

Nd₂Fe₁₄B Synthesis: Effect of Excess Neodymium on Phase Purity and Magnetic Property[†]

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The properties of magnetic material of Nd-Fe-B are highly affected by various factors such as particle size, magnetic anisotropy, phase purity and crystal structure. Incorporation of excess neodymium was carried out in various percentages so that it will adjust the proportion of neodymium in the host crystal after reduction treatment and finally help to improve magnetic property of a material. The interdiffusion of Nd-Fe and boron was studied for various compositions and their effect on magnetic property was understood with theoretical concepts. The factors such as amount of hard and soft phase in the reduction treated product is also responsible for the possible exchange coupling between hard and soft phase magnets for better magnetic properties.

Key Words : Ferromagnetism, Nd₂Fe₁₄B, Reduction-diffusion

Introduction

The combination of intermetallic of rare earth and transition metals with boron such as Nd₂Fe₁₄B is a base material for permanent magnets with high performance with the maximum energy product value among other hard magnets. In hard phase magnetic materials, the key property is their energy product value which improved exponentially within last few years, doubling approximately in every 12 years. The effort for their significant growth is still in progress. The discovery of Nd₂Fe₁₄B by Sagawa *et al.* made a great revolution in the field of magnetic material when people were searching for a material with high coercivity and energy product.¹

The energy product of a magnetic material is defined as the area enclosed in the second quadrant of the B-H loop. Since the energy product of the magnetic material is inversely proportional to its volume, thus to obtain higher energy product value we need to synthesize magnetic material in nanometer regime. The magnetic properties can be optimized by reducing the grain size to the sizes of particle with single magnetic domains and by decoupling of neighboring grain by a paramagnetic Nd-rich inter-granular phase.² The change in intermetallic ratio in the tri-metallic NdFeB magnets makes direct effect on their physical properties and magnetic properties as well. In Nd-rich nanocrystalline, the phenomenon of intergranular phase melting at temperatures far below the melting temperature of the bulk material is observed.³ The inter-diffusion and deformation of Nd and Fe with boron and each other plays an important role in determining the phase pure structure and formation of crystalline domain structures. People have studied the diffusion ability

of Nd and Fe in Nd₂Fe₁₄B magnets with the use of radioactive isotopes of Nd and Fe.^{4,5}

Atomic diffusion of Nd-Fe-B in nanocrystalline solid can be possible in the grains or at the interface of grain boundary. Synthesis of Nd₂Fe₁₄B by chemical route offers this possibility of atomic scale diffusion by optimizing the rate of nucleation and particle growth.⁶ Synthesis of Nd₂Fe₁₄B through glycine nitrate auto-combustion method was successfully carried out by various researchers.^{7,8} In this work we have studied the effect of excess neodymium composition on the synthesis and properties of hard phase Nd₂Fe₁₄B magnetic materials. The excess amount of neodymium in the tri-metallic composition can affect the phase purity and magnetic properties as well. How crystal structure, interdiffusion of Nd and Fe get affected due to increase in neodymium composition has been explained in detail.

Experimental

Materials. Neodymium(III) nitrate hexahydrate [Nd(NO₃)₃·6H₂O, 99.9%, Aldrich Chemicals], iron(II) nitrate nonahydrate [Fe(NO₃)₃·9H₂O, ≥ 98%, Sigma Aldrich], boric acid (H₃BO₃, 99.9%, Katayama Chemicals), glycine (C₂H₅O₂N, 98%, Aldrich Chemicals), were used as received without further purification and de-ionized (DI) water as a solvent.

Synthesis. Synthesis of Metal Oxide Mixtures: The synthesis of NdFeB magnetic materials was carried out by glycine auto-combustion method.⁸ In our previous work the precursors of metal nitrates Nd(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O and boric acid were taken in the molar ratios of Nd:Fe:B:15:77.5:7.5 for synthesis of Nd₂Fe₁₄B phase. In this time, the amount of neodymium precursor was increased from the previously taken (15:77.5:7.5) precursor ratio to 5, 10, 12 and 15 wt % in comparison with the molar ratio to iron precursor. The precursors were dissolved in 25 mL of DI

[†]This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

water in a separate flask with magnetic stirring at room temperature for around 10 min. A 25 mL of glycine solution was prepared by dissolving glycine in DI water in a molar ratio of metal:glycine as 1:1. The glycine solution was added slowly to the metal nitrate solutions. The light orange color changed to dark red after the addition of two solutions. The water was evaporated by heating the solution at 200 °C on a hot plate with continuous magnetic stirring. As the water starts to evaporate the solution viscosity increases. When all of water is evaporated, the remaining viscous mass ignites and burns spontaneously to give a mixture of the metal oxides. The as-prepared metal oxides were washed with DI water to remove any soluble impurities and ethanol to remove any carbon containing impurities. The sample was dried at 60 °C in air before it was reduced.

Reduction Treatment. The metal oxides were reduced to NdFeB nanostructures in an Ar + 5%H₂ atmosphere at 950 °C for 2 h under vacuum. After the reduction treatment, the samples were cooled to room temperature and immediately transferred to an organic solvent, such as hexane, and was stored for further characterization. During the heat treatment at high temperature, the metals, such as neodymium, iron and boron, diffuse into each other to form Nd₂Fe₁₄B alloy. It may also be possible that neodymium and boron diffuse out separately instead of forming a tri-metallic alloy. Thus we obtained different molar ratios for the precursors and final product. The loss of neodymium and boron is only a small fraction of the total mass.

Characterizations. X-ray diffraction (XRD) patterns of the as-prepared metal oxides and reduced NdFeB magnetic materials were recorded using the Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$) of a Rigaku Miniflex-II desktop X-ray diffractometer operating at 30 kV and 15 mA. The samples were scanned at the rate of 0.05° per second in the range of $2\theta = 10\text{--}80^\circ$. The size and shape of the as-synthesized nanostructures were examined with a JEOL JEM 2100 F transmission electron microscope (TEM) operating at 200 kV. For TEM observations, the samples were dispersed in hexane with 1-2 drops of ethanol in it. The drop of the well dispersed nanoparticles was placed over the carbon coated microscopic copper grids (200 mesh size) and was subsequently dried. Elemental mapping and energy dispersive X-ray spectroscopy analysis (EDX) were carried out on a JEOL JEM 2100 F scanning transmission electron microscope equipped with an energy dispersive X-ray spectroscopy analyzer. The magnetic properties of the as prepared magnetic nanostructures were measured at room temperature using vibrating sample magnetometer (VSM) (Lake-Shore 7400) with an external magnetic field up to 14000 Gauss.

Results and Discussion

For the synthesis of phase pure Nd₂Fe₁₄B with enhanced magnetic property, one must understand its crystal structure and the arrangement of atoms in the unit cell. J. F. Herbst *et al.* established exact stoichiometry and crystal structure of

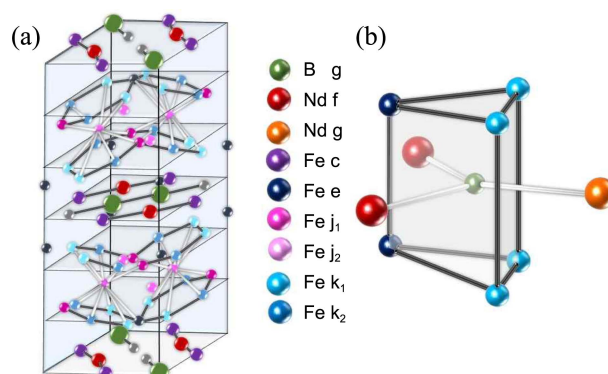


Figure 1. Schematic representation (a) tetragonal unit cell of Nd₂Fe₁₄B ($P4_2/mnm$ space group) and (b) trigonal prism containing a boron atom in the Nd₂Fe₁₄B structure.

Nd₂Fe₁₄B with the help of data available from neutron diffraction analysis.⁹ The schematic representing crystal structure of Nd₂Fe₁₄B and trigonal prism containing a boron atom in the Nd₂Fe₁₄B structure is shown in Figure 1. The tetragonal structure Nd₂Fe₁₄B belongs to $P4_2/mnm$ space group with a unit cell containing 68 atoms and four formula units. It consists of six crystallographically different iron sites and two different rare earth positions for neodymium such as ‘Nd f’ and ‘Nd g’. One site is available for boron which occupies the center of a trigonal prism shown in Figure 1(b). The trigonal prism is formed by the three nearest iron atoms above and the three below the basal plane. These prisms link Fe layers above and below the plane containing Nd and B and contribute for stability of the structure.¹⁰

The mixture of oxide powder was characterized by X-ray diffraction pattern for the determination of number of phases formed after auto-combustion step at 200 °C. The XRD patterns are shown in Figure 2 representing comparison of diffraction patterns of NdFeB samples prepared with 5-15 wt % excess Nd proportion. The crystalline nature of all samples reveals the mixture of three different component particles of Nd₂O₃ (JCPDS # 75-2255), Fe₃O₄ (JCPDS # 88-0315) and NdFeO₃ (JCPDS # 74-1473). The existence of

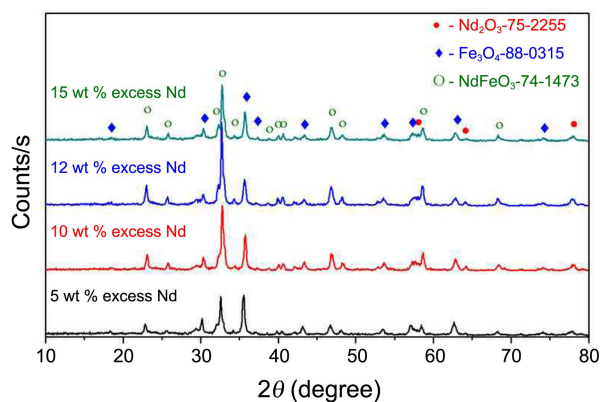


Figure 2. Comparison of X-ray diffraction patterns of as synthesized Nd-Fe-B oxides with different amount of Nd precursor by glycine auto-combustion method at 200 °C.

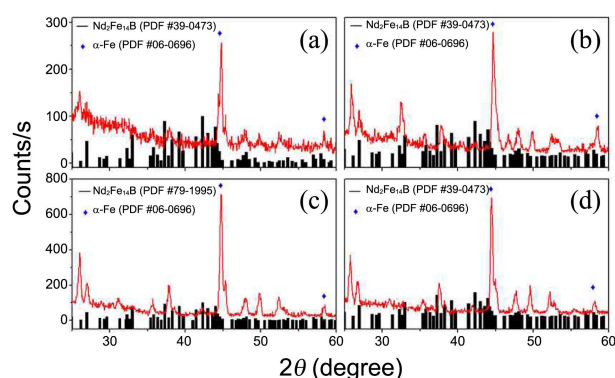


Figure 3. Comparison of X-ray diffraction patterns of Nd-Fe-B oxides with different amount of Nd precursor after reduction treatment at 950 °C. The samples were prepared by glycine auto-combustion method with increasing Nd proportion. 5 wt % excess (a), 10 wt % excess (b), 12 wt % excess (c) and (d) 15 wt % excess Nd.

boron was not detected in any sample due to its amorphous nature. Due to formation of magnetite phase the oxide mixture shows affinity towards magnetic field. These samples were set for reduction treatment at 950 °C under reducing atmosphere to transform the mixtures of various oxides into $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

The corresponding X-ray diffraction patterns after reduction treatment are shown in Figure 3. The crystal structure revealed from diffraction pattern of 5, 10 and 15 wt % excess Nd samples match well with the peaks position of $\text{Nd}_2\text{Fe}_{14}\text{B}$ (JCPDS # 39-0473) and $\alpha\text{-Fe}$ (JCPDS # 06-0696) while the sample prepared with 12 wt % excess Nd matches with the peak positions of $\text{Nd}_2\text{Fe}_{14}\text{B}$ (JCPDS # 79-1995) and $\alpha\text{-Fe}$ (JCPDS # 06-0696). (Different amount of Nd precursor leads to form phase change in alloy composition thus we found that for the sample prepared with 12 wt % excess Nd, shows better resemblance to the peaks of JCPDS # 79-1988 than JCPDS # 39-0473) The variation in diffraction peak intensity can be related to excess proportion of Nd in all samples. Considering the proportion of two components present in all samples, the proportion of hard and soft phase will play an important role in determining magnetic property of the sample. After determining the crystal structure and phase of reduction treated samples, the particle shape and size were estimated through TEM measurement as represented in Figure 4.

Figure 4(a), (b), (c) and (d) represent NdFeB samples prepared with 5, 10, 12 and 15 wt % excess neodymium proportion. From the TEM image, it is shown that the particles are fused with their neighboring particle forming the structures of 150–200 nm size. Due to high temperature reduction treatment large sized fused structures were formed. The HRTEM image of corresponding nanostructures reveals highly crystalline nature and lattice distance matching with diffraction peaks of $\text{Nd}_2\text{Fe}_{14}\text{B}$ in all cases. The peaks are assigned by comparing the lattice distance from XRD patterns of the respective samples. The effect of excess neodymium incorporated in the reaction mixture can be

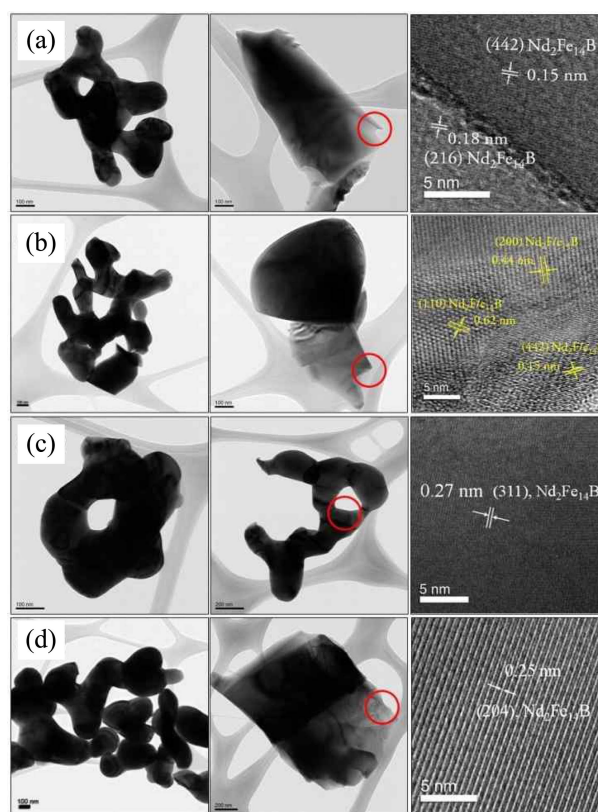


Figure 4. Corresponding TEM and HRTEM images of reduction treated Nd-Fe-B samples prepared with (a) 5, (b) 10, (c) 12 and (d) 15 wt % excess neodymium precursor (all scale bar, 100, 200 and 5 nm).

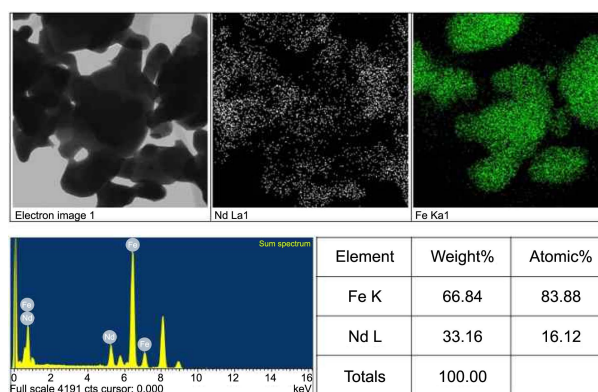


Figure 5. Elemental mapping and EDX analysis of Nd-Fe-B sample prepared with 5 wt % excess Nd concentration. Boron was excluded from the elemental analysis.

understood from the estimation of elemental composition and EDX analysis. Figures 5–8 shows elemental mapping and EDX analysis of NdFeB samples prepared with 5, 10, 12 and 15 wt % excess Nd concentration, respectively. Estimation of boron is not possible with the available technique and instrument as it is a light element.¹¹ In case of sample prepared with 5, 10 and 12 wt % excess Nd, the interdiffusion between neodymium and iron is fairly good one. Above 12 wt % excess concentration of neodymium in the reaction mixture the homogeneity of interdiffusion was not observed.

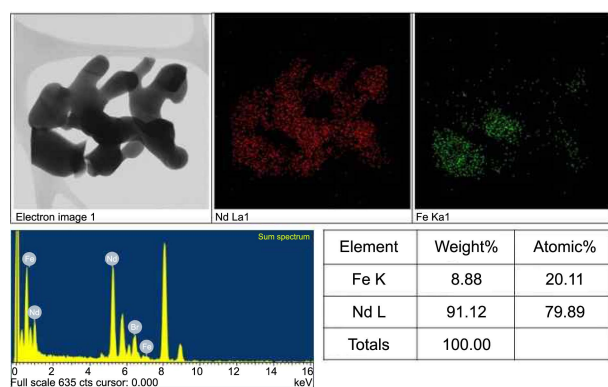


Figure 6. Elemental mapping and EDX analysis of Nd-Fe-B sample prepared with 10 wt % excess Nd concentration. Boron was excluded from the elemental analysis.

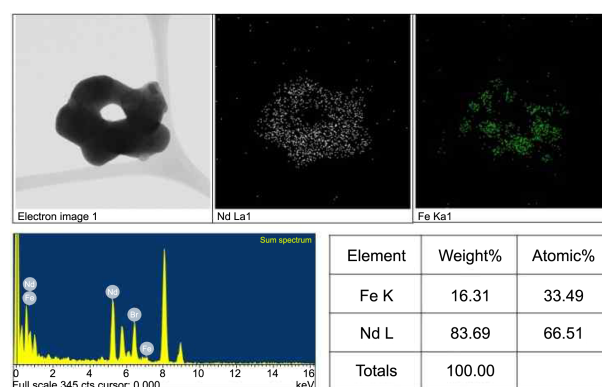


Figure 7. Elemental mapping and EDX analysis of Nd-Fe-B sample prepared with 12 wt % excess Nd concentration. Boron was excluded from the elemental analysis.

The excess neodymium phase separates or segregates from iron phase in the crystal structure. The increasing proportion of neodymium in all samples shows that the scanned area is neodymium rich zone except for the sample prepared with 5 wt % excess Nd concentration. The obtained values of Nd and Fe from EDX analysis are approximate values and they cannot be considered as exact values as the proportion of boron present in the alloy is still unknown.

The response of as prepared NdFeB nanostructures to the applied magnetic field was recorded on vibrating sample magnetometer at 14000 Gauss and represented in Figure 9. The measurement was carried out at room temperature for their practical use and the data obtained from the measurement is shown in Table 1. NdFeB sample with 5 wt % excess of Nd shows highest coercivity value (H_C) of 45.40 G among all samples. Further increase in neodymium composition decreases coercivity value. In case of remanent magnetization, magnetic remanence (M_R) value increases from 5 wt % to 10 wt % excess Nd composition value, 2.27 emu/g. Further increase in neodymium concentration tends to decrease M_R value of NdFeB material. While the saturation magnetization (M_S) follows the similar trend as of coercivity. The sample prepared using 5 wt % excess Nd shows maximum M_S value of 184.26 emu/g. It decreases at 10 wt % excess Nd composition and thereafter further increase in Nd concentration make negligible changes in it.

Theoretically, the maximum coercivity of a nanocomposite (hard-soft combination) magnet can be achieved when the size of soft phase is less than twice the domain wall thickness of the hard phase.¹² If we consider the point of

Table 1. Room temperature VSM measurement data for Nd-Fe-B samples with 5-15 wt % excess Nd composition

Sample	H_C (Gauss)	M_R (emu/g)	M_S (emu/g)
5 wt % excess Nd	45.40	2.01	184.26
10 wt % excess Nd	32.07	2.27	132.66
12 wt % excess Nd	52.12	1.66	131.61
15 wt % excess Nd	32.49	0.95	132.19

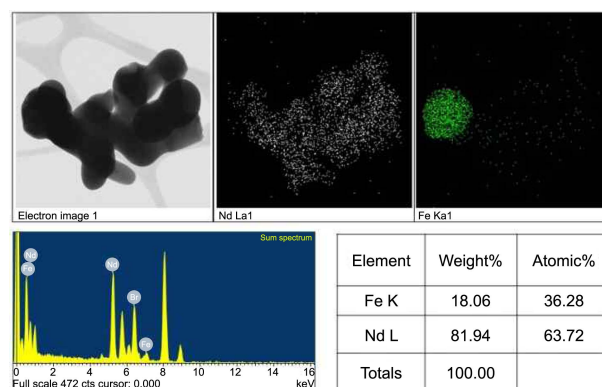


Figure 8. Elemental mapping and EDX analysis of Nd-Fe-B sample prepared with 15 wt % excess Nd concentration. Boron was excluded from the elemental analysis.

particle sizes of hard and soft phase magnetic material, then it is difficult to differentiate from the obtained TEM images whether the particle is of hard phase material or soft phase. Along with size and shape, the magnetic property of the nanocomposite material is dependent on few factors such as chemical composition/phase purity, magnetic anisotropy and crystallinity. Magnetic properties are highly sensitive to impurities or formation of sub-phases along with main phase. The impurity atom shows tendency to occupy interstitial spaces in the host lattice and suppresses the easy formation of the magnetic domains. Increasing neodymium concentration might be responsible for the reduction of phase purity. The sample which was prepared by Jadhav *et al.* using 15:77.5:7.5 compositions for Nd:Fe:B showed coercivity of 500.1326 G with remanence value (M_R) of 3.7627 emu/g and M_S value 10.901 emu/g.⁸ The formation of different sub-phases is also depends upon reduction treatment. In case of neodymium, along with internal diffusion with iron and boron, it can diffuse externally and form another phase with iron. If it is the crystal structure of $Nd_2Fe_{14}B$, majority of neodymium is present near to the surface of the host crystal than inside bulk. During formation of a phase pure crystal structure, neodymium at surface might get segregated due to high thermal energy and tends to form secondary or sub-

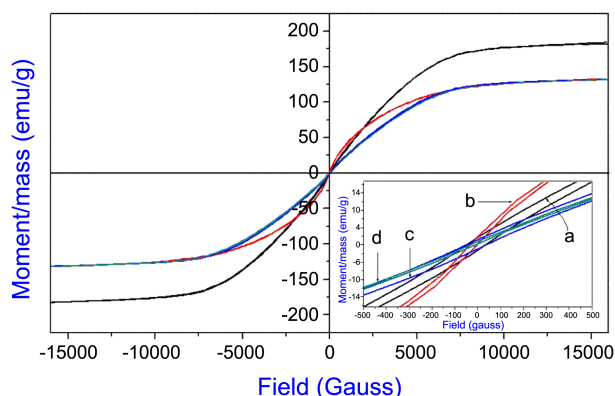


Figure 9. Room temperature VSM measurement of reduction treated Nd-Fe-B samples prepared with a) 5, b) 10, c) 12 and d) 15 wt % excess neodymium concentration. The maximum field of a 14000 Gauss electromagnet was applied for the measurement.

phase. Though we cannot differentiate through X-ray diffraction patterns, the excess addition of neodymium in the reaction mixture increases the chances of formation of sub-phases. Different phases formed during the reduction diffusion process may lead to variation in the magnetic property, generally reduction in the magnetic property.¹³

The coercivity (H_C) of hard phase magnet arises from the large magnetocrystalline anisotropy of the material with non-cubic structure.¹⁴ From HRTEM images of the reduction treated magnetic materials; it is found that most of the lattice distance was matching with hard phase $Nd_2Fe_{14}B$ only. Soft phase α -Fe was not found as a separate phase in the aggregated nanostructures so there is not much exchange coupling between hard and soft phase material. Even with the less particle sizes of hard phase magnetic materials, the exchange coupling might be existed in the mixed product. It is shown well the smooth magnetic hysteresis loop.

Conclusion

Synthesis of NdFeB magnetic materials was carried out by glycine auto-combustion reduction diffusion reaction by increasing amount of neodymium by 5-15 wt % than nominal composition. The incorporation of excess neodymium in the

reaction mixture produced hard phase $Nd_2Fe_{14}B$ as well as soft phase α -Fe as a product with variation in the peak intensity of diffraction peaks. The particle size of reduction treated product was in the range of 150-200 nm range. With increasing in neodymium composition, Nd-rich areas were found to be increased in the reduction treated nanostructures which was responsible for the possible formation of sub-phase of Nd and Fe. The magnetic properties of the reduction treated nanostructures were found low due to various factors such as low phase purity, magnetic anisotropy, interaction of hard-soft domains for exchange coupling.

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