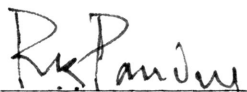# THE EFFECTS OF THERMAL AND MAGNETIC FIELD ANNEALING

ON FERRITE MATERIALS

by

Allen M. Dewey

Electrical Engineering

Texas A&M University
College Station, Texas 77843

Submitted in Partial Fulfillment of the Requirements

of the University Undergraduate Fellows Program

1979-1980

Approved by:

_____
Dr. R.K. Pandey

April 1980

ABSTRACT

The thesis investigates the effects of the annealing process on the magnetic properties of ferrimagnetic materials. Emphasis is placed on how the magnetic properties might be controlled, through the annealing process, in order to meet the requirements of a particular technical application. The thesis covers the general theory and terminology associated with magnetism in materials and then investigates ferrimagnetism in more detail. Next, some common technical applications of ferrites are outlined and the theory of thermal and magnetic annealing is explained. The thesis concludes with a discussion of the experiments conducted during the project. The objective of the experiments was to see if a soft ferrite could be hardened by thermal annealing, in order to make a better permanent magnet without substantially deteriorating the high permeability or low hysteresis loss of the sample. The results of the experiments revealed that by carefully choosing the cooling rate and monitoring the effects of ambient gas in introducing impurities, a 32% increase in coercive field can be realized over an 18% increase in hysteresis loss, 2.9% decrease in permeability, and a 20% decrease in saturation magnetization.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

I. INTRODUCTION

This thesis is the culmination of an independent research project that was conducted to study ferrimagnetism and the annealing process of ferrimagnetic materials. Ferrimagnetism is a type of magnetism due to the presence of several atoms of unequal magnetism coupled antiferromagnetically in a crystal lattice. The annealing process is unusally the last step in the manufacturing process of the ferrimagnetic material that tailors the magnetic properties of the speciem to the particular desired technical application. The objectives of the project were the following:

1) to gain a sound understanding of the basic principles of magnetism and in particular of ferrimagnetism,

2) to understand the crystal structure of some of the common ferrimagnetic materials and its relationship to the ferrimagnetic phenomenon,

3) to apply the knowledge gained in a) and b) to the studying of the annealing process,

4) to become familiar with the experimental procedures used in the annealing process, and

5) to be able to evaluate the experimental results and to determine the technological implications.

The general method of approach taken was that the majority of the theoretical research was conducted during the Fall semester of 1979. Then, the experimental annealing and the analysis of the results were conducted the following Spring semester of 1980. The project was administered as part of the 1979 - 1980 University Undergraduate Fellows Program at Texas A&M University. The research was sponsored by Dr. Pandey of the Electrical

1

Engineering Department's Institute for Solid State Electronics, at Texas A&M University. Due to the vast amount of information available, in varying degrees of detail, concerning ferrimagnetism, the author has elected to present in the following sections what is hopefully a clear, concise, and informative explanation of the magnetic phenomenon.

II. BASIC PRINCIPLES OF MAGNETISM

There are basically two ways that have been used in the past to gener-
ate and explain the governing laws of magnetism. The first method, which
is more commonly found in texts, follows the historical approach to mag-
netism and starts by defining $\bar{B}$ (magnetic flux vector) by the force equation
of a charged particle moving in a magnetic field.

$$\bar{F} = q\bar{v} \times \bar{B} \tag{1}$$

where,

$\bar{F}$ - force

q - charge of the particle

$\bar{v}$ - velocity

$\bar{B}$ - magnetic flux vector

All laws of magnetism can be derived using the $\bar{B}$ vector and then the $\bar{H}$
(magnetic field vector) is derived from $\bar{B}$ [1]. Though this approach has
the advantage of acquainting the reader with the historical significance
of many of the parameters used in magnetics, the author believes that it is
not the simplest approach to take when concerned about specifically the
magnetics of materials. The second method, which is the one that this
thesis will use, starts with the magnetic field vector $\bar{H}$ and develops the
necessary equations Surely, both methods are equally valid and in some
instances to the more knowledgable reader, trivially different. It should
always be remembered that a theory is just a model, and there is no rule
against using several models to explain the same physical phenomenon as
long as the models are not contradicting. Another source of confusion in
explaining magnetics is the use of different dimensional systems. Al-

though the majority of textbooks use the MKS system, the majority of scientific papers on magnetism and magnetic materials still use the CGS system. This thesis will use the CGS system. A conversion table for changing from MKS to CGS units is given in Appendix A. Whenever an equation is given in CGS, the corresponding equation in the MKS system will be given below it in parentheses.

To start with, a useful concept in describing a magnet is the unit magnetic pole. It is defined in a manner similar to Coulomb's Law of electrostatic forces.

$$F = \frac{m_1 \, m_2}{r^2} \tag{2}$$

$$\left(F = \frac{m_1 \, m_2}{4\pi \, \mu_0 \, r^2} \right) \tag{3}$$

where,

    F - force

    m - magnetic pole strength

    r - distance between magnetic poles

    μ_0 - permeability of free space = $4\pi \times 10^{-7}$ henry/meter

Two unit poles (m) of like kind would repel one another in a vacuum with a force of 1 dyne when separated by one centimeter. A bar magnet may be thought of as equivalent to two opposite poles placed more or less at the extremities of the magnet. In an analogy to the electric field $\bar{E}$ being the force per unit positive charge, the magnetic field $\bar{H}$ (a more discriptive name would be the magnetizing force vector) can be defined as the force per unit magnetic pole for a north seeking pole.

Fig. 1

4
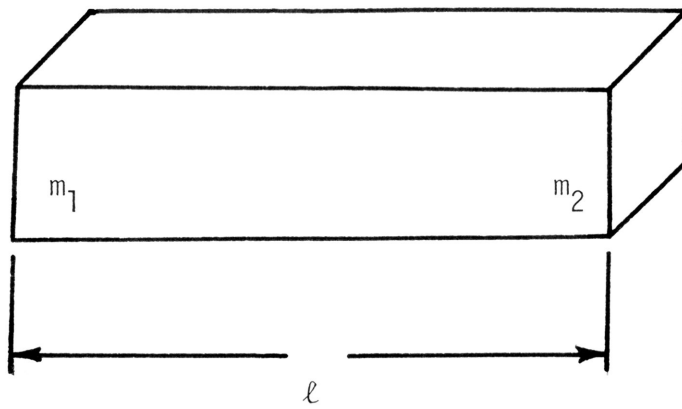
Figure 1 A Conventional Bar Magnet

$$\bar{H} \equiv \frac{\bar{F}}{m} \qquad (4)$$

where,

H - magnetic field strength

F - force

m - magnetic pole strength

The magnetic field can also be defined in terms of a current in a coil of wire. The magnetizing force at the center of a single-turn coil can be easily found from Ampere's law to be

$$H = \frac{2\pi I}{r} \qquad (5)$$

$$\left(H = \frac{I}{2r} \right) \qquad (6)$$

where,

H - magnetic field strength

I - current

r - radius of single-turn coil

Next one can define a magnetic moment,

$$M \equiv ml \qquad (7)$$

where,

M - magnetic moment

m - magnetic pole strength

l - distance between magnetic poles

which can be used to define the intensity of magnetization. The extent to

6

which a body is magnetized is measured by its magnetic moment per unit volume or intensity of magnetization (sometimes called just the magnetization).

$$I \equiv \frac{M}{v} \tag{8}$$

where,

        I - intensity of magnetization

        M - magnetic moment

        v - volume of sample

The process of magnetization can be thought of as a magnetizing force generating a magnetic field, or historically called a magnetic flux density ($\bar{B}$). Both H and I contribute to the flux.

$$B \equiv H + 4\pi I \tag{9}$$

$$(B \equiv \mu_0 H + I) \tag{10}$$

where,

        B - magnetic flux density

        H - magnetic field strength

        I - intensity of magnetization

        μ_0 - permeability of free space

Permeability can be thought of as the ratio of the magnetic flux density to the corresponding magnetic field strength.

$$\mu \equiv \frac{B}{H} \tag{11}$$

where,

        B - magnetic flux density

H - magnetic field strength

μ - permeability of the sample

The permeability need not be a constant. The factor of 4π in Equation (9) arises since a unit pole gives rise to a unit field on the surface of a sphere of unit radius encircling the pole, and this sphere has an area of 4π. Consequently, each unit pole gives rise to 4π lines of flux. The intensity of magnetization is an additional magnetizing force created in the magnetic material owing to its altered physical state, its amplitude being K times the impressed force H

$$\bar{I} = K \ \bar{H} \qquad\qquad (12)$$

where,

$\bar{I}$ - intensity of magnetization

K - susceptibility

$\bar{H}$ - magnetic field strength

The magnetization produces an extra field of its own in the material which may add to the H field already present (if K is positive) or subtract (if K is negative). K is called the susceptibility and has no meaning when a spontaneous magnetization exists within a material without the presence of an external field. Spontaneous magnetization will be discussed later.

The previous discussion did not mention anything about the actual physics involved in the magnetics of materials. Magnetism is, in its most basic form, an atomic phenomenon. In materials where electrons are not paired in opposing spin configurations, a net magnetic moment exists. According to Ampere's law, a moving current (I) encircling an area (A) produces a magnetic field at right angles to the plane of the current loop. At a distance far away, compared to the radius of the loop, the magnetic field

8

Fig. 2   is identical to that of a magnetic dipole (bar magnet). Therefore, it
should be clear that a moving electron in an atom has associated with it a
magnetic field. Actually two kinds of motion must be distinguished. One
is orbital motion, determined by the orbital quantum number ℓ, whose
angular momentum can assume $m_\ell = 2\ell + 1$ specific orientations in space
relative to some external field direction. The other is the moment associated
with the electron spin, which can have either of two opposite directions.
Recall that the quantum numbers (n, ℓ, and m_ℓ) were generated by solving
the time independent Schrödinger equation for the case of the hydrogen
atom [2]. In order to avoid any further confusion the quantum numbers are
defined below.

n - principal quantum number, determines the variation in
the wave function with respect to the radial distance.

ℓ - orbital quantum number, determines magnitude of angular
momentum $\ell = 0, 1, 2, \ldots, (n-1)$

m_ℓ - magnetic quantum number, determines orientation of angu-
lar momentum in space
$m_\ell = -\ell, -(\ell-1), \ldots-1, 0, 1, \ldots(\ell-1), \ell$

s - spin quantum number, determines the magnitude of spin
momentum
$s = 1/2$

m_s - spin magnetic quantum number, determines orientation of
spin momentum in space
$m_s = \pm 1/2$

j - total angular momentum quantum number, determines the
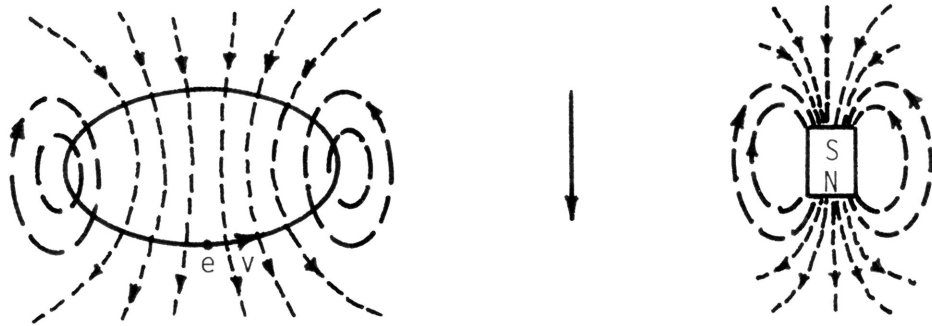magnitude of the total momentum.
$j = \ell \pm s$

9

Figure 2. Magnetic Dipoles

m_j - total magnetic quantum number, determines the orientation

of total momentum in space.

$$m_j = -j, -(j-1), \ldots -1, 0, 1, \ldots, (j-1), j$$

Since an atom consists of a number of electrons occupying various energy levels, it is necessary to know how the orbital and spin momenta of the several electrons are combined or coupled to form the resultant orbital and spin momenta of the atom as a whole. The most common type of coupling is the Russell-Saunders coupling [3] in which the several $\bar{\ell}$ vectors combine to form a resultant $\bar{L}$, and the $\bar{s}$ vectors a separate resultant $\bar{S}$. The $\bar{L}$ and $\bar{S}$ combine to form the resultant $\bar{J}$, which represents the total angular momentum of the whole electron system of the atom. Russell-Saunders coupling can be used when the atom is not heavy, e.g. transition metal ions and rare earth ions use this coupling to compute total angular momenta. So far it has been established that the electron and the atom can be represented by a tiny bar magnet of a fixed magnetic moment. The basic unit of magnetic moment on the atomic scale is the Bohr magneton. By classical means one can derive the following expression for the magnetic moment associated with the orbital motion of the electron.

$$\mu_\ell = \frac{e\hbar}{2m} \sqrt{\ell(\ell+1)} \tag{13}$$

where,

e - charge on the electron = 1.6022×10^{-19} coul

$\hbar$ - $h/2\pi$, h being Planck's constant = 6.62×10^{-34} joule-sec

m - mass of electron = 9.1095×10^{-31} kg

The quantity $(e\hbar/2m)$ consists of only universal constants and is used as a unit for magnetic moment.

11

$$\mu_B = .927 \times 10^{-20} \text{ erg} \cdot \text{gauss}^{-1} \tag{14}$$

$$(\mu_B = .927 \times 10^{-23} \text{ J weber}^{-1} \text{ meter}^{-2}) \tag{15}$$

It should be noted that in an atom the positively charged nucleus is also spinning, so that it has a magnetic moment, usually expressed in nuclear magnetons. The nuclear magneton is about a thousand times smaller than a Bohr magneton so that the nuclear contribution to the magnetizability of an atom is usually neglected.

Now that the atomic physics of magnetism has been outlined, the various types of magnetism will be discussed. The following types of magnetism have been identified:

1) diamagnetism,

2) paramagnetism,

3) metamagnetism,

4) parasitic ferromagnetism,

5) ferrimagnetism,

6) antiferromagnetism, and

7) ferromagnetism.

Diamagnetism is a weak magnetism present in all materials. It is characterized by a negative magnetic susceptibility due to the precession of electronic orbitals about an applied field direction. Paramagnetism is also a weak magnetism characterized by a positive susceptibility, due to the alignment of unpaired electrons with the applied field. In the discussion so far, the possibility of an interaction between the magnetic moments of adjacent atoms has been neglected. This is reasonable for atoms that have closed outer shells, in which case the induced diamagne-

tism is so weak that such interactions can be safely neglected. Similarly the unfilled inner 4f shells of the rare earths are sufficiently screened by outer electrons so that paramagnetism is essentially due to the magnetism of isolated atoms. When the transition metals are considered, however, the outermost shells contain unpaired electrons, and it is reasonable to expect that they can interact with similarly unpaired electrons in neighboring atoms. It has been found that there is an exchange force created by the interaction between the spinning electrons of adjacent atoms. The force acts to keep the atomic moments in a parallel or antiparallel alignment. The nature of this exchange force was first explained by hypothesizing the existence of a "molecular field"[4]. The exchange force was later explained on a quatum mechanical basis, which is beyond the scope of this thesis. However, the proposed force is on the order of 10 million oersted - greater than the strongest steady magnetic fields produced today with many megawatts of power. The aligned atomic magnetic moments form domains. Domain formation is based on the principle that at low temperatures all systems tend toward a state possessing minimum energy. The formation is a result of a compromise that minimizes the work needed to rotate the atomic moments against the exchange force (which acts to keep adjacent moments parallel) as well as the work needed to rotate the moments away form the easy axis of the magnetocrystalline field. Magnetocrystalline fields act to align the atomic moments in a crystalline solid in certain "easy" directions with respect to the crystal lattice. The following figure shows the minimization of energy process between the magnetostatic energy and the domain wall energy. The domain walls are regions where there is a gradual transition in the direction of the atomic moments from one domain to the next domain and are roughly 300 atomic planes thick [6]. Domains can be ob-
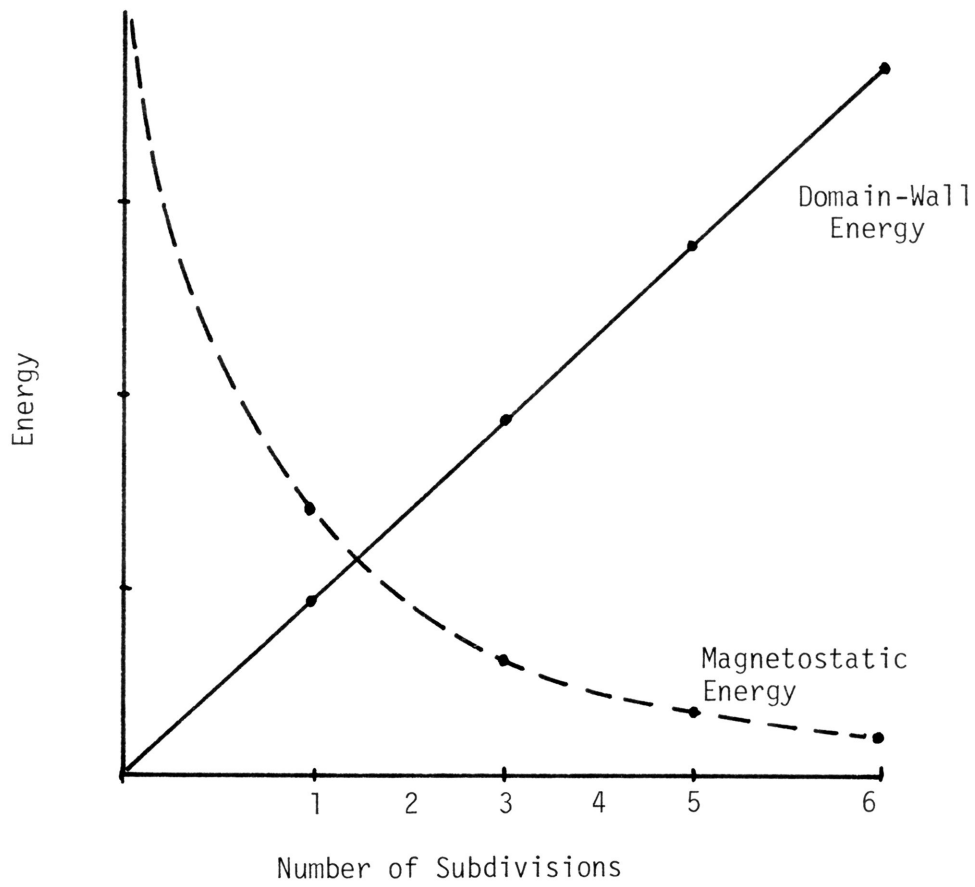
Fig. 3

13

Figure 3   Energy Minimization Reference [5]

14

served and are usually between 0.1 and 0.01 centimeters across. The magnetic strengths of the material is simply the vector sum of the magnetic strengths of its domain. At this point it might be instructive to review

g. 4 the development of this chapter. As shown in Figure 4, first the magnetic moment of the electron was characterized, then the atom's magnetic moment was generated through Russell-Saunders coupling, and now the domain has been generated which also has associated with it a magnetic moment. In the absense of an external magnetic field, the domains are randomly oriented within the material. The magnetic moments of the domains vectorially sum to zero and the material exhibits no net magnetism. Upon application of an external magnetizing force, the domains will align to aid the force. The added intensity of magnetization will be the vector sum of the saturation magnetization (I_s) of each domain. The saturation magnetization is found to decrease with increasing temperature until the Curie temperature is reached, at which point thermal vibration of the atoms exceeds the exchange force and the domains disappear. The material is paramagnetic above the Curie point. As mentioned earlier, the magnetizing force and magnetization (I_s) add to the flux density B. A typical

g. 5 plot of B versus H is given in Figure 5. The hysteresis effect is in part due to inclusions and crystal lattice defects that impede the movement of the domains (more will be said about this subject in the chapter about annealing). The area enclosed by the loop in Figure 5 is the power loss per unit volume per cycle. This chapter will close by finishing the discussion of the different types of magnetism previously listed. Ferromagnetism is characterized by a parallel alignment of the atoms and antiferromagnetism has an antiparallel exchange coupling. Metamagnetism is the name to the phenomenon which is interpreted as a transition from anti-

Bar Magnet

S

N

Minimization of
Total Energy
of Bar Magnet

Domain

S

N

$\begin{pmatrix} \text{Ferro-} \\ \text{Ferri-} \\ \text{Antiferro-} \end{pmatrix}$

Exchange Force

Atom

S

N

(Spin Angular)

Russel Saunders
Coupling

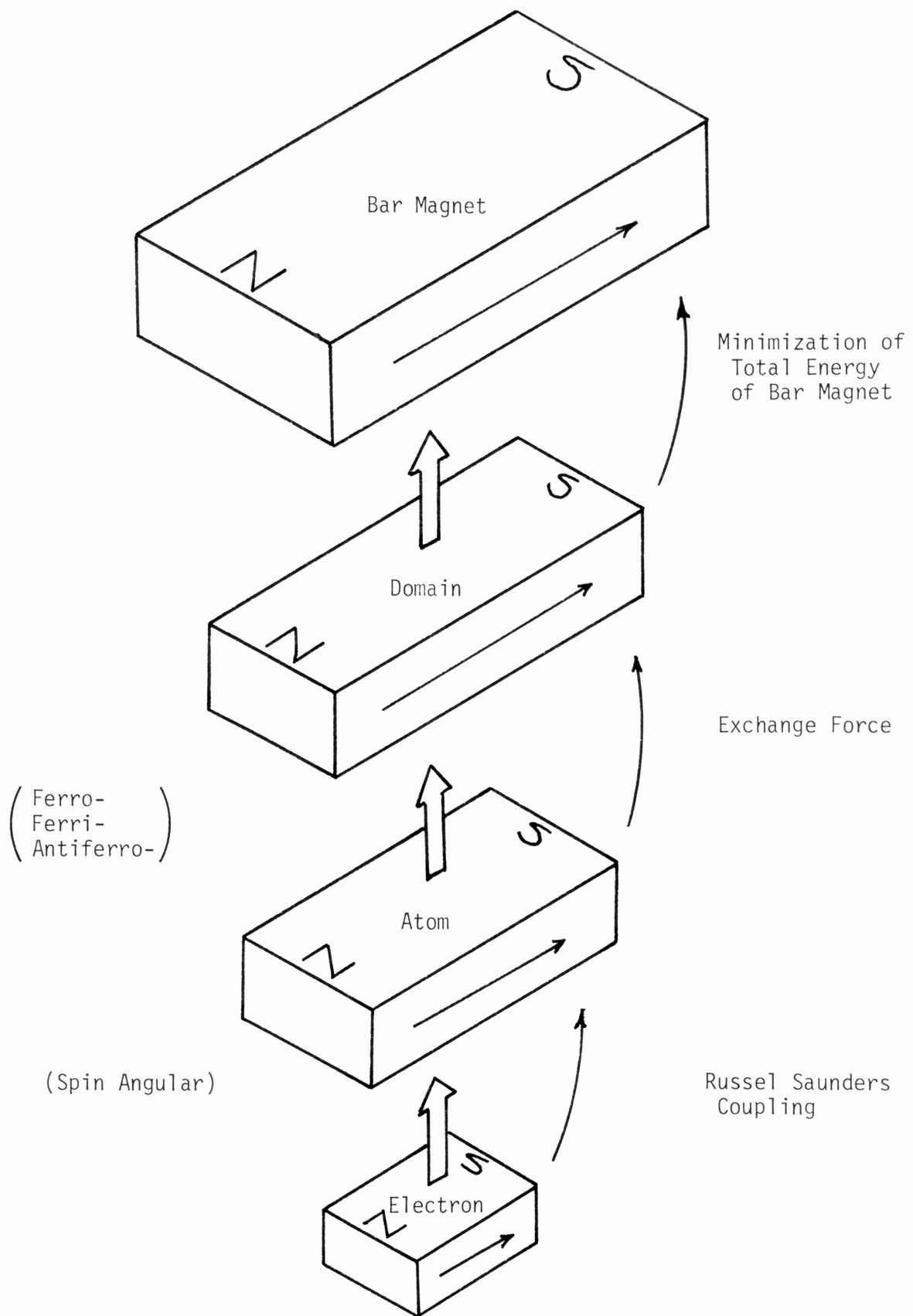Electron

S

N

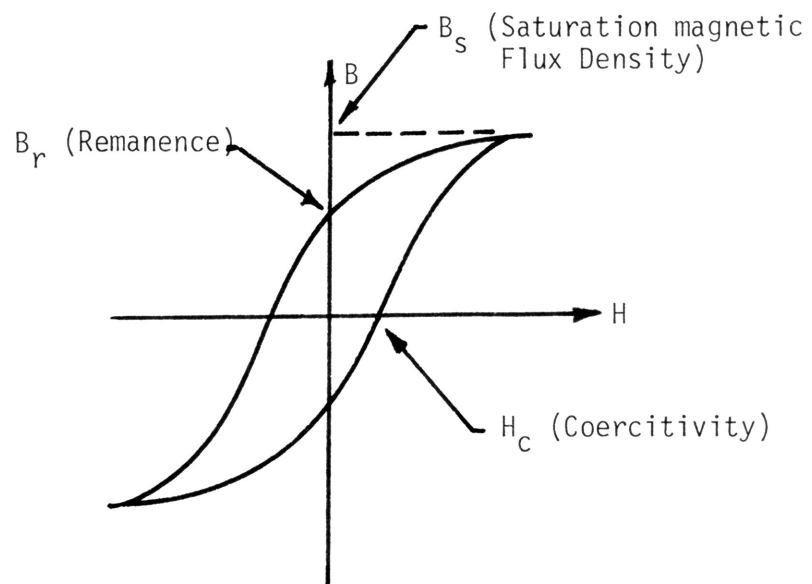Figure 4   Review of Magnetic Phenomenon in
Materials

16

Figure 5 Typical B-H Loop

ferromagnetism to ferromagnetism and vice versa caused by the application
of a strong field or by a change in termperature [7]. Parasitic ferro-
magnetism is the name of a weak ferromagnetism which accompanies antiferro-
magnetism [8, 9, 10, 11]. Ferrimagnetism is the subject of the next
chapter.

III. FERRIMAGNETISM

Ferrites materials exhibiting ferrimagnetism, were developed in the 1940's by J.L. Snoek and his associates at the Philips Research Laboratories in the Netherlands [12]. Their experimental work, together with the basic theory of ferrimagnetism developed by Neel [13], was the starting point for the rapid expansion of research activity on ferrites. Ferrites are ceramic materials, dark grey or black in appearance, very hard and brittle. The typical graph of spontaneous magnetization versus temperature is given in Figure 6. An expression for the paramagnetic susceptibility is given by equation 16.

$$\frac{1}{K} = \frac{T}{C} + \frac{1}{K_o} + \frac{\sigma}{T-\theta} \qquad (16)$$

where c, $1/K_o$, σ and θ are constants that can be calculated form several interaction constants and the assumed distribution of the ions among sites of the crystal lattice [14]. Ferrimagnetic materials can be separated by crystal structure into spinel, garnet, and hexagonal categories.

A spinel structure is face centered cubic. The general formula for a spinel ferrite is $M\,Fe_2\,O_4$. M is one or, in mixed ferrites, more than one of the divalent transition metals Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, My^{2+} and Cd^{2+}. It is also possible to replace some or all of the trivalent iron ions with other trivalent metal ions. The oxygen atoms are arranged in a face centered cubic structure. There are two possible sites, called A and B, in which the metal atoms take up residence between the oxygen atoms. The A sites are tetrahedral sites and are characterized by four oxygen ions and one metal ion. The B sited contain six oxygen ions and
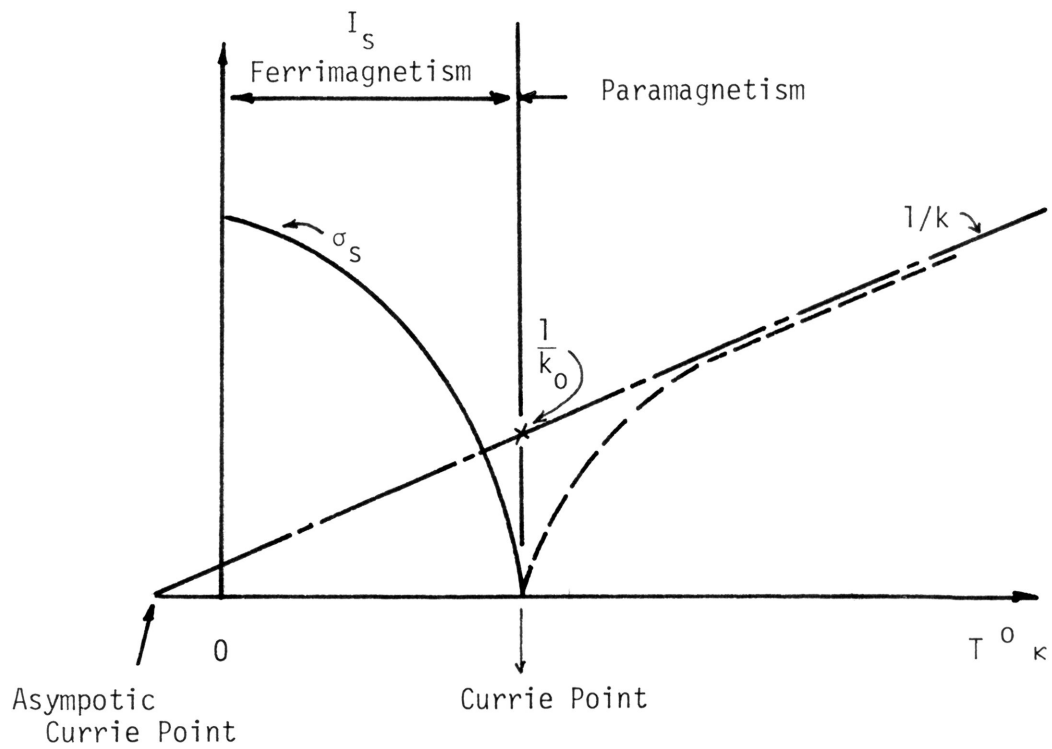
Fig. 6

Fig. 7

19

Figure 6. Spontaneous magnetization and susceptibility versus
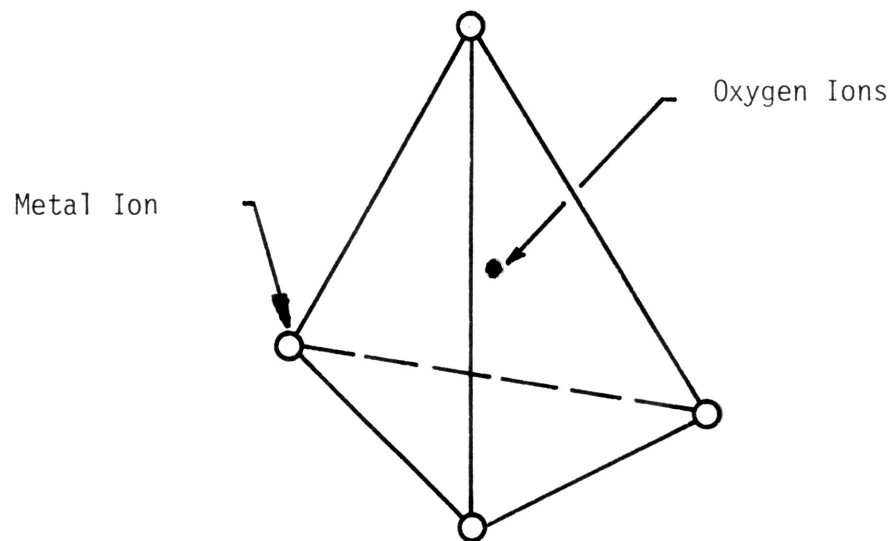temperature σ_s = saturation magnetization, κ = paramagnetic
susceptibility.

Figure 7. Tetrahedral Site

one metal ion.   The sites are referred to as octahedral sites.   Therefore, the unit cell of a spinel ferrite has 64 possible tetrahedral sites and 32 possible octahedral sites; only 8 tetrahedral and 16 octahedral sites are occupied in a full unit cell.   The unit cell contains 24 metal ions and 32 oxygen ions, or from a chemical point of view, 8 molecules having the formula $M Fe_2 O_4$.   If the spinel is "normal", the divalent M ion would occupy a tetrahedral site while the trivalent Fe ions would occupy the two octahedral sites.   In an "inverse" spinel structure, the trivalent Fe ions occupy the tetrahedral and one of the octahedral voids.   Since the bonding mechanism is ionic, the electrons are all tightly bound to the lattice atoms and thus the ferrite acts as an insulator.   Typical re-sistivities are from 10^7 to 10^{10} ohms centimeters, compared to 10^{-6} ohm centimeters for metal magnets.   Among the factors considered to influence the distribution of metal ions over the A and B sites are the radii of the metal ions, the matching of the electronic configuration of the metal-lic ions to the surrounding oxygen ions and the electrostatic energy of the lattice.   Ferrites' versatility comes from the ability to vary the crystal make-up of the material and hence the magnetic properties of the ferrite.   Examples of this kind of "molecular engineering" are the follow-ing:

a)   Manganese substitutes increase electrical resistances, and

b)   Aluminum ions can reduce coercive fields.

It is because the electrons can be thought of as localized in the crystal lattice that enabled Neel to explain the low saturation magnetization (compared to ferromagnets) of many ferrimagnetic materials.   Neel hypothe-sized that when two ferromagnetic atoms are separated from each other by another atom.   For example an oxygen atom in the ferrite $Fe_3 O_4$, the two
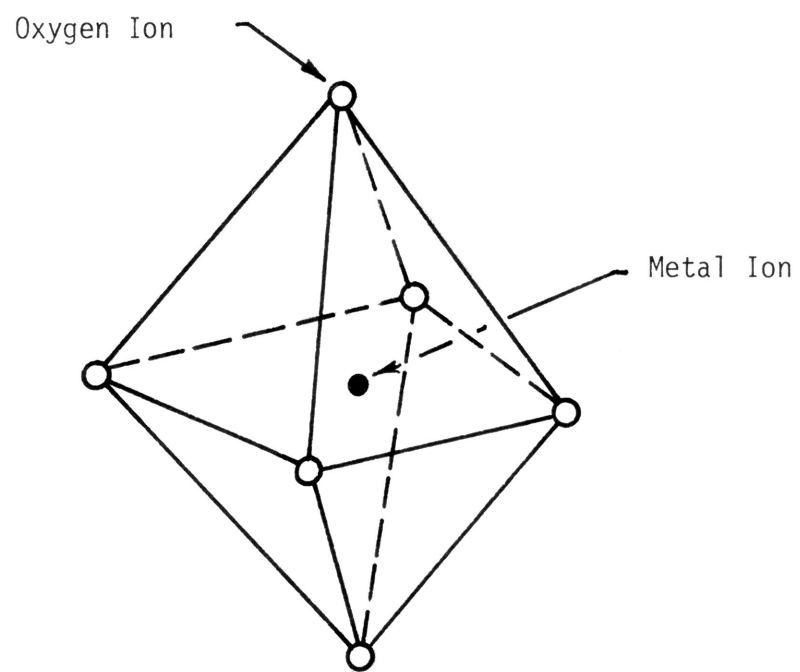
Figure 8. Octahedral Site

metal atoms can still interact with each other in such a way that their unpaired spins are aligned antiparallel. It should be noted that under this analysis the only interaction considered is the A-B exchange. Exchange interactions concerning A-A or B-B are neglected in this thesis. The A-B interaction is sometimes called the "superexchange" process, which is an indirect process that takes place between the cations which carry the magnetic moment in the crystalline lattice by means of an intermediate anion. Neel explained the low saturation magnetization of $Fe_3 O_4$ (iron oxide magnetite) by assuming an inverse spinel structure. If all the iron atoms were assumed to have parallel spin moments (ferromagnetic interactions), it can be shown that the total saturation moment should be about 17 Bohr magnetons. The measured value, however, is 4.08 bohr magnetons. Under an inverse spinel crystal structure, the equal number of Fe^{3+} ions in the octahedral and tetrahedral voids couple antiferromagnetically. The resultant moment of $Fe_3 O_4$ must be due to the Fe^{2+} ions in the octahedral voids. The calculated moment of an Fe^{+2} ion is approximately 4 Bohr magnetons, in good agreement with experimental measurement. If given another divalent ion M that is of the transition series with n electrons in the d shell, the moment would be $n\mu_B$ or $(10-n)\mu_B$, depending on whether the d shell is less than or more than half full respectively. It should be mentioned that the extent to which a crystal lattice is inverted depends on the temperature. In general, the effect of increasing the temperature of a normal spinel is to bring about the excitation of the ions to the inverted position [15].

The garnet structure is the same as the spinel except that it has an additional crystallographic site containing eight oxygen ions and an ion of yitrium or a rare-earth element. The site is called dodchadral.

The general formula of a garnet is $3M_2O_3 \cdot 5 Fe_2O_3$, where M is a trivalent rare earth metal (Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu, or Y). Garnets generally have higher resistivities than spinel ferrites due to the lack of divalent ions.

Hexagonal ferrites are complex compositions of barium oxide, iron oxide, and one or more combinations of transition elements such as nickel, manganese, zinc, magnesium, or cobalt. Some hexagonal crystal ferrites suffer from a serious temperature stability problem that must be solved before they can become practical. Hexagonal ferrites are of interest because of their high magnetocrystalline anisotrophy which is comparable with cobalt, making them suitable for permanent magnets.

25

IV. TECHNICAL APPLICATIONS

This chapter will relate the information presented in the last two chapters to the technical applications of ferrites. The intent is to give the reader some idea of the versatility of ferrites and how the knowledge of ferrimagnetism and "molecular engineering" can be applied to obtain specific characteristics for a particular application. Although ferrites have been used and studied for more than two decades, their wide-spread use has just lately come into being due to the advances made in controlling the manufacturing process. The applications started in the field of telephone communications [16] where the combination of good magnetic properties and high resistivities made these materials very suitable as cores for inductors and transformers. Since the resistivities were at least a million times greater than the values for metallic magnetic materials, laminated or powered cores could be replaced with solid ferrite cores and these could often be made in a more convenient shape than their laminated counterparts. The high resistivities of ferrite materials makes them practically immune to easy currents and therefore reduces power losses in transformers. The application was extended to domestic television receivers where they became and still remain the undisputed core material for the line time-base transformer and the magnetic yoke used in the deflection system. In domestic radio receivers, rods or plates of ferrimagnetic material are used as cores for magnetic antennas.

The development of hexagonal ferrites, having coercivities of 2000 Oe, made ferrimagnetic permanent magnets possible. The crystalline axes may be oriented during manufacturing so that anisotropic properties are induced and greater magnetic energies may be stored. More will be mentioned

about inducing anisotropic properties in the next chapter. These ferrites are used for a wide range of permanent magnet applications, e.g. loud speaker magnets, magnetic chucks, small electric motors, and focussing magnets. Another advantage of ferrite permanent magnets is that they are lighter in weight than their ferromagnetic counterparts.

Another class of application arose when it was found possible to prepare spinel ferrites such as MnMg or LiNi ferrite, having substantially rectangular hysteresis loops. The main use of these materials is for memory cores. The magnetic memory element in a digital computer must be hard enough to retain its forward or reverse magnetization, the states corresponding to a "0" or a "1" in the binary system, indefinitely on being stored. It must also be soft enough to switch states cleanly and rapidly when a small external field is applied in the course of information read-in or read-out.

Applications at microwave frequencies resulted from the discovery that the aligned moments of the electron spins within the crystal lattice may be made to precess at a frequency that depends on the strength of the steady internal magnetic field. Please note that this precession phenomenon is commonly referred to as the gyromagnetic effect or the Larmor Precession [17]. A detailed discussion of the Larmor Precession is beyond the scope and intent of this thesis. An incident circularly polarized electromagnetic wave will only produce precessional resonance (and the accompanying attenuation) if the rotation is in the right sense with respect to the direction of the steady field. This gives rise to non-reciprocal devices in which the transmission properties in one direction are quite different from those in the opposite direction. A variety of microwave devices have been developed which depend basically on this

principle. They include wave guide isolators, switches, circulators, and modulators. Circulators for example, direct the flow of electromagnetic energy and could be used to connect two receivers and two transmitters to a common antenna in order to be able to switch one in if the other fails. Ferrite substrates are currently being used for microwave integrated circuits [18].

This chapter will close by discussing some of the more "unusual" applications of ferrite materials. Due to the fact that ferrites are ceramics, they can be mixed with rubber to form the magnetic gaskets around refrigerators. Some ferrites do not react with stomach acids, and as a result are used for contrast materials in x-ray diagnosis [19]. Recently RCA has shown that ferrimagnetic materials can be locally doped to yield semiconductor materials with high mobilities [20]. In closing, this brief review of technical applications for various ferrites has hopefully demonstrated the wide-spread use of ferrite materials in today's society. The continually increasing need to produce better quality ferrimagnetic materials with improved characteristics has focussed attention on the various manufacturing techniques used to produce a ferrite. Annealing is a manufacturing technique that has a considerable influence over the ferrimagnetic materials eventual characteristics. Therefore it is clear why the study of the annealing process and its effect on the different magnetic parameters which are of importance in considering technological applications, is of scientific interest.

V. THERMAL AND MAGNETIC ANNEALING

It is difficult to prepare a ferrite in a condition as chemically homogeneous or structurally perfect as the metals. In iron for example, chemical inhomogeneity arises only in the form of inclusions (local concentrations of one type of atom in alloy crystals) which can be largely removed by standard purification techniques, but no comparable techniques can be applied to correct gross defects in ferrites. Such considerations help to explain why, although ferrites have been used and studied for more than two decades, their properties are currently being considerably improved by the careful study of manufacturing techniques. The major improvements in the properties of metals date back to the 1930's. Thermal and magnetic annealing are manufacturing techniques that are used to control the magnitude properties of a sample. Thermal annealing attacks the problem of high magnetostatic fields that are induced in the ferrimagnetic material as a result of the "cold work" done during the manufacturing process. Magnetic annealing attacks the problem of high crystal anisotropy and magnetrostriction in the material.

A British scientist in 1885, named Ewing, noted the tendency of an induced magnetization to remain after the applied field was removed. [21] Ewing named this phenomenon "Hysteresis" after the Greek work meaning "to lag". Hysteresis means that a plot of a materials demagnetization path does not overlap its magnetization path. When a weak external field is applied to a magnetic material, the material's domain walls are seen to move. The motion is in a direction that increases the size of the domains whose magnetization is parallel to the applied field and reduces the size of domains whose magnetization is antiparallel. When a stronger external field is applied, the domain walls are often pushed past crystal obstacles,

thereby rendering some of the specimen's magnetism irreversible. When the field is reduced to zero, the domains are trapped behind an energy barrier, so to speak, and cannot change unless an external field of opposite polarity and exceeding some threshold (coercivity) is applied. Crystal obstacles can take many forms. Some of the more common obstacles are inclusions, pores, stress points, radomly oriented crystal grain boundaries and impurities. These defects generate highly localized magnetostatic fields and discontinues that interact with a domain wall.

How are crystal defects created? As mentioned earlier, the cold work of the ferrite material, which includes bending, stretching, rolling, and machining, produces strains in the material that tend to deteriorate the magnetic properties of the ferrite. The eleastic limit of the material is exceeded and plastic deformation of the constituent crystals occures. The crystals become broken up which results in severe distortion of the regular atomic lattice pattern. The distortion gives rise to thermal gradients which set up grain boundaries at the surfaces at which the constituent crystal of the material itself meet. Crystal defects generate magnetostatic fields that tend to oppose the magnetization of the material. Translated into the effects on magnetic properties of device fabrication interest, crystal defects tend to raise the coercivity, raise the hysteresis loss, lower the premeability, and lower the device reliability. Reliability concerns the fact that if the material were not properly annealed, before fabricating a magnetic device, the high internal strains would produce high hysteresis losses and joule heating. The joule heating would act to self-anneal the specimen and hence change the magnetic parameters of the device. This would make the device unreliable.

How does the process of thermal annealing act to "repair the ferrite" The explanation of the annealing process will be restricted to a qualitative explanation. Detailed semi-quantitative theories have been proposed

30

to explain the annealing mechanisms.   But these are beyond the scope of this investigation. [22,23] Thermal annealing is the process by which the material is heated above the Curie point (temperature at which ferrimagnetism disappears and the material exhibits paramagnetic properties)and then cooled to room temperature slowly to reform the magnetic domains. During the cooling process, the thermal energy of the grain boundaries is given up to the material and thereby strains are relieved. In addition, diffusion occurs at the elevated temperatures which reduces inclusions in the ferrite. The result of the annealing process is that the magnetostatic fields produced near crystal defects are reduced and the magnetic properties of the ferrite are improved. Sometimes the thermal annealing process is conducted under controlled atmospheric conditions. Annealing in hydrogen is essentially a purification process and indicates the necessity of keeping impurity levels to a minimum in the manufacturing of magnetic materials. More will be said on annealing in the presence of a gas later in this chapter.

An interesting twist to the above discussion is that not only can the ferrite's magnetic properties be "improved", but additional properties can be further induced by taking the opposite approach. For example, one way to produce hard magnetic materials (large coercivities) is to introduce various internal obstacles. A sudden reduction in temperature will induce internal strains in the material, which is quite undesirable for device applications like power transformers, magnetic relays, amplifiers, and recorders, but quite desirable for device applications utilizing permanent magnets. The experiments conducted during the investigation were concerned with inducing strains into the ferrite sample.

Magnetic annealing is directed towards reducing high crystal anisotropy and magnetostriction in ferrimagnetic materials. Under magnetic field annealing, the cooling and heating take place in the presence of an

31

externally applied magnetic field. In the cooling cycle, the field forces the reappearing magnetic domains (as soon as the temperature reaches the value which is less than the Curie point of the material) to align themselves parallel to the field. Magnetocrystalline antisotropy arises from the coupling between the electron spin and the orbital motion of the electron. The directional properties of the electron orbit are highly oriented with respect to the crystal lattice; thus the effect of an applied magnetic field on the spin moments depends on the spin orientation with respect to the crystal lattice. A preferred direction of magnetization (induced anisotropy) may be induced in a specimen by annealing in a magnetic field. It may be expalined by the direction ordering of atomic pairs in the various sites of the crystal lattice (I.E. AA, AB, BB pairs of atoms). Therefore crystal anisotropy is inherent in the lattice structure. Mechanical strain can cause anisotropy and the shape of grain boundries will nearly always produce anisotropy. The result is that the magnetization is held to a certain direction, or to more than one direction, as if by a string. Translated into the effect on material properties, the greater the anistotropy, the more difficult it is to deflect the magnetization by an external magnetic field, and therefore the lower the permeability. Induced anisotropy has two simple magnetic consequences. First, the domain structure consists of parallel and anti-parallel domains separated by 180° walls lying parallel to the direction of the annealing field. Secondly, the hysteresis loop, when measured in the direction of the annealing field, becomes very rectangular. Magnetic annealing also can act to reduce the effects of magnetostriction on a ferrite. Magnetostriction is an electrostatic interaction that physically stretches each crystal slightly in the direction of magnetization. Magnetostriction adds to hysteresis loss and

32

appears as the humming sound in transformers. If a substance exhibits magnetostriction, then it is bound to be strained when placed in a magnetic field, and the strain will tend to oppose the magnetization, I.E. the permeability of the material will be lowered. In order that a fairly stress-free material be used, it is required that magnetostriction be minimized. One way of doing this is to induce a preferred instead of random orientation for the grains upon subsequent annealing of the ferrite in a strong magnetic field. The resulting ferrite tends to resemble a single crystal and can attain higher permeabilities. Now that thermal and magnetic annealing has been discussed, the actual procedure followed for the experiments conducted in this investigation and the results will be outlined in the next chapter.

VI. EXPERIMENTAL RESULTS

It should be remembered that permeability and coercivity are structural dependent quantities. Therefore, although it is relatively easy to draw up models in which crystal defects are taken into account in the calculation of, E.G. coercive force, it is impossible to make quantitative predictions about coercivity or other magnetic properties of bulk materials. The investigation conducted in this report involved carrying out the experiments and then using the results to make predicitions concerning the manipulation of magnetic properties for device fabrication purposes. Due to the special ferrite that was tested (referred to in the chapter as T-114), magnetic annealing could not be performed, and the effect of thermal annealing on further improvement of the magnetic properties of the ferrite would have been minimal. It was then decided to investigate the effects of inducing strains into the magnetic material. In particular, it was decided to attempt to increase the coercivity (that is to make a stronger permanent magnet) and at the same time keep the increase in hysteresis loss, the decrease in permeability, and the decrease in saturation magnetization low. This aspect was chosen because of its technical value. By a proper annealing process, a manufacturer could "harden" a relatively soft ferrite without substantially deteriorating its magnetic properties, and thereby expand the use of the particular material. The more expensive alternative would be to separately manufacture a hard magnetic ferrite. Given the above objective, the experimental procedure is given below:

1) The T-114 sample was heated at the rate of $25^{\circ}C$ per hour from room temperature $(21^{\circ}C)$ to $280^{\circ}C$.

2) The T-114 sample was left at $280^{\circ}C$ for 175 hours in order to investigate any possible effects of the presence of oxygen on magnetic

parameters.

3) The T-114 sample was then further heated at 25°C per hour from 280°C to 500°C.

4) The T-114 sample was then cooled to room temperature at the rate of 160°C per hour.

Figure 9 gives the experimental set-up used in the investigation. The H-field is derived from the current flowing in the primary windings by using equation 5 or 6. The B-field is obtained by electronically integrating the voltage induced in the secondary winding.

$$V_S = N_S A \frac{dB}{dt} \tag{17}$$

where,

V_S - Secondary voltage

N_S - Secondary turns

A - Cross-sectional area of toroid

B - Magnetic flux density

t - Time

Working in the CGS system, equation 17 can be integrated to generate equation 18.

$$B = \frac{10^8}{N_S A} \int V_S \, dt \tag{18}$$

All parameters are set by switches on the instrumentation panel of the hysteresisgraph. The hysteresisgraph will generate D.C. signals, proportional to the value of H and B, that drive an X-Y recorder that plots the hysteresis loop. The recording accuracy is a function of the number of secondary turns and the drift of the hysteresisgraph. The recording error was $\pm0.12\%$ for the experiment. Please note that more detailed information concerning
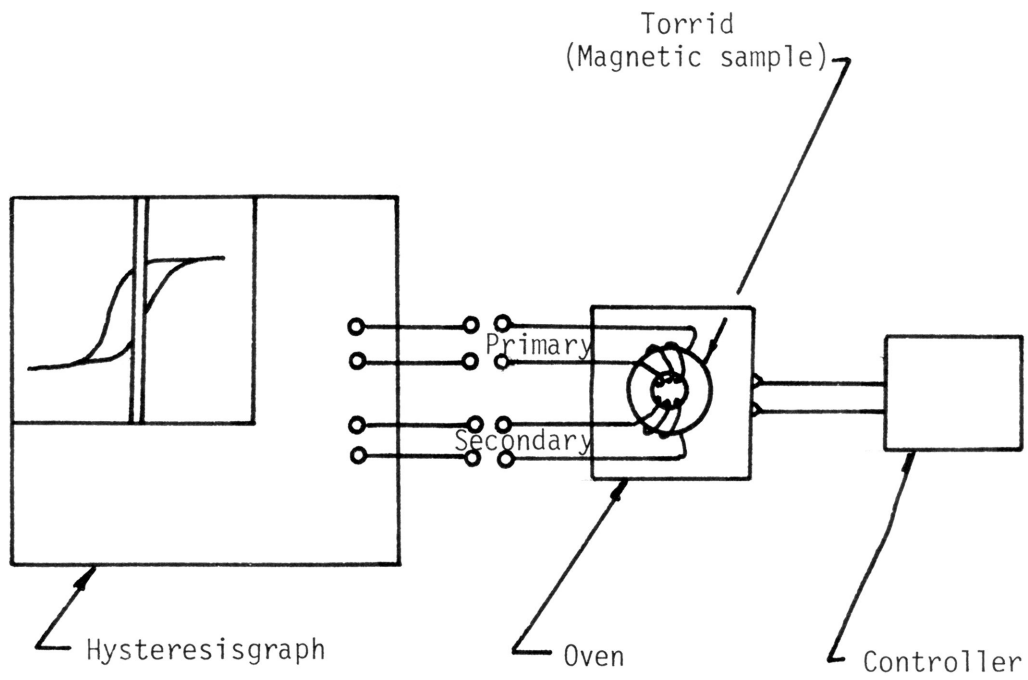
35

Figure 9. Experimental Set-up

the test equipment and the manufacturer's data on of the test sample

is given in Appendix B. The temperature was sensed using a chromium-

aluminum thermocouple that generated a D.C. voltage porportional to the

temperature of the oven. The temperature controller used the D.C. voltage

to regulate the power supplied the heating coils of the oven. The results

10-15   of the experiment are given in Figures 10-15. All data is accurate to

within $\pm$ 1.5%.


% Increase in coercivity (hardness) -   32%

% Increase in hysteresis loss -   18.0%

% Decrease in permeability -   2.9%

% Decrease in saturation magnetization -   20%
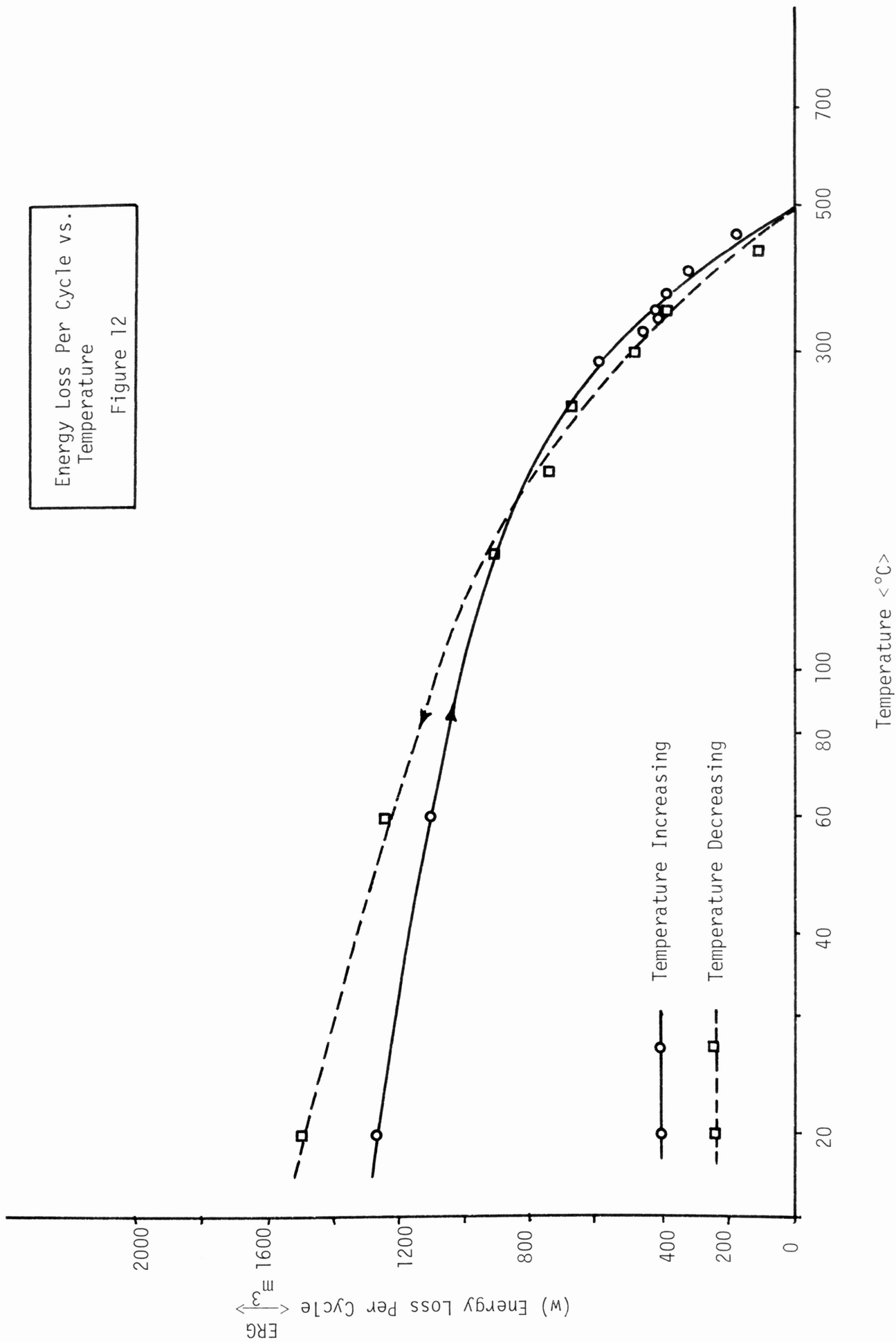
Table 1. Results of Experiment on T-114

The results tabulated in Table 1 show that the material was hardened

without a corresponding deterioration in the hysteresis loss or permeabili-

ty. The investigation also revealed that the presence of oxygen did not

introduce enough impurities into the sample to significantly effect the

mangetic properties. It can therefore be concluded that the results tabu-

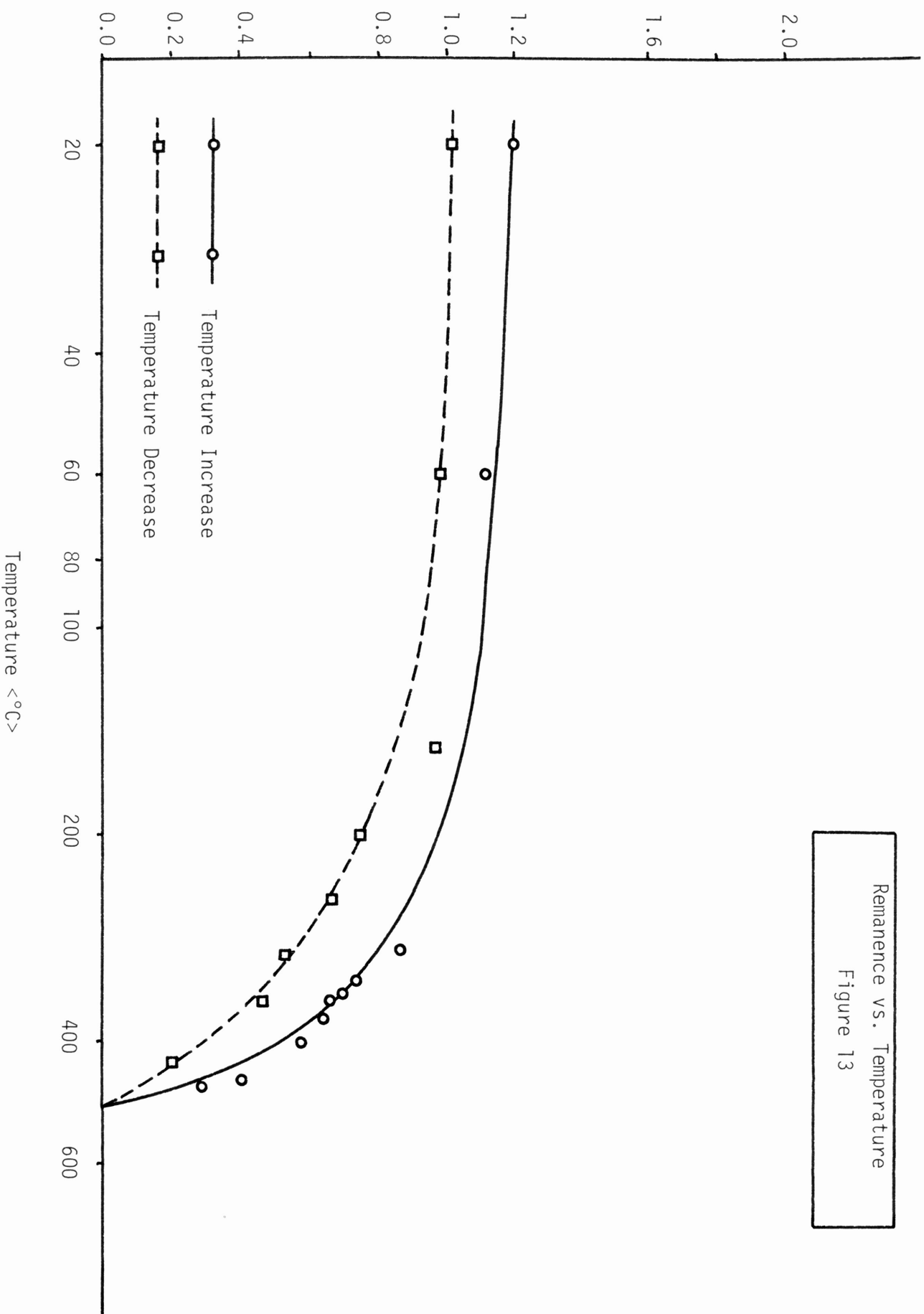lated in Table 1 are a direct result of the chosen cooling rate.
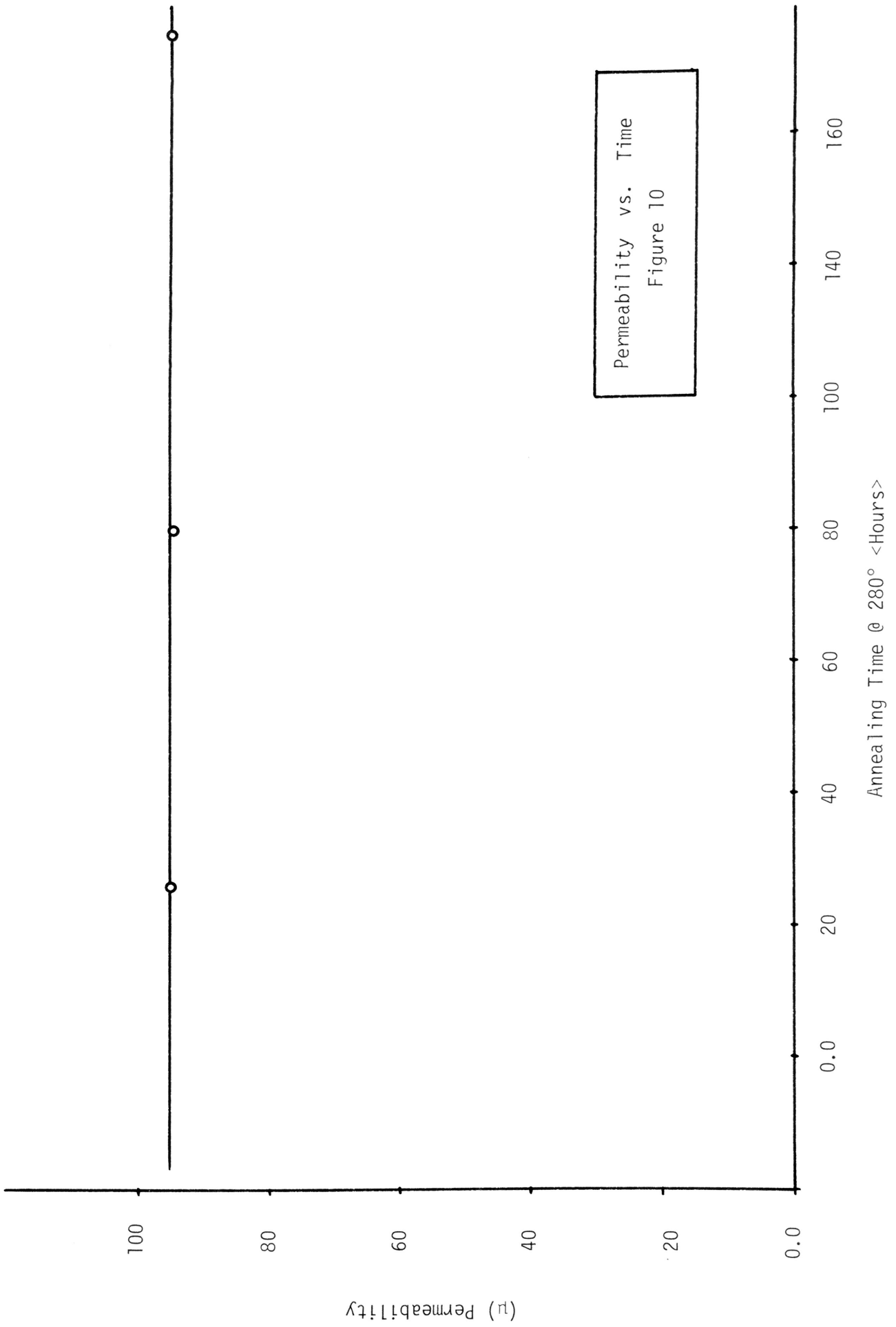
Permeability vs. Time
Figure 10

Annealing Time @ 280° <Hours>

Permeability (μ)

38

Coercivity vs. Temperature
Figure 11
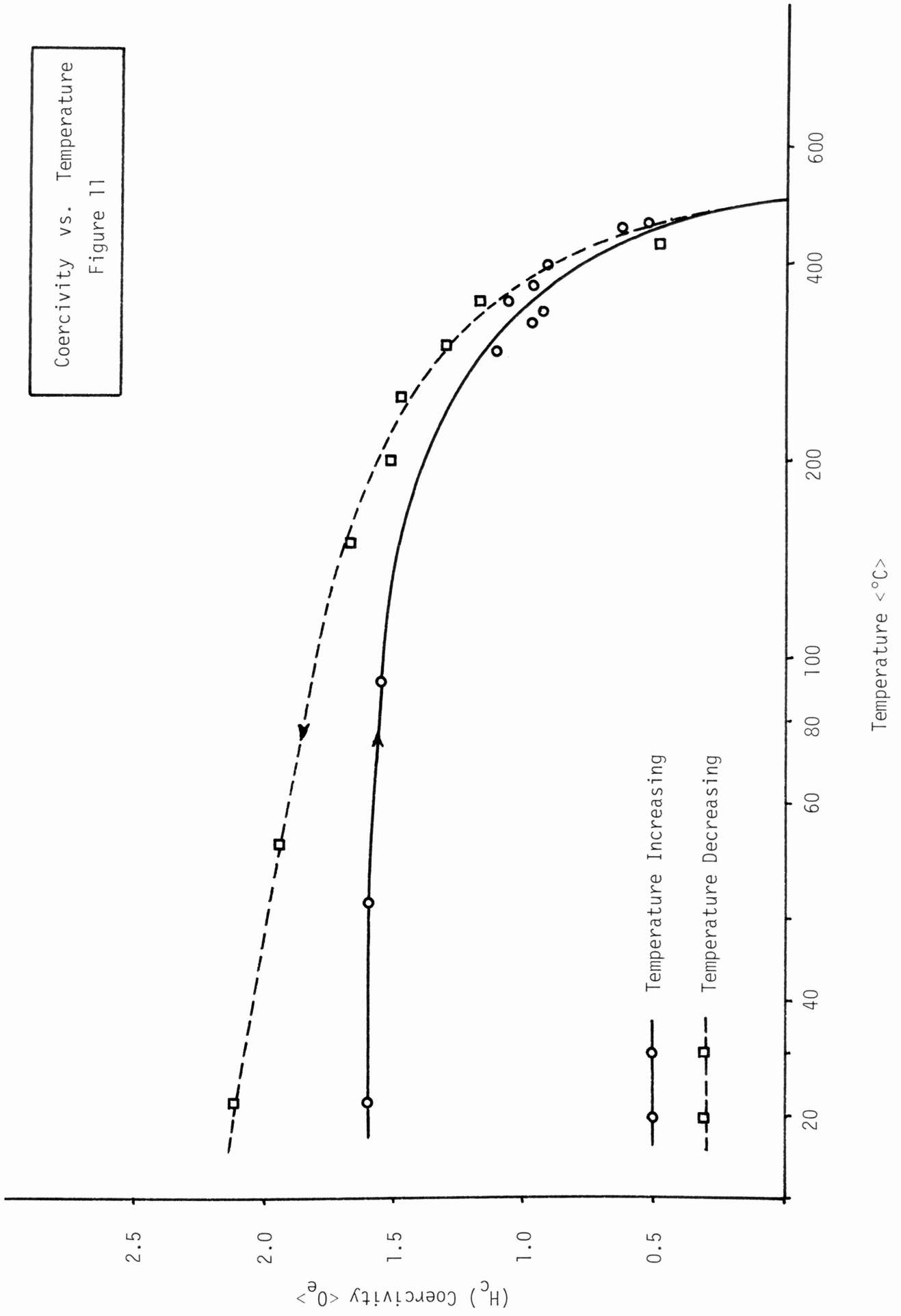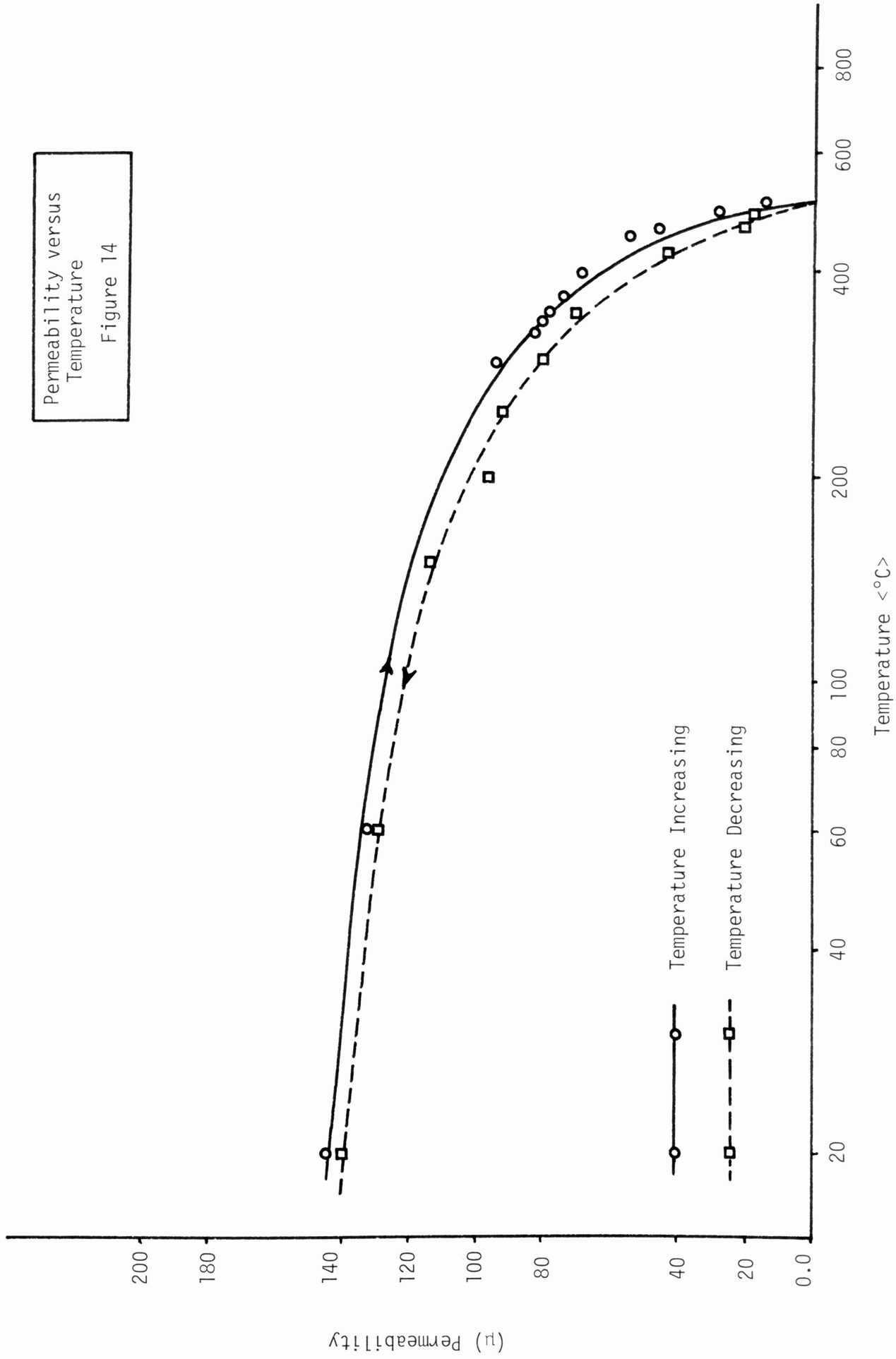
Energy Loss Per Cycle vs. Temperature

Figure 12

Remanence vs. Temperature
Figure 13

41

Permeability versus
Temperature

Figure 14

Temperature Increasing

Temperature Decreasing

Temperature <°C>

Permeability (μ)

Saturation Magnetization versus
Temperature

Figure 15
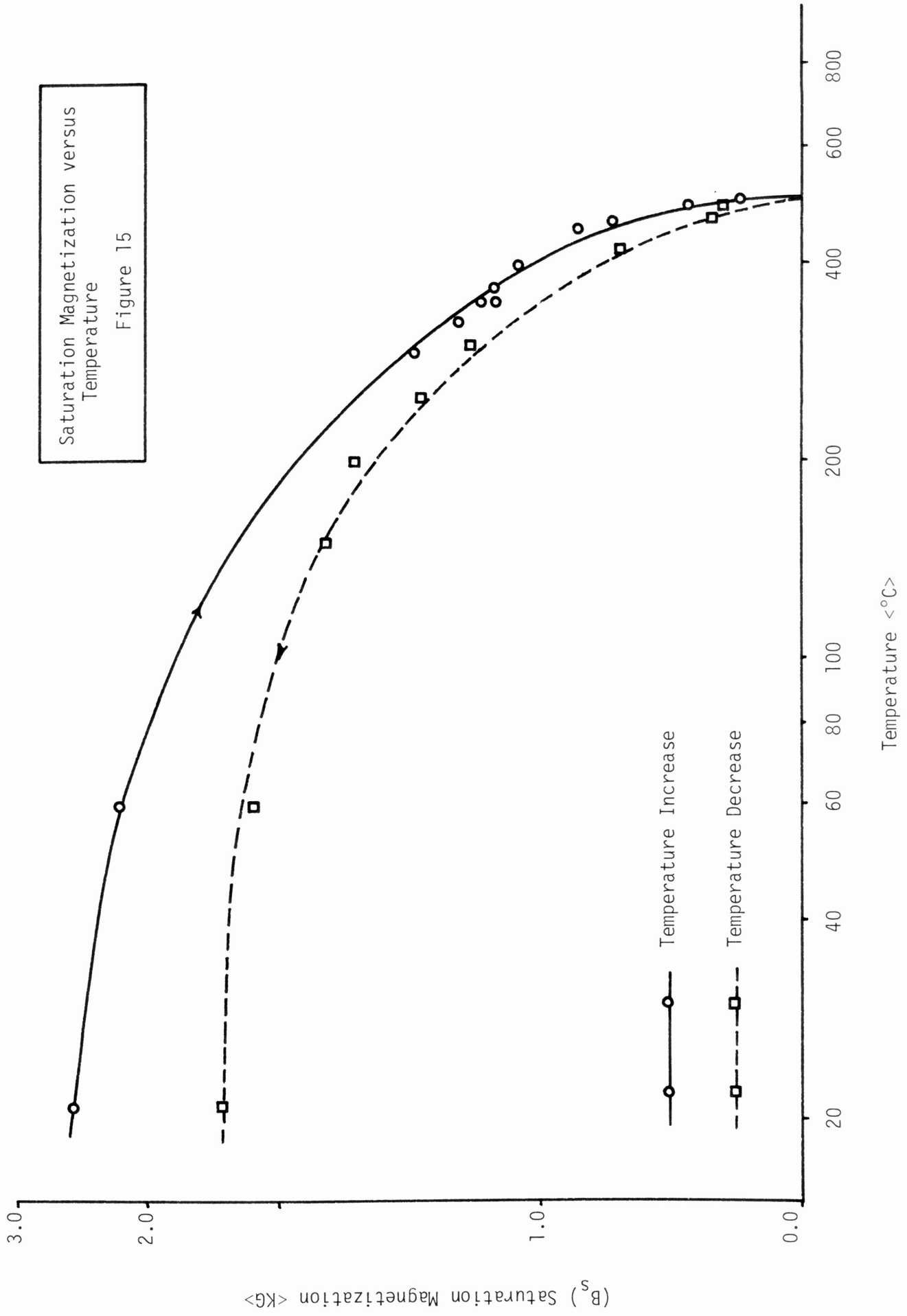
CONCLUSION

In summary, the purpose of this investigation was to investigate ferrimagnetism and the annealing process. The first chapter discussed the basic laws and terminology associated with the field of magnetics. Magnetic phenomena was explained by starting with the electron and building up to the concept of a domain. The particular formation of the domain lead to ferrimagnetism and Chapter 2. Chapter 2 discussed the various types of ferrites, which are spinel, garnet, and hexagonal. Several applications of ferrimagnetic materials were given in Chapter 3. Chapter 3 pointed out how the mangetic parameters (H_c, B_r, and μ) related to device applications. Finally, Chapter 4 discussed the theory of thermal and magnetic annealing and Chapter 5 outlined the experimental phase of the project. The results of the experiments (coupled with the information presented in Chapters 1, 2, 3 and 4) revealed that, by carefully controlling the cooling rate and monitoring the effects of atmospheric gas introducing impurities, thermal annealing can be used to harden a soft ferrite without signficantly deteriorating its magnetic character.

REFERENCES

[1] D. Halliday and R. Resnick, Physic - Part II, John Wiley & Sons, Inc., (1962), pp. 814-943.

[2] E. Schrödinger, Ann. Physic, 80, (1926), p. 437.

[3] H.N. Russell and F.A. Saunders, Astrophys. J., 61, (1925), p. 38.

[4] P. Weiss, J. Phys. 6, (1907), p. 661.

[5] A.H. Bobeck and H.E.D. Scovil, Scientific American, 224, (1971), p. 83.

[6] F. Bloch, Z. Physik, 74, (1932), p. 295.

[7] J. Bequerel and J. Van Den Handel, J. Phys. Radium, 10, (1939), p. 10.

[8] L. Neel, Ann. Physique, 4, (1949), p. 249.

[9] Y.Y. Li, Phys. Rev., 101, (1956), p. 1450.

[10] I. Dzialoshinski, J. Phys. Chem. Solids, 4, (1958), p. 214.

[11] T. Moriya, Phys. Rev., 120, (1960), p. 91.

[12] J.L. Snoek, New Developments in Ferromagnetic Materials, Elsenier Publishing Co., Inc., (1947), pp. 1-10.

[13] L. Neel, Ann. Physique, 3, (1948), p. 137.

[14] Ibid.

[15] A.E. Berkowitz and E. Kneller, Magnetism and Metallurgy, Academic Press, (1969), p. 4.

[16] E.C. Snelling, Soft Ferrites, Properties and Applications, Iliffe Books Ltd., (1969), pp. 2-3.

[17] H. Goldstein, Classical Mechanics, Addison-Wesley, (1959).

[18] R. Gundlach, Electronics, 32, (1968), p. 104.

[19] Ibid.

[20] Y. Hoshino, S. Iida, and M. Sugimoto, Ferrites, Proceedings of the International Conference, University Park Press, (1971), p. 603.

[21] J.A. Ewing, Proc. Roy. Soc. (London), 46, (1889), p. 269.

[22] J.F. Dillinger and R.M. Bozorth, Physics, 6, (1953), p. 279.

[23] L. Neel, Comp. Rend., <u>237</u>, (1953), p. 1613.

BIBLIOGRAPHY

1. A.N. Bobeck and U.F. Gianola, Science and Technology, Feb., (1969), p. 26.

2. A.P. Arya, Elementary Modern Physics, Addison-Wesley Publishing Co., (1976), pp. 202-210, 232-250.

3. D. Wagner, Introduction to the Theory of Magnetism, Pergamon Press, (1972), pp. 5-14, 68-129, 149-225.

4. D.E.G. Williams, The Magnetic Properties of Matter, American Elsevier Publishing Co., Inc., (1966), pp. 1-15, 191-226.

5. D.S. Parasnis, Magnetism, from Lodestone to Polar Wandering, Wiley & Sons, (1960), pp. 1-30.

6. F.J. Lavoie, Machine Design, 43, April '29, (1971), p. 40.

7. J.H. Van Vleck, Science, 201, July '17, (1978), p. 113.

8. J. Smit and H.P.J. Wijn, Ferrites, Physical Properties of Ferrimagnetic Oxides in Relation to their Technical Applications, John Wiley & Sons, (1959), pp. 1-13, 30-42, 136-175, 177-210, 212-214.

9. I.E. Thompson, The Magnetic Properties of Materials, CRC Press, (1968), pp. 1-31, 55-87, 140-150.

10. L.F. Bates, Modern Magnetism, Cambridge University Press, (1951), pp. 1-56, 156-197, 401-490.

11. L.H. Bennett, C.H. Page, and L.J. Swartzendruger, Journal of Research of the National Bureau of Standards, 83, Jan.-Feb. (1978), p. 9.

12. L.V. Azaroff and J.J. Brophy, Electronic Processes in Materials, Mc-Graw-Hill Book Co., (1963), pp. 61-93 , 372-407.

13. M.B. Stearns, Physics Today, April, (1978), p. 34.

14. M.R. Wehr and J.A. Richards, Jr., Physics of the Atom, Addison-Wesley Publishing Co., (1967), pp. 219-264.

15. R.M. Bozorth, Ferromagnetism, D. Van Nostrand, (1951), pp. 14-47.

16. R.S. Tebble and D.J. Craik, Magnetic Materials, John Wiley & Sons, (1969), pp. 1-40, 252-364, 447, 556-637, 663-667.

17. R.S. Tebble, Magnetic Domains, Methuen & Company, (1969), pp. 1-10, 34-43.

18. S. Chikazumi and S.H. Charap, Physics of Magnetism, Robert E. Krieger

Publishing Co., (1964), pp. 1-12, 39-59, 79-99, 113-348.

19. T.H. Haberberger, Ceramic Industry Magazine, Aug. (1971), p. 29.

QUANTITY	MKS Unit	CGS Unit	Factor by which Quantity in MKS is Multiplied by to Convert to CGS
Flux density (B)	Weber-meter^{-2}	Gauss	10^4
Magnetizing Field (H)	Ampere turns meter^{-1}	Oersted	$4\pi\ 10^{-3}$
Magnetic Flux (ϕ)	Weber	Maxwell	10^8
Intensity of Magnetization (I)	Weber-meter^{-2}	emu	$\frac{1}{4\pi} \times 10^4$
Magnetic Moment (M)	Weber-meter	emu	$\frac{1}{4\pi} \times 10^{10}$

APPENDIX B

I. TEST EQUIPMENT:

   - Walker/Magnemetrics Hysteresisgraph - Model MH-20

   - Omega Temperature Controller - Model 4008

II. SAMPLE INFORMATION:

   - Effective Magnetic Cross-sectional Area - 0.0581 in^2

   - Outer Diameter - 1.142 in

   - Inner Diameter - 0.748 in

   - Height - 0.205 in

   - Effective Magnetic Path Length - 2.92 in

   - Surface Area Exposed for Cooling - 2.92 in^2

   - Curie Temperature - 500°C

   - Volume Resistivity - 1 x 10^8 ohm/cm

   - Specific Gravity - 4.7

   - Number of Primary Turns - 81

   - Number of Secondary Turns - 97