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Nd-Fe-B permanent magnets

M. J. O'Shea

Kansas State University

mjoshea@phys.ksu.edu

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1. Introduction

Best permanent magnets known:

Based on either $Nd_2Fe_{14}B$ or $SmCo_5$

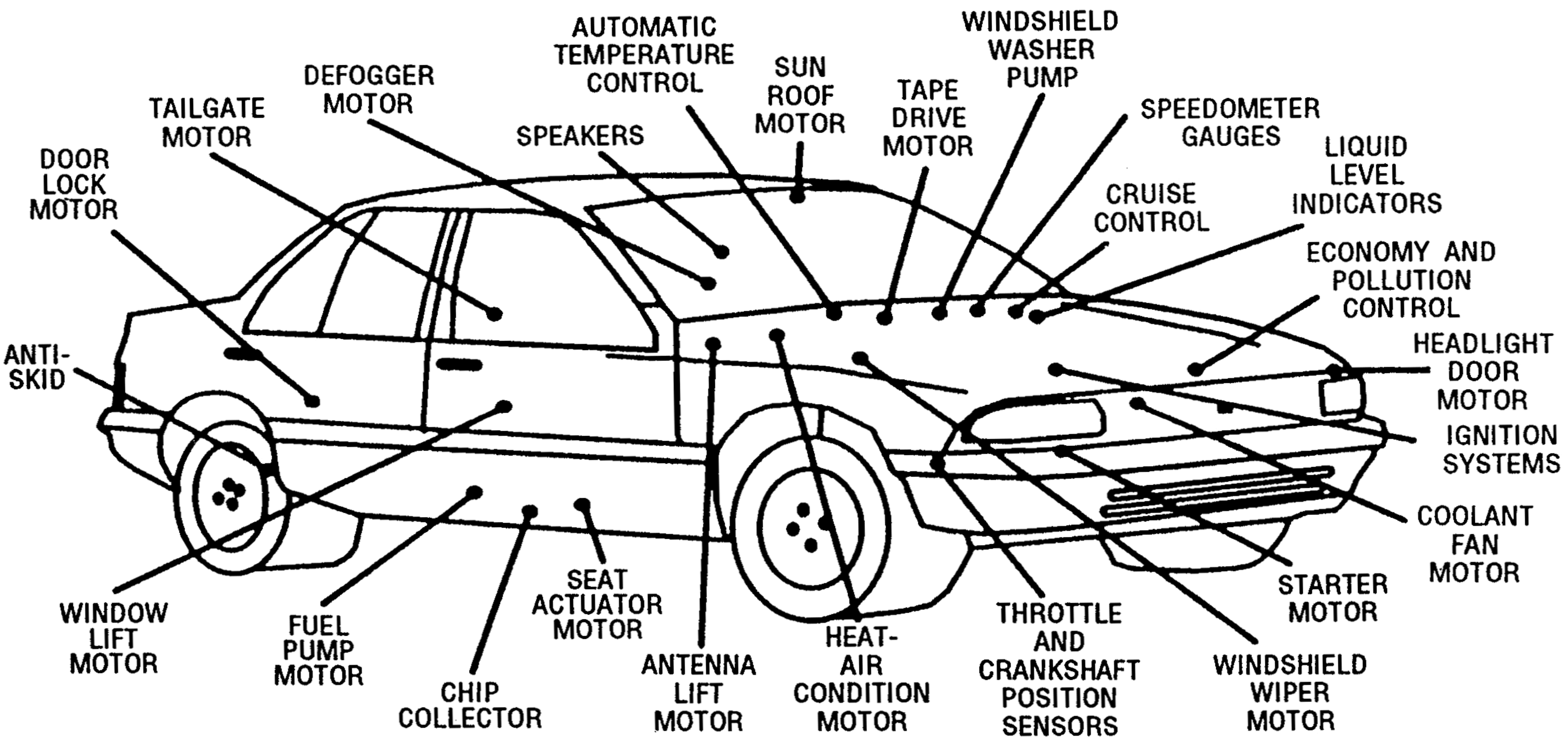
Important figures of merit

Magnetization M_S
- saturation magnetization

Coercivity H_C
-reverse field to reduce magnetization to zero

Energy product BH_{MAX}
-(max. value of product (BH) in 2nd quadrant)

Bulk permanent magnets in motors



PERMANENT MAGNETS IN AUTOMOTIVE APPLICATIONS

Why is nanostructuring important for bulk magnets?

Hard Magnetic Materials (permanent magnets)

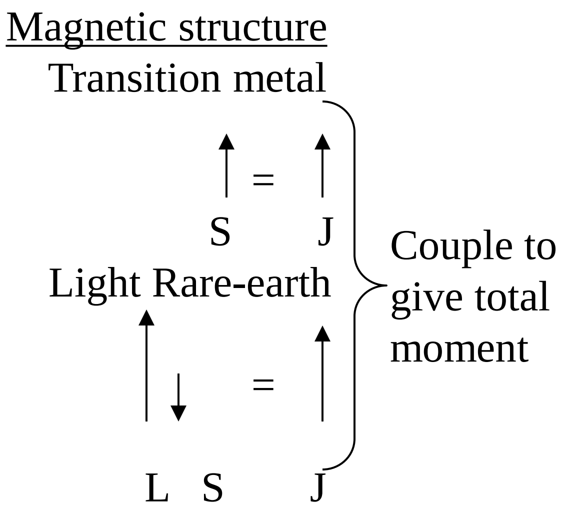
Should have

- a large coercivity (so they are not easily demagnetized)
- a large magnetization so that they create a strong magnetic field

Usually a combination of a rare-earth and a transition metal

High anisotropy

High magnetic ordering temperature



Magnetic structure

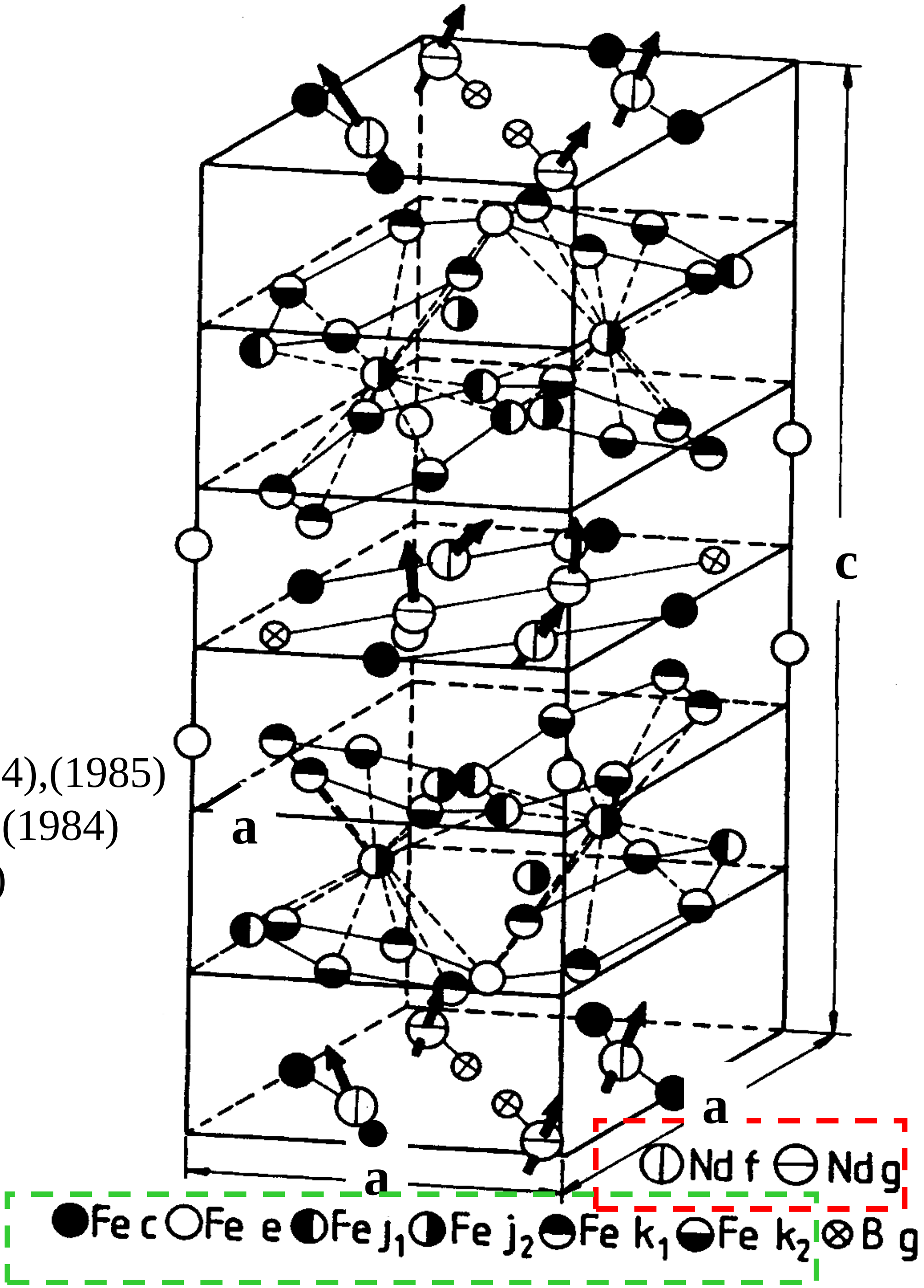
$Nd_2Fe_{14}B$ and $SmCo_5$ → important permanent magnet materials.
(tetragonal) (hexagonal)

Material	$\mu_0 M_s$ (T)	T_c (°C)	K_1 (MJ/m^3)	${}_iH_c$ (MA/m)	$(BH)_{max}$ (MG.Oe)
$SmCo_5$	1.0	700	10	2.9	24
$Nd_2Fe_{14}B$	1.6	312	5	1.6	45
CoPt	0.4	550	5	0.34	12

$Nd_2Fe_{14}B$-Structure

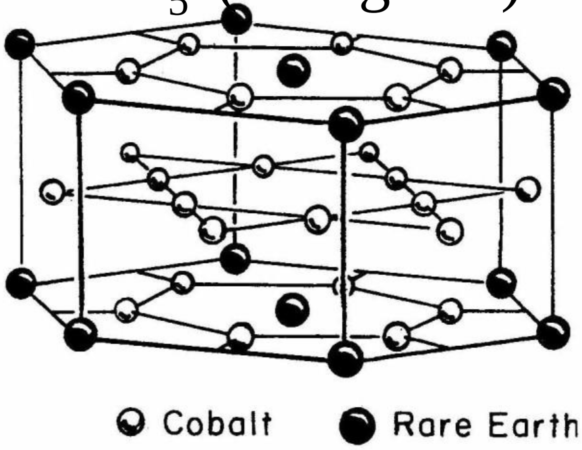
Tetragonal Structure.

See
Herbst et, Phys. Rev. B29,4176 (1984),(1985)
Shoemaker et, Acta Cryst C40,1665 (1984)
Givord et, Physica130B, 323, (1985)

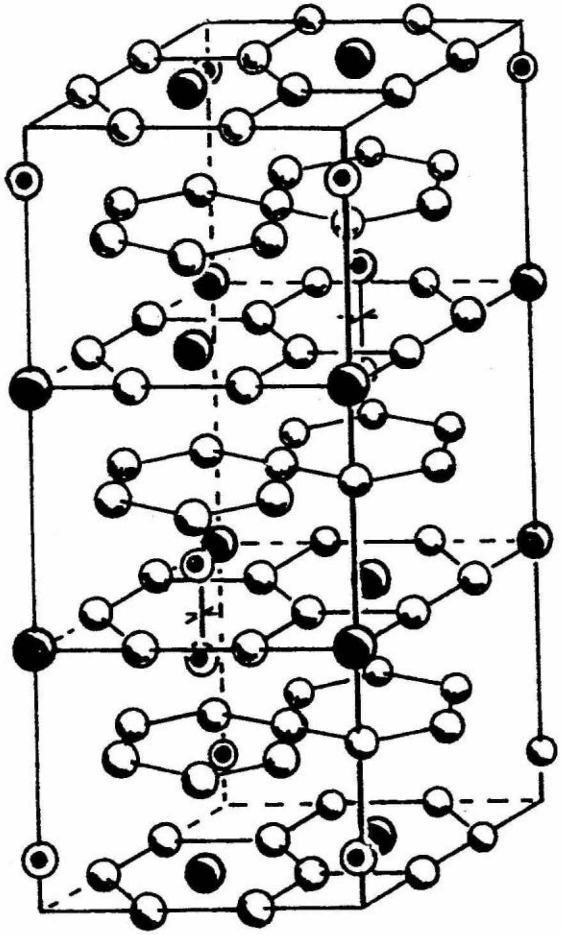


Structure of Sm-Co

$SmCo_5$ (hexagonal)



Sm_2Co_{17} (rhombohedral)



See

O’Handley ‘Modern Magnetic Materials’, John wiley and Sons (2000)

Barret et al ‘Structure of Materials’, Pergamon Press (1980)

Strnat, ‘Ferromagnetic Materials’, Vol 4, Wohlfarth ed., Elsevier Press (1988)

Magnetic Recording

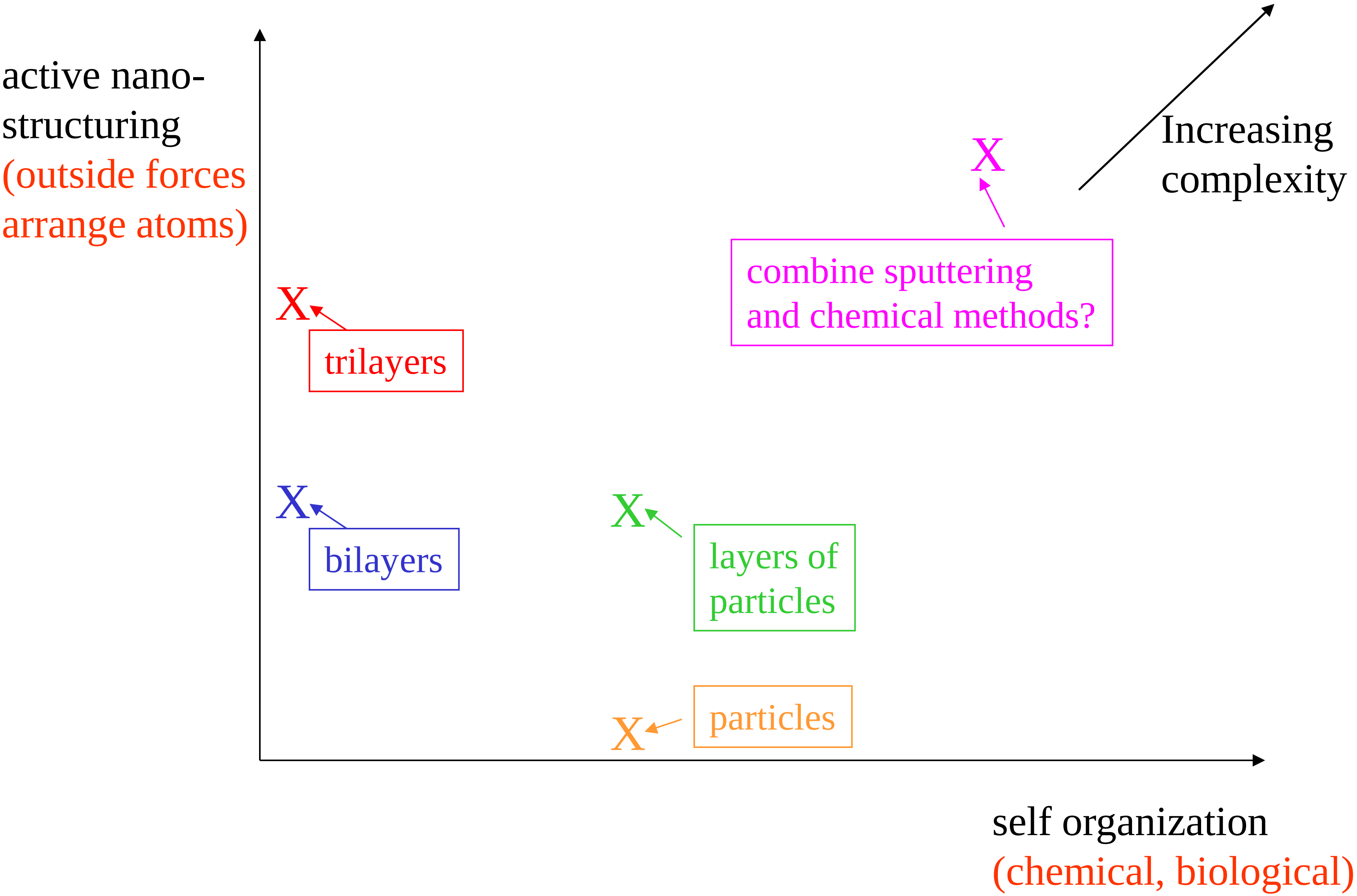
Recording medium- γ-Fe_2O_3 (maghematite), spinel structure
chemically stable
ferrimagnetic
anisotropy is from shape (10:1 ratio of dimensions)
coercivity 350 Oe
Cr added to increase the anisotropy

Type of recoding: longitudinal
perpendicular

Write head- e.g. minature horseshoe magnet.
coil of wire energizes a high permeability magnet
(e.g. NiFe material)
field is created in the gap of the magnet
this field magnetizes the recoding medium
field created in gap>H_c(recording medium)

Read head- i) write head could operate in reverse
ii) giant magnetoresistance read head

Preparation



active nano-
structuring
(outside forces
arrange atoms)

Increasing
complexity

X

combine sputtering
and chemical methods?

X

trilayers

X

bilayers

X

layers of
particles

X

particles

self organization
(chemical, biological)

2. Preparation and structure

This work

- •Nb buffered,
- •540 nm thick NdFeB
- •Influence of anneal time
- •Increase Fe content

Standard (Vacuum) anneal, 20 mins.
or
Rapid anneal, 30 seconds.

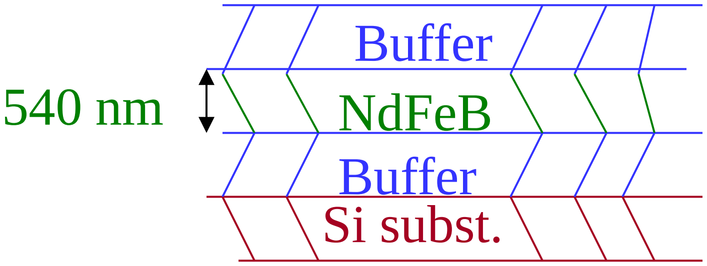
Four compositions:
Fe/Nd ratio: 6, 7.7, 9.4, 11.1 (PIXE)
Nd/B ratio: 1.8 (ICP mass spectroscopy)

Samples are of the form:

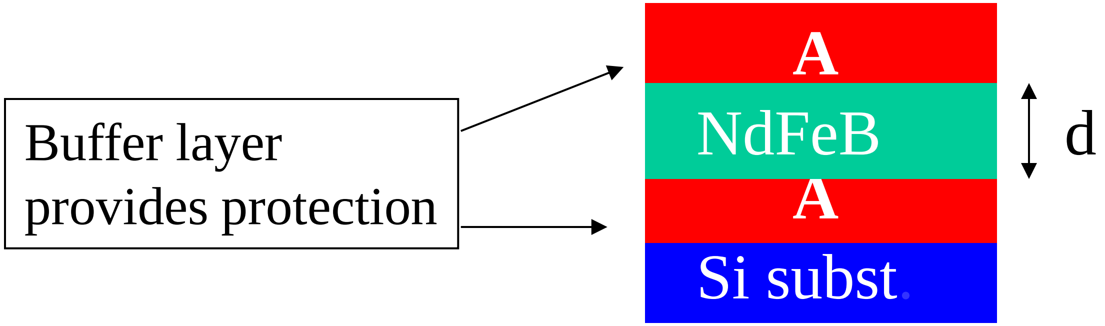
[Nb(20 nm)/NdFeB(d nm)/Nb(20 nm)]/Si subst

Preparation

- Ar ion sputtering
- Water cooled substrate
- Targets: NdFeB+Fe and Nb.



Preparation

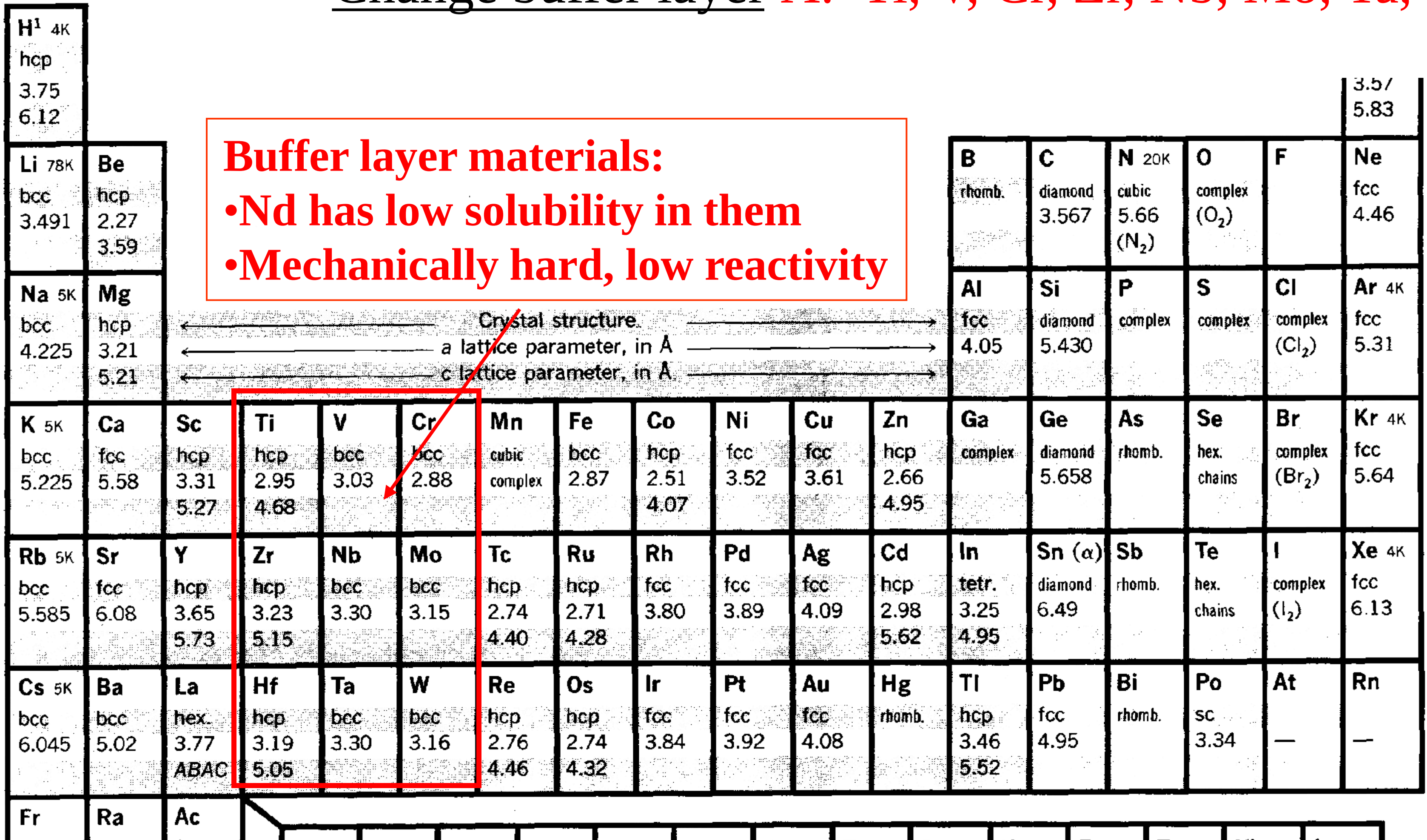


Buffer layer provides protection

Change buffer layer A: Ti, V, Cr, Zr, Nb, Mo, Ta, Hf

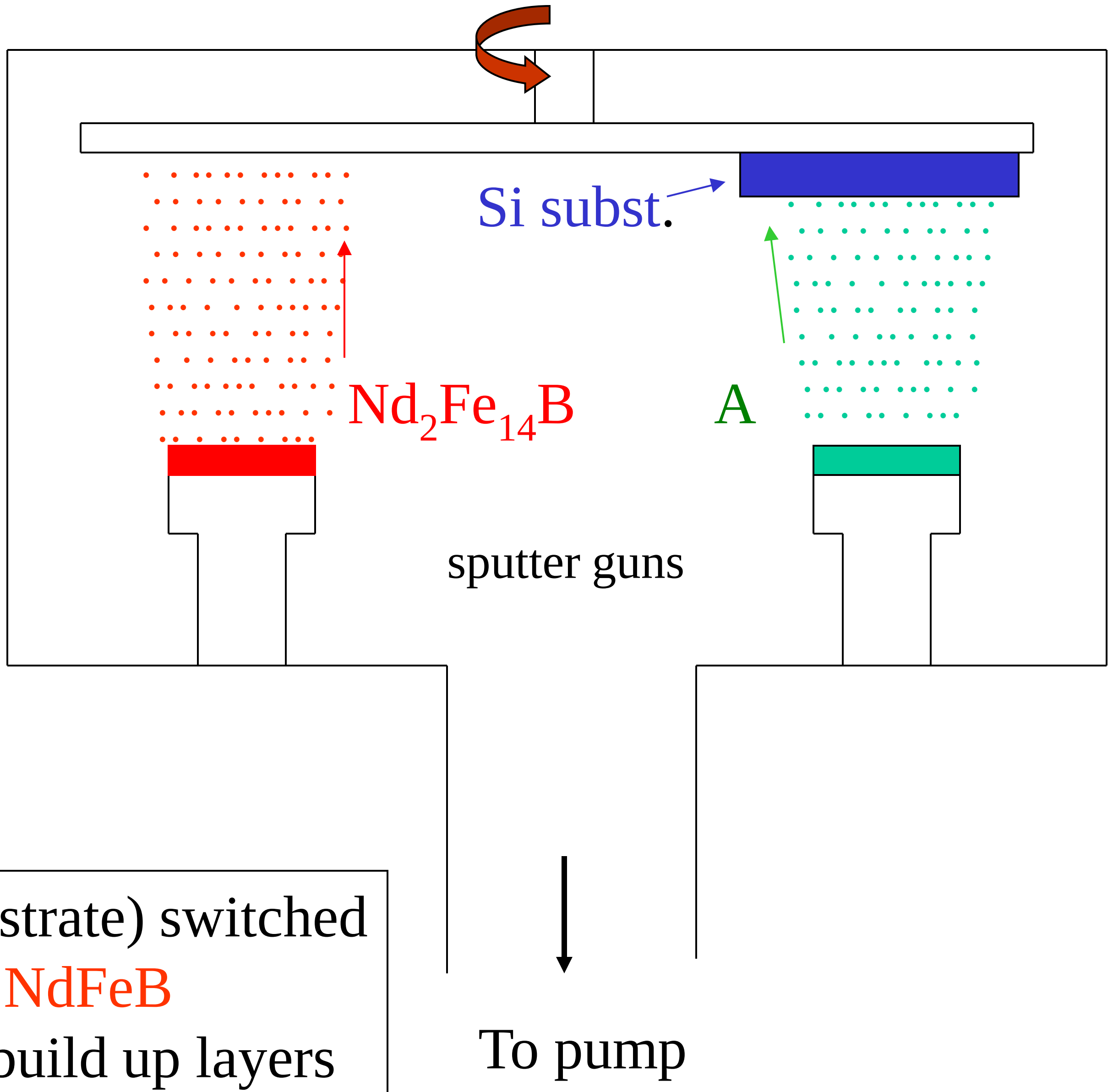
Buffer layer materials:

- **Nd has low solubility in them**
- **Mechanically hard, low reactivity**



H¹ 4K hcp 3.75 6.12																	3.57 5.83
Li 78K bcc 3.491	**Be** hcp 2.27 3.59											**B** rhomb.	**C** diamond 3.567	**N** 20K cubic 5.66 (N_2)	**O** complex (O_2)	**F**	**Ne** fcc 4.46
Na 5K bcc 4.225	**Mg** hcp 3.21 5.21	Crystal structure a lattice parameter, in Å c lattice parameter, in Å										**Al** fcc 4.05	**Si** diamond 5.430	**P** complex	**S** complex	**Cl** complex (Cl_2)	**Ar** 4K fcc 5.31
K 5K bcc 5.225	**Ca** fcc 5.58	**Sc** hcp 3.31 5.27	**Ti** hcp 2.95 4.68	**V** bcc 3.03	**Cr** bcc 2.88	**Mn** cubic complex	**Fe** bcc 2.87	**Co** hcp 2.51 4.07	**Ni** fcc 3.52	**Cu** fcc 3.61	**Zn** hcp 2.66 4.95	**Ga** complex	**Ge** diamond 5.658	**As** rhomb.	**Se** hex. chains	**Br** complex (Br_2)	**Kr** 4K fcc 5.64
Rb 5K bcc 5.585	**Sr** fcc 6.08	**Y** hcp 3.65 5.73	**Zr** hcp 3.23 5.15	**Nb** bcc 3.30	**Mo** bcc 3.15	**Tc** hcp 2.74 4.40	**Ru** hcp 2.71 4.28	**Rh** fcc 3.80	**Pd** fcc 3.89	**Ag** fcc 4.09	**Cd** hcp 2.98 5.62	**In** tetr. 3.25 4.95	**Sn** (α) diamond 6.49	**Sb** rhomb.	**Te** hex. chains	**I** complex (I_2)	**Xe** 4K fcc 6.13
Cs 5K bcc 6.045	**Ba** bcc 5.02	**La** hex. 3.77 ABAC	**Hf** hcp 3.19 5.05	**Ta** bcc 3.30	**W** bcc 3.16	**Re** hcp 2.76 4.46	**Os** hcp 2.74 4.32	**Ir** fcc 3.84	**Pt** fcc 3.92	**Au** fcc 4.08	**Hg** rhomb.	**Tl** hcp 3.46 5.52	**Pb** fcc 4.95	**Bi** rhomb.	**Po** sc 3.34	**At** —	**Rn** —
Fr	**Ra**	**Ac**															

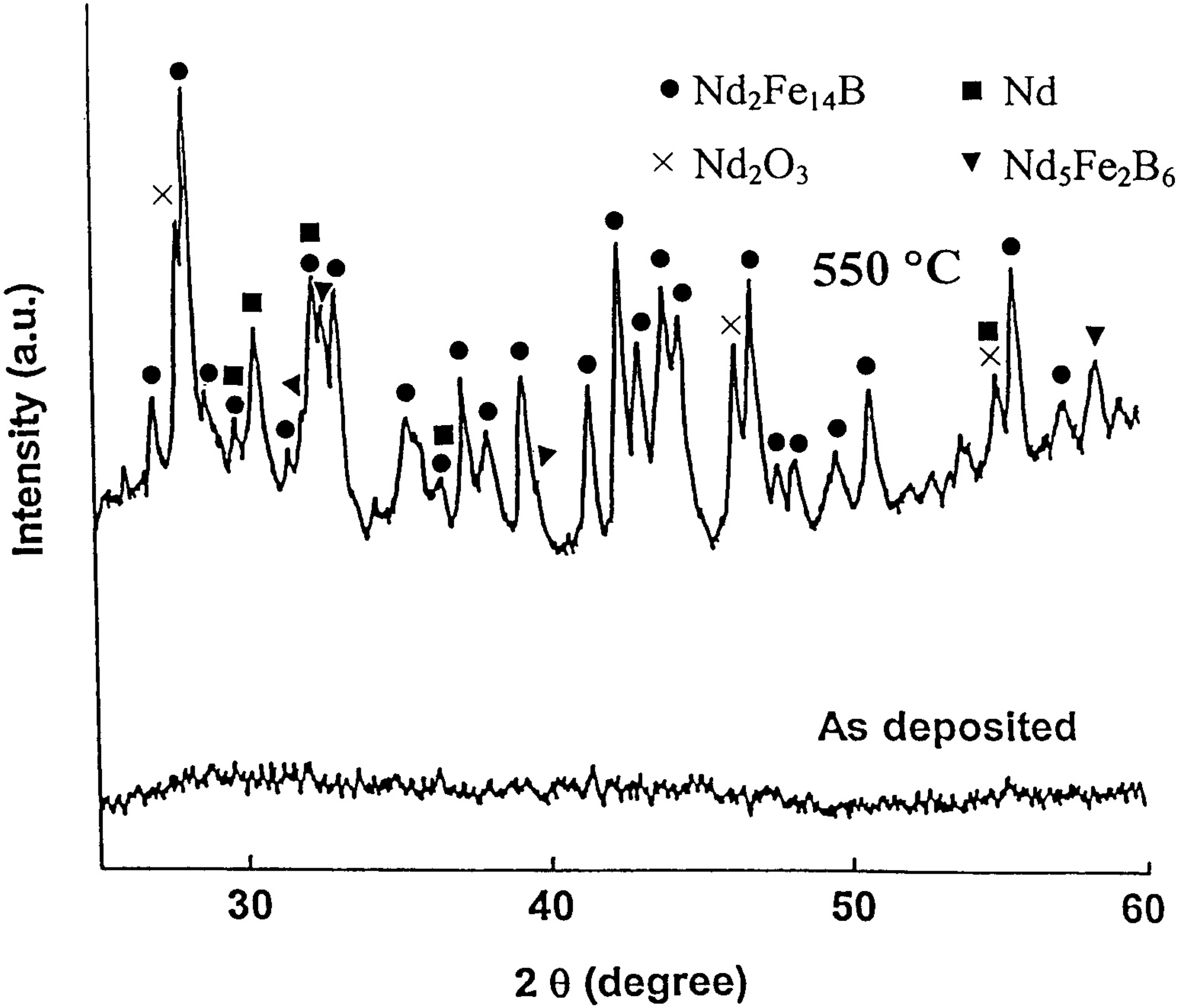
Sputter Deposition



Sample (Si substrate) switched between A and NdFeB sputter guns – build up layers in this way

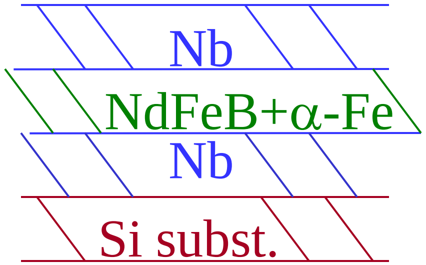
X-ray diffractogram Mo(20nm)/NdFeB(180nm)/Mo(20nm)

-crystallite size 30 nm



Cu K_α x-ray diffraction

$Nd_2Fe_{19}B$ (20 min. anneal).

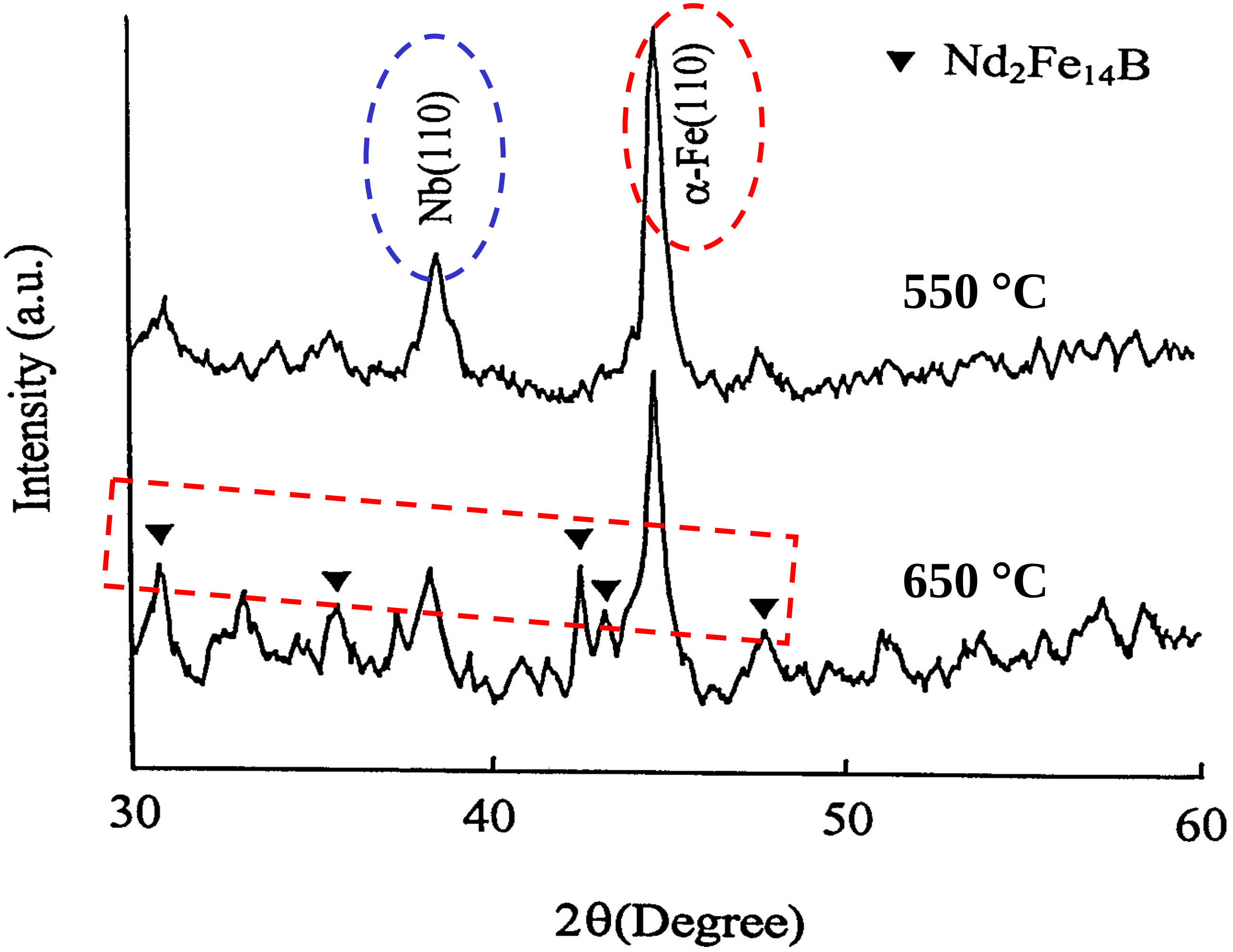


Nb

NdFeB+α-Fe

Nb

Si subst.



Samples with extra Fe have both $Nd_2Fe_{14}B$ and α-Fe phases

3. Annealing rate and varying non-magnetic layer

Parameters varied and their physical effect

Parameter	**Range**	**Possible effect**
A (buffer)	Cr,Mo,Nb,Ta,Ti, V,Zr,SiC,BN	Morphology, Buffer/NdFeB mix
d (thickness)	54, 90, 180, 540nm	Magnetic size effect, morphology
T_{an}(anneal)	450 to 750^{o}C	Morphology
Anneal time	20 mins or 30 secs	Morphology
Fe content	Four compositions	α-Fe formation, BH_{max} enhance.

Annealing

Vacuum anneal(20 minutes)

or

Rapid thermal anneal (30 seconds)

Purpose

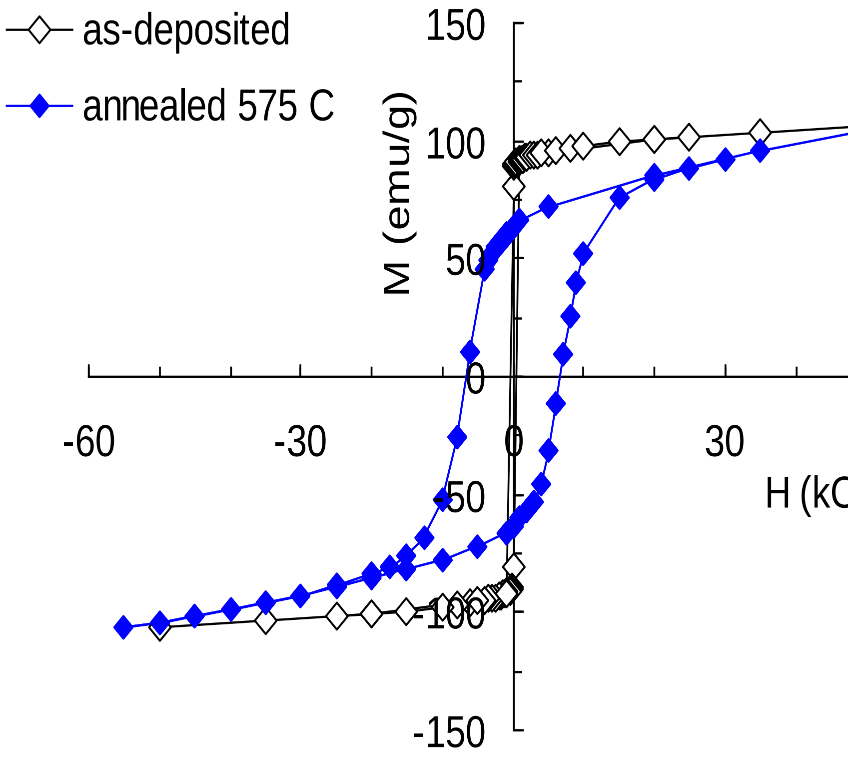
Crystallize the tetragonal $Nd_2Fe_{14}B$

Improve crystal quality (remove defects) from $Nd_2Fe_{14}B$

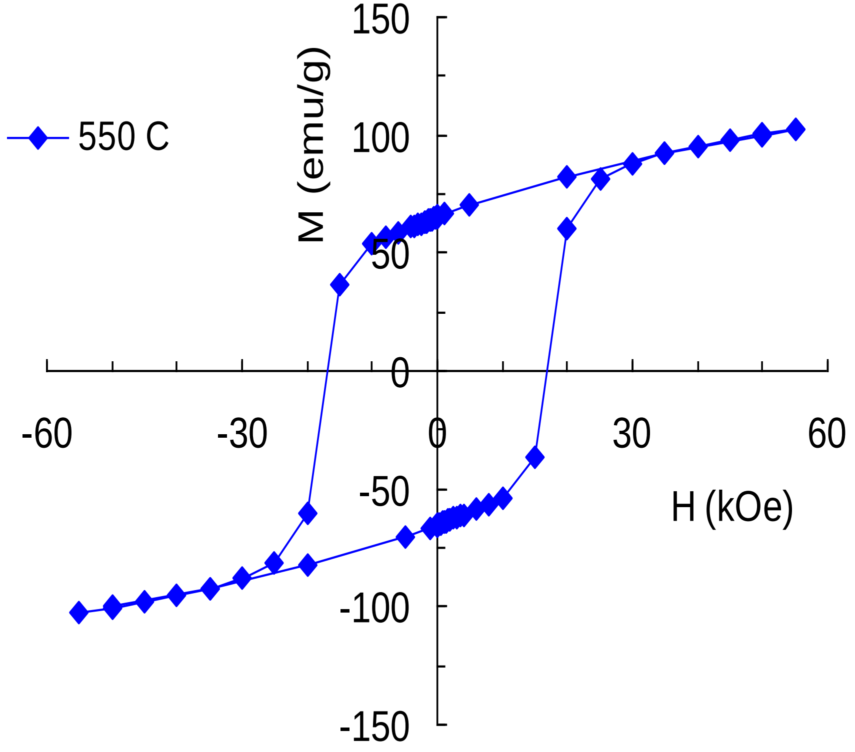
Problem related to annealing:
can lead to a mixing of the buffer layer and the magnetic ($Nd_2Fe_{14}B$) phase.

Can lead to sample-substrate adhesion problems

Cr/NdFeB(180 nm)/Cr

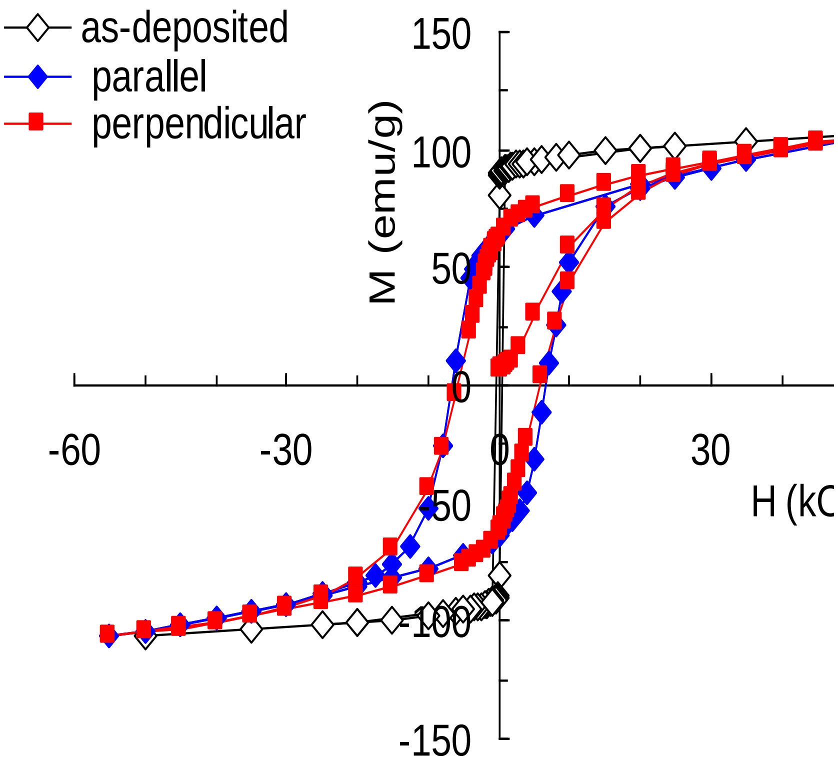


Mo/NdFeB(180 nm)/Mo

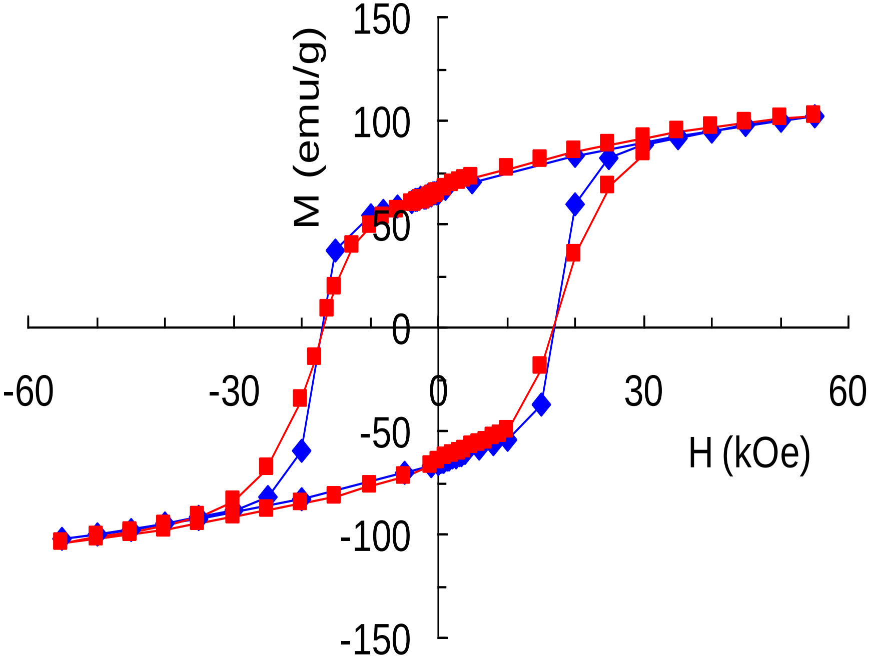


Hysteresis loops

Cr, 180 nm,annealed 575 C



Mo, 180 nm, annealed 550 C



Hysteresis loops

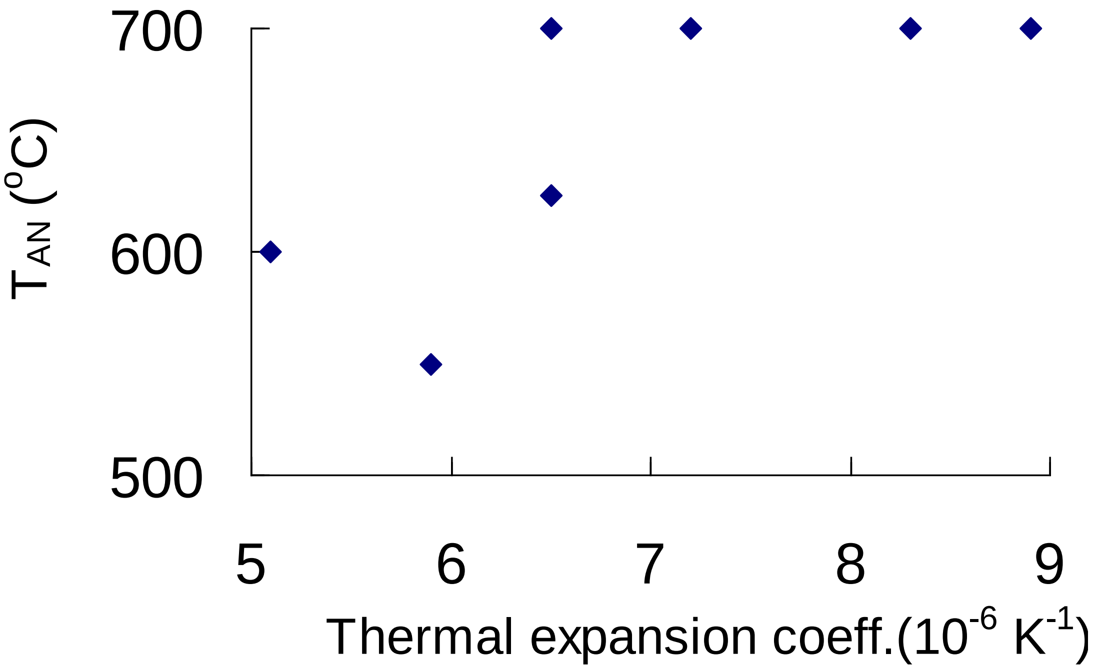
Coercivity summary

Buffer, H_{Ci}

Ti 15 kOe	**V** 2 kOe	**Cr** 6.7 kOe
Zr - -	**Nb** 20 kOe	**Mo** 17 kOe
Hf 14 kOe	**Ta** 10 kOe	**W*** 7.4 kOe *Tsai et al, Jour. Magn.Mag.Mater 196, 728 (1999).

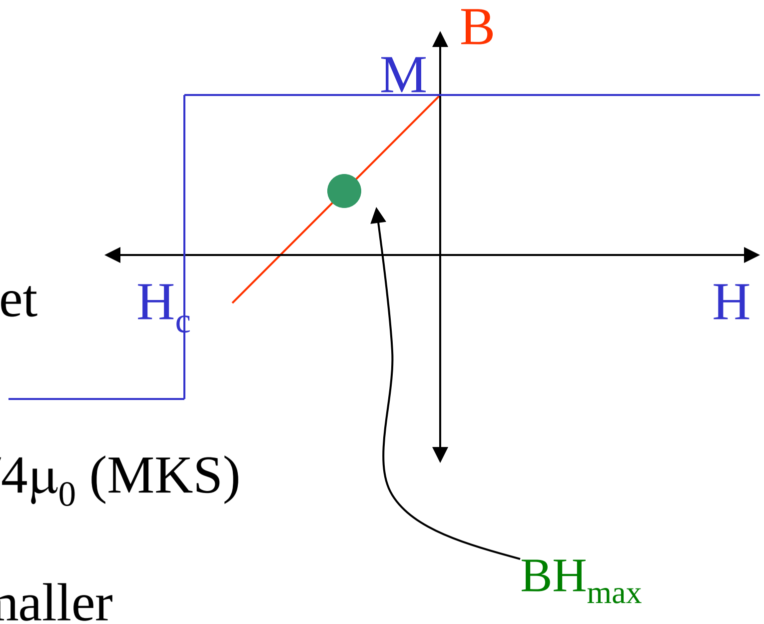
Anneal temperature and Adhesion

Anneal temp at which sample no longer adheres to the substrate



Buffer layer

Theoretical Prediction of BH_{max}



-Largest value of BH in second quadrant

-measures magnetostatic energy stored in magnet

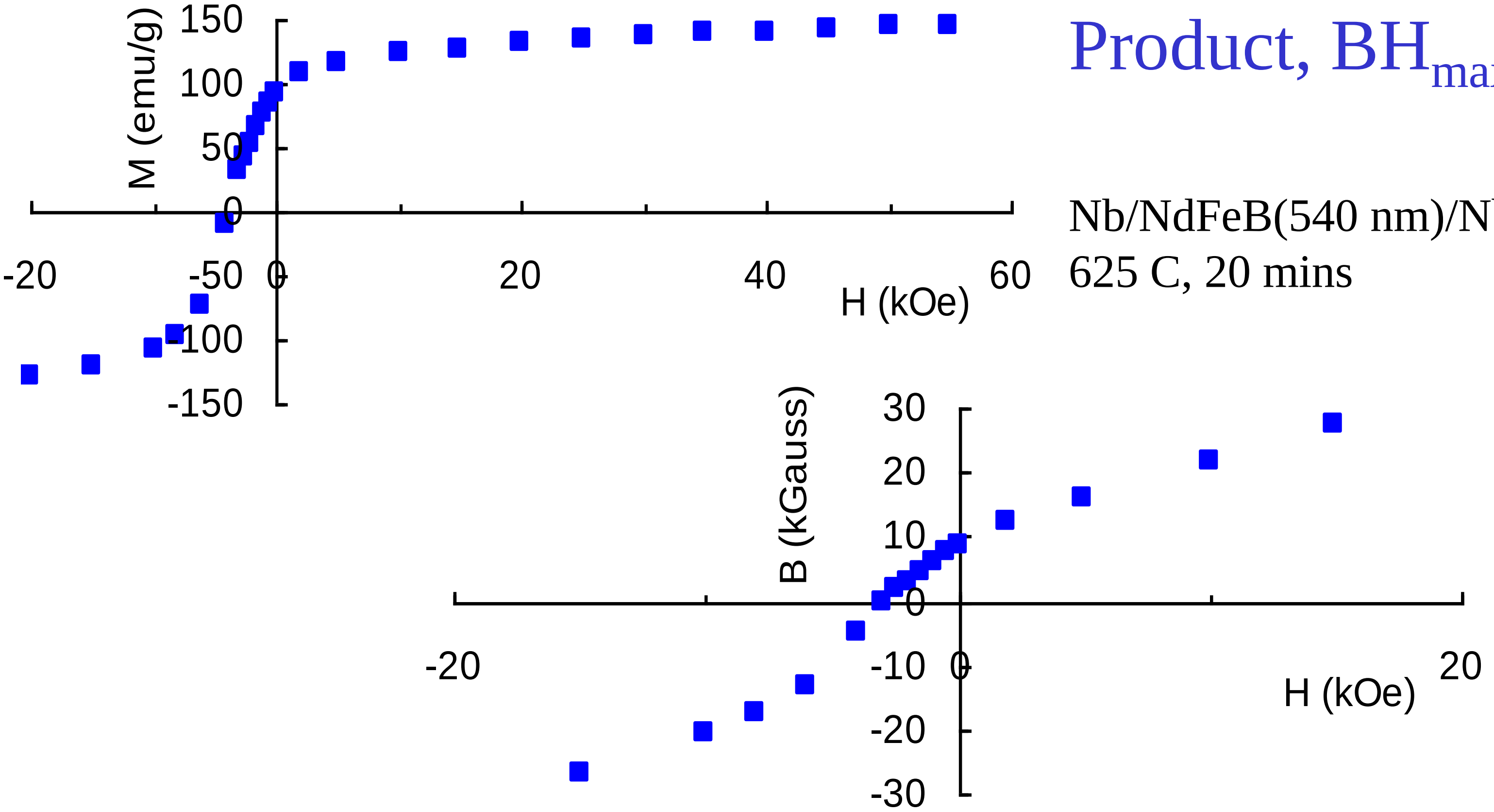
-If coercivity is sufficiently large, $BH_{max} = M_s^2/4\mu_0$ (MKS)

-If coercivity is less than $M_r/2$, then BH_{max} is smaller

e.g. if Fe had a large enough coercivity, $BH_{max} = 0.92$ MJ/m^3,
measured value is ~ 0.001 MJ/m^3
[Skomski, Coey, Phys. Rev. B 48, 15812 (1993)]

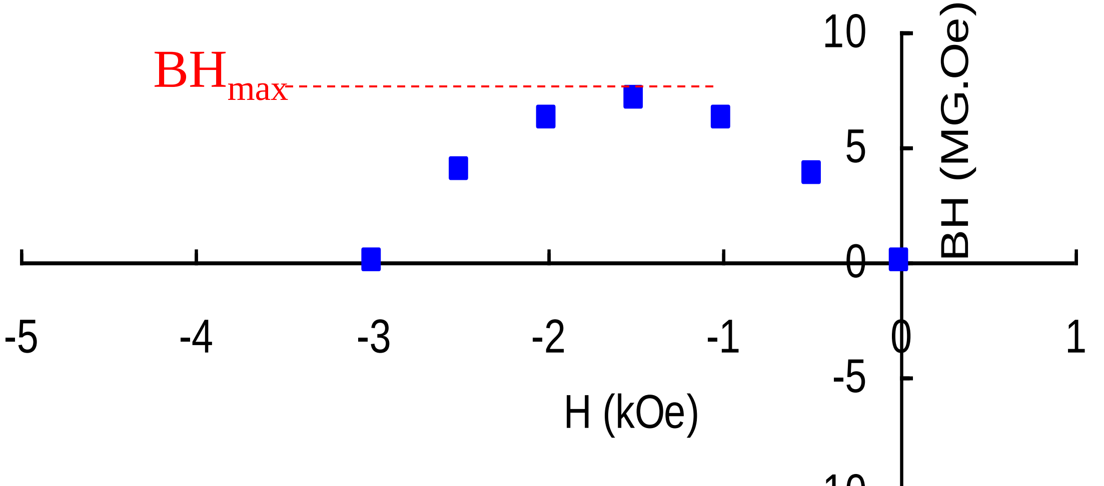
e.g. bulk $Nd_2Fe_{14}B$: BH_{max}(upper limit) = 0.516 MJ/m^3
measured value 0.405 MJ/m^3
[Sagawa et al, Japan. J. Appl. Phys. 26, 785 (1987)]

Maximum Energy Product, BH_{max}



Nb/NdFeB(540 nm)/Nb
625 C, 20 mins

I MG.Oe = 7.96 kJ/m^3



Best Values of H_c, BH_{max} for each buffer

Buffer, H_{Ci}, Max (BH_{MAX})

Ti 15 kOe 9.3 MG-Oe	**V** 2 kOe 2.1 MG-Oe	**Cr** 6.7 kOe 6.8 MG-Oe
Zr - -	**Nb** 20 kOe 7.7 MG-Oe	**Mo** 17 kOe 10.3 MG-Oe
Hf 14 kOe 6.8 MG-Oe	**Ta** 10 kOe 3.2 MG-Oe	**W*** 7.4 kOe *Tsai et al, Jour. Magn.Mag.Mater 196, 728 (1999).

[Jiang, O'Shea, J. Magn. Magn. Mater. 59, 212, (2000)]

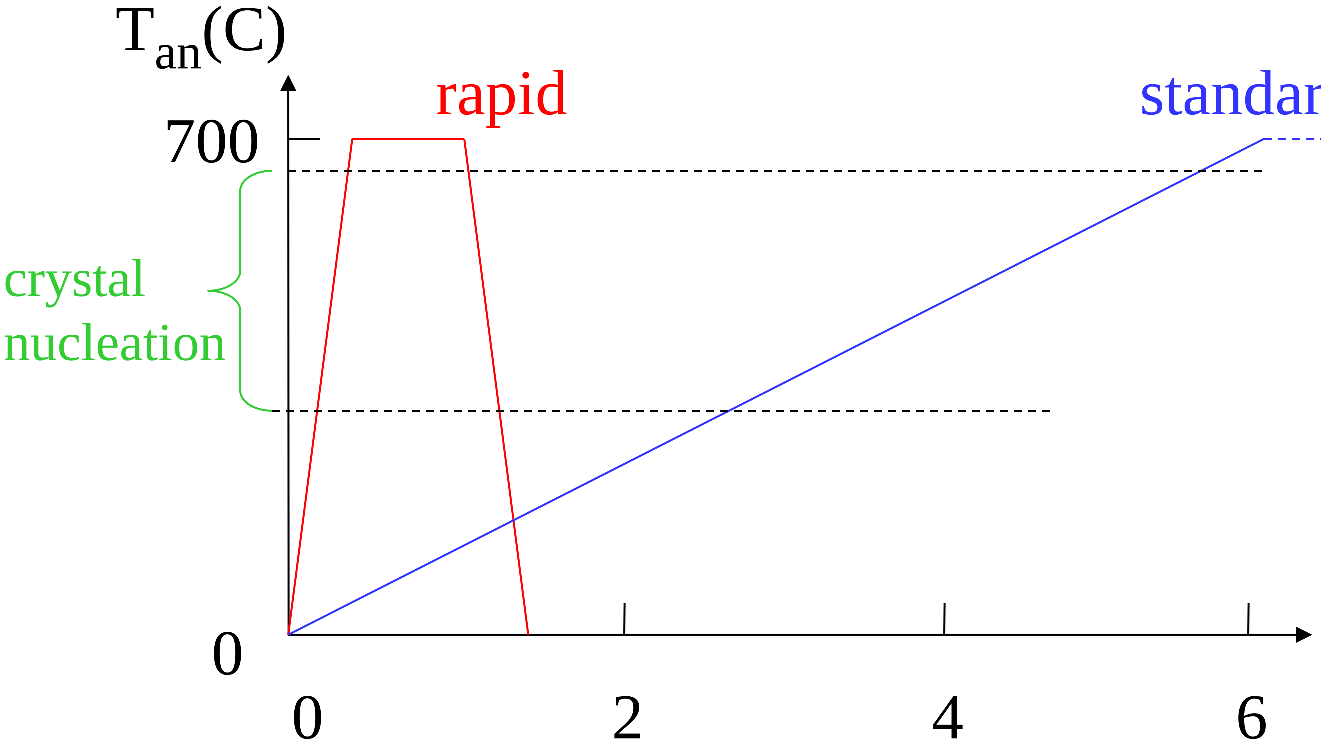
Annealing

Vacuum anneal(20 minutes)

or

Rapid thermal anneal (30 seconds)

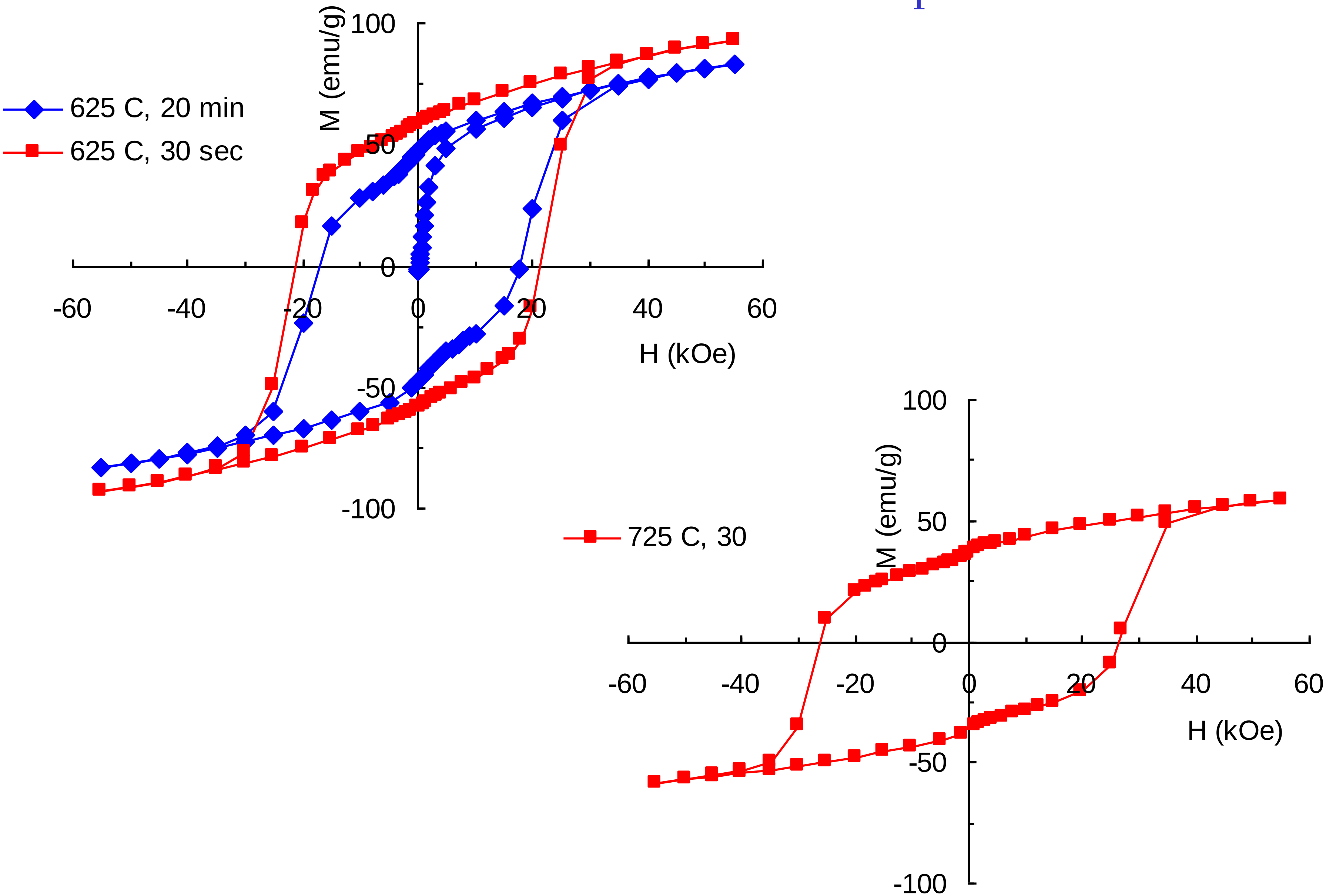
Anneal Temperature profiles



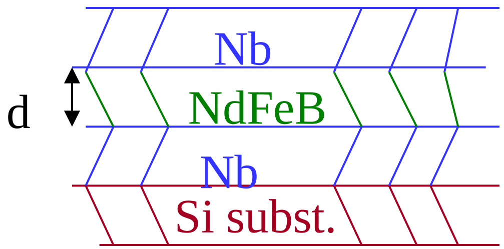
time (mins)

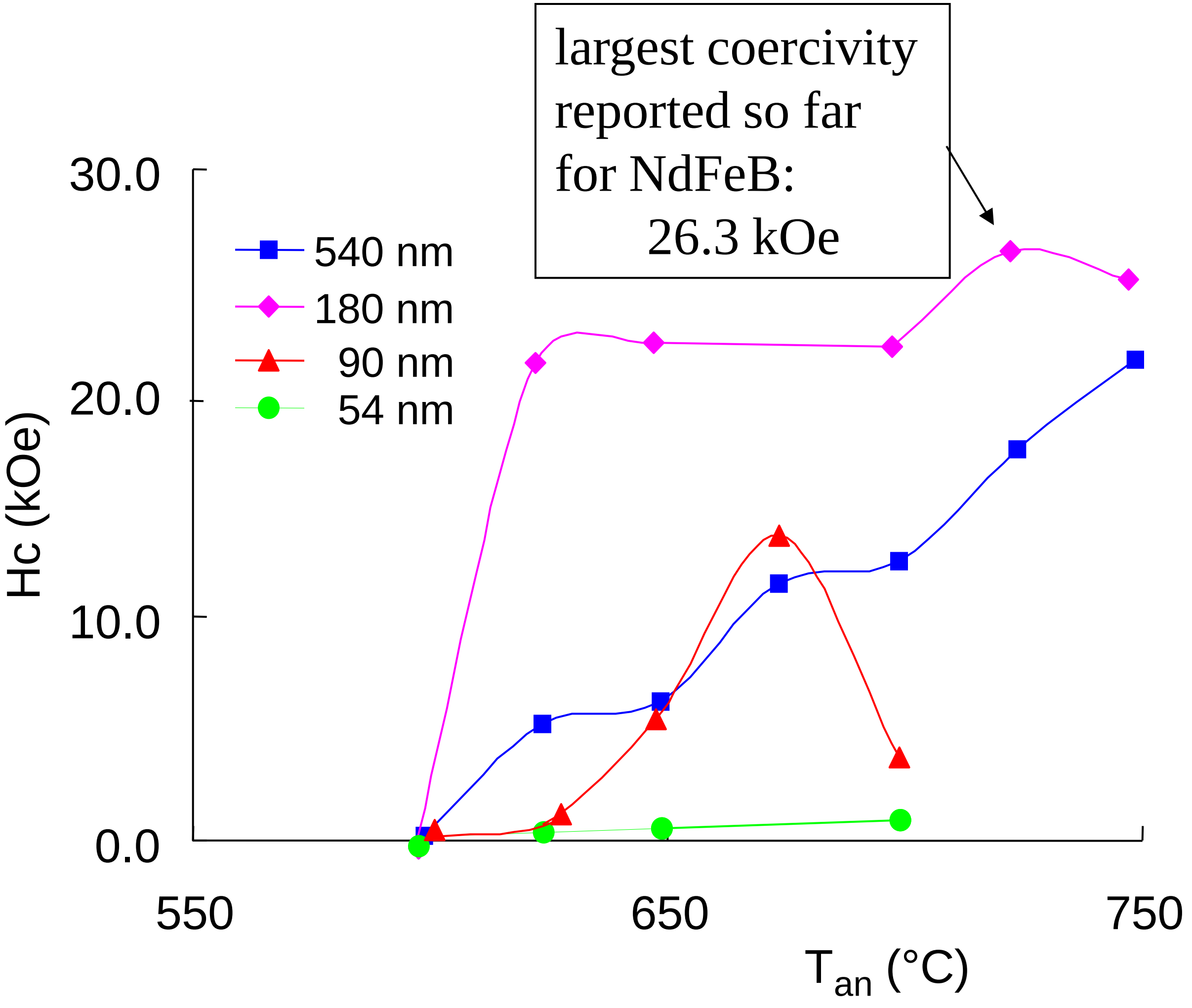
- a rapid anneal should lead to more uniform grain size.

Rapid anneal



H_C as a function of T_{an} ,(rapid anneal)



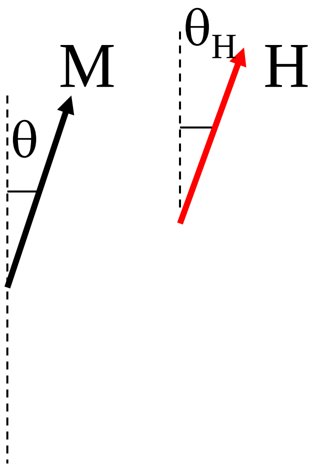

largest coercivity reported so far for NdFeB:
26.3 kOe

To find coercivity for a simple model

Single magnetic domain:

$E_a = K \sin^2\theta$

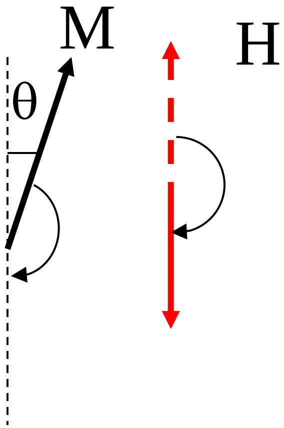
$E_h = -MH \cos\theta_H$



Reverse H :

$\cancel{H} = 2K/M$

H_{C1}



Magnetic domains randomly oriented.

$$H_C = H_{C1}/2 = (K_1 + K_2)/M$$

For $Nd_2Fe_{14}B$ (theory):

$$H_C = 32.4 \text{ kOe}$$

Maximum coercivity

Theoretical maximum (randomly oriented grains) 32.4 kOe

Experiment 26.3 kOe (our thin film), $Nd_2Fe_{8.3}B_{0.8}$
[Jiang, evans, O'Shea, Du, J. Magn. Magn. Mater. 224, 233 (2001)]

Other work: 27.5 kOe (bulk melt-spun), $Nd_{147}Fe_{13}B$
[Girt, Krishnan, Thomas, Altounian, Appl. Phys. Lett. 76, 1737 (2000)]

3. Modeling the coercivity

Magnetic Reversal by Uniform Rotation

[(W. F. Brown, Rev. Mod. Phys. 17, 15 (1945)]

Assuming a single particle with field applied along the uniaxial axis:

$H_C = 2K_1/M_S - N_e M_S$

K_1 - uniaxial anisotropy coeffficent

M_S - saturation magnetization

N_e - difference between parallel and perpendicular demagnetization factors

Modified Brown's Equation

(H. Kronmuller, K.-D. Durst, J. Magn. Magn. Mater. 74, 291 (1988)

$$H_C = (2K_1/M_S)\alpha_\psi\alpha_K - N_e M_S$$

α_ψ - grains not aligned (randomly
oriented, $\alpha_\psi \sim 0.5$)

α_K - grains are not perfect
Both α_ψ and α_K reduce coercivity

Pinning: $\alpha_K < 0.3$
Nucleation: no restriction on α_K

Magnetic reversal by nucleation

[(D. Givord, P. Tenaud, T. Viadieu, IEEE Trans. Mag. 24, 1921 (1988)]

Here reverse magnetic domains nucleate and expand.

$$H_C = \gamma_B \alpha_S \alpha_B / \mu_o v^{1/3} M_S - N_{eff} M_S$$

γ_B – domain wall energy of ideal material

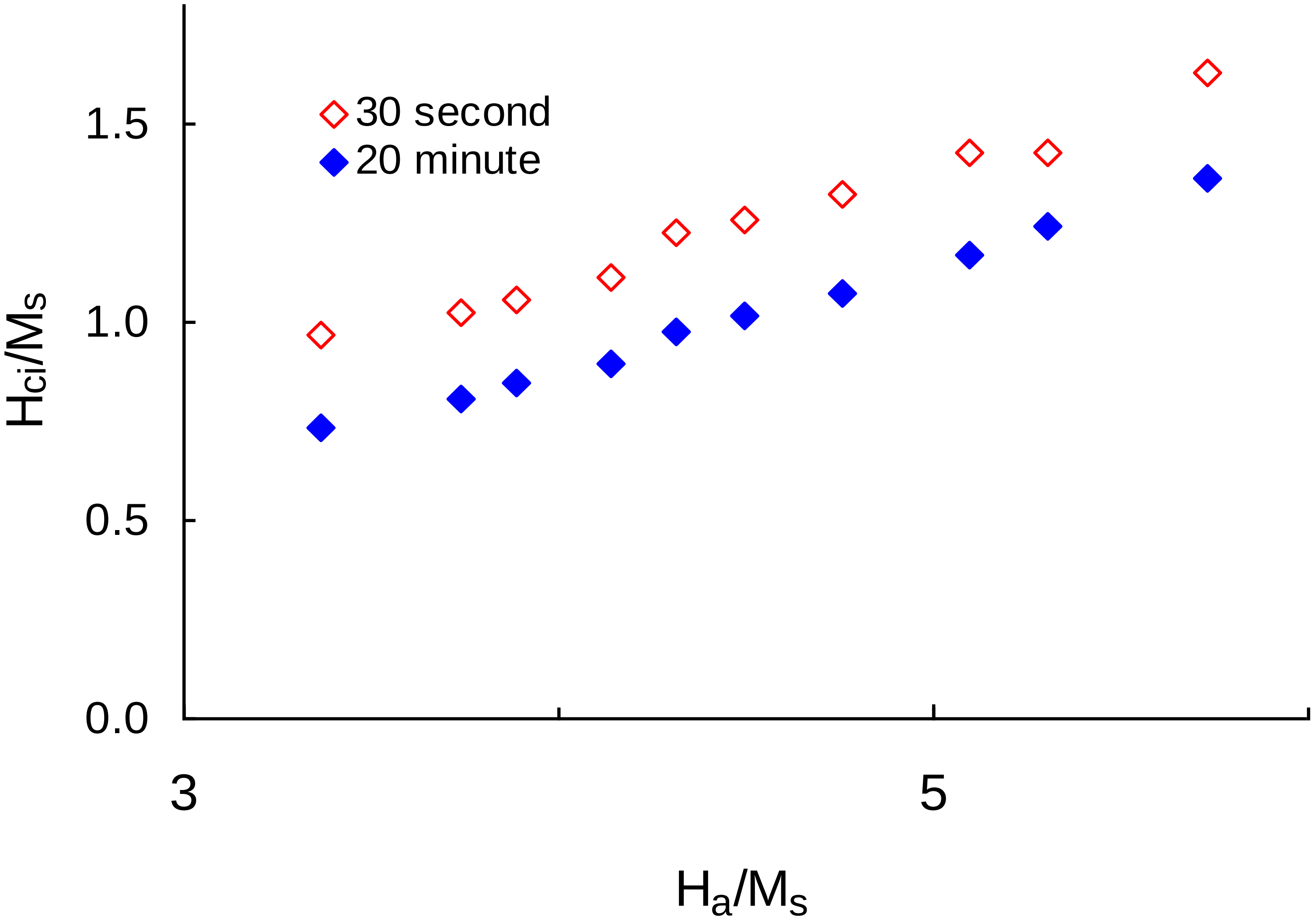
α_S – geometric factor (= $s/v^{2/3}$, s is nucleus surface area and v is volume)

α_B – relates wall energy to ideal wall energy

Both are similar in form!

Modified Brown' plot

Nb/NdFeB(180 nm)/Nb



Modified Brown’s Plot

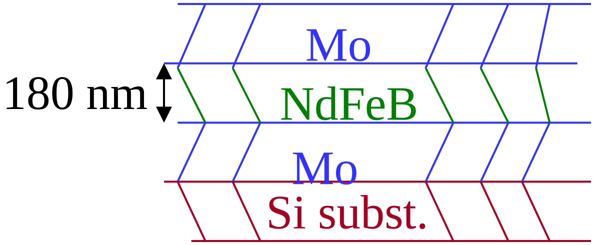
Assume $\boldsymbol{\alpha}_{\psi}$ = 0.5 (no texture)

d (nm)	**Anneal Time (min)**	**Anneal temp (^{o}C)**	**H_{ci} (kOe**	**M_h (emu/g)**	**M_r/M_h**	**N_e**	**α_K** **α_{ex}**
180	20	600	18.0	91.5	0.58	0.19	0.54
180	0.5	650	21.4	100.7	0.63	0.07	0.59

The rapidly annealed sample has:

smaller N_e indicating smaller internal demagnetization fields
larger α_K (indirect argument) suggesting that the grains are of higher quality.
larger remanence ratio

Annealed 550 C



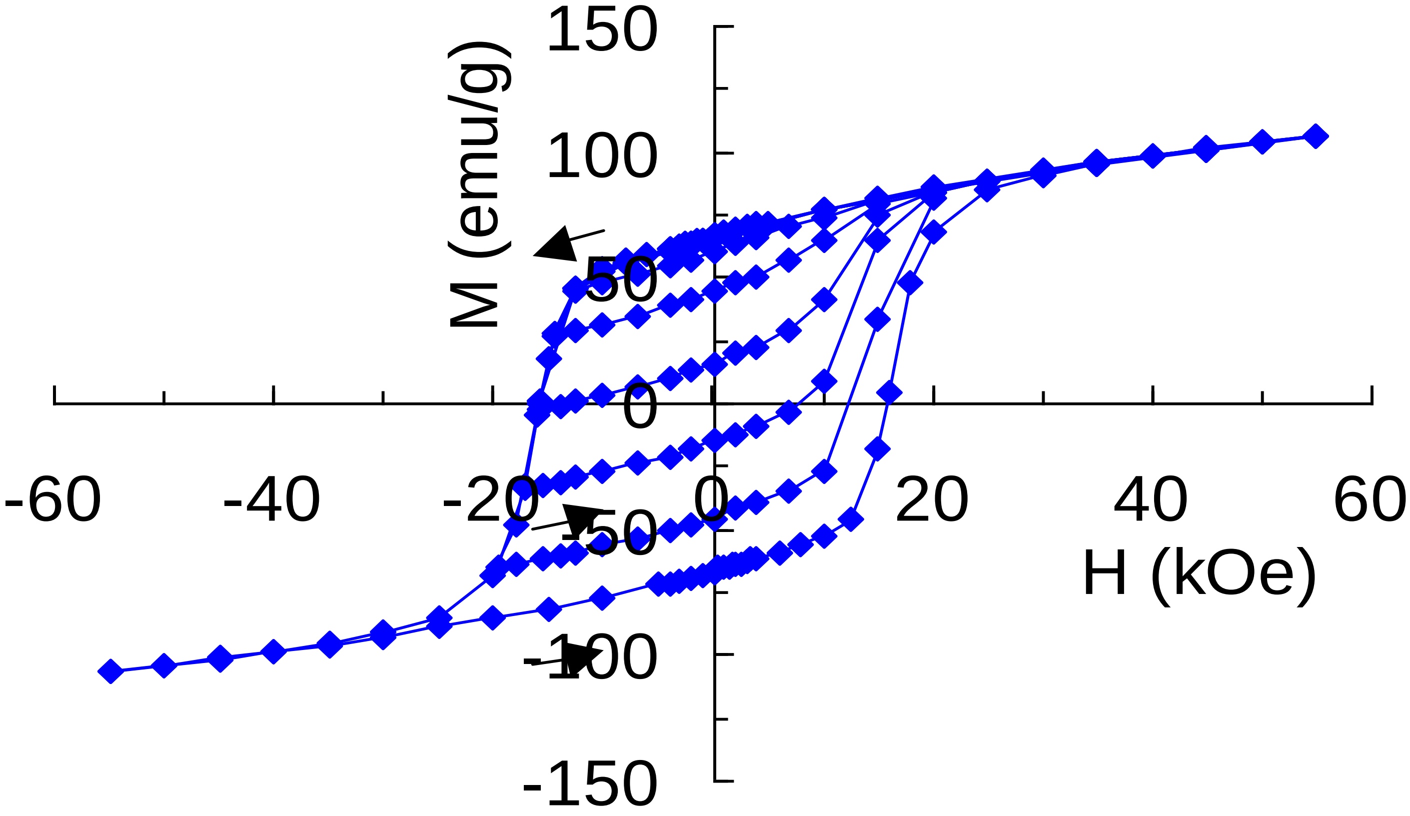
Mo

180 nm

NdFeB

Mo

Si subst.



Largest ‘Maximum Energy Product’, BH_{MAX}:

13 MGauss-Oe (103 kJ/m^3)

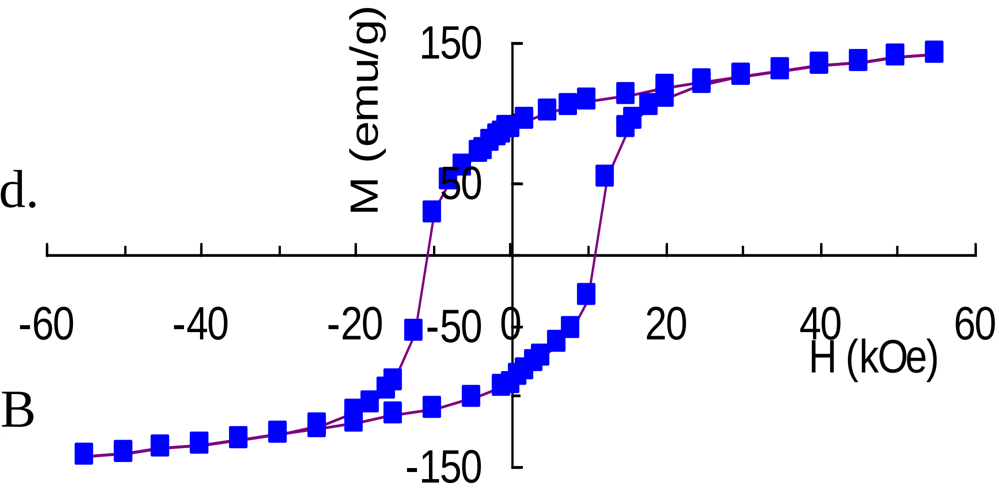
Buffer: Nb

Anneal time,temp:30 sec, 750 ^{o}C

Composition: $Nd_2Fe_{18}B_{0.8}$ (Fe-rich)

Grain size 35-50 nm, randomly oriented.

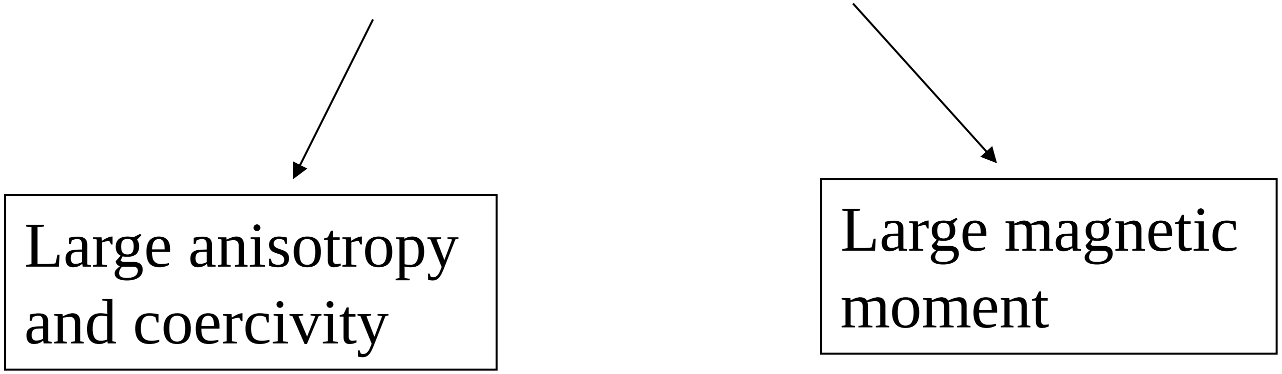
α-Fe is present



- Exchange between α-Fe and $Nd_2Fe_{14}B$ phases leads to a large BH_{MAX},
- Coercivity is 11 kOe
- Others have reported 22.8 MGauss-Oe in oriented films with coercivity of 9.4 kOe.
- Next: Orient the grains to increase BH_{MAX}

4. Exchange coupling

Combine crystallites of $Nd_2Fe_{14}B$ and Fe



Large anisotropy and coercivity

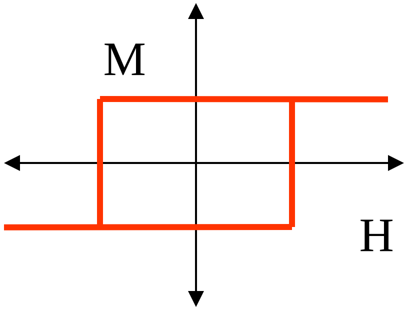
Large magnetic moment

Composite material has a large interface area,
two phases should be strongly coupled magnetically,

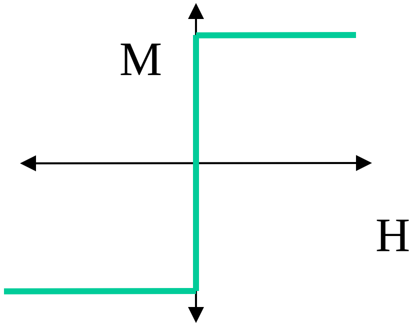
Result: a material with large coercivity, and moderately large magnetization
[Kneller, Hawig, IEEE Trans. Magn. 27, 3588 (1991)]

Two separate materials:

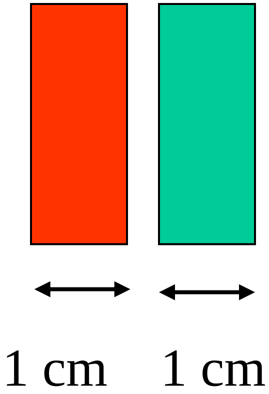
hard (e.g. $Nd_2Fe_{14}B$)

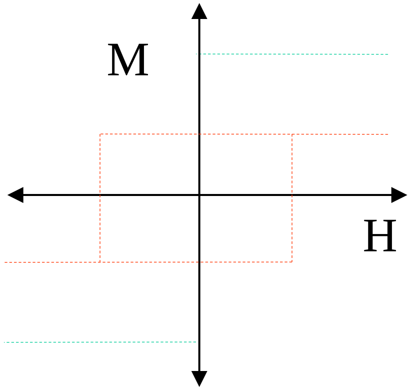


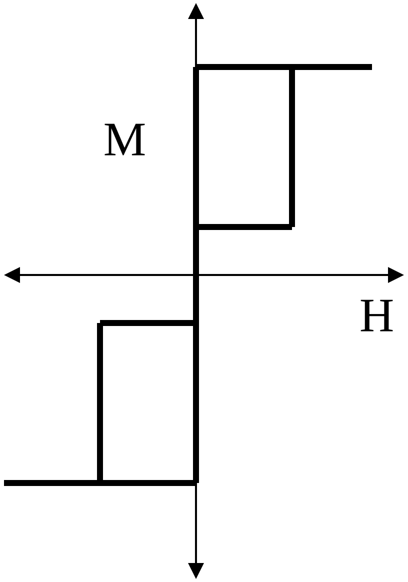
soft (e.g Fe)



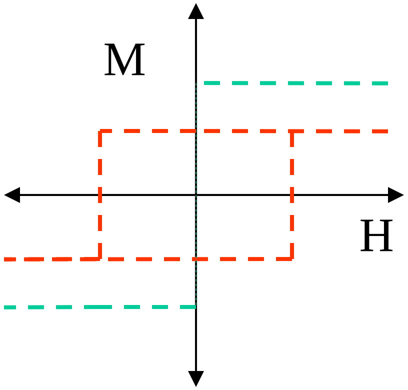
Put them together:



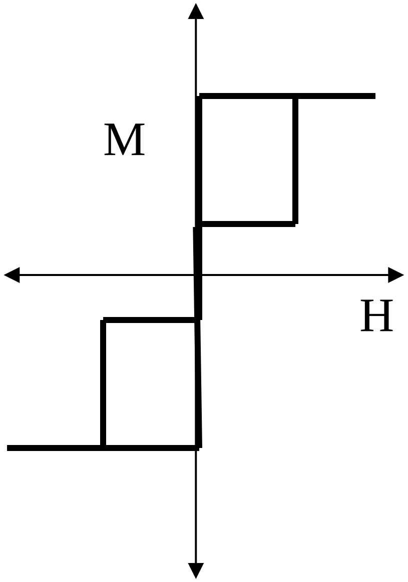




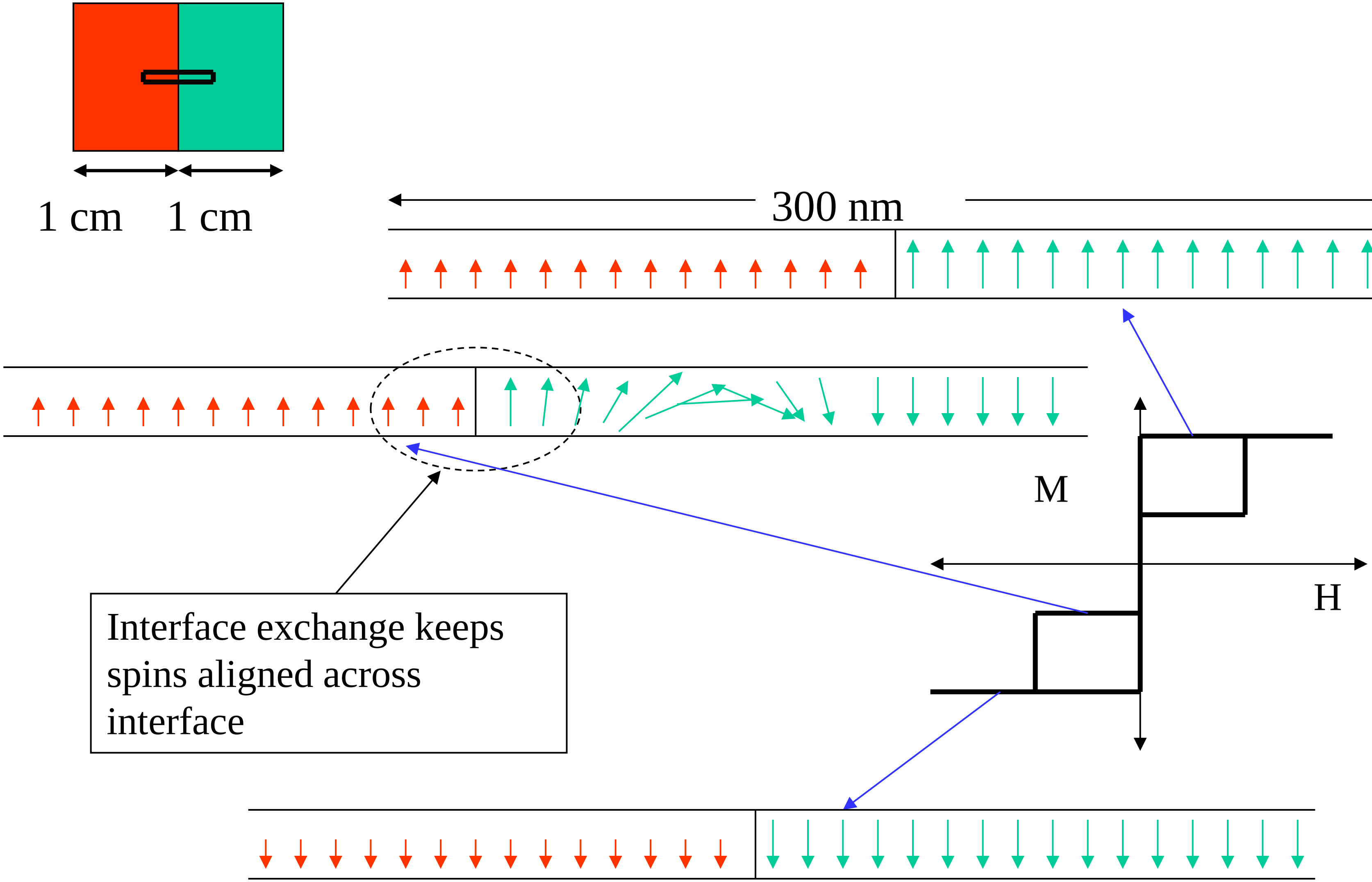
separate loops



added together

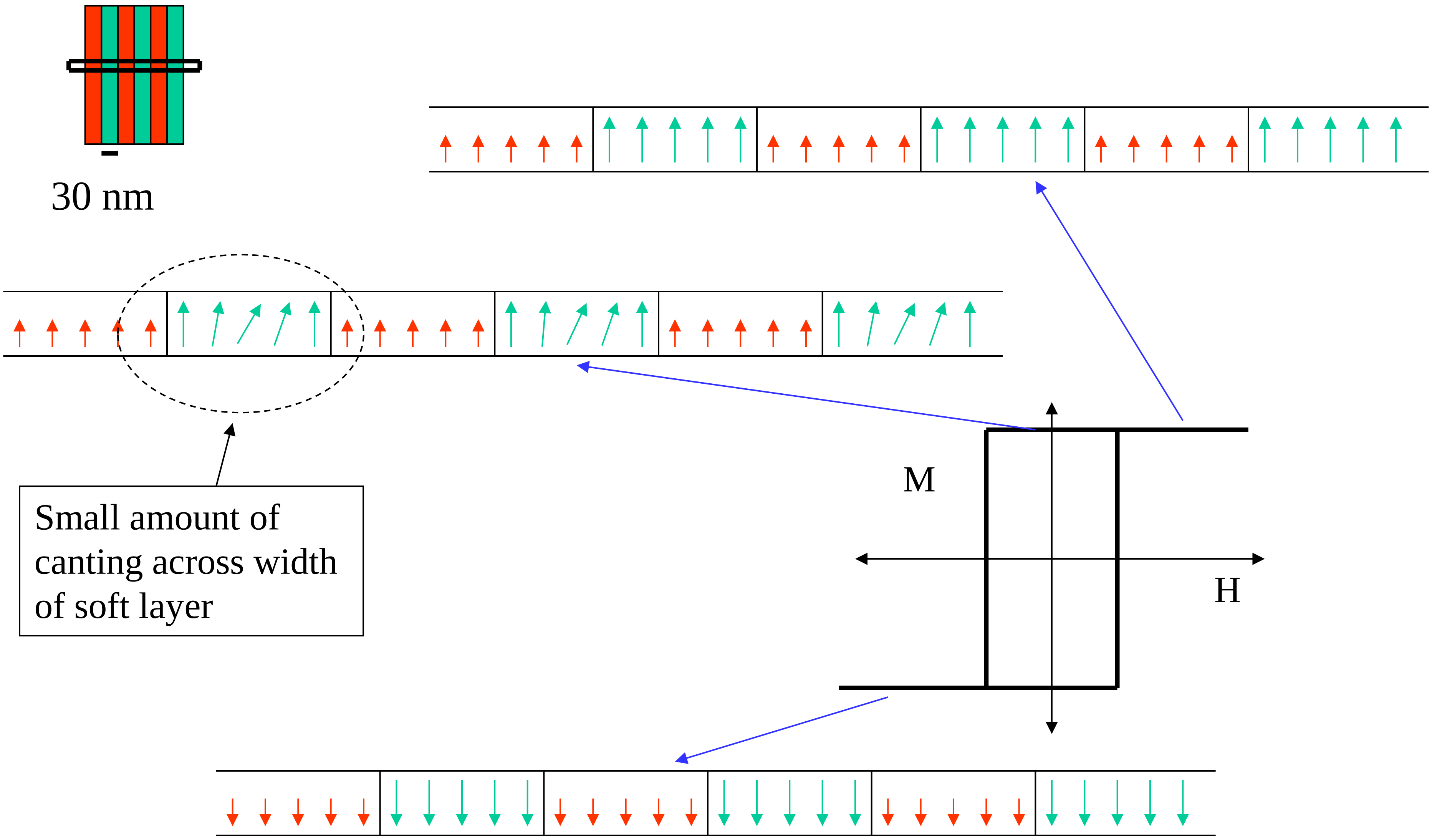


Microscopic view of interface:



Interface exchange keeps spins aligned across interface

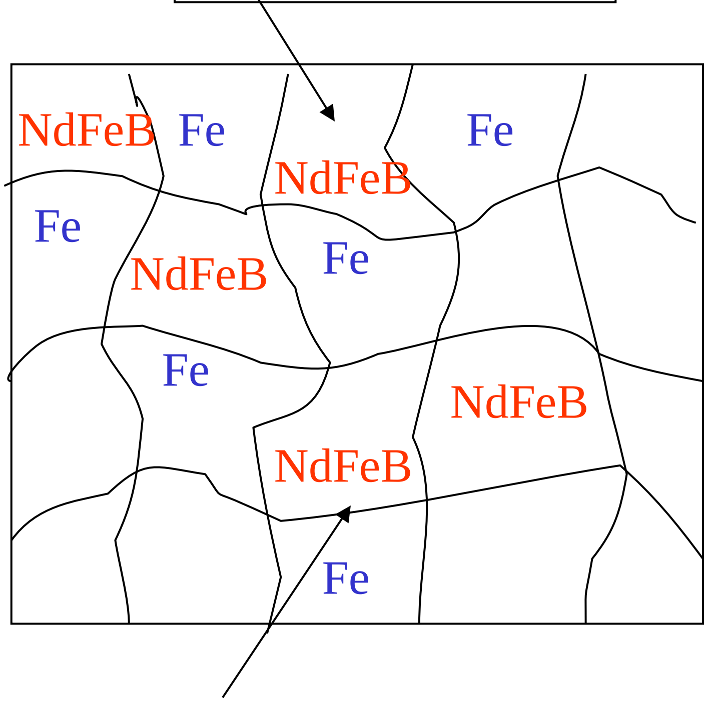
Now lets make the layers 30 nm thick:



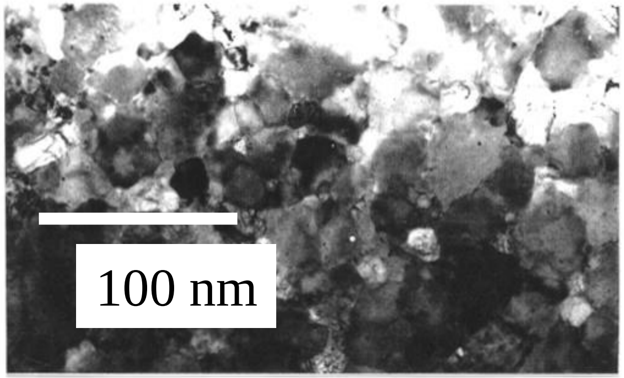
Small amount of canting across width of soft layer

Permanent Magnet

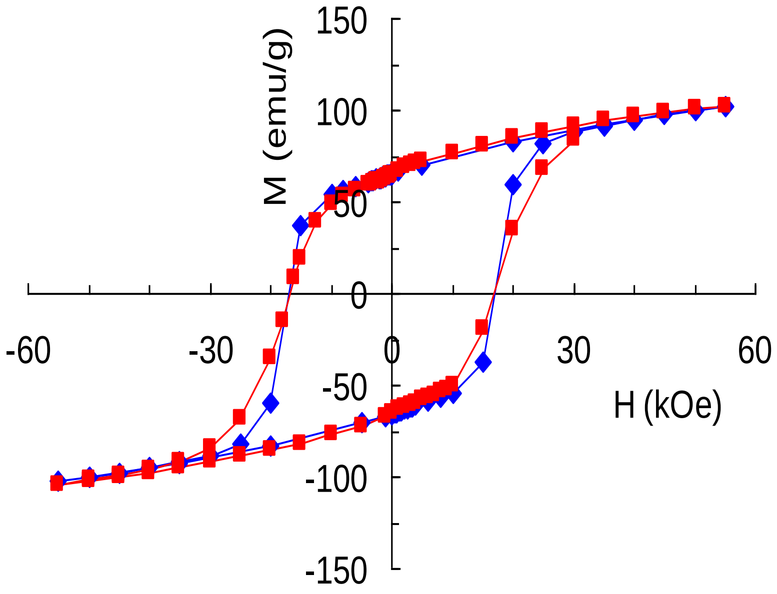
Small crystallite size
→high coercivity



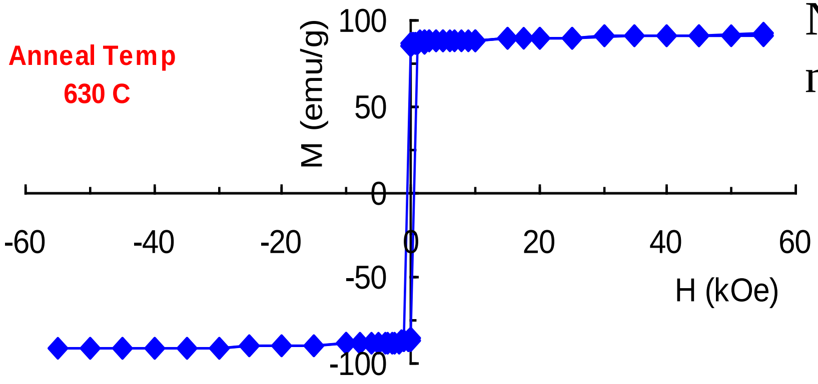
Large interface area
→ NdFeB and Fe coupled.



grain size is 20 – 70 nm.

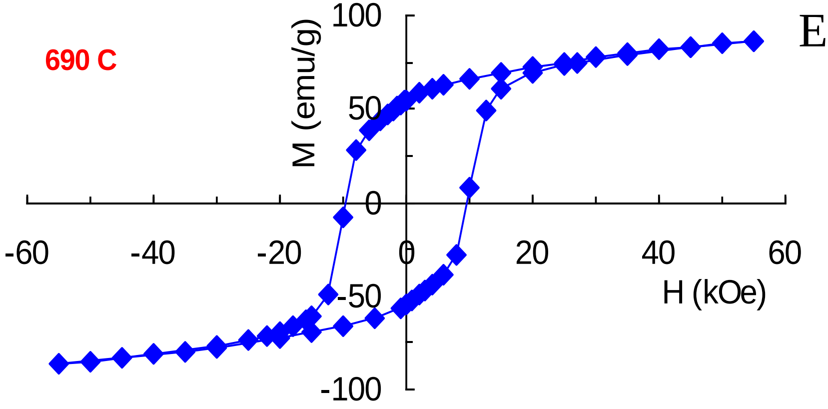


Exchange coupling (Hf/NdFeB/Hf/Si(110)



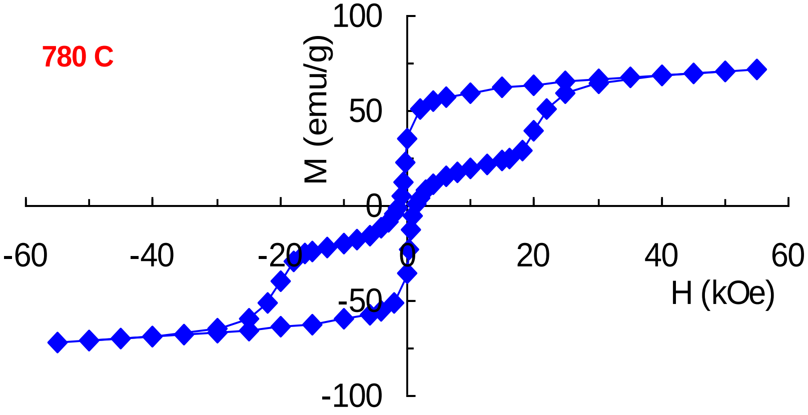
Anneal Temp
630 C

$Nd_2Fe_{14}B$ phase not formed



690 C

$Nd_2Fe_{14}B$, alpha- Fe phases present. Exchange coupled.



780 C

$Nd_2Fe_{14}B$, Fe phases present. Not exchange coupled.

From previous work

Best buffer layers: Nb, Mo

Sample thickness: 180 or 540 nm → largest H_c, MH_{max}

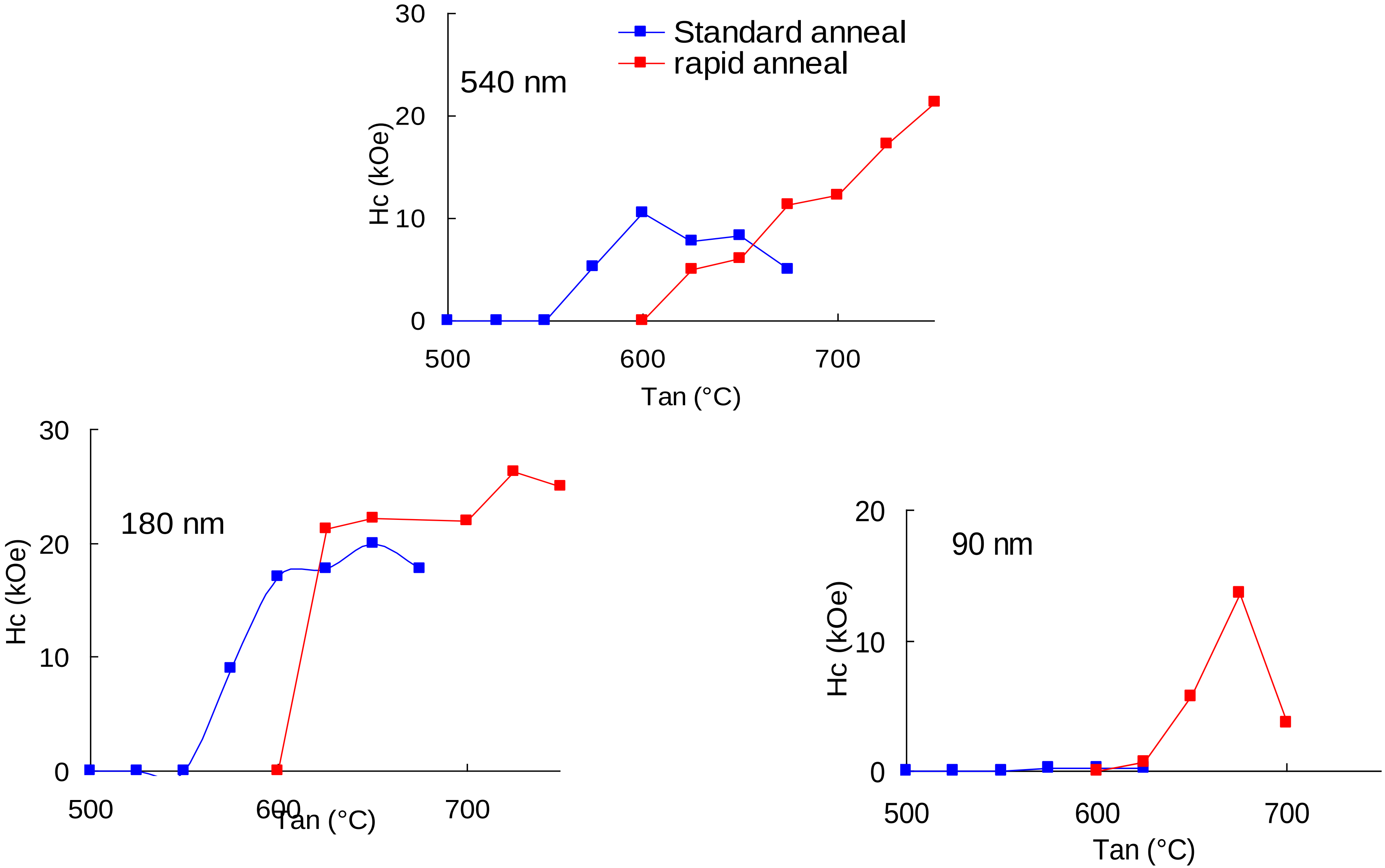
Rapid anneal: larger H_c, MH_{max}

Notes:

The Fe/Nd ratio was determined by PIXE,
7 is stochiometric $Nd_2Fe_{14}B$

The Nd/B ratio was determined by ICP
mass spectroscopy and is 1.8.

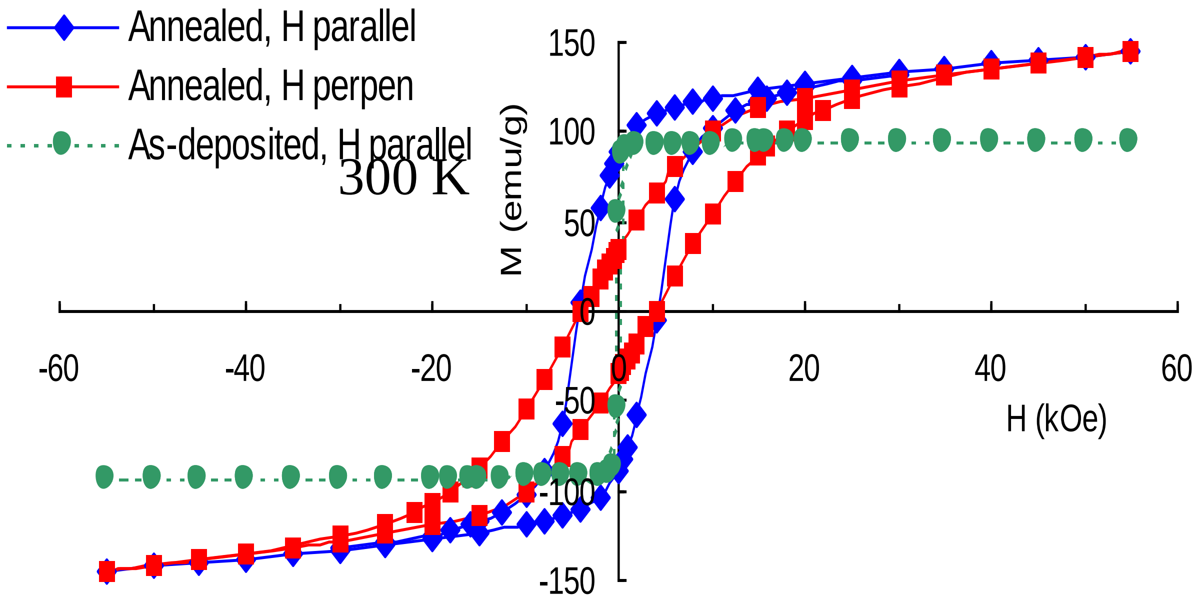
Post anneal: Standard (vacuum) anneal, 20 mins.
Rapid anneal, flowing N, 30 seconds.



[Jiang, O'Shea, to be published in Jour, Magn. Magn. Mat]

Hysteresis loops for:

Nb/NdFeB(540 nm)/Nb/Si,
Rapid (30 sec) anneal at
625 ^{o}C.

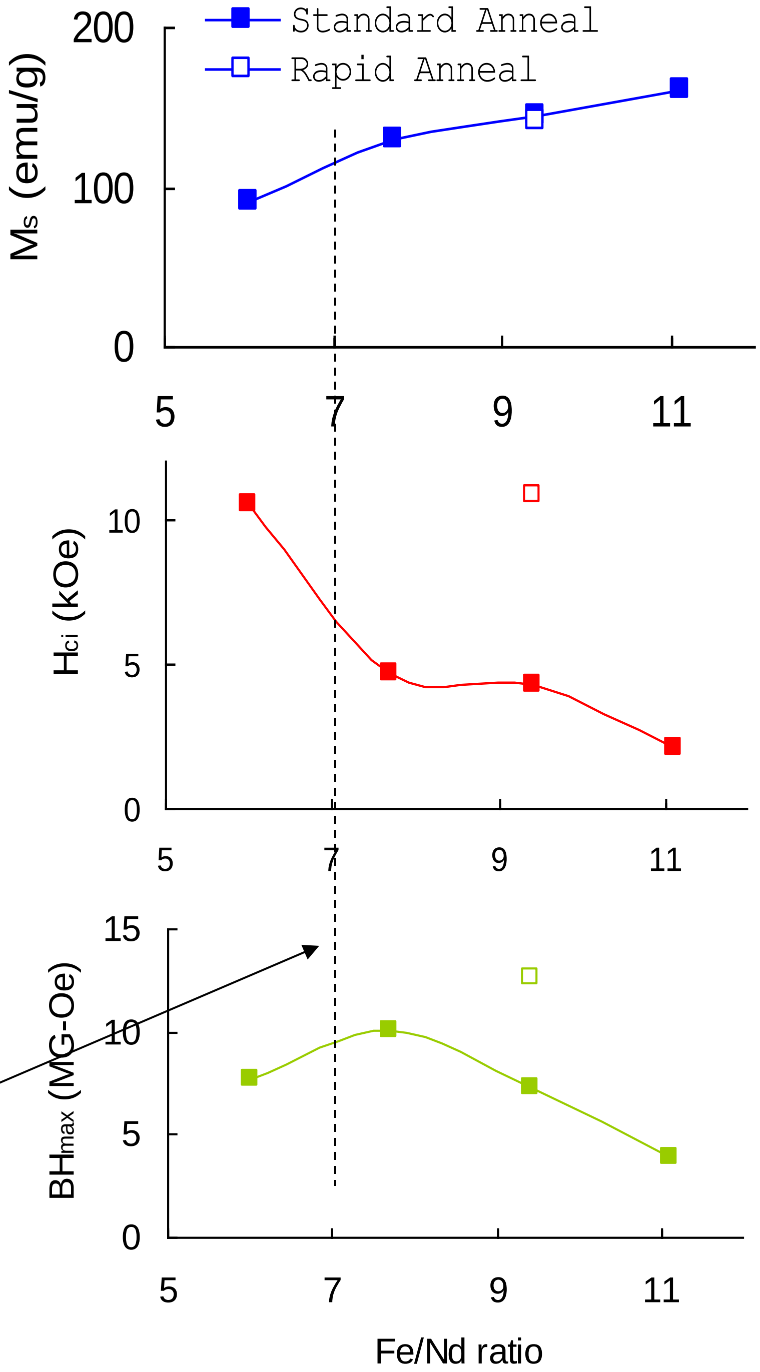


No in-plane or perpendicular magnetic anisotropy apart from demagnetization.

(Quantum Design MPMS5 SQUID magnetometer)

Magnetic Properties as a function of Fe content, d = 540 nm, buffer Nb.

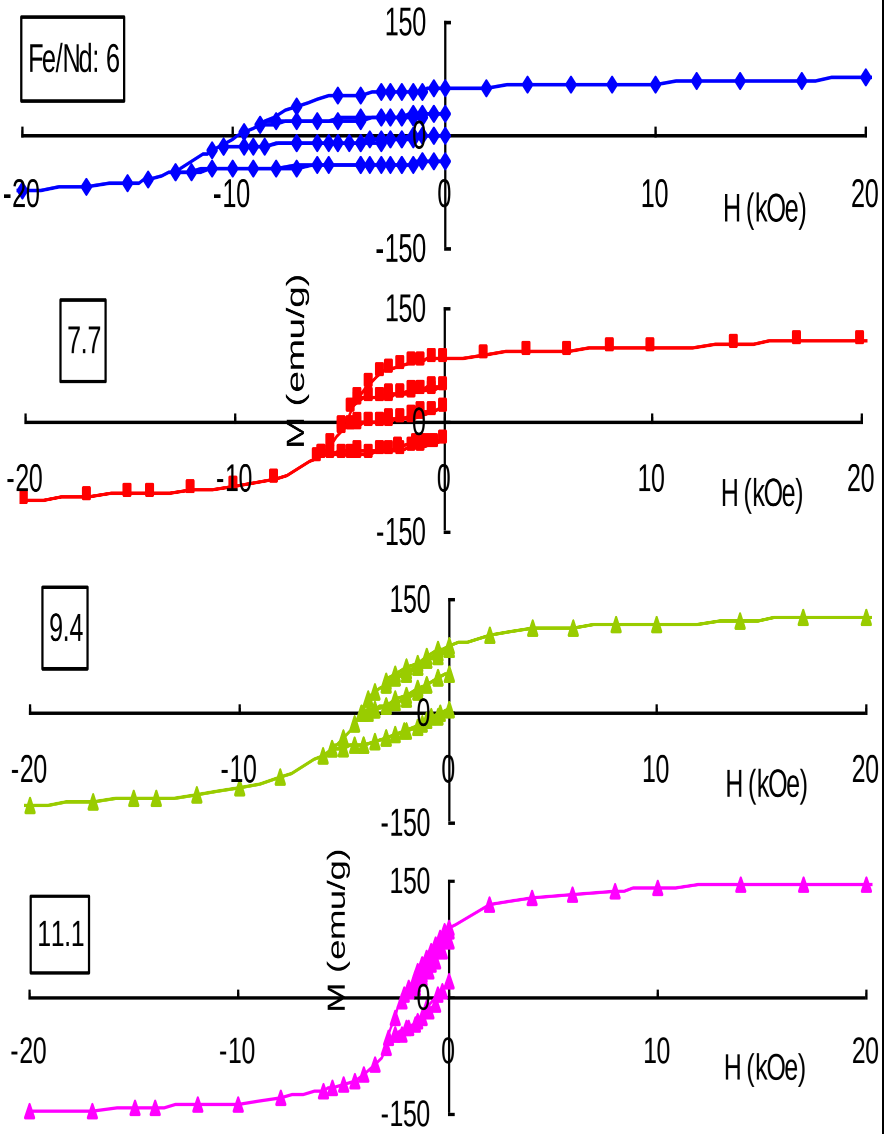
Four compositions:
Fe/Nd ratio: 6, 7.7, 9.4, 11.1 (PIXE)
Nd/B ratio: 1.8 (ICP mass spectroscopy)



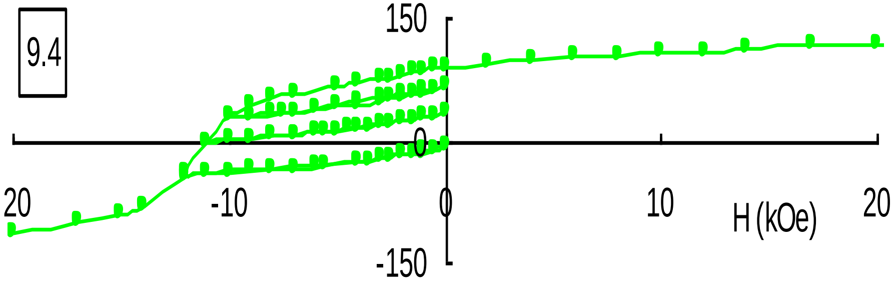
Stochiometric
$Nd_2Fe_{14}B$

Recoil Magnetization- Standard Anneal

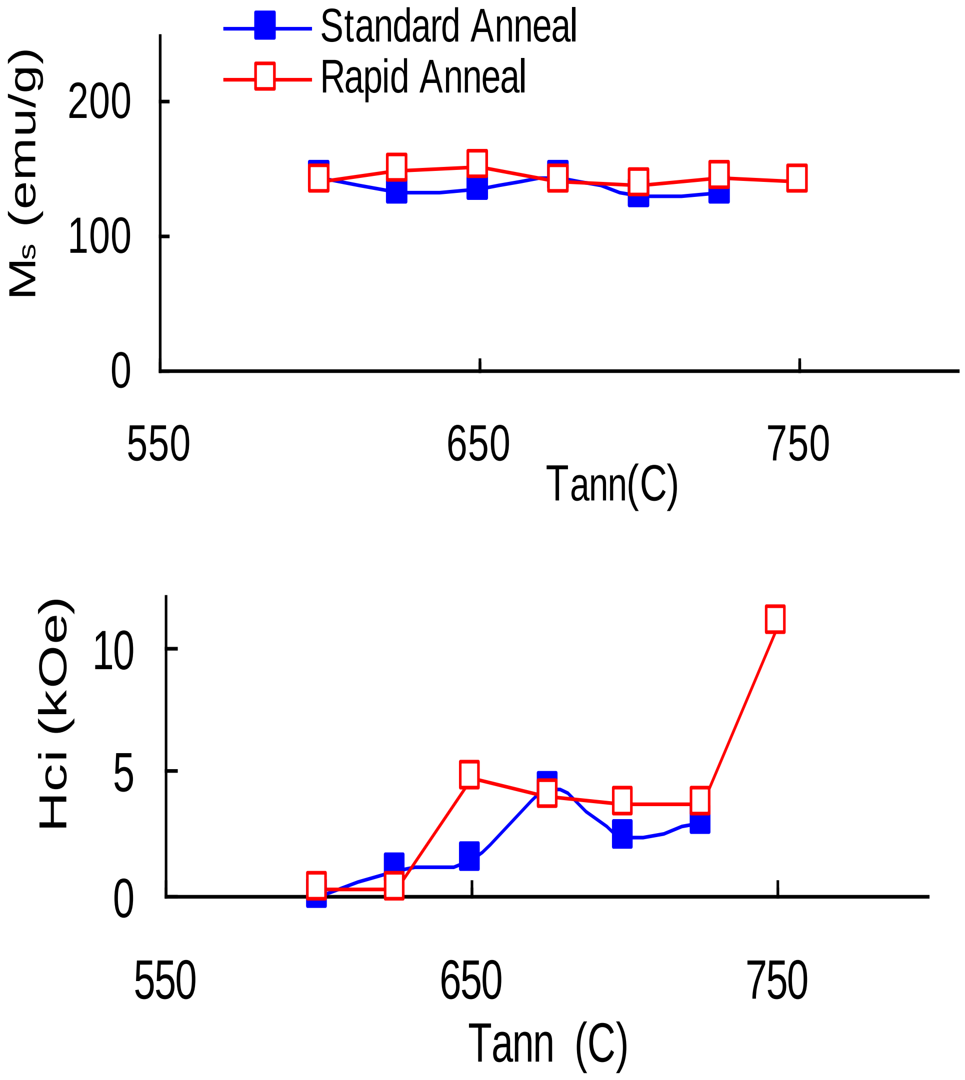
Increasing
Fe content



Rapid Anneal

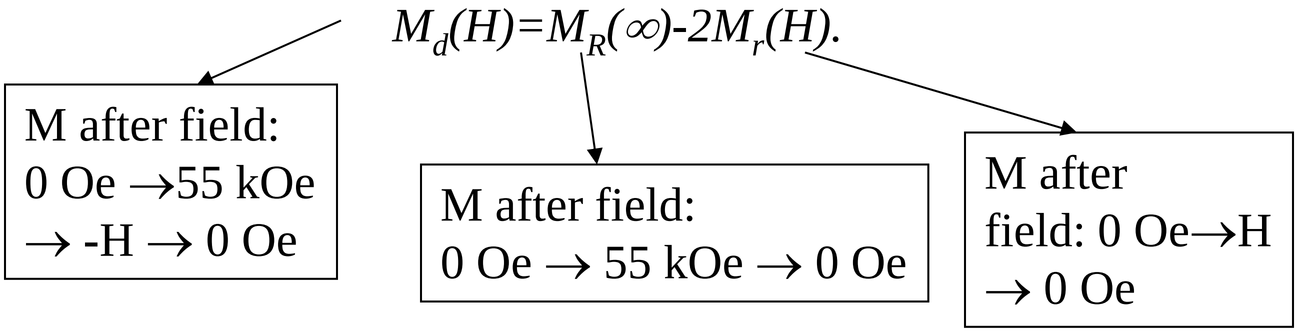


Comparison of a standard and a rapid anneal.
For sample: d = 540 nm, Fe/Nd ratio = 9.4



Interactions

Assuming uniform uniaxial single domain particles with no interactions the remanences are related by:



$$M_d(H)=M_R(\infty)-2M_r(H).$$

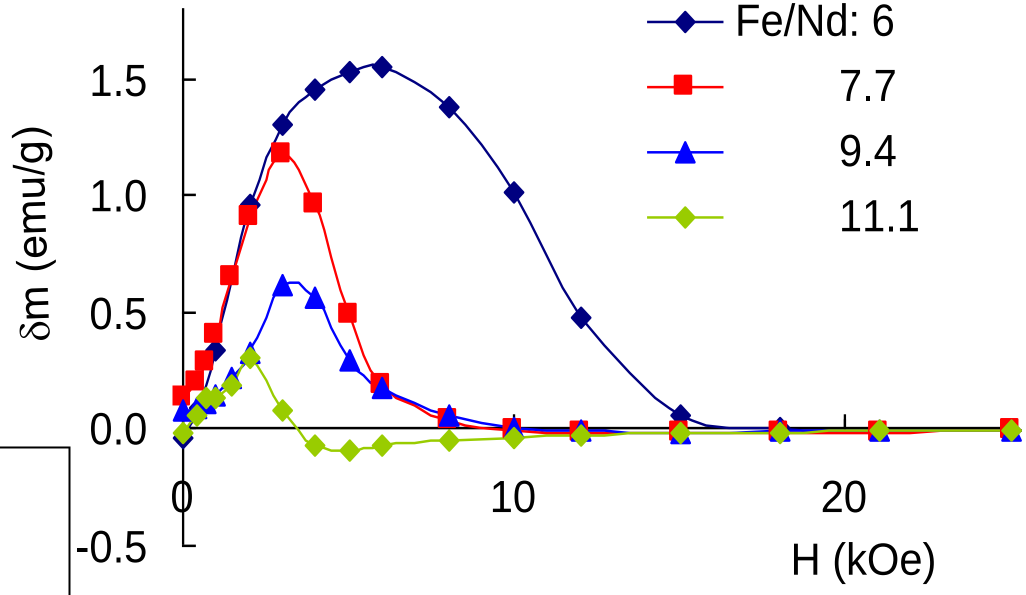
M after field:
0 Oe →55 kOe
→ -H → 0 Oe

M after field:
0 Oe → 55 kOe → 0 Oe

M after field: 0 Oe→H
→ 0 Oe

If interactions are present this no longer holds and the difference between the left and right side is:

$$\delta m= m_d(H)-(1-2m_r(H))$$



- For samples Fe/Nd=6, 7.7, 9.4, strong positive coupling
- For sample Fe/Nd=11.1, evidence for negative coupling due to magnetostatic interactions

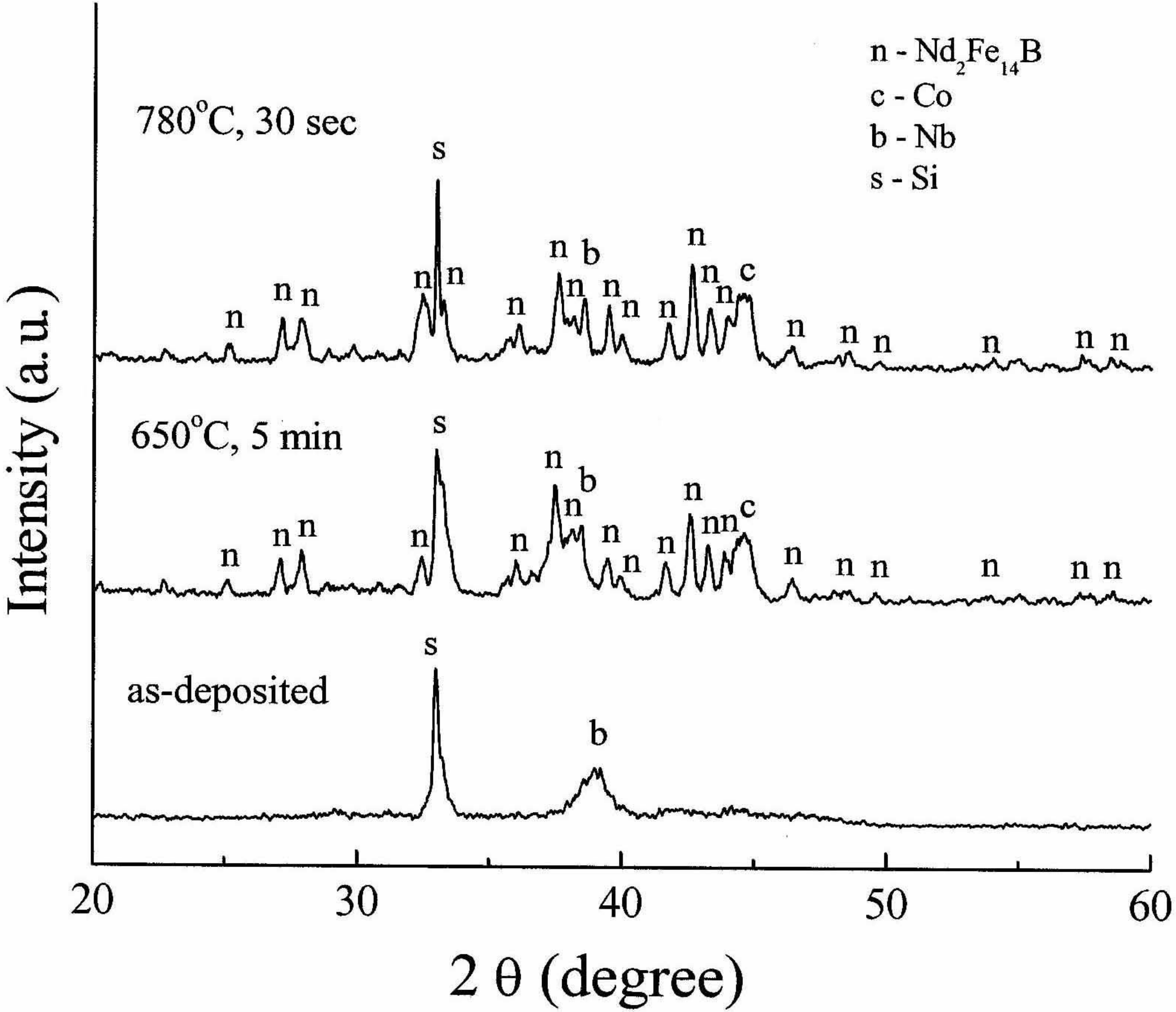
NdFeB/Co –exchange coupled magnets

-Co incorporates a larger moment than $Nd_2Fe_{14}B$

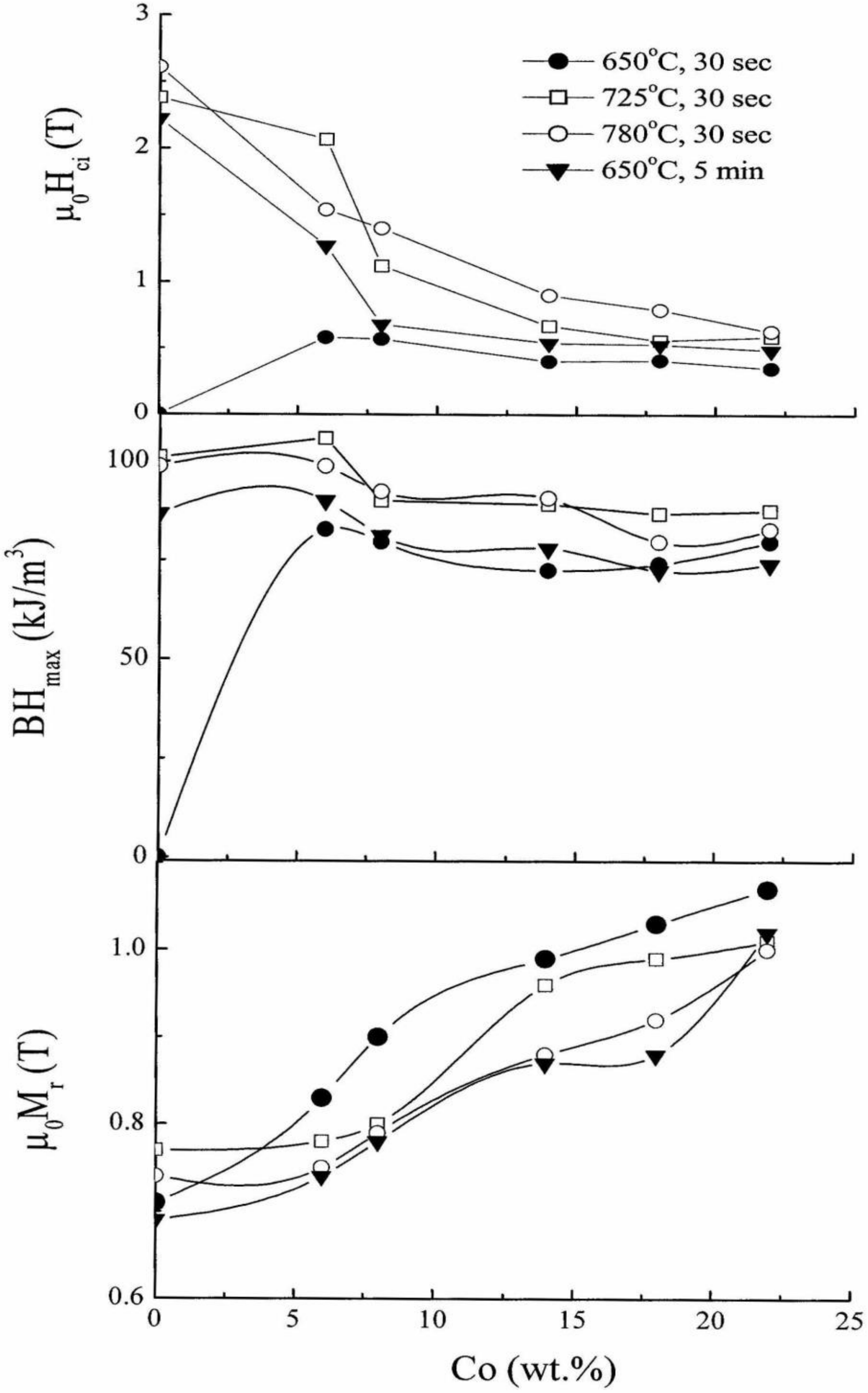
-Co will increase the magnetic ordering temperature

-if Co is incorporated into the $Nd_2Fe_{14}B$ phase [$Nd_2(FeCo)_{14}B$] then the anisotropy of the magnet is lowered.

X-ray diffraction: $Nd_2Fe_{14}B$ +14% Co



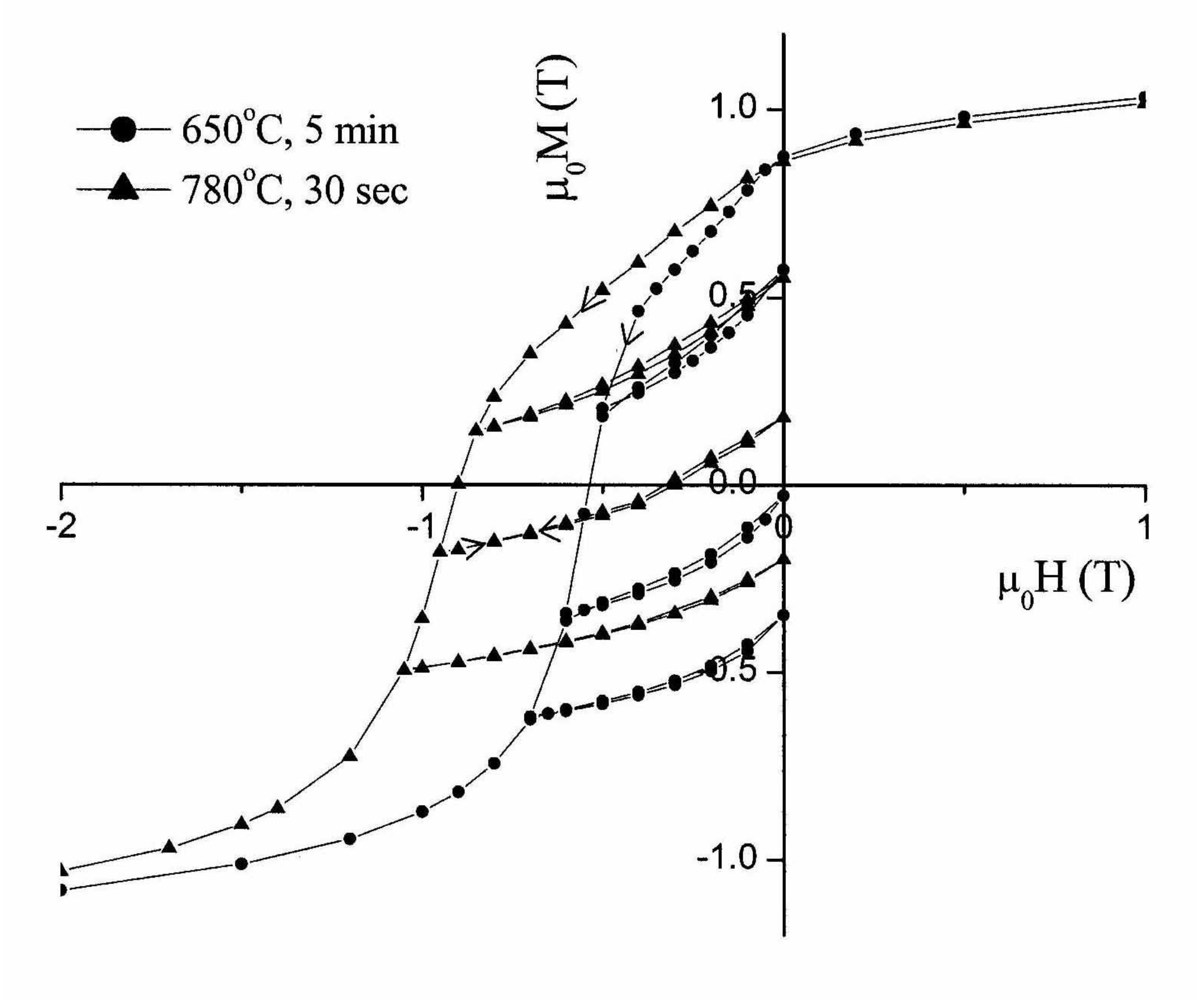
H_c, BH_{max}, μ_0M_r as a function of Co content



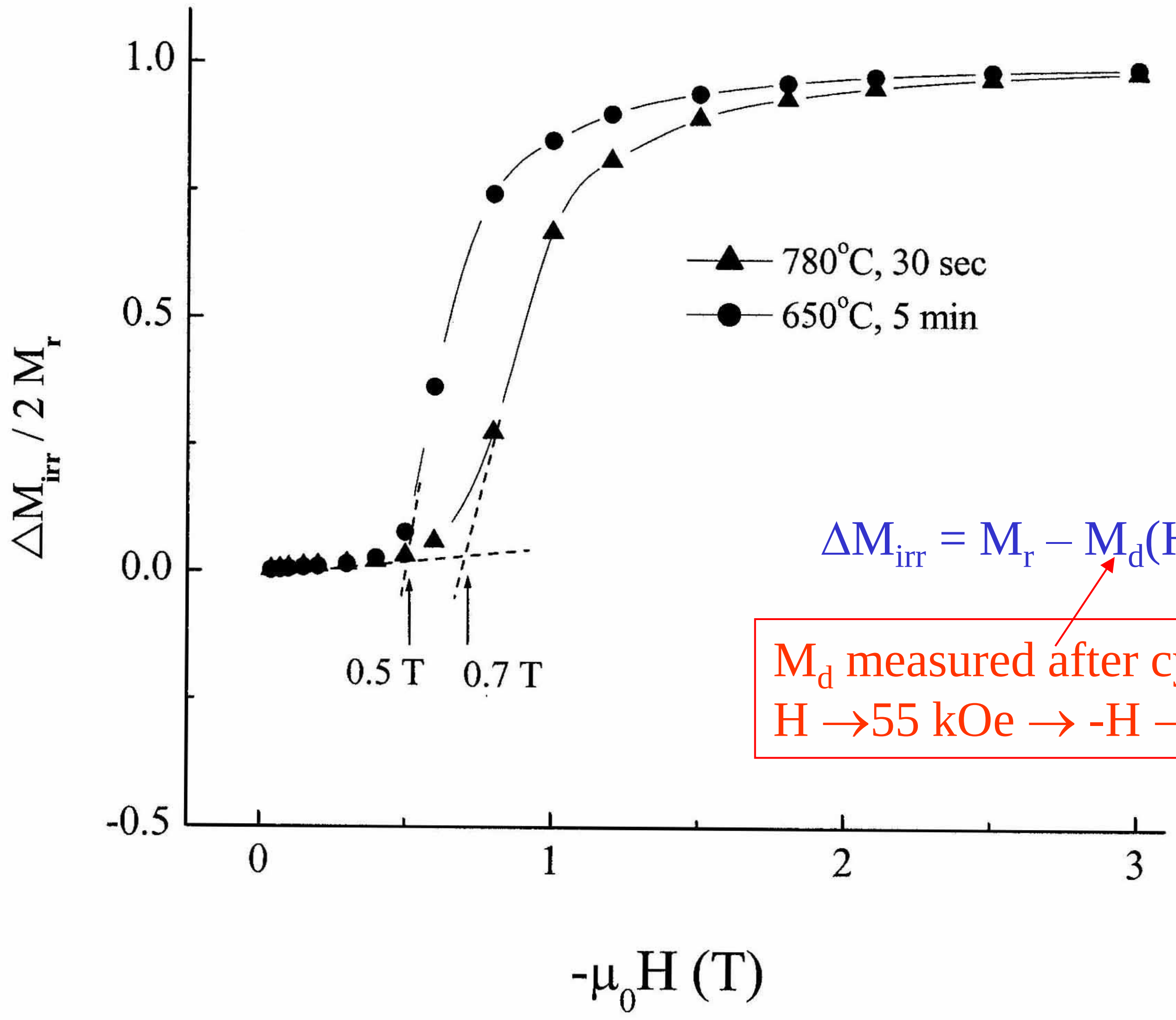
Structure and magnetic properties -two selected samples

						Grain size	
Sample/ T_a (^oC)	x (%)	$\mu_0 M_r$ (T) ±1%	$\mu_0 H_c$ (T) ±1%	BH_{max} (kJ/m^3) ±1%	M_r/M_s ±1%	Co (nm) ±1nm	$Nd_2Fe_{14}B$ (nm) ±3nm
650/ 5 mins	14	0.87	0.54	78.0	0.67	15	31
780/ 30 sec	14	0.88	0.9	90.1	0.67	15	29

Hysteresis and recoil magnetization



Irreversible magnetization

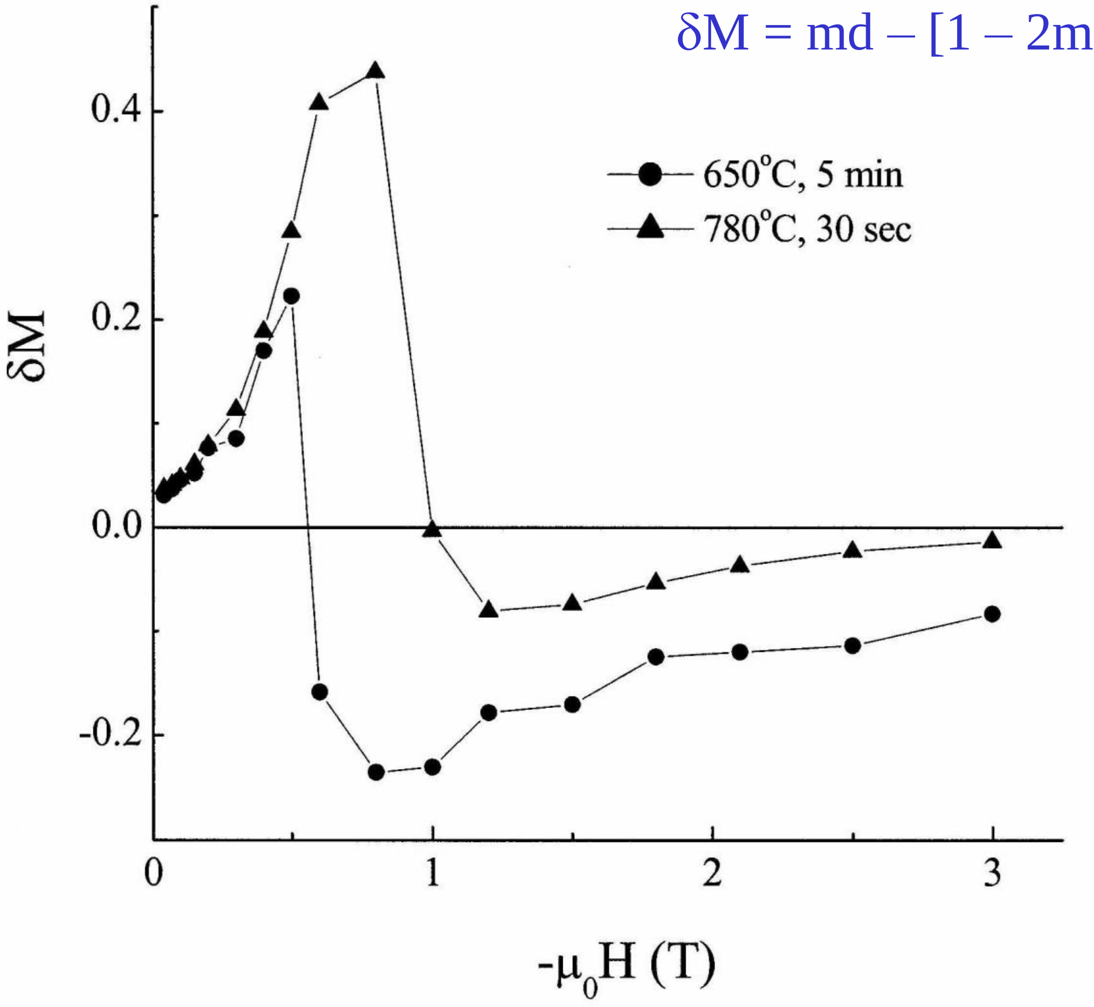


$\Delta M_{irr} = M_r - M_d(H)$

M_d measured after cycling
H →55 kOe → -H →0)e

Henkel Plot

$\delta M = m_d - [1 - 2m_r(H)]$



-grains of rapidly annealed samples have positive inter-grain interactions

Energy product

Largest energy product for NdFeCoB is 106 kJ/m^3 (13.3 MG.Oe)

Found in rapidly annealed sample
(Uniform grain size, strong ferromagnetic interactions)

No other work on thin films to compare to.

For bulk melt-spun: 119 kJ/m^3[1], 95 kJ/m^3[2], 80 kJ/m^3[3], 100 kJ/m^3[4], 55.7 kJ/m^3[5].
After aligning ggrains ref 5 obtains 229 kJ/m^3,

1. H. Chiriac, M. Marinescu, Jour. Appl. Phys 83 (1998)
2. L. H. Lewis and V. Panchanathan, Jour. Magn. Mag. Mater. 196 (1999) 299.
3. Q. Chen, B. M. Ma, B. Lu, M. Q. Huang and D. E. Laughlin, Jour. Appl. Phys. 85 (1999) 5917.
4. J. Bernardi, T. Schrefl, J. Fiddler, Th. Rijks, K. de Kort, V. Archambault, D. Pere, S. David, D. Givord, J. F. O'Sullivan, P. A. I. Smith, J. M. D. Coey, U. Czernik, M. Gronefeld, Jour. Magn. Magn. Mater. 219 (2000) 186.
5. R. W. Gao, D. H. Zhang, W. Li, X. M. Li, J. C. Zhang, Jour. Magn. Mag. Mater. 208 (2000) 239.

Final comments

To date magnets based on Nd-Fe-B discovered two decades ago are the best permanent magnets.

Micro- and nano-structure are important in improving their magnetic properties.

With more control on the precise form of nanostructure it is likely properties can be improved (e.g. larger energy products could be obtained)