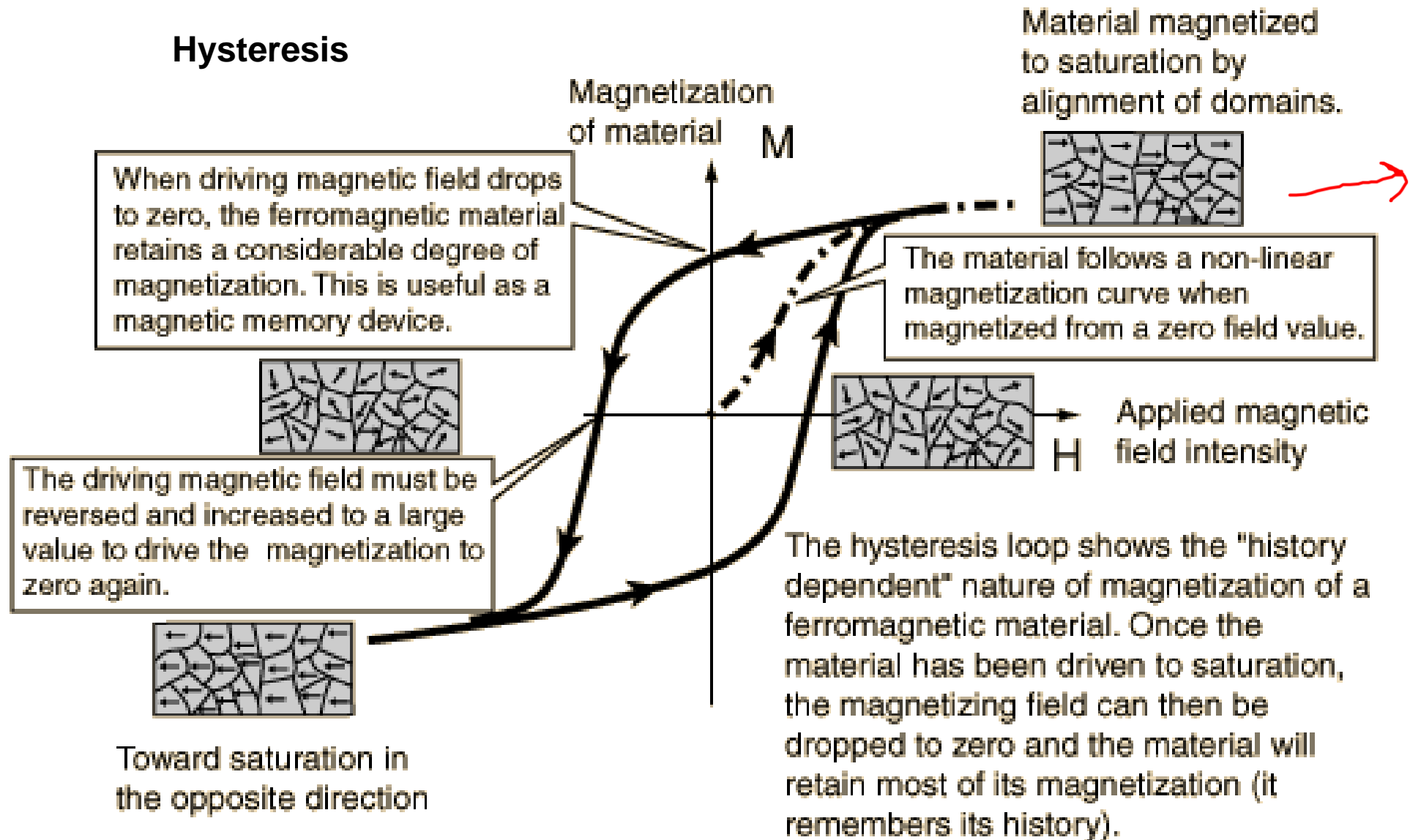


# PYL 102

Monday, Oct. 28, 2024

Nanomagnetism

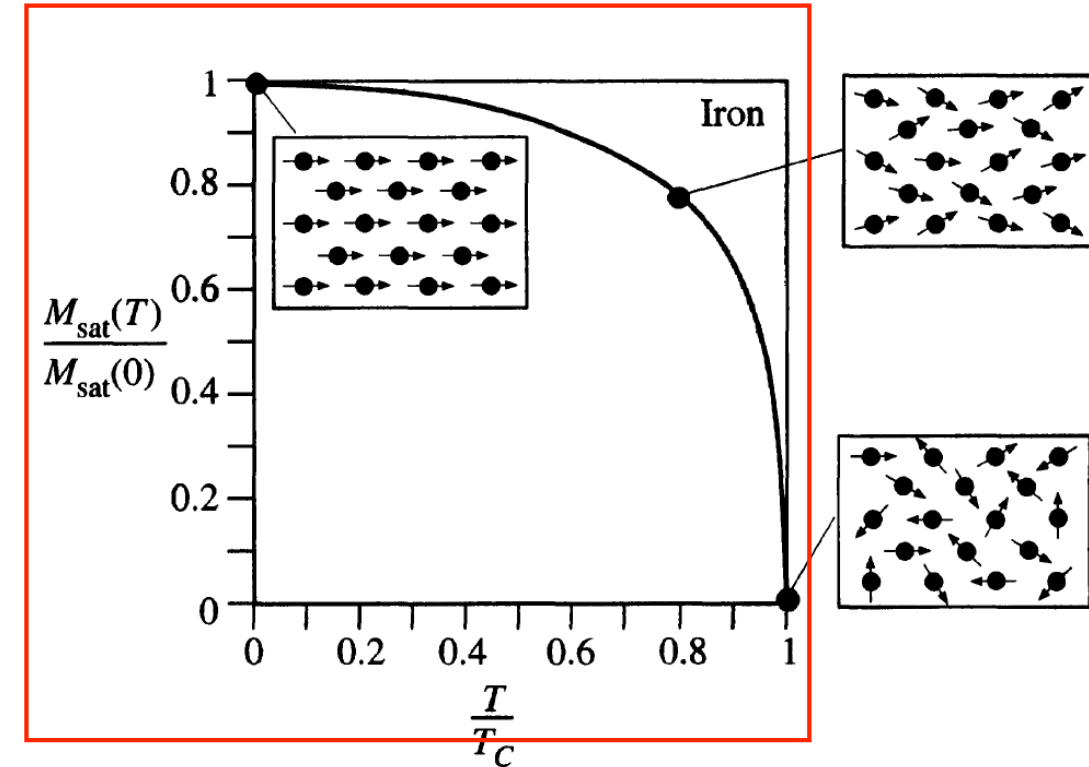
## Hysteresis



## Curie temperature

When all the atomic magnetic moments have been aligned as much as possible is called the saturation magnetization  $M_{\text{sat}}$ . In the iron crystal, for example, this corresponds to each Fe atom with an effective spin magnetic moment of 2.2 Bohr magnetons aligning in the same direction to give a magnetic field 2.2 T. As we increase the temperature, lattice vibrations become more energetic, which leads to a frequent disruption of the alignments of the spins. The spins cannot align perfectly with each other as the temperature increases due to lattice vibrations randomly agitating the individual spins. When an energetic lattice vibration passes through a spin site, the energy in the vibration may be sufficient to disorientate the spin of the atom. The ferromagnetic behavior disappears at a critical temperature called the Curie temperature, when the thermal energy of lattice vibrations in the crystal can overcome the potential energy of the exchange interaction and hence destroy the spin alignments. Above the Curie temperature, the crystal behaves as if it were paramagnetic.

$M_{\text{sat}}$  decreases from its maximum value  $M_{\text{sat}}(0)$  at absolute zero of temperature to zero at the Curie temperature.



# Ferromagnetism

- All ferromagnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation.
- This temperature is called the Curie temperature.
- Ferromagnetic materials respond mechanically to an impressed magnetic field, changing length slightly in the direction of the applied field.
- This property, called **magnetostriction**, leads to the familiar hum of transformers as they respond mechanically to 60 Hz AC voltages.

Difference between exchange interaction and coupling energy :

- Exchange interactions → between individual atomic spins,
- Coupling energy (magnetic anisotropy energy) → on larger scales, like entire particles or domains.

Above Curie temp magnetic domains break.

→ paramagnetic behaviour

For small particles (below  $T_c$ ) (w/o breaking domain)

→ superparamagnetic behaviour

# Ferromagnetic Materials

Material	Treatment	Initial Relative Permeability	Maximum Relative Permeability	Coercive Force (oersteds)	Remanent Flux Density (gauss)
Iron, 99.8% pure	Annealed	150	<b>5000</b>	1.0	13,000
Iron, 99.95% pure	Annealed in hydrogen	10,000	<b>200,000</b>	0.05	13,000
78 Permalloy	Annealed, quenched	8,000	<b>100,000</b>	.05	7,000
Superpermalloy	Annealed in hydrogen, controlled cooling	100,000	<b>1,000,000</b>	0.002	7,000
Cobalt, 99% pure	Annealed	70	<b>250</b>	10	5,000
Nickel, 99% pure	Annealed	110	<b>600</b>	0.7	4,000
Steel, 0.9% C	Quenched	50	<b>100</b>	70	10,300
Steel, 30% Co	Quenched	...	...	240	9,500
Alnico 5	Cooled in magnetic field	4	...	575	12,500
Silmanal	Baked	...	...	6,000	550
Iron, fine powder	Pressed	...	...	470	6,000

# Nano-particle magnetism

The magnetism of small ferromagnetic particles ( $< 1 \mu\text{m}$ ) is dominated by:

- There is a size limit below which the specimen no longer gain a favorable energy configuration by breaking up into domains, hence it remains with one domain.
- The thermal energy can decouple the magnetization from the particle itself to give rise the phenomenon of superparamagnetism.

If the particle size is comparable to the minimum domain size, it would not break into domains.

For a particle (with  $D$  as diameter), the magnetostatic energy is proportional to  $M_s^2 D^3$ . Domain formation requires creation of walls. If  $\gamma$  is the domain wall energy per unit area,  $\gamma D^2$  is the total domain wall energy. So, for large  $D$ ,  $D^3$  term of magnetostatic energy dominates over  $D^2$  term of wall formation and domain form. For very small  $D$ ,  $D^2$  term dominate and wall formation becomes difficult and particle will not break into domains. The critical size  $D_s$  below which a particle will not break into domains is where these two energies are equal. Or  $\gamma D^2 \sim M_s^2 D^3$  i.e.  $D_s \sim \gamma / M_s^2$

Typical values for  $D_s$  range from 10 to 100 nm; Fe(14 nm), Co(70 nm), Ni(55 nm).

It is harder to rotate the magnetization than to move domain wall. Because of this single domain particles have a larger coercivity and remanence compared to multidomain systems.

# Superparamagnetism

In a Ferromagnet below the Curie temperature all the spins are coupled together in a domain and yield a large magnetic moment. The energy of this coupling is  $KV$ , where  $V$  is the volume of the particle. K is anisotropy constant

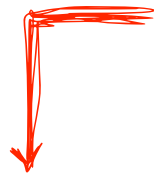
As particle size decrease,  $V$  decreases and becomes smaller than thermal energy  $kT$  !

Therefore, thermal energy can disrupt bonding of total moment of the particle. Then this moment is free to move in response to the applied field. This moment can be quite large thousands of Bohr magnetons.

Therefore, an applied field will tend to align this giant (super) moment but  $kT$  will fight against this alignment as in paramagnetism.

Superparamagnetism is a phenomenon by which magnetic materials may exhibit a behavior similar to paramagnetism even when temperature is below the Curie temperature. This is a small length-scale phenomena.

The superparamagnetism occurs when the material is composed of very small particles ( $<10$  nm).



Coupling energy =  $KV$

Thermal energy =  $kT$

For small particle size  $KV < kT$  so thermal fluctuations can overcome magnetic coupling, so it starts behaving like paramagnets below  $T_C$  but with large magnetic moments

$T < T_c$  thermal energy is not sufficient to overcome the coupling forces between neighboring atoms but the thermal energy is sufficient to change the direction of magnetization of the entire crystallite

Direction of magnetization fluctuates  $\rightarrow$  average magnetic field = 0

So, the material behaves like a paramagnet, except that instead of each individual atom being independently influenced by an external magnetic field, the magnetic moment of the entire crystallite tends to align with the magnetic field.

The anisotropy energy  $KV$  represents an energy barrier to spin reorientation.

Probability of jumping this barrier is proportional to Boltzman factor  $e^{-KV/kT}$ .

Timescale for a successful jump of magnetization vector over the  $KV$  barrier:

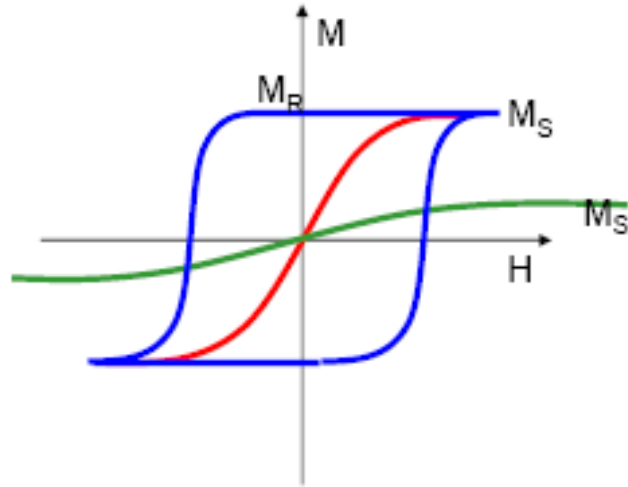
$$\tau = \tau_0 e^{-KV/kT}$$

$\tau_0$  is the attempt timescale ( $\sim 10^{-9}$  s)

A typical experiment with magnetometer takes about 100 s. A critical volume can be determined below which the particle will act as a superparamagnet. At room temperature, Fe (16 nm) and Co (7.6 nm).



# Superparamagnet: The Size Effect

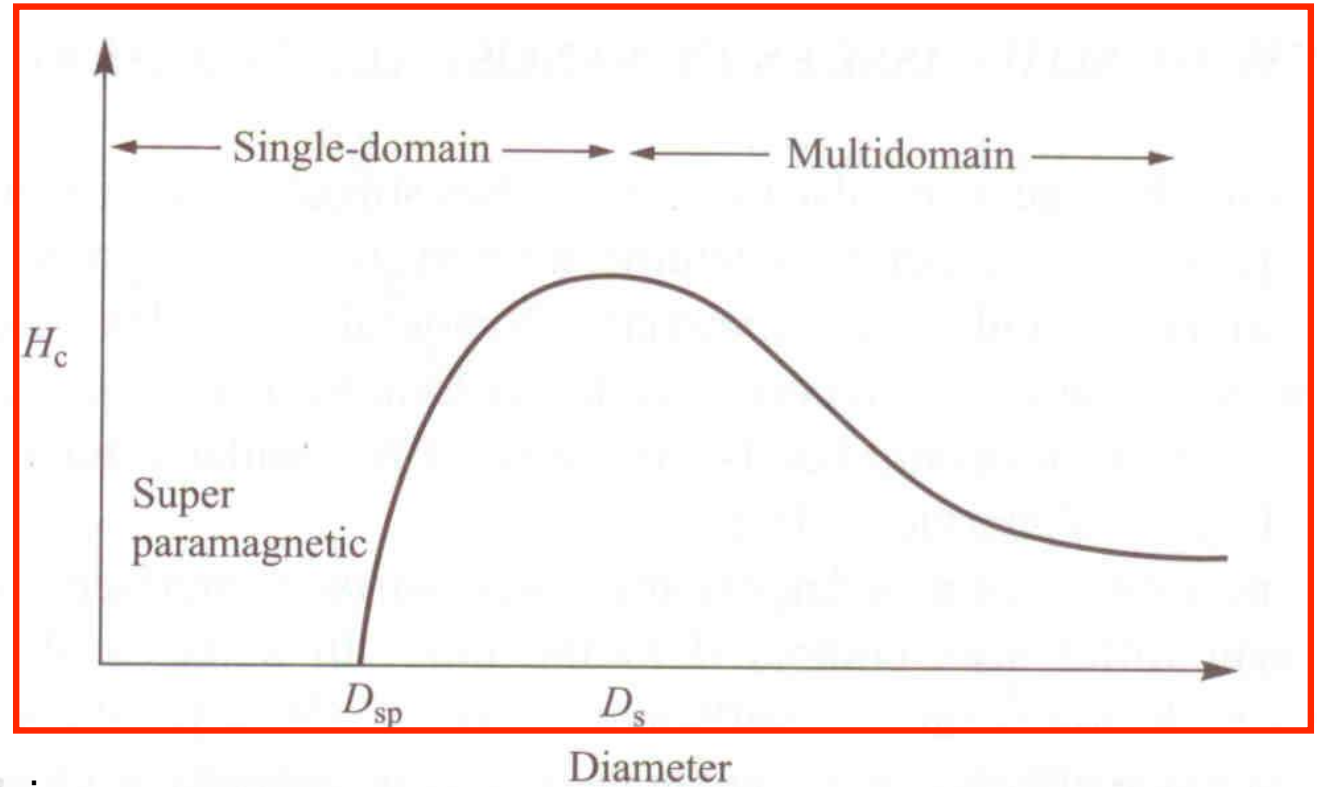


1. High saturation magnetization
2. No hysteresis, remanence  $M_R = 0$

— Ferromagnetisme  
— Paramagnetisme  
— Superparamagnetism

## Dependence of coercivity on particle size

Dependence of coercivity on particle size.  $D_{sp}$  is superparamagnetic size and  $D_s$  is single domain size.

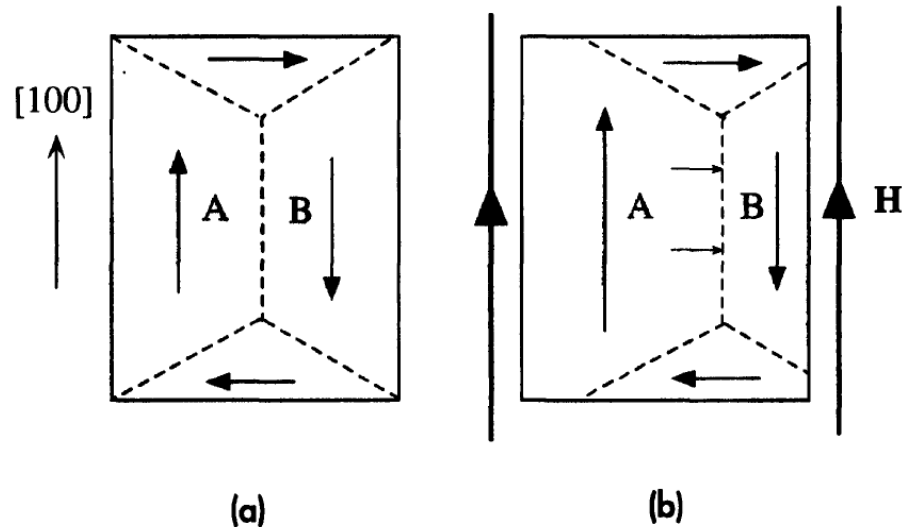


- Larger size particles have many domains.
- Thus magnetization reversal is dominated by domain wall motion, which is relatively easy and hence the coercivity is low.
- However, as particle size decreases, coercivity changes with size  $H_c = a + b/D$  where  $a$  and  $b$  are constants, until single domain (SD) is reached.
- The largest coercivity occur at SD size. Below this  $H_c$  falls off due to thermal activation over the anisotropy barriers and below the superparamagnetic size  $H_c = 0$ .

# Magnetic Anisotropy

Suppose we take a single crystal of ferromagnet like iron, and apply a magnetic field long different crystallographic directions, the magnetization varies with the field depending on the chosen direction for the applied field. Such situation is called magnetic anisotropy. When magnetic anisotropy exists, the total magnetization of a ferromagnet will prefer to lie along a special direction called the easy axis.

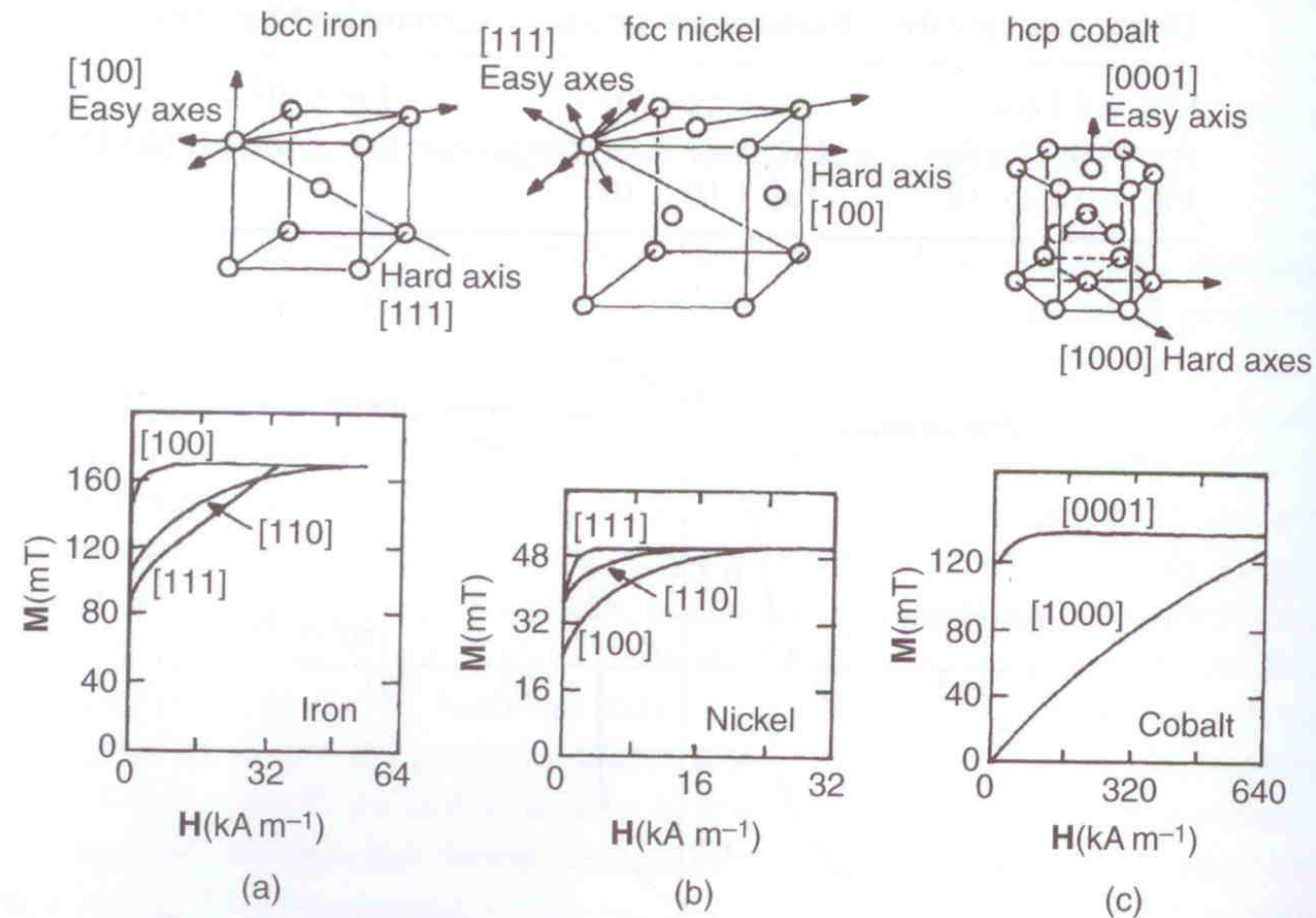
Fe is a bcc solid,  $\langle 100 \rangle$  direction is easy axis (low field required to saturate),  $\langle 110 \rangle$  is the less easy direction and  $\langle 111 \rangle$  is most difficult direction. In certain crystals such as Cobalt, hcp structure, there is only easy axis leading to uniaxial anisotropy. The energy associated with this alignment is called anisotropy energy. The anisotropy energy is maximum when magnetization is  $90^\circ$  to the easy axis.



a) An unmagnetized crystal of iron in the absence of an applied magnetic field. Domains A and B are the same size and have opposite magnetizations.

(b) When an external magnetic field is applied, the domain wall migrates into domain B, which enlarges A and shrinks B. The result is that the specimen now acquires net magnetization.

In Fe, exchange interactions are such that spin magnetic moments are most easily aligned with each other if they all point in one of the six (100) directions. Thus (100) directions in the iron crystal constitute the easy directions for magnetization. If we want to magnetize the crystal along the [111] direction by applying a field along this direction, then we have to apply a stronger field than that along [100]. Saturation is reached at an applied field that is about a factor of 4 greater than that along [100]. The [111] direction in the iron crystal is known as the hard direction. It is apparent that the magnetization of the crystal along [100] needs the least energy, whereas that along [111] consumes the greatest energy. The excess energy required to magnetize a unit volume of a crystal in a particular direction with respect to that in the easy direction is called the magnetocrystalline anisotropy energy and is denoted by K. For iron, the anisotropy energy is zero for [100] and largest for the [111] direction. For cobalt, which has the HCP crystal structure, the anisotropy energy is at least an order of magnitude greater.



*Magnetization curves for single crystals of Fe, Ni and Co along different directions.*

The lowest order anisotropy energy is given as  $E_a = K \sin^2\theta$ , where  $\theta$  is angle between easy axis and magnetization.

Let us now imagine a situation when the system has spontaneous magnetization long the easy axis but a field is applied in another direction. Redirection of the magnetization to be aligned with the applied field requires energy. Crystal anisotropy energy is an intrinsic property of the material. For a uniaxial material such as Co, field necessary to rotate the magnetization  $90^\circ$  away from the easy axis  $H = 2K / M_s$  and  $H \sim K/M_s$  for cubic systems.