Non-rare-earth magnetic materials

Michael A. McGuire

Materials Science and Technology Division
Oak Ridge National Laboratory

May 11, 2011

PM035

Overview

Timeline

- Start: October 2009
- End: September 2013
- Complete: 35%

Budget

- Total project funding
  - DOE $1440K
- Funding received in FY10
  - $360K
- Funding for FY11
  - $360K

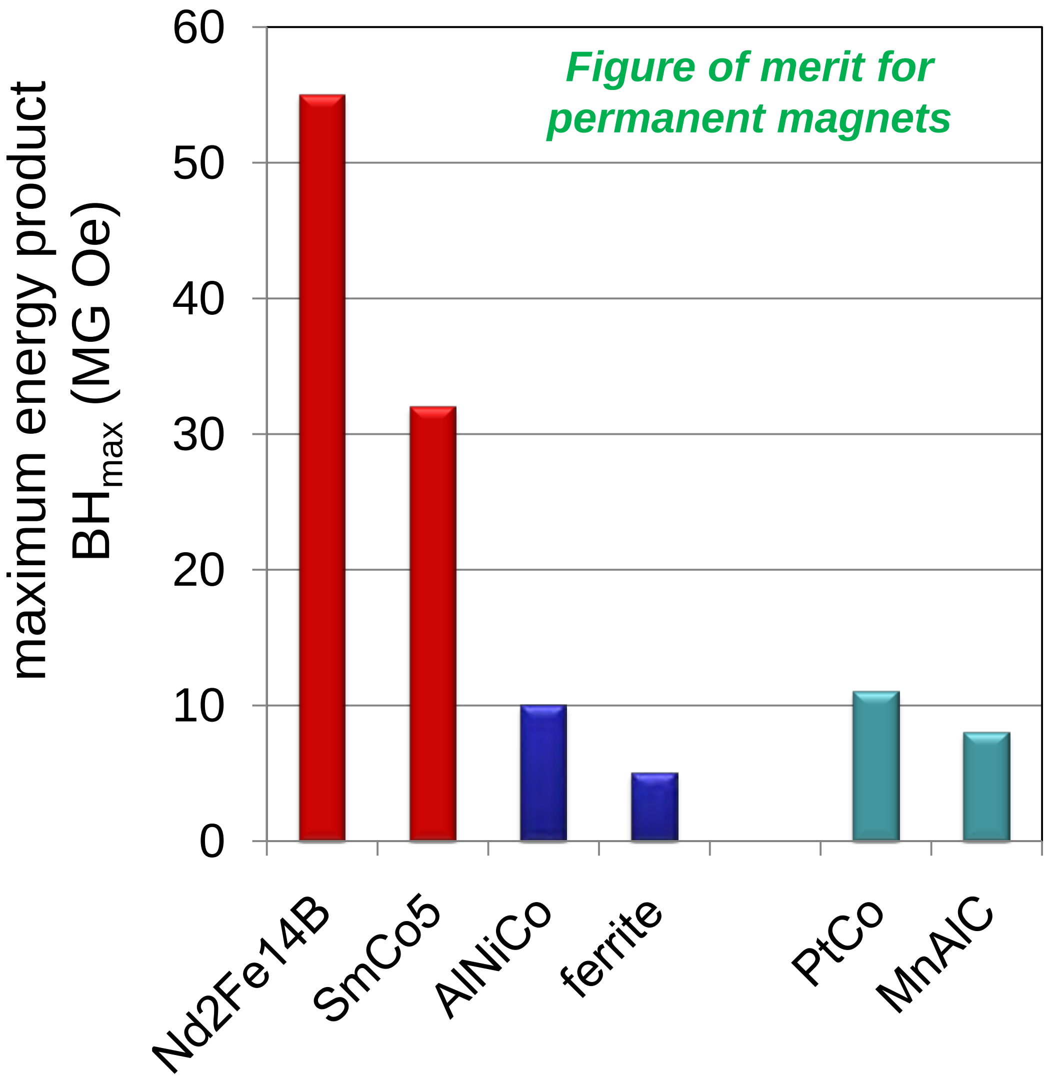
Targets / Barriers

- Relevant Targets
  - lowering the cost of electrical propulsion systems toward
    - 2015 target of 12 $/kW
    - 2020 target of 8 $/kW.
- Relevant Barriers
  - **Rare Earth Minerals:** supply may not meet new demand.
  - **Cost:** magnets currently 30% of motor cost, 60% of 2020 target cost.

Collaborators

- Experimentalists and theorists at ORNL and Univ. of Tenn.

Relevance



- No current permanent magnet (PM) materials are competitive with rare earth element (REE) compounds.
- New demand for PM motors as well as limitations and controls on the current supply of REE present serious cost and availability issues.

Relevance

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

- Objectives of this project
  - Review known magnetic materials and examine those worth further study.
  - Identify new materials in chemical systems which contain elements with the most promise for good permanent magnet properties.
  - Understand the role of heavy transition metals in producing strong 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

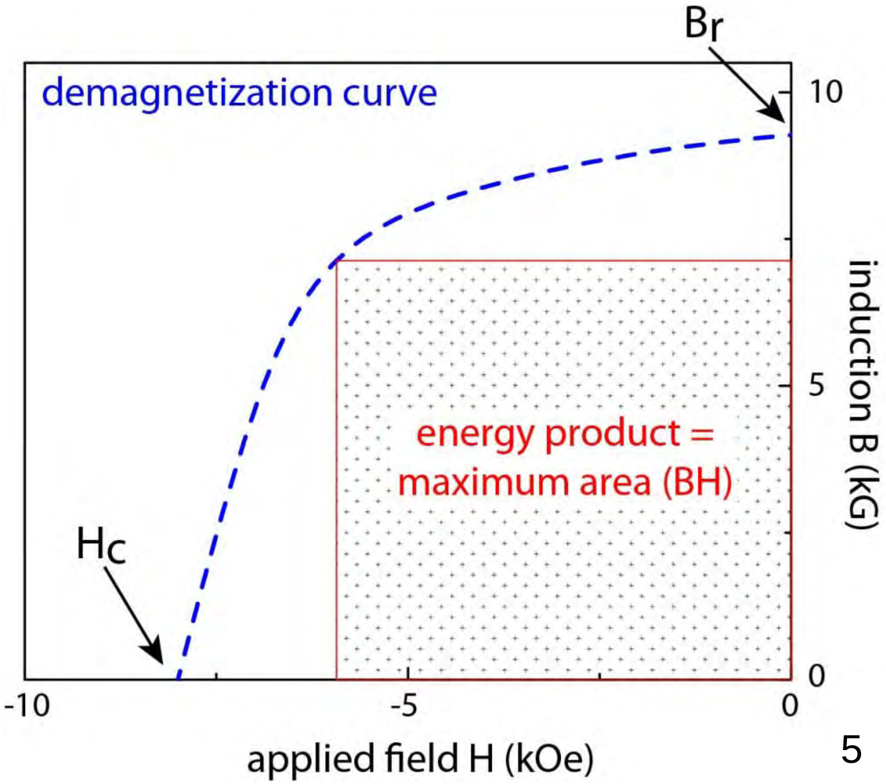
Statement of problem:

To account for likely shortfalls in rare-earth element (REE) supplies and the resulting high cost for PM motors, high performance PM materials that do not contain REEs are needed.

Good PM materials must have high energy products $(BH)_{max}$ at expected operating temperatures.

Large remanent magnetization B_r

Large coercive field H_c



Materials requirements:

- High Curie temperatures
- Large saturation magnetization
- ***Strong magnetic anisotropy***

Approach

REE are particularly important in producing the **strong anisotropy** required for good PM behavior. The main challenge to non-REE PM is achieving strong magnetic anisotropy.

Shape anisotropy

Demagnetization factors are strongest along the shortest axis of anisotropic particles.

Anisotropy is realized in long, thin rods due to the relative ease of magnetization along the long direction.

Magnetocrystalline anisotropy

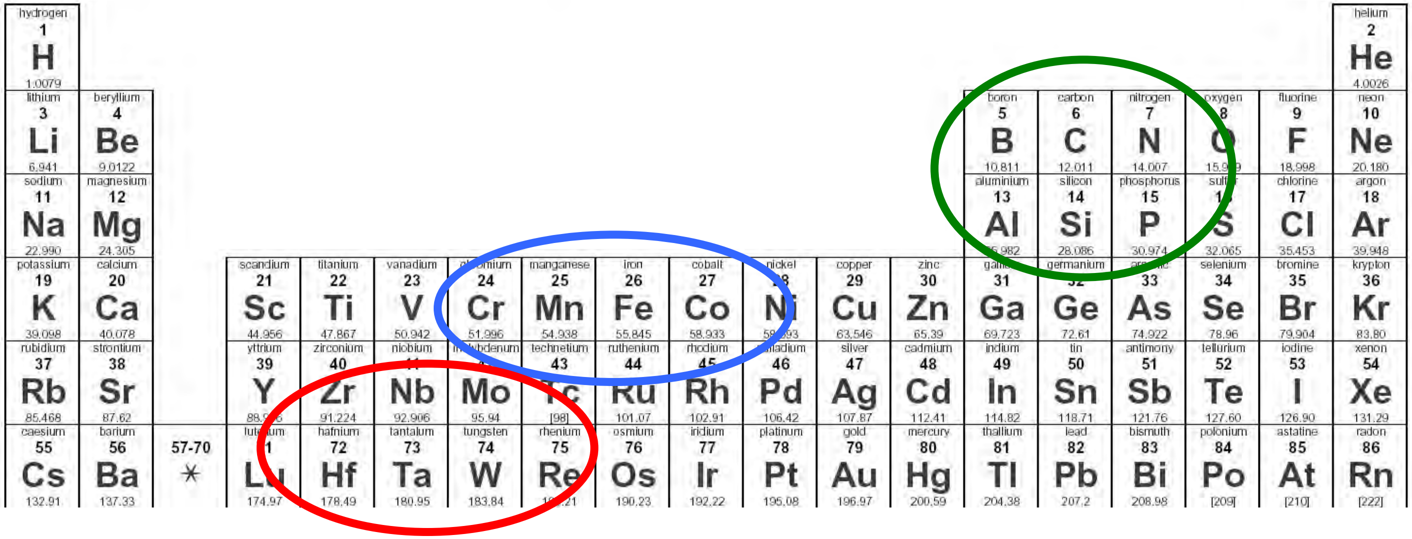
Anisotropic structures and directional bonding can give intrinsic anisotropy to magnetism.

Crystal structure is coupled to magnetic moments through spin-orbit coupling.

Focus on compounds likely to have strong intrinsic magnetocrystalline anisotropy, which could be further enhanced using materials processing techniques.

Approach

- Non-cubic crystal structures rich in 3*d* transition metals and including heavier transition metals with strong spin-orbit coupling are targeted.
- Covalently bonded ternary "interstitials" can increase coupling between 3*d* metals and heavier elements, and produce new, more complex crystal structure types.



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

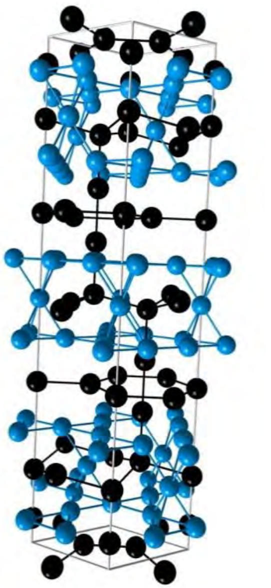
Milestones

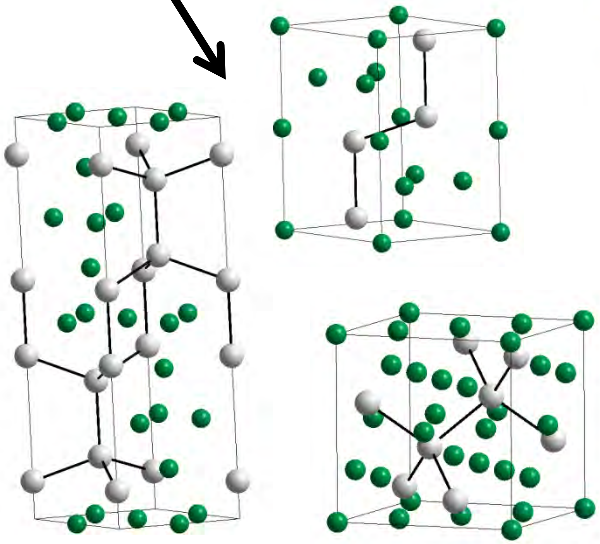
Month/Year	Milestone or Go/No-Go Decision
September 2010	**Milestone:** Identify promising candidate materials not currently used in PM technologies for study and analysis. **Complete:** Several binary intermetallic systems were chosen for study, including Laves phases, μ-phases, and Hf-Co.
September 2011	**Milestone:** Evaluate usefulness of nitrogen as an interstitial in PM materials. **Progress:** Reactivity of some intermetallics with nitrogen has been examined. Review of relevant literature is ongoing. Thermal stability is an issue. **Milestone:** Complete survey of Zr/Hf-Co/Fe systems and identify compositions which warrant further optimization. **Progress:** Effects of processing, chemical manipulations, and thermal treatments on the most promising materials have been studied.
September 2011	**Go/No-Go Decision Point:** Completed analysis of materials initiated in FY2010 will determine whether further study or optimization is warranted. **Progress:** Work on Laves phases, μ-phases wrapping up. Hf-Co shows the most promise. Study of crystal and microstructure are underway.

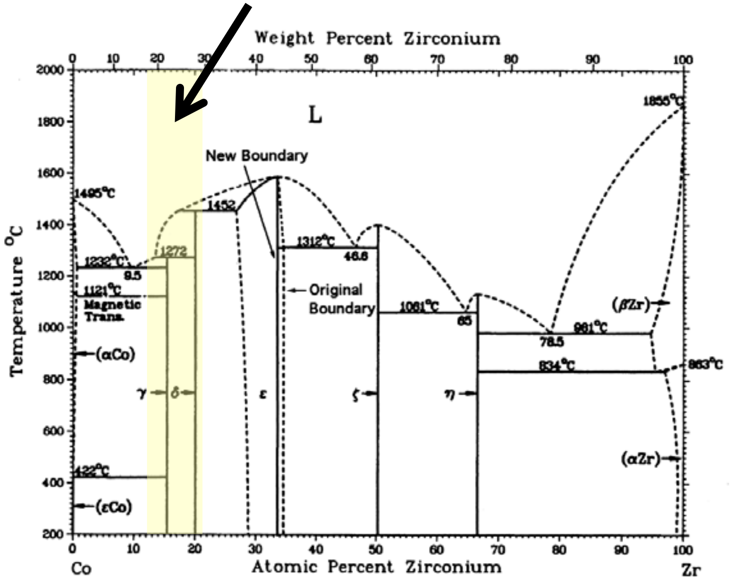
Technical Accomplishments and Progress

Initial materials selection

- Inspect 3d rich side of relevant 3*d*-(4*d*/5*d*) phase diagrams.
- Identify common structure types and examine reports of magnetic properties.
    - Two common classes: (1) Laves phases, (2) μ-phases.
    - Uncommon, interesting compositions in Zr/Hf-Co.



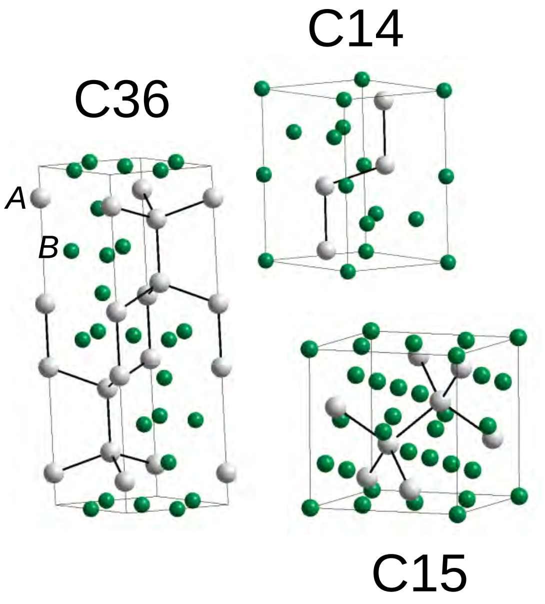




J. H. Zhu and C. T. Liu, Acta Mater. **48** (2000) 2339-2347.

Technical Accomplishments and Progress

Laves phases: composition *AB_2*.



Three prototypes: C14 (hexagonal), C15 (cubic),
and C36 (hexagonal)

Ferromagnetism reported in:

$HfFe_2$ (T_C = 150-300 C)
$HfMn_2$ (nearly FM)
$TaFe_2$ (nearly FM)
$TaCo_2$ (T_C = 19 K)

Some phases are studied as potential hydrogen storage materials.

Computational results in FY2011:

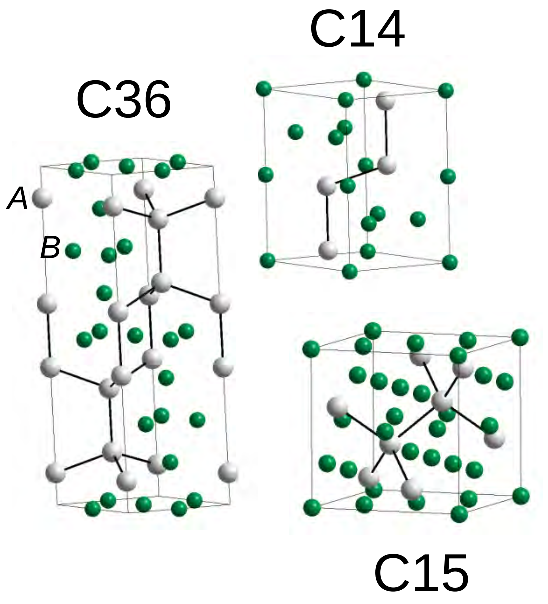
First principles calculations were performed to assess potential PM performance of $HfFe_2$ (C14 structure).

Results indicate little magnetocrystalline anisotropy in this material.

Hard magnetic behavior is not expected to be realized in $HfFe_2$ without further chemical manipulation.

Technical Accomplishments and Progress

Laves phases: composition *AB_2*.



Three prototypes: C14 (hexagonal), C15 (cubic),
and C36 (hexagonal)

Ferromagnetism reported in:
$HfFe_2$ (T_C = 150-300 C)
$HfMn_2$ (nearly FM)
$TaFe_2$ (nearly FM)
$TaCo_2$ (T_C = 19 K)

Some phases are studied as potential hydrogen storage materials.

Experimental results in FY2010:

- Chosen as test system for effects of interstitial nitrogen on magnetic properties.
- Studied reactivity of $TaCo_2$ and $TaFe_2$ with nitrogen.
- No evidence of N-uptake for Laves phase.
- Some decomposition due to TaN_x formation.

Instability of nitrides (relative to oxides and N_2) presents significant synthetic and processing challenges, and instability of eventual products may limit the appeal of this approach.

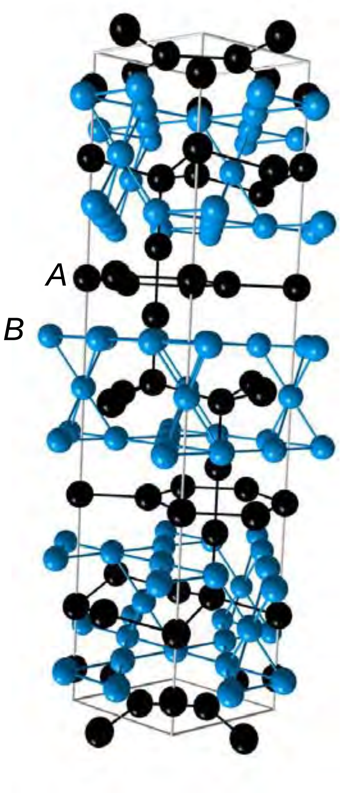
Technical Accomplishments and Progress

μ-phases: W_6Fe_7 structure-type.

Form with compositions ranging form $A_{\sim7}B_{\sim6}$ to $A_{\sim5}B_{\sim8}$.
A = Ta, W, Nb, Mo B = Cr, Fe, Co, Ni

These materials contain the target transition metals, and accept Si, Al, etc. substitutionally.

Very few reports of magnetic behavior in these complex structures, especially ternary variants.



Results in FY2010-2011:

- Synthesized samples at more than 40 compositions.
- Magnetic characterization is underway. No FM at room temperature to date.
- Observed antiferromagnetism in Ta-Fe, Nb-Fe, and Mo-Fe at relatively high temperatures, indicating strong magnetic interactions.
- Weak FM observed in a ternary composition below room temperature.

These materials may not support strong ferromagnetism. Work on these systems is wrapping up.

Technical Accomplishments and Progress

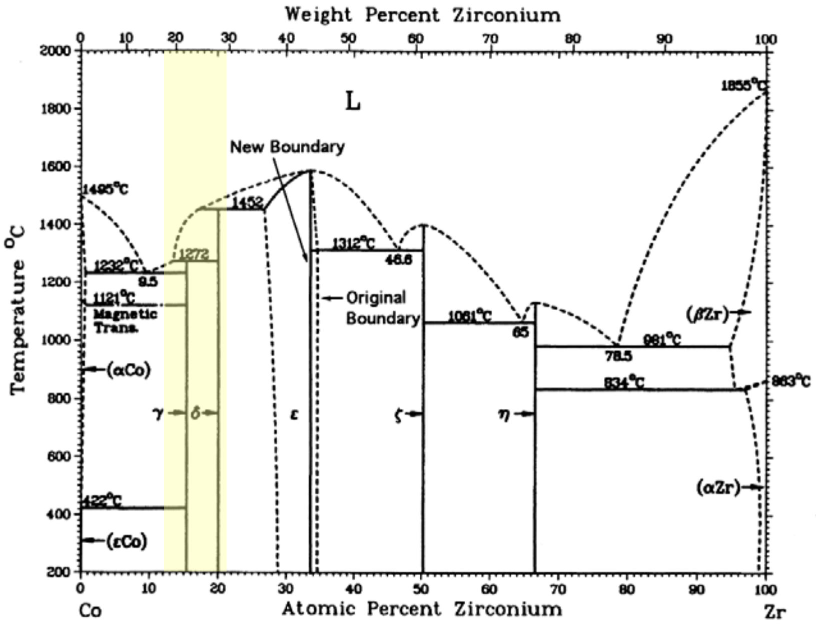
Zr/Hf-Co phases.

Several Co rich phases in Zr-Co and Hf-Co.
Ferromagnetism has been reported in all of them.

Zr_6Co_{23} (Tc = 180 C) cubic
Hf_6Co_{23} (Tc = 480 C)

Zr_2Co_{11} (Tc = 490 C) hexagonal
Hf_2Co_{11} (Tc = 520 C)

Hf_2Co_7 (Tc = 175 C) monoclinic



J. H. Zhu and C. T. Liu, Acta Mater. **48** (2000) 2339-2347.

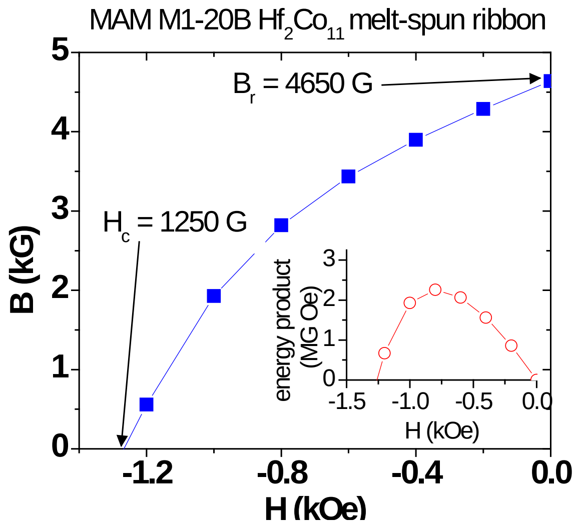
FY2010-2011: Focus on Hf_2Co_{11}

- Synthesized samples by arc-melting, annealing, melt spinning.
- Measured magnetic properties at and above room temperature.
- Examined effects of substitution for Co, and addition of boron.
- Studied magnetic behavior of annealed melt-spun ribbons.
- Initiated structural and compositional analysis.

Technical Accomplishments and Progress

Hf_2Co_{11} alloys.

composition and treatment	saturation magnetization M_S (emu/g)	remnant magnetization B_r (G)	coercive field H_C (Oe)
Hf_2Co_{11} arc-melted	70	390	< 500
Hf_2Co_{11} annealed	71	280	< 500
Hf_2Co_{11} melt-spun	86	4650	1250
$Hf_2Co_{11}B$ melt-spun	66	4500	1550
$Hf_2Co_{10}Fe$ melt-spun	78	3700	450
$Hf_2Co_{10}Mn$ melt-spun	72	3700	<200



Results in FY2010-2011

- Observed significant hard FM behavior in melt-spun ribbons.
- Demonstrated enhancement of coercivity by boron addition.
- Determined Curie temperature of melt-spun alloy (~520 C).
- Showed detrimental effects of Co substitution by Fe, Mn.
- Obtained maximum energy product for ribbons ~ 2.5 MGOe.

Results warrant further study of these materials, but low saturation moment may limit usefulness. Structural characterization is essential to applying theoretical tools.

- ☐ **H_C values comparable to AlNiCo.**
- ☐ **B_r values better than Ferrites.**

Collaborations

- Collaborators at Oak Ridge National Laboratory, Materials Science and Technology Division
  - **David Singh**, Materials Theory Group
    - First principle calculations
  - **Orlando Rios**, Materials Processing Group
    - Material processing and microstructure analysis.
- Collaborators at the University of Tennessee, Department of Materials Science and Engineering.
  - **Nirmal Ghimire and David Mandrus**
    - Sample synthesis and characterization.

Proposed Future Work

FY2011 Milestones:

(1) Evaluate usefulness of nitrogen as an interstitial in PM materials.

(2) Complete survey of Zr/Hf-Co/Fe systems and identify compositions which warrant further optimization.

- Consider alternative synthesis routes to ternary iron nitrides.
- Critically examine thermal stability of relevant compounds.

- Focus on Hf_2Co_{11}.
  - Determine crystal structure of Hf_2Co_{11}.
  - Examine microstructure of melt-spun ribbons.

Given the long history of permanent magnet research and optimization, it is likely that entirely new materials will be required to produce significant advances.

Work in FY2012 (and end of FY2011) will focus on directed discover of new compounds in the most promising rare-earth free chemical systems.

Projected FY2012 milestone:

Determine usefulness of metal flux crystal growth as a route to new transition metal rich ternary compounds.

Summary

To enable progress toward cost targets for electric motors, there is a real need for new strong permanent magnet materials which do not contain rare-earth elements.

- We have identified heavy transition metals are the best candidates to play the important role that rare-earth elements play (strong magnetic anisotropy) in the best available permanent magnet materials.
- We have examined the potential usefulness of several known classes of materials which combine heavy transition metals with magnetic 3*d* metals.
- Hf-Co(-B) alloys show the most promise, and are still under investigation.

It is likely that the most significant advances will come with the discovery of entirely new materials.

- We have identified the most promising ternary chemical systems, and are optimizing synthetic conditions to produce Cr/Mn/Fe-rich compounds.