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A STUDY OF THE RELATION BETWEEN STRUCTURE AND MAGNETIC PROPERTIES IN VAPOR DEPOSITED NI - FE THIN FILMS

by

Samuel J. Horowitz

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

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The magnetic properties of thin films of nickel-iron alloys, and their implementation as computer memory elements have been the subject of an intense study since the early report by Blois.\(^1\) These extensive investigations came about because thin film memory elements were found to have properties which made them potentially superior when compared to the ferrite cores in wide use at that time. Table I from Smith\(^2\) compares the properties of both films and ferrite cores for use in a computer memory. This comparison expresses the optimism displayed by the computer industry in the early 1960's. Since then, however, the superior potential of several of these properties, reliability and competitive cost, have failed to materialize.

Table I  Comparison of ferrite cores and thin magnetic films for use in a computer memory.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ferrite cores</th>
<th>Thin magnetic films</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Bistable</td>
<td>Yes</td>
<td>Yes 3-10 μsec</td>
</tr>
<tr>
<td>2. Speed of coincident-current switch</td>
<td>1 μsec</td>
<td>400 ma into 5Ω (transistor drive)</td>
</tr>
<tr>
<td>3. Drive power</td>
<td>800 ma into 50Ω (tube drive)</td>
<td>At least 5 Mc; probably much higher</td>
</tr>
<tr>
<td>4. Repetition rate before adverse heating</td>
<td>500 Kc</td>
<td></td>
</tr>
<tr>
<td>5. Physical size</td>
<td>1/16-in. diam</td>
<td>1/16-in. diam</td>
</tr>
<tr>
<td>6. Temperature range of operation</td>
<td>Up to 50°C</td>
<td>Should be higher</td>
</tr>
<tr>
<td>7. Reliability</td>
<td>100%</td>
<td>Should be comparable</td>
</tr>
<tr>
<td>8. Number in a system</td>
<td>2½ million</td>
<td>Unknown</td>
</tr>
<tr>
<td>9. Economy of fabrication</td>
<td>Expensive (-5 cents/bit)</td>
<td>Potentially cheap</td>
</tr>
</tbody>
</table>
The characteristics of magnetic thin films which have resulted in their potential usefulness as memory elements in high speed digital computers are derived from a combination of the properties which are a consequence of the thin film geometry, and those which are a consequence of a uniaxial magnetic anisotropy in the plane of the film. When a thin film is prepared in the presence of a magnetic field a uniaxial anisotropy is found to result. This anisotropy gives rise to an energy of the form:

\[ W_k = K_u \sin^2 \theta \]

where \( \theta \) is the angle between the magnetization and the anisotropy or easy direction and \( K_u \) is the uniaxial anisotropy constant which describes the magnitude of the resulting anisotropy. The magnetization will be in its lowest energy state when it is lying along either sense of this axis; hence, the required bistable nature necessary for systems which store information in binary form.

The thin film geometry will insure that the demagnetizing field normal to the plane of the film will be sufficiently large such that the magnetization will be constrained to remain in the plane of the film. In addition, the thin film configuration assures that the film will be stable as a single domain, and the magnetization may be switched from one stable state to the other in the coherent rotation mode. This type of switching is inherently faster than those modes
which require the nucleation and/or propagation of domain walls. The increased switching speed, a desirable property in any memory device, is apparent when thin films are switched in the coherent rotation mode.

The properties of coherent rotation may be described by considering the energy of a single domain film containing a uniaxial anisotropy to which magnetic fields are applied in both the easy and hard directions. The free energy is the sum of the anisotropy energy, given above, and the energy of the interaction of the applied field and the magnetization, $M_s$, of the film.

$$W_H = -\vec{M}_s \cdot \vec{H} = -M_s H_e \cos \theta - M_s H_h \sin \theta$$

$$W_T = K_u \sin^2 \theta - M_s H_e \cos \theta - M_s H_h \sin \theta$$

where, as before, $\theta$ is the angle between the easy axis and the magnetization, $H_h$ is the hard axis component of the applied field and $H_e$ is the easy axis component. The condition that the energy is a minimum at equilibrium requires that

$$\frac{\partial W_T}{\partial \theta} = 0 \quad \text{and} \quad \frac{\partial^2 W_T}{\partial \theta^2} > 0,$$

and predicts the square M-H loop in the easy direction and linear loop with saturation at $H_h = 2K_u/M_s$ in the hard direction. Figure 1 shows such loops and illustrates the anisotropic behavior of a film prepared in the presence of a magnetic field. The value of applied field in the hard
FIGURE 1

EASY AXIS B - H LOOP
Film 9/26/68 - 3 1500 A thick
$H_c = 1.25$ oe.

HARD AXIS B - H LOOP
Film 9/26/68 - 3 1500 A thick
$H_k = 4.74$ oe.
$\theta_{50} = 0.33^\circ$
direction which causes saturation, $2K_u/M_s$, has been labeled the anisotropy field, $H_k$.

The critical curve for rotational switching is predicted by the condition

$$\frac{\partial^2 W_T}{\partial \theta^2} = \frac{\partial W_T}{\partial \theta} = 0$$

which leads to the following relationship

$$\frac{H_e}{H_k}^{2/3} + \frac{H_h}{H_k}^{2/3} = 1$$

In normalized form

$$h_e^{2/3} + h_h^{2/3} = 1$$

This equation generates a figure, called the switching astroid, in the $h_e - h_h$ plane, and Figure 2 shows one quadrant of this astroid. Inside the astroid it is predicted that no rotational switching will occur, while for the choice of applied magnetic fields to lie outside the astroid switching by coherent rotation is predicted. It should be noted that this figure is just a first approximation to the switching behavior of real films. Modes of incoherent or partial rotation, and wall motion do occur, and the astroid must be altered to describe them. Figure 2 also shows the regions of incoherent rotation and wall motion. A complete figure of this type is important as it may serve as a common meeting ground for the engineers charged with integrating associated
FIGURE 2

FILM THRESHOLD PROPERTIES

(after Pohm and Mitchell
IRE Trans. EC, 2, 308(1960))

\[
\frac{H_L}{H_K} = \left( \frac{\text{Longitudinal Field}}{\text{Anisotropy Field}} \right)
\]

\[
\frac{H_T}{H_K} = \left( \frac{\text{Transverse Field}}{\text{Anisotropy Field}} \right)
\]

FIGURE 3

Inverse switching time as a function of longitudinal field strength. Permalloy, thickness unspecified; \(H_c = 0.7\) oe; \(H_k = 3.5\) oe.

(From Hagedorn, J. appl. Phys, 30, 2548(1959))
circuitry and the actual memory arrays, and materials scientists striving to overcome the materials problems imposing constraints on device applications.

Magnetic thin films may be characterized by several measurable parameters which influence the observed switching curve. The anisotropy field, $H_k$, is the field necessary to saturate the film in the hard direction, and is a measure of the magnitude of the uniaxial anisotropy induced during fabrication. The anisotropy constant, $K_u$, is the fundamental quantity, but the anisotropy field is generally the experimentally observable. If one knows the composition of the film, then the saturation magnetization, $M_s$, may be used to calculate the anisotropy constant.

The coercive force, $H_c$, is the threshold for the nucleation and propagation of domain walls in the easy direction, and is generally less than $H_k$. The switching astroid, Figure 2, shows that easy axis fields greater than $H_c/H_k$ and small hard axis fields will result in switching by wall motion. The M-H loop in the easy direction will be square with switching occurring at $H_c$.

One of the assumptions of the coherent rotation model of switching due to Stoner and Wohlfarth, from which the switching astroid was derived, is the presence of a uniform magnetization. In all polycrystalline films the magnetization is found to vary, on a local scale, from the average easy direction. These variations are called magnetization
dispersion or ripple, and are important because many of the observed deviations from the uniform rotation model are attributed to their presence. The opening of the hard axis loop, anomalies in measurement of rotational hysteresis, the presence of hard axis splitting or fallback, and deviations in the initial susceptibility curves, are all examples of these deviations.

Lorentz electron microscopy has provided a technique for direct observation of dispersion or ripple on a microscopic scale, but is not a convenient technique for measurement. In addition, Wohelleben has recently noted the necessity of applying wave rather than geometrical optics to the interpretation of ripple patterns, further complicating analysis. Measurements of the fallback angle, \( a_R \), provide a macroscopic index of the magnetization dispersion. \( a_R \) is defined in terms of the easy axis remnance; the angle a hard axis field would be applied in to result in \( r \) percent remnance, for example \( a_{50} \) or \( a_{90} \). Different authors often refer to different values of \( r \), the two most common are related in the following manner:

\[
a_{50} = .41 \; a_{90}
\]

The terms magnetization ripple and magnetization dispersion are often used interchangeably; in my notation I will refer ripple to microscopic determinations by Lorentz microscopy, and dispersion to macroscopic measurements.
The presence of ripple and dispersion is reflected in the switching behavior of permalloy films. Partial rotation processes, with a slower switching speed, may occur at values of applied field for which coherent rotation would be expected. The threshold curve for partial rotation is shown in Figure 2. The effect of the position and magnitude of the applied field (in the $h_e - h_h$ plane) on the speed of switching is shown in Figure 3. This figure shows the switching time decreasing for a given value of easy axis field, as the hard axis field is increased. The effect of dispersion on the switching speed has been discussed by Telesnin and Nikitina. It has also been suggested that dispersion may be an important mechanism in determining the coercive force.

The vital part played by these three parameters, $H_c$, $H_k$, and $a_50$ in determining the behavior of thin film in a memory application, and the constraints which this behavior imposes on the design engineer, were realized at an early date. Hence, much data is available which relates these parameters to the conditions of fabrication. This approach, that of attempting to control the properties of magnetic films by controlling the fabrication conditions, has been moderately successful in that numerous thin film memories have been developed. Complete success, and widespread conversion to thin film memories has not occurred, and ferrite cores are still in wide use today. This is the case because
industry has not been able to solve the materials problems associated with the requirements of being able to mass produce large arrays of films with identical properties. One important aspect of this limitation is the lack of a complete understanding of the origin of, and the relation between structure and, the observable properties of magnetic thin films. It will be the purpose of this work to attempt to define and shed additional light on some of the basic problems which as yet remain to be solved.

I. The Magnetic Field Induced Anisotropy

When a thin film of any binary or ternary alloy of the nickel-iron-cobalt system is prepared in the presence of a magnetic field, a magnetic anisotropy is observed. The presence of this anisotropy, in a thin film, leads directly to those properties which have made films attractive for memory applications. The most widely studied compositions are those which lie near the zero magnetostriction composition in the nickel-iron system, 81% Ni/19% Fe. Alloys of these compositions are generally called permalloys and have proven to be the most useful for commercial applications.

Films may be prepared by any of several techniques including vapor deposition, sputtering, electroplating, and chemical deposition, and are still found to exhibit the required anisotropy. Vapor deposition has proven to be the most common technique, allowing for the convenient preparation
of polycrystalline films. The anisotropy is observed to be a function of composition, deposition temperature, and the time and temperature of any subsequent annealing.\textsuperscript{4,8,9} The requirements on the magnetic field present during deposition are not stringent; only a field large enough to saturate the film is required. In addition, neither the rate of evaporation, nor the pressure during evaporation, for partial pressures of oxygen less than $5 \times 10^{-5}$ Torr\textsuperscript{10}, have been found to have a large effect on the induced anisotropy in vacuum evaporated films. The origin of this anisotropy is still an area of controversy.

Numerous mechanisms have been proposed to explain the origin of the uniaxial anisotropy in thin films. Those which have withstood the test of time and serious study will now be reviewed.

A. The Mechanism Operative in Bulk Permalloy

The observations of the uniaxial anisotropy in thin films are quite similar to the effects of magnetic annealing observable in bulk material. This phenomenon initially observed for nickel-iron alloys in 1934\textsuperscript{11}, results when bulk samples are heated in the presence of a magnetic field.\textsuperscript{12} The magnitudes of the two effects are similar, but the composition dependencies differ significantly; Figure 4. Magnetic annealing effects in bulk nickel-iron alloys are generally explained by considering directional ordering of
The composition dependence of the anisotropy constant for thin films and bulk alloys.
pairs of iron atoms. This theory was originally proposed independently by Neel\textsuperscript{13} and Taniguchi and Yamamoto\textsuperscript{14,15}, and is based on the following model: When a bulk sample of an alloy is annealed in a magnetic field at a temperature below its Curie temperature, but high enough to allow diffusion to occur, like atom pairs will tend to be aligned parallel to the magnetic field. When the specimen is cooled to a lower temperature, where significant diffusion cannot occur, this non-random arrangement of pairs of atoms will be frozen in, and a magnetic anisotropy will result. For alloys of nickel and iron the driving force behind the preferential ordering of pairs of atoms is the difference between the energies of the dipole-dipole interactions between nickel-nickel, iron-iron, and nickel-iron nearest neighbor pairs. Any deviation from randomness is opposed by thermal fluctuations which tend to randomize the directions of the pairs.

Based on this model Taniguchi has predicted:

\[
K_u = \frac{9}{2} \frac{NC^2 \mu^2 B_1^2(T)B_1^2(T_A)}{2kT_A}
\]

and Neel

\[
K_u = \frac{NC^2(1 - C)^2 \mu A}{2kT_A}
\]

where:

- \(N\) = the number of atoms per unit volume
- \(C\) = the concentration of solute atoms (iron)
\( \lambda \) = the energy change when two nickel-iron pairs are replaced by a nickel-nickel pair and an iron-iron pair

\[
\lambda = \lambda_{\text{Ni-Ni}} + \lambda_{\text{Fe-Fe}} - 2\lambda_{\text{Ni-Fe}}
\]

\( \lambda \) at the measuring temperature

\( \lambda_A \) at the annealing temperature

\( B_1(T) \) = the Brillouin function at temperature \( T \)

\( T_A \) = the annealing temperature (°K)

\( T \) = the temperature where measurement takes place (°K).

Both treatments can describe the observations of magnetic annealing in bulk material. Neel's composition dependence, \( C^2(1 - C)^2 \), provides a better fit to experiments for non-dilute solutions; while Taniguchi's gave the temperature dependence explicitly. These treatments assume that they are treating an ideal solid solution; however, there is evidence that an ordered structure forms in the vicinity of Ni\(_3\)Fe\(^{20}\). The formation of a superlattice would oppose the formation of pair ordering, and in the limit the formation of a perfect superlattice would eliminate all iron pairs. Neel\(^{13}\), Chickazumi\(^{16}\), and Iwata\(^{17}\) have treated the case of non-ideal solid solutions in which both long range ordering (superlattice formation) and the ordering of pairs of iron atoms are occurring simultaneously. The formation of long range ordering in the nickel-iron system, Ni\(_3\)Fe, has been observed to be a sluggish process requiring hundreds of hours of annealing at temperatures above 400°C\(^{18-20}\); hence, it is
not surprising that the composition dependence of $K_u$ in bulk material shows no dip or inflection at the ordering composition.

The pair-ordering theories explain many of the observations of magnetic annealing in bulk material.\textsuperscript{12} The composition dependence is found to be parabolic, proportional to $C^2$, for low solute concentrations, and to vary approximately as $C^2(1 - C)^2$ for higher concentrations. In addition, magnetic annealing experiments on single crystals of cobalt-nickel\textsuperscript{21} and nickel-iron\textsuperscript{22} alloys show the predicted dependence of $K_u$ on the direction of the annealing field with respect to the crystallographic axis. The dependence of the induced anisotropy on the measuring temperature and on the annealing temperature in bulk cobalt-nickel alloys was found to follow the predictions of Taniguchi\textsuperscript{23}, while Ferguson\textsuperscript{24} showed that the behavior of bulk samples of nickel-iron alloys was consistent with the Neel-Taniguchi theory. On the other hand, Prutton\textsuperscript{25} points out the lack of direct evidence for directional ordering of iron pairs in either bulk material or thin films.

B. The Magnetostrictive Constraint Mechanism

The pair ordering mechanism, discussed above, is unable to explain the observations of an induced anisotropy in films of pure nickel, iron, or cobalt, as there can be no solute pairs present in pure material. Therefore, if pair ordering
does apply to nickel-iron alloy films, at least one additional mechanism must be operative. This mechanism is generally associated with the magnetostrictive constraint mechanism, originally proposed by Bozorth and Dillinger\textsuperscript{26} to explain magnetic annealing effects in bulk material, but discarded in favor of the pair ordering models. MacDonald\textsuperscript{27} revived this theory and applied it to explain the induced anisotropy in nickel films, as did Ignatchenko\textsuperscript{28} four years later. In 1962, Robinson applied this mechanism in combination with the pair ordering mechanism in an effort to explain the composition dependence of the induced anisotropy in nickel-iron alloy films. This theory\textsuperscript{4} is based on the following model: A film which is deposited or annealed in the presence of a magnetic field at some temperature \( T \) will be deformed in the field direction by the longitudinal magnetostriction an amount \( \lambda(T) \), where \( \lambda(T) \) is the average magnetostriction constant at temperature \( T \). On cooling in the field, a temperature \( T'_C \) will be reached, below which the atomic mobility of the atoms on the substrate will have decreased to the point where the film cannot adjust to any further changes in magnetostriction. The temperature, \( T'_C \), is the constraint temperature, and \( \lambda(T'_C) \) is the strain for \( T = T'_C \). This strain is equivalent to a stress \( \sigma = \lambda(T'_C)E \), where \( E \) = Youngs Modulus, exerted by the substrate on the film. At the measuring temperature, \( T_m \), a uniaxial anisotropy is observed which is given by
\[ K_\lambda = \frac{3}{2} \lambda (T_m) \sigma = \frac{3}{2} \lambda (T_m) \lambda (T'_c) E \]

For polycrystalline material this average is given in terms of the single crystal magnetostriction constants by

\[ \lambda (T) = \frac{1}{5} \{3\lambda_{111}(T) + 2\lambda_{100}(T)\} \]

where \( \lambda_{100}(T) \) and \( \lambda_{111}(T) \) are the single crystal magnetostriction constants at temperature \( T \). The magnetoelastic energy would then be given by

\[ W_\lambda = K_\lambda \cos^2 \xi \]

where \( \xi \) is the angle between the saturation magnetization and the stress.

West\textsuperscript{31} suggested that this method of calculating the magnetoelastic energy from the average magnetostriction was in error, and proposed that the correct approach was to calculate the magnetoelastic energy by averaging the single crystal magnetoelastic energy over an ensemble of randomly oriented, but non-interacting, crystallites. He further explained that the differences between these two averages could be significant when \( \lambda_{100} \) and \( \lambda_{111} \) are of opposite sign, as is the case for compositions near the zero magnetostriction composition. For cubic symmetry West found:

\[ K_\lambda = \frac{9}{10} \{(C_{11} - C_{12}) \lambda_{100}(T_m) \lambda_{100}(T'_c) + 3C_{44} \lambda_{111}(T_m) \lambda_{100}(T'_c)\} \]

where \( C_{11}, C_{12}, C_{44} \) are the single crystal elastic constants.
West pointed out that the effectiveness of the constraint mechanism was a function of how well the film adhered to the substrate, and that this adhesion was a complex problem related to the cleanliness of the substrate, and the vacuum conditions and substrate temperature during deposition.

The predictions of West and Robinson, and those of Vladimirskij, who suggested a third method of averaging, are compared in Figure 5. The differences are slight in the composition range 65% - 90% nickel. At pure nickel Robinson predicted $K = 3.7 \times 10^3$ erg/cc and West $4.2 \times 10^3$ erg/cc. Experimental scatter does not allow the choice of one theory over the other, but most authors seem to have accepted West's version of the constraint theory over that of Robinson. Recent work by Brownlow and Wilts indicates just the opposite as being the proper choice.

C. Directional Ordered Impurities and Imperfections

It has been observed that vapor deposited thin films in the as-deposited state contain a greater than equilibrium concentration of defects. These defects may form into configurations which exhibit an axis of symmetry and which may be aligned during fabrication or subsequent annealing. Lesnik, Levin, and Nedostup analyzed their annealing data in terms of the annihilation of ordered vacancies by interstitial complexes. Other authors have attributed some part of the relaxation spectrum to vacancies.

The whole problem of non-equilibrium defects is quite
FIGURE 5

THE CONSTRAINT THEORY

CONSTRAINT TEMPERATURE

= 23°C

ANISOTROPY CONSTANT \( K_A \) (\( \times 10^2 \) ERGS-CM\(^2\))

WEIGHT PERCENT NICKEL

WEST

VLADIMIRSKY

ROBINSON
a complex one being related closely to the processes of film formation on the substrate. No comprehensive theory exists which explains the part played by non-equilibrium defects in causing the induced anisotropy. Any model which might be proposed would have to describe the oriented defect complexes which contributed to the anisotropy, as well as changes in this anisotropy with subsequent annealing. In addition, this anisotropy would not be recoverable following annealing at elevated temperatures, as the defect concentration would be expected to relax toward the thermal equilibrium value during annealing.

The presence of large numbers of imperfections in vapor deposited thin films may have a subtle but important influence upon the induced magnetic anisotropy; not through a direct mechanism as discussed above, but through its influence on atomic mobility. Studies of diffusion in radiation damaged material have shown that the diffusion rate is enhanced by the presence of a high concentration of defects. Similarly, Iwata and Hagedorn\(^{37}\) have discussed the annealing behavior of permalloy films by considering the effects of an excess of lattice defects, and the presence of high diffusivity paths, on the annealing behavior of the anisotropy. They observed that the annealing behavior changed as a function of time and temperature of annealing, in much the same manner that defect concentration would change as a result of recovery and recrystallization. Roth\(^{38}\) extended this
idea to include high atomic mobility in the vicinity of grain boundries and surfaces. The effects of sulfur as an impurity, in electrodeposited films, were investigated by Luborsky. He found the annealing behavior to be a strong function of impurity content.

D. The Composition Dependence of the Induced Anisotropy

Most authors have concentrated on the first two mechanisms; the mechanism operative in bulk material, most likely pair ordering, and the constraint mechanism to explain the composition dependence of the induced uniaxial anisotropy in the nickel-iron system, shown in Figure 4. Robinson was the first to combine these two models to explain the composition dependence. He used Ferguson's approximation for bulk alloys

\[ K_{up} \sim (T_c - T_a) C^2(1 - C)^2 \]

and the simpler expression for the constraint,

\[ K_\lambda = \lambda (T_m') \lambda (T_C') E \]

The component due to the mechanism operative in bulk material was scaled by setting it equal to the measured value of \( K_u \) at 82% nickel, the composition where \( \lambda = 0 \). This approach gave a good fit near \( \lambda = 0 \), and a fair fit over the remainder of the composition range. West noted that Robinson's model could be improved if the constraint term was arrived at by
a new averaging method which he, West, proposed. A two component model was also used by Siegle and Beam. They adjusted the relative strengths of the two components and could predict the composition dependence for compositions between 66% and 100% nickel. In this thesis an experimental separation of the magnitudes of these two mechanisms, the constraint mechanism and the mechanism operative in bulk will be reported. This experimental separation is accomplished without the necessity of adjustable parameters.

E. The Temperature Dependence of the Induced Anisotropy

The substrate temperature dependence of the induced anisotropy, characterized by $K_u$ or $H_k$, has been investigated and reported numerous times. These data have been of great value to the design engineer, but have not furthered the understanding of the origin of the anisotropy. Pair ordering theories predict that $K_u$, the anisotropy constant, should be proportional to $^{14,15}$

$$\frac{B^2(T_\text{A}) \cdot B^2(T_\text{m})}{T_\text{A}}$$

For temperatures above 300°C this function may be approximated by $(T_\text{C} - T_\text{A})$, where $T_\text{C}$ is the Curie temperature. Ferguson verified this result in his often referred to experimental paper. Extrapolating this result to lower temperatures, where thin films are usually deposited, and making a
comparison with typical observations on thin films leads to an interesting paradox. Thin films deposited at 240°C exhibit an anisotropy the magnitude of which is characteristic of bulk material which has been annealed above 400°C for a long period of time.

In bulk alloys of nickel-iron magnetic annealing occurs at temperatures high enough to allow sufficient atomic mobility to occur. Ferguson\textsuperscript{24} found a relaxation time of 10\textsuperscript{4} seconds at 450°C, indicating an activation energy of 3.0 eV/atom for the mechanism of magnetic annealing in bulk samples. This result is in good agreement with the activation energies for diffusion of iron in nickel-iron or nickel in nickel-iron.\textsuperscript{41} Thin films, on the other hand, have been observed to undergo magnetic annealing or aging at temperatures as low as 100°C, and complete annealing of the easy axis into a new direction at temperatures as low as 270°C. These results are clearly not compatible with the observations on bulk material. Considerable interest, therefore, has been focused on the annealing behavior of permalloy films.

The early work of Segmuller\textsuperscript{42} and Methfessel and co-workers\textsuperscript{43} established that heat treatment at temperatures above 400°C annealed out the low temperature mechanism and caused films to exhibit relaxation times for magnetic annealing similar to those observed in bulk alloys.\textsuperscript{24,26} In addition, they observed the absence of low temperature processes
in films deposited in vacuums of $10^{-9}$ mm Hg. It was not until the work of Kneer and Zinn\textsuperscript{44,45} that the full annealing spectrum of permalloy films was demonstrated. They performed isothermal magnetic annealing experiments on nickel-iron alloy films, with compositions near the non-magnetostrictive composition, and on films of pure nickel, all prepared by vapor deposition. Values of $H_k$ as a function of time, for hard axis orientation of the annealing field, were continuously monitored without the necessity of cooling to room temperature for measurement. These isotherms were analyzed making the assumption that they could be described as a sum of first order processes, each with its own characteristic relaxation time, $\tau_i$. Values of $\tau_i$ as a function of annealing temperature were calculated by fitting the observed time dependence of $H_k$ to a relationship of the form,

$$H_k(t) = \sum_i H_{ki}(0) \left(2 \exp \left(-\frac{t}{\tau_i(T_A)} \right) - 1 \right)$$

where $t$ is the annealing time (sec), $T_A$ is the annealing temperature ($^\circ$K), and $H_{ki}(0)$ is the initial partial contribution of the $i^{th}$ process, $H_k(0) = \sum_i H_{ki}(0)$. It was found that $\tau_i$ followed an Arrhenius relationship,

$$\tau_i = \tau_{i0} \exp \left(\frac{Q_i}{kT_A} \right)$$

where $Q_i$ is the activation energy for the $i^{th}$ process, $k$ is the Boltzmann constant and $\tau_{i0}$ is the relaxation time for $T_A$ extrapolated to infinity. The results of Kneer and Zinn are
summarized in Table 2. A process which contributed 56% to
the initial value of the anisotropy field in an 81%/19%
nickel-iron alloy film, but which was absent in a pure nic-
kel film, was attributed to the iron-pair ordering mechanism.
The observed activation energy for this process, 1.5 eV, was
low compared to that of the same process in bulk material;
but pretreating an 81%/19% film at 350°C prior to recording
the isotherms increased the contribution of this mechanism
to 85% and increased the activation energy to 2.1 eV. Fur-
thermore, a process which contributed only 16% in Ni/Fe al-
loy films, and which was found to contribute 66% in the pure
nickel film was labeled as due to the constraint mechanism.
The other mechanisms, which disappeared upon pretreatment
at 350°C, were attributed to non-equilibrium defects or
strains.

Similar experiments have been reported on by Smith,
Weiss, and Harte\textsuperscript{46}, by Fujii \textit{et. al.}\textsuperscript{47}, and most recently
by Weidenman and Hoffman\textsuperscript{49}, all of whose results are sum-
marized in Table 2. The work of Smith \textit{et. al.}\textsuperscript{46} was con-
centrated at low temperatures and describes a number of
processes with short relaxation times. The processes de-
scribed vanished rather than reordered during the annealing
processes.

Fujii and coworkers\textsuperscript{47} extended the work of Kneer and
Zinn to compositions between 70% and 90% nickel, and to
deposition temperatures from room temperature to 300°C.
Table 2 Magnetic Annealing Results

Kneer and Zinn\textsuperscript{45}  
81/19\% Ni/Fe  
150\°C-400\°C

<table>
<thead>
<tr>
<th>Process</th>
<th>$%H_k(0)$</th>
<th>$\tau_{i0}$ (sec)</th>
<th>$Q_i$ (eV)</th>
<th>Process</th>
<th>$%H_k(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>20</td>
<td>1.5</td>
<td>.15</td>
<td>I</td>
<td>12</td>
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<tr>
<td>II</td>
<td>8</td>
<td>.03</td>
<td>.4</td>
<td>II</td>
<td>22</td>
</tr>
<tr>
<td>III</td>
<td>16</td>
<td>.30</td>
<td>.4</td>
<td>III</td>
<td>66</td>
</tr>
<tr>
<td>IV</td>
<td>56</td>
<td>2.0x10$^{-8}$</td>
<td>1.5</td>
<td>IV</td>
<td>Absent</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pair</td>
<td></td>
<td>ordering</td>
</tr>
</tbody>
</table>

Fujii et. al.\textsuperscript{47}  
81.5/18.5\% Ni/Fe  
160\°C-320\°C

<table>
<thead>
<tr>
<th>Process</th>
<th>$%H_k(0)$</th>
<th>$\tau_{i0}$ (sec)</th>
<th>$Q_i$ (eV)</th>
<th>Process</th>
<th>$%H_k(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>2x10$^{-4}$</td>
<td>.5</td>
<td>A</td>
<td>magnetoelastic</td>
</tr>
<tr>
<td>II</td>
<td>44</td>
<td>1.1x10$^{-4}$</td>
<td>.5</td>
<td>I</td>
<td>56</td>
</tr>
<tr>
<td>III</td>
<td>9x10$^{-4}$</td>
<td></td>
<td></td>
<td>I</td>
<td>1.73</td>
</tr>
<tr>
<td>IV</td>
<td>25</td>
<td>2x10$^{-5}$</td>
<td>4.8x10$^{-6}$</td>
<td>I</td>
<td>2.0</td>
</tr>
<tr>
<td>V</td>
<td>1.0x10$^{-10}$</td>
<td>2.0</td>
<td>1.1</td>
<td>B</td>
<td>1.1</td>
</tr>
<tr>
<td>VI</td>
<td>31</td>
<td>1.0x10$^{-10}$</td>
<td></td>
<td>C</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Smith et. al.\textsuperscript{46}  
Room temperature-200\°C  
83/17\% Ni/Fe

<table>
<thead>
<tr>
<th>Process</th>
<th>$%H_k(0)$*</th>
<th>$\tau_{i0}$ (sec)</th>
<th>$Q_i$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>6.25</td>
<td>7x10$^{-2}$</td>
<td>.18</td>
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<tr>
<td>II</td>
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<td>IV</td>
<td>6.25</td>
<td>6.0x10$^{-6}$</td>
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<tr>
<td>V</td>
<td>3.75</td>
<td>3.0x10$^{-2}$</td>
<td>.26</td>
</tr>
</tbody>
</table>

*The processes tabulated here account for 25\% of the anisotropy in the temperature range investigated.

Wiedenmann and Hoffmann\textsuperscript{49}  
76/24\% Ni/Fe  
310\°C-410\°C

<table>
<thead>
<tr>
<th>Process</th>
<th>$%H_k(0)$</th>
<th>$\tau_{i0}$ (sec)</th>
<th>$Q_i$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5</td>
<td>Not Determinable</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>15</td>
<td>.5</td>
<td>.5</td>
</tr>
<tr>
<td>III</td>
<td>80</td>
<td>8x10$^{-10}$</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Their results may be grouped as indicated in Table 2. Component A decreased linearly with deposition temperature, and is a minimum near the non-magnetostriction composition; while components B and C were not sensitive to deposition temperature. Component B was not a function of composition, but component C decreased linearly with increasing nickel content. In addition, they observed that component B vanished when the films were evaporated at a rate of 1000 Å/min. rather than 250 Å/min., and in general noted that the relaxation time \( \tau_i \) was an increasing function of deposition temperature. Component A was associated with magnetoelastic anisotropy, and component C with the mechanism operative in bulk material. Their results are shown in Figure 6.

Wiedenmann and Hoffmann 49 analyzed the isothermal annealing behavior of 76%/24% nickel-iron films which were initially annealed for 7 - 10 hours in a field along the easy axis at 390°C. Three different anisotropy sources with different relaxation times and activation energies were separated. These results are also shown in Table 2.

Although the procedure of fitting smooth curves through data points with a sum of exponentials is not guaranteed to produce a unique result, the agreement between the results of different authors working independently is satisfying. In particular those processes labeled pair ordering and those labeled constraint or magnetoelastic anisotropy agree rather well.
FIGURE 6

AFTER FUJII ET. AL.

Dependence of resultant induced anisotropy and anisotropy components on composition (deposition temperature about 30°C).

Influence of deposition temperature upon anisotropy component of 51.5-percent Ni films.
The present work will investigate the origin of the anisotropy in several ways:

1) An experimental separation, not requiring any fitting constants, of the mechanisms contributing to the anisotropy in as-deposited films will be described. This work will show that the anisotropy, in as-deposited films, is a combination of one contribution from the constraint mechanism and one from the mechanism operative in bulk alloys.

2) The annealing kinetics of films which have undergone recrystallization will be investigated. This investigation, carried out on films with a wide range of compositions, will show that the time and temperature dependence of the major component of the induced anisotropy is identical to that observed for bulk permalloy.

II. The Magnetization Dispersion

On a microscopic scale the uniaxial anisotropy varies in both magnitude and direction. The magnetization attempts to follow these variations and magnetization dispersion or magnetization ripple results. The effects of ripple on the behavior of thin films, and the limitations thus imposed on their application as memory elements in high speed digital computers has been discussed. The origin of the magnetization dispersion or ripple will now be examined.
Much of the effort which has been focused on this problem in the past was, as is the case in any fast growing area of technology, phenomenological in nature rather than aimed toward the investigation of basic mechanisms. In a review published in 1968, Wilts and Humphrey\textsuperscript{8} listed 8 parameters of which dispersion had been accused of being a function, and noted the inconsistency in the published data between different laboratories. This variation among different investigators has probably been explained by the work of Paul and Hanson.\textsuperscript{10} They showed that the dispersion was extremely sensitive to partial pressures of oxygen greater than $1 \times 10^{-5}$ Torr, in the range where older vacuum systems operated. Thus much of the scatter in the early literature may originate in the presence of oxygen during film formation. Still a complete picture which will describe the origin of ripple and dispersion has not been proposed.

The first descriptions of magnetization dispersion assumed that the Stoner-wholfforth or uniform rotation model could be applied to separate non-interacting regions in a thin film.\textsuperscript{52} In effect each region had an easy axis and was associated with its own switching asteroid, inclined at some angle to the average easy direction. The dispersion, $a_{90}$, was associated with the statistical distribution of the angle of deviation of the localized asteroids. This model had a qualitative success.

The most successful theories which have been proposed
to describe magnetization dispersion and ripple are derived from micromagnetic theory. Hoffman$^{53-55}$ and Harte$^{56-58}$ have independently developed models to describe ripple based on the micromagnetic approach; both formulations have been reviewed by Cohen.$^{4}$ Hoffmann's results can be more easily compared with experiment, as he extended his theory to describe hard axis domain splitting$^{59}$, upon which most convenient measurement techniques are based.

Ripple theory was developed to explain the observations by Lorentz microscopy of striations within magnetic domains.$^{60}$ The striations were called magnetization ripple. Figure 7 shows ripple structure within magnetic domains; the wave fronts are normal to the direction of the average magnetization at each point. It has been estimated that the wave length of the ripple pattern is about 1 micron, and the average angular deviation roughly 1 degree.

On a microscopis scale a polycrystalline thin film has been shown to possess a highly irregular and imperfect structure, with a small grain size, many stacking faults, a high density of dislocations, point defects, and other imperfections, as well as being highly strained. Hence, it is likely that any successful theory which would describe the presence of ripple would include the local perturbations of this irregular structure on the direction of local magnetization. The work of Hoffmann and Harte has done just that. They began with the simple energy equation we used earlier to
FIGURE 7
MAGNETIZATION RIPPLE IN A 250Å THICK, 77% NI-23%FE FILM
describe the switching behavior of an ideal film, and added
to that the terms required to describe the random anisotropy
originating because of the highly irregular microstructure.

The equation we used earlier may be restated using the
same notation as Cohen\(^4\), Figure 8.

The exchange energy is the same energy from which fer-
romagnetism results. In a ferromagnetic solid the exchange
energy will be a minimum when neighboring spins are parallel
or when the change in spin direction between neighboring
atoms is a minimum. Therefore, the exchange energy will
tend to minimize any sharp gradient in the direction of mag-
netization. The magnetostatic energy has its origin in the
internal poles which are created by local fluctuations in
the direction of magnetization, the creation of which raises
the free energy of the solid. Hence, the magnetostatic en-
ergy will act with the exchange energy to minimize local
fluctuations in the direction of magnetization.

The source of these local fluctuations in the direction
of magnetization, from which ripple results, are accounted
for by a general local anisotropy energy \( E_{kl} = K_s f(\phi,x,y) \).
This energy is associated with a generalized crystallite of
diameter \( D \), a region over which the local perturbing aniso-
tropy is constant. The exact definition of \( D \), and how it
is related to the grain size in the film will depend on the
origin of \( K_s \), the local perturbing anisotropy constant. It
is to this problem we want to address ourselves. \( f(\phi,x,y) \)
Coordinate system for micromagnetic theories. In Hoffmann's theory the x axis is along $\mathbf{M}$, and the y axis is perpendicular to $\mathbf{M}$; in Harte's theory, the x and y axes are parallel to the $EA$ and $HA$, respectively.

External field energy $E_H = -HM \cos(\beta - \phi)$

Uniaxial anisotropy energy $E_{K_u} = K_u \sin^2 \phi$

Exchange energy $E_{ex} = A(\nabla \phi)^2$

Local anisotropy energy $E_{K_l} = K_l(\phi, x, y)$

Magnetostatic energy $E_{mag} = -\frac{1}{2} H_{mag} \cdot \mathbf{M}$

$E_{total} = E_H + E_{K_u} + E_{ex} + E_{K_l} + E_{mag}$
is a trigonometric function involving the position in the film, in the $x-y$ plane, and the angle between the local direction of magnetization and the easy axis. The assumption has been made that the magnetization is parallel to the film plane because of the action of the demagnetizing or shape anisotropy; hence no dependence on the direction normal to the plane of the film.

The problem now is to minimize the total energy and find the angular variation in the direction of magnetization, not as simple a task as for the uniform rotation case we discussed earlier. I will omit the details, as one may refer to the original work or the excellent review by Cohen.\textsuperscript{4} For the linear approximation, the angular variations of the magnetization being restricted to $1^\circ - 2^\circ$, both Hoffmann and Harte have shown that the region of coupling is not the whole film, but an ellipse, simplifying the mathematics. The minor axis of the coupling ellipse lies in the direction of the average magnetization, and the major axis is perpendicular to this direction. The major axis is considerably longer than the minor axis, indicating that the coupling ellipses are narrow bands perpendicular to the mean direction of the magnetization, just as can be observed by Lorentz microscopy. The ripple wave length is proportional to the length of the minor axis. The rms value of the local deviations of magnetization from the average direction of magnetization has been calculated\textsuperscript{53,59}: 
\[
\sqrt{\phi_2} = \frac{1}{2\sqrt{2} \pi^{\frac{3}{2}}} \frac{S}{(M_s \sqrt{A})^{\frac{3}{4}}} \frac{1}{(AK_u)^{\frac{3}{8}}} \frac{1}{h^{\frac{3}{8}}(a)}
\]

where \( d \) is the film thickness,

A is the exchange constant,

\[
h(a) = \frac{2(E_ku + E_m)}{\phi^2}
\]

is the single domain field,

S is the structure constant,

\[
S = K_s D \sigma_1/\sqrt{n}
\]

and where

\( K_s \) is the local anisotropy constant

D is the mean grain diameter of the crystallites,

\( \sigma_1 \) is the standard deviation of the angular functions

\( (\sigma_1 = \frac{1}{\sqrt{2}} \) for randomly distributed uniaxially anisotropic crystallites), and

n is the number of crystallites through the film thickness, \( n = D/d \).

Suzuki and Wilts\(^{61}\) have shown that \( \sqrt{\phi_2} \) and the ripple wave length predict the right order of magnitudes for those observed from Lorentz micrographs. The ripple wave length is proportional to the length of the minor axis of the coupling ellipse.

Although this formulation explains magnetization ripple it does not itself provide a description of microscopic phenomenon such as hard axis fallback or observations of the
initial susceptibility. Hoffmann has extended his work on ripple theory to include a model for hard axis fallback$^{59}$, which along with initial susceptibility techniques are widely used to characterize the magnetization dispersion. These techniques are far more convenient, even though they provide an indirect measurement, than direct observation of $\sqrt{\frac{\phi}{2}}$ or the ripple wave length, by Lorentz microscopy. Hoffmann has shown that the product of $H_k$ and $\alpha_{90}$, the usual indicator of hard axis fallback measurements, is proportional to the structure factor squared.$^{59}$

$$\alpha_{90}H_k = \frac{3}{8\pi A} S^2 = \frac{3}{8\pi A} \left( \frac{K_S D L}{n^2} \right)$$

If we assume the validity of this relationship, the whole problem of the origin of the magnetization dispersion, my primary concern, reverts to establishing a more complete understanding of the origin of $K_s$, the local random anisotropy constant. On the other hand, the bulk of experimental data does not point to the universal validity of this relationship. Some authors use $\alpha_{50}$ rather than $\alpha_{90}$; they may be related in the following manner$^{59}$ $\alpha_{50} = 0.41 \alpha_{90}$.

West and Simmons$^{62}$ found that the magnetization dispersion was a function of increasing grain size, but that the anisotropy field-dispersion product ($\alpha_{50} \cdot H_k$) was nearly independent of grain size and thickness. Hoffmann$^{63}$ found $\alpha_{90}$ proportional to $D^3/dK_u$, but West and Simmons$^{62}$ pointed out the difficulty of separating the dependence on $D$, $d$, and
\( K_u \) in Hoffmann's result. Pocker\textsuperscript{64} investigated the dependence of \( a_{90} \) on \( D \) and \( \delta \) and got relatively good agreement with Hoffmann's prediction. Pocker's results, however, were based on a limited number of films, some of which displayed an unusually high dispersion characteristic of an improperly prepared film. Iwata and Hagedorn\textsuperscript{37} conducted annealing studies and noted that the anisotropy field-dispersion product was not a constant. Landler\textsuperscript{65} deposited films in an elliptical rotating magnetic field to produce changes in induced anisotropy with a minimum change in film structure. He did not find \((a_{50} H_K)\) a constant. Siegle and Beam\textsuperscript{40} noted that \( a_{90} \) varied as \( 1/K_u \), and also observed that the dispersion decreased after an initial two hour easy axis anneal at 250°C. They attributed this change to the relieving of part of the isotropic stress present in evaporated films. Carson\textsuperscript{66} has made similar observations.

These experimental observations, with the exception of Landler\textsuperscript{65}, have in common the fact that the grain size or anisotropy field was varied by annealing or altering the deposition conditions, i.e., substrate temperature. Both of these approaches will change the film structure and alter \( K_s \), the local anisotropy constant, making valid interpretation difficult. In addition, recent work\textsuperscript{66} has shown that magnetization dispersion as well as induced anisotropy is reversible upon annealing, further complicating the picture, as recovery, recrystallization, and grain growth, which occur
during annealing, clearly are not reversible.

The most likely candidates to explain the origin of magnetization dispersion are magnetocrystalline anisotropy, originating in the small grains in a polycrystalline film, and local stress fields acting through the mechanism of magnetostriction. Reports on the composition dependence of $a_{90}$ or $a_{50}$ describe a minimum value in the vicinity of 80% Ni/20% Fe, the region where both the single crystal magnetocrystalline anisotropy constants, $K_1$ and $K_2$, and the single crystal magnetostriction constants $\lambda_{100}$ and $\lambda_{111}$ are small. Suzuki and Wilts$^{61}$ found that the ripple angle was a minimum for compositions near 73% Ni/27% Fe, in good agreement with the report by Baltz.$^{68}$ Baltz and Doyle$^{70}$ did not observe ripple in single crystal films.

The work reported by the group at Nogoya University$^{71-75}$, has contributed significantly to our current understanding of the mechanisms which cause ripple and dispersion. Their work bridged a gap which had developed between the microscopic techniques, i.e., Lorentz microscopy, closely related to ripple theory, and the macroscopic techniques of measurement, convenient for the experimentalist, but difficult to compare with theory. They observed hard axis splitting, in small regions (.05 mm$^2$) in a large film, using a magneto-optic (Faraday effect) technique, and found two components contributing to the macroscopic dispersion: A short wave length periodic variation much like magnetization ripple
observed by Lorentz microscopy, the intrinsic dispersion, and a non-periodic long wave length variation (skew like), the extrinsic component. The short wave length component was found to be relatively constant for a given film, while in a film that had a large macroscopic dispersion the skew or long wave length component was the major component. In addition, it was observed that skew increased with increasing temperature in the same manner as macroscopic dispersion.

Observations on the composition and substrate temperature dependence of the intrinsic dispersion have demonstrated that it originates in a combination of magnetoelastic and magnetocrystalline energies, while the extrinsic component has its origin in the magnetoelastic energy. These observations qualitatively explain many of the early reports on the composition and substrate temperature dependence of magnetization ripple and dispersion. Films prepared at a high substrate temperature will exhibit a minimum in dispersion at the composition where magnetocrystalline anisotropy goes through zero, as the elevated temperature has caused annealing of stresses to occur. On the other hand, a film prepared at low temperature will exhibit a minimum at the non-magnetostrictive composition, 82% Ni - 18% Fe. For intermediate substrate temperatures a broad flat minimum extending through the composition range of 70% to 82% Ni will be observed.

The early reports from the group at Nogoya University
suggested the model described above, but could not find agreement with Hoffmann's predictions for the fallback angle, \( \alpha_{50} \). Recently, however, they have published work\textsuperscript{75} which provides the strongest experimental verification to date. They estimated \( S \), the structure constant, for a large number of films using the transverse bias susceptibility technique\textsuperscript{76}, and independently determined \( K_u \) and \( \alpha_{90} \) for small regions on a larger film using the magneto-optic technique. These results verified Hoffmann's predictions that the anisotropy field-dispersion product was proportional to the structure factor squared, as long as only small regions are being probed. Analysis of the whole film led to marked deviations from theory, attributed to the presence of skew.

At this time there is no quantitative model which describes in detail the mechanisms which contribute to \( K_s \), the local anisotropy constant, and which define \( D \), the generalized grain size. Uchiyama et. al.\textsuperscript{73} used an intuitive formula to describe \( K_s \),

\[
K_s = (K_1^2 + K_\sigma^2)^{\frac{1}{2}}
\]

where \( K_1 \) is the first magnetocrystalline anisotropy constant, and, \( K_\sigma = 3/2 \lambda \cdot \sigma \), is the contribution from the magnetostrictive anisotropy. They fit their observations of the composition and substrate temperature dependence to this formula with \( \sigma \) as an adjustable parameter. The values of stress required were reasonable, being between 0.6 and 2.0 \( \times 10^9 \)
dynes/cm². The only other quantitative result is that of Doyle and Finnegan⁷⁷ who showed that

\[ K_s = [(K_1 + B_s \varepsilon_{33} + \frac{1}{4} B_\sigma \sigma)^2 + \frac{7}{16} (B_\sigma \sigma)^2]^{\frac{1}{2}}, \]

a relationship which includes the effects of an isotropic planar stress, \( \sigma \), an applied strain, \( \varepsilon_{33} \), and the magneto-crystalline anisotropy, \( K_1 \). In this relationship

\[ B_s = \frac{3}{2} (C_{11} - C_{12}) \lambda_{100} + 3C_{44} \lambda_{111} \]

and

\[ B_\sigma = \frac{3}{2} (\lambda_{100} - \lambda_{111}) \]

and \( C \) the elastic constants. Uchiyama et. al.⁷⁴ applied this formulation to their composition and substrate temperature data, assuming \( \varepsilon_{33} = 0 \), and with \( \sigma \) as a free parameter. The fit was comparable to that of the intuitive form discussed above, even to the values of stress required to fit the data to the equation.

Annealing experiments aimed at determining the processes which contribute to the intrinsic dispersion have shown⁷⁴ that it may be described by the sum of three first order processes each with an activation energy equal to 0.5 eV/atom. These processes were associated with the relaxation of the anisotropic stresses. The activation energy suggested that the anisotropic stresses might have their origin in the presence of divacancies, which have an energy of motion of
approximately the right magnitude.

The picture one may draw to describe the long wave length or skew component of dispersion is rather vague in comparison with that described above. The group from Nogoya has noted the part it plays in macroscopic measurements of dispersion, as discussed above, and suggested that its origin lies in a magnetoelastic interaction, but do not provide any qualitative results to support this idea. They also indicated that the scatter observed in measured values of macroscopic dispersion for films prepared in the same manner was due to variations in this skew component, rather than in the short wave length component.

The magnetic properties, particularly the magnetization dispersion, of thin films have been shown to be structure sensitive. It would thus be advantageous to investigate these magnetic properties in films which possess a known structure. In addition, the model for the magnetization dispersion contains terms related to the average crystallite size and their distribution about the mean. It would, therefore, be desirable to measure this average grain size, and the related distribution of grain diameters about the mean. At this time there have been no reports of the grain diameter distribution in vacuum deposited nickel-iron thin films.

Although the group from Nogoya University has indicated the presence of extrinsic and intrinsic magnetization, no significant discussion of the interrelationship between
macroscopic measurements and the microscopic components, extrinsic and intrinsic dispersion, exists. This topic has been the subject of a preliminary investigation to be reported here. A magneto-optic loop checker, able to probe small regions on a larger film, has been constructed, and a study of the relationship between the extrinsic and intrinsic microscopic components and macroscopic measurements has been initiated.

In addition, this thesis will report on easy and hard axis isothermal magnetic anneals performed on a large number of vapor deposited nickel-iron thin films with values of dispersion in the extrinsic region, $a_{50}$ greater than 1° - 2°. These experiments show that after the film has been recrystallized, both the anisotropy field and the magnetization dispersion are reversible, and the relationship

$$a_{50} \sim H_k^{-b}$$

is obeyed, where $b$ is independent of composition and equal to 2.0 ± 0.5.
CHAPTER TWO: PROGRAM OF INVESTIGATION

This thesis will report a series of studies which have been conducted to further the understanding of the relationship between structure and magnetic properties in vacuum deposited nickel-iron thin films. This investigation has been concerned primarily with the uniaxial anisotropy and magnetization dispersion observed by macroscopic techniques. The investigations which have taken place may be separated into four general topics for the purposes of organization. The topics will now be summarized.

I. The Origin of the Uniaxial Anisotropy in Vacuum Deposited Thin Films of Nickel-Iron Alloys

The composition dependence of the anisotropy has, in the past, been described by a model which combined the predictions of the constraint theory with the mechanisms operative in bulk alloys. Previous investigators have fitted this combined model to experimental observations by adjusting the relative strengths of the two components. In this thesis an experimental separation of the magnitudes of these two components, which does not require any adjustable parameters, will be described. These results will be discussed in the light of recent reports.
II. The Kinetics of Magnetic Annealing Recrystallized Thin Films of Nickel-Iron Alloys

Investigations of the annealing behavior of thin films of nickel-iron alloys have demonstrated marked differences in the behavior of the anisotropy in thin films as compared to bulk alloys. Previous investigators have shown that thin film behavior can be made to approach bulk behavior as a function of the degree of prior annealing.

In this thesis the annealing behavior of recrystallized thin films will be investigated during the course of isothermal and isochronal magnetic annealing. This study will demonstrate that the time and temperature dependence of the major component of the induced anisotropy is identical to that observed to result from magnetic annealing of bulk alloys.

III. The Mean Crystallite Size and Structure of Thin Films Which Have Been Recrystallized

The magnetic properties, particularly the magnetization dispersion, of thin films have been shown to be structure sensitive. A standard metallurgical state, not a function of subsequent annealing at lower temperatures, will be induced by a single high temperature recrystallization anneal. The mean crystallite size and the distribution about the mean will be investigated by transmission electron microscopy. This study will show that the mean grain size, following recrystallization, will be comparable to the film
thickness, and will obey a log normal distribution. Subsequent annealing at a temperature below the temperature of the recrystallization anneal, and for times in excess of 100 hours, will not produce significant changes in the mean grain size. The structure of such films will be shown to be characteristic of cold worked metals which have been recrystallized.

IV. The Origin of the Magnetization Dispersion in Recrystallized Thin Films of Nickel-Iron Alloys

The dependence of the macroscopically measured magnetization dispersion on the anisotropy field will be observed during the course of isothermal magnetic annealing of recrystallized thin films. This study will show that the relationship

$$a_{50} = C |H_k|^{-b}$$

is obeyed, where $b = 2.0 \pm 0.5$, and is independent of composition. The disagreement between this result and theory will be discussed in the light of recent observations of the superposition of two components to the dispersion. Preliminary results from a magneto-optic loop checker will also be introduced in an effort to characterize the effects of these two components. This study will demonstrate that the present results describe a special case not adequately described by existing theories.

The division of this work into four separate, but related,
topics as has been done above, will be carried over to later sections of this work. Thus the sections labeled results and discussion, and conclusions will be divided into four sections as indicated above.
CHAPTER THREE: EXPERIMENTAL PROCEDURE

The objective of this research is to study the relation between structure and those magnetic properties which have made permalloy thin films technologically interesting. Detailed discussions of the techniques of fabrication are available\textsuperscript{79,3,51}; therefore, I will describe the fabrication process only to establish the conditions under which samples to be used in later experiments were prepared, highlighting those areas which may have a direct bearing on the experimental results or their interpretation. In the following section I will describe the techniques used to measure the macroscopic magnetic properties, a necessary procedure in later experiments. In subsequent sections I will undertake a discussion of the experimental approach and procedures actually used in investigating the origin and annealing behavior of the magnetic properties of permalloy thin films, and discuss the design of a magneto-optic loop checker.

I. Preparing Permalloy Thin Films by Boat Evaporation

The advantages and disadvantages of boat evaporation have been discussed by Carson\textsuperscript{51}, who was responsible for the design and modification of the vacuum system used in film fabrication. These areas are covered in detail in his dissertation and will not be discussed here. All films to be used in the experiments to be described were prepared in
exactly the same manner; except, of course, those deposited on a thin layer of silicone grease to minimize the effects of the constraint interaction. The vacuum system in which deposition took place was a modified Kinney (Model KDTG-3P) vacuum evaporator with a twelve-inch bell jar. The vacuum system consisted of an oil diffusion pump, ambient and liquid nitrogen baffles, and a mechanical roughing pump, all standard equipment on the Kinney; and a cylindrical liquid nitrogen trap and titanium sublimation pump which was added to the original system during modification. An ultimate pressure in the range 2 to 3 x 10^{-8} Torr was attainable with the aid of these supplementary pumping devices.

A collar with six ports provided power and liquid nitrogen feedthroughs. Pressure in the bell jar was measured with an ionization gage (CVC type GIC-110B) which was connected to a strip chart recorder to continuously monitor the pressure during each evaporation.

Evaporation of small charges of nickel-iron alloys was accomplished by passing a large current through a tungsten boat to which the charge had been spot welded. These boats were 7.7 x 1.9 x 0.055 cm. and were purchased from Fansteel Metallurgical Corporation. The current, which could reach 2500 amperes, was fed into the vacuum system through two water-cooled current feedthroughs. The tungsten boats were fastened to, and supported by, these feedthroughs. The boats were positioned through slots milled in the lower end of
the cylindrical liquid nitrogen trap, such that deposition took place upwards along the axis of the liquid nitrogen cooled cylinder. This configuration kept the pressure rise in the bell jar during evaporation to a minimum. A step down transformer, controlled on the primary side, provided the current necessary for resistance heating of the tungsten boat.

The charge material was either a 0.01 inch diameter, 80.89-19.11 wt. % nickel-iron wire purchased from Materials Research Corporation; or a rolled sheet of an alloy prepared in this laboratory. These alloys were prepared by placing preweighed rolled slugs of pure nickel and iron (Materials Research Corporation Marz Gr) on a water-cooled copper boat and induction melting them in a 5% hydrogen - 95% nitrogen atmosphere. Each alloy was turned over and remelted at least five times to insure a uniform composition. The resulting ingots were rolled out into sheet form, about two millimeters thick. Table 3 lists the charge compositions of those alloys which were used in this work; also shown in this list are the film compositions which resulted from the charges used.

It has been shown$^{51}$ that for boat evaporation, the thickness of the resulting films may be controlled by evaporating a given weight of charge to completion. For a particular source to substrate distance the film thickness is a function of the charge geometry and the heating rate of the
Table 3 Charge Composition and Resulting Film Composition

<table>
<thead>
<tr>
<th>Charge Composition WT % Nickel</th>
<th>Film Composition WT % Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.3</td>
<td>49.5</td>
</tr>
<tr>
<td>65.0</td>
<td>61</td>
</tr>
<tr>
<td>75.5</td>
<td>72</td>
</tr>
<tr>
<td>80.89*</td>
<td>78</td>
</tr>
<tr>
<td>84.0</td>
<td>81.5</td>
</tr>
<tr>
<td>87.8</td>
<td>86</td>
</tr>
<tr>
<td>98.23</td>
<td>97.5</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

*Permalloy wire .01" diameter

tungsten boat.

For evaporations in which the permalloy wire was the charge, a predetermined weight (or length) was wound into a tight flat spiral and spot welded to the center of a tungsten boat. In all other cases, a piece of rolled sheet was cut into a shape about the same as the wound spiral, weighed, and spot welded to a tungsten boat.

A voltage drop of four volts across the boat, causing a heating rate of 2500 amp sec\(^{-1}\) produced films 16,800 Å per gram of charge material. The films produced for the annealing experiments were 1100 Å thick, and required 0.065 grams of charge. Preparation of thin films by the boat evaporation technique allows film formation to occur at a very rapid rate which may approach 2000 Å sec\(^{-1}\). The deposition rate is a function of the heating rate of the
tungsten boat, and the charge weight and geometry. For the 1100 Å films the average deposition rate was 1000 Å/second or greater.

Four 1.58 x 1.58 cm. substrates (Corning type 7059 glass) were supported by a nonmagnetic stainless steel holder. The holder acted as a mask such that each film when deposited was 1 cm. in diameter. The substrate holder could be rotated from its initial position, inside a special substrate heater, to a position over the open end of the liquid nitrogen trap for evaporation (see Figure 9). The substrate temperature was measured before the substrates were rotated out over the tungsten boat. Rotation and the heating of the boat to the evaporation temperature took 5 - 7 seconds; therefore, the actual deposition temperature was 10 - 20°C, less than the measured temperature. Before the substrates were inserted into the vacuum system, lint and dust were removed with a soft brush. In addition, the substrates were baked out at the substrate temperature for evaporation, 240°C, for at least 6 hours prior to evaporation. This procedure was found to be the simplest which would result in films with reproducible magnetic properties.

Films prepared by a boat evaporation technique possess a concentration gradient through their thickness. The vapor pressure of iron is greater than that of nickel, at the deposition temperature; thus, the first layers of the film are iron rich. Depletion of iron in the charge and the
FIGURE 9

THIN FILM DEPOSITION SYSTEM

1) rotating substrate holder
2) substrate heater, shown open
3) titanium sublimation pump
4) liquid nitrogen feed through
5) liquid nitrogen trap
6) high current feed through
7) tungsten boat supports
formation of a nickel-iron-tungsten ternary result in a nickel rich tail. Carson and Rudee\textsuperscript{80} have shown that for films made in the same manner as described above, a composition gradient of 14 weight percent nickel will result. As much as 30\% of the original charge remains on the boat in the form of a ternary alloy as the deposition ends. This remnant is higher in nickel than the charge composition; thus, the average film composition will be high in iron. The iron enrichment is approximately 0.16 weight percent iron per weight percent iron in the charge. Table 3 shows both charge and film compositions. The original calibration upon which these compositions are based was done by X-ray fluorescence, a complete description being given by Carson.\textsuperscript{51}

The films were deposited in the presence of a 75 oe. bias field oriented to lie parallel to the field generated by the current flow in the tungsten boat. This field was much less than the 75 oe. field and thus should not have had an effect on the magnetic properties. The films were allowed to cool in the 75 oe. magnetic field. A temperature drop of 50\(^\circ\)C required thirty seconds, and it took one hour to reach 100\(^\circ\)C.

Table 4 summarizes the conditions for boat evaporation.
Table 4 Conditions for Boat Evaporation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge material:</td>
<td>Permalloy wire or rolled sheet spot welded to a tungsten boat</td>
</tr>
<tr>
<td>Substrate temperature:</td>
<td>240°C</td>
</tr>
<tr>
<td>Pressure prior to evaporation:</td>
<td>$10^{-7} - 10^{-8}$ Torr</td>
</tr>
<tr>
<td>Pressure during evaporation:</td>
<td>$&lt; 2 \times 10^{-6}$ Torr</td>
</tr>
<tr>
<td>Average evaporation rate:</td>
<td>$&gt; 1000$ Å/second</td>
</tr>
<tr>
<td>Substrate material:</td>
<td>Corning type 7059 glass</td>
</tr>
<tr>
<td>Bias field strength:</td>
<td>75 oe.</td>
</tr>
</tbody>
</table>

II. Measurement of the Macroscopic Magnetic Properties

The macroscopic magnetic properties, $H_c$, $H_k$, and $a_{50}$ were measured on every film following deposition, and after each step in the isothermal and isochronal magnetic annealing investigations. As used here, macroscopic magnetic properties mean a measurement representing an average value for the whole film, rather than a measurement representative of some smaller region within the film. These measurements were performed with the aid of a 200 cycle per second inductive pickup M-H loop checker, after a design by Causey. Two sets of pickup coils were available, one which sensed the flux change parallel to the alternating current drive field, and a second which picked up flux changes transverse to the drive field.

Measurements of the anisotropy field were made by the Kobelev technique, which is less sensitive to the presence
of magnetization dispersion than the conventional hard axis extrapolation technique. Crowther's method II$^{83}$ was used to determine the macroscopic magnetization dispersion, $a_{50}$. The coercive force, $H_C$, was determined from the standard easy axis M-H loop. For comparison with theory, measurements of $H_K$ were converted to $K_u$ by the use of the standard relationship:

$$H_K = 2 \cdot K_u / M_s$$

where the values of $M_s$ as a function of composition were obtained from Bozorth.$^{84}$

III. Films Prepared to Minimize the Constraint Energy

In order to minimize the effects of the constraint interaction between the film and substrate, a series of films 1100 Å thick were deposited on liquid like layers of silicone grease. Film formation took place under exactly the same conditions as described in Table 4, except silicone grease was applied to each substrate prior to insertion into the bell jar. At the deposition temperature, 240°C, the silicone grease spread out forming a smooth layer over the substrate surface. Because of this spreading effect all four substrates were covered with silicone grease as well as the substrate holder and heater. Vigorous cleaning in a solvent and a bake out was required before the fabrication of normal constrained films could be resumed. The room temperature
viscosity of the silicone grease was 250.000 centipoise-seconds (Copley Chemical Company, Chelsea, Mass.).

Extreme care in handling was required during measurement of the magnetic properties of these films, as they were easily torn, and were prone to curl up if disturbed.

IV. Magnetic Annealing Experiments

Two types of magnetic annealing experiments were performed; isothermal and isochronal. Isothermal annealing requires that changes in a measurable property, which responds to annealing, be recorded as a function of time at a constant temperature. Several temperatures are required for a complete analysis. Isochronal annealing, on the other hand, requires that changes be recorded as a function of temperature for a constant time interval. After each interval in time or temperature the sample is rapidly cooled to room temperature and a measurement made to determine the change in the property of interest. Implicit in this technique are the requirements that: the cooling rate be rapid enough to retain the state of the property of interest characteristic of the time and temperature of anneal, and that the sample be rapidly reheated back to the proper annealing temperature following measurement. This allows proper determination of the true time and temperature of anneal.

To meet these requirements a special linear motion feed-through was constructed which permitted more than fourteen
inches of linear motion inside the vacuum furnace, allowing the specimens to be moved rapidly in or out of the hot zone. An early design using a magnetic coupled movement was unsuccessful because of an interaction with the bias field required for magnetic annealing. Also unsuccessful, because it did not allow a rapid enough rate of heating and cooling, was moving the furnace with respect to the samples.

The vacuum furnace was a homemade tube furnace, and vacuum system available in our laboratory. The vacuum system consisted of a mechanical vacuum pump, an oil diffusion pump, and ambient and liquid nitrogen baffles connected to a one-inch OD vycor tube thirty-six inches in length. The pressure inside the vycor tube was monitored with an ionization gage (CVC type GIC-110B). All annealing took place in vacuum better than $5 \times 10^{-6}$ Torr. The furnace was a cylindrically wound type, with an inner winding of platinum and an outer nichrome winding. A temperature controller was connected to the platinum winding, the nichrome winding was on all the time. Temperature control was maintained to within $\pm 2^\circ$C.

The magnetic field was produced by a pair of Helmholtz coils, and was oriented along the axis of the cylindrical furnace. Any fields generated by the current in the furnace windings was along this same axis. The magnitude of the magnetic field applied during annealing was fifty oersteds. A sample holder designed to carry nine substrates in three
layers of three each was machined out of copper, and held together with stainless steel screws. The holder is shown in Figure 10. A chromel-alumel thermocouple was clamped to one end of the substrate holder, and used to determine the annealing temperature. The output of the thermocouple was recorded as a function of time to provide a continuous record and to monitor heating and cooling rates. The average initial cooling rate (first six minutes) was 10°C/minute at 350°C and 25°C/minute at 500°C.

The vycor tube was connected to the vacuum system on one end, and to the motion feedthrough on the other with "0" ring seals. Linear motion was achieved by moving a smooth nonmagnetic rod, stainless steel, one quarter of an inch in diameter in an "0" ring seal. A thin layer of vacuum grease was applied to the rod to maintain good vacuum and smooth motion.

Pushing the substrate holder into the furnace, prior to heating, resulted in a burst of gas entering the system, but withdrawal of the substrate holder, at the annealing temperature, could be accomplished without any increase in the pressure within the system.

The usual procedure executed during a typical anneal consisted of the following steps:

1) The films were dusted off with an air blast and loaded into the substrate holder in the order of increasing weight percent nickel. Coded scratch
FIGURE 10

SUBSTRATE HOLDER AND LINEAR MOTION FEED THROUGH

USED IN MAGNETIC ANNEALING STUDIES

1) copper substrate holder, capable of carrying nine films
2) thermocouple used to determine the annealing temperature
3) stainless steel support rod
4) the linear motion feed through
marks on the outer edge of the glass substrates were used to keep track of the various compositions.

2) The holder was fastened together with the two stainless screws.

3) The holder was affixed to the end of the stainless steel rod, and the thermocouple inserted and the two screws retightened.

4) The vacuum system was sealed and pumped down.

5) At a pressure of $1 \times 10^{-7}$ Torr the magnetic field was turned on and the holder was inserted into the furnace. The resulting gas burst was pumped out before a 50°C temperature rise occurred.

6) Time and temperature were recorded on a strip chart recorder.

7) After the prescribed annealing time had elapsed a blower was turned on, cooling the outside of the vycor tube, and the samples were withdrawn and cooled in the magnetic field.

8) When the temperature had dropped to 100°C helium gas was bled into the system and the films removed.

9) The magnetic properties of $H_C$, $H_K$, and $\alpha_{50}$ were measured.

10) The samples were cleaned with an air blast and the next cycle begun.

Isothermal magnetic annealing of thin nickel-iron films was performed at the following temperatures, and for the
following times:

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>Cumulative Annealing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Easy Axis</td>
</tr>
<tr>
<td>252°C</td>
<td>113 hours</td>
</tr>
<tr>
<td>290°C</td>
<td>195 hours</td>
</tr>
<tr>
<td>324°C</td>
<td>195 hours</td>
</tr>
<tr>
<td>325°C</td>
<td>192 hours</td>
</tr>
<tr>
<td>350°C</td>
<td>135 hours</td>
</tr>
<tr>
<td>355°C</td>
<td>125 hours</td>
</tr>
<tr>
<td>383°C</td>
<td>215 hours</td>
</tr>
<tr>
<td>398°C</td>
<td>183 hours</td>
</tr>
<tr>
<td>414°C</td>
<td>161 hours</td>
</tr>
</tbody>
</table>

In addition, a series of isochronal magnetic anneals were performed. These anneals lasted 60 minutes, and were carried out at temperatures between 231°C and 607°C.

Prior to the start of an annealing series the films which had been selected for study were subjected to a pre-anneal, the purpose of which was to completely recrystallize the film, and to establish a standard metallurgical state. These pre-anneals were 60 minutes in length, and were performed at a temperature of 500°C.

V. Grain Size Determination

The grain size of permalloy thin films is an important physical property which is thought to exert a large influence
on the magnetic properties, particularly the magnetization dispersion. It was therefore deemed necessary to measure the grain size and follow any changes which might occur during the course of prolonged magnetic annealing at elevated temperatures.

The grain size was observed by transmission electron microscopy, which required that the films to be analyzed be removed from their substrates. This is a difficult task, as the film and substrate bond is quite strong for films deposited at elevated temperatures. Several different procedures were investigated to accomplish removal of the film from the substrate; one of which was the use of a thin layer of silicone grease discussed in a different context above. The method which was actually used to effect film removal was to prepare films on a glass substrate which had been precoated with a thin layer of copper covered with a thin layer of silicone monoxide. Films prepared in this manner exhibited macroscopic magnetic properties comparable to those observed for films deposited directly onto glass substrates. These special substrates were prepared by vacuum evaporating the copper and SiO underlayers onto standard glass substrate material. Removal of the permalloy film from the substrate was accomplished when the copper underlayer was dissolved away by a mild solution of sodium hydroxide and ammonium hydroxide. This solution did not appear to damage the films surface.
Initial observations of the grain structure by transmission electron microscopy exhibited large variations in contrast from sample to sample. Careful examination of the hydroxide solutions, used to dissolve the copper underlayers, sometimes revealed the presence of the SiO underlayer floating in the solution. The presence of this SiO coating was observed to be a function of the time the film was allowed to soak. An hour was required for the copper to dissolve, but at least four hours were required for the SiO layer to detach itself from the permalloy film. As standard procedure a soaking time of at least four hours was adopted. This procedure resulted in uniformly good contrast when the grain structure was viewed in the electron microscope. The presence of the SiO underlayer along with the film in the microscope had led to the decreased contrast observed earlier because of incoherent scattering of the electrons by the SiO coating.

In several series of isothermal anneals one or two control films, with the copper-silicone monoxide underlayer, were annealed along with seven or eight experimental films. Following pretreatment and successive annealing steps, the substrates of the control films were scored and a small portion removed for study in the electron microscope. The small section of permalloy film was removed, as described above, and the grain structure photographed in the electron microscope.
The crystallite size and distribution were obtained from the electron micrographs with the aid of a particle size analyzer (Carl Zeiss model TGZ 3). This device is a semi-automatic instrument which requires only that imaged particles in the electron micrograph be recognizable to the eye; it is not necessary that the grains be regularly shaped or individually separated. The Zeiss instrument allowed grain diameters between 1.2 and 27.7 mm., on the enlarged micrograph, to be counted. This range of sizes was broken up into 48 segments. It was possible to semi-automatically record either the distribution in each size range or the cumulative distribution of crystallite diameters as a function of the grain diameter. Each micrograph that was selected for analysis was counted completely to remove the possibility of a bias, i.e., the operator might have a tendency to count only the large more easily distinguished grains. In most cases this meant 250 - 500 counts were made on a given micrograph.

The grain size data was recorded in the cumulative distribution function mode to allow a test of whether or not the grain size followed a normal distribution. This was accomplished by plotting the cumulative distribution data, normalized to one, on probability paper. The ordinate on this special graph paper is scaled such that a cumulative distribution, normalized to unity, will plot as a straight line if it obeys a normal distribution. This was found not
to be the case.

There are numerous instances in which grain sizes in metals have been found to follow a distribution in which the logarithm of the grain size obeys a normal distribution. Distributions of this type have a skew toward larger grain sizes, and will appear as a straight line when plotted on log-probability paper. This was found to be the case for the present observations of the grain size in permalloy films. The 0.50 points on the curve indicates the mean grain diameter, and the difference between this point and the 0.8413 point will give the standard deviation which characterizes the central tendency of the distribution.

VI. Design of a Magneto-optic Loop Checker

One of the earliest observations of magnetic domains by the magneto-optic technique was reported by Fowler and Fryer. The arrangement of optical components which they reported is widely used today as a standard apparatus because of its simplicity and good contrast. Figure 11 shows this standard arrangement. Specimens may be viewed in reflection, with contrast resulting from the Kerr effect, or in transmission, for optically transparent or very thin samples, with contrast resulting from the Faraday effect. Figure 11 shows both configurations.

A magneto-optic effect results when a beam of plane polarized light is incident on the surface of a magnetic
Standard apparatus for the magneto-optic observation of domains.

FIGURE 11
material. This interaction is called the Kerr effect when the reflected beam is observed, and the Faraday effect when the transmitted beam is observed. In order for a magneto-optic effect to occur there must be a component of the magnetization in the direction of the incident beam. For the case of a thin film, with its magnetization constricted to lie in the plane of the film, the incident beam must strike the specimen surface at an oblique angle. Contrast results, allowing magnetic domains to be viewed, or switching to be followed, because of the rotation of the plane of polarization which occurs in the transmitted and reflected beams. The angle and direction of rotation is proportional to the angle and magnitude of the magnetization in the illuminated region. Oppositely magnetized regions will result in opposite rotations which may be viewed through an analyzer.

The magneto-optic rotation is larger for the Faraday effect\(^8\); hence, films thin enough to allow sufficient transmission of the incident beam will result in greater contrast when viewed in transmission. This condition is fulfilled for permalloy films less than 1000 Å thick. Figure 11, therefore, shows all the elements required to construct a loop checker making use of the Faraday effect. A device of this type should not be subject to the same type of electromagnetic noise which has plagued the designers of inductive type loop checkers; while the use of a photomultiplier tube rather than an optical detector, i.e., a camera or the eye,
would eliminate the problem of low contrast and light level which has troubled many investigators of domain structure.

A helium-neon laser (Spectra Physics model 133) was selected as a light source. It provided a non-divergent monochromatic beam (6328 Å) roughly one millimeter in diameter. It was chosen largely on the basis of cost and ruggedness. In use its output varied and added significant noise to the system, a problem to be discussed below. All optical components were mounted on a triangular optical bench (Ealing Optical Service). Polarizers were 9.5 cm. diameter linear polarizers (Ealing Optical Service) and were mounted in homemade mounts which allowed 360° rotation about the optical axis. The sample was mounted on a rotary table (Kinematic RT 200, Ardel Instrument Co.) which allowed 360° rotation of the film about its normal. The rotary table was mounted on the optical bench at an angle of 35° to the optical axis. A larger angle 45° - 60° would have resulted in a larger signal, but the requirement of an unobstructed optical path placed a limit on the maximum angle the sample holder could be inclined to the optical axis. With the aid of a vernier scale, rotations as small as 5 seconds of arc about the sample normal could be determined; although in practice, the vernier was never used. Detection was accomplished with the aid of a photomultiplier tube (RCA type 7102). The photomultiplier was the only component not mounted directly on the optical bench. Figure 12 shows
the final arrangement of optical components used in the loop checker.

The rotary table and sample holder were mounted at the center of a set of cube coils which canceled out the earth's magnetic field. A Helmholtz pair was used to switch the film, and could provide a drive field of about 40 oe. The drive coils and earth field canceling coils are also shown in Figure 12.

The Faraday effect loop checker could have been used to measure $H_C$ and $H_K$, as well as dispersion, but as my concern at this point is only the dispersion, only this problem will be discussed. A photomultiplier tube produces a direct current proportional to the light input. As the films used in this work allowed a finite optical transmission, the effect of the Faraday rotation was only a small change on top of a much larger signal. The problem then is the detection of a small change in a much larger background signal. This was accomplished in part with the aid of an operational amplifier with a zero offset. (Union Carbide HC6010) Fujii et. al. 72, used a direct current drive field, and recorded M-H loops directly with the aid of an x-y plotter. Their approach was adopted initially because of the relative simplicity of the instrumentation required, but noise originating in the laser light source forced its abandonment. It seems that inexpensive lasers are constructed with their mirrors physically attached to the gas tube; slight mechanical vibrations thus
THE FARADAY EFFECT LOOP CHECKER

1) laser, 2) polarizer, 3) lens, 4) lens, 5) rotating table, 6) film
7) drive coils, 8) analyzer, 9) photomultiplier housing, 10) optical bench
11) earth's magnetic field cancelling coils
result in variations in the output level. In more expensive systems the mirrors are more rigorously mounted and the output level does not vary. Other instabilities may originate in the laser power supply. The noise thus resulting was of the same order of magnitude as the signal to be detected.

An AC approach making use of a 26 Hz drive field and a lock-in amplifier (Princeton Applied Research Model HR8 or JB4) was finally adopted. Crowther's method was used for the actual measurement of dispersion, such that the magnitude of output signal from the lock-in amplifier was proportional to the net flux change within the region being illuminated by the laser beam. The magnitude of this signal was recorded as a function of the angular position of the film. The angular position which resulted in zero output signal was the average hard direction for that spot. Zero output voltage indicated that 50% of the flux change, in the small illuminated region, was switching in one sense and the remainder in the opposite sense. The angle away from the average hard direction which resulted in one-half of the maximum signal, i.e., 25% switching in one direction and 75% in the other, is the magnetization dispersion. The procedure used in measurement was to record the output voltage, net flux change, as a function of angular position around the average hard direction for the whole film. If this data were normalized, with respect to the maximum value, the average local hard direction and magnetization dispersion
could be easily read from a graph of normalized flux change as a function of angular position.

The annealing investigations already described were performed on films 1100 Å thick. This thickness was found to be too thick for the microscopic dispersion measurement with the magneto-optic loop checker. It was necessary to prepare several groups of films 750 Å thick. These films were prepared in the standard manner. After cooling to room temperature the macroscopic magnetic properties were measured and the films were placed in a second vacuum evaporator where a 1000 Å coating of SiO was deposited over the film. The presence of this coating resulted in a noticeable improvement in the signal-to-noise ratio during magneto-optic measurements. It was verified that no observable change in the macroscopic magnetic properties occurred as a result of the coating of SiO.
CHAPTER FOUR: RESULTS AND DISCUSSION

I. The Origin of the Uniaxial Anisotropy in Vacuum Deposited Thin Films of Nickel-Iron Alloys

A. Experimental Results

A series of films were produced to test the validity of the two component model for the origin of the anisotropy in nickel-iron thin films. This series of films was broken up into two groups. One group was prepared in the usual manner, by deposition onto clean glass substrates; while the second group was deposited onto glass substrates coated with a smooth layer of silicone grease.

The adhesion of the film to the substrate will determine the effectiveness of the constraint mechanism.\(^{31}\) We have observed that for films with compositions near 80% Ni - 20% Fe, the anisotropy field was independent of any intermediate layer introduced between the film and the substrate, for example: silicone monoxide, copper aluminum, gold, or silicone grease. For the case of silicone grease there is no adhesion. These results are consistent with the constraint model, as the predicted contribution to the anisotropy, from constraint, is small in the neighborhood of the zero magnetostriction composition.

However, when unconstrained films were produced on silicone grease-coated substrates, at other compositions, significant differences were evident. These results are shown
in Figure 13. All data points represent the average of at least eight films, the range of scatter being indicated by the error bars. The results for constrained films fall in the middle of the scatter band of the results of several authors compiled by Slonczewski.\textsuperscript{9} Due to limitations in the drive field capacity of the loop checker, films of pure nickel could not be switched, and $K_u$ could not be measured.

In addition to the results for constrained and unconstrained films, and the difference curve, Figure 13 also shows the predictions of the theory used by Robinson and West, assuming that the constraint temperature was that used for deposition, 240°C. The difference curve was drawn assuming that the two high nickel points on the unconstrained curve were artifacts caused either by some partial adhesion of the film to the substrate at compositions of high magnetostriction or by measurement error resulting from the presence of a high dispersion. In any case, there is good qualitative agreement between these experimental results and the predictions of the two component models.

B. Discussion

It is clear from Figure 13 that the difference between constrained and unconstrained films is in reasonable agreement with the predictions of the constraint theory. The difference curve shown in this figure assumes that the two high nickel measurements were artifacts, as discussed above.
The uniaxial anisotropy of both constrained and unconstrained Permalloy films is plotted as a function of composition. In addition, the difference between the two kinds of films is compared to the predictions of the constraint theories.
It seems unlikely that the presence of the silicone grease contributes to the anisotropy in any manner except through the constraint term, since, within the accuracy of these experiments, the difference curve vanishes at the zero magnetostriction composition.

There is a difference between the predictions of the constraint theories and our results for films containing less nickel than the zero magnetostriction composition. The origin of this difference is not readily apparent. Since our measurements exceed the theoretical predictions, it cannot originate in partial adhesion of the unconstrained film to the substrates. It is also doubtful that another mechanism is present since the agreement is quite good in the films that contain more nickel than the zero magnetostriction composition. Perhaps in the higher iron films, where the deviation occurs, the interaction with the substrate is altered in such a manner that a lower effective constraint temperature should be used in the constraint calculation. This deviation will be discussed in more detail below.

The results from the unconstrained films duplicate almost exactly the limiting anisotropies obtained by Chikazumi and Oomura from the slow cooling of bulk alloys in a magnetic field from a temperature of 600°C. The temperature behavior will also be discussed in more detail below.

Similar work by Brownlow and Wilts published simultaneously offers experimental verification of the results
discussed above. They prepared films at various compositions in the nickel-iron and cobalt-nickel systems on a water soluble coating, which enabled the film to be easily detached from the substrate. Measurements of the anisotropy constant, before and after removal from the substrate, was made by the high field torque meter technique. Their results for the nickel-iron system are shown in Figure 14. This figure shows a remarkable agreement between their experimental results and Robinson's predictions over the composition range 50 - 80 weight percent nickel. For compositions with less than 50 weight percent nickel a two phase region exists, and agreement is poor, as one might expect. Their results for the nickel-cobalt system, shown in Figure 15, demonstrate that Robinson's model and experimental results are in accord within the range of compositions known to be a single phase. In this single phase region the deviation between the predictions of West's model and experimental observations are markedly evident. These latter observations, in the cobalt-nickel system, are perhaps the most significant as, in this system, the differences between the models of West and Robinson are large, and a comparison with experiment could be very sensitive. In the nickel-iron system, as shown in Figure 5, the similarity in shape and magnitude of the predictions of the two theories has made meaningful comparison impossible. In the two phase region no valid comparison can be made.
Anisotropy energy, —; change in anisotropy energy, ---; calculation after Robinson, --; and calculation after West, ---, as a function of composition for Ni–Fe alloys.

FIGURE 14

AFTER BROWNLOW AND WILTS

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Anisotropy energy, —; change in anisotropy energy—; calculation after Robinson, ---; and calculation after West, ---, as a function of composition for Ni–Co alloys.

FIGURE 15
The results presented here, and those of Brownlow and Wilts, are in general agreement, and taken together, offer strong support to the two component model of the induced anisotropy in permalloy thin films. There are, however, some differences between the two results in the composition range 50 – 85 weight percent nickel. These differences, in all likelihood, can be attributed to the different measurement techniques used by the two groups. The present results are from a B-H method, while Brownlow and Wilts made use of a high field torque meter technique. Differences between low field B-H loop methods and high field methods have been observed.\(^9\)\(^0\) The high field methods are generally accepted as being the more accurate.\(^9\)\(^0\),\(^8\) It would, therefore, appear that some, if not all, of the difference between these results originate in the measurement error.

II. The Kinetics of Magnetic Annealing Recrystallized Thin Films of Nickel-Iron Alloys

A. Experimental Results

1. Isothermal Magnetic Annealing

The results of easy axis isothermal magnetic annealing of recrystallized permalloy thin films are shown in Figure 16. These results are for changes in \(H_k\) only. Changes in magnetization dispersion will be discussed in later sections. The initial value of \(H_k(t)\), \(H_k(t=0)\), is the value of the anisotropy field after the recrystallization anneal, one hour at 500°C. Figure 17 shows typical results for hard
THE ANISOTROPY FIELD AS A FUNCTION OF TIME FOR ANNEALING AT 383°C (EASY AXIS)

- 61% Ni
- 72% Ni
- 51% Ni
- 77% Ni
- 82% Ni
- 86% Ni

$H_k(\infty) = 11.5$ oe.

$H_k(\infty) = 6.8$ oe.

$H_k(\infty) = 4.5$ oe.

$H_k(\infty) = 3.4$ oe.

$H_k(\infty) = 2.1$ oe.

$H_k(\infty) = 6.5$ oe.

(51%)

FIGURE 16
FIGURE 17

THE ANISOTROPY FIELD AS A FUNCTION OF TIME FOR HARD AXIS MAGNETIC ANNEALING AT 383°C

ANISOTROPY FIELD (Oe.)

TIME (hours) →

77% Ni

72% Ni

61% Ni

61%

M₀(77%) = 4.00e

M₀(72%) = 4.00e

M₀(61%) = 5.20e

M₀(61%) = 10.80e
axis isothermal magnetic annealing, in these cases, $H_k(t=0)$ is either the value of the anisotropy field following the last easy axis annealing step, or that following the easy axis recrystallization anneal. Negative values of the anisotropy field indicate the original easy and hard directions have been changed.

These curves were analyzed assuming that the reactions which they describe followed first order kinetics:

$$\frac{dH_k(t)}{dt} = \frac{H_k(t = \infty) - H_k(t)}{\tau(T)}$$

where $H_k(t=\infty)$ is the value $H_k$ will approach after annealing for an infinite time at temperature $T$. $H_k(t=0)$ is the initial value of the anisotropy field, and $\tau(T)$ is the relaxation time whose temperature dependence is assumed to be given by an Arrhenius relationship. For the boundary conditions of these magnetic annealing studies the anisotropy field is given by:

$$H_k(t) = H_k(\infty) + \{H_k(0) - H_k(\infty)\} \exp(-t/\tau)$$

Similar relationships have been used by other authors^{44-47,49}, but were not general enough to describe both easy and hard axis isothermal magnetic annealing.

For the purposes of analysis this relationship may be rearranged to define a reduced quantity, $H_k^*(t)$

$$\frac{H_k(t) - H_k(\infty)}{H_k(0) - H_k(\infty)} = H_k^*(t) = \exp(-t/\tau)$$
In this relationship $H_k(0)$, $H_k(t)$ and $t$ are determined from experiment and $H_k(\infty)$ and $\tau$ are unknowns. If the observations of the changes in anisotropy field with time describe a first order process, then for the proper choice of $H_k(\infty)$ a plot of \( \log H_k^*(t) \) as a function of time will be a straight line through the origin with a slope of $-\frac{1}{\tau}$. Deviations from this behavior will indicate the presence of more than one process, or that the basic assumption of the first order character of the process was in error. Initial calculations showed that for a choice of $H_k(\infty)$ in agreement with those predicted from the study of magnetic annealing in bulk alloys the above mentioned condition was fulfilled. That is, $\log H_k^*$ versus time was a straight line if, at most, the first one to three data points were omitted. The following calculations were made with the aid of a computer.

1) A value of $H_k(\infty)$ was assumed and the least square slope ($-\frac{1}{\tau}$) and intercept calculated. A value for this initial guess, $H_k(\infty)$ was arrived at with the aid of Ferguson's work on bulk alloys.\(^{24}\)

2) The fitting parameter, the sum of the squares of the differences between the experimental values of $H_k(t)$ and those predicted using the calculated value of $\tau$ and the assumed value of $H_k(\infty)$ was computed.

3) The process was repeated with $H_k(\infty)$ varied in a systematic manner.
4) Plots of $\tau$ and the sum of the squares of the differences as a function of $H_k(\infty)$ were constructed and the best fit values of the relaxation time and $H_k(\infty)$ were chosen. Figure 18 shows typical plots of $\log H_k^*$ as a function of time, while Figure 19 is a typical plot of relaxation time and the mean square deviation (the fitting parameter) as a function of $H_k(\infty)$. This procedure was repeated for each composition and for each annealing temperature.

A plot of $\log \tau$, where $\tau$ was an average relaxation time for the various compositions studied, as a function of the inverse of the annealing temperature in $^\circ$K was found to be a straight line obeying an Arrhenius relationship

$$\tau = \tau_0 \exp(Q/kT)$$

This result is shown in Figure 20. Also shown in this figure are the results of Ferguson\textsuperscript{24} for magnetic annealing in bulk alloys. The least square slope of the straight line through these points indicates an activation energy of 2.41 eV/atom and an intercept, $\tau_0$, of $1.2 \times 10^{-12}$ seconds, in good agreement with the results found for bulk material. The results for annealing at 250$^\circ$C and 290$^\circ$C are shown on this figure, but were not included in the least square calculation. The error bars indicate the scatter for different compositions and easy and hard axis magnetic anneals at each temperature.
LOG \( H_K(t) \) AS A FUNCTION OF TIME FOR HARD AXIS MAGNETIC ANNEALING AT 383°C (FIRST 3 DATA POINTS OMITTED)

61% NICKEL
\( \tau = 6.394 \times 10^5 \) SECONDS
\( H_K(\infty) = -10.8 \) oe

\[ \log H_K(t) = \frac{H_K(t) - H_K(\infty)}{H_K(0) - H_K(\infty)} \]

72% NICKEL
\( \tau = 3.180 \times 10^5 \) SECONDS
\( H_K(\infty) = -5.2 \) oe

77% NICKEL
\( \tau = 5.299 \times 10^5 \) SECONDS
\( H_K(\infty) = -4.0 \) oe

FIGURE 18
FIGURE 19

RELAXATION TIME AND FITTING PARAMETER AS A FUNCTION OF $H_R(\omega)$

RELAXATION TIME

FITTING PARAMETER

SUM OF SQUARES (FITTING PARAMETER)

RELAXATION TIME ($10^3$ SECONDS)
RELAXATION TIME FOR MAGNETIC ANNEALING

$10^3 \frac{1}{T}$ ($^\circ$K$^{-1}$)

PRESENT WORK
FERGUSON (BULK ALLOYS)

FIGURE 20
Figures 21, 22, and 23 are plots of $K_u(\infty)$ as a function of composition, where $K_u(\infty)$ is calculated from the relation

$$K_u(\infty) = M_s/2 \, H_k(\infty)$$

The values of $H_k(\infty)$ are those values derived by the computer fit described above. This data is for annealing at 383°C, 414°C, and for pretreatment at 500°C. The error bars indicate the possible contribution from the constraint mechanism. The values used for the constraint mechanism were those from Robinson's model, and the constraint temperature used was the annealing temperature. The fit is good except for compositions with less than 60 weight percent nickel. Similar comparisons at other annealing temperatures show that agreement becomes worse as the relaxation time for magnetic annealing becomes long with respect to the actual time of anneal.

In addition to the analysis described above, in which data for each temperature was lumped together, without regard to composition, an analysis was made for each composition. The activation energies, as a function of composition, which were calculated by this analysis, are shown in Figure 24. The error bars indicate 90% confidence limits. The prominent dip at a composition near 75% nickel should be noted. The magnitude of this dip is larger than the standard deviation in the data points would predict.
$K_u(\infty)$ AS A FUNCTION OF COMPOSITION FOR BULK ALLOYS AND THIN FILMS ANNEALED AT 383°C

UNIAXIAL ANISOTROPY CONSTANT ($10^3\text{ergs/cc}$)

WT % Ni

FIGURE 21
Figure 22

$K_u (\infty)$ as a function of composition for bulk alloys and thin films annealed at 500°C.
Figure 23

K_0 (001) as a function of composition for bulk alloys and thin films annealed at 414°C

Anisotropy constant K_0(001) (10^5 ergs/cm^2)

Bulk alloys (Ferguson)

Film composition weight percent nickel
FIGURE 24

ACTIVATION ENERGY FOR MAGNETIC ANNEALING AS A FUNCTION OF COMPOSITION

ACTIVATION ENERGY (eV)

PERCENT NICKEL
2. Isochronal Magnetic Annealing

Figure 25 shows the results of 60 minute easy axis isochronal magnetic annealing performed on recrystallized permalloy thin films of various compositions. For the purpose of comparison, the next figure, Figure 26, shows Carson's data for 30 minute isochronal anneals on films which had not been subjected to a recrystallization anneal. The results for recrystallized films, Figure 25, show four regions.

Region I, extending from 230°C to almost 400°C shows only a slight temperature dependence. Region II, extending from 400°C to 460°C exhibits a more marked temperature dependence, with $H_k$ assuming its maximum value in this temperature region. The third region, 460°C to 520°C, is also temperature dependent, with $H_k$ decreasing linearly with increasing annealing temperature. In the final region, 520°C to 600°C, $H_k$ is relatively temperature insensitive. Also shown in Figure 25, in region III, is the straight line indicative of the temperature dependence found by Ferguson for bulk alloys. The agreement between the slope of these lines and the observed temperature dependence in this region is fair.

The annealing temperature dependence of films which were not recrystallized exhibits similar dependence in regions III and IV, but the region I and II behavior is significantly different.
FIGURE 26

ANISOTROPY FIELD AS A FUNCTION OF ANNEALING TEMPERATURE FOR AS-DEPOSITED FILMS (AFTER CARSON 51)
B. Discussion

1. Isothermal Magnetic Annealing

It is clear from Figure 20 that there is good agreement between the present investigation of the annealing kinetics of the induced anisotropy in vacuum evaporated nickel-iron thin films and earlier magnetic annealing investigations performed on bulk alloys. The straight line drawn through both sets of results, from which the relaxation time and intercept, \( \tau_0 \), are calculated assumes that the measured relaxation times at 250°C and 290°C are in error and may be ignored. This is a valid assumption as the expected relaxation times at these temperatures are orders of magnitude larger than the annealing times, 100 - 200 hours. As a result the changes in \( H_k^* \) which occurred between annealing steps was extremely small, and an accurate data fit was not possible. The results, therefore, are questionable and were not included in the least square calculations of the slope and intercept, \( \tau_0 \).

The form of analysis used to deduce relaxation times from the experimental observations of changes in \( H_k^* \) with time required certain assumptions about the functional form they followed. The basic assumption was the applicability of first order kinetics. This led to the conclusion that \( H_k^*(t) \) as a function of time should therefore be a straight line, with a slope of \( -\frac{1}{\tau} \) and which would pass through the origin. We have shown that this is the case; if at most
the first three observations are omitted, i.e., $H^*_K(t)$ versus time is a straight line and does indeed pass through the origin. This result is illustrated for several compositions in Figure 18. No study has been attempted to elucidate further those processes which lead to a deviation from one first order process in the initial points. The relaxation time of this process is of the order of several hours at 350°C, near the lower limit of the resolution of this experimental technique. But the right order of magnitude is to be described by processes observed by Kneer and Zinn\textsuperscript{44,45} and Wiedenmann and Hoffmann.\textsuperscript{49}

A second assumption involved a choice for $H_K(\infty)$, and the subsequent data fitting procedure. The validity of these assumptions is greatly supported by the agreement between those values of $H_K(\infty)$ or $K_u(\infty)$ and the results of Ferguson's study of bulk alloys, Figures 21, 22, and 23. This agreement holds through the whole range of compositions except for compositions which lie in a two phase region. Figure 21 is for prolonged magnetic annealing at 383°C; while Figure 22 summarizes the results for several different 60 minute anneals at temperatures near 500°C. That bulk values would be achieved after only 60 minutes of annealing at 500°C is not surprising, as the indicated relaxation time at this temperature is approximately 20 minutes. The results for magnetic annealing at 414°C are in agreement with those of bulk alloys, except at 61 weight percent nickel. The reason for this discrepancy is not obvious.
The activation energy, \( Q = 2.41 \text{ eV/atom} \), which the present analysis predicts is lower than Ferguson's\textsuperscript{24} prediction of 3.01 eV/atom, but in very good agreement with experimentally determined activation energies for self diffusion in nickel-iron alloys.\textsuperscript{41} This result is also in good agreement with observations of Bozorth and Dillinger\textsuperscript{26} on bulk alloys and Segmüller\textsuperscript{42} on recrystallized permalloy thin films. In addition, these results are consistent with the trend noted by Kneer and Zinn\textsuperscript{45}; i.e., the activation energy for magnetic annealing approached bulk values as a result of high temperature pretreatment.

The present experimental determination of \( \tau_0 = 1.2 \times 10^{-2} \) seconds is also in good agreement with theory as it is the same order of magnitude one might expect for the inverse of the Debye frequency (=\( 10^{-13} \) seconds), i.e., the fundamental frequency of lattice vibration. All earlier investigations of the annealing kinetics of permalloy thin films predicted values several orders of magnitude smaller, a result which was disturbing for a mechanism thought to originate in atomic diffusion.

Figure 24 shows the activation energy as a function of composition for the present data only. The magnitudes indicated are somewhat lower than those calculated from the data of Figure 20, but this might be expected as the temperature range is limited, and thus confidence in the slope and intercept are less. The magnitude of the minimum which occurs in
the neighborhood of 75 weight percent nickel is greater than the standard deviation in the data points; hence, one may regard them as significant. Observations of the diffusion of nickel in nickel-iron alloys indicate a similar minimum in the activation energy for diffusion of nickel in nickel-iron. The diffusion of iron in nickel-iron alloys, on the other hand, does not have a minimum in the neighborhood of Ni₃Fe. Recently Million and Kucera have observed similar behavior in the nickel-cobalt system in the neighborhood of Ni₃Co, a composition which is known to form an ordered structure.

2. Isochronal Magnetic Annealing

Isothermal annealing studies have indicated that the major component of the anisotropy in permalloy thin films, which have been recrystallized, behaves much like bulk alloys when magnetically annealed. Further confirmation is provided by the isochronal magnetic annealing results presented in Figure 25. These films were subjected to the standard 60 minute recrystallization anneal at 500°C prior to the first 60 minute isochronal anneal.

Region I, Figure 25, which extends from 230°C to almost 400°C shows virtually no temperature dependence as the observed relaxation time for this range of temperatures is in excess of 100 hours, larger by orders of magnitude than the time of anneal. Significant atomic movement is not,
therefore, expected during the course of a one hour anneal at these low temperatures. Above 400°C, region II, the annealing time becomes an appreciable fraction of the relaxation time for magnetic annealing; hence, a significant atomic diffusion may occur and observable changes in \( H_k \) result. At approximately 460°C the anisotropy assumes a value equal to its thermal equilibrium value for that temperature and any further increases in temperature results in a decrease in \( H_k \). In this region, region III, the relaxation time is equal to or less than the annealing time and the observed anisotropy will closely follow the expected equilibrium value.

As the temperature is further increased the relaxation time becomes short with respect to the time it takes the films and holder to cool, resulting in values of \( H_k \) characteristic of the cooling rate rather than the annealing temperature. This same behavior, region IV, was also observed by Carson\(^{51}\), and is not due to a memory effect as he proposed, but is just a cooling rate effect as indicated above.

In all cases, except for 51 weight percent nickel films, \( H_k \) reaches its maximum value in region II within 10°C of the line extrapolated from the results on bulk alloys, and decreases linearly in region III. These results are only qualitative; the presence of only 2 - 4 data points in regions II and III makes the calculation of slopes and intercepts of doubtful value.
The results of isochronal magnetic annealing of thin films which were not recrystallized, taken from Carson\textsuperscript{51}, qualitatively supports the present result, although his curves do not as closely follow those of bulk alloys in region III. This may be attributed in part to the much more sluggish heating and cooling rates he observed, and the fewer observations he made over approximately the same temperature range.

3. The Temperature Dependence of the Anisotropy

It has been shown that for the special case of recrystallized permalloy films the temperature dependence of $K_u(\infty)$ is the same as for bulk alloys, $K_u(\infty)$ being the maximum anisotropy which may be induced by prolonged annealing at a given temperature. What we have not touched upon is how this relates to the anisotropy present in thin films in the as-deposited condition. It was noted earlier that the anisotropy present in unconstrained films was equal to that found by Chikazumi and Oomura\textsuperscript{89} to result in bulk alloys which had been slowly cooled, in a magnetic field, from 600°C. The resulting anisotropy was observed to be characteristic of the cooling rate not the annealing temperature. Using Ferguson's\textsuperscript{24} results for bulk alloys, we may calculate the temperature to which the observed anisotropy, in unconstrained films, is equivalent. This result is shown in Figure 27. The indicated composition dependence is probably due to the
composition dependence of the Curie temperature, as magnetic annealing is effective only below the Curie temperature, but at temperatures high enough to allow significant diffusion to occur. Compositions with lower Curie temperatures will be subjected to magnetic cooling for shorter times at temperatures for which the relaxation time for magnetic annealing is longer; resulting, therefore, in less anisotropy being developed. Figure 28 illustrates the equivalence of the anisotropy possessed by a thin film deposited at 240°C, and that possessed by bulk alloys either slowly cooled from 600°C or annealed extensively at temperatures between 400°C and 460°C.

The nickel and iron atoms arriving at the substrate during evaporation possess high kinetic energies and their mobility and effective temperature is greater than the overall substrate temperature. In addition, the presence of extrinsic vacancies and other defects, which are grown in during the rapid formation of the film on the substrate, results in an enhanced mobility of iron and nickel atoms; and consequently, a decreased relaxation time for magnetic annealing. Ferro, Griffa, and Montalenti have shown that magnetic annealing of specimens which possess a high vacancy concentration, as a result of quenching from 1350°C, yields directional ordering for annealing temperatures about 150°C lower than in non-quenched specimens. This decreased relaxation time is characteristic of annealing a bulk alloy or
ANISOTROPY CONSTANT OF UNCONSTRAINED FILMS AND SLOW COOLED BULK ALLOYS AS A FUNCTION OF COMPOSITION

- ■ PRESENT WORK UNCONSTRAINED FILMS
- ○ CHIKAZUMI & OOMURA BULK ALLOYS (SLOW COOLED FROM 600°C)

ANISOTROPY CONSTANT $K_u(QO)$

(10$^3$ ergs/sec)

FILM COMPOSITION (WT % NICKEL)

FIGURE 28
recrystallized film at a higher temperature. Bulk alloys demonstrate a relaxation time of the order of seconds for temperatures only slightly above 600°C. It is, therefore, quite reasonable for anisotropies to develop which are characteristic of temperatures in the neighborhood of 450°C while a film is forming from the vapor onto a substrate maintained at 240°C. Furthermore, Chikazumi and Oomura predicted the same magnitude of anisotropy for bulk alloys slowly cooled, less than 10°C per hour, from 600°C. Their result is quite reasonable considering that the relaxation time at 450°C is of the order of several hours; while at 400°C it is of the order of tens of hours.

4. The Induced Anisotropy in Permalloy Thin Films

The results of the present study of the uniaxial anisotropy possessed by vacuum deposited thin films of nickel-iron alloys leads directly to a model which provides a complete description of its composition, temperature and annealing time dependence. As-deposited films exhibit an anisotropy which is described by a two component model. The major component is the same mechanism operative when bulk alloys are magnetically annealed, most likely the pair ordering mechanism. The magnitude of this component of the anisotropy assumes a value characteristic of the cooling rate rather than the substrate temperature.

The second component may be described by the constraint
mechanism, a mechanism operative only in thin films which are magnetostrictive and constrained by a substrate. This mechanism follows the form proposed by Robinson. During magnetic annealing this process behaves like that observed by Graham and Lommel in films of pure nickel. The activation energy for this process as observed by Graham and Lommel is approximately 0.4 eV.; consistent with more recent investigations performed on nickel and nickel-iron thin films by Kneer and Zinn, Wiedenmann and Hoffmann, Fujii et. al., and with the present result which shows a relaxation time for the minor process of the order of several hours at 350°C.

In recrystallized films the anisotropy attributed to the first mechanism behaves in a manner similar to that observed during magnetic annealing of bulk alloys; while for the case of as-deposited films, the annealing behavior is somewhat more complicated. This complex behavior, which disappears following recovery and recrystallization, must be related to the complex film structure present in the as-deposited film. It would seem likely that lattice defects, i.e., vacancies, interstitials, dislocations, and grain boundaries, known to be present in excess of thermal equilibrium concentrations, would play a role in this complex behavior.

Iwata and Hagedorn have noted that these defects can contribute to the uniaxial anisotropy in two ways.

a) A direct contribution may occur by the presence
of oriented defect configurations such as vacancy atom or divacancy configurations.

b) The contribution may be indirect with the lattice defects affecting the annealing kinetics of the anisotropy but not its magnitude.

The presence of lattice defects may be manifest by a combination of a) and b) above.

a. The Direct Contribution from Lattice Defects

The present observations of the anisotropy present in unconstrained nickel-iron films, in the as deposited state, was adequately described by a two component model, constraint and the mechanism operative in bulk alloys, and did not require, or allow, the presence of a third mechanism. In addition, the results of isochronal magnetic annealing of as-deposited films, Figure 26, did not show any initial decrease in anisotropy even though recovery and recrystallization were occurring and the density of defect was decreasing.

Further support is offered by the present observations of the reversible nature of the induced anisotropy following recrystallization. These observations lead to the obvious conclusion that oriented defect complexes do not contribute significantly to the anisotropy present in as-deposited films. This conclusion is in agreement with that reached by Iwata and Hagedorn \(^{37}\) based on their observations of film behavior following easy axis stabilization annealing, and on the
reports of Luborsky\textsuperscript{39} describing the independence of $H_k$ on impurity sulfur content.

There is, however, one set of results which tend to disagree, or at least modify, this conclusion. Fujii \textit{et al.}\textsuperscript{47} observed the presence of a mechanism which contributed 25\% of the anisotropy to as-deposited 81.5\% nickel films and had an activation energy of 1.1 eV. This mechanism was not a strong function of composition, nor of deposition temperature, between room temperature and 300°C. When the deposition rate was increased from 250 Å/minute to 1000 Å/minute, at a constant pressure of $10^{-5}$ Torr, this component vanished. They suggested that this contribution resulted from the presence of oriented impurity atom complexes trapped during film formation; specifically iron-vacancy or iron-foreign atom pairs. This model is not consistent with the lack of a composition dependence found by Fujii \textit{et al.}\textsuperscript{47} This mechanism was not present in our films since they were produced at $10^{-7}$ Torr and 1000 Å/second. Carson\textsuperscript{51}, however, noted significant changes, and reduced reproducibility, in films produced under conditions approaching the slower rate used by Fujii \textit{et al.}. Paul and Hanson\textsuperscript{10} have observed an increase in $K_u$, similar in magnitude to that resulting from the 1.1 eV. process, for films produced in high oxygen atmosphere. Although Paul and Hanson\textsuperscript{10} used a higher deposition rate, 3000 Å/minute, the ratio of the rate to deposition pressure was comparable to that
used by Fujii et al.\textsuperscript{47} to produce films exhibiting the 1.1 eV process. It seems likely that this process has the same origin as that observed by Paul and Hanson, which appeared when films were produced in a high partial pressure of oxygen.

Carson and Rudee\textsuperscript{50} have produced films under conditions which yield properties equivalent to those observed by Paul and Hanson. Combined bright and dark field transmission electron microscopy reveals that these films contain networks of thin amorphous inclusions, most likely oxide, along the grain boundaries. It thus seems likely that the 1.1 eV process observed by Fujii et al. is related to the formation of these oxide inclusions.

In summary, it appears that oriented configurations of lattice defects do not contribute to the anisotropy as along as films are formed under conditions in which the ratio of deposition pressure to rate does not allow significant oxygen entrapment.

b. The Indirect Contribution from Lattice Defects

Iwata and Hagedorn\textsuperscript{37} and Roth\textsuperscript{38} have discussed the indirect contribution to the anisotropy which results from an enhancement of the atomic mobility by the presence of an excess concentration of lattice defects. The former have observed that the relaxation time for magnetic annealing increases as a function of cumulative annealing time; an
observation consistent with earlier reports.\textsuperscript{44,45} They noted that this increase in the relaxation time took the form of a smooth curve upon which was superimposed a much more rapid increase. The amount of the superimposed change was a function of annealing time in a given configuration, i.e., easy axis or hard axis alignments. The rapid change in relaxation time was attributed to the presence of high diffusivity paths such as grain boundaries or dislocations; while the overall increase with annealing time was attributed to the annealing out of an excess concentration of vacancies. This change in vacancy concentration, and the resulting change in relaxation time, were treated in more detail, and the following relationship was derived:\textsuperscript{37}

\[
v(t^*) = 8n(t^*)v_0 \exp\left(-\frac{E_m}{kT}\right)
\]

where 

- $v(t^*)$ is the relaxation frequency, $\frac{1}{\tau(t^*)}$ as a function of $t^*$, the cumulative annealing time,
- $n(t^*)$ is the vacancy concentration as a function of cumulative annealing time,
- $v_0$ is the Debye frequency, and
- $E_m$ is the activation energy for vacancy motion.

This relationship is similar to that which would be predicted from elementary diffusion theory except for the factor of 8, arrived at by consideration of the lattice geometry of the reorientation of iron atom pairs. This relationship
will prove to be useful for a discussion of the effect of an excess vacancy concentration on atomic mobility.

Ferro et. al.\textsuperscript{92} have reported on the effect of a greater than equilibrium concentration of vacancies, induced by quenching from 1350°C, on magnetic annealing in bulk alloys. They reported an activation energy of 2.4 eV for non-quenched samples and 0.8 eV for quenched alloys. The vacancy concentrations may be calculated as a function of annealing temperature for these results with the aid of the relationship derived by Iwata and Hagedorn.\textsuperscript{37} These calculations are summarized in Figure 29, as is the thermal equilibrium vacancy concentration. Values for the energy of formation and motion of vacancies used were those for pure nickel\textsuperscript{93}, \(E_f = 1.35\) eV and \(E_m = 1.46\) eV respectively. Similar calculations may be made from the results of Kneer and Zinn\textsuperscript{44,45}, and are shown on the same figure. These calculations show that the model of Iwata and Hagedorn does qualitatively explain the variations in relaxation time which have been observed for magnetic annealing of the anisotropy in thin films, and would seem to indicate that even films annealed for two hours at 250°C possess greater than the equilibrium concentration of vacancies. A calculation making use of the present findings almost duplicates that of the bulk alloys which were not quenched. The only unsatisfying aspect of these calculations is the lack of agreement between the unquenched bulk alloy and the calculated thermal equilibrium
TEMPERATURE (°C)

VACANCY CONCENTRATION AS A FUNCTION OF TEMPERATURE

EQUILIBRIUM VACANCY CONCENTRATION

○ Bulk Alloy (Quenched)
□ Bulk Alloy (Ferro et al)
△ Thin Film (As Deposited)
▽ Thin Film (Pre-Annealed 2hrs. 350°C) (Kneer & Zinn)
X Thin Film (Present Data)

\[ \frac{1}{T} \left( \frac{10^3}{°K} \right) \]

FIGURE 29
concentrations of vacancies. Intuitively one would expect these alloys to possess the equilibrium vacancy concentrations. This discrepancy may be due in part to the use of values for $E_f$ and $E_m$ for pure nickel, rather than the values for the alloys. Bulk diffusion experiments predict an activation energy for diffusion of nickel in permalloy of 2.3 eV, but 2.8 - 2.9 eV for pure nickel, almost a 25% difference. A 25% adjustment in $E_f$ and $E_m$ would bring the calculated thermal equilibrium values into agreement with those values calculated from experiment.

Roth\textsuperscript{38} has proposed a somewhat different model to describe the effects of lattice defects on the kinetics of the anisotropy in nickel-iron thin films. He considers two cases:

1) For the special case of annealing which does not result in grain growth he describes a model based on the high atomic mobility existing in the vicinity of grain boundaries and grain surfaces. This contribution may be important in polycrystalline thin films because of the small grain size ~100 Å, hence large ratio of grain surface to grain volume. In bulk alloys the grain diameter is generally much larger thus the effects of grain boundaries on diffusion is not pronounced.

2) In those cases where grain growth occurs atomic mobility is enhanced by the vacancy concentration which follows the moving grain boundaries. During
recrystallization large changes in the anisotropy may occur as most of the film is swept by moving boundaries. Roth maintains that irreversible changes in anisotropy which occur on annealing above the deposition temperature can be explained by the later model.

Qualitatively the enhancement of atomic diffusion by moving grain boundaries is acceptable, but the complex structural changes which occur make it hard to focus on this one mechanism alone. In addition, its effect on the so-called irreversible changes in anisotropy is inconsistent with the present observations of a two component model and the apparent reversibility of the anisotropy following recrystallization.

III. The Mean Crystallite Size and Structure of Thin Films Which Have Been Recrystallized

A. Experimental Results

Transmission electron microscopy has been used to determine the average grain size, and the distribution of the grain size about the average in films which have been magnetically annealed. In a thin film in the as-deposited state, substrate temperature 240°C, the average grain size was found to be about 100 Å, Figure 30. In films 1100 Å thick which had been recrystallized by a 60 minute annealing treatment at 500°C, the average grain diameter was found to be
FIGURE 30
GRAIN STRUCTURE IN AN AS-DEPOSITED THIN FILM, SUBSTRATE TEMPERATURE 240°C, THICKNESS 1100 Å
FIGURE 31

TYPICAL MICROSTRUCTURE IN A FILM RECRYSTALLIZED BY
ANNEALING FOR 60 MINUTES AT 512°C
FIGURE 32

TYPICAL MICROSTRUCTURE FOLLOWING A ONE HOUR ANNEAL

AT 512 °C and 103 HOURS AT 414 °C, FILM THICKNESS 1100Å
MEAN GRAIN DIAMETER AS A FUNCTION OF ANNEALING TIME FOLLOWING RECRYSTALLIZATION

○ 414°C  □ 250°C

MEAN GRAIN DIAMETER (Å)

ANNEALING TIME (hours)

FIGURE 33
PERCENT CUMULATIVE DISTRIBUTION AS A FUNCTION OF GRAIN DIAMETER (ANNEALED 103 hours 414°C)

METER GRAIN DIAMETER 1300 Å

FIGURE 34
approximately 1000 Å. The average grain diameter did not vary from this value even after 100 hours of annealing at 414°C, as seen in Figures 31 and 32. The average grain size as a function of annealing time at 414°C and 250°C is shown in Figure 33.

In addition to determining the average grain diameter, the distribution about the mean was also determined. This distribution was found to be log normal, that is the logarithm of the grain size obeyed a normal distribution. A plot of the cumulative distribution of grain sizes as a function of the logarithm of grain size on probability paper will therefore be a straight line. From a plot of this type one may easily determine the mean grain diameter and the standard deviation characteristic of the grain size distribution. Figure 34 shows such a plot. If the distribution had been normal a plot of the cumulative distribution as a function of grain diameter would have been a straight line on probability paper.

In almost all cases there was an upward deviation away from the straight line characteristic of the log normal type distribution for the largest 10 - 20 percent of the crystallites, i.e., there are more larger grains than one might expect if the log normal distribution were strictly obeyed over the complete range of grain diameters.

Figure 35 shows a high magnification view of the grain structure in a film recrystallized and then subjected to
FIGURE 35

TYPICAL MICROSTRUCTURE, AT HIGH MAGNIFICATION, OF A FILM
RECRYSTALLIZED BY ANNEALING FOR 60 MINUTES AT 512 °C AND
43 HOURS AT 414 °C.
annealing for 42.8 hours at 414°C. The grain structure is characteristic of cold worked metals which have been recrystallized.

B. Discussion

Transmission electron microscopy performed on as-deposited thin films has shown that its structure is much like that of cold worked metals. The presence of highly defected structure, a high density of dislocations and stacking faults, provides a driving force for recovery and recrystallization. Figure 31 shows the grain structure following a 60 minute anneal at a temperature near 500°C. The grain structure is characteristic of cold worked metals which have been recrystallized. This observation is consistent with that of Carson51 who observed complete recrystallization following a 30 minute anneal at a temperature of 450°C. The severity of the annealing pretreatment has also induced grain growth. Following pretreatment the average grain size is comparable to the film thickness. Subsequent heat treatment during the course of the isothermal magnetic anneals, does not result in significant changes in this average grain size. This observation is not unexpected, as the driving force for grain growth is a reduction in the free energy associated with the grain boundary area. Once the grains have grown to a size comparable to the film thickness this driving force is reduced. In addition, there is a pinning which
occurs at grain boundary-surface intersections; hence, the rate of grain growth diminishes once the grain size becomes comparable to the film thickness. Similar observations have been reported during the course of investigations of grain growth in thin sheets and fine wires.

The deviations from log normal behavior which have been observed for large grain size may be a form of secondary recrystallization, also called abnormal grain growth. Secondary recrystallization has been observed to occur in thin sheets when several grains are able to break away from their metastable trapped positions and grow at the expense of still trapped neighboring grains.\(^{94}\)

A stable grain structure characteristic of recrystallized metals has been produced by a one hour anneal at 500°C. The grain size does not appreciably increase during subsequent annealing at lower temperatures.

IV. The Origin of the Magnetization Dispersion in Recrystallized Thin Films of Nickel-Iron Alloys

A. Experimental Results

1. The Dependence of the Magnetization Dispersion on the Anisotropy Field

The dependence of magnetization dispersion, determined by a macroscopic measurement technique, on the anisotropy field has been observed for a large number of films. There was an obvious trend noted. This trend indicated that the magnetization dispersion, \(\alpha_{50}\), varied inversely as some
function of $H_k$, the anisotropy field. Least square fits were made of the values of $\log \alpha_{50}$ as a function of the log of the magnitude of $H_k$ in an effort to find this relationship. The observations of $H_k$ and $\alpha_{50}$ were those derived from the isothermal magnetic annealing of recrystallized permalloy thin films discussed earlier. All the data for a given composition was combined for this calculation, including the several temperatures, and easy and hard axis alignments. These calculations showed that the relationship between $\alpha_{50}$ and $|H_k|$ may be expressed in the following manner

$$\alpha_{50} = C|H_k|^{-b}$$

Within 90% confidence limits the slope, $b$, is independent of composition and equal to $2.0 \pm 0.5$. Results for compositions of 61 weight percent nickel and 72 weight percent nickel are shown in Figures 36 and 37. The results for all compositions are summarized in Figure 38, which shows $b$ as a function of composition. The brackets indicate 90% confidence limits, and the straight line drawn is the mean of the data points, all of which fall within two standard deviations from the mean. As many as 90 observations representing 6 films were combined to calculate these least square slopes. Figure 39 shows the composition dependence of $C$, the constant of proportionality.

The reversible nature of the dispersion and the anisotropy field was verified by hard axis magnetic annealing.
MAGNETIZATION DISPERSION AS A FUNCTION OF ANISOTROPY FIELD.

△ FILM 2-26-65-2 61%
▲ FILM 2-28-69-4 Nickel

SLOPE = -1.753

AS DEPOSITED

FIGURE 36
Magnetization dispersion as a function of anisotropy field

Slope = -2.101

As deposited

Film 2-21-69-2, 72%
Film 2-21-69-4, Nickel

Figure 37
A summary of the least square slopes calculated for seven compositions from plots of the logarithm of $\alpha_{50}$ vs the logarithm of $H_K$. 

FIGURE 38
FIGURE 39

PROPORTIONALITY CONSTANT, C

FILM COMPOSITION (WEIGHT PERCENT NICKEL)
The state of a given film was changed from one of high \( |H_k| \) and low \( \alpha_{50} \) to one of low \( |H_k| \) and high \( \alpha_{50} \) reversibly along the same straight line on a plot of log \( \alpha_{50} \) versus long \( |H_k| \), an example of this typical behavior is shown in Figure 40. This behavior was observed in all cases of hard axis magnetic annealing, through the whole range of compositions, and for those instances where the easy and hard axis were exchanged by prolonged hard axis magnetic annealing. The changes in \( \alpha_{50} \) and \( H_k \) which accompanied easy axis isothermal magnetic annealing also followed straight lines on a log-log plot, Figure 41.

In several cases, plots of log \( \alpha_{50} \) versus log \( |H_k| \) for different films annealed at different temperatures fell on approximately parallel lines, indicating some variation in the proper proportionality constant, C.

2. **The Magnetization Dispersion as a Function of Annealing Time**

The dependence of the magnetization dispersion on time has been observed during the course of isothermal magnetic annealing. Figures 42 and 43 show plots of the magnetization dispersion, in degrees, as a function of annealing time. The magnetization dispersion is seen to follow a smooth
MAGNETIZATION DISPERSION AS A FUNCTION OF ANISOTROPY FIELD

FILM 4-30-69-2 61% Ni
HARD AXIS ANNEAL 383°C

△ Hk DECREASING INITIAL EASY DIRECTION
○ Hk INCREASING NEW EASY DIRECTION

SLOPE AS DEPOSITED -1.844

MAGNETIZATION DISPERSION $\alpha_{90}$ (degrees)

ANISOTROPY FIELD $H_k$ (oe.)

FIGURE 40
Magnetization dispersion as a function of anisotropy field. EASY AXIS ANNEAL 383°C

Value following recrystallization

Film 5-4-69-1 51% Nickel
Film 5-15-69-1 82% Nickel

+ as deposited

Slope = -2.124

Slope = -2.427

As deposited

Figure 41
Magnetization dispersion as a function of time for easy axis isothermal magnetic annealing 383°C

\[ \alpha_{50} \text{ (degrees)} \]

\[ \tau = 3.06 \times 10^5 \text{ seconds} \]

\[ \tau = 5.29 \times 10^5 \text{ seconds} \]

FIGURE 42
MAGNETIZATION DISPERSION AS A FUNCTION OF TIME FOR EASY AXIS ISOTHERMAL MAGNETIC ANNEALING 383°C

MAGNETIZATION DISPERSION $\alpha_{50}$ (degrees)

TIME (hours)

FIGURE 43
curve as it changes with time. The results of the previous section indicate that the magnetization dispersion is not independent of the anisotropy field, thus a straightforward analysis, as carried out for the anisotropy field, cannot be applied in this case. In place of that analysis the following approach has been adopted: The result of the previous section has shown that

\[ a_{50} = C|H_k|^{-b} \quad , \quad b = 2.0 \]  

Combining this with the kinetic equation which was found to describe changes in the anisotropy field,

\[ H_k(t) = H_k(\infty) + \{H_k(0) - H_k(\infty)\} \exp(-t/\tau) \quad , \]

results in

\[ a_{50}^{-1/b}(t) = a_{50}^{-1/b}(\infty) + \{a_{50}^{-1/b}(0) - a_{50}^{-1/b}(\infty)\} \exp(-t/\tau) \quad . \]

This may be rearranged, giving

\[ \log \left[ \frac{a_{50}^{-1/b}(t) - a_{50}^{-1/b}(\infty)}{a_{50}^{-1/b}(0) - a_{50}^{-1/b}(\infty)} \right] = \log a_{50}^*(t) = -t/\tau \quad . \]

As was found previously, this approach will be consistent if a plot of \( \log a_{50}^* \) as a function of time will pass through the origin and be a straight line with slope \(-\frac{1}{\tau}\). Figure 44 is a plot of \( \log a_{50}^* \) as a function of time, and it does obey those conditions described above. This relationship was fitted to the experimental observations shown in Figures 42
\[ \alpha_{50} \text{ AS A FUNCTION OF TIME} \]

77\% NICKEL
383\,°C HARD AXIS
\( \tau = 9.68 \times 10^5 \) SECONDS

61\% NICKEL
383\,°C HARD AXIS
\( \tau = 5.16 \times 10^5 \) SECONDS

77\% NICKEL
383\,°C EASY AXIS
\( \tau = 5.75 \times 10^5 \) SECONDS

\[ \alpha_{50} = \frac{\alpha_{50}(0) - \alpha_{50}(\infty)}{\alpha_{50}(0) - \alpha_{50}(\infty)} \]

TIME (10^4 seconds)

FIGURE 44
and 43, and the smooth curves calculated applying the same techniques used to analyze the $H_K$ isotherms. These curves show that the present analysis does describe the annealing time dependence of the magnetization dispersion. The values of relaxation time, $\tau$, which were calculated from this analysis were consistent with those previously calculated to describe the annealing kinetics of the anisotropy field.

3. **Measurements with the Faraday Effect Loop Checker**

Preliminary observations of the magnetization dispersion in small regions in a larger film have been made with the Faraday effect loop checker. These results have shown that the dispersion measured in this manner was less than that measured by the macroscopic technique. The expected sensitivity of the microscopic dispersion to the size of the illuminated region was not observed. This latter result is surprising, particularly for films possessing macroscopic dispersions of several degrees or more. This problem is the subject of continuing study. Figure 45 shows the results for three measurements on the same film; each measurement was performed with a different spot diameter as indicated. In all cases the microscopic measurement detected dispersions less than that indicated by the macroscopic loop checker technique.
FIGURE 45

NORMALIZED FLUX CHANGE AS A FUNCTION OF ANGULAR POSITION.

FARADAY EFFECT LOOP CHECKER DATA

MACROSCOPIC MAGNETIZATION DISPERSION = 1.16

<table>
<thead>
<tr>
<th>SPOT DIAMETER</th>
<th>2α</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 cm</td>
<td>0.30</td>
</tr>
<tr>
<td>0.2 cm</td>
<td>0.50</td>
</tr>
<tr>
<td>0.5 cm</td>
<td>0.35</td>
</tr>
</tbody>
</table>
B. Discussion

The results which have been presented demonstrate that the macroscopically measured magnetization dispersion and the anisotropy field are related in the following manner:

\[ \alpha_{50} = C |H_k|^b \]

where \( b \) is equal to \(-2.0 \pm 0.5\), and the proportionality constant, \( C \), is a function of composition and is given in Figure 39. These results were found to be consistent for changes in \( H_k \) and \( \alpha_{50} \) occurring over a range of values spanning more than an order of magnitude. Although these measurements were extended to include films possessing values of dispersion in excess of 10° - 20°, where measurements are less reliable, the observed values of \( \alpha_{50} \) and \( H_k \) fell on the same line extrapolated from the low dispersion region. In addition, it has been demonstrated that the annealing time behavior of the magnetization dispersion is consistent with the dependence on the anisotropy field, even in those cases when high values of dispersion were observed. The number of measurements and their reproducibility support the significance of the present observations.

The only theory which is available for a comparison with the present results was derived by Hoffmann\(^{59}\) and is an extension of ripple theory. This theory predicts:

\[ \alpha_{50} = \frac{3}{8\pi A} S^2, \quad S = \left( \frac{K_s D}{\sqrt{2} \sqrt{n}} \right), \]
where $S$, the structure constant, contains the structure dependent terms. Exactly how, and for what values of dispersion this theory may apply to the present work is relevant and will now be discussed.

The present study of the annealing behavior of recrystallized thin films has provided a unique set of conditions under which to investigate the validity of Hoffmann's prediction. The initial high temperature preanneal established a standard metallurgical state in which the various metallurgical parameters, grain size, defect density, and local strains remained constant during subsequent annealing at lower temperatures. Thus the structure sensitive properties in Hoffmann's equation, $K_s$ and $D$, can be considered to be constant. Measurement of the average crystallite size and the observations of the crystallite structure, reported above, have verified this condition.

For the conditions of this investigation, it is clear that the observed dependence of magnetization dispersion on $H_k^{-2.0}$ is inconsistent with the predictions of theory, i.e., $\alpha_{50} = H_k^{-1.0}$. This conclusion is not startling when viewed in the light of the recent report by Fujii et al. They found Hoffmann's predictions correct, but only when $\alpha_{50}$ was measured for small regions on a much larger film, intrinsic dispersion. Macroscopic measurements, reflecting the contribution from both extrinsic and intrinsic magnetization dispersion, were always found to be high with respect to
microscopic measurements, and not to agree with Hoffmann's prediction. As the present observations are of the macroscopic type there is, therefore, no reason to expect agreement with theory.

The earlier results of the group from Nagoya University indicated that most of the macroscopic dispersion, in high dispersion films would originate in the extrinsic component. The present work is in part a preliminary effort to define further this extrinsic component. The results to this point are not conclusive and offer only qualitative support to the earlier observations of the Japanese group. The reports by this group are supported by the annealing study performed by Carson.\(^{51}\) He showed that a 30 minute anneal near 285°C was sufficient to cause the macroscopic dispersion, in as-deposited films, to decrease and assume values equal in magnitude to those observed for microscopic dispersion by Uchiyama et al.\(^{73,74}\) The change was the greatest in magnetostrictive films, and was consistent with the results of Uchiyama et al.\(^{73,74}\) This agreement between macroscopic and microscopic measurements indicated that the short recovery anneal removed the extrinsic contribution. These observations supported by those of the Nagoya group lead to the conclusion that the present study has been performed on films in which the extrinsic component of the dispersion is dominant.

Most observations in the literature are concentrated
on narrow ranges of dispersions in the vicinity of a few degrees. There is, however, one report which discusses values of dispersion as large as $14^\circ$. This is the report by Landler.\textsuperscript{65} He produced films with various values of anisotropy field and magnetization dispersion by deposition in the presence of an elliptically rotating magnetic field. The values of anisotropy field and macroscopic magnetization dispersion possessed by films produced in this manner would, therefore, be independent of film structure for films produced at a given substrate temperature. Landler's result is shown in Figure 46. The curves drawn were calculated from the relationship

$$\alpha_{50} = C |H_k|^{-2.0} \quad \text{for} \quad C = 5, 11$$

These curves do describe the observed dependence of $\alpha_{50}$ on $H_k$ over this extended range of magnetization dispersion. A more exact analysis of Landler's data may be described by

$$\alpha_{50} = 9.5 |H_k|^{-1.94}$$

which is in good agreement with the present observations.

The present results thus seem to describe a special case of magnetization dispersion not adequately described by existing models. This problem is the subject of continuing study.
FIGURE 46

MAGNETIZATION DISPERSION AS A FUNCTION OF ANISOTROPY FIELD (AFTER LANDLER 65)

\[ \alpha_{50} = 5 H_k^{-2} \]

\[ \alpha_{50} = 11 H_k^{-2} \]

MAGNETIZATION DISPERSION, \( \alpha_{50} \)

\[ \text{Substrate temperature} \]
- 25 °C
- 100 °C
- 200 °C
- 300 °C

ANISOTROPY FIELD, \( H_k \) (oe)
CHAPTER FIVE: CONCLUSIONS

I. The induced anisotropy present in as-deposited nickel-iron thin films prepared by vapor deposition may be explained by the two component model, constraint plus directional ordering. The constraint contribution is best described by the model used by Robinson; while the anisotropy due to the directional ordering mechanism is equal in magnitude to the limiting values obtainable by magnetic field cooling of bulk alloys.

II. The magnetic annealing time and temperature dependencies of the major component of the induced anisotropy in recrystallized thin films of nickel-iron alloys is identical to that observed for bulk alloys. This behavior may be described by a first order process in which the relaxation obeys an Arrhenius relationship,

$$\tau = \tau_0 \exp(Q/kT)$$

with $Q = 2.41$ eV/atom and $\tau_0 = 1.2 \times 10^{-12}$. Oriented configurations of non-equilibrium defects do not contribute to the anisotropy directly; but do contribute indirectly by enhancing atomic mobilities.

III. A standard metallurgical state may be induced in vapor deposited nickel-iron thin films by a one hour anneal at 500°C. This treatment results in a recrystallized film with a mean grain diameter comparable to the film
thickness. The distribution of grain diameters about this mean, in recrystallized thin films, obeys a log normal distribution. Subsequent annealing at temperatures below 500°C, the temperature of the recrystallization anneal, does not result in significant grain growth.

IV. Both anisotropy field and macroscopically measured magnetization dispersion change reversibly during the course of magnetic annealing of recrystallized thin films. This reversibility obeys the following relation

\[ a_{50} = C|H_k|^{-b} \]

where b is equal to 2.0 and is independent of composition. This observation is not described by existing theories, but may be explained by recent observations of the existence of skew or extrinsic magnetization dispersion.
CHAPTER SIX: SUGGESTIONS FOR FUTURE RESEARCH

The present observations of the empirical relationship between the anisotropy field and the macroscopically measured magnetization dispersion has opened up an area in which there are many unanswered questions. A more complete understanding of the basis for this observation must be achieved, as well as further defining its realm of validity. The primary avenue for this investigation would seem to be a continuation of the present study making use of the Faraday effect loop checker. In addition, there are still many gaps between ripple theory and macroscopic observations of magnetization dispersion. A complete study, combining macroscopic and magneto-optic observations of the magnetization dispersion, with direct observation of ripple by Lorentz electron microscopy could lead to tremendous insight into this problem.

The electronics industry is presently very much interested in the properties of thin metal layers for use as conductors between elements in micro-electronic semiconductor devices. Problems such as the enhancement of diffusion in the presence of an electric field, electro-migration, have led to increased interest in the relation between structure and electrical properties in metal thin films. An extension of the present work on recrystallized nickel-iron thin films to other alloy systems, film thicknesses, and annealing treatments might prove valuable.
CHAPTER SEVEN: ACKNOWLEDGEMENTS

Many people have contributed to this research. The author is indebted to his thesis advisor, Dr. M. L. Rudee, for initiating interest in this work and for providing guidance during the course of its completion, and to Dr. K. R. Carson who developed the techniques of film fabrication and designed the necessary apparatus. Thanks also go to Dr. R. B. McLellan and Dr. H. C. Bourne for serving on this dissertation committee, and for their helpful suggestions.

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CHAPTER EIGHT: REFERENCES


3. This topic is discussed in several texts and review articles, e.g., Prutton, M., Thin Ferromagnetic Films (Butterworth, London, 1964) p. 54.


5. A complete review has been given by Grundy, P. J. and Trebble, R. S., Adv. in Phys., 17, 153 (1968).


