



# The Search for Enhanced Magnetic Materials

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**TMS2013**  
142<sup>nd</sup> Annual Meeting & Exhibition  
*Linking Science and Technology for Global Solutions*

- Two factors have had a profound affect on the magnetic materials market.
- First, the market has been highly disrupted, especially with respect to rare earth magnets, the strongest commercially available permanent magnets and
- The realization that future demands for magnetic material products will increase dramatically corresponding with increased demand for electric power generation and use.
- This presentation forms the introduction to the series of talks to be heard over the next three days.

## Agenda

- Setting the stage
- The “Millennial Magnet Stakes”
  - Current R&D projects
- Elemental limitations
- Wrapping it up



- We'll start this presentation with a brief description of the market situation.

## Sources of Energy for Production of Electricity

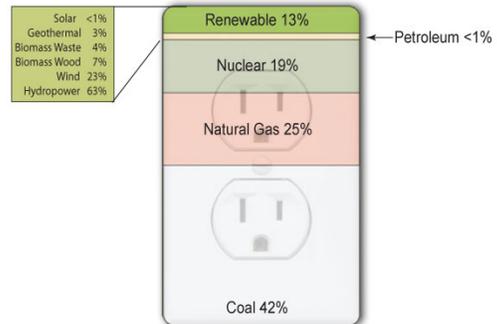
### Non-renewable

- Oil
- Gas
- Coal / Peat
- Nuclear

### Renewable

- Hydro
- Wind
- Bio Fuels and Waste
- Solar
- Geothermal
- Tidal / Wave

USA, Electric only  
Sources of Electricity Generation, 2011



Note: Includes utility-scale generation only. Excludes most customer-sited generation, for example, residential and commercial rooftop solar installations  
Source: U.S. Energy Information Administration, *Electric Power Monthly* (March 2012). Percentages based on Table 1.1, preliminary 2011 data.



- Our survival depends upon successfully thwarting entropy.
- Interestingly, we do that by using energy.
- Energy is, thus, hugely important to our quality of life.
- $\frac{3}{4}$  of the world's population is improving their standard of living and increasing their use of energy.
- We must work on developing renewable sources of energy while simultaneously reducing reliance on and increasing efficiency of generation and use of conventionally produced energy.

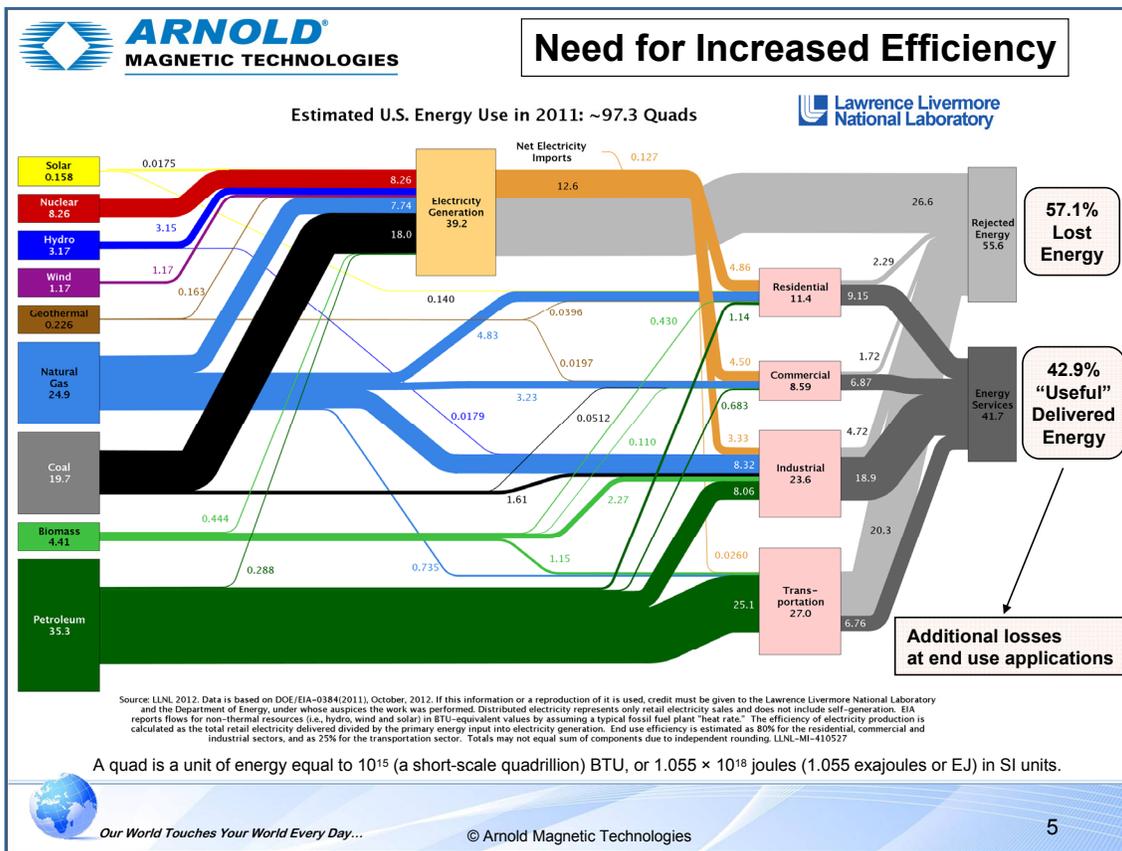
## Energy Sourcing Issues

- Efficiency of fuel extraction & production
  - Net energy balance
    - Example: Ethanol production
- Use of toxic or hazardous materials during exploration and production
  - Environmental impact
    - Example: use of toxic or carcinogenic ingredients in high volume hydro-fracking
- Disposal or storage of end-use by-products (waste)
  - Example: Storage of radioactive waste from nuclear plants
- “Side effects” (law of unintended consequences)
  - Affect on cost of other essential products
    - Example: use of corn for bio-fuel increases price of food and animal stocks dependent upon corn for feed
- Byproducts of use
  - Example: carbon dioxide and noxious gases and particulates

**“There are no simple choices  
- - only intelligent decisions.”**

Series of op-ed pieces by Caterpillar in National Geographic Magazine – 1970's.

- As we progress in the transition to renewable energy sources we need to consider the entire supply chain.
- Through knowledge we can make the best decision related to our technologies – balancing risk and benefit.



- Lawrence Livermore National Laboratories (LLNL) has produced Sankey diagrams for energy production, distribution and use for many countries.
- This is available in a downloadable document at:
  - <https://flowcharts.llnl.gov/content/international/2007EnergyInternational.pdf>
  - <https://flowcharts.llnl.gov/>
  - [https://flowcharts.llnl.gov/archive.html#international\\_archive](https://flowcharts.llnl.gov/archive.html#international_archive)
- Additional information is available from the US Energy Information Administration at:
  - [http://www.eia.gov/energyexplained/index.cfm?page=electricity\\_use](http://www.eia.gov/energyexplained/index.cfm?page=electricity_use)
- This chart shows dramatic low yield of energy in production and delivery to the user. From year-to-year the figures vary but show consistently below 50% arriving at the point of use.

## Role of Magnetic Materials

### Facilitate the...



#### **Efficient production of electrical energy**

Both soft and permanent magnetic materials



#### **Transmission of electrical energy**

Primarily soft magnetic materials



#### **Conversion of...**

Both soft and permanent magnetic materials

- Mechanical energy  Electrical energy



- Permanent and soft magnetic materials are useful in the production, distribution and use of energy, particularly electrical energy.
- In electric power generation and use, permanent magnet materials improve efficiency.
- Improvements in price/performance of permanent magnets (and soft magnetic materials) are increasingly important.

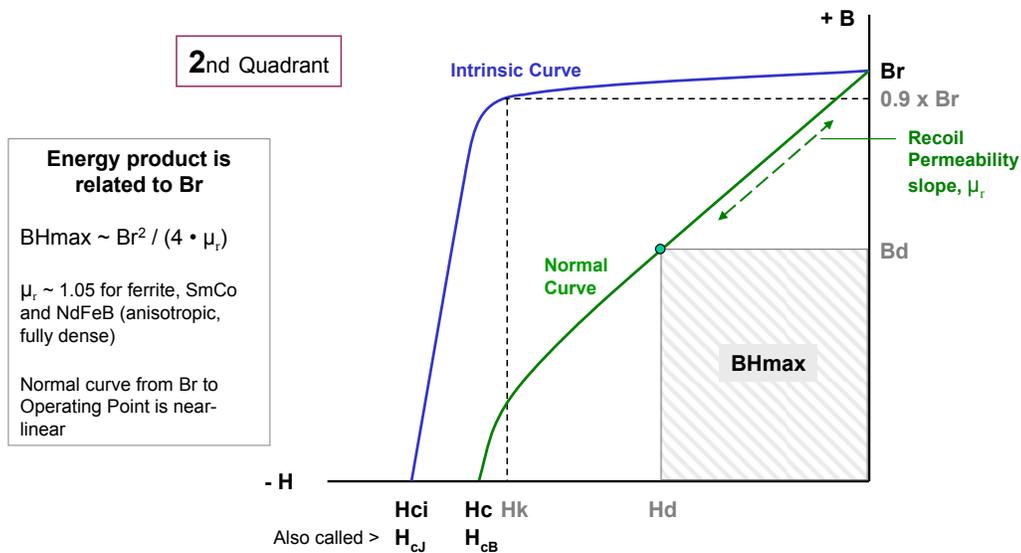
## Agenda

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- The “Millennial Magnet Stakes”
  - Current R&D projects
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- Wrapping it up



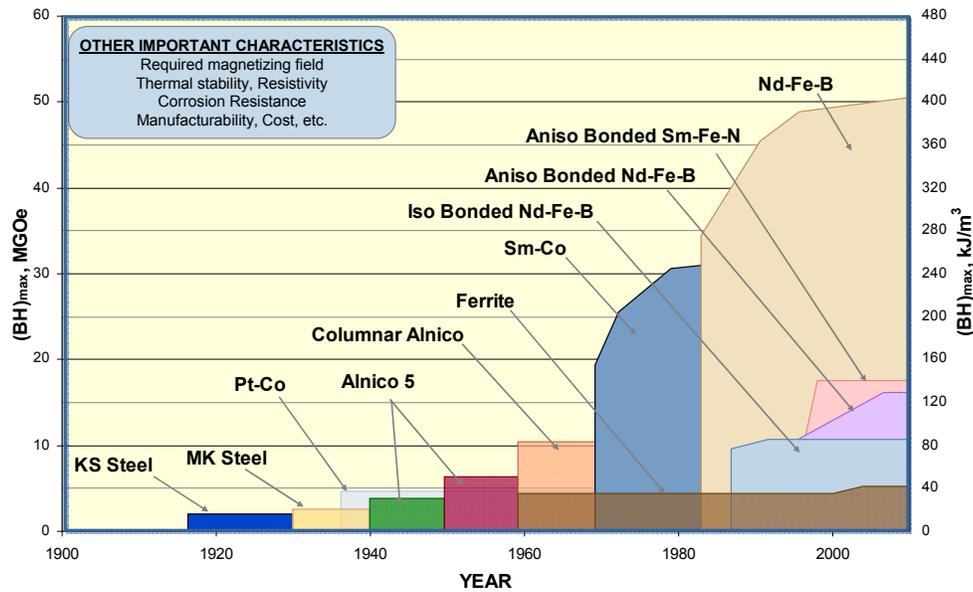
- The importance of the magnetic hysteresis loop dictates that we review the key figures of merit. Here we'll focus on permanent magnet materials.

## Permanent Magnet Key Characteristics



- For permanent magnets, we are primarily interested in the 2<sup>nd</sup> quadrant of the hysteresis loop.
- This illustration is typical of the “demag” curves presented in product literature for ferrite, SmCo and Neo magnets.
- The key figures of merit for permanent magnet materials are indicated on this chart.
- The maximum energy product can be estimated from just the Br as shown in the equation – assuming an appropriate value for recoil permeability.
- Conversely, the Br can be estimated when the maximum energy product is known.
- These calculations can only be made with a “straight line” material (such as ferrite, neo and SmCo magnets).
- As shown here, this material would be considered a straight line (Normal curve) or square loop (Intrinsic curve) material since the Normal curve is straight (at least to the maximum energy point).

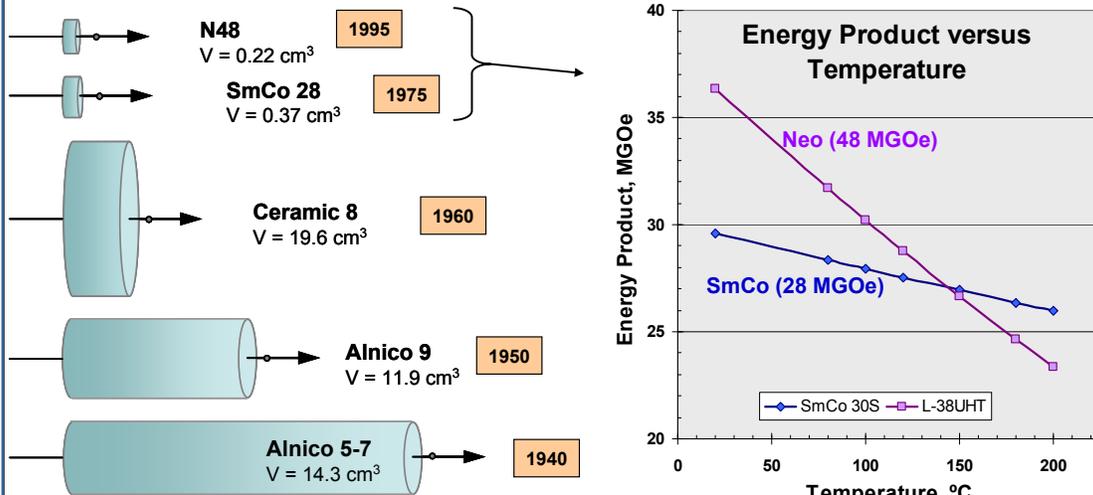
## Improvement in Magnet Strength



- We often present the improvement in energy product in charts such as this – it's visually eye-catching.
- Please note that all the products shown are still used to some extent.
- Each material has a unique combination of properties that makes it well-suited to certain applications.
- This is suggested by the note in the upper left of the chart indicating that many other characteristics must be considered.

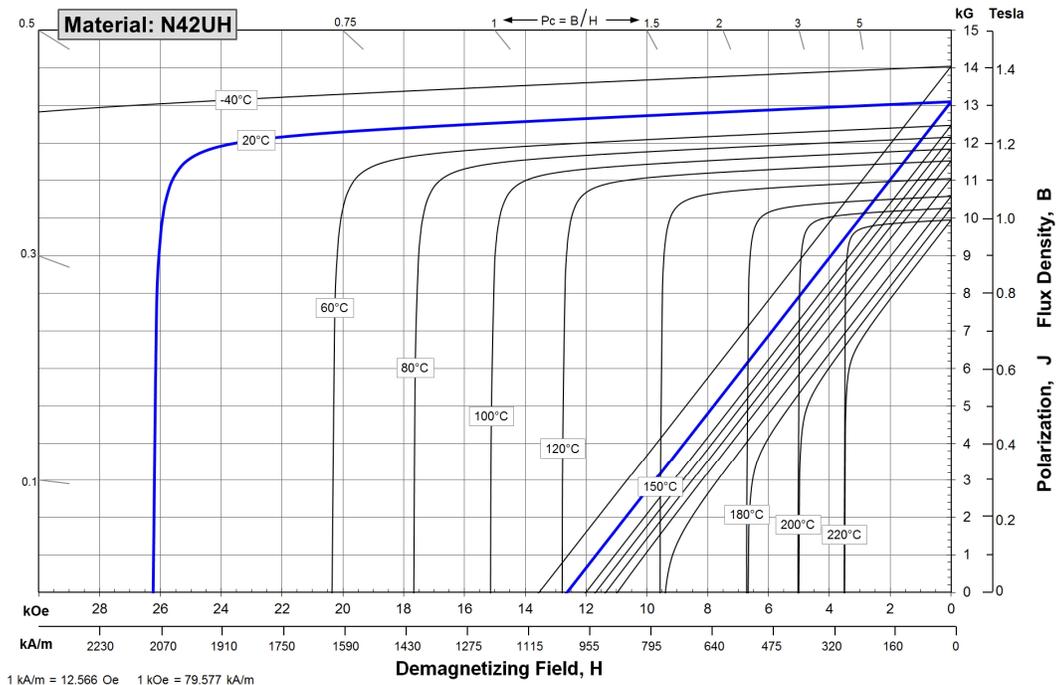
## Relative Magnet Sizes

Relative magnet size and shape to generate 1000 gauss at 5 mm from the pole face of the magnet.



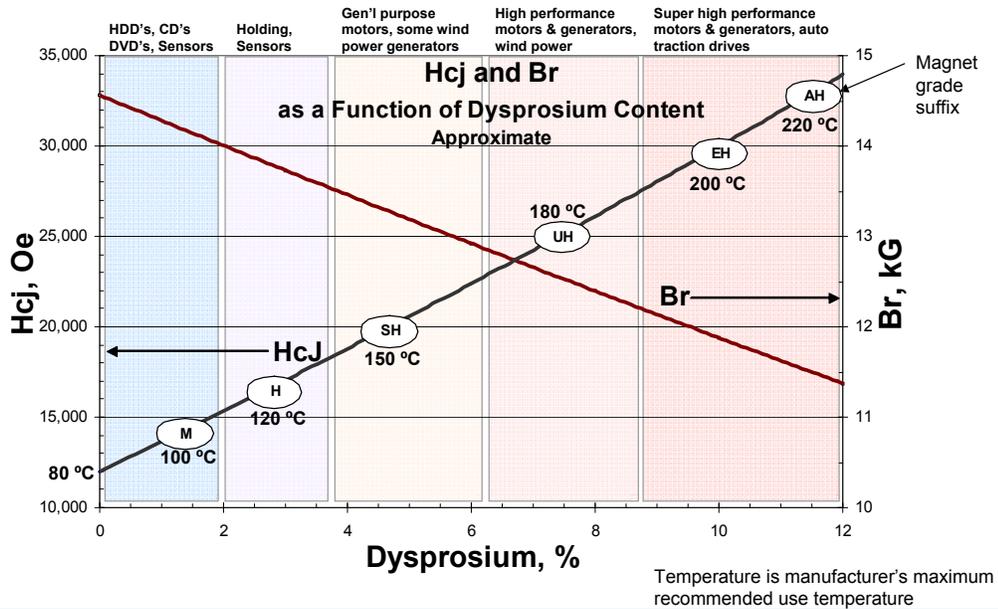
- Improvements in energy product that have facilitated modern applications can be shown pictorially.
- The “V” under each product name is the magnet volume. For example, an N48 magnet with a V of 0.22 cubic centimeters provides the same magnetic field density (strength) near the pole as a ceramic magnet that is 89 times larger.
- Wherever small size and low weight are preferred, rare earth magnets are highly beneficial.
- System size depends also on the steel flux path. For example a larger, weaker magnet requires a larger structure with more steel for the flux return path.

## Typical 2<sup>nd</sup> Quadrant “Demag” Curves



- This is a typical manufacturer’s chart of second quadrant curves as a function of temperature.
- Both Intrinsic and Normal curves are shown.
- This material grade, N42UH, is rated to 180 °C.
- But performance to 220 °C is shown here to emphasize the diminishing Hci.

## Neo Magnet Dysprosium Issue



- As we examine applications for neo magnets more closely, we become aware of the important issue of the forecast “shortage” of dysprosium.
- Hcj is a measure of a magnet’s “resistance to demagnetization.” Br is a measure of a magnet’s field strength. In both cases, generally the larger the number, the better.
- Additions of dysprosium increase Hcj but reduce Br.
- In terms of relative abundance in the crust of the earth, dysprosium is less than 1% of all rare earths and, where it is present in higher percentages, it is most often accompanied by either thorium or uranium, both of which are radioactive.
- The only known occurrence of dysprosium ore without significant radioactive by-products is the ion adsorption clays of southern China.
- Those deposits are estimated to have a 15 to 25 year life at current rates of consumption.
- Dysprosium is required to allow Neo magnets to be used at elevated temperatures, that is above 80 °C, especially in the presence of demagnetizing stress such as in motors and generators.
- We see in this chart that wind power uses Neo with over 4% dysprosium and that traction drives use 8-12% - both represent usage that is considerably higher than the natural abundance.

## Dysprosium is a Short & Long Term Issue

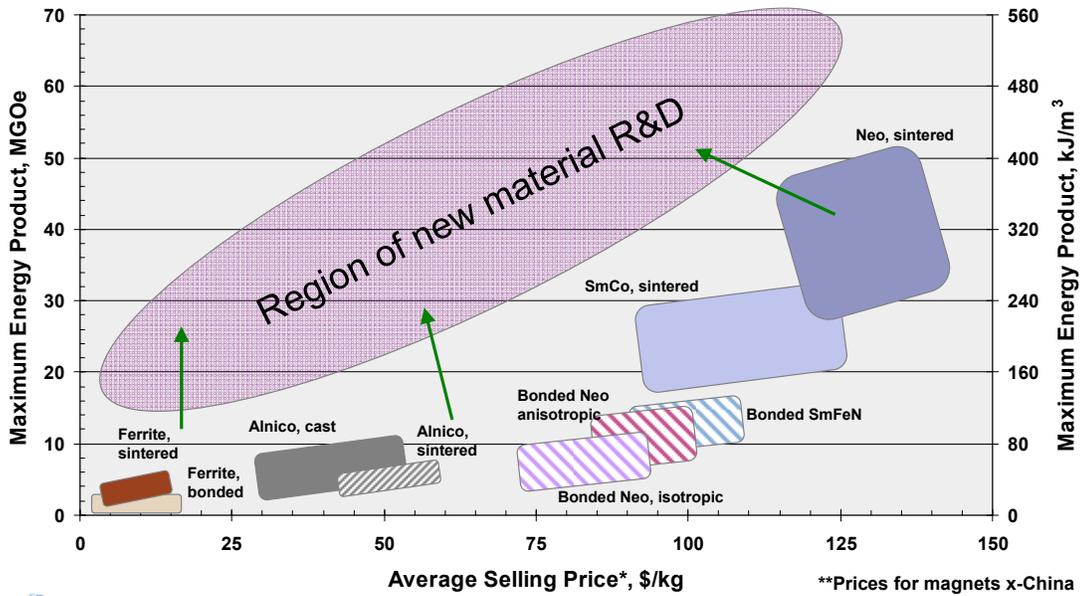
	2010 Production <sup>69</sup>	Potential Sources of Additional Production between 2010 and 2015										Total 2015 Production Capacity	
		United States		Australia			Vietnam	South Africa	Russia & Kazakhstan <sup>70</sup>		India <sup>71</sup>		
		Mt. Pass Phase I <sup>72</sup>	Mt. Pass Phase II	Mt. Weld <sup>73</sup>	NolansBore <sup>74</sup>	Dubbo Zirconia <sup>75</sup>	Dong Pao <sup>76</sup>	Steenkamps-kraal <sup>77</sup>	Russia & Kazakhstan <sup>70</sup>	India <sup>71</sup>			
La	31,000	5,800	6,800	5,600	2,000	510	970	1,100	140	560	54,000		
Ce	42,000	8,300	9,800	10,300	4,800	960	1,500	2,300	290	1200	81,000	Supply Increase	
Pr	5,900	710	840	1,200	590	110	120	250	20	140	9,900		
Nd	20,000	2,000	2,300	4,100	2,200	370	320	830	44	460	33,000	65% increase	
Sm	2,800	130	160	510	240	56	27	125	5	68	4,000	43% increase	
Eu	370	22	26	88	40	2		4	1		550		
Gd	2,400	36	42	176	100	56		83	1	30	3,000		
Tb	320	5	6	22	10	8		4	0.4		370		
Dy	1,600	9	10	22	30	53		34	1		1,700	6% increase	
Y	10,500			66		410	21	250			11,300		
Others	2,000	73	86			75	25	12	3	25	2,300		
Total	120,000	17,000	20,000	22,000	10,000	2,600	3,000	5,000	500	2,500	200,000		

Quantities are metric tons of Rare Earth Oxides  
DOE Critical Materials Strategy, final version January 10, 2012; Table 4.2, p.84



- Rare earth elements are recognized as crucial to the success of clean energy initiatives.
- The United States Department of Energy (DOE) produced a document in December, 2010 called the Critical Materials Strategy.
- It was a thorough document and covered almost every element in the periodic table – more than just rare earths.
- The study continued during 2011 and a second, updated report was issued in late December 2011.
- Be sure to obtain the final version:  
[http://energy.gov/sites/prod/files/DOE\\_CMS2011\\_FINAL\\_Full.pdf](http://energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf)
- This table is from the report. It shows supply of the light magnet rare earths growing by 43% (samarium) and 65% (neodymium) between 2010 and 2015.
- However, dysprosium is shown increasing just 6%. It may be lower than this as many deposits have so little dysprosium as to be uneconomical to separately extract.
- Note that this table is for rare earth **oxides**, not metals.

## Magnet Price versus Energy Product



- Permanent magnet R&D is focused on one or two objectives: increasing magnetic output of low cost materials and/or reducing the net material cost of higher performing materials.

## The Millennial Magnet Stakes

- Exchange Hardening – 2:1 against
- New Phase – 5:1 against
- Strong Ferromagnet – 12:1 against
- Heavy Lanthanide – 20:1 against
- Actinide – 40:1 against

Source: Michael Coey and Ralph Skomski, CEAM c. 1994



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### The Millennial Magnet Stakes

CEAM members will be familiar with the logarithmic plot that shows energy product doubling roughly every twelve years since the beginning of the century, progressing from carbon steel through various grades of Alnico and Sm-Co to Nd-Fe-B. The last point, in 1988, is at 405 J/m<sup>3</sup> for a Nd<sub>2</sub>Fe<sub>14</sub>B magnet. But where do we go next? What chances are there of another doubling of energy product before the end of the century?

The best that can be achieved for any given material is an ideally square hysteresis loop, which gives the upper limit of  $\mu_0 M^2/4$ . For 500 kJ/m<sup>3</sup> we need  $\mu_0 M = 1.59$  T, whereas for 1 MJ/m<sup>3</sup> we need  $\mu_0 M = 2.24$  T. The magnetization of  $\alpha$ -Fe is 2.15T, and some Fe-Co alloys have magnetizations as high as 2.43 T, so it looks as if a megajoule magnet might not be out of the question. Obviously, it cannot be made from Nd<sub>2</sub>Fe<sub>14</sub>B, whose magnetization is 1.60 T, because of the bulkiness of the rare earth which bears almost the same moment as iron at room temperature, but occupies more than three times its volume. In the race to reach 1 MJ/m<sup>3</sup>, there are five runners. Here is an account of their form, with odds on their success.

**New Phase.** This horse comes from the pure 4f-3d bloodstock line which gave us the previous winners SmCo<sub>5</sub> and Nd<sub>2</sub>Fe<sub>14</sub>B. It is increasingly difficult to breed for record energy product, although the latest offspring Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> offers impressive high-temperature performance, but no improvement in magnetization. The aim must be to increase magnetization by reducing rare earth content. A tested breeding method, thermomagnetic analysis of quenched and annealed R-Fe-X mixtures can be applied, together with attempts at isomorphism with H, C, N, ... Odds 5:1 against.

**Strong Ferromagnet.** Here breeders hope is to stabilize a new

combination of qualities in iron, a fully spin-polarized 3d band giving 2.7  $\mu_B$ /atom, and an uniaxial structure as dense-packed as possible. Strongly ferromagnetic iron would have M=2.9 T, but the sign of the anisotropy would probably be wrong. Hopes are raised by confused reports from Japan of very high magnetization in Fe<sub>9</sub>N films, but stewards have been unable to confirm them by on-the-spot band calculations. The moment tends to collapse in dense-packed iron at equilibrium density, so the punters best hope is to stabilize an expanded uniaxial structure with a small amount of some other elements. Three thousand years of practical experience of iron phase diagrams has not yet thrown up a solution. Odds 12:1 against.

**Exchange Hardening.** This is a new, finely-structured hybrid. When exchange coupling extends across the interface of hard and soft material, the anisotropy on the hard side fixes the direction of magnetization on the soft side. It then deviates on a length scale of order  $R\sqrt{\mu_0 M^2/4}$  (2nm for Fe) but if it encounters another hard region coherent with the first closer than this, then the whole composite of hard and soft material may behave as one magnetically hard region, with an effective anisotropy constant of  $f_h K_h$ , where  $f_h$  is the volume-fraction of hard material. The dimensional scale of the hard regions is the domain wall width (2.5nm). (The structure is like a soap film suspended on a comb, sagging a little between the teeth, but never collapsing into bubbles). Possible nanostructures are iron nanomagnets dispersed in a hard rare-earth iron alloy matrix, or a simple multilayer geometry. The hard regions should be at least 1nm thick, which means that  $f_h$  must be 30% or more. Choosing Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> and <sup>60</sup>Fe for the hard and soft phases gives  $M_{sp} = 2.0$  T and  $K_{sp} = 3.6$  MJ/m<sup>3</sup>; higher values are possible with some

cobalt substitution in either or both phases (Fe<sub>95</sub>Co<sub>5</sub> is the 'pole-piece' alloy). The concept of exchange hardening has been demonstrated by isotropic Nd<sub>2</sub>Fe<sub>14</sub>B/Fe<sub>3</sub>B and Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub>/Fe nanocomposites produced by melt spinning and mechanical alloying in the Coehoorn and Street stables, respectively. The latter has an isotropic remanence of 1.4 T. Now the problem is to make oriented material by some deformation or multiple rolling process, or by thin film deposition techniques. Odds 2:1 against (favorite)

**Heavy Lanthanide.** The high atomic moments of 10  $\mu_B$  found on Dy and Ho outweigh the inconvenience of their large atomic volume; and when these dense-packed structures are ferromagnetic,  $\mu_0 M$  can be as high as 3.7 T. There also exist ferromagnetic alloys such as Dy-Al<sub>2</sub> or Ho-Ni, but their Curie temperatures are also below room temperature. Such alloys might be developed as low-temperature permanent magnets, but the problem is the weakness of the 4f-4e exchange coupling. Another line of approach might be to try to couple the 4f orbitals with cerium, where the 4f electrons are mostly delocalized. Odds 20:1 against at RT

**Actinide.** No runners have yet emerged from this stable, although a few pnictides have Curie points approaching room temperature. The attraction is a smaller atomic volume than the lanthanides, but the 5f shell is rather delocalized and they are almost all radioactive and highly toxic. Odds 40:1 against

**Summary of the form.** Ideas on how to raise a new generation of magnets to meet the megajoule challenge are not lacking. Most of them are long shots, but it looks likely that the eventual winner may be a nanostructured two-phase composite rather than a traditional rare-earth iron intermetallic compound. The odds don't add up, because there is one other possibility (No winner, 2:1)

J. M. D. Coey and R. Skomski

- Though we should try, it may not be possible to develop a superior permanent magnet with no rare earth.
- Success should be recognized for superior materials with less rare earth content.
- Actinide magnets are not recommended as the constituents are hazardous (radioactive and toxic) materials.
- Exchange-coupled magnet materials represent the best chance for a new, high performance magnetic material
- Second place goes to development of an entirely new material.

## R&D Activities (U.S.)

### Approaches

- Enhanced Alnico
- New Magnetic Phase
- Nanotechnology forming
- Exchange Coupling
- Diffusion Coating
- Layering Techniques
- Core-Shell structures

Structure-related



### Advanced Research Projects Agency - Energy (ARPA-E) Annual Report for FY2011

Report to Congress  
June 2012

ARPA-E REACT project and others, funded by DOE, EERE and ARPA-E, are focused on finding alternative high performance magnet materials to relieve pressure on rare earth supplies and to facilitate a more robust supply chain for energy critical elements.

United States Department of Energy  
Washington, DC 20585

[http://arpa-e.energy.gov/sites/default/files/ARPA-E FY%202011%20Annual%20Report\\_0.pdf](http://arpa-e.energy.gov/sites/default/files/ARPA-E%20FY%202011%20Annual%20Report_0.pdf)



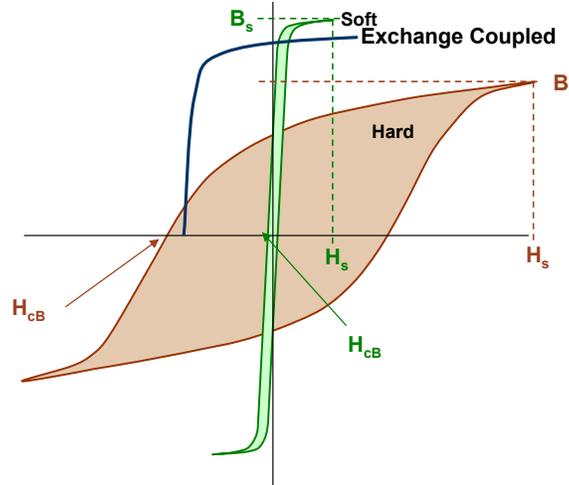
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- Research activities into new magnetic materials include a bottoms-up (design) approach – a search for a new magnetic phase.
- Other thoughts related to a good magnetic material...
- To obtain full benefit from the magnetic material, it should be fully dense (no dilution of the magnetic phase), it should have uniaxial crystalline anisotropy (for maximizing magnetic saturation), and magnetic domains should be oriented within the bulk structure.
- Raw materials need to be widely available and at reasonable cost.
- Raw materials and the finished composition must be non-toxic and environmentally friendly.
- The material should be easily and safely manufacturable.
- The magnets should be recyclable.

## Exchange Coupling - Concept



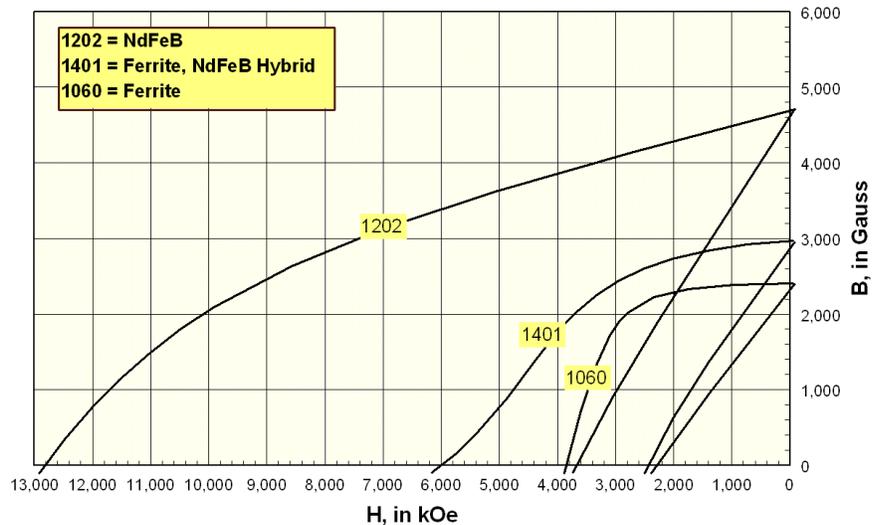
- Exchange coupled magnets derive their name from a synergistic combination of magnetic properties resulting from two dissimilar components: a hard and a soft magnetic phases interacting in a synergistic way.
- The hard phase provides resistance to demagnetization and the soft phase provides exceptionally high saturation magnetization.
- Exchange coupling results in a fortuitous combination of properties: both high saturation and intrinsic coercivity.

## Exchange Coupling

Macroscopic averaging

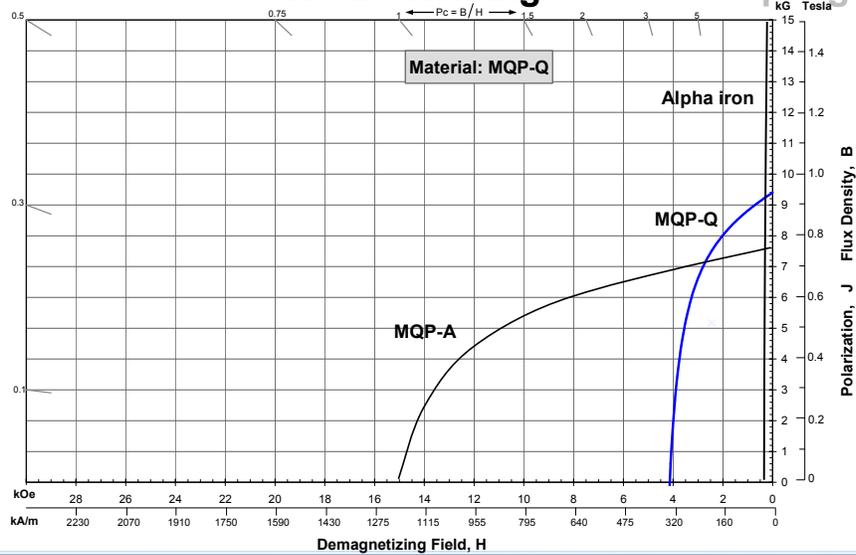
Sub-micron-scale  
Weak exchange

Nano-scale coupling



- In the case of a large microstructure (measured in microns) there is extremely weak coupling.
- Magnet properties are closely approximate to the volume-based average of properties of the individual components.
- In this bonded magnet example, 1060 grade is ferrite, 1202 grade is 100% neo powder and 1401 is a 20% by weight neo-in-ferrite blend.
- As temperature deviates from 20 °C, one notes that neo coercivity decreases while ferrite coercivity increases. At a 20% neo blend, these changes roughly balance creating an interesting mixture.
- However, there is little if any evidence of exchange coupling.

Macroscopic materials      Exchange Coupling      Nano-scale coupling  
Sub-micron-scale  
Weak exchange



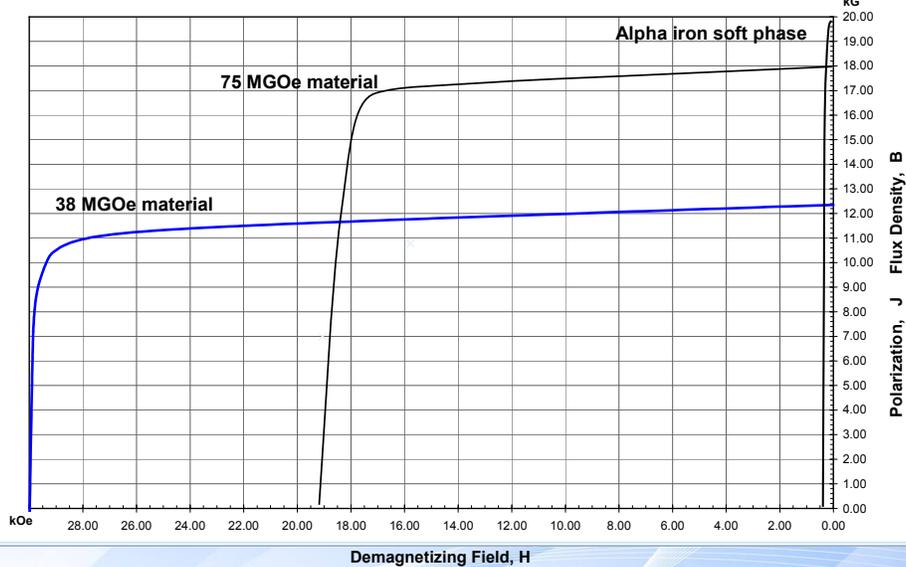
- In this example of Magnequench's MQP-Q, exchange occurs at the nano-scale of between 20 and 30 nano-meters.
- At this scale, it is a weak exchange producing a compromise between  $B_r$  and  $H_{c_j}$ .
- This grade of material is a mixture of Neo (2:14:1) and alpha-iron.
- A similar exchange couple (exchange spring) material was patented by Philips in the late 1980's and consisted of Neo plus  $Fe_3B$ .

## Exchange Coupling

Macroscopic materials

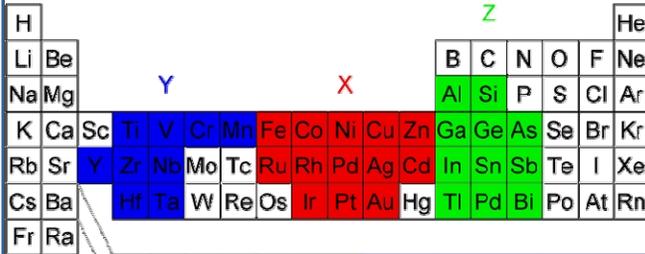
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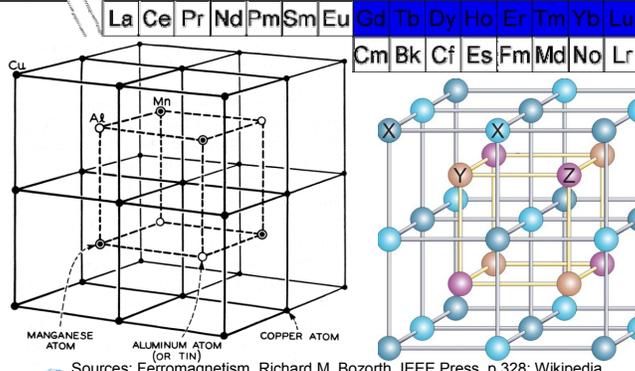


- To achieve beneficial exchange requires coupling at just above the super-paramagnetic size limit.
- In this event, the coupling might be expected to show high  $B_r$ , high  $H_{cJ}$  and a loop shape similar to the hard magnetic phase.
- Achieving this fine a coupled microstructure is challenge number one.
- The second challenge is to have particulate that can be rotated to achieve common domain orientation.
- The last and great challenge is to be able to densify the particulate to full or near-full density.
- It may, alternatively, be possible to freeze-in from the melt a microstructure at very fine sizes, similar to but smaller than those in alnico magnets, so that a dense structure exists naturally.

# Heusler Alloys



"A Heusler alloy is a ferromagnetic metal alloy based on a Heusler phase. Heusler phases are intermetallics with particular composition and face-centered cubic crystal structure. They are ferromagnetic—even though the constituting elements are not—as a result of the double-exchange mechanism between neighboring magnetic ions. The latter are usually manganese ions, which sit at the body centers of the cubic structure and carry most of the magnetic moment of the alloy."



Magnetism and Magnetic Materials, J.M.D. Coey, p.394

	$a_0$ (pm)	$T_C$ (K)	$\sigma_0$ (A m <sup>2</sup> kg <sup>-1</sup> )	$m$ ( $\mu_B$ )
Cu <sub>2</sub> MnIn	621	500	75	4.0
Co <sub>2</sub> MnGa	577	694	93	4.1
Co <sub>2</sub> MnSi <sup>‡</sup>	565	985	141	5.0
Co <sub>2</sub> MnGe <sup>‡</sup>	574	905	116	5.1
Co <sub>2</sub> MnSn	600	829	97	5.1
Ni <sub>2</sub> MnGa	583	360	96	4.2
Ni <sub>2</sub> MnSn	605	360	81	4.2
Pd <sub>2</sub> MnSb	642	247	63	4.4
NiMnSb <sup>‡</sup>	592	730	93	4.0
PtMnSb <sup>‡</sup>	620	572	60	4.0
Mn <sub>2</sub> VAl <sup>‡</sup>	760	730	59	2.0

<sup>‡</sup> Half-metal

- I've included this slide on Heusler alloys due to the interesting crystalline structure.
- They were first identified as a family of materials in 1905 and have found a recent revival in spintronics.
- They exhibit uniaxial crystalline anisotropy.
- They are one example of how structure might be the source of good magnetic properties in a new material.

A Heusler alloy is a ferromagnetic metal alloy based on a Heusler phase. Heusler phases are intermetallics with particular composition and face-centered cubic crystal structure. They are ferromagnetic—even though the constituting elements need not be—as a result of the double-exchange mechanism between neighboring magnetic ions. The latter are usually manganese ions, which sit at the body centers of the cubic structure and carry most of the magnetic moment of the alloy.

(Wikipedia)

## Agenda

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- What are the “elements of magnetics”?

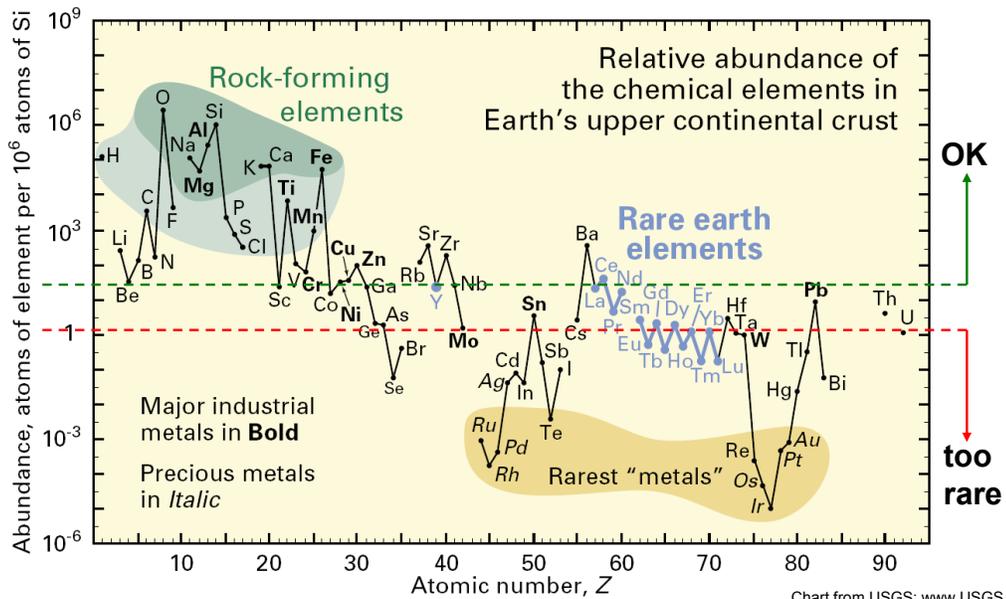
## What are the “Elements of Magnetics”

- Magnetic characteristics that make a material useful
- The economics around those materials
  - Raw material costs and availability
  - Manufacturability and yield
  - Dynamic market changes – when supply cannot keep up with changing demand
- The physical elements that constitute magnetic materials
  - Which elements contribute to the net magnetic moment and magnetic stability of a permanent (or soft) magnetic material
- The ability to transform those materials into a useful product



- These are four “fundamental elements” of the magnetic materials industry.

## Availability of the Elements



- Any discussion of commercial viability has to start with the premise that the raw materials are readily available and at a reasonable cost.
- As a primary ingredient, it's highly recommended to select more readily available materials such as those above the green dashed line.
- Minor ingredients may be from between the green and red lines.
- But elements from below the dashed red line should be avoided except in the very smallest additions.

## Periodic Table of the Elements - Complete

Ref. Vertex42.com

Group 1 IA												13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA																															
1	<b>H</b> Hydrogen [1] 1.00794 +1, -1											5	<b>B</b> Boron [5] 10.811 +3	6	<b>C</b> Carbon [6] 12.0107 +2, -4, 4	7	<b>N</b> Nitrogen [7] 14.0067 +1, 2, 3, 4, 5, 1, 2, 3	8	<b>O</b> Oxygen [8] 15.9994 -2	9	<b>F</b> Fluorine [9] 18.9984 -1	10	<b>Ne</b> Neon [10] 20.1797 0																									
2	3 <b>Li</b> Lithium [3] 6.941 +1	4 <b>Be</b> Beryllium [4] 9.01224 +2											13	<b>Al</b> Aluminum [13] 26.9815 +3	14	<b>Si</b> Silicon [14] 28.0855 +2, -4, 4	15	<b>P</b> Phosphorus [15] 30.9738 +3, -3	16	<b>S</b> Sulfur [16] 32.065 -2	17	<b>Cl</b> Chlorine [17] 35.453 -1, +5, 7, 1	18	<b>Ar</b> Argon [18] 39.948 0																								
3	11 <b>Na</b> Sodium [11] 22.989769 +1	12 <b>Mg</b> Magnesium [12] 24.304 +2											19	<b>K</b> Potassium [19] 39.0983 +1	20	<b>Ca</b> Calcium [20] 40.078 +2	21	<b>Sc</b> Scandium [21] 44.955912 +3	22	<b>Ti</b> Titanium [22] 47.8827 +2, 3, 4	23	<b>V</b> Vanadium [23] 50.9415 +2, 3, 4, 5	24	<b>Cr</b> Chromium [24] 51.9961 +2, 3, 6	25	<b>Mn</b> Manganese [25] 54.938 +2, 3, 4, 7	26	<b>Fe</b> Iron [26] 55.845 +2, 3	27	<b>Co</b> Cobalt [27] 58.9332 +2, 3	28	<b>Ni</b> Nickel [28] 58.6934 +2	29	<b>Cu</b> Copper [29] 63.546 +1, 2	30	<b>Zn</b> Zinc [30] 65.38 +2	31	<b>Ga</b> Gallium [31] 69.723 +3	32	<b>Ge</b> Germanium [32] 72.64 +2, 4	33	<b>As</b> Arsenic [33] 74.9216 +3, -3	34	<b>Se</b> Selenium [34] 78.96 +4, -2	35	<b>Br</b> Bromine [35] 79.904 -1	36	<b>Kr</b> Krypton [36] 83.796 0
4	37 <b>Rb</b> Rubidium [37] 85.4678 +1	38 <b>Sr</b> Strontium [38] 87.62 +2	39 <b>Y</b> Yttrium [39] 88.90584 +3	40	41 <b>Zr</b> Zirconium [40] 91.224 +2, 3, 4	42	43 <b>Nb</b> Niobium [41] 92.90638 +3, 4, 5	44	44 <b>Mo</b> Molybdenum [42] 95.94 +2, 3, 4, 5, 6	45	45 <b>Tc</b> Technetium [43] 98.90625 +4, 5, 6, 7	46	46 <b>Ru</b> Ruthenium [44] 101.07 +3, 4	47	47 <b>Rh</b> Rhodium [45] 101.07 +3	48	48 <b>Pd</b> Palladium [46] 106.367 +2, 4	49	49 <b>Ag</b> Silver [47] 107.8682 +1	50	50 <b>Cd</b> Cadmium [48] 112.411 +2	51	51 <b>In</b> Indium [49] 114.818 +3	52	52 <b>Sn</b> Tin [50] 118.710 +2, 4	53	53 <b>Sb</b> Antimony [51] 121.757 +3, -3	54	54 <b>Te</b> Tellurium [52] 127.603 +4, -2	55	55 <b>I</b> Iodine [53] 126.905 -1	56	56 <b>Xe</b> Xenon [54] 131.29 0															
5	55 <b>Cs</b> Cesium [55] 132.905 +1	56 <b>Ba</b> Barium [56] 137.327 +2	57-71	72 <b>Hf</b> Hafnium [72] 178.49 +4	73	74 <b>Ta</b> Tantalum [73] 180.948 +3, 4, 5	75	75 <b>W</b> Tungsten [74] 183.84 +2, 3, 4, 5, 6	76	76 <b>Re</b> Rhenium [75] 186.207 +4, 5, 6, 7	77	77 <b>Os</b> Osmium [76] 190.23 +4, 6	78	78 <b>Ir</b> Iridium [77] 192.222 +3, 4	79	79 <b>Pt</b> Platinum [78] 195.078 +2, 4	80	80 <b>Au</b> Gold [79] 196.967 +1, 3	81	81 <b>Hg</b> Mercury [80] 200.59 +2	82	82 <b>Tl</b> Thallium [81] 204.384 +3	83	83 <b>Pb</b> Lead [82] 207.2 +2, 4	84	84 <b>Bi</b> Bismuth [83] 208.98 +3, -3	85	85 <b>Po</b> Polonium [84] 209 +2, 4	86	86 <b>At</b> Astatine [85] 210 +2, 4	87	87 <b>Rn</b> Radon [86] 222 0																
6	87 <b>Fr</b> Francium [87] 223 +1	88 <b>Ra</b> Radium [88] 226 +2	89-103	104 <b>Rf</b> Rutherfordium [104] 261 +4	105	105 <b>Db</b> Dubnium [105] 262 +5	106	106 <b>Sg</b> Seaborgium [106] 263 +6	107	107 <b>Bh</b> Bohrium [107] 264 +7	108	108 <b>Hs</b> Hassium [108] 277 +8	109	109 <b>Mt</b> Meitnerium [109] 278 +9	110	110 <b>Ds</b> Darmstadtium [110] 285 +10	111	111 <b>Rg</b> Roentgenium [111] 288 +11	112	112 <b>Cn</b> Copernicium [112] 285 +12	113	113 <b>Uut</b> Ununtrium [113] 288 +13	114	114 <b>Uuq</b> Ununquadium [114] 289 +14	115	115 <b>Uup</b> Ununpentium [115] 289 +15	116	116 <b>Uuh</b> Ununhexium [116] 289 +16	117	117 <b>Uus</b> Ununseptium [117] 289 +17	118	118 <b>Uuo</b> Ununoctium [118] 289 +18																
7	89 <b>La</b> Lanthanum [89] 138.905 +3	90 <b>Ce</b> Cerium [90] 140.12 +3	91 <b>Pr</b> Praseodymium [91] 140.908 +3	92 <b>Nd</b> Neodymium [92] 144.24 +3	93 <b>Pm</b> Promethium [93] 145 +3	94 <b>Sm</b> Samarium [94] 150.36 +3	95 <b>Eu</b> Europium [95] 151.964 +3	96 <b>Gd</b> Gadolinium [96] 157.25 +3	97 <b>Tb</b> Terbium [97] 158.925 +3	98 <b>Dy</b> Dysprosium [98] 162.5 +3	99 <b>Ho</b> Holmium [99] 164.93 +3	100 <b>Er</b> Erbium [100] 167.259 +3	101 <b>Tm</b> Thulium [101] 168.934 +3	102 <b>Yb</b> Ytterbium [102] 173.04 +2, 3	103 <b>Lu</b> Lutetium [103] 174.967 +3	104 <b>Ac</b> Actinium [89] 227 +3	105 <b>Th</b> Thorium [90] 232.038 +2, 3, 4	106 <b>Pa</b> Protactinium [91] 231.036 +3	107 <b>U</b> Uranium [92] 238.0289 +3	108 <b>Np</b> Neptunium [93] 237 +3	109 <b>Pu</b> Plutonium [94] 244 +3	110 <b>Am</b> Americium [95] 243 +3	111 <b>Cm</b> Curium [96] 247 +3	112 <b>Bk</b> Berkelium [97] 247 +3	113 <b>Cf</b> Californium [98] 251 +3	114 <b>Es</b> Einsteinium [99] 252 +3	115 <b>Fm</b> Fermium [100] 257 +3	116 <b>Md</b> Mendelevium [101] 258 +3	117 <b>No</b> Nobelium [102] 259 +3	118 <b>Lr</b> Lawrencium [103] 262 +3																		



- Let's work with the periodic table to see what elements are likely candidates for use in magnetic materials.
- I will use a method similar to that of Bill McCallum of Ames Laboratory who kindly shared his notes with me some time ago (though this approach is solely my responsibility).
- This table was obtained from Vertex in Excel format. It has been modified to simplify the information in each cell. Go to [www.vertex42.com](http://www.vertex42.com) for this and other useful spreadsheets and documents.
- This first table lists all of the elements.

### Periodic Table of the Elements

No: Synthetic, Radioactive, Inert, Toxic, Rare, Salt-forming Elements

																		18 VIIIA	
																		17 VIIA	
																		16 VIA	
																		15 VA	
																		14 IVA	
																		13 IIIA	
																		12 IIB	
																		11 IB	
																		10 VIII	
																		9 VIII	
																		8 VIII	
																		7 VIIB	
																		6 VIB	
																		5 VB	
																		4 IVB	
																		3 IIIB	
																		2 IIA	
																		1 IA	

**Phase at STP**

Gas   Liquid   Solid   Synthetic

**Categories**

Alkali Metals   Alkaline Earth Metals   Transition Metals   Rare Earth Metals   Poor Metals

Noble Gas   Halogens   Non-metals   Metalloids



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- After removing man-made elements, those that are radioactive, inert elements, toxic elements, those elements that are truly rare, the inert (noble) gases, and the rock (salt) forming elements, we are left with the elements in this chart.
- We're down from 90 naturally occurring elements to about 36.
- Let's ask a question: what elements have been used over the last 150 years to make magnetic materials?

## Elements in Existing Magnetic Materials

	Major constituents	Minor constituent: Comments
<b>Soft Magnetic Materials</b>		
Iron	Fe	Low carbon mild steel
Silicon Steel	Fe	Si at 2.5 to 6%
Nickel-Iron	Fe Ni	Ni at 35 to 85%
Moly Permalloy	Ni Fe	Mo at 79%, Mo at 4%, bal. Fe
Iron-Cobalt	Fe Co	V 23 to 52% Co
Soft Ferrite	Fe Mn Ni Zn	O
Metallic Glasses	Fe Co Ni	B Si P Amorphous and nanocrystalline
<b>Permanent Magnets</b>		
Co-Steels	Fe Co	
Alnico	Fe Ni Co Al Cu	Ti Si
Platinum Cobalt	Pt Co	
Hard Ferrites	Fe Sr	Oxygen dilutes; Ba no longer used
SmCo	Co Sm (Gd) Fe Cu Zr	
Neodymium-iron-boror	Fe Nd Dy (Y) B Co Cu Ga Al Nb	
Cerium-iron-boron	Fe Nd Ce B	Limited use in bonded magnets
SmFeN	Fe Sm N	Nitrogen is interstitial; stability issue
MnBi	Mn Bi	Never commercialized
MnAl(C)	Mn Al	Cu C Not successfully commercialized



- This list contains many (though not all) common magnetic materials and the elements used to make them.
- Take a good look and then let's move to the next slide showing them on the periodic table.

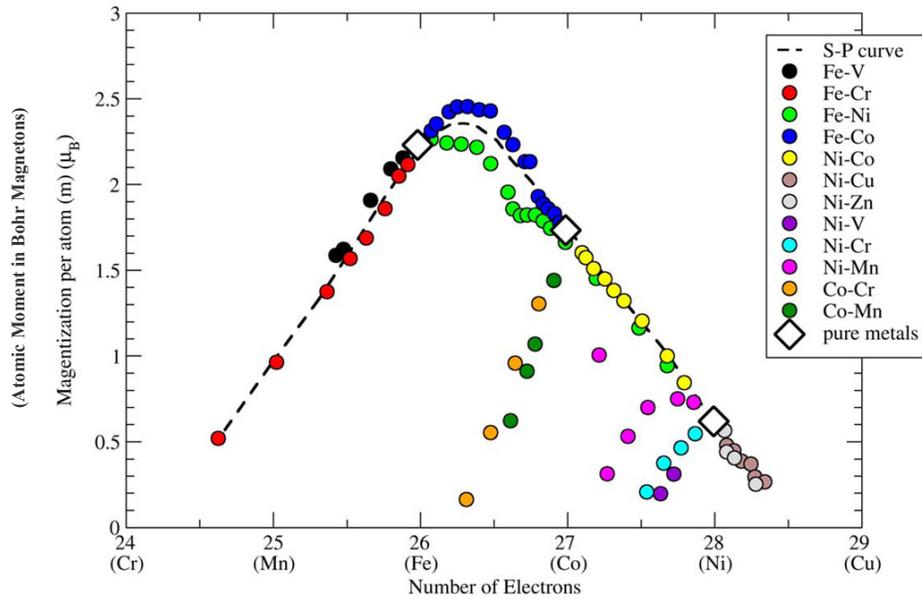
## Elements used in Existing Magnetic Materials

Group 1 IA		Group 2 IIA		Transition Metals										Group 11 IB	Group 12 IIB	Group 13 IIIA	Group 14 IVA	Group 15 VA	Group 16 VIA	Group 17 VIIA	Group 18 VIIIA																		
1	H Hydrogen [1] 1.00794	2	He Helium [2] 4.00260	3	Li Lithium [3] 6.941	4	Be Beryllium [4] 9.0122	5	B Boron [5] 10.811	6	C Carbon [6] 12.011	7	N Nitrogen [7] 14.0064	8	O Oxygen [8] 15.9994	9	F Fluorine [9] 18.9984	10	Ne Neon [10] 20.1798																				
2	Na Sodium [11] 22.9898	12	Mg Magnesium [12] 24.305	13	Al Aluminum [13] 26.9815	14	Si Silicon [14] 28.0855	15	P Phosphorus [15] 30.9738	16	S Sulfur [16] 32.065	17	Cl Chlorine [17] 35.453	18	Ar Argon [18] 39.948																								
3	K Potassium [19] 39.0983	20	Ca Calcium [20] 40.078	21	Sc Scandium [21] 44.9559	22	Ti Titanium [22] 47.88	23	V Vanadium [23] 50.9415	24	Cr Chromium [24] 51.9961	25	Mn Manganese [25] 54.938	26	Fe Iron [26] 55.845	27	Co Cobalt [27] 58.9332	28	Ni Nickel [28] 58.6934	29	Cu Copper [29] 63.546	30	Zn Zinc [30] 65.38	31	Ga Gallium [31] 69.723	32	Ge Germanium [32] 72.64	33	As Arsenic [33] 74.9216	34	Se Selenium [34] 78.96	35	Br Bromine [35] 79.904	36	Kr Krypton [36] 83.798				
4	Rb Rubidium [37] 85.4678	38	Sr Strontium [38] 87.62	39	Y Yttrium [39] 88.9059	40	Zr Zirconium [40] 91.224	41	Nb Niobium [41] 92.9064	42	Mo Molybdenum [42] 95.94	43	Tc Technetium [43] 98	44	Ru Ruthenium [44] 101.07	45	Rh Rhodium [45] 102.9055	46	Pd Palladium [46] 106.42	47	Ag Silver [47] 107.8682	48	Cd Cadmium [48] 112.411	49	In Indium [49] 114.818	50	Sn Tin [50] 118.710	51	Sb Antimony [51] 121.757	52	Te Tellurium [52] 127.6	53	I Iodine [53] 126.905	54	Xe Xenon [54] 131.29				
5	Cs Cesium [55] 132.905	56	Ba Barium [56] 137.327	57	Lanthanide Series					72	Hf Hafnium [72] 178.49	73	Ta Tantalum [73] 180.948	74	W Tungsten [74] 183.84	75	Re Rhenium [75] 186.207	76	Os Osmium [76] 190.23	77	Ir Iridium [77] 192.222	78	Pt Platinum [78] 195.084	79	Au Gold [79] 196.967	80	Hg Mercury [80] 200.59	81	Tl Thallium [81] 204.3833	82	Pb Lead [82] 207.2	83	Bi Bismuth [83] 208.9804	84	Po Polonium [84] 209	85	At Astatine [85] 210	86	Rn Radon [86] 222
6	Fr Francium [87] 223	88	Ra Radium [88] 226	89	Actinide Series					104	Rf Rutherfordium [104] 261	105	Db Dubnium [105] 262	106	Sg Seaborgium [106] 263	107	Bh Bohrium [107] 264	108	Hs Hassium [108] 265	109	Mt Meitnerium [109] 266	110	Ds Darmstadtium [110] 267	111	Rg Roentgenium [111] 268	112	Cn Copernicium [112] 269	113	Uut Ununtrium [113] 270	114	Uuq Ununquadium [114] 271	115	Uup Ununpentium [115] 272	116	Uuh Ununhexium [116] 273	117	Uus Ununseptium [117] 274	118	Uuo Ununoctium [118] 276
7	Lanthanides		57	La Lanthanum [57] 138.905	58	Ce Cerium [58] 140.116	59	Pr Praseodymium [59] 140.908	60	Nd Neodymium [60] 144.24	61	Pm Promethium [61] 145	62	Sm Samarium [62] 150.36	63	Eu Europium [63] 151.964	64	Gd Gadolinium [64] 157.25	65	Tb Terbium [65] 158.925	66	Dy Dysprosium [66] 162.5	67	Ho Holmium [67] 164.930	68	Er Erbium [68] 167.255	69	Tm Thulium [69] 168.934	70	Yb Ytterbium [70] 173.054	71	Lu Lutetium [71] 174.967							
Actinides		89	Ac Actinium [89] 227	90	Th Thorium [90] 232.0377	91	Pa Protactinium [91] 231.036	92	U Uranium [92] 238.02891	93	Np Neptunium [93] 237	94	Pu Plutonium [94] 244	95	Am Americium [95] 243	96	Cm Curium [96] 247	97	Bk Berkelium [97] 247	98	Cf Californium [98] 251	99	Es Einsteinium [99] 252	100	Fm Fermium [100] 257	101	Md Mendelevium [101] 258	102	No Nobelium [102] 259	103	Lr Lawrencium [103] 260								



- They are, with three exceptions, the same elements we selected by narrowing the total list of elements.
- The exceptions:
  - Platinum-cobalt was the first high performance magnet. It was used to make watch drive motor magnets whose very small size compensated for the high material cost. It is still made today but in very limited quantities.
  - Germanium and Tin have not been used, at least to my knowledge, in commercial magnets except as trace constituents, but like aluminum and gallium might make suitable modifying constituents to assist sintering or phase formation.
- If we are to make a new magnet material, it is likely to come from combinations of these elements.

### Slater-Pauling Curve



Color-edited by Dr. Bill McCallum, Ames Lab

R.M. Bozorth, Ferromagnetism, IEEE, 1993, p.438-441



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- The Slater-Pauling curve of energy plotted versus number of valence (3d+4s) electrons teaches us that the highest Ms (saturation magnetization) materials are likely to be constituted largely of iron and cobalt – no surprise there.
- Any compositional additions, such as to create or enhance coercivity, are likely to reduce the Ms and energy product.
- Note that this chart shows only 2-component alloys.

## Sensitivity to Thermal Treatment

**Affect of Thermal Treatment on SmCo 2:17 Magnetic Properties**

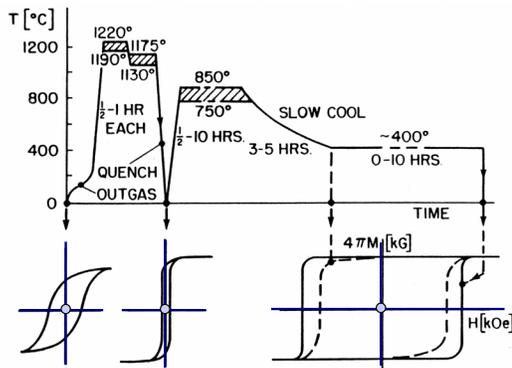


Fig. 32. Typical temperature profile for the sintering and heat-treating of "2-17"-type Sm(Co, Fe, Cu, Zr)<sub>7.2-8.5</sub> magnets.

Source: Rare earth-Cobalt Permanent Magnets, K.J. Strnat, 1988

**Affect of Thermal Treatment in an aligning magnetic field on magnetic Properties of alnico 5**

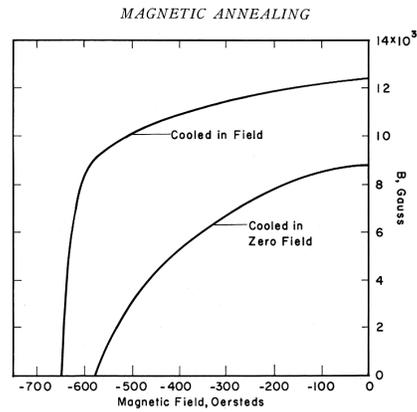


Fig. 8—Effect of Magnetic Annealing of Alnico 5 (142).

Source: Magnetic Properties of Metals and Alloys, published by the American Society for Metals, 1958, Chapter 13, C.D. Graham, Jr., p.307



- In addition to the importance of structure in current research is the importance of thermal processing in the development of optimal microstructure.
- With the exception of ceramic (hard ferrite) magnets, magnetic alloys are just that – alloys.
- Therefore, thermal treatments to form the stable and desirable phase structure are very common.
- In the chart at the left, Karl Strnat teaches regarding the development of the hysteresis loop of SmCo 2:17 during its thermal treatment.
- In the chart to the right, we see the improvement of magnet properties of alnico 5 due to thermal processing in the presence of an aligning magnetic field.

## Alnico Thermal Treatment

### Three treatments

- Solution treatment above 1200 °C
- Isothermal treatment for spinodal decomposition and magnetic alignment
- Draw (precipitation hardening) cycle

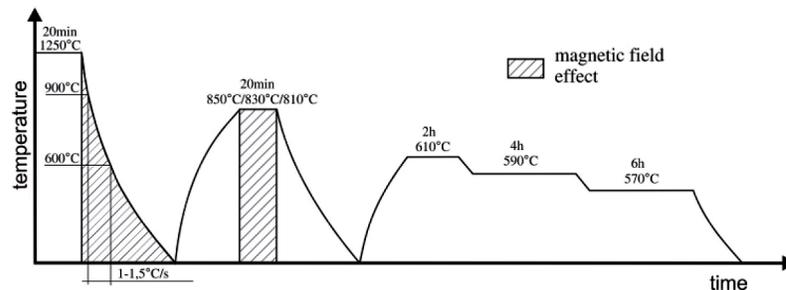


Fig. 3. Scheme of thermo-magnetic treatment of Alnico 8 alloy

Source: Investigations of Thermo-Magnetic Treatment of Alnico 8 Alloy, Stanek et al, Archives of Metallurgy and Materials, Vol 55, 2010 Issue 2



- In another example related to alnico, the material is solution treated at high temperature (about 1250 °C) followed by a conditioning treatment effected by controlled cooling from the solution treatment temperature or by isothermal treatment of the magnets – anisotropic magnets are treated in a field during spinodal decomposition at ~820 °C.
- The third and final treatment is called a “draw” or “coercive aging treatment” to obtain maximum coercivity and optimal loop shape.
- We might say that the right composition provides the opportunity and the right thermal treatment creates the right phase structure.
- As with SmCo 2:17, extending the draw time improves the coercivity – structural kinetics are slow at these low temperatures.

## Consolidation Technologies

- **Cold compaction**
    - With binder (bonded magnets)
    - Plus liquid phase sintering (sintered magnets)
  - **Cold forging; cold rolling**
  - **Hot compaction**
    - Hot uniaxial pressing
    - HIP
    - SPS
  - **Hot forging; friction stir welding**
  - **Hot extrusion (or drawing); hot rolling**
- Challenges**
- Limits to densification using cold compaction
  - Degradation of nanostructure with application of temperature
  - Obtaining uniform alignment of magnetic domains
- \*\*Potential exists to develop magnetic texture through strain

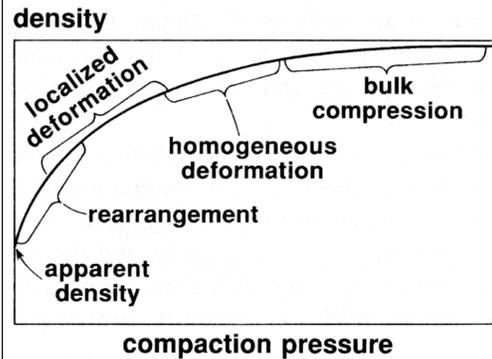
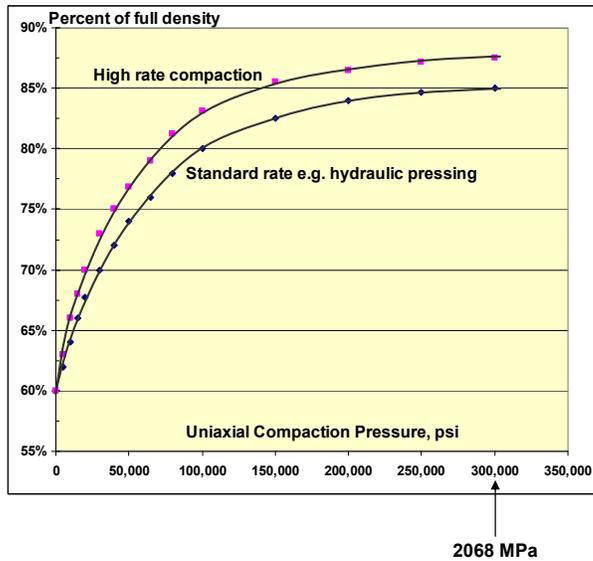


- Every commercially available magnet material since alnico is manufactured by powder metallurgical techniques.
- This includes ferrite permanent magnets, SmCo 1:5, SmCo 2:17, Neo, and SmFeN.
- Except for SmFeN, the materials can be processed into fully consolidated structures via liquid phase sintering or hot deformation (die upsetting).
- The list in this chart shows some of the more common methods for densifying powder into a usable shape.

HIP = hot isostatic pressing

SPS = Spark Plasma Sintering

## Cold Compaction

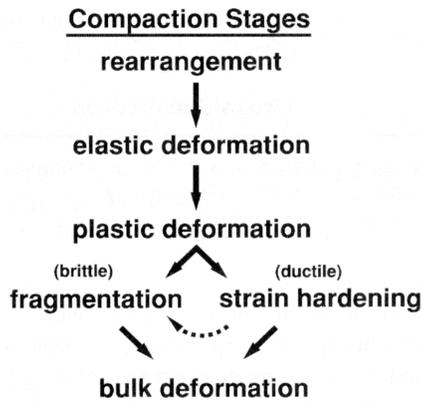


Randall M. German, *Powder Metallurgy Science*,  
2nd ed., MPIF, 1994, p.205

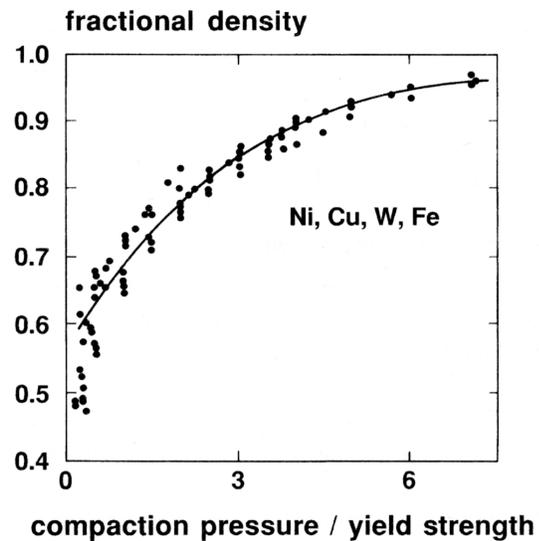


- Shape of a cold compaction curve is dependent upon at least the following:
  - ✓Rate of pressure application
  - ✓Powder particle size and distribution
  - ✓Material hardness
  - ✓Brittleness (or malleability)
  - ✓Included defects (from mechanical working)
- Near full density requires extreme shear and is not possible in cold compaction except with a limited number of “super-plastic” alloys.
- In powder metallurgy, cold compaction is usually followed by a thermal treatment to densify the “green” compact.
- The densifying thermal treatment is called solid or liquid phase sintering

## Cold Compaction



Hot compaction benefits from a lowering of the yield strength of the main alloy or additive constituents.



Randall M. German, *Powder Metallurgy Science*, 2nd ed., MPIF, 1994, p.207, 225



- Randall German wrote two texts on the subject of powder metallurgy. The reference shown here is highly recommended.
- These illustrations reinforce those on the previous slide but go further to show that the material, ductile and deformable at the start of compaction, work hardens and resists continuous compaction through deformation.
- The only ways to continue compaction are to anneal to remove the work hardening or to apply adequate pressure to cause brittle fracture.
- Consolidation to full density will most likely require both pressure and temperature.
- Minimal grain growth requires that the pressure be maximized and temperature minimized.

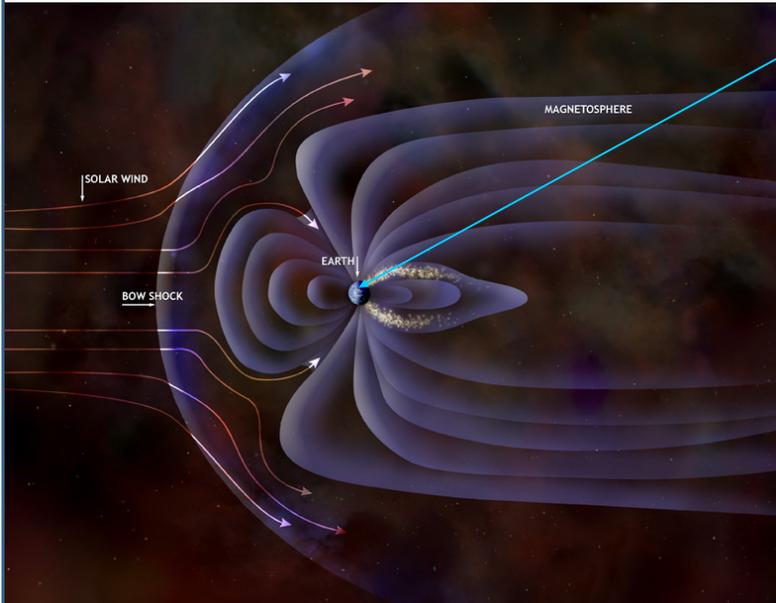


## Wrapping it Up

- New magnetic materials do NOT need to replace existing ones, they need only complement them from the perspectives of price and performance
- They are likely to be developed by a combination of unique atomic structure and thermal treatment
- The largest challenges with nanostructured (particulate) materials will be
  - Co-parallel alignment of magnetic domains
  - Achieving full consolidation (full density)
  - \*\*\*Failing full densification, material must be modifiable for chemical stability in bonded magnets



- Relief on dysprosium shortages does not require a wholesale replacement of neo magnets. It does mean using multiple methods of reducing demand for dysprosium including:
  - ✓ Selective positioning of dysprosium in the structure to minimize content
  - ✓ Reducing temperature of applications so less dysprosium is required
  - ✓ Use of alternate high temperature magnet materials such as SmCo or alnico
  - ✓ Modified designs to reduce demagnetizing stress or provide operation at high permeance coefficient
- New materials will likely use the same elements that have been used for 150+ years. Therefore these new materials will likely depend upon:
  - ✓ A refined structure, perhaps built-up atoms at a time
  - ✓ Sophisticated thermal processing
- The greatest challenges we face with nano-structured material are:
  - ✓ They are more likely to be formed as nano-particulates requiring consolidation with alignment of domains
  - ✓ They are chemically reactive and potentially hazardous during processing thus requiring or benefiting from totally enclosed processing
- In the event that a nano-particulate cannot be fully densified, it must be made adequately passivated for inclusion in a bonding medium such as plastic or metal to form a bonded magnet



San Antonio



<http://chandra.harvard.edu/photo/2005/earth/index.html>

