

# Magnetism and Magnetic Recording Media

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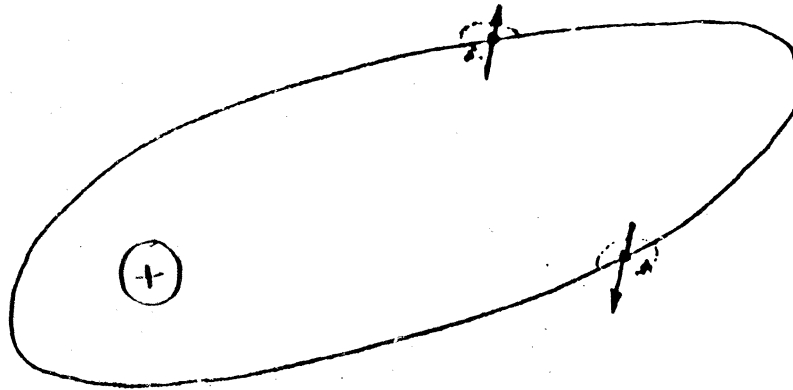
## Contents

- Origin of magnetism; electrons in motion
- The four Quantum Numbers, Pauli Exclusion Principle, Periodic Table
- Diamagnetism, paramagnetism, ferromagnetism, ferrimagnetism and antiferromagnetism
- Exchange interaction: origin of spontaneous moment
- Magnetic properties: intrinsic ( $M_s$ ,  $K_1$ ,  $K_2$ , Curie temperature)  $B$ ,  $H$ , and  $M$ .
- Magnetic properties: extrinsic ( $M_r$ ,  $H_c$ , permeability) Magnetocrystalline Anisotropy
- The hysteresis loop
- Hard and soft magnetic materials
- Single-domain particles
- Shape, crystalline and strain anisotropy
- Particle interactions: The Preisach Diagram
- Particle Orientation and disorientation
- Modes of magnetization reversal in single-domain particles
- Preparation and properties of particles of:
  - $\gamma$ - $Fe_2O_3$ ,  $Co-Fe_2O_3$  (co-substitution, impregnation), isotropic particles
  - temperature-and-stress-dependence of magnetic properties
  - $CrO_2$
  - barium ferrite
  - metals
  - consumption of particles by type, year and application
  - new approaches to making particles
- Particles versus thin films
- Unanswered Questions and Unsolved Problems

IN MAGNETISM ELECTRONS ARE ALL-IMPORTANT

### ORBITAL MOTION AND SPIN

- THE NUCLEUS WILL NOT BE CONSIDERED FURTHER
- ELECTRONS ARE TRAVELLING IN WELL-DEFINED ORBITS
- ELECTRONS SHARING THE SAME ORBIT WILL HAVE OPPOSITE SPIN



- THERE ARE MAGNETIC MOMENTS ASSOCIATED WITH BOTH THE ORBITAL MOTION AND THE SPIN OF THE ELECTRON
- THE ELECTRON SPIN IS THE REAL KEY TO MAGNETISM

Fundamental unit  
of magnetism  
 $\mu_B = \frac{eh}{4\pi m_e c}$

magnetic moment /atom,  $\mu = n \mu_B$

$$\mu_B \text{ (Bohr Magnetron)} = 4.27 \times 10^{-24} \text{ Am}^2$$
$$= 0.927 \times 10^{-20} \text{ erg/g}$$

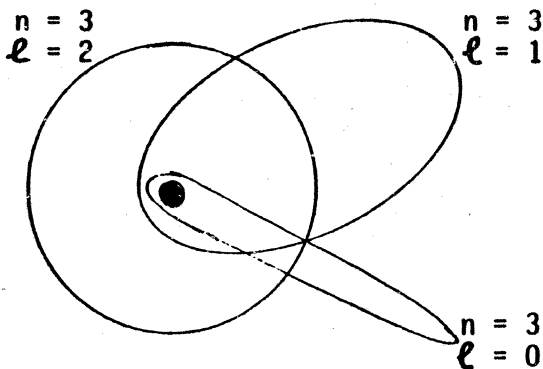
# THE FOUR QUANTUM NUMBERS

(PAULI)

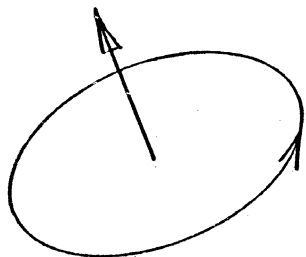
1) PRINCIPAL QUANTUM NUMBER,  $n$

$$mvr = \frac{nh}{2\pi}$$

2) AZIMUTHAL QUANTUM NUMBER,  $l$



3) MAGNETIC QUANTUM NUMBER,  $m_l$



4) SPIN QUANTUM NUMBER

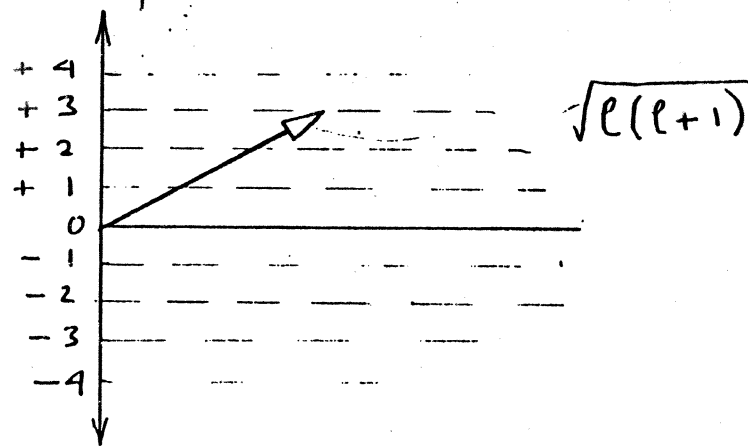
↑  
+1/2

↓  
-1/2

POSSIBLE VALUES

$$l \leq n - 1$$

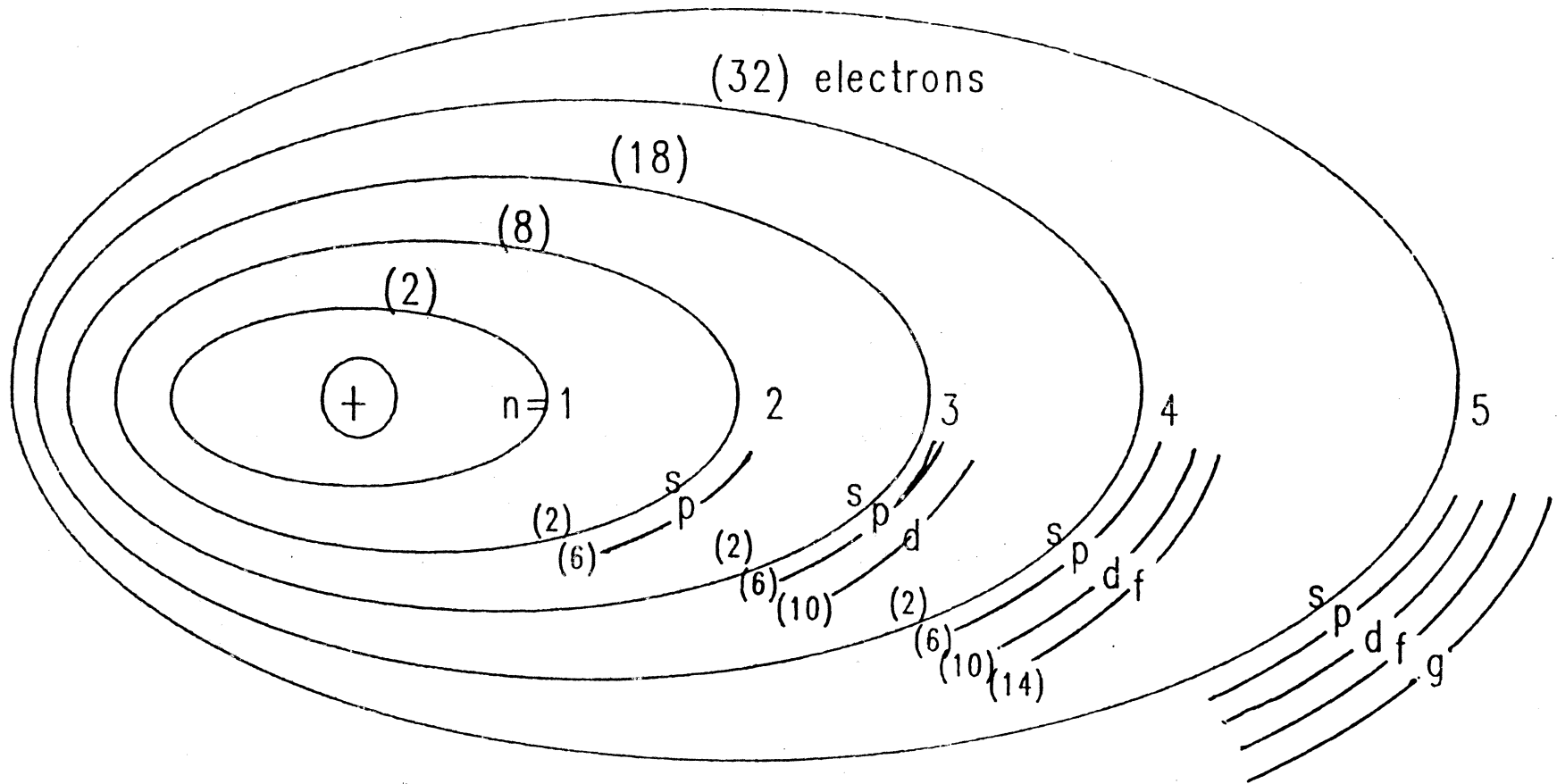
MOST ELLIPTICAL ORBITS = MOST TIGHTLY BOUND ELECTRON  
= LOWEST ENERGY



possible values

$$+l, +(l-1), +(l-2) \dots +1, 0, -1, \dots -l$$

# Atomic Orbitals



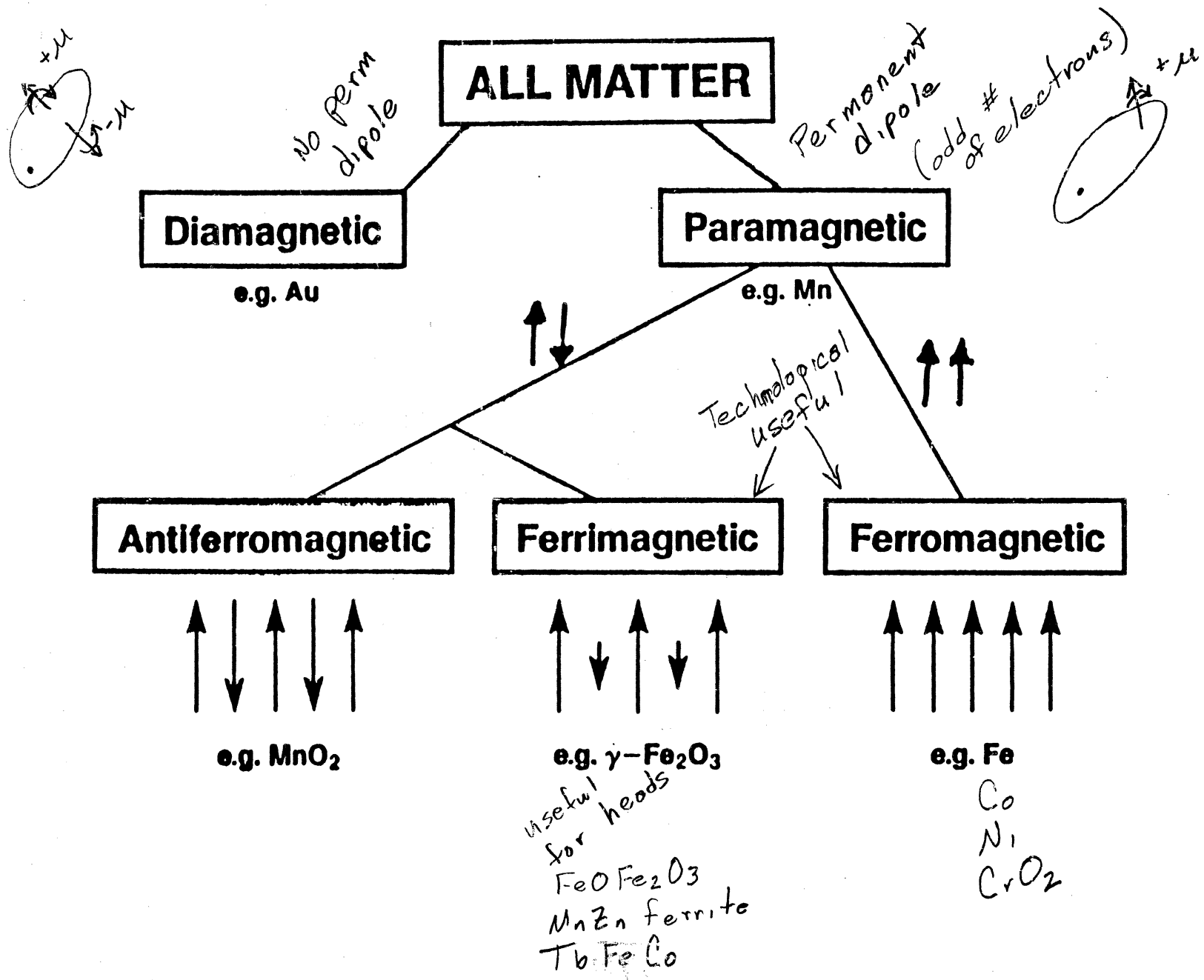
# PERIODIC TABLE, MASS SUSCEPTIBILITIES

	K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p 5d	P 6s 6p 6d	Q 7s	Ground term	$\times 10^6$		
H 1	1							$^1S_0$	-1.97		
He 2	2							$^1S_0$	-0.47		
Li 3	2	1						$^2S_{1/2}$	+0.50		
Be 4	2	2						$^1S_0$	-1.00		
B 5	2	2	1					$^2P_{1/2}$	-0.62		
C 6	2	2	2					$^3P_0$	-0.49		
N 7	2	2	3					$^4S_{3/2}$	-0.8		
O 8	2	2	4					$^3P_1$	+106.2		
F 9	2	2	5					$^4P_{3/2}$	-		
Ne 10	2	2	6					$^1S_0$	-0.88		
Na 11			1					$^2S_{1/2}$	+0.51		
Mg 12			2					$^1S_0$	+0.55		
Al 13			2	1				$^2P_{1/2}$	+0.65		
Si 14		10 Ne core	2	2				$^3P_0$	-0.18		
P 15			2	3				$^4S_{3/2}$	-0.90		
S 16			2	4				$^3P_1$	-0.49		
Cl 17			2	5				$^4P_{3/2}$	-0.577		
A 18	2	2	6					$^1S_0$	-0.48		
K 19				1				$^2S_{1/2}$	+0.52		
Ca 20				2				$^1S_0$	+1.10		
Sc 21				1	2			$^2D_{3/2}$	-		
Ti 22				2	2			$^3F_2$	+1.25		
V 23				3	2			$^4F_{3/2}$	+1.4		
Cr 24			18 A core	5	1			$^7S_3$	+3.08		
Mn 25				5	2			$^6S_5$	+11.8		
Fe 26				6	2			$^5D_4$	Ferro.		
Co 27				7	2			$^5F_4$	"		
Ni 28				8	2			$^5F_4$	"		
Cu <sup>+</sup>	2	2	6	2	6	10		$^1S_0$			
Cu 29				1				$^2S_{1/2}$	-0.086		
Zn 30				2				$^1S_0$	-0.157		
Ga 31				2	1			$^2P_{1/2}$	-0.24		
Ge 32			28 Cu <sup>+</sup> core	2	2			$^3P_0$	-0.12		
As 33				2	3			$^4S_{3/2}$	-0.81		
Se 34				2	4			$^3P_1$	-0.82		
Br 35				2	5			$^4P_{3/2}$	-0.89		
Kr 36	2	2	6	2	6	10	2	6	$^1S_0$	-0.85	
Rb 37					1			$^2S_{1/2}$	+0.21		
Sr 38				1	2			$^1S_0$	-0.20		
Y 39				2	2			$^2D_{3/2}$	+5.8		
Zr 40				1	2	2		$^3F_2$	-0.45		
Nb 41				4	1			$^2D_{3/2}$	+1.5		
Mo 42				5	1			$^3S_1$	+0.04		
Mn 43				5	2			-	-		
Ru 44				7	1			$^5F_4$	+0.50		
Rh 45				8	1			$^5F_4$	+1.11		
Pd 46	2	2	6	2	6	10	2	6	10	$^1S_0$	+5.4

	K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p 5d	P 6s 6p 6d	Q 7s	Ground term	$\times 10^6$						
Ag 47					1			$^2S_{1/2}$	-0.20						
Cd 48					2			$^1S_0$	-0.16						
In 49					2	1		$^2P_{1/2}$	-0.11						
Sn 50			46 Pd core		2	2		$^3P_0$	-0.25						
Sb 51					2	3		$^4S_{3/2}$	-0.87						
Te 52					2	4		$^3P_1$	-0.81						
I 53					2	5		$^4P_{3/2}$	-0.86						
Xe 54	2	2	6	2	6	10	2	6	10	$^1S_0$	-0.84				
Cs 55								$^2S_{1/2}$	-0.22						
Ba 56								$^1S_0$	+0.9						
La 57								$^2D_{3/2}$	+1.04						
Ce 58					Xe core	1		$^1H_1$	+15.0						
Pr 59						1		-	+25.0						
Nd 60						1		-	+36.0						
Ni 61						1		-	-						
Sm 62						1		$^7F_0$	-						
Eu 63								$^6S_5$	+22.0						
Gd 64								$^8D_5$	Ferro.						
Tb 65								-	-						
Dy 66								-	-						
Ho 67								-	-						
Er 68								-	-						
Tu 69								-	-						
Yb 70								-	-						
Lu <sup>+++</sup>	2	2	6	2	6	10	2	6	10	14	2	6	$^1S_0$	-	
Lu 71								$^2D_{3/2}$	-						
Hf 72								$^3F_2$	-						
Ta 73								$^3F_2$	+0.87						
W 74								$^3D_1$	+0.28						
Re 75								$^5S_1$	-						
Os 76								$^3D_1$	+0.05						
Ir 77								$^3D_1$	+0.15						
Pt 78								$^3D_1$	+1.10						
Au <sup>+</sup>	2	2	6	2	6	10	2	6	10	14	2	6	10	$^1S_0$	-
Au 79								$^2S_{1/2}$	-0.15						
Hg 80								$^1S_0$	-0.168						
Tl 81								$^2P_{1/2}$	-0.24						
Pb 82								$^3P_0$	-0.12						
Bi 83								$^4S_{3/2}$	-1.85						
Po 84								$^3P_1$	-						
At 85								-	-						
Rn 86	2	2	6	2	6	10	2	6	10	14	2	6	10	$^1S_0$	-
Fr 87								-	-						
Ra 88								$^1S_0$	-						
Ac 89								$^3D_1$	-						
Th 90								$^3F_2$	+0.11						
Pa 91								$^3F_2$	+2.6						
U 92								$^3D_1$	+1.78						

*elements of  
1st transition  
↓*

*magnetic properties  
rare earth*



## QUANTUM THEORY OF FERROMAGNETISM

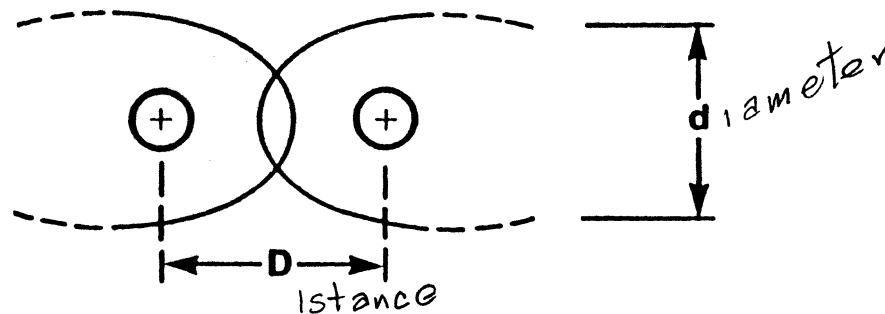
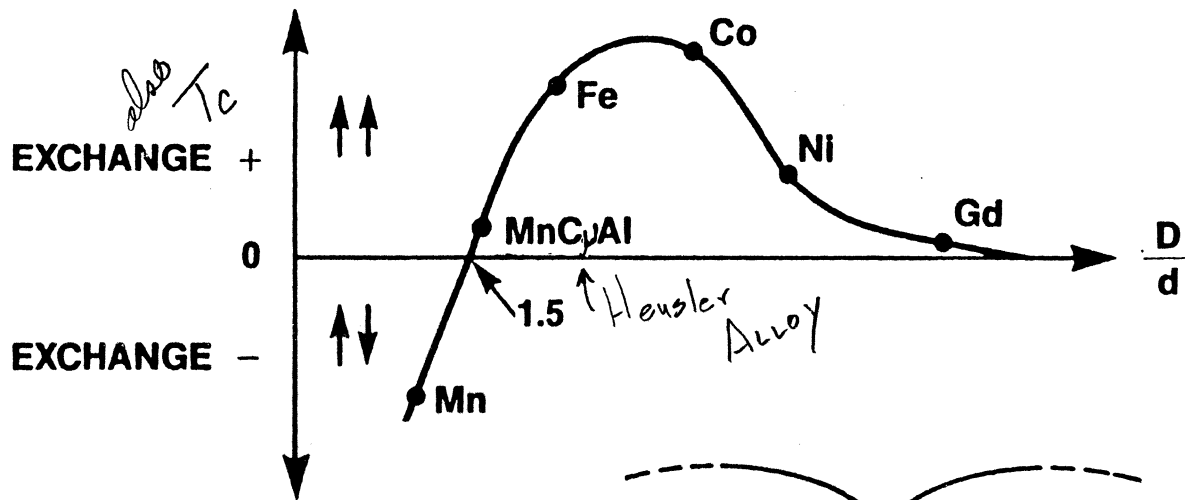
"IF ONE DEMANDS A THEORY THAT WILL PREDICT IN ADVANCE JUST WHICH ALLOYS WILL BE FERROMAGNETIC, WHAT QUANTITATIVELY WILL BE THE REMANENCE, HYSTERESIS, ETC. THEN ONE MUST ADMIT FAILURE.

. . . . IF, ON THE OTHER HAND, WHAT ONE DESIRES OF A THEORY IS A QUALITATIVE UNDERSTANDING OF WHY NATURE WORKS AS IT DOES, AND THE SATISFYING CONFIDENCE OF HAVING A MECHANISM WHICH WOULD, NO DOUBT, EXPLAIN EVEN THE MOST COMPLICATED PHENOMENA IF THE DIFFICULT MATHEMATICAL CALCULATIONS COULD BE MADE THEN THE QUANTUM THEORY OF FERROMAGNETISM IS CERTAINLY A SUCCESS."

JOHN H. VAN VLECK



# EXCHANGE INTERACTION



**Total Interaction = Coulomb Interaction + Exchange**

	Cr	Mn	Fe	Co	Ni	Gd
$D/d$	1.45	1.47	1.63	1.82	1.97	3.1
$T_c$ K			1043	1400	631	287
$T_n$ K	475	100				

*Change distance with Alloy*

# MAGNETIC PROPERTIES

## Intrinsic

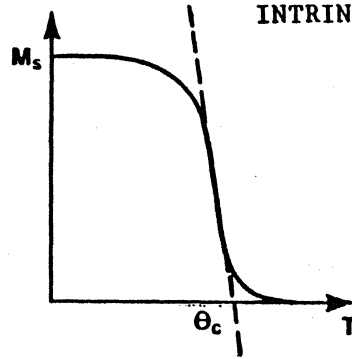
saturation magnetization,  $M_s$

Curie temperature,  $\theta_c$

magneto-crystalline anisotropy,  $K_1, K_2$

magnetostriction  $\lambda$

$$B = H + 4 \pi M_s$$



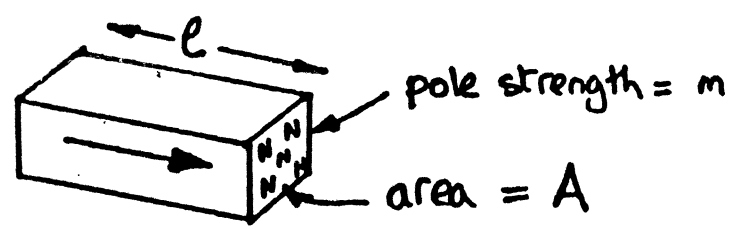
INTRINSIC PROPERTIES DEPEND ONLY ON:

- the type of atom e.g.,  $Fe^{2+}$ ,  $Fe^{3+}$ , Ni, Mn
- the number of atoms
- their arrangement in the crystal
- and the temperature

## SATURATION MAGNETIZATION ( $M_s$ ) In a magnetic field of 100 oersteds

Diamagnetic e.g. Au	$-4 \times 10^{-3}$ emu/cc
Paramagnetic e.g. Mn	$+10^{-1}$
Antiferromagnetic e.g. $MnO_2$	$+10^{-1}$
Ferrimagnetic e.g. $\gamma-Fe_2O_3$	+400
Ferromagnetic e.g. Fe	+1700

# B, H, and M

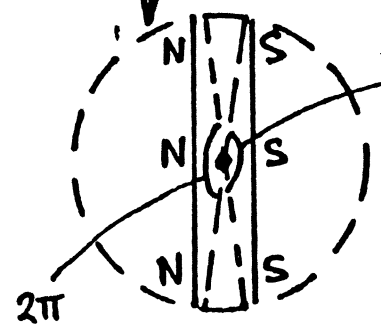
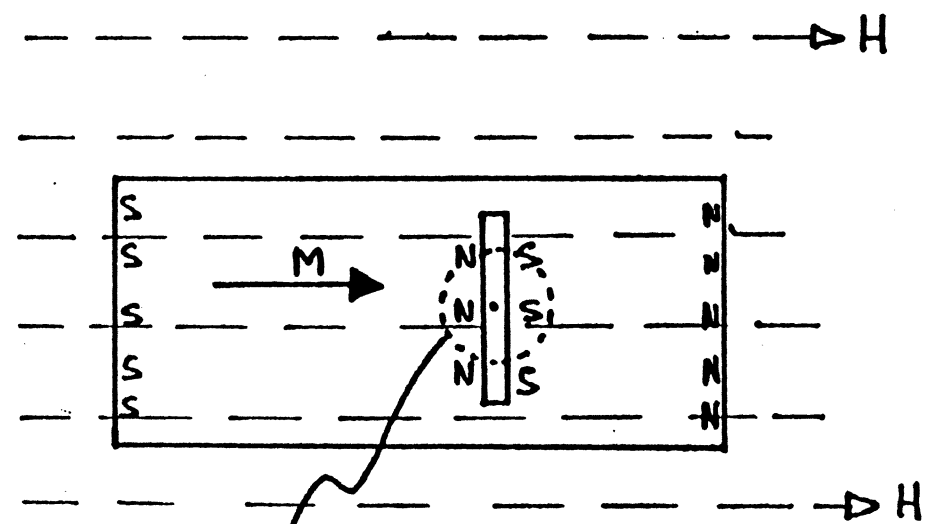


magnetic moment =  $m l$   
 volume =  $A l$

mag. mom. / volume =  $M = \frac{m}{A}$

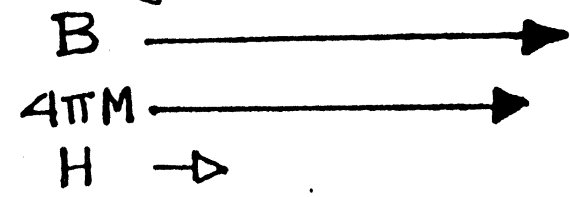
$\text{div } \vec{B} = 0$

normal comp<sup>n</sup>  $\vec{B}$  is continuous  
 tangential "  $\vec{H}$  " "



Mag<sup>n</sup> gives additional  
 Field =  $2\pi \frac{m}{A} + 2\pi \frac{m}{A}$   
 =  $4\pi M$

$\vec{B} = \vec{H} + 4\pi \vec{M}$   
 gauss      oersteds      emu/cc

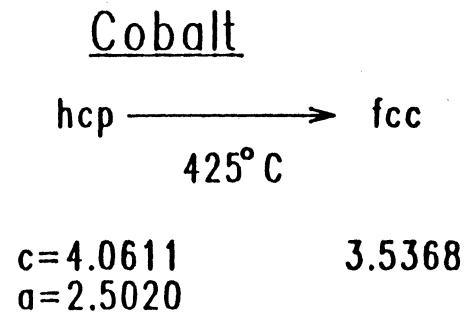
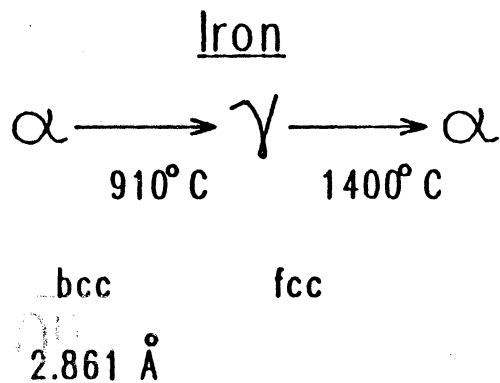


# UNITS IN MAGNETISM

<u>Quantity</u>	<u>Symbol</u>	<u>cgs units</u>	<u>factor</u>	<u>= SI units</u>
		$B = H + 4\pi M$		$B = \mu_0 (H + M)$
• magnetic flux density	B	gauss (G)	$\times 10^{-4}$	= Tesla (T), Webers/m <sup>2</sup>
• magnetic flux	$\Phi$	maxwell (Mx) (G.cm <sup>2</sup> )	$\times 10^{-8}$	= Webers
• magnetic potential diff. (magneto-motive force)	$\mathcal{U}$	gilbert (Gb)	$\times \frac{10}{4\pi}$	= ampere (A)
• magnetic field strength	H	oersted (Oe.)	$\times \frac{10^3}{4\pi}$	= A/m
• magnetization (per volume)	M	emu/cc	$\times 10^3$	= A/m
• " (per mass)	$\sigma$	emu/g	$\times 1$	= A.m <sup>2</sup> /kg
• magnetic moment	m	emu	$\times 10^{-3}$	= A.m <sup>2</sup>
• susceptibility (vol.)	$\chi$	dimensionless	$\times 4\pi$	= dimensionless
• " (mass)	$\kappa$	"	$\times 4\pi$	= "
• permeability (vacuum)	$\mu_0$	"	$\times 4\pi \cdot 10^{-7}$	= Wb/A.m
• " (material)	$\mu$	"	$\times 4\pi \cdot 10^{-7}$	= Wb/A.m
• Bohr magneton	$\mu_B$	$= 0.927 \times 10^{-20}$ erg/Oe.	$\times 10^{-3}$	= A.m <sup>2</sup>
• demagnetizing factor	N	dimensionless	$\times 1/4\pi$	= dimensionless

## Elements of First Transition Series

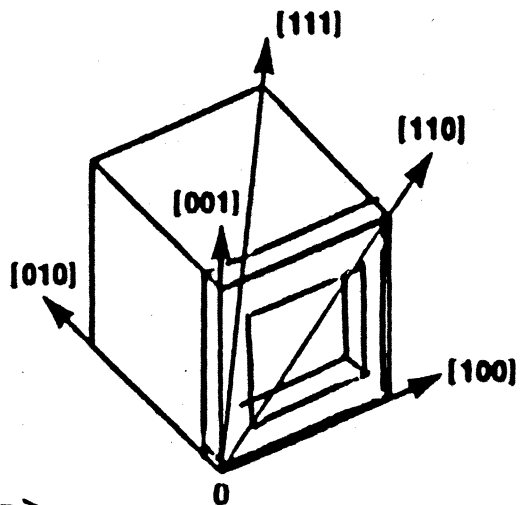
	<u>Fe</u>	<u>Co</u>	<u>Ni</u>
density, g/cm <sup>3</sup>	7.874	8.78–8.85	8.90
Curie point, °C	770	1131	358
melting point, °C	1539	1495	1455
$\sigma$ 20°K, emu/g	217.75	161	54.39
$\sigma$ 0°K, emu/g	221.89	162.5	57.50
$M_s$ , emu/cm <sup>3</sup>	1714	1422	484.1



# MAGNETO-CRYSTALLINE ANISOTROPY

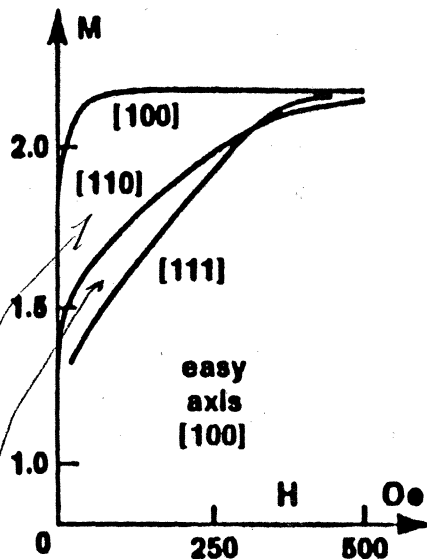
## Iron And Nickel

*Magnetic properties related to crystal properties*



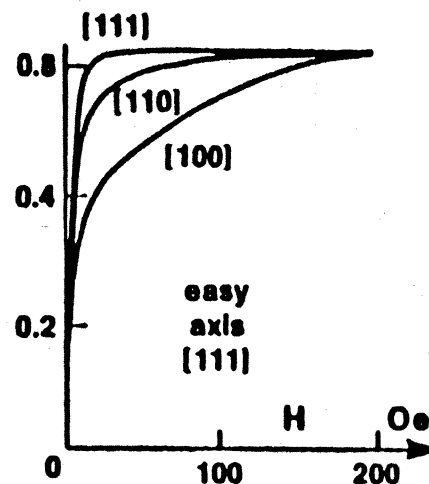
$\langle 100 \rangle$   
 =  $[100], [010], [001]$

IRON



$K_1 = 4.8 \times 10^5 \text{ erg/cc}$   
 $K_2 = 5 \times 10^4$

NICKEL



$K_1 = 4.5 \times 10^4$   
 $K_2 = 2.34 \times 10^4$

magneto-crystalline energy =  $K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) + \dots$

# MAGNETOCRYSTALLINE ANISOTROPY

relationship between  $K_1, K_2$  and EASY directions

Cubic

$K_1$ $K_2$	$+$ $+\infty$ to $-9K_1/4$	$+$ $-9K_1/4$ to $-9K_1$	$+$ $-9K_1$ to $-\infty$	$-$ $-\infty$ to $9 K_1 /4$	$-$ $9 K_1 /4$ to $9 K_1 $	$-$ $9 K_1 $ to $+\infty$
Easiest	[100]	[100]	[111]	[111]	[110]	[110]
Intermediate	[110]	[111]	[100]	[110]	[111]	[100]
Hardest	[111]	[110]	[110]	[100]	[100]	[111]

UNIAXIAL

$$K_1 + K_2 > 0$$

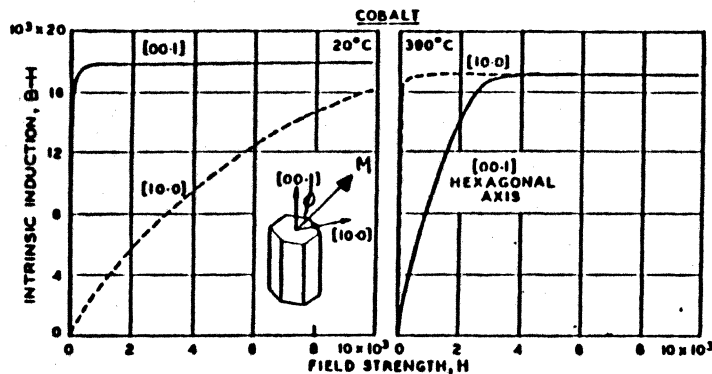
axis (eg. [00.1], [100])

$$K_1 + K_2 < 0$$

basal plane (eg. [10.0])

R.M. Bozorth, Phys. Rev. 50, 1076-81 (1936)

# MAGNETO-CRYSTALLINE ANISOTROPY OF COBALT



25°C

390°C

$$B = H + 4\pi M$$

$$B - H = 4\pi M$$

$$E_K = K_1 \sin^2 \phi + K_2 \sin^4 \phi$$

$$K_1 + K_2 > 0$$

[00.1] easy

(hex. axis)

$$K_1 + K_2 < 0$$

[10.0] easy

(basal plane)

Cobalt

$$K_1 = +3.98 \times 10^6 \text{ erg/cc}$$

$$K_2 = +1.98 \times 10^6 \text{ erg/cc}$$



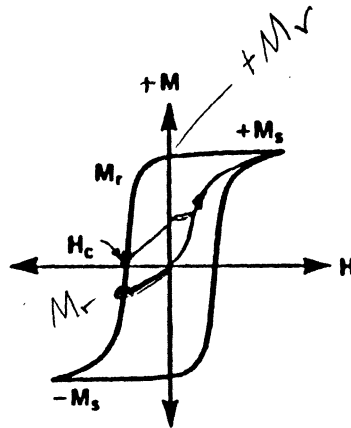
# MAGNETIC PROPERTIES

## Extrinsic

remanent magnetization  $M_r$

coercivity  $H_c, H_r$

permeability  $\mu$



EXTRINSIC PROPERTIES also depend on:

- the type, number, arrangement of the atoms
- and the temperature

but also depend on-

the shape and size of the sample  
and its previous history

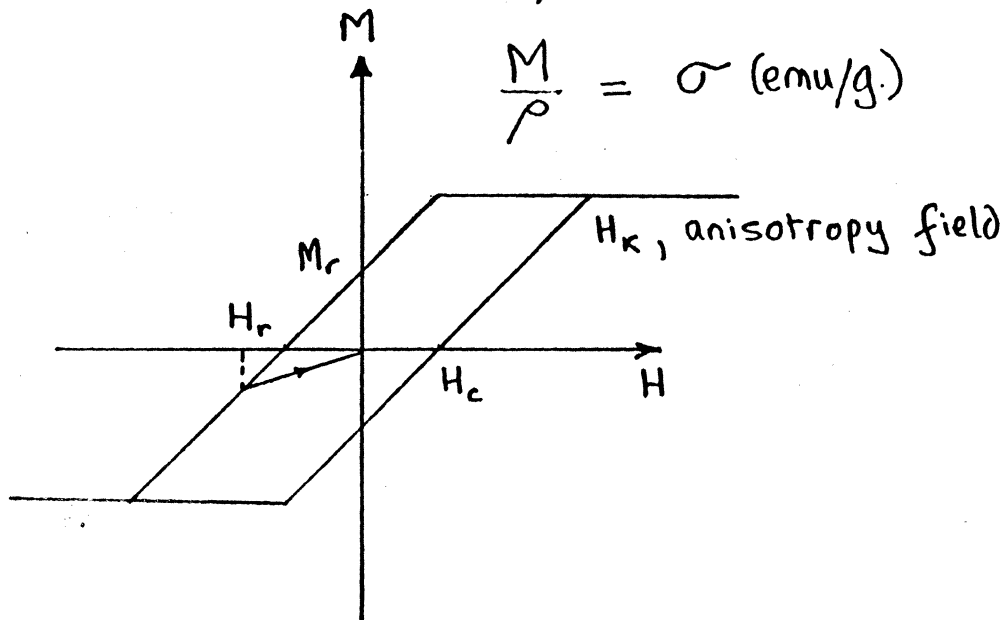
$$B = H + 4\pi M$$

$$\mu = 1 + 4\pi \kappa$$

$$\frac{M}{\rho} = \sigma \text{ (emu/g.)}$$

$${}_{(B)}H_c < {}_{(M)}H_c$$

$$\frac{\kappa}{\rho} = \chi \text{ mass susceptibility}$$



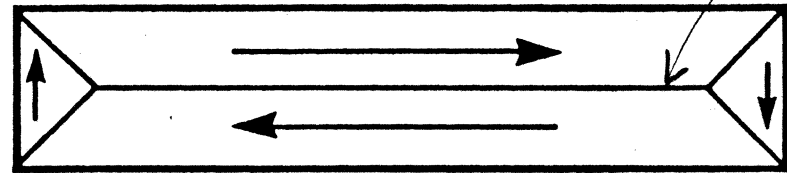
$${}_{SI} B = \mu_0 (H + M)$$

# MAGNETIC DOMAINS

EXTRINSIC PROPERTIES  
MAGNETIC DOMAIN WALL

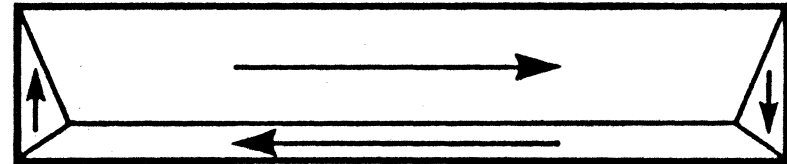
postulated to explain  
why a piece of iron

$$H = 0$$
$$M = 0$$



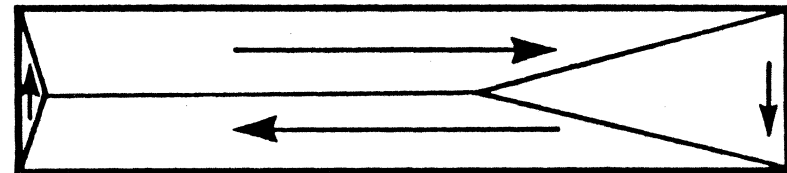
—may not be magnetized

$$H \rightarrow$$
$$M \rightarrow$$



—may then be fully magnetized in small fields

$$H \downarrow$$
$$M \downarrow$$



# WHAT LIMITS THE NUMBER OF DOMAINS?

DECREASE IN MAGNETOSTATIC ENERGY IS BALANCED BY THE INCREASE IN DOMAIN WALL ENERGY AND THE INCREASE IN EXCHANGE ENERGY,  $E_x$

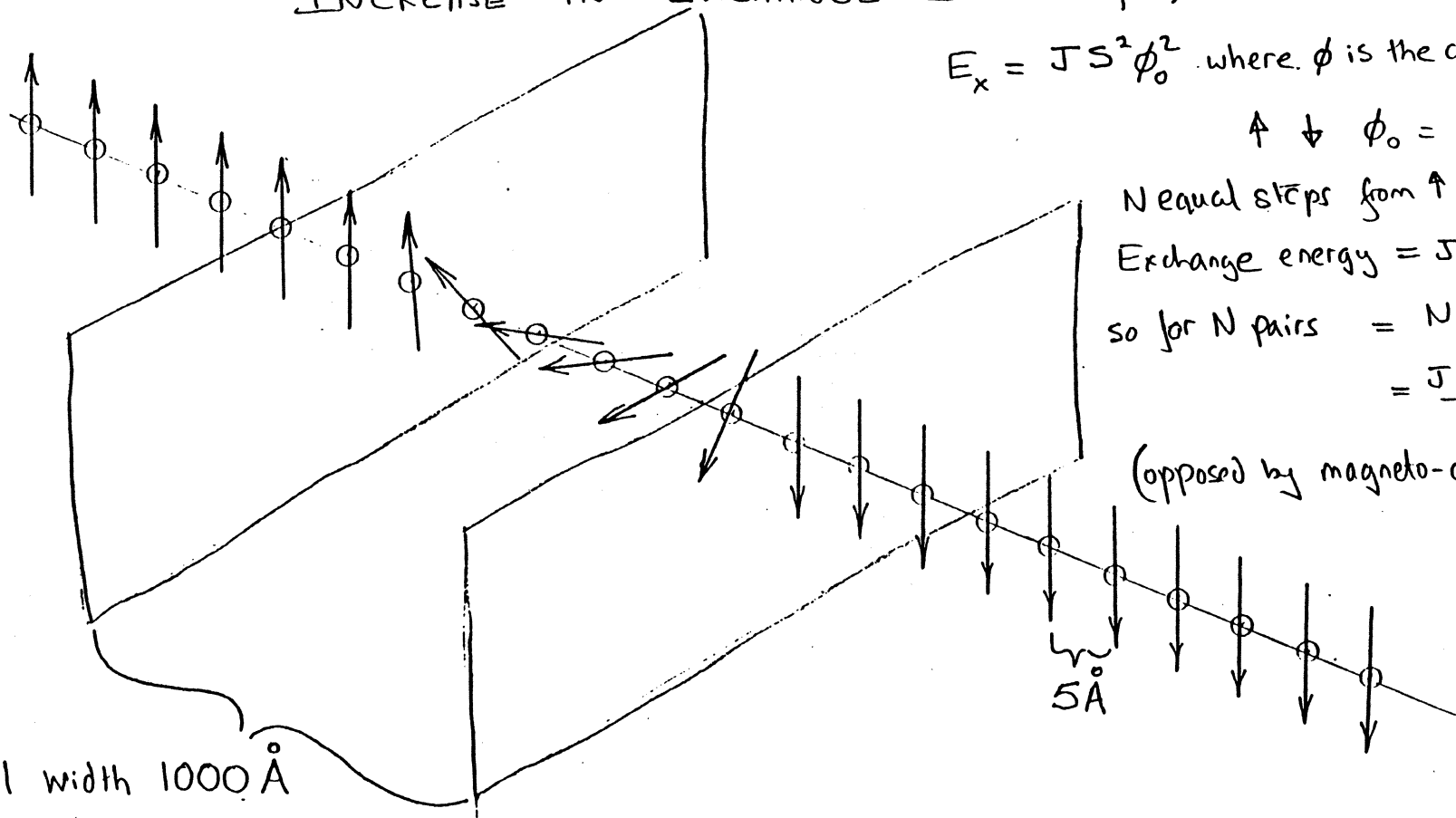
$E_x = JS^2\phi_0^2$  where  $\phi$  is the angle between spins.

$\uparrow \downarrow \phi_0 = 180^\circ$

Nequal steps from  $\uparrow$  to  $\downarrow$   
Exchange energy =  $JS^2\left(\frac{\phi_0}{N}\right)^2$  per p.

so for N pairs =  $NJS^2\left(\frac{\phi_0}{N}\right)^2$   
=  $\frac{JS^2\phi_0^2}{N}$

(opposed by magneto-crystalline energy)



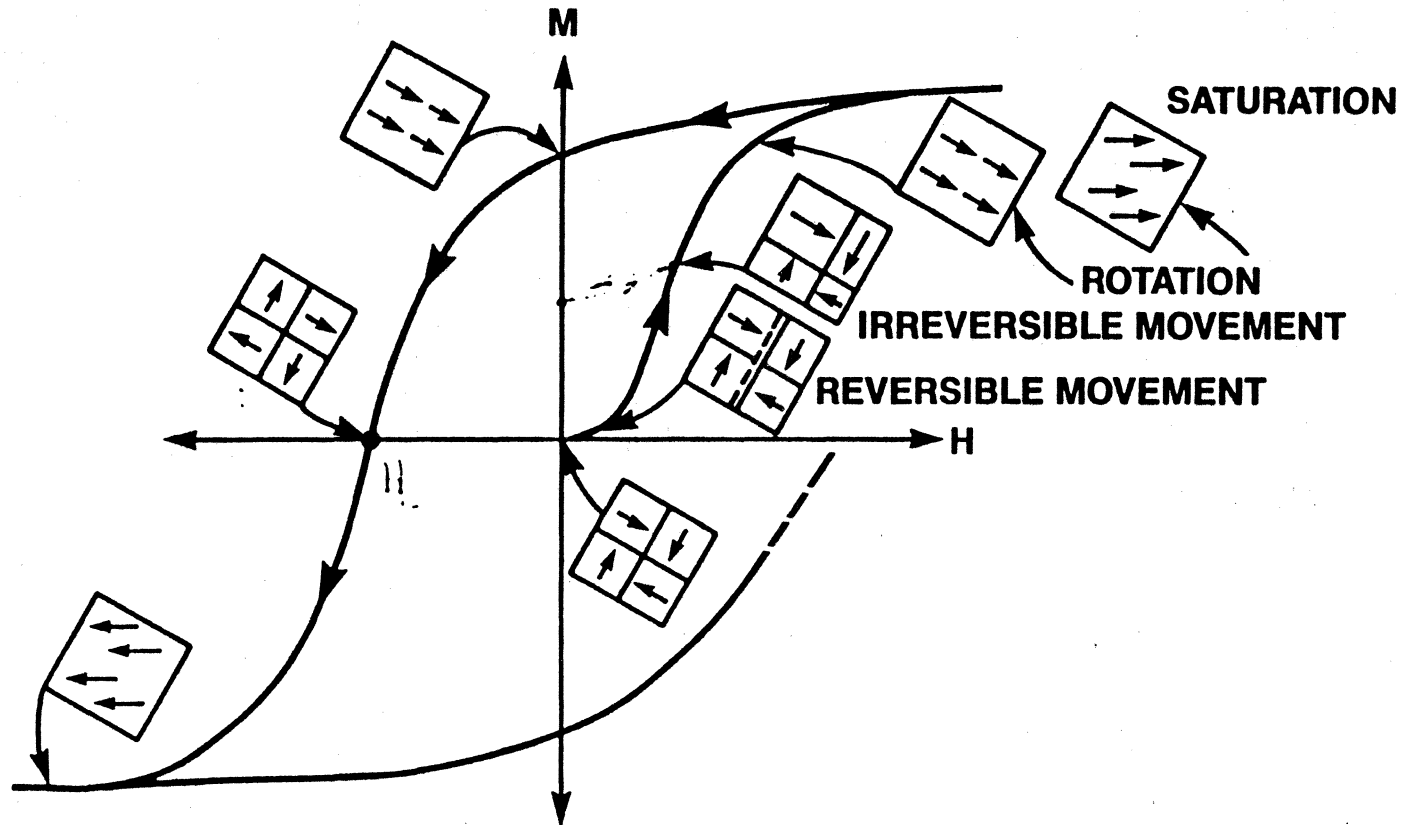
wall width 1000 Å

BLOCH WALLS

$254 \text{ \AA} = \frac{1}{1,000,000}$  "

Bate

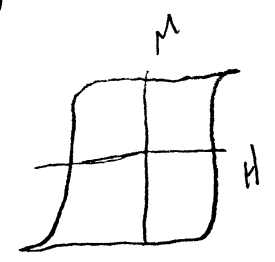
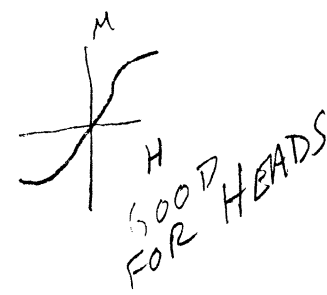
# DOMAINS AND THE HYSTERESIS LOOP

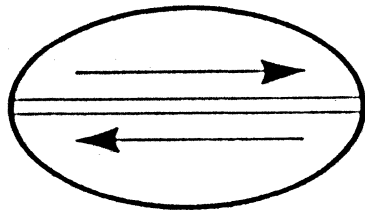


*High Coercivity*
*Low*

## HARD AND SOFT MAGNETIC MATERIALS

<u>Soft</u>	<u>High Ms</u>	<u>Low Hc</u>	<u>Low Mr</u>	<u>High <math>\mu</math></u>
Fe	1700 emu/cc	1 oe	<500	20,000
80Ni20Fe	660	0.1	<300	50,000
MnZn ferrite	400	0.02	<200	5,000
$Co_{70}Fe_5Si_{15}B_{10}$	530	0.1	<250	10,000
<u>Hard</u>	<u>High Ms</u>	<u>High Hc</u>	<u>High Mr</u>	
$\gamma-Fe_2O_3$	400	300-450	200-300	
$BaO.6Fe_2O_3$	360	2000-3000	180	
$SmCo_5$	100	24,000	700	
$Fe_{14}B_{11}$	100	41,000	430	





←  $5\mu$  →

**Multi-Domain**

**coercivity:**

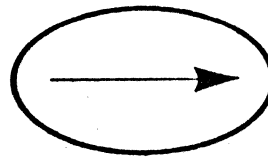
$H_c < 100 \text{ Oe}$

$M_s$

400 – 1700 emu/cc

$\frac{M_r}{M_s}$

$< 0.5$



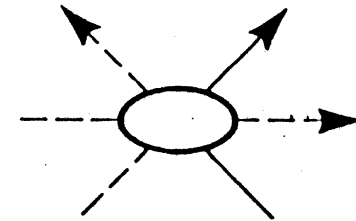
←  $< 1\mu$  →

**Single Domain**

$H_c = 100 - 3000$

400 – 1700

$0.5 < \frac{M_r}{M_s} < 1.0$



$< 0.02\mu$   
← →

**Superparamagnetic**

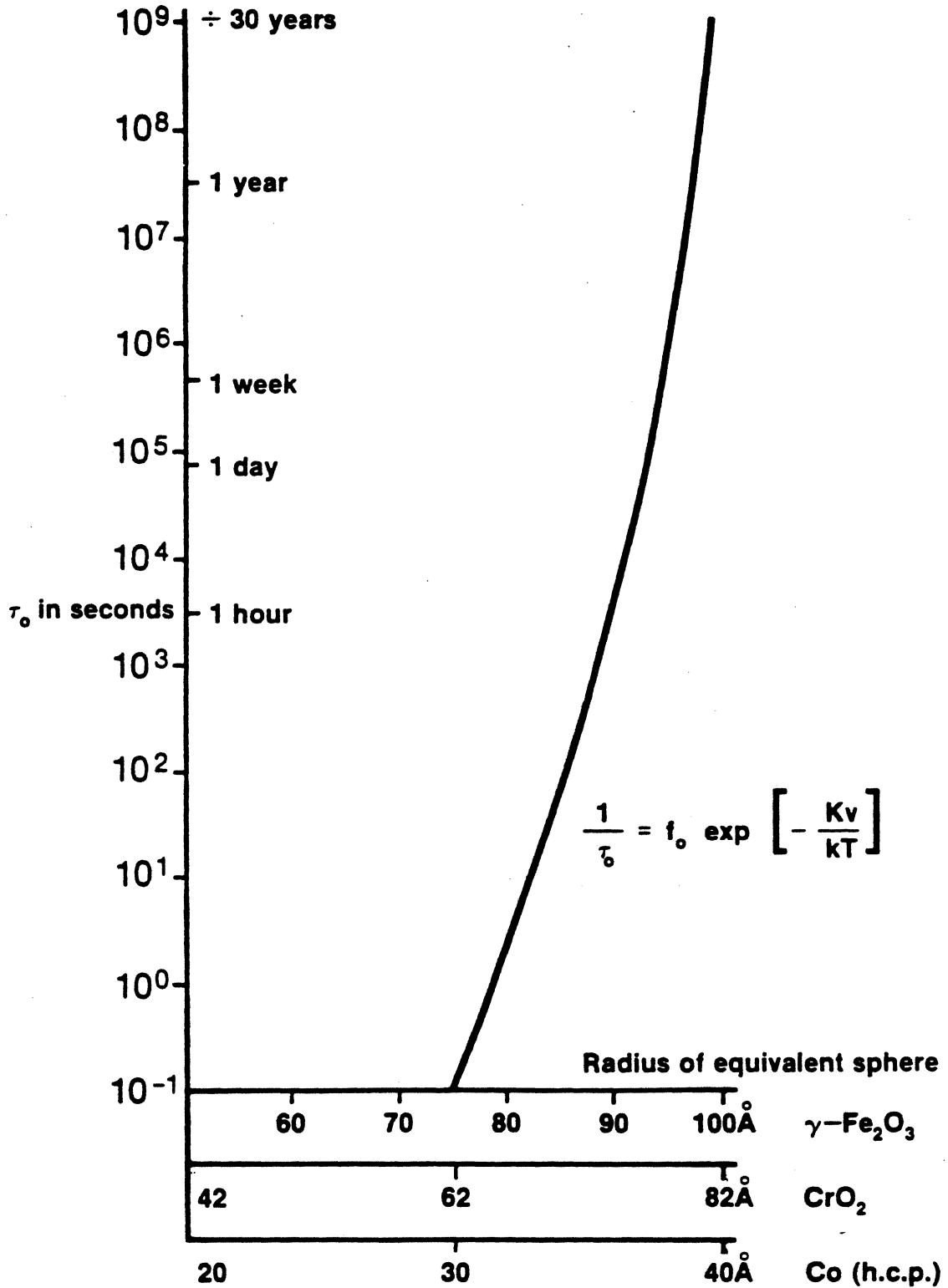
$H_c = 0$

400 – 1700

0



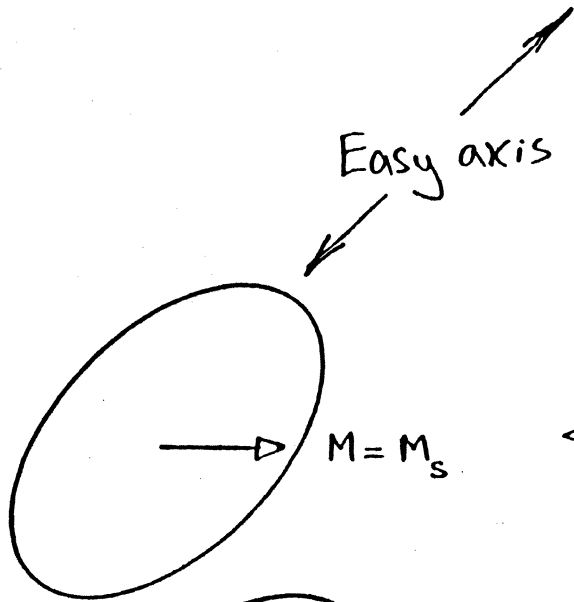
# RELAXATION TIME FOR ACICULAR PARTICLES



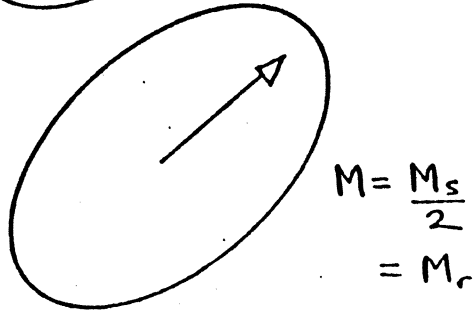
# SHAPE ANISOTROPY

$$\theta = 45^\circ$$

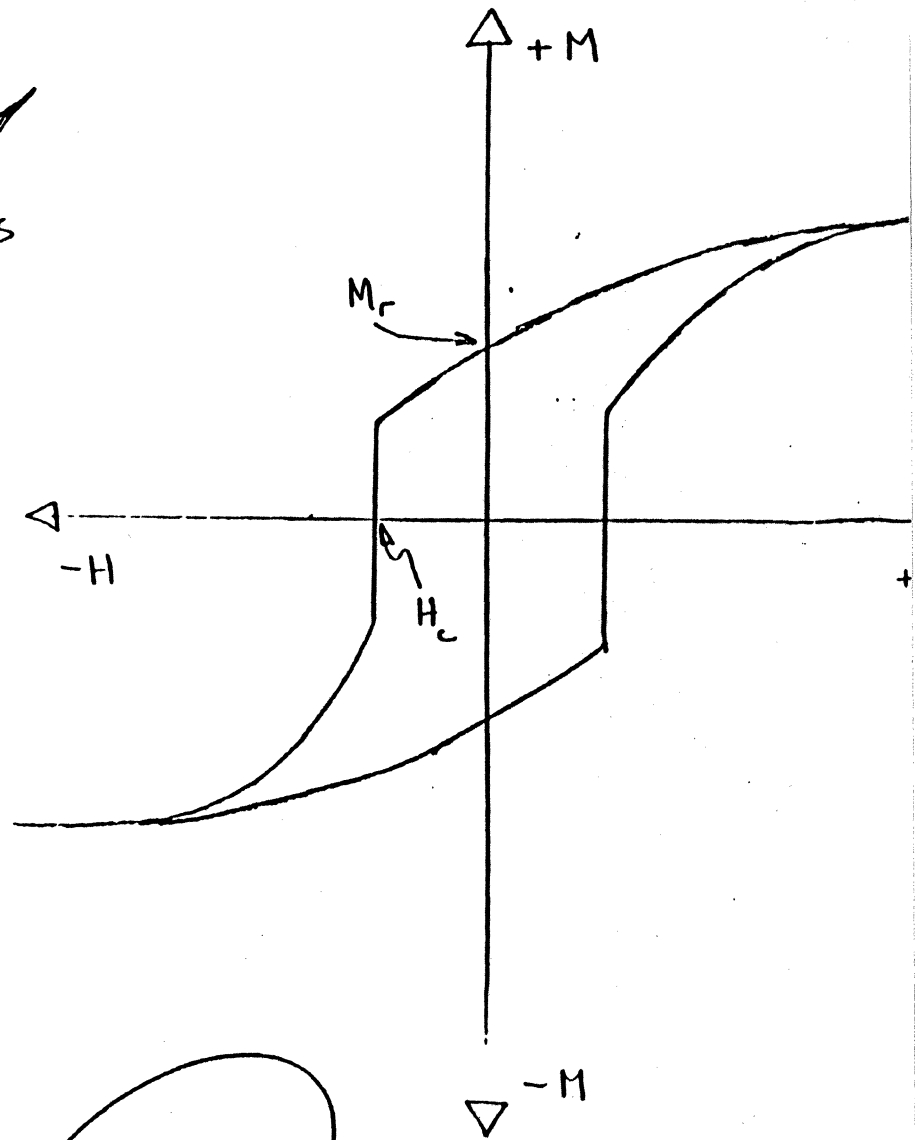
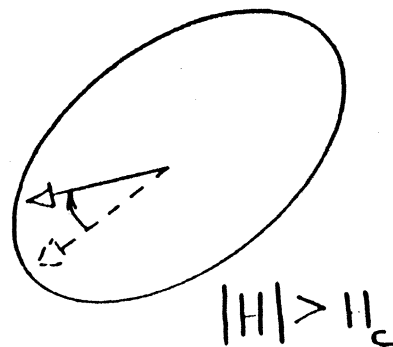
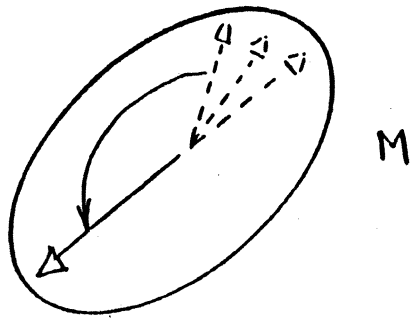
$\longrightarrow$   
 $H = +3000 \text{ Oe}$



$H = 0$



$H = H_c$



Néel 1947

Stoner and Wohlfarth  
1948



# SINGLE DOMAIN PARTICLES

Anisotropy

Maximum Coercivity

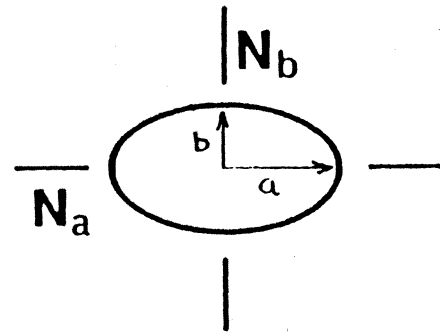
Crystalline

$$H_c = \frac{2 k_1}{M_s}$$

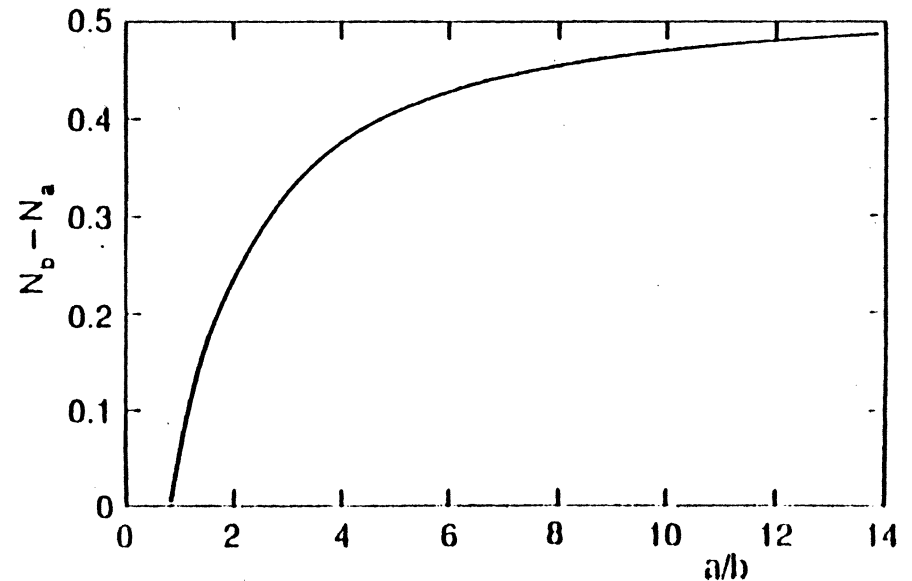
Strain

$$H_c = \frac{3 \lambda_s T}{M_s}$$

Shape



$$H_c = (N_b - N_a) M_s$$

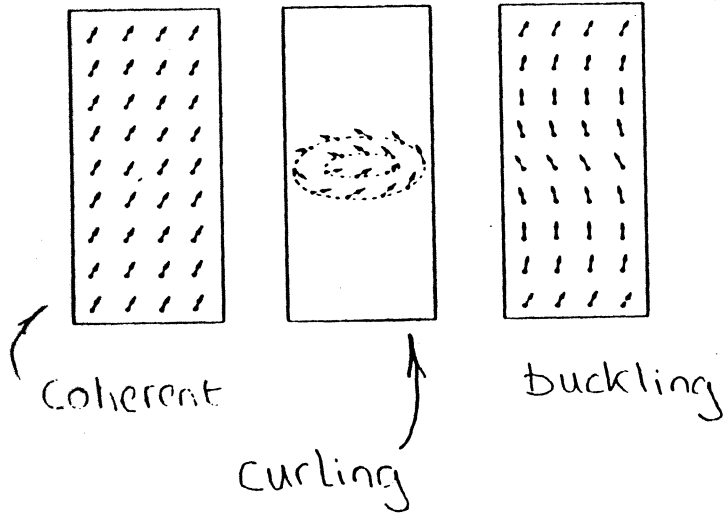


# SINGLE DOMAIN PARTICLES

## Maximum Coercivity

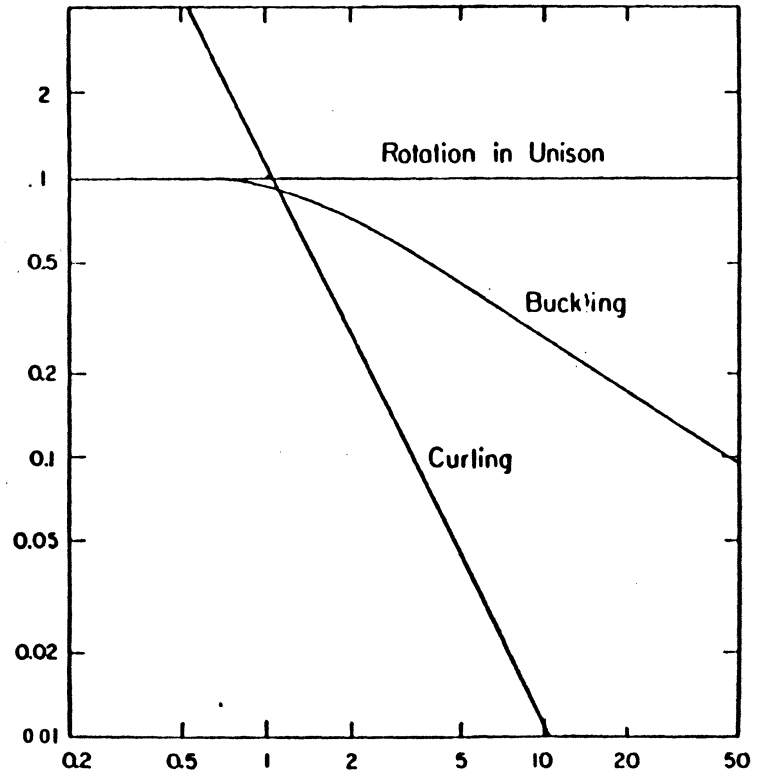
	Iron	Cobalt	Nickel	$\gamma\text{-Fe}_2\text{O}_3$
<i>TEMPERATURE DEPENDANT</i> Crystalline	250	3,000	70	230
Strain	300	300	2,000	<10
Shape (10:1)	5,300	4,400	1,550	2,450

# INCOHERENT MAGNETIZATION REVERSAL



infinite cylinders

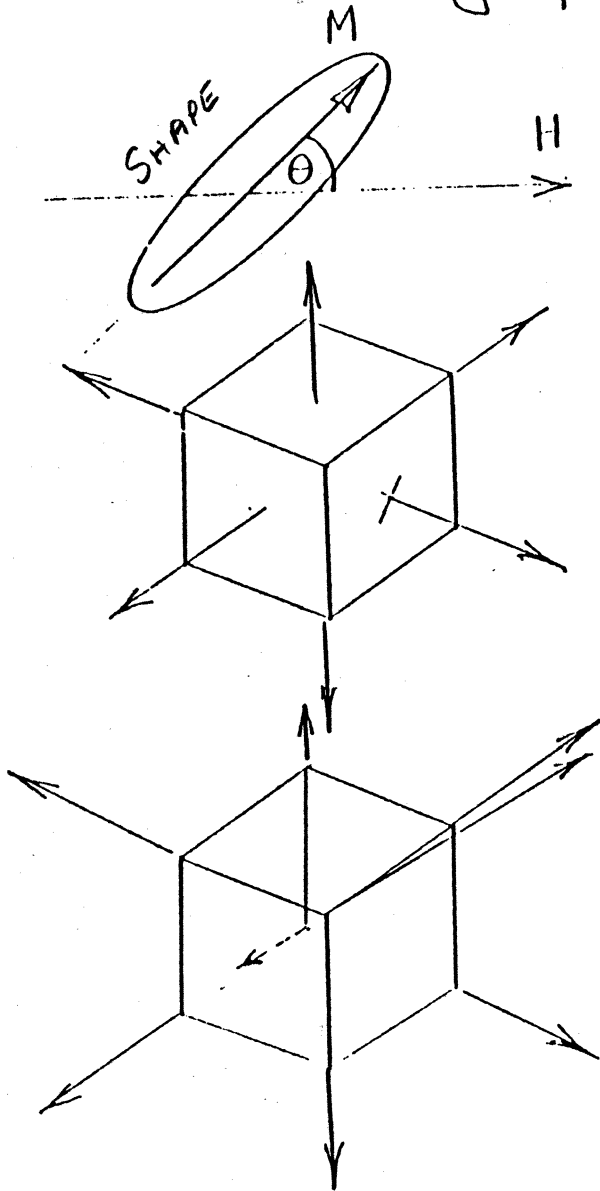
$$\frac{H_c}{2\pi M_s}$$



$S = \frac{\text{cylinder radius}}{\text{cylinder length}}$

# REMANENCE AND PARTICLE ALIGNMENT

random assembly of uniaxial particles.



$n=2$  = number of equivalent easy directions

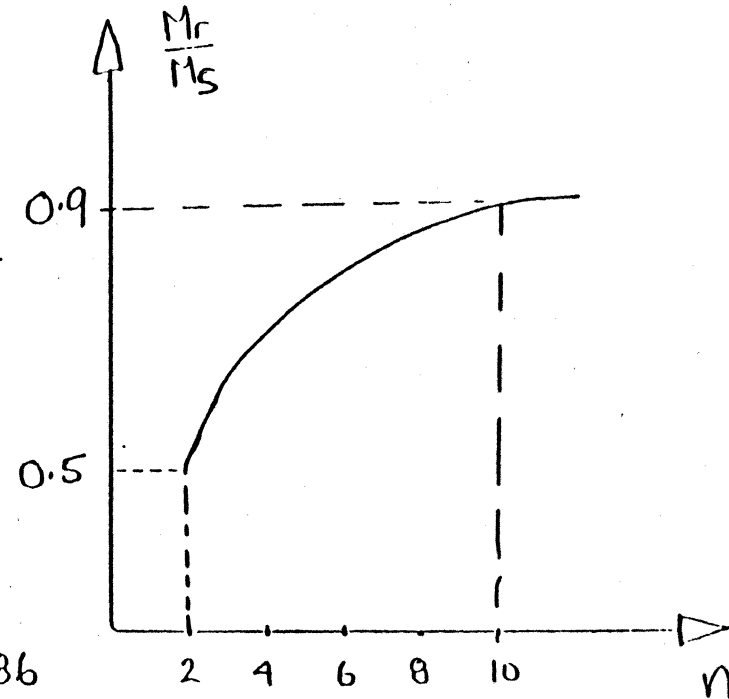
$$\frac{M_r}{M_s} = 0.5$$

$$n=6, \quad \frac{M_r}{M_s} = 0.825$$

easy axes  $\langle 100 \rangle$

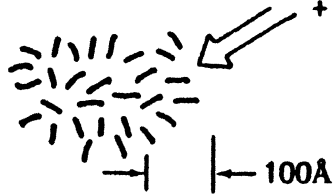
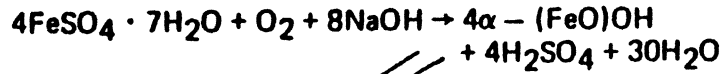
$$n=8, \quad \frac{M_r}{M_s} = 0.86$$

easy axes  $\langle 111 \rangle$

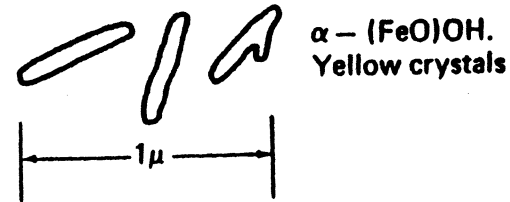


**Acicular  $\gamma - \text{Fe}_2\text{O}_3$**

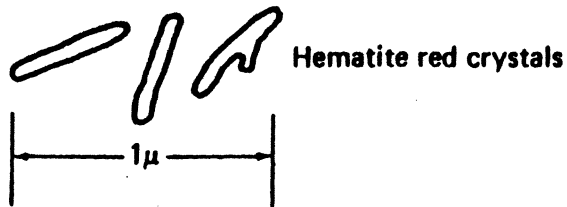
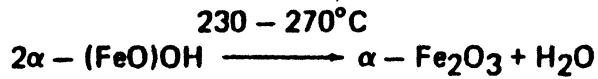
**Step 1 Preparation of colloidal  $\alpha - (\text{FeO})\text{OH}$   
- goethite**



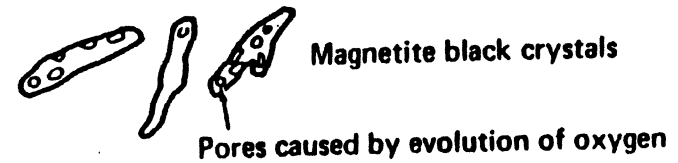
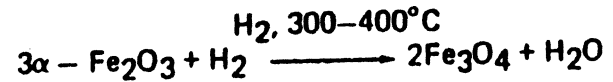
**Step 2 use these as seeds to grow larger crystals of  $\alpha - (\text{FeO})\text{OH}$  with water, scrap iron, air, 60°C, 4 hours.**



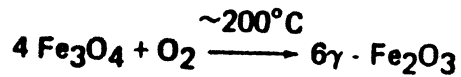
**Step 3 Dehydrate**



**Step 4 Reduce**



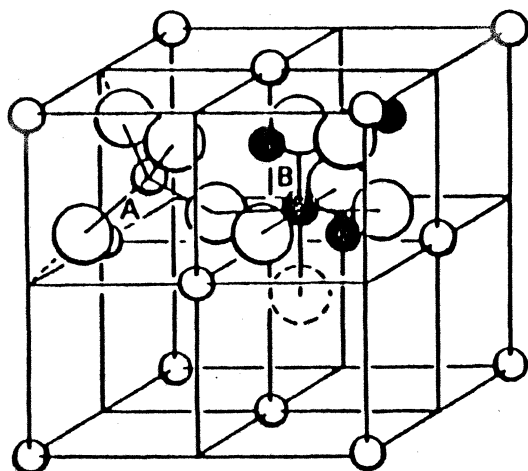
**Step 5 Carefully re-oxidize**



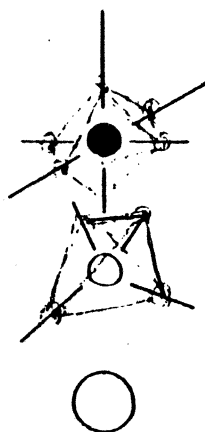
**Transformations**

Pigment  $\rightarrow$  dehydrated oxide  $\rightarrow$  magnetite  $\rightarrow$  maghemite  
 $[\alpha - (\text{FeO})\text{OH}] \quad [\alpha - \text{Fe}_2\text{O}_3] \quad [\text{Fe}_3\text{O}_4] \quad [\gamma - \text{Fe}_2\text{O}_3]$   
 - are Pseudomorphic

# INTRINSIC MAGNETIC PROPERTIES OF $Fe_3O_4$ AND $\gamma-Fe_2O_3$



SPINEL STRUCTURE

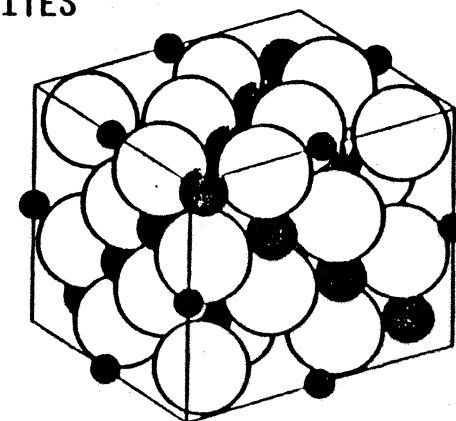


INVERSE SPINEL

$Fe^{2+}$  AND  $Fe^{3+}$  OCTAHEDRAL SITES

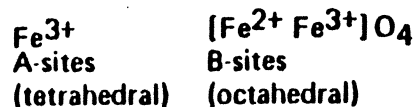
$Fe^{3+}$  . TETRAHEDRAL SITES

○ OXYGEN

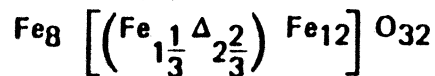


OCTAHEDRAL SITES = 16 . TETRAHEDRAL SITES =  $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) + 4 = 8$

Magnetite – inverse spinel



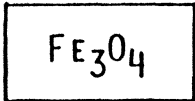
$\gamma$  – Ferric Oxide – same oxygen sublattice  
– vacancies arranged on a tetragonal superlattice ( $c/a = 3$ )



is the formula for  $\frac{1}{3}$  unit cell.

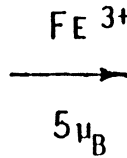
	$Fe_3O_4$	$\gamma-Fe_2O_3$
Moment per molecule	$4\beta$	$2.5\beta$
$\sigma_{so}$	97 emu/g	82 emu/g
$\sigma_s$	87 emu/g	74 emu/g
Density	5.197 g/cc	5.074 g/cc
$I_s$	453 emu/cc	400 emu/cc
Curie temperature	575°C	590°C
Anisotropy constant		
	$K_1 = -1.10 \times 10^5$ erg/cc	$= -4.64 \times 10^4$ erg/cc
	<111> easy	<110> easy
	<100> hard	<100> hard

INTRINSIC PROPERTIES:  $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{Fe}_3\text{O}_4$

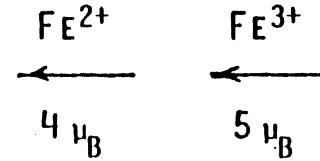


"INVERSE SPINEL"

A SITES



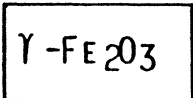
B SITES



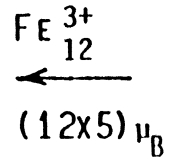
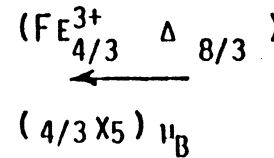
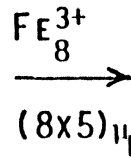
0  
4

NET MOMENT =  $4\mu_B$  PER FORMULA UNIT

$\sigma_0 = \frac{N\mu_B}{M} n_B$  ;  $M = 231.6$  ;  $\therefore \sigma_0 = 97 \text{ EMU/G}$  (EXPT = 94 EMU/G)



MORE Stable



0  
32

NET MOMENT =  $(16/3 \times 5)\mu_B$  per  $\text{Fe}_2\text{O}_3$

MOMENT PER FORMULA UNIT =  $3/32 \times 16/3 \times 5\mu_B = 2.5\mu_B$

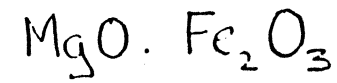
OR 1.25  $\mu$  / IRON ATOM: EXPT = 1.18

$\sigma_0 = 82 \text{ EMU/G}$

$\sigma_0 = 74 \text{ EMU/G}$  ; EXPERIMENT  
 R.T.

# FERRIMAGNETISM

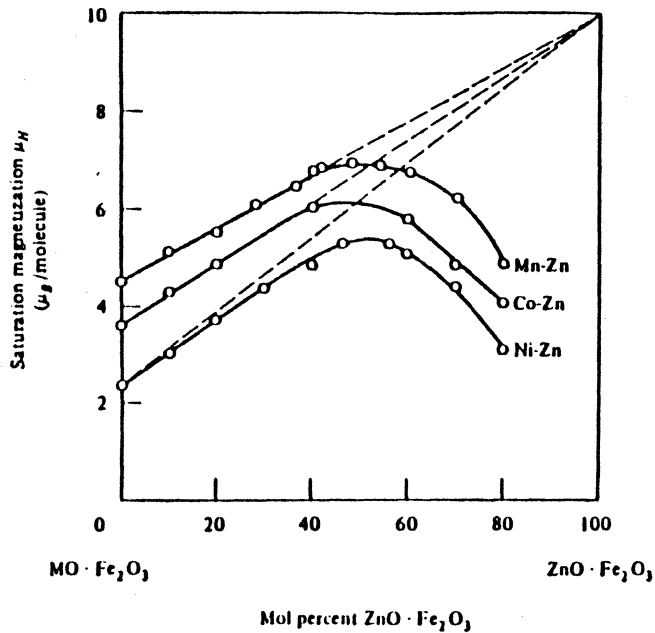
Substance	Lattice parameter $a$ (Å)	Density (g cm <sup>-3</sup> )	0 K		20 C		$T_c$ (°C)
			$\sigma_0$ (emu/g)	$M_0$ (emu/cm <sup>3</sup> )	$\sigma_s$ (emu/g)	$M_s$ (emu/cm <sup>3</sup> )	
MnO · Fe <sub>2</sub> O <sub>3</sub>	8.50	5.00	112	560	80	400	300
FeO · Fe <sub>2</sub> O <sub>3</sub>	8.39	5.24	98	510	92	480	585
CoO · Fe <sub>2</sub> O <sub>3</sub>	8.38	5.29	90	475	80	425	520
NiO · Fe <sub>2</sub> O <sub>3</sub>	8.34	5.38	56	300	50	270	585
CuO · Fe <sub>2</sub> O <sub>3</sub>	8.37*	5.41	30	160	25	135	455
MgO · Fe <sub>2</sub> O <sub>3</sub>	8.36	4.52	31	140	27	120	440
BaO · 6Fe <sub>2</sub> O <sub>3</sub>	$a = 5.88$ $c = 23.2$	5.28	100	530	72	380	450
Fe	2.87	7.87	222	1747	218	1714	770



(pure inverse  $\Rightarrow n_{\mu_B} = 0$ )

0.1 of Mg<sup>2+</sup> } A sites  
 0.9 of Fe<sup>3+</sup> }  $0.9 \times 5 = 4.5 \mu_B$

0.9 of Mg<sup>2+</sup> } B sites  
 1.1 of Fe<sup>3+</sup> }  $1.1 \times 5 = 5.5 \mu_B$

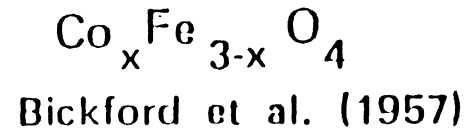
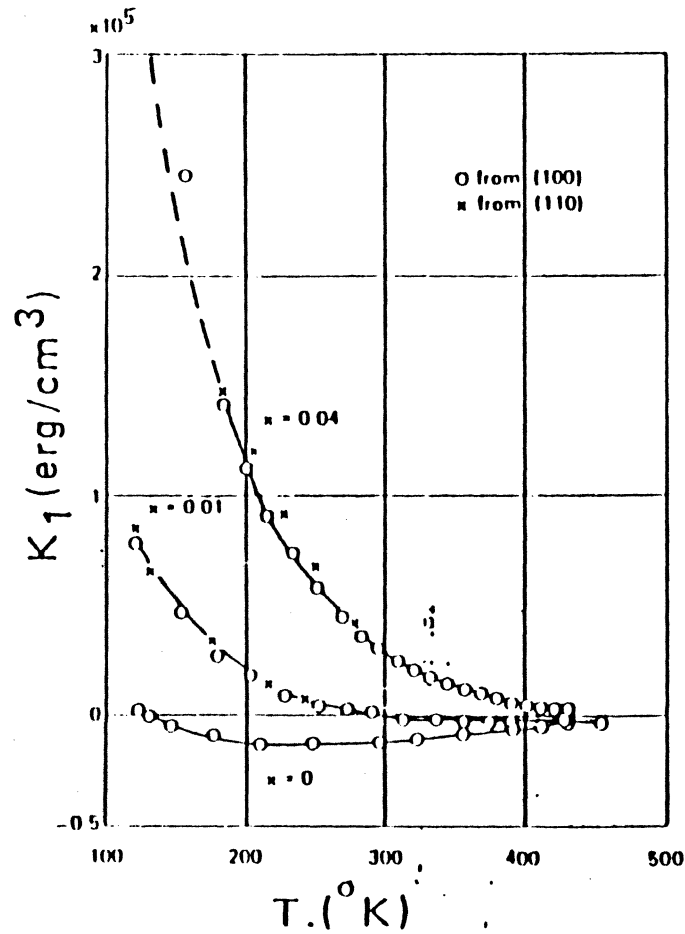


Example	Substance	Structure	Tetrahedral A sites	Octahedral B sites	Net moment ( $\mu_B$ molecule)
1	NiO · Fe <sub>2</sub> O <sub>3</sub>	Inverse	Fe <sup>3+</sup> 5 →	Ni <sup>2+</sup> , Fe <sup>3+</sup> 2 5 ←	2
2	ZnO · Fe <sub>2</sub> O <sub>3</sub>	Normal	Zn <sup>2+</sup> 0	Fe <sup>3+</sup> , Fe <sup>3+</sup> 5 5 ← →	0
3	MgO · Fe <sub>2</sub> O <sub>3</sub>	Mostly inverse	Mg <sup>2+</sup> , Fe <sup>3+</sup> 0 4.5 →	Mg <sup>2+</sup> , Fe <sup>3+</sup> 0 5.5 ←	1
4	0.9 NiO · Fe <sub>2</sub> O <sub>3</sub>	Inverse	Fe <sup>3+</sup> 4.5 →	Ni <sup>2+</sup> , Fe <sup>3+</sup> 1.8 4.5 ←	2.8
	0.1 ZnO · Fe <sub>2</sub> O <sub>3</sub>	Normal	Zn <sup>2+</sup> 0	Fe <sup>3+</sup> , Fe <sup>3+</sup> 0.5 0.5 ←	
			4.5 →	7.3 ←	

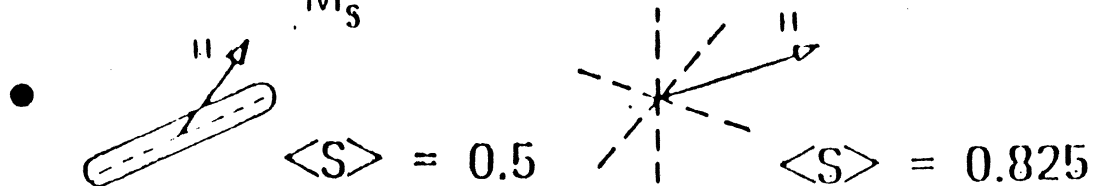


# Cobalt-Modified Iron Oxides

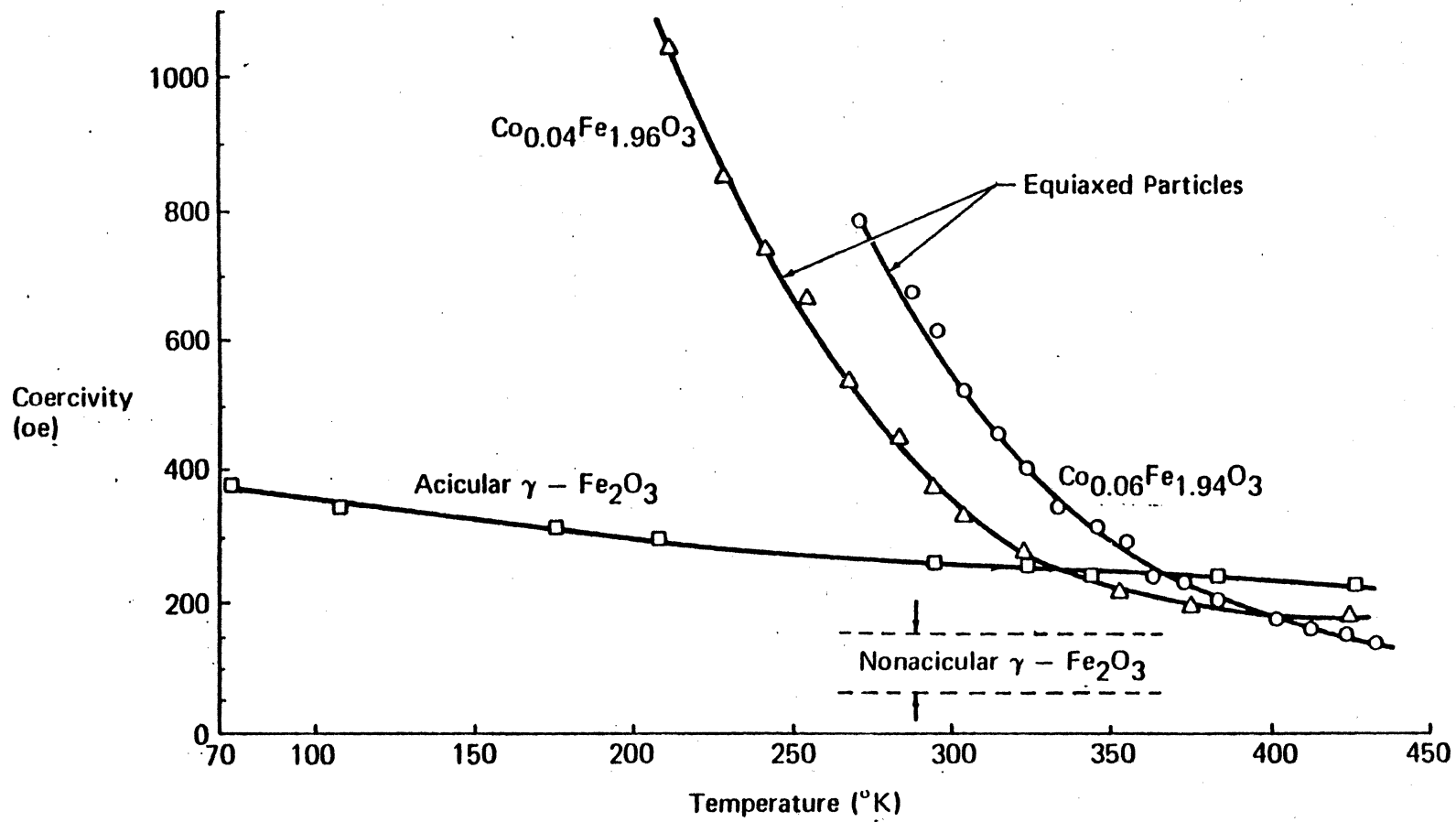
## Cobalt substitution



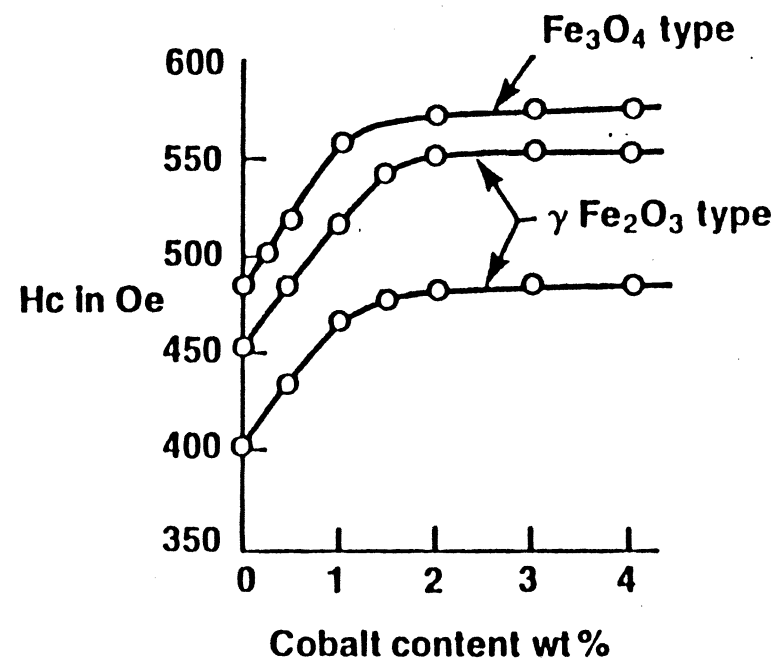
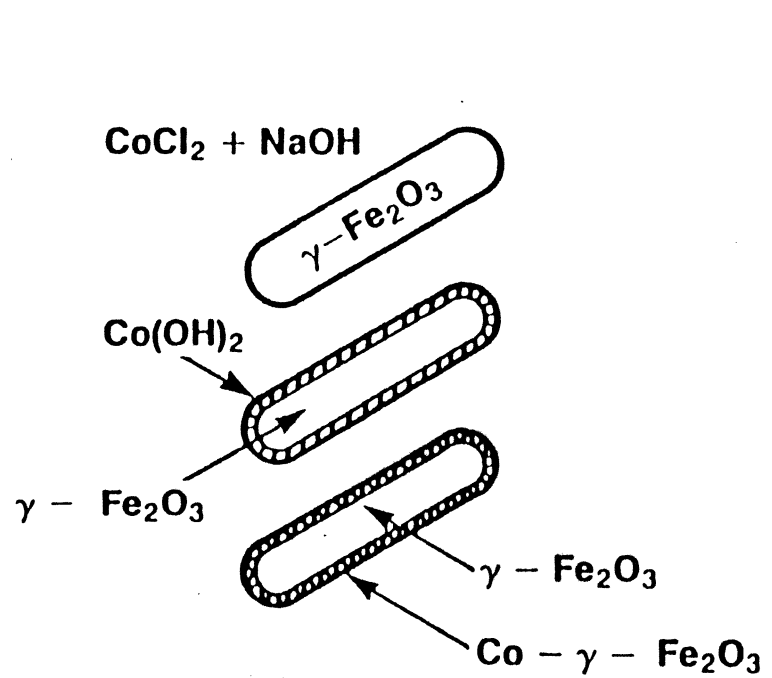
- $H_c = 0.64 \frac{K_1}{M_s}$ , temperature sensitive



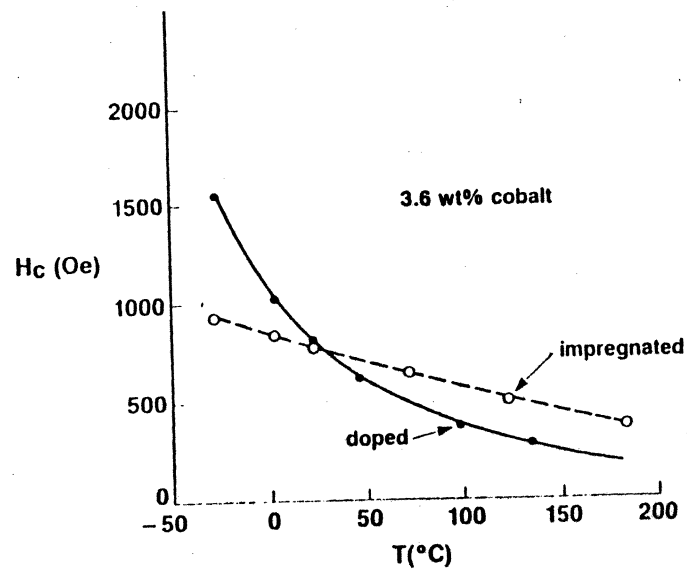
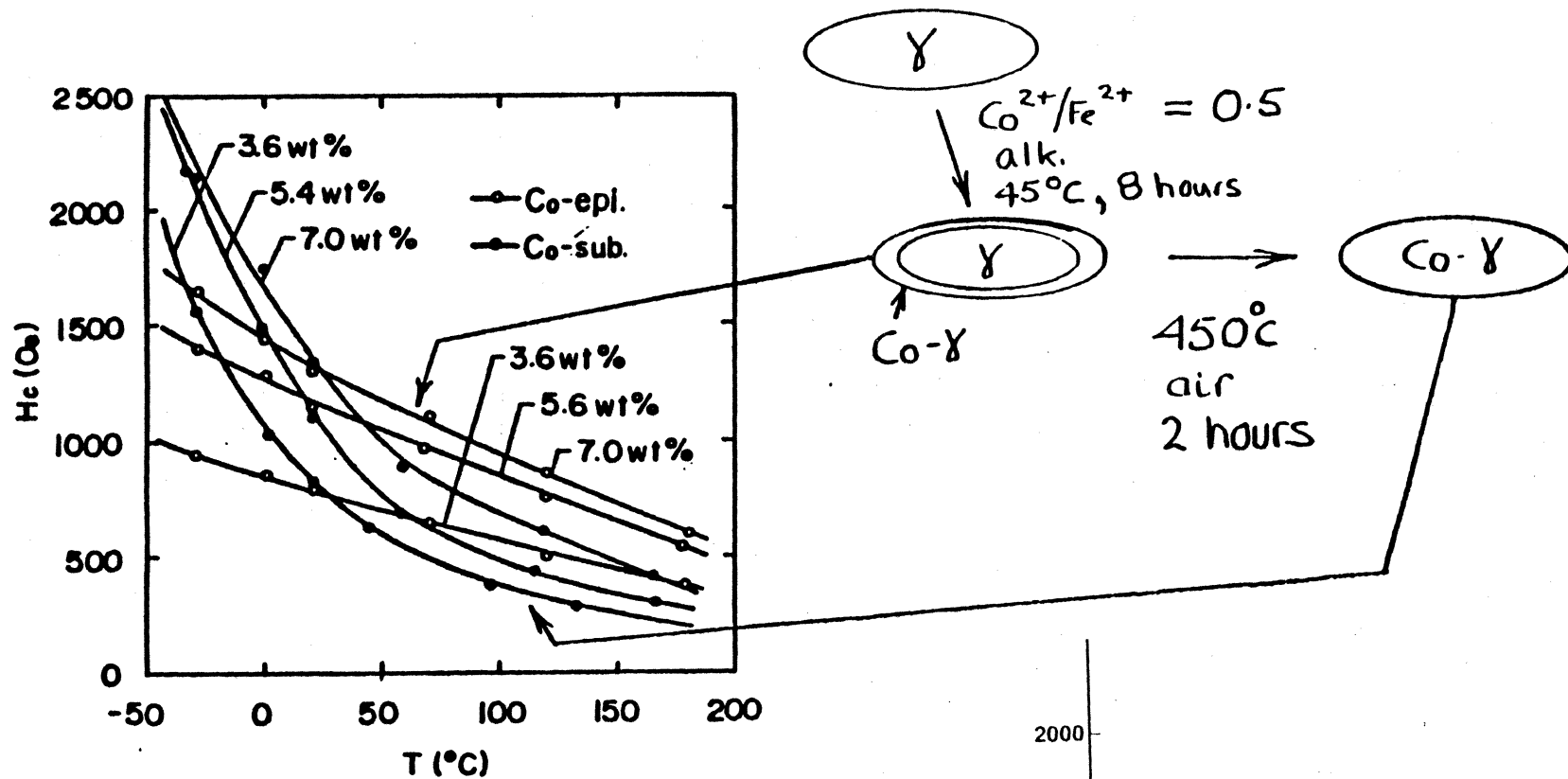
- Remanence time and stress dependent



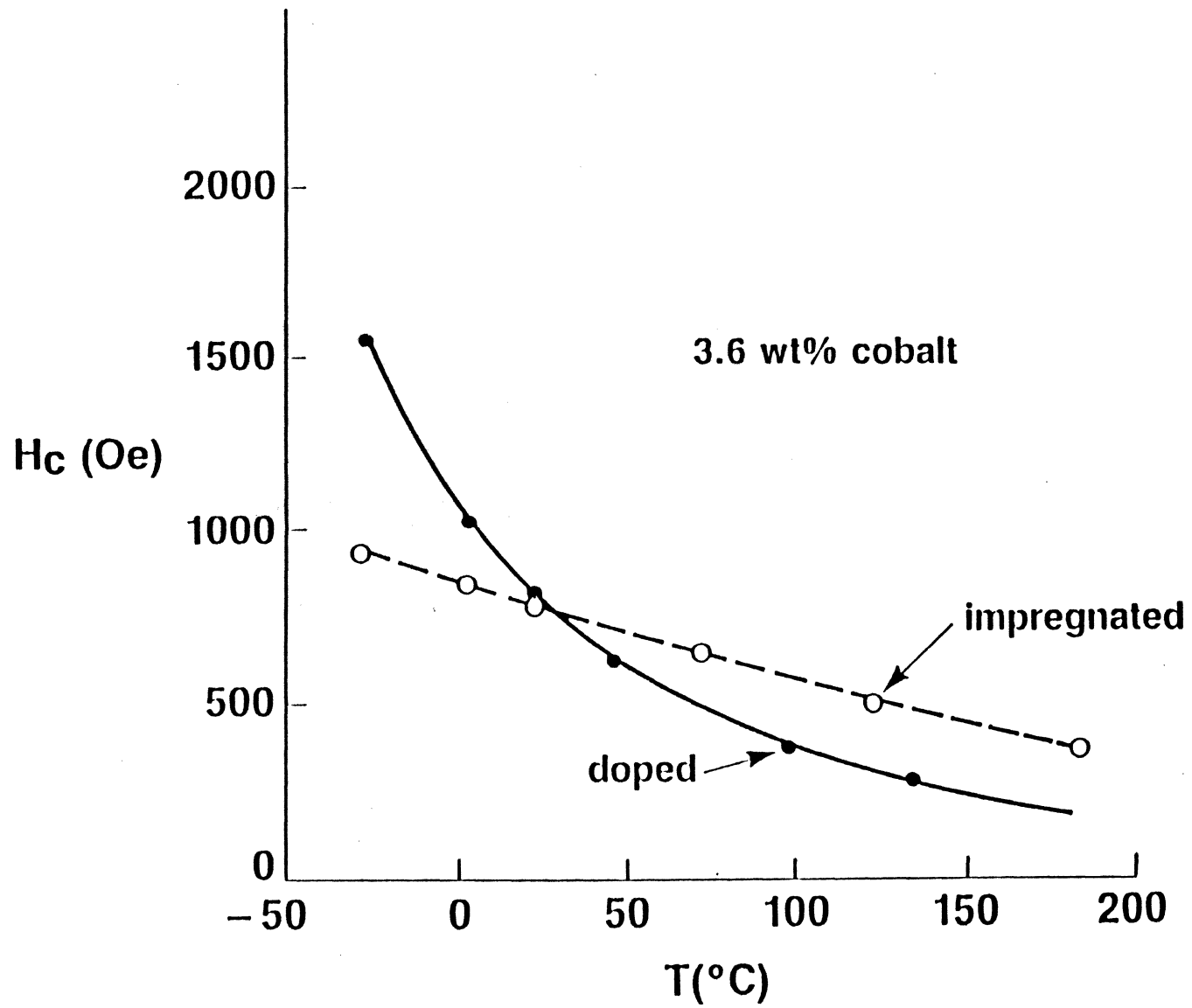
# COBALT-IMPREGNATED IRON OXIDE



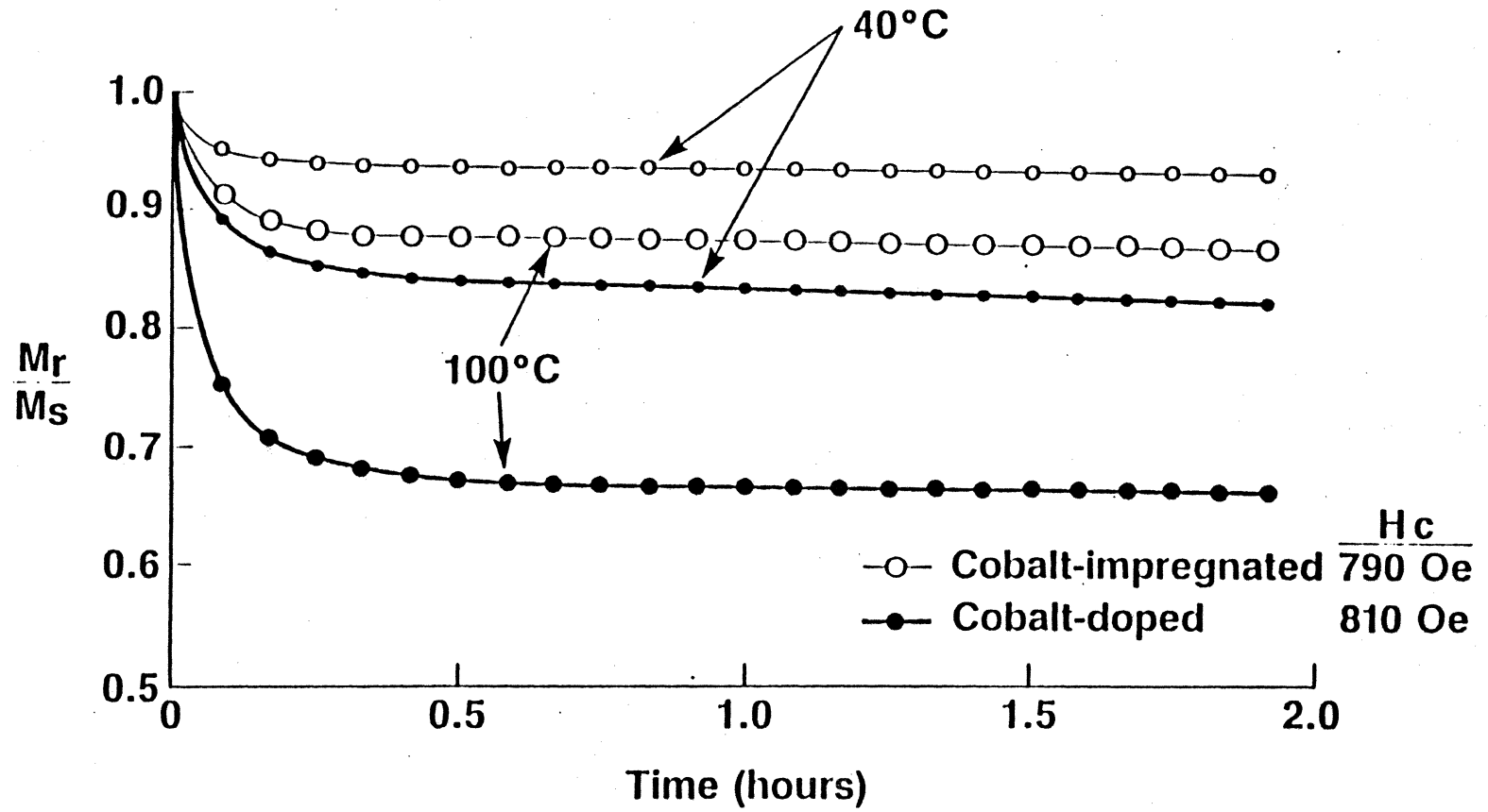
# COBALT - MODIFIED $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> PARTICLES



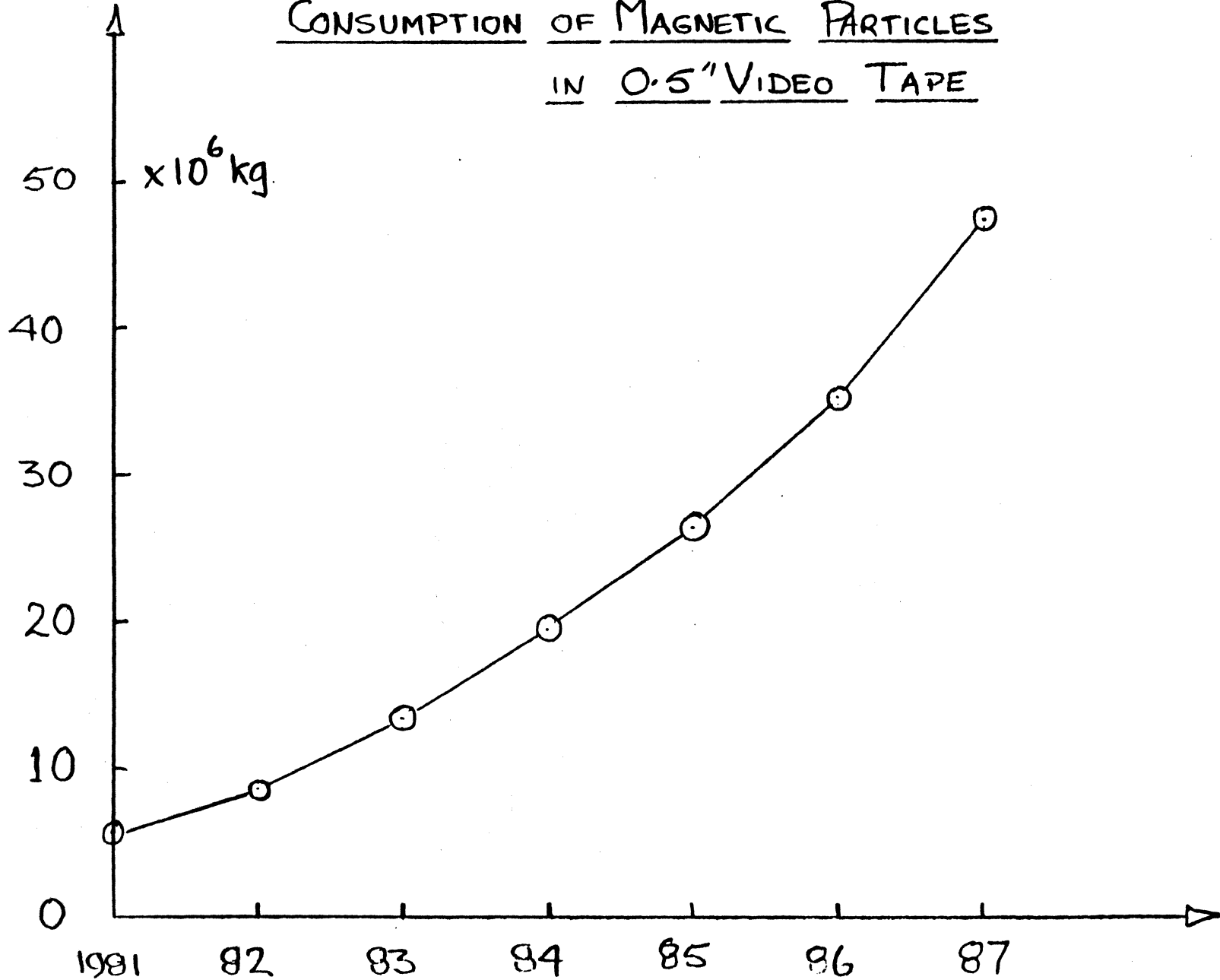
(Ref: hi to Amemiya, Jpn. J. Appl. Phys.)



demagnetizing field = 100 Oe



CONSUMPTION OF MAGNETIC PARTICLES  
IN 0.5" VIDEO TAPE

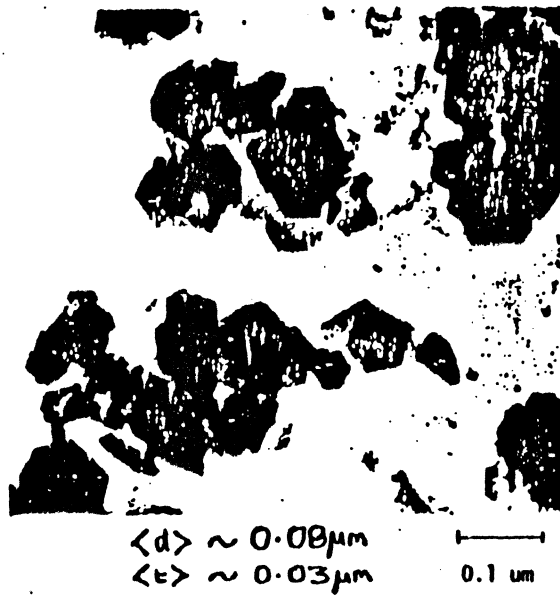
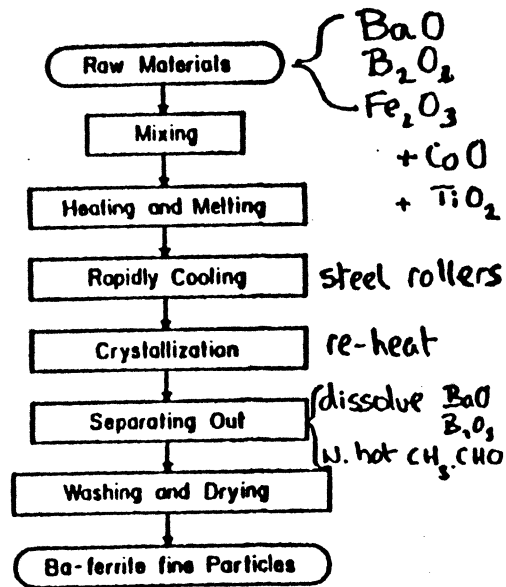


SOURCE: MMIS, p25 November 1983

Property \ Particle	$\gamma\text{-Fe}_2\text{O}_3$	$\text{Co-Fe}_2\text{O}_3$	$\text{CrO}_2$	$\text{Ba}_{0.6}\text{Fe}_2\text{O}_3$ + Co, Ti	Fe	$\text{Fe}_4\text{N}$
saturation magnetization, $\sigma_s$ , emu/g	73-74	73-76.3	70-80	45-70	150-190	110-130
$\frac{\sigma_r}{\sigma_s}$	0.5	0.5-0.8	0.5	0.6-0.7	0.23-0.52	0.47-0.53
Curie Temperature, $T_c$ , °C	[590]	[590]	115-126	320	768	490
magnetocrystalline anisotropy constant, $K_1$ , ergs/cc	$-4.64 \times 10^4$	$-5 \tau_0 + 100 \times 10^4$	$+2.5 \times 10^5$	$+3.3 \times 10^6$	$+4.4 \times 10^5$	
saturation magnetostriction $\lambda_s$	$-5 \times 10^{-6}$	$-5 \text{ to } -15 \times 10^{-6}$	$+1 \times 10^{-6}$		$+4 \times 10^{-6}$	
coercivity, $H_c$ , Oe	250-350	550-750	450-670	320-1970	375-1650	640-1100
switching field distribution, $\frac{\Delta H}{H_c}$	0.26-0.61	0.30-0.6	0.35-0.6	0.16-0.6	0.5-0.75	0.5-0.7
temperature coeff. of coercivity, $\frac{\Delta H_c}{H_c}/^\circ\text{C}$ (20-70°C)	$-1 \times 10^{-3}$	impreg. <sup>d</sup> $-2.4 \times 10^{-3}$ doped $-10 \times 10^{-3}$	$-5 \times 10^{-3}$	$+3.1 \times 10^{-3}$	$-0.6 \times 10^{-3}$	$-0.7 \times 10^{-3}$
specific surface area (BET), $\text{m}^2/\text{g}$	20-40	20-40	25-37	15-31	26	25-40
density, $\rho$ , g/cc	4.60	4.80	4.88-4.95	5.28	5.8	5.8
crystal structure	cubic $a_0 = 25 \text{ \AA}$ , $\text{m}3\text{m}$	cubic	tetragonal $a = 4.4218 \text{ \AA}$ $c = 2.9182 \text{ \AA}$	hexagonal $c = 23.2 \text{ \AA}$ $a = 5.00 \text{ \AA}$	b.c.c. $a = 2.861 \text{ \AA}$	f.c.c. $a = 3.795 \text{ \AA}$
ferro- or ferrimagnetic	ferr	ferr	ferro	ferr	ferro	ferro
particle size, $\mu\text{m}$	needles $l = 0.3$ $d = 0.06$	needles w equilmax. $l = 0.3$ $l = 0.2$ $d = 0.06$	needles $l = 0.5$ $d = 0.05$	hex. platelets $\text{dia} = 0.08-0.1$ thick = $0.01-0.025$	needles $l = 0.3$ $d = 0.06$	$l = 0.5$ $\text{dia} = 0.07$



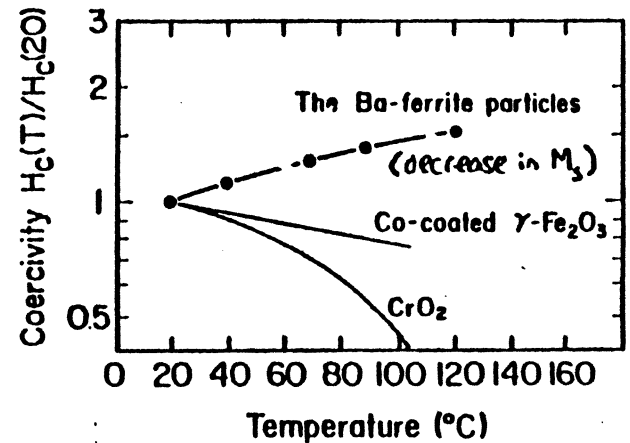
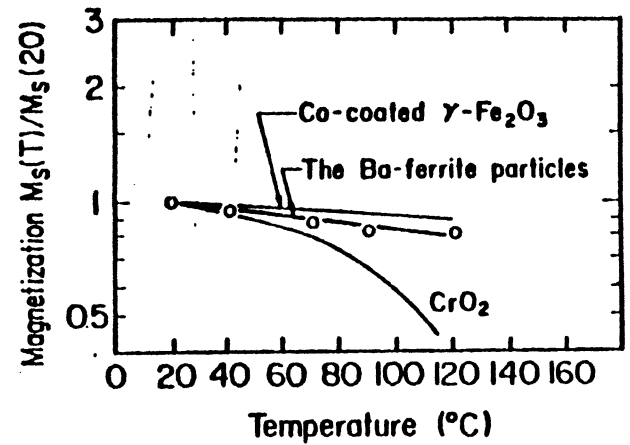
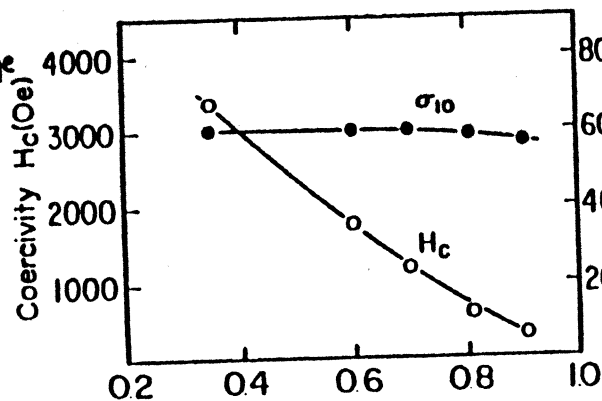
# PREPARATION AND PROPERTIES OF BARIUM FERRITE PARTICLES



Block diagram showing the Ba-ferrite particle preparation process using the glass crystallization method.  $\rightarrow$  uniform nucleation,  $\rightarrow$  small, well-separated, narrow size range

Typical Ba-ferrite fine particles characteristic

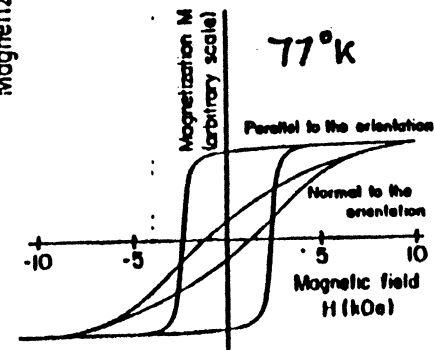
Particle size	0.08 x 0.03 $\mu\text{m}$
Density	5.25 g/ml
Specific surface area	22 m <sup>2</sup> /g
Coercivity	900 Oe
Saturation magnetization	58 emu/g
Curie temperature	350°C
Squareness ratio	0.94



- Co, Ti allow control of H<sub>c</sub> w/o changes in d, t.
- easy axis // c-axis.

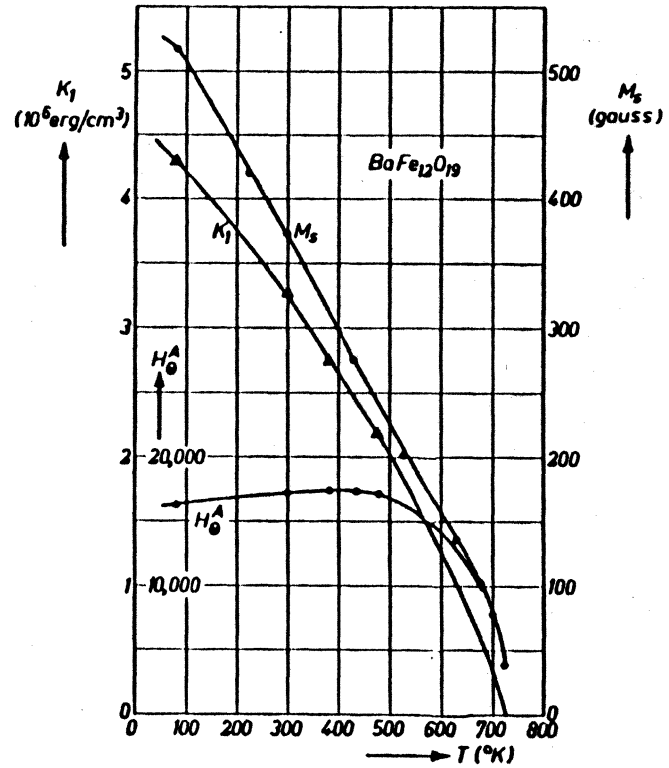
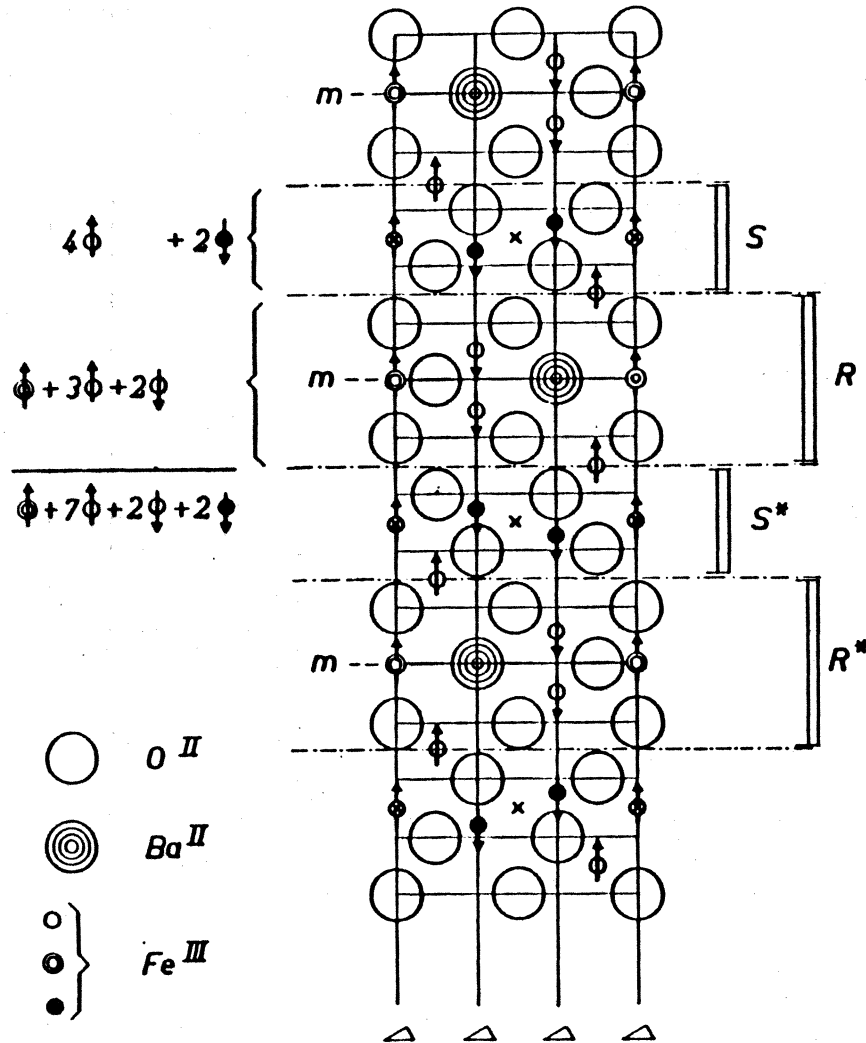
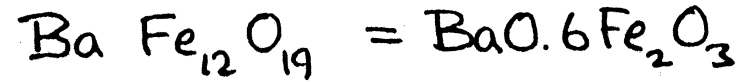
$$H_c = 0.48 \left( \frac{2K}{M_s} - NM_s \right)$$

20°C, x = 0.8  $\rightarrow$  6Koe 4Koe



orienting field  $\leq 10$  Koe

# STRUCTURE AND PROPERTIES OF BARIUM FERRITE



20°C

$$M_s = 380 \text{ emu/cc}$$

$$K_1 = +3.3 \times 10^6 \text{ erg/cc}$$

$$H_A = \frac{2K_1}{M_s} \doteq 17,000 \text{ Oe}$$

Barium

# MATERIALS FOR VERY HIGH DENSITY RECORDING

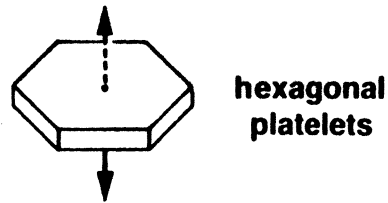
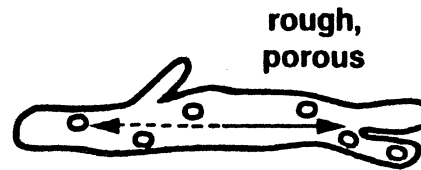
## VHD PARTICLES

Conventional Gamma-Iron Oxide  
(Co-impregnated)  
Example: HDX particles

"Rice Grain" Gamma-Iron Oxide  
(Co-impregnated)

Isotropic Gamma-Iron Oxide  
(Co-doped)

Barium Ferrite



## RECORDING MODE

Longitudinal

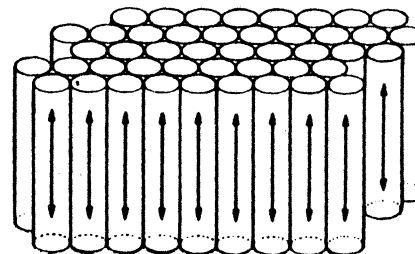
Longitudinal

Longitudinal/Perpendicular

Perpendicular

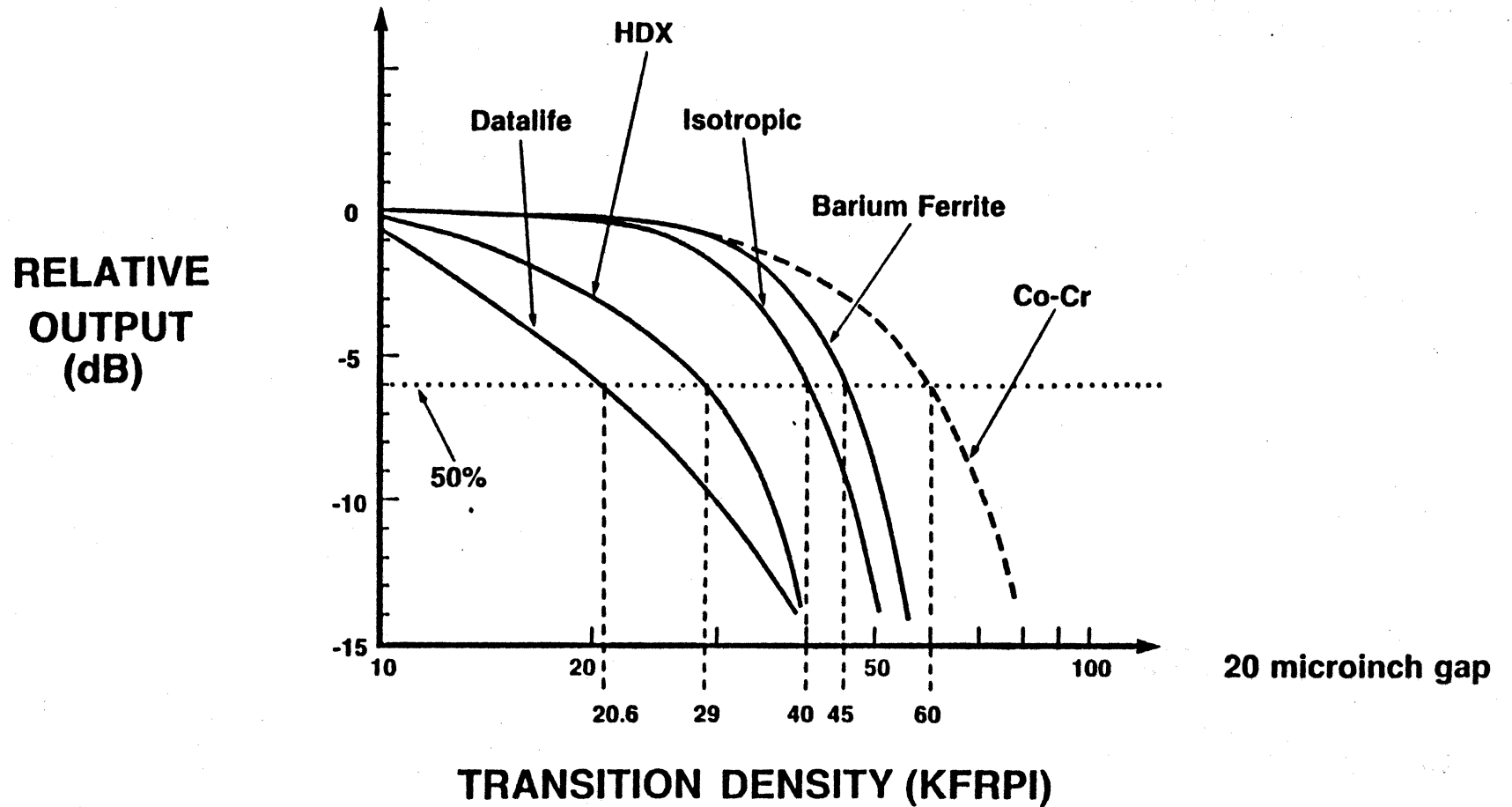
## VHD THIN FILMS

Cobalt - Chrome  
(sputtered)

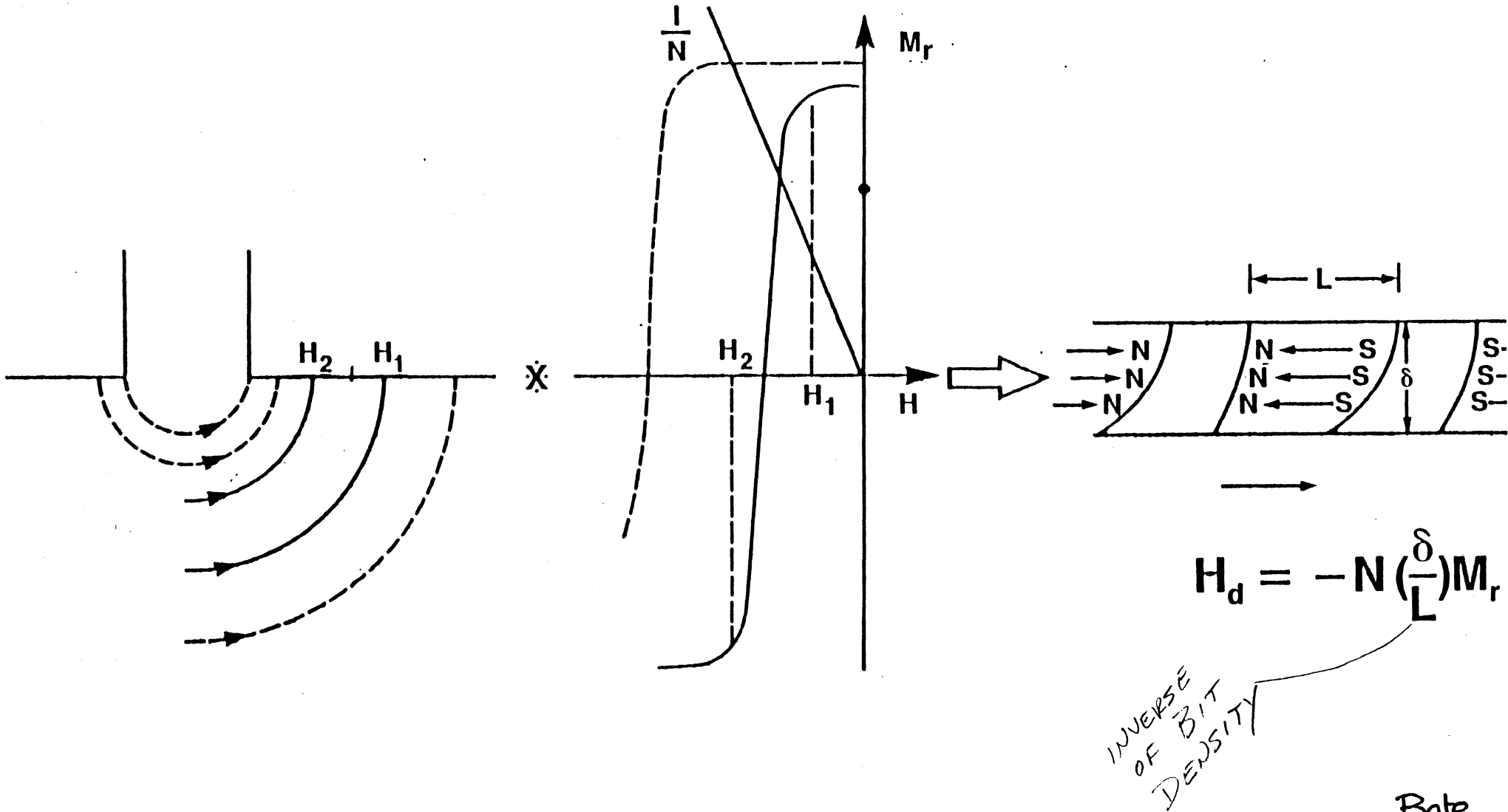


Perpendicular

# RELATIVE OUTPUT VS. TRANSITION DENSITY



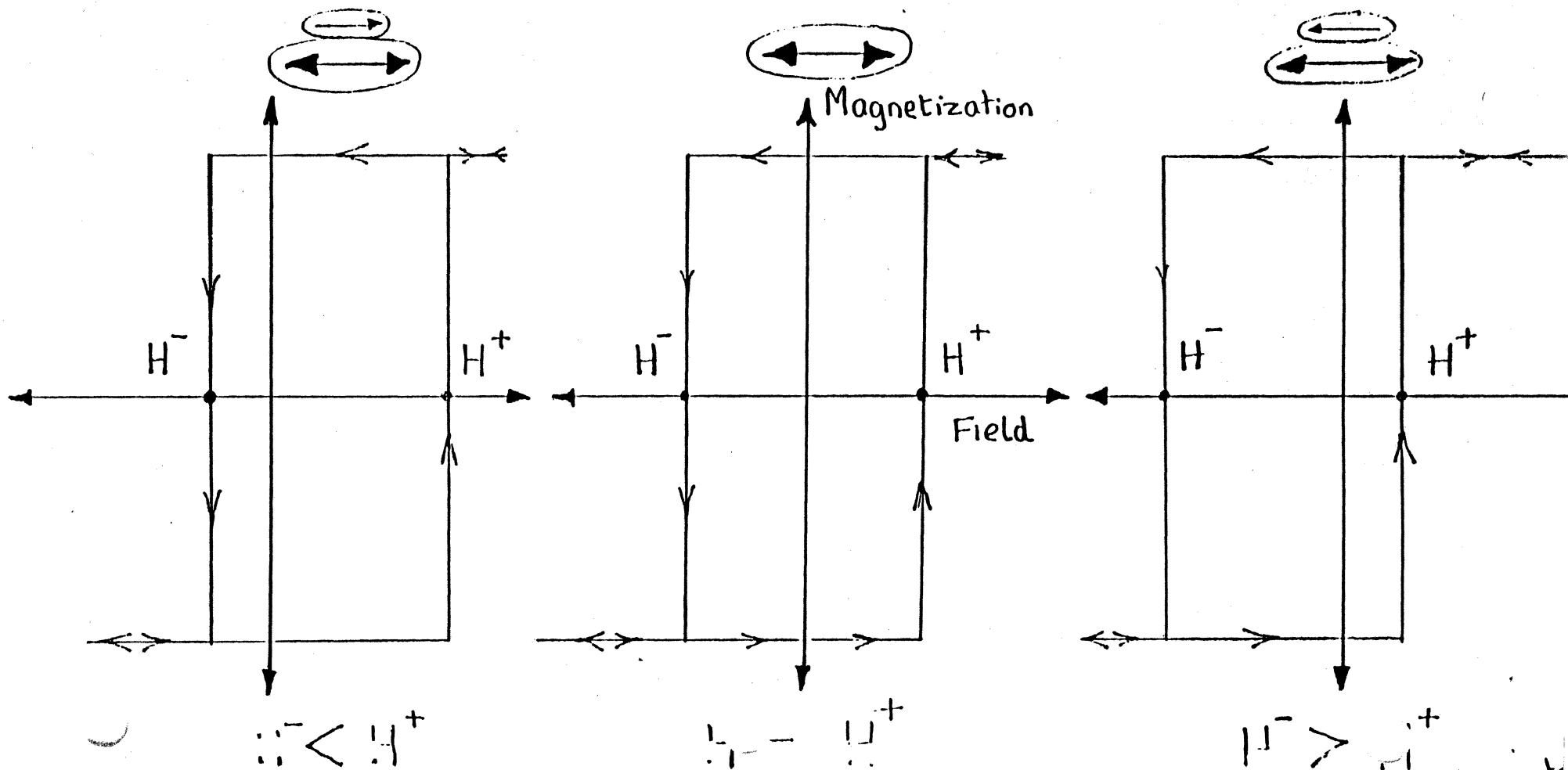
# Writing Process



# PREISACH DIAGRAMS

represent the magnetic interaction between particles in a magnetic tape or disk.

are two-dimensional distribution functions of interaction fields



# PREISACH DIAGRAM

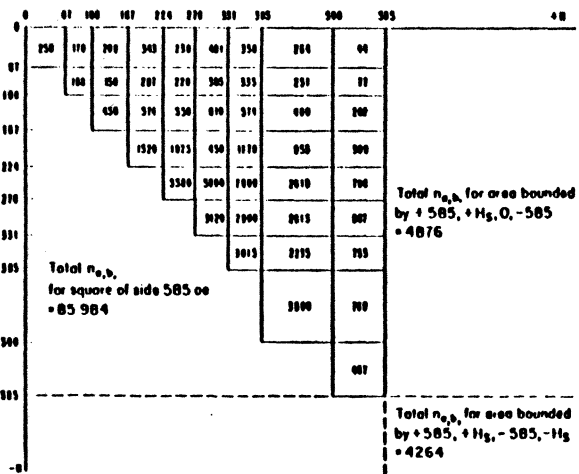


FIG. 6. Part of the Preisach diagram calculated for the nonoriented sample.

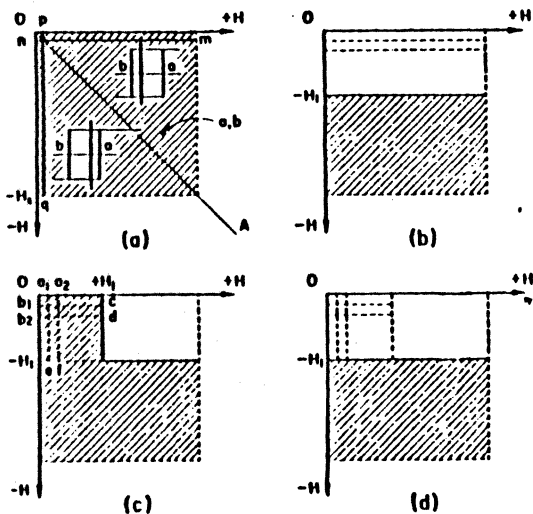


FIG. 1. Preisach diagrams: the shaded area shows the location of particles with positive remanent intensities. Afterfields (a)  $+H_s$ , the remanence is  $I_r$ , (b)  $-H_s$ , the remanence is  $I_r$ , (c)  $+H_s$ , the remanence is  $I_r'$ , (d)  $-H_s$ , the remanence is  $I_r'$ .

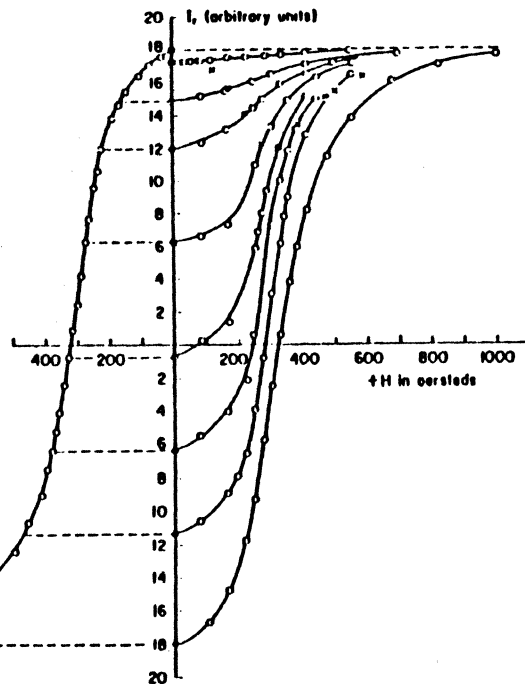
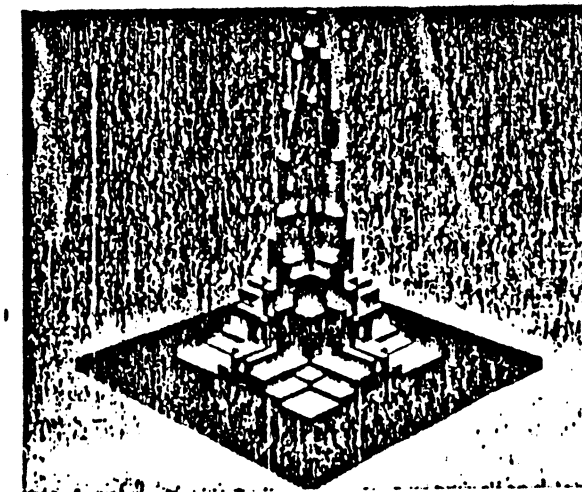
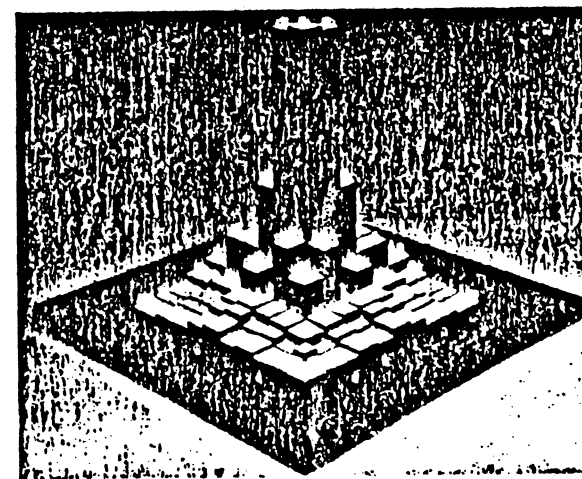
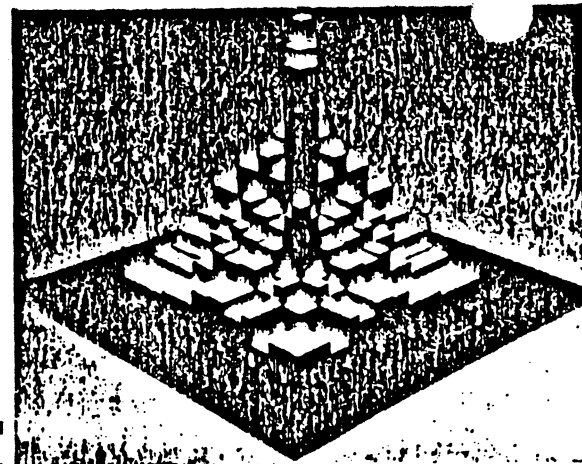
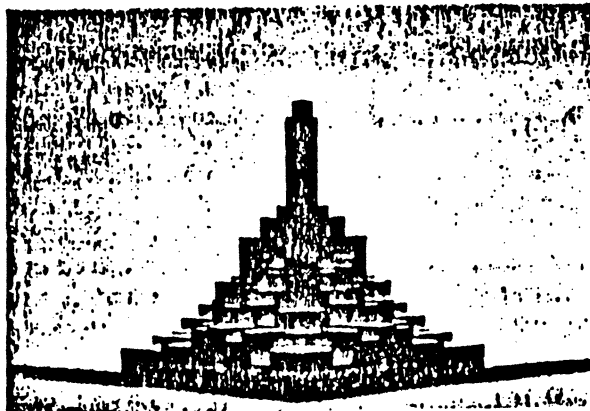
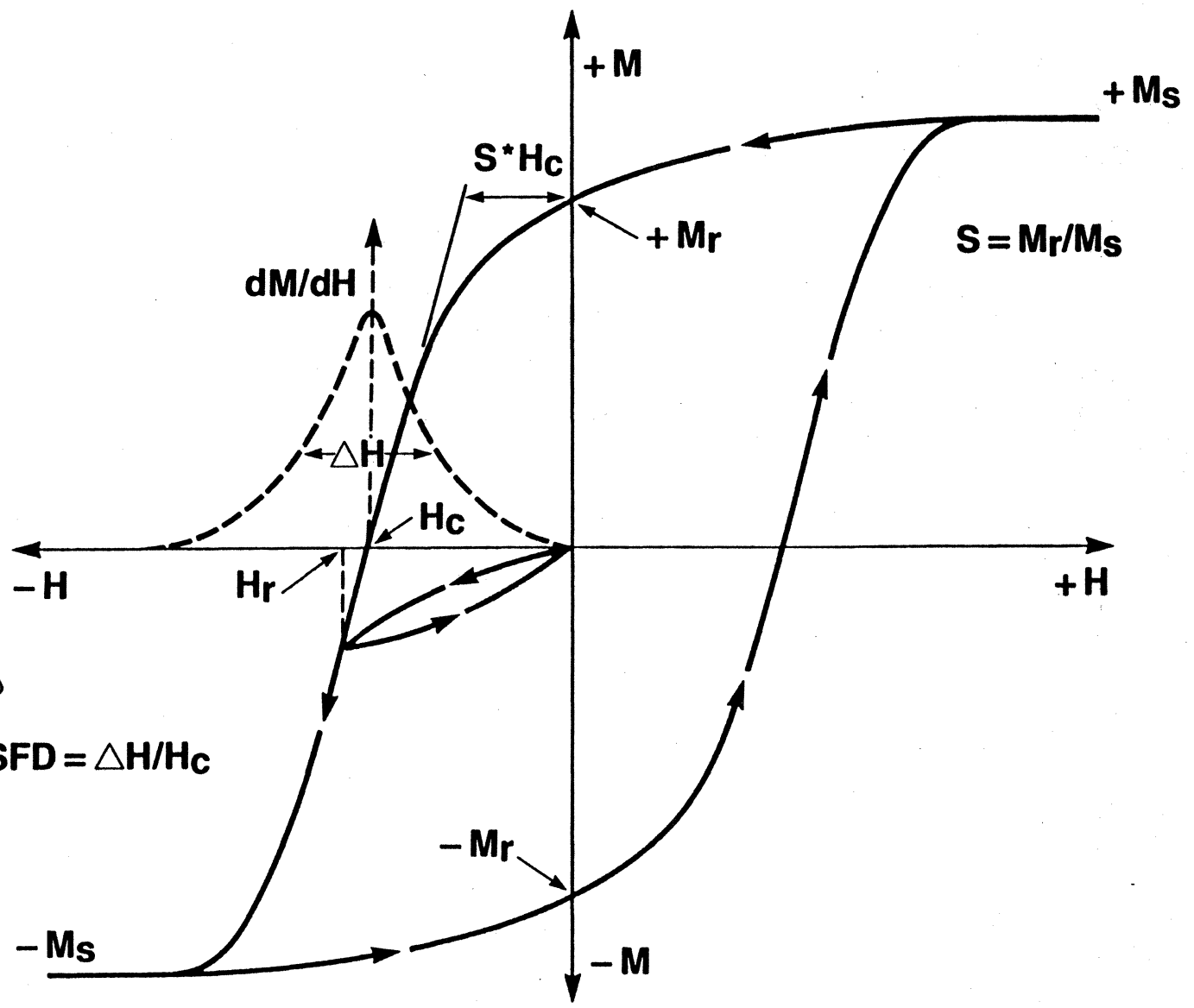


FIG. 2. The descending remanence curve and the ascending curves for the nonoriented sample. The crosses on the ascending curves mark the remanence levels attained after  $-H$  when  $-H$  was the maximum reverse field for that curve. Some of the curves have been omitted for clarity.



C. D. B.



SWITCHING  
FIELD  
DISTRIBUTION

$$SFD = \Delta H/H_c$$

$$S = M_r/M_s$$

$dM/dH$

$S \cdot H_c$

$+M_r$

$+M_s$

$+M$

$+H$

$H_c$

$H_r$

$-H$

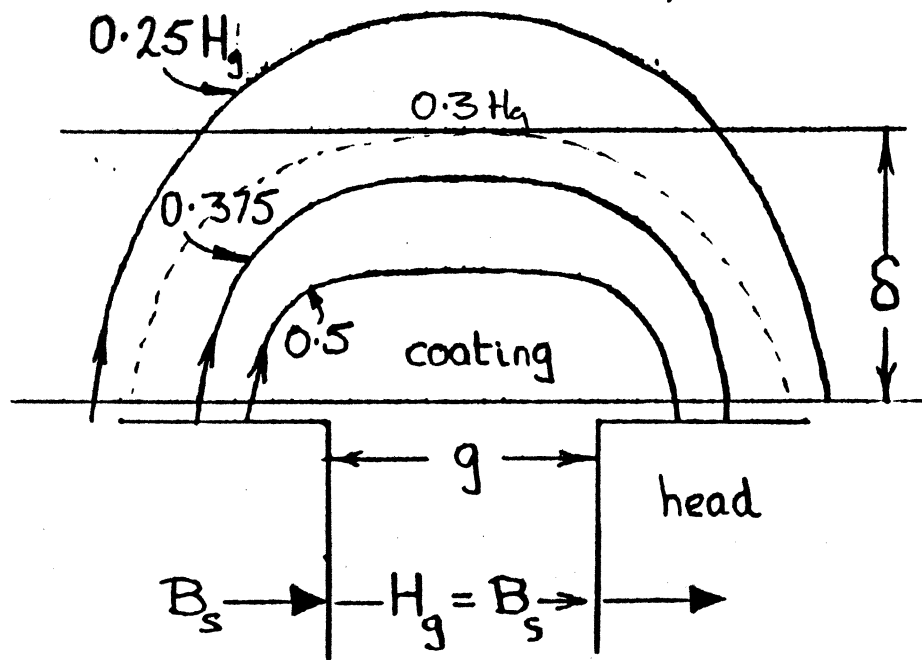
$-M_r$

$-M$

$-M_s$



# THE OVERWRITE PROBLEM

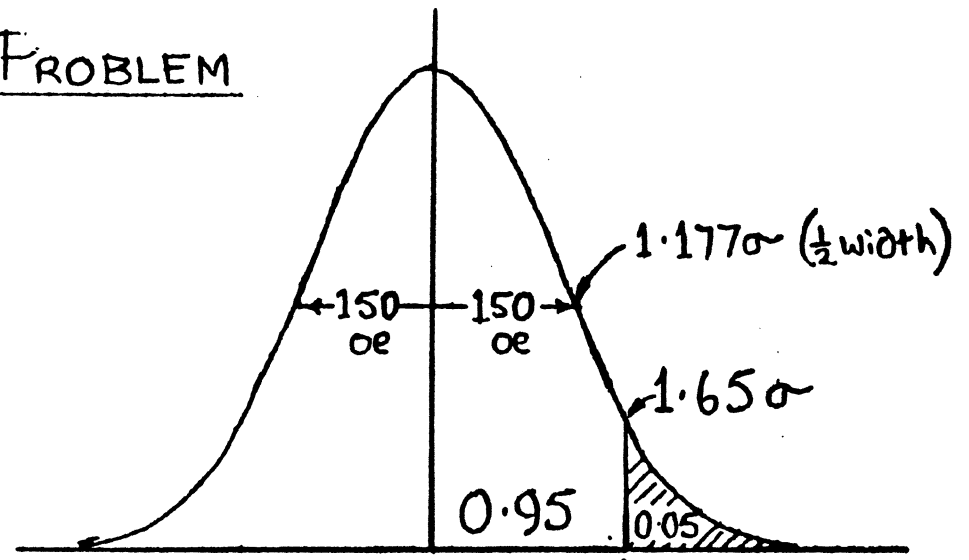


## overwrite test:

- 1) write 1F, measure amplitude
- 2) overwrite with 2F
- 3) read remaining 1F amplitude

overwrite criterion:  $-26\text{dB}$

$$\frac{\text{remaining 1F}}{\text{original 1F}} \leq 0.05$$



$$H_c = 1,000 \quad H_r = 1,050 \text{ oe} \quad 1,260 \text{ oe}$$

Assumptions: Normal Distribution

$S.F.D. = 0.3$

coating thickness,  $\delta =$  head gap,  $g$

## Result

$$0.3 H_g = 1260$$

$$H_g = 4,200$$

Ferrite

$B_s$

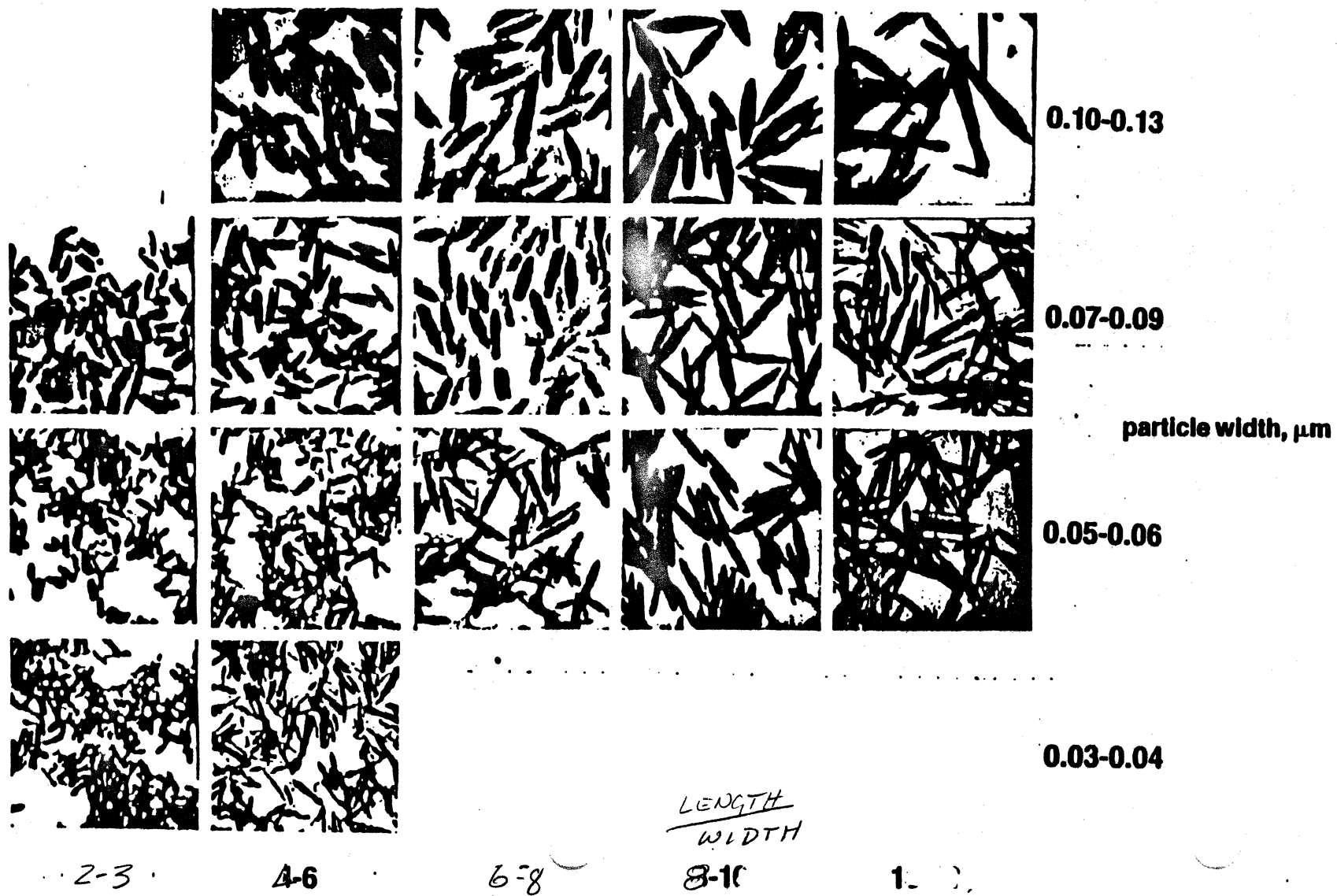
Ni Zn

4,000

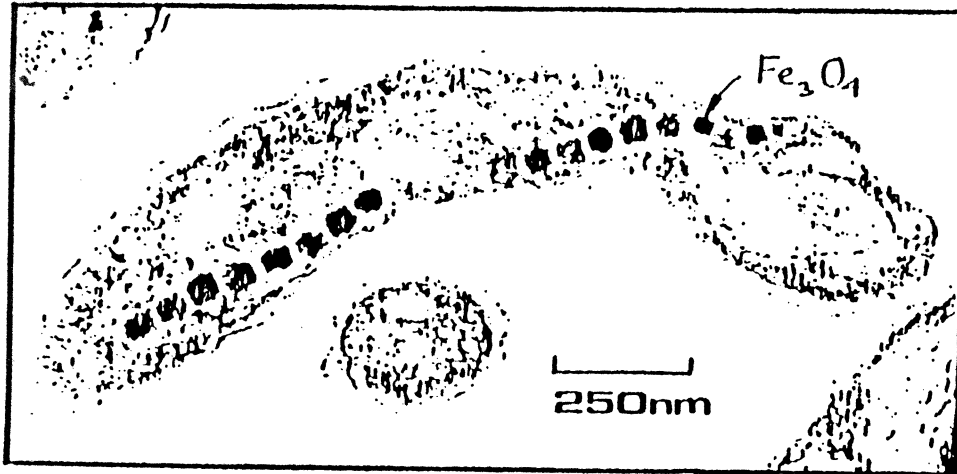
Mn Zn

5,000

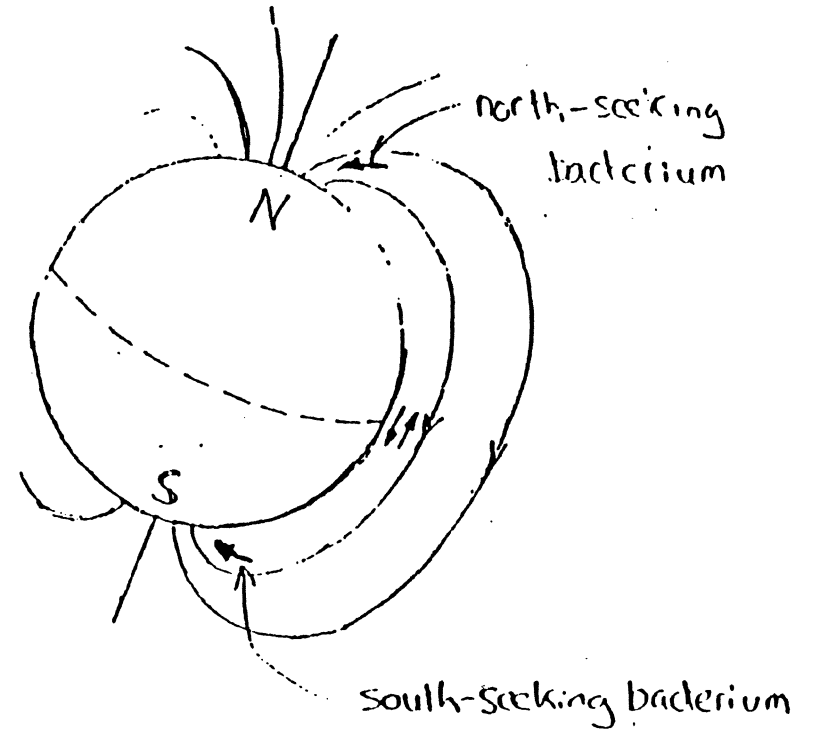
# NP Particles



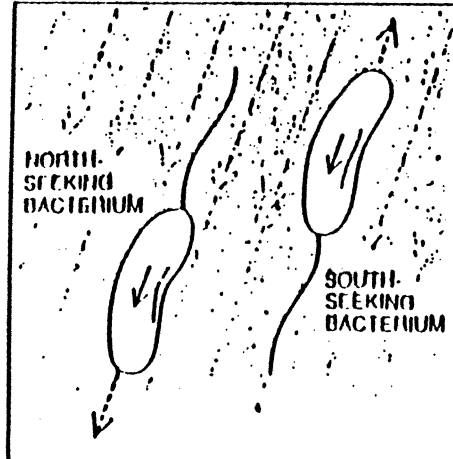
# Magnetic Bacteria



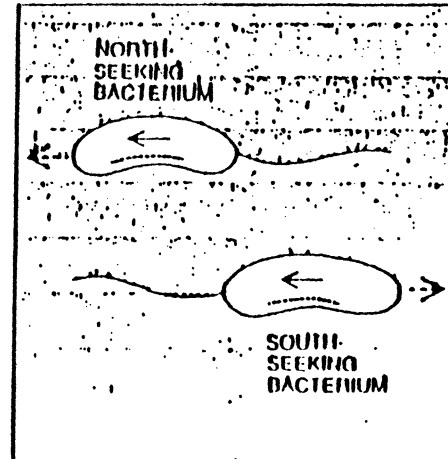
R.D. Frankel 1979



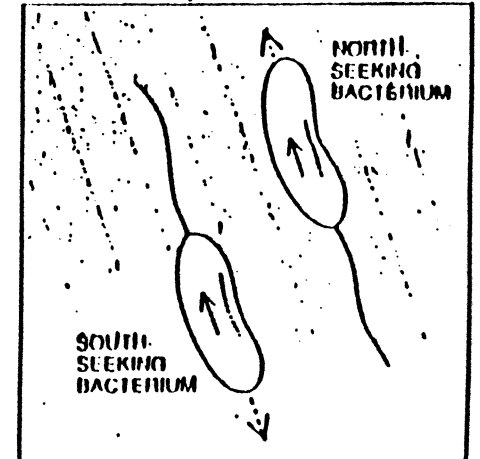
WOODS HOLE, MASS.



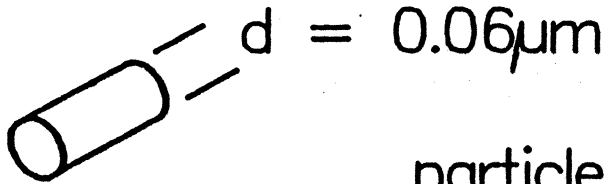
FORTALEZA, BRAZIL



CHRISTCHURCH, NEW ZEALAND



# PARTICLE PACKING DENSITY



$$l = 0.3\mu\text{m}$$

$$\text{particle volume} = \frac{\pi d^2}{4} \cdot l$$

$$= 4.24 \times 10^{-15} \text{particles cc.}$$

$$100\% \text{ packing} \rightarrow 2.3 \times 10^{14} \text{particles/cc.}$$

$$40\% \text{ packing} \rightarrow 10^{14} \text{particles/cc.}$$

---

$$96 \text{ tpi; track width} = 5 \text{ mil} = 1.25 \times 10^{-2} \text{ cm.}$$

$$10,000 \text{ bpi; bit length} = 10^{-4} \text{ in.} = 2.5 \times 10^{-4} \text{ cm.}$$

$$\text{coating thickness of } 40 \text{ microinches} = 1.0 \times 10^{-4} \text{ cm.}$$

$$\text{vol. of one bit} = 3.0 \times 10^{-10} \text{ cc.}$$

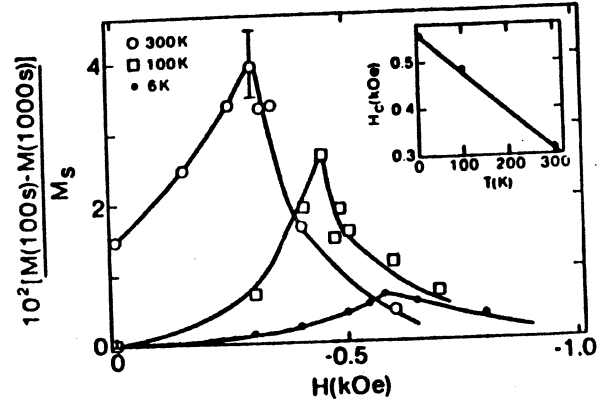
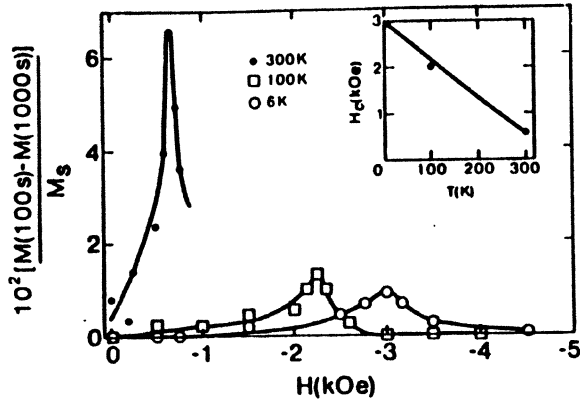
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one bit cell contains  $\sim 30,000$  particles

G. Bate

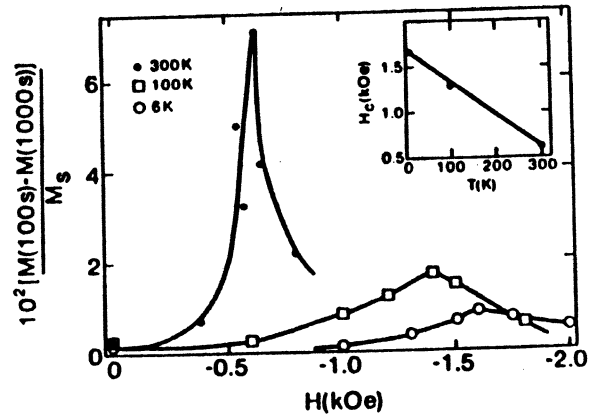
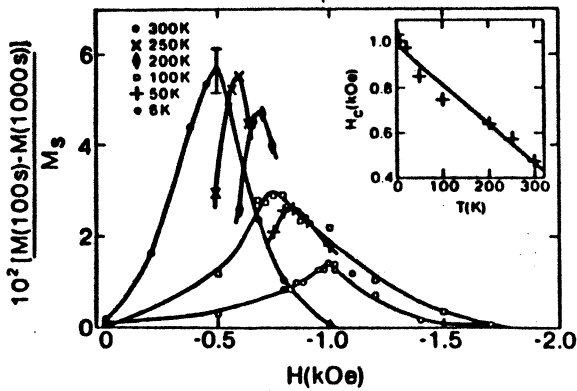
# TIME DECAY OF MAGNETIZATION IN MAGNETIC PARTICLES

CrO<sub>2</sub>



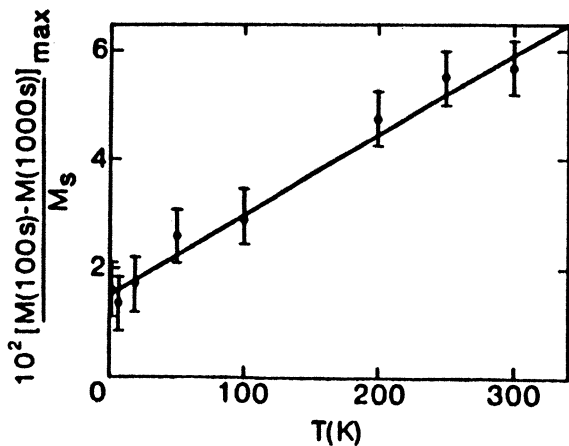
γ-Fe<sub>2</sub>O<sub>3</sub>

CrO<sub>2</sub>



Co-doped  
γ-Fe<sub>2</sub>O<sub>3</sub>

CrO<sub>2</sub>



Oseroff, Clark, Schultz, Shtrikman  
I.E.E.E. Trans. Mag. 1985

## **Particulate Media**

- **wide variety of magnetic properties**
- **magnetic properties from particles**
- **mechanical properties from binder**
- **high coating speeds ( $\leq 130\text{m/min}$ )**
- **wide rolls ( $\leq 1.3\text{m}$ )**
- **uniform, reproducible properties**
- **yields high  $\rightarrow$  low cost**

## **Thin Film Media**

- **thin coatings ( $< 0.25\mu\text{m}$ )**
- **magnetic properties not diluted by binder**
- **magnetic properties varied by changing deposition conditions.**
- **easier to coat on metallic than polymer substrates.**

