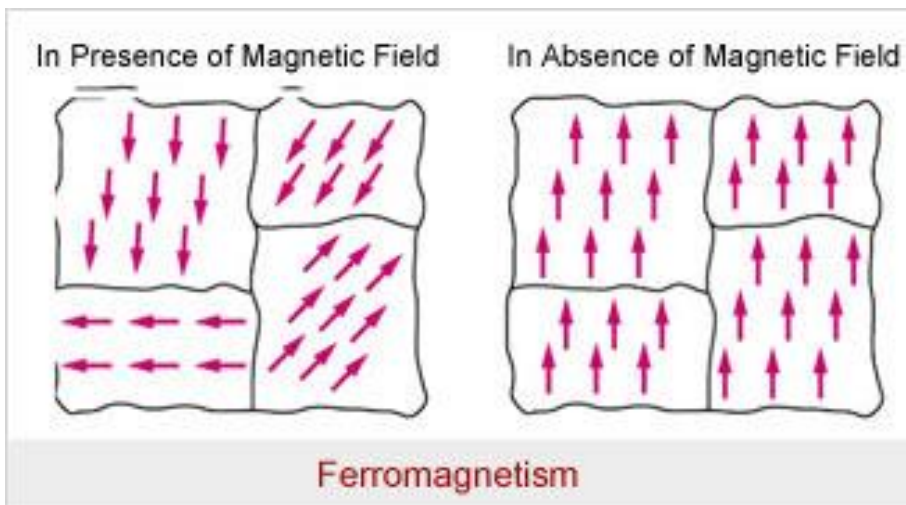
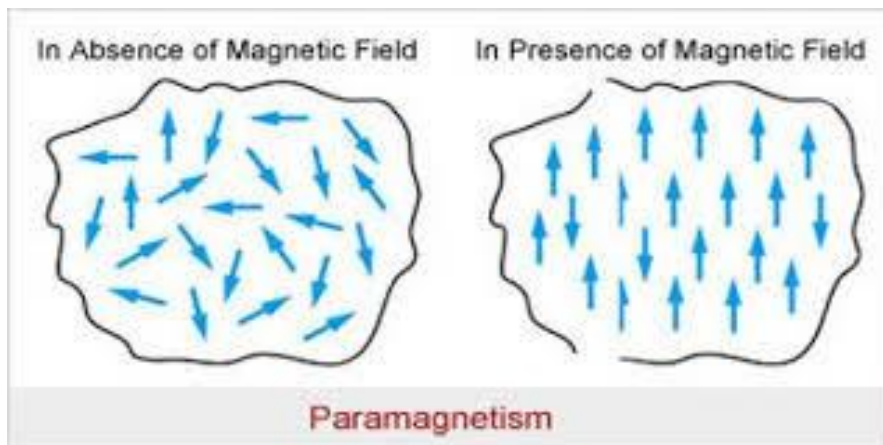
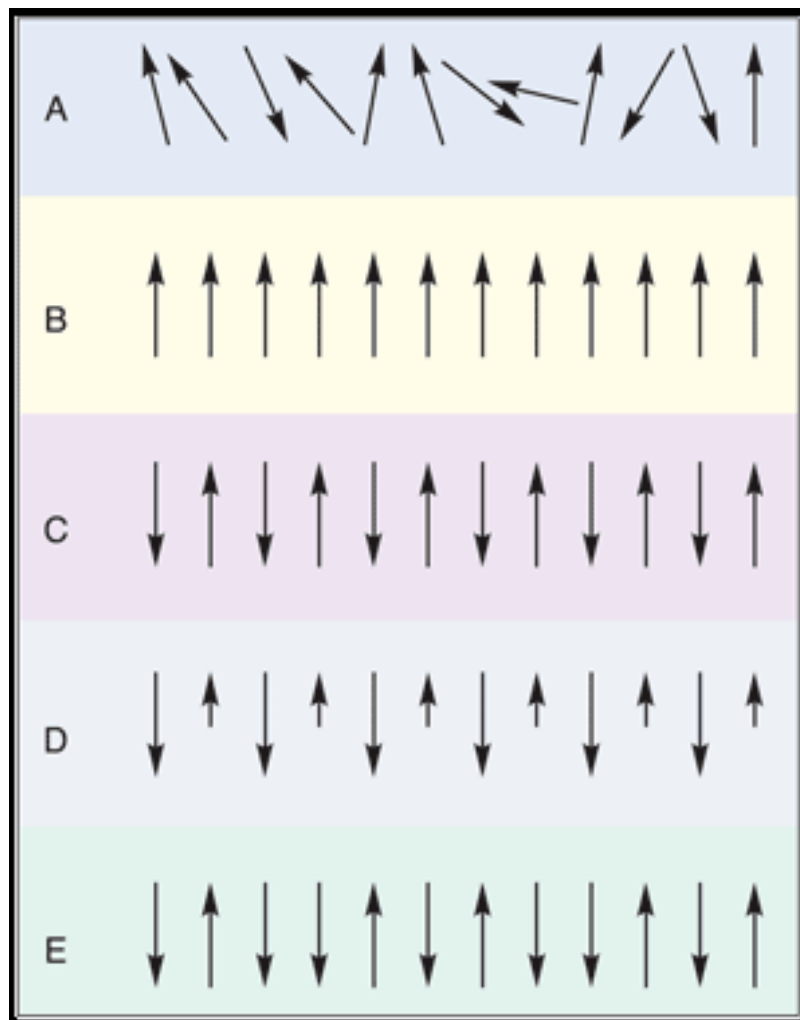


Magnetic nanomaterials

CML102

Magnetic arrangements



Magnetism basics

M = magnetic moment of sample per unit vol.

- Magnetic induction, $B = H + 4\pi M$

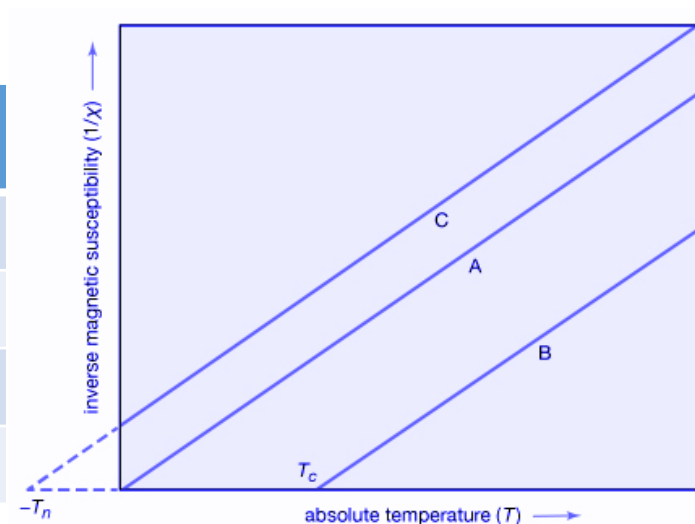
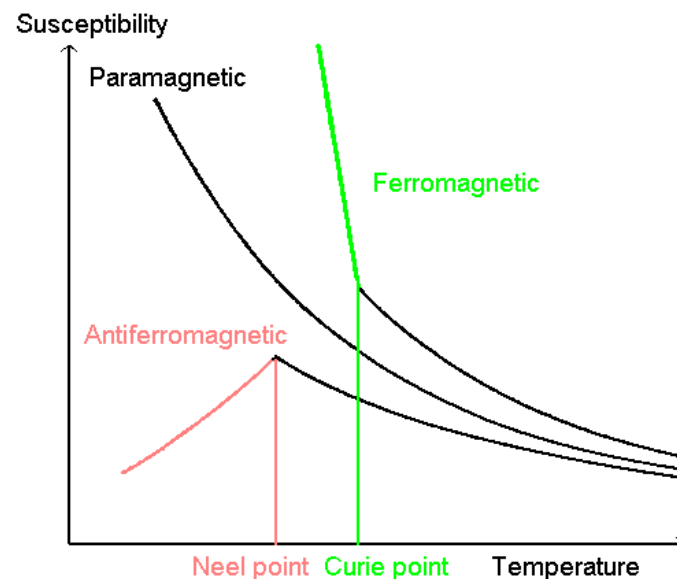
magnetic field

contribution from sample

- Permeability, $P = \frac{B}{H} = 1 + 4\pi\chi_v$,
where $\chi_v = \frac{M}{H}$ and $\chi_{mass} = \frac{\chi_v}{\rho}$
and $\chi_M = \chi_v \times \left(\frac{M_w}{\rho}\right)$

- Curie Weiss Law: $\chi = \frac{C}{T+\theta}$

Behavior	χ_M value	χ vs. inc. T	field dependence
diamagnetism	-1×10^{-6}	no effect	No
paramagnetism	0 to 10^{-2}	decreases	No
ferromagnetism	10^{-2} to 10^6	decreases	Yes
antiferromagnetism	0 to 10^{-2}	increases	Yes



Magnetic moments

- 1BM (Bohr Magnetron) = $\frac{eh}{4\pi mc}$
- $\mu_S = g\sqrt{S(S+1)}$
- $\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$
 - electric fields of surrounding atoms can restrict the orbital motion of electrons and thus wholly or partially quench the orbital angular momentum in solids.

$g = \text{gyromagnetic ratio} \sim 2.00$

- superexchange (NiO)

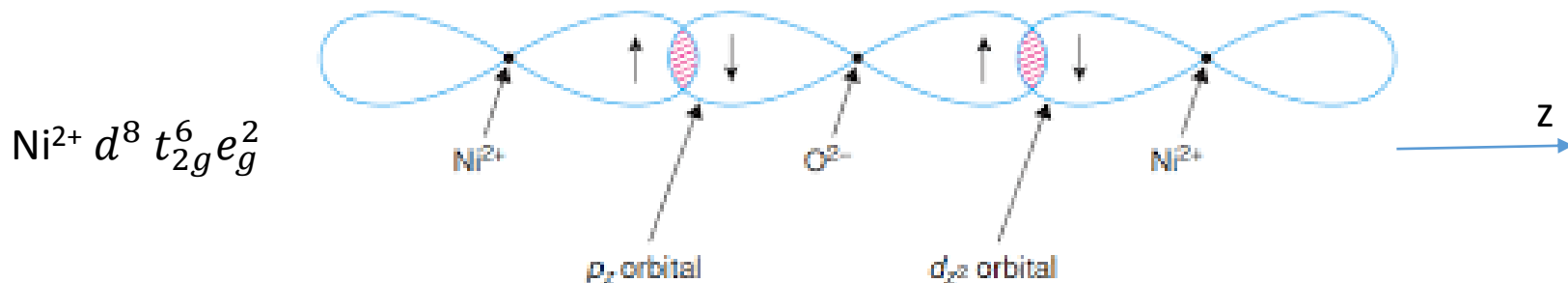
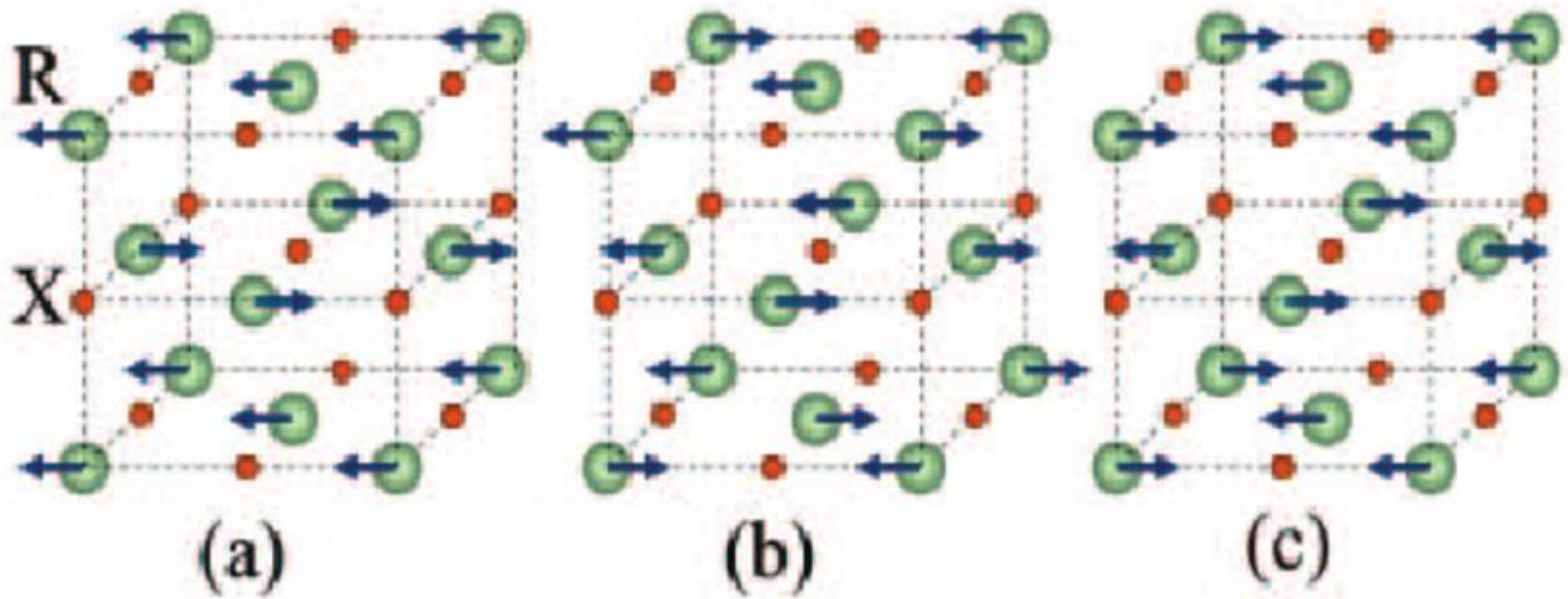
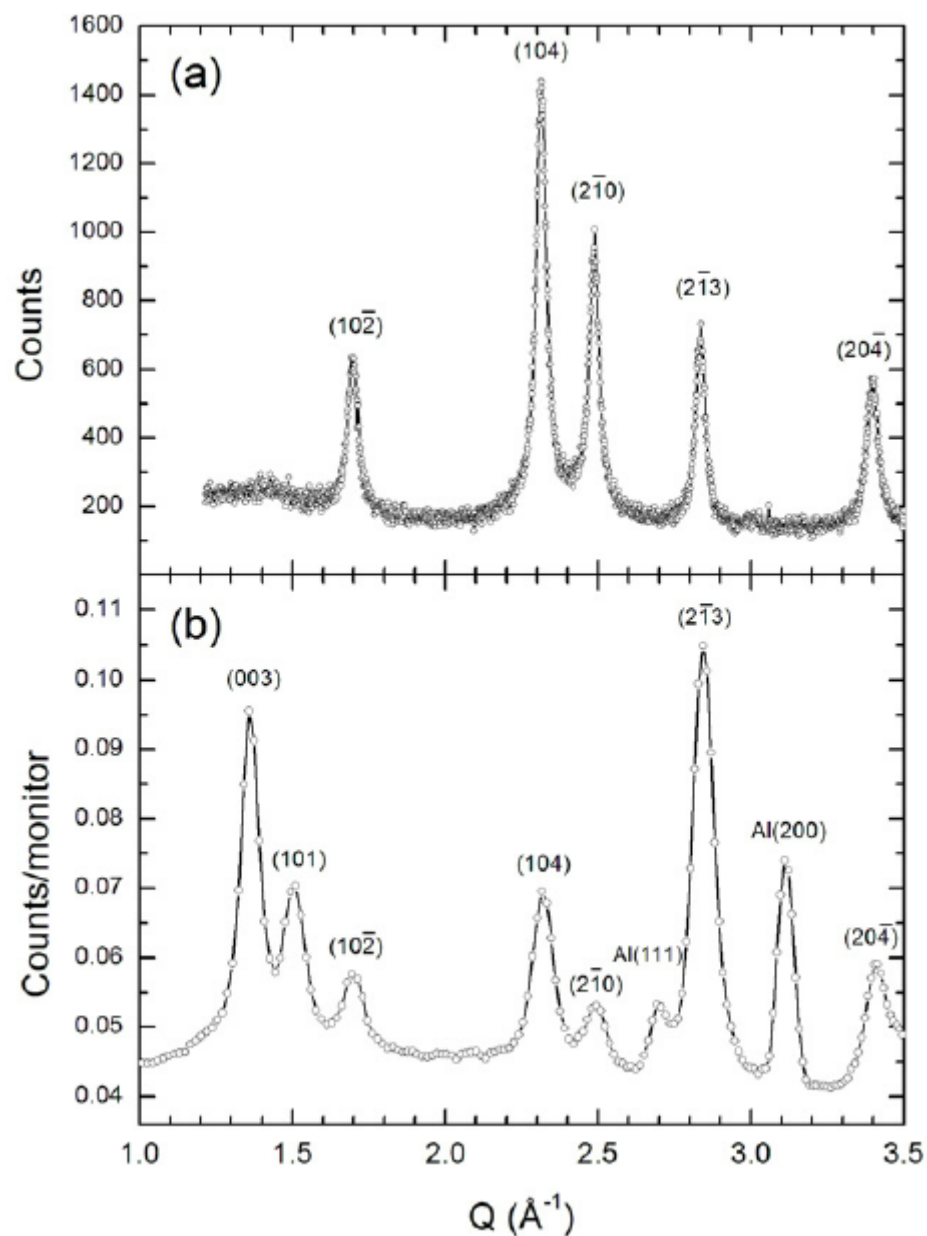


Figure 9.5 Antiferromagnetic coupling of spins of d electrons on Ni^{2+} ions through p electrons of oxide ions.

Antiferromagnetic superstructure

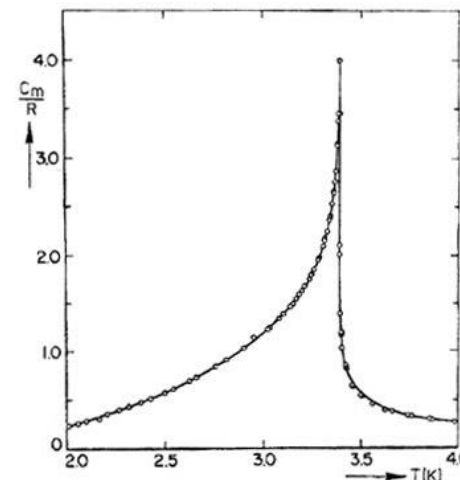


Neutron and x-ray diffraction - AFM



Materials – Metals

- Metals and alloys – Cr, Mn, Fe, Co, Ni and most lanthanides are FM/AFM
 - FM - α -Fe (bcc, [100], T_C 1043 K), Ni (fcc, [111], T_C 631 K), Co (hcp, c-axis, T_C 1404 K)
 - AFM – Mn (complex, 95 K), Cr (bcc, 313 K)
 - Fe d^6s^2 (2.2); Co d^7s^2 (1.7); Ni d^8s^2 (0.6)
 - unpaired e-s
 - band str. calc. show some s e-s go to d orbitals
 - Fe – 7.4 d e-s $\rightarrow$ 4.8 $\uparrow$ and 2.6 $\downarrow$ (unpaired 2.2)
 - max. 2.4 unpaired e-s in $Fe_{0.8}Co_{0.2}$
 - Lanthanides – mostly AFM below r.t.
 - some form both AFM and FM
 - temp dec. para $\rightarrow$ AFM $\rightarrow$ FM
 - e.g. Dy T_C 85 K, T_N 179 K



heat capacity at T_C - λ transition
order-disorder transition



Materials – Oxides

- TiO, VO, CrO – diamagnetic
 - delocalized d e-s – responsible for conductivity and diamagnetism
- AFM – MnO, FeO, CoO. NiO
 - localized e-s, unpaired – responsible for insulating behavior, magnetism

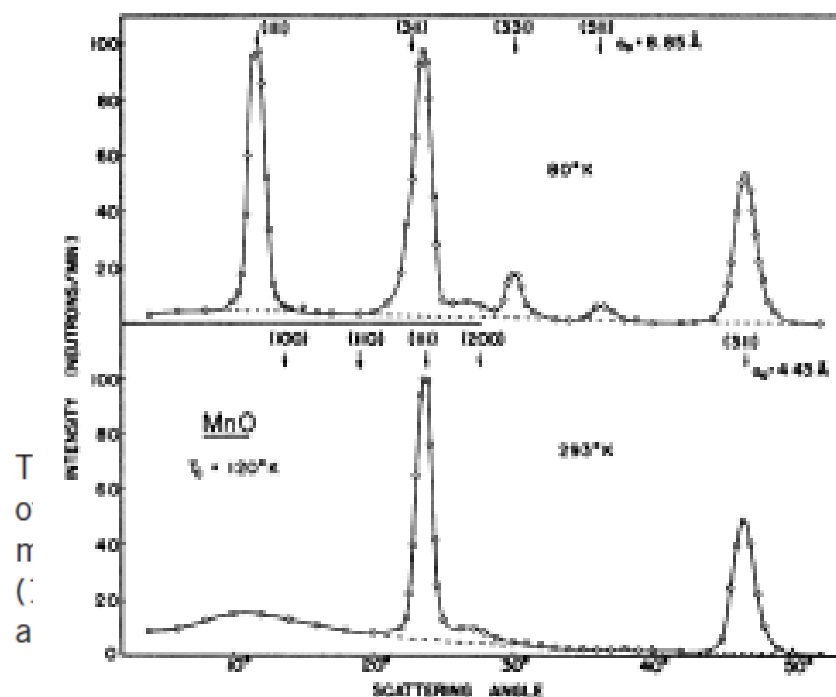
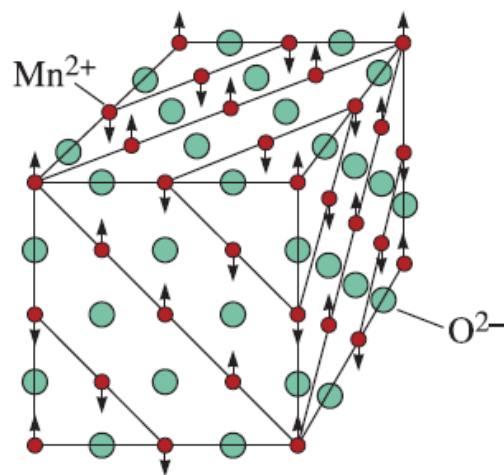


FIG. 4. Neutron diffraction patterns for MnO taken at liquid nitrogen and room temperatures. The patterns have been corrected for the various forms of extraneous, diffuse scattering mentioned in the text. Four extra antiferromagnetic reflections are to be noticed in the low temperature pattern.

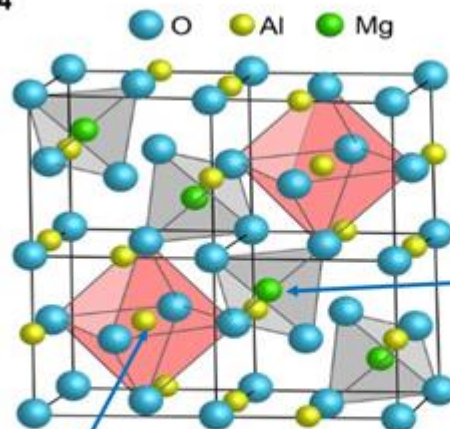
Materials – Spinel

- many different spinels.
 - also with sulfides, halides...
 - Normal: $[A]^{\text{tet}}[B]^{\text{oct}}O_4$,
 - Inverse: $[B]^{\text{tet}}[A,B]^{\text{oct}}O_4$
- Ferrites: MFe_2O_4 , M is divalent Fe^{2+} , Ni^{2+} , Cu^{2+} , Mg^{2+} - all inverse
 - $Fe^{3+} d^5$ – no CFSE, hence the larger divalent ions go into Oh sites
 - $ZnFe_2O_4$ – normal spinel AFM T_N 9.5 K weak coupling, $MgFe_2O_4$ – partly inverse, $MnFe_2O_4$ – 80% normal, 20% inverse - ferri
 - All AFM or ferrimagnets

cation	spinel
2,3	$MgAl_2O_4$
2,4	Mg_2TiO_4
1,3,4	$LiAlTiO_4$
1,3	$Li_{0.5}Al_{2.5}O_4$
1,2,5	$LiNiVO_4$
1,6	Na_2WO_4

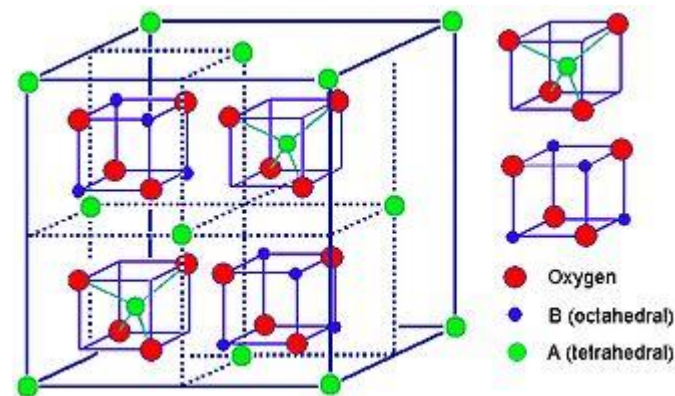
Spinel AB_2O_4

A spinel unit cell is made up of 8 FCC cells. The anions (usually oxide ions: O^{2-}) occupy the FCC lattice points. The divalent A^{II} cations occupy $1/8^{\text{th}}$ of the tetrahedral voids, whereas the trivalent B^{III} cations occupy one half ($1/2$) of octahedral voids.



B site – one metal with six nearest-neighbor oxygens.
Octahedral site

A Site – one metal with four nearest-neighbor oxygens.
Tetrahedral site



More types ...

- Garnets
 - general formula: $A_3B_2X_3O_{12}$
 - $Y_3Fe_5O_{12}$ (YIG) (B and X are the same – Fe^{3+})
- Ilmenites
 - ABO_3 : A = Fe, Co, Ni, Cd, Mg; B = Ti, Rh, Mn
 - rhombohedral structure
- Perovskites
 - ABO_3 :
 - Fe^{3+} , $Mn^{3+,4+}$: FM
 - $[La_{1-x}^{3+}A_x^{2+}][Mn_{1-x}^{3+}Mn_x^{4+}]O_3$ A2+ could be CA, Sr, Ba, Cd, Pb..
- Magnetoplumbites
 - $PbFe_{12}O_{19}$
 - $BaFe_{12}O_{19}$ - BaM



Exchange interaction and dipolar interaction

- spin requires antisymmetric wavefunction

- $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

- Electrostatic energy

- $E = \int \left[\frac{1}{2} \frac{e^2}{r_{12}} \right] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]^2 dV_1 dV_2$

- $= \int \left[\frac{e^2}{r_{12}} \right] [\alpha(1)\beta(2)]^2 dV_1 dV_2 - \int \left[\frac{e^2}{r_{12}} \right] [\alpha(1)\beta(2)\alpha(2)\beta(1)]^2 dV_1 dV_2$

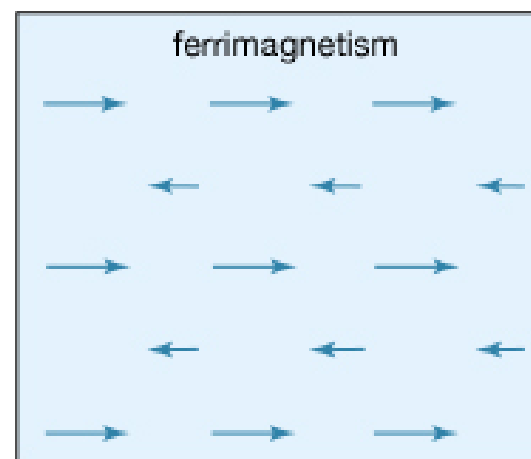
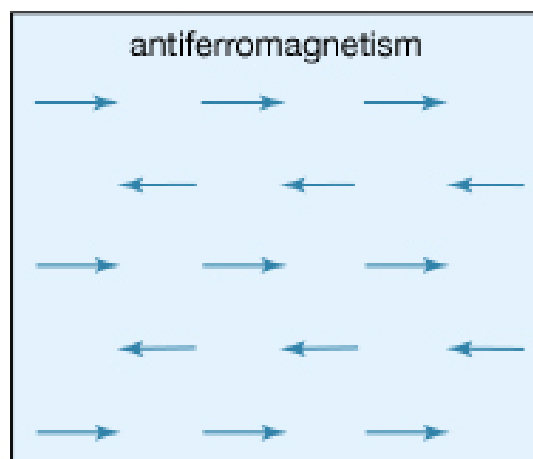
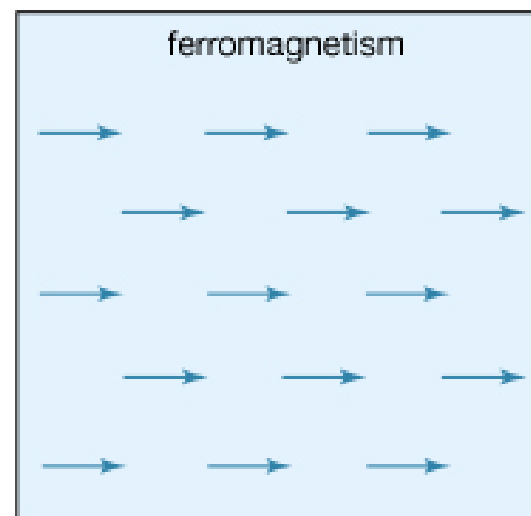
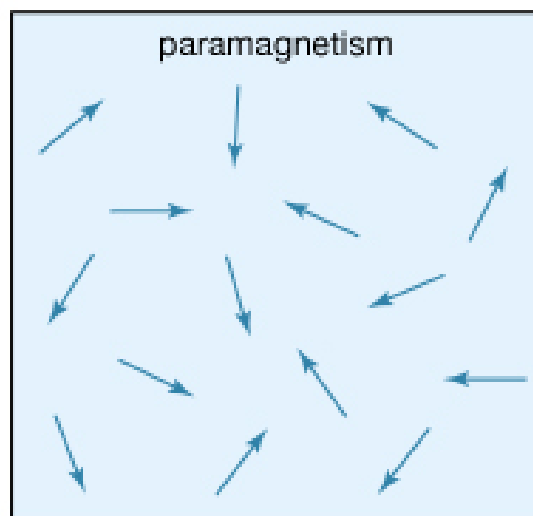
Coulomb integral

exchange integral (difference in Coulomb energy between two electrons with II and anti-II spins = $J \mathbf{S}_1 \cdot \mathbf{S}_2$)

- J exchange interaction constant $\rightarrow$ -ve for FM, +ve for AFM
 - J primarily involves nearest neighbor interactions
 - exchange – dominant interaction
- Dipole-dipole
 - $\frac{(\mu_1 \cdot \mu_2)}{r^3} - 3(\mu_1 \cdot \mathbf{r}) \frac{(\mu_2 \cdot \mathbf{r})}{r^5}$
- Magnetization, M = total magnetic moment per unit volume = vector sum of all the magnetic moments of all atoms divided by the total volume
- $\chi = M/H$
- $\chi = C/(T - \theta)$
- Both M and H have units A/m or emu/g or Oe



arrangement of magnetic moments



Magnetic interactions

- Exchange interaction

- between two spins

$$\int \psi_A(1)\psi_B(1)\psi_A(2)\psi_B(2)d\tau_1d\tau_2$$

$$J \vec{S}_1 \cdot \vec{S}_2$$

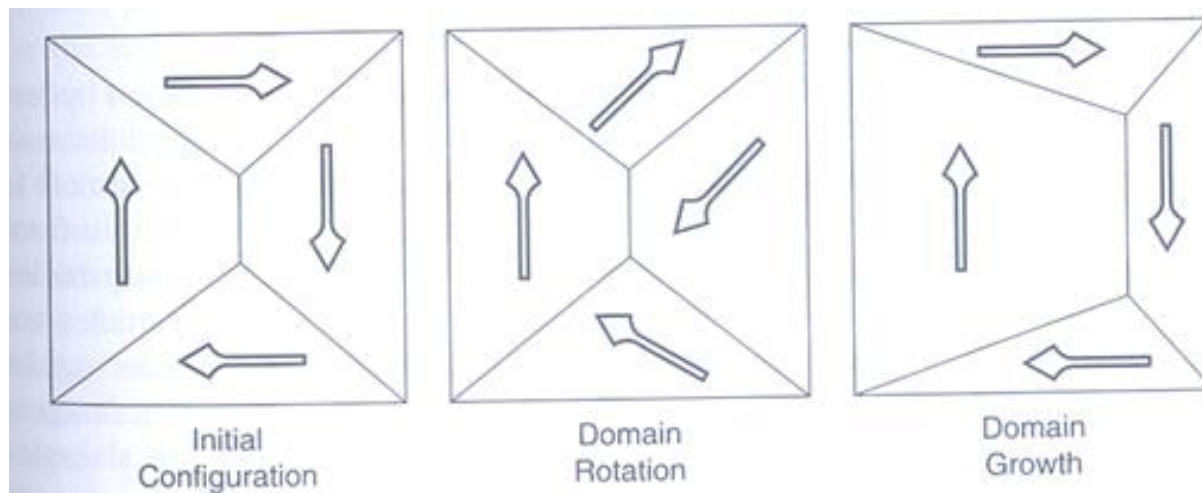
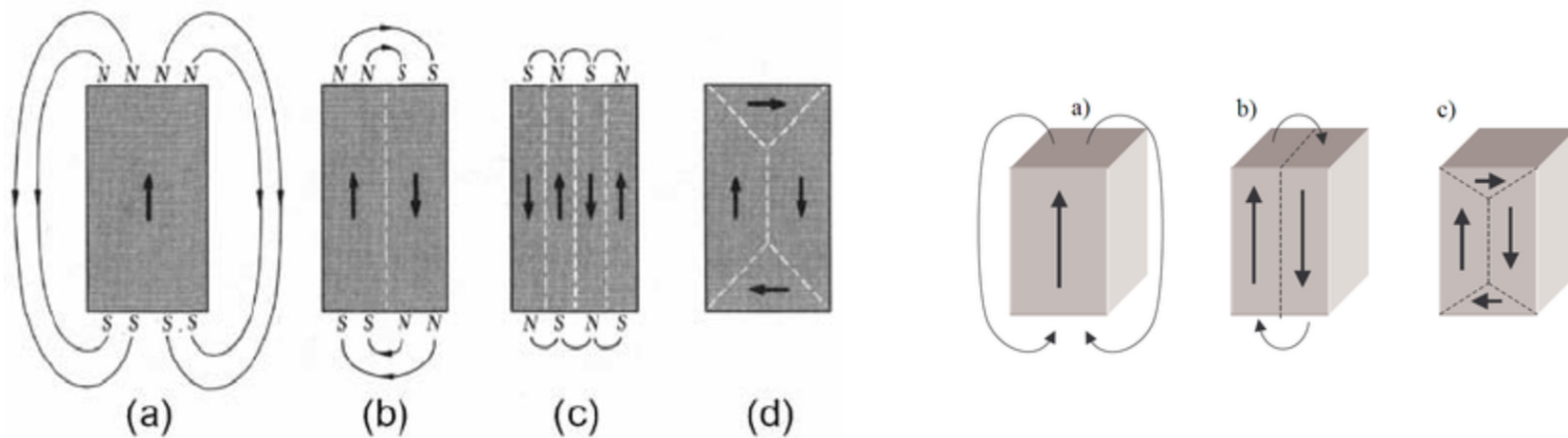
- dipole-dipole interaction

$$\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5}$$

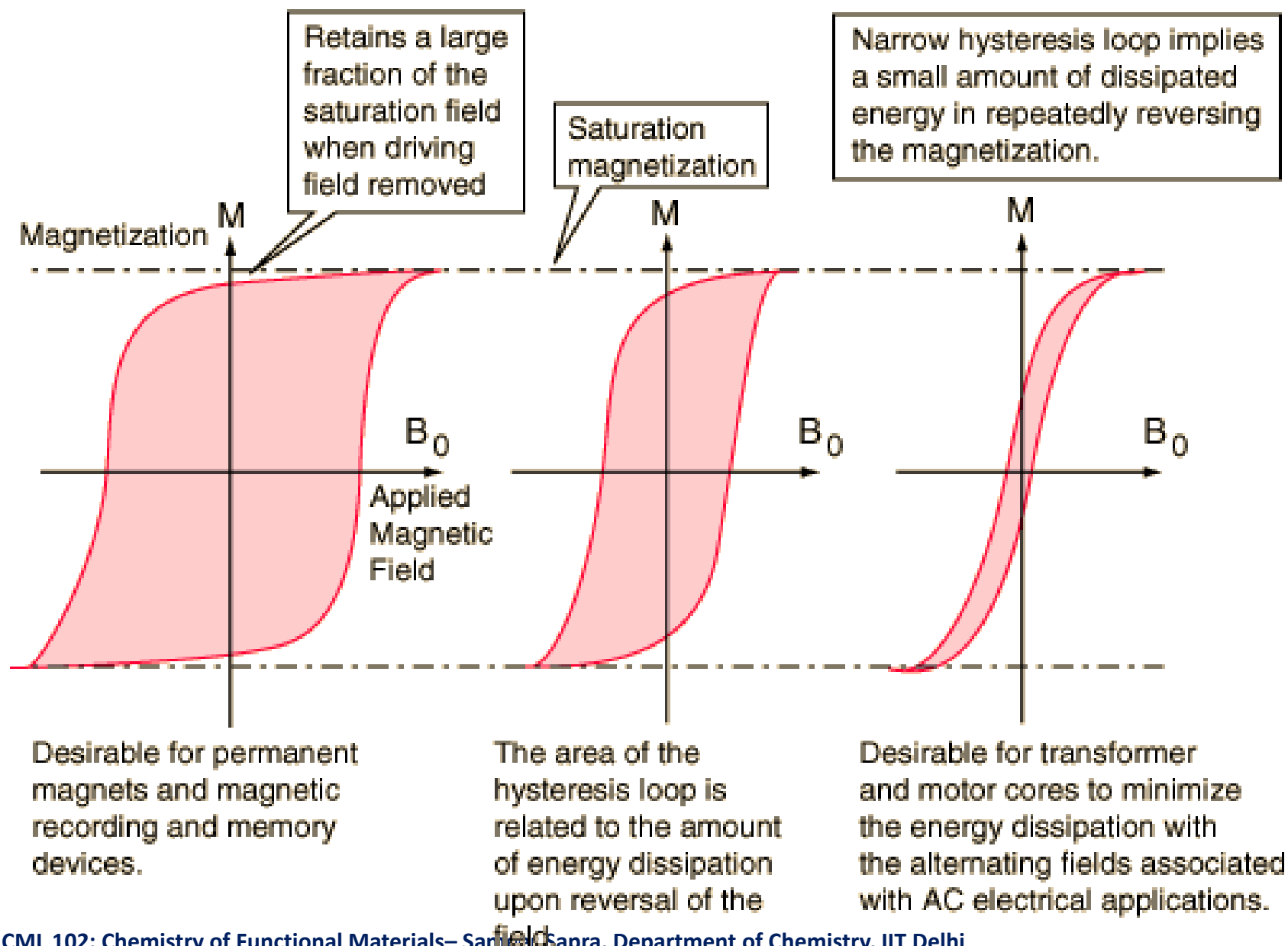


Magnetic Domains

- Weiss 1907



Hysteresis



Superparamagnetism

- single domain
 - $\text{Fe}_2\text{O}_3 < 100 \text{ nm}$
 - $\text{CoFe}_2\text{O}_4 < 50 \text{ nm}$
- apply d.c. field $\rightarrow$ align all particles in the direction of field.
 - inc. T, randomize particles
 - $k_B T$ vs. $\vec{\mu} \cdot \vec{H}$
- for a mono-domain particle, total mag mom $\propto$ # mag atoms N, $\rightarrow N\mu_i$
 - inc. as the size of the NP increases
 - levels off as the particles become multi-domain
 - surface effects – ignored
 - oxides on surface affect magnetic properties. e.g. NiO on surface expands the lattice at the surface for NPs $< 40 \text{ nm}$. This reduces the exchange interaction $\rightarrow$ reduces magnetization



Individual magnetic NPs

- magnetic bits
 - 10 GB / sq. in. $\rightarrow$ 1μ long, 70 nm wide, 30 nm film thickness
 - Co-Cr alloys
- What happens when size is further reduced, say < 10 nm?
- Stoner-Wohlrath (SW) model – particles smaller than single domain
 - spins are all aligned or alternating
 - particle orientation to lower magnetic energy
 - $\exp -E_a/k_B T$ thermal activation to switch over
 - Anisotropy energy of single domain particle, $E_a = KV \sin^2 \theta$
 - K anisotropy constant, V volume of NP, θ angle bet. NP easy axis and applied mag. field
 - quantum mechanical tunnelling
 - Average time between mag. reorientation in superparamagnetic particles – Neel theory $\tau = \tau_0 \exp(KV/k_B T)$
 - particle's magnetic energy is the sum of all the individual moments – depends upon the particle volume
 - neglects surface
 - coercive fields are overestimated



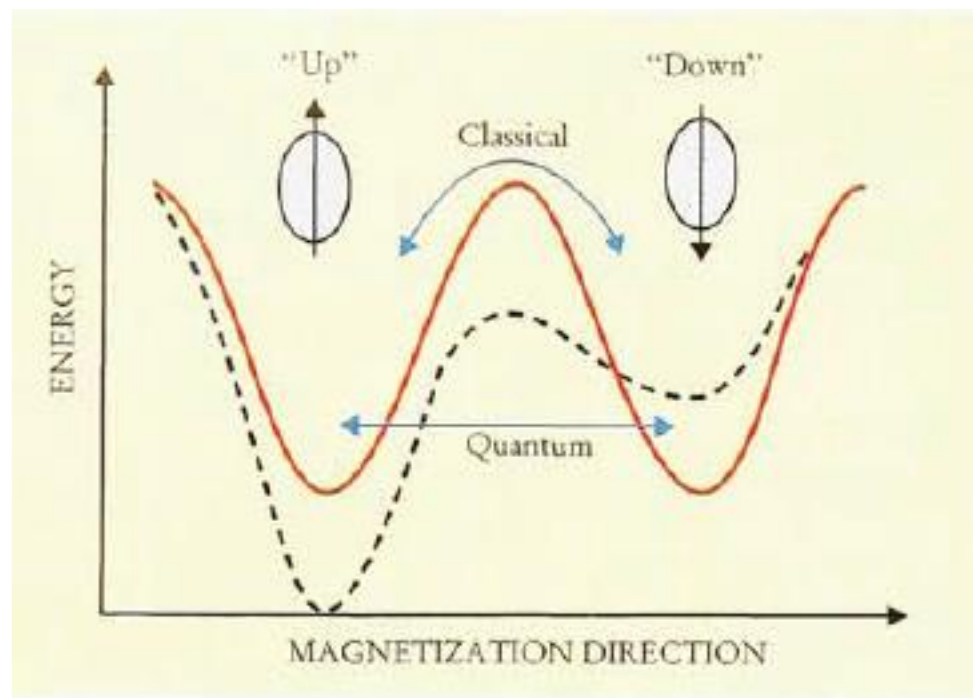


Table 1 Estimated and experimental single domain critical size for common magnetic materials

<i>Estimated</i>		<i>Experimental</i>	
<i>Material</i>	D_{crit} (nm)	<i>Material</i>	D_{crit} (nm)
Co	70 [4], 55 [5]	NiFe ₂ O ₄	40–60 [9,10]
Fe	14 [4], 20 [6]	CoFe ₂ O ₄	50 [9,10]
Ni	55 [4], 65 [7]	Fe ₃ O ₄	< 100 [8]
γ -Fe ₂ O ₃	166 [4]		
Fe ₃ O ₄	128 [4], 50 [8]		

Superparamagnetism

- Small particles < domain size
 - no cooperativity
 - no domain interaction
 - no hysteresis
 - no ferromagnetism – only superparamagnetism
- Blocking temperature T_B
 - temp below which the mag moments are locked, above the temp they are random
 - $kT > \vec{\mu} \cdot \vec{H}$
 - ZFC/FC measurements



Synthesis of Metal caboxylates (Iron oleate)

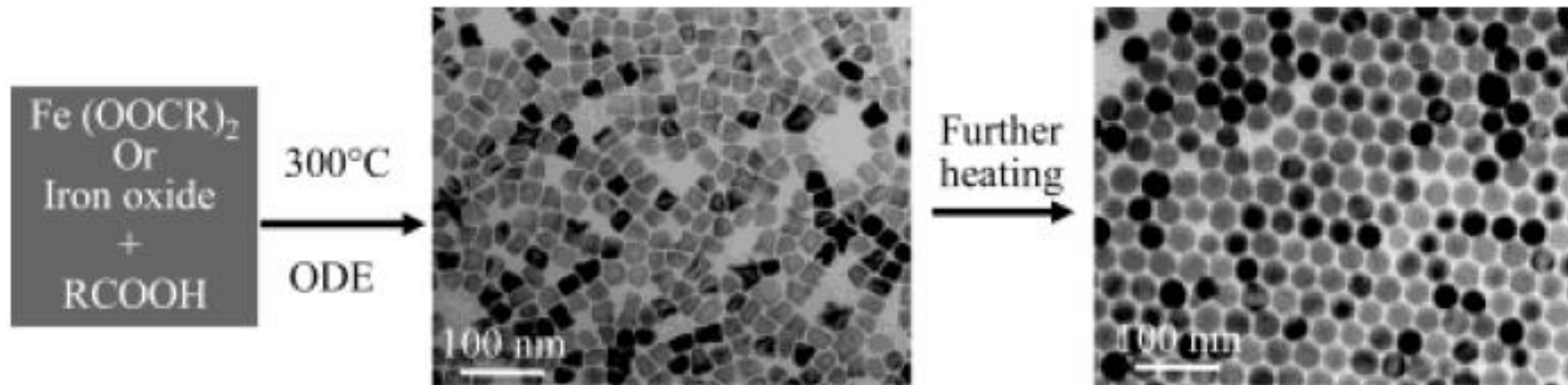
- 5.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or 4 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 100 mL of methanol, and then oleic acid was added in 3 equiv (17 mL) for ferric salt and 2 equiv (11 mL) for ferrous salt. Into one of these two solutions, a NaOH solution with 2.4 g (for ferric) or 1.6 g (for ferrous) of NaOH in 200 mL of methanol was dropped under magnetic stirring conditions. The observed brown precipitate was washed with methanol 4-5 times and dried under vacuum overnight to remove all solvents.
- The salts made by the above procedure (approximately 1 mmol dissolved in 10 mL of CHCl_3) was added dropwise into a stirred concentrate hydrochloric acid aqueous solution for digestion. The brown-colored complex was converted into faint yellow-colored iron chloride complex which was in the aqueous phase. The colorless chloroform extract, containing carboxylic acid, was collected, dried, and weighed. Based on the results, the complex composition was determined as $\text{Fe}^{\text{III}}(\text{oleate})_3$ or $\text{Fe}^{\text{II}}(\text{oleate})_2$.
- The brown-colored solid was dissolved in 20 mL of 1-octadecene (technical grade, 90%) at 60-70 °C and preserved as a stable stock solution at room temperature for the next step.

Chem. Mater. 16, 3931 (2004)



Fe₃O₄ synthesis

- The Fe₃O₄ nanocrystals were prepared by the decomposition of iron-oleate [Fe(II)/Fe(III)] complexes at 300 °C using octadecene as the solvent. The particle sizes can be controlled between 8 and 50 nm without using any activation reagent, by varying the amount of excess oleic acid, or by changing the concentration of the precursor salt during the reaction. Other nonspherical shapes such as cubes or spheroids can also be obtained by freezing the reaction at early stages.
- In a typical synthesis, 1 mL of the stock solution made in the first step was mixed with 4 mL of octadecene and an appropriate amount of oleic acid (from 0.1 to 10 equiv) and the mixture was heated to 300 °C under an argon atmosphere. The reaction progress could be monitored by taking aliquots at different reaction times and observing the nanocrystals in the aliquots under TEM (JEOL 100 CX, 100 kV, copper grids coated with Formvar film). XRD was recorded using the standard methods reported previously.³¹ FTIR was used to verify that the nanocrystals were coated with the corresponding fatty acid in its ionized form (R-COO⁻).



CoFe₂O₄ synthesis

- CTAB [(C₁₆H₃₃)N(CH₃)₃]Br; cetyltrimethylammonium bromide (surfactant)
- n-octane (oil)
- n-butanol (cosurfactant)
- 2 solution
 - microemulsion 1: CTAB/n-octane/n-butanol + Co(NO₃)₂ + Fe(NO₃)₃ (1:2)
 - microemulsion 2: CTAB/n-octane/n-butanol + 10% NH₄OH in excess
 - mix and stir the solutions → NPs ppt → wash with MeOH and CHCl₃.
- Calcine the dried ppt at 600 °C for 5 hours.
- Int. J. Nanotechnol. **1**, 240 (2004)

