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OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Phrama scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Dy-FREE HIGH STRENGTH, HIGH COERCIVITY Nd_2Fe_{14} PERMANENT MAGNETS

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The Ames Laboratory and Department of Materials Science and Engineering
Iowa State University, Ames, Iowa, 50011 USA

3rd International Conference and Exhibition on Materials and Engineering
San Antonio, Texas, USA
October 6, 2014

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U.S. DEPARTMENT OF ENERGY

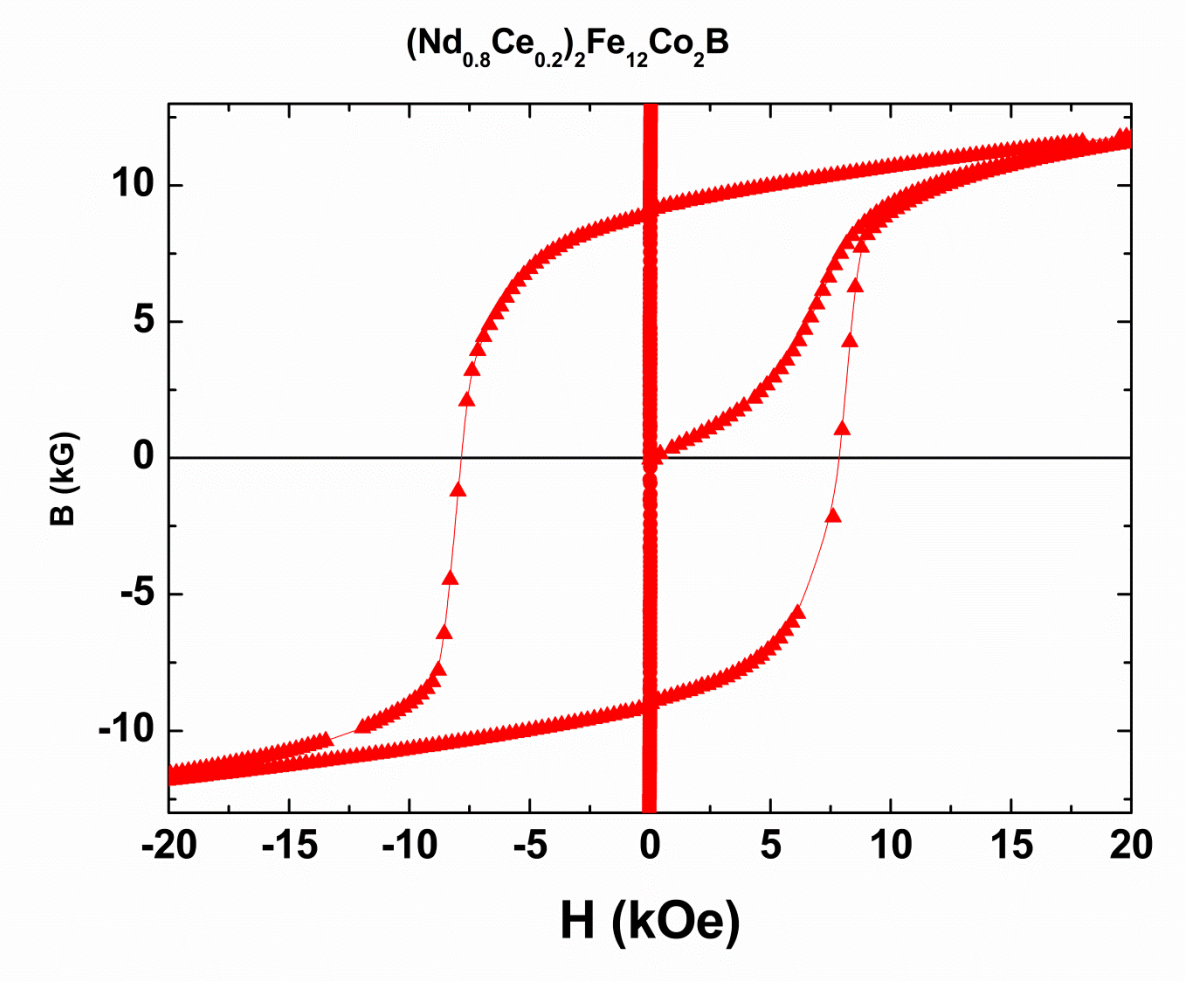
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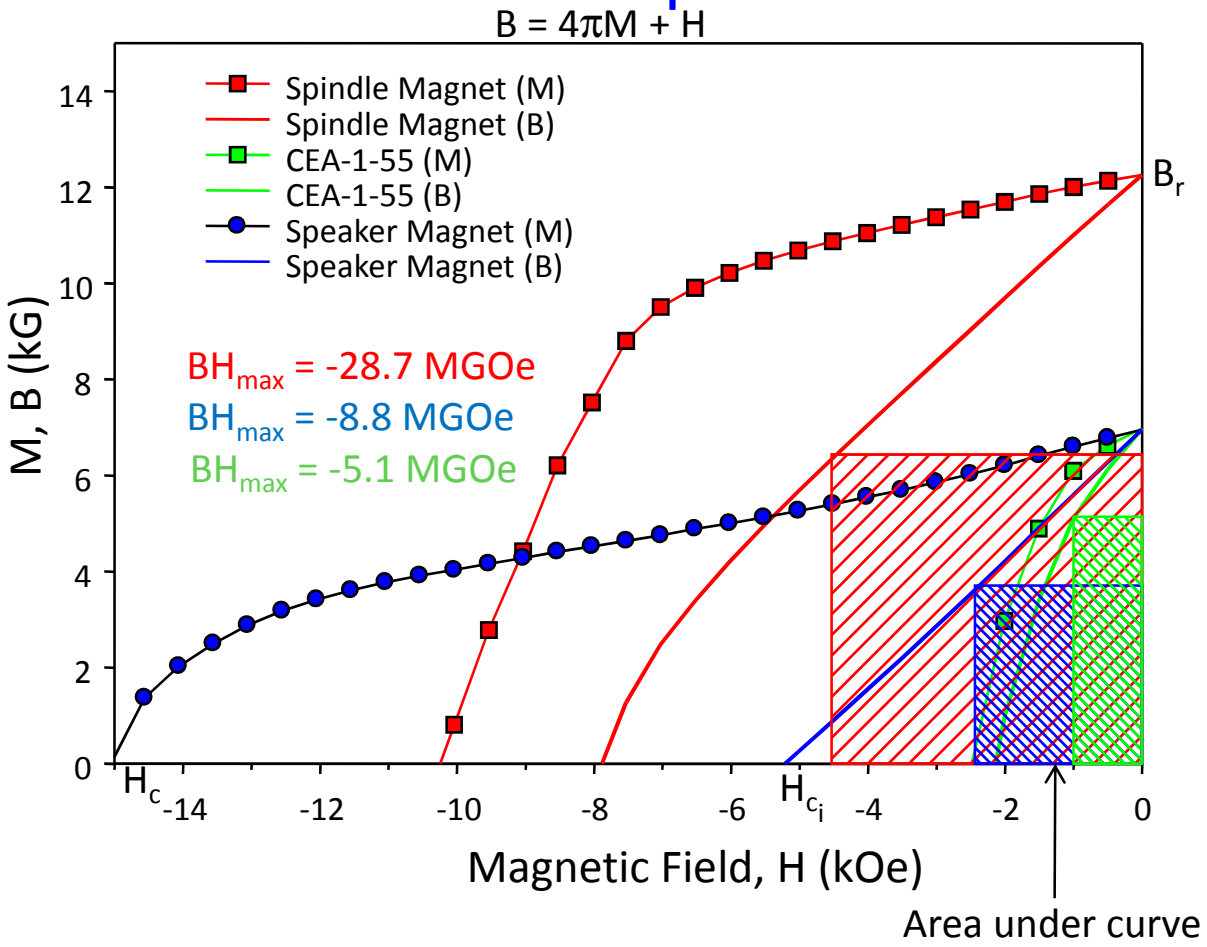
BASIC DEFINITIONS – I

B vs. H Curves



BASIC DEFINITIONS – II

B_r, H_c, H_{c_i}, BH_{max}



B_r Remanence (kG)

H_c Coercivity (kOe) (line with data point)s

H_{c_i} Intrinsic Coercivity (kOe) (solid line)

BH_{max} Maximum Energy Product (MGOe) (largest area under curve)

NEODYMIUM-IRON-BORON PERMANENT MAGNETS $Nd_2Fe_{14}B$

Strongest permanent magnet

Fe – magnetic properties due to iron

Nd – locks the iron magnetic moments, keeps them from rotating (coercivity)

Applications

electric motors (cars, wind turbines, elevators)

spindle magnet of computers

speakers (ear buds)

magnetic refrigerators

Role of Dy

added to $Nd_2Fe_{14}B$ to further increase the coercivity (1 to 10%)

increases the high temperature useful limit

DYSPROSIUM

USEFULLNESS

- Magnet weighs less for the same strength compared to magnets without Dy (automobiles – CART requirements)
- Improves high temperature performance

DRAWBACKS

- Supply of Dy in the world is limited
- One of Dept. of Energy's critical elements (most critical)
- Expensive

DOE's ARPA-E REACT PROGRAM

- Rare Earth Alternatives in Critical Technology for energy
- Get rid of Dy, or reduce the amount needed
- Reduce Nd content, or replace it with new non-rare earth magnets

WHY CERIUM

Most abundant rare earth

Ce needs to be removed to get at the other rare earth elements in the separation process

50% excess Ce supply over demand

General Motors found that in $La_2Fe_{14}B$-$Nd_2Fe_{14}B$ pseudo binary system two phases formed after high temperature anneal – will Ce do the same?

Ce is a mixed valent metal with a history of doing unusual and strange things

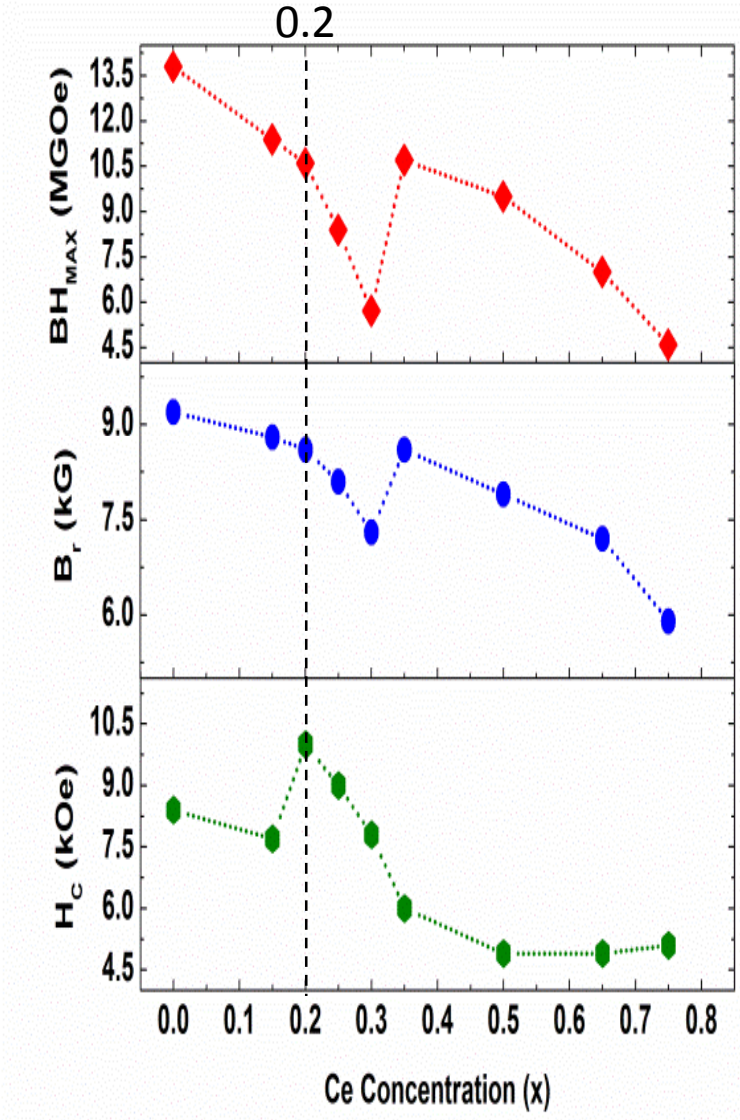
The Ce valence is 3.4 in $Ce_2Fe_{14}B$

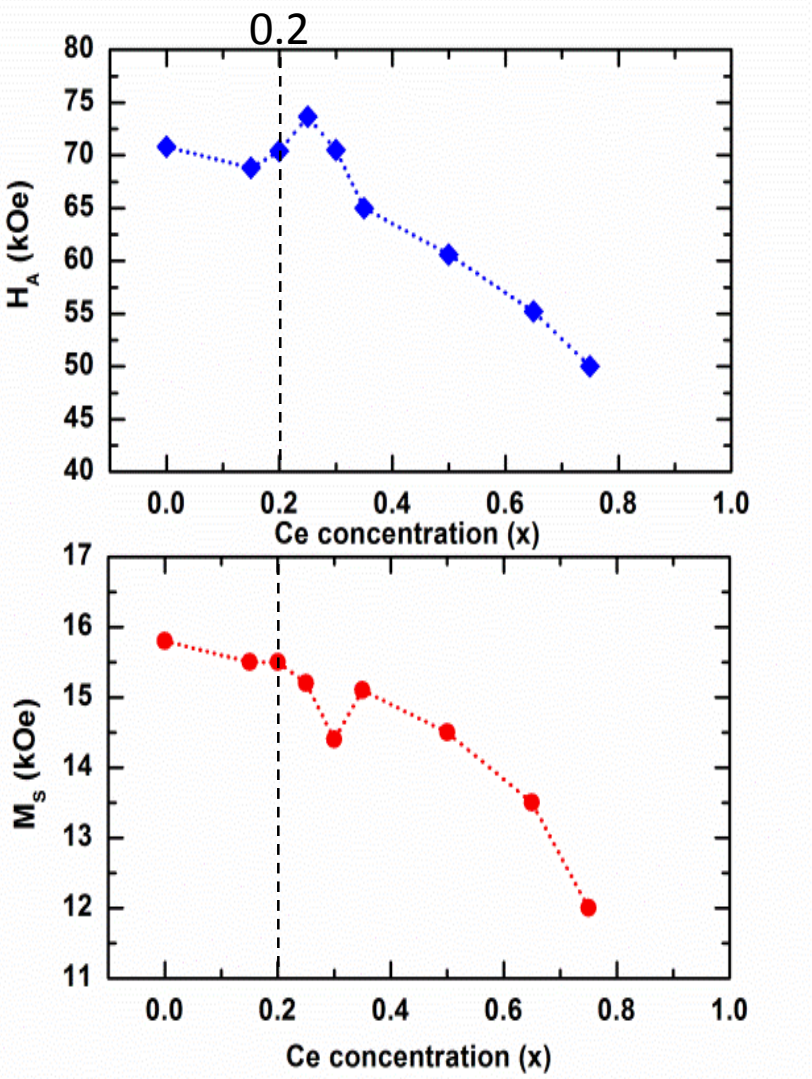
FIRST SURPRISE IN $(Nd_{1-x}Ce_x)_2Fe_{14}B$ SYSTEM

An anomaly in the *c* lattice parameter vs. Ce concentration plot at ~20% Ce substitution for Nd!

An increase in coercive field at ~20% Ce concentration (Slide 8)!

BH_{MAX}, B_r, H_c, H_A AND M_S OF $(Nd_{1-x}Ce_x)_2Fe_{14}B$ RIBBONS



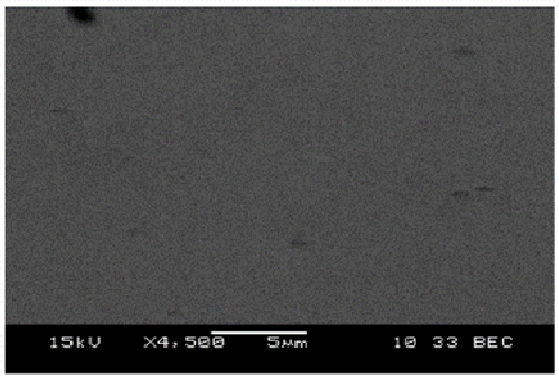


SECOND SURPRISE IN $(Nd_{1-x}Ce_x)_2Fe_{14}B$ SYSTEM

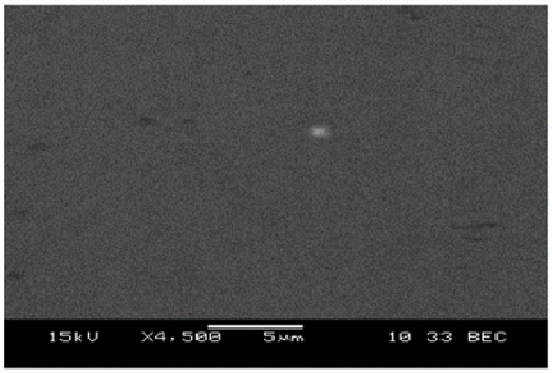
The drop-cast ingots of $(Nd_{1-x}Ce_x)_2Fe_{14}B$ are two phase alloys, with micron size Ce-rich grains in Nd-rich matrix (Slide 10)!

The two-phase region extends from x ~0.15 to x ~0.4 (Slide 10).

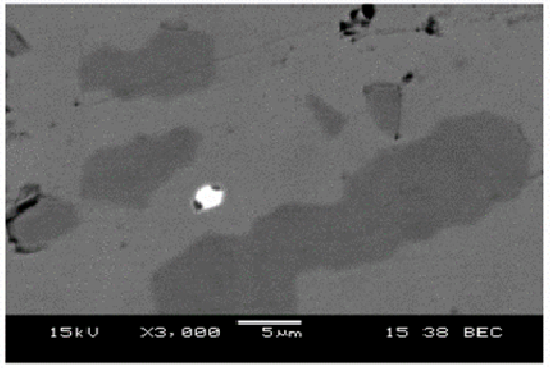
SEM IMAGES OF $(Nd_{1-x}Ce_x)_2Fe_{14}B$ DROP CAST ALLOYS



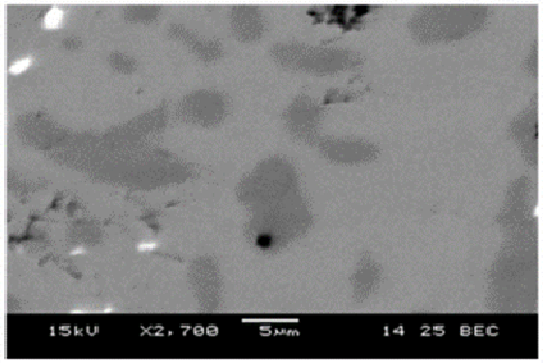
x = 0.0



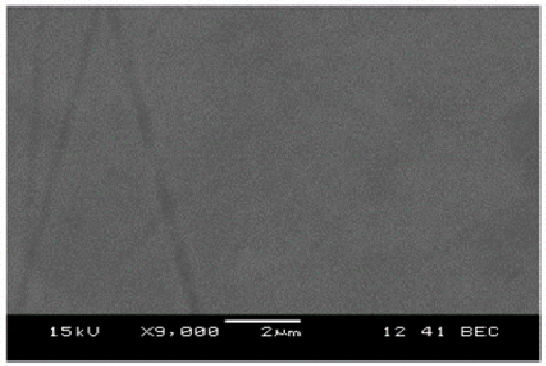
x = 0.15



x = 0.2



x = 0.25



x = 0.5

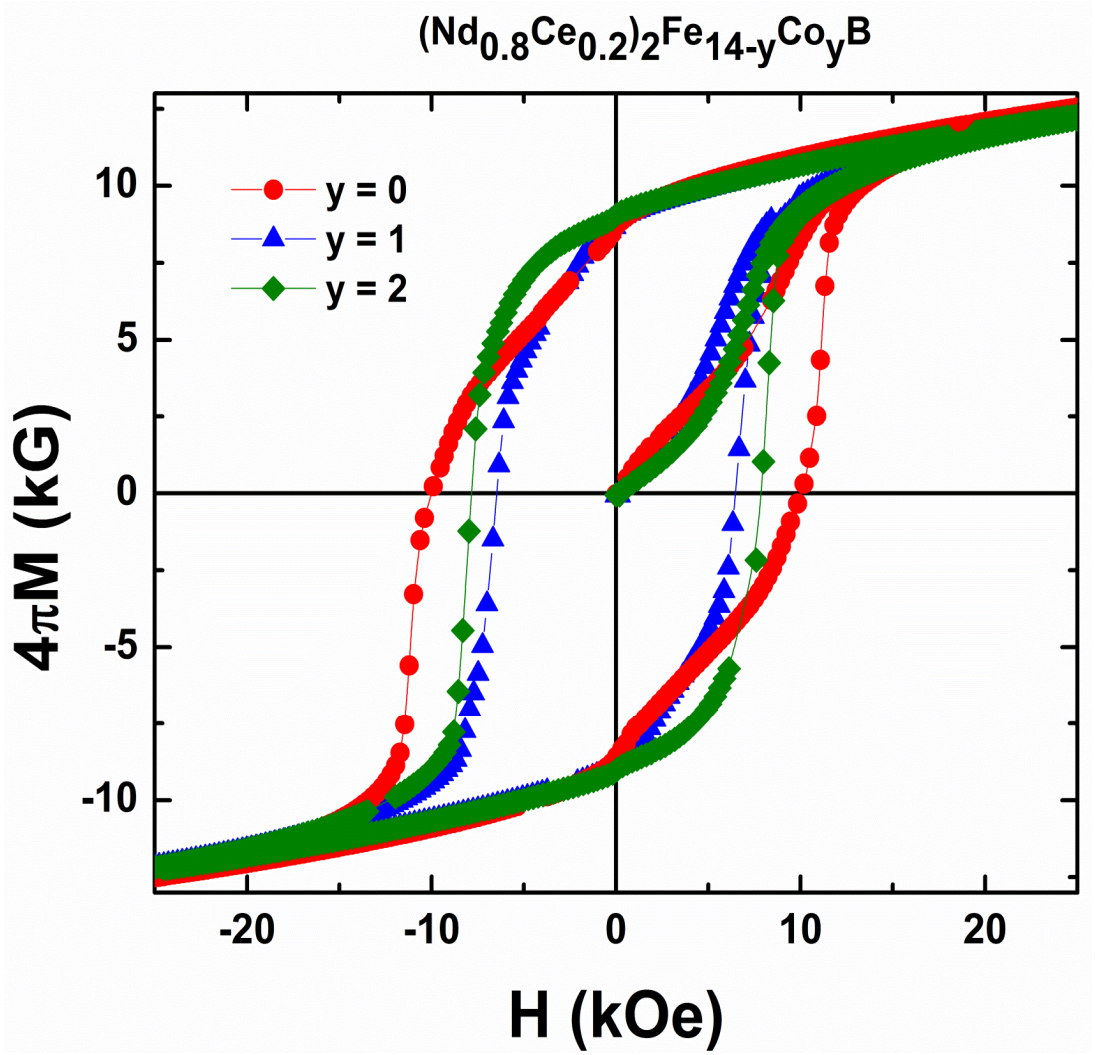
THIRD SURPRISE – THE EFFECT OF COBALT ADDITIONS

Cobalt was added to increase the ordering temperature – which it does

But it squares up the BH loop (Slide 12)!

Wow!

MAGNETIZATION VS. FIELD FOR $(Nd_{0.8}Ce_{0.2})_2Fe_{14-y}Co_yB$ ALLOYS

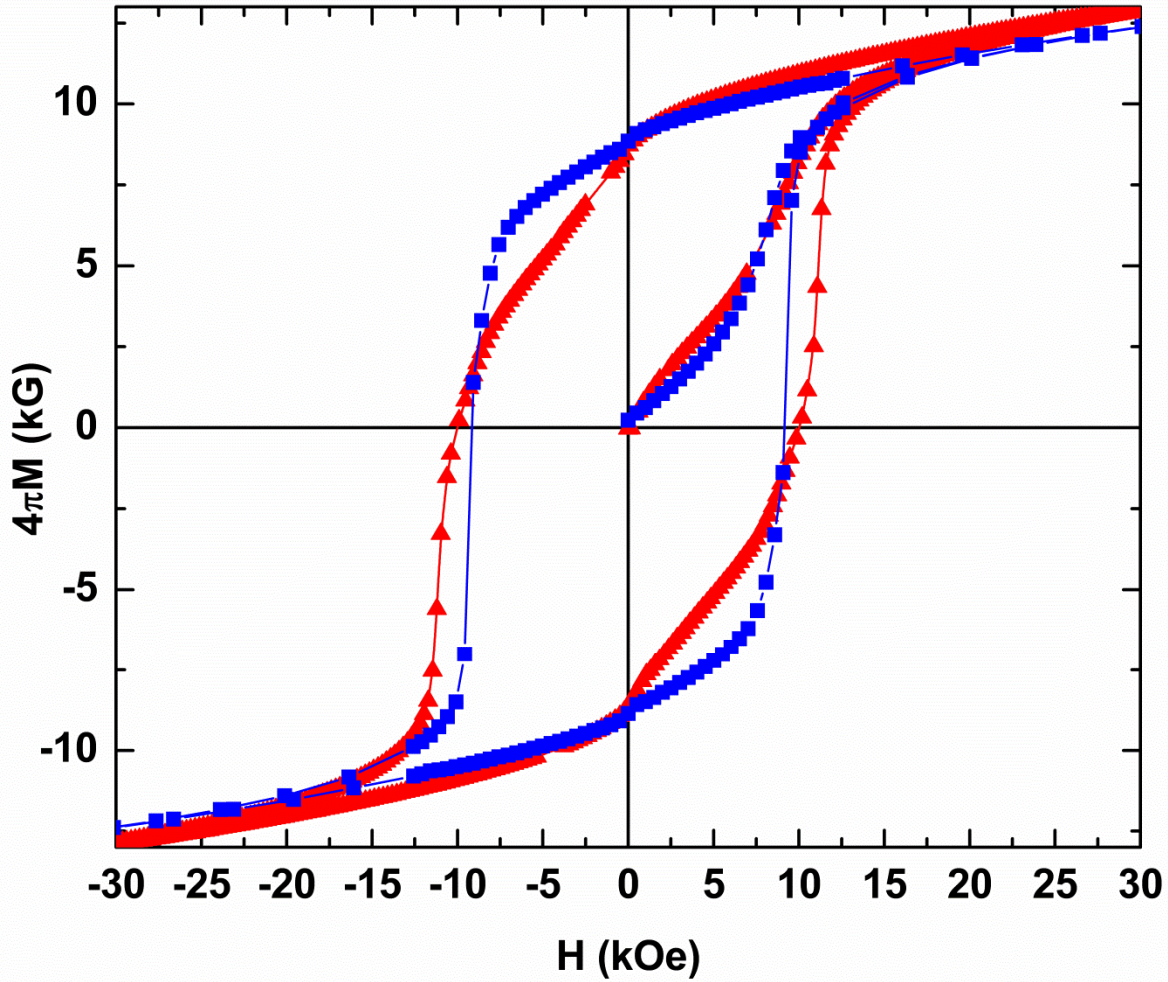


ADDITION OF TiC OR ZrC GRAIN REFINERS

Increased BH_{max} as expected (Slide 14)

ZrC is better than TiC

MAGNETIZATION VERSUS FIELD OF $(Nd_{0.8}Ce_{0.2})_{\sim 2}Fe_{14}B$ WITH AND WITHOUT ADDED TiC MELT SPUN RIBBONS



$(Nd_{0.8}Ce_{0.2})_2Fe_{14}B$

H_C = 10 kOe

BH_{Max} = 10.6 MGOe

$(Nd_{0.8}Ce_{0.2})_{2.2}Fe_{14}B$+ 2.5 % TiC

H_C = 9.1 kOe

BH_{Max} = 15 MGOe

Shape of blue curve is just what the magnet design engineers want in the second quadrant

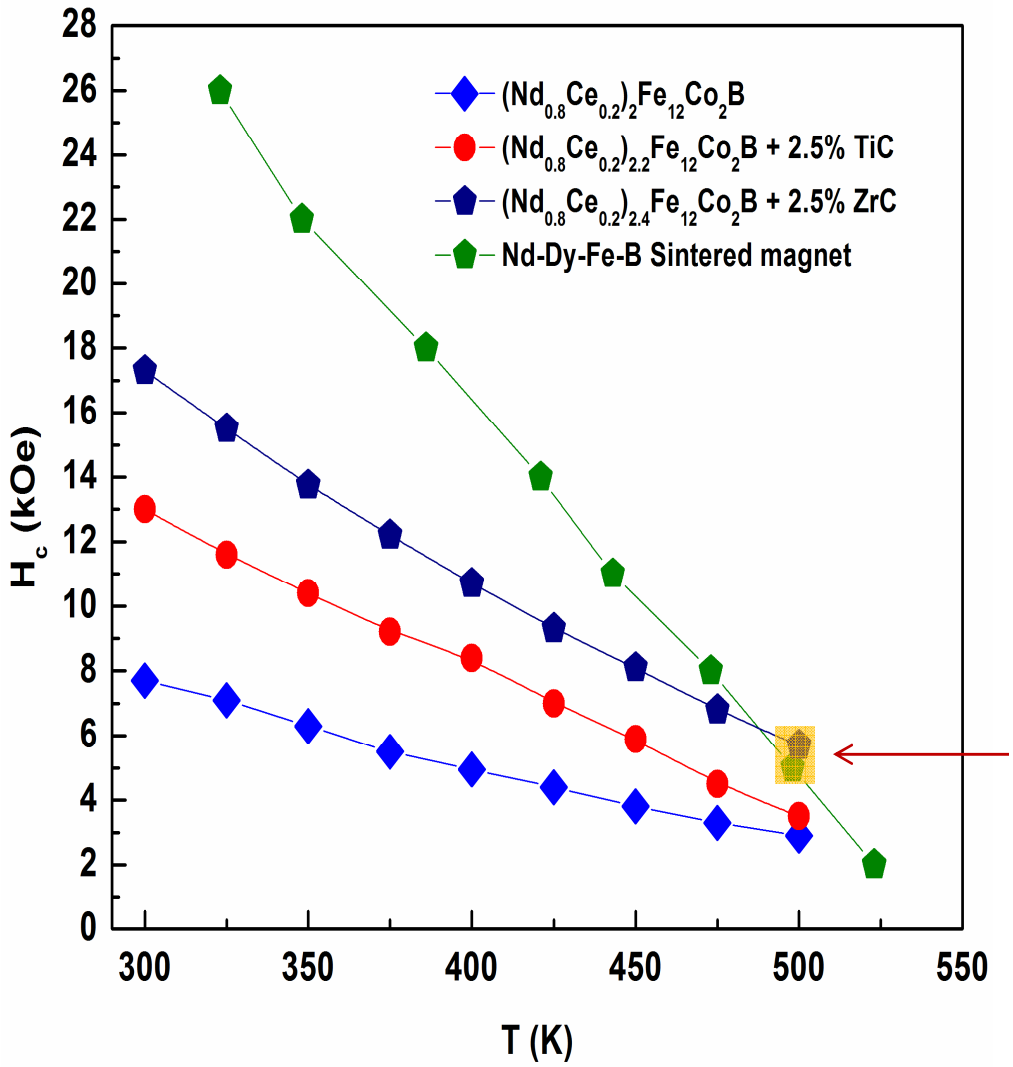
FOURTH SURPRISE – TEMPERATURE DEPENDENCE OF H_c

The temperature dependence of the coercivity drops much slower than that of a sintered Nd-Dy-Fe-B alloy (Slide 16)! Wow!

At ~500 K (~225°C) H_c is larger than that of a sintered Nd-Dy-Fe-B alloy (Slide 16)! Wow! Wow!

The temperature under the hood of an automobile may reach 475 K (200°C) during a hot summer day.

COERCIVITY AS A FUNCTION OF TEMPERATURE FOR $(Nd_{0.8}Ce_{0.2})_{2+z}Fe_{12}Co_2B$ RIBBONS WITH EXCESS RARE EARTH AND/OR TiC, ZrC AS A FUNCTION OF TEMPERATURE.



Note cross-over

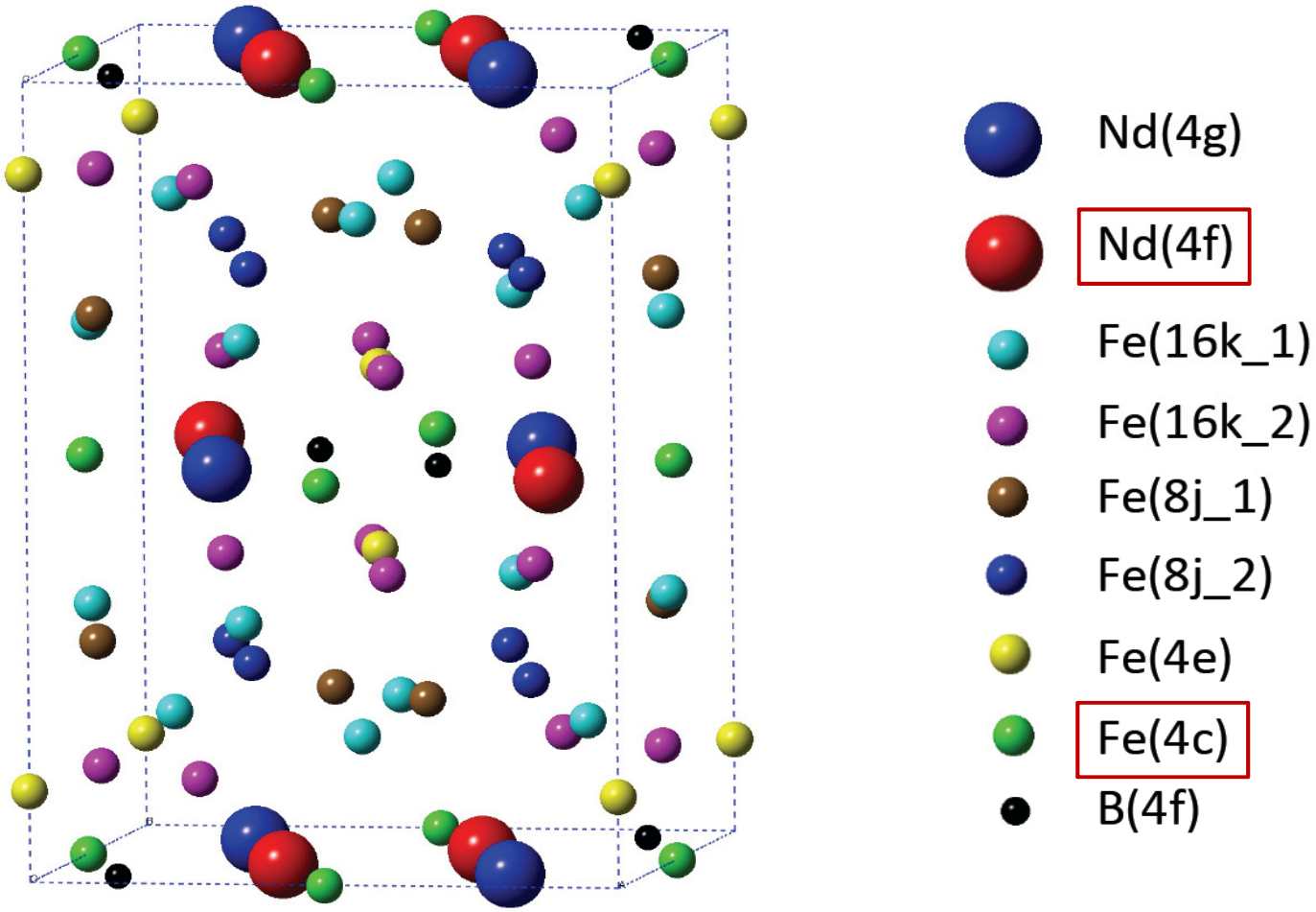
SYNERGISM BETWEEN MIXVALENT Ce AND Co

Cobalt addition:

- Increases T_c as expected
- Increases both H_c and BH_{max} Wow!
- Smaller temperature dependence of H_c and BH_{max};
  - These are better than sintered Nd-Dy-Fe-B magnet above ~475 K (~200°C); i.e. magnetic properties of co-doped Ce,Co better than sintered Dy containing magnets

Ce and Co occupy adjoining crystallographic sites in $Nd_2Fe_{14}B$ structure (Slide 18)

$Nd_2Fe_{14}B$ STRUCTURE



Ce occupies Nd(4f) sites; and Co occupies Fe(4c) sites

Ref.: L. Ke, D. Kukusta, V. Antropov, Ames Laboratory Seminar, March 2014.

PROCESSING COMMERCIAL $(Nd_{0.8}Ce_{0.2})_{2.4}Fe_{12}Co_2B$

Ce and Nd – commercial grade metals (~98 at.% pure)

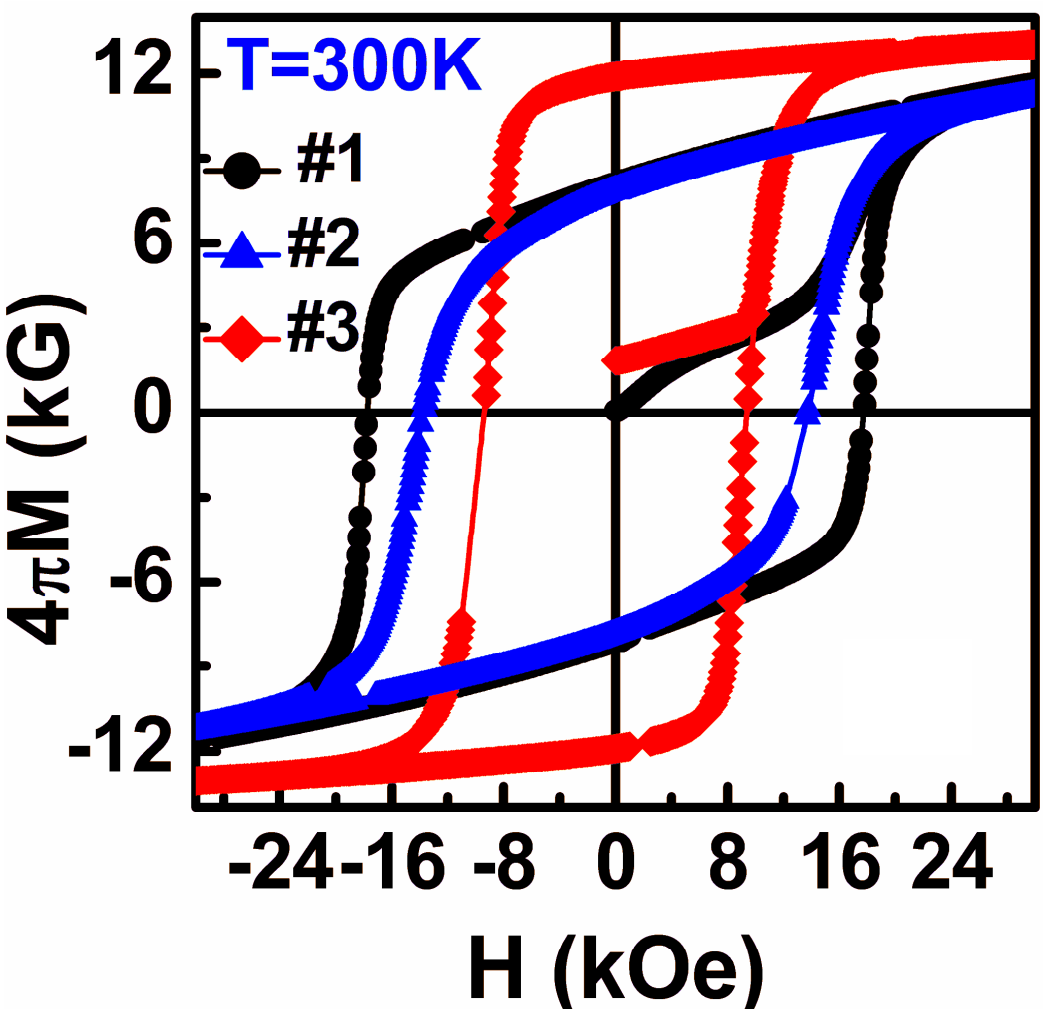
Ferrous boron – commercial grade (~2 at.% non-ferrous impurities)

MQ1(1) melt spun ribbons – isotropic grains

MQ2(2) hot pressed magnet (ingot) – isotropic grains

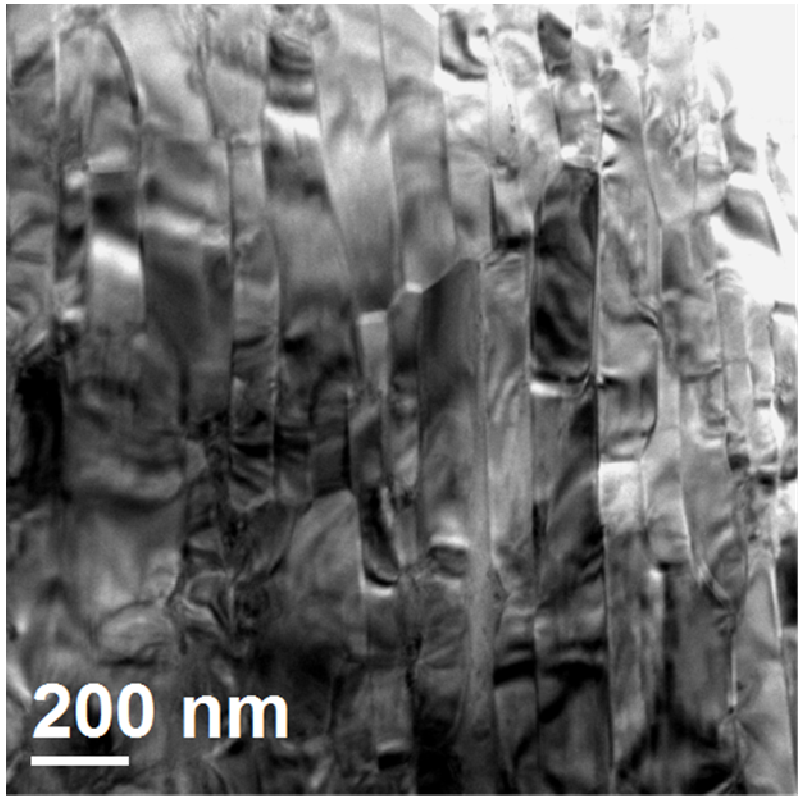
MQ3(3) die upset magnet ingot – anisotropic

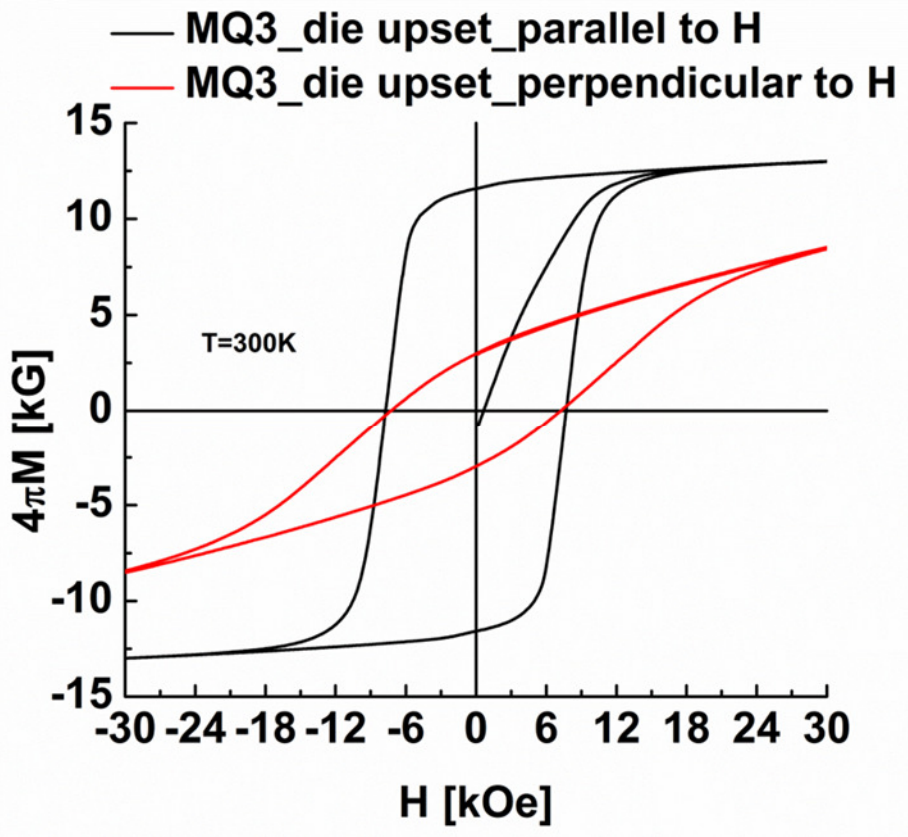
B-H CURVES $(Nd_{0.8}Ce_{0.2})_{2.4}Fe_{12}Co_2B$



#1 – ribbons
#2 – hot pressed
#3 – die upset

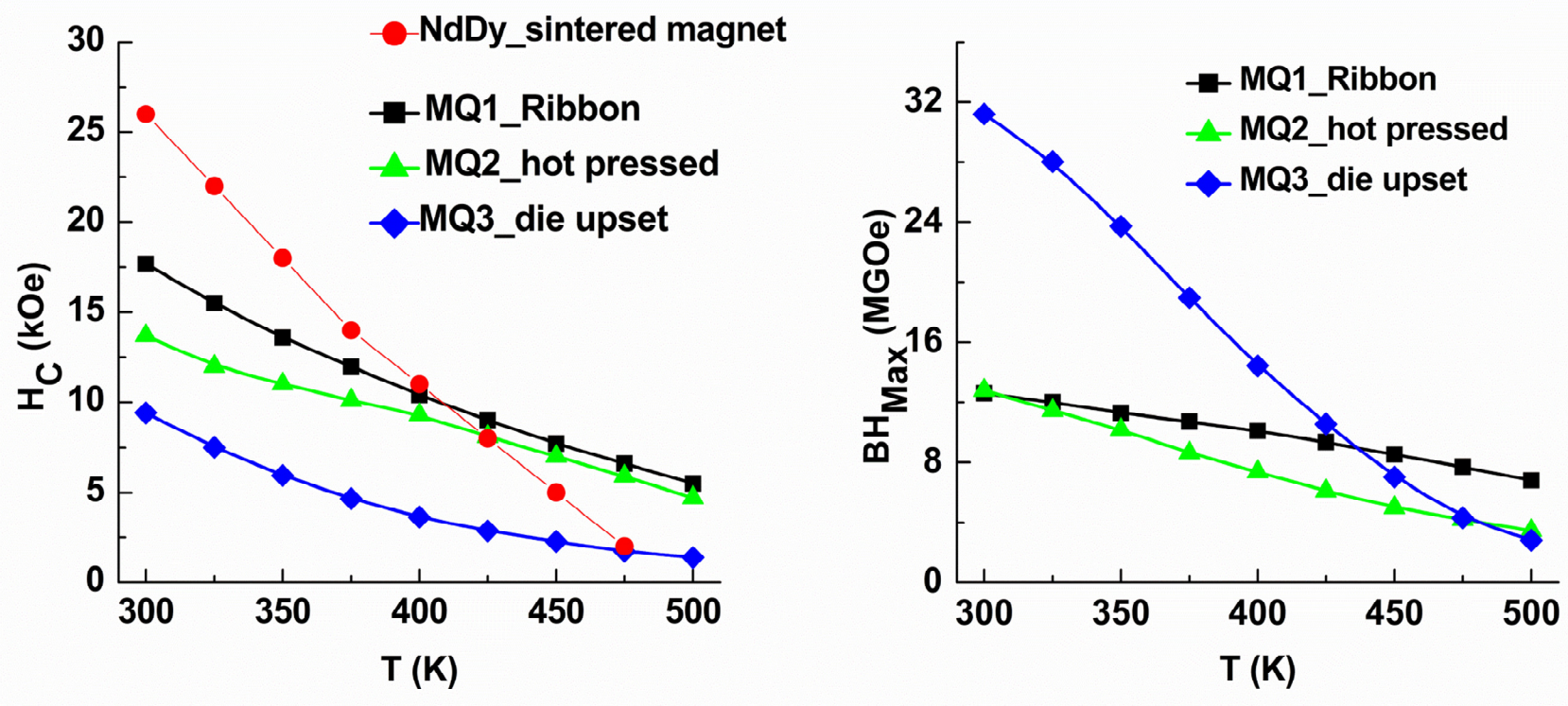
$(Nd_{0.8}Ce_{0.2})_{2.4}Fe_{12}Co_2B$: DIE UPSET





Bright-field TEM images

$(Nd_{0.8}Ce_{0.2})_{2.4}Fe_{12}Co_2B$



CONCLUSIONS

The co-doped Ce,Co $Nd_2Fe_{14}B$ Permanent Magnets are:

1. Competitive with some Dy-doped sintered magnets, especially at T > 475 K (>200°C)
2. Larger $H_c(H_{c_i})$ and BH_{max} values using commercial grade rare earths, and lower purity ferrous boron
3. Will help reduce the strain on Dy markets
4. Will relieve the demand for Nd
5. Will help utilize some of the Ce surplus
6. Mixed valent Ce still has some amazing tricks up her sleeve!

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D. Brown

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C. Zhou

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F.E. Pinkerton

REFERENCE: "Dy-free, Reduced Nd, High Performance $Nd_2Fe_{14}B$-based Permanent Magnets," *Proceedings 23rd International Workshop on Rare Earth and Future Permanent Magnets and Their Applications (REPM 2014)*, G.C. Hadjipanayis, C.H. Chen, J.P. Liu, editors, pp. 403-406, Annapolis, Maryland, USA (August 17-21, 2014)

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