Colloidal Chemical Synthesis of Magnetic Nanoparticles

Review Papers

a) T. Hyeon, *Chem. Commun.* **2003**, 927.
b) J. Park, et al. *Angew. Chem. Int. Ed.* **2007**, 46, 4630.
c) Lu, A. H., E. L. Salabas and F. Schüth, *Angew. Chem. Int. Ed.*, **2007**, 46, 1222-1244.
d) Soon Gu Kwon and Taeghwan Hyeon, *Acc. Chem. Res.* **2008**, 41, 1696-1709.

Applications of Magnetic Nanoparticles

Multi-Terabit/in^2

Magnetic tape

www.columbia.edu/acis/history/media.html

Magnetic Resonance Imaging (MRI) Contrast Agent

- **Hyperthermia for Cancer Treatment**
- **Drug Delivery by Magnetic Field Guiding**
- **Magnetic Fluids for Engineering Applications**

Part I

Introduction to Magnetism

Anthony R. West, "Basic Solid State Chemistry, 2nd Ed."; Wiley 1999.
Lesley Smart and Elaine Moore, Solid State Chemistry: An Introduction, 2nd Ed., Chapman&Hall, 1996; or 4th Ed, 2012.

Magnetic Properties

- Diamagnetism: very weak, closed shell of electrons
- Paramagnetism
- Cooperative Magnetism: Ferro-, Antiferro-, Ferri-magnetism, Spin glass
- Magnetism is characterized by having unpaired electrons: usually metals of d and f elements (Transition metals and lanthanides)

Magnetism

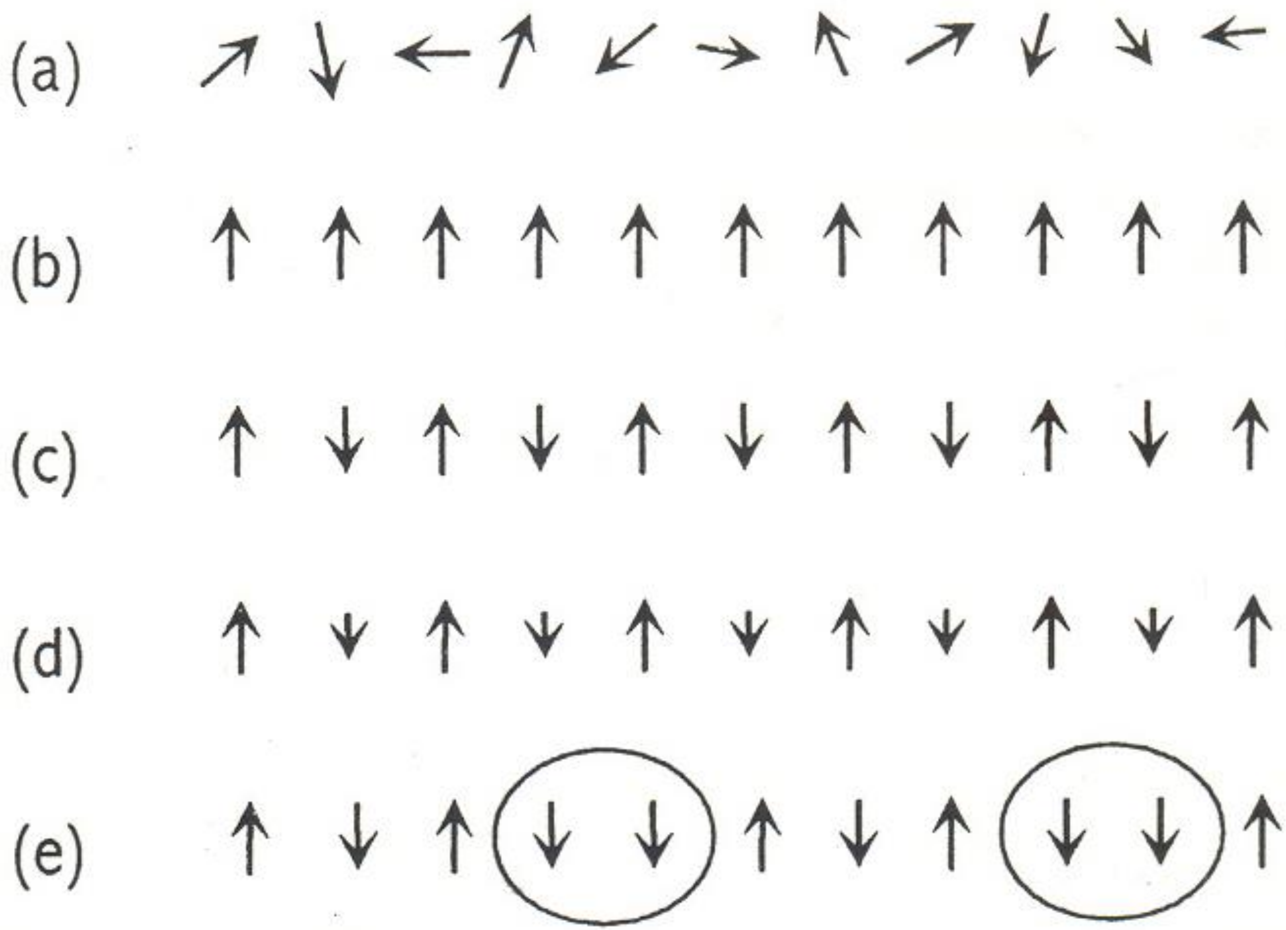


Fig. 8.1 Schematic magnetic phenomena in a 1D crystal: (*a*) paramagnetism; (*b*) ferromagnetism; (*c*) antiferromagnetism; (*d*) ferrimagnetism; and (*e*) spin glass-type behaviour in which an antiferromagnetic array is disrupted or frustrated by enforced ferromagnetic coupling (circled)

Behavior of substances in Magnetic field

In Magnetic field, *H*, Magnetic induction (or Flux density), *B*.

$$B = \mu H$$

$$B = \mu_0 (H + M)$$

$$\chi = \frac{M}{H}$$

$$\mu = \mu_0 (1 + \chi)$$

μ: permeability

μ_0: permeability of free space

***M*: magnetization**

$B = \mu_0 H$ **: Induction generated by applied field**

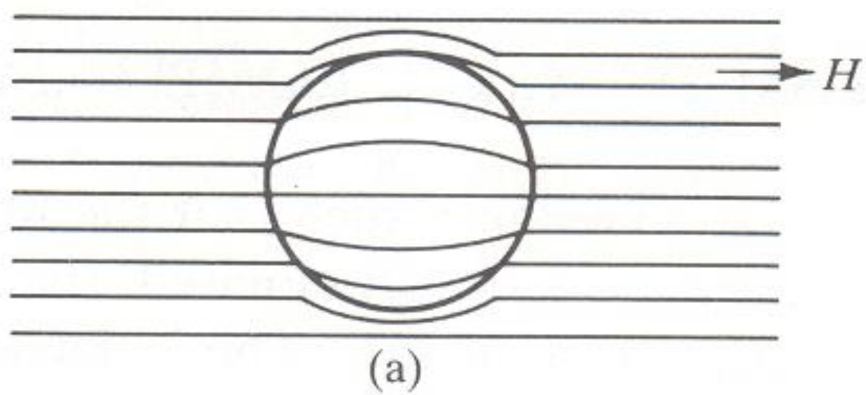
$B = \mu_0 M$ **: Induction generated by Sample**

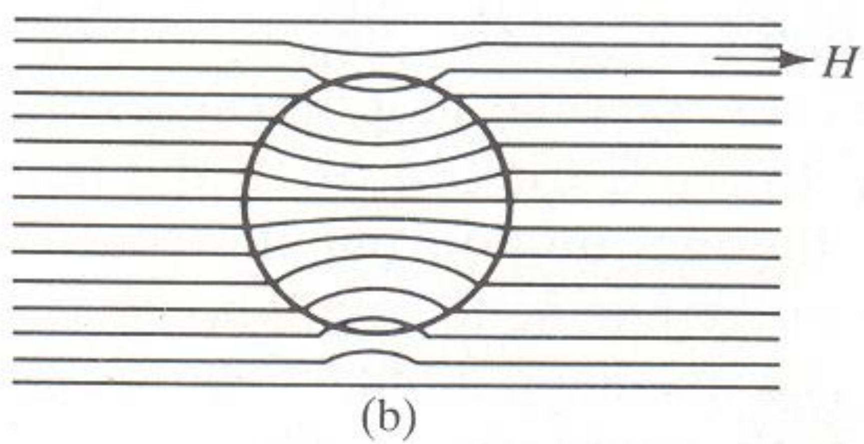
χ: magnetic susceptibility

$$\mu_r = \frac{\mu}{\mu_0} = 1 + \chi$$

Relative permeability

A magnetic field produces magnetic flux. When a magnetic material is placed in the field, increase (paramagnetism) or decrease (diamagnetism) of magnetic flux density.





Flux density in (a) a diamagnetic and (b) a paramagnetic

Effect of χ on temperature

- Simple paramagnetism: isolated unpaired electrons Transition metal complexes, align of magnetic spin with application of magnetic field, opposed by thermal energy
  → Curie law

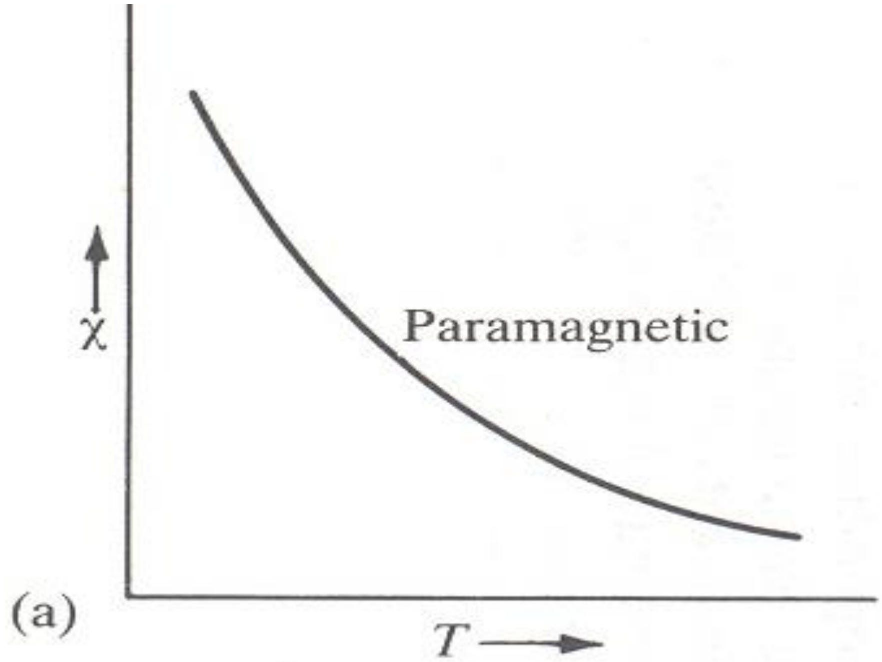
$$\chi = \frac{C}{T}$$

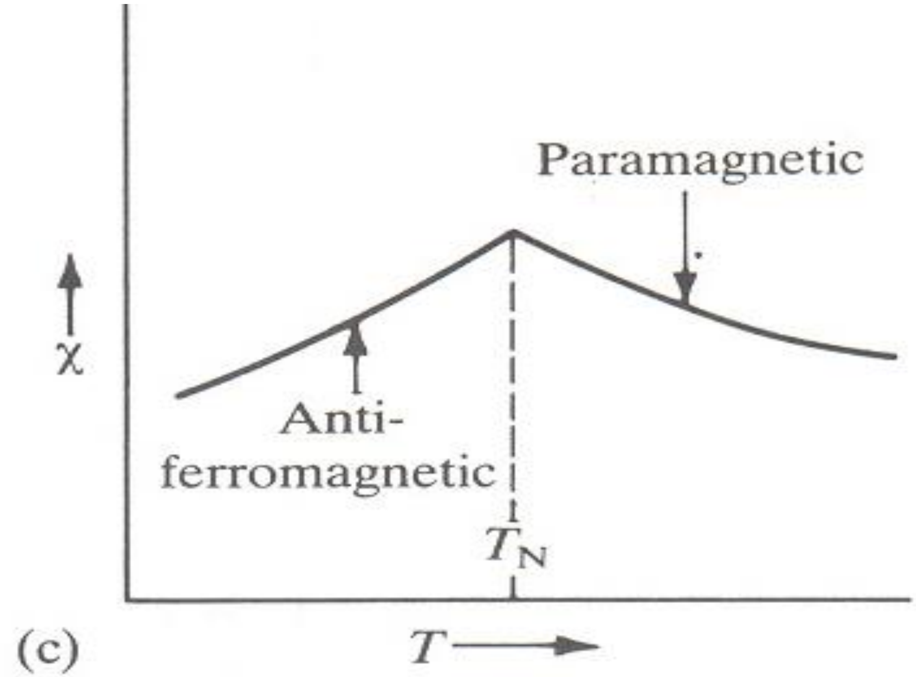
- Cooperative behavior: ferromagnetic and antiferromagnetic: change over from independent to cooperative fashion

$$\chi = \frac{C}{(T - T_C)} \text{ and } \chi = \frac{C}{(T + T_N)}$$

Table 8.1 *Magnetic susceptibilities*

Behaviour	Typical χ value	Change of χ with increasing temperature	Field dependence?
Diamagnetism	-8×10^{-6} for Cu	None	No
Paramagnetism		Decreases	No
Pauli paramagnetism	8.3×10^{-4} for Mn	None	No
Ferromagnetism	5×10^{3} for Fe	Decreases	Yes
Antiferromagnetism	0 to 10^{-2}	Increases	(Yes)





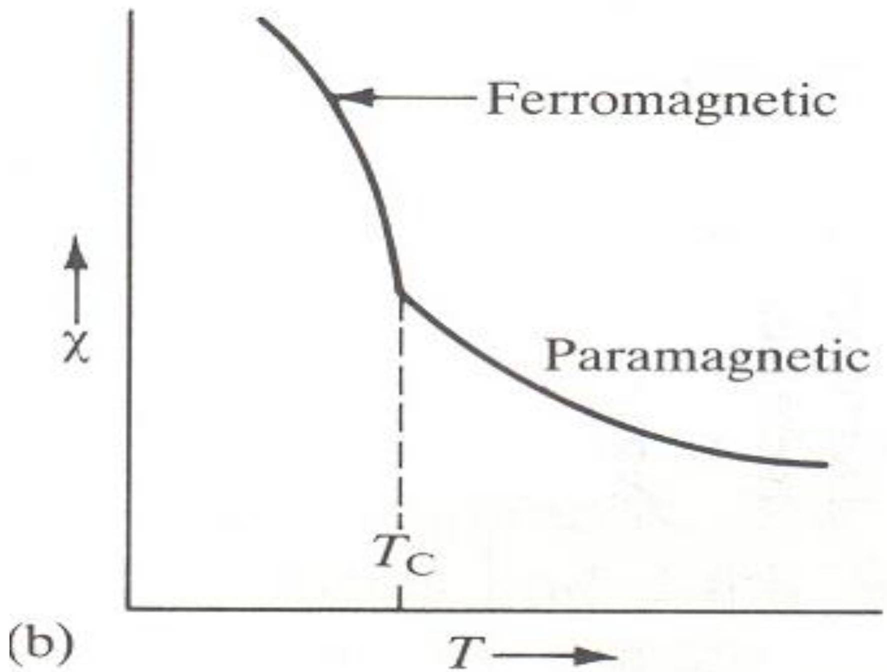


Table 8.2 *Some Curie and Néel temperatures*

Material	T_c (°C)	T_N (°C)
Cr		35
Mn		−173
Fe	770	
Co	1131	
Ni	358	

T1 MRI Contrast Agents using Gd^{3+} complexes

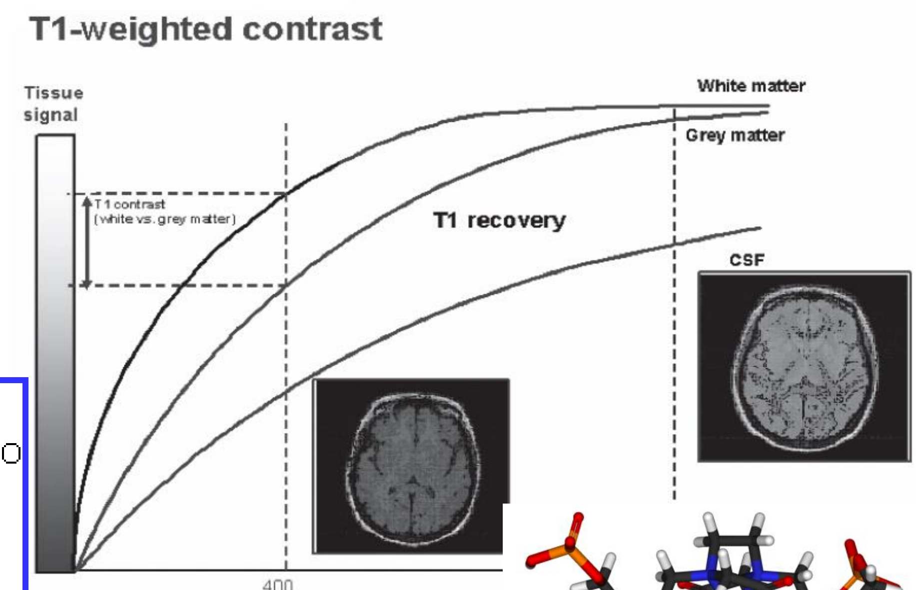
- **Positive Contrast Agents:** **becomes whiter**
  cause a reduction in the T1 relaxation time (increased signal intensity on T1 weighted images)
- Paramagnetic species have unpaired electrons.
- **Gd3+ and Mn2+ ionic complexes**
- **Most of clinically used MRI contrast is T1 Gd-complex**

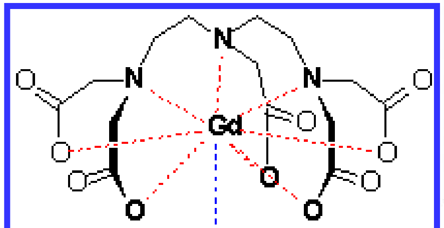
Table 1

Atomic N	Ion	3d	4f	Magnetic moment (Bohr magneton)
24	Cr^{3+}	↑ ↑ ↑		3.8
25	Mn^{2+}	↑ ↑ ↑ ↑ ↑		5.9 (weak field)
26	Fe^{3+}	↑ ↑ ↑ ↑ ↑		5.9 (weak field)
29	Cu^{2+}	↑↓ ↑↓ ↑↓ ↑↓ ↑		1.7-2.2
63	Eu^{3+}		↑↓ ↑ ↑ ↑ ↑ ↑ ↑	(6.9)
64	Gd^{3+}		↑ ↑ ↑ ↑ ↑ ↑ ↑	7.9
66	Dy^{3+}		↑↓ ↑↓ ↑ ↑ ↑ ↑ ↑	(5.9)

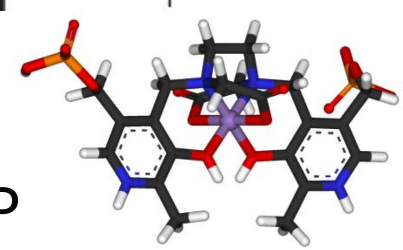
Half-life in urine = 21.0 min after intravenous injection
in blood = 19.6 min

Compound	LD_{50} with intravenous dose in rats (mmol/kg body weight)
Gd-DTPA	10
Gd-EDTA	0.3
Gd-C13	0.4
Meglucamine diatrizoate (common X-ray contrast agent)	18





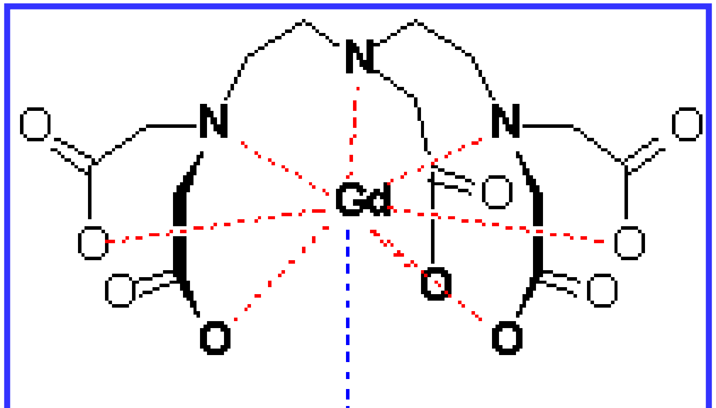
Gd-DTPA



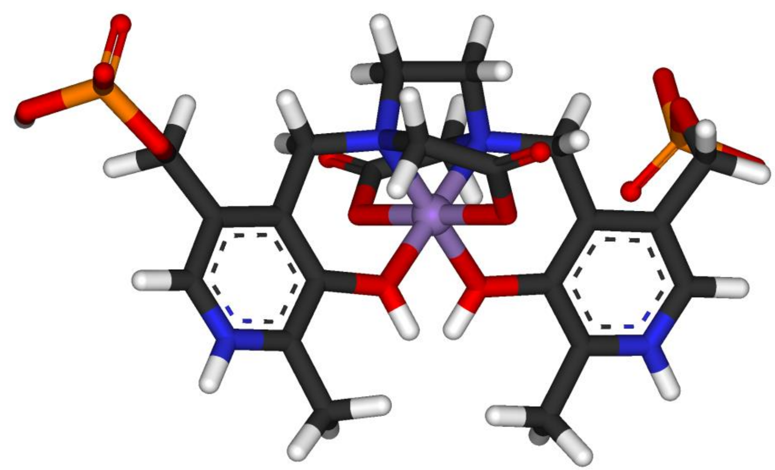
Mn-DPDP

Paramagnetic T1 MRI contrast agents

Atomic N	Ion	3d	4f	Magnetic moment (Bohr magneton)
24	Cr^{3+}	↑ ↑ ↑ _ _		3.8
25	Mn^{2+}	↑ ↑ ↑ ↑ ↑		5.9 (weak field)
26	Fe^{3+}	↑ ↑ ↑ ↑ ↑		5.9 (weak field)
29	Cu^{2+}	↑↓ ↑↓ ↑↓ ↑↓ ↑		1.7-2.2
63	Eu^{3+}		↑↓ ↑ ↑ ↑ ↑ ↑ ↑	(6.9)
64	Gd^{3+}		↑ ↑ ↑ ↑ ↑ ↑ ↑	7.9
66	Dy^{3+}		↑↓ ↑↓ ↑ ↑ ↑ ↑ ↑	(5.9)

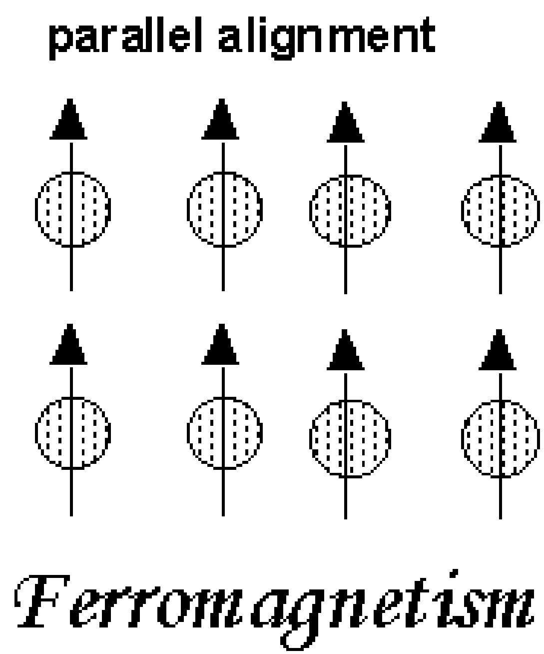


Gd-DTPA


Mn-DPDP

Ferromagnetism

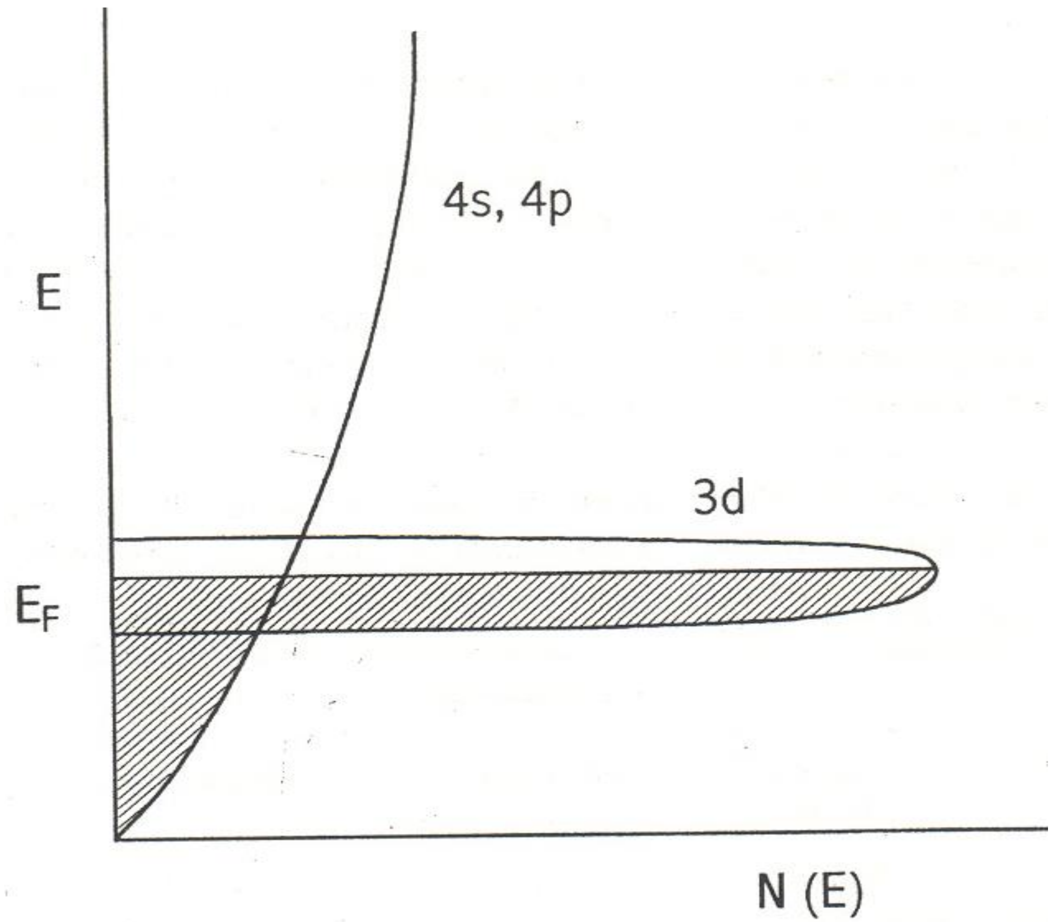
- Ferromagnetic materials exhibit parallel alignment of moments resulting in large net magnetization even in the absence of a magnetic field.
- Two distinct characteristics of ferromagnetic materials
  - Spontaneous magnetization
  - Magnetic ordering temperature



Ferromagnetism

- Ferromagnetism of Fe, Co, Ni. Strong repulsion between d electrons→ can be decreased by aligning electrons with parallel spins. (Hund rule of maximum multiplicity in atomic structure)→ in molecules and solid, however, pairing energy (bonding energy) wins over the exchange energy. → more spin-up electrons than spin-down electrons when Hund's exchange energy wins over bonding (pairing) energy
- K (exchange integral) > W (bandwidth)/5, The smallest bandwidth in Fe, Co, Ni (contracted and weak overlap at later 3d elements)

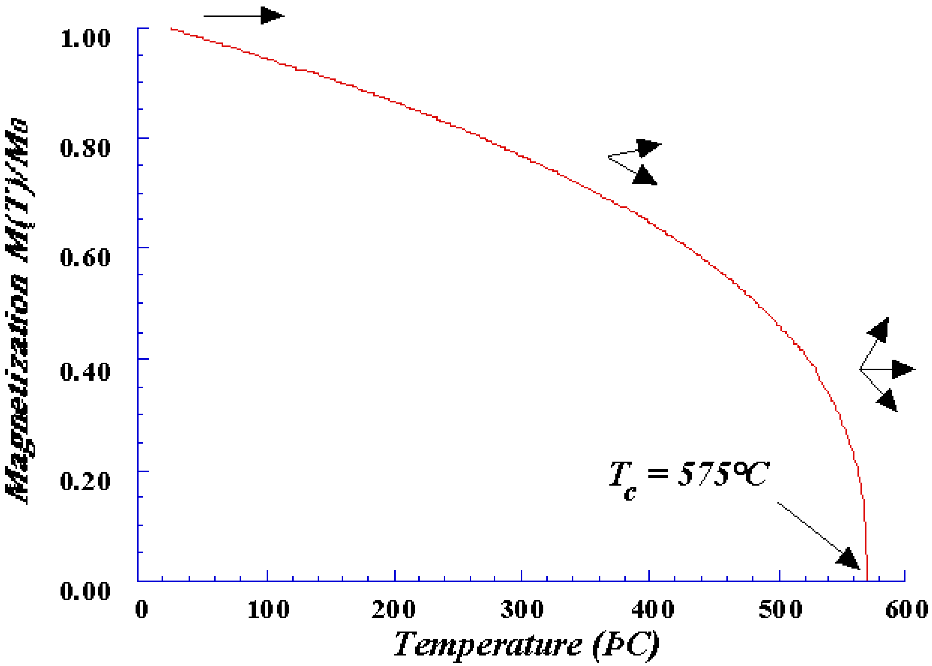
Density of states depends on the nature and degree of overlap of orbitals: 3d orbitals of later transition metals held more tightly to the individual atomic nuclei → poor orbital overlap → narrow band width (s & p orbitals: good overlap, more diffused)

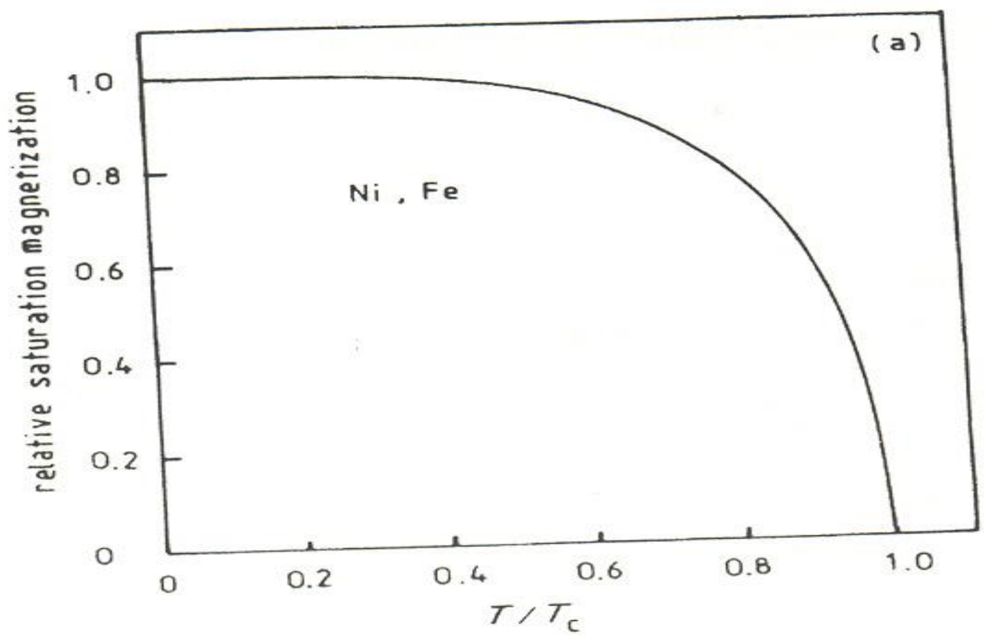


Curie Temperature

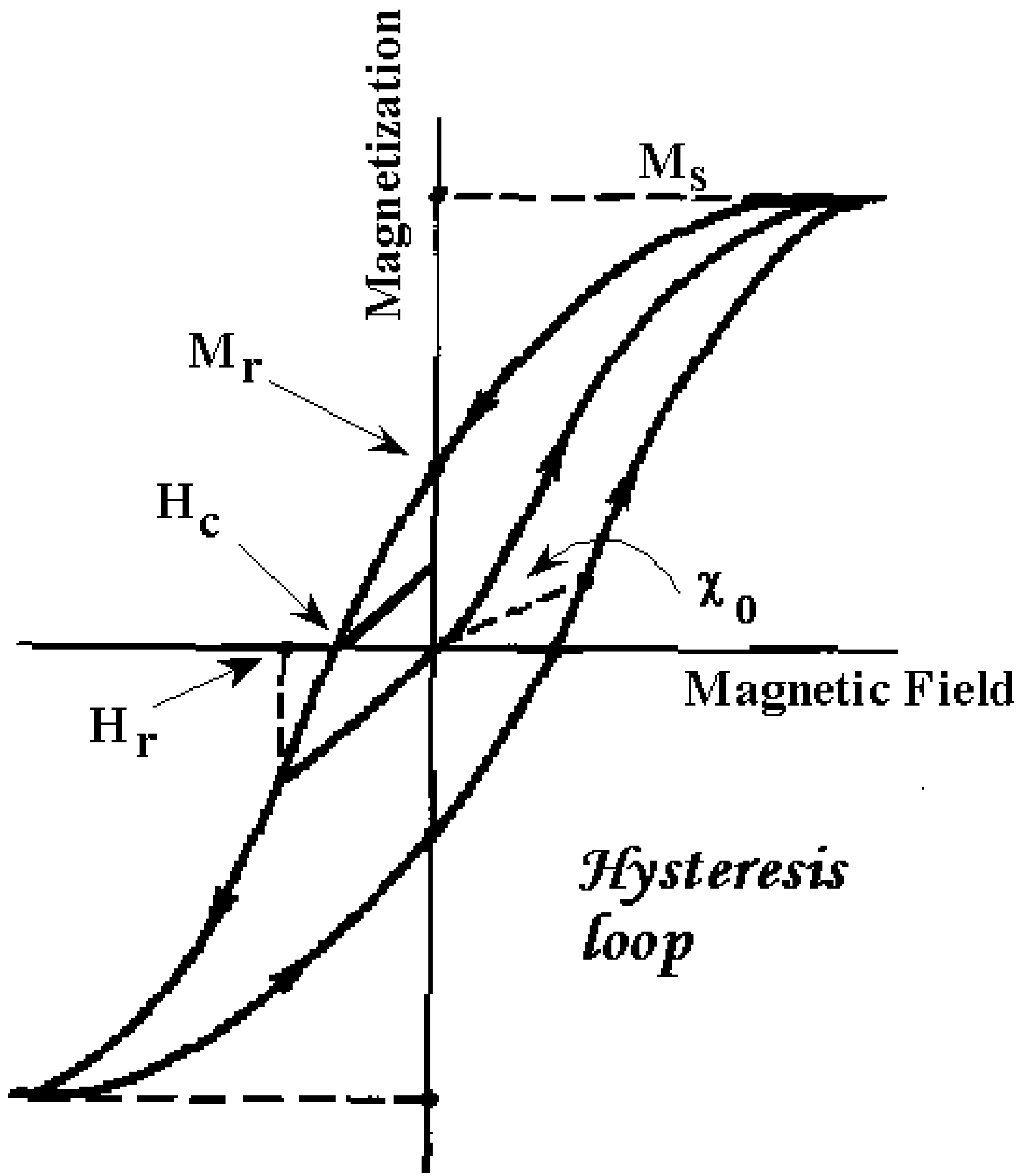
- Even though electronic exchange forces in ferromagnets are very large, thermal energy eventually overcomes the exchange and produces a randomizing effect. This occurs at a particular temperature called the Curie temperature (T_C). Below the Curie temperature, the ferromagnet is ordered and above it, disordered. The saturation magnetization goes to zero at the Curie temperature.

Saturation magnetization goes to zero at the Curie temperature.

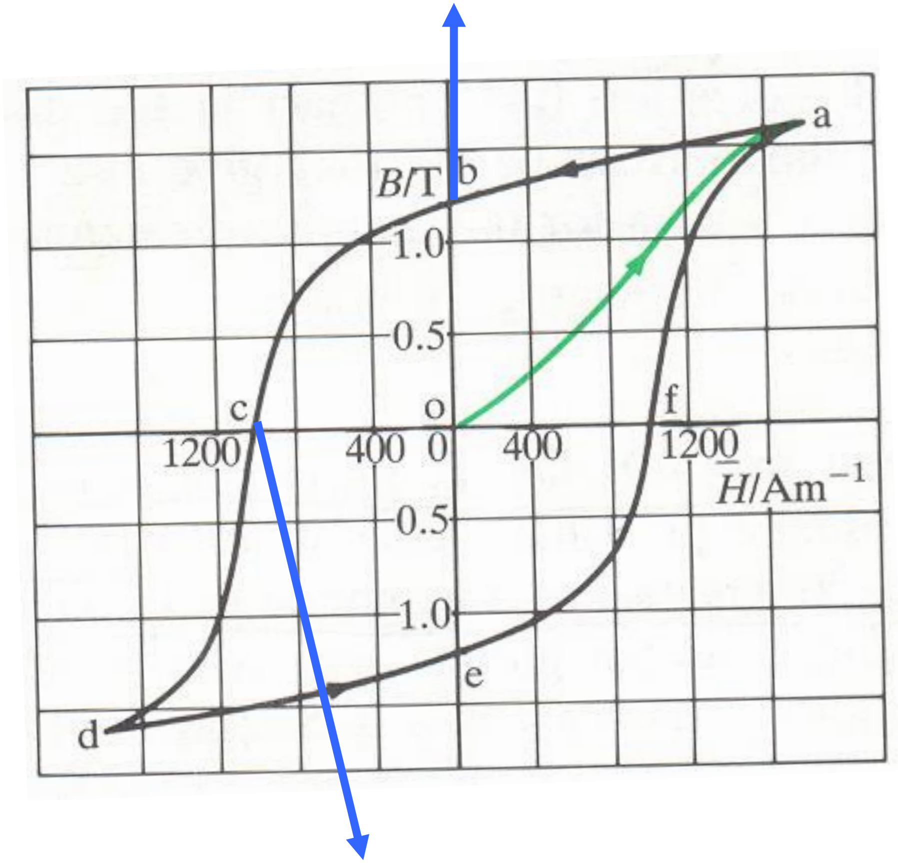




Hysteresis loop



b: remanent magnetization, M_r



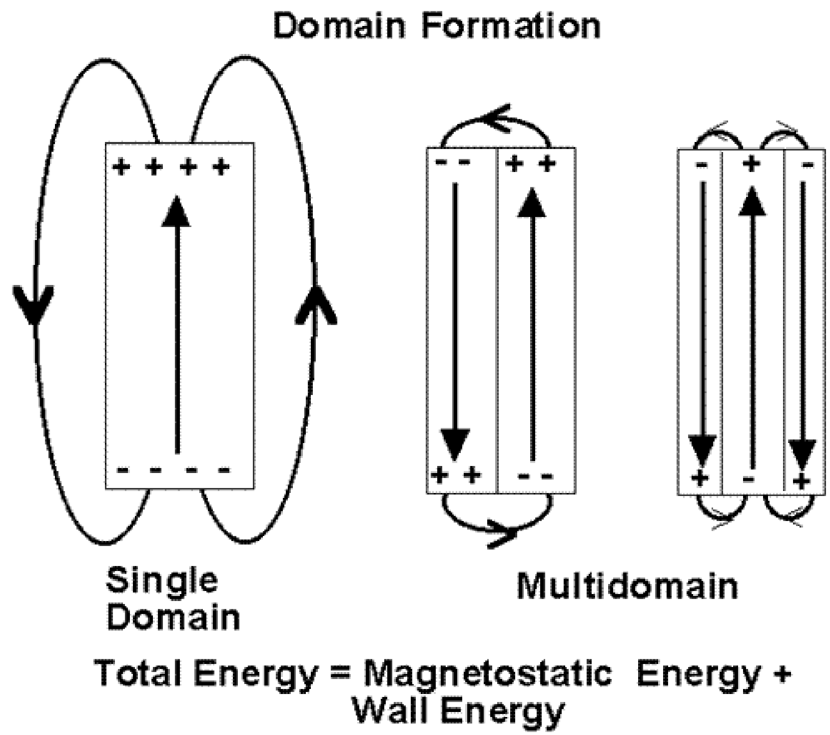
Coercive force, H_c: the field need to reverse the magnetization to zero

Permanent magnets: large coercive force and large remanent magnetization, SmCo5

- 0: nonmagnetic state, the domains are randomly oriented
- 0→ a. increase of magnetic flux density reaching maximum (all the domains aligned with the field), saturation magnetization
- a→ b: When the applied field are reduced the flux density does not follow the initial curve. Difficulty of reversing processes where domains have grown through crystal imperfections: sufficiently large field needed to reverse the aligned spin through the imperfection.

Domain Theory

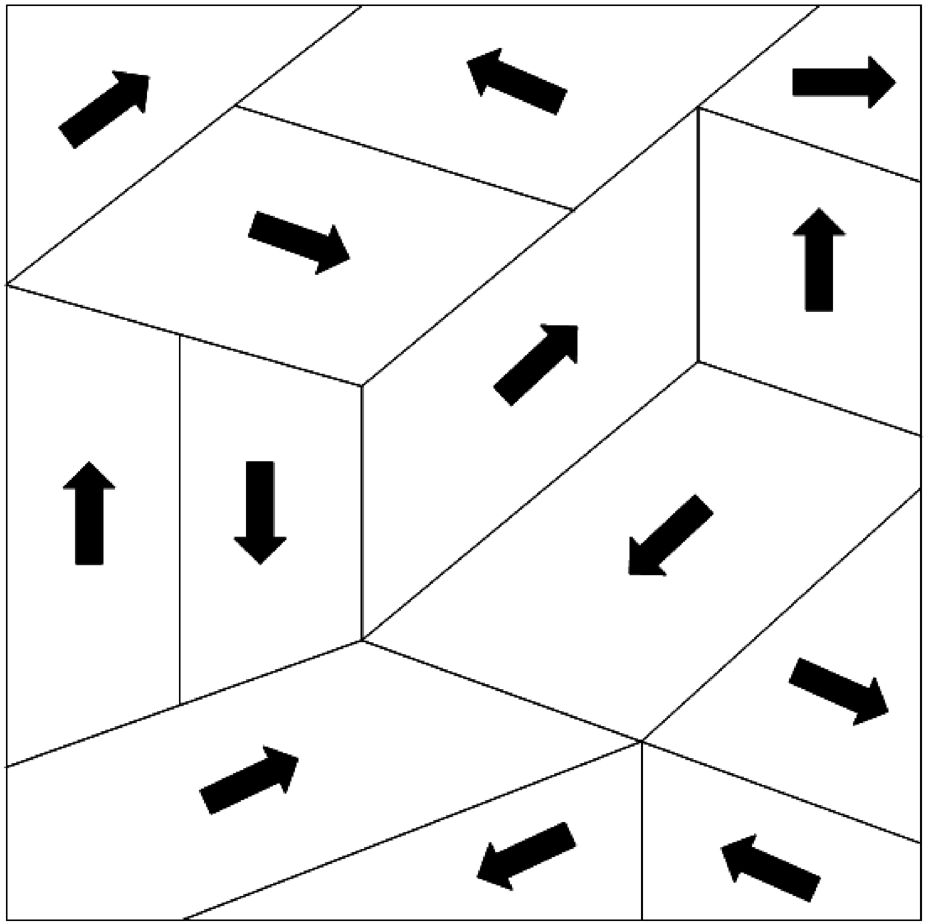
- Below the Curie temperature (Tc), the volume of a bulk magnetic (ferromagnetic or ferromagnetic) material is divided into many magnetic domains to reduce the magnetostatic energy, which is proportional to the volume, D^3, where D is the dimension of the magnetic materials.
- However, the extent of the reduced magnetostatic energy by the multi-domain structure is offset by the energy of the interface between domains which is called domain wall energy, and is proportional to the wall area (D^2).
- Below some critical size, namely, D_c, the domain wall energy surpasses the stabilization energy by the multi-domain structure and the material becomes single domain.

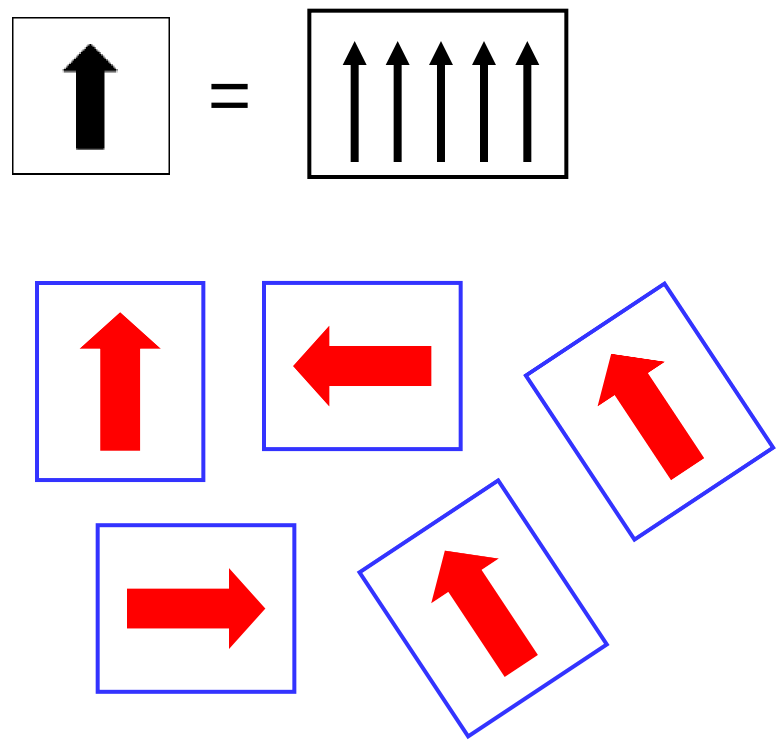


SPM: superparamagnetic
SD: single domain
PSD: pseudo-single domain
MD: multidomain

Cullity, L. C., *Introduction to Magnetic Materials*, Reading, MA: Addison-Wesley, 1972.

Muti-domain (left) and single domain structures (right)





Ferrimagnetism

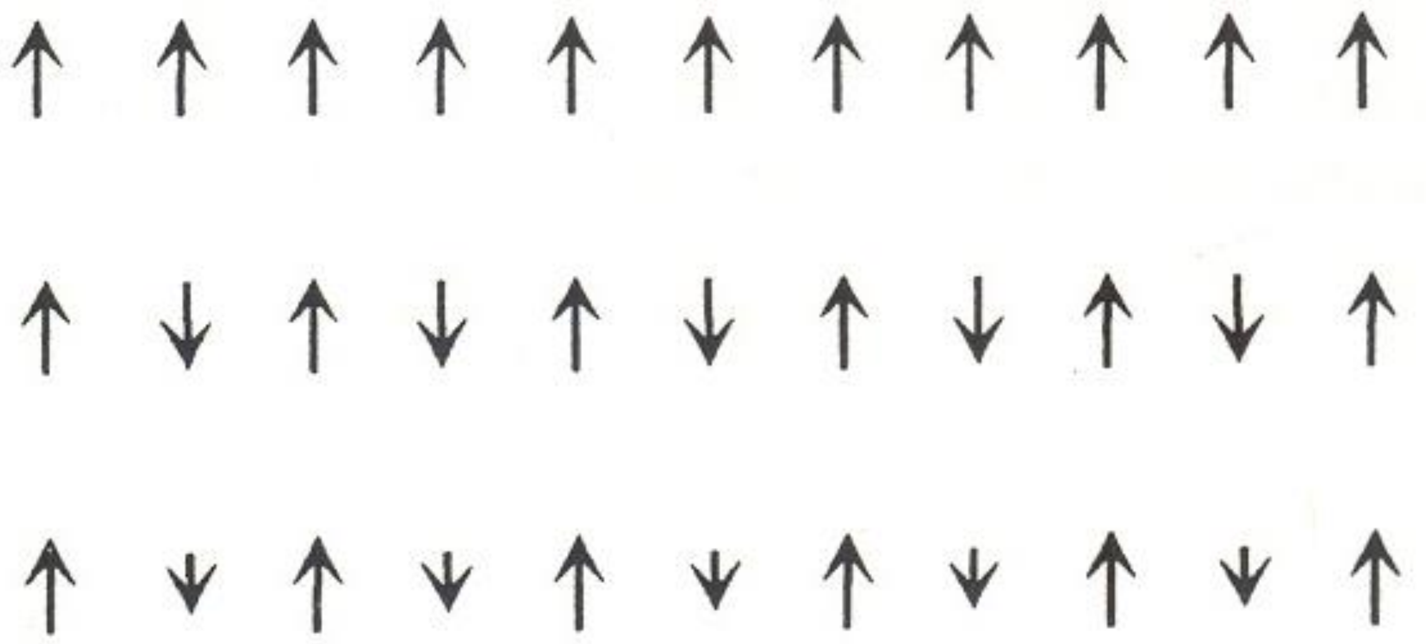
The magnetic structure is composed of two magnetic sublattices (called A and B) separated by oxygens. The exchange interactions are mediated by the oxygen anions. When this happens, the interactions are called indirect or superexchange interactions. The strongest superexchange interactions result in an antiparallel alignment of spins between the A and B sublattice.

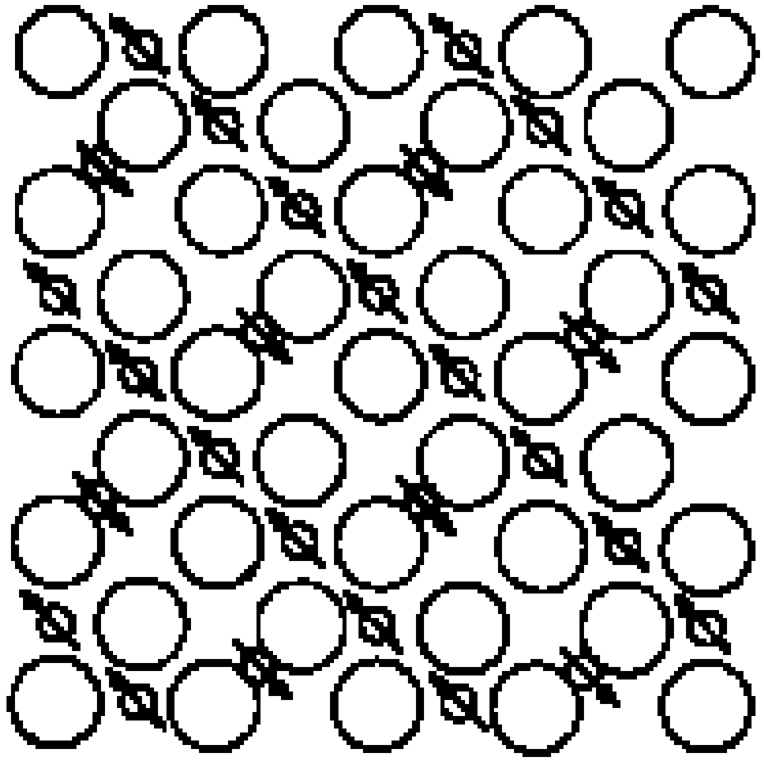
Magnetism

Ferromagnetism

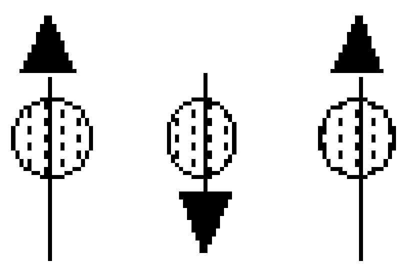
Antiferromagnetism

Ferrimagnetism

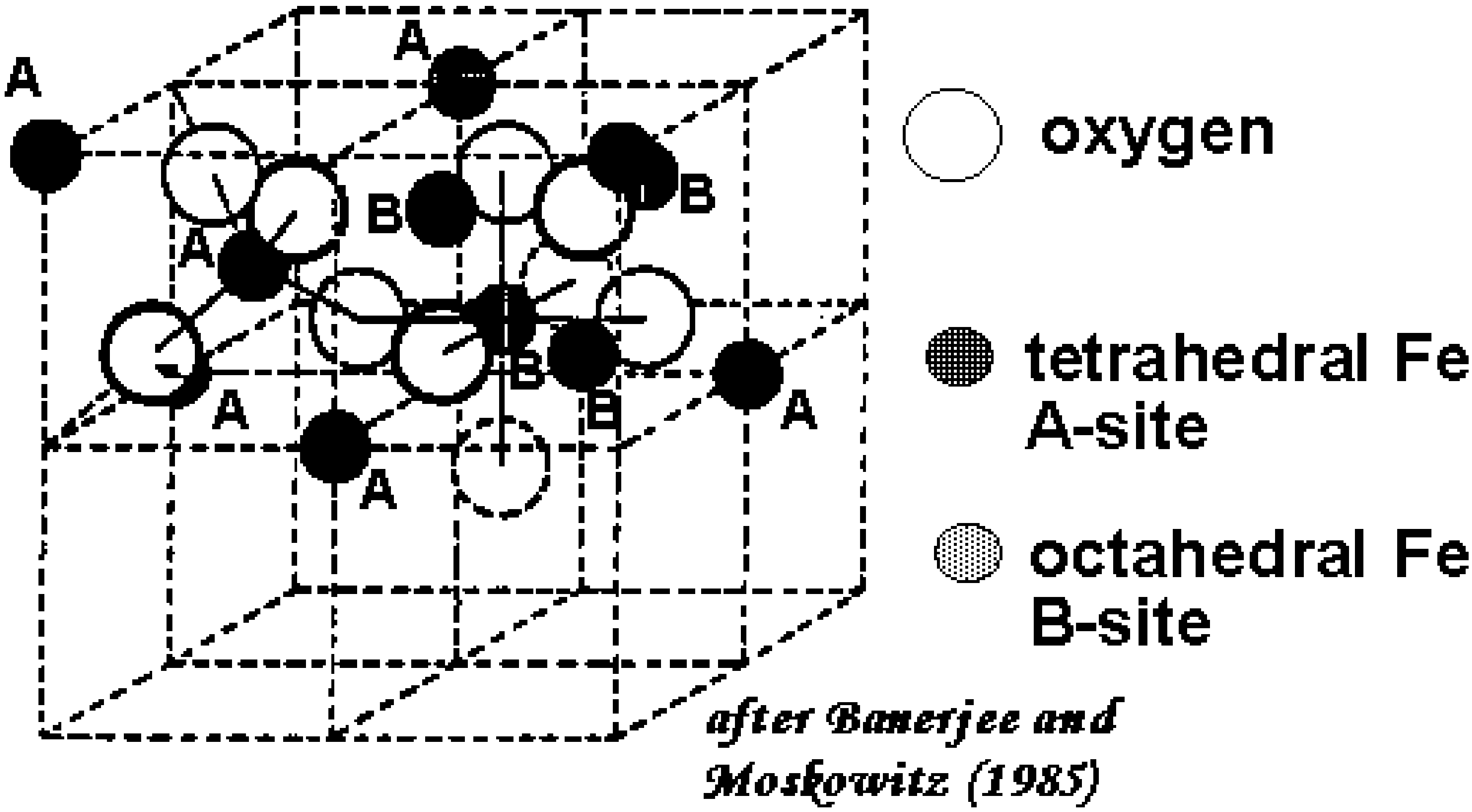




Ferrimagnetism

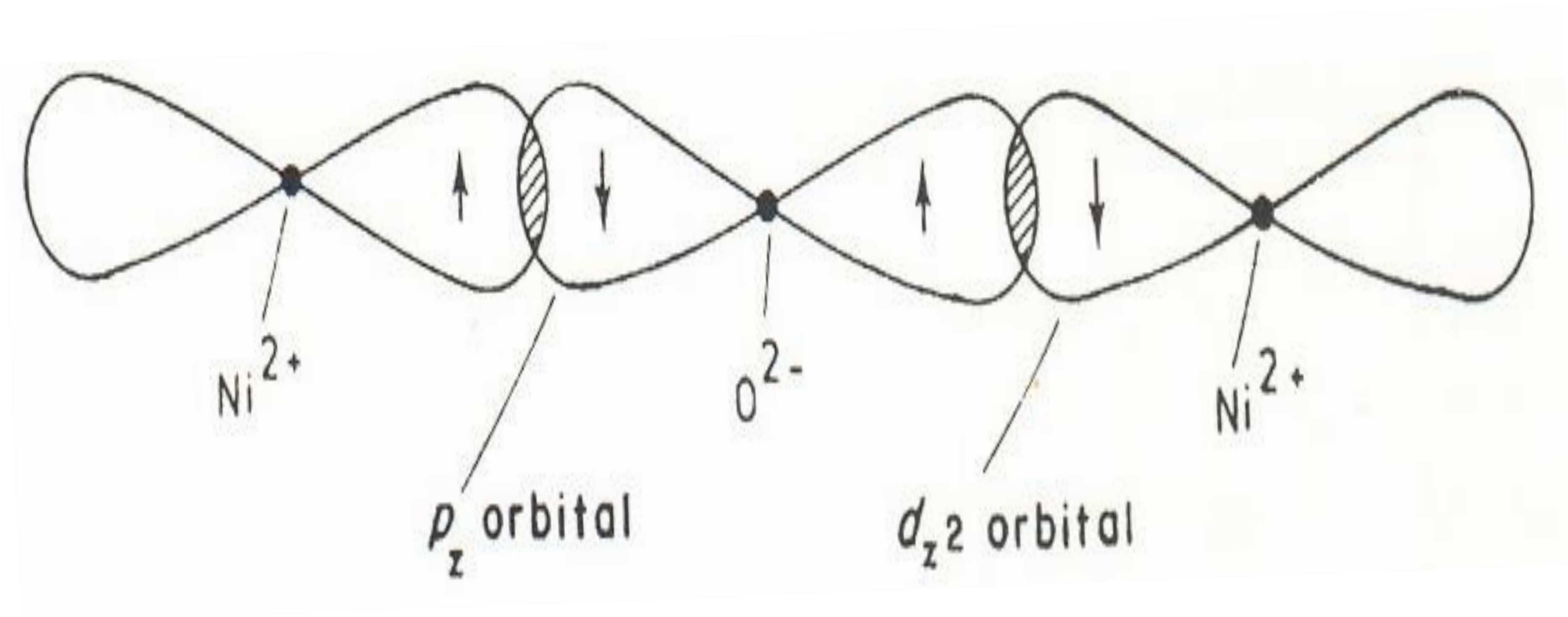


Crystal Structure of Magnetite



Superexchange coupling

Antiferromagnetic coupling of spins of d_{z2} and $d_{x2\text{-}y2}$ on Ni^{2+} ions through *p* electrons of O^{2-} ions



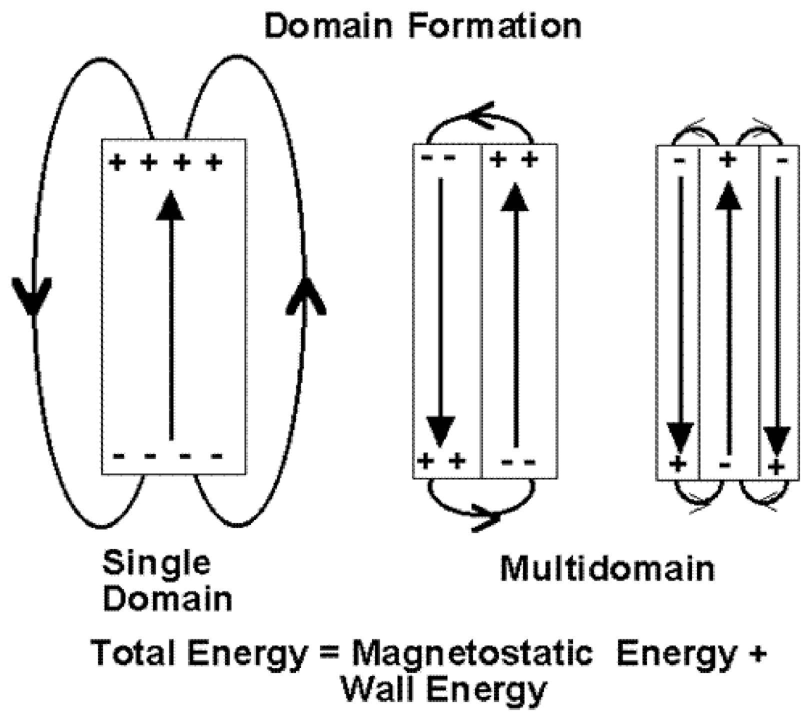
Magnetic Properties of Minerals

Mineral	Composition	Magnetic Order	T_c(°C)	s_s (Am^2/kg)
Oxides				
Magnetite	Fe_3O_4	ferrimagnetic	575-585	90-92
Ulvospinel	Fe_2TiO_2	AFM	-153	
Hematite	aFe_2O_3	canted AFM	675	0.4
Ilmenite	$FeTiO_2$	AFM	-233	
Maghemite	gFe_2O_3	ferrimagnetic	~600	~80
Jacobsite	$MnFe_2O_4$	ferrimagnetic	300	77
Trevorite	$NiFe_2O_4$	ferrimagnetic	585	51
Magnesioferrite	$MgFe_2O_4$	ferrimagnetic	440	21

Mineral	Composition	Magnetic Order	T_c(°C)	s_s (Am^2/kg)
Iron	Fe	FM	770	
Nickel	Ni	FM	358	55
Cobalt	Co	FM	1131	161
Awaruite	Ni_3Fe	FM	620	120
Wairauite	CoFe	FM	986	235

Domain Theory

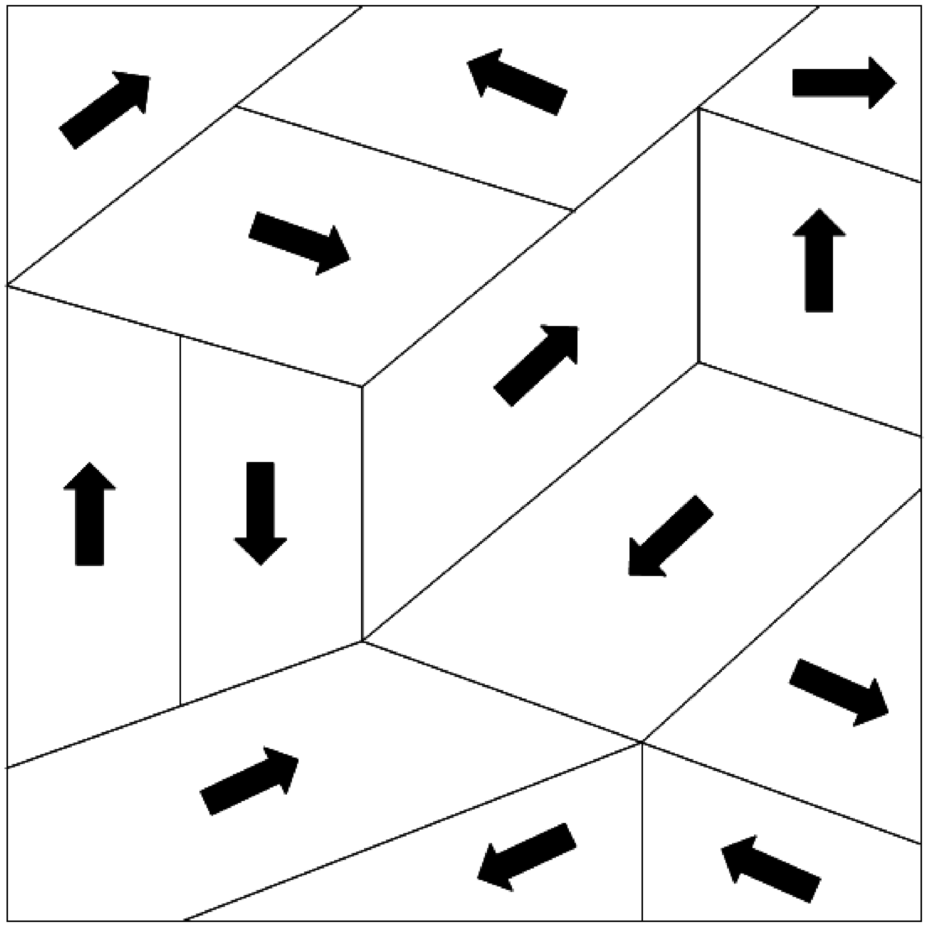
- Below the Curie temperature (Tc), the volume of a bulk magnetic (ferromagnetic or ferromagnetic) material is divided into many magnetic domains to reduce the magnetostatic energy, which is proportional to the volume, D^3, where D is the dimension of the magnetic materials.
- However, the extent of the reduced magnetostatic energy by the multi-domain structure is offset by the energy of the interface between domains which is called domain wall energy, and is proportional to the wall area (D^2).
- Below some critical size, namely, D_c, the domain wall energy surpasses the stabilization energy by the multi-domain structure and the material becomes single domain.

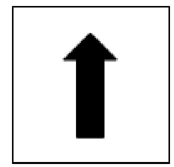


SPM: superparamagnetic
SD: single domain
PSD: pseudo-single domain
MD: multidomain

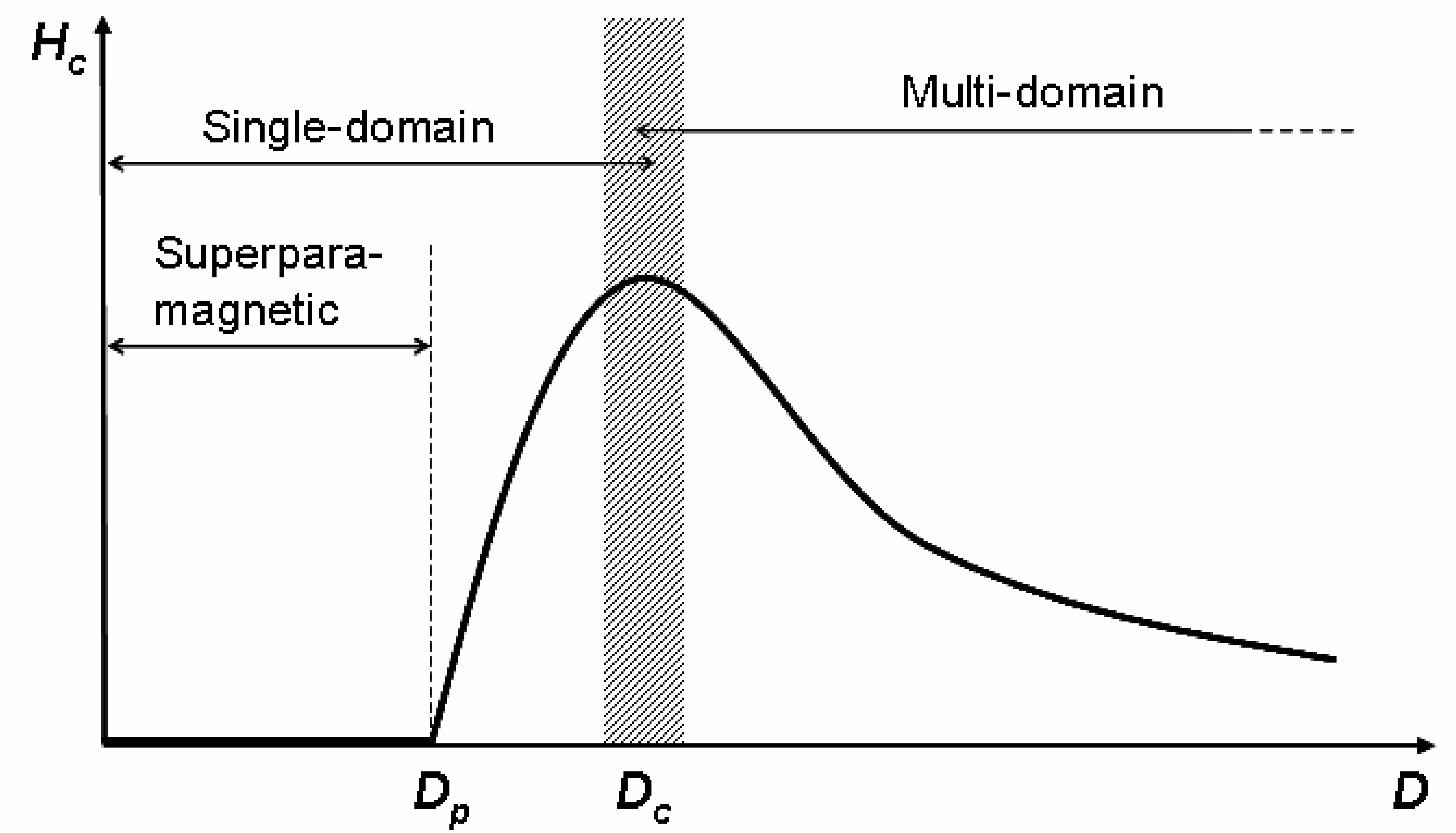
Cullity, L. C., *Introduction to Magnetic Materials*, Reading, MA: Addison-Wesley, 1972.

Muti-domain (left) and single domain structures (right)





Change of the coercive field *Hc* with particle diameter *D*



SPM: Superparamagnetic
SD: Single domain
MD: Multidomain

Cullity, L. C., *Introduction to Magnetic Materials*, Reading, MA: Addison-Wesley, 1972.

Table 1: Estimated single-domain size for different spherical particles.

Material	D_c [nm]
hcp Co	15
fcc Co	7
Fe	15
Ni	55
$SmCo_5$	750
Fe_3O_4	128

Table 2: The influence of the shape of Fe particles on the coercivity.

Aspect ratio (c/a)	H_c [Oe]
1.1	820
1.5	3300
2.0	5200
5.0	9000
10	10 100

Lu, A. H., E. L. Salabas and F. Schüth, *Angew. Chem. Int. Ed.*, Vol. 46, 2007, pp. 1222-1244.

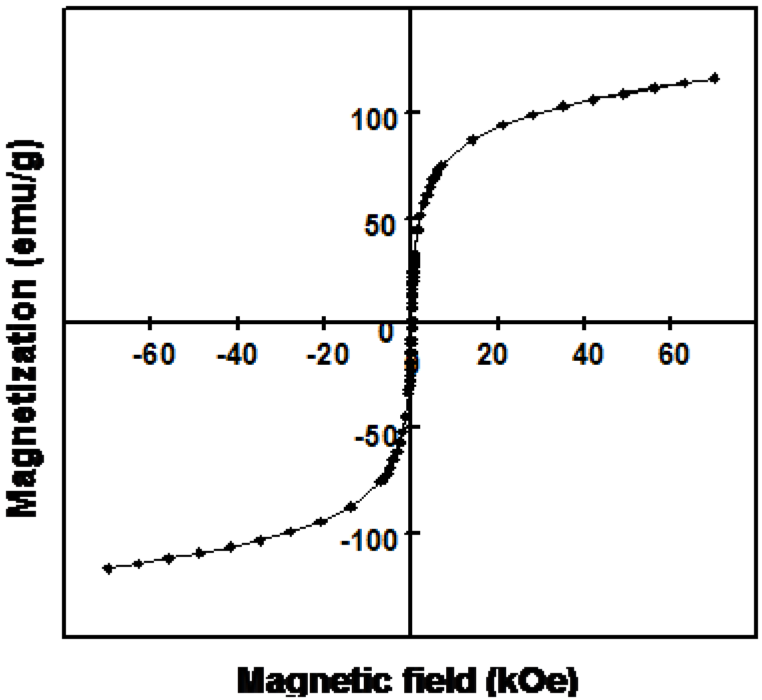
Superparamagnetism (SPM)
→ Magnetic Nanoparticles

• Coercive field, Hc, for a single domain particle decreases with size. When V is so small that *KV* (*K* is magnetic anisotropy constant) is comparable to the thermal energy, *kT*, the magnetization direction is subjected to random thermal fluctuation, which is called superparamagnetism.

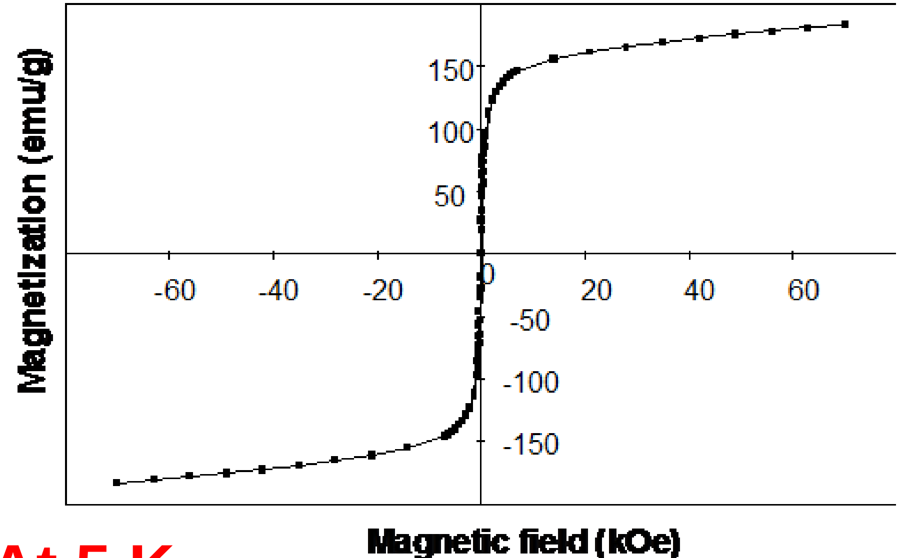
In this condition, Hc is zero (no hysteresis) and the particle has no stable magnetization direction. For a particle of a fixed volume, the minimum temperature required to make it superparamagnetic is called the blocking temperature, T_B, which is expressed in terms of K and V as; $T_B = KV/25k$

Cullity, L. C., *Introduction to Magnetic Materials*, Reading, MA: Addison-Wesley, 1972.

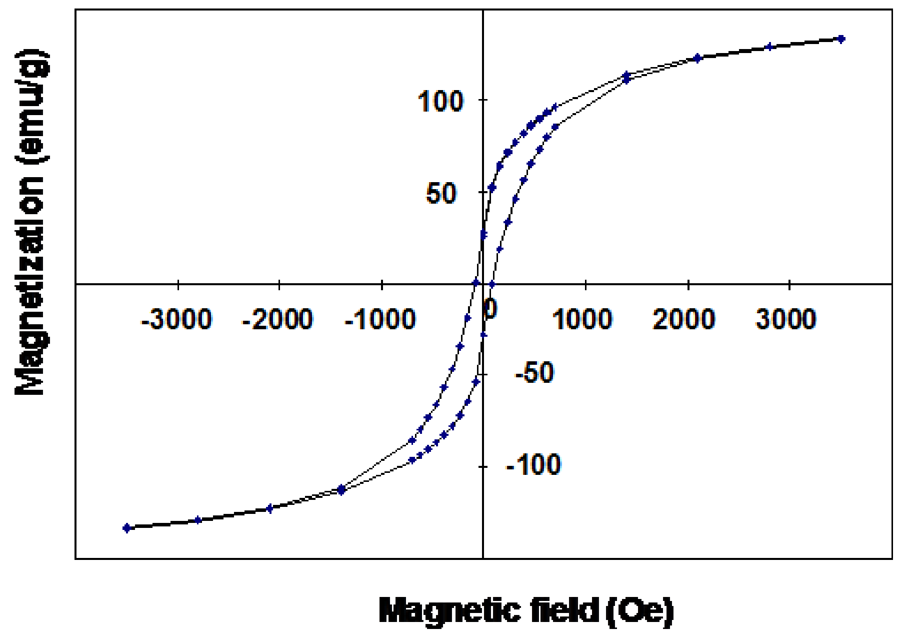
Hysteresis loops of Fe nanoparticles



At 300 K

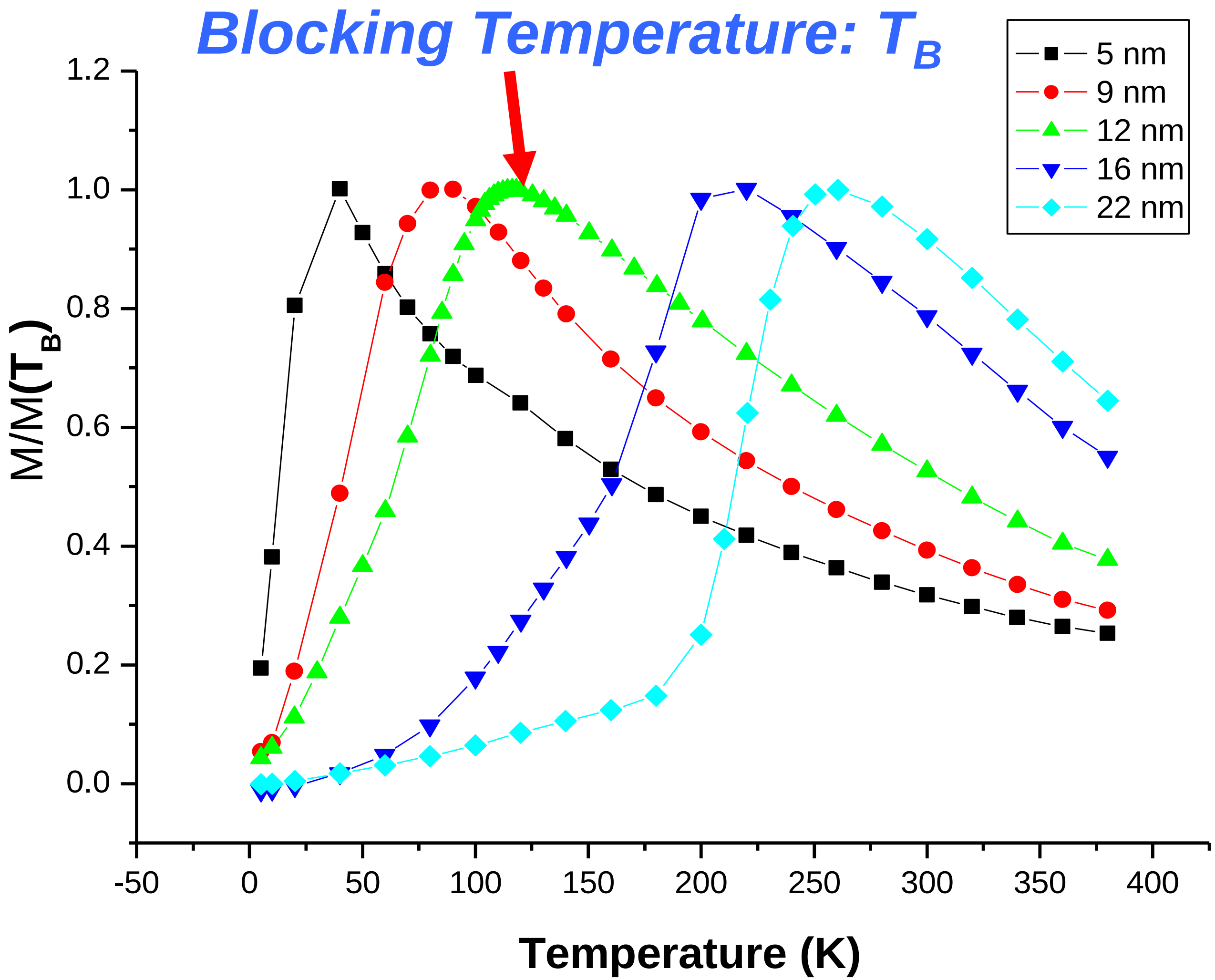


At 5 K



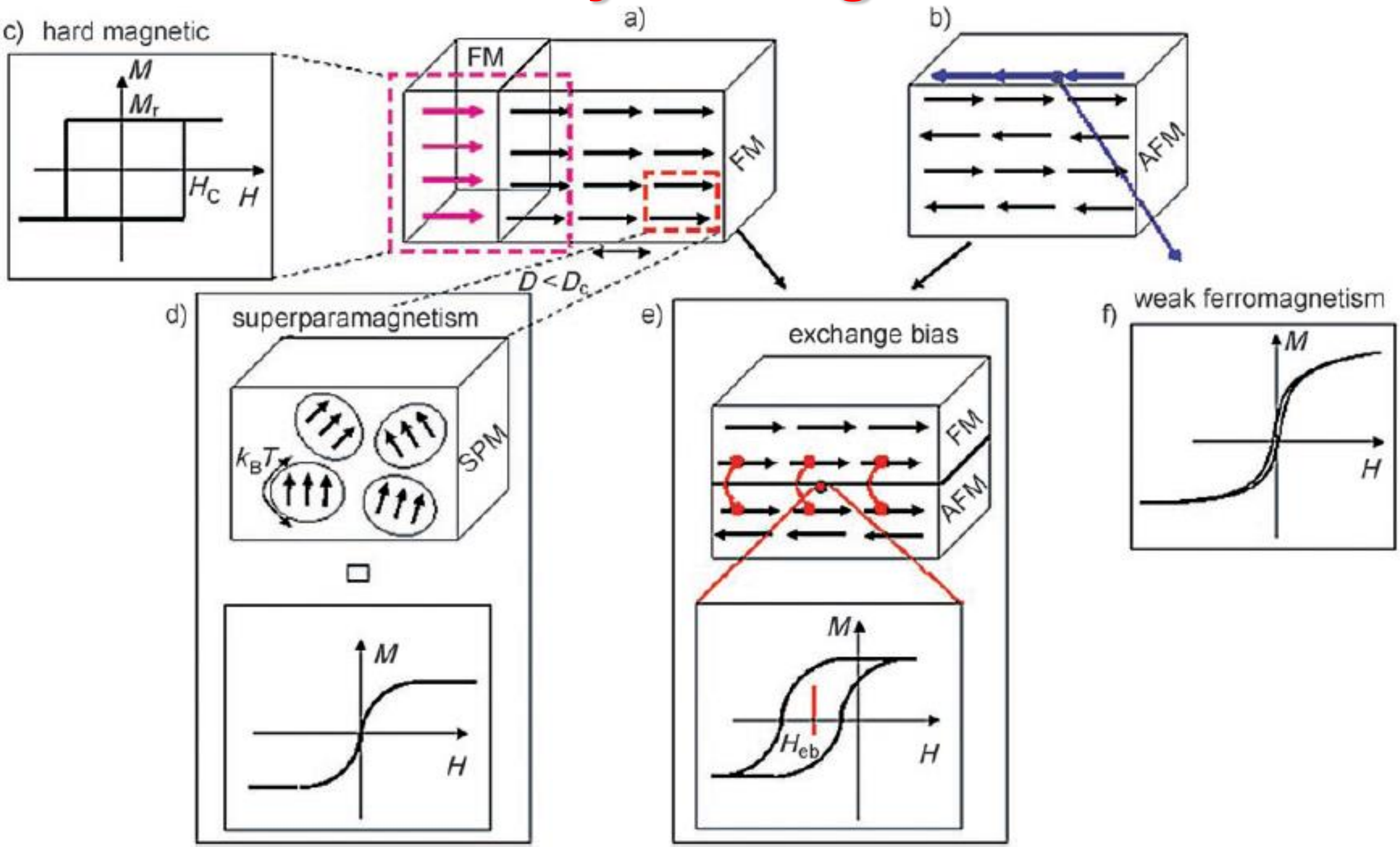
K. S. Suslick, M. Fang and T. Hyeon, "Sonochemical Synthesis of Iron Colloids ," *J. Am. Chem. Soc*. 1996, 118, 11960

Temperature dependence of magnetization measured after zero-field cooling (ZFC) using 100 Oe.



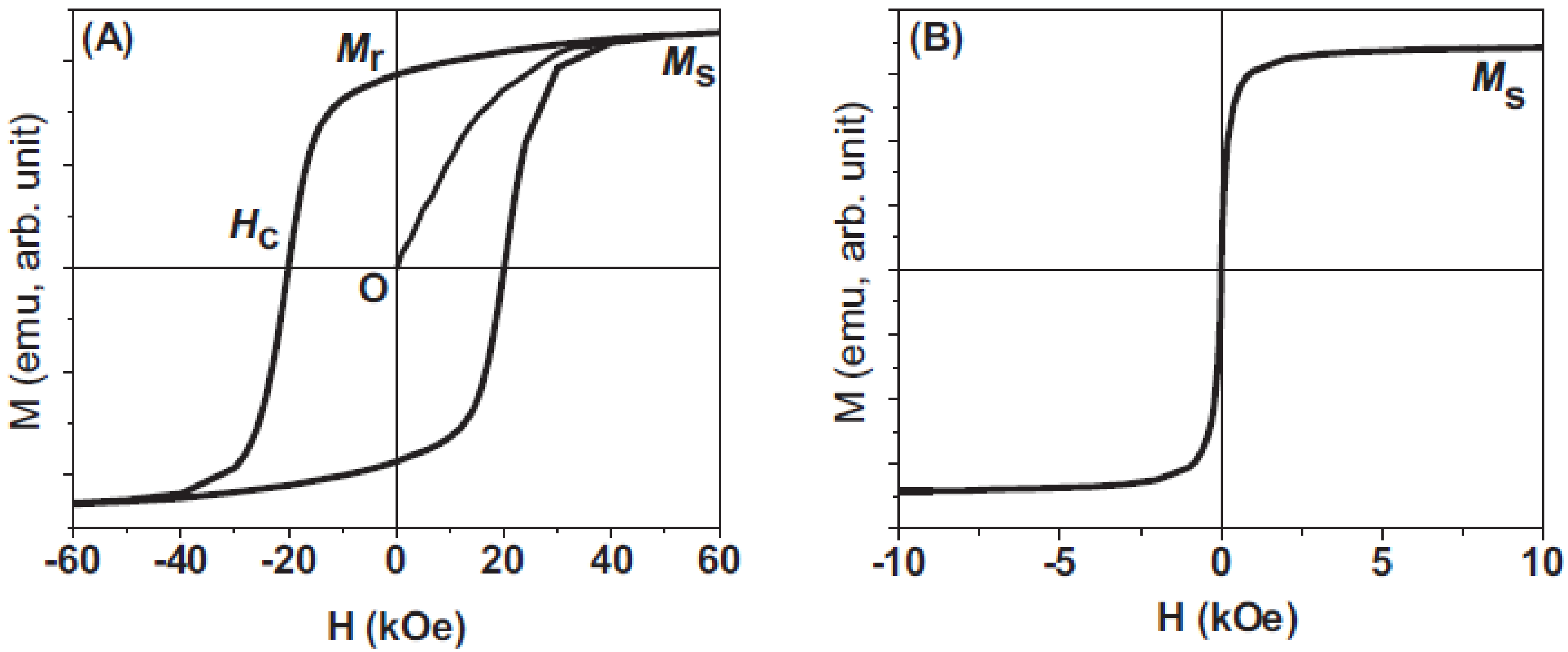
J. Park, et al., *Nature Mater.* 2004, 3, 891.

Summary of Magnetism



Lu, A. H., E. L. Salabas and F. Schüth, *Angew. Chem. Int. Ed.*, Vol. 46, 2007, pp. 1222-1244.

Ferromagnetic vs. Superparamagnetic



S. Sun, *Adv. Mater.* **2006**, 18, 393.