IRG 2: Rare-Earth Free Materials for Spin-Energy Storage and Retrieval Applications

Rainer Schad (IRG Lead), James W. Harrell, Yang-Ki Hong, H. Tim Mewes, Oleg Mryasov, David E. Nikles, Takao Suzuki, Greg Thompson and Pieter Visscher

Introduction:
Modern widely used hard magnets are based on intermetallic compounds of the rare-earths (RE) with Fe or Co. They derive their exceptional magnetic properties from the combination of the RE sublattice providing the high magnetic anisotropy and the 3-d sublattices of Fe or Co giving a large magnetization and a high Curie temperature. To date, the best overall RE hard magnetic materials are the ternary compounds $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$, which exhibits $(BH)_{max}$ of about 50 *MGOe*.[1,2] However, it has been a growing concern that the export of those RE elements from China, which has about 96% of the world production will be further restricted, leading to much higher prices.

While the coexistence of the two main criteria for useful permanent magnets (M_r and H_c) are often incompatible, hard-soft magnetic composite materials are a viable and often-used route for developing novel permanent magnets. Hard-soft magnetic composites are materials composed of two phases; a hard magnetic phase (high H_c) and a soft magnetic phase (high M_r). When the two phases are properly coupled via exchange interactions across the interface, a high $(BH)_{max}$ can be realized. Another way to enhance $(BH)_{max}$ is through the exchange coupling between a high anisotropy hard phase and an anti-ferromagnetic one. An important parameter of such composites is the exchange coupling across the boundary. This can involve grading the boundary over a range of several nm.

This IRG focuses on producing RE-free high-performance hard magnetic materials. The objective is to understand the physics of the coercivity- and magnetic anisotropy-mechanisms and to exploit them in exchange coupled hard/soft magnetic composites. Our goal is to develop RE-free hard magnets with a value of $(BH)_{max}$ higher than 50 *MGOe* at ambient temperature.

Planned work:
A variety of ***materials systems*** will be investigated including: (a) High anisotropy / high moment composites (High K/Low K-High Ms); (b) Isotropic magnets (High K / High K'); (c) Exchange-hardened magnets (High K/High K' (AF)); and (d) High K/High K'(AF)/Low K-High Ms for anisotropic magnets, where K, Ms and AF stand for the magnetic anisotropy constant, saturation magnetization and antiferro-magnetic layer, respectively. (Fig.1) The present work mainly focuses on Fe_3Pt, FePt, MnAl and related alloys for hard materials. The $L1_0$ phase **FePt** exhibits a high magnetic anisotropy of ~7 x 10^7 erg/cc, and is certainly an attractive choice. Harrell and Thompson have studied the structural ordering of FePt films using pulsed laser annealing and determined the temperature-time-transformation curve for this system. Nikles, Harrell and Thompson have extensively studied the chemical synthesis and phase transformation of FePt and related nanoparticles, including core/shell nanostructures.[3,4]

Although **Fe_3Pt** is known to exhibit very soft magnetic characteristics in bulk, it has been reported by Suzuki and his group that Fe_3Pt single crystalline films exhibited a very high magnetic anisotropy of 10^7erg/cc at ambient temperature, with a *m-DO*$_{19}$ type structure, tetragonally-distorted from $L1_1$ type.[5] The τ-phase of bulk **Mn-Al** is known to have a high value of K, a modest magnetization and Curie temperature. Particles of MnAl were successfully fabricated by Nikles using a chemical synthesis method, and exhibited high coercivity of about 20kOe. Recently, Hong proposed composite magnets of MnAl(hard)/FeCo(soft) of a (core/shell) type as possibly higher performing. (Fig.2)

Materials fabrication (Suzuki, Nikles, Hong) The MINT center has excellent capabilities for fabrication of thin films and multilayers including magnetron sputtering and pulsed laser deposition. Furthermore, the center has the expertise to synthesize nanoparticles and core/shell structures with various magnetic properties and size, shape and composition. In the present work, both multilayers and particles of various types mentioned above will be fabricated under various

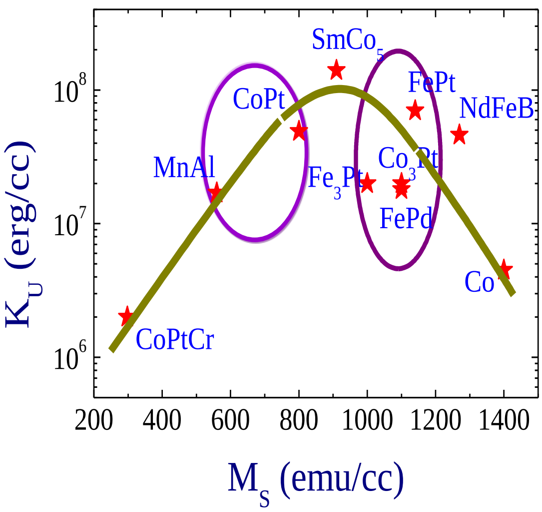

Figure 1 Magnetic anisotropy constant Ku vs. saturation magnetization at 300K

fabrication conditions by sputtering and chemical synthesis methods. We will develop multilayered MnAl/soft magnetic alloy films to understand exchange coupling between the hard (MnAl) and soft (CoFe or NiFe) films and to investigate the effect of interface roughness between the films on the exchange coupling. Sputter deposition will be used to fabricate the multilayered structures.

Magnetic and structural characterization: (Schad, Harrell, Mewes, Thompson) Fundamental magnetic properties can be measured by magnetometry to map the hysteresis. The magnetic anisotropy properties will be estimated using remanence curves, torque magnetometry and FMR. Magnetic interactions will be characterized using δM measurements. The domain structure is investigated using MFM. The domain size, in conjunction with grain sizes will give a better understanding of the reversal mechanisms. Structural analyses will be made by high resolution TEM, SEM and XRD instruments, and a new Local Electrode Atom Probe (LEAP) capable of three-dimensional imaging of structures at the atomic scale, which allows mapping chemical ordering like segregation at grain boundaries.

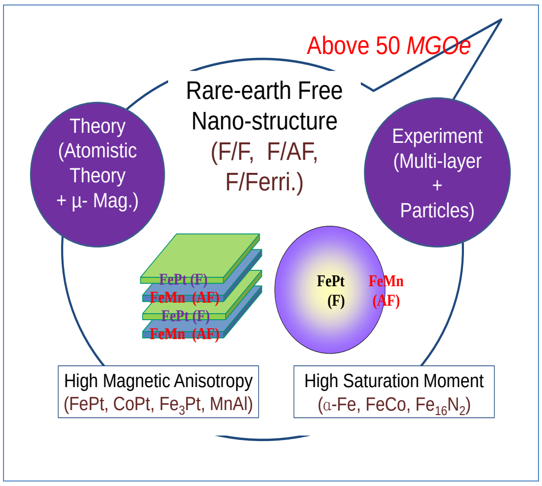

Figure 2. The scope and materials for the present IRG2

The comprehensive characterization of structural and magnetic properties will define the phases of the materials. This will allow a comparison between experimental magnetic data and theoretical modeling by our team.

Theory and Simulation (Mryasov, Visscher) Micromagnetic theory has proven to be essential for understanding the remagnetization process starting from the fundamental magnetic parameters K, A, and M_s. (A; Exchange stiffness constant) Our ability to calculate these parameters from ab-initio or electronic structure based theory of magnetic materials has also improved - the combination of these two condensed matter theory fields gives additional capabilities well suited to support the experimental goals of this proposal.

We will calculate the MH loops of sheet films as well as nanocomposite materials. This will include some direct force simulations in which we simply simulate a very large system and observe the domain patterns that are formed and the resulting loops. However, we believe it is also important to develop some intuitive understanding of the interaction between the component materials. Many 2-component composites can be quite accurately described by a two-macrospin model. We intend to make this idea more quantitatively useful by converting the Landau-Lifshitz (LL) equation for a multi-cell micromagnetic model into an effective LL equation for the evolution of the two macrospins, and extract the parameters describing their interaction. This will make it possible to apply insights obtained from simple models to more complex nanostructures. Visscher has done extensive calculations of reversal mechanisms and rates using an energy landscape approach in exchange-coupled media grains, which present similar problems to the present composites.[6] This systematic approach allows much more efficient optimization of the structure than simply doing brute force simulations of a large number of randomly chosen structures, and picking the best. Mryasov will contribute predictive computational theory for magnetic anisotropy (K_1 and higher order anisotropies such as K_2 to support search for "isotropic" K/K' combinations), interface and bulk exchange interactions, critical temperature for prospective RE-free permanent magnets to support the search for optimum composition, alloy additions, conditions (strain, stress), geometry (shape and dimensions) to maximize $(BH)_{max}$. Mryasov will employ predictive computational materials physics methods to calculate the finite temperature behavior of magnetic anisotropy of ferromagnets and ferrimagnets, and to investigate interface exchange coupling to support the rational design and optimization of two-phase magnets. He will work on extensions of traditional DFT-LDA based theory to account for the many-electron contribution to orbital dependence of effective electron potentials. This improved theory of orbital polarization and magnetic anisotropy will provide an estimate of the DFT-LDA error and will guide a more predictive search for high anisotropy materials.[7] Using state-of-the-art electronic structure and micromagnetic theory, Visscher and Mryasov will help interpret the experimental characterization results and optimize the systems to meet the goals of this proposal.

References: 1.M.Sagawa,*et al., J. Appl. Phys*. 55, 2083 (1984). 2. I.Betancourt and H.A.Davies, *Mater. Sci. and Tech*. 26, 5 (2010). 3. S. Kang *et al., J. Am. Chem. Soc.* 128, 1042 (2006). 4. Y. Inaba *et al., J. Appl. Phys.* 107, 053507-1 (2010). 5. M.A.I. Nahid and T. Suzuki, *J. Appl. Phys.* 97,10K307-1 (2005). 6. P.B. Visscher and D.M. Apalkov, *Magn.and Magn.Materials* 322, 275 (2010). 7. S.V. Faleev, O. Mryasov, and T. Mattsson, *Phys. Rev. B.*, 81, 205436 (2010).

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