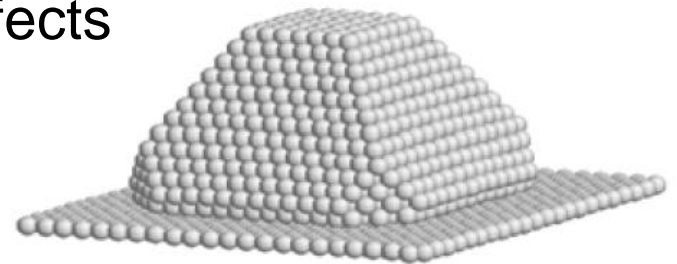# NTNU
Norwegian University of Science and Technology

TMT4320 Nanomaterials
Septemeber 5th, 2016

- Physical properties: size effects
- TNN. Chapter 2.
- NN. Chapter 8.

Last lecture

- Defects
  - ➢ Examples
  - ➢ Problem B

- Physical properties: size effects
  - ➢ Lattice constant
  - ➢ Melting point

Microstructure and defects

Defects in Crystalline materials

How are defects classified?
- Point defects (0D)
  - Metal and alloys → Vacancies, substitutional and interstitial
  - Ionic solids → Schottky (anion-cation vacancy pairs) and Frenkel (vacancy-interstitial pairs) defects
- Line deffects (1D)
  - Dislocations: missing plane of atoms
- Surface defects (2D)
  - Grain boundaries, twins, stacking faults and free surfaces.
- Volume defects (3D)
  - Voids and microcracks.

Physical properties of Nanomaterials

Properties differ a lot between dimensions on an atomic scale and the dimensions which characterize bulk materials

1) Lower **melting point** or **phase transition temperature** and reduce **lattice parameters** due to a huge fraction of surface atoms in the total amount of atoms (More in deep today)

2) **Mechanical properties** may reach the theoretical strength (2 times more than single crystal) due to the reduce probability of defects.

Physical properties of Nanomaterials

Properties differ a lot between dimensions on an atomic scale and the dimensions which characterize bulk materials

3) **Optical properties**. Optical absorption peak of a semiconductor nanoparticle shifts to a short wavelength due to an increased bandgap. Color of metallic nanoparticles may change with size due to surface plasmon resonance.

4) **Electrical conductivity** decreases with reduced dimension due to increased surface scattering. However, it could be enhanced due to better ordering in microstructure.

5) **Magnetic properties.** Ferromagnetism of bulk materials disappears and transfers to supermagnetism in the nanometer scale due to huge surface energy.

Fraction of surface atoms

- Surface atoms are important for chemical reactivity (catalysis) and crystal growth

- Nanoparticles
  - 5 nm: around 8000 atoms
  - 2 nm: around 500 atoms

- Surface/volume ratio
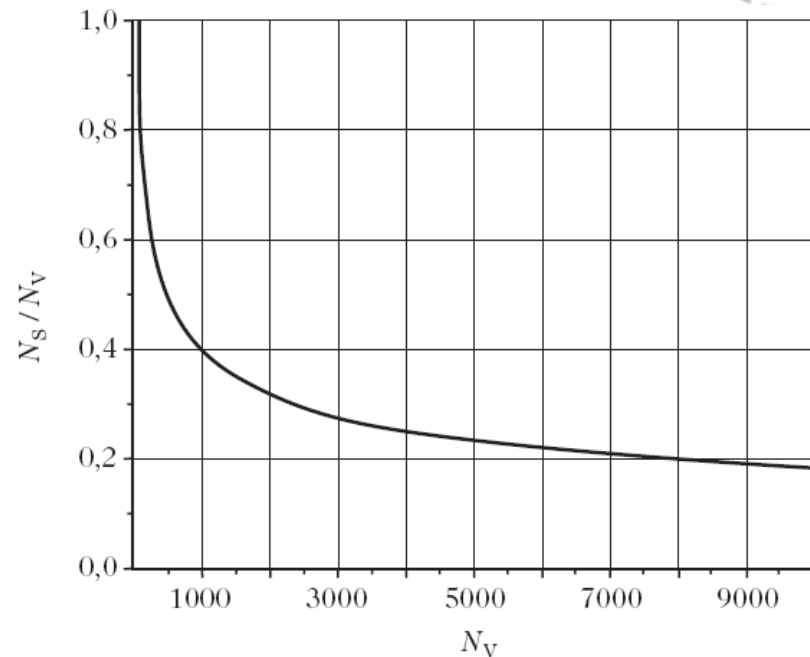
Proportion of surface atoms for a spherical particle comprising N_V atoms with N_S at the surface

Specific surface energy

- γ (J/m²)

- The energy produced by cleaving a crystal divided by the surface area thereby created

- In order to increase the surface area of an object by an amount dA, e.g., by changing the shape of the object, the work required to do this will be:

$$\mathrm{d}W = \gamma \mathrm{d}A$$

- Also expressed as:

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{n,T,P} \quad \text{or} \quad \gamma = N_b \left(\frac{1}{2}\varepsilon \right) = \frac{1}{2} n_a \cdot n_b \varepsilon$$

N_b = number of bonds broken per unit area $\qquad \varepsilon$ = bond energy
n_a = number of surface atoms per unit area $\qquad n_b$ = number of bonds broken per atom

Surface stress

- g_{ij} (J/m^2)
- If one increase the area by stretching it, i.e., keeps the number of surface atoms constant, the work required to do this will be:

$$dW = g_{ij}dA$$

- The surface stress is related to the elastic stresses resulting from deformation of the surface (strain)

Surface curvature

- Surface energies given in handbooks are for flat surfaces
- Surface energy and hence chemical potential (μ) of the surface atoms change with curvature

$$\Delta\mu = \mu_C - \mu_\infty = 2\gamma\frac{\Omega}{r}$$

where μ_C = chemical potential of curved surface

μ_∞ = chemical potential of flat surface

Ω = atomic volume

r = radius of curvature (> 0 for convex surface, < 0 for concave surface, ∞ for flat surface)

- $\mu_{convex} > \mu_{flat} > \mu_{concave}$

Effects on the melting point

Decrease in bonding energy due to enhance surface and grain boundary area in nanocrystalline materials can reduce the enthalpy of fusion and the melting temperature

Melting point → Solid and liquid in equilibrium →

Thermodinamically: $\mu_i^l = \mu_i^s$

Chemical potential

Surface energy

Due to inherent internal pressure: $P_s > P_l$

$$P_s = P_l + \frac{2\gamma}{r}$$

radius

Effects on the melting point

Chemical potential related with pressure: $d\mu = -SdT + VdP$

$\mu_i^l = \mu_i^s$ $\qquad$ $S_l - S_s = \Delta S_m$ $\qquad\qquad$ $\Delta S_m dT = \dfrac{-2V\gamma dr}{r^2}$

Chemical
potential

Entropy at
melting point

Effects on the melting point

Chemical potential related with pressure: $d\mu = -SdT + VdP$

$\mu_i^l = \mu_i^s$ $S_l - S_s = \Delta S_m$ $\Delta S_m dT = \dfrac{-2V\gamma dr}{r^2}$

$\Delta S_m = \dfrac{\Delta H_m}{T_m}$ $\Delta T = \dfrac{2V\gamma T_m}{r\Delta H_m}$

Bulk melting temperature

Change in melting point is inversely proportional to radius on the spere → Grain size is reduced, melting point is lowered

Effects on the melting point

Chemical potential related with pressure: $d\mu = -SdT + VdP$

$$\mu_i^l = \mu_i^s \qquad S_l - S_s = \Delta S_m \qquad \Delta S_m dT = \frac{-2V\gamma dr}{r^2}$$

$$\Delta S_m = \frac{\Delta H_m}{T_m} \qquad \boxed{\Delta T = \frac{2V\gamma T_m}{r\Delta H_m}}$$

Change in melting point is **inversely proportional** to **radius** on the spere → **Grain size is reduced, melting point is lowered**

Effects on the melting point

Examples:

Nano-CdS of diameter ~2.5 nm melts at 600 K (bulk at 1675 K)

Single-walled carbon nanotube melts at 1600 K (bulk at 3800K)

Effects on the melting point

In contrast to nanoclusters and nano-agglomerates, **nanoparticles within a matrix may experience an enhancement in the melting temperature**. Matrix exterts pressure (p) that affects melting temperature

$$p = \frac{2\mu\kappa\Delta V}{3V_o}$$

μ = shear modulus (rigidity/stiffness) of the matrix

κ = Dimensionless particle (presence of other particles)

ΔV = change of V due to thermal expansion

V_o = initial particle volume

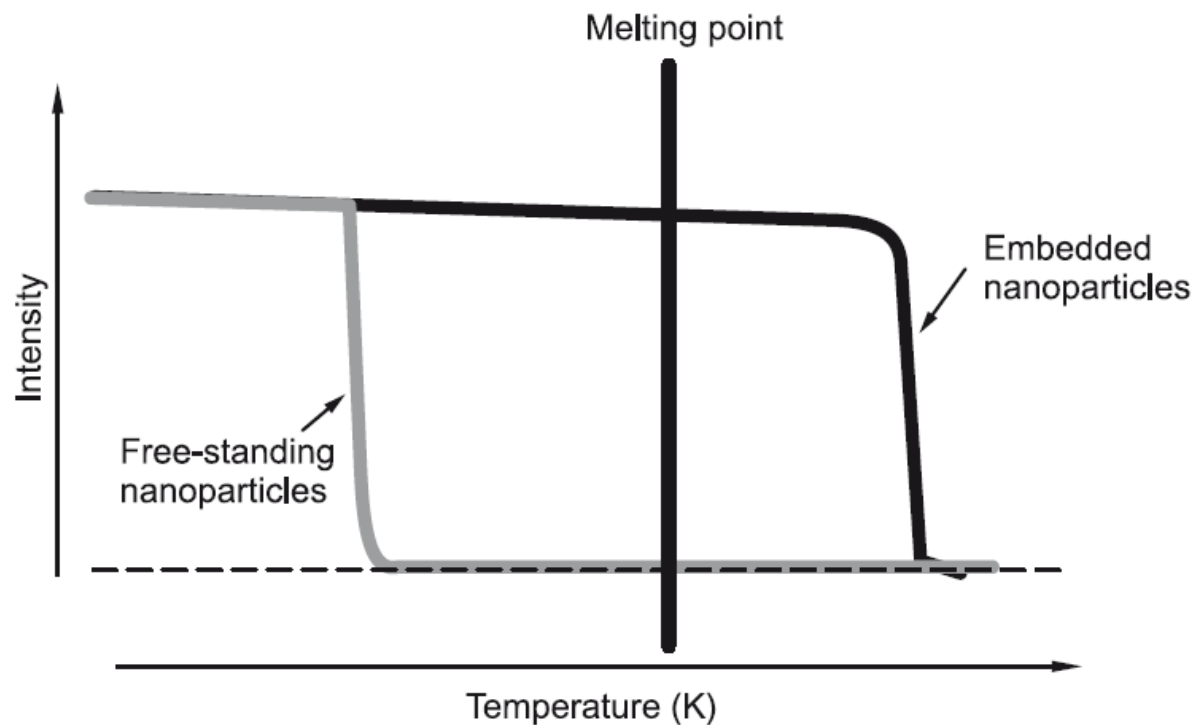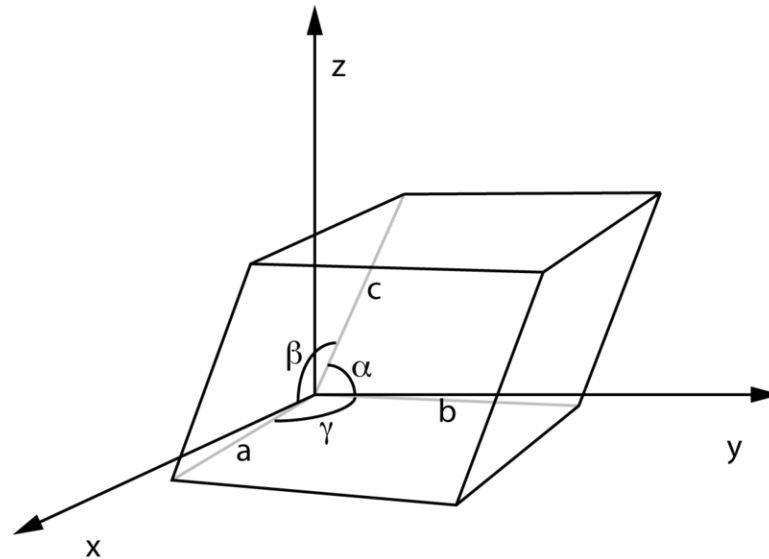# Effects on the melting point

Fig. 2.4 Schematic diagram showing melting of free-standing nanoparticles and that of nanoparticles embedded in a higher melting matrix.

Effect on the lattice parameter

- The lattice parameter (or lattice constant) refers to the constant distance between unit cells in a crystal lattice

- Is the lattice parameter affected by increased surface/volume ratio (decreased nanoparticle size)?

Effect on the lattice parameter

- Ex.: A liquid sphere of diameter $2R$
  - Due to the curvature of the surface, a pressure is generated toward the inside of the sphere
  - The excess pressure ΔP inside the sphere, in the purely hydrostatic case, is given by the Laplace equation

$$\Delta P \mathrm{d}V = \gamma \mathrm{d}A$$

  - $\mathrm{d}V$ is the volume change corresponding to a change $\mathrm{d}A$ in the area of the droplet
  - In the case of a sphere, we obtain:
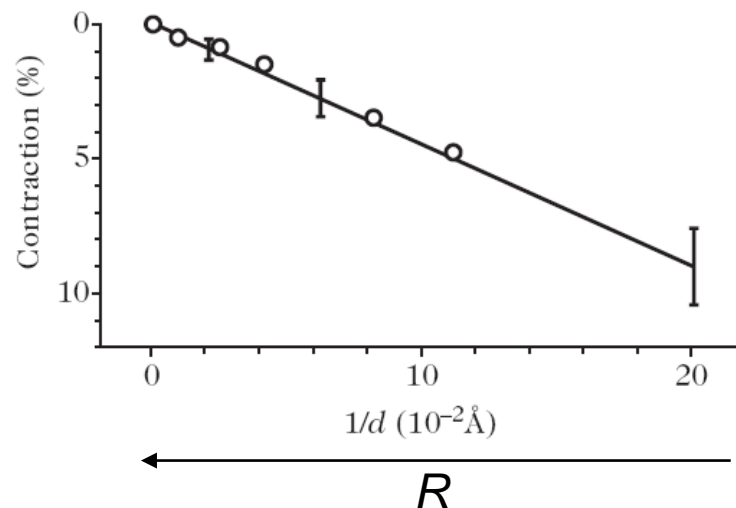
$$\Delta P = 2\gamma/R$$

- For a spherical solid:
  - γ replaced by g_{ij}
  - χ = compressibility
  - a = lattice parameter

$$\frac{\Delta a}{a} = -\frac{2}{3}\chi\frac{g}{R}$$

Effect on the lattice parameter (cont.)

- Contraction of the crystal lattice due to the pressure exerted toward the interior of the particle

    – Proportional to the surface stress

    – Inversely proportional to the particle size

$$\frac{\Delta a}{a} = -\frac{2}{3} \chi \frac{g}{R}$$

Contraction of the lattice parameter of copper clusters as a function of the reciprocal of their diameter

- NB: Here metal nanoparticles

Effect on diffusivity

Nanocrystalline materials exhibit enhanced self-diffusivity in comparison to microcrystalline materials of the same composition

Diffusion kinetics increases with increasing defect content of the material such as vacancy concentration.

Grain boundaries and dislocation provide easy diffusion paths compared to bulk lattice, because the structrue is more open/defective.

Fewer atomic bonds have to be disrupted for difussion along these defects, resulting in lower activation energy paths.

The numerous interfaces in nanocrystalline materials provide a high density of diffusion paths.

Effect on diffusivity

Diffusion coefficient obeys an Arrhenius-type relation with temperature

$$D = D_o \, e^{(-Q/RT)} \qquad\qquad Q = E_a \text{ for diffusion}$$

$Q_l = E_a$ for diffusion in the lattice

$Q_d = E_a$ for diffusion in a dislocation

$Q_{gb} = E_a$ for diffusion in grain boundary

$Q_s = E_a$ for diffusion in a surface

$$Q_l > Q_d > Q_{gb} > Q_s$$

Effect on diffusivity

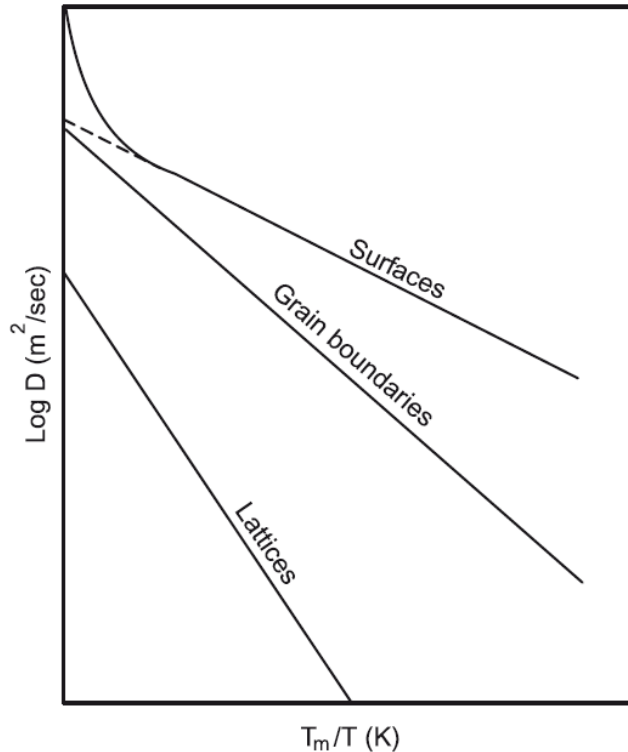Log D vs 1 T → slope proportional to E_a

Fig. 2.5 Schematic showing diffusivity in metals along various diffusion paths. The higher diffusivity along the short circuit paths, such as grain boundaries and surfaces, is demonstrated in the figure.

$$D_{eff} = D_1 + (\delta/d)\,D_{gb} + f\,(V_d/d)\,D_p + f\,(V_s/d)\,D_s$$

Table 2.2 Diffusivities in nanomaterials (in m^2/s at 300 K)

System	Bulk	Glass	Nano
$^{67}Cu/Cu$	10^{-39}	—	10^{-19}
Ag/Cu	10^{-39}	10^{-36}	2×10^{-19}

Grain growth characteristics

Nanocrystalline materials have a significant larger surface area per unit volume fraction of grain boundaries compared to microcrystalline solids

There is always a driving force for reduction in the grain boundary surface area per unit volume → Coarsening of smaller grains involving migration of grain boundaries

Reduction in grain boundary surface area per unit volume is the major driving force for grain coarsening in nanocrystalline materials, in order to reduce the net energy of the system

This is a diffusion limited process that depends on composition and temperature

Grain growth characteristics

Exponential dependence on the temperature

$$r^n = r_0^{\ n} + \exp\left(\frac{-Q_{gb}}{RT}\right)$$

r = radius of the crystal

r_0= material constant

Q_{gb} = E_a for grain boundary migration

N = exponent factor → 2 in microcrystalline materials; much higher in nanocrystalline materials.

Grain growth characteristics

Problematic for high temperature application but sometime and advantage.

Example of Rokas with $BaZrO_3$.

Material very difficult to sinter.

Table I. Sintering Temperature, Density, Cell Parameters, Average Grain Size, Vickers Hardness and Fracture Toughness of $BaZr_{1-x}Y_xO_{3-2/x}$ and $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95}$ Ceramics. Sintering Time was 10 h

Compound	$T_{sintering}$ (°C)	Density (%)	Cell parameter (Å)	Average grain size (μm)	Vickers Hardness (H_v)	Fracture toughness (MPa·m$^{1/2}$)
BZ	1600	97 ± 1	4.1931 ± 0.0001	0.99 ± 0.14	868 ± 23	1.81 ± 0.18
					867 ± 33	*1.78 ± 0.09*
BZY5	1600	95 ± 1	4.1953 ± 0.0001	0.18 ± 0.01	946 ± 34	1.84 ± 0.12
					951 ± 18	*1.83 ± 0.04*
BZY10_1600	1600	95 ± 2	4.1981 ± 0.0001	0.24 ± 0.01	895 ± 19	1.86 ± 0.05
					884 ± 13	*1.80 ± 0.1*
BZY10_1700	1700	95 ± 1	4.1978 ± 0.0001	0.61 ± 0.02	1049 ± 22	1.82 ± 0.07
					1042 ± 28	*1.85 ± 0.04*
BZY10_1600*	1600	95 ± 1	4.2074 ± 0.0001	0.52 ± 0.04	742 ± 7	1.58 ± 0.13
BZY20	1600	95 ± 2	4.2151 ± 0.0001	0.64 ± 0.03	801 ± 20	1.79 ± 0.08
					805 ± 11	*1.81 ± 0.08*
BCZY27_1600	1600	95 ± 2	4.2494 ± 0.0001	0.28 ± 0.04	858 ± 21	1.65 ± 0.11
					857 ± 13	*1.64 ± 0.06*
BCZY27_1700	1700	95 ± 1	4.2492 ± 0.0001	0.63 ± 0.07	842 ± 15	1.56 ± 0.07
					844 ± 22	*1.55 ± 0.07*
BCZY27_1600*	1600	94 ± 1	4.2509 ± 0.0001	0.7 ± 0.08	734 ± 23	1.46 ± 0.03

Italic: Vickers hardness and fracture toughness after exposure to synthetic air at 650°C for 10 h.

Enhanced solid solubility

The solubility of a solute A in a solvent B may be enhanced in nanocrystalline materials in comparision with microcrystalline materials

This is control by the chemical potential (μ) of A in B

Very useful property for the pharmaceutical industry

Enhanced solid solubility

Fig. 2.8 Schematic showing hydrogen adsorption in nanocrystalline material with decreasing grain size.
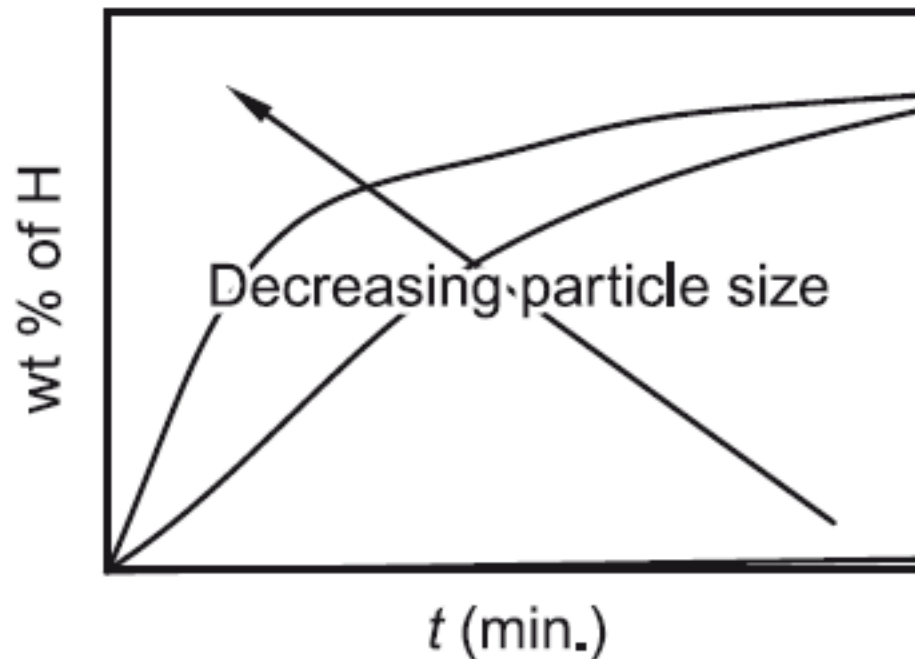
Solubility of H in Pd is increased by a factor of 10 to 100 relative to a Pd single crystal
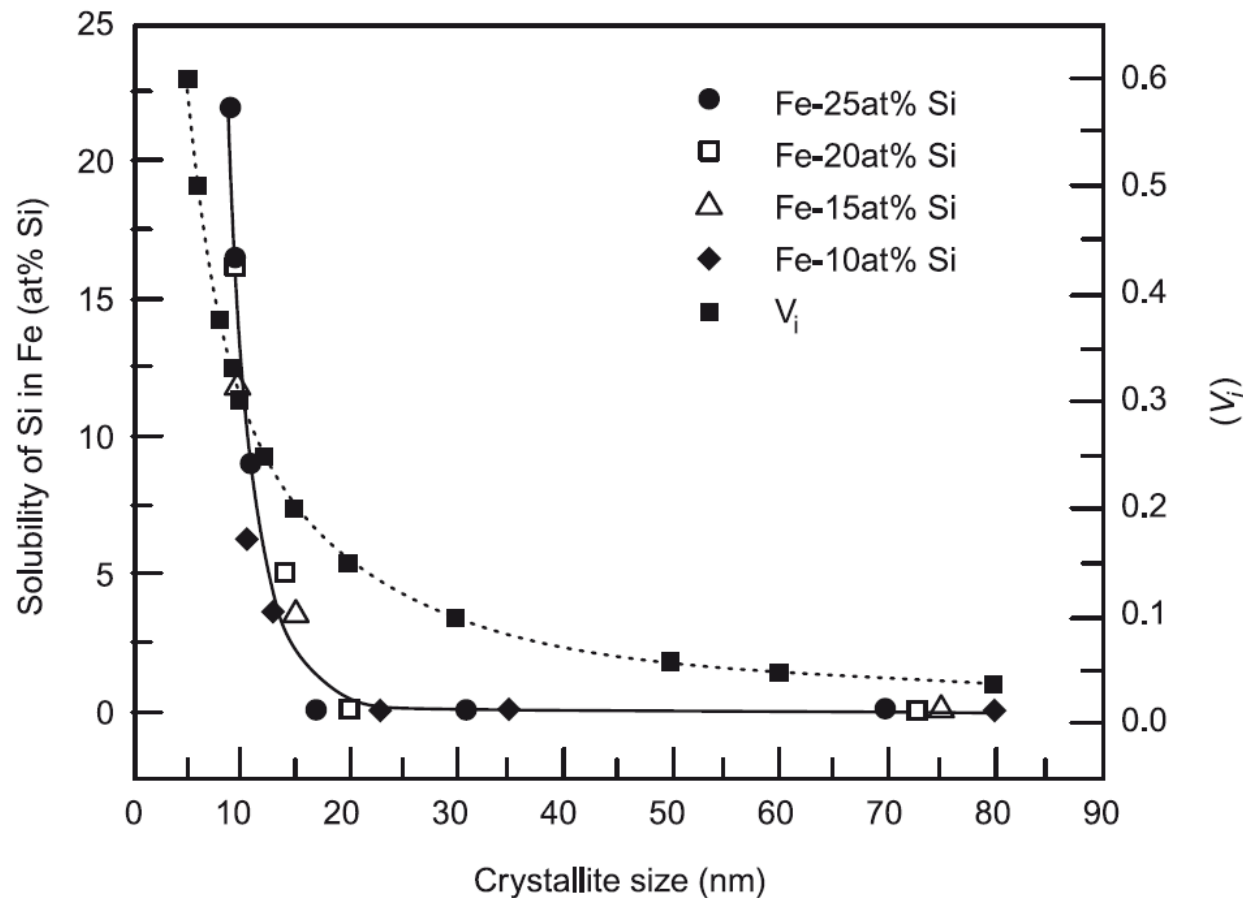
Enhanced solid solubility

Fig. 2.9 Solubility of Si in Fe as a function of crystallite size of Fe. The figure demonstrates significantly higher solubility of Si in nanocrystalline Fe below 20 nm. (*Source:* BS Murty, IIT Madras).

Effect on the magnetic properties

The strength of a magnet is decided by its coercivity (resistance of a material to be demagnetized) and saturation magnetization(effect observed when a materials cannot increase the magnetization applying a magnetic field) values

These values cahnge when the grain size decreases and the specific surface area per unit volume of the grains increases

-Soft Magnetic Nanocrystalline Alloys

-Permanent Magnetic Nanocrystalline Materials

-Giant Magnetoresistance

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

In Microcrystalline soft magnetic alloys, low coercivity has been achieved using coarse-grained materials that magnetic flux pinning at the grain boundaries is avoided.

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

In Microcrystalline soft magnetic alloys, low coercivity has been achieved using coarse-grained materials that magnetic flux pinning at the grain boundaries is avoided.

In nanocrystalline alloys, when the grain size is much smaller that the domain wall width, the magnetic anisotropy is averaged over many grains and orientations and hence the coercivity is significantly reduced and permeability is enhances

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

Fig. 2.10 Amorphous ribbon of Fe–Si–B–Nb–Cu alloy. (*Courtesy:* Bhaskar Majumdar, DMRL, Hyderabad).

Fe-Si-B-Nb-Cu alloy transform to BCC Fe-Si solid solution with grain size of ~10 nm.

Cu → Increase BCC

Nb → retards grain growth

✓ Low core losses

✓ Good saturation induction but still lower than Fe-metalloid alloys

Fe-Zr-B better saturation induction → Higher Fe content

Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

Labels on panel (b) inset: Fe$_3$Si (422), Fe$_3$Si (400), Fe$_3$Si(200), Fe$_3$Si(111), Fe$_3$Si(220), +Amorphous
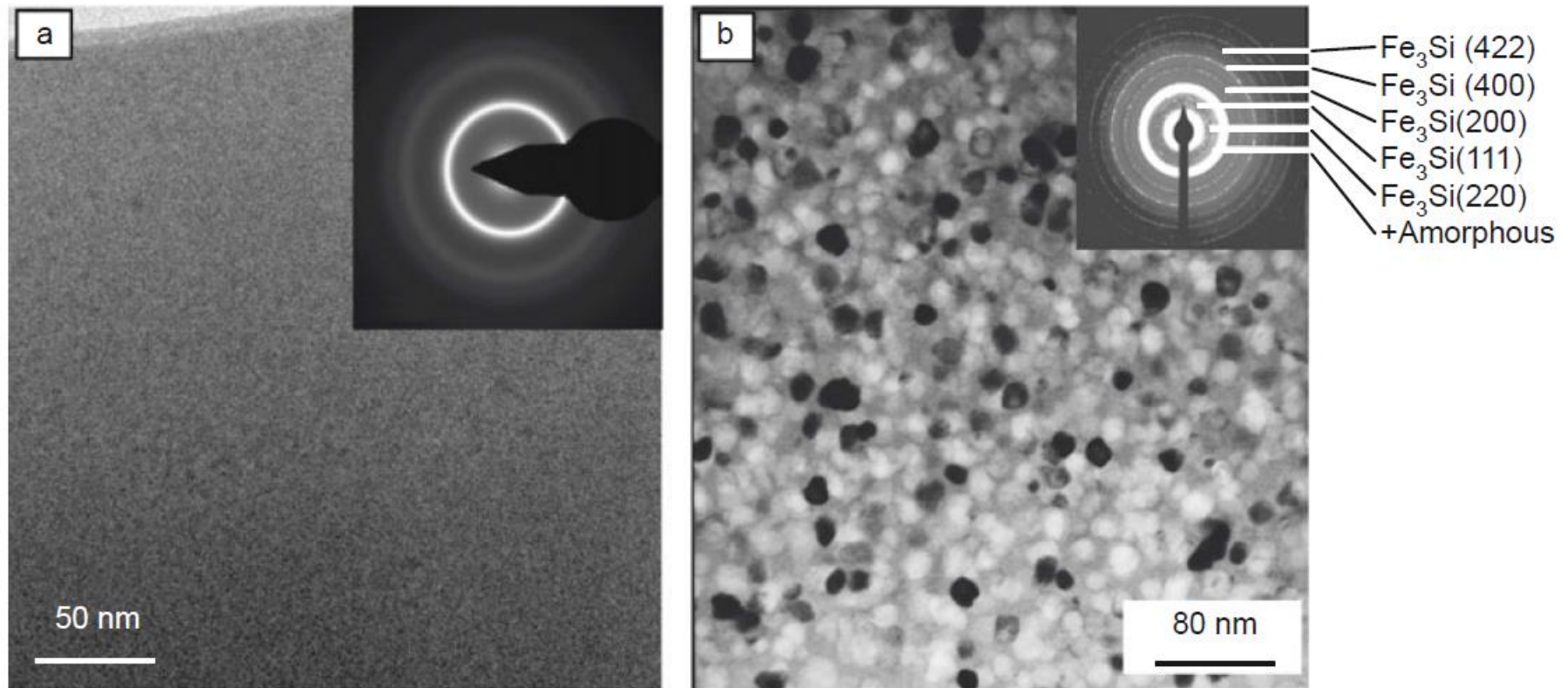
Fig. 2.11 Bright field transmission electron microscopy (TEM) images and corresponding selected area diffraction (SAD) patterns of (a) as melt spun and (b) annealed (525°C for 1 h) ribbons of Fe–Si–B–Nb–Cu alloy. (*Courtesy*: Bhaskar Majumdar, DMRL, Hyderabad).

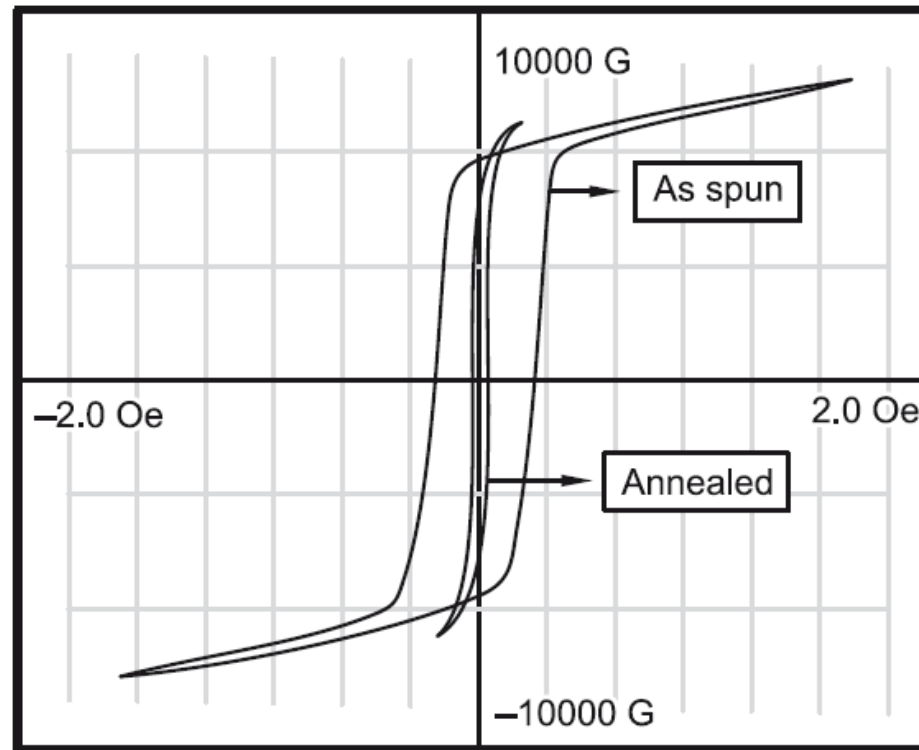# Effect on the magnetic properties

Soft Magnetic Nanocrystalline Alloys

Fig. 2.12 Hysteresis loops of the as-spun and annealed Fe–Si–B–Nb–Cu ribbons. (*Courtesy*: Bhaskar Majumdar, DMRL, Hyderabad).

Effect on the magnetic properties

Permanent Magnetic Nanocrystalline Materials

Mixture of a hard magnetic phase and a soft magnetic phase can exhibit values of remanent magnetization (M_r) greater than the isotropic calue of 0.5 M_s when the phases are nanosize.

This enhancement is obtained when there is an exchange coupling between the two phases due to the nanocrystalline size and the degree of coherence across interphase boundaries

Effect on the magnetic properties
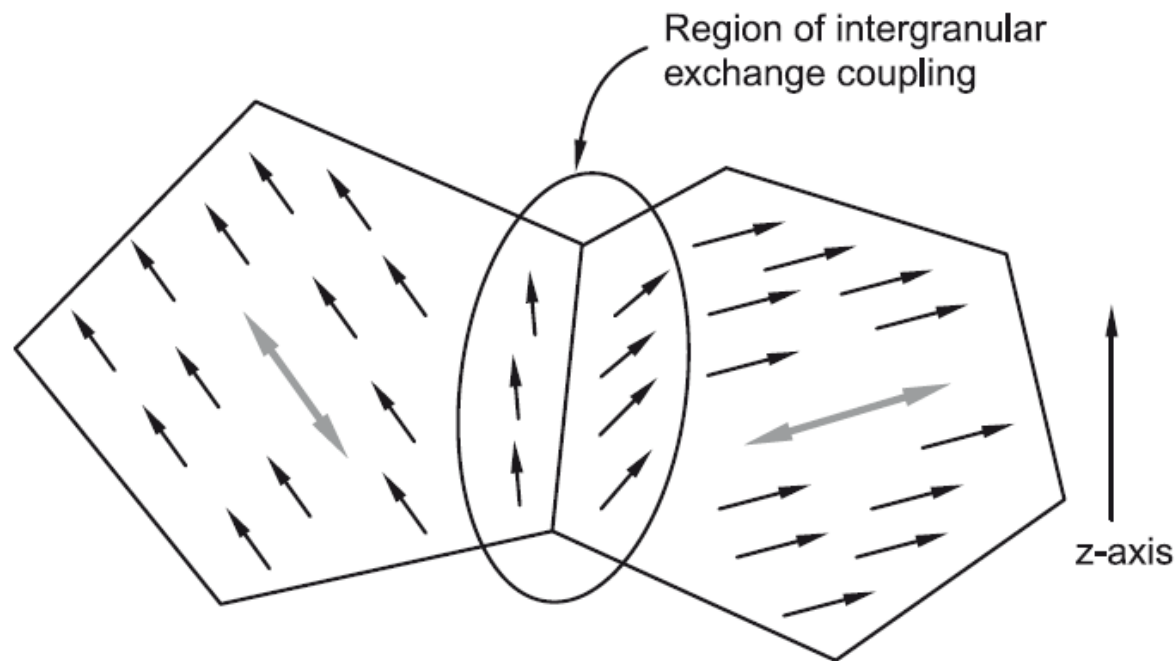
Permanent Magnetic Nanocrystalline Materials

Fig. 2.13 Schematic diagram explaining the principle of exchange coupling in magnetic nanocomposites.

Effect on the magnetic properties

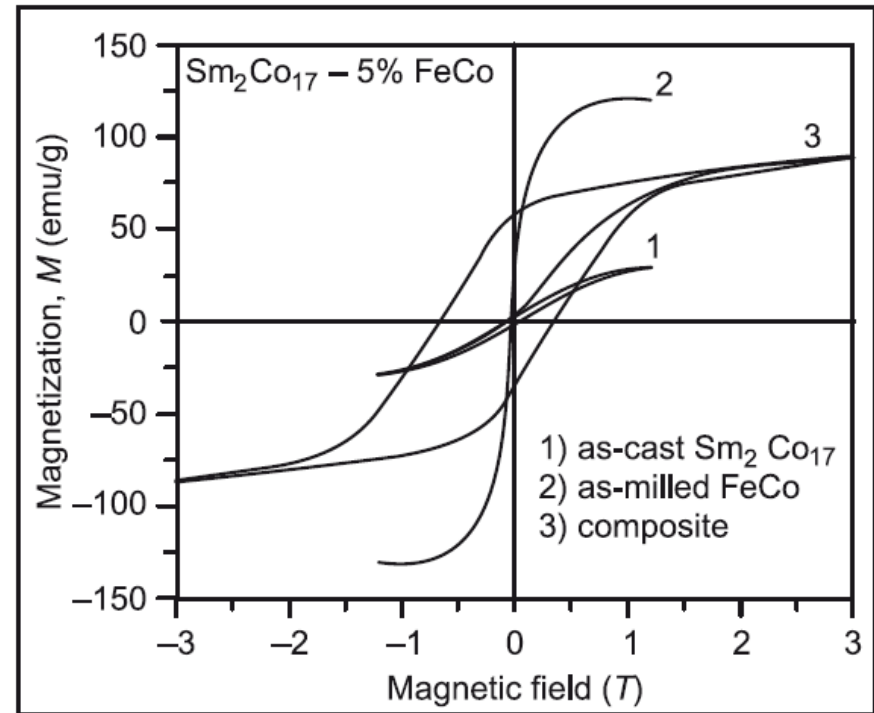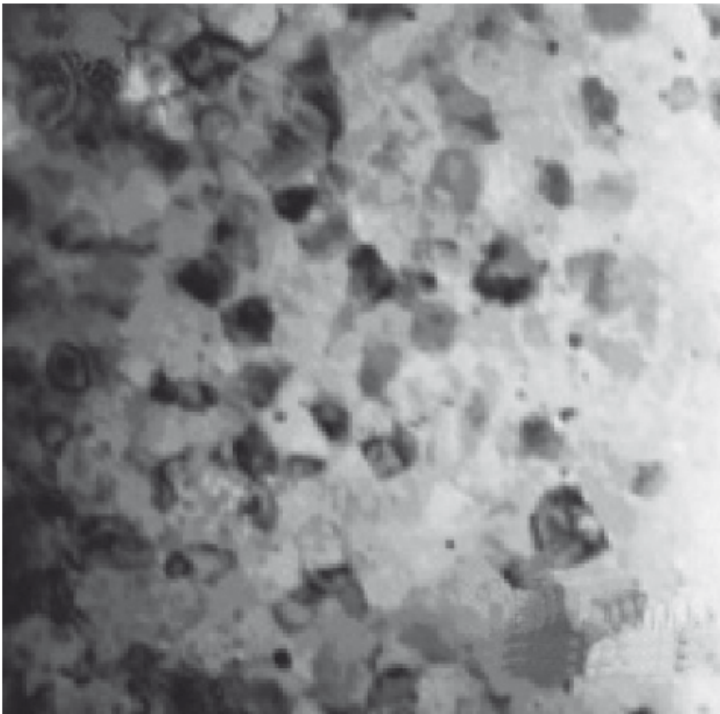Permanent Magnetic Nanocrystalline Materials

Fig. 2.14 Improvement in magnetic properties in Sm_2Co_{17}–FeCo nanocomposites in relation to bulk microcrystalline composites. The improved magnetic properties can be attributed to exchange coupling between the soft and hard magnetic phases in the nanocomposites. (*Source:* BS Murty, IIT Madras).

Effect on the magnetic properties

Giant Magnetoresistance (GMR)

Significant decrease in electrical resistance when a materials is exposed to a magnetic field

Observe in bulk composites consisting of ferromagnetic and non-magnetic phases or in thin film multilayers of these materials as well as in equiaxed granular nanocrystalline materials

Effect on the magnetic properties
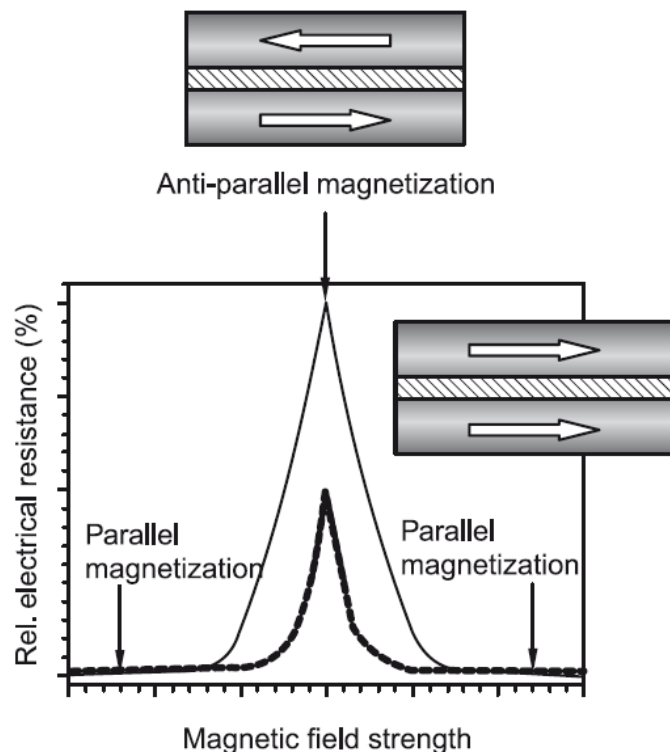
Giant Magnetoresistance (GMR)

Fig. 2.15 Schematic diagram showing GMR effect in magnetic ultrathin films.

A significant decrease in resistance is evident when the external magnetic fields leads to adjacent ferromagnetic layers, aligning in an antiparallel fasion due to weak antiferromagnetic coupling between layers.

Effect on the magnetic properties

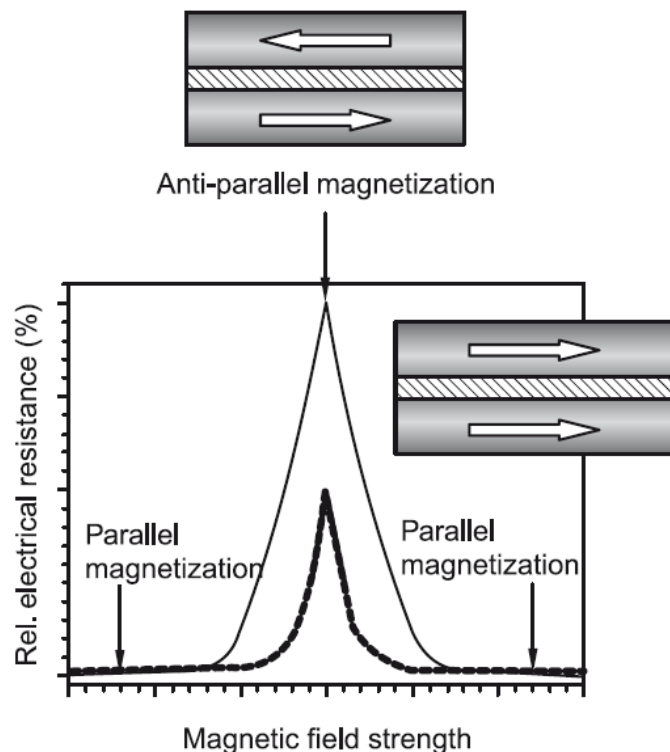Giant Magnetoresistance (GMR)

Anti-parallel magnetization

Fig. 2.15 Schematic diagram showing GMR effect in magnetic ultrathin films.

Granular materials → GMR observe when small ferromagnetic single-domain particles with randomly oriented magnetic axes are embedded in a non-magnetic matrix.

Explanation for GMR is spint-dependent scattering of the conduction electron at the ferromagnetic/non-magnetic interfaces and to a lesser extent, with the magnetic grains.

Effect on the magnetic properties

Giant Magnetoresistance (GMR)

Anti-parallel magnetization

Parallel magnetization   Parallel magnetization

Rel. electrical resistance (%)
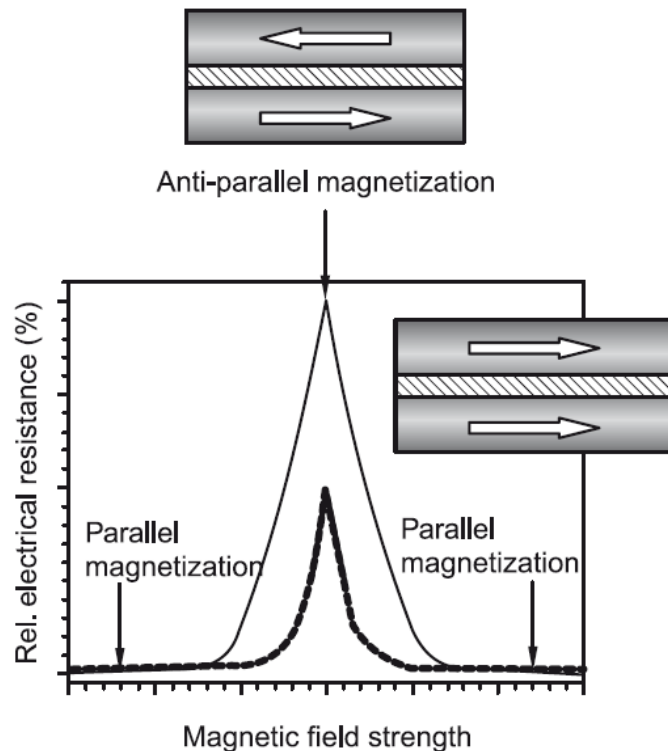
Magnetic field strength

Fig. 2.15 Schematic diagram showing GMR effect in magnetic ultrathin films.

GMR is inversely proportional to the average particle diameters. The effect can be up to 100 % in multiple stacks of ultrathin films. Fe/Cr multilayer ultrathin films Cu/Co nanocompoistes Magnetic reading heads for computer hard discs and position sensors

Effect on the electrical properties

Effects of size on electrical conductivity of nanostructures and nanomaterials are complex, since there are based on distinct mechanisms. These mechanisms are group into 4 categories:

-Surface scattering

- Change of electronic structure

- Quantum transport

- Effect of microstructure

Summary

- Physical properties: size effects
  - ➤ Lattice constant
  - ➤ Melting point
  - ➤ Diffusivity
  - ➤ Enhanced solid solubility
  - ➤ Magnetic properties
  - ➤ Electrical properties

Next

- Physical properties: size effects
  - ➢ Summary of previous effects
  - ➢ Optical properties
  - ➢ Thermal properties
  - ➢ Mechanical properties
  - ➢ Examples of all of them