Non-rare earth magnetic materials

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PM045

Overview

Timeline

- Project start date – Oct. 2009
- Project end date – Sept. 2015
- Percent complete – 57 %

Budget

- Total project funding (FY09-12)
  $1314K
- Funding received in FY12
  $360K
- Funding for FY13
  $234K (est.)

Targets / Barriers

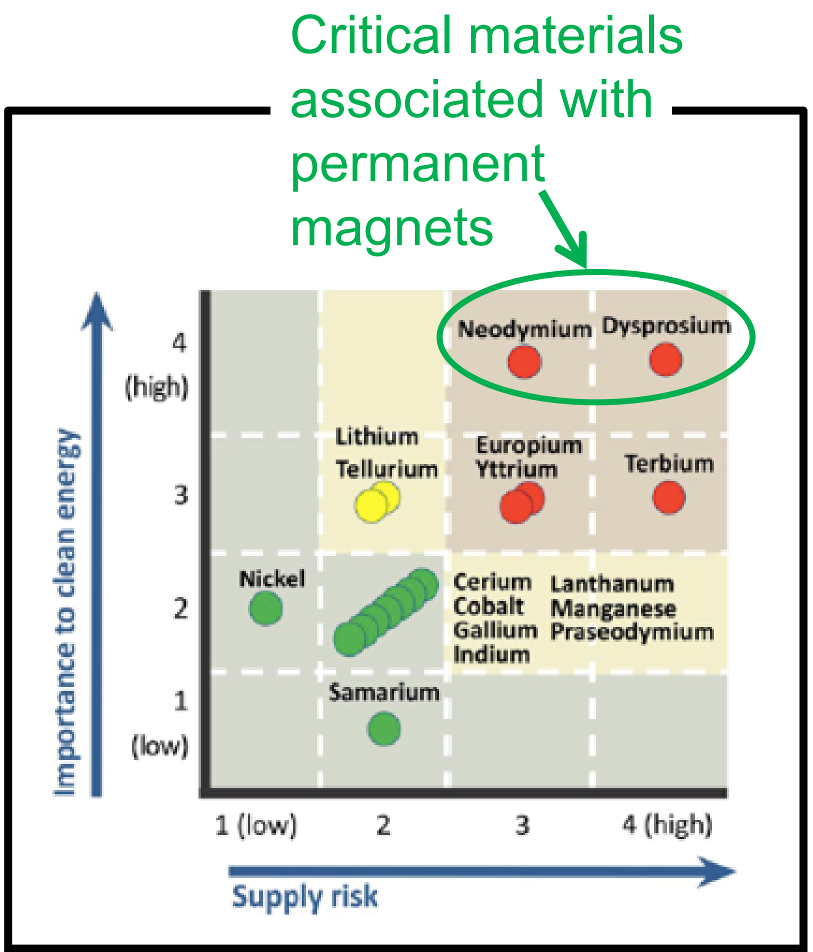
- Relevant Targets
  - lowering the cost of electrical propulsion systems toward
    - 2015 (2020) target of 12 (8) $/kW
- Relevant Barriers
  - **Limited domestic supply:** rare-earth elements.
  - **Cost:** high-performance permanent magnet materials.

Collaborations

- ORNL: *computation, processing*
- Univ. Tenn.: *characterization*
- Georgia Tech Research Institute: *characterization*

Relevance: the problem

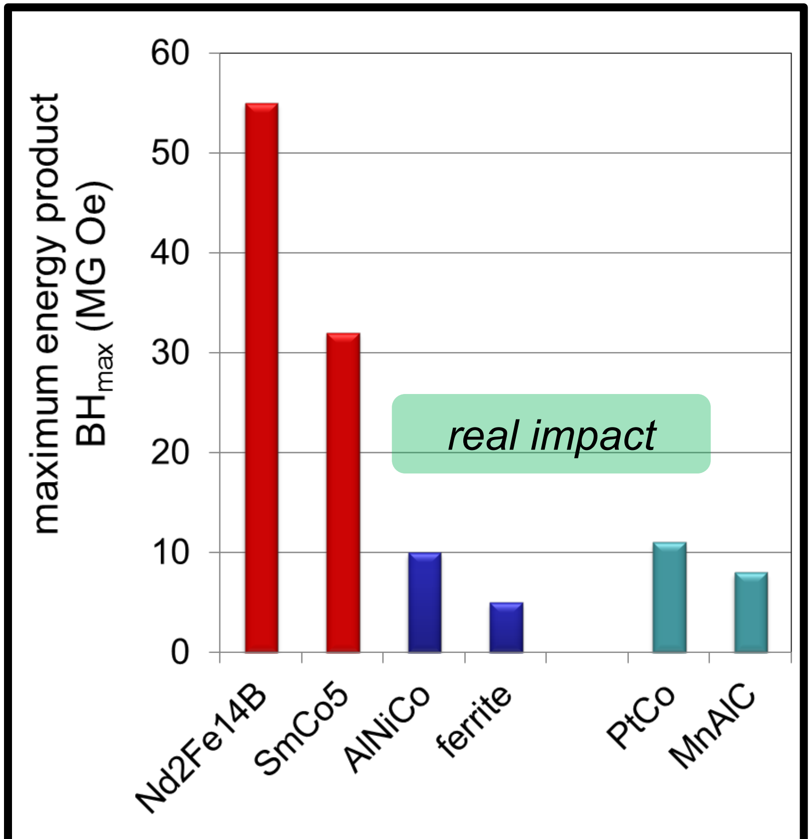
- **Permanent magnet (PM) motors** are key for state-of-the-art electric motors for propulsion.
- Magnets account for:
  - 40% of current motor materials cost.
  - 30% of current motor cost.
  - ***60% of 2020 target motor cost***.
- **Reducing magnet cost** is critical to meeting targets with internal PM motors.
- Available high-performance magnets contain ***rare-earth elements***, which are expensive and subject to supply chain disruptions.



DOE Critical Materials Strategy 2011

Relevance: project objectives

The overall goal of this project is to identify alternative hard ferromagnetic materials which do not contain rare-earth elements and are relevant to PM motor technology.



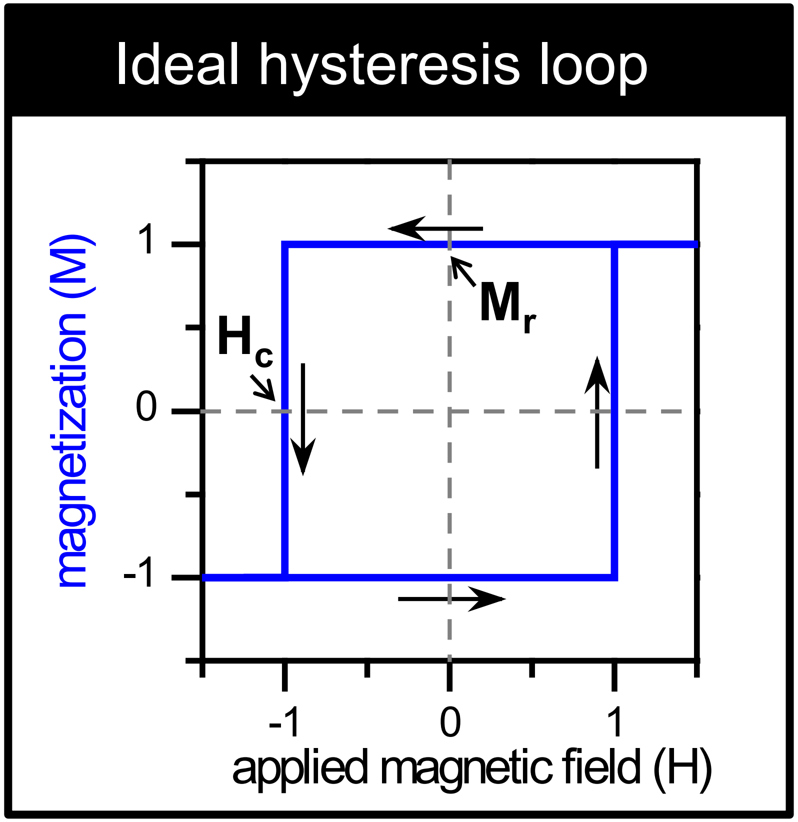
Energy product: amount of magnetic energy available to do work. (1 MG Oe = 8 kJ / m^3)

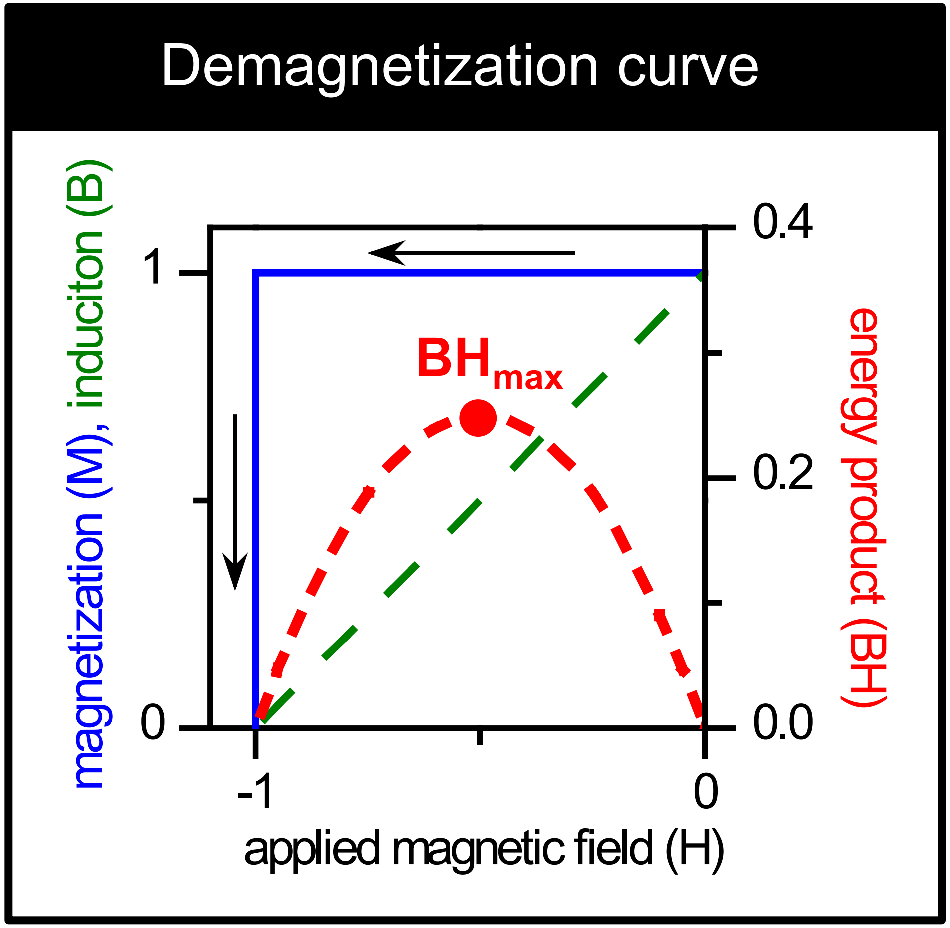
- **Objectives** of this project:
  - Identify new materials in chemical systems which contain elements with the most promise for good PM properties.
  - Examine known materials worth further study.
  - Understand the usefulness of heavy transition metals for magnetic anisotropy.
- **Relevance** to VT program:
  - The availability of alternative PM materials, especially those without rare-earth elements, may enable progress toward cost targets for motors.

Approach: magnetic performance

Parameters characterizing magnetic performance:

- Remanent magnetization (M_r)
- Coercive field (H_c)
- Energy product (BH)
- Curie temperature (T_C)

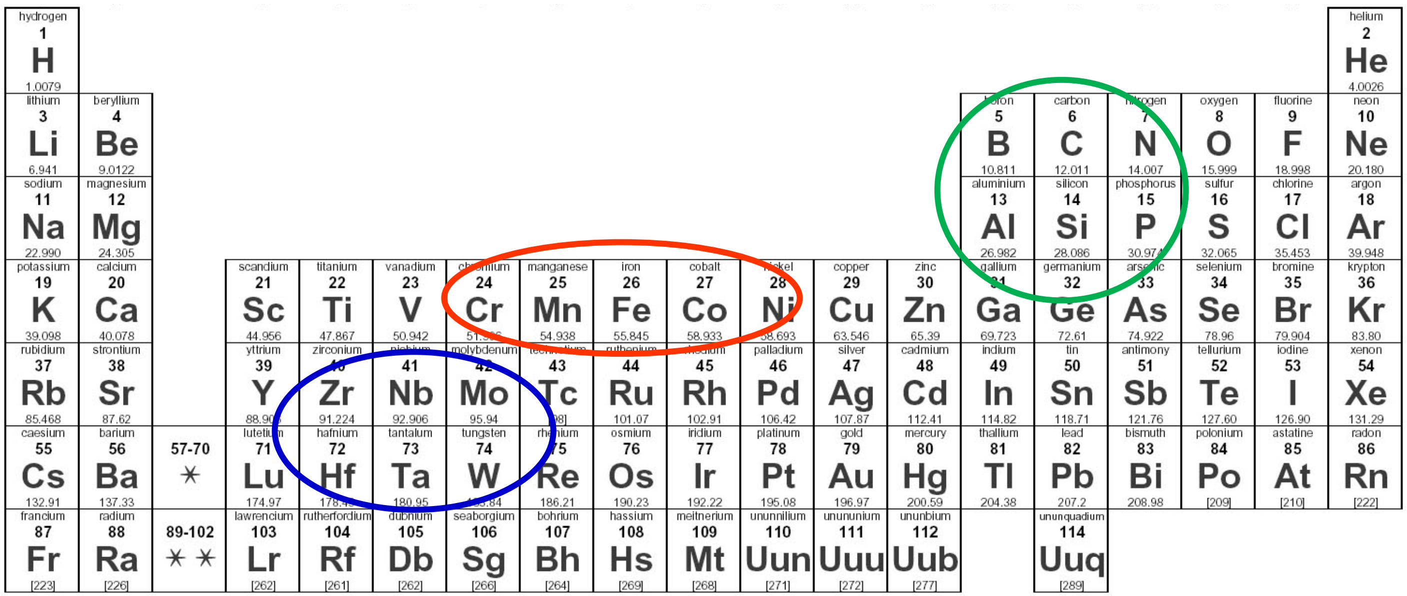




Approach: methodology

This project addresses the **technical barrier of cost and availability of rare-earth elements** by focusing on ***rare-earth free chemical systems***.

Uniqueness: *Utilize **heavy transition metals** instead of rare-earth elements to provide anisotropy. **Focus on new PM materials.***



Target non-cubic crystal structures rich in 3*d* transition metals (strong magnetism), with heavier transition metals (strong spin-orbit coupling), as well as light “interstitials” elements (complex/new materials).

Approach: milestones

Month/Year	Milestone
September 2012	**Milestone:** Determine usefulness of metal flux synthesis technique for producing crystals of new ternary phosphides with high transition metal concentrations. **Complete:** Small crystals or many complex phases produced. Continue with technique.
September 2012	**Milestone:** Develop capabilities to produce sub-nitrides using flowing ammonia gas, and examine effects of mild nitriding conditions on magnetic intermetallic compounds. **Complete:** Poor reactivity of metals with nitrogen and poor thermal stability of products prevented significant progress. This route toward new magnets was determined to be inappropriate for this project.
September 2013	**Milestone:** Identify new ferromagnetic phosphides using metal-flux crystal growth and conventional synthesis methods, and assess their potential for PM applications. **Progress:** Exploratory crystal growth experiments ongoing.
September 2013	**Milestone:** Apply high magnetic field processing capabilities available at ORNL to stabilize ferromagnetic phases in rare-earth-free chemical systems. **Progress:** Initial experiments have demonstrated stability enhancement induced by high magnetic fields.

Progress

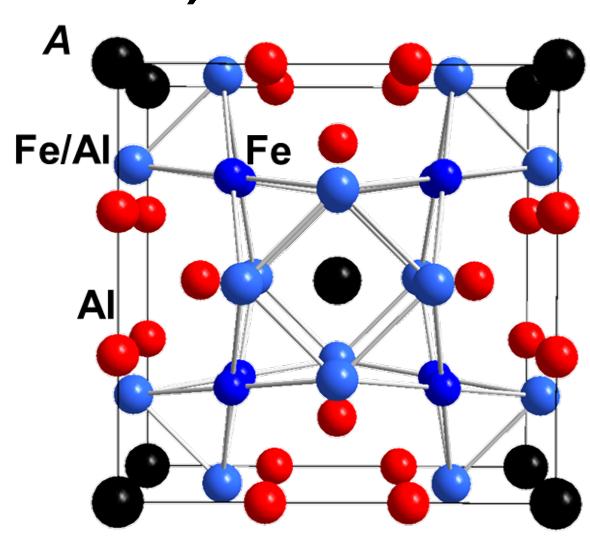
- **New ferromagnets: $ZrFe_{12-x}Al_x$ and $HfFe_{12-x}Al_x$**
  FY11-12

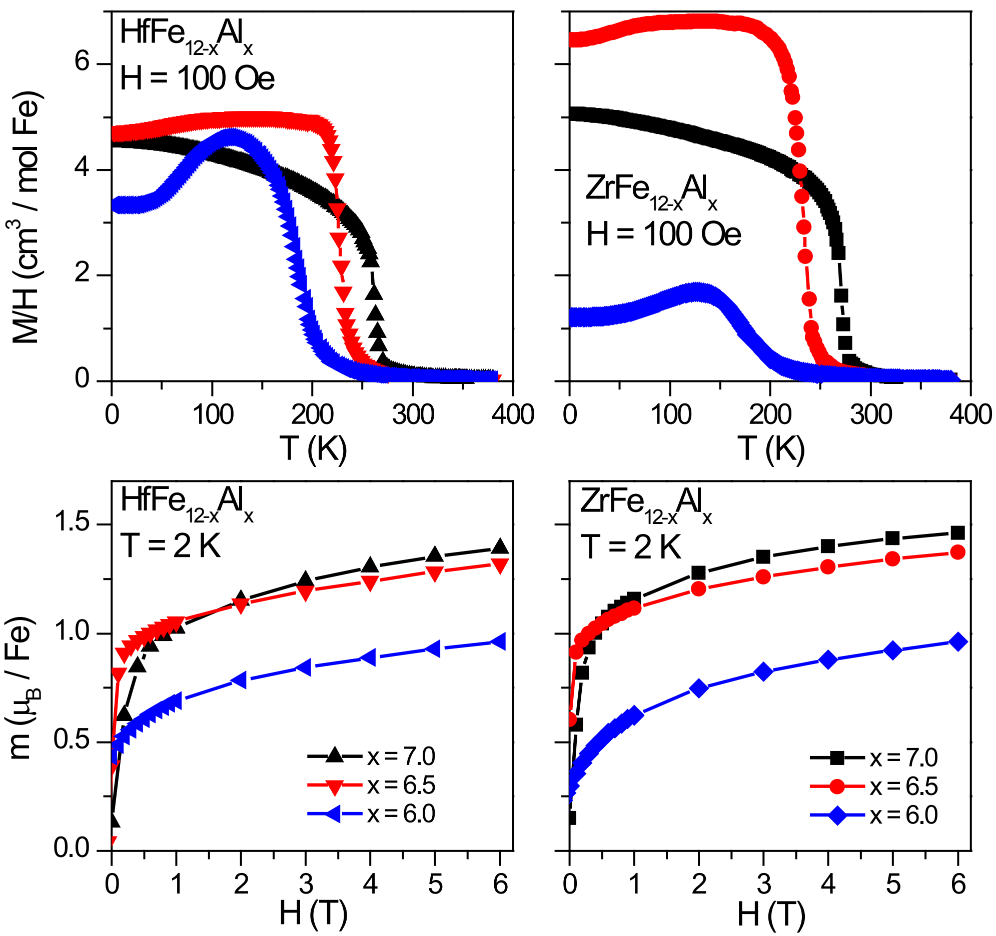
- **Stabilizing $L1_0$ magnetic phases: $FePd_{1-x}Ni_x$**
  FY13

- **Promising new permanent magnet system: $Hf_2Co_{11}B$**
  FY10-13

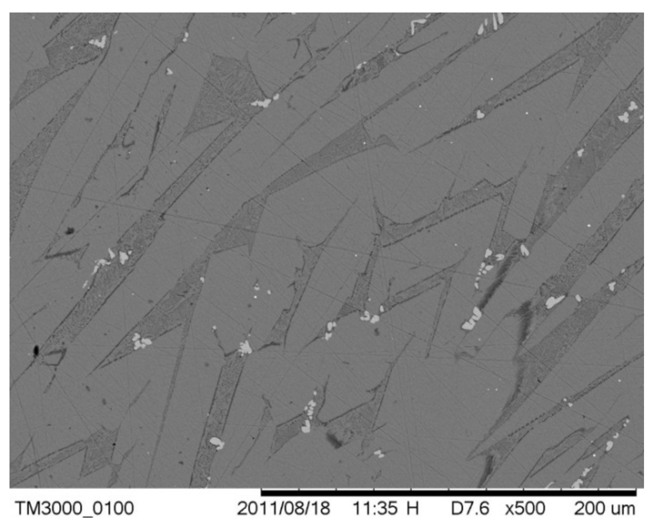
Progress: $A\mathrm{Fe}_{12\text{-}x}\mathrm{Al}_x$ (A = Zr, Hf)

- **Discovered new Fe-Al based ferromagnets**
- Synthesized materials with varying Al contents
- Characterized crystallographic, magnetic, and microstructural properties



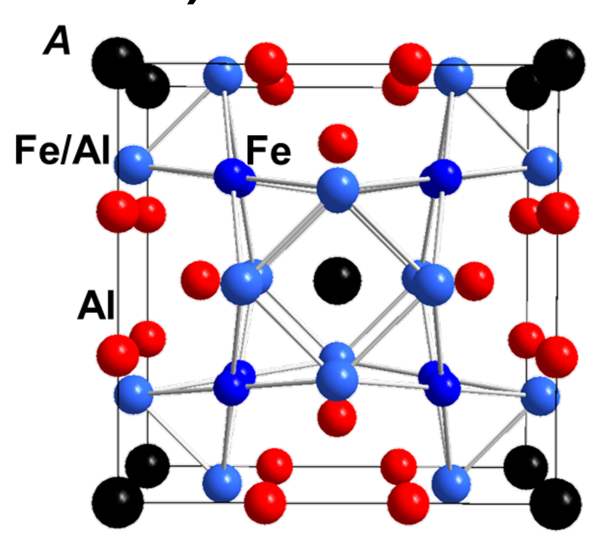


Scanning electron micrograph of $\mathrm{HfFe_6Al_6}$

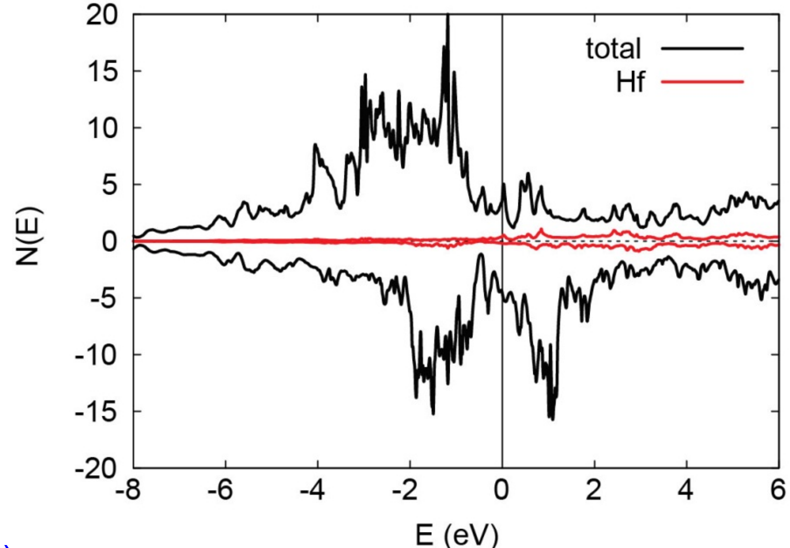


Progress: $A\mathrm{Fe}_{12-x}\mathrm{Al}_x$ (A = Zr, Hf)

- **Discovered new Fe-Al based ferromagnets**
- Synthesized materials with varying Al contents
- Characterized crystallographic, magnetic, and microstructural properties
- Understood experimental data using results of first principles calculations
    - Remanent magnetization may be due to magnetic moments on Zr/Hf.
    - Antiferromagnetic interactions among certain Fe sites suppresses ferromagnetism at high Fe contents



composition	T_C (K)	M_S (μ_B / Fe)	M_r (μ_B / Fe)
$ZrFe_5Al_7$	271	1.46	0.15
$ZrFe_{5.5}Al_{6.5}$	233	1.37	0.6
$ZrFe_6Al_6$	170-190	0.96	0.3
$HfFe_5Al_7$	263	1.39	0.13
$HfFe_{5.5}Al_{6.5}$	230	1.32	0.39
$HfFe_6Al_6$	180-195	0.96	0.44



- Reported findings: J. Appl. Phys. **111**, 093918 (2012).

Progress

- **New ferromagnets: $ZrFe_{12-x}Al_x$ and $HfFe_{12-x}Al_x$**
  FY11-12

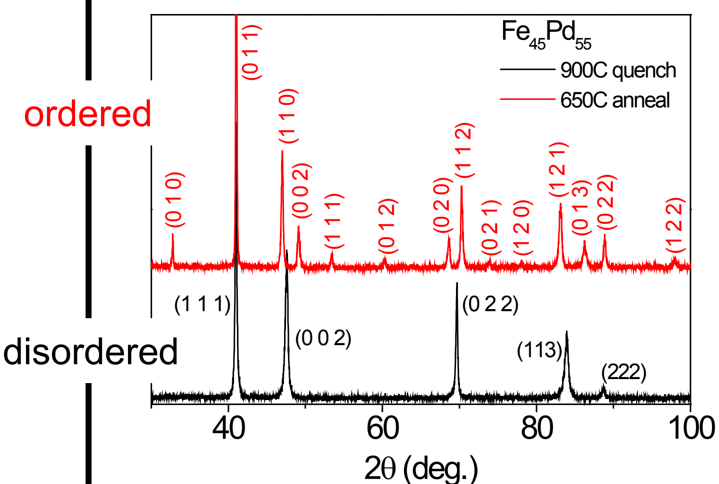
- **Stabilizing $L1_0$ magnetic phases: $FePd_{1-x}Ni_x$**
  FY13

- **Promising new permanent magnet system: $Hf_2Co_{11}B$**
  FY10-13

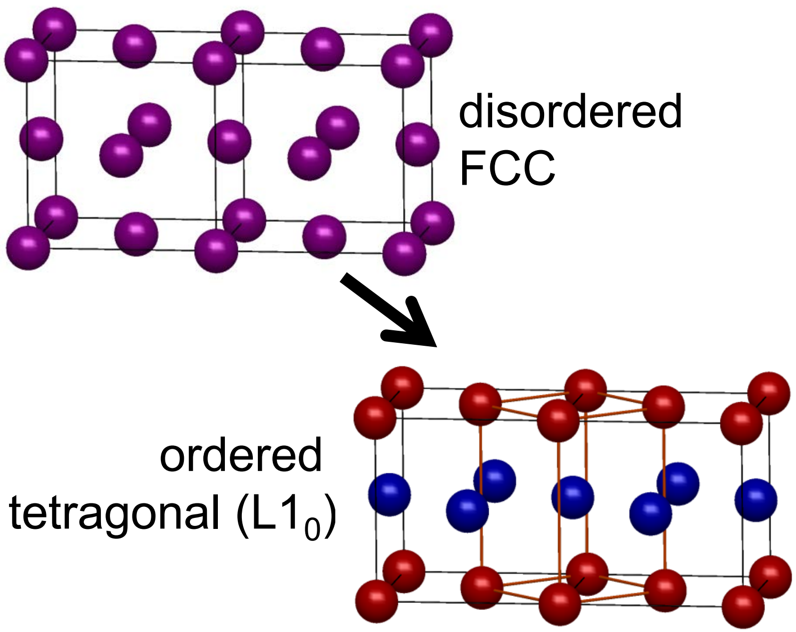
Progress: stabilizing **L1$_0$** compounds

Background information

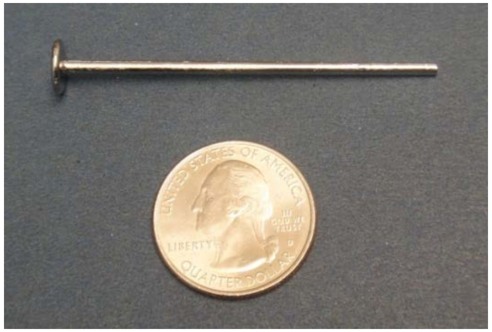
- **Class of strongly anisotropic ferromagnets**
- Binary transition metal compounds with order-disorder phase transitions.



X-ray diffraction pattern: FePd



Suction cast FePd$_{1-x}$Ni$_x$ alloys for thermo-magnetic processing

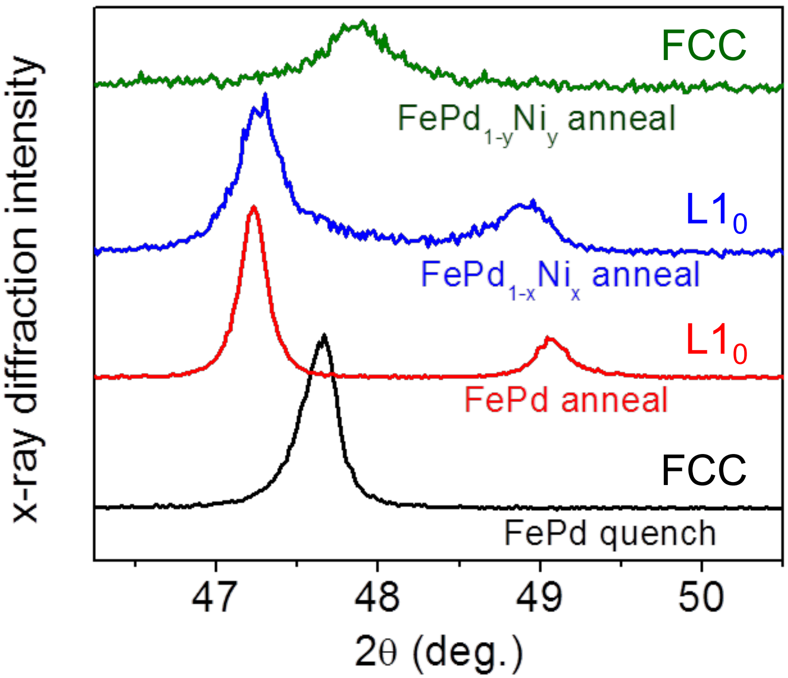


- Examples: MnAl, CoPt, CoPd, FePd, FePt
- **L1$_0$ FeNi is particularly attractive, but *only found in meteorites***

→ ***Investigate FePd$_{1-x}$Ni$_x$ alloys, use high magnetic field processing to stabilize L1$_0$ phase.***

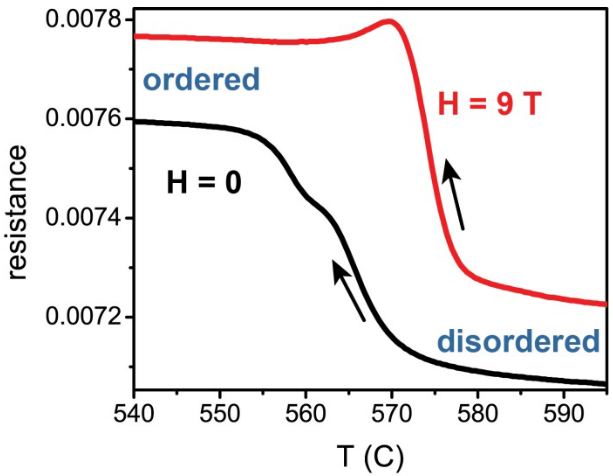
Progress: stabilizing $L1_0$ compounds

- **Produced $L1_0$ $FePd_{1-x}Ni_x$ for low Ni concentrations.**



- Cast alloys for **thermomagnetic processing**
- Performed preliminary processing experiments
- **Observed magnetic-field-induced increase in stability of the $L1_0$ phase.**

Thermo-magnetic processing: $L1_0$ phase stabilized by field



Magnetic field causes order-disorder transition to occur at higher temperature.

Progress

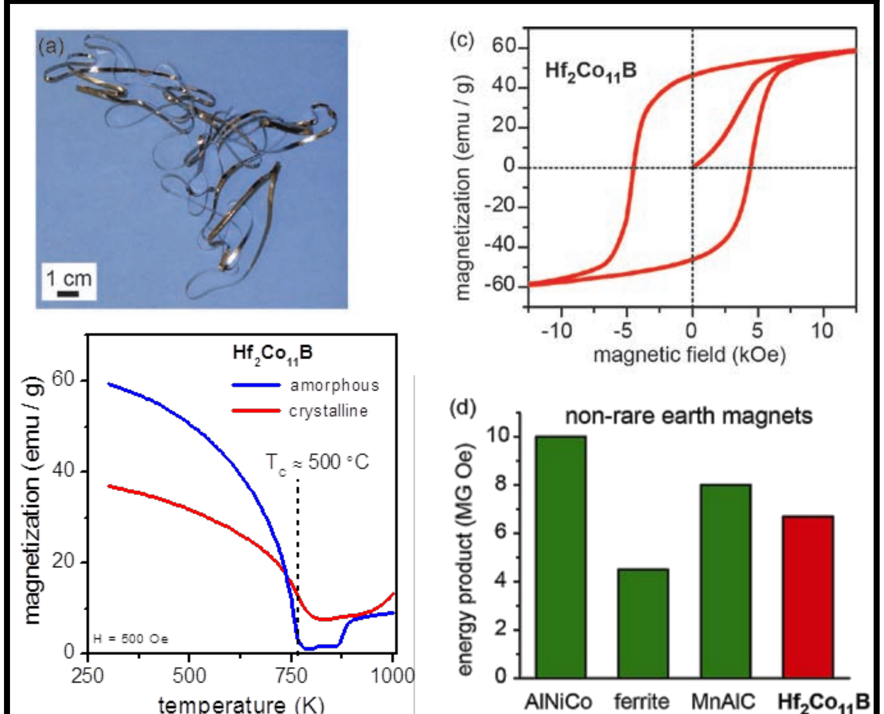
- **New ferromagnets: $ZrFe_{12-x}Al_x$ and $HfFe_{12-x}Al_x$**
  FY11-12

- **Stabilizing $L1_0$ magnetic phases: $FePd_{1-x}Ni_x$**
  FY13

- **Promising new permanent magnet system: $Hf_2Co_{11}B$**
  FY10-13

Progress: $Hf_2Co_{11}B$

$Hf_2Co_{11}B$: melt-spun ribbons and magnetic properties



Continuing study of Hf-Co-B alloys.

- Progress in FY2012-2013
  - **Demonstrated BH_{max} = 6.7 MGOe**
  - Correlated microstructure and magnetism
  - **Filed Provisional Patent Application**

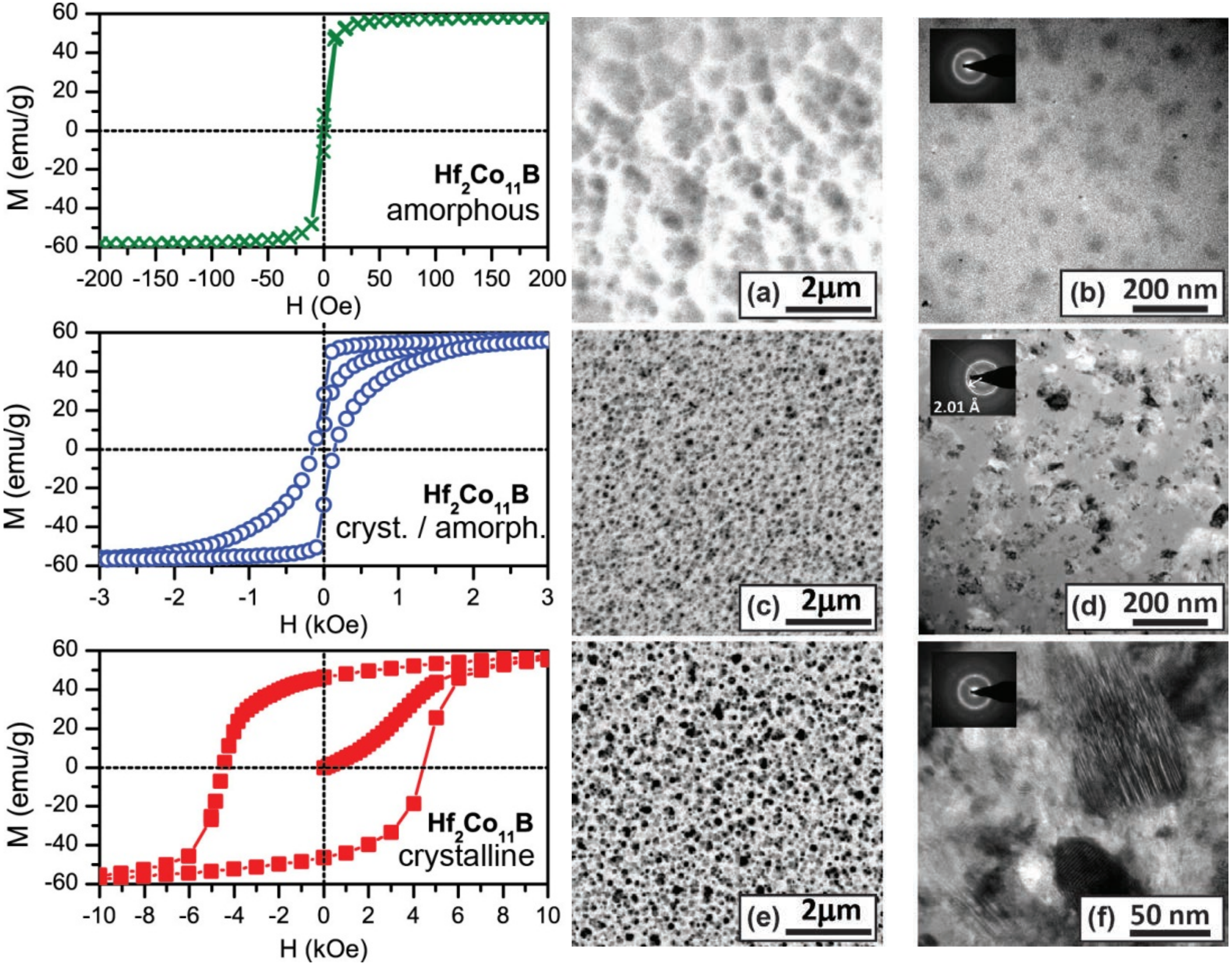
Key findings:

- Energy product competitive with well-established, long-studied non-rare earth magnet materials.
- Energy product near half that obtained in optimized NdFeB melt-spun ribbons.
- Curie temperature ~150°C higher than NdFeB.
- Cost can be reduced by partial Hf → Zr, impact on performance currently under study.

Progress: $Hf_2Co_{11}B$

Magnetism and microstructure

Room temperature M(H) **SEM backscatter** **TEM bright field**



Amorphous material is a very soft ferromagnet

Partially crystallized material show mixed hard/soft magnetism.

Further crystallization produces **hard ferromagnetism**.

Complex structure

Collaborations

- **David Singh**, Materials Theory, Oak Ridge National Lab
  - First principle calculations
- **Orlando Rios**, Materials Processing, Oak Ridge National Lab
  - Magnetic field processing and microstructure analysis
- **Nirmal Ghimire and David Mandrus**, University of Tennessee
  - Sample synthesis and characterization
- **Michael Koehler**, University of Tennessee
  - High temperature magnetic measurements
- **John Schultz**, Georgia Tech Research Institute
  - High frequency magnetic measurements

Proposed Future Work: FY13-14

- $Hf_2Co_{11}B$
  - Continue optimizing processing conditions, melt-spinning, crystallization.
  - Chemical modifications for cost and performance (Zr substitution for Hf, Fe for Co, optimal B content → $Hf_{2-x}Zr_xCo_{11-y}Fe_yB_z$).

- $L1_0$ phases
  - Synthesize $FePd_{1-x}Ni_x$ alloys for x = 0.1,0.2…0.9, 1.0.
  - Characterize magnetic properties: magnetization, curie temperatures.
  - Explore thermomagnetic processing to stabilize the $L1_0$ structure.

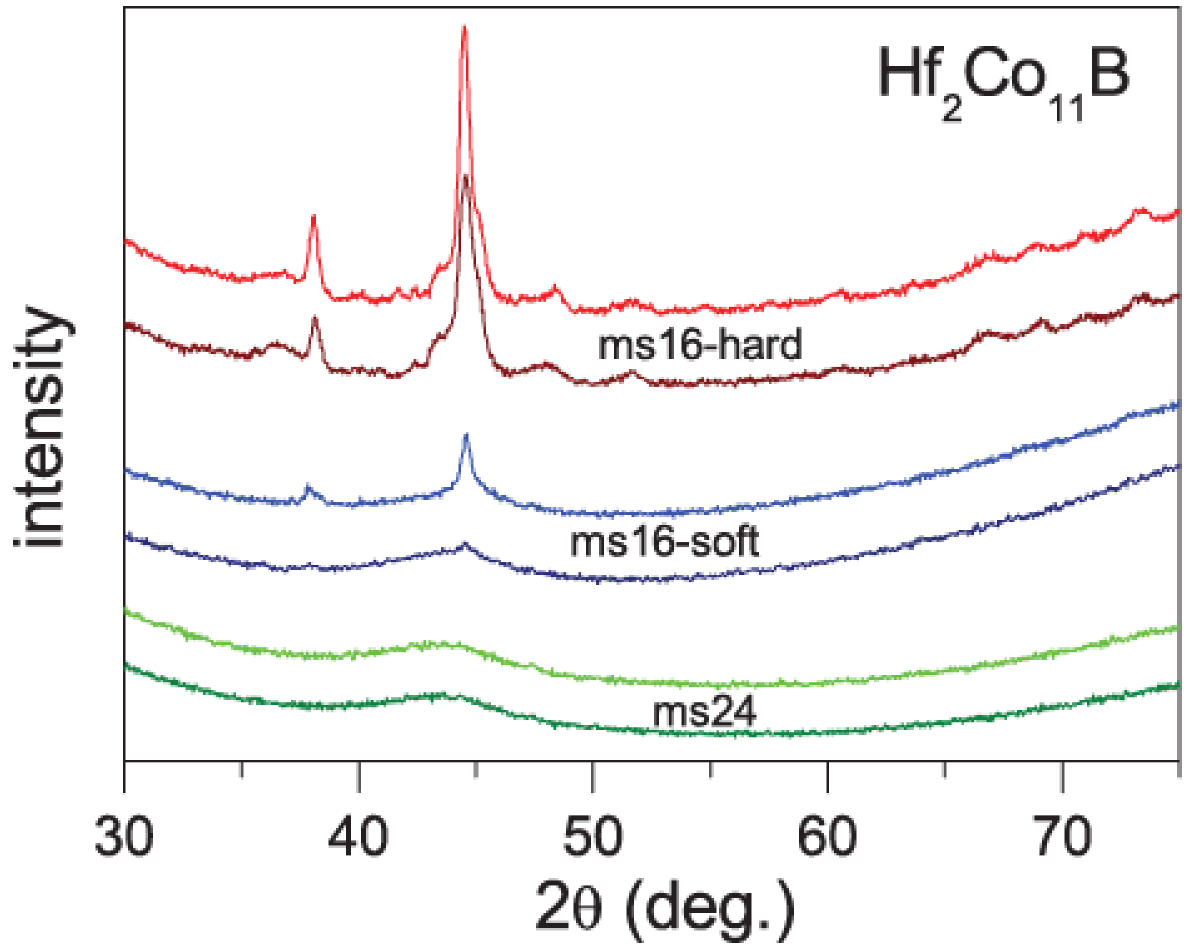
- New transition metal rich phosphides
  - Continue exploratory syntheses in ternary Cr/Mn/Fe/Co-rich phosphide systems.
  - Tune crystal growth conditions (solvent compositions) to favor products with high concentrations of metals.
  - Complement with arc-melting when appropriate (e.g. Fe-phosphides).

Summary

- **Relevance**: Discovery and development of alternative permanent magnet materials addresses the cost and limited domestic supply of rare-earth elements, which are barriers to meeting motor cost targets.
- **Approach**: Focus on new materials discovery and characterization supported by computation, to identify and understand new candidate materials. Combine heavy and light transition metals.
- **Accomplishments and Progress**:
  - Discovered and characterized new rare-earth free Fe-based ferromagnets $AFe_{12-x}Al_x$, and understood performance limits using first principles calculations.
  - Processed $FePd_{1-x}Ni_x$ alloys in high magnetic fields and showed increased stability of the anisotropic magnetic phase and improved kinetics for phase transformation.
  - Demonstrated Hf-Co-B alloys to be competitive rare-earth free permanent magnet materials with high Curie temperature (500 °C), energy products near 7 MGOe, and expectations of further improvement.
- **Collaborations**: Materials theory, processing, and microstructure studies at ORNL, synthesis and characterization at Univ. Tenn., characterization at GTRI.
- **Proposed Future Work**: Improving $Hf_2Co_{11}B$-based alloys by chemical modification, exploration of Cr/Mn/Fe/Co-rich phosphides for new ferromagnets.

Technical Back-Up Slides

$Hf_2Co_{11}B$ x-ray diffraction



$Hf_2Co_{11}B$ differential thermal analysis