• 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.
• We’ll start this presentation with a brief description of the market situation.
• Our survival depends upon successfully thwarting entropy.
• Interestingly, we do that by using energy.
• Energy is, thus, hugely important to our quality of life.
• ¾ 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.”


- 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.
Our World Touches Your World Every Day…

Need for Increased Efficiency

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/
- 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

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.
• Setting the stage
• The “Millennial Magnet Stakes”
  – Current R&D projects
• Elemental limitations
• 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.
• For permanent magnets, we are primarily interested in the 2\textsuperscript{nd} 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).
• 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.
• 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.
• 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.
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 ºC, 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.
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:

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.
• 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.
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

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.

Structure-related

- 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 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.
• 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.
• 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 Br and Hcj.
• 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 Fe₃B.
• 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 Br, high HcJ 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.
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)
• Setting the stage
• The “Millennial Magnet Stakes”
  – Current R&D projects
  • Elemental limitations
• Wrapping it up

• 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.
• 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.
• 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 for this and other useful spreadsheets and documents.

• This first table lists all of the elements.
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

<table>
<thead>
<tr>
<th>Soft Magnetic Materials</th>
<th>Major constituents</th>
<th>Minor constituent</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe</td>
<td></td>
<td>Low carbon mild steel</td>
</tr>
<tr>
<td>Silicon Steel</td>
<td>Fe, Ni</td>
<td>Si…FeSi at 2.5 to 6%</td>
<td></td>
</tr>
<tr>
<td>Nickel-Iron</td>
<td>Fe, Ni</td>
<td>Ni at 55 to 85%</td>
<td></td>
</tr>
<tr>
<td>Moly Permalloy</td>
<td>Ni, Fe</td>
<td>Mo</td>
<td>Ni at 75%, Mo at 4%, bal. Fe</td>
</tr>
<tr>
<td>Iron-Cobalt</td>
<td>Fe, Co</td>
<td></td>
<td>23 to 52% Co</td>
</tr>
<tr>
<td>Soft Ferrite</td>
<td>Fe, Mn, Ni, Zn, O</td>
<td></td>
<td>Amorphous and nanocrystalline</td>
</tr>
<tr>
<td>Metallic Glasses</td>
<td>Fe, Co, Ni, B, Si, P</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Permanent Magnets       | Fe, Co             |                  |
| Co-Steks                | 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-boron    | Fe, Nd, Dy, Y, B, Co, Cu, Ga, Al, Nb | |
| Cerium-iron-boron      | Fe, Nd, Ce, B      | Limited use in bonded magnets |
| SmFeNi                  | Fe, Sm, N          | Nitrogen is interstitial; stability issue |

- MnBi                    | Mn, Bi             | Never commercialized |
- MnBi(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.
• 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.
• 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.
• 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

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
• Shape of a cold compaction curve is dependent upon at least the following:
  ✓ Rate of pressure application
  ✓ Powder particle size and distribution
  ✓ Material hardness
  ✓ Britteness (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

Compaction Stages
- rearrangement
- elastic deformation
- plastic deformation
  (brittle)
  (ductile)
- fragmentation
- strain hardening
- bulk deformation

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


- 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