of the beam and one crystal axis that is perpendicular to the analyzing field. This angle is commonly denoted by φ .

The distance between the sample and the detector is fixed so the direction of the neutron path between the sample and the detector can be specified by two angles, 2θ and χ . The angle 2θ is the angle between the monochromatic beam and the projection of the direction of the neutron path upon the plane perpendicular to the analyzing field. The angle χ is the angle between this plane and the path.

The numerical values of φ , 2θ and χ for a given Bragg reflection can be calculated from the crystal structure of the sample and the wave length of the monochromatic neutrons.

In a conventional polarized beam experiment the intensity of the scattered neutrons is measured for the two spin states of the monochromatic neutrons; the ratio between the two intensities is called the flipping ratio, R . In Equation 2.26 the theoretical expression is given for the flipping ratio of a Bragg reflection. This formula is only valid for the ideal experiment where the polarization P for the two spin states is equal to plus or minus one. In practice the numerical value of P will be

less than one.

The polarization of the monochromatic beam incident on the sample will be denoted by P_i for the spin state that corresponds to the r.f. current in the coil being switched off. The value of P_i is determined by the monochromator and by the depolarization that the beam suffers along the path from the monochromator to the sample. For the spin state that corresponds to the r.f. current being turned on, the polarization will be $-P_i E$, where E is the flipping efficiency. The factor E is related to the probability, e , that a neutron reverses its spin going through the r.f. coil by $E = 2e - 1$. The polarization P_i and the flipping efficiency E are both instrumental constants that can be determined experimentally (32) for a given diffractometer. If the constants P_i and E are included in the cross section in Equation 2.25, the flipping ratio R for a Bragg reflection becomes:

$$R = \frac{1 + q^2 \gamma^2 + 2P_i q^2 \gamma}{1 + q^2 \gamma^2 - 2P_i E q^2 \gamma} \quad (4.1)$$

where $\gamma = p/b$. The quantities p , b and q^2 are discussed in Chapter II.

If one measures the flipping ratio for a particular Bragg reflection, an experimental value of γ for this reflection can be determined from Equation 4.1. By solving this equation one finds:

$$\gamma = P_i \left\{ RE + 1 \pm \frac{1}{P_i} \sqrt{(P_i (RE + 1))^2 - \frac{1}{2} (R-1)^2} \right\} / (R-1) \quad (4.2)$$

The cross section for the Bragg reflection that produces the monochromatic beam is proportional to $b_m^2 (1 + \gamma_m)^2$ or $b_m^2 (1 - \gamma_m)^2$ for the

two possible spin states of the neutrons where b_m is the nuclear coherent scattering length for the monochromator. The ratio γ_m is defined to be p_m/b_m where p_m is the magnetic scattering length for the monochromator. For an ideal polarizing crystal, γ_m is plus or minus one.

The sign of the nuclear coherent scattering lengths, b_m and b , for the monochromator and the sample can be determined experimentally (33) for a given element. For both magnetic scattering lengths p_m and p , the following sign convention will be adopted. If the magnetic moment $\bar{\mu}$ in Equation 2.22 is parallel to the analyzing field, the magnetic scattering length is positive; if $\bar{\mu}$ is antiparallel to the analyzing field, the magnetic scattering length is negative. With this sign convention the polarization P_i in Equation 4.1 and 4.2 has the same sign as γ_m . The flipping efficiency E is positive.

In Equation 4.2 there are two solutions of γ . One can estimate the numerical value of γ from the magnitude of the magnetic moment and the nuclear coherent scattering length b . If the numerical value of γ is estimated to be less than one for a Bragg reflection, the solution with the minus sign has to be used. For numerical values of γ larger than one the solution with the plus sign is correct.

From the experimental value of γ for a Bragg reflection, the value of the form factor, $f(\bar{\tau})$, can be determined if the values of both the magnetic moment and the nuclear coherent scattering length are known. The vector $\bar{\tau}$ is the reciprocal lattice vector of the Bragg reflection. From Equation 2.25 one finds:

$$f(\bar{\tau}) = 3.71 \times \frac{b}{\mu_{\text{ferro}}} \times \gamma(\bar{\tau}) \quad (4.3)$$

where b in units of 10^{-12} cm and μ_{ferro} is measured in Bohr magnetons. The length of the reciprocal lattice vector $\bar{\tau}$ is conventionally measured in units of $1/2d(=\sin \theta/\lambda)$, where d is the plane spacing for the Bragg reflection. By measuring the flipping ratio R of many different Bragg reflections for one sample the shape of the form factor can be determined using Equations 4.2 and 4.3.

The polarized neutron diffractometer that was used for the present investigation is shown in Figs. 2 and 3. The instrument was designed by Drs. L. R. Heaton¹, G. H. Lander¹ and M. H. Mueller¹. It was built by Argonne National Laboratory. The diffractometer is installed temporarily at Ames Laboratory Research Reactor in front of Beam Port No. 4.

The monochromating crystal is a single crystal of the alloy $\text{Co}_{0.92}\text{Fe}_{0.08}$ that has the face-centered cubic structure. The nuclear coherent scattering length b_m (34) and the magnetic scattering length p_m (34) for the (200)-reflection are 0.365×10^{-12} cm and 0.383×10^{-12} cm respectively.

The monochromatic crystal is centered in a collimated beam of thermal neutrons from the reactor; it is oriented so that the monochromatic beam from the (200)-reflection is horizontal. The crystal is held between the poles of a permanent magnet that produces a vertical field of approximately 3 kOe. In order to reduce the radiation coming from the reactor the monochromating crystal is placed in the center of a large shielding drum. The incident beam of thermal neutrons enters the drum through a pie-shaped

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Fig. 2. The ANL neutron diffractometer

Fig. 3. The ANL neutron diffractometer

opening. The scattered beam of monochromatic neutrons goes through a collimator inserted in the drum.

A vertical collimating field between the monochromator and the sample is produced by permanent magnets that are placed in the magnet guides. In the volume where the flipping coil is placed the collimating field is approximately 130 Oe.

The analyzing field in which the sample is placed is produced by the sample magnet. This magnet is an electromagnet and the magnitude of its field can be varied. The stray field from the sample magnet in the vicinity of the flipping coil is strong enough to affect the collimating field. This stray field changes with the D.C. current in the sample magnet. Therefore, the frequency in the r.f. coil is varied in order to obtain maximum flipping efficiency. The optimum frequency decreases from 350 kHz to 325 kHz when the magnet current is increased from 0 to 60 A.

The polarization P_i and the flipping efficiency E were determined at the sample position for several wave lengths of the monochromatic beam. In Table 3 the values used in the present experiments are listed. The symbol λ is the wave length of the monochromatic neutrons and I is the D.C. current in the sample magnet. The symbols dP_i and dE denote the measured standard deviations of P_i and E .

The sample which is centered in the monochromatic beam is mounted in the gap between the pole pieces of the sample magnet; the field in the gap is vertical. The magnet and the pole pieces are constructed in such a way that the sample can be rotated around a vertical axis. This axis is the axis of rotation for the ϕ -motion.

Table 3. Polarization and flipping efficiency

λ in Å	I in A.	P_i	dP_i	E	dE
0.85	20	0.987	0.005	0.985	0.005
0.85	60	0.987	0.005	0.981	0.005
1.02	20	0.980	0.005	0.985	0.005

The sample magnet that is stationary is supported by a pedestal mounted on a table. The height and position of this table are adjusted so that the monochromatic beam goes through the center of the magnet.

The pole pieces are rigidly held together by a thin walled aluminum sleeve. The distance between these pole pieces can be adjusted to the length of the sample attached to one of the pole pieces. For room temperature experiments the assembly of sample and pole pieces is placed in a two-inch diameter vertical hole which runs through the sample magnet. This assembly, called the sample holder, is supported by a bearing mounted on top of the magnet and can rotate around the vertical axis through the center of the magnet. The height of the sample holder can be adjusted so that the sample is in the center of the magnet. For low temperature experiments the sample and special set of pole pieces are placed in the tail section of the cryostat. The bearing on top of the magnet supports the cryostat and its tail section is positioned in the vertical hole through the magnet. The vertical position of the cryostat is adjusted so that the sample is in the center of the monochromatic beam. In order to change the angle ϕ the cryostat containing the sample is rotated. Figs. 2 and 3 show

the sample mounted in the cryostat.

A stepping motor (Slo - Syn) drives the rotation of the sample around the vertical axis through the center of the magnet; this motor is called the φ -drive motor. The value of the angle φ is read to an accuracy of 0.01° by an optical encoder that is mounted on the shaft of the φ -drive motor.

The monochromatic neutrons scattered by the sample are counted by a detector, the counter tube. To reduce the background the counter tube is placed in a cylindrical neutron shield. The assembly supporting the counter shield is constructed in such a manner that the two angles, 2θ and χ , defining the position of the counter tube can be varied automatically. This assembly consists basically of two parts, a counter arm and a frame carrying the counter shield.

The counter arm that supports the frame can rotate around a bearing mounted on the magnet pedestal. The weight of the frame plus counter shield is carried by a set of casters that travel on the table. The axis of rotation for the counter arm is vertical and goes through the center of the magnet. This axis that coincides with the φ -axis is the axis for the 2θ -motion. A stepping motor that drives the counter arm is called the 2θ -drive motor. The value of the angle 2θ is read by an optical encoder to an accuracy of 0.01° .

The counter shield can be raised and lowered in the frame carrying the shield. The motion of the shield is confined by a track in the frame to be a circle in a vertical plane. The track is constructed so that the axis of the counter tube always goes through the center of the magnet.

The angle between this axis and the horizontal plane is χ . The value of χ can be read on a vernier mounted on the frame. A stepping motor drives the shaft, that raises or lowers the counter shield; this motor is called the χ -drive motor. The value of χ is read by an optical encoder mounted on the shaft.

The diffractometer has two separate counting channels. One channel receives pulses from a low efficiency detector, the monitor, that is located in the monochromatic beam between the monochromator and the flipping coil. The other channel records the number of scattered neutrons detected by the counter tube, a high efficiency BF_3 detector. Each channel consists of a detector with a high voltage supply, an amplifier with a pulse height discriminator and a scaler. The counting system of the diffractometer also includes an elapsed time scaler.

The operation of the neutron diffractometer is controlled by an IBM 1130 computer through a specially designed interface. The computer is operated by instructions that are typed in on a keyboard. The computer controls the diffractometer through the following basic instructions to the interface:

- 1) DRIVE (clockwise or counter-clockwise) ϕ -drive motor, 2θ -drive motor or χ -drive motor. All three motors can be driven in a high and low speed.
- 2) STOP χ -drive motor, 2θ -drive motor or ϕ -drive motor.
- 3) READ the optical encoder: ϕ , 2θ or χ .
- 4) RESET, PRESET, START or STOP the three scalers monitor, counter-tube or time.

- 5) FLIP the direction of the neutron spin by turning the r.f. current on or off.

The programs combining these basic instructions are linked together with data processing programs so that the data obtained by the neutron diffractometer include a complete statistical analysis. These programs which were written by Mr. R. Hitterman¹ are all stored on a magnetic disc.

B. Method of Operation

The single crystal samples that are used for the present investigation are in the form of small pillars of the approximate size, 1 x 1 x 8 mm. These pillars are cut so that a given crystallographic direction is parallel to the largest dimension.

In an experiment the sample is mounted with this crystallographic direction parallel to the analyzing field using x-ray diffraction techniques. The accuracy with which the sample can be aligned in the sample holder is $\pm 1^\circ$.

The position of the sample is adjusted so that it is in the center of the monochromatic beam. In order to minimize the background the size of the monochromatic beam is reduced by cadmium slits to be slightly larger than the cross section of the sample.

The crystal structure and the lattice parameters of the sample are assumed to be known. From the wave length of the monochromatic neutrons the value of 2θ can be calculated for a reference Bragg reflection whose reciprocal lattice vector is perpendicular to the analyzing field. With

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the counter in this position the value of φ for the reference reflection is determined by rotating the sample until the reflection is detected by the counter tube. Once the angle is known for one reflection the values of φ , 2θ and χ for all Bragg reflections of interest can be calculated. For each Bragg reflection the angles φ , 2θ and χ are optimized to give maximum scattered intensity.

The monitor counter is used as the time unit to compensate for fluctuations in the power level of the reactor; the intensity of the neutrons that are detected by the counter tube is therefore measured in units of number of scattered neutrons per a given number of monitor counts. For a Bragg reflection the intensity is measured for the two possible spin states of the monochromatic neutrons. The background for this reflection is measured by changing the angle φ to $\varphi + \Delta\varphi$, keeping 2θ and χ constant. The value of $\Delta\varphi$ is determined so that the condition for Bragg scattering is not fulfilled for φ being equal to $\varphi + \Delta\varphi$. The numerical value of $\Delta\varphi$ is chosen to be as small as possible; it is typically of the order of 2° . With the sample in the background position, the intensity of scattered neutrons is also measured for the two spin states of the monochromatic beam. This is done to test that the background measurement is not contaminated by the Bragg reflection.

If the background is small compared to the intensity of the Bragg reflection, one can show that the most accurate determination of the flipping ratio in a given time is obtained if the total number of neutrons counted in the two spin states is the same. For the background measurement the ratio of total number of background counts to the total number of neutrons

counted in the Bragg reflection for one spin state should be inversely proportional to the square root of the ratio between the intensities of the Bragg reflection and the background.

For one Bragg reflection the flipping ratio R and the statistical uncertainty dR are calculated automatically from the measured intensities by the 1130 computer. The diffractometer angles 2θ , φ and χ are set at the values for this reflection before the computer program that is used for the data collection is executed. This computer program has the following input parameters:

- 1) The preset number of monitor counts for one measurement of the number of scattered neutrons.
- 2) The number of measurements with the r.f. current on for each measurement with the r.f. current off. This number will be denoted by F .
- 3) The number of measurements with the r.f. current off for each measurement of the background with the r.f. current off. This number will be denoted by G .
- 4) $\Delta\varphi$ for the background measurements.

By executing this program the data are collected. With the r.f. current on and the sample in the Bragg position the measurement of the number of scattered neutrons per the preset number of monitor counts is repeated F times. These F measurements are followed by one measurement with the r.f. current off. This group of G plus one measurements with the sample in the Bragg position is repeated G times. The value of φ is then changed by $\Delta\varphi$. With the sample in the background position, F measurements with the r.f. current on are followed by one measurement with the r.f.

current off. After the completion of the last measurement the sample is rotated back to the Bragg position. The number of scattered neutrons is printed out for each measurement.

The set of measurements described above will be referred to as one block of data. In a block the total number of measurements is $(F + 1) \times (G + 1)$.

After the completion of the block the flipping ratio R and the standard deviation dR are calculated by the computer. The value of R is determined by:

$$R = F \times \frac{B - G \times D}{A - G \times C} \quad (4.4)$$

where:

A = the total number of scattered neutrons measured with the sample in Bragg position and the r.f. current on.

B = the total number of scattered neutrons measured with the sample in Bragg position and the r.f. current off.

C = the total number of scattered neutrons measured with the sample in background position and the r.f. current on.

D = the total number of scattered neutrons measured with the sample in background position and the r.f. current off.

The standard deviation dR can be calculated from Equation (4.4).

Using counting statistics one finds for dR :

$$dR = \frac{R}{A - G \times C} \times \left\{ A + G^2 \times C + \left(\frac{F}{R} \right)^2 \times (B + G^2 \times D) \right\}^{1/2} \quad (4.5)$$

The contribution to dR from the monitor counts has been neglected in Equation (4.4). This is a good approximation in the present investigation where the count rate in the monitor channel is much higher than the count rates in the detector channel for all reflections.

The results for both the flipping ratio and the standard deviation dR are printed out.

In the experiment the integer constants F and G are chosen to be as close as possible to their respective ideal values of R and $\sqrt{\frac{B}{D}}$. The common value of the preset number of monitor counts is 30,000 counts corresponding to a measuring time of approximately 5 minutes. The typical value of F is two and of G is four; therefore, the total time for one block is approximately 45 minutes.

The computer program continues automatically to collect the data for a new block as soon as one block has been completed. The collection of data for one Bragg reflection is stopped manually after N blocks. The number N is between 30 and 50 blocks for most of the Bragg reflections measured in this experiment.

The mean value $\bar{R}$ and the standard deviation $d\bar{R}$ of the mean are calculated from the N values of both R and dR for the individual blocks. The standard deviation, $d\bar{R}$, is estimated as the mean of the N value of dR divided by the square root of N minus one.

Since N is fairly large, the standard deviation ΔR of R is also computed from the N values of R . The estimate of ΔR is found from:

$$\Delta R = \left\{ \frac{1}{N} \sum_{\text{over all } N \text{ blocks}} (R - \bar{R})^2 \right\}^{1/2} \quad (4.6)$$

After the completion of the N blocks the computer next calculates a flipping ratio R_t and the standard deviation dR_t from Equations 4.4 and 4.5 where A, B, C and D are substituted by the sums of N values of A, B, C and D from the individual blocks.

The internal consistency of all data for one Bragg reflection is checked by comparing $\bar{R}$, $d\bar{R}$ and the average value of dR with R_t , dR_t and ΔR . The measured values of $\bar{R}$ and $d\bar{R}$ are used for the final values for the flipping ratio and its statistical uncertainty. Values of R's and dR's from individual blocks which are obviously affected by non-statistical errors are not included in $\bar{R}$ and $d\bar{R}$.

The experimental value of γ is computed from Equation 4.2 using $\bar{R}$. In this investigation the ratio γ is less than one for all reflections; therefore, γ becomes:

$$\gamma = P_i \left\{ \bar{R}E + 1 - \frac{1}{P_i} \sqrt{(P_i(\bar{R}E + 1))^2 - \frac{1}{q^2} (\bar{R} - 1)^2} \right\} / (\bar{R} - 1) \quad (4.7)$$

The standard deviation $d\gamma$ is calculated from:

$$(d\gamma)^2 = \left(\frac{\partial \gamma}{\partial \bar{R}} \right)^2 (d\bar{R})^2 + \left(\frac{\partial \gamma}{\partial E} \right)^2 (dE)^2 + \left(\frac{\partial \gamma}{\partial P_i} \right)^2 (dP_i)^2 \quad (4.8)$$

where:

$$\frac{\partial \gamma}{\partial \bar{R}} = \frac{(1 + q^2 \gamma^2 - 2P_i E q^2 \gamma)^2}{2P_i q^2 (1+E)(1-q^2 \gamma^2)},$$

$$\frac{\partial \gamma}{\partial E} = \frac{\gamma(1 + q^2 \gamma^2 + 2P_i q^2 \gamma)}{(q^2 \gamma^2 - 1)(1 + E)} \quad \text{and}$$

$$\frac{\partial \gamma}{\partial P_i} = \frac{\gamma(q^2 \gamma^2 + 1)}{P_i(q^2 \gamma^2 - 1)}.$$

The dominant contribution to dy is from $d\bar{R}$ for each of the Bragg reflections which were measured in the present investigation.

The actual orientation of the sample is determined from a least squares analysis of the optimized angles ω , 2θ and χ for all the measured Bragg reflections. In the terbium experiment the value of q^2 in Equations 4.7 and 4.8 is calculated for each reflection from this analysis. The error in q^2 is too small to affect the value of dy ; it has therefore been neglected in the estimate of dy . For the form factor measurement of thulium it is assumed that the magnetic moment is parallel to the c -axis even in an applied field. This implies that the vector product $\bar{q} \cdot \bar{P}$ in Equation 2.24 is not $q^2 P$. The value of $\bar{q} \cdot \bar{P}$ is calculated for each reflection from the least square analysis. The correct value of $\bar{q} \cdot \bar{P}$ can be taken into account by replacing P_i in Equations 4.7 and 4.8 by an effective polarization P_{ie} , where P_{ie} is defined by

$$P_{ie} = \frac{\bar{q} \cdot \bar{P}}{q^2}.$$

The error in the determination of $\bar{q} \cdot \bar{P}$ is small and has been neglected in the calculation of dy .

Since the samples in the present investigation were aligned with an accuracy of $\pm 1^\circ$, the correct values of q^2 and $\bar{q} \cdot \bar{P}$ are only important for reflections with scattering vectors that are not perpendicular to the direction of the moment.

C. Corrections

In polarized neutron experiments the corrections of the experimental results can be divided into two groups: (1) instrumental corrections and (2) corrections due to crystal effects.

The instrumental corrections arise from changes in the beam polarization and contamination of neutrons with the wave length $\lambda/2$ in the monochromatic beam. Both these effects are very important for Bragg reflections which have γ values close to one. Since all the reflections studied in this investigation have γ values less than $1/3$, the corrections due to instrumental effects have been neglected.

The most important crystal effects are depolarization of the beam in the sample, secondary extinction, and simultaneous reflections. In this study the depolarization of the beam was found to be negligible. Intensities of some of the strongest reflections for the thulium and terbium crystals were found to be affected by secondary extinction. Therefore, the results for these reflections are not included in the data presented here. The effect of simultaneous reflections was observed in a few reflections for one of the thulium crystals. The results from these reflections are also excluded from the data.

V. RESULTS

The experimental results for the magnetic form factor for thulium and terbium are presented in this chapter.

A. Thulium

The experimental results for thulium were obtained using two single crystals. These crystals were kindly supplied by Dr. S. Legvold of Iowa State University. The dimensions of the crystals were $0.9 \times 1.1 \times 5.0$ mm and $1.2 \times 1.0 \times 11$ mm with the longest dimension parallel to the crystallographic c-axis in each case. The measurements were performed at two incident wave lengths, $0.85 \text{ \AA}$ and $1.02 \text{ \AA}$.

The crystals were maintained at 4.2°K in an applied field of 10 kOe corresponding to a magnet current of 20 A. The flipping ratio of the $(11\bar{2}0)$ -reflection was observed as a function of the applied field. It was concluded that the crystals were saturated in fields of 3 kOe or more, in agreement with magnetization measurements.

Two samples and two neutron wave lengths were used to test for secondary extinction and simultaneous reflections effects. For the smaller crystal the measured flipping ratios were identical for both wave lengths. In the larger crystal the values for the strong $(11\bar{2}0)$ - and $(10\bar{1}1)$ -reflections were clearly influenced by extinction and therefore rejected; other values were in good agreement with those from the smaller crystal.

The flipping ratio of a nuclear Bragg reflection will be in error if the intensity of a nuclear reflection is contaminated by other Bragg reflections. The second term in equation 2.24 will give rise to purely magnetic reflections that are polarization independent. The Miller indices

for these reflections are $(h, k, \bar{m}, 1 \pm n\tau_m)$, where τ_m is $1/7$. The allowed values of n are 1, 3 and 5 for the magnetic structure of thulium. The angles φ , 2θ and χ for the magnetic satellite reflections corresponding to indices $(h, k, \bar{m}, 1 \pm \tau_m)$ are so close to the values of φ , 2θ and χ for the nuclear $(h, k, \bar{m}, 1)$ -reflection that considerable care was taken to avoid contamination of the nuclear reflection. The detector was scanned through the nuclear and the magnetic satellite reflections to make sure that the peaks were sufficiently resolved. Horizontal Cd-slits in front of the detector were used to improve the instrumental resolution.

A further source of systematic error arises if the thulium nuclei are polarized. Thulium is a single isotope, Tm^{169} , with nuclear spin $1/2$. Since the nuclear polarization effect has a $1/T$ dependence, the flipping ratio of $(11\bar{2}0)$ -reflection was measured at 1.8°K . No change from the value at 4.2°K was observed and the effect can therefore be neglected. The nuclear polarization at 1.8°K has been calculated to be approximately 1% assuming a hyperfine field of 7000 kOe (35) and a nuclear magnetic moment of -0.229 nuclear Bohr magnetons (35). The absence of any change in the flipping ratio sets an upper limit on the incoherent scattering cross section of 0.8 barns.

For both crystals the flipping ratios were measured for a number of different reflections. The values of γ and $d\gamma$ were calculated for each reflections using equation 4.7 and the values of P_i and E given in Table 3. For all reflections the contribution to $d\gamma$ from dR was larger than the contributions from dP_i and dE .

The experimental values for $f(\kappa)$ are given in Table 4. Each value in Table 4 is the average of several equivalent reflections and the

Table 4. Thulium

hkm $\bar{l}$	$\sin \theta/\lambda$	f_{obs}	f_{calc}	$f_{\text{obs}}/f_{\text{calc}}$
10 $\bar{1}$ 0	0.163	0.860 ± 10	0.913	0.942 ± 11
10 $\bar{1}$ 1	0.187	0.829 ± 10	0.892	0.930 ± 11
10 $\bar{1}$ 2	0.244	0.771 ± 8	0.841	0.917 ± 9
11 $\bar{2}$ 0	0.283	0.686 ± 6	0.770	0.890 ± 8
10 $\bar{1}$ 3	0.318	0.740 ± 40	0.756	0.970 ± 60
20 $\bar{2}$ 0	0.327	0.635 ± 8	0.711	0.893 ± 11
20 $\bar{2}$ 2	0.374	0.596 ± 8	0.663	0.900 ± 12
21 $\bar{3}$ 0	0.432	0.505 ± 10	0.571	0.883 ± 17
30 $\bar{3}$ 0	0.490	0.444 ± 6	0.499	0.890 ± 12
22 $\bar{4}$ 0	0.566	0.363 ± 8	0.412	0.883 ± 19
31 $\bar{4}$ 0	0.589	0.353 ± 10	0.388	0.910 ± 26
40 $\bar{4}$ 0	0.653	0.287 ± 13	0.324	0.896 ± 40
32 $\bar{5}$ 0	0.712	0.225 ± 8	0.274	0.822 ± 29
41 $\bar{5}$ 0	0.748	0.220 ± 10	0.245	0.898 ± 40
33 $\bar{6}$ 0	0.848	0.151 ± 8	0.179	0.843 ± 45

quoted error is the standard deviation of the average. In all cases the values from equivalent reflections differed by less than two standard deviations. The values of $f(h)$ were derived from the measured γ values using $b = 0.69 \times 10^{-12}$ cm and $\mu_{\text{ferro}} = 1.001 \mu_B$. The reported errors of b and μ_{ferro} give rise to an error of $\pm 3\%$ in the absolute value of the form factor for all reflections. This uncertainty, which is not included in the errors given in Table 4, introduces a constant scale factor to all measured values.

Also shown in Table 4 are the theoretical form factor, f_{calc} , and the ratio $f_{\text{obs}}/f_{\text{calc}}$. The discussion of f_{calc} and $f_{\text{obs}}/f_{\text{calc}}$ will be given in Chapter VI.

B. Terbium

Four single crystal samples of terbium metal were used in the present investigation. These samples were kindly supplied by Professor F. H. Spedding of Iowa State University. The crystals were all cut in shapes of parallelepipeds. Two of the crystals had their longest dimension parallel to the $(11\bar{2}0)$ crystallographic direction; these will be referred to as the a-axis crystals. The other two crystals were cut so that their longest dimension was parallel to the $(10\bar{1}0)$ crystal axis; these are called b-axis crystals. The dimensions of the two a-axis crystals were $2.0 \times 2.2 \times 7.4$ mm and $0.9 \times 0.9 \times 7.9$ mm. The measurements of the two b-axis crystals were $1.5 \times 1.5 \times 6.2$ mm and $1.0 \times 1.3 \times 8.7$ mm. The samples were mounted with the long axis parallel to the analyzing field. All data in this investigation were obtained for an incident wave length of $0.85 \text{ \AA}$.

Two different crystal orientations were used to test the assumption that crystal field effects can be neglected in the present investigation.

Two crystals with different dimensions were used for each of the two orientations of the crystal. This was done to test for secondary extinction. Furthermore, the mosaic spread (24) of both an a-axis and b-axis crystal was increased by applying mechanical pressure in the direction perpendicular to the longest dimension. Since the effect of secondary extinction decreases by increasing the mosaic spread of a crystal, the flipping ratios of several weak and strong reflections were measured before and after applying the mechanical pressure. Results from reflections that suffered from secondary extinction are not included in the data presented here. The γ -value for the strong $(11\bar{2}0)$ -reflection is given in Table 4. Since the data analysis shows that the $(11\bar{2}0)$ -reflection is probably influenced by secondary extinction, the result for this reflection is not used in the interpretation of the data.

The samples were maintained at room temperature, approximately 25°C . The temperature of the samples was measured several times a day and for each reflection the average sample temperature was recorded. In the course of the experiment the maximum variation in sample temperature was $\pm 1.5^{\circ}\text{K}$. The γ values for all reflections were adjusted to the same sample temperature of 298.2°K using a paramagnetic Curie temperature of 239°K (14). Since the correction is only 1.7% per degree K, the temperature adjustments that have been made are of the same order of magnitude as $d\gamma$. The uncertainty, dT , in the measurement of the sample temperature is approximately 0.1°K . Therefore, the contribution to $d\gamma$ from dT is small and has been neglected.

From the magnetization measurements by Hegland et al. (14) the induced moment can be calculated for terbium. Their results show that the paramagnetic susceptibility for the field parallel to an a-axis is the same as the susceptibility for the field parallel to a b-axis. The magnitude of the induced moment is given by:

$$\mu = 2.12 \times \frac{H}{T - \Theta_p} \quad (5.1)$$

where the field H is measured in kOe and T in degrees K.

The current in the sample magnet was 60 A. for all measurements done on terbium. The reproducibility of the magnet current and the hysteresis in the sample magnet introduced an uncertainty in the magnetic field of approximately 0.4%. Since the standard deviation $\delta\gamma$ was at least 1% for individual measurements of γ , the uncertainty of 0.4% has been neglected.

Three different sample holders were used in the present investigation. One of the a-axis crystals and one of the b-axis crystals were mounted in a special sample holder that had a fixed gap between the pole pieces. Since the results for the two crystals were obtained with the same field on the samples, the susceptibility measurement shows that the induced moment should be the same for the two crystal orientations. The a-axis and the b-axis crystals that were mounted in the special sample holder will be referred to as crystal 1a and crystal 1b, respectively.

The applied field for the second a-axis crystal, crystal 11a, that was mounted in its own sample holder, was approximately 3 kOe larger than the field applied on crystal 1a. The measurements on the two crystals had eleven different $(h\bar{k}l)$ -reflections in common. The ratio of the

values for the two crystals was calculated for each of the eleven reflections. The average of the ratio, γ_{1a}/γ_{11a} , was 0.84 ± 0.01 . All the ratios for the individual reflections differed from the mean by less than twice the standard deviations of the individual ratios. The applied magnetic fields for crystal 1a and crystal 11a were determined by a Rawson probe to be 22.0 ± 0.2 kOe and 25.2 ± 0.2 kOe, respectively. From the magnetic field measurements the average value of γ_{1a}/γ_{11a} was calculated to be 0.87 ± 0.01 . Since the volume sampled by the Rawson probe was larger than any of the samples, the homogeneity of the field was tested by a Hall probe. It was found that the field measured by the Rawson probe was too large for crystal 1a, whereas the measured field for crystal 11a was probably too small. For the present investigation the applied magnetic fields for crystal 1a and crystal 11a were taken to be 21.5 kOe and 25.6 kOe, respectively. Agreement between the neutron data and the field measurement was obtained using these values. All the γ values measured for crystal 11a were multiplied by 0.84. The final values of γ for the a-axis crystals were obtained by averaging the results from crystal 1a and the scaled-values from crystal 11a. The applied magnetic field was taken to be 21.5 ± 0.5 kOe; the uncertainty of ± 0.5 kOe includes the error in the field measurement.

The results from the second b-axis crystal, crystal 11b, were obtained in the field of approximately 26 kOe. The γ -values from this crystal were scaled to the results from crystal 1b in the same way as it was done for the two a-axis crystals. It was found that only five of the measured reflections for crystal 11b were not affected by secondary extinction. The final values for the b-axis crystals were therefore

obtained from the results for crystal 1b and the extinction-free results from crystal 11b. The applied magnetic field for the experimental values was 21.5 ± 0.5 kOe. This was the same field used for the a-axis data.

The results shown in Table 5 are for the measured form factors, $f_a(\kappa)$ and $f_b(\kappa)$, for the a and b axis crystals, respectively. The $f_{\text{obs}}(\kappa)$ is the mean of $f_a(\kappa)$ and $f_b(\kappa)$ for the reflections that have been measured for both orientations. The form factor is calculated using a value of 0.76×10^{-12} cm. for the nuclear coherent scattering length and an induced magnetic moment of $0.77 \mu_B$. The induced moment is calculated from equation 5.1. The standard deviation of f_{obs} does not include the uncertainties in the scattering length and the magnetic moment. These uncertainties will give rise to an error of $\pm 5\%$ in the absolute value of f_{obs} .

In Table 5 the theoretical form factor, f_{calc} , and the ratio, $f_{\text{obs}}/f_{\text{calc}}$, are shown. The discussion of f_{calc} and $f_{\text{obs}}/f_{\text{calc}}$ will be given in Chapter VI.

Table 5. Terbium

hkm $\bar{l}$	$\sin \theta/\lambda$	f_a	f_b	f_{obs}	f_{calc}	$f_{\text{obs}}/f_{\text{calc}}$
10 $\bar{1}$ 0	0.160	0.870 ± 6	0.879 ± 15	0.872 ± 6	0.888	0.98 ± 1
00 $\bar{0}$ 2	0.175	0.820 ± 8	0.810 ± 11	0.816 ± 7	0.870	0.94 ± 1
10 $\bar{1}$ 1	0.182	0.790 ± 7	0.817 ± 15	0.799 ± 7	0.861	0.93 ± 1
10 $\bar{1}$ 2	0.237	0.740 ± 6	0.733 ± 11	0.738 ± 6	0.779	0.95 ± 1
11 $\bar{2}$ 0	0.278		0.619 ± 15	0.619 ± 15	0.716	0.87 ± 2
10 $\bar{1}$ 3	0.308	0.610 ± 5	0.597 ± 7	0.605 ± 5	0.670	0.90 ± 1
20 $\bar{2}$ 0	0.320	0.587 ± 8		0.587 ± 8	0.650	0.90 ± 1
20 $\bar{2}$ 1	0.332	0.557 ± 5		0.557 ± 5	0.632	0.88 ± 1
00 $\bar{0}$ 4	0.351	0.531 ± 6	0.516 ± 6	0.523 ± 6	0.601	0.87 ± 1
20 $\bar{2}$ 2	0.364	0.498 ± 7		0.498 ± 7	0.581	0.86 ± 1
10 $\bar{1}$ 4	0.386		0.487 ± 11	0.487 ± 11	0.548	0.89 ± 2
20 $\bar{2}$ 3	0.415	0.430 ± 7		0.430 ± 7	0.504	0.85 ± 1
11 $\bar{2}$ 4	0.447		0.380 ± 6	0.380 ± 6	0.457	0.83 ± 1
10 $\bar{1}$ 5	0.467	0.369 ± 7		0.369 ± 7	0.429	0.86 ± 2
20 $\bar{2}$ 4	0.476	0.354 ± 7		0.354 ± 7	0.417	0.85 ± 2
30 $\bar{0}$ 0	0.481	0.347 ± 6		0.347 ± 6	0.411	0.84 ± 1
00 $\bar{0}$ 6	0.527	0.301 ± 6	0.302 ± 6	0.302 ± 5	0.353	0.86 ± 1
22 $\bar{4}$ 0	0.555		0.268 ± 7	0.268 ± 7	0.323	0.83 ± 2
22 $\bar{4}$ 2	0.582		0.256 ± 7	0.256 ± 7	0.295	0.87 ± 2
11 $\bar{2}$ 6	0.596		0.242 ± 11	0.242 ± 11	0.280	0.86 ± 4
22 $\bar{4}$ 4	0.657		0.198 ± 7	0.198 ± 7	0.223	0.89 ± 3
00 $\bar{0}$ 8	0.702	0.148 ± 7	0.158 ± 11	0.152 ± 6	0.188	0.81 ± 3

VI. CONCLUSIONS

The experimental results for the magnetic form factor of thulium and terbium will be discussed in this chapter. The results for the two metals will be compared with theoretical form factors.

The experimental form factor for thulium is shown in Fig. 4. The filled circles correspond to Bragg reflections in the basal plane perpendicular to the direction of the moment. The solid curve is a smooth curve drawn through the solid points and through 1.0 for $\sin \theta/\lambda$ equal to zero. This curve is not a theoretical curve. The four open squares in Fig. 4 correspond to Bragg reflections out of the basal plane. The experimental values of the form factor are higher for these four reflections than the form factors for reflections with the same $\sin \theta/\lambda$ values in the basal plane. The larger value of the form factors for these four reflections is a consequence of the fact that the magnetization density of the tripositive thulium ion is oblate with respect to the direction of the moment for the ion in the ordered state.

The experimental form factor for terbium is shown in Fig. 5. The open circles correspond to the data obtained from the b-axis crystals and a cross is used as a symbol for the data points from the a-axis crystals. The solid curve is drawn as a smooth curve through the data points and starts at 1.0 for $\sin \theta/\lambda$ equal to zero. The experimental values for the two crystal orientations fall on the same curve, in agreement with the magnetization measurements. The only exception is the open circle at $\sin \theta/\lambda$ equal to $0.278\text{\AA}^{-1}$. This point corresponds to the $(11\bar{2}0)$ -reflection and will be neglected in the data analysis.

In Chapter III the form factor for terbium is calculated assuming

Fig. 4. The magnetic form factor for thulium

Fig. 5. The magnetic form factor for terbium

that crystal field effects can be neglected. This theoretical form factor depends only on the numerical value of the scattering vector $\bar{\kappa}$; it has no angular dependence. If the crystal field cannot be neglected in the derivation of the form factor, a calculation that takes the crystal field levels into account will give rise to a form factor that is a function of the vector $\bar{\kappa}$. The data points within the statistical uncertainty lie on a smooth curve for all the different reflections. This indicates that crystal field effects are smaller than the statistical uncertainty of the individual points. The effect of the crystal field has therefore been neglected in the interpretation of the results for terbium.

The uncertainties in the values of the ferromagnetic moment and the nuclear coherent scattering lengths will increase the standard deviations of the absolute values of the measured form factor. These additional uncertainties which have not been included in Fig. 4 and Fig. 5 give rise to a common scale factor α for all the points. The factor α is calculated from the magnetization data and the given values of the coherent scattering lengths to be 1.00 ± 0.03 for thulium and 1.00 ± 0.05 for terbium. The factor can be taken into account by assuming that the units of the ordinate axes in Figs. 4 and 5 are α times $f(\kappa)$ instead of $f(\kappa)$. For the smooth curve in both figures α is equal to one. Moon (36) has developed a method by which it is possible to determine α from a form factor measurement alone. However, the data for the experiments presented here do not cover a range of $\sin \theta / \lambda$ large enough for the method to be accurate.

Since the absolute value of the measured form factor is not accurately known, the observed values of the form factor, f_{obs} , are compared directly

to the calculated values, f_{calc} , for each reflection that has been measured. By studying the ratio $f_{\text{obs}}/f_{\text{calc}}$ as a function of $\sin \theta/\lambda$ it is possible to test the shape of the theoretical wave functions that are used to calculate f_{calc} . The radial wave functions that are used for the comparison with the experiment have all been calculated by Freeman and Watson (37).

In Table 4 f_{obs} and f_{calc} are given for thulium. The uncertainty in the scale factor is not included in the values of f_{obs} . The theoretical expression for the form factor is given by equation 3.26 for reflections in the basal plane. Separate theoretical expressions have been derived for the four reflections that are not in the basal plane. The ratios $f_{\text{obs}}/f_{\text{calc}}$ are also given in Table 4.

The values of f_{obs} , f_{calc} and $f_{\text{obs}}/f_{\text{calc}}$ are given in Table 5 for terbium. The theoretical expression for the form factor is given in equation 3.34.

In calculating the magnetic form factor the radial integrals $\langle j_K \rangle$ are needed. These integrals have been calculated for all tripositive rare earth ions as a function of $\sin \theta/\lambda$ by Blume et al. (17) using the wave functions that were computed by Freeman and Watson (37).

The ratios of $f_{\text{obs}}/f_{\text{calc}}$ for the different reflections for thulium are shown in Fig. 6. The error bars on the points are calculated from the standard deviations of the flipping ratio; they do not include the uncertainty in the scale factor. The ratios $f_{\text{obs}}/f_{\text{calc}}$ are also shown for the tripositive ions of samarium, gadolinium, erbium and ytterbium. The ratios were calculated using the solid curve in Fig. 4 for f_{obs} and equation 3.26 for f_{calc} , where the wave functions of

Freeman and Watson (37) for samarium, gadolinium, erbium and ytterbium have been used instead of those for thulium. These curves are shown in order to interpret the deviations of the measured form factor in terms of theoretical wave functions. The ratio $f_{\text{obs}}/f_{\text{calc}}$ approaches the value of the scaling factor α in the limit of $\sin \Theta/\lambda$ going to zero. If the four curves and a smooth curve through the points in Fig. 6 are extrapolated in $\sin \Theta/\lambda$ equal to zero, it is estimated that α for the thulium form factor is approximately 0.97 ± 0.02^1 . This extrapolation is only valid if the experimental form factor is well behaved in the region of $\sin \Theta/\lambda$ between 0 and $0.15 \text{ \AA}^{-1}$.

In Fig. 7 the ratios of $f_{\text{obs}}/f_{\text{calc}}$ are presented for terbium in a graph analogous to the figure in which the thulium results are displayed. It is estimated from the convergence of the curves for the different wave functions that the scale factor for the terbium form factor is 1.00 ± 0.02 . This estimate of α relies as for thulium, on the assumption that the experimental form factor is well behaved in the region of $\sin \Theta/\lambda$ between 0.0 and $0.15 \text{ \AA}^{-1}$. The fact that α is close to one indicates that the value of the applied magnetic field of 21.5 kOe is in agreement with the observed values of γ for terbium.

The ratios of $f_{\text{obs}}/f_{\text{calc}}$ for both thulium and terbium show a very similar behavior. The experimental form factor for all the reflections measured is less than the theoretical calculated for both metals. From this fact it is concluded that the true wave function is more expanded

¹In a recent experiment, Dr. M. Atoji, Argonne National Laboratory, obtained a value of $0.720 \pm 0.006 \text{ } 10^{-12} \text{ cm}$ for the nuclear coherent scattering length of thulium. If this value for b is used, the scale factor for the values of f_{obs} in Table 4 will be 0.958 ± 0.008 in agreement with the value determined from Fig. 6.

Fig. 6. The ratio of the observed and the theoretical form factor for thulium.

The values of the observed and the theoretical form factors are given in Table 4 together with the ratio of the observed and the theoretical form factor. The values of this ratio, $f_{\text{obs}}/f_{\text{calc}}$, are shown in Fig. 6 as open squares for the different reflections. The error bars are calculated from the standard deviations of the flipping ratios. The expression for the theoretical form factor, f_{calc} , is given by equations 3.26 to be

$$f_{\text{calc}} = \langle j_0 \rangle + 0.5952 \langle j_2 \rangle - 0.0828 \langle j_4 \rangle + 0.0095 \langle j_6 \rangle$$

for the basal plane reflections. The values of the integrals, $\langle j_k \rangle$, that have been used in calculating the form factor, f_{calc} , are the ones tabulated by Blume *et al.* (17) for thulium.

From the open squares in Fig. 6, it can be seen that the ratio, $f_{\text{obs}}/f_{\text{calc}}$, decreases with increasing values of $\sin \theta/\lambda$ and is less than unity for all reflections. It has been concluded from this behavior of $f_{\text{obs}}/f_{\text{calc}}$ that the theoretical 4f wave function for thulium used by Blume *et al.* (17) in their calculation of the integrals, $\langle j_k \rangle$, is too contracted.

Since the wave functions for the 4f electrons in the rare earth elements contract with increasing atomic number, the ratios, $f_{\text{obs}}/f_{\text{calc}}$, are shown for samarium, gadolinium, erbium, and ytterbium, as smooth curves where the wave functions for Sm^{3+} , Gd^{3+} , Er^{3+} , and Yb^{3+} have been used instead of the 4f wave function for Tm^{3+} . For these ratios the smooth curve through the experimental points in Fig. 4 has been used for f_{obs} , and the expression for the form factor given above has been used for f_{calc} . The numerical values of the integrals, $\langle j_k \rangle$, have been tabulated by Blume *et al.* (17) for samarium, gadolinium, erbium, and ytterbium.

From Fig. 6 it can be seen that the 4f wave function of gadolinium gives a good fit to the data for the innermost reflections.

Fig. 6. The ratio of the observed and the theoretical form factor for thulium

Fig. 7. The ratio of the observed and the theoretical form factor for terbium.

The values of the observed and the theoretical form factors are given in Table 5 together with the ratio of the observed and the theoretical form factor. The values of this ratio, $f_{\text{obs}}/f_{\text{calc}}$, are shown as crosses and open circles in Fig. 7 for the different reflections. The error bars are calculated from the standard deviations of the slipping ratios. The expression for the theoretical form factor, f_{calc} , is given by equation 3.34 to be

$$f_{\text{calc}} = \langle j_0 \rangle + 0.3704 \langle j_2 \rangle .$$

The values of the integrals, $\langle j_k \rangle$, that have been used in calculating the form factor, f_{calc} , are the ones tabulated by Blume et al. (17) for terbium.

From the crosses and the circles in Fig. 7, it can be seen that the ratio, $f_{\text{obs}}/f_{\text{calc}}$, decreases with increasing values of $\sin \theta/\lambda$ and is less than unity for all reflections. It has been concluded from this behavior of $f_{\text{obs}}/f_{\text{calc}}$ that the theoretical 4f wave function for terbium used by Blume et al. (17) in their calculation of the integrals, $\langle j_k \rangle$, is too contracted.

Since the wave functions for the 4f electrons in the rare earth elements contract with increasing atomic number, the ratios, $f_{\text{obs}}/f_{\text{calc}}$, are shown for cerium, neodymium, samarium, gadolinium, dysprosium, erbium, and ytterbium as smooth curves, where the wave functions for Ce^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , Er^{3+} , and Yb^{3+} have been used instead of the 4f wave function for Tb^{3+} . For these ratios the smooth curve through the experimental points in Fig. 5 has been used for f_{obs} , and the expression for the form factor given above has been used for f_{calc} . The numerical values of the integrals, $\langle j_k \rangle$, have been tabulated by Blume et al. (17) for cerium, neodymium, samarium, gadolinium, dysprosium, erbium, and ytterbium.

From Fig. 7 it can be seen that the 4f wave function of neodymium gives a good fit to the data for the innermost reflections.

Fig. 7. The ratio of the observed and the theoretical form factor for terbium

than the wave functions calculated by Freeman and Watson. In both cases the ratio decreases for $\sin \theta/\lambda$ increasing from 0.0 to approximately $0.3\text{\AA}^{-1}$; for $\sin \theta/\lambda$ in the region between $0.35\text{\AA}^{-1}$ to $0.75\text{\AA}^{-1}$ the ratio is fairly constant. This behavior indicates that for both metals the shape of the calculated wave functions is correct close to the core but that farther away from the core the experimental value of the radial density is higher than the theoretical value. If the scale factors estimated above are taken into account, the value of $f_{\text{obs}}/f_{\text{calc}}$ in the region of $\sin \theta/\lambda$ between $0.35\text{\AA}^{-1}$ and $0.75\text{\AA}^{-1}$ is 0.91 ± 0.02 for thulium and 0.86 ± 0.02 for terbium. This value for terbium is in agreement with the results of Steinsvoll et al. (2).

The wave functions that were calculated by Freeman and Watson for the tripositive rare earth ions are conventional nonrelativistic Hartree-Fock wave functions. The calculation of these wave functions is discussed by Freeman and Watson (37, 38). Recently Synek and Timmons (39) and Ruedenberg(40) have reported calculations of nonrelativistic Hartree-Fock wave functions for tripositive rare earth ions. A comparison between the radial density for Pr^{3+} calculated by Synek and by Freeman and Watson show that the two radial wave functions are so similar that a form factor experiment with the same accuracy as the present cannot distinguish between the two radial functions. A similar comparison of the Gd^{3+} wave functions calculated by Ruedenberg and by Freeman and Watson indicates that the two radial densities for Gd^{3+} are identical in so far as the accuracy of the present experiment is concerned. Ridley (41) has reported Hartree wave functions for Pr^{3+} and Tm^{3+} . These radial wave functions are more expanded than the Hartree-Fock wave functions but the ratio $f_{\text{obs}}/f_{\text{calc}}$ for

thulium using the Hartree wave functions shows that this wave function does not fit the data for thulium any better than the Hartree-Fock functions of Freeman and Watson. It is therefore concluded that the radial densities calculated by Freeman and Watson are the best set of theoretical wave functions to use for the interpretation of the present results.

It has been suggested (42) that the discrepancy between the experimental results for thulium and the theoretical 4f wave functions is due to the conduction electron polarization. In this interpretation the form factor for thulium consists of the combination of two form factors, a 4f form factor plus a 5d form factor. A similar interpretation of the terbium data is not possible for two reasons. First of all, the decrease for small values of $\sin \Theta/\lambda$ of the ratio $f_{\text{obs}}/f_{\text{calc}}$ as a function of $\sin \Theta/\lambda$ extends too far in $\sin \Theta/\lambda$ to correspond to a 5d radial density. Secondly, there is no simple explanation of the loss of 4f-moment in the paramagnetic state. Since the discrepancy between the experimental results and the theory is very similar for the two metals, it will be assumed that the cause of the discrepancy is the same for both metals. The conclusions will therefore be that the effect observed here is due to incorrect 4f wave functions for both terbium and thulium in contrast to the previous interpretation for thulium (42).

The observed expansion of the experimental 4f wave function can be interpreted in two ways. First, the conventional nonrelativistic Hartree-Fock method by which the wave functions for the tripositive ions have been calculated could be in error. Second, the wave functions for the tripositive free ions may not be a good description of the wave functions

In the metal.

The first point has been discussed by Blume et al. (43) and by Newman and Curtis (44). Spin-orbit constants for the tripositive rare earth ions have been computed by Blume et al. (43) using the wave functions calculated by Freeman and Watson (37). A comparison between experimentally determined spin-orbit constants and the theoretical calculated parameters shows that the Hartree-Fock wave functions are too contracted. Relativistic and correlation effects have not been included in the Hartree-Fock calculations but it is not known whether these effects can account for the discrepancy between the free ion form factors by Freeman and Watson and the form factors that have been measured in the present investigation.

The second point has been discussed by Kasuya (45) who has calculated numerical values for the crystal field integrals, $\overline{r^n}$, from the magnetization data for the heavy rare earth metals. The experimental values of $\overline{r^n}$ indicate that the 4f wave functions in the metals are more expanded than those of Freeman and Watson. This observation is in agreement with the present results. Kasuya has analyzed several reasons for the discrepancy between the free ion wave functions and the wave functions in the metal. First, the wave functions for the free atoms is probably a better description of the metal atoms than the wave functions of the tripositive ion. The valence electrons of the free atom becomes the conduction electrons in the metallic state. Since the charge density around each atom associated with the valence or conduction electrons in the metal are contracted from those of the free atom, the 4f electrons in the metal should be expanded. Second, the interaction between the 4f electrons

and the conduction electrons in the metal is strong enough to affect the 4f-electron distribution in the metal. A realistic calculation of the 4f-wave functions in the metal is very difficult and has not yet been done.

The magnetic form factors of rare earth tripositive ions in ionic compounds should be measured in order to determine whether the effects observed in the present investigation are of metallic origin or not. The quantum numbers J for thulium and terbium are both equal to six; the quantum numbers S for thulium and terbium are equal to one and three, respectively. Since the observed effect is larger for terbium than for thulium, it is possible that the cause of the effect is a function of S . Therefore, the magnetic form factor of a light rare earth ion or metal should be studied in order to test this hypothesis.

The experimental results from these two types of experiments will be important in determining the origin of the effect observed in the present investigation.

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IX. APPENDIX A

The magnetic interaction operator $\bar{m}$ for an ion or atom is given by:

$$\bar{m} = \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} [\bar{\kappa} \times \{ (\sum_n \exp(i\bar{\kappa} \cdot \bar{r}_n) \otimes \bar{s}_n) \times \bar{\kappa} \}] \quad (A.1)$$

$$+ \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} \left(-\frac{i}{\hbar}\right) \times [\bar{\kappa} \times \sum_n \{ \bar{p}_n \exp(i\bar{\kappa} \cdot \bar{r}_n) + \exp(i\bar{\kappa} \cdot \bar{r}_n) \bar{p}_n \}]$$

Definitions of the symbols are given in Chapter II. In order to calculate the scattering length of a moment induced by an applied magnetic field, one has to evaluate the thermal average of $\bar{m}$. In thermodynamic equilibrium at temperature T , $\langle \bar{m} \rangle$ is given by

$$\langle \bar{m} \rangle = \text{Tr}(\exp(-\frac{H}{kT}) \bar{m}) / \text{Tr}(\exp(-\frac{H}{kT})) \quad (A.2)$$

where H is the Hamiltonian including the magnetic field. For a rare earth ion in a crystal, H is given by:

$$H = H_0 + H_T - \mu_B g_J \bar{J} \cdot \bar{\mathcal{H}} \quad (A.3)$$

where

H_0 = Hamiltonian for the free ion,

H_T = contribution to H from the crystal field,

and the last term is the contribution to the energy from the magnetic field $\mathcal{H}$.

For H_0 it will be assumed that Russell-Saunders coupling scheme is valid and that Hund's rule applies. Under these assumptions, S , L , and

and J are good quantum numbers. In the ground state J has the value $|L-S|$ or $|L+S|$; for the heavy rare earth ions J is $L + S$. Furthermore, the crystal field energies for the lanthanides (46) are small compared to the Coulomb and spin-orbit energies. Only the states that belong to the ground state value of J will therefore be considered in evaluating equation A.3. The trace will be taken over the $2J+1$ eigenstates, $|JM\rangle$, of J_z . The thermal average of $\bar{m}$ is then calculated from:

$$\langle \bar{m} \rangle = \frac{\sum_{M=-J}^{+J} \langle M | \exp(-\frac{H}{kT}) \bar{m} | M \rangle}{\sum_{M=-J}^{+J} \langle M | \exp(-\frac{H}{kT}) | M \rangle} \quad (A.4)$$

If the temperature T is large, the last two terms in equation A.3 will be small compared to kT . The exponential function will be expanded keeping only terms of first order in $\frac{1}{kT} (H_\Gamma - \mu_B g_J \bar{J} \cdot \bar{\mathcal{H}})$. The result is:

$$\begin{aligned} \exp(-\frac{H}{kT}) &= \exp(-\frac{H_0}{kT}) (1 - \frac{1}{kT} (H_\Gamma - \mu_B g_J \bar{J} \cdot \bar{\mathcal{H}})) \\ &+ \text{terms of the form } (\frac{1}{kT})^n H_0^r [H_\Gamma - \mu_B g_J \bar{J} \cdot \bar{\mathcal{H}}, H_0] H_0^{n-r-2} \end{aligned} \quad (A.5)$$

Since all states that are considered in equation A.4 belong to the same energy level of H_0 , only matrix elements of the first term in equation A.5 will be different from zero. Furthermore, the factors, $\exp(-\frac{H_0}{kT})$, cancel in the ratio in equation A.4. The thermal average, $\langle m \rangle$, can therefore be written as:

$$\begin{aligned} \langle \bar{m} \rangle &= \frac{\sum_M \langle M | \bar{m} - \frac{H_\Gamma}{kT} \bar{m} + \frac{\mu_B g_J \bar{J} \cdot \bar{\mathcal{H}}}{kT} \bar{m} | M \rangle}{\sum_M \langle M | 1 - \frac{H_\Gamma}{kT} + \frac{\mu_B g_J \bar{J} \cdot \bar{\mathcal{H}}}{kT} | M \rangle} \end{aligned} \quad (A.6)$$

The magnetic interaction operator $\bar{m}$ has properties very similar to the magnetic moment operator, e.g. $\langle M | \bar{m} | M \rangle = - \langle -M | \bar{m} | -M \rangle$. Using this fact and the inversion symmetry of the crystal field, equation A.5 reduces to:

$$\langle \bar{m} \rangle = \frac{\mu_B g}{kT} \sum_M \langle M | \bar{J} \cdot \mathcal{H} \bar{m} | M \rangle / \sum_M \langle M | 1 - \frac{H_T}{kT} | M \rangle \quad (A.7)$$

The induced magnetic moment, $\langle \bar{\mu} \rangle$, can be calculated from equation A.7 by replacing the operator $\bar{m}$ by the operator $\mu_B g \bar{J}$.

For $kT \gg H_T$ the denominator in equation A.7 is equal to $2J+1$. Both $\langle \bar{\mu} \rangle$ and $\langle \bar{m} \rangle$ are therefore proportional to $1/T$ at high temperature; the value of the effective moment, μ_{eff} , is $g\sqrt{J(J+1)}$ in the same temperature limit. Since the magnetization measurements for terbium (14) show that the susceptibility at room temperature is proportional to $1/(T-\theta_p)$ with an experimental value of the effective moment very close to $g\sqrt{J(J+1)}$, equation A.7 will be used in the derivation of the form factor for terbium. The thermal average, $\langle \bar{m} \rangle$, can at high temperature be written as:

$$\langle \bar{m} \rangle = \frac{\mu_B g \mathcal{H}}{kT(2J+1)} \sum_M M \langle M | \bar{m} | M \rangle \quad (A.8)$$

where the axis of quantization is parallel to $\mathcal{H}$.

X. APPENDIX B

The magnetic interaction operator $\bar{m}$ for an atom having n unpaired electrons or holes is given by the term in the square bracket in equation 2.8.

$$\begin{aligned} \bar{m} = & \frac{\gamma e^2}{m_e c} \left[\frac{1}{2} (\bar{\kappa} \times \left\{ \sum_n \exp(i \bar{\kappa} \cdot \bar{r}_n) \frac{2}{r_n} \bar{s}_n \right\} \times \bar{\kappa}) \right. \\ & \left. + \frac{1}{2} (\bar{\kappa} \times \left\{ \frac{1}{2} \sum_n (\bar{\ell}_n f(\bar{\kappa} \cdot \bar{r}_n) + f(\bar{\kappa} \cdot \bar{r}_n) \bar{\ell}_n) \times \bar{\kappa} \right\}) \right] \end{aligned} \quad (B.1)$$

where equation 2.9 has been used to transform the orbital part of $\bar{m}$ into an expression depending on the angular momentum $\bar{\ell}_n$.

The function $f(\bar{\kappa} \cdot \bar{r}_n)$ has been given by Trammell (1) to be:

$$f(\bar{\kappa} \cdot \bar{r}) = \frac{2}{(i \bar{\kappa} \cdot \bar{r})^2} \int_0^{i \bar{\kappa} \cdot \bar{r}} x e^x dx$$

Strictly speaking, the transformation in equation 2.9 is valid only for elastic scattering. An additional term in equation B.1 is needed if one is interested in calculating matrix elements between the ground state and the excited states of a free ion. Since the energy required for a transition between two states is much larger than the energy of thermal neutrons, this term has been ignored in equation B.1.

For thulium one wants to calculate matrix elements of $\bar{m}$ between states characterized by the quantum numbers S , L , J , and M where S = total spin, L = total orbital momentum, J = total angular momentum and M = eigenvalue of J_z . The operator $\bar{m}$ is the sum of single electron or hole operators. Therefore, in order to calculate the elements of $\bar{m}$ the

state $|SLJM\rangle$ is normally first expanded in terms of $|SM_SLM_L\rangle$ where $M_S =$ eigenvalue of S_z and $M_L =$ eigenvalue of L_z . The individual states $|SM_SLM_L\rangle$ are then expanded in terms of determinantal product states (47) of the form $\{\Psi_\alpha(K_1)\Psi_\beta(K_2)\dots\Psi_\delta(K_M)\}$ where the $\{ \}$ bracket denotes a Slater determinant. The function $\Psi_\gamma(K_i)$ is a single particle wave function. The argument K_i stands for the one-electron quantum numbers $(\ell_i m_{\ell_i} s_i m_{s_i})$.

The two consecutive expansions are in general very tedious. However, in the case of Tm^{+3} in the 3H_6 -state with $M = J = 6$, there is only one determinantal product state for the two holes in the 4f shell. The state $|SLJM\rangle = |1566\rangle$ is given by:

$$|1566\rangle = \{ \Psi_\alpha(33\frac{11}{22}) \Psi_\beta(32\frac{11}{22}) \} \quad (8.2)$$

The operator $\bar{m}$ in equation B.1 can be written as:

$$\bar{m} = \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} \bar{\kappa} \times \left[\sum_n (\bar{a}_n + \bar{b}_n) \times \bar{\kappa} \right]$$

where

$$\bar{a}_n = \exp(i\bar{\kappa} \cdot \bar{r}_n) \frac{1}{2} \bar{s}_n$$

and

$$\bar{b}_n = \frac{1}{2} (\bar{\ell}_n f(\bar{\kappa} \cdot \bar{r}_n) + f(\bar{\kappa} \cdot \bar{r}_n) \bar{\ell}_n)$$

where $\bar{a}_n$ and $\bar{b}_n$ operate on the wave function for the nth electron.

In equation B.2 the z-axis has been assumed to be the axis of quantization. This implies that the magnetic moment of the ion is in the z-direction. The vector $\bar{l}$, defined to be equal to the matrix

element $\langle 1566 | \sum_n \bar{a}_n + \bar{b}_n | 1566 \rangle$, can now be evaluated using equation B.2.

The result (47) is:

$$\begin{aligned} \bar{I} = \langle 1566 | \sum_n (\bar{a}_n + \bar{b}_n) | 1566 \rangle &= \Psi^* (33 \frac{11}{22}) [\bar{a} + \bar{b}] \Psi (33 \frac{11}{22}) d^4 r \\ &+ \Psi^* (32 \frac{11}{22}) [\bar{a} + \bar{b}] \Psi (32 \frac{11}{22}) d^4 r \end{aligned} \quad (B.3)$$

The integrals on the right hand side are over space and spin coordinates of the single particles.

In the central field approximation the wave function, $\Psi(\ell m_\ell, s m_s)$, is given by:

$$\Psi(\ell m_\ell, s m_s) = \frac{1}{r} R(\ell, r) \Theta(\ell, m_\ell, \Theta) \Phi(m_\ell, \varphi) \delta(s, m_s) \quad (B.4)$$

where the notation of Condon and Shortley (48) has been used.

The spherical harmonic $Y_\ell^m(\Theta, \Phi)$ has been written as the product $\Theta(\ell, m_\ell, \Theta) \times \Phi(m_\ell, \varphi)$, where $\Phi(m_\ell, \varphi) = \frac{1}{\sqrt{2\pi}} \exp(im_\ell \varphi)$. The function $\delta(s, m_s)$ is the electron spin function.

The matrix elements of the spin operator $\bar{a}$ and the orbital operator $\bar{b}$ will be calculated separately. For the spin part, one can easily perform the integral over the spin variable. The result is that only the z-component of $\bar{a}$ is different from zero. The integrals on the right hand side of equation B.3 are therefore of the form:

$$\begin{aligned} \Psi^* (\ell m \frac{1}{2} \frac{1}{2}) \exp(i \bar{\mathbf{a}} \cdot \bar{\mathbf{r}}) 2 s_z \Psi (\ell m \frac{1}{2} \frac{1}{2}) d^4 r = \\ \int \Psi'^* (\ell m) \exp(i \bar{\mathbf{a}} \cdot \bar{\mathbf{r}}) \Psi \Theta(\ell, m) \end{aligned} \quad (B.5)$$

where Ψ' is given by $\Psi = \Psi' \cdot \delta$ (see equation B.4).

If $\exp(i\vec{\kappa} \cdot \vec{r})$ is expanded in terms of spherical harmonics and spherical Bessel functions, the right hand side of equation B.5 becomes:

$$4\pi \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} i^{\lambda} \int_0^{\infty} |R(\ell, r)|^2 j_{\lambda}(\kappa r) dr \times$$

$$\int_0^{\pi} \Theta(\ell, m, \Theta) \Theta(\lambda, \mu, \Theta) \Theta(\ell, m, \Theta) \sin \Theta d\Theta$$

$$\times \int_0^{2\pi} \phi^{*}(m, \varphi) \phi(\mu, \varphi) \phi(m, \varphi) d\varphi \times Y_{\lambda}^{\mu*}(\hat{\kappa}) \quad (\text{B.6})$$

where $j_{\lambda}(\kappa r)$ is a spherical Bessel function, $\kappa = |\vec{\kappa}|$ and $\hat{\kappa} = \vec{\kappa}/\kappa = (\frac{\kappa_x}{\kappa}, \frac{\kappa_y}{\kappa})$.

The first integral, $\int dr$, in equation B.6 can be evaluated if the radial part of the wave function is known. Blume et al. (17) have calculated these integrals as a function of κ for a number of trivalent rare earth ions using Hartree-Fock wave functions. Following the notation of reference 17 the integrals will be written as $\langle j_{\lambda} \rangle$.

The second and third integrals have been evaluated by Condon and Shortley (48). The result of the last integral, $\int d\varphi$, is $\frac{1}{\sqrt{2\pi}} \delta_{\mu, 0}$. The second integral, $\int d\Theta$, will be written following Condon and Shortley (48) as:

$$\int_0^{\pi} \Theta(\lambda, \mu) \Theta(\ell, m) \Theta(\ell, m') \sin \Theta d\Theta = \sqrt{\frac{2\lambda+1}{2}} c^{\lambda}(\ell m, \ell' m') \quad (\text{B.7})$$

where $c^{\lambda}(\ell m, \ell' m')$ (49) has been tabulated for different combinations of ℓ, ℓ', m and m' .

By using equation B.7 and the notation $\langle j_{\lambda} \rangle$ for the radial integral,

equation B.6 becomes:

$$\sqrt{4\pi} \sum_{\lambda=0}^{\infty} i^{\lambda} \sqrt{2\lambda+1} c^{\lambda}(\ell m, \ell m) \langle j_{\lambda} \rangle Y_{\lambda}^0(\hat{\kappa}) \quad (\text{B.8})$$

The contribution from the electron spin operator to the vector $\bar{I}$ in equation B.3 can now be written. The result for the z component is:

$$\begin{aligned} (\bar{I}_{\text{spin}})_z &= \sqrt{4\pi} \sum_{\lambda=0}^{\infty} i^{\lambda} \sqrt{2\lambda+1} (c^{\lambda}(33, 33) + c^{\lambda}(32, 32)) \\ &\quad \times \langle j_{\lambda} \rangle Y_{\lambda}^{0*}(\hat{\kappa}) \end{aligned} \quad (\text{B.9})$$

the x- and y-components are zero.

The z-component of the orbital operator $\bar{b}$ can be calculated in a very similar way. The orbital analog of equation B.5 becomes:

$$\begin{aligned} \frac{1}{2} \int \Psi^*(\ell m, \frac{1}{2}, \frac{1}{2}) (\ell_z f(\bar{\kappa} \cdot \bar{r}) + f(\bar{\kappa} \cdot \bar{r}) \ell_z) \Psi(\ell m, \frac{1}{2}, \frac{1}{2}) d^4r \\ = m \int \Psi^*(\ell m) f(\bar{\kappa} \cdot \bar{r}) \Psi(\ell m) d^3r \end{aligned} \quad (\text{B.10})$$

The function $f(\bar{\kappa} \cdot \bar{r})$ can be expanded in terms of spherical harmonics; the expansion has the same form as the equivalent expansion of $\exp(i\bar{\kappa} \cdot \bar{r})$ except that the spherical Bessels-function $j_{\lambda}(\kappa r)$ is substituted by a function $g_{\lambda}(\kappa r)$ (1, 17). Following the notation of Blume et al. (17), the radial part of the integral in equation B.10 will be denoted by $\langle g_{\lambda} \rangle$. The integrals over Θ and Φ in equation B.10 give the same results as in the calculation of the spin contribution. The orbital analog of equation B.9 can therefore be written as:

$$(\bar{I}_{\text{orbit}})_z = \sqrt{4\pi} \sum_{\lambda=0}^{\infty} i^{\lambda} \sqrt{2\lambda+1} (3c^{\lambda}(33,33) + 2c^{\lambda}(32,32)) \langle g_{\lambda} \rangle Y_{\lambda}^{0*}(\hat{n}) \quad (\text{B.11})$$

In order to calculate the x-component of $\bar{I}$, one has to evaluate integrals of the form:

$$\int \Psi^{*}(\ell m \frac{1}{2} \frac{1}{2}) (\frac{1}{2} \ell_x f(\bar{n} \cdot \bar{r}) + \frac{1}{2} f(\bar{n} \cdot \bar{r}) \ell_x) \Psi(\ell m \frac{1}{2} \frac{1}{2}) d^4 r \quad (\text{B.12})$$

$$= \frac{1}{4} \int \Psi^{*}(\ell m) ((\ell_+ + \ell_-) f(\bar{n} \cdot \bar{r}) + f(\bar{n} \cdot \bar{r}) (\ell_+ + \ell_-)) \Psi(\ell m) d^3 r$$

where $\ell_+ = \ell_x + i\ell_y$ and $\ell_- = \ell_x - i\ell_y$.

The four integrals in equation B.12 can each be calculated using the properties of the angular momentum operators, ℓ_+ and ℓ_- , in a calculation similar to that in which equations B.5 and B.10 were derived. From definitions of $Y_{\lambda}^{\mu}(\hat{n})$ and $c^{\lambda}(\ell m, \ell' m')$ the results of the four integrals can be combined into one expression. The right hand side of equation B.12 then becomes:

$$\frac{1}{2} \sqrt{4\pi} \sum_{\lambda=0}^{\infty} i^{\lambda} \sqrt{2\lambda+1} \times [\sqrt{\ell(\ell+1)-m(m-1)} c^{\lambda}(\ell m, \ell m-1) + \sqrt{\ell(\ell+1)-m(m+1)} c^{\lambda}(\ell m+1, \ell m)] \times \langle g_{\lambda} \rangle \times \text{Re}(Y_{\lambda}^1(\hat{n})) \quad (\text{B.13})$$

where $\text{Re}(Y_{\lambda}^1(\hat{n})) = \text{real part of } Y_{\lambda}^1(\hat{n}) = \frac{1}{2}(Y_{\lambda}^1(\hat{n}) + Y_{\lambda}^{1*}(\hat{n}))$.

For the y-component of $\bar{I}$, one has to calculate the integral on the left hand side of equation B.12 with ℓ_y instead of ℓ_x . The result is given in equation B.13 with $\text{Re}(Y_{\lambda}^1(\hat{n}))$ substituted by $\text{Im}(Y_{\lambda}^1(\hat{n}))$, where

$$\text{Im}(Y_{\lambda}^1(\hat{\kappa})) = \frac{1}{2i}(Y_{\lambda}^1(\hat{\kappa}) - Y_{\lambda}^{1*}(\hat{\kappa})).$$

The x- and y-components of the orbital contribution to $\bar{I}$ are therefore given by:

$$(I_{\text{orbit}})_x = \frac{1}{2}\sqrt{4\pi} \sum_{\lambda=0}^{\infty} c_{\lambda}^1 \text{Re}(Y_{\lambda}^1(\hat{\kappa}))$$

and

$$(\bar{I}_{\text{orbit}})_y = \frac{1}{2}\sqrt{4\pi} \sum_{\lambda=0}^{\infty} c_{\lambda}^1 \text{Im}(Y_{\lambda}^1(\hat{\kappa})) \quad (\text{B.14})$$

where:

$$c_{\lambda}^1 = i\sqrt{2\lambda+1} (2\sqrt{6} c^{\lambda}(33,32) + \sqrt{10} c^{\lambda}(32,31)) \langle g_{\lambda} \rangle$$

The matrix element of the magnetic scattering operator $\bar{m}$ has now been evaluated for thulium. The result is given by:

$$\langle 1566 | \bar{m} | 1566 \rangle = \frac{\gamma e^2}{m_e c^2} \frac{1}{2} (\bar{\kappa} \times (\bar{I} \times \bar{\kappa})) \quad (\text{B.15})$$

The components of $\bar{I}$ are given by equations B.9, B.11 and B.14:

$$I_z = (\bar{I}_{\text{spin}})_z + (\bar{I}_{\text{orbit}})_z$$

$$I_x = (\bar{I}_{\text{orbit}})_x \text{ and}$$

$$I_y = (\bar{I}_{\text{orbit}})_y$$

So far only the direction of the z-axis has been specified. In order to simplify the expressions for the components of $\langle 1566 | \bar{m} | 1566 \rangle$, the x-axis will be taken to be the direction of the projection of $\bar{\kappa}$ onto the plane perpendicular to the z-axis. Since the azimuthal angle

ϕ of $\bar{\kappa}$ is equal to zero, $\text{Im}(Y_{\lambda}^1(\hat{\kappa}))$ is zero. The vector $\bar{\mathbf{T}}$ is of the form $(1_x, 0, 1_z)$. The components of $\langle 1566 | \bar{\mathbf{m}} | 1566 \rangle$ become:

$$\langle 1566 | \bar{\mathbf{m}} | 1566 \rangle_x = - \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} \kappa_x \kappa_z \left(1_z - \frac{\kappa_z}{\kappa_x} 1_x \right)$$

$$\langle 1566 | \bar{\mathbf{m}} | 1566 \rangle_y = 0$$

$$\langle 1566 | \bar{\mathbf{m}} | 1566 \rangle_z = \frac{\gamma e^2}{m_e c^2} \frac{1}{\kappa} \kappa_x^2 \left(1_z - \frac{\kappa_z}{\kappa_x} 1_x \right)$$

or

$$\langle 1566 | \bar{\mathbf{m}} | 1566 \rangle = 2 \, p \bar{\mathbf{q}}$$

where

$$\bar{\mathbf{q}} = \hat{\kappa} \times (\hat{z} \times \hat{\kappa})$$

$$p = \frac{\gamma e^2}{2 m_e c^2} (1_z - \cot \Theta 1_x) .$$

The symbol Θ is the angle between $\bar{\kappa}$ and the axis of quantization (or z-axis).

It is shown below that for thulium:

$\lim_{\kappa \rightarrow 0} (1_z - \cot \Theta 1_x) = 7 = \text{magnetic moment, } \mu, \text{ in } \mu_B$. Therefore, p can be written as:

$$p = \frac{\gamma e^2}{2 m_e c^2} \mu f(\kappa, \Theta)$$

where $f(\kappa, \Theta)$ is the magnetic form factor. The form factor, $f(\kappa, \Theta) =$

$\frac{1}{7} (I_z - \cot \Theta I_x)$. If one evaluates equations B.9, B.11 and B.14 for $\varphi = 0$, $f(\kappa, \Theta)$ becomes:

$$\begin{aligned}
 f(\kappa, \Theta) = & \frac{1}{7} [(2\langle j_0 \rangle + 5\langle g_0 \rangle) P_0(\cos \Theta) \\
 & + 5(\frac{1}{3}\langle j_2 \rangle + \langle g_2 \rangle) P_2(\cos \Theta) \\
 & - \frac{3}{11}(4\langle j_4 \rangle + 5\langle g_4 \rangle) P_4(\cos \Theta) \\
 & - \frac{5}{33}(5\langle j_6 \rangle + 9\langle g_6 \rangle) P_6(\cos \Theta) \\
 & - \cot \Theta \{ \frac{\sqrt{5}}{2} \langle g_2 \rangle P_2^1(\cos \Theta) \\
 & + \frac{3}{11} \langle g_4 \rangle P_4^1(\cos \Theta) \\
 & - \frac{20}{33} \langle g_6 \rangle P_6^1(\cos \Theta) \}] \quad (B.16)
 \end{aligned}$$

In the limit of κ going to zero, one has $\lim_{\kappa \rightarrow 0} \langle j_\lambda \rangle = \lim_{\kappa \rightarrow 0} \langle g_\lambda \rangle = \delta_{\lambda, 0}$.

Therefore, for thulium the limit of $(I_z - \cot \Theta I_x)$ is;

$$\lim_{\kappa \rightarrow 0} (I_z - \cot \Theta I_x) = \lim_{\kappa \rightarrow 0} ((2\langle j_0 \rangle + 5\langle g_0 \rangle) P_0(\cos \Theta)) = 7$$