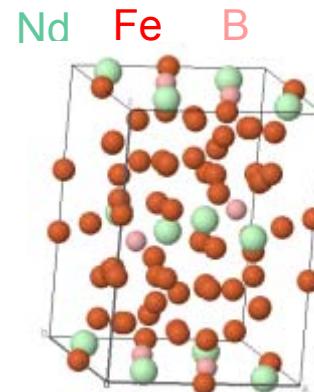
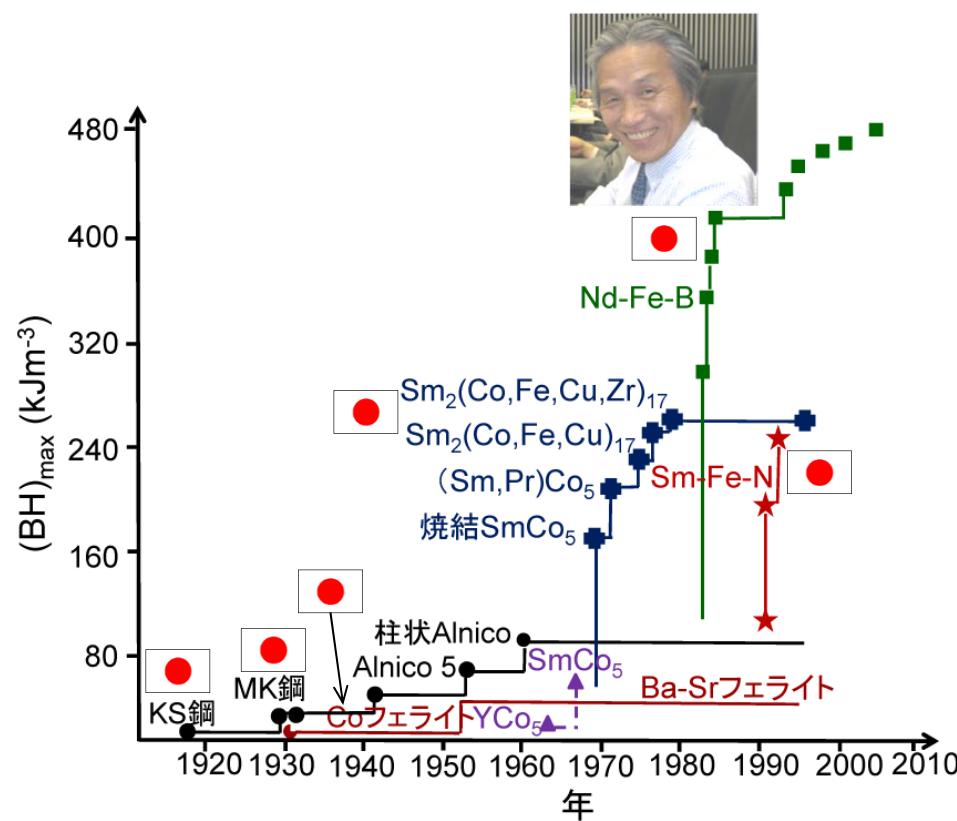




# 永久磁石における問題とその取り組み —計算科学への期待

物質・材料研究機構  
磁性材料ユニット  
&  
元素戦略磁性材料研究拠点  
**宝野和博**

# 磁石の高性能化と小型化



$\mu_0 M_s = 1.61 \text{ T}$ ,  $\mu_0 H_c > 0.8 \text{ T}$   
 $K_u = 4.3 \text{ MJ/m}^3$ ,  $\kappa = 1.54$   
 $(BH)_{\max} < 510 \text{ kJ/m}^3$   
 $T_c = 312^\circ\text{C}$

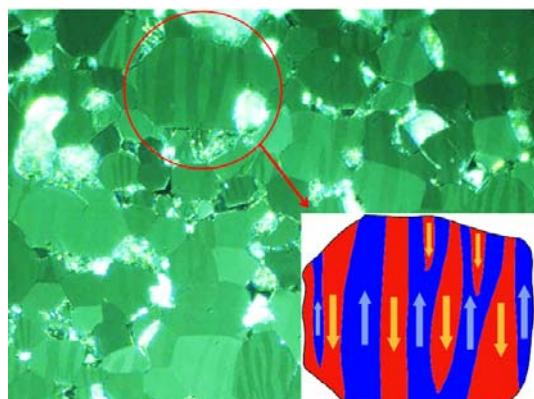
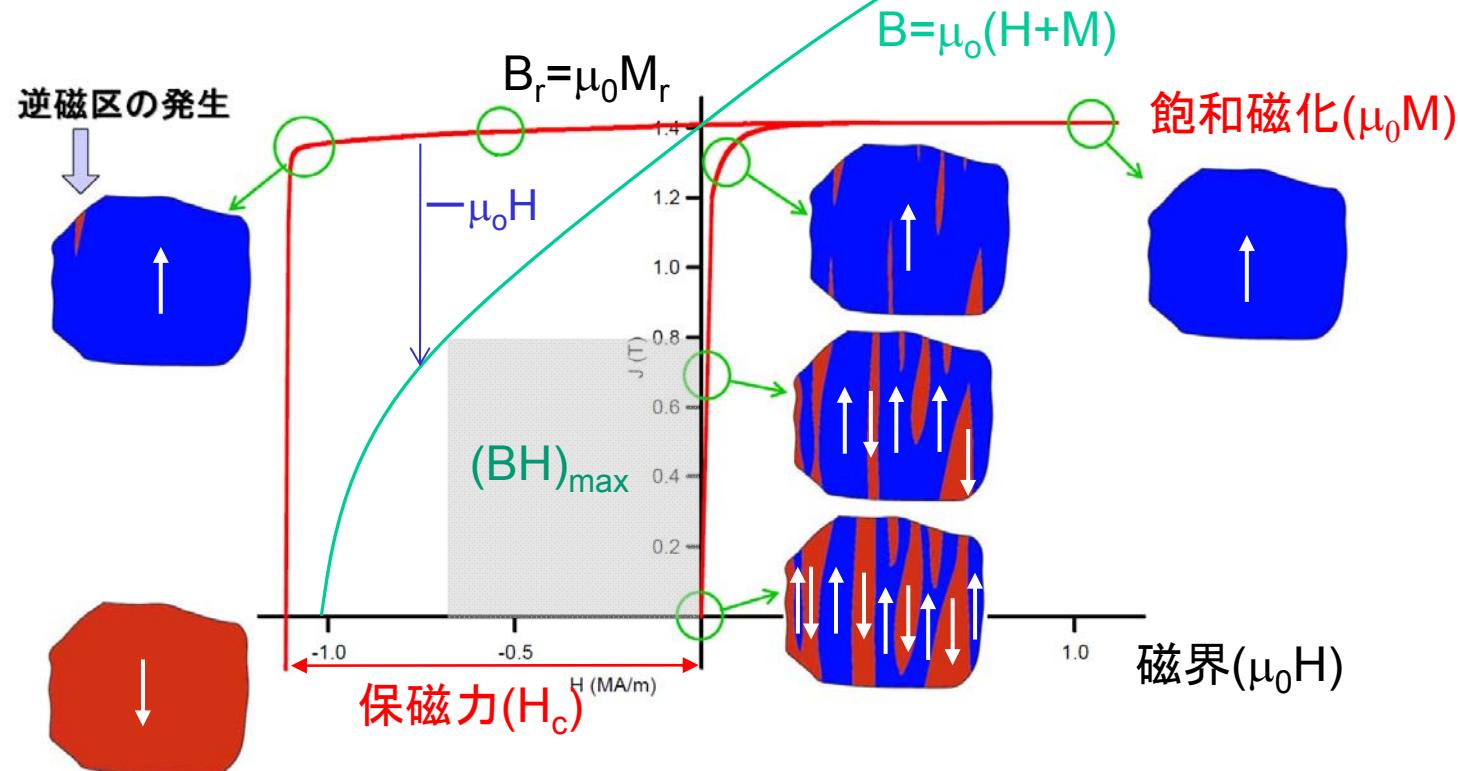
Nd-Fe-B

フェライト



高い  $(BH)_{\max}$  を持つ磁石は 小さな体積で高い磁束を発生できる  
モータや発電機の **小型化** → **省エネ**

# 磁石の性能指数(BH)<sub>max</sub>



原図：信越化学美濃輪氏

**保磁力 $H_c$** : 磁化反転する磁界（耐熱性）

**最大エネルギー積( $BH$ )<sub>max</sub>**:

どれだけの体積で磁束をだせるかの性能指數

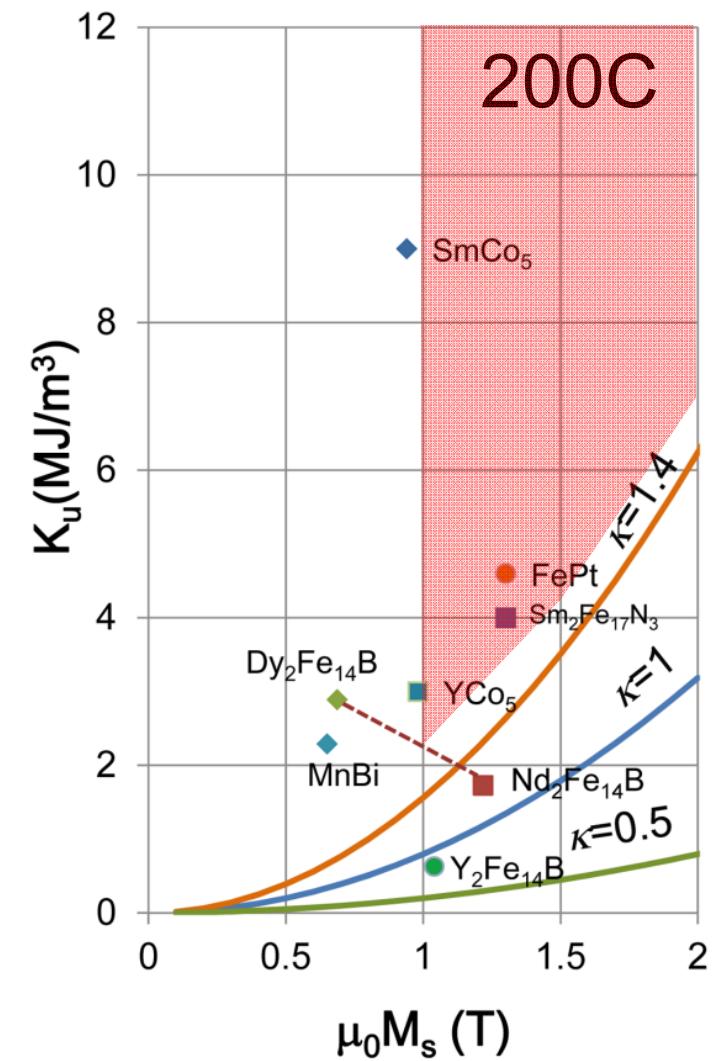
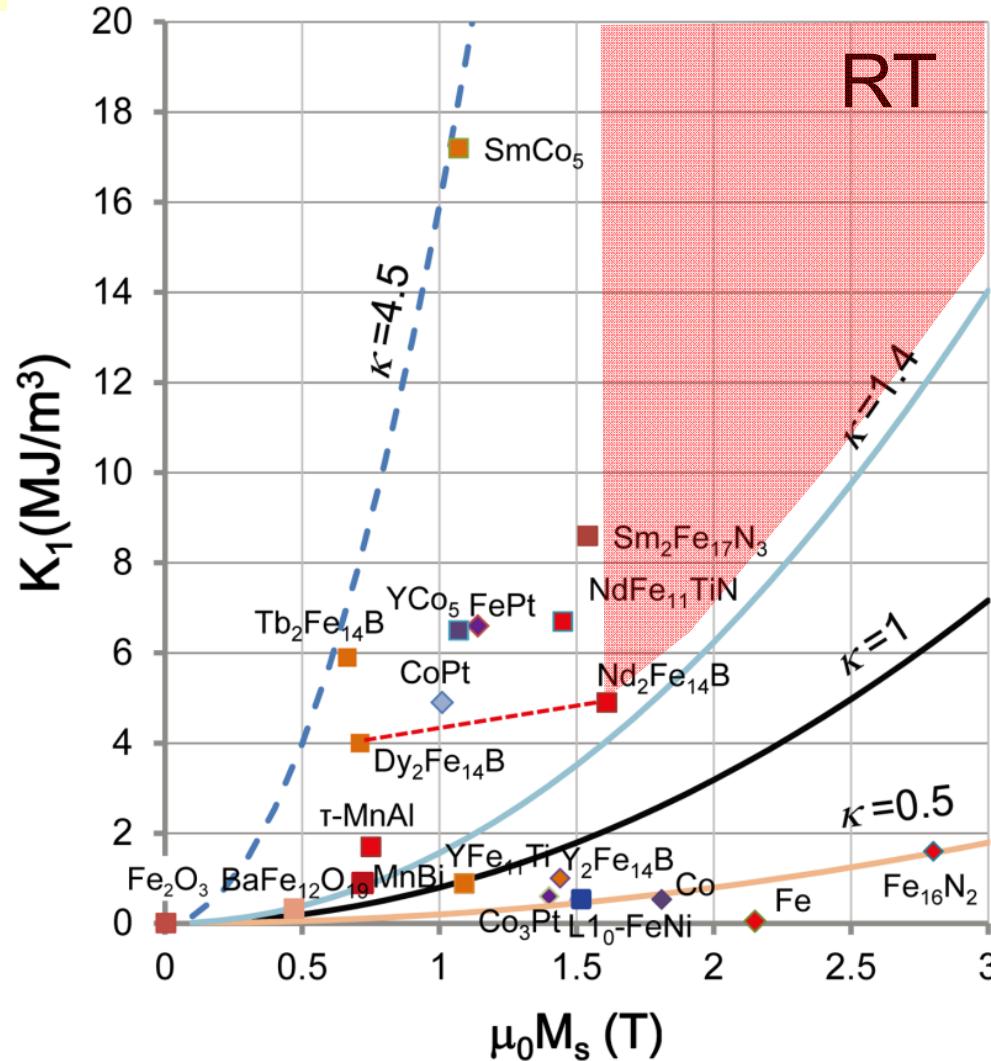
$(BH)_{max} < \mu_0 M_r^2 / 4$  但し  $H_c > M_r / 2$  の場合のみ

$$\kappa = \sqrt{K_1 / \mu_0 M_s^2} > 1$$

# 高性能磁石に要求される結晶磁気異方性 $K_1$ , 磁化 $\mu_0 M_s$ と硬さ係数 $\kappa$

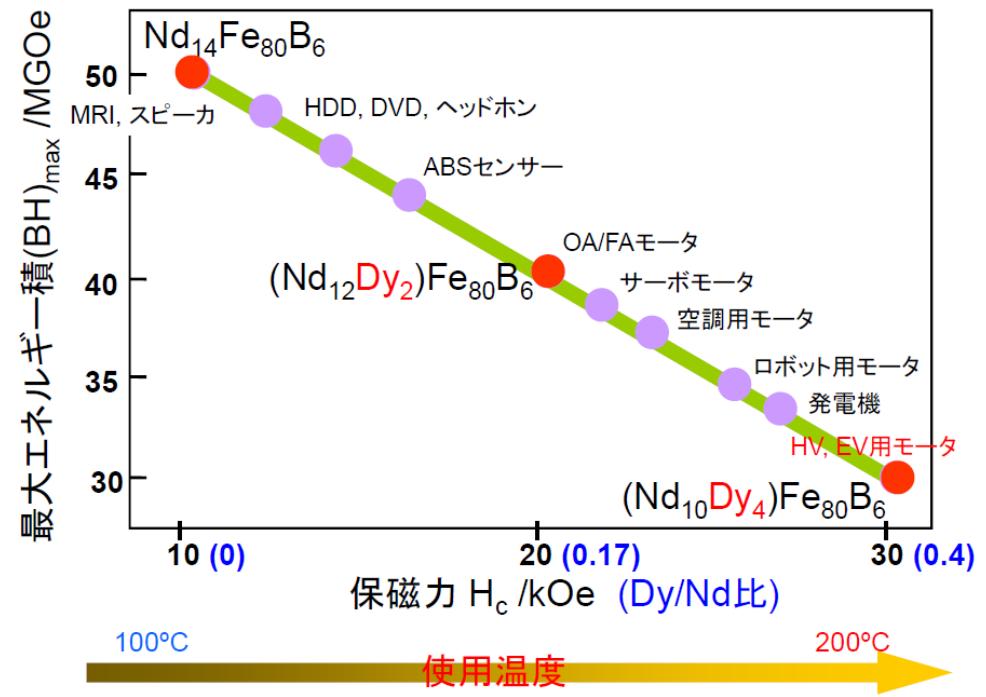
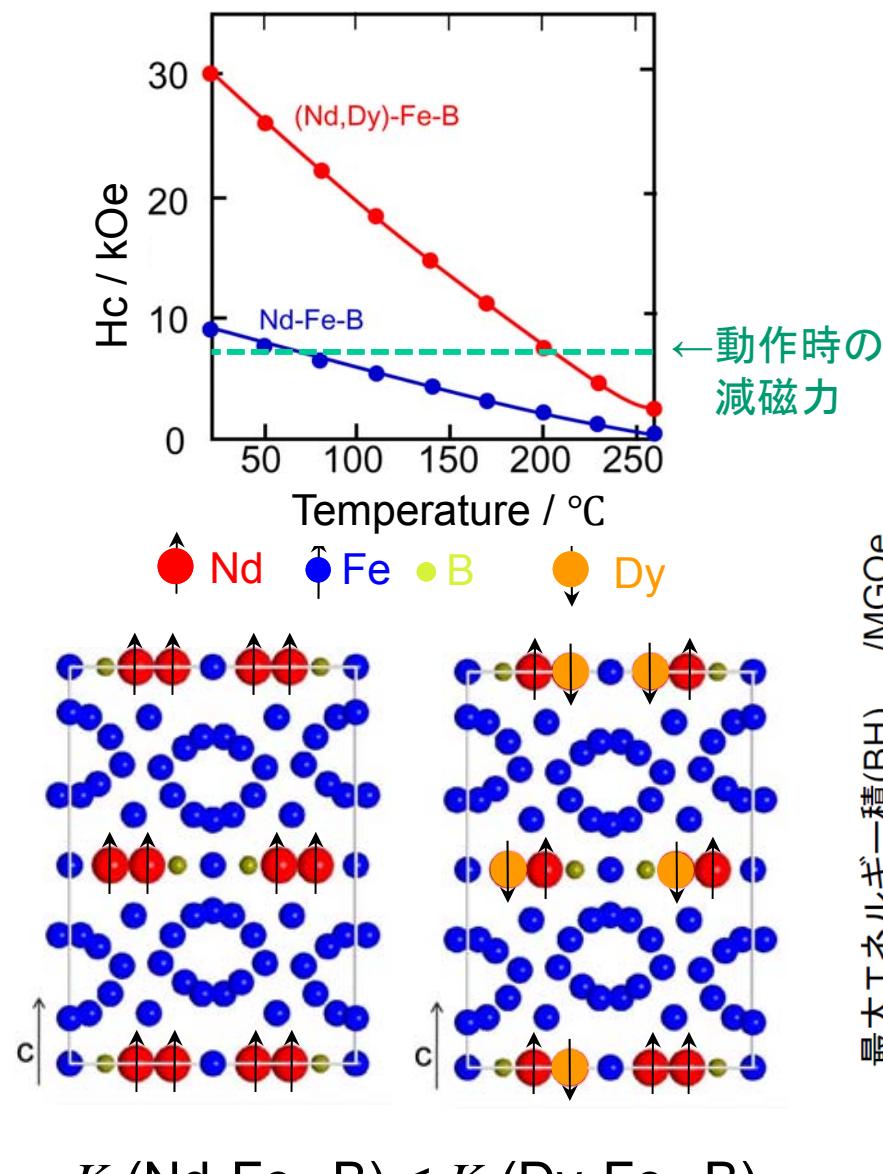
$$(BH)_{\max} = \frac{\mu_0 M_r^2}{4}$$

$$H_c > M_s / 2 \rightarrow \kappa = \sqrt{K_1 / \mu_0 M_s^2} > 1$$

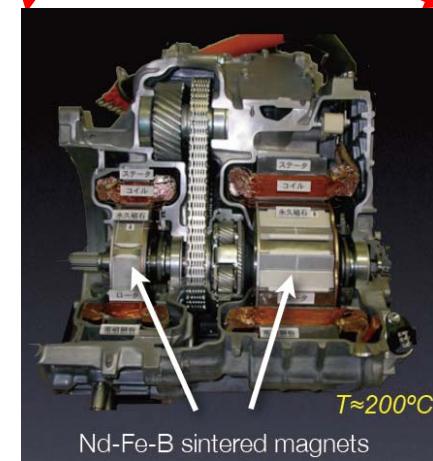


# HV, EV, 風力発電に必要なネオジム磁石

## 耐熱温度を上げるためにジスプロシウム(Dy)が必要



# 省エネ社会における(Nd,Dy)-Fe-B磁石



100万台/年

1.2 kg



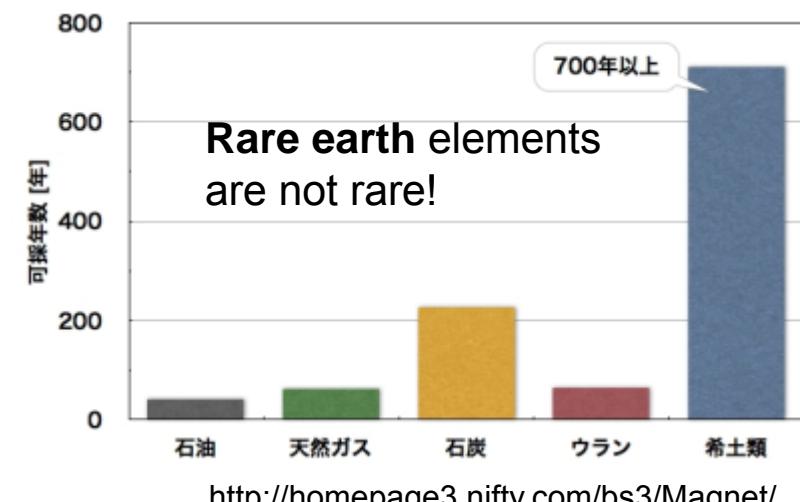
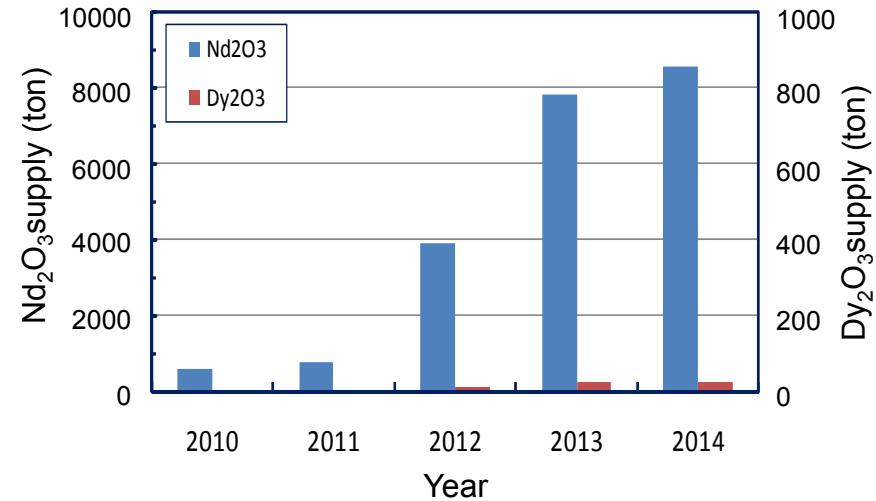
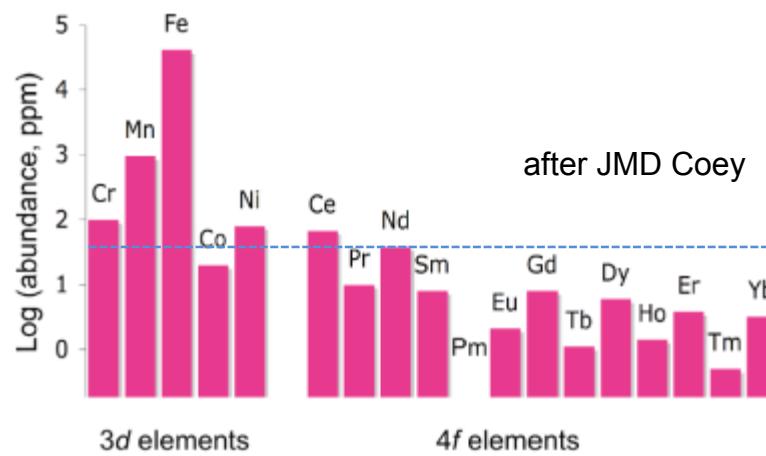
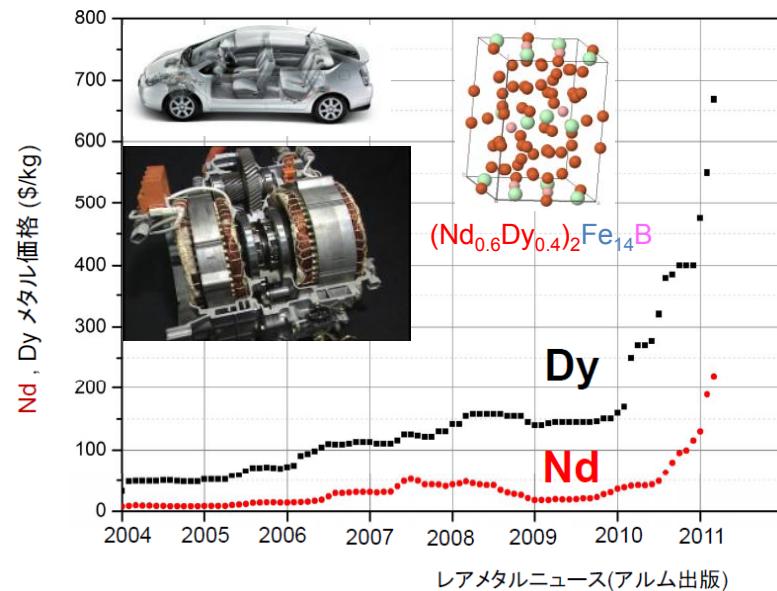
1 t

(Nd,Dy)-Fe-B磁石

$\text{Fe}_{65.5}\text{Nd}_{22}\text{Dy}_{11}\text{B}_1\text{Al}_{0.3}\text{Cu}_{0.1}\text{O}_{0.1}$  (mass.%)

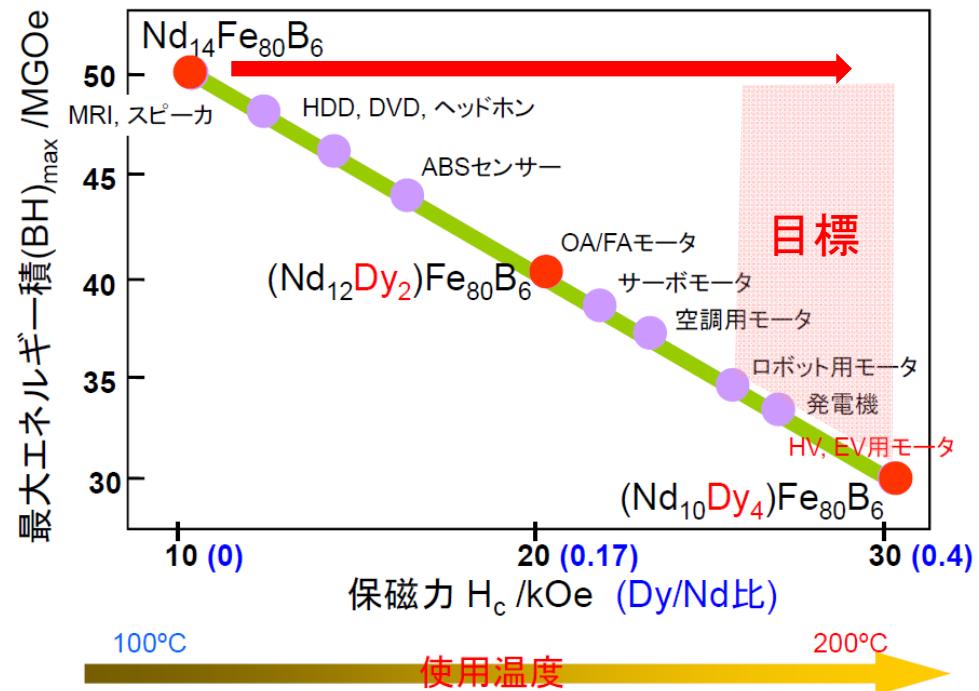
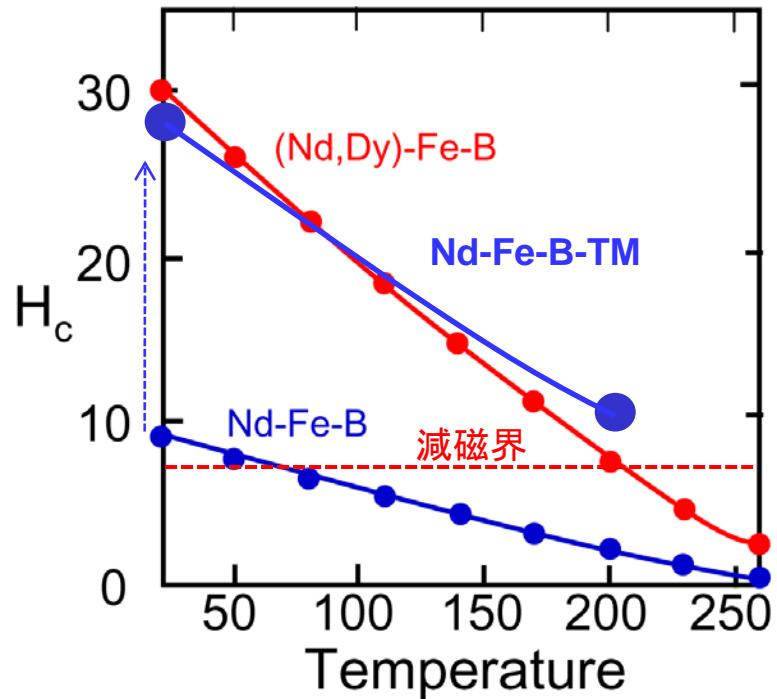
Nd磁石小量消費の時代からNd-Dy磁石大量消費の時代へ

# NdとDyの価格と資源量



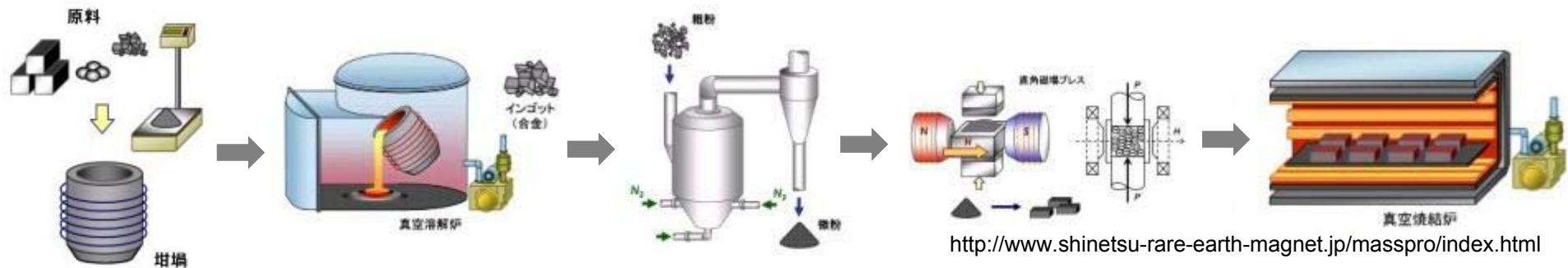
Dyを使わない高保磁力Nd-Fe-B磁石の開発

# Dyフリー磁石の目標



Dyを使わずに現行の(Nd,Dy)-Fe-Bと同等またはそれ以上の $(BH)_{max}$ を持つ $H_c > 25$  kOe以上のNd-Fe-B磁石

# Fe-Nd-B異方性焼結磁石

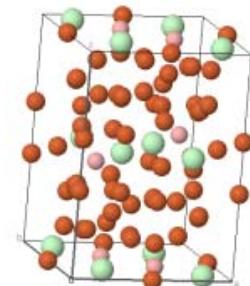
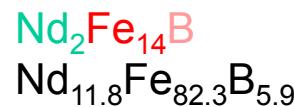
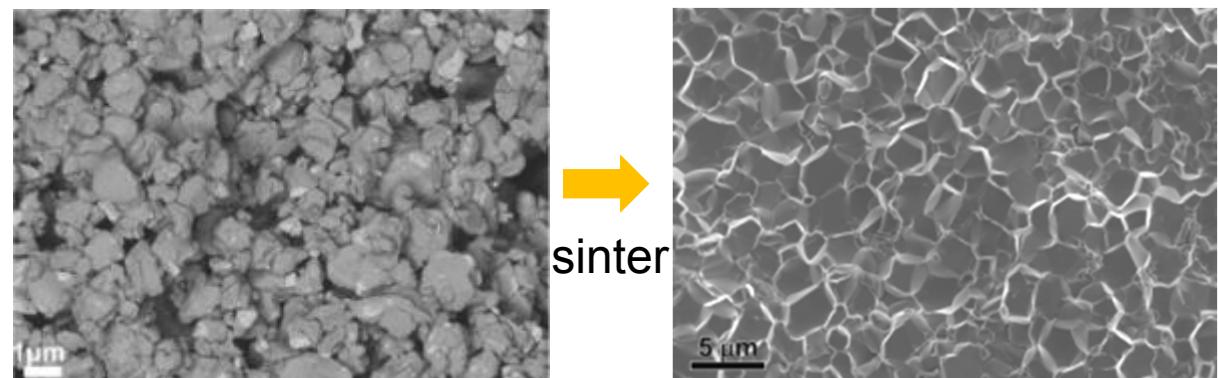


## Alloy composition

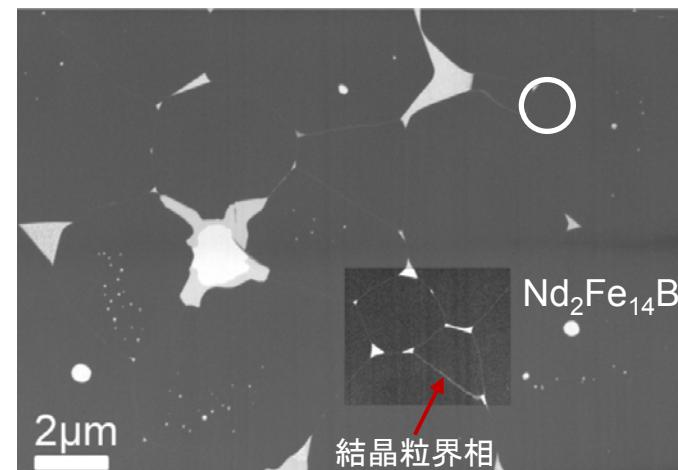
Atomic ratio



Mass ratio



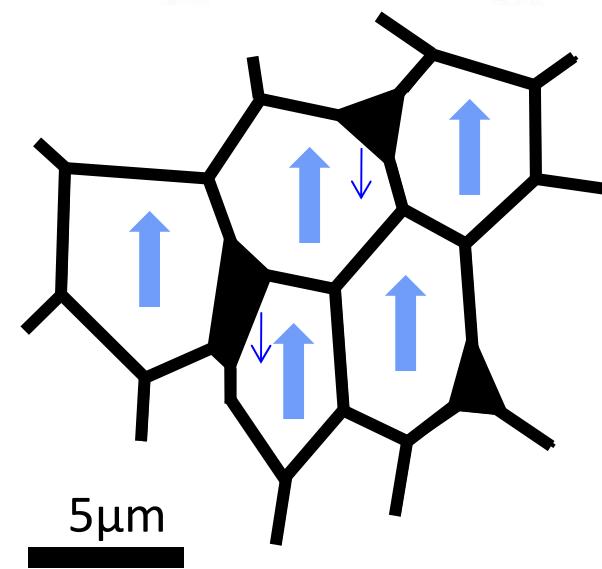
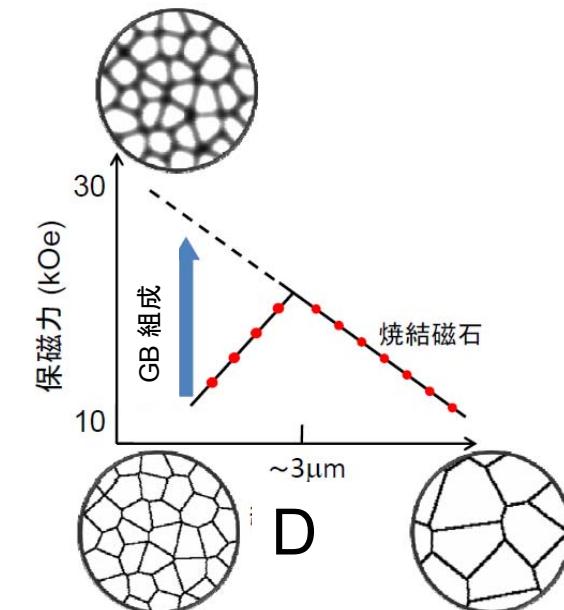
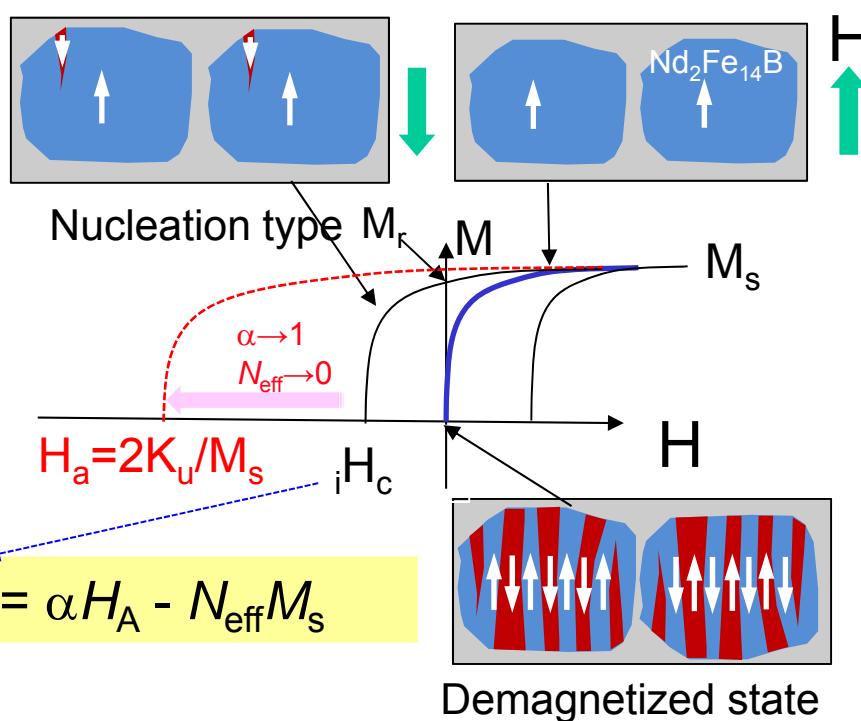
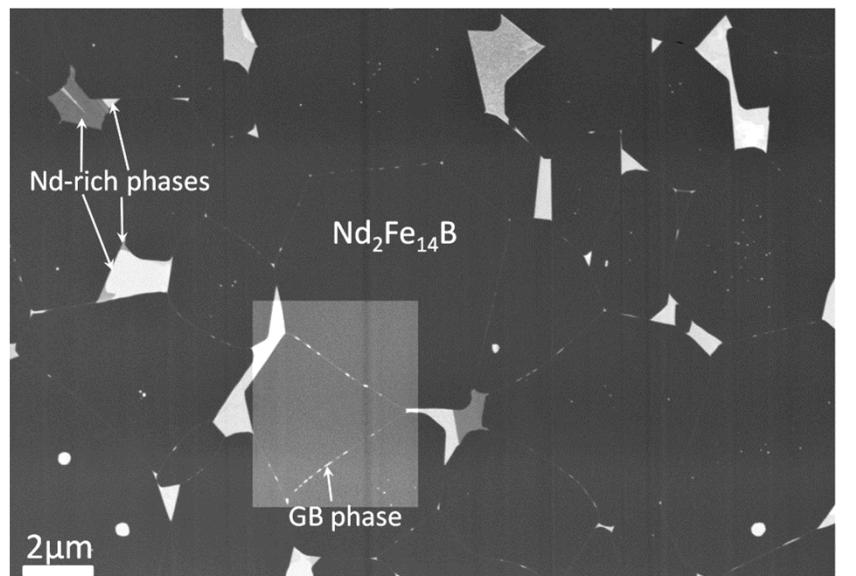
$M=1.61 \text{ T}$   
 $K_u=4.3 \text{ MJ/m}^3$   
 $T_c=312^\circ\text{C}$   
 $(\text{BH})_{\max}<510 \text{ kJ/m}^3$



$D_{\text{GB}} \sim 1.5 D_{\text{powder}}$

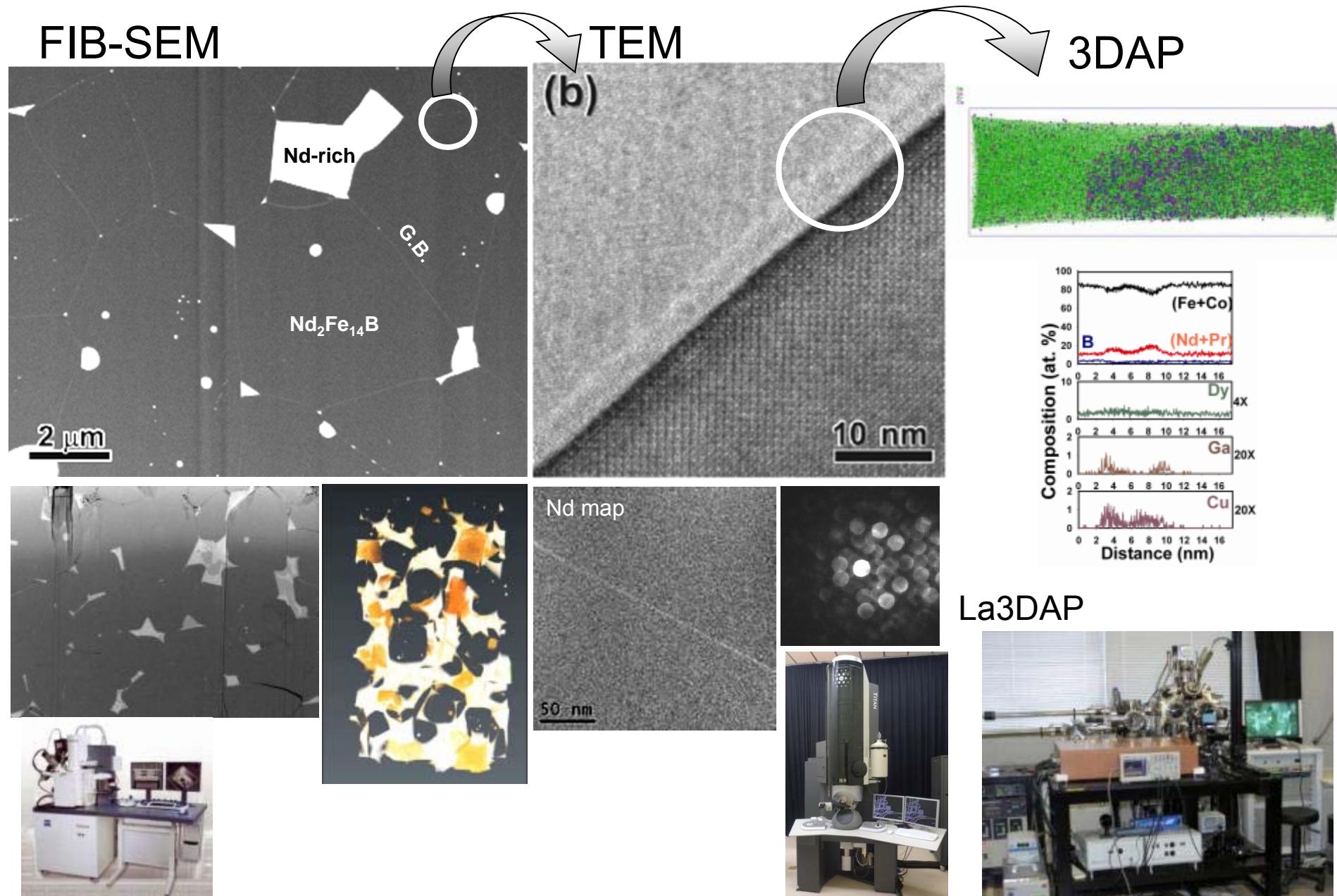


# Nd-Fe-B焼結磁石の微細組織と保磁力

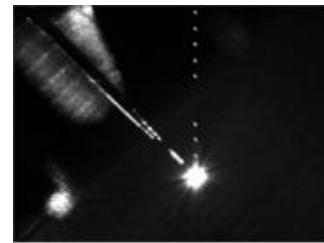
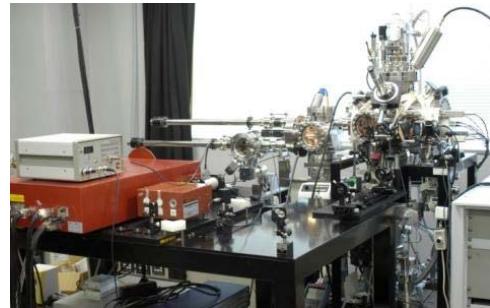


$$H_c = \alpha \uparrow H_a - N_{eff} \downarrow M_s$$

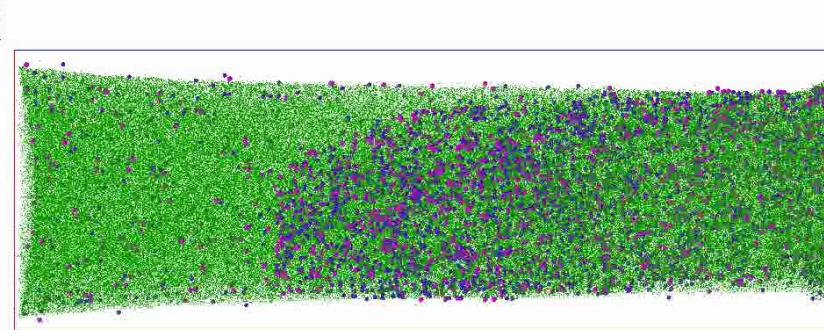
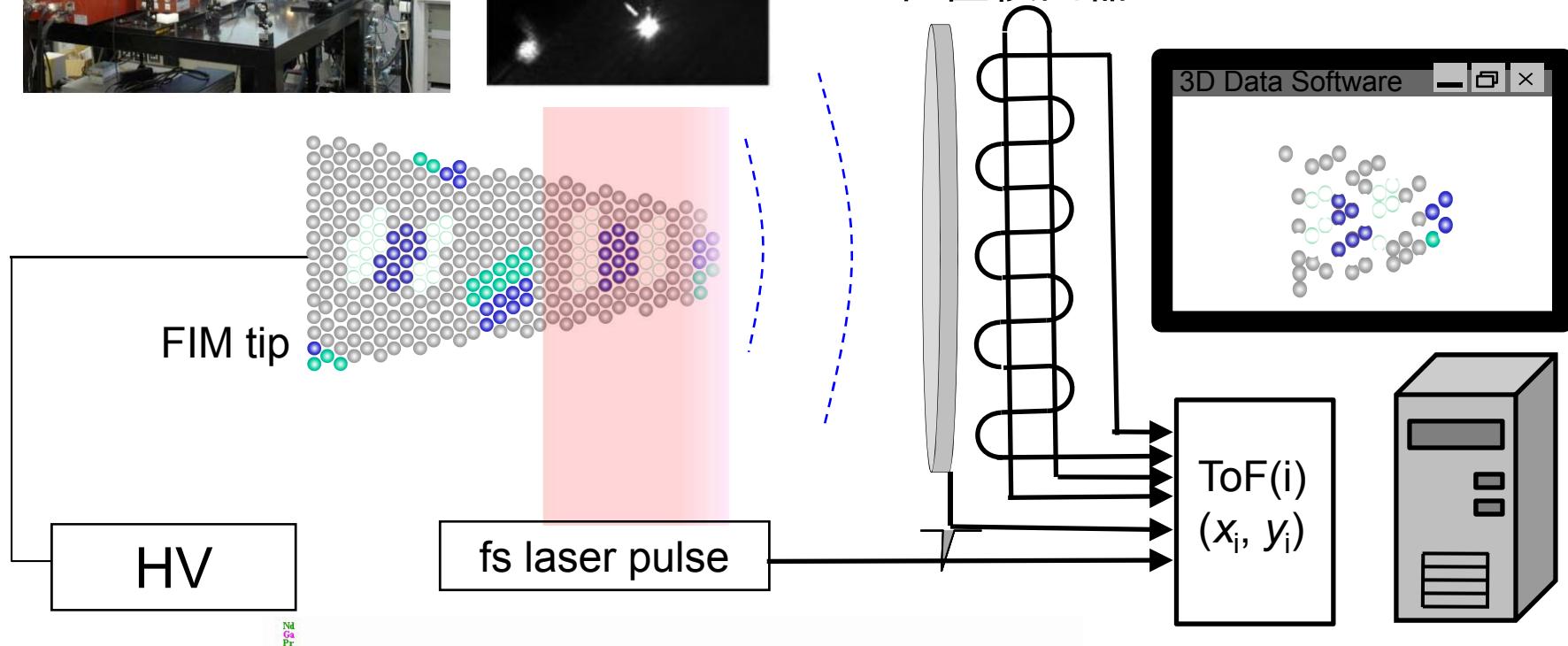
# SEM/TEM/3DAPによるマルチスケール解析



# レーザー補助3次元アトムプローブ



位置検出器

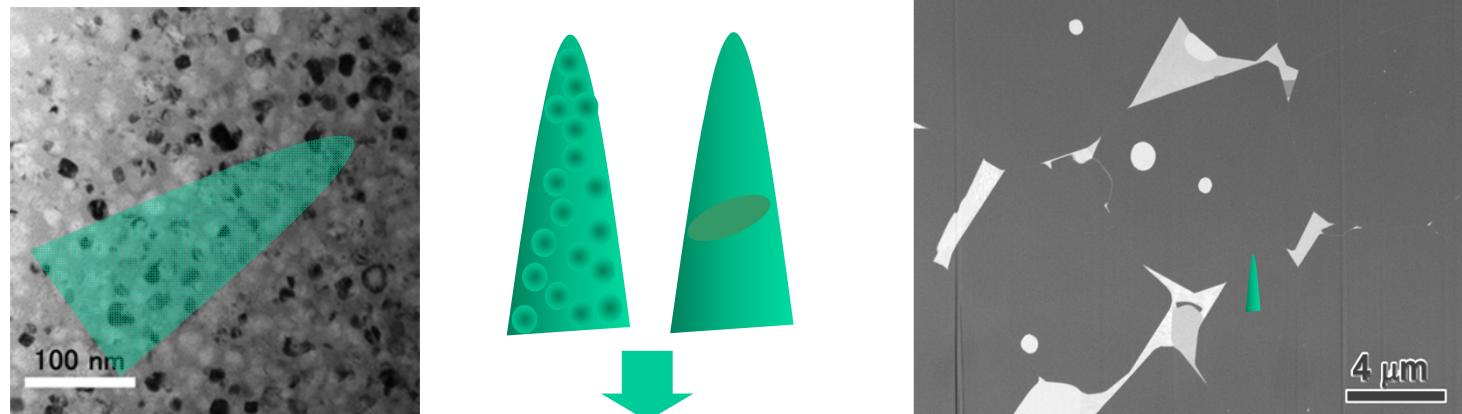


# 3DAP試料形状の制約

## 針状試料

粒界、位相界面、表層などの任意領域の解析が困難

針がつくれる試料のみ解析が可能

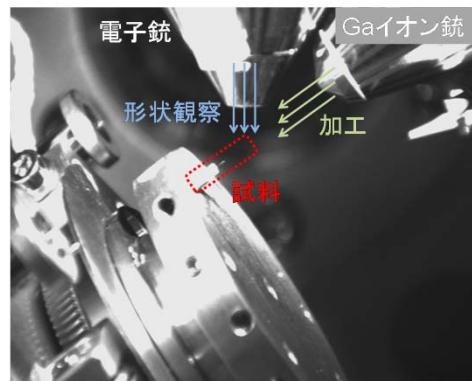


FIBによるあらゆる試料の任意箇所からの試料作製

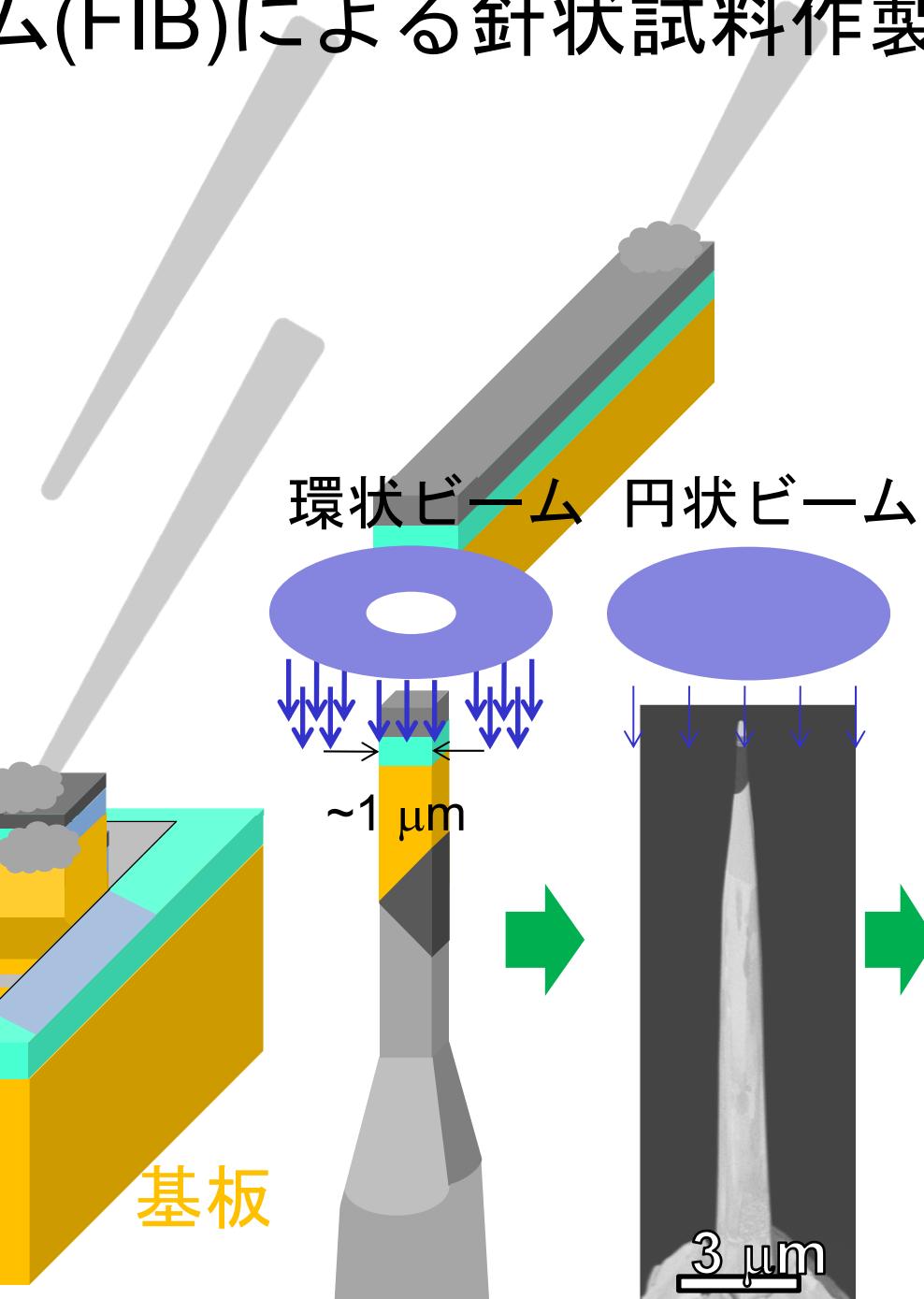
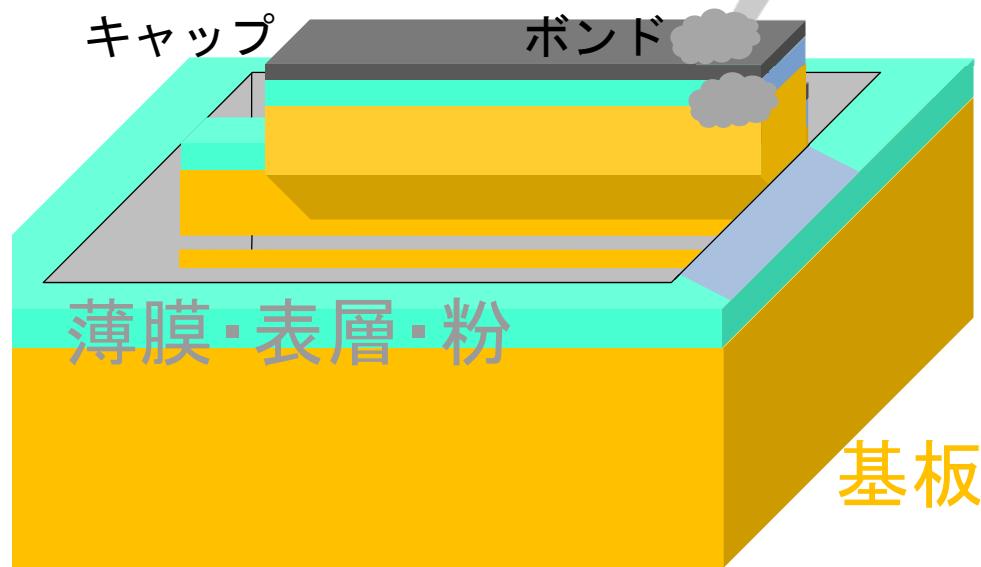


3DAPの応用範囲の拡大

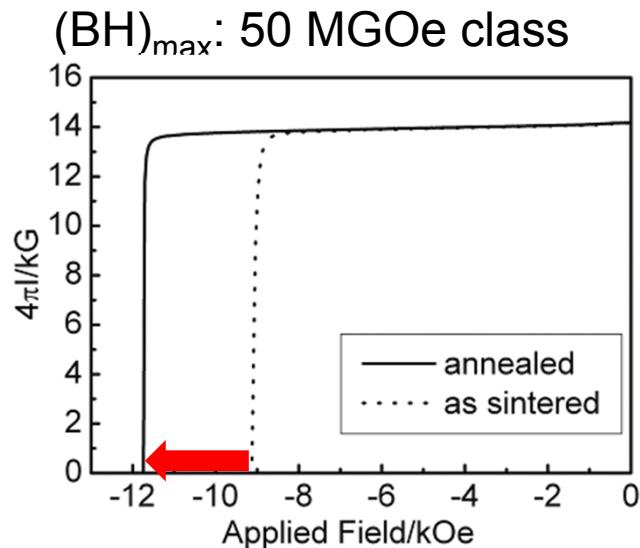
# 集束イオンビーム(FIB)による針状試料作製法



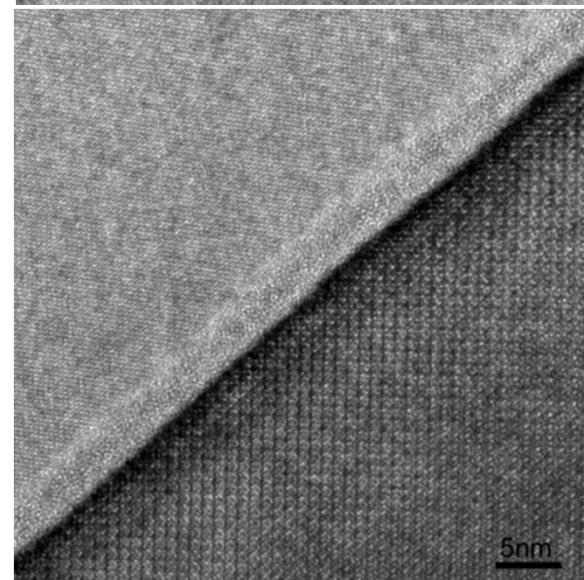
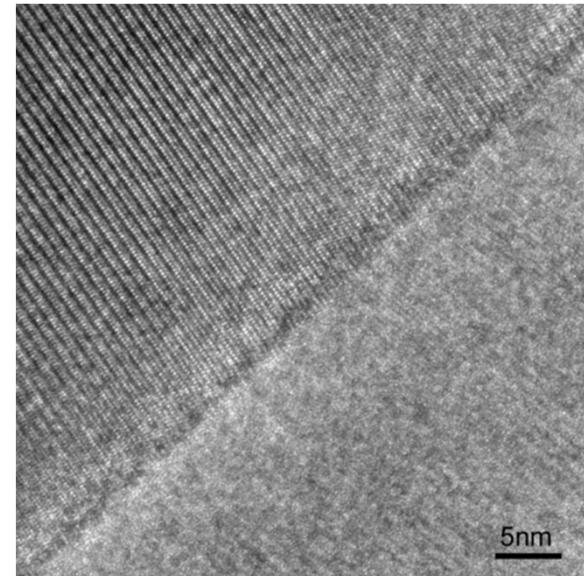
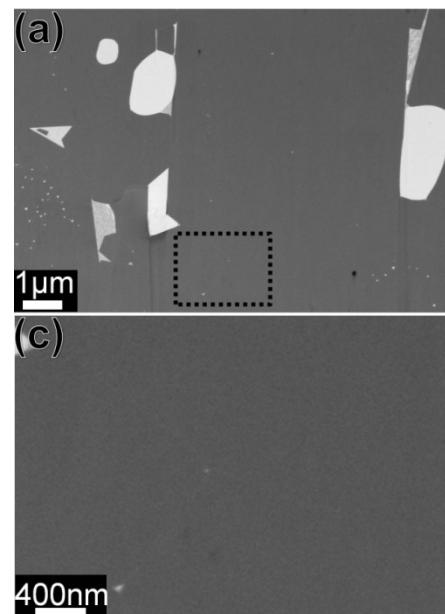
マイクロ  
マニピュレーター



# Nd-Fe-B焼結磁石の保磁力と結晶粒界



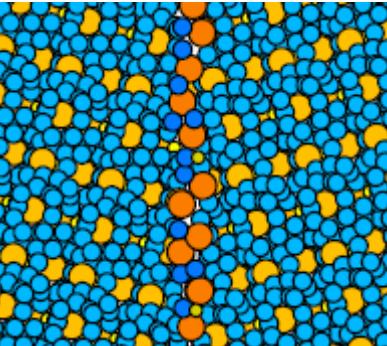
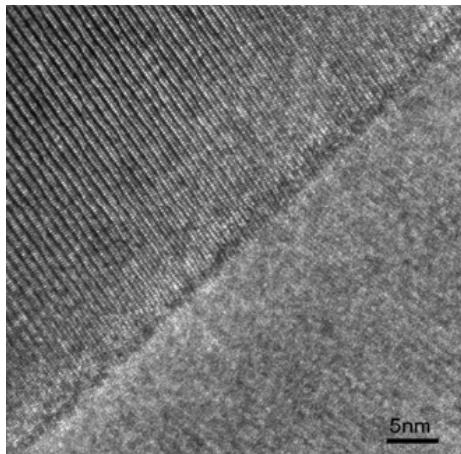
低保磁力



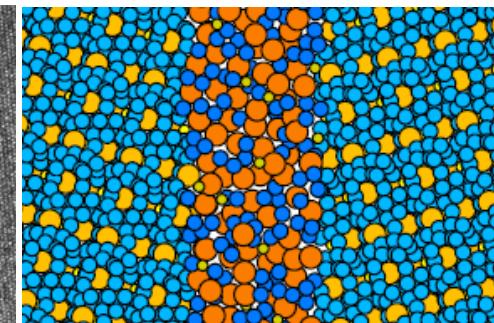
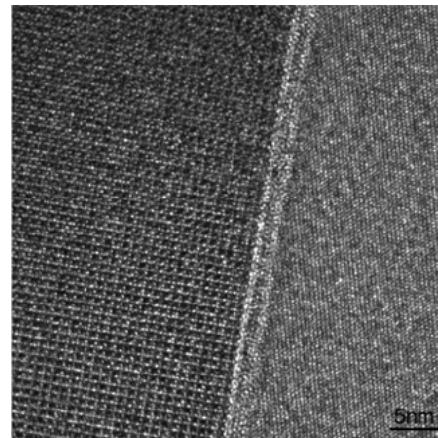
$\text{Nd}_{11.7}\text{Pr}_{2.8}\text{Fe}_{76.8}\text{B}_{6.0}\text{Al}_{0.5}\text{Cu}_{0.1}\text{O}_{2.1}$  (at. %)

# Nd-Fe-B焼結磁石の結晶粒界

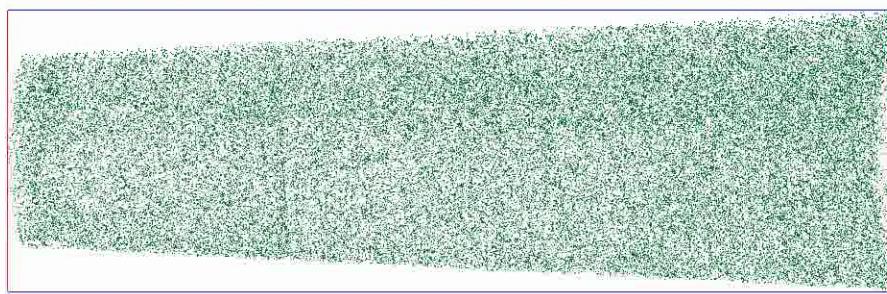
低保磁力



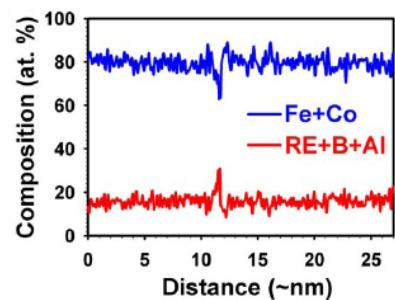
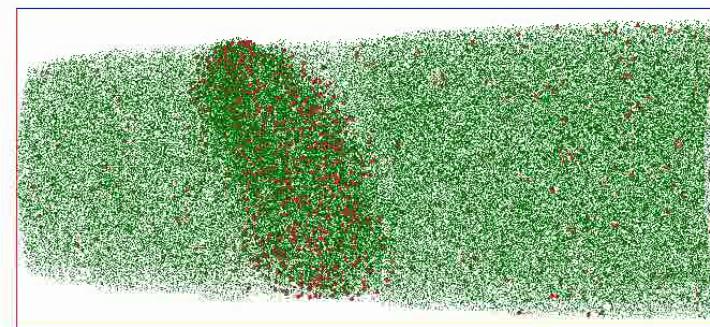
高保磁力



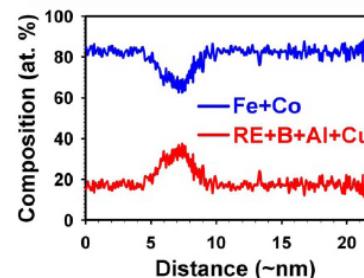
Nd  
Pr



Nd  
Pr

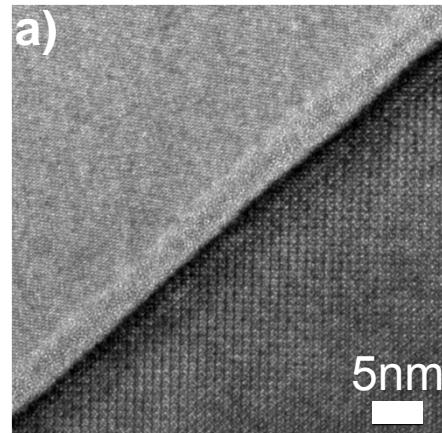


~70nm

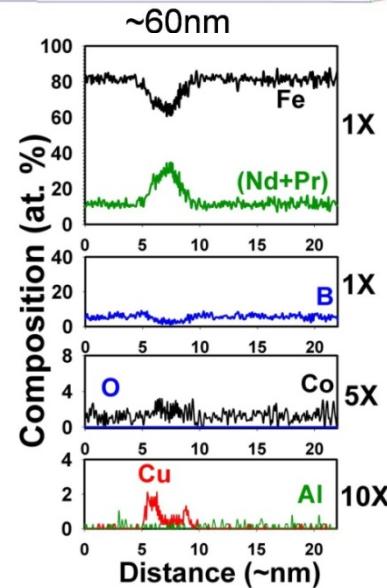
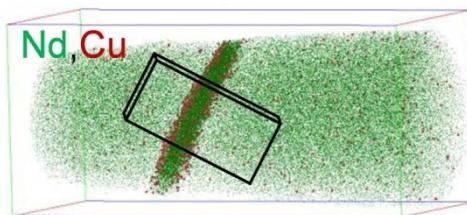


~57nm

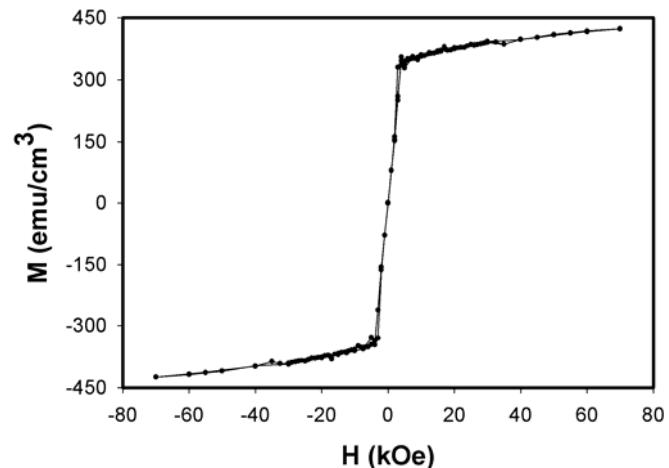
# 結晶粒界アモルファス相Nd<sub>30</sub>Fe<sub>66</sub>B<sub>3</sub>Cu<sub>1</sub>の磁性



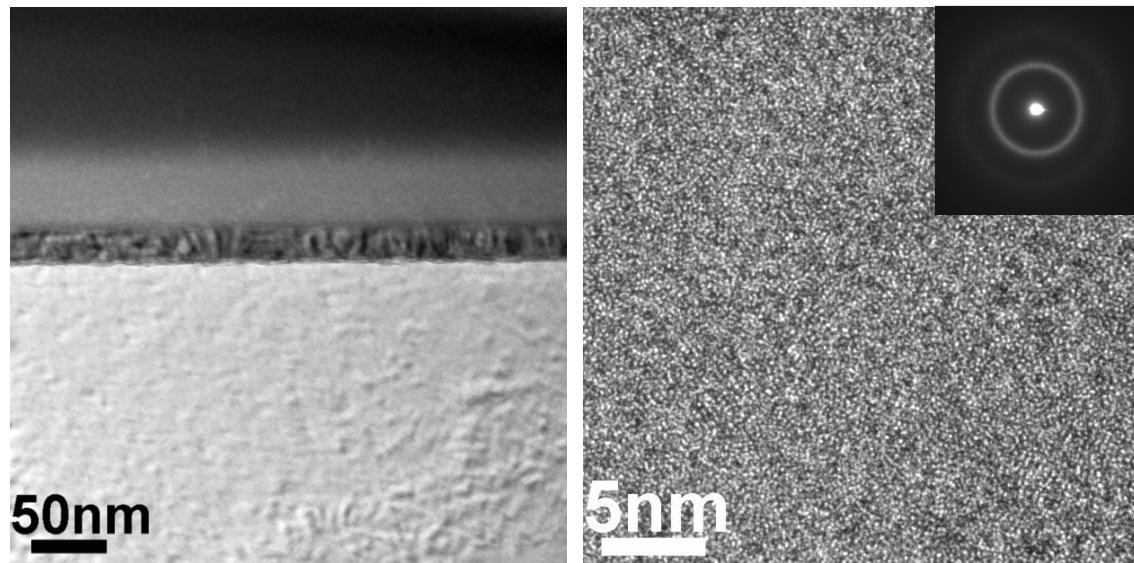
Mo	10nm
Nd-Fe-B-Cu	50nm
Mo	20nm
MgO	



Nd<sub>29.9</sub>Fe<sub>65.8</sub>B<sub>3.1</sub>Cu<sub>1.2</sub>

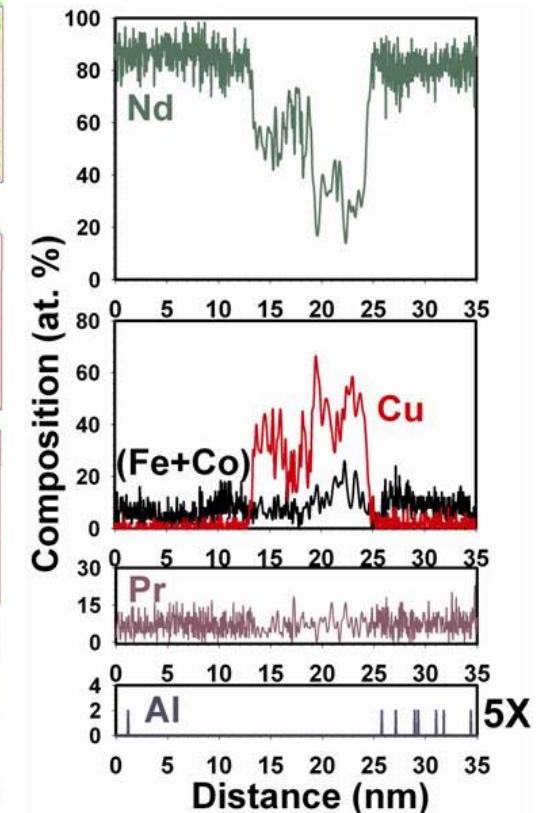
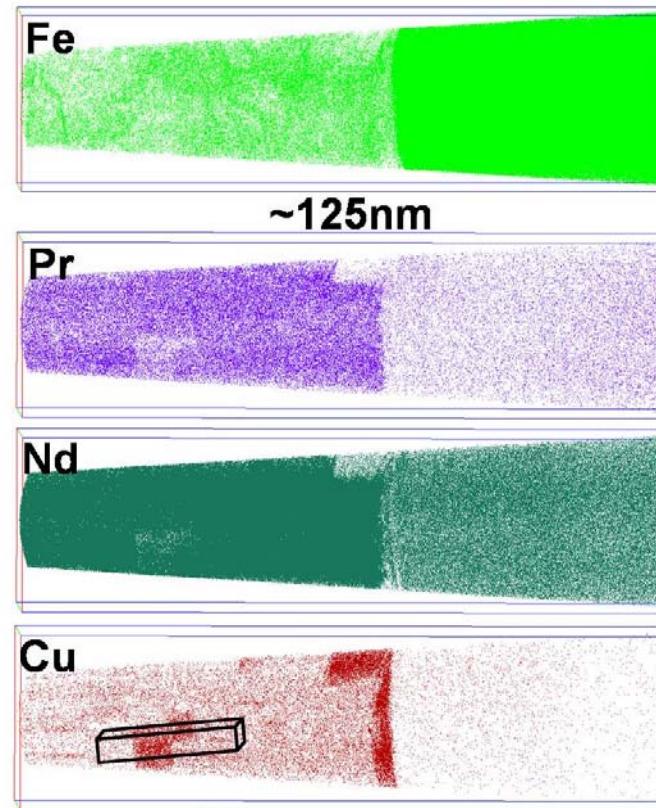
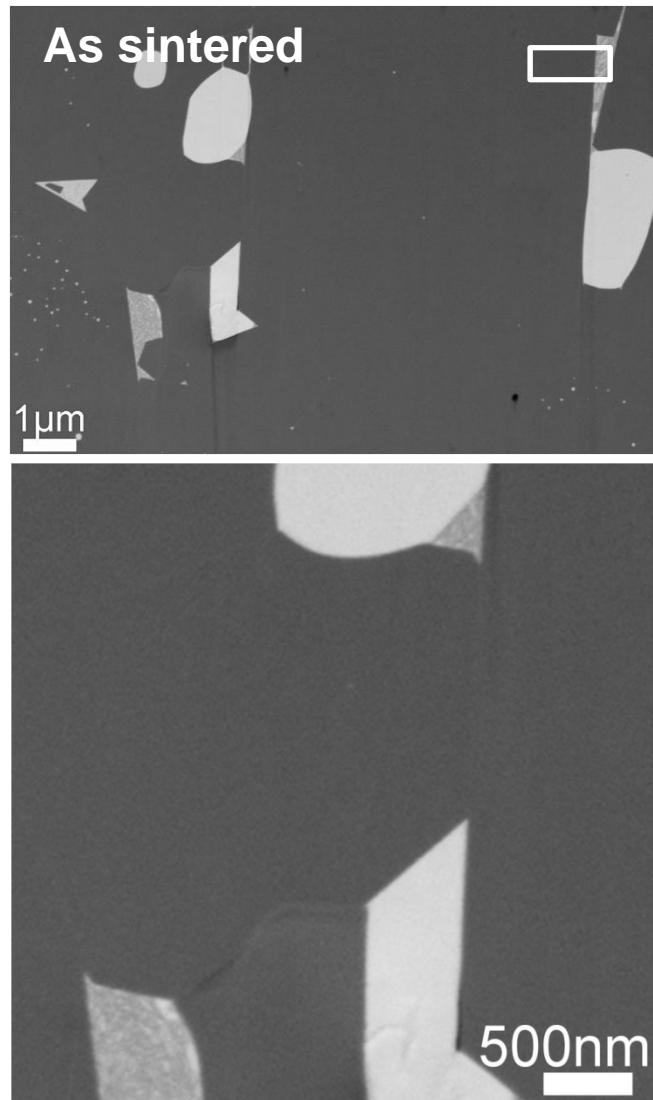


after T. Shima, Tohoku Gakuin



# Nd-リッチ相/Nd<sub>2</sub>Fe<sub>14</sub>B界面

Nd<sub>11.7</sub>Pr<sub>2.8</sub>Fe<sub>76.8</sub>B<sub>6.0</sub>Al<sub>0.5</sub>**Cu<sub>0.1</sub>**O<sub>2.1</sub> (at. %)



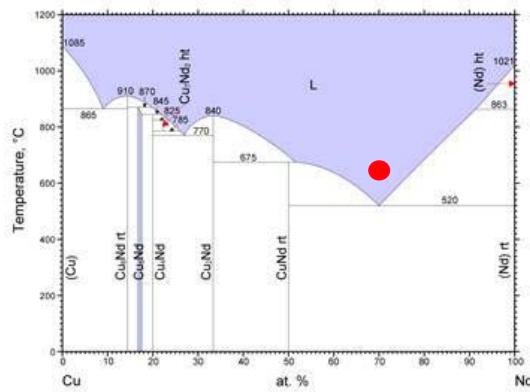
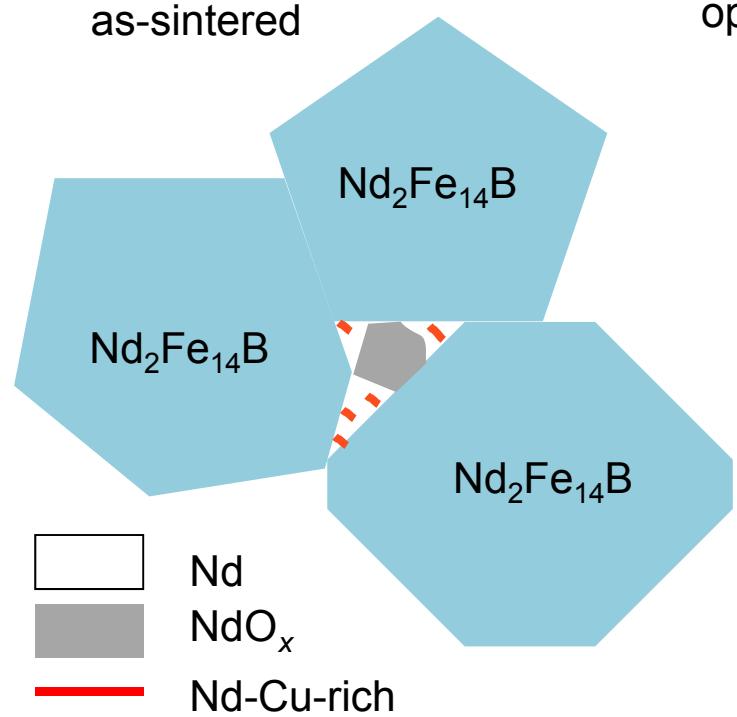
焼結ままの状態では、3重点のMetallic Nd相中に、Cuリッチな相が分散



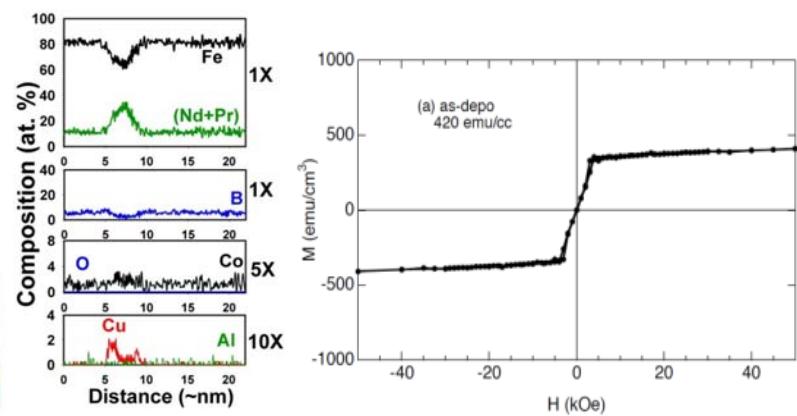
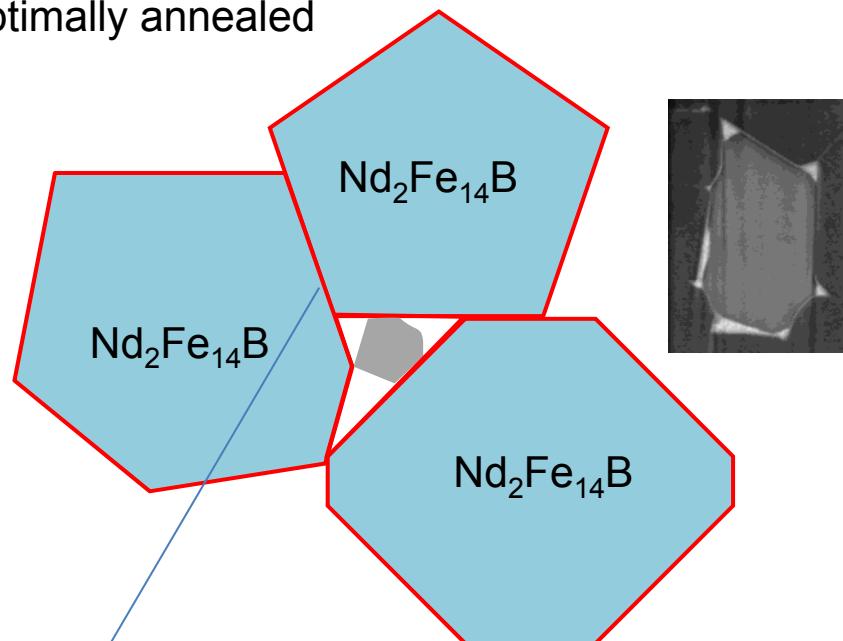
# Nd-Fe-B焼結磁石の最適化熱処理



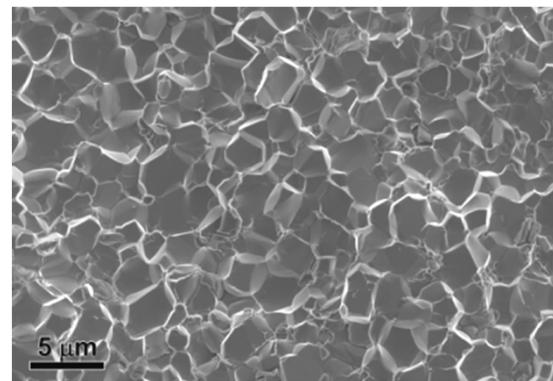
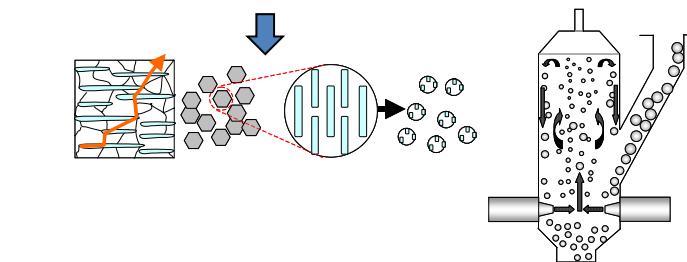
as-sintered



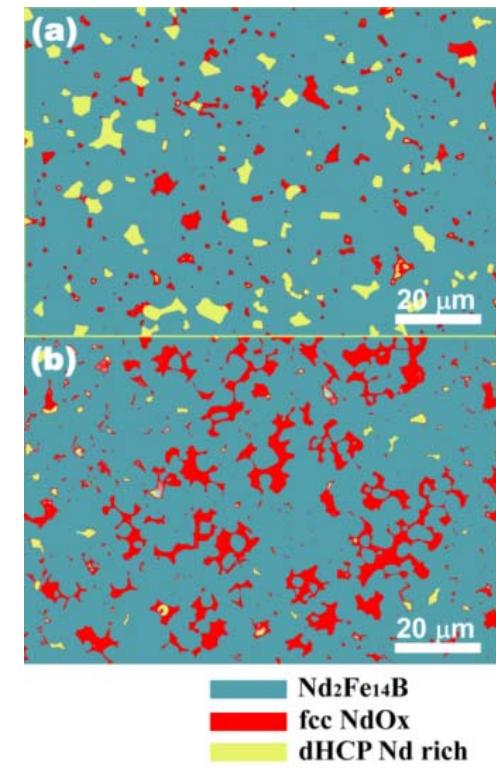
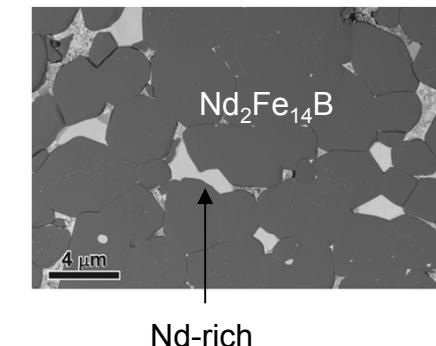
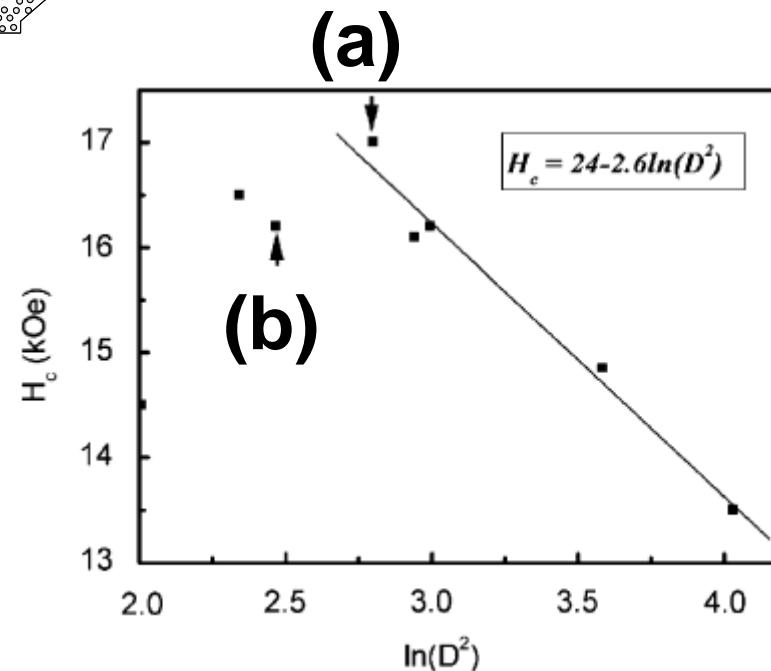
optimally annealed

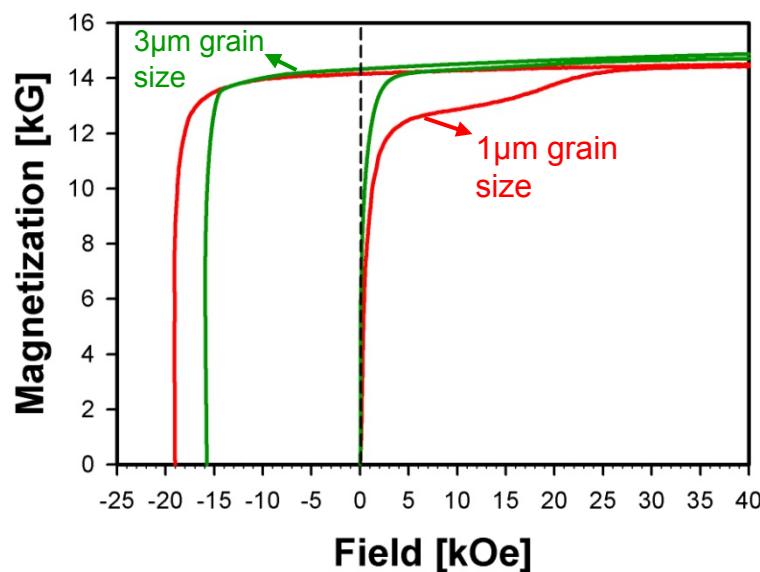
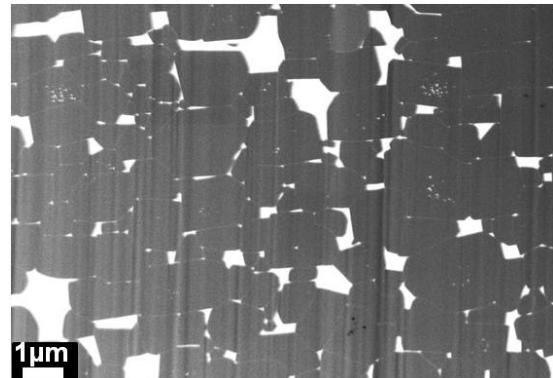


# 焼結磁石における微細化の限界

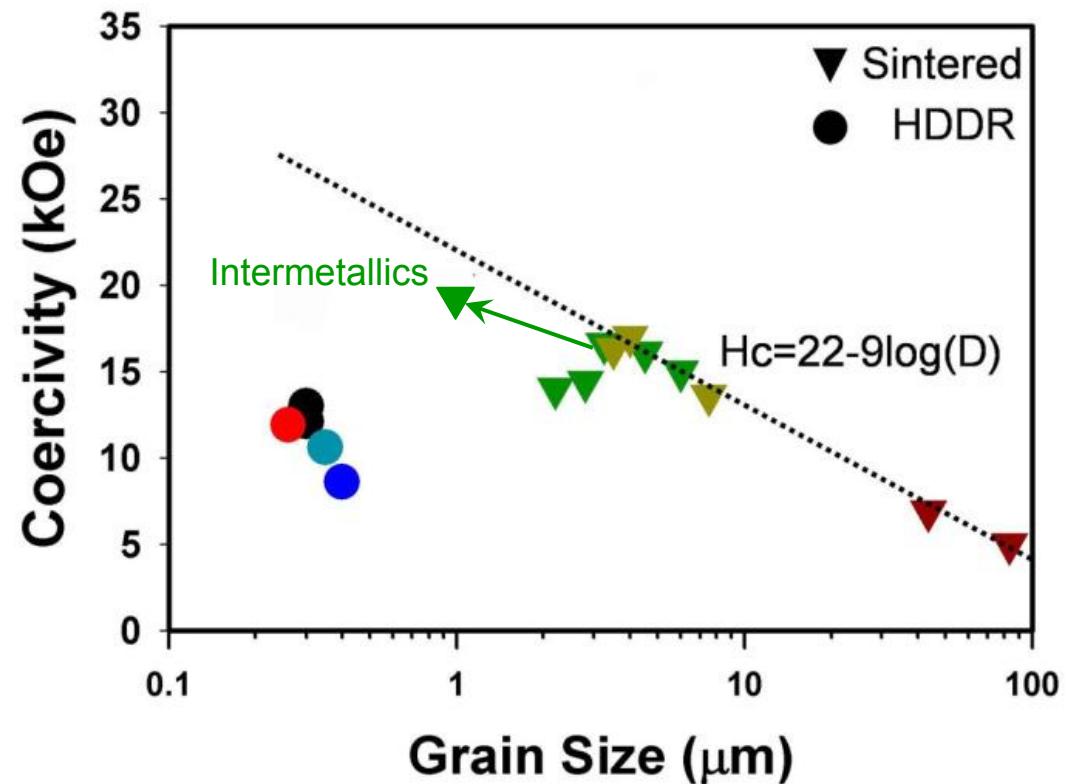


$D_{GB} \sim 1.5 D_{powder}$

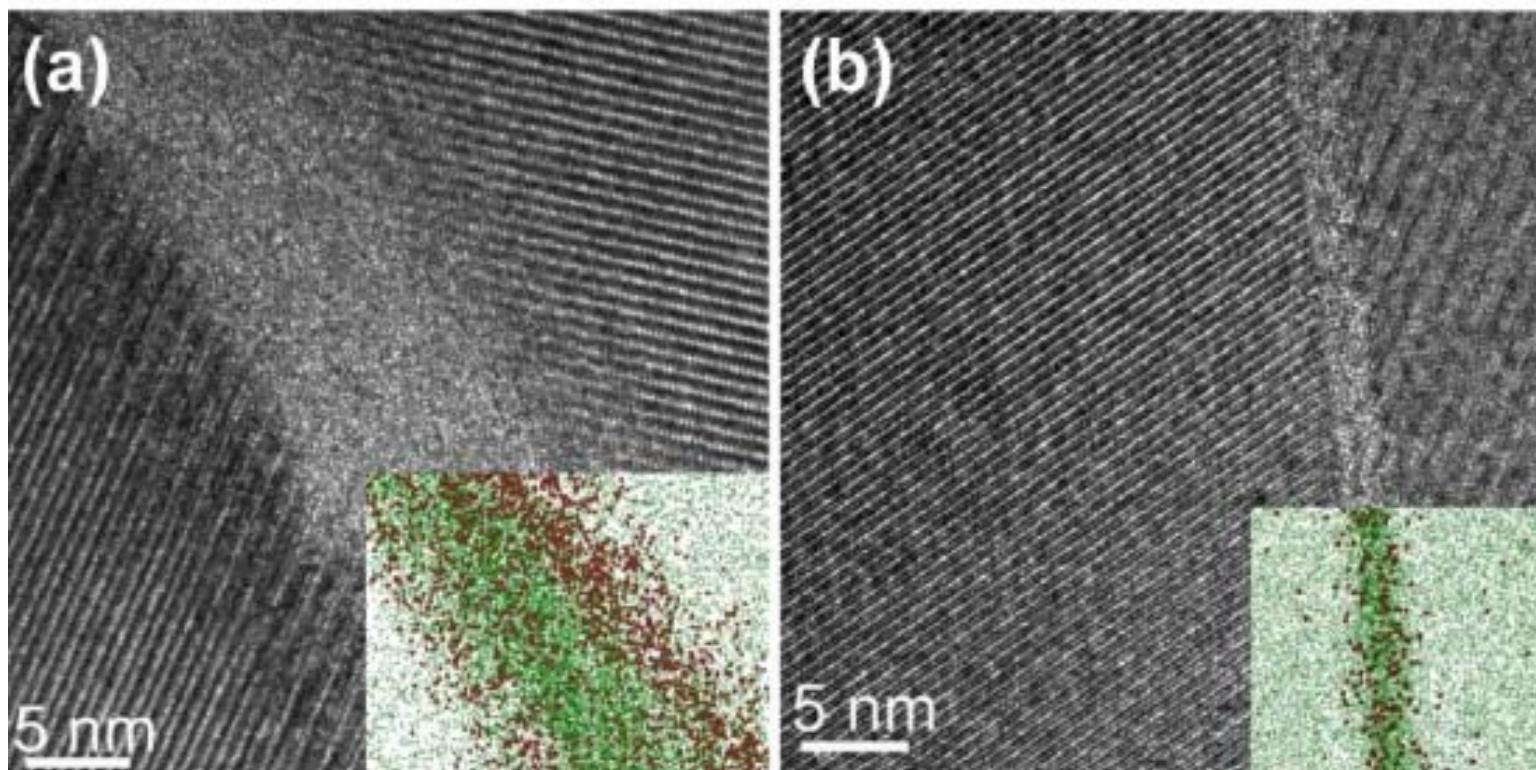
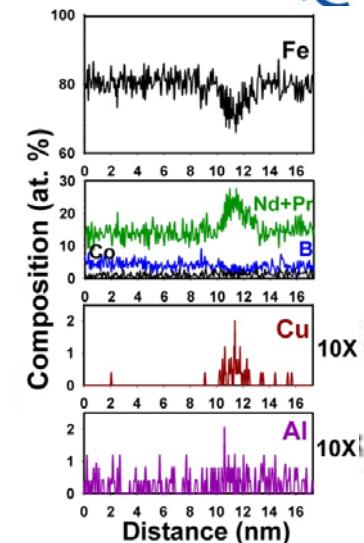
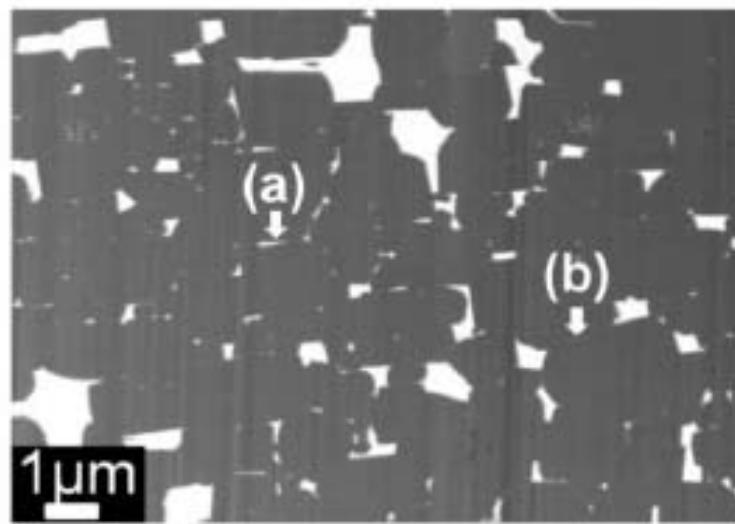
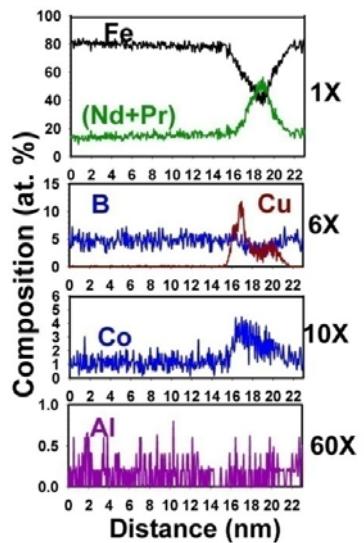




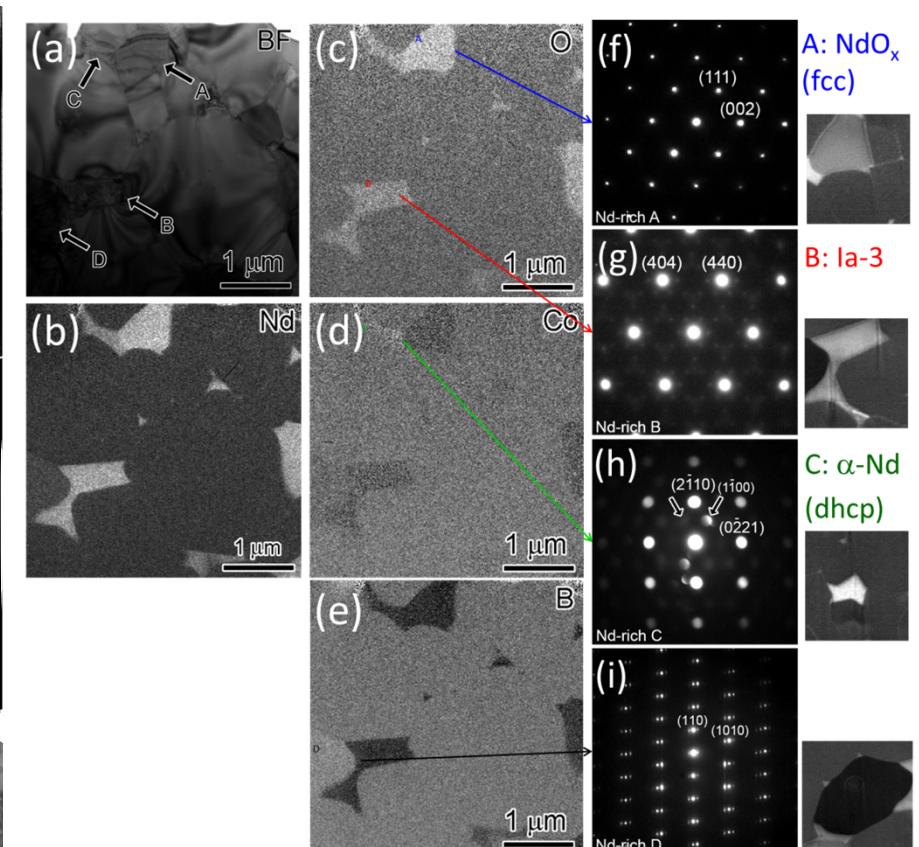
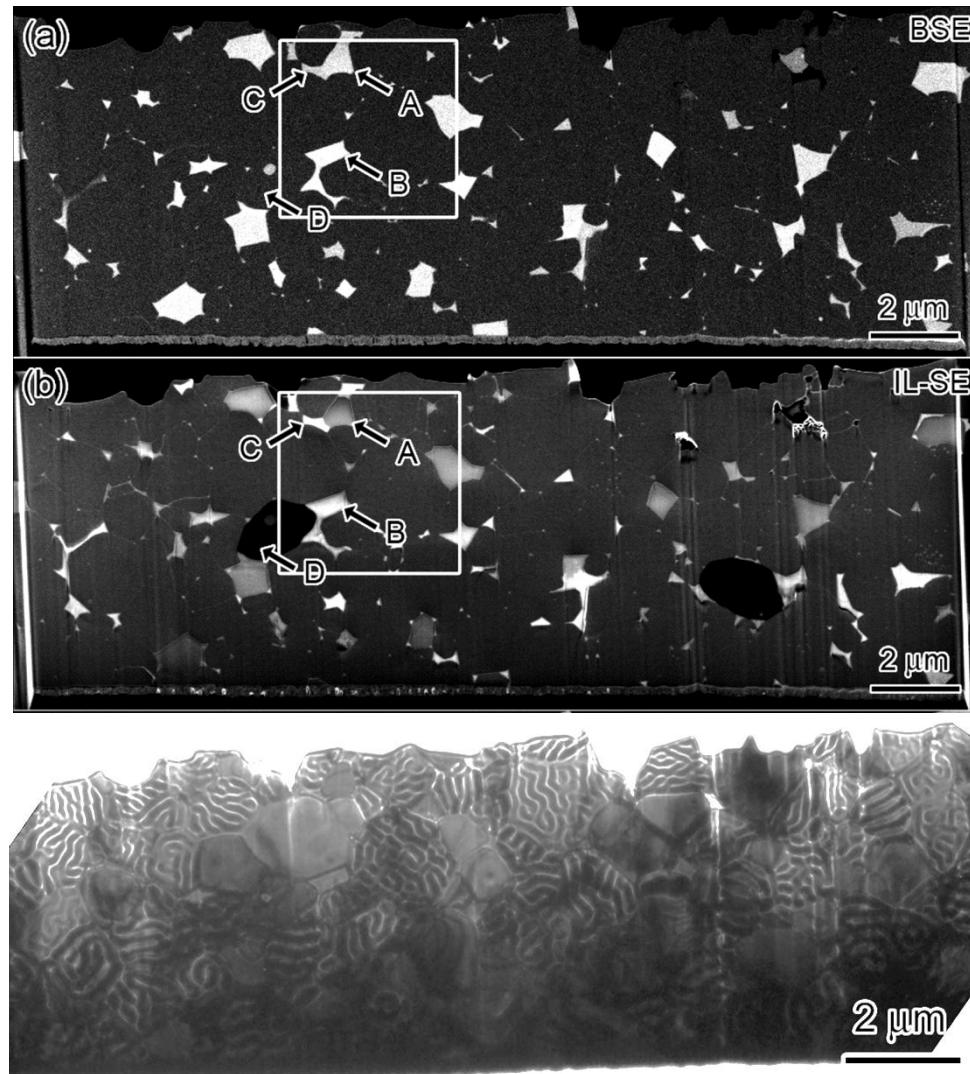
Hc (kOe)	(BH) <sub>max</sub> (MGoe)
20	50



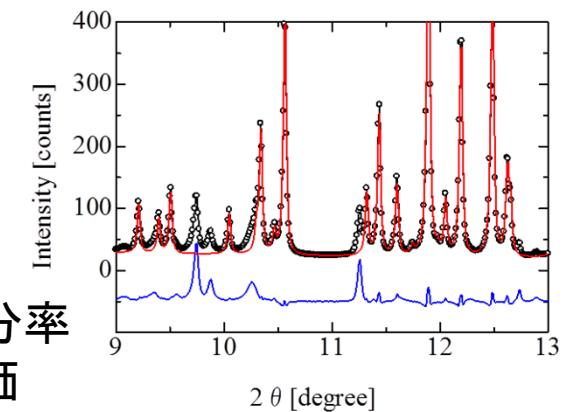
# 厚い粒界層と薄い粒界層



# 複相の体積分率の定量評価

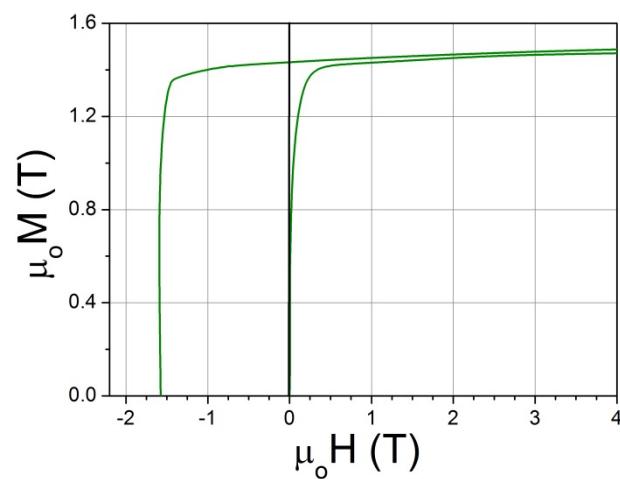
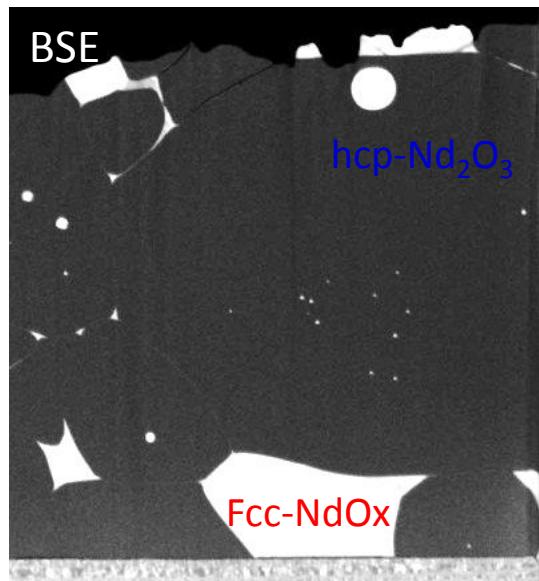


SPring-8  
J-PARC

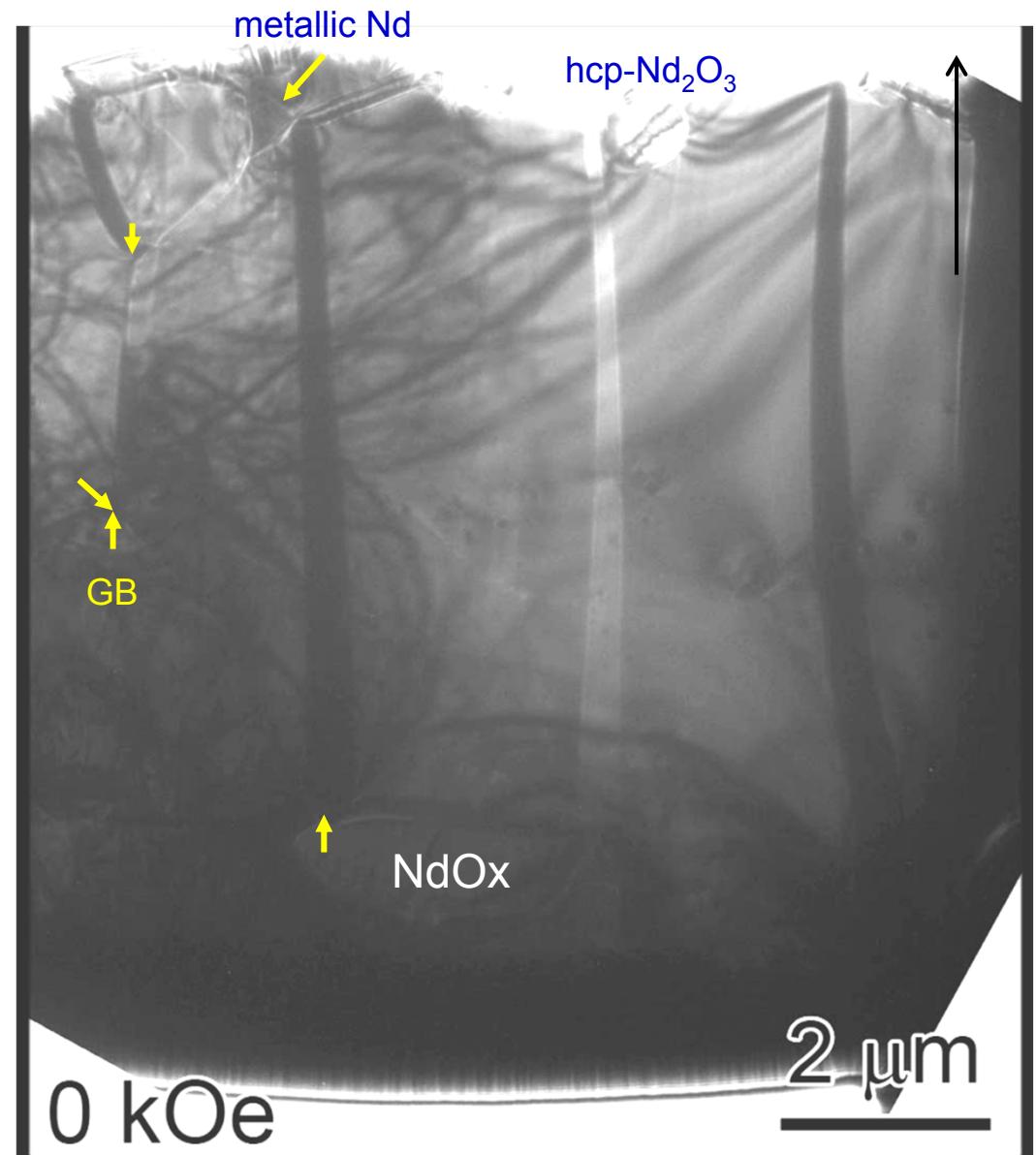


SEM/TEMで同定した複相の体積分率  
をX線回折、中性子回折で定量評価

# 商用磁石における磁壁の結晶粒界によるピニング Lorentz microscopy

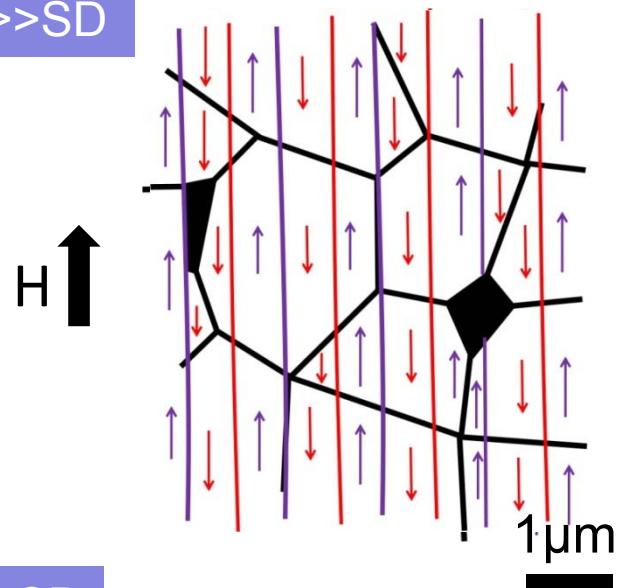


T. T. Sasaki, unpublished.

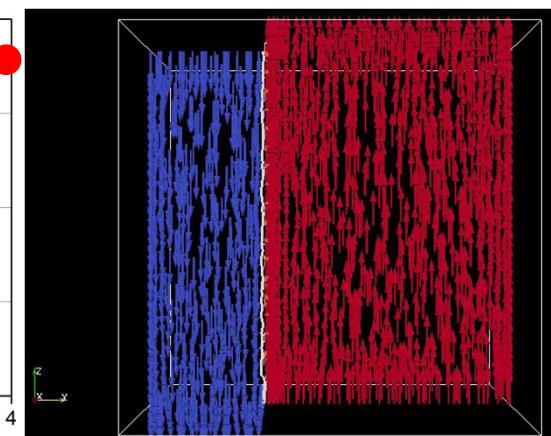
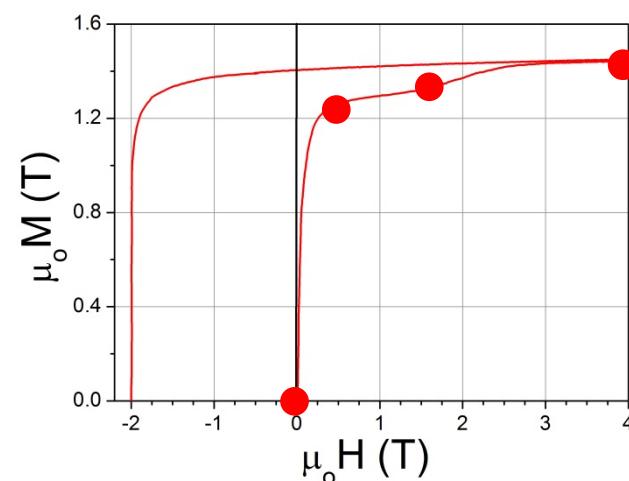
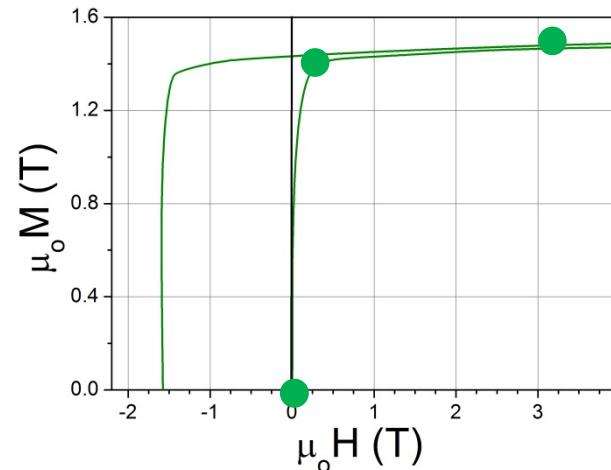
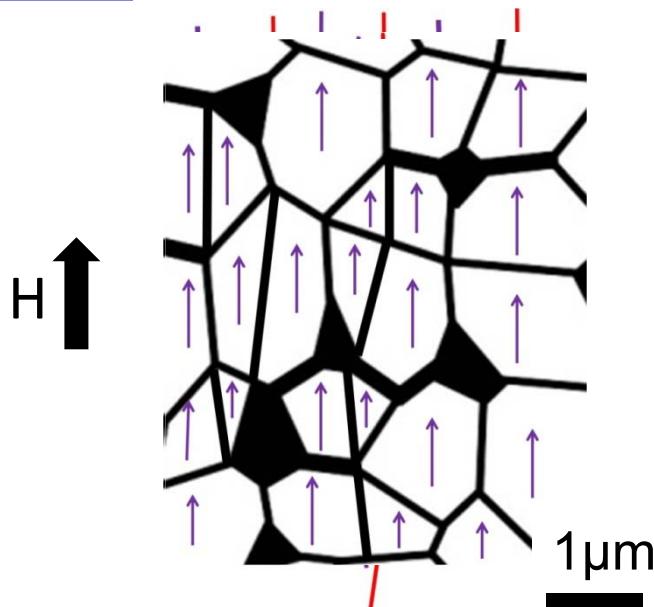


# Initial magnetization curves for D~SD

D>>SD

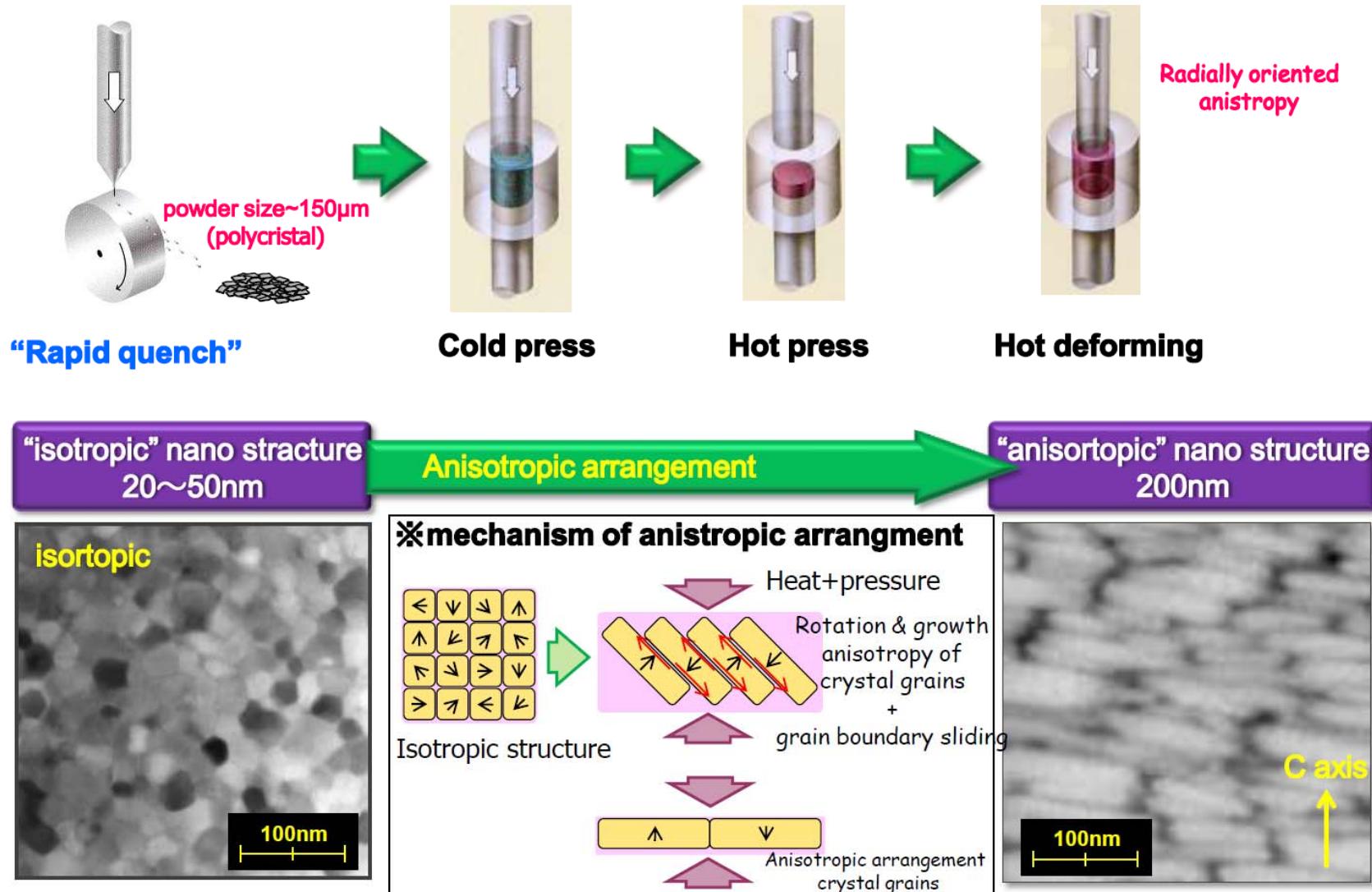


D~SD

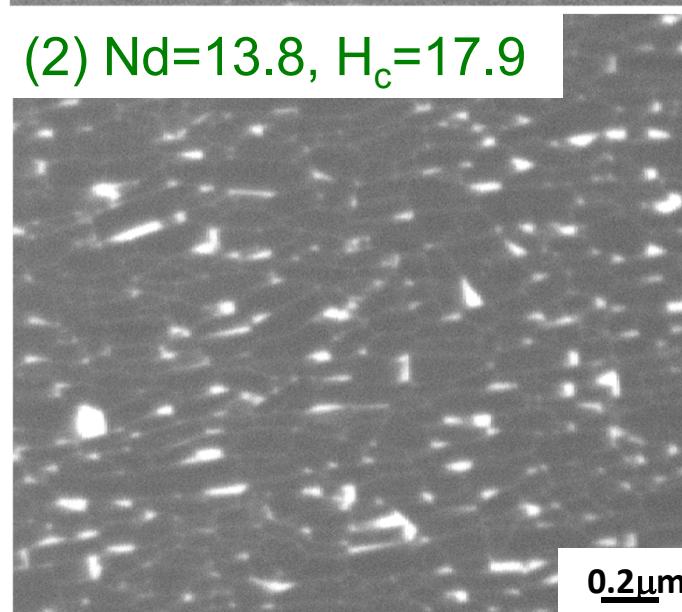
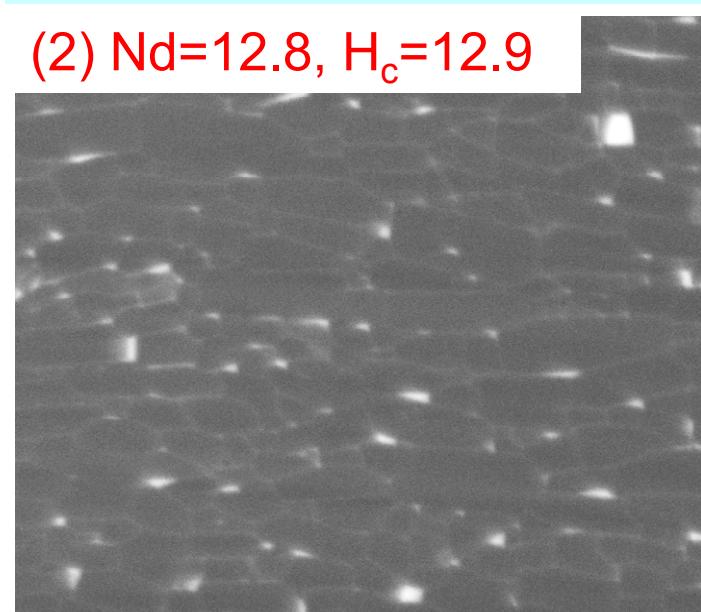
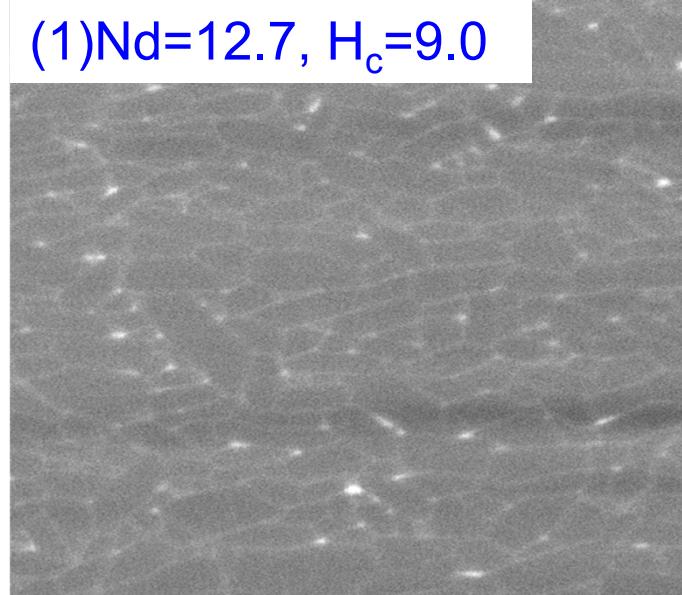
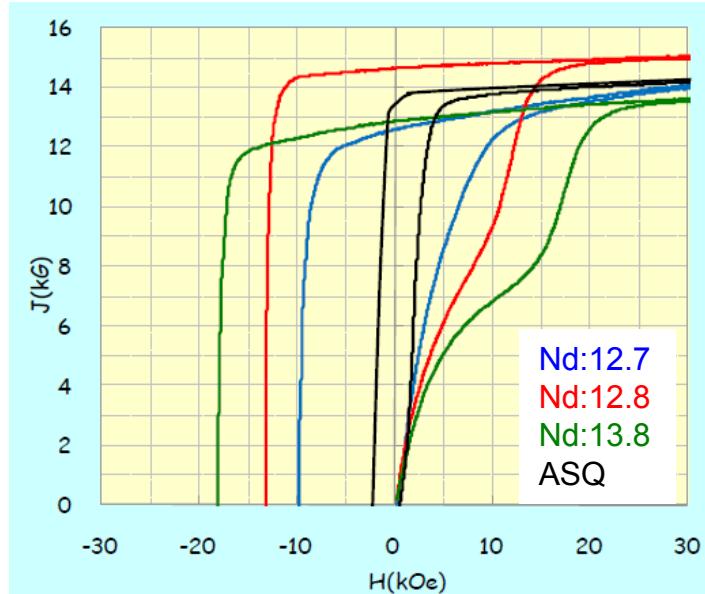


# 熱間圧延異方性磁石

## ■ Manufacture process of MQ3

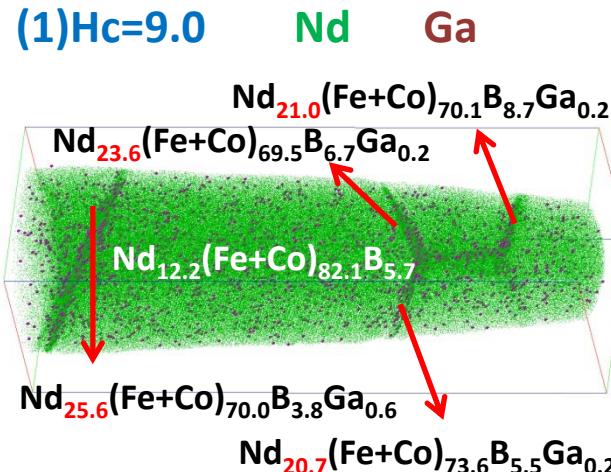


# 熱間加工磁石のNd濃度と $H_c$

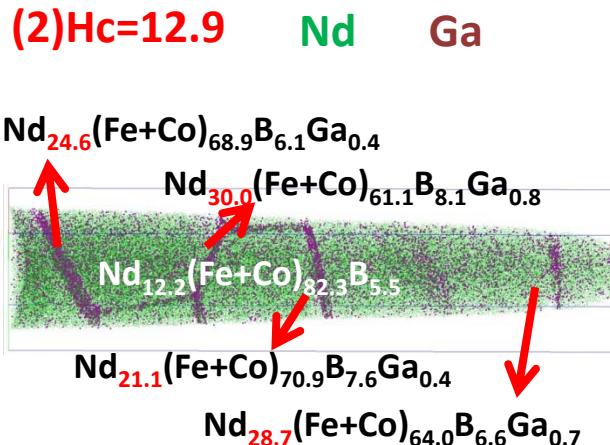


# 結晶粒界のNd濃度とH<sub>c</sub>

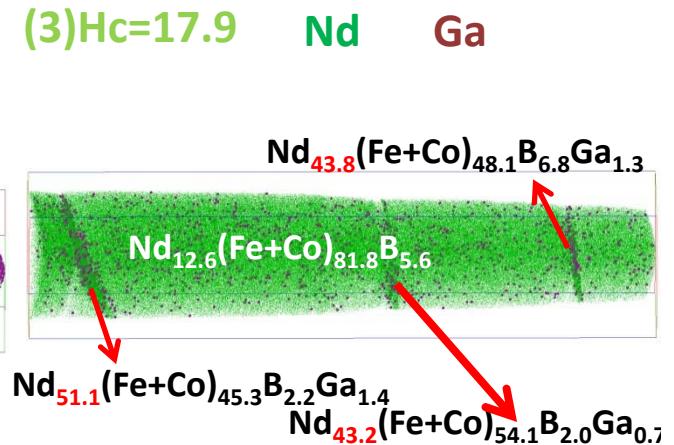
(1) H<sub>c</sub>=9.0



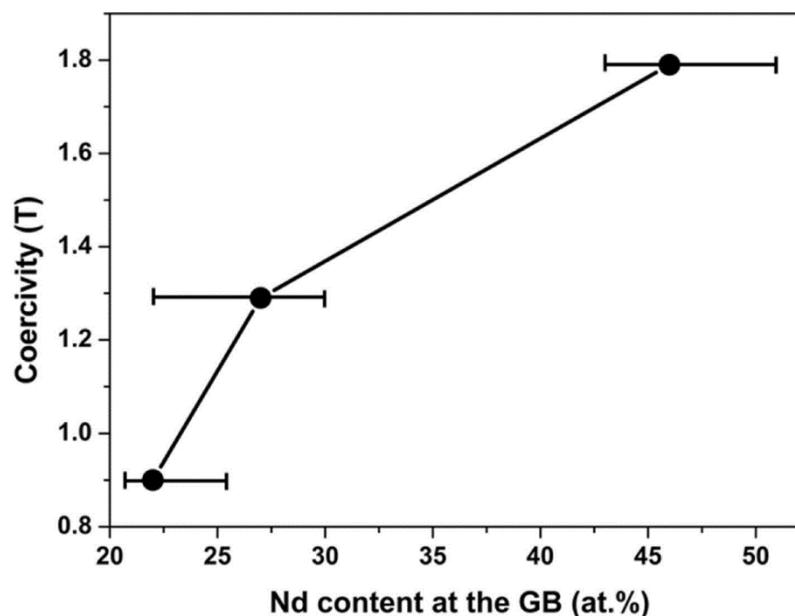
(2) H<sub>c</sub>=12.9



(3) H<sub>c</sub>=17.9

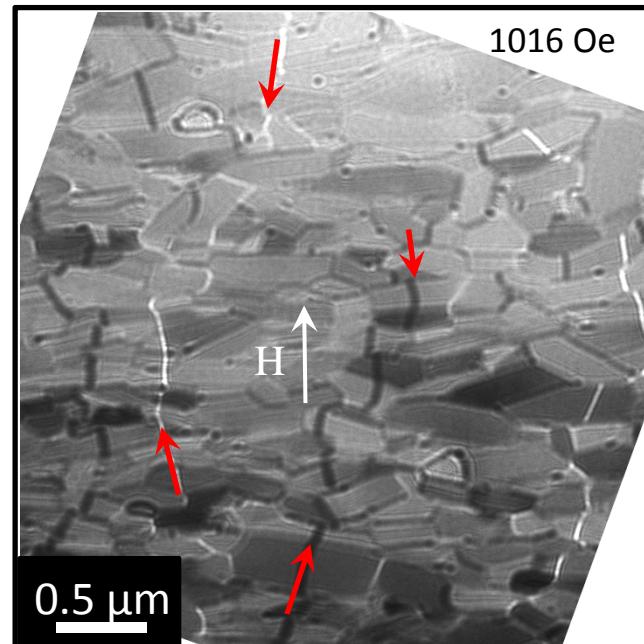
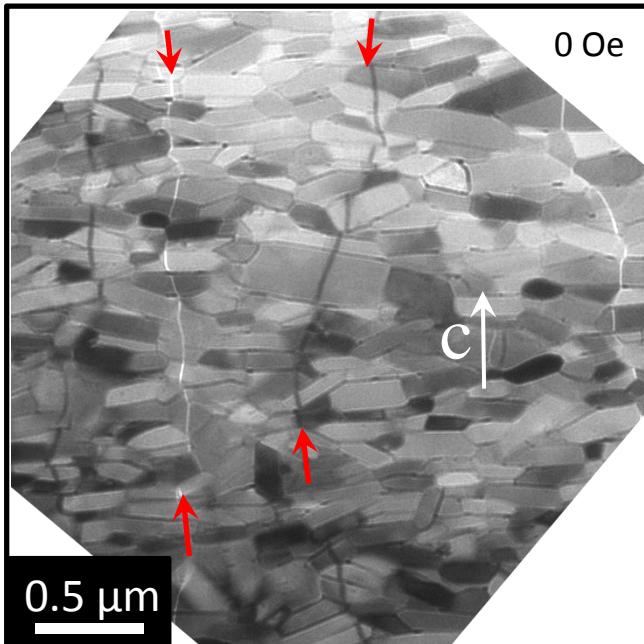


stoichiometry:  
 $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$

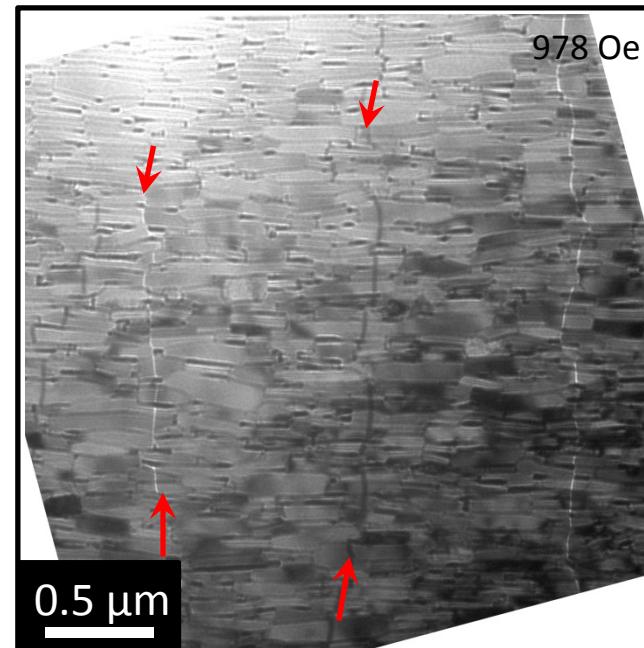
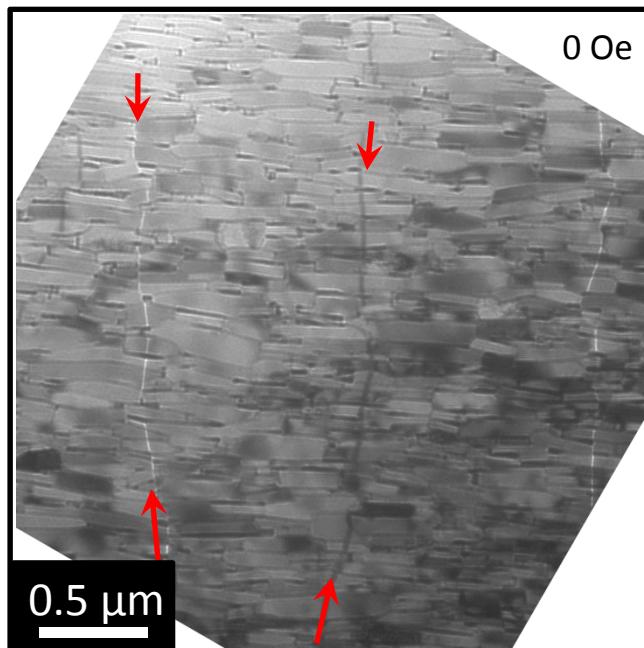


# Lorentz TEM observation

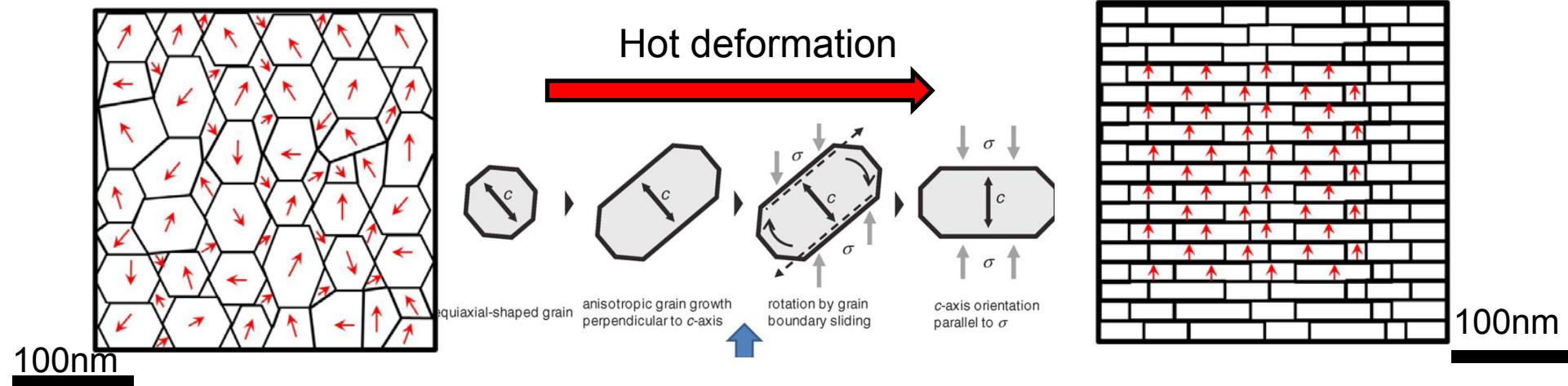
Sample (1)  
 $H_c=0.9T$



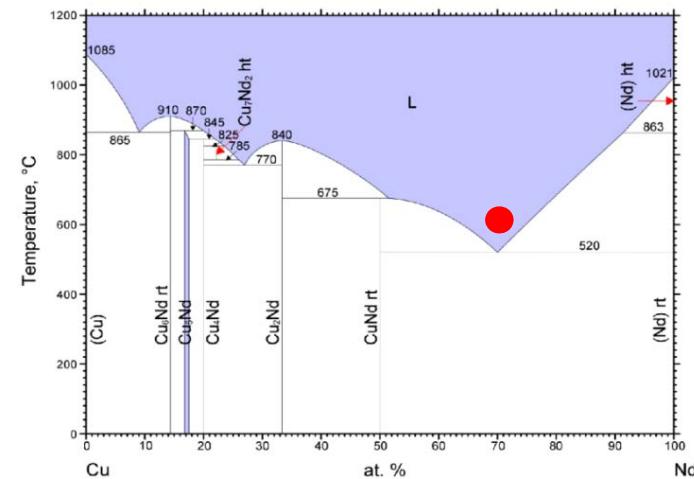
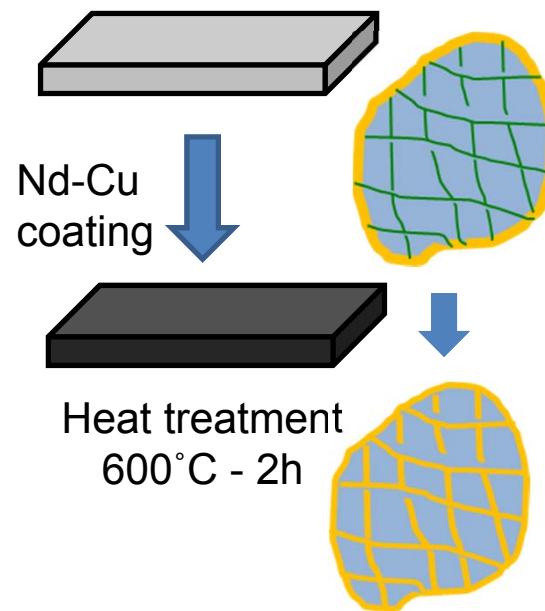
Sample (3)  
 $H_c=1.79T$



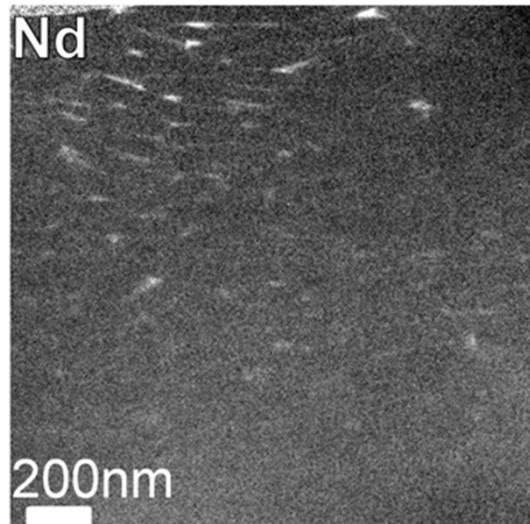
# 熱間加工磁石へのNd-Cu拡散法の適応



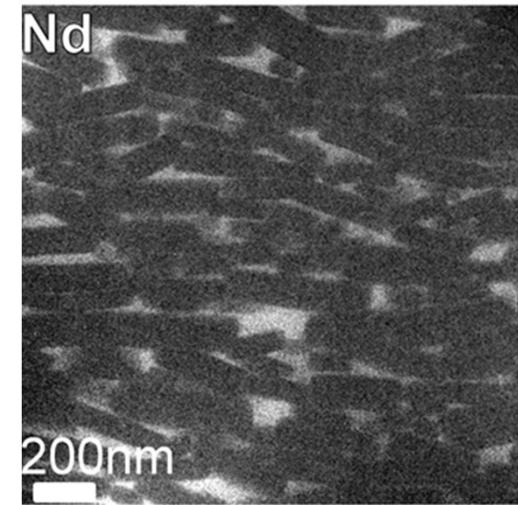
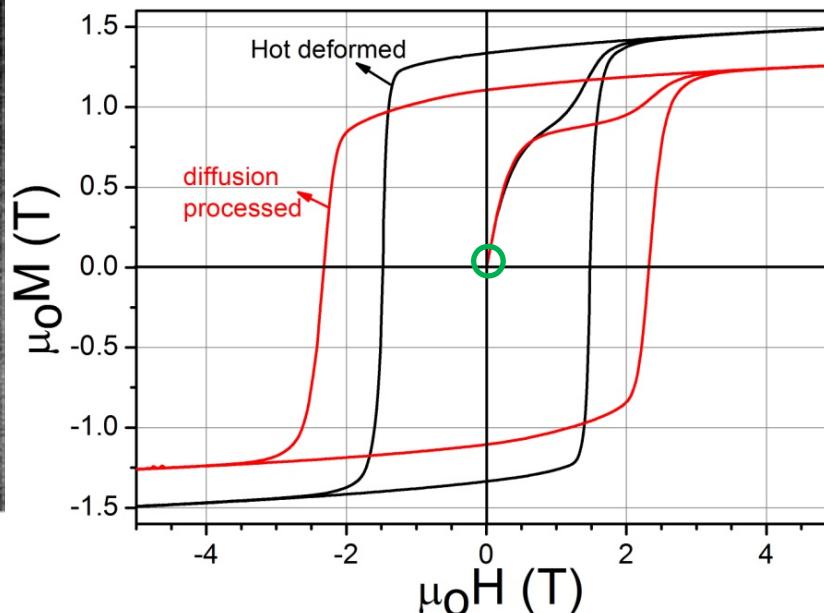
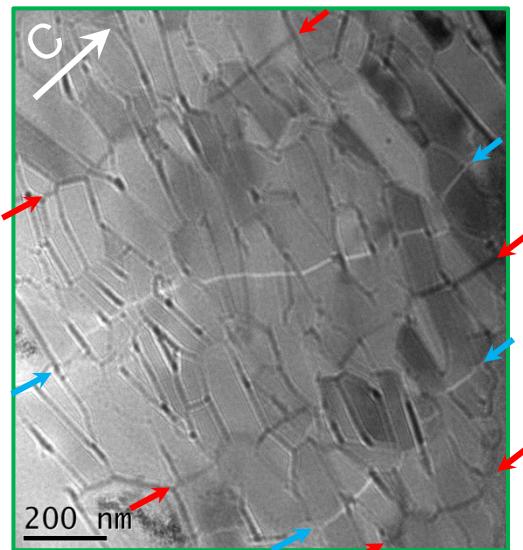
Hot deformed magnet  
 $Nd_{14}Fe_{76}Co_{3.4}B_6Ga_{0.6}$  (at. %)



# 熱間圧延異方性磁石へのNd-Cu拡散処理 **TOYOTA**



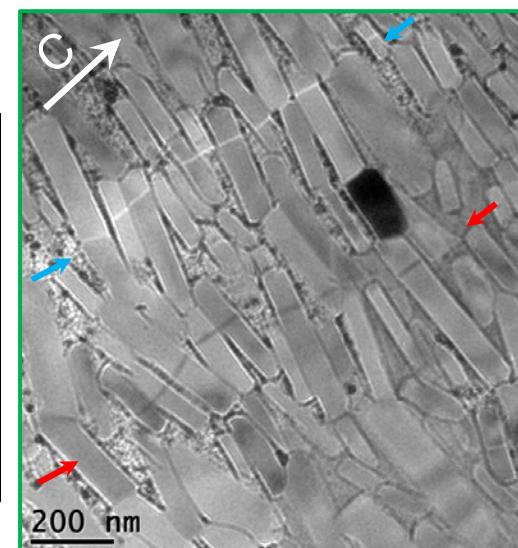
Hot deformed



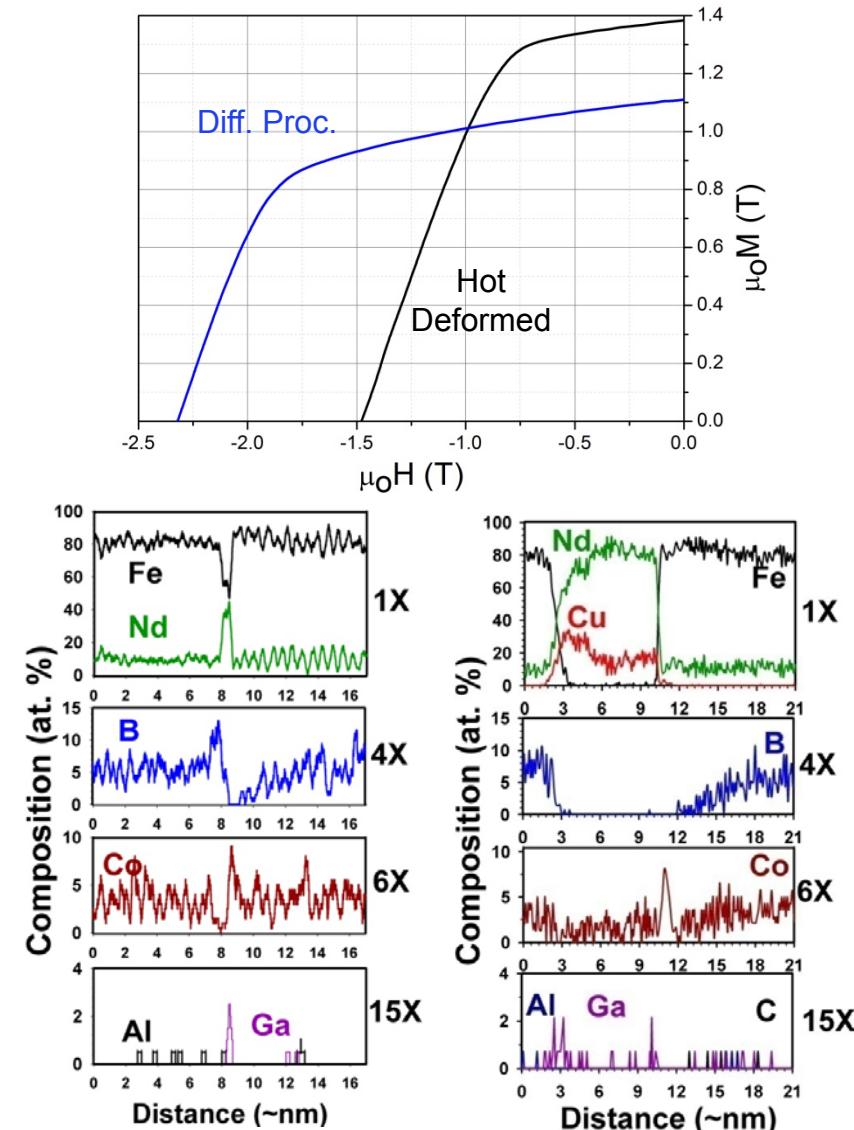
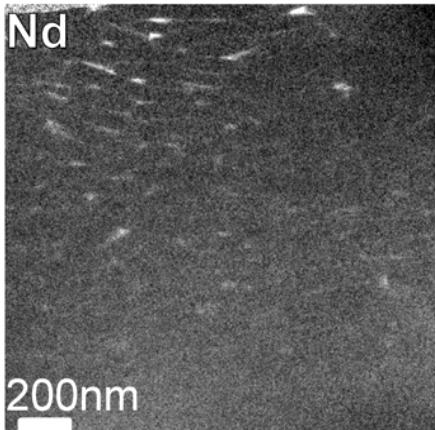
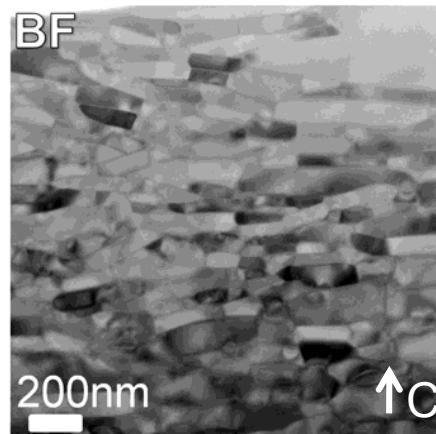
Diffusion Processed

	$\mu_0Mr$ (T)	$\mu_0Hc$ (T)	$(BH)_{max}$ (kJ/m <sup>3</sup> )
Hot Deformed	1.35	1.5	340
Diffusion Processed	1.11	2.3	228
(Nd,Dy)-Fe-B sintered magnets*	1.12	3.0	247

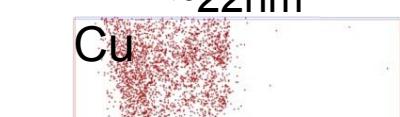
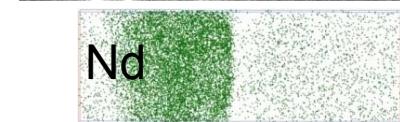
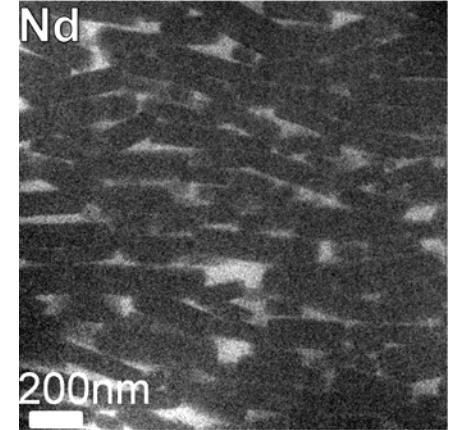
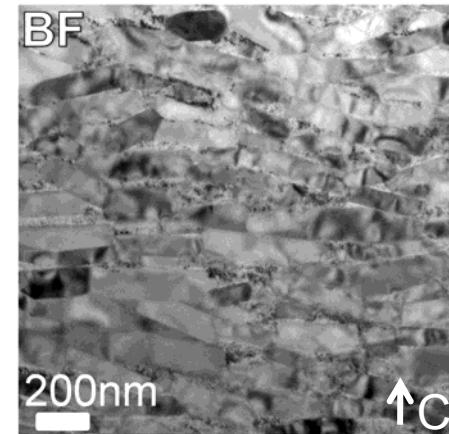
\* Shinetsu N30ZA type magnet: [http://www.shinetsu-rare-earth-magnet.jp/e/products/data\\_nd.html](http://www.shinetsu-rare-earth-magnet.jp/e/products/data_nd.html)



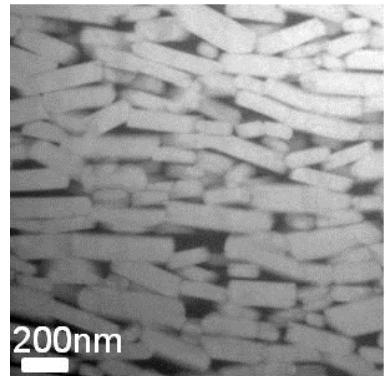
Hot deformed



diffusion processed



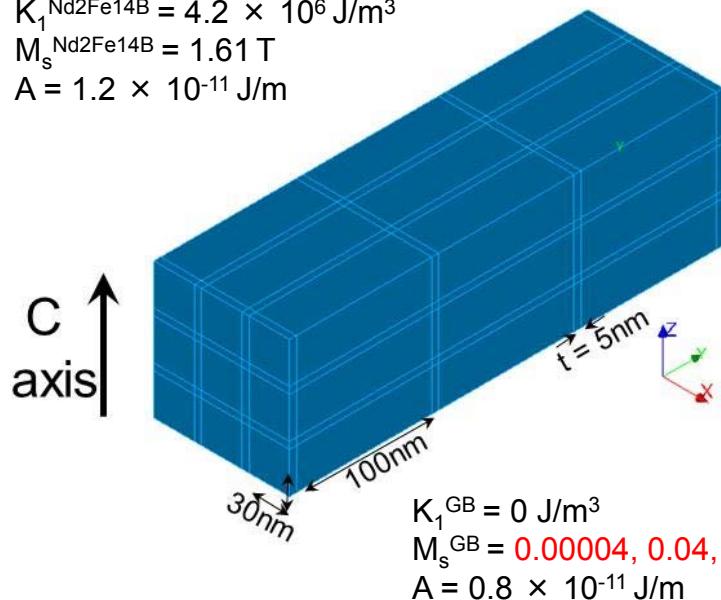
# 結晶粒界の磁性と $H_c$



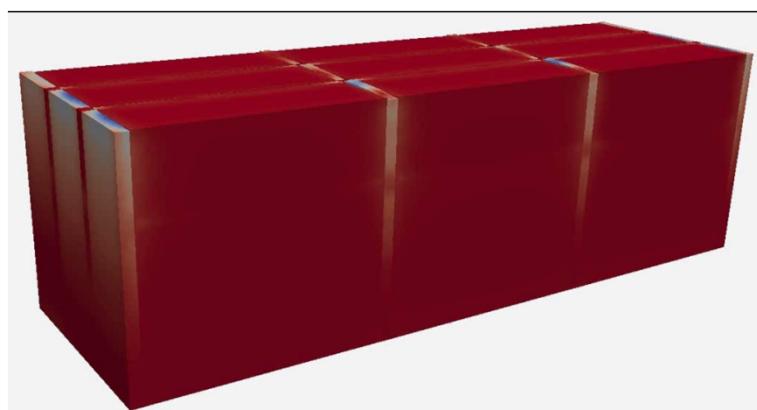
$$K_1^{\text{Nd}2\text{Fe}14\text{B}} = 4.2 \times 10^6 \text{ J/m}^3$$

$$M_s^{\text{Nd}2\text{Fe}14\text{B}} = 1.61 \text{ T}$$

$$A = 1.2 \times 10^{-11} \text{ J/m}$$



$$M_s^{\text{GB}} = 1 \text{ T}$$



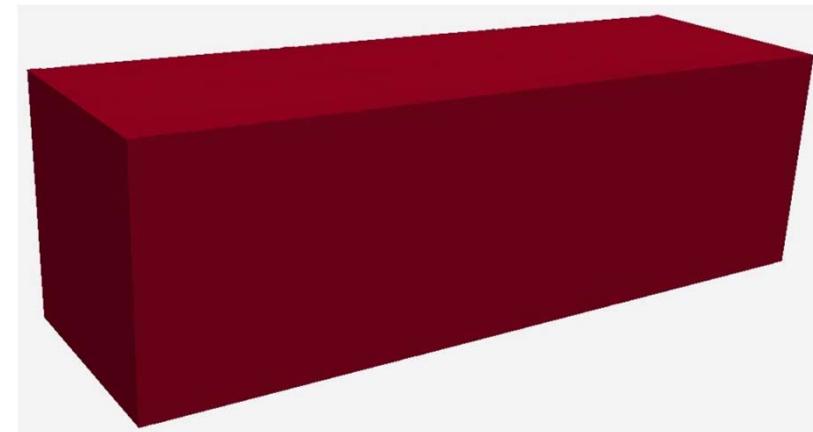
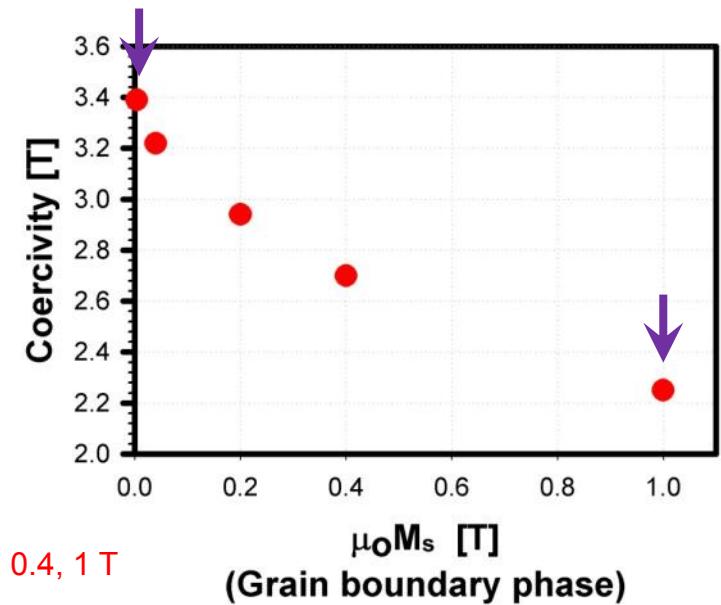
$$\begin{matrix} \uparrow M \\ \downarrow M \end{matrix}$$

$$K_1^{\text{GB}} = 0 \text{ J/m}^3$$

$$M_s^{\text{GB}} = 0.00004, 0.04, 0.2, 0.4, 1 \text{ T}$$

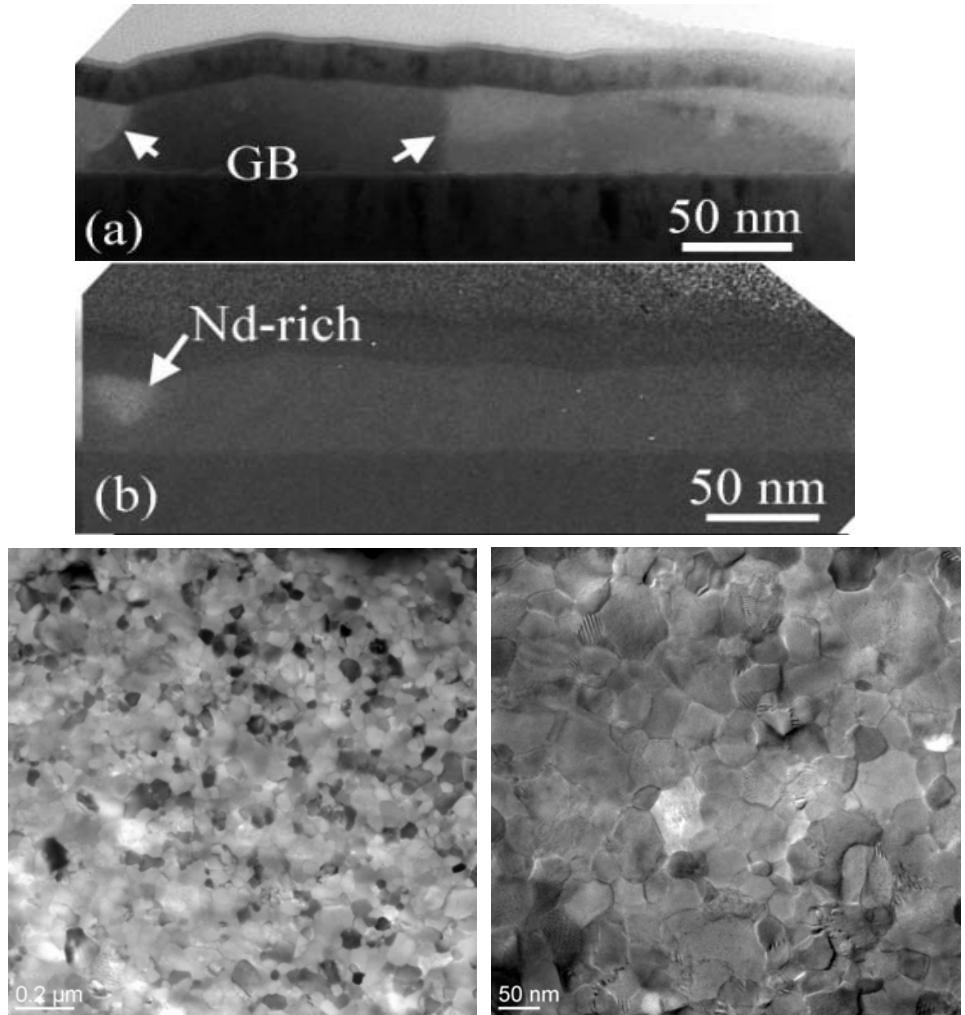
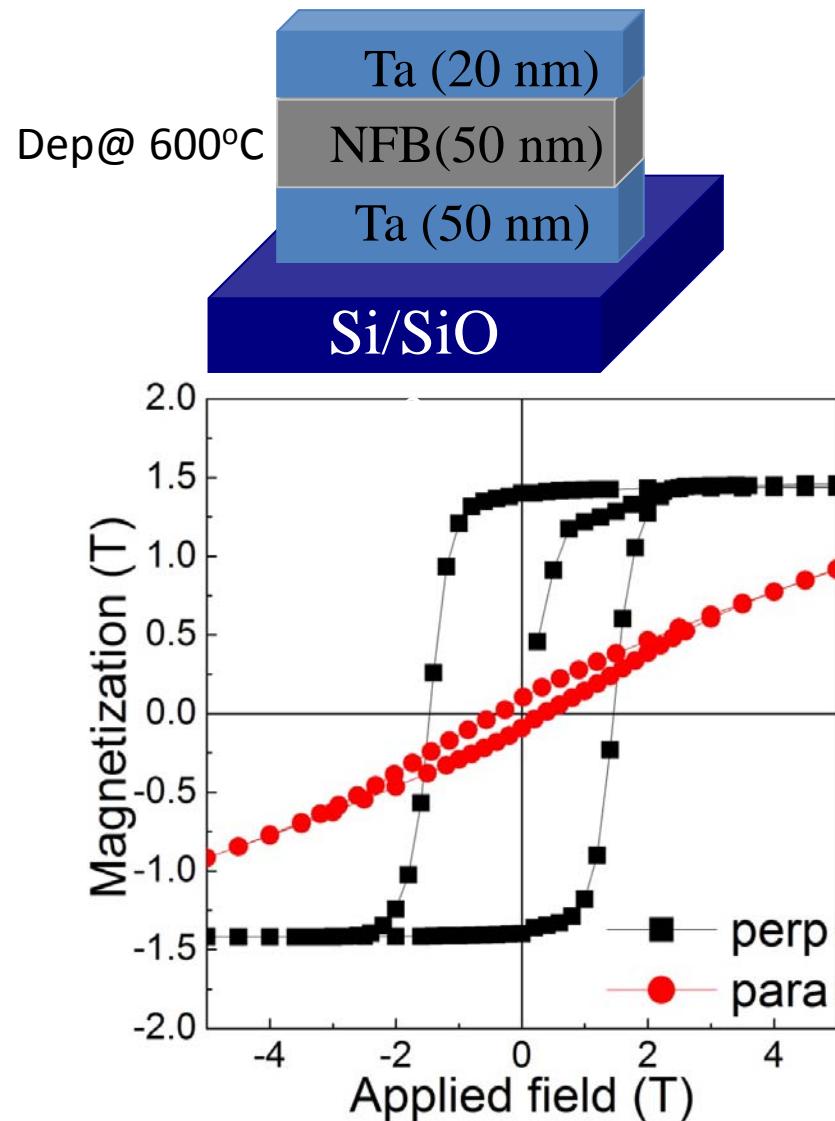
$$A = 0.8 \times 10^{-11} \text{ J/m}$$

$$M_s^{\text{GB}} = 0.00004 \text{ T}$$



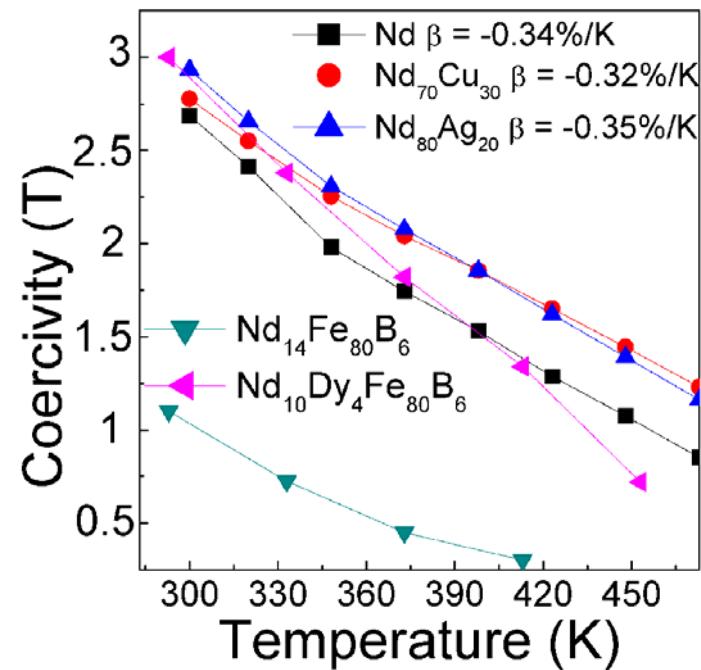
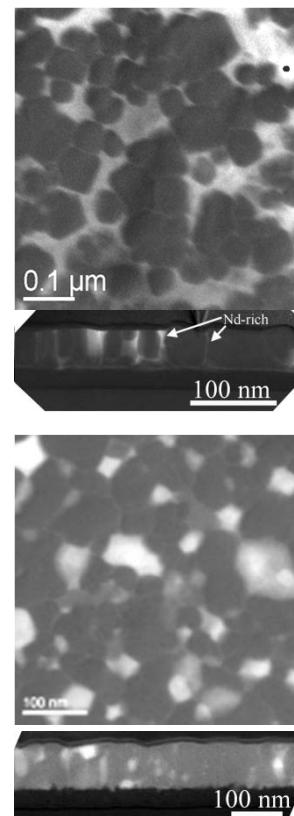
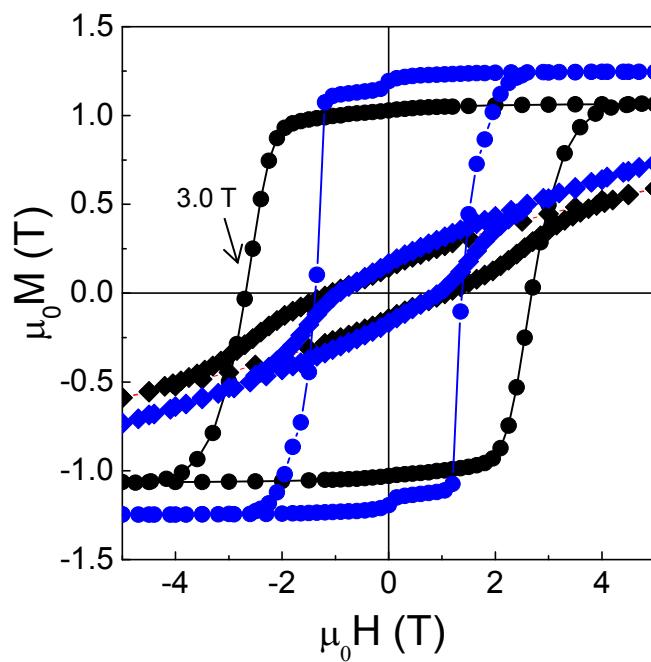
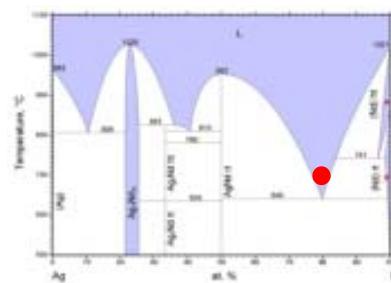
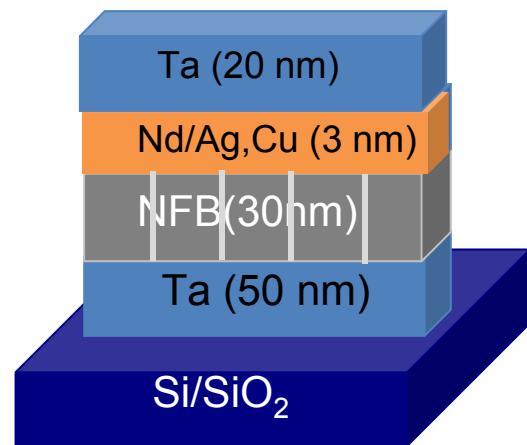
after H. Sepehri-Amin

# モデル薄膜による超微結晶Nd-Fe-B磁石の保磁力

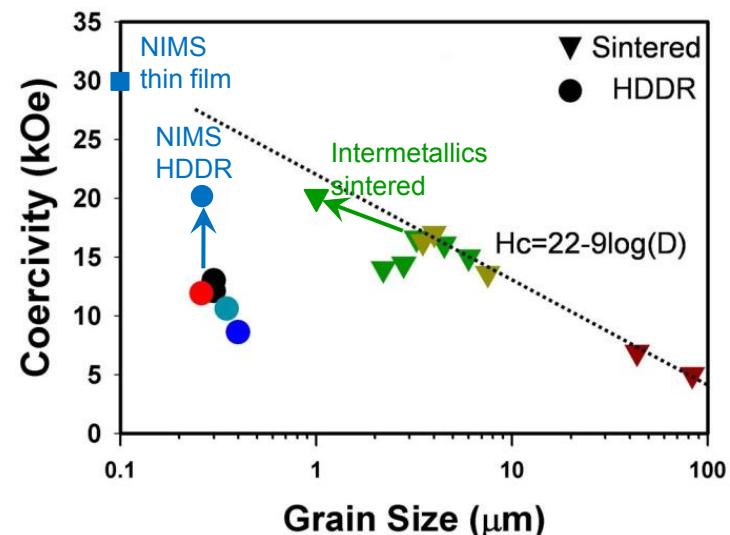


$\mu_0 H_c = 1.4 \text{ T}$ ,  $M_r = 1.4 \text{ T}$ ,  $(BH)_{\max} = 358 \text{ kJ/m}^3$ , comparable to sintered magnets

# モデル薄膜による保磁力の上限の実証

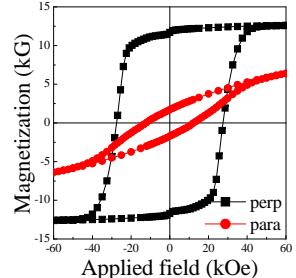


NdCu:  $H_c \approx 12$  kOe@200°C



## モデル薄膜

薄膜を用いた磁石のモデル構造

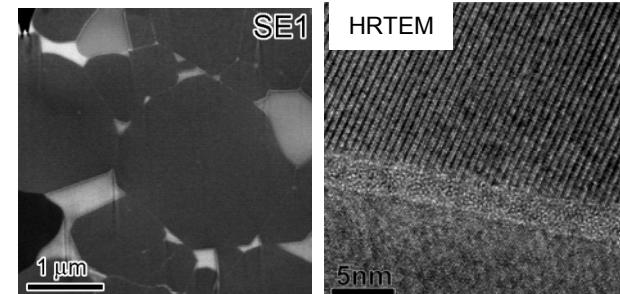


東北学院 嶋

NIMS 宝野

## 微細構造

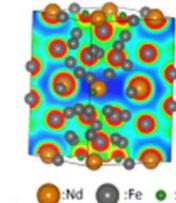
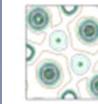
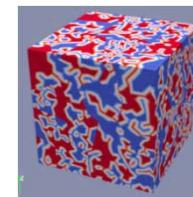
### マルチスケール解析



3DAP analysis  
Nd, Ga

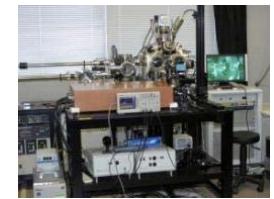
## マイクロ磁気シミュレーション

第一原理計算  
マイクロ磁気シミュレーション



NIMS 大久保

東北大 佐久間



マルチスケール組織解析  
保磁力メカニズムの解明



微細構造・磁気特性最適化のためのプロセス

企業との共同研究

希少元素フリー磁石



# まとめ

- 一般的なNd-Fe-B磁石の保磁力は異方性磁界 $H_a$ の20%程度  
→組織制御で $H_c \sim 0.5 H_a$ を目指す
- 保磁力が低い理由がマルチスケール解析で理解され始めている
- 結晶粒微細化( $\sim 1 \mu\text{m}$ )により焼結磁石の保磁力は2 Tに到達  
(インターメタリクス)
- HDDR磁粉の保磁力はNd-Cu拡散で2 Tに到達 (NIMS, 愛知製鋼)
- 液体急冷等方性磁石の熱間加工による異方性化でも $(BH)_{\max}$ が上がっているので、Nd-Cu拡散法などの保磁力改善で焼結磁石を凌駕する可能性あり (大同特殊鋼)
- Nd-Fe-B磁石の粒界層を非磁性相にした粒径 $\sim 100 \text{ nm}$ の薄膜によるモデル実験で、 $\mu_0 H_c = 3 \text{ T}$ は達成。ナノ結晶だと保磁力の温度依存性係数も小さい。
- Nd-Fe-B磁石の微細構造を最適化すれば $\mu_0 H_c > 2.5 \text{ T}$ の磁石は射程範囲内



# ESICMMの体制概要

代表研究者: 広沢哲  
企画マネージャー: 三俣千春

## 解析評価

GL: 宝野(NIMS)

中村(Spring-8)



小野(KEK)



岡本(東北大)



東北大  
TOHOKU UNIVERSITY

小山(名工大)



名古屋工業大学  
NAGOYA INSTITUTE OF TECHNOLOGY

三谷(NIMS)



鈴木(J-PARC)  
仲谷(電通大)  
小林(東工大)  
竹田(東北大)  
阿部(NIMS)

## 材料創製

GL: 杉本(東北大)

高橋(NIMS)



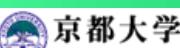
高梨(東北大)



大久保(NIMS)



寺西(京大)



## 電子論

GL: 三宅(AIST)



小倉(阪大)



大阪大  
OSAKA UNIVERSITY

宮下(東大)



東大  
THE UNIVERSITY OF TOKYO

土浦(東北大)



東北大  
TOHOKU UNIVERSITY

胡(NIMS)



合田(東大)



東大  
THE UNIVERSITY OF TOKYO

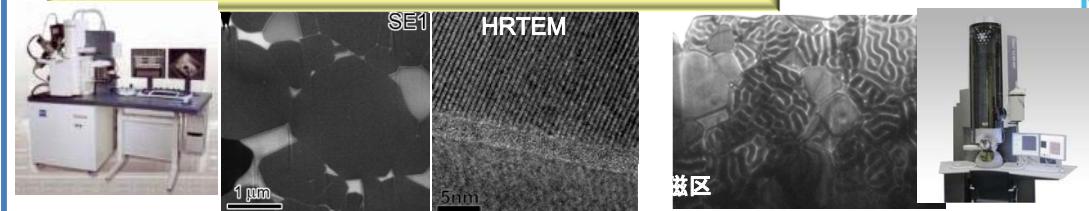
# 解析評価グループ

## 材料創製グループ

新材料試料  
モデル物質  
材料合成プロセスデータ



### マルチスケール組織・界面構造解析



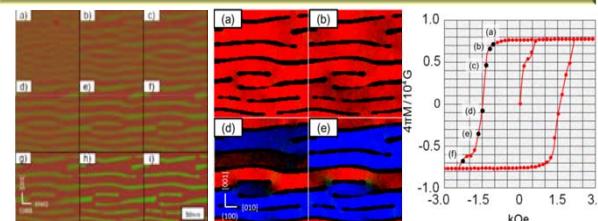
宝野和博 (GL, PI)

## 電子論グループ

電子状態データ  
微細構造データ  
磁気特性データ  
状態図  
熱力学データ

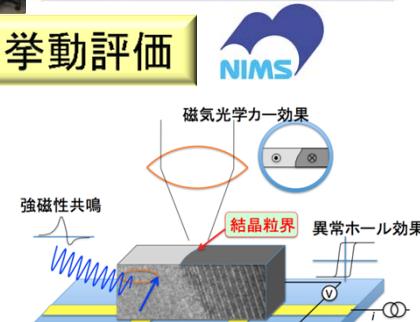


### 材料設計への計算工学集開発



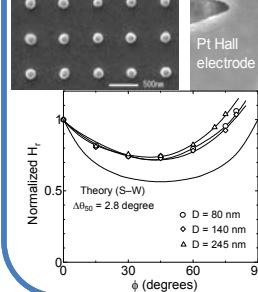
小山敏幸 (PI)

### 粒界磁化挙動評価



三谷誠司 (PI)

### ナノ粒子磁化反転挙動解析



岡本聰 (PI)

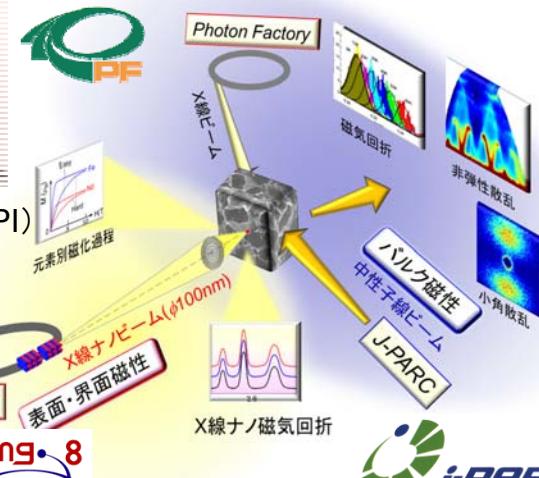


中村哲也 (PI)

### 量子ビーム解析



小野寛太 (PI)



# 電子論グループ : 微細組織制御と新材料設計指針の導出

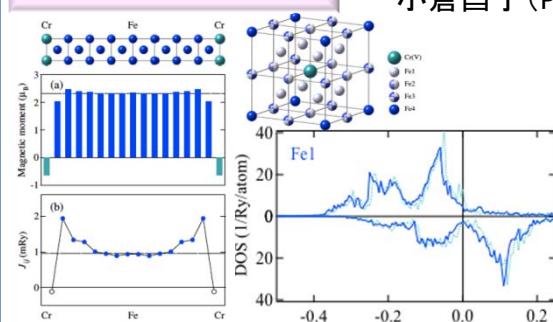
## 解析評価グループ

### 電子論共通基盤



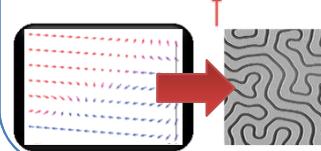
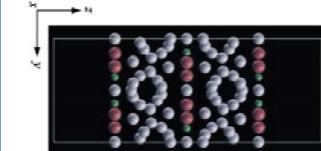
電子状態データ  
微細構造データ  
磁気特性データ  
状態図  
熱力学データ

### 磁気的性質の電子論

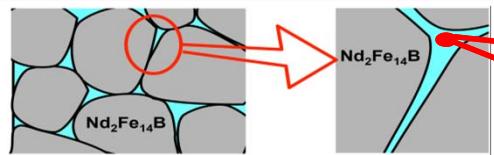


### 保磁力の微視的解析

東北大学  
TOHOKU UNIVERSITY



### 磁気的性質の電子論計算手法創出

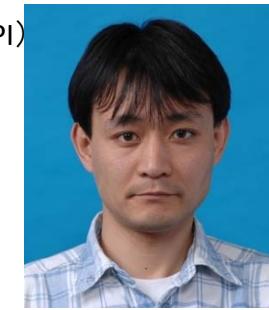
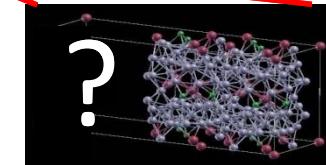


大阪大学  
OSAKA UNIVERSITY



小倉昌子(PI)

三宅隆(GL, PI)  
National Institute of Advanced Industrial Science and Technology AIST

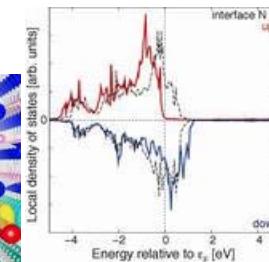
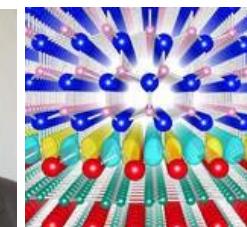


### 第一原理磁石材料探索

東京大学  
THE UNIVERSITY OF TOKYO

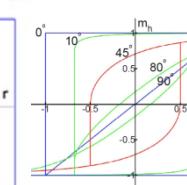
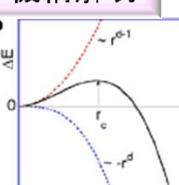
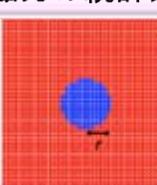


合田義弘(PI)



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### 保磁力の統計力学機構解明



宮下精二(PI)



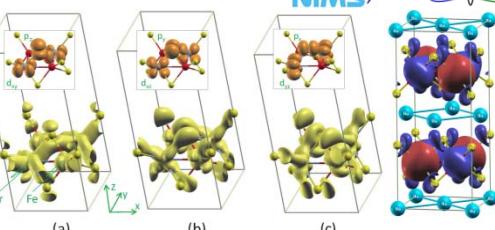
新材料提案  
材料設計指針  
特性発現機構

材料合成プロセスデータ

特性発現機構  
特性予測データ  
構造予測データ

### 新規磁気現象に基く磁石機能創出

NIMS  
 MANA



(a)  
(b)  
(c)

(a)  
(b)  
(c)

(a)  
(b)  
(c)

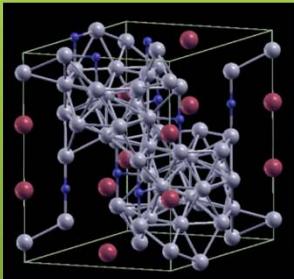
## 材料創製グループ

# 新規磁石の理論的設計

ヒント：Nd-Fe-B磁石の発見から実用化まで

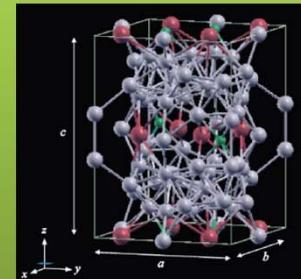
$Nd_2Fe_{17}$   
→ 磁石にならない

Fe-Fe間距離  
が近すぎる



「Bを加えて  
Fe同士を離す」

$Nd_2Fe_{14}B$



Dy添加で  
実用化



RE-Fe-B

(希土類元素の役割)

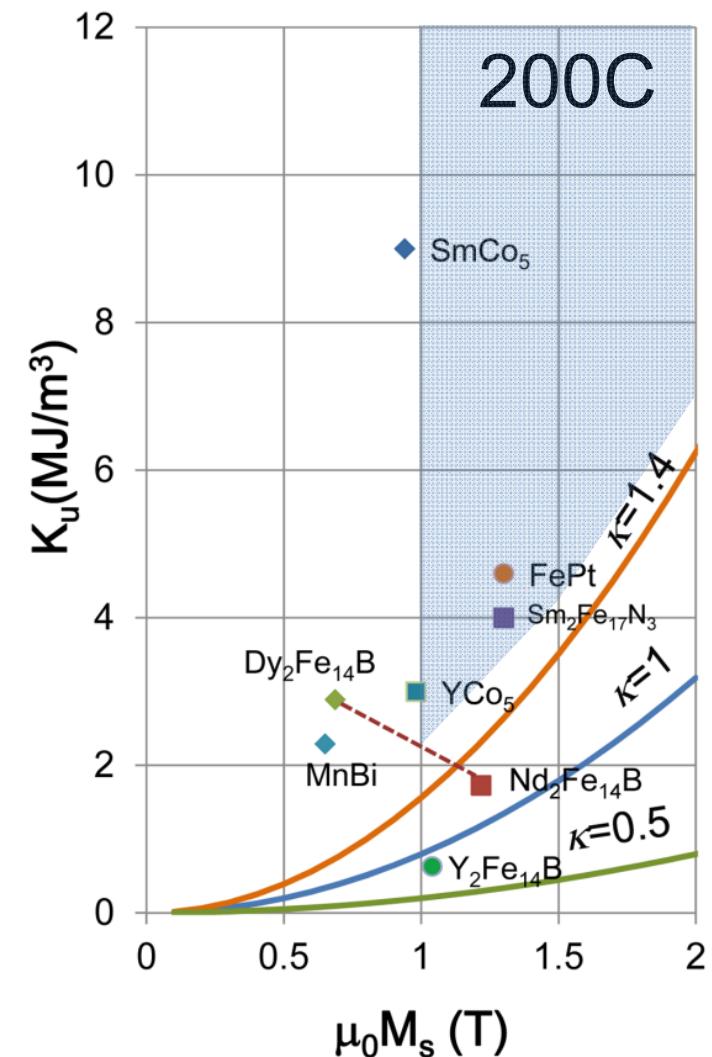
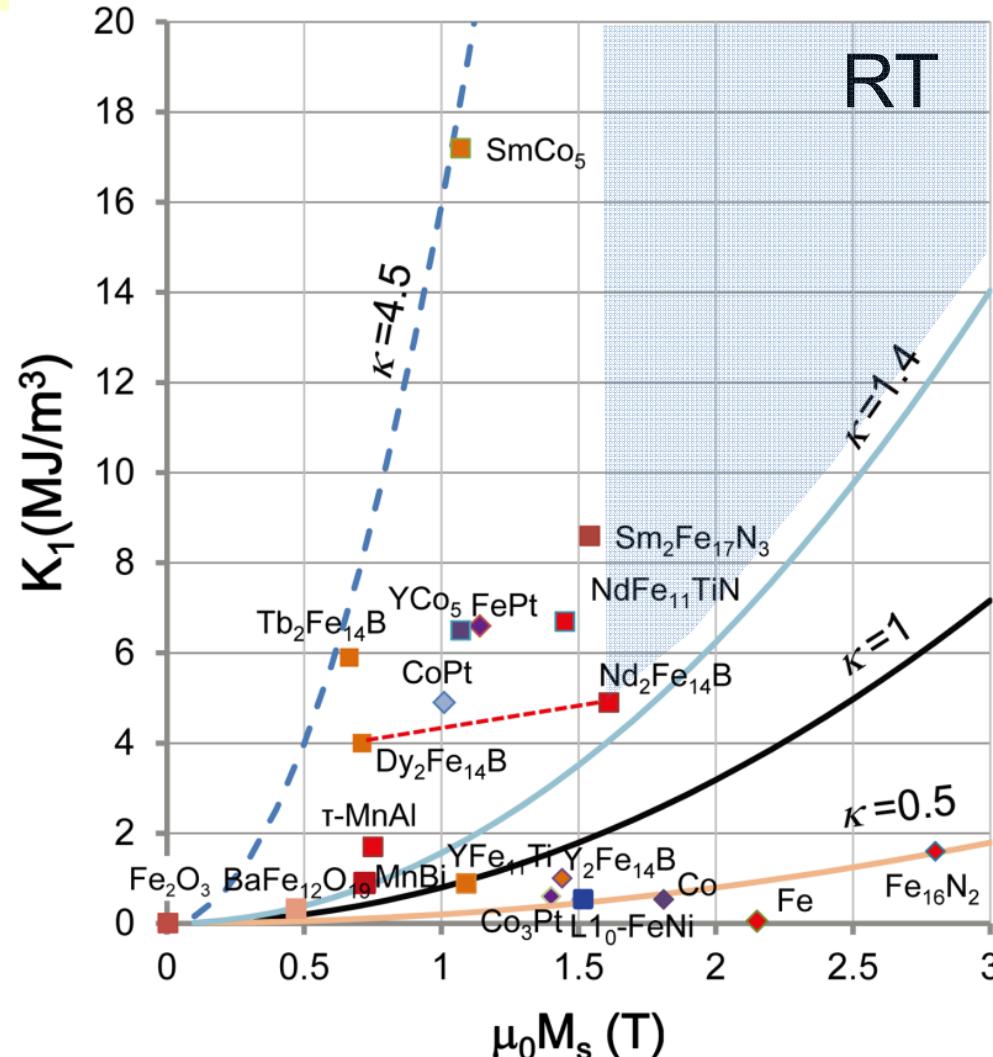
- REによる結晶磁気異方性機構を解明(相対論的第一原理計算)→ RE代替元素の提案
- 粒界相と主相の親和性評価(量子MD計算)

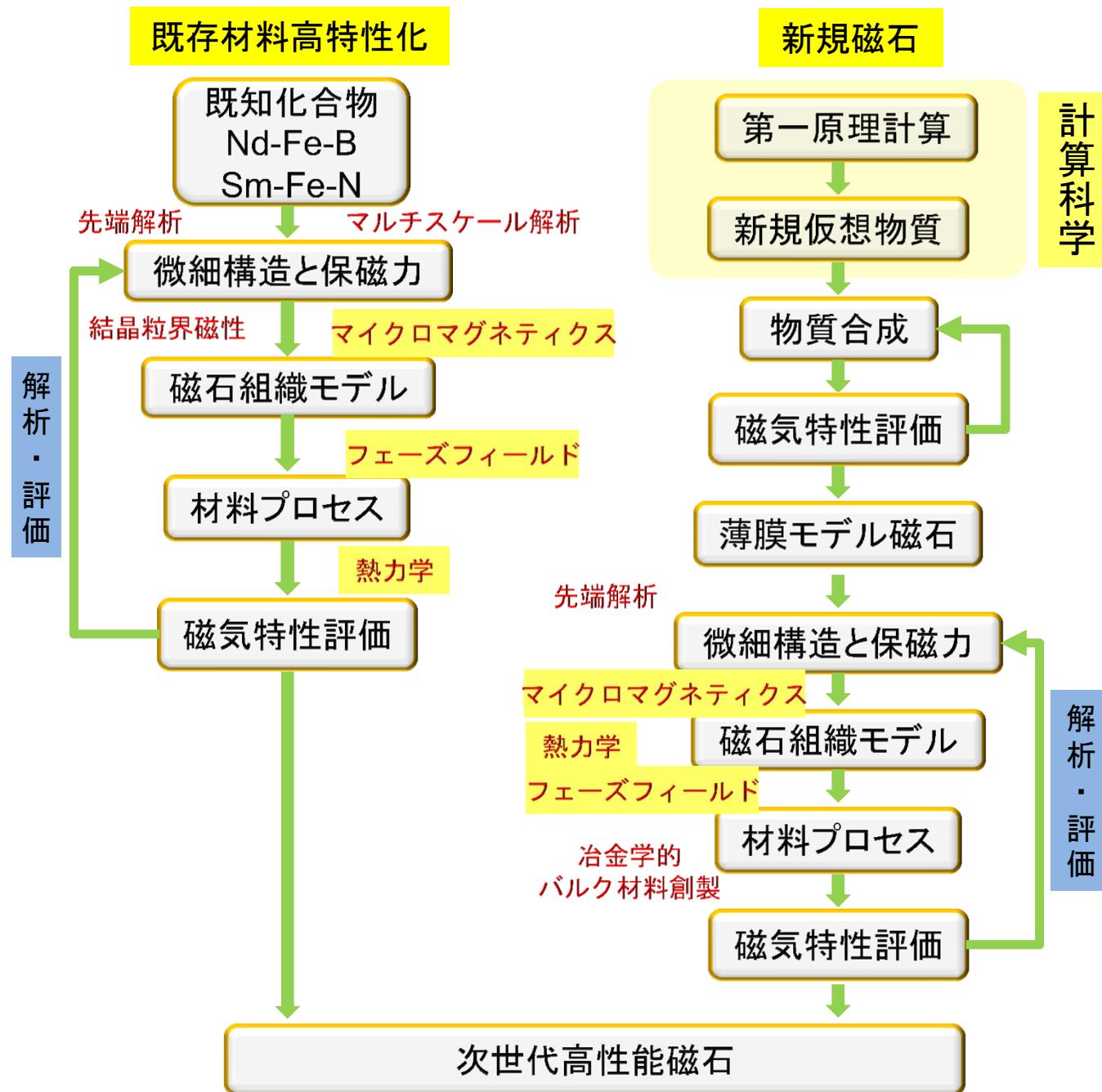
遷移金属化合物(MnAlなど)  
の結晶磁気異方性の起源

- 高い磁化(高精度電子相関計算)・磁気異方性をもつ結晶構造を探索する量子MD計算

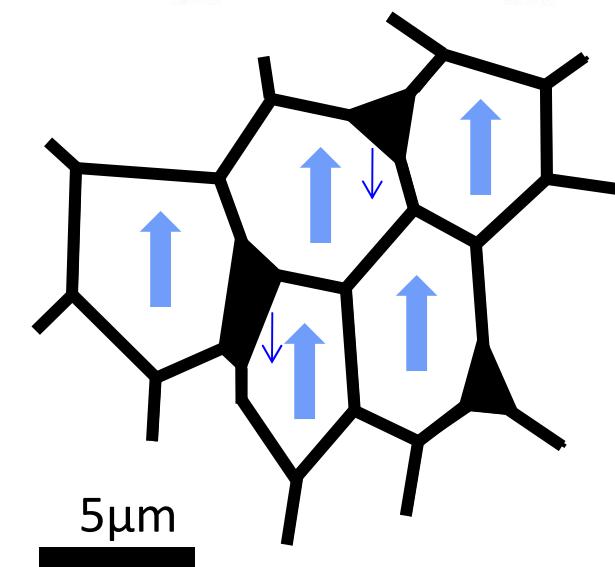
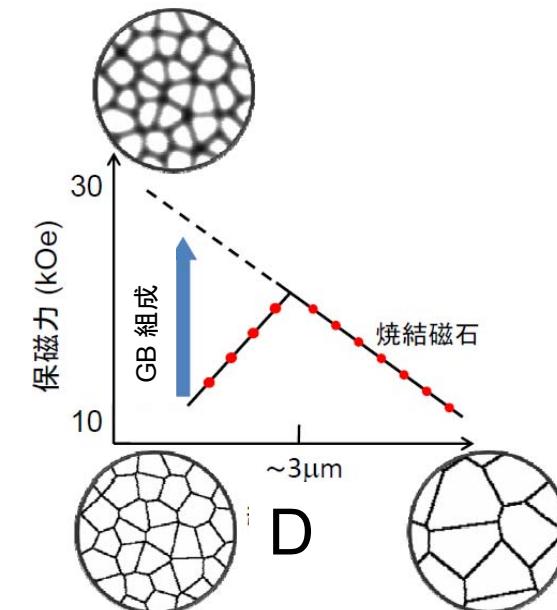
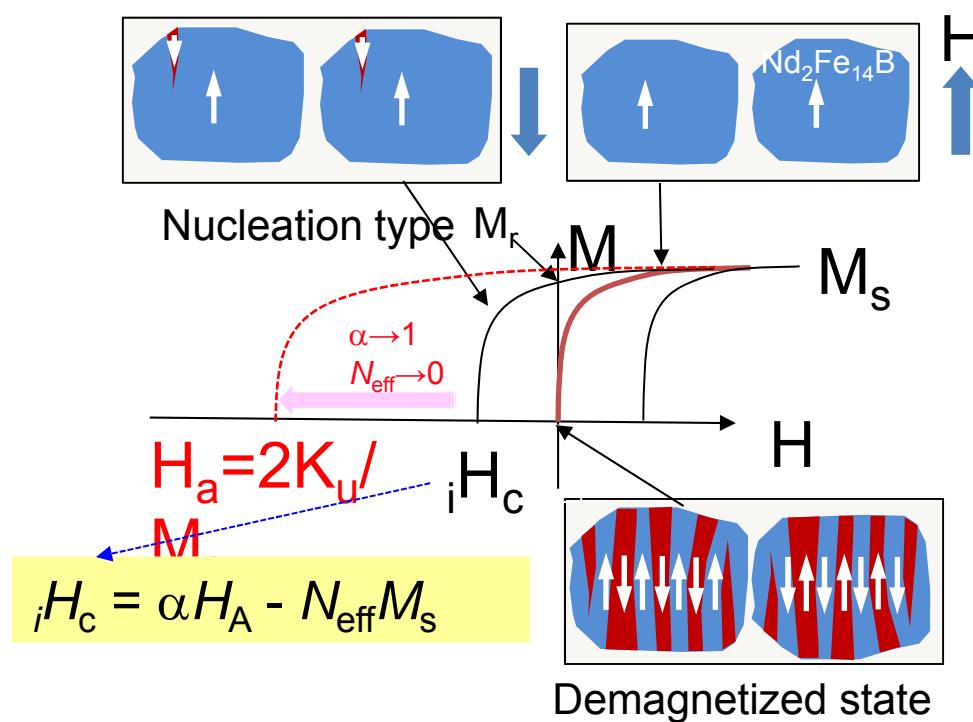
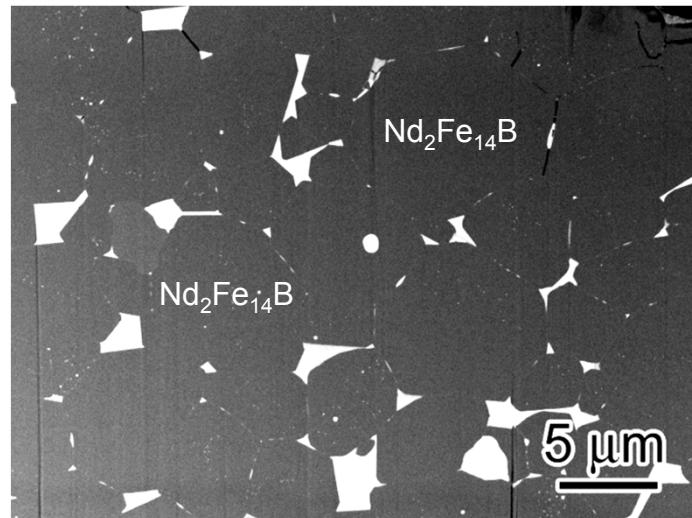
# 磁性化合物の結晶磁気異方性 $K_1$ , 磁化 $\mu_0 M_s$ と硬さ係数 $\kappa$

$$(BH)_{\max} = \frac{\mu_0 M_r^2}{4} \quad H_c > M_s / 2 \rightarrow \kappa = \sqrt{K_1 / \mu_0 M_s^2} > 1$$





# 磁石の保磁力と微細組織



$$H_c = \alpha \uparrow H_a - N_{\text{eff}} \downarrow M_s$$

**Microscopy**

- Micromagnetic**: 3DAP simulation showing Nd, Fe, B atoms.
- Lorentz**: Lorentz microscopy image.
- TEM**: Transmission Electron Microscopy image.
- FIB-SEM**: Focused Ion Beam Scanning Electron Microscopy image.
- 3DAP**: 3D Atomic Potential simulation.
- TEM**: TEM image with 5 nm scale bar.
- SE1**: SEM image with 1 μm scale bar.
- Intensity**: A 2D intensity map with a 10 nm scale bar.
- Hysteresis**: A plot of magnetization  $\mu_0 M$  versus applied field  $\mu_0 H$ .

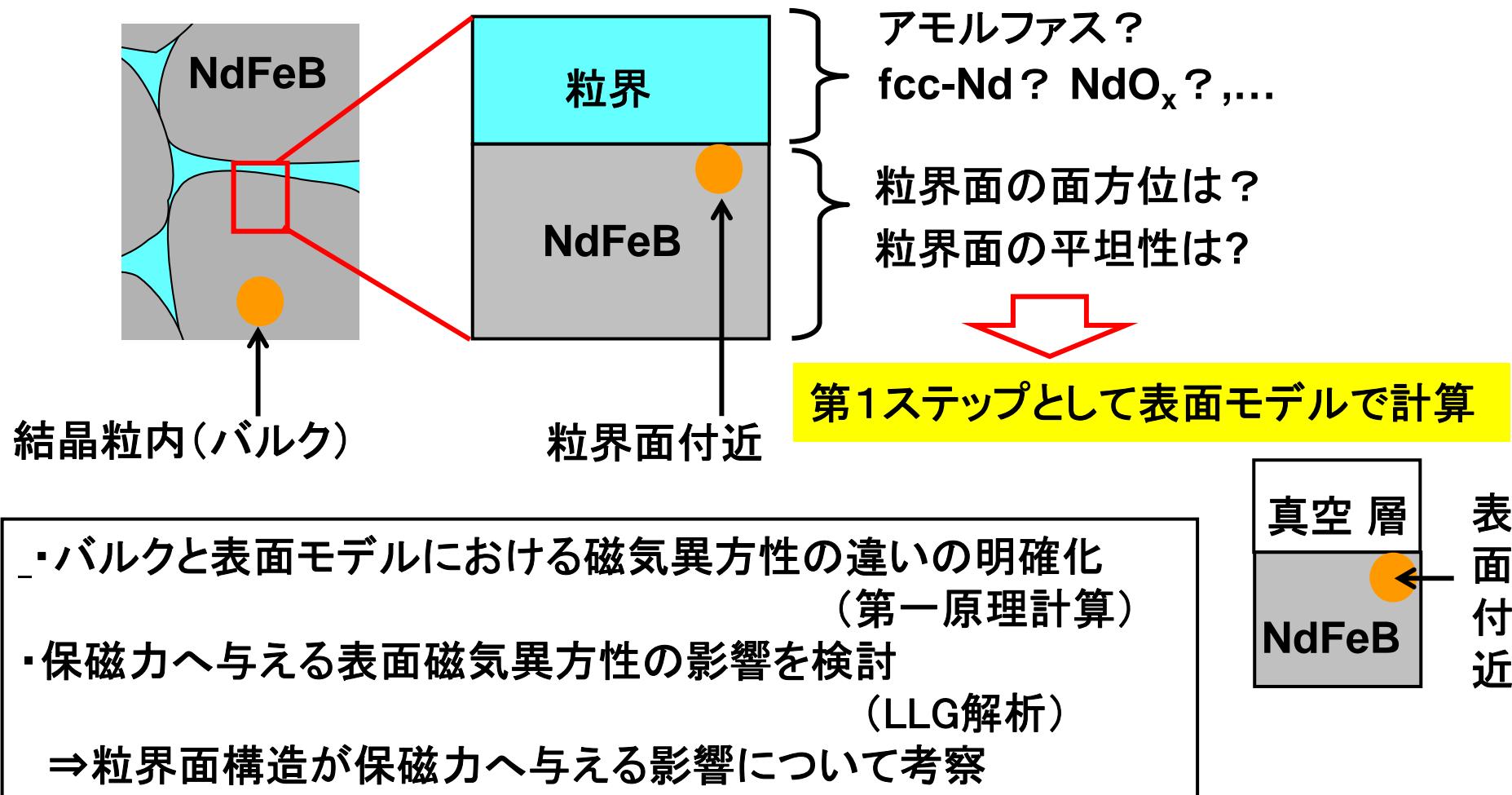
**X-ray, Neutron**

- 界面** (Interface): A 2D intensity map with axes X and Y.
- 表面** (Surface): A 2D intensity map with axes X and Y.
- 薄膜** (Thin Film): A 2D intensity map with axes X and Y.
- 原子** (Atom):
  - 中性子小角磁気散乱**: A 2D intensity map with axes X and Y. Labels:  $I_{\text{Nuc}} + I_{\text{Mag}}$ ,  $I_{\text{Nuc}}$ .
  - STXM**: A 2D intensity map with axes X and Y. Label: "元素別磁区".
  - PEEM**: A 2D intensity map with axes X and Y. Labels: Nd, Dy.
- ナノビームXAS**: A 3D surface plot with axes X, Y, Z.
- ナノビームXMCD**: A plot of XMCD signal versus applied field  $H$ .
- 粒界相磁性**: A plot of magnetization  $M$  versus applied field  $H$ . Labels: Easy, Hard, Fe, Nd.
- 中性子線回折 (In-situ)**: An illustration of a neutron scattering instrument.
- 元素サイト占有率**: A plot of Intensity [counts] versus  $2\theta$  [degree].

# Nd-Fe-B磁石界面における磁気異方性の計算

東北大 佐久間グループ

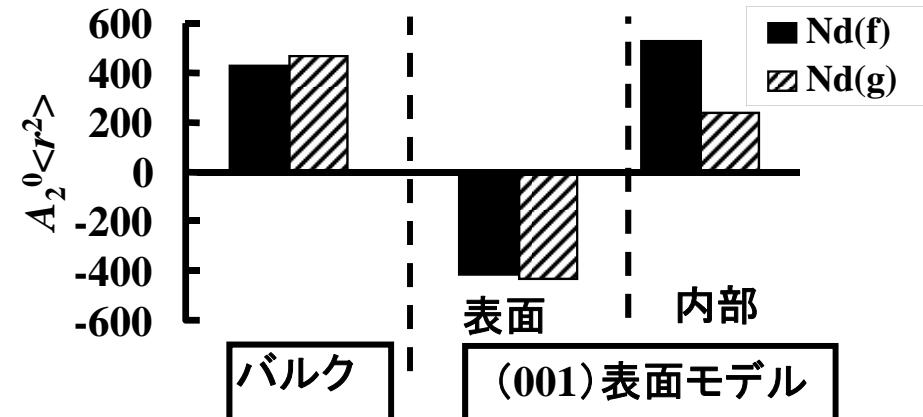
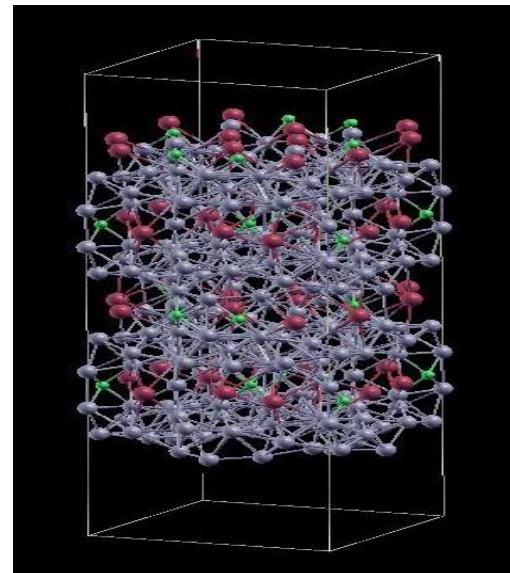
「 $\text{Nd}_2\text{Fe}_{14}\text{B}$ 粒界面近傍の磁気異方性定数を調べる」にあたり、実際の粒界構造(左図)をモデル界面(右図)で代表させて理論計算(第一原理計算)を行



# 界面における異方性の第一原理計算

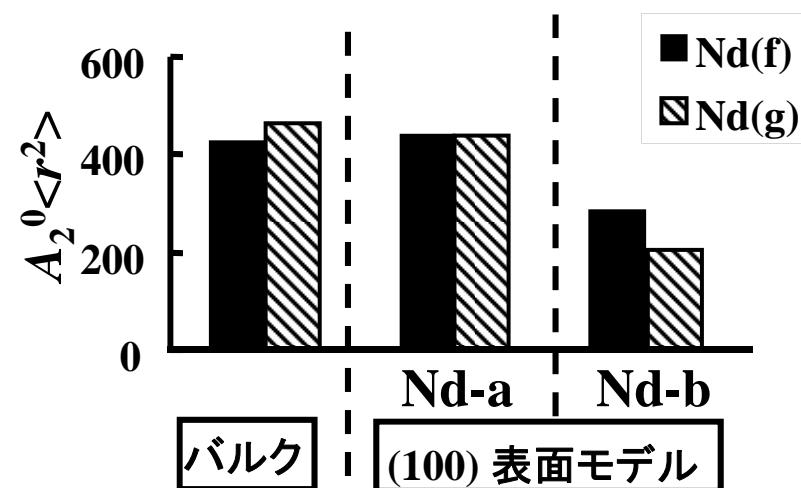
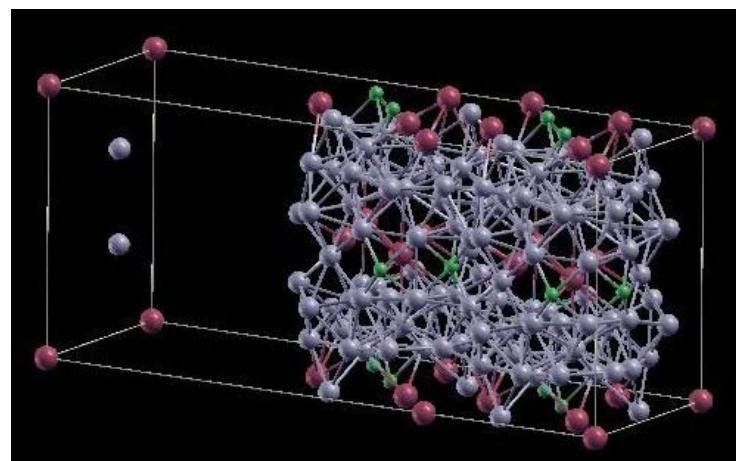
東北大佐久間グループ

## 結晶粒(001)表面の結晶場パラメータ



表面に露出したNdイオンでは結晶場パラメタが負となり、符号がバルクと異なる

## 結晶粒(100)表面の結晶場パラメータ

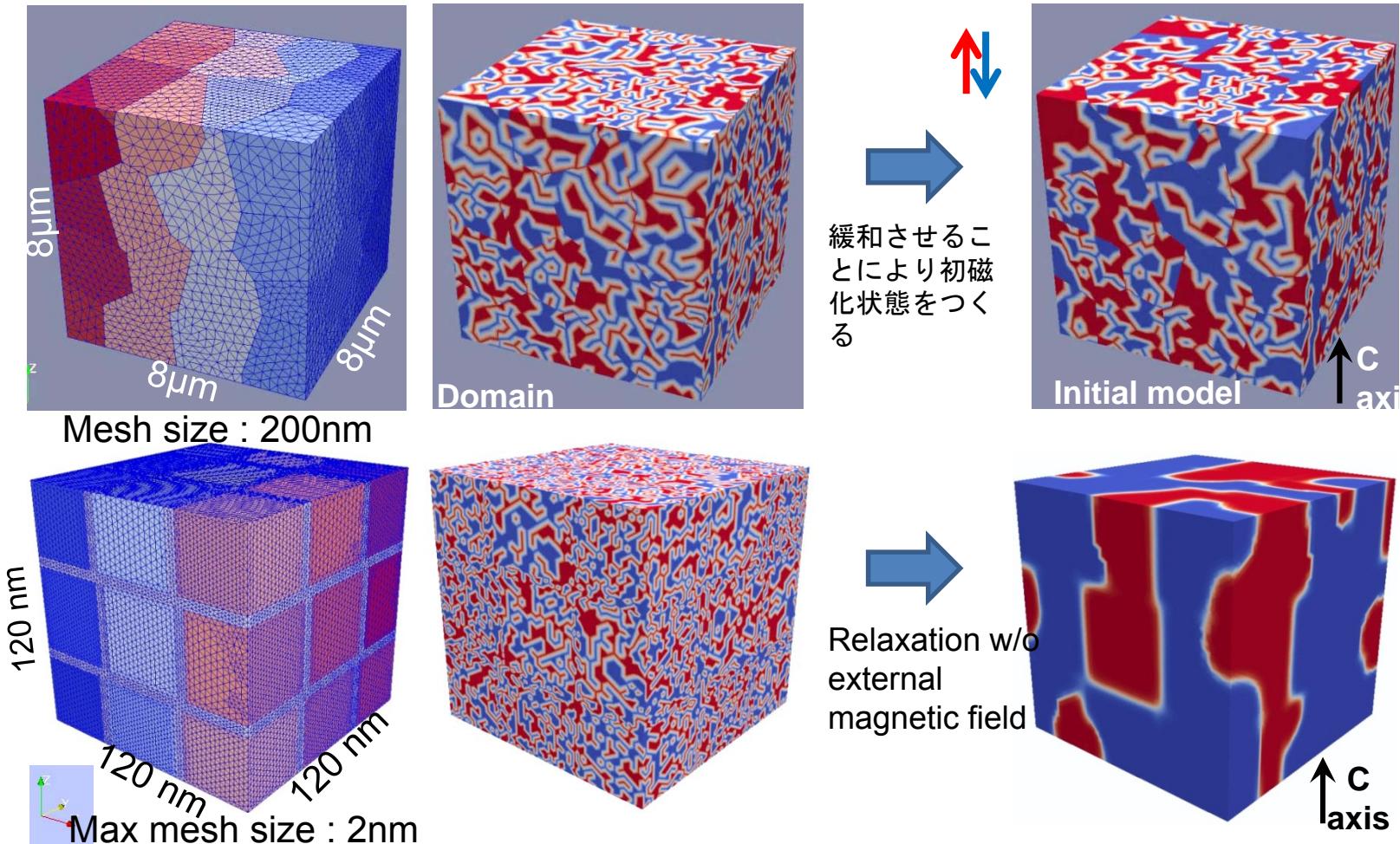


Ndイオンの結晶場パラメターは、バルクと同様に全て正。

# マイクロマグネティクスシミュレーションの問題点

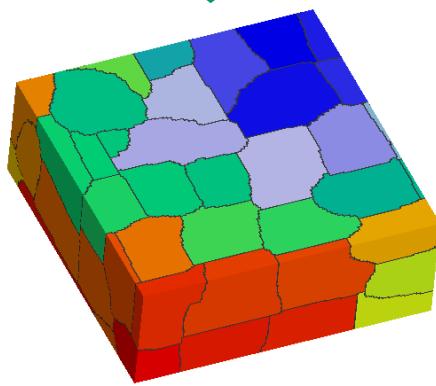
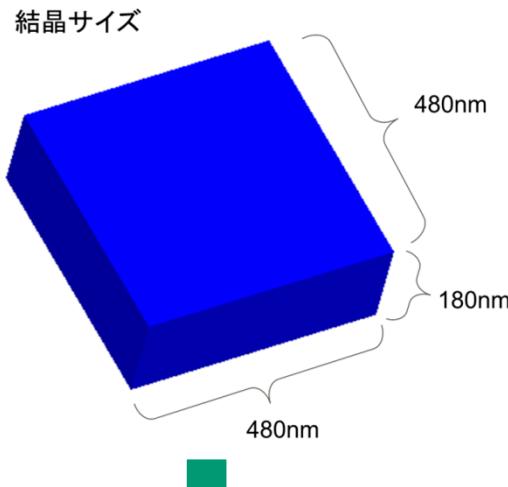
## 保磁力と微細構造の架け橋

### メッシュサイズによる磁区の再現性の問題

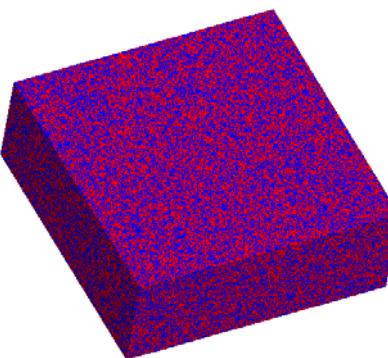


現状ではメッシュサイズの制約により初磁化状態さえ正確に再現できない  
→ メッシュサイズを磁壁幅以下にした現実的なシミュレーションが不可欠

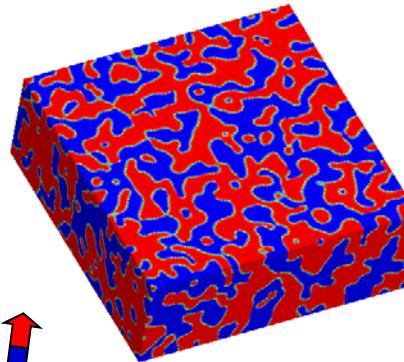
# 磁石の初磁化状態の再現



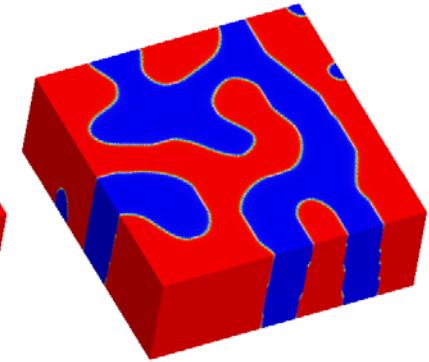
Time=0 psec



Time=50 psec

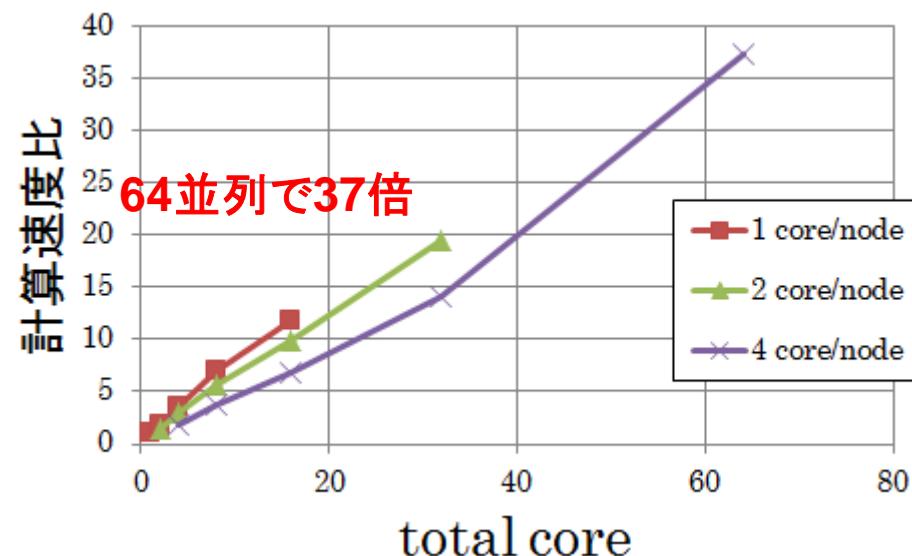


Time=2000 psec



磁化の向き

メッシュサイズの細分化により  
初めて初磁化状態を再現できる





# 今後の展開

- ・ 対象材料として緊急性の高いNd-Fe-B系磁石でスタート。
- ・ さまざまなプロセスで作製されるNd-Fe-B系磁石の微細構造の徹底的な解析と保磁力の因果関係
- ・ 微細構造と保磁力の架け橋マイクロマグネティクシミュレーションと磁区観察により磁化反転過程を明らかにして、高保磁力化の指針を得る
- ・ さまざまな界面における結晶磁気異方性の計算
- ・ 界面における磁気異方性を取り込んだマルチスケールモデル
- ・ メッシュサイズが界面と磁壁幅よりも小さな大規模マイクロマグネティクシミュレーションをツールとして高保磁力磁石設計
- ・ Dyフリーで高保磁力化を実現するための微細構造の提案
- ・ 計算科学によって探索される新磁石化合物に上記を展開