# *Coercivity Mechanism in Hard/Soft Composite Magnets*

# 双相复合磁体的矫顽力机制

**2007年10月，中国，北京、杭州、绵阳**

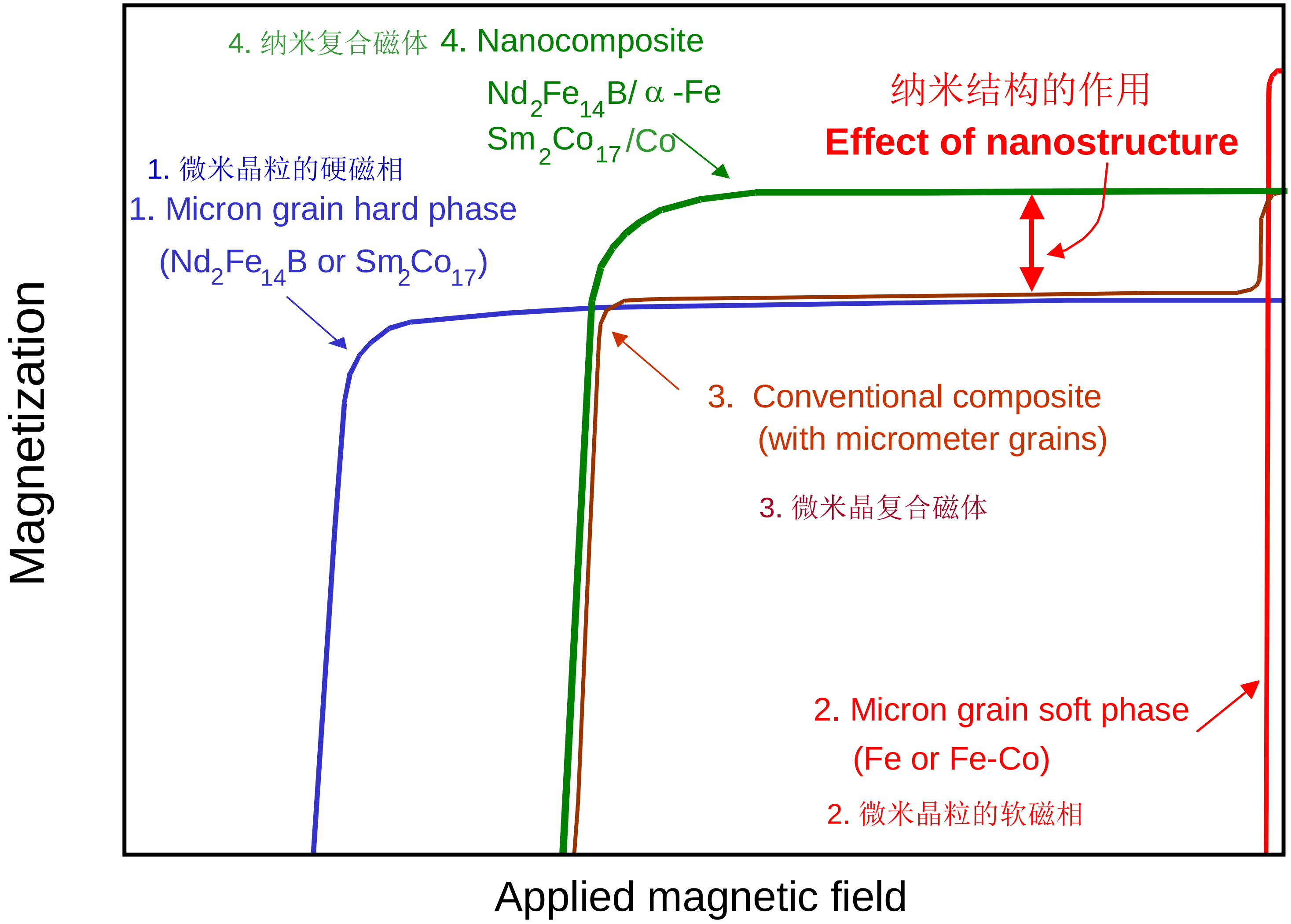
# *Outline*

## 内容提要

- *Concept of composite magnets*
  复合磁体的概念
- *Effect of nanograin structure*
  纳米晶结构的作用
- *Magnetization reversal mechanism*
  反磁化的机制
- *Upper limit size of soft phase*
  软磁相尺寸的上限
- *Future of composite magnets*
  未来的复合磁体

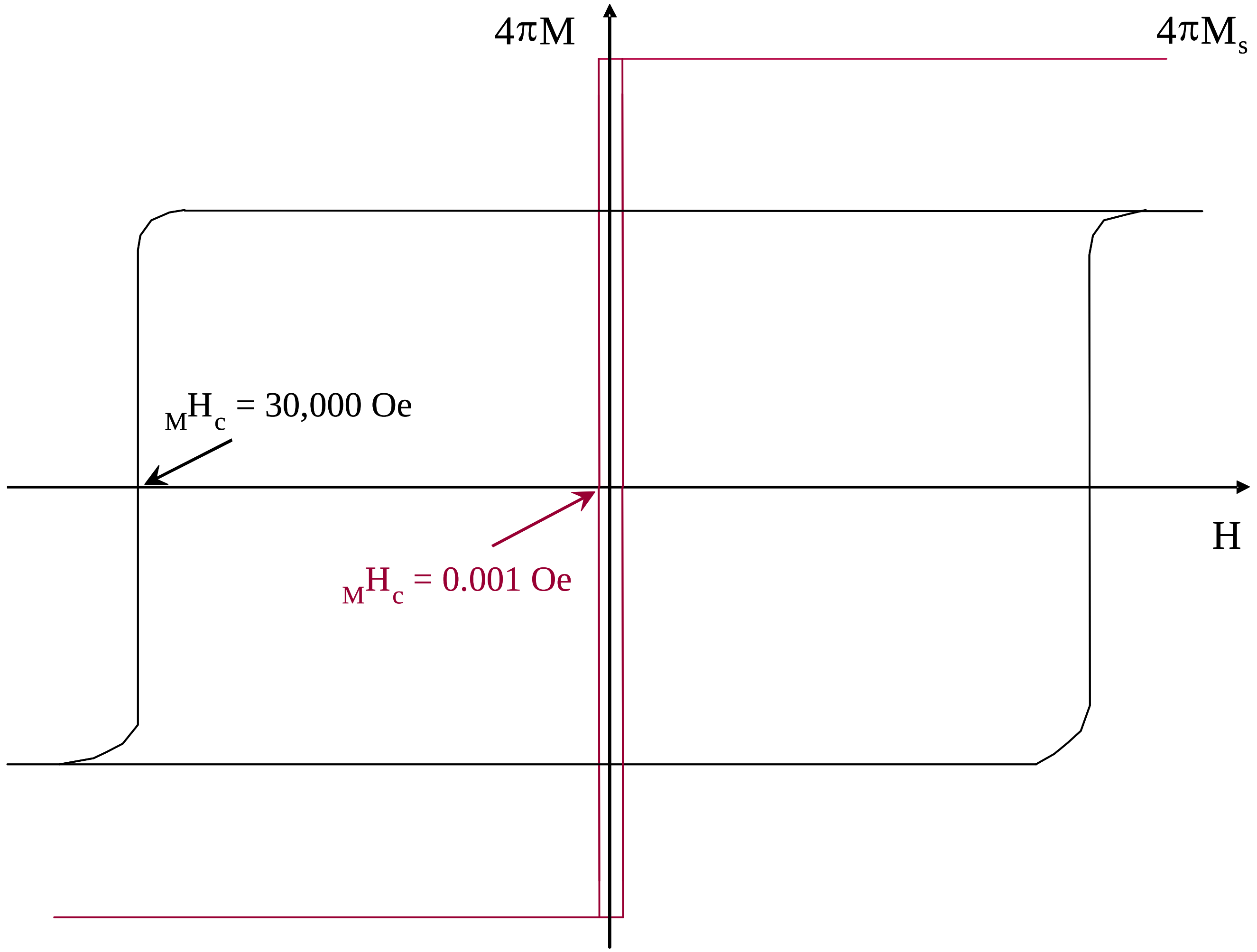
# Effect of Nanostructure

## 纳米结构的作用



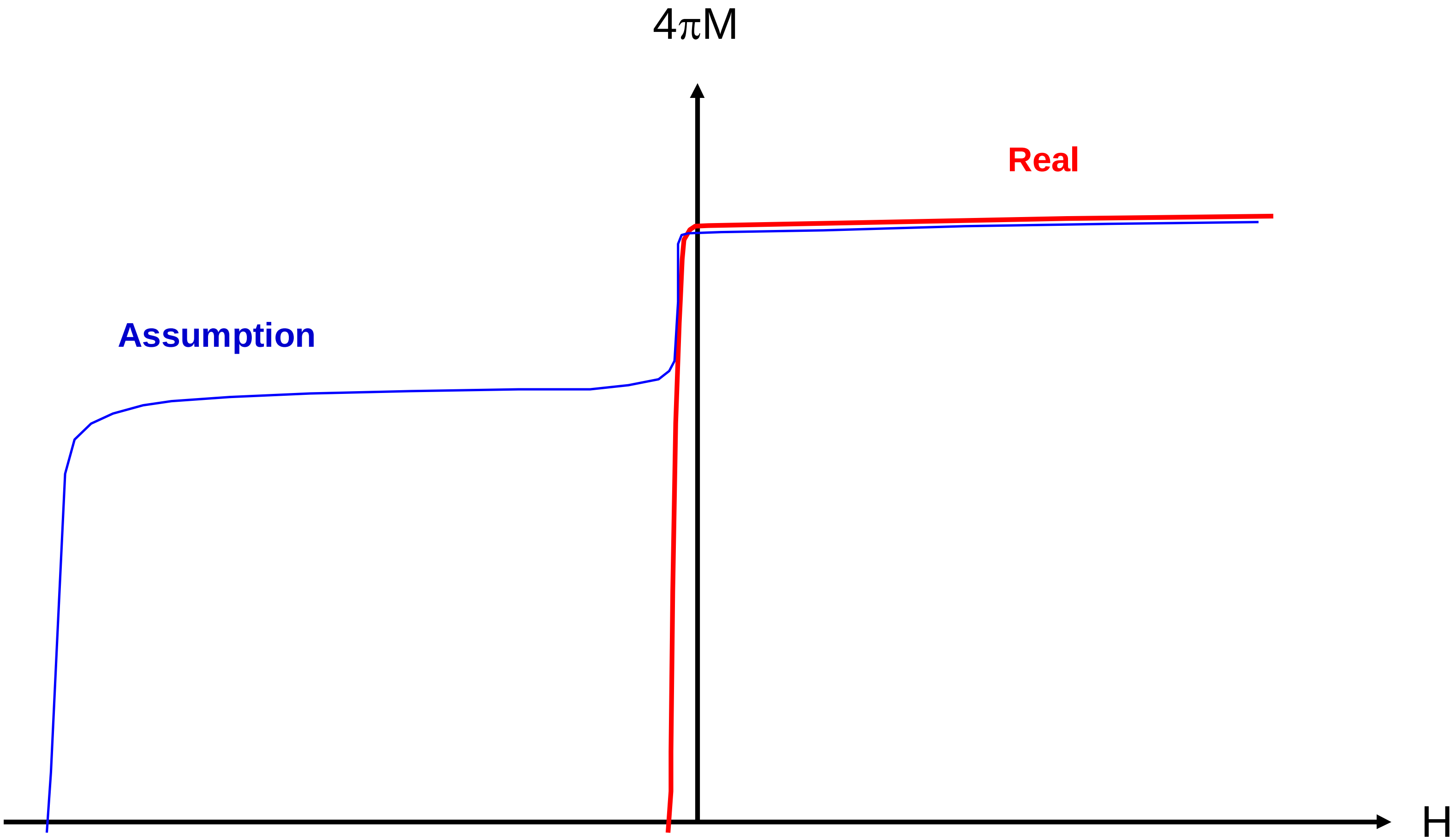
# Concept of Hard/Soft Composite Magnets

软硬双相复合磁体的概念



# Conventional Composite $Nd_2Fe_{14}B/\alpha$-Fe Magnets

微米晶$Nd_2Fe_{14}B/\alpha$-Fe复合磁体



# Coercivity of Nd-Fe-B

Nd-Fe-B磁体的矫顽力

- $Nd_2Fe_{14}B$
  - $4\pi M_s = 16$ kG
  - $H_A = 75$ MGOe
- As a compound or alloy, ${}_MH_c$ of single phased $Nd_2Fe_{14}B$ is very low, ≈ 0 kOe

  纯$Nd_2Fe_{14}B$合金(微米晶粒)的矫顽力很低, 接近于0
- The existence of a minor Nd-rich phase is necessary for coercivity development

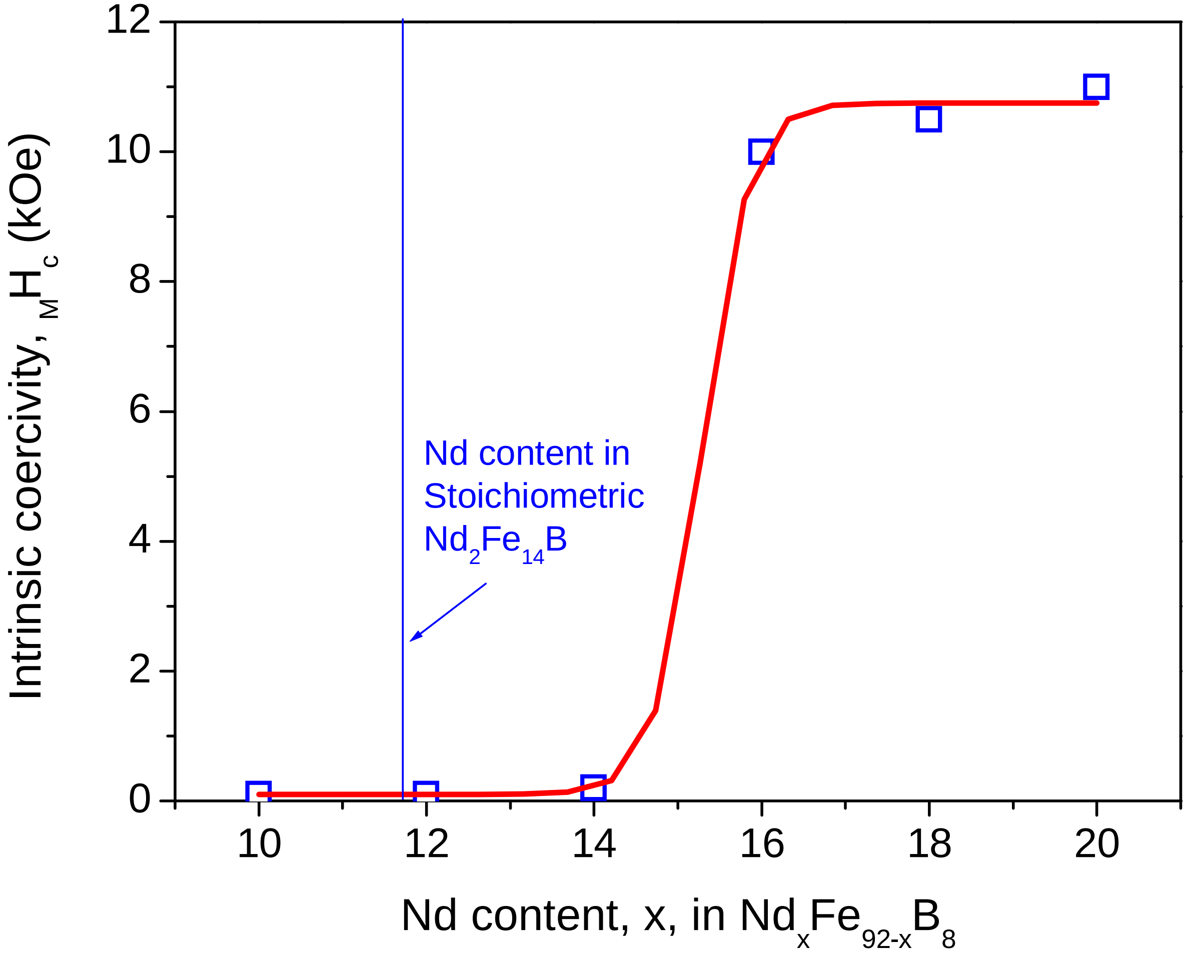
  富Nd相的存在是发展高的矫顽力所必需
- If ${}_MH_c$ of a single phase $Nd_2Fe_{14}B$ is near 0, then ${}_MH_c$ of composite $Nd_2Fe_{14}B/\alpha$-Fe is, of course, near 0 in conventional composites

  既然纯$Nd_2Fe_{14}B$合金的矫顽力接近于0, 那么复合$Nd_2Fe_{14}B/\alpha$-Fe (微米晶粒)的矫顽力自然也接近于0
- In 1988, the Philips group obtained ${}_MH_c = 3$ kOe in **nano**composite $Nd_2Fe_{14}B/Fe_3B$ alloy

  直到1988年, 菲利普才在纳米复合的$Nd_2Fe_{14}B/\alpha$-Fe 中获得3 kOe的矫顽力

# Effect of Nd on Coercivity in Nd-Fe-B Magnets

Nd含量对Nd-Fe-B磁体矫顽力的影响



# Coercivity of $Sm_2Co_{17}$

$Sm_2Co_{17}$的矫顽力

- $Sm_2Co_{17}$ with micron grains

  微米晶粒的$Sm_2Co_{17}$

  - $Sm_2Co_{17}$
    - $K_1 = 3.2x10^7$ erg/cm$^3$
    - $H_A = 65$ kOe
    - $_MH_c < 2$ kOe
  - In order to develop useful coercivity, extra **Sm** and a **Cu** and **Zr** must be added, forming **$Sm(Co_{0.745}Fe_{0.15}Cu_{0.08}Zr_{0.025})_{\sim 7.4}$**

    为了发展矫顽力,必须添加多余的Sm以及Cu和Zr

- 2:17 magnets with nanograins

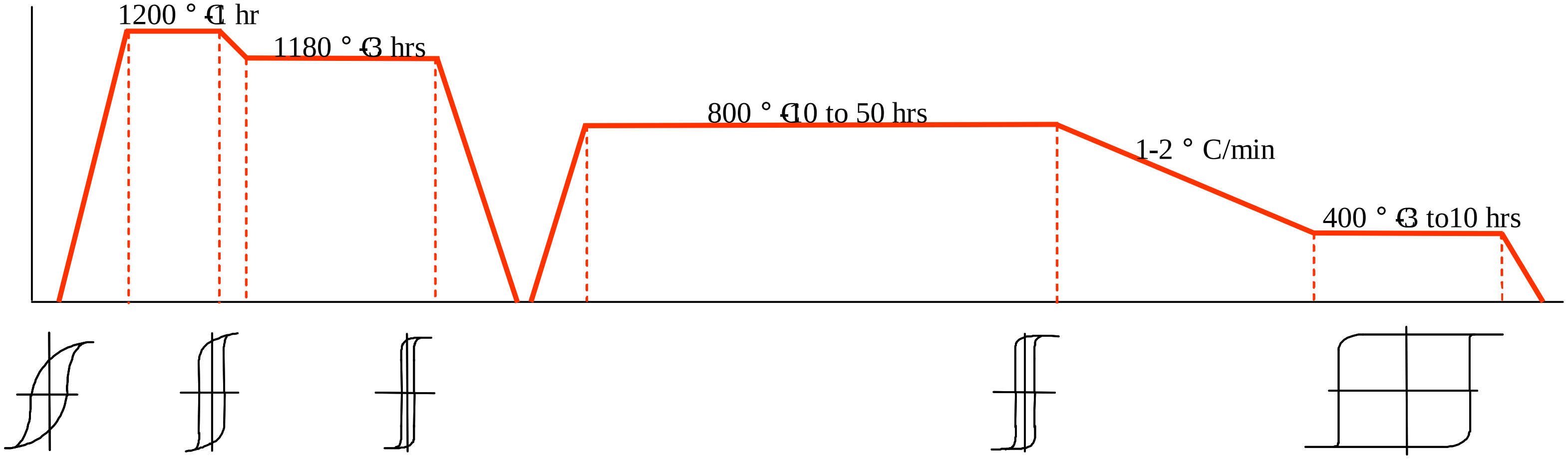
  纳米晶粒2:17磁体

  - J. Wecker et al. 1991, $Sm_2Co_{17}$, 700 ° C-30 m, $_MH_c = 6$ kOe
  - S.K. Chen et al. 1996, $SmCo_{10}$, 750 ° C-20 m, $_MH_c = 4$ kOe
  - U of Dayton, 2002, $Sm_2C0_{17}$, 750 ° C-**1** m, $_MH_c = 15.6$ kOe

# Coercivity Development in Micro- and Nano-Grain $Sm_2Co_{17}$

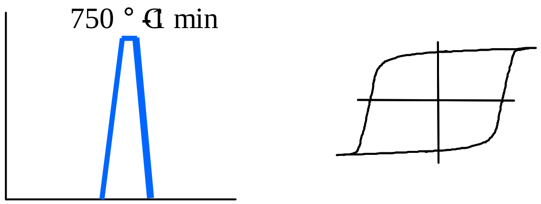
Conventional $Sm_2(Co,Fe,Cu,Zr)_{17}$

微米晶粒2:17

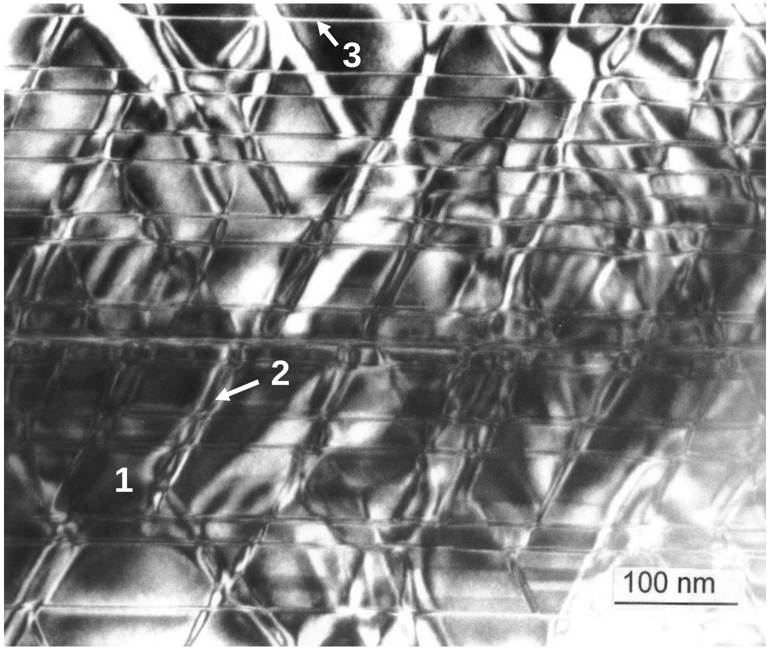


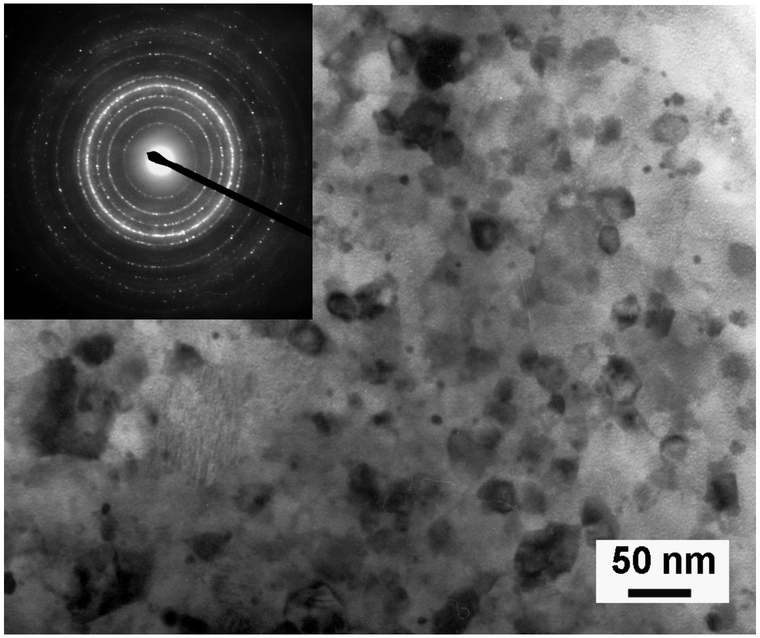
Nanostructured $Sm_2Co_{17}$

纳米晶粒2:17



# TEM Images of Micro- and Nano-grain 2:17 Magnets





$Sm(Co,Fe,Cu,Zr)_{7.1}$
*Sintering: 1200 °C – 1 hr*
*SSHT: 1180 °C – 5 hrs*
*Aging: 800 °C – 50 hrs*
*Slow cooling: 800-400 °C at 1 °C/m*
*Aging: 400 °C-10 hrs*
$_MH_c$ *= 15 kOe*

$Sm_2Co_{17}$
*Anneal: 750 °C - 1 m,*
*MHc = 15.6 kOe*

# *Effect of Nanograin Structure*

## 纳米结构的作用

- *A fundamental change in coercivity mechanism occurs when grain size is reduced from conventional micron size to nanometer range*

  当晶粒尺寸由微米减小的纳米时，矫顽力的机制发生根本性的改变

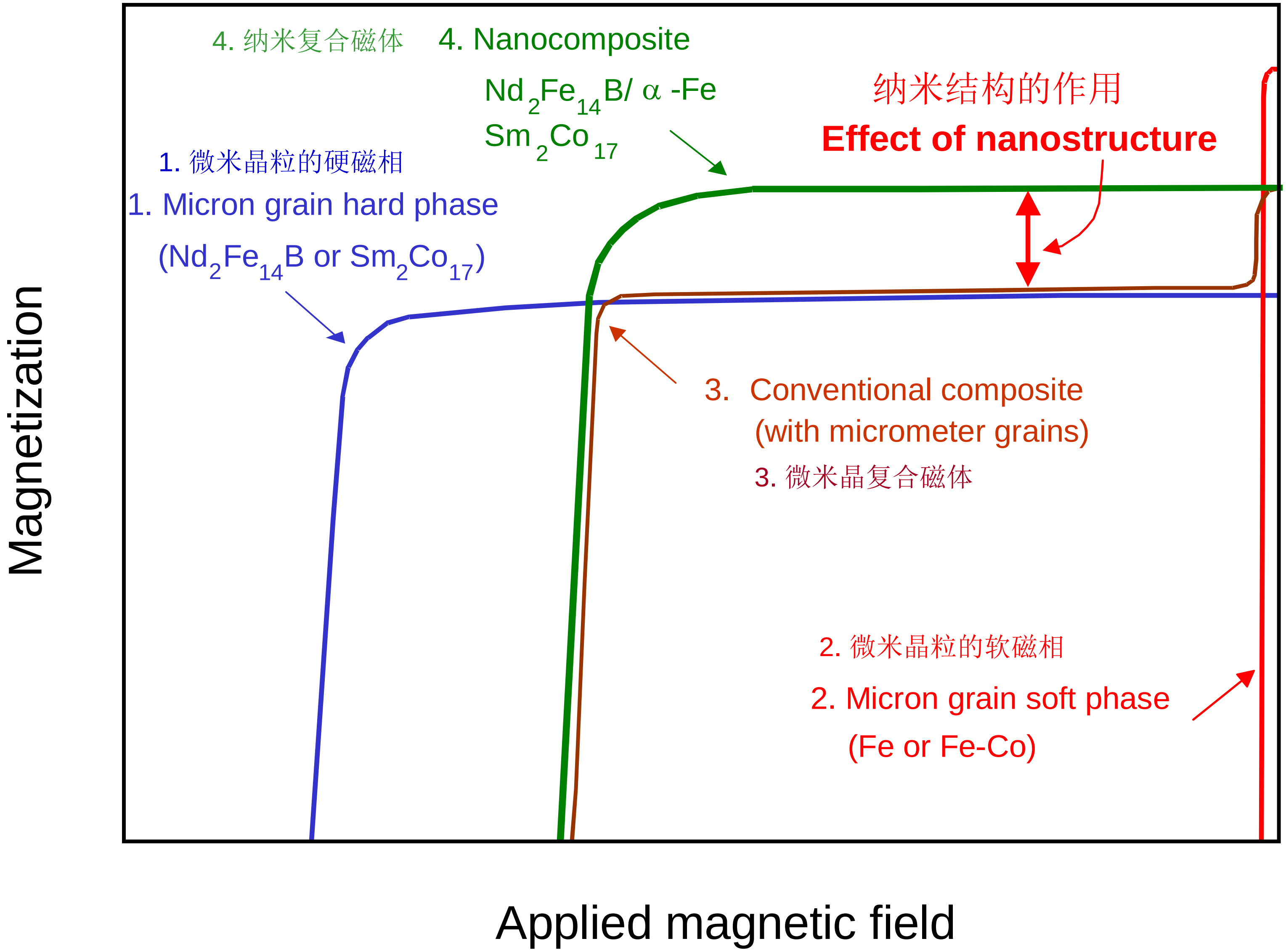
- *High uniaxial magnetocrystalline anisotropy is only a* ***necessary*** *condition for high coercivity, not the* ***sufficient*** *condition in micrograin materials*

  高的磁晶各向异性场在微米晶粒材料中只是获得高矫顽力的必要条件，而不是充分条件

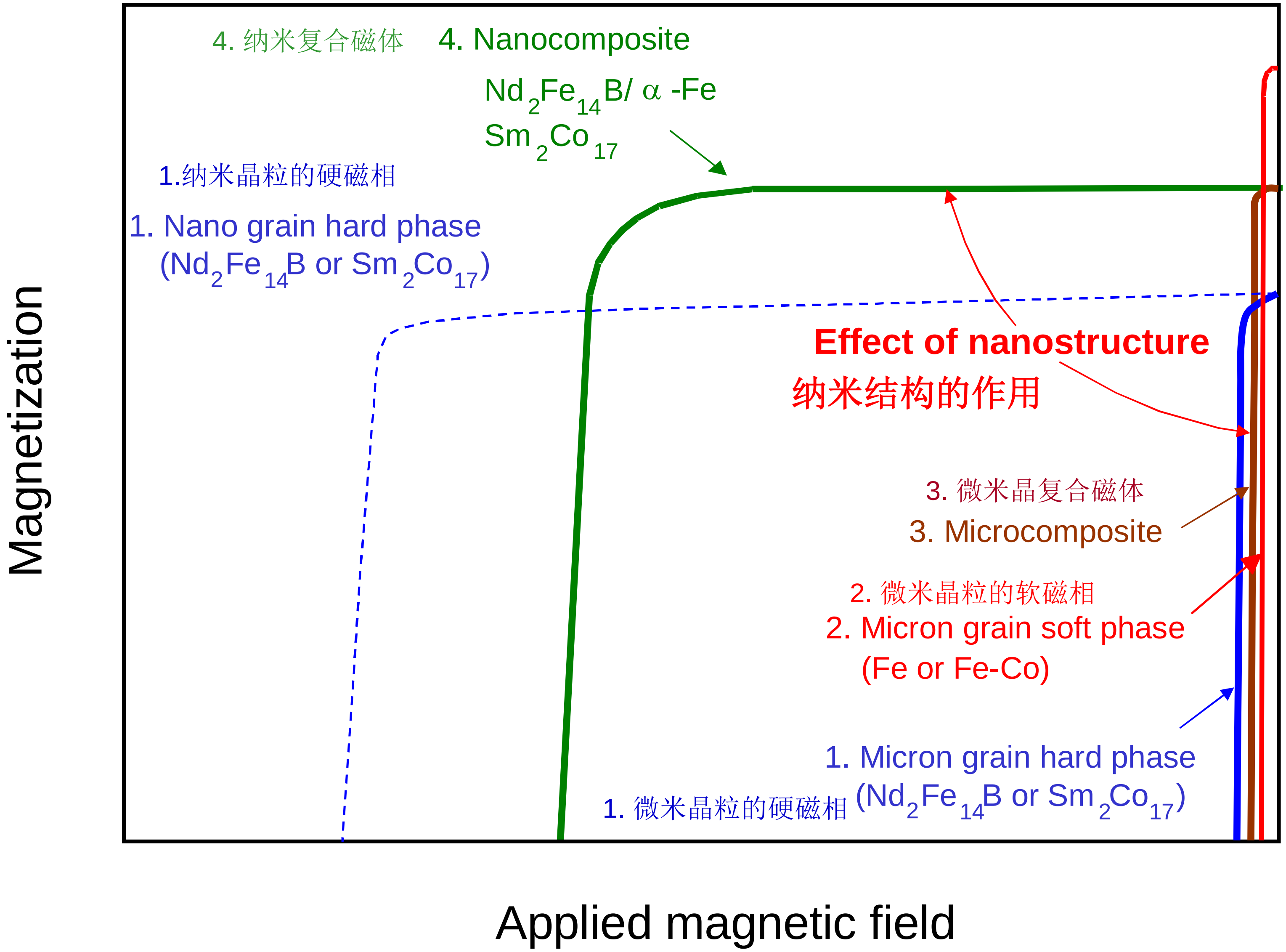
- *High uniaxial magnetocrystalline anisotropy is not only a* ***necessary*** *condition, but also the* ***sufficient*** *condition for high coercivity in nanograin materials*

  高的磁晶各向异性场不但是获得高矫顽力的必要条件，在纳米晶粒材料中，它也成为充分条件

# *Effect of Nanostructure – Old Model*



# *Effect of Nanostructure – New Model*



# *General Accepted Interpretation*

纳米结构作用的流行的解释

- ❑ *Interface exchange coupling exists only in nanostructured materials and it does not exist in conventional micrograin materials*

  界面交换耦合作用只存在于纳米结构材料中，不存在于微米结构的传统材料中

- ❑ *The hard phase, such as $Nd_2Fe_{14}B$ or $Sm_2Co_{17}$, has high coercivity*

  硬磁相，如$Nd_2Fe_{14}B$和$Sm_2Co_{17}$等，都具有高的矫顽力

- ❑ *The microcomposite, such as $Nd_2Fe_{14}B/\alpha$-Fe or $Sm_2Co_{17}$/Co, has kinked demagnetization curves and the high coercivity represents the coercivity of the hard phase*

  微米复合磁体，如$Nd_2Fe_{14}B/\alpha$-Fe和$Sm_2Co_{17}$/Co，呈双相特征的退磁曲线．　高的矫顽力是其中硬磁相矫顽力的表现

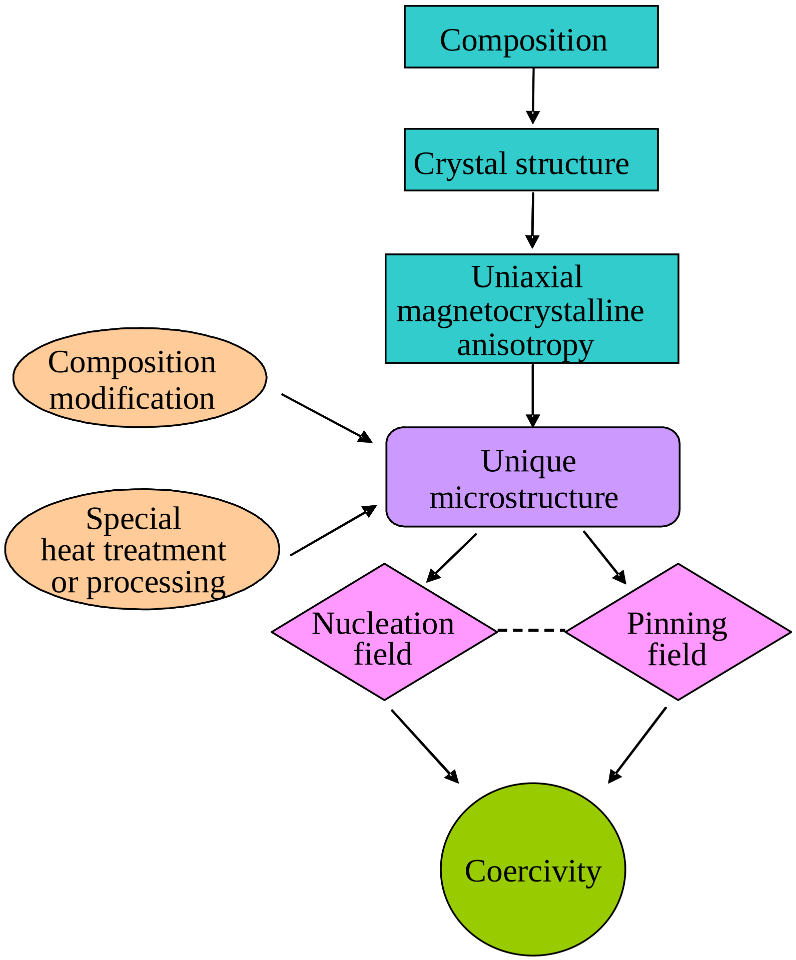
# *New Concept of interface exchange coupling*

- *Interface exchange coupling is a universal phenomenon*
- *In magnetic materials with nanograins, the formation of multiple magnetic domains in a grain is no longer energetically favorable*
- *The magnetization reversal in nanograin magnetic materials is not likely carried out by nucleation of reversed magnetic domains or domain wall motion. Rather, it is carried out by incoherent rotation of magnetization*
- *Therefore, in nanograin magnetic materials there is no longer a need to create a specific microstructure to prevent the formation of reversed magnetic domains or to restrict domain wall motion.*
- *High uniaxial magnetocrystalline anisotropy is not only a necessary condition for high coercivity, as it is in magnetic materials with micrograins, it is also the sufficient condition for high coercivity in magnetic materials with nanograins.*
- *A direct connection between coercivity and magnetocrystalline anisotropy is established in magnetic materials with nanograin structure.*
- *Consequently, high coercivity should be readily obtained for any magnetic materials that have high uniaxial anisotropy, provided that the materials possess nanograin structure.*

# 界面交换耦合作用的新概念

- 界面交换耦合作用是一个普遍现象。它存在于所有多晶磁性材料中，而与晶粒大小并无关系
- 在纳米晶粒磁性材料中，在晶粒内部形成多畴结构，导致整体自由能升高
- 纳米磁性材料的反磁化不是以形成反磁化核或者畴壁移动的方式进行的，而是通过磁化矢量的非一致转动进行的
- 因此，在纳米材料中，就没有必要造成某种特殊的组织结构，防止反磁化核的形成或者阻碍畴壁的迁移
- 高的单轴磁晶各向异性不仅是获得高矫顽力的必要条件，如同在微米晶材料中一样，而且在纳米晶材料中，它也成为获得高矫顽力的充分条件
- 这样，在纳米晶材料中，就建立起矫顽力与磁晶各向异性的直接联系
- 因之，在任何具有高的单轴磁晶各向异性的纳米晶材料中，都可以容易地获得高的内禀矫顽力

# Coercivity Mechanisms in Rare Earth Magnets



Composition

Crystal structure

Uniaxial magnetocrystalline anisotropy

Composition modification

Special heat treatment or processing

Unique microstructure

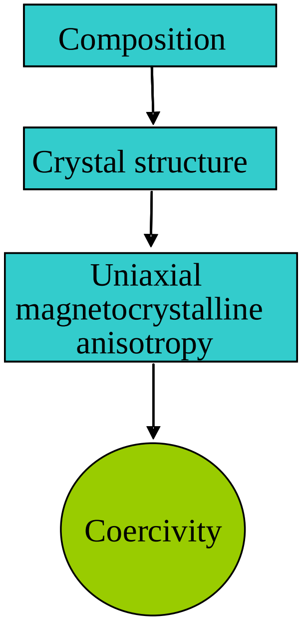
Nucleation field

Pinning field

Coercivity

a. Rare earth magnets with microstructure.

微米晶稀土磁体



Composition

Crystal structure

Uniaxial magnetocrystalline anisotropy

Coercivity

b. Rare earth magnets with nanostructure

纳米晶稀土磁体

# *Exchange Coupling and Magnetization Reversal – Current Models*

- *The exchange energy density can be written as*

  $E_A = A\ (d\psi\ /\ dx)^2$

  *where A is a constant of the order $10^{-11}$ J/m at room temperature, $\psi$ is the angle*
  *between $M_s$ and c axis.*
- *The exchange length, $l_{ex}$, is a critical distance that the hysteresis loop of two-phase magnets consisting of hard and soft phase is a superposition of the two individual loops if the grain size is much larger than $l_{ex}$, and*

  $l_{ex} =$ .
- *The $l_{ex}$ values for Fe, Co, Ni, $SmCo_5$, and $Nd_2Fe_{14}B$ are 1.5, 2.0, 3.4, 4.9, and 1.9 nm, respectively.*
- *Magnetization reversal in nanocomposite two-phase magnets is carried out by nucleation of reversed magnetic domains and/or domain wall motion, the same as in conventional one-phase magnets.*
- *The hard/soft interface exchange coupling exists only when the grain size, especially the grain size of the soft phase, is reduced to nanometer range. The best size of the soft phase is around 10 nm and the upper limit of it is about 20 nm.*

# 交换耦合与反磁化的现有模型

- 交换能密度可以表示为

  $E_A = A\,(d\psi / dx)^2$

  $A$ 是常数，在室温下为$10^{-11}$的数量级; $\psi$ 是$M_s$ 与 $c$ 轴之间的夹角

- 交换长度, $l_{ex,}$ 是一特征长度. 如果晶粒尺寸大于$l_{ex}$, 则退磁曲线呈双相叠加. $L_{ex}$ 的大小为

  $l_{ex} = \sqrt{\dfrac{A}{M_s^2}}$ .

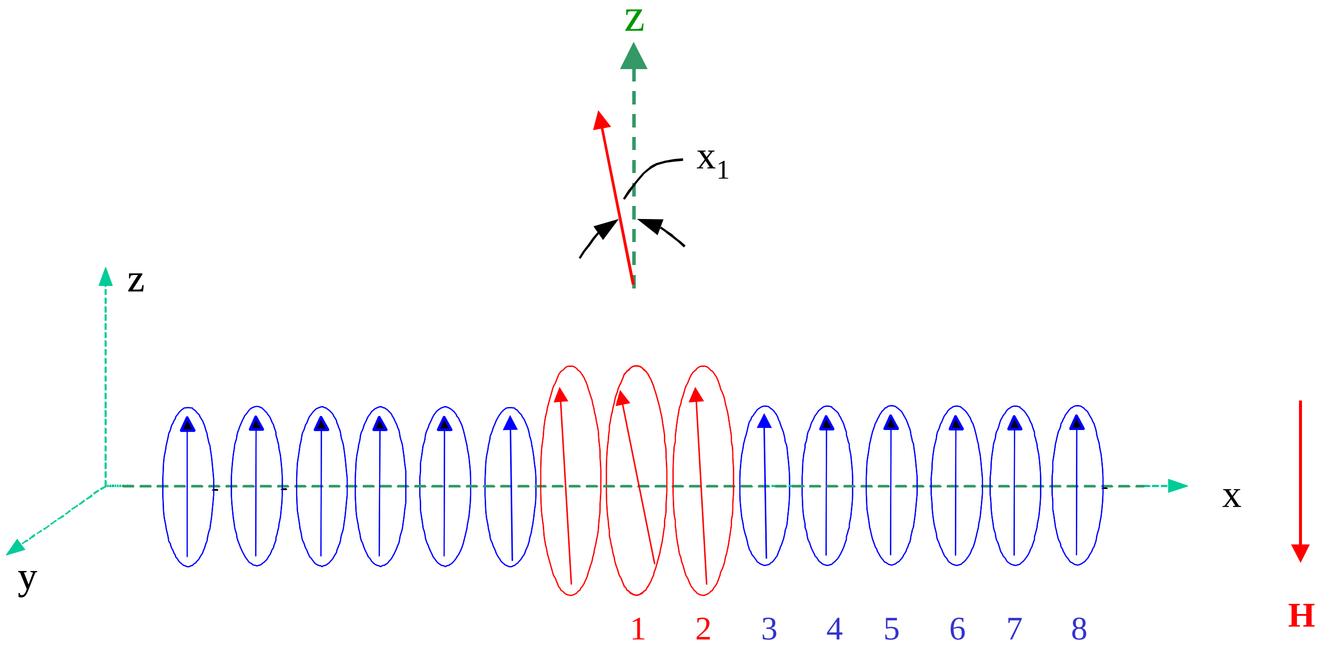
- $Fe, Co, Ni, SmCo_5$, 及 $Nd_2Fe_{14}B$ 的 $l_{ex}$ 值分别为 *1.5, 2.0, 3.4, 4.9, and 1.9 nm,*

- 双相纳米复合磁体的反磁化过程是通过反磁化核的形成以及畴壁移动来进行的, 如同在传统微米晶磁体中一样

- 界面交换耦合只有当晶粒尺寸减小到纳米数量级时才存在. 软磁相的最佳尺寸约为10纳米, 其上限约为20 – 30 纳米

# *Demagnetization of a one-dimensional composite magnet*

## 一维复合磁体的反磁化



- $E_{st} = -M_s H \cos(180° - x_1)$ *(Magneto-static energy)* 静磁能
- $E_a = K_1 \sin^2 x_1$ *(Magneto-crystalline anisotropy energy)* 磁晶各向异性能
- $E_{ex} = -A_{ex} S_1 S_2 \cos(x_1 - x_2)$ *(Exchange energy between moments 1 and 2)*

1 与 2 两相邻原子磁矩之间的交换能

# Energies Involved for Each Magnetic Moment

## 每一磁矩所涉及的能量

- $E_1^s = K_1^s \sin^2 x_1 - M_s^s H \cos (180 - x_1) - 2 A_s S_1 S_2 \cos (x_1 - x_2) ]$
- $E_2^s = 2 [ K_1^s \sin^2 x_2 - M_s^s H \cos (180 - x_2) - A_s S_1 S_2 \cos (x_1 - x_2) - A_s^h S_2 S^3 \cos (x_2 - x_3) ]$
- $E_3^h = 2 [ K_1^h \sin^2 x_3 - M_s^h H \cos (180 - x_3) - A_s^h S_2 S_3 \cos (x_2 - x_3) - A_h S_3 S_4 \cos (x_3 - x_4) ]$

………….

- $E_8^h = 2 [ K_1^h \sin^2 x_8 - M_s^h H \cos (180 - x_8) - A_h S_7 S_8 \cos (x_7 - x_8)]$

# System Minimum Energy Condition

系统最小能量的条件

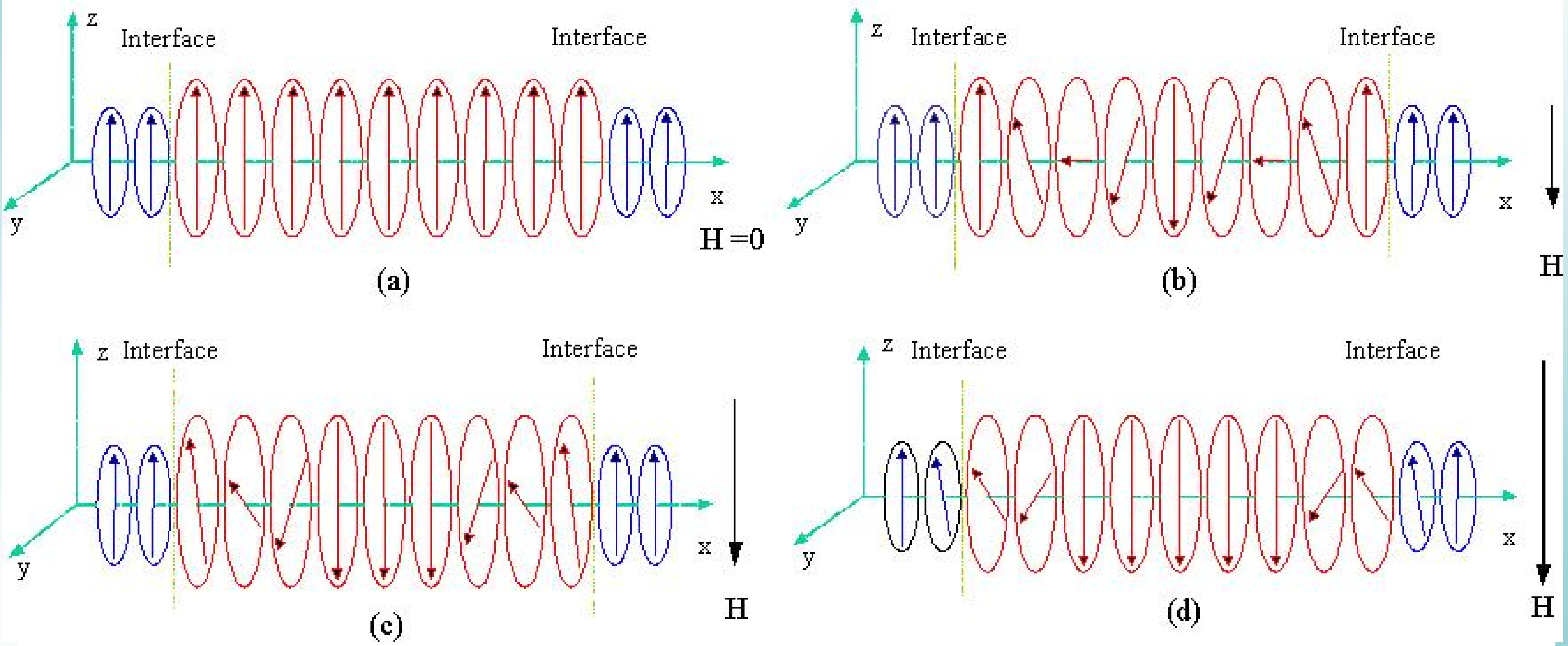
- $d\Sigma E / dx = 0$
- $d^2\Sigma E / dx^2 > 0$

# Magnetization Reversal

## 反磁化过程

→ Magnetization in soft phase

→ Magnetization in hard phase



# Magnetization Reversal

- ❑ ***Magnetization reversal is carried out through rotation of magnetization, rather than nucleation of reversed domains of domain wall motion***
- ❑ ***Exchange coupling at the hard/soft interface makes the rotation incoherent***
- ❑ ***The middle part of a soft grain is a weakest place for demagnetization resistance***
- ❑ ***Reducing the grain size of the soft phase can effectively increase coercivity and improve squareness of demagnetization curve***
- ❑ ***Interface exchange coupling is a universal phenomenon. It exists in all polycrystalline ferromagnetic materials, including materials having micron-sized grains. However, only when the grain size is reduced to nanometer range, the effect of the exchange coupling can be observed***

# 反磁化过程

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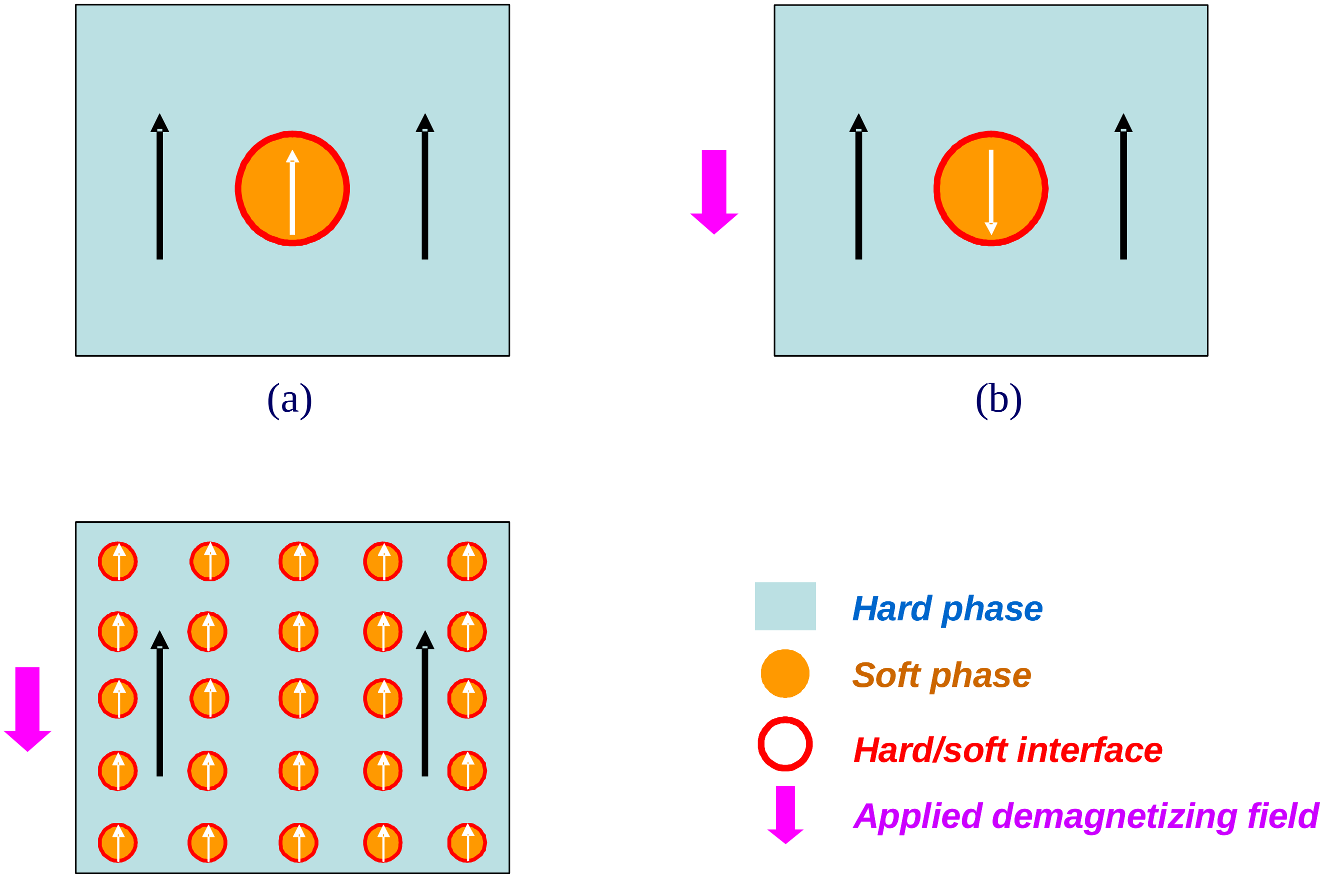
# Effect of Size of Soft Phase

## 软磁相尺寸的作用



(a)

(b)

(c)

▨ Hard phase

● Soft phase

○ Hard/soft interface

⬇ Applied demagnetizing field

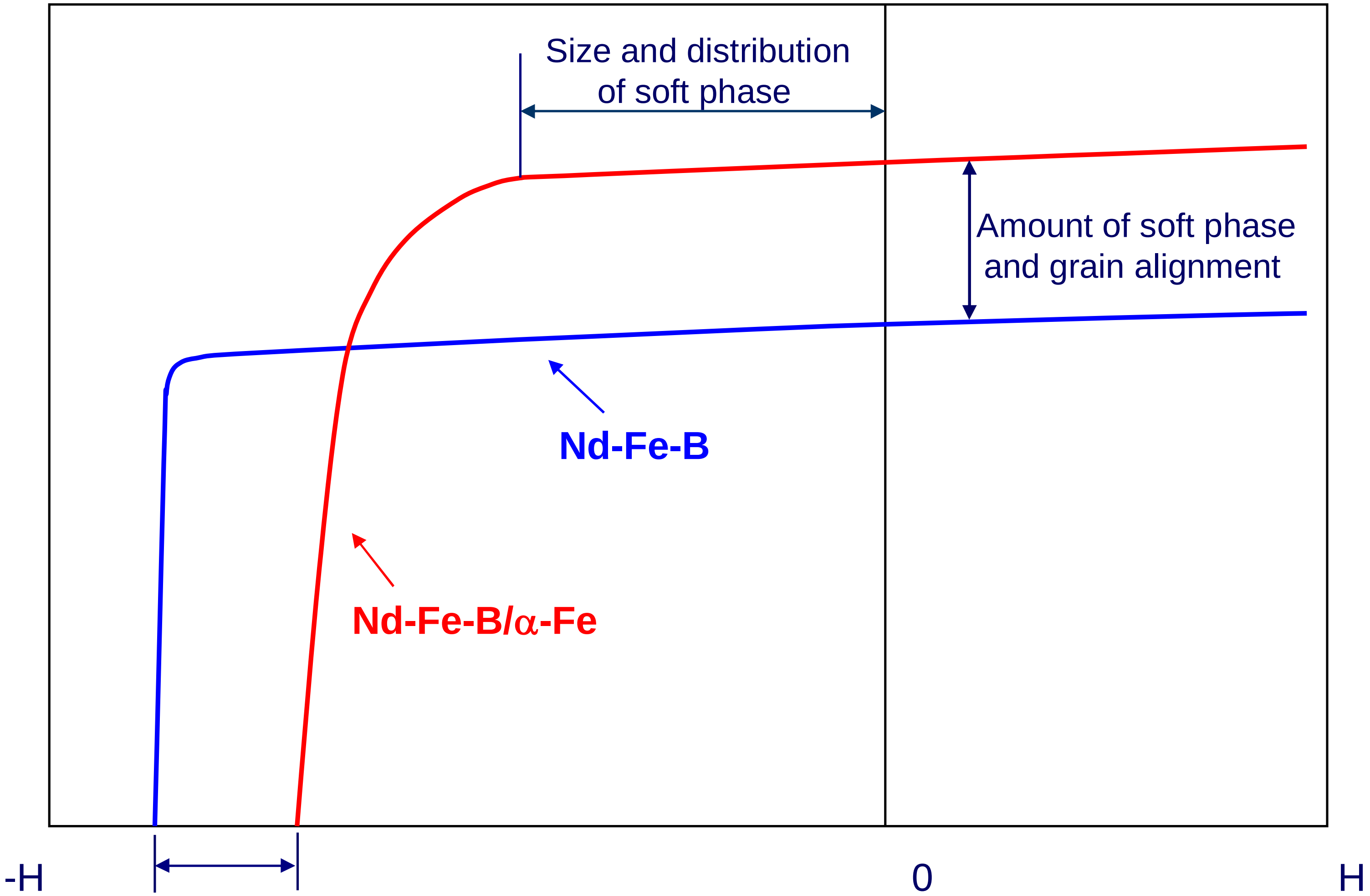
- ❑ $(4\pi M_s)_{comp} = (4\pi M_s)_{hard}\,(1 - v_{soft}) + (4\pi M_s)_{soft}\,v_{soft}$
- ❑ $({}_M H_c)_{comp} = k\,(1 - 1/\rho)\,({}_M H_c)_{hard}$
- ❑ $(H_k / {}_M H_c)_{comp} = k\,(1 - 1/\rho)\,(H_k / {}_M H_c)_{hard}$

$v_{soft}$ is the volume fraction of the soft phase

$\rho = (S / V)_{soft}$, and S and V are the surface area and volume of the soft phase, respectively. $\rho$ will be doubled when the diameter is reduced to one-half while maintaining the original volume.

k is a constant related to $v_{soft}$ and $k \leq 1$.

# Effect of Soft Phase on Demagnetization Curve of a Composite Magnet



1. Size and distribution of soft phase
2. Amount of soft phase

- *Establishment of a direct connection of coercivity and magnetocrystalline anisotropy*
- *A big step forward toward materials design concept*
- *Significant impact to materials R&D*
  - *Improve current magnetic materials*
  - *search for new magnetic materials*

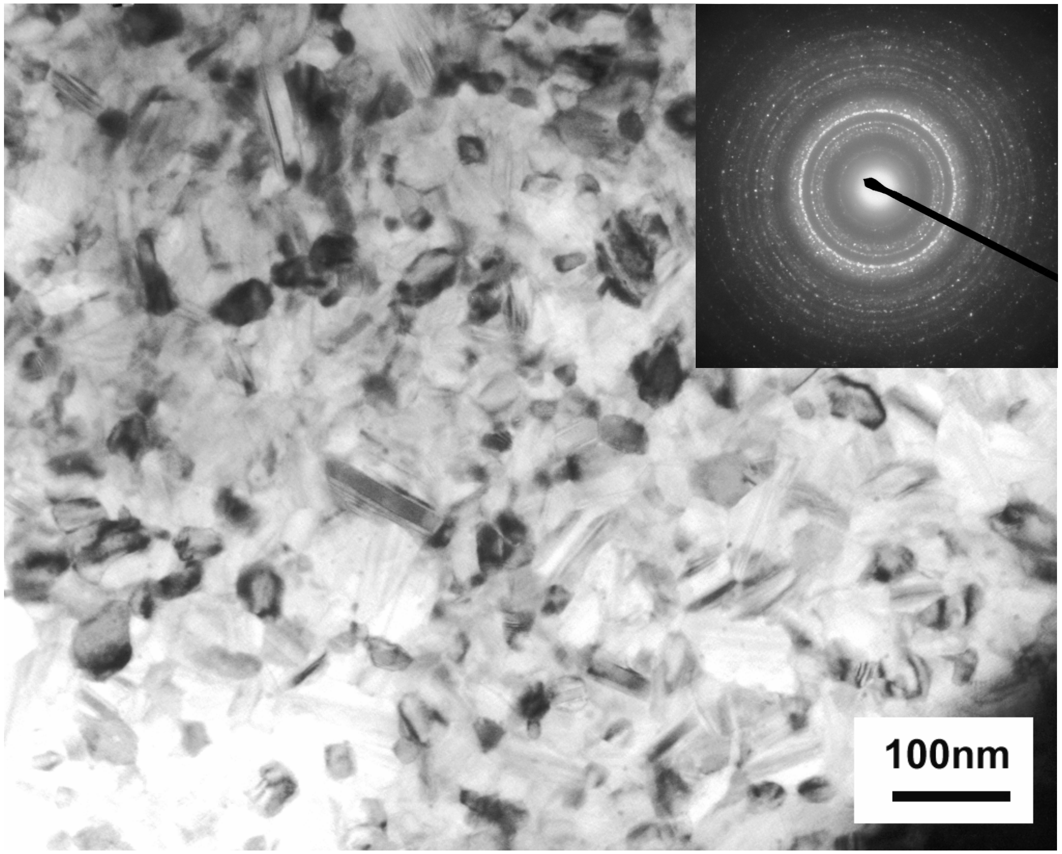
# *A Test of the New Concept*

- *$YCo_5$*
  - *The 1st RE-TM compound studied*
  - *HA = 130 kOe*
  - *High coercivity cannot be developed*

- *Mechanically alloyed $YCo_5$*
  - *${}_MH_c$ = 12 kOe after 750 ° C for 2 min.*

- *Mechanically alloyed $YCo_5/\alpha$-Fe* ***(5 wt%)***
  - *${}_MH_c$ = 7 kOe after 750 ° C for 2 min.*

# TEM Image of $YCo_5/\alpha$-Fe

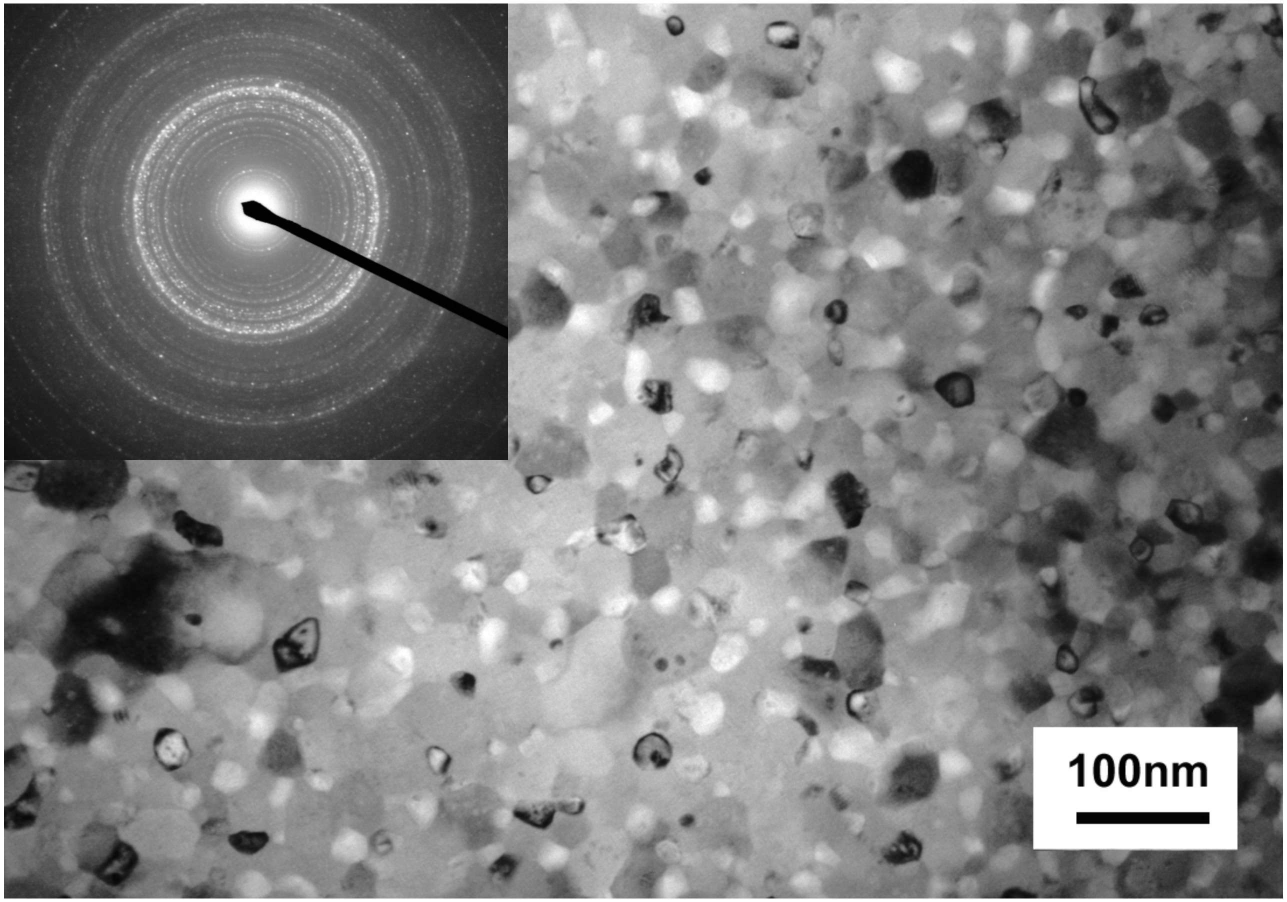


***TEM image and selected area electron diffraction pattern of a mechanically alloyed $YCo_5/\alpha$-Fe specimen after annealing at 750 °C for 2 minutes***

# Soft Phase Size According to the Current Exchange Coupling Model

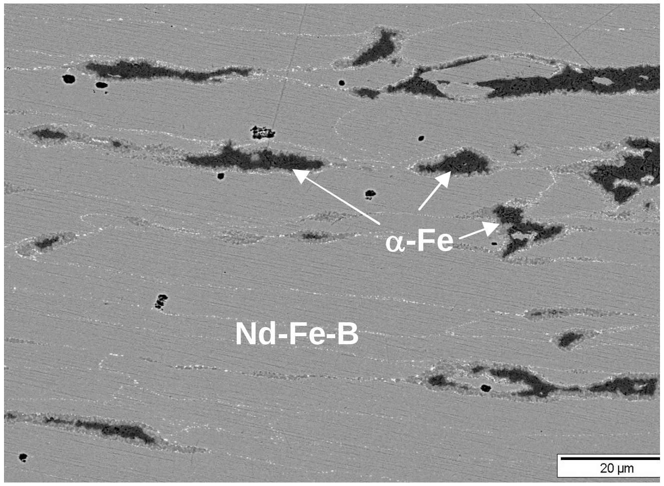
- *Optimum size of soft phase*
  - *9 nm*
- *Upper limit size of soft phase*
  - *20 – 30 nm*

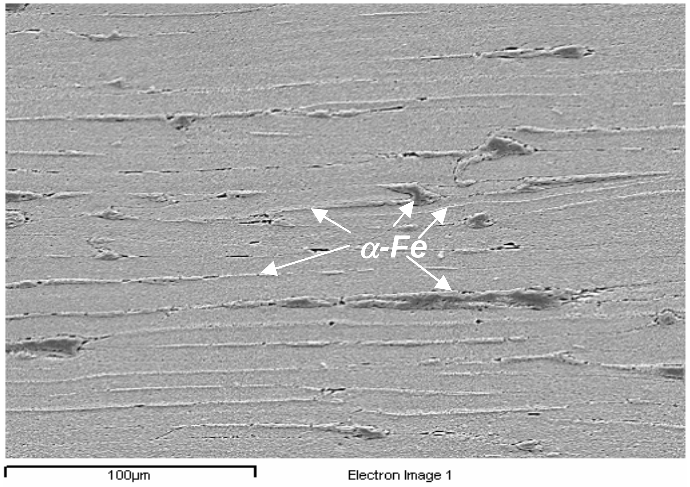
# TEM Image of a Melt-Spun and Annealed $Nd_2Fe_{14}B/\alpha$-Fe Specimen

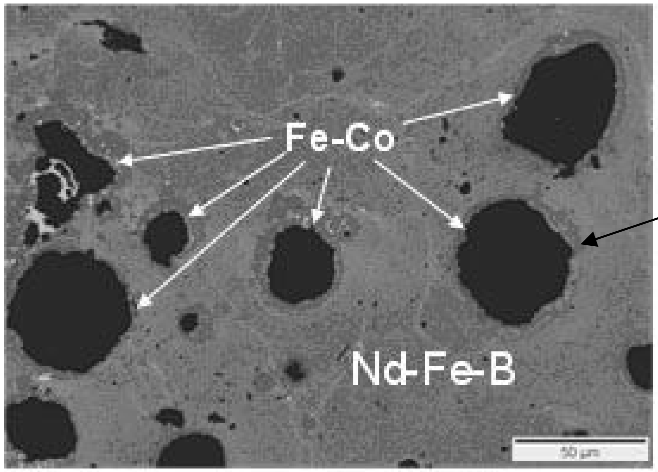


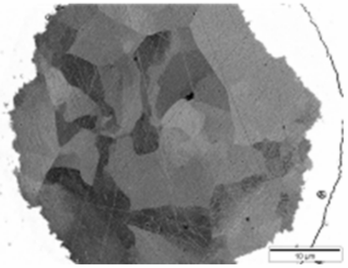
$Nd_{2.4}Pr_{5.6}Dy_1Fe_{85}B_6$, Anneal at 680 °C- 1 m, $_MH_c$ = 6 kOe

# Microstructures Hot Deformed Composite Magnets



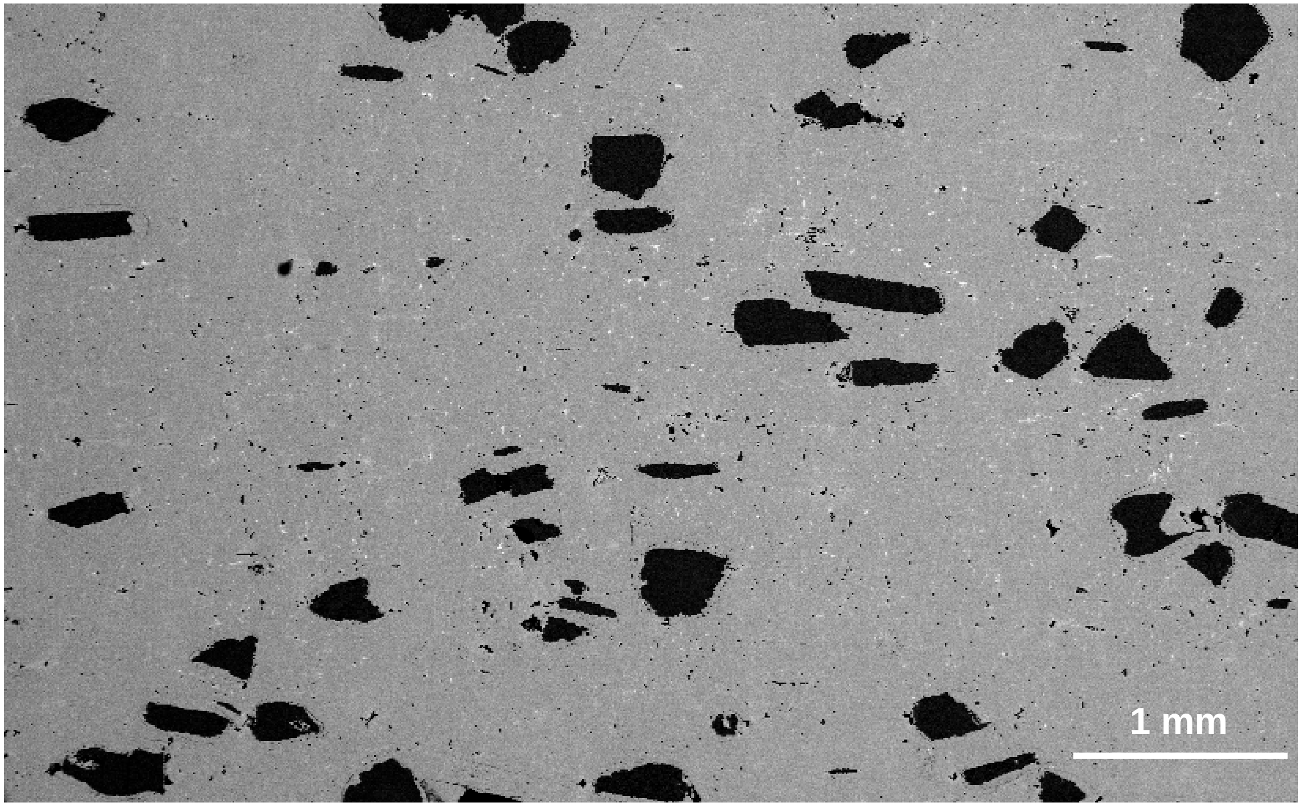






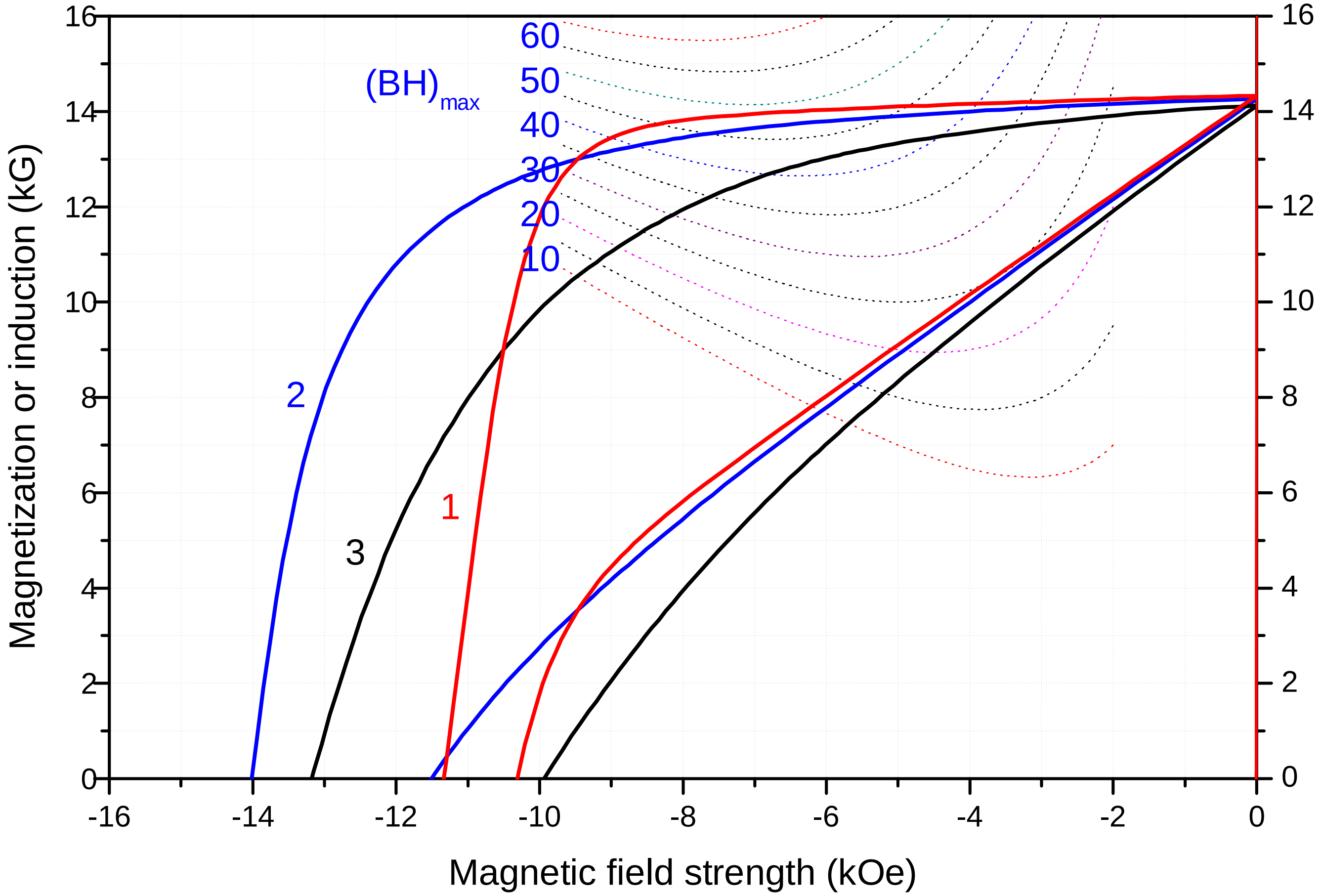
***The soft phase is more than 1000 times as large as the upper size limit predicted by the current model of exchange coupling***

# Size and Distribution of Fe-Co-B in Hard Matrix



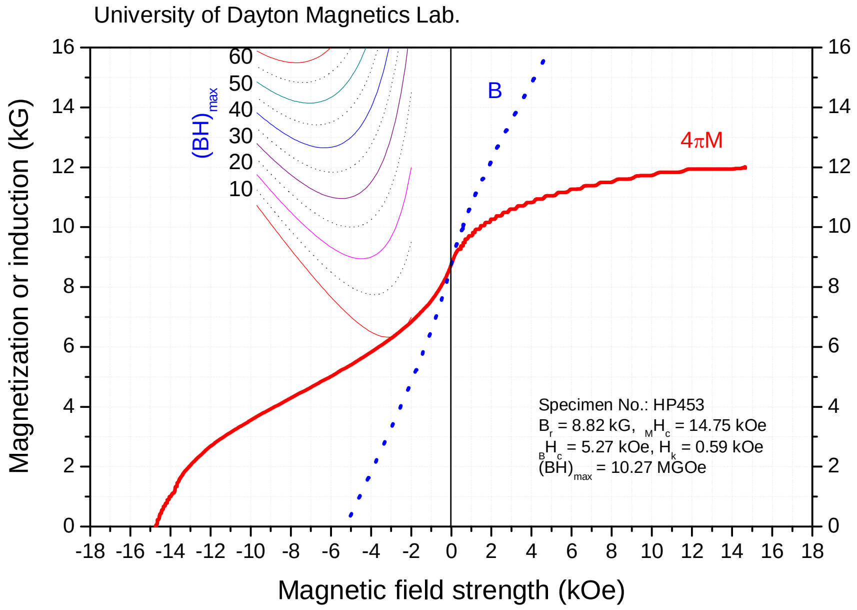
- $Nd_{13.5}Fe_{74.4}Co_{6}Ga_{0.5}B_{5.6}/Fe_{56.7}Co_{35.9}B_{7.4}$ (97 wt%/7 wt%)
- Fe-B alloy preparation: Ball milled for 7 hrs
- **7** wt% Fe-B
- > **53** microns
- $_{M}H_{c}$ = 13.2 kOe, $H_{k}$ = 6.8 kOe, $(BH)_{max}$ = 42.4 MGOe

# Effects of Particle Size of Soft Phase



1. $Nd_{13.5}Fe_{74.4}Co_6Ga_{0.5}B_{5.6}/Fe_{56.8}Co_{35.8}B_{7.4}$ (97 wt%/**3** wt%), ball milled **<** 53 microns
2. $Nd_{13.5}Fe_{74.4}Co_6Ga_{0.5}B_{5.6}/Fe_{56.8}Co_{35.8}B_{7.4}$ (97 wt%/**3** wt%), ball milled **>** 53 microns
3. $Nd_{13.5}Fe_{74.4}Co_6Ga_{0.5}B_{5.6}/Fe_{56.7}Co_{35.9}B_{7.4}$ (93 wt%/**7** wt%), ball milled **>** 53 microns

# *Exchange Coupling in Isotropic and Anisotropic Composite magnets*

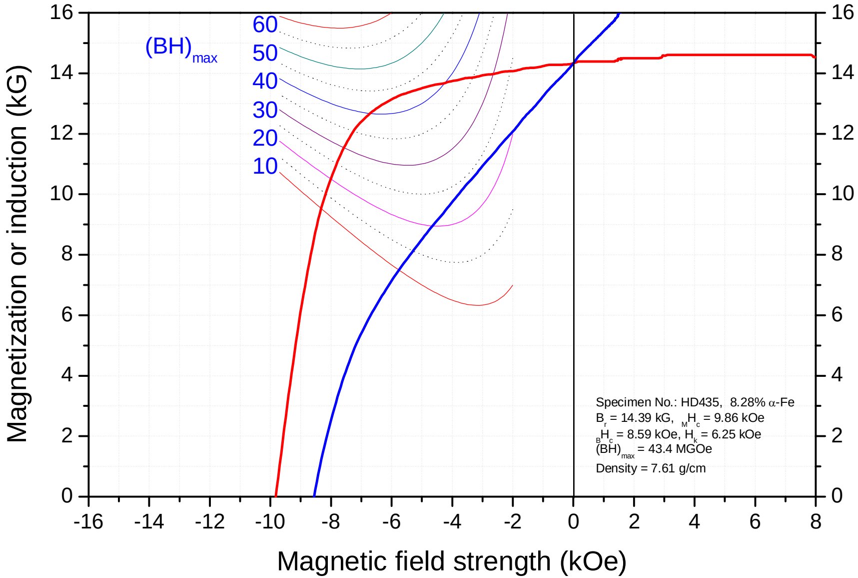


### *Isotropic composite magnet*

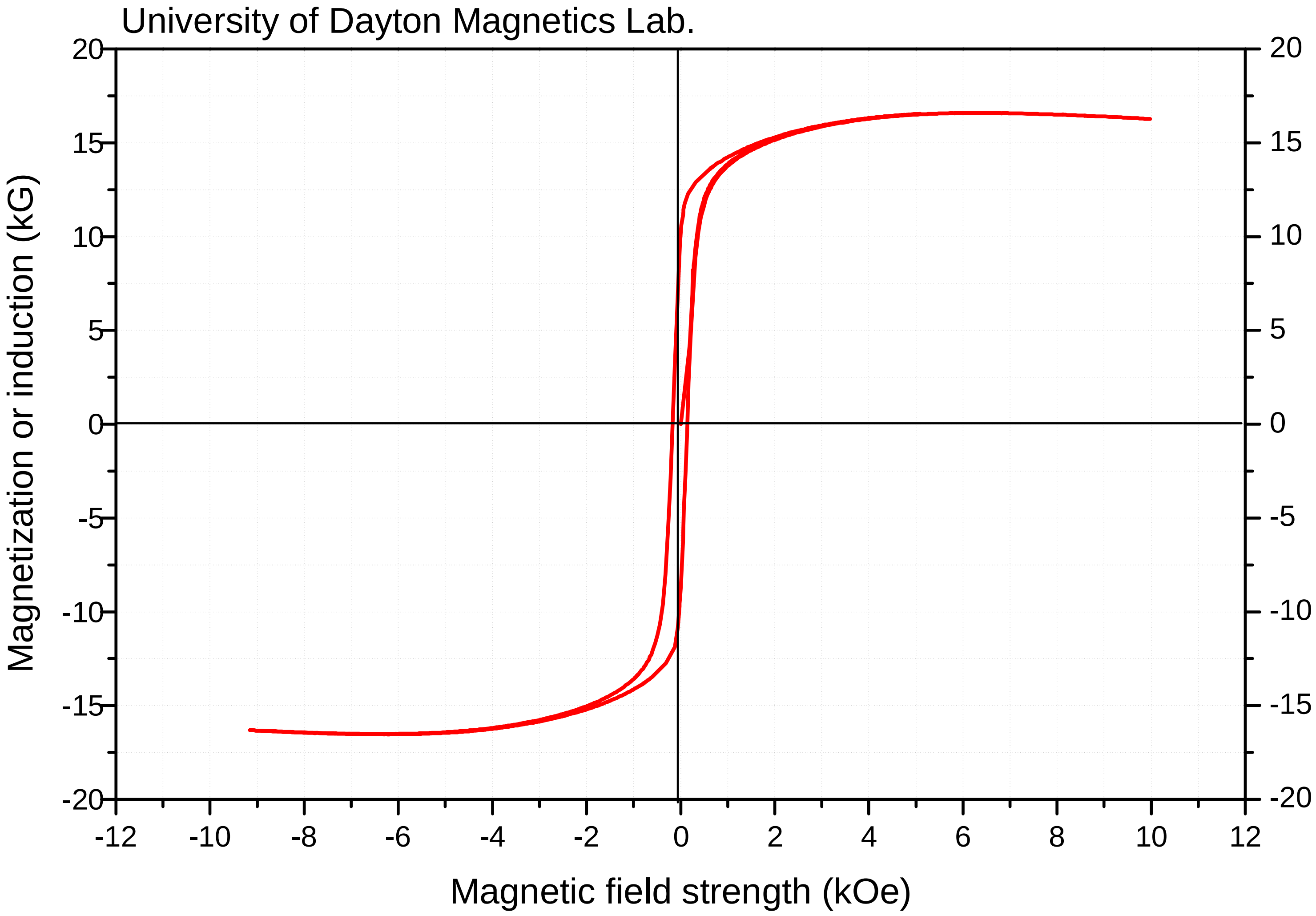
- ❑ *Kinked demagnetization curve*
- ❑ *Not very effective interface exchange coupling*

### *Anisotropic composite magnet*

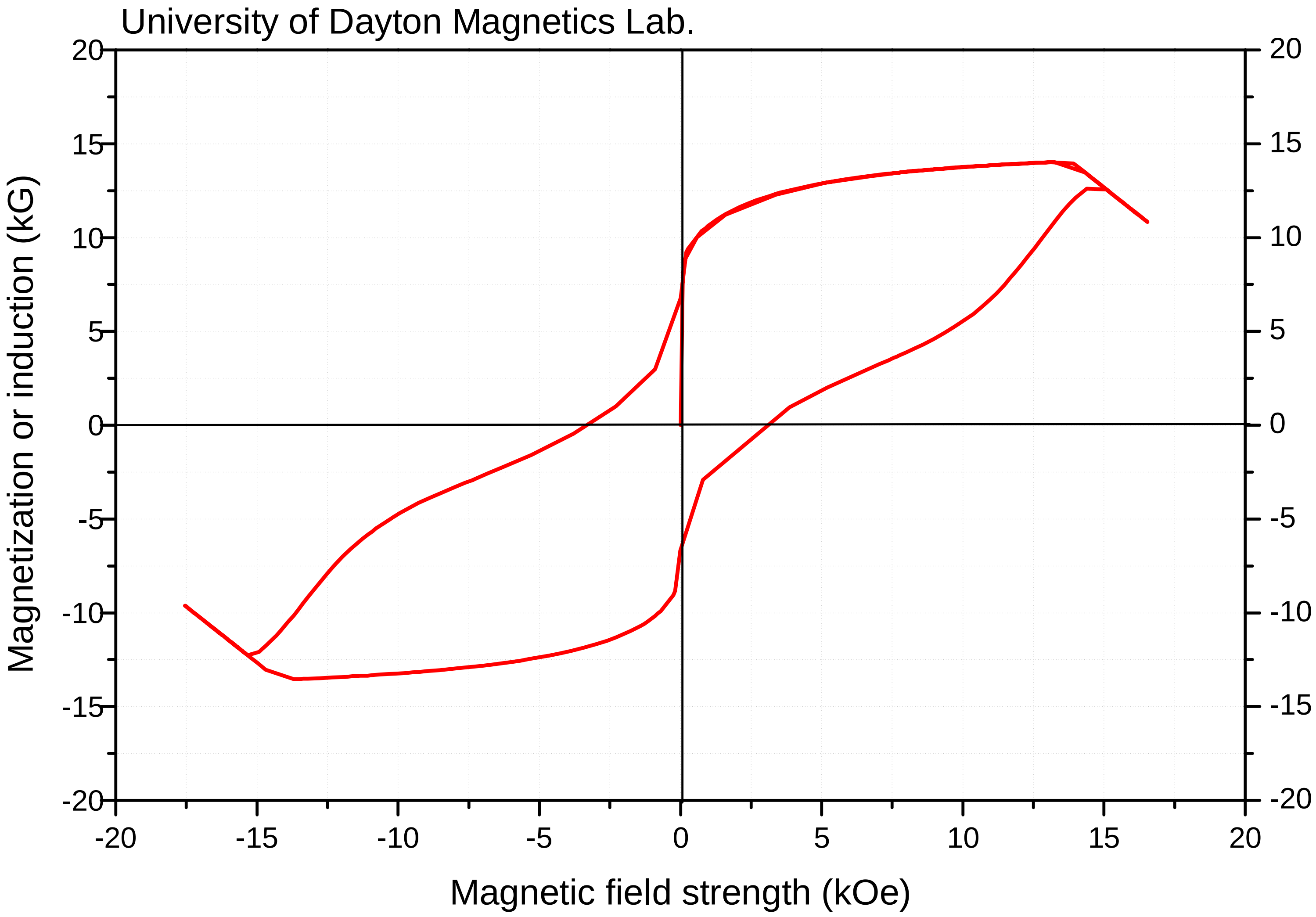
- ❑ *Smooth demagnetization curve*
- ❑ *More effective interface exchange coupling*
- ❑ *Size of soft phase can be very large*



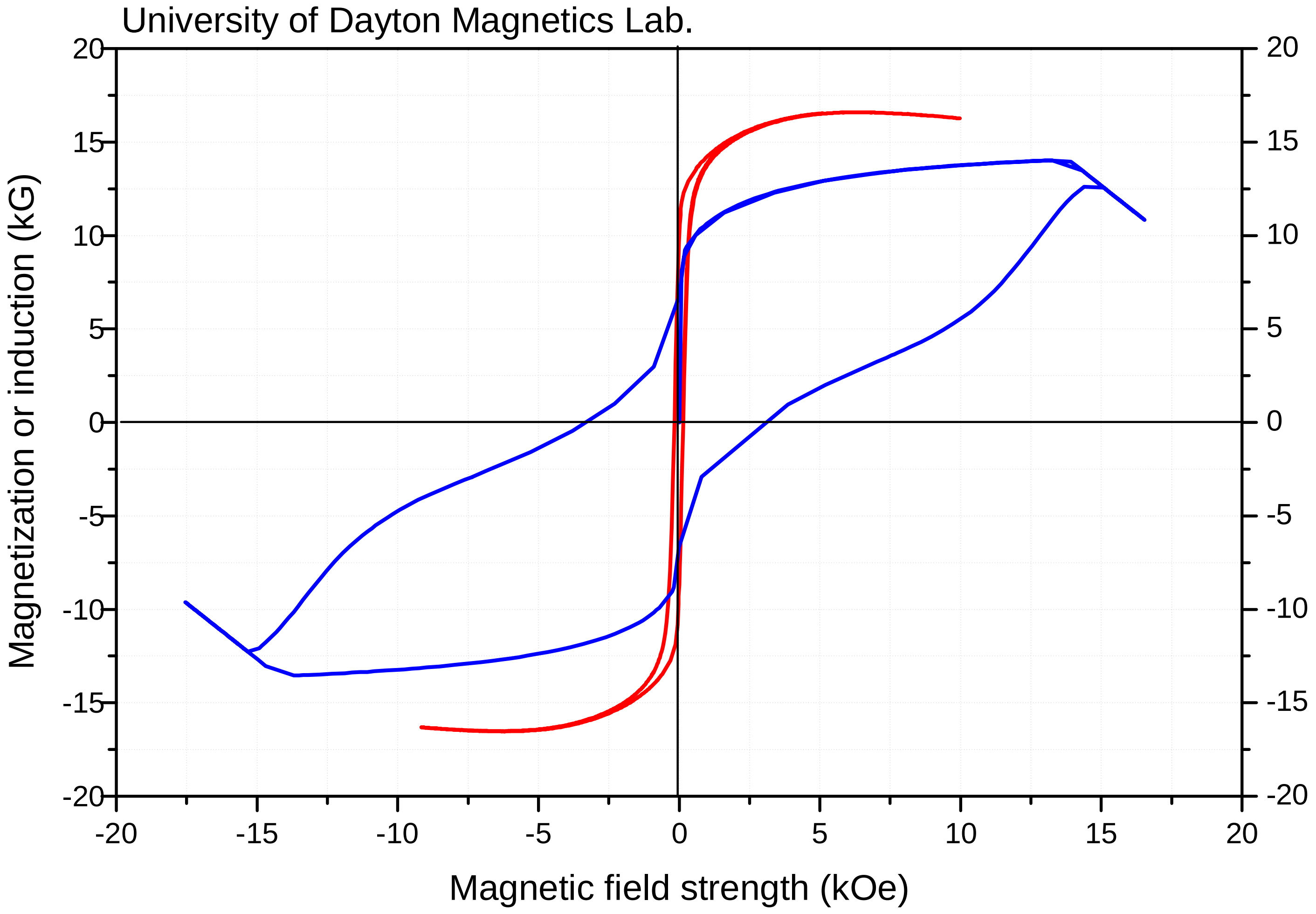
# *Hysteresis Loop of a Nd-Fe-B/α-Fe (60%/40%) Magnet after Hot Deformation*



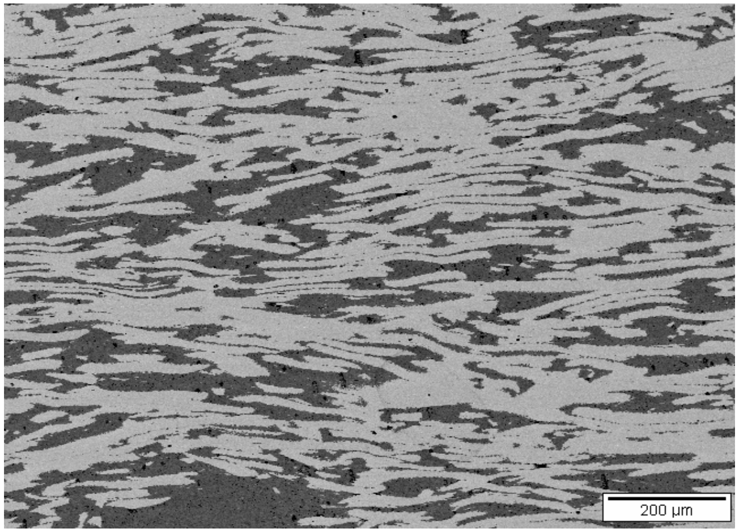
# Hysteresis Loop of a Nd-Fe-B/α-Fe (60%/40%) Magnet after Hot Compaction

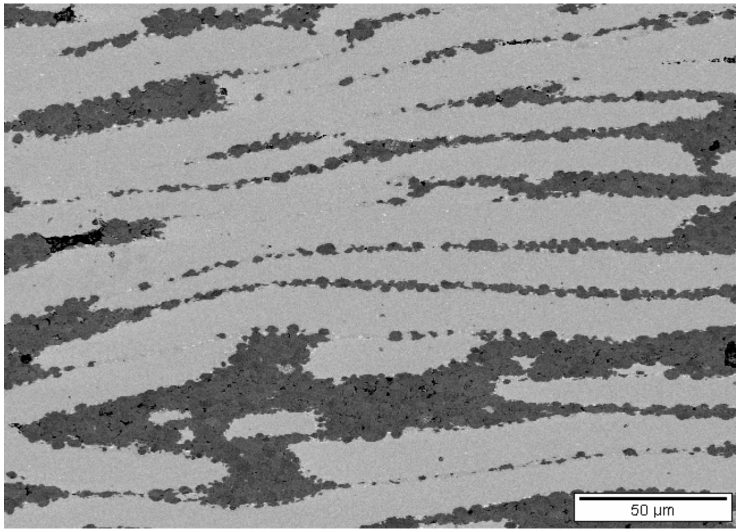


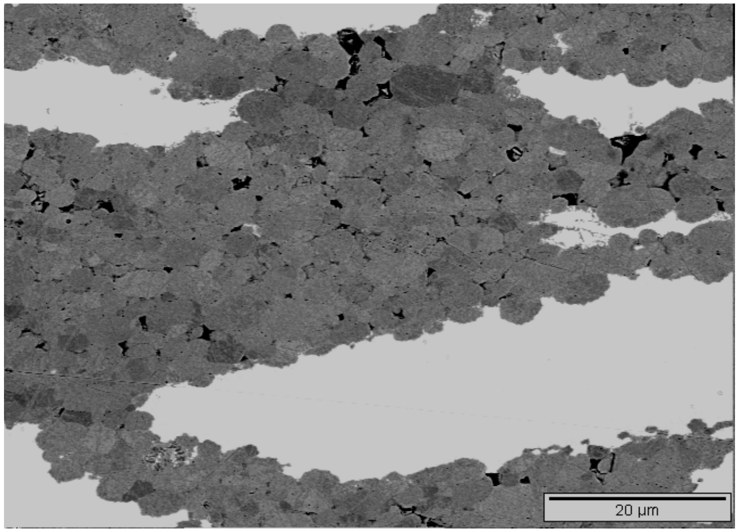
# A Comparison of Hot Compacted and Hot Deformed Magnets

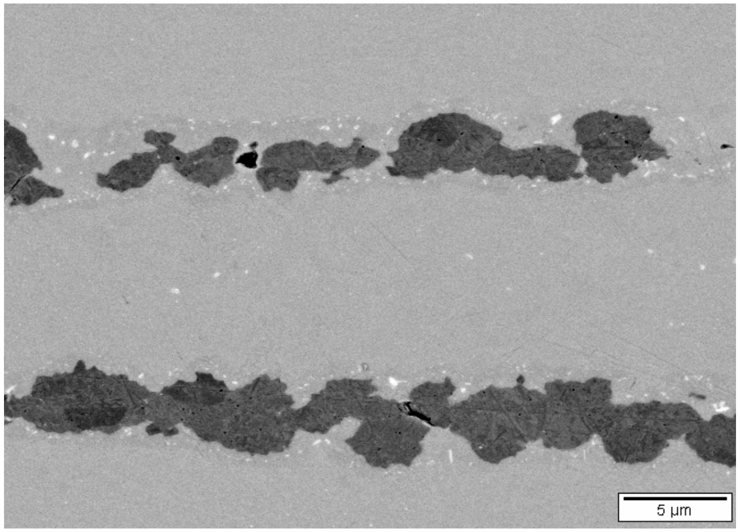


# Microstructure of Nd-Fe-B/α-Fe (60%/40%) Magnet

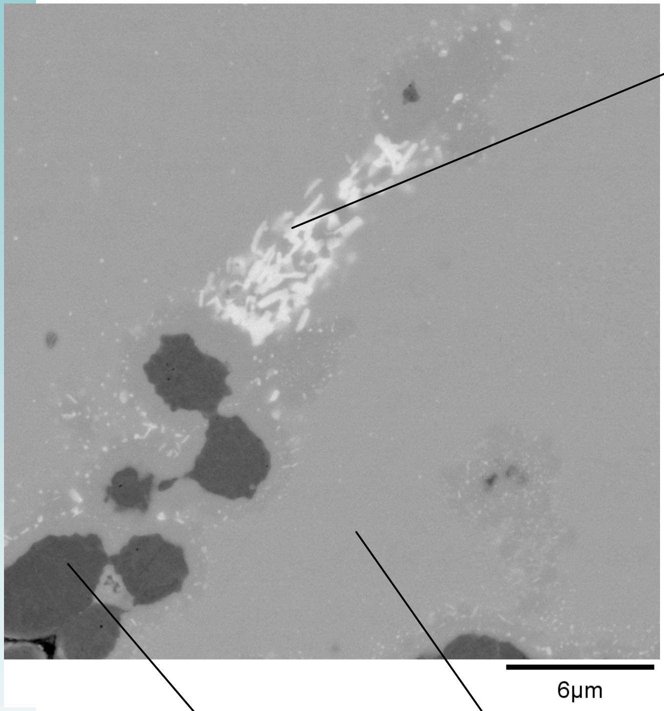


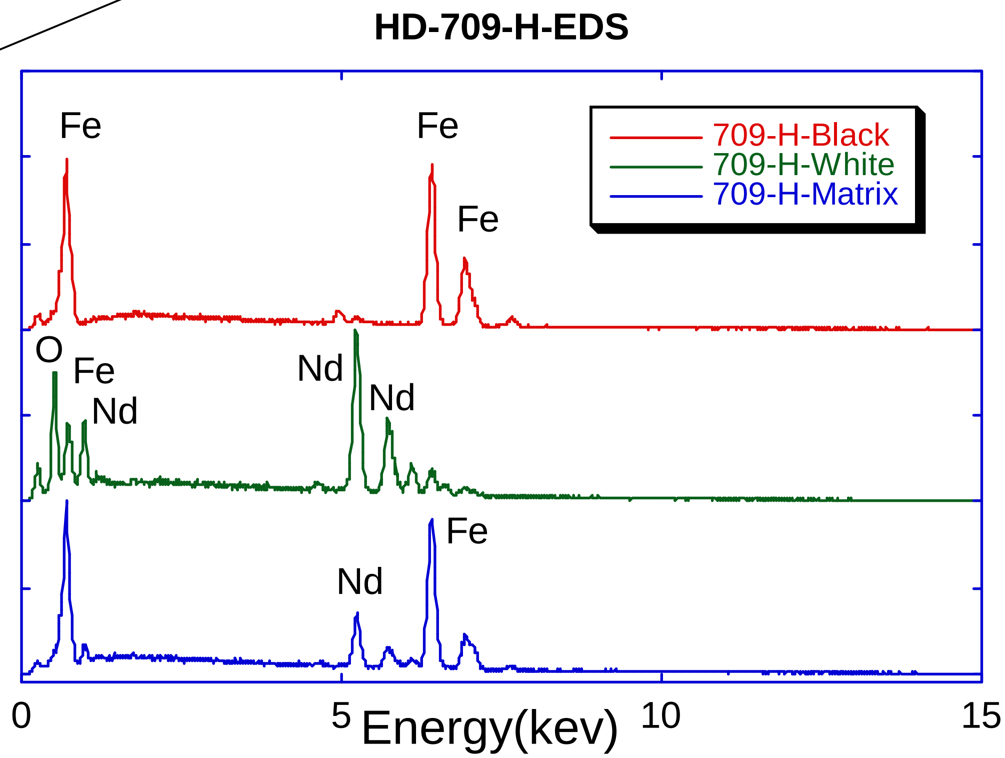




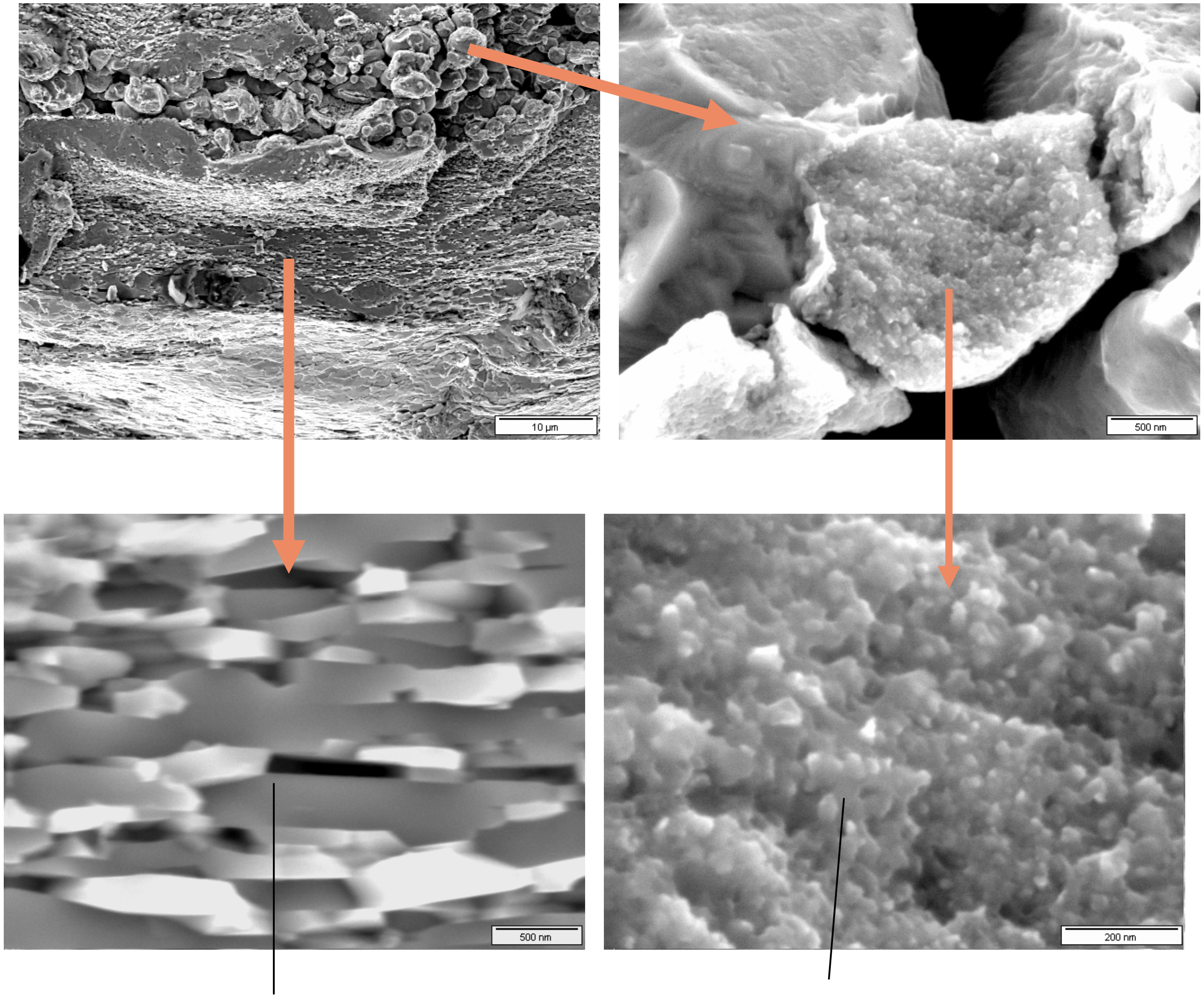


# *SEM/EDS Analysis*





# *Fracture Surface Analyses*



2-14-1 matrix

Inside a Fe particle

# X-Ray Diffraction Result