MASTER IS-T-732

FERMI SURFACE EFFECTS IN TERBIUM ALLOYS

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Ph.D. Thesis Submitted to Iowa State University

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Date Transmitted: October 1976

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PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO. W-7405-eng-82

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Fermi surface effects in
terbium alloys

by

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The relation of magnetic ordering properties in Tb alloys to the geometry of the Tb Fermi surface was investigated. It is believed that the magnetic ordering properties of the rare earths are determined by a generalized susceptibility function that is strongly dependent upon the geometry of the Fermi surface. In this work we varied the Fermi surface geometry through changes in the Fermi energy of Tb and investigated the ordering temperatures as the Fermi energy changed. Specifically, theory predicts that as the Fermi energy is lowered through reduction of conduction electron density the helical ordering structure of Tb should be enhanced. When the Fermi energy is raised the helical structure should be diminished.

In this work the Fermi energy of Tb was lowered through alloying with divalent Mg and Yb and the Fermi energy was raised through alloying with quadrivalent Th. The experimental results are complicated and require a detailed consideration of atomic size as well as Fermi energy effects on the ordering properties. In order to under-

*USERDA Report IS-T-732. This work was performed under Contract W-7405-eng-82 with the Energy Research and Development Administration.

stand the results, a simple theory was developed to account for the effects on band structure which accompany alloying. After application of this simple theory to the experimental results it was found that the results seem to be consistent with the theory. Lowering of the Fermi energy through alloying does produce an enhancement of the helical ordering structure while raising of the Fermi energy produces a decrease in the stability of the helical structure.

1. INTRODUCTION

The rare earth, or lanthanide, series of elements consists of the metals lanthanum through lutetium. These materials all have very similar chemical and physical properties but possess a wide variety of magnetic properties. This situation is a result of the interesting electronic configuration of the lanthanides which can be written schematically as:

where n assumes the values zero through fourteen as one proceeds through the lanthanide series. Most of the rare earth metals have a similar crystalline lattice and consist of triply ionized atoms such that the chemical and gross physical properties of them are similar. The presence of unpaired $4f$ electrons in a highly screened atomic-like level produces large magnetic moments associated with the atoms and accounts for the interesting magnetic properties of the series. Thus, the lanthanide series provides a unique system in which the magnetic properties of metals can be examined in a situation where the crystalline and electronic properties of the materials are quite similar.

It has long been recognized that the magnetic properties of the rare earths are complex but only in recent years has a detailed investigation of these properties been possible. This investigation was made possible by the production of high purity rare earth single crystals by Spedding and Daane¹ and Nigh² at Iowa State University.

Following the production of the high purity single crystals a wide variety of techniques were brought to the problem of understanding the rare earths. Ordinary physical measurements such as investigations of transport properties³ and the classical magnetic properties⁴ produced valuable information concerning the complex nature of the rare earths. Neutron diffraction experiments⁵ were the final key to producing an understanding of the complexity of the magnetic properties of the rare earths.

At the present time it is understood that the complex magnetic properties of the rare earths are brought about by an interplay of various interactions within the crystal. The primary force that brings about ordering is thought to be the Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect exchange interaction⁶ between the localized 4f electrons. The RKKY interaction is one in which the interaction between the localized magnetic moments is mediated by conduction electrons, which are free to propagate throughout the lattice. Qualitatively the interaction is one in which the 4f electrons interact with the conduction electrons through an exchange interaction to polarize the conduction electrons. These polarized electrons then propagate through the crystal and carry the ordering information over a long distance. The indirect exchange process can be described through a generalized susceptibility function which portrays the conduction electron polarization as a wave vector dependent quantity $\chi(\vec{q})$ that is sensitive to details of the Fermi surface. In particular, a complex magnetic ordered structure will result whenever

the $\chi(\vec{q})$ function passes through a maximum where these maxima result from parallel or "nested" regions of the Fermi surface.

The role of Fermi surface "nesting" in determining magnetic properties was first proposed by Lomer⁷ in connection with Cr. Later Williams et al.⁸ proposed that a similar mechanism might be applicable to the rare earths. Energy band calculations by Keeton and Loucks⁹ demonstrated that the Fermi surfaces of the rare earths are extremely anisotropic and indeed do show "nesting" at wavelengths comparable to those observed by neutron diffraction. Evenson and Liu¹⁰ used the bands of Keeton and Loucks to calculate $\chi(\vec{q})$ for several of the rare earths and they were able to obtain good agreement between the calculations and the experimental results.

The pair of bands which determine the shape of the Fermi surface in the heavy rare earths are quite flat so that the "nesting" is quite sensitive to changes in the Fermi energy. In particular, detailed calculations indicate¹⁰ that lowering of the Fermi energy should tend to increase the "nesting" and hence promote complex magnetic ordering. This information provided the motivation for a study by Mellon and Legvold¹¹ wherein Gd was alloyed with divalent Mg to lower the Fermi energy in an attempt to induce a periodic magnetic ordering structure into that simple ferromagnetic material. Unfortunately that study was inconclusive presumably due to failure of rigid band ideas in their alloys.

In this work an investigation of the effects of Fermi energy shifts was undertaken on the element terbium. Tb is believed to be

similar to Gd in that it is a simple ferromagnet at low temperatures but it exhibits anti-ferromagnetic (helical structure) ordering over a narrow temperature range. Therefore, this helical structure could be observed as a function of alloying in a manner similar to Mellon and Legvold¹¹ while avoiding the ambiguities attendant to the absence of an observable periodic ordered structure. The relative stability of the periodic ordering feature was investigated as the Fermi level was shifted upward and downward through alloying. The basic data for this investigation came from magnetic measurements of the alloys which yielded magnetic ordering temperatures. In addition, electrical resistivity and metallographic studies of the alloys were undertaken such that the nature of the alloys could be determined as completely as possible.

II. THEORY

A. Elementary Theory

The rare earths are interesting because they exhibit all of the ordinary forms of magnetism including paramagnetism, ferromagnetism, ferrimagnetism and anti-ferromagnetism often all in the same element. These magnetic properties are a result of various coupling configurations between magnetic moments arising from localized unpaired 4f electrons that are highly screened by the other atomic electrons. In this situation, L and S , the angular momentum and spin quantum numbers, are good quantum numbers and combined give rise to a total angular momentum J . There are $2J+1$ projections of J on the Z -axis that give rise to magnetic moments

$$M_J = g \mu_B; M_J = J, J-1, \dots, -J+1, -J \quad (1)$$

where $\mu_B = 9.2741 \times 10^{-21}$ erg/Oe is called the Bohr magneton. The factor g in Equation 1 is called the Landé g factor defined as:

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (2)$$

Paramagnetism is the high temperature arrangement of the localized magnetic moments and consists of a non-interacting system of the moments in which the orientations of the moments are governed by statistical mechanics. In paramagnetism the magnetic moment per gram is

$$\sigma = \frac{N_o}{A} g J \mu_B B_J(x) \quad (3)$$

where $x = gJ\mu_B H/kT$, N_o is Avogadro's number, A is the atomic weight and $B_J(x)$ is the well-known Brillouin function. In the low field and/or high temperature limit Equation 3 becomes

$$\sigma = \frac{N_o J(J+1) g^2 \mu_B^2 H}{3kTA} = \chi H$$

which is the famous Curie law for the response of a paramagnetic system to a field as a function of temperature.

Certain magnetic materials undergo magnetic ordering in which the moments align themselves parallel to each other. This is called ferromagnetism. A phenomenological description of this behavior was formulated by Weiss.¹² Weiss observed that a ferromagnet seems to have a moment at zero applied field. The spontaneous moment characteristic of ferromagnets implies that an additional internal field must exist in the material. Weiss included the internal field through introduction of a molecular field, H_m , which is proportional to the moment of the material. The total field present in the material is then the sum of the applied field, H , and the molecular field through the relation

$$H_t = H + H_m = H + W \cdot \sigma$$

where W is an interaction constant which indicates how strongly any moment is affected by the average moment of its neighbors. The total field is then placed into Equation 3 by writing $x = gJ\mu_B (H+W\sigma)/kT$.

In low fields and/or high temperatures

$$\sigma = \frac{C}{T - \theta_p} \quad (4)$$

where $\theta_p = WC$ with C identified as the Curie constant which is

$$C = \frac{N_o J(J+1) g^2 \mu_B^2}{3kA} \quad (5)$$

It is observed that the Curie-Weiss law of Equation 4 will describe the experimental magnetization of many materials very well. In an experiment one usually obtains the parameters C and θ_p . The strength of the effective local moment is given as

$$\mu_{\text{eff}} = 2.828 (A \cdot C)^{\frac{1}{2}} \quad (6)$$

It is useful to observe that the paramagnetic Curie temperature, θ_p , is related to the magnetic moment through the relation

$$\theta_p = \frac{WN_o \mu_B^2 \mu_{\text{eff}}^2}{3kA} \quad (7)$$

Finally, a useful quantity that may be obtained experimentally for a ferromagnet is the magnetization at zero temperature in the limit of infinite magnetic field. The experimental saturation moment per gram can be converted to the moment per atom by

$$\mu_{\text{sat}} = \frac{A \sigma_{\infty,0} \mu_B}{5585} \quad (8)$$

The molecular field result for an anti-ferromagnetic material is similar to Equation 4 but with a negative θ_p . This then is all the progress than can be made without a detailed examination of the nature of the molecular field interaction.

B. Exchange Processes

It was shown by Heisenberg¹³ that ferromagnetism could be accounted for by the exchange forces acting between neighboring atoms. In this case the assumed Hamiltonian takes the form

$$H = -2 \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

where J_{ij} is the exchange between atoms i and j and where $\vec{S}_i$ is the spin of atom i . In certain materials the Heisenberg exchange process is undoubtedly the dominant interaction but in the rare earths it certainly is not. The reason that the direct exchange mechanism of Heisenberg is not applicable to the rare earths is that the exchange integral contains the overlap of wavefunctions from neighboring atoms. In the case of the 4f electrons of the rare earths there simply is insufficient overlap of the highly localized 4f wavefunctions to account for magnetic ordering of the localized moments.

Since the direct exchange process is not believed to be applicable to the rare earths, a theory of magnetic ordering to account for coupling between 4f spins through an indirect process is required. Such an indirect process had been proposed by Ruderman and Kittel¹⁴ to explain hyperfine splitting through a nuclear indirect exchange mechanism.

Their ideas were extended to the case of coupling between localized magnetic moments by Kasuya¹⁵ and Yosida.¹⁶ In this model, the conduction electrons, which are free to propagate through the lattice for many atomic distances, interact with the local moments to carry the ordering information. Thus, as the conduction electrons interact with the local moments they are capable of mediating a long range interaction. The indirect exchange interaction between the local moments and conduction electrons is taken to be of the simple form

$$H_{int} = -I(\vec{r}_i - \vec{R}_j) \vec{\sigma}_i \cdot \vec{S}_j \quad (9)$$

where $\vec{\sigma}_i$ is the spin of a conduction electron at $\vec{r}_i$ and $\vec{S}_j$ is the spin of the 4f electrons located at $\vec{R}_j$ and where $I(\vec{r}_i - \vec{R}_j)$ is a position dependent exchange integral. In the rare earths this equation is generally rewritten to reflect the fact that, so long as the exchange energy is not too large, the total angular momentum quantum number J is a good quantum number. Thus, the quantity $\vec{S} = (g-1) \vec{J}$ is put into Equation 9 to yield the modified form:

$$H_{ind} = -I(\vec{r}_i - \vec{R}_j) (g-1) \vec{\sigma}_i \cdot \vec{J}_j \quad (10)$$

Equation 10 is the usual starting point for calculations of the interactions between the localized rare earth ion moments. In general, the interaction Hamiltonian is much more complicated because it must include anisotropic interaction effects which are due to the orbital contribution

to the moment. It is generally believed that ordering effects are dominated by the exchange interaction but if a detailed calculation of the ordering properties is to be carried out the orbital contributions must be considered. If one considers only single ion interactions the orbital contribution to the Hamiltonian can be written as

$$H_{\text{orb}} = H_{\text{an ex}} + H_{\text{cf}} + H_{\text{ms}}$$

where $H_{\text{an ex}}$ is anisotropic exchange caused by the nonsphericity of the 4f wavefunctions, H_{cf} is a crystal field energy due to the non-symmetric distribution of electrical fields within the crystal and H_{ms} is an energy term coming from magnetoelastic forces within the crystal. In general then one must solve $H = H_{\text{ind}} + H_{\text{orb}}$. In principle the Hamiltonian can be solved to explain the complex magnetic structures of the rare earths.¹⁷ However, the essential ordering information is contained in Equation 10 and the rest of this paper will be concerned with a solution of the indirect exchange Hamiltonian.

C. Indirect Exchange

Let us now proceed with a detailed examination of the Hamiltonian of Equation 9. The total energy associated with the exchange between a collection of localized spins in a metal is

$$H_{\text{int}} = - \sum_{i,j} I(\vec{r}_i - \vec{r}_j) \vec{\sigma}_i \cdot \vec{S}_j \quad (11)$$

where the sum extends over all conduction electrons and all local moments.

In general the interaction between the conduction and localized 4f electrons is assumed to be very short range and in fact is approximated as a point contact interaction of the form:

$$I(\vec{r}_i - \vec{R}_j) = I \delta(\vec{r}_i - \vec{R}_j) \quad (12)$$

where I is a constant. Equation 12 is combined with the Hamiltonian of Equation 11 and the exchange energy determined. Following the procedure outlined by Kasuya⁶ the Hamiltonian is second quantized with respect to the conduction electron states to yield

$$\begin{aligned} H_{int} = & -I \sum_j \sum_{k,k',s,s'} [\langle \psi_{k',s'} | \delta(r-R_j) \sigma^z | \psi_{k,s} \rangle S_j^z \\ & + \frac{1}{2} \langle \psi_{k',s'} | \delta(r-R_j) \sigma^+ | \psi_{k,s} \rangle S_j^- \\ & + \frac{1}{2} \langle \psi_{k',s'} | \delta(r-R_j) \sigma^- | \psi_{k,s} \rangle S_j^+] c_{k',s'}^+ c_{k,s}^- \end{aligned} \quad (13)$$

where $c_{k,s}^+$ and $c_{k,s}^-$ are creation and annihilation operators respectively for conduction electrons of momentum k and spin s . If we now observe that the conduction electron wavefunctions are Bloch states in the crystal which are of the form

$$\psi_{k,s} = e^{i\vec{k} \cdot \vec{r}} u_k(\vec{r}) \otimes_s \quad (14)$$

and where $\otimes_s$ is a spin function that carries the information about the conduction electron spin orientation. The wavefunction of Equation 14

is then substituted into Equation 13 to yield

$$\begin{aligned}
 H_{int} = -I/2 \sum_j \sum_{k,k'} u_{k'}^*(\vec{R}_j) u_k(\vec{R}_j) e^{i(\vec{k}-\vec{k}') \cdot \vec{R}_j} \\
 [S_j^z (c_{k'}^+ c_k^- - c_{k'}^- c_k^+) \\
 + S_j^- c_{k'}^+ c_k^- + S_j^+ c_{k'}^- c_k^+] . \quad (15)
 \end{aligned}$$

The Hamiltonian, Equation 15, then provides the basis for the calculations of magnetic ordering in the rare earths. We proceed by performing a perturbation calculation utilizing Equation 15. Notice that the first order perturbation term must be zero since it would be a matrix element between two ground states, and the same spin states, whereas the perturbation Hamiltonian acts to flip a spin in all cases. Thus one must use second order perturbation theory to obtain a non-zero energy term. The second order term is

$$\begin{aligned}
 E^{(2)} = I^2/4 \sum_{i,j} \sum_{k,k'} n_k (1-n_{k'}) [u_{k'}^*(\vec{R}_j) u_k(\vec{R}_i) u_k(\vec{R}_j) u_{k'}^*(\vec{R}_i)] \\
 \frac{e^{i(\vec{k}-\vec{k}') \cdot (\vec{R}_j - \vec{R}_i)}}{(E_k - E_{k'})} 2 \vec{S}_i \cdot \vec{S}_j . \quad (16)
 \end{aligned}$$

Equation 16 is truly remarkable because it shows that the indirect exchange interaction between conduction electrons and the local moments gives rise to an effective direct exchange coupling. This effective direct coupling is of the familiar form

$$E^{(2)} = - \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j = H_{int}$$

where the exchange constant J_{ij} is now a complicated quantity containing the conduction electron information. In a real metal all of the electrons are not in a single conduction band so there is not a unique electron state for each value of momentum and spin. In this situation one must keep track of the band through a band index, b . The band index is put into the Hamiltonian to yield the new form

$$H_{int} = - \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (17)$$

$$J_{ij} = \frac{1}{4} \sum_{\substack{b,k \\ b',k'}} \frac{(n_{b,k} - n_{b',k'}) |\langle bk | I_{ex} | b'k' \rangle|^2 e^{i(\vec{k}-\vec{k}') \cdot \vec{R}_{ij}}}{E_{b,k} - E_{b',k'}}$$

At this point we have the interaction Hamiltonian written in what is essentially its most general form and can begin to examine it for useful information.

In many cases the crude assumption is made that the exchange matrix element $\langle I_{ex} \rangle^2$, which is a function of $\vec{k}$ and $\vec{k}'$, can be written as a function of $\vec{k} - \vec{k}' = \vec{q}$. Then Equation 17 reduces to:

$$H_{int} = - \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

$$J_{ij} = \frac{1}{4} \sum_{\vec{q}} I^2(\vec{q}) \chi(\vec{q}) e^{-i \vec{q} \cdot \vec{R}_{ij}}$$

$$\chi(\vec{q}) = \sum_{\substack{\vec{k} \\ b,b'}} \frac{(n_{b,\vec{k}} - n_{b',\vec{k}+\vec{q}})}{E_{b,\vec{k}} - E_{b',\vec{k}+\vec{q}}} \quad (18)$$

Equation 18 appears to be quite formidable but it is actually a great simplification because the physics of the interaction is then contained in a calculation of $\chi(\vec{q})$ which is relatively simple to perform if the energy bands of the material are known. The quantity $\chi(\vec{q})$ is called the generalized susceptibility and when combined with a matrix element provides a description of the response of conduction electrons to the internal field generated by the localized magnetic moments. Aside from the necessity of having very accurate band calculations, the primary difficulty that is anticipated with respect to application of Equation 18 is the assumption that $I(\vec{k}, \vec{k}') = I(\vec{q})$. This assumption may not be particularly valid because of the complicated wavefunctions associated with the rare earths and in fact Freeman¹⁸ has discussed the role of the matrix elements and concludes that they may be as important as $\chi(\vec{q})$ in determining the nature of J_{ij} . Another caution must be expressed at this point: since the exchange coupling must be expected to produce magnetic ordering at some point, the effects of ordering on the band structure must be considered. In particular, the helical ordering that occurs in those materials we will be considering gives rise to so called magnetic "superzones"¹⁹ because the magnetic structure is incommensurate with the atomic lattice. These "superzones" open up band gaps and can strongly affect the Fermi surface. Therefore, the generalized susceptibility of Equation 18 is actually only applicable in the paramagnetic regime.

It is obvious that $\chi(\vec{q})$ has an important effect on the free energy of the material through the Hamiltonian of Equation 18. To obtain some

understanding of the free energy it is useful to examine the nature of magnetic ordering from a classical point of view by first observing that once a magnetic structure has been established the localized moments assume a stable pattern that is a function of position. The pattern of spins is periodic and can therefore be Fourier transformed to a function of $\vec{q}$. The Fourier transformed spin quantities can be written as $S_{\vec{q}}$ and can then be substituted into Equation 18 to yield the new Hamiltonian

$$H_{\text{ex}} = -N^2/4 \sum_{\vec{q}} I^2(\vec{q}) \chi(\vec{q}) [S_{-\vec{q}} S_{\vec{q}}^* + S_{\vec{q}}^* S_{-\vec{q}}] . \quad (19)$$

Examination of Equation 19 from a classical point of view shows that the free energy of the system is a minimum if the $S_{\vec{q}}$ functions exist for that value of $\vec{q}$ for which $I^2(\vec{q})\chi(\vec{q}) = \mathcal{J}(\vec{q})$ is a maximum. That is, the localized spins will assume a magnetic structure that has a periodicity corresponding to the maximum in the generalized susceptibility function. Therefore, the form of the stable magnetic structure is determined by $\mathcal{J}(\vec{Q})$ which is defined as the maximum value of $\mathcal{J}(\vec{q}) = I^2(\vec{q}) \chi(\vec{q})$ and where $\vec{Q}$ is the wave vector associated with the maximum in the exchange function $\mathcal{J}(\vec{q})$. Thus, a simple "first principles" calculation can be performed that will yield the generalized susceptibility function where the generalized susceptibility describes the nature of the magnetic ordering. The value of $\vec{Q}$ corresponds to the periodicity of the magnetic structure and as this value varies, the complex magnetic structures of the rare earths can be accounted for. In addition, calculations of the gener-

alized susceptibility provide some basis for understanding the ordering temperatures. A simple mean field theory yields the result that the ordering temperature is related to the value of the exchange parameter J . Thus, since the value of J that results in a stable magnetic structure is given in the classical approximation by $\mathcal{J}(\vec{Q})$, we have a value for the ordering temperature of:

$$k_B T_0 = 2/3 \mathcal{J}(\vec{Q}) (g-1)^2 J(J+1) \quad (20)$$

where T_0 is the initial ordering temperature. We have also used the fact that in the heavy rare earths, where spin orbit coupling holds, the spin is given by $\vec{S} = (g-1) \vec{J}$. The quantity $(g-1)^2 J(J+1)$ is known as the de Gennes factor²⁰ and is generally denoted as G . Thus, at least in principle a complete understanding of magnetic ordering in the rare earths results from application of Equation 18.

Up to this point we have treated the problem of magnetic ordering from a strictly formal viewpoint. Therefore, it is essential now to establish the applicability of the formalism to real systems. For the present we will assume that the $I(\vec{q})$ assumption is valid and that $I(\vec{q})$ is a smoothly varying function such that the magnetic structure is indeed determined by $\chi(\vec{q})$. A calculation of $\chi(\vec{q})$ through Equation 18 is simply a summation over all possible initial and final conduction electron energy states where the initial state must be occupied and the final state must be empty. Because of the energy denominator, the summation will be dominated by those allowed transitions that proceed from states imme-

diately below the Fermi energy to immediately above it. Thus, since the summation extends over all states at the Fermi level, the form of the generalized susceptibility will be very sensitive to the nature of the Fermi surface for the material. The simplest calculation that can be undertaken starts by assuming a free electron gas. However, the electron bands of the rare earths are certainly not free electron-like and so a more realistic calculation must be utilized.

Assuming free electron bands in Equation 17 yields a simple result that is known as the RKKY interaction. This particular interaction is of the simple form:

$$J_{ij} = \frac{8mI^2 |u^4(R_{ij})| k_F^4}{(2\pi)^3 \hbar^2} \frac{x \cos x - \sin x}{x^4}$$

where $x = 2k_F R_{ij}$. As can be seen, this equation allows for various interaction strength magnitudes and signs depending on the inter atomic separation R_{ij} . This equation is not particularly valid since it was developed for free electrons. The rare earths have Fermi surfaces that can be represented very crudely by a cylinder with flat ends separated by k_A . Using this Fermi surface and parabolic electron bands we can solve Equation 17 to yield

$$\chi(\vec{q}) = \chi(0) \frac{1}{t} [\ln(1+t/1-t)]$$

where $t = q/k_A$ and where the function passes through a logarithmic singularity at $q = k_A$. In this situation we see that a magnetic structure with

periodicity k_A would result. This rather artificial example provides us with an important bit of information: a periodic magnetic structure will result whenever there are parallel flat pieces of the Fermi surface.

D. Theory of the Rare Earths

It is clear that Fermi surface geometry and periodic magnetic ordering are strongly related if the indirect exchange interaction is the dominant energy. Specifically, if there are parallel and flat regions of the Fermi surface, a well-defined magnetic structure is expected. It has long been felt that this is the proper description of magnetic ordering in the rare earths but only after Keeton and Loucks⁹ demonstrated for the rare earths that there are regions of the Fermi surface where the hole and electron surfaces are parallel was this clearly established. This means that there are nearly one-dimensional pieces of the Fermi surface that will give rise to a peak in the generalized susceptibility.

The calculated Fermi surfaces for the heavy rare earths are characterized by a somewhat cylindrical stalk in the Γ to A direction with a complicated structure extending to the zone edge in the basal plane direction as shown in Figure 1. Extending from the stalk are "toes" which extend to the zone edge around the symmetry point L. Between the "toes", that extend to the zone edge, there is a "webbing" whose thickness and extent is somewhat variable throughout the rare earth series. Evenson and Liu¹⁰ utilized this Fermi surface to calculate the generalized susceptibility function $\chi(\vec{q})$ through Equation 18. They reported that the

Figure 1. The paramagnetic Fermi surface for gadolinium. This is the hole surface in the double zone representation.

generalized susceptibility calculated using constant matrix elements showed a maximum at $\vec{Q}$ where the calculated values of $\vec{Q}$ correspond to the observed magnetic periodicities. The maximum in $\chi(\vec{q})$ corresponds at least roughly to the thickness of the "webbing" between the "toes" of the Fermi surface. The parallel nature of the "webbing" gives rise to many electron states that are separated by a characteristic $\vec{q}$ value. This situation is known as Fermi surface "nesting" and this is the Fermi surface structure which determines the nature of rare earth ordering.

In this work we are especially interested in the heavy rare earth metal terbium. The Fermi surface and generalized susceptibility calculations for Tb were performed by Liu.²¹ The two energy bands that produce the Fermi surface of Tb are shown in Figure 2. These bands were calculated using an RAPW technique that is typical of this work.^{9,10} An important observation from Figure 2 is that the bands are flat and near to the Fermi energy such that the Fermi surface should be very sensitive to any process that moves the bands with respect to the Fermi energy. The Fermi surface generated from the Tb bands is shown in Figure 3 where the Fermi surface appears in cross-section. A generalized susceptibility function was calculated for Tb using this Fermi surface and it is plotted in Figure 3. As can be seen, the generalized susceptibility shows a maximum. The $\vec{q}$ vector of the maximum corresponds to the observed wave vector of the magnetic structure of Tb.

Through the considerations of the preceding sections it is clear that magnetic ordering in the rare earths should be related to the Fermi surface. It would be useful to be able to perform experiments to estab-

Figure 2. Energy bands for terbium along the symmetry axes of the Brillouin zone. The dashed line indicates the Fermi energy.

TERBIUM

Figure 3. The generalized susceptibility and Fermi surface cross-section of terbium.

lish the validity of this theory. Thus, we should look to the theory for specific predictions that can be tested by experiment. Calculations as performed by Liu and associates^{10,22} show certain trends as one proceeds across the rare earth series. One of the most important trends is that the value of $\vec{Q}$ becomes somewhat greater as one advances across the series from Gd to Lu. The experimental ramification of this theoretical result is that the interlayer turn angle in the ordered state should decrease as one goes from Gd to Lu. Neutron diffraction determinations of the magnetic structures²³ are in qualitative agreement with the calculated result. Another specific prediction of the theory is that the height of the maximum in $\chi(\vec{Q})$ can be calculated as a function of lattice volume to yield the pressure derivative of the ordering temperature. The effects of hydrostatic pressure on the heavy rare earths have been calculated²⁴ and are in agreement with the experimental results. Perhaps the simplest experimental confirmation of the theory will result from consideration of the magnetic ordering temperatures which are related to the height of the generalized susceptibility peak.

From the viewpoint of experimental simplicity, the best experiments for investigation of magnetic properties are magnetic susceptibility measurements which yield the magnetic ordering temperatures. Thus, we must consider the role of $\chi(\vec{q})$ in the ordering process. A simple mean field theory^{6,10} shows that the paramagnetic Curie temperature, θ_p , is related to the $\vec{q} = 0$ value of $\mathcal{J}(\vec{q})$ and that the initial ordering temper-

ature, T_i , is related to $\mathcal{J}(\vec{Q})$ so that we may write:

$$k_B (\theta_p - T_i) = 2/3 G[\mathcal{J}(0) - \mathcal{J}(\vec{Q})] \quad (21)$$

or

$$\frac{\theta_p - T_i}{\theta_p} = [1 - \mathcal{J}(\vec{Q})/\mathcal{J}(0)].$$

For a pure metal the de Gennes factor, G , can be calculated for the trivalent rare earth ion through knowledge of Hund's rules. Equation 21 allows us to perform a test of the calculations of $\chi(q)$ since the value of $\mathcal{J}(\vec{Q})/\mathcal{J}(0)$ can be calculated and compared with the experimentally obtained ordering temperatures. Evenson and Liu¹⁰ examined Equation 21 relative to the pure heavy rare earths and conclude that the calculations are consistent with experiment when only minor adjustments of I in Equation 18 are made. Thus, it seems clear that calculations of $\chi(\vec{q})$ can be tested through consideration of the initial ordering temperatures of the pure elements.

Another possible test of the calculations of $\mathcal{J}(\vec{q})$ would be through the ordering temperatures of alloys of two rare earths. In this case we have $G = xG_a + (1-x)G_b$ where x is the concentration of constituent a in the alloy and G_a is the de Gennes factor for constituent a . The role of G in the properties of intra-rare earth alloys has been explored by Bozorth.²⁵ In that work it was found that the main features of the ordering properties of the alloys is determined by G but that since the detailed properties are not so simple, consideration of the interaction strength for the alloys probably is critical.

In the heavy rare earths, ferromagnetic ordering invariably follows the periodic (helical) ordering. Thus, it would be useful if theoretical calculations could explain the second ordering temperature ordinarily encountered, the ferromagnetic ordering temperature T_c . If the free energy of the metal were completely dominated by the exchange energy which is determined by $\chi(\vec{q})$, then the helical structure would be stable at all temperatures. Since the ferromagnetic structure does occur we must ask, what is the mechanism that stabilizes the ferromagnetic structure? There can be several competing processes: first, the $\chi(\vec{q})$ function is generally calculated in the paramagnetic phase which means that it could change drastically in the ordered state, secondly, $\chi(\vec{q})$ does have a temperature dependence that could possibly favor ferromagnetism, finally, there are all the orbital energy contributions given in the Hamiltonian of Section B which could have important temperature effects. Evenson and Liu¹⁰ have examined the problem and conclude that ferromagnetic ordering is driven by magneto-elastic forces in the crystal. Qualitatively this process can be described as mechanical strains developed between adjacent atomic planes by magnetic forces between the non-parallel magnetic moments on the planes. As the material is cooled in the anti-ferromagnetic state, the overall magnetization of the material rises which means that the elastic energy increases very quickly such that at a sufficiently low temperature the exchange energy is overridden and ferromagnetic ordering is the result.

Prediction of the ferromagnetic ordering temperature is difficult because it will be a function of the magnetization, the elastic proper-

ties and of the exchange energy of the system. Assuming that all other forces are unimportant, ferromagnetic ordering will result when the magneto-elastic energy is equal to the tendency of exchange to favor the periodic alignment. The simplest approach to the problem is to assume that the magneto-elastic energy is proportional to some power of the magnetization and to elastic properties of the material as was done by Cooper.¹⁷ If we assume that the elastic properties of the material can be described by an "average" elastic constant, c , we have a magneto-elastic energy proportional to $c M^\beta$. At the ferromagnetic ordering temperature this elastic energy is equal to the part of the exchange energy that favors the periodic ordering structure, $\delta\mathcal{J} = \mathcal{J}(\vec{Q}) - \mathcal{J}(0)$. The exchange energy fraction that favors the periodic structure is then $G\delta\mathcal{J}$ so that when ferromagnetic ordering occurs we have the equation:

$$G\delta\mathcal{J} = A c M^\beta.$$

If we then assume that the magnetization can be written as

$$M = M_0 (1 - T/T_N)^\alpha$$

in the anti-ferromagnetic state, we can then solve the equations for the ferromagnetic ordering temperature, T_C . The solution is

$$T_N - T_C = T_N \left[\frac{G\delta\mathcal{J}}{Ac} \frac{1}{M_0^\beta} \right]^{1/\alpha\beta}.$$

This equation can be utilized to solve for $T_N - T_C$ since many of the parameters are experimentally determined. A more useful formulation is

that for an alloy with one magnetic component. In this case $G = xG_a$ and $M_o = xM_a$ such that the equation for T_c is

$$T_N - T_c = K \frac{(x^{1+1/\alpha\beta})}{(x^{1/\alpha})_c^{1/\alpha\beta}} J(Q) \delta J^{1/\alpha\beta} = \Delta T$$

where x is the concentration of the magnetic constituent. Cooper has argued through dimensional analysis¹⁷ that $\beta \approx 4-6$. Magnetic experiments on several Tb alloys performed for this study show that in the anti-ferromagnetic region $\alpha \approx 1/4$ such that for a single magnetic component alloy we have

$$\Delta T \approx \frac{J(Q)}{x^2} \frac{\delta J}{c^{2/3}} K \quad (22)$$

From this extreme set of assumptions we reach the conclusion that the region of stability of the helical structure is determined by the generalized susceptibility peak height and by the "average" elastic property of the material. It is reasonable that ΔT should be proportional to δJ and inversely proportional to c but it is surprising that the factor x^{-2} has been introduced. The factor x^{-2} arises because magneto-elastic forces decrease very rapidly as the net magnetic character of the material decreases. The surprising ramification of this formulation is that the region of helical structure stability should diverge as x becomes zero. This effect is observed to hold in certain rare earth alloys and therefore may be a valid result although because of the simple assumptions leading to Equation 22, the result should be viewed with caution.

The really important conclusion of Equation 22 is that the ferromagnetic ordering temperature can be calculated through a knowledge of the generalized susceptibility.

It is clear that a knowledge of the generalized susceptibility calculations will allow us to make specific predictions about the magnetic ordering properties of the heavy rare earths. A general conclusion of the work of Evenson and Liu¹⁰ will be useful here: that the extent of Fermi surface "nesting" will increase when the Fermi energy is lowered. In order to test this conclusion, calculations of the generalized susceptibility were performed as a function of Fermi energy for Tb. The calculations were based on a rigid band hypothesis with Tb energy bands supplied by Liu.²¹ Generalized susceptibilities were calculated from Fermi surfaces generated with the Fermi energy raised and lowered by 0.02 Ryd. The results are shown in Figure 4 along with a pure Tb calculation where the pure Tb result is useful in testing the validity of the coarse mesh utilized in the calculation. These results show that lowering of the Fermi energy enhances the generalized susceptibility peak while raising the Fermi energy destroys the peak very quickly.

Experiments that move the Fermi energy would be expected to have important effects upon the magnetic properties of a rare earth. One way of moving the Fermi energy would be through alloying of a rare earth with a material of a different valency. If the additional material is chosen to be non-magnetic, the effects of alloying could be simple movement of the Fermi energy in the bands of the host. The assumption that the Fermi energy could be shifted through a change in electron con-

Figure 4. Generalized susceptibility of terbium calculated when the Fermi energy is 0.51 Ryd and when the Fermi energy is shifted up and down by 0.02 Ryd.

centration without any important changes in the bands of the host is called the rigid band assumption. Beeby²⁶ has discussed the validity of the rigid band model and finds that the model will hold when the energy levels of the constituents interact to form a common band. Stern²⁷ has discussed alloy formation in the rigid band model and finds that the model is valid only if: (a) the excess charge of the solute becomes localized around it; (b) the conduction electrons have long mean free paths; (c) the states of the pure metal near the Fermi energy are in a single band. In the case of Tb alloyed with other transition metals the rigid band criteria are assumed valid since the dominant density of states contributions are from a single d-band in all of the transition metals. Even though a rigid band shift of Fermi energy appears to be a valid viewpoint here, there may be other effects of alloying such as crystal field effects as discussed by Lindgård.²⁸ The bands in the rare earths are sensitive to change in the details of the lattice dimensions such that modifications of the host lattice by the alloying process can be important. The process of host lattice modification through alloying will be called a size effect. The size effect can be a combination of factors that are sensitive to details of the lattice such as the crystalline symmetry through the c/a ratio, the electronic concentration, wavefunction overlap and crystalline electric fields. The size effect can be important especially when the atomic dimensions of the alloy constituents are widely different. The review of intra-rare earth alloys

given by Bozorth²⁵ shows that the size effects from different diluents can have an important effect upon the magnetic properties of alloys.

The experiments performed in this study were an attempt to test the effects of Fermi energy shifts upon the magnetic properties of the rare earths. The specific prediction provided by the theory is that lowering the Fermi energy will enhance the generalized susceptibility peak and raising the Fermi energy will diminish the generalized susceptibility peak. The specific plan is to alloy the trivalent rare earth with divalent and tetravalent diluents to lower and raise the Fermi energy and examine the effects of this alloying upon the ordering properties. As long as rigid band ideas hold, lowering of the Fermi energy should enhance the peak in $\chi(\vec{q})$ and through Equations 21 and 22 we see that the ordering temperatures should be such that the helical magnetic structure will become more dominant. Likewise raising the Fermi energy should make the ferromagnetic structure more dominant. Any deviations away from these predictions probably signal the breakdown of the simple rigid band ideas or the onset of complicated effects such as the crystal field effects discussed by Lindgard.²⁸

III. EXPERIMENTAL PROCEDURE

A. General Description

The experiments performed for this study require accurate determinations of magnetic properties, especially magnetic ordering temperatures, for a set of rare earth alloys. To perform these measurements a magnetometer was designed and built. Accompanying the magnetometer and its dewar system, a device for electrical resistivity measurements was built and used.

Design and construction of a device for magnetic measurements must proceed with careful attention to certain basic requirements: (a) ideally the measurement method should permit simple and rapid sample mounting and change, (b) the measuring technique should be of the required accuracy while having the necessary range of sensitivities to be compatible with the materials to be measured, (c) the sample geometry should be simple and its size should be small enough to be compatible with availability of rare materials, (d) it is advantageous to allow for extreme variation in sample temperature (say 300 to 2 K) while maintaining good sample temperature control, (e) large variations in external field should be available, (f) for single crystal work there should be provisions for simple and accurate sample rotation and finally, (g) it is valuable to have the sample in a stationary external field in order to avoid the complications of sample dynamics in a variable field.

The list of design features is quite varied and in general difficult to realize in one machine. For a magnetometer designed to work with rare earths, the sensitivity does not have to be great since the rare

earths are generally highly magnetic. Even though high sensitivity is not necessary, a wide range of detection sensitivities is advantageous since even in the rare earths magnetization values varying by 10^6 can be encountered. Virtually all of the design features can be met by the vibrating sample magnetometer (VSM). This particular device utilizes the principle of magnetic induction to produce an electrical signal proportional to the sample magnetization. The sample is placed in a uniform external field and is then vibrated in the vicinity of a coil. The time varying position of the sample produces a time dependent field at the coil and therefore an alternating voltage is induced at the coil output that is directly proportional to the sample magnetization. The particular device that was built is of the Foner type²⁹ the overall design of which is shown in Figure 5. The Foner type of VSM is characterized by sample motion that is perpendicular to the external field and a pick-up coil axis that is parallel to the field. A Foner VSM operates at audio frequencies such that ordinary electro-mechanical devices can be used to produce the vibrations. Also, the Foner magnetometer utilizes a reference generator that is coupled to the sample vibrator and produces a signal through vibration of a coil near a permanent magnet. When the sample and a variable fraction of the reference signal are added together 180° out-of-phase, a null condition can be produced that is very reproducible and the fraction of the reference signal required to produce the null is a measure of the sample magnetization. This particular design tends to eliminate instabilities in the amplitude and phase of the vibrations. The Foner VSM has the disadvantage

Figure 5. The major components of the vibrating sample magnetometer.

of being a relative measurement and therefore must be calibrated relative to a known sample. If the machine is built with proper attention to details, accuracy of about 0.2% can be achieved with sensitivity of about 10^{-5} emu.

B. Magnet and Hall Probe

At the heart of any high field magnetometer is the magnet, its power supply and the field determination equipment. In this work a Weiss type of magnet system was utilized which has a field of up to 30.5 kOe. The magnet is a Harvey-Wells Corp. Model L-158 electromagnet with a low carbon iron core. The pole pieces have a 3 inch diameter at the gap with the gap being 1.568 inches wide. The magnet produces from about 80 to 30,500 Oe with a field homogeneity of about 1 part in 10^5 . The power supply is a Harvey-Wells Corp. Model HS-10200 power supply that provides 16 kW of power at 220 amperes that is stable to about 1 part in 10^4 .

Determination of the field strength is provided by a calibrated Hall probe incorporated into the sample coil package. The Hall probe is an F. W. Bell Inc. Model BH-701 Hall element having 1% linearity to 30 kOe and a temperature coefficient of $0.04\%/^{\circ}\text{C}$. This Hall probe was calibrated using a Rawson fluxmeter which had been calibrated relative to an NMR apparatus. By calibrating the Hall probe at many field values and by performing a least squares fit to the calibration points, it is believed that the fields are determined within 1% accuracy. The current was provided by a constant current supply and is 130.00 ± 0.01 mA. Voltages

generated by the probe are measured by a potentiometer. Calibration of the Hall probe yielded a Hall coefficient for this device of 10.205 mV/kOe.

C. Electronics

The most important piece of equipment in the electronics of a VSM is the vibrator-reference generator and the sample coils. For this work a vibrator-reference generator unit was incorporated into a single vacuum tight unit according to a design of Miller.³⁰ The vibrator is an ordinary speaker manufactured by University Speakers Inc. which is capable of dissipating 30 W. Attached to the speaker coil is an aluminum rod which passes through the center of the driver magnet and which is attached to the sample and to the reference generator. The reference generator is a Ling Electronics Model V47/3 vibration generator. The vibrator is capable of producing vibration amplitudes in excess of 1 mm which are apparently quite stable with no noticeable heat produced in the speaker coil. Reference voltages of about 0.3 V are produced by the reference generator which apparently follow the phase and amplitude of the vibrator successfully. Extending from the bottom of the vibrator-reference assembly is a brass rod to which the sample holder is connected by means of a threaded connection.

The coil package used in this magnetometer as the sample pick-up coil consists of four multi-turn coils. Each coil is in the shape of a disk 0.28" thick by 1.02" in diameter with 850 turns of #30 copper wire. The coils were wound on a nylon coil form with a 1/8" center axle. Each layer of the coil was painted with GE 7031 electrical varnish and after

removal from the coil form, the entire coil was given an additional coating of the varnish. This technique produced durable coils of easily reproducible parameters. Four matched coils were chosen with equal external dimensions and with matched electrical properties of about 14.0 ohms and about 4.67 mH of inductance. The four matched coils were placed into holes machined into a plexiglass block such that the axis of each coil is parallel to the field. The coil package is designed such that there are two coils on either side of the sample with one coil on each side above and below the sample. A hole of 0.90" diameter passes through the coil package perpendicular to the coil axes and the coils are mounted as near to the hole as is practical. Each pair of coils on either side of the sample are mounted with their centers 1.035" apart so that their outer edges are in contact. Thus, the coils are positioned as near to the sample location as is possible so that maximum sensitivity can be achieved.

When viewed from one of the magnet pole pieces, on one side of the sample the coils are counter-clockwise wound and on the opposite side of the sample the coils are clockwise wound. On a single side of the sample the coils are wired in series opposition and the opposite sides are wired in series. This particular wiring pattern serves to maximize the induced voltage produced by the sample motion but cancels the effects of fluctuations in the external field. The latter design feature is important since 0.1% variations in the external field at 30 kOe can produce voltage fluctuations in the coils of several volts which must be eliminated if the magnetometer is to possess the necessary sensitivity.

Also, cancellation of the field variations in this way has the additional advantage of tending to eliminate stray pickup from distant sources. Finally, the entire coil package is mounted in a copper box to avoid noise pickup.

The sample voltage is measured in this magnetometer through an ac technique. As the sample is vibrated in the vicinity of the sample coil package, an induced voltage is produced which has the same frequency as the sample vibration frequency. The signal from the sample coil is proportional to the sample magnetization and therefore is the quantity to be measured. In this particular device, a null is produced by adding a determined fraction of the reference voltage to the sample voltage after a 180° phase difference is produced. This procedure requires: (a) a device for producing the required 180° phase change with allowance for some continuous phase adjustment, (b) a reproducible way to obtain a fraction of the reference signal where the fraction is accurately determined and (c) a device to act as a sensitive ac null detector.

The requirement for a continuous phase adjustment is due to possible loss mechanism in the coils and nearby magnetic materials and by phase shifts in the interconnections all of which are not necessarily constants. There are various ways to produce a variable phase but in this application the phase adjustment must not affect the signal amplitude. The final design utilizes an active phase shift using an RC circuit to produce a variable phase in the reference voltage. In this case the resistor and capacitor are in parallel and the resistor is the variable element. An RC circuit will produce a phase shift but will be amplitude constant only

if the RC network is not under load. Thus, a phase shift device was built in which the input and output to the RC circuit have very high impedance. The circuit for the phase shifter is shown in Figure 6. Tests of the phase shifter indicate that it will produce a phase shift of about 10° when the variable resistor is changed from 0 to 120 k Ω and the output over the angular range is constant in amplitude to about 0.1%.

Obtaining a fraction of the reference voltage to be added to the sample voltage can be accomplished by any sort of repeatable voltage dividing process. In this particular application it was found simplest to use a variable transformer which produces the needed voltage division without introduction of unnecessary phase shifts. In this particular case a Gertsch ratio transformer Model 1011 was used to obtain the signal division. The ratio transformer is a useful device for this application because it provides an output that is a known fraction of the incoming signal without a change in phase. In addition, the ratio transformer allows for as little as 10^{-7} of the incoming signal to be placed on the output and where the indicated output is very linear.

Recent developments in ac electronics have produced the dual phase lock-in detector which is very useful for magnetic measurements. The lock-in is essentially a narrow band detector which has the ability to detect those signals that are phase related to a reference voltage. In this particular case a dual phase lock-in was used which has the capability to detect ac voltages that are both in-phase and 90° out-of-phase with respect to a reference. Also, the detection sensitivity of the lock-in is very good (about 0.01 μ V). Thus, the dual phase lock-in amplifier

Figure 6. The circuit diagram of the phase shifter.

is ideal for this magnetometer because it is a sensitive null detector which, because of the phase sensitivity, can be used to check and maintain a true null condition both with respect to amplitude and phase. The particular lock-in detector used in this apparatus was designed by W. Rhinehart of the Ames Laboratory and was built by Ames Laboratory personnel. This device operates at 108.2 Hz because this is an easily reproduced audio frequency and because there are no ordinary harmonics from local power sources in that frequency range.

The final important element in the magnetometer electronics is the local oscillator. The oscillator must provide a signal at 108.2 Hz with very good amplitude and frequency stability with a power output of about 10 W. In this particular case an Optimization Inc. Model AC-15 oscillator was used. The oscillator was in all respects completely satisfactory without modification.

The final circuit for the electronics is shown as Figure 7. All interconnections between the various pieces of equipment were made with shielded coaxial cable. All the pieces of equipment were rack mounted and were electrically isolated from the rack. Grounding was accomplished by tying everything to a common ground.

D. Temperature Control and Measurement

One difficulty of any VSM system is the problem of sample temperature control. Since the sample must be free to move, there can be no rigid contact with the sample except through the drive rod and therefore high quality temperature control is very difficult to achieve. In this case,

Figure 7. The complete circuit diagram for the vibrating sample magnetometer.

the sample chamber is copper and is flooded with helium gas. Therefore, the sample finds itself connected by the exchange gas with an isothermal chamber and will eventually come to equilibrium with the chamber. In this case the sample is cooled by allowing cold vapor from the liquid helium storage area to pass across a temperature controlled copper block and then across the sample. The dewar system was built for this application by Janis Research Co. The dewar is not liquid nitrogen shielded but rather depends on a vapor cooled radiation shield and many layers of "super insulation" in the vacuum wall to provide for effective helium storage. Unfortunately, there is not a good way to provide for liquid nitrogen pre-cooling of the dewar so that the initial transfer into the dewar is somewhat inefficient. When full the dewar holds 1.8 liters of liquid that allows for about 5 hours of experiment time at 4.5 K. The overall design of the dewar system is shown in Figure 5.

Temperature control in this system is provided by careful metering of the quantity of liquid being allowed into the sample chamber and by temperature controlling of a copper heat exchanger. The temperature controller is a PAR Model 152 cryogenic temperature controller using a GaAs diode as the sensing element. In zero field, temperature control is good to about ± 0.01 K below 20 K. There are two primary difficulties encountered in this system: first, the GaAs diode has a sizeable field dependence above about 10 kOe and second, the temperature at which the diode is controlling does not necessarily correspond to the sample temperature. The latter problem arises because as the helium gas flows into the sample chamber and across the sample it may not be in good

equilibrium with the copper heat exchanger. Thus, depending on the gas flow rate, the sample temperature can vary considerably from the temperature of the heat exchanger. In order to overcome the difficulties related to gas flow rate and sample temperature, the temperature of the sample must be measured by an independent device in intimate contact with the sample.

The solution of the temperature control problems depends upon installation of a temperature measuring device directly to the sample holder. A useful feature of the independent measuring device is that a field independent device can be installed to circumvent the field dependence of the controller element. In this work a calibrated thermocouple was used as the temperature measuring device. A thermocouple is useful because it can be made small enough that when fastened to the sample holder it will not interfere with the magnetic measurement. Experience has shown that the field dependence of thermocouple output is very small so that a thermocouple is sufficient for this work. In the high temperature range (40 K to 300 K) a copper versus constantan thermocouple was used and in the low temperature range a gold-0.03% iron versus copper thermocouple was used. The voltage output of the thermocouples was measured by a Leeds and Northrup K-3 potentiometer so that relative temperatures of about 0.01 K could be detected. Calibration of the thermocouples was performed at four fixed temperatures (room temperature, the ice point, 77 K and 4.2 K) and it is believed that the accuracy of these thermocouples was better than 0.5 K. The thermocouple wires were fastened

to the sample drive rod and passed through a vacuum seal at the top of the dewar see Figure 5. The details of the thermocouple position relative to the sample position are shown in Figure 8.

E. Calibration

The vibrating sample magnetometer measures magnetization relative to the output of a reference generator and is therefore an indirect measurement. In order that the measurements can be converted into an absolute value, the magnetometer must be calibrated relative to some known material. Once the machine is calibrated with a known material, the value of magnetization for any other material is determined as a ratio of the unknown magnetization to that of the standard. In order for the calibration scheme to be successful, the magnetometer must be insensitive to the small adjustments that are inadvertently made when samples are changed. The problem of calibration stability arises from several factors: (a) the sample position within the pickup coils must be repeatable, (b) the vibrational stability must be insensitive to sample changes, (c) there must be no extraneous vibrating parts that are sensitive to change and (d) the vibrational amplitude must be sufficiently high that the signal to noise ratio is high enough that the measured signal is indeed determined by the magnetization of the sample. The final consideration that is independent of the magnetometer is the problem of the proper choice of reference materials to be used in calibration.

An ideal sample coil design would be insensitive to sample position so that repeatability of the sample location would be unimportant. Unfortunately, the sample coils used in this device have a sharp peak

Figure 8. The sample holder and drive rod assembly for the vibrating sample magnetometer.

in their response as a function of position at the center of the coils. It is therefore essential that the sample position be repeatable to within 0.2 mm. The necessary position repeatability is accomplished by making sure that the sample holder fits fairly snugly inside the dewar so that no lateral motion is possible. Vertical positioning of the sample is accomplished by a motor driven screw arrangement that can move the entire vibrator-reference assembly. This assembly has a reproducibility of better than 0.1 mm when the sample is changed. The initial positioning of the sample is accomplished by moving the entire assembly vertically until the sample signal is maximized. As long as all moving parts are built with minimum play, the sample position is sufficiently reproducible. The primary difficulty with vertical position is related to the difficulty of maintaining a constant position when the sample drive rod temperature changes by 300 K. In this system the sample drive rod was made from vitreous quartz that has a negligible thermal contraction so that the sample position requires no adjustment.

A useful magnetometer has an apparent sample signal that is independent of vibration amplitude and all other extraneous factors. The Foner type VSM is amplitude independent because of the reference generator as long as the amplitude of vibration is sufficiently large and the reference generator and sample are vibrating synchronously. In general, the condition of amplitude independence is sufficiently met as long as the vibration amplitude is greater than about 0.5 mm. Therefore, the vibration amplitude of this instrument is set to about 1 mm. Vibrations in all the components of the magnetometer will be synchronous so long as

the amplitude is not changing too rapidly and as long as the vibration linkage is sufficiently mechanically rigid. The vibration stability is good enough so long as the vibrator is a high quality speaker capable of the necessary power dissipation. This magnetometer has several connection in the vibration linkage that have a tendency to become loose and spoil the stability. This latter problem is circumvented by properly tightening all parts and painting them with a layer of varnish.

The stability of the VSM can be spoiled by extraneous vibrations. For example, the sample drive rod is a thin quartz rod which can resonate with the vibration frequency to produce an unwanted sample motion. Another problem related to the sample holder concerns the thermocouple wires that pass out of the dewar through a vacuum seal. The thermocouple wires are sufficiently stiff that they produce a damping that is not repeatable and will destroy the magnetometer accuracy. This problem is minimized by wrapping the wires loosely around the top of the drive rod before passing them out through the seal. By thus effectively increasing the free length of the wires, the damping problem is sufficiently small that the reference generator and sample can vibrate synchronously. A subtle problem is encountered with respect to unwanted vibration of the dewar. This problem arises because the dewar is coupled to the vibrator head through the vacuum seal. Since the vibrator head is itself vibrating out-of-phase with respect to the sample because of reaction forces, the dewar is made to vibrate out-of-phase with respect to the sample. Since the dewar is very massive relative to the sample, the dewar vibrations can give rise to large extraneous signals. The

problem was fixed by anchoring the dewar securely to the magnet, by increasing the mass of the vibrator assembly and by anchoring the dewar tailpiece rigidly to the sample coil package.

After all of the stability problems have been solved one can proceed with calibration of the magnetometer. Calibration of a VSM can be performed in two principal ways: determination of the permeability of a standard high permeability material or through the saturation magnetization of a known sample. In general the saturation magnetization method is used because it is very simple to perform and it is insensitive to small errors in temperature and field determination. The usual reference materials are high purity iron or nickel. The chosen standard is subjected to a high external field at a fixed temperature and the signal is measured using the electronics previously described. The quantity that is actually obtained is a ratio transformer dial reading, DR_{sat} , corresponding to the saturation magnetization of the material. The system calibration is then

$$K = \frac{\sigma_{sat}(T, H=\infty) m}{DR_{sat}}$$

where K is the magnetometer calibration, $\sigma_{sat}(T, H=\infty)$ is the previously determined saturation moment at T of the standard sample, m is the mass of the standard and DR_{sat} is the dial reading obtained when the standard sample is saturated. To obtain the magnetization of an unknown sample in absolute units a value of the ratio transformer dial reading, DR' , is obtained and the magnetization is then

$$\sigma' = \frac{DR' \cdot K}{m'}$$

where m' is the mass of the unknown sample. An equivalent and more revealing version of the equation can be written as

$$\sigma' = \frac{DR' \cdot \sigma_{\text{sat}} \cdot m}{DR_{\text{sat}} \cdot m'}$$

It is obvious from this last equation that the magnetization of any unknown sample is determined as the ratio of the unknown sample signal to the signal from the standard sample. Thus, the results of any measurement are no more accurate than the calibration of the magnetometer.

Accuracy of the magnetometer calibration can be assumed to be good if calibration is performed prior to each experiment. It is not simple to know that the standard sample is of high quality so that the published values of magnetization can be assumed to hold for the standard sample. The choice of standards is not trivial since there can be differences of say 0.5% in different samples of iron from one supplier to another even though all of the materials are advertised as 99.999% pure samples. It is apparent that if the materials were indeed 5N pure there would be no difficulty in obtaining accuracies of 0.1%. To search for a good standard it seems best to start with Ni and search for the best sample by recognizing that the principal impurity will be Fe so that the best Ni sample will have the lowest moment. By a similar argument one searches for the Fe sample with the highest apparent magnetization. Through this pro-

cedure, Fe and Ni standards were obtained that agreed with each other within 0.1%. It is not clear why high purity starting materials could exhibit large differences in magnetization except that presumably the purities are habitually overstated by the manufacturers and the materials could be poorly annealed. The primary standard used in this work was a high purity nickel sample that was multiple zone refined. This standard had a resistivity ratio $R_{290}/R_{4.2}$ of 90. The saturation magnetization of this standard was assumed to have a low temperature value of 58.57 emu/gram as was determined for high purity nickel using an absolute determination.³¹

The final difficulty encountered with respect to calibration of a magnetometer is the "image pole" effect encountered at high fields. If one examines the magnetization of nickel at fields in excess of 15 kOe, one should obtain a smooth curve which is essentially field independent. In this magnetometer the apparent magnetization of nickel is observed to drop considerably in the vicinity of 23 kOe. It is thought that this effect has its origins in "image poles" similar to those encountered in electrostatics. In this case, the sample is in the vicinity of the magnet pole pieces such that a magnetic boundary problem exists. The solution of the boundary problem can be accomplished by introduction of image poles, which replace the boundary, that are located inside the pole pieces and are oriented so that the image poles are parallel to the sample orientation. Since the image poles oscillate along with the sample, with a possible phase factor, the sample signal from the magnetometer is enhanced considerably. It is simple to show that the apparent magnetization of the

"image poles" is proportional to the sample magnetization by the relation

$$M_{\text{image}} = M_{\text{sample}} \left[\frac{1-\mu}{1+\mu} \right]$$

where μ is the permeability of the magnet pole pieces. The observed sample magnetization is then given by

$$DR_{\text{obs}} = \frac{M_{\text{sample}}}{K} \left[1 - A \left(\frac{1-\mu}{1+\mu} \right) \right]$$

where A is a constant related to the coupling of the image poles to the sample coils. At low fields where μ is very large (≈ 5000) the observed sample signal is enhanced considerably. At high fields where μ approaches 1, the observed sample signal returns to the true sample signal. Therefore, the image poles disappear as the magnet saturates and so the apparent sample signal decreases significantly in the vicinity of 23 kOe where these particular pole pieces saturate.

It is fortunate that the image poles are proportional to the sample magnetization and that their effect on the observed signal is repeatable so that there is hope of correcting for them. In practice it is assumed that up to 15 kOe the apparent sample magnetization is independent of the image pole problem and that corrections only need to be made at higher fields. At higher fields multiplicative factors are determined that when applied to the observed dial reading will return the signal to the correct level. These correction values are obtained by assuming that the high field magnetization of nickel is a function of $1/H$ and is effectively a constant. The multiplicative correction factors are determined by

finding the ratio of the expected high field dial reading to the observed dial reading. This correction process is thought to be valid since it has a theoretical basis and because it is observed to work well for iron, gadolinium, nickel and a wide variety of ferromagnetic and paramagnetic materials. The image corrections vary from 1.0002 at 17 kOe up to 1.1043 at 30.1 kOe and are shown in Figure 9.

F. Resistivity Measurements

In this investigation the electrical resistivity of each sample was obtained as a function of temperature from 4.2 to 300 K. For this work an apparatus was constructed which uses the standard four probe dc technique. In this technique one passes a dc current through the sample and determines the voltage drop across the sample. Then the resistivity of the sample is

$$\rho = (V/I) (A/l)$$

where V and I are the sample voltage drop and current respectively and where A/l is the ratio of the sample cross-sectional area to the distance between the voltage probes. It is customary to measure V in microvolts, I in amperes and the sample geometrical factor A/l in centimeters such that the resistivity is given in units of $\mu\Omega\text{cm}$.

The sample current is provided by a constant current supply designed and built by Ames Laboratory personnel. The current supply will provide currents from 10 to 150 mA and is stable to 1 part in 10^5 . In all cases the sample current was 100 mA or less. Voltage drop across the sample was

Figure 9. The "image pole" corrections as a function of field. CORR is a multiplicative constant that must be applied to the measured signal to correct for the "image pole" changes.

determined by a Guildline Instruments Ltd. Type 9180-B potentiometer using a Keithley Instruments Model 149 micro-milliammeter as the null detector. The voltage sensitivity of the measuring circuitry is 10^{-8} volts so that resistivities of about $10^{-3} \mu\Omega\text{cm}$ can be resolved with an estimated accuracy of 0.1%.

Accuracy of a resistivity measurement is generally limited by determination of the sample geometrical factor. In this particular experiment the voltage contacts which determine the factor l are fixed as seen in Figure 10. The fixed voltage contacts offer the advantage that the separation can be measured at one time and then is the same for all samples. The separation of the voltage contacts was determined by averaging some twenty measurements of the separation made using a travelling microscope. Fixed voltage contacts also offer the advantage that the leads are not soldered or welded to the sample, which in the rare earths is generally a difficult process. The cross-sectional area of each sample was determined by direct measurement with a micrometer. For convenience the samples were made with a square cross-section of about 1 mm on a side. The sample areas are determined by measuring each of the directions of the square cross-section ten times. By making multiple measurements it is felt that the sample area to length ratios are determined with an accuracy of better than 0.5%.

G. Sample Preparation

The alloys used in this work were prepared by B. J. Beaudry of the Materials Science and Engineering section of the Ames Laboratory USERDA.

Figure 10. The sample holder used for the resistivity measurements.

In all cases the desired alloys were prepared by the melting together of carefully weighed amounts of the high purity constituents. The terbium plus thorium alloys were prepared by arc melting the constituents together over a copper hearth. All other alloys were melted together inside inert gas filled tantalum crucibles by heating the crucibles to the melting point of the constituents inside an induction furnace. The freshly melted alloys were annealed for three days at a temperature near to but below the melting point of the alloy inside the tantalum crucibles. Following annealment the crucibles were cold water quenched to retain a single phase. In all cases the materials were removed from the crucibles by machining away the tantalum and then were polished and stored under vacuum until they were needed.

After the tantalum was machined away, ingots about 10 mm in diameter by about 30 mm long resulted. These ingots were then electro-polished and examined for single crystals by x-rays and visually. Single crystal samples were found only in the terbium plus thorium alloys and single crystal magnetization samples of these were prepared. In all other cases (including all of the resistivity samples) the alloys were polycrystalline. The samples were cut from the ingots with a jeweler's saw into wires about 1.5 x 1.5 x 30 mm. These rough sawn samples were then hand lapped to the final dimensions over sandpaper. In each case a magnetization sample of dimension 1 x 1 x 5 mm and a resistivity sample with dimensions 1 x 1 x 20 mm was prepared. Pieces of the remaining ingots were characterized by x-ray analysis and photomicroscopy under the supervision of B. J. Beaudry. The x-ray analysis yielded the lattice parameters of

the materials. The photomicroscopy analysis was useful in searching for possible second phase and for determination of grain size.

In general, sample purity is an important consideration in any work of this nature. Alloy studies are a bit less restrictive since impurities are generally unimportant when fairly large concentrations of a diluent are introduced into the host. Nevertheless, high purity starting materials were utilized in all of the alloys. The rare earth starting materials typically had other rare earth impurities of about 50 a/ppm, transition metals of about 100 a/ppm and non-metallic impurities of about 1000 a/ppm. The thorium impurities were about 150 a/ppm of transition metals and about 120 a/ppm of non-metallics. The starting magnesium had impurities of about 50 a/ppm transition metals and about 1200 a/ppm of non-metallics.

IV. RESULTS

A. Pure Terbium and Trivalent Diluents

Prior to undertaking alloy studies, the properties of the base material bear investigation. The magnetic and transport properties of terbium were studied previously by Hegland et al.³² A sample of the terbium used as the starting material for this investigation was obtained and the magnetic properties studied. The most important information obtained from the magnetic data are the ordering temperatures. Ordering temperatures are obtained by finding the magnetization as a function of temperature in a fixed external field. At high temperatures the rare earths are Curie-Weiss paramagnets which have a temperature dependence of the form $1/(T-\theta)$. As one cools the Tb, the magnetization passes through a sharp peak. The sharp maximum represents anti-ferromagnetic ordering, which in the case of Tb is the helical structure, and the temperature at which it occurs is called the Néel temperature, T_N . Further cooling of the sample brings on ferromagnetic ordering that is characterized by a large increase in magnetization. The temperature at which the ferromagnetic ordering occurs is called the Curie temperature, T_C . Below T_C , the magnetization of the material is relatively constant down to low temperatures.

The ordering temperatures are in principle simple to obtain from the magnetization data using the properties as outlined. There are certain details that must be considered if the ordering temperatures are to be correctly determined. One of the most important considerations is the choice of external field. Some external field must be applied in order

that the material will have a preferred axis along which to order and so that domain effects can be overcome. A too large external field will tend to "smear out" the ordering effects because Tb will become simple ferromagnetic in fairly small fields. The magnetization peak associated with T_N in Tb is no longer observed in fields of about 1000 Oe. Therefore, in order to have a sufficiently large signal in the alloys and to insure that the helical structure will be properly observed, an external field of 100 Oe was used in all cases. The final detail that requires attention is the actual determination of the ordering temperatures. T_N is simple to obtain since the peak in magnetization is a readily observed feature and it is only about 1 K wide so that T_N is safely chosen to be the temperature at which the maximum occurs. Choosing the correct value of T_C is not so simple because the magnetization rises sharply over a temperature interval of perhaps 5 K. In a simple ferromagnet, T_C is generally associated with the location of the maximum slope in magnetization. In Tb the maximum in slope may not be a correct choice for T_C because immediately prior to ferromagnetic ordering, the turn angle of the helical structure can change rapidly and give rise to a false value for the maximum slope of the magnetization. Using resistivity and neutron diffraction data as a guide it seems that the correct value for T_C must be chosen differently. The magnetization in the vicinity of T_C rises linearly and then levels off sharply on the low temperature side of the transition. T_C is apparently properly chosen as the temperature at which the magnetization breaks away from the sharp linear rise. Because of the uncertainties in the procedure, the values of T_C are known to only about

± 2 K. The magnetization results obtained for pure Tb are shown in Figure 11. The ordering temperatures obtained from those data are

$$T_N = 229.5 \text{ K and } T_C = 221 \text{ K} .$$

These results compare favorably with those of Hegland et al.³² Ordering temperatures can also be obtained from the resistivity data and are indicated by sharp changes in slope at the critical temperatures. In fact, the sharp slope change in resistivity is generally a better indicator of T_C than is magnetization. Thus, T_C is best obtained from resistivity and T_N from magnetization. The resistivity results for the host material indicate that the resistivity ratio $R_{290}/R_{4.2} = 37$ and the room temperature resistivity agreed with that obtained by Hegland et al.³² Therefore, the resistivity of Tb was not examined in detail.

Because of the remarkable similarity of the rare earths, solid solution alloys of two rare earths can be made continuously over the entire composition range. This particular property of the rare earths is very useful for obtaining alloy information over a wide range of compositions. In general, an alloy of two rare earths has complicated properties because, even though both constituents will be trivalent and otherwise similar, the fact that both constituents are magnetic will produce complicated ordering effects. It is helpful when only one of the alloy components is magnetic for then the resulting magnetic properties are related only to the one magnetic constituent. Thus, the alloys which are most useful for understanding Tb alloy physics are the alloys of Tb with

Figure 11. The magnetization of pure terbium versus temperature in an applied field of 100 Oe.

Sc, Y, La and Lu. These alloys are solid solutions over the entire composition range and contain a trivalent non-magnetic diluent. The alloys of Tb with Lu were investigated by Bozorth²⁵ while the alloys of Tb with Sc, Y and La were investigated by Child and co-workers.³³⁻³⁵ The ordering properties of these alloys are considerably different from each other even though they are all trivalent non-magnetic diluents. The ordering temperatures for the Tb with Sc, Y, La and Lu alloys are shown in Figure 12. The most remarkable feature of Figure 12 is the fundamental difference between the properties of the La and Sc alloys. We see that La stabilizes the ferromagnetic structure while Sc is effective in stabilizing the helical structure. Apparently this difference is a result of a size difference between the various materials. This problem will be discussed further in Chapter V but it is immediately clear that an understanding of alloying will not be complete without a knowledge of the effects of constituent size.

The data for the alloys of Lu and La with Tb were not complete for Tb-rich alloys. Therefore, for completeness, two alloys each of La and Lu with Tb were prepared and studied for this work. The results of the magnetic measurements are shown in Figure 13 for the La alloys and Figure 14 for the Lu alloys. The ordering temperatures for those four alloys were determined and can be summarized as follow:

Alloy	T_N	T_C
Tb ₉₆ La ₄	209	206
Tb ₉₀ La ₁₀	-	189
Tb ₉₅ Lu ₅	218	190
Tb ₉₀ Lu ₁₀	204	151 .

Figure 12. The ordering temperatures as a function of alloy concentration for alloys of terbium with non-magnetic trivalent diluents. Open symbols represent the Néel temperatures and filled symbols represent the Curie temperatures.

Figure 13. The magnetization as a function of temperature for the terbium-lanthanum alloys in an external field of 100 Oe.

Figure 14. The magnetization as a function of temperature for the terbium-lutetium alloys in an external field of 100 Oe.

The electrical resistivity of each of these alloys was obtained as a function of temperature. The resistivity data for the La alloys are shown in Figure 15 and for the Lu alloys in Figure 16. These data are interesting because they illustrate what values of resistivity are typical of a non-magnetic diluent in Tb. One of the useful quantities that can be derived from the resistivity data is the spin resistivity, which is defined as the difference between the zero temperature extrapolation of the high temperature linear resistivity and the actual zero temperature resistivity. The spin resistivity is a measure of the strength of the interatomic coupling in the alloys. Another useful quantity is the residual resistivity, which is the zero temperature limit of the resistivity. The residual resistivity per diluent atom is a measure of the incompatibility of the alloy constituents. The experimental values of residual and spin resistivity are ($\mu\Omega\text{cm}$)

Alloy	ρ_{res}	ρ_{spin}
Tb ₉₆ La ₄	23.5	77
Tb ₉₀ La ₁₀	45.7	52
Tb ₉₅ Lu ₅	13.3	78
Tb ₉₀ Lu ₁₀	24.6	71

These data show that the effect of atomic size can be important for resistivity since Lu and Tb are quite similar in size while La is much larger than Tb. Thus, it seems that because of the large size difference, La has an unusually large effect upon the conduction electron scattering process. The corresponding values of residual and spin resistivity for pure Tb are

Figure 15. The electrical resistivity as a function of temperature for the terbium-lanthanum alloys.

Figure 16. The electrical resistivity as a function of temperature for the terbium-lutetium alloys.

Pure Tb: $\rho_{\text{res}} = 3.1$ and $\rho_{\text{spin}} = 87 \mu\Omega\text{cm}$

where it should be noted that ρ_{res} is determined by purity.

B. Divalent Diluents

The theory presented in Chapter II tells us that addition of a divalent diluent to a trivalent rare earth host should be interesting with respect to the magnetic ordering properties. All alloy studies where the constituents have a different valency are made difficult by the unfortunate fact that an arbitrary choice of two elements will not likely form a solid solution alloy. The classical rules of alloying behavior were first laid down by Hume-Rothery³⁶ where it was shown that size, valency and electronegativity of the constituents are all important in deciding if the alloy can form. In particular, if the constituents are too different in size the local disorganization of the lattice will cause a loss of binding energy and will not favor solid solution formation. Electronegativity differences that are too great will result in such a strong tendency towards formation of an ionic compound that formation of the desired alloy is not favored. These two factors are combined in a diagram of atomic size and electronegativity of the elements called a Darken-Gurry plot.³⁷ Consideration of a Darken-Gurry plot constructed for the rare earths shows that there are few elements, which will form a solid solution with the rare earths, that are of a different valency.

On the basis of a Darken-Gurry plot there are only four divalent or monovalent materials that could alloy successfully with Tb: Mg, Yb, Ca and Li. The phase diagrams of Tb with Ca and Li are not known but

experiments performed in the course of this study show that the region of solid solubility of these materials is very small. The phase diagram of Gd with Mg³⁸ shows that the solubility of Mg in Gd is about 14 a/o so that the solubility of Mg in Tb is about 12 a/o. Similarly, the phase diagram of Gd with Yb³⁹ shows that the solubility of Yb in Tb should be about 17 a/o. Therefore, this study is limited to alloys with divalent Mg and Yb. In both cases, the size difference between the atomic sizes of the divalent atom and Tb is sufficiently great that single crystals of the alloys could not be obtained and therefore the quoted results are for polycrystalline samples.

Two alloys of Mg with Tb were prepared for this study and the results of the magnetic measurements are shown in Figure 17. The ordering temperatures obtained from the magnetic data are

Alloy	T_N	T_C
Tb ₉₄ Mg ₆	171	101
Tb ₈₈ Mg ₁₂	136	-

In the 12% Mg alloy no ferromagnetic ordering was observed down to 2 K. Thus, the addition of divalent Mg to Tb has been remarkably successful in enhancing the stability of the helical structure. The observed response of the ordering properties to lowering of the Tb Fermi energy is in accordance with the prediction of Chapter II where it was predicted that the generalized susceptibility would be enhanced by lowering of the Fermi energy.

Figure 17. The magnetization as a function of temperature for the terbium-magnesium alloys in an external field of 100 Oe.

The resistivity results for the Tb with Mg alloys are shown in Figure 18. These results are interesting because of the high residual resistivities encountered. The resistivity results yield ordering temperatures that agree with those obtained from magnetic measurements. Because of the very high residual resistivities, it is not possible to obtain what would seem to be meaningful values for the spin resistivities. The residual resistivities of 134 and 179 $\mu\Omega\text{cm}$ for the 6 and 12% alloys respectively are not understood but must be due to some unusual scattering mechanism such as formation of a resonant bound state or perhaps lattice strains. The unusually high residual resistivity values may correlate with the small size of the Mg atom with respect to Tb. It is certain that in these alloys one must be particularly cautious of alloying effects because of the short electron mean free paths indicated by the high resistivity values.

Five alloys of Yb with Tb were prepared with Yb concentrations of up to 13 a/o. Magnetic measurements were made and gave the results shown in Figure 19 that can be summarized as

Alloy	T_N	T_C
Tb _{97.5} Yb _{2.5}	216	201
Tb _{95.5} Yb _{4.5}	208	193
Tb ₉₃ Yb ₇	200	188
Tb ₉₀ Yb ₁₀	186	180
Tb ₈₇ Yb ₁₃	-	178

No helical ordering structure was found in the 13 a/o Yb alloy. It is expected that Yb would be divalent in Tb so that the Fermi energy would

Figure 18. The electrical resistivity as a function of temperature for the terbium-magnesium alloys.

Figure 19. The magnetization as a function of temperature for the terbium-ytterbium alloys in an external field of 100 Oe.

be lowered and the helical structure favored according to the arguments of Chapter II. As can be seen, the end result of Yb addition is elimination of the helical structure which is contrary to the predictions. It is interesting that the initial effect of Yb addition is a widening of the region of helical structure stability. Thus, it seems that interpretation of this result may not be simple and in fact will require consideration of both valency and size effects.

The resistivity data as shown in Figure 20 are interesting because the values of spin and residual resistivity are virtually identical for the Yb and for the La alloys. This result agrees with the conclusion that size effects must be important since the atomic radii of Yb and La are similar:

$$\text{La}^{3+} = 1.15 \text{ \AA} \text{ and } \text{Yb}^{2+} = 1.13 \text{ \AA} .$$

Thus, it seems that the similar sizes of La and Yb make their effects on the electronic properties quite similar. In addition it is interesting to note that the addition of La to Tb also tends to eliminate the helical structure. Therefore, we see another bit of evidence indicating that a complete understanding of the alloy results will require consideration of valency and diluent size effects. The resistivity data are summarized by:

Alloy	ρ_{res}	ρ_{spin}
$\text{Tb}_{97.5}\text{Yb}_{2.5}$	12.6	80
$\text{Tb}_{90}\text{Yb}_{10}$	49.2	59

Figure 20. The electrical resistivity as a function of temperature for the terbium-ytterbium alloys.

A possible explanation for the difficulties encountered with interpretation of the Yb data is that Yb is not divalent when in the Tb lattice. This would seem possible since the Yb 4f shell is relatively near to the Fermi level making it possible for sufficient lattice contraction to delocalize an additional 4f electron into a conduction band state. The possibility of electron delocalization can be tested by any property of the material that is sensitive to electron concentration. One such property is density of the metal. Since the binding of a metal is sensitive to the extent of electron delocalization, the density of the metal would be greater if an additional electron were to become a band electron. Density measurements for the Tb with Yb alloys were performed and the values of density fall slightly above a linear interpolation between the densities of Tb and divalent Yb. The slightly high density values are evidence that the Yb may exhibit some trivalent character but this evidence is considered weak. The most direct method for determining the valency of Yb is through magnetic measurements. Yb in the divalent state has a filled 4f shell and is non-magnetic while in the trivalent state Yb has a magnetic moment of $4.0 \mu_B/\text{atom}$. The difference in moment between the two valence states is observed as a significant difference in the saturation moments of the alloys. The difficulty in this method of valency determination is that Tb is magnetically hard so that moderate magnetic fields are not able to completely saturate the magnetization except in properly oriented single crystals. Efforts to obtain a Tb with Yb single crystal failed and thus, determi-

nation of the saturation moments were not successful. High field magnetization values for the Tb with Yb alloys were consistent with the divalent state but were not conclusive.

An indirect method for determination of the valency of Yb in Tb is the measurement of the valency of Yb in Gd. The saturation moment of Gd alloys can be measured in the available fields because Gd is much more magnetically soft than is Tb. Alloys of Yb in Gd were produced and the saturation moments were obtained by examining the magnetization of the material as a function of field at high fields. The saturation magnetization was obtained by noticing that the magnetization is expected to approach saturation as $1/H$. Therefore, the magnetization is plotted as a function of $1/H$ and the infinite field limit to the magnetization is read directly from the graph. The results of these measurements are shown in Figure 21 and can be summarized as:

Alloy	$\mu_{\text{sat}}/\text{Gd atom}$
Pure Gd	7.55
Gd ₉₅ Yb ₅	7.52
Gd ₉₁ Yb ₉	7.50
Gd ₈₆ Yb ₁₄	7.48

where the saturation moments are quoted in terms of the moment per Gd atom in the alloy in units of Bohr magnetons. It should be noted that the saturation moments were obtained at 4.5 K and not in the zero temperature limit. However, since the Curie temperatures for all of the alloys are in excess of 240 K, the quoted results should be very nearly the zero temperature and infinite field limit of magnetization. The fact that the

Figure 21. The magnetization as a function of inverse field for the gadolinium-ytterbium alloys obtained at a temperature of 4.5 K.

moment per Gd atom is almost constant indicates conclusively that Yb is divalent when in Gd. Therefore, it seems most reasonable to assume that Yb is divalent in Tb also. This interpretation of the results is open to debate since the Tb lattice is slightly more compact than the Gd lattice so that Yb could possibly delocalize in Tb when it does not in Gd. Without further information it is most reasonable to assume that Yb is divalent in Tb. Therefore, the Tb with Yb alloys are apparently a situation where the divalent character of the diluent must be combined with consideration of its atomic size to account for the effects of alloying on the ordering properties of Tb.

C. Tetravalent Diluents

According to a Darken-Gurry plot there are few materials with a valency greater than three that will form a solid solution alloy with terbium except in very dilute alloys. There are only two candidates for a higher valency alloy which are Zr and Th. Experiments have shown that the solubility limit of Zr in Tb is only about 5%⁴⁰ which was not expected to be sufficient to show a large effect. The solubility limit of Th in Tb is fairly large⁴¹ and alloys of up to 8 a/o of Th concentration were actually made. Tb and Th are sufficiently similar in size that single crystals of a moderate size were obtained. Therefore, the magnetic measurements were made on single crystal samples where the magnetization axis was chosen as an easy axis. The resistivity samples are much longer than the magnetization samples so that no single crystals of a sufficient size were found. Thus, the resistivity measurements

were made on multi-crystalline samples. These samples contained fairly large grains of random orientation but should not be considered as polycrystalline since all possible grain orientations probably did not exist in any one sample.

Three alloys of Tb with Th were made for this study. In all three cases sufficiently large single crystals were found to serve as magnetization samples. The single crystals were found by visual inspection, were oriented by a Laue x-ray technique and were then cut from the ingots with a spark erosion apparatus. In all cases, both basal plane and c-axis crystals were identified but only the basal plane results will be reported here. The magnetic measurements of the basal plane crystals of the Th alloys are shown in Figure 22. The ordering temperatures are

Alloy	T_N	T_C
$Tb_{99}Th_1$	222	218
$Tb_{96.5}Th_{3.5}$	-	213
$Tb_{92}Th_8$	-	192

For those alloys with greater than 1% Th content there was no observable helical ordering. Since the addition of tetravalent Th to trivalent Tb is expected to raise the Fermi energy of Tb, the effectiveness with which Th suppresses the helical ordering is consistent with the arguments of Chapter 11.

Resistivity data for the Tb with Th alloys were obtained and are shown in Figure 23 and are quite similar to the resistivity data obtained

Figure 22. The magnetization as a function of temperature for the terbium-thorium alloys in an external field of 100 Oe.

Figure 23. The electrical resistivity as a function of temperature for the terbium-thorium alloys.

for the Tb with La alloys. The values of residual and spin resistivity are a bit anomalous with respect to La and are summarized as:

Alloy	ρ_{res}	ρ_{spin}
Tb ₉₉ Th ₁	20.0	73
Tb _{96.5} Th _{3.5}	34.8	59
Tb ₉₂ Th ₈	68.6	32

The fact that the resistivities of the Tb with Th alloys are different from those of the Tb with La alloys could arise from two sources namely size effects and Coulomb scattering. The size effect would arise if the atomic size of Th is much different than that of Tb so that the Th atoms would act as scattering sites. Since Th has a metallic radius of 1.82 Å while La has a metallic radius of 1.88 Å, Th is likely more compatible with Tb (radius = 1.80 Å) so that the size effect is probably not the origin of the extra scattering. Probably the scattering of Th is a result of the charge associated with the Th site when in the trivalent Tb lattice. Because of the extra charge on the Tb site, there would be strong Coulomb scattering of electrons from the Th atoms. At this time it seems reasonable to assume that Th should be considered as similar to La with respect to its effects on the lattice since in both cases the lattice is being expanded. The fact that Th is more effective than La in eliminating the helical structure might be evidence that raising the Fermi energy in Tb follows the predictions of Chapter II.

D. X-ray Results

The lattice parameters of the alloys utilized in this work were obtained through x-ray studies by B. J. Beaudry. The x-ray method involved obtaining diffraction patterns in a Debye-Scherrer camera using filtered Cu radiation. The samples used in this work were in the shape of thin wires that were cut from the ingots of material and electro-polished. Since this method of obtaining lattice parameters depends on having many crystallites of random orientation, the results for the Tb with Th alloys were obtained from annealed filings of the material. In all cases the lattice parameters were obtained with typical calculated uncertainties of about 1 part in 3000.

The lattice parameters for pure Tb were previously determined by Spedding and Beaudry.⁴² The results of this investigation are compatible with the previous data. Results of the lattice parameter measurements can be summarized as

Alloy	$a(\text{\AA})$	c/a	$V \text{ (cm}^3\text{/mole)}$
Pure Tb	3.6055	1.579	19.31
Tb ₉₄ Mg ₆	3.5814	1.583	18.97
Tb ₈₈ Mg ₁₂	3.5613	1.586	18.68
Tb ₉₃ Yb ₇	3.6162	1.581	19.50
Tb ₈₇ Yb ₁₃	3.6319	1.583	19.78
Tb ₉₉ Th ₁	3.6061	1.581	19.34
Tb _{96.5} Th _{3.5}	3.6060	1.583	19.35
Tb ₉₂ Th ₈	3.6061	1.585	19.39

V. DISCUSSION

It is clear from the results of Chapter IV that an understanding of the data will require a detailed theory of magnetic ordering in alloys. Such a theory must be capable of explaining the ordering of intra-rare earth alloys as well as those with Sc, Y and La. This theory must be capable of including not only the effects of variable atomic moments but also must incorporate an understanding of diluent size effects. A theory of this type does not exist at this time so that analysis of the data is very difficult to perform in detail. In the course of the data analysis performed for this work, a phenomenological theory has been developed that allows for a quantitative explanation of magnetic order in the rare earth alloys. This theory is very simple and must be treated as conjecture at this time. However, when applied consistently the theory is useful for the data analysis.

A. Elementary Considerations

Up to now the usual analysis of rare earth alloy data has been performed using simple mean field ideas. If we consider the initial ordering temperature, T_i , of an alloy through Equation 20, we have

$$k_B T_i = \frac{2}{3} J \bar{G}$$

$$\bar{G} = x_a (g_a - 1)^2 J_a (J_a + 1) + x_b (g_b - 1)^2 J_b (J_b + 1) \quad (23)$$

where J is the exchange coupling strength that we have argued is equal to $J(\vec{Q})$ and where the average de Gennes factor for the alloy consisting

of components a and b is denoted as $\bar{G}$. In this case we have denoted the initial ordering temperature as T_i because even though the initial ordering temperature is ordinarily a Néel temperature, there are cases depending on the nature of $\rho(\vec{Q})$ where the initial ordering is not anti-ferromagnetic. Often it is assumed that J is a constant for all rare earth materials so that Equation 23 should describe all rare earth alloys. If we consider the simplest case where an alloy consists of only one magnetic constituent, we have

$$T_i = AGx \quad (24)$$

where A is a constant, x is the concentration of the magnetic rare earth constituent and G is the de Gennes factor for that magnetic constituent. Thus, rare earth alloys should all be described by Equations 23 and 24 depending on the nature of the alloy. The rare earths provide a unique test of the validity of the simple theory because of the wide range of G values that are available and because of the continuous solubility range of the rare earths when alloyed with each other. The formidable task of mixing the rare earths and determining their ordering properties was undertaken by Bozorth²⁵ and it was found that $\bar{G}$ seems to be a valid variable but the Equation 23 must be

$$T_i = A \bar{G}^{-2/3} \quad (25)$$

in order to properly describe the rare earth alloys. Equation 25 seems to indicate that the simple mean field explanation of rare earth alloys

is sufficient although the origin of the exponent $2/3$ is not understood. Apparently the exponent $2/3$ is connected in some way with the exchange strength but more specific conclusions require a more detailed analysis.

Equation 24 tells us that all of the alloys consisting of a particular magnetic rare earth with any non-magnetic diluent should be similar. Thus, the effects of Sc, Y and La in a heavy rare earth should be identical. Of course, these materials do not have the same effects on the ordering properties of other rare earths which means that Equation 25 is only partially valid at best. One of the great difficulties with Equation 24 is that it predicts that T_i becomes zero only when the concentration of the magnetic material becomes zero. The experimental results for alloys of Gd with Sc,⁴³ Y and La⁴⁴ and of Tb with Sc,³³ Y³⁴ and La³⁵ show that especially in the Sc alloys, the initial ordering temperatures of the alloys fall to zero at small but non-zero values of concentration. Thus, Equation 24 clearly fails in that case. Finally, La for example promotes helical ordering in Gd but eliminates the helical structure in Tb. This means that not only are the various non-magnetic diluents different but their action on the various rare earths is different. Thus, a more detailed theory of magnetic ordering in the rare earths is clearly required.

B. Consideration of the Interaction Strength

The failure of Equations 23 and 24 to describe magnetic ordering in the rare earth alloys is apparently related to a too simple view of the role of the interaction strength J . In the past J has generally

been viewed as a constant that is the same for all of the rare earths. Presumably this is not correct and in fact if the exponent $2/3$ in Equation 25 is to be viewed as a ramification of the non-constant character of J , there must be considerable variation of the interaction strength. Some useful observations concerning the interaction strength were made recently by Wollan.⁴⁵ Wollan observed that the ordering temperatures of the rare earth alloys can be written in a different form from Equation 25:

$$T_i = C \bar{G} - B \bar{G}^2$$

where the parameters B and C can be chosen to describe the ordering properties of the intra-rare earth alloys. By noticing that the inter-layer coupling energies contain phase factors given by the magnetic turn angle ω and by deriving a simple form for the RKKY interaction Hamiltonian, Wollan arrived at a new form for the initial ordering temperatures:

$$T_i = C \bar{G} - b(\cos \omega_i - \cos \omega_0)^{1/2} \bar{G}$$

where ω_0 is the turn angle for an alloy with $\bar{G} = 0$ and ω_i the initial turn angle for a particular alloy. This form of the ordering temperature relationship is interesting because the last term is equivalent to $B \bar{G}^2$ because, as noted by Wollan, the relationship of turn angle to alloy composition happens to follow the required dependence. The final form for T_i arises because deviations in interlayer coupling happen to have a

systematic variation with alloy composition. The formulation of Wollan actually does not offer any insight into the origin of the extra dependence of interlayer coupling on concentration, but it does demonstrate that the complex nature of the ordering temperatures in the rare earths can be understood through a proper understanding of J .

From the considerations of Chapter II we recall that the coupling strength J can be understood as being the value of the generalized susceptibility evaluated at its maximum. The value of $\mathcal{J}(\vec{Q})$, which can be calculated, determines the nature of the ordering temperatures in the rare earths. It is very interesting to note that the initial turn angle ω is directly determined by the magnitude of $\vec{Q}$. This is significant because it means that the nature of the ordering temperatures and the turn angle will be related just as concluded by Wollan. It seems that we should be able to calculate the generalized susceptibility functions for the rare earths and test the hypothesis that the discrepancy between Equations 23 and 25 can be eliminated by $\mathcal{J}(\vec{Q})$. There are two difficulties involved with trying to resolve the mystery through use of $\mathcal{J}(\vec{Q})$: first, $\mathcal{J}(\vec{Q}) = I^2(\vec{Q}) \chi(\vec{Q})$ is not directly calculable in any simple way, only $\chi(\vec{Q})$ can be obtained and secondly, the value of $\chi(\vec{Q})$ is not actually known for the alloys. Thus, we need some understanding of the nature of the matrix elements before we can derive the required $\mathcal{J}(\vec{Q})$ values. Finally, some notion of the $\chi(\vec{Q})$ values for the alloys must be obtained. If these two difficulties can be overcome we should be able to use Equations 22 and 23 to explain the ordering temperatures of all the alloys.

The nature of the matrix element $I^2(\vec{k}, \vec{k}')$ is rather complicated since it is essentially an overlap integral between the atomic 4f wavefunctions and conduction electron wavefunctions. Since a calculation of $I^2(\vec{k}, \vec{k}')$ would require a detailed knowledge of all the wavefunctions, it is generally approximated as a function of $\vec{q}$ only and then is assumed to follow some simple form. Evenson and Liu¹⁰ have proposed a phenomenological form for the matrix element:

$$\frac{I^2(\vec{q})}{I^2(0)} = \exp(-aq^2) + \exp(-a(4\pi/c - q)^2) .$$

This simplified form for the matrix element is then multiplied into the calculated generalized susceptibility functions to obtain $\chi(q)$. Using the assumed matrix element produces a decreasing function with some structure in it that is in qualitative agreement with observed $\chi(q)$ functions.⁴⁶ Thus the assumed matrix element is sufficiently realistic that it makes the $\chi(\vec{q})$ function decrease as a function of $\vec{q}$ in about the correct manner to reproduce the observed magnon spectra. In addition, by choosing the parameter a correctly, the proper turn angles for the rare earths are reproduced including the ferromagnetic ordering structure of Gd. Thus, the simple form for the matrix element has been quite successful in reproducing the observations.

If we accept the simplified matrix element we can proceed with a calculation of the expected initial ordering temperatures of the pure rare earths. In this case the generalized susceptibility functions as

calculated by Liu, Gupta and Sinha²² were used since they are the best available. Using Equation 20 we can reproduce the observed ordering temperatures of the pure rare earth elements if we make two assumptions: first, it is necessary to assume that $J(0)$ is a constant for all of the rare earths and second, it was necessary to let the peak height ratio $J(\vec{Q})/J(0)$ be equal to the calculated ratio $\chi(\vec{Q})/\chi(0)$. The first assumption means that the overall magnitude of the interlayer coupling is independent of the material. That assumption seems reasonable but since $\chi(0)$ is proportional to the density of states at the Fermi level, which is not a constant, the nature of that assumption is not understood. The second assumption is equivalent to making the matrix element a more slowly decreasing function of $\vec{q}$ than is given by the simple assumed Gaussian form in the vicinity of the maximum. The latter assumption is not particularly disturbing since the Gaussian form is likely an approximation at best. Using the calculations²² and two simple assumptions the initial ordering temperatures of the pure rare earths are reproduced quite well which implies that the ordering temperatures can be understood by a detailed consideration of the $J(\vec{q})$ functions.

As we have seen, the greatest difficulty encountered in an understanding of the pure rare earths is related to the assumed form of the matrix elements as used here. Basically the two difficulties as outlined previously can be overcome if $I^2(0)$ is not a constant and if the matrix element is more complicated than the simple Gaussian form that was assumed to be correct. Detailed calculations performed by Harmon and Freeman⁴⁷ show that using $I^2(\vec{k}, \vec{k}') = I^2(\vec{q})$ is a very questionable

procedure. In fact, the matrix element can have more structure than $\chi(\vec{q})$. If this is the case, the simple Gaussian form for the matrix element may not be even remotely valid. Evenson and Liu¹⁰ have argued that at larger $\vec{q}$ values $I^2(\vec{k}, \vec{k}')$ might have so much structure that much structure that much cancellation occurs and gives rise to the approximate validity of the Gaussian form. Bearing in mind that the simple assumption seems to be qualitatively correct and because there is no simple and useful alternative at this time, the simple formulation of the matrix element will be used as a guide in this work.

The major problem to be resolved in this discussion now is, what is the nature of $\chi(\vec{q})$ for an alloy? Since the properties of $\chi(\vec{q})$ are determined by the band structure, we actually need a simple procedure for calculation of band structures in rare earth alloys that is not as complicated as performing detailed calculations in each case. Further, since the concepts of lattice periodicity are not valid in an alloy, it is not clear how to calculate the bands in an alloy correctly. Since the properties of the rare earths are all so very similar it is reasonable to assume that the band structure of any alloy would be similar to that of the primary constituent. Further, since the bands for the pure constituents are known, the band structure for any alloy should be a combination of the bands of the constituents with possible corrections that account for modification of the bands by alloying. If we take the viewpoint that the rare earth bands are all similar but vary somewhat between the elements because of lattice dimension changes, it would seem reasonable that the principal effect of alloying would be a minor modifi-

cation of the lattice dimensions and therefore of the bands. Since empirically we can assume that the lattice dimensions of an alloy of two rare earths is simply a linear interpolation between those of the pure elements, the bands of an alloy should be a weighted average of the bands of the pure elements. The generalized susceptibilities are an average over the bands so that it is probably safest to represent the effects of alloying by examination of $\chi(\vec{q})$ because then we would have a tendency to smooth out small errors introduced by crude assumptions.

For the purposes of this paper we will make use of the empirical observation that the properties of the rare earths are similar enough that linear interpolation between the pure elements will describe the properties of the alloys. Thus, we assume that the generalized susceptibility of an alloy is given by

$$\chi_{\text{alloy}}(\vec{q}) = x \chi_A(\vec{q}) + (1-x) \chi_B(\vec{q}) \quad (26)$$

where x is the concentration of constituent A. We view this equation as a simple empirical way of dealing with the effects of alloying on the band properties of the alloy. Equation 26 is expected to yield the generalized susceptibility peak height for the alloy by simply combining the properties of the pure elements. Because of the fact that a sharp generalized susceptibility peak would not necessarily arise from the alloying, it is not obvious that this procedure would reproduce the correct turn angle for the alloy but the peak height should be useful.

If we accept Equation 26 and then specialize to a situation where there is but one magnetic constituent we can arrive at a useful form for the initial ordering temperature:

$$k_B T_i = A \times G_A \mathcal{J}(\vec{Q}) = A \times G_A I^2(\vec{Q}) [x \chi_A(\vec{Q}) + (1-x) \chi_B(\vec{Q})] \quad (27)$$

where A is equal to 2/3 according to simple mean field theory. Equation 27 gives the initial ordering temperature in a situation where the exchange strength is variable through alloy concentration. If we now make the observation that in all of the rare earths the $\chi(\vec{q})$ functions are quite similar except for peak height differences and small changes in $\vec{Q}$, we can write that:

$$\chi_B(\vec{Q}) = \chi_A(\vec{Q}) + \delta$$

where this equation has ignored the small difference in $\vec{Q}$ between the two constituents. As long as the value of $\vec{Q}$ is not too different in the two constituents, δ can be considered to be a constant that can be obtained from calculations. Using this relationship for the generalized susceptibility we can rewrite Equation 27 to obtain a new form of the equation:

$$k_B T_i = A \times G_A \mathcal{J}_A(\vec{Q}) [1 + (1-x)B\delta] \quad (27b)$$

As can be seen, for an intra-rare earth alloy where the generalized susceptibility functions of the constituents are not too different, the initial ordering temperature can be written as:

$$T_i = Dx - Ex^2$$

which is just the empirical equation proposed by Wollan⁴⁵ to describe the pure rare earths and the intra-rare earth alloys. Thus, through a proper choice of the parameter δ the initial ordering temperatures of the rare earth alloys can be reproduced. An example of the application of Equation 27b is shown in Figure 24 as the solid line through the open data points. In this case Equation 27b has been applied to alloys of Tb with Y where the experimental points are data obtained by Child et al.³⁴ As can be seen in Figure 24, using a derived value for δ produces a fit to the data that is quite good and which seems to indicate that the functional form of Equation 27b is correct. In order to fit the data two assumptions were used: first, it was assumed that $\mathcal{J}(0)$ is the same for Tb and Y and second, that the peak values of $\mathcal{J}(\vec{Q})$ are obtained from the calculated values of Liu et al.²² These are the same two assumptions that were used in fitting the data for the pure rare earths. Thus, it seems that through a proper choice of the generalized susceptibility functions of the constituents the ordering properties of rare earth alloys can be predicted. Since the generalized susceptibility functions that correctly fit the Tb with Y alloys are those as calculated, it seems that Equation 27b is likely of physical significance. It must be noted

Figure 24. The ordering temperatures for terbium-yttrium alloys as a function of normalized moment per atom. The curve through the open data points represents the fit of the theory to the Néel temperatures while the curve through the filled data points represents the theoretical fit to the Curie temperatures of the alloys.

that because of the simple nature of the "rigid band" scheme represented by Equations 26 and 27, the surprising success of the formalism in fitting the experimental data could be fortuitous.

The ferromagnetic ordering temperature and therefore the temperature region over which the helical structure is stable is determined by a complex interplay of exchange and anisotropic energies. Because of this fact it is not easy to find an exact relationship for the ferromagnetic ordering temperature. By the simple theory of Chapter II, as given by Equation 22 it seems reasonable that the region of helical structure stability, ΔT , is a function of the height of the $J(\vec{q})$ peak and of the elastic properties of the material. If we make the simple assumption that c is the elastic constant of the material and is independent of alloy composition following Equation 22 we have:

$$\Delta T_{\text{alloy}} = \frac{K J(\vec{Q})_{\text{alloy}}}{x^2 c} \delta J_{\text{alloy}}$$

where this equation applies for an alloy with one magnetic constituent. If we now combine Equations 22 and 26 we can derive an equation to describe ferromagnetic ordering in the alloys. To simplify Equation 22 we can use the assumption of Equation 26.

$$J(\vec{Q})_{\text{alloy}} = x J(\vec{Q})_A + (1-x) J(\vec{Q})_B$$

$$\text{and if, } J(\vec{Q})_B = J(\vec{Q})_A + I^2(\vec{Q})\delta$$

$$\text{then, } J(\vec{Q})_{\text{alloy}} = J(\vec{Q})_A + (1-x) I^2(\vec{Q})\delta .$$

where $\delta \mathcal{J}_A = \mathcal{J}(\vec{Q})_A - \mathcal{J}(0)_A$. This equation can be used to fit the region of helical structure stability but caution must be used because of two principal factors: first, the derivation of Equation 28 involves a series of very simple assumptions which are not necessarily valid and second, the parameter δ can be chosen to represent the ΔT values for any alloy system at least approximately but the validity of δ as a physically meaningful quantity is not clearly established.

A partial test of the validity of Equation 28 is shown in Figure 24 where the solid line passing through the filled data points is the fit of Equation 28 to the data. As can be seen, a fair fit to the experimental data points for Tb with Y alloys³⁴ results from this formalism. The fit required that $\delta = 10$ which is a rather high value for that parameter. At this time it is not known if such a large generalized susceptibility peak could occur but the primary difficulty involved with such a high value for δ is the fact that a significantly smaller value was required to fit the initial ordering temperatures. It would seem that the same value for δ should be used to predict both ordering temperatures, if the theory is to be valid. Possible Fermi surface modifications in the ordered state might make the value of δ dependent on which magnetic structure is in question. It is also possible that the theory for ferromagnetic ordering is too simple and would thus give rise to an erroneously high value for δ . Probably the strongest statement that can be made is that the theory provides a useful fitting function that will be useful if applied consistently. The important conclusion

is that a $\mathcal{J}(\vec{Q})$ function for intra-rare earth alloys can be derived in a simple fashion that will adequately represent the ordering temperatures for the alloy.

C. Interaction Effects in Trivalent Diluents

From the discussion of the preceding section it seems clear that the ordering properties of the rare earth alloys can be described adequately through a proper choice of the $\mathcal{J}(\vec{q})$ function. The interpretation of the fitted function may not be obvious but when applied consistently it should allow for the description of ordinary band effects on the ordering properties of the alloys. Let us now use the formalism to describe the ordering temperatures of alloys of Tb with trivalent diluents especially Sc and La. These two cases are particularly important because they involve a rather large change in atomic volume that must be accounted for in some way. The volume effect that is felt to be important in the valence change alloys Mg, Yb, and Th can be accounted for by deriving a $\mathcal{J}(\vec{q})$ function for a trivalent diluent with a similar volume change and then assuming that the derived function will describe the band modifications due to volume change in other alloys.

Referring to Figure 12 we see that the alloys of Tb with Sc are anomalous with respect to the temperature region over which the helical structure is stable. The initial ordering temperatures of these alloys are normal with respect to those of Y and La. Thus, a complete description of the Sc alloys requires that the peak height, $\delta\mathcal{J} = \mathcal{J}(\vec{Q}) - \mathcal{J}(0)$, is strongly enhanced while the actual value of $\mathcal{J}(\vec{Q})$ is left relatively

constant. This could in fact result if $\mathcal{J}(0)$ is decreasing quite strongly as Sc is added to the Tb host. Since the principal effect of Sc addition to Tb is a contraction of the lattice, it is possible that the density of states at the Fermi level could decrease strongly while the Fermi surface "nesting" would in fact tend to increase. Thus, it seems possible to obtain at least a qualitative explanation of the nature of the Sc alloys through analysis of the interaction effects. There are possible complications because of the rather large changes in volume that accompany addition of Sc to the Tb lattice. Those properties that are sensitive to inter-atomic spacing will be modified significantly by the addition of Sc to Tb. One of the factors that could change significantly is the elastic properties of the material. In this case one might expect that the more compact Sc lattice would be more stiff. The elastic properties of pure Tb and Sc are different by perhaps 15% so that the effects of differences in c should not account for the anomalous properties of the Sc alloys. Because of the large decrease in lattice spacing, the anisotropic effects such as the crystalline electric field could increase significantly. If such fields tend to follow a power law of the form r^{-n} (n can be as large as 7 depending on the nature of the crystalline fields in the solid) so that the strength of the crystalline fields can be very sensitive to atomic volume. The large increase in crystalline field that could result from the decrease in lattice volume through Sc addition might account for the anomaly that T_1 becomes zero at a small but non-zero value of Tb concentration. Since the effects of volume on factors such as the crystalline field are not simple, we will assume that

all such complications can be absorbed in a proper choice of $J(\vec{q})$. From this discussion it becomes clear that consideration of interaction strength cannot explain all the properties of magnetic ordering in the rare earths but it is a good first step. Thus, when we derive a value of $J(\vec{Q})$ that will give the observed ordering temperatures for the alloys such as those with Sc, it may include implicitly a number of factors that we are not aware of that are volume dependent.

Derivation of $J(\vec{Q})$ for the Sc alloys is made by utilizing Equation 28. Equation 28 would seem to be the appropriate choice because the initial ordering temperatures do not vary by a large amount while ΔT can be quite different. A value for δ is found that will give the correct width of the helical structure at say 10% of Sc concentration. It is assumed that the correct $J(\vec{Q})$ for Tb is known from the calculations.²² It should be observed that the generalized susceptibility function found using this procedure is valid only in the helically ordered regime. Since we have argued that this function may not correspond to that required in the paramagnetic region, application of the derived $J(\vec{Q})$ function for Sc in Tb to other materials can only be done in the helical regime of the other material. This final point is well illustrated by the fact that $J(\vec{Q}) = 17$ for Sc will reproduce the initial ordering temperature (this is essentially identical to that of Tb) while $\delta J = 13$ is required of Sc to fit the width of the helical regime. The requirement that $J(\vec{Q})$ for Tb and Sc be similar in the paramagnetic phase as implied by the initial ordering temperature is in agreement with calculations of Liu et al.²² and by Rath and Freeman.⁴⁸ According to these calculations the $\chi(\vec{q})$

functions of Tb and Sc are quite similar except that Sc may have a somewhat more dominant peak. The difficulty is in understanding the origin of the large susceptibility peak required to fit the ferromagnetic ordering. Perhaps the most satisfactory explanation of the difficulty is that the parameters used in deriving Equation 28 are in error. To resolve this problem would require that either the magneto-elastic energy is rising slower than M^4 or that the temperature dependence of the magnetization is slower than $(1-T/T_N)$. We, therefore, have some evidence that Equation 28 is in error although it is felt that the qualitative information derived through application of that equation is useful. Thus, the value of $\chi(\vec{Q})$ that is derived from this discussion is likely overestimated, but it should still be useful as an indication of the nature of the generalized susceptibility in that material.

As can be seen in Figure 12, the alloys of Tb with La are anomalous because of the tendency of La to promote ferromagnetic ordering. This particular result is perhaps reasonable since the metallic radius of La is somewhat larger than that of Tb while that of Sc is smaller than that of Tb. Thus, La should act oppositely to Sc if lattice volume, or atomic size, is the factor responsible for the difference among the various alloys. We should be able to make arguments similar to those used for the Sc alloys to derive a $\chi(\vec{Q})$ that will reproduce the La results. There is an additional complication that should be considered in the case of La alloys: La promotes ferromagnetic ordering in Tb³⁵ and La favors helical ordering in Gd.⁴⁴ Because of this difficulty we must be very cautious because the theory presented herein makes no provisions for

$\mathcal{J}(\vec{q})$ of La being different in the various rare earths which means that the same generalized susceptibility function should work in both the Gd and Tb alloys. At this time it is believed that the origin of the difficulty is that La favors the dhcp crystal structure in the Gd alloys. Since the Gd alloys change to the dhcp structure at the concentration of La at which the helical structure arises, it is apparent that the crystal structure modification gives rise to the helical structure. The crystal structure change is relevant because the crystallographic phase change corresponds to a change in lattice symmetry with a sudden modification of the axial ratio which could easily change the nature of the Fermi surface drastically. In the Tb case, the addition of La simply expands the lattice without introduction of the phase change over the concentration range studied. Thus, it is possible that the Tb with La alloys represent a case where the lattice is simply being expanded while the Gd with La alloys are much more complex. This again illustrates that application of this simple theory must be performed cautiously and very consistently.

Derivation of the proper $\mathcal{J}(\vec{Q})$ for La in its alloys with Tb can be made with some confidence through Equation 28. In this case we notice that the helical structure disappears at some La concentration which can be read from Figure 12. The helical structure disappears when $\mathcal{J}(\vec{Q}) = \mathcal{J}(0)$ so that the Equation 28 can be utilized to yield the simple relation:

$$0.94 \mathcal{J}(\vec{Q})_{\text{Tb}} + 0.06 \mathcal{J}(\vec{Q})_{\text{La}} = \mathcal{J}(0) .$$

In obtaining this equation we have assumed that $\mathcal{J}(0)$ is constant for the Tb with La alloys and that the generalized susceptibility function for pure Tb is known. The value of $x = 0.94$ was read directly from Figure 12. The generalized susceptibility function derived for La can now be used to understand the volume effect of expansion of the lattice and can only be safely applied to a situation where the helical structure is made to disappear.

D. Interaction Effects in Valence Change Alloys

We can now use the analysis techniques of the preceding section to understand the alloys in which an electron concentration change was induced through alloying of Tb with a material having a different valency. The first situation to be considered is that of Tb alloyed with Mg. The experimental data for this alloy system is summarized in Figure 25 where we see the remarkable tendency of Mg to promote the helical ordering structure, a result which is in agreement with the predictions of Chapter I. However, because of the large atomic size difference between Mg and Tb this result must be considered not only from the viewpoint of valency change but also with respect to volume differences. In this case we consider the metallic radius of Mg = $1.60 \text{ \AA}$ to notice that it can be properly compared to that of Sc = $1.62 \text{ \AA}$. On this basis we assume that Mg can be directly compared to remove the effects of lattice size modification. Qualitatively we can observe that Mg and Sc tend to contract the lattice to a comparable degree and because of that they both tend to promote the helical structure. The important problem is to decide if the

Figure 25. The ordering temperatures as a function of alloy concentration for the alloys of terbium with those diluents which raise (thorium) and lower (magnesium and ytterbium) the Fermi energy.

valency characteristics of Mg have an effect in addition to the volume effect. The analysis procedure is to derive a δ that will reproduce the width of the helical region for the Mg alloys using Equation 28 and then subtract from it the value of δ_{Sc} derived for the Sc alloys in order to remove the volume effects. The end result of this procedure should be a generalized susceptibility function that reflects changes in Fermi surface "nesting" due to electron concentration changes. This procedure is equivalent to making the observation that Mg in Tb promotes the helical structure even more strongly than does Sc which implies that Fermi surface "nesting" is increased by the divalent nature of Mg. This simple qualitative interpretation was previously made by Burgardt and Legvold⁴⁹ but was not at that time quantitative. Thus, the primary advantage of the formalism presented herein is that it allows us to place a quantitative estimate on the increase in Fermi surface "nesting." It is interesting to note that the spectacular ability of Mg to promote the helical structure is due to the cooperation of the volume and the Fermi surface effects.

The generalized susceptibility function for Mg is derived from an experimental value for ΔT such as that for 10% of Mg in Tb as read from Figure 25. The enhancement of the generalized susceptibility function thus derived is $\delta_{Mg} = 50$. After subtracting the peak height of Sc, to remove the effects of volume change, we obtain the generalized susceptibility of Tb with the Fermi energy lowered. If we approximate the Fermi energy of Tb with its Fermi energy lowered with addition of 10% Mg through a very simple rigid band approximation we have

$$E_F = 0.494 \text{ Ryd and } g(\vec{Q}) = 18.0 \text{ states/Ryd/atom.}$$

Thus, since $g(\vec{Q})$ for Tb is 15.1 states/Ryd/atom, we see that lowering of the Fermi energy by 0.015 Ryd has produced a very substantial increase in the generalized susceptibility peak just as predicted.

Analysis of the Tb with Th alloys is undertaken through Equation 28 by observing that $g(\vec{Q}) = g(0)$ at the alloy concentration where the helical structure disappears. The Th alloys are particularly interesting for observation of the disappearance of the helical structure because the helical structure is suppressed with only 2% Th concentration. Since Th tends to increase the conduction electron concentration when added to Tb, the experimental results are in accordance with the prediction of Chapter II. The complication is, of course, that there could be other competing effects such as a volume effect. In this case we argue on the basis of metallic radius that Th is comparable to La since Th has a radius of 1.82 Å and La has a radius of 1.88 Å. This interpretation is not necessarily valid since the metallic radius of Th is almost identical to that of Tb and Th is certainly smaller than is La. The x-ray results of Chapter III prove that Th does tend to expand the lattice and since the properties of the Th and La alloys are otherwise quite similar, we will assume that Th can be directly compared to La. Using this assumption it becomes clear that the remarkable ability of Th to suppress the helical structure in Tb is related to a combination of a volume effect and of raising the Fermi level as was noted by Burgardt and Legvold.⁴⁹

We derive the value of $\mathcal{J}(\vec{Q})$ for Th in Tb by using the same procedure that was applied to La. In this case we observe from Figure 25 that the helical structure in Th alloys disappears at 2% of Th concentration. Therefore, one can solve for the $\mathcal{J}(\vec{Q})$ of Th and remove from that value the change in peak height due to volume effects as derived from the La alloys. Using that analysis of the 2% alloy we find that

$$E_F = 0.512 \text{ Ryd and } \mathcal{J}(\vec{Q}) = 14.7 \text{ states/Ryd/atom.}$$

It should be noted that the Fermi energy was computed using a simple rigid band assumption. As can be seen, raising of the Fermi energy has acted to lower the peak in the generalized susceptibility from the pure Tb value of 15.1 down to 14.7 which is in agreement with the predictions of Chapter II. Since Th is not likely to expand the lattice as much as does La, the direct comparison of La and Th may not be completely valid. Because of this possible difficulty, the value of $\mathcal{J}(\vec{Q})$ derived by assuming that Th and La are identical should be treated as an upper limit on the correct value.

The final alloy system to be considered is the complicated case of Tb alloyed with Yb. In this situation Yb is thought to be divalent so that the helical structure should be promoted according to the predictions of Chapter II. Experimentally it was found that adding Yb to Tb eventually eliminated the helical structure in a manner similar to Th. The apparent solution of this difficult situation comes from a consideration of atomic size. Yb is much larger than Tb which means that

it tends to expand the lattice and thus should tend to eliminate the helical structure through the volume effect. Thus a proper interpretation of the results will require a consideration of both volume and valency effects where the volume effect is in fact dominant. To analyze the data we argue on the basis of metallic radii that Yb and La can be directly compared since the metallic radius of Yb = 1.92 Å and the radius of La = 1.88 Å. Since the addition of Yb to Tb does not suppress the helical structure as quickly as does La, the effect of lowering the Fermi energy is qualitatively seen to be a promotion of the helical structure. This interpretation was made by Burgardt and Legvold⁴⁹ where they noticed that apparently Yb does tend to promote the helical structure as expected.

Data analysis is made by noticing that the helical structure in the Yb alloys disappears at 13% of Yb concentration. The $\mathcal{J}(\vec{Q})$ for Yb is derived in a manner similar to that used for Th and the volume effect is removed by subtracting the change in generalized susceptibility induced by La. The final results are

$$E_F = 0.491 \text{ Ryd and } \mathcal{J}(\vec{Q}) = 17.5 \text{ states/Ryd/atom}$$

where E_F was obtained through a very simple rigid band approach. As can be seen peak height is greatly increased over the pure Tb value of 15.1 so that the theoretical prediction apparently is confirmed. Since Yb has a larger metallic radius than does La it could have even a larger volume effect than does La so that the peak height derived for Yb should

be treated as a lower limit on the correct value. The important conclusion is that the apparent tendency of divalent Yb to promote the ferromagnetic structure is a result of a strong volume change and that the true result of lowering of the Fermi energy by addition of Yb is an increase in the peak in the generalized susceptibility of Tb.

E. Conclusion

The work reported in this paper was intended as a test of the relation of the generalized susceptibility (and therefore, the ordering properties) for Tb to the Fermi energy of Tb. The experimental results are complicated and require a detailed consideration of atomic size as well as valence for a correct analysis. In order to properly analyze the data a simple theory was developed which attempts to account for the effects on band structure which accompany alloying and attendant lattice size changes. Using this simple theory, the alloys of Tb with Mg are understood as a fortuitous combination of Fermi energy lowering and of lattice contraction. The remarkable tendency of Th to promote the ferromagnetic structure in Th is understood as a combination of the Fermi energy being raised and of the lattice being expanded. The theory was also useful in explaining the interesting behavior of the Tb with Yb alloys which upon preliminary analysis did not seem to follow the theoretical predictions. After proper consideration of the volume effect, indeed the Tb with Yb alloys showed promotion of the helical structure as predicted. The complicated behavior of the Tb with Yb alloys is a case where the volume and valence effect compete. The results of the

analysis can be summarized as the following:

E_F (Ryd)	$\mathcal{J}(\vec{Q})$ (states/Ryd/atom)	Alloy
0.512	14.7	Tb ₉₈ Th ₂
0.509	15.1	Pure Tb
0.494	17.8	Tb ₉₀ Mg ₁₀
0.491	17.4	Tb ₈₇ Yb ₁₃

As can be seen, lowering of the Fermi energy does produce an enhancement of the peak in the generalized susceptibility which implies additional Fermi surface "nesting". Raising of the Fermi energy seems to decrease Fermi surface "nesting" as evidenced by the diminished generalized susceptibility peak. These results are in agreement with the rigid band predictions of Chapter II. Thus, even though there is considerable speculation attached to the quantitative conclusions of this paper there can be little doubt that the magnetic ordering properties of the rare earths are intimately related to the Fermi surface geometry through the generalized susceptibility.

VI. ACKNOWLEDGEMENTS

I would like to extend my thanks to my major advisor, Dr. Sam Legvold, for making my graduate career exciting and most rewarding. His patience in enduring my independent manners and headstrong attitudes is particularly appreciated.

I would like to recognize the long and particularly fruitful discussions with my metallurgist friends particularly Mr. B. J. Beaudry, Dr. K. A. Gschneidner, Jr., Mr. J. O. Moorman and Dr. D. T. Peterson. These gentlemen aided greatly in my training as a materials scientist and their willingness to share experience and samples made my research possible.

Special thanks are in order for Dr. S. H. Liu and Dr. B. N. Harmon who tried to teach me a bit about solid state physics. I particularly thank them for removing some of my more naive attitudes towards the nature of solids.

Finally, I would like to thank my parents. Without their constant encouragement and sacrifice my career in physics would never have been possible.