2010 凝聚态物理-北京大学论坛

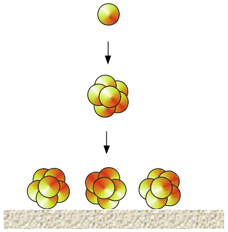
# 纳米粒子组装薄膜的物理特性

## --从纳米粒子合成及其物理特性研究到纳米粒子组装材料的制备--

**彭栋梁**

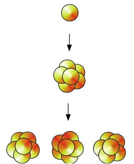
厦门大学材料学院
低维纳米功能材料实验室

2010年3月18日 北京大学



# Short Outline

- 研究背景
- 金属和合金纳米粒子的物理气相合成
- 磁性纳米粒子组装薄膜的制备及其结构、磁学和电学特性
- 高频软磁薄膜制备与性能研究
- 总结与展望

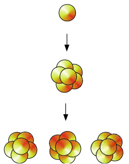


# 纳米粒子组装体系及其制备的重要性

◆制备纳米粒子组装体系是构筑新型纳米结构的重要方法之一，在纳米器件上有潜在应用。利用纳米粒子来制备具有新型纳米结构的高性能、多功能材料不仅是本世纪新材料研究和开发的重要手段之一，而且其基础研究和应用研究均具有极其重要的意义。

◆通过化学方法（液相法）控制的纳米粒子生长，以及纳米粒子自组装的一维、二维和三维点阵被广泛地研究。

◆物理气相法是另一种制备纳米粒子组装材料的方法，该方法将纳米粒子在真空当中直接沉积或组装到一个基片上或基体里，是一个具有应用前景的制备新型纳米结构材料的重要方法，近年来受到人们的广泛关注。

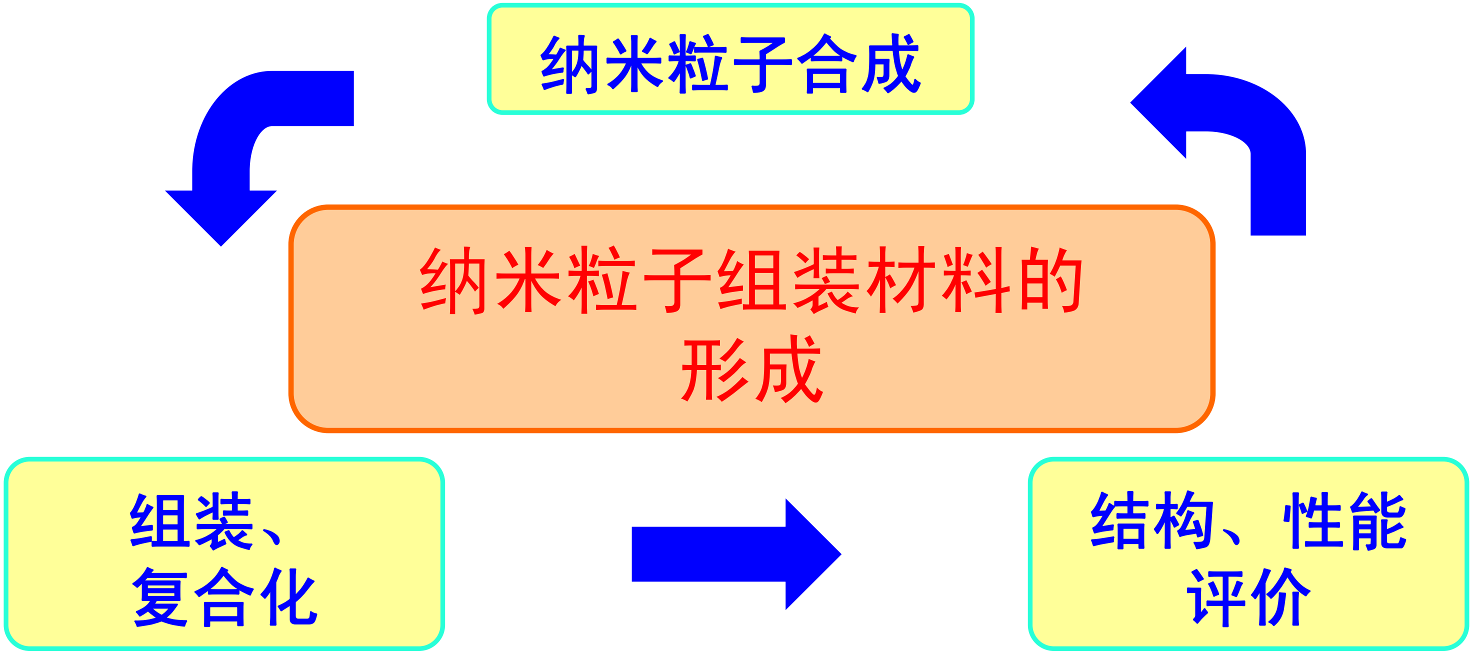


# 利用纳米粒子的特异性进行新材料的开发

## 液相法、气相法

主要是过渡金属（磁性纳米粒子）

纳米粒子的尺寸均一化、平均尺寸控制、形状控制



**纳米粒子合成**

纳米粒子组装材料的形成

**组装、复合化**

**结构、性能评价**

控制沉积或自组装
大面积（量）化、超晶格、
取向控制

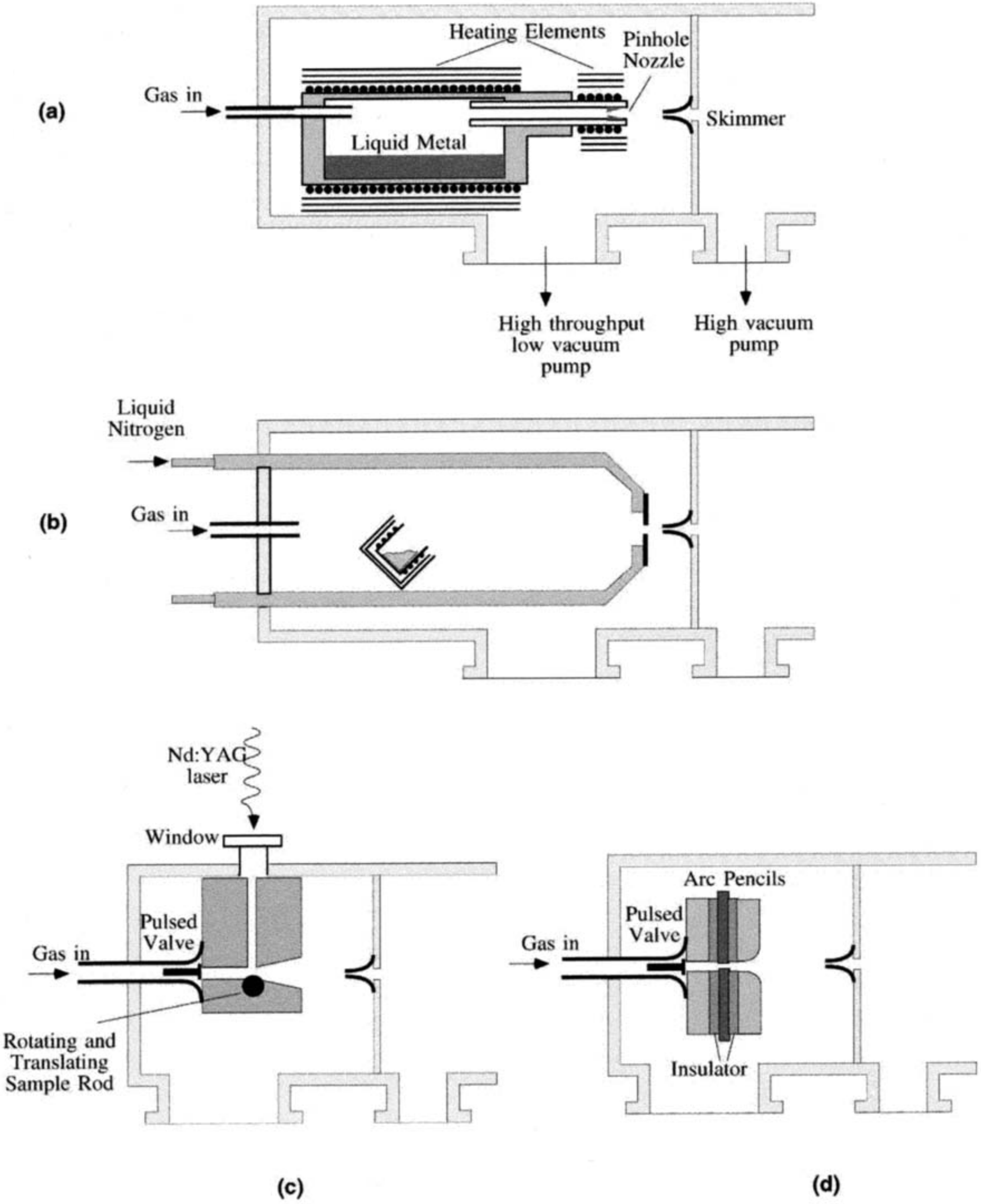
TEM，SEM，XRD
磁性、电学性质、光学性质等

# 纳米粒子的制备方法

- 液相法（化学方法）
- 气相法（物理方法）
  - 加热蒸发
  - 激光蒸发
  - 脉冲弧光放电蒸发
  - 等离子体辉光放电蒸发

**惰性气体冷凝法**

# 几种纳米粒子的产生源示意图

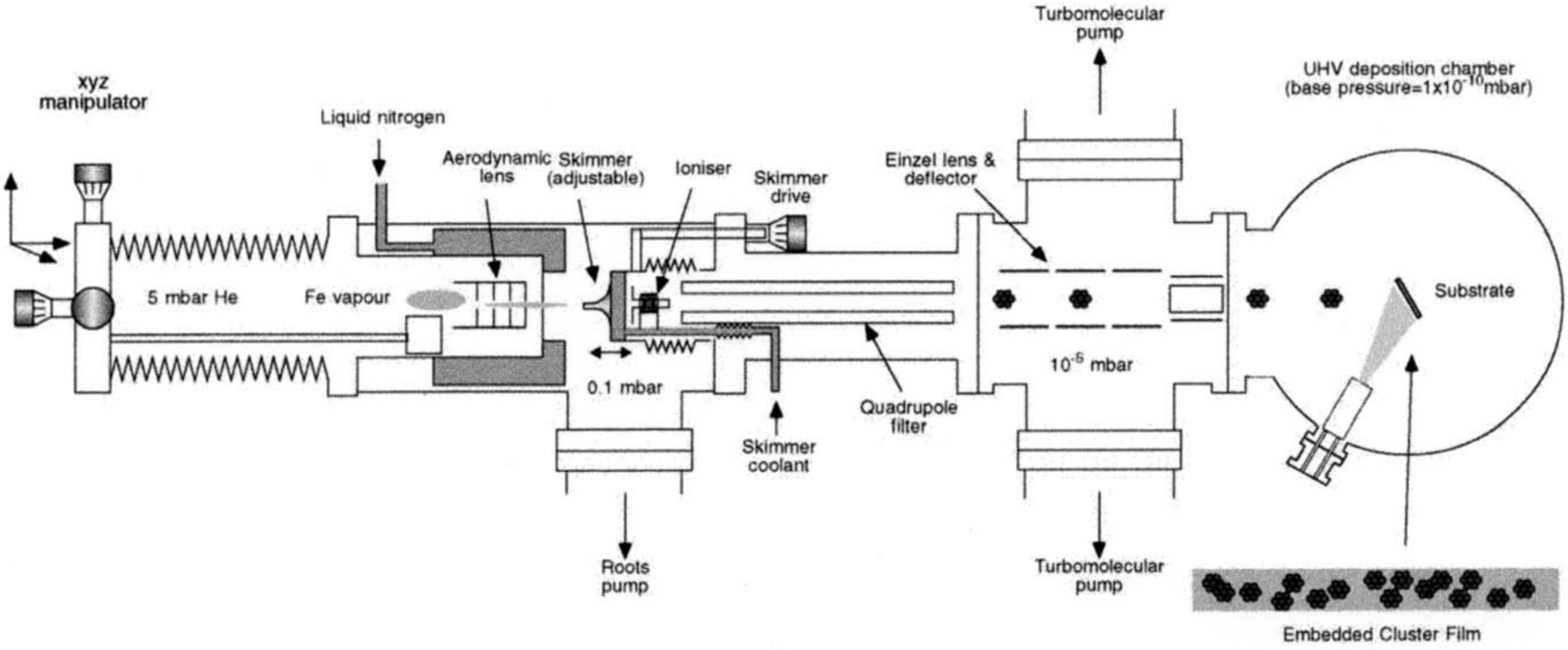


**(a)、(b)** 加热蒸发

**(c)** 激光蒸发

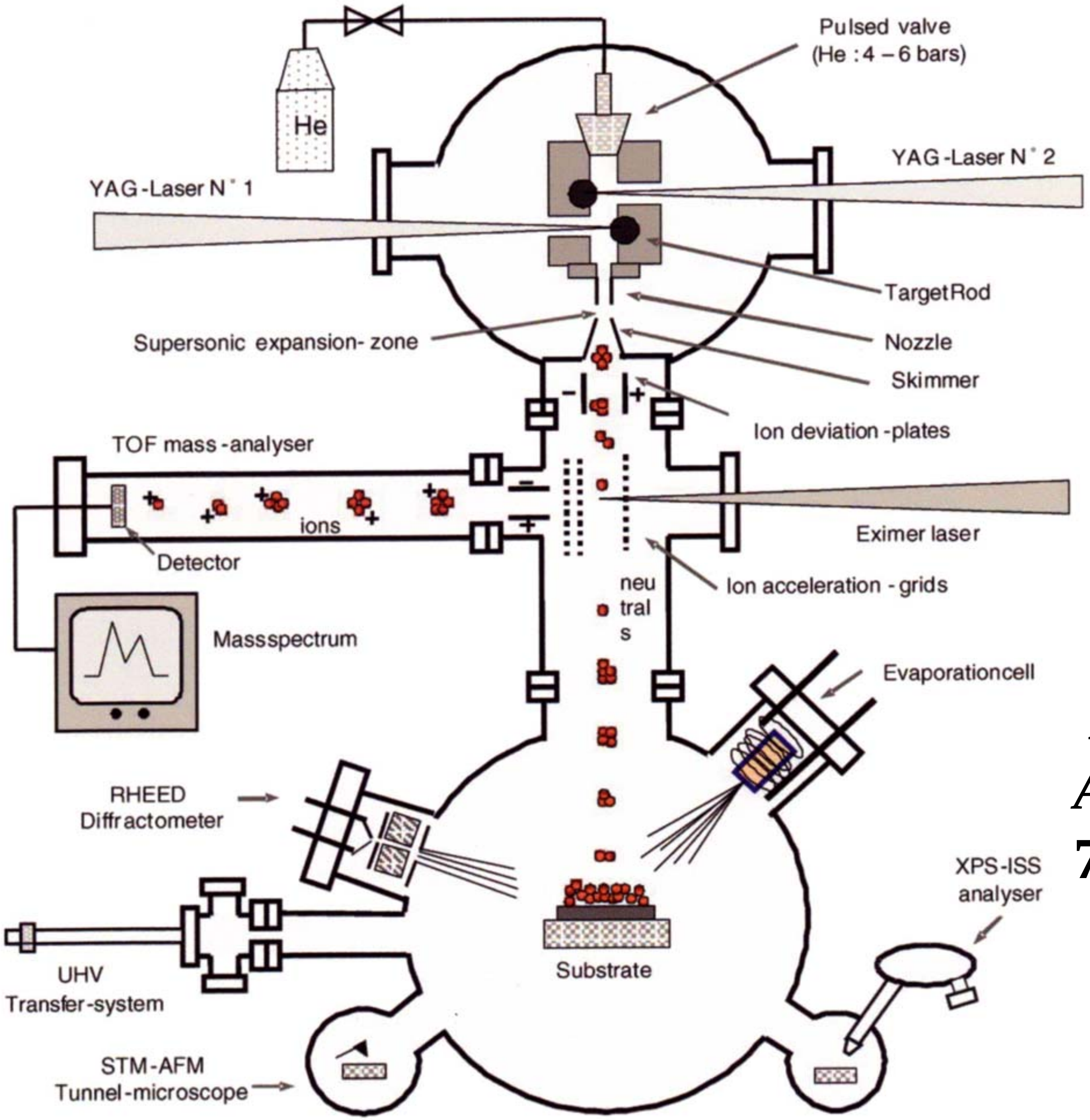
**(d)** 脉冲弧光放电蒸发

# Set-up of the Binns' group, UK



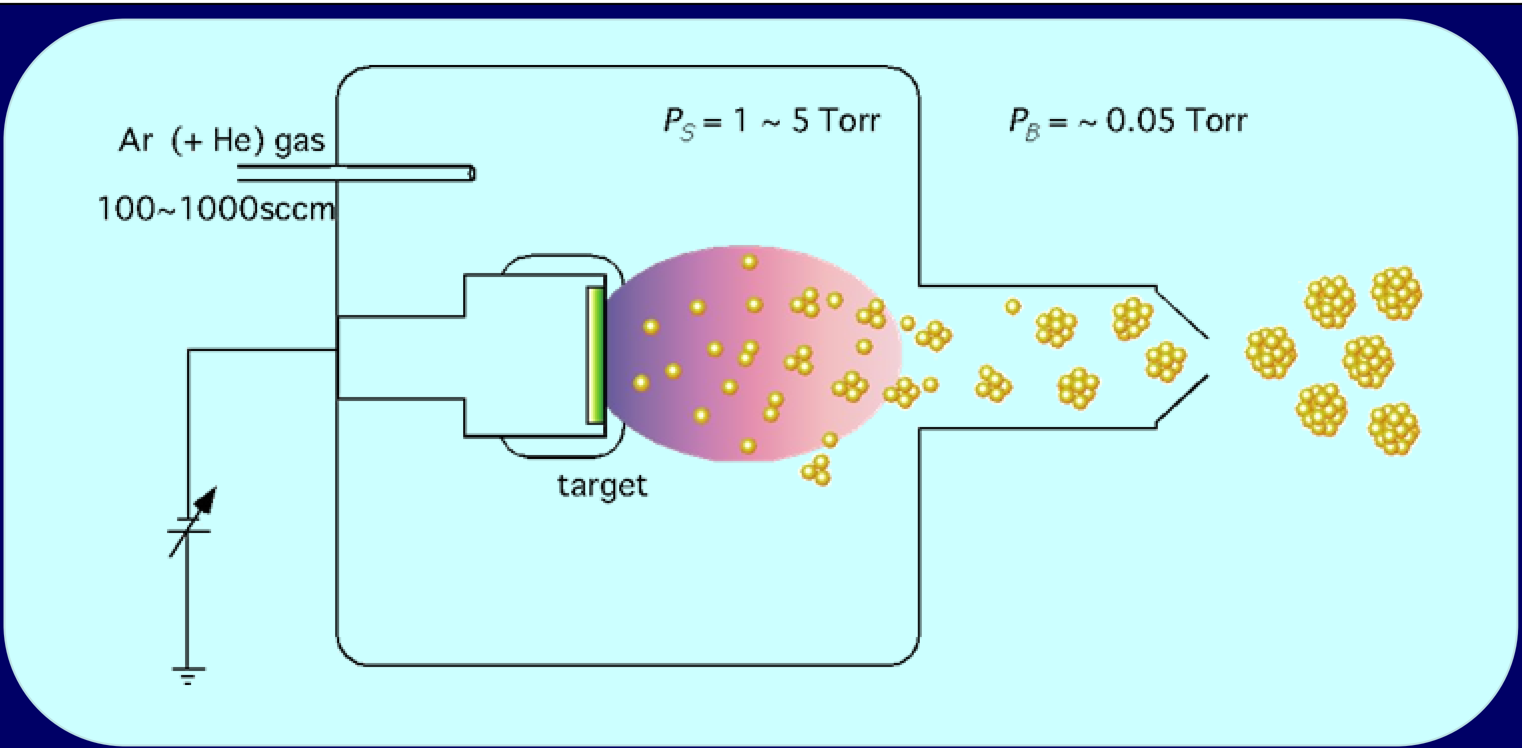
**S.H. Baker *et al*., *Rev. Sci. Instrum*. 71 (2000) 3178.**

# Set-up of the Perez's group, France



**A. Perez *et al.*,**
***Adv. Eng. Mater.*,**
**7 (2005) 475**

# Plasma-Gas-Condensation (PGC) Cluster Source (The original Haberland source, Germany)

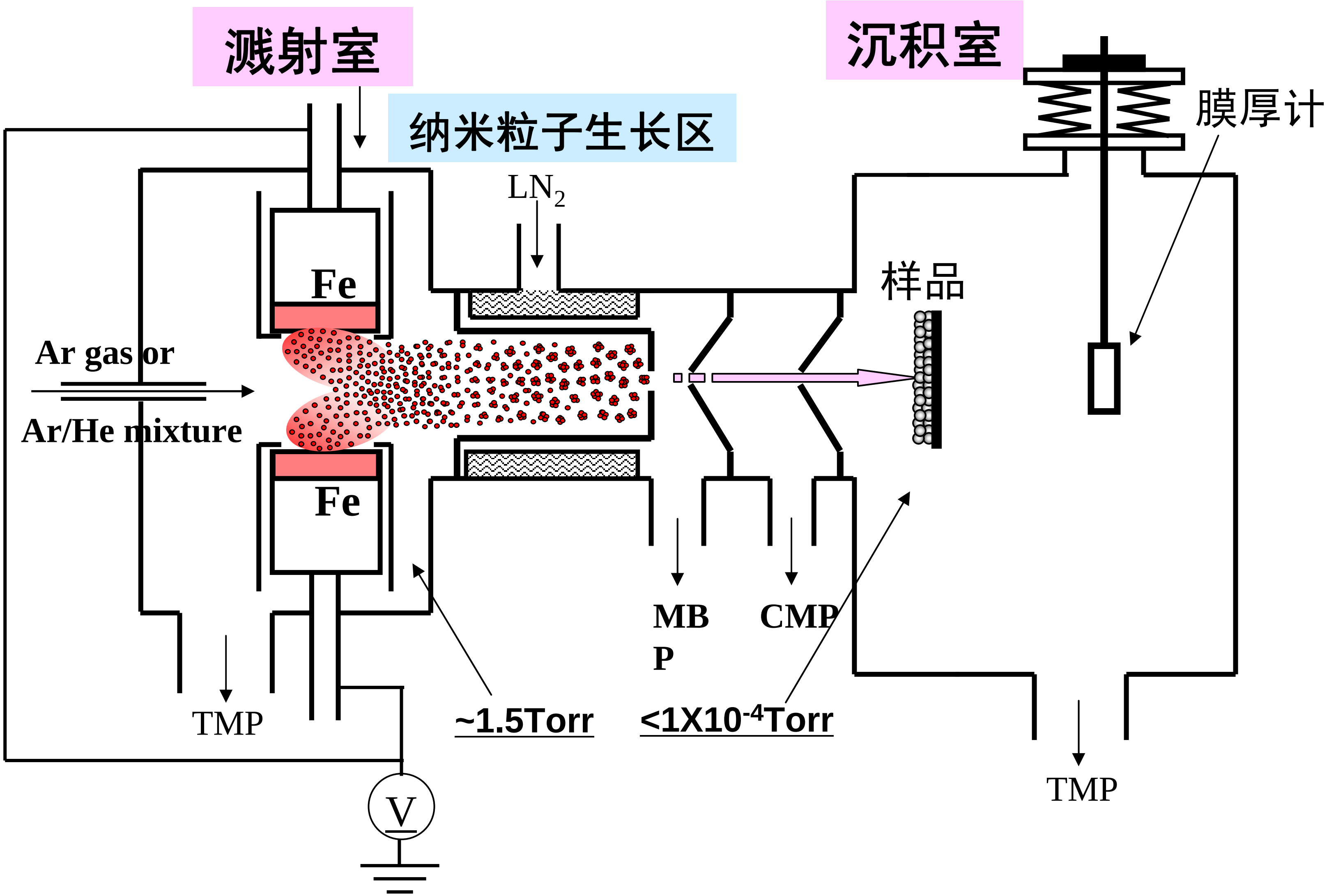


**溅射法** + **惰性气体冷凝法**

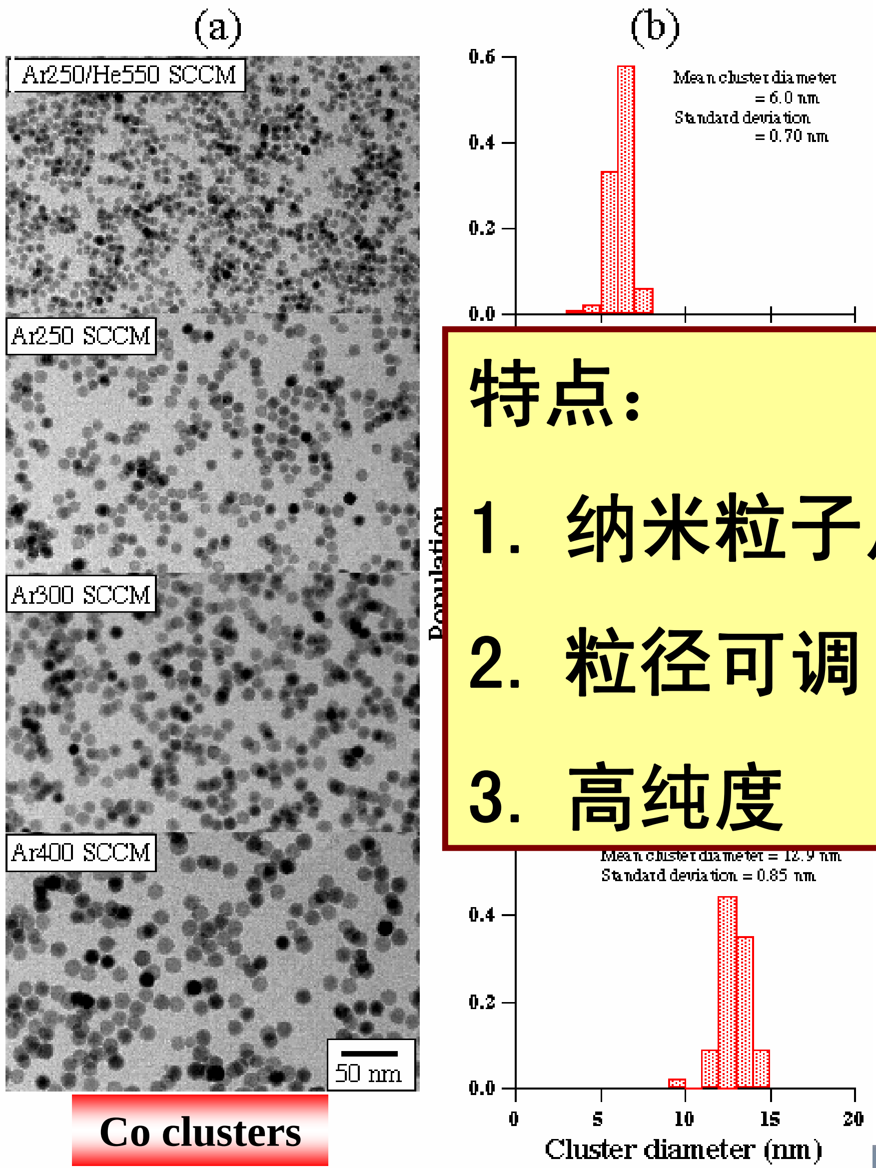
高熔点、难融化金属
高通用性

粒子尺寸控制性好
产率高

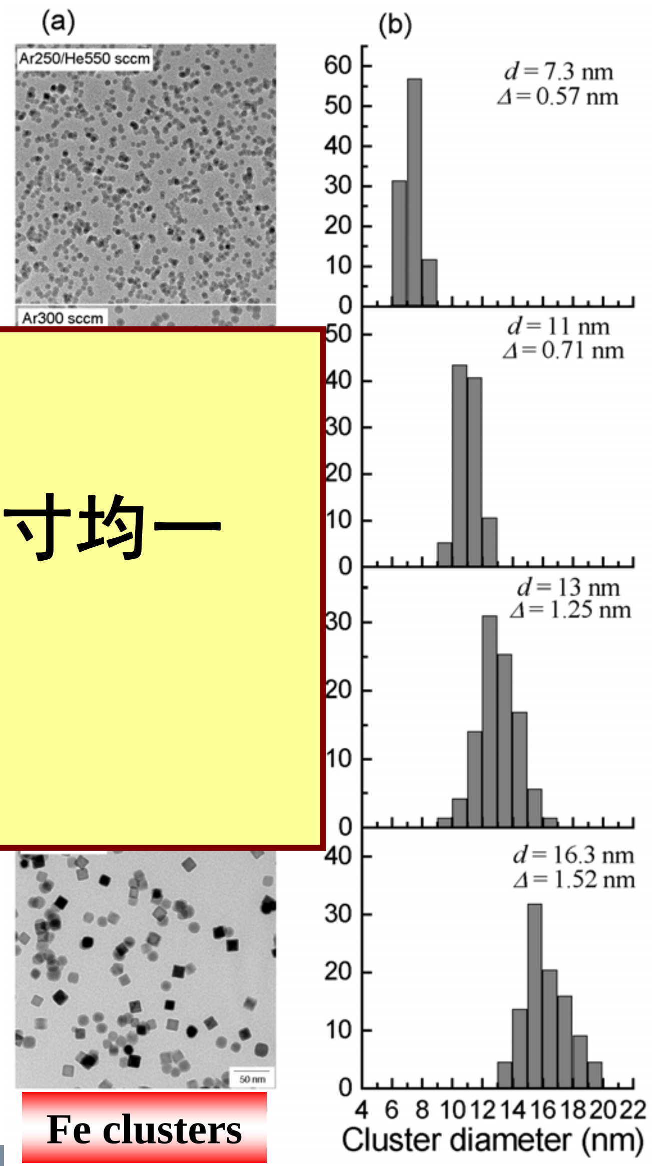
# 物理气相法制备纳米粒子组装材料原理图



# 例：尺寸均一的Fe金属纳米粒子（TEM照片）



**Co clusters**

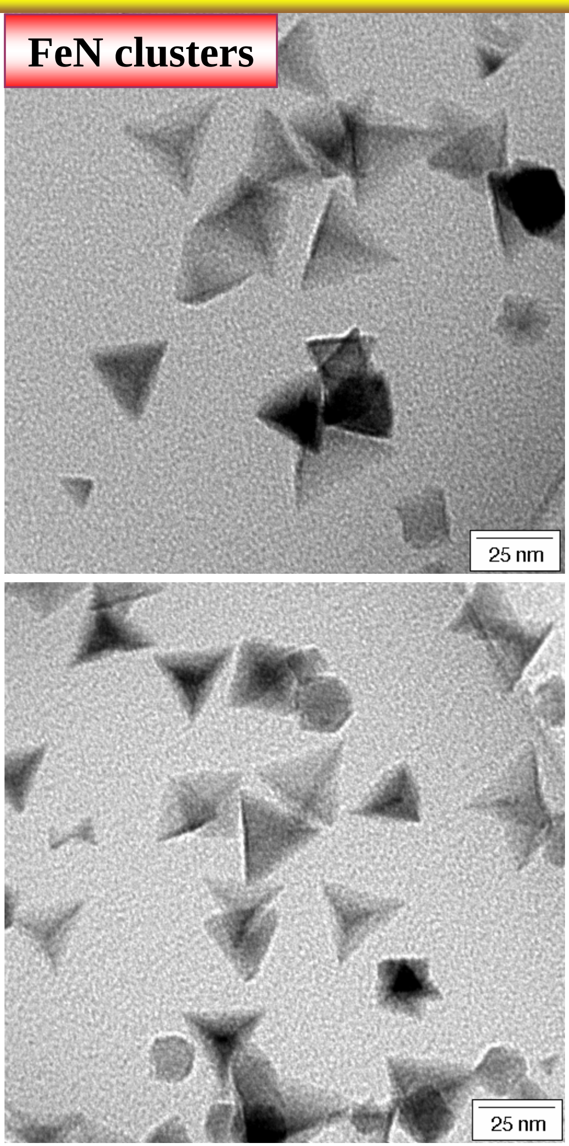


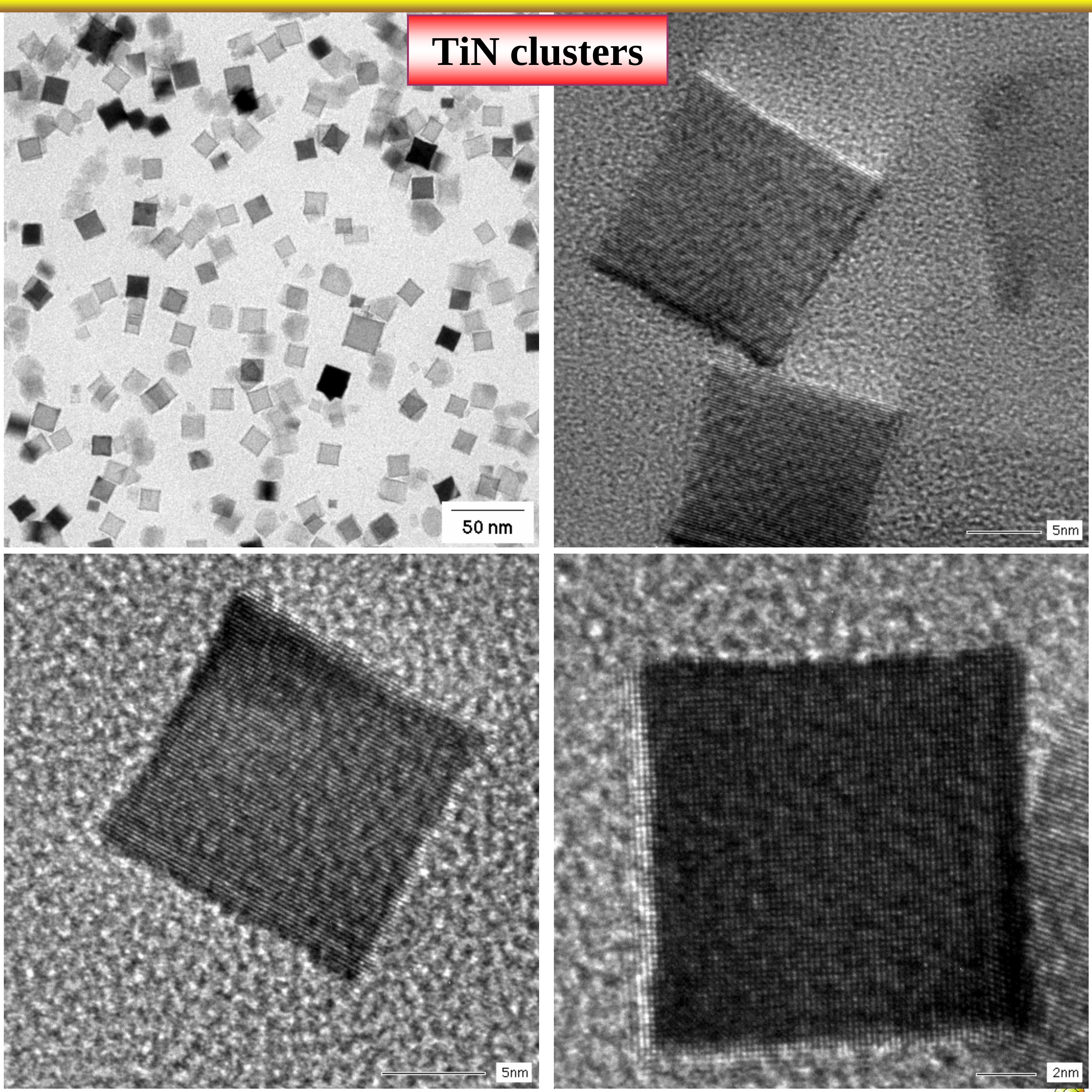
**Fe clusters**

**特点：**

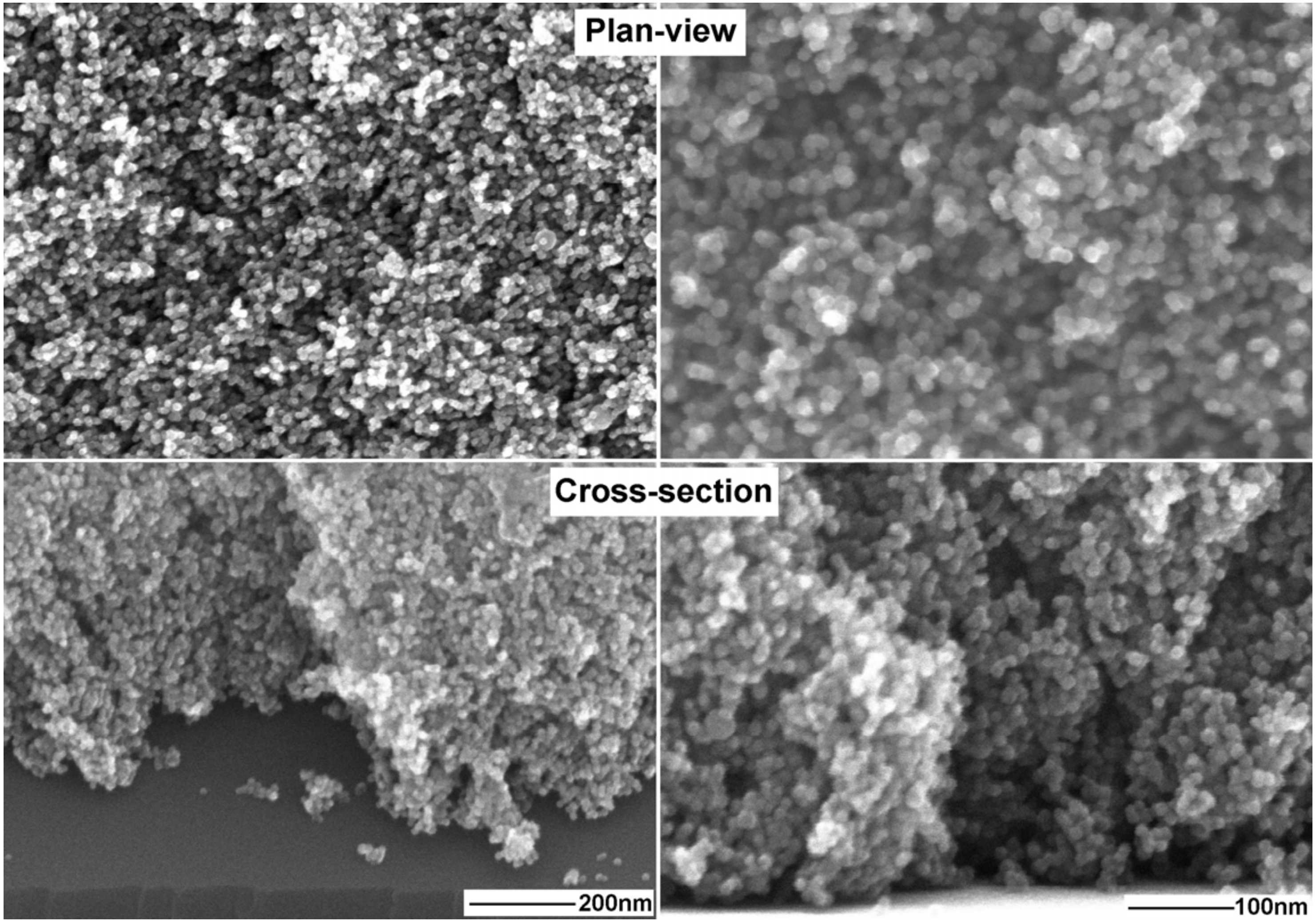
1. 纳米粒子尺寸均一
2. 粒径可调
3. 高纯度

# 例：特定形状的化合物纳米粒子（TEM照片）



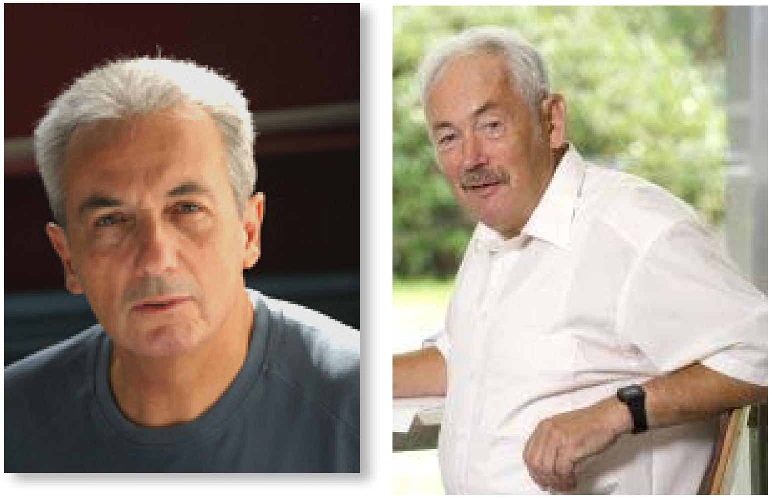


# 例： Fe纳米粒子集合体膜的SEM照片



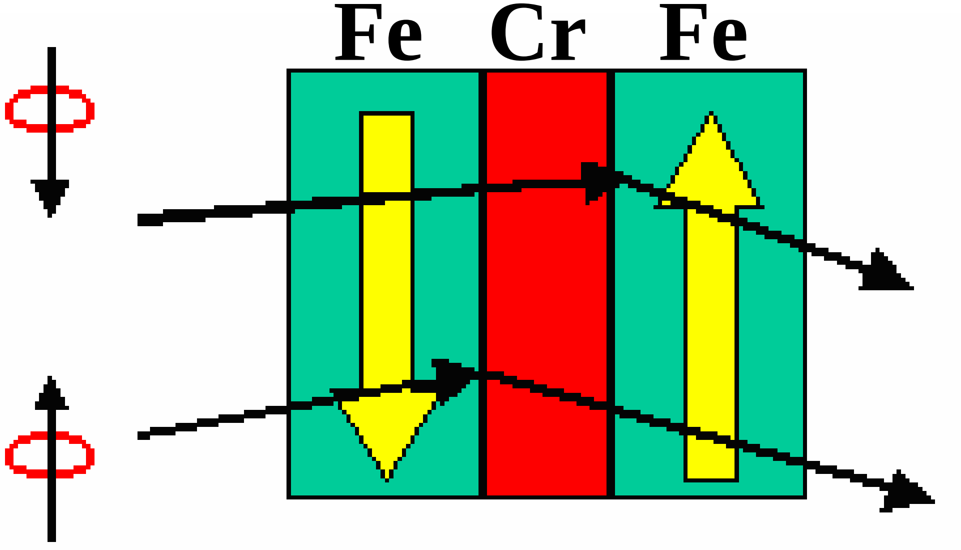
# 巨磁电阻效应（GMR）

**A. Fert和P. Grünberg**



1988年发现巨磁阻
2007年度的诺贝尔物理学奖

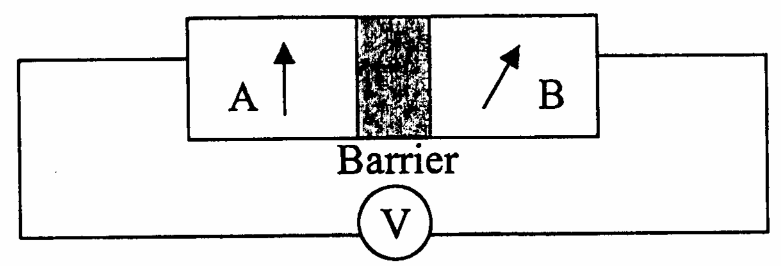
巨磁阻

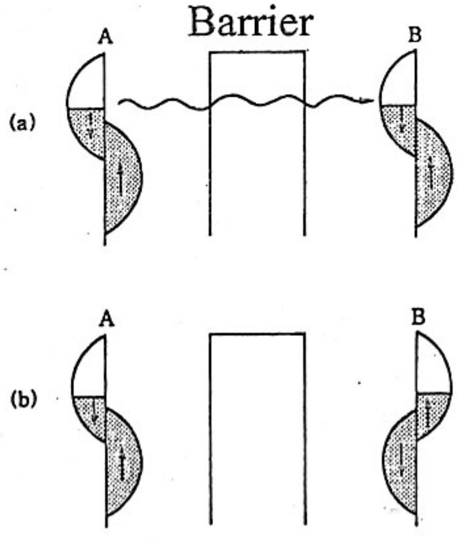


1986年德国的Peter Gruenberg教授首先在Fe/Cr/Fe多层膜中观察到反铁磁层间耦合。
1988年法国巴黎大学的Albert Fert教授研究组首先在Fe/Cr多层膜中发现了**巨磁电阻效应**。

# 自旋依赖隧穿型巨磁电阻效应（TMR）

- **TMR of ferromagnetic tunnel junction**





(a) $M_A \uparrow\uparrow M_B$

(b) $M_A \uparrow\downarrow M_B$

$$G = \sum_{\sigma=\pm} |T|^2\, D_{A\sigma}(E_F)\, D_{B\sigma}(E_F+eV)$$

$$|T|^2 \propto \exp(-2s\kappa),\quad \kappa=(2m\varphi)^{1/2}/\hbar$$

$$G_{\uparrow\uparrow} \propto D_{A\uparrow}D_{B\uparrow} + D_{A\downarrow}D_{B\downarrow}$$

$$G_{\uparrow\downarrow} \propto 2\, D_{A\uparrow}D_{B\downarrow}$$

$$TMR = (G_{\uparrow\downarrow}^{-1} - G_{\uparrow\uparrow}^{-1})/G_{\uparrow\downarrow}^{-1}$$

$$= 2P_AP_B/(1 + P_AP_B)$$

$P_A$, $P_B$ : Spin polarization

$$P_\zeta = (D_{\zeta+} - D_{\zeta-})/(D_{\zeta+} + D_{\zeta-})$$

$$(\zeta = A, B)$$

**$P_{Fe} = 44\%$, $P_{Co} = 34\%$, $P_{Ni} = 11\%$**

# 自旋依赖隧穿型巨磁电阻效应（TMR）

- **TMR of magnetic metal-insulator granular system**

$$G \propto (1+P^2\cos\theta)\,\exp(-2ks-E_c/k_BT)$$

$$\boxed{MR = \frac{P^2m^2}{1+P^2m^2}}$$

$E_c$: charge energy

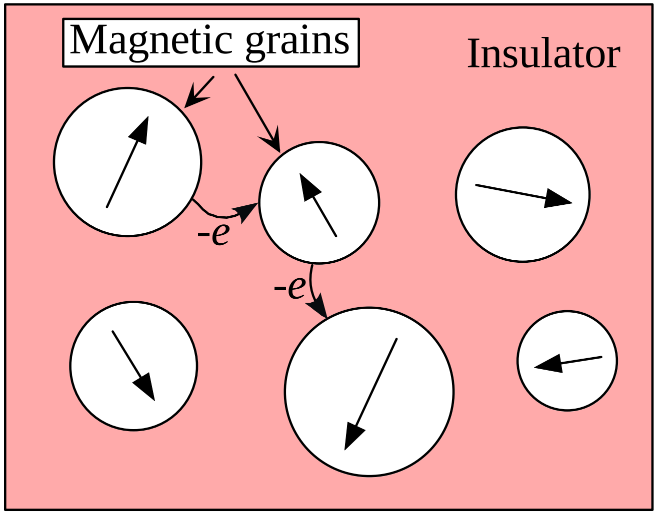
$P$: spin polarization

$m$: relative magnetization

$P_{Fe} = 0.44 \Rightarrow MR \propto m^2$

Maximum theoretical value

$$\boxed{MR_{Fe} = 16\%}$$

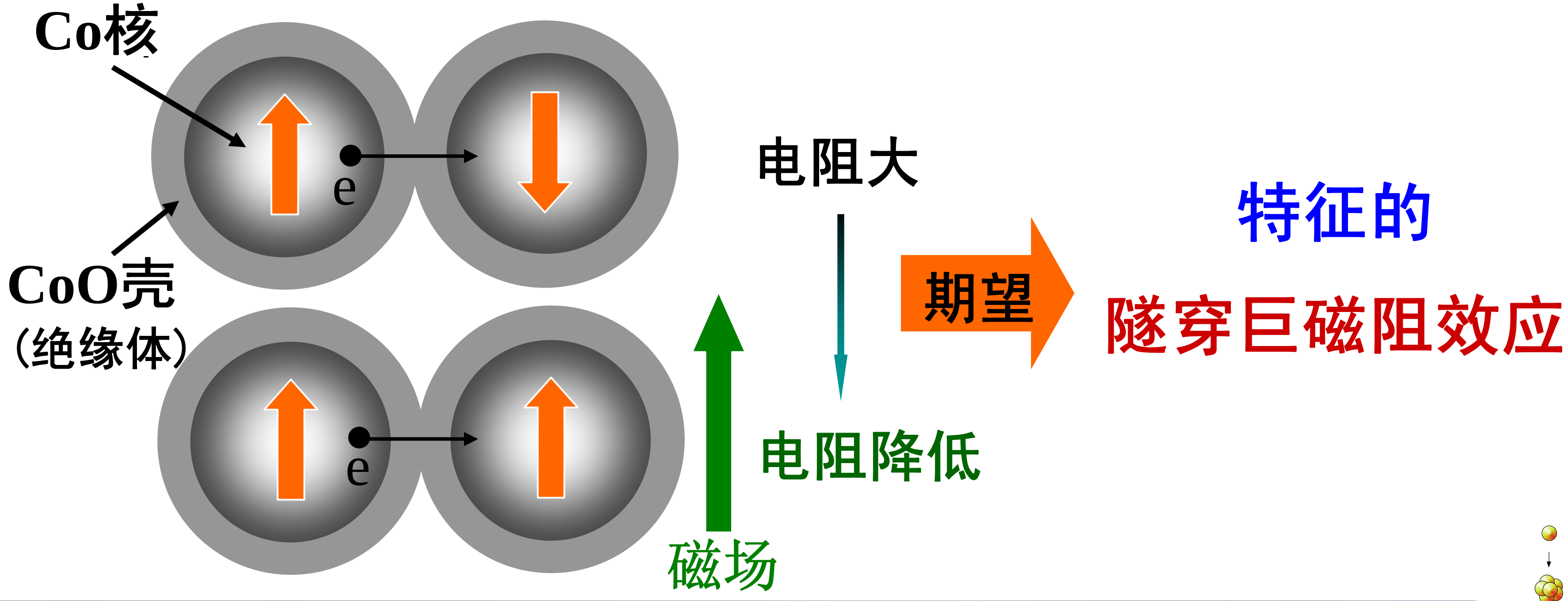


# 核-壳型纳米粒子集合体中是否存在巨磁阻效应

核-壳结构纳米粒子 → 是否 → 隧穿巨磁阻(TMR) ??

尺寸均一 → 独特的性质 ??

## 研究构思



Co核

CoO壳

(绝缘体)

e

e

电阻大

电阻降低

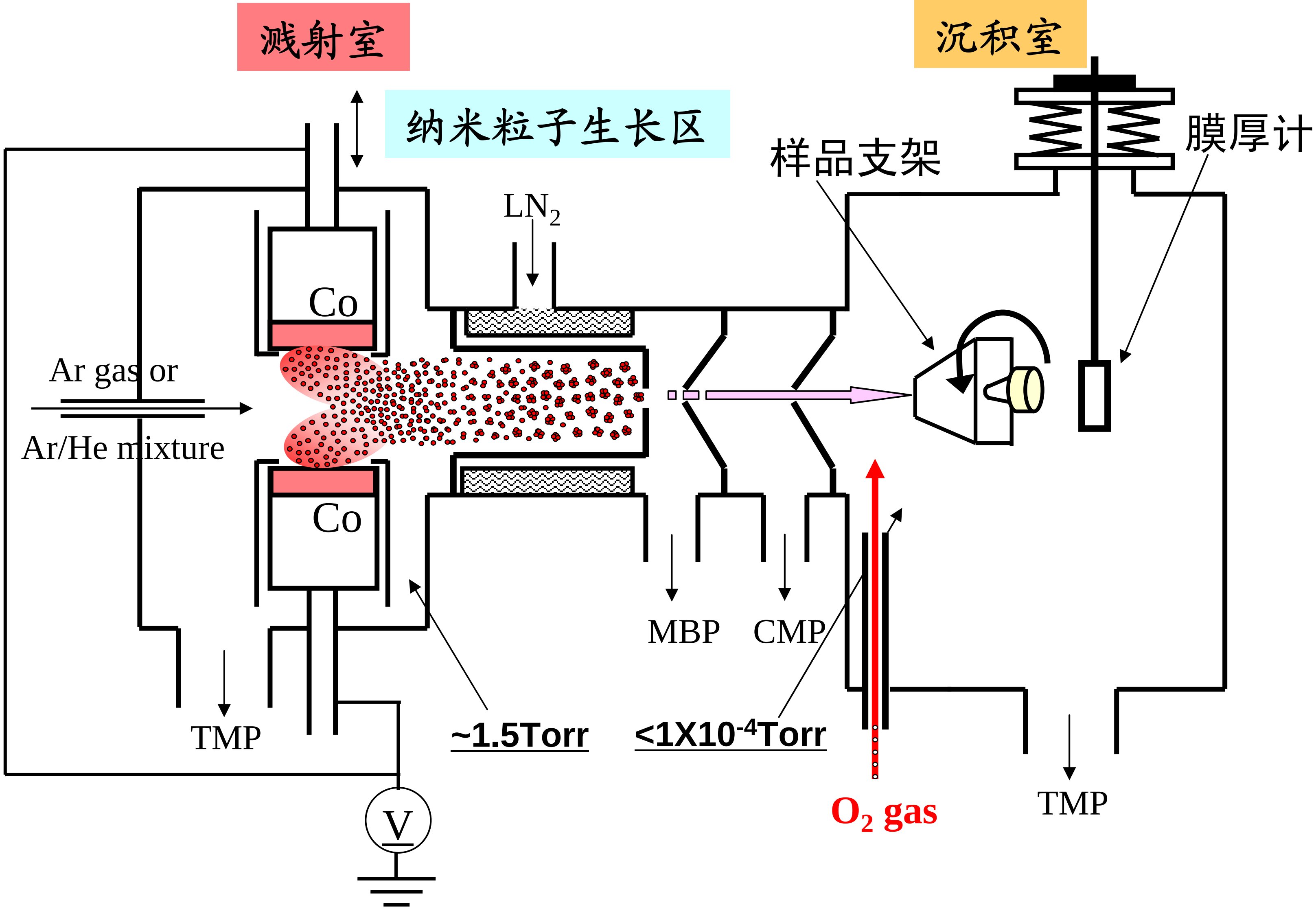
磁场

期望

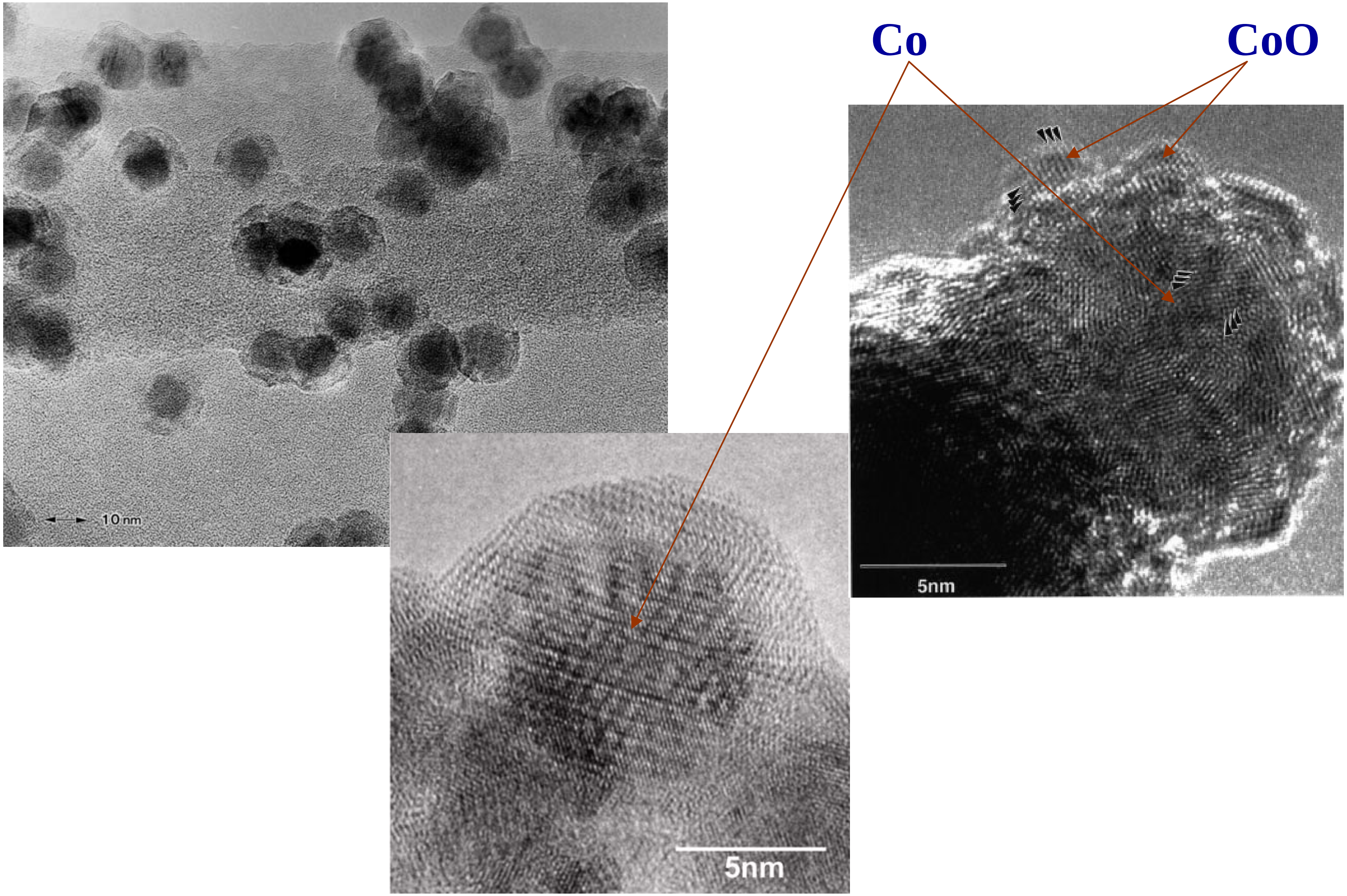
特征的

隧穿巨磁阻效应

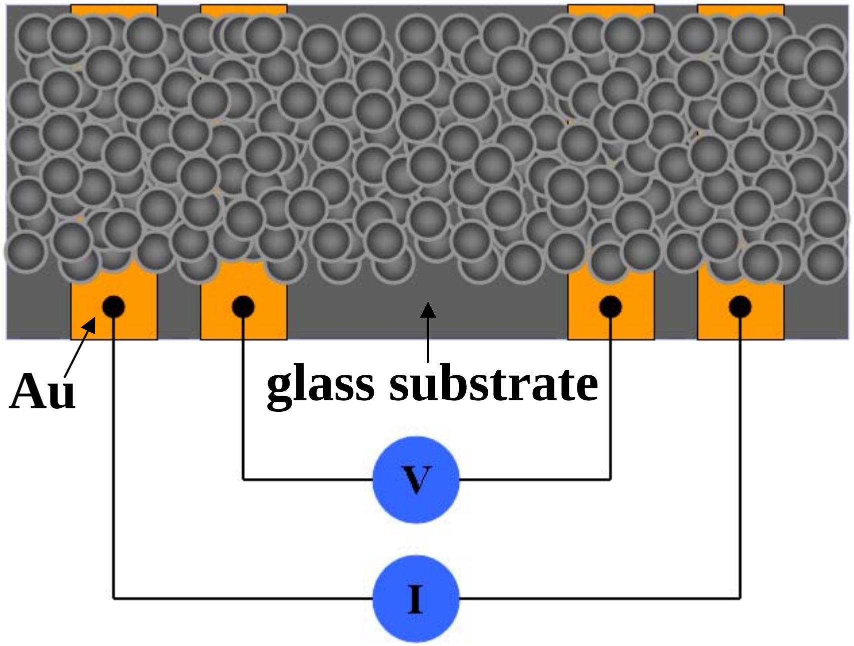
# Co/CoO核-壳结构纳米粒子的制备方法

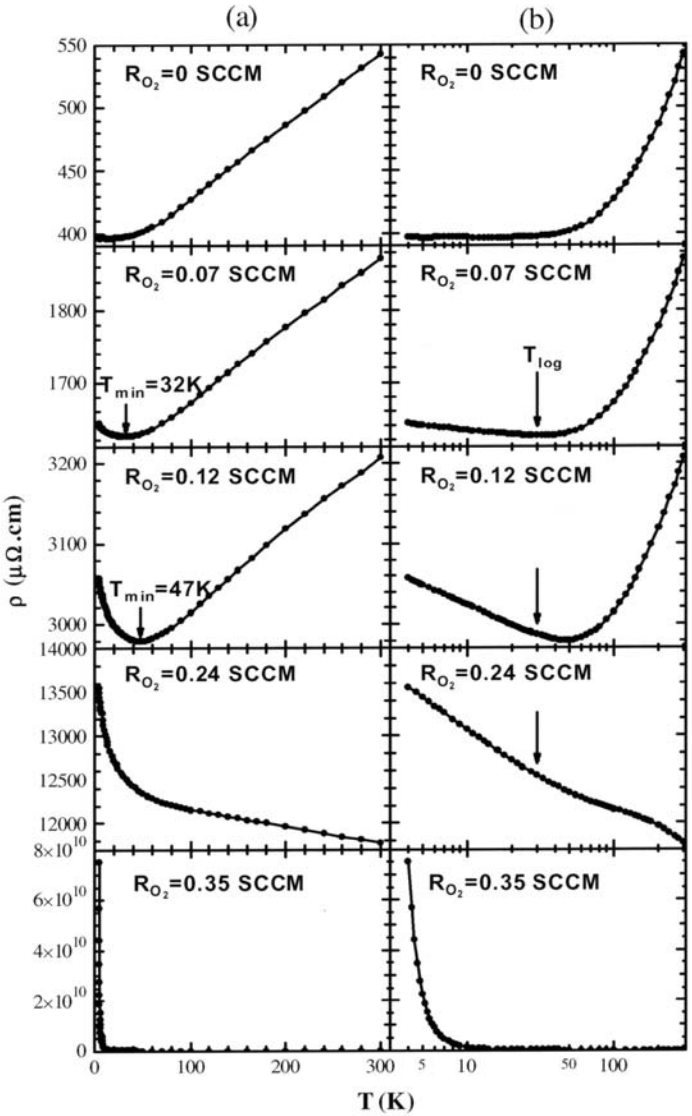


# 形成的Co/CoO核-壳结构纳米粒子



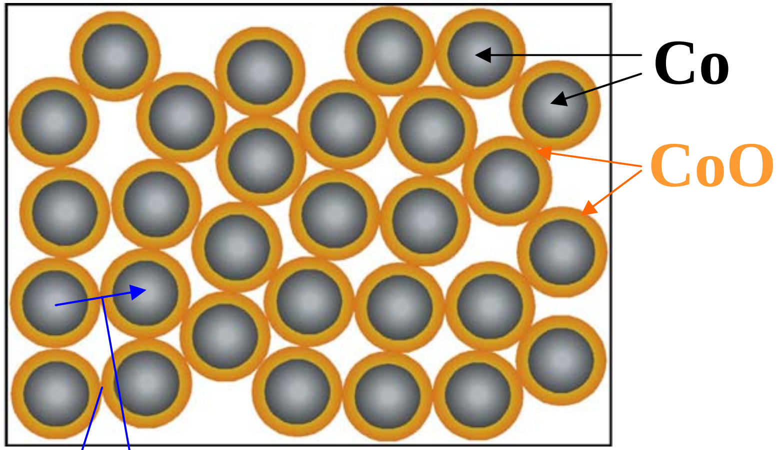
# Co/CoO纳米粒子集合体膜电阻率的温度依赖关系

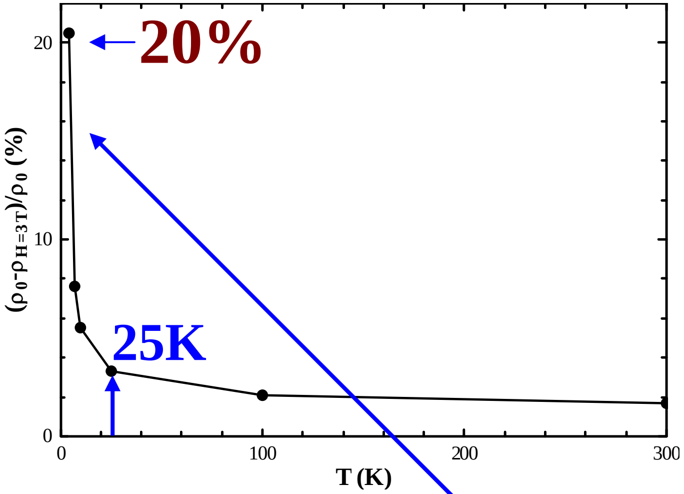




D. L. Peng *et al.*, Phys. Rev. B, **60** (1999) 2093

# 观察到不同于非均一尺寸颗粒膜的隧穿现象



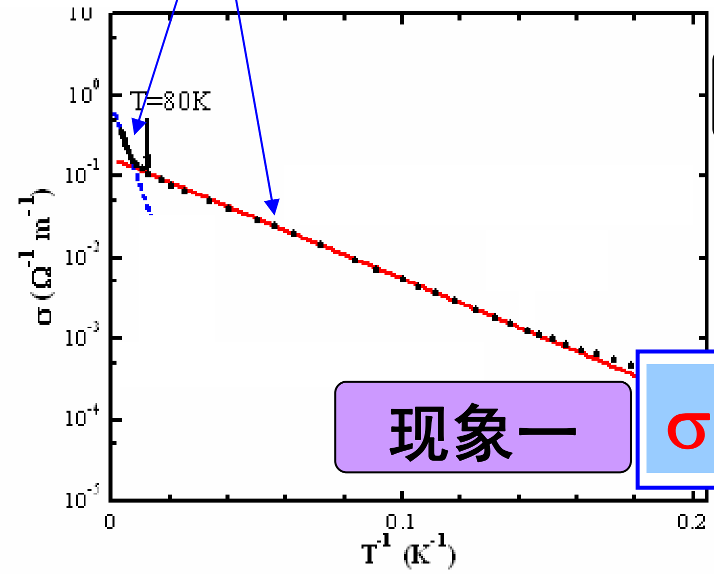


**现象二**

**Co/CoO:低温磁阻率剧增**

**磁阻率 > 20%**

**纯Co: 磁阻率 < 0.01%**



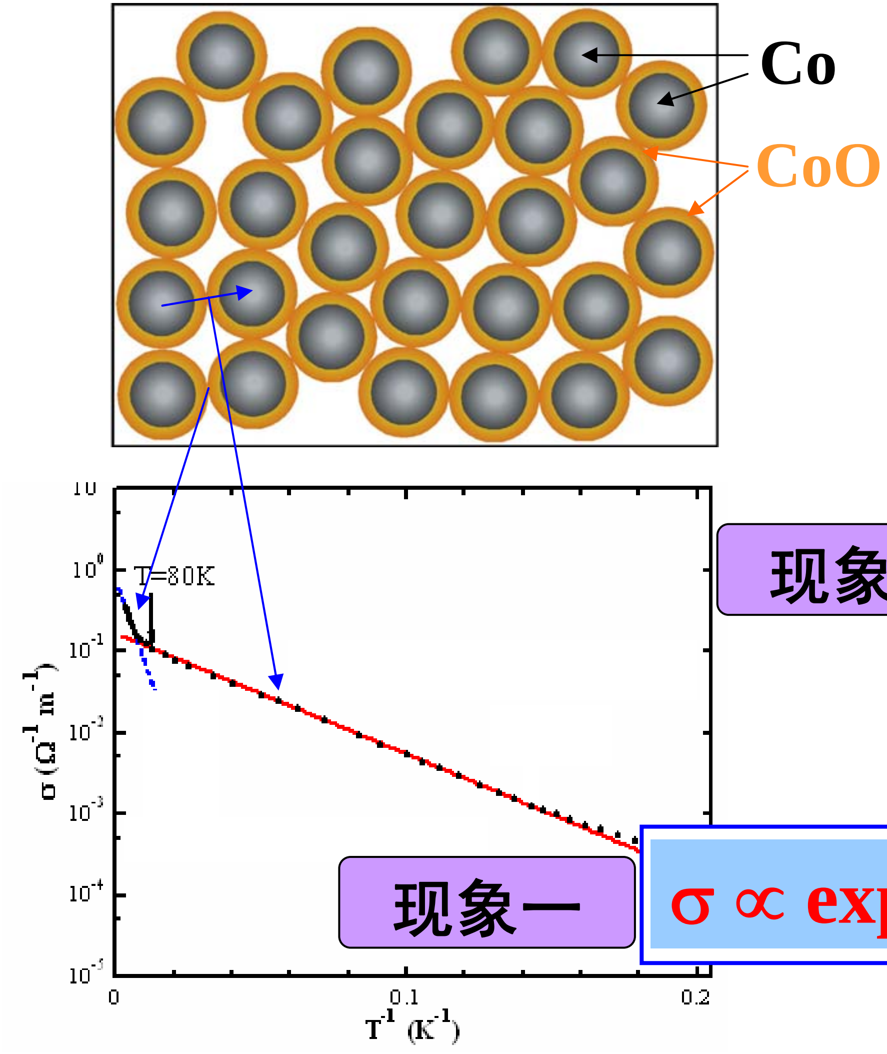
**现象一**

$$\sigma \propto \exp(-1/T) \neq \sigma \propto \exp(-1/T^{1/2})$$

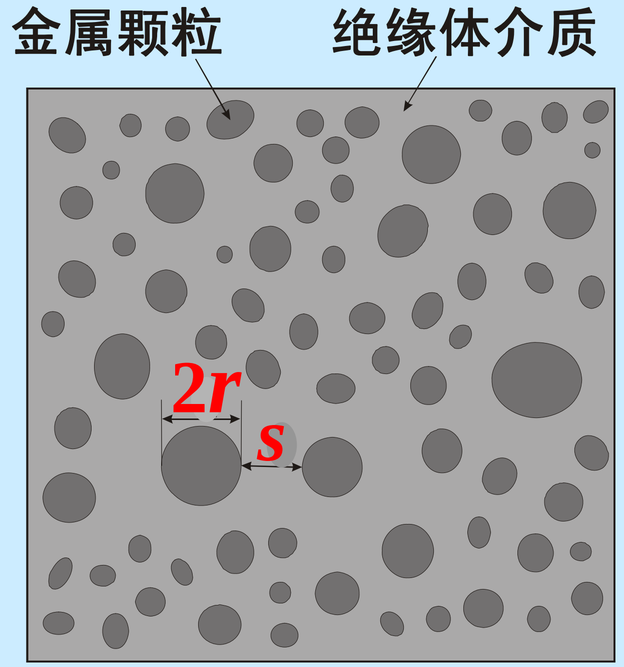
(金属-非金属颗粒膜)

D. L. Peng *et al*., Appl. Phys. Lett., **74** (1999) 76

# 观察到不同于非均一尺寸颗粒膜的隧穿现象



**现象二**



金属-非金属颗粒膜

**现象一**

$\sigma \propto \exp(-1/T)$ $\neq$ $\sigma \propto \exp(-1/T^{1/2})$

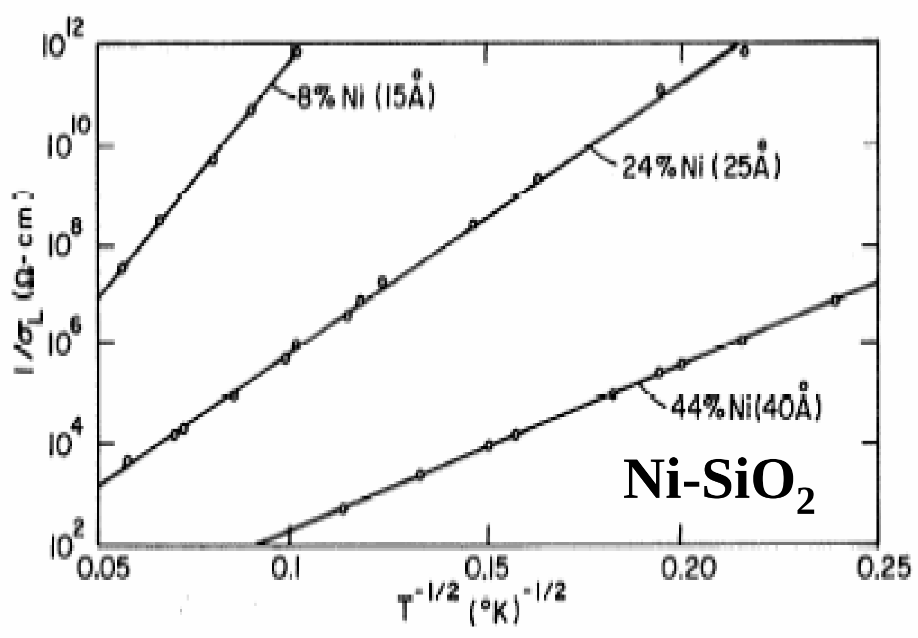
(金属-非金属颗粒膜)

D. L. Peng *et al.*, Appl. Phys. Lett., **74** (1999) 76

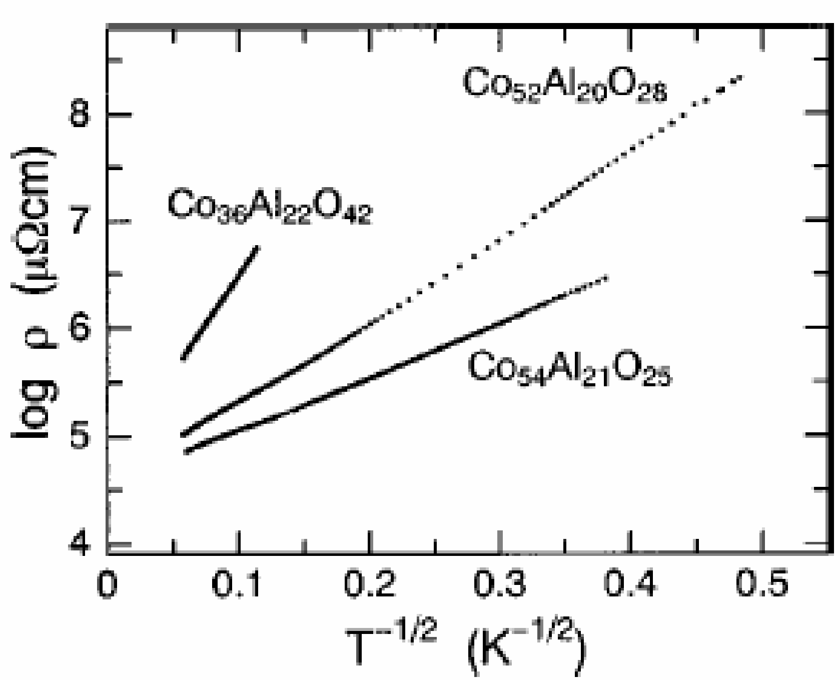
# 普遍观察到的“隧穿电导率温度依赖关系”

## (在尺寸非均一纳米颗粒薄膜(Granular films )中)

## 文献中报道：



Ping Sheng et al., *PRL*, 31(**1973**)44



S. Mitani et al., *JAP*, 83(**1998**)6524

**25年间观察到的结果均呈现 $\sigma \propto \exp(-b/T^{1/2})$**

# $\sigma \propto \exp(-bT^{-1/2})$ 的理论解释和模型

## Sheng & Abeles' Tunneling Conduction Theory in Granular Metals

*PRL* 37(1976)1429

$$\sigma \propto \int_0^\infty \int_0^\infty ds\, dr\, D(s,r) \exp(-2\kappa s - E_c/2k_BT), \quad (1)$$

**Charging energy:** $E_c \propto 1/r$

**On the basis of the assumption:**

$sE_c = C$ (constant) or $s \propto r$ ,

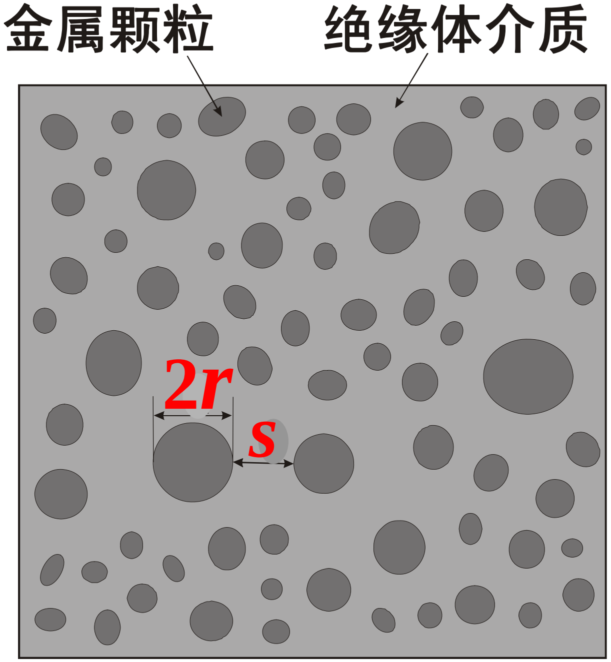
$$\sigma \propto \int_0^\infty ds\, D(s) \exp(-2\kappa s - E_c/2k_BT),$$

$$\exp(-2\kappa s - E_c/2k_BT) \longrightarrow \text{maximum}$$

$$s_m = (C/4\kappa k_BT)^{1/2}.$$

**The dominant temperature dependence:**

$$\boxed{\sigma \propto \exp(-b/T^{1/2})} \quad (2)$$



金属-非金属颗粒膜

# 现象一：$\sigma \propto \exp(-bT^{-1})$ 的起因分析

Neugebauer and Webb, *JAP* 33(1962)74

**Conductivity:**

$$\sigma \propto \int_0^\infty \int_0^\infty ds\, dr\, D(s,r) \exp(-2\kappa s - E_c/2k_B T), \qquad (1)$$

**$\kappa$ is the tunneling exponent of electron wave functions in the insulator, $\kappa = [2m^*(\phi + E_F - E)/h^2]^{1/2}$.**

**Charging energy: $E_c \propto 1/r$**

**$r$ : the size of metal grains**

**$s$ : the separation of neighboring metal grains**

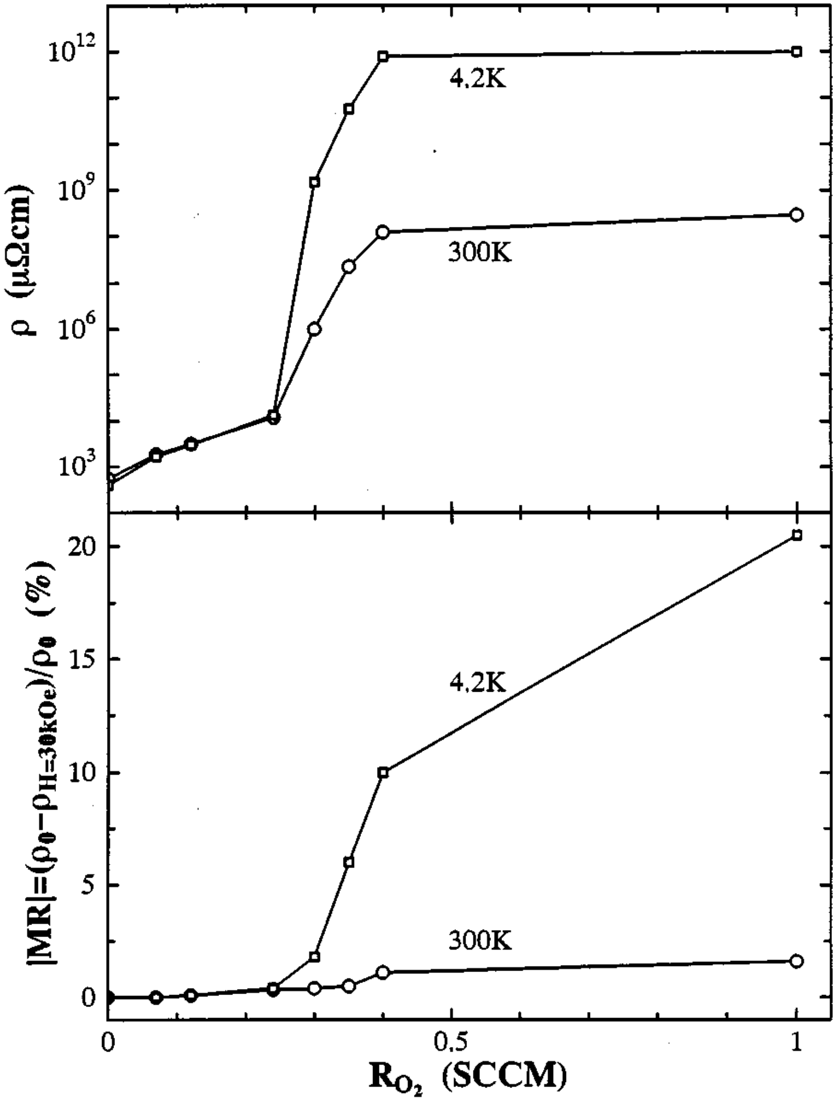
**When the cluster size is monodispersed and the intercluster distance is uniform,**

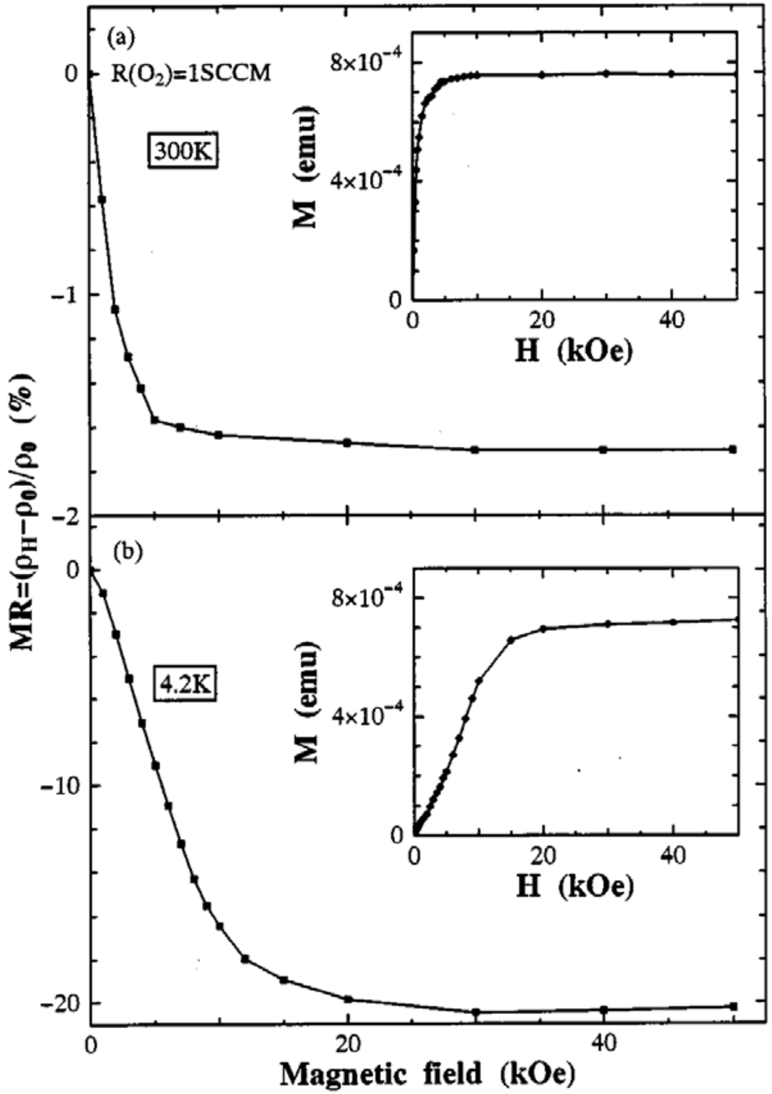
$$\sigma(T) \propto \exp(-E_c/2k_B T) \propto \exp(-1/T)\,. \qquad (2)$$

**纳米粒子尺寸和绝缘层厚度的均一性**

D. L. Peng *et al.*, Phys. Rev. B, **60** (1999) 2093

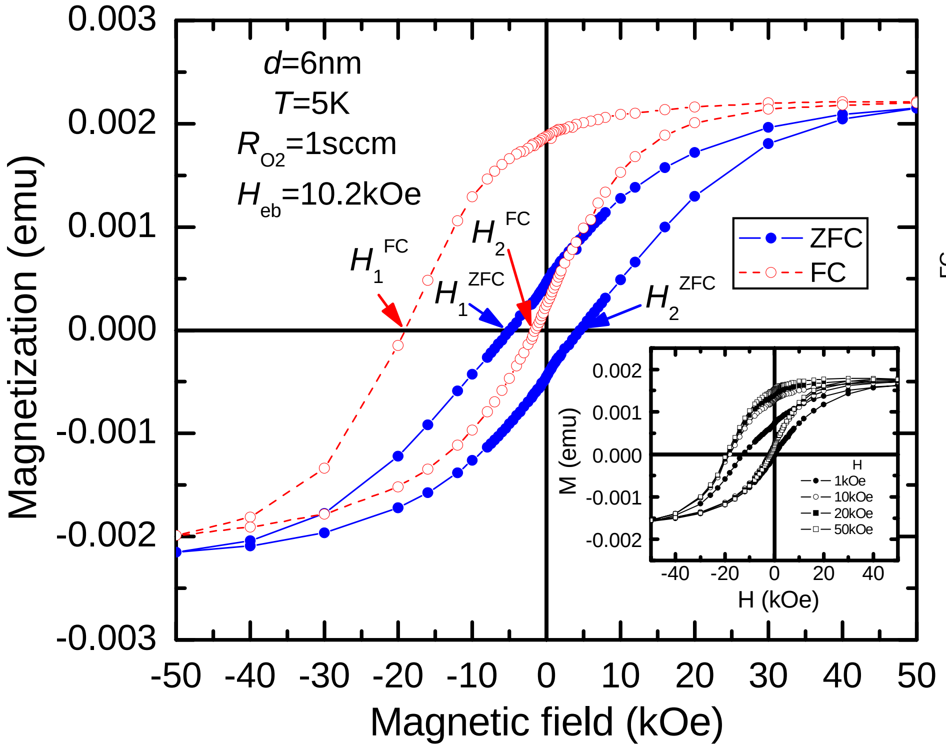
# Co/CoO核壳型纳米粒子集合体膜的隧穿巨磁阻

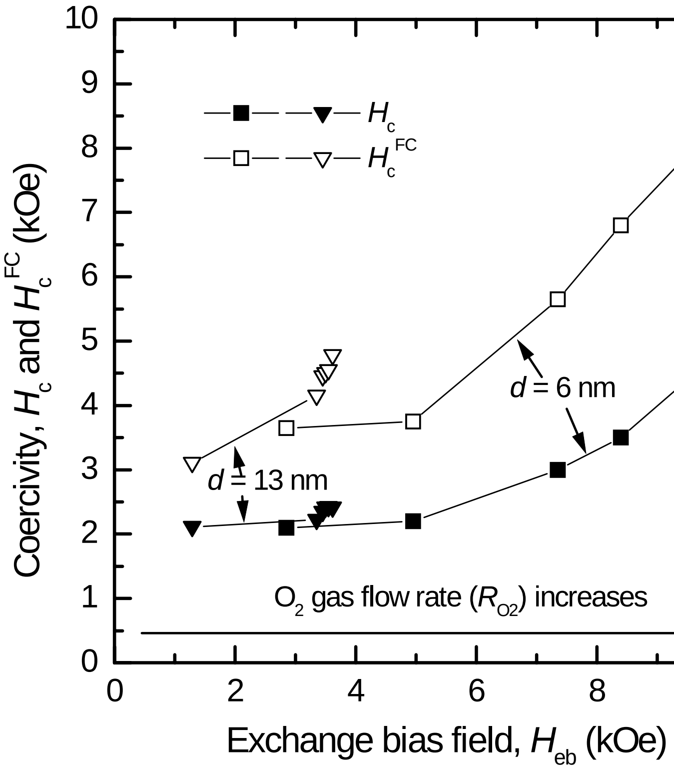




D. L. Peng *et al.*, Phys. Rev. B, **60** (1999) 2093

# Co/CoO核壳界面交换偏置引起的Co核纳米粒子单轴磁各向异性的增强





Exchange bias field: $H_{eb} = |H_1^{FC} + H_2^{FC}|/2$

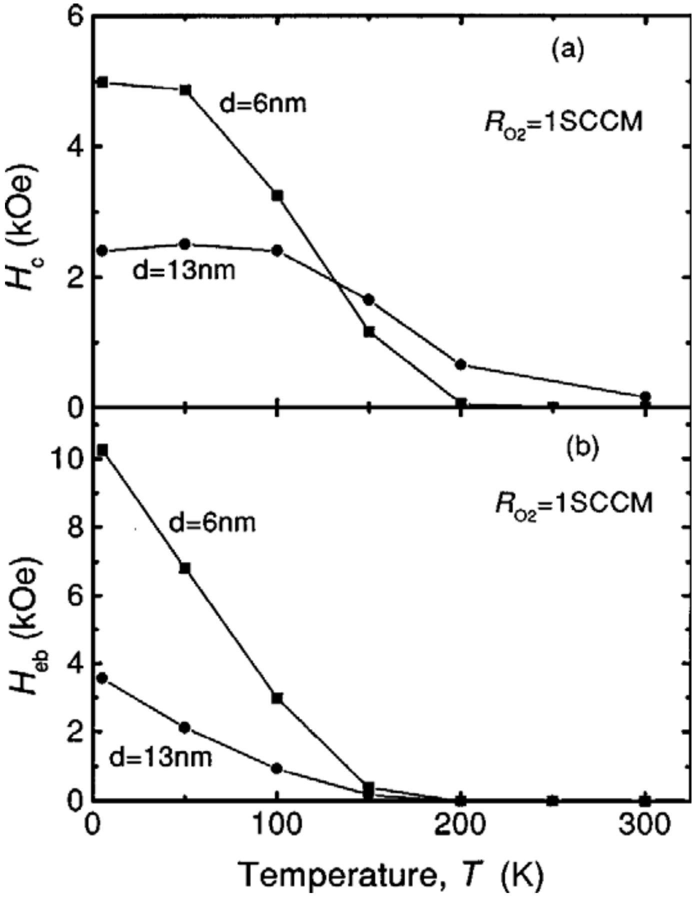
Coercivity: $H_c = |H_1^{ZFC} - H_2^{ZFC}|/2$;

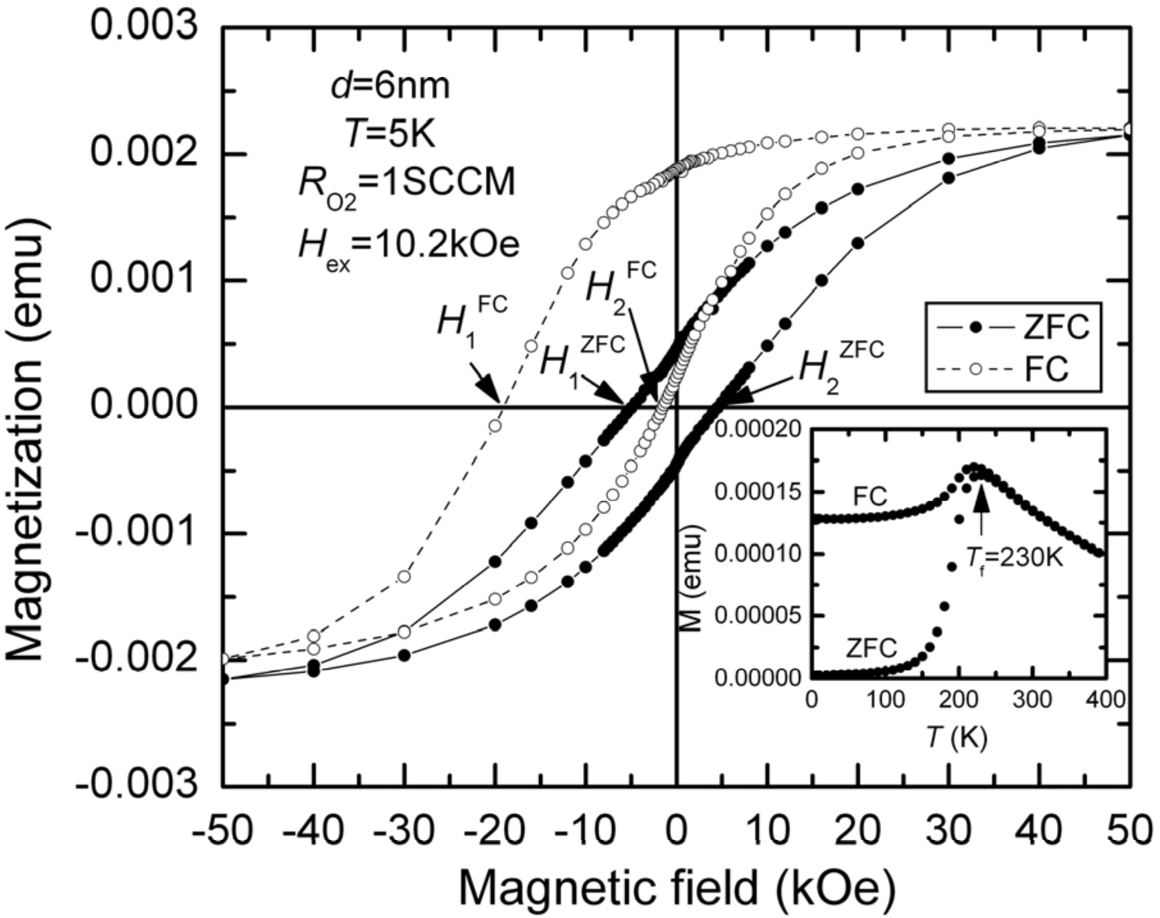
$H_c^{FC} = |H_1^{FC} - H_2^{FC}|/2$

- 交换偏置场 $H_{eb} > 1$ T
- 矫顽力显著增大

D. L. Peng *et al*., Phys. Rev. B, **61**(2000)3103 (引用98次)

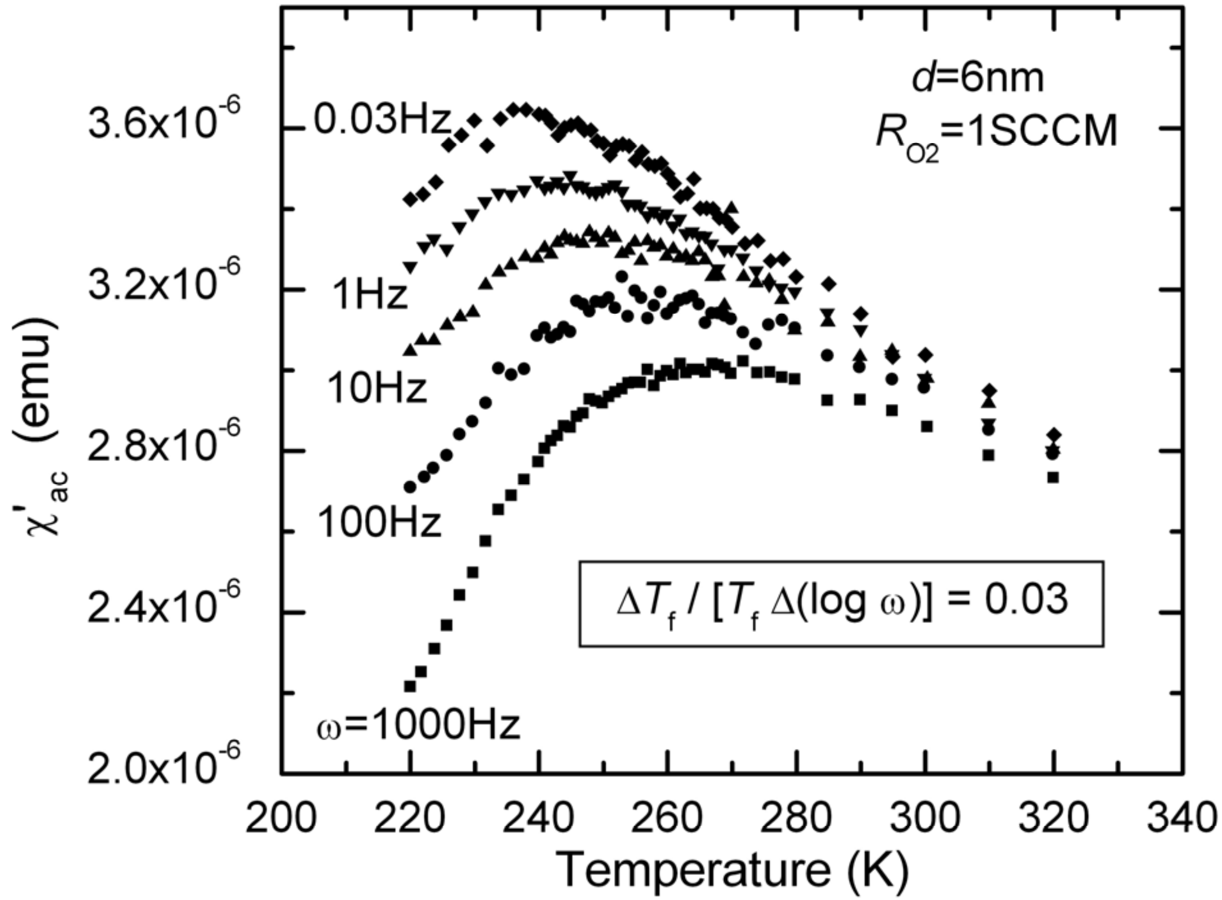
# 交换偏置场引起矫顽力显著增大的起因分析





D. L. Peng *et al.*, Phys. Rev. B, **61**(2000)3103

# 交换偏置场引起矫顽力显著增大的起因分析

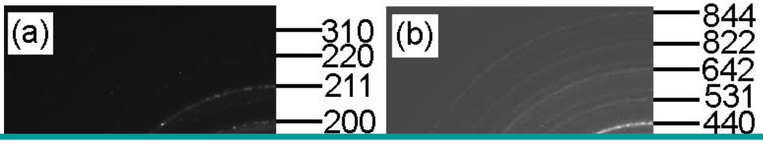


**Spin-glass-like state in the interfacial layer.**

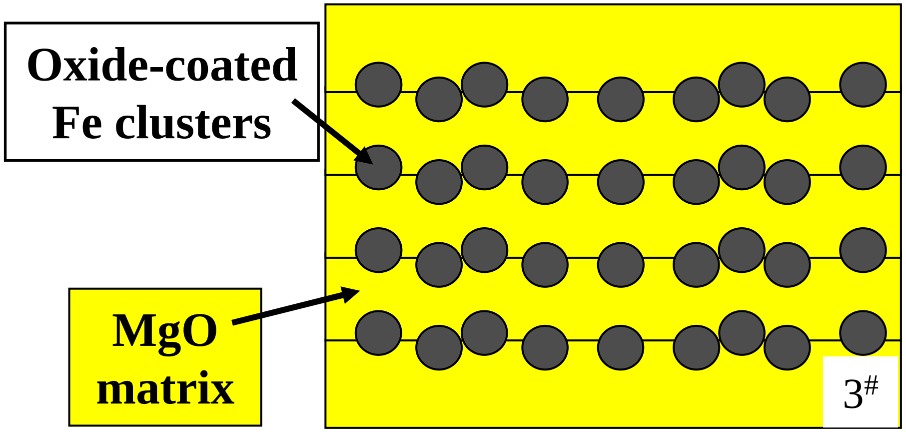
**$\Delta T_f/[T_f\ \Delta(\log\omega)]$ is the same order as those of the spin glasses and smaller than the values (0.2-0.3) of the superparamagnets.**

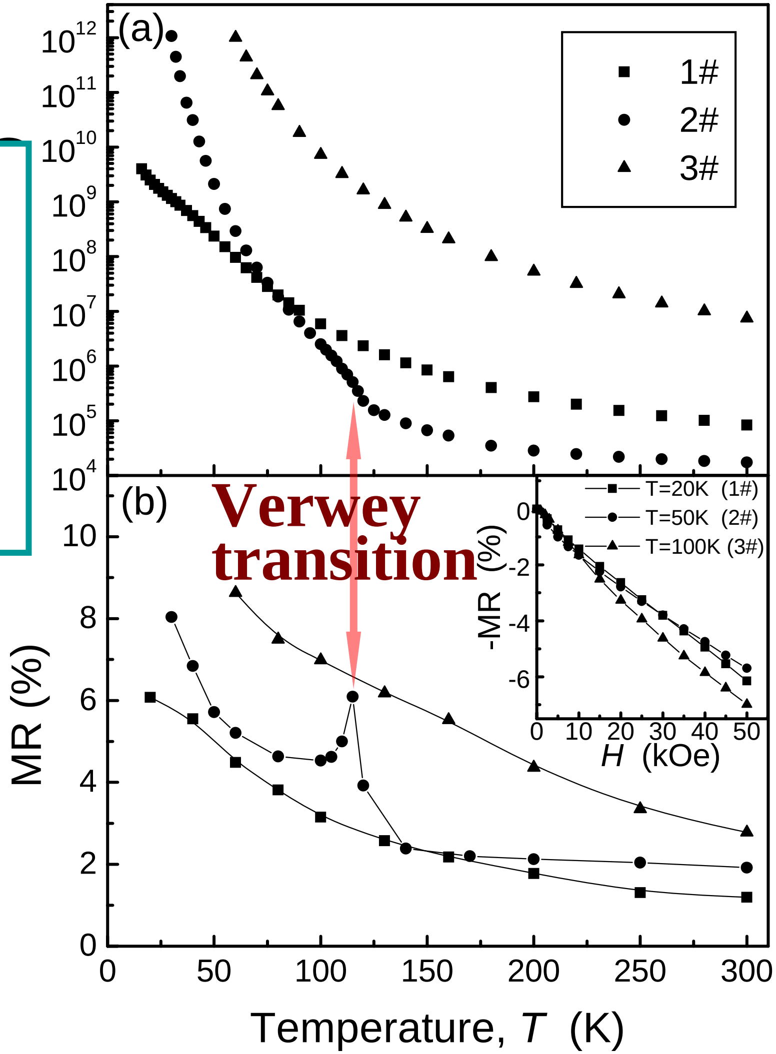
D. L. Peng *et al*., Scripta Mater., **44**(2001)1471

# 表面氧化Fe纳米粒子组装膜的巨磁阻效应



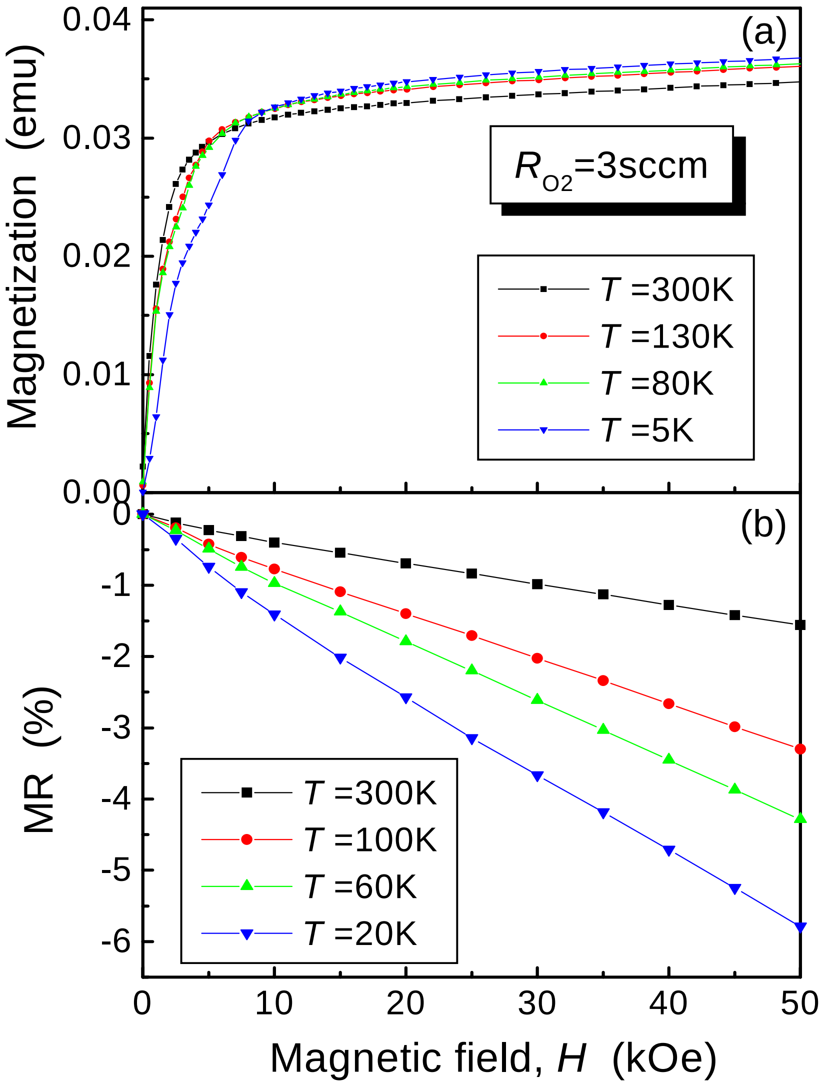
在表面氧化Fe核－壳结构的纳米粒子组装体系统中隧穿巨磁阻效应显示特殊规律性；非常小的表面氧化物颗粒导致了高磁场非饱和磁阻特性；为了增强高温巨磁阻效用，非磁性障碍层的引入是非常重要的。



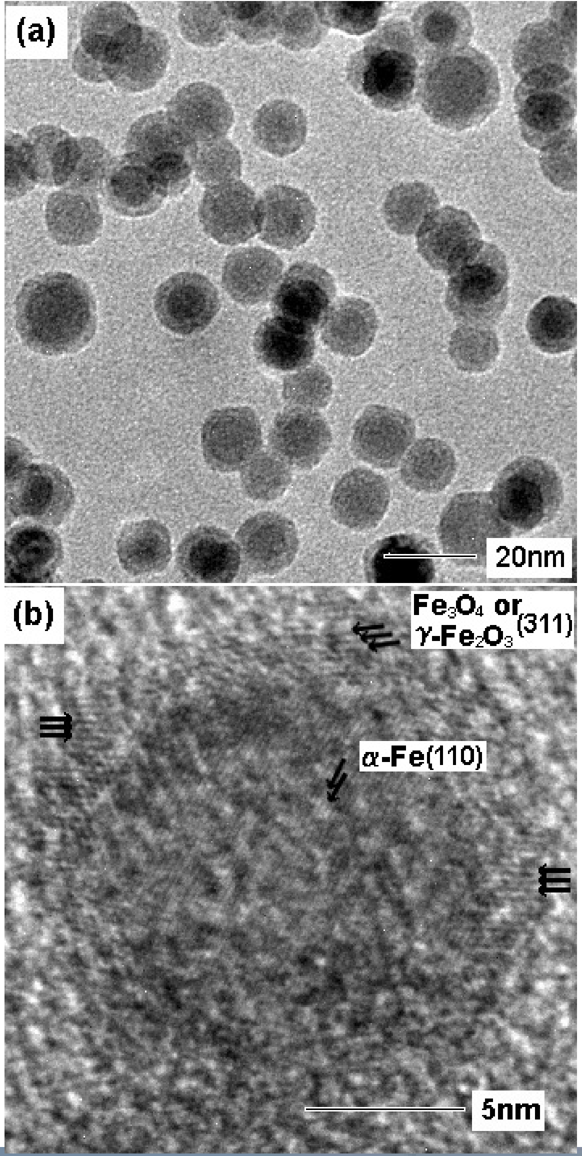


D. L. Peng et al., *Appl. Phys. Lett.*, 81 (2002) 4598

# Comparison of magnetic field dependence of magnetization and *MR*

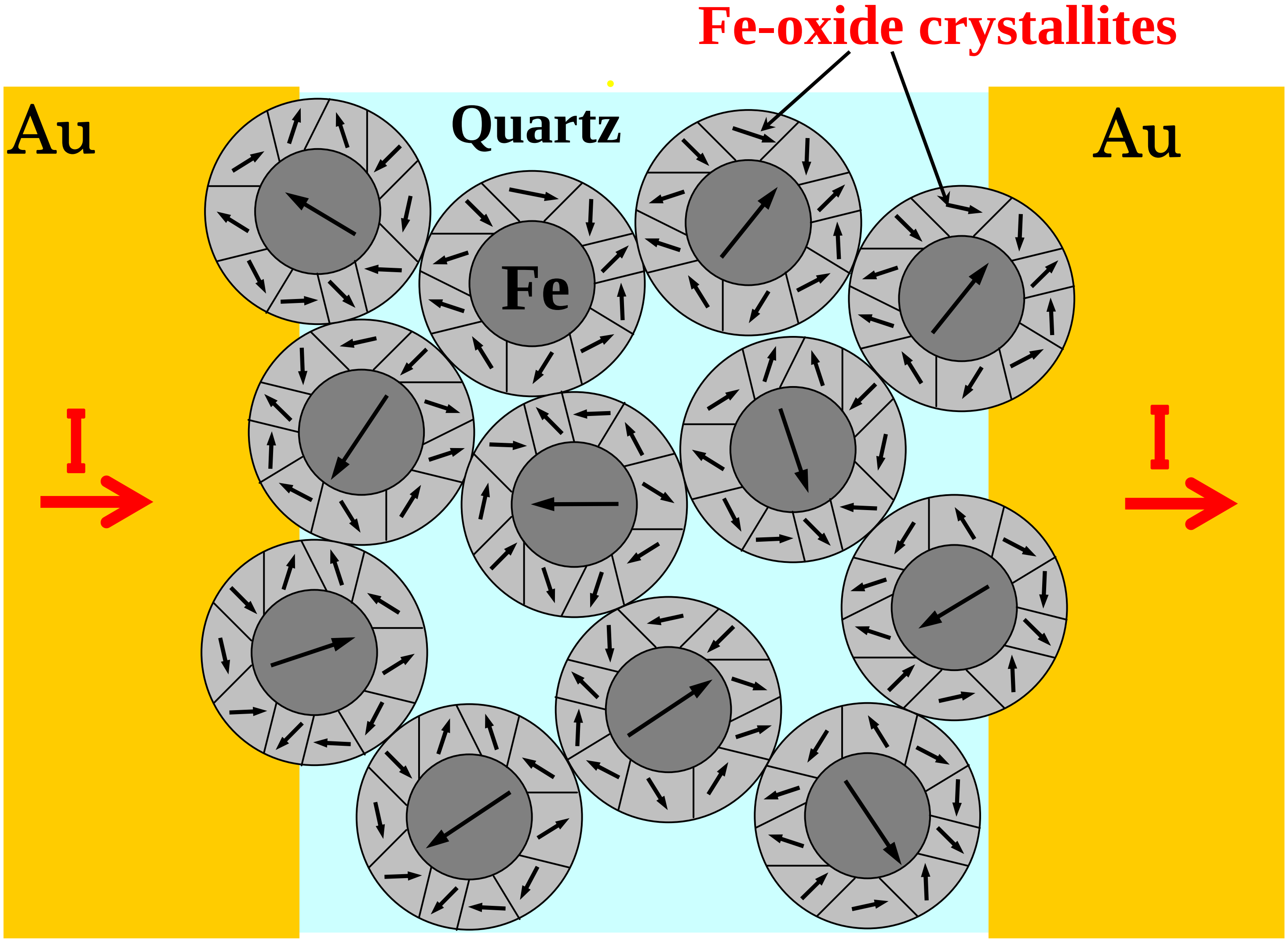


# TEM images of the oxide-coated Fe clusters with $d$ = 13 nm



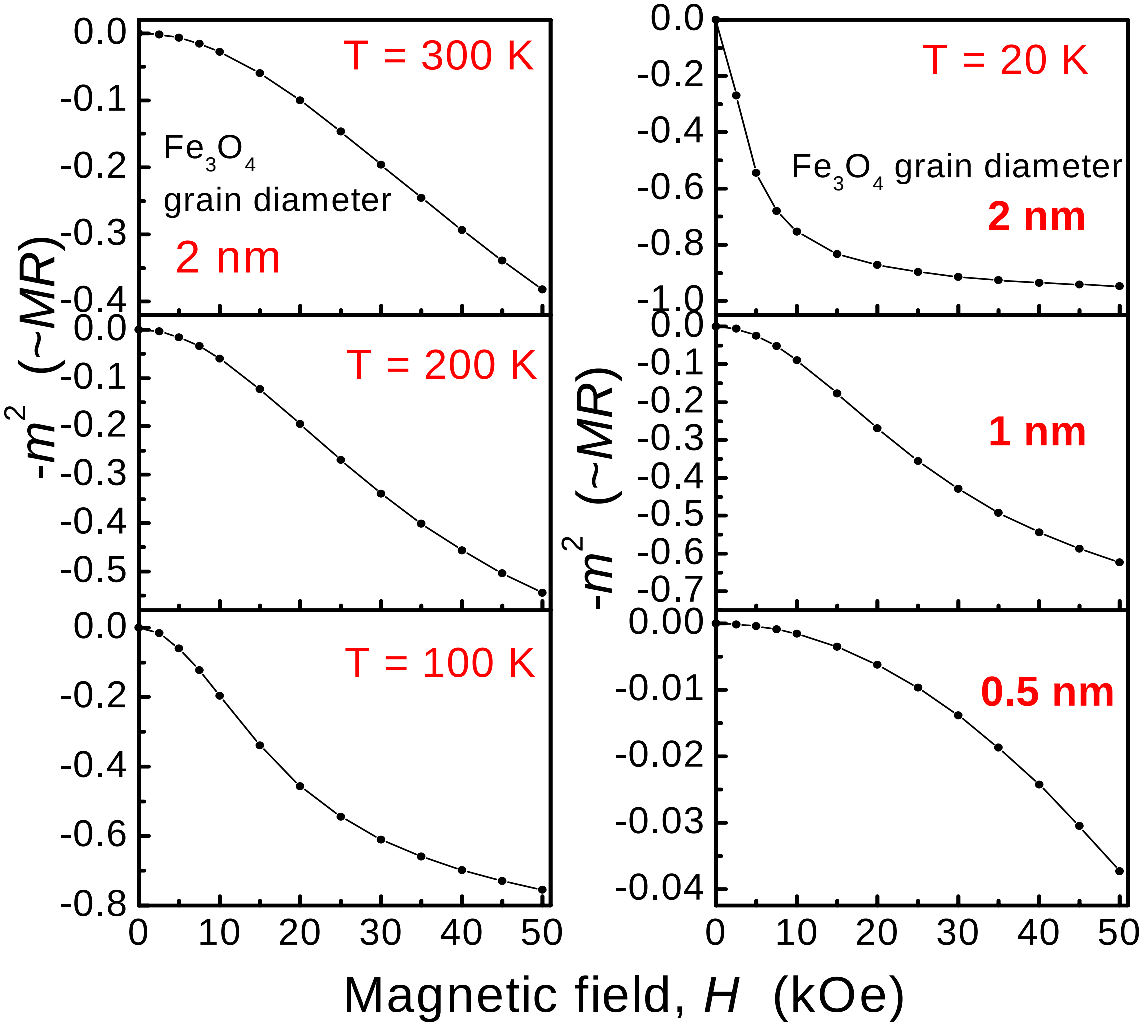
**Core-shell structure and small oxide shell crystallites**

# Schematic illustration for tunneling conduction in this core-shell-type oxide-coated Fe cluster assembly

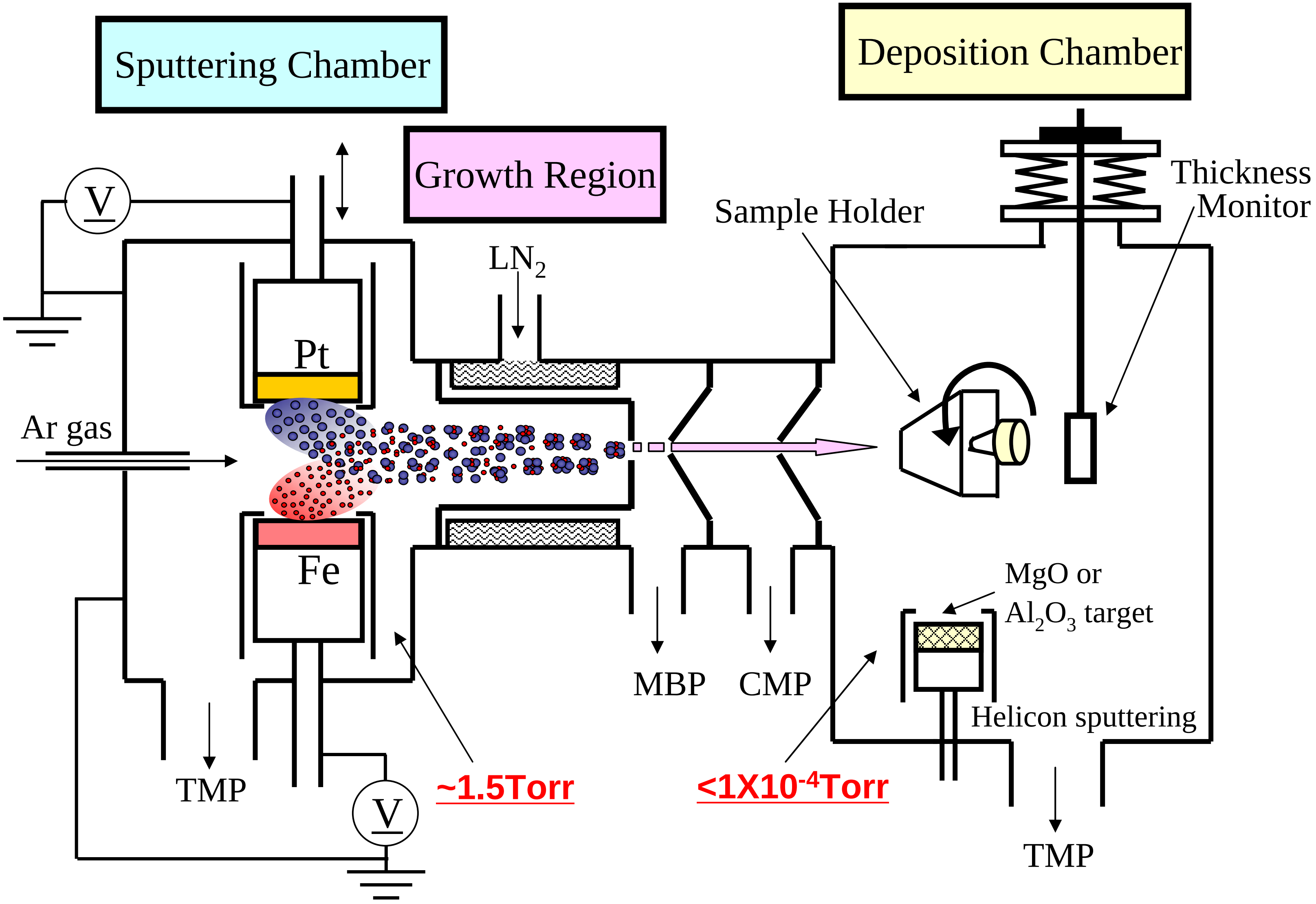


# Magnetic field *H* dependence of *m*² and *MR* when a superparamagnetic state is assumed

Calculated result using Langevin function L($\mu H/kT$)



# 均一尺寸Fe-Pt合金纳米粒子的气相合成

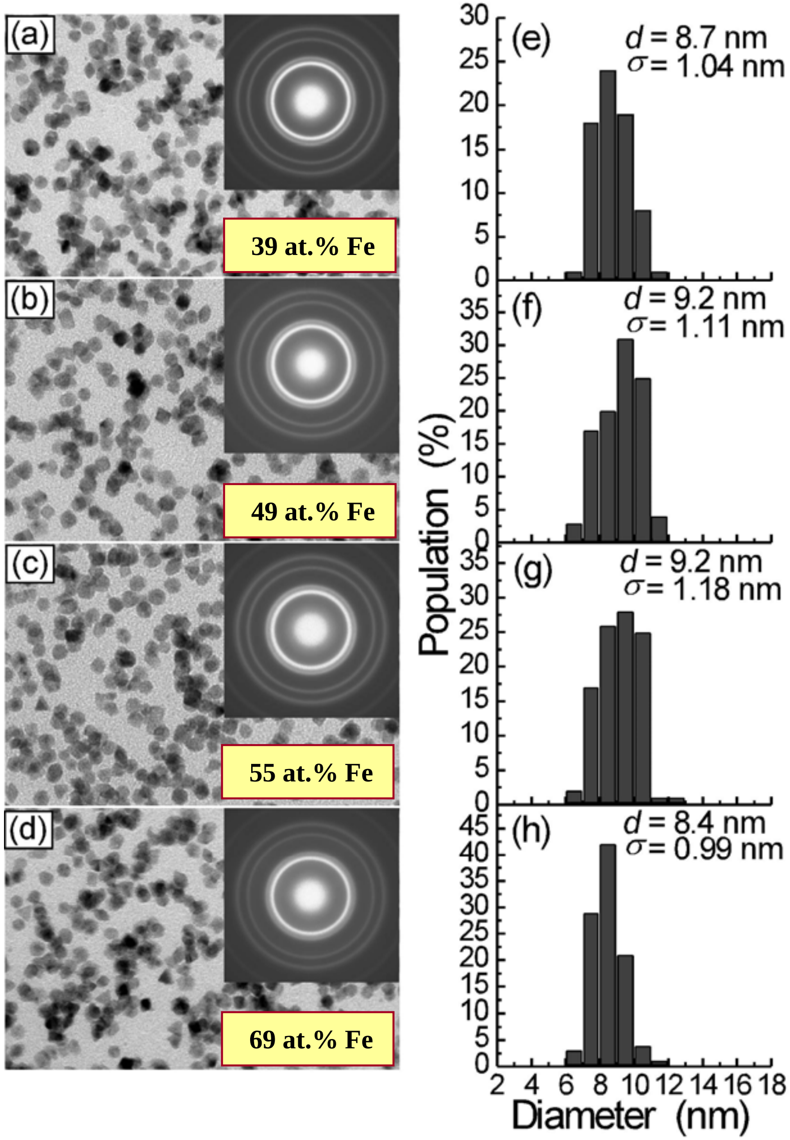


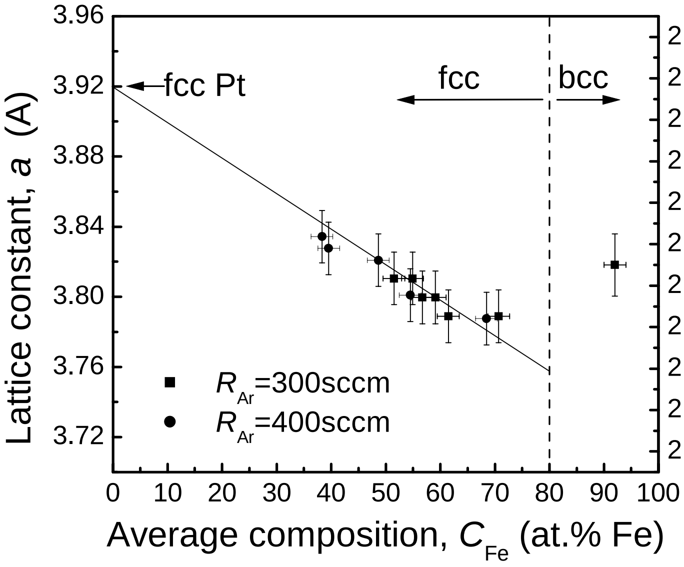
~1.5Torr

<1X10$^{-4}$Torr

D. L. Peng *et al*., Appl. Phys. Lett., **83** (2003) 350

# Fe-Pt合金纳米粒子的尺寸、成分和结构





**尺寸均一、成分均匀且可调**

对异种单质靶材进行溅射合金化，可以获得成分可控的合金纳米粒子。

D. L. Peng *et al*., Appl. Phys. Lett., **83** (2003) 350

# TEM images and ED patterns of $Fe_{49}Pt_{51}$ cluster-assembled film with a thickness of *t* = 30 nm (*d* = 9 nm)

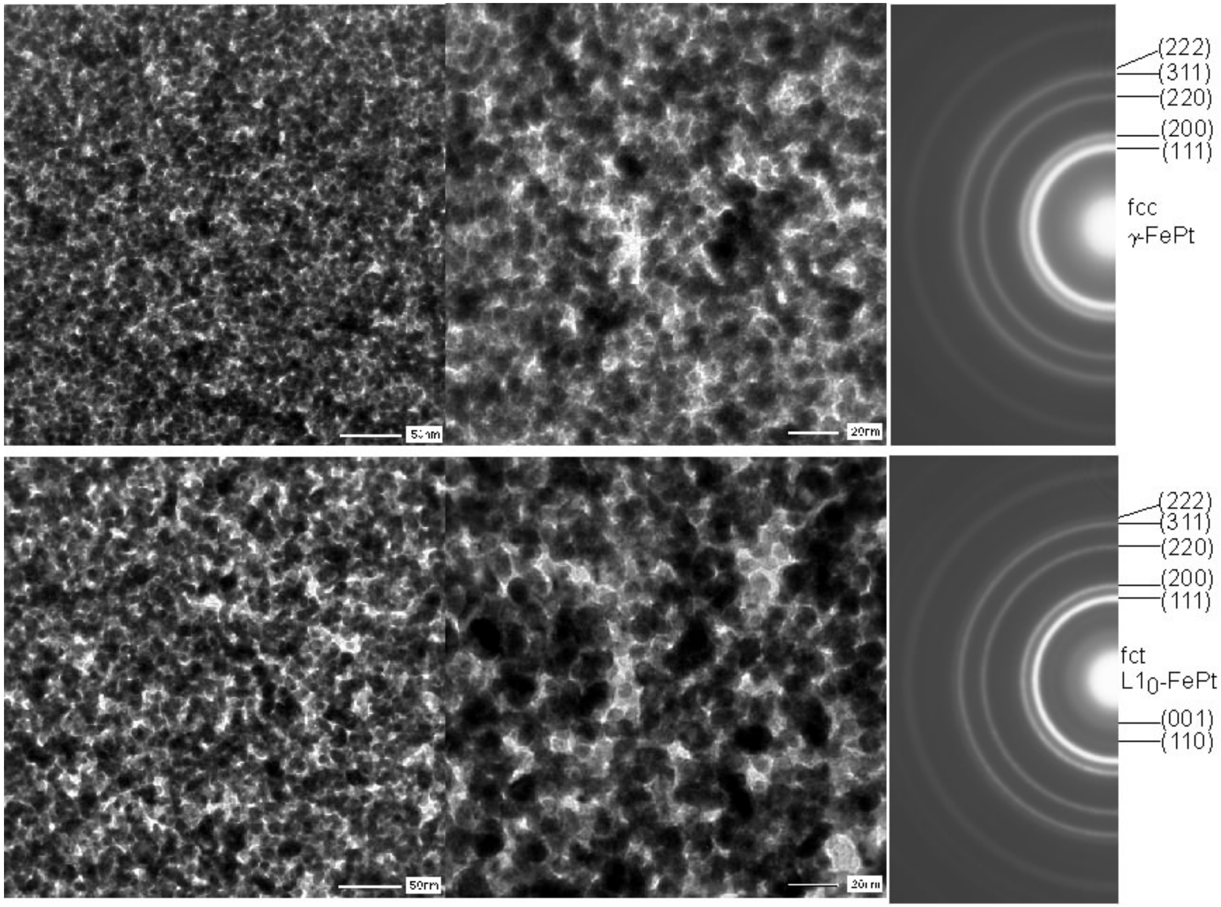
x 50k

x 100k

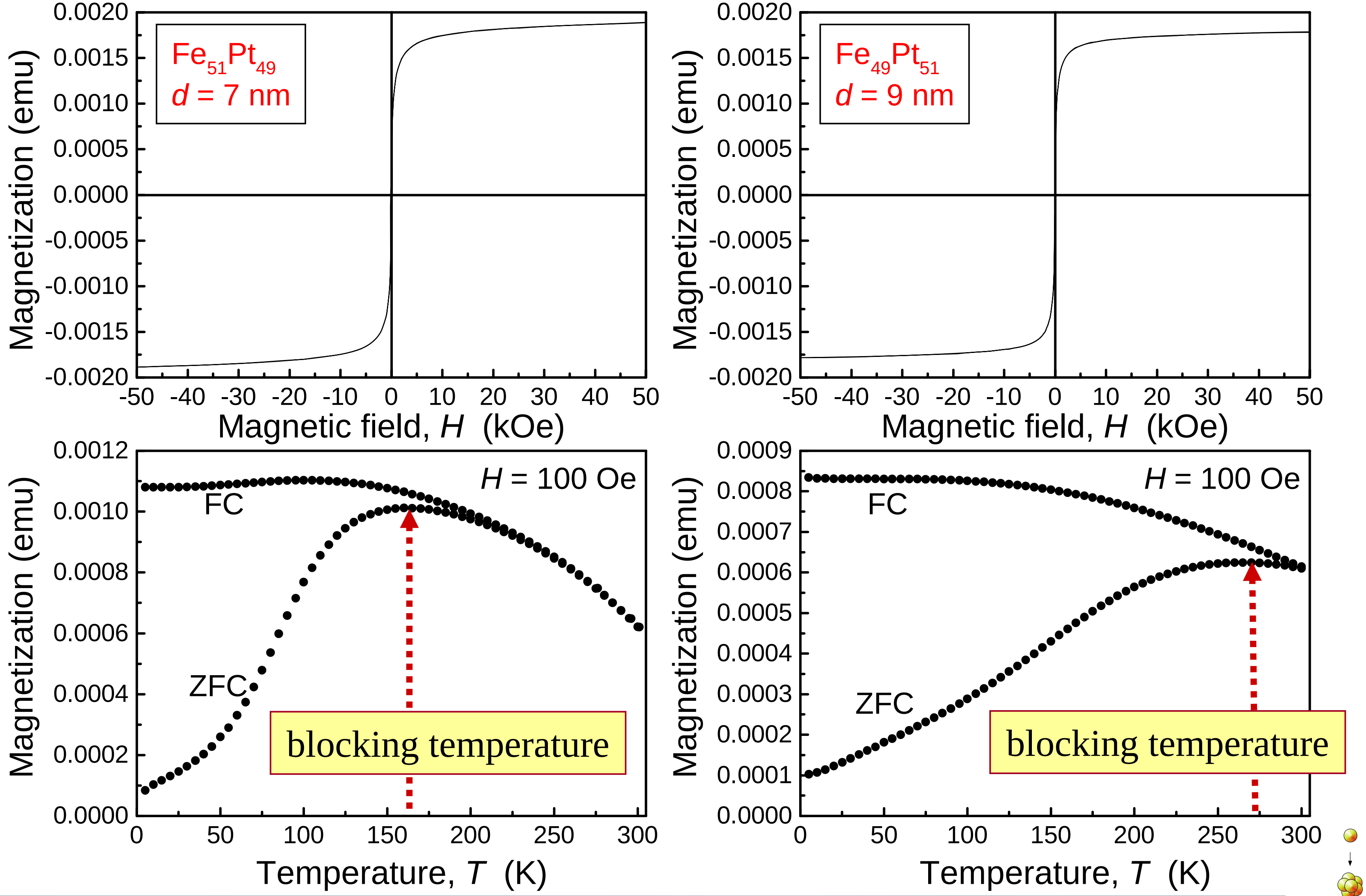
**As-deposited**

**After annealing**

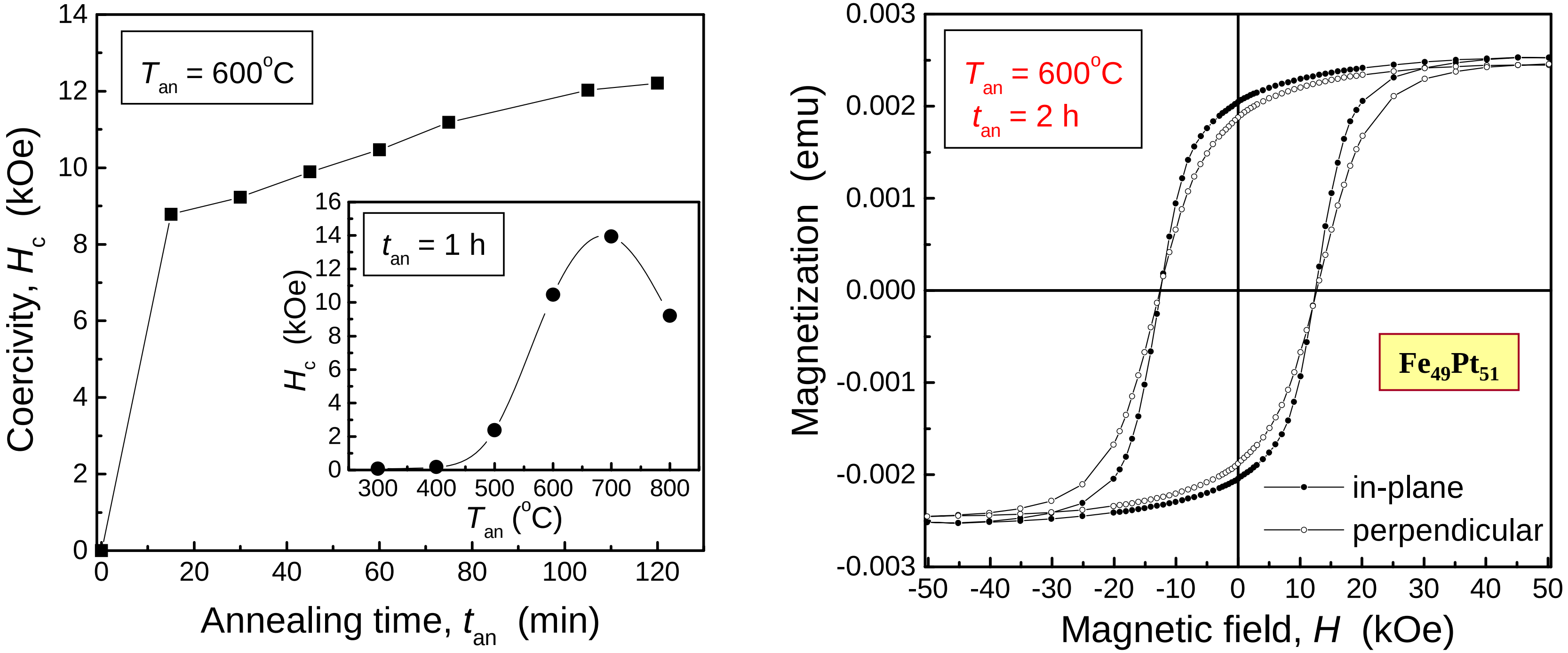
$T_{an}$=600°C
$t_{an}$=60min



# Magnetic measurement results of as-deposited FePt alloy cluster-assembled films



# Fe-Pt合金纳米粒子的组装体膜的磁学特性



D. L. Peng *et al*., Appl. Phys. Lett., **83** (2003) 350

# 趋势：smaller and faster

需求：信息；通讯；抗电磁干扰；微波隐身

**电子器件“两高两低”发展趋势**

- 高频化 高效率 低维化 低损耗

## 软磁薄膜材料性能要求

- 高饱和磁化强度 低矫顽力 高电阻率 高磁导率 高铁磁共振频率 良好的热稳定性…

# 几种常见的软磁薄膜材料

- 铁氧体软磁薄膜材料
- 非晶(CoZrNb, CoZrTa等)软磁合金薄膜材料
- 磁性金属-绝缘介质纳米结构复合颗粒膜材料
- Fe基纳米晶合金软磁薄膜材料

➢ 高频用FeCo纳米晶合金软磁薄膜材料的研制

√ 最高的饱和磁化强度

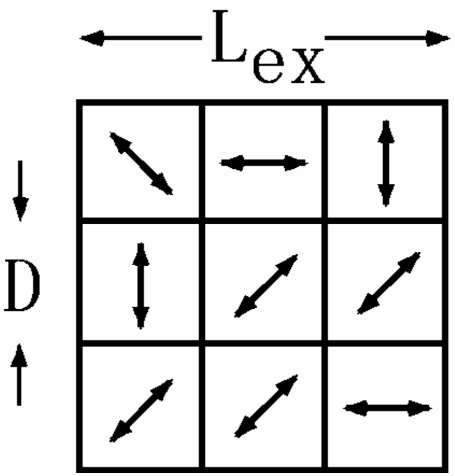
× 大的磁致伸缩

× 低的电阻率

# 纳米晶磁性合金的软磁性原理

## Herzer’s random anisotropy model (RAM)

(G. Herzer, *IEEE Trans. Magn.* 26 (1990) 1397)



$$N = (L_{ex}/D)^3$$

$$L_{ex} = \left(\frac{A}{K_{eff}}\right)^{\frac{1}{2}}$$

$$K_{eff} = \frac{K_c}{\sqrt{N}} = K_c\left(\frac{D}{L_{ex}}\right)^{\frac{3}{2}}$$

$$\boxed{K_{eff} \approx \frac{K_c^4 D^6}{A^3}}$$

$$\boxed{H_c = P_c\frac{K_c^4 D^6}{M_s A^3}}$$

$L_{ex}$： 交换相关长度
$K_c$： 晶体磁各向异性常数
$K_{eff}$： $L_{ex}$范围内的平均磁各向异性常数

磁晶各向异性常数被平均化

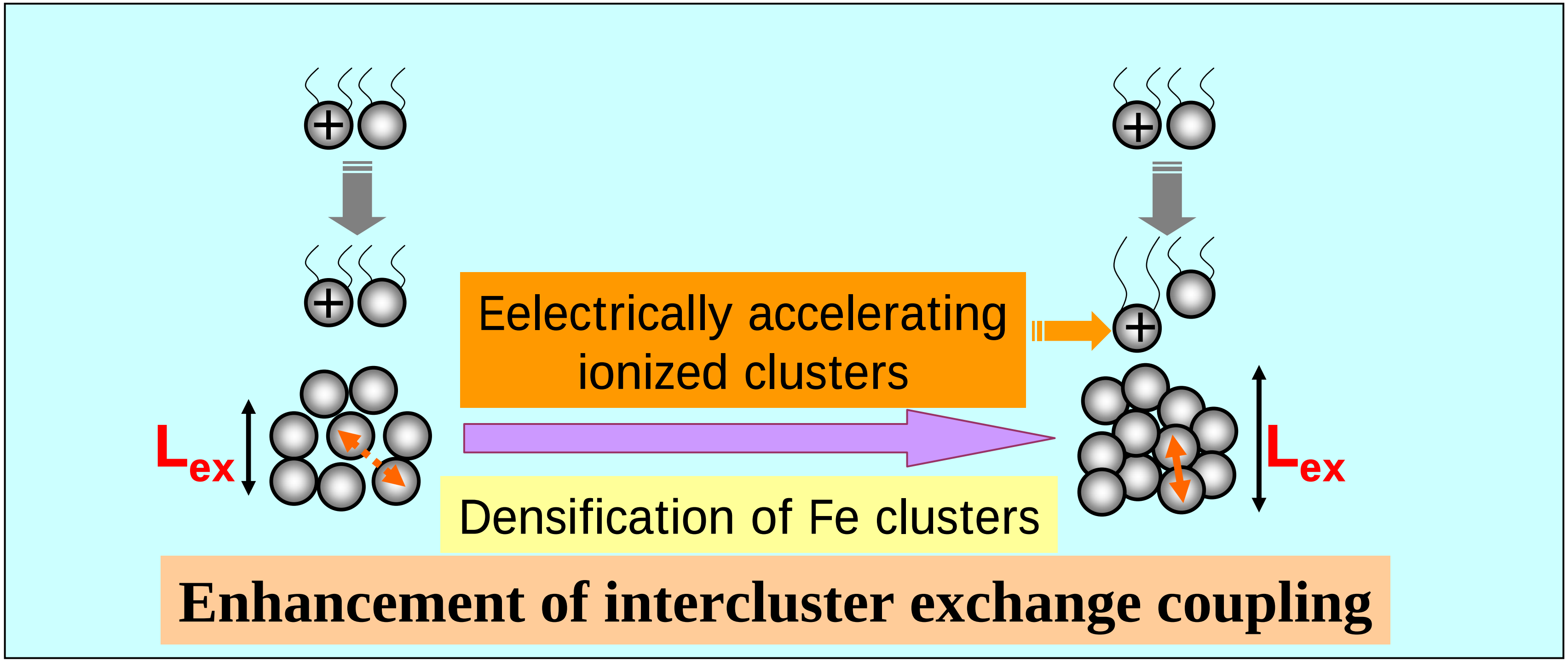
软磁性

# 研究构想

提高纳米粒子组装膜材料致密度

降低有效磁各向异性常数

实现优良软磁性能薄膜材料的室温制备

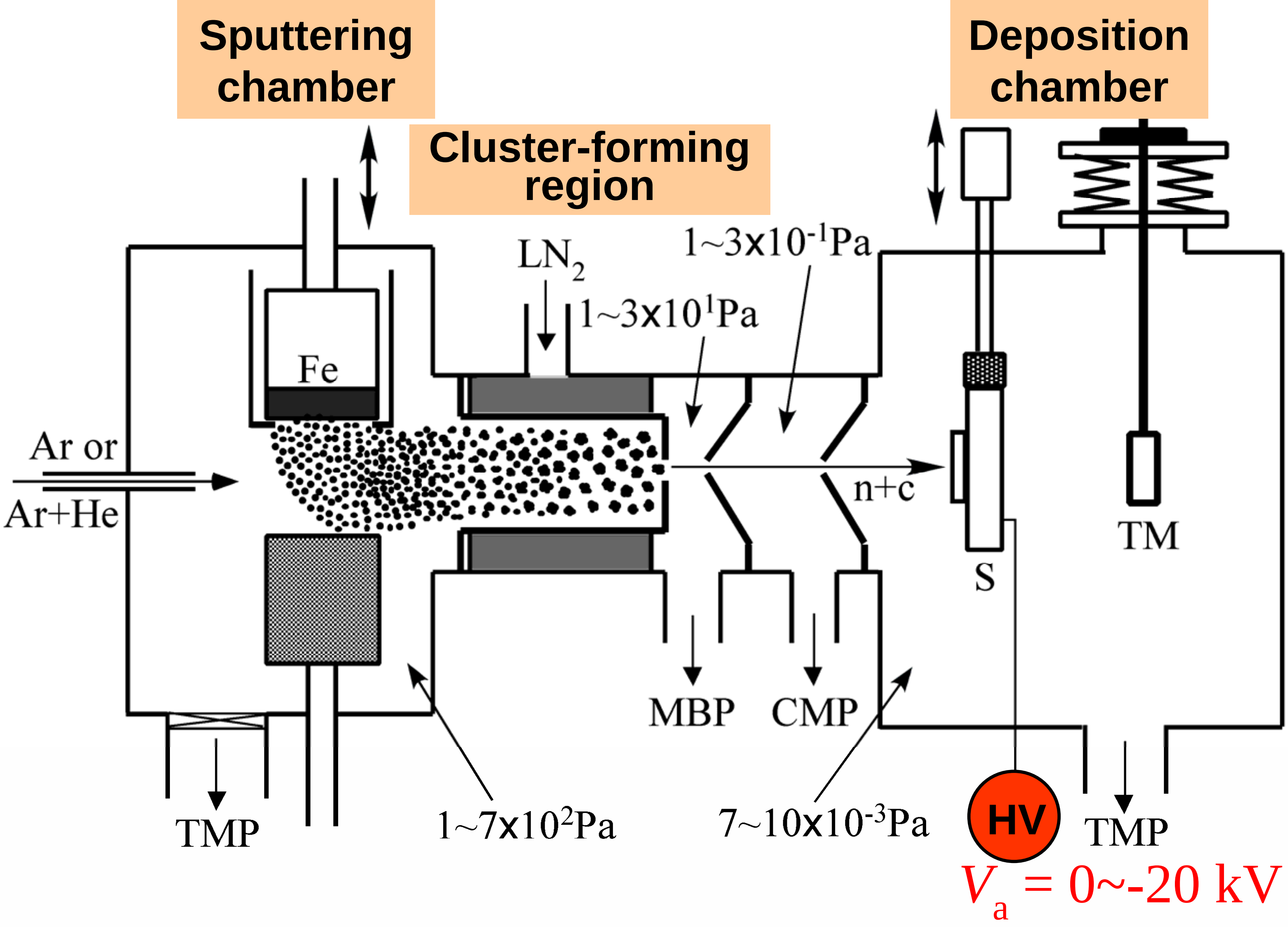


Eelectrically accelerating ionized clusters

Densification of Fe clusters

**Enhancement of intercluster exchange coupling**

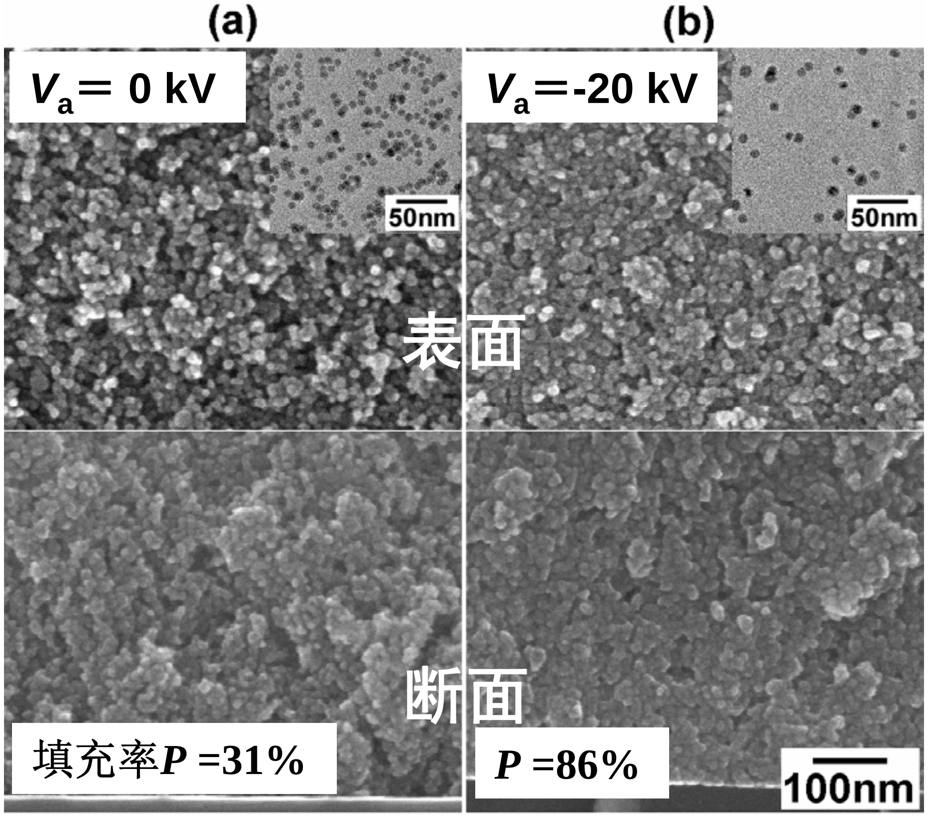
# 软磁性Fe纳米粒子集合体膜的室温气相制备

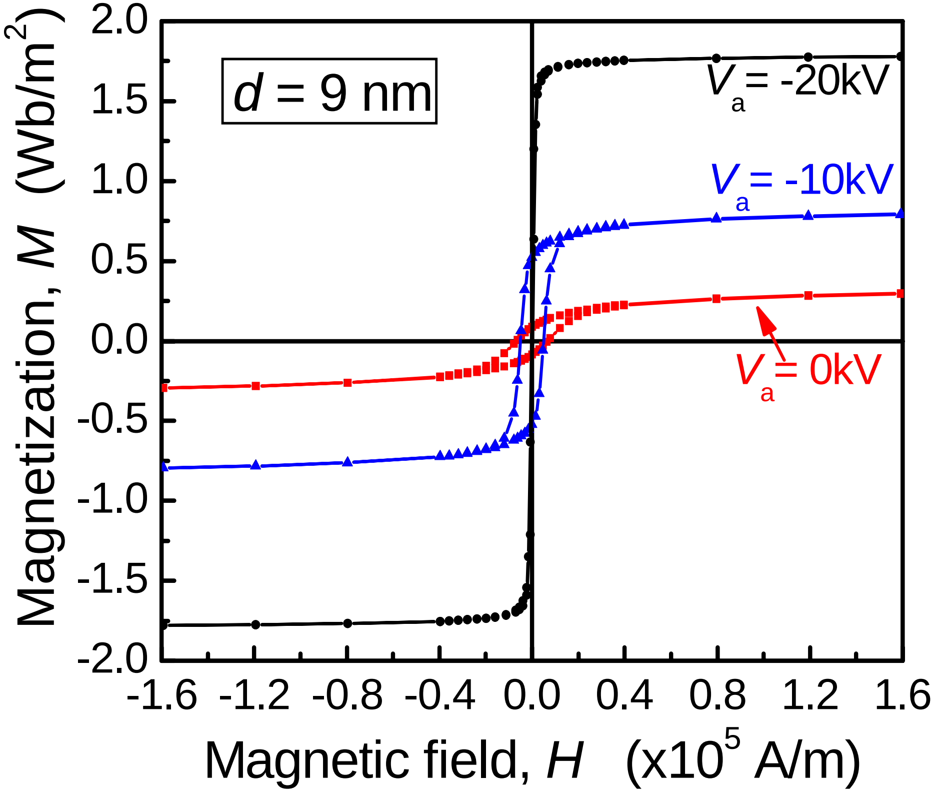


$V_a$ = 0~-20 kV

D. L. Peng *et al*., ***Appl. Phys. Lett.***, 85 (2004) 2935

# Fe纳米粒子集合体膜的结构和磁学特性

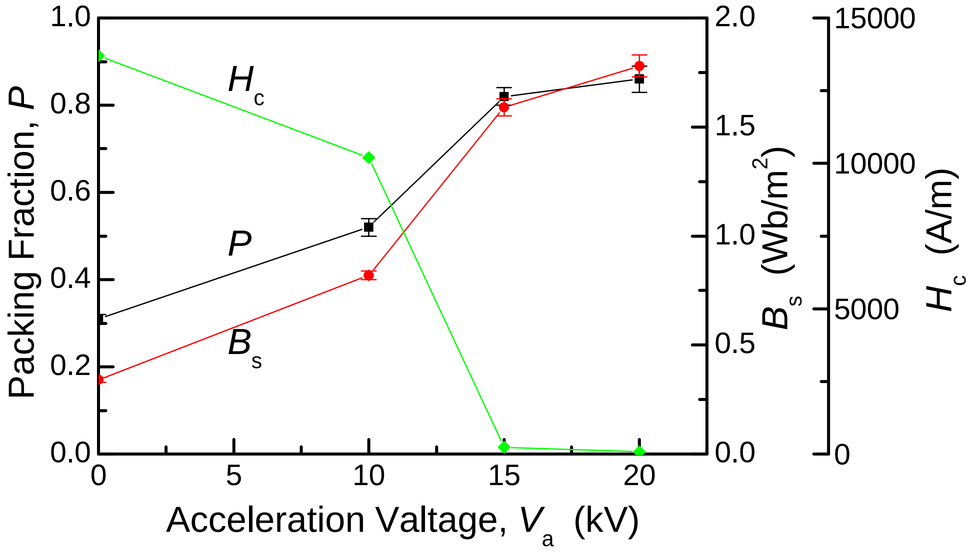


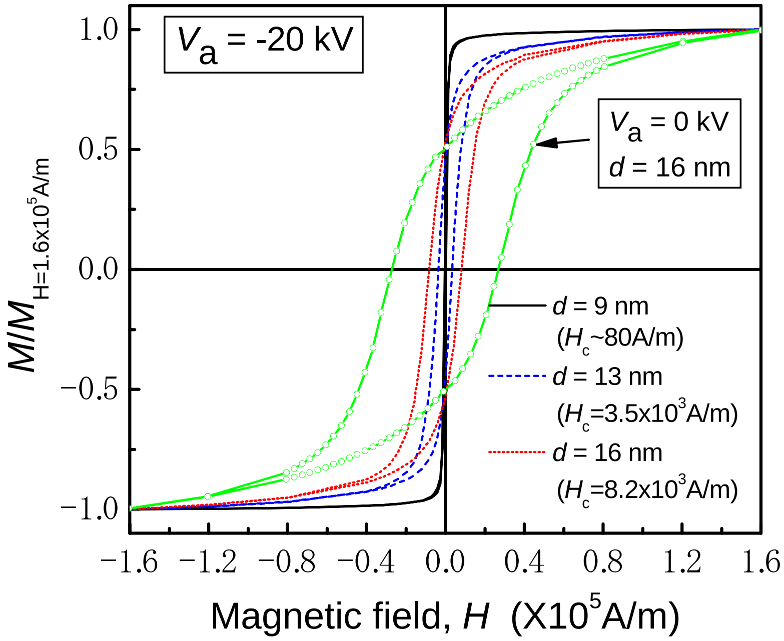


→ **致密化** → **软磁性**

D. L. Peng *et al*., ***Appl. Phys. Lett.***, 85 (2004) 2935

# 加速电压和纳米粒子尺寸对磁学特性的影响

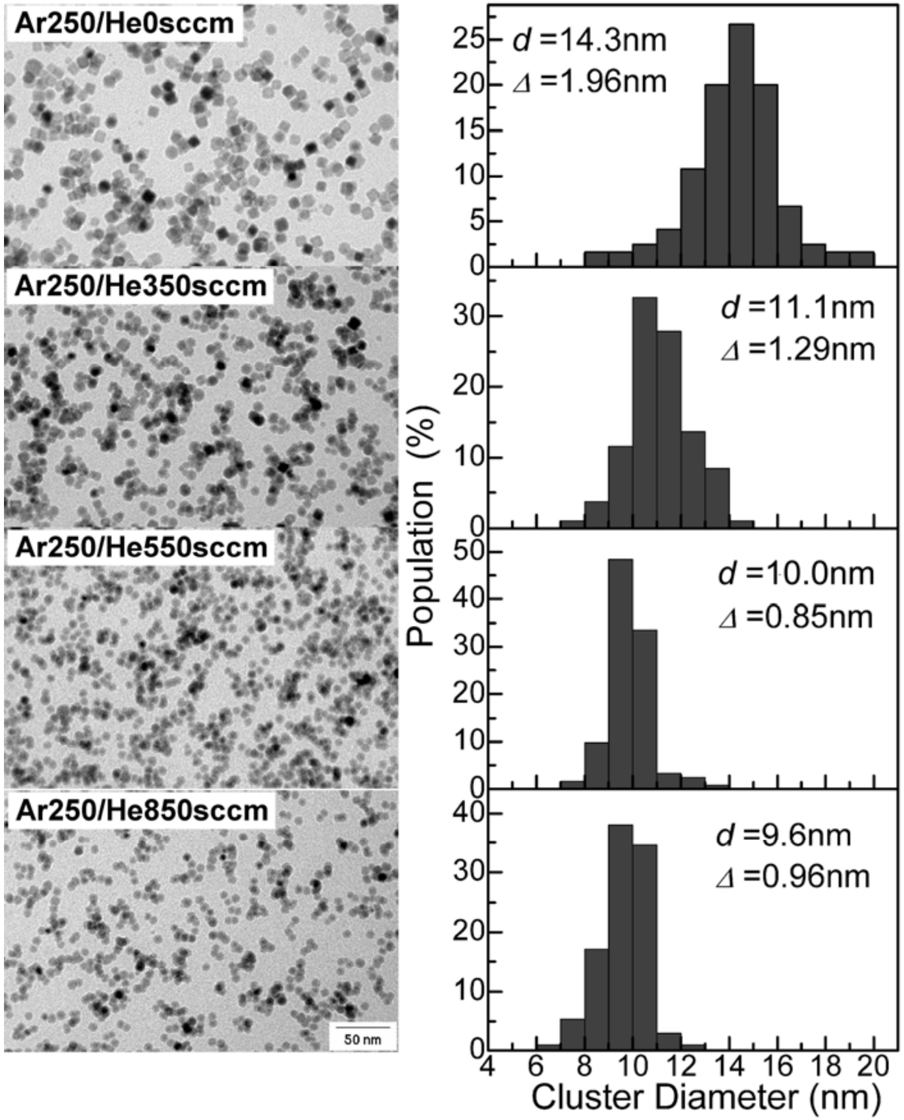




$$M_s = 1.86\ \mathrm{Wb/m^2};\quad H_c < 1\ \mathrm{Oe}$$

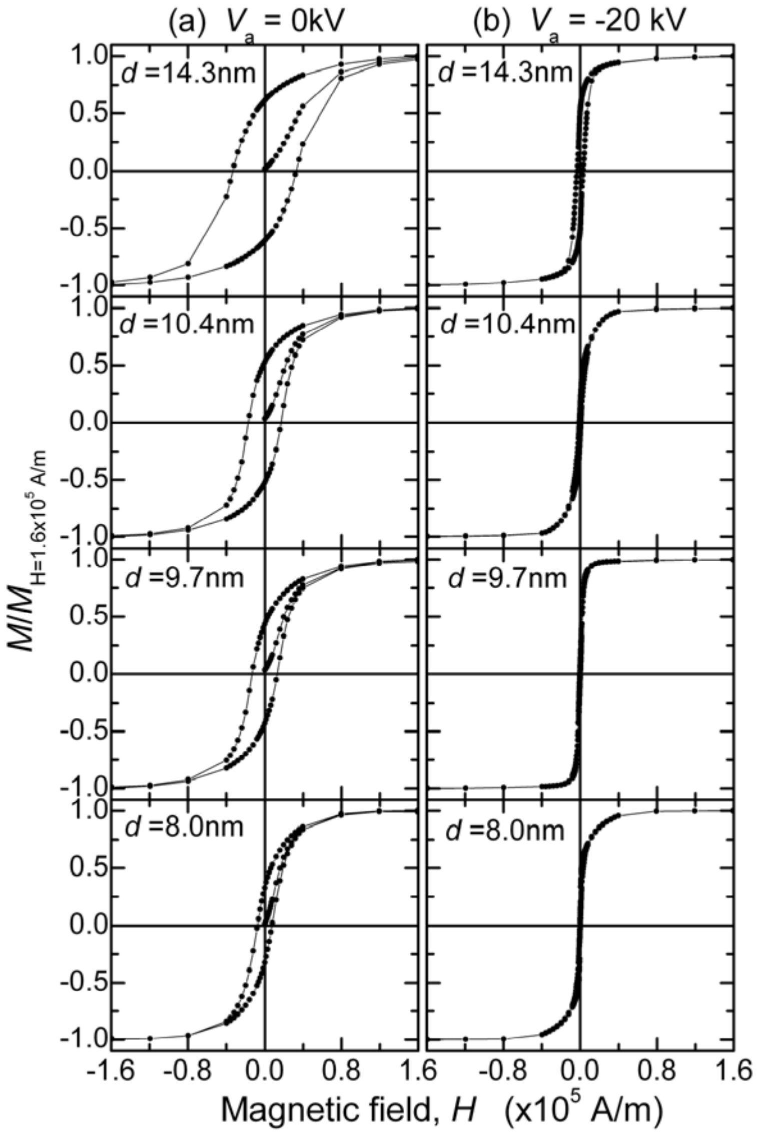
D. L. Peng *et al.*, ***Eur. Phys. J. D***, 34 (2005) 173-176

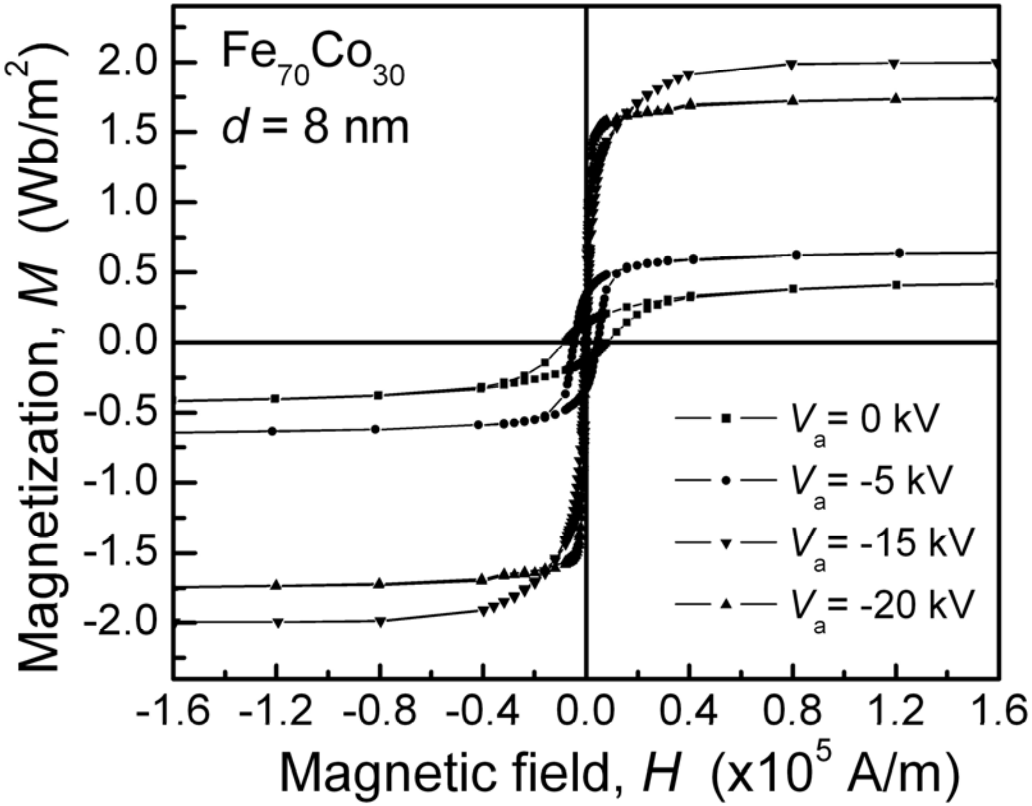
# 合成的Fe-Co合金纳米粒子



D. L. Peng *et al.*, ***J. Appl. Phys.***, 102 (2007) 033917

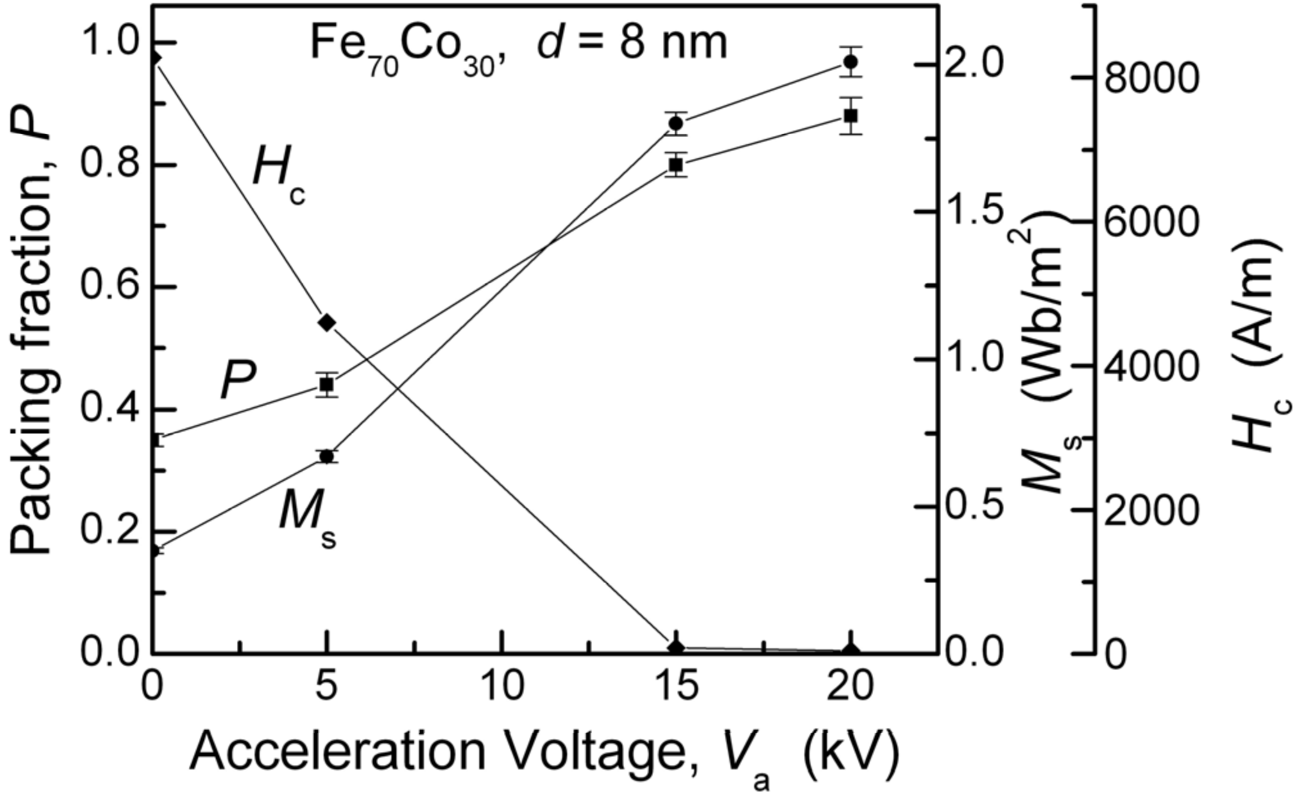
# Fe-Co合金纳米粒子集合体膜的磁学特性





D. L. Peng *et al.*, ***J. Appl. Phys.***, 102 (2007) 033917

# 加速电压对薄膜结构和磁学特性的影响

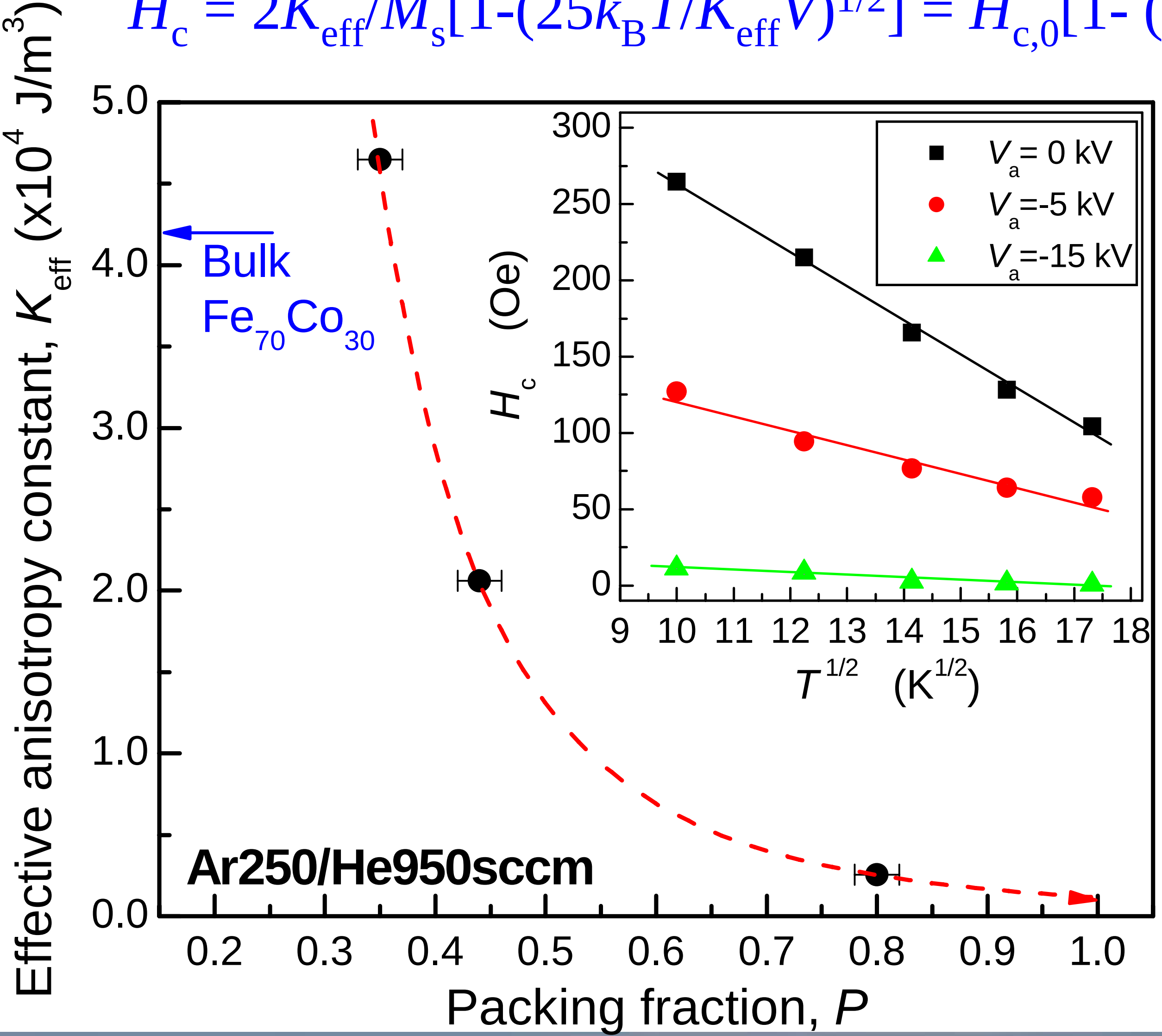


$M_s$ = 2.01 Wb/m$^2$;   $H_c$ < 1 Oe

D. L. Peng *et al.*, ***J. Appl. Phys.***, 102 (2007) 033917

# Fe-Co合金纳米粒子集合体膜磁各向异性常数

$$H_c = 2K_{eff}/M_s[1-(25k_BT/K_{eff}V)^{1/2}] = H_{c,0}[1- (25k_B/K_{eff}V)^{1/2}(T)^{1/2}]$$



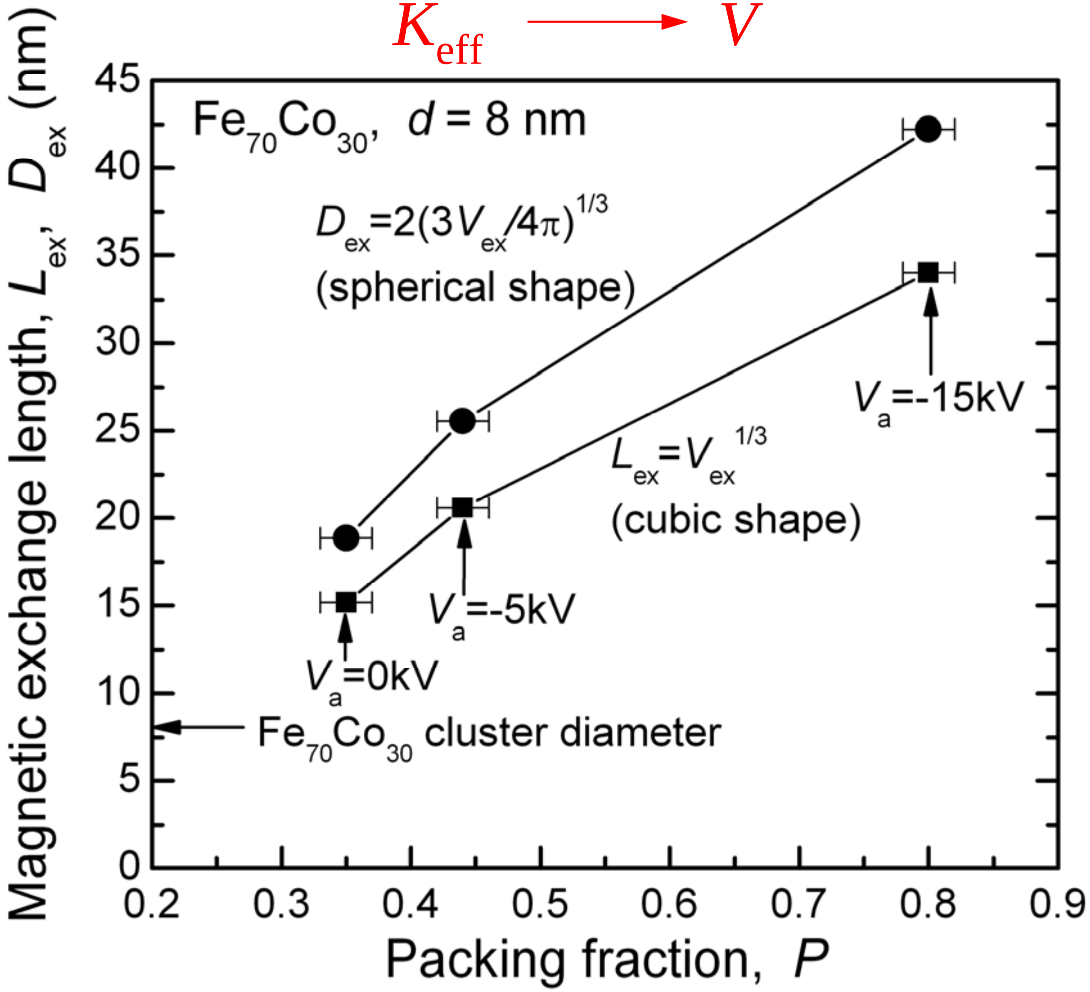
$$K_{eff} = H_{c,0}M_s/2$$

D. L. Peng *et al.*, ***J. Appl. Phys.***, 102 (2007) 033917

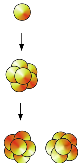
# 对Fe-Co合金纳米粒子集合体膜估算的磁交换耦合长度

$$H_c = H_{c,0}[1- (25k_B/K_{eff}V)^{1/2}(T)^{1/2}]$$

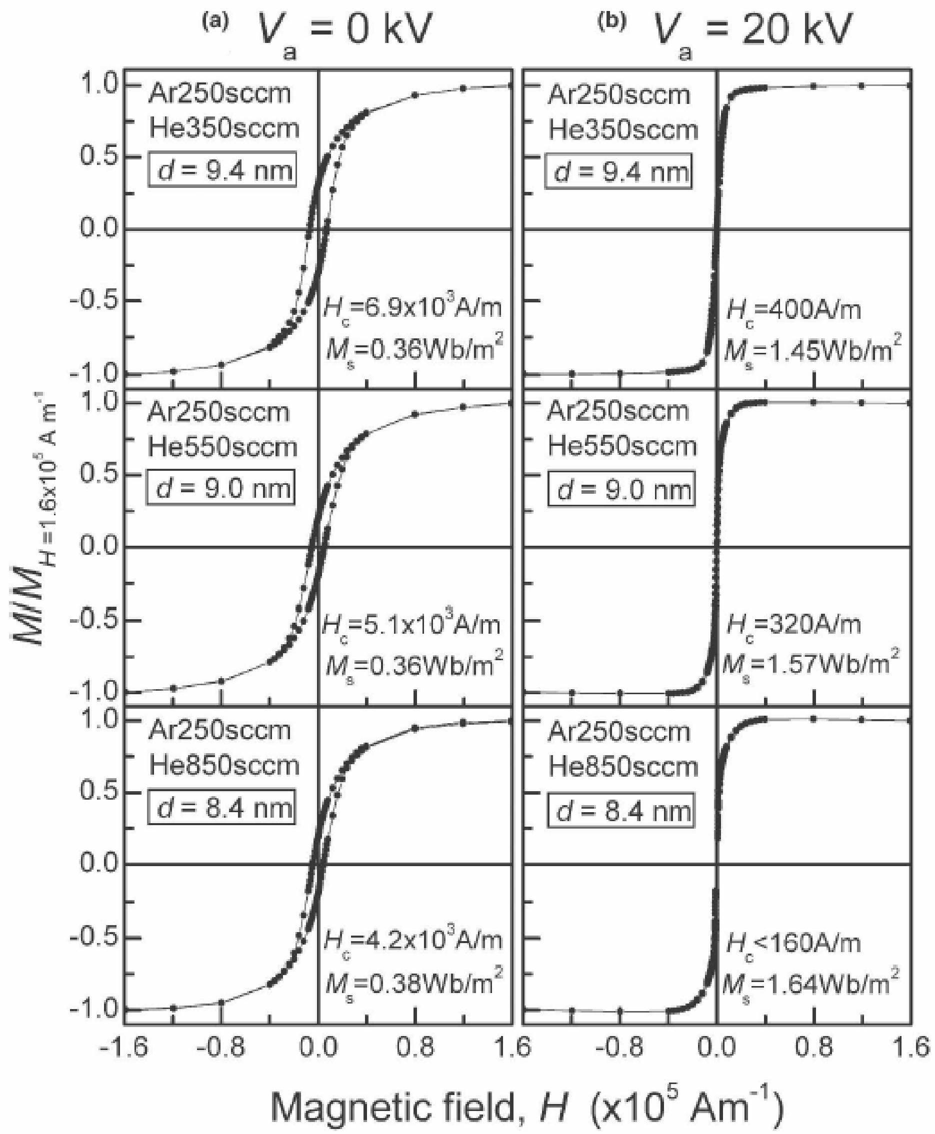
$$K_{eff} \longrightarrow V$$



D. L. Peng *et al.*, ***J. Appl. Phys.***, 102 (2007) 033917

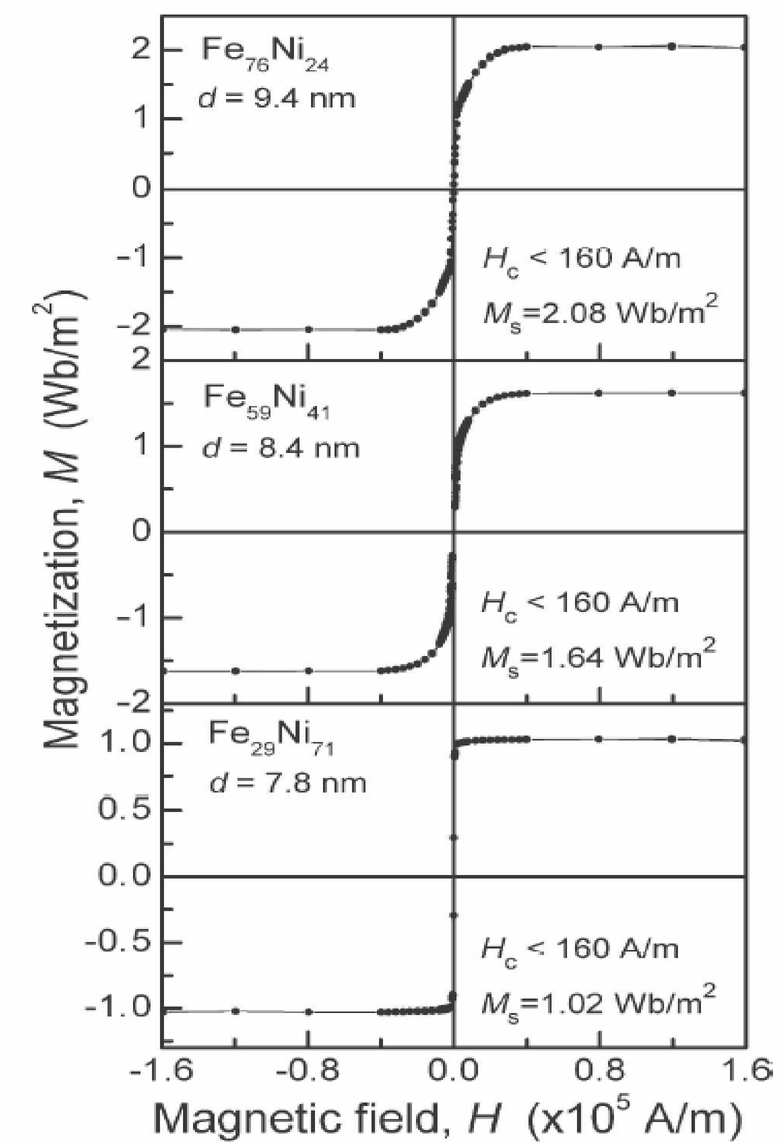


# 高密度Fe-Ni合金纳米粒子集合体膜的磁化曲线



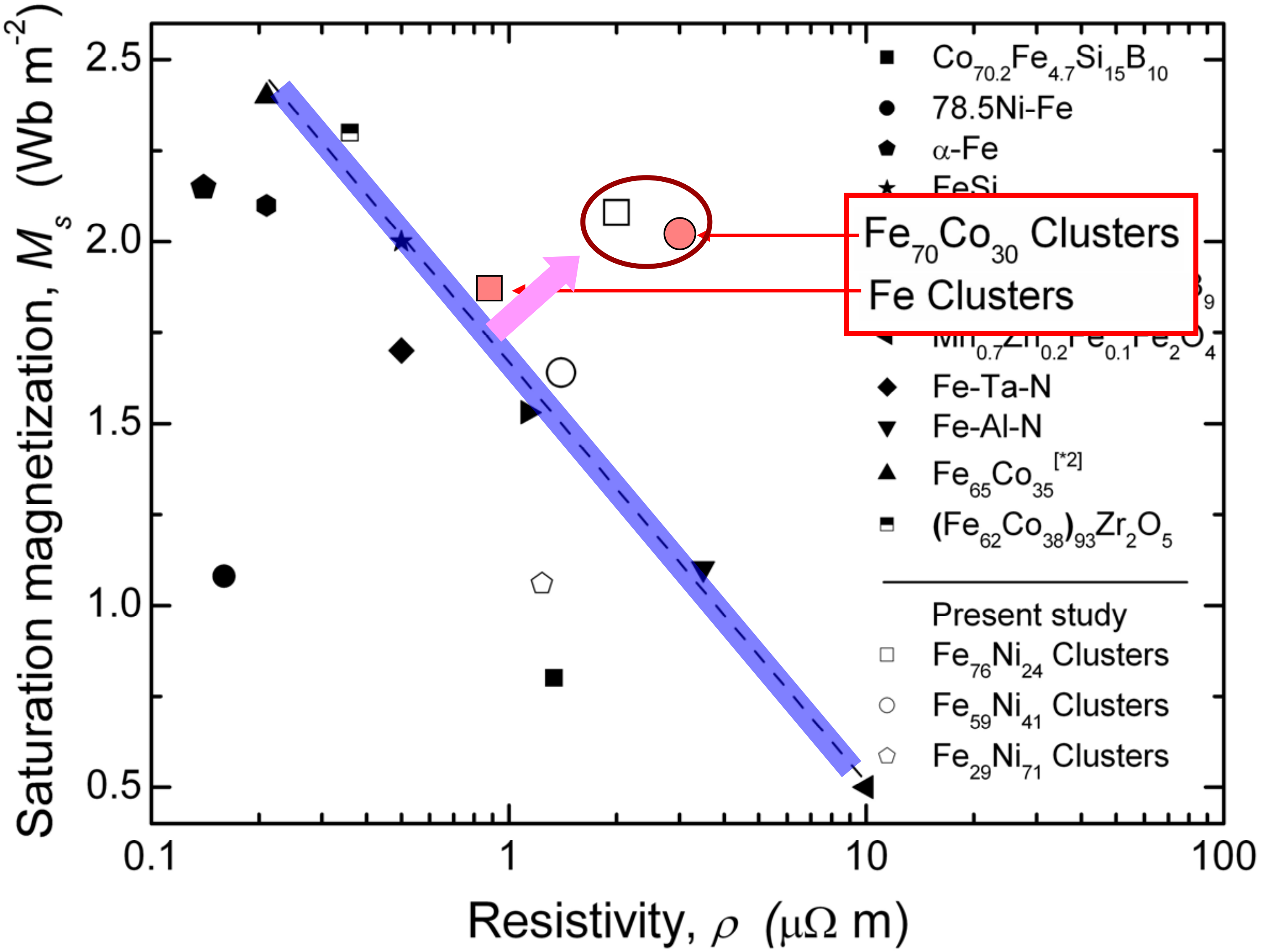
D. L. Peng *et al*., ***J. Mater. Res.***, 23 (2008) 189-197.

# 不同成分Fe-Ni合金纳米粒子集合体膜的磁化曲线



D. L. Peng *et al.*, ***J. Mater. Res.***, 23 (2008) 189-197.

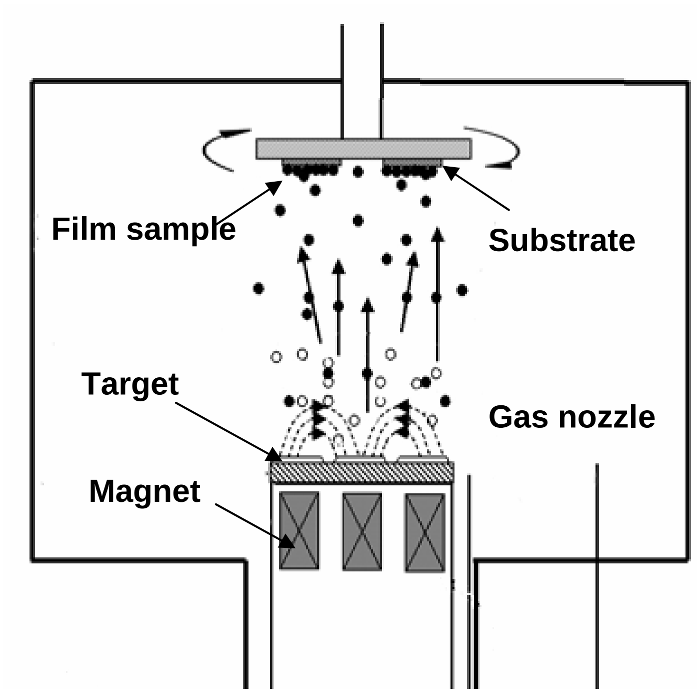
# 纳米粒子组装软磁膜与几种典型软磁材料的特性比较



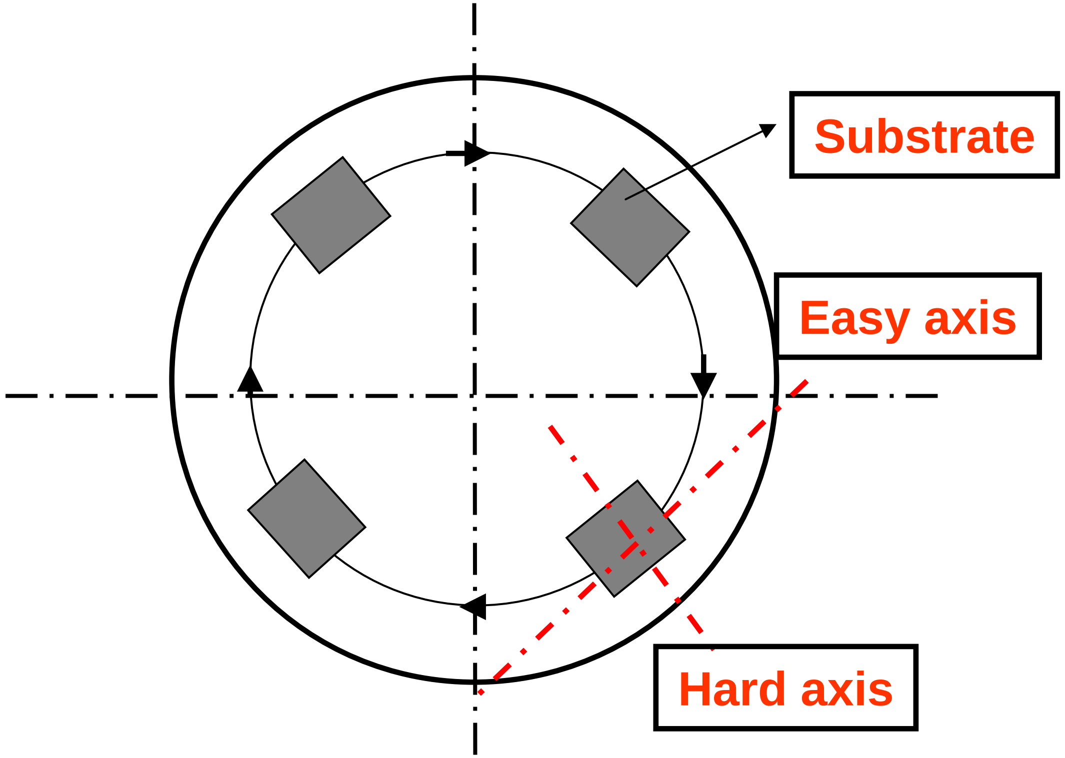
D. L. Peng *et al.*, ***J. Mater. Res.***, 23 (2008) 189-197.

# 传统磁控溅射法制备高频软磁薄膜

磁控溅射原理图



基片旋转俯视图

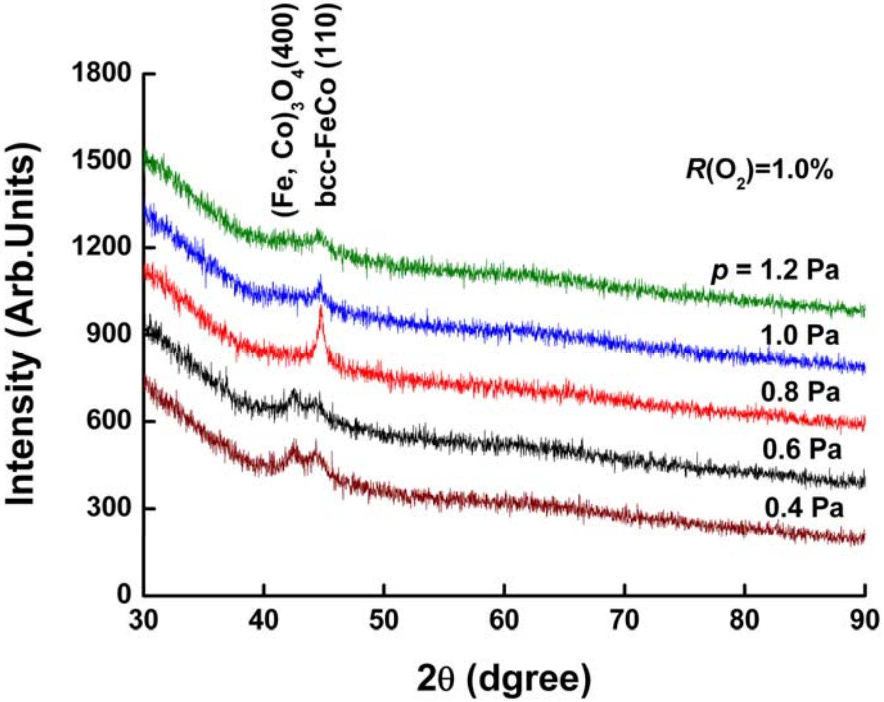


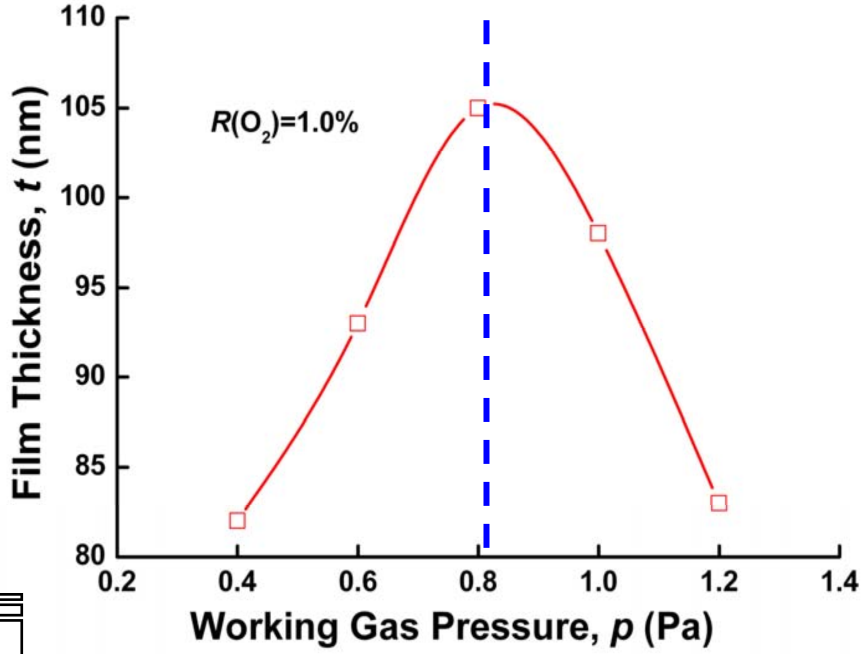
实验材料：$Fe_{65}Co_{35}$合金靶 、$O_2$ 、玻璃片、硅片

研究方法：XRD SEM EDX Four-probe Surface profiler VSM Permeameter

# 结构与性能分析

## $Fe_{65}Co_{35}$-O纳米晶合金薄膜

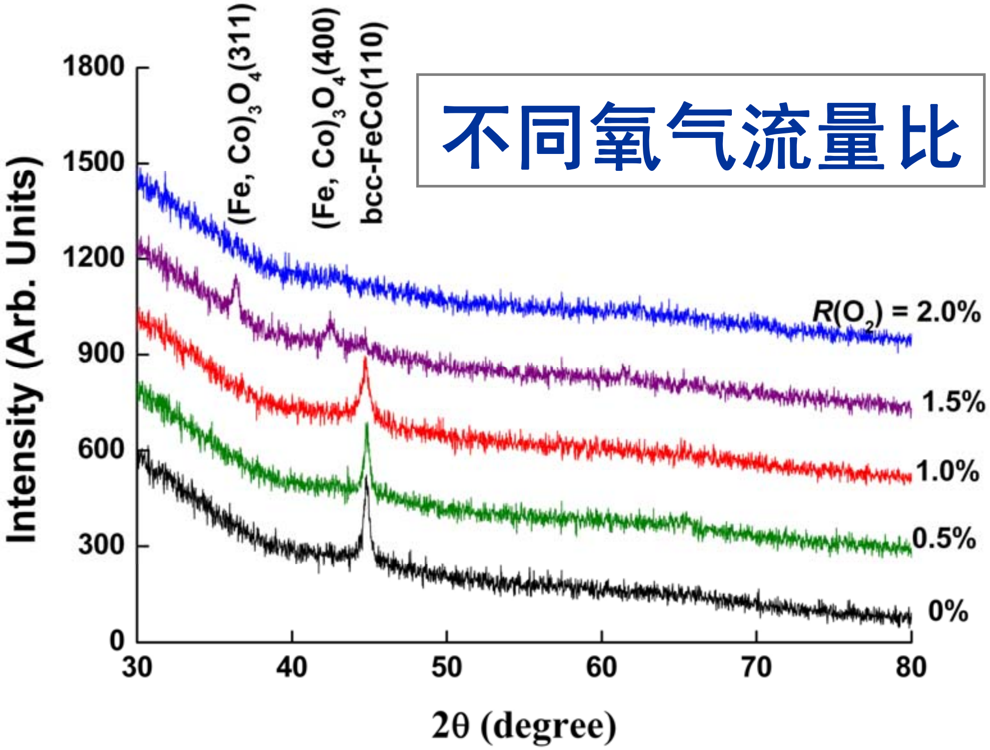


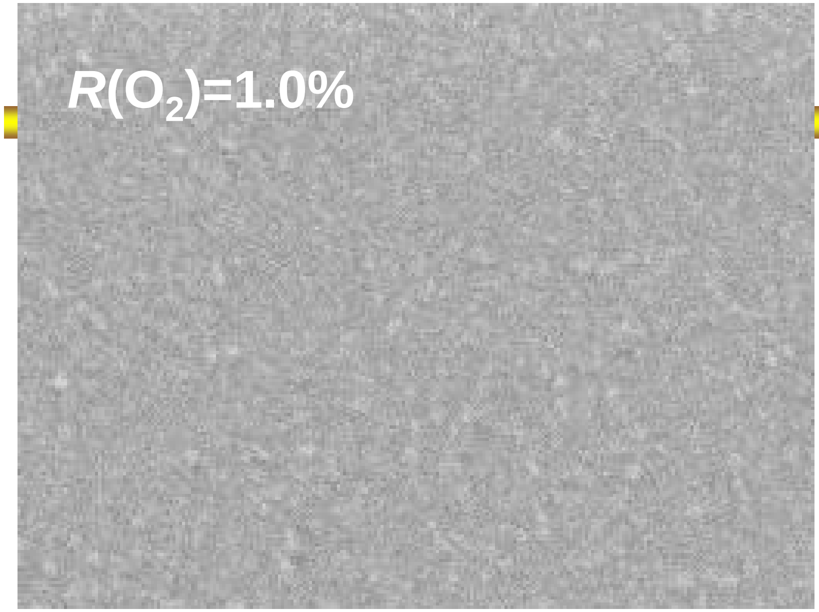


**工作气压 $p$ = 0.8 Pa**

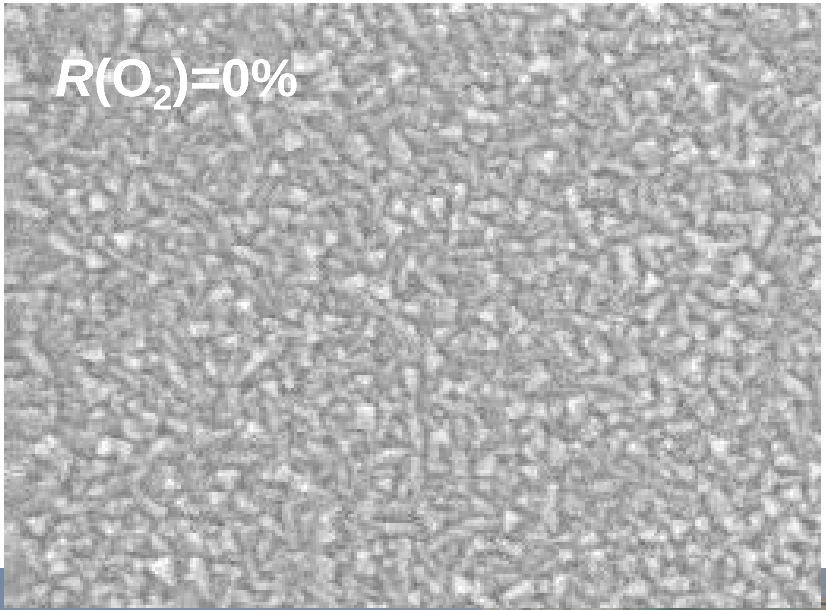
W. Wang *et al.*, ***J. Appl. Phys.***, 106 (2009) 013912

# 不同氧气流量比

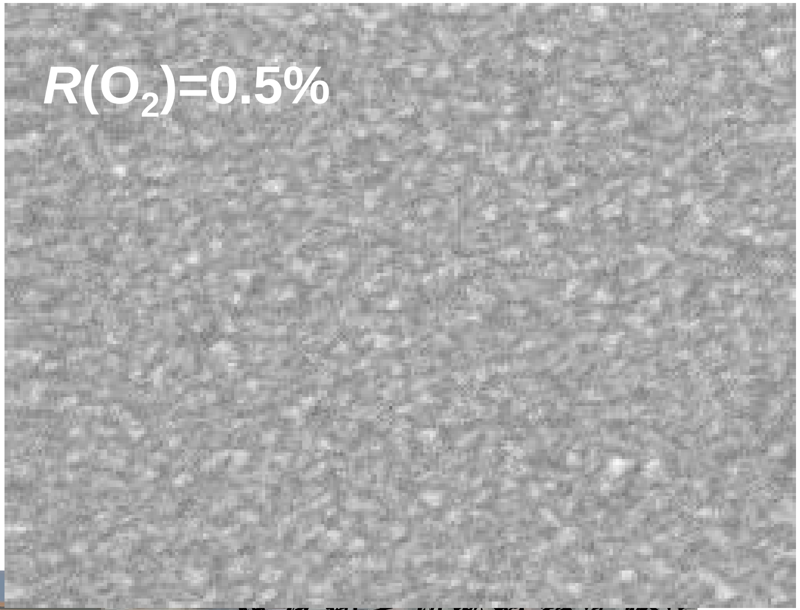




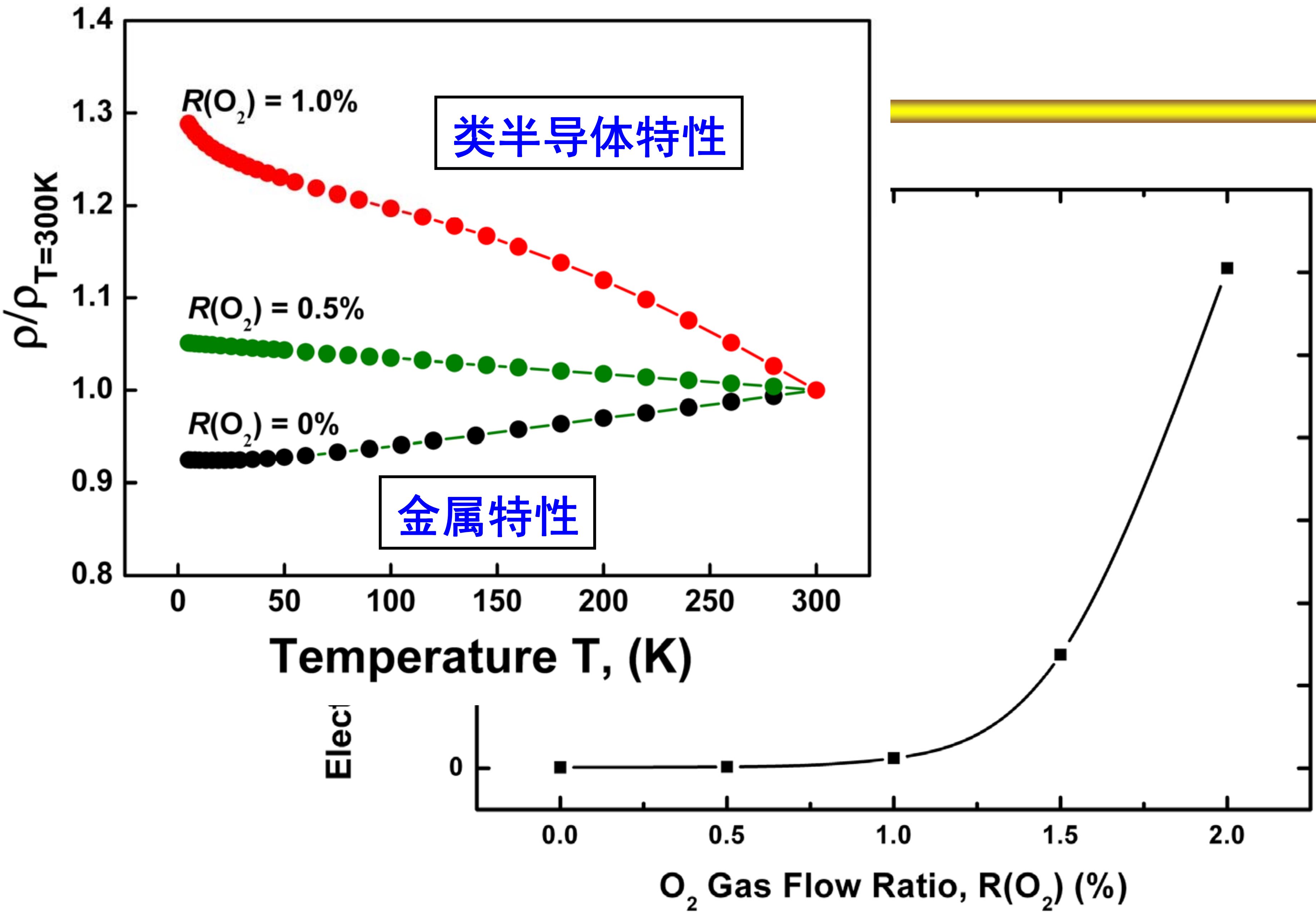
$R(O_2)$=1.0%



$R(O_2)$=0%

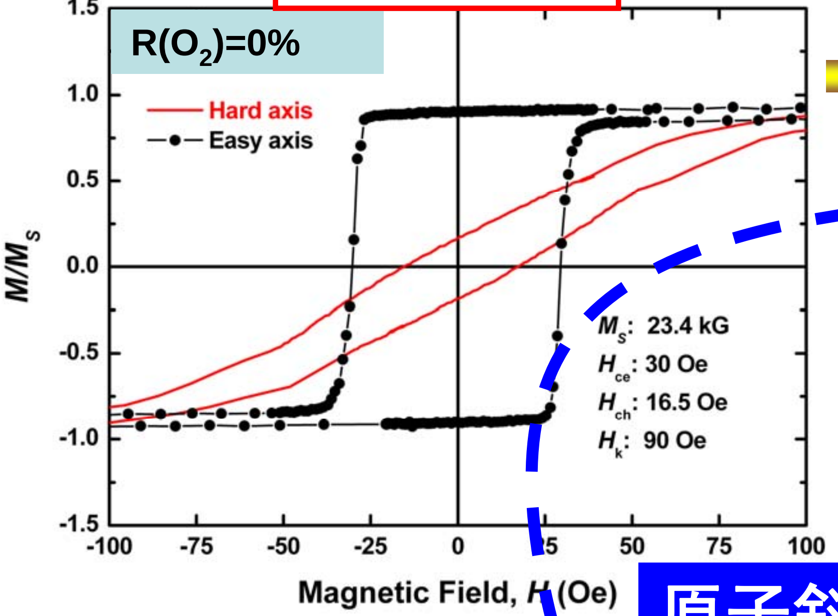


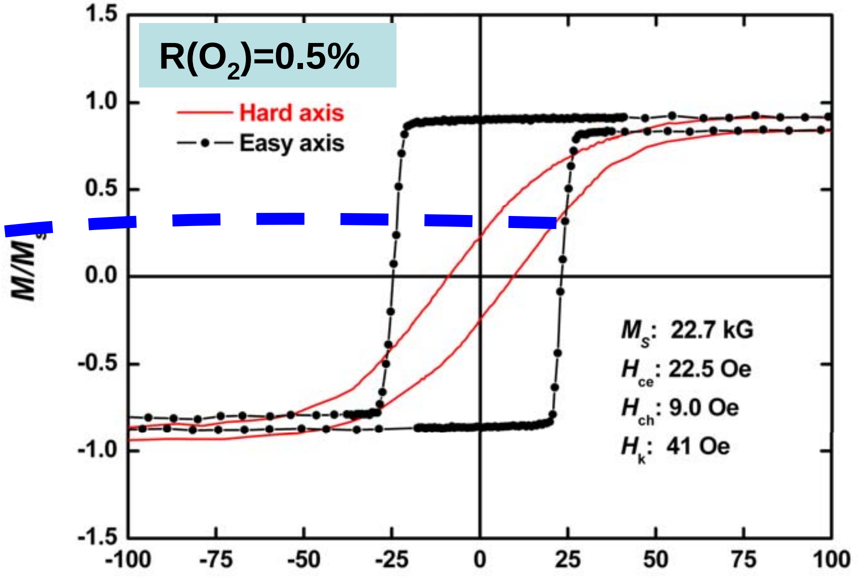
$R(O_2)$=0.5%



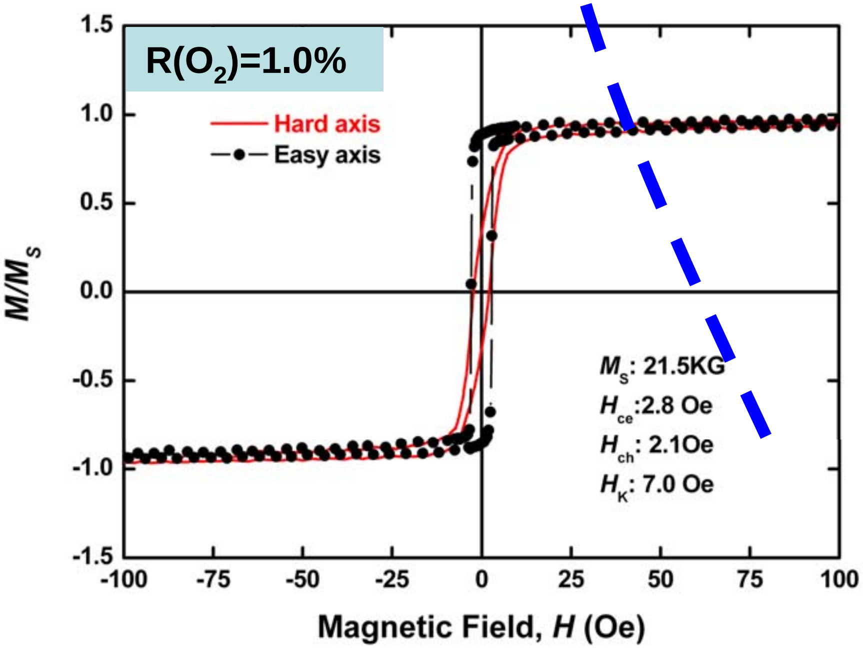
W. Wang *et al.*, ***J. Appl. Phys.***, 106 (2009) 013912

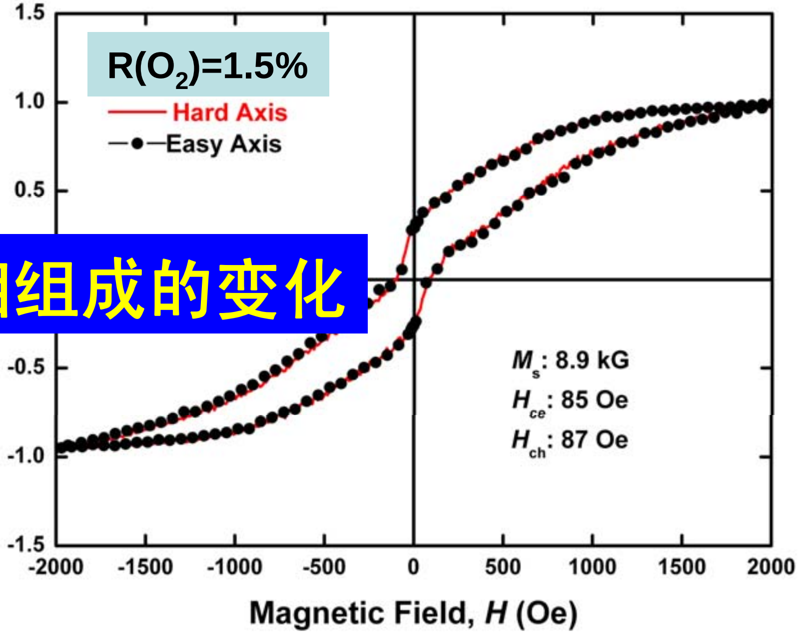
# 磁学特性





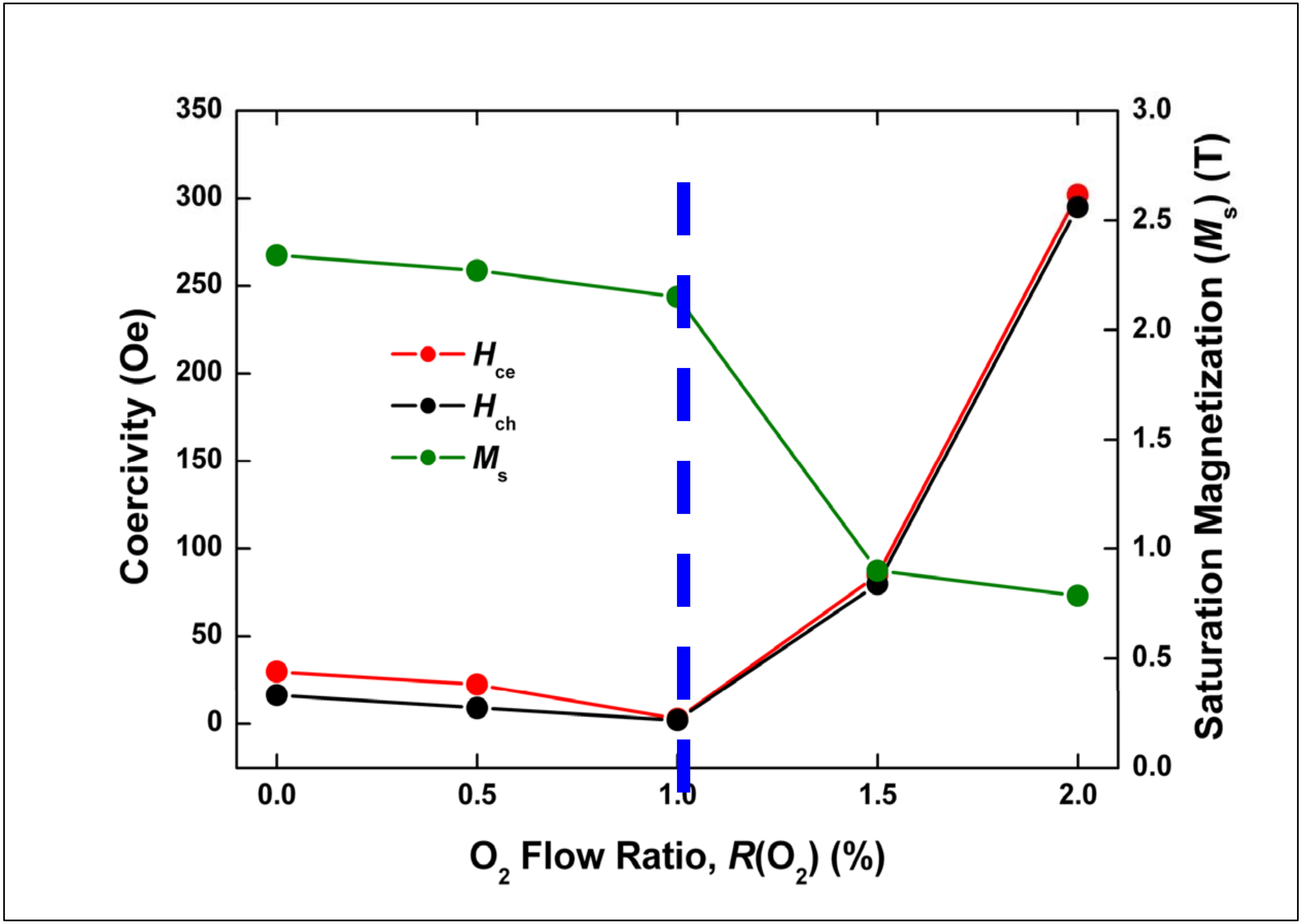
原子斜入射 晶粒沿旋转方向取向生长





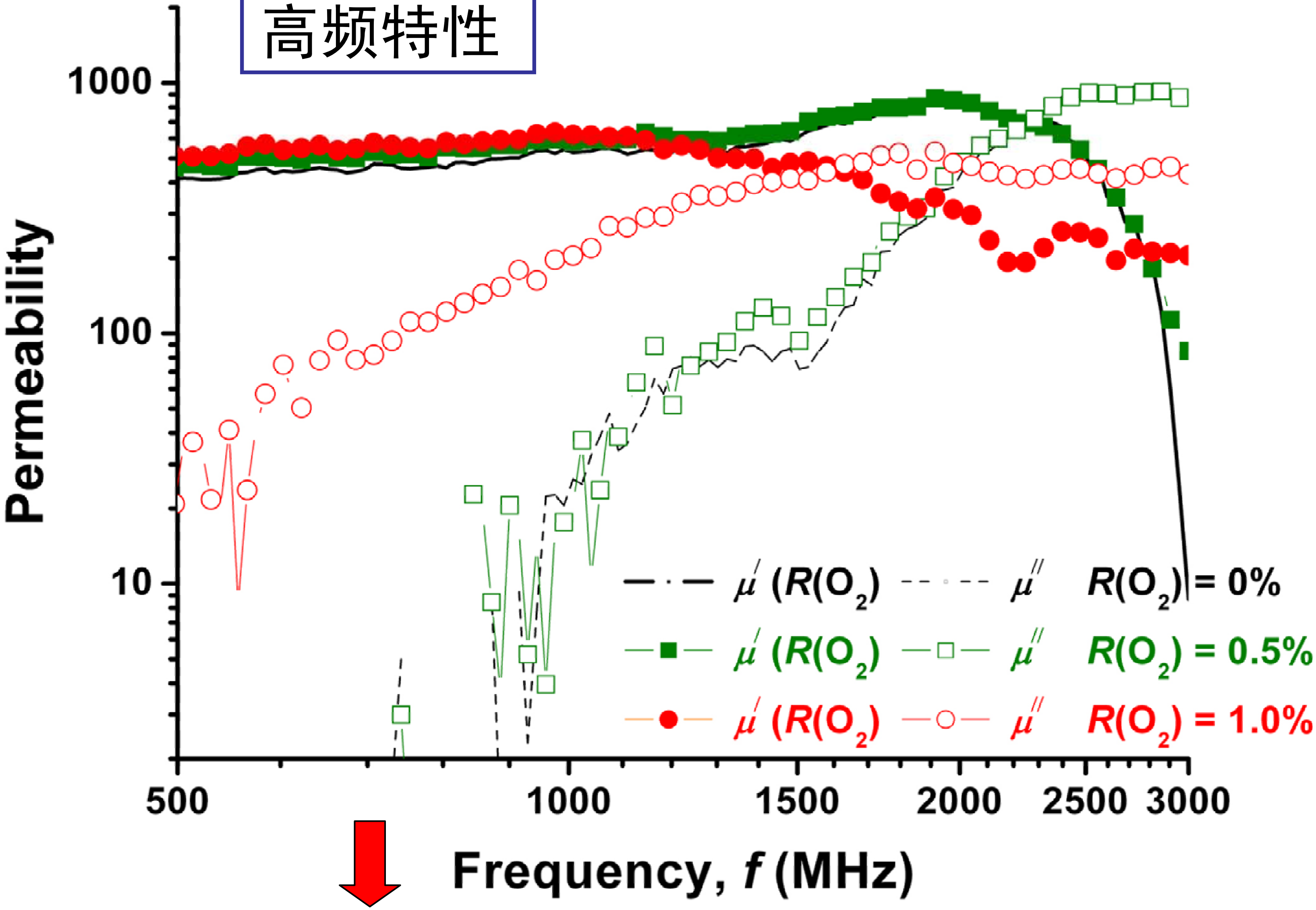
相组成的变化

# 磁学特性



W. Wang *et al.*, ***J. Appl. Phys.***, 106 (2009) 013912

# 高频特性



少量氧的导入有利于高频下磁导率的维持

W. Wang *et al.*, ***J. Appl. Phys.***, 106 (2009) 013912

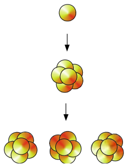
# 总结与展望

- 纳米粒子组装薄膜显示独特的物理性质，具有重要的应用前景。

- 纳米粒子束流沉积方法可将产生的纳米粒子在真空当中直接地沉积或组装到一个基片上或基体里 ，从而可防止纳米粒子的表面污染，有望使得纳米粒子本身所特有的功能性在应用上得到极大程度地发挥 。

- 采用纳米粒子束流沉积可获得可控密度的纳米粒子组装膜，并可实现金属和合金纳米晶软磁性薄膜材料的室温制备；纳米粒子的轻微表面氧化或者纳米尺度多晶界面处的轻微氧化可获得优良的高频磁导率特性。

- 通过利用纳米粒子束流组装和常规的薄膜溅射相结合的新方法，有望获得具有优异性能的纳米结构新材料。



# 研究合作者

- Prof. K. Sumiyama, Nagoya Institute of Technology, Japan
- Prof. T. Hihara, Nagoya Institute of Technology, Japan
- Associate Prof. S. Yamamuro,
  Nagoya Institute of Technology, Japan

- 陈远志 副教授（博士）
- 岳光辉 讲师（博士）
- 王来森 博士研究生
- 温瑞涛 硕士研究生

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