Accelerating Energy Innovations

Critical Materials Institute

AN ENERGY INNOVATION HUB

Developing Substitutes

Magnets – Phosphors – Materials Development Framework

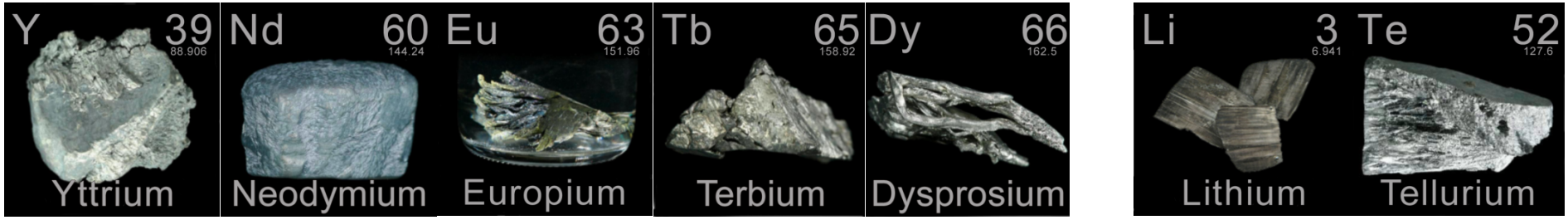
Adam Schwartz and Brian Sales

U.S. DEPARTMENT OF ENERGY

LLNL-PRES-643614

The Mission of CMI

Eliminate materials criticality as an impediment to the commercialization of clean energy technologies for today and tomorrow



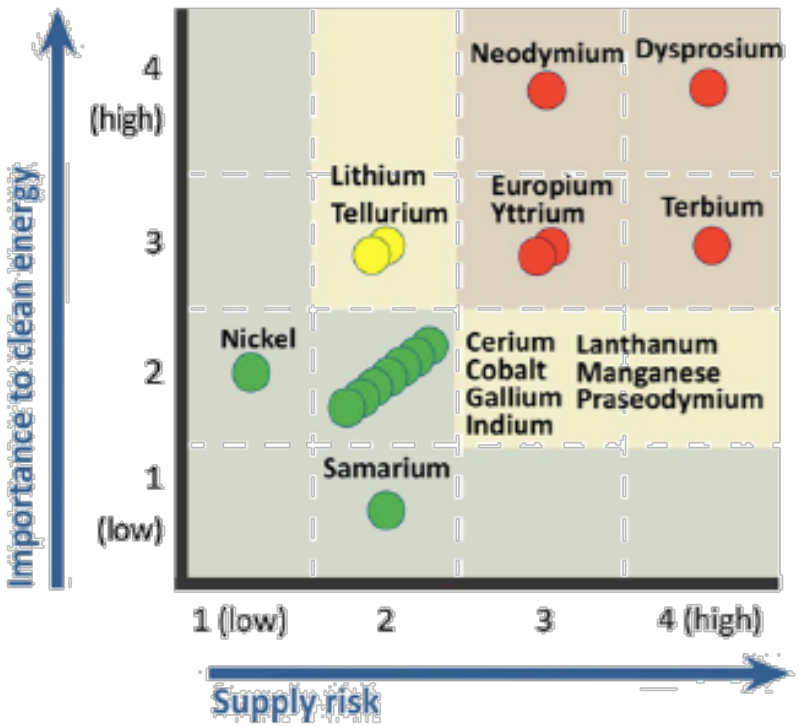
Long term goal of Developing Substitutes

Invent and qualify new materials that use little or no critical materials

Critical Materials Institute

Objectives: Developing Substitutes

- A substitute permanent magnet that exhibits properties similar to current $(Nd,Dy)_2Fe_{14}B$ magnets, but containing less Dy and Nd
- New phosphors that eliminate Eu^{3+} (red) and Tb^{3+} (green) from fluorescent lamp phosphors
- A closely coupled theoretical and experimental framework that can accelerate the invention and deployment of new substitute materials at a reduced cost



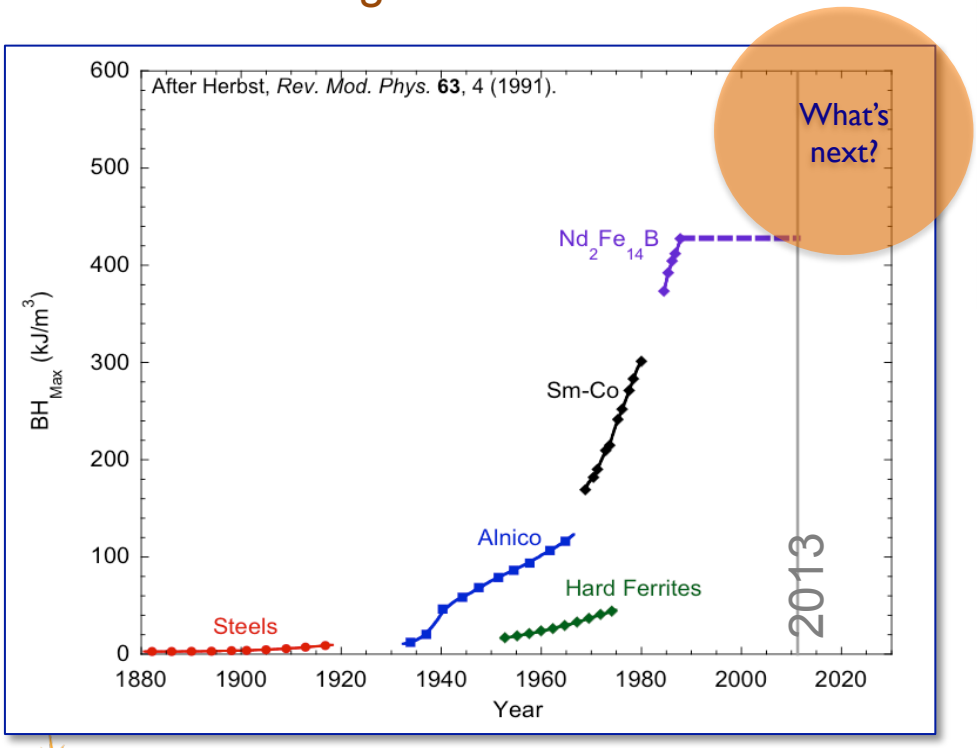
Medium Term Outlooks: 2015 – 2025

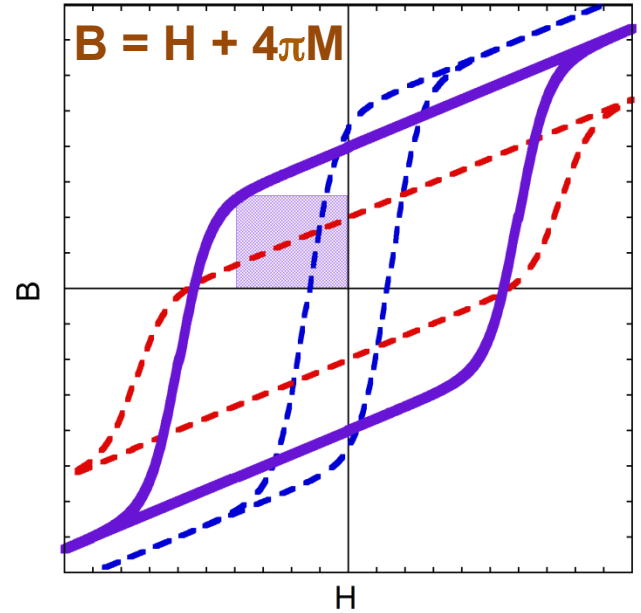
Critical Materials Institute

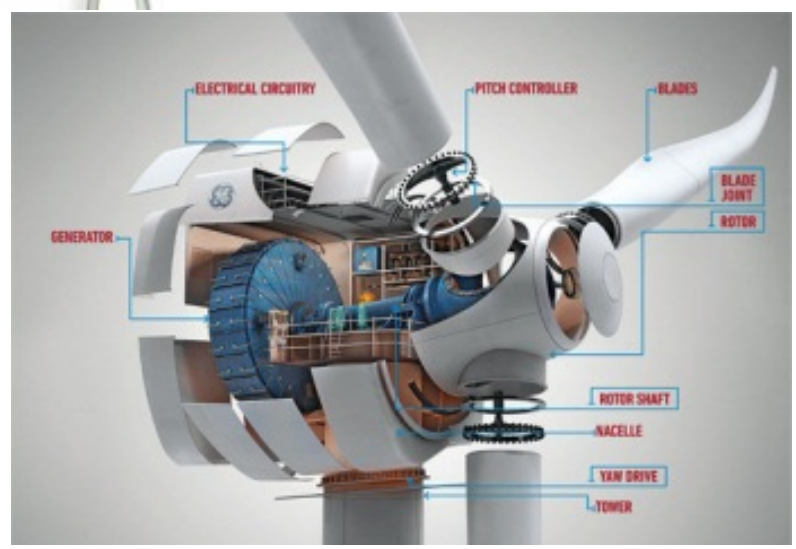
Developing Substitutes Magnets Team

The best permanent magnets are largely based on rare earth elements

- Hard disk drive spindle motors
- Portable electronics - speakers & microphones
- Small motors in vehicles
- Traction motors in electric vehicles
- Wind turbine generators

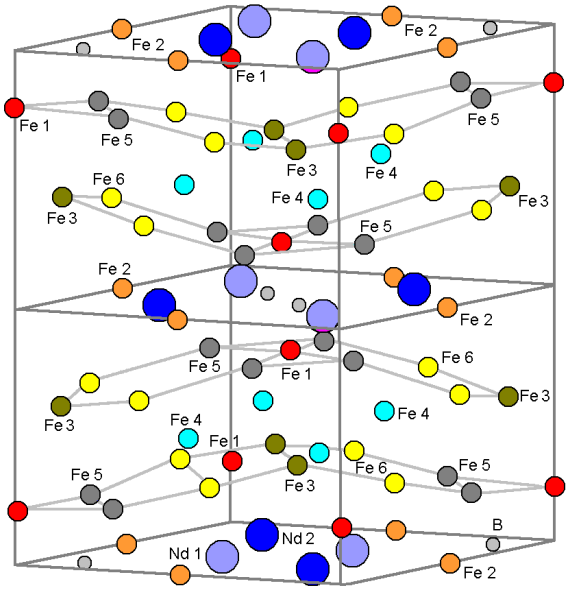


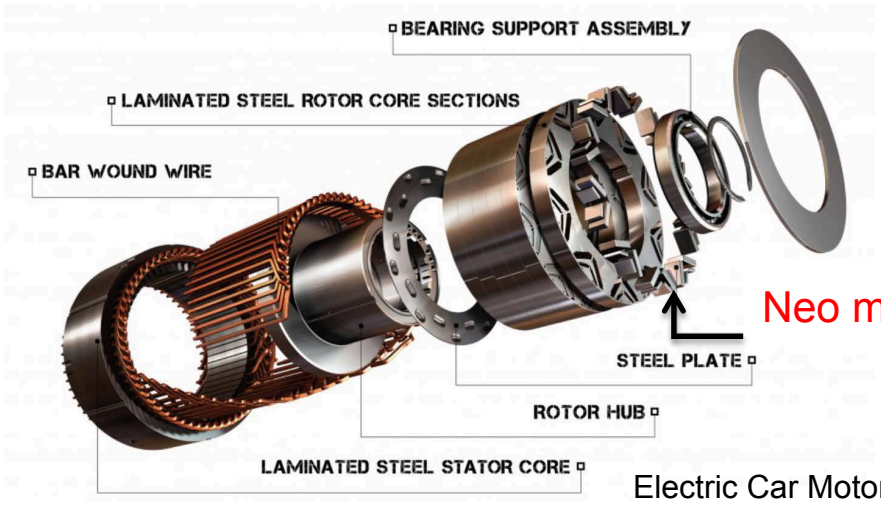




Critical Materials Institute

The best of the best permanent magnets are based on $Nd_2Fe_{14}B$





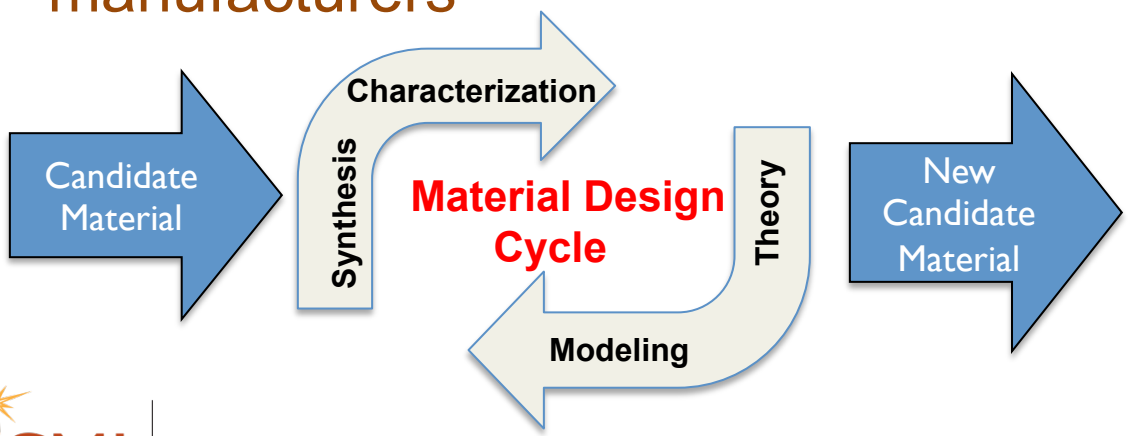
Neo magnets

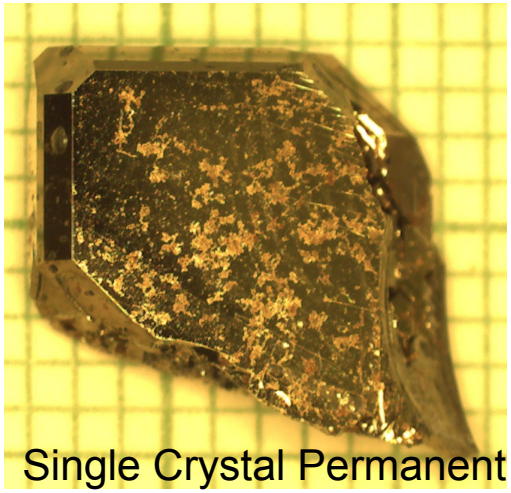
Electric Car Motor (GM)

- $Nd_2Fe_{14}B$ discovered/developed in 1984 to replace $SmCo_5$- partially as response to instability of cobalt supply from Zaire
- An expensive heavy rare earth, Dy, is added to improve magnet performance in electric motors and generators
- Both Nd and Dy in short supply

CMI will discover and develop new permanent magnets that use less rare earths

- Integrate theory, simulation, and modeling with synthesis, characterization, and testing
- Explore selected ternary phase compositions for transition metal rich magnets
- Develop and apply theory, modeling, and simulations to understand results and suggest improved compositions
- License new magnets with reduced rare earth content to US manufacturers





Single Crystal Permanent Magnet Material

Critical Materials Institute

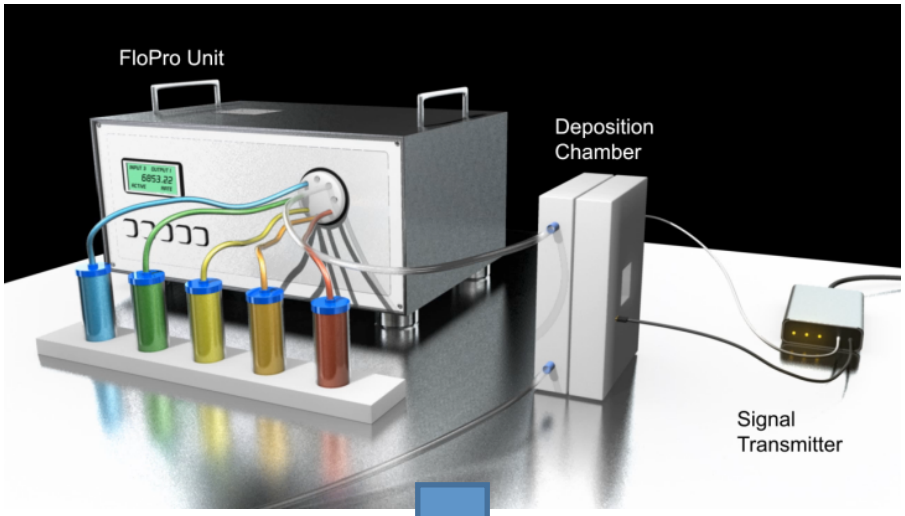
$Nd_2Fe_{14}B$ magnets are made with lots of waste

- **Powder metallurgical techniques employed include:**
  - Melting and casting
  - milling and hydrogen decrepitation
  - aligning followed by sintering
  - finally finishing that involves cutting and/or grinding
  - During this last step a lot of material is wasted and very difficult to recover

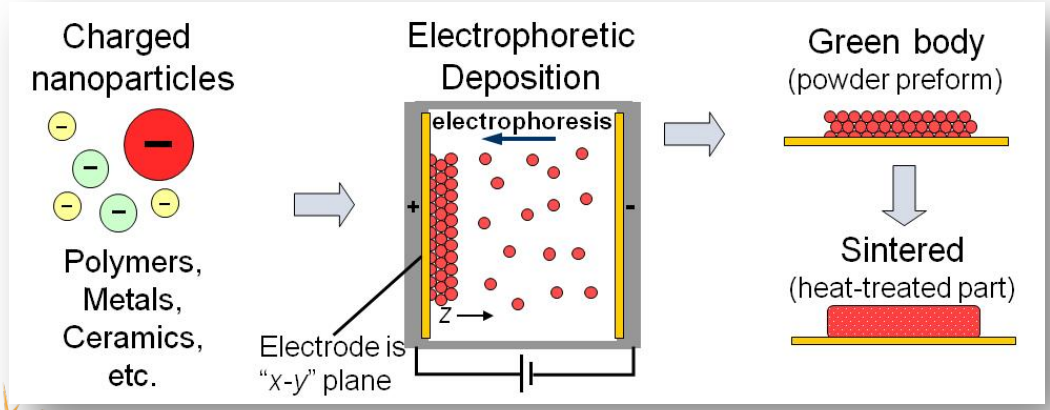
Develop additive manufacturing of permanent magnets with less rare earths and no waste

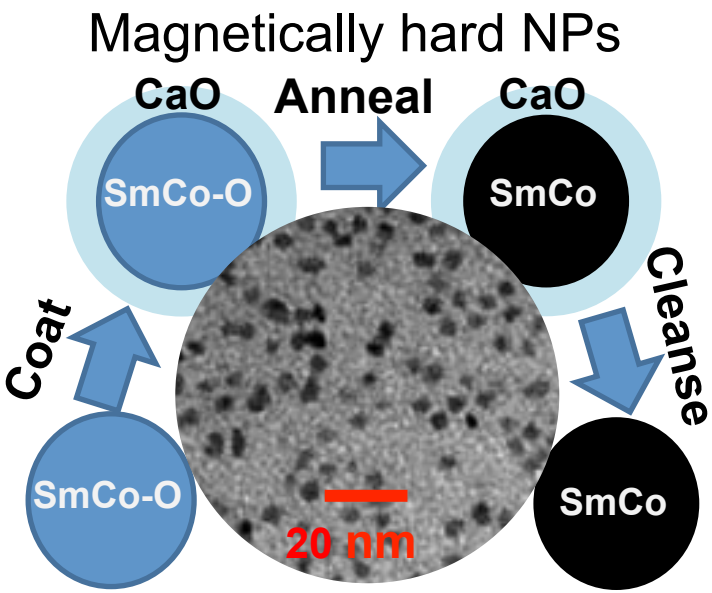
- Additive Processing of Permanent Magnets
- Functionally modifying sintered magnets to minimize the need for Dy
  - Ink-jet printing and pulsed thermal processing for improved magnet properties
  - Electron beam and laser-based additive manufacturing techniques for the near net shape production of sintered and bonded permanent magnets
  - Discover new permanent magnets through transition metal substitution

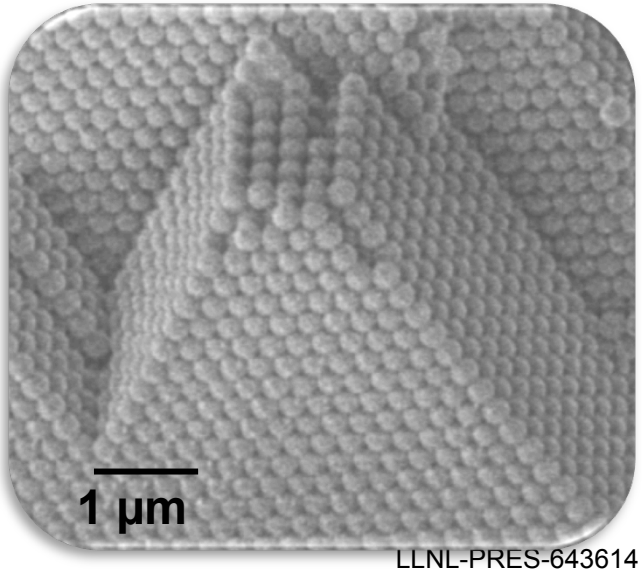
Exchange Spring Magnets: Requires precise control of size and position



Position controlled via electrophoretic deposition

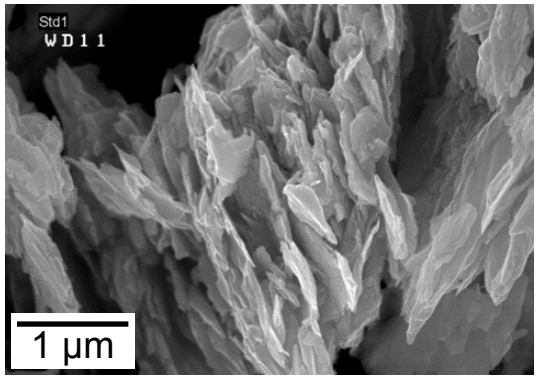




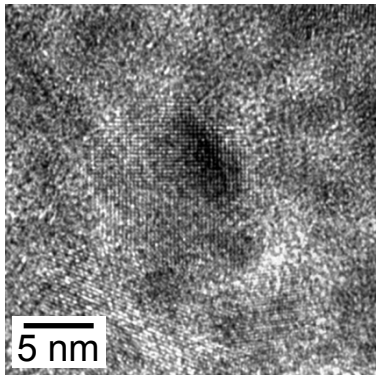


Critical Materials Institute

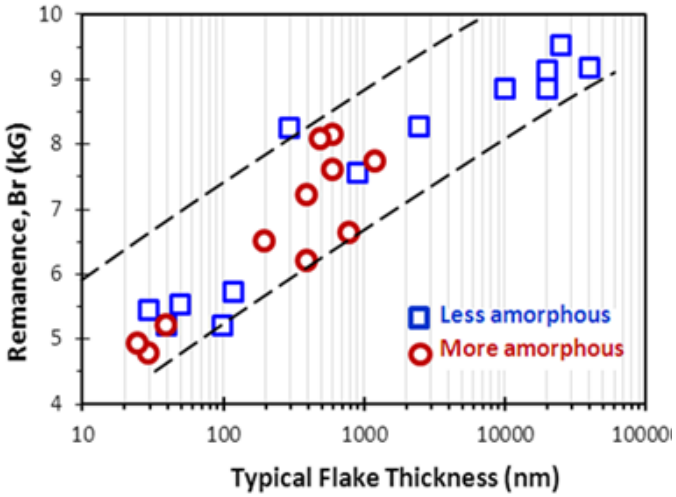
Optimization of grain boundaries and interfaces in fine particle magnets



$SmCo_5$ nanoflakes made by mechanical milling



$SmCo_5$ nanoparticle made by chemical synthesis



Property deterioration at small size

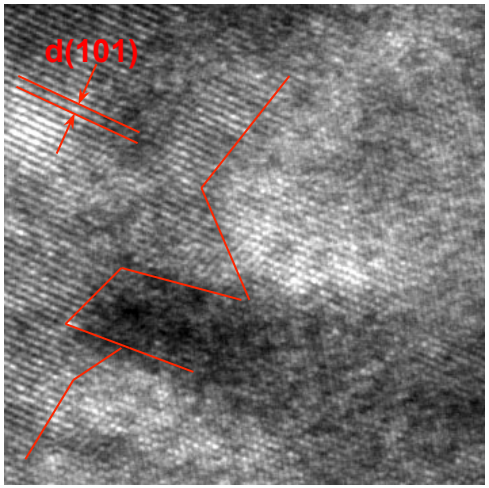
- Nanoparticles of permanent magnets are essential building blocks of high performance nanocomposite magnets
- Nanoparticles made by chemical and mechanical methods
- Magnetic properties substantially deteriorate with decreasing particle size

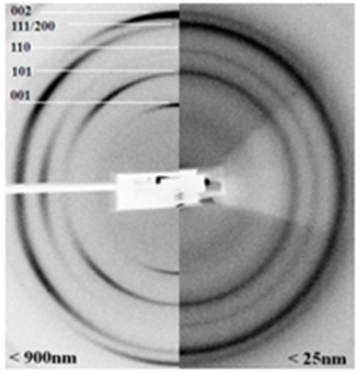
Critical Materials Institute

Optimization of grain boundaries and interfaces in fine particle magnets

- Use advanced microscopy techniques to probe nanostructure of permanent magnet nanoparticles
- Develop structure/processing/property relationships to identify root causes of magnetic property deterioration
- Identify processing routes that lead to improve magnetic particle properties
- Microscopically verify improved nanoparticle structure

High resolution transmission electron microscopy of the $SmCo_5$ nanoflakes showing irregular boundaries and considerable local disorder of the lattice





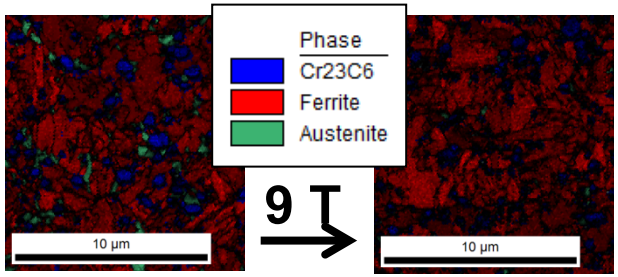
Transmission x-Ray diffraction pattern comparing $SmCo_5$ nanoflakes milled to different sizes

Critical Materials Institute

Thermo-magnetic processing: a powerful tool for microstructural control

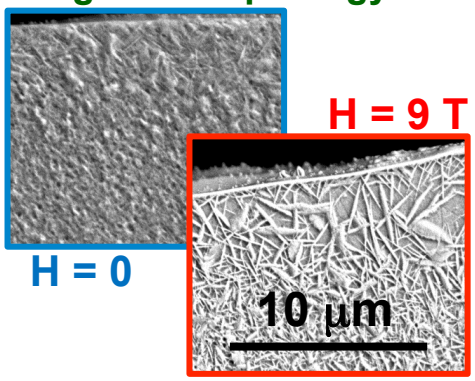
- Employ unique high-magnetic-field processing techniques to refine the microstructures of rare-earth magnet materials to increase anisotropy which will allow reduced rare-earth content.
- High magnetic fields drive crystallographic alignment and have significant kinetic and thermodynamic effects, facilitating phase transformations and altering equilibrium phase diagrams.

Examples of microstructural changes produced by thermomagnetic processing.



Processing steel in a 9 Tesla magnetic field minimizes retained austenite.

Crystallizing ferromagnetic alloy in a magnetic field changes grain morphology.

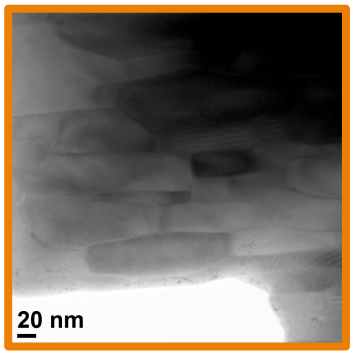


Commercial-scale systems enable crystallization, annealing, sintering, compacting, extruding, sonicating etc. in fields to 9 Tesla and temperatures exceeding 2000 °C.

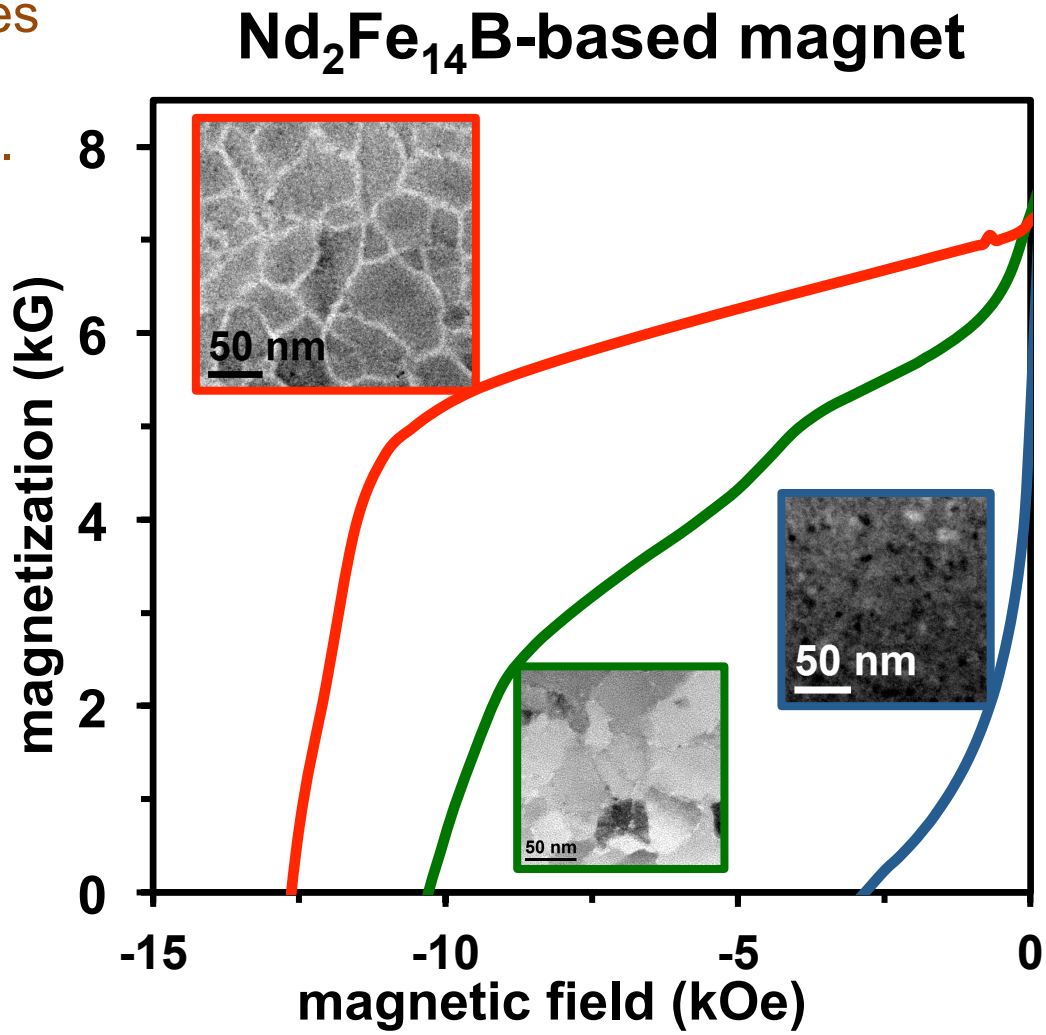
Critical Materials Institute

Microstructure determines magnetic performance

- Carefully tailored microstructures will allow more efficient use of rare-earth elements in magnets.
- Rapid solidification results in high coercivity but low energy product due to random grain alignment.
- Ideal nanostructure: aligned crystallites separated by a thin (~3nm) magnetically soft phase with smooth grain boundaries.



Aligned grains in an anisotropic rare-earth magnet.



Refining microstructure of a rapidly quenched alloy by controlled annealing promotes an isolated nanoscale structure with enhanced coercivity

Critical Materials Institute

Developing Substitutes Phosphor Team

Mao-Hua Du | Bill Cohen | Steve Payne | Kiel Holliday | Nerine Cherepy | Vanita Mani | Adam Schwartz

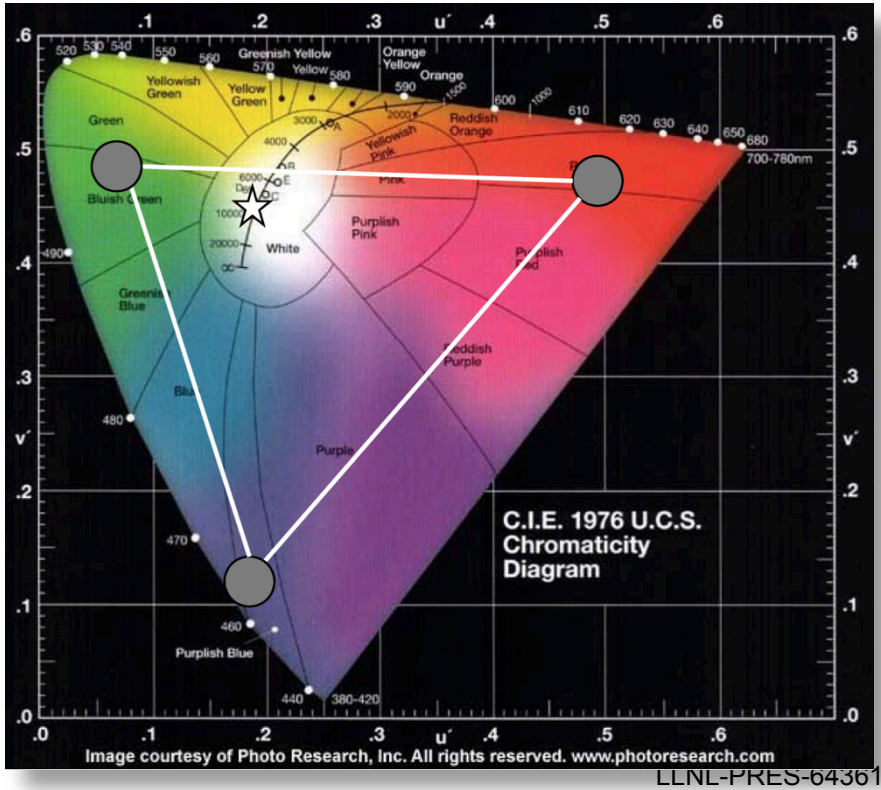
Alok Srivastava

Lynn Boatner

Critical Materials Institute

Terbium & Europium

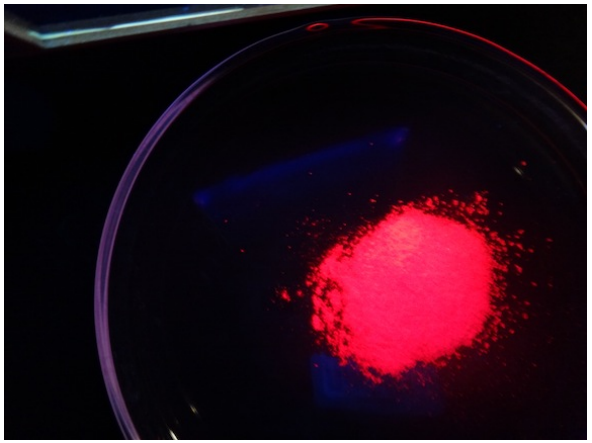
- Provide green and red light emission
- Traditional uses:
  - CRTs
  - Long-tube fluorescent lamps
  - Flat panel color displays and TVs
- Current uses:
  - Compact fluorescent lamps
  - Personal electronics
- Future uses:
  - LED lighting
  - OLED displays



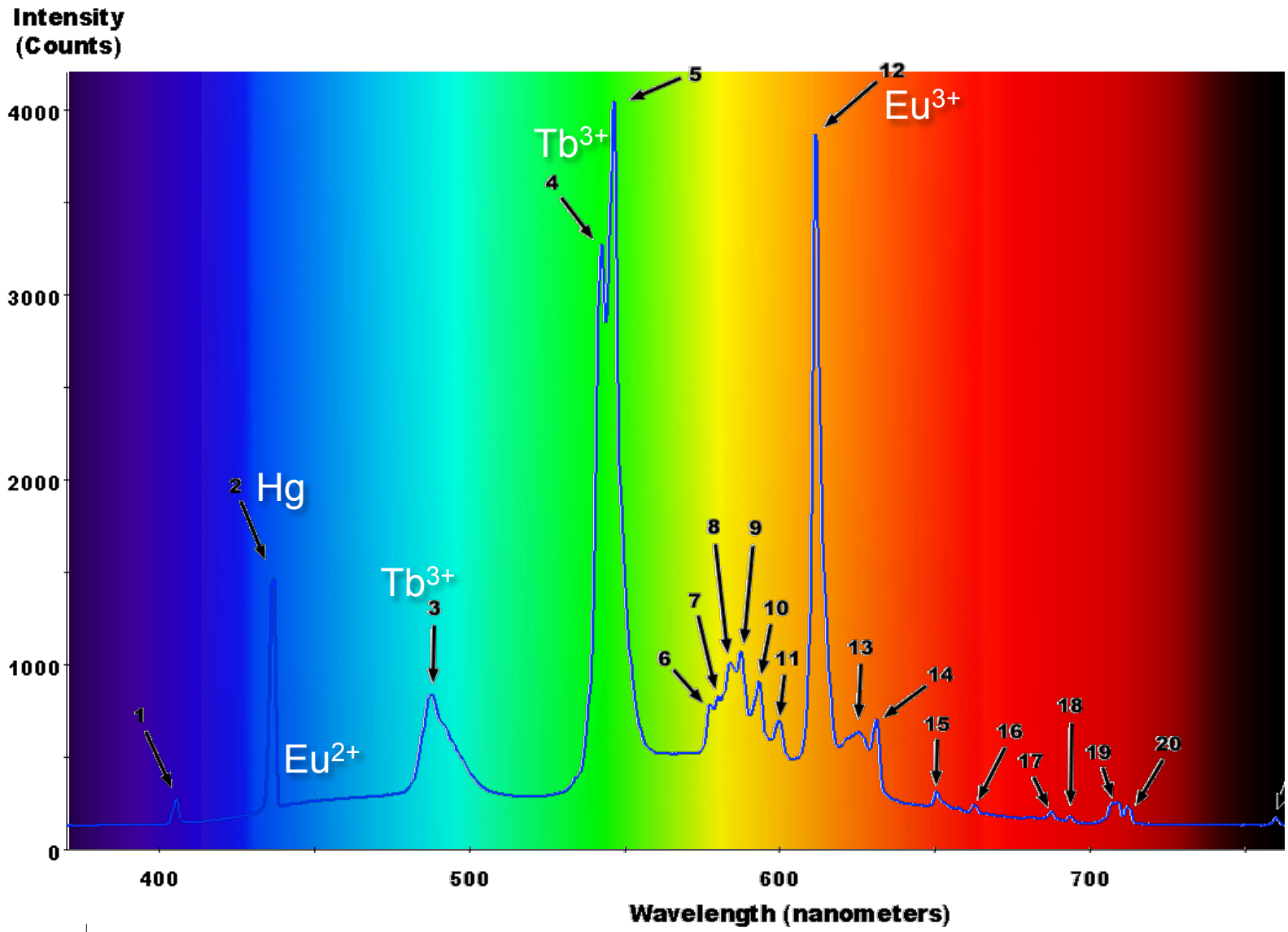
Critical Materials Institute

Phosphor strategy considerations

- Current fluorescent lamps use Eu3+ (red) and Tb3+ (green)
- ~1 billion fluorescent lamps remain in use
- Use may decline when LEDs replace fluorescents (10-20 yrs?)
- Use of phosphors is currently expanding as fluorescent lights (particularly CFLs) gain market share
- Solid state lighting is gaining momentum
- LEDs still use phosphors, but are more efficient and need less
- Short and mid-term solutions are needed
  - Recycling of Eu and Tb from used lamps
  - Replacement with less-critical materials



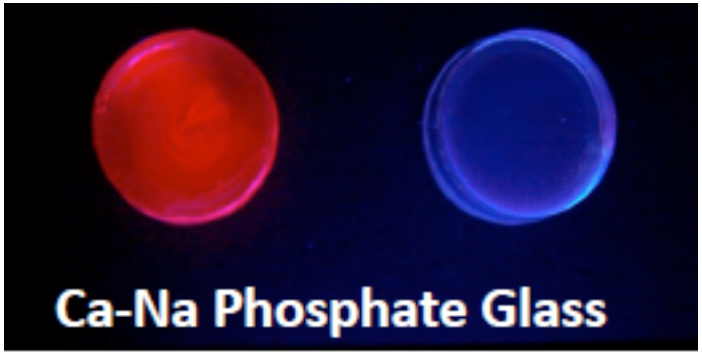
Phosphor design

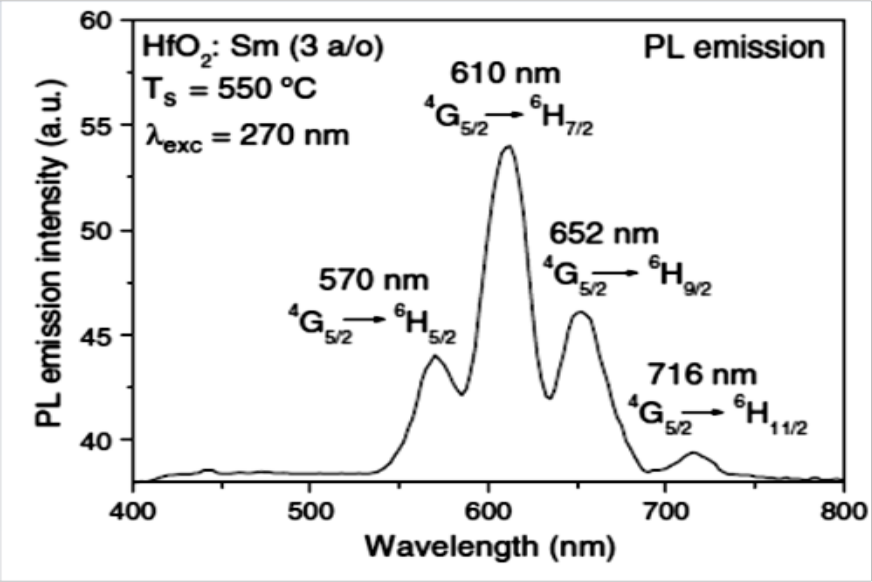


Critical Materials Institute

New phosphors with less rare or no rare earths

- Replace Eu^{3+} with Sm^{3+} or Mn^{4+}
- Replace Tb^{3+} with Mn^{2+}
  - Predict, control, and tailor crystal field splitting for optimization
  - Synthesize, characterize and test candidate phosphors
  - Evaluate lamp performance
  - Scale up production
- Integrate expertise across LLNL, ORNL, AMES, GE

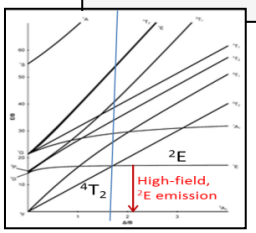




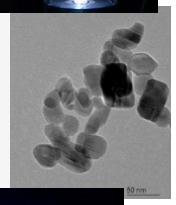
Critical Materials Institute

Substitution efforts address four key areas

Candidate Selection
- Literature & databases
- Classic models: Judd-Ofelt; Tanabe-Sugano; Crystal field
- Advanced quantum models

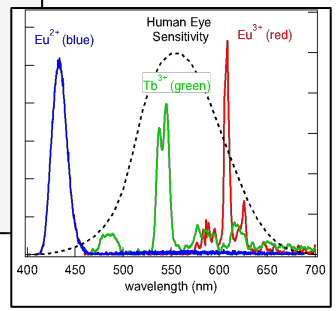


Synthesis
- Combustion
- Precipitation (e.g. urea)
- Solid state reaction
- Flame synthesis
- Vapor doping
- Post-treatments



New phosphor meeting all specifications

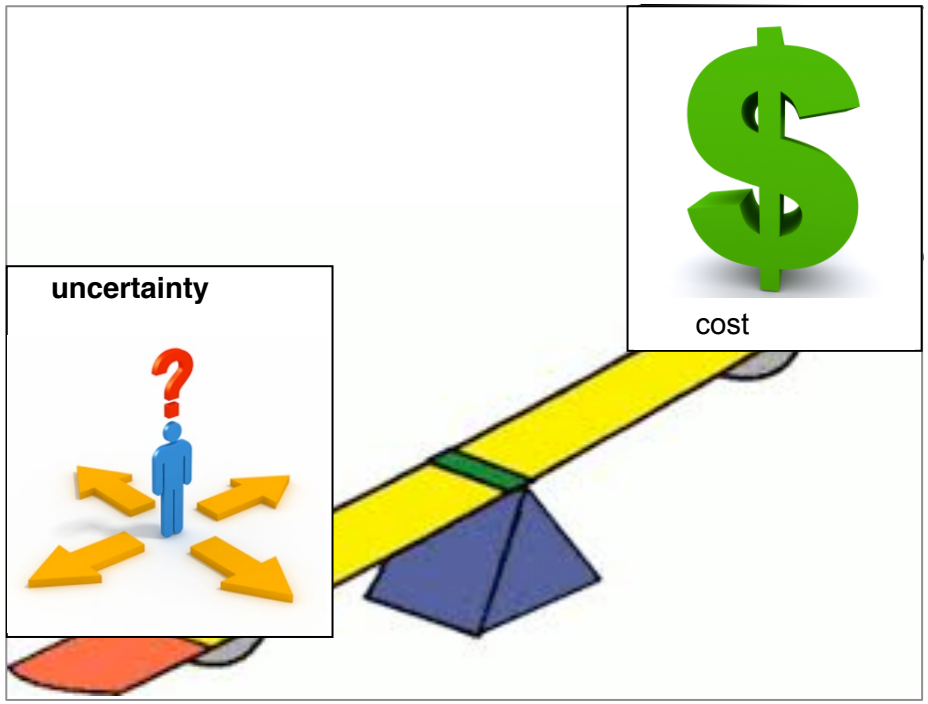
Characterization
- Emission (CIE)
- Absorption
- Decay time
- Photo-stability
- Structure
- Composition



Lamp Performance
- Mercury resistance
- Water insensitivity
- Firing stability
- Radiation resistance
- Protective coating (?)
- *Long-term stability*

Quantitative framework for cost-efficient material development

How to balance theory and experiment in materials R&D?



Material simulations are becoming more accurate but more expensive (ditto for material experiments).

All measurements and calculations have uncertainties.
"In life, the only certainty is uncertainty."

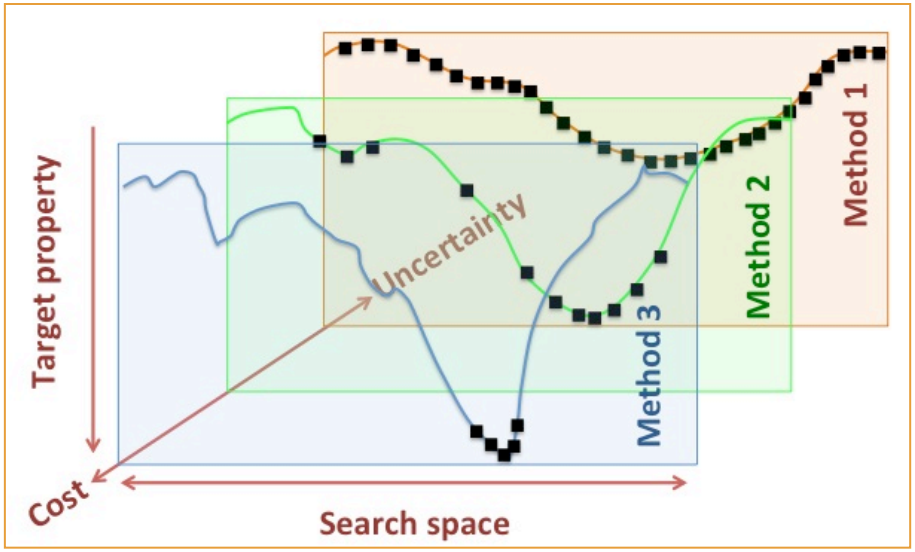
Utility of experiments and calculations for material R&D can be defined and quantified on an equal footing, on the balance of their uncertainties and costs.

Quantitative framework for cost-efficient material development

Multi-fidelity cost-efficient adaptive search/optimization algorithms

$$\text{Method utility} = \text{Accuracy} \times \text{Efficiency} = \frac{1}{\text{Uncertainty} \times \text{Cost}}$$

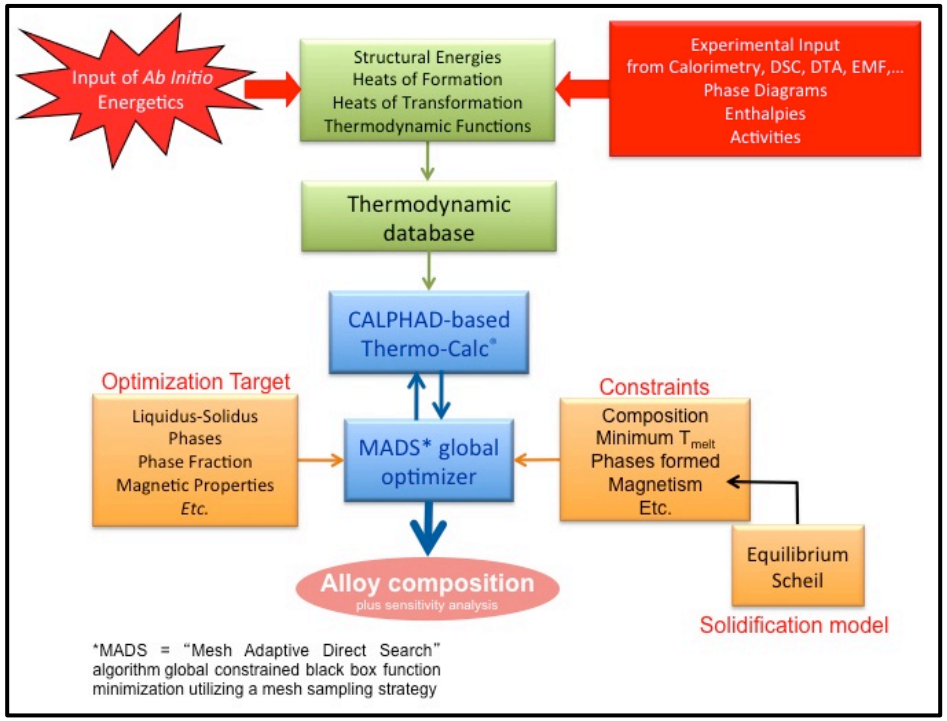
- **Multi-fidelity: Explore material search space by taking samples of varying quality**
- **Cost-efficient: Select next sampling point & sampling method to maximize the expected model improvement per unit sampling cost**
- **Adaptive: The uncertainty/cost ratios of the sampling methods are re-evaluated to make subsequent search more efficient**



Critical Materials Institute

Efficient prototyping of rare earth-based alloys from *ab initio* electronic structure and thermodynamics

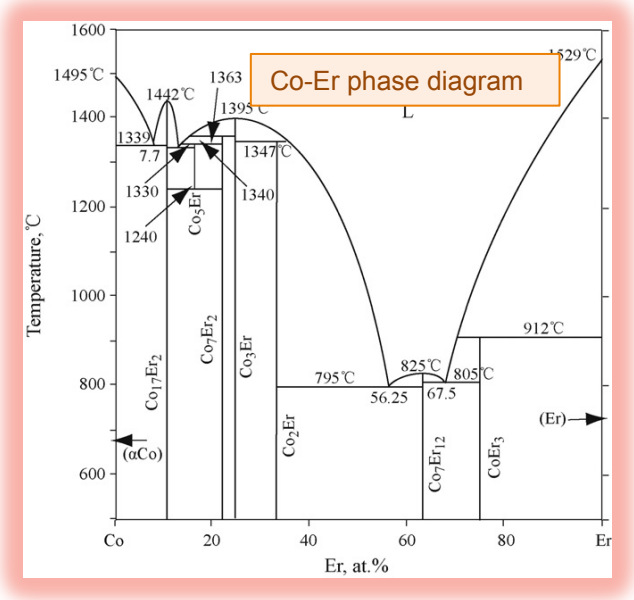
- Prediction of *phase-stability* trends and *phase diagrams* of RE-based multi-component alloys is crucial for predicting materials properties and performance
- A *Materials Design Simulator* (MDS) will be implemented to search for solute replacements to RE that provide materials stability and performance

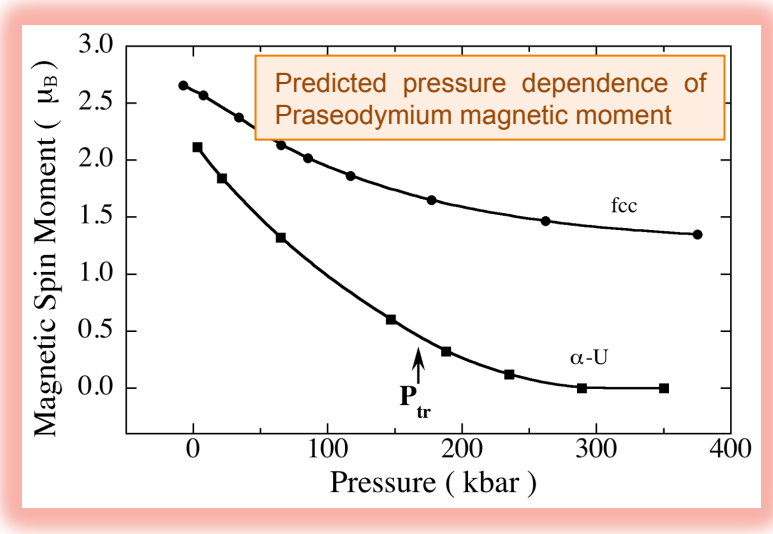


Critical Materials Institute

Efficient prototyping of rare earth-based alloys from *ab initio* electronic structure and thermodynamics

- Solution: Improved *ab initio* – CALPHAD thermodynamics – experiments coupling, and efficient search engine to optimize properties of new complex RE systems, *e.g.*, melting temperature, preferred phases, magnetism, *etc*
- Output: Prediction of the role of solutes on stability and magnetism in RE-based alloys
- Output: Guidance from MDS for experimental design of new RE alloys and compounds, and accelerated and safe insertion of materials into application

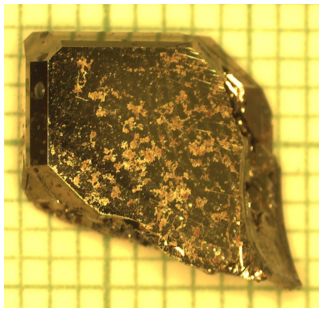


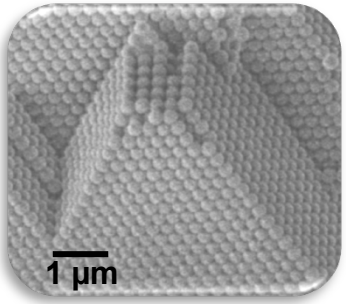


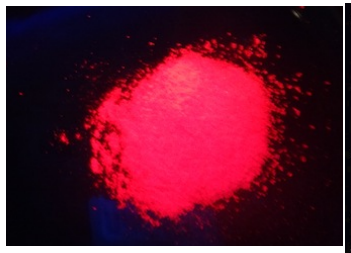
Critical Materials Institute

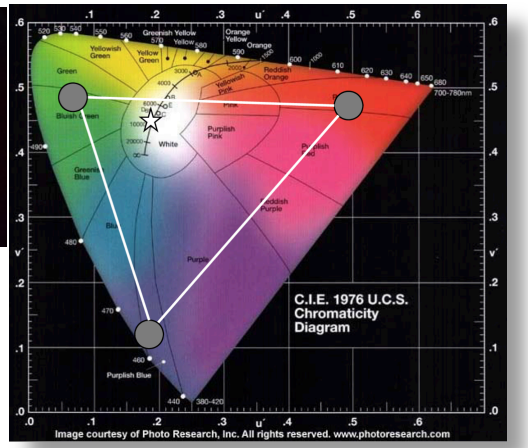
Developing Substitutes will invent and qualify new materials that use little or no critical materials

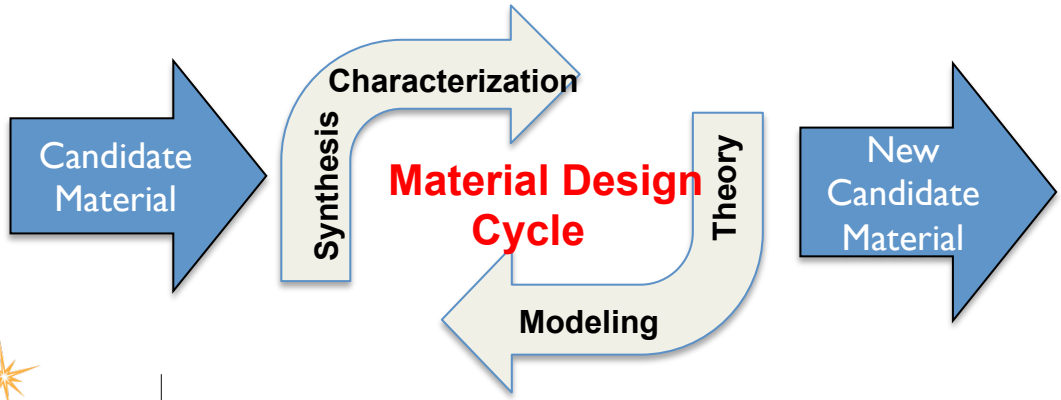
- A substitute permanent magnet that exhibits properties similar to current magnets, but contains less Dy and Nd
- New phosphors that eliminate Eu^{3+} and Tb^{3+} from fluorescent lamp phosphors
- A closely coupled theoretical and experimental framework that accelerates the invention and deployment of new substitute materials at a reduced cost

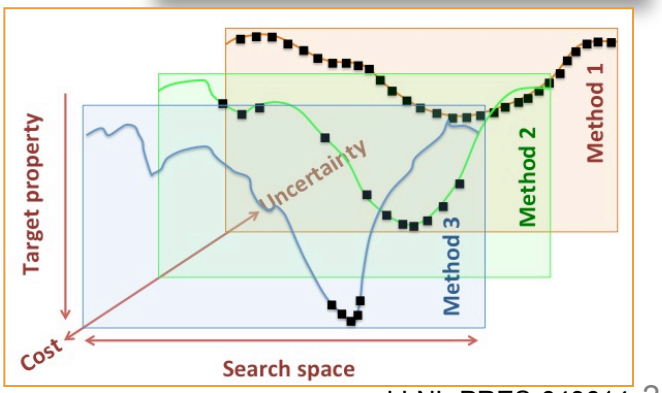












Critical Materials Institute

Thank You!

Questions?