JST Japan-EU workshop,
Nov. 22, 2011

Rare Elements in Magnetic Materials

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My Research Experience

- **1972-1975 : hcp Ni, fcc Co, Fe-Co-Ni**
- **1975-1985 : Rapidly quenched amorphous materials, Sndust (Fe-Al-Si) alloys**
- **1985-1991 : Amorphous thin films (Gd-Co, ･･･）, Spin-glass (Fe-based alloy), Magnetiresistance (Fe,Co,Ni)**
- **1991-1993 : Tunnel magnetoresistance, Soft magnetic materials, Multilayer films, Kerr effect of alloy films**
- **1993-2007 :Tunnel magnetoresistance, (Magnetism of organic materials), (Permanent magnet), HDD, MRAM**
- **2007- : MRAM materials, Organic/In-organic hybrid materials**

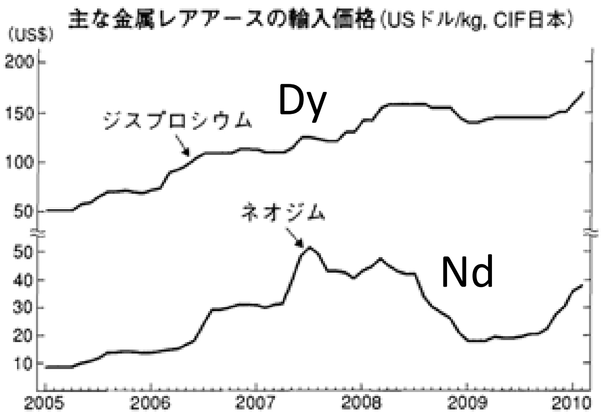
Price of the Elements used for Magnetic Materials

Elements	Price ($/kg)
B	0.65
N	
Mg	2.7 (2005)
Al	2.2 (2010)
Si	2.49
V	16
Cr	7.6
Mn	0.003
Fe	0.06
Co	67
Ni	37
Zn	3.2

Elements	Price ($/kg)
Ga	530
Ge	1240
Ru	1400 (2011)
Pd	11500
Ir	37000 (2011)
Pt	42100
Nd	45→460
Sm	250
Gd	140
Tb	800 →4900
Dy	150 →3800

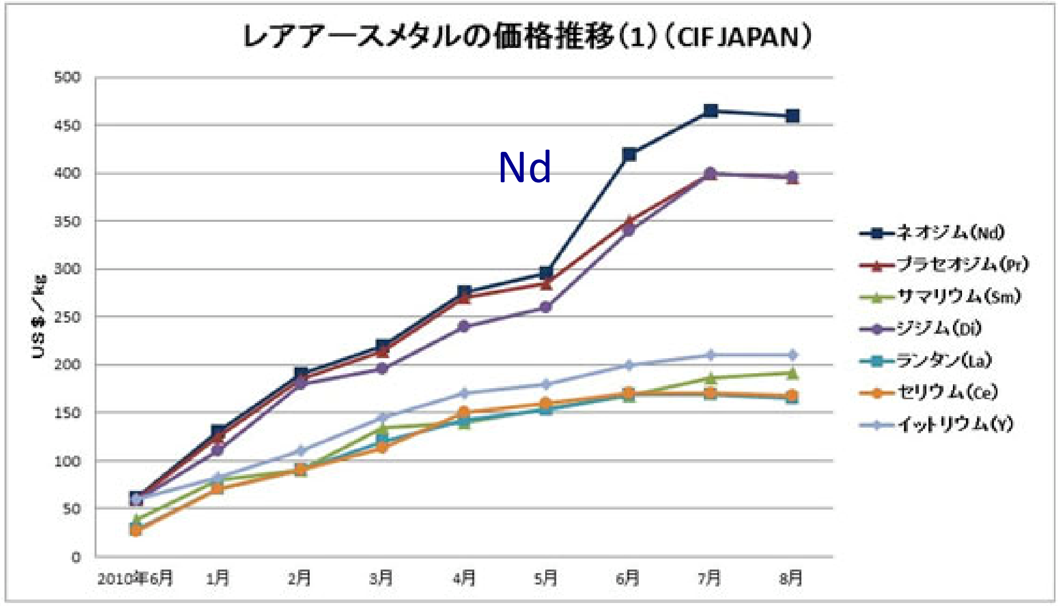
At 2007

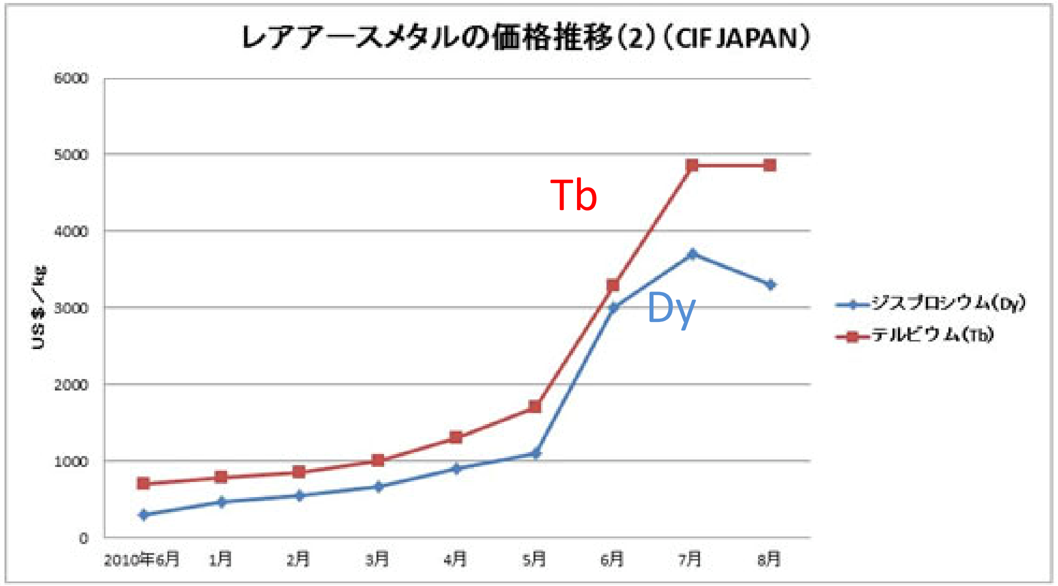
Price of rare earth elements



2005〜2010

レアメタルニュース(発行元:アルム出版社)2010年 03 月 24 日p01 抜粋

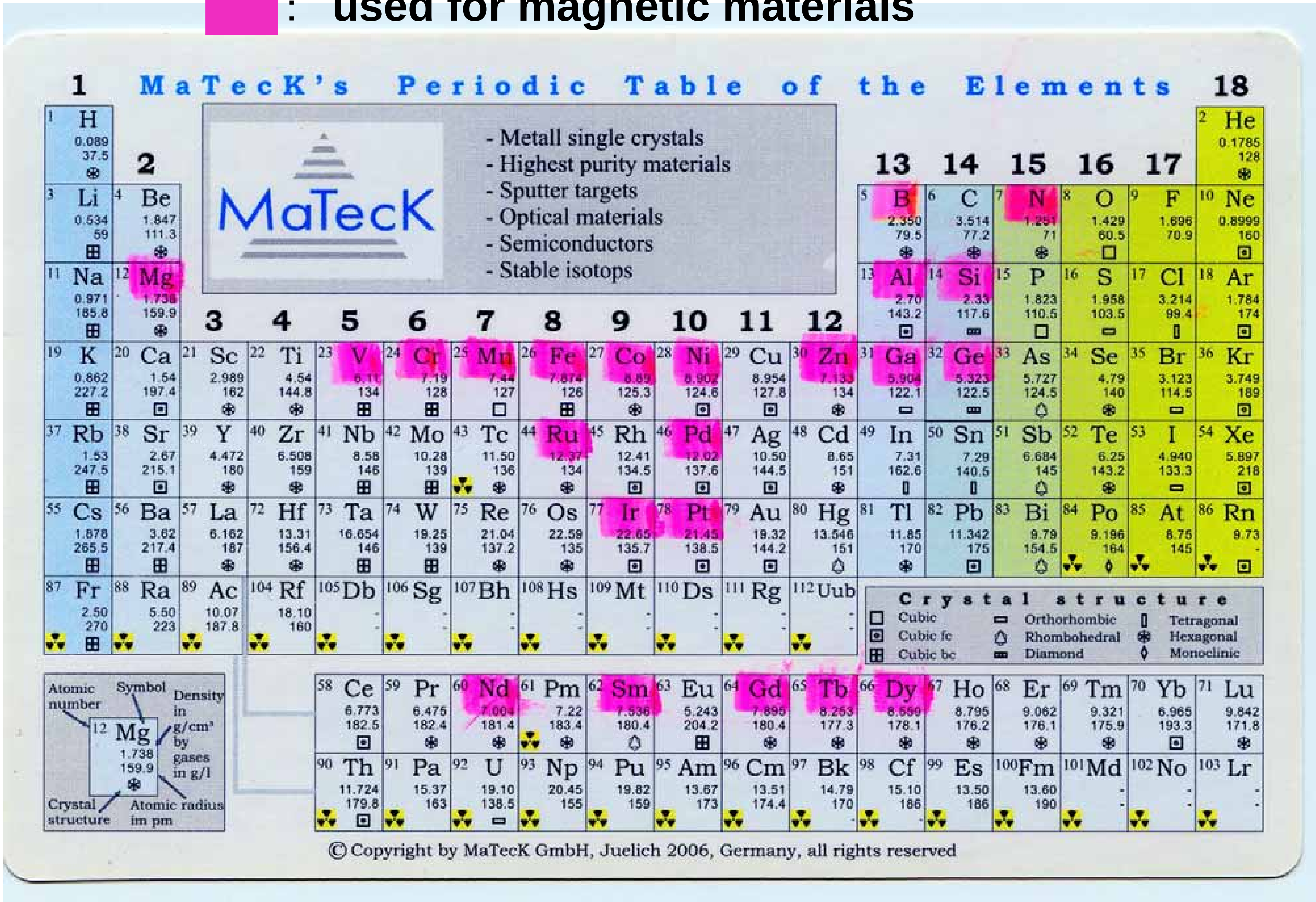




June 2010〜August 2011

NeoMag
www.neomag.jp

: **used for magnetic materials**



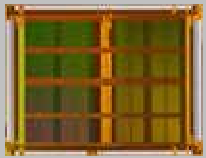
Classification of magnetic materials

- Spintronics materials : Fe-Co-B, Heusler alloys (Co_2MnSi), Pt-Mn, Ir-Mn, Co-Pt, Fe-Pt, CoCrPt , Mn-Ga
- Hard magnetic materials : NdFeB+Dy, SmCo, FeSmN
- Soft magnetic materials : Fe-Ni, Permendur (CoFe), Fe-based amorphous alloys, Sendust (Fe-Al-Si)

Except oxides

Staff of Spintronics Materials Group and Collaboration

TOSHIBA



T. Miyazaki

S. Mizukami

T. Kubota

Q. Ma

Materials physics in AIMR

Dept. Appl. Phys RIEC

Our Target

Finding a new material which will be used as the electrodes of MTJ in high density MRAM

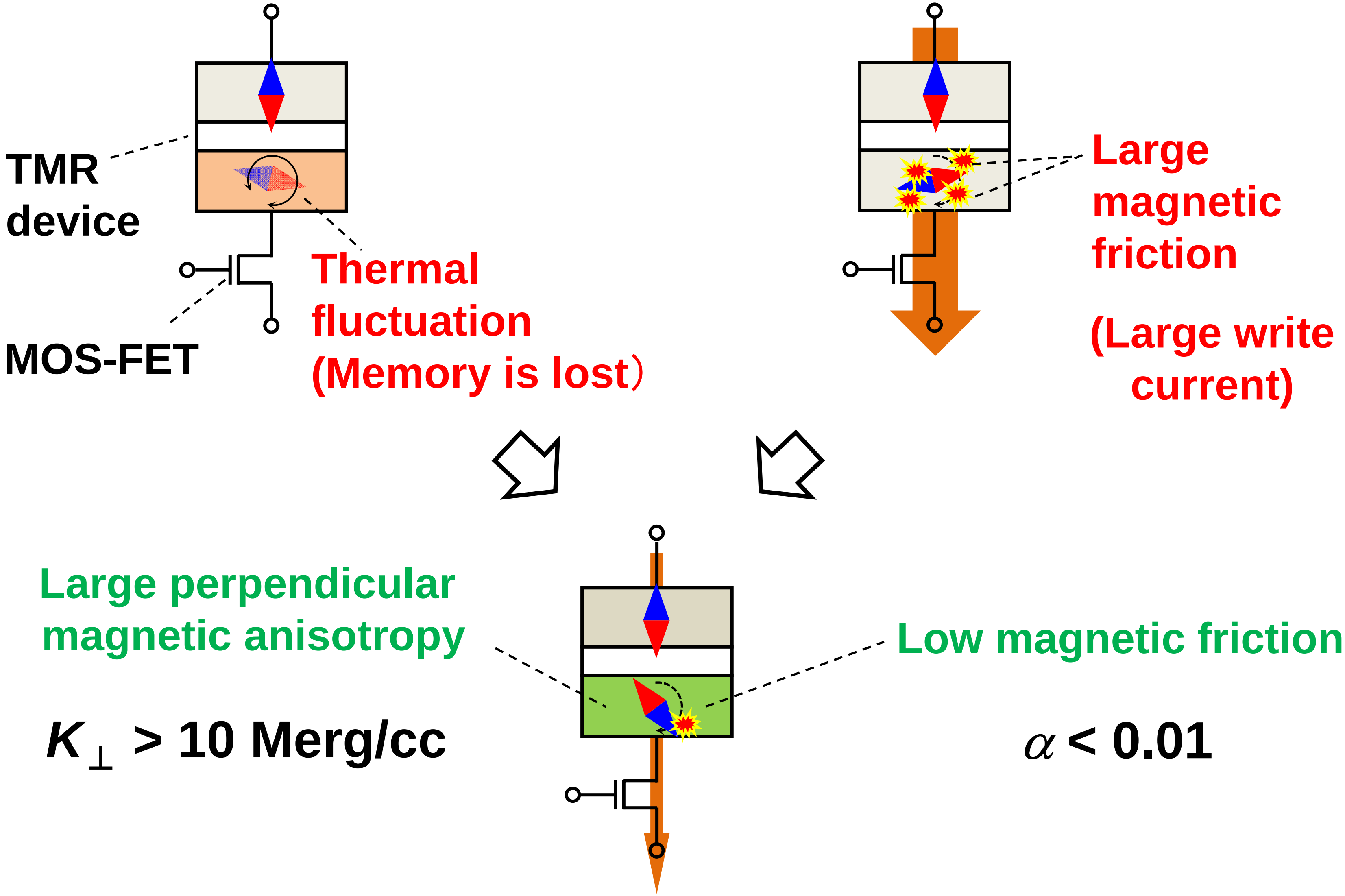
$M_s < 300$ Gauss

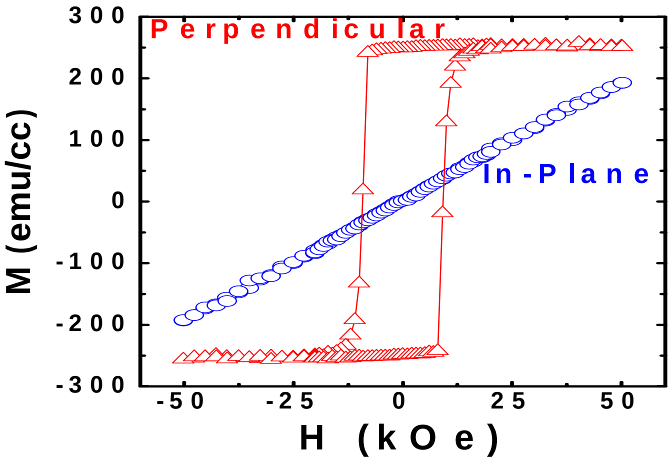
$K_{\perp} = 1\text{x}10^7$ erg/cc

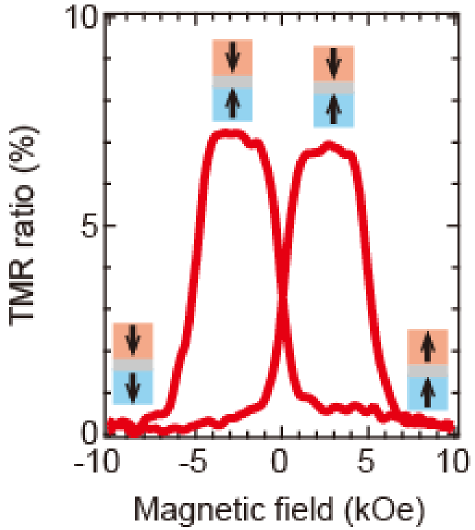
$\alpha < 0.01$

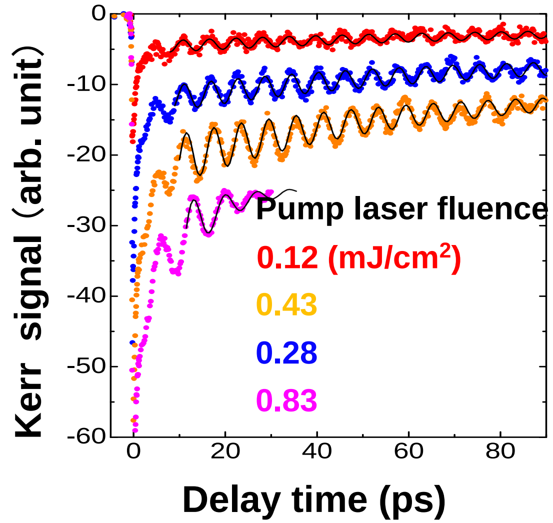
TMR ratio > 100 %

Spintronics Materials for Gbit STT-MRAM









Typical magnetic and transport properties for Mn-Ga thin film (green Material) developed in our group

Large ($K_{\perp}$ =1－2x10^{7} erg/cc) perpendicular anisotropy

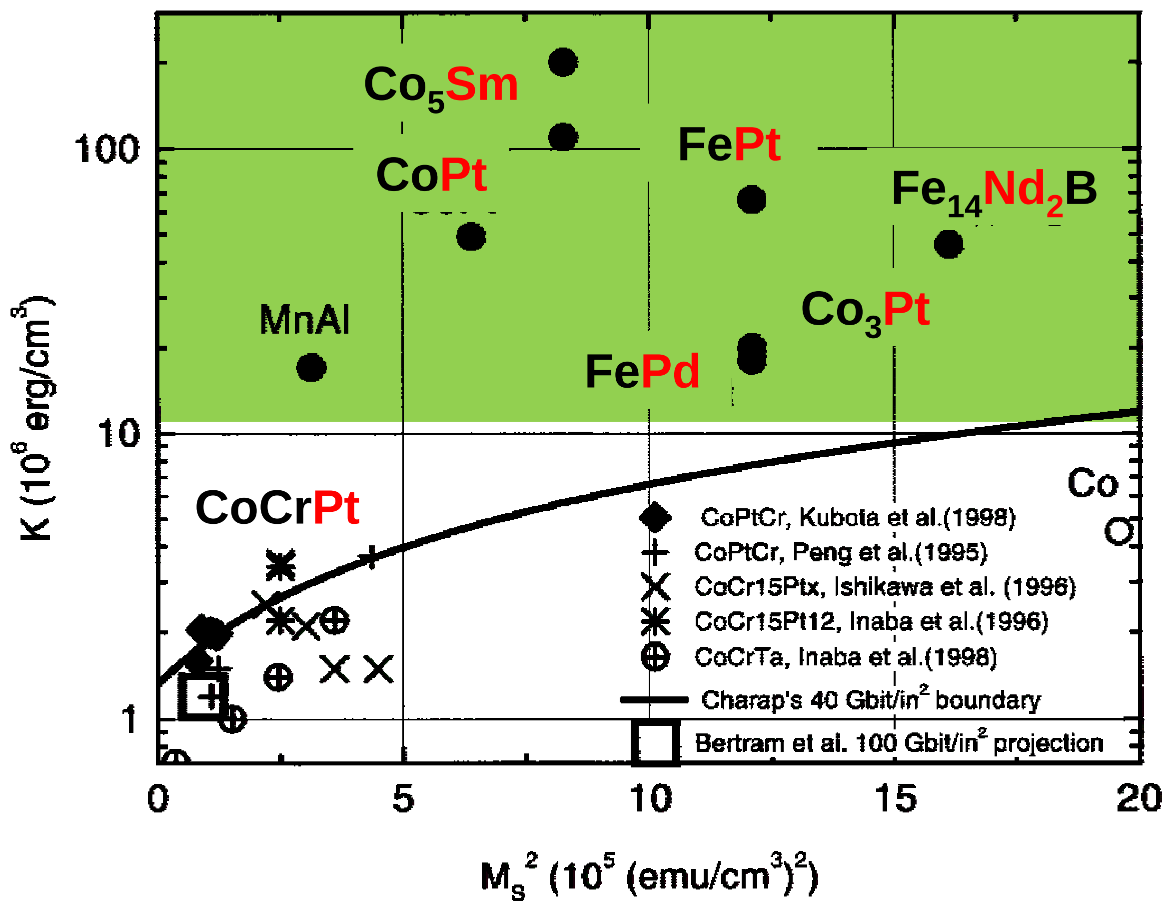
TMR ratio
We must improve this point

Small damping constant

α ＝0.01－0.02

Wu et al, APL 94, 122503 (2009), Mizukami et al, PRL 106, 117201 (2011), Kubota et al, APEX 4, 043002 (2011)

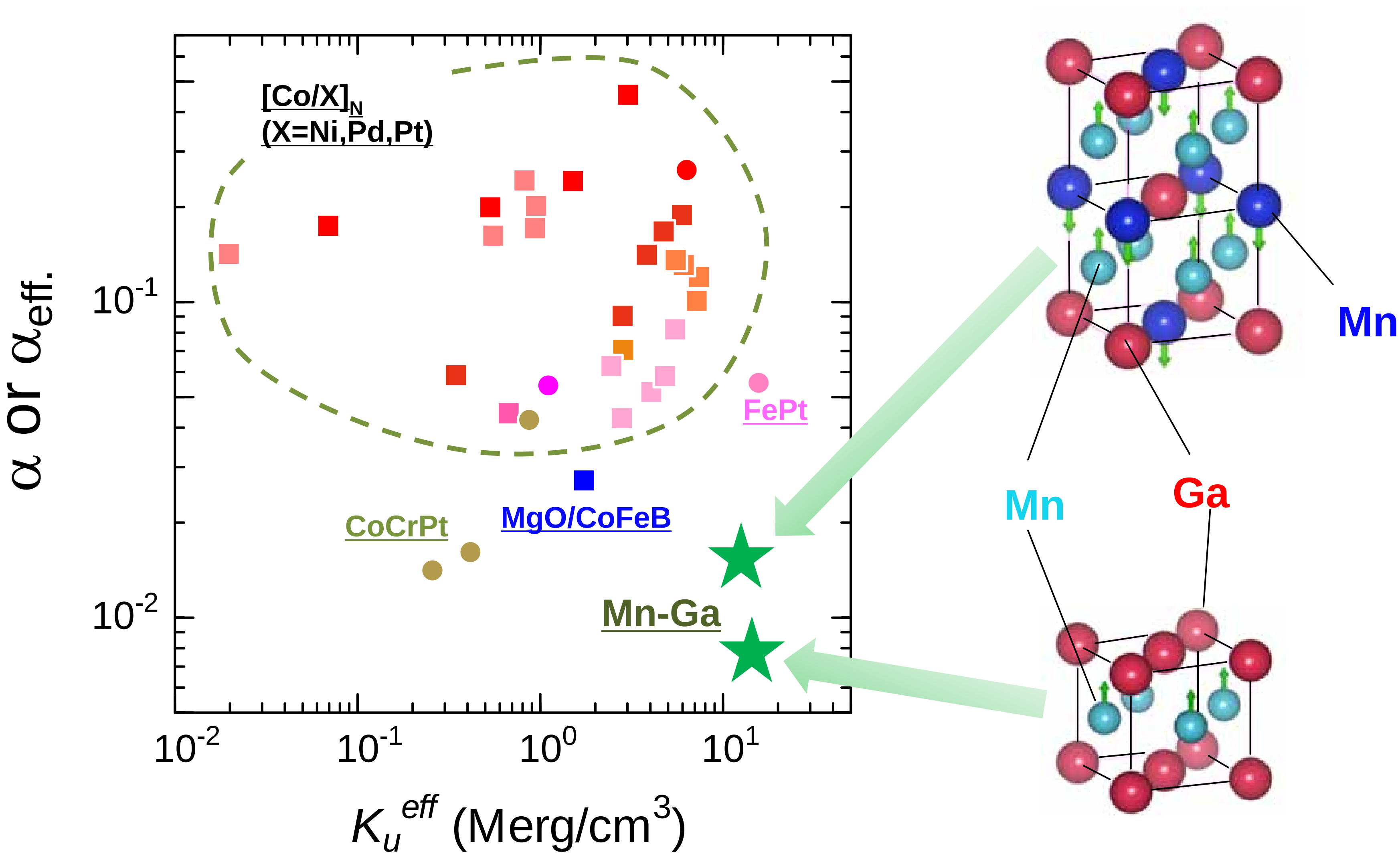
Perpendicular magnetic anisotropy, $K_\perp$ > 10 Merg/cc



D. Weller et al. IEEE Trans Mag. 36 10 (2000)

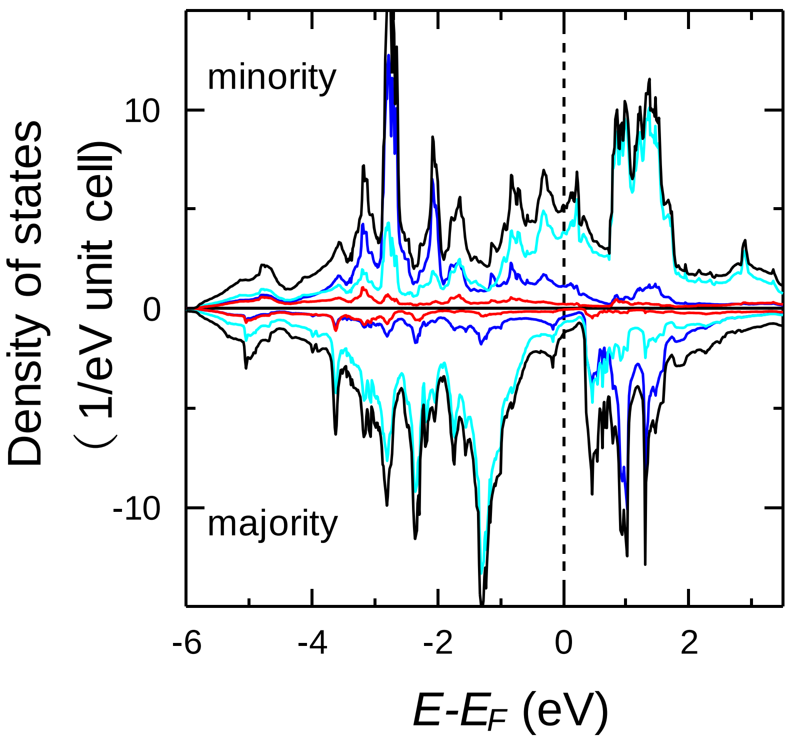
Noble or Rare-earth metals are crucial ?

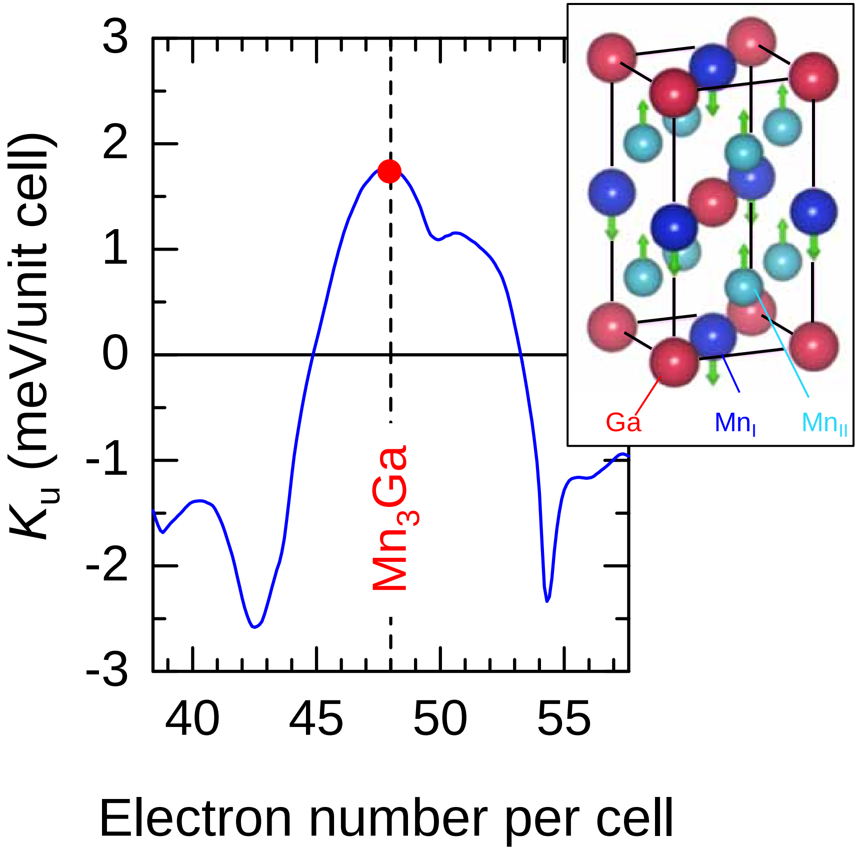
Mn-Ga alloys exhibit large-$K_{\perp}$ as well as low-α



And also low-cost

Comparison between experiments and theory





LMTO-ASA with LDA approximation

Mn_{II} : 2.48 μ_B

Mn_{I} : -3.09 μ_B

M_s = 306 emu/cc

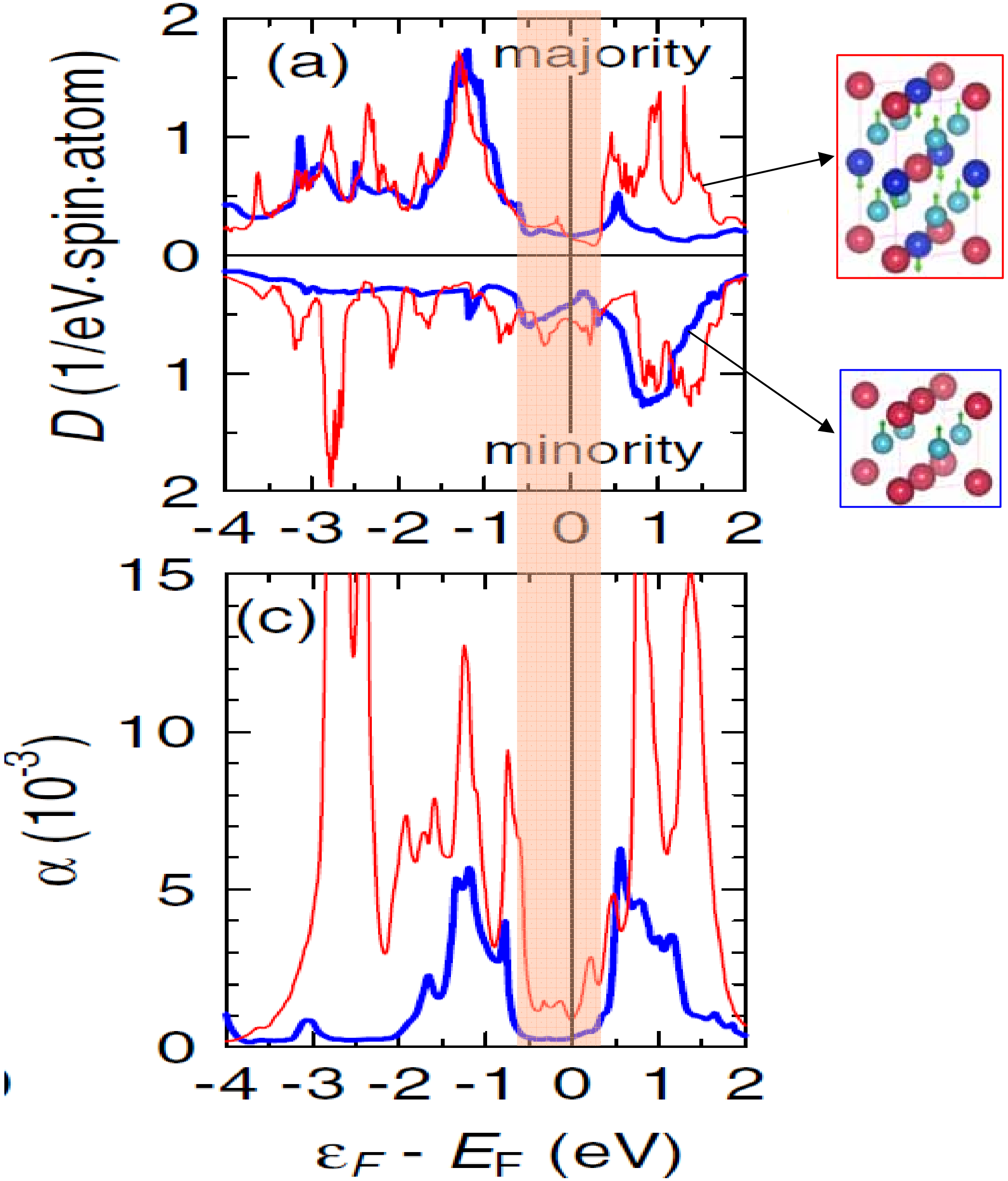
Calc. including spin-orbit interaction

$K_\perp$ = 26 Merg/cc

Roughly consistent with exp. values

S. Mizukami et al., Phys. Rev. Lett. 106, 117201 (2011).

Possible story ?



Small damping is only around E_F, (between DOS peaks)

$$\alpha \propto \boxed{\frac{\xi_{so}^2}{\Delta E^2}} \boxed{D(E_F)}$$

small

$$K_\perp \propto \boxed{\frac{\xi_{so}^2}{\Delta E}}$$

large

(still under investigation)

Physics of Magnetic Materials Group (Yamagata University)

Prof Kato

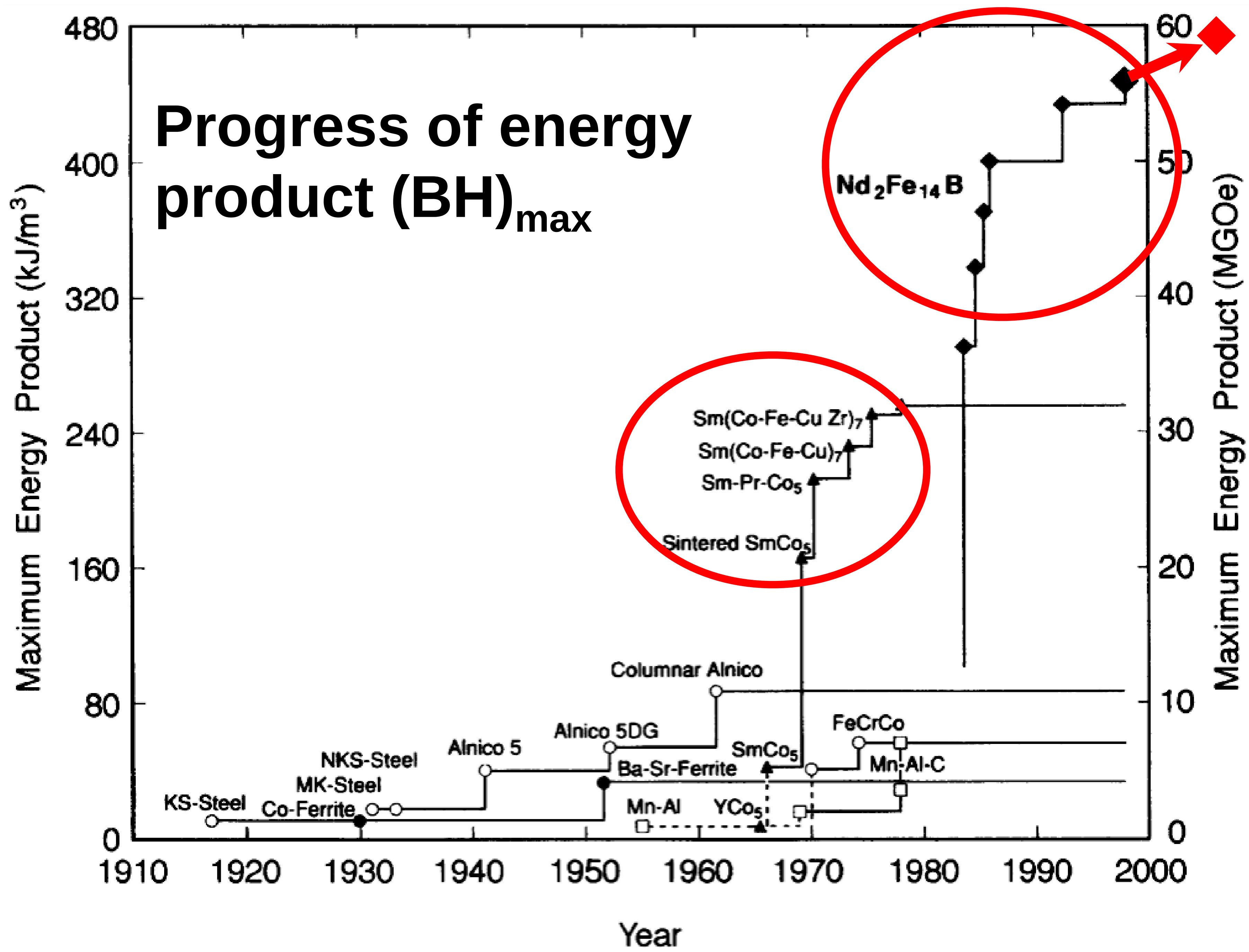
- **Development technology for reducing Dy usage in a rare-earth magnet**

METI-NEDO Project : Rare Metal Substitute Materials Development Project (H19ーH23)

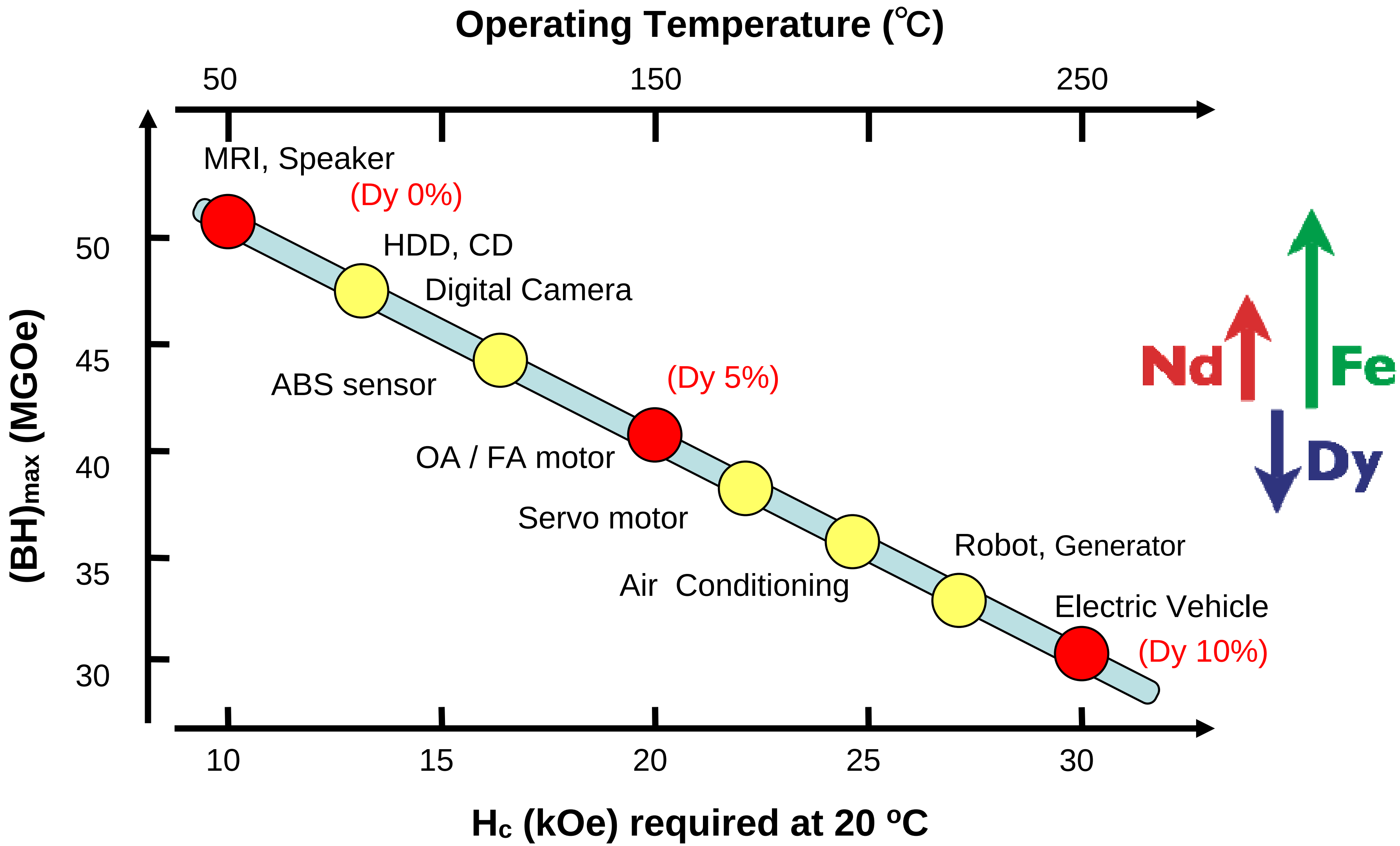
Yamagata Univ. + 2 Univ. +2 Institute + 4 Companies

- **Coercivity enhancement in bulk Nd-Fe-B by high-magnetic field process**
- **Coercivity mechanism study by using model-interface sample made by thin-film process**

Progress of energy product $(BH)_{max}$

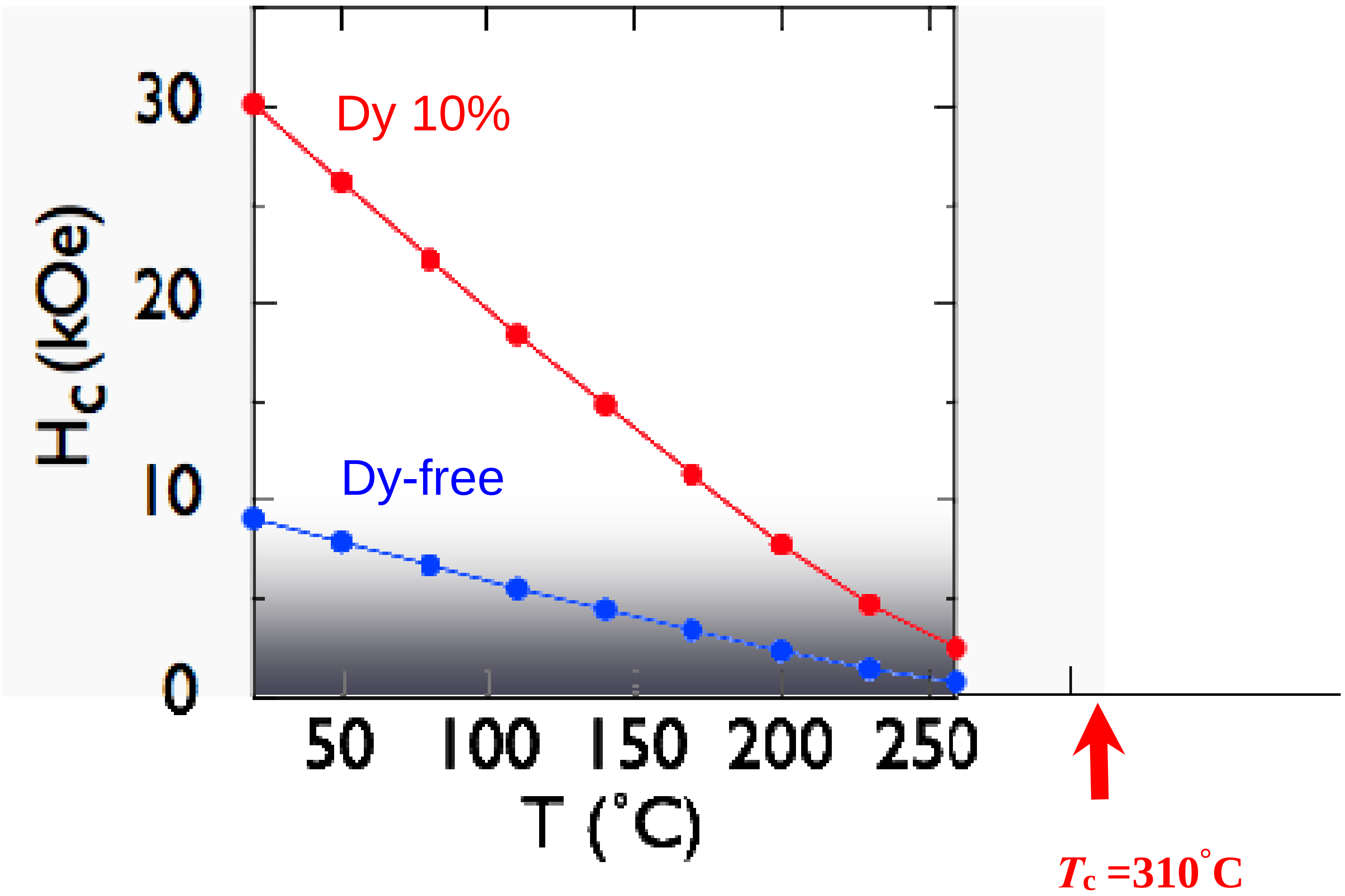


Main use and corresponding magnetic properties of Nd-Fe-B permanent magnet



Natural Abundance : Dy << Nd

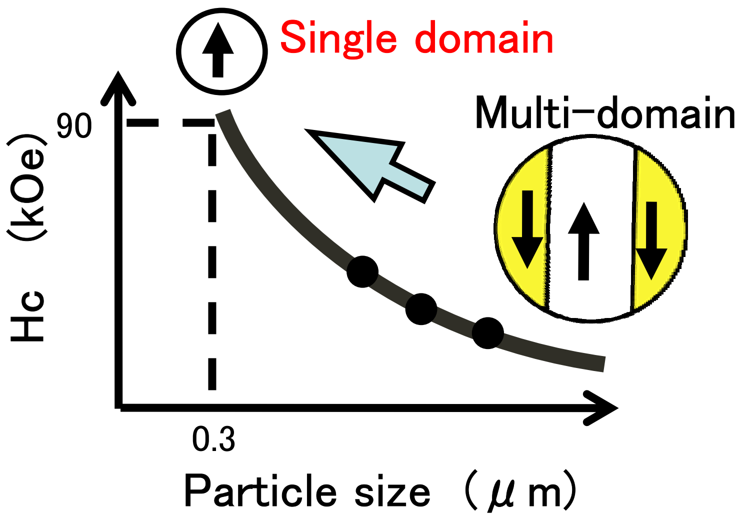
Nd-Fe-B permanent magnet



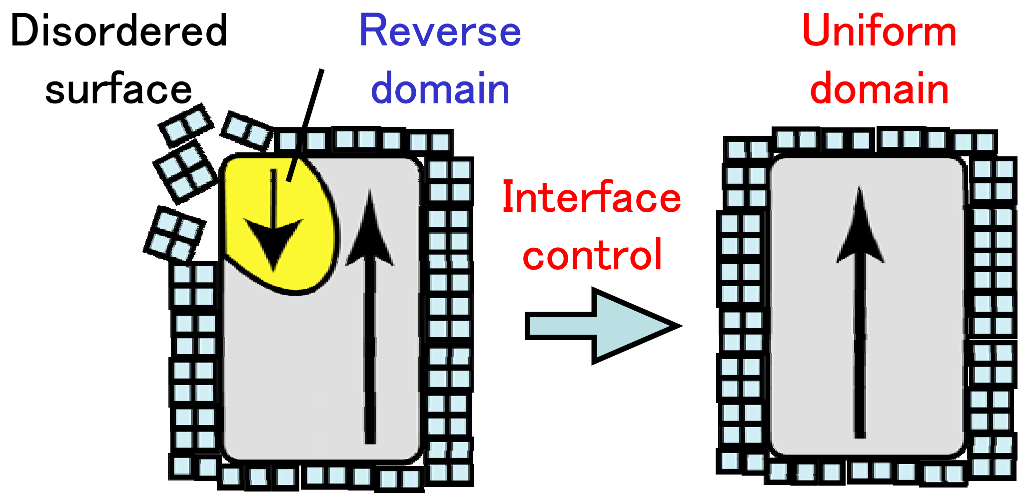
How to increase the coercive force without Dy?

Two approaches to increase Hc of Nd-Fe-B magnet without Dy

Ⅰ. Reduction of particle size



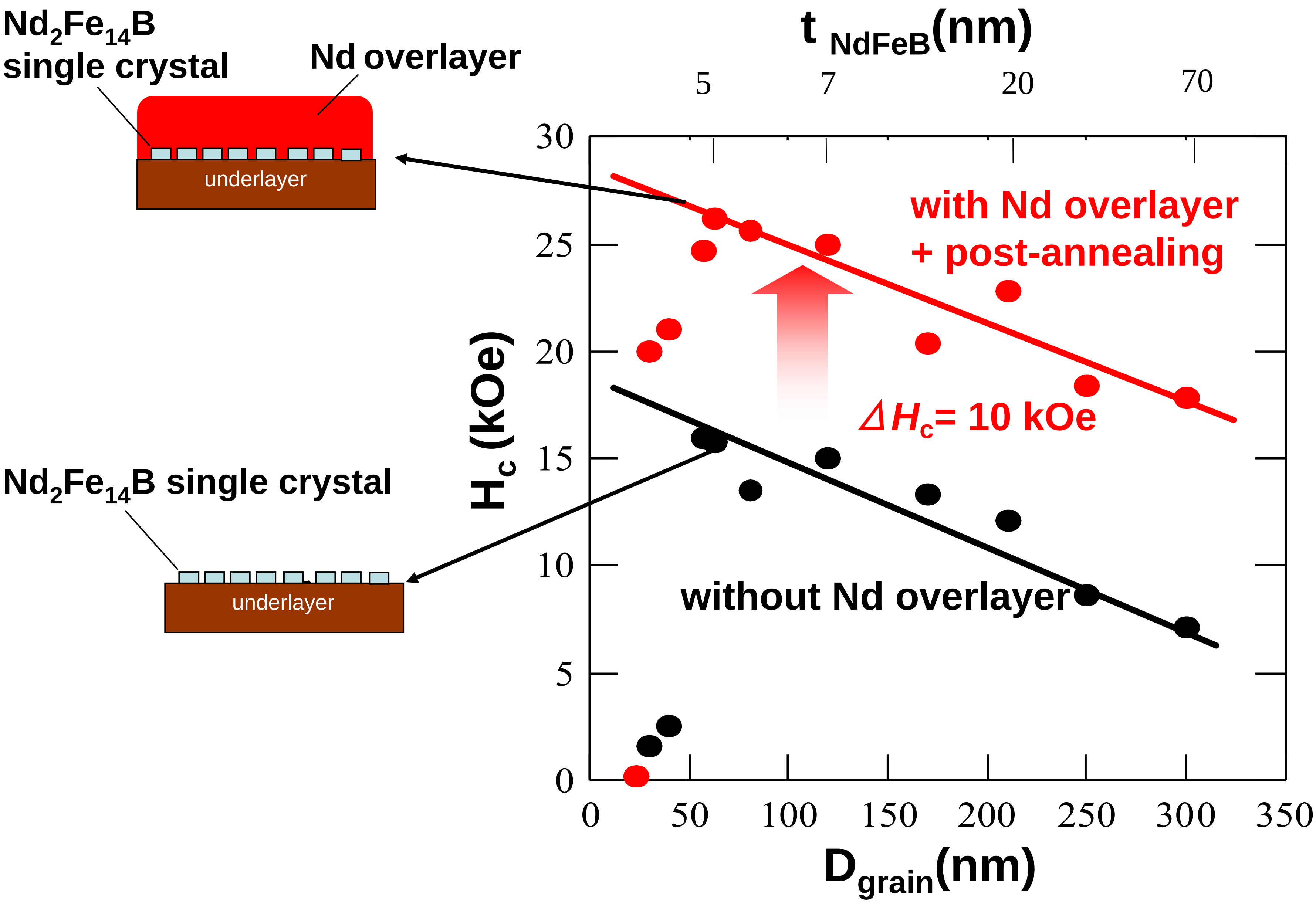
Ⅱ. Control of particle surface



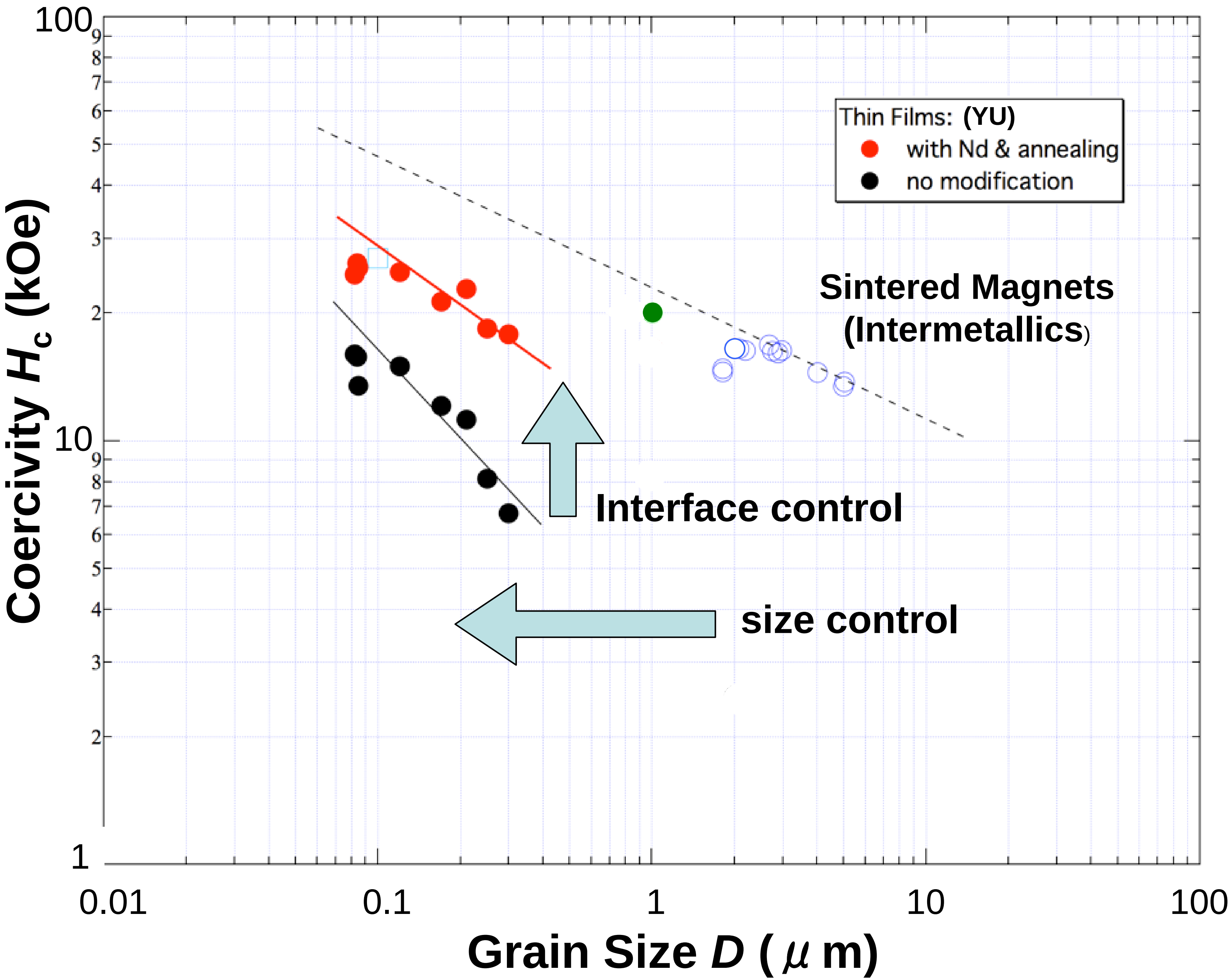
H_c (Dy-free Nd-Fe-B) ≒ 10 kOe

This value is approximately 10 % of the theoretically expected value

H_c enhancement in Nd-Fe-B film by Nd capping



H_c versus size



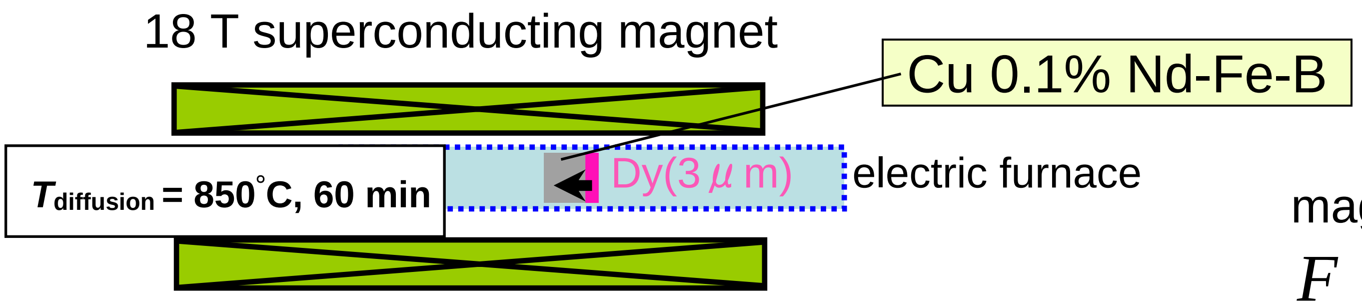
Effect of Strong Field Gradient on H_c in the grain boundary diffusion process

Problems of Dy diffusion process

- **Max. diffusion depth : ３－5 mm**
- **Strong Dy-content gradient from surface to inside**

Any effect of mag. force by field gradient ?

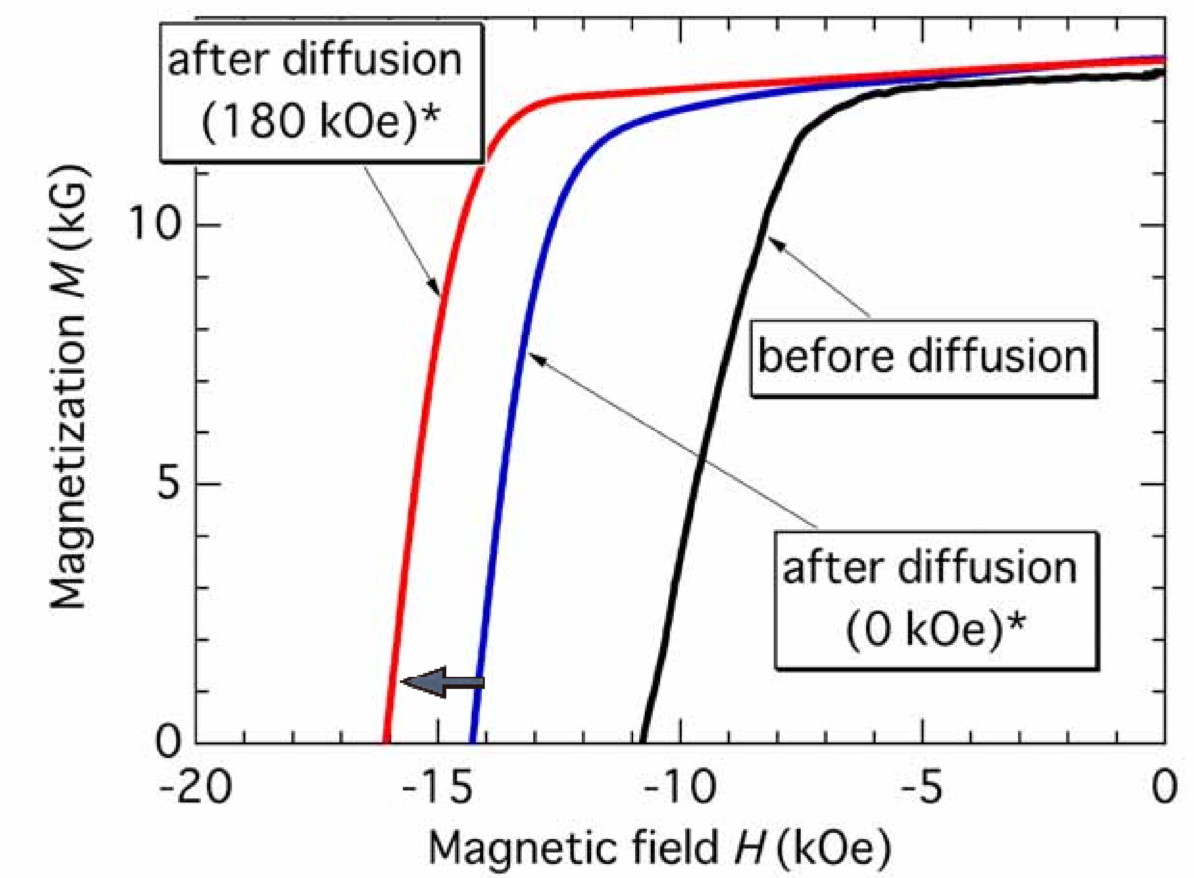
Dy diffusion experiment in strong field gradient

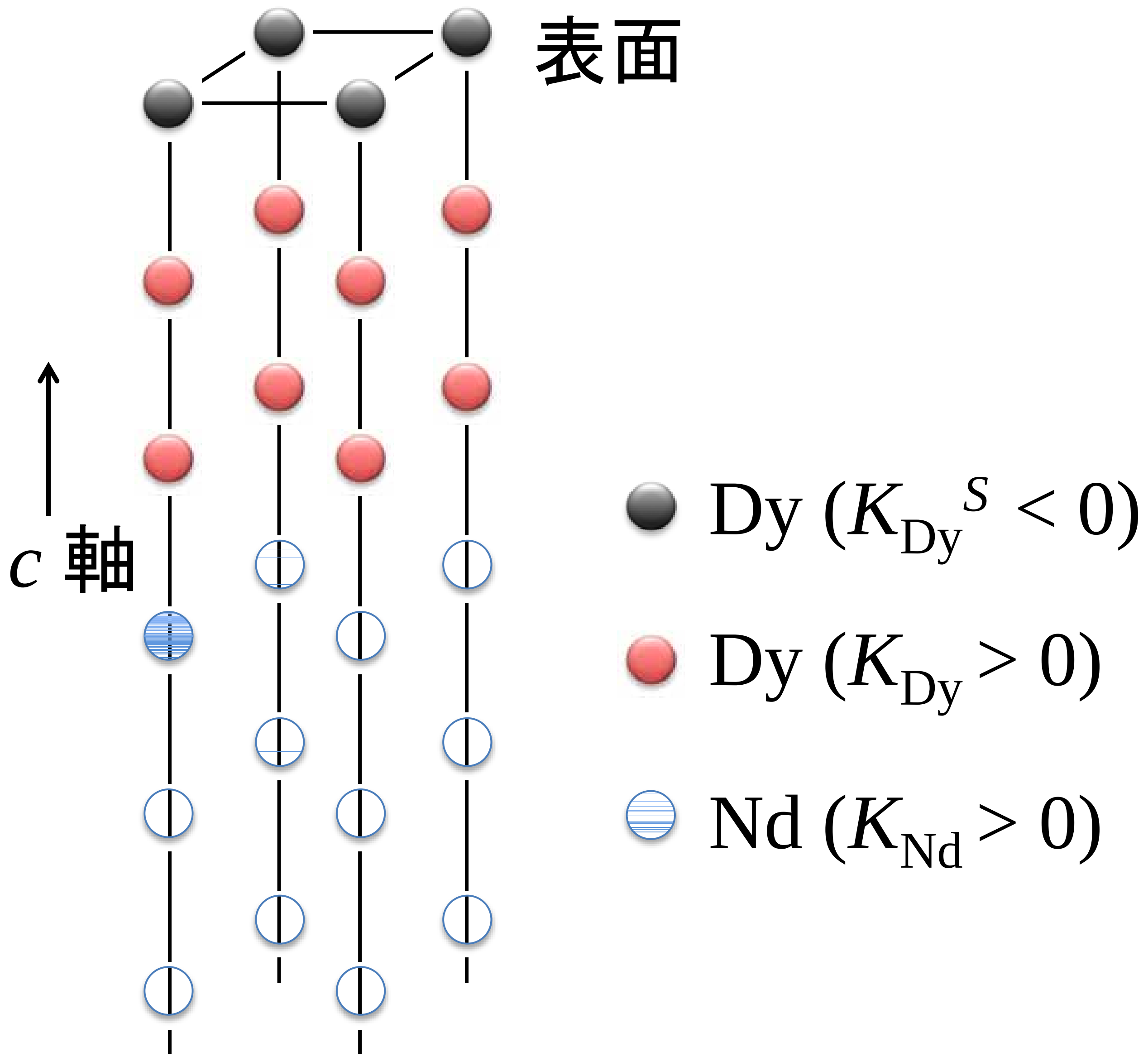


magnetic force:

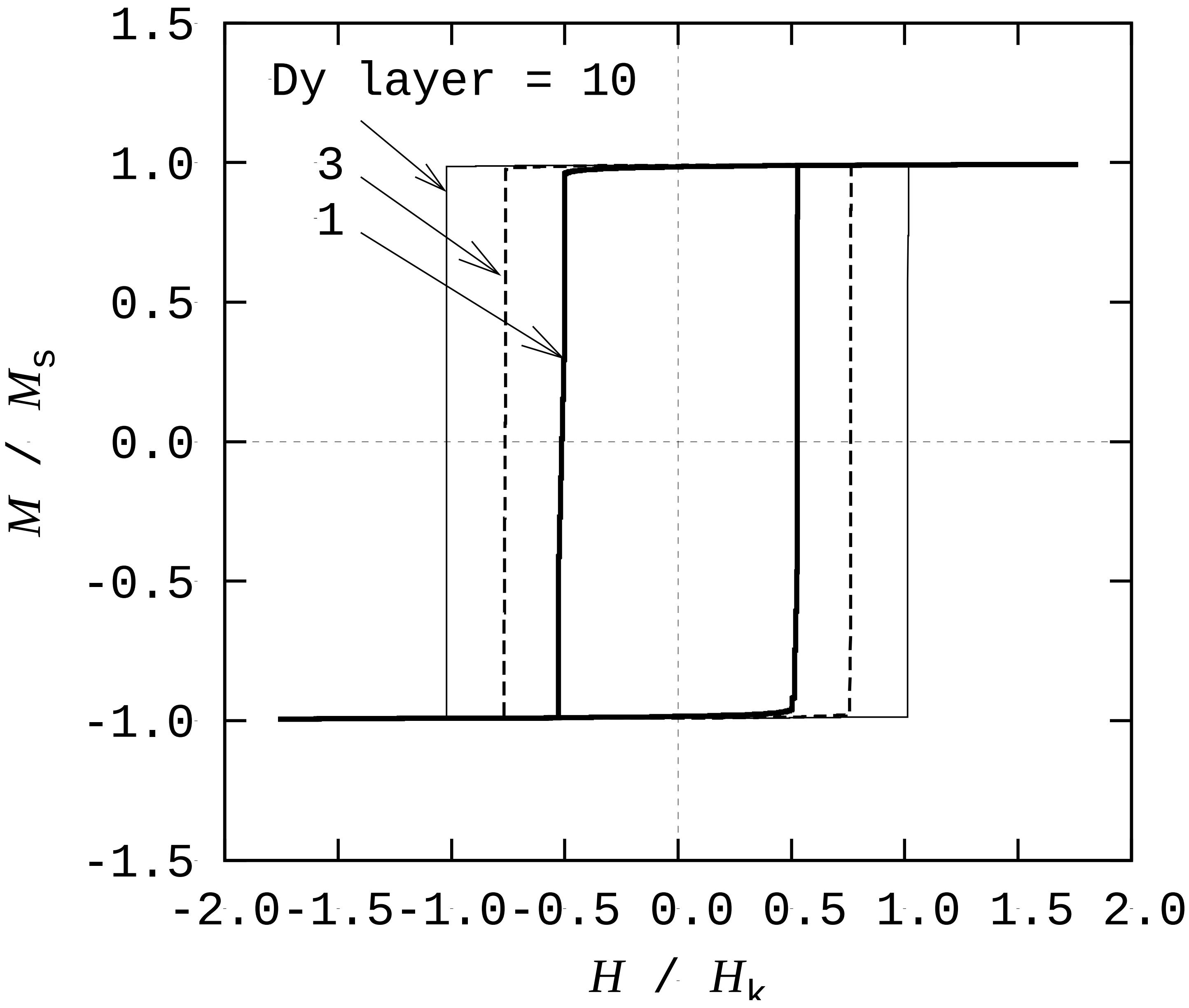
$$F \propto H \cdot dH/dz$$

*annealed at T_a=500°C after diffusion

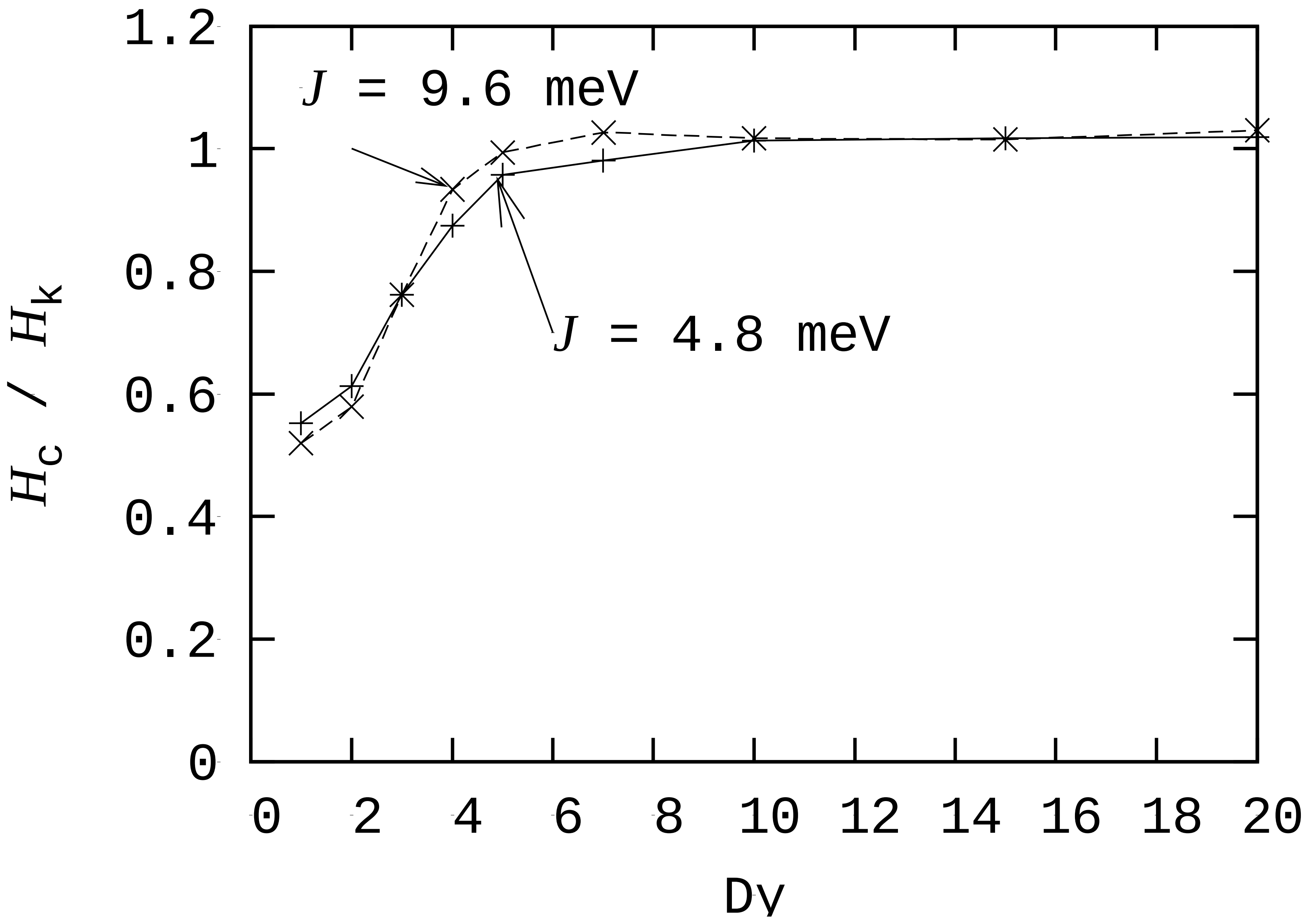




土浦ら、固体物理**14**, 677 (2009), まてりあ **50**, 389 (2011)



Dy layer = 10
3
1
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
M / M_S
H / H_k



1.2
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
16
18
20
Dy
H_c / H_k
J = 9.6 meV
J = 4.8 meV

How to get replaced materials ?

Morphology Change

- Multilayer film
- Fine particle
- Hybrid
- Nano-porous
- Interface control
- Topological control
- …

We need beyond these changes

Technical Methods

- Rapid quenching
- Sputtering
- MBE
- Atomic layer deposition
- High magnetic field processing
- …

We must find further other new methods