Fundamental and Magnetic-Hardening Studies of Rare-Earth and Nanocomposite Magnets

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I. Introduction

In this project we study new nanocrystalline and nanocomposite structures that have high potential for permanent-magnet development. These materials, which can be synthesized to have either very high or intermediate coercivities, have many applications in electric power, transportation, and information-storage industries. There is great interest in further development of understanding and application of these materials.

Following are brief discussions of recent research highlights for the present grant.

II. Project Reports

A. Fundamental Electronic, Magnetic and Micromagnetic Studies

1. Nanostructured Exchange-Coupled Magnets

We have summarized in a major review the key features of exchange-coupled permanent magnets. Exploiting exchange coupling is an important tool to improve the remanence of isotropic magnets (remanence enhancement) and to enhance the saturation magnetization of oriented magnets. However, the improvement of the remanence is limited by the requirement of maintaining a minimum coercivity of the order of $M_s/2$. The idea behind these systems is to break out of the straitjacket of natural crystal structures by artificially structuring new materials.
The concept is similar to that of the 4f-3d intermetallics themselves, but on a different scale, where the atoms are replaced by a mesoscopically structured hard-magnetic skeleton with surplus anisotropy and small soft-magnetic blocks.

Analytical calculations yield a well-defined and realistic upper limit of the order 1 MJ/m³ to the energy product of permanent magnets. This energy product is predicted for suitable multilayered and random hard-soft nanostructures. The main problem is to ensure a sufficiently high coercivity. The above-mentioned energy-product predictions are valid for ideal nanostructures, but in reality there are always imperfections which reduce the coercivity and undermine the energy product. From a basic point of view, this coercivity reduction is well understood, but in practice it is often difficult to identify the structural features governing the coercivity of a given material. This task amounts to the determination of the micromagnetic spin configurations as a function of the magnet’s real structure. One issue is the exchange at grain boundaries, which affects the coupling between nanograins and, indirectly, the coercivity and the maximum energy product. Both continuum and layer-resolved analytic calculations yield a quasi-discontinuity of the magnetization between misaligned and incompletely exchange-coupled grains. This discontinuity is accompanied by a moderate reduction of the intergranular exchange and facilitates the switching of soft phase. By contrast, anisotropy changes in the grain-boundary region have no major effect on the spin structure, because the effect of anisotropy inhomogeneities averages over at least a few nm. Future developments in the field will exploit our ever-increasing knowledge of the microstructure and reversal mechanisms of the materials to fully realize the potential of magnetic nanostructures and to explore new applications.

2. High-Temperature Sm(Co,Fe,Cu,Ti)z Permanent Magnets

The effects of transition-metals such as Fe, Cu, Zr, and Ti substitutions in Sm-Co permanent magnets have been subject of thorough investigation for many years. Recently, they have found renewed attention in the context of high-temperature permanent magnets. For example, Ti-substituted Sm₂Co₁₇-type permanent magnets have excellent high temperature magnetic properties with $H_c = 12.3$ kOe at 500 ºC. We investigated how Fe and Ti affect the magnetic properties of sintered Sm-Co magnets by varying the Fe content of Sm(Co, Fe, Cu, Ti)z samples. A coercivity of 10.8 kOe at 500 ºC has been achieved for a transition-metal ratio of 7.3. In combination with the positive effect of the Fe on the magnetization, this coercivity makes the material a promising candidate for high-temperature applications. Higher transition-metal ratios cause the coercivity to drop, as expected from the phase structure of Sm-Co magnets. The temperature dependence of the coercivity is explained in terms of the temperature dependence of the magnetic properties of the grain-boundary phase. TEM is used to investigate the difference between Ti-containing and Zr-containing magnets. Both compositions exhibit the cellular microstructure characteristic of sintered Sm-Co magnets, with cell sizes of about 100 nm. The main difference is the absence of the lamellar phase in the Ti-containing samples.

3. Finite-Temperature Micromagnetism of Sm-Co Permanent Magnets

The finite-temperature coercivity of Sm-Co-Cu-Ti and other Sm-Co based permanent magnets was investigated theoretically. There are two main contributions: the intrinsic
temperature dependence of atomic-scale properties and thermally activated micromagnetic processes. For planar walls subjected to an arbitrary but weak anisotropy inhomogeneity, a closed expression for the pinning energy was found. Thermally activated jumps yield a nonequilibrium correction to the finite temperature coercivity. Since the phase-space trajectories responsible for thermally activated magnetization reversal are very close to the static trajectory, ‘giant’ thermodynamic fluctuations can be ignored, and the reversal is always described by a power-law exponent 3/2.

B. Magnetic and Structural Studies of Nanocrystalline and Nanocomposite Rare Earth-Iron-Carbides

1. Nd$_{10}$Fe$_{82}$-$y$M$_{y}$B$_{6}$C$_{2}$ Nanocomposite Ribbons ($M = \text{Nb, Zr}$)

Our previous studies revealed that in carbon substituted Nd-Fe-(B,C) nanocomposite ribbons, the best hard magnetic properties were obtained for Nd$_{10}$Fe$_{82}$B$_{6}$C$_{2}$ with values $H_C = 8.7$ kOe and $(BH_{\text{max}}) = 15.2$ MGOe. We tried to improve further the properties by forming a more uniform microstructure using grain growth inhibitors (Nb, Zr). Zr substitutions up to 1 at.% and Nb up to 4 at.% were used, since the latter one was proven to be more beneficial. Coercivity increases monotonically with the amount of additions and especially with Nb. The maximum value of 10.6 kOe is obtained for Nd$_{10}$Fe$_{78}$Nb$_{4}$B$_{6}$C$_{2}$. The reduced remanence $m_r$ is enhanced for certain compositions, indicating stronger exchange coupling between the hard and soft magnetic phases. The later is also confirmed by the enhanced positive peak in δM-plots. More specifically $m_r$ increases slightly from 0.64 for Nd$_{10}$Fe$_{82}$B$_{6}$C$_{2}$ to 0.66 for Nd$_{10}$Fe$_{80}$Nb$_{2}$B$_{6}$C$_{2}$ and to 0.69 for Nd$_{10}$Fe$_{81.5}$Zr$_{0.5}$B$_{6}$C$_{2}$. Another feature that is greatly improved with Nb substitutions is the shape of the demagnetization curves, which becomes more square. The enhancement of coercivity and reduced remanence according to TEM studies are a consequence of a finer and more uniform microstructure. $(BH_{\text{max}})$ has a maximum value (17.2 MGOe) for $y = 2$, and then decreases slowly with further Nb addition. The reason for this trend is the simultaneous decrease of remanence, which despite the coercivity enhancement cannot preserve the maximum energy product. From the above discussion it is evident, that Nb substitution is more beneficial to the coercivity and hysteresis squareness, but Zr has a better effect on the remanence. Therefore, a proper combination of these two elements could lead to a higher energy product magnet.

From the X-ray diffraction studies it is found that the melt-spun ribbons become more amorphous with the Nb substitution. In annealed ribbons, in which the 2:14:1 and α-Fe phases are present, there is not any shift of the 2:14:1 and α-Fe diffraction peaks, suggesting that Nb atoms do not enter into the crystal lattice of these two phases. DSC measurements revealed only one exothermic peak for all Nb-containing samples. This transformation corresponds to the crystallization of the amorphous material to the magnetically hard 2:14:1 phase and α-Fe. The position of the peak maximum does not change significantly for $y = 0$, 0.5 and 1, but it shifts rapidly to higher temperatures with further increase of the Nb content. Therefore, the addition of Nb reinforces the formation of amorphous state. The same trend was observed in the activation energy, which is approximately the same (~325 kJ/mol) for $y =$0, 0.5 and 1 and it increases rapidly (376 kJ/mol) for $y = 2$. 
2. \( \text{Nd}_{10}\text{Fe}_{82-y}\text{Zr}_y\text{B}_2\text{C}_6 \) Nanocomposite Ribbons

The promising result obtained in the previous work with 1 at.% of Zr substitution, motivated us to examine further the effect of Zr on the magnetic properties of the high-carbon-containing nanocomposites. Thus, Zr content was increased gradually up to 4 at.%. The coercivity was found to benefit with this substitution, which is increasing dramatically from 3.2 for \( y = 0 \) to 10.6 kOe for \( y = 4 \), being comparable to that of \( \text{Nd}_{10}\text{Fe}_{78}\text{Nb}_{4}\text{B}_6\text{C}_2 \) ribbons. The reduced remanence values have also become similar to those of the boron-rich composition. Nevertheless, the maximum energy product is still lower (13 MGOe for \( \text{Nd}_{10}\text{Fe}_{81}\text{Nb}_{2}\text{C}_6 \) versus 17.2 MGOe for \( \text{Nd}_{10}\text{Fe}_{81}\text{Zr}_{4}\text{B}_6\text{C}_2 \)). The explanation lies in the squareness of the demagnetization curve. The carbon rich ribbons despite the substitutions, still have a significantly smaller squareness than the boron-rich samples. The large difference in the magnetic parameters is attributed to the different microstructure. The grains in the \( \text{Nd}_{10}\text{Fe}_{82}\text{B}_6\text{C}_2 \) ribbons are from 60-100 nm, with some even larger \( \alpha \)-Fe grains of 250 nm. In \( \text{Nd}_{10}\text{Fe}_{78}\text{Zr}_{4}\text{B}_6\text{C}_2 \) ribbons though, the grain have become significantly smaller with average values of 25 nm and 42 nm for the 2:14:1 and \( \alpha \)-Fe phases, respectively.

X-ray patterns of melt-spun ribbons showed three phases: 2:17, 2:14:1 and \( \alpha \)-Fe. The amount of the \( \alpha \)-Fe phase is significant reduced with the Zr content. For \( y = 2 \) and 4 a ZrC phase appears in addition. DSC studies showed two exothermic peaks that move to higher temperatures with Zr content. The lower-temperature peak corresponds to a transformation of the amorphous phase into 2:17 and \( \alpha \)-Fe and the higher-temperature one to a transformation of the 2:17 into 2:14:1 and \( \alpha \)-Fe.

3. Cobalt Substituted \( \text{Nd}_{10}\text{Fe}_{82-x}\text{Co}_x\text{C}_2\text{B}_6 \) (\( x = 0, 10, 20, 30 \)) Melt-Spun Ribbons

We have investigated the effect of cobalt substitution on the structure and magnetic properties of \( \text{Nd}_{10}\text{Fe}_{82-x}\text{Co}_x\text{C}_2\text{B}_6 \) (\( x = 0, 10, 20, 30 \)) ribbons. The XRD diffraction patterns of the as–spun ribbons show the presence of two phases. The magnetically hard 2:14:1 and soft \( \alpha \)-Fe(\( \text{Co} \)) phase. The amount of \( \alpha \)-Fe(\( \text{Co} \)) phase increases with Co content. The diffraction peaks get broader with Co indicating that Co makes the as- spun ribbons more amorphous. With the addition of Co the Curie temperature of the both phases shifts slightly to higher temperatures (588 °C). The increase indicates that Co atoms enter the crystal structure of both the 2:14:1 and \( \alpha \)-Fe phases enhancing the 3d magnetic interactions. DSC measurements performed on fully amorphous samples show that there is one exothermic peak at 613°C for \( x = 0 \) and two peaks at 592°C and at 635°C for \( x = 30 \). X-ray diffraction patterns for the samples those were DSC-annealed at this first exothermic peak show that the amorphous phase transforms directly into 2:14:1 and \( \alpha \)-Fe. The exothermic peaks moves from 613°C for \( x = 0 \) to 592°C for \( x = 30 \).

Hysteresis loop measurements showed that \( H_c \) in optimally quenched and annealed samples has a small increase with cobalt content. The highest achieved coercivity is 8.2 kOe and it was obtained for \( x = 20 \) with a corresponding remanence of 98 emu/g. The TEM images showed a typical nanocomposite structure. It consists of a mixture of 2:14:1 and \( \alpha \)-Fe(\( \text{Co} \)) phases. The grain sizes were 20-50 nm for cobalt free ribbons and 60 nm for \( x = 20 \). With the increase in Co substitution the micro structure becomes non uniform leading to deterioration of magnetic properties.
4. Magnetic, X-Ray Diffraction, and Mössbauer Spectroscopy Studies of Nd$_2$Fe$_{15}$Ga$_2$Cx Magnets

X-Ray diffraction pattern for Nd$_2$Fe$_{15}$Ga$_2$Cx $0 \leq x \leq 2$ show that all the alloys studied have the Th$_2$Zn$_{17}$ rhombohedral structure. The lattice parameters and the unit cell volume are found to increase linearly with increasing carbon concentration. Structural measurements on magnetically aligned powder samples show that the samples studied possess magnetic anisotropy with a basal easy axis. Magnetization measurements at 5K and at room temperature show that all samples under investigations are ferromagnetic, and the saturation magnetization increases with increasing x, reaching a maximum at x=1, and then decreases slowly for larger values of x. Mössbauer spectra show that all the samples are magnetically ordered at room temperature and the average hyperfine field behaves similar to the saturation magnetization, where it reaches a maximum of 242 kOe for x=1. The isomer shift is negative and it increases with increasing carbon concentration. The results are explained in terms of volume expansion and the magneto-volume effects.

C. Nanostructured and Nanocomposite Films

1. Exchange Coupling and Remanence Enhancement in Nanocomposite Multilayer Magnets

After experimental evidence of intergrain exchange coupling was reported, nanocomposite magnets with high remanence and large energy products were predicted. However, the experimental values of the maximum magnetic energy product of nanocomposite bulk magnets have been much less than the theoretically predicted ones. We have observed exchange coupling and remanence enhancement in nanocomposite (Nd,Dy)(Fe,Co,Nb,B)$_{5.5}$/$\alpha$-Fe thin films prepared by sputtering and heat treatments. The coercivity of a single Ti-buffered (Nd,Dy)(Fe,Co,Nb,B)$_{5.5}$ layer is as large as 1.85 T, while a high remanence of $J_r = 1.31$ T and a high maximum energy product of $(BH)_{\text{max}} = 203$ kJ/m$^3$ are achieved in the nanocomposite multilayer films. Well-designed multilayer films consist of magnetically hard Nd$_2$Fe$_{14}$B-type phase with the grain dimension of 40 nm and magnetically soft $\forall$-Fe phase existing in the form of the continuous layers. Our results suggest that the nanocomposite multilayer films with well-distributed fine grains of the hard and soft magnetic phases could constitute the new generation of permanent-magnet materials.

2. Magnetism of Sputtered Sm-Co-Based Thin Films

Granular Sm-Co and Sm-Co-Cu-Ti thin films were produced by thermal processing of sputtered Sm-Co single layers and SmCo$_x$/(CuTi) multilayers. Single layer SmCo$_x$ films with nominal compositions ranging from SmCo$_3$ to SmCo$_{7.5}$ were prepared by co-sputtering. In-plane anisotropy was found in the composition range of $z < 5.5$, whereas for $z > 5.5$ the films exhibit three-dimensional random anisotropy. A coercivity of 49.6 kOe at 300 K was obtained in a film with the nominal composition SmCo$_4$. Sm-Co-Cu-Ti films were sputtered on Si substrates with a Cr underlayer of 90 nm and coverlayer of 18 nm. The structure of the multilayer is $(\text{SmCo}_{245A}/\text{CuTi}X)$$_n$, ($X = 2-10$, $n = 38 - 44$), corresponding to a total thickness of the Sm-Co-Cu-Ti layers of about 200 nm. X-ray diffraction patterns show that after annealing between 500 °C and 550 °C for 30 minutes, the hexagonal 1:5 phase forms with average grain size of
8 nm. Electron micrographs of the processed films show that grains with diameters of 5 to 10 nm are embedded in a matrix. Both the grains and the matrix phase exhibit the CaCu$_5$ structure, but the matrix is probably Cu-rich. The hysteresis loops show that these films have large coercivities of up to 50.4 kOe. Ti plays an important role in realizing the coercivity, in spite of the quite small fraction of Ti in the films. A SmCo$_5$ single layer and SmCo$_5$/Cu and SmCo$_5$/Ti multilayers do not exhibit the granular structure observed in the Sm-Co-Cu-Ti thin films, and the coercivities of the annealed SmCo$_5$/Ti and SmCo$_5$/Cu films did not exceed 25 kOe and 10 kOe, respectively. This behavior is reminiscent of the coercivity mechanism in Cu- and Ti- substituted bulk Sm-Co magnets, where Ti-helps to form Cu-rich grain boundaries necessary to realize domain-wall pinning. The magnetization reversal in the films is analyzed using jm plots.

3. Nanotube Magnetism

FePt and Fe$_3$O$_4$ nanotubes have been fabricated by hydrogen reduction in nanochannels of porous alumina templates and investigated by structural and magnetic measurements. Ferromagnetic FePt nanotubes were formed by loading the templates with an Fe and Pt chlorides mixture followed by hydrogen reduction at 560 °C. Using an Fe nitrate solution, thermally decomposed at 250 °C and reduced in hydrogen for 2.5 hours at the same temperature, yields Fe$_3$O$_4$ tubes. The length of the nanotubes is about 50 µm and their diameters are 200 nm. Reflecting the different magnetocrystalline anisotropies of the compounds, the coercivities range from 0.61 kOe and Fe$_3$O$_4$ to 20.9 kOe for FePt. The hysteresis is explained in terms of a tubular random-anisotropy model, which yields a diameter and anisotropy dependent transition from a curling-type mode (Fe$_3$O$_4$) to a localized mode (FePt).

III. Publications on DOE-Supported Work (2001 - Present)

1. M. Daniil, Z.M. Chen, G.C. Hadjipanayis, A. Moukarika, and V. Papaefthymiou, STRUCTURE AND MAGNETIC PROPERTIES OF THE INTERMETALLIC La$_2$Co$_{17-x}$Mo$_x$ (x = 0.5, 1, 1.5, 2) AND La$_2$Co$_{16-y}$Fe$_y$Mo (y = 0, 1, 2, 3, 4, 6) COMPOUNDS, J. Magn. Magn. Mater. 234, 375 (2001).


