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Fundamental and Magnetic-Hardening Studies of Nanocrystalline and Naaocomposite Magnets

David J. Sellmyer
University of Nebraska-Lincoln, dsellmyer@unl.edu

George C. Hadjipanayis
University of Delaware, hadji@udel.edu

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by
David J. Sellmyer, University of Nebraska
George C. Hadjipanayis, University of Delaware

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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

A low concentration of rare earths (R) plays an important role in magnetic materials because of their large anisotropy. However, the Curie temperature ($T_c$) has a decreasing trend with increasing Fe concentration in R-Fe compounds. In order to understand the variation of $T_c$ as a function of iron concentration we have carried out self-consistent spin-polarized electronic structure calculations for the sequence $YFe_2\rightarrow YFe_3\rightarrow Y_2Fe_2\rightarrow YFe_{12}$ where yttrium is a prototype R element. The exchange interaction parameters were derived using the infinitesimal angle approach. The Monte Carlo simulations based on the Heisenberg Hamiltonian were carried out to derive $T_c$ of Y-Fe compounds and results are in very good agreement with experimental data. The changes in the magnetic properties with Fe concentration were understood in terms of the local environment and magneto-volume effects.
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The nature of intergranular interactions in nanostructured two-phase magnets has been investigated. Boundaries between misaligned grains store magnetic energy, but only a small fraction of the energy is concentrated at the interface. A consequence is, for example, that a reduction of the quantum-mechanical exchange by a factor 5 reduces the effective exchange between the grains by only 35%. Grain boundaries are therefore likely to act as pinning centers unless there is complete decoupling. At interfaces between hard and soft regions, the majority of the energy is stored in the soft phase. It is indicated that a systematic approach towards the description of two-phase magnets is the use of micromagnetic Green functions, although in the short- and long-wavelength limits there are diverging contributions associated with sharp grain boundaries and extended soft regions, respectively. Finally, a novel two-phase phenomenon has been predicted: the projective remanence enhancement, being equal to 11.8% of the soft phase's magnetization for an exactly solvable heteroanisotropic random-layer model.

The effect of intergranular exchange on the energy product of nanostructured permanent magnets has been investigated. In the limit of well-textured and strongly anisotropic magnets, the calculation yields analytic energy-products in terms of known materials parameters, and approximate hysteresis loops have been obtained for a number of cases. In single-phase nanocrystals there is a critical grain size below which a high magnetocrystalline anisotropy reduces the energy product by undermining the remanence enhancement. Together with the well-known cooperative coercivity reduction in the strong-coupling limit, this yields a comparatively narrow window where exchange enhancement improves the permanent-magnet performance. In two-phase magnets, the energy product is determined by the anisotropy and saturation magnetization ratios of the hard and soft phases. As a rule, high energy products require well-textured and fine-grained structures with a high fraction of the soft magnetic high-magnetization phase. On the other hand, very high anisotropies deteriorate the energy product unless they are necessary to ensure coercivity. These requirements are reasonably well satisfied high-energy-product Fe-Pt films recently developed in our laboratories.

B. Intrinsic and Magnetic Hardening Studies of Carbides and Alloys

1. Synthesis of 1:12 Carbides

We tried to fabricate carbides based on stoichiometry NdFe<sub>12+y</sub>Mo<sub>y</sub>C<sub>y</sub> (y = 0.5, 1), using the arc-melting method. Generally, it is not easy to form the 1:12 carbides from the melt because Mo alloys with carbon to form Mo-C, and therefore does not leave enough carbon to enter into the 1:12 unit cell. In order to reduce the amount of MoC and a-Fe and therefore to increase the amount of the 1:12 carbide phase we varied the stoichiometry and the heat-treatment conditions (temperature and time). Best results were obtained with NdFe<sub>10</sub>Mo<sub>1.5</sub>Ti<sub>0.5</sub>C<sub>0.5</sub> sample heat-treated at 1000°C for 3 days, where an almost single 1:12 phase was obtained.

2. Magnetic Hardening Studies in Melt-Spun Nd-Fe Carbides

Most of our efforts were focused on the fabrication of arc-melted nanocrystalline carbides based on the 2:14:1 structure. The initial as-cast samples had the following stoichiometry: Nd<sub>6.4</sub>Fe<sub>96.8</sub>Nb<sub>5.6</sub>C<sub>5.6</sub>, Nd<sub>6.4</sub>Fe<sub>96.8</sub>Nb<sub>5.6</sub>C<sub>5.6</sub>, Nd<sub>10</sub>Fe<sub>92</sub>Nb<sub>8</sub>C<sub>5.6</sub>, Nd<sub>12</sub>Fe<sub>80</sub>Nb<sub>20</sub>C<sub>6</sub>, Nd<sub>14</sub>Fe<sub>77</sub>Nb<sub>3</sub>C<sub>6</sub> and they were melt-spun using both low (23.7 m/s) and high wheel speeds (83.4 m/s).
X-ray diffraction (XRD) analysis showed that all the samples (as-made and annealed) contain a very large amount a-Fe. It was also found that it is easier to obtain the 2:14:1 phase after annealing, when low wheel speeds are used to make the as-made ribbons, and when the Fe content is less than 82%. The highest coercivity of 1.2 kOe was obtained in Nd$_{15}$Fe$_{77}$Nb$_2$C$_6$ ribbons, after annealing at 800°C for 15 minutes. This value is much lower than the value obtained in the Nd-Fe borides with the corresponding composition. It may be that Nb takes C to form NbC and therefore impedes the formation of the Nd$_2$Fe$_{14}$C phase. This was confirmed in the Nb-free samples, which showed much higher coercivities, after annealing, with the highest value of 9.4 kOe observed in Nd$_{13.5}$Fe$_{80.5}$C$_6$.

In order to help the formation of the 2:14:1 phase a small amount of boron was introduced in one of the above alloys with the stoichiometry Nd$_{15}$Fe$_{77}$Nb$_2$C$_6$B. The effect of the wheel speed on the formation of the 2:14:1 phase was studied by making ribbons with 3 different wheel speeds (23.7, 29.05 and 34.4 m/s) (XRD patterns showed that only the ribbons made with 34.4 m/s and annealed above 800°C have a considerable amount of the 2:14:1 phase plus a-Fe. The highest coercivity (13.05 kOe) was obtained after annealing at 800°C for 5 min. Nb-free samples have also been prepared and are ready to be studied.

3. Structure and Magnetic Properties of the Intermetallic La$_x$Co$_{17-x}$Mo$_x$ ($x = 0.5, 1, 1.5, 2$) and La$_x$Co$_{16-x}$Fe$_x$Mo ($x = 0, 1, 2, 3, 4, 6$) Compounds

It is well known that from the whole series of the R$_2$Co$_{17}$ compounds, only the one with R = La does not exist, because of the small ratio of the La atomic radius to the Co one. Recently we successfully stabilized the La$_2$Co$_{17}$ compounds by replacing a few Co atoms by Mo atoms.

The effect of Mo and Fe atoms on the crystal structure and magnetic properties of the intermetallic La$_x$Co$_{17-x}$Mo$_x$ ($x = 0.5, 1, 1.5, 2$), La$_x$Co$_{16-x}$Fe$_x$Mo ($x = 0, 1, 2, 3, 4, 6$) compounds were studied. X-ray diffraction patterns revealed that most of the samples are single phase and they belong to the rhombohedral Th$_2$Zn$_{17}$-type structure. The lattice parameters a and c, increase both with Mo and Fe content (Table I). From the x-ray diffraction patterns on aligned powdered samples it was seen that from the La-Co-Mo compounds only the one with x=0.5 presents planar anisotropy, whereas from the La-Co-Fe-Mo compounds only the x=1 has uniaxial anisotropy. The magnetization MS and the Curie temperature $T_c$ decrease upon Mo substitution, whereas the anisotropy field $H_a$ = 2.3T does not change significantly. In the Fe-substituted compounds $M_s$ increases, but the Curie temperature increases slightly for $0 < x < 4$ and decreases for $x=6$. In the magnetization versus temperature measurements (in the low temperature region) a discontinuity of the magnetization was observed in the La$_{15}$Co$_{85}$FeMo at $T = 260K$, which can be attributed to a spin reorientation process. Mössbauer spectroscopy measurements are being performed for verification of the above statement.
Table I. Lattice parameters as obtained from the Rietveld analysis, and magnetic data for the La₂Co₁₇₋ₓMoₓ and La₂Co₁₆₋ₓFeₓMoₓ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>V(Å³)</th>
<th>Tₘ(°C)</th>
<th>Mₛ (emu/gr)</th>
<th>μ₃d (µB)</th>
<th>EMD</th>
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<tr>
<td>La₂Co₁₆₋ₓMoₐ₅</td>
<td>8.515</td>
<td>12.362</td>
<td>776</td>
<td>738</td>
<td>103.0</td>
<td>1.45</td>
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<td>La₂Co₁₆Mo</td>
<td>8.522</td>
<td>12.387</td>
<td>779</td>
<td>613</td>
<td>92.9</td>
<td>1.37</td>
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<tr>
<td>La₂Co₁₅₋ₓMo₁₅</td>
<td>8.525</td>
<td>12.397</td>
<td>780</td>
<td>594</td>
<td>82.8</td>
<td>1.28</td>
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<td>La₂Co₁₅Mo₂</td>
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<td>12.412</td>
<td>783</td>
<td>587</td>
<td>72.6</td>
<td>1.17</td>
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<td>La₂Co₁₅FeMo</td>
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<td>12.404</td>
<td>781</td>
<td>638</td>
<td>95.5</td>
<td>1.40</td>
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<td>12.425</td>
<td>785</td>
<td>639</td>
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<td>12.449</td>
<td>788</td>
<td>644</td>
<td>106.8</td>
<td>1.53</td>
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<td>8.561</td>
<td>12.475</td>
<td>792</td>
<td>648</td>
<td>114.0</td>
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<tr>
<td>La₂Co₁₀₋ₓFeₓMo</td>
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<td>12.509</td>
<td>797</td>
<td>626</td>
<td>117.0</td>
<td>1.68</td>
<td>plane</td>
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</tbody>
</table>

C. Nanostructured and Nanocomposite Films

Magnetic properties of nanocomposite Fe-Pt films with Fe concentration higher than 50 at % have been investigated. Fe/Pt multilayers were produced by sputtering and magnetic hardening was observed after heat treatment including rapid annealing. The final nanocomposite films, denoted as FePt:FeₚPt, consisted of the hard face-centered tetragonal FePt phase and a soft face-centered-cubic phase of approximate composition FeₚPt. The maximum energy products of the optimally processed samples approached 53 MGOe, very close to the world record value of 54 MGOe for NdₓFeₓ₋ₚB. Evidence for exchange coupling of the hard and soft phases was found.

Magnetic properties of FePt/Fe multilayers of alternating hard and soft magnetic regions were calculated using linear-muffin-tin-orbitals and Green function methods. The changes in the magnetic properties of hard and soft phases with their relative thicknesses were studied via self-consistent calculations of local magnetic moments, effective exchange interaction parameters and the anisotropy energy. The calculations show that this system is a promising permanent-magnet candidate with large-energy product (up to 90 MGOe) uniaxial anisotropy, and high Curie temperature.

SmCoₓ/Co (x = 3.5, 4 and 5) nanostructured multilayers have been prepared by DC and RF sputtering. Magnetic hardening has been found in the as-deposited thin films. The effects of the Co and hard-phase layer thicknesses and the effect of the Cr underlayer have been studied. Further magnetic hardening has been achieved by heat treating the samples to produce hard-soft nanocomposites of the form SmCoₓ₋ₚCo. A remarkable increase of the coercivity has been obtained in the nanocomposite films, with coercive force up to 42 kOe. TEM, AFM, and MFM observations have been performed to understand the nanostructure and the domain structure.
First-principles calculations have been carried out to study the exchange coupling of (SmCo$_2$)/Co$_{1-x}$Fe$_x$ multilayers. The multilayers stacked along the c-axis of the hexagonal hard phase (SmCo$_2$) and the <111> direction of the fcc soft phase (Co$_{1-x}$Fe$_x$) are well matched structurally. The self-consistent spin-polarized electronic structure results were used to calculate the magnetic moments and the exchange-interaction parameters. The average magnetic moments of the soft (Co,Fe) and hard phases are 1.83µB and 1.2µB per atom respectively. A continuum model of the periodically layered hard/soft composite predicts the optimum thickness of the soft phase to be about 13 nm independent of the thickness of the hard phase. Calculated exchange parameters predict the Curie temperature of the hard/soft system to be between the values for each phase (1000-1388 K) depending on the relative thicknesses of the two phases. The optimum theoretical limit to the energy product of the composite is ~65 MGOe which is almost twice the value for the hard phase.

III. Publications on DOE-Supported Work (1995-Present)


21. Z. Chen and G.C. Hadjipanayis, STUDIES ON THE FORMATION, STRUCTURE AND MAGNETIC PROPERTIES OF Cr SUBSTITUTED Sm₃(Fe,Cr)₁ₓCₓ COMPOUNDS, JMMM 171, 261 (1997).


38. Z. Chen and G.C. Hadjipanayis, EFFECTS OF Cr SUBSTITUTION ON THE FORMATION, STRUCTURE AND MAGNETIC PROPERTIES OF Sm$_x$$(Fe,Co)$_{17}$C$_x$ ALLOYS, IEEE Trans. Mag. 33, 3856 (1997).


53. Z.M. Chen, M. Daniil, G.C. Hadjipanayis, ENHANCEMENT OF CURIE TEMPERATURE OF THE 2:17 PHASE IN NANOCOMPOSITE Sm$_9$(Fe, Co)$_{11}$Cr$_2$C$_2$/Fe,Co MAGNETS, to be submitted to J. of Applied Physics.

54. M. Daniil, Z.M. Chen, G.C. Hadjipanayis, 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$_{16-x}$Fe$_3$Mo (x = 0, 1, 2, 3, 4, 6) COMPOUNDS, to be submitted.