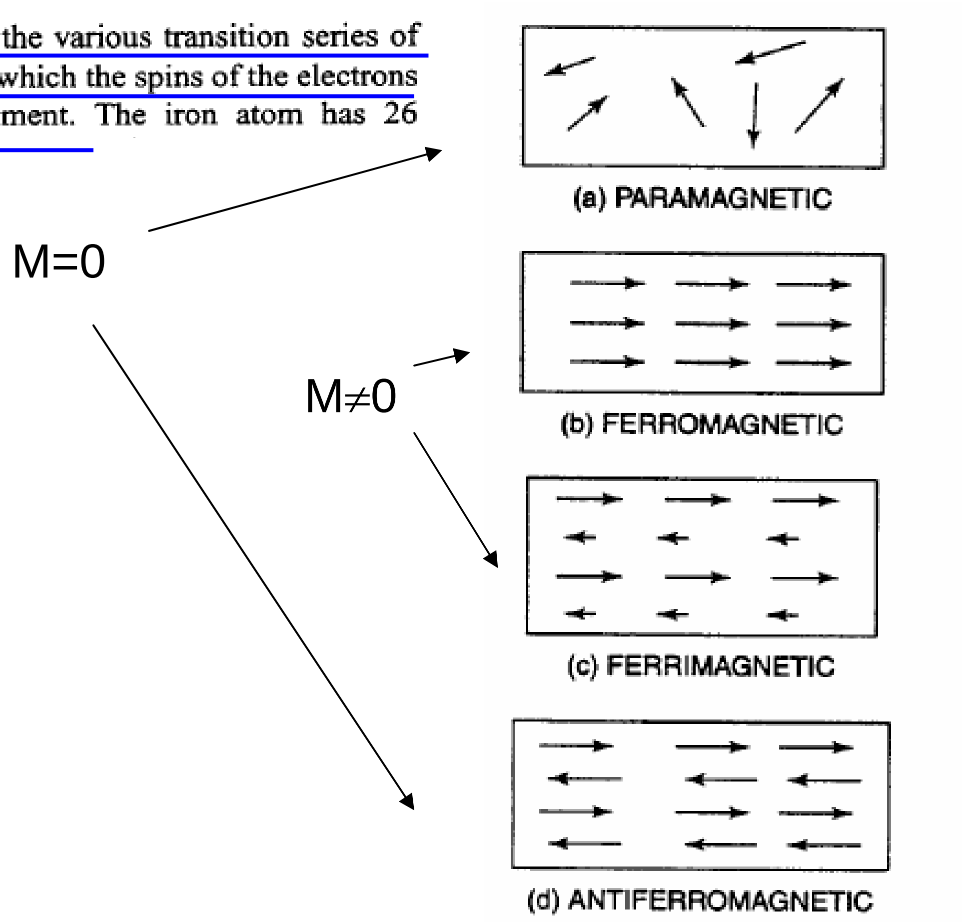
Chapter 7 Nanostructured Ferromagnetism

strength of the magnetism that is present. Atoms in the various transition series of the periodic table have unfilled inner energy levels in which the spins of the electrons are unpaired, giving the atom a net magnetic moment. The iron atom has 26



ious arrangements of individual atomic

The interaction between atomic magnetic moments is of two types:

- 1. Exchange interaction

$$E = \iint \left[\frac{\frac{1}{2}e^2}{r_{12}}\right][\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1)]^2 dV_1\, dV_2 \qquad (7.1)$$

which involves carrying out a mathematical operation from the calculus called *integration*. Expanding the square of the wavefunctions gives two terms:

$$E = \iint \left[\frac{e^2}{r_{12}}\right][\Psi_A(1)\Psi_B(2)]^2 dV_1\, dV_2 - \iint \left[\frac{e^2}{r_{12}}\right]\Psi_A(1)\Psi_B(1)\Psi_A(2)\Psi_B(2) dV_1\, dV_2 \qquad (7.2)$$

The first term is the normal Coulomb interaction between the two charged particles. The second term, called the *exchange interaction*, represents the difference in the

Heisenberg model of magnetism E= *J* $S_1.S_2$
J>0 is antiferromagnetism
J <0 is ferromagnetism

2. Dipolar interaction $\frac{\mu_1 \cdot \mu_2}{r^3} - 3(\mu_1 \cdot r)\frac{\mu_2 \cdot r}{r^5}$ (7.3)

1. Exchange interaction

In the case of a small particle such as an electron that has a magnetic moment, the application of a DC magnetic field forces its spin vector to align such that it can have only two projections in the direction of the DC magnetic field, which are $\pm\frac{1}{2}\mu_B$, where μ_B is the unit magnetic moment called the *Bohr magneton*. The wavefunction representing the state $+\frac{1}{2}\mu_B$ is designated α, and for $-\frac{1}{2}\mu_B$ it is β. The numbers $\pm\frac{1}{2}$ are called the *spin quantum numbers* m_s. For a two-electron system it is not possible to specify which electron is in which state. The Pauli exclusion principle does not allow two electrons in the same energy level to have the same spin quantum numbers m_s. Quantum mechanics deals with this situation by requiring that the wavefunction of the electrons be antisymmetric, that is, change sign if the two electrons are interchanged. The form of the wavefunction that meets this condition is $\frac{1}{2}^{-1/2}[\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1)]$. The electrostatic energy for this case is given

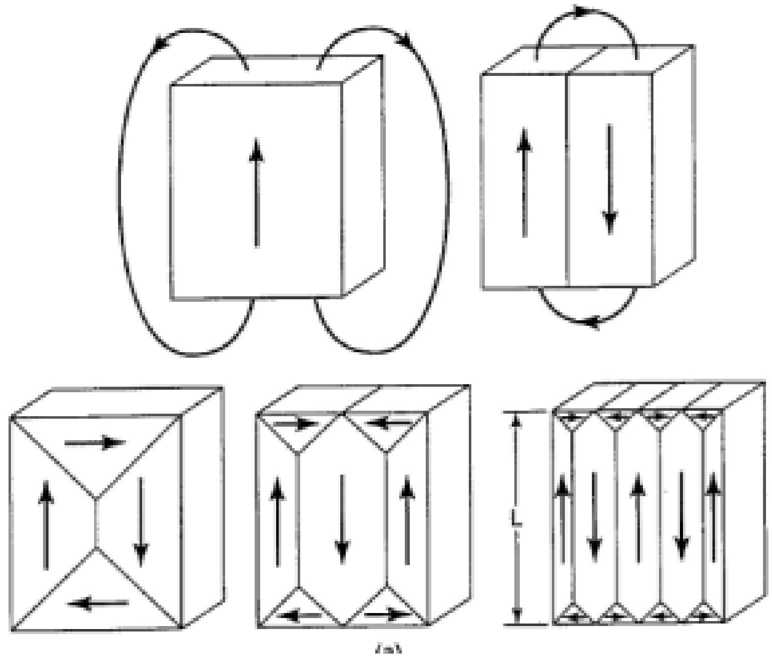
Magnetization M of a bulk

Is the total magnetic moment per unit volume

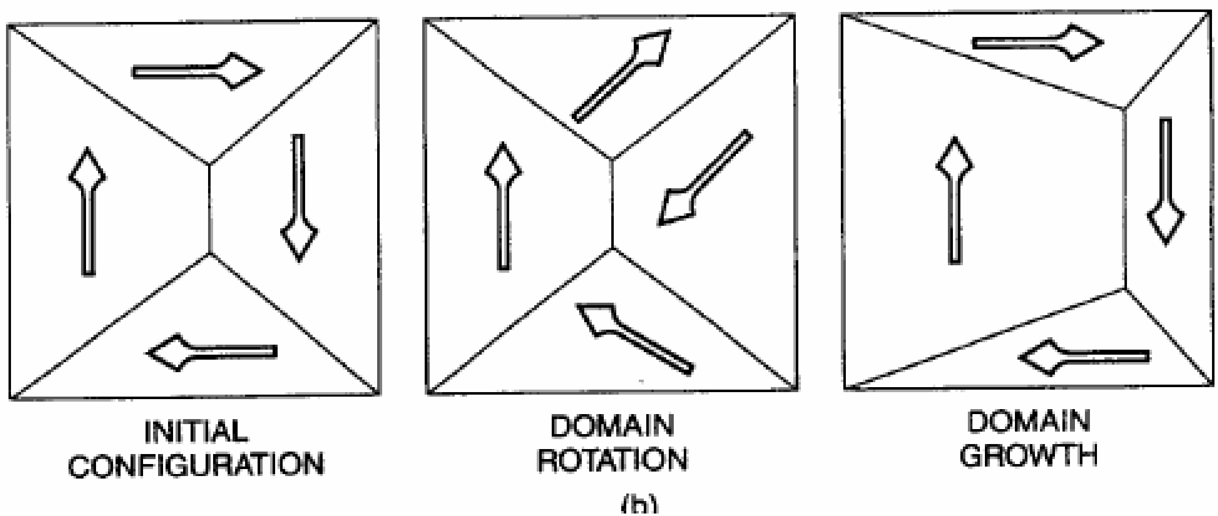
$$M(T) = M(0)(1 - cT^{3/2}) \tag{7.4}$$

For T<< Tc   Tc is Curie temperature

$$\chi = M/H.$$



H=0

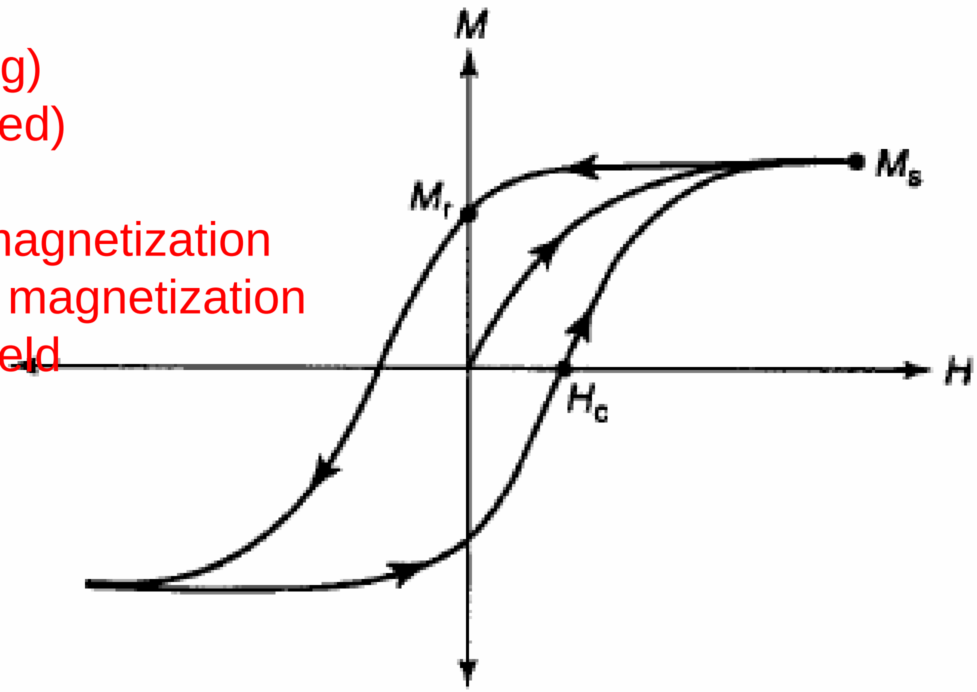


H>0

Remnant magnetization, Coercive field, Saturation magnetization Hysteresis (loop)

CGS M(emu/g)
H(oersted)

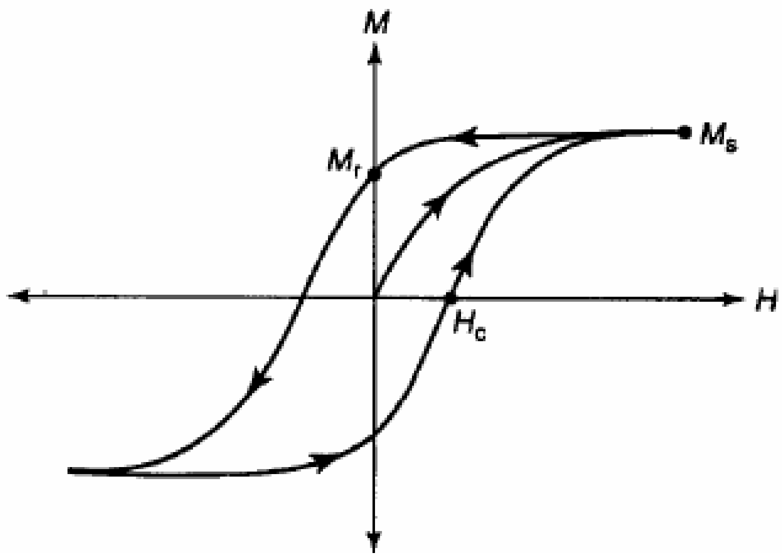
M_r : remnant magnetization
M_s: Saturation magnetization
H_c: Coercive field



7.3. Plot of the magnetization M versus an applied magnetic field H for a hard agnetic material, showing the hysteresis loop with the coercive field H_c, the remnant tization M_r, and the saturation magnetization M_s, as indicated.

7.2 Effect of bulk nanostructuring on magnetic properties

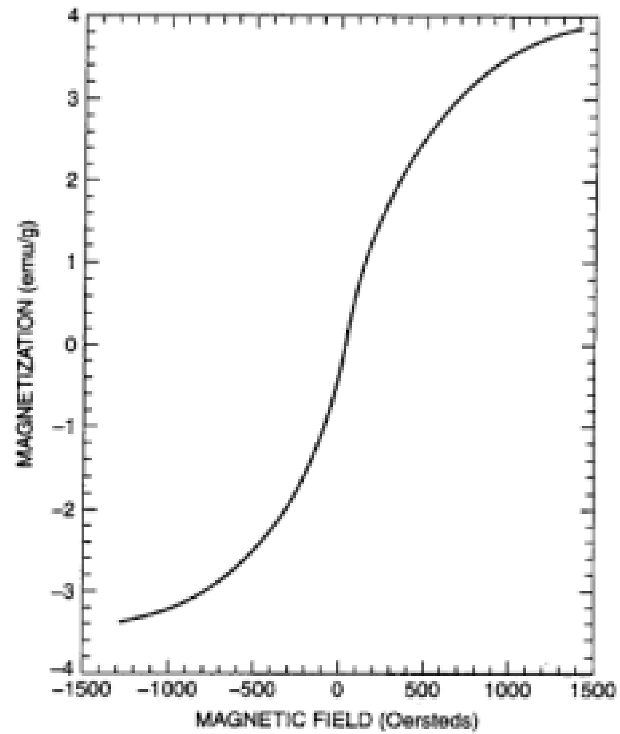
The amount of energy loss meaning the amount of heat generated is proportional to the area of loop



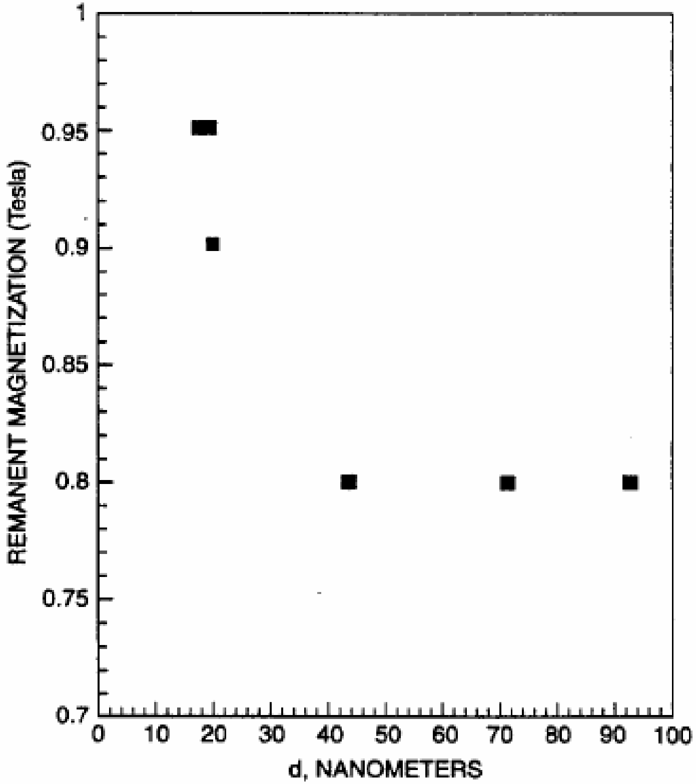
Soft magnet H_c->0

Hard magnet H_c> 0

tion curve. Amorphous alloy ribbons having the composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ prepared by a roller method, and subjected to annealing at 673 to 923 K for one hour in inert-gas atmospheres, were composed of 10-nm iron grains in solid solutions. Such alloys had a saturation magnetization M_s of 1.24 T, a remnant magnetization M_r of alloy powders of $Fe_{69}Ni_9CO_2$ having grain sizes of 10–15 nm prepared by decom- us



ure 7.4. Reversible magnetization curve for nanosized powders of a Ni–Fe–Co alloy ibits no hysteresis. An oersted corresponds to 10^{-4} T (tesla). [Adapted from K. Shafi e *later. Res.* **15**, 332 (2000).]



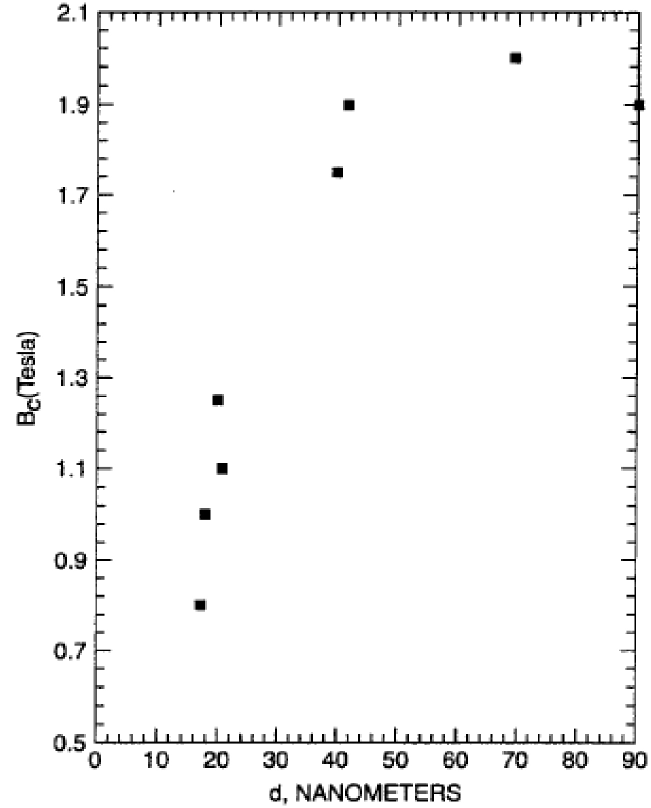
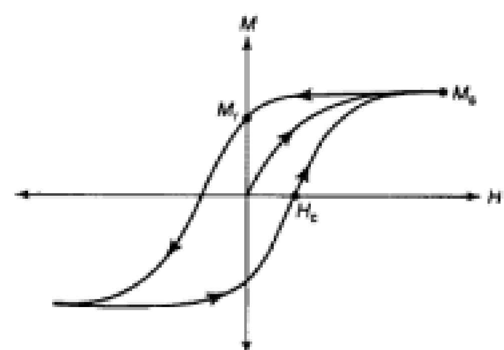
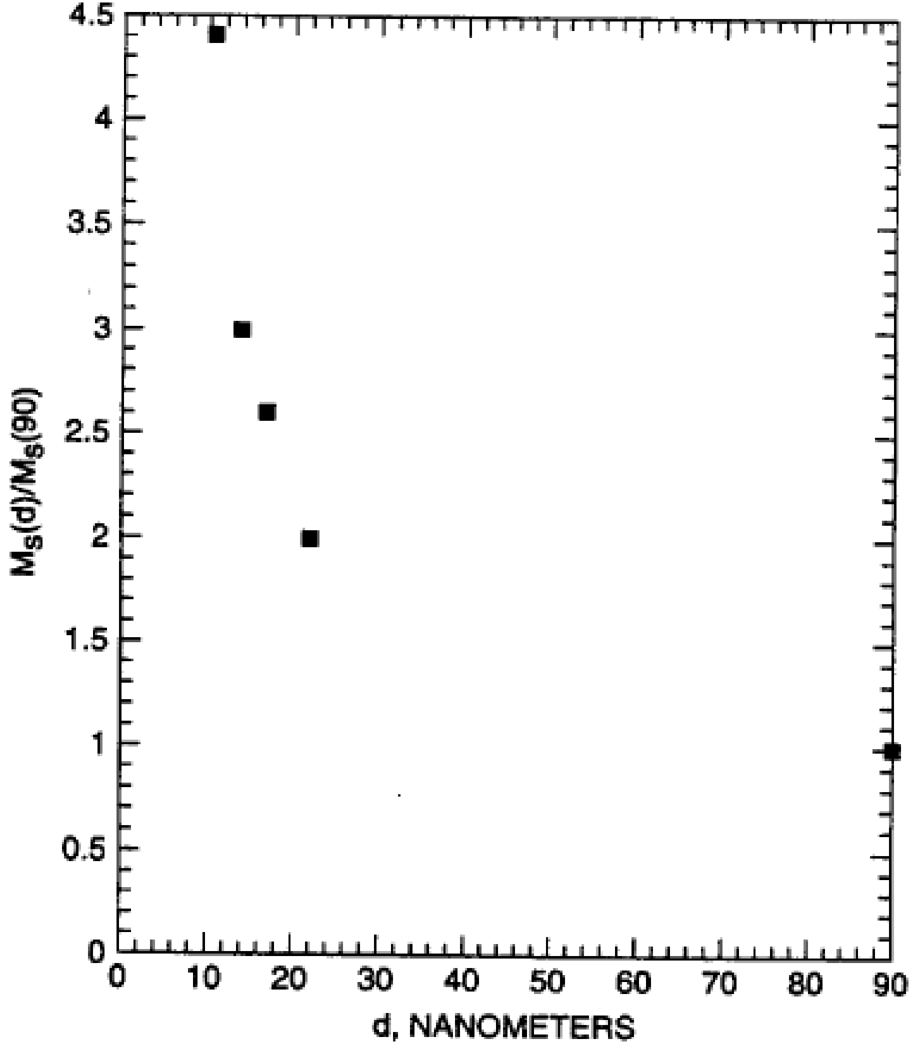


Figure 7.6. Dependence of the coercive field B_c (i.e., H_c) on the granular particle size *d* o
Nd–B–Fe permanent magnet. [Adapted from A. Manaf et al., *J. Magn. Magn. Mater.* 1

$Nd_2Fe_{14}B$ Grain d

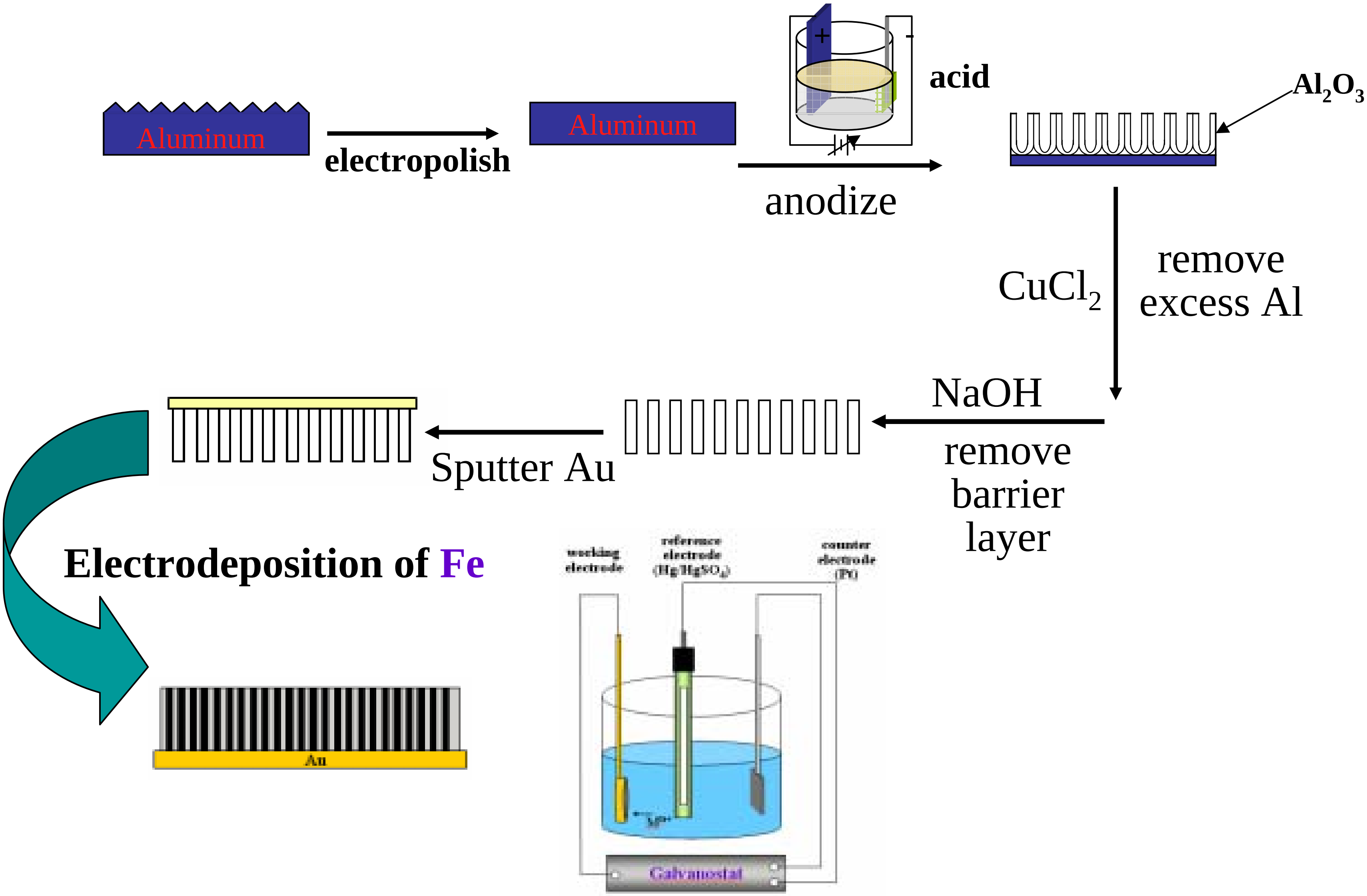




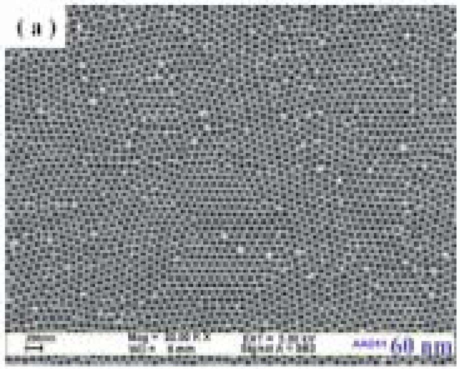
7.7. Dependence of the saturation magnetization M_s of zinc ferrite on the granular size *d* normalized to the value $M_s(90)$ for a 90-nm grain. [Adapted from C. N. Chinnasamy,

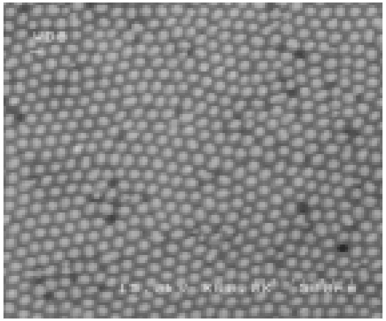
7.4. nanopore containment of magnetic nanowires

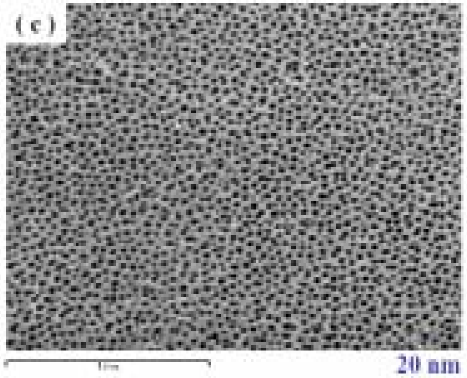
Fabrication of Fe Nanowire Arrays

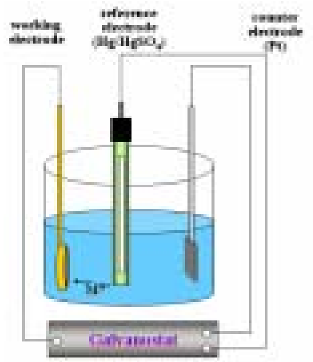


Size dependence of magnetization in Fe **nanowires**

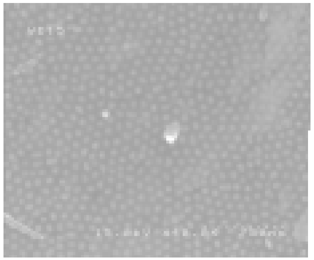




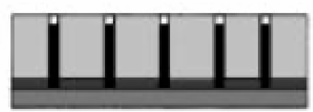




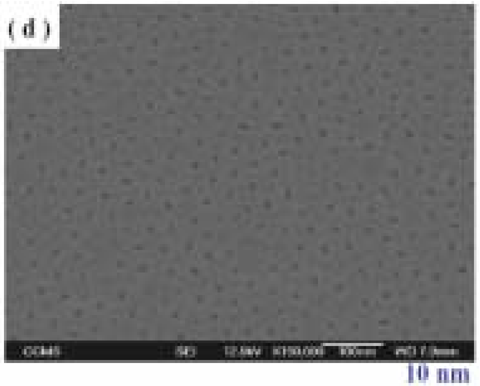
AAO method



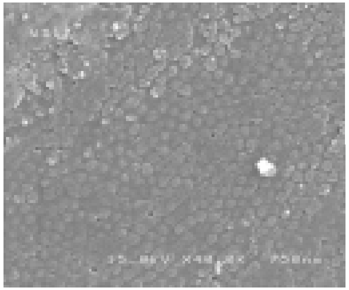
Cu **nanowire**



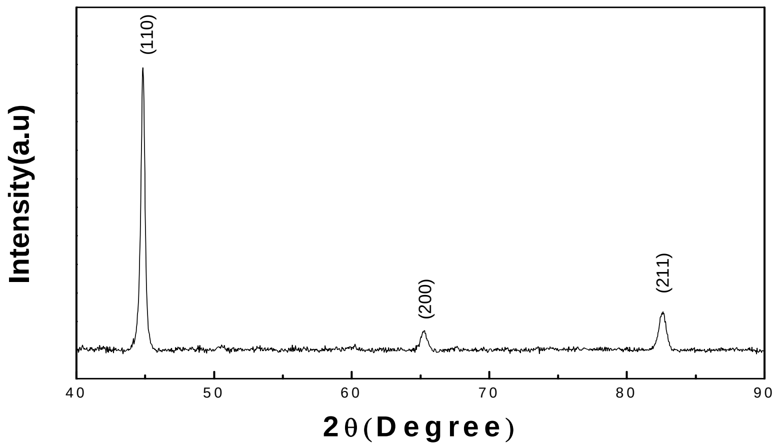
$CuSO_4.5H_2O$,
pH~2

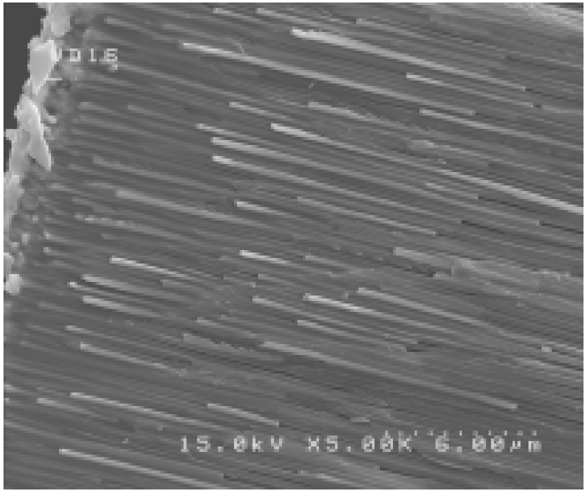


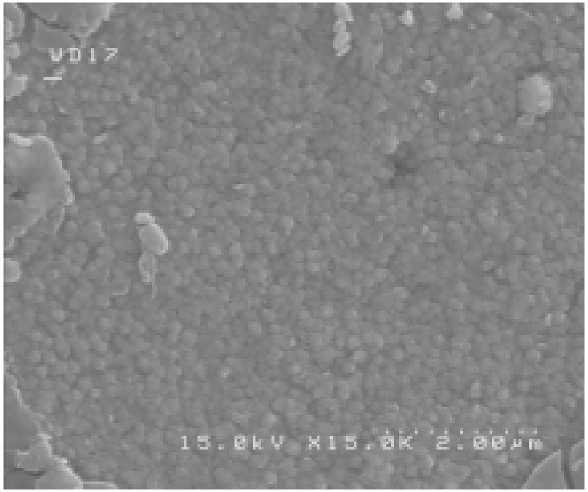
70nm Al nanowires



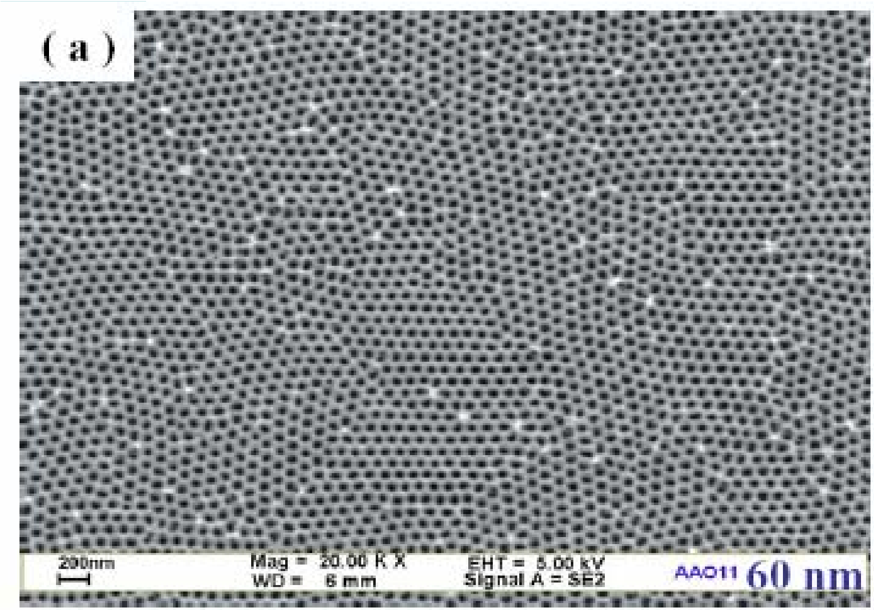
Fe

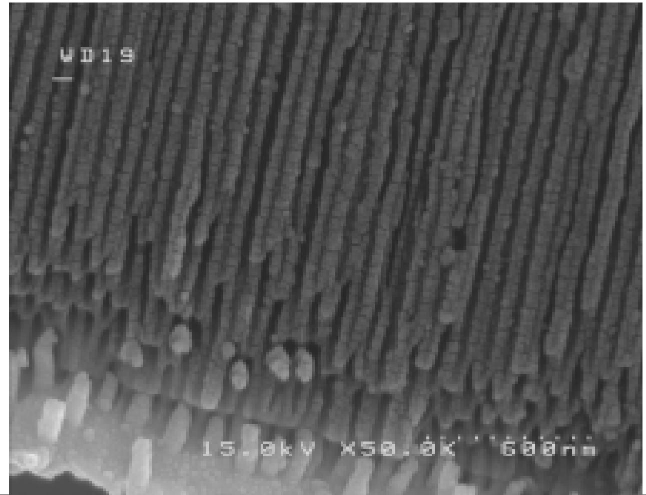


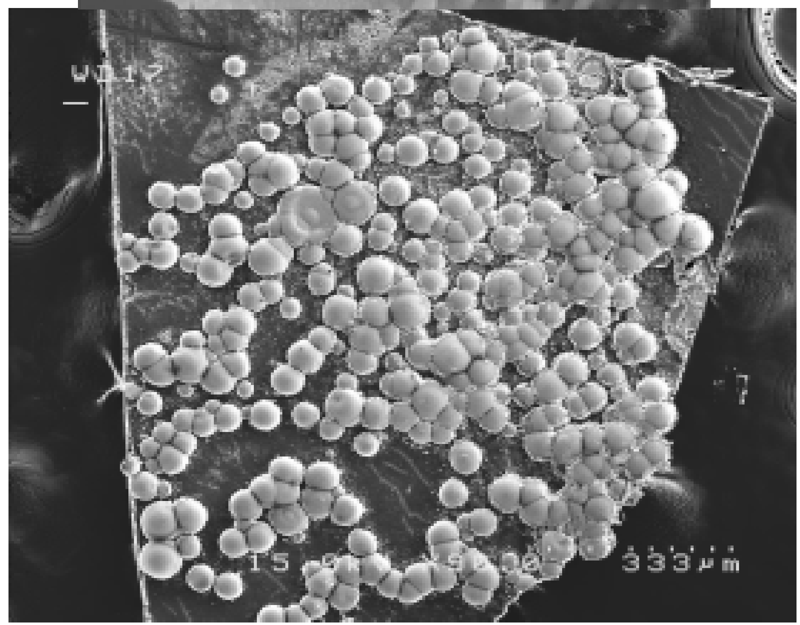


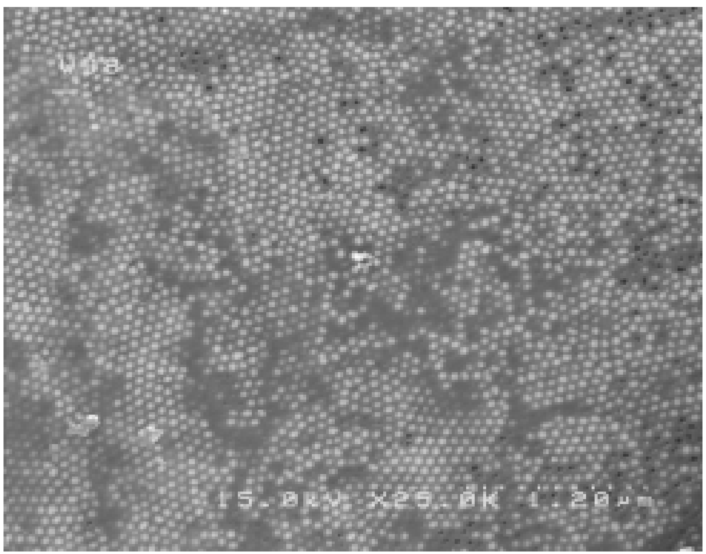


Fe nanowire ~200 nm



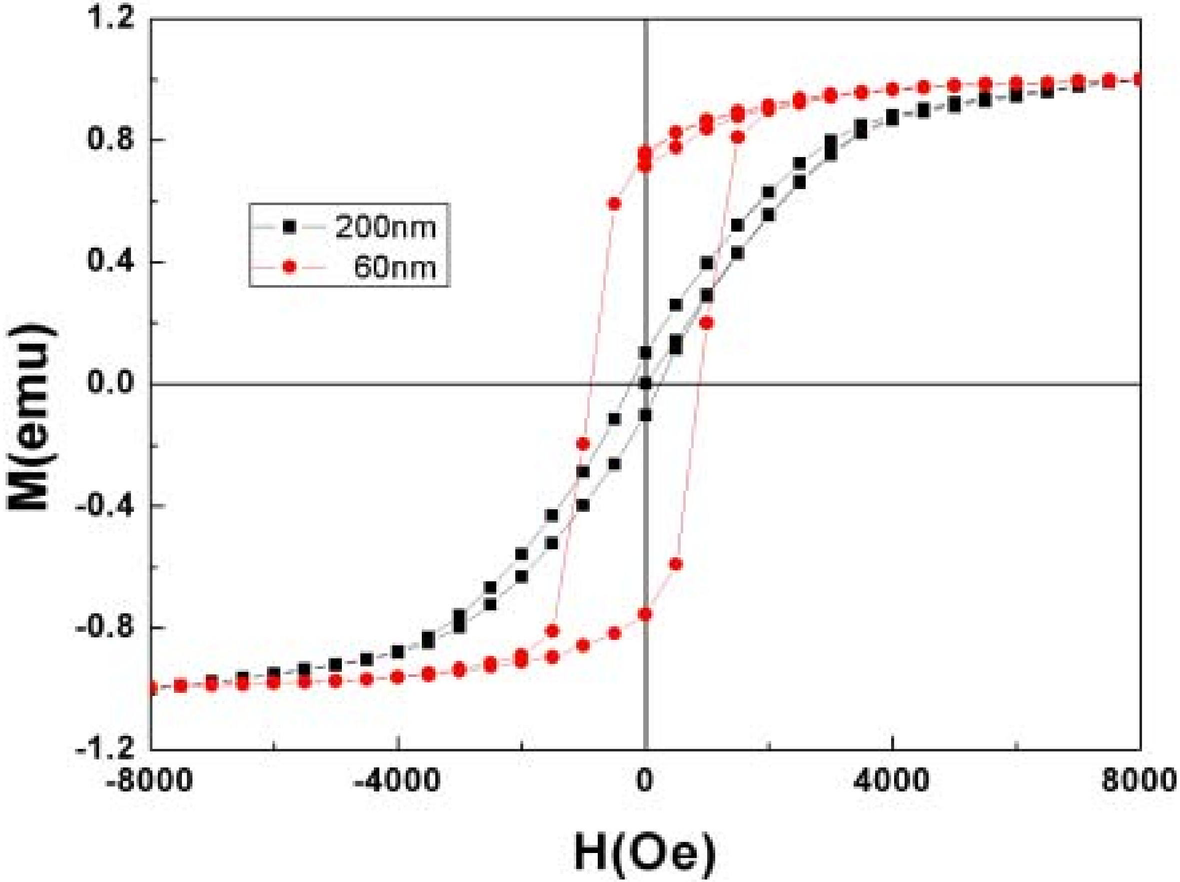




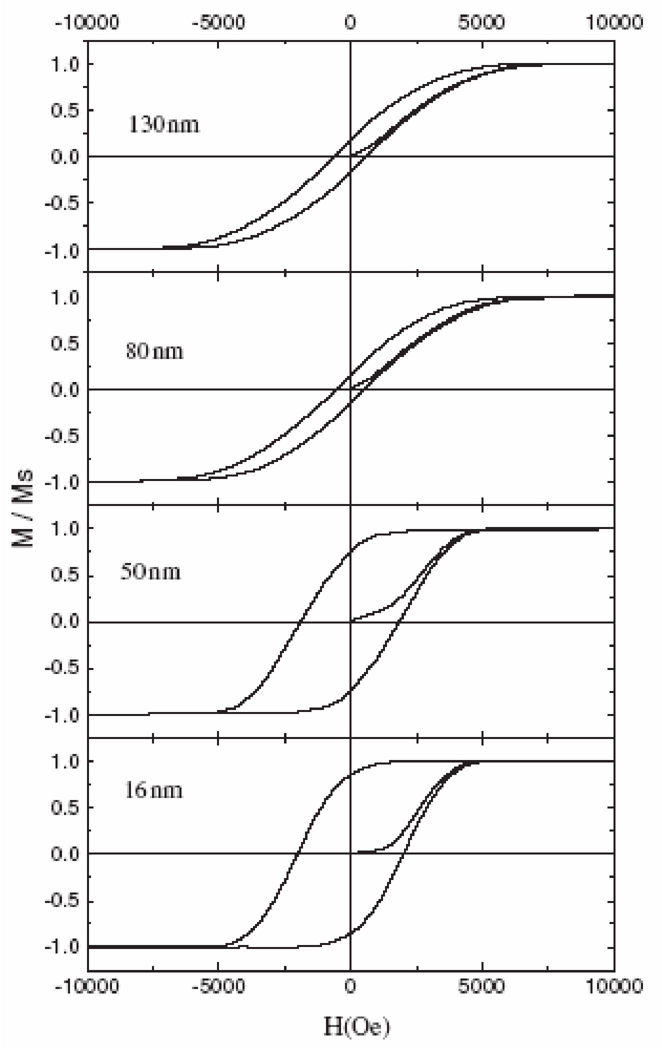


Fe nanowire ~60 nm

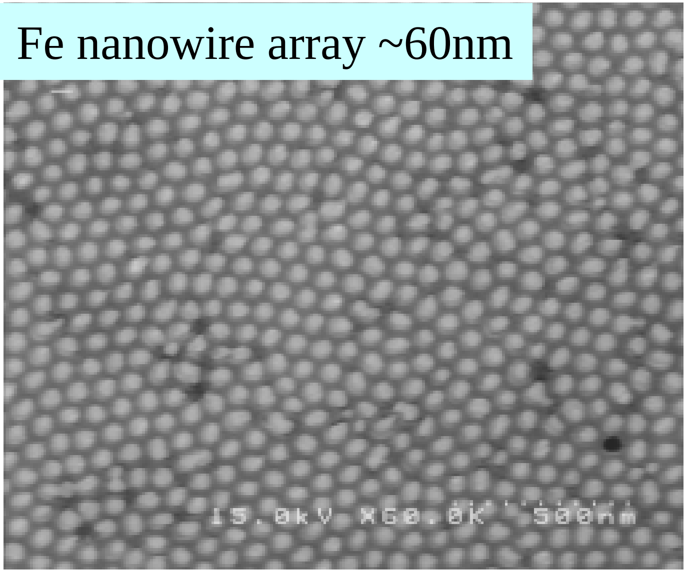
Normalized (M/Ms)-H

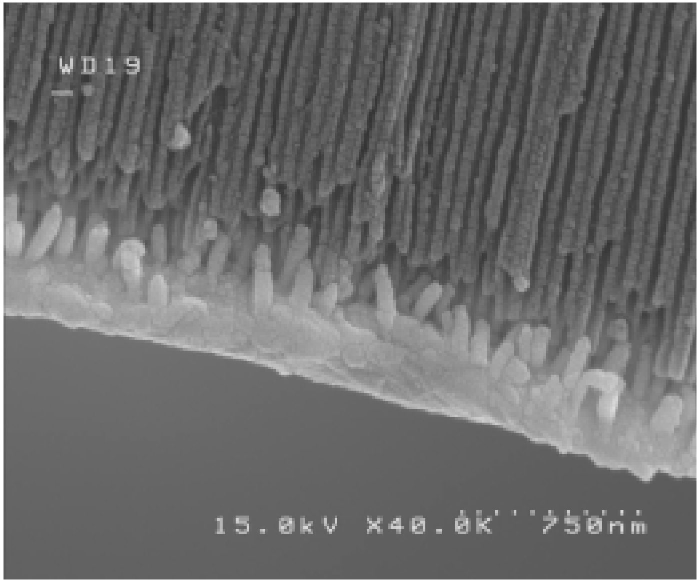


Magnetic texture of nanowire arrays



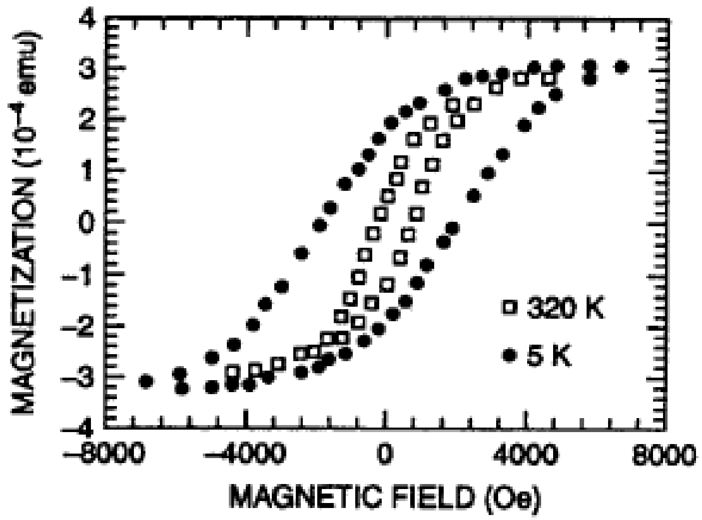
Fe nanowire array ~60nm

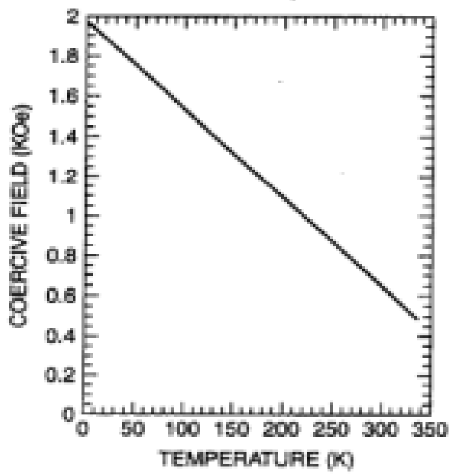




7.5 Nanocarbon ferromagnets

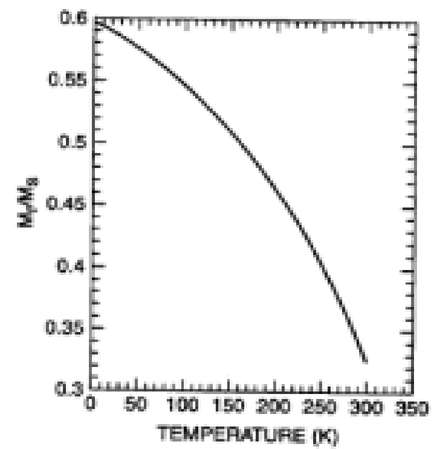
gure 7.11. Scanning electron microscope image of iron particles (light spots) on the tips of igned carbon nanotubes. [With permission from Z. Zhang et al., *J. Magn. Magn. Mater.* 231, I (2001).]





ıt of coercive field H_c versus temperature T for iron part

gnetizatior



the tips

o of remnant magnetization M_r to saturation magnetization M_s

Quantum size effects 量子尺寸效應：

Phonon quanum size effect : 聲子與表面積之改變。

Electronic quantum size effect : 電子結構改變與能階劈裂。

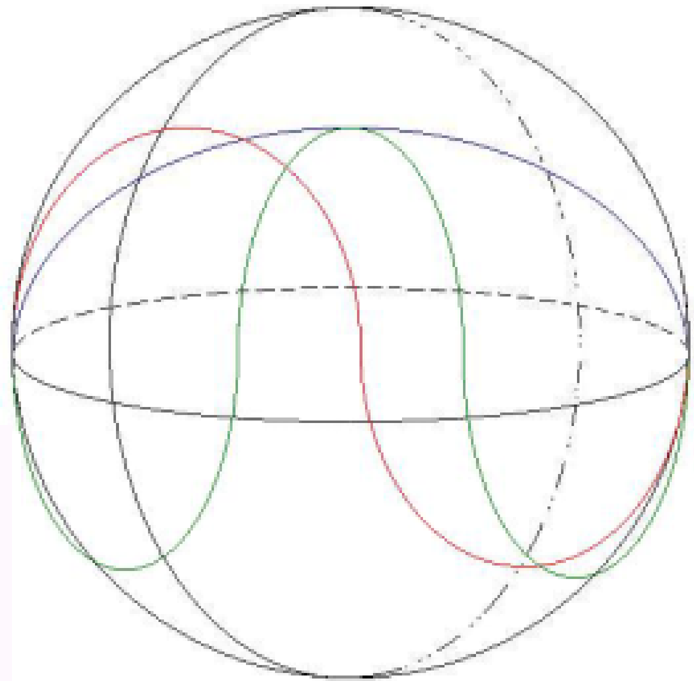
Phonon quanum size effect： 聲子與表面積之改變。

Wave mode:
Spherical Bessel Function

$$C_p = \gamma T + \sum_l \sum_s \frac{V_m (2l+1) K_B z^2 e^z}{4R^3 (e^z - 1)^2}$$

with

$$z = \frac{\hbar c a'_{l,s}}{K_B R T}$$



Nanoparticle：

聲子量子尺寸效應：聲子與表面積之改變。

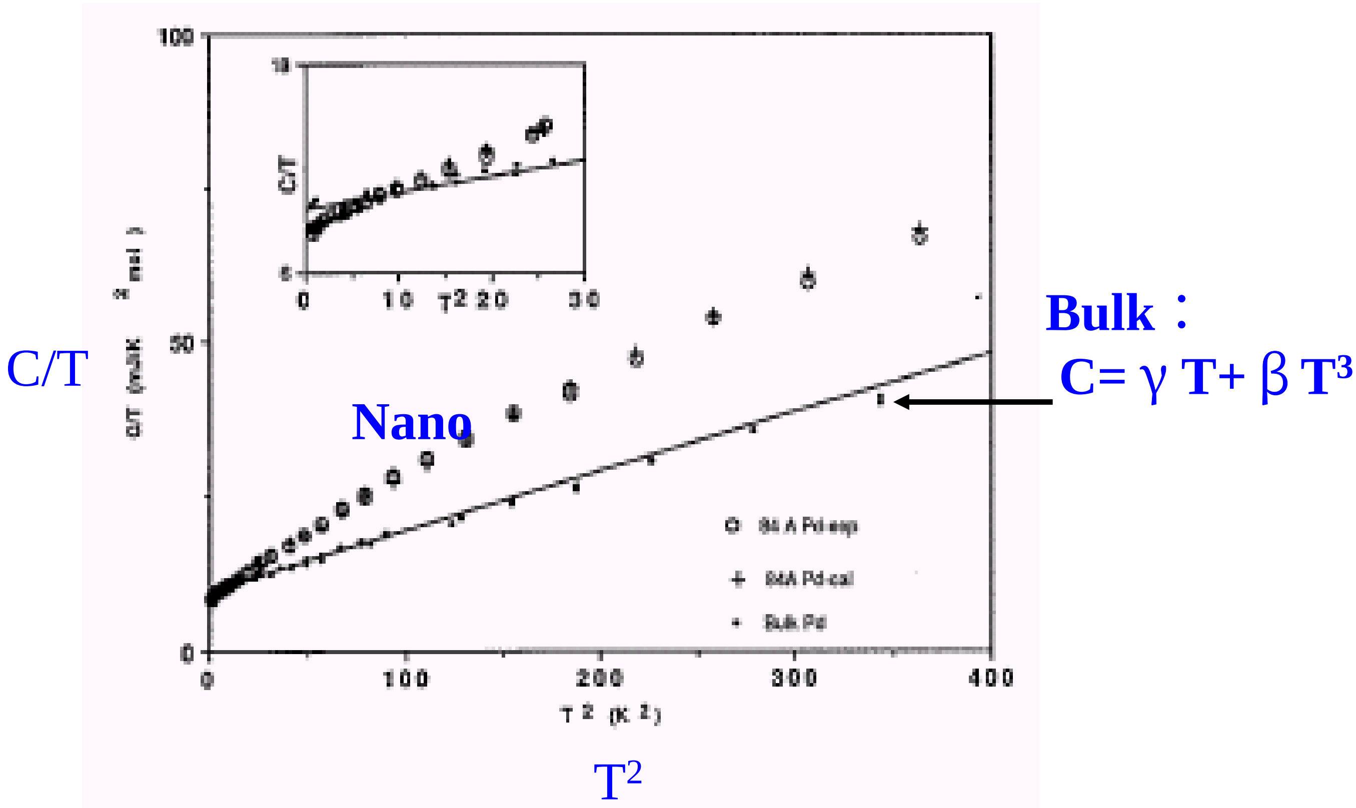
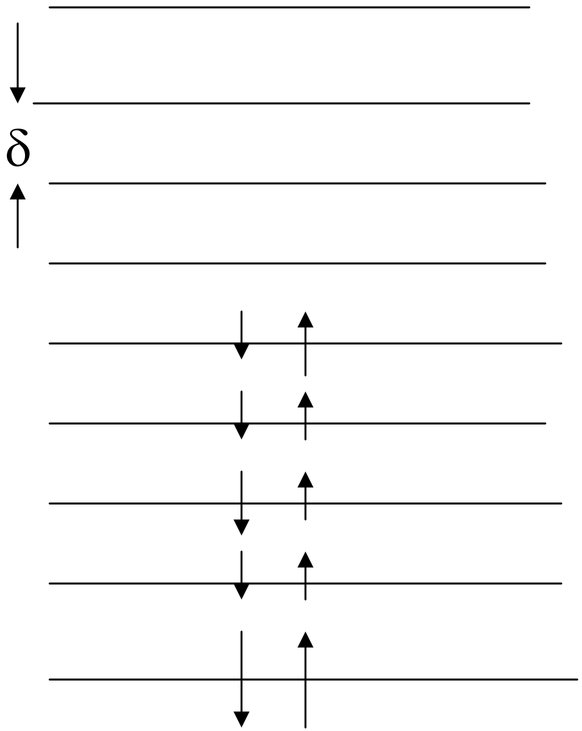


FIG. 3. The specific heat of bulk palladium and 84-Å Pd nanocrystals. The small dots represent bulk Pd and the solid

<u>**Y.Y. Chen etc, PRB 52, 9364, 1995**</u>

Electronic quantum size effect： 電子結構改變與能階劈裂。



$\varepsilon_F \sim 10^4$ K

$$\delta \approx E_F / N \propto V^{-1}$$

Bulk Pd **δ ~10e^{-30}K**

80 Å Pd **δ ~ 0.5K**

No. of atoms~ 8000

Magnetic field

H=0

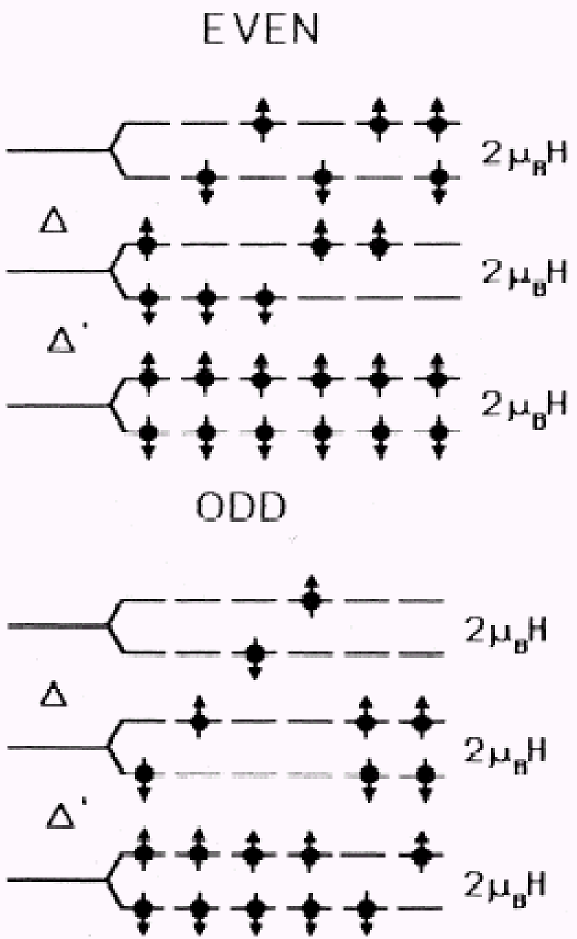


FIG. 2. Electron-level structure diagrams for the two cases of particles with an even number of electrons, and for particles with an odd number of electrons. Only the lowest-energy configurations are shown with the ground state at the left and progressively higher excited states to the right for each of the even and odd cases.

Rev. Mod. Phys., Vol. 58, No. 3, July 1986

H>0

Partition of C(T)

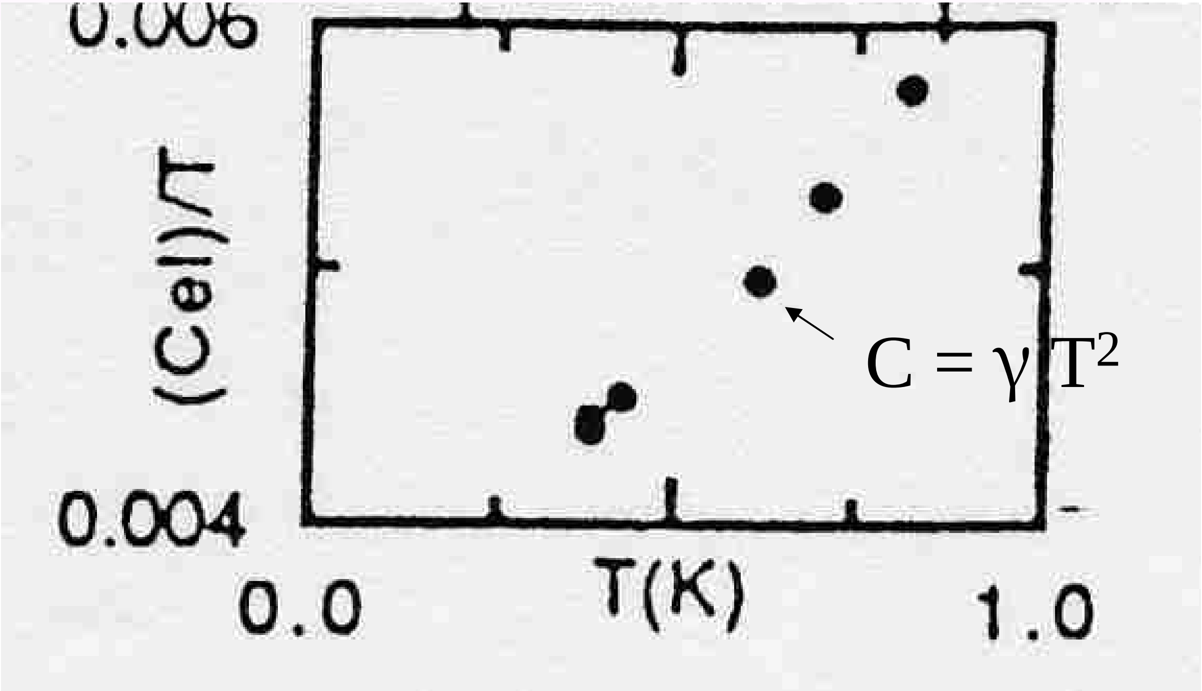
$$Z_{even} \approx 1 + 2(1+\cosh 2\beta\mu_B H)(e^{-\beta\Delta}) + e^{-2\beta\Delta},$$

$$Z_{odd} \approx 2(\cosh\beta\mu_B H)(1+e^{-\beta\Delta}+e^{-\beta\Delta'}).$$

$$C^1_{even}/k_B = 30.2(k_B T/\delta)^2,$$

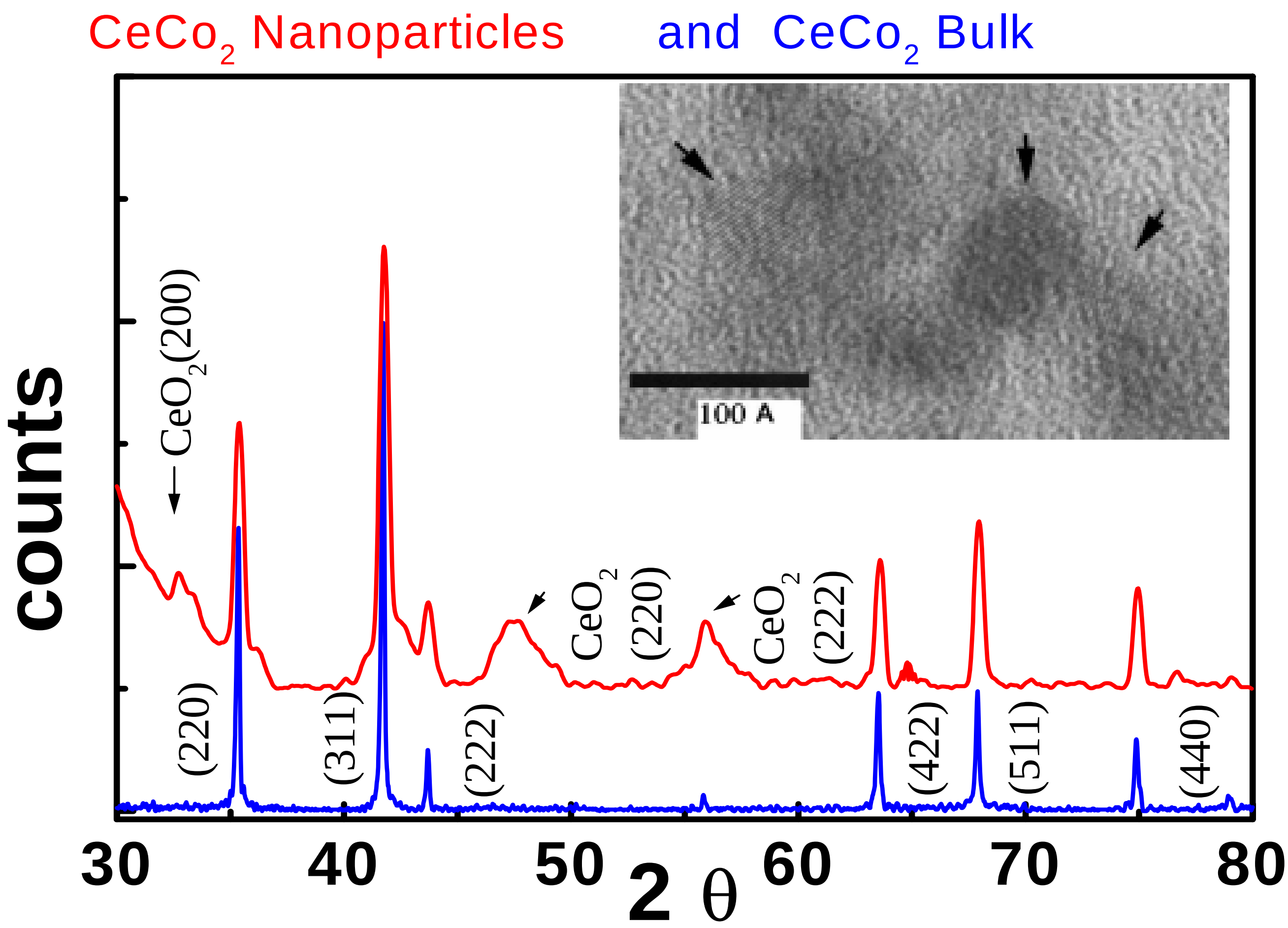
$$C^1_{odd}/k_B = 17.8(k_B T/\delta)^2,$$

orthogonal

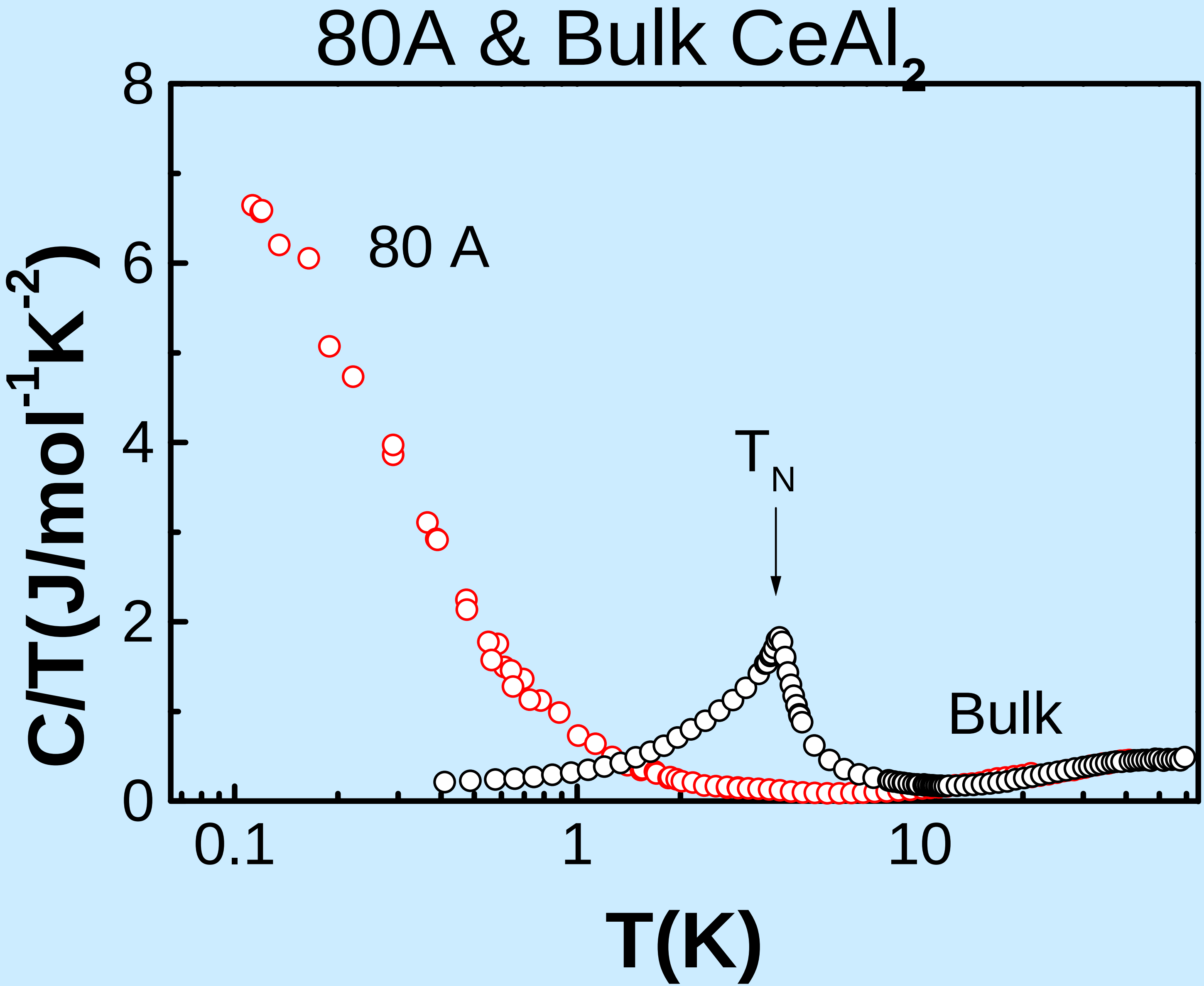


Y.Y. Chen, LT21 Proceeding 2369 Aug.1996

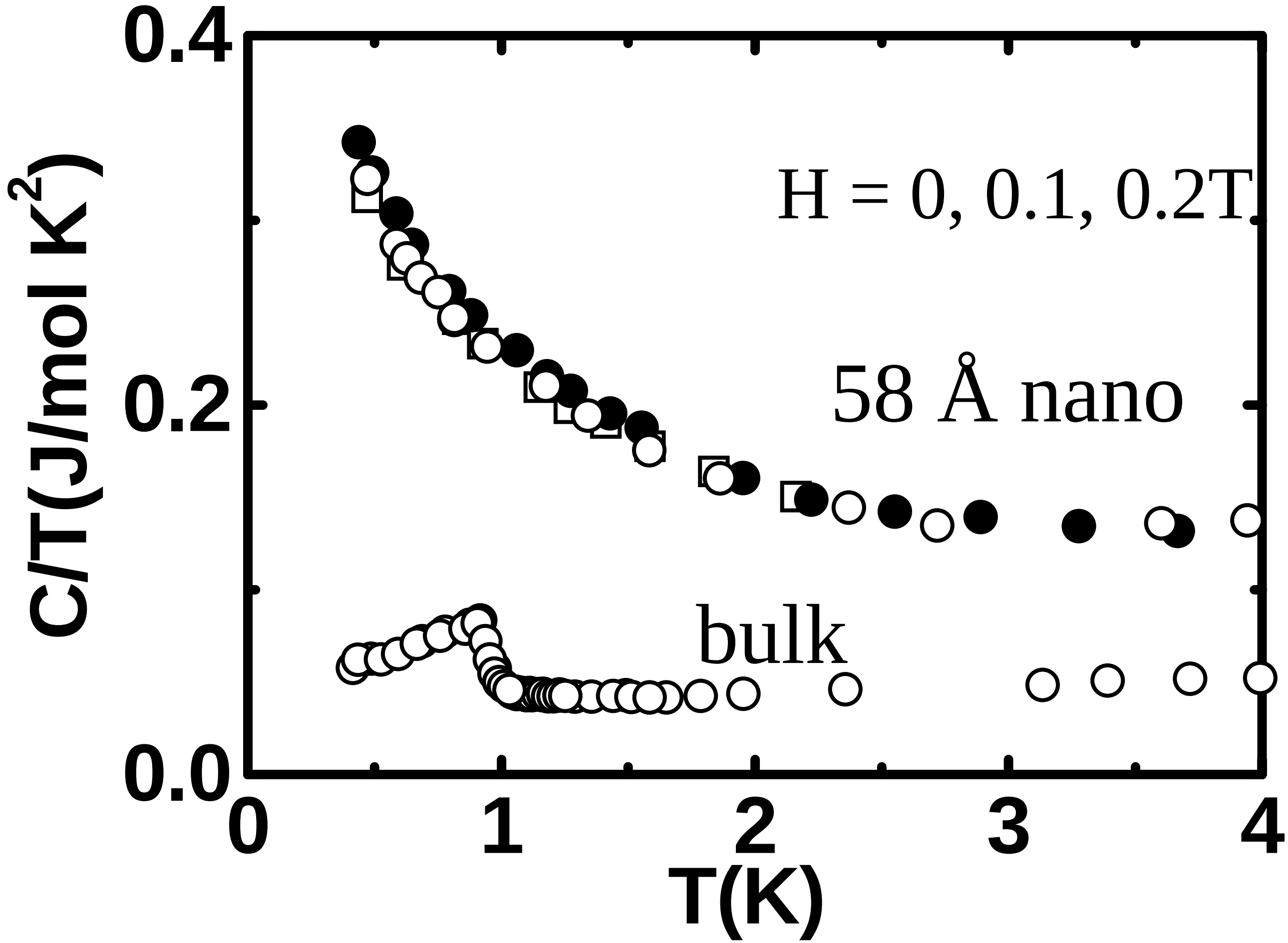
X-ray & HRTEM



CeCo2 Nanoparticles
and CeCo2 Bulk
counts
CeO2(200)
CeO2
(220)
CeO2
(222)
(220)
(311)
(222)
(422)
(511)
(440)
100 A
30
40
50
60
70
80
2 θ


80A & Bulk CeAl2
80 A
T_N
Bulk
C/T(J/mol-1K-2)
8
6
4
2
0
0.1
1
10
T(K)

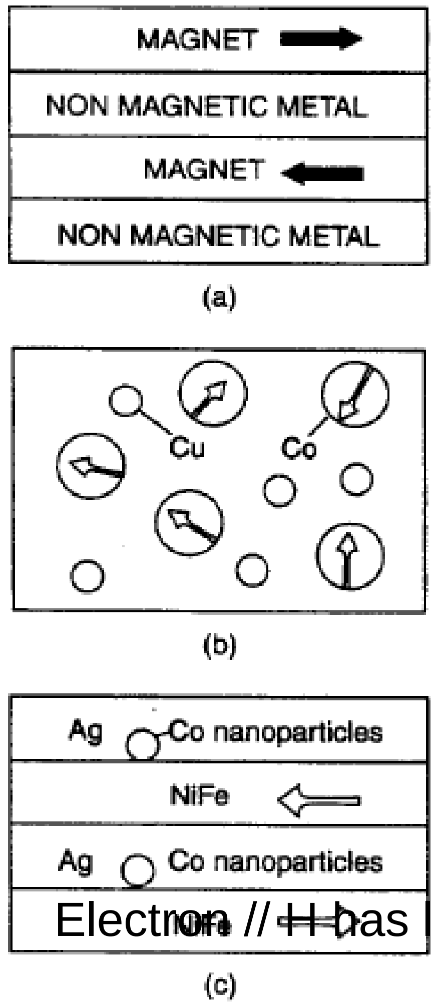
C (H) of 58A CeCo2



7.6 Giant and colossal magnetoresistan

- Metal:
- 1. The conduction electrons being forced to move in helical trajectories about an applied magnetic field.
- 2. Field curves the electron trajectory within a length of its mean free path
- Cu at 4 K with H=10 T , resistance R increases 10 times

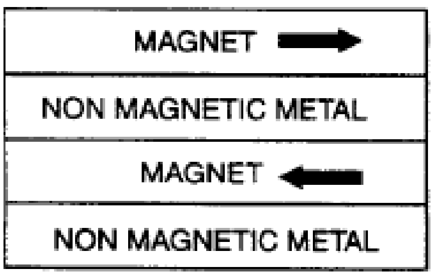
Giant magnetoresistance (GMR)



Electron // H has less scattering

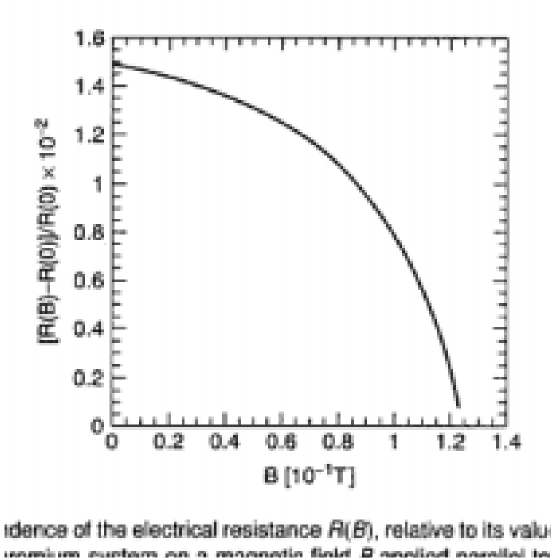
Giant magnetoresistance (GMR)

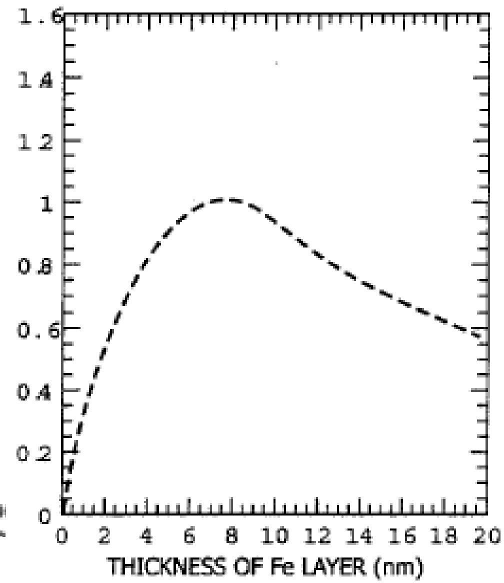
Alternate layers of FM and Non-FM



(a)

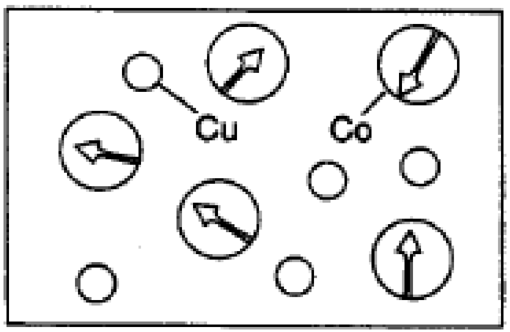
Fe-Cr



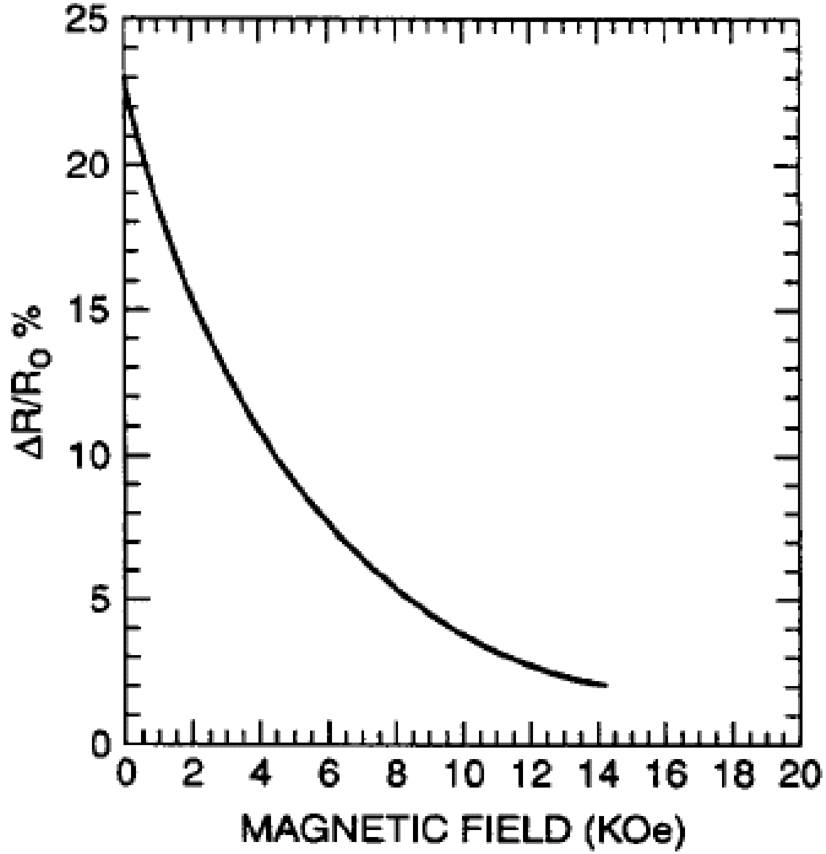


Electron // H has less scattering

Giant magnetoresistance (GMR)



(b)



ence of the change of magnetoresistance ΔR versus
Co nanoparticles in a copper matrix. A kilooersted

Electron // H has less scattering

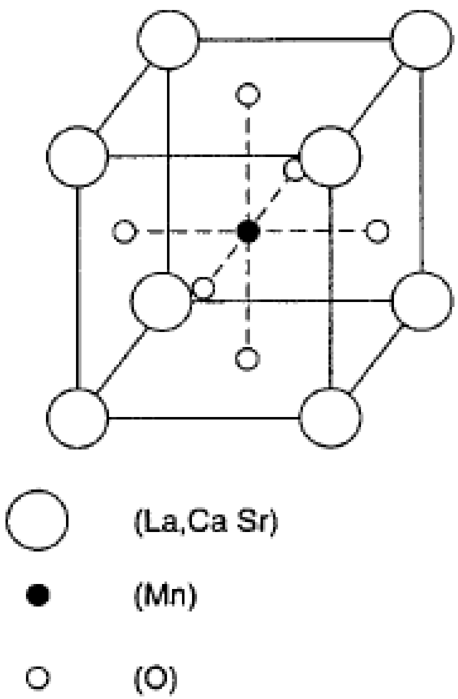
Colossal magnetoresistance (CMR)

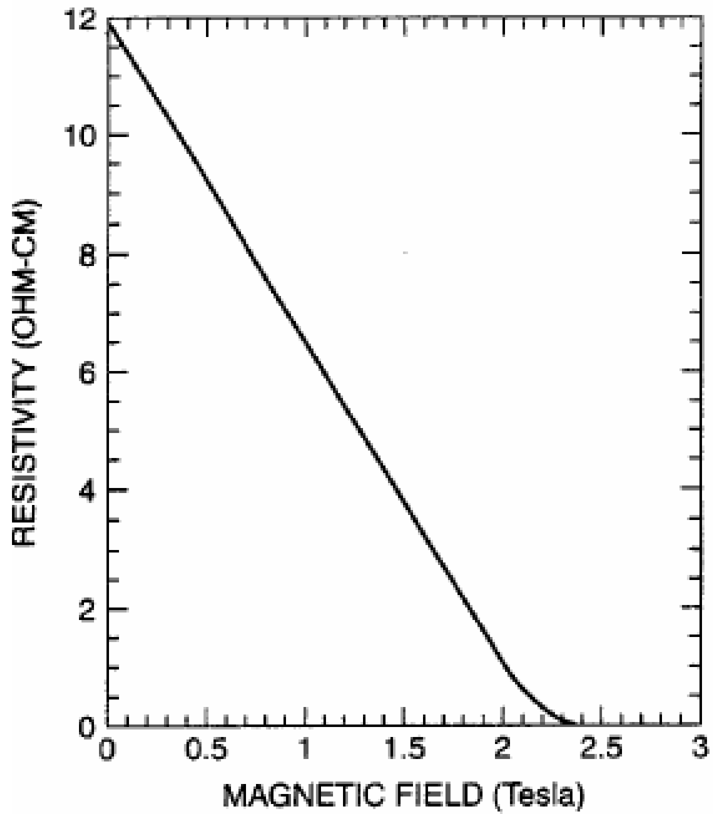
Materials have been discovered having larger magnetoresistive effects than the layered materials, and this phenomenon in them is called *colossal magnetoresistance*

$LaMnO_3$

magnetic recording heads, or as sensing elements in magnetometers. The perovskite-like material $LaMnO_3$ has manganese in the Mn^{3+} valence state. If the La^{3+} is partially replaced with ions having a valence of 2+, such as Ca, Ba, Sr, Pb, or Cd, some Mn^{3+} ions transform to Mn^{4+} to preserve the electrical neutrality. The result is a mixed valence system of Mn^{3+}/Mn^{4+}, with the presence of many mobile charge carriers. This mixed valence system has been shown to exhibit very large magneto-

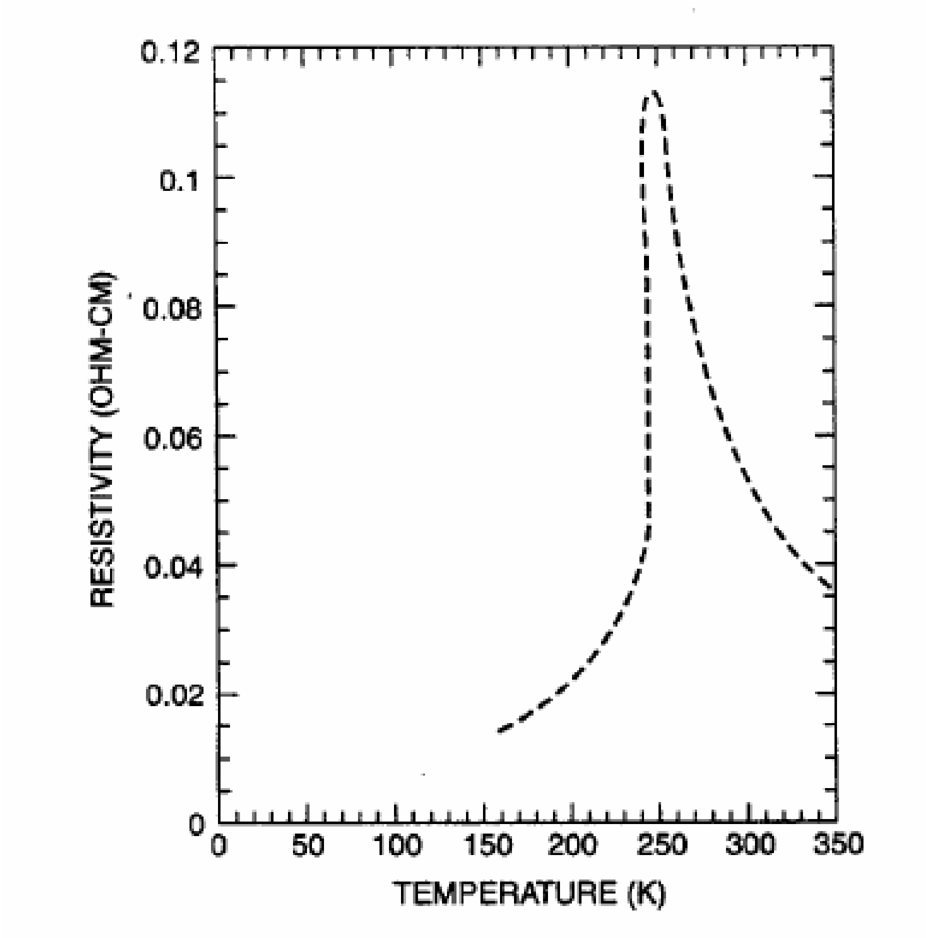
Colosal magnetoresistance





ence of the resistivity (normalized magnetoresistance) of La–Ca–Mn–O on
field in the neighborhood of the Curie temperature at 250 K. (With

La-Ca-Mn-O



0.12
0.1
0.08
0.06
0.04
0.02
0
RESISTIVITY (OHM-CM)
0
50
100
150
200
250
300
350
TEMPERATURE (K)

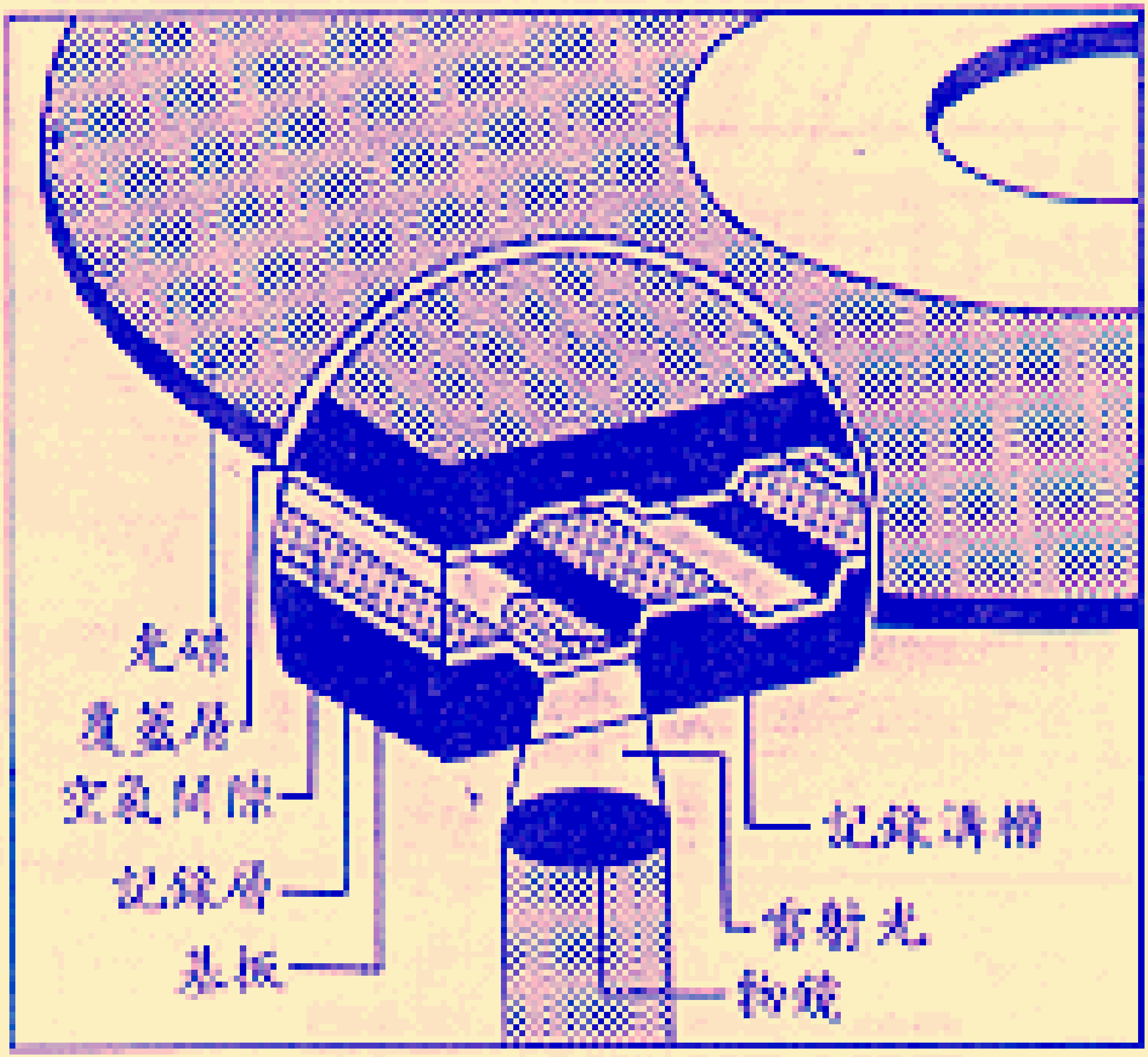
Magnetic storage

- 1. Induction coils to induce and read the magnetization

- 2. The magnetoresistive reading is more sensitive than Induction coils

Magnetic storage

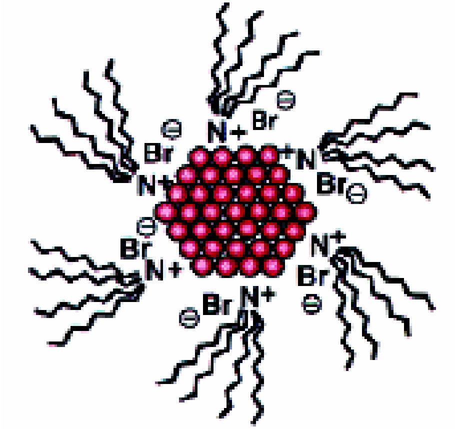
- 1. Induction coils to induce and read the magnetization
- 2. The magnetoresistive reading is more sensitive than Induction coils



光碟片的結構圖

7.7 Ferrofluids

- 1. Nanoparticles are single domain ~ 10 nm
- 2. Coated with a surfacetant to prevent aggregation
- 3. Suspended in a liquid of transformer oil or Kersene



Magnetic-field-dependent anisotropic optical properties

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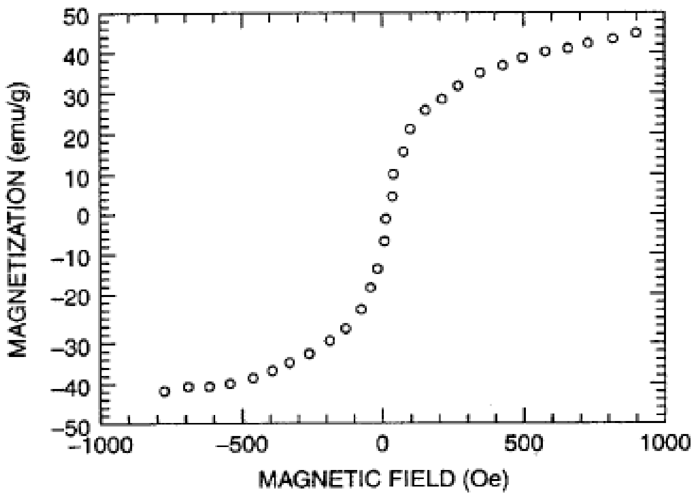
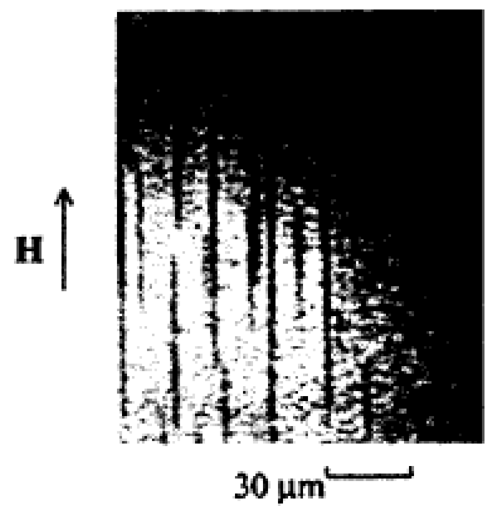
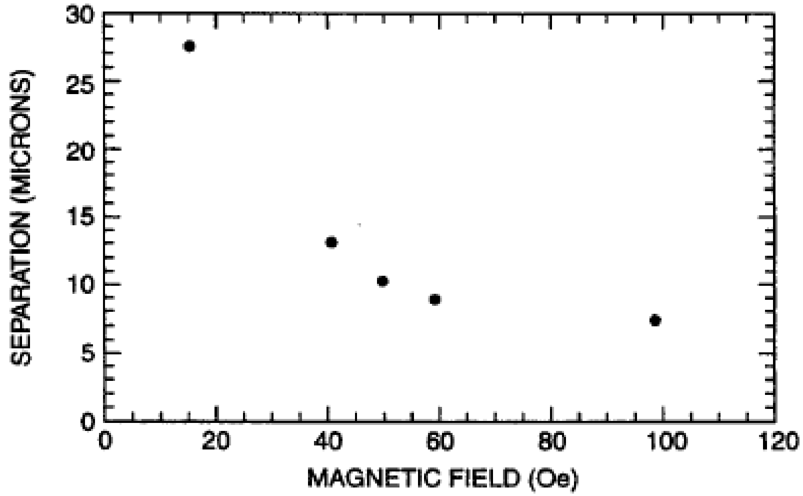


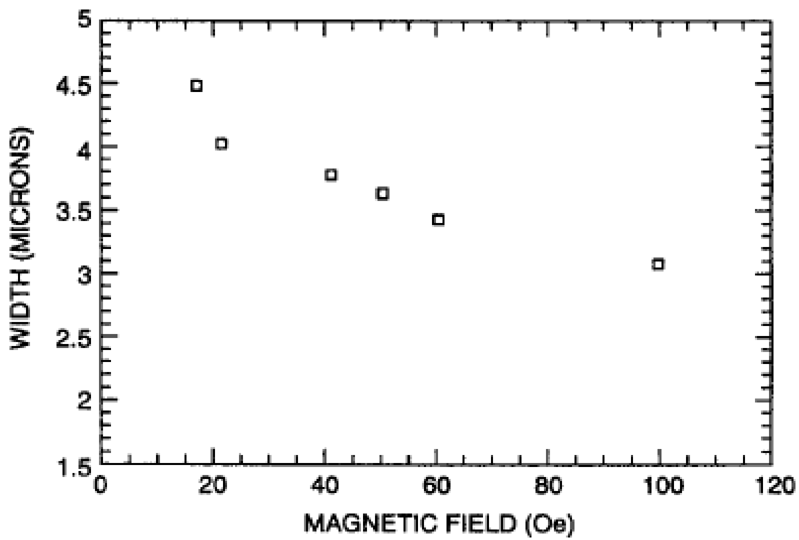
7.22. Magnetization curve for a ferrofluid made of magnetite, Fe_3O_4, nanoparticles




30
25
20
15
10
5
0
SEPARATION (MICRONS)
0
20
40
60
80
100
120
MAGNETIC FIELD (Oe)

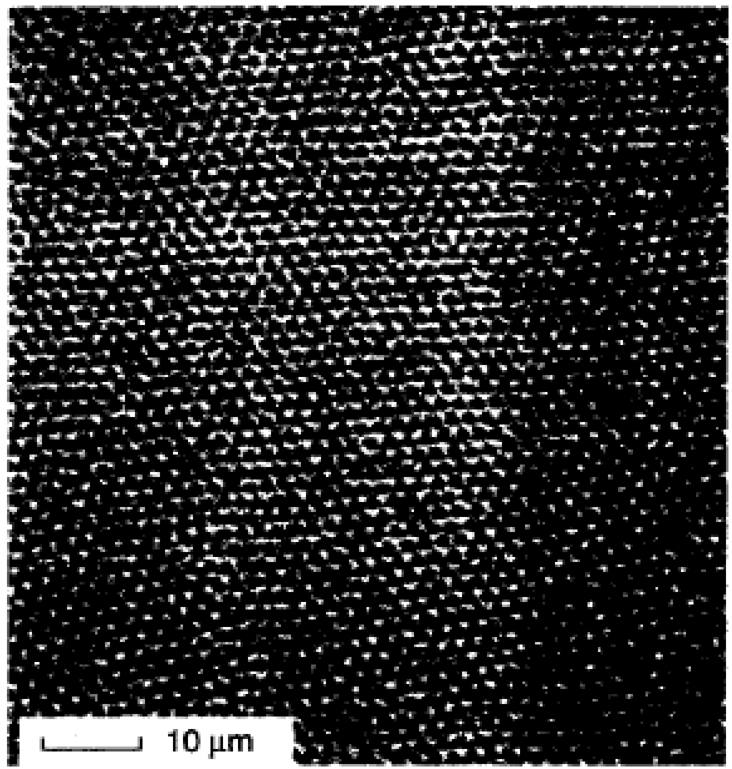
(a)

H // Surface


5
4.5
4
3.5
3
2.5
2
1.5
WIDTH (MICRONS)
0
20
40
60
80
100
120
MAGNETIC FIELD (Oe)

(b)

H is perpendicula to the surface



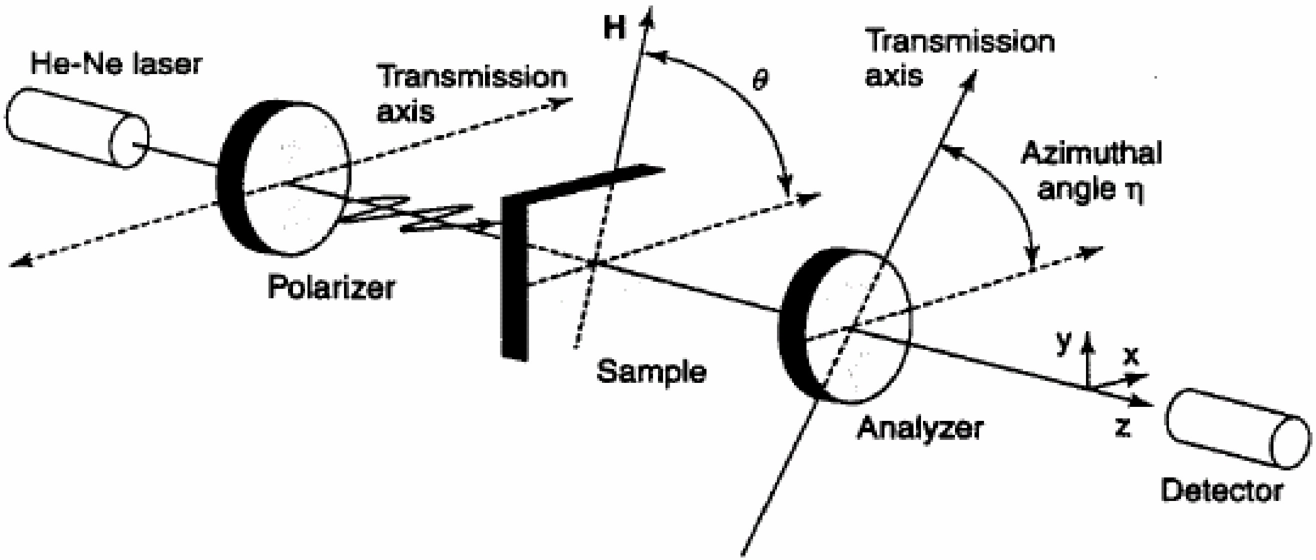


Figure 7.26. Experimental arrangement for measuring optical polarization effects in a ferrofluid film that has a DC magnetic field *H* applied parallel to its surface. [With permission from H. E. Hornig et al., *J. Phys. Chem. Solids* **62**, 1749 (2001).]