SPring-8利用推進協議会 先端磁性材料研究会

窒素侵入型化合物を活用した新規磁石用材料

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Co-workers

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Outline

1. Motivation
   - Present status of permanent magnet-

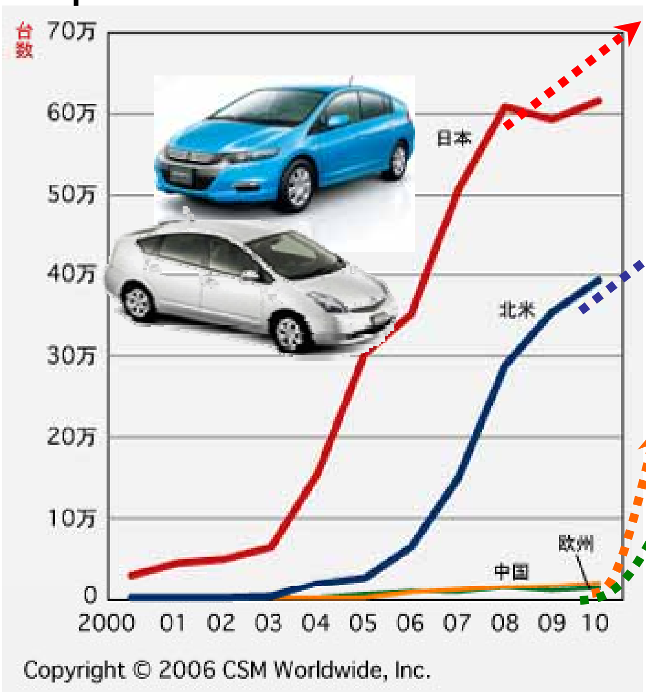
2. Magnetism of α', α" $Fe_{16}N_2$
   - Physical interest (high K_u and high M_s material) -

3. Synthesis of α"- $Fe_{16}N_2$ nanoparticles
   via chemical route
   - Direct and/or indirect synthesis

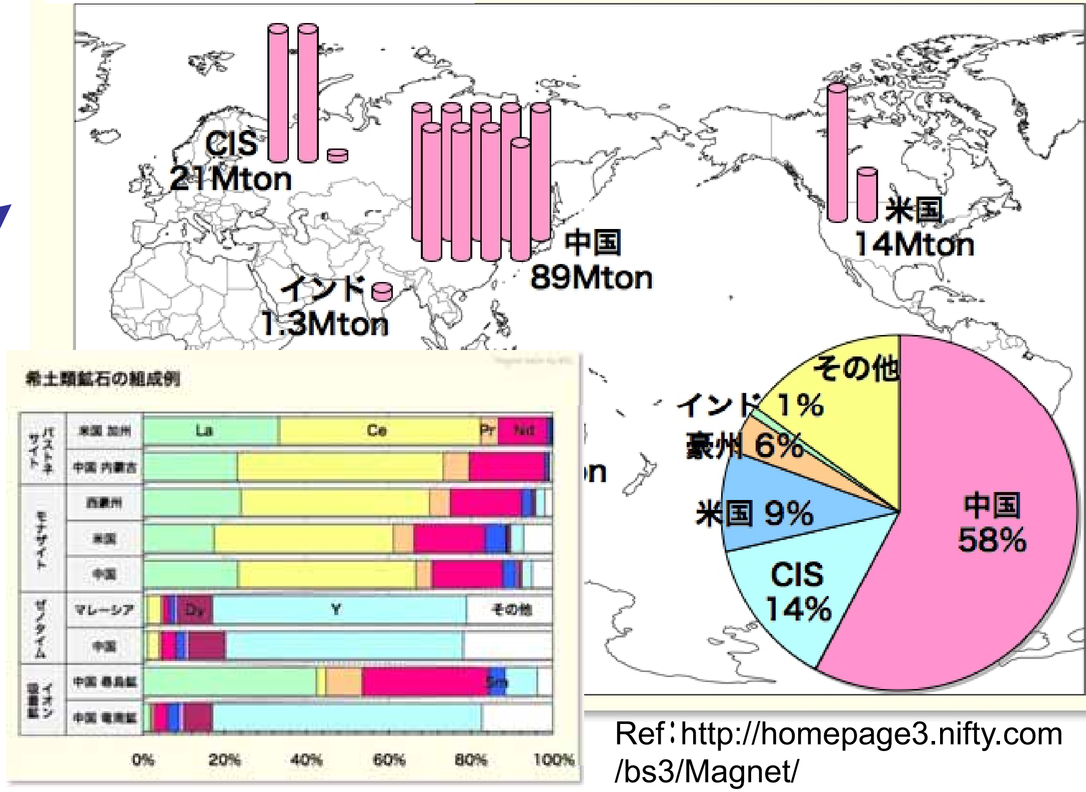
4. Summary

Present status of permanent magnet

Shipment of HEV & EV



Deposits of REE



Ref：http://homepage3.nifty.com
/bs3/Magnet/

High performance permanent magnet is indispensable for highly qualified motor (powerful torque, miniaturized, light weight)

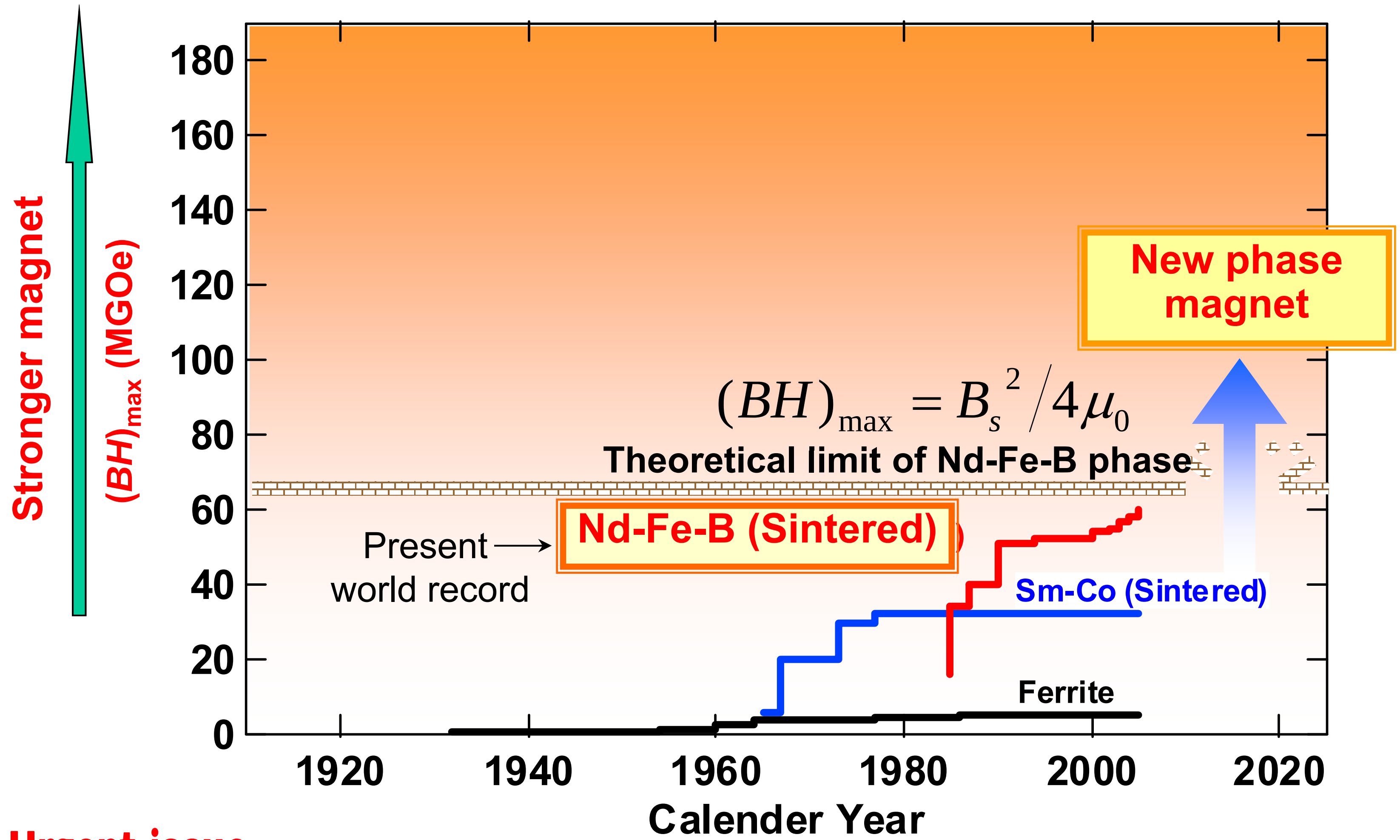
Social problems For REE

- **Imported mainly from China. Especially, Dy depends only on China.**
- **Restriction of export rate from China by 10-40% every year**
- **Mineral resources → Drying up in the future**
- **Increment of Dy demand up to three times as much as until 2020**

Nd-Fe-B magnet with Dy less →
- **Dy free**
- **Alternative materials**

(2020：Break away from the REE risk)

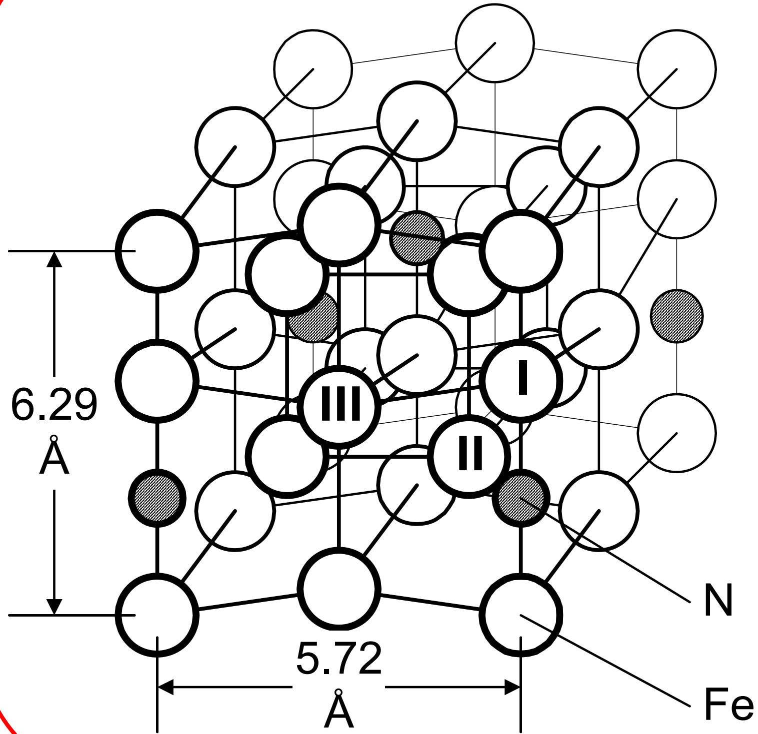
Change of $(BH)_{max}$ of permanent magnets



- Urgent issue -

REE less/free new magnet with equivalent or higher $(BH)_{max}$ of Nd-Fe-B magnet

α”-$Fe_{16}N_2$ interstitial compound



M_s of α"-$Fe_{16}N_2$: 240 emu/g ~ 2.4 T

(Equal to max. M_s of $Fe_{70}Co_{30}$ In the Slater-Pauling curve)

Migaku Takahashi, et al.; *J. Appl. Phys.*, 76, 6642 (1994).

Migaku Takahashi, et al.; *J. Magn. Magn.Mater*, 208, 145 (2000).

K_u of α"-$Fe_{16}N_2$: ~1 x 10^7 erg/cm^3

(Originally reported

$B_s \approx 2.9$ T $\approx$ 280 emu/g

T.K.Kim and M.Takahashi; *Appl. Phys. Lett.*, 20, 492 (1972).)

Review: M. Takahashi et al., *J. Magn. Magn. Mat.*, 208, 145 (2000).
(Title: α"-$Fe_{16}N_2$ problem – giant magnetic moment or not)

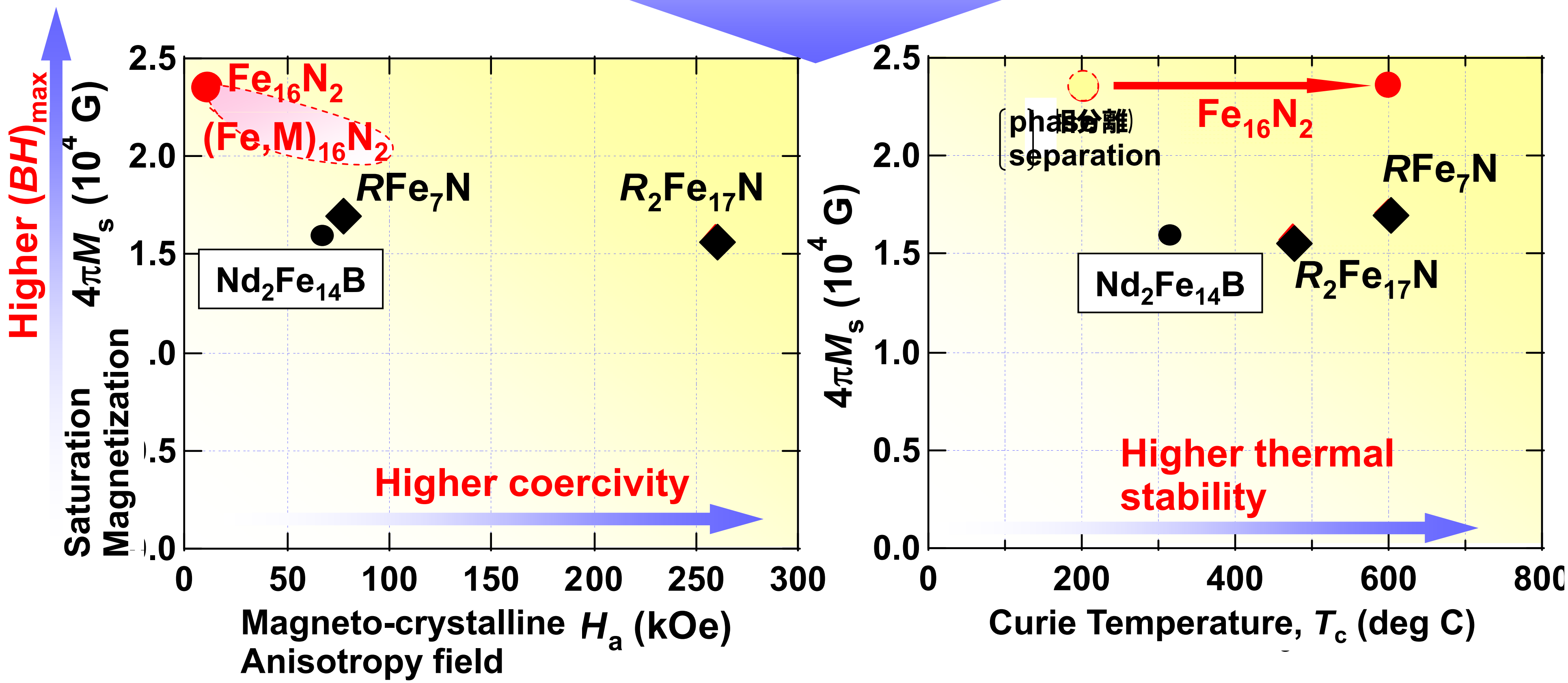
New candidate for the futured permanent magnetic material with rare earth element free

Highly potential iron nitride materials

REE less/free

- **High B_s**
- **Free from drying up of mineral resources**
- **Constitutience of Fe and N elements**

" $((Fe,M)_{16}N_2)$ " materials



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4. Summary

2. Magnetism of a’, a” Fe16N2
- Physical interest (high Ku and high Ms material) –

2-1 Non-equilibrium structure formation

2-2 Substitution effect
- Nitrogen site → H, B, C, O,…
  (p electron number control)
- Iron site → Co, Ni, … etc.
  (d electron number control)

2-3 Thermal stability

2-4 N content ; Stoicheometry (11 at.%) or off-stoicheo.
and chemical ordering

2-5 Enlargement of unit-cell volume; Magneto-volume effect

How do these factors relate to intrinsic K_u and M_s?

Non-equilibrium structure formation

Thin film

- Flash evaporation (glass sub.) ('72 original)
  ➡ M_s = 2200 emu/cm^3

- Plasma control (MgO sub.)
  - Plasma evaporation
  - Facing target type sputtering

  ➡ M_s = 240 emu/g

- MBE method (using an E-gun) (InGaAs sub.)
  ➡ B_s = 2.9 T

M. Komuro *et al.*, *J. Appl. Phys.* **67**, 5126 (1990).

Fight without humanity and justice !! ('92 ~ '98)

Nanoparticles (Since 2000)

- Reduction/Nitridation

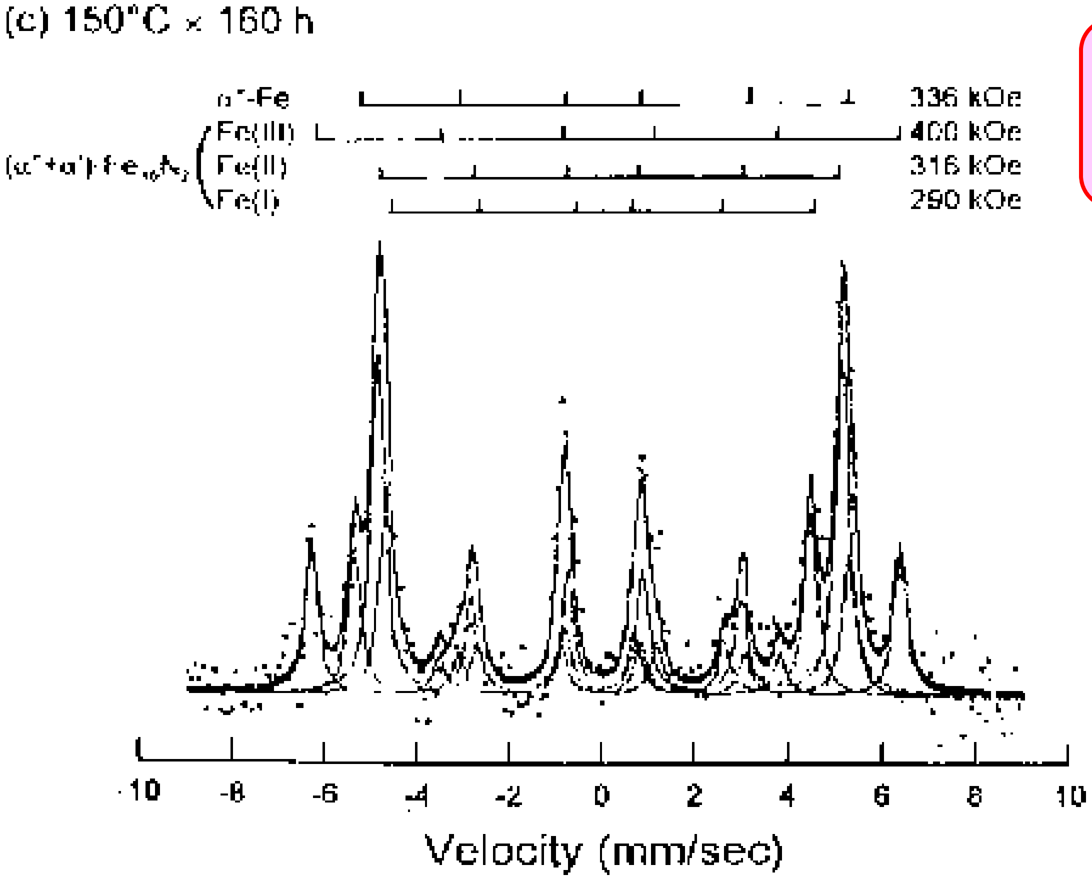
T. Hattori *et al.*, *J. Magn. Soc. Jpn.* **25**, 927 (2001).
S. Kikkawa, *et al.*, *Mater. Res. Bull.* **43**, 3352 (2008).
E. Kita *et al.*, *J. Magn. Magn. Mater.* **310**, 2411 (2007).
Y. Sasaki *et al.*, *IEEE Trans. Magn.* **41**, 3241 (2005).

M_s = 200 ~ 225 emu/g
86 emu/g_{net} (core-shell)

K_u = ~4 x 10^6 erg/cm^3

- Mixture phase (Fe, α"-$Fe_{16}N_2$, …)
- Low reproducibility of the synthesis

Analysis of Mössbauer spectra of pseudo-single crystalline sputtered thin film



Clear splitting of H_i

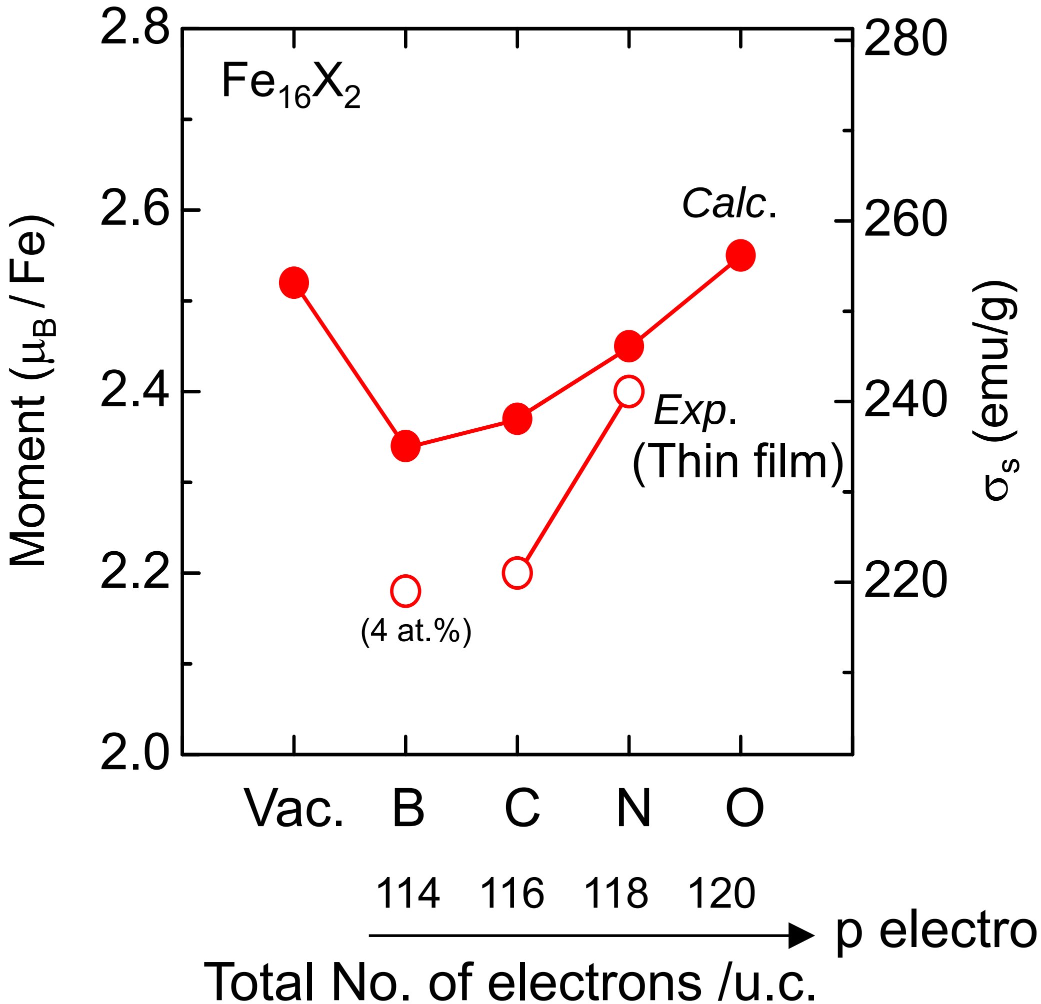
H_i^{ave}: 330 kOe (≈ H_i of α-Fe)

- Fe (I) : 290 kOe
- Fe (II) : 316 kOe
- Fe (III) : 400 kOe

- α''-$Fe_{16}N_2$ volume 82 %
- α-Fe-N volume 18% with relatively high isomer shift

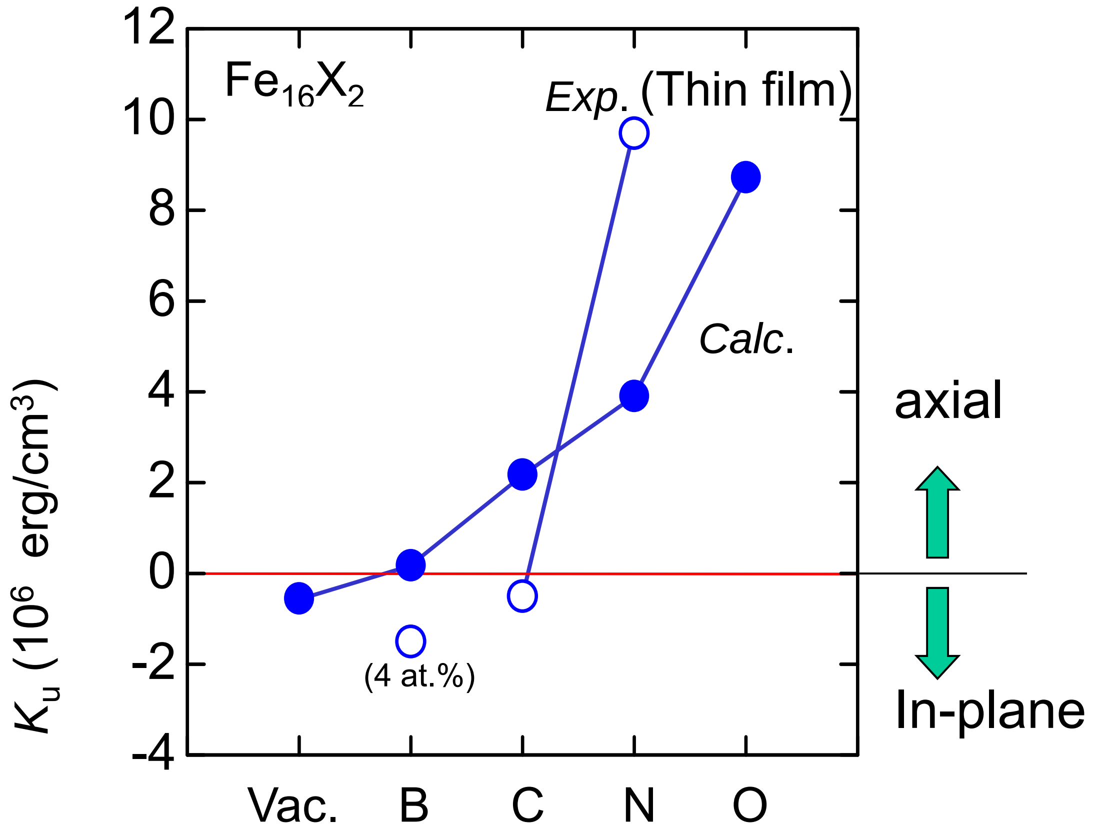
Experimental evidence of α'' – $Fe_{16}N_2$ phase!!

Substitution effect of N site
- Magnetic moment -
(Theoretical and experimental results)



Calc.: A.Sakuma: *JAP*, **79**, 5570 (1996).
Exp.: M.Takahashi *et al*.: *JMMM*., **239**, 479 (2002).
(Pseudo-single crystalline sputtered thin film)

Substitution effect of N site
- Magnetocrystalline anisotropy constant -
(Theoretical and experimental results)

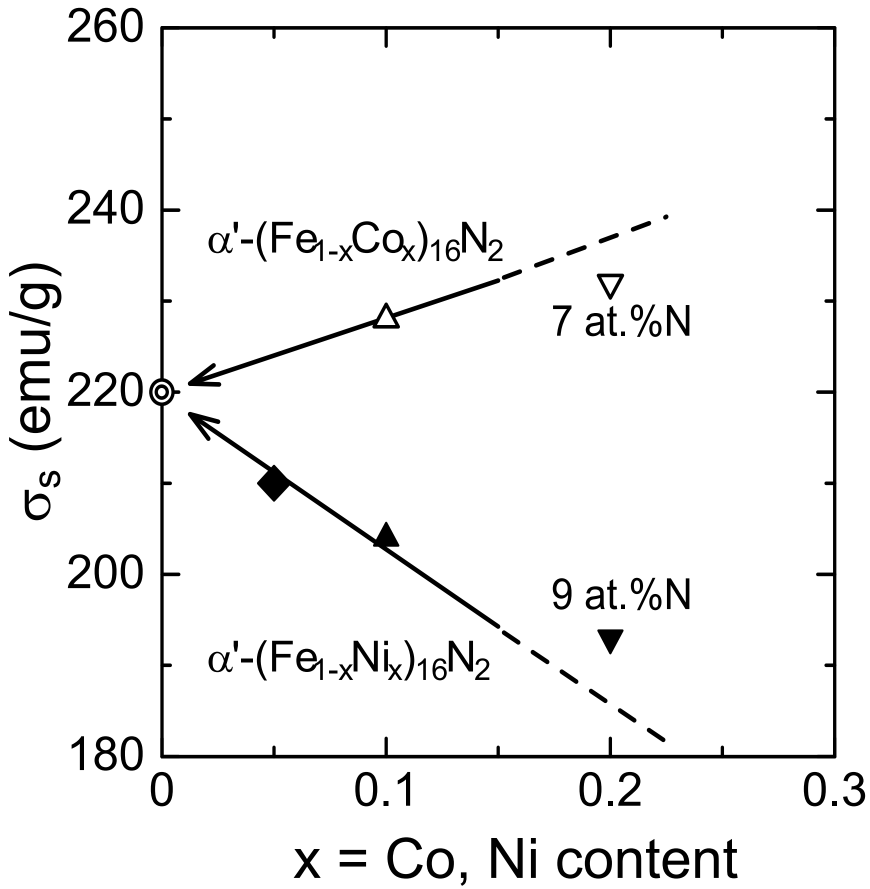


Calc.: A.Sakuma: private communication.

Exp.: M.Takahashi *et al.*: *JMMM*, **239**, 479 (2002).
(Pseudo-single crystalline sputtered thin film)

Substitution effect of Fe site - Magnetic moment -

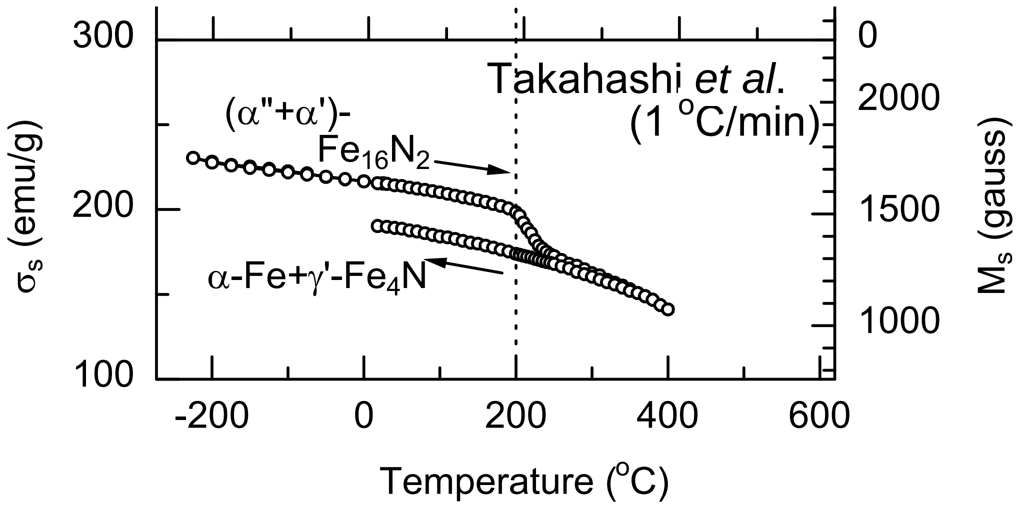
Pseudo-single crystalline sputtered thin film



Thermal stability

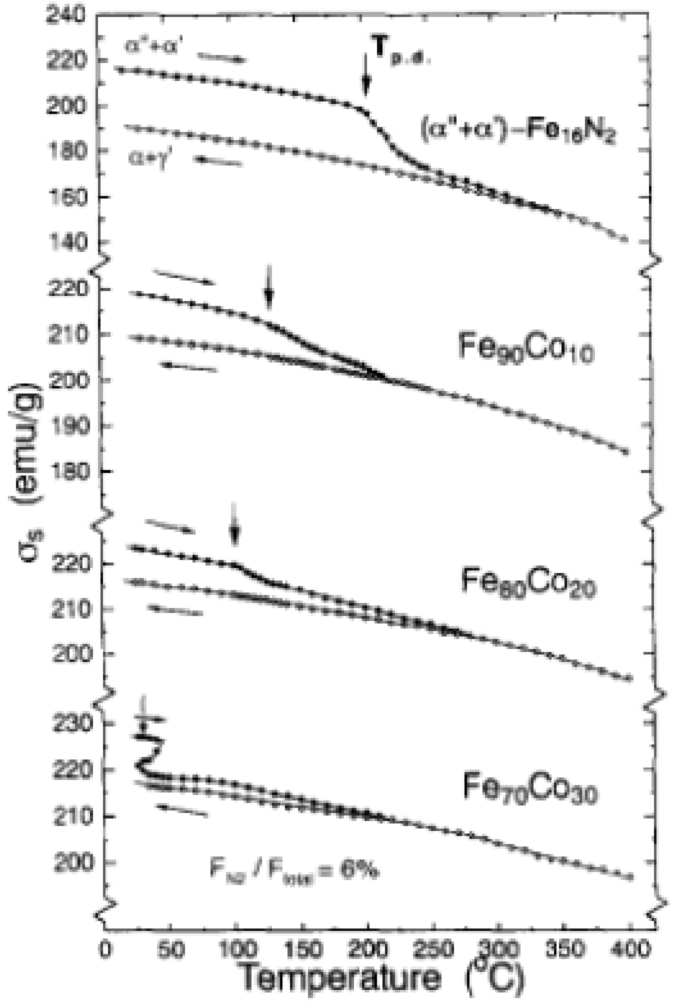
(Pseudo-single crystalline sputtered thin film)

$\alpha'' - Fe_{16}N_2$



$\alpha'' - (Fe,Co)_{16}N_2$

H. Shoji *et al.*: *JMMM*, **162**, 202 (1996).

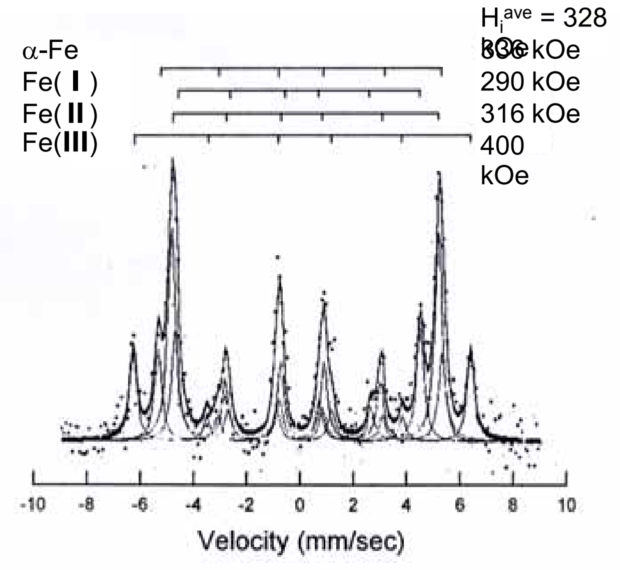


- Phase separation over 200 ℃

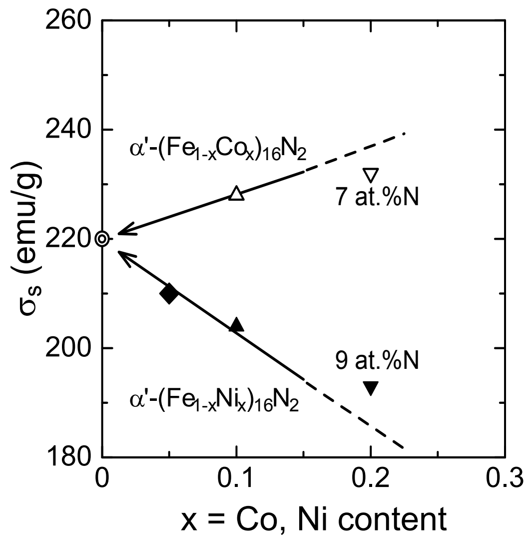
- Phase stability
  degraded by Co substitution

Experimental conclusion of magnetism of α"-$Fe_{16}N_2$ phase

Synthesis of α" phase



Saturation magnetization of α" phase

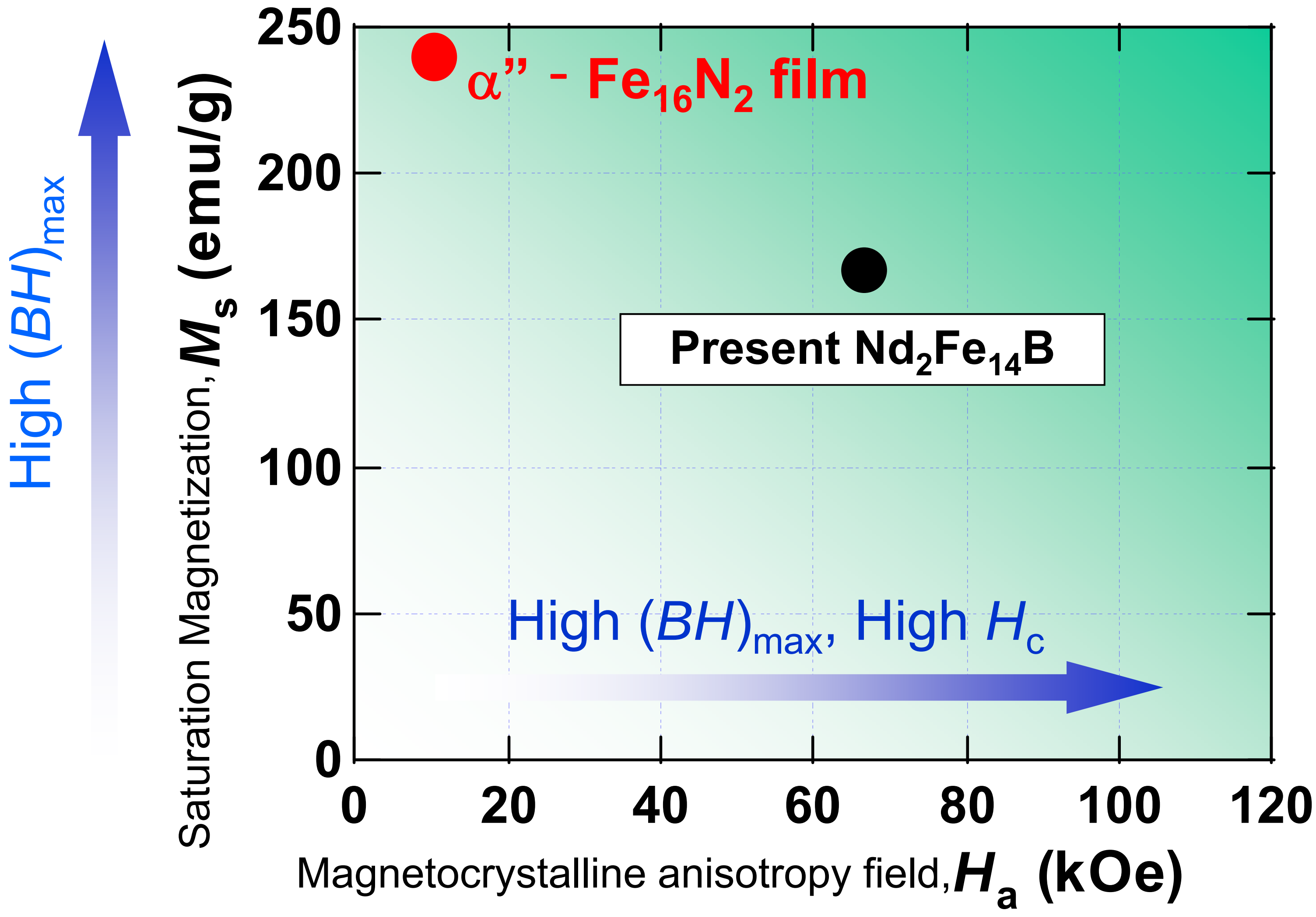


$Fe_{16}N_2$
$(Fe\text{-}Co)_{16}N_2$
$(Fe\text{-}Ni)_{16}N_2$
$Fe_{16}N_2$(-H)
$Fe_{16}(N,C)_2$
$Fe_{16}C_2$

Dependency of N content
Impurity effect(H_2O, CO_2, etc.) ➡ UC process
3d electron number effect ➡ $(Fe_{1-x}Co_x)_{16}N_2$ (bct), $(Fe_{1-x}Ni_x)_{16}N_2$ (bct, fct)
N, C, B interstitial effect ➡ $Fe_{16}(N_{1-x}C_x)_2$, $Fe_{16}(N_{1-x}H_x)_2$
Thermal stability
Unit cell volume effect

Not so large magnetic moment for α"-$Fe_{16}N_2$ phase！
M_s = 240 emu/g (300 K), K_u ~ 1 x 10^7 erg/cm^3

Short summary



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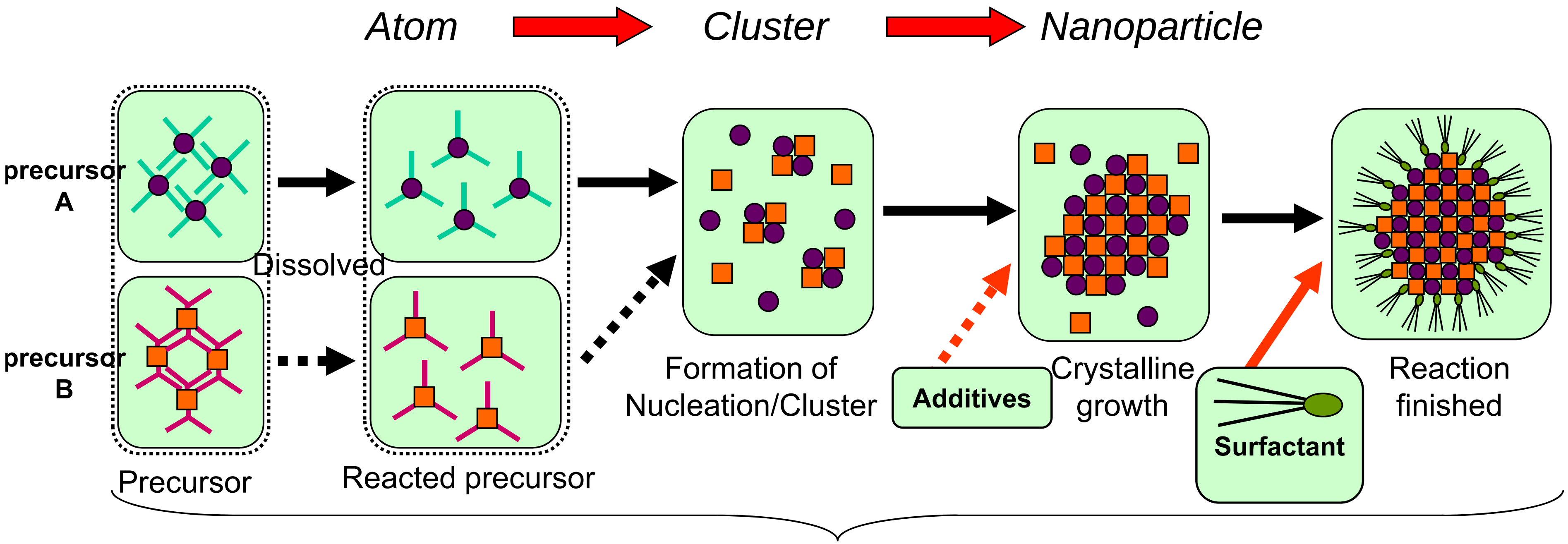
4. Summary

α" - $Fe_{16}N_2$ nanoparticle via chemical route

- Direct synthesis -

Free from influence of substrate/under layer

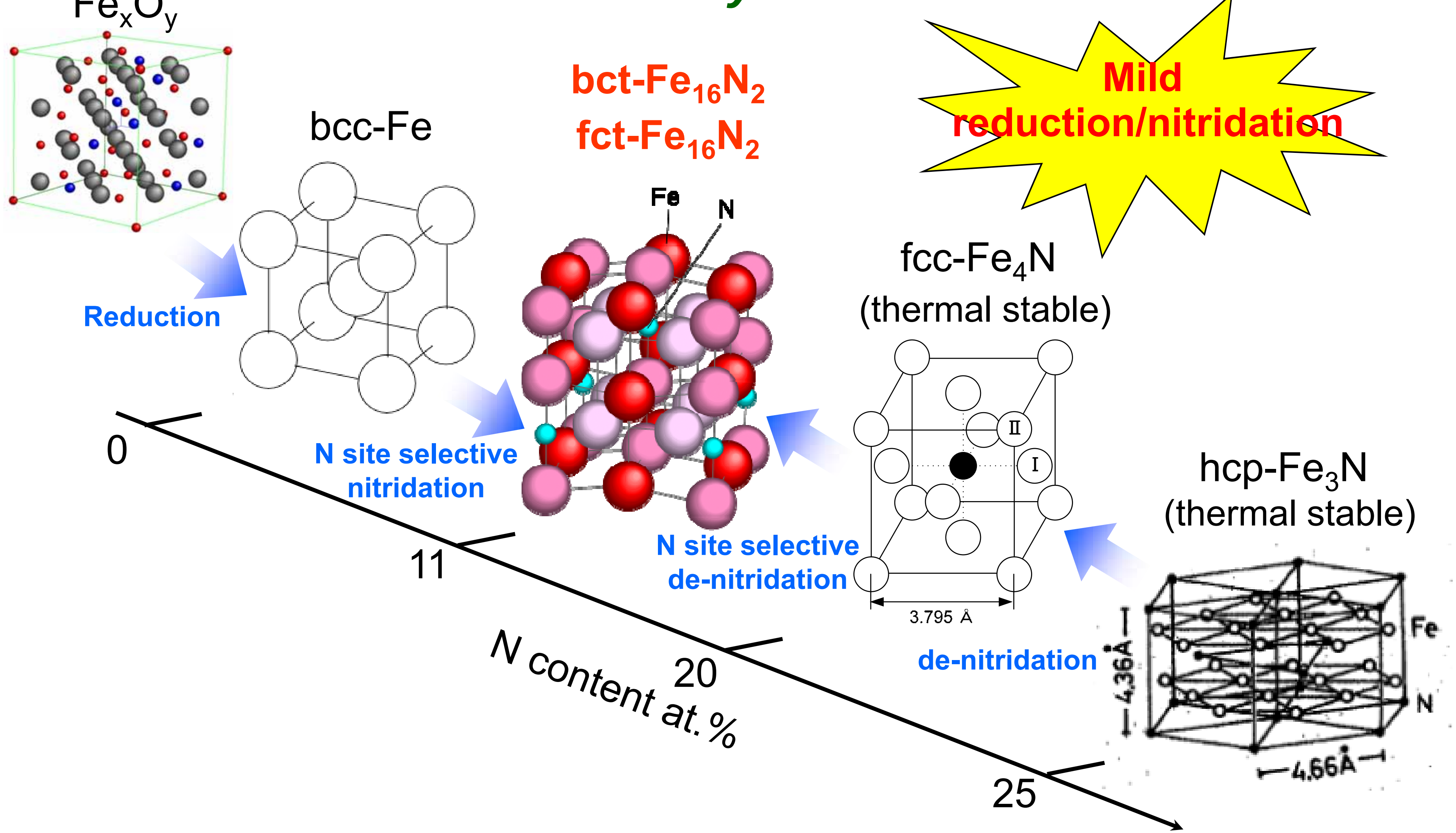


Wide variety of process parameter

Synthesis of non-equilibrium α"-$Fe_{16}N_2$ phase

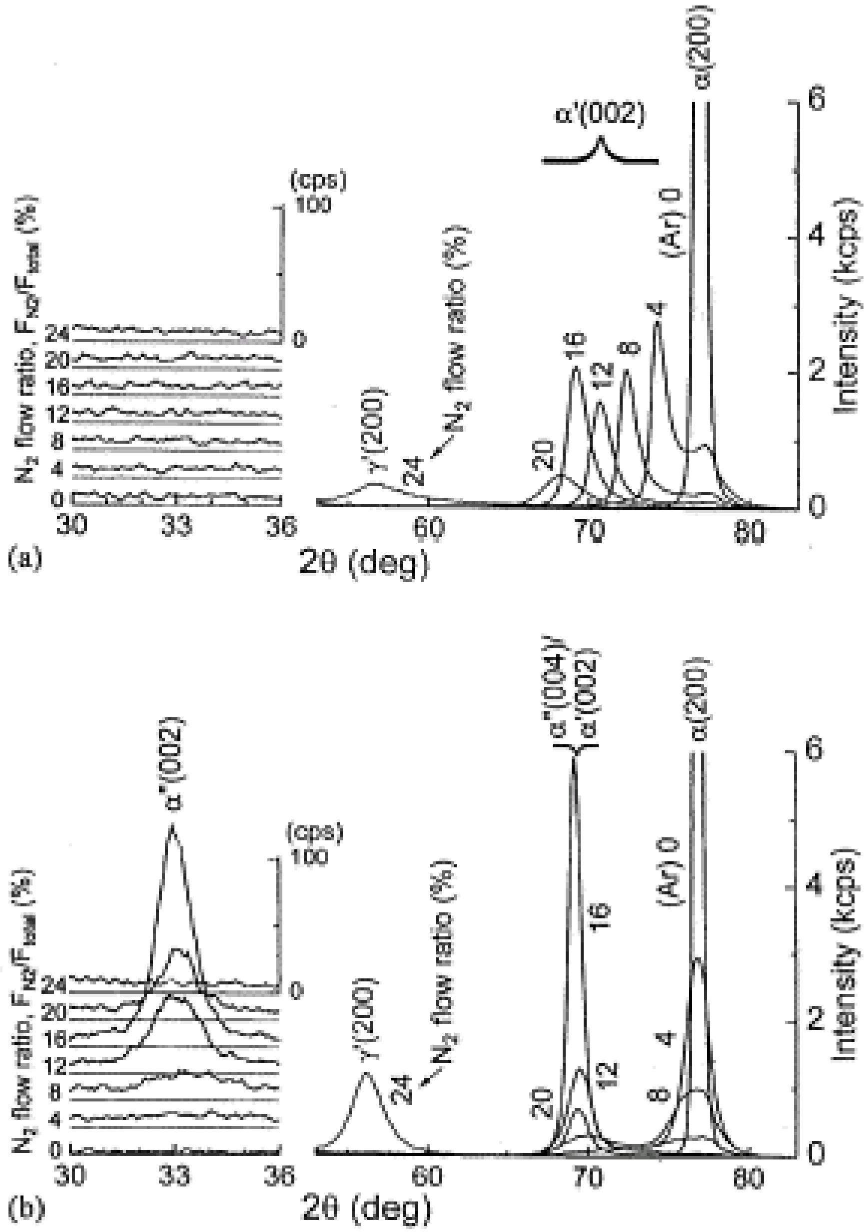
α" - $Fe_{16}N_2$ nanoparticle via chemical route

- Indirect synthesis -

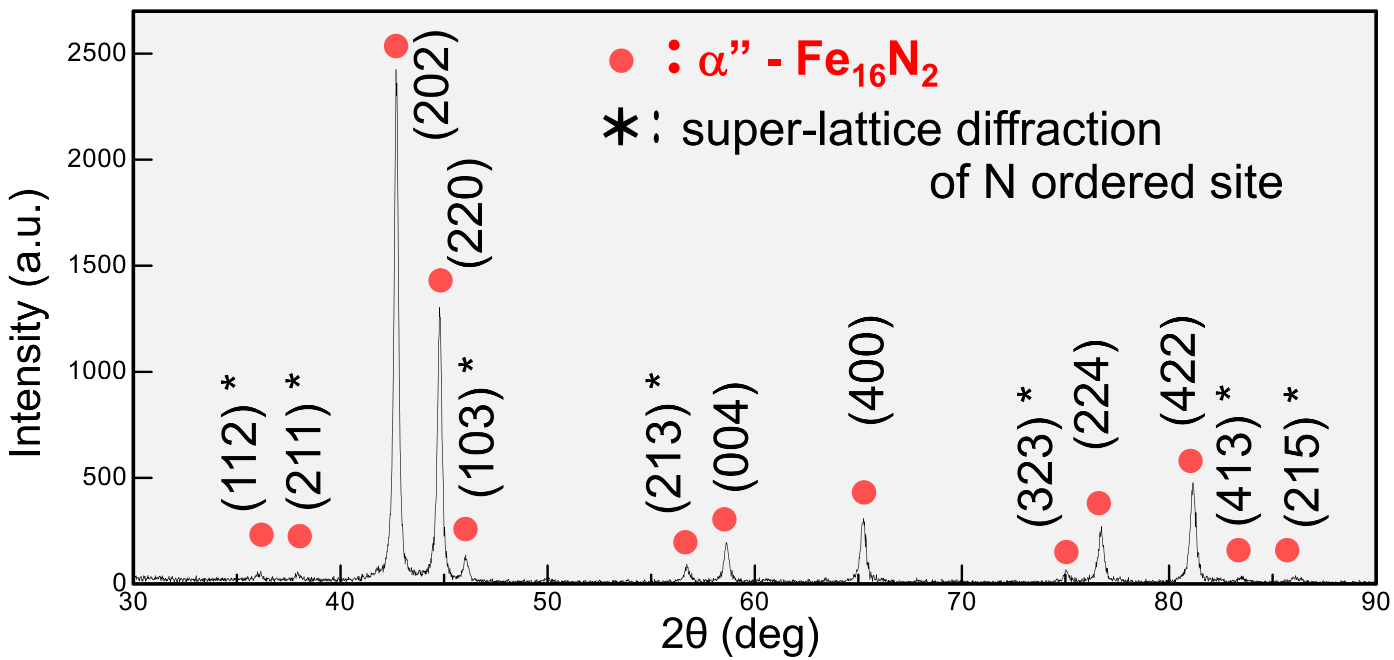


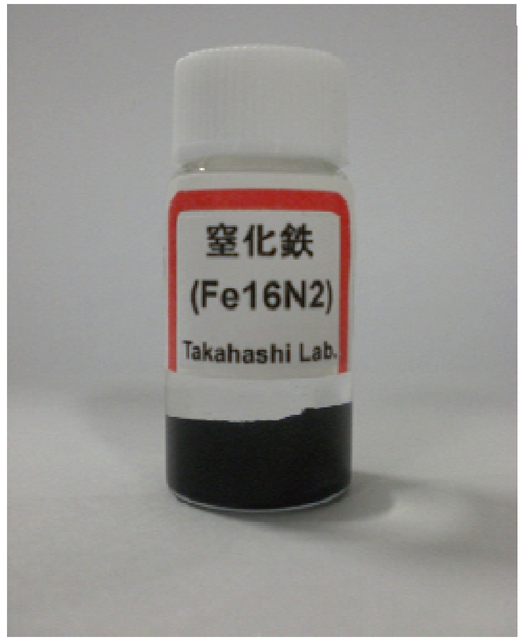
XRD profiles for α”-$Fe_{16}N_2$ pseudo-single crystalline sputtered thin film

(001) Plane orientation



XRD profiles for α”-$Fe_{16}N_2$ nanoparticles

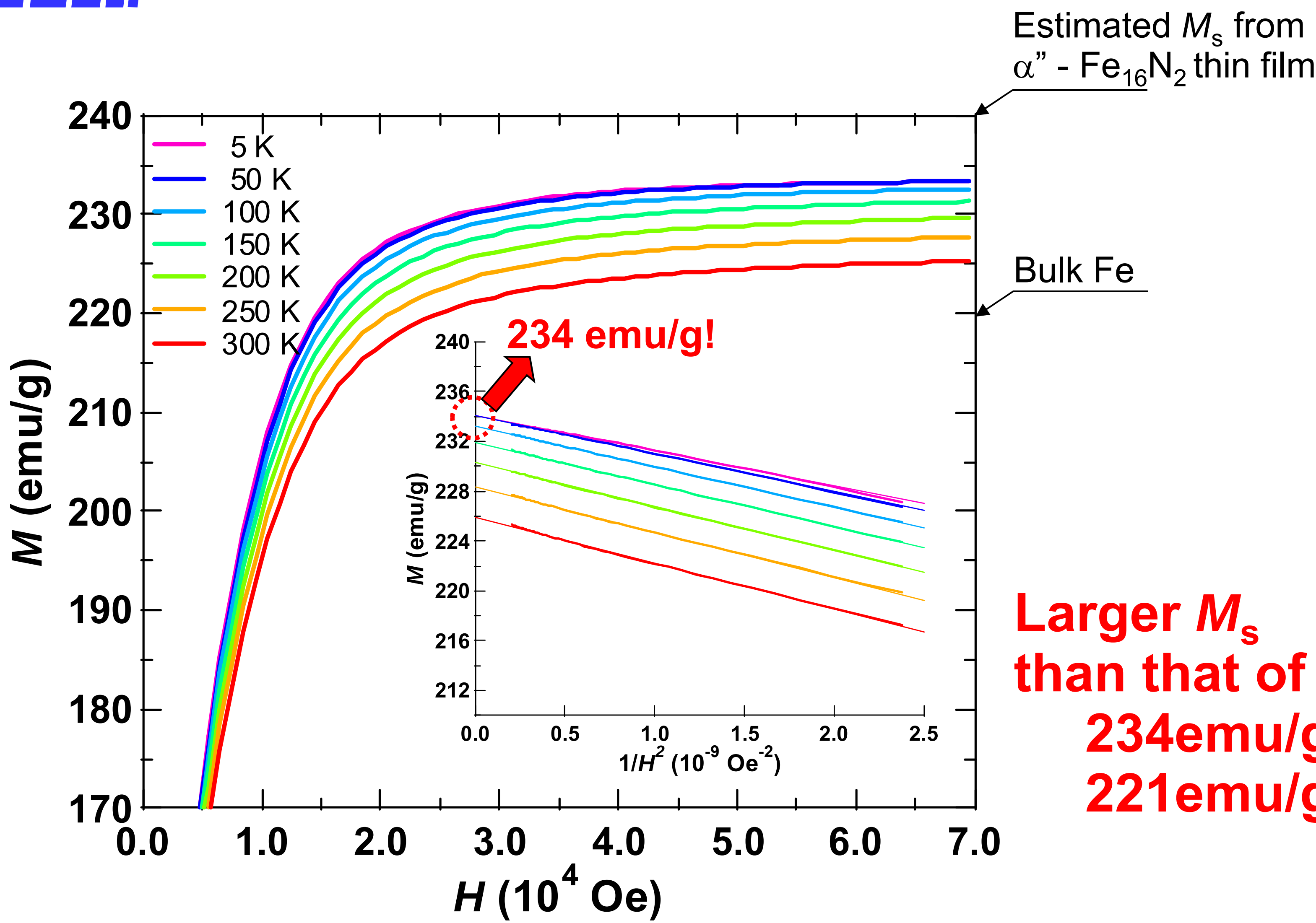




- Success of gram scale synthesis of single phase α” - $Fe_{16}N_2$ nanoparticles !!

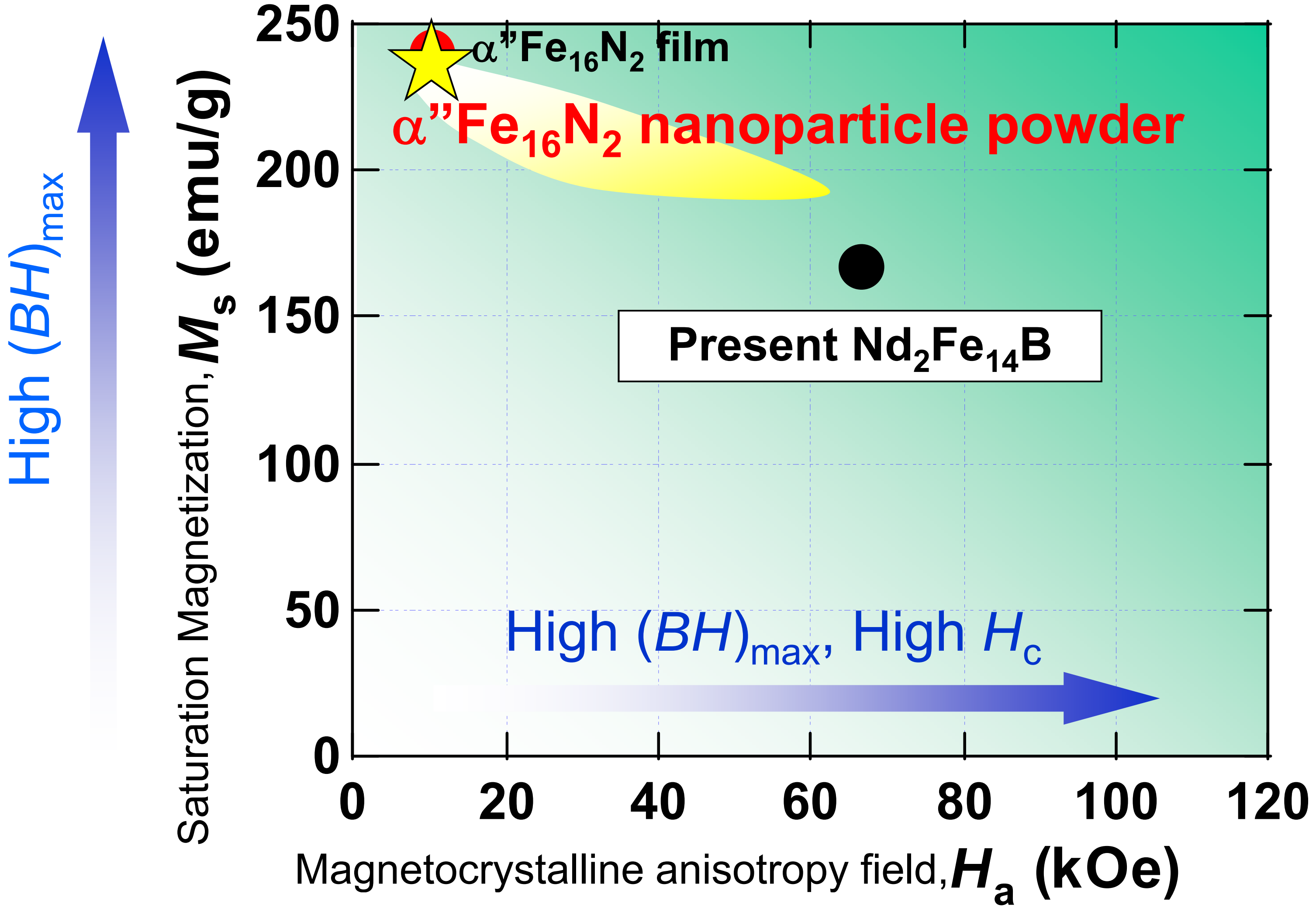
- Lattice constants (*a* & *c*) well agree with those of thin film!

Magnetization



Larger M_s
than that of α-Fe
234emu/g@5K
221emu/g@300K

Magnetic potential of α" $Fe_{16}N_2$ phase for permanent magnetic material



Summary

- Establishment of stable synthesis of α"- $Fe_{16}N_2$ nanoparticles

- Single crystalline, single phase with stoicheometry N concentration (11 at.%) and same lattice constant as bulk precipitates

- Magnetism of α"- $Fe_{16}N_2$ phase

$$\begin{cases} M_s \sim 240 \text{ emu/g} \\ K_u \sim 1 \times 10^7 \text{ erg/cm}^3 \end{cases}$$

⇒ Agree well with our former thin film results!!