AN INVESTIGATION OF MAGNETIC HARDENING PROCESSES IN PLATINUM-COBALT AND PLATINUM-NICKEL-IRON ALLOYS

ΒY

G. C. HADJIPANAYIS

A thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Winnipeg: March, 1979.

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ABSTRACT

Magnetic hardening in $Co_{52}Pt_{48}$ and $FePt_{0.7}Ni_{0.3}$ has been examined through X-ray diffraction, electron microscopy and electron diffraction in correlation with magnetic measurements.

Both alloys can be quenched from a high temperature to retain a disordered f.c.c cubic structure. Aging at lower temperatures produces an ordered tetragonal phase of type AuCu I with $(\frac{C}{a}) \sim 0.97$. The c-axis is an easy axis of magnetization with an anisotropy constant of $\sim 10^7$ erg/cc. Upon ordering the alloys become magnetically hard. The crystal structure and morphology of the alloys has been examined by electron microscopy.

In $\operatorname{Co}_{52}\operatorname{Pt}_{48}$, at the early stages of ordering, ordered regions of diameter 50 - 100 Å were found with their c-axes oriented at random parallel to one of the three original disordered cubic "a" axes. In the optimum high coercivity state, particles with the same c-axis having a diameter of ~200 Å group together on {110} planes with their c-axes at 45° to the {110} plane. In the overaged state like particles coalesce to form lamellae of one particular c-axis, the other two orientations being consumed.

Conventional domain walls could not be seen in an optimum Co₅₂Pt₄₈ using Lorentz microscopy although macroscopic domains were observed on a mechanically polished sur-

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face with the Bitter technique.

In the optimum $\text{FePt}_{0.7}\text{Ni}_{0.3}$ the {110} lamellar structure was found; the c-axis of the tetragonal lamellae being at 90° to the dominant tetragonal matrix. Lorentz microscopy revealed 180° domain walls parallel to the matrix c-axis.

In an attempt to elucidate the origin of magnetic hardening in both alloys, the hard magnetic properties were examined in different ordering stages and at temperatures from 4.2 to 600 K. The large values of the reduced remanence ratios are explained in terms of exchange interactions between the particles of different c-axis. This interaction being proportional to the overall sample magnetization (λ I) modifies the Stoner and Wohlfarth magnetization curves of single domain particles and allows the reduced remanence ratio to be higher than 0.5. Values of the interaction parameter λ were found from the measured remanence ratio.

The coercivity increases on cooling below room temperature. This increase can be attributed to the decreased probability of the thermal activation of domain wall segments over barriers as temperature falls (thermal effects) and to the change of the intrinsic properties (magnetocrystalline anisotropy and saturation magnetization) with temperature.

Magnetic viscosity measurements were used over a wide range of temperatures (4.2 to 600 K) to separate thermal

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activation from intrinsic temperature effects. No observable time effects were seen in optimum $Co_{52}Pt_{48}$ at 4.2 K.

In addition, values of the saturation magnetization and magnetocrystalline anisotropy were obtained by least squares fitting to the law of "approach to saturation". Magnetization measurements were taken in fields up to 100 kOe and at temperatures from 4.2 to 300 K. It was found that some of the magnetization curves could be superimposed on the overaged magnetization curve after translating the H axis by a proper amount, λI . This is also an indication of the exchange interaction hypothesis and the values of λ obtained by this way were consistent with those obtained from the reduced remanence ratio.

From the picture of the experimental observations a model has been set up to explain the magnetic hardening in $FePt_{0.7}Ni_{0.3}$. It is assumed that the lamellar junctions are the pinning centres of domain walls and, therefore, the source of magnetic hardening. A linear variation of coercivity with temperature is predicted through continuous pinning of domain walls provided the intrinsic effects are not important.

No simple domain interaction is consistent with the structure observed in $Co_{52}Pt_{48}$ at its optimum state. However, the applicability of a recent coherent rotation random anisotropy model of coercivity is discussed.

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CHAPTER I

INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

A ferromagnetic material is characterized by the phenomenon of hysteresis or irreversibility in magnetization M as shown in Fig. 1.1.

The value which the magnetization acquires at high magnetic fields H is called the saturation magnetization M_s . After the removal of the field, the magnetization does not reduce to zero but to a definite value called the remanent magnetization or remanence M_R . The reverse field required to bring the magnetization to zero is called the coercive force or coercivity H_c . Similarly, the field required to bring the remanent magnetization M_R to zero is called the remanent magnetization to zero is called the coercive force or coercivity H_c . Similarly, the field required to bring the remanent magnetization M_R to zero is called the remanent the remanent coercivity H_R (Fig. 1.1).

Weiss (1907) tried to explain this irreversibility by assuming the existence of "domains" inside which the magnetization is saturated, but various domains have different directions of magnetizations so that in the absence of the field there is no net magnetization. The boundary layers between these domains are known as "domain walls".

This study is mainly concerned with the properties of hard magnetic materials which resist demagnetization well and are characterized by high coercivities and remanences.



Fig. 1.1 Demagnetization curves.

There are two possible mechanisms of magnetic hardening.

- a) The reversal of anisotropic single domain particles as shown by Stoner and Wohlfarth (1948). (The subdivision of the crystal into domains reduces the magnetostatic energy, but a domain wall energy must be introduced to effect this reduction. As the size of the crystal is reduced the diminution in magnetostatic energy falls off more rapidly than the increase in domain wall energy and below a critical size the crystal prefers to stay in the single domain state.) It is found that large fields are needed to reverse these single domain particles if they are magnetized in the anisotropic direction.
- b) The pinning of domain walls by inhomogeneities is the alternative mechanism of magnetic hardening as first suggested by Becker (1932) and Kersten (1943).

The second mechanism is responsible for the magnetic hardening of the alloys examined in this study since they are mainly consisted of multidomain grains.

Consider an area A of a 180° domain wall interacting with a pinning site of interaction energy U(x), Fig. 1.2.

Assuming that when the field is zero the minimum of the interaction energy U(x) lies at x = 0 then the total magnetic energy in a field H can be written as:





$$E_{+} = U(x) - 2HIAx \qquad 1.1$$

Where I is the magnetization per unit volume and x is the distance the wall moved after the application of the field H.

The equilibrium state can be found when

$$\frac{dE_t}{dx} = 0 \quad \text{or} \quad \frac{dU}{dx} - 2\text{HIA} = 0 \quad 1.2$$

and is one of maximum or minimum energy depending on whether $\frac{d^2 U}{dx^2}$ is less or greater than zero.

At zero field the domain wall will sit on the positions of minimum energy facing a barrier of height $\Delta E = \Delta U$, Fig. 1.2b. As the field slowly increases the domain wall will move from A to B reversibly and there is no hysteresis. One can actually see that the action of the field is to bring the positions of maximum and minimum energy closer together thus decreasing the height of the energy barrier, Fig. 1.2c, which is then

$$\Delta E = \Delta U - 2HIAx \qquad 1.3$$

At a particular value of the field the domain wall reaches position B, where the slope of the interaction energy is a maximum and where there ceases to be an energy barrier. The wall then suffers an irreversible jump to a new position F which has the same slope as B. This leaves the sample with an increased remanent magnetization.

At absolute zero T = 0, there is no thermal activation. The particular value of the magnetic field required to push the wall past the energy barrier, corresponds to the coercivity of that barrier and is given from Equation 1.2 by

$$H_{c,o} = \frac{1}{2IA} \left(\frac{dU}{dx}\right) \max.$$
 1.4

At any other temperature T, there is always a finite probability that the wall will cross the energy barrier through thermal activation in a lower field than $H_{c,o}$. The probability that the wall will pass the energy barrier ΔE in time τ is given by

$$\tau^{-1} = C e^{-\Delta E / kT}$$
 1.5

Where k is Boltzman's constant and C a constant equal to exp(25) Hz (Bean and Livingston, 1959). Assuming that thermal activation is the only contribution to the temperature variation of the coercivity, then H_c should follow the relation derived by Gaunt (1972).

$$H_{C,T} = \frac{\Delta U}{2IA\Delta x} - \frac{25kT}{2IA\Delta x}$$
 1.6

It is obvious from the previous arguments that if one attempts to calculate the coercivity H_c , he must have an expression for the interaction energy U(x). That is the purpose of this study; to elucidate the origin of magnetic hardening by looking at the nature and distribution of these imperfections throughout the crystal.

1.2 SUMMARY

For this purpose,

- a) The crystal structure and the crystallographic ordering of the alloys were examined by X-ray diffraction analysis (Chapter III).
- b) The hard magnetic properties (H_c, H_R, M_R) were examined for various ordering stages and at different temperatures (Chapter IV). The variation of coercivity H_c with temperature is mainly due to:
 - i) thermal activation
 - ii) the change of saturation magnetization M_s and magnetocrystalline anisotropy K with temperature (intrinsic effects).
- c) Magnetic aftereffect or magnetic viscosity measurements were used (Chapter V). This is a relaxation effect in the magnetization of the sample after the sudden application or the removal of a magnetic field. It is the result of thermal activation of domain walls over the energy barriers. With the

use of magnetic viscosity measurements one can separate thermal activation from the intrinsic effects. Finally, these measurements have to be consistent with the model set up to explain the magnetic hardening.

- d) High field magnetization measurements were used to determine the saturation magnetization M_s and the magnetocrystalline anisotropic K, by least squares fitting to the "law of approach to saturation" (Chapter VI).
- e) The Curie temperature was measured in order to estimate approximately the exchange constant J_{ex}
 (Chapter VII). This value was then used to calculate the domain wall energy (Chapter VIII).
- f) Finally, optical and electron microscopy were employed to image the imperfections and their interactions with domain walls (Chapter IX).

Most of the present work has been devoted to the study of an $\text{FePt}_{0.7}\text{Ni}_{0.3}$ and a $\text{Co}_{52}\text{Pt}_{48}$ alloy. Both of these systems undergo a disorder/order transition below a critical temperature. This transition is from a face-centred cubic to a face-centred tetragonal structure. Hard magnetic properties are produced by appropriate heat treatment.

CHAPTER II

EXPERIMENTAL TECHNIQUES

2.1 SAMPLE PREPARATION

The alloys were melted by arc casting from high purity materials in a water cooled copper boat under an atmosphere of purified argon. To ensure homogeneity the alloys were melted several times. The cast weights were recorded in order to detect any significant melting losses. Weight losses ranged from 0.5 to 1% and were attributed to the tendency of the alloys to splatter when melting.

After the alloys were prepared, samples were cut off using the diamond wheel. A final spherical or oblate spheroidal shape of the specimens was obtained using a grinding apparatus, Fig. 2.1b. (The method is based on the principle that a spinning body which is free to choose its axis of rotation will spin about its axis of maximum moment of inertia. If, then, it touches an abrasive surface it will reduce its largest diameter).

Subsequently, the samples were etched in concentrated HCl acid and they were ready for the heat treatment.

2.1.1 Heat Treatment

The samples were sealed into a clean vycor tube under argon pressure and they were homogenized at a temperature of 1100° C for several hours. Subsequently, the temperature was



Fig. 2.1 (a) High temperature annealing furnace. (b) Apparatus for grinding small spheres.

reduced to $\sim 1000^{\circ}$ C and the samples were quenched by breaking the vycor tube under tap water. Furthermore, the specimens were annealed at various fixed temperatures (600 - 700°C) for different times at the end of which they were quenched in the above way.

All the annealing was done in tube furnaces with temperature control of $\pm 2^{\circ}$ C. Since the highest available temperature from the tube furnaces was 1100° C, a modified single crystal furnace (Fig. 2.1a) was used for higher temperatures. The sample was held with a molybdenum wire inside an alumina tube around which there was a carbon resistance heater. A mixture of argon with 1% H gas was flowing into the tube to prevent oxidation of the sample. The advantage of this system is that the sample can be quenched quickly into the water by cutting the molybdenum wire.

2.2 MAGNETIZATION MEASUREMENTS

The extraction method was used for all the magnetization measurements. This method is based on the flux change in a search coil when the specimen is removed from the coil. The total flux through the coil in an applied field H_a is given by

$$\Phi_1 = BA = (H_1 + 4\pi I)A = (H_a - H_D + 4\pi I)A$$

Where B is the magnetic induction, I is the magnetization of the specimen, A is the area of the sample (it is assumed to be the same as the area of the coil), and N is the demagnetizing coefficient

$$H_{D} = -NI$$

After the sample is removed from the coil the flux through the coil is given by

 $\Phi_2 = H_a A$

The change in flux $\Delta \Phi$, therefore, is

$$\Delta \Phi = \Phi_2 - \Phi_1 = (N - 4\pi) IA$$
 2.1

And is proportional to the magnetization of the specimen I. The emf (e_i) generated on the coils due to the change in flux is

$$e_i \propto \frac{d\Phi}{dt}$$
 2.2

2.3 MAGNETOMETER FOR LOW FIELD MEASUREMENTS

The magnetometer consists of an electromagnet, a power supply, a pick-up coil and an integrator. Through a cold finger, temperatures down to 4.2 K were achieved. For high temperatures up to 700 K a hot finger was used.

2.3.1 Electromagnet

A water cooled Magnion electromagnet driven by a 25 amp regulated power supply was used for all the low field magnetic measurements. The maximum available field was 16 k0e and it could be reversed by a switch in the output of the power supply. The latter was shorted out while the polarity of the coils was reversed, because of the large inductance of the coils of the electromagnet. A 9 mm diameter hole was bored in the pole faces along the axis of the core.

The magnetic field was set by a ten turns potentiometer in the control circuit and it was calibrated against this setting by a flip coil fluxmeter.

i) Field Profile Curves

A small sensing coil was used to determine the field profile in the longitudinal and radial directions of the pole faces of the electromagnet. It was found that in the longitudinal direction the field falls off from the centre (Fig. 2.2) by an amount given by

$$h_1 = - 0.126 x^3 \%$$

Where x is in mm and h_1 is the percentage change of the field. Along the radial direction (perpendicular to the hole axis)



Fig. 2.2 Field profile curves in the electromagnet pole faces; h₁ and h₂ are the longitudinal and radial fields, respectively.

the field increases from the centre by

$$h_r = 0.121 y^2 \%$$

Therefore, for centered specimens of length L and radius R the average change of the field relative to the central field is

$$\bar{h}_1 = -\frac{0.126}{32} L^3 \%$$
 and $\bar{h}_r = \frac{0.121}{3} R^2 \%$

The specimens used for the magnetic measurements had dimensions of L \sim 6 mm and R \sim 2 mm. That would give

$$\bar{h}_1 = -0.85\%$$
 and $\bar{h}_r = 0.165\%$

which are within the expected experimental error.

2.3.2 Coils - Integrator

A compensated pick-up coil of 15,000 turns of no. 44 B.S copper wire was used. The coil was sitting between the pole tips of the electromagnet so that its centre was coaxial with the pole tips.

When the sample was removed from the coils to the interior of the magnet core an emf (e_i) was generated on the coils due to the change in flux (Equation 2.2). This emf (e_i) was, subsequently, integrated through an electronic

integrator (Fig. 2.3) based on a chopper stabilized operational amplifier to produce an output emf e_0

$$e_{o} = -\frac{1}{(R_{i}+R_{s})C} \int e_{i}dt \qquad 2.3$$

Where R_i , R_s and C are defined in Fig. 2.3. Using Equations 2.1, 2.2 and 2.3 one can easily see that e_o is proportional to the magnetic moment of the sample.

$$e_{0} = -\frac{1}{(R_{i}+R_{s})C} \int \frac{d\Phi}{dt}dt$$
$$= -\frac{1}{(R_{i}+R_{s})C} (N - 4\pi)IA$$
$$e_{0} \propto I$$

For static measurements the output voltage was displayed on a digital voltmeter and for magnetic aftereffect measurements on a chart recorder whose full-scale sensitivity varied from 0.5 mV to 500 V. The output drift rate is typically 10 mV/sec when offset voltage and curvent have been adjusted (Fig. 2.3).

2.3.3 Image Effect

The measurements which were made with an electromagnet had to be corrected for the image effect. This is due to the magnetic image of the specimen (Fig. 2.4a) which is present because of the high permeability μ of the pole faces.







(a)



(a) Image effect. (b) Field dependence of the magnetometer output for a constant emu source (V_L) and the image effect factor L such that LV_L is constant.



The magnetic moment of the image equals that of the specimen for infinite permeability μ pole faces, decreases as μ decreases and becomes zero for a perfect diamagnet, $\mu = 0$. It interacts with the specimen and increases the flux density around it. It, therefore, increases the fluxmeter deflection due to the removal of the specimen from the search coil.

The image effect depends strongly on the field, even when the magnetic moment of the specimen is kept constant. The higher the field, the closer the pole caps to saturation and the lower the permeability. This variation causes the magnetic output for a constant moment sample to decrease as much as 5% at 16 k0e.

A small coil of the same size as the specimen carrying constant current to produce a constant magnetic moment was used to find the correction image factor. Fig. 2.4b shows the variation of the magnetometer output V_L due to the image effect and the correction factor L so that LV_L is constant.

2.3.4 Calibration of the Magnetometer

An annealed nickel specimen was used to calibrate the magnetometer. The readings after being corrected for the image effect, produced constant results for the field range of 8-16 kOe, establishing thus a confidence for the image correction factor. By using M = 55.11 emu/g for the magnetic moment of nickel (Crangle and Goodman, 1971) the calibration factor is found to be

calibration factor = (0.1078 ± 0.0005) emu/mV

This was also checked and verified with an iron sample.

2.3.5 Cold Finger

The spatial constraints imposed by the proximity of the pole faces allowed the use of a cold finger arrangement shown in Fig. 2.5 in order to achieve a temperature range from 4.2 K up to room temperature (300 K). This consists of four co-axial stainless steel tubes. Liquid helium (or liquid nitrogen) flows down the inner tube which is isolated by a vacuum space. The two inner tubes are soldered to an oxygen-free high conductivity copper block. At the top of the block there is a hole for the escape of helium gas through the space between the second and third tube.

The copper block is used for the heater and the sample holder. The heater is made out of nichrome wire having a resistance of 40 Ω . At the end of the heater, there is a Au 0.03% at Fe thermocouple used for the temperature controller.

The sample holder is made out of aluminum. At its end there is a copper-constantan thermocouple for measuring the temperature of the sample.

Bellows are used in some places to give more flexibility to the cold finger and reduce the possibility of breaking the joints due to thermal contraction. To prevent the tubes





from touching each other, teflon spacers were used. The sample was centered through the position adjustment shown in the figure. Liquid helium is transferred into the cold finger through the transfer tube shown in the block diagram of Fig. 2.6.

2.3.6 Hot Finger

Fig. 2.7 shows a schematic diagram of the hot finger. It basically consists of a copper block thermally isolated from the surroundings by a stainless steel tube and a vacuum jacket. The heater is made out of nichrome wire with a total resistance, $R = 32 \Omega$ and it is wound around the copper tube. The sample is mounted on the end of the copper block close to the thermocouple. A piece of glass served as a spacer for thermal isolation of the heater.

2.4 MAGNETOMETER FOR HIGH FIELD MAGNETIC MEASUREMENTS

2.4.1 Superconducting Magnet

The "approach to saturation" magnetization measurements were made in fields produced by a superconducting magnet from S.H.E. Manufacturing Company (Superconducting Helium Electronics). The magnet (Fig. 2.8) consists of a solenoid of type II superconducting wire layer wound to a non-magnetic former. It has a working bore of 40 mm and an overall length of 220 mm. Test results show a maximum field at 4.2 K of



- 1. Mercury manometer, 0 to 20" Hg or pressure gauge on Helium dewar.
- 2. Accessory flow control panel.
- 3. Accessory temperature controller, manual or automatic.

Fig. 2.6 Typical set up for the cold finger use.




Fig. 2.8 Circuit for a superconducting magnet.

87 kG and a quench field greater than 85 kG. At temperatures below 4.2 K a field higher than 100 kG can be obtained.

i) Superconducting Switch

A switch (Fig. 2.8) including a thermally isolated superconducting wire is connected across the terminals of the magnet to allow the magnetic field to be maintained for a long time without passing current into the cryostat. When the switch is closed the wire is superconducting. When it is open a heating coil heats the superconductor above its transition temperature and the switch becomes resistive.

ii) Power Supply

A constant current power supply (DPS - 100) is used to supply the current to the superconducting solenoid. Its long-term stability is 1 in 10^3 . It provides a steady sweep rate because of the large inductance of the solenoid. The field can be reversed by switching the terminals of the power supply.

iii) Field Profile

The shape of the winding of the superconducting wire is arranged to provide adequate homogeneity of the magnetic field in the working bore. Test results (Table 2.1) show that the homogeneity of the field is 0.041% in a vertical distance of 4 cm across the centre of the magnet. (In 공영화지율지

Table 2.1 Field profile in the superconducting magnet.

Z (cm)	R (cm)	$\left(\frac{H}{I}\right)_{\text{axial field}}\left(\frac{kG}{A}\right)$	$\left(\frac{H}{I}\right)_{radial field}\left(\frac{kG}{A}\right)$
0.00	0.00	1.19948E+03	
1.00	0.00	1.19968E+03	
2.00	0.00	1.19907E+03	
3.00	0.00	1.19372E+03	
4.00	0.00	l.17657E+03	
5.00	0.00	l.13769E+03	
6.00	0.00	1.06527E+03	
0.00	0.10	1.19948E+03	0.00000E-01
1.00	0.10	1.19968E+03	-1.05319E-02
2.00	0.10	1.19907E+03	1.03273E-01
3.00	0.10	1.19372E+03	4.90138E-01
4.00	0.10	1.17657E+03	1.30718E+00
5.00	0.10	1.13769E+03	2.67890E+00
6.00	0.10	1.06527E+03	4.66247E+00
0.00	2.20	1.18759E+03	-4.76837E-07
1.00	2.20	1.18906E+03	-1.75167E+00
2.00	2.20	1.19288E+03	-1.28359E+00
3.00	2.20	1.19618E+03	4.91144E+00
4.00	2.20	1.19160E+03	2.11698E+01
5.00	2.20	1.16765E+03	5.03740E+01
6.00	2.20	1.11154E+03	9.42397E+01

Table 2.1, z is the vertical distance from the centre of the bore, R is the radial distance and the field is represented by the sensitivity of the superconducting coil $\frac{H}{I}$ ($\frac{kG}{A}$) at 4.2 K).

2.4.2 Cryostat and Vacuum Systems

The magnet was vertically suspended inside a Pope dewar through some stainless steel tubes of 0.010" wall thickness (Fig. 2.9). This dewar was filled with liquid helium so that the superconducting magnet is at liquid helium temperature (4.2 K) during operation. The helium dewar is also immersed in another Pope dewar which is filled with nitrogen. The top of the helium dewar is connected through an o-ring to the cryostat head which is made out of brass. Both dewars and the cryostat head are fixed to a thick aluminum plate which is the top of a cage enclosed on four sides by plexiglass and plywood to protect the dewars and the magnet.

The current from the power supply is carried down the magnet by lead coated brass tubes. Liquid helium is transferred into the helium dewar through a stainless steel tube which ends below the magnet. The flap valve is kept open during operation for the escape of helium gas, in case the superconducting magnet goes normal (magnet quench).

This apparatus was designed for a variety of experiments so inserts were made to fit into the cryostat which could be decoupled from the vacuum systems. A flow diagram of the



Fig. 2.9 Cyrostat assembly.

vacuum system is shown in Fig. 2.10.

2.4.3 Inserts

Three inserts were used for the experimental observations. Two of them were designed to be used for different temperature ranges. The third one was made to be used with a new set of very sensitive and well compensated coils.

i) High Temperature Insert

This insert was initially designed to be used for the temperature range of 4.2 K to 600 K. It basically consists of a nitrogen dewar jacket (Fig. 2.11) made out of copper which is vacuum isolated from the sample and helium spaces. The nitrogen dewar serves as a sink for the heat generated by the furnace, so that less liquid helium boils off. It also decreases the heat loss from the furnace due to radiation processes.

The furnace is made out of a copper tube along which there is a groove with a flat end. A nichrome wire is used as the heater. It runs up and down the groove having a total resistance of 15 Ω . A platinum resistance thermometer is placed on the flat end for the temperature control. The furnace is isolated from the nitrogen dewar by a quartz glass spacer.

The coils are fixed at the end of the outside part of the insert which is immersed into the magnet bore.



Fig. 2.10 Vacuum system flow diagram.



Fig. 2.11 High temperature insert.

Since this insert could not go below 30 K, another one was designed to be used at liquid helium temperatures. (An insert is constructed in such a way that the bottom part is made out of copper for uniform temperature and the top is made out of stainless steel so that less heat is transferred from the outside down to the helium bath).

ii) Low Temperature Insert I

Fig. 2.12 shows a schematic diagram of the low temperature insert. A vacuum is necessary to isolate the furnace from the helium bath. The sample could also be isolated from the furnace by a vacuum space. The furnace is similar to that used with the high temperature insert. Thermistors are used for the temperature control because the platinum resistance thermometer is field dependent below 30 K.

This insert could be used from 4.2 K up to 100 K.

iii) Low Temperature Insert II

This insert could only be used at 4.2 K. The demand for high accuracy in the high field magnetization measurements $(1:10^{4})$ made necessary the use of extremely well compensated coils (new coils) whose restricted dimension forced the design of the insert shown in Fig. 2.13. The sample is thermally isolated from the helium bath by a vacuum jacket.



Fig. 2.12 Low temperature insert I.

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Fig. 2.13 Low temperature insert II.

2.4.4 Additional Parts of the Magnetometer

Other accessories which are needed to complete the apparatus for the high field magnetization measurements include the sample holder, the piston chamber for moving and positioning the sample, the liquid nitrogen blow-off, the integrator and the temperature controller.

i) Sample Rod

The sample rod consists of a stainless steel tube joined with a glass rod (for isolation) through a copper tube (Fig. 2.14). The end of the glass rod is connected with a copper block where the thermocouple sits and at the bottom of which the sample is held with an aluminum holder. The glass rod is fixed to the copper block with "Plio-bond" glue. The top end of the sample holder is made out of a stainless steel plug through which the thermocouple wires pass. The wires were brought out of the vacuum space via a silicon rubber seal.

ii) Piston Chamber - Sample Positioning

The sample rod is fixed to a piston (Fig. 2.15) which is driven by a solenoid valve with the help of helium gas (Fig. 2.16). In phase 1, valves B and D only are opened and the piston is moving to the right, while in phase 2, B and D are closed and the piston is moving to the left.

Adjustment screw A (Fig. 2.15) is used only with the new coils for the vertical positioning of the sample in the



Fig. 2.14 Sample rod.

·_y. 2.1



Fig. 2.15 Piston chamber and sample positioning attachment.





centre of coil 2 (sample in up position) while screw B is used with the new coils to centre the sample in coil 1 in the down position or with the old coils to centre the sample in the main coil.

iii) Liquid Nitrogen Blow-off

The liquid nitrogen blow-off is used to blow all nitrogen which was used to pre-cool the superconducting magnet in the helium dewar. It is made out of copper having the schematic diagram shown in Fig. 2.17. This fits into the fill tube of the helium dewar. On the fill tube there is a hole to prevent oscillation of the liquid helium bath. That is why the two o-rings were used to help in building up a pressure on the surface of the liquid nitrogen which is subsequently pushed out of the dewar through the tube.

iv) Integrator

The integrator used with the high field magnetometer was the same one used with the electromagnet as described earlier in Section 2.3.2.

v) Temperature Control Unit

Temperatures above 4.2 K were obtained by slowly heating up the furnace which is then coupled to the sample with some helium gas. The temperature was controlled by the unit shown in Fig. 2.18. The control element is a thermistor. The IR



Fig. 2.17 Liquid nitrogen blow off.



Fig. 2.18 Block diagram for temperature control unit.



drop across the thermistor created by a constant current I is backed-off by a reference set point voltage V_s . The difference V_s - IR is fed into a null-detector, the analogue output from which is used as the input of the dc temperature controller supply. Temperatures were measured with a copper-constantan thermocouple and then regulated to ±1 K.

2.4.5 Instructions for the Use of Superconducting Magnet

There are some steps which should be followed when the superconducting magnet is used. The following instructions referred to the case where the high temperature insert is used. If other inserts are used avoid the steps associated with the high temperature insert.

- a) Flush (air) and pump He vacuum space (glass dewar)
 several times, then seal in mechanical vacuum.
- b) Flush (air) and pump N₂ vacuum space (insert)
 several times then seal in diffusion pump vacuum.
- c) Flush (He) and pump sample and furnace spaces (insert) several times then seal in exchange gas (½ atm. He).
- d) Flush (dry N₂) and pump magnet space several times then seal in 1 atmosphere N₂ gas.
- e) Cool down system.
 - i) Fill liquid N₂ dewar (glass).
 - ii) Put LiN₂ to top of magnet (He dewar).
 - iii) Fill LiN₂ dewar (insert).

- f) Wait.
- g) Blow LiN, out of magnet space.
- h) Flush (He gas) and pump magnet space.
- i) Fill magnet space with LiHe.
- j) Adjust exchange gas pressures.

One can change the sample while the liquid helium is still in the dewar with the following steps.

- a) Release pressure in piston chamber.
- b) Disconnect polyflow tubing from the piston chamber.
- c) Remove sample holder having helium gas flowing in the sample space.

2.4.6 Flux Creep - Coils

i) Flux Creep

The phenomenon of flux creep accompanying the displacement of the sample inside the superconducting magnet was studied thoroughly by J. P. Rebouillat (1972). If a sample is placed in the magnetic field of a superconducting magnet, it will concentrate the lines of force. The flux through the space between the sample and the magnet will not attain immediately its equilibrium value but it will increase with time creeping back to the sample through the superconducting material (Fig. 2.19a). If the sample is then removed from the magnet, the flux will decrease with time creeping back



Fig. 2.19 (a) Flux creep through a superconducting loop when a sample is brought at its centre.
(b) A dipole moment represented by a planar loop carrying current i inside a sensing coil carrying current I.

to its original place through the superconducting material.

The sensing coil which is around the sample will, thus, measure a change in flux $\Delta \Phi$ due to creeping of the lines of force.

It was found by J. P. Rebouillat that the change of flux $\Delta \Phi$ due to creep is a logarithic function of time up to 140 sec (\propto a M log ($\frac{t_0+t}{t_0}$), "a" constant, M moment of the sample and t₀ a constant depending on the base of logarithim) and beyond this time it is constant. He also observed that the flux $\Delta \Phi$ is proportional to the magnetic moment of the sample and it is field independent. Sensing coils, therefore, should be designed in order to minimize the flux creep.

ii) Coils

The construction of a sensing coil is based on the assumption that $\frac{B}{I}$ should be large and constant over a large volume within the coil. B is the magnetic field produced inside the coil after a current I passes through it. This condition would be easily understood after considering Fig. 2.19b. The moment M of the sample is represented by a planar circular loop of surface S, carrying a current i, M = Si. If the sample is ellipsoidal of uniform magnetization, it can be represented by a dipole as above. Around the loop there is a sensing coil carrying current I. The mutual inductance between the loop and the sensing coil is L. If the field produced by the sensing coil at the loop

is B then the flux through the loop is

 $\Phi_1 = BS = LI$

On the other hand, the flux passing through the sensing coil due to the loop is

$$\Phi_2 = \text{Li} = \frac{\text{BS}}{\text{I}} \text{i} = \frac{\text{B}}{\text{I}} \text{M} \qquad 2.4$$

Therefore, the flux is proportional to the dipole moment to be measured through the constant $\frac{B}{I}$. The coil is thus more sensitive when $\frac{B}{I}$ is large and constant over a large distance within the coil (so that small displacements of the sample from the centre of the coil will not affect the readings).

a) Old coils system

The old coils system (original coils which can be used at 4.2-600 K) consists of the three coils shown in Fig. 2.11. The two compensating coils B and C are connected in series to each other and in opposition to the main sensing coil A.

The coils are made out of no. 44 gauge "P-bondal magnet wire". The superimposed film of thermoplastic bonding material make the wire to be bonded turn by turn after heating it at 100°C. The main coil has 100,000 turns with R = 80 k Ω . It is sixth order corrected with $\frac{B}{I}$ constant to 1:10⁴ over an inch at its centre.

However, this system does not correct for the flux creep. It is found experimentally that the flux creep after 15 secs corresponds to 1% of the total signal of the sample.

b) New coil system

For the high field magnetization measurements one needs high accuracy in the data in order to detect small changes in moment corresponding to susceptibilities of $\chi \sim 10^{-6}$ emu/g/0e. That would correspond to a resolution of more than $1:10^{-4}$. The coils, therefore, must have the right sensitivity to detect a change in flux of $1:10^{-4}$. This will be the result if the coils are corrected for the flux creep.

The dimension and the relative positions of the coils in the new coil system are shown in Fig. 2.20 (5:1 scale). The two main coils (coil 2, coil 3) are corrected independently for the flux creep by having around them co-axial compensation coils (coil 1, coil 4). The coil dimensions were adjusted experimentally for the best compensation. They are made out of no. 44 gauge wire of 0.002" thickness. Each of the main coils have 10,941 turns at the slot and an extra 1,312 turns at the ends. Their total resistance is $R_1 =$ 10,560 Ω . The two compensating coils have 912 turns each with a total resistance of $R_2 = 1,912 \Omega$.



For a high resolution in the magnetic measurements a plateau on the $\frac{B}{I}$ curve was found at the centre of the two effective coils. That was done by computer and the results are shown in Fig. 2.21. $\frac{B}{I}$ is constant to 2:10⁻⁴ over a distance of 4.7 mm at the centres of the two main coils.

In this new system the main coils are placed near the sample and the compensating coils are near the superconductor. When the sample leaves the main coil 2, the trapped flux near this coil will tend to decrease (by creep). The same effect will be observed in the compensating coil 1, which is around the main coil 2. However, the total change of flux is considerably reduced since the two coils are connected in opposition. Similarly, when the sample reaches the main coil 3, the flux near this coil will tend to increase. This, however, is balanced by the decrease of flux creep in coil 4 since the two coils are connected in opposition.

The flux which has crept through the superconductor in 15 secs represents a change of 0.1% of the total change in flux due to the displacement of the sample. Thus, flux creep correction for these coils is an order of magnitude better than in the old coil system.



2.4.7 Magnetization Measurements - Calibration

i) Magnetization Measurements

Magnetization measurements were made by the extraction method as described earlier in Section 2.2. Because of the desired high accuracy in the readings an attempt was made to correct for the integrator drift and the remaining flux creep due to the non-perfect compensation of the pickup coil. Fig. 2.23 shows the intervals at which a magnetization reading was taken.

Initially, the sample is in the down position labelled as "in", for a certain time t1. If the rate of the integrator drift is b then the reading at A is

 $R_A = bt_1$

The sample is then moved in the up position labelled as "out", and it stays there for a time t_2 at the end of which a reading R_B is taken

$$R_{B} = bt_{1} + M + aM ln(\frac{t_{0}+t_{2}}{t_{0}}) + bt_{2}$$

Where M is the moment of the sample and aM $\ln(\frac{t_0+t_2}{t_0})$ is related to the flux creep during the time interval of t_2 . This cycle was repeated several times and the magnetization readings R_C , R_D , were taken.





$$R_{C} = bt_{1} + M + aM \ln(\frac{t_{0}+t_{2}}{t_{0}}) + bt_{2} - M - aM \ln(\frac{t_{0}+t_{3}}{t_{0}}) + bt_{3}$$

The difference between the "out" and "in" readings is named $\ensuremath{\mathtt{d}_1}$

$$d_1 = R_B - R_A = M + aM \ln (\frac{t_0 + t_2}{t_0}) + bt_2$$

And it includes the integrator drift, bt₂. On the other hand, the difference between the "in" and "out" readings is given by

$$d_2 = R_C - R_B = M + aM \ln(\frac{t_0 + t_3}{t_0}) - bt_3$$

If, however, the time intervals are the same, $t_1 = t_2 = t_3$, one can find a reading \overline{d} proportional to the moment of the sample by averaging d_1 and d_2

$$\bar{d} = \frac{d_1 + d_2}{2} = KM$$
 , $K = 1 + a \ln(\frac{t_0 + t}{t_0})$

It was, therefore, important to make the measurements at regular intervals to obtain a reproducible value. The time for which the sample stays in the "in" position should be equal to the time it stays in the "out" position. That was made possible by a timer which activated the solenoid valve and moved the sample in and out. A number of measurements had to be taken in the "in" and "out" positions since after a few cycles the measurements tended towards a final steady value. Therefore, in the final analysis a number of "in" and "out" differences were averaged with "out" and "in" differences giving a value proportional to the moment of the sample.

ii) Calibration

The magnetometer was calibrated with an annealed iron sphere. By using J. P. Rebouillat's (1972) magnetization values of Fe at different fields a calibration factor K(H) was found in the range of 20 - 70 k0e.

$$M_{Fe}(H) = K(H) (e_0)_{Fe} = \frac{K(H)}{R_C} \int e_i dt$$

then

 $K(H) = \frac{M_{Fe}(H)}{e_{O}}$ (e_o is the integrator output)

Values of K(H) at different fields were least squares fitted to a third degree polynomial in H for the old coils and to a sixth degree polynomial in $\frac{1}{H}$ for the new coils giving the following expressions for K(H)

 $K(H)_{old coils} = 52.71356 + 6.79682H + 13.93258H^2 - 5.88728H^3$

$$K(H)_{\text{new coils}} = 53.82651 - \frac{5.81619}{H} + \frac{3.75412}{H^2} - \frac{1.38369}{H^3} + \frac{0.29453}{H^4} - \frac{0.003377}{H^5} + \frac{0.00162}{H^6}$$

The sample moment is then found by

$$M_{sample}(H) = K(H) (e_{o})_{sample}$$

In the case where magnetization measurements were taken above 70 KOe, a correction for the magnetoresistance of the coils was necessary. Figures 2.23 and 2.24 show how the resistance of the coils varies with the field. If above 70 KOe

$$M_{Fe}(H) \propto e_{O}(R + R_{COII}(H))$$

Where $R_0 = 10 \ k\Omega$, is the input resistance of the integrator and R_{coil} (H) is the resistance of the coils at field H, then

$$K(H)_{H>70 \text{ kOe}} = K(H_{O}) \frac{(R_{O}+R_{coil}(H))}{(R_{O}+R_{coil}(H_{O}))}$$

Where $K(H_0)$ is found from Equation 2.5 with $H_0 = 70$ k0e.

2.5 X-RAY TECHNIQUES

Ordering in $\text{FePt}_{0.7}^{\text{Ni}}_{0.3}$ and $\text{Co}_{52}^{\text{Pt}}_{48}$ has been studied both photographically and by diffractometer using a copper or cobalt radiation with the appropriate filters.

The diffractometer tracings were taken with chemically etched samples in the form of thin foils. Bulk specimens having a plate-like shape with sharp edges were used for





the powder camera method. These samples were aligned in such a way that while they were rotating about the camera axis, the collimated x-ray beam was striking the same edge all the time. This method gave an accurate estimate of the lattice parameters using the high angle lines in the final analysis. Exposure times ranged from 4 - 6 hours with an anode current of 20 mA at 40 kV for a copper tube and 15 mA at 40 kV for a cobalt tube.

The single crystal grains were oriented using a back reflection Laue photograph and its stereographic projection with the use of Greninger's chart.

2.6 OPTICAL AND ELECTRON MICROSCOPY

2.6.1 Optical Microscopy

Surface microstructure observations were made on specimens which were cut from the bulk sample by the diamond saw. The flat surface of these specimens was then mechanically polished and examined with an ordinary optical microscope.

Extra care was taken for the surface of the samples which were used for the domain wall observations. In this case the surface was polished down to $\frac{1}{2}\mu$ diamond powder. In some cases etching followed polishing for the removal of the damaged surface layer. The samples then were annealed at 1000° C for 16 hrs for the relief of the remaining surface strains and they were ready for the application of ferro-
fluid. That was supplied by the Ferrofluidics Corporation and is a magnetic fluid consisting of 300 Å particles in a water carrier. A total amount of ½ drop was satisfactory for a specimen 1 cm diameter. The ferrofluid had to be pressed down carefully on the specimen surface by a glass cover slip so that the thinnest possible fluid layer existed. This is important since the ferrofluid layer must be transparent to observe the microstructure.

2.6.2 Electron Microscopy

Samples with thinned areas (~1000 Å) for the electron microscopy observations were produced by electropolishing. Specimens in the form of plates of 5 mm thickness were cut from the bulk ignot by a diamond saw and they were cold rolled down to 0.005". Since the specimens are fairly brittle, especially in their ordered state, a cycle of rolling and annealing was repeated several times, before the desired thickness was obtained.

Using the common window technique a 1 x 1 cm² sample whose edges were laquered was electropolished in a concentrated HCl acid bath using a voltage of 2 - 3 V. In some cases thin foils were prepared by cutting discs of 3 mm diameter with a spark cutting machine and electro-jetting them with an electrolyte of HCl acid using a current of approximately 100 mA. These discs were finally electropolished in the previously described way. In any case, the samples

were heat treated just before they were electropolished. They were examined in a 100 kV Philips EM 300 electron microscope.

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CHAPTER III

CRYSTAL STRUCTURE AND ORDERING

3.1 INTRODUCTION

A review of the crystal structures of FePt and CoPt alloys is given.

FePtNi alloys were made by substituting some of the platinum atoms with Ni and they were examined crystallographically. The ordering process has been investigated for an $^{\rm FePt}_{0.7^{\rm Ni}_{0.3}}$ and a $\rm Co_{52}^{\rm Pt}_{48}$ alloy.

3.2 IRON - PLATINUM

Below the solidus iron and platinum form a continuous series of solid solutions which on being cooled to lower temperatures undergo transformations. Their constitution diagram Fig. 3.1a (A. Kussmann, 1950) shows three stable superstructures: Pt_3Fe , PtFe, and $PtFe_3$. The γ -solid solution of the Fe-Pt system has a disordered face centered cubic structure of the Cu type. Fig. 3.2a shows the unit cell of Cu type. The variation of the lattice spacing of this phase with composition is shown on Fig. 3.2b.

The superstructures Fe_3Pt and FePt_3 have an ordered cubic structure of the Cu₃Au type. Their unit cells are shown in Fig. 3.2 b and 3.2 c and they can be thought of in terms of four interpenetrating simple cubic sublattices.

Pt, at. %







(b)

Fig. 3.1 (a) Phase diagram of Fe-Pt. (b) Lattice parameters of disordered Fe-Pt alloys as a function of composition.



Unit cells of the FePt system (a) Disordered cubic FePt (b) ordered FePt₃ (c) ordered Fe₃Pt (d) ordered tetragonal FePt. Fig. 3.2

The ordered FePt phase which according to the phase diagram exists in the range of 30-65 atomic % Pt has a tetragonal structure of the CuAu type. In this specific case, the ordering transformation involves a decrease in dimensions along the Z axis and an increase along Y and X leading to tetragonality with $\frac{c}{a} < 1$. Fig. 3.2d shows its unit cell. Fe and Pt atoms are disposed in layers parallel to {100} planes.

A. Z. Menshikov (1974) has recently studied the type of structure and magnetic ordering, the lattice parameters and the degree of long range order of a number of FePt alloys with different compositions.

The existence of a disordered f.c.c. state in the equiatomic FePt alloy could not be shown so far. This is because in FePt, ordering is so rapid that it cannot be suppressed by quenching so that the alloy is overaged after any form of heat treatment. Kussman et. al. (1950) supposed from investigation on off-stiochiometric alloys the critical temperature for the order/disorder transition near 1300°C.

P. Gaunt and G. Hadjipanayis (1976) prepared alloys in which some of the platinum was replaced by nickel. These alloys retained the cubic phase on quenching and while ordering one can easily control the volume fraction of the ordered phase by the appropriate heat treatment.

3.3 IRON - PLATINUM - NICKEL

The three binary compounds formed from the elements of iron, nickel and platinum have a number of ordered phases with either Cu₃Au structure (Fe₃Pt, Ni₃Pt, FePt₃, FeNi₃) or the CuAu tetragonal superstructure (FePt, NiPt). Paulene (1962) has also reported a tetragonal superlattice in neutron irradiated FeNi. Shôtaro Shimizu and Eigô Hashimoto (1971) have studied the ordering in PtFe-PtNi alloys by replacing some of the Fe atoms with Ni. Fig. 3.3 shows the variation of the lattice parameters of disordered and ordered FePt-PtNi alloys.

Alloys of composition $Pt_{1-x}Ni_xFe$ have also been examined crystallographically (G. Hadjipanayis, 1974). Compounds with composition x = 0.2 and 0.3 showed a disordered face-centered cubic structure after quenching from 1000° C. Both of these form a tetragonal ordered structure of CuAu type at lower temperatures with Pt/Ni atoms at [000] and $[\frac{1}{2}\frac{1}{2}0]$ and Fe atom at $[0\frac{1}{2}\frac{1}{2}]$ and $[\frac{1}{2}0\frac{1}{2}]$.

The alloy with x = 0.4 showed the cubic ordered structure PtFe₃ on subsequent annealing with Pt/Ni atoms at [000] and Fe atoms at $[\frac{1}{2},\frac{1}{2}0]$, $[\frac{1}{2}0,\frac{1}{2}]$ and $[0,\frac{1}{2},\frac{1}{2}]$.

These results agree with the recent observations of G. T. Stevens et. al. (1978) who determined qualitatively the form of the 600[°]C isothermal section of the ternary equilibrium diagram FePtNi (Fig. 3.4).



Fig. 3.3 Lattice parameters of PtFe-PtNi alloys.



3.3.1 Ordering in FePt_{0.7}Ni_{0.3}

Ordering during isothermal tempering has been examined in a foil of FePt_{0.7}Ni_{0.3} alloy which has been homogenized at 1000°C and quenched in water. The change in x-ray diffraction lines during ordering at 600°C and 700°C is described as continuous. The fundamental cubic lines gradually broaden into bands that are later resolved into the tetragonal lines corresponding to the ordered structure. This process is best studied from a (311) reflection. The profiles of (311) lines are shown in Fig. 3.5. The original (311) cubic line broadens in the process of ordering and gradually divides into two smeared (311) and (113) tetragonal phase lines which then shift to their final position and become more distinct.

The lattice parameters and the $\frac{c}{a}$ ratios are shown in Table 3.1 for tempering at 700^oC; $(\frac{c}{a})_{str}$ is the ratio determined from the main lines (311) and (113) and $(\frac{c}{a})_{super}$ is determined from (203) and (312) super structure lines.

During tempering at 700°C the value of $(\frac{c}{a})_{str}$ gradually falls as ordering proceeds. Even in the early stages of ordering, the $(\frac{c}{a})_{super}$ ratio is significantly lower than one and less than $(\frac{c}{a})_{str}$. This supports the conclusion that ordering involves the nucleation and growth of ordered phase domains with a relatively high degree of long range order S.

States for which $(\frac{c}{a})_{str}$ and $(\frac{c}{a})_{super}$ do not coincide have frequently been reported by E. V. Kozlov et. al. (1967), G. V. Ivanova et. al. (1975) and L. M. Magat et. al. (1971).



Fig. 3.5 Diffractometer curves of 311-113 reflection taken on polycrystalline FePt_{0.7}Ni_{0.3} after annealing at 700^oC.

Table 3.1	Variation in $(\frac{C}{a})$ ratio of FePt _{0.7} Ni _{0.3} in the
	process of isothermal annealing at 700°C (esti-
	mated error ±0.002).

Annealing Time	^a f.c.c ^(A) *	$\left(\frac{c}{a}\right)_{str}$	$\left(\frac{c}{a}\right)$ super
l min	3.758		
5 "	3.756	-	0.989
20 "	-	0.988	0.982
40 "	· _	0.983	0.979
2.5 hr	-	0.980	0.979
48 "	-	0.979	0.978
500 "	-	0.978	0.977

* Lattice parameter of the disordered cubic phase.

This is due to the fact that $\left(\frac{c}{a}\right)_{super}$ corresponds to the level of long range order inside antiphase domains, while $\left(\frac{c}{a}\right)_{str}$ corresponds to the average level of long range order inside the alloy. At the early stages of ordering (Chapter VIII) the entire volume is occupied by small ordered nuclei of the tetragonal phase but due to their partial or complete coherence the structure reflections give an average pattern of the tetragonal phase with a lower tetragonality (lower S thus higher $\left(\frac{c}{a}\right)$) or even that of a distorted cubic phase.

The smaller the nuclei are the more the difference is. However, when the nuclei are grown in size they give the independent x-ray pattern. This can be seen from the converging of $(\frac{c}{a})_{str}$ and $(\frac{c}{a})_{super}$ as annealing continues.

The same alloy has been homogenized at $1350^{\circ}C$ (high homogenization), quenched from $1000^{\circ}C$ and subsequently annealed at $700^{\circ}C$. The x-ray results are identical to the previously discussed.

3.4 COBALT - PLATINUM

Below the crystallization temperature, cobalt and platinum form a continuous series of solid solutions although transformations occur at lower temperatures.

J. B. Newkirk et. al. (1951) demonstrated the existence of discrete regions of order in equilibrium within regions of disorder at composition on either side of the 50 atomic percent alloy. These observations, together with the sharp discontinuities found on the resistance temperature curves (Fig. 3.6), confirmed that the ordering process based on the equiatomic cobalt-platinum alloy is a phase change of the first kind.

The phase diagram Fig. 3.7 shows two stable superstructures CoPt and CoPt₃. The ordered CoPt phase has a tetragonal structure of CuAu type similar to that of FePt, Fig. 3.2d. As a result of careful x-ray work, Rudman et. al. (1957) established the true critical temperature as $833^{\circ} \pm 2^{\circ}$ C. The long range parameter unity at 615° C was found to be 0.78 at the critical temperature.

The superstructure compound CoPt_3 was reported by Geisler et. al. (1952). The symmetry of the lattice is undisturbed by this ordering process which results in a movement of cobalt atoms to the corner sites and platinum atoms to the face centres of the original unit cell (Fig. 3.2c). The critical temperature of this transformation is between 700[°] and 800° c.

The lattice parameters for the disordered alloys quenched from 1000° C are shown in Fig. 3.8a.

The axial ratio is strongly influenced by the temperature of the heat treatment. As shown by P. S. Rudman et. al. (1957), it increases from 0.9680 at 600[°]C to 0.7800 at the critical temperature for the equiatomic CoPt alloy (Fig. 3.8b).

The lattice parameter of the $CoPt_3$ disordered alloy at 800°C is 3.829Å after quenching and 3.831Å after ordering at



Per cent Change in Resistance





Wt. % Co

Fig. 3.7 E

Equilibrium diagram of the Co-Pt system.





Fig. 3.8 Lattice parameters for Co-Pt alloys. (b) Variation of $\binom{C}{d}$ ratio with temperature in the equiatomic CoPt alloy.

700[°]C, as shown by A. H. Geisler et. al. (1952).

3.4.1 Ordering in Co₅₂Pt₄₈

Ordering during isothermal tempering has been examined in a Co₅₂Pt₄₈ alloy at 600°C and 700°C after being homogenized at 1000°C and quenched in water. X-ray studies reveal two modes of ordering as has been reported earlier by J. B. Newkirk et. al. (1951) and H. N. Southworth and B. Ralph (1969). Ordering at 600°C is described as "discontinuous". Tetragonal phase lines appear immediately beside the cubic lines and become stronger as time goes on. For a time the f.c.c. lines coexist with them, then they become weaker and eventually disappear and only tetragonal phase lines are observed. This is shown in Fig. 3.9 for the (311) profiles.

The superlattice lines initially appear diffuse and in later stages become sharp in the centre with shoulders on either side of the peak (Fig. 3.10). As it will be seen from electron microscopy observations, the broadening of these lines is mainly due to coherency strains between regions of ordered and disordered material. The sharp peaks which appear on the top of the ordered diffuse lines are due to large ordered domains which grow irregularly and rapidly at the grain boundaries.

The variation of the lattice parameters and $(\frac{c}{a})$ ratios are shown in Table 3.2a. $(\frac{c}{a})_{str}$ was determined from the positions of (311) and (113) lines while $(\frac{c}{a})_{super}$ was deter-





Table 3.2 Results of X-ray diffraction analysis of Co₅₂Pt₄₈. (a) Annealed at 600°C; (b) annealed at 700°C; and (c) annealed at 700°C after being homogenized at 1350°C (high homogenization).

Annealing Time	af.c.c ^(A)	$\left(\frac{c}{a}\right)_{str}$	(<u>c</u>) a) super
5 hr	3.761	0.975	0.972
12 "	3.762	0.969	0.970
16 "	3.760	0.970	0.969
32 "	-	0.969	0.969

(a)

(b)

Annealing Time	$(\frac{c}{a})_{str}$	(^C _a) super	
2 min	-	0.982	
7 "	0.991	0.976	
17 "	0.985	0.972	
16 hr	0.974	0.973	

(c)

Annealing Time	$\left(\frac{c}{a}\right)_{str}$	(^C a) super
17 min	-	0.985
42 "	0.981	0.977

mined from the (203) and (312) superstructure lines.

Ordering at 700[°]C is similar to that of $\text{FePt}_{0.7}\text{Ni}_{0.3}$ (Fig. 3.6). The process is described as "continuous". The disordered f.c.c lines initially broaden and later are resolved into the tetragonal lines corresponding to the ordered structure. The $(\frac{C}{a})$ ratios are shown in Table 3.2b.

The axial ratios $(\frac{c}{a})_{str}$ and $(\frac{c}{a})_{super}$ differ markedly for the same polycrystalline specimens during tempering at 700°C but they are practically the same at 600°C. Tempering at 700°C produces a homogenous finely dispersed structure with comparatively high degree of long range order. The degree of long range is higher at 600°C but the structure is very inhomogenous.

The fact that $(\frac{c}{a})_{super}$ is much less than $(\frac{c}{a})_{str}$ supports the idea that ordering in CoPt proceeds via the nucleation and growth of discrete ordered domains in a disordered matrix. This is also supported by the examination of precipitation-hardening aging curves of CoPt alloys, (Fig. 3.12 by J. B. Newkirk et. al. (1950)). It is obvious that the maximum hardness occurs when the alloy is not fully ordered so that the high strength can be interpreted in terms of a domain-size hardening.

The same procedure has been repeated with the same alloy homogenized at 1350° C (high homogenization) and quenched from 1000° C in water. After being annealed for 17 minutes at 700° C the alloy was ordered with no detectable splitting of the



(a)



(b)

Fig. 3.11 Precipitation aging curves for (a) $Co_{48}^{Pt}_{52}$ and (b) $Co_{42}^{Pt}_{58}$ alloys.

tetragonal lines. The superstructure lines are broad and diffuse and this is due to the very small size of the ordered regions. Further annealing produces splitting of the main lines. The lattice parameters are shown in Table 3.2c.

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CHAPTER IV

HARD MAGNETIC PROPERTIES

(Initial Magnetization, Remanence and Coercivity)

4.1 INTRODUCTION

It has been seen from earlier discussions that coercivity $H_{\rm C}$ and remanence $M_{\rm R}$ (technical magnetic properties) are important parameters in determining the magnetic hardening of a material.

In this chapter these technical magnetic properties are being investigated at different temperatures and for various stages of ordering.

4.2 HYSTERESIS AND REMANENCE LOOPS

Wohlfarth (1958) has shown that for an assembly of noninteracting single domain particles with uniaxial anisotropy the equation

 $M_D(H) = M_R(\infty) - 2M_R(H)$ is obeyed. 4.1

 $M_{\rm R}\,({\rm H})$ is the initial remanence of freshly aged specimens, $M_{\rm D}\,({\rm H})$ is the remanence obtained after saturating the specimen and applying a reverse field H and $M_{\rm R}\,(\infty)$ is the saturation remanence.

However, McCurrie and Gaunt (1964) showed that a similar relation holds for specimens containing energy barriers to domain wall motion. Suppose a specimen consisting of grains which contain obstacles to domain wall movements. The mass of grains with barriers which require a field H to allow free wall motion is given by

$$dm = m(H) dH$$

In a freshly aged specimen the resultant magnetization of each grain is zero. After the application of a field H the specimen acquires a remanence $M_R(H)$ given by

$$M_{R}(H) = \frac{M_{S}}{m} \int_{O}^{H} m(H) dH$$

Where $m = \int_{O}^{\infty} m(H) dH$ is the total mass of the specimen and $M_{\rm S}$ is the saturation magnetization (m(H) is a distribution function).

After saturating the specimen and reversing the field, the grain of coercivity less than the reverse field will be completely reversed and will not return to the zero magnetization initial state. Thus

$$M_{D}(H) = M_{R}(\infty) - 2\frac{M_{S}}{m}\int_{O}^{H} m(H) dH \quad or$$
$$M_{D}(H) = M_{R}(\infty) - 2M_{R}(H)$$

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4.1

This relationship is satisfied as long as the coercivity of a grain is much higher than the field required to sweep a domain wall through the grain in the absence of barriers and if the density of barriers is high.

4.2.1 Corrections for the True Remanence Loop

i) Correction for Applied Field

In order to find the remanence one must take into account the effect of the demagnetizing field due to the shape of the specimen. In a uniformly magnetized body, a demagnetizing field H_D always exists which acts in the opposite direction to the magnetization which creates it and is given by

$$H_{D} = -NI = -N\rho M \qquad 4.2$$

Where N is the demagnetization factor known from the shape of the specimen, I is the magnetization per unit volume and ρ is the density. The total field acting on the material is generally known as the "internal" H_i and is given by

$$H_{i} = H_{a} - N\rho M \qquad 4.3$$

Where H_a is the applied field. This is the appropriate field for Equation 4.1.

ii) Correction for Remanence

The true saturation remanence $M_R(\infty)$ is found from the ordinary hysteresis loop after correcting for the demagnetizing field and it is the value of the magnetization when $H_i = 0$. All the other remanence measurements were taken in zero applied field H_a , but what actually is measured is the magnetization in a small demagnetizing field H_D . One, therefore, has to make certain corrections in order to plot the true zero field remanence loop. These corrections are different for the various parts of the loop.

a) Initial Remanence

In the freshly demagnetized specimen the magnetization and remanence are zero. One can assume the simplified case where the specimen consists of regions of different coercivities distributed in such a way, Fig. 4.1a, that in the absence of a field, the net remanence is zero.

When a small field H_a is applied some of the soft regions $(H_C \leq H_{11}, H_{11} = H_a - N\rho M(H_a))$ which originally opposed the field will flip over towards the field direction so that the remanence has a nonzero value $M_R(H_{11})$ (Fig. 4.1b). If the applied field H_a is switched to zero, a demagnetizing field $H_D = -N\rho M_R(H_{11})$ is acting on the specimen so that $H_{12} = -N\rho M_R(H_{11})$. This field is of opposite direction to the remanence so it causes some of the soft

regions, $(H_{C} \leq H_{12})$ to turn towards its direction thus reducing the remanence (Fig. 4.1c). So the observed remanence in zero applied field is always smaller than the actual value. The correct remanence is found in the following way. First, plot the ordinary demagnetization curve using the internal field H_{i} instead of the applied field H_{a} (Fig. 4.2a). Because in the region of interest, $H < \frac{2K}{I_s}$, it can be assumed that the magnetization of all regions is either parallel or antiparallel to the local easy directions (i.e. eg. 4.1 holds for this part of the curve). Plot also the remanence $M_R(H_1)$ as a function of the internal field H_{i} , Fig. 4.2b. If the measured remanence at ${\rm H}_{\mbox{il}}$ is ${\rm M}_{\rm R}({\rm H}_{\mbox{il}})$, that would correspond to a demagnetizing field $H_D = H_{12} = -N\rho M_R(H_{11})$. This field would lower the remanence to the value of M(Hi2) as shown in Fig. 4.2a.

To find the correct remanence $M_R(H_{i1})$ one has to add the difference $M_R(\infty) - M(H_{i2})$ to the observed value $M_R(H_{i1})$.

As the applied field is increasing, more and more regions turn towards its direction so that the remanence is increasing until it is saturated at high fields, Fig. 4.1d.















Fig. 4.1 Schematic representation of a remanence distribution function. The direction of the arrows shows the remanence direction and their size indicates the magnetic hardness of the individual domains.

М M_R(∞) M(H_{i2}) H_{i2} $^{\rm H}$ i





Fig. 4.2 (a) Demagnetizing curve. (b) Remanence loop.

b) Demagnetizing Remanence

The application of a small negative field H'_a will cause some of the soft regions (having coercivities $H'_c \leq H'_{11}$, $H'_{11} = -H'_a - N\rho M_R(H'_a)$) to turn back in the field direction, Fig. 4.1e, so that the remanence is decreasing from the saturation value $M_R(\infty)$ of Fig. 4.1d. When the applied field is reduced to zero, Fig. 4.1f, there will be a demagnetizating field $H_D = H'_{12} = -N\rho M_R(H'_{11})$ acting on the specimen which is in the same direction as the applied negative field. It is, however, less than the effective applied and, therefore, no correction is required as no further reversals take place. However, in the region where the magnetization becomes negative the demagnetizing field is of opposite direction to the applied field H'_a , Fig. 4.1g.

In the absence of the applied field $H_a^{"}$ this demagnetizing field will cause some of the soft regions to turn towards its direction thus reducing the remanence (Fig. 4.lh). One, therefore, has to increase the observed remanence in the same way as it was shown for the initial remanence.

After all the corrections have been made, the application of relationship 4.1 to both $\text{FePt}_{0.7}\text{Ni}_{0.3}$ and $\text{Co}_{52}\text{Pt}_{48}$ systems has been examined carefully.

4.2.2 FePt_{0.7}Ni_{0.3}

An FePt_{0.7}Ni_{0.3} sample with the shape of an oblate spheroid was used for the remanence measurements. The plane of the sample was parallel to the applied field having a demagnetizing factor N = 2.168. Fig. 4.3 shows the hysteresis loops of two different stages of the sample. It is closely seen that for the early stages of ordering (12 min. at 700[°]C) the remanence has a value of $M_R(\infty) = 57$ emu/g which is much higher than one-half the saturation magnetization (M_S^{84} emu/g, see Chapter VI). This value drops to $M_R(\infty) = 49$ emu/g for the optimum state to $M_R(\infty) = 6.4$ emu/g for the overaged case, Table 4.1.

The remanence curves are shown in Fig. 4.4. A feature worth noting is the observed decrease in remanence as the applied field increases. It always appears in the initial remanence curve and it disappears after the sample has been cycled. This effect is stronger for the sample at the early stages of ordering, (Fig. 4.4) and it might be associated with some kind of interaction between the individual domains. The type of interaction is not yet clear but is being investigated.

Fig. 4.5 shows the plot of $\frac{M_R(H)}{M_R(\infty)}$ against $\frac{M_D(H)}{M_R(\infty)}$. The values of these ratios were taken from the remanence curves of Fig. 4.4. One can easily see that the remanence relationship

$$M_{D}(H) = M_{R}(\infty) - 2M_{R}(H)$$



Fable	4.1	The room	temperature	remanence in	FePto 7Nio 3
		following	g an isotherm	al annealing	at 700°C.

Annealing Time	M _R (emu/g)	M _R /M _s *	
12 min	57.0	0.67	
23 "	49.5	0.58	
l hr	45.0	0.53	
36 "	6.7	0.08	

* M_s = 91.0 emu/g.




is satisfied in the field range of $H_i = 0$ to $H_i = H_c$ for the sample at the optimum state. The deviations which are observed above this field are associated with the observed anomaly in the initial remanence which makes the measured remanence higher than the saturation $(M_R(\infty))$. The largest deviations are observed for the early ordering sample.

The remanent magnetization increases on cooling the sample down to 77 K as shown by the hysteresis loops of Fig. 4.6. However, the ratio $\left(\frac{M_{R}(\infty)}{M_{S}}\right)_{T}$ remains fairly constant. The temperature dependence of remanence is shown on Table 4.2.

4.2.3 Co₅₂Pt₄₈

All the magnetization and remanence measurements were taken with a specimen in the shape of an oblate spheroid. The equiatorial plane of the sample was perpendicular to the applied field H_a having a demagnetizing factor N = 5.480.

Figures 4.7 and 4.8 show the hysteresis and remanence loops for a $Co_{52}Pt_{48}$ sample in two different ordering stages. The applied field H_a is apparently not big enough to saturate the remanence as it was for $FePt_{0.7}Ni_{0.3}$. That is probably the reason why the anomaly in the initial remanence is not seen in this case.

In Fig. 4.9 $\frac{M_{R}(H)}{M_{R}(\infty)}$ was plotted against $\frac{M_{D}(H)}{M_{R}(\infty)}$. The solid line represents the theoretical curve predicted by the remanence relationship, Equation 4.1. It is obvious that this relationship is obeyed fairly well for $Co_{52}Pt_{48}$ in the two

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Heat Treatment (700°C)	Τ(Κ)	M _R (emu∕g)	M _R /M _s *
12 min	4.2	64.6	0.71
	300	56.9	0.67
17 "	4.2	62.1	0.68
	77	60.0	0.68
	300	54.0	0.64
23 "	4 0		
	4.2	55.5	0.61
	200	54.0	0.60
	300	49.5	0.58
l hr	4.2	52.8	0.58
	300	45.0	0.53

Table 4.2 Temperature dependence of remanence in FePt 0.7^{Ni}0.3'

 Values of M were used from high field magnetization measurements (Chapter VI).







different ordering stages.

The temperature variation of remanence is shown in Table 4.3. However, the ratios $(\frac{M_R}{M_S})_T$ remain fairly constant. Table 4.4 shows the variation of remanence with ordering.

4.3 VARIATION OF COERCIVITY WITH ORDERING

The transformation of the disordered phase to an ordered phase involves the nucleation and growth of ordered particles at the expense of the disordered matrix (Chapter IX).

The changes in the coercivity that occur during this transformation for an accumulative aging at 700°C are shown in Fig. 4.10. The disordered cubic phase has coercivities less than 50 0e. The coercive force increases to a maximum and then decreases with additional aging time. After long aging times the coercivity comes to a constant value of 200 0e which is higher from that of the disordered state. The highest levels of coercive force correspond to states at which the alloys consist predominantly of an ordered tetragonal phase.

It is obvious from Fig. 4.10 that the coercivity peak of $Co_{52}Pt_{48}$ is much higher (3500 0e) than that of FePt_{0.7}Ni_{0.3} (1600 0e). This peak is reached much faster in $Co_{52}Pt_{48}$ than in FePt_{0.7}Ni_{0.3}.

It is worth noting that for $Co_{52}Pt_{48}$ the coercivity is significantly affected by the slight difference of heat treatment.

Table	4.3	Variation	of	remanence	with	temperature	in
		Co52Pt48.					

Heat Treatment	Т(К)	M _R (emu/g)	M _R /M _s *
Quenched from 1000 ^O C, annealed for 2 min	4.2	38.8	0.74
at 700°C (early ordering)	300	35.0	0.69
Quenched from 1000 ⁰ C, annealed for 17 min	4.2	29.4	0.57
at 700°C (optimum)	300	26.9	0.53

* Values of M_s were obtained from high field magnetization measurements (Chapter VI).

Table	4.4	The	remanence	at	300	Κ	as	а	function	of	ordering
		in (Co ₅₂ Pt ₄₈ .								

Annealing Time (700°C)	M _R (emu∕g)	M _R /M _s *
2 min	35.0	0.69
4 "	30.0	0.59
17 "	26.9	0.53
50 "	23.0	0.45
2.5 hr	18.5	0.37
l6 "	13.2	0.26

*

 M_s has been taken as 50.76 emu/g.

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4.4 TEMPERATURE DEPENDENCE OF THE COERCIVITY AND REMANENT COERCIVITY

The coercive field H_{c} and the remanent coercivity H_{R} were both found to be strongly temperature dependent and increased markedly on cooling to liquid helium temperatures. Thermal activation of the domain walls over the energy barriers will make the coercivity increase as the temperature decreases (eg. 1.6). This is because at low temperatures thermal activation is small and higher fields are required to push the domain walls over the energy barriers. Another reason for this variation of the coercivity is the change of the intrinsic properties (saturation magnetization M_{S} and magnetocrystalline anisotropy K) with temperature. This will affect the interaction energy U(x) and consequently, the coercivity H_c, Equation 1.6.

4.4.1 FePt 0.7^{Ni}0.3

The variation of the coercive field H_C and the remanent coercivity H_R with temperature for an $FePt_{0.7}Ni_{0.3}$ sample in its optimum state is shown in Figures 4.11 and 4.12. The low temperature measurements (T<300 K, Fig. 4.11) were taken at a different time with the sample not in the same state as it was used for the high temperature measurements (T>300 K, Fig. 4.12). The temperature dependence of H_C and H_R appears to be linear in these two sets of measurements. From Fig. 4.11 the values of the coercivity and remanent coercivity at





absolute zero are $H_{\rm C}$, o = 2450 Oe and $H_{\rm R}$, o = 2650 Oe. A feature worth noting is the apparent kink in these curves at about 77 K where the slope $\frac{\rm dH_C}{\rm dT}$ changes from 3.2 Oe/K to 2.4 Oe/K, Fig. 4.11.

Fig. 4.13 shows again the variation of $H_{\rm C}$ and $H_{\rm R}$ with temperature for FePt_{0.7}Ni_{0.3} in its early ordering stages. This change appears to be linear in the range of 77 - 300 K but at higher temperatures it slows down and it deviates from the straight line. At these high temperatures the values of $H_{\rm C}$ and $H_{\rm R}$ move closer together.

4.4.2 Co₅₂Pt₄₈

The temperature dependence of H_C and H_R for $Co_{52}Pt_{48}$ in its optimum state is shown in Fig. 4.14. It is obvious that the variation is not linear, leveling off at low temperatures. The extrapolated values of the coercivity and remanent coercivity to absolute zero are H_C , o = 6250 Oe and H_R , o = 6500 Oe respectively.

The value of $\frac{H_{C}}{H_{R}}$ is 1.04 indicating a sharply defined distribution of anisotropies.

In order to separate the thermal contribution to the variation of the coercivity with temperature from that due to the change of the intrinsic properties (K and M_S) magnetic aftereffect measurements were used.

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CHAPTER V

MAGNETIC AFTEREFFECT

5.1 INTRODUCTION

If the magnetic field applied to a ferromagnetic substance is suddenly increased or decreased, the magnetization continues to change with time after the field change as shown in Fig. 5.1. The magnitude and the change of the magnetization for some ferromagnetic materials is too big to be accounted for by eddy currents. This phenomenon is called "magnetic viscosity" or "magnetic aftereffect" and is due to the thermal activation of domain walls over the energy barriers (domain wall creep).

In this study, as in the case of the majority of others, the magnetization is found to vary linearly with lnt over the entire measurement time interval t

$$M = const + Slnt$$
 5.1

where S is the magnetic aftereffect constant.

5.2 THERMAL ACTIVATION THEORY OF MAGNETIC VISCOSITY

The many attempts to derive a universal theory for the magnetic aftereffect produce different expected temperature and field dependences for the phenomena. Street and Woolley (1949) were the first to derive Equation 5.1 from thermal





activation considerations. They found that this equation is obeyed for a wide range of ferromagnets and over several decades in time of observation. They also predicted a coefficient S proportional to the temperature T (Street and Woolley, 1956).

$$S = -\frac{kTX}{\left(\frac{\partial E}{\partial H}\right)_{T}}$$
 5.2

where X is the irreversible susceptibility, E the activation energy for a single barrier jump and H the magnetic field. Hahn and Paulus (1973) presented Equation 5.2 in the form

$$S_{v} = -\frac{kT}{\frac{\partial\Delta F}{\partial H}}$$

where $S_v = \frac{S}{\chi}$ and ΔF is equivalent to E.

In a recent paper, P. Gaunt (1976) has reviewed the thermal activation theory of magnetic viscosity. His principles are shown in the following discussions.

5.2.1 Viscosity With a Single Activation Energy

In this theory each activation is characterized by an individual coercivity H_0 differing from process to process. The basic equation of thermal activation phenomena gives the probability dp (<<1) of a change occuring in a short time dt in terms of the activation energy E, that is the height of the energy barrier which must be overcome for the change to occur, and the absolute temperature T.

$$dp = Ce^{-E/kT}dt$$

Where C is $\exp(25) \sec^{-1}$ (Bean and Livingston, 1959).

The characteristic time for a process which appears as a relaxation time τ is given by

$$\frac{1}{t} = \frac{dp}{dt} = Ce^{-E/kT}$$
 5.3

For a static experiment where the time of measurement varies from 1 second to 1,000 seconds, barriers whose heights are $\stackrel{<}{=}$ 25kT (for T = 1s, 1 = Ce^{-E/kT} or E = kT lnC = 25kT) have already been passed. Those whose heights are between 25kT and 31.9kT will contribute to magnetic aftereffect during this time interval. Barriers of higher energy will have no measurable effect on magnetic aftereffect.

Suppose a ferromagnet with saturation magnetization Mo. At a time t after the sudden application of a reverse field H, there are n regions with activation energy E not reversed. The rate of reversal $\frac{dn}{dt}$ is

$$\frac{dn}{dt} = -nCe^{-E/kT}$$
 5.4

 $\frac{M}{M_{O}} = \frac{n-n'}{n_{O}} = \frac{2n-n_{O}}{n_{O}}$ 5.5

But

Where n' is the number of regions reversed and $n_0 = n' + n$ total number of such activation processes.

The rate of change in magnetization $\frac{dM}{dt}$ is found by differentiating Equation 5.5

$$\frac{1}{M_0}\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{2}{n_0}\frac{\mathrm{d}n}{\mathrm{d}t}$$

Substituting $\frac{dn}{dt}$ from Equation 5.4 one gets

$$\frac{1}{M_o}\frac{dM}{dt} = -\frac{2}{n_o}nCe^{-E/kT}$$
 5.6

and because from Equation 5.5

$$n = \frac{1}{2} \left(\frac{M}{M} + 1\right) n_0$$

then Equation 5.6 becomes

$$\frac{dM}{dt} = -C (M + M_{o}) e^{-E/kT}$$
 5.7

Which gives the rate of change of magnetization due to thermal activation. Integration of Equation 5.7 gives an exponential change of magnetization

$$M = 2M_{o} \exp (-Ct^{-E/kT}) - M_{o}$$
 5.8

The exponential decay of magnetization is an unusual case which has never been confirmed by experiments. However, the lnt dependence can be derived if there is a spectrum of activation energies.

5.2.2 Viscosity With A Range Of Activation Energies

Suppose that the barriers can be classified according to their activation energies so that

$$\int_{-\infty}^{\infty} f(E) dE = 1$$
 5.9

Where f(E) dE is the number of regions having activation energies between E and E + dE. Equation 5.8 thus becomes

$$M = 2M_{O_{O}} \int_{0}^{\infty} \exp(-Cte^{-E/kT}) f(E) dE - M_{O}$$
 5.10

The integral in Equation 5.10 is taken from o to ∞ since negative activation energies correspond to instantaneous reversals with no waiting time.

By differentiating Equation 5.10 with respect to lnt

$$-S = \frac{dM}{dlnt} = -2M_0 \int_0^\infty \lambda e^{-\lambda} f(E) dE$$
, $\lambda = Cte^{-E/kT}$

If, however, f(E) is a slowly varying function compared to $\lambda e^{-\lambda}$, it can be taken out of the integrand and after integration,

$$S \simeq 2M_kTf(E)$$
, Ct>>1 5.11

The change in M associated with a particular energy barrier E, when the field is changed by δH , can be found from Equation 5.8.

$$\delta M = 2M \exp (-Cte^{-E/kT}) f(E) (\frac{\partial E}{\partial H})_T \delta H$$
 5.12

Assuming again that f(E) and $(\frac{\partial E}{\partial H}) f(E)$ are slowly varying functions an expression for the irreversible susceptibility can be found from Equation 5.12.

$$\chi = \left(\frac{\partial M}{\partial H}\right)_{T} = 2M_{O} f(E) \left(\frac{\partial E}{\partial H}\right)_{T} \qquad 5.13$$

By dividing Equations 5.11 and 5.13, one gets

$$S = -\frac{kT\chi}{\left(\frac{\partial E}{\partial H}\right)_{T}}$$
 5.14

This equation is model free and it allows one to determine $(\frac{\partial E}{\partial H})_{T}$ from measurements of X, S and T.

In order to investigate $\left(\frac{\partial E}{\partial H}\right)_T$ for a particular set of barriers in the total distribution f(E) one has to make sure that he is looking at the same set all the time as H and T vary. Usually, one looks at the set of barriers corresponding to the maximum value of S,S₀. This peak of S occurs near the coercive field of the specimen, defined as H_s . The behaviour of this maximum value reflects the behaviour of the most numerous barriers of energy ε . For a particular temperature of observation, Equation 5.14 then becomes

$$S_{O} = -\frac{kTX}{\left(\frac{\partial \varepsilon}{\partial H}\right)_{T}}$$
5.15

5.2.3 Intrinsic Temperature Of The Activation Energy

In general, the activation energy E is a function of both the magnetic field H and the temperature T. Thus

$$\frac{dE}{dT} = \left(\frac{\partial E}{\partial H}\right)_{T} \frac{dH}{dT} + \left(\frac{\partial E}{\partial T}\right)_{H}$$
 5.16

In a viscosity experiment over a time range of 1 to 1,000 seconds only energies from 25kT to 31.9kT will be activated. Thus, the average activation energy is 28.5kT. Then Equation 5.16 becomes

$$28.5k = \left(\frac{\partial E}{\partial H}\right)_{T} \frac{dH}{dT} + \left(\frac{\partial E}{\partial T}\right)_{H}$$

 $\left(\frac{\partial E}{\partial H}\right)_{T} = \frac{28.5 \text{ k} - \left(\frac{\partial E}{\partial T}\right)_{H}}{\frac{dH}{dT}}$

or

If one looks at the most numerous barriers of energy ϵ corresponding to the maximum value of So at $\rm H_{c}$ then

$$\left(\frac{\partial \varepsilon}{\partial H_{s}}\right)_{T} = \frac{28.5 k - \left(\frac{\partial \varepsilon}{\partial T}\right)}{\frac{d H_{s}}{d T}}$$
 5.17

 $\frac{dH_s}{dT}$ is the temperature variation of the coercive field at which S is maximum. Thus, experimental measurements of S_o , χ , T and $\frac{dH_s}{dT}$ with Equation 5.15 and 5.17, allow $\left(\frac{\partial \varepsilon}{\partial T}\right)_H$ the intrinsic temperature dependence of the barrier energy to be determined. It is, therefore, possible to separate thermal activation and intrinsic temperature contributions to the coercive force. Equation 5.17 becomes particularly simple if $\frac{\partial \varepsilon}{\partial T} = o$ since

$$\left(\frac{\partial \varepsilon}{\partial H_{s}}\right)_{T} = \frac{28.5k}{\frac{dH_{s}}{dT}}$$
 5.18

If this equation is not found it indicates that intrinsic temperature effects are important. Any further analysis of the viscosity parameters is not possible without a model for the energy barrier.

5.3 QUANTUM MECHANICAL TUNNELING

The previous calculations have been carried out employing classical models, whereas quantum mechanical effects may be found when the walls become extremely narrow. The most important quantum effect appears to be domain wall tunneling through the energy barrier.

Egami (1973) has examined this case for some heavy rare earth metals and their compounds which have extremely narrow domain walls. In his calculations he showed that a domain wall behaves like a particle with a finite effective mass. The concept of tunneling, therefore, applies when the motion of the wall through the barrier takes place.

Quantum mechanical tunneling might become detectable at low temperatures where thermal activation is very small. One, therefore, may observe a coefficient S temperature independent.

Experimental observations on Dy (Egami, 1973) show a temperature independent magnetization rate below liquid helium temperatures. Theoretical calculations predict a transition from tunneling to thermal activation at about 3 K. Similar discussions have been made by J. Hunter and K.N.R. Taylor (1977) for the $Dy(Co_7Ni)_2$ system.

5.4 EXPERIMENTAL OBSERVATIONS

Magnetic aftereffect has been measured in the following way:

The sample is first saturated and withdrawn from the field. Then it is re-inserted into a chosen stable reverse field. The change in magnetization with time is then integrated and displayed on a chart recorder giving the output trace shown in Fig. 5.2. Subtracting the instrumental drift rate and plotting ΔM (change in magnetization) against ln (time) gives Fig. 5.2 which shows a linear relationship up to 32 seconds. The slope S of ΔM against lnt curves shows a maximum S_O at H_S .

This maximum and the shape of the S against H curves closely mirror the shape and maximum of the irreversible susceptibility χ $(\frac{dM_R}{dH})$ against H curves. This is illustrated in Fig. 5.3.

As it was mentioned earlier, attention is directed towards the maximum value S_0 , because it reflects the behaviour of the most numerous energy barriers. In a viscosity experiment one, therefore, has to know for a particular temperature T the value S_0 , the field H_s at which it occurs and the irreversible susceptibility χ at this field. It is then possible by using Equations 5.15 and 5.17 to separate thermal activation and intrinsic temperature contributions to the coercive force.

5.4.1 FePt0.7^{Ni}0.3

The magnetic aftereffect has been investigated for the early ordering and the optimum state of an $\text{FePt}_{0.7}\text{Ni}_{0.3}$ sample over a wide range of temperatures (4.2 - 600 K). The sample

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Fig. 5.2 (a) Output trace from integrator and chart recorder after insertion of specimen into a stable demagnetizing field. (b) Change in magnetization against time after insertion into a reversed demagnetizing field.



has been quenched from $1000^{\circ}C$ and annealed at $700^{\circ}C$ for 11 minutes for the early state and 22 minutes for the optimum state.

Fig. 5.4 shows the magnetic aftereffect coefficient S as a function of the temperature T. It is obvious that the aftereffect is larger for the early stages of ordering for which it peaks around room temperature (300 K) while S is still increasing at 440 K for the optimum state.

The temperature dependence of $\left(\frac{\partial E}{\partial H}\right)_{T}$ for both the stages of ordering is shown in Fig. 5.5. The shape of this curve for the early ordering sample is different from the optimum state, having a peak at about 420 K.

All the experimental observations are tabulated on Tables 5.1 and 5.2.

5.4.2 Co₅₂Pt₄₈

The magnetic viscosity has been measured for a $\text{Co}_{52}\text{Pt}_{48}$ sample in its optimum state from 77 K up to 460 K. The values of S and $\left(\frac{\partial E}{\partial H}\right)_{T}$ as functions of the absolute temperature T are shown in Fig. 5.6. In this temperature range S increases with the temperature, while $\left(\frac{\partial E}{\partial H}\right)_{T}$ increases with T at low temperatures, then it levels off and starts increasing again at about 300 K.

Values of all the measured experimental quantities are listed on Table 5.3.







(<u>\</u> <u>\</u>) S

Т(К)	X(10 ⁻² mV/0e)	S(mV)	H _s (0e)
4.2	7.4	0.12	2626
11	7.3	0.24	2618
20	7.5	0.34	2590
60	7.2	0.69	2500
77	7.6	0.87	2458
114	8.0	1.07	2342
136	8.1	1.29	2271
152	8.1	1.35	2223
174.5	8.1	1.45	2143
194	8.0	1.66	2087
210	8.2	1.79	2037
2 32	8.2	1.87	1961
253	8.2	2.09	1889
293	7.9	2.14	1711
315	7.7	2.27	1608
335	7.6	2.36	1537
352	7.7	2.44	1463
371	7.7	2.50	1399
394	7.7	2.57	1314
413	7.7	2.61	1230
433	7.7	2.64	1137

Table 5.1

Experimental values of the magnetic viscosity parameters in an optimum FePt_{0.7}Ni_{0.3} sample.

Т(К)	$\chi(10^{-2} \text{mV}/0\text{e})$	S(mV)	H _s (0e)
77	12.0	1.66	1350
103	12.0	2.14	1180
124	12.0	2.26	1050
145	12.4	2.49	980
173	12.6	2.82	880
249	12.8	3.43	800
290	13.0	3.57	750
345	11.0	3.01	560
500	5.0	2.06	450
562	3.3	1.61	400

Table 5.2 Experimental values of the magnetic viscosity parameters in an FePt_{0.7}^{Ni}_{0.3} sample at its early ordering stages.
Т(К)	$\chi(10^{-2} \mathrm{mV/0e})$	S(mV)	H _s (oe)
77	1.70	0.30	5520
124	1.75	0.35	5200
171	1.80	0.43	4 725
2 35	1.90	0.56	4400
290	2.00	0.70	4100
322	1.80	0.67	3678
356	1.86	0.68	3380
407	2.00	0.75	2950
478	2.20	0.81	2350

Table 5.3 Experimental values of the magnetic viscosity parameters in an optimum Co₅₂Pt₄₈ sample.

No detectable time effect was observed in $Co_{52}Pt_{48}$ at liquid helium temperature although a measurable effect was found for FePt_{0.7}Ni_{0.3}.

For both $\text{FePt}_{0.7}\text{Ni}_{0.3}$ and $\text{Co}_{52}\text{Pt}_{48}$ Equation 5.18 does not hold (the deviation is not very large) indicating the presence of some intrinsic temperature effects. These effects are due to the variation of the magnetrocrystalline anisotropy K and the saturation magnetization M_s with temperature. The values of K and M_s were obtained by fitting some high field magnetization measurements to the law of approach to saturation.

CHAPTER VI

HIGH FIELD MAGNETIZATION MEASUREMENTS

6.1 INTRODUCTION

The variations of the magnetocrystalline anisotropy K and the saturation magnetization M_S with temperature and ordering have been investigated. Since all the experimental observations have been carried out on polycrystalline specimens, high field magnetization measurements were taken in order to determine K and M_S by least squares fitting to the law of "approach to saturation".

6.2 SATURATION AND SPONTANEOUS MAGNETIZATION

At very high fields the magnetization increases slowly and almost linearly with the applied field. This is the saturation magnetization within a domain. In this state, even all magnetization vectors lie close to the field direction, the magnetization increases slowly because of the effect of the strong applied fields in the redistribution of the spin states within the domain.

The value of the saturation magnetization does not go to zero when the external field is zero but to a value slightly lower than its value in a high field. This is the spontaneous magnetization which is spontaneously present within domains when no external field is applied. It, thus, slightly differs from the saturation magnetization measured in a strong field. However, this effect is nearly always small and can be allowed for by suitable extrapolation.

The large values of the spontaneous magnetization were explained by Weiss (1907) on the basis of a hypothetical molecular field within the material. The internal molecular field H_m is proportional to the magnetization M and is responsible for the alignment of the magnetic carriers against thermal forces

$$H_{\rm m} = \gamma M \qquad 6.1$$

Where γ is the molecular field coefficient. However, in his theory, Weiss was unable to postulate any mechanism for the origin of this molecular field. In seeking for a physical origin, Heisenberg (1928) showed that the molecular field is caused by quantum mechanical exchange forces. The magnetic moments of neighbouring electrons are coupled via an exchange interaction which tends to align them. The exchange energy between two adjacent atoms with spins Si and Sj, respectively, is given by

$$E_{ex} = -2J_{ex} \vec{S_1} \cdot \vec{S_1}$$
 6.2

Where J_{ex} is the exchange integral which occurs in the calculation of the exchange effect. The exchange energy depends on the relative orientation of the spins and is minimum when

the spins are aligned parallel, (Morrish, 1965).

6.3 MAGNETOCRYSTALLINE ANISOTROPY

According to the molecular field theory in a demagnetized single crystal, the domain magnetizations could lie in all directions. This would mean that the measured magnetization curves for the crystal would be the same whatever the direction of the applied field relative to the crystal axes. However, experimental magnetization curves show that the approach to saturation differs according to the orientation of the field with respect to crystal axes, Fig. 6.1. Some directions are directions of easy magnetization and others are hard directions. This is a fundamental effect called magnetocrystalline anisotropy. The anisotropy energy of a cubic crystal can be written as

$$E_{K} = K_{0} + K_{1}(\alpha_{1}^{2}\alpha_{2}^{2} + \alpha_{1}^{2}\alpha_{3}^{2} + \alpha_{2}^{2}\alpha_{3}^{2}) + K_{2}\alpha_{1}^{2}\alpha_{2}^{2}\alpha_{3}^{2} + \dots$$
6.3

Where K_0 , K_1 , and K_2 are the anisotropy constants and α_1, α_2 , and α_3 are the direction cosines of the magnetization direction with respect to the cubic axes of the crystal (usually K_0 is ignored because it is independent of the angle). For a uniaxial ferromagnet the anisotropy is given by

$$E_{K} = K_{1} \sin^{2}\theta + K_{2} \sin^{4}\theta \qquad 6.4$$





Magnetization curves for a single crystal of (a) nickel and (b) cobalt.

Where θ is the angle between the magnetization vector and the direction of the crystallographic c-axis.

Magnetocrystalline energy plays a large part in determining the thickness, energy and the mobility of domain walls. It is believed this is mainly due to the spin-orbit coupling. When an external field tries to reorient the spin of an electron the orbit of that electron tends to be reoriented. But because of the strong orbit-lattice coupling, the orbit resists the attempt to rotate the spin axis. The magnetocrystalline anisotropy energy is the energy required to break this spin-orbit coupling.

6.4 APPROACH TO SATURATION

The approach to saturation is a complex mechanism. It becomes even more difficult when one attempts, in formulating the theory, to allow for the quite considerable effect the structure of the material has on the magnetization processes. This is because the structure effect varies from sample to sample whereas the theory tries to establish certain universal regularities of the phenomenon. The measurements presented here are not directed towards a systematic study of the process.

6.4.1 Magnetization Processes

The approach to saturation as a function of field is illustrated in Fig. 6.2. In the low field region (1) numerous contributions including strains, impurities and anisotropic effects limit complete saturation. In this region magnetization changes occur by domain wall displacements. Region (2) involves high fields where most of these limiting interactions are overcome but anisotropic contributions and spin wave excitations may still be present (in addition to band contributions to the high field susceptibility X). The total magnetization varies only by rotations. Region (3) is reversed for ultra-high fields where the interaction between the applied field and the magnetic system may be large enough to produce magnetic phase transitions.

6.4.2 Expressions for the Law of Approach to Saturation

The anisotropy produced by the crystalline defects and the magnetocrystalline anisotropy are the origin of the difficulties in achieving the state of the magnetic saturation of the samples. For a long time one has attributed to these two contributions, laws of variation in $\frac{A}{H}$ and $\frac{B}{H^2}$, respectively. But the laws become very much different as the calculations become more sophisticated.

According to Brown (1941) crystalline defects or stresses lead to laws in $\frac{1}{\frac{n}{H}^2}$ with n = 1, 2 or 3 for point,



Fig. 6.2 General features of magnetization versus field. In region (1) domain wall motion takes place; in region (2) anisotropic contribution and spin wave excitations play a role. In the ultrahigh field region (3) magnetic phase transitions may occur. line and plane geometry, respectively. Néel (1948) from his part taking into account the role of cavities and inclusions has determined one complex law changing continuously from $\frac{1}{H}$ in weak fields to $\frac{1}{H^2}$ in high fields.

It is generally believed that experimental values of magnetization in high fields (much larger than the coercive force of the specimen) can be analyzed as

$$M = M_{s} (1 - \frac{A}{H} - \frac{B}{H^{2}} - \frac{C}{H^{3}} - \dots) + p(H) \qquad 6.5$$

p(H) is known as the parasitic paramagnetism or the high field susceptibility term. Any limitations of the number of turns in series (6.5) depends considerably on the values of the anisotropy constants as well as on the field strength H.

6.4.3 Physical Nature of Terms

To ascertain the physical nature of the coefficients in the law governing the approach of magnetization to saturation, one must find out what are the forces against which work must be carried out in the process of magnetizing single crystals in different crystallographic directions.

i) $\frac{B}{H^2}$ and $\frac{C}{H^3}$ terms.

If it is assumed that the magnetization in the field range of interest takes place by rotations then the course of magnetization curve in high fields should be determined by the influence of $\frac{B}{H^2}$ and $\frac{C}{H^3}$ terms. Akulov (1931) has shown that for a polycrystalline cubic structure, the coefficient B in the term $\frac{1}{H^2}$ is a function of the magnetocrystalline energy, represented here with one single constant K

$$B = \frac{8}{105} \frac{K^2}{J_s^2}$$
 6.6

Vergne (1966) showed that the influence of $\frac{C}{H^3}$ term is not negligible up to internal fields of 500 Oe in the case of Ni and 1000 Oe in the case of iron. However, one expects this term to be important at low temperatures since usually there is a substantial increase of the second anisotropy constant K₂ at these temperatures (C is a function of K₁ and K₂ as shown by Equations I.5 and I.8 in Appendix I).

ii) $\frac{A}{H}$ term

It is very difficult to find the origin of this term so that a rigorous law like the one stated in Equation 6.5 cannot be established. A representation including $\frac{A}{H}$ term would lead to infinite magnetization energy

$$E = \int_{H_O}^{\infty} H dM = \int_{H_O}^{\infty} H \frac{dM}{dH} dH = A \int_{H_O}^{\infty} \frac{dH}{H} + B \int_{H_O}^{\infty} \frac{dH}{H^2} + \dots 6.7$$

Therefore, one has to find a mechanism leading to a magnetization law in which $\frac{A}{H}$ in medium fields is transformed to a law of $\frac{B}{H^2}$ in high fields. Néel (1948) showed that a substance whose magnetization varied irregularly from point to point obeys in internal fields a complex magnetization law analagous to that stated in the previous paragraph.

On the other hand, Brown (1941) considering the effect of high localized forces acting on the spins at crystalline defects, observed a law leading to the $\frac{A}{H}$ term.

iii) p(H), the parasitic paramagnetism or high field susceptibility term

This term represents the increase of the magnetization within one domain over the spontaneous value. It probably originates from the redistribution of the populations of spin states in high fields. It is an increasing function of temperature and is important near the Curie point and at high fields. The paramagnetic terms are contributed by

a) the high field susceptibility X, so that p(H) = XH. X is the sum of X_p , X_{vv} , and X_{dia} , $\chi = X_p + X_{vv} + X_{dia}$, where $X_p (~10^{-6} \text{emu/g/0e})$ is the Pauli spin paramagnetic contribution, $X_{vv} (~10^{-5}-10^{-6} \text{emu/g/0e})$ is the Van Vleck paramagnetism (Place and Rhodes, 1968) and $X_{dia} (~10^{-6} \text{emu/g/0e})$ is the contribution from the diamagnetism of the core electron and the Landau conduction electrons (Danan, 1968). X is found to be high in alloys and it is greater in polycrystalline specimens than in single crystals. b) the Holstein-Primakoff (1940) spin-wave amplitude reduction due to the magnetic field H. The expected increase in magnetization, p(H), is predicted to be roughly proportional to $(H)^{\frac{1}{2}}$.

6.4.4 Derivation of B and C Coefficients

Various authors have studied the law of approach to saturation of a polycrystalline ferromagnet free of all external constraints. They have calculated the variation of magnetization due to the rotation of spontaneous magnetization, considered as a vector of constant modulus $\boldsymbol{J}_{\text{S}},$ under the influence of the applied magnetic field H. In this type of calculation one assumes that the polycrystal is composed of randomly oriented crystallites free of internal stresses, microscopic defects (lattice defects) and macroscopic defects (holes, inclusions and grain boundaries). A further assumption is also made that the applied field is sufficient to make each crystallite a single domain. The law of approach to saturation is then determined by finding the equilibrium position of the magnetization vector J_S in a crystallite for fields sufficiently large that the angle θ between the field and the magnetization can be regarded as small. For this, one finds the free energy of the crystal with respect to the angle θ and minimizes it. The magnetization of the polycrystal as a function of the field is then found by averaging the single crystal expression taking into account all the possible orientations of the crystallites (Appendix I).

6.4.5 Influence of Interactions on the Law of Approach to Saturation

The interactions among the crystallites come in the calculations in such a way that the total field acting on the crystallite is the sum of the external field and the internal field created by the neighbouring crystallites. The interactions modify strongly the law of approach to saturation.

According to Holstein and Primakoff (1940) and Néel (1948) the expansion series in Equation 6.5 is multiplied by a factor of $\frac{G}{2}(\frac{4\pi I_S}{H})$ varying from .5 in zero field to 1 in infinite fields. For very high fields (H>>4\pi I_S)

$$G \simeq \frac{1}{(1 + \frac{4\pi I_{S}}{3H})^{2}}$$
 (A. Herpin, 1968).

By substituting back to Equation 6.5 one can easily see that the effect of the interactions is to change the field into a total magnetic field H_t which is the sum of the internal field H_i and the Lorentz field $\frac{4\pi}{3}I$.

$$H_{t} = H_{i} + \frac{4\pi}{3}I = H_{a} - H_{D} + \frac{4\pi}{3}I$$
 6.8

6.4.6 Determination of Magnetocrystalline Anisotropy and Saturation Magnetization

A specimen has attained a state of an effective saturation at $H = H_S$, if for $H > H_S$ the variation of the magnetization with the field is linear. The saturation magnetization M_S is then found by extrapolating the linear part of the magnetization curve to zero internal fields (Fig. 6.3). The slope of this line is the susceptibility X. This is also verified by the fact that the values of X and M_S , found by least squares fitting the high field magnetization measurements to the law of approach to saturation, are very similar to those found by extrapolation.

Generally, whether or not a state of an effective saturation is obtained, values of X, M_S and the magnetocrystalline anisotropy K can be found by least squares fitting the high field magnetization measurements (H>20 k0e) to a "law of approach" having the form

$$M = M_{s} (1 - \frac{B}{H_{t^{3}}} - \frac{C}{H_{t^{4}}} - \frac{D}{H_{t^{5}}}) + \chi H_{t}$$
 6.9

Where Ht is the total field shown in Equation 6.8. M_S and X were varying until a best fit was found. The values of the coefficient Band the saturation magnetization M_S corresponding to the best fit were used to determine the anisotropy constant K_1 with the help of Equation I.5 and I.8 (Appendix I) assuming $K_2 = 0$. This is because the second term $(\frac{C}{H_{+}^3})$ in

Equation 6.9 is very sensitive to the chosen form of the total field H_t while the first term $(\frac{B}{H_t^2})$ is not. In fact, small variations of the field could cause rapid variations in the second term coefficient C (Equation 6.10). Let the field H_t change by a small amount ΔH , then Equation 6.9 becomes

$$M = M_{s}(1 - \frac{B}{(H_{t} \pm \Delta H)^{2}} - \frac{C}{(H_{t} \pm \Delta H)^{3}} -) + \chi(H_{t} \pm \Delta H)$$

$$M = M_{s}(1 - \frac{B}{H_{t}^{2}(1\pm\frac{\Delta H}{H_{t}})^{2}} - \frac{C}{H_{t}^{3}(1\pm\frac{\Delta H}{H_{t}})^{3}}) + \chi(H_{t}\pm\Delta H)$$

$$M = M_{s}\{1 - \frac{B}{H_{t}^{2}}(1\pm\frac{2\Delta H}{H_{t}}) - \frac{C}{H_{t}^{3}}(1\pm\frac{3\Delta H}{H_{t}})\} + \chi(H_{t}\pm\Delta H)$$

$$M = M_{s}[1 - \frac{B}{H_{t}^{2}} - \frac{1}{H_{t}^{3}}(C\pm2B\Delta H) - \dots] + \chi(H_{t}\pm\Delta H)$$

6.10

For this reason no reliable values of the second anisotropy constant K_2 could be obtained.

The sensitivity of this method was tested using the numerical results of Lee and Bishop (1966) for magnetization as a function of field of an assembly of non-interacting single domain particles.

The root mean squares deviation (RMS)

$$RMS = \sqrt{\frac{(M_{exp} - M_{cal})^2}{n}}$$

was used to show how well the calculated curves fit to the experimental points (n is the number of experimental points). This was found after fitting the expression $(M_{exp} - M_s - \chi H_t)$ of Equation 6.9 to a fourth degree polynomial in $H_t (\frac{B}{H_t^2} + \frac{C}{H_t^3} + \frac{D}{H_t^4})$. As stated earlier, by varying X and M_s a best fit was found. The values of B', C', D', X', and M'_s corresponding to the best fit were used to find the calculated value of magnetization M_{cal} .

$$M_{cal} = M_{s}^{t} + \frac{B'}{H_{t}^{2}} + \frac{C'}{H_{t}^{3}} + \frac{D'}{H_{t}^{4}} + \chi' H_{t}$$

6.5 EXPERIMENTAL OBSERVATIONS

The accuracy of the above method was checked with samples of known saturation magnetization and magnetocrystalline anisotropy such as Nickel (Ni) for the cubic case and Cobalt (Co) for the uniaxial case.

6.5.1 Ni-Co

Annealed samples of Ni and Co with ellipsoidal shapes of known demagnetizing factors were used for the high field magnetization measurements. Figures 6.3 and 6.4 show the magnetization curves for Ni and Co, respectively at 4.2 K.

In the case of Ni an effective saturation has been achieved at $H_s = 58$ kOe (Fig. 6.3). By extrapolating the linear part of the magnetization curve a value of $M_s = 58.43$ emu/g is obtained. The susceptibility X is found to be





Table 6.1	Experimental	values of K,	$M_{\rm S}$ and λ	(in annealed
	samples of C	o and Ni at 4.	. 2 K.	

Samples	M _S (emu∕g)	K(10 ⁶ erg/cc)	X(10 ⁻⁶ emu/g/0e)	RMS
Ni	58.430	1.57	3.7	0.002
Co	162.130	9.33	3.0	0.006
	······································			

 N_{CO} (demagnetizing coefficient) = 5.2894

N_{Ni} = 3.3653.

 $3.5 \ 10^{-6} \ \text{emu/g/0e}.$

The listed values of M_s , K and X (Table 6.1) were found after fitting the experimental points of Figures 6.4 and 6.5 to a law of approach having the form shown in Equation 6.9. The values obtained for M_s , K and X are very close to those reported by J. Rebouillat (1972):

> $M_s = 58.53 \text{ emu/g}$ $K_1 = 1.24 \ 10^6 \text{ erg/cc}$ $\chi = 1.98 \ 10^{-6} \text{ emu/g/0e}$ for Ni

and

$$M_{s} = 161.90 \text{ emu/g}$$

$$K_{1} = 7.66 \ 10^{6} \text{ erg/cc}$$

$$\chi = 4.5 \ 10^{-6} \text{ emu/g/0e} \qquad \text{for Co.}$$

6.5.2 FePt_{0.7}Ni_{0.3}

The variations of the magnetocrystalline anisotropy K and saturation magnetization M_s of FePt_{0.7}Ni_{0.3} have been investigated for different ordering stages and at different temperatures.

 Influence of ordering on magnetocrystalline anisotropy and saturation magnetization.

Fig. 6.5 shows the magnetization curves at 4.2 K of an ellipsoidal FePt $_{0.7}$ Ni $_{0.3}$ sample through the course of ordering

from the initial cubic phase to the overaged tetragonal.

The magentization curve of the cubic phase is shown on a finer scale in Fig. 6.6. By extrapolation the values of $M_s = 89.44$ emu/g and $X = 3.75 \ 10^{-6}$ emu/g/0e were found.

Table 6.2 shows the values of M_s , K and X which were found by fitting the experimental points to the law of approach in the same way as before.

The sample while ordering shows a slight increase in saturation magnetization and a drastic change in the magnetocrystalline anisotropy constant. Similar increases in the saturation magnetization with ordering has been reported by V. Kussman (1964) for an FePd alloy. The obtained values of susceptibilities are of the same order as those calculated theoretically (6.4.2, Sec. iii). The change in M_S and K as the susceptibility X varies from 0 to 5 10^{-6} emu/g/0e is .5% and 3%, respectively.

For the overaged sample, the magnetization measurements above 70 kOe were taken at 1.5 K while those below 70 kOe were taken at 4.2 K. That was the result after the temperature of the helium bath was decreased to 1.5 K. This increased the critical field of the superconducting magnet and extended the maximum available field to 100 kOe. The calibration of the magnetometer was done in fields up to 70 kOe so that for the measurements in higher fields the magnetoresistance of the coils was used for calibration. But the magnetoresistance was measured to three figures while the wanted accuracy was





Table 6.2	Experimental	values	of K	C, M_	and	χ	in	FePt	-Ni-	~
	at 4.2 K.			5				Ο.	/ 0.	3

Heat Treatment	M _s (emu∕g)	K(10 ⁷ erg/cc)	χ(10 ⁻⁶ emu/g/0e)	RMS
Quenched from 1000 ⁰ C (cubic)	89.47	0.37	3.6	0.002
Annealed 12 min at 700 ⁰ C (early ordering)	89.89	1.83	3.0	0.020
Annealed 23 min at 700 ⁰ C (optimum)	90.05	3.28	2.0	0.070
Annealed for 1 hr at 700 ⁰ C	91.26	4.20	1.0	0.030
Annealed for 48 hr at 700 ⁰ C (overaged)	92.11	6.78	5.0	0.100

N = 1.3661.

1:10⁴. That was probably the reason for the observed relatively high values of RMS.

ii) Temperature dependence of magnetocrystalline anisotropy and saturation magnetization.

The magnetization curves of the same FePt_{0.7}Ni_{0.3} sample at different temperatures are shown in Fig. 6.7. A least squares fit to the law of approach to saturation gave the values listed in Table 6.3.

The considerable change in magnetization between 4.2 K and 300 K is due to the relatively low Curie temperature of $FePt_{0.7}Ni_{0.3}$ (T_c~760 K, Sec. 7.4.1). The unexpected increase in magnetocrystalline anisotropy at 150 K might be associated with the observed kink in the coercivity at ~100 K.

6.5.3 Co₅₂Pt₄₈

i) Influence of ordering on the saturation magnetization and magnetocrystalline anisotropy.

An oblate spheroid of Co₅₂Pt₄₈ was used for the magnetization measurements which are shown in Fig. 6.8. It is obvious from the shape of the curves that the sample becomes harder to saturate while ordering. This is associated with an increase in magnetocrystalline anisotropy.

The magnetization curve of the cubic phase is shown on a finer scale in Fig. 6.9. By extrapolation the values of $M_s = 51.16 \text{ emu/g}$ and $X = 3.3 10^{-6} \text{ emu/g/0e}$ were obtained.



Table 6.3 Temperature dependence of K, $M_{\rm S}$ and X in an optimum ${}^{\rm FePt}0.7{}^{\rm Ni}0.3{}^{\rm \cdot}$

T(K)	M _S (emu∕g)	K(10 ⁷ erg/cc)	X(10 ⁻⁶ emu/g/0e)	RMS
4.2	90.05	3.28	2	0.07
77.0	88.92	2.93	2	0.08
150.0	87.92	3.40	6	0.03
300.0	84.74	3.03	2	0.06



(ɓ/nɯə) W



Table 6.4 Variation of K, M_s and χ with ordering in $Co_{52}Pt_{48}$ at 4.2 K.

Heat Treatment	M _s (emu∕g)	$K(10^7 \text{ erg/cc})$	χ (10 ⁻⁶ emu/g/0e)	RMS
Quenched from 1000°C (cubic)	51.16	0.184	3.3	0.004
Annealed for 2 min at 700 ⁰ C (early ordering)	52.20	2.5	-	0.005
Annealed for 17 min at 700 ⁰ C (optimum)	51.95	4.96	-	0.070
Annealed for 16 hr at 700 ⁰ C (overaged)	50.17	5.76	4.0	0.100

N = 5.4796

Following the same technique of least squares fitting, the listed values of M_s , K and X were found at 4.2 K (Table 6.4).

ii) Temperature dependence of saturation magnetization and magnetocrystalline anisotropy.

Temperature has very little effect on the shape of the magnetization curves as shown on Fig. 6.10. Table 6.5 shows the values of Ms, K and X found by the usual way. The slight decrease in saturation magnetization in the temperature range of 4.2 - 300 K is due to the high Curie temperature of $Co_{52}Pt_{48}$ ($T_C \sim 900$ K). The anisotropy constant changes very little in the above range of temperature and it is consistent with the results shown by O. A. Ivanov (1972) who reported high values of magnetic anisotropy even at temperature tures close to the Curie point.

The values obtained for K and M_S are comparable to those found by Y. A. Shur (1968) for a single cyrstal of $Co_{50.5}$ Pt_{49.5}.



Table 6.5 Temperature dependence of K, M_s and X in an optimum $Co_{52}Pt_{48}$.

T(K)	M _s (emu∕g)	K(10 ⁷ erg/cc)	χ(10 ⁻⁶ emu/g/0e)	RMS
4.2	51.95	4.96	-	0.07
7.7 ``	51.23	4.50	-	0.06
300	50.76	4.26	2	0.05

CHAPTER VII

CURIE TEMPERATURE

7.1 INTRODUCTION

In a ferromagnetic material the spontaneous magnetization depends on temperature having a maximum value at absolute zero (Fig. 7.1). The magnetization falls with an increasing rate with increasing temperature and becomes zero at a characteristic temperature called the Curie point T_c .

At this temperature thermal agitation is sufficient to destroy the strong interaction which tends to align the atomic moments.

Measurements of the Curie temperature will give an approximate value of the exchange integral J_{ex} . The value of this exchange integral will be used to calculate the domain wall energy.

7.2 DETERMINATION OF THE CURIE TEMPERATURE

The Curie temperature of a ferromagnet is not obviously identified in a superficial examination of the magnetization measurements because of the disturbing influence of the magnetic field at which the measurements were taken. A sharp second order phase transition exists when there is no field. However, the Arrot method (Arrot, 1971) for determining the Curie temperature is suitable to be applied when a set of I(H,T) curves is available (I is the magnetization per unit



Fig. 7.1 Reduced saturation magnetization of Fe as a function of relative temperature.
volume).

Close to Curie temperature the magnetization I is very small so that the free energy F of a ferromagnetic body can be expanded in power series of I and in the presence of a field H it can be written as

$$F = F_{0} + a_{1}I + a_{2}I^{2} + a_{3}I^{3} + a_{4}I^{4} + \dots - I \cdot H$$
 7.1

Under the condition that the Curie point must represent a stable state (Landau and Lifshitz, 1964) Equation 7.1 transforms to

$$F = F_0 + a_2 I^2 + a_4 I^4 + \dots - I \cdot H$$
 7.2

With $a_4 > 0$ and $a_2 > 0$ for $T > T_C$ and $a_2 < 0$ for $T < T_C$. At $T = T_C$, $a_2 = 0$. Close to the Curie temperature a_2 can be expanded in powers of the difference $T - T_C$ at constant pressure

 $a_2 = a(T - T_C) + \dots a > 0$

Thus, for small I, Equation 7.2 can be written as

$$F = F_{c} + a(T - T_{c})I^{2} + a_{A}I^{2} - HI$$
 7.3

The equilibrium condition

$$\frac{\partial F}{\partial I} = 0$$
, $\frac{\partial^2 F}{\partial I^2} > 0$ leads to

$$\frac{\partial F}{\partial I} = 2a(T - T_C)I + 4a_4I^3 - H = 0$$
 7.4

From this, one can find the initial susceptibility $\chi = \left(\frac{\partial I}{\partial H}\right)_{H=0}$ above and below the Curie point.

By differentiating Equation 7.4 one gets

$$2a(T - T_C)\frac{\partial I}{\partial H} + 12a_4I^2\frac{\partial I}{\partial H} = 1$$

For $T \ge T_C$ where I = 0 at H = 0

$$\chi = \left(\frac{\partial I}{\partial H}\right)_{H=0} = \frac{1}{2a(T - T_c)} = \frac{C}{T}$$

Which is the Curie-Weiss law (1907). Equation 7.4 can be rewritten in the form

$$H = 2a(T - T_{C})I + 4a_{4}I^{3}$$
 or

$$\frac{H}{I} = a'(T - T_{C}) + b'I^{2}$$
 7.5

$$a' = 2a, b' = 4a_{4}$$

It thus follows from Equation 7.5 that magnetization field data plotted as I^2 versus $\frac{H}{I}$ should result in a straight line for each temperature of measurement. The intercept of the straight line plot with $\frac{H}{I}$ axis should be negative when $T < T_c$; positive when $T > T_c$ and zero when $T = T_c$. Thus, the line with $T = T_c$ passes through the origin and separates the paramagnetic from the ferromagnetic region.

For routine measurements the Curie point can be found roughly by considering that the magnetization I measured at a field strength H sufficient to align the domains (but not very large) approximates to the spontaneous magnetization at temperatures around the Curie point. The Curie temperature is then found by plotting I^2 versus T and extrapolating I^2 to the temperature axis.

7.3 RELATIONSHIP BETWEEN THE EXCHANGE INTEGRAL AND THE CURIE TEMPERATURE

Since the ferromagnetic state depends on the magnetic interactions represented by the molecular field or exchange interaction there will be a relationship between them and the Curie temperature at which the ferromagnetic state breaks down.

The molecular field and exchange interaction are equivalent so there is a relation between them (J. D. Patterson, 1971).

$$H_{\rm m} = \gamma M = \frac{2 z J_{\rm ex}}{\mu_{\rm H}} S^2$$
7.6

Where z is the number of nearest neighbors (assume exchange forces to be effective in nearest neighbors), and $\mu_{\rm H}$ is the magnetic moment of the atom in the field direction. But the molecular field is related to the Curie temperature by

$$H_{m} = \gamma M = \frac{3kST_{C}}{\mu_{H}(S+1)} \qquad (J = S) \\ pure spin) \qquad 7.7$$

By substituting Equation 7.7 to Equation 7.5

$$J_{ex} = \frac{3kT_{C}}{2z(S+1)S}$$
7.8

The exchange integral J_{ex} is thus proportional to the Curie temperature T_{c} .

7.4 EXPERIMENTAL OBSERVATIONS

In determining the Curie Temperature an experiment has been done on FePt $0.7^{Ni}0.3$ while a reference is used for the Curie point of $Co_{52}Pt_{48}$.

7.4.1 FePt_{0.7}Ni_{0.3}

Fig. 7.2 shows the temperature dependence of the magnetization of FePt_{0.7}Ni_{0.3} around the Curie temperature for different applied fields H. Values of $(\frac{H_i}{I})_T$ can be deduced from these curves after the proper correction for the demagnetizing field. The plot of I^2 versus $(\frac{H_i}{I})_T$ is shown in Fig. 7.3 for different temperatures of measurement, and it results in a straight line according to Equation 7.6. The line with $T = T_c$ passes through the origin. Such a line and, consequently, the Curie temperature lies between 460° and 465°C for the case of ordered FePt_{0.7}Ni_{0.3}. The deviations observed at high fields are expected since the conditions of the approxi-



The magnetization at different external fields as a function of temperature around the Curie point in FePt 0.7^{Ni}0.3



mations will not hold at these fields. In Fig. 7.4 values of I^2 are plotted versus T. The values of I have been taken from Fig. 7.2 and from the curve corresponding to the lowest applied field H = 717 Oe. By extrapolating I^2 to the temperature axis a rough value of the Curie temperature T = 458°C is found. The value of J_{ex} is found from Equation 7.8 by substituting z = 12 for the number of nearest neighbors, $T_C = 733$ K and $S = \frac{1}{2}$.

$$J_{ex} = \frac{3 (1.38 10^{-16}) 733}{(2) (12) (3/4)} erg$$

$$J_{ex} = 1.686 10^{-14} erg$$
7.9

7.4.2 Co₅₂Pt₄₈

The variation of the Curie temperature with the composition for cobalt-platinum alloys is shown in Fig. 7.5 (A. S. Darling, 1963). The depression in the Curie point due to ordering in the vicinity of the 25 atomic per cent cobalt alloy is obvious. The Curie temperature of $Co_{52}Pt_{48}$ is $T_{\rm C}$ = 900 K consistent with the value reported by J. B. Newkirk et. al. (1950). By substituting back to Equation 7.8, z = 12, $S = \frac{1}{2}$ and $T_{\rm C}$ = 900 K

$$J_{ex} = \frac{(3)(1.38 \ 10^{-16})(900)}{(2)(12)(3/4)} \text{ erg}$$





Magnetization squared as a function of temperature close to the Curie point. By extrapolation the Curie temperature is found to be 458°C.



Fig. 7.5 Variation of Curie temperature with composition in cobalt-platinum alloys.

$$J_{ex} = 2.07 \ 10^{-14} \ erg$$
 7.10

The values of the exchange integral J_{ex} will be used in the next chapter for the calculation of domain wall energy and width.

CHAPTER VIII

DOMAIN WALL ENERGY

8.1 INTRODUCTION

The change in direction of the magnetization between one domain and the next does not occur in a discontinuous jump but it takes place gradually over many atomic planes. Inside the wall the spins are no longer parallel to each other or to the easy directions. Therefore, the exchange and the magnetocrystalline anisotropy energy increase and then contribute to the domain wall energy. While the exchange energy tries to make the wall as wide as possible, in order to make the angle between adjacent spins as small as possible, the anisotropy energy tries to make the wall thin, in order to reduce the number of spins pointing in non-easy directions.

8.2 BLOCH WALLS

Fig. 8.1 shows the structure of a 180° domain wall. This type of boundary is often referred to as a 180° "Bloch" wall and it is here assumed that the rotation of the magnetization across the wall is such that the magnetization always lies parallel to the plane of the wall, itself assumed planar. The domain wall energy per unit area is given by the sum of the exchange and anisotropy energy

 $\gamma = \gamma_{ex} + \gamma_{an}$



Fig. 8.1 Structure of a 180° wall (by B. D. Cullity, 1972).

For the particular case of a 180° domain wall in a simple cubic structure of edge 'a' and parallel to a cube face $\{100\}$, the domain wall energy is a function of the thickness δ of the wall and it is shown in Fig. 8.2. The thickness of the wall is a compromise between the opposing influences of exchange energy and magnetocrystalline anisotropy energy. It is found (J. Crangle, 1977) to be

$$\delta = \sqrt{\frac{JS^2\pi^2}{Ka}}$$
 8.1

The smaller the anisotropy the thicker the wall. Therefore, wall thickness increases with temperature, because K almost always decreases with rising temperatures. The corresponding domain wall energy is given by

$$\gamma = 2 \sqrt{\frac{JS^2 \pi^2 K}{a}}$$
 8.2

8.3 NÉEL WALL

In recent years great interest has developed in the properties of thin films. In this case the thickness of the specimen is comparable with the thickness of the domain wall so that it is no longer possible to neglect the interaction between the strips of the free poles formed at the intersections of the domain wall with the surface of the specimen.





By taking into account this interaction a new type spin transition was predicted. This new domain wall, called Néel wall, is characterized by the fact that the magnetization rotates from one domain into the other without leaving the plane of the sample (Fig. 8.3, by Carey et. al., 1966).

8.4 CALCULATED VALUES OF DOMAIN WALL ENERGY AND WIDTH

Equation 8.2 was used to calculate the domain wall energies of the cubic and tetragonal phase of the samples. Since there is an uncertainty about the exact theoretical relationship between T_c and J_{ex} an order of magnitude treatment has been worked out.

Assuming $S = \frac{1}{2}$ and $a^3 = \frac{\text{volume of unit cell}}{\text{number of magnetic atoms in cell}}$ the listed values of domain wall energies were found (Table 8.1). Values of the domain wall width δ were determined by using Equation 8.1.



Fig. 8.3 Schematic representation of (a) Block wall and (b) Néel wall in a thin specimen.

Table 8.1 Calculated values of domain wall energy and width.

$\gamma = 2\sqrt{\frac{J_{ex}S^{2}\pi^{2}K}{a}}$ $\delta = \sqrt{\frac{J_{ex}S^{2}\pi^{2}}{Ka}}$	K(10 ⁷ erg/cc)	J _{ex} (10 ⁻¹⁴ erg)	o a(A)	$\gamma(erg/am^2)$	δ (Å)
FePt _{0.7} Ni _{0.3}					
cubic	0.37	1.7	2.61	4.9	66
tetragonal	3.30	1.7	2.61	14.5	22
Co52Pt48					
cubic	1.80	2.1	2.98	3.6	98
tetragonal	5.00	2.1	2.98	18.4	19

CHAPTER IX

MICROSTRUCTURE OBSERVATIONS

9.1 INTRODUCTION

Before a model is set up to explain the observed magnetic properties of the samples, it is very important to look at the microstructure of the specimens and determine the nature of the interaction responsible for their magnetic hardening. For this electron microscopy has been employed where one can actually see the microscopic inhomogeneities and their interactions with domain walls (Lorentz microscopy). The Bitter technique was used for the observation of magnetic domains in $\text{Co}_{52}\text{Pt}_{48}$ because no domains could be seen on a sample in its optimum state using Lorentz microscopy.

9.2 ELECTRON MICROSCOPY IMAGING AND DIFFRACTION

A parallel beam of electrons accelerated by a potential V is transmitted through a specimen (thin foil) and is diffracted in a number of directions by the crystal (Fig. 9.1). The diffracted electron beams are brought into focus in the back focal plane of the objective lens, forming a diffraction pattern. This pattern can be suitably magnified and studied if subsequent lenses in the microscope are arranged to focus on the rear focal plane of the objective. The diffraction pattern consists of an approximately two dimensional array of spots, each spot corresponding to a particular set of reflect-





Fig. 9.1 Electron microscope image and diffraction.

ing planes. From the diffraction pattern one can find the orientation of the foil. The objective lens also forms an image of the lower surface of the specimen in the image plane. This image can be magnified subsequently by other lenses of the instrument and finally is projected into the fluorescent screen (Fig. 9.1).

9.2.1 Bright and Dark Field Images

It can be seen from Fig. 9.1 that the transmitted and diffracted beams from the same area of specimen meet in the image plane. If the diffracted beams are allowed to contribute to the final image, the quality of the image is poor mainly because of lens aberrations. However, this can be avoided if only the transmitted beam or one of the diffracted beams is allowed to contribute to the final image. This is achieved by using a small aperture which can block either the transmitted or the diffracted rays. If the aperture is centred on the main transmitted beam blocking the diffraction rays a so-called bright field image is produced. A dark field picture is obtained when the aperture is centred on one of the diffracted beams thus blocking the direct beam.

9.2.2 Contrast Theory

In order to explain the contrast observed at lattice defects, it is necessary to calculate the diffracted intensity from a perfect crystal and then try to see how this intensity

is modified by the presence of lattice defects. It is simple to base the discussion on the kinematical theory of diffraction.

An incident beam of unit intensity is directed vertically onto the foil (Fig. 9.2). The foil is assumed to be oriented in such a way that only one beam, with indices hkl corresponding to the reciprocal vector \dot{g} , is being diffracted at the Bragg angle θ . According to the kinematical theory the foil is divided into small rectangular columns such as AB. The amplitude of the diffracted beam from that column is

$$A_{D} = \sum_{j} F_{j} e^{-2\pi i (\vec{g} + \vec{s}) \cdot \vec{r}_{j}} = \sum_{j} F_{j} e^{-2\pi i \vec{s} \cdot \vec{r}_{j}} \qquad 9.1$$
(for a perfect crystal $\vec{g} \cdot \vec{r}_{j}$ is integer)

 F_j is the scattering factor for electrons from the atoms in the unit cell located at a distance \vec{r}_j within the column \vec{s} is the deviation of the reciprocal vector \vec{g} from the Ewald sphere measured along the length of the column.

The intensities of the diffracted and transmitted beams are $I_D^{=}|A_D|^2$ and $I_T^{=1-I_D}$, respectively. For a perfect crystal both transmitted and diffracted intensities at the bottom of the foil will be uniform from one area to the next and no contrast is observed. If, however, a planar defect is present along the line CD one portion of the crystal is displaced with respect to the other by a vector \vec{R} . The amplitude, therefore, of the diffracted beam by this region is

incident beam



Fig. 9.2

Schematic representation of the way in which the transmitted and diffracted electron wave intensities vary within the foil. The planar fault gives rise to a change in phase in the diffracted or transmitted beam.

$$A_{D} = \sum_{j} F_{j} e^{-2\pi i (\vec{g} + \vec{s}) \cdot (\vec{r}_{j} + \vec{R}_{j})} = \sum_{j} F_{j} e^{-2\pi i \vec{g} \cdot \vec{R}_{j}} e^{2\pi i \vec{s} \cdot \vec{r}_{j}}$$

$$j$$
9.2

Thus, if a fault is present, the intensity of the diffracted beam is modified by an additional phase angle α given by

The difference between this intensity and that of the surrounding perfect crystal gives rise to the contrast observed at the crystal defects.

9.3 OBSERVATION OF DOMAIN WALLS

Among the techniques which are currently in use for the observation and investigation of magnetic domain structures, the Bitter pattern and Lorentz microscopy method are the most fruitful and still the most widely used. Both of these models disclose domain walls. The individual domains appear the same but the domain walls are delineated.

9.3.1 Optical Microscopy - Bitter Technique

In the Bitter method (or the Colloid technique) devised by Bitter in 1931, an aqueous suspension of extremely fine particles of magnetite, Fe_3O_4 , is applied to a strain-free and highly polished surface of the specimen. These particles are attracted to regions of high magnetic field gradient which are produced near domain walls. Imagine a 180° wall intersecting the surface as in Fig. 9.3a, where the spins in the wall are represented simply by the one in the centre normal to the surface. This gives rise to a free north pole and to localized fields spread in the directions shown in the figure. Using an optical microscope, in the "bright field" conditions, Fig. 9.3b, the domain walls will appear as dark lines on a light background and vice versa for the "dark field" conditions, Fig. 9.3c.

9.3.2 Lorentz Electron Microscopy

Lorentz microscopy has been used commonly in studying domain walls because of its high resolution. It allows the examination of the fine details of domain structures and it permits the direct observation of inhomogeneities and their interactions with domain walls. Electrons with velocity \vec{v} passing through a magnetic sample of magnetization \vec{M} experience a force \vec{F} , known as the Lorentz force, given by

$$\vec{F} = -e(\vec{\upsilon} \times \vec{B}) = -4\pi e(\vec{\upsilon} \times \vec{M}) \qquad 9.4$$

Where \vec{B} is the magnetic induction, $\vec{B} = \vec{H} + 4\pi \vec{M}$ and neglecting the effect of the applied and demagnetizing fields.

Because of this force, the electron beam passing through the specimen will be deviated by an amount and in a direction determined by the magnitude and direction of the local \dot{M}_{s}



Fig. 9.3 Observation of domain walls by the Bitter method (Cullity, 1972).

vector. In adjacent domains this will lead to a deficiency of electrons in some places and an excess of electrons to others (Fig. 9.4). If one, therefore, observes the foil out of focus the positions of domain walls will appear as white lines for the deficient in intensity places or black lines for the places of excess in intensity. Switching from the underfocused to the overfocused state the white lines become black and vice-versa.

9.4 DOMAIN MICROSTRUCTURE

Both alloys examined in this study undergo a disordered cubic — ordered tetragonal transition by means of nucleation and growth. Electron diffraction microscopy and X-ray analysis reveal that the transition takes place in the following way.

- a) Nucleation of coherent ordered particles in the disordered matrix.
- b) Clustering of particles having parallel c-axes into common crystallographic planes.
- c) Growth of clustered nuclei to coalesce forming lamellae. Adjacent lamellae are twin related.
- d) Growth of lamellae of dominant c-axis converting the entire crystal into a mosaic of perfectly ordered domains.



Fig. 9.4 Lorentz microscopy method of observing domain walls.

A detailed examination of the microstructure of $Co_{52}Pt_{48}$ and FePt_{0.7}Ni_{0.3} through the course of ordering has been carried out. Since the results are very similar for both systems, $Co_{52}Pt_{48}$ was chosen to serve as an example of the disordered-ordered reaction.

An analysis of the observed structure features and their modification was carried out by means of a correlation of bright and dark field micrographs with selected area diffraction patterns.

9.4.1 Ordering and Microstructure in Co₅₂Pt₄₈

As has been seen earlier (Sec. 2.4.1), ordering in $Co_{52}Pt_{48}$ can be suppressed by quenching from $1000^{\circ}C$. Aging at 700°C orders the alloy which becomes magnetically hard.

Microstructure observations were reported for four different aging stages: early (2 min. at 700° C), optimum (17 min. at 700° C), intermediate (150 min.), and overaged (960 min.).

Penisson et. al. (1971) also examined the microstructure of an equiatomic CoPt alloy after an isochronous thermal treatment, but they did not correlate their observations with the magnetic properties of the sample. Since the magnetic properties are very sensitive to the exact composition and heat treatment, it was very difficult to correlate the observed magnetic properties with their microstructure

observations.

i) Early Ordering State

As stated earlier, X-ray analysis shows broad superstructure lines with no evidence of splitting of the main lines.

Electron microscopy observations show a mottling contrast in all grains on the bright and dark field micrographs (Figures 9.5 and 9.7). The electron diffraction pattern of (001) plane shows the presence of three superlattice spots, 100, 010, and 001. This is because the c-axes of the ordered crystallites always remain effectively parallel to one of the cube axes of the original crystal. Thus, the ordering of a single crystal results in a formation of three classes of crystallites referred to as a reference system consisting of the cube axes of the original disordered matrix.

Dark field micrographs, using all three different superstructure spots (Fig. 9.5) revealed different ordered regions consisting of randomly distributed quasi spherical particles having a 50 - 100 Å diameter. This suggests that the ordered nuclei have the CoPt tetragonal structure. The ordered phase covers a large proportion of the grain volume.

Since ordering involves a change in symmetry, the reaction is accompanied by sizable internal strains due to the lattice misfit between the mutually coherent parent and product phases. The strains, being very large at the beginning, tend to relax in later stages of ordering. The strain Fig. 9.5 Dark field image taken from a 010 superlattice reflection of a (001) foil at the early stages of ordering.

Fig. 9.6

Diffraction pattern of a (101) zone. Superlattice reflections appear to be washed out; the appearance of some "streaking" indicates the presence of strains in the matrix.

D effect is seen on the diffraction pattern (Fig. 9.6), by the appearance of asymmetric streaks along <110> directions on the diffraction spots. (As a result of the strains, striations are observed in the bright field micrographs). The shape of the main spots is modified because all three orientations of the ordered phase are superimposed on each other in the reciprocal lattice of the disordered matrix.

An interesting result is shown on micrographs 9.7a and 9.7b. The dark field pictures were taken using the OlO superlattice spot and the O2O main spot of a (101) foil. The spacing of the observed thickness fringes is different on the two micrographs and it is consistent with the predictions of the kinematical theory of diffraction. According to the latter, the extinction distance ε_g is given by (Hirsch et. al. 1965)

$$\varepsilon_{g} = \frac{\pi u}{F\lambda}$$

Where u is the volume of the unit cell, F is the structure factor and λ the wavelength of the electrons at 100 kV. (The extinction distance is a measure of the depth periodicity of the thickness fringes appeared in the micrographs).

Since ε_{g} is inversely proportional to F, and F is smaller for the superlattice spot

Fig. 9.7 Dark field images from a (010) superlattice reflection (a) and (020) main reflection (b) of a (101) foil.





12.



(b)

$$(F_{hkl})_{super} = S(f_{Co} - f_{Pt})$$

The spacing of the thickness fringes is much larger for the micrograph taken with the superlattice spot.

ii) Optimum State

Further aging of the sample results in a process characterized by

- The change in size and shape of nuclei from spherical to an ellipsoidal form.
- 2) A change of the spatial distribution showing the existence of alignment of the nuclei along {110} crystallographic planes. This produces on the micrographs alignment directions which are consistent with intersections of {110} planes with the foil plane. The c-axis makes a 45[°] angle with the normal to the {110} planes.
- 3) The presence of distinct streaks on the electron diffraction patterns. These streaks lie along <110> on {110} planes.

a) The (012) Foil.

The above features are shown on micrograph 9.8. This is a dark field picture using the 100 superlattice spot of

Fig. 9.8 Dark field picture from a 100 superlattice reflection of a (012) foil at the optimum state showing ordered nuclei along [221] and [221].




Fig. 9.9

Stereographic projection of (012) zone showing the six possible {110} planes. The points A and D are parallel to alignment directions in Fig. 9.8; these are also the directions of the streaks observed on the diffraction pattern (Fig. 9.10). The point E shows the direction at which the particles are elongated.

Fig. 9.10 Diffraction pattern of the (012) foil for the area shown in Fig. 9.8. The distinct streaks are along the [221] and [221] directions.



the (012) foil plane. It gives a picture of the projection to the plane of observation of the collection of ordered nuclei whose c-axis corresponds to this particular diffraction spot (100). The length of the ordered nuclei ranges from 200 - 300 $\stackrel{\circ}{A}$ with $\frac{\text{length}}{\text{width}} = 3 \div 5$. These nuclei are clustered in [221] and [221] directions in the foil plane. These are consistent with the intersections of (110) and (110) planes with the foil plane as shown in the stereographic analysis (Fig. 9.9). The c-axis is at 45° to both of these planes. In addition, the ordered nuclei appeared to be elongated along the [100] direction shown on the (012) stereographic projection (Fig. 9.9).

The diffraction pattern of this area is shown on Fig. 9.10. Asymmetric streaks are observed in directions close to $[\overline{22}1]$ and $[2\overline{2}1]$. But the angle between the traces $[\overline{22}1]$ and $[2\overline{2}1]$ as measured from the micrograph is 96° while the angle between the streaks is only 80°. It is, therefore, believed that these streaks are projections of $[\overline{11}0]$ and $[1\overline{10}]$ directions to the plane of the foil. In fact, the projection of $[\overline{11}0]$ into the (012) plane is

 $[012] \times [\overline{110}] \times [012] = [\overline{542}]$

Similarly, the projection $[1\overline{1}0]$ into the (012) is $[5\overline{4}2]$. The angle between $[\overline{5}\overline{4}2]$ and $[5\overline{4}2]$ is 83.6°, close to the measured angle between the streaks (80°).

The asymmetric streaking observed on the diffraction spots is characteristic of relrods in the reciprocal lattice. The elastic distortions induced by the cubic-tetragonal transformation cause displacement and streaking of the lattice points in a direction parallel to the distortion. That would lead to the formation of relrods in the reciprocal lattice. The intersection of the Ewald sphere with the relrods will give rise to the streaks observed on the diffraction pattern (the diffraction pattern is a planar section through reciprocal space).

Streaks due to coherency strains are distinguishable from those due to particle shape. The former are asymmetric; they do not appear at the origin or in reflections unaffected by the strains and their length increases with increasing order of reflection. The streaking observed at the origin is believed to be the result of double diffraction (Hirsch et. al. 1965).

In summary, the ordered nuclei are aligned in (110) and (110) planes and they are elongated along the [100] direction. The streaks on the diffraction spots and, therefore, the shears on the lattice points are along the [110] direction which lies on the (110) plane and along the [110] which lies on the other alignment plane (110) (Fig. 9.9).

The alignment of nuclei in certain crystallographic planes is believed to be due to the asymmetric strains induced by the cubic tetragonal transformation (Tanner, 1968).

The ordered nuclei which initially are randomly distributed in the matrix become centers of tetragonal distortion and they impose a bias on nucleation in their vicinity. In order to minimize the strain energy, the succeeding nuclei take the same orientation as their nearest predecessor.

A dispersion in size of the nuclei as well as a shape irregularity has been also observed on the micrographs. This could be explained as follows. Starting with an initial random distribution some nuclei which are well placed will develop preferentially while others tend to disolve. This leads to a dispersion in size. The shape of the nuclei is also irregular since the direction of growth varies from one nuclei to the other with each nuclei tending to grow in certain directions which are energetically favoured.

b) The (111) Foil Plane

One sees on the reciprocal lattice that the spots corresponding to the three different c-axes are present only in certain planes like {001}, {111} and {210} whereas in {110} and {112} planes only one type of nucleus is observable.

The spatial distribution of the ordered nuclei corresponding to the three different c-axes (100, 010 and 001) are shown in Figures 9.12, 9.13 and 9.14. These are dark field pictures using the 011, 101 and 110 superlattice spots of a (111) foil. The nuclei corresponding to the [001] c-axis (110 spot) are aligned in [121] and [211] directions



Fig. 9.11 S

Stereographic projection of the (111) zone showing the six possible {110} planes. Points A, C and E are the alignment directions of the nuclei in micrographs 9.12, 9.13, and 9.14. Point H shows the elongation direction of nuclei. Points K and L are the direction of the streaks observed in the diffraction pattern.

Fig. 9.12 Dark field picture from the 101 superlattice reflection of a (111) foil showing ordered nuclei corresponding to one kind of c-axis [010]. Ordered nuclei are along [112] and [211].

Fig. 9.13 Dark field image of the same area as in Fig. 9.12, from the 110 superstructure reflection showing ordered nuclei corresponding to a different c-axis [001]. Nuclei are along [121] and [211].



Fig. 9.14 Dark field picture of the same area as in Fig. 9.12, from the Oll superlattice reflection showing ordered nuclei corresponding to the third c-axis [100]. Ordered nuclei lie along [112] and [121] directions.



(Fig. 9.13). These are consistent with intersections of $(\overline{1}01)$ and $(0\overline{1}1)$ planes with the (111) plane (Fig. 9.11). The c-axis makes an angle of 45° with the normal to both these planes. The average length of nuclei is 150 Å with an average ratio of $\frac{\text{length}}{\text{width}} = 1.7$. The separation between the rows of the aligned particles is 140 Å. The dark field micrograph with the $\overline{1}01$ spot (Fig. 9.12) lights the nuclei of [010]c-axis. The clustering of the nuclei is along $[\overline{1}\overline{1}2]$ and $[\overline{2}11]$ directions, which again are consistent with intersections of ($1\overline{1}0$) and ($0\overline{1}1$) planes with the plane of observation (111) (Fig. 9.11). The c-axis is at 45° to both of these planes. The average length of nuclei is 150 Å and the ratio of $\frac{\text{length}}{\text{width}}$ = 2.5.

The third kind of nuclei corresponding to [100] c-axis (dark field with 011 spot, Fig. 9.14) show alignment along [112] and [121] which as seen previously (Fig. 9.11) are consistent with intersection of {110} planes with the (111) plane.

In all three different cases, the ordered nuclei are elongated along the [Ī01] directions. The streaks appearing on the diffraction spots are along the [0Ī1] and [lī0] directions (Fig. 9.11).

c) Short Range Order

P. Eurin et. al. (1973) claimed a short range order in the spatial distribution of the ordered nuclei. They proposed

that same ordered nuclei are arranged locally in a b.c.c. lattice, forming a three dimensional pseudoperiodic structure. That was shown by optical Fraunhofer diffraction.

A similar technique was used to examine the possibility of any periodical arrangement of nuclei. A photographic plate associated with the dark field micrograph of Fig. 9.14 was illuminated by a parallel beam of coherent light of a laser (.1W). The diffraction pattern (Fig. 9.15) was obtained in the focal plane of a converging lens. It is similar to that obtained by P. Eurin et. al. However, it is not uniform but rather dense lines of spots appear in two directions which are identified as normals to the alignment directions of nuclei. (That was actually the hint to re-examine the results of P. Eurin et. al. since the optical diffraction patterns obtained with the dark field micrographs of three different foils (001), (110) and (111) showed dense lines perpendicular to the direction of alignment of nuclei). This is the kind of diffraction pattern which is formed when coherent light falls on a rectangular hole.

The spacing of the grating d which is formed by the nuclei and gives the observed optical diffraction pattern is found to be ~900 Å by measuring the distance D between the maxima and using the relation $d = \frac{\lambda L}{D}$; where L is the distance from the dark field micrograph to the diffraction pattern and λ is the wavelength of the light of the lazer. This spacing corresponds to rectangular holes of this size, observed on

Fig. 9.15 Optical diffraction pattern obtained from the dark field micrograph of Fig. 9.14 after illuminating the photographic plate by coherent light from a laser.



the dark field micrographs (Figures 9.13 and 9.14), which are formed by the aligned nuclei. The density of nuclei is high around these holes and if the coherent light happens to hit one of them the observed pattern is obtained. However, these holes are not periodically distributed and the obtained pattern is not uniform.

iii) Intermediate and Overaged State

Upon prolonged aging

- 1) A fine lamellar structure was developed.
- Lamellar size increases and is characterized by a maze pattern which is a manifestation of antiphase domain structure.
- 3) Intensity of superlattice spots on the diffraction pattern increases and the tetragonal split is distinct indicating a more advanced stage of ordering.
- a) Intermediate State.

At this aging state, ordered nuclei having parallel c-axes coalesced to form fine lamellae shown on Fig. 9.16. The bright regions of the dark field micrograph represent lamellae corresponding to one of the three different c-axes (dark field picture was taken with the 100 superlattice spot of a (012) foil). The relationship of the contrast between the lamellae is inverted with the use of the superlattice spots corresponding to the other two c-axes. This suggests Fig. 9.16 Dark field picture from a 100 superlattice reflection of a (012) foil of an intermediate ordering stage. Lamellar traces are along the [221] and [221] directions.



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a twin structure with the c-axes between each successive lamellae having a sequence 1, 2, 1, 2,... The twin interface is parallel to {110} planes (Fig. 9.17).

The lamellar traces on Fig. 9.16 are along [221] and $[\overline{22}1]$ and then are consistent with intersections of ($\overline{110}$) and ($\overline{110}$) with the (012) foil as shown in Fig. 9.9. They are 150 - 200 Å wide and 700 - 800 Å long.

The process of twinning is a good example of the reduction of the strains built up in the cubic-tetragonal transformation. Since twinning is equivalent to a systematic shear on each successive atomic planes, it can relieve some of the stresses (Hanson et. al., 1964). In addition to the stress relief by shear, there is an extra relief due to the rotation of the c-axis by 90° resulting from twinning since the stress in the twinned region will no longer augment that due to the matrix, (Marcinkowski, 1963).

b) Overaged State.

In an overaged sample there is a progressive growth of the lamellar size. Antiphase domains (APD) become visible in the interior of the ordered lamellae. These may be regarded as lattice domains in which the configuration of the cobalt and platinum atoms has been reversed so that the atoms of two adjacent domains are out of step by a displacement vector \vec{R} . For cobalt-platinum \vec{R} may be equal to any one of the following vectors; $\frac{a}{2}$ [101], $\frac{a}{2}$ [101], $\frac{a}{2}$ [011] and $\frac{a}{2}$ [011]





Fig. 9.17 (a) Schematic representation of the microstructure. (b) Angular relationships of the matrix structure and resulting twins $(\tan(\frac{\pi}{4} + \phi) = \frac{c}{a})$.

(Fig. 9.18). The boundaries separating the out-of-step domains are called antiphase domain boundaries.

An interesting feature of the antiphase domain structure is the observed complex maze pattern. This can be explained satisfactorily on the basis of the kinematical theory of diffraction contrast. The phase difference α between the diffracted beam on either side of the antiphase boundary is given by $\alpha = 2\pi \vec{g} \cdot \vec{R}$ (Equation 9.3) where \vec{R} is of the type $\frac{1}{2}$ a[101]. For a main reflection (hkl) the phase shift is zero or $\pm \pi$. But for a superlattice reflection α is $\pm \pi$ and contrast for antiphase domains becomes visible.

These features are shown on Fig. 9.19. The dark field micrograph was taken with the 100 superlattice spot of a (012) foil. The bright regions correspond to lamellae of a particular c-axis [100] and they lie along the [221] and [221] directions. These are consistent with intersections of (110) and ($\overline{1}10$) planes with the (012) foil (Fig. 9.9). Both of these planes make an angle of 45° with the [100] c-axis. The lamellar width now varies from several thousand to 200 Å. Antiphase domain boundaries are visible in the interior of the lamellae. Each lamella is decorated with fringes. This is not surprising and it can be explained by considering Fig. 9.20. A lamella of definite width W is inclined to the foil at an angle ϕ . If the lamella is a perfect crystal (with no defects) there exists a region ABCD where no contrast is observed. This is because the thickness



Fig. 9.18 Antiphase vectors in CoPt. Displacements such as $\vec{R} = \frac{1}{2}a[101]$ place Co and Pt atoms to wrong sites. On the other hand, no antiphase boundaries are formed by displacements such as $\vec{R} = \frac{1}{2}a[110]$. There are four possible antiphase vectors.

Fig. 9.19 Dark field micrograph from a 100 superstructure reflection of a (012) foil at an overaged state. Lamellar traces are along the [221] and [221] directions.

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Fig. 9.20 A lamella of width W is inclined to the foil at an angle ϕ . In the region ABCD no contrast is observed. On either side of this region, thickness fringes appear on the micrographs.

t

of this column is constant and the diffracted beams at any point on the bottom of the column will be identical. However, the regions on either side of the column will give a fringe contrast because the diffracted intensity oscillates with depth in the crystal (Equation 9.1). As the lamellar width decreases the region of no contrast diminishes and beyond a critical size it is no longer observed. The fringes then cover all the width of the lamellae. From the length 1 of fringes and the angle ϕ the plane of the lamella makes with the foil the thickness t of the foil can be determined by

$$t = ltan\phi$$
 9.11

1 is found from the micrograph to vary from 100 $\stackrel{0}{A}$ (place labeled A) to 170 $\stackrel{0}{A}$ (B). The angle between (110) or ($\overline{110}$) and (012) is 71°34'. Substituting these values to Equation 9.11 t is found to vary from 300 to 500 $\stackrel{0}{A}$ in the regions of interest.

Inspection of the corresponding selected area diffraction patterns (Fig. 9.21) disclosed an increased splitting of the reflections indicating a more advanced ordering stage. From the tetragonal split of the 200 spot an approximate value of $\frac{c}{a}$ can be found

$$\frac{c}{a} = \frac{d_1}{d_2} = \frac{30.0 \text{ mm}}{30.8 \text{ mm}} = 0.974$$

Fig. 9.21 Diffraction pattern of the (012) foil corresponding to the area shown on Fig. 9.19. The assymetric streaks have not yet disappeared and the tetragonal splitting is now distinct.



(d₁ and d₂ are the corresponding distances of 200 and 002 from the central spot of diffraction pattern). This value of $\frac{c}{a}$ ratio is very close to the value obtained by X-ray dif-Asymmetric streaks are also observed on the diffracfraction. tion spots suggesting the presence of some strains. These are long range strains caused by the structural misfit at the junction of the growing lamellae with different c-axes. These strains may eventually relax by further twinning. Coarse twin lamellae, twin bands, may be formed in the interior of which exist microtwin lamellae (P. Eurin et. al., 1973), or by further expansion of a dominant orientation as shown on Fig. 9.22. One of the c-axes predominates over the other two and plays the role of matrix inside which exist lamellae following the twin relations. Eventually, the size of the ordered lamellae diminishes to the profit of the ordered matrix, producing large monodomain areas with antiphase domain contrast.

iv) Magnetic Hardening and Microstructure

Besides the observations made in the previous sections the relation between the microstructure and magnetic hardening was examined in additional ordering stages giving the results shown on micrographs, (Figures 9.23a - 9.23f). The coercivity is small in the early ordering, it peaks at the optimum and settles down to a low value in the overaged.

a) At the early ordering, ordered tetragonal nuclei having a nearly spherical shape with 50 - 100 $\stackrel{\rm O}{\rm A}$

Fig. 9.22 Dark field image from a 010 superlattice reflection of a (101) foil at the late stages of ordering. One of the c-axis predominated over the other two.



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diameter are randomly distributed in the cubic matrix. This is shown on the dark field micrograph (Fig. 9.23a) using the OlO superlattice spot of a (101) foil. The coercivity measured is 350 Oe.

- b) At an intermediate stage to the optimum the nuclei start aligning in groups as shown by the dark field micrograph (Fig. 9.23b) using the 100 superstructure spot of a (012) foil. The ordered nuclei have a ratio of $\frac{\text{length}}{\text{width}} = 2$, with a length of 80 - 100 Å. The coercivity increases to 2500 0e.
- c) Near the optimum state the ordered nuclei are aligned in certain directions and their dimensions are increased to a length of 100 - 140 ^O/_A with <u>length</u> width = 2. This is shown on the dark field micrograph (Fig. 9.23c) using the <u>1</u>10 superlattice spot of a (112) foil. The coercivity is further increased to 3000 0e.
- d) Further annealing causes the nuclei to grow in one dimension leading to a $\frac{\text{length}}{\text{width}} = 4$, with an average length of 160 Å. The dark field micrograph (Fig. 9.23d) was taken using the 010 superstructure spot of a (101) foil. The measured coercivity is 3500 0e.
- e) At an intermediate state to the overaged, the ordered nuclei having parallel c-axes start joining together forming twin lamellae of 100-200 Å thick-

Fig. 9.23 Dark field micrographs from

- (a) 010 superlattice reflection of a (101) foil (2 min. at 700 °C).
- (b) 100 superstructure reflection of a (012) foil (12 min. at 700° C).
- (c) $\overline{110}$ superlattice reflection of a (112) foil (17 min. at 700°C).
- (d) 010 superstructure reflection of a (101) foil (20 min. at 700° C).
- (e) $\overline{102}$ superlattice reflection of a (241) foil (150 min. at 700° C).
- (f) 100 superstructure reflection of a (012) foil (960 min. at 700° C).



(a)



(b)











(d)



ness. This is shown on the dark field micrograph (Fig. 9.23e) using the $\overline{1}02$ superlattice spot of a (241) foil. The measured coercivity has dropped to 2000 0e.

f) At the overaged state the lamellar thickness increases from several thousand to 200 Å, as shown on Fig. 9.23f. The dark field picture was taken using the 100 superstructure spot of a (012) foil. The coercivity measured is only 200 0e.

v) Aging at 600°C - Inhomogenous Ordering

As stated earlier in the X-ray analysis the ordering at 600°C is discontinuous. Tetragonal lines appear from the beginning besides the cubic and they grow at the expense of the latter on further aging. The profile of a superlattice line shows a sharp peak with a broad shoulder at either side.

Microstructure observations of an alloy at its optimum state (H_c ~1800 0e) revealed that the structure is not homogenous. Fig. 9.24 shows large ordered regions which were observed next to very small ordered nuclei of 50 Å diameter. The dark field micrograph was taken with the 010 superlattice spot of a (101) foil. The lamellae lie along [11] directions consistent with intersections of (10) and (011) planes with the (101) foil. Both of these planes make an angle of 45° with the c-axis.
Fig. 9.24 Dark field image from a (010) superstructure reflection of a (101) foil. The large ordered regions lie along [111].



The interface between these ordered domains and the matrix is irregular and somewhat diffuse. These large irregular ordered domains are responsible for the sharp peak observed in the X-rays and the very small nuclei give rise to the broad shoulder of the superstructure lines.

Complete disordered regions were also observed (Fig. 9.25) in some areas of the foil suggesting that ordering is not homogenous as was the case for aging at 700° C. The diffraction pattern of Fig. 9.25 belongs to a (220) foil where the absence of 010 and $\overline{101}$ superlattice spots is obvious.

9.5 SURFACE MORPHOLOGY AND MAGNETIC DOMAINS IN Co52Pt48

9.5.1 Surface Microstructure

The surface of some mechanically polished samples has been examined with an optical microscope. After homogenizing the specimens there was a noticeable grain growth especially for those which were homogenized at 1350° C. This effect was more pronounced in $Co_{52}Pt_{48}$ for which grains of a few millimeters were observed.

Fig. 9.26 shows the surface of a $\text{Co}_{52}\text{Pt}_{48}$ sample after being mechanically polished and annealed for 17 minutes at 700^oC (in its optimum magnetic hardness). A stereographic analysis of all the traces observed is shown in Fig. 9.27. Markings labeled with 1, 3 and 4 lie close to <110> and <111> directions. However, some of these are believed to Fig. 9.25 Diffraction pattern of a (220) zone. The absence of the 010 and 101 superstructure spots is obvious, indicating the presence of the disordered cubic structure.



Fig. 9.26 Surface microstructure of a Co₅₂Pt₄₈ sample at its optimum state after being mechanically polished.





Fig. 9.27 Stereographic projection of the Co₂₂Pt₄₈ grain shown on Fig. 9.26. Marking 5 is the domain wall direction as it appears on Fig. 9.29 after the application of the ferrofluid.

be annealing twins lying in <111> directions since they are formed in the cubic state and they do not disappear after the surface layer is removed. (In fact, they travel from one side to the other side of the thin foil). Markings labeled 2 lie along <110> directions and these as well as some of the 1,3 and 4 traces are assumed to be associated with the stresses built up in the sample during the cubictetragonal transformation.

Trace 5 is the direction of domain walls appearing in the polished surface of the grain after the ferrofluid was applied.

9.5.2 Magnetic Domains

Although Lorentz microscopy was employed to image domain walls no magnetic contrast was observed for a $\text{Co}_{52}\text{Pt}_{48}$ sample at its optimum state. On the other hand, conventional 180° domain walls were observed in the overaged samples where the microstructure consists of ordered lamellae embedded to a tetragonal matrix. However, magnetic domain walls were macroscopically present on the polished surface of a $\text{Co}_{52}\text{Pt}_{48}$ specimen. Since a strain free surface is required the polished specimen was annealed at 1100°C for 24 hours and then it was brought up to the optimum state by the appropriate heat treatment (17 min. at 700°C).

The domain structures were typical of those for strongly uniaxial materials. Fig. 9.28 shows domain structures

characteristic of planes parallel to the easy axis (area A) or making an angle between 0 and 180° with the easy axis of magnetization (area B).

A series of observations was carried out on a single grain (Fig. 9.26) which was oriented by X-rays. The domain structure of the grain in the demagnetized state is shown on Fig. 9.29. Most of the sample's area is occupied by 180° domain walls with the easy axis on the plane. It is found by stereographic analysis that these domains are parallel to a [001] direction (Fig. 9.27).

The application of a field of 2000 0e changes the pattern to that shown on Fig. 9.30. Some of the domain walls grow in size at the expense of the others and at the new remanent state are arranged in the way shown on Fig. 9.30. At the overaged state the magnetic domains grow in size as shown on Fig. 9.31. This is consistent with the electron microscopy observations of large ordered mono-domain regions.

However, in spite of the precautions taken, it was not certain that ordering did not occur to a greater extent near the surface than throughout the bulk specimen so that the observations do not represent a true picture of the interior of the specimen. An attempt was made to remove the surface layer by electropolishing. However, this technique is tricky because of the difficulty in electropolishing these alloys. In most of the cases the surface was rather etched than electropolished failing to reveal any domain

Fig. 9.28 Bitter domain patterns in $Co_{52}Pt_{48}$ characteristic of uniaxial materials with the easy axis on the foil plane (A) or at the angle θ between $0 - 90^{\circ}$ (B).

Fig. 9.29 Bitter domain pattern of the Co₅₂Pt₄₈ grain at the demagnetized state.



Fig. 9.30 Magnetic domains on the same grain as in Fig. 9.29 after the application and removal of a field of ~2000 0e.

Fig. 9.31 Magnetic domain structure of the Co₅₂Pt₄₈ grain in an overaged demagnetized state.



structures. But in a few cases electropolished grains were obtained showing the same domain contrast observed on the previously shown Figures 9.29.

9.6 MAGNETIC DOMAINS IN FePt_{0.7}Ni_{0.3}

Ordering in FePt_{0.7}Ni_{0.3} is similar to that of $Co_{52}Pt_{48}$ so that the change of microstructure through the course of ordering will not be presented here. However, the crystal morphology of the sample (Fig. 9.32) in its optimum state (H_c 1400 0e)closely parallels the intermediate state of $Co_{52}Pt_{48}$. The bright field micrograph of a (001) foil (P. Gaunt, 1977) shows lamellar traces with multiantiphase domain boundaries. This confirms the idea that each lamella does not develop from a single nucleus but from a group of nuclei having parallel c-axes. The lamellar traces lie along {110} directions and they are in twin relations with their c-axis at 90° to that of the tetragonal matrix. That was confirmed for six different orientations by trace analysis and dark field micrographs from the superlattice spots.

Fig. 9.33 is an overfocused image of the same area shown on Fig. 9.32. Each lamellar trace is decorated with black and white contrast and these are identified as 90° domain walls, since the c-axis rotates through 90° in crossing from the lamellae to the matrix. The long black and white lines, parallel to [001] are 180° domain walls. They are determined from the matrix whose c-axis and therefore the easy direction of magnetization is parallel to [001]. When a 180[°] domain wall crosses a lamellar trace the black and white contrast of the lamellae reverses. This is shown on the ringed areas of figures and is sketched in Fig. 9.33.

After the application and removal of a field of 2000 0e the domain walls are displaced and in the new remanent state seem to show preference in crossing 90° lamellar junctions (Fig. 9.34).

Fig. 9.32 Bright field image of an FePt_{0.7}Ni_{0.3} sample at its optimum state. Lamellar traces are along the [011] and [011] directions.



Fig. 9.33 Overfocused image of the area shown on Fig. 9.32. The walls parallel to [001] are 180° domain walls. The (011) and (011) lamellae are decorated by pairs of 90° domain walls. The ringed area shows the reversal of lamellae contrast on crossing a 180° wall.



Fig. 9.34 Overfocused image of same area as in Fig. 9.33 after the application and removal of a 2000 Oe field parallel to [001]. Ringed area shows 180° wall crossing a lamellar junction.



CHAPTER X

PROPOSED THEORY OF MAGNETIC HARDNESS AND DISCUSSION OF RESULTS

10.1 INTRODUCTION

Based on the electron microscopy observations a model is set up to explain magnetic hardening in $\text{FePt}_{0.7\text{Ni}0.3}$. The model leads to a linear variation of coercivity with temperature through continuous pinning of domain walls.

The applicability of the random anisotropy model on the $\text{Co}_{52}\text{Pt}_{48}$ alloy is also investigated. The model explains the measured high values of the remanent magnetization in both systems.

10.2 PROPOSED MODEL FOR FePt 0.7^{Ni}0.3

The micrographs (9.33-9.34) of an FePt_{0.7}Ni_{0.3} sample at its optimum state show 180° domain walls crossing 90° lamellar junctions after the application and removal of a field of 2000 Oe. These lamellar junctions are assumed to be the pinning centres of the magnetic domain walls.

When a 180° domain wall crosses a lamellar junction there is no need for extra domain wall segments or uncompensated poles within the lamellae (Fig. 10.1a). However, the application of a field will cause the wall to move a distance z introducing an extra segment of a 180° domain wall and the uncompensated poles within the lamellae (Fig. 10.1b).





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Fig. 10.1 (a) Change in lamellar 90° wall contrast on crossing a 180° domain wall and 180° wall meeting lamellar junctions; B and W indicate lines of black and white contrast. (b) 180° wall leaving lamellar junctions.

The interaction energy U(z) arises from the increase in domain wall energy E_{γ} and the demagnetizing energy E_{D} . Both of these will act like a barrier to domain wall motion after the application of a field. However, the wall crosses this barrier at the coercive field H_o given by (Chapter I)

$$H_{O} = \frac{1}{2IA} \left(\frac{dU}{dz}\right)_{max}$$
 10.1

In order to evaluate H₀ the maximum value of $\left(\frac{dU}{dz}\right)_{max}$ is required. But for an order of magnitude treatment,

$$\left(\frac{\mathrm{d}U}{\mathrm{d}z}\right)_{\mathrm{max}} = \frac{\Delta U}{\Delta z} = \frac{\mathrm{E}_{\mathrm{Y}} + \mathrm{E}_{\mathrm{D}}}{\mathrm{z}/2} \qquad 10.2$$

assuming that the maximum of the slope of the energy barrier occurs halfway between the minimum and maximum energy at $\Delta z = z/2$.

From Fig. 9.33 the lamellar spacing $d_1 = 10^{-5}$ cm the other dimension d_2 normal to the figure is 10^{-5} cm $\leq d_2 \leq 10^{-4}$ cm and the lamellar thickness t = 7 10^{-7} cm. The domain wall energy introduced when the wall moves a distance $z = \sqrt{2}$ t is given by

$$E_{\gamma} = \gamma z d_2 = \gamma \sqrt{2} t d_2 \qquad 10.3$$

Substituting to Equation 10.3, the above values of t, d_1 and $\gamma = 14.5 \text{ erg/cm}^2$ (Chapter VIII) a value of E_γ is found $E_{\gamma} = 1.44 \ 10^{-10} \ \text{erg.}$

The demagnetizing energy of the uncompensated poles can be approximated to $E_D = 2\pi d_1 d_2 t I^2$. (This is found after treating the uncompensated poles like a capacitor whose charged plates are separated by d_1). Substituting the measured values of z, d_1 and I = 1191 emu/cc, E_D is found to be

$$E_D \simeq 4 \ 10^{-10} \text{ erg.}$$

The demagnetizing energy is thus comparable to the domain wall energy. Therefore, to an order of magnitude treatment the barrier energy ΔU is given by

$$\Delta U = E_{\gamma} + E_{D} \simeq 5 \ 10^{-10} \, \text{erg.}$$

A substitution back to Equation 10.2 leads to

$$H_{\sim} \simeq 5 \text{ kOe}$$

This is higher than the observed value of coercivity. However, H_0 is very sensitive to the value of $(\frac{dU}{dz})_{max}$ and, therefore, to the right choice of the interaction energy. In this treatment the interaction energy was oversimplified but more exact calculations are required to determine the true form.

10.3 CONTINUOUS AND DISCONTINUOUS PINNING

There are two modes of domain wall pinning: the continuous and discontinuous mode. Continuous domain wall pinning refers to the case of continuous pins. In the other mode, domain walls tend to bow out between discrete obstacles.

In this study the pinning centres are actually lines (lamellar junctions) and continuous pinning probably takes place. However, there is a certain criterion for one of the two modes to occur.

10.3.1 Discontinuous Domain Wall Pinning

Consideradomain wall and a planar pin lying on an xy plane. The planar pin is assumed not continuous having an area " α " associated with an area A of domain wall per pin.

In the absence of a field the domain wall is pinned at z = -b. However, the application of a field will cause the domain wall to bow between discrete pins. If the interaction energy of the pin per unit area is V, the equilibrium condition is determined by minimizing the total energy G associated with the wall with respect to the displacement z.

 $G = V\alpha - 2HIA (z + b)$ $\frac{dG}{dz} = \alpha \frac{dV}{dz} = 2HIA = 0$ 10.4 $\frac{dV}{dz} = 2HIA/\alpha$

The simplest solution to this equation will be two values of z; one corresponding to a minimum value of G and the other one to a maximum value.

If V is assumed antisymmetrical about z it has to be an odd function of z plus a constant. In the region of interest z is small so the simplest form of V is given by

$$V = F\{b + z - (\frac{z^3 + b^3}{3b^2})\}$$
 10.5

Where F is a force constant and a,b are constants at fixed temperature. Substituting back to Equation 10.4

$$\frac{dV}{dz} = F\left(1 - \frac{z^2}{b^2}\right) = \frac{2HIA}{\alpha}$$

$$\frac{z}{b} = \pm \frac{\left(F - \frac{2HIA}{\alpha}\right)^{\frac{1}{2}}}{F^{\frac{1}{2}}}$$
10.6

The positive sign corresponds to a maximum value of G and the negative sign to a minimum value.

The absolute value of coercivity, ${\rm H}_{_{\scriptsize O}},$ corresponds to the inflection point at z = 0

 $F = 2HIA/\alpha$

By substituting Equation 10.6 back to Equation 10.4

$$G_{\max} = \frac{2}{3}F\alpha b \left(1 - \frac{H}{H_0}\right)^{\frac{3}{2}} + Q$$

$$G_{\min} = -\frac{2}{3}F\alpha b \left(1 - \frac{H}{H_0}\right)^{\frac{3}{2}} + Q$$

$$Q = (\alpha F - 2HIA)b - \frac{\alpha Fb^3}{3b^2}$$

The energy barrier preventing escape of the wall is given by

$$E = G_{max} - G_{min} = \frac{4}{3}F\alpha b (1 - \frac{H}{H_0})^{\frac{3}{2}}$$

This energy barrier may be overcome by thermal activation if E = 25kT (Bean et. al. 1959)

$$25 \,\mathrm{kT} = \frac{4}{3} \,\mathrm{Fab} \,\left(1 - \frac{\mathrm{H}}{\mathrm{H}_{\mathrm{O}}}\right)^{\frac{3}{2}} \,10.7$$

Equation 10.7 leads to the coercive force at temperature T, which is given by

$$\frac{H_{\rm T}}{H_{\rm O}} = 1 - \left(\frac{75 \, \rm kT}{4 \, \rm F\alpha b}\right)^{\frac{2}{3}}$$
 10.8

10.3.2 Continuous Pinning

Equation 10.4 can be used for the total energy per unit area U associated with a domain wall,

$$U = V - 2HI(z + b)$$
 10.9

V has the same form as Equation 10.5 and the stationary states are found at

$$\frac{z}{b} = \pm \left(\frac{F-2HI}{F^{\frac{1}{2}}}\right)^{\frac{3}{2}}$$

The corresponding energy barrier is given by

$$\Delta E = \frac{4}{3} FAb \left(1 - \frac{H}{H_0}\right)^{\frac{3}{2}}$$
 10.10

It is obvious from Equation 10.10 that for a continuously pinned domain where A is large $(A \rightarrow \infty)$ the domain wall will not escape until $H \rightarrow H_{O}$. However, in a recent theory (P. Gaunt et. al. 1978) have shown that a "blister" could be formed on the plane of a domain wall which would allow the domain wall to break away at fields much lower than H_{O} .

The activation energy required to form the "blister" is given by the sum of the extra domain wall energy necessary to create the blister and the field and interaction energies $E_{\rm I}$.

$$E = E_{\gamma} + E_{I} = 2\pi N\gamma b^{2} (1 - \frac{2HI}{F})$$
 10.11

Where N is an integral equal to 4.93. This energy can be thermally activated when E = 25kT.

$$25kT = 2\pi NYb^2 (1 - \frac{2HI}{F})$$

The coercivity at temperature T is given by

$$H = \frac{F}{2I} \left(1 - \frac{25 \, kT}{(2\pi NY b^2)} \right)$$
 10.12

If, thus, F, I and Y are independent of temperature the coercivity H_C should vary linearly with temperature.

10.3.3 Criterion for Continuous and Discontinuous Pinning

Both of the pinning modes are allowable. Unpinning of domain walls through thermal activation should take place at the lower of the coercive fields given by Equations 10.8 and 10.12. The continuous pinning mode will dominate when

$$\left\{\frac{75kT}{4F\alpha b}\right\}^{\frac{2}{3}} < \frac{25kT}{2\pi N\gamma b^2}$$
 10.13

10.3.4 Comparison With Magnetic Viscosity Experiments

The parameter $(\frac{\partial E}{\partial H})_T$ which was derived in the magnetic viscosity discussion (Sec.5.2.2), can be determined for continuous pinning by differentiating Equation 10.11

$$\left(\frac{\partial E}{\partial H}\right)_{\rm T} = -\frac{4\pi\,{\rm INY}\,{\rm b}^2}{{\rm F}} \qquad 10.14$$

After eliminating b^2 between Equations 10.14 and 10.12 the following expression for F is found

$$\frac{F}{F_{O}} = \frac{I}{I_{O}} \left(\frac{H_{C}}{H_{O}} - \frac{25kT}{\left(\frac{\partial E}{\partial H}\right)} \right)$$

$$10.15$$

$$F_{O} = 2I_{O}H_{O}$$

Where H_{O} is the coercivity at absolute zero. This allows the calculation of $\frac{F}{F_{O}}$ since the quantities in the right hand side are experimentally measured.

Similarly, an expression for b^2 is found after combining Equations 10.14 and 10.12

$$b^{2} = \left\{ \frac{-H_{C} \left(\frac{\partial E}{\partial H}\right)_{T} + 25kT}{2\pi\gamma N} \right\}$$
 10.16

Values of $\left(\frac{\partial E}{\partial H}\right)_T$ were determined in Chapter IV from magnetic viscosity measurements. These were used to evaluate F and b² according to Equations 10.15 and 10.16. Finally, the calculated values of F and b² are used to check the validity of continuous domain wall pinning through the criterion shown in Equation 10.13. Thus, a self-consistent method was developed.

The temperature dependence of the calculated $\frac{F}{F_{O}}$ is shown on Fig. 10.2 together with the variation of the reduced coercivity with temperature. The 15% reduction in the value of F between 4.2 K and 300 K is consistent with the 10% drop of the magnetocrystalline anisotropy observed in this range (Sec. 6.5.2).



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The separation between the two curves shown in Fig. 10.2 represents the reduction of the coercive field by thermal processes. It is clear from this curve that the reduction of coercivity, with temperature rise, comes from thermal activation effects.

The calculated values of b^2 are listed on Table 10.1 together with the values of the criterion expression $\frac{(2\pi N\gamma)^2}{6.67 \text{ F/kT}}$. The criterion for continuous domain wall pinning is satisfied since in this case $\alpha = 2\sqrt{t} d_2$. Substituting the observed values of $t = 7 \ 10^{-7} \text{ cm}$, $d_2 = 10^{-4} \text{ cm}$, a value of $\alpha = 10^{-10} \text{ cm}^2$. It is clear from the values listed on Table 10.1 that $\frac{\alpha}{b^2}$ is always bigger than $\frac{(2\pi N\gamma)^2}{6.67 \text{ F/kT}}$ throughout the temperature range covered.

However, the calculated values of b appeared to be very small ~10 $\stackrel{\rm O}{\rm A}$. Since, b is a measure of the interaction range attention has to be paid to this point because the demagnetizing energy $E_{\rm D}$ might dominate the domain wall energy and must be taken into account when formulating the theory.

Similar calculations have been carried out on an early ordering $\text{FePt}_{0.7^{\text{Ni}}0.3}$ sample and on an optimum $\text{Co}_{52}^{\text{Pt}}_{48}$ sample. The results are listed on Tables 10.2 and 10.3.

Calculated values of the reduced interaction strength $\frac{F}{F}_{0}$ and the interaction range b for an optimum FePt $_{0.7}^{Ni}$ $_{0.3}^{..}$. Table 10.1

ŧ ۰.

T (K)	H _C (0e)	$(\min_{\substack{i \in S \\ i \in S \\ i \in K}} (\lim_{j \in K} (u_j + i_j)) $	F(dyn/cm ²)	0 मि मि	$b^{2} (10^{-15} cm^{2})$	$\frac{a}{b^2}(10^4)$	<u>(2тNY) 2</u> *; 6.677.74-т (10 ³
4.2	2626	2.59	6 35				TVIATION
11	2618	3.35	СС • У	00°T	2.12	4.7	9.8
20	7590		- -	T0.1	2.78	3.6	5.7
) J		4•41	6.42	1.01	3.66	2.7	4.2
	0067	6.26	6.47	1.02	5.27	1.9	2.4
/ /	2458	6.73	6.43	1.01	5.67	1.8	- C - C
L 14	2342	8.52	6.26	0.99	7.00	2 V	3 C
1 36	2271	8.54	6.23	0.98	200	₽ ₹ • -	α ι -
152	2223	9.12	6.14	0.97	7 30	₩ ₹ • -	/•T
174.5	2143	9.75	5.99	0.94		т. - т	7•0
194	2087	9.35	6.00	чо 0			- 2
232	1961	10.17	5.78	16.0	04.1	н. С.	1. 5
253	1889	9 . 93	5.73			г. Г.	L • 4
300	1711	10 82		0.00	1.10	1 .3	1. 3
315	1600		0r•n	0.84	7.72	1.3	1. 3
0.2.C		TU.69	5.20	0.82	7.70	1. 3	1. 3
	/ £ CT	10.79	5.09	0.80	7.66	1 •3	۲. ۲
265	, 1463	11.11	4.92	0.78	7.69	, ,	, c
371	1399	11.43	4.78	0.75	7 76) c • • -	
394	1314	11.81	4.60	0.72	7.79	1.3	г. Ч.
* Values	$Of (\frac{\partial E}{\partial E})$						
2) 5 5 7 7 7 7 7 7 7	ΔT (<u>9H</u>) T w	ere caken irom	Chapter V.				27
$\Sigma = 2\pi N \simeq 3$	Γ	$= 14.5 era/cm^{2}$					4

 $\gamma = 14.5 \text{ erg/cm}^2.$

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Fu
Calculated values of the interaction strength for $\text{FePt}_{0.7}^{\text{Ni}}_{0.3}$ in the early ordering stages.
. 2
10
Table

T (K)	Н _С (0е)	$(\frac{\partial E}{\partial H})_{T}$ (units of k)	$F(dyn/cm^2)$ b	b ² (10 ⁻¹⁵ cm ²)
77	1350	5.57	00 7	ţ
201			00.4	2.9
C 0 T	1180	5.78	3.80	c c
124	1050			4. 7
	0704	6.58	3 . 55	г. С
145	980	7.22	VV E	+ (•) (
ר <i>ה</i> ר			rr • • • • •	
T/3	880	7.73	3.33	ر د
249	800			•
	000	9.29	3.33	4 2
290	750			J •
)	9C • NT	3.20	4.7
345	560	12.61	57 6	· · ·
			6. I J	4.8
Calculated values of the interaction strength F and the interaction range b for ${\rm Co}_{52}{\rm Pt}_{48}.$ Table 10.3

77	H _c (0e)	$(\frac{\partial E}{\partial H})_{T}$ (units of k)	F(dyn/cm²)	$b^{2} (10^{-15} cm^{2})^{*}$
77				
	5520	4.44	9,65	ţ
124	5200	6.29	9, 23	0 C
171	4800	7.16		α. /
235	4400	8.03	4/ O	9.4
290	4100	8 34	T Z •0	10.0
322	3800	ייי ני רי רי רי	7.95	10.0
356	3500	2 · /2	7.56	10.0
407	2000	د/ . <i>و</i> .	7.10	10.4
	1	/8.OT	6.22	10.2

 $\gamma = 18.4 \text{ erg/cm}^2$.

*

10.4 REMANENT MAGNETIZATION

The large values of the observed remanent magnetization are explained satisfactorily using the random anisotropy model of Callen et. al. (Callen, 1977). Since their discussion is based on a Stoner and Wohlfarth (1948) model modified to include the exchange interaction, it is easier to understand the theory by first discussing the original Stoner and Wohlfarth theory of single domain particles.

10.4.1 Stoner and Wohlfarth Theory of Single Domain Particles

Stoner and Wohlfarth (1948) have calculated the field dependence of the magnetization for non-interacting single domain particles possessing a certain form of anisotropy (shape, magnetocrystalline or strain anisotropy). The total energy E_t of a particle with uniaxial anisotropy K and magnetization I_s in a field H is the sum of the magnetocrystalline energy E_K and the magnetostatic energy E_m

 $E_{t} = E_{K} + E_{m}$ 10.17

If the magnetization and easy axis make an angle θ and φ respectively with the field H, then to the first order

$$E_{K} = K \sin^{2} (\phi - \theta) \qquad (K_{2} = 0)$$

and

$$E_m = -HI_c \cos\theta$$

Therefore, the total energy can be written as

$$E_{t} = K \sin^{2} (\phi - \theta) - HI \cos \theta \qquad 10.18$$

In an equilibrium state the magnetization of the particle in a given field H, points to the direction where E_t is minimum

$$\frac{dE_t}{d\theta} = 0 , \qquad \frac{d^2 E_t}{d\theta^2} > 0 \qquad 10.19$$

But

$$\frac{dE_{t}}{d\theta} = 2 K \sin(\phi-\theta) \cos(\phi-\theta) + HI_{s} \cos\theta = 0$$
$$-\frac{1}{2}h \sin 2(\phi-\theta) + h \sin\theta = 0 \qquad 10.20$$
$$h = \frac{HI_{s}}{2K}$$

Equation 10.20 provides a relation between h and the angle θ and ϕ . In the final analysis, θ is given as a function of ϕ and h, $\theta = \theta(\phi, h)$, and the magnetization is found from the average value of $\cos \theta$.

$$m = \frac{I}{I_s} = \langle \cos \theta \rangle$$
 10.21

Stoner and Wohlfarth solved the problem numerically and have calculated hysteresis curves for various values of ϕ shown on Fig. 10.3a. The hysteresis curve for a random array of non-interacting single domain particles is shown on Fig. 10.3b. According to this, the remanence ratio





I I_s

Fig. 10.3 (a) Calculated magnetization curves for uniformly magnetized prolate ellipsoids. (The numbers on the curves are the values in degrees of the angle ϕ between the polar axis and the field. (b) Calculated magnetization curves for a random array of non-interacting single domain particles.

m(0) is 0.5 and the coercivity $\rm h_{C}$ = 0.480. Therefore, $\rm H_{C}$ can be written as

$$H_{c} = 0.960 \frac{K}{I_{s}}$$
 10.22

The critical field H_{cr} where the magnetization changes abruptly ($(\frac{dm}{dh})_{H_{cr}} = 0$) occurs at h = 0.5 and is given by

$$H_{cr} = \frac{K}{I_s}$$
 10.23

10.4.2 Random Anisotropy Model

Callen et. al. (1977) in a recent theory discussed the properties of amorphous Rare-earth-iron alloys in terms of a Stoner and Wohlfarth theory modified by an effective field H_{eff} to include an exchange term ($\lambda \overline{I}$) proportional to the average magnetization,

 $H_{eff} = H + \lambda \bar{I}$ 10.24

By the same arguments as before the total energy E_t of a magnetic spin possessing uniaxial anisotropy K can be written as

$$E_{t} = K \sin^{2}(\phi - \theta) - (H + \lambda \overline{I}) I_{c} \cos\theta \qquad 10.25$$

The equilibrium state is given by $\frac{dE_t}{d\theta} = 0$ and leads to

$$-\frac{1}{2} \sin 2 (\phi - \theta) + h' \sin \theta = 0$$

$$h' = h + \lambda' m$$

$$10.26$$

$$h' = \frac{\lambda I_{S}^{2}}{2K}$$

$$10.28$$

$$m = \langle \cos \theta \rangle$$

The graph of m against h' is identical to that of Stoner and Wohlfarth shown on Fig. 10.3b. However, the solutions of m must lie on the curve shown by Equation 10.26 and on the straight line of Equation 10.27. For a given value of field h, the problem was solved using the "load line" technique. The intersections of the straight line with the curve m(h') are possible solutions. However, only those with an m, a positively increasing function of h, are allowed. By varying h from large positive values to negative, the self-consistent magnetization is found, (Fig. 10.4).

Callen et. al. distinguished three different regions. For a high value of $\lambda' = \lambda'_1$ (small slopes) the straight line passes through the origin (h'= 0) and is tangent to the m(h') curve at A. Therefore, by reducing h to zero, the magnetization m is decreasing until h = 0 where it switches abruptly to a negative value, giving a zero coercivity. For negative h the stable solution is the one with the most negative m (Fig. 10.4).



Fig. 10.4 Stoner and Wohlfarth magnetization curve for an array of non-interacting single domain particles. Straight lines are plots of reduced magnetization m versus reduced field h' according to Equation 10.27, $h' = h + \lambda' m$.

For $\lambda'_2 < \lambda' < \lambda'_1$, as h is decreased the solution moves toward smaller m. However, at a certain negative value of h the straight line is tangent to the curve at A and the magnetization drops to a negative value giving a definite coercivity and a high remanence. (The value of the field h where this occurs is the coercivity h_c).

When λ' reaches the small value λ'_2 (at very large slopes) all lines pass through point E with co-ordinating m = 0 and h = 0.5. The coercivity is thus given by $h_c = 0.5$ and the remanence by m(0) = 0.5.

The predicted dependence of the remanence and coercivity on the exchange parameter λ' is shown on Fig. 10.5. For large values of λ' the coercivity drops drastically from that of Stoner and Wohlfarth and the remanence is higher than 0.5. However, when $\lambda \rightarrow 0$, the results approach the values predicted by Stoner and Wohlfarth.

i) Experimental values of the exchange parameter λ .

As stated earlier for a given value of λ one can construct the corresponding magnetization loop (m = m(h')) from the Stoner and Wohlfarth curve where $\lambda = 0$ with the help of Equations 10.26 and 10.27. The calculated loop can then be transformed to an m = m(h) curve by changing the field h' to h with the use of Equation 10.27, h = h' - λ 'm. This is shown on Fig. 10.6 for $\lambda = 46$ ($\lambda' = \frac{\lambda I_S^2}{2K} = 1.67$). It is clear that the exchange interaction shifts the curves to lower



Fig. 10.5 Reduced coercivity (a) and reduced remanence (b) as a function of the interaction parameter λ' .



fields. The stronger the interaction, the larger the separation between the curves is.

ii) Calculation of λ from the observed remanence ratio.

Inversely, one can find λ from the observed remanence ratio. In h = 0, with no exchange interaction, the remanence ratio should be 0.5. However, with exchange interaction present, in h = 0, the effective field equals the exchange field and the corresponding magnetization ratio appears higher than 0.5. In other words, the exchange term is equal to the field which is required to shift the observed value of the remanence ratio to the Stoner and Wohlfarth curve with $\lambda = 0$. A sample calculation is shown below.

The observed reduced remanence ratio in $FePt_{0.7}^{Ni}0.3$ at the early stages of ordering and at 4.2 K is 0.71. That would correspond to an exchange field of h' = 0.39 (Fig. 10.6). Using Equation 10.28 with $M_{\rm S}$ = 1204 emu/cc and K = 6.8 10^7 erg/cc, λ is found to be 52. Values of the exchange parameter λ for FePt 0.7^{Ni}0.3 and Co₅₂Pt₄₈ are listed on Table 10.4. The large values of λ at the early stages of ordering are consistent with the electron microscopy observations. There will be exchange interaction between the surface layers of particles with different 'c' axes. If the particles are small, therefore, the interaction energy per unit volume of particle will be significantly greater than for larger particles. The low value of the remanence ratio in the over-

Table 10.4	Calculated values of the parameter λ for (a) is $Co_{52}Pt_{48}$.	ne exchange interaction ^{FePt} 0.7 ^{Ni} 0.3 ^{and} (b)
	(a)	
Annealing Ti (at 700°C)	.me λ *	λ **
12 min	52.0	_
23 "	28.5	24.33
l hr	23.9	25.20

	(b)	
Annealing Time (at 700 ⁰ C)	λ *	λ **
2 min	108.0	_
17 "	37.2	37.00

* Found from the measured remanence ratio.

** Found from the superposition of the high field magnetization curves. aged state suggests that domain walls have been activated. However, one can assume that the overaged state represents the case with $\lambda = 0$, since the particles have grown substantially in size and the exchange interaction among them is almost negligible and can be neglected.

iii) Calculation of λ from the high field magnetization measurements.

Since the effective field includes the exchange term $\lambda \overline{i}$, the law of approach to saturation is modified to take this into account. However, it is found that some of the magnetization curves, Fig. 10.7, can be superimposed on the overaged state curve with $\lambda = 0$ after shifting them by an amount $\lambda \overline{i}$. One, therefore, can find λ from the amount they are shifted. The agreement between the λ 's found by this way and those derived from the remanence ratios is surprisingly good (Table 10.4). The superimposed curves are shown on Fig. 10.7.

The fact that the magnetization curves of the samples at different ordering stages could be superimposed suggests that they have the same saturation magnetization and anisotropy constants. However, some discrepancy was observed for the early ordered state in both systems. The corresponding magnetization curves could not be superimposed on the overaged state curve. However, after using the λ found from the observed remanence ratio and shifting the curve by the



proper amount, $\lambda \bar{1}$, the new curve shown on Fig. 10.7 was found. Its shape suggests that it has a higher anisotropy than the overaged state. But the behaviour is not as simple since as shown from the fitting of the new curve to the "law of approach to saturation", the relation between the anisotropy constants K_1 and K_2 has changed from the early ordered state to the overaged state.

10.5 DEGREE OF LONG RANGE ORDER

The previous result was initially surprising since the phenomenological reduction of the $\left(\frac{c}{a}\right)$ ratio while ordering suggested that the overaged state had a higher degree of order than the early ordered state. However, a careful analysis of the diffractometer tracings showed that the degree of long range order S was the same throughout the course of orderings (Table 10.5) (from the early ordered to the overaged state). The parameter S was found from the ratio of the integrated intensities of the 201 superlattice and 200 fundamental reflections after using the right formula

$$S^{2} = \frac{A_{S}}{A_{f}} = \frac{m(LP) (f_{A} + f_{B})^{2}}{m(LP) (f_{A} - f_{B})^{2}}$$
 10.29

Where A_s , A_f are the areas under the superlattice (201) and the fundamental (200) peaks, respectively, m is the multiplicity factor, LP is the Lorentz polarization factor $(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta})$ and f_A , f_B are the atomic scattering factors. In FePt $0.7^{Ni}0.3$ Table 10.5 Values of the long range order parameter S.

Samples	S
Co ₅₂ Pt ₄₈	0.77
FePt0.7 ^{Ni} 0.3	l.00

the equivalent Pt atom was assumed to be $Pt_{0.7}(Ni_{0.3}Fe)_{0.3}$ and the equivalent Fe atom $(Ni_{0.3}Fe)_{1.3}$

10.6 ELASTIC STRAIN IN THE INITIAL STAGES OF ORDERING

The fact that the sample has the maximum degree of long range order from the early stages of ordering while the measured $(\frac{c}{a})$ ratio is very close to 1, suggests that the sample is under considerable strain so that the measured $(\frac{c}{a})$ does not reflect its true state. This strain energy arises from the cubic-tetragonal transformation, (Eshelby, 1957).

A tetragonal particle is in a strain-free state when it is completely isolated from its surroundings. In the early stages of ordering the specimen consists of randomly distributed ordered nuclei which are highly constrained. (Any change in the nuclei will create an internal stress due to the constraints imposed by its surroundings). However, the specimen does not relax its strain by expanding to the equilibrium tetragonal state because each nuclei tends to expand in different directions. Since this would probably cause a further increase in energy, the nuclei prefer to stay in this "squashed" state.

In later ordering stages the nuclei are aligned in {110} crystallographic planes. However, it is possible, in this state, to factorize the strain energy into two shears. The first shear occurs on the plane of alignment and causes

a macroscopic shape change. The other shear takes place in another {110} plane at 60° to the previous and is followed by an internal slipping of the specimen which will depend on the size of the nuclei. In the small strain approximation ($\varepsilon <<1$, Burkhart et. al., 1953) a shear on a (011) can be represented by

Therefore, according to the previous argument, one has $\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1-\varepsilon & 0 \\ 0 & 0 & 1+\varepsilon \end{vmatrix} \times \begin{vmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1-\varepsilon & 0 \\ 0 & 0 & 1\end{vmatrix} = \begin{vmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1-2\varepsilon & 0 \\ 0 & 0 & 1+\varepsilon \end{vmatrix}$ 10.30

The product of these two shears is the tetragonal structure shown in the right hand side of Equation 10.30. (In the exact treatment the final tetragonal crystal is slightly rotated with respect to the initial cubic).

The internal slip will depend on the total number of dislocations in the sample. For a particle of radius r the total number of dislocations n is given by

 $d\pi r^2 = n$

Where d is the density of dislocations approximately equal to $\sim 10^{11}-10^{12}$ dislocation lines/cm². Therefore, one can find roughly the particle size before the tetragonal transformation could take place

$$r^{2} = \frac{1}{d\pi} \approx \frac{1}{10^{12}}cm^{2}$$
,
r $\approx 100 \text{ Å}$

10.7 MAGNETIC HARDENING IN Co52Pt48

The predicted coercivity for $Co_{52}Pt_{48}$ according to the Stoner and Wohlfarth theory should be

$$H_{c} = 0.96 \frac{K}{I_{s}} = \frac{0.96 \times 5.8 \ 10^{7}}{810} \ 0e^{2}69 \ k0e$$

This, however, is much higher than the experimentally observed value.

According to the random anisotropy exchange model, the coercive field required for the coherent rotation of domain is much lower. Using the values of the calculated parameter λ , the following coercivities were found from the graph of Fig.

^Hc, early ordering
$$\lambda' = 105$$
 = 33 k0e

^Hc, optimum
$$\lambda' = 37$$
 = 63 k0e

These values again exceed the 1.5 and 6 k0e coercivities measured at 4.2 K. This implies that a domain wall reversal process has been activated at a lower value of coercive field than that required for coherent rotation of domains.

The existence of large scale domains (Fig. 9.29) suggests the applicability of theories based on domain wall impedance. The walls were parallel to a <100> direction. If they are a true reflection of the underlying surface, they suggest the existence of a dominant c-axis over macroscopic regions of the sample. This could not be observed in electron microscopy because of the high magnification. One, therefore, has to confirm this hypothesis in order to construct a domain wall impedance model for magnetic hardening consistent with the structural and magnetic data.

Domain walls could possibly occur in a ferromagnet with random magnetic anisotropy as was recently suggested by T. Egami (1978) who tried to explain the temperature dependence of the coercivity of amorphous TbFe₂.

APPENDIX I

Expressions for the coefficients B and C of the law of approach to saturation.

i) Uniaxial Crystal

Assume a crystallite whose spontaneous magnetization J_s makes an angle θ with the applied field H (Fig. I.1). If the angle between the easy axis and the field is ϕ , then the total energy E is the sum of the magnetocrystalline energy E_k and the magnetostatic energy E_m .



Fig. I.1

 $E = E_{K} + E_{m} = K_{1} \sin^{2}(\phi - \theta) + K_{2} \sin^{4}(\phi - \theta) - HJ_{s} \cos\theta \qquad I.1$

The equilibrium condition is found by minimizing Equation I.1

$$\frac{\partial E}{\partial \theta} = -\sin(2\phi - 2\theta) - 2\frac{K_2}{K_1}\sin^2(\phi - \theta)\sin(2\phi - 2\theta) + h\sin\theta = 0$$
$$h = \frac{HJ_s}{K_1}$$

In high fields the crystallite will be almost saturated so that the magnetization will be very close to the field direction and the angle θ will be very small. Therefore, one can express θ in a series expansion $\frac{1}{H}$ as shown in Equation I.3.

$$\theta = \frac{\alpha}{h} + \frac{\beta}{h^2} + \dots, \quad \theta^2 = \frac{\alpha^2}{h^2} + \frac{2\alpha\beta}{h^3} + \dots$$
 I.3

Equation I.2 can be rearranged by approximating $\sin\theta \approx \theta$ and expanding $\cos\theta$ in series of θ and neglecting the terms beyond second order. If one substitutes for θ the expression given in Equation I.3, and equates the coefficients of the same order $\frac{1}{h}$ terms, he will get α and β as functions of ϕ . But

$$\frac{I}{I_{s}} = \cos\theta = 1 - \frac{\theta^{2}}{2}$$
or from Equation I.3
$$\frac{I}{I_{s}} = 1 - \frac{\alpha^{2}}{2h} - \frac{\alpha \cdot \beta}{h^{3}} - \dots$$
I.4

 α and β being functions of ϕ could be substituted in Equation I.4 and averaged over all possible values of ϕ (all orientations of easy axis). By carrying out the calculations the coefficients B and C of Equation 6.5 can be found and they are equal to

$$B = \frac{4}{15} \left(1 + \frac{16}{7}R + \frac{32}{21}R^2\right) \frac{K_1^2}{I_s^2}$$

$$C = \frac{16}{105} \left(1 + \frac{8}{3}R + \frac{32}{11}R^2 + \frac{512}{429}R^3\right) \frac{K_1^3}{I_s^3} , \quad R = \frac{K_2}{K_1} \quad I.5$$

ii) Cubic Crystal

For the cubic case the calculations are more difficult (Becker and Döring, 1939). The total energy can be written in the form

$$E = F(\vec{\alpha}) - HJ_{s_{i}} \sum_{i}^{\alpha} \alpha_{i} \beta_{i}$$
 I.6

Where F($\dot{\alpha}$) is the magnetocrystalline energy, α_{i} and β_{i} are the directional cosines of magnetization and field, respectively. Following the same procedure as for the uniaxial case one minimizes Equation I.6 with the condition $\sum_{i} \alpha_{i}^{2} = 1$. In high fields $\alpha_{\mbox{i}}$ is very close to $\beta_{\mbox{i}}$ so it can be expressed as

$$\alpha_{i} = \beta_{i} + XA_{i} + X^{2}B_{i} + \dots , X = \frac{1}{HJ_{s}}$$
 I.7

It can be shown that

$$\frac{1}{I_{s}} = \cos\theta = \sum_{i} \alpha_{i} \cdot \beta_{i} = 1 - \frac{X^{2}}{2} \sum_{i} A_{i}^{2} - X^{3} \sum_{i} A_{i} \cdot B_{i}$$
With
$$\sum_{i} A_{i}^{2} = \sum_{i} F_{i}^{2} - (\sum_{i} F_{i}\beta_{i})^{2}$$
and
$$F_{i} = (\frac{\partial F}{\partial \alpha_{i}})_{\alpha_{i}} = \beta_{i}$$

and

By expressing F $_{i}$ and F $_{i}\beta_{i}$ as functions of β_{i} and knowing that

$$F(\alpha) = K_{1} (\alpha_{1}^{2} \alpha^{2} + \alpha_{2}^{2} \alpha_{3}^{2} + \alpha_{3}^{2} \alpha_{1}^{2}) + K_{2} \alpha_{1}^{2} \alpha_{2}^{2} \alpha_{3}^{2}$$

the coefficients B and C of Equation 6.5 can be calculated

$$B = \frac{8}{105} (1 + \frac{2}{11}R^{2} + \frac{3}{11 \cdot 13}R^{2}) \frac{K_{1}^{2}}{I_{s}^{2}}$$

$$C = \frac{8}{105} (\frac{72}{11 \cdot 13} - \frac{8}{11 \cdot 13}R - \frac{104}{11 \cdot 13 \cdot 17}R^{2} - \frac{136}{11 \cdot 13 \cdot 17 \cdot 19}R^{3}) \frac{K_{1}^{3}}{I_{s}^{3}},$$

$$R = \frac{K_{2}}{K_{1}}$$
I.8

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