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MAGNETIC PROPERTIES OF SOME AMORPHOUS RARE EARTH–TRANSITION METAL ALLOYS PREPARED BY DUAL-SOURCE EVAPORATION

by

Gary E. Roberts

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Thesis Director's Signature

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I. INTRODUCTION

I.1 Scope of the Thesis

The announcement by Chaudhari, et al. [1] in 1973 that amorphous sputtered films of Gd-Co and Gd-Fe can support magnetic bubble domains and have some attractive properties for device applications has stimulated a great deal of interest in amorphous rare earth-transition metal (RE-TM) alloys. In this thesis, the room temperature magnetic properties of amorphous Ho-Co, Dy-Co, Gd-Fe, and Tb-Fe thin films are reported. These particular binary alloys are selected because (1) facilities for measuring the magnetic properties as a function of temperature are not available and all of the above alloys are ordered at room temperature over a wide range of composition, and (2) it is hoped that comparison of Ho-Co with Dy-Co and Gd-Fe with Tb-Fe will enable some conclusions to be drawn about the effect on the magnetic properties (particularly the uniaxial anisotropy) of varying the rare-earth constituent for a fixed transition-metal constituent. In this work, particular emphasis is placed on those properties most useful for the characterization of bubble domain materials. These properties, some of which are interrelated, are: (1) the magnetization, \(M\), (2) the uniaxial anisotropy constant, \(K_u\), and the anisotropy field, \(H_K = 2K_u/M\), (3) the quality factor, \(Q = H_K/4\pi M = K_u/2\pi M^2\), (4) the wall energy density per unit wall area, \(\sigma_w\), (5) the characteristic length, \(l = \sigma_w/4\pi M^2\), and (6) the exchange
constant or stiffness, A. Although none of the amorphous RE-TM alloys reported on here are at present, nor may they ever be, primary contenders for device applications, a broader understanding of the properties of this class of materials, and the origins of those properties, is essential if their full potential in applications is to be realized.

The next section of this chapter discusses the magnetic properties which are desirable for a bubble domain material. It points out that all of the requirements cannot be optimized simultaneously and that some trade-offs are a necessity.

The final section of this chapter gives a history of bubble materials selection. It places the emergence of amorphous materials in historical perspective and provides a basis for the comparison of their properties with alternative materials, principally the rare-earth iron garnets.

Chapter II reviews the literature on amorphous rare earth-transition metal alloys and discusses some of the concepts necessary to an understanding of these materials. It is divided into three sections. The first section discusses amorphous alloys in relation to bubble domain applications. The second section reviews experimental results on the uniaxial anisotropy in both sputtered and evaporated films and discusses the attempts to explain those results. The last section presents some of the differences and similarities between amorphous RE-TM alloys and the intermetallic
RE-TM compounds, with a view toward obtaining a better understanding of amorphous magnetism.

Chapter III describes the experimental techniques used in this investigation.

Chapter IV presents and interprets the results which were obtained, drawing on the material in Chapter II for background and comparisons.

The last chapter summarizes the major findings and conclusions.

I.2 Material Requirements for Bubble Domain Devices

The material requirements for bubble domain devices are analyzed in detail by Thiele [2] and are summarized in papers by Gianola, et al. [3], Nielsen [4], and Koblishka, et al. [5]. The discussion presented here is based upon these sources.

The magnetic materials used in bubble memories must be in the form either of thin plates or thin films. The magnetization must be along the normal to the plane of the film, and hence the easy axis of magnetization must also be in this direction. Since the demagnetizing field, which is proportional to the moment of the material ($4\pi M$), tends to rotate the magnetization back into the plane of the film, the anisotropy field must be greater than the moment of the material, i.e. $H_K > 4\pi M$ or $Q = H_K/(4\pi M) > 1$ where $Q$ is the quality factor.

For a film which satisfies this requirement, the lowest energy state in the absence of an applied field is
one in which there are equal volumes of oppositely directed magnetization. This state is characterized by a serpentine or maze-like pattern of strip domains. When a bias magnetic field is applied normal to the plane of the film, the domains in which the magnetization is aligned parallel to the field expand at the expense of the other domains. At a critical field, those domains in which the magnetization is anti-parallel to the bias field, and which are bounded by a domain wall that does not intersect the edge of the film, collapse into cylindrical domains with a circular cross-section. These circular cylindrical domains are referred to as bubbles. A further increase in the magnetic field causes the bubbles to decrease in diameter until a second critical field is reached at which the bubbles collapse. At this point the film is saturated and consists of a single domain.

Before discussing the static stability of bubble domains, it is convenient to define the characteristic length of a bubble material as

$$\ell = \frac{\sigma_w}{4\pi M^2}$$

where $\sigma_w$ is the wall energy density per unit area of wall and $4\pi M$ is the magnetization. Since the wall energy density for a 180° Bloch wall in a material with uniaxial anisotropy $K_u$ is given by $\ell = 4\sqrt{AK_u}$, the characteristic length may also be written

$$\ell = \frac{\sqrt{AK_u}}{\pi M^2}.$$
For a thin film uniformly magnetized normal to the plane of
the film, the magnetostatic energy density per unit volume
is given by \( -\frac{1}{2} \mathbf{H}_D = 2\pi M^2 \), where \( \mathbf{H}_D = -4\pi M \) is the demagne-
tizing field. Hence, the characteristic length may be re-
garded as \( 1/2 \) of the ratio of the wall energy density to
the magnetostatic energy density. An alternate interper-
tation of the characteristic length is that \( 2l \) represents
the distance of closest approach for domain walls, since if
the walls are brought closer, the increase in energy due to
more walls would exceed the energy decrease corresponding to
the complete elimination of the magnetostatic energy [6].
This can easily be seen by considering a square film with
edge length \( a \) and thickness \( h \) which is divided into parallel
strip domains of width \( w_s \) (see Fig. 1). The total wall
energy is \( \sigma_w ha(a/w_s) \) and the energy gained by eliminating
the magnetostatic energy is \( 2\pi M^2 a^2 h \). The ratio of these two
energies is

\[
\frac{\sigma_w}{w_s 2\pi M^2} = \frac{2l}{w_s}
\]

which is greater than one if \( w_s < 2l \).

Considerations of the static stability of bubble
domains indicate that the film thickness should be \( h \approx 4l \).
At approximately this thickness, domain diameter is mini-
mized, the ability of the domain to recover from fluctua-
tions in size and shape in the presence of coercivity is
maximized, and the dependence of the domain diameter on
thickness is minimized. At this thickness, the ratio of the
bias field at collapse, \( H_0 \), to the bias field at runout, \( H_2 \),
Fig. 1. Parallel strip domains in a magnetic thin film with the easy axis normal to the film plane.
is $H_0/H_2 = 1.4$. At the center of the stable bias field region, $H_{bias} = 1.2 H_2 = 0.3(4 \pi M)$ and the domain diameter is $d \approx 8l$ so that $d/h \approx 2$. Hence, the film thickness $h \approx 4l$ and bubble diameter $d \approx 8l$ are called the preferred values. However, it should be pointed out that this requirement need not be satisfied with great precision since devices with $d \approx h$ seem to work well.

Since the data rate in memory applications is directly proportional to the velocity with which bubbles can be propagated, an additional material requirement is the need for fast bubble propagation. The speed of bubble domains depends upon their mobility and the driving field. The mobility of a domain wall is given by [7]

$$\mu_w = \frac{\gamma}{\alpha} \sqrt{\frac{A}{K_u}} = \frac{\gamma}{4\alpha} \frac{\sigma_w}{K_u}$$

where $\mu_w$ is the mobility, $\gamma$ is the gyromagnetic ratio and $\alpha$ is the Gilbert damping parameter. Using the preferred bubble diameter $d = 8l = \frac{2\sigma_w}{\pi M^2}$

the mobility relation can be rewritten in the form,

$$\mu_w = \frac{\gamma}{16\alpha} \frac{4\pi M}{H_k} = \frac{\gamma}{16\alpha} \cdot \frac{1}{Q}$$

From this expression, it can be seen that for a given value of domain diameter the mobility is inversely proportional to the quality factor, Q. Hence, it is desirable for Q to be as small as possible. On the other hand, while $Q > 1$ is sufficient for static bubble stability, the necessity to
propagate bubbles without spurious nucleation of unwanted bubbles in actual devices calls for $Q \geq 2.5$ [8].

In general, minimizing the power required to propagate the bubbles requires minimizing the coercivity, $H_C$. However, in T-bar type devices, the lowest practical rotating field for bubble propagation depends strongly on $M$ as a result of the interbar gaps [9]. Therefore, the propagating power is not increased significantly as long as $H_C \leq 0.01(4\pi M)$. However, in contiguous disk devices [10] that do not have gaps and in bubble lattice devices [11] that propagate bubbles by means of bubble-bubble interactions, it is always desirable to have the lowest possible coercivities.

One final requirement is that the material have its magnetic ordering temperature above room temperature and that the material properties be reasonably independent of temperature at room temperature. Hence, the exchange constant $A$ must be sufficiently large to ensure a Curie point well over 100°C.

I.3 A Brief History of the Evolution of Bubble Materials

In 1966 A. H. Bobeck and P. Michaelis were working on a new type of magnetic memory known as the waffle-iron, which was intended to be an improvement over core memories. Their experiments with the waffle-iron structure led them to the discovery that a thin permalloy film could sustain an isolated reverse domain with the magnetization lying in the plane of the film. They also found that the domain could be
moved intact over the surface of the film in two dimensions. However, these reverse domains were not considered attractive for use in a memory application because of their large size, the slowness with which they moved, and the anisotropy in their motion due to the easy and hard directions in the plane of the film. Consideration of the ideal magnetic properties of a material for a memory consisting of reversed domains that could be stored and moved around in two dimensions led to the conclusion that the magnetization should be normal to the film surface and that the magnetic properties should be nearly isotropic in the plane of the film. It was first pointed out by R. C. Sherwood that these requirements were met by the rare-earth orthoferrites, whose general formula is RFeO$_3$, where R is a rare-earth or yttrium [12]. Using orthoferrite crystals in the form of thin plates supplied by Sherwood and Williams, Bobeck was soon able to observe stable bubble domains and use them to make simple devices. These discoveries were announced in a now famous paper published in 1967 [13].

Subsequently, extensive research on the magnetic properties of the orthoferrites and their application to bubble devices was performed [14,15]. This work clearly demonstrated the potential of bubble domain memories, established design criteria for bubble materials, and provided information on circuit performance. However, it soon became clear that there were serious problems with the orthoferrites as a bubble domain memory material. They
combine a low moment \((4\pi M \approx 60-150 \, \text{G})\) and a large \(Q(>1000)\), which gives rise to bubble domains on the order of 100 \(\mu\text{m}\) in diameter. This results in an uneconomically low bit packing density. Because the net moment of the orthoferrites is due to canted antiferromagnetism, it was not possible to increase \(4\pi M\) to achieve a smaller bubble size. Since the exchange constant \(A\) could also not be changed significantly, the only approach left to reduce the bubble size was to reduce the anisotropy (recall the expression for characteristic length). An attempt to do this was made by utilizing the spin reorientation temperature range.

The easy axis for an orthoferrite is the \(a\) axis of the orthorhombic structure from absolute zero temperature up to the spin reorientation temperature range. As the temperature is raised through this range of approximately 20\(^\circ\)C the easy axis changes from the \(a\) to the \(c\) axis, and remains the \(c\) axis up to the Néel temperature. For all orthoferrites except SmFeO\(_3\), the \(c\) axis is the easy axis at room temperature.

These facts indicated that a lower room temperature \(K_u\) could be achieved by employing a mixture of Sm and other rare earths in order to adjust the reorientation range closer to room temperature \([16,17]\). A solid solution of Sm\(_{0.55}\) Tb\(_{0.45}\) FeO\(_3\) did exhibit a bubble diameter of 25 \(\mu\text{m}\) \[16\], but this was still larger than the 1-10 \(\mu\text{m}\) range desired at that time. In addition, since reorientation occurred just below room temperature, the properties of such
mixtures had too strong a temperature dependence at room temperature.

The next materials to be considered for bubble applications were the hexagonal ferrites, whose chemical formula is $\text{MFe}_{12-3} \text{O}_{19}$ where $\text{M}$ is $\text{Ba}$, $\text{Ca}$, $\text{Sr}$, or $\text{Pb}$. The room temperature values of $4\pi M$ were large (e.g. $4\pi M = 4700$ G and $H_K = 17,000$ Oe for $\text{BaFe}_{12} \text{O}_{19}$), and hence these materials could support very small bubble domains (typically $< 0.3 \, \mu m$). Substituting $\text{Al}$ for $\text{Fe}$ ($\text{MFe}_{12-x} \text{Al}_x \text{O}_{19}$) reduced both $4\pi M$ and the anisotropy constant $K_u$, although $4\pi M$ decreased more rapidly and consequently $H_K$ increased. In this way, bubble domains as large as $10 \, \mu m$ could be obtained. Unfortunately, the poor dynamic properties of the hexagonal ferrites rendered them unsuitable for bubble applications. The initial domain wall mobilities were extremely low $[18,19]$. For example, that of $\text{PbFe}_8 \text{Al}_4 \text{O}_{19}$ was only $3 \text{cm/sec/Oe}$. Moreover, the wall velocities saturated at rather low values in the 100-600 cm/sec range as the drive field was increased.

At this point (1969), bubbles were in danger of being relegated to the status of a laboratory curiosity because of the materials problem. The orthoferrites exhibited large domain wall mobilities (5000 cm/sec/Oe for $\text{YFeO}_3$), but the bubbles were too large to achieve an economical bit packing density. On the other hand, bubbles in the appropriate size range were found in the hexagonal ferrites, but they could not be propagated fast enough. Then, in 1970, Bobeck et al. announced the discovery that some flux-grown ferrimagnetic
garnet crystals possessed an anomalous uniaxial anisotropy that was induced during crystal growth and that stable bubble domains with properties desirable for device use existed in these crystals [20].

The simplest chemical formula for the ferrimagnetic rare-earth iron garnets is \( \text{R}_3\text{Fe}_5\text{O}_{12} \) where \( \text{R} \) is a rare-earth or yttrium. These materials have been in use for some time, ever since the discovery of the very versatile yttrium iron garnet or YIG (\( \text{Y}_3\text{Fe}_5\text{O}_{12} \)) in the 1950's [21]. Because of their intrinsic cubic crystalline anisotropy, the garnets were not considered for bubble applications at first. However, Bobeck's discovery that sufficient uniaxial anisotropy could be growth-induced in flux-grown garnet crystals led to the adoption of the material which is now being used in device development.

The materials used in Bobeck's original work were garnet crystals which had to be sliced into thin platelets for bubble applications. It was soon discovered that epitaxial magnetic garnet films grown on non-magnetic substrates by either chemical vapor deposition (CVD) [22,23] or liquid phase epitaxy (LPE) [24] also exhibited growth-induced anisotropy. At present, LPE is the method universally used to grow magnetic garnet films because of better reproducibility, lower defect density, and greater ease in adjusting film composition [25]. The "dipping" technique of LPE consists of immersing a polished, single-crystal, non-magnetic garnet substrate suspended by a
platinum wire into a solution containing the constituents of the desired garnet. The substrates are mounted horizontally and rotated at 50-250 rpm to ensure uniform film growth. When the solution is at the proper temperature and state of saturation, a garnet film nucleates and grows on the substrate at a rate of 0.1 to 1 μm per minute [26]. After the desired thickness has been achieved, the substrate is withdrawn from the solution. Fig. 2 shows a cross section of a furnace used for epitaxial growth.

The most important requirement for successful garnet epitaxy is that the lattice parameters of the substrate and the magnetic garnet film should nearly match [27]. The most extensively used substrate compositions are the rare-earth gallium garnets such as Gd₃Ga₅O₁₂ (gadolinium gallium garnet or GGG). Substrate preparation is extremely important because any dislocations, inclusions or other defects on the substrate surface will nucleate growth defects in the deposited magnetic garnet films.

The attractiveness of the magnetic garnets for bubble domain applications stems from the versatility of the garnet structure in accepting various substitutions, and the consequent wide range of possible magnetic properties. The use of multiple rare earths makes possible adjustment of the growth-induced anisotropy and hence of the quality factor Q. Choice of the rare earths used makes possible temperature insensitive compositions by adjustment of the magnetic compensation temperature. Finally, substitution of non-
Fig. 2. Cross section of a furnace used to grow garnets by liquid phase epitaxy. Substrates can be mounted either horizontally or vertically. From [27].
magnetic ions on the iron sublattices, particularly $\text{Al}^{3+}$ or $\text{Ga}^{3+}$, enables one to precisely adjust the room temperature magnetization. Indeed, the room temperature $4\pi M$ of the magnetic garnets can be adjusted from zero to over 1800 G [25], although the values chosen for bubble applications are usually in the low hundreds of gauss. Two examples of compositions which have been used in device development work are $\text{Y}_{2.62}\text{Sm}_{0.38}\text{Fe}_{3.85}\text{Ga}_{1.15}\text{O}_{12}$ ($4\pi M = 200$ G) and $\text{Y}_{2.35}\text{Eu}_{0.65}\text{Fe}_{3.8}\text{Ga}_{1.2}\text{O}_{12}$, both of which have bubble diameters in the 6 $\mu$m range [28,29]. This corresponds to a density of $10^6$ bits/in$^2$ for a field-access T-bar type device. According to Almasi [30], as of 1973 the state of the art using garnet materials was about 5 $\mu$m bubbles operating at 500 KHz.

In the effort to find garnet compositions which would have high mobilities suitable for use in high speed memories, two difficulties were encountered. The first of these was the discovery of "hard bubbles" [31]. Hard bubbles are characterized by a diameter variation of 10:1 over a stable bias range of about 0.23 M as compared to a 3:1 diameter variation over a stable bias range of 0.1 M for the normal bubbles described by Thiele's theory. This unusual stability is not objectionable, but hard bubbles also have an undesirably low mobility and they also move down a magnetic field gradient at an angle to the gradient instead of parallel to it. The behavior of hard bubbles can be explained by assuming that the domain wall sur-
rounding a bubble domain is divided into Bloch wall segments of opposite polarity separated by Neel wall segments usually referred to as Bloch lines [31]. The "hardness" of a bubble depends upon the number of Bloch lines. One of the two possible bubbles with two Bloch lines behaves most like a normal bubble. While a bubble with no Bloch lines moves at an angle with respect to a field gradient, it does conform to the predictions of Thiele's theory with regard to static stability. Several methods for suppressing the formation of hard bubbles have been found [32,33,34], but the simplest and quickest is probably ion implantation. Hard bubbles are never observed in the orthoferrites because their magnetic properties are not quite isotropic normal to the easy axis (recall \( a \neq b \) for the orthorhombic structure) and this favors the formation of bubbles with two Neel wall segments.

The second problem which arose was the wide scatter in bubble velocity seen in the same sample with the same drive field as the speed of the bubbles was increased. This phenomenon was called dynamic conversion and was explained as the result of a change in the spin configuration of the bubble wall to a spin structure of lower mobility while in motion. While large maximum velocities could still be observed in some cases, the wide scatter in velocity made reliable high speed propagation in devices impossible. Vella-Coleiro [35] found that garnet compositions containing rare-earth ions with a larger Gilbert damping constant \( \alpha \) showed a reduced tendency toward dynamic conversion,
while low $\alpha$ materials exhibited dynamic conversion at low drive fields. Unfortunately, the high $\alpha$ materials had smaller mobilities, and this threatened to limit the use of garnets to memories where the data rate was less than $2 \times 10^6$ bits/sec. The solution to this difficulty was found by Le Craw et al. [36], who noted that Slonczewski's equation for the critical velocity above which uniform motion for a plane wall is not possible [37],

$$v_p = \frac{\gamma A}{h \sqrt{K_u}}$$

contained the gyromagnetic ratio $\gamma$, and hence the Lande $g$-factor also, in the numerator. Using the fact that Eu$^{3+}$ has a very high $g$ because of its $J = 0$ ground state, they designed a material, Eu$_{1.45}$Y$_{0.45}$Ca$_{1.1}$Fe$_{3.9}$Si$_{0.6}$Ge$_{0.5}$O$_{12}$, for which $g > 30$, $\mu_w = 1400$ cm/sec/Oe, and $v_p \approx 30,000$ cm/sec.

Because of the desire to increase the storage density as much as practicable in order to build large capacity memories, efforts have been made to fabricate garnet materials that will support micron and sub-micron bubbles. Plaskett, et al. [38] reported that Eu$_2$Y$_1$Fe$_5$O$_{12}$ films deposited on Sm$_3$Ga$_5$O$_{12}$ substrates could support stable bubbles as small as 0.6 $\mu$m in diameter with $4\pi M \approx 1500$ and $Q \approx 3$. However, the anisotropy in this case was stress-induced by a mismatch between the film and substrate lattice parameters, which usually results in a lower mobility than in materials where growth-induced anisotropy is the dominant contribution to $K_u$. Nevertheless, using a
garnet of this type, they were able to operate a 100-bit T-bar shift register at 100 KHz with 0.8 μm bubbles, giving a storage density of 6.7 X 10^7 bits/in^2 [39]. The narrow-linewidth permalloy patterns for this device were prepared by electron-beam lithography. Giess et al. [40] reported 1 μm diameter bubbles on (EuTm)₃ (FeGa)₅ O₁₂ films approximately 0.7 μm thick. A Q of 2.8 was claimed with 4πM ≈ 700 G. This material also exhibited good temperature stability of magnetic properties. Bullock, et al. [41] reported device operation on Luₓ Sm₃₋ₓ Fe₅ O₁₂ (1.5 ≤ x ≤ 1.9) with large growth-induced anisotropy (∼ 3 X 10⁵ ergs/cm³). Bubble diameters were ∼0.8 μm, the magnetization was approximately 1700 G, and Q ranged from 1.5 to 2.5. Using a bias field of 1200 Oe, straight line T-bar propagation at quasistatic frequencies was achieved with a 100 Oe rotating field. These efforts indicated that the major limitations of garnets for micron and sub-micron bubble applications may result from the fact that the Q values of 1.5-3 are uncomfortably low. George [42] has made an analysis which suggests that Q should be in the 4.5-5.0 range for 1 μm bubbles that operate at 6-8 MHz.

The last group of materials discovered for use in bubble memories are the amorphous rare-earth transition-metal alloys. Chaudhari, et al. [1] found that films of Gd-Co or Gd-Fe prepared by RF or dc sputtering would support bubble domains. These amorphous materials will be discussed more thoroughly in the next chapter.
A convenient graphical method of comparing the properties of different classes of bubble materials is the materials status chart first used by Gianola, et al. [3], and shown in Fig. 3. This a log-log plot of $H_K$ vs. $\frac{4\pi M}{H}$ on which lines of constant bubble diameter (assuming $d \approx 8l$), quality factor $Q$, and anisotropy $K_u$ are indicated. Hence one can see at a glance the strengths and weaknesses of different types of materials for bubble applications.
Fig. 3. Materials status chart.
II. AMORPHOUS RARE EARTH-TRANSITION METAL ALLOYS

II.1 Amorphous Alloys for Bubble Applications

The first experimental work on the properties of amorphous rare-earth transition-metal alloys was that of Orehotsky and Schroder in 1972 who investigated amorphous Gd-Fe thin films [43]. Films with 15-94 atomic % iron were prepared by co-evaporation onto substrates held at 77°K. All the alloys had an amorphous structure that was stable at room temperature. The alloys were found to exhibit ferri-magnetic order in which the magnetic moments of the iron atoms were aligned opposite to the moments of the gadolinium atoms. Some films with lower net magnetizations could not be saturated in the plane of the film even in fields up to 18,000 Oe. This led to the conclusion that the films were magnetically anisotropic with an easy axis normal to the film plane. It was conjectured that this anisotropy was associated with an isotropic stress in the plane of the film due to substrate constraints.

Although the existence of perpendicular anisotropy in amorphous Gd-Fe films did not attract wide attention at first, Orehotsky's and Schroder's discovery did lead workers at IBM to investigate amorphous Gd-Fe and Gd-Co for bubble applications. Chaudhari, Cuomo, and Gambino [1] prepared films by both RF and dc sputtering using arc-melted targets, and found that under certain conditions of fabrication alloys of the appropriate compositions satisfied Thiele's
condition, $H_K > 4\pi M$, and would support bubble domains. Bubbles ranging in size from a few microns to less than one micron were observed. The room temperature magnetization data for amorphous Gd-Co showed a minimum near 79 atomic % Co (see Fig. 4.). This variation of $4\pi M$ with composition was explained by antiferromagnetic coupling between the Co and Gd atoms (as in Gd-Fe), with the minimum interpreted as a room temperature ferrimagnetic compensation point where the moments of the two sublattices cancel. The dependence of the compensation temperature on composition is shown in Fig. 5 [44]. Application of a negative bias voltage to the substrates during sputtering varied the composition of the films by as much as 10 atomic % from the target composition. Coercivities were found to vary from one-half to a few percent of the saturation magnetization. The anisotropy constant $K_u$ was determined by ferromagnetic resonance, and typical values of $Q$ were well in excess of one. The anisotropy was not considered to be stress-induced, since a film deposited on a NaCl substrate showed no change in domain strip width after the substrate was dissolved in water. Magnetocrystalline anisotropy was also eliminated since diffraction data showed that if any coherently scattering regions did exist in the films, they were less than 25 Å in diameter. Pair ordering and shape anisotropy were considered to be two remaining possibilities that might contribute to $K_u$. Within a short time, Chaudhari and his co-workers built and operated shift registers on Gd-Co in
Fig. 4. Magnetization dependence on composition for sputtered amorphous Gd-Co.
Fig. 5. Compensation temperature versus composition for amorphous Gd-Co alloys.
which the bubble diameter was 2 μm. They also deposited films on a variety of substrates, including silicon, and found that the film properties were independent of the substrate, whether it was amorphous, polycrystalline, or single crystal [1,45]. This is one of the most important features of amorphous Gd-Co for bubble applications, since it raises the possibility of fabricating a completely integrated memory in which both the bubble memory and the associated semiconductor circuitry are on the same chip. Amorphous bubble materials also offer the advantage of simpler and less expensive preparation, particularly on a large scale, than the complicated process described for garnets in Chapter I.

After this initial work, extensive effort aimed at a better understanding of the properties of amorphous Gd-Co continued. Cronemeyer [46] studied the anisotropy by ferromagnetic resonance and found values ranging from $0.5 \times 10^5$ - $4 \times 10^5$ ergs/cm$^3$. Gambino, et al. [44] attributed the observed anisotropy to Co pair ordering in which there were about one per cent more Co pairs oriented parallel to the film plane than perpendicular to it. They theorized that this preferential orientation came about as a result of the resputtering of atoms in the film due to the substrate bias voltage. This was the first publication in which the key role of substrate bias in producing films with uniaxial anisotropy was acknowledged.
Using a molecular field approximation, Hasegawa [47] calculated that the exchange constant $A$ increased linearly from $5.7 \times 10^{-7}$ to $6.6 \times 10^{-7}$ ergs/cm for Gd$_{1-x}$Co$_x$ films with $0.75 < x < 0.85$. In addition, he found that postdeposition thermal annealing in the presence of a 3kOe field applied perpendicular to the film plane resulted in a lower coercivity, $H_C$. It also tended to reduce $4\pi M$ and $K_u$ for films with less than 80 atomic % Co. Ion radiation was found to be another means of reducing $H_C$ by as much as a factor of two [48]. Using these two treatments, coercivities of less than one oersted were obtained for films suitable for bubble applications. Shirakawa, et al. [49] found coercivities that were much larger than those reported by Hasegawa for his unannealed films. They reported that $H_C$ rose to several hundred oersteds for films very close to compensation. Chaudhari et al. [50] and Matsushita et al. [51] showed that the large values of coercive force near compensation made Gd-Co films a suitable material for the storage of information by thermomagnetic compensation point writing.

Bourne et al. [52] prepared amorphous films of Gd-Co using RF sputtering with dc substrate bias, whereas other investigators had used an effective substrate bias that was RF in origin. They found that the optimum bias range for inducing perpendicular anisotropy with $H_K > 4\pi M$ was $-50v$ to $-100v$. They also noted that a uniform bias electric field configuration was essential to achieving uniform film properties.
Sputtered amorphous Gd-Fe films for bubble applications were investigated by Kobayashi, Imamura, and Mimura\[53,54,55]\ and by Zwingman, et al. [56]. The Japanese group found $H_K > 4\pi M$ for films with 65 to 83 atomic % iron, with compensation at 74 atomic % iron. Anisotropy constants ranged from $1 \times 10^5$ to $4 \times 10^5$ ergs/cm$^3$. They concluded that the magnetic properties of Gd-Fe were very similar to those of Gd-Co, except that the smaller value of the exchange constant resulted in a smaller characteristic length for films with the same magnetization. Zwingman reported lower anisotropy energies on the order of $4 \times 10^4$ ergs/cm$^3$ ($Q < 5$) and $H_K > 4\pi M$ over a composition range of only two atomic percent. He concluded that the anisotropy in his films was due to an isotropic in-plane stress, the origin of which was attributed to the sputter deposition process and not to differing coefficients of thermal expansion between film and substrate.

From the magnetization data for Gd-Co in Fig. 4, it can be seen that in order to have a magnetization small enough to form bubble domains of sufficient size to permit device fabrication, the alloy composition must be close to the compensation point. However, the properties of compositions close to the compensation point are extremely temperature sensitive. In order to make a temperature insensitive composition, both the Curie point and the compensation temperature must be far from room temperature, as shown in Fig. 6. Satisfying this condition with a sufficiently low
Fig. 6. The desired positions of the Curie point and compensation point relative to room temperature in order for the magnetic properties to be relatively independent of temperature at room temperature.
value of room temperature magnetization requires a ternary alloy. Chaudhari, et al. [57] studied the systems Gd-Co-X where X = Cu, Au, Mo, or Cr. They found that each ternary system could be described in terms of a paramagnetic boundary, defined by compositions with Curie points at room temperature, and a compensation line, defined by compositions which are compensated at room temperature. The ternary system Gd-Co-Mo is shown in Fig. 7. In the Mo and Cr systems, the lowering of the Co moment dominated and less Gd was required to compensate. The effect of Mo on the moment per Co atom is shown in Fig. 8. In the Au and Cu systems, the Gd-Co exchange was weakened by dilution faster than the Co moment was reduced, and more Gd was required to obtain a compensated composition at room temperature. The effectiveness of Mo in reducing the exchange constant A was shown graphically on a log-log plot of $\lambda$ vs. $4\pi M$. For Gd-Co, the data could be fitted by a straight line with a slope of negative one. Since the definition of the characteristic length could be written in the form

$$\lambda = \frac{\sqrt{32\pi \sqrt{AQ}}}{4\pi M} \approx \frac{10 \sqrt{AQ}}{4\pi M}$$

this implied that the product AQ was nearly constant. For binary Gd-Co, AQ was approximately $12.5 \times 10^{-6}$ erg/cm. As shown in Fig. 9, increasing the Mo content decreased the value of the AQ product, primarily by decreasing A.

Chaudhari, et al. found that the addition of 16 atomic % Mo
Fig. 7. Magnetic properties of the Gd-Co-Mo system.
Fig. 8. Saturation moment for cobalt per atom versus fraction of Mo \((y/[y+(1-y)x])\).
Fig. 9. Characteristic length versus magnetization. Values are shown plotted for films prepared from targets containing various concentrations of Mo. The Mo(I) target contained 7% Mo, Mo(II) 10% Mo, and Mo(III) 15% Mo.
to a particular Gd-Co alloy reduced $4\text{TM}$ from 1260 G to 480 G and AQ from $12.5 \times 10^{-6}$ ergs/cm to $1.0 \times 10^{-6}$ ergs/cm, while maintaining a stable bubble size of 2 m.

One of the difficulties in assessing ternary systems has been the necessity to prepare many alloy targets, since only a limited range of compositions could be achieved using a single target with different substrate biases. This difficulty was circumvented by using "mosaic" type targets [52,53] or a multiple target sputtering system [58,59]. Another approach to this problem was that of Hasegawa [60]. He formulated a two sublattice molecular field model based on Néel's theory of ferrimagnetism which enabled him to predict the properties of various film compositions based on limited experimental data. Application of this model to Gd-Co-Mo [60] and Gd-Co-Au [61] confirmed that agreement between its predictions and experiment was adequate. Subsequently, Hasegawa extended the model to predict the temperature dependence of $L$, $Q$, and the collapse field $H_o$ for Gd-Co-Mo alloys tailored to support 0.25, 0.5, and 1.0 $\mu$m bubbles [62]. He concluded that 0.5 $\mu$m bubbles showed the most promise from the standpoint of temperature stability. However, it should be pointed out that his results were based on the assumption that the temperature dependence of $K_u$ could be represented by $K_u(T) = k [M_{Co}(T)]^2$, where $k$ was a constant and $M_{Co}$ was the magnetization of the Co sublattice. This assumption is of questionable validity [63].
Minkiewicz et al. [64] reported that research on Gd-Co-Cu resulted in an alloy with a large quality factor $(Q = 7.9)$ capable of supporting $1 \mu m$ bubbles with $4\chi_M = 930$ G. They also concluded that Cu does not dilute the Co sublattice as rapidly as Mo. Investigation of the Gd-Co-Cr system by Schneider [65] showed no advantage in using Cr as the third element.

These results on the ternary alloy systems Gd-Co-X, where X is a nonmagnetic additive, have led to the conclusion that Mo is the preferred substituent because of its strong affect on the Co moment (recall Fig. 8). Development work on devices using amorphous materials has focused on Gd-Co-Mo. A recent review of Gd-Co-Mo for micron and sub-micron bubble applications has been given by Kobliska et al. [5].

Hasegawa [66] pointed out that the temperature dependence of the magnetization for the Gd-Co-Mo and Gd-Co-Au systems has the same characteristics as for Gd-Co, except that $4\chi_M$ and the Curie temperature are reduced. This was because the ratio of the Gd-Co exchange interaction $(J_{\text{Gd-Co}})$ to the Co-Co exchange interaction $(J_{\text{Co-Co}})$ was not changed appreciably $(J_{\text{Gd-Co}}/J_{\text{Co-Co}} \sim .14$ for Gd-Co and Gd-Co-Mo and $\sim .11 - .25$ for Gd-Co-Au). He concluded that a system such as Gd-Co-Ni where the ratio $J_{\text{Gd-Co}}/J_{\text{Co-Co}}$ was smaller $(\sim .06 - .10)$ might offer better temperature stability [66]. Meyer and Jove [67] have also suggested substitution of Ni for Co to improve the properties of Gd-Co.
The dynamic properties of amorphous bubble materials were first studied by Kryder and Hu [68]. Their results showed typical mobilities ranging from 500 cm/sec/Oe to 2000 cm/sec/Oe for Gd-Co, Gd-Co-Au, and Gd-Co-Cu. These values compared favorably with the properties of the better garnet materials. Bubble velocities in excess of 10,000 cm/sec were measured with no evidence of non-linearity in the plot of velocity versus difference in bias field across the bubble diameter. No particular correlation of mobility or coercivity with doping element was found. Hard bubbles and dynamic conversion were observed in some samples, as discussed in connection with epitaxial garnets in Chapter I. Subsequently, Kryder and co-workers [8,9] operated a $10^7$ bit/in$^2$ memory chip using 2 μm bubbles in Gd-Co-Mo at data rates up to 1 MHz. Preliminary results indicated that rates up to 10 MHz might be possible.

Following the original announcement of Chaudhari et al. that Gd-Co and Gd-Fe were potential bubble domain materials, many other amorphous RE-TM alloys were examined both for their potential in applications and to achieve a better understanding of this new and important class of materials. Heiman, et al. [69] reported that evaporated amorphous films of Tb-Co, Tb-Fe, Ho-Co, Ho-Fe, Ho-Ni, and Gd-Fe all possessed a $K_u$ sufficient to cause the magnetization to be normal to the film plane. Gd-Co was found to be anomalous in that bias sputtering was required to produce $K_u > 2\pi M^2$. Jouve et al. [70] studied amorphous R-Co films with
R = Gd, Dy, Ho, Er made by d.c. sputter deposition. Strip domains were observed at room temperature for Gd, Dy, and Ho alloys and the Gd-Co and Ho-Co films exhibited similar anisotropy energies. They concluded that the existence of perpendicular anisotropy was independent of the rare-earth constituent, but was influenced by bias conditions during sputtering.

Noting that evaporation offered some advantages over sputtering as a preparation method, Taylor [71] studied Gd$_{1-x}$Fe$_x$ films prepared by electron beam coevaporation of the elements. He found $Q > 1$ for $0.69 < x < 0.81$ with compensation at $x = 0.74$. $K_u$ increased monotonically from $2 \times 10^5$ erg/cm$^3$ at $x = 0.67$ to $3.8 \times 10^5$ erg/cm$^3$ at $x = 0.82$ (see Fig. 10). As measured on samples with Fe-dominated magnetization, the characteristic length $l$ varied from 0.35 $\mu$m for $4K_M = 450$ G to 0.038 $\mu$m for $4K_M = 2200$ G. The magnetization data, which is shown in Fig. 11, was closely approximated by the expression $4\pi M = |36,800 - 49,700 x|$.

II.2 Anisotropy and Structure of Amorphous RE-TM Thin Films

The source of the uniaxial anisotropy in both bias sputtered and evaporated amorphous films has been a source of considerable speculation. Magnetic uniaxial anisotropy has been found to be a common feature of these films, but its exact nature appears to be dependent upon preparation methods and conditions [69,72]. For example, evaporated films of Gd-Fe, Ho-Co, Ho-Ni, Ho-Fe, Tb-Co and Tb-Fe all
Fig. 10. Room temperature uniaxial anisotropy energy as a function of composition for evaporated Gd-Fe films. Gd$_{0.08}$Fe$_{0.92}$ is polycrystalline. From [71].
Fig. 11. Room-temperature saturation magnetization as a function of composition for evaporated Gd-Fe films. From [71]
possess a $K_u$ sufficient to cause the magnetization to be normal to the film plane [69]. Gd-Fe films sputtered with or without bias also satisfy this condition [59,53], as do bias sputtered Dy-Co and Ho-Co [70]. Gd-Co is unusual in that only bias sputter deposition produces $K_u > 2\pi M^2$; thermal evaporation or sputtering without bias results in films with in-plane magnetization. Indeed, evaporated Gd-Co films exhibit a hard-axis normal to the film plane [72,76]. In this section, some of the ideas which have been put forward to explain these observations will be reviewed, including attempts to correlate the magnetic anisotropy with structural anisotropy in the films.

In general, anisotropy in magnetic materials can arise from four principle mechanisms: 1) Magnetocrystalline anisotropy 2) Stress 3) Shape anisotropy 4) Atomic short range ordering [44]. Magnetocrystalline anisotropy is the magnetic manifestation of long range atomic order. Using dark field electron microscopy on a Gd-Co sample, Herd and Chaudhari [73] found no evidence of microcrystallites. If any coherently scattering regions did exist in the sample, they concluded that their maximum size would have to be less than the 15 Å resolution limit of the microscope. X-ray diffraction data have also confirmed the amorphous structure of these RE-TM alloys. Therefore, magnetocrystalline anisotropy can be ruled out as a contributor to $K_u$.

Stress-induced anisotropy has also been discarded as the cause of $K_u$ for bias sputtered Gd-Co because films
deposited on NaCl substrates showed no appreciable change in domain strip width before and after the substrate was dissolved [44]. Since the strip width is proportional to the characteristic length, \( \ell \), and \( \ell \) is given by
\[
\ell = \frac{\sqrt{AK_U}}{\pi M^2}
\]
Gambino, et al. concluded that \( K_U \) was not sensitive to substrate constraint. The only investigators to attribute the anisotropy observed in their films to a stress-induced mechanism have been Zwingman et al. [56], who found anisotropies in bias-sputtered Gd-Fe one order of magnitude smaller than the values measured for either sputtered or evaporated Gd-Fe by other researchers.

Shape anisotropy arises because of the geometry of the magnetic regions. For example, an ordered cluster of atoms in a region of substantially unordered material will have a magnetization along the long axis of the atom cluster because strong demagnetizing fields would exist along the short axis of the cluster. Since it does arise from demagnetizing effects, this type of anisotropy has a theoretical upper limit of \( K_U = 2\pi M^2 \). The observed anisotropy in amorphous RE-TM thin films is typically several times greater than this, and hence shape anisotropy has generally been ruled out as the predominant source of the observed \( K_U \). Moreover, by studying the effect of non-perpendicular incidence of atoms during film growth, Onton and Lee [72] concluded that shape anisotropy, due to a tendency for columnar
growth caused by self-shadowing, has no significant effect in the anisotropy of thermally evaporated Gd-Co.

Recently, however, Esho and Fujiwara [74] described a mechanism whereby shape anisotropy could provide $K_u > 2\pi M^2$ for bias-sputtered Gd-Co. They proposed that the growth-induced anisotropy was due mainly to shaped voids elongated along the film thickness direction caused by Argon inclusion. Such voids could give rise to $K_u > 2\pi M^2$ if a shell surrounding each void had a high Co-rich composition, and consequently a large saturation magnetization. The composition difference between the shell and the surrounding areas of the film was assumed to be a consequence of the preferential resputtering of Gd-atoms caused by applying a negative substrate bias voltage. Under the assumption that the void volume is negligibly small, the shape anisotropy energy per unit volume was given by

$$E_A = -\frac{1}{2} (N_{||} - N_{\perp}) \Delta M^2 \beta (1 - \beta)$$

where $N_{||}$ and $N_{\perp}$ are the demagnetizing factors of the shell parallel and perpendicular to the long shell axis, $\Delta M$ is the magnetization difference between the shell and the environment, and $\beta$ is the partial volume of the shells. If $\Delta M$ was higher than 400 emu/cm ($\Delta 4\pi M > 5000$ G), $E_A$ gave an anisotropy energy comparable to the observed levels of $K_u$ with reasonable values for $N_{||}$, $N_{\perp}$ and $\beta$. As evidence to support this model, they noted that $K_u$ increases with bias voltage, and hence also with argon content, for
films within a limited range of saturation magnetizations (200-600 G). They also found that the density of the films sputtered at high bias voltages was lower. Since the observed decrease would have corresponded to 25 At% Ar, which seemed too high to be reasonable, they concluded that part of the decrease was due to void formation. Finally, it was observed that the Kerr rotation decreased more rapidly with time for films sputtered at high biases. Since this decrease was associated with oxidation of constituents, an increase in void concentration with bias voltage was inferred.

Most of the attempts to explain the growth-induced anisotropy have focused on atomic short range ordering and pair ordering, which can be regarded as a special case of short range order involving nearest neighbors only. The first attempt to explain the anisotropy in bias sputtered Gd-Co was that of Gambino et al. [44], who attributed $K_u$ to a preferential orientation of Co-Co pairs. From studies of hcp cobalt they concluded that the easy direction associated with a Co-Co pair was perpendicular to the pair axis and that the associated anisotropy was $10^{-15}$ to $10^{-16}$ ergs/pair. The number of excess nearest neighbor pairs in the film plane required to account for the observed anisotropy ($\sim 10^5$ erg/cm³) was $10^{20}$ to $10^{21}$ pairs/cm³. This corresponded to 0.1 to 1.0% more pairs in-plane than out-of-plane.
The excess of the in-plane pairs was attributed to the sputter deposition process. Since Co-Co or Gd-Gd bonds were less stable than Gd-Co bonds, an atom bonded to a like surface atom had a higher respattering probability. This increased the statistical probability of a Gd-Co pair oriented perpendicular to the plane of the film and reduced the probability of Co-Co pairs oriented perpendicular. The excess Co-Co pairs in the plane of the film resulted from the decreased concentration perpendicular to the plane. The following evidence was offered to support this model. The anisotropy was found to be relatively independent of temperature at room temperature, indicating that it was associated with the Co sublattice. Ion radiation damage experiments showed that a dosage of $7 \times 10^{15}$ argon ions/cm$^2$ (2 MeV) was sufficient to destroy the uniaxial anisotropy when no magnetic field was applied to the sample. It was also observed that a dosage of $5 \times 10^{14}$ argon ions/cm$^2$ was capable of inducing perpendicular anisotropy in the presence of an applied perpendicular magnetic field of 1.6 kG [48,75]. The level of radiation used was calculated to be sufficient to cause displacement of approximately half the atoms in the sample, but not sufficient to fill voids or level surface structure. In addition, it was argued that radiation damage would be extremely unlikely to cause oriented voids, and even if such shape effects did occur, the presence of an applied field should not have much effect. On the other hand, pair ordering should be
more sensitive to ion radiation damage, and the formation of ordered pairs might be expected to be influenced by an external magnetic field.

Heiman, et al. [69] studied the temperature dependence $K_u$ for sputtered Gd-Co and found it to be relatively flat except in the neighborhood of the compensation temperature, where a sharp decrease was noted. This decrease was also observed by Cronemeyer [46], although more recent results [63] indicate that it may be a spurious effect stemming from the difficulties in accurately measuring $K_u$ near compensation, where $H_K$ becomes very large. From the generally weak temperature dependence, Heiman et al. concluded that $K_u$ was most likely associated with the Co sublattice magnetization, as previously suggested by Gambino, et al. [44]. However, they cited unpublished x-ray diffraction results which seemed "to rule out pair order", and argued that the anisotropy was more likely due to a "preferred pseudo-crystalline coordination" or "anisotropic local coordination," i.e., short range order involving a larger cluster of atoms than just simple pairs.

Heiman and co-workers also sputter deposited Gd-Co films on substrates canted with respect to the target. They found perpendicular or in-plane magnetization depending on the presence or absence of bias, but found no evidence that the easy axis was also canted. Noting that $K_u$ also increased monotonically with increasingly negative bias for a fixed target, they concluded that the pre-
dominant influence on the uniaxial anisotropy was the bias field directed resputtering.

Chaudhari and Cronemeyer [63] measured the temperature dependence of the uniaxial anisotropy in sputtered Gd$_{1-x-y}$Co$_x$Mo$_y$ films by ferromagnetic resonance. They found that it was impossible to fit the observed $K_u(T)$ variations to be proportional to $M_{co}^n$ where $n = 2$ to $3$ and $M_{co}$ is the cobalt sublattice magnetization. This was a blow to the cobalt pair ordering hypothesis of Gambino et al. [44]. A fit for $n = 4$ was obtainable, but they found "no justification for a quadrupolar type variation under the circumstances". Instead, to fit the data it was necessary to use the pseudo-dipolar hypothesis [76]

$$K_u = C_{11} M_1^2 + C_{12} M_1 M_2 + C_{22} M_2^2$$

where $M_1$ and $M_2$ are the sublattice magnetizations and $1 = \text{Gd}, 2 = \text{Co}$. For two samples they found the following values of the $C_{ij}$'s:

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{22}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>$x = .74$</td>
<td>$y = .11$</td>
<td>$-0.558$</td>
</tr>
<tr>
<td>Sample B</td>
<td>$x = .71$</td>
<td>$y = .16$</td>
<td>$-0.041$</td>
</tr>
</tbody>
</table>

These results showed the Gd-Co coupling to be dominant and that even the Gd-Gd coupling was of considerable importance. In terms of a pair model, since all the coefficients were negative, the Gd-Co pairs contributed to perpendicular anisotropy and the Co-Co and Gd-Gd pairs to in-plane anisotropy (one sublattice was regarded as positive and the other
negative, so that the net magnetization was $M = M_1 + M_2$.

Although these results were both interesting and surprising, it was concluded that they did not really unveil the physical situation which was responsible for the anisotropy.

Although Orethosky and Schroder [43] noted the existence of perpendicular anisotropy in their evaporated Gd-Fe films, Heiman and Lee [77] were the first to measure values of $K_u$ for evaporated RE-TM alloys. They reported anisotropies of about $3 \times 10^6$ ergs/cm$^3$ for co-evaporated Ho-Co films at 4.2K. Stress-induced anisotropy was ruled out because films prepared on carbon foils supported on Collodion-coated grids showed uniaxial anisotropy. The $K_u$ values were considered to be too large to be explained by shape anisotropy. In a subsequent publication, Heiman et al. [69] reported the temperature dependence of $K_u$ for Ho-Co. Since the anisotropy of Ho-Co was an order of magnitude larger than that for Gd-Co at low temperature, and since it exhibited a strong temperature dependence, they suggested that $K_u$ was dependent at least in part on the orbital moment of the Ho atom. They postulated that local anisotropy fields, though basically random, might have a preference for the direction perpendicular to the film plane. It was also noted that if substrates were canted so that the incident atomic beam made an angle to the substrate normal, then the easy axis was tilted toward the incident beam direction. Based upon these observations, they suggested that the anisotropy in evaporated films is princi-
pally due to a short-range pseudo-crystalline coordination on the order of 10 Å which has a growth-induced preferred direction due to the unidirectionality of the incident beam.

As mentioned in the previous section of this chapter, the anisotropy in evaporated Gd-Fe thin films was studied by Taylor [71]. From the monotonic increase in $K_u$ with increasing Fe content over the range from 67 to 83 At % Fe, he concluded that ordering in the Fe component was principally responsible for the anisotropy. While not excluding pair ordering, he suggested that longer-range structural ordering was more likely, primarily because the anisotropy in a polycrystalline Gd$_{0.08}$Fe$_{0.92}$ film was consistent with that of the amorphous films (see Fig. 10).

In two subsequent papers, Taylor and Gangulee [78,79] investigated the magnetic anisotropy in evaporated Gd-Co and Gd$_x$(Fe$_{1-y}$Co$_y$)$_{1-x}$ films. For Gd-Co (60 to 95 At % Co) they found a hard axis perpendicular to the film plane for less than 91 At % Co and easy and moderate directions within the film plane. The data is shown in Fig. 12. The anisotropy data were fitted with the dipolar equation

$$K_u = 0.660 M_{Co}^2 + 2.218 M_{Co} M_{Gd} + 0.097 M_{Gd}^2$$

where $M_{Co}$ and $M_{Gd}$ are the sublattice magnetizations. Interpreting this result in terms of a pair ordering mechanism, they concluded that Gd-Co pairs contribute to in-plane anisotropy while Gd-Gd and Co-Co pairs contribute to perpendicular anisotropy. This was exactly the opposite of the findings of Chaudhari and Cronemeyer [63] based on the tem-
Fig. 12. Perpendicular anisotropy constant as a function of composition for evaporated Gd-Co films. Open and filled circles are experimental force balance and FMR data respectively. Solid line is calculated from

\[ K_u = 0.660M_{Co}^2 + 2.218M_{Co}M_{Gd} + 0.097M_{Gd}^2 \]

From [78].
temperature dependence of $K_u$ in sputtered Gd-Co-Mo films. However, it should be noted that the Gd-Co interaction was dominant in both cases. The anisotropy for evaporated Gd-Co also showed little temperature dependence, ranging from $-5.3 \times 10^5$ at $4.2^\circ K$ to $-4.6 \times 10^5$ at room temperature for Gd$_{0.25}$Co$_{0.75}$.

Apparently dropping his previous objections to pair ordering in Gd-Fe, Taylor noted that his $K_u$ data for Gd-Fe could be fitted by the dipolar equation

$$K_u = 0.922 M_{Fe}^2 + 1.356 M_{Fe} M_{Gd} + 0.799 M_{Gd}^2.$$ 

Therefore, it appeared that for both Gd-Co and Gd-Fe the unlike RE-TM pairs contributed to in-plane anisotropy while the like pairs, RE-RE and TM-TM, contributed to perpendicular anisotropy. On this basis, the presence of a hard axis magnetization normal to the film plane, instead of an easy axis, in evaporated Gd-Co is due to the dominance of Gd-Co pairs, while Fe-Fe and Gd-Gd pairs control the anisotropy in Gd-Fe. Taylor and Gangulee were able to extend this analysis to the ternary system Gd-Fe-Co [79]. They found that the model satisfactorily described the data for all films that were amorphous. The additional contribution due to Fe-Co pairs was found to contribute to perpendicular anisotropy.

Several attempts have been made to find a structural basis for the observed anisotropy using x-ray techniques. A useful characterization of the atomic arrangements in an amorphous solid is the radial distribution function (RDF).
The RDF of an arrangement of identical atoms describes the average number of atoms at distances between \( r \) and \( r + dr \) from some chosen atom as origin, further averaged by taking each atom in turn as the origin [80]. Cargill [81] determined two RDF's for an amorphous sputtered Gd_{0.18} Co_{0.82} alloy. One was obtained from x-ray scattering data taken with the scattering vector perpendicular to the film surface and one from data taken with the scattering vector parallel to the film surface. The results suggested a deficiency of in-plane Gd-Gd nearest neighbor pairs, but detected no difference in the number of Co-Co or Gd-Co pairs oriented perpendicular and in-plane. However, since experimental uncertainties were on the order of 3%, the 1% preferential orientation of Co-Co pairs suggested by Gambino et al. [44] could have gone undetected.

Wagner et al. [82] also measured x-ray intensities in both transmission and reflection in an attempt to detect a preferred atomic orientation. Transmission and reflection data on a bias sputtered alloy of the composition 77-17-6 (Co-Gd-Ar) showed no structural differences. They concluded that no large scale preferred orientation appeared to exist in the film. They also obtained reduced radial distribution functions, \( G(r) = 4\pi r [\rho(r) - \rho_s] \) where \( \rho_s \) is the average atomic density of the alloy, for Gd-Co films sputtered with and without bias. The peaks in \( G(r) \) at larger values of \( r \) (i.e. \( r > 6 \, \text{Å} \)) exhibited larger heights in the biased film than in the unbiased film. This seemed to in-
dicate that the biased film, the one with magnetic anisotropy, possessed structural order over longer distances than the unbiased film.

Onton et al. [83] and Covault [59] et al. found a correlation between the structure of amorphous Gd-Co, as revealed by x-ray diffraction, and the bias voltage present during sputter deposition. Films sputtered with zero bias voltage typically showed one broad peak in the x-ray diffraction spectrum, while films sputtered with -100 volts bias showed two broad peaks with a shoulder between them. These are the type of results which Heiman et al. [69] had used to argue against pair ordering (see p. 44), presumably on the basis that pair ordering alone could not give rise to such a pronounced change in the diffraction spectrum. Onton and co-workers were also able to match the x-ray diffraction spectrum from a Gd-Co$_{3.1}$ film sputtered at -100 v. bias using a microcrystalline model based on 11 Å Gd Co$_5$ crystallites. Since Gd Co$_5$ has an easy plane anisotropy constant of $4 \times 10^7$ ergs/cm$^3$, only about 1% alignment of the local easy planes would be required to explain the observed net anisotropies on the order of $10^5$ ergs/cm$^3$[84].

Onton and Lee [72] found that the x-ray diffraction spectrum of thermally evaporated amorphous Gd-Co exhibited the same features as the spectrum of the bias sputtered film discussed above. The thermally evaporated films were characterized by hard axis anisotropy normal to the film plane with $K_U \sim -5 \times 10^5$ ergs/cm$^3$. Although the nature of
the anisotropy is different, thermally evaporated and bias sputtered Gd-Co give rise to similar x-ray diffraction patterns. However, for Gd-Co sputtered without bias, which exhibits little or no anisotropy, the x-ray pattern is distinctly different. According to Onton and Lee, these results continued "the findings that magnetic anisotropy in amorphous Gd-Co correlates with a prevalent structural unit within the amorphous matrix."

II.3 Magnetism in Amorphous RE-TM Alloys and the Intermetallic RE-TM Compounds

The concept of an amorphous material exhibiting long range ordered magnetism despite the lack of long range structural periodicity is of relatively recent origin. The first theoretical evidence that translational invariance was not a requirement for ferromagnetic order was given by Gubanov [85] in 1960. Using a molecular field model, he showed that the effect of the structural disorder was to introduce fluctuations into the exchange interaction which modify the Curie temperature and the magnetization.

The first experimental observation of amorphous ferromagnetism was by Brenner et al. [86] in 1950. They observed ferromagnetic behavior in an amorphous film of Co-P prepared by electrodeposition. Until recently, most experimental studies of ferromagnetism in amorphous solids employed alloys of transition metals (Fe,Co,Ni) with elements of Groups III A, IV A, or V A (B,C,Si,P) [81]. In general, such materials are amorphous for only a limited composition
range, typically 75 to 85 atomic percent of the transition metal. These "metal-metalloid" alloys have been produced as amorphous solids by rapid quenching from the liquid state (e.g. by "splat cooling"), by evaporation in vacuum and condensation on cooled substrates, by electrodeposition from aqueous solutions, and by "electroless" (chemical) deposition. Interpreting the magnetic properties of these materials is complicated by the fact that their equilibrium crystalline forms are usually mixtures of two or more phases. This rules out comparisons of properties between amorphous and single phase crystalline materials of the same composition and makes it difficult to separate effects of composition and structural disorder [81].

Beginning in 1972, RE-TM alloys which are amorphous over wide composition ranges (unlike the "metal-metalloid" alloys) have been made by vacuum evaporation and by d.c. and r.f. sputtering. Aside from their technological importance in applications such as magnetic bubbles and thermomagnetic writing, these alloys offer a unique opportunity to gain a greater understanding of amorphous magnetism since there are a number of intermetallic RE-TM compounds whose magnetic properties can be directly compared with those of the corresponding amorphous alloy of the same composition. In this section, some of the common features of magnetism in the amorphous and crystalline states, and some of the differences, will be discussed.
Primarily because of the difference in atomic radii, the equilibrium phase diagrams of the rare earths with the 3d transition metals do not exhibit any large homogeneity regions. In the processes of vacuum evaporation and sputtering, where a rapid transition from the vapor state to the solid state takes place, this lack of solubility results in the formation of amorphous alloys. However, under equilibrium conditions, compounds are formed with elements to the right of chromium in the periodic table, i.e. with manganese, iron, cobalt, and nickel [37]. In general, such intermetallic compounds can be defined as mixtures of two (or more) metals which have a well defined and simple stoichiometry. These RE-TM compounds have been the subject of extensive investigations stimulated by the search for better permanent magnet materials, a search which finally proved successful with the RECo$_5$ materials. The observed compound stoichiometries in the RE-Mn, RE-Fe, RE-Co and RE-Ni phase diagrams are shown in Fig. 13. The only compound common to all these systems is that represented by the basic formula RB$_2$, where B = Mn, Fe, Co, or Ni. The RB$_2$ compounds crystallize in the cubic Laves phase structure shown in Fig. 14. The unit cell of this structure is a cube with RE atoms at each corner and at each face center. If this cube is subdivided into eight smaller cubes, then four of the small cubes have a RE atom positioned at their centers. The other four cubes are occupied by tetrahedra
Fig. 13. The observed compound stoichiometries in the R-Mn, R-Fe, R-Co and R-Ni phase diagrams.
Fig. 14. The atomic positions in the MgCu$_2$ Laves phase structure.
whose vertical axes coincide with the [111] direction and on whose corners the TM atoms are situated.

Experimental magnetization values for the compounds with the heavy rare earths (Gd, Tb, Dy, Ho, Er) indicate the existence of ferrimagnetic order in which the transition-metal moment is coupled antiparallel to the rare-earth moment. On the other hand, compounds with the light rare-earths Pr, Nd, Sm are ferromagnetic, with parallel moment alignment. This reversal in the sign of coupling can be understood in terms of an antiferromagnetic coupling of the spin angular momentum of the rare earth to that of the transition metal, since for the heavy and light elements $J = L+S$ and $J = L-S$ respectively (see Fig. 15). The same features also exist in amorphous RE-TM alloys. These similarities arise from the fact that the major features of the d-band structure in the crystalline phase are also present in the amorphous phase [44]. From this point on, our discussion will be limited to alloys involving the heavy rare earths and the transition metals Fe and Co, since they are the ones of interest here. An extensive review of the intermetallic rare-earth compounds, including those formed with elements besides the 3d transition metals, has been given by Taylor [87].

The magnetic 4f electrons of the rare earths are considered to be well localized and may not be described as band electrons. To illustrate this point, the relative outer radial extent of the atomic electrons in Gd is shown
Fig. 15. A simple view of the relative spin orientations in the RE-TM compounds and amorphous alloys.
in Fig. 16. Also indicated is the Wigner-Seitz radius appropriate for pure Gd in its metallic state. As can be seen from Fig. 16, the 5d and 6s atomic orbitals on different atomic sites do overlap one another to a considerable extent. Consequently, they will form an s-d conduction band of considerable width. In the RE-TM alloys, the 4s electrons of the 3d-metal will also contribute to this conduction band. On the other hand, the 4f electrons are tightly bound to the atom and do not overlap neighboring atoms appreciably. Note that their maximum occurs well inside the outer maxima of the closed 5s and 5p shells. Hence, in the metallic alloys, the rare earths may be regarded as localized tripositive ions, with corresponding localized moments, immersed in a sea of conduction electrons to which each rare-earth atom contributes its three outer electrons. For convenience, the basic properties of the rare earth ions are summarized in Table I.

Because the 4f electrons are so well localized, the 4f wave functions on different atoms overlap negligibly. Consequently, the direct exchange interaction between 4f electrons on different sites is insignificant. Magnetic ordering involving the rare earths is accomplished through the mechanism of indirect exchange between the localized 4f electrons and the conduction band electrons. The indirect exchange mechanism was first proposed by Ruderman and Kittel to explain the long range coupling between nuclear spins interacting via the Fermi hyperfine interaction. It
Fig. 16. The relative outer radial extent of the atomic electrons in gadolinium.
<table>
<thead>
<tr>
<th>Configuration $4f^n$</th>
<th>$j^+$ ion</th>
<th>$L$</th>
<th>$S$</th>
<th>$J$</th>
<th>$g$</th>
<th>$(g-1)^2J(J+1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>La Ce$^{4+}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>Ce</td>
<td>3</td>
<td>1/2</td>
<td>5/2</td>
<td>6/7</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>Pr</td>
<td>5</td>
<td>1</td>
<td>4</td>
<td>4/5</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>Nd</td>
<td>6</td>
<td>3/2</td>
<td>9/2</td>
<td>8/11</td>
<td>1.84</td>
</tr>
<tr>
<td>4</td>
<td>Pm</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>3/5</td>
<td>3.20</td>
</tr>
<tr>
<td>5</td>
<td>Sm</td>
<td>5</td>
<td>5/2</td>
<td>5/2</td>
<td>2/7</td>
<td>4.46</td>
</tr>
<tr>
<td>6</td>
<td>Eu</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Gd Eu$^{2+}$</td>
<td>0</td>
<td>7/2</td>
<td>7/2</td>
<td>2</td>
<td>15.75</td>
</tr>
<tr>
<td>8</td>
<td>Tb</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>3/2</td>
<td>10.50</td>
</tr>
<tr>
<td>9</td>
<td>Dy</td>
<td>5</td>
<td>5/2</td>
<td>15/2</td>
<td>4/3</td>
<td>7.08</td>
</tr>
<tr>
<td>10</td>
<td>Ho</td>
<td>6</td>
<td>2</td>
<td>8</td>
<td>5/4</td>
<td>4.50</td>
</tr>
<tr>
<td>11</td>
<td>Er</td>
<td>6</td>
<td>3/2</td>
<td>15/2</td>
<td>6/5</td>
<td>2.55</td>
</tr>
<tr>
<td>12</td>
<td>Tm</td>
<td>5</td>
<td>1</td>
<td>6</td>
<td>7/6</td>
<td>1.17</td>
</tr>
<tr>
<td>13</td>
<td>Yb</td>
<td>3</td>
<td>1/2</td>
<td>7/2</td>
<td>8/7</td>
<td>0.32</td>
</tr>
<tr>
<td>14</td>
<td>Lu Yb$^{2+}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
was later extended by Kasuya and Yosida to treat local moment-conduction electron interactions in magnetic materials and is now referred to as the RKKY interaction. In the RE-TM alloys, indirect exchange produces the effective 4f-3d interaction (shown schematically in Fig. 15) which couples the RE and TM sublattices antiferromagnetically. It also produces an effective 4f-4f exchange which promotes ferromagnetic alignment of the rare earth ions, although this is of secondary importance compared to the 4f-3d exchange.

The dominant contribution to the total exchange is usually the TM-TM interaction. The exchange mechanism coupling the 3d ions to one another is referred to as a direct interaction since overlap of the 3d orbitals is involved. Here, certain features of this interaction which are important to the understanding of RE-TM alloys will be discussed. For this purpose, the direct exchange may be pictured in terms of a band model in which the magnetic moment is associated with the electrons (or holes) in the unfilled 3d band. In the absence of exchange effects, one may consider two sub-bands equally populated with spin-up $\uparrow$ and spin-down $\downarrow$ electrons. In order for a net moment to exist, $n$ electrons per atom must be transferred from the $\downarrow$ to the $\uparrow$ states. The energy necessary for the electron transfer arises from the exchange interaction and may be depicted by the displacement of one sub-band with respect to the other along the energy axis by a distance $\Delta E$. 
(see Fig. 17). For cobalt, the electron transfer from the ↓ to the ↑ sub-band results in the filling of all the ↑ states, but this is not the case for iron. The incomplete polarization in Fe results from the trapping of the Fermi level at a minimum in the ↑ sub-band since the exchange field cannot provide the large excess energy necessary to move $E_F$ through this region of low density of states.

The effect of the electrostatic crystal field on the rare-earth ions is also important to an understanding of RE-TM alloys. In contrast to the 3d transition metals, the interaction of the rare-earth ions with the crystalline electric field is known to be much less than the spin-orbit interactions within the ion. This is a consequence of the limited spatial extent of the 4f wave functions compared with those for the 3d electrons plus the screening effects of the 5s and 5p electrons. Since the spin-orbit interaction is dominant, the total angular momentum is a good quantum number for the rare-earth ions, and the effects of the crystal field may be taken as a perturbation of the (2J+1) fold degenerate ground state $J$(recall $J=L+S$ for the heavy rare-earths). Hence, the minimization of the crystal field energy causes a preferential orientation of the magnetic moments. Classically, this may be viewed as resulting from the action of the crystalline electric field on the anisotropic 4f charge distribution. The large spin-orbit coupling then ensures that the spin, as well as the orbital moment, follows the charge distribution. Thus,
Fig. 17. Schematic representation of the splitting of the spin-up and spin-down subbands of an itinerant electron ferromagnet by the exchange interaction.
the anisotropy is large in terbium, which has a highly anisotropic 4f charge distribution, while it is small in gadolinium, which has an almost spherical ion. The anisotropy arising from the crystal field interaction is often referred to as single-ion anisotropy. The single-ion model has been used, with some success, to explain the huge magnetocrystalline anisotropies found in the rare-earth metals [38] and in the cubic rare earth-Fe$_2$ compounds [39].

To calculate the energies involved in the crystal field interaction, one frequently uses a point-charge model in which the electrostatic potential at the origin is written

$$V_C(\vec{r}) = \sum_i \frac{Z_i}{|\vec{r} - \vec{R}_i|}$$

where $Z_i$ is the ionic valence and the $\vec{R}_i$ are the positions of the atoms in the crystalline or amorphous alloys with respect to a typical reference ion at the origin. The electric field at the position of the reference ion is a solution of Laplace's equation. Expanding in spherical harmonics,

$$V_C(r, \theta, \phi) = \sum_{l} \sum_{m=-l}^{+l} a_{lm} r^l Y^m_l(\theta, \phi)$$

where

$$a_{lm} = (-1)^m \frac{4\pi}{2l+1} \sum_i \frac{Z_i}{R_i^{l+1}} Y^{m*}_l(\theta_i, \phi_i)$$

and

$$\vec{r} \rightarrow (r, \theta, \phi)$$

$$\vec{R}_i \rightarrow (R_i, \theta_i, \phi_i)$$
Calculation of the crystal field splitting requires a knowledge of the matrix elements of $V_c$ in the ground state manifold of the ion, $|J, M_J\rangle$. Time reversal invariance guarantees that terms with $\ell$ odd are zero, while for $4f$ electrons with an orbital angular momentum quantum number of 3, terms with $\ell > 6$ are zero [90].

In the cubic Laves phase, only fourth and sixth order terms appear because of the cubic symmetry [87]. Hence,

$$V_c = V^0_4 + V^4_6 + V^6_6 + V^6_6$$

where

$$V^m_\ell = a^m_\ell r^\ell \gamma^m_\ell(\Theta, \Phi)$$

For an amorphous material, only the terms $V^0_2$ and $V^0_4$ need be considered. Using binary dense random packing of hard spheres to model the amorphous structure, the magnitude of the crystal-field potential is found to be surprisingly uniform, exhibiting only a 2% rms deviation over the material [91]. However, because of the lack of a regular crystal structure, the minimum energy directions have a random spatial distribution, and do not give rise to any macroscopic easy magnetic direction. These local "crystal" fields are often referred to as local anisotropy fields.

Until recently, it was commonly believed that a comparison between the crystalline and amorphous phases of the same alloy would always show that the Curie temperature for the amorphous phase was lower. The first clear-cut evidence to support this hypothesis was given by Rhyne et al. [92]. For bulk amorphous TbFe$_2$ prepared in the form of millimeter thick plates by rapid d.c. sputtering, they found a
Curie temperature, $T_C$, of $388^0K$ and a spontaneous moment at $0^0K$, $M(0)$, of $2.8\mu_B$ per formula unit. This was in contrast to $T_C = 710^0K$ and $M(0) = 4.7\mu_B$ for the crystalline TbFe$_2$ Laves phase. Subsequently, Harris et al. [93] proposed a model for magnetism in amorphous RE-TM alloys. They assumed that the most important characteristic of the amorphous state was the existence of local anisotropy fields of random orientation. Using this model, they were able to obtain qualitative agreement with the experimental data on TbFe$_2$. Moreover, they predicted that amorphous RE-TM alloys containing S-state or nonmagnetic RE atoms, such as Gd, Y, or Lu, would not exhibit a significant decrease in magnetization or Curie temperature compared with their crystalline counterparts.

Just a few months later, however, Tao et al. [94] reported that $T_C$ for amorphous GdCo was about $565^0K$, which was a sizable increase over the $T_C$ of $395^0K$ for crystalline GdCo. This could not be explained on the basis of the model proposed by Harris et al. [93]. They also found that the Co atoms carried a larger moment in the amorphous state, $1.4\mu_B$ as opposed to $1.02\mu_B$ in the crystal. Both values were smaller than the $1.7\mu_B$ found in pure Co metal. Moreover, while the Laves phase GdCo$_2$ had a density of $9.66\text{ g/cm}^3$, the density of amorphous GdCo was $8.35\text{ g/cm}^3$. From these facts, they concluded that the change in $T_C$ could be accounted for qualitatively by assuming that less charge transfer from the rare earth ions to the transition
metal ions takes place in the amorphous films. Since Co has vacant states in only one of the d sub-bands, transfer of charge to Co should decrease both $T_C$ and the cobalt moment. Since Fe has unfilled spin states in both d sub-bands, the iron moment and $T_C$ could either increase or decrease. Hence, charge transfer could provide a mechanism to explain the increased $T_C$ for amorphous GdCo$_2$ and its decrease for amorphous TbFe$_2$.

Subsequent work involving other Gd-Co compositions [95] as well as other RE-TM alloys [69,77] has tended to support the charge transfer model, while discounting the role of local anisotropy and orbital moment of the RE in the altered exchange of the RE-TM alloys. Lee and Heiman [96] found $T_C$ for RE-Co and RE-Ni alloys to be higher in the amorphous state than the crystalline state, while the reverse was true for RE-Fe alloys, results which are consistent with charge transfer. However, they also noted that amorphous RE-TM alloys, as opposed to the crystalline alloys, exhibited enhanced Co-Co and Ni-Ni exchange, reduced Fe-Fe exchange, and reduced RE-RE and/or RE-TM exchange. On the basis of Cargill's [97] radial distribution function analysis of amorphous GdFe$_2$ and a comparison with the Laves phase compound, they proposed that these effects could be accounted for by the differences in interatomic spacings and in coordination.

To summarize, the signs of the various exchange interactions are the same for both the crystalline and amorphous
states. Hence, both exhibit a similar ferrimagnetic order. However, the magnitudes both of the exchange interactions and of the transition metal moment are altered in the amorphous state. These facts can be accounted for qualitatively on the basis of charge transfer and altered coordination and interatomic spacing. Crystal field effects in the form of local anisotropy fields do not appear to play a significant role in the altered exchange. However, their effect on other aspects of the magnetic behavior of the amorphous alloys cannot be discounted.
III. EXPERIMENTAL TECHNIQUES

In order to gain additional insight into the properties of amorphous rare earth-transition metal thin film alloys, an investigation of the following binary alloy systems was undertaken: Ho-Co, Dy-Co, Gd-Fe, and Tb-Fe. The rare earth-transition metal films studied in this investigation are prepared by simultaneous evaporation from two Varian e-Gun evaporation sources. The distance between the centers of the e-Gun crucibles is 5.8 cm. The substrates are Corning 0211 glass, 1.59 cm. square by .06 cm. thick, and they are mounted 27 cm. above the sources. The substrates are partially covered by masks so that the resulting films are circular in shape with a 1 cm. diameter. The substrates are at room temperature during deposition. Before being exposed to atmosphere, the films are passivated with approximately 500 Å of SiO.

The vacuum chamber consists of an 18 inch diameter by 30 inch high Pyrex bell jar together with a Type 304 stainless steel baseplate equipped with eleven 1-1/2 inch I.D. feed-through ports. Roughing is provided by three Varian VacSorb pumps, whose ultimate pressure is approximately 5 microns. The high vacuum pumps are a 250 liter per second VacIon pump and a titanium sublimation pump. Hence, the vacuum chamber is completely free of oil or organic contamination. In a typical pumpdown, the pressure is reduced to 1-3 X 10⁻³ Torr before beginning film deposition. Once
the pressure reaches $10^{-7}$ Torr, gettering of the vacuum chamber is aided by two evaporations of the rare-earth metal of approximately 60 sec. duration each. The pressure during film deposition is $2-6 \times 10^{-7}$ Torr.

In order to record the progress of the evaporation from each source, the sensor heads of two Sloan Deposit Thickness Monitors are mounted in the vacuum system. This instrument has the ability to determine accurately the mass deposited on a quartz crystal by measuring the frequency shift of a crystal controlled oscillator housed inside the sensor head. The frequency shift is related to the thickness of the deposit by the formula

$$\Delta f \cong \frac{\rho h}{2},$$

where $\Delta f = \text{frequency change of oscillator in Hz.}$

$h = \text{film thickness on sensor crystal in Å.}$

$\rho = \text{bulk density of deposited material in gm/cm}^3.$

Aluminum shields are positioned so that each crystal is exposed to the vapor emanating from a single source. This arrangement is shown in Fig. 18.

In order to produce films which have uniform composition as a function of thickness, it is necessary that the rate of evaporation from each source remain constant once deposition begins. Since the control unit of each Sloan monitor has a recorder output which provides a voltage proportional to the oscillator frequency, the thickness of the material deposited on each sensor crystal can be plotted as a function of time using an X-Y recorder. The first attempt to achieve rate control was to have an operator manually
Fig. 18. Schematic of the evaporation system showing the positions of the e-guns, aluminum shields, and monitor sensor heads.
adjust the power to each e-Gun so that the thickness increased linearly with time. However, this method proved unsatisfactory since composition sometimes varied as much as 10% with film thickness despite the best efforts of the operators. Therefore, a device was constructed which utilized automatic feedback to control the power to the e-Gun. This evaporation controller works as follows. First, the voltage from the recorder output of the Sloan Thickness Monitor is compared with a voltage that increases linearly with time. This ramp voltage is generated by a Hewlett Packard Moseley 17108 A Time Base. The difference between the two voltages is then amplified and used to control the timing of a sequence of pulses applied to the gate of a triac placed in the primary of the e-Gun filament transformer. If the recorder output voltage is less than the ramp voltage, the power to the filament is increased. On the other hand, if the recorder output voltage is greater than the ramp voltage, the power to the filament is decreased. In this way, the frequency shift of the oscillator, and hence the deposit thickness on the crystal, is made to track the voltage ramp with time. The rate of evaporation is adjusted to the desired value simply by attenuating either the ramp voltage or the recorder output. A block diagram of the rate control system is shown in Fig. 19. Further details on the operation of the evaporation controller can be found in Appendix I. Two of these controllers were constructed, one for each e-Gun.
Fig. 19. Block diagram of the rate control system.
Figure 20 shows the thickness of iron deposited on the sensor crystal during the fabrication of Gd-Fe films. The linear increase of thickness with time confirms that accurate rate control was achieved. Similar recordings are made for each source during each evaporation. These recordings provide a permanent record of the evaporation and enable any irregularities which might cause anomalous film properties to be spotted.

One final problem in achieving accurate rate control should be noted. Both holmium and dysprosium do not melt and then evaporate. Instead, they sublimate at rather low power levels. Because of the low power required to maintain the desired deposition rate, the control system tends to oscillate. The result is that the holmium or dysprosium is deposited in short rapid bursts rather than smoothly and continuously. Once the size of the charge in the e-Gun becomes sufficiently small, and hence the power required for the desired deposition rate sufficiently large, the oscillations cease. Unfortunately, however, the remaining charge is usually sufficient to make a film only about 0.2 microns thick. This difficulty is circumvented by arranging the charge in a special way. Since the holmium and dysprosium are purchased in the form of 1/4 inch diameter rods, disc shaped sections about 0.1 inch thick are cut off the rods. Four of these discs are then arranged in the dimple of the e-Gun crucible (see Fig. 21) so that the electron beam strikes in the middle of the group of discs. Since the beam
Fig. 20. Thickness of iron deposited on the sensor crystal (in Hertz) versus time.
Fig. 21. Top view of the e-gun showing the arrangement of the Ho or Dy disks.
hits only the edge of each disc directly, a larger amount of power is necessary for a reasonable deposition rate, and yet the size of the charge is sufficient to allow a longer deposition.

Although the sensor crystals are mounted at approximately the same distance from the sources as the substrates, the films are approximately eight-tenths as thick as the total thickness of the material deposited on both crystals as determined by the formula $h = (2/\rho)\Delta f$. This indicates a non-uniform distribution of flux from the sources. The total deposition rate at the substrates is typically $7-9 \, \text{Å/sec.}$ and deposition times are from 500-800 sec. The films are usually 0.4-0.6 microns thick. Films thicker than 0.6 microns tend to crack and then peel from the substrate within 24 hours unless the substrates are heated during deposition.

Because of the unavoidable displacement between the two sources, the films exhibit a composition gradient along the direction of a line passing through the position of the charge in each e-Gun. This gradient can be reduced by increasing the source-to-substrate distance, but this lengthens the deposition time and makes it more difficult to fabricate films of even moderate thickness (say 0.3 microns). The source-to-substrate distance of 27 cm. used in the present system represents a compromise between these two requirements. However, the composition gradient does allow one to make films of different average composition
during a single deposition simply by locating substrates at different positions relative to the two sources. Because of the desire to minimize any possible angle of incidence effects, no substrate locations are used for which the angle of a line from either source to the substrate center exceeds 12° from normal. From the difference in average composition of films made during the same deposition and from the distance between the centers of the films during deposition, the composition gradient across a 1 cm. diameter film is estimated to be 0.6 to 0.7%.

Room temperature hysteresis loops for the normal component of magnetization are made by plotting the Hall voltage as a function of magnetic field applied normal to the film plane [106]. The magnetic field is produced by an adjustable gap electromagnet with 4 inch diameter pole pieces, and the field is measured by a semiconductor Hall probe. The Hall current used was 50 ma, which provided a large signal but did not cause heating of films with thicknesses from 0.4-0.6 microns. Electrical contact to the films is made by pressure, and the four pressure contacts are arranged in a square configuration. Because of the finite area of each metal contact, any Hall voltage originating from the edges of the film is short-circuited. Hence, the observed hysteresis loops are due to a central region of each film approximately 0.6 cm. in diameter.

Thickness measurements are made using an optical interferometer with a green filter that has maximum trans-
mission at \( \lambda = 5460 \, \AA \). Hence, the spacing between fringes is 2730 \( \AA \) and a shift of one fringe spacing at the edge of the film corresponds to a film thickness of 2730 \( \AA \). By photographing the fringes and measuring the fringe shift from the photograph, variations in thickness at least as small as 1/10 of the fringe spacing can be detected. Therefore, the absolute error in the thickness measurement is \(< 300 \, \AA\).

For films with observable strip domains, strip periods are measured using polar Kerr contrast microscopy. The SiO layer used for passivation enhances the Kerr contrast by reducing the background reflection of light. Strip domains are first photographed with a 35 mm Nikkon camera and the period is then measured from the resulting photomicrograph. The photomicrographs are calibrated by measuring the distance between two defects in a film using a calibrated eye-piece with a vernier adjustment, and then photographing these same two defects. Because of the crossed polarizers which are needed for the Kerr effect, exposure times of 2-3 minutes are required even with a fast black-and-white film (Kodak Tri-X Pan Film). Although the strips could not be seen with the eye, a strip period as small as 0.8 microns has been measured with the aid of the camera. Once the strip period and film thickness are known, the characteristic length can then be determined using relations by Shaw, et al. [107]. The characteristic length is always calculated from the strip period at the exact center of the
film as determined by translators on the microscope stage. This point will be commented upon further when the measurement of magnetization is discussed.

The magnetization, $\mathcal{M}$, and the anisotropy field, $H_K$, are measured with a Princeton Applied Research Model 150A Parallel Field Vibrating Sample Magnetometer (VSM). The magnetometer is mounted on an electromagnet with 4 inch diameter pole pieces. With a 2 inch gap, the maximum field is $14$ KG. Because their mass is so much greater than that of the film, the plexiglass holder and glass substrate are found to contribute an appreciable signal at high fields due to their diamagnetic susceptibility. This signal is opposite in sign to that of the film and is a linear function of the applied field. The signal due to the film alone is found by adding the signal measured for the holder and a blank substrate to the signal measured for the film-holder-substrate combination. In order to reduce the diamagnetic contribution from the substrates, they are cut down to a lcm X lcm square, just large enough to accommodate the lcm circular film. Films with compositions close to compensation, where $H_K$ varies more rapidly with composition, are cut to a width of .5 to .6 cm. in the direction of the composition gradient. Unless the range of composition across a given film straddles the compensation point, $\mathcal{M}$ is very close to a linear function over this composition range since it is less than 1%. Therefore, the magnetization measured with the magnetometer, which represents an
average over the volume of the entire film, is the magnetization at the center of the film. This is the reason that the strip period is always measured at the center of the film.

In order to obtain reproducible magnetization measurements with the VSM, it is important that the sample be placed at the saddle point where the signal is least sensitive to small shifts in sample position. Consider a system of coordinates in which the x axis is parallel to the applied field, the z axis is parallel to the direction in which the sample vibrates (vertical direction), and the y axis is perpendicular to the other two. For a one centimeter diameter circular film oriented with the plane of the film parallel to the applied field, the measured signal as a function of the position of the center of the film along the z axis (x and y are held fixed) takes the form shown in Fig. 22. It is obvious that the sample should be placed at the position of the maximum, since this gives the largest signal and since a displacement of ±0.05 inches results in a difference of only about 1% in the measured signal. A similar maximum is observed for translation in the y direction, while a minimum occurs for translation in the x direction. Hence, the sample should be positioned so that the signal is simultaneously at a maximum for displacement in the y and z directions and at a minimum for displacement in the x direction. In this way reproducible readings can be obtained for the same sample at different times. This
Fig. 22. VSM signal for a 1 cm. diameter film as a function of the position of the film center along the z direction.
is especially important since the magnetization for a given film is calculated by comparing its signal with that of a standard of known moment.

Because of the relatively large size of the films (1 cm diameter) with respect to the signal pick-up coils, it was felt that a standard of exactly the same dimensions should be used. Hence a 1 cm diameter nickel film was made using material of 99.8% purity. This film was deposited at 200°C and annealed for several hours at 250°C so that its density would be close to that of bulk nickel. The thickness of the nickel film is 2.234 ± 0.02 μm. The magnetization of the standard is assumed to be $4\pi M = 6095$ Gauss at room temperature [99,109]. Nickel is chosen as the standard material since a nickel film can be saturated both parallel and perpendicular to the plane of the film with available fields. This is necessary since some films with large anisotropies (primarily Dy-Co and Tb-Fe) could only be saturated with the field applied parallel to the easy axis, i.e. normal to the plane of the film.

To check the calibration of the nickel standard, films of pure iron and cobalt were also made. The magnetization of these films was calculated using the nickel standard and compared with the published values for bulk iron and cobalt. The results are listed in the table below:

<table>
<thead>
<tr>
<th></th>
<th>Thickness (μm)</th>
<th>$4\pi M$ (calculated)</th>
<th>$4\pi M$ from ref. [99]</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Film</td>
<td>.245</td>
<td>21,085</td>
<td>21,488</td>
<td>.981</td>
</tr>
<tr>
<td>Co Film</td>
<td>.335</td>
<td>19,230</td>
<td>17,982</td>
<td>1.069</td>
</tr>
</tbody>
</table>
In both cases, the difference between the calculated and published values of $H_{\text{NI}}$ is less than the possible error due to uncertainties in film thickness.

A typical hysteresis loop measured with the VSM for a Ho-Co film is shown in Fig. 23. The data was taken with the field applied parallel to the plane of the film (i.e. perpendicular to the easy axis of magnetization). Two features of this loop should be noted. First, an abrupt transition takes place at low fields. This is partly an artifact of the electromagnet since the field reversal switch causes some oscillations in the applied field which have a demagnetizing effect on the film. A smooth transition through zero field would probably result in a loop with more hysteresis in the low field region. Nevertheless, there is a clear indication that a layer of the film exists which is easily saturated in-plane. This effect is probably due to the lack of a well developed uniaxial anisotropy in the initial layer of deposited material. A similar thickness dependence of $K_u$ for sputtered Gd-Co has been noted by Chaudhari et al. [1]. Using the fact that $h = 4800$ Å for the film in Fig. 23, a comparison of the signal for a field of approximately 100 G to the saturation value indicates that this initial layer is about 700 Å thick. This is consistent with the observation that films 400 Å thick do not exhibit uniaxial anisotropy, while films 1200 Å thick do.
Fig. 23. VSM hysteresis loop for a Ho-Co film with the applied field parallel to the film plane.
The second feature of the loop in Fig. 22 that should be noted is the large susceptibility at high fields above technical saturation. This susceptibility is due to local anisotropy fields of the type discussed in Chapter II. In calculating the magnetization of these films, the linear portion of the magnetization curves above technical saturation has been extrapolated back to the demagnetizing field to obtain the spontaneous moment, $4\pi M_0$. This is also the convention adopted by Rhyne et al. [101] for bulk amorphous TbFe$_2$ and by Tao et al. [95] for sputtered Gd-Co. This choice is appropriate, rather than an extrapolation to infinite field, since in the next chapter the magnetization data will be compared with the spontaneous magnetization calculated from a molecular field model. It should be noted that magnetization measurements on the same film taken at different times with the sample oriented either parallel or perpendicular to the applied field almost always agree within 5%, the discrepancy being smaller for films with larger moments.

The anisotropy energy is determined from the plot of magnetization versus applied field with the field aligned parallel to the plane of the film. For a film in a single domain state, the field required for saturation would be $H_K - 4\pi M$ due to the demagnetizing energy. However, in the absence of an applied field, these films are usually in a multi-domain state in which the demagnetizing energy is greatly reduced. Hence, it is more appropriate to adopt
the convention that the saturation field is equal to the anisotropy field. This has also been the practice adopted by numerous other workers in this area [69,71,78,109,53]. For the film in Fig. 22, $H_K = 4000$ Oe. Once the anisotropy field, $H_K$, is known, the anisotropy constant is calculated from the expression $K_u = \frac{1}{2}MH_K$.

As a check on the method for determining $H_K$ described above, the anisotropy fields of two Gd-Fe films were measured using the susceptibility technique described by Zwingman, et al. [56]. In this technique, $H_K - 4\pi M$ rather than $H_K$, is the quantity measured directly. A comparison of the measurements is shown below:

<table>
<thead>
<tr>
<th>4\pi M(VSM)</th>
<th>$H_K$(VSM)</th>
<th>$H_K-4\pi M$(suscept.)</th>
<th>$H_K$(suscept.)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2470</td>
<td>4750</td>
<td>1900</td>
<td>4370</td>
<td>1.09</td>
</tr>
<tr>
<td>3980</td>
<td>1400</td>
<td>-2280</td>
<td>1700</td>
<td>0.82</td>
</tr>
</tbody>
</table>

The relative difference between the two methods is larger for the film with $Q<1$ ($H_K - 4\pi M$ negative). For the film with $Q>1$, agreement within 10% is observed.

Film composition is determined by x-ray fluorescence. Counts are taken on the $K_\alpha$ line for the transition metal and on the $L_\alpha$ line for the rare-earth and compared with the intensities measured for pure metal standards of known thicknesses. The method used to analyze the data is described in detail in Appendix 2.

X-ray diffraction tests were run on several samples to confirm their amorphous structure. No diffraction peaks
were observed for any of the RE-TM alloys, although they were detected for films of pure Ho and pure Co. An electron diffraction pattern for a thin (~800 Å) Gd-Co film made in the evaporation system also showed it to be amorphous.
IV. RESULTS AND DISCUSSION

IV.1 Magnetization and Molecular Field Calculations

The spontaneous magnetization as a function of composition for the four alloy systems, (Ho-Co, Dy-Co, Gd-Fe, Tb-Fe) is shown in Figs. 24, 25, and 26. Ho-Co and Dy-Co both exhibit a maximum at a cobalt atomic fraction, $x$, of .66 to .67, and then the magnetization decreases as the cobalt fraction is reduced further. The value of the magnetization at the maximum is 2800 G for Dy-Co and 1000 G for Ho-Co. The larger maximum for Dy-Co is a consequence of the larger effective spin, $(g-1)J$, of Dy since the exchange coupling is between spins (recall Fig. 15). Ho-Co samples with $x < .55$ are paramagnetic at room temperature.

For Gd-Fe, compensation at room temperature occurs at $x = .765$, a larger iron fraction than $x = .74$ as reported by Taylor [71]. However, if one corrects for this difference in compensation composition, the magnetization data presented here agree well with Taylor's data (see Fig. 11). This can be seen readily by considering the linear approximation for the range $.65 < x < .85$ given by Taylor,

$$4\pi M = |36,800 - 49,700 x| .$$

If a change of variables $x = x' - .02$ is made, then the resulting expression,

$$4\pi M = |37,794 - 49,700 x'|$$

provides a good fit to the data reported here. The reasons for the difference in compensation composition are not clear,
Fig. 24. Magnetization versus composition for Ho-Co and Dy-Co.
Fig. 25. Magnetization versus composition for Gd-Fe.
but two possible factors are the following. First, Taylor
determined the compositions of his films by electron micro-
probe, whereas x-ray fluorescence was used here. Second,
differences in impurity levels and types in the starting
materials may also have affected the results.

The solid lines in Figs. 24-26 represent molecular
field fits to the magnetization data using the exchange con-
stants, moments, and g-factors shown in Table II. The
molecular field model for ferrimagnetism was formulated by
Néel and was first applied to the amorphous RE-TM alloys
by Hasegawa [47,62]. In this model, the sublattice mag-
etizations are represented by a pair of coupled Brillouin
functions:

\[ M_1 = N_1 \varepsilon_1 \mu_B J_1 \mathcal{B}_1 \left( \frac{g_1 \mu_B J_1}{kT} H_{m1} \right) \]  

\[ M_2 = N_2 \varepsilon_2 \mu_B S_2 \mathcal{B}_2 \left( \frac{g_2 \mu_B S_2}{kT} H_{m2} \right) \]  

where \( l = \text{RE}, 2 = \text{TM} \), and

\( M_1 \) is the RE or TM sublattice magnetization
\( N_1 \) is the number of RE or TM atoms per unit volume.
\( \varepsilon_1 \) is the g-factor for the RE or TM.
\( J_1 \) is the RE angular momentum (\( J_1 = L_1 + S_1 \))
\( S_2 \) is the TM spin.
\( H_{m1} \) is the molecular field acting on a RE or TM atom
\( \mu_B \) is the Bohr magneton
\( T \) is the temperature in °K
\( k \) is Boltzmann's constant
\( \mathcal{B}_j(\cdot) \) is the Brillouin function
### Table II

<table>
<thead>
<tr>
<th></th>
<th>Ho-Co</th>
<th>Dy-Co</th>
<th>Gd-Fe</th>
<th>Tb-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{comp}}$</td>
<td>0.72</td>
<td>0.77</td>
<td>0.765</td>
<td>0.78</td>
</tr>
<tr>
<td>$\mu_{\text{RE}} (\mu_b/\text{RE atom})$</td>
<td>8.75±0.25</td>
<td>8.5±0.25</td>
<td>7.0</td>
<td>8.0</td>
</tr>
<tr>
<td>$\varepsilon_{\text{RE}}$</td>
<td>1.25</td>
<td>1.33</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>$\varepsilon_{\text{TM}}$</td>
<td>2.22</td>
<td>2.22</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$J_{\text{TM-TM}} (10^{-16} \text{ergs})$</td>
<td>200</td>
<td>200</td>
<td>45.0</td>
<td>45.0</td>
</tr>
<tr>
<td>$J_{\text{TM-RE}} (10^{-16} \text{ergs})$</td>
<td>24.8±1.5</td>
<td>29.0±1.5</td>
<td>22.0</td>
<td>26.0</td>
</tr>
<tr>
<td>$J_{\text{RE-RE}} (10^{-16} \text{ergs})$</td>
<td>1.70</td>
<td>1.48</td>
<td>1.60</td>
<td>1.60</td>
</tr>
<tr>
<td>$\varepsilon J_{\text{RE}}$</td>
<td>10</td>
<td>10</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>$(\varepsilon-1)J_{\text{RE}}$</td>
<td>2</td>
<td>2.5</td>
<td>3.5</td>
<td>3</td>
</tr>
</tbody>
</table>
The net magnetization is then \( 4\pi M = 4\pi |M_1 - M_2| \). The molecular fields are given by,

\[
H_{m1} = \lambda_{11} M_1 + \lambda_{12} M_2
\]
\[
H_{m2} = \lambda_{21} M_1 + \lambda_{22} M_2
\]

where the \( \lambda_{ij} \) are the molecular field constants. These molecular field constants can be related to the exchange integrals by equating the energy of a RE or TM moment in the molecular field to the exchange energy given by a Heisenberg Hamiltonian (see, for example, Morrish [98], p. 282).

The results are:

\[
\lambda_{11} = \frac{2Z_{11}(g_i-1)^2 J_{11}}{N_1 g_i^2 \mu_B^2}
\]
\[
\lambda_{12} = \frac{2Z_{12}(g_i-1) J_{12}}{N_2 g_1 g_2 \mu_B^2}
\]
\[
\lambda_{21} = \frac{2Z_{21}(g_i-1) J_{12}}{N_1 g_1 g_2 \mu_B^2}
\]
\[
\lambda_{22} = \frac{2Z_{22} J_{22}}{N_2 g_2^2 \mu_B^2}
\]

where \( J_{11} \) is the RE-RE exchange integral
\( J_{12} \) is the RE-TM exchange integral
\( J_{22} \) is the TM-TM exchange integral
\( z_{ij} \) is the number of nearest neighbor type \( j \) atoms for a type \( i \) atom
(i.e., \( z_{12} \) is the number of TM nearest neighbors for a RE atom).
On the basis of x-ray data [81,97], we assume that the atoms are randomly distributed over the atomic sites with an average coordination number of 12. Hence, for a RE$_{1-x}$ TM$_x$ alloy with TM atomic fraction $x$, we have

$$z_{11} = z_{21} = 12(1-x)$$

$$z_{22} = z_{12} = 12x$$

Since $N_1 = (1-x)N$ and $N_2 = xN$, where $N$ is the total number of atoms per unit volume, one can show that

$$\lambda_{12} = \lambda_{21} = \frac{2(12)(9_i - 1) J_{12}}{Ng_1g_2\mu_0^2}$$

A comment on the calculation of $N$ is in order. If the density, $\rho$, of the RE$_{1-x}$ TM$_x$ alloy is known, then

$$N = \frac{\rho N_0}{(1-x)A_{RE} + xA_{TM}}$$

where $A_{RE}$ and $A_{TM}$ are the atomic weights of the RE and TM respectively and $N_0$ is Avogadro's number, 6.0225 x 10$^{23}$ cm$^{-3}$.

Tao, et al. [94] have reported that the densities of amorphous Gd-Co films vary smoothly with $x$ and that, within measurement error, the density is given by a linear interpolation between pure Co and pure Gd. Hence, for all four binary alloys it was assumed that

$$\rho = (1-x)\rho_{RE} + x\rho_{TM}$$

where $\rho_{RE}$ and $\rho_{TM}$ are the densities of the rare earth and transition metal respectively.
Due to the form of the Brillouin function, an analytic solution of eqns. (1) and (2) for the sublattice magnetizations is not possible, and the two equations must be solved either graphically or numerically. Here, an iterative solution was obtained by guessing initial values of $M_1$ and $M_2$, and then converging on the correct solutions within a tolerance of $|M_i(\text{new value}) - M_i(\text{old value})| < 1$.

In order to fit the room temperature magnetization data, the following parameters must be specified: $J_{11}, J_{12}, J_{22}, g_1, g_2, \mu_1, \mu_2$ where $\mu_1 = g_1 J_1$ and $\mu_2 = g_2 S_2$ are the RE and TM moments respectively in units of Bohr magnetons. All of these quantities are assumed to be independent of composition except for the transition metal moment $\mu_2$, which decreases with increasing rare earth content due to charge transfer from the conduction band to the d band of the transition metal. Physical arguments can be used to assign values to some of these parameters, and the others are then adjusted to give the best fit to the data.

The Co-Co exchange interaction is taken as $2.0 \times 10^{-14}$ ergs after Hasegawa [47]. This value is calculated from the estimated Curie temperature $T_c = 1400^\circ$K for alloys with a high cobalt concentration using the formula

$$J_{\text{Co-Co}} = \frac{3kT_c}{2xZ S_{\text{Co}} (S_{\text{Co}} + 1)}$$

where $S_{\text{Co}} = \mu_{\text{Co}} / g_{\text{Co}}$ is the spin of cobalt for the corresponding value of $x$ and $z$ is the number of nearest neigh-
bors, which was assumed to be 12 as previously noted. The RE-RE exchange constants are calculated from the Curie temperatures for the amorphous RE$_{0.33}$ Ni$_{0.67}$ alloys. Since nickel does not have a moment in these alloys due to the filling of its d-band by charge transfer, it is assumed that $J_{\text{RE-RE}}$ is responsible for the entire exchange interaction [100]. Hence,

$$J_{\text{RE-RE}} = \frac{3kT_c}{2(1-\lambda)Z(q_{\text{RE}}-1)^2 J_{\text{RE}}(J_{\text{RE}}+1)}$$

The g-factor for cobalt is assigned the value $g_{\text{Co}} = 2.22$ based on resonance experiments performed by Cronemeyer [46]. This is very close to the value $g_{\text{Co}} = 2.19$ given by Tebble and Craik [99]. The g-factor for Fe is assumed to be $g_{\text{Fe}} = 2$ [100], although it too may deviate from the spin only value of 2. For example, Tebble and Craik given $g_{\text{Fe}} = 2.09$, although this difference would have only a minor effect on the other parameters. For the rare earths, the values of $g$ for the free $j^+$ ions, as listed in Table I, are used.

The RE-TM exchange interaction is selected to give the appropriate compensation composition in conjunction with the rare-earth moment. It should be noted that the compensation composition is not very sensitive to variations in the transition metal moment since the rare-earth sublattice is ordered primarily by antiferromagnetic coupling to the transition metal sublattice, and not by
ferromagnetic coupling among the RE atoms. Although reasonable fits to the data can be obtained by using the rare-earth moments for the free $3^+$ ions, it is found that the fit can be improved by reducing $\mu_{\text{RE}}$ from 10-15% for the non S-state ions. Accordingly, the moments of Tb, Dy, and Ho are reduced from $9\mu_B$, $10\mu_B$, and $10\mu_B$ to $8\mu_B$, $8.5\mu_B$, and $8.75\mu_B$ respectively. Physically, this reduction corresponds to an incomplete alignment of the RE moments due to random local anisotropy fields [93,101], the origin of which was discussed in Chapter II. The high field susceptibility mentioned in the chapter on experimental techniques confirms that local anisotropy exists in the films studied. This point will be discussed again later.

As mentioned previously, the TM moment is reduced by charge transfer as the RE concentration increases. The variation in the cobalt moment shown in Fig. 27 was determined empirically and was found to result in an excellent fit for both Ho-Co and Dy-Co. For comparison, the variation in $\mu_{\text{Co}}$ used by Taylor, et al. [78] to fit their data on evaporated Gd-Co,

$$\mu_{\text{Co}} = 1.72 - 1.88\left(\frac{1-x}{x}\right)^{1.5}$$

is shown by a dashed line. Even with adjustments in the other parameters, a good fit to the data presented here could not be found using Taylor's formula. Moreover, since his films all had more than 60 atomic percent Co, he
Fig. 27. Transition metal moment as a function of composition.
probably did not intend the formula to be valid for lesser Co concentrations. Certainly, the rapid decrease of $\mu_{\text{Co}}$ to zero in the range $0.5 < x < 0.6$ is a non-physical result which is not consistent with other magnetization data on amorphous Gd-Co [95].

Also shown in Fig. 26 are the values of $\mu_{\text{Co}}$ given by Burzo [102] for the following Gd-Co intermetallic compounds: Gd$_3$Co, Gd$_4$Co$_3$, GdCo$_2$, GdCo$_3$, Gd$_2$Co$_7$, GdCo$_5$, and Gd$_2$Co$_{17}$. Based on neutron diffraction results, Burzo also reports $\mu_{\text{Co}} = 1.00 \mu_B$ for HoCo$_2$ and DyCo$_2$ as well as for GdCo$_2$. Comparison with the variation in $\mu_{\text{Co}}$ used here shows $\mu_{\text{Co}} = 0.92 \mu_B$ for amorphous HoCo$_2$, a smaller value than in the crystalline compound. This is not consistent with the charge transfer model proposed by Tao et al. [94] to account for the generally higher Curie temperatures of the amorphous RE-Co alloys. However, this should not be construed as serious evidence against the charge transfer model, since their findings were based on magnetization measurements of amorphous Gd-Co at 4.2K, certainly a much more direct method of determining the cobalt moment. Most probably, the discrepancy is due to the assumption that the exchange constants are independent of composition, whereas a decrease in $J_{\text{Co-Co}}$ and $J_{\text{RE-Co}}$ with decreasing cobalt concentration would be more realistic. Since the value of $J_{\text{Co-Co}}$ is based on samples with a high cobalt concentration, it may well be too large for $x < 0.70$ and consequently a more rapid decrease in $\mu_{\text{Co}}$ in this region would be required in order
to fit the data. However, in the absence of magnetization versus temperature data for several samples of different compositions, there is no basis on which to determine the variation of the exchange constants with composition. The amorphous Ho-Co and Dy-Co alloys investigated here definitely do exhibit higher Curie temperatures than their crystalline counterparts. For example, both amorphous DyCo₂ and HoCo₂ are ordered at room temperature, while the compounds have Tᵦ = 159⁰K for DyCo₂ and Tᵦ = 85⁰K for HoCo₂ [87].

For Gd-Fe and Tb-Fe, the following formula for the iron moment as a function of composition is used:

\[ \mu_{Fe} = 2.2 - (1-x) \left[ 4.6 - 0.94(g-1)J \right] \]

This expression was derived by Heiman et al. 100 from Mossbauer effect data. Since (g-1)J takes the values 3.5 and 3 for Gd and Tb respectively, the resulting equations are

\[ \mu_{Fe} = 2.2 - 1.31(1-x) \] for Gd-Fe
\[ \mu_{Fe} = 2.2 - 1.78(1-x) \] for Tb-Fe.

These equations are plotted in Fig. 27. By comparison with Co, the percentage reduction in the Fe moment for the same TM atomic fraction is much less. This is due to the presence of vacancies in both d sub-bands for Fe, whereas only one d sub-band has unfilled states for Co.

The iron-iron exchange constant, \( J_{Fe-Fe} = 45.0 \times 10^{-16} \) ergs, is selected empirically. Heiman et al. [100] found that the Curie temperatures for amorphous Gd-Fe decreased
with increasing iron content. Extrapolation of the $T_C$ data to 100% Fe yielded $T_C = 270^0K$ for "amorphous iron." This fixed $J_{FE-FE}$ at $20.5 \times 10^{-16}$ ergs. However, it was noted that $J_{FE-FE}$ increased significantly as the iron fraction was reduced. For this reason, it was felt that a larger value would be needed for the composition range $0.65 < x < 0.85$ containing the magnetization data reported here. Subsequently, the value $45.0 \times 10^{-16}$ ergs was determined by trial and error.

Although only limited magnetization data for Tb-Fe was taken due to a break-down in the evaporation system, a fit to the available data is easily obtained drawing on the experience gained with Gd-Fe. The availability of more data would probably necessitate only minor changes, if any, in the fitting parameters.

From the values of the constants listed in Table II, it is obvious that there is little variation in the RE-TM and RE-RE exchange interactions among the different alloys. The major differences in alloy properties result from the stronger Co-Co, as opposed to Fe-Fe, exchange coupling, the more rapid reduction in the cobalt moment than the Fe moment with increasing RE content, and the different spins and moments of the RE atoms. The first of these items results in generally higher Curie temperatures for the RE-Co alloys, while the second causes the Curie temperature of RE-Co alloys to depend much more strongly on composition.
For the same TM, an alloy containing a RE with a smaller effective spin will exhibit a lower Curie temperature than an alloy of the same composition with a RE of higher spin. Hence Ho-Co becomes paramagnetic at room temperature at a composition containing approximately 55 atomic percent Co, while Dy-Co is still ordered at room temperature for this composition.

Using the parameters in Table II, additional molecular field calculations were performed to construct plots of the Curie temperature and compensation temperature as a function of composition for Ho-Co and Gd-Fe (see Figs. 28 & 29). Although these plots may be considered only qualitatively correct, they do exhibit important general features that are nonetheless valid. First, the Curie points of the iron alloy are much lower over a wide range of composition, but they show a much smaller dependence on composition than the Curie points of the Co alloy. Second, because of their lower Curie temperatures, Gd-Fe alloys exhibit a compensation temperature only over a narrow composition range of approximately 5 atomic percent. On the other hand, compensation temperatures for Ho-Co exist over a range of almost 20 atomic percent cobalt. It should be noted that direct experimental observation of Curie points in excess of 600°K is usually not possible due to the onset of crystallization.

Using the sublattice magnetizations obtained from the molecular field model, the effective g-factor, $g_{\text{eff}}$, 

Fig. 28. Curie temperature and compensation temperature as a function of composition for Ho-Co.
Fig. 29. Curie temperature and compensation temperature as a function of composition for Gd-Fe.
for Ho-Co, Dy-Co, and Gd-Fe has been calculated from the formula

$$g_{\text{eff}} = \frac{M_{\text{RE}} - M_{\text{TM}}}{g_{\text{RE}} - g_{\text{TM}}}$$

The results are plotted in Fig. 30. As can be seen from the formula above, $g_{\text{eff}}$ passes through zero at compensation and then diverges where $(M_{\text{RE}}/g_{\text{RE}}) = (M_{\text{TM}}/g_{\text{TM}})$. Divergence occurs at $x \cong 0.83$ for Ho-Co and at $x \cong 0.845$ for Dy-Co. Over the region where strip domains are observed with Co dominated magnetizations, $g_{\text{eff}}$ is negative for both Ho-Co and Dy-Co. For Gd-Fe with $g_{\text{Gd}} = g_{\text{Fe}} = 2$, $g_{\text{eff}} = 2$ regardless of composition. If $g_{\text{Fe}} = 2.09$ is assumed after Tebble and Craik [99], then $g_{\text{eff}}$ for Gd-Fe diverges very sharply at $x \cong 0.77$ as shown in Fig. 29. For the region $x > x_{\text{Comp}}$ where strip domains are observed, $g_{\text{eff}}$ is approximately 2 to 6. Large $g$-factors are desirable since they result in higher mobilities and larger bubble velocities without dynamic conversion (recall the discussion for garnets in Chapter I).

IV.2 Characteristic Length, Wall Energy, and Exchange Constants

The characteristic length as a function of magnetization for Ho-Co, Dy-Co, and Gd-Fe is shown in Fig. 31. Strip domains are not observed on Tb-Fe films due to large coercivities. For Ho-Co and Dy-Co, all data points represent films with cobalt-dominated magnetizations (i.e. $x > x_{\text{Comp}}$). The magnetization ranges where strip
Fig. 30. Effective G-factor as a function of composition for Ho-Co, Dy-Co and Gd-Fe.
Fig. 31. Characteristic length versus magnetization.
domains were observed and the corresponding values of characteristic length are as follows:

\[
\begin{array}{ccc}
4\pi M \text{ (Gauss)} & \lambda(\mu m) \\
\hline
\text{Ho-Co} & 600-2500 & 0.40-0.06 \\
\text{Dy-Co} & 2500-5400 & 0.11-0.04 \\
\text{Gd-Fe} & 800-3200 & 0.30-0.025 \\
\end{array}
\]

Also shown in Fig. 31 are two dashed lines with slopes of negative one. Remember that since the characteristic length can be written

\[
\lambda = \frac{\sqrt{32\pi} \sqrt{AQ}}{4\pi M}
\]

such lines represent contours of constant AQ. The value of AQ for the upper line is that which gave the best fit to the data for sputtered Gd-Co of Chaudhari et al. \cite{57},

\[
AQ = 12.5 \times 10^{-6} \text{ (see Fig. 9.)}
\]

For the lower line,

\[
AQ = 7 \times 10^{-6} \text{ erg/cm}, \text{ the value corresponding to Gd-Co-Mo films sputtered from a target with 15 atomic % Mo.}
\]

The characteristic lengths for the three alloys studied here all lie between these two lines, indicating that similar values can be obtained in the Gd-Co-Mo system with generally lower magnetizations. However, the region with \(Q > 1\) extends to smaller characteristic lengths for these evaporated films, particularly for Gd-Fe and Dy-Co.

The straight lines drawn through each set of data points in Fig. 31 represent least squares fits to an equation of the form \(\lambda = D(4\pi M)^n\). The values of \(D\) and \(n\) are:

\[
\begin{array}{ccc}
\text{Gd-Fe} & \text{Dy-Co} & \text{Ho-Co} \\
D & 70100 & 7560 & 1510 \\
n & -1.84 & -1.42 & -1.29 \\
\end{array}
\]
The slope for Gd-Fe, -1.84, is very close to the -2 value which corresponds to a constant wall energy density. Since \( \mathcal{G}_w = 4\sqrt{AK_u} \), and since the trend in \( A \) should be the same as for \( K_u \), one would expect \( K_u \) for Gd-Fe to exhibit a weaker dependence on magnetization, and hence on composition, than \( K_u \) for Ho-Co and Dy-Co. Measurements of \( H_K \) and \( K_u \) presented later confirm this conclusion.

As noted previously, all data points for Ho-Co and Dy-Co in Fig. 31 represent films for which \( x > x_{\text{comp}} \). Due to a lower wall energy, films with \( x < x_{\text{comp}} \) exhibit a significantly smaller strip period and characteristic length than films of the same magnetization with \( x > x_{\text{comp}} \). In fact, only parallel strip domains are observed for Ho-Co and Dy-Co films with rare-earth dominated magnetizations (see the photographs in Fig. 32). This fact, together with the shape of the Hall effect hysteresis loops for such films, indicates the existence of an in-plane component of the magnetization, even though \( Q \) is in excess of one. This behavior may result from the fact that all directions in the plane of the film are not equivalent. The presence of hard and moderate directions in the plane of the film and an easy axis normal to the plane of the film would be similar to the observations on coevaporated Gd-Co by Taylor and Gangulee [78], who found easy and moderate directions in the plane of the film and a hard axis normal to the film. For Ho-Co and Dy-Co films with \( x > x_{\text{comp}} \) where the uniaxial anisotropy is stronger, the energy difference of the in-plane
$X > X_{\text{comp.}}, \ x = .837, \ 4\pi M = 4000, \ \rho_0 = 1.0 \mu m$

$X < X_{\text{comp.}}, \ x = .716, \ 4\pi M = 2270, \ \rho_0 = 1.1 \mu m$

Fig. 32. Stripes on Dy-Co
directions is apparently not large enough to affect the a.c. demagnetized domain configuration.

Using the characteristic length data and magnetization measurements, the wall energy density can be calculated from

$$\sigma_w = \frac{l}{4\pi M^2} = \frac{l}{4\pi} (4\pi M)^2$$

The results are plotted against composition in Figs. 33, 34, and 35. For Ho-Co the data has been replotted in Fig. 33b with the compositions corrected to lie on the molecular field magnetization curve. This is done under the assumption that the magnetization measurement is more accurate than the composition measurement, an assumption that appears to be justified since the scatter in the data is definitely reduced.

Both Ho-Co and Dy-Co show a definite increase in wall energy with increasing cobalt content. As will be seen shortly, this results from increases in both A and $K_u$ (recall $\sigma_w = \sqrt{AK_u}$). The large wall energies for Dy-Co are indicative of large anisotropies, since A should be comparable for Ho-Co and Dy-Co. Gd-Fe exhibits little variation in $\sigma_w$ over the entire region where strip domains can be observed, both above and below compensation. This is consistent with the -1.84 slope of the fit to the characteristic length data. From the relatively constant Curie temperatures of Gd-Fe over the same composition range, one can infer that A is also relatively constant. Hence, the behavior of the $\sigma_w$ data indicates that $K_u$ does not vary rapidly for these compositions.
Fig. 33. Wall energy versus composition for Ho-Co.
Fig. 34. Wall energy versus composition for Dy-Co.
Fig. 35. Wall energy versus composition for Gd-Fe.
Noting that the wall energy is given by \( \sigma_w = 4 \sqrt{AK_u} \), it is possible to calculate the exchange constant \( A \) from the following formula:

\[
A = \frac{\sigma_w^2}{16K_u} = \frac{\lambda^2 (4\pi M)^3}{32 \pi H_K} = \frac{\lambda^2 (4\pi M)^4}{(16\pi)^2 K_u}
\]

The resulting values of \( A \) are shown in Figs. 36, 37, and 38. As expected, the exchange constants for Ho-Co and Dy-Co increase with increasing cobalt atomic fraction. On the other hand, \( A \) for Gd-Fe shows a smaller variation with composition.

The exchange constant can also be calculated from the molecular field model using the following equation given by Hasegawa [60]:

\[
A = \frac{n_{11} J_{11} \overline{J_1} (1-x)^2}{a_{11}} + \frac{(n_{12}+n_{21}) J_{12} \overline{J_1} \overline{S_2} x (1-x)}{a_{12}} + \frac{n_{22} J_{22} \overline{S_2} x^2}{a_{22}}
\]

where 1 = RE, 2 = TM,

- \( J_{11}, J_{12}, J_{22} \) are the exchange constants
- \( a_{11}, a_{12}, a_{22} \) are the RE-RE, RE-TM, and TM-TM interatomic distances respectively

\( \overline{J}_1 = J_1 B_{J_1} \)

\( \overline{S}_2 = S_2 B_{S_2} \)

\( n_{11}, n_{12}, n_{22} \) are the number of RE-RE, RE-TM and TM-TM pairs per volume extending to the first nearest neighbors.
Fig. 36. Exchange constant versus composition for Ho-Co.
Fig. 37. Exchange constant versus composition for Dy-Co.
Fig. 38. Exchange constant versus composition for Gd-Fe.
Based on structure studies of amorphous GdFe$_2$ by Cargill [97] and TbFe$_2$ by Rhyne et al. [103], we take $a_{11} = 3.5$ Å, $a_{12} = 3.0$ Å and $a_{22} = 2.5$ Å. Following Hasegawa [62], it is assumed that $n_{11} = n_{12} = n_{22} = 2$. The dashed lines in Figs. 36-38 show the exchange constant as calculated from the molecular field model. Agreement between values of $A$ calculated by the two different methods is not particularly good, although in view of the indirectness of each method, better agreement might be merely fortuitous. For example, as calculated from the formula

$$A = \frac{\kappa^2 (4\pi M)^4}{(16\pi)^2 K_u}$$

the relative error in $A$ is approximated by

$$\frac{\Delta A}{A} \approx 2 \frac{\Delta \kappa}{\kappa} + 4 \frac{\Delta (4\pi M)}{4\pi M} + \frac{\Delta K_u}{K_u}$$

If we assume a 10% uncertainty in $\kappa$, 5% in $4\pi M$, and 20% in $K_u$, then the error in $A$ may be as large as 60%. The molecular field calculation is also subject to large uncertainties due to possible errors in the exchange integrals and sublattice magnetizations. It should be noted that the molecular field results are consistently smaller than the values of $A$ calculated from $\kappa$, $4\pi M$, and $K_u$. This also appears to be the case for amorphous Gd-Co prepared by sputter deposition. As mentioned previously, Chaudhari, et al. [57] found that their characteristic length data for Gd-Co could be fitted with an AQ value of 12.5 $\times$ 10$^{-6}$.
ergs/cm. Assuming typical Q's of 5-10, this implies that A varies from $1.25 \times 10^{-6}$ to $2.5 \times 10^{-6}$ ergs/cm. On the other hand, Hasegawa's [47] molecular field calculation showed A for Gd-Co to be in the range $5.7 \times 10^{-7}$ to $6.6 \times 10^{-7}$ ergs/cm over the same composition range ($0.75 < x < 0.85$).

IV.3 Anisotropy

As noted previously, all four of the amorphous RE-TM alloys investigated here exhibit uniaxial anisotropy normal to the plane of the film with $H_K \geq 4\pi M$ over broad composition ranges. The anisotropy fields, $H_K = 2K_u/M$, for Ho-Co, Dy-Co, and Gd-Fe are plotted against composition in Figs. 39, 40, & 41. The molecular field magnetization curves are also indicated in each figure so that Q values can be estimated. The dashed lines are not fitted curves, but merely represent trends in the data. In Fig. 39a, considerable scatter in the data for Ho-Co is seen. However, correcting the compositions so that each point lies on the magnetization curve suppresses some of the scatter and reveals a clearer trend in the data, as shown in Fig. 39b. This type of correction was not used in plotting the data for Gd-Fe and Dy-Co.

From these graphs, conservative estimates for the composition regions where $H_K > 4\pi M$ are as follows:

- Ho-Co $0.66 < x < 0.78$
- Dy-Co $0.66 < x < 0.88$
- Gd-Fe $0.71 < x < 0.82$
Fig. 39. Anisotropy field versus composition for Ho-Co.
Fig. 40. Anisotropy field versus composition for Dy-Co.
Fig. 41. Anisotropy field versus composition for Gd-Fe.
For Dy-Co this region extends over a change in $x$ of 0.23, whereas for Ho-Co and Gd-Co the change in $x$ is 0.12 and 0.11 respectively. The anisotropy fields for Gd-Fe are slightly larger than those for Ho-Co, while $H_K$ for Dy-Co is much larger than for either of the other two alloys. Although only a few data points for Tb-Fe have been compiled, preliminary results indicate that it has the largest room-temperature anisotropies. Because the anisotropies of only three Tb-Fe films have been measured, they were not plotted on a graph, but instead are listed below in the following table:

<table>
<thead>
<tr>
<th>$x$</th>
<th>$4M(G)$</th>
<th>$H_K$(Oe)</th>
<th>$Q$</th>
<th>$K_u$(ergs/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.663</td>
<td>4340</td>
<td>12,500</td>
<td>2.9</td>
<td>$2.2 \times 10^6$</td>
</tr>
<tr>
<td>0.688</td>
<td>3850</td>
<td>15,000</td>
<td>3.9</td>
<td>$2.3 \times 10^6$</td>
</tr>
<tr>
<td>0.719</td>
<td>3050</td>
<td>22,000</td>
<td>7.2</td>
<td>$2.7 \times 10^6$</td>
</tr>
</tbody>
</table>

The data for the anisotropy energy, $K_u$, of Gd-Fe, Ho-Co, and Dy-Co are plotted against composition in Figs. 42 and 43. For all three alloy systems, the anisotropy increases monotonically as the transition-metal fraction increases. In order to investigate the possibility that pair ordering may contribute to the anisotropy in these films, the data for each alloy has been fitted with the dipolar equation

$$K_u = C_{TM-TM} M_{TM}^2 + C_{TM-RE} M_{TM}M_{RE} + C_{RE-RE} M_{RE}^2,$$

where the $C$'s are coupling constants and $M_{TM}$ and $M_{RE}$ are the TM and RE sublattice magnetizations [63,78]. The
Fig. 42. Anisotropy energy versus composition for Ho-Co and Gd-Fe.
Fig. 43. Anisotropy energy versus composition for Dy-Co.
sublattice magnetizations are obtained from the molecular field fits previously discussed. The values of the dipolar coupling constants are listed in Table III, and the resulting curves are indicated by solid lines in each figure. Both sublattice magnetizations are considered to be positive quantities, and hence a term with a positive coupling constant contributes to perpendicular anisotropy while a negative one contributes to in-plane anisotropy. For convenience, the results of Taylor and Gangulee [78,79] for evaporated Gd-Fe and Gd-Co are also included in Table III. Their data was discussed in Chapter II and can be seen in Figs. 10 and 12.

Before discussing the results, a word about the fitting procedure used to determine the coupling constants is in order. The results in Table III were obtained by trial and error to give the best eyeball fits to the data. A direct least-squares

<table>
<thead>
<tr>
<th></th>
<th>C_{TM-TM}</th>
<th>C_{TM-RE}</th>
<th>C_{RE-RE}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho-Co</td>
<td>5.28</td>
<td>-10.32</td>
<td>5.41</td>
</tr>
<tr>
<td>Dy-Co</td>
<td>2.93</td>
<td>1.99</td>
<td>2.17</td>
</tr>
<tr>
<td>Gd-Fe</td>
<td>0.74</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>Gd-Fe (Taylor et al. [79])</td>
<td>0.922</td>
<td>1.356</td>
<td>0.799</td>
</tr>
<tr>
<td>Gd-Co (Taylor et al. [78])</td>
<td>0.660</td>
<td>2.218</td>
<td>0.097</td>
</tr>
</tbody>
</table>

fit is not possible since the sublattice magnetizations are expressed in terms of Brillouin functions. An attempt to
circumvent this difficulty was made using the following variable transformation:

\[ M_1 = \frac{M g_1}{g} \left( \frac{g_2 - g}{g_2 - g_1} \right) \]
\[ M_2 = \frac{M g_2}{g} \left( \frac{g_1 - g}{g_2 - g_1} \right) \]

where \( 1 = \text{RE} \) and \( 2 = \text{TM} \). The inverse transformation is

\[ g = \frac{M_1 - M_2}{M_1 - \frac{M_2}{g_1} - \frac{M_1}{g_2}} \]
\[ M = M_1 - M_2 \]

For this transformation to be valid, it is obvious that one must require \( g_1 \neq g_2 \). If \( g_1 \) and \( g_2 \) are the RE and TM \( g \)-factors, then \( g \) is the effective \( g \)-factor discussed previously. However, it is not necessary to use these values, since the results are independent of \( g_1 \) and \( g_2 \) as long as they are not too close together. Substituting the equations for \( M_1 \) and \( M_2 \) in

\[ K_u = C_{11} M_1^2 + C_{12} M_1 M_2 + C_{22} M_2^2 \]

results in the following expression:

\[ K_u = M^2 \left( a_0 + a_1 g^{-1} + a_2 g^2 \right) \]

or

\[ \frac{K_u}{2 \pi M^2} = H_K = \frac{1}{2 \pi} \left( a_0 + a_1 g^{-1} + a_2 g^2 \right) \]

where the constants \( a_0, a_1, a_2 \) are related to \( C_{11}, C_{12}, C_{22} \) by algebraic equations \([63]\). Since this is a
second order polynomial, a least squares fit of the $H_K$ data as a function of $\frac{1}{T}$ is easily accomplished, where $g$ is calculated using $M_1$ and $M_2$ as determined from the molecular field fit. From the values of $a_0$, $a_1$, and $a_2$, the coupling constants $C_{11}$, $C_{12}$, and $C_{22}$ can be computed. This procedure was followed for Dy-Co with the following results: $C_{11} = 2.50$, $C_{12} = -1.65$, $C_{22} = 2.60$. However, when $K_U$ was plotted as a function of $x$ using these values, the resulting curve obviously did not fit the data as well as that found by trial and error. Apparently, this is due to the indirectness of the fitting procedure. However, these results are similar to those obtained from an eyeball fit and encouraged the belief that the earlier results were not unduly distorted by personal bias.

An alternative method of fitting the data numerically is to express each sublattice magnetization as a polynomial in the TM atomic fraction $x$. Preliminary work indicated that a fourth order polynomial would be required. Therefore, the expression for $K_U$ would have involved an eighth-order polynomial with nine coefficients, all of which could be expressed in terms of $C_{11}$, $C_{12}$, $C_{22}$. Due to a lack of time and the feeling that a maximum of additional effort would be required to obtain a minimum of additional information, this approach was not pursued further.

Returning to the results presented in Table III, one can see that the signs of the coupling constants are in agreement with the results of Taylor and Gangulee. In terms
of a pair ordering model, RE-TM pairs contribute to in-plane anisotropy while TM-TM and RE-RE pairs contribute to perpendicular anisotropy. It should be noted that the TM-TM coupling constant appears to be affected by the rare-earth constituent and the RE-RE coupling constant by the transition metal.

Comparison of the present results for Gd-Fe with those of Taylor et al. shows comparable values of \( C_{\text{TM-TM}} \). However, their values of \( C_{\text{TM-RE}} \) and \( C_{\text{RE-RE}} \) are much larger. This is a consequence of the fact that their data indicates a constant value of \( K_u \) for films with \( x < x_{\text{Comp}} \) instead of the continuing gradual decrease found in this work. (compare Figs. 10 & 42). If the curve for Gd-Fe shown in Fig. 42 were raised to a nearly constant value of approximately \( 3.5 \times 10^5 \text{ erg/cm}^3 \) for \( x < .75 \), then the magnitudes of the coupling constants would be much closer to those found by Taylor. This example illustrates the fact that the C's are very sensitive to some variations in the fitted curve, although the signs remain the same as long as the curvature is unaltered.

In fitting the anisotropy data with a dipolar equation, it was assumed for the moment that the anisotropy is due to pair ordering. The consequences of that assumption as reflected in the values of the coupling constants must now be examined. The results for both Gd-Fe and Dy-Co are definitely plausible. The magnitudes of the \( C_{ij} \)'s for Dy-Co are reasonable in view of the large anisotropies involved.
Moreover, the ability of Taylor and Gangulee to explain the easy-plane anisotropy (i.e. hard axis normal to the film plane) of evaporated Gd-Co in terms of the pair model lends it added credibility. However, it seems anomalous that Ho-Co, which exhibits room temperature anisotropies comparable to or less than those of Gd-Fe, should have by far the largest coupling constants. The values shown in Table II imply that each of the contributions to the anisotropy is an order of magnitude larger than the observed net anisotropy (note that $C_{\text{TM-TM}} + C_{\text{TM-RE}} + C_{\text{RE-RE}} = 0.37$).

Despite the success in fitting observed anisotropy variations with the dipolar equation, it may be that pair ordering is merely an approximation to a more complex form of structural ordering. For example, the critical dependence of the Co-Co coupling constant on the rare-earth might be interpreted to indicate the presence of short-range order extending beyond pairing. On the other hand, results to be discussed presently suggest that there is an appreciable contribution to the anisotropy from single-ion effects in alloys with a rare earth other than gadolinium.

In any event, in the process of making the fits to the dipolar equation, it was definitely established that the anisotropy cannot be accurately described by an equation of the form $K_u = C M_i^n$ where $C$ is a constant and $M_i$ is either the RE or TM sublattice magnetization. This indicates that $K_u$ cannot be attributed entirely to either the RE or the TM. Hence a major contribution to the anisotropy
must be due to a mechanism involving interactions between
the two, whether it is pair ordering or a more complex short
range order.

As mentioned previously, the magnetization versus ap-
plied field curves for Ho-Co, Dy-Co, and Tb-Fe exhibit a
relatively large high-field susceptibility above technical
saturation. This result is attributed to incomplete order-
ing of the RE moments in zero field due to random local
anisotropy fields. A high field (HF) susceptibility has
been observed by Rhyne et al. [101] in magnetization
measurements on bulk amorphous TbFe$_2$, but they noted the
absence of a large susceptibility for amorphous GdFe$_2$. The
susceptibilities for Ho-Co and Dy-Co are plotted against
composition in Figs. 44 and 45. The data were calculated
from the slopes of the magnetization versus applied field
curves at high fields. Since this slope is small, sub-
stantial errors are possible. The accuracy is estimated
to be about $\pm 0.5 \times 10^{-3}$. Nevertheless, the trend toward
larger susceptibilities at lower TM atomic fractions is con-
sidered to be valid. The increase in susceptibility for
Ho-Co over the range $0.70 < x < 0.80$ is believed to be due to
two factors. First, as $x$ decreases there are more RE ions
present to contribute to the susceptibility. Second,
although the Curie temperature remains well above room tem-
perature, it does decrease quite rapidly in this region with
the result that the strength of the local anisotropy fields
at room temperature is reduced. For samples with Curie
Fig. 44. High field susceptibility versus composition for Ho-Co.
Fig. 45. High field susceptibility versus composition for Dy-Co.
points quite close to room temperature, the local anisotropy fields should be negligible, and the susceptibility is that usually observed in ferromagnetic materials close to their Curie temperature. A Ho-Co film that was paramagnetic at 20°C showed $\chi \approx 3 \times 10^{-3}$. Smaller MF susceptibilities ($< .7 \times 10^{-3}$) also seemed to be present in Gd-Fe, but pure TM films also exhibited such behavior occasionally. This may have been due to imperfect cancellation of the holder signal or to an artifact of the magnetometer caused perhaps by poorer regulation of the magnet current at high fields. For this reason, a definite conclusion about the existence of local anisotropy in Gd-Fe has not been reached. If such local anisotropy does exist, it must have an origin other than the single-ion effect.

Although a perfectly random orientation of the local anisotropy axes would not result in a macroscopic easy axis, it is possible that there may be a slight preferential ordering due to the evaporation process. This possibility is suggested by a computer simulation of the structure of thin amorphous films grown from a unidirectional vapor beam [104]. To determine if this effect could contribute appreciably to the anisotropy of evaporated films containing rare earths other than gadolinium, an estimate of the possible anisotropy contributed by this mechanism in amorphous TbFe$_2$ will be calculated.

Cochrane et al. [91] have found that the structure of amorphous RE-TM alloys may be modeled by a computer-generated
cluster of randomly close-packed hard spheres of two sizes. Computer generated RDF's based on this model showed reasonable agreement with neutron diffraction results on amorphous TbFe₂. Utilizing a point charge model, they also calculated the electrostatic potential at RE-sites in the cluster. Taking the parameters for terbium, the second order potential V₂⁰ was found to be dominant with an interaction energy of ΔE₂ = 0.403 eV/Tb ion. Somewhat surprisingly in view of the random structure, ΔE₂ was found to have a standard deviation of only 2% over a large number of sites in the cluster. The distribution of the local easy axes over the unit sphere for the computer generated cluster was uniform.

If all the local easy axes could be perfectly aligned, then the resulting anisotropy would be huge:

\[ K_2 \approx 0.403 \text{ eV/Tb ion} \times 1.6 \times 10^{-12} \text{ergs/eV} \times 2 \times 10^{22} \text{ Tb ions/cm}^3 \]
\[ \approx 1 \times 10^{10} \text{ ergs/cm}^3 \]

at 0°K. Callen and Callen [105] have shown that the temperature dependence of single-ion anisotropy may be predicted by

\[ K_2(T) = K_2(0) \hat{I}_{5/2} \left[ \mathcal{L}^{-1}(m_{\text{RE}}(T)) \right] \]

where \( \hat{I}_{5/2} \) is a normalized hyperbolic Bessel function, \( \mathcal{L}^{-1} \) is the inverse of the Langevin function, and \( m_{\text{RE}}(T) = M_{\text{RE}}(T)/M_{\text{RE}}(0) \) is the reduced rare-earth sublattice magnetization. This equation is plotted in Fig. 46. From
Fig. 46. Temperature dependence of single-ion anisotropy.
a molecular field calculation (see Fig. 47) it is estimated that \( M_{\text{TB}}(300^\circ K)/M_{\text{TB}}(0) \approx 0.5 \) for amorphous TbFe\(_2\). Hence, \( K_2(300^\circ K)/K_2(0^\circ K) \approx 0.15 \). Therefore, the room temperature anisotropy corresponding to perfect alignment of the local easy axes would be on the order of

\[ K_2(300^\circ K) \approx 10^9 \text{ ergs/cm}^3. \]

Since the anisotropy of an amorphous Tb\(_{34}\)Fe\(_{66}\) film is found to be \( 2.2 \times 10^6 \) ergs/cm\(^3\), this result indicates that preferential alignment of only about 0.1% of the local easy axes would be necessary to make a substantial contribution to the observed anisotropy.

To summarize, it appears probable that the anisotropy in Tb-Fe, Dy-Co, and Ho-Co is partly due to a slight preferential alignment of the local anisotropy axes. However, the results from fitting the anisotropy data with the dipolar equation indicate that this cannot be the sole origin of the anisotropy and that the transition-metal also plays a vital role. Since crystal field effects are small for gadolinium, the anisotropy in evaporated Gd-Fe (and Gd-Co) cannot be attributed even in part to the single ion mechanism, and may be primarily the result of pair ordering.

IV.4 Coercivity

The coercivity of the evaporated RE-TM films is determined from Hall effect hysteresis loops. The results are plotted in Figs. 48-51. Ho-Co and Gd-Fe exhibit comparable values of coercivity, but \( H_C \) increases dramatically for Dy-Co and Tb-Fe. In fact, for a composition range of about
Fig. 47. Net magnetization and terbium sublattice magnetization as a function of temperature for Tb.34Fe.66. From a molecular field calculation.
Fig. 48. Coercivity versus composition for Ho-Co.
Fig. 49. Coercivity versus composition for Gd-Fe.
Fig. 51. Coercivity versus composition for Tb-Fe
atomic percent in the neighborhood of compensation 
(\(x = .78\)), \(H_C\) for Tb-Fe exceeded the largest available 
fields for the Hall effect measurement (10 koe) and loops 
could not be plotted. Irregular domains characteristic of 
a coercive film in its virgin state were observed on such 
films when they were first removed from vacuum. Even after 
being placed in an applied field of 10 koe, the same domain 
structure was still observed.

Consider a domain wall of length \(L\) in a film of thick-
ness \(h\). For a shift \(dx\) of the wall parallel to itself, 
the increase in the energy of the system must be equal to 
the work performed on it. Hence

\[
2H_A M h L \ dx = \frac{\partial (\sigma_w h L)}{\partial x} \ dx
\]

where \(H_A\) is the applied field. The critical field at which 
the wall motion becomes irreversible is the coercivity, \(H_C\). 
Thus

\[
H_C = \frac{1}{2MhL} \ \frac{\partial (\sigma_w h L)}{\partial x}
\]

Using the expression for wall energy \(\sigma_w = 4\sqrt{AK_u}\) and taking 
the appropriate partial derivatives, one can show that

\[
H_C = \frac{\sigma_w}{2M} \left( \frac{1}{2A} \frac{\partial A}{\partial x} + \frac{1}{2K_u} \frac{\partial K_u}{\partial x} + \frac{1}{h} \frac{\partial h}{\partial x} + \frac{1}{L} \frac{\partial L}{\partial x} \right)
\]

Assume that the domain wall is in a local potential well of 
half-width equal to the domain wall width \(\delta\). This assumption
is valid since if $S$ is very much greater than the width of the potential well, the wall will not be perturbed by it \([44]\). Substituting $\frac{3A}{3x} = \frac{A}{b}$ etc. and $S = \sqrt{A/K_u}$ leads to

$$H_c = \frac{2K_u}{M} \sum_i \frac{\Delta X_i}{X_i}$$

where $x = K_u, A, L,$ and $h$. Since there is no basis on which to expect appreciably larger relative fluctuations $\Delta K_u/K_u$ and $\Delta A/A$ for any particular alloy, much of the difference in observed coercivity is related to variations in the quantity $2K_u/M = H_K$. This observation is supported by the fact that both $H_c$ and $H_K$ increase through the series Ho-Co, Gd-Fe, Dy-Co, and Tb-Fe.

Although the measurement of $H_c$ from the Hall hysteresis loops does not have good resolution for low values of $H_c$, the smallest coercivities observed in Ho-Co and Gd-Fe films appear to be on the order of 5-10 Oe. These are undesirably large values for a bubble material, although reductions may be possible by means of post deposition heat treatments or radiation damage \([48,75]\). Gambino et al. \([44]\) report $H_c$ of 0.5 to 1 Oe for as deposited sputtered Gd-Co films. If evaporated films should prove to have process limited coercivities on the order of several oersteds, then evaporation may not be suitable for the fabrication of amorphous bubble materials.

IV.5 Materials Status Chart

The properties of amorphous evaporated Ho-Co, Dy-Co, and Gd-Fe are summarized in the materials status chart in
Fig. 52. Comparison of this chart with the one in Fig. 3 shows that Gd-Fe and Ho-Co fall into roughly the same area as Gd-Co and Gd-Co-Mo. Dy-Co is just to the high anisotropy side of this region and seems to bear the greatest similarity to the hexagonal ferrites. From the point of view of bubble applications, Dy-Co and Tb-Fe are obviously unsuitable because of their large coercivities. It may be possible to fabricate Gd-Fe and Ho-Co films with sufficiently low coercivities, but addition of a third element would be necessary to improve the temperature stability. Due to the larger damping associated with holmium, Ho-Co films may well exhibit undesirable dynamic properties. The combination of high coercivities and low Curie points makes Tb-Fe suitable for thermomagnetic information storage by Curie-point writing.
Fig. 52. Materials status chart.
V. CONCLUSIONS

In this chapter, the major conclusions about the magnetic properties of the evaporated amorphous RE-TM alloys are summarized.

1) Analysis of the room temperature magnetization data using a molecular field model confirms the important influence of charge transfer on the magnetic properties. This is particularly true for the two cobalt alloys, where the rapid reduction in the cobalt moment with composition for films with more than 15 atomic per cent rare earth results in a strong composition dependence for the exchange constant A and the Curie temperature, \( T_C \). Since Fe has vacancies in both d sub-bands, the reduction in the iron moment with increasing rare-earth content is much more gradual, as the molecular field analysis confirms. Hence, A and \( T_C \) for Gd-Fe are relatively constant over the composition range studied.

2) The stronger Co-Co, as opposed to Fe-Fe, exchange coupling results in generally higher exchange constants and Curie temperatures for the Co alloys. Consequently, the Co alloys exhibit a compensation temperature over a composition range of approximately 20 atomic per cent, as opposed to 5 atomic per cent for the iron alloys.

3) For the same TM, an alloy containing a RE with a smaller effective spin will exhibit a lower Curie temperature
than an alloy of the same composition with a RE of higher spin. Hence, Dy-Co is ordered at room temperature over a wider range of composition than Ho-Co.

4) There is little variation in the RE-TM and RE-RE exchange constants among the various alloys.

5) Both Ho-Co and Gd-Fe exhibit smaller values of characteristic length for a given magnetization than sputtered Gd-Co. Dy-Co has large values of $l$ at high magnetizations due to large anisotropy energies.

6) Wall energies for Ho-Co and Dy-Co vary from 0.5 - 3.5 ergs/cm$^2$ and 2 - 9 ergs/cm$^2$ respectively. In both cases, $\sigma_w$ increases monotonically with increasing Co content. Since the two alloys have comparable values for the exchange constant $A$, the larger wall energies for Dy-Co are due to its larger anisotropies. Wall energies for Gd-Fe vary from 1.5 to 2.0 ergs/cm$^2$ and are nearly independent of magnetization and hence also composition for Fe atomic fractions of .65 - .85.

7) The anisotropy data can be fitted with a dipolar equation of the form

$$K_u = C_{11} M_1^2 + C_{12} M_1 M_2 + C_{22} M_2^2.$$  

Interpretation of the results in terms of pair ordering indicates that RE-TM pairs contribute to in-plane anisotropy, while TM-TM and RE-RE pairs contribute to perpendicular anisotropy. The magnitudes of the coupling constants show that all three interactions are important in contributing to the observed anisotropy.
Hence $K_u$ cannot be attributed entirely to either the RE or the TM. Despite the success in fitting the observed anisotropy variations with the dipolar equation, it may be that pair ordering is merely an approximation to a more complex form of structural ordering. For example, the critical dependence of the Co-Co coupling constant on the rare earth might be interpreted to indicate the presence of short-range order extending beyond pairing.

8) The alloys containing rare earths other than gadolinium have a significant susceptibility at high fields above technical saturation. This susceptibility is interpreted to indicate the existence of strong local anisotropy fields which cause incomplete ordering of the rare-earth moments.

9) An order of magnitude calculation indicates that preferential alignment of at most 0.1% of the local anisotropy axes would be necessary to make a significant contribution to the observed macroscopic anisotropy. Since the rare-earth ions Dy and Tb are more anisotropic than Ho and Gd, such a contribution would be consistent with the observations that Dy-Co and Tb-Fe show larger anisotropies than Ho-Co and Gd-Fe respectively. The fact that Ho-Co shows a stronger temperature dependence for $K_u$ than either evaporated or sputtered Gd-Co is additional evidence to support this contention [69,78].
10) Since $K_u$ for Ho-Co and Dy-Co increases monotonically with increasing cobalt atomic fraction over the composition range where the rare-earth sublattice magnetization is decreasing, the structural anisotropy giving rise to a slight preferential ordering of the local easy axes must also result in a contribution to the magnetic anisotropy from the TM. This is also indicated by the results from fitting the $K_u$ data with the dipolar equation, as noted in 7). The fact that Gd-Fe, for which local crystal field effects should be negligible, shows strong uniaxial anisotropy demonstrates conclusively that another anisotropy mechanism besides single-ion anisotropy is important.

11) The coercive force and $H_K$ appear to be related, since both increase through the series Ho-Co, Gd-Fe, Dy-Co, and Tb-Fe.

12) From the point of view of bubble domain applications, both Dy-Co and Tb-Fe show anisotropies and coercivities which are much too large. It may be possible to fabricate Gd-Fe and Ho-Co films by evaporation with sufficiently low coercivities. However, because of the larger damping associated with holmium, Ho-Co may exhibit undesirable dynamic properties. Moreover, Ho-Co exhibits a rather low negative effective $g$-factor ($0 > g_{eff} > -2$) over the composition range most favorable for the formation of bubble domains.
Appendix 1

Operation of the Evaporation Controller

The first step in fabricating films is to choose the desired composition and then select appropriate evaporation rates to give that composition. Since the change in frequency of the crystal monitor is proportional to the mass of material deposited on the crystal,

$$\frac{\Delta f_{RE}}{\Delta f_{TM}} = \frac{\text{RE weight fraction}}{\text{TM weight fraction}} = \frac{1-y}{y} = \frac{1}{y} - 1$$

where $\Delta f_{RE}$ and $\Delta f_{TM}$ are the frequency changes of the respective crystal monitors for a fixed time interval and $y$ is the TM weight fraction of the deposited material. The weight fraction and atomic fraction are related by

$$y = \frac{A_{TM} x}{A_{TM} x + (1-x) A_{RE}}$$

where $A_{TM}$ and $A_{RE}$ are the atomic weights of the TM and RE respectively and $x$ is the TM atomic fraction. It is easy to show that

$$\frac{\Delta f_{RE}}{\Delta f_{TM}} = \frac{A_{RE}}{A_{TM}} \left( \frac{1-x}{x} \right)$$

For the binary alloys investigated here the values of $A_{RE}/A_{TM}$ are: Ho-Co, 2.7986; Dy-Co, 2.7574; Gd-Fe, 2.8157;
Tb-Fe, 2.8457. From the expression for $\Delta f_{RE}/\Delta f_{TM}$ one can easily determine the relative rates of evaporation needed for a given TM atomic fraction either graphically or algebraically. The next step is to pick the actual rates, bearing in mind that the TM usually cannot be evaporated faster than 5 Å/sec at the monitor with the 2 kW power supplies available.

Potentiometers on the evaporation controller enable one to set the rate of the corresponding source by attenuating the input voltages from the monitor control unit and the Moseley 17108 A time base. Usually, only the voltage from the monitor is attenuated. The time base is always set on the 50 sec/in scale. The monitor is usually set so that full scale deflection of the frequency meter corresponds to 30 kHz, unless a very slow rate of evaporation is desired (1-2 Å/sec). The attenuators are set with the aid of the x-y plotter using the following procedure:

1. Using the x-y plotter, let the ramp voltage from the time base rise to the value corresponding to an elapsed time of 500 sec (i.e. a horizontal deflection of the plotter pen of 10 inches). Although the time base should be set at 50 sec/in during the evaporation, one can use the 5 sec/in setting to do this, thus saving time.

2. From the selected evaporation rate, calculate the frequency change, $\Delta f_{500}$, for an elapsed time of 500 sec.
3. Adjust the variable frequency oscillator (VFO) on the crystal monitor control unit so that the frequency meter reads $\Delta f_{500}$. This can be done more accurately by connecting a digital frequency counter to the "frequency" jack on the back of the control unit. At this point the vertical gain of the x-y plotter should be set so that the pen will not run off scale during the evaporation. Usually the vernier scale between 1 v/in and 10 v/in is used and the gain adjusted so that the pen will trace a straight line with a slope of one-half (i.e. 5 in. vertical deflection after 500 sec.) An evaporation longer than 500 sec. can be recorded by using both the vertical and horizontal zero knobs to move the pen back on scale (see Fig. 20).

4. Two LED's on the front of the evaporation controller indicate deviations from the desired evaporation rate. Simply attenuate the voltage from the monitor so that both LED's are extinguished. Now the source will track the desired rate.

5. Follow the same procedure for the second source.

6. Rezero the time base and the oscillator and you are ready to go.

One usually begins an evaporation with the toggle switch on the evaporation controller set in the "no feedback" position. The power to the e-gun is then adjusted manually for approximately the right deposition rate. At this point, the VFO knob is set so that the LED's are both
momentarily out. Then the switch is flipped to "feedback" and controlled evaporation begins.

For reference, circuit diagram of the controller is included in Fig. 1-1. The unity gain input stages provide an input impedance of 100 K and prevent loading of the time base and the monitor voltage from the "recorder" jack. The large capacitors on each stage reduce the gain for 60 Hz noise on the input voltages, which can cause the current through the triac to have a d.c. component. This saturates the core of the filament transformer, causing the power supply fuse to blow every time. The same time base is used to drive both x-y plotters and both evaporation controllers. The input impedance of the four devices in parallel is about 50 K, whereas the time base will drive a minimum load of 20 K.
Fig. 1-1. Circuit diagram for the evaporation controller.
Appendix 2
X-Ray Fluorescence Data Analysis

X-ray fluorescence was used to determine film composition and thickness. If the film to be analyzed is sufficiently thin, each atom within it will absorb and emit x-rays independently of the others without significantly altering the incident beam. Under such conditions, the intensities of the transition metal (TM) $K_\alpha$ and rare earth (RE) $L_\alpha$ emission lines excited in the film are directly proportional to the respective numbers of TM and RE atoms in the film. The proportionality constants are obtained simply by determining the intensities from pure metal standard films of known thickness. Of course, corrections must be made for background intensity and for differences in atomic density between the RE and TM standard films and the amorphous alloy film.

It should be emphasized that the method described above is used properly only when the films to be analyzed are sufficiently thin. If they are too thick, matrix absorption effects between the RE and TM atoms become important, and the measured film composition will be in error. Secondary fluorescence is not a consideration in any event, as the following numbers show. Examination of this table shows

<table>
<thead>
<tr>
<th></th>
<th>$K_{\alpha_2}$</th>
<th>$K_{\alpha_1}$</th>
<th>$L_{\alpha_2}$</th>
<th>$L_{\alpha_1}$</th>
<th>$K$</th>
<th>$L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.9399</td>
<td>1.9360</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1.7928</td>
<td>1.7889</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>2.0568</td>
<td>2.0460</td>
<td>1.9863</td>
<td>1.9755</td>
<td>1.709</td>
<td>1.648</td>
</tr>
<tr>
<td>Tb</td>
<td>1.9198</td>
<td>1.9088</td>
<td>1.8558</td>
<td>1.8447</td>
<td>1.579</td>
<td>1.535</td>
</tr>
</tbody>
</table>
that the RE L_\alpha emission line is always to the low energy side of the TM K absorption edge, and the TM K_{\alpha} emission line is always to the low energy side of the RE L_{\alpha} absorption edge. Hence, secondary fluorescence will not occur.

The film to be analyzed must also be sufficiently thin to permit the incident beam to penetrate without significant attenuation. If this is not the case, atoms toward the base of the film will be exposed to a less intense x-ray beam and will be excited less frequently than those near the top of the film. This will lead to errors in thickness measurements and also in composition if there is a significant difference in attenuation between the standards and the alloy film.

The assumptions stated at the beginning are believed to be justified for the films studied here based upon the following observations:

1. X-ray thickness measurements show good agreement with interferometer thickness measurements for films where the latter measurement gives values of 0.6 \mu m or less.
2. Compositions measured using standards of varying thicknesses from .15 to .35 \mu m varied by at most 1.5%.

The absolute accuracy of the analysis is limited by how well the thicknesses of the standard films are known. These thicknesses were measured with an interferometer. As stated in the text, the nominal accuracy of this technique is less than 300 \AA, a rather large percentage error for a standard film with a nominal thickness of 3000\AA. However,
by taking special care and averaging a large number of measurements, the error can be reduced to $<100 \, \text{Å}$. As noted above, good consistency was obtained using different standards.

Data was taken on two instruments:
1) a GE XRD-5 spectrometer equipped with a molybdenum fluorescence tube operating at 50 kv and 44 ma.; 2) a Phillips Norelco spectrometer equipped with a chromium fluorescence tube operating at 50 kv and 40 ma. The Phillips spectrometer had a vacuum path for the x-rays which could be evacuated to a pressure of 300 microns. Composition measurements taken on the same instrument at intervals as long as one year apart agreed within 1%. Reproducibility for measurements taken on different instruments with the same standards was almost as good. A mask was used in taking data so that the area of film exposed to the x-rays was the same for all films.

The following equations were used to calculate composition and thickness:

Notation:

$I = \text{number of counts corrected for background intensity}$

$N = \text{atomic density (atoms/cm}^3\text{)}$

$h = \text{thickness}$

$x = \text{transition metal atomic fraction}$

Subscripts:

$T = \text{transition metal}$

$R = \text{rare earth}$

$S = \text{standard}$
$U = \text{unknown}$

e.g. $N_{TU} = \text{atomic density of transition metal atoms in the film to be analyzed}$

$I_{TU} = \text{number of corrected counts on the transition metal } K_{\alpha} \text{ line for the film to be analyzed.}$

$$\frac{I_{TU}}{I_{TS}} = \frac{N_{TU} h_u}{N_{TS} h_{TS}} \quad \frac{I_{RU}}{I_{RS}} = \frac{N_{RU} h_u}{N_{RS} h_{RS}}$$

Therefore

$$N_{TU} = \frac{I_{TU} h_{TS}}{I_{TS} h_u} N_{TS}$$

$$N_{RU} = \frac{I_{RU} h_{RS}}{I_{RS} h_u} N_{RS}$$

and,

$$\chi = \frac{N_{TU}}{N_{TU} + N_{RU}} = \frac{\frac{I_{TU}}{I_{TS}} h_{TS} N_{TS}}{\frac{I_{TU}}{I_{TS}} h_{TS} N_{TS} + \frac{I_{RU}}{I_{RS}} h_{RS} N_{RS}}$$

Since $N_{TS} = \frac{\rho_T}{A_T} N_0$

where $\rho_T = \text{density of transition metal}$

$A_T = \text{atomic weight of transition metal}$

$N_0 = \text{Avogadro's number}$

and similarly $N_{RS} = \frac{\rho_R}{A_R} N_0$.

Therefore

$$\chi = \frac{\frac{I_{TU}}{I_{TS}} \rho_T h_{TS}}{\frac{I_{TU}}{I_{TS}} \rho_T h_{TS} + \frac{I_{RU}}{I_{RS}} \rho_R h_{RS} \frac{A_T}{A_R}}$$
The thickness, $h_u$, is calculated from

$$h_u (N_{Tu} + N_{Ru}) = \frac{I_{Tu}}{I_{TS}} h_{TS} N_{TS} + \frac{I_{Ru}}{I_{RS}} h_{RS} N_{RS}$$

Since $N_{Tu} + N_{Ru} = N_u$,

$$h_u = \frac{\frac{I_{Tu}}{I_{TS}} h_{TS} N_{TS} + \frac{I_{Ru}}{I_{RS}} h_{RS} N_{RS}}{N_u}$$

where

$$N_u = \frac{\rho_u}{x A_T + (1-x) A_R} N_0$$

Substituting the equation for $x$

$$h_u = \frac{\frac{I_{Tu}}{I_{TS}} h_{TS} \rho_T + \frac{I_{Ru}}{I_{RS}} h_{RS} \rho_R}{\rho_u}$$

A linear approximation for $\rho_u$, after Tao et al. [95], has been used.

$$\rho_u = x \rho_T + (1-x) \rho_R$$
REFERENCES


42. P. K. George, First International Conference on Bubble Domain Memories, San Jose, California, December, 1974.


