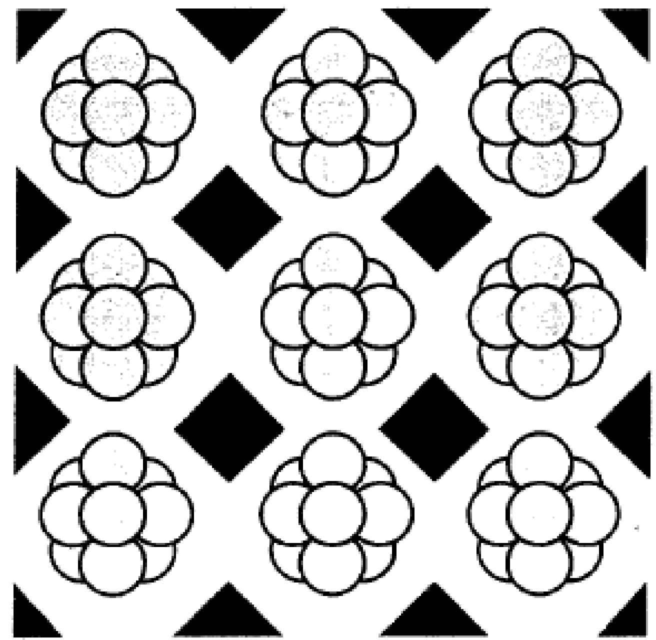
6.2.3 Arrays of nanoparticles in Zeolites

- Zeolites: Cubic mineral
- $(Na_2,Ca)Al_2Si_4)O_{12}.8H_20$
- Porous materials

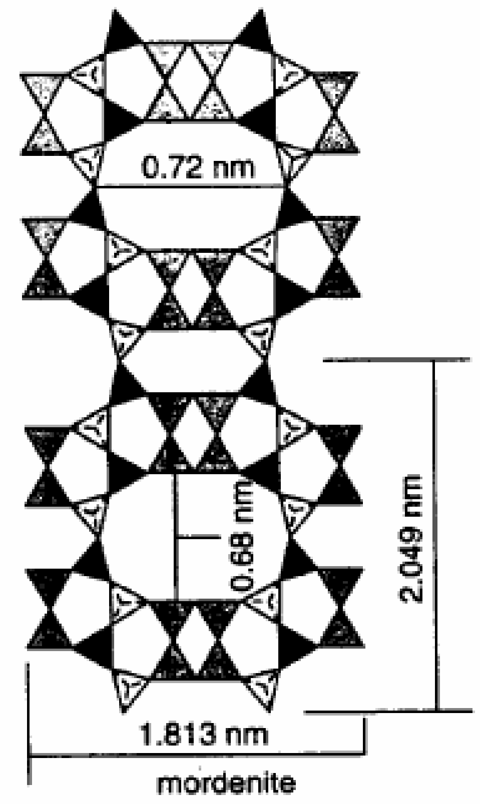


3chematic of cluster assemblies in zeolite pores. (With
ov et al., in *Handbook of Nanostructured Materials and*
1., Academic Press, San Diego, 2000, Vol. 4, Chapter 4, p. 23

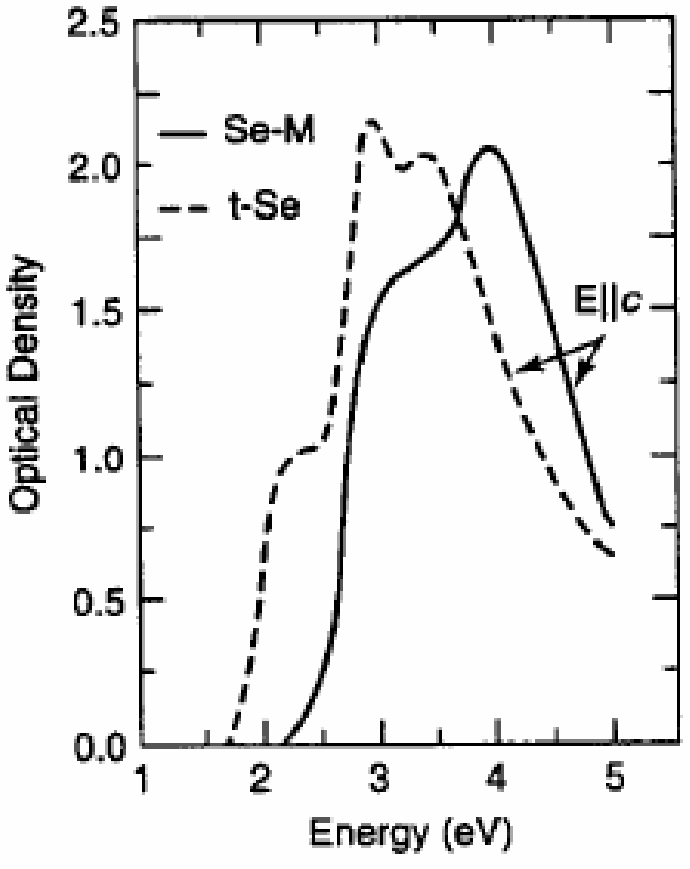
Zeolite--Mordenite

- $(Ca,Na,K_2)(Al_2Si_{10})O_{24}.7H_2O$
- Orthrorhombic
- Long parrel channels
- With d= 0.6 nm

- Se atoms fill into the channel
- to form chains of single atom
-



Optical absorption



The electronic structure of Se chains is different from Se crystal

6.2.4 Crystals of metal nanoparticles

Chemical reduction !

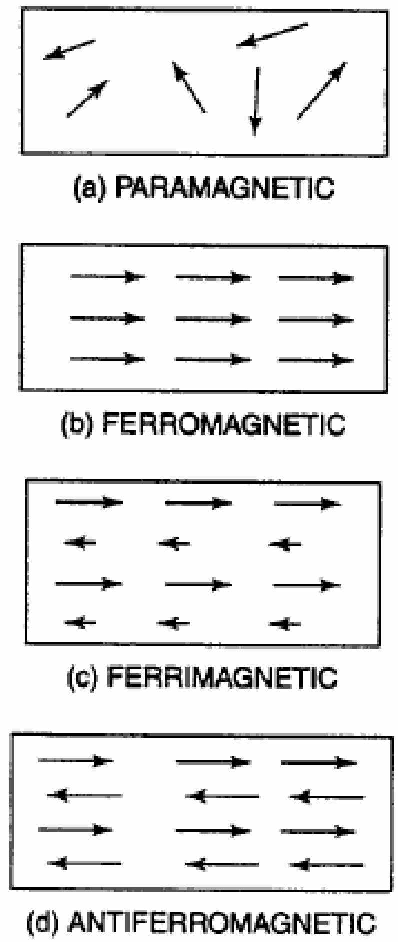
6.2.4. Crystals of Metal Nanoparticles

A two-phase water toluene reduction of $AuCl_4^-$ by sodium borohydride in the presence of an alkanethiol ($C_{12}H_{25}SH$) solution produces gold nanoparticles Au_m having a surface coating of thiol, and embedded in an organic compound. The overall reaction scheme is

$$AuCl_4^-(aq) + N(C_8H_{17})_4 + (C_6H_5Me) \rightarrow N(C_8H_{17})_4 + AuCl_4^-(C_6H_5Me) \quad (6.10)$$

$$mAuCl_4^-(C_6H_5Me) + n(C_{12}H_{25}SH)(C_6H_5Me) + 3me^- \rightarrow 4mCl^-(aq) + (Au_m)(C_{12}H_{25}SH)_n(C_6H_5Me) \quad (6.11)$$

Chapter 7 Nanostructured Ferromagnetism



ious arrangements of individual atomic

The interaction between atomic magnetic moments is of two types:

- 1. Exchange interaction

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

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

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

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

2. Dipolar interaction

$$\frac{\mu_1 \cdot \mu_2}{r^3} - 3(\mu_1 \cdot r)\frac{\mu_2 \cdot r}{r^5} \tag{7.3}$$

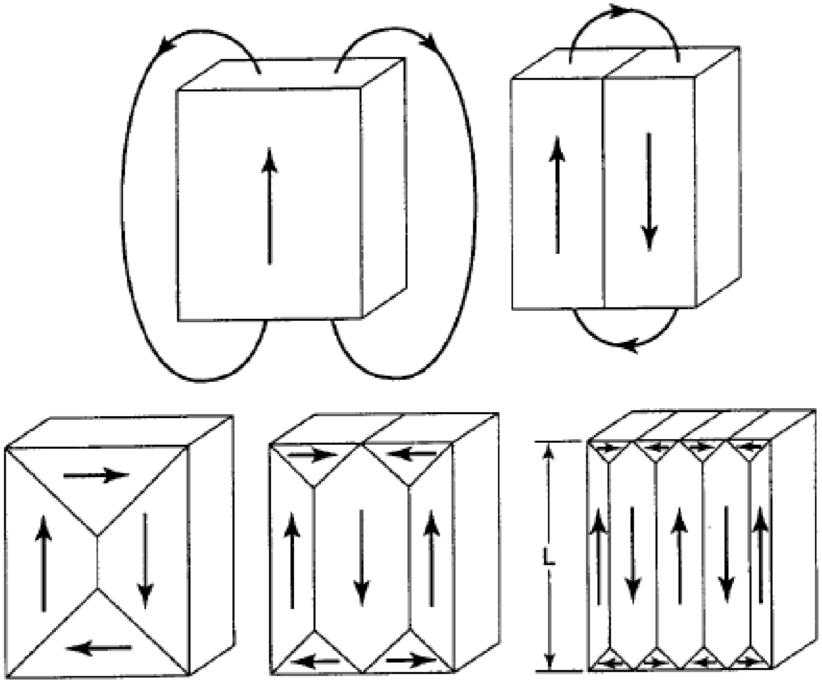
Couiomb interaction and exchange interaction for m_s=-1/2

Magnetization M of a bulk

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

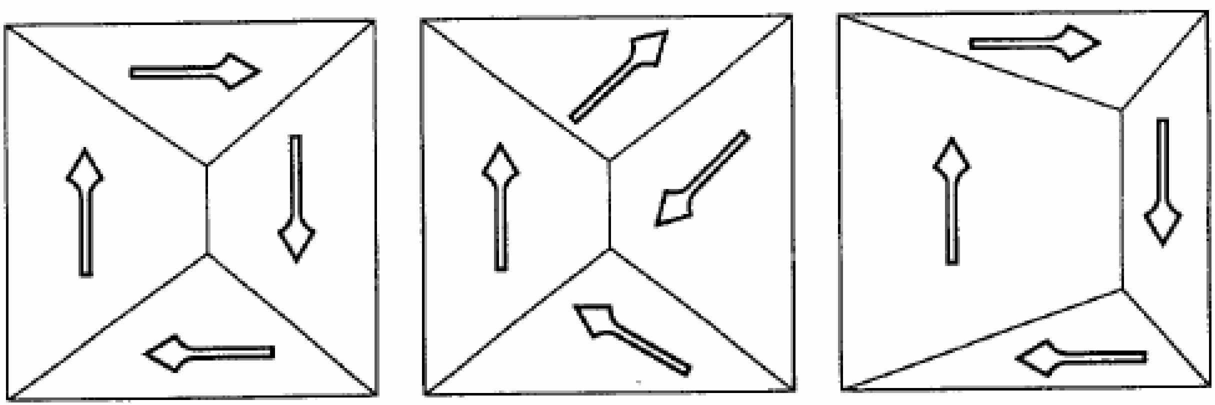
For T<< Tc

$$\chi = M/H.$$



(a)

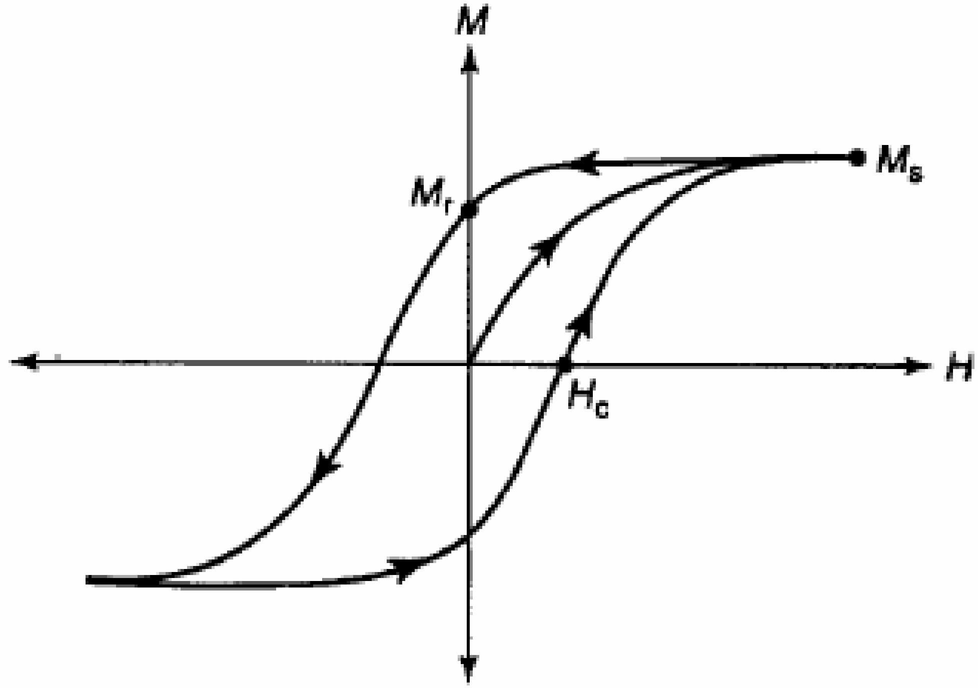
H=0



(b)

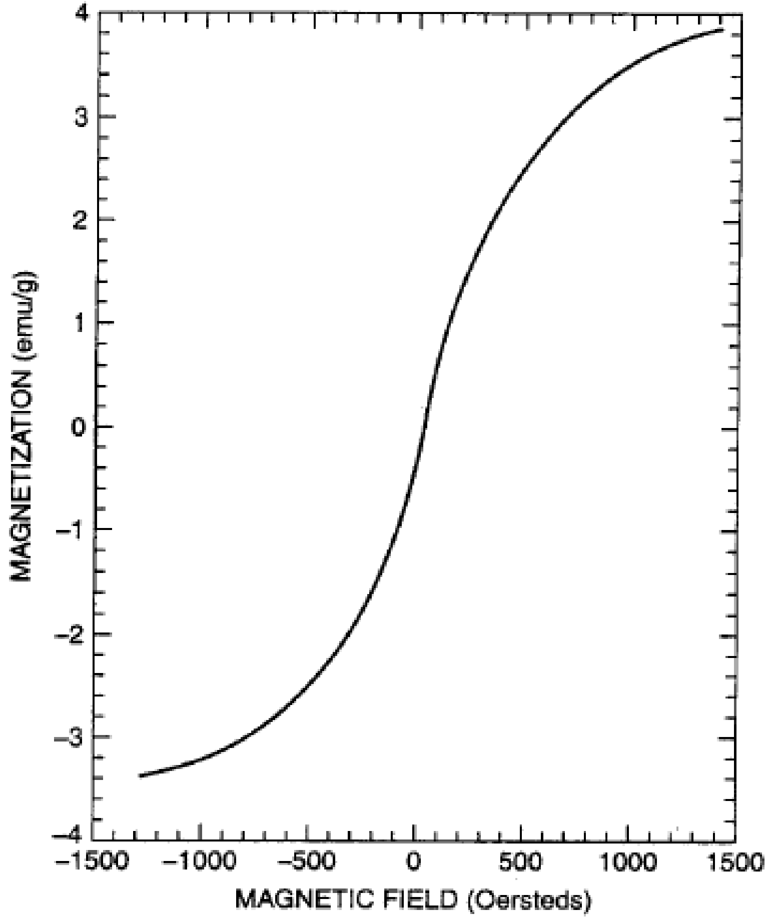
H>0

Remnant magnetization, Coercive field, Saturation magnetization



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



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 *Mater. Res.* **15**, 332 (2000).]

Superparamagnetism

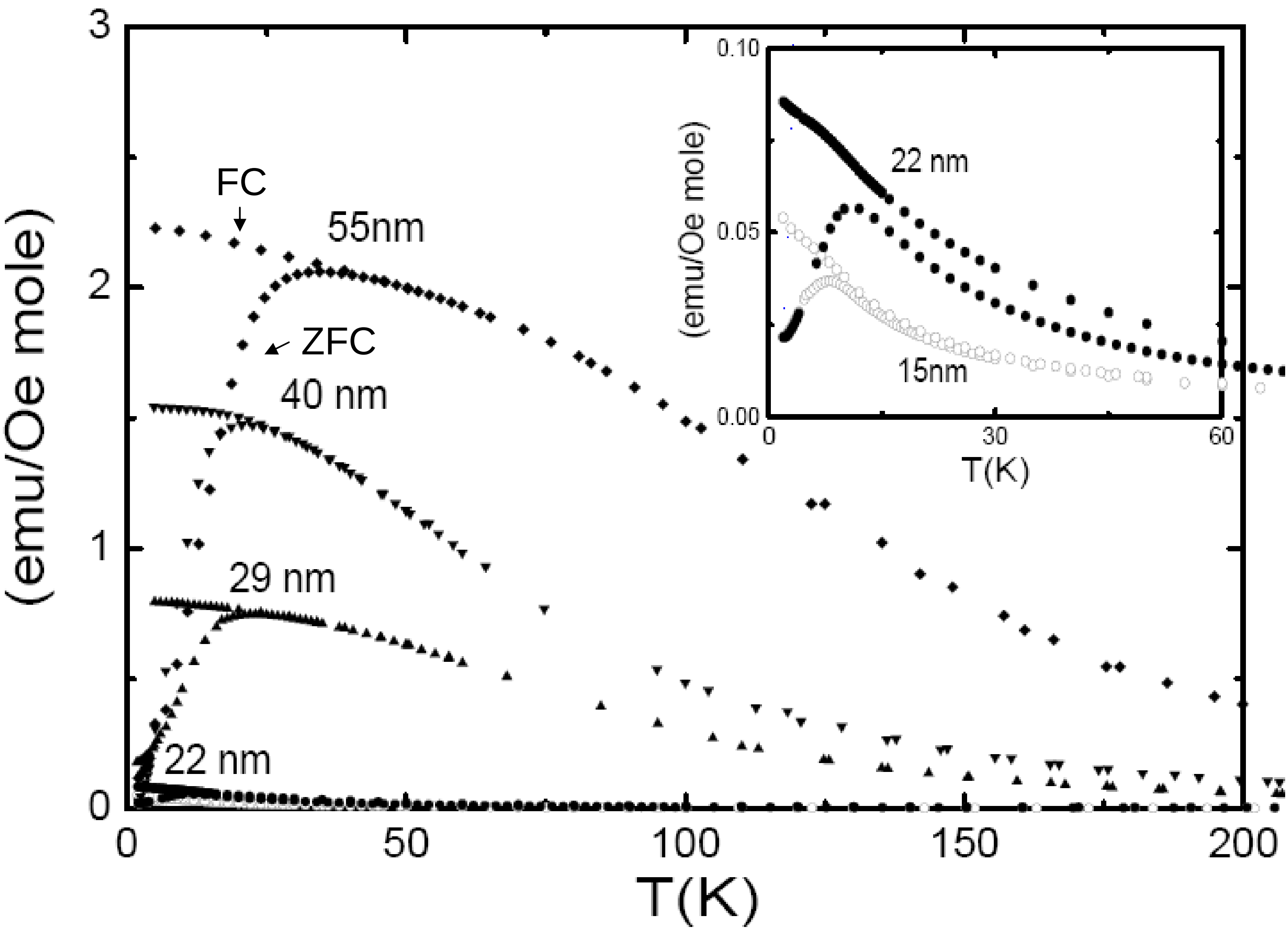
⇒Monodomain particles

- Below 100 nm

⇒Fluctuation of the magnetic moment like in a paramagnet

⇒Ferromagnetic particles with moment (T_c is high)

⇒Moment dependent on particle volume



此圖為$FeSi_2$奈米粉末的DC磁化率-溫度曲線

Temperature dependence of χ

- 1. The temperature of peak value of χ in ZFC is defined as the Blocking temperature T_B。
- 2. χ of ZFC and χ of FC deviate at T_B
- 3. Above T_B, χ of ZFC and χ of FC are overlap.

Blocking Temperature

$$T_B = \frac{KV}{25k_B}$$

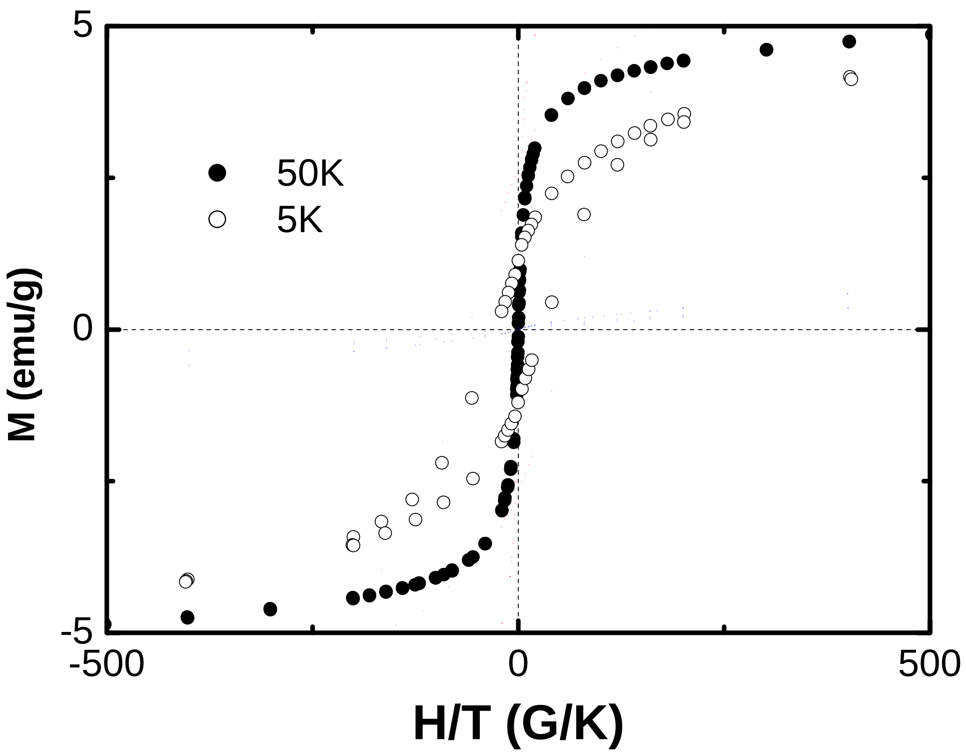
k_B is the Boltzmann constant

K is the anisotropic constant

V is the volume of nanoparticle

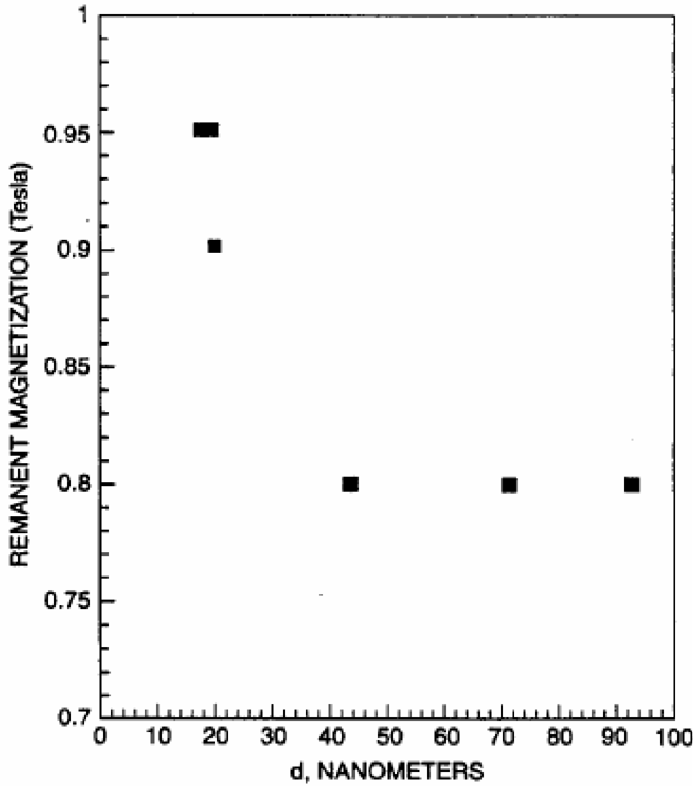
Analysis of size-dependent blocking temperature

M-H曲線



- 1. T< T_B, Hysteresis appears in M-H. Due to thermal energy is less than the interactions among particles
- 2. T> T_B, No hysteresis appears in M-H. Since thermal energy is larger than the interactions among particles

$FeSi_2$ 40nm particles



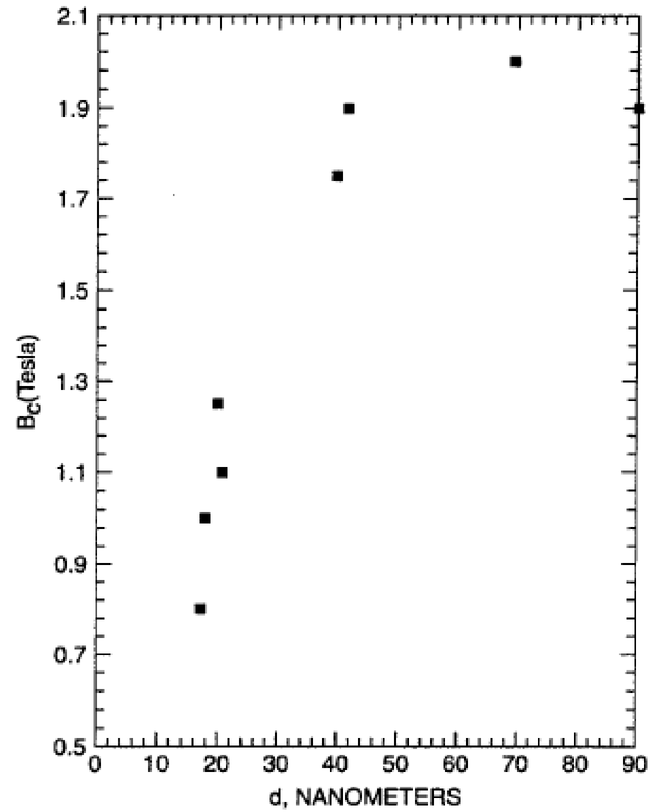


Figure 7.6. Dependence of the coercive field B_c (i.e., H_c) on the granular particle size d (
Nd–B–Fe permanent magnet. [Adapted from A. Manaf et al., *J. Magn. Magn. Mater.* 1

$Nd_2Fe_{14}B$ Grain d

7.4 nanopore containment of magnetic particles

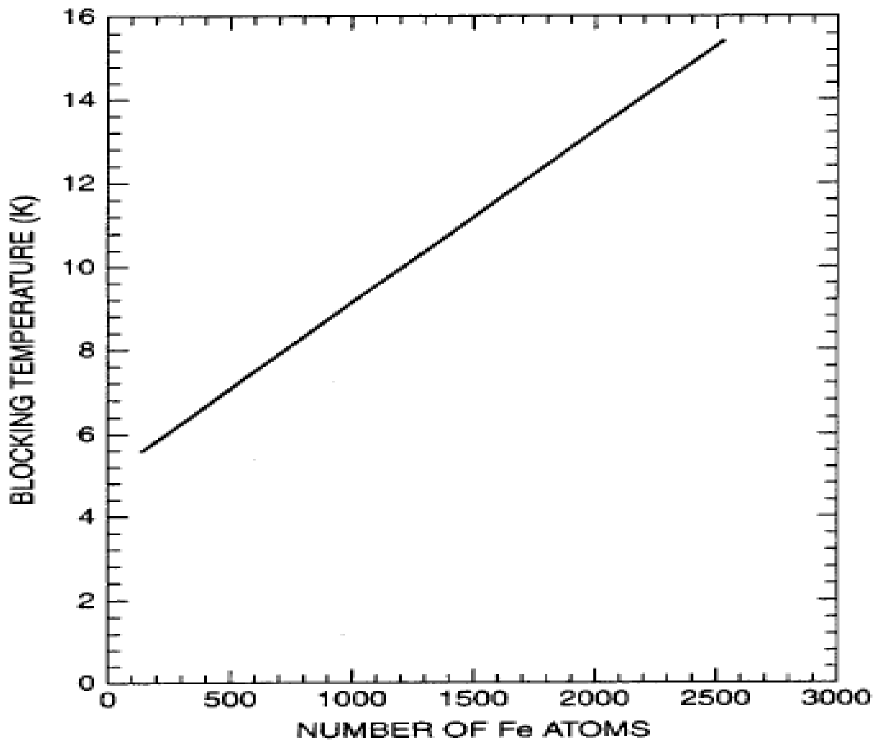
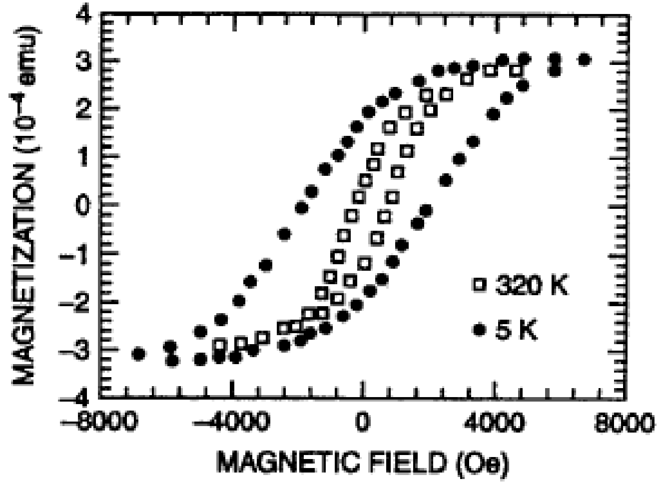


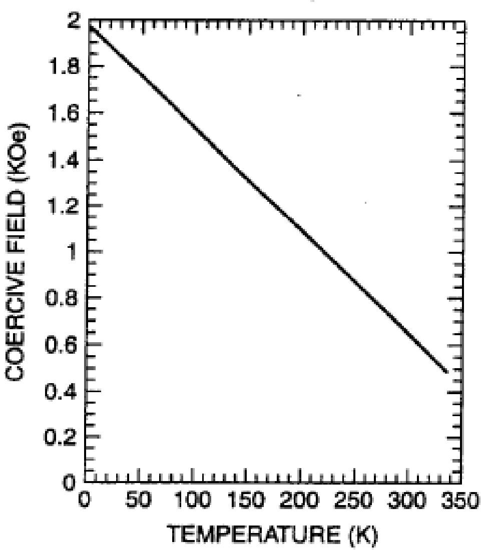
Figure 7.9. Plot of blocking temperature T_B versus the number of iron atoms in the cavity of ferritin. [Adapted from D. D. Awschalom and D. P. DiVincenzo, *Phys. Today* (April 1995).]

7.5 Nanocarbon ferromagnets

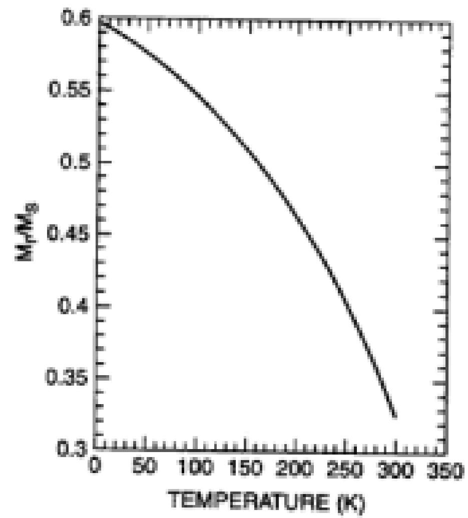
igure 7.11. Scanning electron microscope image of iron particles (light spots) on the tips of igned carbon nanotubes. [With permission from Z. Zhang et al., J. Magn. Magn. Mater. 231, I (2001).]



jnetization curve hystersis loops for iron particles on the tips



ɔt of coercive field H_c versus temperature T for iron part



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。

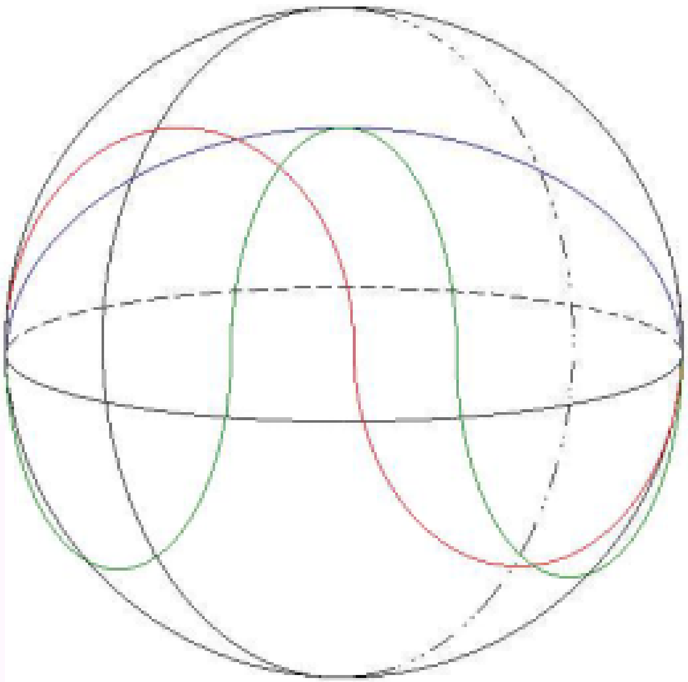
Phonon quanum size effect：聲子與表面積之改變。

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。

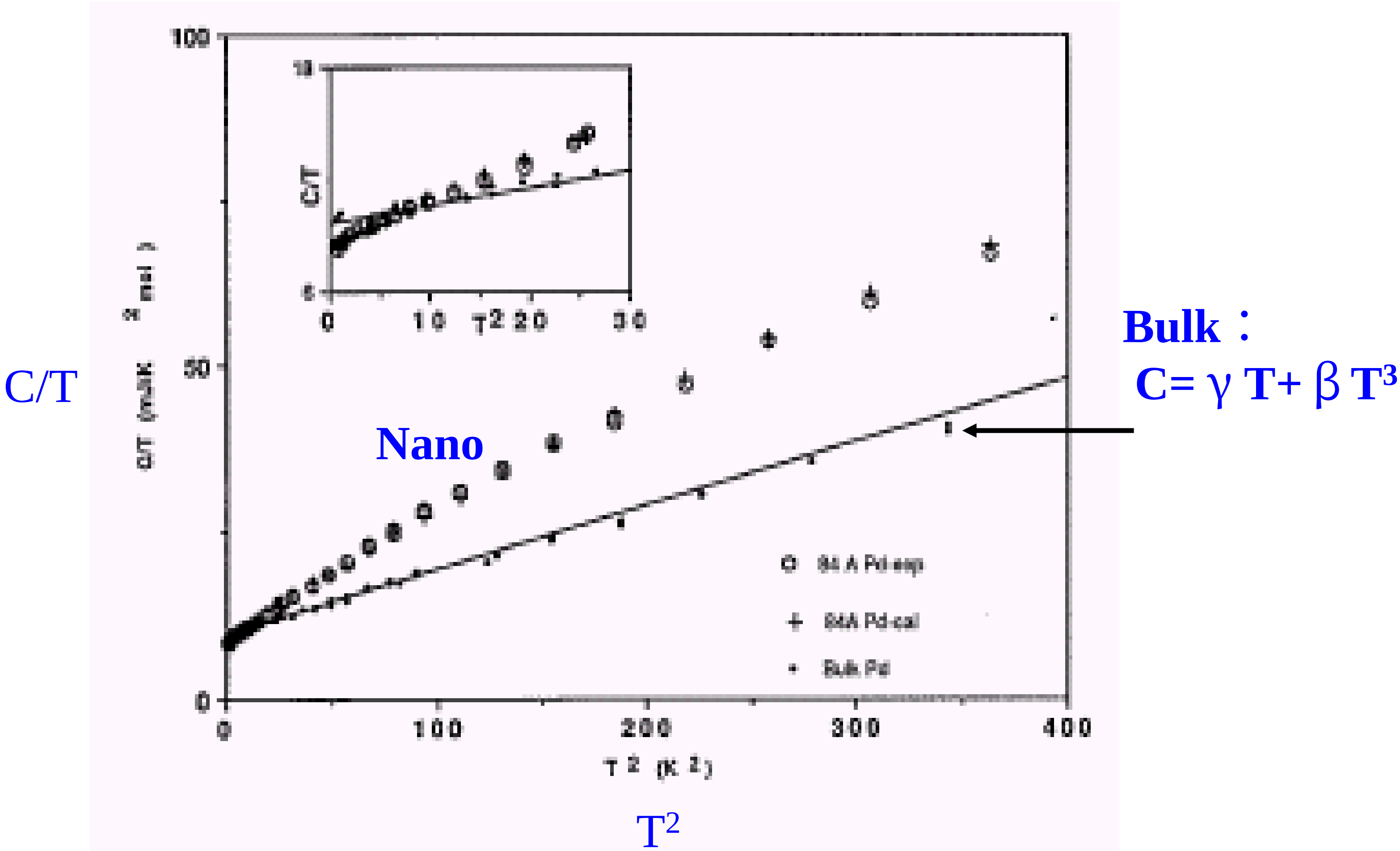
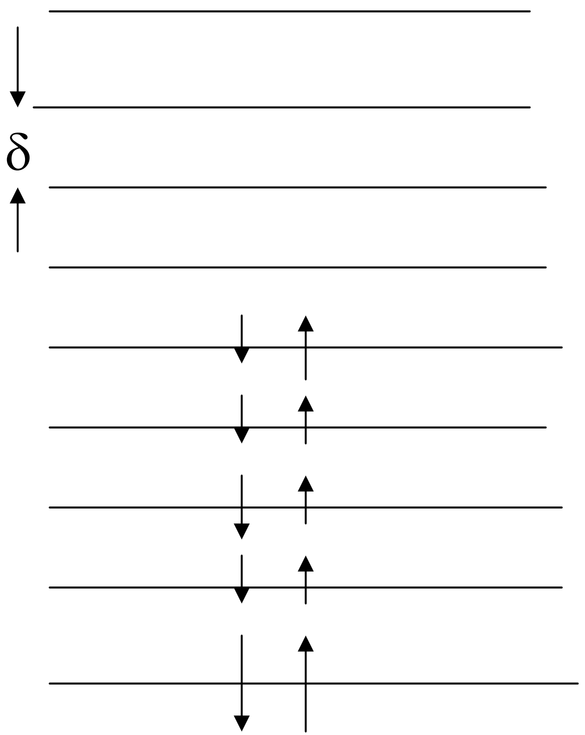


FIG. 3. The specific heat of bulk palladium and 84-Å Pd nanocrystals. The small dots represent bulk Pd and the solid

Y.Y. Chen etc, PRB 52, 9364, 1995

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

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



$\varepsilon_F \sim 10^4$ K

Bulk Pd **δ ~10e^{-30}K**

80 Å Pd **δ ~ 0.5K**

No. of atoms~ 8000

Magnetic field

H=0

H>0

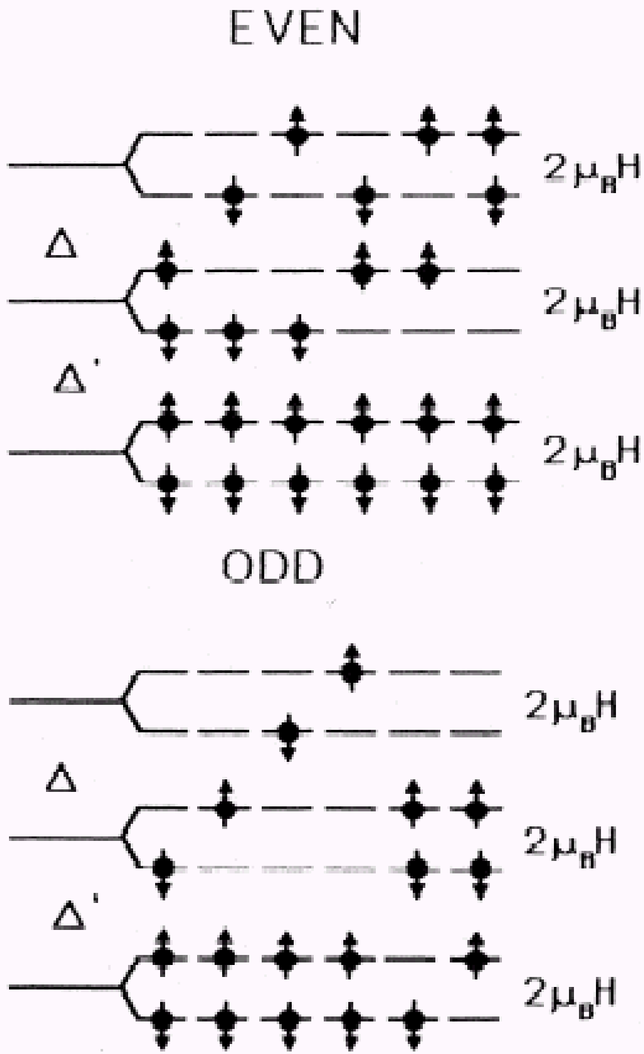


FIG. 2. Electron-level structure diagrams for the two cases of particles with an even number of electrons, and for particles with an odd number of electrons. Only the lowest-energy configurations are shown with the ground state at the left and progressively higher excited states to the right for each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

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

Partition of C(T)

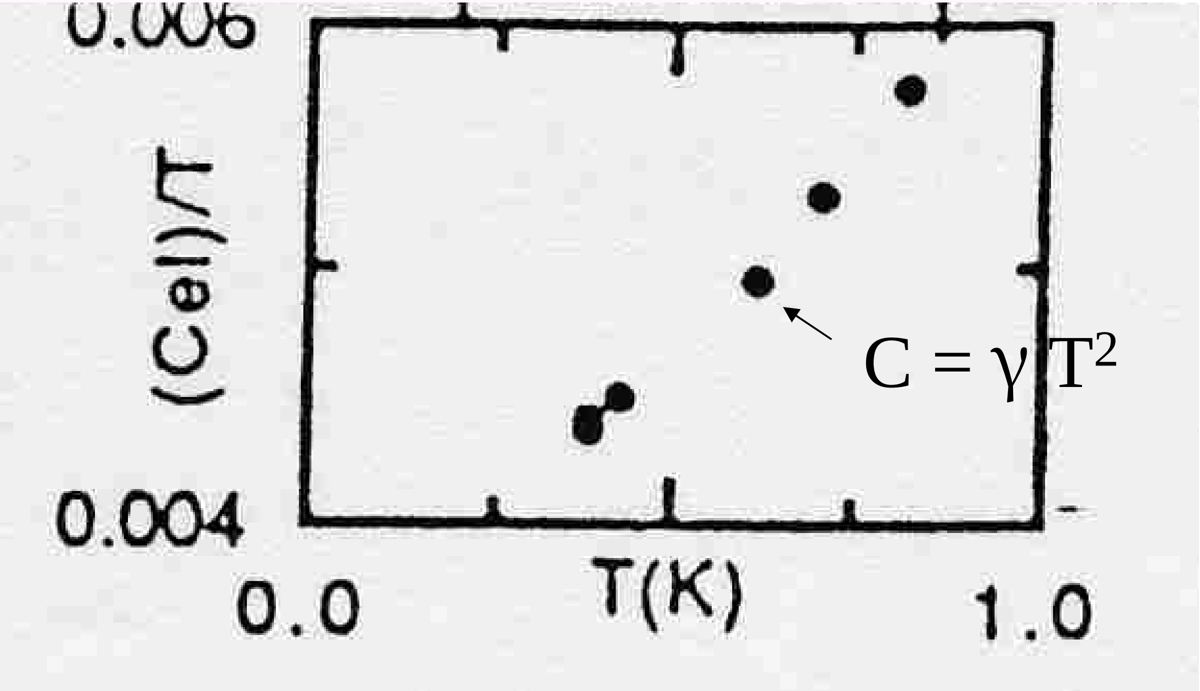
$$Z_{even} \approx 1 + 2(1+\cosh 2\beta\mu_B H)(e^{-\beta\Delta}) + e^{-2\beta\Delta} ,$$

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

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

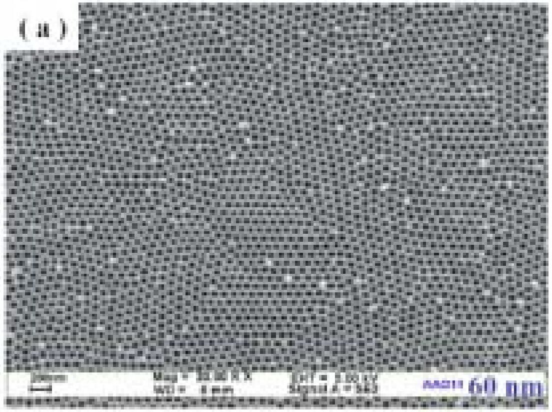
$$C^1_{odd}/k_B = 17.8(k_B T/\delta)^2 ,$$

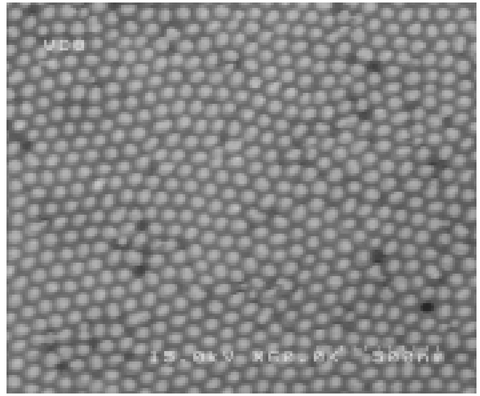
orthogonal

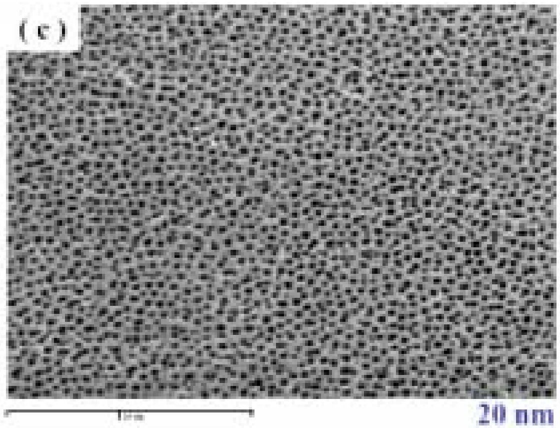


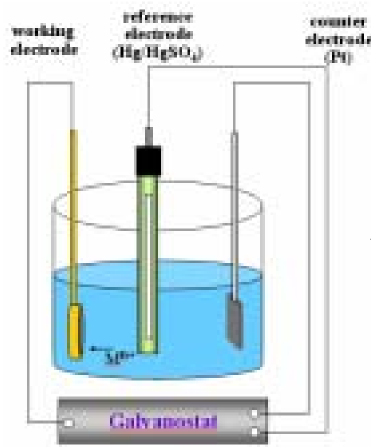
Y.Y. Chen, LT21 Proceeding 2369 Aug.1996

Size dependence of magnetization in Fe **nanowires**

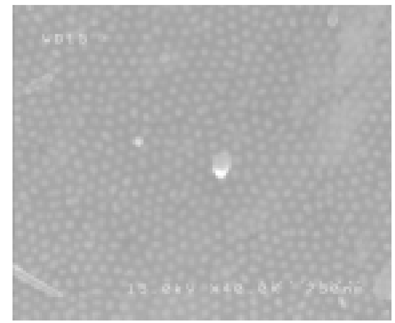




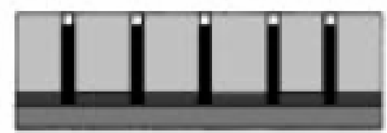




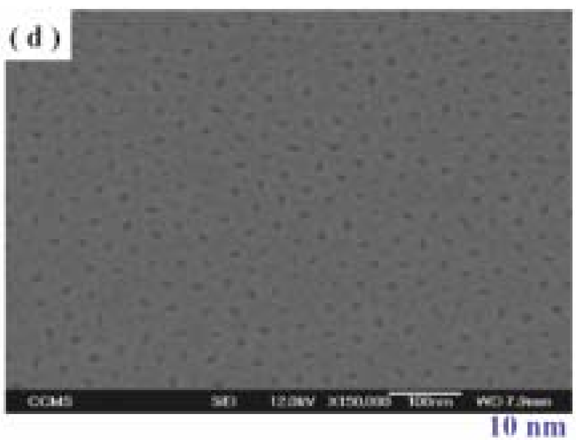
AAO method



Cu **nanowire**

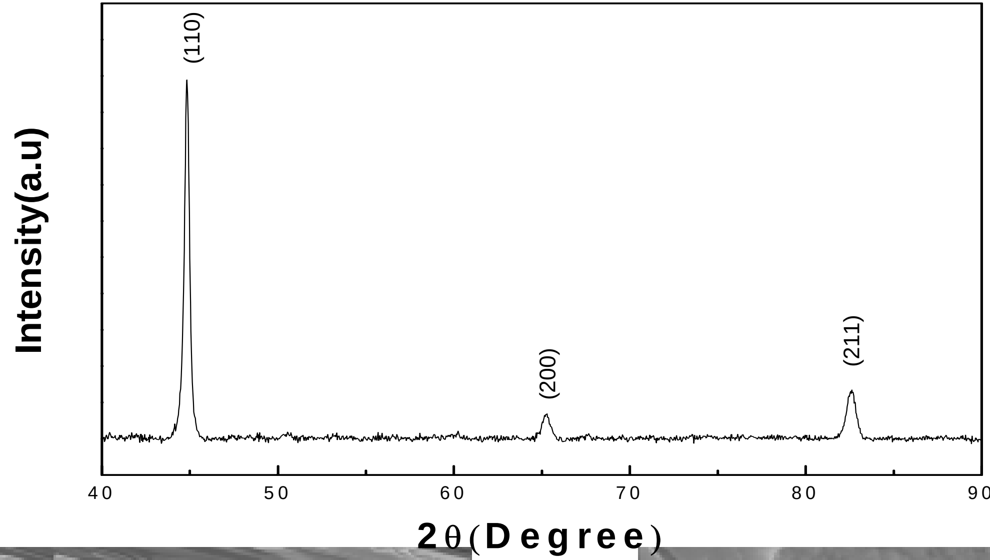


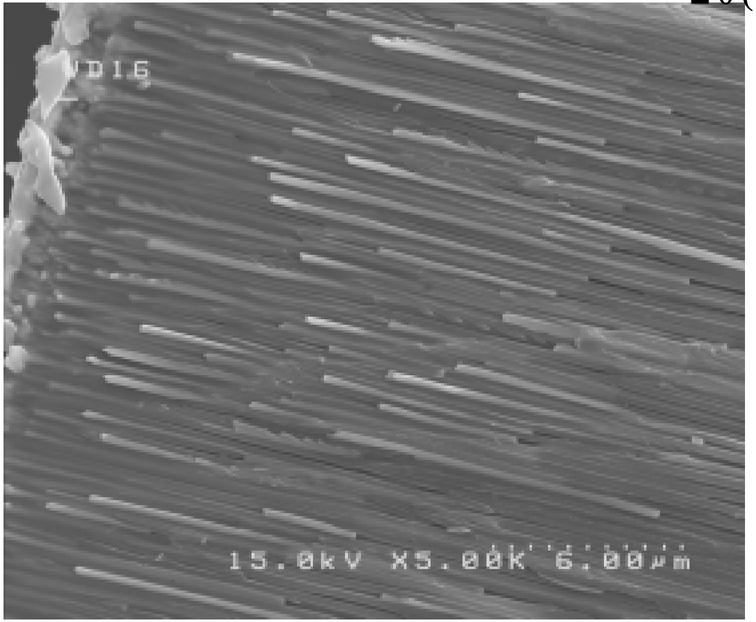
$CuSO_4.5H_2O$, pH~2

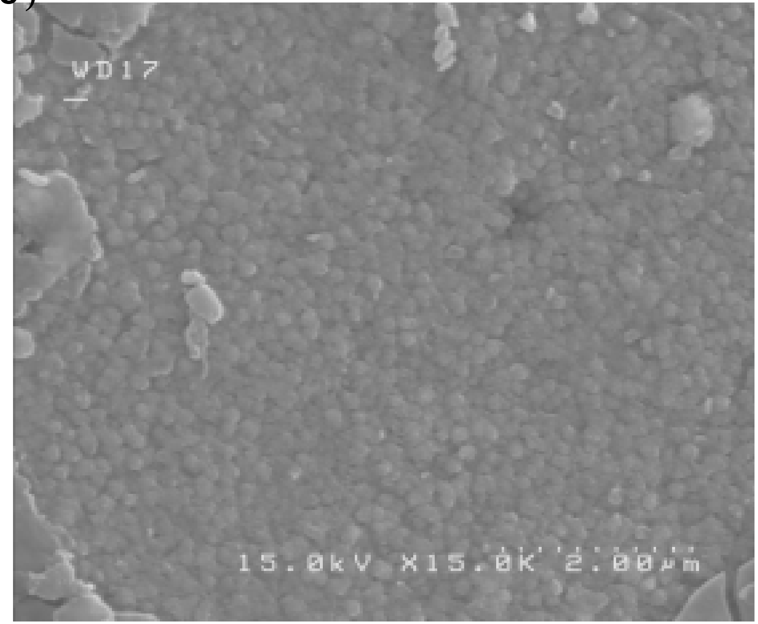


70nm Al nanowires

Fe

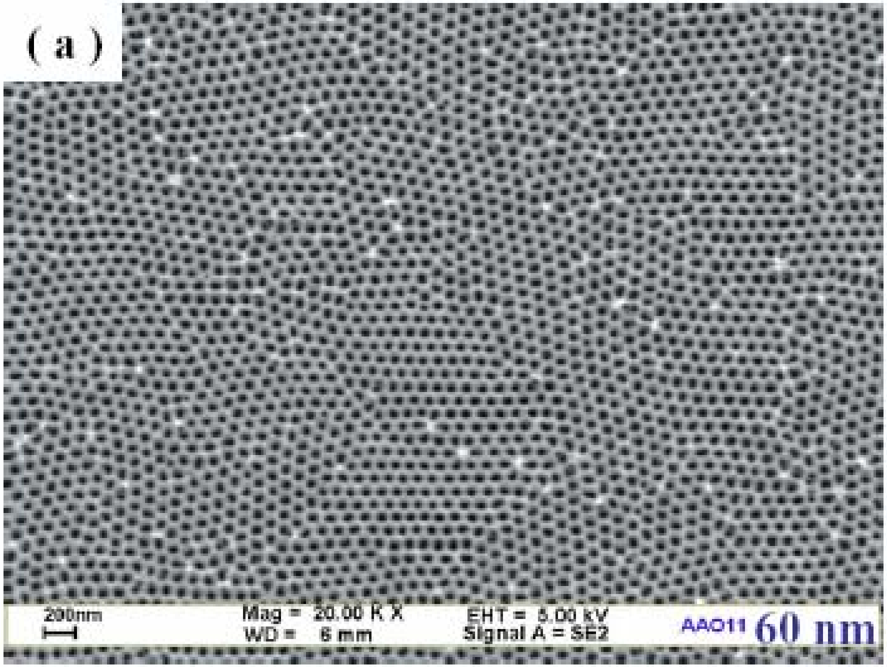


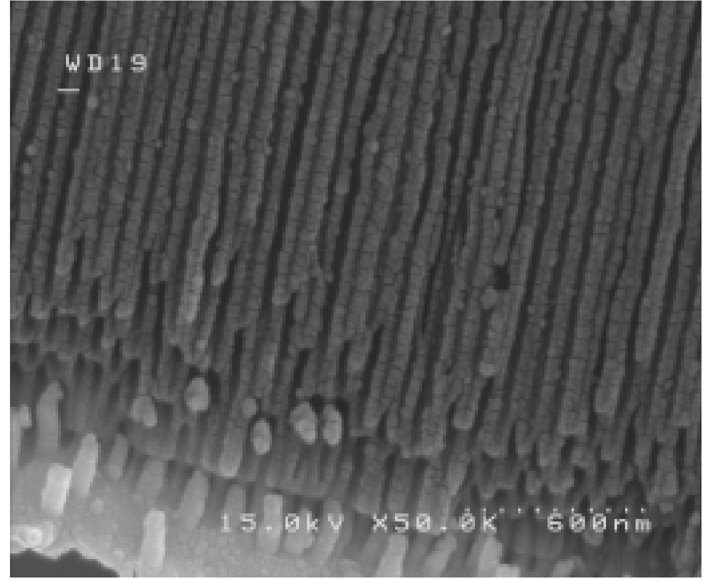


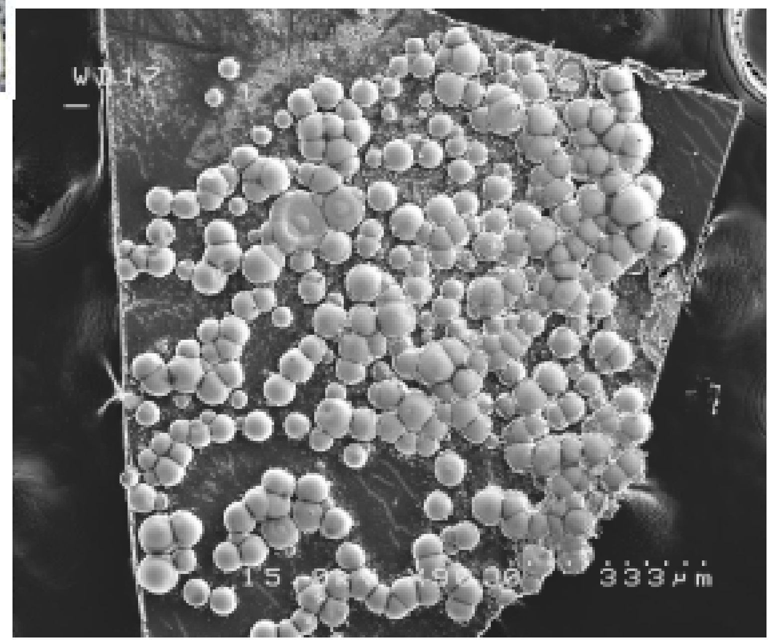


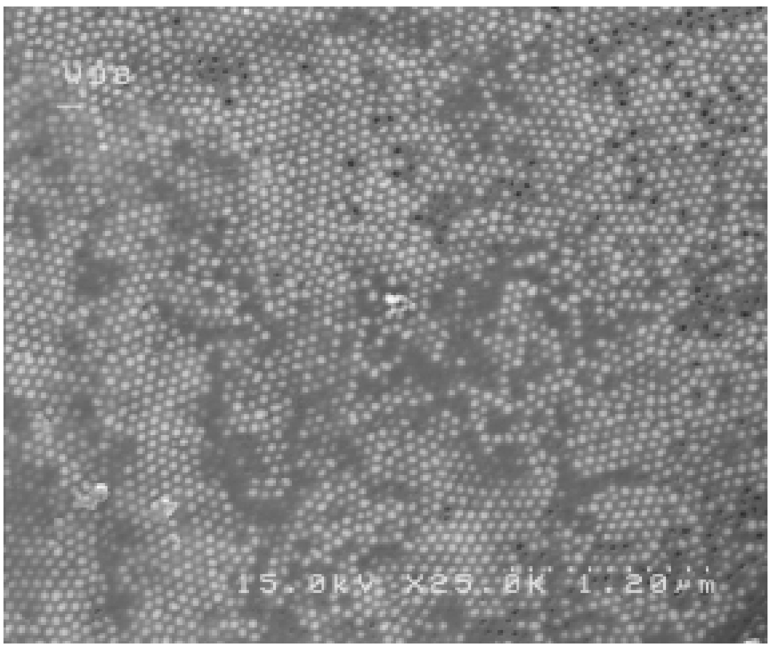
Fe nanowire ~200 nm

Fe



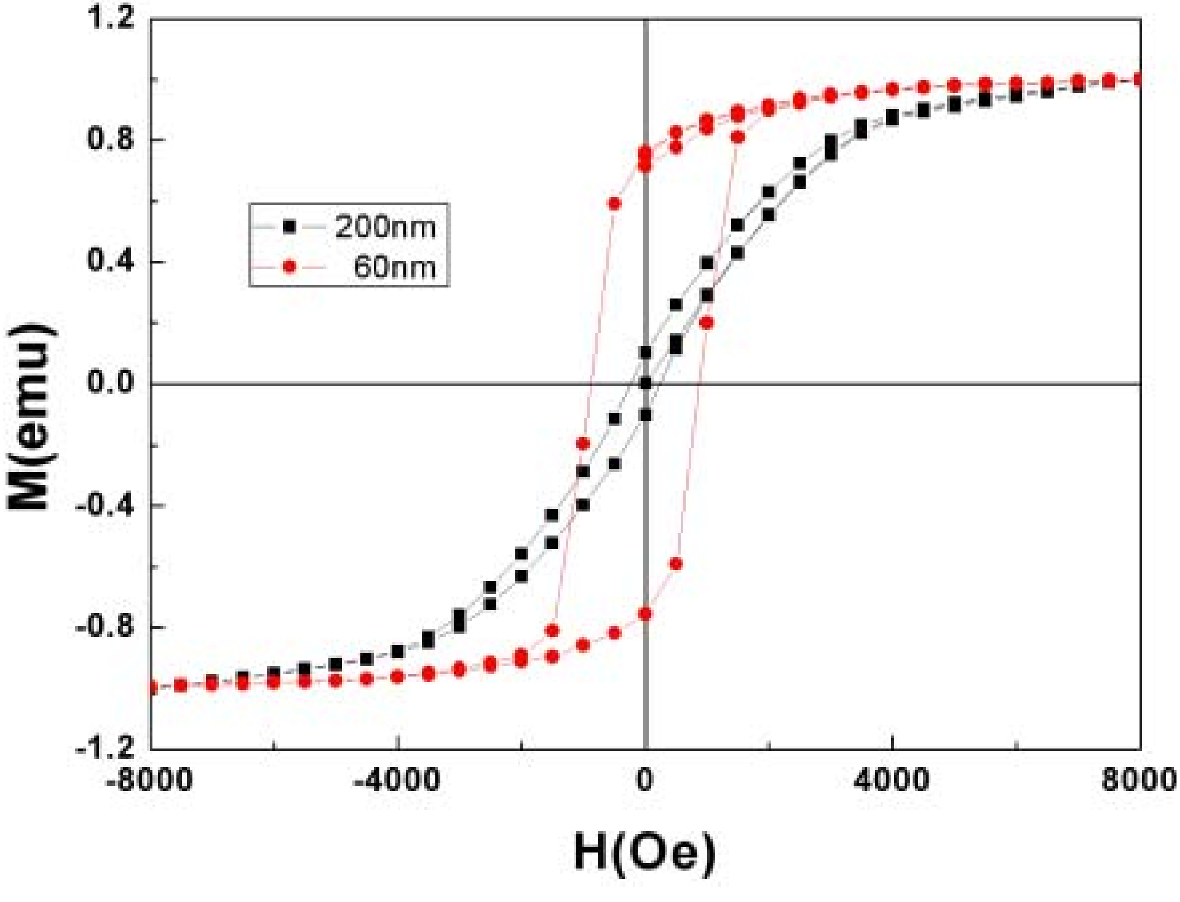




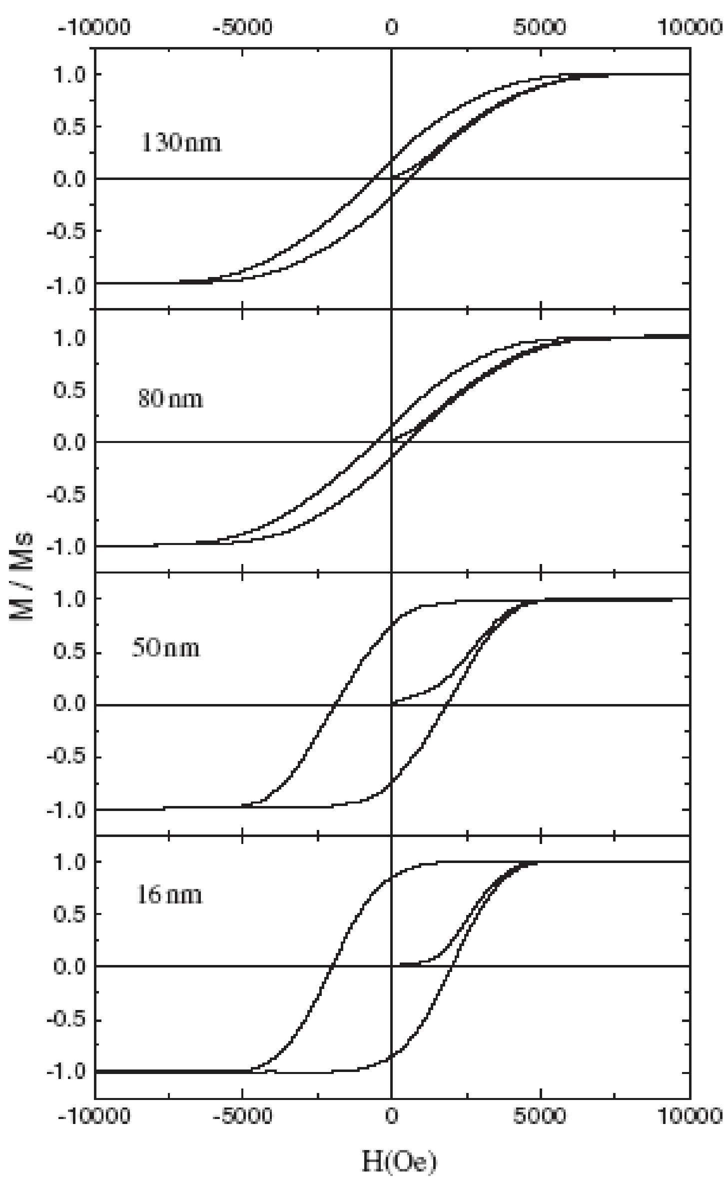


Fe nanowire ~60 nm

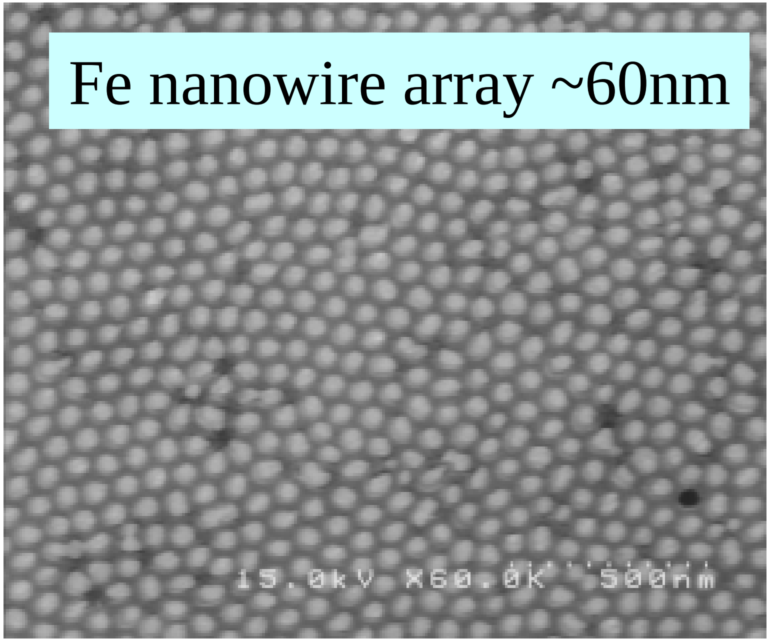
Normalized (M/Ms)-H

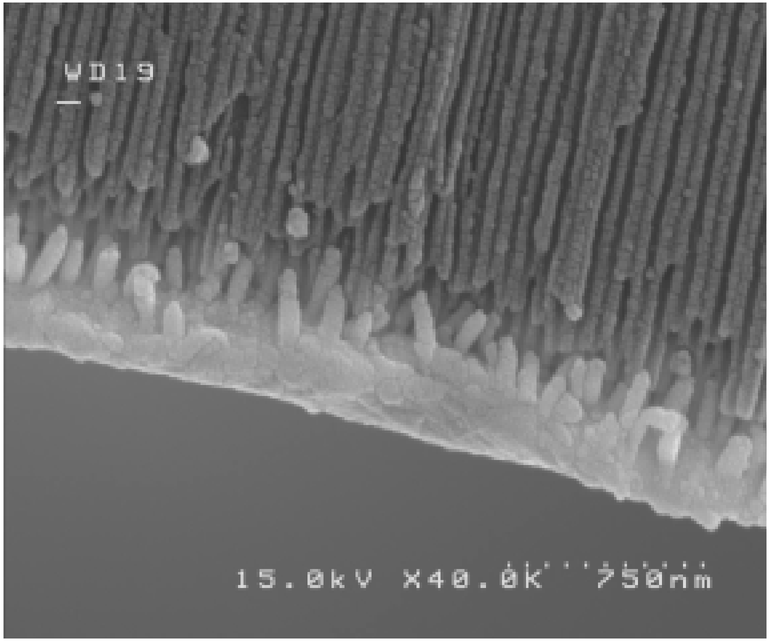


Magnetic texture of nanowire arrays



Fe nanowire array ~60nm

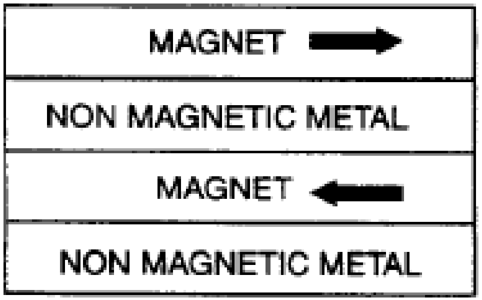




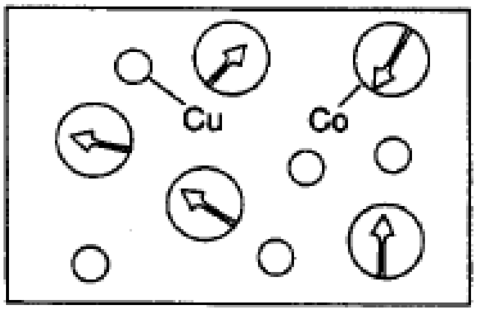
7.6 Giant and colossal magnetoresistan

- 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
- R increases 10 times

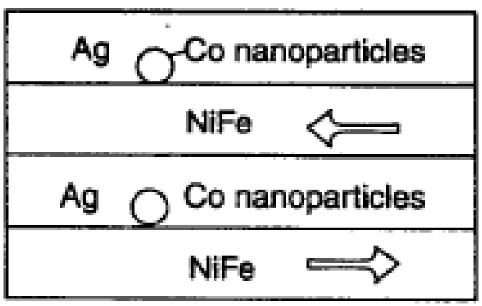
Giant magnetoresistance (GMR)



(a)



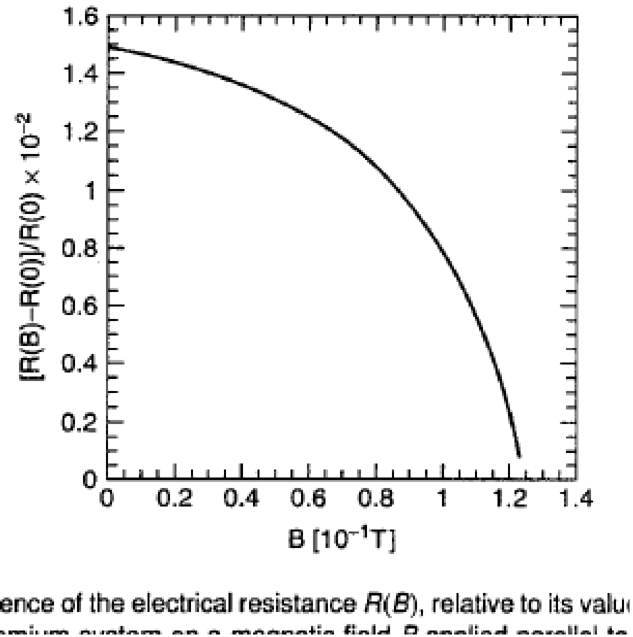
(b)

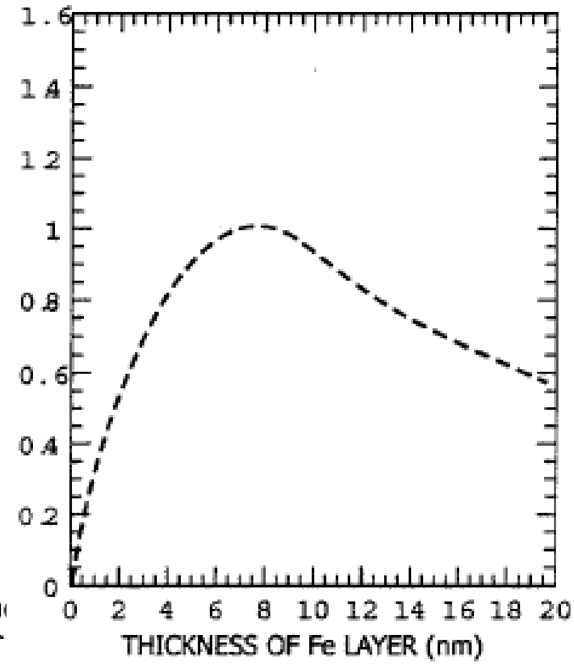


(c)

Alternate layers of FM and Non-FM

Fe-Cr

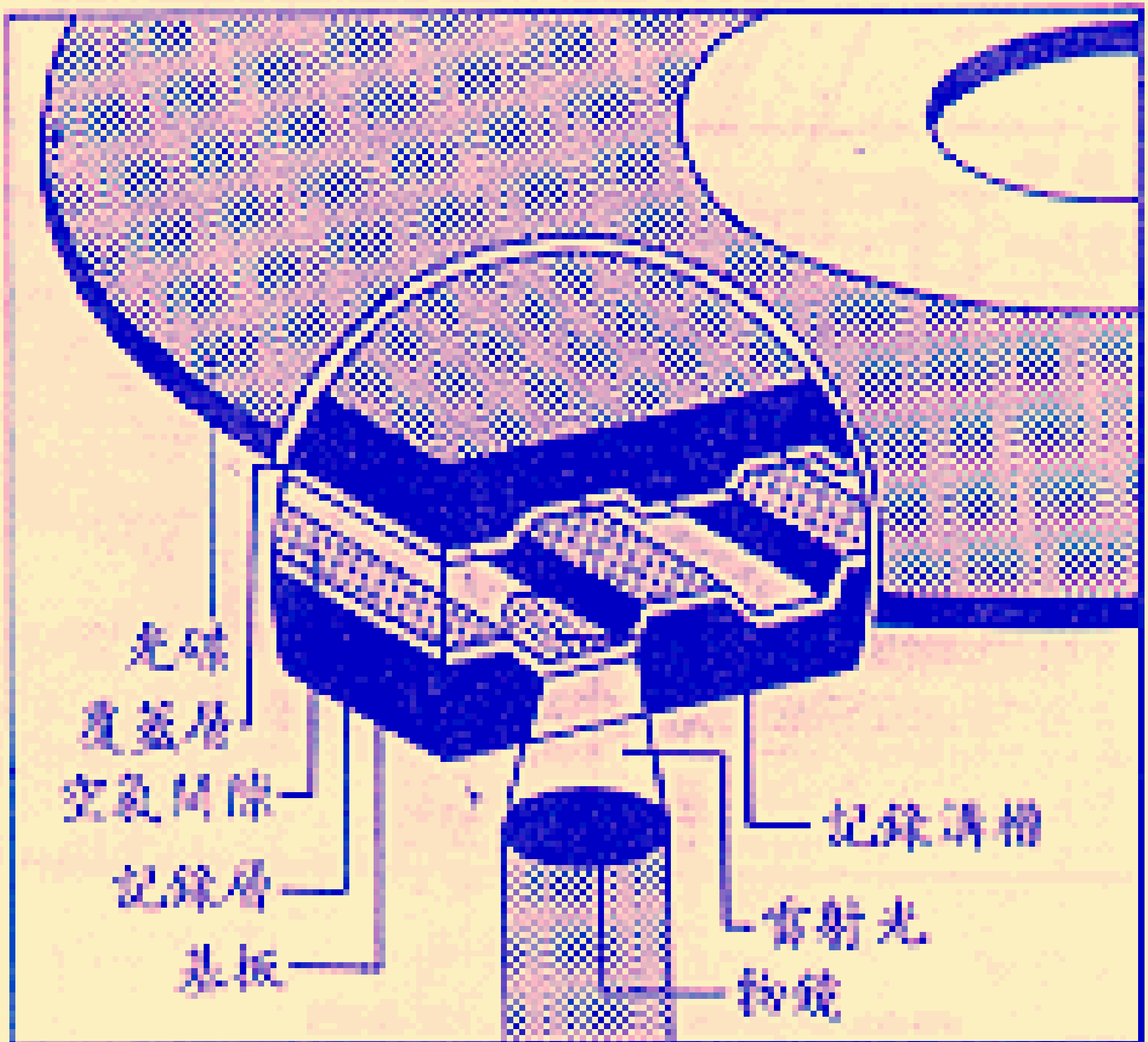




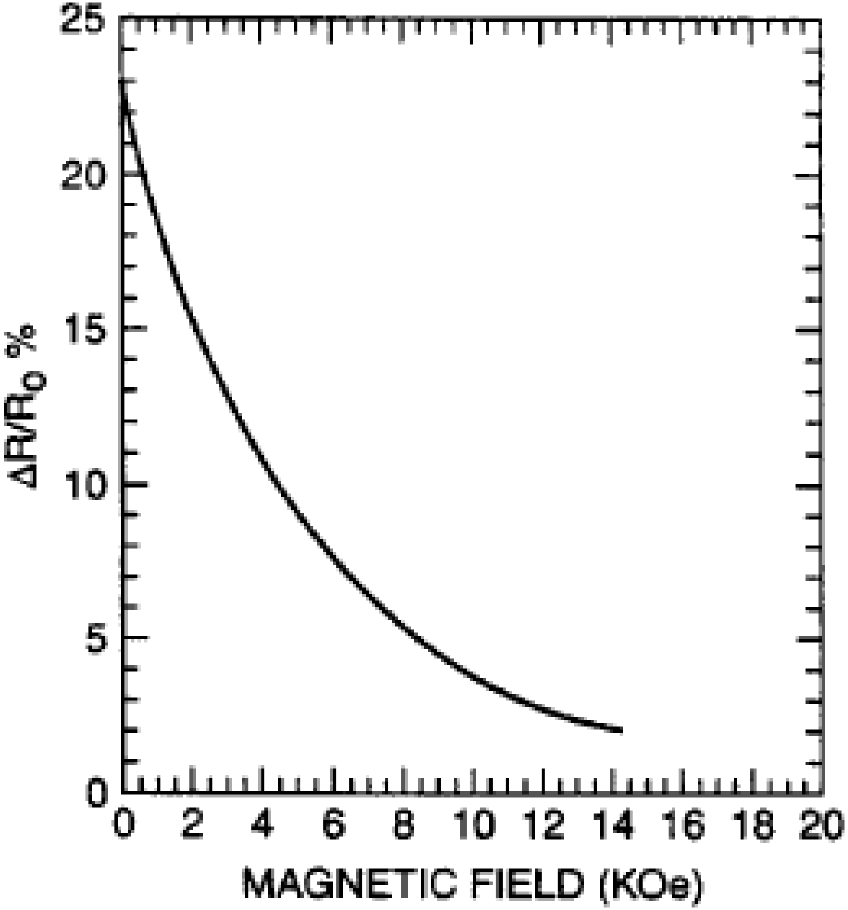
Electron // H has less scattering

Magnetic storage

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

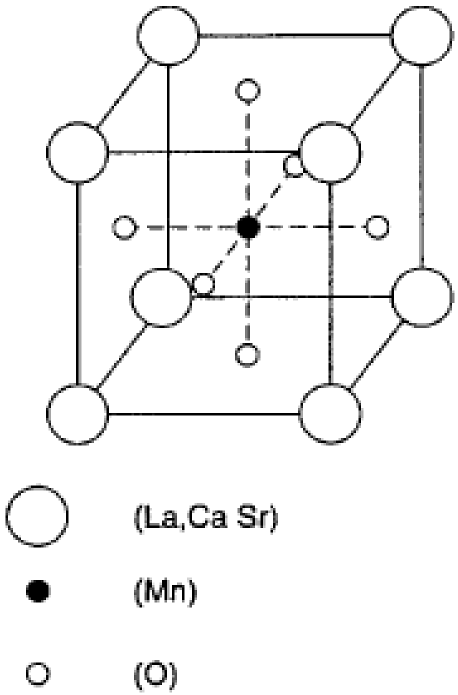


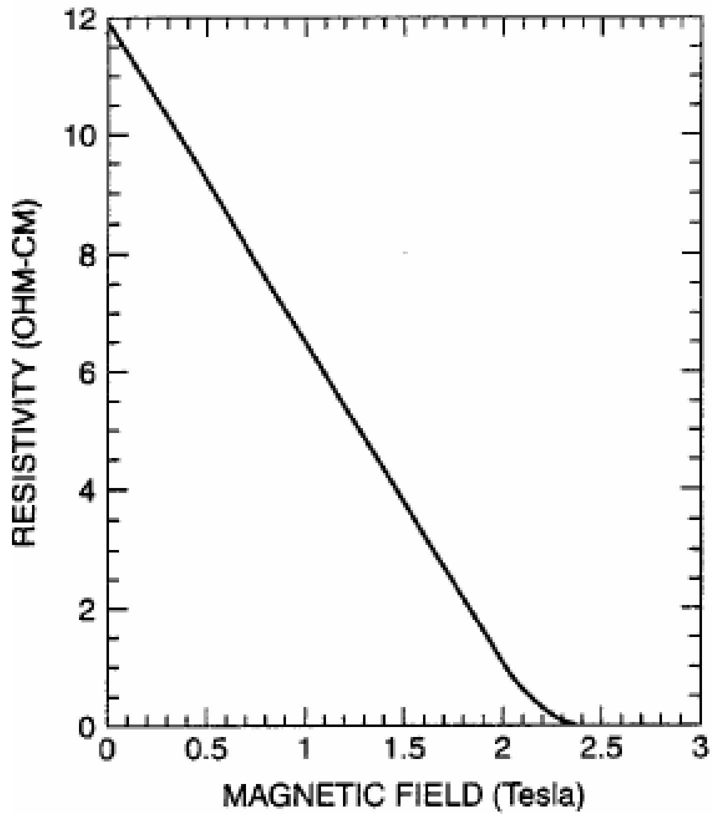
光碟片的結構圖



Dependence of the change of magnetoresistance ΔR versus the
film of Co nanoparticles in a copper matrix. A kilooersted co

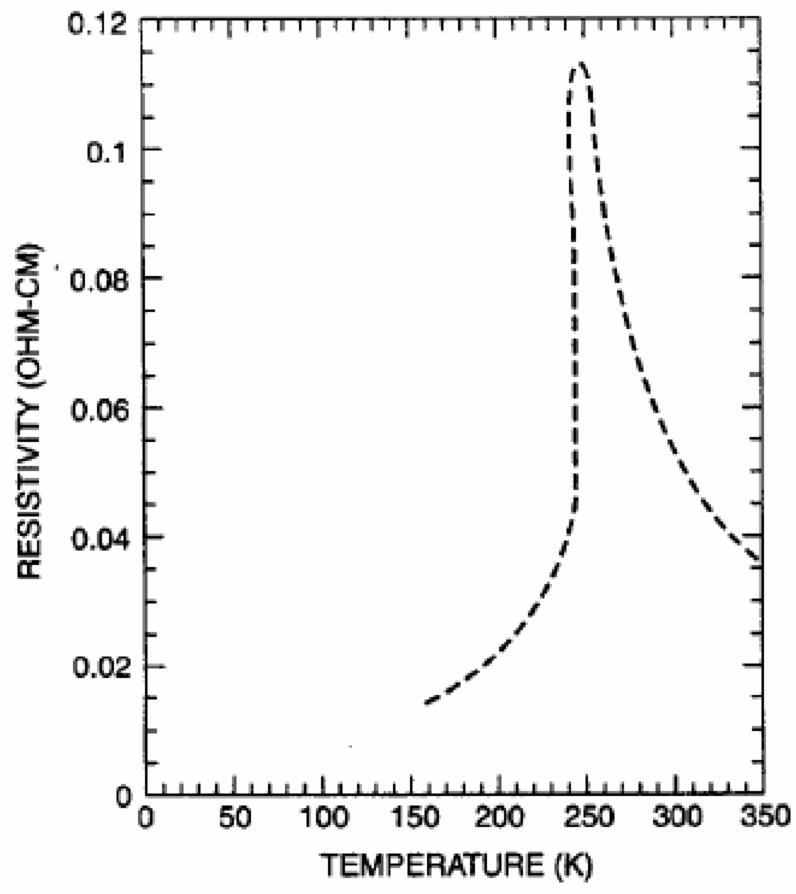
Colosal magnetoresistance





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

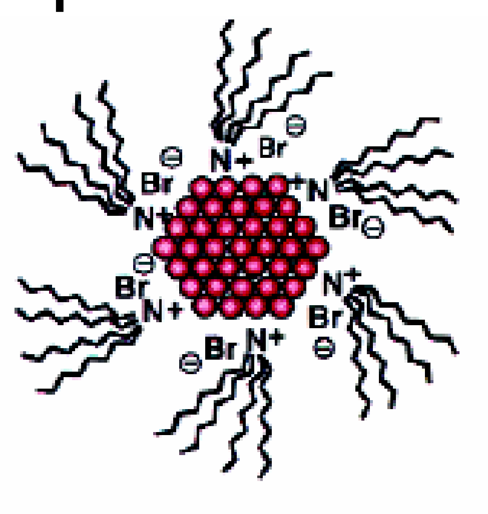
La-Ca-Mn-O



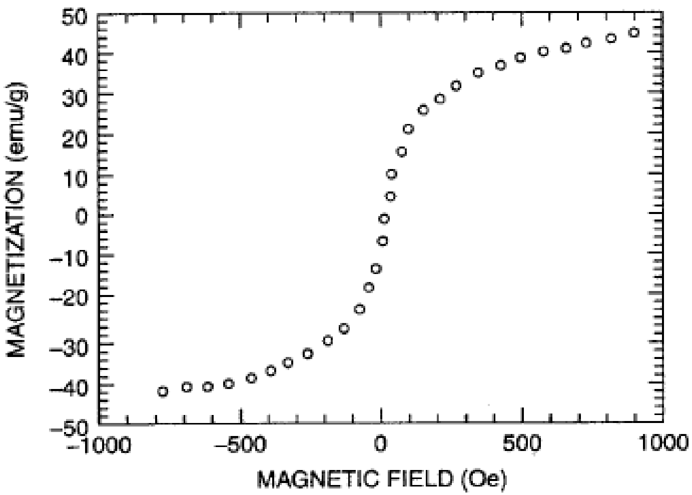
0.12
0.1
0.08
0.06
0.04
0.02
0
RESISTIVITY (OHM-CM)
0
50
100
150
200
250
300
350
TEMPERATURE (K)

7.7 Ferrofluids

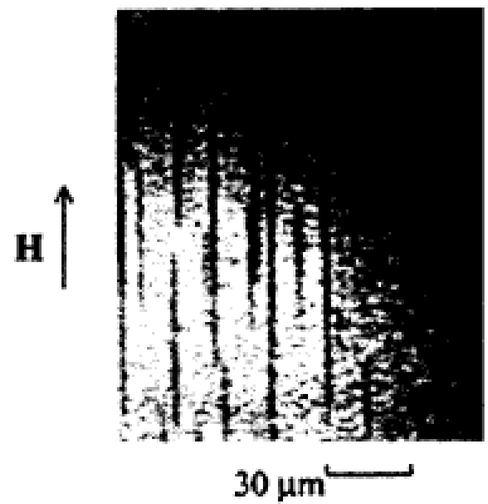
- 1. Nanoparticles are single domain ~ 10 nm
- 2. Coated with a surfacetant to prevent aggregation
- 3. Suspended in a liquid of transformer oil or Kersene

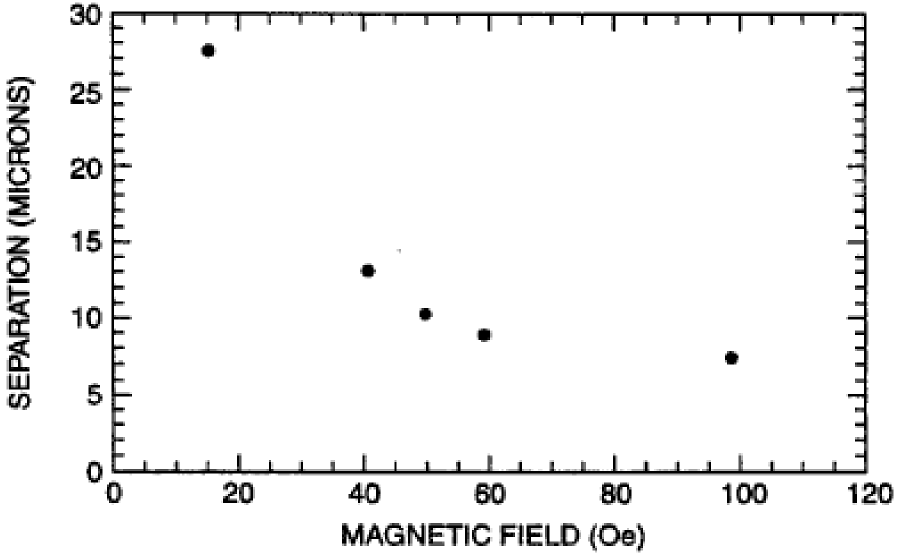


Magnetic-field-dependent anisotropic optical properties



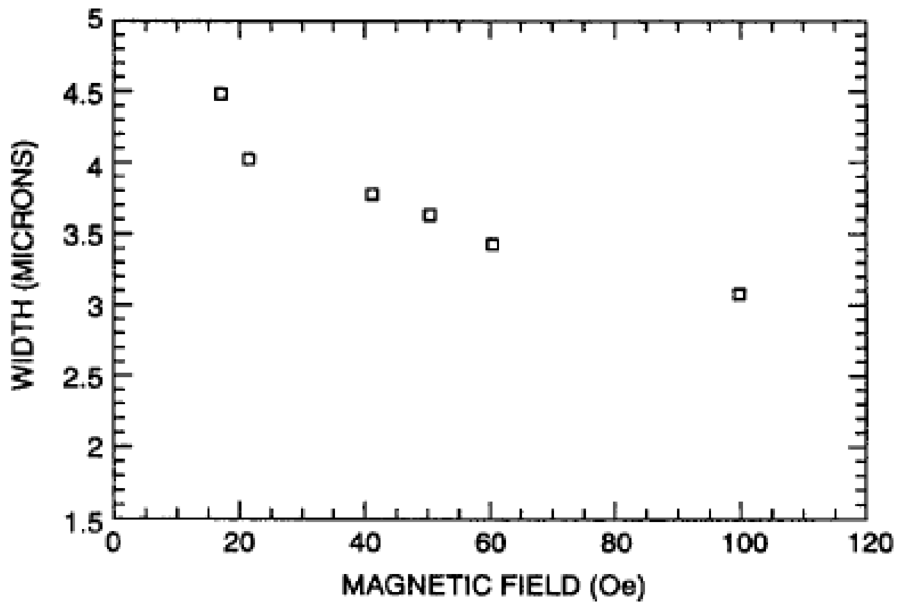
7.22. Magnetization curve for a ferrofluid made of magnetite, Fe_3O_4, nanoparticles




SEPARATION (MICRONS)
MAGNETIC FIELD (Oe)

(a)

H // Surface


WIDTH (MICRONS)
MAGNETIC FIELD (Oe)

(b)

H is perpendicula to the surface