Critical Materials for Magnetism

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Dublin 2, Ireland

1. Materials used for applications of magnetism
    - *Permanent magnets*
    - *Soft magnets*
    - *Magnetic recording*

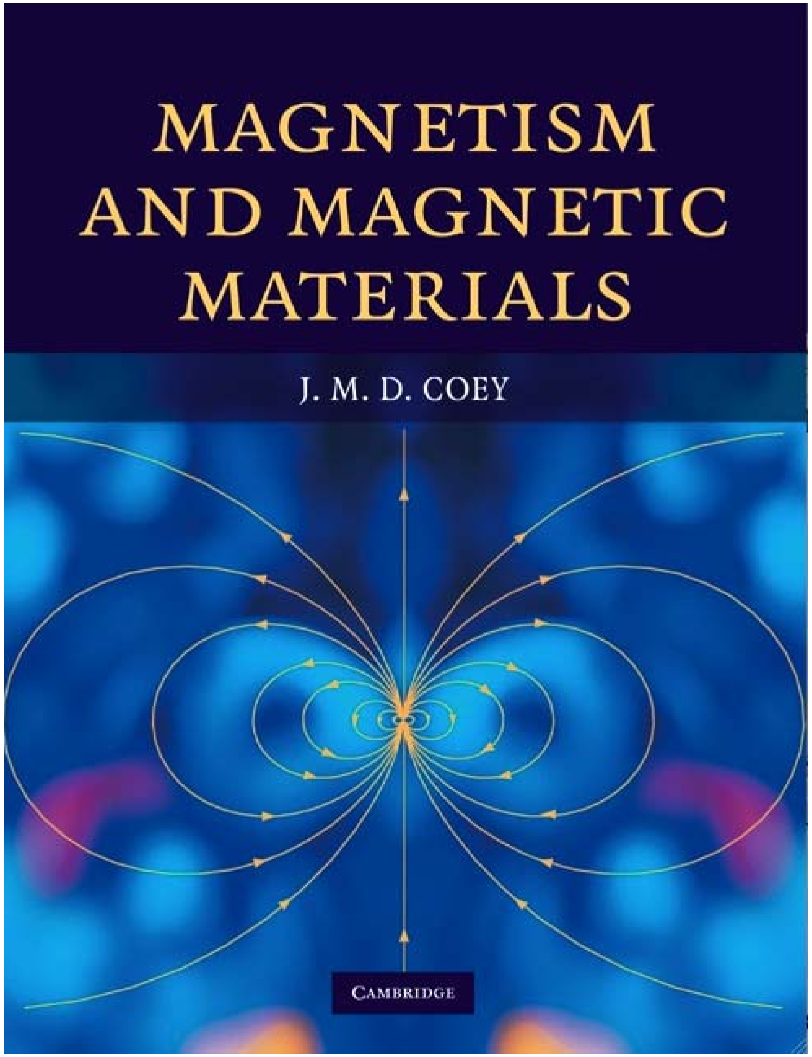
2. Permanent magnets — filling the gap

3. Perpendicular magnetic media and memory

science foundation ireland

www.tcd.ie/Physics/Magnetism

Tokyo, 21xi 2011



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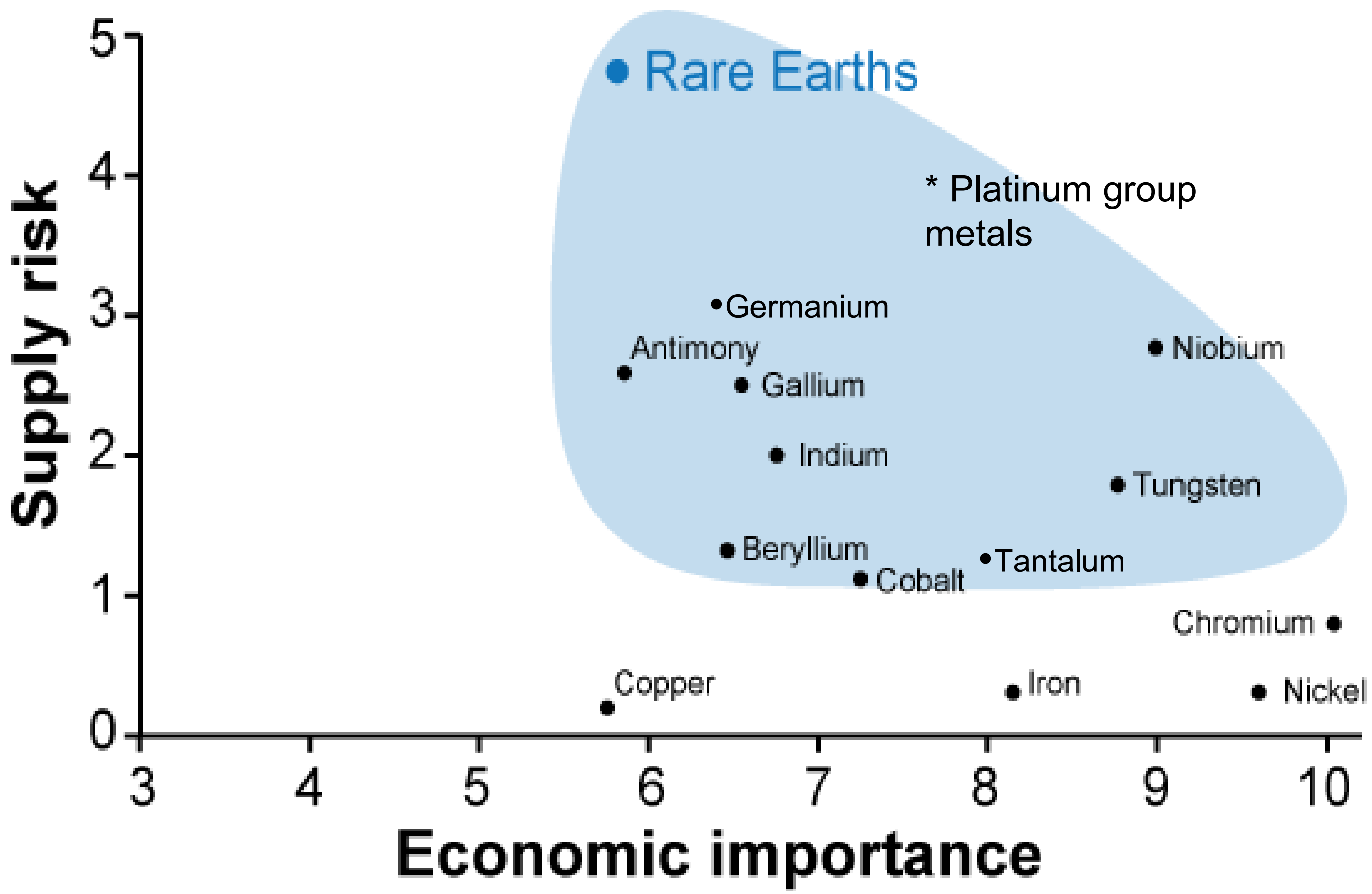
Critical raw materials – EU report



1. Materials used for applications of magnetism

Magnetic Periodic Table

Key (66 Dy): Atomic Number → 66; Atomic symbol → Dy; Atomic weight → 162.5; Typical ionic change → $3 + 4f^9$; Antiferromagnetic T_N(K) → 179; Ferromagnetic T_C(K) → 85

1 H 1.00																	2 He 4.00
3 **Li** 6.94 $1 + 2s^0$	4 Be 9.01 $2 + 2s^0$											5 **B** 10.81	6 C 12.01	7 **N** 14.01	8 **O** 16.00 35	9 **F** 19.00	10 Ne 20.18
11 **Na** 22.99 $1 + 3s^0$	12 Mg 24.21 $2 + 3s^0$											13 **Al** 26.98 $3 + 2p^6$	14 Si 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 Ar 39.95
19 **K** 38.21 $1 + 4s^0$	20 Ca 40.08 $2 + 4s^0$	21 **Sc** 44.96 $3 + 3d^0$	22 **Ti** 47.88 $4 + 3d^0$	23 **V** 50.94 $3 + 3d^2$	24 **Cr** 52.00 $3 + 3d^3$ 312	25 **Mn** 55.85 $2 + 3d^5$ 96	26 **Fe** 55.85 $3 + 3d^5$ 1043	27 **Co** 58.93 $2 + 3d^7$ 1390	28 **Ni** 58.69 $2 + 3d^8$ 629	29 **Cu** 63.55 $2 + 3d^9$	30 Zn 65.39 $2 + 3d^{10}$	31 **Ga** 69.72 $3 + 3d^{10}$	32 Ge 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 Kr 83.80
37 **Rb** 85.47 $1 + 5s^0$	38 Sr 87.62 $2 + 5s^0$	39 **Y** 88.91 $2 + 4d^0$	40 **Zr** 91.22 $4 + 4d^0$	41 **Nb** 92.91 $5 + 4d^0$	42 **Mo** 95.94 $5 + 4d^1$	43 **Tc** 97.9	44 **Ru** 101.1 $3 + 4d^5$	45 **Rh** 102.4 $3 + 4d^6$	46 Pd 106.4 $2 + 4d^8$	47 **Ag** 107.9 $1 + 4d^{10}$	48 Cd 112.4 $2 + 4d^{10}$	49 **In** 114.8 $3 + 4d^{10}$	50 Sn 118.7 $4 + 4d^{10}$	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 Xe 83.80
55 **Cs** 13.29 $1 + 6s^0$	56 Ba 137.3 $2 + 6s^0$	57 **La** 138.9 $3 + 4f^0$	72 **Hf** 178.5 $4 + 5d^0$	73 **Ta** 180.9 $5 + 5d^0$	74 W 183.8 $6 + 5d^0$	75 **Re** 186.2 $4 + 5d^3$	76 **Os** 190.2 $3 + 5d^5$	77 **Ir** 192.2 $4 + 5d^5$	78 **Pt** 195.1 $2 + 5d^8$	79 **Au** 197.0 $1 + 5d^{10}$	80 Hg 200.6 $2 + 5d^{10}$	81 **Tl** 204.4 $3 + 5d^{10}$	82 **Pb** 207.2 $4 + 5d^{10}$	83 **Bi** 209.0	84 **Po** 209	85 **At** 210	86 Rn 222
87 **Fr** 223	88 Ra 226.0 $2 + 7s^0$	89 **Ac** 227.0 $3 + 5f^0$															
			58 **Ce** 140.1 $4 + 4f^0$ 13	59 **Pr** 140.9 $3 + 4f^2$	60 **Nd** 144.2 $3 + 4f^3$ 19	61 **Pm** 145	62 Sm 150.4 $3 + 4f^5$ 105	63 **Eu** 152.0 $2 + 4f^7$ 90	64 **Gd** 157.3 $3 + 4f^7$ 292	65 **Tb** 158.9 $3 + 4f^8$ 229 221	66 **Dy** 162.5 $3 + 4f^9$ 179 85	67 **Ho** 164.9 $3 + 4f^{10}$ 132 20	68 **Er** 167.3 $3 + 4f^{11}$ 85 20	69 **Tm** 168.9 $3 + 4f^{12}$ 56	70 Yb 173.0 $3 + 4f^{13}$	71 **Lu** 175.0 $3 + 4f^{14}$	
			90 **Th** 232.0 $4 + 5f^0$	91 **Pa** 231.0 $5 + 5f^0$	92 **U** 238.0 $4 + 5f^2$	93 **Np** 238.0 $5 + 5f^2$	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 Bk 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 260	

Nonmetal
Metal
Radioactive

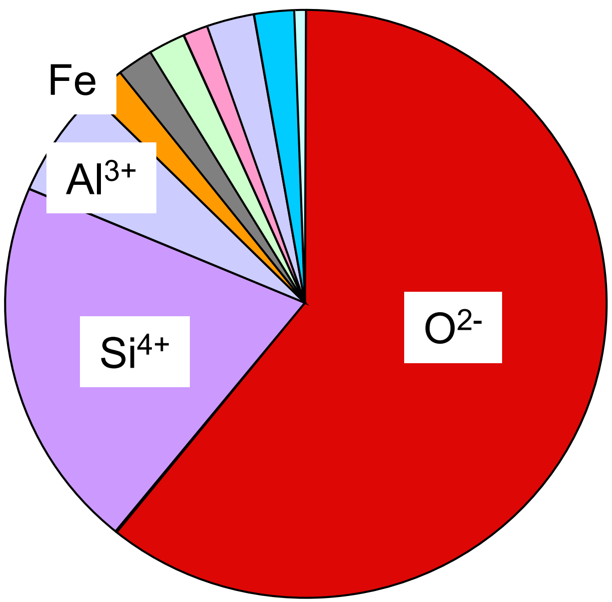
Diamagnet
Paramagnet
BOLD Magnetic atom

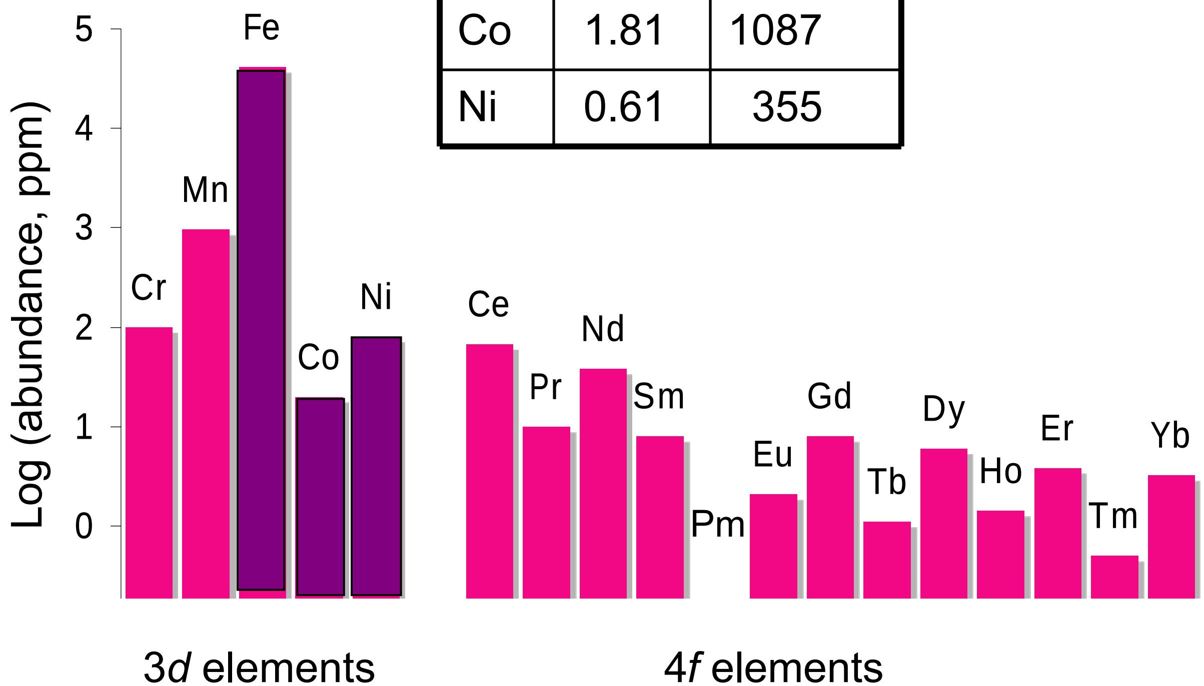
Ferromagnet T_C > 290K
Antiferromagnet with T_N > 290K
Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

Tokyo, 21xi 2011

Crustal abundances of magnetic elements

	J_s (T)	T_C(°C)
Fe	2.15	771
Co	1.81	1087
Ni	0.61	355



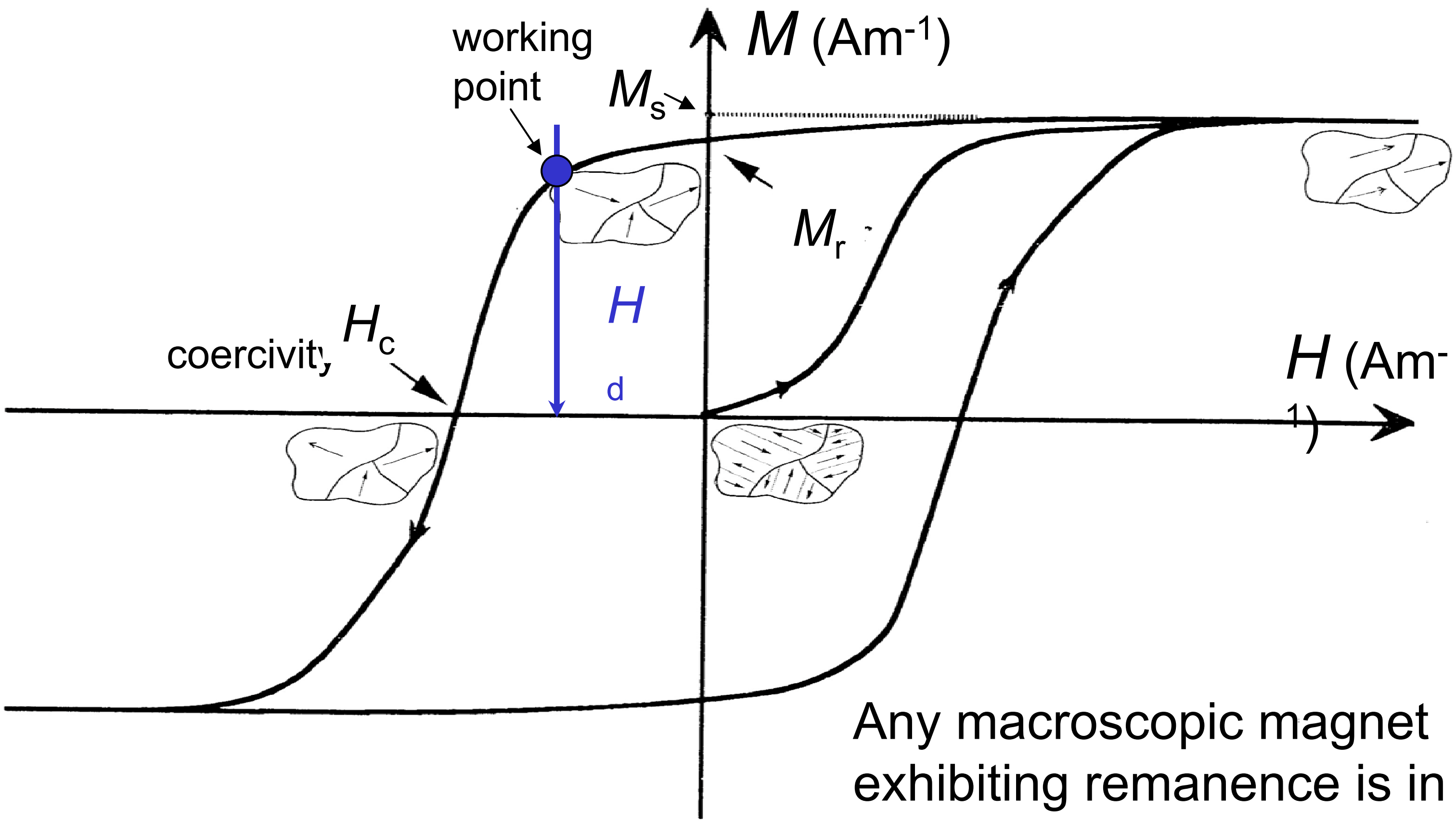


Crustal abundances (top 9)

All magnetic elements (log scale}

Iron is 40 x as abundant as all the other magnetic elements taken together.

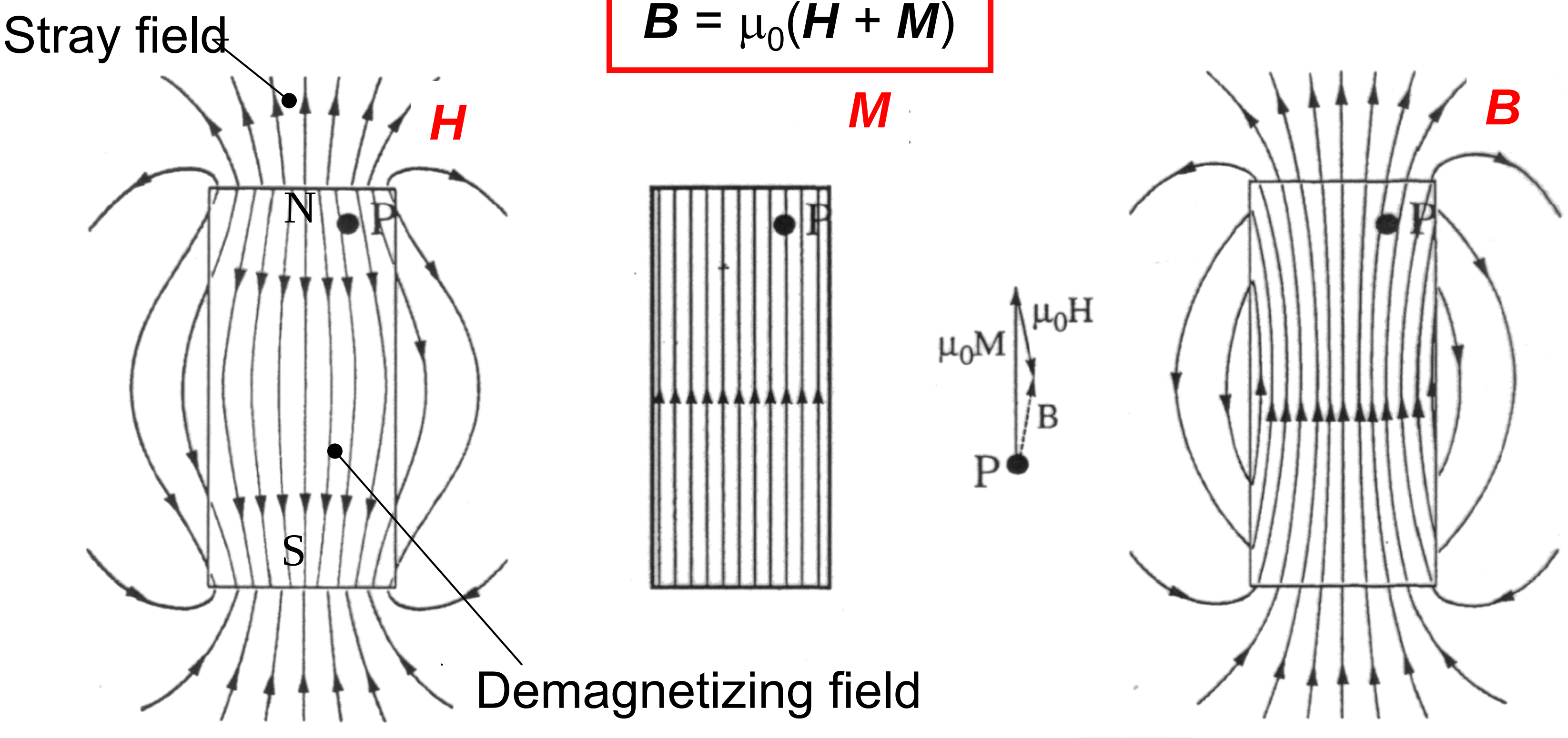
Hysteresis



Any macroscopic magnet exhibiting remanence is in a *thermodynamically-metastable* state.

The demagnetizing field

$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M})$$

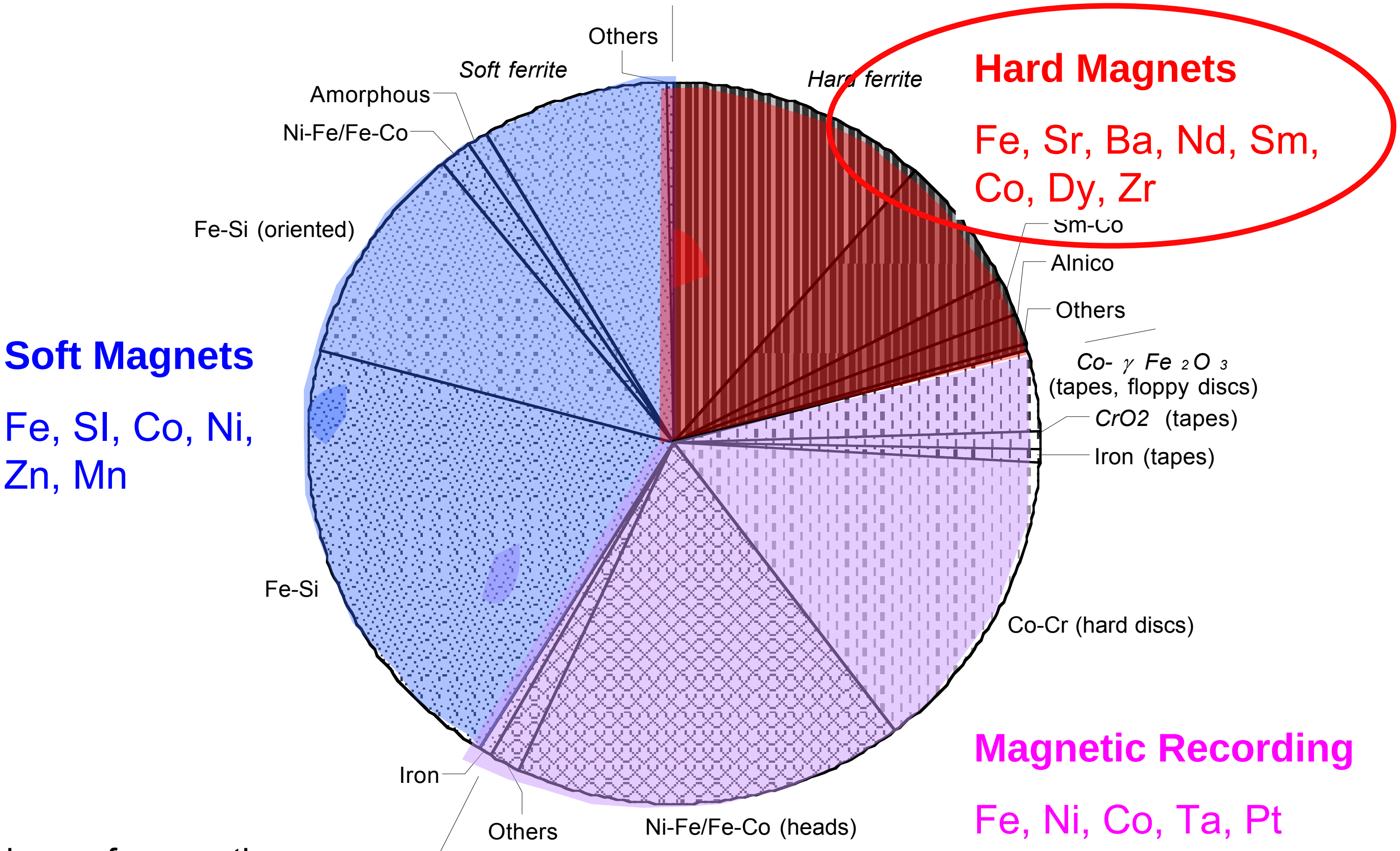


$$\boldsymbol{H}_d \approx -\mathcal{N}\boldsymbol{M}$$

demagnetizing factor $0 \leq \mathcal{N} \leq 1$

$$\nabla \boldsymbol{B} = 0$$

Magnetic materials for applications

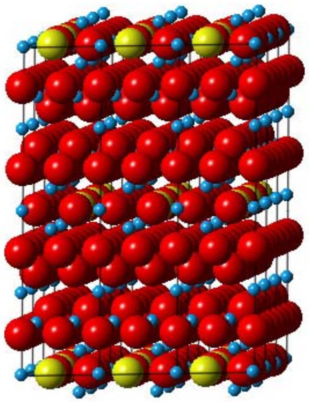


Breakdown of magnetic materials in 2000 - 30 B$

Summary of magnetic properties of useful materials

	T_c (°C)	M_s (MAm^{-1})	K (kJm^{-3})	λ (10^{-6})
$SmCo_5$	847	0.86	17200	-
$Nd_2Fe_{14}B$	315	1.28	4900	-
CoPt	567	0.81	4800	-
FePt	477	1.14	1800	-
$SrFe_{12}O_{19}$	467	0.38	330	-
$Fe_{94}Si_6$	770	1.68	48	-7
$Co_{35}Fe_{65}$	940	1.95	20	-60
$Ni_{80}Fe_{20}$	570	0.83	-1	2
$(MnZn)Fe_2O_4$	300	0.50	-3	-5
$(NiZn)Fe_2O_4$	590	0.33	-7	-25
$Y_3Fe_5O_{12}$	287	0.14	-2	-1

The permanent magnet market (~$10B)



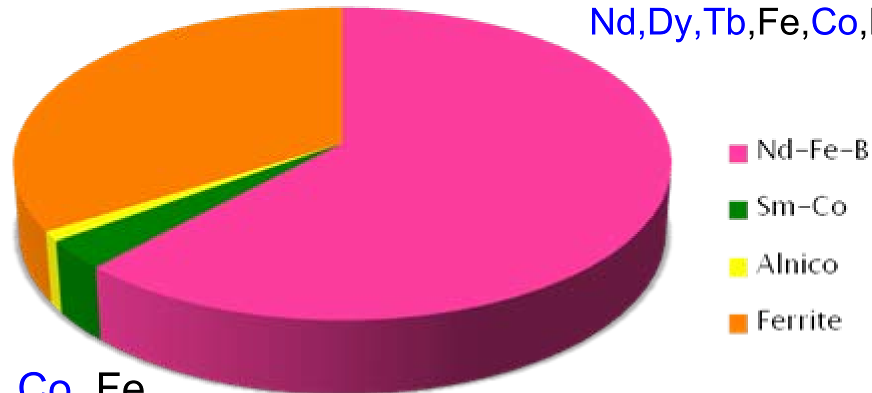
$SrFe_{12}O_{19}$

Sintered Ferrite

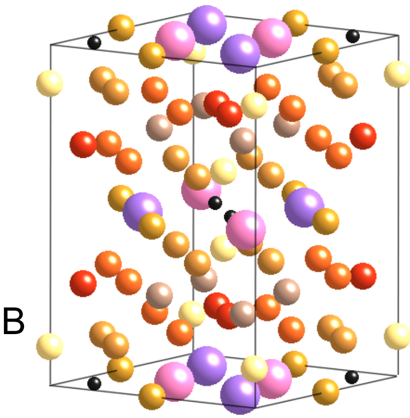
Bonded Ferrite

Alnico;
Fe,Co,Ni,Al

Sm-Co; Sm, Co, Fe, Zr,Cu

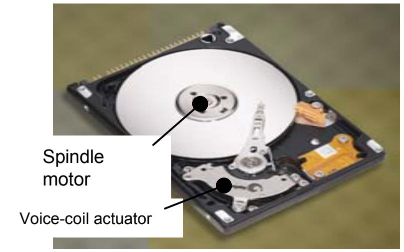


Sintered Nd-Fe-B
Nd,Dy,Tb,Fe,Co,B



$Nd_2Fe_{14}B$

Bonded Nd-Fe-B



Tonnage production:

Ferrite; 1,000,000 Nd-Fe-B; 80,000

The Limits

Curie temperature T_C. Should be > 550 K for RT applications

Magnetization M_s. Should be as large as possible. Many applications depend on M_s^2

Energy product $|BH|_{max}$ Should be as large as possible for a permanent magnet $|BH|_{max} < \frac{1}{4}\mu_0 M_s^2$

Coercivity H_c . Should be 0 for soft magnets, > $\frac{1}{2}M_s$ for hard magnets.

Cost. As low as possible

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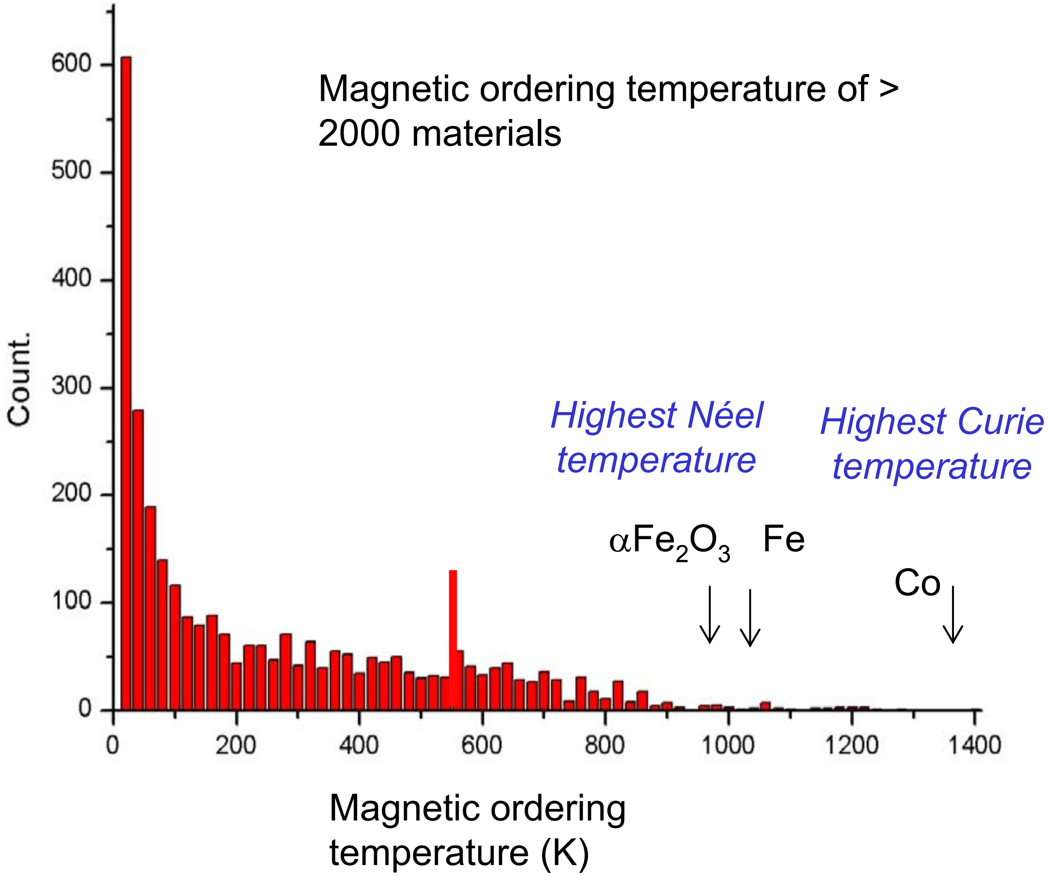

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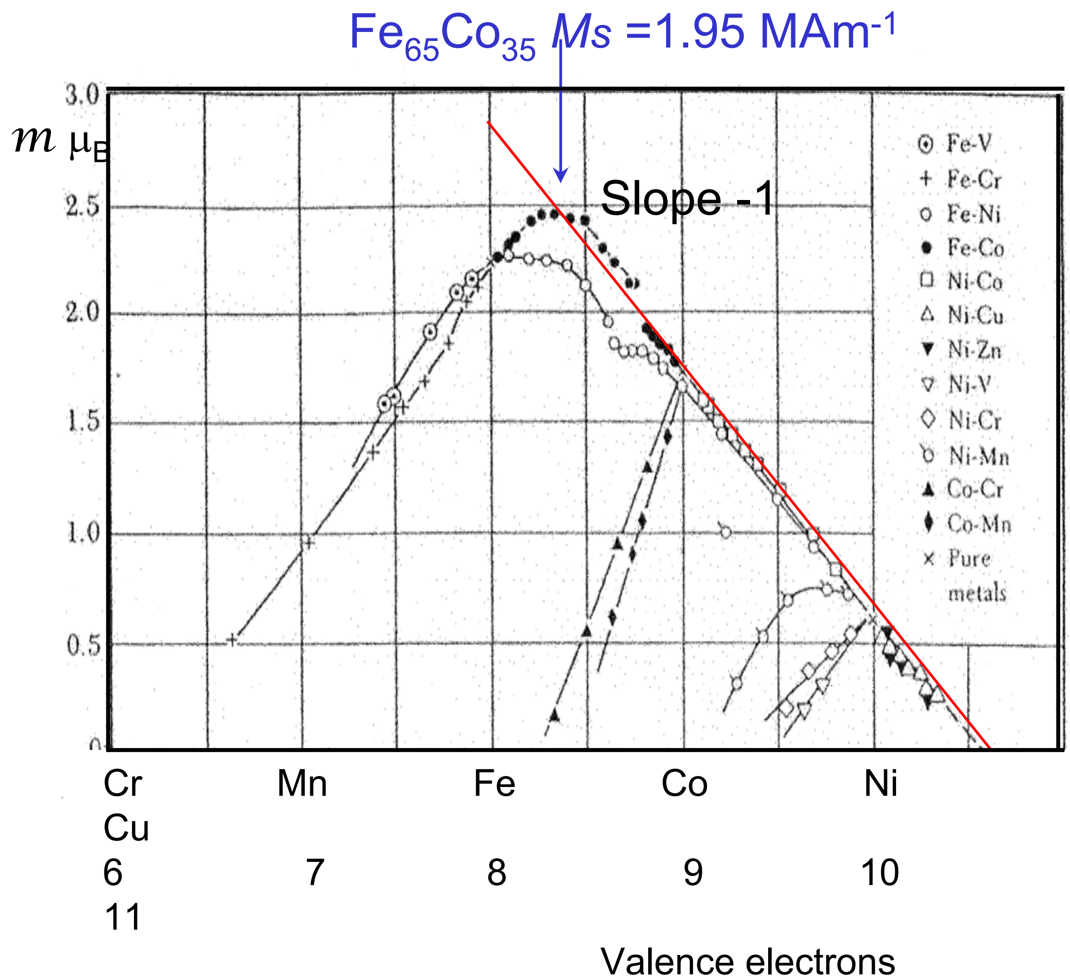
Slater-Pauling Curve



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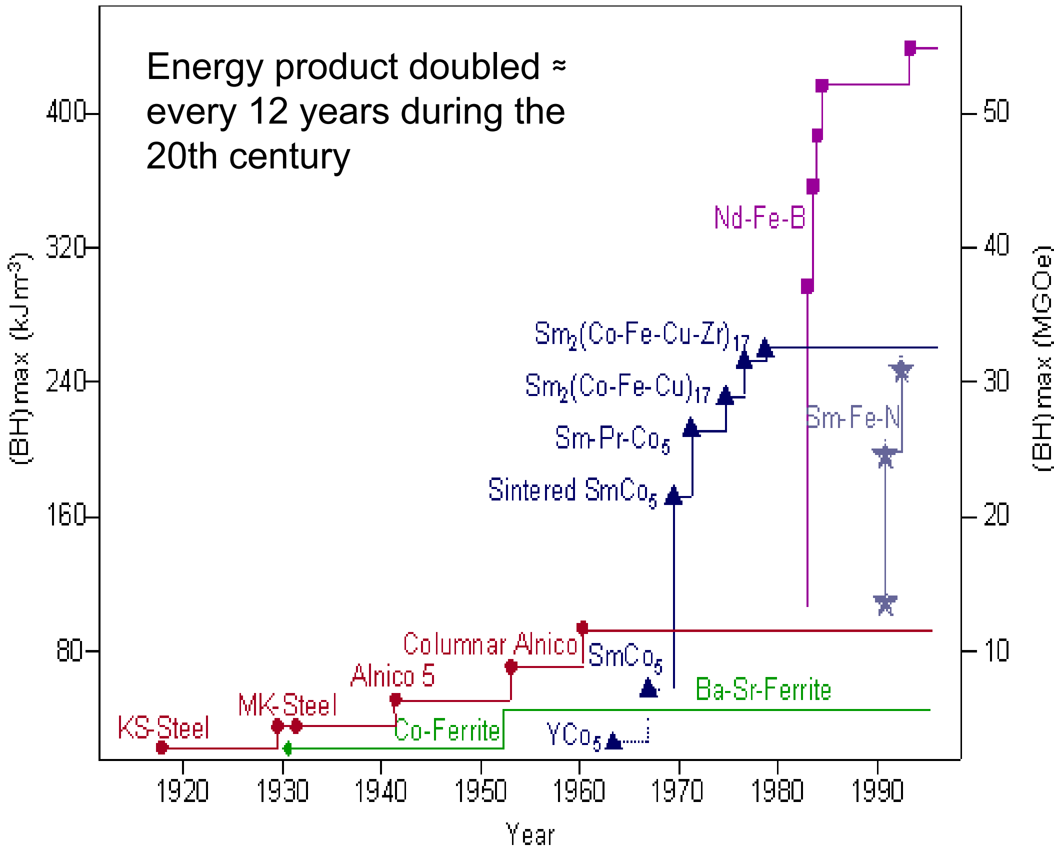

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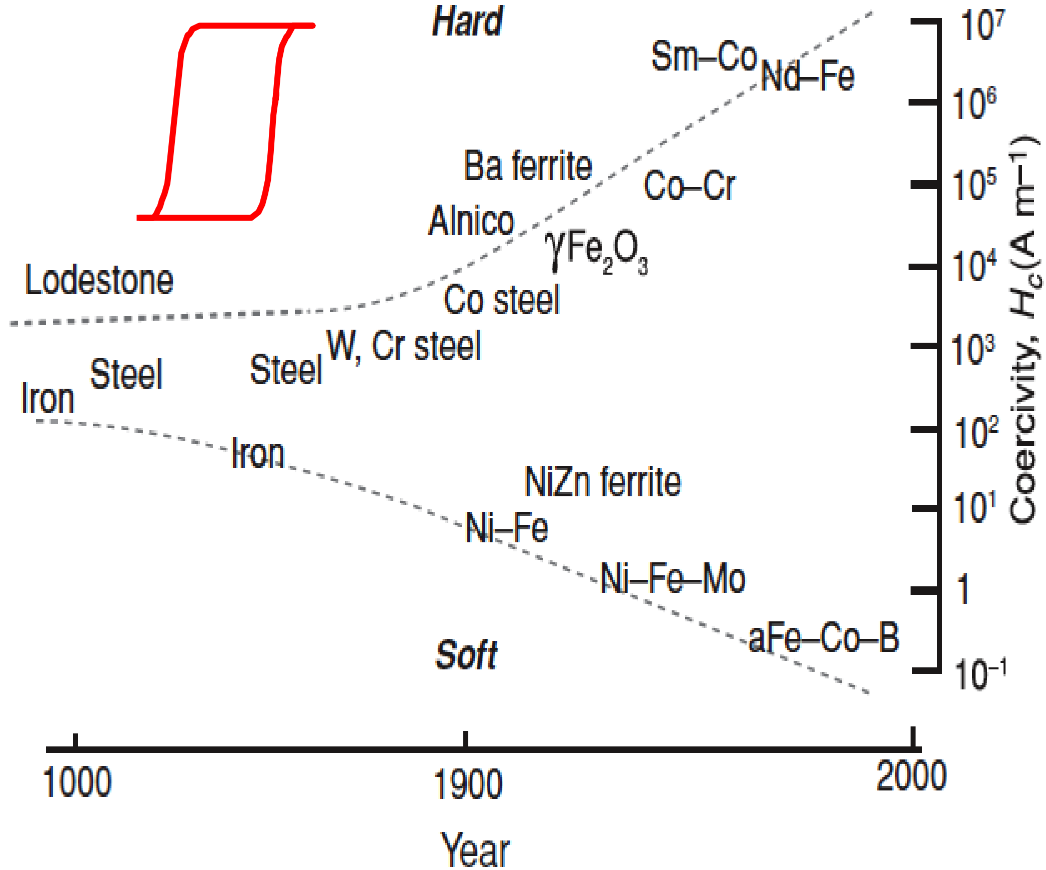
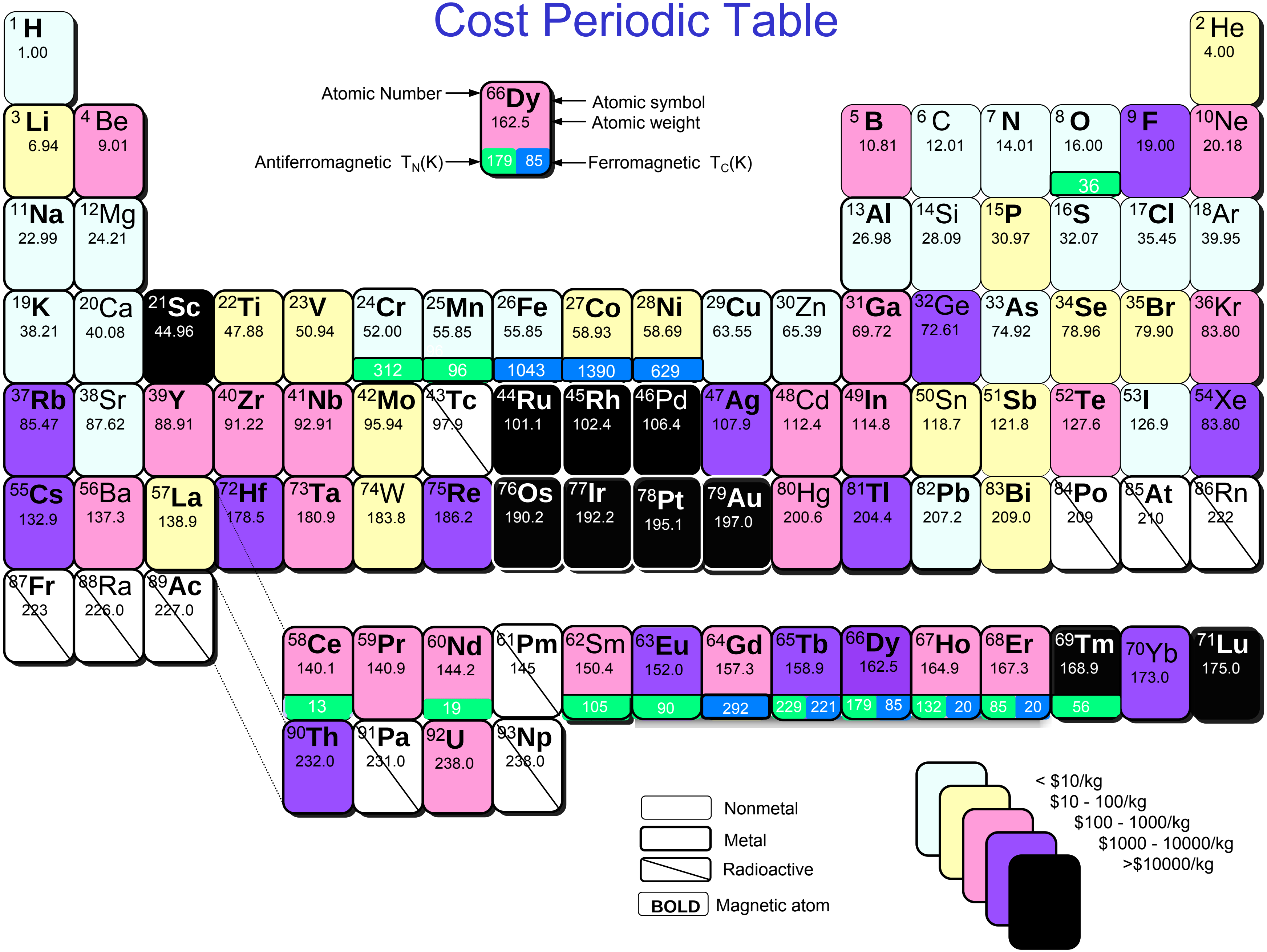


The main achievement of technical magnetism in the 20th century was *mastery of coercivity*

1900: $10^3 < H_c < 10^5$ A m^{-1}

2000: $1 < H_c < 2\ 10^7$ A m^{-1}

Cost Periodic Table



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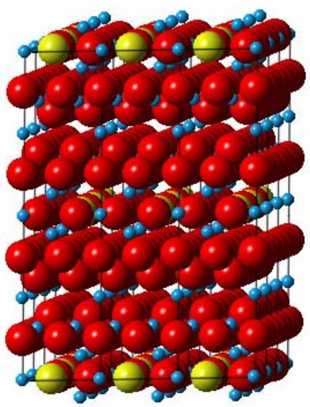
2. Permanent Magnets – Filling the Gap

The permanent magnet market (~$10B)



$SrFe_{12}O_{19}$

M_s = 0.38 MA m^{-1}

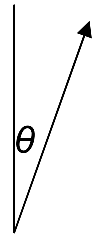
K = 330 kJ m^{-3}

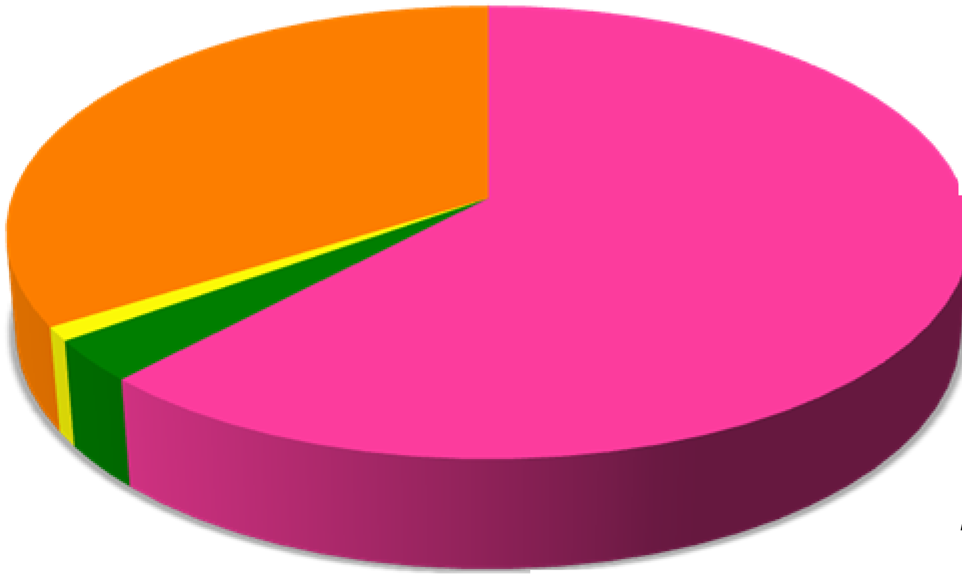
T_C = 740 K

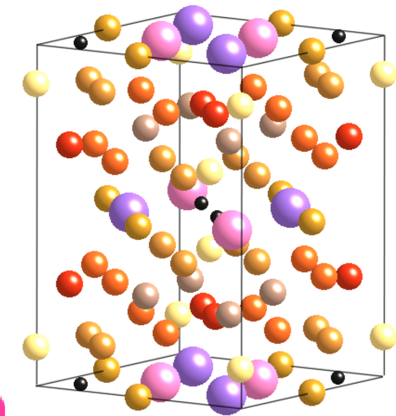
$|BH|_{max}$< 35 MJm^{-3}

Cost ~ 5$ kg^{-1}

$K = \sin^2\theta$







$Nd_2Fe_{14}B$

M_s = 1.28 MA m^{-1}

K = 4.9 kJ m^{-3}

T_C = 588 K

$|BH|_{max}$< 400 MJm^{-3}

Challenges

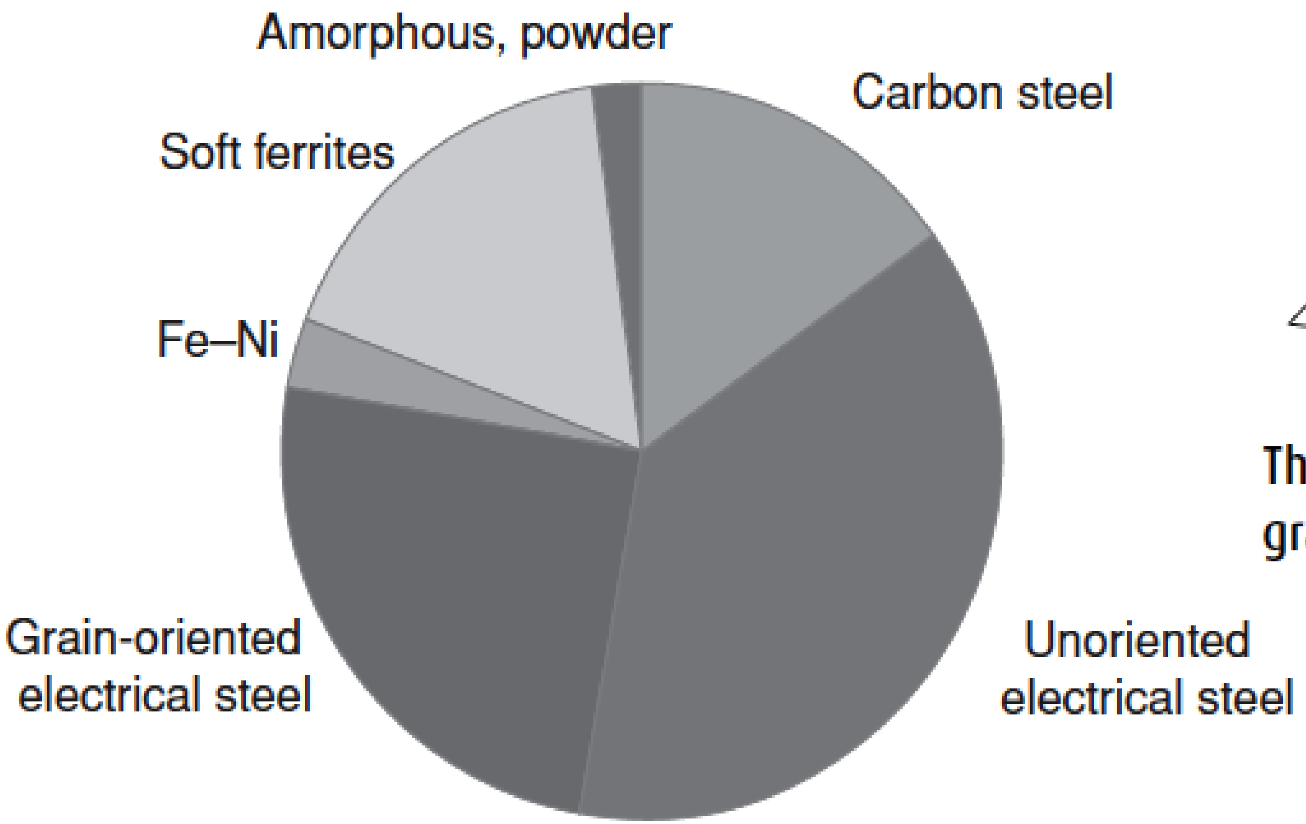
The 2 MA m^{-1} material. Find a usable soft material with $M > 2$ MAm^{-1}

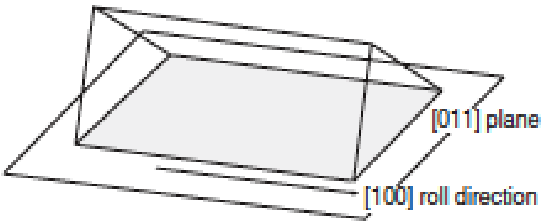
The megajoule magnet. Double $|BH|_{MAX}$ again to 1000 kJ m^{-3}.

The rare-earth free/reduced replacement of Nd-Fe-B. Should be as large as possible. Many applications depend on M_s^2

The gap magnet. Find a new material intermediate between ferrite and RE magnets.

Soft magnets $\approx$ 10 B\$ a^{-1}





The Goss texture of grain-oriented Si-Fe.

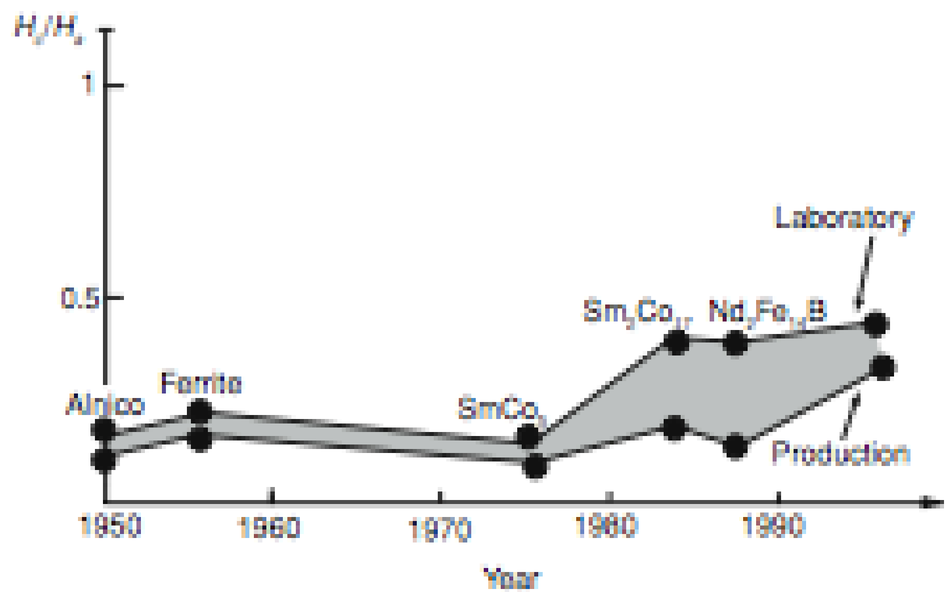
Targets in the gap

$\|BH\|_{MAX}$	T_C	M_s	K	Raw materials cost
kJm^{-3}	K	MAm^{-1}	kJm^{-3}	\$/kg
A 100	> 550	570	400	10
B 150	> 550	690	600	20
C 200	> 550	800	800	30

$$H_c < H_a = 2K_1/M_s$$

$$\kappa = (K/\mu_0 M_s^2)^{1/2} > 1;$$

$$K > \mu_0 M_s^2$$



Tok

Properties of some uniaxial ferromagnets

	MnAl	MnBi	Mn_2Ga	$Y_2Fe_{14}B$	$Fe_{16}N_2$	Fe_3C	YCo_5
M_s ($MA\ m^{-1}$)	0.60	0.58	0.47	1.10	1.92	1.09	0.85
K_1 ($MJ\ m^{-3}$)	1.7	0.90	2.35	1.1	1.0	0.45	6.5
T_C (K)	650	628	>770	590	810	560	987
κ	1.95	1.46	2.35	0.85	0.43	0.55	2.7
Materials cost ($ kg^{-1})	<10	< 20	> 100	< 30	< 10	< 10	<50

$|BH|_{max}$ 50 kJ m^{-3}
Yamaguchi et al
(89)

How do we find a suitable new material ?

Combinatorial Materials Science

Magnetocrystalline anisotropy

Shape anisotropy is limited to $K_{sh} = \frac{1}{4}\mu_0 M_s^2(1-3\mathcal{N})$; it implies $\kappa < \frac{1}{2}$. A better source is magnetocrystalline anisotropy, mainly due to spin-orbit coupling and the crystal-field interaction.

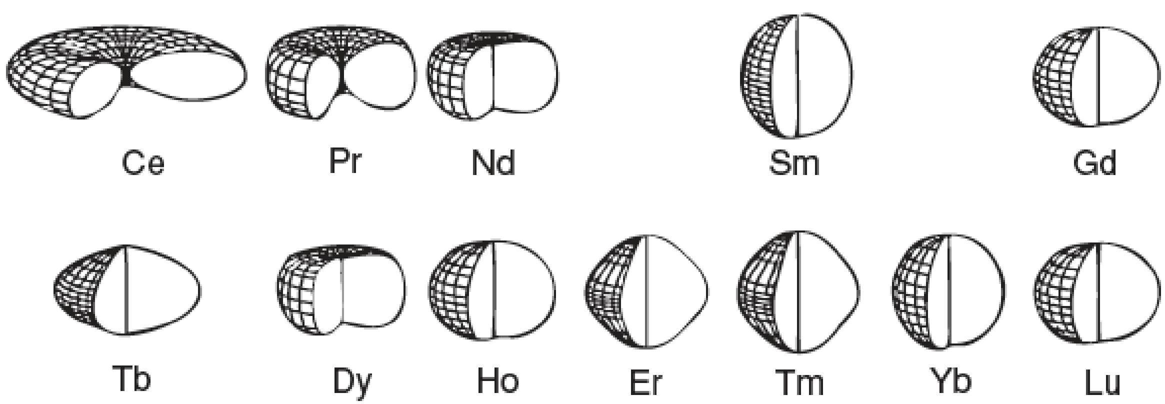
$$E_a = K_1 \sin^2\theta + \ldots\ldots$$

The leading term in the crystal-field interaction is

$$H_{cf} = B_2^0\{3J_z^2 - J(J+1)\}$$

$$B_2^0 = A_2^0\,\theta_2$$

$K_1^{cf} \sim B_2^0 J^2$. It varies as the electric field gradient x atomic quadrupole moment



Spin-orbit coupling is stronger for 4*f* than 3*d* atoms.
Hence the use of rare-earth intermaetallics as permanent magnets.

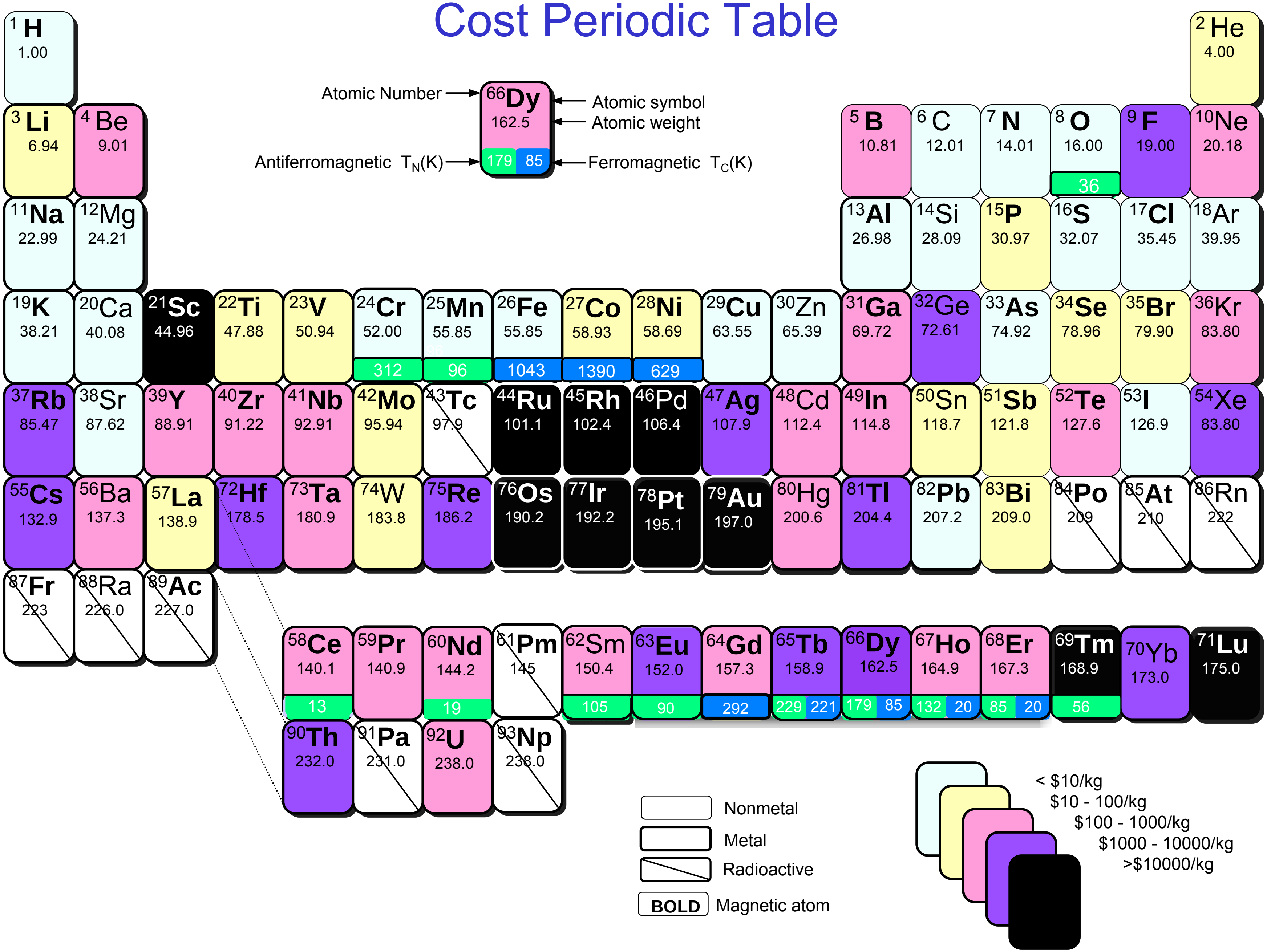
3. Perpendicular magnetic media and memory.

Cost – the constraint

- For bulk permanent magnets, we must choose elements which are easily available and cheap. 10 g for everyone on earth requires a million moles of magnet.

- This constraint does not apply for thin film devices. One mole is enough to provide everyone with a microchip containing a magnetic film a few nanometers thick.

Cost Periodic Table



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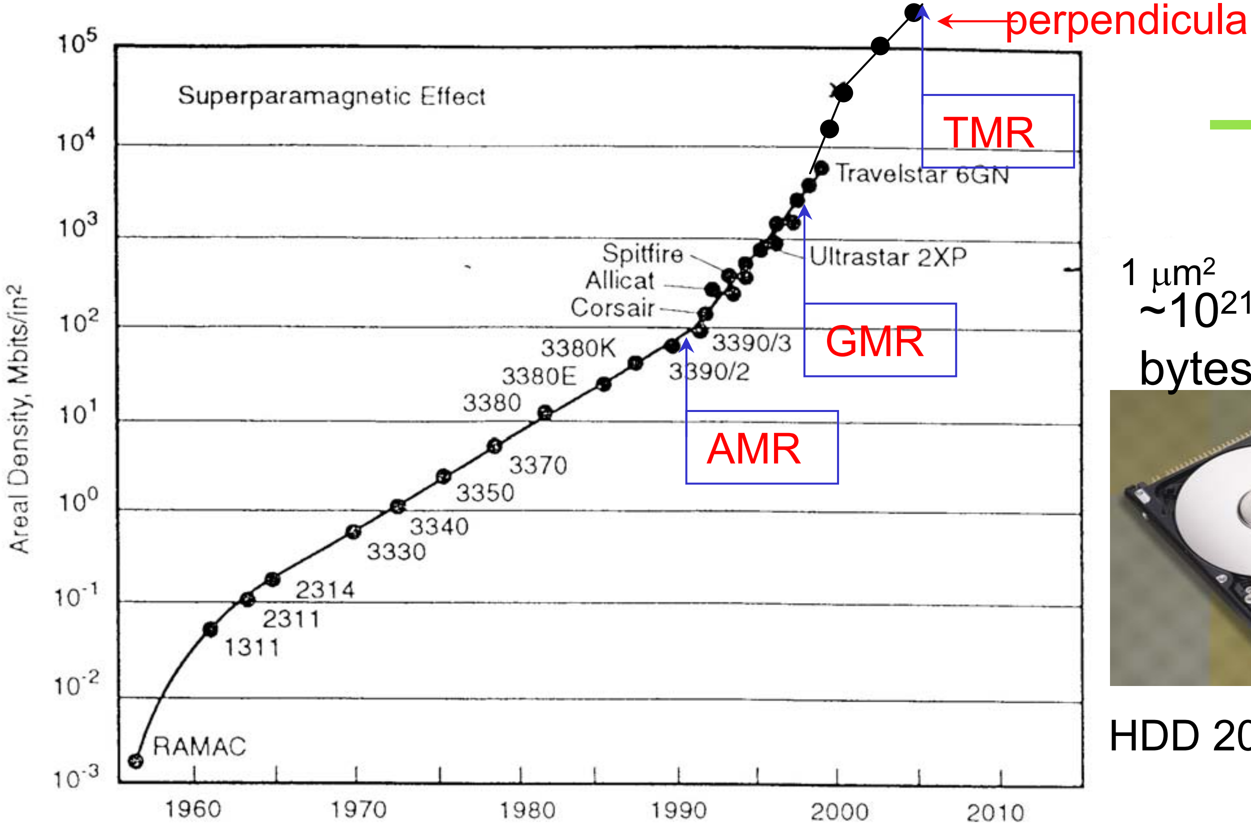
$\sim 10^{10}$ bytes/year

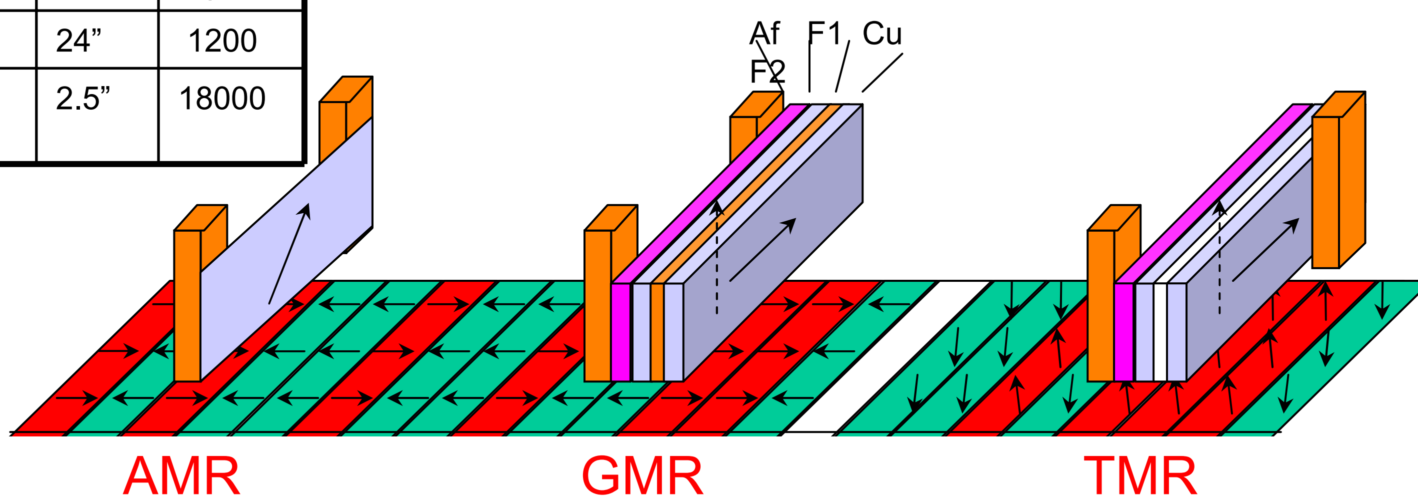
RAMAC 1955 40 Mb



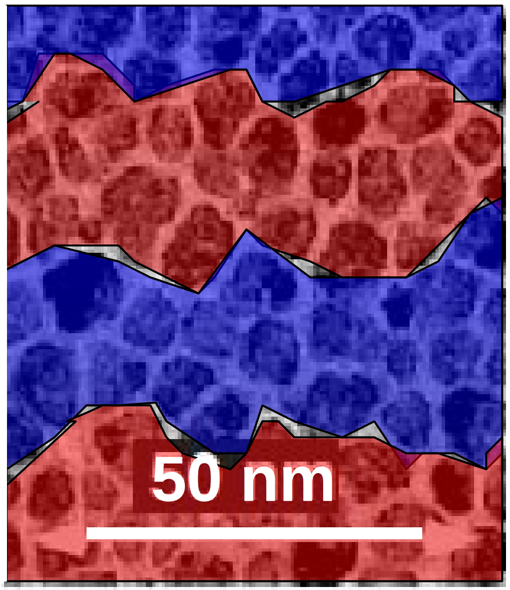
1 μm²
$\sim 10^{21}$ bytes/year

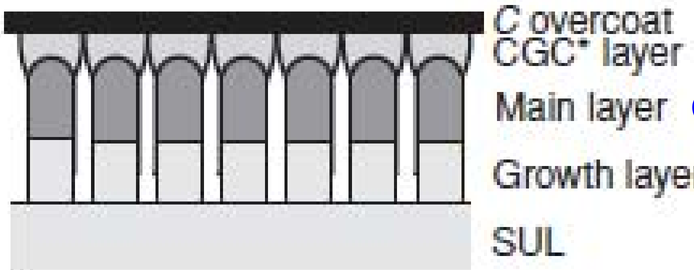
HDD 2005 160 Gb

year	caapcity	platters	size	rpm
1955	40 Mb	50x2	24”	1200
2005	160 Gb	1	2.5”	18000

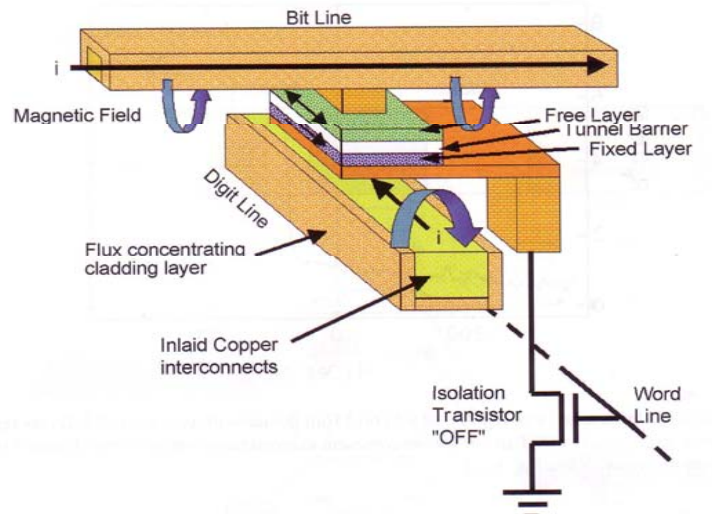


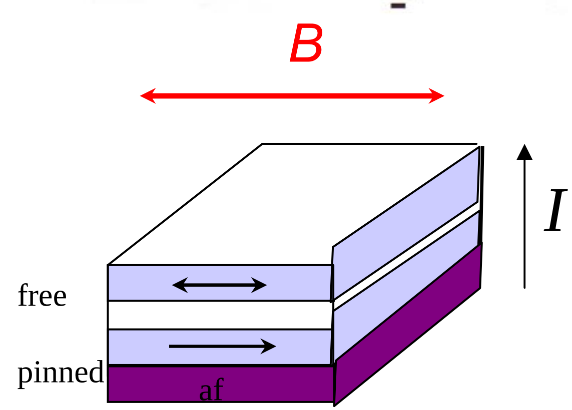
Perpendicular thin film media and memory





Next step – bit patterned media





planar magnetic tunnel junction (MTJ)

Thin film media and memory

Tetragonal $L1_0$ structure

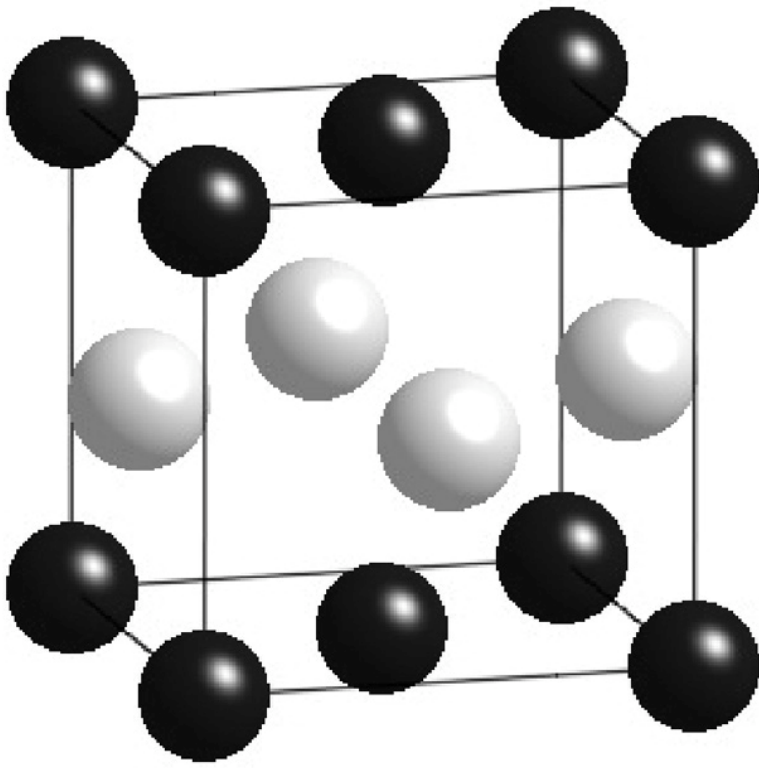
FePt

FePd

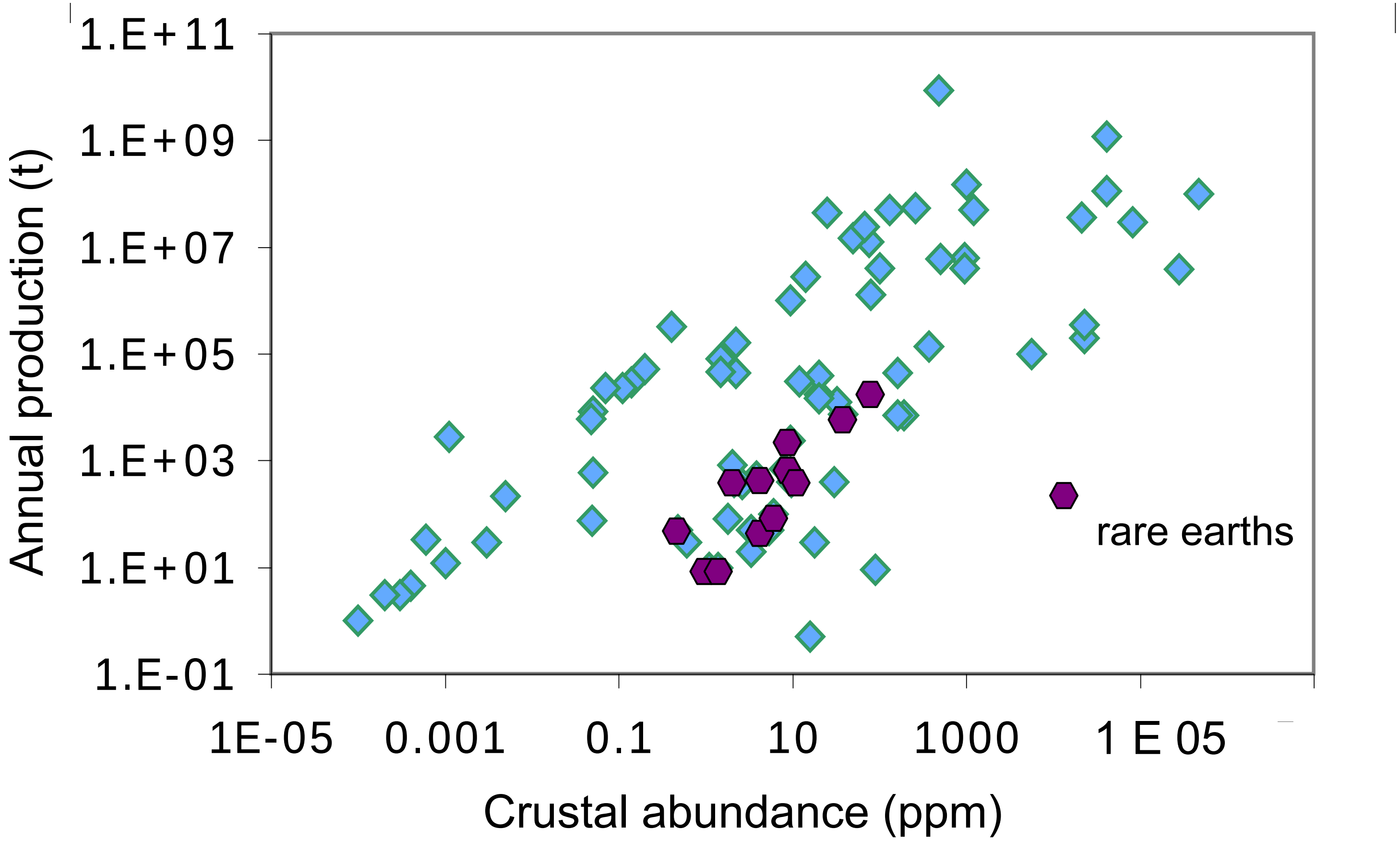
CoPt

NiFe ?

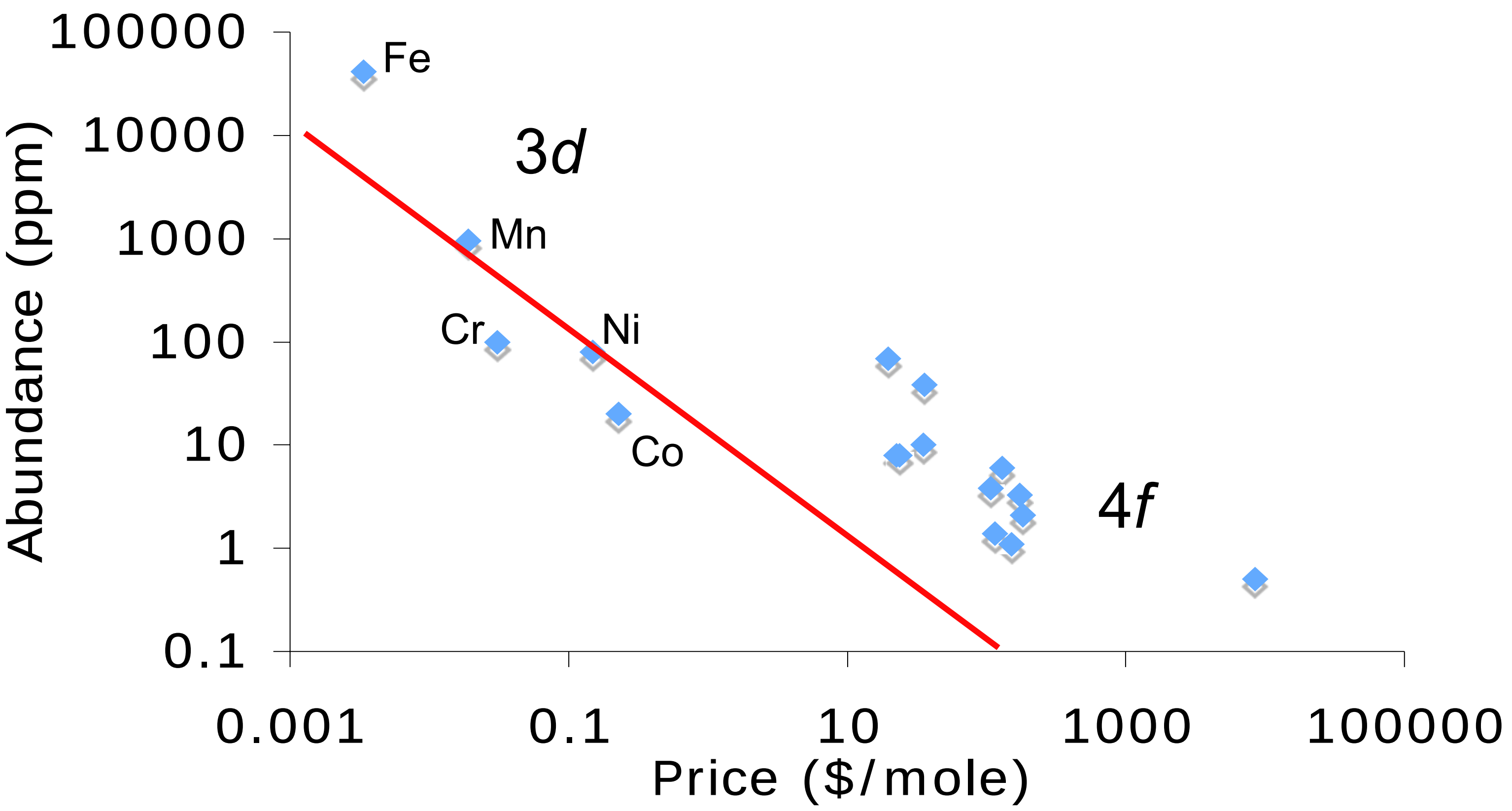
CoFe ?



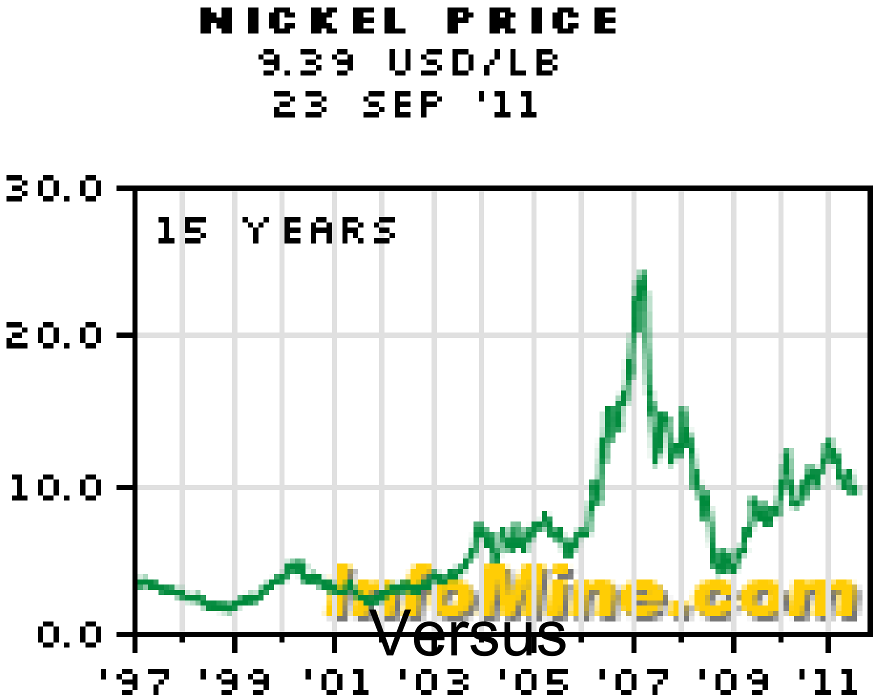
Production/abundance



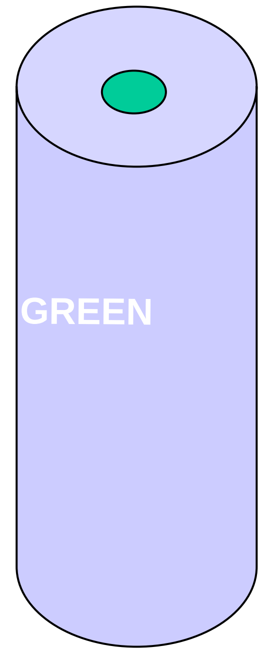
Abundance/cost



Gambling



Versus



Science is sane.
Physicists have saved space,time,energy
Can they save the world ?

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4. Summary and conclusions

Summary – Where are the limits?

- Polarization $\mu_0 M_s$ 2.45 T improvement unlikely (bulk)
- Curie Temperature 1380 K improvement unlikely
- Anisotropy Field 40 T improvement pointless
- Energy product $(BH)_{MAX}$ 512 kJ m^{-3} depends on M_{s},
- Energy product $(BH)_{max}$ 475 kJ m^{-3} depends on loop shape

Conclusions

- The era of exponential improvement of energy product is over.
- Emergence of a new permanent magnet material superior to $Nd_2Fe_{14}B$ is unlikely.
- Rare earths are overpriced; prices should fall as production increases, but Dy will remain problematic.
- Rare-earth free bulk magnets can be envisaged. Materials should be Fe or Mn based; >100 kJm^{-3} should be achievable, maybe 200 kJm^{-3}
- The challenge for two-phase hard/soft nanostructures is to align the hard nanoparticles. The megajoule magnet seems to out of reach
- Good prospects exist for new perpendicular thin films for magnetic recording or spin electronics.


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